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Stefano Passerini · Linda Barelli ·
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Emerging Battery Technologies to Boost the Clean Energy Transition

Cost, Sustainability, and Performance Analysis

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Editors' Foreword

Batteries are a crucial element for the world's future energy systems built upon renewable energy sources of strongly intermittent nature such as solar and wind. While the market for lithium-ion batteries, the currently dominating technology, keeps growing at stunning pace and technological boundaries are being pushed further, also concerns about the corresponding demand for raw materials and associated environmental and societal impacts are becoming stronger. This has led to an increase of research activities in the field of recycling, material demand and sustainability of lithium-ion batteries, but also to the search and development of new battery technologies based on more abundant, less toxic and broadly available materials. To this regard, technologies based on materials such as sodium, magnesium or aluminium could play a crucial role since they are expected to offer advantages in terms of performance, costs and sustainability. However, these systems are still in an early stage of development, while many sustainability problems do not arise until a technology is broadly implemented and creates market forces strong enough to trigger changes in the industrial landscape, global resource and material streams and corresponding mining and waste handling activities. Here, the principal challenge is to identify promising technologies in an early research stage, extrapolate their possible future deployment at the large scale and thereby assess potential sustainability hotspots in a prospective, foresight-oriented view, anticipating recycling and circular economy challenges. This requires a combination of different perspectives including electrochemistry and material science, energy system modelling, market projections and material flow analysis, system analysis and environmental assessments, as well as societal expectations regarding technology and sustainability.

The present book analyses the most relevant technological developments in the field of batteries, taking a prospective and interdisciplinary view with a broad sustainability angle, including environmental, societal and economic aspects. By assuming a broad introduction of the considered emerging technologies in the markets, potential environmental, societal and economic implications are anticipated from a system and technology assessment perspective, providing a glimpse on the energy storage demand answered by future batteries systems. As such, the book will be relevant to all scholars working on or interested in the development or the assessment of new battery technologies or other energy storage technologies and their integration in the power system or in on-board applications.

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Overview of the Book

Rechargeable batteries are everywhere, from our mobile phone and its wireless earphones, our cars, trucks, and buses up to large battery installations replacing conventional power plants for guaranteeing stability of the electricity grid. However, the sustainability of this booming market is repeatedly being questioned, with the energy-intensive cell manufacturing, resource demand and shortages, or limited recyclability just being some of the keywords frequently heard in this context. Moreover, also limitations of current technologies are remarked in addressing seasonal energy storage needs. New battery technologies are being developed aiming at solving at least some of these issues by using earth-abundant materials, applying design-for-recycling principles, or pushing performance and economic boundaries far beyond the current state of the art of current lithium-ion batteries. But can these expectations be ever fulfilled? This book tries to give a first answer on this critical question by combining the perspectives of technology developers with those of system analysts, presenting emerging battery technologies that could contribute to short- and long-term storage in different application areas. Moreover, prospective analyses of the potential sustainability challenges and opportunities of these emerging technologies in a future decarbonized economy are provided. In this way, the reader has the opportunity to gather knowledge not only at the technology level, but also on a systemic scale, analyzing the whole sector from both a micro- and a macro-scale perspective.

Acknowledgments

The editors want to thank all the authors that supported this project from the very beginning with their expertise and their valuable time. In addition, the editors acknowledge the financial support from the Institute of Technology Assessment (ITAS) of the Karlsruhe Institute of Technology, in particular the Helmholtz Program Energy System Design and Materials and Technologies for the Energy Transition, the EU-Project Storage Research Infrastructure Eco-System[1] and the European Energy Research Alliance Joint Programme for Energy Storage.[2]

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[1] https://www.storiesproject.eu/

[2] https://www.eera-energystorage.eu/

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Part I
Batteries for the Clean Energy Transition

Preface

Accelerated global warming evidences the need for a drastic change of our present society towards a world economy operating within the planetary boundaries. This implies, among others, a rapid and profound decarbonization with all activities ultimately based on renewable energies. To overcome the intrinsic variable nature of renewable energy sources, the integration of energy storage devices, particularly batteries, is considered as a key enabler, allowing to store electricity for use on demand in areas that have traditionally been run on fossil energy. These include a wide set of grid-connected and mobility services and, possibly, new fields such as drones and robotics.

This chapter prepares the ground for the subsequent chapters of the book by introducing the general concepts and challenges related with these transitions. Specifically, Chapter 1 picks the mobility sector as one of the sectors that is undergoing fundamental changes and elaborates on the specific trends to be expected in near future and the role that batteries play for these. This includes not only electrification of vehicles but also aspects of intelligent vehicles, interconnections, and charging infrastructure. Chapter 2 then takes a circular economy perspective by introducing the key challenges and opportunities related with the transition toward a closed loop economy. It tackles the limitations of the present linear economy model and introduces the “R”-imperatives of the circular economy and then applies these to the emerging battery recycling sector to highlight the most important bottlenecks for a circular battery economy.

Chapter 1
Mobility and Future Trends

Seyed Mahdi Miraftabzadeh, Michela Longo, and Federica Foiadelli

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1.1 Introduction

The world is rapidly changing, and the transportation and mobility industry is no exception. Mobility, a paramount part of modern society, helps people to access jobs, education, healthcare, and other destinations. There has been a significant shift in thinking about mobility, with a growing emphasis on sustainability and the need to reduce the environmental consequence of transportation. Mobility is an essential aspect of modern society, encompassing everything from personal transportation to public transit, logistics, and infrastructure. With the rapid advancements in technology, mobility is undergoing a significant transformation, with new technologies and services emerging that have the potential to revolutionize the way we move [1–3]. Mobility has seen a surge in development over the past few decades, and it is worthwhile to follow the latest trends in recent years.

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One of the most significant development and trends in mobility is the transition toward electric vehicles (EVs) from internal combustion engine vehicles. Electric vehicles are powered by batteries rather than fossil fuels, and they produce zero emissions while in operation [1, 4, 5]. Thus, EVs are more sustainable options compared to traditional fuel-powered vehicles. Additionally, the cost reduction of batteries and advancements in charging infrastructure make EVs a more reasonable choice for all people.

Furthermore, another trend in mobility is the rise of ride-sharing services like Uber and Lyft, which allow individuals to hail a ride from their smartphones and pay for it through the app, making transportation more accessible and convenient for many people, especially in urban areas where public transport may not be as well-developed [1, 6]. However, the convenience of ride-sharing comes with a cost, as these services have been criticized for exacerbating traffic congestion and air pollution. Also, the rise of ride-sharing has led to a decrease in public transportation and personal car ownership, which can negatively impact the environment and the economy [7]. Additionally, the employment status of ride-sharing drivers has also been a topic of debate, as some argue that they should be classified as employees rather than independent contractors. Despite these challenges, ride-sharing continues to grow in popularity and is expected to impact the future of transportation significantly.

The remainder of this chapter is organized as follows: toward the electrification of mobility is presented in Sect. 1.2. Section 1.3 presents the e-mobility and future trends. Electromobility charging infrastructure is given in Sect. 1.4. Section 1.5 discusses the importance of 5G technology in mobility and its applications. Finally, the future trends in mobility are presented in Sect. 1.6.

1.2 Toward the Electrification of Mobility

Electrification will play an essential role in the modification of the transportation and mobility industry and has offered major opportunities in recent years, including the environmental impacts and CO_2 emission reductions of transportation [1, 4]. In general, mobility electrification refers to the use of electric power for transportation, such as electric vehicles, electric bikes, and electric scooters. The shift to e-mobility has been increasing in recent years; however, several factors, as presented in Fig. 1.1, enhance such a transition.

Several factors reinforce mobility electrification as follows [7–9]:

Government policies and incentives: Many countries have implemented policies and incentives to encourage the adoption of electric vehicles, such as tax breaks, grants, and subsidies.

Advancements in technology: The new development and improvements in battery technology have directed to cost reduction of batteries. Also, the introduction of new modules of fast and ultrafast charging has surpassed the so-called “range

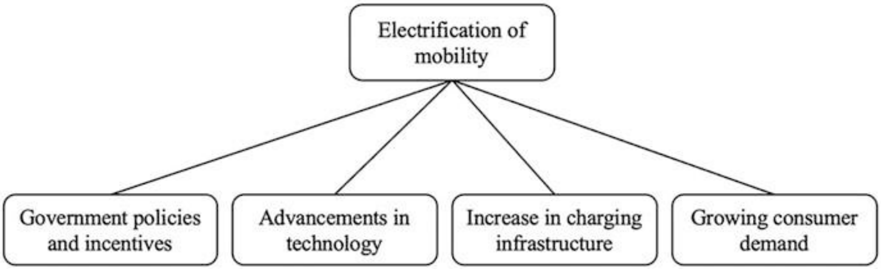

Fig. 1.1 Factors driving mobility electrification

anxiety" issue of new e-mobility customers. Thus, electric vehicles are a more reasonable and affordable option for a wider range of customers.

Growing consumer demand: The transportation sector is one of the main responsible actors for climate emissions. As the concerns about climate change have grown, more people have become aware of the negative environmental impact of transportation as well. Therefore, more consumers have been choosing e-mobility, particularly electric vehicles, which are considered a sustainable alternative compared to traditional ones.

Increase in charging infrastructure: Governments and private companies are investing in the development and expansion of charging stations, both in residential and public spots, to sustain the growth of e-mobility. These investments resulted in finding more charging stations in cities and on roads in many countries.

Government and industry entities will persist in working together to promote further mobility electrifications in various areas. The availability of charging infrastructures requires to be expanded to provide more convenience for consumers to charge their EVs outside their homes as well. The improvement in the range and performance of electric vehicles reduces consumer concerns about long-distance travel with electric vehicles. The development of a thorough strategy for end-of-life battery management minimizes the environmental impact of EV batteries. Finally, customers' concerns regarding the cost, recent advances in electric vehicle performance, and sustainability of e-mobility need to be constantly updated.

1.3 E-Mobility and Future Trends

E-mobility refers to any means of transportation (electric vehicles, electric bikes, electric scooters) that work by electric power. E-mobility is considered a sustainable option compared to conventional diesel and gasoline vehicles since it produces no emissions while in operation and can be powered by renewable energy sources (RESs) such as wind and solar energy, which significantly reduce the carbon footprint of transportation.

E-mobility is a promising solution for decreasing harmful pollutants and greenhouse gas emissions from transportation. However, maximizing the environmental benefits of e-mobility depends on the source of electric energy used to charge the vehicles, the manufacturing process of EVs, and the disposal of the battery at the end of its life span. Additionally, more strategies are required to achieve zero-emission transportation than only the transition to e-mobility, including sustainable urban planning, bike-sharing, and expanding public transportation systems to decrease the overall dependence on personal motorcars.

One of the main trends in e-mobility is the increasing adoption of electric vehicles since battery technology has advanced; the cost of batteries decreased from $1000 per kWh in 2010 to $227 per kWh in 2016, and it is predicted that it will be lower than $100 per kWh by 2030 [10]. As a result of the reduction in battery costs, the number of electric vehicles on the roads has significantly increased. Many countries, such as European countries, have set ambitious targets for replacing traditional cars with electric versions in the coming years. Another trend in e-mobility is the development of charging infrastructure. As more electric vehicles are in operation, it becomes increasingly necessary to have a reliable and convenient charging infrastructure. Many governmental and private companies are investing in developing charging stations, both in residential and public, to satisfy future needs of charging e-mobilities ubiquitously.

Further development in e-mobility technology is expected to emerge in the near future, as it is summarized in Fig. 1.2. Currently, EVs have a limited driving range; however, since there are many advancements in battery technology and capacity, EVs are expected to have a more extended driving range. Ultrafast and wireless charging are other important predictions in e-mobility technology to provide more convenience for drivers to charge their vehicles on the go or without physical connections [11]. Smart charging technology allows scheduling the electric vehicles charging smartly, considering the electricity demands and prices or the electric grid pressure in peak hours. Another interesting aspect of the future of e-mobility is vehicle-to-everything (V2X) solutions that enable EVs to transmit their surplus

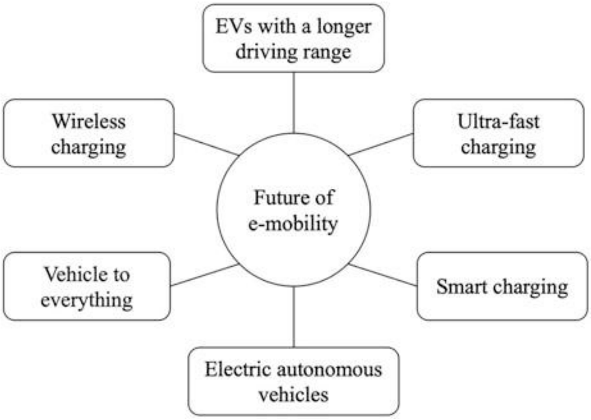

Fig. 1.2 Expected future trends in e-mobility

energy to electric grids, houses, buildings, or any other energy consumption destinations [12, 13]. Finally, thanks to advanced artificial intelligence, autonomous electric vehicles will not only increase the efficiency of mobility but also reduce greenhouse gas emissions.

The future of e-mobility includes using electric vehicles and steady technological advancements to support them. As the demand for electric vehicles grows, the development of charging infrastructure will become increasingly important. In the future, it is expected to see more convenient and efficient charging options such as wireless charging, ultrafast charging stations, and even faster home charging systems. Furthermore, electric vehicles will be integrated with autonomous and connected vehicle technologies, allowing for more seamless integration into smart cities and a more efficient transportation system with zero carbon emissions.

1.4 Electromobility Charging Infrastructure

The charging infrastructure for e-mobility is defined as the charging stations and equipment required to charge electric vehicles, including both home charging and public charging stations. The accessibility and availability of charging infrastructure are the key factors in speeding up the transition to e-mobility. Table 1.1 presents the different current types of charging infrastructure [4, 14, 15]. Level 1 charging is the slowest and safest type of charging, usually used for overnight charging at home. Level 2 charging charges an EV in several hours and is widely operated in public charging stations. Finally, DC fast charging harnesses high power in order to recharge an electric vehicle (EV) in a few minutes. This type requires a specific protection system for monitoring and communication between EV charging equipment and the vehicle.

There are several challenges and limitations associated with the expansion of charging infrastructure:

- High costs: The installation and maintenance of charging stations can be expensive, and governments and private companies may solely be keen to invest in them if they guarantee adequate demand. Therefore, identification of best

Table 1.1 Different types of charging infrastructure

Type	Voltage (volt)	Typical power (kW)	EV miles of range per hour	Setting
Level 1	120 AC	1.2–1.4	3–4 miles	Standard 120-volt household outlet
Level 2	208–240 AC	3.3–6.6	10–20 miles	Often used at public charging stations and at home
DC fast charging	400–1000 DC	50 or more	150–1000 miles	Typically located along highways and in urban areas to support long-distance travel

locations for charging stations and choosing the best charging infrastructure type are necessary to address this concern.

- Limited accessibility: In some locations, mainly remote regions or rural, it can be challenging to install charging stations due to a lack of available electricity or other infrastructure.
- Charging station compatibility: There is no universal standard for EV charging; for example, the EV plug-in type or charging connector differs across geographies and models. Thus, not all charging stations are compatible with all EVs in operation, which can cause inconveniences and confusion for customers.

Governmental and industrial organizations have strong cooperation to overcome these challenges by developing comprehensive solutions and actions. For instance, many countries focus on standardizing charging equipment to ensure compatibility with all EVs. Also, many funds are offered to research and development divisions so as to improve charging station technology and reduce the costs of creation, installation, and maintenance.

1.5 5G Application in Mobility

5G, the fifth and newest generation of mobile technology, has the potential to significantly impact various aspects of society, particularly in terms of mobility [16–20]. Some of the key applications of 5G in mobility include the following:

- Connected vehicles: 5G networks offer faster and more reliable connectivity compared to previous versions, making it possible for vehicles to communicate with each other and with infrastructure in real time. Consequently, it can improve traffic flow, reduce congestion, and make it possible for vehicles to drive themselves.
- Remote driving: 5G networks have low latency, high bandwidth, and ultra-reliability, which enables the remote control of vehicles and equipment in real time; thus, using 5G enables remote driving and operation of vehicles in dangerous or difficult environments.
- Intelligent transportation systems: 5G networks can enable the real-time collection and analysis of data from traffic cameras, sensors, and other sources, allowing for the optimization of traffic flow and the reduction of congestion.
- Automated transportation: The high-speed, low-latency connectivity of 5G networks can support the communication and connectivity needed to operate automated transportation systems, such as drones, self-driving cars, and autonomous buses.
- Enhanced safety: 5G networks can enable communication between vehicles, infrastructure, and passengers to improve the overall safety of transportation by allowing real-time data exchange and providing faster response times and more accurate information necessary for safety issues.

- In-vehicle experiences: 5G networks enable faster and more dependable connectivity inside vehicles, promoting new services such as infotainment, online shopping, and streaming high-definition videos. Additionally, 5G networks can provide passengers with high-speed Internet access, allowing them to work or entertain themselves during their journey.

5G networks have the potential to revolutionize mobility by making transportation safer, more efficient, and more convenient. The technology promotes the development of new applications such as connected and automated vehicles, intelligent transportation systems, and enhanced in-vehicle experiences, which can help reduce congestion and improve traffic flow and overall mobility ventures.

1.6 Future Trends

It is likely to see the continued development and expansion of electric vehicles and ride-sharing services in the future. Besides, various other trends are expected to shape the future of mobility, which are listed below.

- Autonomous vehicles: Self-driving vehicles have the great potential to diminish traffic congestion and accident while additionally making transportation more reliable and accessible to people who are incapable of driving, such as the disabled or elderly. Many scientists and companies are actively working on developing autonomous vehicles, such as Tesla, Uber, and Waymo.
- Connected vehicles: The advances on the Internet of things and communication technologies, such as 5G, connect vehicles through their sensors and communication devices [16]. The connected vehicles communicate with other vehicles and infrastructures, including traffic lights and road signs, to relieve traffic congestion and enhance the mobility flow.
- Micromobility: Micromobilities, lightweight vehicles such as electric scooters and bikes, are created for short trips and are becoming increasingly widespread in urban areas to save time and traffic. Furthermore, they are convenient options that not only reduce traffic congestion but also minimize the negative environmental impact of traditional transportation.
- MaaS (mobility as a service): MaaS is an emerging concept that enables the provisioning of transport services with a single access point for all different types of mobility, including public transportation, bike- and car-sharing, taxis, ride-hailing, and more [21, 22]. Many mobility companies leverage joint digital channels or applications, enabling people to plan and book rides to discourage private vehicle ownership. One of the interesting ideas of MaaS is that users pay a monthly fee to access transportation services rather than pay for each means of mobility separately. Implementing the MaaS concept or eMaaS reduces traffic congestion and lowers pollution.
- Hyperloop: Hyperloop is a high-speed ground transportation system that uses magnetic levitation technology to move passengers and cargo at speeds up to

1130 km per hour. This system includes connected mobility hubs worldwide through a network of tubes that pods can move in a vacuum at ultrahigh speeds. This concept still needs to be developed because of the limitation of nowadays technology and safety issues. Hyperloop can solve the problem of long-distance travel.

The future of mobility is likely characterized by a shift toward more sustainable and efficient forms of transportation, such as electric vehicles, and micromobility options, such as bicycles and e-scooters. Integrating autonomous vehicles and connected vehicle technologies is also expected to play a key role in shaping the future of mobility. The concept of mobility as a service (MaaS) is also gaining popularity, where transportation is seen as a service and not just a product, allowing for a more seamless, integrated, and convenient user experience. Hyperloop technology, which uses high-speed trains in vacuum-sealed tubes, is also being researched and developed as a new transportation mode. The 5G networks will also play a vital role in the future of mobility by enabling new services such as automated transportation and in-vehicle connectivity. On the other hand, as ride-sharing services become more prevalent, they are likely to significantly impact the way we move around cities, reducing the need for personal car ownership and changing the way we think about transportation. These technological and transportation advancements will significantly help reduce traffic congestion and air pollution and increase accessibility.

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Chapter 2
Principles of a Circular Economy for Batteries

Christoph Helbig and Martin Hillenbrand

Contents

2.1 Definition of Circular Economy

The rapidly growing market for batteries in mobility and stationary applications leads to increasing amounts of battery material demand and returned waste batteries [45]. Battery materials like cathodes, anodes, the separator and electrolyte, connectors, casing and housing, safety equipment, and the battery management system cause environmental impacts in their supply chain, in the mining, processing, and fabrication stage [32]. These environmental impacts cause concern, not only because of the greenhouse gas (GHG) emissions related to resource extraction and processing [22] but also exposure to toxic substances, air pollution, water depletion, and land use [12]. One strategy to reduce these material-related impacts is to use products longer and use more recycled materials in their production—subsumed under the label of circular economy measures [42]. Other strategies include improving

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batteries' energy and power density, extending their cycle stability, reducing fabrication waste, and reducing battery production's energy and carbon intensity. Such strategies, however, are not the focus of this chapter.

The circular economy is a concept to keep materials in the loop. It is an alternative to a conventional, linear economy in which resources are used in production and consumption to provide utility to people and society. In contrast, the circular economy generates less to no waste, minimizing the need for final disposal and raw material extraction from the lithosphere [2]. In the circular economy, materials are still used in production and consumption, but their wastes are used again for the same or different purposes. This cycling, or at least cascading, minimizes the amount of material extracted from the lithosphere. Ideally, mining and quarrying would be limited to what is required to expand in-use stocks and replace unavoidable irreversible material losses [39]. The expansion of in-use stocks has been the norm for most material systems in the past century [25], and it is likewise crucial for modern technologies, like batteries [45], that have not yet reached some level of demand saturation [44].

Cyclical ecosystems formed by the circular economy are considered more sustainable than linear ecosystems because they reduce resource consumption and environmental impacts and provide an economic benefit. The reduction of primary material requirements comes from the increased use of materials recovered from waste, replacing materials mined or quarried from the lithosphere. Recycling generally reduces energy requirements, carbon footprints, and other environmental impacts. Of course, there is a risk for a circular economy rebound, nullifying the environmental savings [47]. For very high recycling rates, high energy requirements for collection, sorting, and processing can also reduce secondary production's environmental and cost benefits [41]. Implementing a circular economy reduces the negative environmental impacts of material extraction and expansion and increases raw mYaterial supply security. Therefore, the circular economy addresses resource scarcity concerns and reduces environmental impacts. In addition, it is also expected to provide economic benefits due to the value generation of material recovery, savings from extraction reduction, and avoidance of disposal [28].

Various definitions for the circular economy exist [24]. The interdisciplinary nature of the challenge can partially explain this. Closing the material loops is not just about understanding the material flows in society or developing recycling processes and long-living products designed for recycling. It also includes policy aspects of providing the proper legislative framework to foster the use of materials recovered from waste, installing take-back schemes, and many other material efficiency measures. Sociological aspects of understanding how behavior changes contribute to the use of fewer products, the use of more sustainable products, and the most efficient use of waste management systems also play their role in establishing a circular economy. An actual circular economy can be implemented by combining the micro-, meso-, and macro-systems perspectives [24].

The overall status of the implementation of the circular economy can be measured with two simple metrics: first, a perfect circularity would be achieved if recovered end-of-life material outputs met all material demand, and second, in an ideal circular economy, this would be happening without material quality losses, meaning that no extra energy would be required to recover materials [6]. Of course, this ideal is not practically achievable because of numerous material, metallurgical, and product design challenges [39]. Every loop in the circle creates dissipation and entropy, attributed to losses in quality (mixing, downgrading) and quantity (material losses, by-products) [20], making a fully closed loop impossible. Nevertheless, for the various reasons outlined above, it is desirable to close the loop as far as possible [6]. In addition, the technical, economic, and sociological challenges to closing material cycles of different materials, like base metals, specialty metals, plastics, pulp and paper, or construction minerals, are fundamentally different.

Batteries are an exciting sector for establishing a circular economy because they represent a rapidly growing market, with significant material demand, in parts, even Critical Raw Materials [19]. The battery sector is currently subject to technological changes, and the realization of circular economy benefits within this technological change would foster the transition to low-carbon technologies.

2.2 R-Imperatives of the Circular Economy

Many measures to install a circular economy are subsumed under so-called R-imperatives. Starting with short lists of just three “3Rs” like “reduce, reuse, recycle” and “recycle, remanufacture, reuse,” the lists have gotten longer [24]. One list even consists of ten R-imperatives: refuse, reduce, resell/reuse, repair, refurbish, remanufacture, repurpose, recycle materials, recover energy, and re-mine [38]. Probably, talented wordsmiths will be able to extend these lists almost indefinitely. According to Walter R. Stahel, the R-imperatives in the concept of circular economy replace production with sufficiency: “reuse what you can, recycle what cannot be reused, repair what is broken, remanufacture what cannot be repaired” ([42], p. 435). In the Waste Hierarchy, a concept from the Waste Framework Directive of the European Union, waste prevention comes before preparation for reuse, recycling, recovery, and disposal [11]. Therefore, the R-imperatives can be hierarchical. Each R-imperative’s potential for the circular economy depends on the maturity of a technology, its industrial sector, and inherent material properties.

Even the longer lists of R-imperatives follow three basic ideas to change the material cycles, corresponding to the three Rs of reducing, reusing, and recycling:

1. **Narrowing** material cycles (use less material overall).
2. **Slowing** material cycles (keep materials in use for longer).
3. **Closing** material cycles (keep materials in the loop).

Distinguishing between R-imperatives at different stages of material cycles ensures that various actors are addressed. Material cycles can be narrowed, slowed, and closed by bringing together consumers, producers, legislation, and the waste management sector. Figure 2.1 shows a product’s different life cycle stages, from

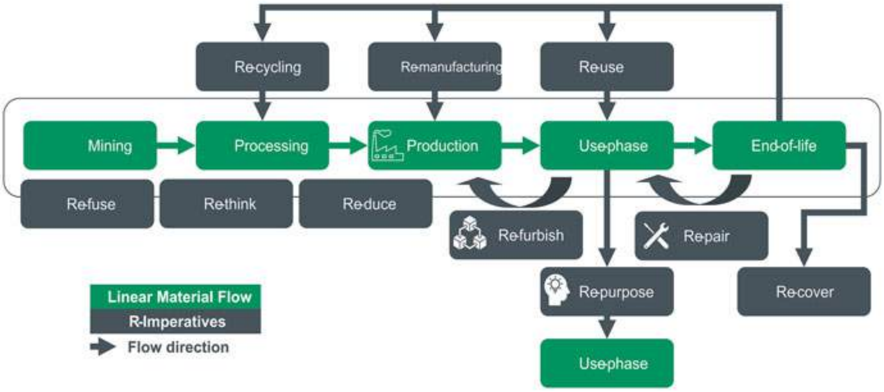


Fig. 2.1 Schematic visualization of the ten R-imperatives, refuse, rethink, reduce, reuse, repair, refurbish, remanufacture, repurpose, recycle, and recover, and their corresponding impact on narrowing, slowing, and closing the material cycles

extraction to waste management, and ten corresponding R-imperatives along these stages.

Narrowing material cycles means that, overall, less material is used. **Refusing** to use a product is the first option to use less. An example is the "flygskam" initiative to reduce the need for air transport [5]. **Rethinking** a product in a circular economy means providing the same service with a wholly changed product design that is much less resource intensive. An example is film photography, which has been largely replaced with digital photography, making the production of photographic films obsolete, resulting in significantly lower demand for film development, reducing silver losses [8]. **Reducing** material use can be achieved by making products smaller and lighter or making the production process more efficient. For example, reducing floor space in private households reduces the construction material requirements and the energy demand for heating and cooling the building [35].

Slowing material cycles is achieved by implementing measures to prevent a product from becoming end-of-life waste. **Reusing** products means despite the will to dispose of a product by one consumer, the product in its current state still has value for another consumer and can still be used by someone else [4]. The used clothing market is the most prominent example. **Repairing** products extends their usage by investing just a minimal maintenance effort, much smaller than what would be needed for a replacement. Repair is common practice for valuable, intensively used mechanical products like cars, machines, and infrastructure [40]. **Refurbishing** goes a bit further than repairing as you don't just want to reestablish functionality, but you might also invest in modernization. Apartments and houses are typically refurbished [37]. **Remanufacturing** means that parts of a product are used in a new product. The market for classic cars has a lot of experience with remanufacturing, and modular desktop PCs allow the reuse of individual components [15]. **Repurposing** extends the material life by changing the purpose of the product.

Batteries of electric vehicles can still be used in stationary applications if their capacity is not satisfactory for mobility applications anymore [13].

If the product and its components are unsuitable for these lifetime-extending measures, its materials can still be valuable. **Recycling** means obtaining materials that can be used as inputs for new products. Although that is desirable, recycled materials do not necessarily have to be of the same quality. Even downcycling counts as recycling [20]. Metals are materials where quality is generally maintained, and low loss rates result in relatively high recycling rates [14]. Some materials may be hard to recycle but provide a heating value. In these cases, thermal **recovery** is the last option in the Waste Hierarchy. An example of recovery is mixed waste plastics replacing fuels for energy recovery [18].

2.3 Battery Material Flows

Annual growth rates of the battery industry were about 30% in the past decade and are expected to be about 20% in the next two decades [36]. Until 2010, most global electrochemical storage capacity was in lead-acid batteries (LAB), with about 300 GWh of new electrochemical energy storage installed yearly, used chiefly as vehicle starter batteries [36]. LABs are positive examples of the circular economy being a mature market with established take-back schemes and recycling facilities. LABs are the main reason lead achieves relatively high circularity values compared to other base metals [21].

Since 2010, however, the focus has shifted to lithium-ion batteries (LIBs). Initially, LIBs were chiefly used in portable electronic devices; now, LIBs for electric vehicles dominate the market [36]. With this rapid market growth, concerns about resource availability and the environmental impact of LIB production have become increasingly important in recent years [19, 32].

For LIBs, the challenge of installing a functional circular economy is more prominent than for LABs. LIBs have vastly different sizes, shapes, types, and material compositions, affecting waste separability and the metallurgy of the recycling process. Battery cells for LIB consist of aluminum and copper foil current collectors, cathode and anode active materials, carbon binders, the electrolyte, and a porous separator. The cell, housing cover, and connection interface form the battery module. On the pack level, you can add a management controller, cooling system, frame and crash structure, and a battery pack housing cover [26, 33].

Technologically, there have been an extensive debate and a lot of development in terms of the cathode active materials, with the most prominent options for battery electric vehicles being nickel-cobalt-aluminum, nickel-manganese-cobalt (with various stoichiometric combinations of transition metals, from NMC111 to NMC811) [27], and iron-phosphate active materials. LIBs can also contain various critical materials, for which the establishment of material cycles is even more important and challenging [3, 26, 46].

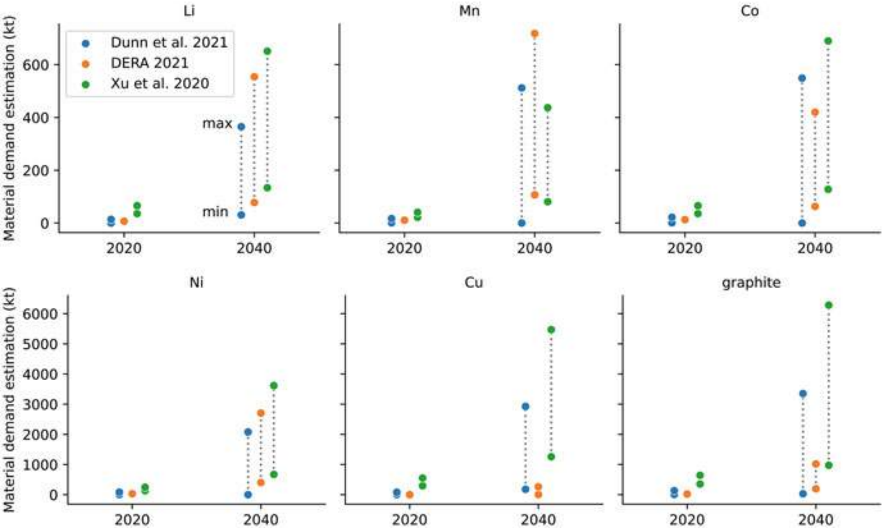


Fig. 2.2 Minimum and maximum estimations for the material demand of Li, Ni, Co, Mn, Cu, and graphite for batteries for 2020 and 2040 in scenarios of Xu et al. [45], Marscheider-Weidemann et al. (DERA 2021), and Dunn et al. [7] in kilotons (kt). The base year for material demand in Marscheider-Weidemann et al. [30] is 2018, not 2020, as no 2020 values were provided in the source. Furthermore, only one data point is specified for 2020

In the future, new battery technologies are expected to make additional raw materials and materials necessary, for example, sodium, calcium, or aluminum [1]. Some of these developments are explicitly undertaken to reduce the dependence on Critical Raw Materials, like cobalt, or other expensive metals, like nickel. It is crucial to close material loops to meet future material demands and reduce the environmental impact of battery production, especially for expensive, scarce, or environmentally harmful materials [32].

In the meantime, material demand and end-of-life material flow for lithium, cobalt, and nickel are expected to continue to increase [45]. Figure 2.2 shows the range of estimations of current and future material demand for lithium, nickel, cobalt, manganese, copper, and graphite in recent battery material flow studies. This ever-increasing material demand causes an issue in implementing the circular economy. The International Energy Agency estimates that by 2040, recycled copper, lithium, nickel, and cobalt from spent batteries could reduce the combined primary supply requirements for these minerals by around 10% [23]. The main reason is that you can only recycle what you have used in the past because of the time lag of the product's lifetime. From a resource savings perspective, product lifetimes should be extended to reduce the demand for new batteries, but the market has grown significantly when a battery becomes waste. Therefore, even with high end-of-life recycling rates for battery materials, the recycled content in batteries will remain low until some saturation level has been achieved and the in-use stock is not multiplying anymore. Such saturation is not expected to happen before the mid-century simply because of the massive demand for electrification in mobility and stationary storage applications.

2.4 Battery Design for Circularity

In the broad definition of the circular economy, more sustainable material cycles for batteries are not only a question of recycling. The goal is a holistic implementation of circular economy measures to reduce overall resource requirements and material-related environmental impacts. So how can the material cycles for batteries be narrowed, slowed, and closed comprehensively?

Narrowing material cycles in a rapidly growing market is a challenging task. However, significant efforts have already been made to reduce, for example, the required housing. Cell-to-pack technologies, for example, for LFP, have eliminated the module component and increased the battery's energy density, effectively reducing the amount of steel, aluminum, or plastic packaging that is not an active material in the battery. At its core, this is a "reduce" strategy, although here, it is chiefly used to increase the capacity of the vehicle battery. Circular economy strategies narrowing the material cycles are chiefly used for their Critical Raw Materials content, particularly for the partial or complete substitution of cobalt in batteries due to its high cost and conflict potential [3].

Battery material cycles can be slowed by prolonging battery life by designing cells that last for a long time and many charging cycles. Significant improvements have been made in terms of the aging stability of batteries, so it is now conceivable that an electric vehicle can drive on the same battery for 20 years and one million miles [16]. At the same time, electrolytes have been developed to allow faster charging without compromising cycle stability [29]. Batteries can also be leased to vehicle owners and afterward be used in less demanding applications, a strategy which can be identified as reuse, remanufacture, or repurpose strategy, depending on the amount of processing required and nature of the alternative use [3].

Battery material cycles can be closed by recycling the battery components [10]. Generally, one can distinguish many pyrometallurgical and hydrometallurgical processes and direct recycling routes [26]. The recoverability of contained Co, Ni, Li, Mn, Al, Cu, C, Fe, electrolytes, and plastics depends on the chosen process. Pack, module, and cell design also significantly impact battery dismantling and repair, remanufacture, and recycling options [43].

In general, the pyrometallurgical processes are more versatile regarding the battery chemistries and geometries. They have a high recycling capacity, require no sorting or pretreatment, and enable high recovery of valuable metals (Co, Ni, Cu). They are established and well-understood processes with industrial know-how [17]. On the downside, certain materials (graphite, plastics, and electrolyte) are burned and thus lost. The obtained products are often low purity and downcycled (e.g., Li and Al) or need further hydrometallurgical refinement. The pyrometallurgical process is expensive because of its high energy consumption and the need for off-gas treatment to remove toxins [17, 26].

Hydrometallurgical processes have high recovery rates, high purity of the products, low energy consumption, and low GHG emissions [17]. They have low recycling capacities. The batteries must be crushed to meet the purity and pretreatment requirements, which leads to safety problems. In addition, efficient methods for electrolyte deposition still need to be demonstrated industrially. The complex processes, the needed treatment of the final effluent (neutralization), the treatment of the contaminated wastewater, and other aspects of the process (e.g., solvents) lead to high operating costs [26].

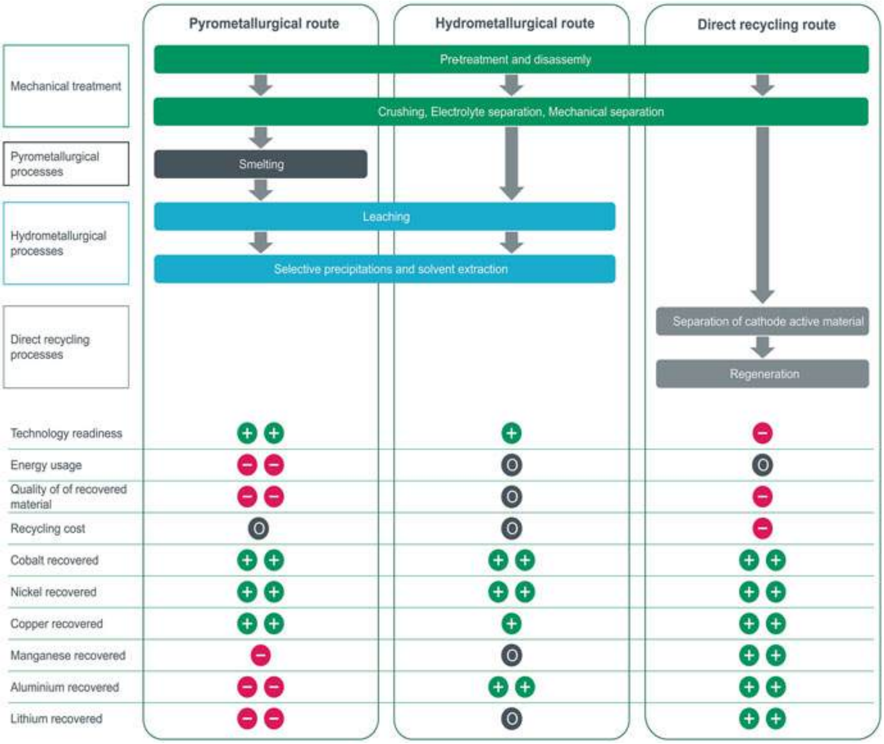
Disassembly and pretreatments are always the first steps. In the case of the pyrometallurgical processes, the second step is directly smelting the pretreated LIBs. In addition, the alloy and the slag can be further refined by leaching, selectively precipitation, and solvent extraction. Alternatively, the disassembled and pretreated material can be converted into the so-called black mass through further mechanical treatment, which includes crushing, electrolyte separation, and mechanical separation. Afterward, the black mass can be processed through hydrometallurgical or direct recycling route. In the hydrometallurgical route, leaching, selective precipitation, and solvent extraction are used to recover the contained materials. In the direct recycling route, separating, regenerating, and producing new cathode active material are the goals [26]. While the direct recycling route provides the opportunity to obtain higher quality recyclates, it is not as mature as the pyrometallurgical or hydrometallurgical routes. Figure 2.3 shows the main process routes, advantages, and disadvantages for pyrometallurgical, hydrometallurgical, and direct recycling routes. For a more detailed description of the most important recycling processes and the corresponding efficiencies, the reader is referred to Chap. 4.3 of this book or to the work of Ekberg and Petranikova [9].

Mohr et al. [32] show that recycling could reduce the environmental impacts of lithium-ion battery production, both in the case of pyrometallurgical and hydrometallurgical processes. They highlight that the savings depend on the cell chemistry, particularly the cathode active material, and the environmental impact category, like abiotic depletion or global warming potential. Additionally, it is not always the process with maximum recycling depth that provides the most considerable environmental savings, which will become even more critical if the share of expensive materials in the battery decreases [32].

2.5 Circular Economy in the EU Battery Regulation

The European Commission adopted a new Battery Regulation with severe implications for the circular economy of batteries [31]. Among other things, the regulation also addresses various issues concerning the material cycles of batteries.

The Battery Regulation is meant to narrow material cycles if successful. It enables and guides the rise of batteries in electric vehicles and stationary applications, where



	Pyrometallurgical route	Hydrometallurgical route	Direct recycling route
Technology readiness	⊕⊕	⊕	⊖
Energy usage	⊖⊖	O	O
Quality of of recovered material	⊖⊖	O	⊖
Recycling cost	O	O	⊖
Cobalt recovered	⊕⊕	⊕⊕	⊕⊕
Nickel recovered	⊕⊕	⊕⊕	⊕⊕
Copper recovered	⊕⊕	⊕	⊕⊕
Manganese recovered	⊖	O	⊕⊕
Aluminium recovered	⊖⊖	⊕⊕	⊕⊕
Lithium recovered	⊖⊖	O	⊕⊕

Fig. 2.3 Summary of pyrometallurgical, hydrometallurgical, and direct recycling routes for battery materials and their respective main advantages and disadvantages. (Adapted from Latini et al. [26] and Harper et al. [17])

they serve as electrochemical energy storage enabling the reliable use of renewable energy and thus replacing, at least in part, fossil fuels, which are by design not circular. Several articles of the regulation are relevant to the circular economy. The previously mentioned slowing and closing of material cycles are taken up, but the narrowing of material cycles is not considered.

Articles 9 to 11, 73, and 74 have an impact on slowing the material cycles. Articles 9 and 10 describe performance and durability requirements for batteries. Article 11 mandates the removability and replaceability of portable batteries in appliances, ensuring that the appliance stays in use in case batteries have a shorter lifetime than the appliance itself. Article 73 supports the repurposing and remanufacturing of batteries. Article 74 mandates producers to provide information on the dismantling and removal of batteries to support repair, remanufacture, preparation for reuse, treatment, and recycling.

Articles 8, 59, 69, and 71 close the material cycles. Article 8 mandates that the cobalt, lead, lithium, and nickel present in new EV batteries fulfill the requirements for minimum shares of material recovered from waste for each of the metals present.

As proposed, these minimum shares will be implemented in 2030 and raised in 2035. Article 59 sets targets for producers and article 69 for member states for minimum collection targets for waste of portable batteries. The proposed targets are gradually raised until 2030 when a 73% minimum collection rate shall be reached. Article 71, in combination with Annex XII, sets targets for recycling processes regarding their minimum recycling efficiencies based on the average weight of batteries, and levels of materials recovery, for cobalt, copper, lead, lithium, and nickel, respectively. By 2030, according to the proposal, an 80% recycling efficiency for lead-acid batteries and 70% for lithium-ion batteries shall be reached, enabling by 2031 a recovery of 95% for cobalt, copper, lead, and nickel and 80% for lithium.

The regulation is supported by various initiatives, such as the European Battery Alliance, and financial aid packages to support research and innovation along the entire battery value chain. But those benefits also come with risks, such as higher compliance costs, hindering innovation, technology adaptation, and competitiveness [31].

If implemented as the battery regulation proposal foresees, the contribution of recycling to meeting the raw material demand of battery production in Europe could be more than 40% for cobalt and more than 15% for lithium, nickel, and copper by 2040. Those numbers are based on a recycling volume of 150 to 300 kilotons of lithium-ion batteries and battery components per year in 2030 and 600 to 2500 kilotons in 2040 [34].

The Battery Regulation also proposes a battery passport with information on repair, disassembly, and, importantly, the carbon footprint of the battery from raw material extraction to the end-of-life phase, without the use phase. Such a mandatory carbon footprint, and in the future also carbon footprint classes and a threshold for marketing batteries in the European Union, supports the goal to reduce the overall environmental footprint of battery production. Therefore, the overall goal of the circular economy, avoiding unintended harmful environmental impact, is just as much tackled with the battery regulation proposal as the various mentioned R-imperative actions.

2.6 Outlook

In a way, batteries are already a contribution to the circular economy because they allow using reversible electrochemical processes for energy storage and, thereby, replacing single-use fossil fuels. However, the circular economy of batteries will be incomplete unless batteries are recycled after their product lifetime. Linear material flows for fossil fuels would only be replaced by take-make-waste processes for lithium, nickel, cobalt, natural graphite, and other battery materials. The battery regulation proposal is a cornerstone to prevent such linear material flows.

One should never forget that recycling alone cannot meet the material demand for building up the in-use stock in a growing market. Securing Critical Raw Materials supply is equally important to allow batteries to fulfill their purpose in the required transitions in the energy sector for global net zero carbon emissions. The R-strategies and recycling technologies mentioned above are necessary to reduce the total material demand for batteries, but they will not eliminate the demand. They are necessary but not a silver bullet. Therefore, the circular economy of batteries needs to be accompanied with material research and embedded in a more general sustainability strategy.

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Part II
System Perspective for a Clean Energy Transition

Preface

This chapter provides an overview on the key role of batteries for the clean energy transition. First, recent projections for the development of global and European demand for battery storage out to 2050 are presented and discussed in Chapter 3, with separate insights for the power system and the mobility sector.

The impact of the projected rise in battery production is analyzed also with reference to the battery cost reduction's trend and, on the other hand, to the consequent strong increase in demand for critical minerals. Increasing the supply of these critical minerals in lockstep with demand is essential in order for battery costs to continue to decline.

Chapter 4 then provides a review of energy storage technologies, going beyond batteries. It compares and discusses the most relevant storage technologies, such as power-to-x or pumped hydro, and highlights their main features and performance characteristics, including their ecological footprint. Chapter 5 picks up on this and highlights the specific advantages of batteries, whose specific performance and technical characteristics make them a specifically promising technology for a wide set of applications. Focus is placed on applications related to both grid-connected and mobility services. For the former, this includes bulk energy services, transmission, and distribution network support and capacity firming coupled to highly variable RES plants. With regard to transport applications, electric mobility, and perspectives relative to electric vehicles (EVs), interaction with the electric infrastructure is presented and discussed.

Chapter 3
Projected Global Demand for Energy Storage

Max Schönfisch, Amrita Dasgupta, and Brent Wanner

Contents

3.1 Introduction

Long-term projections of the development of the global energy system foresee a dramatic increase in the relevance of battery storage for the energy system. This is driven primarily by the proliferation of electric vehicles and a growing demand for electricity storage, connected to rising shares of variable renewables in the electricity supply mix.

At the same time, electric vehicles are projected to continue to make strong inroads in the transport sector, leading to a dramatic increase in battery production geared toward the automotive sector.

Across scenarios, major outlooks published recently foresee a rapid global expansion of variable wind and solar PV-based electricity generation, as well as a rising share of electricity in total final energy consumption (see, e.g., [7, 9, 12, 26–

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28, 30]). The integration of these rising volumes of variable electricity requires key enabling technologies such as battery storage to grow as well.

This chapter provides a detailed look at recent projections for the development of global and European demand for battery storage out to 2050 and analyzes the underlying drivers. It draws primarily on the International Energy Agency (IEA)'s World Energy Outlook (WEO) 2022 [26], to which the three authors contributed.

The WEO 2022s long-term projections of the development of the global energy system foresee a dramatic increase in the relevance of battery storage for the energy system. As a result of falling costs and supportive policies, electric vehicles become the dominant technology in the light-duty vehicle segment in all scenarios in 2050, contributing to a massive increase in the demand for automotive batteries. In the electricity sector, battery energy storage systems emerge as one of the key solutions to provide flexibility to a power system that sees sharply rising flexibility needs, driven by the fast-rising share of variable renewables in the electricity mix. Batteries are also increasingly tapped to provide firm capacity as traditional generators, such as coal- or gas-fired plants, are retired.

As a result of the growing demand for batteries, the demand for critical minerals used in battery production, such as lithium, cobalt, nickel, graphite, copper, or manganese, is expected to increase substantially as well.

3.2 Methodology

The projections and findings on the prospects for and drivers of growth of battery energy storage technologies presented below are primarily the results of analyses performed for the IEA WEO 2022 [26] and related IEA publications.

The IEA WEO 2022 explores the potential development of global energy demand and supply until 2050 using a scenario-based approach. It does so through three scenarios. It should be noted that these scenarios do not represent predictions but rather analyze in detail possible versions of how the energy system might develop given different policy targets and assumptions on their implementation ([26], p. 105).

The first two scenarios, the Stated Policies Scenario (STEPS) and the Announced Pledges Scenario (APS), are descriptive. The third scenario, the Net Zero Emissions by 2050 Scenario (NZE Scenario), is prescriptive:

- STEPS describes the development of the energy system considering only the current policy setting, based on a country- and sector-specific appraisal of policies that are in place or have been announced as of late 2022.
- APS assumes that all climate commitments, including nationally determined contributions (NDCs) and country-level net zero targets that have been announced as of late 2022, are achieved in full and on time (even though supporting policies may not yet have been put into place), representing a more aggressive emission-reduction pathway than STEPS.

- The NZE Scenario describes a cost-effective pathway for the global energy system to reach net zero emissions by 2050, maintaining at least a 50% probability of keeping the global temperature rise below 1.5 degrees Celsius until 2050 while achieving universal access to modern energy services (primarily electricity and clean cooking) by 2030 ([15], p. 48, [26], p. 463).

The scenario projections are derived using a bottom-up, partial-optimization model of the global energy system, called the Global Energy and Climate Model (GEC-M), modeling energy demand, transformation, and supply in high detail for 26 regions (11 countries and 15 country groupings). A comprehensive description of the model, the key assumptions, and data sources used can be found in the documentation [21]. Of particular relevance to the representation of battery energy storage in the model are the power and transport sector modules of the GEC-M. The technology-rich power sector module combines an investment model with a high-resolution dispatch model to simulate the evolution of the regional power systems, ensuring that there is sufficient generating capacity to cover peak demand plus a reserve margin, as well as sufficient production to meet the annual demand of all end uses, including grid losses ([21], p. 45). The transport sector module consists of dedicated, regional bottom-up models for aviation, maritime, rail, and road transport. The road transport model projects the evolution of the regional vehicle fleets and their fuel consumption based on, among other things, activity drivers such as historical trends, GDP and population, vehicle scrappage functions, and cost-competitiveness assessments of different drivetrain technologies ([21], p. 32).

3.3 Development of Demand for Battery Energy Storage

The electricity[1] and transport sectors are the key users of battery energy storage systems. In both sectors, demand for battery energy storage systems surges in all three scenarios of the IEA WEO 2022. In the electricity sector, batteries play an increasingly important role as behind-the-meter and utility-scale energy storage systems that are easy to scale, site, and contribute to system reliability and flexibility. In the transport sector, the increasing electrification of road transport through plug-in hybrids and, most importantly, battery electric vehicles leads to a massive rise in battery demand.

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[1] In the context of this chapter, we define “electricity sector” as encompassing the production and all stationary end uses of electricity.

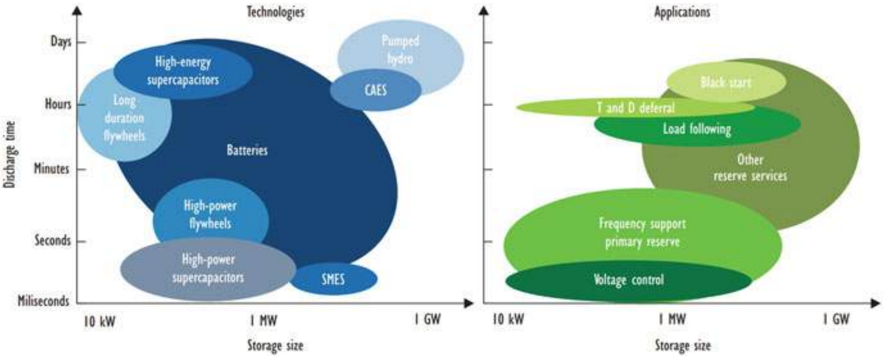

Fig. 3.1 Storage technologies and potential power system applications based on discharge times. Note: T and D deferral = transmission and distribution investment deferral. (Source: IEA [22], p. 64)

3.3.1 Electricity Sector

Energy storage, in particular battery energy storage, is projected to play an increasingly important role in the electricity sector. Storage technologies provide vital system services, ranging from short- to long-term balancing, the provision of operating reserves and ancillary services like voltage control or black start capability, to the management of congestion in the electricity grid. Currently, pumped storage hydro is the most widely deployed storage technology, accounting for 90% of total storage capacity ([22], p. 64), and there is significant additional potential in certain regions. Other emerging options include compressed air and gravity storage for the short-term and hydrogen as an option for long-term storage (IEA, [24]). An overview of several established and emerging storage technologies, as well as their typical capacities and applications, is provided in Fig. 3.1. It shows that, depending on the volume of the battery, battery energy storage systems can dispatch on timescales ranging from seconds to days, over a broad range of capacities. In contrast to other technologies with more specific use cases, batteries are able to provide a broad range of services to the electricity system. Accordingly, battery energy storage systems are the fastest growing storage technology today, and their deployment is projected to increase rapidly in all three scenarios.

Battery storage systems can be distinguished between two classes: utility-scale battery energy storage systems and behind-the-meter battery energy storage systems. Utility-scale battery energy storage systems are directly connected to the distribution or transmission systems. They typically offer much higher capacities and greater storage volumes than behind-the-meter systems. They are relatively compact and highly modular, which allows for scalable battery storage systems to be deployed rapidly in almost any location, an advantage compared to traditional large-scale electricity storage solutions such as pumped hydro. In addition to energy storage, which allows operators to engage in energy arbitrage, helping balance the power system and more cost-effectively match demand and supply, they provide important flexibility services to the system. They can be tapped to provide operating reserves and important ancillary services such as frequency control or helping with the restoration of grid operations after a blackout. Due to their scalability and modularity, they are also promising solutions for the provision of localized flexibility in distribution or transmission systems, helping to address bottlenecks and reducing the need for costly investments into new transmission and distribution infrastructure [5, 24]. Furthermore, there are more and more cases of batteries being colocated with variable renewables in order to "firm up" the latter's electricity production, for example, in Germany or India, where pairing renewables with storage is rewarded through dedicated support mechanisms. Also, where eligible, batteries are increasingly tapped to provide firm capacity in capacity markets ([25], p. 55).

Behind-the-meter battery energy storage systems are connected to the distribution grid behind the utility meter of an individual electricity consumer, typically a household or a small business. Behind-the-meter battery energy storage systems are usually paired with a distributed energy resource, in most cases rooftop solar PV. Behind-the-meter batteries enable consumers to lower electricity bills by maximizing the consumption of self-generated electricity and enabling them to engage in energy arbitrage, i.e., shifting consumption from high to low price periods. The overall magnitude of savings is highly dependent on the level and structure of electricity tariffs and the remuneration consumers receive for feeding electricity into the grid. Variable or time-of-use electricity and feed-in tariffs offer greater potentials for savings using behind-the-meter battery energy storage systems than fixed rates. Another common motivation for the installation of behind-the-meter battery energy storage systems is to improve resilience against interruptions in the power supply from the grid, where behind-the-meter battery storage systems coupled with a distributed energy resource increasingly compete with traditional solutions such as diesel generators [6].

Across all scenarios in the WEO 2022, utility-scale systems account for the majority of battery storage deployment, though the development of both utility-scale and behind-the-meter storage are heavily dependent on the prevailing regulations. In many jurisdictions, net metering[2] regulations that underpin the growth of rooftop solar ([14], p. 36) are holding back investments into behind-the-meter electricity storage. Stronger growth in behind-the-meter systems can be expected should regulation change in ways that encourage self-consumption, such as time-of-use tariffs, and introduce a time-dependent, market-based remuneration for electricity fed into the grid by small-scale generators. However, that growth would not necessarily come on top of the projected growth of utility-scale systems, since (aggregated) behind-the-meter storage can, with the right regulation and the appropriate control technology, provide some of the flexibility to the system that would otherwise be provided by utility-scale batteries.

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[2] Net metering is a billing mechanism that allows consumers to credit self-generated against consumed electricity irrespective of when that electricity was generated.

3.3.1.1 Development of Stationary Battery Energy Storage

In recent years, the pace of installations of battery storage systems has picked up significantly. In 2021 alone, more than 9 GW were installed globally, a nearly 90% increase on 2020. At the end of the year 2022, total global installed stationary battery storage capacity stood at more than 27 GW ([26], p. 311). The speed of the increase has been substantial: just 10 years ago, the global installed battery energy storage was less than 1 GW in total.

Moving forward, battery storage capacity is projected to grow massively in all three scenarios (see Fig. 3.2). In the STEPS, installed global, grid-connected battery storage capacity increases tenfold until 2030, rising from 27 GW in 2021 to 270 GW. Deployments accelerate further after 2030, with the global installed capacity reaching nearly 1300 GW in 2050. Accounting for all announced pledges and policies leads battery storage capacity to grow to 425 GW in 2030 and close to 2300 GW in 2050, a near doubling compared to the STEPS. The pace of deployments is even faster in the NZE Scenario, where installed capacity reaches about 780 GW in 2030 and nearly 3900 GW by 2050, as the electricity sector is the first to be fully decarbonized, by 2035 in advanced economies and by 2040 in emerging market and developing economies.

In the European Union, total installed battery storage capacity rises from nearly 5 GW today to 14 GW in 2030 and almost 120 GW in 2050 in the STEPS, which achieves the agreed objectives, including reaching 32% of renewable energy by 2030, and fulfills all the National Energy and Climate Plans and major policies as of late 2022. In the APS, which reflects discussions on higher ambitions for renewable energy, including the goal to reach a 40% share in gross energy consumption by 2030 within the Fit for 55 package [11] and the G7 commitment to achieve predominantly decarbonized electricity by 2035 [8], battery storage capacity increases to 50 GW by 2030 and more than 200 GW in 2050. In the NZE Scenario, which requires similar emissions reductions by 2030 and 2035, higher energy efficiency and a more responsive demand side require slightly less battery capacity deployments, with installed capacity reaching 180 GW in 2050 [26].

3.3.2 Transport Sector

Despite the massive growth projected in all scenarios of the WEO 2022, stationary battery energy storage capacity in the electricity sector is—depending on the scenario—only equivalent to 7–10% of the combined storage capacity of electric vehicle batteries. This makes the transport sector the by far biggest user of batteries.

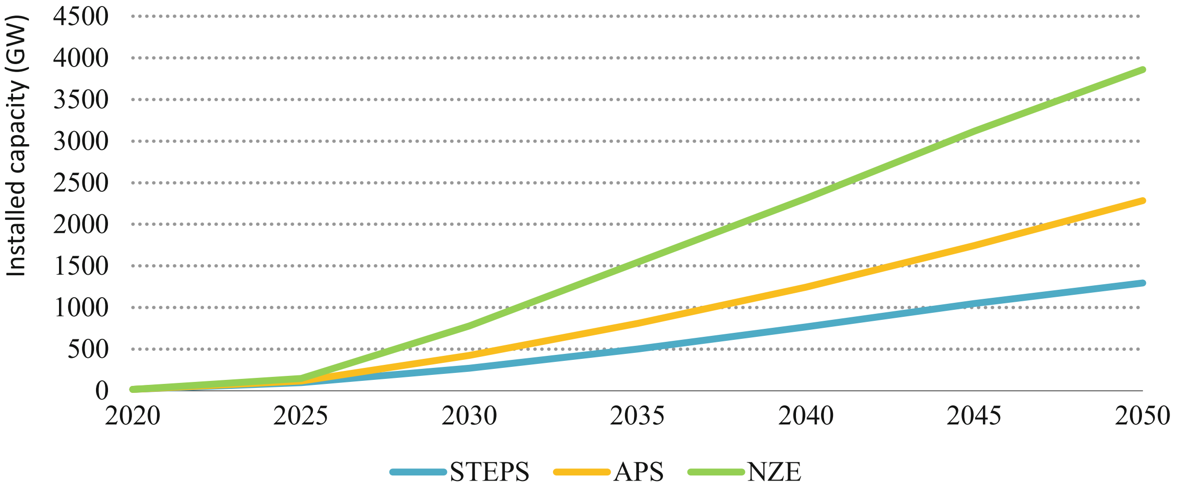

Fig. 3.2 Global installed stationary battery energy storage capacity by scenario, 2020–2050. (Source: IEA) [26]

3.3.2.1 Deployment of Battery Electric Vehicles

In the sector, the vast majority of batteries are used in electric and plug-in hybrid electric vehicles.

Electric vehicles are projected to make up increasing shares of newly registered vehicles across all types of road vehicles (passenger/commercial light-duty vehicles, medium and heavy-duty vehicles, buses and two−/three-wheelers) in all three scenarios.

In 2021, demand for automotive lithium-ion batteries was 340 GWh per year, doubling from 2020 ([26], p. 167), with global electric vehicle sales reaching a record-breaking 6.6 million ([20], p. 4), bringing the global electric vehicle fleet (excluding two−/three-wheelers) to 18 million ([20], p. 99). Nearly 9% of all new passenger vehicles sold were fully electric. China led the world in sales, followed by Europe and the USA [23].

In the STEPS, which considers only policies already in force as of late 2022, the global electric vehicle fleet (excluding two−/three-wheelers) grows to 200 million vehicles by 2030, representing over 20% of all road vehicle sales ([20], p. 99). In the APS, which assumes that all existing targets are met in full and on time, electric vehicle adoption is more rapid, with their share in total sales growing to over 35% in 2030 and total stock reaching 270 million vehicles in the same year ([20], p. 99). In the NZE Scenario, electric vehicle uptake proceeds even faster, and globally, 60% of all new vehicles sold in 2030 are fully electric, with the number of electric vehicles growing to 350 million ([20], p. 99).

The bulk of the growth comes from the light-duty vehicle segment, most notably passenger electric vehicles. In 2021, electric light-duty vehicles accounted for 95% of the global electric vehicle fleet (excluding two−/three-wheelers), and they continue to maintain this share through 2030 in the STEPS. Electric light-duty vehicle sales grow more rapidly in the APS, reaching a share of 35% of total light-duty vehicle sales by 2030. In the NZE Scenario, more than 60% of all light-duty vehicles sold in the same year are electric ([20], pp. 99–100). The rapid expansion of electric vehicle sales is projected to continue after 2030. In the APS, electric vehicles reach a two-thirds share in total new light-duty vehicle sales by 2040. Slow turnover in the vehicle stock means, however, that even in this scenario, the share of electric vehicles in the global light-duty vehicle fleet will exceed two-thirds only by 2050 ([26], p. 275).

Electrification is projected to proceed more slowly in the medium and heavy-duty vehicle segment. While electric trucks are well suited for roles like urban delivery, with relatively short driving distances and the possibility of overnight charging, larger batteries and a high-power charging infrastructure are required to enable long-distance electric trucking. In the STEPS, electric trucks reach a sales share of under 10% in 2030, while in the APS and NZE Scenario, they account for 10% and 25% of sales, respectively ([20], pp. 100–101).

Electric buses are the second most common type of electric vehicle in use today (excluding two−/three-wheelers). Their share in the bus stock is projected to increase to 11% by 2030 in the STEPS, 15% in the APS, and 25% in the NZE Scenario ([20], p. 100).

Although excluded from the total number of electric vehicles presented above, electric two−/three-wheelers are the most common type of electric vehicle today and are projected to remain so through 2030. In many regions, they are already cost-competitive with internal combustion engine two−/three-wheelers on a total cost of ownership basis and projected to see strong growth in Asia in particular. Electric two−/three-wheelers account for over 25% of the stock in 2030 in the STEPS, up from around 6% in 2021. In the APS, 35% of the total stock is electric, while in the NZE Scenario, that share is even higher ([20], p. 101).

The electrification of road transport is proceeding at different speeds across the world. In terms of the distribution of sales, advanced economies and China act as trailblazers, with battery electric vehicles accounting for more than 50% of the cars sold by 2030 in China, the European Union and the USA ([26], p. 274). In Europe, supportive policies ensure that it remains one of the key electric vehicle markets: in the STEPS, light-duty electric vehicles account for 35% of all light-duty vehicle sales in 2030. In the APS, assuming additional policy pledges are implemented, this share rises to over 50%. The 2030 sales shares are 50% for buses and 7% for trucks in 2030 in the STEPS and 55% for buses and 20% for trucks in the APS ([20], p. 104).

The impact on the demand for automotive batteries is substantial. In the NZE Scenario, which sees the strongest growth of electric vehicles to 2030, demand grows 16-fold, from 340 GWh per year in 2021 to more than 5500 GWh per year in 2030 ([26], p. 167).

3.4 Drivers of Demand for Battery Energy Storage

As shown above, demand for batteries is projected to increase substantially until 2050 in all scenarios both in the transport and in the electricity sector.[3]

In the transport sector, this is driven by the rising adoption of electric vehicles, which, thanks to falling costs and supportive government policies, are becoming an increasingly attractive choice compared to conventional internal combustion engine vehicles. and supportive government policies.

In the electricity sector, the adoption of batteries is driven mainly by the rising demand for flexibility, adequacy, and energy balancing that accompanies the rise in the share of variable renewables in decarbonizing power systems.

Rising demand for batteries in both sectors can create a virtuous cycle of falling costs through technological improvements, learning, and improved economies of

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[3] It should be noted that the faster scale-up projected for the APS and NZE Scenario (compared to the STEPS) will require policy and regulatory frameworks to evolve in a manner that reflects the contribution that battery energy storage systems are able to make to the system.

scale, which in turn accelerates deployment, although raw materials costs are likely to play an increasingly significant role ([25], p. 55).

3.4.1 Electricity Sector

In the electricity sector, clean energy transitions change the nature of power systems. Maintaining capacity adequacy—the ability to match demand and supply at all times with a high degree of reliability—is central to energy security, calling for contributions without adding to overall emissions. Rising flexibility needs, linked primarily to the fast-rising share of variable renewables in the electricity mix, bolster the value of dispatchable technologies, particularly low emissions options. Growing demand for solutions that provide power system flexibility and capacity adequacy is the main driver underpinning the rapid increase in battery energy storage capacity projected in the WEO 2022, as falling costs for battery storage improve their economics compared with competing sources of flexibility and adequacy.

3.4.1.1 Rising Electricity System Flexibility Needs

Electricity system flexibility needs are projected to increase significantly compared to today in all scenarios modeled for the WEO 2022. Rising flexibility requirements follow from the increase in variable wind and solar PV-based electricity generation in markets around the world. Furthermore, the electrification of additional end uses, such as electric heating, electric vehicles, or certain industrial processes, raises peak demand, as well as the hourly, daily, and seasonal variability of electricity demand ([26], p. 307).

At the same time, the retirement of a large part of the existing fleet of conventional coal- and gas-fired power plants will increase the demand for alternative sources of flexibility and firm capacity ([23], pp. 308). Battery energy storage systems play an increasingly important role in the provision of system flexibility (the ability of the system to respond to fluctuations in supply and demand) and capacity adequacy (maintaining available electricity supply to meet demand in all hours of the year). Additionally, battery energy storage is projected to become increasingly relevant as a component in renewables-based off-grid electricity supplies, supplanting fossil fuel-based generators.

Battery energy storage systems are highly responsive and able to charge or discharge quickly. The energy-to-power ratios of stationary battery energy storage systems, typically ranging from below 1 to 8 hours of storage at full capacity ([26], p. 312), make them well suited to providing flexibility over timescales measured from minutes and hours to a few days [24]. The change in net load from one hour to the next is thus a helpful indicator for flexibility needs that can be usefully served by batteries.

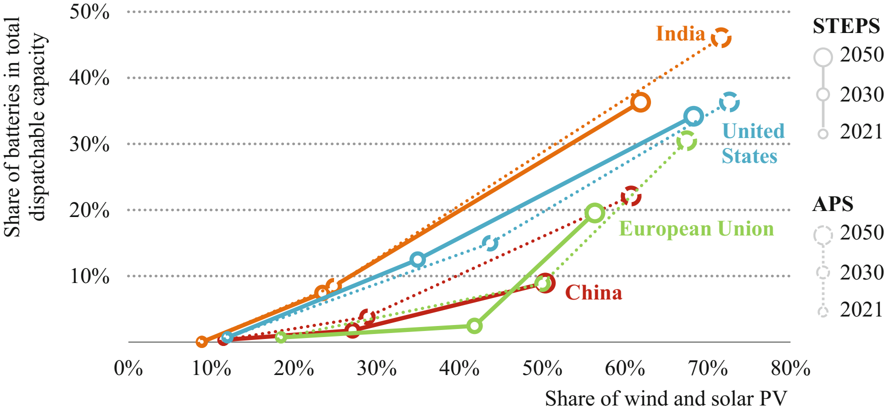

Fig. 3.3 Share of batteries in total dispatchable capacity and share of variable renewables in total electricity generation for the European Union, China, India, and the USA, 2021–2050. (Source: IEA [26], p. 311)

The rising contribution by variable wind and PV increases the variability of the net load.[4] In the STEPS, the share in the global electricity mix of wind and solar PV together doubles from 10% in 2021 to 20% in 2030 and rises above 40% until 2050. In the APS, it increases to 30% by 2030 and reaches nearly 60% in 2050. In the NZE Scenario, it increases to nearly 70% by 2050. As a result, global flexibility needs[5] triple until 2050 in the STEPS, rise more than 3.5-fold in the APS, and quadruple in the NZE Scenario. However, there is significant regional variation: systems which today have relatively small shares of wind and solar PV see a much stronger relative increase in flexibility demand. In India, for example, flexibility requirements rise sixfold until 2050 in the APS, whereas in the European Union—where the combined share of wind and solar PV in the electricity mix was already 18% in 2021—they double over the same time period ([26], pp. 214, 299).

The relationship between the rising share of variable renewables in the electricity mix (and thus increasing flexibility demand in the electricity system) and the increase of stationary battery energy storage capacity (as a share of total dispatchable capacity) is illustrated in Fig. 3.3. It shows that across the four regions displayed, battery capacity rises in tandem with the share of variable renewables in the electricity mix. There are, however, differences between regions and scenarios. In the APS, battery storage capacity rises faster relative to the share of renewables in the system than in the STEPS, since renewables are deployed faster and alternative sources of flexibility, such as coal-fired power plants, retired earlier. Regional

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[4] The net load is the load that remains after deducting the production of wind and solar PV from electricity demand.

[5] In the WEO 2022, flexibility needs are measured by the hour-to-hour ramping requirements after removing hourly wind and solar PV production from hourly electricity demand, divided by the average hourly demand for the year ([26], p. 308).

differences are also the result of the relative share of solar PV and wind in the respective electricity system, as solar in particular is increasingly paired with batteries. Battery deployment thus tends to be larger in places with high proportions of solar PV compared to wind power, like the USA or India, than in regions where wind power predominates, like China or the European Union ([26], p. 312).

3.4.1.2 Contribution to System Adequacy

In addition to providing flexibility, battery energy storage systems also play an increasingly important role in meeting the adequacy needs of the electricity system. In the APS, for example, battery storage is the primary replacement, in terms of system adequacy, for coal, which is mostly phased out globally until 2050. Battery energy storage accounts for nearly 45% of the replacement capacity, followed by dispatchable renewables, most notably hydropower (15%); solar PV and wind (slightly below 15%); nuclear, fossil fuels with carbon capture utilization and storage (CCUS), hydrogen, and ammonia (7–8% each); and new natural gas-fired capacity (4%) ([19], p. 82).

However, the speed of the shift to batteries as a system adequacy resource varies. Advanced economies, which see the rapid phasing down of their remaining coal fleets in the 2030s, see a surge in investments into battery energy storage systems for system adequacy at around the same time, with emerging market and developing economies following suit in the 2040s, coinciding with a major drop in coal capacity there ([19], p. 82).

3.4.1.3 Falling Costs

Innovations in battery chemistry, learning effects, and economies of scale are another key driver of rising deployment, since they continue to drive down the cost of battery packs and components that comprise the balance of system of utility-scale battery energy storage systems, making them increasingly cost-competitive with alternative flexibility options. Spillover effects from the electric vehicle industry play an important role in decreasing the cost of battery packs available for stationary applications ([26], p. 311). "Second-life" electric vehicle batteries are projected to play an increasingly important role, providing an option to cheaply expand stationary battery energy storage [24].

Due to increasing economies of scale and continuous innovation along the supply chain, costs for lithium-ion batteries have already declined by nearly 90% between 2010 and 2021 ([26], p. 167). The average installed cost of battery energy storage systems designed to provide maximum power output over a 4-hour period is projected to decline further, from a global average of around USD 285/kWh in 2021 to USD 185/kWh in the STEPS and APS and USD 180/kWh in the NZE Scenario by 2030. Until 2050, costs are projected to drop to around USD 135/kWh in all scenarios ([26], p. 473), with costs in the STEPS slightly above this value and costs in the APS and NZE Scenario slightly below. This makes renewables, in particular solar PV, combined with utility-scale battery energy storage one of the most cost-competitive solutions to provide dispatchable capacity in many markets in 2050, with the levelized cost of electricity falling below that of new combined-cycle gas turbines ([26], p. 406).

It should be noted, however, that as innovation and learning make batteries cheaper and cheaper to produce, the relative contribution of mineral resource prices to the cost of battery packs increases. In 2022, sharp increases in the prices of key minerals like lithium, cobalt, nickel, graphite, copper, or manganese contributed to a 7% increase in the average price of lithium-ion battery packs, despite an ongoing shift to lower cost chemistries that require lower volumes of certain critical minerals [4]. The projected future cost declines presented above are thus contingent on prices of important minerals returning closer to their historical averages.

3.4.1.4 Policy Frameworks and Regulation

However, while batteries are certain to continue to grow, to get on track for the high levels of deployment seen in the APS and the NZE Scenario, the two more ambitious scenarios of the World Energy Outlook 2022, policies and regulatory frameworks need to evolve.

In the electricity sector, governments should consider energy storage, alongside other flexibility options such as demand response, power plant retrofits, or smart grids, as part of their long-term strategic plans, aligned with wind and solar PV capacity as well as grid capacity expansion plans. Business cases for grid-scale storage can be complex and may not be viable under legacy market and regulatory conditions. In liberalized electricity markets, measures to increase incentives for the deployment of flexibility that is able to rapidly respond to fluctuations in supply and demand could help improve the business case for grid-scale storage. These include decreasing the settlement period and bringing market gate closure closer to real time, as well as updating market rules and specifications to make it easier for storage to provide ancillary services. The business case for storage improves greatly with value stacking, i.e., allowing it to maximize revenue by bidding into different markets. Regulatory frameworks should continue to be updated to level the playing field for different flexibility options, which would help to build a stronger economic case for energy storage in many markets. Transmission and distribution investment deferral (using storage to improve the utilization of, and manage bottlenecks in, the power grid), for example, is another potential high-value application for storage, since it can reduce the need for costly grid upgrades. To capture the greatest benefit, storage should be considered, along with other non-wire alternatives, in the transmission and distribution planning process. A key issue is ownership: in many markets, storage is considered a generation asset, and system operators (transmission as well as distribution) are not allowed to own storage assets. One solution is to allow them to procure storage services from third parties. However, regulatory frameworks need to be updated carefully to minimize the risk of storage assets receiving regulated payments and undercutting the competitive power market [24].

Behind-the-meter battery energy storage is facing challenges on its own. In many jurisdictions, legacy electricity tariff structures do not reward the deployment of behind-the-meter battery storage, which continues to fall behind grid-scale battery energy storage in the projections of the World Energy Outlook 2022. Regulatory changes, such as changes to tariff structures that reward shifting consumption with the help of batteries, could greatly enhance the prospects for behind-the-meter battery energy storage.

3.4.2 Transport Sector

In the transport sector, a combination of falling electric vehicle costs, government subsidies and support for the development of a charging infrastructure, as well as standards favoring electric and other zero emission vehicles is projected to lead to a massive increase in the global electric vehicle fleet.

3.4.2.1 Improving Economics of Electric Vehicles

Falling costs, most importantly for the battery packs, driven by ongoing innovation and improving economies of scale, ensure that electric vehicles become the cost-effective choice for most types of road transport after 2030 in all scenarios, especially in the light-duty vehicle segment. In many emerging market and developing economies, electric two−/three-wheelers are, depending on use, already cheaper than internal combustion engine alternatives on a total cost of ownership basis, and this is projected to become the case for most models by 2025 ([17], p. 76; [18], p. 122). The rising attractiveness of electric vehicles to consumers is reflected in the model range. In 2021, around 450 different models of electric vehicles were available on the market, 5 times more than in 2015 ([20], p. 4).

3.4.2.2 Subsidies and Infrastructure Build-Out

Countries are increasingly looking to boost the uptake of electric vehicles to address concerns around CO_2 emissions and local air pollution. Building on the improving competitiveness of electric vehicles, governments across the world are seeking to accelerate the adoption of electric vehicles through subsidies. Direct per vehicle subsidies like cash bonuses or tax rebates lower the cost of electric vehicles, making them more attractive compared to internal combustion engine vehicles.

Other ways to subsidize electric vehicles include exemptions from tolls and charges, as well as the provision of free or subsidized public charging. Increasing investments in charging infrastructure is necessary to make electric vehicle use more practical and alleviate the problem of range anxiety among current and future electric vehicle users, as well as to make electric long-distance trucking more practical ([23], pp. 275). Furthermore, initial public investments in charging infrastructure are essential to overcome the "chicken-and-egg problem" of providing enough chargers to make electric vehicles more attractive and practical to use while at the same time sustaining an infrastructure that is unlikely to be profitable initially due to the low number of users.

Total expenditures by governments in support of electric vehicles almost doubled in 2021. Some countries, including in the European Union, India, and Japan, have introduced or expanded subsidies, while some markets, such as China, Korea, and the UK, have used the opportunity provided by falling electric vehicle costs to reduce per vehicle subsidies, recognizing the narrowing cost gap between electric and conventional internal combustion engine-powered vehicles ([20], p. 59).

3.4.2.3 Standards and Targets

Standards and targets are projected to play a major role accelerating the adoption of electric vehicles. As of mid-2022, 36 countries and several US states have committed to ending sales of internal combustion engine-powered cars and, in some cases, light trucks, by a certain year ([26], p. 273). With the "Fit for 55" package, the European Union has pledged to ensure that all new cars and vans registered in the block will have to be zero emission by 2035. In an intermediate step, new vehicles will have to comply with CO_2 standards that will require emissions drop by 55% until 2030 for cars and 50% for vans (from a limit of 95 g/km for cars and 147 g/km for vans in 2021) [10]. Globally, 25% of the present light-duty vehicle market is covered by pledges or targets to bring the share of zero emission vehicles to 100% by 2035 ([20], p. 57) (Table 3.1).

Table 3.1 Selected targets to end sales of new internal combustion engine-powered vehicles, by country or state

Year	Country/state	Type of vehicle
2025	Norway	LDVs
2030	Austria, Slovenia, Washington (USA)	LDVs
	Denmark, Iceland, Ireland, Netherlands, Singapore	Passenger cars
2035	European Union, Cape Verde, Canada, Chile, UK	LDVs
	California, Massachusetts, and New York (USA)	Passenger cars
2050	Costa Rica, New Zealand, Connecticut, Maryland	Passenger cars
	New Jersey, Oregon, Rhode Island, Vermont (USA)	

Source: IEA ([26], p. 273)

Notes: LDVs, light-duty vehicles (passenger cars and light trucks). This table covers countries and states with legislation, a target, or stated ambition in place to phase out the sales of internal combustion engine light-duty vehicles

Major automakers are responding by turning increasingly to electric vehicles—not only to respond to regulation but also to maintain or capture market share and retain or gain a competitive edge [20]. A general overview of the electrification plans of different automakers is provided in the IEA Global Electric Vehicle Outlook 2022 ([20], p. 32).

While electric vehicle sales are projected to continue to grow strongly in all scenarios, a slow turnover in the vehicle stock means that the process of electrifying significant portions of the global vehicle fleet will take time and not be completed until after 2050 in the STEPS and APS. The NZE Scenario therefore assumes an end of new internal combustion engine vehicle sales globally by no later than 2035. This will require significant efforts to step up electric vehicle and battery production ([26], p. 276).

3.5 Resource Demand for Batteries

Clean energy technologies, including batteries, require far larger volumes of critical minerals than fossil fuel-based technologies. Copper is a key component of most technologies that produce or consume electricity; silver and silicon are needed for solar PV; rare earth elements are an important component of most wind turbine motors and electric motors, while lithium, nickel, cobalt, manganese, and graphite are crucial minerals for the production of lithium-ion batteries ([16], p. 5), the dominant battery chemistry for electric vehicles and utility-scale energy storage applications, both today and under the projections of the World Energy Outlook 2022 ([26], p. 217).

The energy sector is becoming a substantial consumer of critical minerals as the accelerating transition to a clean energy system is expected to significantly raise demand. For the majority of minerals, the energy industry only made up a minor portion of total demand until the middle of the 2010s.

The energy sector's share is projected to increase significantly over the next two decades: electric vehicles and stationary battery energy storage systems have already outclassed consumer electronics as the largest consumer of lithium and are projected to overtake stainless steel production as the largest consumer of nickel by 2040 ([16], p. 5).

Lithium-ion batteries have emerged as the dominant battery technology in both electric vehicles and stationary battery energy storage applications. They are far more energy dense than competing solutions such as lead acid or nickel cadmium batteries. The production of lithium-ion batteries is mineral-intensive. A battery pack is made up of modules which are composed of individual cells. Cells account for around 70–85% of the weight of the total weight of a battery pack. They contain several minerals, mainly lithium, nickel, cobalt, and manganese (in the cathode), graphite (in the anode), copper (in the current collector), as well aluminum, steel, and microelectronics (for other components of the modules and pack) ([16], p. 90).

3.5.1 Dominant Lithium-Ion Battery Chemistries

Lithium-ion batteries are often categorized and commonly referred to by the chemistry of their cathodes. The choice of chemistry determines a battery's energy density and longevity, which varies significantly between chemistries, and is a key determining factor for the type and amount of minerals required. The most commonly used cathode chemistries for lithium-ion batteries are lithium cobalt oxide (LCO), lithium manganese oxide (LMO), lithium iron phosphate (LFP), lithium nickel cobalt aluminum oxide (NCA), and lithium nickel manganese cobalt oxide (NMC) ([16, 32], p. 90; [29]).

Of the types mentioned above, LCO batteries have the greatest energy density and a relatively high specific energy (150–190 Wh/kg). The primary choice for consumer electronics is a mature technology, with the disadvantage, however, of a comparably short life cycle (500–1000 full cycles). This, coupled with an inherent thermal instability, means they are generally not employed in electric vehicles or as stationary electricity storage solutions ([16], p. 90).

The LMO battery has a high specific power, a longer life cycle (1000–-1500 cycles), and much better thermal stability than LCO. Being cobalt-free is often considered as a key advantage of this chemistry. However, it has a notably lower energy density, in the range of 100–140 Wh/kg. Presently, it finds use in the production of electric bikes and some commercial vehicles ([16], p. 90).

LFP batteries offer high thermal stability and a longer life cycle (more than 2000 full cycles) ([16], pp. 90). Its lower energy density and specific energy (90–140 Wh/kg) mean that the technology has been thus far favored for large-scale stationary energy storage applications and heavy-duty vehicles, where the size and weight of a battery are secondary considerations over safety and durability, rather than passenger electric vehicles or behind-the-meter home storage systems [24]. Nevertheless, owing to several social, geopolitical, and resource constraint concerns, LFP batteries, which do not require nickel, manganese, or cobalt, are today witnessing a massive resurgence in R&D spending to improve their energy density and make them suitable for passenger EVs. These efforts were spearheaded by automakers in China, where in the past year, both domestic and international OEMs like Tesla Motors and Volkswagen have focused on producing LFP-based entry-level EV models.

The NCA battery has the highest specific energy range (200–250 Wh/kg) in the current class of technologies as well as high specific power, combined with a lifetime of 1000 to 1500 full cycles. NCA is the technology preferred by manufacturers like Tesla and has immense potential for use in power systems in backup and load shifting applications. However, they are more expensive than other chemistries ([16], p. 91).

NMC batteries have longer life cycle (1000–2000 cycles) compared to NCA, but a lower energy density (140–200 Wh/kg). They have dominated the BEV and PHEV markets since its commercialization in the early 2000s. While NCA batteries have higher specific energy to their name, NMC batteries possess longer lifetimes, which makes them the favored choice for PHEVs. Manufacturers producing both BEVs and PHEVs, such as General Motors, are known to use NMC variants of lithium-ion batteries ([16], p. 91).

Advancement in lithium-ion battery technology involves more than just the challenge of improving energy density, durability, safety, and cost. It also includes the effort to do so while minimizing the environmental, social, and political costs of acquiring their constituent materials. Owing to price spikes and concerns over ethical mining practices in the 2010s, EV producers have been working to reduce the amount of cobalt in batteries over the past several years—this implies, in many cases, an increase in the quantity of nickel. NCA batteries transitioned to NCA+, a nickel-rich variant of NCA, and NMC 111 batteries have moved increasingly toward NMC 532, NMC 622, and NMC 811 and could move to even more nickel-rich chemistries. This trend of moving away from cobalt could therefore have major implications for the requirement for nickel, which also has a highly concentrated supply chain today ([16], p. 91).

Anodes must complement cathode chemistries. Anode materials are selected for their charge collection capability. Graphite is currently the dominant choice for the anode in most lithium-ion batteries, although certain manufacturers also use lithium titanate instead of graphite. Efforts to replace some or most atoms of carbon in the graphite anode with silicon atoms are underway (e.g., Tesla, Porsche) and are expected to drastically improve the energy density of the cells. However, silicon anodes swell during charging, causing its surface to crack and performance to drop. Another alternative to the graphite anode is pure lithium metal, which also has far greater charge collection capability than graphite. But this anode cannot be used with liquid electrolyte batteries due to undesirable chemical interactions between the electrolyte and the metal anode, which drastically reduces the lifetime of the cell. The use of a lithium metal anode may increase significantly with the advent of all-solid state batteries (ASSBs) ([16], p. 92).

The future technology mix will have a significant impact on the amount of specific mineral resources required for the production of batteries. As shown in Fig. 3.4, different battery chemistries require different minerals in varying quantities. Different assumptions about the evolution of the technology mix can thus have a substantial effect on the amounts of certain minerals consumed for battery production.

Nickel manganese cobalt oxide (NMC) batteries, for instance, usually require roughly eight times more cobalt but only half as much nickel than nickel cobalt aluminum oxide (NCA) batteries. While nickel, cobalt, and manganese are needed for lithium iron phosphate (LFP) batteries, approximately 50% more copper is required compared to NMC batteries ([16], p. 88).

Further uncertainty is introduced by the potential for disruptive leaps in battery technology. As we reach the physical limits of density and life cycle improvements with current technology and materials, notable cost reductions can only be achieved by the disruption of the current technology—for example, in the form of ASSBs with

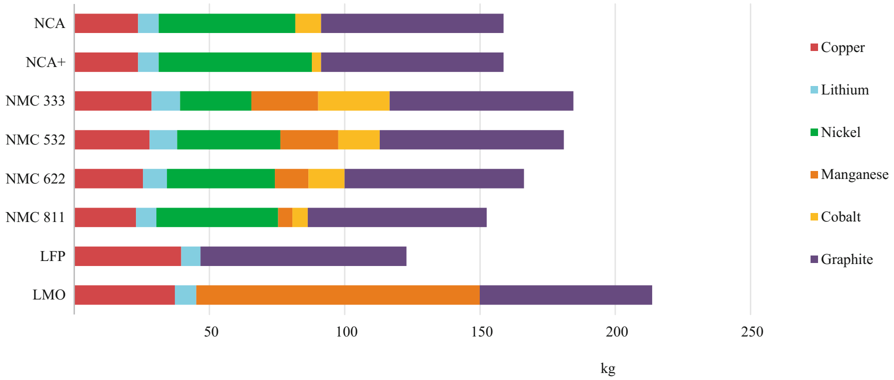

Fig. 3.4 Critical minerals required for the production of a 75-kWh automotive lithium-ion battery using selected cathode chemistries. (Source: Adapted from Ref. [16], p. 89), based on Refs. [1–3, 13, 31]

lithium anodes or through the increased used of silicon in graphite anodes for existing liquid electrolyte chemistries, or through all together new chemistries such as sodium-ion batteries. Therefore, a continued cost decline at the pace observed during the past decade cannot be taken for granted without a further acceleration in technology innovation, and this will be accompanied by changes in mineral demand projections.

3.5.2 Mineral Resource Requirements for the Production of Batteries

While mineral resource requirements for battery production were not quantified for the STEPS, APS, or the NZE Scenario presented in the WEO 2022, the IEA published detailed minerals demand projections in a preceding report. They are based on the IEA Sustainable Development Scenario (SDS) which describes a global pathway for the energy system that achieves the goal of the Paris Agreement, in addition to meeting the United Nations' Sustainable Development Goals.

In the SDS, the transport sector sees battery demand from EVs grow by nearly 40 times between 2020 (160 GWh) and 2040 (6200 GWh). The base case chemistry assumptions project a shift away from cobalt-rich chemistries. This is achieved in both NCA batteries and NMC variants, where the ratio of nickel and manganese is increased in the transition from NMC 111 to NMC 532, NMC 622, and ultimately NMC 811 ([16], p. 97). While most heavy trucks are reliant on LFP batteries in the medium term, the base case also sees growth in the market share of LFP for cars due to its increasing use in China. The base case also sees ASSBs becoming commercially available by around 2030 and requiring another 5 years for manufacturing capacity to build up. Even in 2040, ASSBs remain more expensive than liquid electrolyte lithium-ion batteries and are therefore limited to premium vehicles and advanced economies. In the longer term, heavy trucks operating long haul are likely to use ASSBs as soon as they become available because of the great benefits of energy density improvement in these applications. They would enable increased payload, greater operating range, and shorter charging times ([16], p. 96).

For the anode, natural graphite is expected to continue to account for the majority of market share. Even as artificial graphite starts to replace natural graphite for reasons of improved purity and hence energy density, a small number of manufacturers choose lithium titanate (LTO) instead of graphite for heavier vehicles due to its fast-charging advantages. The dominance of graphite declines very slightly over the years to make way for nanocomposite graphite doped with silicon and for lithium metal that emerges with the advent of ASSBs ([16], p. 96).

Overall annual demand for minerals under the base case chemistry assumptions grows by 30 times between 2020 and 2040, from 400 kt to 11,800 kt. Nickel demand grows by 41 times to 3300 kt, while cobalt increases by only 21 times, as cathode chemistries shift away from NMC 111 toward lower-cobalt chemistries (NMC 622 and NMC 811). Lithium demand grows by 43 times, while copper grows 28 times. Graphite demand grows 25 times from 140 kt in 2020 to over 3500 kt in 2040. Silicon registers the largest relative growth, up over 460 times, as graphite anodes doped with silicon grow from a 1% share in 2020 to 15% in 2040 ([16], p. 97).

In the electricity sector, battery storage grows by 11 times between 2020 (37 GWh) and 2040 (420 GWh). In the base case chemistry assumptions, safe and cheap LFP batteries for utility-scale storage are expected to dominate the overall battery storage market. The remaining demand is covered by the more expensive, but energy dense, NMC 111 and NMC 532 used predominantly for home energy storage. The NMC variants transition toward NMC 622 and NMC 811 in a similar way to the market for EV batteries, albeit with a delay owing to the time needed for transfer of technology and sufficient reduction in prices. Vanadium flow batteries (VFBs) first become commercially suitable in 2030 with a small share, growing modestly to capture a wider market for storage applications in large renewables projects.

Overall demand for minerals in the base case grows by 33 times between 2020 and 2040, from 26 kt to nearly 850 kt. Overall mineral demand outpaces battery demand growth, as the market share for LFP batteries is displaced by more mineral-intensive NMC chemistries. The largest relative growth is seen in nickel, which grows more than 140 times from 0.4 kt in 2020 to 57 kt in 2040. Cobalt demand increases by 70 times while manganese demand increases by 58 times.

The base case projections are founded on a set of assumptions, which, when altered due to reasons of technology advancements, could result in scenarios that produce very different results.

The base case for electric vehicle batteries, for example, assumes an ongoing shift away from cobalt toward nickel-rich cathode chemistries. Growing concerns around nickel supplies, for example, due to price spikes triggered by delays to and cost overruns at planned nickel mining projects, could conceivably slow the shift toward nickel-rich chemistries. The impact on minerals volumes could be substantial: compared to the base case, a delayed shift could result in a nearly 50% higher demand for cobalt and manganese for electric vehicle batteries by 2040. Similarly, a much more rapid shift toward ASSBs could result in higher lithium demand than in the base case but would also reduce the demand for graphite and silicon ([16], p. 99).

The base case for energy storage systems is built on the assumption that utility-scale storage forms a major proportion of the demand, wherein cost (and not space) is the primary concern for the technology selection. However, several alternative scenarios could change the base case projections. For instance, more rapid adoption of wall-mounted home energy storage would make size and thus energy density a prime concern, thereby pushing up the market share of NMC batteries such as those already used by the Tesla Powerwall. Conversely, if the technology for flow batteries, which have the advantage of virtually unlimited energy capacity and very long lifetimes, reaches a stage of widespread commercialization earlier than expected, then utility-scale storage technology could shift away from LFP batteries toward VFBs ([16], p. 105).

The mineral demand projections presented in this section show that the proliferation of batteries in the electricity and transport sectors will lead to a significant increase in the demand for various critical minerals essential for battery production. Scaling up the production of these minerals in a sustainable manner is critical to achieving the deployment rates and cost reductions projected in the scenarios presented above. Today already, raw material prices account for 50–70% of total battery costs. A doubling of lithium or nickel prices, for example, would lead to 6% increase in battery costs ([16], p. 107). It is important to note that in addition to primary production (mining), battery recycling has the potential to be a significant source of secondary supply of the critical minerals needed for future battery demand. IEA analysis suggests that the recycling and reuse of batteries from electric vehicles and stationary storage could reduce primary mineral supply requirements by more than 10% by 2040 ([16], p. 187). Targeted policies, including minimum recycled content requirements, tradable recycling credits, and virgin material taxes, all have potential to incentivize recycling and drive growth of secondary supplies. International coordination will be crucial because of the global nature of the battery and critical minerals markets [24].

3.6 Conclusion

Long-term projections of the development of the global energy system foresee a dramatic increase in the relevance of battery storage for the energy system. This is driven primarily by the proliferation of electric vehicles and a growing demand for electricity storage, connected to rising share of variable renewables in the electricity supply mix.

The IEA WEO 2022 projects electric vehicles to become the dominant technology in the light-duty vehicle segment in all scenarios in 2050, contributing to a massive increase in the demand for batteries. In the electricity sector, battery energy storage systems emerge as one of the key solutions to provide flexibility to a power system that sees sharply rising flexibility needs, driven by the fast-rising share of variable renewables in the electricity mix. Batteries are also increasingly tapped to provide firm capacity as traditional generators, such as coal- or gas-fired plants, are retired.

The ongoing decline in the cost of battery packs is crucial to this. It enables electric vehicles to compete on cost with their internal combustion engine counterparts in more and more use cases. Policies and targets play an important role as well. Zero emission vehicle sales targets, such as the European Union's commitment to 100% zero emission vehicles in sales by 2035, provide guidance to carmakers, many of whom are responding by expanding the model range and setting their own fleetwide electrification targets. Direct and indirect electric vehicle subsidies, as well as investments into charging infrastructure, are boosting the competitiveness of electric vehicles and their practicality of use.

On the stationary battery energy storage side, falling costs, driven mainly by the battery pack, which benefits from spillover effects from the EV industry, but also ongoing learning and economies of scale on the rest of the balance of system, are increasingly making battery energy storage a cost-competitive choice for the provision of flexibility and secure capacity.

The projected rise in battery production leads to a strong increase in demand for critical minerals like lithium, cobalt, nickel, graphite, copper, or manganese. Increasing the supply of these critical minerals in lockstep with demand is essential in order for battery costs to continue to decline.

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Chapter 4
Overview of Energy Storage Technologies Besides Batteries

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Contents

4.1 Introduction

Energy storage systems are grouped by their types of energy storage media into mechanical, electrical, electrochemical, chemical, and thermal energy storage systems. Mechanical storage systems consist mainly of pumped hydro storage, air energy storage, and flywheel storage systems.

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Electrical storage systems store electricity directly in supercapacitors and superconducting magnetic energy storages. Electrochemical storages are commonly referred to as batteries and include lead-acid, Li-Ion, Na-S, as well as redox-flow batteries. Chemical and thermal energy storage systems include, for example, hydrogen, synthetic fuels, and warm water. In addition to the other energy storage systems, they are also essential elements for the energy transition by enabling sector coupling.

The central point for establishing the concept of sector coupling and additionally the concept of power-to-X is the importance of renewably produced electricity for the energy transition and the need to integrate this electricity into the various economic sectors. Power-to-X technologies are technologies that enable this integration and include besides energy storage also material utilization paths. They can be grouped by their concepts into, e.g., power-to-power, power-to-gas, power-to-liquid, or power-to-heat [5].

Regarding the energy storage technologies focused on here, Fig. 4.1 shows the different energy storage technologies sorted by energy storage capacity and storage duration. Storage systems with high capacity and high storage duration are called long-term energy storage and can be used as seasonal storage or for sector coupling with the heating and mobility sector. In contrast, technologies with lower capacity and short storage duration are called short-term storage and are generally used for short-term balancing applications.

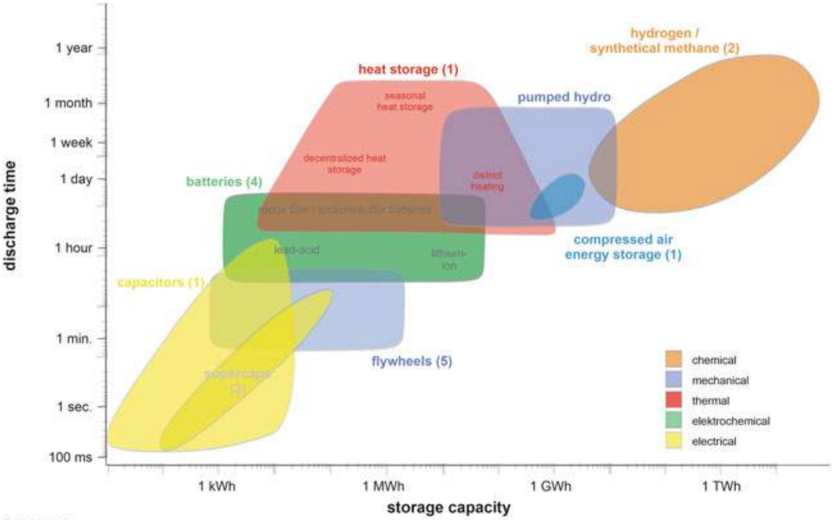

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Fig. 4.1 Overview over different types of energy storage system sorted by storage capacity and discharge time

Electric, mechanical, and electrochemical energy storage applications generally refer to power-to-power applications which remain within the power sector in their function. These can be grouped according to the corresponding segment of the energy system. Figure 4.2 shows an overview of these applications. Depending on the type of application, different storage technologies are better suited to provide the required services.

Power-to-X concepts that connect the power sector with another sector, e.g., the heat, industry, or the transport sector, are referred to as sector coupling. Sector coupling is an important element of the energy transition, as it can make decisive contributions to defossilization in the various sectors [35].

The ecological footprint of energy storage technologies includes a variety of aspects. From a cradle-to-grave perspective, there are different life cycle stages. Firstly is the production stage that includes both the production including all necessary materials and the construction including the transport processes as well as the energy and water and the resulting emissions and waste. Secondly are replacement measures and additional emissions that are caused by the energy storage system itself requiring energy during its operation. In addition, there is an energy loss associated with storing energy due to nonideal efficiencies <100 % of the storage operation. At "end-of-life," the focus is on dismantling, separating, and

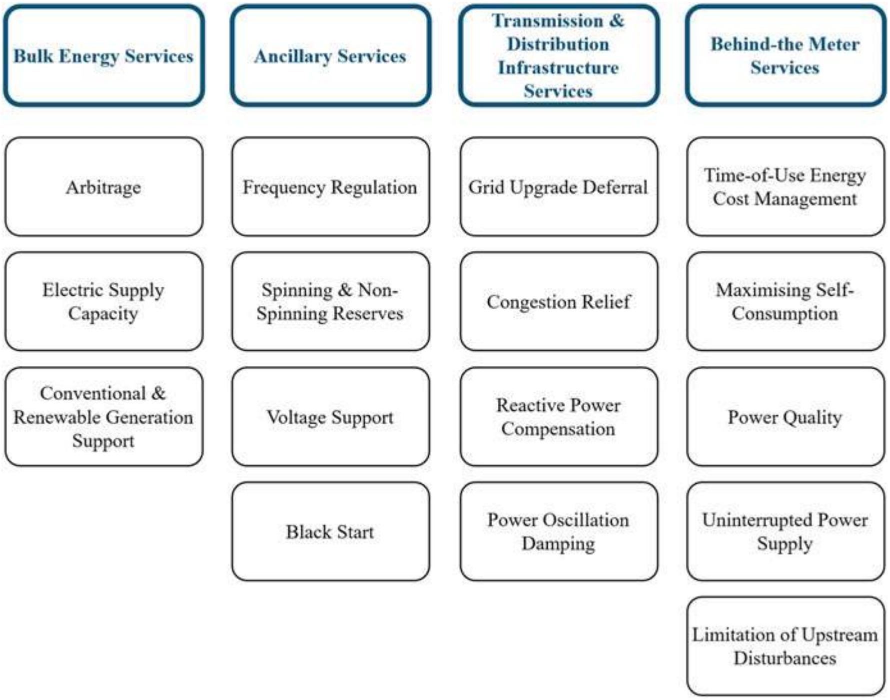

Fig. 4.2 Overview of power-to-power energy storage applications sorted by the corresponding segment of the energy system

disposing of the materials and recycling, including the energy consumption and emissions required for this [14]. Especially the emissions of the respective process chains as a whole are crucially dependent on the emissions of the upstream energy system (fossil or renewable) and the round-trip efficiency of the energy storage system. With a primarily emission-free energy mix, technical aspects such as service life, capacity, and efficiency become the decisive influencing factors [22].

4.2 Mechanical Energy Storage: Pumped Hydroelectric Storage

4.2.1 Operating Principle

Pumped hydroelectric storage (PHES) is one of the most common large-scale storage systems and uses the potential energy of water. In periods of surplus of electricity, water is pumped into a higher reservoir (upper basin). In demand times, this process is reversed, and the potential energy is transformed into electrical power by a generator within a short reaction time [20].

The energy density depends on the height difference between upper and lower reservoir and ranges between 70 and 600 meters, which corresponds to energy densities of 200–1600 Wh/m^3 [21].

There are two different design principles: the tandem design and the use of pump turbines. In the tandem design, pumps and turbines are designed as independent units, whereas pump turbines can function both as pumps and turbines. Pumped storage power plants are characterized above all by high storage capacities and rapid operational readiness.

More than 96 % of installed storage capacity worldwide consists of pumped hydro storage systems. Table 4.1 shows the installed rated power and capacity of pumped hydro in the world since 1990.

With a storage duration ranging from a couple of hours up to several days and reaction times within seconds, pumped hydro storage systems are used for bulk energy services as well as ancillary services.

Table 4.1 Worldwide installed rated power and rated capacity of pumped hydro storage systems [8]

Year	Installed rated power in MW	Installed rated capacity in MWh
2020	181.041	601.684
2010	133.348	448.477
2000	106.841	396.301
1990	84.989	330.191

4.2.2 Ecological Footprint

Of all energy storage systems, pumped hydro storage systems have the longest service life of 50–150 years [2]. Due to their design, they show neither a degradation of the high round-trip efficiency nor the capacity. Because of their low volumetric energy density, however, pumped storage power plants require large areas for storage lakes and a sufficiently high gradient between the upper and lower reservoirs. In practical terms, this means that PHES are primarily implemented in areas with natural height differences.

The main materials in the construction of PHES are concrete[1] and steel. Although these materials have significant CO_2 emissions during production, these are put into perspective by their long service life. The required materials are available worldwide, so they do not have any criticality worth mentioning. The operation and commissioning, which mainly consists of damming rivers or connecting existing lakes, can lead to many negative consequences for the local ecosystems. In particular, the constantly changing water levels can be negative for flora and fauna, but also for possible tourist use. Even if pumps, pipes, or turbines are hardly visible in modern designs such as cavern power plants, the intervention in nature is often viewed with skepticism or completely rejected by those affected. Therefore, "since the 1970s, especially in European countries, this has led to a continuously decreasing acceptance of these energy storage devices among the population" [1].

Decommissioning, dismantling, and recycling play a subordinate role with PHES because of the particularly long service life. At the same time, hardly any materials that are critical for disposal are installed here.

4.3 Mechanical Energy Storage: Compressed Air Energy Storage

4.3.1 Operating Principle

Compressed air energy storage is based on the compression of air and storage in geological underground voids (e.g., salt caverns) at pressures of around 100 bar. When discharging, the compressed air is released and expanded to drive a gas turbine to generate electricity. As air cools down during expansion, it has to be heated while releasing. Here, a distinction is made between diabatic and adiabatic compressed air energy storage.

When discharging a diabatic compressed air energy storage (D-CAES), the released air is heated via combustion using natural gas or fuel. Therefore, a

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[1] The production of steel requires sand as raw material, which has become a scarce resource. However, it is not part of the 2020 EU Critical Raw Materials List, which has been the basis for the evaluation of critical materials in this chapter.

Table 4.2 Worldwide installed rated power and rated capacity of compressed air energy storage systems [8]

Year	Installed rated power in MW	Installed rated capacity in MWh
2020	1.614	40.087
2010	400	2.860
2000	400	2.860
1990 (While [8] doesn't mention any installed CAES before 1990. The CAES plant in Huntorf, Germany, was built in 1978 and is included in this table, based on data from Ref. [30])	290	560

D-CAES system is a hybrid system composed of a natural gas fired open cycle turbine and an electrical storage system.

In an adiabatic compressed air energy storage (A-CAES), the heat produced during the compression cycle is stored using thermal energy storage (TES). During discharging, the stored thermal energy is used to heat the released air. The compressor discharge temperature can reach more than 600 °C. The hot air is sent to a TES which is designed for the applied internal pressure and which is sufficiently insulated to minimize heat losses. The TES can be made of ceramic, concrete, or natural rock materials. In this setup, no additional combustion cycle is required.

Two large-scale D-CAES were installed in 1978 and 1991 in Huntorf, Germany, and McIntosh, USA, respectively. They were used for energy time-shift and spinning reserve for a generally conventional energy system. Since diabatic storage systems still depend on fossil fuels, research has been focusing on A-CAES since then. First commercial A-CAES have been commissioned in 2020 in China and the USA, to support the increased integration of renewable generation in these systems. Table 4.2 provides an overview of the worldwide installed rated power and capacity of compressed air energy storage systems.

4.3.2 *Ecological Footprint*

CAES have the second highest service life of 30–50 years for the machines and even longer for the cavern. Also, they show neither degradation of the medium nor the capacity. Because of their low volumetric energy density, however, compressed air storage power plants require large, pressure-resistant, mostly underground volumes for storing the compressed air. These caverns are mostly salt caverns that are specifically created by leaching. Other types of storage volumes have not yet been implemented for cost reasons. Therefore, only areas where salt caverns exist or can be created have been considered for CAES.

The use of materials (steel, concrete) is significantly lower for CAES compared to PHES and focuses primarily on the machine house with the compressors and turbines.[2] In contrast to PHES, the CO_2 emissions in the production of the components for a CAES are rather low. However, it must be noted that when the salt cavern is drained, extremely high salt loads have to be disposed of by rinsing with warm water. This can cause further emissions during construction through long pipelines or affect flora and fauna through discharge into rivers.

During operation, the CO_2 emissions that result from the additional firing of natural gas for D-CAES systems are dominant. It can be assumed that approx. 98 % of the total CO_2 emissions occur during operation [24]. Modern concepts with heat storage (A-CAES) do not require additional natural gas and are therefore significantly more attractive from an emissions point of view. Both types of construction require little space, as most of the system is underground. For this reason, CAES are hardly viewed with skepticism or rejected by those affected, except during in the leaching and construction phase.

Decommissioning, dismantling, and recycling play a subordinate role with CAES due to the particularly long service life. At the same time, hardly any materials that are critical for disposal are used.

4.4 Mechanical Energy Storage: Flywheel Storage

4.4.1 Operating Principle

Flywheels store electrical energy in the form of rotational energy. The flywheel is set in motion, or its speed is increased with the aid of an electric motor, thus storing energy. The amount of energy that can be stored depends on the rotational speed, since this is proportional to the mass moment of inertia and the square of the angular velocity. If required, the kinetic energy is converted back into electrical energy via a generator. Since the speed of the wheel changes both when energy is stored and when it is discharged, a frequency converter is required to adapt the voltage generated to the grid frequency [20, 26].

Under optimum operating conditions, flywheels can achieve an efficiency of up to 95 %. To keep the relatively high rest losses (approx. 20 % per hour), which are mainly caused by friction on the bearings and on the flywheel itself, as low as possible, the flywheels usually run in vacuum chambers. Furthermore, magnetic bearings with superconductors are used, which significantly reduce losses compared to roller bearings or plain bearings [11].

Flywheels show fast discharge times (within seconds) with high power densities of up to 10,000 W/kg [20].

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[2] For PHES, the use of materials for the machine house is small in comparison with the required materials for building the reservoirs.

Table 4.3 Worldwide installed rated power and rated capacity of flywheel energy storage systems [8]

Year	Installed rated power in MW	Installed rated capacity in MWh
2020	972	97
2010	865	0.2
2000	0	0

Flywheel energy storage systems are mainly used for short-term storage application lasting from milliseconds up to minutes such as power quality services [1]. This can also be seen in Table 4.3, where the installed rated power of flywheel energy storage systems is significantly higher than the installed rated capacity.

4.4.2 *Ecological Footprint*

Compared to battery storage systems, flywheel storage systems have a long service life of more than 20 years in most cases. Also, due to their design, they show neither a degradation in round-trip efficiency nor in capacity. However, self-discharge, which mainly results from air and bearing friction, must be considered in the emissions balance.

Since flywheels—in contrast to PHES and CAES—do not store the energy in the medium of water or air, but in a rotating mass, the use of materials is relevant. The materials used are primarily fiber-reinforced composite materials (e.g., CFRP) or steel. The materials are to be classified as not very critical in terms of procurement, but steel production brings increased CO_2 emissions into the balance, whereas recycling of composite materials is very difficult if not impossible. In terms of safety, flywheels must be secured against bursting, since the usually very fast rotating masses have a high-risk potential. This is often taken into account by building a containment for the flywheel or sinking the flywheels in the ground. Therefore, acceptance problems with this technology are not to be expected [1].

During operation, fundamental losses occur due to self-discharge. With slowly rotating steel flywheels, these tend to be higher than with composite flywheels, but even there they are not negligible compared to other storage technologies. Therefore, the mode of operation (average storage period) is of great relevance, i.e., the losses are higher with longer storage periods, so that in this case the CO_2 emissions—assuming a fossil energy mix—are much higher during operation than during production [24].

Decommissioning, dismantling, and recycling play less of a role with flywheels than with battery storage due to their long service life. At the same time, hardly any materials that are critical for disposal are installed. With composite flywheels, the materials still are a challenge to dispose of, and, unlike steel, they cannot yet be recycled.

4.5 Electrochemical Energy Storage: Redox-Flow Batteries

4.5.1 Operating Principle

Flow batteries are rechargeable batteries which use two different electrolytes—one with a positive charge and one with a negative charge—as storage medium. The most used electrolyte systems are vanadium-vanadium or the iron-chromium. One of the biggest advantages of this technology is the decoupling between power and energy ratings, as tank volume and stack size (active surface area) can be scaled independently.

The electrolytes are stored in external tanks and only pumped through the battery cell for charging and discharging in two separate hydraulic circuits. When operating, oxidation and reduction processes take place at the anode and cathode, which convert the electrical energy into chemical energy during charging and back into electrical energy during discharging. The two half-cells are separated by an ion-selective membrane. As the anolyte and catholyte are stored in separate tanks, the self-discharge rate of flow batteries is nearly zero. Additionally, as the battery electrodes do not actively participate in the chemical reactions, flow batteries are deep discharge proof [12].

Redox-flow batteries have been continually under development and have become more commonly used since 2010 as can be seen in Table 4.4. Applications range from small scale behind-the-meter applications in private households to providing bulk energy and ancillary services. The most common type of redox-flow battery is vanadium redox-flow batteries [1].

The advantage of redox-flow batteries in comparison with Li-Ion batteries is the separation of storage power and storage capacity, which can therefore be chosen individually to fit the application.

4.5.2 Ecological Footprint

In terms of ecological assessment, redox-flow batteries differ from conventional batteries in many respects. The crucial point here is that the energy is usually stored in two liquids, which are stored in conventional containers, mostly made of plastic. The decisive advantage in the design is that the capacity can be precisely adapted to

Table 4.4 Worldwide installed rated power and rated capacity of redox-flow battery storage systems [8]

Year	Installed rated power in MW	Installed rated capacity in MWh
2020	319	1.236
2010	9	19
2000	3	0.8

the application, regardless of the output, so that there is no unnecessary material consumption due to oversizing in output or capacity.

It is advantageous that the materials mostly used (plastic, aluminum) have no or rather low criticality (vanadium), since there are many new exploration projects at an advanced stage worldwide [9, 28, 33]. Nevertheless, it must be considered that the storage medium—in contrast to, for example, pumped storage power plants—is an expensive recyclable material and that vanadium, the electrolyte most used, requires safe containment, since it is a heavy metal that must not be released into the environment. At the same time, however, these mostly double-walled storage containers offer safety advantages compared to some lithium-ion batteries, which have risky materials (e.g., cobalt in NMC cells) finely distributed in each cell due to their design. Likewise, the mostly water-based electrolytes do not pose any fire hazards, in contrast to lithium-ion batteries.

During operation—if neither storage nor withdrawal occurs—only a small amount of self-discharge occurs. When storing and withdrawing, however, the pumps that pump the anolyte and catholyte through the cells of the stack are the main consumers of energy, which is equivalent to self-discharging. As a result, the round-trip efficiency of vanadium redox-flow batteries at around 70 % is also significantly lower than that of other battery types. Therefore, the mode of operation is of great relevance, i. e., the losses are lower with longer storage periods, but significantly higher with frequent charging and discharging. In this case, the CO_2 emissions—assuming a fossil energy mix—are much higher during operation than with more efficient storage systems. This aspect does not apply to a primarily renewable energy mix.

From an ecological point of view, the greatest advantage is that the storage fluids are usually of a single type, uncontaminated, and in liquid form. They can be easily regenerated during operation and simply pumped out at the end of their life and recycled with almost no material loss (related to vanadium). From a purely economic point of view, the value of the electrolyte is an advantage here since recycling is more worthwhile [3]. At the same time, recycling has a positive effect on the criticality of vanadium since the vanadium can be recovered and used in new VRFBs. The aging of the storage media and the associated degradation are also significantly lower than with conventional batteries. A service life of up to 20 years is assumed, which puts the production emissions into perspective [15].

4.6 Thermal Energy Storage: Power-to-Heat

4.6.1 Operating Principle

Power-to-heat applications use electric power to generate or redistribute heat. Consequently, they serve to couple these two sectors. The heat is generated, for example, in electrode boilers, in electric boilers, or by using heat pumps.

In electrode boilers, the operating principle of direct resistance heating [16] comes into effect, where the flow of the electric current through the medium to be heated leads to heat generation. The electric boiler works according to the operating principle of electrical resistance heating, in which a current-conducting heating element heats up and then transfers this heat to the surrounding medium that can be stored. Both boilers are also suitable for steam generation. Both processes are established technologies and are structurally simple and low maintenance storage solutions that can be implemented in different scales. They are therefore suitable for household, commercial, or industrial applications. Electrode boilers in large-scale applications are mainly used in combination with heat networks or to produce superheated steam [18].

In heat pumps, electricity is used to transfer heat from a heat reservoir to a location to be heated using a carrier medium. The transfer occurs in a circular process in which the carrier medium is compressed, liquefied, expanded, and evaporated. During evaporation, it absorbs the heat energy, which it then releases to the location or medium to be heated during condensation. Overall, the transported heat is raised to a higher temperature level in the circular process [27]. Heat pumps make use of ambient heat. The amount of electrical energy required for the circular process is thus less than the amount of energy yielded by the process. The thermal efficiency of heat pumps is therefore very high but varies greatly depending on the type of system and ambient conditions. There is a large number of different types of heat pumps, which differ in terms of process (compression/evaporation or use of other physical principles) and heat sources (e.g., groundwater, ambient air, waste heat) [6].

If the heat pump is combined with a heat storage system, a higher-value utilization concept is created for the energy transition: by storing the heat from power-to-heat processes, the technologies contribute both to meeting the heat-side demands and to integrating renewable electricity into the energy system in the best possible way and providing required flexibilities. In this way, they couple the electricity sector with the heating sector in a beneficial way to the energy transition.

The electricity-based generation of cold by refrigerators (power-to-cold) also belongs to the field of thermal technologies and is also combined with suitable storage solutions [32]. However, electricity-based thermal utilization without intermediate storage is also conceivable, for example, for the provision of space heating by resistance heaters or process heat in industry. Such technologies fulfill a “power-to” purpose if they contribute to the electrification of processes that were previously operated differently.

4.6.2 Ecological Footprint

Power-to-heat systems must be considered separately ecologically for energy conversion unit and thermal energy storage. The thermal storage tanks, which are mostly designed as simple hot water tanks with insulation, have a very long service life and contain no risk materials. The service life of heat pumps is in the range of 10–15 years.

When looking at the materials used, the focus is primarily on heat pumps, as they often have critical refrigerants—the other materials are to be regarded uncritical (standard metals). The refrigerants primarily used to date are fluorinated or partially halogenated refrigerants, the use of which is restricted by the EU regulation (EU 517/2014, F-Gas Regulation) [1]. At the same time, these PFAS (perfluorinated alkyl substances) are very much part of the ecological debate because they are considered persistent and potentially toxic. Therefore, the development goes in the direction of natural refrigerants such as propane. Here, however, the potential flammability and explosiveness of the refrigerant must be considered. This is probably the only aspect that can lead to a slightly reduced acceptance of the power-to-heat technology.

During operation, there are practically no losses. The thermal storage—depending on the storage period—has a low level of self-discharge through heat losses to the outside. Due to their high efficiency, heat pumps have significantly reduced CO_2 emissions compared to natural gas and even electric boilers. Also, no degradation in conversion efficiency or storage efficiency or capacity is to be expected.

Decommissioning, dismantling, and recycling play only a minor role in power-to-heat systems, especially in the storage tanks, due to their long service life. Only the refrigerants of the heat pumps must be disposed of safely.

4.7 Chemical Energy Storage: Power-to-Gas

4.7.1 Operating Principle

Power-to-gas technologies are associated with material conversion processes. Various chemical reactions can be triggered using electric current. Gaseous products are obtained, for example, from various electrolysis processes, from the electric arc process, microwave plasma activation, or single-stage electrosynthesis using CO_2 [10]. Via the electrolysis of water, hydrogen and oxygen are obtained as products. The associated electrolysis processes differ in flexibility and degree of efficiency and in their technology readiness levels. Most developed and market-ready is the alkaline electrolysis (AEL), followed by the proton exchange membrane electrolysis (PEM) and—with a larger distance—the electrolysis using a solid oxide electrolysis cell (SOEC) operating at high temperatures. In an electrolyser, water is split by means of the electric current applied to electrodes which are surrounded by an electrolyte and separated by a semipermeable diaphragma into the anode and the cathode compartment, so that hydrogen and oxygen can be collected separately. AEL uses an alkaline electrolyte and an ionic conductive membrane as diaphragma, while PEM uses solid electrode membrane assemblies to realize the necessary separation. The SOEC also operates with a solid electrolyte as diaphragma. Here, water steam is used instead of liquid water due to the high operating temperatures [29].

Via co-electrolysis, syngas (hydrogen, carbon monoxide) can be produced from the reactants water and carbon dioxide [4]. The electric arc process produces ethyne and hydrogen from methane [17]. Microwave plasma activation decomposes carbon dioxide to carbon monoxide and oxygen [25]. Electrosynthesis can be used to produce alkenes, especially ethene, from carbon dioxide and water [34]. In addition to these direct power-to-gas products, further indirectly electricity-based gaseous products can be synthesized. Via the hydrogen path, methane is, for example, obtained as an indirect power-to-gas product by means of chemical or biological methanation [13]. The electric arc process and the chemical methanation operate at high technology readiness level (TRL), the co-electrolysis and the biological methanation at medium TRL and the electrosynthesis and the microwave plasma activation at low TRL.

The gases produced by power-to-gas processes contribute to sector coupling, since they can be used in a material or energetic way in different sectors, and their storability enables sector-specific requirements to be decoupled from electricity production over time. The power-to-gas products hydrogen and methane are particularly important for the energy storage system, as they can be converted back into electricity in combined heat and power (CHP) systems or fuel cells and thus used energetically.

4.7.2 Ecological Footprint

Up to now, the service life of electrolysers has been in the single-digit range, depending on the type of electrolysers (AEL or PEM) and operating parameters. And—comparable to battery storage—there is a degradation in efficiency.

The materials used (membranes, catalysts) are expensive and some (catalysts) can be recovered, but membranes cannot. Since some catalyst materials are particularly rare (e. g., iridium), the development of a recycling industry parallel to the development of electrolysers production is necessary [19].

In electrolysis mode, the CO_2 emissions can be reduced by around 90 %—compared to the natural gas reforming that is common today [31]. Since the electrolysis process has so far only had an efficiency of approx. 60–70 %, it is obvious that a high proportion of fossil energies in electrolysis would lead to more CO_2 being emitted in extreme cases than if hydrogen would be from natural gas. In addition, it must be considered that—if hydrogen is stored under high pressure (300–700 bar)—additional energy expenditure is required for the compression.

Decommissioning, dismantling, and recycling play an important role in electrolysers because of the rare and expensive catalysts, but also because of the shorter service life [1].

4.8 Conclusion

This overview of energy storage and conversion technologies shows the wide range of possibilities of storing energy as well as providing services to other sectors. It also shows that no single technology alone can provide all the necessary services for a successful energy transition. From short-term storage needed for power applications to medium term storage for balancing applications to long-term storage for seasonal balancing, the different types of energy storage systems offer individual benefits to the energy system. However, they also come with their individual drawbacks, from the use of critical materials to costs and overall efficiency to the issue of recycling. Which of the various energy storage technologies will become the key technologies for a successful energy transition depends on the—changing—boundary conditions such as costs and recycling but also the availability of critical materials. However, it is already certain that energy storage itself is a key technology to enable the energy transition.

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Chapter 5
Batteries: Advantages and Importance in the Energy Transition

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Contents

5.1 Battery Energy Storage Systems Composition

Wind and photovoltaic generation systems are expected to become some of the main driving technologies toward the decarbonization target [1–3]. Globally operating power grid systems struggle to handle the large-scale interaction of such variable energy sources which could lead to all kinds of disruptions, compromising service continuity. Electricity storage systems can help reduce some of the inefficiencies and gaps in the system, helping to increase its reliability, helping to facilitate the integration of renewables, and effectively managing energy production. Furthermore, through the reasoned use of electric energy storage systems, it is possible to facilitate the regulation between supply and demand of electric energy, through a decoupling of electricity production from the load or from the user. Finally, the use

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of storage systems allows distributed accumulation for the increasingly widespread microgrids, which significantly increase the certainty of electricity supply [4].

There are therefore different types of storage systems, and they are defined as mechanical, electrical, thermal, and electrochemical. Among the categories of storage systems, in recent years, the one linked to electrochemical systems, also known as batteries [5], is becoming more and more interesting. Battery uses are commonly divided into two categories—in front of the meter (FTM) and behind the meter (BTM)—depending on where they are placed within the electrical supply chain. FTM batteries can be found in distribution and transmission networks, utilities, substations, and generation plants. In general, the sizes in terms of capacity of FTM storage systems are in the order of MWh. On the other hand, talking about BTM storage systems, generally they are batteries that are positioned in the final part of the supply chain, the user side. Typically, these batteries are smaller in terms of capacity size and are used in residential, industrial (as backup generators), commercial, and transportation [6–8]. Among the various categories of batteries, those based on lithium ions are increasingly used; however, there are different chemical compositions that are used depending on the applications. Lithium-ion batteries, among the most common today, thanks to their high specific energy value (3.86 Ah/g), are used in electric vehicles and also as storage systems to support the grid and can be of different sizes. With that type of chemistry, it is also easy to avoid the memory effect of the batteries; they also have a low self-discharge and are also safe in environmental terms. In addition to high specific energy and high load capacity, power cells have long cycle life and long service life, with little need for replacement. They are characterized by their high specific energy density, low internal resistance, and relatively short recharging time. Among the disadvantages, however, there are the high temperatures and charge levels, which accelerate the degradation in terms of accumulation and, moreover, require a protection circuit that prevents heat dispersion during overloads. This means that high value of C-rate must be avoided, in order to prevent undesired temperature raise, able to generate thermal runaway phenomena, which affect the storage system with fire risk. Another type of battery is lead-acid, cheaper than the previous ones, but less efficient in charge, less durable, and with a limited specific energy and power compared to other technologies [9, 10]. Even if the treatment for their disposal is easier with respect to Li-ion, where innovative methods are studied to recover materials, also lead-acid batteries require a special operation for the disposal; otherwise, they risk becoming harmful to the environment. Nickel batteries, on the other hand, have longer life cycles than lead-acid battery and have a higher specific energy; however, they are more expensive than lead batteries [11–13]. Open batteries, usually indicated as flow batteries, have the unique capability to decouple power and energy based on their architecture, making them scalable and modular with moderate cost of maintenance. They are used as energy backup, covering long duration energy storage timeframes up to 1 or 2 weeks, but also load leveling and peak shaving applications for the transmission and distribution of electricity. These batteries have a specific energy significantly lower with respect to Li-ion, generally used for shorter timeframes (up to 8 hours), but flow batteries are simple to update and easily integrated, however, they are an innovative technology and are still being studied and improved today. There are currently new flow batteries in development, but also more mature technologies such as vanadium redox flow batteries (VRFB). In this case for high capacity to power ratio, the cost per stored kWh is lower than for lithium-ion batteries [14]. The batteries are then integrated with other systems, with which they create a more complex architecture defined as battery energy storage system (BESS), which can work with a centralized or distributed architecture. Conventional centralized architectures consist of the following:

- The battery pack: the electrochemical storage system, which transforms electrical energy into chemical energy during the charge phase, while the opposite occurs during the discharge phase. The energy released during discharging can be used by the user for the various purposes previously described.
- The battery management system (BMS): The BMS takes care of the correct and safe functioning of the battery. Since each battery has preferential operating conditions, the BMS ensures that these conditions are met. Furthermore, the BMS takes care of monitoring the residual energy inside the battery and its state of health (SOH), so as to optimize performance.
- The power conversion system (PCS): The PCS is the interface with the grid and allows the DC terminal of the battery to communicate with the AC terminal of the grid. Since the AC current has a certain mains frequency, an electronic circuit called phase-lock-loop (PLL) is used to synchronize the current leaving the battery with that of the mains.
- The energy management system (EMS): The EMS control unit is the equivalent of the BMS applied not to the battery but to the entire BESS. EMS links all elements of the BESS together and optimizes the performance of the entire system.
- The safety system: It is generally structured on several levels, each responsible for a specific task.

Subsequently, it should be remembered that each type of BESS has certain technical specifications that characterize the efficiency of the system [15]. It is clear that the first characteristic parameter is the storage capacity, i.e., the amount of electric charge that the battery can accumulate and that the BESS can make available. Another parameter of primary importance is the nominal power, a characteristic that specifies the amount of power that the BESS can transmit. The round-trip efficiency represents the ratio between the energy emitted during the discharge phase and the energy supplied during the battery charge phase. The depth of discharge (DoD) represents the percentage of energy discharged with respect to the maximum capacity. Battery lifetime is also a relevant parameter for choosing the storage system and is calculated through the number of battery charge and discharge periods; otherwise, it can be expressed as the total amount of energy that a battery can supply during its life. Finally, the safety parameter is important in determining the suitability of the battery for a particular use.

5.2 BESS Application as Grid Integration

Therefore, considering the decarbonization trend in the field of electricity production, it is clear that the development of these storage systems can facilitate the energy transition. In fact, following the decarbonization trend of the various sectors, the national electricity requirement is only increasing, rising the electrical demand. The typical electrical demand curve has peaks at certain times of the day, one in the morning and one in the evening. This demand is compensated for by various energy sources, in a manner compatible with the national energy production mix. Energy sources, both renewable and nonrenewable, have precise start-up times; in fact, depending on the time of day, a specific energy source is used. For example, coal-fired plants require very long start-up times; therefore, the fund of energy demand is met through the use of these plants. Conversely, systems whose start-up is much faster, such as gas cycles, for example, can compensate for the momentary peaks encountered during the day. Qualitatively, the shape of the demand curve is similar in the various days of the week; therefore, the presence of these peaks is almost constant. Finally, the production curve will have to be capable of punctually following the demand curve. However, starting up these gas-fired plants is both expensive and polluting. Therefore, the integration of storage systems within the electricity grid could contribute to the damping of these peaks, making it possible to avoid the start-up of gas-fired plants. This attempt to dampen peak loads is also called peak shaving. The application of the peak shaving technique, through the use of accumulation systems, also helps to avoid grid oversizing, which would be necessary for peak hours. Furthermore, it must also be considered that sudden variations in demand generate grid instability, in terms of voltage and frequency [16]. Such fluctuations would risk damaging the quality of the supply service. The use of the peak shaving technique would therefore make it possible to absorb electricity when demand is lower, and then release it when it is higher. However, it should be considered that the integration of the various renewable resources within the electricity grid, however, only increases the variability of the production curve. Following the principle described above, there is another technique that is establishing itself to facilitate the integration of renewables. If peak shaving technique aims to remove the generation peaks, load leveling is a technique that is used to level the load curve [17, 18]. The operating principle is similar to that of peak shaving, absorbing power from the grid when demand is lower and then returning it when demand reaches its maximum daily values. Therefore, the damping of peak power demand can be facilitated, if accompanied by a prudent tariff policy which, by combining the price of power and energy supplied, makes it convenient for a user to purchase such storage systems. Therefore, the two techniques end up combining perfectly, since the user's peak shaving operation leads to load leveling for the supplier. Therefore, the user, through an automatic BMS, applies a daily peak shaving, optimizing the management of electricity and, consequently, saving the user. In fact, in doing so it is possible to stipulate a contract with the distributor at a lower peak power, since the peak beyond the maximum established level required by the loads would be filled by the accumulation system. For the supplier, however, this procedure means a leveling of demand (load leveling), improving efficiency in the power generation and transmission phases, avoiding construction costs linked to infrastructural upgrades.

Furthermore, as previously mentioned, the network may be subjected to instability. Among these instabilities are voltage dips. Voltage dip is defined as the temporary reduction of voltage below 90% of the declared voltage for a period greater than or equal to 10 milliseconds and not greater than 1 minute, where the conditions for interruption do not exist (definition taken from standard CEI EN 50160); the unipolar voltage dip is a voltage dip that affects only one phase [19]. These instabilities generally originate from faults in the public network or in network systems, sometimes linked to overloads of starting transients of large motors or to the insertion of significant loads. These holes are unpredictable, and their annual frequency is variable and is not attributable to the network operator or local distributor. In addition, data processing and control equipment can experience data loss and require time-consuming maintenance in the event of a significant voltage sag. In addition to this, voltage sags lead to economic losses. If previously diesel generators such as UPS (uninterrupted power supply) were used to compensate for the existence of voltage dips, today the use of electrochemical storage systems would facilitate the management of voltage dips, thanks to BMS systems [4]. Similarly, it has been studied that when there are fluctuations in the network frequency, due, for example, to the variation of the rotation speed of synchronous generators, the use of batteries considerably facilitates frequency regulation [20–22]. Therefore, to condense the various uses applied to the network, it is possible to state the FTM applications to which the BESSs should be applied:

- Bulk energy services: mass energy service process, which increases the capacity that can be supplied by the electricity system, thanks to the accumulation of massive quantities of energy to meet the peaks. At the same time, it is possible to accumulate electricity in the time slots in which it has a low cost, to sell it at a time in which the demand is higher and the cost of energy is higher.
- Ancillary services: e.g., all those systems that support the transmission of energy from the production site to the user and that help to maintain the usability of the system. Ancillary services can be generators or connected service providers capable of rapidly increasing the output of potential reserves, regulation, and flexibility (e.g., frequency regulation, voltage regulation, black start).
- Transmission and distribution network support: Expansion of the transmission network to avoid unwanted congestion can be expensive, and installing a BESS can be more cost-effective. Furthermore, with the growing contribution of renewables to the local distribution system, the power fluctuations in their output can create voltage fluctuations and damage the equipment connected to the system. A BESS can take part in voltage regulation, stabilizing the system.
- Integration of renewables: The integration of batteries into variable renewable energy production systems helps to give greater stability to the electricity grid. Capacity firming is widely used, for example, with the production of wind and

solar energy and has advantages such as the optimization of the generation profile, supply, and exchange of reactive power in support of renewables and balancing of load currents [23].

5.3 BESS Integration in Transport Sector

If on the side of the electricity system, electrochemical storage systems represent a great opportunity, within the transport sector they represent a necessity. Indeed, the use of batteries within the mobility sector has become the engine of the decarbonization of this sector. Although electric means of transport have already existed for some time, electrification through battery-mounted vehicles has undergone significant development in recent years. Furthermore, the different needs related to the different types of vehicles have also favored the study of new accumulation chemistries related to the different types of vehicle that use them. NMC (nickel-manganese-cobalt), LFP (lithium-iron-phosphate), and NCA (nickel-cobalt-aluminum) batteries are among the most used onboard road vehicles. Meanwhile, other studies of electric vehicles that require more effort in power use other types of chemical compositions such as LTO (lithium-titanate) [24]. In any case, batteries represent a fundamental prerogative for the electrification of electric vehicles, as much as they represent for the creation of a recharging infrastructure capable of supporting the electrification of the mobility system. With the increase in the number of electric vehicles on the market and in use, local distribution networks risk running into overloads. This is due to the fact that some users, such as those who are driving along a motorway, suddenly need high power to quickly recharge their exhausted vehicle through fast charging. The use of a distributed storage system helps to reduce the maximum load that must be supported by the transmission and distribution infrastructure by implementing BESSs in the vicinity of the electrical loads. The integration of BESS systems within the electricity grid brings various advantages, such as the provision of ancillary services for the distribution system operator (DSO) and transmission system operator (TSO). Based on these considerations and with the increase in the use of electric vehicles, the attention on the integration of BESSs, based on Li-Ion batteries, in charging stations has increased. Interest has been brought both to the domestic use of these batteries, to integrate the solar home systems (SHS), for vehicles, and with public recharging infrastructures.

Indeed, it is evident that, despite all the benefits that follow the electrification of means of transport, there is an increase in the demand for electricity to power them, with a considerable impact on the electricity grid. In fact, the presence of multiple charging infrastructure systems that require very high powers easily creates voltage dips and voltage instability, which represent one of the main causes of blackouts, since, as mentioned, the supply system works very close to the limit of stability, since the power demand is very high. The electrical loads associated with the rapid recharging of vehicle batteries, in addition to requiring significant amounts of power from the grid, are also highly nonlinear. The characteristics of nonlinear loads have a non-negligible impact on the network; therefore, it is advisable to recognize them. Such nonlinearities, for example, affect voltage stability, making in-depth studies in this regard fundamental. It is recognized that careful planning of the use of charging infrastructure can smooth out voltage fluctuations [25]. At the same time, careful planning of the charging phases of electric vehicles prevents the emergence of unwanted peaks in the demand curve [26]. Among the other critical issues that can be encountered are those that are identified as power quality (PQ) problems, deriving from harmonics and voltage imbalances that occur in the event of crowding in the recharge. In addition to voltage dips, unwanted peaks in demand, and PQ problems, an increase in the EV penetration rate can increase grid power losses, proportional to the number of feeders in the destruction system, augmented by the additional losses inherent in the recharge [27, 28]. The last of the critical issues to be submitted is the overload and overheating of distribution transformers, which are particularly stressed in the event of a request for high powers. Operation of transformers at temperatures higher than the nominal ones causes premature aging, reducing the useful life of the transformer [29]. However, despite the critical issues reported, electric mobility, if properly integrated with the smart grid, can assist in the dynamics of peak shaving. In fact, it is known that for most of the time during a day, the cars of private users remain parked and consequently unused or are used for limited trips. Based on this consideration and on the recent developments of the intelligent grid, which has evolved in a bidirectional perspective, thanks to the advent of distributed generation, we thought about how to optimize the times in the stall phase of the cars. The vehicle-to-grid (V2G) technology was born from this idea.

5.4 Electric Vehicle and Infrastructure Interaction

With the increase in technological availability and sensors in the field of mobility, it is correct to say that the entire sector, by imitating the distributed generation of dispatching, has evolved from a bidirectional perspective. If previously, the vehicle had a one-way interaction with the infrastructure, this is no longer the case. In fact, previously four charging methods have always been considered, which differ in power and protections, which transferred electric power from the charging infrastructure to the vehicle, stationed in a dedicated space. The traditional one-way charging procedure was then renamed as V1G, which means intelligent charging. Through intelligent recharging, the vehicle is able to change the recharging timing dynamically, since in addition to power, the vehicle and the infrastructure exchange information, which allows recharging to be regulated, helping to minimize its costs. Among the advantages of V1G, in addition to charging monitoring and timing optimization, there are also the infrastructure localization tool and the possibility of charging the vehicle at certain times of the day, so as to have greener and at the same time cheaper energy [30]. If sensoring and artificial intelligence (AI) have been fundamental in the development of intelligent recharging, the integration of a bidirectional power inverter connected to the car battery and to the grid represents the heart of V2G technology. The improvement that V2G brings to V1G is the possibility of having a vehicle that is not only able to draw power from the grid to recharge the battery but is also able to return power to the grid at times of the day when it is most stressed. These energy flows are obviously managed by a control unit, which ascertains the needs of both the network manager and the user. Following the description of the increase in electricity demand, the need to dampen peaks, the need to level the load, and the value that electrochemical storage systems will have to meet all the needs of the network, the V2G technology, which exploits the power that could be supplied by vehicles that remain parked and unused for most of the day, is perfectly combined with the demands of the network. In doing so, from an electrical point of view, the vehicles are seen by the network as many distributed accumulation systems from which it is possible to draw power to level the load curve [31, 32]. If this technology is seen from the point of view of a broad distribution network, in the various bibliographic studies, its applicability at the local level has not been overlooked. When the V2G technology is applied locally, and therefore on a building or at home, it takes the name of vehicle-to-building (V2B) or vehicle-to-home (V2H), respectively. The operating principle of V2B and V2H is the same and very similar to that of V2G but limited to a single building: with the integration of renewables and their variability, the generated power becomes fluctuating, sometimes creating power excesses or imbalances; therefore, vehicles are used as real batteries to receive or deliver energy according to the demand curve. In that case, the power transmitted by the vehicle can be applied to prevent service interruptions and blackouts locally [33]. Finally, to complete the description of the interactions between the vehicle and the surrounding world, vehicle-to-everything (V2X) should be mentioned. The V2X is based on the interaction of the vehicle with any object that surrounds it—vehicles, infrastructures, people, and traffic—in order to improve the driving experience. This technology is also strictly dependent on the high level of sensing. What prompted private companies to invest in V2X technology was the better management of roads and traffic, which are supported by AI through various algorithms and predictive models, but at the same time it encourages safer driving, thanks to continuous communication of data with the surrounding vehicles and infrastructure and energy savings. Today with V2X, we mean the possibility that the vehicle has to interact, in a bidirectional way, with any object that surrounds it [34]. It is clear that, with the increase in the diffusion of renewables and the electrification of the transport sector, the possibility of having energy storage systems available in a distributed manner represents an important push toward decarbonization, since they would help to combat the variability of the production and demand. At the moment, however, a remuneration policy has not yet been clearly defined for those who decide to join the sharing of energy toward the grid. Remuneration to those who subscribe to the V2G service is important, not only because users are actively supplying energy to the grid rather than recharging but also because users are subjecting their vehicle to continuous charge and discharge cycles in the process, potentially contributing to battery aging [35].

5.5 BESS Lifetime

Although today we have a thorough knowledge of electrochemical storage systems, still today there are several limitations related to BESSs, and the most relevant is precisely the useful life of rechargeable batteries, which degrade with aging. This event represents a problem for applications such as electric vehicles, since battery degradation implies a reduction in capacity and consequently a limitation of the vehicle's travel range. As a result, EV manufacturers have a tendency to oversize the battery, to make the driving range appear constant, over the life of the battery. However, this technique only increases the cost and mass of the battery. Complicating matters is the fact that the degradation process of lithium-ion batteries is nonlinear, requiring knowledge of the materials that make up the battery, internal reactions and knowledge of aging processes. Normally, the useful life of the battery is characterized by a predefined number of charge and discharge cycles to which it can be subjected, which can vary depending on some factors during the life cycle, decreasing its efficiency. For batteries, there is a specific parameter that indicates the condition of the battery, called state of health (SOH). SOH indicates the level of performance of the storage system, based on voltage, self-discharge, and internal resistance. This parameter varies in the range 0–1, and an SOH equal to 1 indicates a battery at the beginning of its useful life, in which the capacity, in kWh, is maximum. Among the factors that influence the useful life of the battery, the first is the aging and degradation of materials. After that, the working environment is one of the factors that influence the useful life of the batteries. Specifically, if a battery worked in an environment with a temperature that was too high or too low for its operating range, the activity of the electrode would end up decaying. Therefore, maintaining an operating temperature range in line with the nominal one has a positive impact on battery life. Maintenance and cleaning factors, which facilitate the functioning of the components, should not be overlooked. Another factor that impacts battery life is the charge and discharge cycle. The succession of charge and discharge cycles implies a decrease in capacity, also due to the internal degradation of the materials. The factor that most significantly impacts the useful life of the batteries is the depth of discharge (DoD). The higher the DoD, the shorter the useful life of the battery; therefore, a charge and discharge cycle with a controlled and optimal DoD helps to significantly extend the useful life of the battery. The different chemistries of the storage systems will then have operating ranges and different DoD [36–38]. For example, for lithium-ion batteries, which have a wide range of uses since they are excellent for both power and energy applications, they have an optimal state of charge (SoC) operating range between 20% and 80%. Within this range, the duration of the useful life of the lithium-ion battery is maximized. Furthermore, by respecting this range, the amount of energy stored in the batteries is optimized with respect to the recharge time [39]. Current also has a major impact on the life span of the cells and consequently on the battery and the number of cycles it can withstand. Batteries that are subjected to higher discharge currents have a shorter life.

5.6 BESS Dismission and Second Life

Downstream of the knowledge of how the useful life of the batteries works and is interpreted, it is useful to describe how these storage systems are decommissioned. When it comes to decarbonization and reducing the environmental impact through electrification, it is often mentioned that the disposal of batteries is a complicated and not always green process. In addition, despite the lowering of battery costs relative to capacity, batteries still have a significant cost, for example, for an electric vehicle the battery can be worth 50% of the total cost. Therefore, to respond to these two needs, various stakeholders have undertaken various studies on the second life of batteries. Second life has the purpose of ensuring a recovery of the functionality of the batteries at the end of the life cycle, converting them into stationary accumulation systems. For example, the useful life of a lithium-ion battery applied to electric vehicles has a duration in charge and discharge cycles equivalent to 8–10 years. After this time, the battery is removed from the vehicle even if it still has some remaining capacity, as this is not sufficient to meet the standards for electric vehicles. However, the battery can still be useful for other energy storage purposes, such as, for example, the inclusion of storage systems in the charging infrastructure for electric vehicles, which help to sustain the grid. The three main benefits that can be generated to the smart grid by reusing batteries after their first life are as follows:

- Defer and limit expenses related to the production and sale of new batteries.
- Provide energy reserves that allow continuity of service, especially in industrial processes powered by other energy sources.
- Use the available energy previously accumulated in times of absence or high cost of raw materials.

Typically, end of life (EOL) is considered to occur when actual capacity reaches 80% of rated capacity. Similarly, the end of the second life is considered to occur when the actual capacity reaches 30% of the nominal capacity. For this reason, half the nominal effective capacity is considered for stationary applications where batteries are used during their second life, since it is considered the middle ground between 80% maximum nominal capacity and 30% minimum rated capacity. The theoretical value 50% of the nominal capacity is considered for practical purposes, since it is approximately possible to have a desired capacity value with a number of second life batteries equal to twice the number of first-life batteries that would be needed to have the same capacity [40].

Among the BTM areas of application with the greatest interest in the second life of batteries are the fast-charging systems (DC fast-charging stations) with which it is possible to reduce charging times. Using batteries during their second life to assist recharging stations, it is possible to guarantee high peak currents, accelerating recharging times, avoiding oversizing of the network. This solution also represents an opportunity for savings or income for car manufacturers, which have resalable batteries in proportion to the range of vehicles they put on the market. Instead, the FTM applications that best lend themselves to a second life are those related to transmission services and energy shifting, a practice that aims to distribute energy production throughout the day. These applications present marginal installation space problems; in fact, it should be remembered that second life batteries occupy twice as much space as first-life ones.

On the basis of these considerations, therefore, it is possible to deduce that some BESSs are particularly suitable for use as storage systems during their second life, such as those based on lithium ions. Among the applications that these storage systems can perform during their second life are as follows:

- Peak shaving: process of damping power demand peaks through the activation of local energy sources or using an accumulation system.
- Power upgrade deferral: Through the BESS, it is possible to provide additional capacity, and with low growth rate loads, it is possible to postpone infrastructural interventions.
- Time-of-use energy cost management: BESSs can help end users reduce the cost of the service by smoothing demand into preset daily peaks.
- Self-production optimization: A BESS can assist standby generators by extending uninterrupted service time, reducing inefficient start-ups, and reducing fuel requirements for diesel powered UPS systems.
- Integration of renewables: Renewable energy sources are fluctuating by nature and depend on several variable parameters. These variations cause frequency and voltage fluctuations, causing grid instability. A BESS system even in its second life can help compensate for grid imbalances.
- Energy independence applications: Batteries during their second life can be integrated into microgrids, useful for powering users, which can range from buildings to neighborhoods. Microgrids are often powered by renewables; therefore, BESSs prevent grid imbalances.
- Support for fast-charge recharges: The possibility of integrating BESSs during their second life into high-power infrastructures helps to reduce energy costs and avoid grid peaks. The station could also move toward net-zero energy consumption with the assistance of a BESS.

Despite the existence of different applications for batteries during their second life, there are applications where high-power density and instantaneous service with a high C-rate are required, which do not make second life batteries suitable for the task. Among the high-performance applications, there are those of backup or support to the network to increase the power quality. Therefore, even reactive power compensation operations require too high performance and significant stress levels for batteries during their second life [41–43].

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Part III
Battery Markets

Preface

The market for batteries, in particular lithium-ion batteries that constitute the presently dominating technology, keeps growing at stunning pace, and technological boundaries are being pushed further. There are several markets for stationary, mobile, and portable applications, which are all characterized by different requirements and that are subject to high dynamics in line of the ongoing energy transition. For example, new policy regulations, the pandemic, and the ongoing war in Ukraine have triggered several developments that lead to an increased demand of batteries for stationary and mobile applications. One of the most striking developments is the fast growth of electric mobility which is gaining a high momentum triggered by China and the USA. At the same time, batteries are gaining more and more attention for stationary applications, starting from residential on a kWh size to bulk storage with multiple MWh capacities. The first section, i.e., Chapter 6, analyzes in detail the battery market fragmentation, upcoming requirements, main drivers, and challenges of stationary, mobile, and portable applications. In the following Chapter 7, foreseeable developments in battery technologies, markets, key performance indicators, and demand scenarios are discussed along with most relevant battery use cases. In addition, new research trends for future market developments are assessed and broken down to lithium, new cell materials, cell and manufacturing design, recycling, and the use of raw materials.

Chapter 6
Battery Market Segmentation

Stefan Wolf and Javier Olarte

Contents

6.1 Introduction

Batteries are used in a large number of different applications. The spectrum ranges from grid-connected stationary battery storage in the megawatt-hour range to extremely small batteries in the microwatt-hour range that can be integrated into electronic systems. Each use case places different demands on the battery. Accordingly, there are major differences between the battery technologies used, both at the level of the cells and at the battery systems level. In many applications at the system design phase, engineers select the battery technology in a tradeoff between cost and application requirements. The sweet spot in this tradeoff is different from one application to another. Scientific literature provides a set of KPIs to describe battery characteristics that allow to compare them with each other. In many cases these

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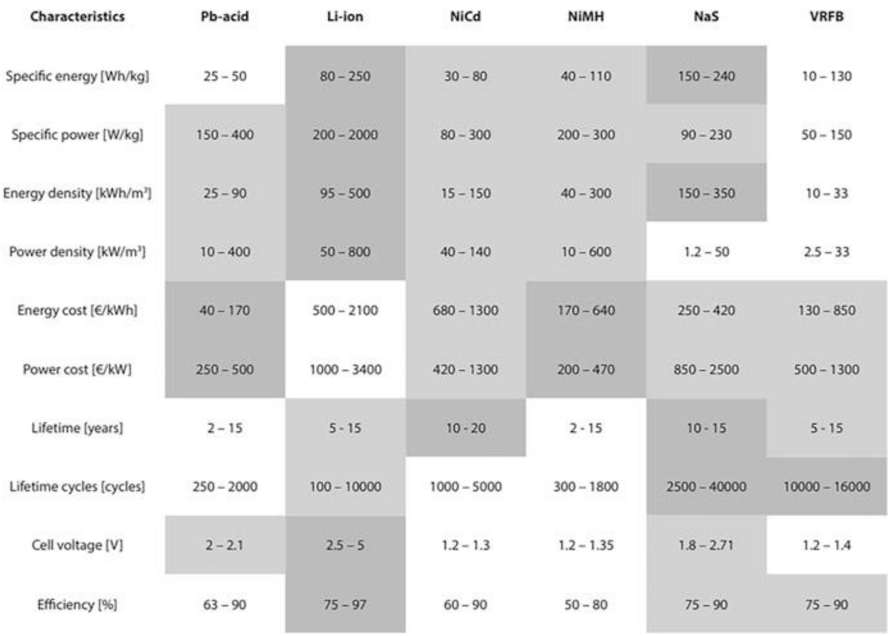


Characteristics	Pb-acid	Li-ion	NiCd	NiMH	NaS	VRFB
Specific energy [Wh/kg]	25 – 50	80 – 250	30 – 80	40 – 110	150 – 240	10 – 130
Specific power [W/kg]	150 – 400	200 – 2000	80 – 300	200 – 300	90 – 230	50 – 150
Energy density [kWh/m³]	25 – 90	95 – 500	15 – 150	40 – 300	150 – 350	10 – 33
Power density [kW/m³]	10 – 400	50 – 800	40 – 140	10 – 600	1.2 – 50	2.5 – 33
Energy cost [€/kWh]	40 – 170	500 – 2100	680 – 1300	170 – 640	250 – 420	130 – 850
Power cost [€/kW]	250 – 500	1000 – 3400	420 – 1300	200 – 470	850 – 2500	500 – 1300
Lifetime [years]	2 – 15	5 - 15	10 - 20	2 - 15	10 - 15	5 - 15
Lifetime cycles [cycles]	250 – 2000	100 – 10000	1000 – 5000	300 – 1800	2500 – 40000	10000 – 16000
Cell voltage [V]	2 – 2.1	2.5 – 5	1.2 – 1.3	1.2 – 1.35	1.8 – 2.71	1.2 – 1.4
Efficiency [%]	63 – 90	75 – 97	60 – 90	50 – 80	75 – 90	75 – 90

Fig. 6.1 Most valuable characteristics or KPIs for battery technology comparison [25]

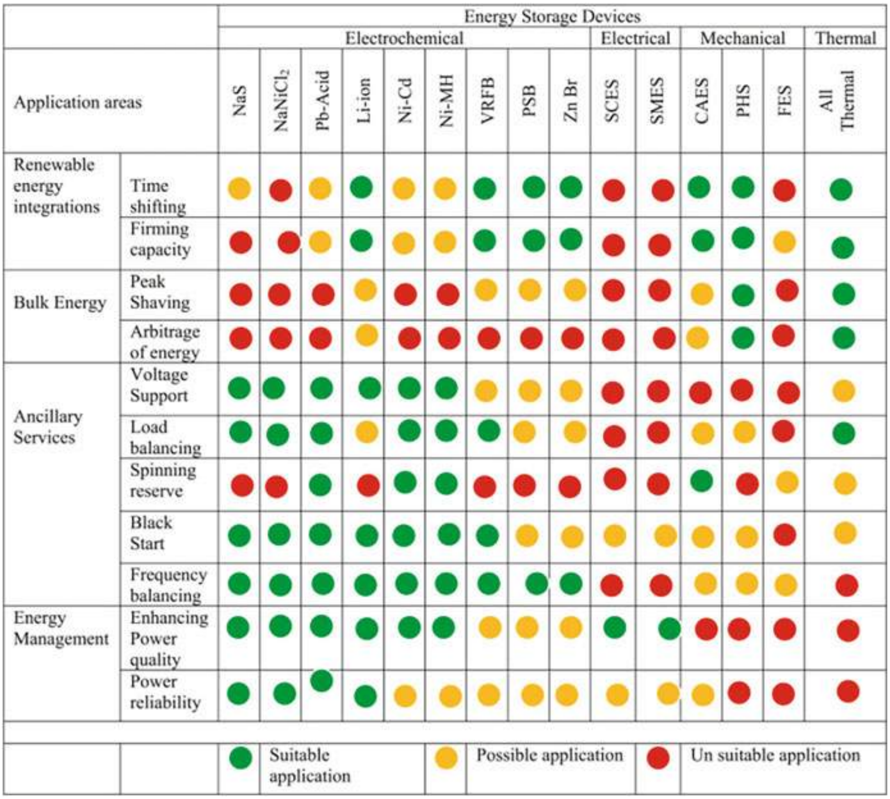
KPIs serve as a first orientation for which battery technology is is best suited for which application as shown in Fig. 6.1.

However, when the application requirements are analyzed in more detail, other aspects appear as relevant in the decision-making process, namely, cost, safety, environmental, and social, among others.

The battery market is therefore fragmented into many market segments that differ considerably not only in terms of the technology used but also in terms of market volume. The most important market segment by market size is batteries for road vehicles. Nevertheless, different market segments are described below and classified in terms of their specific requirements. These market segments are grouped into the classes stationary, mobile, and portable.

6.2 Stationary

Stationary battery storage systems are usually connected to an electricity grid. They provide services that serve the grid operation and decouple the generation and consumption of electricity over time. This facilitates the integration of volatile renewable power generation. In addition, they can be used to dampen peak loads and thus facilitate the integration of new consumers such as electric vehicles and heat pumps. Thus, stationary battery storage represents a key technology for the energy



		Energy Storage Devices														
		Electrochemical									Electrical		Mechanical			Thermal
Application areas		NaS	$NaNiCl_2$	Pb-Acid	Li-ion	Ni-Cd	Ni-MH	VRFB	PSB	Zn Br	SCES	SMES	CAES	PHS	FES	All Thermal
Renewable energy integrations	Time shifting	🟡	🔴	🟡	🟢	🟡	🟡	🟢	🟢	🟢	🔴	🔴	🟢	🟢	🔴	🟢
	Firming capacity	🔴	🔴	🟡	🟢	🟡	🟡	🟢	🟢	🟢	🔴	🔴	🟢	🟢	🟡	🟢
Bulk Energy	Peak Shaving	🔴	🔴	🔴	🟡	🔴	🔴	🟡	🟡	🟡	🔴	🔴	🟡	🟢	🔴	🟢
	Arbitrage of energy	🔴	🔴	🔴	🟡	🔴	🔴	🔴	🔴	🔴	🔴	🔴	🟡	🟢	🔴	🟢
Ancillary Services	Voltage Support	🟢	🟢	🟢	🟢	🟢	🟢	🟡	🟡	🟡	🔴	🔴	🔴	🔴	🔴	🟡
	Load balancing	🟢	🟢	🟢	🟡	🟢	🟢	🟢	🟡	🟡	🔴	🔴	🟡	🟡	🔴	🟢
	Spinning reserve	🔴	🔴	🟢	🔴	🟢	🟢	🔴	🔴	🔴	🔴	🔴	🟢	🔴	🟡	🟡
	Black Start	🟢	🟢	🟢	🟢	🟢	🟢	🟢	🟡	🟡	🟡	🟡	🟡	🟡	🔴	🟡
	Frequency balancing	🟢	🟢	🟢	🟢	🟢	🟢	🟢	🟢	🟢	🔴	🔴	🟡	🟡	🟡	🔴
Energy Management	Enhancing Power quality	🟢	🟢	🟢	🟢	🟢	🟢	🟡	🟡	🟡	🟢	🟢	🔴	🔴	🔴	🔴
	Power reliability	🟢	🟢	🟢	🟢	🟡	🟡	🟡	🟡	🟡	🟡	🟡	🟡	🔴	🔴	🔴

		🟢	Suitable application	🟡	Possible application	🔴	Un suitable application	

Fig. 6.2 Stationary energy storage systems and their use cases [3]

transition in the electricity grid. Figure 6.2 provides an overview of different storage technologies and their areas of application in the electricity grid.

Home Storage Home battery storage is mostly used "behind the meter" to optimize self-consumption via time-shifting of locally generated renewable energy. The most common combination is a battery home storage system with a rooftop photovoltaic system. Energy is stored during the midday hours. In the morning and evening hours, it is fed into the home grid to supply electrical appliances. The optimal storage size depends on electricity and system costs, load and generation profiles, energy consumption, and the size of the installed photovoltaic system. In addition, battery home storage systems can also be used to bridge interruptions in the power supply. The typical usable battery capacity of such storage systems is in the range of 2–15 kWh [27]. In contrast to other applications, the esthetics of the battery storage unit is also a purchase-relevant decision criterion here.

The demand for home battery storage will continue to increase in the coming years. The driving forces for market development are listed below:

- Renewable energies and electrification: Residential buildings are increasingly being equipped with photovoltaic systems. Additionally, new electrical consumers such as heat pumps and electric vehicles are being added. Time-shifting of generated electricity behind the meter significantly increases the self-consumption rate and lowers energy supply costs.
- Rising energy costs: Fossil greenhouse gas emissions are increasingly being factored into energy costs. Taxes and levies are designed to provide incentives to conserve energy. Political and economic crises repeatedly cause fluctuating prices on the energy markets. Home storage systems serve as enablers for personal energy cost optimization.
- Guaranteed electricity supply: Not in every country electricity is reliably available 24/7. Blackouts or scheduled brownouts restrict the quality of life and can lead to consequential damages. Home storage systems make it possible to bridge gaps in the electricity supply.
- Technological progress: The technology offers potential for further improvement. New battery chemistries like sodium ion promise a rapid further decrease in battery costs. Optimized software and electronics will increase round-trip efficiencies. This will improve economic efficiency. With increasing sales figures, economies of scale can be realized in production resulting in a further improvement of economic efficiency.

Industrial and Commercial Storage The focus of industrially and commercially used battery storage systems is on peakshaving and uninterruptible power supply (UPS). Peakshaving serves to reduce the connected load, which is particularly relevant for companies in the manufacturing sector. The “behind-the-meter” battery storage system can reduce load peaks. For particularly short load peaks with steep power gradients, a combination with ultracapacitors can be useful. In UPS applications, battery storage ensures the power supply for machines and ICT systems. Especially for the operation of data centers, such UPS systems are an absolute necessity. Furthermore, the roofs of factory and office buildings are increasingly being equipped with photovoltaic systems. Even if the generation and consumption profiles usually have a considerably greater overlap here than in residential buildings, time-shifting can be used to optimize self-consumption. Comparing different companies for storage systems, the size of such battery storage systems typically ranges from 20 kWh to 2 MWh [10]. While the energy density plays a subordinate role for such applications, the price and potential energy cost savings have a major influence on the purchase decision.

The use of battery storage systems will continue to increase in industrial and commercial applications [4]. The main drivers for this are listed below:

- Energy cost optimization: Grid connection costs are usually calculated on the basis of the maximum electrical power used. Peakshaving can reduce power peaks and thus energy costs. The same applies to optimizing self-consumption by time-shifting renewable energy production.

- Sustainability reporting: Low greenhouse gas production and on-site generation and use of renewable energies have a positive impact on the sustainability of the company. Battery storage is an enabler for the optimal use of renewable energy. Positive sustainability reports can be used in advertising. Furthermore, sustainability reports are used by investors to analyze the company’s exposure to climate legislation. This can have an effect on the company’s cost of capital.
- Security of supply: Power failures or voltage drops can affect technical systems. Considerable damage to plants and products can be the result. Battery storage works like an insurance against this risk. The willingness to pay is accordingly based on the amount of risk that can be avoided.

Utility Storage Grid-integrated battery storage can provide various ancillary services listed in Fig. 6.2. The integration of battery storage systems is possible in the distribution grid as well as in the transmission grid. In the distribution grid, stationary battery storage systems primarily serve to stabilize the grid in the event of short-term fluctuations. The feed-in of fluctuating renewable energies and new consumers such as electric vehicles or heat pumps leads to an increased strain on the distribution grids. This can lead to voltage fluctuations. However, maintaining certain voltage bands (+/− 10%) is a crucial prerequisite for the reliable operation of electrical devices [16]. Grid-integrated battery storage systems can stabilize the grid voltage by feeding in or consuming active power. Via the inverter, battery systems can also provide reactive power, which also affects grid voltage. In addition, battery storage systems can have a dampening effect on voltage gradients and thus improve the voltage quality. In time-shifting and peakshaving operation, battery storage systems reduce grid load. In this way, the need for grid expansion can be reduced or delayed. In the event of a grid collapse, grid-integrated battery storage can maintain the power supply in smaller grid areas for a short time. If the grid does collapse completely, such storage systems can also be used for black-starting the grid.

When used in the transmission grid, the main focus is on providing control power. There must be a constant balance between generation and consumption in the electricity grid. If this balance is disturbed, balancing measures take effect, which are classified according to their time of provision as instantaneous reserve, primary control reserve, secondary control reserve, minute reserve, and reserve by the balancing group manager. The instantaneous reserve is the immediate compensation of power imbalances. In conventional power plants, it is provided from the energy of the rotating masses in turbines and generators. Therefore, it is also called spinning reserve. Primary control power must be activated within seconds and held for a period of minutes. In Germany, activation time is 15 s and power must be held for up to 15 min [9]. The following activation times are valid for power balancing in Germany, but there are comparable requirements in other electricity markets [24]. These requirements are similar in different electricity markets. Secondary control power must be capable of being fully activated within 5 min. The minute reserve must be fully activated within 15 min and be provided for at least 15 min. However, the provision period can also be up to several hours. If these measures are not sufficient, the balancing group manager activates further reserve capacities.

Battery storage systems are able to provide all these balancing measures positively (energy injection) or negatively (energy absorption).

The demand for grid-integrated utility scale battery storage is much related to the chosen power generation mix. The continuing global trend toward the expansion of weather-dependent renewable energies indicates that the market will expand much further. However, the extent of market growth is difficult to estimate. The main influencing factors are listed below:

- Grid relief: The integration of weather-dependent renewable energies and new electricity consumers creates major challenges, especially at distribution grid level. Grid-integrated battery storage can relieve the load on the electricity grid. In this way, grid operators can save costs and gain time for grid expansion or make it unnecessary.
- Cost reduction: In control devices, power electronics, and battery technology, there is still great potential to further reduce the total cost of ownership. With regard to battery technology, cost reductions can be achieved through new cell chemistries such as sodium-ion batteries and possibly also second life batteries.
- Demand side integration: It is uncertain to what extent the consumer side can be integrated into grid operation and to what extent consumers behind the meter will make their own optimizations. For example, electric vehicles have a huge storage capacity in total. However, it is uncertain to what extent the vehicle electronics, the cycle stability of vehicle batteries, and the charging infrastructure will enable the grid integration of electric vehicles.

Non-battery Stationary storage In addition to battery systems and different cell chemistries, there are a number of other energy storage technologies that need to be mentioned here (also see Fig. 6.2) in order to compare battery technology.

- Ultra-/Supercapacitor energy storage (SCES) is primarily suitable for very short-term, high-power electricity storage. Their use is particularly worthwhile in the case of rapid successive charging and discharging cycles. This is the case, for example, in the improvement of power quality. When electrifying applications with this requirement profile, combined systems with batteries and capacitors are increasingly being used.
- Superconductive magnetic energy storage (SMES) can store energy in magnetic form in superconducting coils. They have a high-power density. The field of application corresponds to that of supercapacitors.
- Compressed air energy storage (CAES) uses compressed air to store energy. Air is sucked in and compressed by a compressor and stored in a tank. Since large volumes are required, underground caverns, for example, in salt domes, are often used for storage. When energy is needed again, the compressed air can be expanded via a gas turbine. Heat recovery can significantly increase circulation efficiency. The shorter the cycle duration, the better heat can be recovered. Therefore, CAES are used as spinning reserves and for time-shifting.
- Pumped hydro energy storage (PHS) stores electricity in positional energy. For this purpose, water is pumped into a higher basin. When energy is needed, the

water is drained from the basin and passed over a turbine, which then generates electricity again. Due to its very fast reactivity, PHS is suitable for peakshaving and arbitrage trading but also for longer term energy storage.

- Flywheel energy storage (FES) stores electricity in rotational energy. For this purpose, a heavy cylinder is rotated or decelerated by an electric motor. The energy that can be stored is comparatively limited. That is why there are only a few applications for this type of storage.

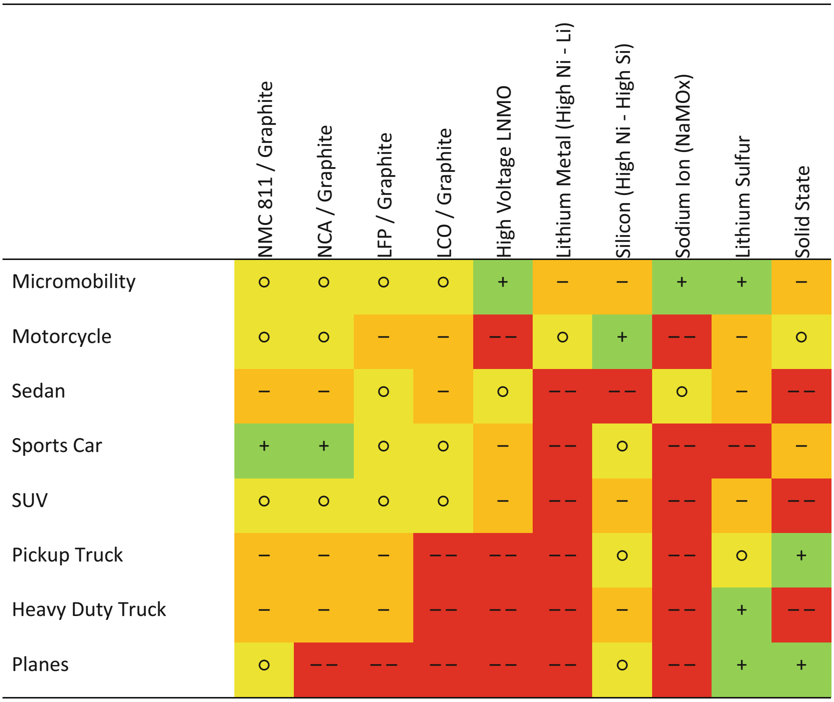
6.3 Mobile

Batteries are increasingly being used to power vehicles of all kinds—a domain previously primarily occupied by petrochemical fuels and internal combustion engines. However, fuels of fossil origin are not compatible with mitigating climate change. Therefore, governments around the world have taken steps to phase out internal combustion engines in the transport sector. In the European Union, for example, with a few exemptions, only zero-emission vehicles can be newly registered from 2035 [13]. Japan and China are aiming for full electrification of new car sales by 2035 [17]. Battery-electric vehicles are the most advanced technology to meet these requirements. However, the trend toward electrification is not limited to road transport. Electrification with the use of battery technology is also advancing in other areas such as micromobility, commercial vehicles, shipping, rail transport or aviation. As different as these application areas are, the suitable battery technologies are also very different. Each battery technology has its characteristic properties, just as each mobility application has its characteristic requirements. Table 6.1 shows a utility value analysis of which battery technology is suitable for which application [6].

Micromobility Micromobility includes e-bikes, electric scooters, and other small electric means of transport. They are mainly used for shorter distances in urban environments. Electric scooters in particular are offered as mobility as a service products by various providers in cities. Batteries are usually integrated into the product or can be removed and replaced completely in form of an encased battery pack. The design and size of the product is decisive for the degree of integration of the battery. Typical battery sizes range from a few 100 Wh to a few kWh [4]. Important criteria for the selection of suitable battery technologies in this market segment are cost, energy density, and charging rate.

Micromobility devices became possible due to low-cost batteries, compact and powerful electric motors, and advances in power electronics and control components. Due to the great success of e-bikes, powered scooters, powered self-balancing boards, powered skate boards, and many other devices, market diffusion is already more advanced compared to other mobile battery applications. Yet significant growth potential remains in the micromobility market, even if year-on-year growth rates are declining to single-digit percentages. The key growth drivers are listed below:

Table 6.1 Battery technology to mobility application fit overview



	NMC 811 / Graphite	NCA / Graphite	LFP / Graphite	LCO / Graphite	High Voltage LNMO	Lithium Metal (High Ni - Li)	Silicon (High Ni - High Si)	Sodium Ion (NaMOx)	Lithium Sulfur	Solid State
Micromobility	○	○	○	○	+	–	–	+	+	–
Motorcycle	○	○	–	–	– –	○	+	– –	–	○
Sedan	–	–	○	–	○	– –	– –	○	–	– –
Sports Car	+	+	○	○	–	– –	○	– –	– –	–
SUV	○	○	○	○	–	– –	–	– –	–	– –
Pickup Truck	–	–	–	– –	– –	– –	○	– –	○	+
Heavy Duty Truck	–	–	–	– –	– –	– –	–	– –	+	– –
Planes	○	– –	– –	– –	– –	– –	○	– –	+	+

Legend: – – bad, – poor, ○ average, + good, + + great

- Growing urbanization: The global trend toward urbanization is changing mobility behavior as well. Congestion and growing environmental awareness lead to an increased use of alternative modes of transport. Battery-powered micromobility on short distances and paved surfaces in urban centers is a viable alternative to other modes of transport.
- Convenience and accessibility: Battery-powered micromobility devices are a low-barrier complement to public transport in urban centers. For disabled people, they can facilitate access to mobility. It is also the most affordable form of motorised individual mobility.
- Government incentives: Cities create incentives to improve air quality and decarbonize mobility. Battery-powered micromobility benefits from this.

Passenger Vehicles This class of mobile applications represents the largest market segment in terms of market volume. Therefore, the class of passenger vehicles deserves further subdivision into motorbikes, cars, buses, and trucks.

For the application of batteries in motorcycles, the charging rate and the volumetric and gravimetric energy density are primarily relevant decision variables. The reasons for this are the limited construction space available and the narrow limits in the tolerable vehicle weight. Typical battery sizes are in the range of 5–20 KWh [4]. For less heavily motorized mopeds and scooters used in urban traffic, exchangeable batteries may also be an option. In those cases, priorities shift toward gravimetric energy density and cost. Such vehicles are typically equipped with batteries of 1–5 kilowatt-hours [4].

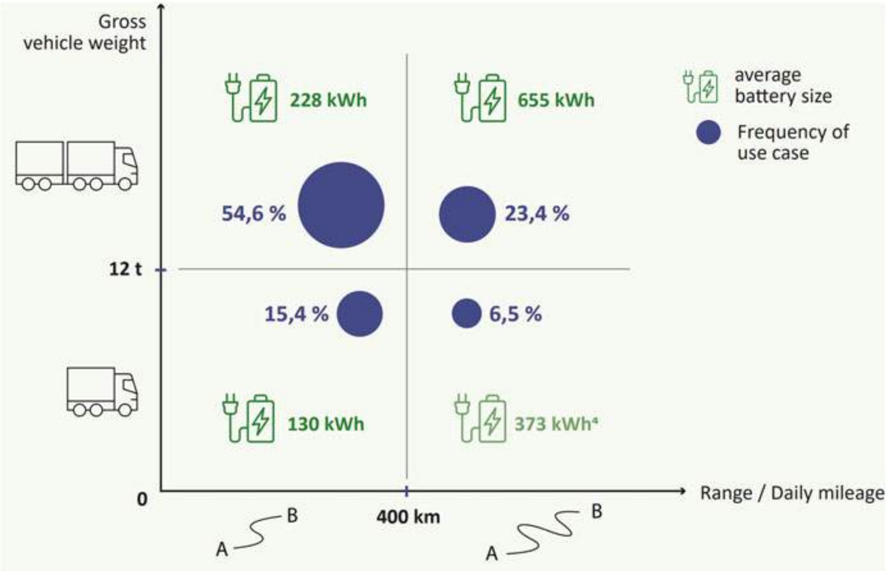
Battery-electric cars represent the single largest market segment. Depending on the size and weight of the vehicle as well as the intended use, different requirements for the battery technology apply (compare Table 6.1). Battery-electric cars are typically equipped with batteries from 30 to 110 KWh [14] with a growth trend. NMC cell chemistries are widely used. In cheaper vehicles with a shorter range, LFP is also used. For small vehicles with low range, the use of sodium-ion batteries may also be conceivable. For the selection of battery technologies for electric cars, the most important priorities are cost, volumetric energy density, and life cycle. Batteries are usually permanently installed in the vehicle in the form of a battery pack although some vehicle manufacturers also offer interchangeability of battery packs. These batteries are usually equipped with a conditioning system that can cool or heat the battery. Cooling is particularly necessary for fast charging. While charging, heat is generated due to the internal resistance of battery cells that must be managed in order not to endanger the thermal stability of cells. Moreover, the battery can be preheated in cold ambient temperatures to prepare it for charging and enable a higher charging rate. With regard to the integration of batteries into the vehicle, there are two opposing trends. Manufacturers like Tesla and BYD work on making the battery pack a structural part of the vehicle [28]. This saves weight and reduces the necessary installation space. Other manufacturers, above all nio, are opting for battery swap systems. This allows for greater flexibility and gentler charging. However, this greater flexibility comes at the price of disadvantages due to the standardized form factor of the battery pack and the more difficult thermal management. In addition, the construction and operation of the swapping infrastructure is associated with comparatively high costs. Therefore, vehicle-integrated battery systems are likely to be sufficient for most applications. Cars with swappable batteries primarily address the customer segment of businesspersons and travelling salespersons, since a costly battery-swapping infrastructure must be built and operated. Due to the cost premium, it is to be expected that cars with swappable batteries will initially be offered in the premium segment and purchased by people with high mobility needs and a high willingness to pay.

For buses, there are two different use cases. Most buses are used in urban public transport. This use case is characterized by frequent starts and stops as well as fixed routes. Longer stops, e.g., at terminus stations, allow for recharging of the batteries. Recharging can be done in different ways. However, automated pantograph systems are becoming increasingly popular. Depending on the route and charging opportunities, city buses are equipped with 200–500 kWh batteries [1, 7]. Due to frequent starting and stopping, there is a great potential for recuperation. For maximum utilization of the recuperation potential, batteries can also be combined with ultracapacitors. Here is also the biggest difference to coaches, since they are usually travelling at a constant speed over longer distances. In addition, there are fewer opportunities for charging breaks. For this reason, coaches are also offered with larger batteries beyond 500 kWh [1].

Battery-electric vehicles are the largest market segment for the application of batteries for the foreseeable future. More than 80 million passenger vehicles are sold globally [11]. By 2050, battery-electric vehicles will make up most of this market. In its net zero-emissions scenario, the IEA projects that by 2030 the global market share of electric vehicles will be around 60% [18]. This significant market growth is driven by several factors, which are listed below:

- Environmental and climate regulation: In order to mitigate climate change and improve air quality in urban areas, governments are taking regulatory measures against internal combustion engine vehicles. Since this does not fundamentally change mobility behavior, battery-electric vehicles are among the beneficiaries.
- Government incentives: In order to accelerate the market ramp-up, many governments provide substantial financial incentives for the purchase of zero-emission vehicles. In particular, countries with a strong automotive industry also directly promote the development and production of batteries.
- Comfort: Even if charging pauses on long-distance journeys have a detrimental effect on comfort, battery-electric vehicles do offer some advantages. The interior can be designed more generously; the vehicle is significantly more quiet and less prone to wear and tear.

Commercial Vehicles Commercial vehicles fulfill transport applications from urban delivery services to freight transport on international long-haul routes. The requirements for performance and range differ accordingly. In delivery applications, smaller vehicles below 12 t gross vehicle weight are commonly used. The requirements for these vehicles are similar to those for large cars and pickup trucks. Heavier trucks are used for short-distance transport logistics and retail deliveries. Due to the relatively short daily routes of less than 400 km, moderate battery sizes of 100 kWh to 500 kWh are mostly sufficient [26]. Long-distance road transport of goods is usually done with heavy duty long-haul trucks with larger batteries in the range of 350–1000 kWh [5, 26]. Figure 6.3 gives an overview of the frequency of the different applications and the average battery sizes installed [8]. The most common cell chemistries in commercial vehicles are NMC, LFP [20], and, coming up soon, LMFP [19]. The most important criteria for choosing the right battery technology are gravimetric energy density, life cycle, and cost. Compared to passenger vehicles, life cycle is of particular importance. Especially in long-distance traffic, mileages of more than 1000,000 kilometers must be achieved over the lifetime of the vehicle. Despite the disadvantages of batteries in terms of weight and charging time, the high degree of utilization of batteries in long-haul transport leads to unexpectedly positive cost-effectiveness.



Snapshot of the percentages of medium-haul (up to 400 km) and long-haul transport and their distribution on medium-weight (up to 12 metric tons) and heavy-weight (above 12 metric tons) vehicles. The battery sizes of each quadrant were averaged based on the manufacturers' data.

Fig. 6.3 Use cases for battery-electric heavy duty transport [8]

Shipping Shipping is a difficult field for the application of battery-electric propulsion systems. Large and heavy vessels require a lot of energy and thus also exceptionally large batteries. Nevertheless, battery-electric propulsion systems are increasingly being used in shipping. The first applications are pleasure crafts, touristic riverboats, and ferries. These applications combine relatively short routes and nearby charging opportunities. Norway is the global pioneer in the electrification of shipping. As of 2026, the country has declared its fjords to become the world's first maritime zero-emission zone [21]. The first battery-powered ferries are already in operation. The Bastø Electric, for example, began operation in the Oslo Fjord in 2021. The ferry is 143 m long and has room for 200 cars, 24 trucks, and 600 people. Batteries with a total capacity of 4300 kWh store the energy [12]. In addition, it can be useful in regions that are less well connected to the electricity grid to set up buffer storage at piers to charge the ships' batteries. Beyond that, battery-electric marine propulsion systems could also be used in coastal cargo shipping. A study published in 2022 concludes that the total cost of propulsion (TCP) of battery-electric vessels is competitive to internal combustion engine powered vessels up to a distance of 1000 km [22]. The authors estimate that the competitive route length will increase to around 3300 km in the near future. This is due to expected further reductions in battery costs and higher energy density as well as increasing TCP for internal combustion engine ships.

Battery-electric drives are becoming increasingly relevant in shipping. The largest number of sold propulsion systems is achieved in the segment of pleasure crafts. Passenger and container ships, however, require considerably larger batteries, so that a relevant market is emerging here as well. The most important market drivers are listed below:

- Comfort: In the pleasure craft market segment, comfort plays a very significant role. Battery-electric drive systems are compact and low maintenance. They are also quiet and do not produce exhaust emissions. Integrated systems can also provide power for electrical devices on board. It is also possible to charge these batteries with onboard solar panels. Accordingly, a dynamically growing market is already developing here.
- Environmental regulation: Emissions of pollutants from shipping are the subject of public debate. The example of Norway shows how states are setting regulatory frameworks that benefit battery-electric propulsion systems. Besides the Norwegian fjords, also pollutant emissions from ships on inland waterways in densely populated areas are relevant.
- Corporate sustainability: Sustainability is becoming an increasingly strong selling point. This is especially true in tourist shipping.
- Costs: Especially in the pleasure craft segment, there are synergy effects that justify higher costs. In commercial shipping, the economic competitiveness is much more important. The competitiveness of battery-electric propulsion depends on two opposing trends: firstly, the further cost degression of battery storage system and, secondly, cost increases of fossil fuel powered propulsion systems. Here, factoring in of the damage caused by CO_2 emissions is a major cost driver.

Aviation Aviation is one of those industries where avoiding greenhouse gas emissions is particularly difficult. One obstacle to the electrification of aviation is the very tight weight limits. Consequently, propulsion systems must provide a high energy density and, for takeoffs, also a high-power density. In addition, very strict safety requirements apply, because problems during flight can have devastating consequences. This combination of requirements poses a major challenge for new climate-friendly propulsion systems. Despite this, the use of battery-electric propulsion systems is being considered in aviation. Prototypes and demonstrators from various manufacturers have already proven the technical feasibility of battery-powered aircraft. This concerns small short-haul aircraft or vertical takeoff and landing (VTOL) devices. If batteries are to play a relevant role in aviation, however, battery technologies with significantly higher energy densities must be developed. Studies assume that at least 400 Wh/kg to 750 Wh/kg are necessary for regional air traffic. If traditional narrow-body aircraft designs are to be equipped with battery-electric propulsion systems, at least 600 Wh/kg to 820 Wh/kg will be required for commercial operation on regional routes [2]. Current lithium-ion technology cannot meet these requirements. Lithium sulfur batteries could theoretically achieve the required energy densities but are still under development. Key challenges would be higher discharge rates and a longer life cycle. Greater hope lies in the use of solid state batteries. Here, too, many challenges still need to be solved, especially to improve manufacturability. If solid state batteries with high energy density and good safety characteristics become available by the end of the 2020s, aviation will be one of the most interesting market segments for their commercial application. But the challenge of battery-electric flying is bigger than just changing the propulsion system. New aircraft designs are necessary to exploit all efficiency potentials. Decades of further development are necessary to enable widespread adaptation of battery-electric aviation in passenger transport. The first applications of this technology will be small short-haul aircraft for only a few passengers.

Aviation is a market segment in which battery-electric propulsion systems may play a role in the future. The prerequisite for this, however, is significant technological progress. Therefore, this market segment is prone to become a test field for novel high-performance batteries. Whether battery-electric designs will play a larger role in regional air traffic also depends on the progress made in the development of alternative drive technologies and synthetic fuels. The key market drivers are listed below:

- New aviation concepts: VTOLs enable flight connections over short distances that were previously restricted to other modes of transport. Especially in densely populated areas, low noise and pollutant emissions as well as high safety standards are mandatory acceptance criteria for this technology. Electric propulsion systems with multiple rotors can meet these requirements. Various companies are developing and testing such concepts already. Another rapidly growing market segment is unmanned drones, which are being used in various fields of application. Military applications are a strong technology and market driver in this area.
- Environmental regulations: Aviation is also experiencing increasingly stricter regulation of pollutant and greenhouse gas emissions. To some extent, it is already included in emissions trading systems. Regulatory requirements and rising costs associated with fossil fuels may improve the economic viability of battery-electric propulsion systems in aviation in the future.

Rail Rail transport can be subdivided into light urban and tram transport, regional and long-distance passenger transport, and heavy freight transport. Overall, rail transport is already a very efficient and climate-friendly mode of transport. Nevertheless, there are use cases in the different areas where batteries should be considered. Urban rail passenger transport is already electrified to a large extent. Here, batteries can be used to make optimal use of the energy recovery potential of regenerative braking. Depending on the topology of the terrain and the dimensioning of the catenary network, the amount of energy that can be fed back into catenaries may be limited. Small batteries sometimes in combination with ultracapacitors can act as buffer storage and help to stabilize the voltage quality in the overhead contact line network. This can save up to 30% energy [15]. In addition, the construction of tram lines and catenaries in dense urban areas can lead to spatial conflicts with other infrastructures. With small batteries, trams can bridge shorter distances without catenary. This can simplify the traffic planning of intersections, for example.

Long-distance passenger transport is usually equipped with overhead lines, as long-distance routes are often at high capacity. In regional transport, the share of electrified routes is significantly lower. Here, battery-electric trains are an alternative to diesel-powered trains. This is especially true if parts of the route are electrified with catenaries. The trains' batteries can then be recharged in these sections of the route. The first battery-electric trains are already in operation. Due to the good integration into the existing infrastructure, battery-electric regional trains are an interesting market segment. Depending on the route length, batteries with more than 300 kWh capacity are used. Due to the high total weight and the large transport capacity, the energy consumption of battery-electric trains is 3–8 kWh/km. Where there is no catenary infrastructure at all, battery-electric trains will eventually have to compete with other propulsion technologies such as hydrogen fuel cells and synthetic fuels.

In heavy freight transport, the comparatively low energy density of batteries becomes a problem especially over long distances. However, the use of battery-electric power trains would also be technically feasible here. More realistic, however, is the use of battery-electric freight locomotives in shunting operations, on factory premises, and on short regional routes.

Batteries for rail transport require a high energy density. This is particularly important when longer distances are to be covered. In addition, a high-power density is necessary to exploit the full potential of regenerative braking and quick acceleration. Another important aspect is the requirement for a very long life cycle. Trains are in continuous operation and cover several million kilometers over their lifetime. Accordingly, the battery must be able to withstand many charging cycles. In addition, there are high demands on safety and reliability. Particularly in freight transport, hazardous goods are also transported. Fire risks must therefore be avoided. Furthermore, in the event of a defect, a train may block a section of the track. This can lead to high consequential costs.

Rail transport is an interesting market segment for a relatively small number of large battery systems. Whereas in the past it was mainly hydrogen drives that were seen as a future technology here, interest is increasingly moving in the direction of battery-electric trains. The main market forces are listed below:

- Environmental regulation: Stricter climate and environmental legislation also affects rail transport. Moreover, many railway companies around the world are partly or fully state-owned. Therefore, politics can exert more direct influence on investment decisions and accelerate the switch to more climate-friendly technologies.
- Energy costs: Electric trains can recover energy when braking. With battery-powered trains, this is becoming possible even in areas without catenaries. Energy costs can be reduced through increased energy efficiency. The magnitude of this effect, of course, depends on the difference between electricity and fuel prices.

- Improved performance: Compared to diesel engines, electric motors can be controlled better, and they provide full torque already at low speed. This has a positive effect on acceleration.
- Comfort: In passenger transport, passenger comfort is also an important decision criterion. Diesel engines cause nuisance through exhaust fumes, noise, and vibrations, which have a negative impact on the passengers' perception of comfort and quality.

6.4 Portable

Portable batteries have been the largest market segment in the past. This market segment covers a wide range of applications. These include consumer electronics, power tools, medical devices, and numerous other applications. The typical battery capacity is in the range of a few watt-hours. Batteries with a capacity of up to 1 kilowatt-hour are used in power tools. Portable batteries are usually directly integrated into the product. Depending on the size, energy requirements, and usage characteristics of the product, there are very different requirements for the battery technology. Accordingly, this market segment offers many small niches for manufacturers of special batteries. The various niche applications also offer interesting market entry opportunities for the first-time commercialization of new battery technologies. Due to the great diversity of battery applications, with relatively small market volumes, the individual applications are only briefly described below [4].

- Telecommunications: The market segment is very established and the products are mature. The market is saturated and the number of smartphones sold has been declining slightly since 2017. Lithium-ion battery cells in laminated cell formats with form factors specially adapted to the product are used to a large extent. The capacity of these batteries is in the range of 4–20 Wh. This market segment is very cost-sensitive.
- Laptops and tablets: The market for laptop and tablet batteries is saturated. Laptops reached peak demand in 2011 and tablets in 2014. Since then, sales figures have stagnated. In the past, 18,650 format round cells were more common, but in the competition for thinner and lighter laptops, many manufacturers are increasingly switching to specially designed pouch formats. Nearly all batteries used are lithium-ion.
- Power tools: The market for power tools continues to grow dynamically. More than one million units are sold annually. The market covers a broad spectrum from low-end solutions for occasional users (6 V, 10 Wh) to powerful professional tools (36 V, > 50 Wh). Increasingly, Li-Ion batteries are prevailing over NiCd batteries. The power-tool manufacturers expect from batteries above all low prices, fast charging, and high energy density. For professional tools, an improved life cycle of more than 500 cycles is also important.

- Medical devices: Batteries are used in medical devices such as implants, defibrillators, hearing aids, and prostheses. Particularly in the case of implants and hearing aids, extreme requirements are placed on batteries due to the small packaging space. As these requirements can be very specific, various cell chemistries are used in special cell formats. The market for medical battery applications is growing dynamically. On the one hand, this is due to the constant expansion of the product range, but also to an aging population in wealthy industrial countries.
- Household devices: Batteries are increasingly being used in household appliances such as shavers, toothbrushes, or vacuum cleaners. The market is growing dynamically, even if there are major differences between the individual product categories. Lithium-ion batteries have replaced other cell chemistries in many product categories. The market segment is very price-sensitive. In addition, short charging times and low self-discharge are expected.

Besides the market segments mentioned, there are numerous others, such as toys, mobile video game consoles, sports equipment, smartwatches, or wearable electronics, which will not be discussed in detail. However, the large number of applications shows the great potential for smaller manufacturers of special batteries. The special requirements create the necessary conditions for the introduction of new battery technologies. For this reason, the small-scale consumer battery market cannot be neglected.

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Chapter 7
Future Battery Market

Stefan Wolf and Michael Lüken

Contents

7.1 Introduction

The global battery market has been growing very dynamically since the beginning of the 2010s, with annual growth rates of more than 30%. According to data from Avicenne Pillot (2022), the market volume of the entire battery market in 2020 was

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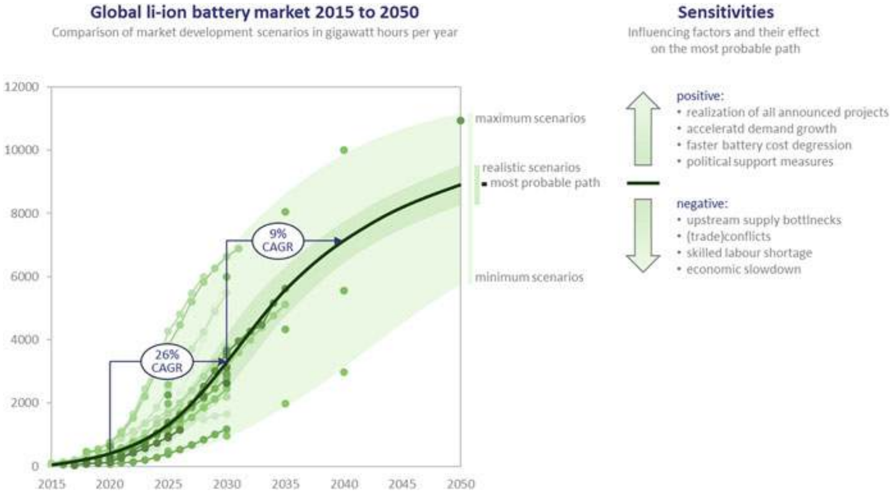


Fig. 7.1 Evaluation of the global battery market outlook [14]

USD 93 billion. Lead-acid batteries accounted for USD 37 billion of this, of which 414 GWh were produced in 2020. The production volume of Li-ion batteries was just over half that at 250 GWh. However, the market volume of Li-ion batteries was already USD 39 billion in 2020.

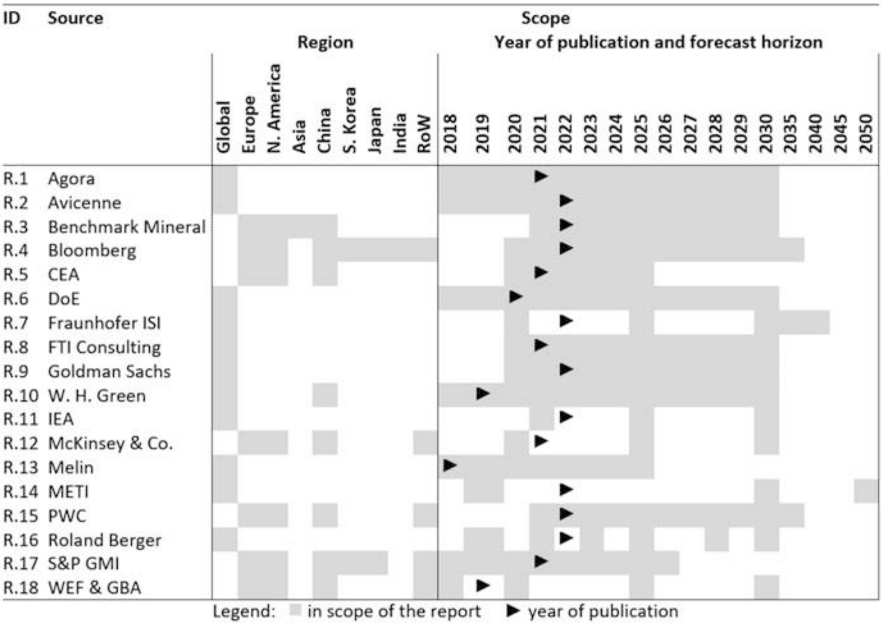
7.2 Market Outlook

The market outlook is characterized by strong growth in the production of Li-ion batteries. Figure 7.1 shows the battery market development based on an assessment of market reports listed in Table 7.1. This growth is predominantly caused by the transition from internal combustion engine vehicles to battery-electric vehicles. The most likely growth path reaches a global production capacity of 3200 GWh/a in 2030, 7100 GWh/a in 2040, and 8900 GWh/a in 2050 [14].

In terms of regional breakdown of the global market, Asia, and China in particular, remains in the leading position. Based on the announced production capacities, a substantial change in regional market shares is not to be expected. The studies evaluated conclude that Europe will be able to cover a large part of its battery cell demand itself by 2030. Europe's share of the global market will be 16% to 27% in 2030, depending on the assumptions applied. Due to the multitude of influencing factors, there is a great degree of uncertainty in this result.

In the decade from 2020 to 2030, the compound annual growth rate (CAGR) of the global market is projected to be 26% [14]. This rapid growth provides a good market entry opportunity for many new companies. As market diffusion of battery technology continues, the CAGR will drop to single digits in the following decade

Table 7.1 Evaluated market reports projecting the future development of the battery market



ID	Source	Scope																									
		Region									Year of publication and forecast horizon																
		Global	Europe	N. America	Asia	China	S. Korea	Japan	India	RoW	2018	2019	2020	2021	2022	2023	2024	2025	2026	2027	2028	2029	2030	2035	2040	2045	2050
R.1	Agora	▨									▨	▨	▨	▨ ▶	▨	▨	▨	▨	▨	▨	▨	▨	▨				
R.2	Avicenne	▨									▨	▨	▨	▨	▨ ▶	▨	▨	▨	▨	▨	▨	▨	▨				
R.3	Benchmark Mineral		▨	▨	▨	▨								▨	▨ ▶	▨	▨	▨	▨	▨	▨	▨	▨				
R.4	Bloomberg		▨	▨		▨	▨	▨	▨	▨			▨	▨	▨ ▶	▨	▨	▨	▨	▨	▨	▨	▨	▨			
R.5	CEA		▨	▨		▨							▨	▨ ▶	▨	▨	▨	▨									
R.6	DoE	▨									▨	▨	▨ ▶	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨				
R.7	Fraunhofer ISI	▨											▨		▶			▨					▨	▨	▨		
R.8	FTI Consulting	▨											▨	▨ ▶	▨	▨	▨	▨	▨	▨	▨	▨	▨				
R.9	Goldman Sachs	▨											▨	▨	▨ ▶	▨	▨	▨	▨	▨	▨	▨	▨				
R.10	W. H. Green	▨				▨					▨	▨ ▶	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨				
R.11	IEA	▨												▨	▶			▨					▨				
R.12	McKinsey & Co.		▨	▨		▨				▨			▨	▶				▨					▨				
R.13	Melin	▨									▨ ▶	▨	▨	▨	▨	▨	▨	▨									
R.14	METI	▨										▨			▶								▨				▨
R.15	PWC		▨	▨		▨				▨				▨	▨ ▶	▨	▨	▨	▨	▨	▨	▨	▨	▨			
R.16	Roland Berger	▨										▨		▨	▶	▨		▨			▨		▨				
R.17	S&P GMI		▨	▨		▨	▨	▨		▨	▨	▨	▨	▨ ▶	▨	▨	▨	▨	▨								
R.18	WEF & GBA		▨	▨		▨				▨	▨	▶	▨					▨					▨				

Legend: ▨ in scope of the report ▶ year of publication

from 2030 to 2040. This will start a market consolidation phase which many of the new companies will not survive. The unsuccessful companies will be bought up by the better performing ones. Therefore, an aggressive growth strategy is necessary to survive in the mass market. In the second half of the 2020s, companies will need to secure significant market share and strategic alliances with automakers to survive in the long term. This conflicts with the limited experience of European and North American start-ups in particular. It will be a matter of not only scaling quickly but also learning more efficiently and faster than established companies that have been active in the market for years. Another possible strategy is specialization. By building up know-how and serving the needs of a smaller market segment, a technological advantage over competing companies can be achieved. This approach can enable survival with lower revenues compared to the mass market, but possibly more attractive margins.

The Li-ion battery market projection in Fig. 7.1 shows an assessment of 25 market development scenarios from 18 market reports. The market projections are classified into maximum, minimum, and realistic development paths depending on the assumptions on which they are based. The maximum scenarios are mostly based on the expansion targets announced by battery manufacturers. However, it can be assumed that not all of the announced battery production capacities will actually be created. Some of the players on the market today will not be able to survive and will withdraw their announcements. The minimum scenarios are mostly based on regulatory requirements. Particularly in the vehicle sector, many countries have already passed resolutions to phase out the internal combustion engine. One example of this is the CO_2 fleet limits for passenger cars and light commercial vehicles that apply in the European Union [6, 7]. The minimum scenarios use these regulatory requirements as a basic assumption for estimating the expected market diffusion. The realistic scenarios are based on the historically observable market diffusion of battery technology.

Battery-electric passenger cars will be by far the most important market segment. Other, much smaller, market segments are commercial vehicles, stationary power storage, consumer electronics, power tools, and similar. Projections for the marine, aviation, and stationary power storage market segments are subject to the greatest uncertainties. Stationary power storage in particular has less limiting requirements for KPIs such as energy or power density neither gravimetric nor volumetric. This allows significantly more freedom in the choice of cell chemistry. One example of new battery chemistries with disruptive potential is sodium ion batteries. It is likely that this battery technology will capture a significant portion of the market volume outlined in Fig. 7.1. The properties of sodium ion batteries make them suitable for use cases that do not necessarily require high energy densities. However, manufacturers are also considering putting sodium ion batteries in vehicles with a range of up to 400 km in the future [3]. Breakthroughs in the industrialization of such cheaper batteries for stationary electricity storage can lead to significantly accelerated market diffusion. Nevertheless, even in this case, passenger cars would be expected to form the largest market segment.

The actual development of the battery market is difficult to estimate because it depends on a variety of influencing factors. The most probable path indicated in Fig. 7.1 reflects the mean value of the realistic scenarios. Realistic scenarios are considered to be those that make probable assumptions for the future impact of key influencing factors while weighing up various options. The consistent scenario descriptions resulting from this approach allow a projection for the future development of the battery market based on the state of knowledge in 2022. The real development of the battery market can deviate considerably from the most probable path. The following developments can lead to a positive deviation [14]:

- Realization of all announced projects: The construction, commissioning, and ramp-up of battery factories are a complex task that poses considerable challenges, especially for start-up companies. The supply of raw materials, active materials, and components must also be ensured. It is therefore to be expected that not all announced production capacities will actually be built, commissioned, and fully utilized. Time delays also have a negative impact on the availability of production capacities. If these assumptions are not correct and the production capacities are actually realized as announced, the market development will shift into the area of maximum scenarios.

- Accelerated demand growth: The realistic scenarios are based on the established regulatory framework. In the past, it was observed that the speed of market diffusion of new technologies has been increasing. Accordingly, it is possible that the market for batteries, especially in the automotive segment, could grow much faster than previously assumed.
- Faster battery cost degression: With every battery produced, the knowledge about possible cost savings increases. Accordingly, the realistic scenarios extrapolate the future development of battery costs in line with the observed learning curve. New technical developments, for example, in production technology or through the introduction of cheaper battery cell chemistries, can accelerate the cost degression. Accordingly, a new market equilibrium would be expected to emerge resulting in a larger battery market volume.
- Political support measures: Political measures can have a significant impact on the development of the battery market. The realistic scenarios are based on a business as usual assumption derived from the current and expected political framework conditions. More ambitious policies and actual compliance with the 1.5 °C target of the Paris climate agreement would shift the market development into the range of the maximum scenarios.

However, there are also a number of factors that can have a negative impact on the development of the battery market:

- Upstream supply bottlenecks: The rapid growth of battery production capacities requires an equally rapid growth of upstream supply chains. Capacities along the entire supply chain must be ramped up in parallel. However, especially in the commodity sector, scaling up capacities is much more time-consuming (5–10 years) than building battery factories (2–4 years). Therefore, realistic scenarios assume that not all announced battery production capacities will actually be built. If significantly greater challenges arise in the development of upstream supply chains than expected today, this will have a negative impact on the development of the battery market. Influencing factors that are difficult to assess are the actions of governments in local protests against mining projects and the discovery of new raw material deposits.
- (Trade) conflicts: International trade went into crisis as early as the 2010s, triggered by trade disputes between the USA and China. Russia's invasion of Ukraine and the subsequent sanctions also have an impact on the battery industry, since Russia is a major nickel supplier with a global market share of slightly less than 10%. Such conflicts can therefore have a significant impact on the development of the battery industry. However, they are difficult to predict. Even more difficult to assess are their consequences. New conflicts and a further acceleration of the economic decoupling between the USA, Europe, and China can lead to problems along the supply chains with negative effects on the development of the battery market.
- Shortage of skilled labor: Many thousands of skilled workers are needed to build up the battery industry and its supplier industries. These workers must be trained and educated. This is a major task that requires the cooperation of the

governments, industry, and educational institutions. However, the battery industry competes with other emerging industries for talents. This is further exacerbated by the demographic trends in major battery producing countries. However, there is an opportunity for the battery industry to tap into skilled labor that is being laid off in the production of internal combustion engines. Advances in automation can also further reduce labor intensity. If the demand for skilled labor cannot be met, delays are to be expected, which will shift market development into the realm of the minimum scenarios.

- Economic slowdown: A general economic slowdown is likely to result in restrained consumer spending and thus reduced demand for batteries. Recessions are expected and occur at regular intervals. The realistic scenarios continue the patterns observed in the past. If instead a prolonged stagnation phase or even a depression occurs, this will lead to a slower development of the battery market.

The market reports evaluated in Fig. 7.1 are listed in Table 7.1 together with additional information on the level of detail of those reports. Most of the reports consider the world market in aggregated form. Some break down the market into individual regions or countries. The table also shows the period covered by the reports. Few reports make statements beyond 2030; as such, long-term projections are subject to great uncertainty. The year in which the publication appeared is also indicated.

7.3 Market Entry of New Battery Technologies

The fundamental challenge of the future battery market lies in the mutual interdependence of market demands and technological advances. The advancement of battery application in various sectors (especially in aviation and medical devices) requires a market maturity of high-performance battery solutions, while in turn technological development progress is—at least partially—determined by market potential. This section hence provides an outlook on foreseeable developments in battery technologies (not limited to cell chemistry but including management systems and further components) and how their market introduction might interact with demand scenarios in various segments.

KPIs play a crucial role in bridging the gap between market assessments and technological outlooks by defining the most important characteristics of a battery system with respect to their applicability. They serve as a measure of "how a battery can be used" (for market scenarios) as well as a guideline for "what a battery can provide" (in technology roadmaps). Our analysis will hence focus on current definitions of and trends in KPIs.

This section is structured as follows: we will first give a short overview of KPI target values for batteries on an international level. We will then discuss KPI trends in relation to both battery market segments and technologies. Finally, we derive conclusions for future market developments on the background of current research trends.

7.4 Overview of Target KPIs for Batteries

The set of KPIs for a particular battery application defines the main properties of battery performance in the respective application. It typically encompasses a wide range of technical parameters as well as cost parameters. For the sake of our analysis, we will mainly focus on the KPIs used in the most recent battery Strategic Research and Innovation Agenda (SRIA) [2]:

- Gravimetric and volumetric energy density at cell level (Wh per kg and Wh/l, resp.)
- Power density at cell level (W per kg and W/l, resp.)
- Cycle life (for high-capacity and high voltage applications, resp.)
- Cost at pack level (€ per kWh).

Besides of upcoming improvements of lithium-ion-based cell chemistry, SRIA provides KPI estimates for so-called "beyond lithium" approaches based on natrium ion and metal-air concepts. Another stream of innovation is the concept of solid-state batteries (SSBs) with polymer electrolytes. KPI estimates are taken from a recent report by the Fraunhofer ISI [12].

With the advancement and market introduction of new cell technologies, significant improvements in all KPIs can be expected (see Table 7.2), although the respective year of market availability bears uncertainty. For example, assuming the availability of systems with a lifetime of more than 6000 cycles in the year 2030 and over 15,000 cycles in the years after is well reasonable. The reader should keep in mind though that these numbers represent goals related to ongoing or foreseeable developments until the year 2030 rather than safe forecasts. However, a recent overview [15] of manufacturers announcements indicates an earlier market upscaling of sodium ion batteries than expected by SRIA.

7.5 KPI Trends in Relation to Both Battery Market Segments and Technologies

The next step in the analysis is to summarize current expectations for particular KPI levels from the demand/application perspective and compare them to the above results. For the purpose of our analysis, we aggregate market subsegments up to a reasonable degree and omit niche applications with relatively small market sizes. The results of the comparison are summarized in Table 7.3.

A differentiated picture emerges in the comparison of KPI requirements in different market sectors with current KPI projections of various battery technologies. For large market segments, esp. light- to heavy-duty vehicles, the needs on the demand side and the projections for generation 4–5 lithium-ion batteries on the supply side are in fair agreement. However, further research is needed to satisfy the needs of smaller segments such as airborne transport.

Table 7.2 Objectives and outcomes of advanced material development, based on the Batteries European Partnership Association [2] and Schmaltz et al. [12]

Technology/application	KPI goals: technological parameters	KPI goal: cost at pack level	Time to market
Generation 3 Li-ion batteries for mobility applications	50–400 Wh/kg, 750–1.000 Wh/l 700 W/kg, 1500+ W/l 3000+ cycles (high-capacity applications)/ 2000+ cycles (high voltage applications)	< 100 €/kWh	2025+
Generation 4 Li-ion batteries for mobility applications	400+ – 500+ Wh/kg, 800+ – 1.000+ Wh/l Up to 3000 cycles	< 75 €/kWh	2030+
Generation 5 Li-ion batteries for mobility applications	500+ Wh/kg, 1.000 Wh/l At least 800 cycles at 80% DoD	< 75 €/kWh	2030+
Li-ion batteries for stationary storage applications (commercial high-power applications) (a longer lifetime of 10,000+ cycles is defined for utility-scale applications)	500+ Wh/l 6000+ cycles	< 75 €/kWh	2030
"Beyond lithium"	Na-ion systems: 180 Wh/kg, 500 Wh/l 15.000+ cycles Metal-air systems: 200+ Wh/kg, 800+ Wh/l 2.000–5.000 cycles	<0.05 €/kWh/cycle corresponds to 100 €/kWh for 2.000 cycles, e.g.	2030+
Solid-state battery (SSB) with polymer electrolyte	440 Wh/kg, 900 Wh/l	n.a.	2030

"+" denotes "or more than"/"or later." Li: lithium. Na: sodium

Light-duty battery-electric vehicles for passengers are the largest market segment within the mobility sector. However, the KPI requirements of this segment cannot fully be met by generation 3 Li-ion batteries (1000 W/kg/2.200 W/l of power density in 2030). The same holds for plug-in hybrid electric vehicles. While their future market share is significantly smaller than for BEVs, they still constitute a demand of over 100 GWh [2] of battery capacity in the year 2030. Market maturity of generation 4 and 5 solutions improves the situation, while the power density remains a challenge.

Sodium (Na) ion-based systems are an option to satisfy the cycle life needs of medium to heavy-duty BEV applications (up to 6000 cycles) in the near future. The market introduction of these systems, expected to allow for a lifetime of over 15,000 cycles, is highly desirable to support a large-scale electrification of road freight transport. Likewise, expectations for cycle lifetime in stationary applications can—according to current projections—only be met by Na-ion systems. The power

Table 7.3 Comparing KPI goals on the demand side (market segments/applications) to KPI projections on the supply side (technology-specific)

Market segment, market size (2030)	KPI goals	Comparison to KPI projections			
		Gen. 3 Li-ion	Gen. 4-5 Li-ion	Na-ion, metal-air	SSB with polymer electrolyte
Mobility: light-duty BEV (1.000 - 2.500 GWh/a) and medium to heavy-duty BEV (200 GWh/a)	450 Wh/kg, 1.000 Wh/l	(+)	(+)	(-)	(-)
	1.000 W/kg, 2.200+ W/l	(-)	n. a.	n. a.	n. a.
	2.000 cycles (light)	(+)	(+)	(+)	n. a.
	6.000 cycles (medium to high)	(o)	(+)	(+)	n. a.
	85 EUR/kWh (light),	(o)	(+)	(-)	n. a.
	150 EUR/kWh (medium to high)	(+)	(+)	(-)	n. a.
Mobility: light duty PHEV (100 – 150 GWh/a)	350 Wh/kg, 800 Wh/l	(+)	(+)	(o)	(+)
	1.750 W/kg, 3.850 W/l	(-)	n. a.	n. a.	n. a.
	>2.000 cycles	(+)	(+)	(+)	n. a.
	120 EUR/kWh	(+)	(+)	(+)	n. a.
Mobility: Off-road mobile machinery[1] (30 GWh/a) and BE or hybrid electric ship with energy battery (4 GWh/a)	350 Wh/kg, 800 Wh/l (Ship: 1.000 Wh/l)	(+)	(+)	(o)	(+)
	>6.000 cycles (Ship: > 10.000)	(o)	(-)	(+)	n. a.
	200 EUR/kWh (Ship: 75 EUR on cell level)	(+)	(+)	(+)	n. a.
Mobility: BE or hybrid electric aircraft with power battery (up to 5 GWh/a)	450 Wh/kg, (power density n/a)	(+)	(+)	(-)	(-)
	>3.000 cycles	(o)	(-)	(+)	n. a.
	200-300 EUR/kWh	(+)	(+)	(+)	n. a.
Stationary applications	>250 Wh/kg, >700 Wh/l	(o)	(+)	(-)	(+)
	>700 W/kg, >1.400 W/l	(+)	n. a.	n. a.	n. a.
	15.000 cycles	(-)	(-)	🟩	n. a.
	70 €/kWh on module level	🟩	(o)	🟩	n. a.

Colors: goals are met (+, green), application goals are not met (−, red), ambiguous (o, yellow) because the KPI goals on the supply side are not clearly defined or specified. "n.a.": KPI estimate is not available in the considered literature

density projections for Na-ion systems (500 Wh/l) do not satisfy the requirements of stationary applications yet.

Off-road mobile machinery (up to 30 GWh per year in the year 2030), often characterized by continuous operation and robustness, requires large battery systems of up to 1000 kWh in size, optimized for a high energy (rather than power) density and outstanding lifetime requirements of up to 6000 cycles. Similarly, most water-borne transport applications (approx. 4 GWh/a in 2030) require even larger scales (up to several hundreds of MWh) and lifetimes (over 10,000 cycles). The latter requirement can neither be met with generation 3–5 battery concepts for mobility applications nor with metal-air systems. Li-ion batteries for stationary storage applications but also Na-ion systems would meet the cycle lifetime requirements but not the energy density demands. Improved solid-state batteries with polymer electrolytes might provide the power density required in these market segments by 2030 [12].

To conclude, while the technological development of batteries achieved remarkable results, solutions beyond current Li-ion batteries are needed to enable large-scale mobility and stationary applications. Particularly, power density levels beyond those of the coming Li-ion battery generations for road vehicle applications and improved cycle lifetimes for marine/aviation mobility and stationary applications are desirable. While sodium ion battery technologies are a promising option to allow for the high cycle lifetimes needed in most airborne and waterborne transport applications, energy density needs to improve to fully match the requirements of current aircrafts and long-distance vessels for a full electric operation. A mature market battery solution for the electrification of maritime and particularly airborne transportation might have a high symbolic value, beyond its limited market size and relatively modest contribution to current greenhouse gas emissions.

7.6 Current Research Trends and Conclusions for Future Market Developments

Current challenges in battery research and development span over the whole range of the battery ecosystem. The European Battery Partnership defines in its recent Strategic Research and Innovation Report six focus areas to support the development and market introduction of future battery technologies along the value chain: Raw Materials and Recycling, Advanced Materials and Manufacturing, Battery End Uses and Operations, Crosscutting Topic Safety, Crosscutting Topic Sustainability, and Coordination [2]. The report outlines strategic actions and a timeline of Technology Readiness Level (TRL) estimates in each area. The main trends and TRL projections in the areas of materials and manufacturing are summarized in Fig. 7.2.

7.7 Lithium-Ion Batteries

Innovative cell chemistries are catching up, but the current Li-ion battery will most probably remain the dominating battery type until 2030 due to successful market uptake and an established industrial value chain. The Li-ion battery concept is subject to continuous improvement and still bears potential for optimization. Current research focuses on improving the energy density while delivering on the other application relevant KPIs [1].

Fig. 7.2 Timeline of selected future battery developments, based on Batteries European Partnership Association [2], pp. 56 and 61, complemented by estimates on SSB development based on Schmaltz et al. [12] (pp. 92–93). The numbers indicate TRL estimates

- Intensive research is being carried out into nickel-rich NMC materials on the cathode side. Increasing the nickel content increases the specific capacity while reducing the cobalt content. Suitable composites are required to assure a high cycle stability. Nickel-rich 811-NMC cathodes are close to market launch.
- On the anode side, research aims at increasing the silicon content of graphite electrodes (up to 10% Si/SiOx in generation 3) and thus the specific capacity without large loss of cycle stability.
- Research on electrolytes focuses on compatibility with the electrode by developing additives for organic liquid electrolytes and on solid electrolytes, to improve battery safety and render the use of metallic lithium anodes possible.
- Coated separator membranes improve lifetime, temperature tolerance, and safety properties of batteries, e.g., through hydrogen fluoride absorbing ceramic particles. Extra costs for coating need to be compensated for by optimizing the manufacturing process.

7.8 Innovative Cell Chemistries

Substantial improvements of battery KPIs can be expected from so-called post-lithium-ion batteries. Most technologies have a high theoretical energy density. A variety of challenges still need to be overcome before market maturity can be achieved.

- Major progress in solid-state batteries (SSBs) with polymer electrolytes is expected in the coming years, bearing large potential to fulfill energy density KPIs in mobility applications [12].
- The lithium solid-state battery logically connects to the Li-ion battery. The application of solid electrolytes, in the form of ceramics, polymers, or hybrid, allows for the use of metallic lithium in cell chemistry.
- Na-ion and Ka-ion batteries follow a similar operating principle as Li-ion batteries but bear the advantage of less raw material scarcity compared to lithium. Due to the larger ion radius and lower redox potential, lower energy densities are expected for these two technologies. Na-ion batteries have already entered the market but fill only a small market niche for stationary storage so far due to high costs.
- The Zn-O_2 battery (as an example of metal air batteries) has already reached technological maturity. However, the energy density is still far below the predicted energy density, making this system mostly suitable for stationary applications. Improving reversibility and thus cycle stability remains a challenge.
- Redox flow batteries, e.g., based on vanadium, potentially allow for high cycle stability ($>$10,000 cycles) but have only a very low energy density.

7.9 Cell Design and Manufacturing Processes

Next to advanced material development, innovations in cell design and manufacturing processes provide chances especially for cost reductions. Trends in this area are the following:

Ongoing improvements in particular steps of the manufacturing process contribute to production efficiency. Prominent examples are 3D printing (allowing for individual cell designs), 3D inkjet processes (facilitating the production of anodes and cathodes), selective laser melting (SLM, enabling complex filigree geometries, e.g., in electrode production), and selective laser sintering (SLS, saving additional assembly steps).

Advanced environmentally sustainable processing techniques for Li-ion batteries (denoted as “Step 2 Advanced Cell Manufacturing Processes” in the SRIA report) will become mature in the second half of the decade, with positive effects on the environmental footprint of battery production, in particular energy efficiency (and, hence, costs). First improvements on coating processes are expected already by 2025. The expected impact on KPIs is a 20% cost reduction, and carbon intensity might drop by 25% [2].

Progress in digitalization improves testing and manufacturing processes in the second half of the decade. A major role plays the development of data-driven or physics-driven so-called digital twins—an advanced method for monitoring and managing complex battery systems [10]. A 25% reduction in energy consumption and lower capital costs of manufacturing processes can be expected. The integration of smart functionalities in battery cells allows for improved performance, reliability, and lifetime of 20% and more [2].

7.10 Battery Systems and End Use

Manufacturing is not the end of the process to ensure a large-scale market uptake of novel battery technologies in mobility and stationary applications. Improvements to the level of battery systems and end use are important to ensure high performance and safety. Current trends focus on improved safety (e.g., Battery4Europe defines the action item to introduce safe-by-design solutions by 2028) [2]; optimized battery management systems allow for accurate and robust determination and active control of cell states (e.g., current of individual cells), improved balancing schemes, and error diagnostics [9].

7.11 Raw Materials, Recycling, and Sustainability

Recent supply chain disruptions raised concerns on the availability and costs of raw materials in battery production. A recent report by the IEA provides an overview of current trends and challenges in battery supply chains [8]. The stability of the supply chain depends on a reliable supply of scarce materials. Many of them, most prominently lithium, are limited to a few production sites and suppliers. On this background, measures to improve the resilience of the supply chain are highly desirable:

- Regional diversification of material sources and suppliers.
- Improving social sustainability standards of material suppliers, not only as an ethical necessity but also as an essential contribution to supply chain resilience.
- Improved recycling processes and additional measures for supply chain efficiency, such as tracing and labeling procedures. For example, the Battery4Europe network defines the action item to develop a tracing and labeling scheme over the full life cycle by 2028 [2]. Also, the concept of a "digital battery passport" receives growing attention [5].

Recycling plays a crucial role in reducing material scarcity and the ecological footprint of batteries. With growing battery production, a massive increase in recycling volume can be foreseen. Recent estimates of the volume of lithium-ion batteries components in Europe amount to 230 kilotons per year in 2030 and about 1500 kilotons per year in 2040 [11].

Current recycling approaches suffer from the fact that production processes do not take end of life treatment into account, so that huge efforts are required for the separation of materials. Besides direct mechanical separation, pyrometallurgical and hydrometallurgical methods are currently applied. Pyrometallurgical methods require substantial energy and material input for chemical calcination and combustion. Hydrometallurgical approaches are more complex and require less energy but use large amounts of toxic substances and require water purification. Both result in high costs and a low material recovery rate. The savings achieved by using recycled material compared to never used material is currently in the range − 5 to +20% [13]. A ready-for-recycling approach in cell design and battery pack assembly is hence the most effective action in this field.

More generally, the environmental sustainability of batteries receives growing awareness. For example, water use of mining is a serious concern in lithium mining regions such as Chile [4]. Due to current uncertainty in energy costs, substantial progress in material recycling and efficient production processes is of vital interest for the battery industry and not only an environmental concern anymore. The development and introduction of sustainability standards and regulations clearly contributes to improved material supply security and the resilience of manufacturing and distribution processes. The widespread implementation of circular designs in industry can be expected in the second half of this decade.

7.12 Conclusions for Future Market Developments

The overview of current research and development trends leads to the following conclusions for future market developments:

1. Significant improvements in Li-ion batteries can be expected by 2030. According to the above analysis of KPI needs in various applications, post-generation 3 systems can contribute to future market maturity of light- and medium to heavy-duty vehicles in road transportation.
2. Stationary applications and air/marine mobility would benefit from further efforts to improve cycle lifetimes of Li-ion batteries, production ramp-up of Na-ion batteries, and market introduction of improved solid-state batteries.
3. The main application of Na-ion, metal air, and redox flow batteries is currently expected in stationary applications due to their relatively low energy density. As discussed above, their high cycle lifetime might be beneficial in some mobility applications, too. With growing demand for electricity storage, the market share of these innovative concepts will increase substantially, bearing the potential for cost decreases from economies of scale.
4. Improvements in cell design and manufacturing processes as well as advanced material recycling concepts bear a large potential to improve the efficiency of the overall battery supply chain. Substantial cost reductions can be expected, although there is hardly any reliable estimate for the total reduction potential.
5. Growing awareness of risks for supply chain resilience and environmental footprint initiates a trend toward a more circular, diversified, and sustainable approach of the battery supply chain. From a market perspective, this trend translates into improvements of supply and cost stability.
6. Enforced technological research and development are inevitable to secure the accelerating market growth for batteries and the expectations for future cost decreases. Collaboration within the battery industry, public funding, and a stringent strategic research agenda are essential to achieve this goal.

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Part IV
Economics and Materials of Present Batteries

Preface

To date, lithium-ion batteries (LIBs) are unrivaled in terms of energy density and performance, making them the technology of choice for virtually all mobility applications but also stationary storage systems. However, they are not the only energy storage option and compete with numerous other technologies in terms of cost and performance but also (to an increasing extent) in terms of sustainability such as material intensity or criticality. This chapter gives an overview of the present state of the art in batteries under these aspects. As such, it is mainly focused on lithium-ion technology, treating the main drivers for their success, but also the problems that might arise from the high material intensity of the battery sector and the corresponding limitations that might arise from them in the future. Specifically, Chap. 8 treats the challenges posed by the different energy storage applications and how electrochemical storage systems are typically tailored to match these in terms of performance and costs. From there, Chap. 9 establishes the link to the circular economy principles as introduced in Chapter 2, treating the presently prevailing and near-future recycling processes and the potential (but also limitations) of them to close the material circles. Finally, a spot is also put on safety aspects, which have important implications especially for end-of-life handling and logistics and thus also the efficiencies and corresponding impacts of battery recycling.

Chapter 8
Performance and Cost

Johannes Büngeler and Bernhard Riegel

Contents

8.1 Introduction

Over the past few decades, a wide variety of electrochemical storage systems have been developed and made commercially available. Today's prominent electrochemical storage systems encompass technologies like lead-acid, nickel-cadmium, and nickel-metal hydride alkaline batteries, sodium-nickel chloride and sodium-sulfur high-temperature batteries, and lithium-ion technology.

Each of these unique electrochemical storage systems possesses specific features. Product variants, adjusted to meet the requirements of individual applications, are offered with tailored performance characteristics [20]. These tailored performance characteristics primarily encompass energy and power density, life cycle, design life, and the operating temperature range.

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Consequently, certain applications are dominated by specifically adjusted electrochemical systems. Due to the complexity of application-specific requirements, selecting the most suitable electrochemical storage technology based solely on tabulated performance data can be challenging. Additional necessary system components, such as thermal management and battery management, can significantly impact the performance of the overall system and should not be overlooked.

A technology substitution within a particular application only occurs if a technology reaches its performance limits and can no longer meet the changed or increased requirements of the application. Other reasons for a technology change in specific applications are usually economical (e.g., total cost of ownership) or environmental (e.g., bans on heavy metals, safety concerns).

Sustainability aspects, such as the recycling and recovery of battery materials, will become increasingly important for end customers seeking to reduce the CO_2 footprint of their applications.

The following subchapters will discuss the main performance criteria and costs associated with the different technologies, addressing each technology separately.

8.2 Lead-Acid Batteries

Lead-acid batteries accounted for the largest share of the global battery market, at around 90%, until 2010. From then on, the market share of lithium-ion batteries has been growing steadily, and in 2021, the market share of lithium-ion batteries was already slightly higher than the market share of lead-acid batteries, due to the upcoming demand for electromobility.

For the automotive and industrial market, the lead battery has been the predominant energy storage system for over 100 years.

The lead-acid batteries are on the market in two major different construction designs. On the one side, there is the flooded or “vented” construction design, requiring maintenance. On the other side, there is the maintenance-free valve-regulated (VRLA) batteries [1].

Today, the share of maintenance-free lead-acid batteries has increased to about 80% of the total lead market. There are two types of VRLA batteries, which differ in the way the electrolyte (sulfuric acid) is fixed. In one type, the electrolyte is fixed in a silica gel; in the other, it is in an AGM (absorbent glass mat) material.

Lead-acid batteries with AGM technology have become the most important technology in the field of automotive and industrial applications [3]. The share of AGM types, which are more efficient than gel types, is 85% of the VRLA market.

The lead-acid battery innovation has historically been market driven, primarily by the end-user applications. This explains the very wide range of specific battery products, sizes, and construction designs.

The positive electrodes in lead-acid batteries can have either a tubular, flat grid plate design or plante design, while the negative electrodes are always constructed as a flat grid plate design.

Table 8.1 Main performance and cost parameters of the most important positive electrode designs used with the lead-acid technology

Electrode design	Cost	Performance			
		Performance classification	Cycle-life	HP (high power)	HE (high energy)
Planté	Very high	High power	< 100	+++	+
Grid	Low	Low to high	> 100–1.000	++	+++
Tubular	Medium	Medium	> 1.600	+	++
Bipolar	Low (target)	High	> 1000 (target)	+++	+++
Total range	50–250 €/kWh		Up to >1600	<700 W/kg	<60 Wh/kg

(+) is good
(+++) very good

Table 8.1 shows the most important positive electrode designs and their main performance characteristics and cost. It is evident that there are significant differences between the various types of electrodes and their properties. For instance, the plante electrode exhibits high-power density but comes with a higher price tag and a lower life cycle. In contrast, the tabular electrode has a lower power density. The grid electrode, currently employed in VRLA batteries, offers lower costs and a higher power density compared to the tabular electrode. Additionally, ongoing development is focused on the bipolar electrode, as outlined in the "Further Development" section. This electrode aims to combine high performance, extended cycle-life, and a lower price.

The main application fields for lead-acid batteries are as follows:

- Automotive mobility applications (grid electrode)
- Material handling and logistics applications (tabular electrode)
- Stationary energy storage applications (grid, tabular, and plante electrode)

Advantages

- High-power densities
- Very robust and abuse tolerant (safe without an additional battery management system (BMS)
- Cost-effective with low maintenance cost
- Application approved
- High recyclability

Disadvantages

- Low gravimetric energy density
- Mandatory ventilation for flooded lead-acid batteries
- Water loss that requires maintenance in flooded cells
- Contains lead.

Further Development

In recent years, the lead-acid battery has undergone many relevant improvements in terms of lifetime and performance.

These include material innovations such as the addition of novel carbon additives and expanders to the anode to avoid negative electrode sulfation and the use of innovative separator materials and the development of more resistant alloys for high-temperature environments. The outstanding feature in this process is that these improvements have been tailored to the specific application. These novel designs are referred to as "advanced lead-acid batteries," which include bipolar, lead-carbon, and pure lead thin plate technologies [2].

Bipolar Lead-Acid Batteries

While bipolar and monopolar designs share the same lead-based chemistry, they differ in that in bipolar batteries, the cells are stacked in a sandwich construction so that the negative plate of one cell becomes the positive plate of the next cell. Stacking these cells next to one another allows the potential of the battery to be built up in 2 V increments. Since the cell wall becomes the connection element between cells, bipolar plates have a shorter current path and a larger surface area compared to connections in conventional cells. This construction reduces the power loss that is normally caused by the internal resistance of the cells. At each end of the stack, single plates act as the final anode and cathode. This construction leads to reduced weight since there are fewer plates and bus bars are not needed to connect cells together. The net result is a battery design with higher power than conventional monopolar lead-based batteries.

Until recently, the main problem limiting the commercialization of bipolar lead-acid batteries was the availability of a lightweight, inexpensive, and corrosion resistant material for the bipolar plate and the technology to properly seal each cell against electrolyte leakage.

Architectural advantages are as follows:

- Lower inner resistance, i.e., higher power density
- Increased energy density up to 63 Wh/kg

The lead-acid battery technology has a well-established circular economy. At the end of their life, lead-based batteries are collected for recycling. Within the EU, almost 100% of lead-based batteries are returned and recycled in a closed loop with a high efficiency of over 80% [20]. The market for lead-based batteries in the EU is mainly served by recycled material, and the demand for primary lead reserves is low.

8.3 Li-Ion Technology

As lithium shows the most negative normal potential of 3.05 V against hydrogen, Li-Ion batteries achieve higher gravimetric and volumetric energy densities compared to other widely used technologies like lead-acid or nickel-based systems.

In the past few decades, lithium-ion batteries have replaced the NiMH batteries in the field of portable and mobility applications due to their higher energy densities (80 Wh/kg vs. up to about 300 Wh/kg).

Currently, the expected market growth for Li-Ion batteries will be more than 3 TWh by 2030 and will largely serve with up to 85–90% the e-mobility and the energy storage markets [20].

The high market growth will most likely result in lower cost per kilowatt-hour due to standardization and mass production.

Due to the variety of possible combinations of cathode and anode materials, the resulting Li-ion batteries show specific and individual performance characteristics suitable for different kinds of applications. The development of Li-ion technologies suitable for industrial and automotive applications is still a challenge in terms of material research process, production, development, recycling, safety, and transportation [4].

Typical cathode active materials are as follows:

- LCO—lithium cobalt oxide ($LiCoO_2$).
- LMO—lithium manganese oxide spinel ($LiMn_2O_4$).
- LFP—lithium iron phosphate ($LiFePO_4$).
- NCA—lithium-nickel-cobalt-aluminum oxide ($LiNiCoAlO_2$).
- NMC—lithium-nickel-cobalt-manganese oxides ($Li(NiCoMn)O_2$).

The most relevant cathode material for the e-mobility is the NMC material, which is currently further developed to meet the major requirement for higher energy densities to achieve an increased driving range. This results in modifications of nickel-cobalt-manganese oxide (NMC) materials, from NMC 111 to NMC 811, with increased nickel and reduced cobalt content. Typically, these NMC materials are combined with anode materials of high capacity (Fig. 8.1).

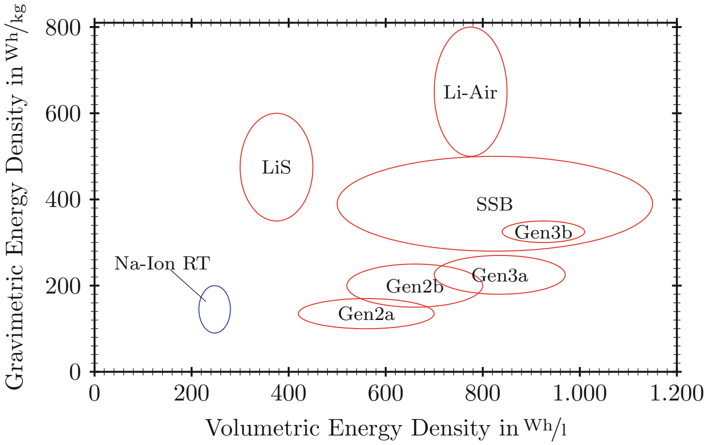

Fig. 8.1 Gravimetric and volumetric energy densities of most relevant Li-Ion and post-lithium battery technologies

Table 8.2 Cost and performance data of most relevant anode/cathode combinations for NMC batteries

Generation	2a	2b	3a	3b
Cathode	NMC 111	NMC 523–622	NMC 622	NMC 811
Anode	100% C	100% C	C + Si (5–10%)	Si/C composite
Gravimetric energy density in Wh/kg	100–170	150–250	180–270	300–350
Volumetric energy density in Wh/l	420–700	520–800	700–970	850–1000
Cost in €/kWh	100–110	90–100	85–95	65–95

Table 8.2 and Fig. 8.1 show the performance and cost parameters of the most relevant anode/cathode combinations.

The electrolyte composition is usually LiPF6 in organic solvents with additional additives in order to improve certain properties. Field of developments is electrolytes that can withstand higher voltages and consequently higher energy densities.

Depending on the active material combinations, some advantages and disadvantages become less or more apparent.

Advantages
- Very high energy densities.
- High cell voltages: up to 3.7 V nominal.
- Can be optimized for specific application performance requirements.
- Tolerate to high discharge currents (discharged rate > 40 C).
- Fast charging possible.
- Batteries can be almost completely discharged without affecting cycle durability, lifetime, or high current output.
- Very low self-discharge rate (3–5%/month).

Disadvantages
- Sensitivity to deep discharge, overcharge, and excessive temperatures requires active battery management and monitoring.
- Relatively high sensitivity to high or low temperatures.

8.4 Post-Li-Ion Battery Technologies

In response to the growing demand for energy-efficient and environmentally sustainable energy storage, researchers are seeking alternatives to conventional lithium-ion batteries. This exploration is motivated by the need to address not only energy efficiency but also the ecological and social impacts of current battery technologies. A key challenge is developing electrodes that are durable and stable while also offering high energy densities and quick charge-discharge rates.

To address these challenges, studies are concentrating on materials that are more abundant and environmentally friendly compared to traditional lithium sources.

The exploration of post-lithium battery technologies, based on alternative materials, presents both challenges and unique opportunities.

8.4.1 Lithium All-Solid-State Battery Technologies

Structure of Solid-State Batteries

The electrochemical system of lithium solid-state batteries is similar to lithium-ion batteries. The major difference is that, at the very least, the electrolyte is in a solid state.

All-solid-state batteries are generally considered to be a class of batteries that will enable higher energies in the future (see Table 8.3 and Fig. 8.2). The actual increase in energy comes only through the elimination of the graphite by the metallic Li anode.

Solid-state batteries use an electrolyte made of solid material instead of the usual liquid electrolyte. The electrodes are also made of solid material in terms of an all-solid-state battery [5].

Currently there are solid/liquid hybrid cells on the market which are also described as a certain kind of solid-state system.

The main components of the SSB cell are the anode and cathode active materials and the solid electrolytes. Various materials are suitable for use in SSB.

Anode Active Material

The most promising anode active materials in order to achieve high energy density are lithium metal and silicon. Lithium metal anodes are considered the most promising, as they enable the highest possible energy density on the anode side.

Cathode Active Material

Soon, Ni-rich layered oxides (NMC, NCA) and lithium iron phosphate (LFP) will become the most likely to be dominant cathode active materials. These materials are already commonly used in state-of-the-art LIB.

Table 8.3 Cost and performance data of most relevant post-Li-Ion and sodium-ion battery technologies

	Li-SSB	Lithium-air	LiS	Sodium-ion RT[a]
Gravimetric energy density in Wh/kg	280–500	500–800	180–270	90–160 (200)
Volumetric energy density in Wh/l	500–1150	700–850	300–450	215–280
Cost in €/kWh	Not commercially available	Not commercially available	Not commercially available	40–65

[a] Adelhelm [17]

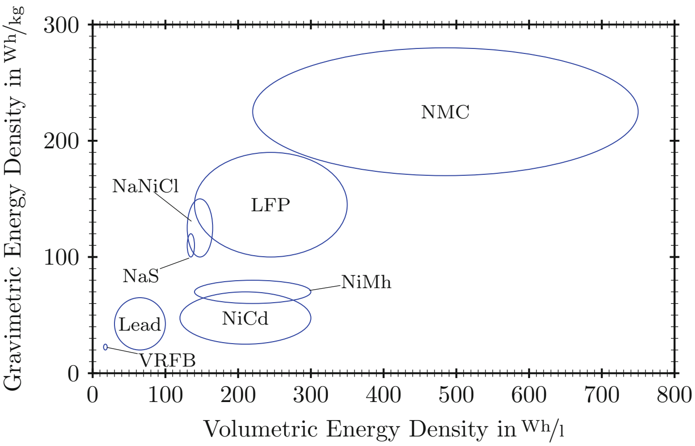

Fig. 8.2 Gravimetric and volumetric energy densities of different battery technologies

Electrolyte

With solid-state batteries, there is the possibility that part of the solid electrolyte can be incorporated into the electrodes. The main advantages of future solid-state batteries are that the energy density of the cells would increase significantly in the future and the risk of fire would also decrease due to the less pronounced flammability of the electrolyte.

Compared with Li-ion cells, high-power densities cannot be achieved with the solid-state technology. The reason for this is usually the high Li^+ contact resistance at the phase boundary between the cathode and the solid electrolyte.

Solid-state cells are being developed with both polymeric and inorganic solid electrolytes. Inorganic electrolytes can be distinguished between sulfide and oxide solid electrolytes.

The specific energy/energy density of solid-state cells can be increased by the following:

- Lower electrolyte/separator thickness
- Use of Li anodes
- Use of nonporous active materials
- Increase in cell voltage due to the higher electrochemical stability (electrochemical window) of the electrolyte

Advantages of solid-state batteries compared to liquid electrolyte Li-Ion batteries are as follows:

- Higher energy density than Li-ion
- Safety—instead of flammable organic liquid electrolyte, use of a solid-state electrolyte (ceramic, polymer)
- No electrolyte leakage
- Can fit easier casing shapes

- Solid-polymer Li-ion cells can be made as thin as 0.1 mm or about one-tenth the thickness of the thinnest prismatic liquid Li-ion cells
- Potentially lower manufacturing costs

Disadvantages of solid-state cells compared to liquid electrolyte cells are as follows:

- Power limited by low ionic conductivity of electrolyte
- High interfacial resistance
- Poor interface contacts

In addition, due to the non-combustibility (at least of the ceramic electrolyte) and the higher temperature resistance of the electrolyte, safety-relevant components can be reduced in the module/pack, thus achieving a volume/mass reduction for the battery system.

8.4.2 Li-S Batteries

Lithium-sulfur batteries represent a new type of battery that promises high gravimetric energy densities at a moderate cost (see Table 8.3 and Fig. 8.2).

Design

Li-S batteries usually have a cathode consisting of sulfur and carbon and an anode of lithium metal to take advantage of the high specific capacity of the sulfur cathode [6].

Currently, there are also approaches of using a liquid polysulfide solution instead of a solid-state sulfur electrode. This idea is not new and was published as early as 1975.

Challenges and Opportunities

The cathode material of common lithium-ion cells is the most expensive component of a battery (more than 20% of the cell cost). It contains cobalt and nickel. Both are rare raw materials whose costs tend to rise rather than fall when batteries are mass-produced. In lithium-sulfur batteries, this cost item is eliminated, potentially saving more than 20% of the cost, because sulfur is very inexpensive and available in large quantities. Dry electrode manufacturing processes can also reduce production costs.

The theoretical gravimetric energy density of around 2500 Wh/kg is almost ten times that of conventional lithium-ion batteries.

However, the Li-S battery has disadvantages in terms of volumetric energy density. Future applications could be for situations in which the low weight of the battery is more important than its size, such as quadcopters, aircrafts, and ships. These appear to be more realistic applications for Li-S batteries.

The cycle stability, i.e., the lifetime of Li-S batteries, is currently still very low (limited to less than 200 cycles). Cells from pre-commercial production achieve only about 100 cycles at an energy density of 350 Wh/kg. However, cells with a significantly longer service life of several thousand cycles have already been achieved on a laboratory scale.

Advantages

- Main advantage of Li-S batteries is the potentially high gravimetric energy density, estimated up to 600 Wh/kg in perfect systems.
- Hope for low cost: Compared to LIB, it is hoped that the low cost of sulfur will result in significantly lower prices for energy storage. However, this is partially offset by the higher cost of metallic lithium (compared to graphite).
- The usage of pure materials allows higher recyclability.

Disadvantages

- Volumetric energy density lower than lithium-ion batteries (currently about 50%). Even in fully developed cells, at most the level of today's lithium-ion batteries can be achieved.
- Achievable performance lower than in commercial lithium-ion batteries.
- Current prototypes can only be operated at currents of approx. C/2.

The low cost and high abundance of sulfur (i.e., the active cathode material) make LiSB more appealing than Li-ion batteries, given the fact that the latter use critical materials, such as cobalt and nickel, in the manufacturing of the cathodes. LiSB are promising because of the high energy density, low cost, and natural abundance of sulfur.

8.4.3 Lithium-Air Battery Technologies

Lithium-air batteries possess a great potential for efficient energy storage applications in order to resolve future energy and environmental issues. The extremely high theoretical energy density is attractive, but there are still various technical limitations to overcome. The performance of lithium-air batteries is governed mainly by electrochemical reactions that occur on the surface of the cathode [7]. Widespread interest in various carbons and their applicability as cathode materials in lithium-air batteries are a result of their highly specific surface area and porosity, their lightweight, and their low production cost.

Among the group of metal-air batteries, intensive research is being carried out in particular on the development of lithium-air batteries. Since lithium has the highest electrochemical potential of all metals, these batteries offer the highest energy density by far of all metal-air systems that can theoretically be achieved [8, 18]. Compared with the state-of-the-art, it is hoped that energy densities can be achieved that are about ten times higher in practice, in order to make the ranges of electric vehicles based on such batteries competitive with today's gasoline-powered cars.

However, it may result in the need for a lot of additional technology and electronics (e.g., to clean the air), so that the weight and space this takes up reduces the theoretical energy density to such an extent that the batteries hardly have any advantages over more advanced lithium-ion batteries. For example, the theoretical material energy density of a lithium-air system is up to 3450 Wh/kg, but if the entire periphery is taken into account, the possible energy density is reduced to about 1000 Wh/kg. Currently available primary cells achieve energy densities of around 800 Wh/kg.1.

Major challenges currently lie in achieving an acceptable number of charge cycles and reducing voltage losses during charging and discharging.

8.4.4 Sodium Ion Room-Temperature Technology

In comparison with the state-of-the-art high-temperature sodium batteries, the upcoming new sodium-ion battery technology operates at room temperature. The sodium-ion battery has a similar working principle to the Li-ion battery. Sodium ions also shuttle between the cathode and the anode to store and release energy [16].

The significantly higher global equal distribution of sodium and absence of critical raw materials like cobalt and nickel in the cathode lead to cost reductions and lower environmental impact of the sodium system compared to lithium-ion [15]. Due to the technological similarities with existing Li-ion batteries, the industrialization process of sodium-ion batteries can be accelerated. A significant advantage is that the sodium-ion battery can be manufactured with the same production facilities as lithium-ion cells.

For cathode materials, the most important part of sodium-ion batteries, Prussian blue analog, layered metal oxides, and NASICON (sodium (Na) super ionic conductor) have their own advantages in different aspects. The most critical indicators based on potential application scenarios are higher energy density, longer life cycle, and better low temperature performance. Overall, the cost and safety advantages of sodium batteries will gradually gain in prominence. Therefore, it is likely that sodium-ion batteries will be used in different automotive and industrial applications.

So far, the technology is not yet fully developed and still needs to be tested in practical applications. Safety concerns have also not been conclusively assessed, especially given the lower melting point of sodium in potential sodium plating scenarios. It is believed that its properties at low temperatures are superior to those of lithium-ion batteries.

8.5 Nickel-Based Batteries

Alkaline batteries that use nickel hydroxide as a cathodic material belong to the mainstream battery systems.

The most important representatives of this technology are the nickel-cadmium (NiCd), nickel-metal hydride (NiMh), as well as nickel-zinc (NiZn) and Ni-iron (NiFe) systems. In past decades, only NiCd and NiMH technology has played an important role in portable, automotive, and industrial applications. Therefore, only the cost and performance of the NiCd and NiMH systems will be discussed below.

It can already be pointed out that neither NiCd nor NiMh play a significant role in the current markets and are only used to a small extent exclusively in niche applications.

Due to the performance and the costs of these systems, it can be assumed that they will be substituted by other technologies, such as Li-Ion, by 2030.

8.5.1 Nickel-Cadmium Batteries

Nickel-cadmium batteries played a major role in the past, competing with lead-acid batteries in certain applications.

The general advantages of the very reliable NiCd battery system is the higher energy density, the robustness, and a high deep discharge cycle-life—even at low temperatures when compared with lead-acid batteries.

The electrodes for NiCd systems are classified into five electrode types: pocket electrodes, sintered electrodes, plastic-bonded electrodes, nickel foam electrodes, and fiber electrodes [9].

Table 8.4 presents the key properties and costs of these electrodes. The pocket plate electrode, characterized by its relatively thick electrode, is primarily used in applications that require low to medium performance. It has been the dominant choice for standby applications like uninterruptible power supplies (UPS) and emergency power supply systems for railway rolling stock. On the other hand, sintered electrodes are designed for high-power cells that can deliver significant power output. However, the sintered structure undergoes mechanical stress during charge and discharge cycles, which can potentially affect the overall durability and longevity of the system. Moreover, this technology is associated with higher costs compared to other alternatives. Despite these limitations, this energy storage system

Table 8.4 Cost and performance data of most relevant NiCd electrode designs

Electrode design	Cost	Performance			
		Performance classification	Cycle-life	HP (high power)	HE (high energy)
Pocket plate	Low	Low	< 1.000	–	+
Sintered	High	High	> 2.500	+++	+++
Fiber	Medium to high	Medium to high	> 3.500	++	++
Foam	Medium to high	High	> 2.500	++	+++
Total range	300–450 €/kWh		Up to >3500	200–500 W/kg	25–60 Wh/kg

(+) is good
(+++) very good

finds application in demanding sectors such as aircraft, military, railway, and vehicles where high performance and reliability are crucial requirements.

The fiber electrode enables the fabrication of both high-power and high-energy cells by adjusting the electrode thickness accordingly. These cells exhibit long life due to their ability to compensate for volume changes in the active material during cycling, thereby preventing shedding of the active material. They also offer fast rechargeability, facilitating quick energy replenishment. This versatile system finds applications in various domains, including standby and mobile applications such as railway rolling stock and automated guided vehicles (AGVs). Additionally, it is suitable for use in aviation and space flight applications where high performance, durability, and reliability are essential.

The foam technology emerged in the late 1980s to address the need for energy cells with higher volumetric and specific energy capacities. Unlike sintered technology, which allows only a maximum of 50% of the electrode volume for active material loading, the foam approach utilizes a metallic nickel substrate. The electrode structure is formed by electrolytic nickel plating of polyurethane foam, followed by the removal of the organic core material under high-temperature conditions in a reducing atmosphere. The resulting isotropic reticulated substrate exhibits exceptionally high porosity exceeding 95%. As a result, the available porosity for active material loading increases by approximately 30% compared to sintered substrates. Overall, this technique offers enhanced active material utilization and provides higher porosity for improved energy capacity, meeting the requirements for higher volumetric and specific energy cells.

Cell designs for NiCd batteries are prismatic or spiral wound, flooded, or maintenance-free valve regulated.

Nickel-cadmium cells have been manufactured as maintenance-free, sealed battery system since the 1950s.

The sale of new cadmium-containing batteries in the EU has only been permitted for a few applications since December 2009, and it must be ensured that batteries are returned for recycling at the end of life. The few exceptions are portable batteries for emergency or alarm systems, including emergency lighting and medical equipment, and certain industrial applications.

The NiCd battery system has become a subject of environmentally related discussions, due to the fact that cadmium is a hazardous heavy metal and has been banned from many applications. This has resulted in the NiCd being substituted in many applications by the NiMh technology.

Advantages

- High-power capability
- Fast rechargeability
- Good low temperature performance (−40 °C)
- Good energy density

Disadvantages

- Poor environmental compatibility: Cadmium is a toxic heavy metal
- High self-discharge rate
- Low cell voltage of 1.2 V/cell

8.5.2 Nickel-Metal Hydride Batteries (NiMH)

Since the 1990s, NiCd batteries in the consumer markets for portable devices have been displaced by NiMH batteries. The reason for this was the higher energy storage capability achievable with NiMH and the general concern about cadmium as an environmentally hazardous material. Beneficial for an easy substitution of the NiCd technology by NiMh is the similar cell voltage of 1.2 V/cell [10].

The NiMH system was developed in the 1980s for electronic devices with high energy demand. During the 1990s, NiMH was the dominating electrochemical storage system for portable devices, which was replaced by Li-ion battery system in the middle of the 1990s. The Li-ion technology has shown even higher gravimetric and volumetric energy densities, which are essential for advanced portable devices. Another major application where NiMH played a very important role was the introduction of the first hybrid electrical vehicles at the beginning of the twenty-first century. In particular, the high-power performance of the NiMH battery systems was the greatest attraction for automotive applications.

The basic technologies for the electrodes as well as for other components used in NiMH cells are very similar to what has been developed for NiCd cells in a variety of applications.

The preferred electrode types of NiMH are the sinter-type and the foam-type electrode.

Two major designs for NiMH batteries are realized, the cylindrical and prismatic types.

Advantages

- High energy and power density
- Robust, but not as robust as NiCd for deep discharge and overcharge
- Temperature operation range from −15 °C to 40 °C
- Fast rechargeability
- Environmentally friendlier compared to NiCd (no heavy metals)
- Good recyclability

Disadvantages

- Need for battery management system
- High self-discharge rate.
- Low cell voltage of 1.2 V/cell

8.6 Sodium-Based Batteries

8.6.1 High-Temperature Sodium Batteries

High-temperature sodium batteries consist of liquid electrodes and a solid electrolyte (usually an ion-conducting (e.g., Na+) ceramic). These batteries require relatively high operating temperatures of >300 °C to maintain the sodium-based electrode in the liquid state as well as to increase the conductivity of the solid electrolyte.

Mainstream technologies are the sodium-nickel-chloride (NaNiCl) and the sodium-sulfur battery (NaS).

NaNiCl and NaS batteries have a service life of around 4500 cycles and an efficiency of 75–86%. Thermal losses due to the heating required to maintain the cell temperature must be considered if there are longer periods of time between charging and discharging. This can be influenced to a certain extent through a corresponding effort in thermal insulation.

8.6.1.1 Sodium-Nickel-Chloride Batteries

Sodium-nickel-chloride ZEBRA batteries were developed in 1985 in South Africa. The name ZEBRA stands for Zeolite Applied to Battery Research Africa. The cathode mainly consists of a porous nickel matrix which serves as a current conductor with nickel chloride ($NiCl_2$), which is impregnated with sodium aluminum chloride ($NaAlCl_4$). The anode is made of sodium [11].

Ceramic β-aluminum oxide is used as the separator and electrolyte, but the sodium ions do not allow electrons to pass between the anode and cathode. The operating temperature of this type of battery is between 270 °C and 350 °C, so that the electrodes (active material) are in the liquid state (melted) and the ceramic separator achieves high conductivity for sodium ions [12]. The specific energy of the cells is approximately 120 Wh/kg at a nominal voltage of 2.3 V to 2.6 V. Advantages over the sodium-sulfur battery are the inverse structure with liquid sodium on the outside, which allows the use of inexpensive rectangular steel housings instead of cylindrical nickel containers. The assembly is simplified in that the battery materials can be used in the uncharged state as sodium chloride and nickel, and the charged active materials are only generated in the first charging cycle. Sodium-nickel-chloride batteries have been used in the past for small series of electric vehicles in fleets and for stationary storage applications.

8.6.1.2 Sodium-Sulfur Batteries

The cells consist of an anode made of molten sodium and a cathode made of graphite fabric soaked with liquid sulfur to achieve electrical conductivity, as sulfur is an insulator. As in the case of the NaNiCl battery, the solid electrolyte β-aluminum oxide is used as the electrolyte, which becomes conductive for Na + ions above a temperature of approx. 300 °C. The optimum temperature range is between 300 °C and 340 °C. During the discharge process, positively charged sodium ions enter the solid electrolyte from the liquid sodium, releasing electrons. The sodium ions migrate through the electrolyte to the positive electrode, where they form sodium polysulfides. The cell voltage is 2 V. This process is reversed during charging.

A major advantage of the sodium-sulfur battery is that the internal resistance of the cell is almost independent of the state-of-charge. It only rises sharply toward the end of the charge because there is a decrease in sodium ions in the electrolyte. The required operating temperature is maintained in normal operation by the power dissipation of the cells themselves; in standby operation, it is achieved by an additional electric heater, which increases the battery's own consumption.

One advantage of this battery is a long calendar life of over 15 years [13]. The technology has been commercialized since 2002, mainly for large-scale storage with more than 1 MWh of energy [14].

8.7 Redox Flow Batteries

Redox flow batteries have been under development since the 1970s. The vanadium redox flow battery, developed in the 1980s, is considered the best-studied redox flow battery system.

Research efforts are currently focused primarily on reducing equipment and maintenance costs and searching for new electrolyte systems for higher energy densities, electrode optimization for higher performance, membrane development for lower maintenance costs, and electrical system development.

In redox flow batteries, the electrolytes are stored in two circuits in external tanks, while the electrochemical reaction takes place in a "power stack" (reversed fuel cell). Unlike other battery technologies, redox flow batteries thus allow independent scaling of power and energy capacity, making them suitable for a wide range of stationary applications [8, 18].

RF batteries are suitable as stationary energy storage mainly for industrial applications (backup power, load management), at distribution grid level (MW and MWh range, grid management), and for off-grid applications and minigrids (kW and kWh range, long-term storage).

A characteristic of this type of battery is that the power (size of the reactor) can be scaled independently of the capacity (electrolyte volume), because the electro-active materials (electrolytes) can be stored in external tanks [19].

Lifetime.

A lifetime of 20 years is generally expected for VRFB (vanadium redox flow batteries), where temperature control (against precipitation) and regular internal re-initialization of the electrolyte (which is state-of-the-art) are established.

The electrolyte, which represents a significant part of the capital cost of the vanadium redox flow battery, has an unlimited lifetime due to the possibility of reprocessing.

Vanadium redox flow batteries are considered to have an unlimited lifetime, since there are no classical aging mechanisms as in typical battery systems.

Up until now, more than 50 different RFB systems have been described in the literature, of which only a small number have been commercialized or are in the commercialization phase.

The most relevant systems currently are as follows:

- Iron/chromium (Fe2+/Fe3+; Cr2+/Cr3+)
- Bromine/polysulfide (Br-/Br3-; S22-/S42-)
- All-vanadium (V2+/V3+; V4+/V5+)
- Vanadium/bromine.

Advantages
- Good energy efficiency: 60–85%
- Very long service life (> 20 years)
- Electrolyte recyclable and reusable
- Cycle stability (> 10,000 cycles)
- Good response time (some micro- to milliseconds)
- Scalable, modular design
- Independent scaling of power and capacity
- Due to separation of energy storage and converter
- Overcharge and deep discharge tolerance
- Low maintenance
- Almost no self-discharge

Disadvantages
- Low energy densities
- Investment costs

8.8 Conclusion

The selection of an appropriate electrochemical storage system involves consideration of various performance factors such as energy and power density, cycle-life, design life, efficiency, and self-discharge. However, the compatibility of a storage system with specific application requirements is the most crucial factor in its selection. Additionally, factors like investment costs, total cost of ownership, system safety, reliability, and sustainability have gained importance in recent years, particularly with the introduction of the new European Batteries Regulation [21].

Traditional technologies, such as lead- and nickel-based systems, have undergone continuous application-specific development over the years. These developments have focused on adapting the design (including external dimensions, shape, and internal electrochemical design) to meet specific electrochemical requirements, such as high cycle-life for traction applications or an optimized design life for charge retention in UPS applications. The performance data ranges for these systems, listed in the overview in Table 8.5, are a result of appropriate internal designs aimed at achieving high performance in various areas or meeting high energy demands.

Usually, power density and energy density, as shown in Fig. 8.2, or cost per unit of energy are commonly compared. However, this approach can be misleading. For instance, a common mistake is often made when comparing systems based on cost per unit of energy content (€/kWh), as there are many applications where the cost per required power (€/kW) is more relevant. High-performance battery systems are typically more expensive in terms of energy content (€/kWh) due to their internal design.

Moreover, considering the cost based on energy throughput (cycle-life) for many applications is less meaningful, especially when such systems are used as backup systems for emergency power.

The progress of lithium-ion batteries for electric vehicle (EV) applications serves as a prime example. Lithium-ion batteries have undergone significant development to meet the specific demands of the EV industry. Initially utilized in consumer electronics, this technology has been tailored and tested in fleet trials to address the requirements of electric vehicles. These trials have emphasized the importance of maximizing energy density while accommodating reduced cycle lives, typically ranging from 1000 to 1500 energy throughputs, for EVs.

In contrast, stationary large-scale storage applications necessitate life cycles surpassing 6000 energy throughputs and extended design lives of up to 20 years. These requirements are significantly higher compared to EVs, highlighting the divergent needs of different applications in terms of battery longevity and reliability.

The development of lithium-ion batteries for electromobility applications illustrates the need for application-specific development to cater to the unique requirements of different applications. This example highlights the importance of tailoring battery technologies to meet specific demands, as seen in the progression of lithium-ion batteries for electric vehicles. Similarly, emerging technologies such as sodium-ion batteries (RT, room temperature) are expected to undergo a similar development process, where their characteristics and performance will be optimized to address the specific needs of various applications. This approach ensures that future energy storage solutions are customized and efficient, aligning with the diverse requirements of different industries and sectors.

In conclusion, the demand for electrochemical storage systems is increasing due to the electrification of the mobility sector and the integration of renewable energy sources. There is no universal battery system that fits all applications. The market and applications indicate that there will be a need for different mainstream and upcoming storage systems in the future.

Therefore, when selecting the optimal energy storage system for a specific application, it is crucial to carefully consider the application-specific requirements in order to choose the most optimal and sustainable system for the given application.

Table 8.5 Main performance and cost parameters of the most important battery technologies

	Lead-acid	NiCd	NiMH	Li-ion NMC	Li-ion LFP	NaS	NaNiCl	VRFB
Gravimetric energy density in Wh/kg	20–60	25–60	60–80	170–280	100–190	100–120	100–150	20–25
Specific power in W/kg	75–700	200–500	200–1000	200–2000	200–1000	60–100	100–300	5–15
Volumetric energy density in Wh/l	30–100	120–300	140–300	220–580	140–350	130–140	130–165	15–20
Open circuit voltage in V/cell at 100% state-of-charge	2.12	1.3	1.3	3.7	3.2	2.08	2.58	1.3
Full cycle equivalents	500–2000 (80% DoD)	1000–3500 (100% DoD)	2000–4000 (80% DoD)	1500–3500 (100% DoD)	2000–5000 (100% DoD)	2000–10,000 (100% DoD)	2000–10,000 (100% DoD)	10,000–16,000 (100% DoD)
Charging time	Hours	Minutes to hours	Minutes to hours	Minutes to hours	Minutes to hours	Hours	Hours	Hours
Energy efficiency in %	75–90	75–85	75–85	90–95	90–95	75–85	75–90	70–75
Operational temperature range in°C	−25 to +50	−40 to +60	−20 to +50	−20 to +55	−20 to +55	−20 to +60	−40 to +80	−10 to +60
Cost in €/kWh	50–250	300–450	750	130	120	400–600	550–750	600

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Chapter 9
Raw Materials and Recycling of Lithium-Ion Batteries

Shannon Helen Davies, Paul Christensen, Thomas Holberg, Joao Avelar, and Oliver Heidrich

Contents

9.1 Introduction

Electric vehicles (EVs) powered by lithium-ion batteries (LIBs) have quickly emerged as the most popular replacement for petrol- and diesel-powered vehicles. In the next 5–10 years, the LIB market is set to grow exponentially due to a push toward EVs by both policymakers and vehicle manufacturers [25]. Such a push will inevitably lead to an increase in demand for raw materials, which is of particular concern for critical raw materials (CRMs) such as lithium and cobalt which are of

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high economic importance [25]. Moreover, with a life span in EV of only 8–10 years, the LIB waste stream will increase considerably [39]. This is particularly important considering that, by 2025, the UK's dynamic stockpile of spent LIBs could exceed 100,000 battery packs or 42,000 tons of LIB waste [39].

Due to the economic value of the materials contained within spent LIBs and the volume of waste predicted in the coming years, the most economical and environmentally friendly option is to reuse or to recycle them. This is even more important considering that 2022 has seen the first ever increase in LIB pack prices since records began in 2010 [24]. Such increases are primarily due to rising raw material and battery component prices and the increasing inflation.

The development of recycling processes in the last decade has led to a sharp increase in the purity of materials recycled which can reduce the reliance on raw materials and alleviate some of the pressure on the natural reserves of materials such as nickel and cobalt. The most advanced recycling processes are pyrometallurgical, hydrometallurgical, and direct recycling [37]. However, even the most advanced technologies have challenges with regard to recycling efficiencies, significant environmental impacts, and safety hazards [22]. The safety hazards extend from the battery's primary use through to their final disposal, with 48% of waste fires in the UK attributed to LIBs [4]. It is worth noting that, these fires will increase significantly if the sale of EVs increases as forecasted.

This chapter starts with a brief review and analysis of the value chain of LIBs, their supply risks associated with raw materials, as well as the global impacts of using these materials, in both their original and secondary usage. This is followed by a detailed description of the three existing recycling processes for LIBs and the material yield from each of these processes, as well as a discussion on the opportunities and problems that come with these recycling processes. We briefly discuss battery recycling legislation and describe some of the safety risks associated with the transportation, processing, and recycling of LIB. The primary risks of LIB fires and how to prevent the fires are highlighted. This chapter concludes by summarizing the key findings of this work. For more details on general circular economy considerations related with batteries, including reuse and second life, the reader is referred to Chap. 2 of this book.

9.2 Battery Contents

9.2.1 Battery Families and Their Cathode Chemistries

To understand the supply and safety risks associated with the materials used in LIBs, it is important to consider the various active cathode chemistries of the numerous LIBs currently available. LIBs currently on the market use a variety of lithium metal oxides as the cathode and graphite as the anode [29].

Most existing LIBs use aluminum for the mixed-metal oxide cathode and copper for the graphite anode, with the exception of lithium titanate (Li_4Ti_5, LTO) which uses aluminum for both [23]. The cathode materials are typically abbreviated to three letters, which then become the descriptors of the battery itself. For example, lithium cobalt oxide ($LiCO_2$) becomes LCO, which was presented in 1991 as the first major commercially available LIB technology [50]. Due to the high-cobalt content, and soaring cobalt costs, LCO batteries have become very expensive to manufacture. Problems also lie in LCO's lack of thermal stability and quickly fading capacity. Despite this, they are heavily used in mobile devices [46].

The next LIB emerged in 1996 with a cathode made of lithium manganese oxide ($LiMn_2O_4$, LMO) [23]. Replacing cobalt in the cathode with nickel and manganese does make LMO cheaper than LCO but has resulted in a lack of cycling stability at high temperatures [46].

Most commonly used in medium- and high-range electric vehicles (EVs), due to their high energy density and low power consumption [45], is the lithium nickel manganese cobalt battery ($LiNi_xMn_yCo_{1-x-y}O_2$, NMC). The NMC battery is a so-called "family" as any combination of the three metals is possible, giving rise to a variety of cathode chemistries within one family. The four chemistries which are most common are NMC-111, NMC-532, NMC-622, and NMC-811, with the numbers referring to the ratio of nickel-manganese-cobalt in the active cathode material. First commercialized in 2004, the NMC battery family boasts very good specific power, life span, cost, safety, and specific energy [31].

Similar to NMC is the lithium nickel cobalt aluminum oxide cathode ($LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$, NCA). NCA also has a high specific energy, power, and life span, but it is more expensive than NMC [31].

The final example is the lithium iron phosphate battery ($LiFePO_4$, LFP), widely used in medium- and low-range EVs, which has sacrificed energy density for safety, improved environmental performance, and low production costs, coming from the lack of cobalt in the cathode [45]. The market share of LFP batteries has grown substantially in recent years, from 10% of the global EV market share in 2018 to approximately 40% in 2022 [9]. One reason for this is the popularity of LFP batteries in the Chinese market, with Tesla recently announcing they will use LFP batteries in their Model 3 for the Chinese market [13]. The drive towards the electrification of public transport has also played a part in this. This is due to factors such as the absence of cobalt in the cathode reducing the production costs, the use of phosphate to increase stability, enhanced electrode stability against overcharging, and a higher tolerance to heat. All of which has lead to LFPs being commonly used in buses [44].

9.2.2 Whole Battery Pack

Most of the focus from recyclers is extracting the valuable metals such as copper, nickel, and cobalt [40] contained within the active cathode material. Despite this, the active cathode material only makes up a maximum of 35% of a LIBs' relative weight, as seen in Fig. 9.1. Pouch cells can weigh between 75 and 225 g, depending on the battery cathode chemistry.

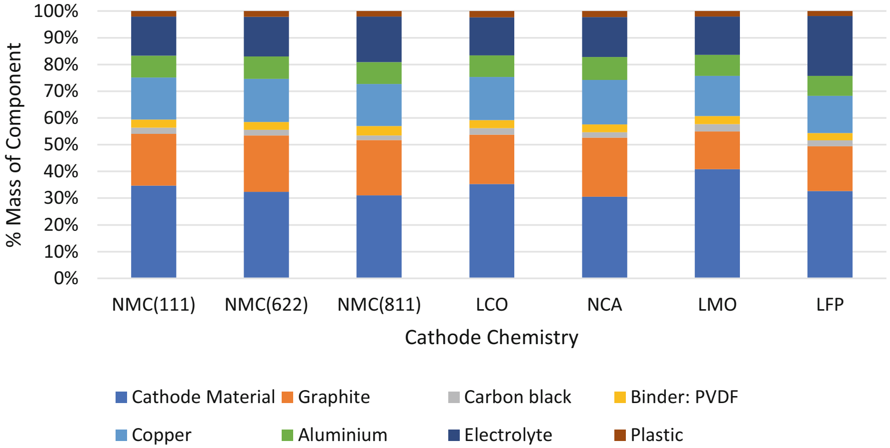

Fig. 9.1 Relative weight percentages of LIB. (Based on Sommerville [40])

Lithium-ion cells come in three principal shapes and sizes: cylindrical, pouch, and prismatic. All three "form factors" are employed in the larger applications of LIBs including EVs and battery energy storage systems (BESS). In an EV pack, the cells are arranged in series, parallel, or mixed configurations to form a module.

Each module will also have its own electrical and thermal control components [38]. The modules are then connected in series, parallel, or a combination of the two, to form a battery pack. The modules can be mechanically locked into place or welded or glued together, which is a considerable disadvantage in their manufacturing, as it makes them particularly difficult to disassemble. The packs themselves are housed in a plastic or metal container, also containing a whole pack battery and thermal management systems.

9.3 Battery Cathode Materials and the Associated Supply Risks

A LIB's active components are an anode and a cathode, separated by an organic electrolyte, i.e., a conductive salt ($LiPF_6$) dissolved in an organic solvent. The anode is typically graphitic carbon, but silicon has emerged in recent years as a replacement with a significantly higher specific capacity [51]. The inactive components include a polymer separator, copper and aluminum current collectors, as well as a metal or plastic casing.

Table 9.1 Typical raw material requirements (Li, Co, Ni and Mn) for three battery cathodes in kg/kWh [20]

	Type	Lithium	Cobalt	Nickel	Manganese
LCO		0.11	0.96	0.00	0.00
NCA		0.10	0.13	0.67	0.00
NMC	111	0.15	0.40	0.40	0.37
	622	0.13	0.19	0.61	0.20
	811	0.11	0.09	0.75	0.09

The majority of materials that are constrained by resource limitations are those contained within the cathode, as well as the electrolyte due to its lithium content [35]. The majority of LIBs on the market today have cathodes which include lithium, cobalt, nickel, and manganese due to their high energy densities. Table 9.1 shows an estimate of the amount of these metals, in kilogram required per kilowatt-hour for five popular cathode materials.

Batteries with lithium cobalt oxide (LCO) cathodes typically require approximately 0.11 kg/kWh of lithium and 0.96 kg/kWh of cobalt (Table 9.1). Nickel cobalt aluminum (NCA) batteries, however, typically require significantly less cobalt, approximately only 0.13 kg/kWh, as they contain mostly nickel at approximately 0.67 kg/kWh. Nickel manganese cobalt (NMC) batteries vary on their raw material requirements depending on which member of the battery family is being used. For example, the NMC-111 contains approximately 0.40 kg/kWh of nickel, manganese, and cobalt, whereas NMC-811 requires 0.75 kg/kWh of nickel and only 0.19 and 0.20 kg/kWh of cobalt and manganese respectively. In practice, this means a Tesla Model S, which uses a 100kWh NCA battery [25], would require 10 kg of lithium, 13 kg of cobalt, and 67 kg of nickel.

The following section describes the supply chains associated with the elements used in the manufacturing of LIBs, particularly those contained in the cathode.

9.3.1 Cobalt, Lithium, and Nickel

It is projected that, just for EV batteries and energy storage, the EU will need 18 times more lithium and 5 times more cobalt in 2030, with this increasing another three-fold by 2050, compared to the current supply to the whole EU economy [1]. This will inevitably lead to supply issues not just in the EU, but globally, and has resulted in both materials being added to the EU's Critical Raw Materials (CRMs) list [14].

The significant increase in demand for cobalt, lithium, and nickel is demonstrated in Fig. 9.2, where it is easy to see that the adoption of LIBs with cathode chemistries with very low or even no cobalt is appealing. In both scenarios modeled in Xu et al. [49], the known global reserves for cobalt could be depleted by 2050. Cobalt reserves also have the added challenge of being very geographically concentrated, partly in areas with political and social conflict [49]. The Democratic Republic of the Congo (DRC) in particular plays a dominant role in current and future cobalt supply,

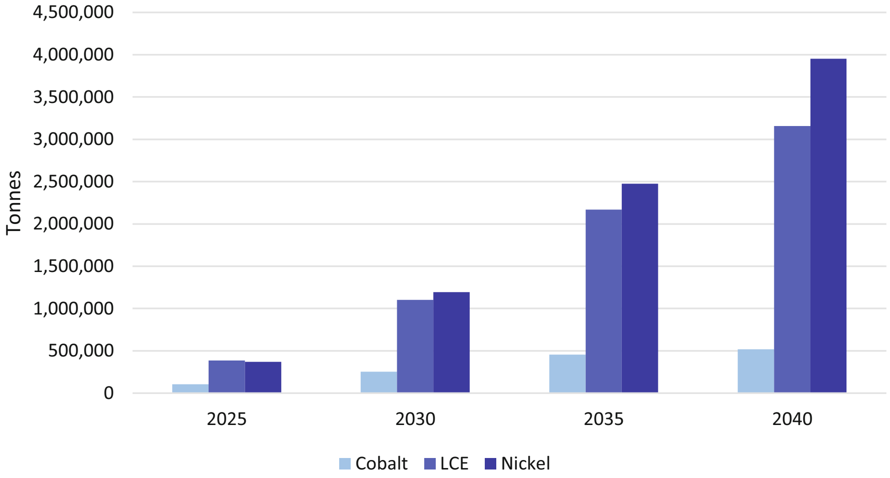

Fig. 9.2 Global demand for raw materials to 2040 [20]

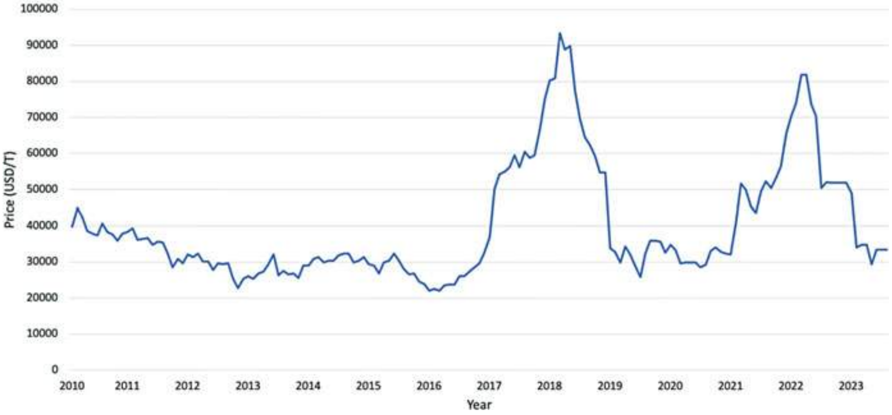

Fig. 9.3 Cobalt price volatility from February 2010 to August 2023 [43]

accounting for 60–75% of global mine production [2]. Cobalt mining also has the disadvantage of being reliant on the nickel and copper markets, as cobalt is primarily mined as a by-product of the two [2300], so the expansion of new cobalt mines will only occur if the nickel and copper markets are strong [2].

Due to this, cobalt markets are volatile, rising from $31,000 per ton in 2012 to $93,000 per ton in 2018, with another peak in 2022 [2300, 28]. The volatility is well demonstrated in Fig. 9.3. This increase resulted in a 5–64% increase in cathode material costs per technology, proving the high dependence on raw materials in the industry [46]. Moreover, the supply risk score of cobalt has risen sharply from 49 in

2007, meaning the element was uncritical, up to 60 in 2017, making it the most critical element contained within battery cathodes [46].

Cobalt plays an important role within the battery chemistries, providing high energy densities and stable batteries, and so it is unlikely that cobalt will be eliminated from LIB cathodes in the near future [2]. This benefits the recycling industry as cobalt is the main driver of the revenue produced from pyrometallurgical and hydrometallurgical recycling. With appropriate recycling facilities and further development, the industry can move away from mined cobalt and begin to use recycled cobalt from spent LIBs.

Lithium has much the same supply issues as cobalt. By 2025, it is possible that lithium demand could outgrow current production capacities [49], with one of the scenarios in Xu et al. [49] concluding that known reserves of lithium could be depleted before 2050.

Battery manufacturers are attempting to decrease their reliance on cobalt, but not lithium; this is perhaps due to lithium reserves being less concentrated in conflict areas. Despite this, in the year 2012–2013, lithium's supply risk score jumped considerably, from 52 to 57 [46]. The issue with lithium is that the industry does not appear to be trying to relieve their reliance on it at this present time. This further solidifies how efficient, cost-effective recycling is necessary to recover lithium from spent LIBs and ensures the recovered lithium is of a high enough quality to be used in future LIB manufacturing.

Lithium and cobalt also have a variety of other uses, outside of LIBs. For example, cobalt is magnetic and so when alloyed with aluminum and nickel, it can be used to produce particularly powerful magnets. Cobalt's high-temperature strength also makes it particularly important in the development of jet turbine generators. More superficially, for centuries cobalt has been used to produce blue paint. While lithium is a very light metal, it is often alloyed with others to make light-wear armor plating, and aluminum-lithium alloys are used in aircraft and high-speed trains. Interestingly, lithium carbonate can be given to people suffering with severe depression as a mood stabilizer, but the full effect of the drug on the brain is not fully understood.

Although not as critical as lithium and cobalt, nickel reserves are still a concern, with the prediction that by 2040 EVs alone could require as much nickel as the global primary nickel production in 2019 [49]. As with lithium, one scenario in Xu et al. [49] predicts known reserves for nickel to be depleted by 2050. This is mostly corroborated by Wentker et al. [46] which predicts that with the current rates of extraction, nickel reserves will be depleted in 35 years. This is concerning when it is widely accepted that the adoption of battery chemistries with high-nickel and low-cobalt content has been faster than expected and could lead to a 60-times increase in nickel demand for the EU alone from 2017 to 2060 [2].

The industry's move from high lithium content batteries just shifts the burden onto nickel reserves. This is depicted well by the projected dramatic increase in nickel demand compared to cobalt demand displayed in Fig. 9.4. Although LIBs with high-nickel chemistries have a higher energy density and therefore reach the desired range for EVs, there is some concerns over the stability of these batteries

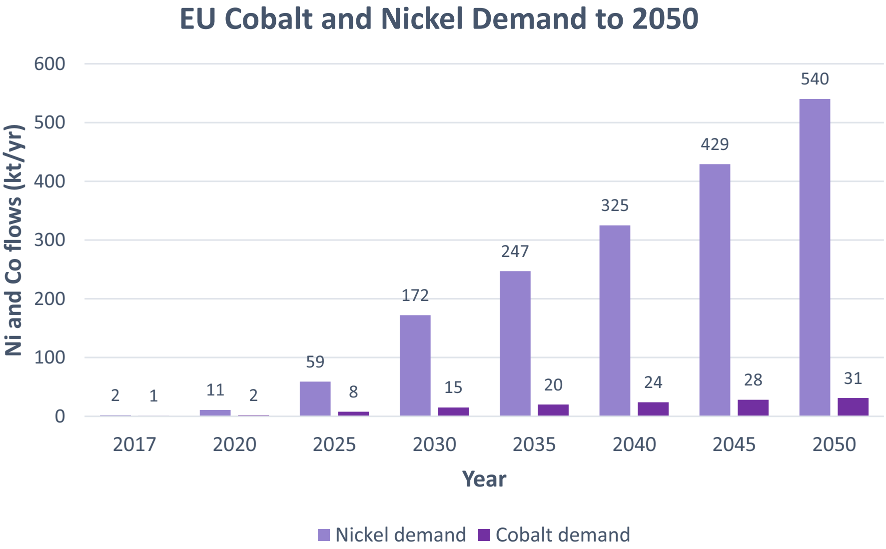

Fig. 9.4 Cobalt and nickel demand for European EVs for high adoption of high-Ni cathodes [2]

particularly the lithium nickel oxide battery which, after two decades of intensive research, still are not commercially ready [2]. However, the revenue generated from recovered nickel is much lower than that of cobalt which, due to the move toward high-nickel low-cobalt battery chemistries, may impact economic viability of recycling, as it will depend more on the volatile price of nickel [2].

9.3.2 Manganese

The supply of manganese comes from the mining of ore and scrap, with the ore including both manganese and iron ore [42]. The majority of mined manganese comes from South Africa and Australia, with shares of 26% and 17%, respectively, with China dominating processing and consumption [42]. Helbig et al. [23] find that the supply risk score for manganese, 52 points, is particularly average for all the raw materials used in LIBs. The most notable supply risk indicators for manganese come from the static reach reserves and the substitutability. The static reach reserves are only 34 years, the third lowest out of the raw materials, and the substitutability has a score of 4 which is second lowest [23]. This means that the current easy-to-access manganese reserves will be depleted in only 34 years and manganese as a component of LIBs has very limited materials that could replace it while maintaining the battery capacity and life span. Both of these factors mean it is imperative that the purity of recycled manganese is adequate to be reused in LIBs, taking away the reliance on reserves.

9.3.3 Other Materials

Copper, steel, aluminum, and graphite are also materials found in the spent LIBs. Xu et al. [49] predict that for copper, aluminum, and graphite, all known reserves exceed demand from EV manufacturing until at least 2050. However, there is a slight concern about natural graphite, as in 2019 64% of it was produced in China, which may lead to low supply reliability through political conflicts among global powers [49]. As much as this would not be ideal, it is true that synthetic graphite has begun to dominate the LIB anode market, with a 56% share in 2018, due to both its increased performance and decreased cost [49].

However, the shift toward silicon-based anodes, as appears to be the trend, would alleviate these concerns, with 25.8% abundance of silicon in the Earth's crust [26]. Silicon-based anodes also provide good chemical stability in the electrolyte, improving safety of the battery, and the abundance of silicon in the Earth's crust reduces the overall cost.

As much as these materials are necessary to the manufacturing, and therefore the recycling, of LIBs, their lack of criticality in comparison with the other materials makes them of low concern. However, to achieve increasing recycling efficiencies according to the new regulatory framework for batteries in, for example the EU, USA, and China, it is vital to recover these fractions, no matter how small.

9.4 Lithium-Ion Battery Recycling

9.4.1 Available Recycling Processes

Due to the value of the materials contained within LIBs, it is vital that they are safely and effectively recycled. All recycling is either open-loop or closed-loop. Open-loop recycling is the most common form, in which materials recovered from the recycling process have to undergo a series of refining processes before they can be used again [37]. Closed-loop recycling, considered the best case scenario, is when the materials recovered from the recycling process are in the correct chemical form and sufficient purity levels to be reused directly in the products they were recycled from [37].

There are a growing number of recycling facilities across the globe, as depicted in Fig. 9.5. Each company achieves different recycling yields, due to having their own unique take on one of the three available recycling processes or employing a combination of two.

Three main recycling processes for spent LIBs are commonly used: pyrometallurgical, hydrometallurgical, and direct cathode recycling (which will be referred to as direct recycling). Pyro- and hydrometallurgical processes are both employed to effectively recover metals from e-waste. The recoverable materials from each of these processes are listed in Table 9.2. None of the recycling processes listed are

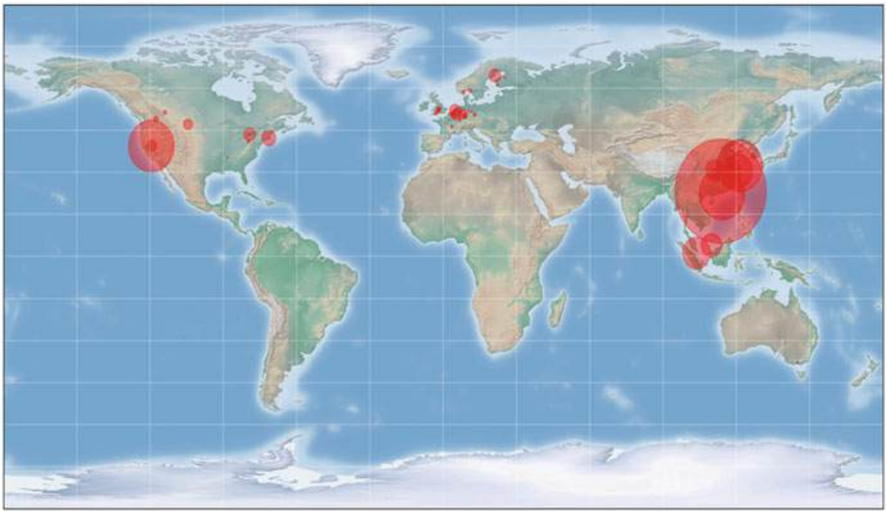

Fig. 9.5 Locations of recycling facilities globally, with the size of the red dot representing the recycling capacity in tons/year

Table 9.2 Recoverable materials through different recycling technologies

Pyrometallurgical	Hydrometallurgical	Direct
(1) Copper compounds (2) Iron compounds (3) Co^{+2} in output (4) Ni^{+2} in output (5) Lithium compounds (6) Aggregate (from slag)	(1) Copper (2) Steel (3) Aluminium (4) Graphite (5) Plastics (6) Lithium carbonate (7) Co^{+2} in output (8) Ni^{+2} in output (9) Mn^{+2} in output (10) Electrolyte solvents (11) Electrolyte salts	(1) Copper (2) Steel (3) Aluminium (4) Graphite (5) Plastics (6) NMC (7) Electrolyte solvents (8) Electrolyte salts

perfect, and work is being done to improve the processes in some way. Most of the improvements are based around increasing yield or purity, reducing the use of raw materials or energy, and reducing waste [18].

Pyrometallurgical Recycling Process

Pyrometallurgical recycling is one of the most ubiquitous metal recycling technologies used today. Pyrometallurgical processes use high temperatures to extract and purify raw materials. Fig. 9.6 depicts the process flow of a generic pyrometallurgical recycling process, in which spent LIBs, either shredded or intact, are sent to a smelter which burns off electrolyte and plastics in the battery to supply heat and the gas produced through the smelting process is treated.

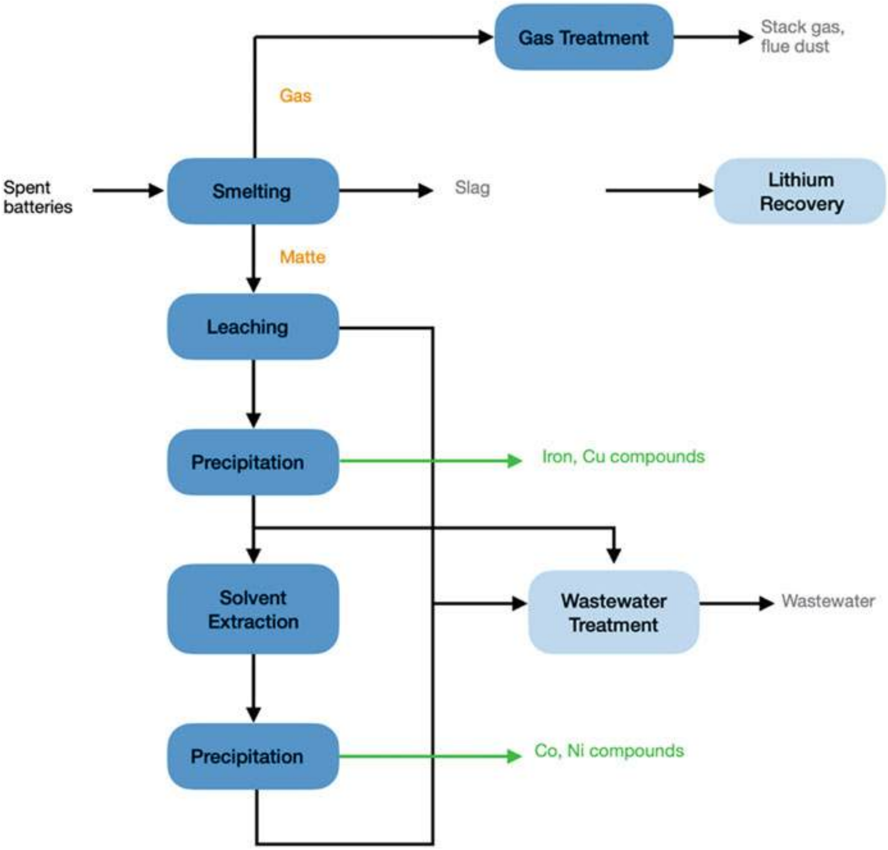

Fig. 9.6 Process diagram of pyrometallurgical recycling processes

Graphite/carbon and aluminum in the LIBs act as reductants for the metals and are oxidized, while cobalt, nickel, copper, and iron in the LIBs make up the matte. The rest of the materials, including oxidized aluminum and lithium, end up in the slag. It is important to note that the slag may be used as aggregate for pavement or as supplementary material for cement production and there is ongoing research into the lithium recovery process from the slag [40].

The matte undergoes an acid leaching process and then precipitation to produce iron and copper compounds. Following this, the matte can be further processed to produce cobalt and nickel compounds; the processes used are solvent extraction followed by precipitation. These compounds can also be separated fully through hydrometallurgy.

The facilities which currently utilize pyrometallurgical recycling are Accurec and Umicore [40]. In Umicore's facility in Hoboken, Belgium, only modules or packs larger than a shoebox require disassembly prior to the recycling process [40]. See Table 9.2 for a list of recoverable materials through pyrometallurgical recycling.

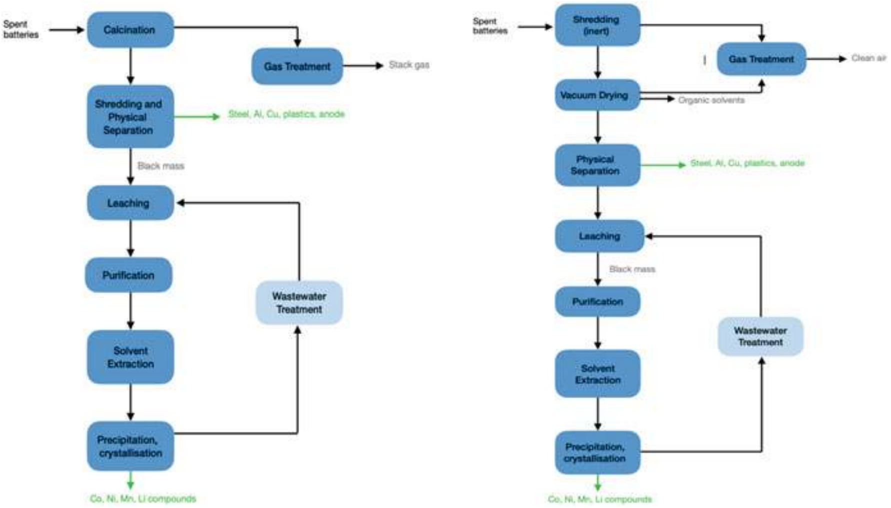

Fig. 9.7 Left: calcination resp. drying of spent LIB and subsequent generic hydrometallurgical recycling process. Right: the hydrometallurgical process used by TES

Hydrometallurgical Recycling Process

Figure 9.7 depicts the process flow of a generic hydrometallurgical recycling process. Hydrometallurgy uses aqueous solutions, such as acids and salts, to dissolve the metals, and then subsequent steps recover the metals from the solution.

Spent LIBs which are hydrometallurgically recycled must first be discharged and disassembled, before they are shredded. This is important as, for hydrometallurgy to be cost-effective, it is necessary to ensure that minimal extraneous material is exposed to the process [40]. In some cases, organic compounds such as the binder and solvents from the electrolyte are then burned off and carbon dioxide will be emitted. TES, a global LIB recycling company, uses shredding under inert atmospheric conditions and vacuum drying followed by condensation for this, as shown in the right image of Fig. 9.7. The organic solvent from the electrolyte will be recovered, and residual fluorine and phosphorus will be removed at the purification step of the hydrometallurgical process.

After shredding, the process is made up of several physical separation processes to separate out aluminum, copper, and steel as metal scraps, plastics, and black mass followed by a leaching process for the black mass. The final step includes solvent extraction and precipitation to produce cobalt-nickel-manganese compounds, with the potential for lithium carbonate extraction which can be used in the production of new cathode materials [11]. However, market demand for high purity materials in the correct ratios justifies further separation into individual cobalt-nickel-manganese compounds. Both Duesenfeld in Germany and Recupyl in France use this process, however only at a small scale, selling most of their black mass to the metallurgical industry [40]. Umicore performs hydrometallurgy after pyrometallurgy to further separate the compounds of transition metals [40].

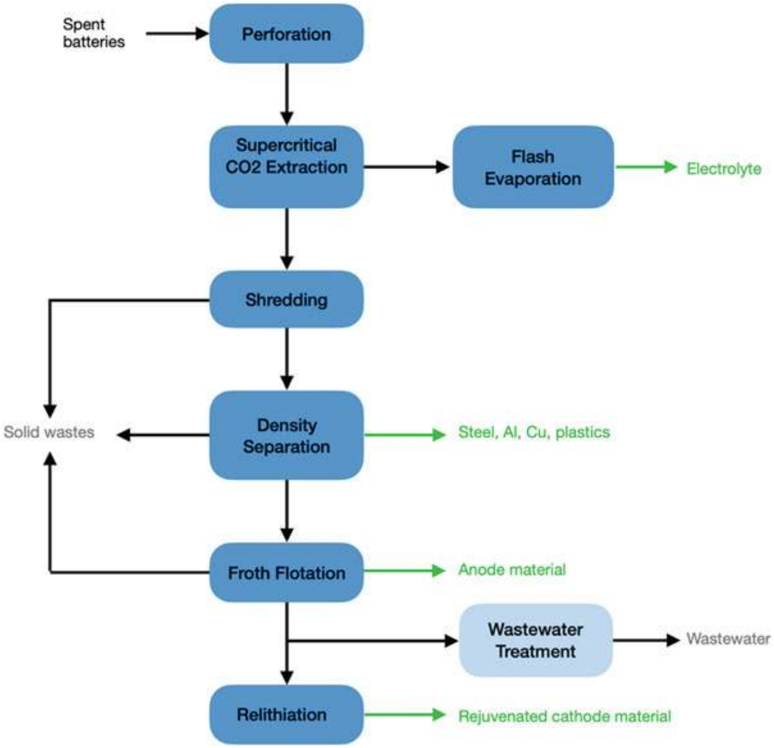

Fig. 9.8 Process diagram of a generic direct recycling process

Direct Recycling

Figure 9.8 depicts the process flow of a generic direct recycling process. Direct recycling describes the process by which the battery components are recycled without breaking down their chemical structure. For this, spent LIBs must first be discharged and disassembled before they can be perforated.

To recycle the electrolyte solvent and salts, they then undergo supercritical CO_2 extraction. The rest of the LIBs can then be shredded before going through several physical separation processes, density separation, and froth flotation, which recover plastics, metals, anode material, and cathode material, respectively [11]. The final step sees the recovered cathode material relithiated, which is the process by which they restore lithium stoichiometry of the cathode by bathing it in a heated lithium solution, to produce rejuvenated cathode powder.

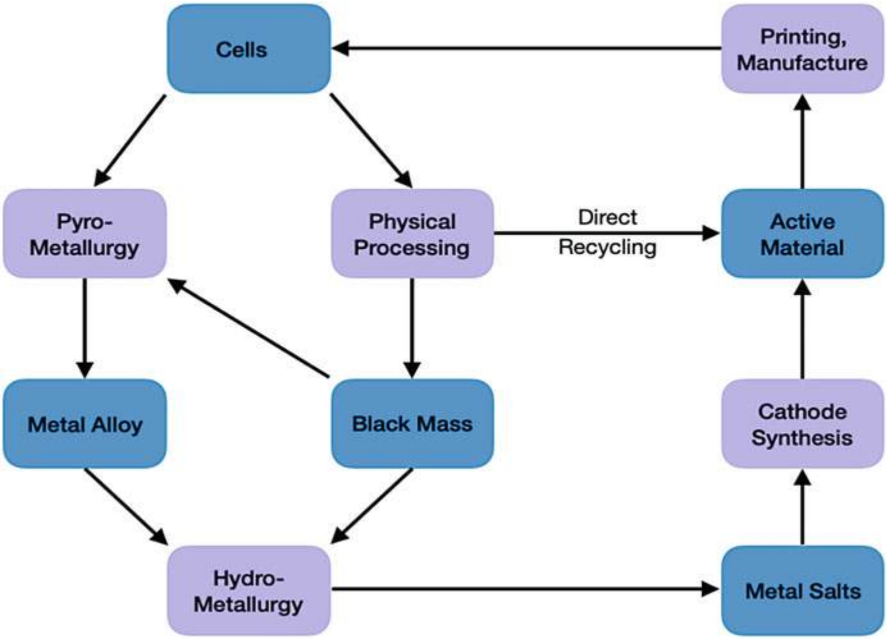

Fig. 9.9 Generalized recycling loop. Processes are in purple and intermediate products in blue. (Based on Sommerville et al. [40])

Direct recycling is not currently used anywhere in industry, but it is the preferred method as the active material is reused without it having to be returned to the constituent raw materials as compounds or salts [40].

9.4.2 *Yield for the Different Recycling Processes*

As mentioned previously, the uniqueness of each company's recycling process leads to differing material recovery percentages and purities. This section will give statistics as produced in generalized processes modeled in Everbatt [11]. It cannot be overstated how essential high material recovery percentages and purities are to the alleviation of pressure on material reserves globally. Striving for closed-loop recycling across the industry should be an ultimate goal.

A generalized recycling loop showing the potential routes in which LIB cells may be recycled is shown in Fig. 9.9, with processes in purple and intermediate products in blue. In practice, some large-scale recyclers follow the loop to the left, using a combination of pyro- and hydrometallurgical processes. Not shown in Fig. 9.9 is that some recyclers produce only a "black mass" of active material, i.e., metal oxides and carbon, which will then be sold on for pyro- or hydrometallurgical recovery [40].

Both pyrometallurgical and hydrometallurgical processes recover 98% of the cobalt from the input, and, with such a high efficiency, there should be a consistent drive to ensure spent LIBs are recycled so the cobalt can be reused, particularly due to the high volatility of the cobalt markets and low natural reserves [11].

Material recovery of lithium is not as efficient as cobalt, at only 90%, and to recover lithium using pyrometallurgical recycling, the slag must undergo a hydrometallurgical process, thus increasing recycling costs making it less attractive to recyclers [11]. This means recyclers are less likely to recover lithium, increasing the reliance on virgin materials. Luckily, like cobalt, material recovery efficiency of nickel is 98% for both pyrometallurgical and hydrometallurgical recycling [11]. Only hydrometallurgical recycling recovers manganese, but this is also at 98% efficiency [11]. Copper and steel have 90% material recovery efficiencies from all three recycling processes. Meanwhile, aluminum and graphite have 90% material recovery efficiencies from only hydrometallurgical and direct recycling [11].

9.4.3 Opportunities from Recycling

The primary advantage of LIB closed-loop recycling is that it can save raw materials. When materials such as lithium, cobalt, and nickel are so critical to the operation of LIBs but are relatively scarce, it is vital to develop recycling processes which will alleviate some of the pressure on natural reserves. It is estimated that recycling can save up to 51% of the extracted raw materials, in addition to the reduction in the use of fossil fuels and nuclear energy in both the extraction and reduction processes [8].

One benefit of a LIB compared to a primary battery is that they can be repurposed and given a second life. A LIB in an EV is classed as EOL once the warranty, usually 8–10 years, has been exceeded; however, both manufacturers and developers agree that LIBs still retain 70–80% of their initial capacity after this time [39]. Some changes to the LIB may be necessary before it can be repurposed, such as replacing damaged cells or reconfiguring the pack for non-EV use [5], but it is estimated that LIBs which are repurposed in stationary energy storage applications have a second life span of an additional 10 years before they reach their absolute EOL [39]. Another benefit of second life LIBs is both environmentally and economically valuable, as they can reduce direct energy consumption from the electricity grid [39].

The idea of a second life for LIBs from small devices such as mobile phones has been trialed in the developing world, mostly in isolated areas that are not connected to the national grid. The second life LIBs can be connected to solar panels and allowed to charge and then used to power LED-based systems [8]. This is a safe, reliable, and sustainable way to light homes, aiding in the replacement of candles and kerosene lamps. Costa et al. [8] find that a LIB that was used in the standard life of a mobile phone, 2 years, still contains 1250 cycles. This means a 12 V, 3.1A battery will be able to power a 5 W LED lamp for 4 hours every night for 3 years and the unit itself will cost only $35 whereas kerosene lamps cost an average of $54 per year of use [8].

Pyrometallurgical recycling has been proven to be economically feasible and conducive for large-scale operations [30]. Hydrometallurgical recycling has a number of environmental benefits, such as a low operating temperature and lower CO_2 emissions compared to the pyrometallurgical process [5]. Economically, hydrometallurgical recycling is preferable due to the increase in recoverable materials and their increased quality. The hydrometallurgical process allows most of the metals contained within EOL batteries to be recovered after extraction and separation through using strong inorganic acids to leach the metals into solvents. Inorganic acids such as hydrochloric, sulfuric, and nitric can be used to achieve 99% solubilization of lithium and cobalt [30].

9.4.4 Limitations of Recycling

The primary limitation of LIB recycling is that closed-loop recycling does not exist; the materials cannot be used in like-for-like products and instead have to be downcycled. This is due to the waste treatments, namely, shredding, involving some degree of material intermixing and small-scale dispersion of metals into those recovered in bulk, such as aluminum and steel, reducing their quality. Although recycling cobalt from LIBs can be used in samarium-cobalt magnets for sensors and electric motors [34], the majority of recycled materials go on to be used in products with lower material quality requirements. To compensate for this, primary and secondary materials are often mixed to match material requirements in other products.

The pyrometallurgical recycling process may have generated relatively successful business models up until now, but this is likely to change. Despite the fact that the process is simple and mature and requires no sorting prior to recycling, there are a number of disadvantages [5]. Pyrometallurgical recycling requires a significant amount of energy to treat waste gases before they are safe to release into the environment [47]. This is in addition to the process itself requiring very high temperatures, making it very energy intensive [30]. Moreover, metals such as lithium, aluminum, and manganese cannot be recovered at such high temperatures, and the growing trend toward manufacturing LIBs with lower cobalt content means the revenue generated from this process will decrease. This is due to recovered cobalt generating 50–70% revenue for pyrometallurgical recycling, so lower cobalt leads to lower revenue and a lack of profit. Unfortunately, recent trends suggest that batteries with higher nickel and lower cobalt content, such as the NMC-811 batteries, are becoming more popular due to increased energy density, environmental sustainability, and reduced manufacturing cost [48].

Another disadvantage of the pyrometallurgical process is that both lithium and aluminum are entrained in the process slag and therefore require further processes to recover. The UK currently exports most of its spent LIBs to Umicore in Belgium, which uses the pyrometallurgical process; this meant lithium and aluminum were lost to the slag as it was not economically feasible to process it [47]. However, Umicore have recently employed further processing to recover lithium from the slag [5]. Although this is a positive in terms of material recovery, an additional process increases not just the total recycling cost but the environmental one too.

As with pyrometallurgical recycling, hydrometallurgical recycling does rely on cobalt recovery for the majority, in this case 40–60%, of its generated revenue. As above, the low nickel, high-cobalt content means it is not economically feasible to hydrometallurgically recycle NMC-811 batteries. However, unlike pyrometallurgical recycling, a profit is still generated per kg of NMC-532 and NMC-622 batteries when hydrometallurgically recycled. In addition to this advantage, the materials produced from hydrometallurgical processes are of a high purity while recovering most of the LIB constituents [5].

Unlike pyrometallurgical, the hydrometallurgical process does require manual deep-discharging and dismantling before recycling can begin, which requires considerable storage space, which adds to overall costs, due to an increase in labor costs, and overall complexity [5].

Hydrometallurgical recycling also produces a considerable amount of wastewater through the leaching and precipitation operations. The treatment this requires adds to both the environmental burden and overall recycling cost. Another increase in cost comes from the challenge of separating some elements in the solution, such as cobalt, nickel, manganese, iron, copper, and aluminum, due to their similar properties [5], more specifically cobalt and nickel in aqueous medium. This requires solvent extraction and consequently large amount of organic solvent with organophosphate additives to be stored and processed. Purification steps generate, e.g., $Al(OH)_3$, FeO.OH, CaF_2, $CaPO_4$, which potentially need to be treated as hazardous waste.

Direct recycling is the newest of the modeled recycling processes and is still in its development stages for EV LIB recycling [25], which is its primary disadvantage. Another disadvantage of direct recycling is that it requires rigorous sorting before the recycling process can begin, as the exact cathode chemistry must be known prior to recycling. This is due to the inflexibility of the process: what goes in must come out [5]. This raises questions of whether the process is appropriate for an ever-changing reality; with a market already saturated by differing cathode chemistries, how can a process which can only recycle one specific chemistry at a time be sustainable? Although this is an important question, it is true that direct recycling produces the highest revenues of all the recycling processes and, due to this, it has the highest net recycling profit by a considerable margin [25]. The overarching economic benefits suggest that research into direct recycling must continue, ensuring it can be used sustainably on a commercial scale.

9.4.5 Battery Recycling Legislation

With battery recycling comes battery recycling legislation. Current legislation across all three major markets, China, the EU, and the USA, focuses on the protection of local environment and human health [32].

While the EU's original battery directive was published in 2006, the new Battery Regulation, published in 2023, will build upon and replace the 2006 EU Battery Directive, with a direct focus on the challenges that have come with rapid development of the industry [16]. Melin et al. [32] divide the new Regulation into four key elements, all of which are imperative to improving the sustainability of LIBs: The first is the Regulation aims to increase both transparency and traceability across the battery life cycle; second, it mandates carbon footprint declaration throughout the life cycle and establishing maximum thresholds, addressing climate impact of the batteries; third is an emphasis on circularity through increased collection and recycling efficiencies and mandating the use of recycled materials, particularly in batteries above 2kWh; and finally, fourth are including waste processors to the Battery Management System (BMS), verifying the battery's state of health in real time, and determining if the battery has the potential to be reused or repurposed before it is recycled.

While the EU has a number of directives to support in research and innovation across the entire battery chain, it has failed to secure key elements of the supply chain, such as raw material extraction, refining, and battery manufacturing [32]. Much is the same in the USA who, through Tesla, have been at the forefront of manufacturing but rely on global markets for refinement, production, and recycling of battery raw materials [2300].

The market is dominated by China, who occupy more than two-thirds of it [32]. This has been possible through a booming EV battery sector and strong government support in the form of subsidies and investment stimulus [32]. China also implemented the Interim Measures for the Administration of the Recycling and Utilization of Power Batteries for New Energy Vehicles from 2018 [32]. These cover minimum standards for the reclassification of batteries for second life applications, the recycling efficiency of plants treating EOL batteries, and requirements necessary to qualify for subsidies. When these measures were tightened further in 2019, they were made stricter than the regulations the EU plan to enforce a decade from now [16].

While in the USA, the Biden administration has declared the electrification of transport a top priority and produced an investment proposal of up to $174 billion, they still lag behind both the EU and China in mandating EPR or promoting circular economy principles. The stringent measures imposed on Chinese companies, who already dominate in material refining, battery production, and mature recycling infrastructure, have allowed them to easily comply with EU regulations. This imbalance between new and mature markets has led to a variety of unintended consequences. For example, such stringent measures can lead to distorted innovation through increased compliance costs, hindering competitiveness. Moreover, European EV manufacturers having to adhere to the new, stricter regulations will be more constrained in their options than the less regulated USA and also risk losing out to Chinese competitors due to their bigger, more mature share of the market [32].

EU regulation does aim to responsibly develop supply chains for Europe's EV industry, with recycling being at the forefront of this. However, the regulations do not require recycled material to be sourced in Europe, nor does it restrict the source of recyclables to EOL batteries [16]. This will put companies who have operated in markets such as China and South Korea, with much greater experience in battery material production, including in the use of recycled materials, in a much better position to meet these regulations. This could lead to European material producers and battery manufacturers being essentially eliminated from their own market.

One new regulation being proposed by the industry is a digital battery passport (DBP) for each battery entering the market. Digital product passports themselves are not novel; they have existed for some time to assist value chain stakeholders in achieving sustainable product management [36]. However, the concept has recently caught the attention of battery policymakers, and the European Commission is implementing DBPs [15]. The policy explicitly calls for the implementation of DBPs for industrial and EV batteries by January 2026 [16]. The EU has implemented three main EOL battery polices: maximum carbon footprint thresholds, minimum shares of recoverable materials, and DBPs. The main goal of DBPs is to enable sustainable product life cycle management and promote value-retaining processes, which in turn facilitates sustainable and circular value chains [3]. However, due to DBP development currently being pursued by nongovernmental institutions, there is a lack of clear specifications for the scope of DBPs, leading to inconsistency across the industry.

Battery legislation covers the entire life cycle of a LIB, from manufacture to initial use through to collection, processing, recycling, and disposal. The life cycle itself comes with a number of impacts, covered under environmental, social, and economic.

The steps of a LIB's life have been covered throughout this chapter; however, one important element which runs throughout the life cycle of a LIB that has not yet been addressed is the safety risks that come together with LIB's use and disposal and the social impacts these have. The way these risks fit into the life cycle of a LIB is demonstrated with the flowchart in Fig. 9.10. In the next section, we will discuss these risks, as well as addressing how it is best to reduce them.

9.5 Current Safety Concerns of End-of-Life Batteries

9.5.1 End-of-Life Management and Recycling

At present, there are very few LIB recycling facilities in the UK and Europe, despite the crucial role the industry has in the decarbonization of the planet. However, there are almost daily reports of fires caused by LIBs in both bin lorries and recycling

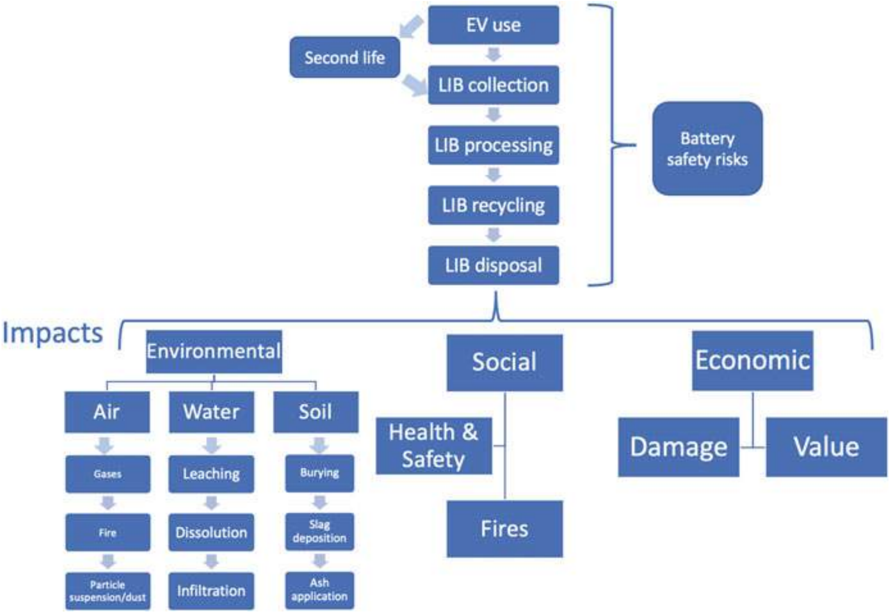

Fig. 9.10 Flowchart of the life cycle of a LIB

facilities [33]. In the USA, the cost is even greater, and not just financially, they have seen injuries and even deaths. This had led to material recovery facilities in the USA being increasingly reluctant to admit LIB related fires due to insurance concerns.

A report from Eunomia found that there are approximately 201 waste fires each year caused directly by LIBs [4]. While the fires do vary significantly in terms of severity and duration, it is estimated that the fires cost the UK £158 million annually [4]. The majority of these costs are found to be incurred by waste site operators; however, the cost to society, the environment, and the fire service is approximated to be £16 million. The report also breaks the waste fires into four categories, with 1 being the most severe and 4 being the least, finding that it is fires of severity level 3 which occur most frequently and therefore have the highest cost implications at over £128 million annually [4].

In the USA, the situation is even more bleak with a Fire Rover report estimating the cost of LIB waste fires to be $1.2 billion annually [17]. Even with the report's author believing fires are underreported, there is still an alarming year-on-year increase in waste fires. Although they have not all been directly linked to LIBs, LIBs are listed as 1 of the 4 causes of the increasing number of facility fires which have resulted in 49 injuries and 2 deaths, an increase in injuries of 158% from Fire Rover's 2018 report [17].

At present, these fires are caused by small LIBs from or in small rechargeable devices such as mobile phones. However, the battery industry is ever-changing and, most importantly, ever-growing, with an onslaught of EOL LIBs from EVs and second life applications coming very soon. This will diversify the waste stream recycling facilities have to manage, and it may be that the global drive to replace fossil fuels could mean the fiery epidemic in recycling facilities is the calm before the storm [33].

LIBs can store large amounts of energy, but this energy must be released in a safe, controlled fashion. If this energy is released through abuse of the batteries, toxic, flammable, and potentially explosive gases, as well as fine particles of heavy metals, are released; this process is known as thermal runaway. This can easily be caused by crushing and penetration of the batteries, which are common practices in recycling facilities. When the batteries are crushed, the separator may be pierced, which in turn allows the anode and cathode to come into contact and a short circuit to develop. When this occurs, the heat generated causes pyrolysis of the organic solvent and other exothermic reactions which generate a mixture of gases that includes hydrogen (up to 50%), carbon dioxide, carbon monoxide, small organic molecules such as ethane and ethene, hydrofluoric and hydrochloric acid, and hydrogen cyanide. When these vent from the cells, via safety caps on cylindrical and prismatic cells, or pouch cells bursting, the gases take with them small droplets of the remaining organic solvent producing a thick, white vapor cloud [6]. Thermal runaway produces very large volumes of vapor cloud, e.g., up to c.a. 6000 L/kWh [21], and hence when this is vented, it does so at high pressure: immediate ignition of the cloud thus results in flares that can be several meters long. Delayed ignition can, and has, resulted in unconfined vapor cloud explosions (UVCE) [10], and such large volumes of vapor cloud have also led to UVCEs from small LIBs including e-scooters and e-bikes.

One common practice is the storage of road traffic collision (RTC) vehicles in vertical piles and moving them with magnetic claws and forklifts. This cannot be the case for EVs due to the risks posed by potentially damaged battery packs, which have been known to ignite hours, days, or even weeks after the initial incident [41]. Thus, it has been generally accepted that RTC EVs should be stored with a 10–20 m exclusion zone.

Although the biggest concern does lie with damaged or abused LIBs, it has been known for EVs to apparently spontaneously ignite, and, while the cause is still unclear, BMS failure, defects in design and/or manufacture, or some contamination during manufacturing are the most common postulations [7].

The lack of understanding of the risks and hazards of LIBs is concerning; while there seems to be some in governments, the public appears to be wholly unaware: an example is the incidents of fires due to members of the public assembling spare e-bike batteries bought online and doing so by soldering. Companies are currently able to sell secondhand EV battery packs, even batteries that are damaged or missing their BMS, to the public, with no safety warning. While this may not be illegal at present, it is wildly irresponsible. Without the appreciation for the complexity of the protection systems or the hazards of abused batteries, the risk of personal and municipal harm cannot be understated [7]. It is evident that abuse of batteries, such as rapid charging, does destabilize them and can reduce the onset of thermal runaway to room temperature [27], and damaged EV batteries have an increased risk of explosion. LIBs are safe and stable to use under specified limits of temperature and charge, but where does liability lie when misuse leads to injury or death?

9.5.2 Reducing Waste Fires

The most obvious way to reduce waste fires caused by LIBs is to ensure the batteries do not end up in the residual and mixed recycling waste streams in the first place. There are two easy to implement, short term measures which may help with this. Firstly, separate kerbside battery and small waste electronic and electrical equipment (WEEE) collection from households, and, secondly, increase the number of retail collection points for batteries and small WEEE [4].

However, the responsibility cannot be placed only on the consumer; instead, there must be supporting policy mechanisms that would fund systemic change in the collection of spent LIBs. The most effective way to do this is to financially incentivize or deter consumers from incorrectly disposing of batteries, alongside an improved collection system. These policies may include the banning of batteries from residual and mixed recycling waste streams, fining those who do not comply; enforcing enhanced extended producer responsibility (EPR) for batteries and small WEEE to pay for and coordinating, improving collection, and reflecting the cost of fires; creating a deposit return scheme (DRS), or other incentivization method, to encourage consumers to return spent LIBs and small WEEE for recycling; and introducing fee modulation within WEEE EPR system that allows producers to pay lower fees for design features that facilitate easier battery removal by consumers [4].

Moreover, there is evidently a problem in the WEEE management stream, with the increase in fires being an indicator of the need for change. The GRINNER project aims to rectify this. Funded through the European Union's (EU) Horizon Europe program, the GRINNER project will focus on the reduction of fires caused by LIBs in the WEEE management chain [12]. The plan is to develop an AI-powered battery detection system utilizing data from X-ray detectors and pick-and-place robots. The system will use X-ray detectors to analyze X-ray data and detect waste containing batteries that can then be removed by a vision-based pick-and-place robot [12]. The robots will be commercially available and easily incorporated into existing WEEE and other recycling environments, to extract batteries and other e-waste safely and effectively before they are damaged by machines that crush and consolidate waste.

Batteries themselves do contain several methods to improve their thermal stability. For example, each battery contains a BMS which controls and prevents conditions which could lead to failure, such as overcharging and overdischarging [19]. The BMS also operates the battery for the best application performance and a long life span. In addition to BMS, all batteries contain a thermal management system (TMS) which maintains the optimum operating temperature of between 20 and 40 °C and keeps temperature changes between the modules to a minimum [19]. As a whole, the battery compartment is also built with fire prevention in mind, being designed to survive structurally and containing a vent to let out any pressure buildup [19].

9.6 Conclusions

It is evident that the EV revolution is well underway, with a vast number of raw material requirements and battery waste being created.

With such a diverse product market, there is a great amount of choice for battery manufacturers, from the low cost LFP batteries to the high capacity NCA batteries. The diversity of this market does not come without its problems, with many of the materials used to produce the battery cathodes coming with considerable material criticality issues, particularly lithium and cobalt. While the market does appear to be moving away from batteries with a high-cobalt content, the use of lithium is here to stay, due to its stabilizing properties. Moreover, this move away from cobalt has led to the development of batteries with a higher nickel content, simply shifting the burden onto nickel reserves.

Made up from a variety of toxic and rare materials, stockpiling and landfilling spent LIBs is not an option, so the waste streams generated from them need sustainable, cost-effective, high-yield management systems, such as recycling. The recycling market has already undergone change: pyrometallurgical recycling began as the most popular recycling method; however, there is no lithium recovery under this method. This has led to the growing popularity of hydrometallurgical recycling which produces high material yields, for low environmental cost. As direct recycling is still in its relative infancy, it is not yet available for commercial use; however, this method of recycling is the industry's best chance at achieving closed-loop recycling.

There are some very clear advantages of recycling LIBs, with the main one being the alleviation of pressure on reserves of the raw materials. It is important, however, to consider second life applications of LIBs that have reached their EOL in their first application. For example, LIBs in EVs reach their EOL in an EV after only 8–10 years, but they retain 70–80% capacity. These batteries can go on to have a second life in stationary energy storage, storing renewable energies such as solar to be released in times of high demand, alleviating pressure on the national grid. Smaller LIBs from small electronic devices can also be used in such a way to power individual electronic devices.

As closed-loop recycling, the method by which recycled products are used in like-for-like products, has not yet been achieved, the recycled products must be downcycled. Mostly, the recovered materials are mixed with other raw materials to contain the correct mix to be used in products with lower material quality requirements. This is only one of the limitations of LIB recycling; the others include the hazardous waste produced from the recycling processes and the fact that LIB recycling is still not economical, with government grants needed to fill the gap.

Safety in recycling plants has already proven to be a real concern, and that is without the addition of a very large number of very large EV batteries entering the waste stream. To date, fires caused by LIBs have cost the UK and US economy billions and will continue to do so without sufficient policy intervention which prevents spent LIBs from finding their way into conventional waste streams. Due to the high chance of thermal runaway, spent LIBs cannot be handled in the way lead-acid batteries are; long gone are the days of scrap vehicles being stored in piles 20 meters high.

This chapter has presented the cathode chemistries and the supply risks that come with the most important raw materials for each cathode. There is a discussion to move away from high-cobalt chemistries, the impacts on nickel reserves, as well as the low substitutability of other materials such as manganese. The different recycling processes, with a simple explanation of each, accompanied by a flow diagram were presented. The yield of each process was discussed followed by the opportunities and problems we are presented with when recycling LIBs, namely, the environmental benefits and down-cycling of products. This chapter covers battery recycling legislation, including DBPs and how they aim to aid in the adoption of a circular economy. We finish with an overview of the safety issues which come throughout the life cycle of a LIB, with a particular focus on how the LIB waste stream is incredibly high risk.

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Part V
Emerging Battery Chemistries

Preface

Batteries are playing a central role within the European Green Deal roadmap that targets climate neutrality by 2050. Indeed, rechargeable batteries of high energy density and round-trip efficiency and designed by a sustainable approach represent the key technology for many applications, from sustainable and smart mobility, clean, affordable, and secure energy from intermittent renewable sources, smart environments, and communications. However, the search for battery chemistries offering even higher energy and/or power density in combination with enhanced sustainability is still open. This chapter takes a technology perspective and introduces the fundamental technical and electrochemical concepts and working principles of the most relevant battery chemistries. As such, it is fundamental for understanding the general principles of battery energy storage. Within this, Chapter 10 focuses on "classic" closed systems, with the most prominent representative being lithium-ion batteries, but tackles also other emerging systems such as sodium-ion or solid-state technologies. Chapter 11 then deals with open systems, mainly redox-flow batteries, where energy and power can be scaled independently.

Chapter 10
Closed Battery Systems

Akiko Tsurumaki, Sergio Brutti, Giorgia Greco,
and Maria Assunta Navarra

Contents

10.1 Lithium Metal Batteries

Electrochemical plating/stripping of lithium metal at the negative electrode of aprotic batteries can in principle provide significant functional improvements compared to Li ion intercalation electrodes, in terms of the outstanding performance of the Li metal electrode (theoretical capacity = 3860 mAh g^{-1} and E° = −3.04 V vs. SHE, standard hydrogen electrode, cf. 372 mAh g^{-1} and ≈ − 2.9 V vs. SHE for graphite) [1]. A high energy density of 400–600 Wh kg^{-1} can be achieved when lithium metal anode is combined with intercalation-type cathode materials such as $LiFePO_4$, $LiCoO_2$, lithium–nickel–manganese–cobalt oxide (NMC), and lithium–nickel–cobalt–aluminum oxide (NCA). The use of Li metal anode is also proposed in Li–sulfur (Li–S) batteries and Li–oxygen (Li–O_2) batteries, thus enabling further increase in the energy density of these

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next-generation battery chemistries. However, and despite the extraordinary research efforts made in the last five decades by researchers all over the word, lithium metal electrodes in secondary, i.e., rechargeable, batteries are still far from being commercially feasible. In fact, there are fundamental limitations that hinder the reversibility of lithium metal stripping/deposition in aprotic electrolytes based on liquid, polymer, or crystalline components [2].

In the lithium metal battery (LMB) technology, the reduction potential of Li is below that of conventional organic electrolytes. Therefore, lithium metal electrodes show Coulombic efficiencies upon cycling lower from unity in batteries. This fact makes the electrolyte a critical component in the development of LMB. In addition, the uneven deposition morphology of Li and inhomogeneous electrochemical dissolution lead to dendrite and dead lithium formation, lowering the Coulombic efficiencies [3]. A wide variety of approaches has been proposed to tackle these drawbacks, rooted in thermodynamics and kinetics of the lithium stripping/deposition. Overall, the electrochemical reversibility of lithium metal electrodes can be enhanced by the following four main strategies [4]:

1. Optimization of the electrolyte formulation to control the solid electrolyte interphase (SEI) formation over the electrodes
2. Pre-deposition of an artificial SEI over the lithium metal electrode
3. Exploitation of open three-dimensional scaffolds with controlled meso- or nanomorphologies to buffer volume expansions and self-heal the formation of dead lithium
4. Substitution of liquid electrolytes with solid polymer and inorganic materials, and their combination into hybrid electrolytes, to limit side reactions at the lithium metal surface

10.1.1 Mechanism of the Electrochemical Lithium Stripping/Deposition in Liquid Electrolytes

Lithium metal is an extraordinary reducing agent with the redox potential of $E^\circ = -3.04$ V vs. SHE. Almost all aprotic liquid solvents with polar groups suitable for the formulation of secondary battery electrolytes are thermodynamically unstable in contact with lithium. This thermodynamic constraint causes an immediate degradation of solvent molecules in contact with the surface of lithium metal through a pseudo-corrosion mechanism [5]. The degradation is initiated by the irreversible reduction of one solvent molecule:

$$\mathsf{solvent} + \mathsf{Li} \rightarrow \mathsf{solvent}^{\bullet\,-} + \mathsf{Li}^{+}\ (\mathsf{solv})$$

and this reaction unavoidably creates pitting holes over the lithium metal through the release of solvated Li^+ ions in the electrolyte, simultaneously generating the unstable radical $\text{solvent}^{\bullet\,-}$ anion in a doublet state [6]. This radical molecule easily undergoes further reactions with other solvent molecules:

$$\mathrm{solvent}^{\bullet -} + \mathrm{solvent} \rightarrow (\mathrm{solvent{-}solvent})^{\bullet -}$$

to form a short-chain radical polymer $(\mathrm{solvent{-}solvent})^{\bullet -}$. The radical can also react with the salt anion (e.g., $LiPF_6$) to form insoluble lithium salts like lithium fluoride:

$$\mathrm{solvent}^{\bullet -} + \mathrm{LiPF_6\ (solv)} \rightarrow \mathrm{LiF\ (solid)} + (\mathrm{PF_5{-}solvent})^{\bullet -}.$$

In turn, unstable alkyl carbonate–fluorophosphate adducts, i.e., $(\mathrm{PF_5{-}solvent})^{\bullet -}$, are formed that easily further degrade through irreversible multistep processes, leading to a precipitation of the insoluble species and/or an alteration of the electrolyte composition. Another degradation process of the $\mathrm{solvent}^{\bullet -}$ radical anion is its intramolecular breakup promoted by a further reduction, leading to the formation of gaseous species (i.e., molecular hydrogen, ethylene, and other small volatile organic molecules like formaldehyde, acetylene, etc.) [7]. These multifarious radical chain reactions, initiated by the inevitable reduction of solvent molecules, lead very rapidly to the precipitation of insoluble inorganic and organic by-products (e.g., Li_2CO_3, Li_2O, lithium alkyl carbonates, esters, etc.) over the surface the lithium metal, thus forming a passivation film (i.e., a natural solid electrolyte interphase, namely, n-SEI) [8]. This n-SEI completely passivates the surface of lithium metal, within the pitting holes as well as in the outer areas, but the pseudo-corrosion is not remarkable in the latter. Therefore, the n-SEI is unavoidably inhomogeneous in the nanometer scale, with significant compositional and morphological differences. Furthermore, in the initial electrochemical lithium deposition or oxidation of the lithium electrode, further electrolyte degradation occurs ending in the complete passivation of the surface by a thick passivation n-SEI film that is reminiscent of the original natural SEI [9].

The compositional inhomogeneity of the n-SEI originates from the so-called weak points, where the accumulation of organic by-products makes the local electric resistance larger compared to the surrounding areas of the electrode. These weak points become the most favorable nucleation sites for the electrochemical deposition of lithium metal and the electrochemical stripping of lithium ions. Overall, the surface of the lithium metal electrodes upon cycling will alter, driven by the local fluctuation of the n-SEI transport properties, thus leading to the aggravation of the original morphological inhomogeneities with formation of dendrites and pitting holes [10].

Once formed, dendrites increase remarkably the volume of the lithium metal electrode and grow preferentially toward the counter-electrode, following the electric field lines. This growth leads to internal short circuits and catastrophic cell failures. Moreover, dendrite formation exposes additional fresh lithium surface to the electrolyte, thus leading to further electrolyte degradation and accumulation of n-SEI. This mechanism is particularly unfavorable as it drives the formation of dead lithium upon stripping. This is because dendrites can be electrochemically dissolved during discharge, and therefore it is possible that a portion of the metallic lithium dendrite, passivated by the unfavorable n-SEI, may lose an electronic contact with

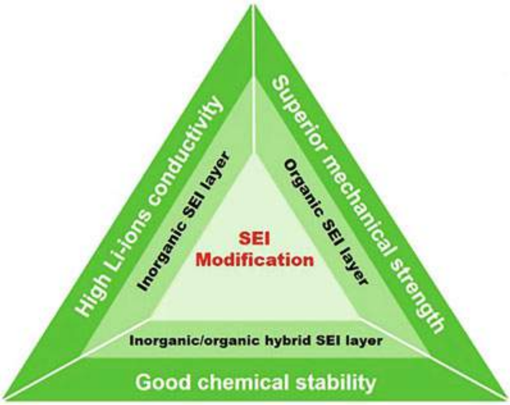


Fig. 10.1 Optimal properties of SEI layers over metallic lithium [12]

the bulk of the electrode. Unavoidably, these isolated lithium dendrites cannot undergo further electrochemical reactions leading to the loss of active material [11].

In general, the n-SEI grown on lithium metal before and upon cycling should meet several requirements to mitigate the dendrite growth, enhance the reversibility of plating/stripping, and suppress the formation of dead lithium as schematically summarized in Fig. 10.1.

Unfortunately, the n-SEI layer formed in typical LIB electrolytes is unable to fulfill these demands, and, as already mentioned, different strategies have been considered to tackle this challenge, in particular forming artificial SEI layers or altering the nature of the n-SEI. Another radical approach is to replace liquid electrolytes moving to solid-state (electrolyte) batteries.

10.1.2 SEI Modulation via In Situ Formation

The formation of the SEI can be modulated by electrolyte additives that can alter the degradation mechanism to form more homogeneous and stable passivation films over the surface of the lithium metal electrodes. These sacrificial chemical species initially consume some metallic lithium of the electrode, but this consumption is generally limited and will end once the lithium electrode surface is passivated in situ by a modified solid electrolyte interphase (m-SEI). These electrolyte additives belong to two main groups depending on their main effect, i.e., reduction-type and reaction-type additives [13].

Reduction-type additives have a relatively high redox potential and are reduced upon lithium deposition prior to any unfavorable effect on the electrolyte [14]. Their decomposition products form an insoluble film, protecting the electrode/electrolyte interface, with enhanced transport properties compared to the n-SEI formed spontaneously without the additive. Reduction-type additives are divided into two subgroups. The first subgroup consists of reactive compounds containing unsaturated bonds like vinylene carbonate (VC) or fluoroethylene carbonate (FEC) and promotes the accumulation of polymerized organic species over the surface of the lithium metal electrodes. The second subgroup includes reductive agents aiding the SEI formation. This class of reductive additives is electrochemically reduced before the electrolyte decomposition by-products precipitate onto the lithium surface. These additives can also react with radical species generated during the initial solvent reduction process, thus terminating the radical chain reaction that leads to the uncontrolled n-SEI formation. The most common chemical species that belong to this class are sulfur-containing chemical like sulfolane, ethylene sulfite, or dialkyl-sulfone [15]. Their degradation ends with the formation of insoluble lithium sulfites or alkyl lithium sulfites.

Reaction-type additives are typically molecules with scavenging abilities. These species can react with intermediates of the natural degradation radical chain reaction of the electrolyte in contact with lithium surfaces, altering the final composition of the SEI by promoting the accumulation of electrochemically inert species with favorable transport properties. (Trimethylsilyl)isothiocyanate can easily scavenge PF_5 as well as phosphite-containing compounds, thanks to their strong nucleophilic character [16].

Besides reaction-type and reduction-type additives, it is important to mention the possible use of co-salts of multivalent cations (e.g., Mg^{2+}, Ca^{2+}, Zn^{2+} Fe^{2+}, In^{3+}, and Ga^{3+}). Many of these cations can alloy with lithium upon reduction worsening the ionic transport properties across the entire electrode surface. This effect leads to a smaller ionic conductivity but mitigates the uncontrolled growth of lithium dendrites [17].

10.1.3 Ex Situ Deposition of Artificial SEI

The second general strategy to improve the reversibility of lithium stripping/deposition is the ex situ preformation of an artificial SEI layer (a-SEI) on the surface of the metallic electrode. This strategy cannot fully prevent the spontaneous reactivity of the electrolyte with the lithium surface but can strongly mitigate its occurrence and therefore strongly reduce the chemical and morphological inhomogeneity of the lithium electrode surface. In general, a-SEIs over lithium metal electrodes can be synthesized by atomic-layer deposition (ALD), aeration, or chemical coating in a liquid precursor solution [18].

ALD is an advanced thin-film fabrication technique capable of producing homogeneous and ultrathin films at room temperatures or slightly above [19]. The final surface film is extremely thin, thanks to the careful control of the mass-loading of the a-SEI allowed by the technique. These ultrathin films are typically constituted by Al_2O_3 that, during the electrochemical deposition of lithium, firstly converts into the highly conductive lithium aluminate $Li_xAl_2O_3$ that stabilizes further the a-SEI and allows a remarkable limitation of the dendrite growth [20].

Aeration is a chemical deposition method from the gas phase, in which the lithium metal surface reacts with almost permanent gaseous species like N_2 or O_2 to form homogeneous nitride or oxide layers. Since Li_3N is an electrochemically stable and fast ion conductive chemical species, the precipitation of a continuous and homogeneous thin film of lithium nitride over the surface of lithium metal acts to prevent side reactions between lithium metal and the electrolyte without hindering the lithium ion mobility [21].

The a-SEI, starting from selected liquid precursor solutions, can be obtained by using the so-called dip-coating or drop-casting method. A suitable chemical composition of the precursor solutions promotes the formation of a-SEI with controlled compositions and surface moieties. In fact, the constituent species of the precursor solution degrades due to the direct chemical reaction with the metallic lithium forming a preliminary passivation film [22]. This a-SEI can mitigate the unavoidable reactivity of the metallic lithium surface with the electrolyte upon cycling. The composition of the precursor solutions can modulate the composition of the resulting a-SEI allowing the control of the transport and mechanical properties of the a-SEI. An almost innumerable number of precursor solutions have been proposed in the literature, all leading to an improvement in the overall reversibility of the lithium plating/stripping. Among the many possibilities, one that should be mentioned is the use of polyphosphoric acid solution in organic solvents like dimethyl sulfoxide that promotes the formation of a Li_3PO_4-rich a-SEI, with excellent chemical stability, high Young's modulus (10–11 GPa), and high lithium ion conductivity [23].

10.1.4 3D Engineering of the Electrode Morphology

The third possible approach is to modify the morphology of the surface where Li is plated (either Li metal or directly the current collector) by an engineering at the nanoscale. Mechanically robust and chemically inert three-dimensional scaffolds or generic frameworks are used to facilitate homogeneous deposition of lithium metal, thus indirectly limiting the degradation of the electrolyte over fresh lithium surface [24]. The coating of lithium metal electrodes with very thin amorphous carbon-based hollow nanostructures can modulate the Li^+ ion transport pathways toward the metal surface, leading to the nucleation and growth of the lithium deposits either over Li or the current collector. Furthermore, lithium metal can deposit within the hollow nanostructures with a minimal contact with the electrolyte, thus mitigating any further degradation. Also, the use of two-dimensional materials like graphene or hexagonal boron layer can modulate the lithium stripping/deposition reaction by inducing specific growth morphologies and the formation of a tailored a-SEI [25].

The use of open nickel foams as a current collector and support for the lithium deposition is also an effective strategy to accommodate the huge volumetric changes experienced by conventional host-less flat electrodes to lead homogeneous lithium deposition. In fact, the 3D open foam can be infused with molten lithium by capillary force forming a composite scaffold with a minimized interfacial resistance and empty spaces to buffer volumetric changes upon stripping and deposition [26].

10.2 All-Solid-State Lithium Metal Batteries

The use of commercially available organic liquid electrolytes in LMBs, as well as in Li ion batteries (LIBs), unavoidably poses major safety issues because of their flammability and strongly exothermic reactivity with lithium that can easily self-heat the battery in case of accidents, leading to catastrophic explosions. The replacement of liquid electrolytes with a solid electrolyte (SE) allows to tackle this serious drawback drastically and reduces the risk of fire and explosion even in case of major thermal, mechanical, or electrical abuse. As a further advantage, the use of SEs as an electrolyte having a function of separator increases the overall volumetric energy density of the batteries, thus improving the overall performance [27].

The ideal set of properties of SEs is [28, 29]:

1. High ionic conductivity ($>10^{-4}$ S cm^{-1}, better $>10^{-3}$ S cm^{-1} in the case of thick composite electrolytes) with a high Li$^+$ transference number ($t_{\mathrm{Li+}}$), especially at low temperatures
2. Good chemical compatibility with other battery components including lithium metal
3. Good thermal and electrochemical stability at a wide range of temperatures and voltages for the constant operation of cells, including the thermal stability also in terms of the absence of phase transition so as to avoid the formation of low conductive solid phase
4. Minimal interfacial resistance between SE and electrodes
5. High electronic area-specific resistance, resulting in conductivities $<10^{-12}$ S cm^{-1}, to prevent self-discharge
6. Appropriate mechanical strength to resist dendrite growth
7. Good affordability in terms of less environmental impact, allowing for simple and low cost fabrication of both SE itself and devices

All-solid-state batteries with lithium metal electrodes (ASS-LMB) are classified as “generation 4b batteries” by the EU commission. However, despite the excellent functionality of SEs, several drawbacks hinder their development beyond the lab-scale and the final commercialization. The most relevant challenges are the unsatisfactory ionic conductivity compared to classical liquid electrolytes, the large impedance at the electrode–electrolyte interfaces, and the electrochemical instability against lithium metal of SE constituents.

10.2.1 Classification of Solid Electrolytes

Solid-state electrolytes can be either inorganic solid electrolytes (ISEs), solid polymer electrolytes (SPEs), or their composites. The former electrolyte can further be divided into oxide types, sulfide types, and others including hydride, borate, and phosphate types. The oxide-type ISEs have good chemical and electrochemical stability. The design of a material with a good air stability and low toxicity is possible. They exhibit a fast ionic conductivity in bulk, up to 10^{-3} S cm^{-1} at room temperature; however, to achieve this ionic conductivity, a sintering procedure at high temperatures, conventionally at around 1000 °C, is necessary to reduce grain boundary resistance between electrolyte particles. In contrast to this, sulfide-type ISEs have a low oxidation stability and high reactivity in the presence of moisture but exhibit a high ionic conductivity merely by pressing the materials at room temperature (so-called low-temperature sintering). This is because of a larger size S^{2-} which broadens ion conduction pathways in the electrolyte structure and the higher polarizability of S^{2-} which weakens the interaction with Li^+. On the other hand, SPEs have several advantages in manufacturing processes, such as simple production of large-area films, easy formation of a seamless interface with the electrodes, and possible handling of SPE in ambient air. However, it is not easy to find a suitable combination of a polymer matrix and additive salt that can exhibit ionic conductivity higher than that of ISEs, except for the combinations forming gel polymer electrolytes.

10.2.2 Ion Conduction Mechanisms of Solid Electrolytes

ISEs normally consist of two sublattices: a crystalline framework composed of immobile ions and a sublattice of mobile ions [30]. Therefore, Li^+ ions move within an essentially static framework through ion hopping (i.e., the Grotthuss mechanism), which is favorable with regard to a faster ion conduction. The mobile species in a crystalline solid need to pass through periodic bottleneck points, which defines migration energy. To reduce the energy barrier and achieve faster ion conduction, (1) the number of mobile ions and their hopping sites, as well as the vacancy of the mobile ions, (2) the size of bottleneck points, (3) the degree of structural order in a mobile ion sublattice, and (4) the presence of highly polarizable anions in sublattices are critical factors [31]. In glassy inorganic materials, the ion conduction mechanisms are quite like those in crystalline structures. The ions at local sites, being excited to neighboring sites, diffuse collectively on a macroscopic scale. In contrast to these, in SPEs, the motion of Li^+ ions is mediated by the dynamics of the host polymer, i.e., the vehicular mechanism, thereby restricting the ion conduction to a relatively slow speed. The segmental motions of polymer chains create free volumes that allow for the migration of ions coordinated by the polymer polar groups, and ions migrate from one coordinate site to another, promoted by the segmental motions. The ionic conductivity, in this case, is strongly dependent on the crystallinity of the host polymer.

10.2.3 Development of Inorganic Solid Electrolytes

The diffusion of ions in crystalline solids is significantly affected by both ion valence and ionic radius of the migrating species because these influence electrostatic interactions between mobile ions and cations forming the structural skeleton [31]. In addition to this, the natures of the ligands and metals composing the skeleton of the host framework have large impacts on the performance of ISEs because they determine the channel size for ion migration. In the case of Li^+ diffusion, since controlling the bottleneck size for the ion diffusion has been successful in enhancing Li^+ conductivity and reducing the activation energy, structural tuning by cation substitutions within a given structural framework has been intensively studied. Among those investigated, the most attractive Li^+ conductors, based on oxides such as natrium super ionic conductor (NASICON) type, garnet type, and perovskite type, as well as sulfides such as lithium super ionic conductor based on sulfides (thio-LISICON) type, $Li_{10}MP_2S_{12}$ (LGPS) type, argyrodite type, and $Li_7P_3S_{11}$ type, are summarized in this section and Table 10.1.

NASICON-Type (e.g., LATP/LAGP) NASICON-type Li^+ conductors are represented by the general formula of $AM_2(PO_4)_3$, in which $A = Li$ and $M = Ge$, Ti, Zr, etc., forming a three-dimensional framework of MO_6 octahedra alternatively connected with PO_4 tetrahedra by sharing their vertices [31]. Lithium ions occupy two different sites in the structure, so-called A1 and A2 sites, and their migration occurs via ion hopping between these sites. The limitation for the ion motion comes from triangular oxygen windows, which separate the A1 and A2 sites, known as the bottleneck [38]. Therefore, optimization of the bottleneck size effectively improves the ionic conductivity and reduces its activation energy.

The first strategy for this issue is the use of larger M ion in $AM_2(PO_4)$ structure [33]. For example, the ionic conductivity of $LiGe_2(PO_4)_3$ is only 6.62×10^{-9} S cm^{-1} [32]. In the case of $LiTi_2(PO_4)_3$ and $LiZr_2(PO_4)_3$, where Ge^{4+} is replaced with larger ions, their ionic conductivities improve to 2×10^{-6} S cm^{-1} and 3.8×10^{-5} S cm^{-1} at room temperature, respectively. The second strategy is the aliovalent substitution, resulting in $A_{1+x}M'_xM_{2-x}(PO_4)_3$, in which $M' = Al$, Ga, La, etc. This increases the Li^+ concentration and also its mobility [33]. The concentration of M^{3+} needs to be limited to ~15% ($x = 0.3$) to avoid the formation of a secondary phase due to an ionic radius mismatch [31]. Al-doped NASICON-type materials, such as $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ (LATP) and $Li_{1+x}Al_xGe_{2-x}(PO_4)$ (LAGP), are known to exhibit ionic conductivities of ~3×10^{-3} S cm^{-1} (when $x = 0.3$) [31] and 1.0×10^{-3} S cm^{-1} (when $x = 0.5$), respectively [33]. Both LATP and LAGP are stable at relatively high potentials and in air, while they are unstable at low potentials because Ti^{4+} is easily reduced. The formation of a protective layer based on polymers, LiPON, or other ISEs allows the use of this kind of materials with lithium metal anodes [39].

Garnet-Type (e.g., LLZO) The general formula of garnet-type materials is $A_3B_2(XO_4)_3$, in which $A = Ca$, Mg, Y, La, etc., $B = Al$, Fe, Ga, Ge, Mn, Ni, V, etc., and $X = Si$, Ge, Al, etc., forming eightfold, sixfold, and fourfold coordinated

Table 10.1 Properties of different kinds of ISEs

Structure type	Basic structure	Particular composition	Conductivity at R.T./ S cm^{-1}	Advantage/ disadvantage	[Ref]
Oxides					
NASICON	$AM_2(PO_4)_3$ A site for Li^+	$LiTi_2(PO_4)_3$	2×10^{-6}	High air stability/incompatible with lithium metal anode because of Ti^{4+} with poor resistance to reduction	[32]
		$Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ (LATP)	~ 3×10^{-3} ($x = 0.3$)		[31]
		$Li_{1+x}Al_xGe_{2-x}(PO_4)_3$ (LAGP)	1.0×10^{-3} ($x = 0.5$)		[33]
Garnet	$A_3B_2(XO_4)_3$ X site for Li^+	$Li_7La_3Zr_2O_{12}$ (LLZO)	1.63×10^{-6} (tetragonal)	Stable against lithium metal/ lithiophobic	[34]
		$Li_7La_3Zr_2O_{12}$ (LLZO)	2.44×10^{-4} (cubic)		[32]
		$Li_{6.24}Al_{0.24}La_3Zr_2O_{11.98}$	4×10^{-4}		[35]
		$Li_{6.4}Ga_{0.2}La_3Zr_2O_{12}$	1.32×10^{-3}		[35]
Perovskite	ABO_3 A site for Li^+	$Li_{3x}La_{2/3-x}\square_{1/3-2x}TiO_3$ ($0 < x < 0.167$, LLTO)	$\sim 10^{-3}$	Presence of grain boundary resistance, incompatible with lithium metal anode because of Ti^{4+}	[32]
Sulfides					
Thio-LISICON	$Li_xM_{1-y}M'_yS_4$	$Li_{3.25}Ge_{0.25}P_{0.75}S_4$	2.2×10^{-3}	High ionic conductivity (merely after pressing)/limited stabilities in the contact with moisture and lithium	[36]
LGPS	$Li_{10}MP_2S_{12}$	$Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$	2.5×10^{-2}		[32]
Argyrodite	Li_6PS_5X	Li_6PS_5Cl Li_6PS_5Br	1.9×10^{-3} 6.8×10^{-3}		[36]
$Li_7P_3S_{11}$	$Li_2S–MS_n$	$Li_7P_3S_{11}$	1.7×10^{-2}		[37]

structures centered on A, B, and X cations, respectively [32]. Li^+-conductive garnets have the general composition of $A_3B_2(LiO_4)_3$. The Li^+ content can be increased by the aliovalent doping, and several materials with different stoichiometry such as the Li3 series, $Li_3Ln_3Te_2O_{12}$ (Ln = Y, Pr, Nd, etc.), Li5 series, $Li_5La_3M_3O_{12}$ (M = Nb, Ta, Sn, etc.), Li6 series, $Li_6ALa_2M_2O_{12}$ (A = Ca, Sr, Ba, etc., and M = Nb, Ta, etc.), and L7 series, $Li_7La_3M_2O_{12}$ (M = Zr, Sn, Hf, etc.), have been reported [32]. Garnets with Li^+ concentration > 3, e.g., $Li_7La_3Zr_2O_{12}$ (LLZO), are identified as stuffed lithium garnets [40]. In these stuffed lithium garnets (i.e., Li5-7 series), Li^+ occupies both tetrahedral and highly distorted octahedral coordination sites, while in the conventional garnets (i.e., Li3 series), Li^+ occupies only a tetrahedral coordination. Li ions in octahedral site migrate easily, while those in the tetrahedral site are not.

In the case of Li7 series garnet-type materials, including LLZO, the material can possess a cubic phase featuring a disordered lithium arrangement in addition to a tetragonal phase featuring a fully ordered lithium occupancy [32, 35]. The formation of a cubic structure is critical to achieve a high level of ionic conductivity. Aluminum doping is known to stabilize the cubic phase of LLZO and enhance Li^+ conductivity in one to two orders of magnitude compared to undoped tetragonal LLZO [35]. Furthermore, the ionic conductivity can be increased to 1.32×10^{-3} S cm^{-1} by doping Ga^{3+} [35]. Regarding the electrochemical stability, garnet-type electrolytes are favorable in terms of showing a stability against lithium metal. In the case of LLZO, however, the material is lithiophobic [41], resulting in a formation of the interphase with a high charge transfer resistance. Softening of the lithium at 170–175 °C (about 5–10 °C below Li melting temperature) [1] and the formation of lithiophilic coating such as those based on ionic liquids or polymers [42, 43] are known to be an effective solution for this problem. Instability at the interface with cathode has also been reported. The coating formation is effective also in this case in preventing oxidations of the electrolyte.

Perovskite-Type (e.g., LLTO) Perovskite structures are described as follows: ABO_3, in which the A-site ions (typically divalent alkaline earth metal ions) locate at the corners of a cube structure, B ion (typically transition metal ions, such as Ti^{4+}) at the center, and oxygen atoms at the face-centered positions. Based on this framework, 12-fold coordination is formed around A sites and sixfold coordination (BO_6) around B sites by a sharing corner with each other [31]. A Li^+ conductor can be obtained by replacing the divalent alkaline earth metal ions at A sites with the trivalent rare-earth element such as La^{3+} and monovalent Li^+. Just like the other ISEs, the bottleneck size for the ion conduction needs to be controlled to improve ionic conductivity, and this has been done by introducing large rare-earth or alkaline earth metal ions in the A site [31]. The presence of vacancy in the material, more specifically $Li_{3x}La_{2/3-x}\square_{1/3-2x}TiO_3$ (LLTO, $0 < x < 0.167$, $\square$ represents vacancy), for example, also allows for the enhanced bulk conductivity of $\sim 10^{-3}$ S cm^{-1} at room temperature. In such materials, La-rich and La-poor (i.e., Li-rich) layers are formed and alternately stacked. Within this structure, Li^+ transport is restricted to the Li-rich layers, and minimal transport occurs between these layers, which limits Li^+ transport to be two-dimensional. In polycrystalline structures, Li-rich layers in each grain are misaligned, and this reduces the ionic conductivity of the materials one to two orders of magnitude lower than that of the bulk [44]. As observed in other materials containing Ti^{4+} with less resistance to reduction, LLTO is not stable in a low-potential region, making it incompatible with the lithium metal anodes. Therefore, the partial or complete substitution of Ti^{4+} with Sn^{4+}, Zr^{4+}, Mn^{4+}, and Ge^{4+} has been reported. These modifications need to be carried out so as not to form a secondary phase and not to decrease the Li^+ concentration in the materials [45].

Thio-LISICON-Type and LGPS-Type Thio-LISICON-type electrolytes can be obtained by substituting O^{2-} by S^{2-} in a LISICON structure, specifically from $Li_xM_{1-y}M'_yO_4$ to form $Li_xM_{1-y}M'_yS_4$ (M = Si or Ge; M' = P, Al, Zn, Ga, etc.) [29]. The thio-LISICON-type electrolytes exhibit higher ionic conductivity compared with the LISICON electrolytes [31]. This is because of a larger size and higher polarizability of sulfide ions as discussed before for the classification of SEs. Depending on the valence of the cations, lithium vacancies in the structure can be controlled which affect Li^+ conduction significantly [46]. The maximum conductivity of the thio-LISICON family can be as high as 2.2 × 10^{-3} S cm^{-1} in the case of $Li_{3.25}Ge_{0.25}P_{0.75}S_4$ [36]. Thio-LISICON-type electrolytes tend to be unstable faced with lithium metal. However, their high ionic conductivity established this class of electrolytes as potential ISEs for the future of ASS batteries.

$Li_{10}MP_2S_{12}$ (M = Si, Ge, or Sn) and $Li_{11}Si_2PS_{12}$ are frequently considered as one of the thio-LISICON-type electrolytes [31]. However, thio-LISICON-type and these electrolytes have different crystalline structure, specifically based on orthorhombic and tetragonal crystal systems, respectively [47], and therefore can be regarded as different class of materials, namely, LGPS type. The electrolyte consists of $(Ge/P)S_4$ tetrahedra alternating with LiS_6 octahedra, forming a one-dimensional chain along the c-axis by sharing a common edge. These linear chains are connected to each other by PS_4 tetrahedra by sharing a vertex with LiS_6 octahedra [36], forming a backbone structure. Lithium ions locate in the empty space of the backbone structure by forming LiS_4 tetrahedra and create a one-dimensional LiS_4 chain along the c-axis, which is available for Li^+ conduction. In addition to this conductive channel, Li^+ diffusion is possible between neighboring conduction paths through the LiS_6 tetrahedra. Aliovalent doping enhances ionic conductivity, and, in particular, $Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$ exhibits ionic conductivity of 2.5 × 10^{-2} S cm^{-1} [32].

Argyrodite Type Lithium argyrodite, Li_6PS_5X (with X = Cl, Br, or I), is also one of the sulfide-based Li^+ conductors, having a face-centered cubic lattice of X^-, in which PS_4 tetrahedra locate as if isolated by the anions [31]. Li^+ ions form Li_6S octahedra and distribute over the remaining tetrahedral interstices [31]. In the case of Li_6PS_5Cl and Li_6PS_5Br, the halide ions can partially occupy the place of S^{2-} in the Li_6S octahedra due to an X^-/S^{2-} site disorder, which promote Li^+ mobility significantly. As a result, annealed Li_6PS_5Cl and Li_6PS_5Br exhibit high ionic conductivities of 1.9 × 10^{-3} S cm^{-1} and 6.8 × 10^{-3} S cm^{-1}, respectively [36]. In contrast to these, the site disorder does not occur in the case of Li_6PS_5I due to a large size of I^-, and annealed Li_6PS_5I shows the low ionic conductivity of 4.6 × 10^{-7} S cm^{-1} [36].

$Li_7P_3S_{11}$ Type $Li_7P_3S_{11}$ is glass-ceramic-type sulfide-based electrolytes, which can be obtained through the crystallization of glassy electrolytes formed by a binary mixture of $Li_2S–P_2S_5$. Binary mixtures of $Li_2S–MS_n$, such as $Li_2S–P_2S_5$, $Li_2S–B_2S_3$, and $Li_2S–SiS_2$, mixed by a mechanical milling technique exhibit glassy phase with conductivities of 10^{-5}–10^{-4} S cm^{-1} at room temperature. The conductivity can be improved in the order of 10^{-3}–10^{-2} S cm^{-1} by heat treatments because the glassy electrolyte softens and reduces the grain boundary resistance during the crystallization process [36]. Particularly, $Li_7P_3S_{11}$, obtained in 70% Li_2S–30% P_2S_5 in molar ratio, exhibits the ionic conductivity of ~1.7 × 10^{-2} S cm^{-1} [37]. $Li_7P_3S_{11}$ consists of $P_2S_7{}^{4-}$ di-tetrahedra and slightly distorted PS_4 tetrahedra. An inherent flexibility of readily fluctuating $P_2S_7{}^{4-}$ polyhedra enables the fast Li^+ migration in the material [48]. The ionic conductivity of $Li_7P_3S_{11}$ phase is higher than those of highly conductive thio-LISICONs, which mainly contain $PS_4{}^{3-}$ [45].

Overall, sulfide-type ISEs possess considerable high ionic conductivities. However, their drawback is their instability. Several Li_2S–P_2S_5 binary systems are known to generate H_2S upon an exposure to moisture [45]. In addition, at the interface with lithium metal, multiple solid phases including Li_2S, Li_3P, $Li_{17}Ge_4$, and polyphosphide are usually formed, and the most common solution for this problem is the formation of a-SEI on lithium metal [1]. Also, for the cathode side, the formation of a protective layer, so-called a buffer layer, usually based on lithium metal oxide (e.g., $LiNbO_3$, Li_2ZrO_3) or lithium borate (e.g., $Li_3B_{11}O_8$), is effective [1].

10.2.4 Solid Polymer Electrolytes

Non-swollen dry polymer solid electrolytes, so-called SPEs, with suitable physicochemical and mechanical properties can be easily processed into thin separators. The advantages of SPEs as compared to the ISEs are easy fabrication, better scalability, high levels of safety, and flexible shapes. Some polymers with a high polarity, such as poly(ethylene oxide) (PEO) and poly(ethylene carbonate) (PEC), dissolve a large variety of lithium salts, such as lithium triflate ($LiCF_3SO_3$), lithium bis (fluorosulfonyl)imide (LiFSI), and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI). The cations and anions dissociated in the polymer matrices are both mobile, and therefore SPEs act as a dual-ion conductor. Since the ion motion in the polymer matrices is assisted by the segmental motion of polymer chains, it mostly occurs within the amorphous fraction of the polymer matrix above its glass transition temperature (T_g). In this temperature range, the SPEs exhibit an ionic conductivity of around 10^{-3}–10^{-4} S cm^{-1}. To reduce T_g, but to still retain the solid state, copolymerization, insertion of a branch structure, and cross-linking have been undertaken [49]. In addition, the use of inorganic additives such as Al_2O_3-, ZrO_2-, TiO_2-, SiO_2-, and Li^+-conductive ceramic fillers (i.e., ISEs) has been confirmed to improve ionic conductivity and, mainly, enhance the mechanical strength of the resulting polymer membranes [50].

Despite these promising features, many drawbacks hinder the application of SPEs in LMB such as:

1. Small t_{Li+}, generally lower than 0.5
2. Occurrence of lithium dendrite growth and dead lithium formation, leading to poor efficiency and limited reversibility upon cycling
3. Low electrochemical anodic limit, around 4–4.1 V vs. Li^+/Li, that limits the choice of cathode.

Many efforts are presently devoted to tackle these issues. The fixation of an anion structure such as carboxylate, sulfonate, sulfonylimide, etc., onto a polymer backbone allows the SPEs to have the t_{Li+} of unity. In this case, the effective dissociation of the immobilized anions and Li^+ is essential for the ion conduction. Recently, fixation of sulfonylimide on SPEs is dominating the material development because a delocalized negative charge of the anion is favorable for the ion dissociations [51]. In addition, since an enlarged conjugation structure adjacent to the anion structure can reduce the ionic interactions, several polystyrene derivatives with functional structures at the para position have been designed as Li^+-conductive SPEs [51].

Besides PEO, also PEC has been proposed and demonstrated as a potential polymer matrix having the favorable combination of good physicochemical properties and satisfactory conductivity even at low temperatures. PECs show also a better anodic stability compared to PEO, thus allowing the use of high-voltage cathode such as layered oxides. On the other hand, the mechanical properties of PECs counterbalance the benefits, and relevant dendrite growth occurs at the lithium metal side [52]. In such cases, the use of dual or multiple polymer layers, having different functions, may help the homogeneous lithium metal plating/stripping, thus suppressing the dendrite growth.

10.3 Sodium and Sodium Ion Batteries

10.3.1 Battery Technologies Based on Na Metal

Among the emerging battery technologies alternative to LIBs, sodium-based batteries, in particular sodium metal batteries (NMBs), sodium ion batteries (NIBs), all-solid-state sodium metal battery (ASS-NMB), Na–S, and $Na–O_2$, show attractive benefits such as sustainable precursors, secure raw material supplies, and, in principle, low costs [53–56].

Figure 10.2 shows a schematic view of the most common Na batteries [55]. NIBs are represented by a porous Na-free negative electrode, a liquid electrolyte, and a Na-rich positive electrode; the full battery is assembled in the discharged state (Fig. 10.2a) like LIBs. The most common negative electrodes are composite films constituted by insertion-type active material, but also conversion and alloying materials have been proposed and tested. On the other side of the battery, the most common positive electrode materials tested successfully are layered ternary oxides that exploit the reversible insertion/de-insertion of Na^+ ions driven by the redox reactions such as Mn^{4+}/Mn^{3+}, Ni^{4+}/Ni^{3+}, or Co^{4+}/Co^{3+}. Regarding liquid electrolytes, formulation closely matching those of LIBs based on organic carbonate solutions has been demonstrated for the utilization in NIBs by simply substituting lithium salts with sodium salts. An appealing advantage of NIBs compared to LIBs is the possible use of Al as the negative electrode's current collector instead of Cu, thanks to the inability of Al to alloy with Na above the Na^+/Na plating/stripping redox potential [57].

ASS-NMBs are based on positive and negative electrodes, like that of NIBs, whereas the electrolyte is a solid composite (Fig. 10.2b). ASS-NMBs are recognized as a promising future battery technology because of their highly improved thermal stability, although there is room for performance improvement. Other advanced systems are $Na–O_2$ and Na–S batteries. The former exploits the plating/stripping

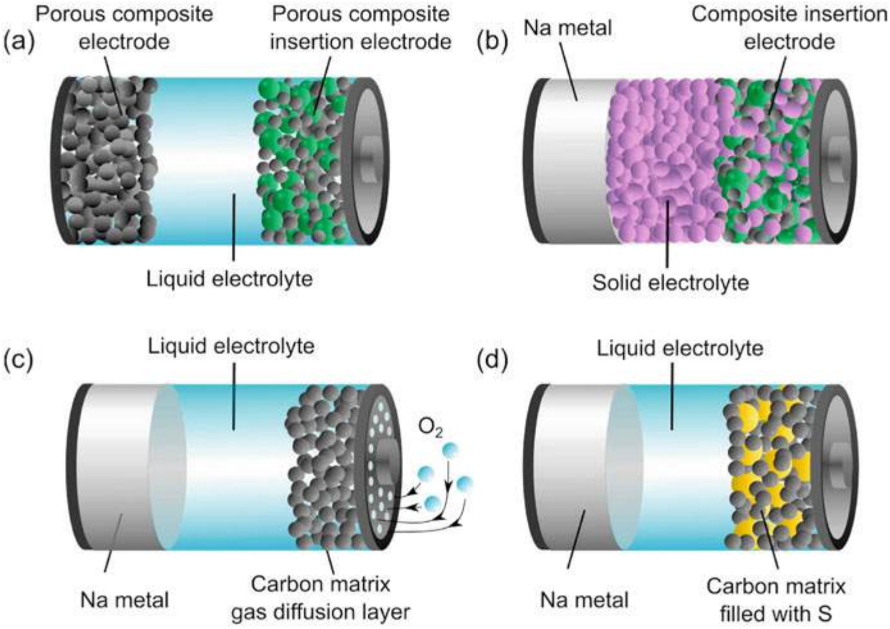


Fig. 10.2 Schematic view of the most common Na battery concepts, (**a**) Na ion battery, (**b**) solid-state Na metal battery, (**c**) Na/O_2, and (**d**) Na/S [55] (License n. 5,396,641,494,902)

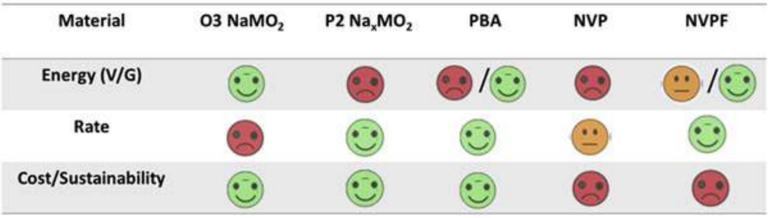
reaction of a Na metal at the anode side, whereas porous conducting carbon-based composites in contact with O_2 are used as the cathode, as depicted in Fig. 10.2c. The electrolyte can be either aqueous or aprotic. The latter, Na–S batteries, has very similar configuration compared to Na–O_2 ones, the most relevant difference being the presences of a sulfur–carbon composite at the positive electrode and the exclusive use of either liquid or solid aprotic electrolyte.

This section addresses an overview of state-of-the-art Na batteries, which represent an attractive solution almost suitable to replace Li ion technology in many future applications [53–56].

10.3.2 Toward Sodium Ion Batteries: Cathode Materials

Research on active materials for cathodes in NIBs can take advantages from all similar previous studies for LIBs. Table 10.2 visually summarizes the relative merits of many of the most promising cathodes for NIBs, namely, O3-$NaMO_2$ and P3-Na_xMO_2, Prussian blue analogs (PBA), sodium vanadate phosphates (NVP), and sodium vanadate fluorophosphates (NVPF), belonging to layered oxides (O3-$NaMO_2$ and P3-Na_xMO_2), hybrid materials (PBA), and polyanionic phases (NVP and NVPF) [55, 58–61].

Table 10.2 Comparison of performance for the most promising NIB’s cathodes. The different colors of the symbols represent high (green), average (orange), and poor (red) performance. Acronyms of the compounds are described in the main text [55] (License n. 5,396,641,494,902)



Material	O3 NaMO$_2$	P2 Na$_x$MO$_2$	PBA	NVP	NVPF
Energy (V/G)	🙂	☹	☹/🙂	☹	😐/🙂
Rate	☹	🙂	🙂	😐	🙂
Cost/Sustainability	🙂	🙂	🙂	☹	☹

Layered Oxides These materials have a two-dimensional layered structure, in which the Na ions intercalate and deintercalate reversibly. The general formula of the most advanced materials within this class is Na$_x$MM’M”M“‘O$_2$, where M, M’, M”, and M”’ = transition metals, Sn, Al, Mg, etc. This family of materials has a small molecular weight and therefore a large theoretical capacity; their stoichiometries and redox mechanisms are comparable to those of their Li analogs successfully used in LIBs [62]. Differently from the lithium layered oxides, Na ions can be coordinated by both prismatic (P) and octahedral (O) sites in the layered oxide structure, giving rise to a large variety of phases with different transition metals and stacking structures. From the performance point of view, capacities can reach as large as 200 mAh g^{-1} [62, 63]. The most critical drawback of these materials is the anticorrelation between Na content and cycling stability. In fact, materials with a Na/M ratio close to unity show large initial specific capacities but suffer from a remarkable capacity fading. On the other hand, layered phases with Na/M ratios close to 0.7 show excellent stability for prolonged cycling at the expense of the overall capacity [62, 63]. Presently, research efforts are placed on adding extra-capacity to layered phases arising from excess sodium and anionic redox activity. However, true Na-rich phases, i.e., Na$_{1+x}$M$_{1-x}$O$_2$, similar to the so-called lithium-rich layered oxides, are still elusive due to dimension of the Na atom, being larger than the Li one.

Polyanionic Compounds Polyanionic compounds are also under study as positive electrodes for NIBs. Their working potentials can be easily tuned by changing the composition of the cations and polyanions in the structure, thanks to the close interplay between the variable intensity of the inductive effect provided by different polyanionic groups and the redox activity of the different transition metals [64, 65]. The most common polyanionic compounds for NIBs crystallize in typical prototype lattices, like tavorite, alluaudite, olivine, and NASICON. The crystalline structure of these materials is more stable compared to layered oxides and allows a full intercalation/de-intercalation of one or two Na ions. The best performances reported in a full cell are delivered by V^{3+}-containing compounds [65]. In particular, the NASICON-like $Na_3V_2(PO_4)_3$ (NVP) [66] and $Na_3V(PO_4)_2F_3$ (NVPF) in a full cell with hard carbon (HC) as the negative electrode and a liquid aprotic electrolyte can deliver specific capacities as large as 120 mAh g^{-1} at 3.4 V vs. Na^+/Na with a good capacity retention even at high current rates [65, 66].

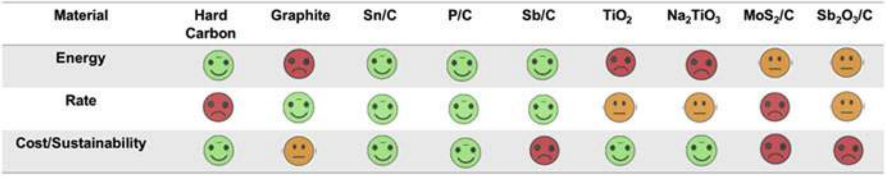
Prussian Blue Analogs (PBAs) PBAs are very attractive materials for positive electrodes in NIBs. Their general stoichiometry is $A_xM[M'(CN)_6]_{1-y}\bullet zH_2O$, where A is an alkali metal, M and M' are a transition metal ion, and y is the fraction of vacancies in the crystal structure [67, 68]. Like in the case of layered oxides and polyanionic structures, also for PBA the choice of specific transition metal blends allows to tune the redox potential of NIBs [58, 69], allowing the materials to work either as cathode or anode. PBAs have been proposed by the US company Natron that demonstrated the ability of PBAs to operate simultaneously as positive electrodes in the form of sodium hexacyanoferrate and as negative electrodes in the form of hexacyanomanganate, reaching very promising performance [70].

10.3.3 Toward Sodium Ion Batteries: Anode Materials

A visual comparison among the promising materials for negative electrodes in NIBs is summarized in Table 10.3. Materials can be grouped depending on the reaction mechanism upon Na^+ incorporation/de-incorporation: insertion (HC, graphite, TiO_2, Na_xTiO_3), alloying (Sn/C, P/C, Sb/C), conversion (MoS_2/C), and mixed alloy conversion (Sb_2O_3/C).

Insertion Materials The most promising insertion-based materials are the so-called hard carbons (HCs) having their specific capacities in the range of 300–350 mAh g^{-1}, with a Coulombic efficiency in the first cycle as high as 80% [71] and a working potential below 1 V vs. Na^+/Na. On the other hand, soft carbons (SCs) show a much smaller capacity compared to HCs, i.e., 200–250 mAh g^{-1}, but at lower working potential 0.5–0.6 V vs. Na^+/Na. Overall, despite the capacity retention in prolonged

Table 10.3 Comparison of performance for the most promising NIB's anodes. The different colors of the symbols represent high (green), average (orange), and poor (red) performance [55] (License n. 5,396,641,494,902)



Material	Hard Carbon	Graphite	Sn/C	P/C	Sb/C	TiO_2	Na_2TiO_3	MoS_2/C	Sb_2O_3/C
Energy	🟢	🔴	🟢	🟢	🟢	🔴	🔴	🟠	🟠
Rate	🔴	🟢	🟢	🟢	🟢	🟠	🟠	🔴	🟠
Cost/Sustainability	🟢	🟠	🟢	🟢	🔴	🟢	🟢	🔴	🔴

cycling being better for SCs compared to HCs, the latter phases (i.e., HCs) are the most promising active materials due to the much smaller accumulation of irreversible capacity compared to SCs, both in the first cycle and cycle-by-cycle, thus minimizing the waste of charge and the sacrificial positive electrode masses in a full NIB configuration. To improve the performance of HC, two main strategies are presently explored [72]. One is the optimization of the HC microstructure and surface composition to enhance the specific capacity through pseudo-capacitive and pseudo-plating sodium incorporation mechanisms [73, 74], whereas the second one is the incorporation of additional and different sp^2 carbon structures (like SCs or graphene) in HC-based carbon electrodes [75]. Both strategies can increase the capacity unfortunately at the expense of the Coulombic efficiency [75]. Beyond the improvement of performance, keeping sustainability and low environmental impact of these kinds of materials is important because these are critical characteristics. With this respect, it is also crucial to choose the correct precursors for these materials to keep the low costs and the sustainable philosophy of HC [76].

Alloying Materials This type of anode material shows a higher specific capacity compared to HC and operates at low voltages [77]. The alloy-forming materials gain attention due to the ability to incorporate/de-incorporate more than one Na atom per redox atom, but as a trade-off, they suffered from huge volumetric changes upon cycling. Different strategies have been proposed to address this issue, such as minimization of active material particles into a nanometric scale to reduce the mechanical strain per one particle, the formation of core–shell materials to physically restrict the volume change, and the utilization of carbon-based additives as a buffer space [78]. At the same time, however, it is necessary to evaluate whether these improvements are essential from different perspectives. For instance, carbon-based additives are added as stabilizing components for alloy-forming materials, but it also commits as “dead weight” and affects practical capacity of total electrode mass.

The alloy-forming materials are classified into group 4 elements (Si, Ge, Sn), group 5 elements (P, As, Sb, Bi), and their binary or ternary alloys. Among the group 4 elements, Si and Sn are attractive materials because of their abundance. Despite the successes of Si in LIBs, Si has not been that successful in NIBs. In the case of Sn, there are a number of similarities between the Sn in NIBs and LIBs. Among group 5 elements, P is the element with highest theoretical capacity 2596 mAh g^{-1} arising from the formation of Na_3P [79], but due to its high flammability, its practical applications have been hindered [80]. Most of developments are centered on P/carbon composites due to large volume changes during cycling as well as low electric conductivity. P/graphene composites are known to show outstanding performances [81], as well as Sb/carbon composite which can reversibly deliver up to 3 Na per atom and reach a specific capacity of 610 mAh g^{-1} with 95% of capacity retention over 100 cycles [82]. Unfortunately, however, due to the high cost, toxicity, and low sustainability of the latter material, its practical application is not recommended.

Metal Oxides Like in the case of LIBs, a variety of metal oxides have been investigated as anode materials for NIBs, and they are known to show distinctive mechanisms of anode functionality. Among these materials, the most representative one is titanium oxide, which operates through an insertion mechanism changing its structure from crystalline to amorphous [83]. Despite the high operating voltage and the low Coulombic efficiency, this material is very promising because of the low cost, low toxicity, and availability [83]. Since the conductivity of titanium oxide is low, the use of dopant has been proposed to increase its electronic conductivity. To this end, the materials such as TiO_2 nanosheets/graphene oxide composites have been developed and demonstrated to show a capacity above 175 mAh g^{-1} at 1C for 200 cycles and 90 mAh g^{-1} at 20C for 10,000 cycles [84].

Conversion Materials The reaction of this type of materials with Na is known to form a new phase which is structurally very different from the starting one, specifically $M_aX_b + (bc)\cdot Na \rightleftarrows aM + bNa_cX$, in which M is a metal (Cu, Fe, Sn, etc.) and X is an anion (O, S, P, etc.). Despite their high theoretical capacity, there are different issues related to the conversion materials, such as a low first cycle Coulombic efficiency, an insulating property, a voltage hysteresis, and a large volumetric expansion upon cycling together with consequent electrode degradation in long term due to the deep structural transformation. The electrode composition design and the right choice of the electrolyte are two investigated strategies to improve and solve the issues listed above. MoS_2 represents a typical conversion-type material with a theoretical capacity of about 670 mAh g^{-1} [85]. The electrochemical performance and its stability can be improved by engineering the materials such as the formation of different heterostructures or the combination of MoS_2 layers with different carbon-containing species [86]. Yet, due to the complexity to scale up a controlled synthesis of MoS_2, the large-scale application of this material has not been successful.

New emerging candidates are the metal phosphides [87] because they sustain the conversion reaction of the phosphorus within a metal atom network which provides electric conductivity. Moreover, in these materials, the volumetric expansion and long-term degradation are mitigated [88].

10.3.4 Liquid Electrolytes and SEI Formation in NIBs

In the case of LIBs, there are various standard electrolytes, which are also commercially available. In contrast to this, the optimal electrolyte of NIBs is still under development [89]. Like the electrolytes for LIBs, the performance of electrolytes for NIBs is strongly dependent on the electrode chemistry and electrode combination, making the optimization of an electrolyte composition complex. Especially in the case of NIBs, the ability of electrolyte to form SEI at the anode side is crucial because the SEI based on sodium salts has a higher solubility compared to that based on lithium salts; thus, the SEI undergoes continuous creation and destruction [90].

The main salts used in literature are sodium perchlorate ($NaClO_4$), sodium hexafluorophosphate ($NaPF_6$), sodium triflate ($NaCF_3SO_3$), and sodium bis (trifluoromethanesulfonyl)imide (NaTFSI), which are combined with ether or carbonate solvents [89]. $NaClO_4$ was chosen in the early stage of NIB research, but it is not ideal because of its explosive nature. As an alternative salt, $NaPF_6$ has been employed most frequently, although its performances are strongly affected by the presence of impurities [91].

The main solvents used together with these salts are the same for LIB technology, such as propylene carbonate (PC), ethylene carbonate (EC), and dimethyl carbonate (DMC), or their mixtures, which are known to form a stable SEI in the case of LIBs [91]. Since, in the case of NIBs, there is a problem in the stability of SEI as mentioned before, the use of additives has been recommended to form a compact, uniform, and more stable SEI, such as FEC and VC [92], which is the same additive used to create m-SEI in LIBs. In addition to these, sodium difluoro(oxalato)borate (NaDFOB), succinonitrile (SN), and 1,3-propane sultone (PS) have been reported as potential additives. It should be noted that in the case of NIBs, also ether-based electrolytes show very good performances for different active materials [93] including high surface carbons [94]. The use of ether-based electrolytes allows the co-intercalation of solvated Na^+ into graphite and enables the formation of stable SEI with enhanced Na plating/stripping efficiency.

Several ionic liquids and aqueous-based electrolytes are also proposed as more sustainable and stable electrolytes [89, 95]. The use of ionic liquids has positive effect on the stability of SEI. Because of this, very promising results have been obtained, for example, when ionic liquids are combined with TiO_2 anode material [96]. Due to the high cost of this class of electrolytes, practical application is not yet realized. In contrast to this, aqueous electrolytes have advantages in terms of their low cost, good sustainability, and safety [60]. However, the structural stability of the electrodes in water and the possible side reactions need to be assessed carefully [60]. Recently, the concept of the "water-in-salt" (WiS) electrolytes has been proposed. This class of electrolytes is defined as the concentrated aqueous solution of salt, in which the number of water molecule per ion is far below the solvation number [60]. These electrolytes consist of contact ion pairs (CIPs) and aggregated cation–anion pairs, which decrease the availability of water and improve its electrochemical stability. By employing the WiS electrolyte, symmetric NIBs based on a dual V^{3+}/Ti^{4+} NASICON-structured $Na_2VTi(PO_4)_3@C$ bifunctional electrode were successfully investigated, showing a stable performance over 2500 cycles at 10C [97]. This result demonstrated that the fluorine-rich SEI can suppress the electrode dissolution [97]. Important results of the advances in electrolyte/electrode optimization, related to formulation of advanced electrolyte system, are well summarized in the review of Chen and co-workers [98].

10.3.5 Next-Generation Sodium Batteries

An important step is being taken toward an all-solid-state configuration of the NIB to eliminate the serious problems related to the flammability of liquid electrolytes [99]. The first solid-state sodium ion conductor dates to the 1960s, when a fast two-dimensional sodium-ion-transport phenomenon was discovered in β-alumina ($Na_2O•11Al_2O_3$). In the same period, NASICON-type compounds were first studied leading to the development of $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ ($0 \leq y \leq 3$). Many efforts have been made to elucidate the mechanism of Na^+ transport and to achieve the optimal compositions. Recently, the inclusion of NaF at the synthesis step of NASICON was found to be effective for the fast ion transport (resulting in a conductivity of about 4×10^{-3} S cm^{-1}). In addition, different kinds of solid-state electrolytes have been reported, such as those based on SPEs as well as oxide and sulfide ISEs, as summarized by Zhao et al. [100]. The ionic conductivity and electrochemical stability of Na^+-conductive solid-state electrolytes are still low, and further development is necessary for the commercial use [99].

Other state-of-the-art systems for future sodium technologies are Na–S and Na–O_2 batteries [101]. As a closed system, in this section, focus is placed on Na–S batteries only, but both are promising systems. Na–S batteries were patented by Ford Motor Company in the 1960s, which were made of a β-alumina ceramic electrolyte and cycled at high temperature around 300 °C [102]. At this temperature, Na and S are both molten and need to be separated by the solid electrolyte. For a practical application, the working temperature of Na–S batteries must be reduced, and thus room temperature or intermediate temperature Na–S batteries are being reconsidered [103]. The important difference between Li–S and Na–S batteries is the thermodynamically stable species of alkali metal polysulfides, which should be considered for further development, possibly being both advantageous and disadvantageous.

10.4 Battery Technologies Based on Alkaline Earth Metals

10.4.1 Rechargeable Magnesium Ion Batteries

Magnesium ion batteries (MIBs) have attracted intensive attention due to their high capacity, high security, and low-cost properties. However, the performance of MIBs is seriously hindered by the intense polarization and slow diffusion kinetics of Mg^{2+} ions. To solve these issues, numerous efforts based on both experimental and theoretical studies have been proposed [104, 105]. In this section, the latest advancement in anode and cathode materials as well as electrolytes for MIBs is summarized and discussed.

10.4.1.1 Negative Electrode Materials for MIBs

Metallic Magnesium Anodes The volumetric energy density of Mg is higher than that of Li (3833 vs. 2046 mAh cm^{-3}), which is beneficial for the energy storage systems [106]. Different from the lithium metal, Mg was considered for a long time as a metal whose plating is homogeneous without formation of any dendritic structures [107, 108]. This, together with the low reduction potential of Mg^{2+} (–

2.37 V vs. SHE), makes Mg metal an ideal anode. Despite these merits, recently some authors pointed out the potential hazards related with a formation of dendritic forms or needlelike structures due to uneven deposits on magnesium metal [109–111]. Moreover, surface side reactions are known to occur on the anode side resulting in the accumulation of passivation films during the initial cycles of batteries. Unlike the formation of the SEI on the lithium metal, many reports assume that the passivation layers on the metallic magnesium have low ionic conductivity for magnesium cations [112]. Related to the formation and passivation properties of the interphase, the Coulombic efficiency of magnesium stripping and plating is the most critical parameter, and this is strongly affected by the electrolyte, its chemical properties, purity, and concentration of salt(s). Early generation of nucleophilic electrolytes [113, 114] in ether-based solvents is known to keep magnesium surface at least partially active (non-passivated). Acting on the metal anode itself, Liang et al. synthesized ultrasmall Mg particles with a diameter of ~2.5 nm [115]. The ultrasmall nanoparticles reduced the thickness of the passivation film, which improved the deposition of Mg. Chemical modification is another feasible way to control the reactivity of Mg metal. Lv et al. used a $SnCl_2$–dimethoxyethane (DME) solution to treat Mg foil and obtained a modified Mg anode with a tin-based artificial layer [116]. The Mg anode can maintain stable plating/stripping for more than 4000 cycles at a high current density of 6 mA cm^{-2}. In the same manner, by adding $GeCl_4$ into $Mg(TFSI)_2$–DME electrolyte, the Ge-based artificial layer was also formed on the Mg surface, showing a self-repairing process [117].

Alloying Anodes Some elements from block p are known to electrochemically react with magnesium ions to form an alloy. Alloying materials, such as bismuth (Bi), tin (Sn), and phosphorus (P), are promising alternatives to Mg metal anode [118]. Alloy materials may have synergistic effects in MIBs, bringing new properties that single Mg metal does not have. Bi anode (theoretical volumetric capacity is 3783 mAh cm^{-3}) [119] can rapidly insert and extract Mg^{2+}, with the ion dynamics being related to defect chemistry. In general, gravimetric and volumetric capacities related to the electrochemical alloying are very high (theoretically up to 900 mAh $g^{-1}{}_{(Sn)}$ and 6570 mAh $cm^{-3}{}_{(Sn)}$ for the formation of Mg_2Sn). Synergistic effects have been expected by combining multiple elements such as Bi–Sb (solid solution), Bi–Sn (composite), or intermetallic compositions of InBi, SnSb, or InSb [120–122]. Like the alloying-type electrode materials in LIBs, the volumetric changes due to the alloying and de-alloying process hamper the long-term cycling of the electrode. However, with a good electrode formulation, high reversible cycling has been demonstrated especially with Bi-based electrodes (Fig. 10.3) [123]. It is also important to consider that alloy electrodes might be easier to produce than magnesium metal electrode foils. Indeed, alloys can be synthetized in the form of powder by ball-milling or high-temperature reactions, which can be easily integrated in the battery industry. Moreover, alloys are certainly less surface sensitive than magnesium metal and might be of interest for protecting the Mg surface from the dendritic growth.

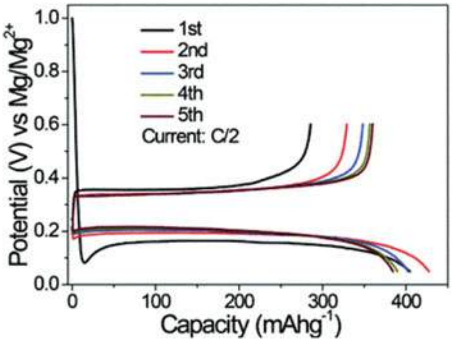


Fig. 10.3 Electrochemical behavior of Bi nanowires in a Bi|Mg half-cell at C/2 with an organohaloaluminate electrolyte [123] (License n. 1,322,765)

Intercalation-Type Anodes Although graphite has been widely employed in conventional LIBs, it is difficult for Mg^{2+} to be inserted into graphite due to its high ionization potential (7.65 eV for Mg and 5.39 eV for Li) [124]. However, Kim et al. proved that the co-intercalation of Mg^{2+} and linear ether solvents is possible through the density functional theory (DFT) calculations [125]. The Mg^{2+} storage properties of carbon nanotubes (CNTs) have also been studied by the DFT. Aslanzadeh et al. studied the influence of CNTs' diameter on the voltage of MIBs by calculating the adsorption energies of zigzag CNTs [126] and demonstrated that the cell voltage increased with the increase of CNTs' diameter. Recently, research interest was shifted to graphene to explore its potential as the anode material for MIBs. Graphene with 25% double-vacancy defects can achieve a Mg^{2+} capacity of 1042 mAh g^{-1} [127]. In addition to these, many other two-dimensional materials have been studied, such as transition metal carbides (MXene) [128] and borides (MBene) [129]. Regarding metal oxide insertion materials, TiO_2 is a very common anode for various secondary batteries. However, the limited capacity of 110 mAh g^{-1} at 0.1 C seriously obstructs its application in MIBs [130]. According to the research of Luo et al., proton charge compensation in Ti-deficient TiO_2 (B) nanowires ensures more thermodynamic feasibility and sufficient intercalation sites for Mg^{2+}, thereby increasing the capacity.

10.4.1.2 Positive Electrode Materials for MIBs

The cathode material, a key component of MIBs, predominantly determines the energy density of batteries. However, most of the cathode materials of MIBs show small capacity and poor rate capability, which seriously hinder the battery performance. Most studies on Mg batteries focus on the combination of Mg metal with inorganic cathodes based on transition metal redox centers. As of today, inorganic oxide, polyanionic, and sulfide compounds are the focus of attention of the research community, but they all present their pros and cons. Moreover, research on inorganic cathodes for magnesium batteries is sometimes quite perplexing as the lack of highly oxidative stable Mg electrolytes prevents the evaluation of Mg insertion reactions at high voltages.

Chevrel Phase Mo_6S_8 Research on the cathode materials for Mg insertion was accelerated by the seminal work of Aurbach et al. with a prototype full Mg cell based on the Chevrel phase Mo_6S_8 [114] and opened a large avenue of research on chalcogenides. These structures are very promising due to the weak electrostatic interactions between Mg^{2+} ions and the sulfide/selenide-based anion framework. The low operating voltage (~1.1 V vs. Mg^{2+}/Mg) and low specific capacity (~100 mAh g^{-1}) of Mo_6S_8, related to an incomplete de-insertion of Mg ions due to the trapping of partial charges at room temperature, are limiting factors for commercial application of the given technology. Substituting sulfur by selenium allows for a 100% capacity usage [131] but at the expense of the specific capacity value. Although the voltage and capacity values are too modest to obtain energy densities competitive with Li ion batteries, Chevrel structures remain the benchmark electrodes for Mg batteries as they offer remarkable insertion/de-insertion kinetics and good reversibility.

Layered Cathode Materials Layer materials possess two-dimensional transmission channels, which enable rapid Mg^{2+} migration. The reported layered cathode materials for MIBs include both transition metal oxides and transition metal sulfides, such as V_2O_5, MnO_2, MoS_2, and TiS_2 [132]. As a representative, V_2O_5 has attracted great attention due to its high theoretical capacity (~295 mAh g^{-1} for MgV_2O_5) and working voltage (~2.35 V vs. Mg^{2+}/Mg). Compared with transition metal oxides, the relatively low ionization degree of S in transition metal sulfide weakens the electrostatic interaction between Mg^{2+} and negative charge, which is favorable for the migration of Mg. Yang et al. studied the diffusion kinetics of Mg^{2+} in MoS_2 (theoretical capacity of 223.2 mAh g^{-1}) [133].

Polyanionic Cathode Materials Polyanionic compounds have been widely used in MIBs because of their versatile variety, stable structure, and strong inductive effect [134]. In $MgMSiO_4$ ($M = Mn$, Co, Fe, etc.), Mg^{2+} diffuses from the octahedral (O) site to the tetrahedral (T) site [135], with an energy barrier of 740÷770 meV [136]. Despite olivine $FePO_4$ performing well in LIBs, its capacity in MIBs is only ~13 mAh g^{-1} at 20 mA cm^{-2} [137], which can be attributed to the amorphous phase produced on the material surface during the discharge process, preventing Mg^{2+} from entering the bulk phase of $FePO_4$.

Organic Cathode Materials Although inorganic materials have widely dominated the field of rechargeable batteries, a great amount of attention has been recently placed on organic materials because they possess many crucial advantages, like safety, sustainability, green, low cost, and high theoretical capacity [138]. Carbonyl conjugates are a large group possessing many C=O functionalities, essentially determining properties such as diversity, fast reaction kinetics, and high specific volume. Therefore, compared to other types of organic cathode materials, carbonyl-conjugated compounds are expected to develop as the next generation of cathode materials for Mg batteries. Quinone-based monomers are particularly suitable as an active storage unit, and most of recent reports [139] provided highly attractive properties in terms of energy and power density as well as cyclability. Other reports showed applicability of imides and radical organic compounds [140], which in theory are less attractive in terms of energy density. As well known, electrochemical characteristics depend also on type of electrolyte, where both salts and solvents play important roles [141]. It has been demonstrated that the use of $Mg(TFSI)_2$ salt can increase the capacity utilization of organic electrodes, while the use of $AlCl_3$ can upshift the potential of redox active compounds [142]. Although redox active organics in the form of different polymers show the best properties in terms of cycling and rate capability, there are still some important challenges that need to be addressed before their potential commercialization.

10.4.1.3 Electrolytes for MIBs

To make MIBs commercially available, further breakthroughs in the electrolyte chemistry development are needed. As for other battery technologies, the electrolytes for MIBs should fulfill multiple criteria such as low toxicity, low cost, wide electrochemical stability window, and high ionic conductivity. The following main types of the electrolytes have been explored in MIB technologies: (i) liquid-organic solvent electrolytes, (ii) solid-state electrolytes, (iii) polymer electrolytes, and (iv) ionic liquid-based electrolytes [104].

Liquid electrolytes based on organic solvents or ionic liquids are up to now the best performing materials for Mg deposition/stripping processes. The former electrolytes present a wider electrochemical stability window, while the latter group shows a lower overvoltage in the Mg deposition process, a higher thermal and chemical stability, and a negligible flammability.

For the electrochemical reactivity at the Mg metal anode, even traces of water or other oxygenated coordination ligands must not be present in the electrolyte, to avoid any compromise in the anodic reversibility, cyclability, and current density [143]. Actually, oxygenated species cause the formation of a compact $MgO_x(OH)_y$ layer on the magnesium metal anode, which hinders the anode–electrolyte charge exchange processes promoting on its surface the growth of dendrites. On the other hand, as demonstrated by Novak et al. in the early 1990s [144, 145], water is necessary in the cathodic side to efficiently and reversibly exchange magnesium ions between the solid cathode active material and the electrolyte during insertion and de-insertion processes. This is because water molecules can exfoliate the cathode layered structure and enhance the Mg^{2+} diffusion into the bulk cathode materials by solvating the ions and facilitating their solid-state migration phenomena [146, 147]. Taking all together, developing electrolytes for MIBs able to address the so-called “devil” (at anode) and “holy” (at cathode) water dilemma is a very difficult target.

10.4.2 Calcium Batteries

Calcium (Ca) batteries are emerging as a promising next-generation electrochemical energy storage system, due to the abundant reservation of calcium and the competitive redox potential of Ca^{2+}/Ca. However, the practical realization of rechargeable Ca and Ca ion batteries (CIBs) still relies on the identification of suitable electrodes and electrolytes. Despite reversible calcium plating–stripping being recently demonstrated [148], efforts are still needed to improve both kinetics and efficiency and to allow a wider range of electrolyte formulations. Widening the electrochemical stability window of the electrolyte is crucial to lead the development of positive electrodes operating at high potential [149, 150].

10.4.2.1 The Benefits of Calcium Batteries

Calcium is a divalent alkaline earth metal with an extraordinarily strong oxidative ability in consideration of the -2.87 V vs. SHE redox potential for the Ca^{2+}/Ca couple [151, 152], to be compared to the -3.04 V vs. SHE of the lithium metal electrode. In comparison to other elements under development for battery applications, calcium is the multivalent metal with the most negative redox potential and an ionic radius of 114 pm, very similar to Na^+, that is the cation easily intercalated/deintercalated in/from a variety of materials [153]. The theoretical properties of calcium metal electrodes, in terms of gravimetric and volumetric specific capacities, surpass those of potassium, sodium (both gravimetric and volumetric), and zinc (gravimetric) and are like that of lithium (volumetric), thanks to the favorable combination of intermediate atomic weight and density [149]. In addition, compared to aluminum and magnesium, calcium has a larger ionic radius and a smaller electronegativity [154, 155], thus suggesting on the one hand a lower coordination binding in the liquid phase, thanks to the smaller charge density, and on the other hand a less covalent bonding in solid lattices. Furthermore, it is highly abundant on Earth's crust and industrially inexpensive, much more than Li, Na, K, Mg, and Zn [150, 156, 157]. Even though calcium has an atomic weight seven times larger than lithium, the specific capacities of the calcium-based oxides vary in the 100–250 mAh g^{-1} range, comparable with lithium intercalation positive electrodes, also for what concerns the thermodynamic potentials. Similar to the anode materials available for LIBs, silicon, phosphorus, and carbon negative electrodes can reach large theoretical capacities at relatively low redox potentials also in the case of CIBs. On the other hand, calcium carbide is expected to suffer from large kinetic limitations and overpotentials being the crystal structures of all CaC_2 polymorphs remarkably different from graphite [158]. Moreover, outstanding theoretical performance is achievable for $Ca–O_2$, as well as for Ca–S, leading to the formation of calcium peroxide and calcium sulfide.

A tentative evaluation of the relative merit of various calcium-based batteries in comparison with LIBs can be made using the theoretical performance of the $LiCoO_2$/C LIB as the baseline (360 Wh kg^{-1}, calculated assuming a $\Delta E° = 3.6$ V and a specific capacity normalized by the sum of both positive and negative electrode materials) [159]. The CIBs constituted by $CaMn_2O_4$ and Si can disclose a theoretical energy density of about 520 Wh kg^{-1}, being superior to the benchmark LIB (mentioned above) and approaching the desirable figures of the $LiMn_{1.5}Ni_{0.5}O_4$/Si and $LiFePO_4$/Li configurations [159]. Both sulfur battery chemistries, i.e., Ca–S and Li–S, have a comparable theoretical performance (approximately 1800–2000 Wh kg^{-1}) that is, in both cases, exceeded by the Ca–O_2 and Li–O_2 ones (~2400 and ~ 3500 Wh kg^{-1}, respectively).

Overall, calcium-based battery chemistries can theoretically achieve performance of interest, not far from those of lithium-based ones, but research in the field is still in its infancy. To date, the serious exploitation of cathode materials for CIBs just started because of the pioneering work of Ponrouch et al., demonstrating the successful Ca plating/stripping using conventional organic solvents in 2016 [148]. However, the field being in its early stage, the number of reports on positive electrode materials in the literature is still limited [159–165].

10.4.2.2 Challenges in Developing Calcium Batteries

The operating principle of typical calcium batteries is depicted in Fig. 10.4, using inorganic framework as cathode and metallic Ca as anode. In this process, a series of limiting steps occurs [166]. Firstly, the slow diffusion of Ca^{2+} in the positive

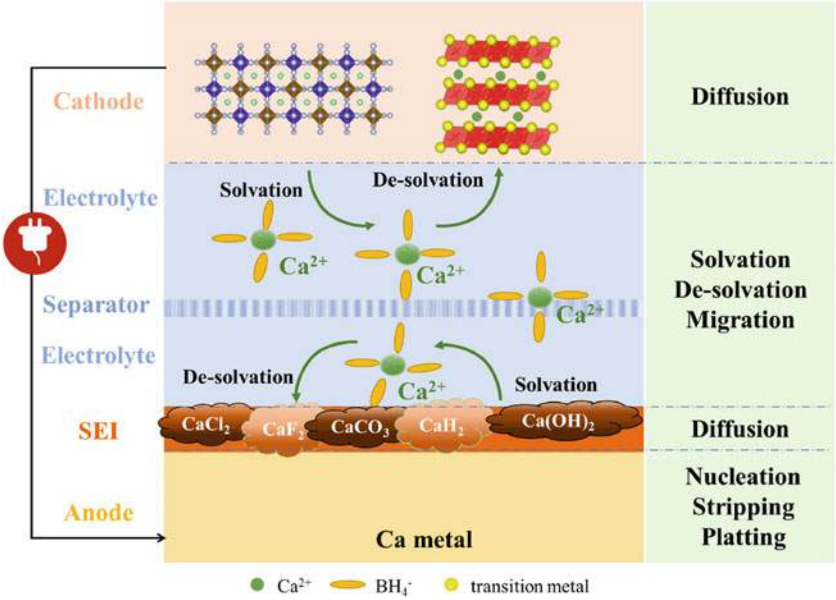


Fig. 10.4 The diffusion, migration process of Ca^{2+} in a typical calcium battery [166] (License n. 5,487,100,248,324)

electrode is inevitable. Although the charge density of Ca^{2+} is small (52 C mm^{-3}, the same as Li^+), its diffusion rate is significantly affected by its large ion radius (0.99 Å, compared to 0.76 Å for Li^+), which is a dominant limiting factor. Secondly, Ca^{2+} forms solvated calcium in the electrolyte. In some cases, the formed solvated group is relatively large, making it difficult to migrate in the electrolyte. Moreover, when the solvated cluster moves to the electrodes, it needs to be de-solvated. A higher voltage beyond the reorganization energy is needed to break the interatomic bonds in the solvation cluster. This voltage needs to be within the electrochemical stability window of the electrolytes; otherwise, it is easy to decompose the electrolyte. Thirdly, the shuttle of de-solvated calcium ions in SEI is also a matter to be discussed. SEI is a thin film with a thickness of several nanometers between the electrolyte and the anode. This layer can protect the anode from continuous damage and the electrolyte from side reaction with the anode. Ideally, the SEI film is a good ion conductor but needs to be an electronic insulator. As for CIBs, the main components of SEI are $CaCl_2$, $Ca(OH)_2$, $CaCO_3$, CaF_2, CaH_2, etc. [167]. These substances undergo structural changes during the calcium ion diffusion process. Due to the strong interatomic bond, many components are thought to be unable to transmit Ca^{2+} (such as $CaCl_2$, $Ca(OH)_2$, $CaCO_3$, etc.). Also, continuous insertion/de-insertion of Ca^{2+} induces a large volume change of SEI, which may rupture the thin film. Once Ca^{2+} passes the SEI and arrives at the anode, the intercalation, nucleation, or plating of Ca happens [168]. Owing to these complex steps, it is extremely challenging for calcium to deposit.

The main issues and their current state, to be carefully addressed to allow the calcium technology being widely applicable, are summarized as follows:

- The Ca^{2+} ion hosting materials that must be stable enough during the Ca^{2+} diffusion and insertion/de-insertion: Prussian blue analogs, transition metal compounds, and organic compounds are known as potential materials for this requirement [169, 170].
- The reversible stripping/plating of Ca metal at moderate temperature: the proof-of-concept batteries, as of today, showed an average Columbic efficiency of 96% for 50 cycles, which is not sufficient for the practical application [160, 171].
- The efficient solvation/de-solvation process of Ca^{2+}-based electrolytes: different from Li^+-based electrolytes, which can form Li^+-conducting SEI, the reactions between electrolytes and calcium tend to generate Ca^{2+}-blocking phases when contacting with organic electrolytes [172].

Overall, although great efforts have been made to change the electrolyte and modify the anode–electrolyte interface, the reversible plating/stripping of Ca metal is still tricky and complicated matter. The complexity of working directly with a Ca metal anode drives the search for alternative anodes, which can be categorized into three types based on the calcium ion storage mechanism, including alloying anodes, intercalation anodes, and organic anodes [166, 173], showing the direction toward CIBs.

10.5 Conclusions

Among the emerging battery technologies, Na ion batteries as well as alkali metal batteries, probably solid state, are those expected to become commercially available in the near- (2–5 years) to mid-term (5–10 years) future. Na ion batteries are already being developed by several industries following the CATL announcement made at the end of 2021. Polyvalent metal-based battery chemistries appear to be in the early stage of development with a few hurdles to be addressed in the next few years.

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Chapter 11
Open Battery Systems

Eduardo Sanchez Diéz, Federico Poli, and Francesca Soavi

Contents

11.1 Redox Flow Batteries

In RFBs, the electroactive species are dissolved in solutions (anolyte and catholyte) that are stored in tanks external to the cell and that are flown in the cell core that is made by the anode and cathode current collectors, intercepting the anolyte and catholyte flows, respectively, and separated by the separator (Fig. 11.1a).

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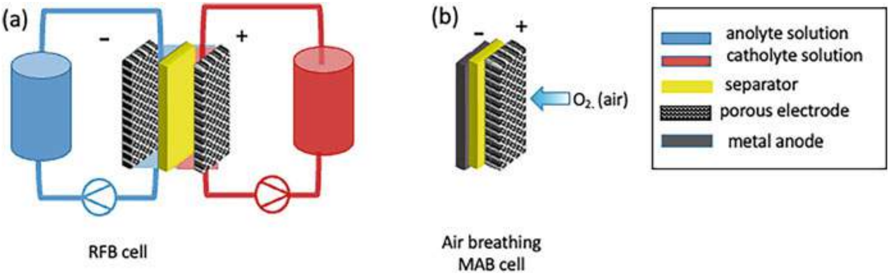


Fig. 11.1 Schemes of open battery systems: (**a**) redox flow battery (RFB) and (**b**) air-breathing metal–air battery (MAB)

MABs typically consist of a metal anode, a separator soaked in the electrolyte, and an air (oxygen) cathode that has one face exposed to the environment (Fig. 11.1b). To solve kinetics and cyclability issues that are still slowing MAB development, flow MABs (FMABs) have been proposed. FMABs exploit the RFB design, with the anolyte and/or the catholyte (only one half-cell or both) acting as carrier of the anodic metal species or of the oxygen, respectively [1].

The main advantage of RFBs relies on their peculiar architecture that allows for decoupling of power and energy but also enables easy maintenance and scale-up of the system. However, as the active materials are in solution, their solubility severely limits the energy density of the system.

Under this open system concept, many chemistries have been postulated looking at SET plan targets in terms of cost and durability, which are primarily determined by the active materials' availability and stability [1]. In this context, vanadium-based RFBs have demonstrated their supremacy considering their long lifetime (20 years) and high performance. The scarcity of the raw material is the main reason behind the need to replace vanadium. Thus, systems such as the H_2/Br_2 battery, which offer high power density and a cell voltage of 1.09 V, are also paving their way to market.

Alternatively, the so-called hybrid redox flow batteries contain at least one solid active material that is plated or stripped within the cell. Zn/Br and Zn/Fe are successful examples of this concept [2], while all-iron (ca. 1.2 V) and all-copper (ca. 0.6 V) RFBs can be listed as sustainable options considering the abundance and the low toxicity of the employed materials when compared with the most used vanadium-based compounds [1]. The problems inherent to the plating process are the main hurdles to be solved. Despite the benefits in terms of energy density of using a solid metal as anode, a direct consequence is that power and energy cannot be independently regulated.

Back to conventional RFBs, flow batteries based on organic active materials have been postulated as real candidates to dare VRFB, and based on the ubiquitous nature of carbon-based materials, they may offer a global solution. Indeed, there is a bloom of start-ups working on organic flow batteries.

11.1.1 Organic-Based Chemistries

Irruption of organic active materials in RFBs is an open door to a vast chemical space. Thus, beyond the abundance and the potential inexpensive manufacturing at large scale, the high tunability of those compounds is the main reason for the interest aroused by aqueous organic redox flow batteries (AORFBs) [3].

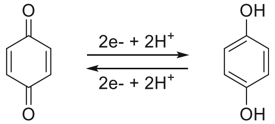
A wise design of active material should allow to determine the redox potential, the solubility, the chemical and electrochemical stability, the reaction kinetics, the gravimetric capacity, and even the crossover rate. In this regard, selection of the functionality of the active site, the inclusion of polar groups, and the definition of the molecular weight and the number of active sites would serve to modulate the properties. The ideal electrolyte is still to come, and a compromise has to be accepted. The most relevant examples on AORFB are either based on quinone-type or on viologen-based anolyte solutions (Table 11.1).

Quinone–Fe System Quinone-type molecules can undergo a fast and reversible $2e^-$ and $2H^+$ transfer according to Eq. 11.1:

Table 11.1 Comparison of the parameters reported for various AORFBs

Electrolyte Anolyte/catholyte	Theor. electrolyte capacity (Ah L^{-1}) Anolyte/ catholyte	Capacity decay (%) day^{-1}	EE (%) at current density (mA cm^{-2})	Ref
DPPEAQ/$K_4[Fe(CN)_6]$ alkaline pH	26.8/10.7	0.014 (12)	65 (100)	[5]
DPivOHAQ/$K_4[Fe(CN)_6$ alkaline pH	26.8/8.0	0.0018 (16)	85 (100)	[4]
DHPS/$K_4[Fe(CN)_6]$ alkaline pH	37.5/8.3	0.682 (14)	82 (100)	[6]
$(SPrN)_2V/NH_4[Fe(CN)_6]$ alkaline pH	9.6/9.6	0.018 (17)	63 (40)	[7]
Dex-Vi/BTMAP-Fc neutral pH	40.2/20.1	N.O. (30)	N/A (50)	[8]
BTMAP-Vi/ N2TEMPO neutral pH	13.4/13.4	N.O (9)	60 (60)	[9]
$(ATBPy)Cl_4$/ $(TPABPy)Cl_3$ neutral pH	26.8/26.8	0.445 (2)	86 (60)	[10]

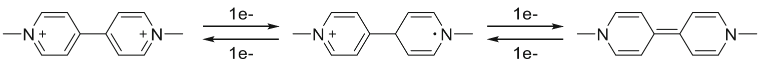
N.O. not observed



(11.1)

Among the multiple examples in the literature, anthraquinone–iron couples have shown the highest stability. Recent efforts have been devoted to further push the stability of those compounds to capacity decays as low as 0.0018% day^{-1} [4]. This has been possible by including highly stable carboxylate (DBEAQ), pivalate (DPivOHAQ) [5], or phosphonate (DPPE) [6] moieties in anthraquinone core structure, which can be coupled with ferrocyanide leading to a cell voltage of 1.0 V and operated in alkaline media with high energy efficiencies (>80% at 100 mA cm^{-2}). The lack of a more competitive catholyte solution is identified as the main limitation, while despite the high solubility of the anthraquinones, the system has only been validated for low-energy-density electrolytes (0.5 M anthraquinone). With a similar reaction mechanism, pyrazines have been employed in alkaline batteries leading to high cell voltages (1.2–1.4 V) and good cell performance when coupled with ferrocyanide [6].

Viologen-Based Systems with Neutral pH Bipyridinium salts can undergo 1e^{-} or 2e^{-} reduction processes (2); the first reduction is considered as fully reversible, while the capacity retention is generally lower if the second process is involved. No protons are involved in the redox equilibrium of viologens neither in the case of the materials selected as catholyte counterparts, i.e., iron complexes or TEMPO derivatives mainly. Those batteries are operated under mild conditions, close to neutral pH values. This may elongate the durability of the battery's components, but it also entails a challenge in terms of conductivity due to the low proton and hydroxyl concentration in the electrolyte media. Thus, the efficiency of neutral pH systems ranges between 40% and 80% energy efficiency (EE) for current densities between 50 and 100 mA·cm^{-2}. The low cell voltage (ca. 0.8 V) [7, 8] of the viologen–iron complex systems is their main weakness, while the most stable viologen–TEMPO systems employ low-energy-density electrolytes (0.5 M) [9]. Molecular engineering works are still in progress, and stable 2e^{-} storage extended bipyridinium compounds have been developed [10] boosting potential energy density of viologen systems.



(11.2)

The stability of organic materials is still under debate, and comparison of different systems is not straightforward even if the capacity fade over time has been taken as a more reliable parameter [11]. Cycling conditions, capacity utilization, and concentration of active materials among other factors may impact the electrolyte stability.

In a lower extent, polymer redox active materials have been employed as a measure to mitigate crossover [12], and organics have also been combined with a metal anode to boost energy density [13]. However, those trends remain as a secondary option after weighing pros and cons.

The use of nonaqueous organic redox flow batteries (NARFBs) has been also explored. This full organic electrolyte could theoretically mitigate the energy density problems of RFB as the cell voltage can be increased over 3 V and the solubility of the active materials is significantly higher in organic solvents. However, this ideal scenario is hurdled by the poor conductivity of the electrolytes, the high viscosity of high concentrated solutions, and the low chemical compatibility of the membranes and the organic solvents. Thus, high concentrations >2 M cannot be exceeded without compromising diffusion properties [14]. NARFBs are generally operated at low current densities (< 40 mA·cm^{-2}) [15] or at low concentrations [16].

11.2 Metal–Air Batteries

11.2.1 *Steady Metal–Air Batteries*

Metal–air (oxygen) batteries (MABs) have the advantage of using the lightest cathode material available in nature: oxygen. Furthermore, O_2 is not stored inside the cell, but it is continuously supplied from air or tanks outside the cell. Therefore, cell capacity is not limited by cathode active material depleting. In addition, in conventional (not-flow) MABs, the anode is a thin metal foil with an extremely high density. Combining a metal anode and an O_2 cathode enables to use most of the system volume for the anode material, and this results in a battery with an extremely high energy density.

Several MAB chemistries have been proposed, including those based on alkali, transition, and multivalent metals [17–19]. Table 11.2 summarizes the cell reactions, the metal and discharge product densities, the nominal cell voltage, and the theoretical specific capacity and specific energy and energy density of different MABs.

Table 11.2 Cell reactions, metal and discharge product densities, nominal cell voltage, theoretical specific capacity and specific energy and energy density of different MABs. The energy density values have been calculated referring to the metal (first value) and the discharge product (second value) densities

Cell reaction	Metal density (kg L^{-1})	Discharge product density (kg L^{-1})	Cell voltage (V)	Theor. specific capacity (Ah L^{-1})	Theor. specific energy (kWh kg^{-1})	Theor. energy density (kWh L^{-1} metal product)
$2Li + O_2 \leftrightarrows Li_2O_2$	0.534	2.3	2.96	1.17	3.5	1.9–8.0
$2Na + O_2 \leftrightarrows Na_2O_2$	0.968	2.8	2.33	0.69	1.6	1.6–4.5
$K + O_2 \leftrightarrows KO_2$	0.890	2.3	2.48	0.37	0.9	0.8–2.2
$Mg + {}^1/_2O_2 + H_2O \leftrightarrows Mg(OH)_2$	1.738	2.3	3.09	0.92	2.8	4.9–6.6
$4Al + 3O_2 + 6H_2O \leftrightarrows 4Al(OH)_3$	2.700	2.4	2.71	1.03	2.8	7.5–6.8
$Zn + ½ O_2 \leftrightarrows ZnO$	7.140	5.6	1.65	0.66	1.1	7.7–6.1
$3Fe+2O_2 \leftrightarrows Fe_3O_4$	7.874	5.2	1.28	0.46	0.6	4.6–3.1

Li, Na, K, Mg, and Al-MABs feature cell voltages higher than 2 V and therefore require the use of nonaqueous electrolytes. In the case of Li and Na, which are not stable in water, organic/inorganic hybrid electrolytes have been proposed. In these systems, the metal is in contact with an organic electrolyte, and the cathode operates with an aqueous electrolyte. Anode and cathode are alienated by a solid ionic conductor separator. Zn- and Fe-MABs featuring cell voltages lower than 2 V can operate with aqueous electrolytes, and they typically make use of alkaline solutions.

The specific capacity evaluated based on both metal and oxygen contents depends on the number of electrons exchanged for mole of reactants and mainly on the atomic mass of the metal. It spans from 0.46 Ah kg^{-1} of the Fe–O_2 cells (four-electron process) to 1.17 Ah $kg^{-1}$of the Li–O_2 (two-electron process), which features the lightest metal, i.e., lithium.

All the MABs listed in Table 11.2 feature high theoretical specific energy densities that are about two- to tenfold higher than that of today's lithium-ion batteries. Among the nonaqueous MABs, the Li–O_2 cells exhibit the highest value that in theory can be as high as 3.5 kW kg^{-1}. Among the aqueous MABs, Zn–O_2 holds the best promises with 1.1 kW kg^{-1}.

In MABs, at the anode, metal stripping/deposition occurs. At the cathode, the sluggish kinetics of the oxygen reduction and evolution reactions (ORR/OER) are promoted by catalysts (or mediators) that are supported on the electrode surface, typically a porous carbon with high surface area. Like in fuel cells, in static MABs, the optimization of the cathode three-phase boundary (catalyst–electrolyte–gas) is of paramount importance to achieve a high conversion efficiency and fast cell response under high-current regimes. Today, typical discharge currents are lower than 0.5 mA·cm^{-2} for nonaqueous Li-MABs and 500 mA·cm^{-2} for aqueous Zn-MABs. In air-breathing cells, the slow natural diffusion of O_2 to the cathode is one of the processes that cause not negligible cell overvoltages during discharge at high currents. Furthermore, during the discharge, insoluble by-products are deposited on the surface of the metal anode and air cathode, therefore passivating the electrodes, clogging cathode pores, and further limiting the diffusion of oxygen. These passivating products limit the discharge capacity of MABs to values that can be 50% lower than the theoretical ones. They also cause high recharge overvoltages and, consequently, low recharge energy efficiency that is typically lower than 70%.

As it concerns the metal anode, stripping/deposition inherently induces changes in the metal surface morphology, dendrite growth, and metal fragmentation into particles with subsequent loss of electric contact and of material. Here, the electrolyte can play a role by forming a suitable solid electrolyte interphase that protects the anode and controls the uniform metal deposition.

11.2.2 Flow Metal–Air Batteries

Despite such promising theoretical performance, still many challenging problems need to be solved to let MABs become a consolidated technology. Combining MAB chemistries with a flow cell design in flow metal–air batteries (FMABs) can be an answer. FMAB cell commonly consists of a metal anode (tin foil or a flowable anolyte), a separator soaked in the electrolyte, and a flowable air (oxygen) cathode. At the anode, the metal stripping/deposition occurs. At the cathode side, an electrolyte enriched with oxygen is flowed across a porous current collector where the oxygen reduction and evolution reactions (ORR/OER) occur. As in their static counterparts, to overcome the sluggish kinetics of the ORR/OER, the surface of the porous electrodes is decorated with catalysts or mediators.

The exploitation of a flowable cathode (catholyte) is a smart strategy to overcome some of MAB's intrinsic challenges, such as the slow oxygen diffusion at the cathode and the passivation of electrodes by deposition of insoluble by-products [1]. The convective transport of the catholyte allows for overcoming the mass transport limitations due to the oxygen diffusion [20, 21]. To reduce the current collector passivation, driven by the deposition of the insoluble discharge products (such as metal oxides), a valuable strategy is the exploitation of slurries rather than solutions, in which the suspended particles act as nucleation centers [1, 22]. Moreover, to alleviate the dendrite formation, while increasing the current density at the anode, a possible solution is the exploitation of anolyte slurries [23]. The main drawback is the nontrivial design of the flow frame, which strongly depends on the cell chemistry and the rheological properties of the electrolyte.

Nowadays, zinc, aluminum, and lithium are the main metallic anodes on which the research activity in MAFBs has been focused. According to the metal reactivity, both aqueous and nonaqueous electrolyte media have been explored [24, 25].

Zn-MAFBs are the most mature technology. Indeed, the company "Zinc 8" is currently manufacturing 100 kW, targeting 1 MW installation, forecasting a price below 100 € kW^{-1}. Li-MAFBs, for their exceptionally high theoretical energy density, are holding great promises for energy storage.

By using the abundant, readily available seawater as catholyte, the seawater battery (SWB) arises as an attractive option for low-cost, large-scale energy storage [26–28]. During its charge, at the cathode, the electrolysis (oxidation) of seawater occurs, contemporary with the reduction of Na^+ ions, extracted from seawater on the anode side. Indeed, seawater features a salinity of ≈3.5% (35 g L^{-1}) in which Na^+ and Cl^- ions account for most of the dissolved salts. The metallic sodium requires an anhydrous anolyte, aprotic solvent solutions with sodium-based organic salts, e.g., 1 M sodium trifluoromethanesulfonate ($NaCF_3SO_3$) in tetraethylene glycol dimethyl ether (TEGDME) or 0.1 M sodium bis(fluorosulfonyl)imide (NaFSI) in ionic liquid solutions [27]. The anolyte chamber must be physically separated from the aqueous catholyte while being in ionic contact. Therefore, Na-ion conducting, solid electrolytes (e.g., NASICON) that separate the anhydrous anodic chamber and the aqueous cathodic chamber are adopted [26–28]. To improve the kinetics of the ORR and OER, Pt/C- and Ir/Ru-based catalysts could be exploited [29]. However, in SWB, the presence of Cl^- in the catholyte requires the use of a proper current collector to control its oxidation reactions during charge, and this represents an additional problem.

SWB features a theoretically high cell voltage ≈3.48 V, with reported practical voltage of 2.2 V. Although extremely promising, today, this technology is still in R&D phase, and efforts are required to decrease the cost of the components to efficiently scale up [26].

11.3 Conclusions

The open batteries might change the paradigm of storing, using, and distributing energy. Besides their inherently higher safety, especially when compared to LIBs, they feature great flexibility, and a variety of materials and cell design are under exploitation. RFBs and MABs are interesting open systems that may play an important role in stationary energy storage application. In RFBs, the electrolyte is identified as the most critical component of those batteries, and there is an ongoing search for the most stable, cost-effective, safe, and abundant active materials. Thus, systems relying on safe aqueous electrolytes comprising organic active materials are gradually closing the gap with vanadium and have the potential to compete or coexist with lithium to fulfil the global demand.

MABs, even based on abundant metals, hold the promise of extremely high volumetric energy density because light and multivalent metals can be exploited. However, in MABs, low cycling stability and power are still the main limitations that could be overcome by exploiting the RFB architecture in the emerging flow and semisolid flow MABs.

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Part VI
Prospective Assessments of Emerging Batteries

Preface

There are several challenges related to current lithium-ion battery (LIB) technology, including safety, the need for scarce resources, environmental impacts, resource availability, cost, or social implications. Such doubts are addressed in new regulations and frameworks such as the EU Battery Regulation and Critical Raw Materials Act, as well as in a wider way in the Sustainable Development Goals (SDGs). The development of new battery technologies is considered as a way to overcome some of the named challenges related to LIB. However, requirements towards more sustainability make it necessary to also adequately provide corresponding prospective assessments that cover economic, environmental, and social dimensions over the entire life cycle of new battery types. Prominent methods for this purpose are, among others, environmental and social life cycle assessments and techno-economic and acceptance studies. Typically, these generate complex, multidimensional results that are difficult to communicate and where trade-offs have to be made. This requires the involvement of relevant stakeholders, e.g., via the use of integrated methods as multi-criteria decision-making methods to aid decision-making towards sustainability and the most appropriate battery technology for a given application. All the named methods face several challenges which have to be addressed carefully. After discussing general challenges of prospective assessments in Chapter 12, an overview of the most relevant methods to assess the environmental (Chapter 13), the techno-economic (Chapters 14 and 15) and the social (Chapters 16 and 17) impact of battery systems is provided in the following. Finally, multicriteria decision analysis methods for battery sustainability assessment are presented in Chapter 18.

Chapter 12
Methodological Challenges of Prospective Assessments

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and Nicolas von Drachenfels

Contents

12.1 Introduction

Environmental and social impact assessments have been developed from an environmental accounting perspective to identify the impacts and hotspots of a present or past technology retrospectively [33]. The increased use of those assessment methodologies as an engineering tool calls for alternative assessment methods that enable

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guiding innovations towards sustainability. This is the case for emerging technologies that are at an early stage of the development process [2]. Emerging technologies include both innovative products and processes that are not yet on the market, such as novel battery technologies, as well as novel advances to products and technologies that already exist on the market [4]. To evaluate the impacts of these technologies, predictions of future markets or future production technologies must be made that account for changes in economic, environmental, and social conditions over time [18].

Prospective assessment is a future-oriented method that can be used to assess environmental, economic, and social impacts of emerging technologies as well as mature technologies that are predicted to change significantly in the future [6]. Prospective assessment is also sometimes referred to as ex ante, future-oriented, early-stage, anticipatory, explorative, and scenario-based assessment, although the definitions of these methods, and whether they refer to the same method or slight variations of a method, are inconsistently reported across literature [4, 6, 9]. For this section, the definition of prospective assessment is taken as the systematic assessment of a future point in time, considering developments in society, technology, economy, and policy, that potentially influences the technology, its societal conditions, and its environmentally relevant flows [2, 18, 48].

A key benefit of prospective assessment is that decisions can be made proactively, at an early stage of the development process, to minimise or even prevent future potential adverse environmental, economic, and social impacts of the technology being assessed [22, 31, 50]. Prospective assessments, like retrospective assessments, provide guidance to decision-makers, including technology developers, policymakers, and manufacturers. The results of prospective assessments can be used in multiple ways depending on the goal and scope of the study. For example, results can inform technology developers of valuable changes that can be implemented at an early stage of development, support stakeholders in terms of investment opportunities that can enable further research and technological development, inform policymakers of recommendations based on assessed policy implementation scenarios, and guide manufacturers towards assessed applications of a technology that are considered relatively more sustainable [7, 9]. Therefore, the future potential and future challenges of the innovative technology are defined prior to the technology being implemented at larger production scales [50].

Prospective assessment is therefore valuable for assessing emerging battery technologies that have not yet penetrated the market and are still in the development phase. By assessing these technologies at an early stage, mitigation measures can be implemented more readily and influence the production technology as it is upscaled to industrial production. A standard method for conducting a prospective assessment of emerging battery technologies, or for other technologies, presently does not exist. This leads to challenges when using the results in a decision-making context [4, 17]. Although such challenges also exist for retrospective assessments, Hetherington et al. argue that challenges in prospective assessment are more prominent due to the time sensitivity to apply the results within the technology development timeframe [19]. These challenges are largely related to data availability, scaling issues, uncertainty, and comparability of results [19].

This section focuses on the challenges for applying prospective assessment to emerging battery technologies. Within the following sections, four key challenges of prospective assessments are defined and discussed. These challenges include data availability and quality (Sect. 12.2), scaling issues (Sect. 12.3), uncertainty management (Sect. 12.4), and comparability (Sect. 12.5). Section 12.6 concludes with an outlook on research and development in prospective assessment of emerging battery technologies.

12.2 Data Availability and Quality

The availability of data is limited and often of lower quality than preferred to meet the goal of prospective assessments [9]. Primary data, or measured raw data, are often scarce and/or confidential. While this is also a known challenge for retrospective LCA, key difference for prospective assessments is that data is simply not yet available or based on a laboratory scale [33]. Material input and energy consumption data are difficult to collect at this scale since production conditions are not yet optimised and the production processes themselves are still under investigation for their feasibility. Measurements on laboratory scale typically lead to energy consumptions that are not representative of production conditions at larger scales and material consumptions that suffer from high input quantities and poor product yields [11, 15].

The availability and quality of data is therefore largely related to the technology readiness level (TRL) and manufacturing readiness level (MRL) of the technology being assessed. The TRL indicates the level from 1 (concept development) to 9 (small-scale production) that addresses the maturity and functional readiness of a technology, whereas the MRL indicates the manufacturing maturity level of the technology's components and subsystems [15]. For emerging technologies, the TRL ranges from 2 (concept feasible) to 5 (laboratory-scale production validated), with corresponding MRLs from 2 (new manufacturing concepts identified) to 5 (prototype production simulated) [31]. Gavankar et al. found that the environmental burden per unit output is likely to reduce significantly with increased technology and manufacturing maturity levels [15].

In terms of battery technologies, Greenwood et al. [16] have criticised the TRL for being too generalised for consistent application to batteries. They have taken inspiration from the TRL, MRL, and other readiness levels, to develop the Battery Component Readiness Level (BC-RL) framework. In the BC-RL, three types of technologies are defined depending on the extent to which the technology can use existing production and cell assembly processes, and nine stages are identified, from laboratory production (stage 1) to commercialisation (stage 9).

As highlighted in Table 12.1, on each BC-RL stage, different data sources can be used for assessments of battery components and cells. For example, in the theoretical

Table 12.1 Battery Component Readiness Levels by Greenwood et al. [16] and examples of assessments for battery components and cells

Battery Component Readiness Level	Assessment example
1. Theoretical concept development	Environmental screening of nanomaterials for batteries [13]
2. Determination of fundamental component properties	Estimation of material cost for fictive dual-graphite cells [37]
3. Determination of electrochemical properties for small-format full cells – system-level proof of concept	LCA based on lab-scale coin cell with a sulphide solid electrolyte [55]
4. Determination of electrochemical properties for commercial-scale cells – system-level prototype	LCA based on a lab-produced pouch cells with a $Sn_{0.9}Mn_{0.1O2}$ anode powering a remote-controlled vehicle [5]
5. Development of proof of concept for scalable component production	Combination of pilot and lab-scale data to predict the environmental impact of processing battery-grade cobalt sulphate [38]
6. Development of industrial-scale component production processes	Cost and energy estimates of industrial production of $LiPF_6$ based on process modelling [43]
7. Development of proof of concept for scalable cell production	LCA for a cell based on a pilot-scale production line [11]
8. Development of industrial-scale cell production processes	Gate-to-gate GHG emissions of a 7 GWh cell production line based on calculations [10]
9. Establishment of commercial plants for component and cell production	Top-down LCA of an automotive lithium-ion battery pack produced in an existing 30 GWh factory [42]

concept development phase, data availability is insufficient to conduct a full LCA. In this case, streamlined LCA approaches (e.g. ignoring some up- or downstream processes, mixing qualitative and quantitative data, etc.) are more suitable and applied for screening purposes [3, 12]. Similarly, in phase 3, lab-produced coin cell prototypes can be used to establish simplified LCAs of novel technologies. When using simplified LCA however, complex challenges arise with emerging technologies that should be understood by all stakeholders to enable effective development decisions to be made [19]. For example, the function of the product might not yet be clearly defined (such as for nanomaterials), systems change when scaled up – lack of knowledge on how they will function at larger scales, processing stages might not be fully defined, coproduct use is unclear, and end-of-life treatment is unknown. Additional techniques (e.g. proxies, process simulation) are therefore used to fill data gaps and assess the technology in a production-scale environment (addressed further in Sect. 12.3).

For prospective assessments, the background data is also of significance [8, 17, 35]. Foreground data is data related to the technology being assessed, including its relevant components and processes, whereas background data refers to data for processes further upstream and downstream of the technology being assessed. For example, background changes in the electricity mix can influence the future impacts of electric vehicles and battery technologies [30, 35, 54]. Therefore, changes in the electricity mixes must also be included in the background data used for the assessments in order to more accurately capture the future impacts of battery electric vehicles [8].

The available data and quality determine the extent to which results can be applied for comparative assertion or hotspot assessments [56]. The goal of the study needs to be transparent and adapted to the data quality. It is furthermore essential to consider both the quality level and the time required for assessment, as well as the timing of the results needed to impact effectively the design and development stage.

12.3 Scaling Issues and Modelling Choices

Additional modelling choices are made for prospective assessments to determine the expected impacts of an emerging product system, including defining the functional unit, system boundary, allocation methods, and scaling factors. These challenges are not unique to prospective assessments, but due to data gaps and several unknowns such as the future application of the product system and how the production processes will be implemented at larger scales, these challenges become more prominent in prospective assessment [19].

The reliance on laboratory-scale data to perform prospective LCAs presents a significant challenge. It requires the upscaling of foreground inventory data. In a typical scaled-up process, the process is first optimised in the lab, followed by several steps to upscale the technology before building a large-scale facility [45]. This includes preliminary validation of lab-scale process and constructing a mini-plant, followed by a pilot plant to validate processes and finally simulate industrial-scale production. Due to the time-intensive nature of actual upscaling, prospective assessments utilise various data projection techniques to predict the future implementation of technology on an industrial scale [47]. In the case of emerging batteries, there are different methods for scaling products, and the scales defined for this context are at the level of electrodes, cells, or packs.

12.3.1 Upscaling at the Product Level (Cells and Packs)

Upscaling at the product level includes the tasks of determining the material composition of the product to which other material and energy flows are related. For incremental innovations that build on existing technology, for example, an increase of the electrode thickness, the already existing cell design needs to be adapted. Performance-mass models are the most used tools to calculate the effects of the changed cell design to the material composition. Those types of models are typically spreadsheet based and are available for a variety of different cell chemistries and cell formats as they are often used within cost assessments. Prominent examples for conventional Li-ion technology are the BatPaC model [32], the CellEst model [52], or the mass model developed by Schünemann [39].

Prospective assessments on new technology for batteries are typically based on lab-produced prototype cells (e.g. coin cells or small pouch) used for experimental purposes. However, prototype cells produced on a lab scale are not always comparable with those used in industry [27] and using these as a base of assessments might result in under- or overestimations of impacts. For example, lab-scale-produced solid-state cells typically contain a relatively thick solid electrolyte (typically 80–200 μm for solid polymer and composite polymer and up to 1 mm for inorganic electrolytes) but need to be reduced to below 25 μm to realise high energy densities [58]. Zhang et al. [55] illustrate how such thick inorganic solid electrolyte (1 mm) in a lab-produced coin cell is responsible for 97.1% of the total manufacturing energy consumption and has roughly double the global warming potential impact compared to a conventional LIB cell.

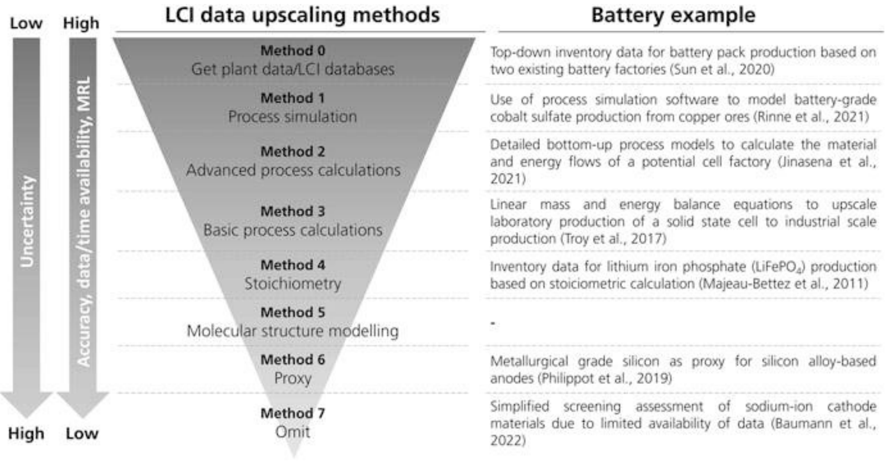
Different methods can be applied to upscale novel battery technologies from lab-scale or theoretical conceptual cells in prospective assessments on new technology. These include the use of basic calculation project cells produced in a lab environment, adapted spreadsheet-type models, and more advanced electrochemical models. The first approach uses basic (linear) calculations to estimate how the lab-produced prototype cells might scale in the future. For example, Zhang et al. [55] linearly scale the 1-mm-thick solid electrolyte used in a coin cell down to thickness of 20 μm to quantify the environmental benefits. Similarly, Wolff et al. [53] use a set of linear equations to scale a lithium-sulphur lab-produced coin cell to represent a 50 kWh automotive battery. While such simple scaling is useful for approximations, they typically neglect the technical complexity of batteries. To include such technical complexity, more advanced models are used to simulate specific cell designs used as an input to the inventory data. Due to the structural similarity of different battery types, existing spreadsheet-based models can be adapted for new cell chemistries. Peters et al. [34], for example, use a modified BatPaC model to obtain the inventory data and related life cycle environmental impacts of different sodium-ion battery types based on the electrochemical parameters of different sodium-ion active materials.

The two discussed types of models are important to develop the LCI for the raw materials, the production, and the end-of-life life cycle stage. For a holistic analysis as is foreseen in LCA, the use phase of the battery needs to be understood. This task requires more advanced electrochemical models to understand the aging mechanisms and the performance of the battery over its life cycle. Electrochemical models have been linked to LCA to enable a more systematic evaluation of battery design parameters (e.g. electrode thickness, porosity, and ambient temperature) and operating conditions on energy density and life cycle and related environmental impacts of lithium-ion batteries [24, 25]. Such coupling between detailed electrochemical models and system analysis models such as LCA or cost assessments has only recently been proposed and is presently not widely adopted or available.

12.3.2 *Upscaling at the Unit Process Level*

In the context of the production life cycle stage, an upscaling method for the unit process level can be defined as the procedure to project how a new process presently available at a low MRL might function at a higher MRL [47]. The goal of this upscaling process is to generate the potential material and energy flows of the unit process as well as potential emissions and waste flows. Following Parvatker and Eckelman [33] and van der Giesen et al. [48], a range of general LCI generation methods can be identified (see Fig. 12.1). The choice of method is largely dependent on the data and time available for the assessment and the MRL of the assessed technology. Scaling up the data from lower TRLs and MRLs to commercial scale also impacts the accuracy and introduces uncertainty into the results (discussed in more detail in Sect. 12.4).

When inventory data cannot be directly obtained from a commercial plant or LCI database, the first LCI generation method choice is the use of process simulation. Process simulation refers to steady-state and dynamic simulation models using process simulation software (e.g. Aspen Plus, CHEMCAD, or HSC Sim) and is commonly used in chemical and process engineering to analyse, design, and improve production processes. As such models typically require detailed process operational parameters, the manufacturing readiness level of the process has to be relatively high. Following process simulation, the second method is manual calculation [47] which includes advanced process calculations, basic process calculations, and calculation based on stoichiometric relations. As opposed to basic process calculations, advanced process calculations include more details such as production scale, equipment efficiencies, equipment sizing, and calculation of the energy



LCI data upscaling methods	Battery example
Method 0 Get plant data/LCI databases	Top-down inventory data for battery pack production based on two existing battery factories (Sun et al., 2020)
Method 1 Process simulation	Use of process simulation software to model battery-grade cobalt sulfate production from copper ores (Rinne et al., 2021)
Method 2 Advanced process calculations	Detailed bottom-up process models to calculate the material and energy flows of a potential cell factory (Jinasena et al., 2021)
Method 3 Basic process calculations	Linear mass and energy balance equations to upscale laboratory production of a solid state cell to industrial scale production (Troy et al., 2017)
Method 4 Stoichiometry	Inventory data for lithium iron phosphate ($LiFePO_4$) production based on stoiciometric calculation (Majeau-Bettez et al., 2011)
Method 5 Molecular structure modelling	-
Method 6 Proxy	Metallurgical grade silicon as proxy for silicon alloy-based anodes (Philippot et al., 2019)
Method 7 Omit	Simplified screening assessment of sodium-ion cathode materials due to limited availability of data (Baumann et al., 2022)

Fig. 12.1 Methods to generate life cycle inventory data with respect to uncertainty, accuracy, data availability, and manufacturing readiness level (MRL). (Adapted from van der Giesen et al. [48] and Parvatker and Eckelman [33])

requirement of each piece of equipment used in a production process [33]. On the lowest MRL, molecular structure-based models and proxies can be used to generate process inventory data. Molecular structure-based models are not widely applied to generate inventory data.

Amongst the presented methods, process calculations are mostly adopted for scaling calculations for the production life cycle stage. In many cases, the process design can be anticipated with the help of production engineering knowledge. If the production processes are similar to existing ones, dimensional analysis can be a powerful tool to scale LCI [57]. This is particularly the case for chemical production systems, for which several scale-up frameworks based on process calculations have been developed [36, 40]. However, as the battery production process chain includes process engineering, manufacturing, and electrical processes, a transfer of the scale-up frameworks comes with additional challenges. In scaling the LCI from a lab- or pilot-scale to large-scale production, the following factors describe the situation at low MRL [11]:

- Significantly lower material efficiencies
- Lower process efficiencies, energy efficiency, and throughput of the processes
- Overvaluation of technical building services like the dry room
- Lack of systemic efficiencies within the production system like the use of waste heat, energy recovery, or solvent recovery
- Unoptimised product design compared to industrial-scale batteries

Taking these factors into consideration, the scale-up of unit processes needs to include the production system perspective. In the battery production cell system, the dry room plays a key role for the energy demand. Modelling approaches for the dry room have become increasingly accurate but at the same time more complex [1, 49]. During scaling, it can be a viable option to use dry room area related key parameters, such as presented by Vogt et al. [49]. Depending on the location of the dry room, the energy demand is typically within a range of 0.85–0.975 kWh h^{-1} m^{-2} and 0.05–0.7 kg CO_2-eq h^{-1} m^{-2}.

The presented LCI generation and scaling approaches can be applied to most life cycle stages. However, the use phase of batteries requires different scaling approaches, for example, electrochemical models which were explained in the previous subsection. Additionally, learning rate or experience curves can be applied to estimate the future development of technical performance parameters [44]. While these have been applied in techno-economic assessments, the application of learning rates to generate LCI data for foreground systems is a relatively new concept.

12.4 Uncertainty Management

Prospective LCA of emerging technologies has been identified as a challenging area within the field of LCA due to the lack of empirical data available to perform assessments. This entails the need for assumptions to be made about future developments. The absence of empirical data, combined with the high degree of uncertainty in the future scenarios being evaluated, can lead to uncertainties in the results between studies performing a prospective LCA [48]. This can make it challenging for decision-makers to use the results of the assessment in a meaningful way. Due to such challenges, the management of uncertainty becomes a critical aspect in the prospective LCA of emerging technologies.

To address these challenges, it is important to have robust and transparent methods for uncertainty management in prospective LCA of emerging technologies. This will ensure that the results of the assessment are reliable and that decision-makers can have confidence in the results. Several methods have been proposed for uncertainty management in prospective LCA, including sensitivity analysis, scenario analysis, and Monte Carlo simulation [45]. These methods can be used to identify the key sources of uncertainty in the results and to assess their impact on the results of the assessment. In addition, several types of uncertainties exist, including parameter uncertainty, scenario uncertainty, and model uncertainty [23]. This section focuses on parameter and scenario uncertainty, which are the most found ones in prospective LCAs of emerging technologies.

Parameter uncertainty refers to the variability and unreliability of the input data used in an LCA study [29]. This type of uncertainty is prevalent in every type of product assessed using an LCA, but it is especially pronounced at emerging technologies. Input data can be uncertain due to a lack of information or due to variability in the data collected. There are several factors that can cause variability in the input data. Some of the most common sources of variability include data collection, data quality, model uncertainty, and measurement uncertainty. For example, data on energy consumption, emissions, or material use can be subject to measurement error, variability in production processes, or changes in the market energy mixes. To account for parameter uncertainty, LCA practitioners often use sensitivity analyses to examine how changes in input parameters affect the overall results of an LCA. The Monte Carlo method is another commonly used approach to account for parameter uncertainty, where the input data is modelled using probability distributions and then simulated multiple times to account for variability.

The uncertainty in LCA scenarios arises from the choices made in the modelling process, such as the assumptions made in the goal and scope phase or the upscaling calculations [45]. This type of uncertainty is especially prevalent in prospective LCAs of emerging technologies, where information is limited and there is a high degree of uncertainty about the future development of the technology [23]. For instance, when making assumptions about the development of the electricity grid in the background datasets, the results of the LCA can be highly uncertain due to the selection made. To mitigate scenario uncertainty, researchers frequently employ sensitivity analyses to investigate how changes in key assumptions or boundary conditions impact the overall results of the LCA [26]. Additionally, prospective LCAs can be used to explore extreme-case scenarios (or anticipatory LCAs) or to assess the robustness of the results under different boundary conditions [51].

Several studies have been conducted to address uncertainty in prospective LCAs, including Cooper and Gutowski's approach for selecting probability distributions

[7], Lacirignola et al.'s procedure for examining the robustness of global sensitivity analysis results [23], Marini and Blanc's method for identifying parameters that contribute to uncertainty using the Sobol indices [26], Ravikumar et al.'s statistical test for significant differences in LCA results (Ravikumar et. al. 2018), and Wender et al.'s development of anticipatory LCAs [51].

In conclusion, uncertainty management is a critical aspect of prospective LCA of emerging technologies. Applying the existing methods to document the uncertainties in the results of LCA will aid in wider acceptance of the results. Regardless of the choice of method used to mitigate uncertainty, considering uncertainty is essential to ensure the reliability and credibility of the results of a prospective LCA study. Failing to consider uncertainty can result in unreliable and misleading results, making it difficult to make informed decisions about the sustainability of emerging technologies.

12.5 Comparability

LCA has become a widely used method for evaluating the environmental impact of emerging technologies. However, comparability of results between studies can be challenging due to several factors, and they can be related to the aim of the LCA study, the functionality of the LCA, system boundaries, and specified life cycle impact assessment methodologies [45].

12.5.1 Aim of the Study

In prospective life cycle assessments, the aim of the study plays a crucial role in determining the comparability of results. The aim of the study can be generally categorised into (i) comparisons of technologies or (ii) identifications of hotspots, both of which are predominantly used in retrospective assessments. Unlike retrospective assessments, prospective assessments require differentiation between comparisons at different technology readiness levels (TRLs), such as laboratory-scale compared to industrial-scale production, or comparisons at a similar TRL but different maturity readiness level (MRL), such as laboratory-produced Li-ion battery cells compared to laboratory-produced solid-state battery cells. Assessing technologies at different TRLs can prove to be the most challenging task and often result in less accurate comparisons. To improve the comparability and interpretability of results, it is essential to communicate the readiness levels and production scale of the technology as part of the prospective assessment and clearly state them in the study [15]. The use of various upscaling methods, as discussed in Sect. 12.2, can also aid in comparing technologies with different TRLs.

The aim of the LCA study also plays a crucial factor in determining the comparability of results between studies. For example, a study that aims to compare the environmental impact of different materials used in a product will have a different system boundary than a study that aims to compare the life cycle impact of different production processes for a specific material. The choice of system boundary affects the results of the study and, therefore, the comparability of results between studies with different aims [6].

Finally, the goal of the LCA study can also influence the functional unit, which is a crucial aspect of the LCA methodology. The functional unit is the unit of measurement that allows for the comparison of different technologies or products. The choice of functional unit must be clearly defined and consistent between studies for results to be comparable [46].

12.5.2 Functionality

The functional unit is a crucial component in conducting an LCA as it quantifies the performance of a product system. The challenge in defining the functional unit lies in the fact that the future function of emerging technologies may not be fully known. Systems at an early stage are susceptible to change, and additional functionality may develop as the product matures. This was evident in a study by Hischier et al. who found that the main factor for variations in the LCA outcome depends on a well-defined functional unit [20].

To overcome this challenge, it is necessary to either define ranges for the functional unit or to consider multiple functional units. A framework described by Simon et al. [41] that includes the functional analysis of a lab-scale process can be useful in defining the system functions. The authors must also be aware of the issues concerning the definition of the functional unit and should investigate the effects of different functional units to analyse the full function along the life cycle. However, it is important to note that defining the functional unit can be challenging, especially when the application of the product is not yet apparent. This can lead to inaccurate results due to the uncertainty in upscaling and a potential change or decrease in functionality.

For example, different functional units, such as one battery pack or cell, 1 kilogram of battery, 1 kilowatt hour of storage capacity, or 1 kilometre driven, may be used to evaluate variations when assessing the environmental impact of electric vehicle batteries [28]. In this case, normalising the LCAs based on a common functional unit, such as 1 watt hour of capacity, can help facilitate comparison of the assessment results of different emerging battery technologies. By including multiple functional units in the assessment and analysing the sensitivity of the functional unit choice, a more in-depth understanding of the environmental performance can be obtained.

12.5.3 System Boundary

The system boundary is a critical factor in the comparability of results between LCA studies. The system boundary determines the extent of the life cycle to be included in the study, and the choice of system boundary can have a significant impact on the results of the study. For example, a study with a narrow system boundary may not include all environmental impacts associated with a technology or product, while a study with a broad system boundary may include environmental impacts that are not related to the technology or product [6].

The choice of system boundary can also impact the level of detail and accuracy of the results. For example, a narrow system boundary might provide a detailed analysis of specific processes within the technology but may not fully capture the overall environmental impact of the technology. On the other hand, a broad system boundary might provide a comprehensive view of the technology but may not provide the level of detail necessary to evaluate specific processes or impacts. Therefore, it is essential to indicate the extent of inclusion or exclusion of the processes in the system boundary. Studies comparing similar systems should attempt to include the necessary processes required for a fair comparison and evaluation with existing technologies.

12.5.4 Life Cycle Impact Assessment

The choice of life cycle impact assessment methodology is another key factor in the comparability of results between LCA studies. Different methodologies have different strengths and weaknesses, and the choice of methodology can have a significant impact on the results of the study. For example, some methodologies may be more suitable for assessing the impact of emerging technologies, while others may be better suited for comparing the impact of different production processes [45].

In the impact assessment phase, the methodologies used to calculate the impacts can also vary, leading to different results. Some methodologies have additional regionalised impact categories, while others use global impact categories, which can result in significant differences in the results. Therefore, an appropriate choice of methodology representing the impacts for the system is necessary [33]. In addition, to improve comparability with previous and upcoming studies, it would be beneficial to include as many impact categories and methodologies as possible.

Using outdated LCIA methods can lead to incorrect conclusions as emerging technologies can cause unknown impacts in the future that are not captured by existing LCIA categories. Additionally, different characterisation factors are available for various impact categories, and it is suggested to perform the LCA with different characterisation factors [20].

Data availability is often limited in early-design-stage assessments, making it difficult to determine all impact categories [11]. Moreover, the potential environmental impacts of new substances may be overlooked, due to missing LCIA categories, insufficient LCI data, or a lack of knowledge about new impacts. Therefore, there is a need for using a standardised LCIA method when performing prospective LCA of emerging technologies.

12.6 Conclusion and Outlook

This section discussed the definition of prospective assessment as well as the use of its results to inform technology developers, policymakers, and manufacturers. The section also highlighted that there is presently no standard method for conducting a prospective assessment. Several challenges related to data availability, scaling issues, uncertainty, and comparability were identified and discussed. These challenges are highly interconnected and largely linked to the availability of data and choice of upscaling methods, leading to increased uncertainties and difficulty to compare results with existing technologies.

The use of prospective assessments for emerging technologies, such as electric vehicle batteries, poses significant challenges that must be transparently reported and understood by all stakeholders. The lack of transparency in LCA results, especially in a prospective context, requires clear descriptions and justifications of all assumptions made during the assessment process. The results of prospective assessments can provide valuable insights in identifying the environmental impacts of emerging technologies, and results can be used to envisage mitigation strategies.

However, it is important to note that prospective LCAs do not predict the future but rather explore a range of possible scenarios that define the space in which the technology may operate. This allows for a fair comparison of emerging technologies with incumbent technologies and the verification of design options that could steer the technology towards a preferred future state.

In conclusion, the use of prospective LCA in evaluating emerging technologies has the potential to provide valuable insights into the future development of these technologies. By exploring various scenarios and implementing systematic uncertainty management, prospective LCA can support decision-makers in steering the technology towards a preferred future state. It is crucial that the results of these assessments are transparently reported and understood by all stakeholders, including technology developers, policymakers, industry decision-makers, and society, to ensure their effective use in decision-making.

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Chapter 13
Life Cycle Assessment of Emerging Battery Systems

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Contents

The scale of battery capacity that may need to be produced and subsequently managed to enable compliance with regional clean energy use and emissions reductions goals highlights the importance of minimizing the life cycle environmental impact of battery technologies. Here, the life cycle of a battery technology encompasses the material and energy inputs and outputs associated with materials extraction, manufacturing, use, and end-of-life handling processes. Each battery technology requires different processes for each of these stages. In addition, improvements and changes in these processes are continually being developed and implemented. Accounting for the material and energy inputs and outputs associated with a product's life cycle and translating the results to material resource requirements and environmental impacts are encompassed in life cycle assessment (LCA).

Conducting an LCA of a given product requires data that tracks the required materials and energy inputs and outputs associated with the production, use, and end-of-life management processes for that product. These data consist of both direct inputs to and outputs from processes directly involving the product itself, as well as inputs and outputs associated with the systems that provide those inputs. These

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datasets are developed from multiple data sources including but not limited to material supplier data, manufacturer data, trade data, academic literature, and regional government databases. Datasets for a particular product can be updated as supply chains and product designs are changed, but due to the lengthy time requirement and institutional barriers (i.e., manufacturers protecting their proprietary data) required to produce LCA data, these may not always keep up with emerging developments.

Certain battery technologies have relatively mature LCA datasets and subsequently a robust literature of LCAs that characterize them. For example, batteries that have been deployed at a commercial scale for a long time, such as lead-acid, nickel-metal hydride, and variations on lithium-ion batteries, have been the subject of many LCA studies due to their ubiquity in consumer electronics and, more recently, electric vehicles and electric grid-tied energy storage [6, 14, 17, 35, 41, 43]. Improvements are continually being made in terms of reducing the environmental impacts of their product supply chain, in-use performance, and end-of-life handling procedures for some of these chemistries. Additionally, technological improvements in battery performance are being assessed and reflected in updated LCAs that build on the results of previous studies.

Newer battery technologies, as discussed in Parts V, do not yet enjoy the benefit of a robust literature on their environmental impacts due to their relative immaturity and/or lack of scale of deployment, combined with the time and effort required to compose datasets for these technologies that are sufficient to perform informative LCAs. However, prospective LCAs for some of these battery technologies have been conducted, whether for full battery packs or installations or for materials and components that are essential to these systems (i.e., anode materials). This section will summarize the literature of prospective LCAs for presently emerging battery technologies and comment on the needs for the scope of future assessments to improve our understanding of these technologies such that these can be compared on a consistent basis with incumbent battery technologies.

13.1 Closed Battery Systems

A closed battery system in this discussion refers to a system where all the fundamental components of the battery – the anode, cathode, and electrolyte – are contained within the same physical space and no outflow of matter occurs. This contrasts with an open system, which will be the focus of Sect. 13.2. For closed systems, emerging battery technologies of interest for improving performance characteristics (e.g., higher energy density) over incumbent technologies consist of new battery chemistries based on novel lithium chemistries enabled using metal anodes or solid electrolytes or chemistries based on different anode materials such as sodium, magnesium, aluminum, potassium, and calcium.

13.1.1 Solid-State Lithium Batteries

An emerging development in lithium-based battery chemistries is the use of solid-state electrolytes instead of the typical liquid- or gel-based electrolytes used in incumbent lithium-ion batteries.

A recent LCA of a solid-state lithium-ion battery performed by Zhang et al. [45] focused on characterizing the environmental impacts of producing a small-scale coin cell with a solid-state lithium-aluminum-titanium-phosphate (LATP) chemistry and comparing its impacts to a cell with a conventional liquid-based electrolyte for lithium-ion batteries. That study demonstrated that production of one solid-state LATP cell in the CR2032 form factor required higher primary energy inputs than a conventional lithium-ion cell of the same form factor (2.6 MJ vs. 1.1 MJ) and produced roughly double the greenhouse gas emissions (0.1 kg CO_2e vs. 0.05 kg CO_2e). This was primarily driven by the energy intensity of producing the inorganic solid electrolyte. Efforts to reduce the required thickness of the electrolyte layer were found to reduce all the environmental impact indicators considered in the study significantly, highlighting the need for manufacturing improvements for this technology. A previous LCA for a solid-state lithium battery performed by Troy et al. [32] focused on the production of a pouch cell based on a lithium-lanthanum-zirconium-oxide (LLZO) chemistry. Troy et al. did not compare the environmental impact results with incumbent battery technologies due to the relative immaturity of the solid-state cell with commercial technologies at the time, but their results show that on-site electricity use for cell production is the largest contributor to impacts. Depending on where manufacturing occurs, the environmental impacts from electricity use can vary dramatically.

Focusing on the pack level, Keshavarzmohammadian et al. [18] conducted an LCA for a solid-state lithium-ion battery pack with a pyrite cathode (iron sulfide) for application in electric vehicles. The study scope more closely mimics the production processes that would be used to produce real-world battery systems. The study found that cumulative energy demand and contributions to greenhouse gas emissions from the pyrite-based solid-state pack are on the same order of magnitude as that of conventional lithium-ion batteries. The largest contribution toward these impacts was again the energy use for cell production, more specifically the operation of clean dry rooms and the production of cathode paste.

In perhaps the earliest LCA study of solid-state batteries, Lastoskie and Dai [19] performed a comparative LCA to assess the environmental impacts of producing a solid-state cell relative to that of a laminated cell with a gel electrolyte for electric vehicle applications. They examined various cell chemistries for each type and scaled the results into battery packs and vehicle assemblies. The study demonstrated that, compared to laminated cell chemistries, solid-state batteries had lower environmental impacts across multiple indicators, depending on the chemistry chosen. Specifically, solid-state lithium vanadium oxide electrolytes exhibited the lowest environmental impacts across all the environmental impact indicators considered. The solid-state batteries specifically provided benefits during the use phase of the electric vehicles due to higher energy density that reduced energy consumption during vehicle operation. Cell chemistry variations had a significant effect on production phase impacts.

Overall, present literature on LCAs of solid-state battery technology shows that there is still much uncertainty regarding the existence or extent of environmental benefits from using solid-state batteries compared to conventional lithium-ion batteries. The environmental impacts of these systems are generally found to be similar to that of conventional lithium-ion batteries but, depending on the scope of the assessment and the specific chemistries used, can be higher or lower than conventional batteries. In designing future solid-state battery systems, care must be taken to identify and avoid unintended consequences that contribute to high environmental impacts.

13.1.2 Metal Anode-Based Lithium Batteries

Another emerging development for batteries based on lithium is the use of lithium metal anodes instead of traditional graphite-based anodes. Lithium metal anodes potentially provide the benefit of increased energy and power densities compared to batteries with conventional anodes but are presently subject to multiple material stability issues during use [37]. Nonetheless, prospective LCAs of battery systems or components containing lithium metal anodes have been conducted. Berg and Zackrisson [8] conducted a cradle-to-grave LCA of metal anodes for lithium battery packs used in electric vehicles using computer simulations of the battery cells as opposed to physical fabrication, focusing on greenhouse gas emissions from a life cycle perspective. They showed that lithium iron phosphate (LFP) and nickel manganese cobalt (NMC) batteries based on lithium metal anodes exhibit lower life cycle greenhouse gas emissions compared to their conventional counterparts used in Nissan Leaf and Tesla Model S vehicles. Emissions reductions for the Nissan Leaf ranged from 50% to 58% of the original pack, while that for the Tesla Model S ranged from 20% to 39% of that of the original pack. This study shows the potential environmental benefits of batteries with lithium metal anodes, but these results require validation by assessment of physically produced cells.

Vandepaer et al. [34] performed a cradle-to-grave LCA of LFP batteries comparing the use of lithium metal anodes (lithium metal polymer or LMP) versus traditional graphite anodes in a stationary grid-connected application, differentiating between systems deployed at the distributed vs. centralized scale. This study showed that LMP batteries exhibited lower contributions to detrimental human health impacts (~18% reduction) and climate change (~23% reduction) but similar contributions to ecosystem damage and resource use compared to conventional graphite anode batteries, for both the centralized and distributed systems. These results are strongly driven by the assumptions for the sourcing and production of battery materials – aluminum from China produced using coal power in the graphite anodes versus aluminum sourced from Canada using hydropower in the metal anodes.

Therefore, the study highlights the key factor of emissions generated from metal production and their sensitivity to the energy source used for production.

Wu and Kong [40] also performed a comparative cradle-to-gate LCA of lithium-ion battery production with three different anode materials: lithium metal, silicon nanowire, and traditional graphite anodes, all used in batteries with a common chemistry (NCM). When focusing on the production of a given mass of anode material alone, this study found that the conventional anode material exhibited the lowest contributions toward six of eight midpoint environmental indicators examined, with lithium metal anodes exhibiting the lowest contributions toward metal depletion potential and marine eutrophication potential. The silicon nanowire anode exhibited the highest impacts across all categories. In translating these results to the production of full battery systems of the same energy capacity (1 kWh), however, the batteries made with lithium metal anodes exhibited the lowest contributions toward all eight environmental impact indicators considered in the study, with the most significant benefits occurring for marine eutrophication potential. This results from differences in the specific energy of the different anodes: anodes with higher specific energy will require a lower mass of anode to be produced to enable a battery with a given energy capacity. Lithium metal anodes have specific capacities of roughly ten times that of conventional graphite anodes but do not have ten times the environmental impacts; therefore, full battery systems produced with lithium metal anodes exhibited the lowest environmental impacts. The study demonstrated, however, that these benefits occur when the cycle life of the lithium metal-based battery is similar to that of batteries with conventional anodes; lower cycle life will reduce or eliminate the cradle-to-gate environmental benefits of lithium metal batteries.

Padashbarmchi et al. [23] performed a comparative, cradle-to-grave LCA of the lithium-ion batteries produced using three different metal oxide nanoparticles as the anode active material, iron oxide, cobalt oxide, and copper oxide, and compared these against a battery with a traditional graphite anode. The study presented environmental impacts using an aggregated metric of Eco-indicator points from the *Eco-indicator99* framework. Based on this metric, batteries produced with two of the metal oxide-based anode materials (iron oxide and cobalt oxide) exhibited lower environmental impact scores than batteries with traditional graphite anodes, with batteries based on copper oxide obtaining higher environmental impact scores. For individual endpoint indicators, all three metal oxide anodes showed lower resource depletion impacts than the traditional graphite anode, while copper oxide exhibited a very high contribution to human health impacts that drove its total indicator score. This study shows that metal anodes have the potential to have a lower impact than conventional anode materials depending on the materials chosen.

The present literature on LCAs of metal anode technology for lithium-ion batteries shows that wider use of this technology have the potential to reduce environmental impacts compared to conventional anode batteries in both mobile and stationary applications.

13.1.3 Non-lithium Chemistries

Concerns regarding the criticality and geopolitics of access to lithium resources have also driven interest in developing and scaling battery chemistries that depend on elements other than lithium for their active anode element. Specifically, other alkali metals (sodium, potassium), alkaline earth metals (magnesium, calcium), and metals such as aluminum are of interest for lithium alternatives, described in Part V, as well as organic materials.

Peters et al. [24] performed the first-of-its-kind LCA of the production (cradle-to-gate) of a sodium-ion battery pack and compared its impacts using six midpoint environmental indicators with those for different lithium-ion battery packs. They also explored the sensitivity of these impacts to cycle life, round-trip efficiency, and material substitution of anode hard carbon precursors. They found that with a cycle life of 2000 cycles, sodium-ion environmental impacts were lower than lithium-ion batteries on two indicators (freshwater eutrophication and human toxicity), within the range of lithium-ion batteries for three indicators (global warming, fossil depletion, and terrestrial acidification), and higher impacts than lithium-ion batteries for marine eutrophication potential. Battery cycle life was found to be a major factor in comparing sodium-ion battery environmental impacts versus lithium-ion batteries: a drop to a cycle life of 1000 caused sodium-ion batteries to generally perform worse than lithium-ion across indicators, while increases to 3000 or higher led to lower impacts than most lithium-ion battery types. This study also highlights the potential for improvement in these impacts from material selection for the anode and cathode as well as its precursors and production method.

Jasper et al. [16] included a sodium-ion battery in a comparative, cradle-to-grave life cycle assessment of a home battery system operated to increase the use of otherwise curtailed solar electricity generation, where it was compared against three lithium-ion chemistries based on a functional unit of 1 kWh of electricity delivered. A sodium nickel magnesium manganese titanium oxide cathode and a hard carbon anode were selected to represent the sodium-ion battery. For the full life cycle of these systems, sodium-ion batteries were found to have higher contributions to global warming potential, resource depletion, and freshwater toxicity than the three lithium-ion battery systems. These results were driven by the relatively lower energy density of the sodium-ion battery compared to the lithium-ion batteries at the time of publishing, which requires a larger material mass to be produced to deliver 1 kWh of electricity. Since this larger material mass increases the scale of all life cycle processes, their emissions also increased. It is important to note that between the time of the study [16] and that of the initial study by Peters et al. [24], the energy density of lithium-ion battery technology has improved, which explains the difference between the results of these studies. Another recent study by Carvalho et al. [10] that conducted a comparative cradle-to-gate LCA of lithium-ion and sodium-ion batteries also found that producing a sodium-ion battery contributed more to climate change and resource use than lithium-ion batteries on a per-unit energy capacity basis, also due to its lower energy density.

For mobile applications, Marmiroli et al. [20] performed a cradle-to-grave LCA of a sodium-nickel-chloride battery used in commercial light-duty vehicles, which was then compared on a consistent basis with the results of an LCA of an NMC lithium-ion battery and that for a diesel vehicle used in the same application by Accardo et al. [1]. These studies found that per kWh of battery capacity across their entire life cycle, the sodium battery contributed the most toward 7 of the 12 midpoint indicators with their assumed production location, increasing to 8 of 12 indicators when the batteries are assumed to be produced in Europe. Generally, the impacts from the sodium battery were higher than that of the NMC lithium-ion battery.

Present literature on sodium and sodium-ion batteries initially showed promise for this technology to offer a lower environmental impact option for meeting the battery capacity needs of the transition to a clean energy system. Improvements in the energy density of lithium-ion batteries, however, have reduced this prospect with many studies showing higher life cycle environmental impacts for sodium-ion batteries. Depending on the criticality of lithium as battery demand grows over time, sodium-ion batteries may still offer an important alternative in some applications.

Beyond sodium-based batteries, LCAs of closed system batteries based on other alternatives to lithium are relatively sparse. Potassium and calcium batteries have been discussed from materials performance standpoints [2, 5, 12, 25, 26] but have not yet been the subject of a formal life cycle assessment. Aluminum and magnesium batteries have been the subject of some initial assessments.

Delgado et al. [28] performed a comparative, cradle-to-grave LCA of an aluminum-ion and a lithium-ion battery (NMC chemistry) cell, focusing on their contributions to global warming potential on per-cell and per-energy capacity bases. This study found that on a per-cell basis, the aluminum-ion battery contributed 30% lower greenhouse gas emissions than lithium-ion but on a per-energy capacity basis contributed as much as 12 times the greenhouse gas emissions of the lithium-ion battery. These results were driven by the significantly lower energy density of the aluminum-ion battery, resulting in much more material mass required to achieve a given energy capacity.

Melzack et al. [21] conducted a cradle-to-gate LCA of an aqueous aluminum-ion battery and compared these results to those of supercapacitors on a per-power capacity basis. This application better suits the aluminum-ion battery which has high specific power but low energy density. This study found that the aluminum-ion battery exhibited lower or similar impacts than graphene and activated carbon-based supercapacitors on multiple environmental impact indicators, including but not limited to global warming potential, terrestrial eutrophication, and ozone formation. The relatively early development stage of the aluminum-ion battery implies the potential for improvements to its environmental performance. In applications requiring high specific power, it is more competitive with incumbent technologies.

Montenegro et al. [22] conducted a cradle-to-gate LCA of a magnesium-sulfur (MgS) battery cell with three different cell construction designs and compared it to those for lithium-ion batteries (LFP, NMC, and lithium-sulfur or LiS). The cell construction design for the MgS battery was found to be a major driving factor in its environmental impact profile, with designs that optimize the cell separator thickness and pouch housing reducing contributions to global warming potential and fossil fuel depletion to be similar to or lower than that of the lithium-ion batteries. The optimized cell design for the MgS battery did exhibit higher material depletion and ozone depletion potential than the initial design, but these impacts fell within the range of values spanned by lithium-ion batteries. This study highlights the importance of fundamental cell design in driving larger-scale environmental impacts and competitiveness of the MgS battery. This work was expanded in a study by Bautista et al. [7], which takes the optimized cell design from Montenegro et al. [22] and expands the scope of the LCA to a full modeled battery pack, including the use phase of different battery applications on the electric grid, and compares the results against three lithium-ion battery chemistries. This study found that the modeled MgS battery still contributed environmental impacts that were similar to or lower than the range spanned by lithium-ion batteries across all of the environmental impact indicators included and across the different grid applications. The environmental impacts of the MgS battery were found to be most sensitive to the assumption for the round-trip efficiency of the system in all applications.

The literature on magnesium-based batteries shows promise for this technology in competing against lithium-ion batteries from an environmental impact standpoint, but this potential needs to be verified by LCAs based on physically produced packs and tracked as production methods for this technology scales up to maturity.

Organic alternatives for battery materials are also of interest due to their potential benefits for reduced environmental impact and resource depletion potential. A study by Zhang et al. [46] performed a cradle-to-gate LCA of a fully organic closed system battery based on organic polymers. This study did not perform a direct comparison to other battery technologies but rather focused on identifying hotspots and major contributors to environmental impacts to inform future needs for changes in production processes and material selection. This study found that the dominant contributor to environmental impacts was the production of the organic cathode backbone due to the large number of steps involved requiring significant quantities of solvents. For future improvements, optimizing the cathode backbone production processes to reduce or eliminate the need for solvents will be important for reducing the environmental impacts of this battery at scale.

13.2 Open Battery Systems

An open battery system refers to one where the fundamental components of the battery are not physically contained within the same space and the flow of matter (e.g., electrolyte and oxidant) occurs between them. Open systems have the potential to exhibit high energy density (i.e., in metal-air batteries) or ease of decommissioning due to the partially deconstructed configuration of these systems. For open systems, emerging battery technologies of interest for improved performance, safety, or environmental impact profiles are different chemistries of redox flow batteries including organic-based systems and metal-air batteries.

13.2.1 Inorganic Flow Batteries

Many flow battery chemistries exist at different stages of technological and commercial maturity; therefore, relatively few of them have been the subject of LCA studies. The earliest flow battery to reach commercial scale and presently the most mature is the vanadium redox flow battery (VRFB), which has been the subject of multiple LCAs. The first LCA including a vanadium redox flow battery was conducted by Rydh [27] in 1999, which compared the life cycle environmental impact of the VRFB with a lead-acid battery and found that the VRFB exhibited lower environmental impact (using an aggregated environmental impact score) than lead-acid batteries.

A more recent LCA was conducted by Weber et al. [38], which conducted a cradle-to-cradle LCA of a VRFB based on a more detailed, up-to-date dataset of this technology compared to the original inventory from Rydh [27] that was used in multiple studies and compared the results to a lithium titanate-based LFP battery. This study demonstrated that for the VRFB, components related to the electrolyte were the strongest drivers of multiple environmental impacts including contributions to global warming potential, due to the large weight fraction of the electrolyte and related components and the environmental impact of vanadium production. When compared to the lithium-ion battery, the VRFB exhibited lower or similar environmental impacts for three of the four environmental impact indicators (global warming, human toxicity, abiotic depletion) when electricity inputs to battery life cycle processes were assumed to come from clean sources such as wind and solar. When electricity inputs are fossil-based, VRFB impacts are higher than lithium-ion due to its lower round-trip efficiency, requiring more fossil-based generation (and subsequent environmental impacts) for each unit of electricity delivered by the battery.

Additional LCA studies have also focused on or included the VRFB. A study by AlShafi and Bicer [4] conducted a comparative LCA between the VRFB, compressed air energy storage, and molten salt thermal storage based on per kWh of electricity delivered from solar energy. Of these systems, the VRFB was found to contribute the most toward all five of the environmental impact indicators considered, driven by the dominance of copper in the system and the environmental impacts of solar PV. A study by da Silva Lima et al. [30] conducted a comparative, cradle-to-grave LCA of a VRFB and an NMC-based lithium-ion battery on a per kWh of renewable electricity delivered basis. Across their whole life cycle, the environmental impacts of the VRFB were found to be similar or lower than that of the lithium-ion battery when both were constructed with virgin materials but generally lower than that of lithium-ion batteries when 50% of the VRFB electrolyte is recycled. This study also highlights the prominence of the VRFB electrolyte in driving environmental impacts due to its large mass fraction in the overall system and energy-intensive production processes.

Recent LCAs have also started to assess new flow battery chemistries that have only recently reached commercial scale. A study by He et al. [13] conducted a comparative cradle-to-gate LCA of three flow battery chemistries: the VRFB, the zinc-bromide flow battery (ZBFB), and the iron flow battery (IFB), based on up-to-date manufacturer data for commercial systems. This was the first study to conduct LCAs of the ZBFB and IFB systems, despite these systems already being deployed at a small commercial scale. This study found that of these three systems, the IFB generally exhibited the lowest environmental impacts in six of eight midpoint impact indicators due to its use of relatively benign materials, the exception being freshwater ecotoxicity and ozone depletion potential due to materials used in the cell membranes. The ZBFB generally exhibited the second largest contribution to environmental impacts but contributed the most to abiotic resource depletion. The VRFB exhibited the highest environmental impacts on seven of the eight impact indicators included in the study, strongly driven in five of those impact categories by the production of the VRFB electrolyte based on vanadium pentoxide. The VRFB results, however, were shown to be highly sensitive to the assumed production process of the vanadium pentoxide electrolyte, with lower emissions processes potentially reducing environmental impacts in four of the eight categories to be competitive with the IFB. This study highlights the importance of not only material selection but also reducing the emissions intensity of production processes for key materials that are required for flow battery operation. The results of this study were used in a further study by Tian et al. [31] that assessed how the emissions saved from the deployment of the three different flow batteries on a renewable electric grid scale versus the emissions contributed from producing these batteries as the installed capacity of these batteries on the grid increases. Extending the themes from the study by He et al. [13], the IFB enabled the largest capacity of batteries to be installed while ensuring that the emissions benefit outweighed battery production emissions due to the low greenhouse gas emissions intensity of IFB production. Conversely, the VRFB had a much lower ceiling on how much capacity can be installed before battery production emissions overtook the emissions saved on the grid. Selecting lower emissions intensity production methods for vanadium pentoxide increased this capacity ceiling, however.

13.2.2 Organic Flow Batteries

Flow battery systems with organic electrolytes are also an emerging technology with the possibility to reduce the potential environmental impacts and resource depletion effects associated with inorganic electrolytes [9, 39]. Organic flow batteries are relatively new and as of this writing (mid-2022) are just starting to be commercialized. Therefore, LCAs of this class of technologies are relatively sparse in the research literature, but one very recent (published 2022) study focused on performing LCAs of flow batteries with organic electrolytes.

A study by Di Florio et al. [11] performed a comparative, cradle-to-gate LCA of a semi-organic flow battery using anthraquinone disulfonic acid and hydrobromic acid as electrolyte materials and compared the impact results against a VRFB on a per 1 MWh of electricity delivered basis for renewable energy shifting. This study found that the semi-organic flow battery exhibited lower environmental impacts on 8 of the 11 categories of environmental impacts considered. The three exceptions were stratospheric ozone depletion, mineral resource scarcity, and cumulative energy demand; however, the semi-organic flow battery and the VRFB exhibited similar contributions in these cases, and their differences were found to be within the band of uncertainty for the analysis. These results were largely driven by the lower contributions to environmental impacts from electrolyte production, highlighting the benefit of the semi-organic electrolyte. However, the semi-organic electrolyte was assessed for two different production pathways, air oxidation and dichromate oxidation, and the beneficial results apply to the air oxidation pathway, with the dichromate oxidation pathway exhibiting higher environmental impacts for the electrolyte production.

13.2.3 Metal-Air Batteries

Metal-air batteries are an emerging technology of interest due to their advantages over conventional lithium-ion batteries in energy density. By using ambient air as the external cathode for the system, these systems can weigh significantly less than closed system batteries. From an LCA standpoint, lithium-air batteries have been the primary focus of study due to their energy density.

Iturrondobeitia et al. [15] performed a cradle-to-gate LCA of seven different chemistries of lithium-oxygen batteries. The study results were compared against lithium-ion, lithium-sulfur, and sodium-ion batteries when used in electric vehicles on a per-unit energy capacity basis. This study found that compared to the lowest emission closed system battery (lithium-ion), five of the seven lithium-air chemistries produced lower greenhouse gas emissions. The two exceptions were the cobalt carbonate-based and gold/nickel-based lithium-air batteries, which produced 208% and 175% of the greenhouse gas emissions produced by the lithium-ion battery, respectively, largely driven by emissions from the production of the battery cathode. For the average of the seven lithium-air chemistries across all the 18 environmental impact indicators considered, lithium-air batteries exhibited improved environmental impacts compared to any of the closed system batteries in 10 out of 18 environmental impact indicators. Notably, lithium-air batteries required significantly larger land use than the closed system batteries, 17 times more than the lithium-sulfur and 7.6 times more than the lithium-ion battery, but the study did not explicitly elaborate on the driver of this result. Certain lithium-ion chemistries, such as the battery based on porous carbon, exhibited lower environmental impacts than the lowest impact closed system battery on 16 of the 18 environmental impact indicators. This study highlights how, depending on the chemistry, lithium-air batteries may or may not provide environmental benefits over closed system batteries even with their higher energy density.

Uludag and Yay [33] conducted an LCA of a lithium-air battery based on a tetraethylene glycol dimethyl ether and lithium hexaphosphate electrolyte, produced with and without electrolyte stabilizers. The study results were compared with closed system batteries for contributions to greenhouse gas emissions. This study found that the lithium-air batteries on average exhibited similar greenhouse gas emissions when produced without stabilizers or when produced with aluminum oxide stabilizers, but markedly lower greenhouse gas emissions when produced with silicon dioxide stabilizers. The configuration with silicon dioxide stabilizers enabled a higher energy density, almost twice that of the configuration when produced with aluminum oxide stabilizers and 43% more than the configuration without stabilizers. This caused the silicon dioxide configuration to exhibit the lowest environmental impacts across all four of the environmental impact indicators considered. When compared to closed system lithium-ion batteries, the silicon dioxide configuration exhibited only 61% of the greenhouse gas emissions of the lowest emission lithium-ion battery (lithium manganese oxide in this study). This study further highlights the importance of optimizing battery production pathways to realize the environmental benefits of lithium-air batteries over incumbent technologies.

Wang et al. [36] performed a comparative, cradle-to-grave LCA of a lithium-oxygen battery and a closed system NMC lithium-ion battery when used in electric vehicle applications. Production of the negative electrode was found to be a major or driving contributor to 11 of the 13 environmental impact indicators in the production phase of the system, with the exceptions being global warming potential and fossil depletion potential, where cell assembly is the major contributor. The impacts from the negative electrode are driven by the impacts associated with the production and use of copper, whereas impacts from cell assembly are driven by the production and use of carbon nanotubes. From the cradle-to-grave perspective, the lithium-oxygen battery exhibits lower environmental impacts in 9 of the 13 environmental impact indicators, with the exceptions being terrestrial ecotoxicity, ozone depletion, human toxicity, and fossil depletion.

Zackrisson et al. [44] conducted the initial LCA of lithium-air batteries, applying a cradle-to-grave approach to assessing a prototype lithium-air battery intended for use in an electric vehicle. At the time of this study [44], environmental impacts contributed by the lithium-air battery were dominated by the production phase of the system. Impacts from the use of copper dominated impacts on ecotoxicity, human toxicity (cancer and non-cancer), and abiotic depletion, while emissions from electricity use dominated contributions to global warming potential. This initial study projected that as lithium-air battery technology develops, the use phase will come to represent the majority of environmental impacts.

Metal-air batteries based on metals other than lithium have not been investigated extensively with LCA tools. Yang and Knickle [42] conducted a preliminary analysis of an aluminum-air battery in 2002, well before the large-scale commercialization of electric vehicles, and focused on life cycle cost instead of environmental impacts. From an environmental standpoint, Santos et al. [29] performed a cradle-to-gate LCA of a zinc-air battery based on the laboratory-scale fabrication of the cell. A comparison of the zinc-air environmental impacts to incumbent technologies was not provided due to the use of a laboratory-scale production process; this study highlighted major contributors to the environmental impacts of this technology. This study found that cathode production was the largest contributor to 12 out of 14 environmental impact indicators, the two exceptions being non-cancer human toxicity and mineral/fossil/renewable resource depletion – where the zinc anode was the largest or dominant contributor. From a cost standpoint, this study also found that the zinc-air battery exhibited the lowest costs compared to incumbent battery technologies on a per-power capacity basis (kW) but one of the higher costs on a per-energy capacity basis.

Lithium-air technologies potentially offer promising environmental impact reduction benefits compared to incumbent battery technologies, but the careful configuration of material selection and production pathways is required to realize these benefits. Due to the relatively immature state of metal-air technologies, repeating LCAs for these batteries if they achieve scale will be required. Knowledge of the environmental impacts of metal-air batteries using metals other than lithium is presently too sparse in the literature to estimate their potential for providing reduced environmental impacts. Additionally, in real-world operation, certain metal-air batteries are sensitive to air purity; substances such as water vapor in the air, for example, can degrade and damage such systems [3].

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Chapter 14
Techno-economics Analysis on Sodium-Ion Batteries: Overview and Prospective

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Contents

14.1 Sodium-Ion Battery Basic Raw Materials

The total global battery demand is expected to reach nearly 1000 GWh per year by 2025 and exceed 2600 GWh by 2030 [1]. The expandability of lithium-ion batteries (LIBs) is one of the options; however, with the increasing shortage of lithium minerals and their uneven distribution around the world [2], the long-term development of LIBs could be constrained. In fact, the raw material demand driven by battery applications is estimated to experience unprecedented growth in the coming years. In detail, four battery metals are impacted the most by this growth towards 2030: lithium by a factor of 6, cobalt by a factor of 2, class 1 nickel by a factor of 24, and manganese by 1.2 [1].

In this context, sodium-ion battery (SIB) might become an important alternative considering its abundant resources, high cost-effectiveness, and high safety.

The early SIB development took place in parallel with the LIB development in the 1970s/1980s. Subsequently, their development slowed down considerably due to the higher energy density lithium-ion chemistry in the 1990s/2000s [3].

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On the other hand, due to availability and price issues of Li-ion basic raw materials, related to the fast increase of demand from mobility, mobile electronics, and stationary applications confronted with limited availability of the supply side [4, 5], recently, the studies of sodium-ion batteries have rapidly become highly topical, as evidenced by the sharp increase in the number of research papers.

SIBs have the most similarities with LIBs in terms of working principle, typical electrode materials, and electrolyte formulations. Moreover, SIBs in principle can use the same technologies of LIB manufacturing lines, reducing development costs and timescales [6]. SIBs have the same working principle as LIBs, with the difference that the charge transfer relies on sodium ions instead of lithium ions and electrode RedOx reactions involve Na instead of Li. Both electrodes are deposited on metallic current collectors, immersed in a liquid electrolyte allowing for mobility of ions between electrodes, and separated by electrically non-conductive, porous (to allow ion mobility) layer preventing internal short circuit [3].

Moreover, sodium-ion chemistry allows to use aluminium, which is inactive in terms of reacting with sodium, for both anode and cathode current collectors, substituting in this way copper otherwise used as anode current collector in LIBs [2]. Therefore, changing the current collector from copper to aluminium cannot only greatly reduce the cost of the cell but also addresses the over-discharge issue, especially in organic solutions, and decreases the battery weight. According to [7], the cost shares of the current collector foils are 11.6% for copper and 2.7% for aluminium in terms of the total cost of a lithium-ion cell. Replacing the copper foil with an aluminium foil in a SIB would result in a cell material cost reduction of about 9%, with a corresponding battery cost reduction of about 3%. The exchange would consequently result in a 55% mass reduction but also a 50% volume increase relative to the exchanged foil.

On the other hand, since commercial graphite cannot be directly used as anode for SIBs, due to intercalation problems and a lack of stable Na–C compounds [8], SIBs might show a significant increase of the anode contribution to the total price. The commonly proposed alternative anode for SIBs is hard carbon, although it re-acts less with sodium than the lithium in graphite per unit mass and volume. In fact, hard carbon shows lower specific density than graphite, and thus thicker laminates are needed, and as the irreversible capacity is also larger, more active material is required, which could increase the costs [9].

Although different works investigated the use of hard carbon as anode for SIBs, in order to make it more practical [10–12], commercial hard carbon prices kg^{-1} are not available. But it has been reported that higher price comes from the high-cost precursors [10, 11]. However, in order to reduce SIB cost and increase its performances, there are different studies that focus on low-cost/high-yield synthesis of hard carbon using cheaper precursors (e.g. cellulose, corn stalks, phenolic resin) [10, 12]. Vaalma et al. used \$15 kg^{-1} as a price of hard carbon; however, it can be lowered up to \$8 kg^{-1}, considering the efforts are being done to enhance the properties of the hard carbon [7, 10].

For the electrolyte, the differences are comparably small: the amount of lithium in the electrolyte is very low (0.5% for a 1 M LiPF6 solution in organic solvent), and correspondingly low is the potential for cost reductions by substituting it with an electrolyte using a less expensive sodium salt [13].

However, SIBs compared with LIBs show some drawbacks, which have slowed down its widespread diffusion, including a higher redox potential (−2.71 V for sodium compared with −3.04 V for lithium, both versus the standard hydrogen electrode), a higher atomic mass (23 g mol^{-1} and 7 g mol^{-1} for sodium and lithium, respectively), and a larger size (the Shannon ionic radii are 1.02 Å and 0.76 Å for sodium and lithium, respectively), which lead to a decrease in the theoretical energy density [5, 7]. At the cell level, these factors contribute to a decrease in performance.

14.2 Sodium-Ion Battery Cost Analysis

While there are several works available in the literature on the costs of lithium-ion battery materials [14], cells, and packs, there is relatively little available analysis of these for sodium ion [15]. Moreover, most of the works focus on costs of material preparation and the electrodes/electrolytes taken in isolation, without considering the costs of the whole cell or battery system [16]. However, the cost percentage for active components (cathodes, anodes, and electrolytes) in cells is generally lower than 50% [7], while the costs of the inactive components (current collectors, binders, separators, etc.) are even higher than for those electrode materials. Therefore, the lack of a cost analysis makes it hard to evaluate the long-term feasibility of this storage technology.

For realistic cost predictions, calculations must be done for a certain battery cell with defined kWh. As sodium has a higher molecular weight and a larger size than that of lithium, the theoretical energy density may decrease, and the cost at the cell level can increase [5, 10].

A detailed cost analysis using the Argonne National Lab's BatPaC model (a commonly applied battery cost model, with specifications for many common cathode chemistries, including SIB technology) has been undertaken by Faradion and suggests that material costs at a manufacturing scale will be less than \$150 kWh^{-1} [17]. This makes sodium technology cost competitive with the most inexpensive lithium technologies. The cost breakdown for the components for a Faradion 12 Ah pouch cell is as follows: anode active material = 26%, cathode active material = 28%, electrolyte = 12%, separator = 3%, current collectors = 13%, and miscellaneous components to a fabricate pouch cell-type battery = 18%.

Hirsh et al. [18] investigated the use of Na-ion batteries for grid energy storage, included a cost analysis of Na-ion cells for various sodium cathode chemistries, and included a comparison with the cost ($ per kWh) of $LiCoO_2$. The calculated values compare very favourably with those calculated by Faradion showing that cobalt-free Na ion to be between 40% and 60% lower cost in $ per kWh than $LiCoO_2$/graphite (which they calculate to be at 99 $ per kWh). The authors attribute this significant decrease in cost to the transition metal elements, particularly Co and Ni, which in

Na-ion cathodes can be absent or minimised without the detrimental effect on performance observed in equivalent Li-ion cathodes of the same B-site composition.

Schneider et al. [19] compared cost and GHG emissions of LIBs and SIB reporting that current automotive LIB cell cost based on NMC111|C (186 $ (kWh)) is significantly below the evaluated sodium-ion alternatives. According to the authors, this finding is mainly due to the lower specific charges and voltage of the active materials of sodium-ion batteries, leading to higher material requirements and longer processing times per kWh of capacity. They further show current LIB superiority regarding greenhouse gas emissions and attribute this fact to the same mechanism. Consequently, the authors state that sodium-ion batteries can only become competitive if a performance similar to LIBs is achieved.

Vaalma et al. [7] compared SIB and LIB costs, considering 11.5 kWh, 7 kW battery, with a fixed number of cells as the model system. In detail, the authors compared the cell materials and battery costs of three LIB different chemistries (LMO–sG ($LiMn_2O_4$ with synthetic graphite), NCM(622)–nG ($Li_{1.05}(Ni_{0.6}Co_{0.2}Mn_{0.2})_{0.95}O_2$ with natural graphite), and NCM(622)–SiC ($Li_{1.05}(Ni_{0.6}Co_{0.2}Mn_{0.2})_{0.95}O_2$ with silicon/carbon composite)) with three different SIB chemistries (NMO–sHC (β-$NaMnO_2$ with standard hard carbon), ASC–PHC (advanced sodium-ion cathode material with phosphorus-hard carbon composite), and FSC–aPHC (future sodium-ion cathode (the working potential is increased by 0.2 V compared to ASC) with advanced PHC)). The LIB chemistries have been selected to illustrate the development of LIBs with increased energy density and lower cost, while the SIB chemistries are representative examples of a present (NMO–sHC), advanced (ASC–PHC), and future (FSC–aPHC) SIB.

The results of the study are shown in the following Table 14.1. Comparing the LIBs, large cost reductions in terms of the total cost of the cell materials result from changing the cathode material from LMO to NCM (622). Considering NMO–sHC, an example of a present SIB, a substantial increase in the cost of the cell materials relative to the three investigated LIBs is reported. More specifically, the anode cost increases with the use of sHC compared with natural or synthetic graphite owing to the lower density (1.50 g cm^{-3} for sHC versus 2.24 g cm^{-3} for graphite), which leads to increased electrolyte cost. Furthermore, the anode cost also increases because of the lower energy density of sHC (300 mAh g^{-1} and 360 mAh g^{-1} for sHC and graphite, respectively), and thus more active material is needed to achieve the target energy of the battery. Finally, the price of the active materials is higher with sHC (\$15 kg^{-1}) than with natural graphite (\$10 kg^{-1}). On the other hand, considering SIBs that are more advanced, a substantial cost decrease is calculated for ASC–PHC and FSC–aPHC owing to the use of anode materials that have a higher capacity (300 mAh g^{-1} for sHC versus 700 mAh g^{-1} for PHC and 900 mAh g^{-1} for aPHC) and, in particular, exhibit a higher volumetric energy density despite the average working potential increasing by about 0.2 V with respect to hard carbon22. Again, the smaller amount of required electrolyte results in a large cost decrease. Therefore, the development of anode and cathode materials with higher volumetric energy densities is important because it simultaneously leads to a notable decrease in

Table 14.1 Cost comparison of model sodium-ion and lithium-ion batteries, considering as assumption an 11.5 kWh, 7 kW battery [7]

	LMO–sG	NCM622–nG	NCM622–SiC	NMO–sHC	ASC–PHC	FSC–aPHC
Cell material cost ($)	1022	878	841	1164	943	781
Positive active material (%)	31	40	43	20	37	37
Negative active material (%)	16	13	10	24	12	9
Carbon and binders (%)	4	3	3	5	4	4
Positive current collector (%)	3	2	3	3	3	4
Negative current collector (%)	12	10	11	3	4	4
Separator (%)	20	18	19	23	25	27
Electrolyte (%)	15	13	11	22	15	16
Battery pack ($)	2981	2760	2689	3300	2920	2704
Mass (kg)	89.5	68.1	57.9	111.6	78.4	69.4
Volume (l)	51.3	41.3	34.9	73.9	49.3	43.9
Specific energy density (Wh/kg)	128.5	169.0	198.5	103.1	146.8	165.8
Price per energy ($/Wh)	1022	878	841	1164	943	781

the cost of the conductive carbon and binder and, especially, the cost of the electrolyte.

With regard to the entire battery pack, the NMO–sHC battery shows different disadvantages with respect to the LIBs such as increased volume, mass, and cost. On the other hand, the FSC–aPHC cell chemistry would be competitive with NCM (622)–SiC in terms of cost, and although it has a higher mass and volume, these parameters may be less crucial for stationary applications.

However, as stated by the authors, the lifetime, energy efficiency, and safety influence on the cost of the final batteries were not considered in the analysis. These parameters strongly influence the costs of a storage system. In fact, for example, a NCM–graphite battery with a cost of about $3,000 and a cycle life of about 5,000 cycles would have a cost per kilowatt hour ($0.060 kWh^{-1}) that is more than twice that of a LFP–LTO battery with a cost of about $5,000 and a cycle life of 20,000 cycles ($0.025 kWh^{-1}).

Another similar study was conducted by [13] modifying BatPaC from a prismatic cell model to a cylindrical 18,650 cell model. In detail, the authors compared layered oxide SIB cells with two different LIB cell chemistries: lithium–nickel–manganese–cobalt–oxide cathodes and lithium–iron–phosphate cathodes. The study results show that the lithium–iron–phosphate battery shows the highest price per kWh of storage capacity (229 €/kWh), followed by the SIB at 223.4 €/kWh. On the other hand, the lithium–nickel–manganese–cobalt–oxide battery is the cheapest (168.5 €/kWh), due to its high energy density. When looking at the contribution of the battery materials to the final cell costs (per single 18,650 cell), the benefits of the SIB on a material level become clearer. Here, the SIB shows the lowest costs per single cell (0.50 €/cell), whereas the materials for the NMC-type cells are the most expensive (0.72 €/cell). However, these are costs per single cell and do not consider the storage capacity.

Moreover, since fluctuations in raw material prices are a major factor of concern for battery manufacturers [20], the authors perform a sensitivity analysis varying raw material prices. The results show a high sensitivity to fluctuations in the graphite/hard carbon prices. This is more severe for the SIB, where the share of anode active material is higher. Regarding the cathode materials, the highest fluctuations can be observed for cobalt and nickel. Lithium and copper, despite the variations in their price, which have a stronger impact on the final cell price, are comparably stable metals that did not fluctuate heavily over the past 10 years. However, recent increases in the price of lithium have been significant and might be triggered by an increasing demand for batteries, leading to potentially stronger impacts in LIB prices than previously noted. Thus, the high dependency of the actual NMC price on current nickel market prices, and cobalt market prices to a great degree, produces significant uncertainty for future price predictions. Since this situation also affects the SIB due to the high nickel content in the cathode, alternative nickel-free, SIB cathode chemistries could be an interesting option in this regard.

At this time, a direct comparison of the cost-effectiveness of LIBs and SIBs is not possible because SIBs have not been produced on a comparable scale to LIBs. In fact, although the commercialisation and production of these systems are still at a very infant stage as compared to LIBs, presently, there are few companies worldwide developing commercial Na-ion batteries for some niche applications:

- Faradion Limited, established in 2011, was the first nonaqueous Na-ion battery company in the world. It is an owner of >20 patent families (2019) covering a range of materials, technologies, and system designs. Its main product uses high-energy-density oxide cathode with hard carbon anode and liquid electrolyte. Its pouch cells have demonstrated 140–150 Wh/kg at cell level with good rate performance up to 3 C and cycle life of 300 (100% DoD) to 1000 (80% DoD) [17]. It demonstrated viability of its solution for e-bike and e-scooter applications.
- Tiamat was founded in 2017 in France. Its solution is a 18,650 cell based on polyanionic materials, with energy density of 100–120 Wh/kg at cell level [21]. The company targets fast charging applications for both mobility and stationary storage use. Durability of more than 4000 cycles and rate capability of >80% retention for a 10 C rate have been recorded. The company has demonstrated working prototypes of e-bikes, e-scooters, Start&Stop 12 V and 48 V batteries.
- Novasis Energies, Inc., originated from University of Texas at Austin, further developed at the Sharp Laboratories of America. Based on Prussian blue analogue as the cathode and hard carbon as the anode, its battery delivered 100–130 Wh/kg with cyclic stability of 500 cycles and rate capability up to 10 C.

- HiNa Battery Technology Co., Ltd., a spin-off from the Institute of Physics, Chinese Academy of Sciences (IOP-CAS), was established in 2017. Its batteries are based on Na–Fe–Mn–Cu oxide cathodes and anthracite carbon anode and can deliver 120 Wh/kg. In 2019, it was reported that HiNa installed a 30 kW/100 kWh Na-ion battery in East China. Its NIB pouch cells with a cycle life of 2000 cycles have been developed and demonstrated in e-bike, mini electric vehicle, and household energy storage system applications.
- Altris AB:301 is a spin-off company from the Ångström Advanced Battery Centre with links to Uppsala University and EIT InnoEnergy. The company is selling Fennac®, an iron-based Prussian blue analogue for the positive electrode in nonaqueous sodium-ion batteries. Batteries containing Fennac® utilise hard carbon as the anode.
- Natron Energy, a spin-off from Stanford University, is another newly founded company that uses Prussian blue analogues for both the cathode and anode but in this case utilises an aqueous electrolyte. At the expense of lower energy density values than those of organic-based batteries, this cell configuration allows run times as short as 30 s achieving power values of 775 W kg^{-1} (or 1550 W L^{-1}). The cells are able to run over 25,000 cycles at 12 C rate accessing about 70% of the total capacity and with only 6% degradation measured over the duration of the test (6 months).

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Chapter 15
Techno-economics of Open Battery Systems

Christine Minke

Contents

15.1 Bottom-Up Approach in Techno-economics

Techno-economics of emerging technologies require a bottom-up approach. Ideally, it should consist of three different interlinked modeling levels (Fig. 15.1). The basis is built by the electrochemical level. The calculation of the battery performance considering thermodynamic constraints (open cell voltage, OCV) and losses allows for the assessment of the achievable power *P*, while the available amount of redox-active species in the electrolyte determines the energy content *E*. On the component level, the costs for the key elements of the cells (membranes, electrodes, bipolar plates) and the electrolyte are determined. Finally, the system level must consider the technical system design including power electronics and balance of plant (BOP) for the considered application.

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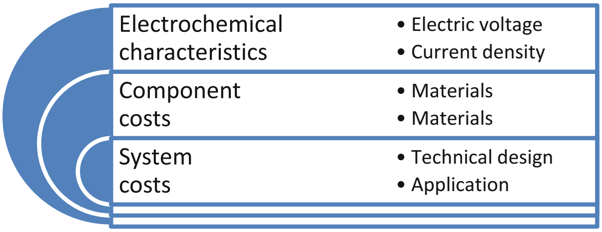

Fig. 15.1 Interlinkage of levels in techno-economic modeling of flow batteries. (Source: Christine Minke)

15.1.1 Electrochemical Characteristics of Flow Batteries

The achievable power P in a FB can be calculated with the number of cells N and the power of a single cell, which is given by the cell voltage U_{cell}, the applied current density I, and the cell area A_{cell}:

$$P = N \cdot P_{\text{cell}} = U_{\text{cell}} \cdot i \cdot A_{\text{cell}}$$

The cell voltage can then be easily calculated on the basis of the open cell voltage U_0 and losses R_{cell}:

$$U_{\text{cell}} = U_0 - R_{\text{cell}} \cdot i$$

The open cell voltage is dependent on the thermodynamic equilibrium potential and the composition of the electrolyte, i.e., the state of charge (SOC) of the battery, as well as different losses. Its precise calculation with the Nernst equation is quite complex, because the concentrated electrolyte mixture exhibits nonideal behavior [4]. Even more demanding is the determination of the current density-dependent losses caused by the ohmic resistance of the electrolyte and the battery components (membrane, electrodes, bipolar plates), the kinetic overpotentials of the half-cell reactions, and the additional concentration polarization through mass transfer resistances [1]. Moreover, side reactions such as hydrogen evolution [16] and transport of redox-active species through the membrane, i.e., crossover [15], are further effects, which have to be taken into account for a precise description of the dynamic FB performance.

However, for a simplified yet sufficiently exact assessment of these losses in the view of the techno-economic analysis, an overall cell resistance R_{cell} is employed [17], which can be conveniently obtained from measured polarization curves or from more detailed physicochemically based FB models. The resulting equation for the battery power is:

$$P = N \cdot (U_0 - R_{\text{cell}} \cdot i) \cdot i \cdot A_{\text{cell}}$$

The energy content E of the battery is the product of the power P and the charge/discharge time t:

$$E = P \cdot t$$

With Faraday's law, one can calculate the required molar flow rate $\dot{n}_R$ of the redox-active species in the electrolyte with the elementary charge e, the number of transferred electrons z, and the Avogadro number N_A:

$$\dot{n}_R = \frac{P}{U_{\text{cell}} \cdot e \cdot z \cdot N_A}$$

The volumes of the positive electrolyte PE and the negative electrolyte NE are then obtained with

$$V_{\text{PE}} = V_{\text{NE}} = \frac{\dot{n}_R \cdot t}{c_R \cdot \text{DOD}}$$

Here, c_R is the concentration of the redox-active species, and DOD is the depth of discharge, which is the difference between the minimum and maximum SOC of the battery.

Finally, the pumping power P_{pump} can be estimated with the electrolyte flow rate through the cells $\dot{V}$ and the corresponding pressure drop Δp:

$$P_{\text{pump}} = \dot{V} \cdot \Delta p = f \cdot \frac{\dot{n}_R}{c_R} \cdot \Delta p$$

The factor f is a reasonably chosen multiple, e.g., tenfold, of the theoretically required flow rate in order to maintain approximately constant concentrations in both half-cells, while the pressure drop is usually calculated with Darcy's law.

With the quantities given above, one can also calculate the energy efficiency of the FB cell stack or system:

$$\eta_E = \frac{P_{\text{discharge}} - P_{\text{pump}}}{-P_{\text{charge}}} = \eta_C \cdot \eta_V$$

Here, the coulombic efficiency η_C and the voltage efficiency η_V of the cell are defined as the ratio of discharge and charge voltage, respectively. The coulombic efficiency is mainly affected by side reactions and crossover processes and usually has values above 95%. On the other hand, the voltage efficiency is determined by the current density-dependent losses with typical values in the range of 80% for properly chosen current densities.

15.1.2 Component Costs of Flow Batteries

The key components of FBs are the electrolyte containing the redox-active species and the core elements of the stack, i.e., membrane, bipolar plates (BPPs), and electrodes.

Detailed techno-economics of membranes have been provided in previous work [13]. It has been shown that for cation exchange membranes with relatively high price, i.e., Nafion™, the membrane has a significant impact on total costs. Moreover, given the complex production process and the costly raw materials, it is unlikely that these prices will fall significantly. Alternatives are cost-effective membranes based on sulfonated poly ether ether ketone (SPEEK) or other low-cost materials [3] or even more cost-effective nanoporous separators. However, the enhanced convective flow compared to dense membranes would require an effective control of the pressure difference between the two half-cells [20].

BPPs show the second highest impact on costs as demonstrated in techno-economics of carbon-polymer BPPs [10]. In particular, the choice of graphite raw materials determines the processability of the compound, the production costs, and the electrochemical performance. A remaining challenge is the manufacturing of large-area BPPs. For square meter size, standard methods, i.e., injection molding, are no longer applicable, and appropriate extrusion techniques have yet to be developed for commercial applications [12].

Considering that two electrodes are required per unit cell, the electrode costs for the carbon electrodes can be set at about the same level as the costs for BPPs. However, considerable differences might occur depending on the raw materials used for the carbon electrode production [11].

Last but not least, the electrolyte shows very high significance for the overall FB costs. A detailed analysis for the most advanced all-vanadium flow battery (VFB) system has shown that depending on the E/P ratio of the battery, up to 50% of the overall costs can be attributed to the vanadium raw material [14]. Huge problems in this context are the strongly fluctuating vanadium prices and the uncertain future prospects for the price development. In spite of the possible development of more cost-effective electrolyte production processes based on vanadium pentoxide [5, 8], the raw material costs for VFB will remain high.

For this reason, the development of FB technologies based on (potentially) more inexpensive redox-active components has been recently intensified. One prominent example is the all-iron FB with very low electrolyte costs [19]. Other researchers have proposed organic redox-active components such as quinones [7]. However, in contrast to inorganic energy carriers with practically unlimited lifetime, these organic substances are prone to chemical and electrochemical degradation. Thus, the stability of these materials is a key parameter for their cost-effectiveness [2, 6].

The calculation of the required quantity of key components is straightforward for a FB with given nominal power P and energy content E [12]:

- The number of membranes is equal to the number of cells N.
- The number of BPPs is equal to the sum of cells and stacks ($N + N_{\text{stack}}$).

- The number of electrodes is twice the number of cells ($2N$).
- The total electrolyte volume is the sum of positive and negative electrolyte volume ($V_{PE} + V_{NE}$).

15.1.3 System Costs of Flow Batteries

The system description may be defined individually. Nevertheless, a linear and comprehensive system definition is highly recommended for accuracy and transparency of techno-economic studies. In Fig. 15.2, a detailed technical system definition for a flow battery is illustrated.

It is structured in the energy subsystem with the key component electrolyte, the power subsystem with the cell stacks, the power electronics, and balance of plant components. Other aspects, e.g., building and site, are usually not considered in detail in a technical model but may be included within a full-system definition in the techno-economic model.

15.2 Data Basis and Quality in Techno-economics

The quality of input data is crucial for any quantitative assessment. Input data consist of technical and economic data. Data quality covers the nature and origin of data (primary, secondary, estimate) combined with aspects of uncertainty (accuracy, validity, time dependency).

15.2.1 Input Data

Input data is required in terms of technical and economic figures. Technical data should at least include the following key figures:

- Nominal power P in kW
- Energy-to-power ratio E/P in h
- System efficiency η

In a preferably more detailed technical description, the list of key figures is completed with:

- Depth of discharge DOD
- Current density i in mA cm^{-2}
- Single cell area A_{cell} in m^2
- Number of cells N and stacks N_{stack} in a system
- Active material concentration in electrolyte c_R in mol l^{-1}

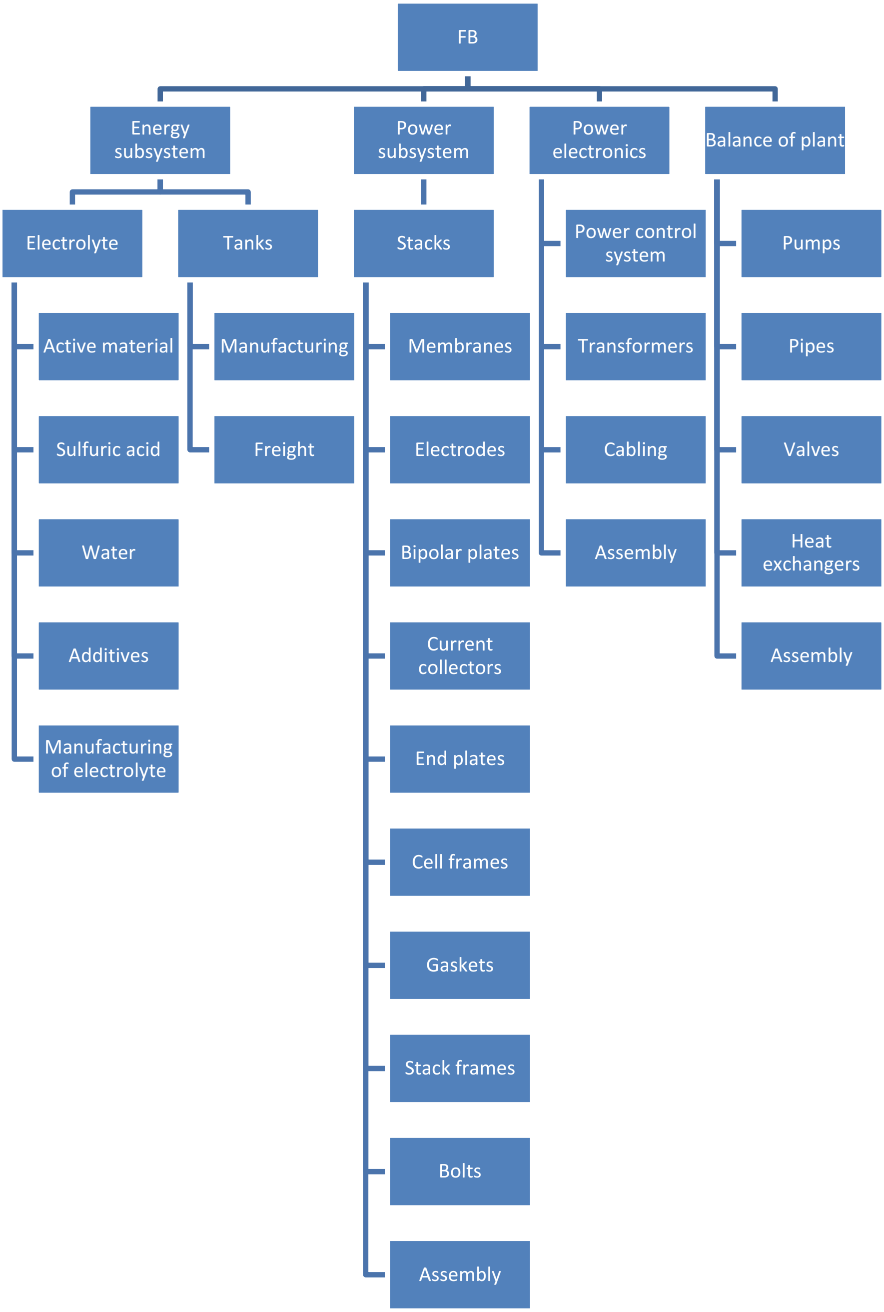

Fig. 15.2 Detailed technical system definition of a flow battery. (Source: Christine Minke)

Considering the manufacturing of a battery system, data on materials, cell geometries, and manufacturing processes, including energy demand, should be provided. The battery operation requires detailed data derived from electrochemical measurements in order to give a quantitative description of performance, lifetime, and cycle life.

Economic input data has to be provided in analogy to the technical bottom-up system description. Thus, in a first processing step, price data has to be adapted to the technical component description, which is for FB typically specified areal or power specific and volume or energy specific. Price data for materials, components, or systems are usually complemented by manufacturing or at least assembly costs. Furthermore, detailed cost data are often limited to key components, whereas costs of further system components, e.g., BOP, are calculated using supplement factors.

15.2.2 Data Quality

Input data may be derived from primary or secondary sources. Primary data is a type of data that is procured directly from main sources, i.e., specific manufacturing processes or specific batteries at operation sites. It is rarely possible to collect all data as primary data. Therefore, secondary or generic data are widely used. These include data from literature, databases, or handbooks. In case of any data gaps, estimates and analogies may be used and carefully documented. By their very nature, estimates have the lowest data quality. To conclude, data quality is closely linked to data availability.

A reasonable exception of this data quality ranking is price data. Price data may be highly volatile over time due to complex market and socioeconomic developments. Thus, discrete primary data in the form of specific price information from a vendor might be less reliable. In this perspective, generic data derived from a database with reasonable technical, geographic, and temporal assessment limits are preferable.

Aspects of uncertainty cover accuracy, validity, and time dependency of data. Accuracy addresses reliability and completeness of data. Additionally, a balance in accuracy for all system components is preferable in order to prevent asymmetries within the model. Validity and time dependency refer to the applicability and temporal correlation of data to the date of study. It is not uncommon for input data to be recited while the design of the battery is being adjusted, e.g., a scale-up from kilowatt to megawatt scale. Temporal correlations are especially important in prospective techno-economics aiming on the prediction of future developments. These are generally subject to uncertainties which have to be appropriately reflected by means of sensitivity analyses.

15.3 Target Figures in Techno-economics

In this section, economic modeling approaches for five widely used economic target figures in techno-economics of open battery systems are presented. These are production costs C, capital and operational expenditures CAPEX and OPEX, and derived total cost of storage as well as levelized cost of storage LCOS.

15.3.1 Capital Costs

A common goal of a techno-economic assessment is the calculation and sensitivity analysis of capital costs C (synonyms are system costs or production costs) of FB systems. For this purpose, an accurate and detailed bottom-up modeling approach in combination with high-quality input data is favorable. A common level of detail is an inventory of component listing mass-, volume-, area-, or unit-specific costs. In literature, a wide variety in the level of detail can be found. On the one hand, the inventory may be limited to key components. On the other hand, each production process of any component may be described in a detailed process model covering input materials, machining, and labor, in order to provide a maximum detail degree.

Capital costs C may be expressed as absolute costs in EUR (or any other currency) per FB or in the form of specific costs. These may be power- or energy-specific costs, usually related to nominal system power (EUR/kW) or nominal energy capacity (EUR/(kWh)). In any techno-economic model, the dependence of results on the E/P ratio cannot be overemphasized. Thus, the cost structure in techno-economic assessments does usually reflect the independent scalability of energy E and power P. Two different approaches are commonly used [14]. In one approach, all items are allocated to either a predefined power or energy subsystem. This leads to a mathematical equation describing total system costs C in EUR as the sum of power and energy subsystem costs:

$$C = P \cdot c_{P,\mathrm{sub}} + E \cdot c_{E,\mathrm{sub}}$$

with cost rates of power and energy subsystem $c_{P,\mathrm{sub}}$ in EUR/kW and $c_{E,\mathrm{sub}}$ in EUR/(kWh), respectively. The individual summands of $c_{P,\mathrm{sub}}$ and $c_{E,\mathrm{sub}}$ are costs of components listed in Fig. 15.2.

In another approach, fixed costs C_{fix} are added to the equation following the idea that not everything can be allocated to the energy and power subsystems:

$$C = P \cdot c_{P,sub} + E \cdot c_{E,sub} + C_{fix}$$

In order to calculate specific system costs in EUR/kW and EUR/(kWh), total system costs may be divided by nominal system power $c_P = C/P$ or energy capacity $c_E = C/E$.

The informative value of these figures is limited and must always be considered in the context of the *E/P* ratio. An illustrative example is the application to VFB in a power range of 10 to 1000 kW providing energy for $E/P = 2$ to 10 h:

$$C_{\mathrm{VFB}} = P \cdot 1000\,\mathrm{EUR/kW} + E \cdot 300\,\mathrm{EUR/(kWh)}$$

This empirical formula is based on a detailed qualitative and quantitative analysis of literature and prices [12].

15.3.2 Total Cost of Storage

Total cost of storage is a common term in techno-economics, especially in comparative studies on different energy storage technologies. Nevertheless, this term is not standardized in the form of an appropriate mathematical definition. In general, seen from a user's perspective, it includes all expenses associated with purchasing and using the battery system.

A more standardized term in this context is levelized cost of storage (LCOS). It is defined and applied in analogy to levelized cost of energy (LCOE) which is calculated for electric energy generation technologies, e.g., photovoltaic systems. The basic idea is to calculate the price of a kilowatt hour of energy emitted by the system. Thus, LCOS is defined as the total cost of ownership over the investment period divided by the energy delivered by the energy storage system.

In order to calculate LCOS, the above-described capital cost assessment approach may be extended in two ways: first, by considering additional cost items for CAPEX and thus for the investment and, second, by considering the operation phase with associated OPEX. LCOS are expressed in EUR/(kWh) of energy E emitted by the FB over its lifetime in a total number of charge-discharge cycles N_{cycle}. Thus, LCOS is dependent on the system's energy efficiency, DOD, lifetime, and the electricity price. A simplified mathematical description of these interrelations is:

$$\mathrm{LCOS} = \frac{\mathrm{CAPEX} + \mathrm{OPEX}}{E \cdot N_{\mathrm{cycle}}}$$

Referring to the nature of an extended capital value method, the full mathematical equation including time dependency of monetary values is formulated as follows:

$$\mathrm{LCOS} = \sum_{t=0}^{n} \frac{\mathrm{CAPEX}_t - R_t + \mathrm{OPEX}_t + c_{\mathrm{el},t} \cdot \frac{E_t}{\eta}}{(1+i)^t \cdot E_t}$$

with considered lifetime from $t = 0$ to year n, residual value R of storage components at their end of life, electricity price c_{el}, energy emitted from the battery in each year E_t, system energy efficiency η, and discount rate i.

Additional cost items for the calculation of CAPEX are interest rates and other costs incurred in connection with borrowing of funds and asset management as well as freight and installation costs for FB components and systems.

OPEX usually include operating and maintenance rates as well as costs of energy that is fed into the battery. These have to be divided by the system efficiency in order to calculate the amount of energy that can be discharged from the system. Resulting energy losses are considered in techno-economics when it comes to profitability assessments, where CAPEX and OPEX are compared to revenues over lifetime. Some examples for economic parameters used in techno-economics of FBs [18] are listed below:

- Freight cost in USD/mile
- Effective income tax rate in %
- Cost of capital in %
- Annual taxes and insurance premiums as fraction of capital investment in %
- Fixed charge rate in %
- Capital recovery factor in %
- Rate of general inflation in %
- Escalation rate for capital costs and operating and maintenance costs in %

This key figure is very complex, so some sample figures for VFB are given below for reference. In analogy to the considerations in the previous section on capital costs, for an *E/P* ratio between 2 and 10 h, LCOS = 0.05 to 0.30 EUR/(kWh) are calculated, decreasing with increasing *E/P* [17]. Two comparable studies consider VFBs with *E/P* = 4 h [9, 18]. These three independent studies show a consensus on a probable range of LCOS = 0.10 to 0.25 EUR/(kWh). However, when considering maintenance costs in order to increase the service life of VFB, higher LCOS in a range of 0.15 to 0.35 EUR/(kWh) are assumed, increasing with increasing maintenance efforts [9].

15.4 Conclusion

To conclude, there are no standards defined on scope or level of detail concerning techno-economics for FBs. This subchapter provides an assessment framework for techno-economics of emerging technologies that are usually subject to uncertainties. FBs are developed in many variants covering a wide range of active species, nominal power, energy capacity, cell geometry, choice of materials, and operation strategies. With this degree of complexity, detailed and transparent techno-economics are all the more important.

In consequence, a special emphasis should be put on the highly complex technical dimension of FBs. The technical model may be kept quite simple but should at least include key figures, i.e., *E/P* ratio, overall ohmic cell resistance, current density, system energy efficiency, and lifetime of components and system.

Techno-economics with transparent technical data lead to more relevant results, especially when validated by measurement data.

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Chapter 16
Social Implications

Viera Pechancová, Petr Sáha, and Drahomíra Pavelková

Contents

16.1 Battery Industry Vulnerabilities

Professor Stanley Whittingham, the Nobel Prize laureate, states in his article [1], ‘our efforts have emphasized better and better batteries, higher energy, higher power, longer life, and lower cost. We have neglected to investigate the afterlife of batteries and the devices they are in’. In the meanwhile, these and similar thoughts have leaked into strategic documents, such as the **Vision for a Sustainable Battery Value Chain** by the World Economic Forum and Global and Battery Alliance [2].

Based on the Paris Agreement target 2 °C scenario, ‘a circular battery value chain’ should create 10 million safe, fair and good-quality jobs globally by 2030. In addition, the battery industry should envisage safeguarding human rights, foster just energy transition and economic development and be in line with the UN Sustainable Development Goals (SDGs). Last, but not least, the battery industry is estimated to

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provide 600 million people with access to electricity, reducing the gap of households without electricity by 70% before 2030.

Energy storage represents key enabling technology in the energy transition, especially with **batteries** being promising technology for the zero pollution ambitions of the European Green Deal. The Strategic Action Plan on Batteries was adopted in 2018 and is a comprehensive set of measures to develop an innovative, sustainable and competitive battery 'ecosystem' in Europe. Batteries are considered key components in mobile and stationary energy storage systems. They enable the transition to smart energy systems by compensating for the variability of supply and demand.

Although there are relevant energy and environmental benefits in the battery operation phase, the exploitation of critical raw materials, such as cobalt, lithium, manganese, nickel and graphite, needed to produce batteries, involves not negligible impacts. Recently, the European Commission put forth a new battery regulation that includes compulsory sustainability requirements, requiring supply chain due diligence for minerals utilised in batteries.

Battery-driven low-carbon transition bears impacts and risks in several directions. What the authors call 'decarbonisation divide', the **battery industry vulnerabilities** might be divided into *(i)* e*nvironmental risks, (ii) gender discrimination, (iii) child labour and (iv) geopolitics and ethnics* [3].

The **environmental and public health risks** concern the resource depletion, human toxicity and ecotoxicity, mainly associated with copper, cobalt, nickel, thallium and silver, with partial results for lithium and aluminium [4]. As an example, raw material mining is connected with environmental pollution, but serious health impacts could be identified along the whole battery supply chains and life cycles [5].

Gender discrimination and the marginalisation of women relate to the diversity-specific issues. Some examples of gender-specific acceptance research include lab-on-skin or telemedicine platforms for wearable biosensors [6, 7]. Another research study found significant differences in attitudes, perceptions and values regarding BEVs between males and females, which could be potentially useful for designing more effective policy measures [8]. The integration of gender analysis into materials research and engineering is crucial to address the gender-related implications of wearable electronics with bio-related applications. Yet another gender perspective offered by the International Renewable Energy Agency (IRENA) and the International Labour Organization (ILO) is that women account for only 32% of the overall renewable energy workforce [9].

It is often the case that no existing labour regulations restricting **child labour and exploitation** are present in the originating countries [10]. An estimated 23% of children in the Democratic Republic of Congo, many of whom are orphans, work within cobalt mining where they are exposed to physical, physiological and sexual abuse in order to provide food for themselves and their families. Despite moving towards less cobalt content in batteries, Fig. 16.1 shows cobalt content of the NMC811 cathode battery (6.6 kg for 75 kWh battery pack), assuming production

Fig. 16.1 The consequences of a cobalt-containing cathode production. (Used with permission of Royal Society of Chemistry from [11]; permission conveyed through Copyright Clearance Center, Inc.)

of 26 million BEVs by 2030, which will result in 25,000 children working 10 hours per day [11].

Subjugation of ethnic groups and geographical issues point out the situation of dominance and control of raw material (cobalt) mining and e-waste treatment leading to lock-in of ethnic group inequalities, ethnic discrimination and refugees/migratory workers. The vulnerabilities are highly geographically concentrated with a lot of focus on China, which claims most of the energy sector employment growth, predicted to target in total 122 million in 2050 under the 1.5 °C pathway, compared to 114 million under present policies [9]. Speaking of the geographical spread, several countries, such as the USA, Japan or the Netherlands, were more successful in BEV adoption than others, e.g. South Korea or China [12].

The successful achievement of the renewable energy sources (RES) targets and other energy-related ambitions amplifies therefore the importance of questions related to the **social aspects** of the energy technology transitions [3]. Nevertheless, the energy transitions seem to suffer from a vicious cycle syndrome – consumers are not interested in less developed technologies, which are then priced higher, and investors are less interested to invest in a product with low demand. The clean energy transition technologies, including battery electric vehicles (BEVs), are still seen as somewhat innovative and therefore might be perceived as immature or risky [13].

As demand for the critical resources, such as metals, minerals, land and water, continues to lever up, just transitions, and specifically **just energy transition**, span throughout different disciplines including critical resource geography, a subfield of human-environment geography **transitions** [14]. According to [15], the emerging landscapes of energy storage consider site-specific **environmental justice** concerns, such as mineral mining, extraction and toxicity during production and disposal of devices. Moreover, increased use of key strategic minerals and metals imposes spatial consequences and political and justice dilemmas. As a consequence, concepts such as resource nexus thinking [16] and social engineering of extraction [17] are being brought into discussions.

In the context of environmental, social and governance (ESG) development of sustainable energy materials, priority has been recently given to nickel-rich cathode materials, and efforts continue for the development of organic/green batteries

[18]. To sum up, the **key sustainability challenges of the battery sector** might be summarised as follows:

1. Battery production has non-negligible GHG emissions.
2. The battery value chain bears also significant social risks.
3. The viability of battery-supported applications is uncertain [9].

Balance needs to be found between the needs of modern society, social aspects and environmental conservation [5]. Advanced battery technologies need to be assessed via a combination of techno-economic simulation tools, cost-benefit analysis and business model innovation, including the social and socio-economic impacts on workers, local community and the society.

The following Sect. 16.2 addresses these issues with the technology acceptance lenses concentrating on battery applications in e-mobility, grid storage and in the context of social innovations. The same issues are addressed also in the next Chap. 17 focused on the social impact assessment method s-LCA, which gained a lot of attention with scholars recently due to the need for more sustainable battery life cycle from 'cradle to grave'. Both approaches, type I s-LCA and type II s-LCA, are explained and compared in Chap. 17.

16.2 Acceptance Issues

The technology adoption and diffusion are associated not only with the performance and cost, but there are social factors entering the adoption process as well. Several theories might be useful to explain these inter-relations; however, the **theory of social acceptance** and **diffusion of new technologies** play a central role. The technology acceptance studies on users' adoption of specific technologies and products are built, among others, on the technology acceptance model, which emphasises the primary role of the perceived usefulness and the perceived ease of technology use as predictors of an individual's attitude towards using and behavioural intention to use a technology [19].

In broad terms, acceptance refers to the passive or active approval of socio-political and community stakeholders towards large-scale energy technologies or related policy strategies, encompassing their willingness to embrace or support such initiatives [20]. According to the seminal work introduced by [21], there are three **dimensions of social acceptance** in the field of renewable energy innovations: socio-political, market and community acceptance (Fig. 16.2). The *socio-political acceptance* relates to the governmental decision-making processes and adoption of energy policies. NIMBY (not in my backyard) effects and people's motives are attributed to the second dimension – *community acceptance*. Finally, the *market dimension*, being a consequence of market adoption of technologies, is helping to overcome barriers to larger diffusion.

When speaking about the social acceptance of energy storage technologies specifically, the clustering across applications and sectors is helpful. These clusters

Fig. 16.2 The triangle of social acceptance of renewable energy innovation. (Reprinted from Wüstenhagen et al. [21], with permission from Elsevier)

include especially RES for stationary applications, e-mobility and portable/wearable electronics to a certain extent, which will be elaborated in the following sections.

16.2.1 E-Mobility and the Range Anxiety Phenomenon

The IRENA and ILO (2021) indicated that about 11% of GHGs were generated globally by the road transportation sector, with 5.8 Gt CO_{2eq} in total. Furthermore, sales predictions suggest that more than 50% of new passenger cars sold by 2035 will be electric [22]. BEVs are thus considered to be important element in the clean energy transition, whereby battery represents key technology affecting technical performance and cost factors.

Despite the urgent need for the **transportation sector decarbonisation**, several studies have indicated barriers to the EV diffusion. The BEV cost, limitations in the battery capacity and vehicle weight represent just a few of the obstacles to full BEV commercialisation [23, 24]. On the other hand, higher driving range, more frequent charging infrastructure, lower prices and pro-environmental attitudes represent factors facilitating the BEV adoption based on the scientific studies (see Fig. 16.3).

Although the environmental perspective is crucial with respect to the low-carbon transport systems, the social perspective started to gain attention among scholars as

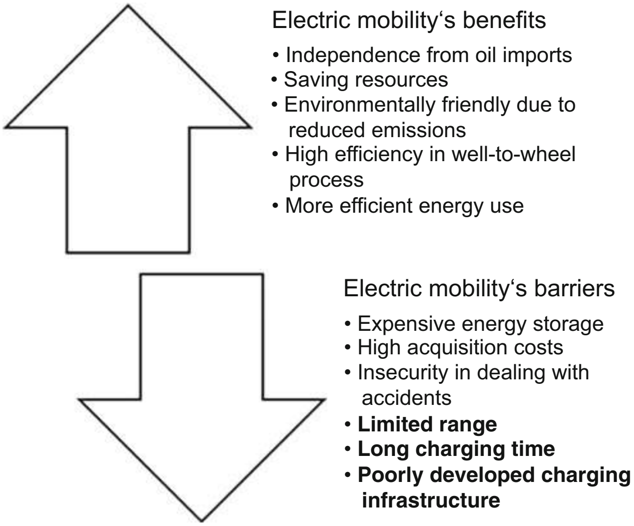

Fig. 16.3 Electric mobility’s benefits and barriers [25], distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license

well. Consequently, hand in hand with the technical improvements, the **users’ experience** (satisfaction, usefulness and attitude) has attracted scholarly interest including the **phenomenon of range anxiety** [25]. In addition to that, there are **determinants of acceptance** identified, such as *contextual* (charging availability), *cost* (purchase, operation), *attitudinal and behavioural* (travel habits), *BEV experience* (familiarity), *sociodemographic* (income, education) and *social* (norms).

The **charging limitations** (both the infrastructure network and charging time) are the main barriers of electric mobility nowadays. Based on some studies, the consumers are willing to wait more than 6 hours when the BEV is charged at home, while charging outside should be done in less than 30 minutes. Furthermore, based on a Flemish acceptance study of various charging infrastructure systems, consumers expressed interest in inductive charging as long as the cost of the system does not exceed that of conventional charging methods [26].

Nevertheless, certain studies have revealed that the negative association between battery electric vehicle (BEV) acceptance and cost-related drawbacks, such as high purchasing costs or limited driving range, is influenced by social identity variables, which carry significant weight [27, 28]. These findings emphasise the need to consider factors beyond individual cost/benefit considerations and focus on social identity elements like social norms and collective efficacy [29].

To conclude, most consumers concerned about the driving range have had no user experience with BEVs. One of the solutions could be the smart charging systems for BEVs, once technical reliability is improved and access to smart charging from other devices is provided, as well as improvements of technical performance of BEV are done [30].

16.2.2 Social Aspects of Grid Storage

Although energy mix is shifting towards intermittent renewables across most markets, the power sector accounted still for considerable 23% of global GHG emissions in 2017 totalling 11.9 Gt CO_{2eq} [9].

The definition of **social acceptance of energy infrastructure** elucidates what factors contribute to the social acceptance of the three types of infrastructure (wind, transmission lines and pump hydro-storage as examples), i.e. ‘social acceptance of new infrastructure occurs when the welfare decreasing aspects of the project are balanced by welfare increasing aspects of the project to leave each agent at worst welfare neutral and indifferent to the completion of the project, or better off and supportive of the project’ [31].

[32] works with four factors in their assessment: general vs. *local acceptance, public concerns, trust in stakeholders and attitudes towards financial support/funding*. Although social **acceptance of RES** has been assessed as relatively high across Europe, differences exist between general social acceptance and local social acceptance. The factors include trust in public authorities, distribution of quality information, public involvement and economic benefits [33]. In the latter case, the challenge is that the cost-benefit analysis (CBA) of smart batteries overlooks usually nonfinancial drivers. Some consumers are dissatisfied with the technology even with a favourable CBA [34].

In nations where there is generally high public acceptance of various energy technologies, the lack of local community acceptance, particularly in areas directly affected by the construction of renewable energy plants, can lead to the failure of otherwise promising renewable energy projects. This highlights the importance of considering local community attitudes as both drivers and barriers to acceptance in the successful implementation of renewable energy initiatives [35, 36].

Although research results on the acceptance of grid-scale stationary battery storage systems, which are likely to play an increased role in smoothing the supply-demand curves, are scarce, the majority of respondents point to the overall positive attitudes [37–39]. Some examples of battery storage local barriers to acceptance include some landscapes, loss of living space, the risk of fire and explosion as safety concerns [39].

Another perspective to the **social role** of grid-level storage has its background in a price suppressing effect, decreasing the probability of remaining in the high price regime during peak hours and the probability increase of remaining in the standard regime during off-peak hours [40]. Yet a different social perspective is represented by the so-called platformisation, enabling new ways of energy provisioning and consumption [41]. The worldwide increase in using digital platforms for energy exchange raises, namely, new questions such as how the interactions of people with energy infrastructures will look like in the future.

16.2.3 Social Innovation and Neighbourhood Batteries

Social innovation in energy is linked to a variety of concepts ranging from community energy, business models, energy self-sufficiency and savings to energy nudging. Avelino et al. [42] characterise social innovations as concepts, objects and/or actions that bring about changes in social relationships, encompassing novel approaches to energy utilisation, thinking and organisation. Examples include social practices of charging and managing the power of **portable electronics** (mobile phones) [43], **connection of PV and batteries** [40] and also **adoption of home batteries** [44].

Neighbourhood batteries represent new dimension of energy storage (alternatively community energy storage) building on the collaboration between a network operator and renewable energy initiatives. Neighbourhood batteries have the potential to reflect societal values responsibly, in line with principles of energy justice and in the context of responsible research and innovation [45]. The idea of a neighbourhood battery entails making strategic decisions, and potentially strategic innovations, whose transformative impact largely relies on the perceptions and actions of the individuals involved [46]. To tackle these challenges, it is imperative to integrate social aspects into materials research and engineering, promoting technology advancements that are inclusive and equitable [47].

16.3 Conclusions

In conclusion, this chapter presents insights into vulnerabilities and sustainability challenges within the battery industry, emphasising the crucial role of social issues. It highlights the historical emphasis on battery performance and cost, neglecting the afterlife of batteries and the social implications of their production and usage. The adoption of a circular battery value chain aligned with the Paris Agreement 2 °C scenario holds significant promise for creating safe, fair and quality job opportunities while driving economic development and promoting just energy transitions. However, the exploitation of critical raw materials raises environmental concerns and poses risks such as resource depletion, human toxicity and child labour.

Addressing these challenges necessitates incorporating social aspects into materials research and engineering to ensure inclusive and equitable technological developments. Gender-specific research has shed light on differences in attitudes and perceptions towards battery electric vehicles (BEVs) and wearable biosensors, calling for more effective policy measures that consider diverse perspectives. Furthermore, social acceptance plays a pivotal role in the widespread adoption of renewable energy technologies and energy storage systems. Understanding factors that influence the acceptance of battery technologies, such as charging infrastructure limitations, range anxiety and economic considerations, is essential for driving successful energy transitions.

The discussion on grid storage underscores the need to strike a balance between general and local acceptance, considering the impact of renewable energy projects on communities. Smart battery solutions, local collaboration and responsible research and innovation are potential pathways to enhance social acceptance and advance energy justice. Overall, the pursuit of advanced battery technologies should go hand in hand with a thorough assessment of their social and socio-economic impacts. Efforts must be made to align the needs of modern society with environmental conservation, enabling a sustainable and equitable energy future. By fostering an inclusive approach and embracing social innovation, the battery industry can become a powerful driver of positive change, leading us towards a greener, more resilient and socially responsible energy landscape.

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Chapter 17
Social Life Cycle Assessment of Batteries

Maurizio Cellura, Anna Irene De Luca, Nathalie Iofrida, and Marina Mistretta

Contents

17.1 Guidelines for Social Life Cycle Assessment

Managing social issues requires the implementation of specific evaluation tools. Life cycle methodologies have gained great consensus among academics and practitioners for the assessment of the impacts of the whole life cycle of a product or service. Among them, social life cycle assessment (s-LCA) is the latest methodology developed, specifically devoted to the evaluation of potential positive and negative social impacts of a product or service, taking into account all activities that are related to the extraction and processing of raw materials, manufacturing, distribution, use, maintenance, recycling and final disposal. The life cycle approach can

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prevent the shifting of burdens between geographical areas, supply chain steps or life cycle phases when evaluating impacts, as well as highlighting possible hotspots.

S-LCA methodology is similar to the environmental LCA methodology, as both methods are based on the ISO 14040 framework. However, while the procedures of goal and scope definition, inventory analysis, impact assessment and interpretation are common, s-LCA differs in the data that is collected. S-LCA highlights the social consequences of the activities and assesses their organisational and societal context in the supply chain.

Social impacts are considered as the effects on the different typologies of stakeholders involved, such as workers, local communities, value chain actors, consumers, societies and children [1]. S-LCA seeks to improve the product's supply chain by providing information on social aspects for decision-makers. Its specific objective is to assess social impacts in the same way environmental LCA does it for environmental ones. But, while LCA is regulated by specific ISO standards (14040-44:2021, in the updated version), about s-LCA there is not still a standardised methodology, and the most diverse methodologies have been proposed in the literature. The s-LCA guidelines from UNEP [1] are based on social and socio-economic impact categories (e.g. human rights, working conditions, health and safety, etc.) with 40 subcategories and five stakeholder groups (society, worker, consumer, value chain actors and local community) and on context-dependent inventory indicators. The UNEP guidelines do not provide an agreed and standardised framework for social indicators that reflect and measure the social impacts of technologies and processes along product life cycles and supply chains. However, they represent the present landmark in the field.

Presently, a specific ISO standard, the 14075 'Principles and framework for social life cycle assessment', is under development (in the preparatory phase), and recently UNEP (2020) updated the Guidelines for s-LCA and the Methodological Sheets for subcategories in s-LCA [2], providing a methodological overview for practitioners about possible evaluation procedures. According to them, there are two main impact assessment approaches, and each of them responds to different practical research aims: the reference scale approach (type I) and the impact pathway approach (type II). The Methodological Sheets provide a list of possible stakeholder groups to be considered in the evaluation processes, namely, workers, local communities, value chain actors, consumers, society and children; for each of them, subcategories of assessment are suggested (40 in total).

17.1.1 The Reference Scale Approach

Type I s-LCA assesses the social performance or risks of companies or organisations involved in the product system, by comparing their behaviour to a reference scenario (e.g. specific legal regulations or norms). The comparison is made according to specific primary or secondary data and information or stakeholders' opinions, and therefore the evaluation consists in the description of a current status (in the short term) and not in the accounting of the links between the activity and long-term impacts. Therefore, the characterisation process is mainly based on interpretation. Results are expressed in performance reference points (PRPs), which are ‘thresholds, targets, or objectives that set different levels of social performance or social risk’ [1]. PRPs consent estimating the magnitude and significance of potential social impacts associated with organisations in the product system, but they are context-dependent, often based on international standards, local legislation or industry best practices and, therefore, not generalisable.

Type I s-LCA methodology suffers many issues because it comprises a multiplicity of qualitative approaches in terms of data collected and their significance, the use of the functional unit (FU) to scale inventory input is very often optional and the characterisation step consists in an implicit or explicit value judgement on the collected data [3, 4]. Furthermore, studies framed within this typology often disregard the main typical elements of life cycle studies such as the system boundaries, the time boundaries, the cutoff criteria and the evaluation of each single life cycle phases. They provide a qualitative assessment of the social performance of behaviours and activities linked to a product or service system [5], by means of value judgements made on collected data and result characterisation made with different relative weights [3, 4]. The most used characterisation methods applied within type I s-LCA found in literature are based on comparisons to norms and best practices, socio-economic contexts, stakeholders’ judgements on companies’ compliance, experts’ evaluations or comparison of alternatives [5]. Moreover, weighting is mainly conducted to give a relative importance judgement to specific categories of impact or stakeholder group, sometimes by means of multicriteria methods or other participative approaches.

Some specific databases are available for type I s-LCA, such as PSILCA (Product Social Impact Life Cycle Assessment), which provides information on social aspects of products over their life cycles, for almost 15,000 industry sectors and commodities and for 69 qualitative and quantitative indicators, considering global supply chains and services, and to detect social hotspots. Similarly, the Social Hotspots Database (SHDB) consists of a multiregional economic input-output data which provides local and global supply chains and links these to a broad range of social metrics aligned per sector and per country. It is a tool to help companies and organisations to manage their social responsibility; it enables quick identification and prioritisation of social risks in supply chains through data classified by country and sector, as well as a methodology for quantifying social impact. They are effective to identify social impacts at the country level but only by means of aggregated data showing averages across different technologies and geographical areas; therefore, these databases are of limited value in distinguishing between alternative operations and locations for products and services [6].

17.1.2 The Impact Pathway Approach

Type II s-LCA is aimed at predicting the consequences of the product system, and it evaluates actual or potential social impacts through causal or correlation/regression-based relationships (the impact pathways) between the product or service life cycle and social impacts in the short or long term. The characterisation process is based on an analytical and quantifiable identification of the consequences of the life cycle.

According to [7] and [1], type II s-LCA is epistemologically and methodologically in line with environmental LCA, where inventory inputs are quantitatively linked with environmental impacts. To harmonise all the life cycle approaches (life cycle assessment and life cycle costing), a type II s-LCA methodology could be more suitable, because it allows:

- an objective assessment of potential impacts aligned with ISO norms 14040-44: 2021.
- Connecting quantitatively inventory input to possible impacts.
- A rational use of elements such as the functional unit, the setting of system boundaries and the rational choice of cutoff criteria, which are often blurred and confused in type I s-LCA approaches.
- Generalising the insights to similar productive sectors.

Many methods have been proposed within this group. [8] reviewed 28 studies and highlighted three main paths to include impact pathways in s-LCA:

(i) applying more variables composing impact pathways, or frameworks gathering several pathways.
(ii) Using and testing already existing pathways empirically (mainly linking income data with health impacts at a macroscale).
(iii) Applying known and already quantified characterisation models or factors from other research works to case studies.

Examples of impact pathways can be found in the work [9], which proposed the Preston pathway to assess the social impacts of banana industry in terms of relations between the increased economic activity and the growth in income, which leads to improvements in the health of a country’s population.

[10] proposed the Wilkinson pathway to assess the anticipated change in the infant mortality rate caused by a change in income distribution in the population of a country, itself generated by an important change in a life cycle.

Recently, the psychosocial risk factor (PRF) impact pathway [11] has been proposed to assess the social impacts of a product life cycle by quantifying the risk of psychosocial impacts on different typologies of stakeholders, according to the duration of exposure to certain living and working conditions that can lead to health issues. According to the definition by [12], PRFs are the aspects and characteristics of work planning and management that can potentially lead to physical or psychological damage. The psychosocial risks are measured in odds ratios (ORs), a statistical measure of the intensity of association between two variables, e.g. as the ratio between the odds of exposure for people with a disease and the odds of exposure for healthy people [13]. Measuring the psychosocial risks with the ORs is a retrospective analysis of a phenomenon, expressed with a nondimensional value, and it can assume values between 0 and $+\infty$. A value of 1 indicates that there is no association between disease and exposure, while values >1 indicate a positive association (the risk factor can provoke the disease/disorder); higher values show a stronger association between exposure and disease [14].

Data are retrieved from previous scientific studies that analysed the relationships between specific living and working conditions and diseases (or disorders), for example, the association between low income and myocardial infarction (OR: 3.53) and stroke (OR: 3.73) [15] or long working hours and metabolic syndrome (OR: 1.66) [16].

All possible stakeholder groups can be potentially covered: workers (from entrepreneurs to labourers), consumers, local communities' members, citizens, value chain actors and children.

Operatively, s-LCA is divided into four steps, the same as indicated in the ISO norms 14040-44 [17, 18]:

1. *Goal and scope*: definition of the system boundaries, categories of impact, functional unit, cutoff criteria, foreground and background processes, taking into account all possible phases of the system under study.
2. *Inventory analysis*: data collection can be conducted both using primary sources (surveys, interviews, participatory approaches) and secondary sources (scientific and grey literature). All required data should be properly allocated to their life cycle phases (e.g. planning, manufacturing, transport, use and disposal).
3. *Impact assessment*: it consists in choosing the most appropriate impact assessment method, according to the objective of the study. Qualitative and quantitative methods are available. As mentioned in the previous paragraphs, it is possible to pay attention to the companies' behaviour as well as to the functioning of the product' or service's life cycle.
4. *Interpretation* of results obtained, retrieving insights useful for stakeholders (private or public ones), practitioners and academics.

This methodological diversity in s-LCA studies is due to the specific characteristics of social sciences, which are multiparadigmatic, and many worldviews can be held: indeed, many scientific methods are available for the assessment of social phenomena, such as quantitative, qualitative and mixed methods [7]. Therefore, up to now, both interpretivist and post-positivist epistemological positions have been applied in the s-LCA scientific literature [7]. Most of the studies published have been evaluating in a qualitative or normative way a wide range of impact categories mostly linked to companies' behaviour (e.g. child labour, corruption, fair wages, safety, etc.), rather than to the life cycle functioning; few studies can be found in literature quantifying cause-effect relationships between life cycle functioning and areas of protection (AoP) in an objective and generalisable way [7].

Further efforts should be made on standardisation possibilities and the alignment to other life cycle methodologies, and testing of methods is necessary to overcome present obstacles and increase the applicability and interpretability results [19].

17.2 Experiences in the s-LCA of Batteries

While literature is rich of studies focused on the environmental impacts of battery production, the social aspects have been little investigated or are limited to social acceptance.

Indicators for s-LCA are often based on qualitative information rather than quantitative, given the nature of the social aspects under assessment. No standardised set of social indicators exists; thus, the choice of social indicators in s-LCA is challenging and possibly subjected to bias.

The typology of s-LCA methodology (type I or type II) strongly influences the typology of data to be collected, as well as the results to be obtained. In the case of type I, site-specific data should be collected, and the social impacts retrieved would be mainly linked to the company's conduct in a specific geographic and sociocultural context. In the case of type II, both primary and secondary data can be collected, and social impacts are quantifiable and directly linked to the life cycle processes.

Identifying the social impacts of battery supply chain must necessarily include all life cycle phases, such as the extraction and processing of raw materials, the production of intermediates, the production of battery cells, the assembly of the battery pack as final product and the disposal or recycling. Raw materials come from different mining sites, often concentrated in few countries. For example, cobalt is mainly extracted in Congo (about 60%), followed by Russia and Australia, from where lithium predominantly comes from. China is the largest producer of aluminium and graphite but also copper and manganese.

To review the specific literature on the topic, a search on the principal scientific research engine (e.g. Scopus, Web of Science) has been made using the keywords 'social life cycle assessment' or 'SLCA' and 'batteries'. Eight contributions have been found (Table 17.1), mostly published since 2019. Only three of them are focused specifically and solely on the assessment of social impacts [20–22], while all the other papers make a multidimensional assessment, taking into account more sustainability dimensions, and therefore combining more methods, in some cases by means of multicriteria decision-making (MCDM) methods [23–26]. Among the studies reviewed, three analyse specifically the production sustainability of batteries [21, 23, 24], three are focused on the production of battery electric vehicles (BEV) [20, 25, 26] and two are devoted to the assessment of the mining phase [22, 27]. Indeed, it is widely shared among reviewed papers that significant risks originate from raw material extraction [21, 22, 27].

All the studies reviewed had the goal of proposing an assessment framework able to address decision-making towards more sustainable solutions, since early phases of the product or project. The most recurring impact category concerns workers'

Table 17.1 Review of social life cycle assessment of batteries

Author	Field of application	Objectives	Methods	Social categories or indicators	Involved actors	Affected stakeholders	Main results
Egbue [20]	Electric vehicle (EV) Li-ion batteries	To assess the social and socio-economic impacts along some parts of the lithium life cycle, in particular extraction and production impacts	s-LCA	Not available	Not available	Society, workers, local communities	Understanding and tracking impacts of lithium for EV batteries over some of its life cycle processes. s-LCA can be used by engineering managers to improve social and socio-economic conditions of production and consumption of lithium
Sansa et al. [23]	Batteries	Proposing a new model for the selection of sustainable design options, able to deal with the uncertainties and the imprecisions due to the technological choices and their potential impacts since early design phase of the product	Environmental LCA (ELCA), economic LCA (EcLCA), s-LCA and the fuzzy analytic network process		Experts, involved to confirm results	Employees, consumers, managers, governors	The design option PDO_1 (lithium iron phosphate, 2 volts, durability of 1000–2000 cycles and specific energy of 90–120 Wh/kg) is considered the most suitable for the design of the product since it generates the minimum impacts through all the life cycle phases

(continued)

Table 17.1 (continued)

Author	Field of application	Objectives	Methods	Social categories or indicators	Involved actors	Affected stakeholders	Main results
Guo [24]	Lead-acid battery, Li-ion battery, Nas battery and NiMH battery	Developing a life cycle sustainability decision-making framework for the prioritisation of electrochemical energy storage under uncertainties by combining MCDM method and life cycle sustainability assessment	LCA, LCC, s-LCA and two MCDM methods: Bayesian best-worst method (BWM) and fuzzy TOPSIS (technique of order preference similarity to the ideal solution)	Social acceptance, electric power system reserve capacity reduction	Five top-tier experts of energy storage including three professors and two practitioners, involved in the weighting process	Society	Result indicates the Li-ion battery has the best life cycle sustainability performances according to eight sustainability criteria from four pillars: economy, environment, society and technology
Thies et al. [21]	Lithium-ion batteries	Assessing the social sustainability hotspots of lithium-ion batteries with a spatially differentiated resource flow model of the supply chain. Comparing three supply chain configurations	s-LCA: Social Hotspots Database in openLCA	Child labour, corruption, occupational toxics and hazards, poverty	Not available	Children, workers, society	The Germany-focused production entails much lower risks in the cell production and pack assembly stage compared to the China-focused production. The results confirm that significant risks originate from the production of raw materials, with graphite production, cobalt sulphate production

							and nickel sulphate production being the main contributors based on actual production shares
Wang et al. [25]	BEVs	To assess the life cycle sustainability of BEVs in China, and the results obtained by comparison with internal combustion engine vehicles (ICEVs) will be used to analyse the developmental advantages and problems of BEVs	LCA, LCC, s-LCA, TOPSIS	Freedom of association and collective bargaining, child labour, fair salary, forced labour, equal opportunities/discrimination, health and safety for workers and consumers, feedback mechanism, access to material resources, local employment, contribution to economic development, technology development, policy and subsidy	Questionnaires and on-site interviews with stakeholders in the three phases of manufacturing, operation and recycling of the vehicles for data gathering	Workers, consumers, local community, society, government	A comparison of BEVs and ICEVs. The study found that the life cycle sustainability of ICEVs in China was better than that of BEVs
Wilken et al. [26]	Electric vehicles and internal combustion engine vehicles	Presenting a novel approach to analyse ICEV-, BEV- and FCEV-type (fuel cell electric vehicle) passenger cars on a	LCA, LCC, PROMETHEE (Preference Ranking Organization Method for Enrichment Evaluations)	The social assessment was realised through the application of specific weighting scenarios as part of the MCDM process	To exclude bias and keep the assessment feasible, neither stakeholder representatives nor 'experts' were	Car owners or users	The weights and preference thresholds only marginally affect the rankings: the BEV alternatives based on renewable

(continued)

Table 17.1 (continued)

Author	Field of application	Objectives	Methods	Social categories or indicators	Involved actors	Affected stakeholders	Main results
		multidimensional basis			involved in this study		electricity (i.e. BEV_wind/PV) share the upper ranks with the conventional vehicles (i.e. ICEV_diesel/gas) in the majority of scenario combinations, whereas BEV_EU-mix and all of the FCEV alternatives are mostly ranked lower
Mancini et al. [27]	Responsible sourcing initiatives for cobalt	Comparing the situation of two pilot projects about the general situation at cobalt small-scale mining sites in Congo (DRC). Providing the basis to discuss the lessons learned for the assessment and monitoring of responsible sourcing programmes and	OECD Guidance, CCCMC (China Chamber of Commerce of Metals, Minerals and Chemicals Importers and Exporters) guidance, IFC (International Finance Corporation) Performance Standards, s-LCA	Local community: health and safety, local employment and economy, social benefits/losses, cultural heritage and land rights, discrimination, forced migration/resettlement and land rights and poverty Workers: health and social well-being,	Interviews to miners, miners' representatives, pilot initiative implementers, ex-child workers for data gathering	Local communities, workers	Results show that the systems analysed are rather effective in implementing the changes that they are designed to make, especially in the case of life-threatening working conditions, child labour and corruption. However, the risk

		of due diligence schemes and possible implications for policy		wages, social benefits, working conditions, discrimination, freedom of association and collective bargaining, training and education, job satisfaction and engagement			categories addressed by these projects are dictated by downstream expectations and do not necessarily correspond to the demands of the miners they are designed to protect. For instance, price calculation and income as well as gender considerations are particularly salient aspects and are not captured by responsible sourcing programmes but are part of the s-LCA framework
Muller et al. [22]	Flexible and modular mining plant (MMP)	The goal of this study is to assess the social implications of a new mining paradigm, small-scale ‘switch-on switch-off’ (SOSO) mining, which is based on the design	s-LCA (PSILCA v2.0 database)	Society: contribution to economic development, value chain actors, corruption, fair competition and promoting social responsibility Local community:	Interviews with members of the project in charge of the MMP development, deployment and operations	Society, local communities, workers, children	Switching the electricity supply system increases the overall risk due to the increase in potential impacts occurring on the renewable energy supply chain

(continued)

Table 17.1 (continued)

Author	Field of application	Objectives	Methods	Social categories or indicators	Involved actors	Affected stakeholders	Main results
		of a flexible and modular mining plant (MMP) and aims at exploiting quickly and safely European small high-grade deposits of raw materials, including critical		access to raw material resources, safe and healthy living conditions, local employment and migration, respect of indigenous rights Workers: health and safety, fair salary, social benefits, working time, child labour and freedom of association			(e.g. battery manufacturing). When switching the country of operation to Greece, the overall potential impacts are predicted to decrease

conditions, especially in terms of health and safety, freedom of collective bargaining, fair wages and child labour. Of studies, 50% also take into consideration local communities and 62% also the whole society. Lithium-ion battery production is the most assessed scenario.

Concerning results [23] affirmed that batteries with lithium iron phosphate, voltage of 2 V, durability of 1000–2000 cycles and specific energy of 90–120 Wh/kg can be considered the most suitable for the design of the product because of lower impacts through all the life cycle phases. [24] compared different typologies of batteries and concluded that lithium-ion battery has the best life cycle sustainability performances according to eight sustainability criteria from four pillars (economy, environment, society, technology). [21] highlighted that when the cell production and pack assembly stage is conducted in Europe (Germany, in their case study), it entails much lower risks compared to the China-focused production: they confirm that significant risks originate from the production of raw materials, with graphite production, cobalt sulphate production and nickel sulphate production being the main contributors based on actual production shares. Concerning the production of the vehicles, contrasting results are obtained in [25, 26], which both applied multicriteria decision-making methods. In the first case, comparing battery electric vehicles and internal combustion engine vehicles (ICEVs), the authors found that the life cycle sustainability of ICEVs in China was better than that of BEVs. In the second study, [26], weights and preference thresholds only marginally affected the rankings. BEV alternatives based on renewable electricity (i.e. wind or photovoltaic plants) share the upper ranks with conventional vehicles (i.e. diesel/gas) in many scenario combinations, whereas BEV with electricity from the European Union (EU) 2012 electricity mix (BEV_EU-mix) and all the fuel cell electric vehicle alternatives are mostly ranked lower.

17.3 Conclusions

Results from the literature review on the batteries or electric vehicle supply chain showed that, while the environmental impacts are mainly and regularly investigated by scholars, the social repercussions of this production process are very poorly considered or are limited to social acceptance. Probably this is due to the difficulty with the different s-LCA methodologies, not yet standardised in one unique approach, the complexity of the indicators' choice and the obstacles to obtaining data from the specific production sector and for all life cycle phases. This is especially for raw material extraction and processing which seems to be the riskiest stage in terms of impacts but also the production of intermediates, the production of battery cells, the assembly of the battery pack as final product and the disposal or recycling. It is interesting to note that although social is little applied to the sector analysed, most existing studies prefer to conduct integrated analyses with other impact assessment methodologies, in the light of a multiperspective approach, by confirming the need to conduct analyses to assess the sustainability of production processes as holistically as possible. On the other hand, from an exclusive social point of view, the inclusion in the same investigation of impact evaluations on different types of stakeholders remains a very challenging issue; in fact, those most analysed are always the workers' group, with the recurring impact category on work conditions (health and safety, freedom of collective bargaining, fair wages and child labour). The major conclusions that can be retrieved are about the necessity of more research to clearly define the possible social impacts of batteries, especially objective analyses that can clearly quantify the impacts deriving from the life cycle phases and that allow comparisons among different scenarios, which can be highly variegated.

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Chapter 18
Multicriteria Decision Analysis for Sustainability Assessment for Emerging Batteries

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Contents

18.1 Introduction

The origin of the concept of sustainability is commonly associated with the definition of sustainable development given by the Brundtland Report and the Rio Conference “Environment and Development” in 1992: “Sustainable development meets the needs of the present without compromising the ability of future generations to meet their own needs.” From this, different concepts emerged to give better

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understanding to sustainability such as the triple bottom-line model [3], the Sustainable Development Goals (SDGs) [54], the Integrative Concept of Sustainable Development (ICoS) [32], etc.

However, defining and assessing sustainability in a specific context is a challenging task. Considering different dimensions and perspectives results in conflicting goals when trying to select the best solution. In the context of batteries, the development and implementation of sustainable technologies is especially challenged by aspects such as materials availability (resources and geographical location), economic feasibility, and technology readiness levels.

Going beyond techno-economic factors, these challenges require methodologies that comprehensively analyze the sustainability issues and allow discussion and interaction among relevant stakeholders, e.g., researchers, technology developers, and policymakers. Multicriteria decision analysis methods are an adequate tool to assess sustainability in different contexts given their flexibility and capability to integrate stakeholders in decision-making processes. The process of conducting MCDA sustainability assessment has important implications regarding the identification of sustainability criteria and indicators, selection of MCDA methods, and identification of stakeholders and their involvement in the assessment. The aim of this chapter is to provide an overview of the MCDA methodology and how this can be applied in the context of sustainability assessment of emerging batteries. First, the definition of important concepts in MCDA sustainability assessment is given. This is followed by a review of MCDA studies in the field of battery storage. Then, a use case for cathode material selection for sodium ion batteries is presented as example for the use of PROMETHEE II. Discussion on the results with a focus on the methodology and their meaning is presented. The chapter ends with conclusion and outlook for MCDA sustainability assessment for emerging storage technologies.

18.2 MCDA for Sustainability Assessment

Multiple criteria decision analysis (MCDA) is a technique that supports decision-making processes through the comparison of potential solutions or alternatives using relevant, often conflicting, criteria. The process of MCDA generally consists of the following steps: identification and involvement of stakeholders, problem definition, selection of criteria (and indicators), definition of alternatives, preference modeling (criteria weighting and aggregation), comparison and evaluation of alternatives, sensitivity/robustness analysis, and problem resolution [21].

The three main challenges for the application of MCDA methods in sustainability assessment are stakeholders' integration, selection of sustainability criteria and indicators, and selection of MCDA methods. They are briefly described in the following paragraphs.

18.2.1 Stakeholder Integration

Identification and involvement of relevant (and diverse) stakeholders is of great importance for MCDA sustainability assessment. Stakeholders should be involved in the construction of the model from definition of the problem and identification of sustainability issues to the evaluation of the results [33]. In practice, this has some drawbacks since it demands high amount of resources such as time, people, and money. Therefore, it is common to find applications or models in which stakeholders' integration is limited to weighting using different formats again depending on the resources available, e.g., workshops, online surveys, and interviews.

18.2.2 Sustainability Criteria and Indicators

Guidelines for general applications of MCDA methods indicate that criteria/indicators are required to be unambiguous, comprehensive, operational, and understandable [31]. In the context of sustainability assessment, they should as well reflect the concept of sustainability used (e.g., triple bottom-line model) and the sustainability issues related to the object of study [4, 22, 48]. At this point, the integration of stakeholders facilitates and strengthens the process of identifying sustainability issues. It is also important to consider the nature of the criteria/indicators for sustainability assessment. It is recommended that they include a life cycle perspective "not to divert some negative impacts from one stage to the other" [12].

18.2.3 Selection of MCDA Method

This subchapter is divided into two sections. First, a general description of MCDA methods is presented, including more detailed information about three selected methods to illustrate their capacities and differences. Second, the presentation and description of the requirements of the MCDA methods to conduct sustainability assessment and a brief comparison of how those three methods perform on these requirements.

18.2.4 Classification of MCDA Methods

MCDA methods can be distinguished into multi-objective decision-making (MODM), multi-attribute decision-making (MADM), and combinations of MODM and MADM [35]. MADM methods can be categorized into (i) elementary methods (e.g., weighted sum method), (ii) single synthesizing criterion (e.g., TOPSIS, AHP), (iii) outranking methods (e.g., PROMETHEE, ELECTRE), and (iv) mixed methods [23]. These methods have different strengths and weaknesses, and their application depends on the decision problem and type of information available [35]. For example, Cinelli, Kadzinski, Gonzalez, and Roman [13] and Wątróbski, Jankowski, Ziemba, Karczmarczyk, and Zioło [56] present "guidelines" to help users to select the most adequate method based on categories such as criteria structure (flat, hierarchical), capacity to handle missing information, and easiness of use. The following paragraphs include a brief description of three methods (WSM, TOPSIS, and PROMETHEE) commonly used in the context of energy management.

18.2.5 WSM

The WSM (weighted sum method) is a way to combine criterion values according to their preferences into a ranking value for each alternative. Its main advantage lies in its simplicity, allowing stakeholders without background knowledge to understand how the ranking is achieved. WSM requires unitless criterion values of comparable scale and therefore usually operates on normalized criterion values, weighting them by normalized preference values and summing them up:

$$R_j = \sum w_i \cdot N_i(C_i) \text{ for } i$$

where R_j is the ranking value for alternative j, w_i the normalized weight for criterion $\underline{i}$, and C_i the normalized criterion value for criterion i. The normalized criterion values must be profit oriented, i.e., higher values are better than lower ones. If this is not the case as for, e.g., costs, this can be achieved by an according normalization.

WSM is frequently chosen because it feels obvious and comes to stakeholders naturally.

18.2.6 TOPSIS

The Technique for Order Preference by Similarity to Ideal Solution (TOPSIS) starts with the normalization and weighting of the input data [10]. With the normalized and weighted input data, the different alternatives can be interpreted as points depending on the chosen criteria. Besides, two theoretical points are calculated: a point that corresponds to the best values in each category over all considered alternatives (theoretical best alternative) and a point which corresponds to the worst value over all alternatives (theoretical worst alternative). With TOPSIS, the best alternative is calculated based on the shortest and farthest Euclidean distances from the theoretical best and the theoretical worst alternative, respectively (cf. Hwang and Yoon [28] and

García-Cascales and Lamata [18]). To determine the so-called performance value P_i of an alternative, the named distances are determined and related to each other:

$$P_i = S_i{}^{-} / (S_i{}^{+} + S_i{}^{-})$$

where S_i^{-} is the distance to the theoretical worst alternative and S_i^{+} is the distance to the theoretical best alternative. TOPSIS requires a limited subjective input compared to other approaches, e.g., PROMETHEE. Its logic is rational and understandable, and the computation processes are straightforward [18].

18.2.7 PROMETHEE

The PROMETHEE family of outranking methods includes several versions which are suitable for different decision-making situations: PROMETHEE I and II, for partial and complete rankings, PROMETHEE III for interval order, PROMETHEE IV for continuous extensions, PROMETHEE V for problems with segmentation constraints, PROMETHEE VI for the human brain representation, and PROMETHEE Group Decision Support Systems (GDSS) for group decision-making [9]. The principle of PROMETHEE is based on pairwise comparisons of alternatives along each criterion. These pairwise comparisons depend on preference functions assigned to each criterion with the aim of translating the difference between two alternatives from the criterion scale to a 0–1 degree of preference. PROMETHEE I provides partial rankings of the alternatives with the outranking flows Φ + and Φ-. The higher Φ + and the lower Φ- are, the better is the overall rank of the analyzed option. PROMETHEE II adds a step to derive a complete ranking of the alternatives (outranking flow Φ) by calculating the difference between the two flows. The challenge or complexity associated with this method when compared to elementary or single synthetizing methods relies on the cognitive effort by the decision-maker to define parameters associated with the preference functions. The next paragraphs describe weighting and preference function selection for PROMETHEE II.

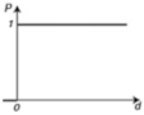
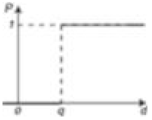
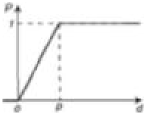
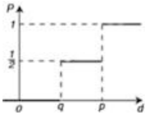
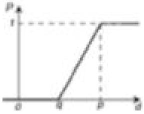
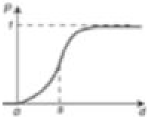
(a) Weighting

There is no specific methodology to determine the weights in PROMETHEE II, and commonly other methods are used for this task. An important consideration for the selection of weighting methods is that in PROMETHEE II the weights represent importance coefficient, i.e., the voting power of the criteria in the decision problem [11].

(b) Preference Function and Parameters

The selection of preference functions allows to identify the degree of preference among alternatives where 0 means indifference and 1 strict preference. Depending

Table 18.1 PROMETHEE preference functions [38]

Preference function	Thresholds	Graphical representation
Type I – Usual	None	
Type II – U-shape	q– Indifference	
Type III – V-shape	p– Preference	
Type IV – Level	q,p	
Type V – V-shape with indifference (linear)	q,p	
Type VI – Gaussian	S – Gaussian threshold	

on the type of function selected, preference thresholds (p) and/or indifference thresholds (q) can be defined. Q indicates the largest difference that can be neglected and p the smallest difference that represent a total preference [38]. Table 18.1 shows the six preference functions in PROMETHEE. PROMETHEE II is equivalent to the WSM when all criteria have the type III–V-shape preference function and the same value for the preference threshold P [19, 37].

The selection of the preference parameters P and Q is meant to be done by the decision-makers based on their perceptions on the decision problem [51]. However, this is commonly not a simple task, and several strategies or approaches have been proposed to simplify this in different contexts, e.g., uncertainty of life cycle impact assessment (LCIA) [58], and using the difference between the maximum and minimum value of each criterion and making then p and q equal to 10–30% and 5–15% of this difference, respectively [34].

18.3 Properties of MCDA Methods for Sustainability Assessment

In the context of sustainability assessment, there is a set of desirable properties when selecting an MCDA method [12, 45]:

- Handling qualitative and quantitative data: when conducting sustainability assessment, different information can be obtained in different forms, i.e., ordinal, cardinal, or mixed.
- Type of weights: within an MCDA model, there are two types of weights: trade-offs when the weights reflect intensity of preference and importance coefficients which represent voting power [44]. In the case of sustainability assessment, the weights should be modeled as importance coefficients. Therefore, special attention should be paid when selecting the methods for preference elicitation.
- Partial/null compensation between criteria: compensation implies the existence of trade-offs in the aggregation of criteria, i.e., the extent to which bad performance of one criterion can be offset by good performance of another. Compensation is associated with the concept of weak sustainability and low compensation with strong sustainability (a more detailed description can be found in Ziemba [60]).
- Threshold values: these can be useful in complex preference models where not all preferences have the same intensity or relevancy.
- Ease of use: simple structure facilitates the experience of the users. Some methods are commonly preferred because of their simplicity. For example, full compensatory methods such WSM are easier to implement compared to low-compensatory methods that could require high cognitive effort such ELECTRE III or PROMETHEE II. However, it is a task of the analyst to properly understand the methods and be able to explain it to stakeholders.
- Handling uncertainty: sustainability issues are inherently related to uncertainty. In order to account for this imprecision or vagueness in the information, the multicriteria evaluation needs to either model the uncertainty of the input data, i.e., stochastic analysis, or include sensitivity analysis [42].
- Software support and graphical representation: several software exist that facilitate the implementation of different MCDA methods. Given their importance on the implementation of MCDA methods, an additional subchapter is dedicated to this topic.

Table 18.2 presents the performance of commonly used MCDA methods related to the desired properties for sustainability assessment in the context of energy technologies. It can be seen why outranking methods are more suitable for sustainability-related decision-making problems. Their ability to offer thorough understanding of how the problem is structured to accurately represent the decision-maker's preferences, and to account for uncertain information using techniques like probability distributions, fuzzy sets, and threshold values, makes them highly valuable [25].

Table 18.2 MCDA method performance with respect to the desired properties for sustainability assessment [12, 14]

	MADM methods		
	Elementary methods	Single synthesizing criteria	Outranking methods
Properties/characteristics for sustainability assessment	WSM	TOPSIS	PROMETHEE II
Handle qualitative and quantitative data	Quantitative	Quantitative	Quantitative, qualitative
Weights as importance coefficients	Trade-offs	Trade-offs	Relative importance coefficients
Threshold values	No	No	Preference, indifference
Partial/null compensation between criteria	Full	Full	Null, partial
Handling uncertainty	Yes	Yes	Yes
Ease of use	High	High	Medium
Software support and graphical representation	Definite [30], MCDA KIT Tool [43], diviz [41]	Triptych, PyTOPS [59], MCDA KIT Tool [43], diviz [41]	Visual PROMETHEE [39], D-Sight [27], MCDA KIT Tool [43], diviz [41]

18.4 MCDA Software

MCDA software supports users through decision-making processes by providing different methods. High diversity of MCDA software is available to match the various needs of the different users which could depend on characteristics such as MCDA methods available, structuring of preferences, graphical representation, usability, platform (desktop, website), and last but not least type of license (commercial, free). Inventory of some available MCDA software can be found in Beekman [8], International Society on MCDM [29], and Weistroffer and Li [57]. Commercial MCDA software stand out for offering good technical support and documentation. However, a great deal of MCDA software has been developed by the scientific community to meet specific needs (e.g., specific MCDA methods, context-based software) or simply to eliminate the barriers that licenses impose. The following subchapter presents the freely available software MCDA KIT tool, originally developed by the Karlsruhe Institute of Technology to support decision-making processes in the context of nuclear emergency management, yet with the original goal to avoid specific constraints and to provide a broadly applicable tool for both the scientific and the operational communities. This tool is still continuously improved in the context of the projects where it is applied, e.g., by adding a specific plug-in to meet the requirements of sustainability assessment.

18.4.1 MCDA KIT Tool

The MCDA KIT tool is a standalone java desktop application with the goals to teach and demonstrate multiple available MCDA methods as well as to apply MCDA in an operational environment. The former manifests in a flexible design which allows for easy and fast integration of new methods resulting in an already comprehensive collection. The latter leads to a clear and user-friendly graphical interface, displaying analyses and results in various ways. The MCDA KIT tool provides many interactive possibilities to edit and analyze an MCDA task. Figure 18.1 shows some of the more common interactions beginning from top left rank bar chart, normalization, report, stability analysis, values, and direct weighting.

The tool is designed in a modular and most generic way to allow combination and comparison of the different methods of the MCDA process. Many different algorithms have been implemented for the various tasks. Weights can be determined by the use of direct weighting, SMART, SWING, and AHP (analytical hierarchy process). Normalization is possible by many methods, starting with simple linear min-max functions up to nonlinear methods like Softmax or piecewise linear. So far, the method for aggregation can be chosen from WSM (weighted sum), WPM (weighted product), some voting methods, VIKOR, TOPSIS, or PROMETHEE. By design, other algorithms can be added easily, expanding the collection of methods over the course of time.

The software is also capable to address uncertainties, both in weights and values, by evaluation of ensembles. Uncertainties can be defined as histogram distributions, naturally supporting stakeholder surveys, or probability distributions with the need to specify the distributions and their parameters. Furthermore, the software features

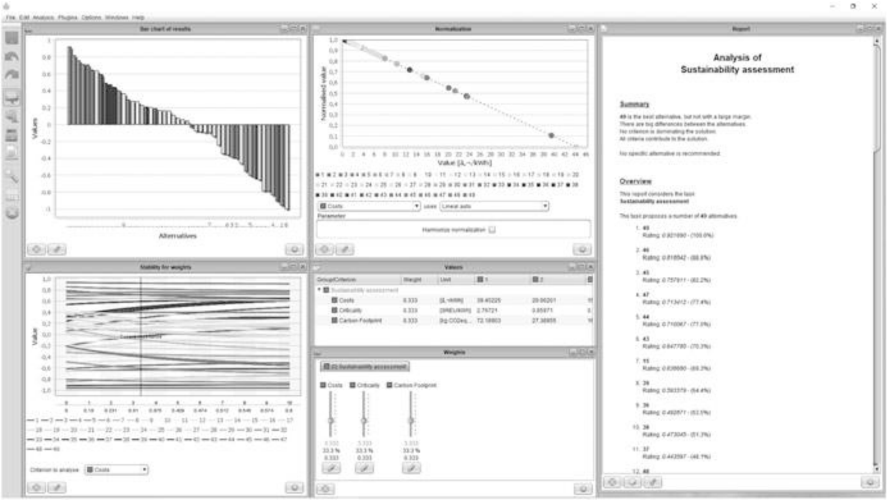


Fig. 18.1 Screenshot of MCDA KIT tool

the generation of documents which textual outline the input conditions, the applied MCDA methods and parameters, and the results as well as analyses like stability estimates and potential correlations. Several import and export methods allow to connect to other tools like MS Excel. A plug-in interface allows third parties to easily add functionality. The tool is also translated in several languages and provides different modes to address color blindness.

18.5 MCDA for Sustainability Assessment in the Field of Batteries

There are several MCDA studies available in the field of batteries, aiming at different technologies (different Li-based chemistries, redox-flow, or high-temperature batteries), as well as different applications reaching from stationary to mobile applications. Depending on the specific scope, corresponding methods and criteria are selected for the assessment of batteries as indicated in Table 18.3. This is not intended to be an exhaustive review but to provide some example of applications and perhaps identify common practices. A wide range of MCDA methods are applied in the selected studies, including mostly compensatory approaches. Criteria selected include mostly LCA indicators. In addition to that, some studies include a wide set of stakeholders, while others do not include any in their assessments. A major factor that should also be kept in mind is that technologies that are being compared might have different technology readiness levels. This can be challenging as some technologies already experienced a large learning curve, while others are just being presently developed. Having this heterogeneity in mind makes it difficult to directly compare the results of different studies. Consequently, it is not possible to determine the best technology via a single study.

18.6 Use Case MCDA Sustainability Assessment for Early-Stage Cathode Materials for Sodium Ion Batteries

In this chapter, the MCDA process (problem definition, selection of criteria, definition of alternatives, and preference modeling) for sustainability assessment is illustrated based on an example of early-stage cathode material screening for sodium ion batteries. The assumptions and calculations here presented correspond to the ones made by the authors in the original publication [6], except for the application of the MCDA method for which PROMETHEE II is used instead of WSM. More details on the made assumptions, considered chemistries, and used data can be found in Baumann et al. [6].

Table 18.3 Overview of selected MCDA studies in the field of battery storage with different chemistries, applications, criteria, and stakeholder involvement

Source	Technologies / alternatives	Application	Criteria	MCDA methods (w = weighting, a = aggregation)	Number and categories of stakeholders involved (participant/category description)	Results
Haase et al. [24]	Battery electric vehicle (BEV), fuel cell electric vehicle (FCEV), internal combustion engine vehicle (ICEV)	Electric vehicles	Environmental (LCA) Economic (total costs) Social (domestic value added)	TOPSIS (a)	None	Under given assumptions, the BEV with wind power was assessed as most sustainable option in 2020 as well as in 2050
Domingues, Marques, Garcia, Freire, and Dias [16]	BEV, FCEV, ICEV, plug-in hybrid (PHEV)	Electric vehicles	Life cycle impact assessment	ELECTRE TRI (a)	None	BEV and PHEV are the only vehicles that can achieve the top class
Baumann, Peters, and Weil [7]	Lithium–iron–phosphate (LFP), lithium–iron–phosphate/lithium titanate (LFP–LTO), lithium–manganese oxide (LMO), nickel–cobalt–aluminum oxide (NCA), and nickel–cobalt–manganese oxide (NMC)	Utility scale Battery storage technologies: Primary regulation, energy time shifting, wind energy support, decentralized grid	Environmental (damage to ecosystem DE, damage to human health DHH, damage of resources availability DRA) Economic (life cycle costs LCC) Social (socioeconomic values, acceptance, regulation, and frame) Technological (maturity, technology performance, tech. flexibility)	AHP (w), TOPSIS (a)	72 people/civil society, regulation, policymakers, researchers (university), municipal utility, network operator, utility company, RES production/retail, automotive sector, battery manufacturer, energy storage business	LIBs seem to be the most Recommendable technology among the evaluated BESS for most application areas (with exception of the LIB–LTO, which is only suitable for low E/P ratios)

(continued)

Table 18.3 (continued)

Source	Technologies / alternatives	Application	Criteria	MCDA methods (w = weighting, a = aggregation)	Number and categories of stakeholders involved (participant/category description)	Results
Ma et al. [36]	Nas battery, lead-acid (LA) battery, NiMH battery, and Li-ion battery (LIB)	Electrochemical energy storage for renewable energy-based power generation stations	Environmental (CO_2 intensity) Economic (capital intensity and operation cost) Social (social acceptance and electric power system reserve capacity reduction) Technological (cycle life, energy efficiency, and self-discharge rate)	Bayesian BMW (w), TOPSIS (a)	Five people/experts	LIB is the optimal solution
Albawab, Ghenai, Bettayeb, and Janajreh [1]	LA batteries, LIBs, super-capacitors, hydrogen storage, compressed air energy storage, pumped hydro, and thermal energy storage	Not given	Environment (area and material intensities, energy, CO_2, and capital intensities of the construction, life cycle greenhouse gas emissions) Economic (operating cost, current installed capacity, growth rate) Social indicators (health and safety issues)	Extended SWARA (w)/ ARAS (a)	Three people/experts from engineering, energy storage, sustainability, energy and climate change, renewable energy	Ranking: (1) thermal energy storage, (2) compressed air, (3) LIBs, (4) pumped hydro, (5) LA batteries, (6) hydrogen storage (onboard), and (7) supercapacitors

			Technological: cycle lifetime, cycle efficiency, discharge time at rated power, and adaptability for mobile systems Resource (specific energy, specific power, energy density)			
Salameh et al. [49]	PV-BES based on nickel–iron (Ni–Fe), LIB, and LA battery technologies at different depths of discharges (DOD)	PV/battery technology microgrid system for a desalination plant	SDG 7: Affordable and clean energy (round-trip efficiency, energy density, number of life cycles, lifetime years, storage duration) SDG 8: Decent work and economic growth SDG 15: Life on land (environmental impact) Economic (annual levelized cost, levelized cost of energy) Size: NPV, NBAT	TOPSIS, WSM, NEW (a)	None	The PV-LIB at 50% DOD was the best option among all cases

(continued)

Table 18.3 (continued)

Source	Technologies / alternatives	Application	Criteria	MCDA methods (w = weighting, a = aggregation)	Number and categories of stakeholders involved (participant/category description)	Results
Murrant and Radcliffe [46]	Power to gas, a distributed battery system, battery storage integrated with solar PV and demand from an airport, liquid air energy storage, battery storage integrated with wave energy, and thermal energy storage at a new residential development	Energy storage projects	Environmental co-benefits Economic growth (innovation), economic viability, increasing self-consumption, economic co-benefits Deferral of grid upgrades, technology viability	MAVT (w,a)	18 people/local and national businesses, academia, community energy groups, and CC	Top-ranking project: Battery storage integrated with solar PV and demand from an airport

18.6.1 Stakeholder Integration

Material researchers from KIT were selected as relevant stakeholders given the scope of the analysis (screening of early-stage cathode materials). Their integration includes the stages of problem definition, selection of criteria, and alternatives and excludes weighting of criteria. In the following subchapters, these will be referred as stakeholders.

18.6.2 Problem Definition

Sodium ion batteries (SIBs) are considered as promising, sustainable alternative to lithium ion batteries (LIBs) regarding the use of critical and expensive materials and the high carbon footprint of the same [6]. Although there is a wide set of different cathode active materials (CAMs) available for SIB, they are considered to be in a lower technology readiness level (TRL) than CAMs for LIB, which are a state-of-the-art technology. Under these uncertainties, how to determine the most sustainable cathode types that are under development and to prioritize certain electrodes types becomes a challenge.

18.6.3 Selection of Criteria

The MCDA is based on a comprehensive bottom-up screening approach using three different criteria: (1) CAM cost, (2) raw material criticality, and (3) carbon footprint. These were selected considering the sustainability issues mentioned in Sect. 18.6.2, a literature review and workshops with stakeholders. Table 18.4 presents the information related to the criteria, indicators, and sources of the data.

18.6.4 Definition of Alternatives

The alternatives consist of 49 CAMs selected using literature screening and from workshops conducted with stakeholders. An overview of the used SIB CAMs and their properties as well as results for the three different criteria is provided in Table 18.5. Here, each SIB CAM chemistry is benchmarked to eight selected LIB CAMs (Nos. 1 to 7 and No. 30 in Table 18.4). From this, lithium–nickel–manganese–cobalt (No. 5) and lithium–iron–phosphate (No. 30) are among the most prominent CAMs. All CAMs are separated into oxidic and polyanionic cathode types for a more differentiated comparison.

Table 18.4 Overview of used criteria for SIB cathode evaluation

Sustainability issues	Criteria	Indicator	Unit	Description	Methods for quantification/ source of data
Resource management (global supply concentration, country governance, import reliance, trade restriction, recycling)	Raw material criticality (criticality)	Supply risk (SR) for the EU	SREU/ kWh	Collective term describing the economic value and dependency on certain materials as well as the probability of supply chain disruptions [50]	SR for Europe [17]
Global warming, emissions to air and water	Carbon footprint (CF)	GHG emissions	kg CO_2eq./ Wh	Greenhouse gas emissions of the CAM precursors and their synthesis process	LCA
Competitiveness	CAM cost (cost)	Costs	€/kWh	Costs of raw materials and precursor materials	Literature and market search inflations and inflation adjusted median values of costs from the last 11 years

A major challenge is to gather the specific mass composition of all cathodes on a common functional unit, here the specific energy of the CAM without an anode. This was realized via a literature review, complemented by laboratory data and stoichiometric calculations for a reference case without anode. All criteria are calculated on a Wh base.

18.6.5 Preference Modeling

PROMETHEE II is selected to model preferences in this chapter based on the description and requirements for sustainability assessment presented in Table 18.2.

18.6.6 Weighting

There is no direct involvement of stakeholders for the weighting process as stakeholders preferred the use of equal weights in combination with a sensitivity analysis with different weighting sets.

Table 18.5 Overview of assessed CAM and corresponding results for the three assessment criteria

No.	CAM name	Theoretic capacity (mAh/g)	Reversible capacity (mAh/g)	Reversible specific energy without anode (Wh/kg)	Cost (€/kWh)	Criticality (SREU/kWh)	CF (kg CO_2eq.-kWh)
Layered oxide materials							
1	$LiCoO_2$	274	150	585	39.45	2.77	72.19
2	$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA)	279	188	696	20.06	0.86	27.39
3	$LiNi_{0.5}Mn_{0.5}O_2$	280	150	585	15.98	0.90	16.51
4	$LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (NMC111)	278	160	592	23.62	1.51	34.92
5	$LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC622)	276	170	629	21.25	1.12	29.40
6	$LiMn_2O_4$ (LMO)	148	110	472	8.01	1.29	5.04
7	$LiNi_{0.5}Mn_{1.5}O_4$ (LNMO)	147	140	644	10.33	0.67	10.62
8	P2-$Na_{0.67}CoO_2$	168	115	369	44.06	3.76	99.05
9	a-$NaMnO_2$	244	185	509	1.97	0.88	2.16
10	ß-$NaMnO_2$	244	190	523	1.92	1.14	2.77
11	$Na_{0.44}MnO_2$	122	120	336	3.22	1.52	2.86
12	P2-$Na_{0.67}MnO_2$	175	175	490	2.14	0.99	2.08
13	P2-$Na_{0.67}Mn_{0.72}Mg_{0.28}O_2$	191	220	572	1.74	1.16	2.23
14	P2-$Na_{0.67}Mn_{0.95}Mg_{0.05}O_2$	177	175	455	2.29	1.13	2.33
15	P2-$Na_{0.67}Mn_{0.5}Fe_{0.5}O_2$	174	190	523	1.26	0.72	1.51
16	O3-$NaMn_{0.5}Fe_{0.5}O_2$	243	110	303	2.12	1.16	2.92
17	P2-$Na_{0.67}Ni_{0.33}Mn_{0.67}O_2$	173	161	596	5.16	0.69	7.78
18	P2-$Na_{0.8}Li_{0.12}Ni_{0.22}Mn_{0.66}O_2$	214	118	415	7.14	0.97	9.26

(continued)

Table 18.5 (continued)

No.	CAM name	Theoretic capacity (mAh/g)	Reversible capacity (mAh/g)	Reversible specific energy without anode (Wh/kg)	Cost (€/kWh)	Criticality (SREU/kWh)	CF (kg CO_2eq.-kWh)
19	P2-$Na_{0.83}Li_{0.07}Ni_{0.31}Mn_{0.62}O_2$	214	140	490	6.60	0.80	9.40
20	P2-$Na_{0.83}Li_{0.25}$ $Mn_{0.75}$ O_2	237	185	500	4.35	0.85	3.54
21	O3-$NaFe_{0.5}Co_{0.5}O_2$	238	160	502	15.61	1.55	35.18
22	O3-$NaNi_{0.33}Co_{0.33}Fe_{0.33}O_2$	238	165	487	15.12	1.24	31.68
23	O3-$NaNi_{0.5}Mn_{0.5}O_2$	240	125	377	10.13	0.93	16.28
24	$Na[Mn_{0.4}Fe_{0.5}Ti_{0.1}]O_2$	244	110	308	2.38	1.18	6.30
25	$NaMn_{0.33}Fe_{0.33}Ni_{0.33}O_2$	240	100	481	5.51	0.66	9.00
26	$Na_{0.6}Fe_{0.11}Mn_{0.66}Ni_{0.22}O_2$	159	120	324	7.25	1.29	10.50
27	$NaMn_{0.3}Fe_{0.4}Ni_{0.3}O_2$	241	130	390	6.19	0.80	10.16
28	P2-$Na_{0.6}Fe_{0.2}Mn_{0.65}Ni_{0.15}O_2$	158	200	620	2.97	0.67	4.16
29	$Na_{0.6}Ni_{0.22}Al_{0.11}Mn_{0.66}O_2$	164	225	675	3.63	0.62	5.33
Polyanionic materials							
30	$LiFePO_4$ (LFP)	170	165	569	5.70	0.81	5.08
31	$Na_3V_2(PO_4)_3$	118	110	381	15.33	1.59	34.99
32	$Na_4MnV(PO_4)_3$	111	110	380 a)	8.01	1.30	18.79
33	$Na_3MnTi(PO_4)_3$*	117	114	410[a]	1.87	1.14	5.55
34	$Na_3MnTi(PO_4)_3$**	176	172	506[b]	1.51	0.93	4.50
35	$Na_3MnZr(PO_4)_3$	107	110	402[b]	1.41	1.12	3.23
36	$NaFePO_4$	154	152	410	0.57	0.87	3.06
37	$Na_{1.7}0_2Fe_3(PO_4)_3$	87	140	406	0.55	0.93	2.95
38	$Na_4Fe_3(PO_4)P_2O_7$**	152	129	406	0.62	0.87	3.27

39	Na_2MnPO_4F*	249	178	651	0.99	0.76	2.29
40	$NaV(PO_4)F$	143	82	303	23.42	2.52	51.79
41	$Na_{1.5}VPO_{4.8}F_{0.7}$	130	134	509	12.69	1.30	28.27
42	$Na_2Fe(PO_4)F$	124	110	360	0.78	1.09	3.52
43	$Na_3MnPO_4CO_3$*	192	125	490	1.08	0.61	2.80
44	$Na_2MnFe(CN)_6$*	171	140	490	1.32	0.50	2.06
45	$Na_{0.61}Fe[Fe(CN)_6]_{0.94}$[1]	61	170	493	0.80	0.58	2.06
46	$Na_{0.81}Fe[Fe(CN)_6]_{0.79}$[1]	90	149	447	0.88	0.46	1.67
47	Na_2FeSiO_4*	276	181	724	0.87	0.44	3.14
48	Na_2MnSiO_4*	278	210	630	1.66	0.68	4.00
49	$Na_2Fe_2(SO_4)_3$*	120	102	418	0.40	0.45	0.87

Data based on Baumann et al. [6]

[a] Specific energy is directly from the literature and the average potential is calculated

[b] Specific energy is calculated from the integration of the potential capacity

*2Na exchange; **3Na exchange; [1] Prussian blue analogs

Table 18.6 Preference function and parameters selected for use case

Criteria	Cost (€/kWh)	Criticality (SREU/kWh)	CF (kg CO_2eq.-kWh)
Preference function	Linear	Linear	Linear
Maximum value	44.06	3.76	99.05
Minimum value	0.40	0.44	0.87
Q	0	0	0
P	0.89	0.07	2

18.6.7 Preference Function and Parameters

In this example, we use the type V-shape with indifference function (linear preference function) for each of the three criteria since they all have a continuous numerical scale, and while comparing them, very small differences can be neglected. P and Q are defined as suggested in Haralambopoulos and Polatidis [25], P being equal to the difference between the maximum and the minimum value for each criterion divided by n (49 CAMs) and Q being equal to zero (Table 18.6).

18.6.8 Results

In this section, the results of using the MCDA method PROMETHEE II for the aggregation of criteria and ranking of materials are presented. Additionally, sensitivity analyses of weights are carried out. All calculations are carried out using the MCDA KIT tool (see Sect. 18.2.4).

18.6.9 Comparison and Evaluation of Alternatives (Ranking)

In Fig. 18.2, the resulting net flows of materials using the method PROMETHEE II are displayed for equal weighting of the three considered criteria. The higher the resulting net flow, the better the alternatives perform from a sustainability point of view. In Fig. 18.2a, alternatives are sorted from left to right according to their CAM number (see Table 18.5), whereas, in Fig. 18.2b, alternatives are sorted from left to right according to their net flows, i.e., ranking. Some trends can be observed in the ranking. First ranks are achieved by polyanionic SIB CAMs (Nos. 49, 46, 45, 47), from which Nos. 45 and 46 correspond to Prussian blue analogues (PBAs), and Nos. 49 and 47 to Si- and S-containing SIBs. Most LIB layered oxide materials (CAM Nos. 1–7) show negative net flows (ranks 32 and higher). Only LIB CAM LFP (CAM No. 30) has a positive net flow. CAMs containing cobalt or vanadium perform lower in the rank, whereas those that contain Mn show preferable rankings. A detailed overview on the results can be found in Baumann et al. [6]. It is important to notice that varying the energy densities can have a high impact on the results. Also, the performance on a cell level can be very different and has thus to be analyzed in detail for further assessments.

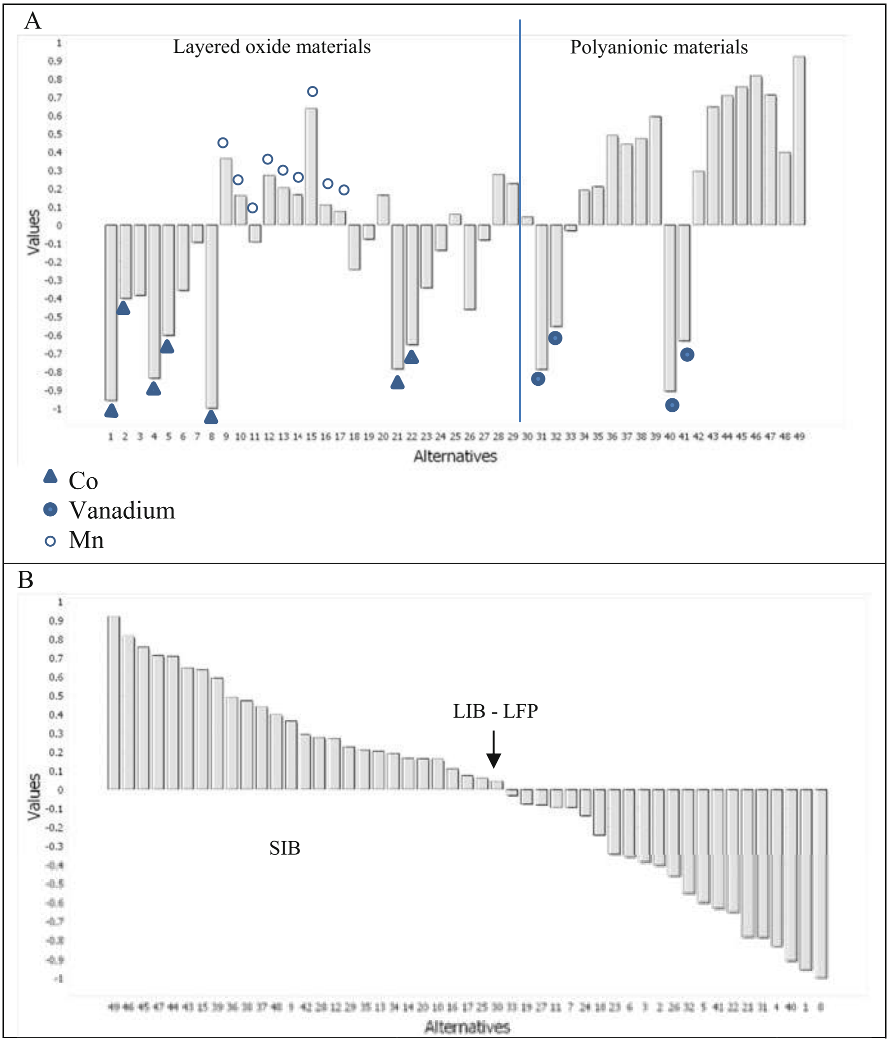


Fig. 18.2 Resulting net flows and rankings of CAMs using PROMETHEE with equal weighting of criteria, sorted according to material numbers (**a**) and rankings (**b**)

18.6.10 Sensitivity Analysis

Table 18.7 presents the rankings with different importance coefficients (weights) up to the 15th place for the cases of (i) equal weights for all criteria, (ii) higher importance to costs (25% criticality and 25% CF), (ii) higher importance to criticality (25% costs and 25%CF), and (iii) higher importance to CF (25% criticality and 25% costs). There is low variation in the ranking when considering different importance coefficients for the criteria.

Table 18.7 Net flows of cathode materials of first 15 ranks

	Equal weights (original case)			Sensitivity analysis		
				50% costs	50% criticality	50% CF
Rank	Net flow	CAM No.	CAM name	CAM No.		
1	0.921	49	$Na_2Fe_2(SO_4)_3$	49	49	49
2	0.818	46	Na0.81Fe[Fe(CN)6] 0.79[a]	46	46	46
3	0.757	45	Na0.61Fe[Fe(CN)6] 0.94[a]	45	47	45
4	0.713	47	Na_2FeSiO_4	47	45	44
5	0.710	44	$Na_2MnFe(CN)_6$	44	44	15
6	0.647	43	$Na_3MnPO_4CO_3$	43	43	47
7	0.638	15	P2-Na0.67Mn0.5Fe0.5O_2	15	15	43
8	0.593	39	Na_2MnPO_4F	39	39	39
9	0.492	36	$NaFePO_4$	36	48	36
10	0.473	38	$Na_4Fe_3(PO_4)P_2O_7$	38	36	38
11	0.443	37	Na1.702$Fe_3(PO_4)_3$	37	38	37
12	0.399	48	Na_2MnSiO_4	42	28	9
13	0.365	9	a-$NaMnO_2$	48	29	12
14	0.294	42	$Na_2Fe(PO_4)F$	9	37	48
15	0.276	28	P2-Na0.6Fe0.2 Mn0.65Ni0.15O_2	35	9	13

[a]Prussian blue analogs

18.7 Discussion

As the intention of this exercise is to reflect on the application of MCDA on sustainability assessment for emerging technologies, only a brief analysis on the results will be presented, and the main attention relies on the process. For a deeper analysis about the results (although using a different MCDA method), the original publication can be consulted [6].

18.7.1 Meaning of Results

The results presented provide insights into the process of CAM selection for SIBs according to MCDA-assisted sustainability assessment. The ranking of CAMs can be understood only as indicative for research and development trends on the material level and cannot be extrapolated into the cell level. Having this in mind, it can be said that the ranking suggests that considering the criteria CF, criticality, and costs, the most promising CAMs for SIBs could be Prussian blue analogs and Si- and

Mn-based chemistries. Some of these CAMs perform even better than commercial LIB CAMs used as benchmark here.

18.7.2 MCDA Procedure

The challenges of conducting MCDA sustainability assessment (see Chap. 2) sharpen when dealing with early-stage technologies. The following paragraphs elaborate on them.

Selection of Criteria The experience with existing energy technologies facilitates the identification of the sustainability issues associated with this decision problem, e.g., high CO_2 emissions, social acceptance, and resources availability. In this use case, this task is limited by the availability of data to compare the impacts of the energy technologies shrinking the potential set of criteria to the mentioned three. Values taken from literature were used to perform calculations, e.g., specific energy values and CAM production costs taken from the literature and estimation of precursor price via stoichiometric calculations. High effort was required for this task, and yet the uncertainty of the results is still very high due to the low TRL of the technologies and lack of robust primary data. Non-existing LCA, unknown social impacts, and volatile market prices challenge the application of MCDA for emerging technologies. Existing methods like prospective LCA could play an important role in this task [26, 47, 53], providing a systematic methodology for obtaining data.

MCDA Method Selection The use case demonstrates that the application of low-compensatory methods such as PROMETHEE II can be facilitated through the use of software and existing approaches to (initially) determine threshold values (preference parameters, p and q). In this type of problem, uncertainty analysis should be conducted carefully. The approach used here represents a deterministic MCDA with sensitivity analysis. However, sustainability assessment of emerging materials/technologies might require stochastic MCDA methods ([42]; [55]). When searching MCDA methods that fit to the sustainability assessment requirements and account for the uncertainty in the performance data (using Cinelli, Kadziński, Miebs, Gonzalez, and Słowiński [14]), the following candidates result: fuzzy PROMETHEE II [20], PANSEM II [2], SMAA III (stochastic multicriteria acceptability analysis) [52], and SMAA-PROMETHEE [15]. Van Schoubroeck et al. [55] present an example of application of SMAA-PROMETHEE for sustainability assessment of emerging biotechnologies.

Stakeholder Integration The integration of material researchers (experts) within the MCDA process was very important for the identification of alternatives and accessing the laboratory data. However, the low diversity within the group of stakeholders hinders deeper reflections on sustainability. Integration of a diverse group of stakeholders is not only relevant for sustainability but also for technology development [40]. To the best of the author’s knowledge, there are not so many studies on applications of MCDA approaches to emerging technologies. Some examples found show the integration of stakeholders from academia, government, and industry [5, 55]. Further research should be conducted on determining how diverse the group of stakeholders within sustainability assessment of emerging technologies could be.

18.8 Conclusion

In this chapter, we have presented the general requirements for MCDA sustainability assessment and an overview of their application in the field of batteries. Some recent applications of MCDA in the field of batteries show diverse approaches with a trend for deterministic, compensatory MCDA methods and inclusion of stakeholders. Available data from a use case of early-stage cathode material screening for sodium ion batteries was selected to illustrate and analyze the suitability of MCDA for assessing emerging battery technologies. In this type of decision problems, identifying the sustainability criteria is not as challenging as evaluating the performance of the alternatives. The lack and/or the high uncertainty of the performance data, e.g., laboratory data, calculations based on literature values, makes it difficult not only to evaluate but to derive concrete conclusions after conducting MCDA. However, the results obtained can be used as indicative to identify promising materials/technologies that could potentially be taken forward in their TRL.

Further development or improvement of the presented model would include exploring different alternatives to address uncertainty in weights and values, such as evaluation of ensembles, probability distributions, or using suitable stochastic MCDA methods (e.g., SMAA- and fuzzy PROMETHEE). Expanding the categories of stakeholders and its participation on the MCDA sustainability assessment is needed to improve the task of preference modeling.

In the context of sustainability assessment, it is very important to understand MCDA as an iterative process in which information, priorities, and stakeholders (categories) are constantly changing. The use of systematic approaches and specialized MCDA software is very important to keep pace with this task.

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