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ROADMAP

2024 roadmap for sustainable batteries

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Abstract

Modern batteries are highly complex devices. The cells contain many components—which in turn all have many variations, both in terms of chemistry and physical properties. A few examples: the active materials making the electrodes are coated on current collectors using solvents, binders and additives; the multicomponent electrolyte, contains salts, solvents, and additives; the electrolyte can also be a solid ceramic, polymer or a glass material; batteries also contain a separator, which can be made of glass fibres, polymeric, ceramic, composite, etc. Moving up in scale all these components are assembled in cells of different formats and geometries, coin cells and Swagelok cells for funamental testing and understanding, and pouch, prismatic and cylindrical cells for application. Given this complexity dictated by so many components and variations, there is no wonder that addressing the crucial issue of true sustainability is an extremely challenging task. How can we make sure that each component is sustainable? How can the performance can be delivered using more sustainable battery components? What actions do we need to take to address battery sustainability properly? How do we actually qualify and quantify the sustainability in the best way possible? And perhaps most importantly; how can we all work—academia and battery industry together—to enable the latter to manufacture more sustainable batteries for a truly cleaner future? This Roadmap assembles views from experts from academia, industry, research institutes, and other organisations on how we could and should achieve a more sustainable battery future. The palette has many colours: it discusses the very definition of a sustainable battery, the need for diversification beyond lithium-ion batteries (LIBs), the importance of sustainability assessments, the threat of scarcity of raw materials and the possible impact on future manufacturing of LIBs, the possibility of more sustainable cells by electrode and electrolyte chemistries as well as manufacturing, the important role of new battery chemistries, the crucial role of AI and automation in the discovery of the truly sustainable batteries of the future and the importance of developimg a circular battery economy.

Contents

Introduction

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It is unanimously recognised by EU, DoE and many other associations, governments and organisations that batteries are a central technology to combat man-made climate change and to reach and maintain our net zero CO_2 targets. They contribute to the storage and balancing of intermittent renewable energy for the grid and to the decarbonisation of transportation using electrical vehicles (EVs), ships, and possibly planes. This comes alongside other areas where batteries are instrumental, such as powering portable electronic devices, the internet of things, and future personalised health care devices—just to mention a few key applications.

The lithium-ion battery (LIB), commercialised in 1991 by Sony, is today the standard commercially viable battery technology used to reach the highest gravimetric energy densities, *ca.* 250–300 Wh kg^{-1} at cell level, which renders them the solution for EVs, enabling driving ranges of *ca.* 500 km.

The progress achieved for LIBs is impressive with continuous improvements in performance alongside the very vast cost decreases, down by *ca.* 90% the last decade, much due to Wright's law of production at scale. Yet, there are new challenges emerging, not the least the availability of the supply chains needed to reach the estimated needed battery capacity production of *ca.* 2.5 TWh globally by 2030.

As the pressure on raw battery materials has increased, the US, EU, UK, and others have come up with several lists of critical elements classified according to the resource's natural availability *vs.* the economic importance. More or less all minerals and elements needed for LIBs are critical(!).

This, together with unsustainable practices in LIB manufacturing, such as the use of toxic poly(vinylidene fluoride) (PVdF) as binders and N-Methyl-2-pyrrolidone (NMP) as solvent, both are carcinogenic and reprotoxic, and the use of toxic and flammable fluorinated electrolytes and toxic glues during the pack assembly, have all made battery scientists and engineers alike think about the development of more sustainable battery practices.

Our 2024 Roadmap on Sustainable Batteries is a reflection from representatives of the sustainable battery R&D community, with some bias towards Europe and European perspectives, on what most crucially needs to be addressed (and how) so that we in the future can construct truly sustainable batteries which will have a low(er) impact on the environment, not only in terms of mineral depletion and global warming potential, but across all the categories including all resource depletion water, toxicity, eutrophication, and acidification. Such more sustainable batteries must still also be performant and safe to use.

The Roadmap starts with a chapter by Crespo and Au providing a definition of sustainability of a battery, involving not only the use of sustainable and/or recycled supply chain, but using a holistic approach across all the life cycle of a battery. The importance of life cycle assessment across all the life stages of a battery is further emphasised in the chapter by Passerini *et al* in chapter 3, Petavratzi *et al* present critical minerals in relation to future battery manufacturing and the importance of creating sustainable and available supply chains. The regulatory developments (*i.e.* new legislation) are key to strengthen the sustainability and circularity of batteries, and this is addressed by Tidblad from Volvo Cars Corporation in chapter 4. Naylor and Younesi provide an industrial perspective on sustainable batteries in chapter 5, emphasising the importance of embedding materials sustainability from the very start of a spinout creation. In chapter 6, Pasta *et al* introduce zero-excess lithium batteries, emphasizing reduction of the material needed alongside higher energy densities. Somewhat similarly, Reynaud *et al* in chapter 7 describe cathodes for LIBs either totally without or containing minimal amounts of critical metals, predominately by using Mn or Fe-based oxides, which is followed by a chapter on sustainable anodes for alkali batteries, including Li and Na, and the bottlenecks of the existing alternatives. Komaba *et al* move on and discuss alternative battery chemistries based on Na and K that are closer to commercialisation, and the needed for battery diversification and materials sustainability for these chemistries. In chapter 10 Ponrouch and Bitenc discuss yet another class of alternative batteries, multivalent batteries, which are still in their fundamental research stages, but with potential to increase not only the sustainability but also performance of batteries.

In the Roadmap it is really recognized that the role of the battery electrolyte is key; more sustainable electrolytes are discussed by Armand *et al*, including solid (polymer) electrolytes as well as ceramic and glasses by Grant; Maria Forsyth *et al* discuss the opportunities and remaining gaps for the use of ionic liquids as safer electrolytes; and finally Alexis Grimaud *et al* take on super-concentrated aqueous electrolytes, where most water molecules are cation coordinated and not 'free' and thereby not having water nature at large. We do acknowledge that no Roadmap is complete, and that we here, despite serious and multiple attempts, do not have a sustainability assessment of the prevailing carbonate liquid electrolyte included, which would be highly important and clearly is warranted, while we do in the above chapters focus on future electrolyte concepts.

Not only does each individual component play a crucial role in the overall battery sustainability, but also the electrode, cell and pack manufacturing. In chapter 12 Berecibar *et al* discuss sustainable alternatives for binders and separators. This is followed by a chapter by Kendrick *et al* on the use of more sustainable solvents to prepare the electrode slurries. Chapter 14 by Huang *et al* describes sustainable production of thick electrodes with maintained fast ion transport by aligned channels produced via ice templating.

The chapter by Franco *et al* emphasises the need for a holistic approach to automation through digital twins and machine learning to accelerate discoveries, to help standardisation and eliminate experimental errors, while at the same time addressing the sustainability in an accelerated fashion. Indeed, a holistic mindset is important; when talking about sustainable batteries, the importance of creating a circular economy for battery manufacturing via recovering raw material and other components using recycling is of uttermost importance. We therefore finish the roadmap with a chapter on battery recycling and the importance of a circular economy by Néstor Antuñano *et al* while also pointing our the readers of this roadmap to the the fantastic 'Roadmap for a Sustainable Circular economy in Lithium-ion and Future Battery Technologies' by Emma Kendrick, Paul Anderson *et al* [1].

It is clear that battery sustainability is a truly complex issue, but at the same time it is one that perhaps not yet has been encompassed by all. The battery industry is currently more or less entirely focused on hard performance numbers and sales figures, and more or less completely neglects sustainability. Legislation such as the newly updated 2006 Battery Directive, however, aims to ensure that the growth of the battery industry is done sustainably. In July 2023 the EU Battery Regulation Amendment was adopted by the EU Council, laying out the structure to achieve sustainable batteries in practice. This includes a digital record system to enable the transfer of key information, containing a unique identifier on the battery type and model, more statistics on performance and durability, and the use of increasing amounts of recycled materials into each battery. This will be an important tool to raise awareness for battery companies of the importance of sustainability in future battery technologies—much along the lines of what is covered more in-depth and more widely in this Roadmap. Therefore, we hope and think that the Roadmap of Sustainable Batteries should be a source of both knowledge and change for both academia and industry.

1. What are sustainable batteries?

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Status

The global transition to a net-zero carbon economy will rely heavily on the development of new battery technologies. Commercialised in 1991 by Sony, lithium-ion batteries (LIBs) dominate the market, ubiquitous in applications from mobile phones and small medical devices to electric cars. However, the critical minerals found in LIBs, including lithium, nickel, cobalt and graphite, and our ever-growing energy demands mean that new technologies must and are being developed to alleviate the environmental burden and pressure on supply chains. Indeed, this year, large-scale production of sodium-ion batteries (NIBs) commenced in China, which will allow us to move away in part from certain critical materials. Typically, however, investment in battery technologies is still driven only by cost and performance. The environmental or social repercussions of mining and processing raw materials, manufacturing batteries and logistics of distribution are not taken into consideration in the strategy towards achieving net zero targets. Moreover, as growing volumes of batteries reach their end-of-life, more efficient approaches towards recycling and repurposing, beyond the current hydrometallurgical and pyrometallurgical processes, must be developed.

Sustainability not only encompasses the irreversible damage to biodiversity and human health, but also growth that minimises the disruption risks to fragile supply chains contingent on changing geopolitics [2]. Current LIBs and even stationary redox-flow batteries are largely based on materials whose extraction and refinement are 90% dominated by China alone, while assembly and manufacture also mostly occur in Asian countries including Japan and South Korea [3]. Most countries have weak supply chains and are therefore vulnerable in managing their energy production and storage requirements, a situation that will only worsen as we transition towards a fully electric society. The disruption to the supply of battery grade nickel arising from uncertainty around the trading relationship with Russia is a timely example of supply chain susceptibility. Meanwhile, China leads in their huge investment into diversifying, implementing, and researching new battery technologies, with other countries and regions falling largely behind.

Current LIBs suffer from a more acute concentration of supply than that of fossil fuels. The level of global market control exerted by a few dominant countries and companies places the global reliance on LIBs at a susceptibility level comparable to that for oil. Thus, concerted advances in developing diverse battery chemistries, securing sustainable and local supply chains and applying circular design (figure 1) will not only ease the environmental costs associated with the battery life cycle, but also enable the democratisation of renewable energy, energy equity and security.

Current and future challenges

At present, there is no universally agreed-upon set of metrics from which to objectively evaluate battery sustainability. Comparison of one metric in isolation, for example, the commonly used carbon dioxide equivalent (CO_2-eq) [4], is still non-trivial, with underlying assumptions varying across different case studies. This absence of a universal standard therefore allows easy green washing. A contributing factor is that we are only now reaching sufficient volumes of end-of-life LIBs to provide statistically significant data to feed into life cycle assessment (LCA) models. Reporting of this data is, however, frequently omitted or incomplete since the hugely negative contributions of certain LCA segments (e.g. biodiversity destruction) are hidden behind relatively easy-to-implement practices (e.g. electrification of transportation fleets).

Challenges to sustainable batteries arise across the whole life cycle. Due to the high concentration of particular minerals, many mining practices cause significant damage to local ecosystems [5]. Furthermore, they often produce large volumes of waste tailings, rocks, and wastewater, which can pollute local soil and water systems [6].

The environmental footprint of manufacturing processes is governed by the choice of materials, energy source, synthesis routes and the complexity of logistics connecting separate processes. These typically rely on large volumes of toxic solvents (i.e. N-methylpyrrolidone, NMP) or fluorinated polymeric binders (i.e. polyvinylidene fluoride), and high temperature heat treatments [7]; moreover, manufacturing is generally dominated by a minority of Asian countries who depend on coal for electricity generation [8].

To offset the environmental costs of manufacturing, it is crucial to increase the amount and efficiency of energy delivered over the battery's lifetime. Not all chemistries are suitable for all applications, and it is important to match cell characteristics with the requirements of specific applications to prolong battery life. Certain tentative moves into repurposing used battery packs for second-life have been made; for example, spent EV batteries provide back-up power to Amsterdam's Johan Cruijff Arena [9]. However, lack of

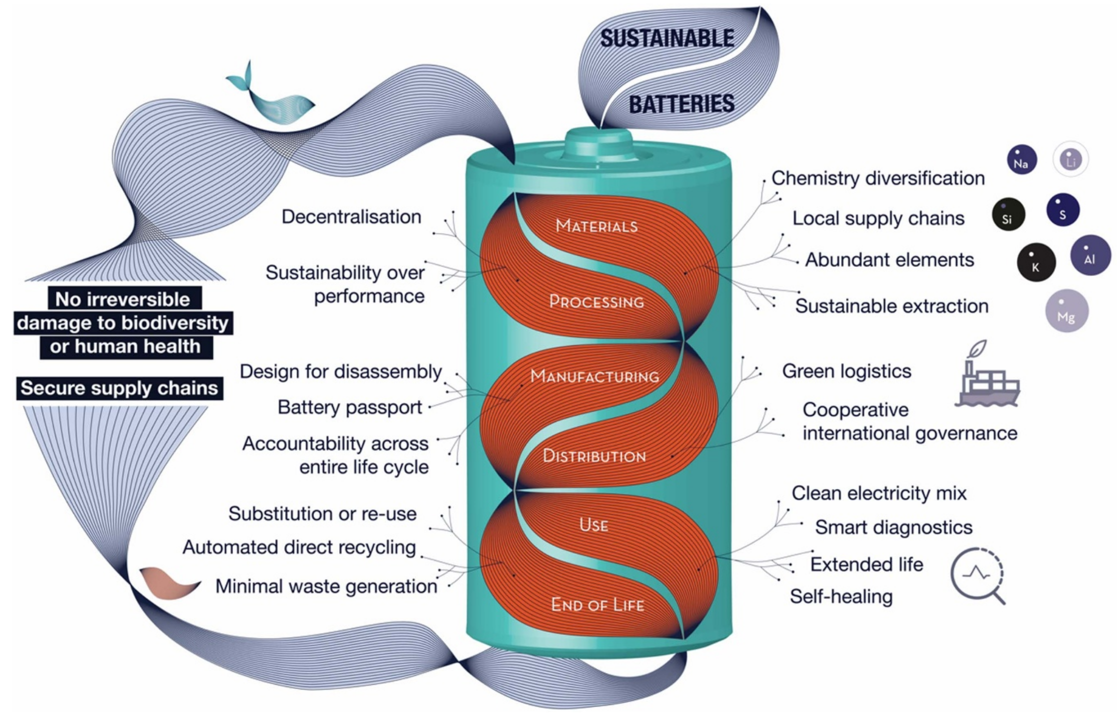

Figure 1. Sustainable batteries will be realised through the holistic implementation of good practices at all stages of the battery lifetime: materials, processing, manufacturing, distribution, use, and end of life.

information about the battery state of health at the end of first life make it challenging to deploy these batteries safely and effectively in their second.

At the end of life, energy- and solvent-intensive processes are employed to recycle spent batteries, but they are largely resource inefficient, recovering only high-value materials such as Co. Differences in chemistry and pack design, and lack of transparency over battery characteristics present major issues preventing wider-spread recycling.

A more concerted drive towards improvement is unfortunately prevented by the perceived lack of profitability, inhibiting the large-scale investment that would be required. Moreover, lack of governance or incentives to drive the economy towards sustainable industry, coupled with far lower production costs in Asia, result in manufacturing being highly localised in one region. For emerging technologies such as NIBs, China also dominates at all stages along the value chain. Sustainable battery growth in the UK or Europe has until now been held back by lack of unity between regions, and insufficient legislation on battery reusability, recyclability and traceability. New EU legislation [10] has introduced requirements regarding carbon footprint declaration, supply chain responsibility, labelling, and end of life management. Despite the recent publication of the UK Battery Strategy, the UK is yet to set out its own legislation in response; however, since three quarters of cars produced in the UK are exported overseas, there is a strong economic incentive for the UK automotive industry to comply with EU regulation in order to continue placing products on the EU market.

Advances in science and technology to meet challenges

With the development of new technologies, we have the opportunity to design future batteries holistically, considering the full life cycle sustainability and resource-efficiency whilst minimising costs. Diversifying chemistries to match technical specifications could reduce reliance on critical minerals, in turn alleviating pressure on ecological hotspots. Where certain materials are indispensable, more sustainable extraction methods must be deployed; for example, lithium extraction from geothermal brine is less land-, water- and energy-intensive, and can co-produce renewable energy [11]. New methods of processing waste, including microbial biomining of tailings, reduce the ecotoxicity of waste streams whilst also extracting further value from the ore [12].

Innovations in battery design to contain fewer components and allow easy dismantling will enable reduced resource costs during assembly, and at end-of-life. Shifting to greener solvents or, indeed, solvent-free methods, greatly reduces the environmental impact of manufacturing. However, these advances must occur in parallel to materials discovery, as many cathode materials are highly moisture sensitive.

Technologically, integration of recycling facilities into manufacturing plants will promote self-sufficiency and minimise transportation emissions at end-of-life.

Advances in battery performance are being made in both academic and industrial settings. On the materials level, for example, switching to lithium iron phosphate cathodes provides access to longer lifetimes and higher thermal stability, while for higher Ni-content lithium-nickel-manganese-cobalt-oxide, the increased energy density can offset manufacturing environmental impacts per kWh [13]. Developments within the emerging chemistries, such as NIBs, lithium-sulfur batteries or all-solid-state batteries, as well as chemistry-agnostic strategies from self-healing binders to thermally stable electrolytes, will all contr1ibute to greater diversity of storage options to suit targeted applications requiring faster charging, higher energy or extreme use conditions. High-throughput testing, advanced characterization, and multifunctional designs are needed to accelerate the uptake of these technologies by industrial stakeholders.

On the industrial level, artificial intelligence and machine learning are finding many applications for predictive maintenance and early fault detection. Data on energy usage is collected through smart battery management systems and analysed in real time, enabling regulation of the battery's operation to improve efficiency, lifespan and safety. Such datasets should be openly shared between all stakeholders to improve models for the precise prediction of state-of-charge and state-of-health of batteries from a given usage profile.

An important hurdle for recycling is recovery efficiency. Advances in automated sorting, disassembly and direct recovery should be targeted, to ensure greater efficiency and safety, and facilitate reduction of costs. Greater transparency regarding battery chemistry, manufacturing methods and cell design will be necessary; one such example is the EU digital 'battery passport' [10], where technical specifications (e.g. chemistry, capacity, voltage), manufacturer production data, usage history, maintenance and servicing records, and end-of-life and recycling instructions would need to be provided by all manufacturers. Ultimately, a globally unified system would eliminate risks of improper disposal, given the current variation in recycling standards and regulations. Cooperation and standardisation across the entire battery ecosystem is therefore crucial, alongside incentives for investors in new battery technology commercialisation, manufacturing and recycling.

Concluding remarks

A sustainable battery landscape will be based on secure supply chains, ethical and minimally invasive materials extraction processes, resource- and energy-efficient manufacturing, extended energy delivery over the battery's lifetime, and resource recovery at the battery's end of life. Battery diversification holds the key for mitigating supply chain risks whilst maximising the potential of energy storage technologies, by enabling us to address specific application requirements without compromising sustainability or scalability. Diversification is thus crucial to creating a resilient and sustainable energy framework, but it will only be achieved by promoting innovation, incentivising cooperative industrialisation, and enforcing all stakeholders in the supply chain to commit to prioritising sustainability at every level. Current practices across extraction, refining, manufacturing and distribution logistics of LIBs must be reformed for future battery generations to ensure compliance with environmental and social sustainability principles. Research and development must focus on abundant elements and environmentally friendly chemicals, while manufacturing practices should minimise energy intensive methods and strive to increase resource efficiency. Wider implementation and legislation for recycling will alleviate the demand for primary resources. Governments must establish clear regulations and create programmes to facilitate the production and adoption of new battery technologies. Implementation of clear labelling will increase awareness and empower investors and consumers to choose sustainable battery options. Standardisation of labelling and reporting of cell data will be key to building a productive recycling system to accommodate the variety of battery chemistries that will come into circulation; governance, policy agreements and financial incentives will be instrumental in this decisive shift towards a sustainable battery future.

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2. The life cycle assessment of batteries

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Status

The Life Cycle Assessment (LCA) is a formal methodology used for the assessment of the environmental impact of a certain system, whether it is a product, process, or service. When applied to batteries, LCA allows to estimate with quantitative indicators their 'level of sustainability', considering all the material and energy flows of the production phase, the use phase, and the end-of-life phase (figure 2) [14]. Since nowadays batteries are primarily aimed to promote the decarbonization of the transport and energy sectors by facilitating electrification, it is important that a quantitative comparison can be made between the environmental performance of traditional technologies, as internal combustion engines and conventional power plants, and their battery-enabled equivalents, as electric vehicles (EVs) [15] and renewable power plants with battery energy storage systems (BEESs) [16]. Equally important, LCA can be used also to critically analyze battery technologies themselves, for example, by comparing different cathode materials for lithium-ion batteries [17], or by considering the impact of innovative chemistries such as sodium-ion or solid-state batteries [18, 19]. LCA on commercial lithium-ion batteries has been applied since the early 2000s [20], and the number of academic, industrial, and governmental studies focusing on this topic has steadily grown thereafter [21]. This increasing interest in such sustainability analyses is being also fueled by legislative requirements: for instance, from 2024 batteries will require a carbon footprint quantification to allow their sale in the European Union market [22]. Moreover, the variety of new battery materials that are being proposed as alternatives to lithium-ion batteries are very often labelled as more sustainable and greener than the current dominant technology, but these claims are almost never substantiated with a rigorous LCA. Therefore, there is a great potential for an extensive application of this methodology, and the LCA can be then considered as a fundamental tool in this ever-growing field. Nevertheless, a proper use of LCA in the battery sector faces some pitfalls that could hinder its utilization in a reliable way and the sound, reproducible interpretation of its results.

Current and future challenges

In general, there is a consensus in the pertinent literature that battery LCA lacks standardization in terms of the analysis boundaries, functional unit(s), and life cycle inventory. The end-of-life phase of the battery life cycle, despite having a significant influence on the final LCA results, is the one with the highest associated uncertainties, since there are still no fully established practices regarding the disposal, recycling and eventual reuse of packs, modules and cells [14, 23, 24]. Regarding the use phase, not only batteries can be employed in applications with very different requirements (EVs, BEESs), but these same applications can be characterized by various load profiles and environmental conditions which affect the efficiency and the cycle life, hence the definition of a univocal and comprehensive functional unit is difficult [25]. Frequently, inventory data used for defining material or energy flows are derived from other LCAs (i.e. secondary data), are obtained from outdated works, or even have unspecified origins [21, 25, 26]. Although the use and reporting of reliable primary data from direct measurements are becoming more prevalent, it is not yet a widespread practice. Furthermore, the production scale considered in the studies must be carefully accounted for, as battery assembly at the laboratory level, in a pilot plant, or in a gigafactory relies on distinct equipment, processes, and methods, and economies of scale significantly influence the final environmental performance [21]. Same goes for the geographical location, which has a fundamental impact on the input raw materials and the electricity mix [25]. For instance, Bouter and Guichet [22] performed a statistical analysis of the global warming potential resulting from LCA studies on batteries published in the last thirteen years. They found a range of 27–271 kg CO2-eq.$\cdot$kWh^{-1} strongly depending on the specific energy of the considered battery, the assumed or calculated manufacturing energy, and even the nationality of the studies' authors (figure 3). All these factors together severely limit the comparability of the studies in the field and poses questions on the validity of the values obtained for the indicators, which can vary between one or two orders of magnitude between LCAs performed by different authors. The abovementioned issues have been mostly identified in works on lithium-ion batteries, the current commercial technology, but the LCA of new solutions for battery energy storage is still in its infancy. Only few, recent analyses, mostly at a laboratory scale, dealt with innovative chemistries such as sodium-ion batteries [18, 27, 28], solid-state batteries [19, 29], lithium-sulfur batteries [30], organic batteries [31], or non-insertion anodes [32]. Since it will be necessary to reliably assess the sustainability of these solutions for their potential industrialization, the challenges of obtaining

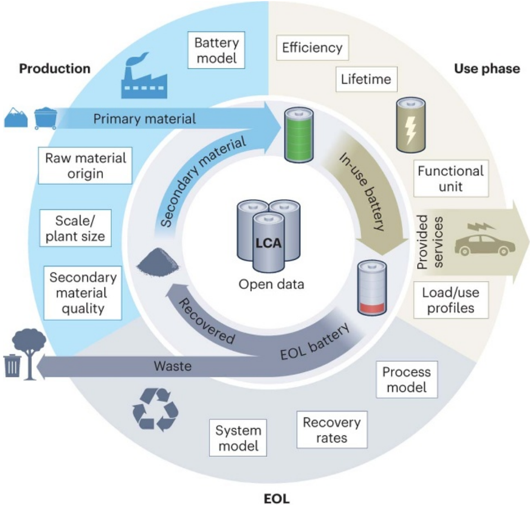

Figure 2. A visual depiction illustrating the life cycle assessment (LCA) process for batteries, where the main material flows are shown in the inner circle, while the outer circle highlights the major stages of the life cycle and key considerations for best practice. Reproduced from [14], with permission from Springer Nature.

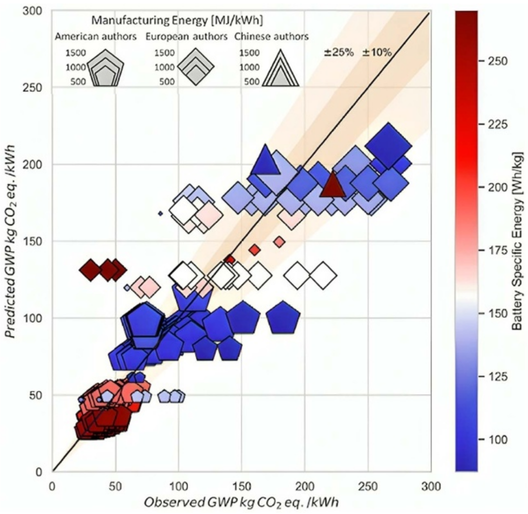

Figure 3. Global warming potential (in kg CO_2eq. kWh^{-1}) of lithium-ion battery production from seveal Europeam, American and Chinese LCA studies. The x-axis shows the global warming potential reported in the analysed studies, with the y-axis shows the results of a predictive model developed by the study's authors. Reprinted from [22], Copyright (2022), with permission from Elsevier.

high-quality inventory data for these very diverse systems and modeling upscaled production lines will need to be addressed.

Advances in science and technology to meet challenges

A proper implementation of LCA for batteries that can overcome the obstacles described in the previous section relies mainly on a drive to normalize the methodology and the data inventories. There have been considerable efforts in the review and the systematic analysis of the battery LCA literature, with the objective of identifying the weaknesses and inconsistencies of the numerous works of the last two decades [14, 20–23, 25, 26]. These studies set guidelines for the definition of rigorous criteria to obtain reproducible and comparable results, such as the choice of reasonable functional units according to the intended use of the battery, the definition of realistic use phase load profiles, and the clear reporting of the source of the inventory data. To be fully effective, it is desirable that these or analogous guidelines are crystallized in national and international standards. The expected rapid growth of the number of battery production sites, both pilot plants and gigafactories [33], will foreseeably increase the availability of state-of-the-art primary data regarding material and energy flows, hence enhancing the quality of LCAs on realistic industrial scenarios. Due to the dynamic conditions under which batteries are produced, used, and disposed, LCAs should also reflect this ever-changing reality. For instance, the impact of depleting a certain resource may change over time according to the discovery of new reserves, or the future deployment of more and more renewable energy plants connected to the power grid could lower the environmental burden of electric energy use. Therefore, it is crucial to emphasize the importance of reporting sensitivity analyses of the LCA outcomes to enhance the validity of the results by accounting for reasonable variations in the input parameters [25]. Finally, the further development of the alternative chemistries to lithium-ion batteries would improve the availability of inventory data and increase the level of knowledge about the processes involved in the production, use and disposal of such post-lithium solutions.

Concluding remarks

In conclusion, LCA is definitely a valuable tool for evaluating the environmental impact of batteries, particularly in the context of promoting the sustainability of the transport and energy sectors. LCA allows for a comprehensive assessment of the entire life cycle of batteries, from production to use to end-of-life and provides quantitative indicators to gauge their environmental performance. However, challenges remain in the lack of standardization of this type of analysis. Efforts to normalize the methodology and data inventories, as well as the development of national and international standards, are essential to ensure the reliability and comparability of LCA results in the battery sector, particularly as new battery technologies emerge. The collaboration among stakeholders for data reporting and sharing is key to address these challenges and harness the full potential of LCA as a fundamental tool in the field of battery sustainability assessment.

Acknowledgments

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3. Critical raw materials for batteries

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Status

Global battery production capacity is forecast to reach over 5 terawatt hours (TWh) annually by 2030 [34]. Battery manufacturing requires a range of mineral raw materials, including lithium, nickel, graphite, cobalt, manganese and phosphorous. These are considered 'critical' by many countries, owing to their supply risk, associated with production concentration and bottlenecks in the supply chain, and economic importance. Demand projections for battery raw materials (BRM) exist at global, national and industry-levels. Whilst differences exist in the forecasting approach, they all foresee exponential demand growth in BRM, significantly exceeding current levels of supply in the medium- to long-term (figure 4). It is essential to increase supply through expansions, the development of new mining and refining capacity, and embracing a circular economy (CE) for batteries. It is also vital to avoid trade-offs between upstream material production and decarbonising the economy [35]. Accordingly, our aim must be to develop resilient and equitable value chains that provide benefits to as many stakeholders as possible. This is challenging because of the short timescales necessary to achieve net zero targets, security of supply concerns and global competition for critical raw materials (CRMs), and rapidly shifting geopolitics [36]. Favourable, long-term industrial policies, a strong emphasis on research and development, and recognition of the importance of secure supplies of raw materials, means China dominates the mining, processing and refining of many CRMs, and has a vertically integrated lithium-ion battery ecosystem that is difficult to challenge.

Furthermore, the rate of innovation in battery technologies and associated changes in material requirements, makes it both challenging for the supply-side to respond and inhibits investment due to the uncertain demand outlook. The investment risk is compounded by the influence of China on CRM markets, the lower cost of domestic production, including overcapacity for certain minerals, and a willingness to subsidise low-margin parts of the supply chain, to control the entire value chain. New investment in BRM supply has been orders of magnitude lower than for battery manufacturing, contributing to concerns about mineral supply deficits [39]. Environmental, social and governance (ESG) standards are of increasing importance to consumers of BRM. Applying strict responsible sourcing criteria further limits supply options. Growing tension is likely to emerge between the desire of the automotive sector to source ESG-compliant materials at an acceptable price and the market availability of battery-grade chemicals. All of these factors mean that consumers of BRM have valid concerns about future availability.

Current and future challenges

A significant disconnect exists between the policy objectives of many countries on net zero, and the levels of investment and rate at which global material supply chains are responding to increased mineral demand [40]. There are three critical materials lists one by the EU [41], one by US [42] and one from the UK [43]. Policy makers and businesses have to recognise that key nodes in the battery supply chain must develop in parallel, so that they combine to form a coherent and resilient ecosystem that permits the timely supply of responsibly sourced raw materials and encourages investment across the entire supply chain. A unique feature of the battery value chain is the very rapid technological innovation, which has led to market segmentation by region and end use. The diversification in battery chemistry is driven by the demands of different applications, the push to reduce battery pack costs, despite increasing material prices, and ESG and security of supply concerns. Over the past five years there has been a trend to more nickel-rich chemistries at the expense of cobalt that require lithium hydroxide instead of lithium carbonate, and substantial growth in the deployment of lithium iron phosphate batteries [44]. Sodium-ion batteries are an emerging technology that have the potential to be commercialised in 2023. In the longer-term, solid-state battery technologies are improving and expected to be in use in EVs before the end of the decade. Other chemistries, including lithium sulfur and zinc air batteries will play a role in the continued diversification of batteries.

Assessing 'responsible' CRM supply is problematic due to a lack of internationally agreed standards, poorly defined metrics and tools, and an absence of data, to monitor sustainability. The timescales under which compliant supply chains have to be developed are very short, which may result in security of supply considerations being prioritised at the expense of ESG performance. New global initiatives (e.g. COP15—global biodiversity framework) and investors are increasingly driving compliance and monitoring of the ESG performance of BRM value chains.

Tracing BRM in products, understanding their content and material forms, and determining their fate in end-of-life products is challenging [36]. Greater end-to-end visibility of battery materials supply chains could assist in mitigating supply risk, by improving understanding of market requirements and enabling

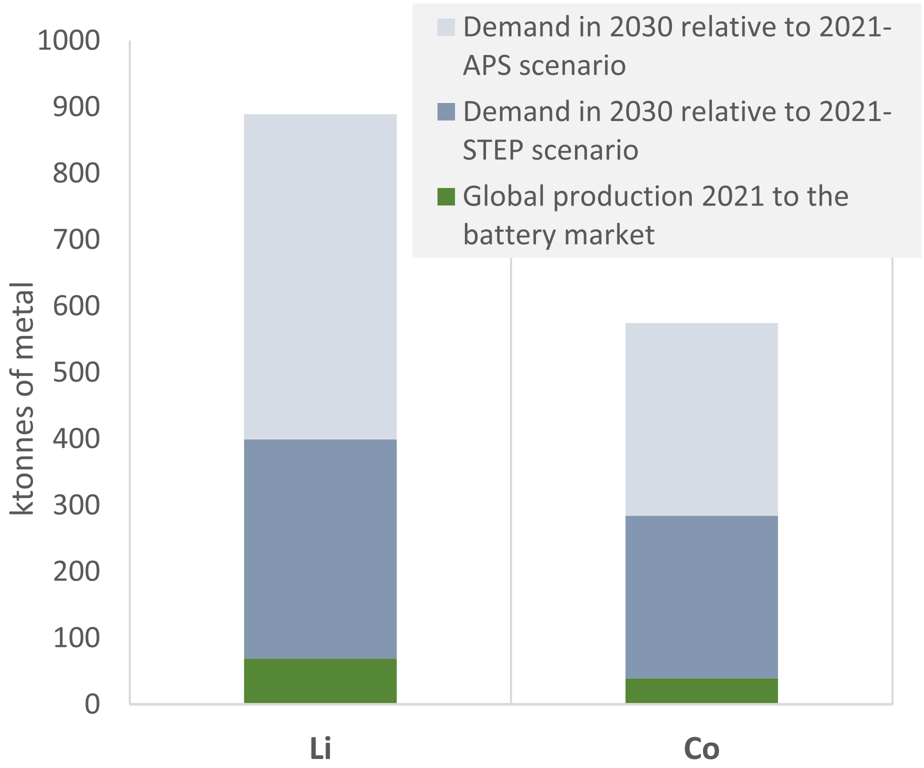

Figure 4. Electric vehicle lithium demand in 2030 under the Stated Policy Scenario (STEP) and the Announced Pledges Scenario (APS) compared with the 2021 global lithium supplied to the battery market (own calculations based on data from [37, 38].

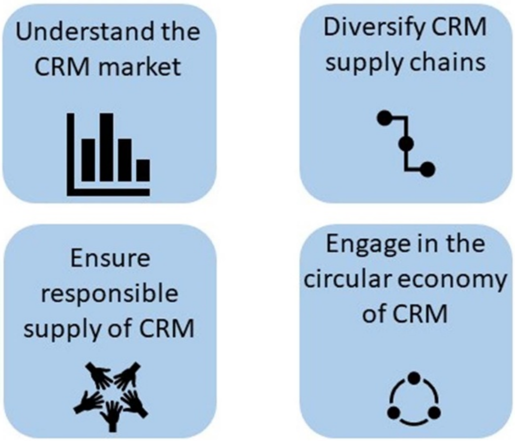

Figure 5. Key pillar to mitigate risk in global battery raw materials supply chains.

reliable, fit-for-purpose upstream material provision (e.g. battery compounds). Greater understand would also support circular business models. However, the current situation of increasing global competition for BRM and poor market transparency, coupled with vertically integrated supply chains, results in poor understanding of the actors involved and material flows.

Advances in science and technology to meet challenges

Addressing these challenges has focused on policy, technology, and improving supply chain resilience (figure 5).

The EU and the US have established policies and legislation that are influencing CRM sourcing and investment decisions across the value chain. For example, the EU Critical Raw Materials Act [45] and the EU Battery Regulations [46] incentivise the development of domestic mining projects and the importance of a CE for batteries. In the US, the Inflation Reduction Act [47] places conditions on the sourcing of CRMs and battery components to be eligible for tax credits. Other countries e.g., the UK, Canada and Australia have published strategies on critical minerals. Global initiatives, including the Minerals Security Partnership and the Global Battery Alliance, are important commitments towards developing more resilient and sustainable BRM supply chains.

Responsible BRM supply requires improved end-to-end supply chain visibility and traceability, understanding of the interdependencies of relevant stakeholders, and technical standards that promote international best practice. For example, the OECD due diligence guidance for responsible supply [48], the Responsible lithium partnership [49] and the Cobalt Industry Responsible Assessment Framework [50], and certification schemes (e.g. the Initiative for Responsible Mining Assurance [51], the International Finance Corporation Performance Standards on Environmental and Social Sustainability [52]) aim to promote compliance. However, a lack of coordination and consistent datasets to underpin assessment is problematic and may lead to inconsistent and incomparable outcomes.

Blockchain technology is of great interest and under development to allow BRM supply chains to be transparent and auditable [53]. Battery passports represent a digital record of a physical battery, containing information on material provenance, battery chemistry, manufacturing factors and sustainability indicators. Several battery passports are under development, with some pilot schemes established [54], however, universal uptake by industry is potentially years away, given the challenges that have to be overcome (e.g. interoperability, adherence to regulatory systems, accessibility issues etc).

The CE will be of fundamental importance in battery ecosystems, as it can provide additional material supply and incorporate mechanisms for extending product life, resulting in a lowering of total material demand. Established battery ecosystems (e.g. East Asia) have expanded their capacity to process end-of-life batteries as an integral part of the manufacturing process. However, several challenges persist, including the lack of data to map BRM flows, the scale of collection, dismantling, refurbishment and recycling infrastructure, and an absence of clear policy targets, standards, industrial strategy and skills gaps in certain countries and regions.

Concluding remarks

Demand for BRM is forecast to grow exponentially and global mining and refining capacity will require rapid scaling to meet this demand. The challenge is the time available to do this, to decarbonise the energy system and meet net zero targets. The key challenges and areas for intervention include:

- Data on battery values chains is currently uncertain, fragmented and lacks harmonisation and interoperability, which obscures traceability and makes it difficult to assess ESG performance and opportunities for CE interventions. New, internationally agreed data, metrics, and tools are required.
- The rate of innovation in battery technologies means raw material supply chains struggle to respond, leading to market deficits. Innovation also effects investment in new capacity, due to the uncertainty about future BRM demand.
- The supply of BRM will be strongly influenced by ESG factors, which need to be considered on a jurisdictional and project basis in order to fully appreciate the complexities and risks.
- Policy frequently lags technological innovation. Furthermore, there is a strong effort in the 'west' to decouple from China, with an emphasis on 'friend-shoring'. China's dominance in CRM value chains, owing to decades of domestic and international investment, means this is unrealistic over short times scales.
- Developing a CE for batteries is vital for security of supply and sustainability. However, its benefits are unlikely to be apparent until sufficient in-use stocks exist. Establishing a CE requires robust data and models, industrial capacity, regulatory frameworks, investment in skills and social acceptance.

Acknowledgments

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4. Regulatory developments to strengthen sustainability and circularity of batteries

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Status

December 2020, the European Commission (EC) proposed a new Battery Regulation for Europe [55] to replace the Battery Directive from 2006 [56]. The new Battery Regulation implements the Strategic Action Plan on Batteries [57] as part of European Green Deal [58], and follows the Circular Economy Action Plan [59] from 2020, which states that new regulatory framework for batteries will consider sustainability and transparency requirements, taking into account carbon footprint of battery manufacturing, ethical sourcing of raw materials and facilitate establishment of a circular value chain for reuse, repurposing and recycling of batteries to recover critical materials. To reach the objectives and address the entire lifecycle of all batteries placed on the Union market, the Battery Directive is replaced by a Regulation, thus safeguarding the integrity of the internal market, ensuring uniform application for all operators across the Union and avoiding divergent implementation by Member States, which could distort competition and create trade barriers [55]. Following the co-decision process and the trilogue between the European Parliament, the Council and EC, a compromise text of the EU Battery Regulation was published 18 January 2023 [60]. The European Parliament and council adopted the Battery regulation on 12 July 2023 [61]. The regulation was published in the Official Journal on 28 July 2023 and entered into force in all member states on 18 August 2023.

In addition to the categories of the Battery Directive portable, SLI (starter, lighting, ignition) and industrial batteries, the regulation identifies traction batteries for electric vehicles (EV) and light means of transport (LMT) as two new categories, based on their large and growing part of the market [60]. Stationary energy storage as well as traction batteries for aviation, maritime, rail and off-road machinery fall under the industrial batteries. Figure 6 provides an overview of key technical provisions for sustainability and circularity and their applicability to the different battery categories. New sustainability requirements are introduced in stages, with several provisions targeting EV, industrial and LMT batteries only, such as recycled electroactive materials content, carbon footprint, battery passport, and certain performance and durability requirements. For portable batteries, there is a long-term target to phase out non-rechargeable batteries of general use [55, 60].

The Battery Regulation is the first legislation that covers the entire product lifecycle, from cradle to cradle. According to Carrol [62], the Battery Regulation will make batteries produced in Europe the most sustainable in the world and may become a benchmark for the entire global battery market as it applies to all batteries that are placed on the EU market.

Current and future challenges

IEA [63] reports that the EV market has seen exponential growth in 2022, as sales exceed 10 million, or 14% of global new car sales. The global outlook for 2030 is that EV will increase to 35% of new car sales based on existing policies. While this contributes to the decarbonization of the transport sector, the increasing demand and use of lithium-ion batteries (LIB) can lead to scarcity of critical raw material resources [64–66] as well as pose a risk of a huge future waste problem [67]. Improved recycling technologies and more efficient collection of end-of-life batteries to create a circular value chain of materials has been identified as key elements to mitigate both concerns [64–68]. However, the value of recovered materials must be greater or equal to the cost for extracting new materials for recycling to be economically viable [65]. Recycling of LIB is complex due to extremely variable formulations which complicates separation and engineering designs [67]. Both positive and negative environmental impacts can be achieved by using recovered materials to produce new batteries, depending on the LIB cell chemistry and the recycling process chosen [66]. It is critical that the regulation provides the decisive incentives to implement a resilient circular economy system [66].

The objective of circular economy is to optimize the use of objects and to preserve the use of the stocks of objects and the materials they comprise at their highest utility and value levels [69]. It is generally accepted that circularity is facilitated by fast return to use, i.e. relatively short lifecycles in each loop. EV and energy storage batteries are typically designed for relatively long life. EV battery lifespan estimates in the literature range from 8–20 years [68]. Repurposing of end-of-life EV batteries further delays recycling and recovery of materials. The assumed life-expectancy of batteries has a major impact on the availability of recycled materials for new batteries. Calculations by Hoarau and Lorang [68] indicate that available metals from recycling barely reach 4% of all metal inputs with an assumed lifespan of 12 years. Thus, there is a potential conflict of interest in the Battery Regulation when it simultaneously pushes for extended useable battery life by durability requirements in first life followed by additional life through repurposing while enforcing

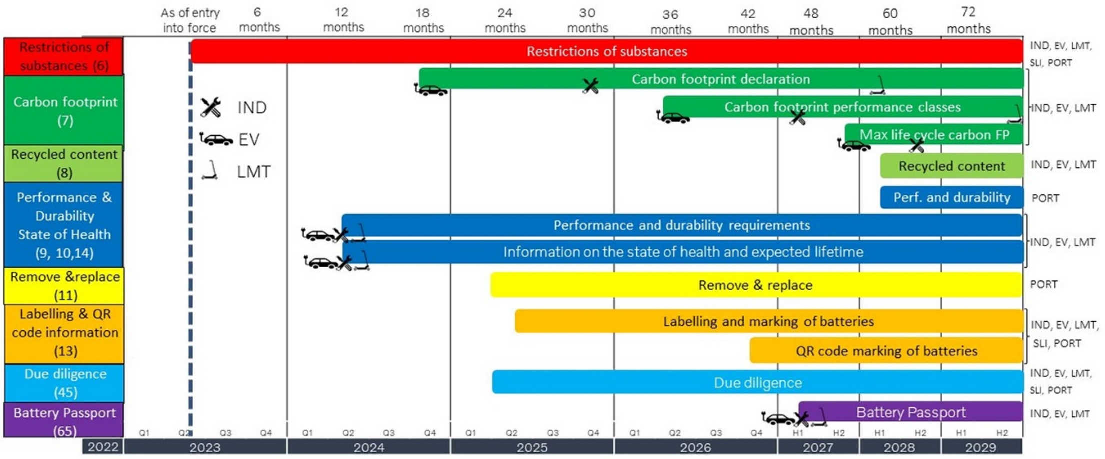

Figure 6. Projected time plan for entry into force of key provisions in the EU Battery Regulation until 2030, assuming adoption in June 2023, based on the compromise text in [60]. The symbols indicate when a provision starts to apply to different applications. IND = industrial batteries > 2 kWh; EV = electric vehicle batteries; LMT = light means of transport batteries; SLI = starter-, lighting- and ignition batteries; PORT = portable batteries. The respective regulation article numbers are given in parenthesis to the left in the figure.

aggressive provisions on recycled content for lithium (6%), nickel (6%) and cobalt (16%) in 2030, increasing to 12%, 15% and 26%, respectively, by 2035.

Advances in science and technology to meet challenges

Several authors stress the need for improved recycling processes to guarantee supply of critical materials [64–68]. Most methods proposed in literature are based on lab-scale experiments and the applicability into large-scale industrial recycling remains to be confirmed [70]. The effects of differing impurity profiles between virgin materials and secondary raw materials also need to be clarified. Copper, aluminium, iron, carbon, fluorine and phosphorous contaminants are expected in recycled battery materials. There is a lack of knowledge on how these affect materials properties and the electrochemistry of the battery. Inclusion of copper can decrease the initial specific capacity [71] and aluminium can increase capacity fade [72].

Development of new battery chemistries will continue, driven by demands for higher energy densities, faster charging capabilities and longer cycle lives. Recycling technologies will have to continually evolve to meet the challenges of new chemical formulations. Hydrometallurgical processes are promising, as new battery precursors can be produced with sufficient purity [66, 70]. However, direct recycling, i.e. recovery of the electroactive materials themselves rather than substance separation, is gaining interest [68]. This process requires relithiation of the cathode material to replenish lithium lost during the use of the battery, and technology is needed to address this challenge. Furthermore, contaminating rock salt phases need to be removed from the recovered layered oxide cathode materials [70].

Traceability of static and dynamic data for each individual battery during its entire lifecycle is another challenge. Figure 7 shows a schematic of the data collection and processing needs required to develop a digital twin and provide data for the battery passport for EV batteries.

This puts high demands on connected internal data sources as well as the ability to remotely access data from both installed and detached traction batteries. Blockchain is a powerful tool to manage and track digital identities of batteries through the entire lifecycle from material extraction, though production and use to disposal and recycling [65]. However, the technology is expensive and there may be resistance from stakeholders to share certain data. Furthermore, scalability and high energy consumption create barriers to wide adoption that need to be resolved.

Finally, new business models that enable internalization of social and environmental costs and benefits in the economic valuation are needed [73]. In-depth studies on the diversity of implemented circular economy strategies is lacking, including stakeholder interactions, relationships and roles in order to understand how the strategies work in practice.

Concluding remarks

The new EU Battery Regulation will bring about both technical and non-technical challenges to industry and society, as new business models need to be developed to support a sustainable and circular battery value chain and more efficient use of critical resources. A key element for a resilient circular economy is reliable data sharing between all stakeholders.

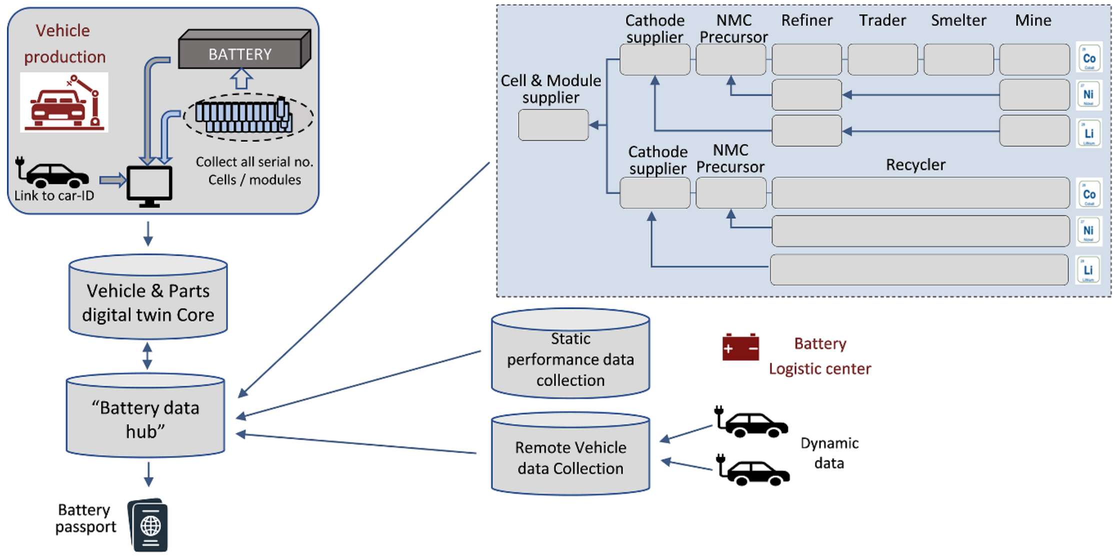

Figure 7. Schematic example of the data collection and processing steps towards the electric vehicle battery passport.

The strategic importance of batteries for reaching the EC's overall goal of climate neutrality is highlighted and reflected in the EU Battery Regulation addressing environmental, social and internal market aspects across the entire battery value chain. The new EU Battery Regulation is likely to influence future battery legislation in other parts of the world and inspire similar legislations in other geographic regions as the global battery market continues to grow exponentially and the geopolitical challenges and needs to secure supply chains intensify.

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5. An industrial perspective on the future of sustainable batteries

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Introduction

The development of sustainable batteries can be considered from a number of different perspectives, as can be understood by considering the United Nations' 17 Sustainable Development Goals [74]. While the most obvious goal, justifying the development of energy storage technologies, is number 7 (affordable and clean energy), there are many others that are relevant to improving the sustainability factors of batteries. These include, for example, goals 3 (good health and well-being), 12 (responsible consumption and production), 14 (life below water), and 15 (life on land).

With these in mind there are several strategies that can be considered in the development of more sustainable batteries. For example, there are a number of Critical Raw Materials (CRMs) employed in batteries, which as defined by the European Union are those materials which currently present a supply risk when set against their economic importance [40, 75]. The replacement of CRMs, or materials which raise ethical concerns for their sourcing, or those which are becoming prohibitively expensive (preventing adoption of technology) is one route to improving battery sustainability. Another is the use of materials that are safer to human health; for example, employing less toxic or less flammable materials inside batteries themselves, or removing toxic process chemicals during manufacture. Such measures may furthermore have the additional benefit of cost savings. Moreover, the use of less toxic materials, for example fluorinated polymers and electrolytes, can offer environmental benefits in the event that the device is improperly disposed of or to aid during recycling processes.

Batteries could also become more sustainable via decreasing the CO_2 footprint in the whole supply chain, from mining to cell and package production, as well as recycling. Electrification of the mining industry and expansion of localized mining to decrease transportation of raw materials will in the future have an impact on making batteries more sustainable. There is also a high interest to decrease energy consumption during material synthesis, cell production, and recycling.

Active materials, electrolytes and other components

A large number of compounds are used already in lithium-ion batteries (LIBs), and can vary widely with a diverse range of battery chemistries available on the market. Since the initial commercialisation of LIBs, the revolutionary $LiCoO_2$ (LCO) cathode material has now evolved into what we know as the NMC ($LiNi_{1-x-y}Mn_xCo_yO_2$) family of materials [76]. This is a result of replacing some of the cobalt in the structure with nickel and manganese to, for example, create $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ ('NMC111'). The removal of cobalt (a CRM, according to the EU) is seen as a way to, not only improve the sustainability factors of the cathode, but also results in higher capacities the more nickel is introduced and reduces cost with greater fractions of manganese [77]. However, the trade-offs may be greater reactivity to moisture and the electrolyte, and lower stability, respectively, while removing cobalt could result in poor performance at high rates. Meanwhile, other cathode materials are also being considered for large-scale use, including lithium iron phosphate (LFP, $LiFePO_4$) and spinel-phase lithium nickel manganese oxide ($LiNi_{0.5}Mn_{1.5}O_4$) [78]. The use of iron and manganese, and the removal of cobalt from these materials, presents an improved sustainability. However, they each pose challenges, for example, maintaining comparable energy densities and long-term cycling stability [79].

On the anode side, natural graphite is another material categorised by the EU as a CRM. In recent years, silicon has become an interesting material to use in place of graphite, especially for batteries in automotive applications, but it is not yet used in large scale in commercial cells. Silicon offers an approximate ten-fold theoretical specific capacity and 2–3 times higher volumetric energy density compared to graphite [80]. However, silicon is an example of how the sustainability topic for batteries can be complicated. While silicon is an abundant element in Earth's crust and thus quite cheap, most state-of-the-art technologies to make a practical silicon anode involve some rather complicated and expensive engineering, in which toxic silane gas is used to produce silicon. This highlights that though using naturally abundant elements is an important criterion, the whole process from mining, to active material production, and recycling needs to be considered to provide a full picture of sustainability.

One of the main strategies for developing more sustainable batteries is to move away completely from lithium (also one of the EU's CRMs) towards batteries based on naturally abundant elements such as sodium, potassium, magnesium, calcium, and aluminium. Among those, sodium-ion batteries have been developed faster and are currently being commercialized in China, while under industrialization in EU and

US [81]. The sodium-ion battery technology has the potential to improve the sustainability of batteries to a completely new level, especially when no cobalt, nickel, copper, lithium, and graphite compounds are used. Such independency from CRMs and expensive materials will decrease the cost of battery cell production. However, the recycling of sodium-ion batteries is still largely unexplored as such batteries contain no expensive elements to make recycling profitable. Similarly, the use of non-flammable and halogen-free electrolytes is also seen as a progression towards sustainability as they offer enhanced safety and reduced toxicity of the battery [82, 83].

Electrode processing/coating

The use of fluorine-free binders in recent years, particularly in the preparation of graphite-based electrode sheets, has allowed for the growth of aqueous processing [84, 85]. The use of water as a solvent rather than, for example *N*-methyl-2-pyrrolidone (as used for polyvinylidene fluoride), enables a safer preparation of the slurry that is used for electrode preparation. There are several water-based binders available, but some of the most common are carboxymethyl cellulose and styrene-butadiene rubber.

Another approach is to remove solvents altogether from the electrode fabrication process and opt for a recently-developed method known as dry-coating [86]. Dry-coating has the advantage of not needing large quantities of solvent as used in the traditional coating method. This not only reduces the risk to workers of exposure to toxic chemicals, but also saves on materials costs and potential damage to the environment through the disposal of solvent waste.

Cell production

The production of Lithium-ion batteries has been considered to be profitable via ‘economies of scale’ as the profit margin for cell production is not substantial. Therefore, there is an intense effort to decrease the cost at any possible step of cell production. Electrode materials constitute the major cost of LIBs, however, different steps of cell production especially formation/ageing increase the cost of cell production [84, 87]. In addition, a high amount of energy is consumed through dry room environments and in drying and solvent recovery processes, *i.e.* about 29% and 47% of the total energy consumption during cell production [87]. Therefore, optimization of all steps in cell production to decrease the energy consumption could improve the sustainability of LIBs.

Recycling

Along with the rapid increase in the number of ‘gigafactories’, the recycling of LIBs has become very important to ensure electrification of different sectors fulfilling sustainability aspects. The volume of waste produced during mining and cell production and the number of batteries at the end of life will soon become a large amount, requiring well-stablished large scale recycling facilities. There are a few major recycling methods, namely hydrometallurgical, pyrometallurgical and direct recycling, used to recycling LIBs [70]. The main challenge, however, is to ensure the recycling processes produce few side products and negative environmental impacts while they remain economically profitable. As industry is moving towards lowering or eliminating use of CRMs, recycling of LIBs becomes less economically favourable. Therefore, this requires united policies to ensure industries and societies seriously take suitability aspects into consideration when considering profit.

6. Zero-excess lithium batteries

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Status

Lithium metal is considered the 'holy grail' anode for battery technology because of its high energy density resulting from its lowest reduction potential (−3.04 V vs the standard hydrogen electrode) and low atomic weight (3860 mAh g^{-1}, 2060 Ah l^{-1}). For these reasons lithium metal batteries have been investigated as far back as the 1970s by Whittingham and Dahn for commercial applications before they had to be taken off the market due to safety concerns [88]. Zero-excess lithium batteries (ZELBs) contain all lithium within the cathode on assembly, forming a lithium metal anode on the initial charge. This architecture is required to reach the highest possible energy densities. Recently, the push for longer driving ranges on electric vehicles (EVs) and lightweight batteries for aerospace applications have driven renewed interest in ZELBs as commercial Li-ion batteries with traditional graphite anodes are reaching their theoretical energy limits. As shown in Figure 8, ZELBs with high energy cathodes could push gravimetric energy densities over 450 Wh kg^{-1} and volumetric energy densities over 1200 Wh l^{-1} [89].

Commonly, excess high-purity lithium metal foil is used as the anode to compensate for irreversible capacity loss during cycling. Lithium metal production is expensive and energy-intensive potentially raising the cost/kWh metric above some Li-ion options [90]. Typically, Li_2CO_3 is converted to LiCl and purified via electrowinning at 380 °C–500 °C requiring 30–40 kWh $kg_{Li}{}^{-1}$ while producing toxic chlorine gas [91]. Forming a lithium foil for manufacture requires passivation for handling even in dry rooms due to its high reactivity, which can lead to contamination and inconsistent performance due to the difficulty in reproducing the passivation layer [92]. By contrast, in ZELBs all the lithium is contained in the cathode so similar manufacturing methods to commercial Li-ion batteries can be used. By using a minimal amount of lithium and incorporating it into the cathode where it is easier to handle, ZELBs are a more sustainable alternative to achieve the highest energy density batteries.

To be practical for high energy density applications such as transport, ZELBs must also have a cycle life and safety record comparable to Li-ion batteries. Significant safety improvements have been made by moving away from the flammable carbonate electrolytes used in commercial Li-ion batteries to low volatility solvents, flame retardant salts, or solid electrolytes [93]. The lack of excess reactive lithium also increases safety. However, capacity retention remains a major barrier to obtaining a practical cycle life; to retain 80% of the initial capacity after 1000 cycles a coulombic efficiency (CE) of 99.978% is required [94]. The initial plating of lithium is of particular concern in ZELBs as it regularly shows the poorest CE.

Current and future challenges

Some of the challenges of ZELBs are the same as those faced by excess lithium metal batteries, such as the formation of inactive 'dead' lithium and lithium-electrolyte reactions forming a thick solid electrolyte interphase (SEI) [94]. However, without excess lithium, ZELBs must maintain a CE of 99.978%. The initial half cycle normally experiences an unacceptably low CE due to plating lithium directly onto the current collector (CC). A high nucleation barrier on the CC encourages non-uniform growth and exacerbates the challenges experienced by lithium metal [93]. Exposing copper and lithium to an electrolyte leads to the additional complication of galvanic corrosion, which is detrimental to calendar life and highly dependent on SEI quality [95]. Unfortunately, anode volume change with lithium and particularly in ZELBs causes fracture of the SEI unless it has exceptional fracture toughness [96].

The current collector can be modified to protect lithium and promote uniform plating. It was determined computationally that CCs, including lithium alloys, within an optimal adsorption free energy range cause good lithium adherence ('lithiophilicity') while maintaining sufficient surface diffusion to facilitate smooth deposition morphologies [97, 98]. 3D host structures which contain and direct lithium growth have also been investigated, however their thickness can significantly reduce energy density [89]. Alternatively, thin, mechanically stable, ionically conducting, and electronically insulating surface coatings have been shown to encourage dense lithium growth and limit parasitic reactions. Metal oxide surface coatings via atomic layer deposition (ALD) have demonstrated improved CEs with depositions thin enough not to significantly impact energy density [99]. The efficacy of each approach is mainly evaluated using CE, but use of different cut-off potentials and cycling parameters make it difficult to determine the origin of inefficiencies and compare data across the literature [96].

While most reported ZELBs use liquid electrolytes, solid state electrolytes promise improvements in energy density and safety. A 2020 Samsung paper sparked interest in mixed ionically and electronically

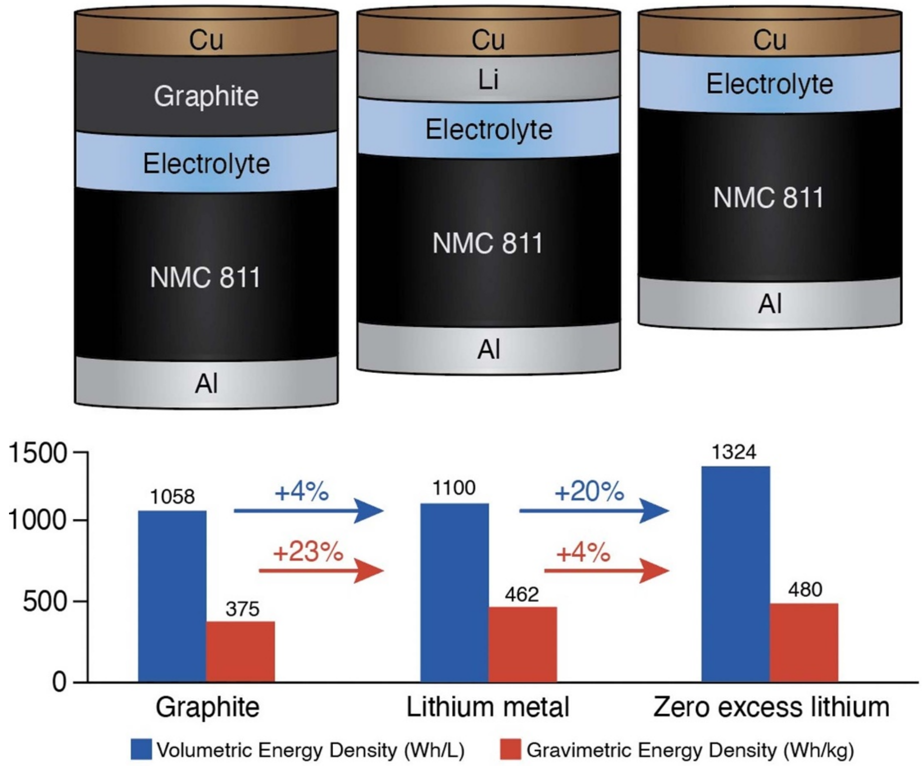

Figure 8. Summary of energy densities of batteries at the stack level with a NMC811 cathode and graphite, excess lithium with a N/P ratio of 2, or a zero-excess lithium anode. All cells assume an areal capacity of 4 mAh cm^{-2} and volumetric energy densities are calculated at the charged state. Schematics not to scale. Calculated values based on those reported by Lohrberg *et al* [89]. Adapted from [89]. CC BY 4.0. © 2023 The Authors. Advanced Functional Materials published by Wiley-VCH GmbH.

conductive interlayers as their use of a carbon interlayer containing silver nanoparticles with a Li_6PS_5Cl solid electrolyte demonstrated >80% capacity retention after 1000 cycles at 60 °C and 2 MPa of applied pressure [100]. This performance is promising, but the underlying mechanism is not well understood yet [101].

Advances in science and technology to meet challenges

For ZELBs to achieve the required performance, strategies to improve plating morphology and lithium protection must be used in tandem. Improving the lithiophilicity of surfaces by using lithium alloys should be combined with thin surface layers which can protect lithium after deposition. Optimisation of these layers is required to ensure they are thin enough not to cause high impedance or reduce energy density while being thick enough to sufficiently passivate lithium even through high volume change cycling. Additionally, optimised cycling protocols have been shown to significantly aid in maintaining a high CE, specifically asymmetric slow charge fast discharge and formation cycles prior to running the cells to create a stable SEI [102]. Higher current densities are still needed to compete with Li-ion batteries.

For all areas of improvement, in particular solid state, a better understanding of the underlying mechanisms affecting CE are needed. Characterisation advances have improved understanding of the underlying degradation mechanisms in ZELBs, notably with the application of cryo-microscopy and quantification of inactive lithium [103, 104]. However, the highly air and beam sensitive nature of battery materials, particularly Li and the SEI, means often the techniques which have been developed are resource-intensive, destructive, and ex-situ potentially leading to the introduction of artifacts in the data, such as has recently been observed with x-ray photoelectron spectroscopy [105]. Therefore, further work is needed to develop characterisation techniques *in-situ* or preferably *operando* to capture the state of the lithium and SEI with both spatial and temporal resolution so their evolution mechanisms and the impact this has on battery performance can be better understood.

Even with these advances, maintaining a CE of 99.978% will be difficult. Therefore, methods of introducing excess lithium within the cathode to maintain sustainability advantages on assembly should be investigated further. The 'reservoir' method limits depth of discharge after the first half cycle, leaving excess lithium metal at the anode without cathode modifications [102]. Alternatively, sacrificial additives such as $Li_2[Ni_{0.8}Mn_{0.1}Co_{0.1}]O_2$ have been added to the cathode creating an excess of lithium on first charge that is not reincorporated into the $Li[Ni_{0.8}Mn_{0.1}Co_{0.1}]O_2$ cathode on discharge [106]. Both methods have demonstrated improvements in cycle life, however the'reservoir' approach can reduce energy density below cells using graphite-Si anodes [89]. Therefore, sacrificial additives are more promising, but this is a relatively new field and further work is needed to better understand the interaction between additives and cell performance.

Concluding remarks

Achieving functional, zero-excess lithium metal batteries is a major challenge which would enable higher energy densities, while using cheaper and less energy intensive manufacturing than batteries with excess lithium. The major problem facing their implementation is maintaining at least a 99.978% coulombic efficiency. While there have been significant advances made, the required cycle life to make them competitive with Li-ion batteries has not yet been achieved under practical conditions. Therefore, perhaps urban aerospace applications where both volumetric and gravimetric energy densities are critical, but cycle life is less so would be a good fit for ZELBs [107]. Here, we have outlined some of the promising areas of research to further improve performance. However, with all these advances researchers should bear in mind the methods of materials procurement, battery production, and potential for end-of-life recyclability. This will enable ZELBs to be developed while fitting into a wider infrastructure of sustainable batteries.

Acknowledgments

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7. Sustainable cathodes for lithium-based chemistries

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Status

Cathode active materials (CAMs) for lithium-ion batteries (LIBs) rely on three main families of inorganic compounds: layered oxides, spinel, and polyanionic compounds. Over the last decades, extensive research efforts have focused on developing novel CAMs with improved performance in terms of energy and power density, lifespan, safety and cost. Cost is probably one of the most determining criteria for large-volume applications. The cathode indeed accounts for ∼20% of the total cost of LIBs, and in the meantime, significantly impacts the energy and power density of the battery [108].

As the demand for LIBs grows, sustainability considerations have become increasingly important in CAMs selection. For instance, cobalt, which is a key element in layered oxide CAMs, is expensive and raises ethical and environmental concerns associated with its mining and processing. To address these issues as well as to increase the energy density, cobalt has been partially substituted in the pioneer $LiCoO_2$ with more sustainable metals, and $Li[Ni_xCo_{1-x-y}Al_y]O_2$ (NCA) and $Li[Ni_xMn_yCo_{1-x-y}]O_2$ (NMC) are currently well-established cathode chemistries in commercial LIBs [109].

Spinel $LiMn_2O_4$ (LMO) provides a remarkable cobalt-free alternative. It exhibits intrinsic structural stability, reducing the risk of thermal runaway compared to layered oxide materials. However, its lower energy density compared to NMC and NCA materials, as well as issues with manganese dissolution have limited its widespread adoption. LMO is however commonly used in blends with NMC/NCA to gain power performance [110–112].

Polyanionic compounds based on Earth-abundant elements like iron offer a large variety of compositions and structures, that in general, provide enhanced stability compared to oxides, but operate at lower potentials. LFP, which has been established as the optimal environmentally friendly CAM, can be prepared at moderate temperatures using various synthetic approaches which differ in terms of atom economy and management of the gases released [110]. Carbon coating of LFP is an integral feature of the production process to cope with its low electronic conductivity. Therefore, the use of inert or partially reducing atmospheres increases costs but simultaneously promotes the Fe^{2+} oxidation state required for the target phase. Although at present, the economic advantages of LFP technology compared to less sustainable technologies like NMC materials are still under debate [113], some recent studies predict trajectories to lower prices for LFP technology in the LIBs market by 2030 [114].

Current and future challenges

One of the major challenges of LIBs remains improving their energy density, which is to a great extent limited by the positive electrode [115]. Substituting iron with manganese in polyanionic compounds has the potential to increase their energy density by raising their redox potential. The lower power capability of Mn-based polyanionic compounds compared to Fe-based ones is being addressed at industrial level by developing blends of $Li(Mn,Fe)PO_4$ and NMC materials, whose synergistic behaviour enables fast kinetics.

Spinel $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) is a promising candidate for Co-free cathodes for high voltage applications, offering excellent thermal stability and reduced synthesis cost. Successful implementation of LNMO in commercial LIBs requires however the development of stable electrolytes for high-voltage operation and addressing capacity fading of full cells caused by transition metal dissolution [79].

As for layered oxides, Ni-rich chemistries (e.g. NMC-622, NMC-811, and beyond) allow to enhance energy density while decreasing the use of controversial Co, but face challenges such as lower cycling and thermal stability. Different approaches can mitigate these issues, including secondary particles engineering, development of single crystalline materials and/or designing gradient-concentration particles with Ni-rich cores and Mn-rich shells [116]. Ni-rich NCA chemistries, on the other hand, inhibit transition metal dissolution and delay surface degradation and capacity fading [117].

Another strategy for enhancing the energy density is pursued with lithium-rich layered oxides, which offer extra capacity by involving the anionic redox reactions in the overall redox process. However, these materials face challenges such as low initial coulombic efficiencies, voltage fading due to structural transformations, and poor rate capability in full cells [118]. Anionic redox was also predicted in N-doped polyanionic compounds [119], although experimental demonstration has not yet been achieved. In the last years, significant efforts have been dedicated to comprehending the mechanisms underlying anionic redox in order to fully harness this promising approach [120].

An alternative approach for improving Li-based battery technology involves replacing 3D-metal-based CAMs by renewable organic materials synthesized from natural sources via green chemistry. However, hurdles such as their low redox potential and low volumetric energy density still prevent their practical implementation [121].

Besides the CAMs performances, challenges also arise in scaling up production maintaining sustainable practices regarding manufacturing processes and responsible sourcing of raw materials. For instance, the production and processing of Ni-rich and Li-rich materials are particularly sensitive to humidity, leading to higher costs. Furthermore, as nickel is a finite resource, the growing demand for nickel-rich cathodes raises concerns about future availability and cost, emphasizing the need for recycling efforts. In terms of electrode processing, the development of suitable binders, preferably fluorine-free for improved sustainability, is crucial for fabricating high mass loading electrodes with excellent mechanical properties, thus increasing energy density and meeting industry requirements. Shifting from organic to aqueous and dry processing is a current challenge that researchers and industry are actively addressing [122].

Advances in science and technology to meet challenges

Increasing the energy density of current LIBs continues to require important research efforts on novel CAMs. Material Acceleration Platforms (MAPs) can significantly accelerate the R&D process by efficiently screening and evaluating a wide range of materials, accelerating the development of new CAMs with improved performance and sustainable characteristics [123].

Another critical aspect is the development of comprehensive characterization techniques for a deep understanding of CAMs and their reaction mechanisms [124]. In particular, this knowledge is essential for tailoring and controlling anionic redox processes. By gaining insights into the complex electrochemical processes within CAMs, scientists can optimize their design and performance.

Next, advancements in coatings of highly reactive CAMs as well as cathode-electrolyte interface (CEI) engineering are required to improve electrode processing and longevity of LIBs. These are also necessary to integrate CAMs in polymer and ceramic solid-state batteries, developing new processing methods scalable at industrial level [125].

Besides, battery recycling also presents a significant challenge [1]. Since the integrity of CAMs is often not the primary cause of battery failure, there is a great potential in developing Direct Recycling methodologies to recover and refurbishing of CAMs without reducing them down to raw metal precursors and subsequent resynthesis, thereby enabling their reuse in new batteries. However, the feasibility of such an approach at a competitive cost compared to conventional recycling methods remains uncertain. Additionally, finding economically viable approaches to recycle low-cost elements like iron for LFP-based batteries is crucial for establishing a sustainable battery ecosystem. Another complexity arises with the lack of transparency and consistency in the chemistry of recovered batteries, preventing them from being categorized based on their chemistry, and hindering the implementation of an efficient recycling process. Addressing these issues necessitates the formulation of new policies that incentivize and support investments in more environmentally friendly recycling practices, see chapter 16 for more details on recycling.

Concluding remarks

Developing sustainable cathodes for LIBs is a complex and multifaceted challenge that requires interdisciplinary collaboration between materials chemistry, materials engineering, manufacturing technology and recycling solutions, which involve academic research, industry, and policy makers. Advances in these areas will help to accelerate the development of more sustainable and efficient cathode materials for Li-based batteries, which can in turn help to accelerate the transition to a more sustainable energy future.

Acknowledgments

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8. Sustainable anodes for alkali metal batteries

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Status

Since their introduction in 1990, rechargeable Li-ion batteries have transformed portable electronics and are the leading energy storage technology for electric vehicles and grid-scale applications [126]. However, concerns about future lithium costs, sustainability, end of life, social equity, and material distribution [127] have fuelled the exploration of alternative and sustainable battery materials and technologies.

Currently, natural graphite is the predominate anode material used in commercial Li-ion batteries with a market share of over 98%. This non-renewable material is only mined in select few countries leading the EU to label it as a critical resource [128]. Synthetic graphite is an alternative, but its more expensive and derived from petroleum resources hampering its sustainability. Furthermore, graphite has a limited capacity of 372 mAh g^{-1} as only a single Li^+ can be stored for every six carbon atoms, thus limiting the overall energy density of Li ion batteries [126]. Substituting the graphite anode with materials that can store a higher number of Li^+ per unit volume will reduce the size of the anode, lowering the amount of material needed to create a Li-ion battery while improving the energy density. Realistically, we need to shift away from pure graphite anodes as the next generation of electric vehicles will require a significant leap in overall energy density, from 250 to 500 Wh kg^{-1}, however at the same time we need to also maximise lifetime. Thus, significant scope exists to improve the sustainability of Li-ion batteries via increasing the capacity of the anode, however sustainability (including lifetime) still needs to be placed at the forefront over pure performance in the development of these materials. Another thing that ust be considered in volumetric energy density whereby the density of the elecrodes must be considered.

Alternatively, the sustainability can be enhanced by changing the ion chemistry from Li to a more sustainable alkali metal ion, such as Na and K. Swapping Li with Na has several benefits, Na is more abundant, can use Al instead of Cu current collectors, and the hard-carbon anode can be synthesised from renewable biomaterials [129]. However, Na and K-ion batteries currently suffer from significantly lower energy density than Li-ion, limiting their commercial applications. This is due to issues with the hard-carbon anode, such as understanding specifically how Na^+ are stored, preventing tailoring the anode for maximum performance [130]. Thus, further development of the anode is needed before they can be a viable alternative to Li-ion.

Current and future challenges

Several potential alternatives to the graphite anode in Li-ion batteries exist, including synthetic graphite, metal oxides, alloying metals, polymers, MOFs, and biobased carbon materials. Of these, metal oxides and alloying materials (Si, Sn, Ge, Mg, and Al) are the most promising as they offer significantly higher storage capacities [131]. Silicon is the most investigated as it has the highest capacity (4200 mAh g^{-1}) [131], however it is problematic from a sustainability perspective. The manufacture of metal grade silicon produces between 10.2 and 12.6 metric tonnes of CO_2 per ton of silicon as it needs H2 which is curently made from fosil resources. This figure comes before any additional refinement needed to create Si based anodes. Thus, alternative alloys and metal oxides need to be pursued (e.g. phosphorus based).

Graphite's success in Li-ion is due to its limited volume expansion (<10%) when Li-ions are inserted and removed under cycling. Comparatively, Si, Sn and P anodes experience 250%–400% volume expansion [131]. This has two major impacts, (i) pulverisation of the electrode leading to delamination from the current collector, and (ii) broken solid electrolyte interface (SEI) layer that in-turn creates a new SEI layer in each cycle trapping Li. The result in rapid capacity loss and ultimately premature cell failure. Solving the issue of anode expansion is one of the major challenges for incorporating these materials as anodes.

Na and K-ion batteries can also use various alloying or metal oxides to improve the capacity, but they also suffer from the volume expansion issue. One approach is to integrate metal oxides or alloys with carbon materials that can accommodate the volume expansion, provide conductivity, and protect the SEI layer. Additionally, these carbon materials can be sourced from sustainable biomaterials, while reducing the amount of alloy in the electrode. Unfortunately, as the ratio of carbon to alloy increases, the overall capacity of the anode suffers. Thus, the challenge is to maintain the higher capacity of these materials but still allow for the long term cyclability.

Finally, current manufacturing processes need to be overhauled to remove fluorinated binders and problematic organic solvents. Switching to aqueous solvents or removing binders entirely will reduce the environmental impact. Consideration also needs to be given to by-products of the manufacturing process

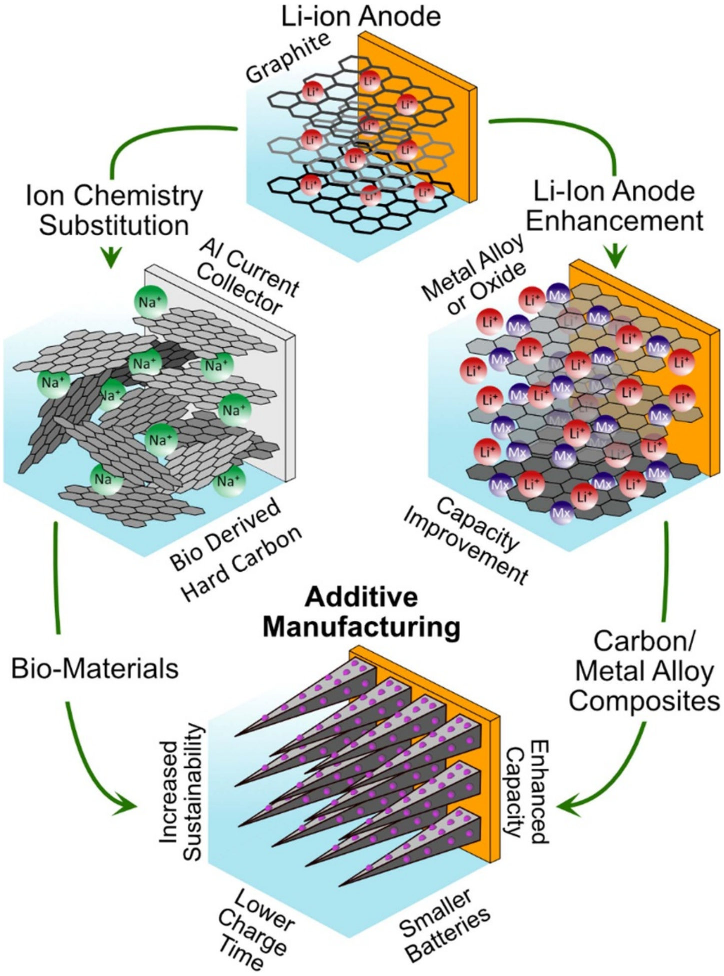

Figure 9. Pathways to improve the performance of the anode material in alkali metal batteries while improving the sustainability of the anode.

(e.g. HF in silicon processing), which need to be easy to dispose of safely, or integrated into other applications.

Advances in science and technology to meet challenges

To achieve high capacity, sustainable, composite material-based anodes (e.g. P/C), it is critical to move past slurry-cast stacked anodes using in conventional battery manufacturing. These offer limited control of the geometry and architecture while making it difficult to control volume expansion. Shifting towards additive manufacturing and free-standing electrodes offer the possibility of creating unique architectures that improve ion and electrical conductivity, remove components (e.g. binder, current collector), impart mechanical properties (e.g. flexibility), and can be integrated around the components they are powering (figure 9).

Free-standing electrodes from spinning techniques (e.g. electrospinning) can create flexible binder-free conductive electrodes. For example, 986 mAh g^{-1} (1 A g^{-1}) was achieved after 2000 cycles using a hollow $Sn/SnO_2@C$ nanofiber anode (li-ion) from electrospinning and controlled annealing [132]. Biomaterials, such as lignin, can also be used as the carbon precursor for forming the carbon fibers, improving the sustainability of these anodes considerably [133]. Industrial scale production of electrospun fibers is already possible, with several commercial companies offering large scale equipment to produce meters to kilometres of material on roll-to-roll reels. Future advances here will come from improving fiber throughput to lower costs and investigating spinnable biomaterials to remove the relance on petrochemical based polymers (e.g. PAN).

Additive manufacturing (3D printing) offers another solution to advance sustainable anodes (figure 9). It enables the fabrication of desirable complex architectures, precise control of the shape and thickness of electrodes, potential for lowered manufacturing cost, and potentially eliminating the need for device assembly. For example, Liu printed a comb-like 3D SiO@C/graphite anode and 3D $LiFePO_4$ cathode that interdigitated into a full cell that had an impressive aerial capacity of 33.2 mAh cm^{-2} [134]. Recent progress in additive manufacturing has also shown the possibility of printing the entire battery, which can significantly reduce manufacturing requirements. Considering that industrial scale additive manufacturing equipment is now commercially available for a wide range of different materials and projects, it is likely that battery manufacturing will be headed in the same direction. However, the big challenge for additive manufacturing is reducing the amount of binder needed for stable printing, improving print times, and developing print heads that can print architectures smaller than the microscale currently available. Printing at the nanoscale will allow the development of architectures that efficiently move ions through the anode, improving cycle stability and charge rate.

Lastly, the end-of-life considerations for all these anode materials needs to be also be gven importance in adition to performance metrics, as they are curently not recycled. If this cannot be achieved, at the least the anode materials need to be easy to disassemble without risk, reused or bioderaded.

Concluding remarks

To enhance the sustainability of Li-ion batteries, it is crucial to explore alternative materials and ion chemistries beyond graphite anodes. For anode materials to be considered fully sustainable, they need to originate from abundant or renewable sources, obtained through ethical means, as well as being biodegradable or recoverable. Improving the capacity or life of the anode is also critical as it means the battery is likely to ‘pay back’ the energy lost from production. Performance remains the key consideration in anode development, however there is an increasing focus on investigating sustainable materials, with both factors now driving materials discovery.

In addition to material advancements, sustainability can be further improved by adopting new manufacturing technologies that reduce the number of battery components and enable specific architectures. For example, batteries can be moulded around the components they power, minimizing the need for excessive cabling and reducing resistance. Consequently, achieving truly sustainable battery materials necessitates not only exploring sustainable materials but also embracing innovative manufacturing techniques that align with the principles of a circular economy.

Acknowledgments

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9. Na-ion and K-ion batteries

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Status

Na-ion and K-ion batteries (NIBs and KIBs) have gained interest as sustainable next-generation batteries. The main advantage of these batteries is the abundant resources of Na and K compared with Li. Li is present in the Earth's crust at about 20 ppm, while Na and K exist at >1% (figure 10(a)) [135, 136]. In addition, neither Na nor K thermodynamically forms the binary intermetallic compounds with Al [137, 138], unlike Al–Li formation in the Li system. This allows cheaper Al foil as the current collector, rather than the Cu foil commonly used in LIBs, for NIB and KIB negative electrodes.

The different carrier ions impart unique characteristics to NIBs and KIBs. Although the increased atomic weight will disadvantage weight per electric charge, there are also advantages to utilizing these heavier and larger carrier ions. Their larger ionic radii would enable high-power batteries due to their lower surface charge densities, which reduce their interaction with Lewis bases, such as solvents and electrolyte salts, resulting in lower electrolyte viscosity and higher ionic conductivity [136]. The activation energy of desolvation at the electrode interface is also expected to be lower. As a result, NIBs and KIBs may have even better fast charge–discharge performance and power density than Li-ion batteries.

The development of Na batteries has spanned decades. Some cathode and anode materials, including Na_xCoO_2 [139], have been investigated in the 1980s. We note that $NaCoO_2$ //Pb-poly(*p*-phenylene) full cell was first demonstrated by Hitachi, Showa–Denko, and Allied-Signal [137]. Due to the LIB big wave since 1991, the research motivation and activity of NIB materials almost disappeared. In the 2000s, reversible sodium insertion into HC was reported [140], and the operation of full cells combining hard carbon (HC) anodes and $NaVPO_4F$ [141] or P2-$NaNi_{1/2}Mn_{1/2}O_2$ [142] cathodes was achieved. These first-generation NIBs demonstrated reversible operation, whereas the energy densities were lower than that of graphite//$LiFePO_4$ (LFP) cells (figure 10(b)). Subsequent active development of cathode (e.g. $Na_2Mn[Fe(CN)_6]$ (NMHCF) and $Na_3V_2(PO_4)_2F_3$ (NVPF)) and anode (e.g. high-capacity HC) materials has enabled state-of-the-art NIBs to achieve energy densities equal to or higher than graphite//LFP cells per active material (figure 10(b)). Recently, some major manufacturers have announced the upcoming commercialization of NIBs, and their use in electric vehicles was also announced. Thus, the R&D activity of NIB is still increasing because high-performance NIBs are realistic alternatives to LIBs.

Compared with NIBs, KIBs are an emerging technology. Although the chemical synthesis of K graphite intercalation compounds (GICs) was reported in the 1920s, the electrochemical synthesis of K-GICs and application for KIBs' negative electrodes were first reported in 2015 [138, 143]. Further, electrochemical potassium insertion into Prussian blue, $K_xFe[Fe(CN)_6]$, was reported as early as 2004 [144]. More than a decade after this pioneering work, a KIB combining the PBA, $K_2Mn[Fe(CN)_6]$ (KMHCF), and graphite achieved a high energy density (figure 10(b)) [145].

Current and future challenges

Demonstrating sustainable batteries will certainly require not only the use of abundant elements as carrier ions, but also the development of sustainable cathode and anode materials. We summarized the minimum weight of active materials and their elements to constitute 1 kW cells for some LIBs, NIBs, and KIBs, as shown in figure 11(a). The NIBs and KIBs shown here consist only of abundant elements such as Fe and Mn, except for NVPF.

Life Cycle Assessment (LCA) is a widely accepted methodology for evaluating environmental impacts. Peters *et al* performed an LCA of NIBs and demonstrated the promise regarding environmental impacts, such as CO_2 emissions and fossil fuel consumption [18]. This work also highlighted essential challenges for sustainable material development and performance improvement. Figure 11(b) displays the contribution of major components of $HC||Na_{1.1}Ni_{0.3}Mn_{0.5}Mg_{0.05}Ti_{0.05}O_2$ to environmental impacts. The greater environmental impact of the HCs compared to the layered oxides highlights the importance of investigating its manufacturing process and raw materials like bio-wastes. However, it is important to note that sacrificing performance would not reduce the environmental impacts on an energy-density basis. Likewise, exploration of high-performance and low-Ni cathode materials is critical due to the significant environmental impact of Ni. Indeed, a recent analysis has shown that some state-of-the-art cathode materials, such as NMHCF, have lower supply risks and carbon footprints than LFP [146]. Although KIBs have not yet been subjected to a comprehensive LCA, the use of Ni-free positive electrodes and graphite negative electrodes may make them as promising as NIBs (figure 11(a)).

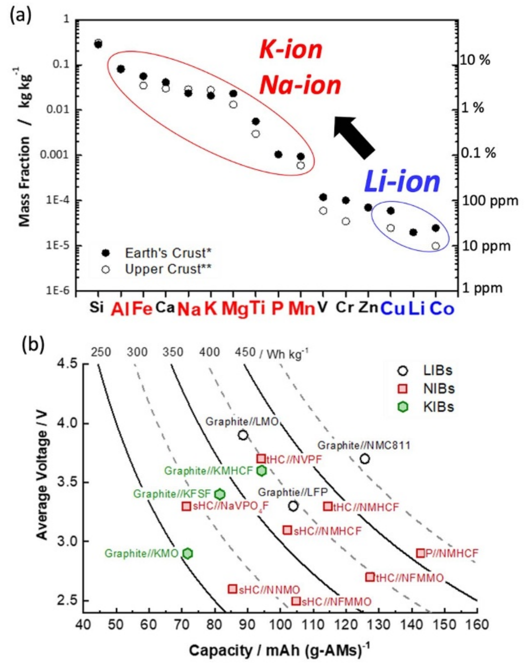

Figure 10. (a) Abundance of elements in the Earth's crust and (b) Calculated energy density per active material for several Li-ion, Na-ion and K-ion batteries. Irreversible capacity and excess capacity of negative electrode are not considered. Abbreviations for active materials are as follows: NMC811 ($LiNi_{0.8}Mn_{0.1}Co_{0.1}$), LMO ($LiMn_2O_4$), LFP ($LiFePO_4$), sHC (standard hard carbon, capacity of 250 mAh g^{-1} and potential of 0.3 V vs Na^+/Na), tHC (templated hard carbon, capacity of 480 mAh g^{-1} and potential of 0.1 V vs Na^+/Na), NVPF ($Na_3V_2(PO_4)_2F_3$), NMHCF ($Na_2Mn[Fe(CN)_6]$), NNMO ($NaNi_{1/2}Mn_{1/2}O_2$), NFMMO ($Na_{5/6}Fe_{1/3}Mn_{1/2}Mg_{1/6}O_2$), KMHCF ($K_2Mn[Fe(CN)_6]$), KFSF ($KFeSO_4F$), and KMO ($K_xMnO_2$). (a) [137] John Wiley & Sons. © 2018 The Chemical Society of Japan & Wiley-VCH Verlag GmbH & Co. KGaA, Weinhe.

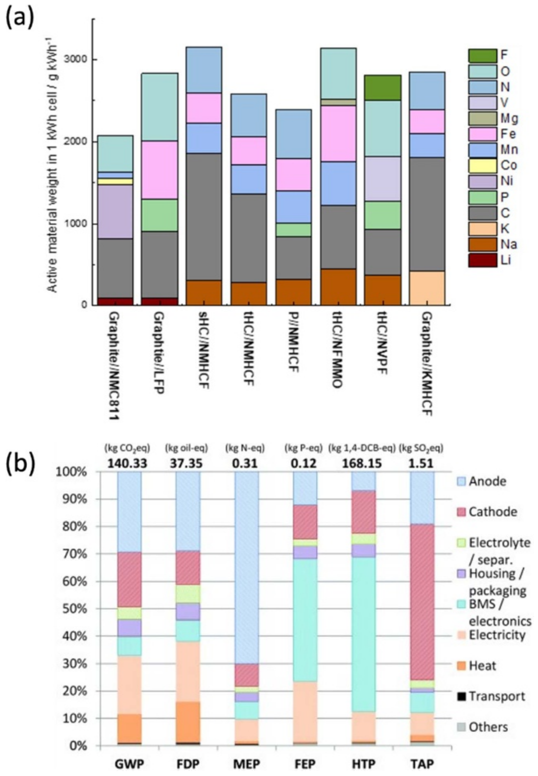

Figure 11. (a) Calculated minimum weight of active material and its elements to constitute 1 kW LIBs, NIBs, and KIBs. (b) Characterization results for the production of 1 kWh of a SIB with sugar-derived hard carbon and layered oxide of $Na_{1.1}Ni_{0.3}Mn_{0.5}Mg_{0.05}Ti_{0.05}O_2$ and contribution of the principal battery components to the overall impact per category. GWP = global warming potential, FDP = fossil depletion potential, MEP = marine eutrophication potential, HTP = human toxicity potential, TAP = terrestrial acidification potential. (b) Reproduced from [18]. CC BY 3.0.

In terms of performance, the energy density, lifetime, and charge/discharge energy efficiency significantly affect the environmental impacts [18]. Increasing the energy density of the electrodes reduces the usage of the active materials as well as the current collector, separator, electrolyte, and outer casing, resulting in a decrease in energy/material consumption per kWh. Battery life is of paramount importance. Although the degradation modes are quite complex, they primarily include active material degradation and side reactions at the electrode/electrolyte interface [147, 148]. Thus, we expected significant improvements in the cycle life by optimizing all electrode components, electrolytes, and electrolyte additives [147, 149].

In addition to the cost and sustainability, NIBs and KIBs should establish their unique strong points to compete favorably with LIBs. Based on the weak Lewis acidity of Na^+ and K^+ ions, the possible characteristics include high-power density and low-temperature operation. However, the actual reaction resistances of NIBs and KIBs, especially for the negative electrodes at low temperatures, are often reported to be higher than LIBs, possibly due to SEI-related resistance of the negative electrodes [150]. Indeed, several studies have demonstrated significant improvements in rate and low-temperature performance through electrolyte optimization [149, 151].

Advances in science and technology to meet challenges

Based on the previous discussions, the development of sustainable NIBs and KIBs will take two paths: increasing the energy density and improving the cycle life. For high energy density NIBs, O3-type layered oxides have great potential. Recent studies have reported that optimal transition metal substitution increases moisture stability, cycle life, and operating voltage [137, 152]. Thus, metal-substituted Fe- or Mn-based O3-type layered oxides, such as O3-$NaFe_{1/2}Mn_{1/2}O_2$, would be potential candidates. For the negative electrode materials, the synthesis of high-capacity HCs is a promising strategy. Recent successes in synthesizing HCs with capacities ca. 480 mAh g^{-1} [153] suggest that NIBs can match current Li-ion batteries in terms of energy density (figures 10(b) and 11(a)). Furthermore, the use of alloying or P electrodes, which have even higher capacities, and mixtures of these materials with HCs could be considered to further increase energy densities [148].

Compared with LIBs and NIBs, high-energy-density layered oxides for KIBs are limited. Thus, a more feasible strategy is to create long-life KIBs using polyanionic compounds or PBAs. Indeed, stable operation of graphite||KMHCF full cells for over 500 cycles in nonaqueous electrolytes has been achieved by developing suitable nonaqueous electrolytes and additives [149].

The realization of high-power NIBs and KIBs requires in-depth consideration of active materials, electrode structure, and liquid/solid electrolytes. Actually, previous studies suggest that the electrode/electrolyte interface or interphase design is critical [148]. Although this is a complex process lacking a unified theory, automation of electrochemical experiments, virtual screening with advanced simulations, and performance prediction by machine learning are being explored to mitigate these challenges.

All-solid-state NIBs and KIBs are of high potential for future batteries. Because of no electrochemical formation of Li–Al alloy, there are remarkable merits for cell configuration of bipolar-type stacked cells. In the case of bipolar configuration of LIB, a double-layered current collector of Al and Cu will be necessary for collecting current for positive and negative active materials. On the contrary, single-layered Al foil will be applicable for bipolar NIBs and KIBs. We emphasize that all-solid-state NIBs and KIBs will possibly be recognized as post all-solid-state LIBs.

After the long story of research and development since the 1970s, when the pioneering work of Delmas, Whittingham, and others took place, NIBs are now entering the stage of practical application. The accumulation of knowledge from practical battery operation will realize more high-performance and reliable battery technology. Considering that more than 40 years of fundamental research have paved the way for the commercialization of NIBs, the importance of fundamental research is obvious. Meanwhile, the sharing of challenges between industry and academia is expected to facilitate the development of more efficient and sustainable battery technologies.

Concluding remarks

NIBs and KIBs are emerging as viable, sustainable alternatives to Li-ion batteries owing to the abundance and unique properties of sodium and potassium. Despite their heavier weight of atoms affecting specific capacities, their larger ionic sizes offer potential advantages such as higher power densities. The state-of-the-art NIBs can achieve specific energy densities similar to graphite//$LiFePO_4$ batteries. Although KIBs are still in the early stages of development, the results show that energy density and sustainability competitive to NIBs are feasible. The key challenges for their sustainability include developing environmentally friendly electrode materials and improving battery performance, such as energy density, cycle life, and charge/discharge energy efficiency. Further development of NIBs and KIBs will require a focus on enhancing their performance. Advances in science and technology and closer collaboration between academia and industry would overcome these challenges and drive the growth of sustainable battery technologies.

Acknowledgments

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10. Multivalent batteries (Ca/Mg/Al)

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Status

A silver bullet technology is unlikely and rather a solid progress in very diverse technologies is required. In order to embrace large-scale applications more sustainable battery alternatives based on abundant materials are needed, ideally avoiding the use of Li, natural graphite, Co, Cu, Ni etc. Concepts such as Na-ion batteries are currently rapidly making their way to proper commercialization (see previous section). Other concepts are very much still in their infancy—and within these all multivalent ion based rechargeable battery technologies [154, 155]. In terms of sustainability, Mg, Ca and Al, respectively, the 7th,5th and 3rd most abundant elements on the Earth's crust, are very promising compared with Li (being 33rd) at 18 ppm even though Mg is currently being listed as a critical raw material by EU mostly due to the absence of European production [156], In addition, organic cathode materials are currently the most promising electrode for multivalent cation based batteries further enhancing the sustainability aspect of such battery technology. For any battery using metal negative electrodes, the density and redox potential of the metal itself are keys to high performance. Indeed, Ca volumetric capacity is on a par with Li, while Mg and Al are *ca*. 2 and 4 times higher, respectively (figure 12). Also metal negative electrode standard potentials are slightly higher for calcium when compared to Li (170 mV). While Mg and Al are 670 mV and 1.38 V higher than Li, respectively. Use of currently available alternative to metal anode would result in significant capacity drop leading to low energy density of full cells.

In addition, the number of M^{n+} needed to be intercalated in a positive electrode host structure is 1/n the number of Li^+ (or Na^+) necessary for an equivalent charge transfer and higher capacities are theoretically achievable. However, the maximum practical reversible capacity is limited by the number of redox centers in the host as well as the variability of their oxidation states. Also, even though small cation radius (figure 12) can arguably easily be accommodated in a host, the strong Coulombic interactions resulting are highly prohibitive and commonly results in sluggish cation mobility—both in solids and liquids. High desolvation energy barrier and poorly ion conducting passivation layers further challenge high reversibility and power performances. Overall, Ca, Mg and Al metal anode based batteries hold promises for very high energy density and low cost batteries but are currently facing many challenges which still need to be overcome before commercialization could be envisioned.

Current and future challenges

Multivalent electrolytes should enable highly efficient metal plating and stripping above 99.9% to realize the potential of multivalent metal anodes in practical cells. Targeted high efficiency of metal plating and stripping means that electrolyte must be completely stable at the metal/electrolyte interface or alternatively metal anode has to be covered by stable solid electrolyte interphase (SEI), which prevents further electrolyte decomposition while allowing cation transport. The stability of the multivalent electrolyte depends on specific multivalent metal since they vary quite a lot in their redox potential. Ca metal having the lowest redox potential, very close to Li metal, hence, it is very unlikely that decomposition of electrolyte could be completely avoided. On other hand, Mg and Al metal have considerably higher redox potentials enabling better stability at metal/electrolyte interface. Hence, state-of-the-art Mg and Al electrolytes also exemplify significantly better metal plating/stripping efficiencies than Ca ones [157, 158]. However, electrolytes stable at metal/electrolyte interface might experience significant limitations of the anodic stability, especially in combination with high-voltage cathodes. In the last years significant progress in the field of multivalent electrolytes has been achieved by utilization of weakly coordinating anions based on fluorinated alkoxy groups and carborane compounds (table 1) [159–162]. Multivalent metal anodes are often presented as alternative anode materials that circumvent the limitations of Li metal anode connected with dendrite formation and uneven deposition. For Mg, while surface diffusion barriers for adatoms might be lower before charge transfer and nucleation and growth favouring smoother deposit morphology [163, 164], studies have shown that uneven deposition in multivalent batteries can indeed occur and can lead to similar safety issues as in Li metal batteries [165, 166]. It is worth mentioning, however, that reliable value of the critical current density at which Mg dendrites start to form could not be concluded from these latter works since the Mg electrode used presented very sharp edges and was most likely, at least partially, passivated, significantly enhancing the inhomogeneity of the Mg plating. More systematic investigation regarding deposit morphology and estimation of critical current density at which dendrite are formed is much needed,

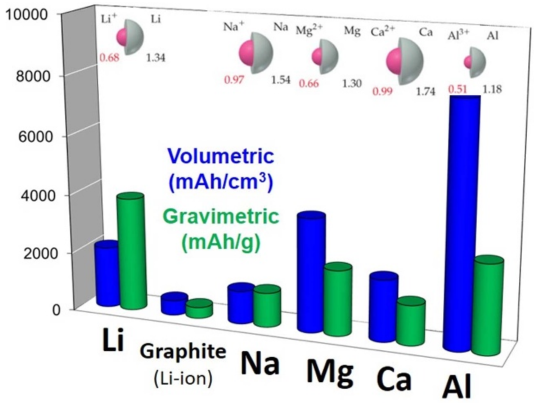

Figure 12. Theoretical gravimetric and volumetric for anodes—Li-ion and metal (with respective ionic and atomic radius).

Table 1. Overview of some of the state-of-the-art multivalent electrolytes with their key properties. CE denotes Coulombic efficiency. Voltage window is typically assessed through linear sweep voltammetry, which typically overrates the stability due to low surface area of metal electrodes and relatively fast sweep rate. DME—dimethoxyethane, THF—tetrahydrofuran G2—diglyme, TGM—tetraglyme. EMIMCl-1-ethyl-3-methylimidazolium chloride.

Electrolyte	CE	Stability vs. M/M^{n+} (V)	Morphology	References
$Ca(B(hfip)_4)_2$ DME	80%	4.2 V	Small deposits, intertwined with separator	[161]
$Ca(CB_{11}H_{12})_2$ DME/THF	88%	4.0 V	Granular, intertwined with separator	[162]
$Mg(B(hfip)_4)_2$ DME	98%	4.3 V	No information	[160]
$Mg(Al(hfip)_4)_2$ G2	99.4%	3.5 V	Large granular deposits	[157]
$Mg(CB_{11}H_{12})_2$ TGM	99%	3.8 V	Granular	[159]
$AlCl_3$:EMIMCl	99%	2.1 V	Uneven deposition	[158]

especially considering the fact that high Young modulus of these metals might increase the risk of short circuit.

Development of inorganic cathode materials has been seriously impeded due to difficult insertion, slow solid-state diffusion, solvent co-intercalation and tendency towards irreversible conversion reactions [167]. Hence, there are only a handful of inorganic materials that enable reversible insertion of multivalent cations like Mo_6S_8. However, even Mo_6S_8 as a literature standard does not enable reversible insertion of Ca^{2+}. Hence, alternative types of cathodes are being actively pursued like sulfur and organic electrodes, which undergo conversion and coordination electrochemical mechanism, respectively [168, 169]. Both types of electrodes enable reversible electrochemical activity, however, suffer from similar limitations as in Li–S and Li-organic battery systems. Organic electrodes are troubled by dissolution of simple organic molecules, low volumetric energy density, incomplete capacity utilization, utilization of cation–anion pairs in the electrochemical mechanism and sulphur positive electrodes by polysulfide shuttle, loss of active material and incomplete conversion. However, reaction mechanism going beyond conventional ion insertion might offer a more realistic path towards realization of practical multivalent high-energy batteries. Especially, organic cathode materials have in the last year exemplified long-term cycling stability in the range of several hundreds and even thousands of cycles. Especially, those employing anthraquinone type and similar type of compounds [170, 171]. However, currently used compounds possess only moderate voltages and capacities leading to very modest energy densities of multivalent metal organic cells. A major issue is also the fact that cation–anion pair utilization in electrochemical mechanism has be noticed pointing to the need to improve the salt dissociation in the electrolyte. Such ion pairs formation always comes at a cost of severely decreased energy density due to utilization of electrolyte in the reaction mechanism [172]. For instance, insertion of complex ions like $AlCl^{-}_{4}$, in Al based batteries resulted in extremely low specific capacity [173].

Advances in science and technology to meet challenges

The less mature Mg, Ca and Al batteries currently also suffer from a lack of reliable electrochemical setups for careful assessment of new material (positive and negative electrodes or electrolyte). Considering the difficulty of the development of new battery chemistries in which both electrodes and electrolytes must be studied in parallel, the use of reliable electrochemical protocols is crucial (and not trivial) in order not to discard potentially interesting material candidates due to poor performance based on half-cell testing.

While the main interest in multivalent cation based battery technology development does arise from the possibility to use metal negative electrodes, the use of Ca, Mg or Al metal also involve significant technological challenges. Indeed, by contrast with Li metal which is commercial using polymer electrolyte technology, handling Ca, Mg or Al would require even more stringent conditions such as: (i) chambers with an ultra-high purity atmosphere in order to avoid any traces of oxygen, water, or any other kind of contaminant which could react at the electrode surface and completely block plating/stripping or (ii) development of metal pre-passivation strategies allowing for easier handling in conventional dry rooms. It is worth noting that the first case scenario would most likely result in a significant cell production cost increase.

Another technological challenge associated with metal negative electrode involve the mechanical properties of such metal. Indeed, while Li metal polymer cells are currently produced by metal extrusion, this will most likely be difficult for Mg and Ca which possess higher Young's modulus, respectively 45 and 20 GPa (only 4.9 GPa for Li). Alternative production strategies will thus be needed in order to produce high purity foils, possibly via evaporation methods and/or by clever alloying strategies mitigating both mechanical properties and electrochemical performances of the metal negative electrodes. For Al the situation is very different; although the pure metal also presents a high Young's modulus (70 GPa) the assembly of commercial cells would likely benefit from the vast knowledge available from the Al industry.

Concluding remarks

Magnesium, calcium or aluminium batteries hold promise for the applicability of metal anodes and hence large capacities. Nonetheless, the development of suitable cathodes and the achievement of highly reversible metal plating and stripping is a must and will requires novel electrolyte formulations enabling a wider electrochemical window, better interfaces and improved interfacial processes (for instance lower desolvation energy). While the development of organic positive electrodes clearly constitutes a breakthrough in terms of cell cycle life and overall electrochemical performances, significant additional efforts will be needed in order to further increase energy density (especially volumetric) and power of multivalent cation based batteries. In addition to these specific material science challenges, one can foresee that these post-Li batteries will also need to overcome several technological challenges associated with handling highly reactive and stiff metals.

Acknowledgments

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11a. Sustainable polymer electrolytes

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Status

Insufficient energy and safety of the contemporary lithium-ion batteries (LIBs) have significantly incentivized the development of solid-state batteries (SSBs) built with solvent-free electrolytes and high-energy electrode materials [174, 175]. Among all the possible electrolyte candidates, polymer electrolytes (PE) stand out due to their superior flexibility and ease in film preparation at large scale (e.g. square meters with microscale thickness).

In the late 1980s, the replacement of triflate anion with a more delocalized anion, bis(trifluoromethanesulfonyl)imide ($TFSI^-$), was proposed, which leads to nearly an order of magnitude increase in ionic conductivity of poly(ethylene oxide) (PEO)-based dry PEs [176]. In the late 1990s, lithium iron phosphate ($LiFePO_4$) cathode was discovered and the carbon-coating strategy was suggested to improve its electronic conductivity [176, 177]. These early pieces of excellent findings enabled the debut of dry PE-based SSBs in electric vehicle (EV) market in the 2010s [176, 177]. Presently, the dry PE-based SSBs, consisting of a thin membrane of LiTFSI/PEO, metallic lithium (Li°) anode, and $LiFePO_4$ cathode, have been employed as power source for EVs (e.g. Bluecars®, Bluebuses®) and grid storage (e.g. Bluestorage®). These results clearly testify the technological feasibility of employing dry PE films as electrolytes for large-format 5–8. Furthermore, the abundance of the raw materials used in dry PEs (e.g. carbon, hydrogen, and oxygen, etc.) adds further value in terms of technological sustainability for developing dry PE-based SSBs.

Current and future challenges

Despite the decent cycle life (>4000 cycles at ca. 100% depth of charge) of the above dry PE-based SSBs, the energy density and rate capability are still insufficient for future applications (e.g. long-range EVs, drone-taxis, etc) [176, 177]. To achieve a driving range comparable to that of fossil fuel powered vehicles (>600 km per charge), the energy density of the state-of-the-art (SOA) dry PE-based SSBs has to be substantially improved, including both gravimetric (>400 Wh kg^{-1}) and volumetric (>800 Wh l^{-1}) energy densities. Therefore, remarkable improvement in the molecular design and production of PE components are critical for satisfying aforesaid requirements for next-generation PE-based SSBs. Specifically, the following challenges have to be addressed (figure 13).

(a) Low cation-only conductivity

The transport of ionic species in bulk electrolyte is tightly related to the rate-capability of SSBs; yet, it has to be highlighted that, instead of total ionic conductivity, the cation-only conductivity overweighs, since the migration of anionic species is likely to generate concentration polarization in SSBs (figure 13(a)) [178]. In this scenario, the cation-only conductivity of an ideal dry PEs has to reach $\geq 1.0 \times 10^{-3}$ S cm^{-1} at the operating temperature of SSBs. Obviously, the dry PEs with PEO or other kinds of polymer matrices show significantly lower cation-only conductivities at room temperature (ca. 2.0×10^{-5} S cm^{-1} at 25 °C), as compared to the threshold value above [178].

(b) Poor electrochemical stability

The electrochemical stability of neat PEs is relatively a straightforward concept; yet, it is of paramount difficult to estimate the intrinsic stability of PEs on different kinds of electrode materials under the operating conditions (e.g. potential, temperature, etc) [179]. To couple high-energy anodes with high-voltage cathodes in PE-based SSBs, the electrolyte components and the resulting PEs should remain stable at high potentials of >4 V vs. Li/Li^+. However, this is beyond the stability domain of PEO-type PEs ($\leqslant$3.8 V vs. Li/Li^+), requiring the design of alternative polymers [180]. To allow the implementation of high-energy conversion-type cathode (e.g. sulfur, oxygen), the chemical reactions between PEs and aggressive electrode intermediates (e.g. polysulfide) should be minimized (figure 13(b)). This excludes the use of polycarbonate or polyesters, though their ionic conductivities seem to be moderate ($>1.0 \times 10^{-4}$ S cm^{-1} at 25 °C) [181].

(c) Unstable electrode-electrolyte interphase/interfaces

The interphase or interface formed between electrode and PEs are of vital importance for the operation of SSBs. For the anode side, relatively stable interphases could be built between PEs and metallic anodes at low

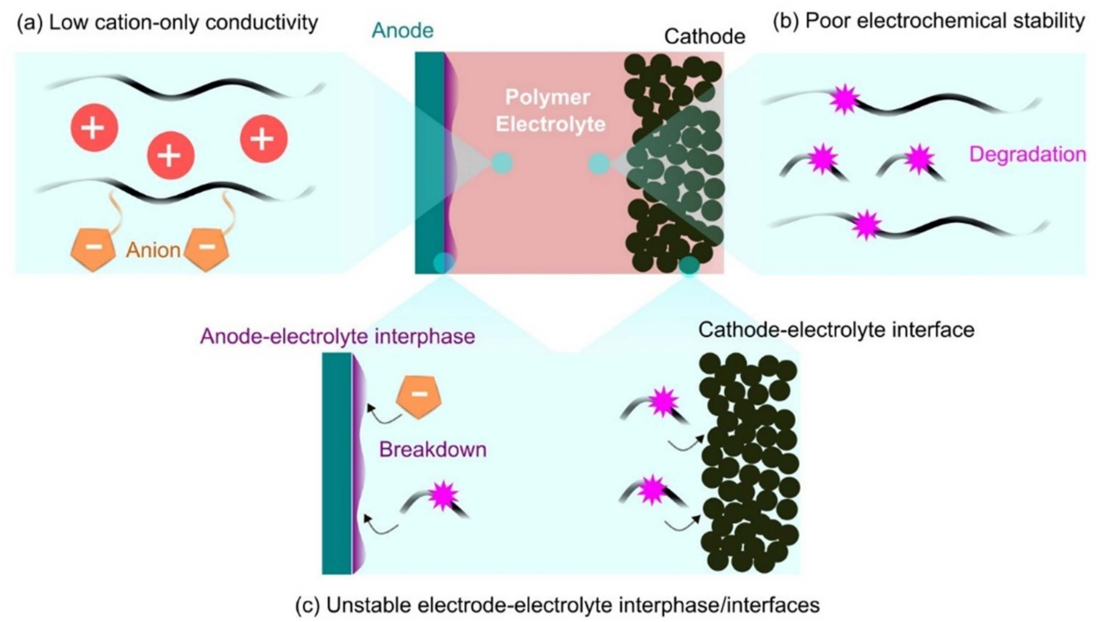

Figure 13. Remaining challenges for developing high-performant PE-based SSBs. (a) Low cation-only conductivity, (b) poor electrochemical stability, (c) unstable electrode-electrolyte interphase/interfaces.

current densities (<0.1 mA cm^{-2}); however, inhomogeneous nucleation and growth of metal particles readily occur at higher current densities, which induces internal short-circuit of SSBs (figure 13(c)) [181]. For the cathode side, the oxidation of PEO and polyethers are unavoidable when coupling with high-voltage cathodes, which causes the formation of gaseous compounds and particle pulverization (figure 13(c)) [181].

Advances in science and technology to meet challenges

To circumvent the aforesaid challenges in developing PE-based SSBs, intensive effort has been made in recent years [182]. First, the selective and efficient transport of cationic species in PEs is closely related to the nature of conducting salt and polymer scaffold. By replacing semi-crystalline PEO with amorphous polyethers, the ionic conductivities at room temperature region are largely enhanced, reaching a moderate value of 1.0×10^{-4} S cm^{-1} at 25 °C (figure 14(a)) [180]. Instead of perfluorinated sulfonimide (e.g. TFSI$^-$), the utilization of hydrogenated anions, (difluoromethanesulfonyl)(trifluoromethanesulfonyl)imide (DFTFSI$^-$), effectively slows the migration of anionic species and leads to an improved selectivity in cationic transport (figure 14(b)) [183]. Furthermore, grafting anionic moieties to a polymer backbone can quell the migration of anions in PEs [184], but it requires profound delocalization of negative charges and adequate solvating segments (e.g. ether, or carbonyl groups) in the polymer architecture.

Second, to cope with the electrochemical stability requirement, double-layer PEs seem to be an effective approach. For example, the Li-ion conducting glass ceramic (LICGC) is not stable against lithium metal; however, separating the LICGC-based composite PEs with an aluminum oxide (Al_2O_3)-based one not only increases the utilization of sulfur in cathode but also mitigates the side reactions between LICGC and Li° anode (figure 14(c)) [186]. Moreover, replacing the discrete anions with polyanion is considered to be necessary to prevent the interdiffusion of salt anions due to their different activity coefficients in two polymer layers [187].

Last, the anode-electrolyte interphases/interfaces are critical for cell performance, and could be regulated via structural modifications of salt anions and polymers [181, 182]. The hydrogenated anion mentioned above is likely to be reduced on the surface of metal anode, forming a mixture of lithium fluoride (LiF) and lithium hydride (LiH) which could increase the transport of lithium ions across the anode-electrolyte interphases (figure 14(b)) [185, 188]. By increasing the perfluoroalkyl chains in the sulfonimide anions, efficient stabilization of cathode-electrolyte interface could be also achieved [189].

Concluding remarks

Developing next-generation PE-based SSBs with high-energy and high rate-capability lies in the innovative design of salt anions and polymer matrices. In recent years, significant improvement has been achieved in the structural regulation of salt anions; yet, it seems to be rather difficult to replace PEO or polyether with other kinds of polymers (e.g. polycarbonate, polyesters). It has to be noted that the implementation of new

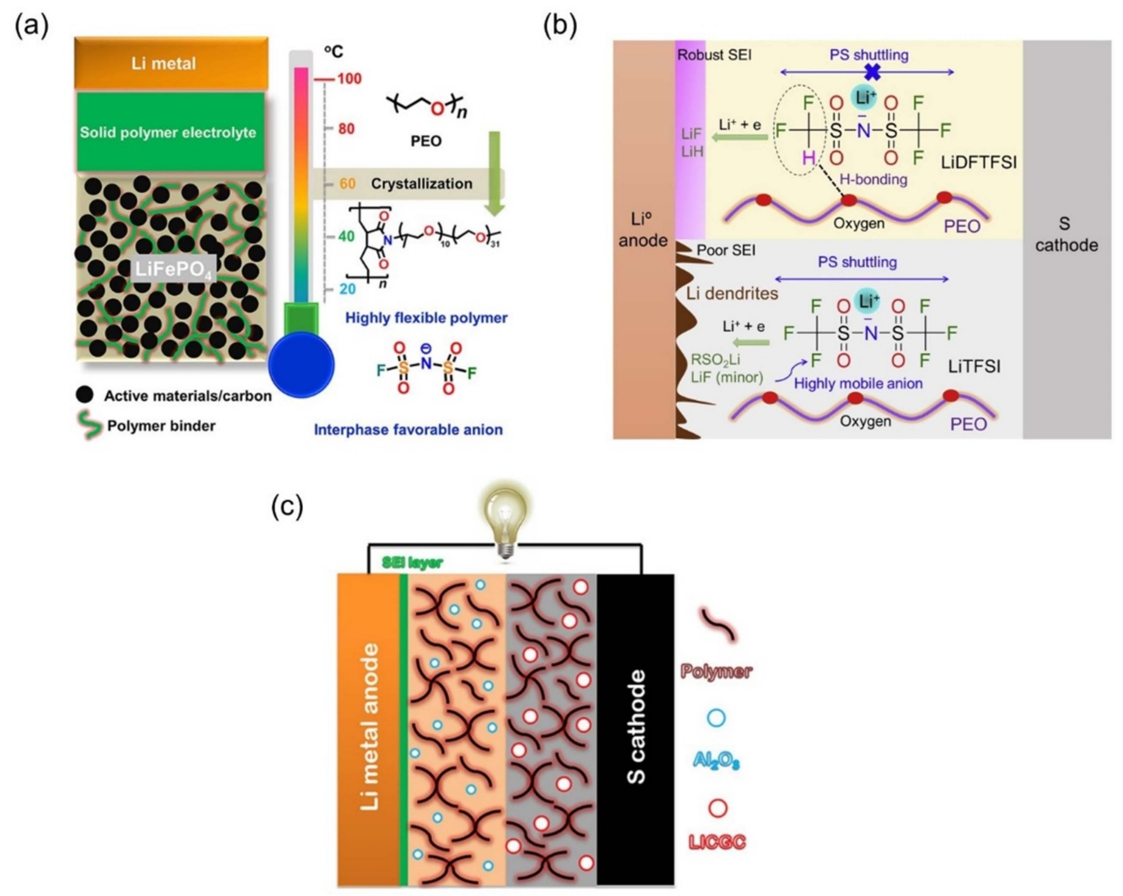

Figure 14. Possible pathways to improve the performance of PE-based SSBs. (a) Amorphous polyethers. Reprinted from [180], Copyright (2018), with permission from Elsevier. (b) Hydrogenated anion. Reprinted from [185], Copyright (2019), with permission from Elsevier. (c) Double-layer PEs. Reprinted with permission from [186]. Copyright (2017) American Chemical Society.

polymer matrices should be aligned with the structural modification of salt anions, including the dissociation and solvating processes of metal salts.

Furthermore, with increasing concerns on the use of polyfluoroalkyl substances (PFASs; being harmful to human and animals), excluding long perfluorinated chains from polymers and salts would be important for attaining sustainable technology with PE-based SSBs. In addition, solvent-free processing techniques (e.g. extrusion) for preparing PE films will be also desired for the exclusion of volatile and toxic organic solvents (e.g. acetonitrile) towards a more sustainable SSB technology. For other kinds of SSBs, it unlikely to obtain highly conductive PEs with Mg^{2+} and Al^{3+} cations owing to their low Eigen values [346, 347]; yet, the introduction of some mono- (e.g. Na^{+}, K^{+}) and multi- (e.g. Zn^{2+}) valent cations seems to be possible, and, in particular, the know-hows accumulated in Li-based PEs could be somehow useful for developing these kinds of SSBs.

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11b. Sustainable battery electrolytes: ionic liquid-based electrolytes

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Status

Over the past 25 years, a number of families of ionic liquid (IL) electrolytes have exhibited exceptional performance characteristics relative to organic electrolytes for advanced battery chemistries based on lithium metal, silicon, sodium-ion and Li/Na-sulfur [190–194]. Much of this success can be attributed to recent developments around IL electrolytes that contain a high, typically around 50 mol%, concentration of alkali metal salt [193–196]. The dramatic differences in structuring that occur in this compositional window both in the bulk and at the electrode surface has seen new and unexpected behaviours relating to the alkali cation transport properties and SEI formation. Through co-design of IL chemistry and electrode formation conditions, the behaviour of these high salt concentration electrolytes at the electrode interface can be tailored to promote the formation of favourable SEI products, being typically composed of more Li/Na-conductive, Li/Na-rich inorganic species [197].

ILs have also been explored for their ability to play a role in the development of solid polymer electrolyte chemistries through their incorporation into ionomeric materials (such as polymerizable ILs) to form ionogel polymer electrolytes. Polymer and ionogel polymer electrolytes enable the implementation of conventional high-throughput, low-cost manufacturing processes. By incorporating IL-based additives to form ionogel polymer electrolyte systems, the lithium-ion transport properties and membrane mechanical integrity can be enhanced without sacrificing the non-volatile nature along with the thermal and electrochemical stability [198, 199].

The current best-in-class lithium battery electrolyte chemistries are based, at least in part, on lithium salts with fluoride-containing anions such as hexafluorophosphate for lithium-ion, and bis(fluorosulfonyl)imide for emerging lithium metal-based chemistries [195]. The inclusion of fluorine-based compounds in the electrolyte chemistry is, to date, ubiquitous as a pathway to promote the targeted formation of lithium fluoride, known to be a favourable SEI component in lithium batteries. In addition to this, the fluorine can also serve to passivate the aluminium current collector through the formation of insoluble AlF_3. However, at high fluorine content this incurs considerable upstream and downstream costs in terms of environmentally damaging chemical processing routes and challenges in the recycling processes. Safety risks and hazards also arise from the release of fluorine-containing toxic gases in the case of a venting or fire event during cell operation. Advancements by way of a reduction in, or removal of, the electrolyte fluorine content serves as the lynchpin to realising further improvements in safety and addressing environmental aspects of electrolyte manufacturing and recycling.

Current and future challenges

ILs offer a number of attractive advantages compared to traditional carbonate-based electrolyte systems. However, they invariably suffer from limitations in other areas of performance. The areas of deficiency that work to inhibit the commercial uptake of IL electrolytes are generally associated with the following characteristics:

(i) Inferior rate capability at low to mid-temperatures.
(ii) Poor wetting of the separator and electrodes.
(iii) High cost of IL manufacture.

The first two of these persisting issues stem from two materials properties that are common to most high alkali salt concentration IL electrolytes, namely a high viscosity at ambient temperatures and a high surface energy (relative to other traditional cell components). The third point speaks to the high overall cost stemming from process challenges in the development of large-scale low-cost manufacturing routes.

There have been a number of positive claims made about IL electrolytes. While many of these rest on evidence of the inherent materials properties, there remains much research to do in order to validate whether these claims translate to characteristics of a device in operation. These proposed advantages include the following;

(i) **The ability to reduce the fluorine content.** Electrolyte materials based on low-fluorine chemistries is an area of high importance for traditional electrolyte systems, with efforts focusing on chemistries including boron, sulfur, phosphorous, cyano-based chemistries (figure 15) [200, 201]. In this regard, the use of IL solvents opens the door to new chemistries presented to the electrode surface (and

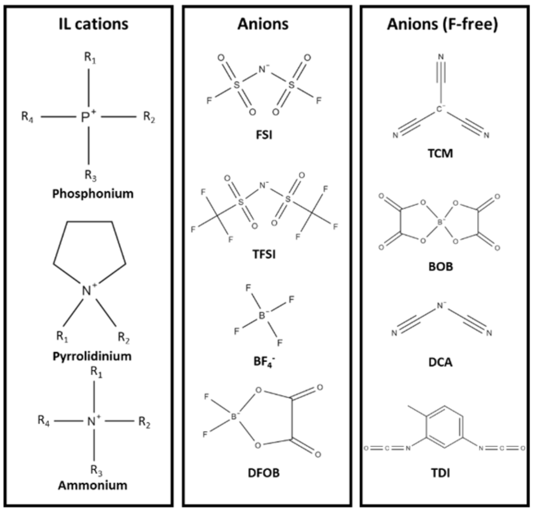


Figure 15. Chemical structures of common cationic and anionic species present in an ionic liquid electrolyte. F-free anion chemistries are also shown. FSI = bis(fluorosulfonyl)imide, TFSI = bis(trifluoromethanesulfonyl)imide, DFOB = difluoro(oxalato)borate, TCM = tricyanomethanide, BOB = bis(oxalate)borate, DCA = dicyanamide, TDI = 4,5-dicyano-2-(trifluoromethyl)imidazolium.

aluminium current collector) at significantly different molar ratios for the formation of alternative high-performing SEI compositions with additional scope for improvement in room-temperature rate performance, lower cost, and faster wetting of the separator and electrodes. Lowering the fluorine content is also a promising path to reducing costs and improving sustainability by avoiding costly and environmentally impactful fluorine-based chemistry.

(ii) **Inherent fire safety advantages.** The most prominent candidate IL electrolytes are generally known for having low vapour pressures and thermal stabilities well above 150 °C, which should make them more resistant to a device fire resulting from a thermal runaway event. Safety performance is often reported via inference from the materials properties or preparing small pouch or cylindrical cells. However, the true measure of safety performance of a battery is not reflected by testing small cells in isolation, but is given by testing larger format cells as well as in pack or module configuration with the appropriate enclosures.

(iii) **The ability to be recycled to a greater extent.** The battery recycling industry is still catching up to the surge in lithium-ion battery manufacturing. The development of new recycling methods can take advantage of the non-flammability and non-volatility of IL electrolytes, such as adapting solvent extraction methods to recover electrolytes.

Advances in science and technology to meet challenges

Non-fluorinated, sustainable chemistry

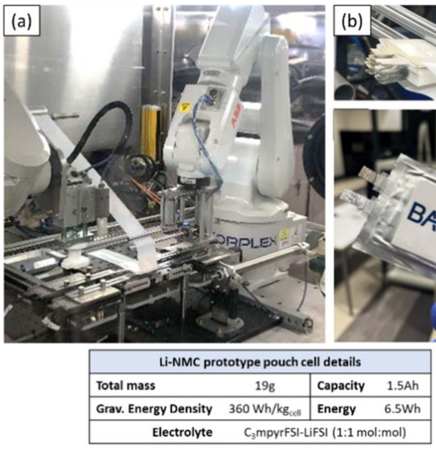
Conventional computing methods impose a considerable demand on limited and costly processing capacity. New computational modelling techniques paired with artificial intelligence are now starting to be developed for chemical and physical processes [123, 202] and are going to play an increasing role for accelerated design of potential chemistries and IL structures.

Low cost ionic liquid manufacturing

Cost estimates for mass produced ILs still sit 5–10 times higher than carbonate-based solvents. In addition to new low-cost and sustainable chemistries, new approaches to synthesis at scale are needed to bring down the cost. A translation of this technology to the process engineering and chemical engineering disciplines is needed to realise this. Continuous flow chemistry is a promising pathway to reduce the cost of ILs through high volume production, but needs to be further developed for ILs [203].

Cell manufacturing challenges and opportunities

As with any new material, the barrier to implementation often arises from the need for a concerted effort to understand and adapt the manufacturing process to accommodate different materials behaviours. Scale prototyping is vital to the discovery and solving of these challenges. While upscaling the manufactured cell size reveals new challenges not seen in the laboratory (figure 16), this comes paired with opportunities for



Li-NMC prototype pouch cell details			
Total mass	19g	Capacity	1.5Ah
Grav. Energy Density	360 Wh/kg_{cell}	Energy	6.5Wh
Electrolyte	C_3mpyrFSI-LiFSI (1:1 mol:mol)		

Figure 16. Photos from Deakin University's Battery Research and Innovation Hub (BattRI-Hub) prototyping line showing (a) custom-designed pouch cell robotic stacking unit that allows for flexible materials selection, (b) lithium metal electrode-separator stack, (c) a 1.5 Ah, 360 Wh kg^{-1} prototype lithium metal-NMC pouch cell using an IL electrolyte.

innovation and smarter design. The slow wetting of the separator and porous electrodes with IL electrolytes challenges the speed of cell production. The low volatility and high thermal stability of IL electrolytes present opportunities for new processing techniques that can incorporate, for example, high vacuum wetting or solvent-free electrode extrusion [204].

Proving and quantifying the safety advantages

A stronger correlation between sensitive operando techniques such as calorimetry [205] performed at the coin cell level with the safety performance at module/pack scale is required to provide a basis for claims of the safety performance of IL materials [206]. A detailed understanding of this correlation can provide a pathway for standard materials testing methods as a means to quantify the safety performance.

Operando methods

There is still much that operando methods can help us to uncover about the behaviour of materials inside current lithium-ion battery technologies. IL electrolytes offer another avenue of versatility due to their ability to operate under high-vacuum conditions, broadening the range of techniques and approaches that can be applied. An important component of electrolyte design lies in an understanding of the SEI formation, which remains a poorly characterised process. Electrode and separator wetting, along with ion transport under different operating conditions are two phenomena that can be interrogated by operando NMR and neutron scattering techniques [207, 208].

Concluding remarks

IL electrolytes are a class of electrolyte material with some inherent properties that can overcome some of the lasting challenges faced when using traditional electrolyte systems. However, due to the sheer vastness of the chemical composition space, decades of research has only begun to scratch the surface of their possibilities. Their implementation into commercial devices faces additional barriers with traditional manufacturing, but also presents vast opportunities to develop new approaches for mass-scale production and cell manufacturing in the foreseeable future taking advantage of the unique properties of ILs.

11c. Super-concentrated aqueous electrolytes: a WISE choice?

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Status

Aqueous rechargeable batteries (ARBs) offer a range of benefits that include sustainability and safety, specifically, eco-friendliness and non-flammability. Following the past development of lead-acid or Ni–Cd/Ni-Metal hydride batteries, the introduction of the first aqueous rechargeable lithium-ion battery (ALIB) by Li *et al* in 1994 created a drive to further develop water-based electrolytes for Li-ion batteries [209]. However, water has a limited electrochemical stability window (ESW) of 1.23 V, with the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) occurring on the negative and positive electrode, respectively. Albeit due to slow kinetics for water oxidation and reduction at electrochemical interfaces a ≈2 V electrochemical window can be achieved. Still, this limited ESW restricts the choice of electrode materials and thus severely limits the energy density [210]. Based on the past developments in super-concentrated organic electrolytes, Suo *et al* proposed in 2015 the concept of water-in-salt electrolyte (WiSE), where the salt outweighs water in mass and volume. They utilised lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) salt at a concentration of 21 mol kg^{-1} (m), which equates to ∼5.5 mol l^{-1} [211–213]. By harnessing two effects, the ESW could be extended. Firstly, the high concentration of anions results in a modified solvation sheath which promotes the formation of a solid electrolyte interphase (SEI) on the negative electrode, thus minimising HER and extending the limit on reduction (figure 17(a)) [214]. Secondly, the formation of hydrophobic double layer at the positive electrode minimises OER, extending the limit on oxidation [215]. The result is an electrolyte with an ESW of ≈3 V (figure 17(b)), enabling the use of previously inaccessible electrode materials (figure 17(c)). As a proof-of-concept, a 2.3 V aqueous Li-ion battery (ALIBs) using $Mo_6S_8 \,||\, LiMn_2O_4$ was developed to showcase the potential of a WISE. This work led to a surge of interest in super-concentrated aqueous electrolytes, with Yamada *et al* almost simultaneously proposing the water-in-bisalt electrolyte (WiBS) in 2016, boosting the salt concentration to 28 m with the addition of 7 m lithium bis(pentafluoroethanesulfonyl)imide (LiBETI) to 21 m LiTFSI, pushing the operating potential to 3.1 V with a $Li_4Ti_2O_{12} \,||Li_{0.5}Ni_{0.5}Mn_{1.5}O_4$ battery [216]. Since, the solubility limits have been extended further, up to 63 m with a 42 m LiTFSI: 21 m $Me_3EtN.TFSI$ mixture [217]. Following the demonstration for LIB, WiSEs have then been used for developing aqueous Na-ion, K-ion and Zn-ion batteries with extended potential windows, making important advancements in these respective fields [218–220]. Following the initial excitement, many challenges still need to be addressed to envision any practical applications for WISE-based systems.

Current and future challenges

Unlike aprotic solvents, the formation of an SEI in aqueous Li-based electrolytes was previously believed to be impossible due to two factors: (1) the greater solubility of inorganic compounds in water, and (2) the inability of salts to decompose to form passivating components. Although still debated, the SEI formation mechanism indicates that while WiSEs enable the reactivity of salt anions and drastically limit the dissolution of SEI components, they do not prevent the HER. Instead, the HER is directly involved in the SEI formation in two ways: (1) by producing OH^- ions, which triggers the chemical decomposition of the anions, most commonly $TFSI^-$ which forms LiF and CF_x, and (2) by decreasing the amount of water and inducing salt precipitation. Unfortunately, it has been established that the thus formed-SEI is not fully passivating. Under normal cycling and resting conditions, the partial dissolution of the SEI results in the gradual loss of passivation, leading to self-discharge and capacity fade [214, 222]. These problems are intensified at elevated temperatures, drastically hindering the practicality of the WISE (21 m LiTFSI). In fact, when considering the aforementioned frailties, conventional WiSE-ALIBs (i.e. 21 m LiTFSI or 21 m LiTFSI + 7 m LiBETI) are unable to outperform Ni-metal hydride batteries with regards to rate capability, self-discharge and range of operating conditions [222].

Aside from limited performance in practical conditions, the sustainability of using such high concentrations of salts can be questioned. For instance, when considering molarity, WISE requires 5.5 times the amount of lithium in moles compared to a conventional 1 mol l^{-1} organic electrolyte. Hence, assuming a commercial 18 650 cell requires ∼5 ml of electrolyte, using WISE over a conventional organic electrolyte result in an overall 20% increase in lithium content, on a molar basis. Furthermore, the use of fluorinated salts such as LiTFSI, typically employed in most WISE, is less than ideal due to their toxicity and corrosive

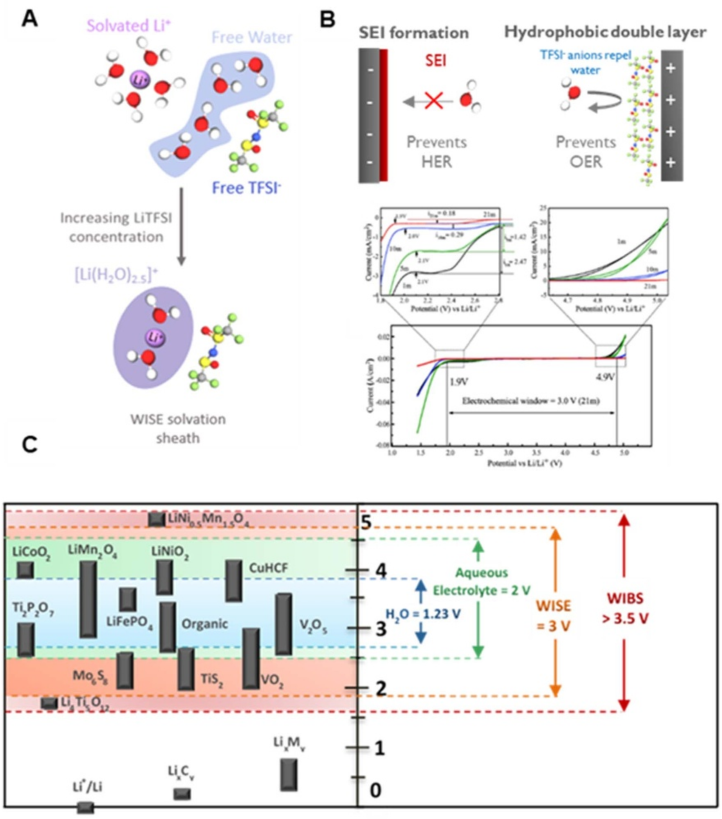

Figure 17. (a) Modification of solvation sheath when moving from salt-in-water (top) to water-in-salt regime (bottom) [213], (b) Expansion of ESW with WISE as a result of SEI formation and hydrophobic double layer formation, the latter is a simplified scheme depicting previous findings from MD calculations [213]. From [213]. Reprinted with permission from AAAS. (c) ESW of WISE and WIBS compared to traditional aqueous electrolytes and pure water superimposed with the redox potential of various electrode materials adapted from [221]. Reproduced from [221], with permission from Springer Nature.

nature. These issues run counter to the initial clean and green ethos of using an aqueous electrolyte. Thus, strategies are required to reduce the Li content and the need for a high concentration of fluorinated salts.

Advances in science and technology to meet challenges

To circumvent the aforementioned issues, diluents have been recently employed leading to promising results. For instance, Xu *et al* proposed a unique electrolyte, 4.5 m LiTFSI–Urea–KOH–H_2O; urea plays a key role, acting as a sustainable diluent to reduce the salt concentration while also forming strong interactions with Li^+ and water to alter the solvation sheath [223]. This solvation enables urea to form a polymerisation product on the negative electrode, providing a passivating organic layer in addition to the inorganic SEI. The formation of the latter is catalysed by the use of KOH, which provides the OH^- required to react with $TFSI^-$ to form the LiF-based SEI (figures 18(a) and (b)). The strategy enabled a $Li_4Ti_5O_{12}$ || $LiMn_2O_4$ cell exhibiting 99.9% Coulombic efficiency in both coin and pouch cell formats (figure 18(c)), as well as a lower self-discharge rate compared to WISE. The use of diluents similar to urea is common way to reduce the concentration of Li salt while altering the Li solvation, examples being poly (ethylene glycol) (PEG), sulfolane, dimethyl sulfoxide (DMSO) and dimethyl carbonate (DMC), although the use of organic solvents goes against the goal of a sustainable electrolyte [221, 224–226]. Figure 18(b) showcases the mass of each component required to make 1 kg of WISE, and electrolytes containing urea, PEG and sulfolane. The amount of Li salt is drastically reduced compared to WISE, however, this comes as the cost of water content. Indeed, the quantity of water used in each system accounts for a small fraction of the electrolyte mass, drastically less than the already low quantity required for WISE. Despite showing promise, diluting strategies do raise a question: are these electrolytes really aqueous? Furthermore, all still utilise fluorinated salts to generate the LiF-based SEI. Interestingly, recent studies have shown that LiF, often attributed as the key component of the SEI, may not be responsible for SEI stability in organic-based electrolytes [227]. Thus, an interesting perspective for ALIBs is to develop novel, non-fluorinated salts that focus on solvation chemistry and/or super-concentration while using diluents, such as urea, or additives to induce passivation.

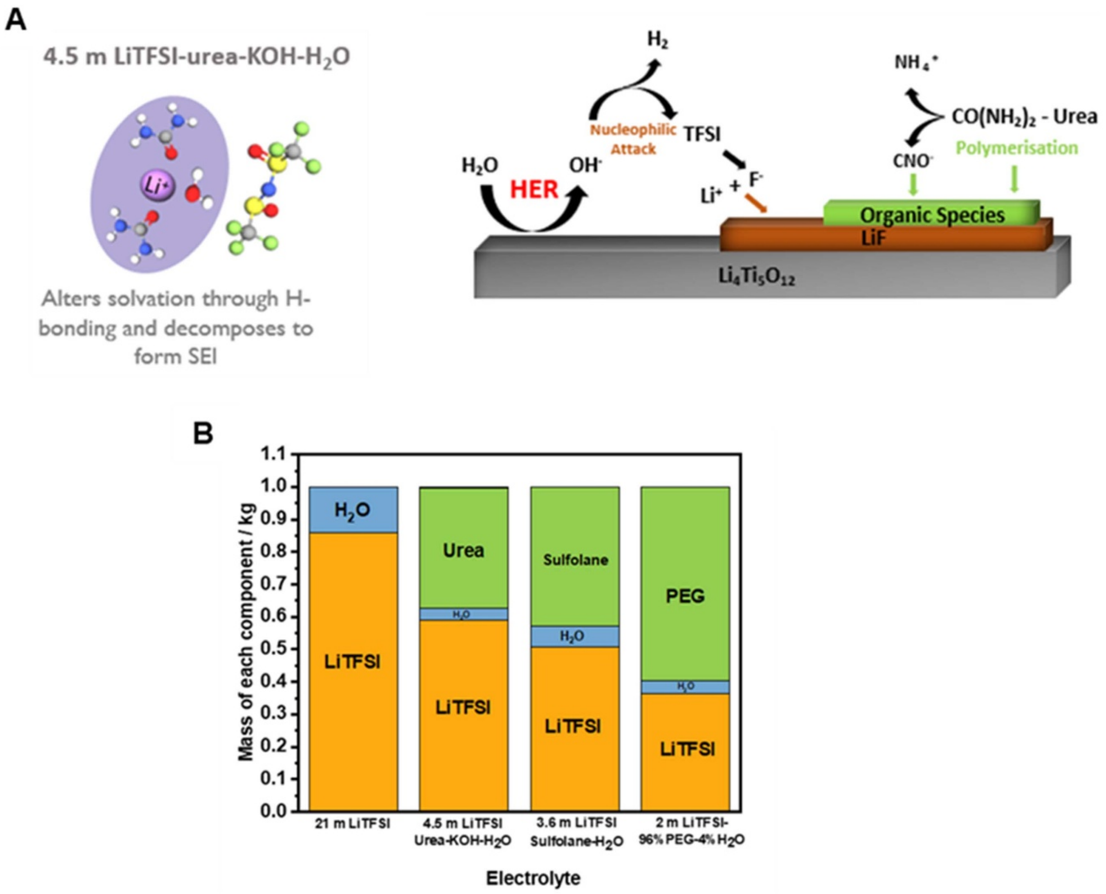

Figure 18. (a) Schematic representation of solvation sheath for 4.5 m LiTFSI–Urea–KOH–Water electrolyte (left), which enables unique SEI formation (right) [223]. Reproduced from [223], with permission from Springer Nature. (b) Mass of each component of a WISE and three electrolytes using diluents [213, 221, 223, 224].

It is worth noting that super-concentration is not just utilised to stabilise interfaces, but also to reduce the solubility of intercalation/redox active compounds. This can enable the use of more sustainable alternative battery chemistries compared to Li-ion, such as Na-ion or K-ion. Jiang *et al* developed an aqueous K-ion rechargeable battery (AKIB) using a super-concentrated 22 mol l (M) KCF_3SO_3 electrolyte. This super-concentrated electrolyte enables the use of 3,4,9,10-perylenetetracarboxylic diimide (PTCDI) as an organic-anode material and Prussian blue $K_xFe_yMn_{1-y}[Fe(CN)_6]_w\cdot zH_2O$ as a cathode material, through minimizing the dissolution of both active materials, albeit a fluorinated salt was used [228]. The combination of aqueous electrolytes and organic electrode materials is an attractive proposition from a sustainability standpoint. Meanwhile, despite K-ion batteries being a rather fresh technology and associated with limited energy density compared to Li-ion, K-ion batteries do exhibit a lower environmental and cost footprint. The convergence of sustainable battery chemistries requires additional advancements, but it presents an opportunity to develop a truly sustainable battery for the future, especially for large-scale stationary applications.

Concluding remarks

The introduction of super-concentrated aqueous electrolytes has progressed ALIBs to new heights, through expanding the ESW to allow the use of electrode materials previously out-of-reach. To tackle the concerns surrounding SEI stability and the need for high concentration of Li-based fluorinated salts, green diluents are used which play on the solvation chemistry while reducing the salt concentration. However, one can question the aqueous nature of such electrolytes with the low quantity of water present. Moreover, in light of recent research efforts identifying the role of LiF in SEI stability for organic electrolytes, focus should shift towards developing novel, non-fluorinated salts. Doing so, one can decouple the role of salts on inducing super-concentration and/or modifying the solvation structure, while additives and/or diluents are used to trigger passivation. Outside of ALIBs, the use of super-concentrated electrolytes has been beneficial for more environmentally friendly chemistries compared to Li-ion, such as K-ion, that can address less energy demanding applications. The use of more sustainable intercalation compounds, free of critical raw materials is enabled through mitigating dissolution and this concept is of particular interest when prioritizing sustainability, granted these systems are far away from any practical application. There is still plenty to explore for super-concentrated electrolytes for aqueous batteries. However, it remains to be seen whether they will remain a laboratory curiosity or find practical applications in the real world.

Acknowledgments

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11d. The challenge of sustainable inorganic solid-state electrolytes

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Status

Lithium-ion batteries (LIBs) are the most widely used energy storage devices in electric vehicle and portable electronic applications due to their high specific capacity and energy density, affordability, and long cycle life. However, LIBs have some limitations associated with their use of flammable organic liquid electrolytes whereby overcharging may induce overheating, electrolyte combustion, and even explosion [229]. The liquid electrolytes used in LIBs are also usually too reactive to be used with metallic Li anodes that are the focus of intense research activity due to the step-change increase in battery capacity they can provide. Consequently, more electrochemically stable solid-state electrolytes (SSEs) are a pivotal component for the development of solid-state batteries (SSBs) that can both exploit metallic Li anodes and provide improved safety [230]. SSEs may be broadly classified into organic solid electrolytes (polymers), inorganic solid electrolytes (ISEs) that includes garnet, NASICON, sulfide, perovskite, anti-perovskite and glassy electrolytes, and composite solid electrolytes (organic and inorganic) [231]. Because of their comparatively high electrochemical and mechanical stability, and relatively high ionic conductivities, ISEs have received the most R&D attention.

Although sustainability considerations have so far not been a significant facet of SSB development, a sustainable ISE will be imperative for their widespread application beyond niche markets. Oxide-ISEs have been considered promising because of their wide electrochemical stability window, high chemical stability for compatibility with high voltage (>4 V) cathodes, and have relatively low environmental impact. For example, oxide ISEs with relatively abundant, non-toxic, and sustainable elements include garnets such as popular $Li_7La_3Zr_2O_{12}$ (LLZO) and its derivatives, and NASICON-type oxides including $Na_3Zr_2Si_2PO_{12}$, $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP) and $Li_{1+x}Al_xGe_{2-x}$ $(PO_4)_3$ (LAGP). ISEs based on phosphates (LATP and LAGP) have good stability to moist air (lower tendency for the formation of Li_2CO_3) and a lower volumetric density (3 $g\cdot cm^{-3}$) than LLZO (5.1 $g\cdot cm^{-3}$), but their ionic conductivities are generally considered low at 10^{-5}–10^{-4} S cm^{-1} [232]. The NASICON family of compounds, with a typical formula $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ ($0 \leqslant x \leqslant 3$) (NZSPO) have higher ionic conductivity of approximately 6×10^{-3} S cm^{-1}, compositional tunability, mechanical strength, and air stability in sodium-ion batteries. In terms of earth abundance Si (282 000 ppm), Na (23 600 ppm), P (567 ppm) are considered readily available whereas Zr (132 ppm) is rarer (and more expensive). Nonetheless, a mature supply chain is predicted to be able to provide NASICON at a cost, scale and environmental compatibility suitable for competitive grid-scale energy storage [232]. However, oxide ISEs must overcome continued challenges of high processing temperatures required for high density, which also promote thermal degradation and/or reactions (e.g. with C additives), and low intrinsic mechanical compliance (high stiffness) that leads to poor inter-particle contact and a tendency to micro-/macro-cracking.

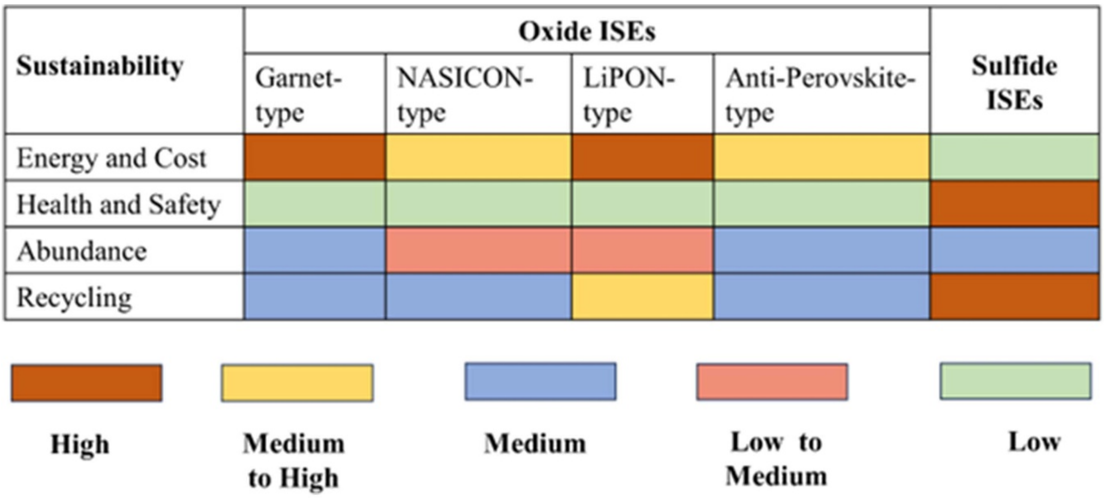
More recently, sulphur-based fast ionic conducting ISEs have emerged for SSBs, and have eclipsed oxide-ISEs in some aspects. Examples include $Li_{10}GeP_2S_{12}$ (LGPS) and its derivatives, and lithium argyrodites such as Li_6PS_5X ($X =$ Cl, Br, I), both with ionic conductivities as high as >1 mS cm^{-1} [175]. The abundance of sulphur is intermediate at approximately 400 ppm, which is higher than the abundance of the rare earth elements usually present in oxide-ISEs. The principal disadvantage of sulphur-ISEs, and challenge to environmental compatibility, is their ready reaction with water vapour to produce toxic H_2S gas. Otherwise, sulphur-ISEs offer low temperature synthesis and the ability to be densified at temperatures as low as room temperature, albeit with very high pressures up to 500 MPa—avoiding costly and energy intensive high temperature sintering steps.

Finally, anti-perovskites such as the recently emerging Li_3OCl (LOC) and longstanding amorphous, thin LiPON films further add to the diversity of inorganic solid electrolytes [233, 234].

Current and future challenges

In laboratory studies, the principal research direction has concerned identifying ISE compositions that provide a balance between high ionic conductivity, and mechanical and chemical stability. For example, many candidate ISEs exhibit excellent conductivity at elevated temperatures, but maintaining this conductivity at ambient temperatures of commercial devices remains a hurdle. For beyond-the-laboratory applications, ISEs must additionally meet the challenges of environmental sustainability over the product lifetime, cost of production, abundance and accessibility of elements, health and safety, and recycling solutions (table 2).

Table 2. Sustainable ISEs and risk factors.



Sustainability	Oxide ISEs				Sulfide ISEs
	Garnet-type	NASICON-type	LiPON-type	Anti-Perovskite-type	
Energy and Cost	🟧	🟨	🟧	🟨	🟩
Health and Safety	🟩	🟩	🟩	🟩	🟧
Abundance	🟦	🟥	🟥	🟦	🟦
Recycling	🟦	🟦	🟨	🟦	🟧

🟧	🟨	🟦	🟥	🟩
High	**Medium to High**	**Medium**	**Low to Medium**	**Low**

Energy and cost

Oxide-ISEs are based on relatively complex synthesis, high-temperature precursor calcination, and high sintering temperatures for solid electrolyte processing, which are energy and usually carbon intensive. For example, the high ionic conductivity cubic garnet LLZO phase requires synthesis at 1000 °C–1300 °C and sintering to adequate density at 1100 °C–1200 °C and 50–100 MPa [235, 236]. NASICON processing is similarly energy intensive. Although sulphur-ISEs offer lower temperature synthesis, their reactivity demands a protective environment (Ar atmosphere, dry room) and appropriate safety infrastructure that is both expensive and energy intensive. Processing of LIPON-type thin films requires high vacuum conditions, relatively high-cost precursors, has low throughput, and is restricted to thin film battery with a small area format.

Elemental abundance

Garnets and NASICON contain less abundant elements that are also energy intensive to extract and purify, such as rare earths (lanthanum, yttrium, zirconium, etc). Many sulphur-ISEs are composed of comparatively abundant elements but the mining sulphur ores and refinement to sulphur is notorious for its negative environmental impact, including habitat disruption, water and soil contamination, and emissions of sulphur dioxide (SO_2) during smelting and refining processes [237].

Health and safety

Oxide-ISEs are considered generally low risk materials, although handling of all fine-scale particulates carries risks relating to potential ingestion and aerosol dispersion. In particular, nanoparticles (diameters < 100 nm) can irritate the respiratory system and cause lung damage, and so coarser particles (>5 μm) are preferred in industrial settings. Sulphur-ISEs are toxic if ingested, inhaled, or in contact with the skin or eyes and readily formed H_2S is a highly toxic gas that can cause respiratory irritation, headaches, and even death at high concentrations [238].

Recycling of ISEs

Consideration of ISE recycling is in its early stages, and will remain immature until there is greater consensus of the materials embodied in a commercial SSB, especially the ISE, and only a few studies have considered the issues in depth e.g [239]. As with LIBs, a key consideration for ISE recycling will be the extent to which a battery is dissembled to recover specific valued components (and the materials therein), or whether cells are processed largely intact in a smaller number of steps but with less discrimination and separation of elements. The application of recovery/purification steps such as pyrometallurgy and hydrometallurgy are likely to be energy intensive, and must be able to separate a wide range of elements. As with manufacture, where sulphur-ISEs are present, additional infrastructure or novel processes will be required to manage H_2S-related risks. Given their higher as-manufactured energy density, SSBs might find end of primary life re-use in secondary markets where a degraded, low cost SSB might still offer residual performance that is cost-competitive with newer LIBs or other batteries.

Advances in science and technology to meet challenges

In the LIB industry, solvent-free processing has rapidly gained traction for its in principle capability to reduce significantly factory size, energy consumption, and reduce health and safety infrastructure and overheads by eliminating the use of toxic, flammable and expensive organic solvents used in the slurry casting of LIB cathodes [240]. This dry processing approach has successfully been applied to SSB pouch cell [241] and if it can be scaled up to commercial SSB packs, for example by the large-scale dry processing of ISE-based electrolyte sheets, it would make a major sustainability contribution to the emerging SSB industry.

Despite progress in ISE formulations for practical SSBs (oxides, sulphides, etc.) there remains a strong need for more inert, safer ISEs with ionic conductivities >1 mS cm^{-1}, high intrinsic grain boundary toughness to resist crack and dendrite propagation issues, and low energy synthesis and fabrication. Recent work suggests the ongoing potential for the discovery of new ISEs that meet some if not all of these requirements, and a large unexplored formulation space [242]. The algorithms increasingly used to identify promising candidate formulations can be extended readily to include consideration of earth abundance, toxicity, accessibility (supply chain and geographical consideration), recyclability, re-use, etc. The weighting of each the factors in the optimization function can also be varied to reflect the different requirements for the laboratory, usually focused on high electrochemical performance, or the more holistic and multi-faceted commercial requirements. Alongside experimental, computational or hybrid approaches to finding new crystalline sustainable ISEs, glassy or semi-crystalline and high disorder materials might provide a further pathway to formulations that balance performance with greater sustainability.

Concluding remarks

Sustainable ISEs are set to play an enabling role in the growth of energy storage technologies, but must have managed environmental impact and be composed of elements that facilitate a sustainable SSB industry, across all phases of their lifetime. While obstacles persist, such as a relatively small palette of viable ISEs each with their own advantages and disadvantages, it is a comparatively immature field technologically and consequently there remains considerable potential for breakthroughs in materials design with abundant and accessible elements, computational modelling, safety, re-use and recycling, and manufacturing innovations.

Acknowledgments

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12. Overview on challenges and possibilities of sustainable binders and separators

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This chapter is based on the knowledge generated in the Battery 2030+ [243] projects BAT4EVER [244] and HIDDEN [245], where binders and separators are studied. All sections have been divided into two, containing the overview of binders and separators.

Status

Binder is an indispensable member of the Li-ion battery (LiB) electrode recipe. The commercial base for the binders is now set between 2 and 5 wt.% in electrode composition. They are polymeric materials that are included in the electrode slurry to improve the particle–particle and particle–current collector adhesion. They also contribute to maintain the mechanical integrity of the battery electrodes leading to an improved cycling stability. However, they are insulators where a certain loss of electronic conduction should be considered. In this sense, the key expectations from the binders can be summarized as; high degree of dissolution with an excellent solution stability, high mechanical flexibility, the highest possible electronic conductivity and sufficient electrochemical stability under operating voltages. Binders are required to be dissolved in solvents and reprecipitate onto the particles after coating & drying. Hence, they play an important role in sustainable manufacturing of LiB electrodes as the selection of solvent depends on the type of binder.

Separators are crucial parts of batteries that provide ionic conductivity and electrical insulation between the anode and cathode. In the first type of LiBs, microporous polyethylene (PE) separators were used, which provided good performance and low cost. However, with the increasing demand for higher energy density and better safety, new separator materials have been developed. Later, ceramic-coated separators were introduced to improve the safety and thermal stability of the batteries. These separators have a higher melting point and are less prone to thermal shrinkage and melting. In newer types of LiBs, nanofiber and composite separators were developed to improve the ion conductivity, mechanical strength, and thermal stability of the batteries. These separators have smaller pore sizes and higher porosity, which enables faster ion transport and reduces the risk of short circuits. The next generation of LiBs is expected to feature solid-state separators, which can offer even higher energy density and better safety compared to liquid electrolyte batteries. However, the development of solid-state separators still faces technical challenges such as high interfacial resistance and limited ionic conductivity. Researchers are actively working to overcome these challenges and bring solid-state batteries closer to commercialization.

Current and future challenges

Figure 19 lists the current challenges of binders and separators in advanced LiBs. Additional challenges do exist for other battery generations (e.g. solid-state), which are briefly discussed in the text, but were left out from the image for clarity.

Binders

As a key component determining the sustainability of the battery manufacturing processes, sustainable binders are well-documented in the advanced LiBs. Yet, the industry is still seeking best performing binders in the solid-state systems, and there are still a lot to do in the sustainability perspective.

There are non-aqueous binders and aqueous binders depending on the solution media. Non-aqueous binders are conventional binders that are used in organic solvents in the slurry recipe. A popular example for the non-aqueous binders is polyvinylidene fluoride (PVDF). It is widely used in batteries having a graphite anode with its excellent electrochemical stability and binding strength. However, PVDF fails to accommodate the large volume changes in the anodes due to weak Van der Waals bonds. Besides, as a fluorinated compound, PVDF is not sustainable [246].

Aqueous binders such as Carboxymethyl Cellulose-Styrene-Butadiene Rubber (CMC-SBR), Polyacrylic Acid (PAA), Alginate, Polyethylene Glycol (PEG), Chitosan and Lignin can be processed in aqueous media during electrode manufacturing. They not only provide a cheaper solution by removing N-methyl pyrrolidone (NMP) solvents in the slurry composition, but they are also greener alternatives to PVDF in production. Yet, they do not have the scaled-up competency, although battery prototypes with aqueous-processed electrodes are recently launched [247].

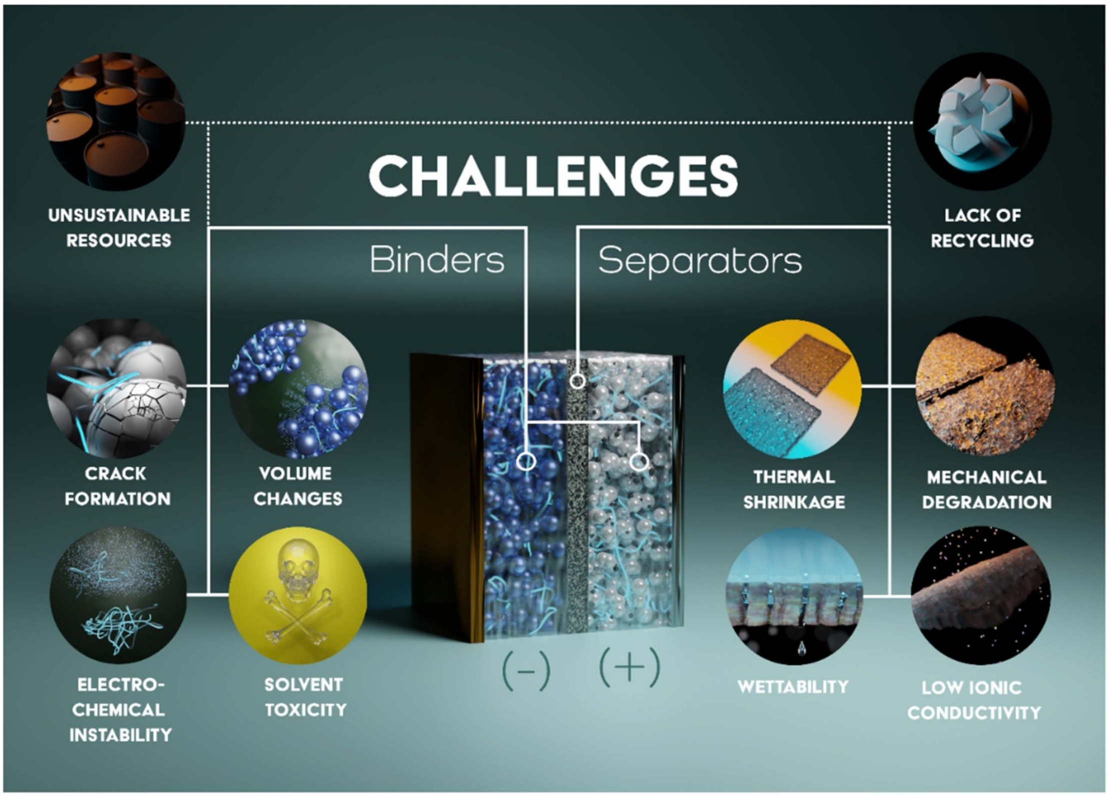

Figure 19. Current challenges of binders and separators in advanced LiBs. (Image design by Szymon Wiktorowicz/Labartory.com.).

Recyclability of the binders for reaching fully sustainable batteries is also not mature, yet. There is ongoing research in relatively small-scale recycling of binder materials via supercritical CO_2 extraction [248] and magnetic separation [249].

Separators

Intensive increase in the battery temperature, mechanical damage to the cell and metallic lithium dendrite growth would cause separators to fail [250]. PE separators are commonly used in LiBs due to their good thermal stability and low cost. However, PE separators also face challenges such as poor wettability with the electrolyte, which can lead to low ion conductivity and poor battery performance. Additionally, PE separators are susceptible to thermal shrinkage and melting at high temperatures, which can cause short circuits and safety hazards. Moreover, their low mechanical strength limits their application in high-power and high-energy-density batteries [251]. Many of the materials used in polyethylene and polypropylene, are derived from non-renewable resources, and can have significant environmental impacts. To achieve high power and high energy battery targets, the thickness of the separator should be minimized, which is 20–25 μm for commercial separators [252].

Advances in science and technology to meet challenges

Binders

Considerable research is being conducted to overcome the as-mentioned challenges. They originated to address challenges such as mechanical flexibility for the volumetric changes of Si anode, improved transport kinetics, sustainable manufacturing, and recycling [247].

For the sake of switching to water-based slurry systems, lignin and cellulose based binders stood forward with their advantages such as low-cost and sustainability. They are convenient for both anode and cathode slurries. Yet, the binder content is limited to reduce to the technological targets as transport kinetics are largely affected [253].

Self-healable binders are also demonstrated especially for the Si based anodes. This approach plays an important role when particle cracking occurs during lithiation and provides the overall electrode's integrity thanks to the reformation of the polymeric bonds [254]. Although, the technology has been proven with self-healable behavior, the common binders are also needed in the slurry composition to maintain sufficient binding strength and interface stability.

Binder morphology has also been studied to accommodate the volume changes. In a recent study, water-soluble PAA based binder was developed in a web morphology, inspired by spider web, boosting the high-rate performance and long-term cyclic stability [255].

Separators

To address the challenges faced by PE separators, new technologies include the development of nanofiber and composite separators that can improve wettability and ion conductivity [256]. These separators can also provide enhanced mechanical strength and thermal stability, reducing the risk of short circuits and safety hazards. Additionally, research is being conducted to explore the use of sustainable materials for separator production, such as bio-based materials [257]. Another approach is the use of additive manufacturing or 3D printing techniques to create complex separator structures with improved properties [258]. Advancements in thermal management, battery management systems, machine learning and artificial intelligence can help to reduce the risk of thermal runaway and other safety hazards associated with PE separators.

Separators with self-healing properties are also a promising new technology that could address some of the challenges associated with conventional LiB separators. These self-healing separators can autonomously repair defects or damages that occur during battery operation, which can lead to longer battery lifetimes and improved safety. These materials can heal themselves by re-forming the crosslinks that were broken or damaged due to dendrites [259]. Another approach is the use of microcapsules containing healing agents that can be released to repair any damage to the separator. Self-healing separators have the potential to significantly improve the sustainability and performance of LiBs. On the other hand, solid-state separators can address safety and performance issues, offering higher energy density (larger potential window) and longer cycle life, but face challenges such as high interfacial resistance and limited ionic conductivity. Researchers are exploring interface engineering, composite electrolytes, and new materials to bring solid-state batteries closer to commercialization.

Concluding remarks

Sustainable binders and separators are important for improving battery performance and reducing environmental impact. The current state-of-the-art binders are not sustainable, but technology is evolving in this direction, with water-soluble and solvent-free alternatives being regarded as sustainable. It is realistic to see more sustainable binders in the battery field soon. Next-generation bio-based separators are critical for addressing challenges in Li-based batteries and improving energy density and safety. Efforts must focus on efficient bio-based, solid-state, and smart separators, and strategies for developing sustainable cells from single to whole battery components could be developed. Advanced modelling, machine learning, industry 4.0, and standardization of methodologies can accelerate material discovery and reduce time to market.

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13. New electrode manufacturing: sustainable solvent and binder systems

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Status

Replacing traditional solvents with 'greener' alternatives will promote responsible and sustainable practices in the manufacture of battery electrodes, and solvent replacement is therefore an active area of research and development. The traditional solvents used in commercial battery electrode manufacturing include N-methyl-2-pyrrolidone (NMP) [260], dimethylformamide (DMF) and dimethylacetamide (DMAc); these are derived from fossil fuels, and all have implications for the environment and human health [261, 262].

Polyvinylidene difluoride (PVDF) is a desirable binder material in batteries, owing to its chemical inertness; however, this inertness makes it soluble in few organic solvents (as illustrated in figure 20), and manufacturers have therefore traditionally used NMP as one of the few solvents that will solubilise PVDF within an accessible temperature range [263]. However, NMP is a significant hazard to human health and as a result, there has been growing interest in developing alternative solvent-binder systems that can replace NMP-PVDF [87].

Several alternative solvent-binder systems have been proposed and studied in recent years, including systems based on water or employing less toxic organic solvents than NMP. These systems aim to reduce the environmental and health risks associated with NMP-PVDF and improve the performance and stability of battery electrodes. Water would be an ideal solvent to reduce the toxicity of the electrode slurry, combined with soluble bio-polymers as binders (such as sodium carboxymethyl cellulose (CMC), sodium alginate, carrageenan gum, or guar). These binders are non-toxic and biodegradable, and their use can reduce the overall manufacturing costs of the electrodes.

Making binder-solvent systems more sustainable can be achieved by making the solvent more environmentally sustainable (for example, using solvents derived from biomass instead of fossil fuels) to reduce the environmental impact of battery production [265]. Alternatively, the focus can be on using less toxic solvents such as terpineol [266] instead of NMP.

However, there are still challenges in developing alternative solvent-binder systems, such as achieving comparable performance to NMP-PVDF systems, optimizing the manufacturing process, and ensuring scalability and commercial viability. Therefore, further research and development are needed to advance the use of alternative solvent-binder systems for lithium-ion battery electrodes.

While there have been some successful experiments with using sustainable solvents in electrode manufacturing [267], further development and optimization are needed to make these solvents commercially viable for large-scale production. Additionally, the cost and availability of sustainable solvents need to be considered in relation to traditional solvents used in electrode manufacturing.

Current and future challenges

The battery and electrode manufacturing industry faces several challenges, both currently and in the future. These include:

Material supply chain: The supply chain for battery materials, including lithium, cobalt, and nickel, is currently vulnerable to disruption due to geopolitical risks, resource scarcity, and environmental concerns. In addition, the solvents and binders also have environmental impacts and upstream supply chains, which need to be considered when assessing the overall environmental impact of the materials [268].

Cost: While the cost of battery manufacturing has decreased significantly in recent years, further cost reductions are needed to make batteries competitive with traditional energy sources [269]. The use of green solvents, alternative binders, and sustainable manufacturing processes may increase the cost of electrode production.

Safety: The safety of batteries remains a critical concern, as incidents of battery fires and explosions have been reported in recent years. Improving battery safety is crucial for ensuring consumer confidence and avoiding potential regulatory setbacks [270]. Fluorinated polymers such as PVDF and PTFE are known to decompose and form HF which have significant safety concerns.

Performance: The performance of batteries needs to improve to meet the increasing demand for longer-lasting, faster-charging, and higher-capacity batteries. Research and development efforts are focused on developing new materials, designs, and manufacturing processes to achieve this goal. Green solvents and alternative binders may not perform as well as traditional solvents like NMP and PVDF, in terms of adhesion

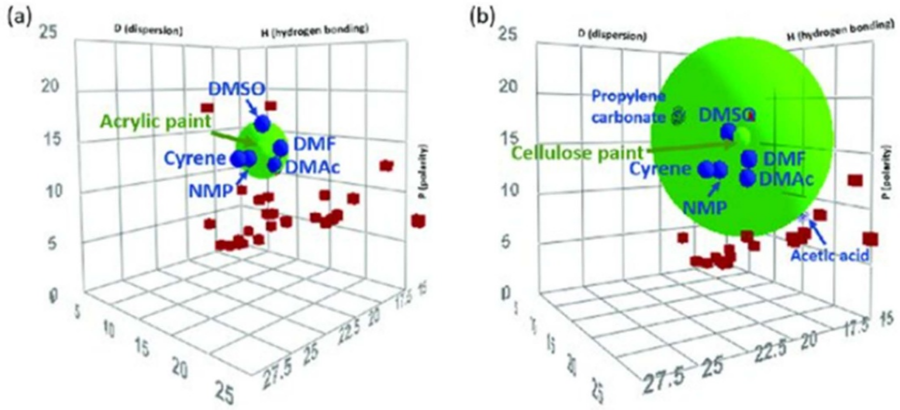

Figure 20. The Hansen spheres of two example polymers, with good solvents (blue), poor solvents (red) and the boundary defining good solvents (green) centred on the calculated position of the substrate. Polymer (a) is similar to PVDF in that it has a small solubility sphere and a limited number of viable solvents, all of which are polar aprotic. Polymer (b) is a cellulosic polymer with a rather larger solubility sphere. Reproduced from [264]. CC BY 4.0.

and cohesion of the electrode to the current collector [271]. Other adhesion enhancers may be needed to ensure that the performance of the electrode is not compromised when using these alternatives.

Environmental impact: Battery production has a significant environmental impact due to the extraction of raw materials, the use of energy in manufacturing, and the disposal of used batteries. Developing sustainable manufacturing processes and recycling technologies can reduce the environmental impact of battery production [272]. Green solvents are designed to reduce the environmental impact of electrode manufacturing and many of them can be used in recovery of the active materials from recycling processes. However, the production and disposal of these solvents can still have an environmental cost and the environmental impact of the entire manufacturing, and recycling process must be considered [273].

Scalability: current manufacturing processes may not be compatible with green solvents, which may require new equipment or processes, leading to additional costs and longer development times.

In the future, demand for sustainable electrode manufacturing is expected to increase as consumers and companies become more environmentally conscious. Meeting this demand will require significant investments in research and development, as well as in scaling up production capacity of promising solvents and binders. It will also require addressing the challenges mentioned above, including performance, scalability, cost, environmental impact, and material supply chain.

Advances in science and technology to meet challenges

Current research efforts in this area are focused on generating advances via the following approaches:

Water-based solvents: Water-soluble binders, such as carboxymethyl cellulose (CMC) and sodium alginate, are biodegradable, non-toxic, and have a low environmental impact. These materials are being developed and optimized for use in electrode manufacturing.

'Benign' solvents: solvents with lower toxicity than NMP are being investigated as replacements. Candidate solvents include dimethylsulfoxide (DMSO) [274], triethyl phosphate (TEP) [275] and ketone-containing compounds such as cyrene [265]. See figure 21 for the molecular structures of these examples. DMSO is REACH registered and does not have associated GHS hazards [276], however in applications such as cryogenic storage of embryos or in certain in vivo studies, toxicity concerns have been raised [277]. New polar aprotic solvents that can dissolve PVDF are under continual development [278]. The use of *in-silico* modelling has significantly eased this process, allowing for new solvent structures to be rapidly screened against either target replacements or for specific solvating powers [279].

Solvent-less manufacturing or lower solvent manufacturing processes: the development of solvent-free processes, such as the formation of electrode coatings by techniques such as electrospraying, automatically solves the problem of unsustainable solvent use [280].

Sustainable material sourcing: Efforts are being made to improve the sustainability of the material supply chain for battery electrode manufacturing. For example, the use of recycled materials and the development of more sustainable mining and extraction practices can reduce the environmental impact of the raw material supply chain.

Certification: One of the most well-known certification programs is the European Chemicals Agency's REACH (Registration, Evaluation, Authorization, and Restriction of Chemicals) regulation, which aims to

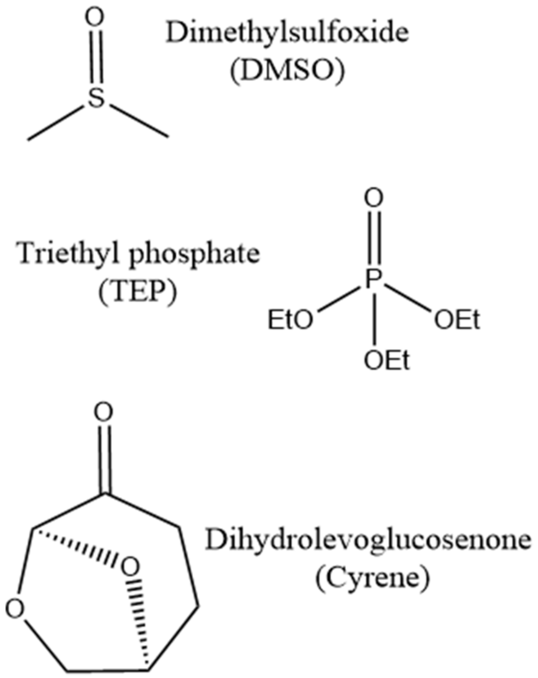

Figure 21. Molecular structures of examples of solvents that can be considered either less toxic (TEP, Cyrene, DMSO) or more sustainably produced than NMP (DMSO, Cyrene).

ensure the safe use of chemicals in Europe. Under REACH, companies that manufacture or import chemicals, including solvents and fluorine compounds used in electrode manufacturing, must register these substances with the European Chemicals Agency and provide information on their properties, uses, and potential risks. The regulation also includes authorization and restriction processes for certain hazardous substances [281]. In addition to REACH, the International Organization for Standardization (ISO) has developed standards such as ISO 14001 for environmental management systems and ISO 9001 for quality management systems, which can be used by manufacturers to ensure the responsible use of solvents and fluorine compounds in their processes.

Concluding remarks

Solvents are a key part of the electrode manufacturing process, and it is therefore in the interest of the battery manufacturing industry to promote the use of sustainable solvents wherever possible. Usable solvents are, however, dictated by the choice of binder included in the electrode; at present, there are no commercial 'greener' alternatives that work as reliably well as the PVDF-NMP polymer-solvent system. This is, however, an active area of research, with the clear and valuable goal of promoting the sustainability and lowering the toxicity of materials used to manufacture electrodes. Possible approaches to this problem tend to focus on either replacing the PVDF binder with a material that is soluble in water or another benign solvent, or on finding more sustainable solvents for PVDF.

Acknowledgments

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14. New electrode manufacturing: morphology and processes

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Status

The conventional method of making electrodes for different types of batteries is slurry coating: dispersing electrode active material, polymeric binder, electrical conductivity enhancer, e.g. carbon black, in a solvent, and coat the electrode slurry on a metallic foil before drying to evaporate the solvent and form a random mixture of constituent materials and microstructure. Aqueous processing is used in most anode processing, while toxic organic N-methyl pyrrolidinone (NMP) solvent and polyvinylidene difluoride (PVDF) binder are used for most cathodes. Some of the electrodes are then calendered to increase electrical conductivity and electrode density. While slurry coating is highly productive, the range of fabricated electrode thicknesses is restricted ($\leqslant 300\ \mu$m) before electrode cracking and it cannot control the resulting electrode microstructure [282, 283], hence, typical electrodes have pore tortuosity of 3–4 through the electrode thickness (the kinetically favourable direction for ion diffusion during (dis)charge) that restrict ion diffusion and capacity especially during fast (dis)charge [284]. The electrodes for new types of sustainable batteries still tend to use the existing slurry coating method, and consequently the electrochemical performance at the cell level remains constrained. One such example is of Li–S batteries (LSBs). When compared with Li metal oxide cathode materials, S is non-toxic, highly abundant and cost-effective. Combined with a high theoretical capacity (1675 mAh g^{-1}) and energy density (2600 Wh kg^{-1}), LSBs are a promising sustainable battery option [285, 286]. However, current electrode manufacturing and materials developments have not addressed the insulative properties of S and polysulfide (PS) shuttle effects that have restricted the electrochemical performance of LSBs at the cell level. There has been an accelerating emergence from the research base of innovative manufacturing processes (for conventional and new chemistries such as LSBs) in two areas. One is to develop dry processing that removes the needs for the liquid solvent used in slurry coating with significant sustainability benefits. The other is to manipulate electrode microstructure to arrange the material particles in a more controlled way to exploit the intrinsic properties of electrode active materials more efficiently and improve electrochemical performance [287, 288]. For example, modelling results show that the optimum porosity of 10% at the current collector and 50% at the electrode surface reduces ohmic resistance by 15%–33% than a uniform porosity of 30% throughout the electrodes [289]. Novel manufacturing methods such as the ones use aqueous processing or dry processing have the potential for reducing energy used for production by a quarter [290] as less energy is required in the electrode drying process for solvent evaporation (boiling points of NMP and water are 202 °C and 100 °C, respectively) and recovery of the evaporated NMP. Additionally, electrodes made of aqueous binder also do not require the use of NMP to re-dissolve the PVDF binder and separate the cathode material for battery recycling [291], reducing life cycle CO2 equivalent emission for a 10 kWh battery by 1000 kg [292].

Current and future challenges

For aqueous processing that replaces NMP with water, water may hydrolyse cathode materials, e.g. $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC811), causing Li leaching and change the morphology of the PVDF binder in the electrodes. The higher surface tension of water results in higher capillary forces during drying and cracking in thick ($>200\ \mu$m) electrodes [293]. C-based S cathodes in LSBs also exhibit high degrees of cracking. After the formation of Li_2S in the initial discharge, up to 80% volume expansion can occur. This is due to the large difference in densities of S (2.07 g cm^{-3}) and Li_2S (1.66 g cm^{-3}) [294]. The impregnation of S in C hosts to reduce the shuttle effect has challenges such as containing PS chains with polar nature in non-polar C hosts such as C nanofibres (CNFs) and nanotubes. For dry processing, ensuring sufficient mixing of dry slurry components, temporally inducing flow behaviour to a mixture of dry powders for casting, shaping the mixture into a coherent layer of defined width and thickness, and ensuring its adhesion to the current collector are the current challenges [295]. Another challenge is to reduce the proportion of inactive components such as binder and increase speed. For processing of making design electrode microstructure, the challenges are control over the resulting microstructure and scalability.

Advances in science and technology to meet challenges

Surface coatings of Al_2O_3 on NMC811 particles using techniques such as atomic layer deposition have been investigated to facilitate aqueous processing and prevent surface-initiated layered-to-spinel phase transitions [296]. Electrospinning of CNFs with or without binders has been developed to achieve higher degrees of

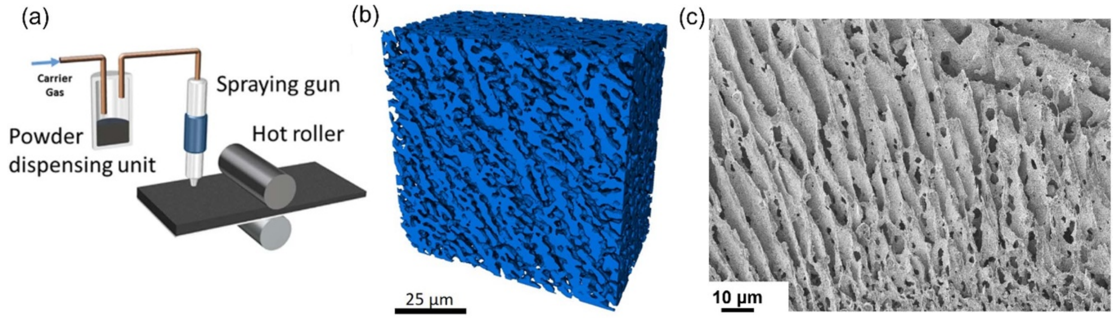

Figure 22. (a) Schematic of the manufacturing system of dry electrode processing [295]. Reproduced from [295], with permission from Springer Nature. (b) 3D volume rendering of the electrodes made by directional ice templating [290]. Reproduced from [290] with permission from the Royal Society of Chemistry. and (c) cross-sectional scanning electron microscopy (SEM) image of the fabricated electrode with vertically aligned pore channels and porosity gradient (lower porosity at the bottom) [298]. Reproduced from [298] with permission from the Royal Society of Chemistry.

orientation in CNFs and prevent drastic volume changes and cathode cracking in LSBs that exhibited an initial capacity retention of ∼93% after 150 cycles at 0.2 C [297]. Electrostatic coating or dry painting of the active material, binder and conductivity enhancer powders onto the current collector, followed by hot pressing that melts the polymer binder form a 3D network to effectively hold the active material and carbon additive together in a flexible web, creating a free-standing electrode film (figure 22(a)) [298]. Atomisation spray deposition of a suspension of electrode materials through a nozzle by compressed air and depositing on a current collector on a heating plate to evaporate solvent has been developed to make either layered [299] or graded electrode composition [300]. A three-layer electrode containing C in the top and bottom layers and Si/SiO$_x$ in the middle layer by spray improved electrical contact and reduced pulverisation of Si/SiO$_x$ [288]. There have also been developments in innovative manufacturing technologies to make electrodes with designed pore microstructures to improve ion diffusion kinetics through the electrode thickness which is the kinetically favourable ion diffusion direction during battery charge and discharge that improved capacity at faster (dis)charge rates [293]. Scalable directional ice templating processing has been developed to make electrodes with both vertically aligned pore channels that were filled with a standard liquid electrolyte during battery assembly, and improved ion diffusivity and capacity especially at faster (dis)charge rates, e.g. 15% capacity increase at 1 C (figures 22(b) and (c)) [293, 301]. Another directional freezing and polymerisation method has been developed to make electrodes with vertically aligned channels filled with a solid polymer electrolyte within a single process that increased effective ion diffusivity by 2 orders of magnitude at room temperature for solid-state batteries [302]. Other methods such as laser patterning [303] and 3D printing [304] have also been developed to manipulate electrode microstructure with high aspect ratio pores.

Concluding remarks

As the capacity of battery manufacturing increases, it is important to develop sustainable manufacturing methods that can be applied across existing and new battery chemistries. Innovative techniques are being investigated to enhance battery performance whilst improving sustainability, including developing aqueous and dry processing, and making designed electrode microstructure to enhanced ion diffusion.

Acknowledgments

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15. Battery manufacturing: a holistic approach to automation through digital twins and machine learning

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Status

Effective reduction of greenhouse emissions to circumvent climate change is a global challenge. One solution to achieve a low-carbon future relies on the energy transition enabled by lithium-ion batteries. Europe is poised to prohibit the production of fossil-fuel vehicles by 2035, while the European battery gigafactory industry is flourishing to meet the demands of the automotive sector's electrification. In this landscape, there remains a constant need to enhance battery cell energy and power densities, that together with durability, safety, and cost, constitute properties that depend on the manufacturing process. This process is highly complex, involving numerous parameters: material chemistry, composition, cell assembly, electrochemical protocols for stable Solid Electrolyte Interphase formation, among many others [305, 306]. Optimization solutions based on design of experiments for improving battery cell properties exist since it is a globally used technology. Nevertheless, there is significant room for optimizing the optimization and to reduce scrap rates in battery cell prototyping, as well as making the whole process more sustainable. Digital twins, originated in aerospace [307], constitute a promising concept in this regard: they are virtual representations of the manufacturing process that allows for monitoring, analysis, and simulation of its behaviour, and to predict the quality of the produced battery cells in real-time. This concept requires using data collected from sensors to create a digital model that can be used to optimize the quality of the produced battery cells in an autonomous fashion. This is particularly interesting for battery prototyping and pilot lines where a significant variability of manufacturing parameters exists [306]. The ARTISTIC project [308] has provided a pioneering approach to create such battery cell manufacturing digital twins, illustrated in figure 23. This approach integrates real manufacturing with physics-based process modeling and machine learning (ML) to perform inverse design of manufacturing parameters for optimal battery electrode or cell properties. These properties can be related to the product quality and/or to the environmental impact of the manufacturing.

The wide adoption of digital automation, particularly using digital twins, will significantly offer benefits to the battery industry. Implementing predictive maintenance [309], quality control [310], process optimization [311], resource planning [312], and real-time monitoring [312] can lead to increased efficiency, improved quality control, enhanced sustainability, better product performance, and reduced costs. Ultimately, using digital automation and ML in the battery industry can lead to a more sustainable and efficient energy landscape through many paths: the fast and automatic optimization loop that is enabled by this approach accelerates prototyping and testing of new battery designs, resulting in faster innovation and the development of more efficient, sustainable, and cost-effective batteries [307].

Current and future challenges

ML lends itself for digital automation purposes because of its ability to provide accurate representations of physical systems and predict their behaviour in quasi-real time by learning from existing data. However, the complexity of the battery manufacturing process requires a large amount of data, which can be difficult to obtain. In addition, the lack of accepted standards for data management hinders the exchange of information between academic research groups (disposing of battery prototyping or pilot lines) and the creation of collaborative large databases. Furthermore, its accuracy is crucial, as even small errors can result in significant impacts on the designed digital twins.

Current challenges for extensive experimental data collection to parametrize ML methods include an entirely consistent and systematic variation of manufacturing tests. Training a ML model with an inadequate small data set will not succeed in capturing the complex features that characterize battery fabrication and functioning [313]. Accessible manufacturing, prototyping, or laboratory battery production that implements robust procedures is necessary for accurate prognostics by in (un)expected input conditions. This experimental data production depends on the ML objective. For instance, building ML models for predicting battery safety might require atypical input conditions of several cells to minimize contradictory prognostics [314]. In comparison, ML models built for the purpose of optimizing fabrication, may use fewer

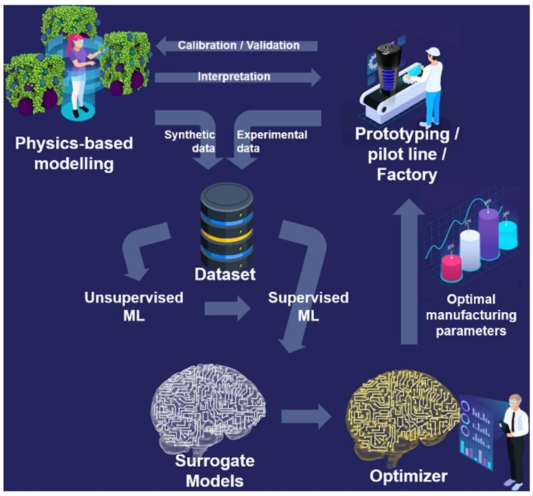

Figure 23. The ARTITIC concept for inverse design of battery cell manufacturing. Input and output data is generated by physics-based models and a prototyping or pilot line. The stored hybrid datasets are filtered and processed either automatically or by users, and fed into ML models for applying optimization methods that find the required manufacturing parameters to attain the desired battery electrode or cell properties [308]. Adapted with permission from Freepik.

experimental data or data from physics-based process models [315]. Notably, optimizing sustainability parameters such as durability or resource utilization might even require data from long after the product has left the factory or before the materials arrive at it.

Therefore, future research challenges include developing more advanced ML models that can accurately represent the manufacturing process and to automatically identify areas where improvements can be made, as well as advanced methods to filter redundant and noisy data and artificially augment training datasets. Improving the explainability of ML methods to facilitate the human understanding of the optimization results is also needed to allow identifying the origins of possible failures while the digital twin operates.

Another challenge is the integration of digital twins with real systems (figure 23), as it requires a high degree of synchronization and coordination between the physical and the virtual worlds. There is also a particular need for physics-informed ML to improve the accuracy of digital twins in modelling and twinning enabling technologies while guaranteeing the scalability of the results. This might involve incorporating knowledge of the physical principles underlying the manufacturing process into the ML models used to create digital twins.

Advances in science and technology to meet challenges

To address the challenges of integrating digital twins with real systems, advanced ML models capable of handling large amounts of unstructured data generated by battery prototyping and physics-based computer simulations are necessary. These models should be able to detect anomalies in real-time (in both real manufacturing and in computer simulations) for accurate predictions. Thus, the interaction between existing and new ML algorithms and non-relational databases [316] should be promoted, optimized and adapted to the problem to reduce computational costs and improve accuracy. This would also enable the integration of data generated by different sources and users, even if they follow different standards. Additionally, data filtering methods that can identify and remove irrelevant data and noise are essential.

Furthermore, simulation (synthetic) data generated by physics-based models at both micro and macro scales are necessary to complement scarce experimental data. It is still essential to optimize the scalability and parallelization of simulation codes to reduce computational costs [317]. To overcome these problems, it would be essential to enhance the existing computing infrastructure and the consequent adaptation of existing simulation codes to emerging technological paradigms such as quantum computing. Work in this direction should also aim to address at the same time phenomena such as heterogeneity along the electrode band at the cm-scale, and heterogeneity along electrode thickness at the µm-scale [307]. Moreover, further research should be oriented towards the extension of existing models [318] towards different and greener chemistries [319–321], and alternative manufacturing methods that do not use hazardous solvents such as extrusion [322], as basic research evolves, and new materials and methods are developed. Materials scrap recovery and battery cell recycling should be also considered in the digital twins.

Another challenge is to integrate generative ML models into physics-based simulation generation *i.e.* to move from pre-set to predictive models generation. This approach not only has the potential to improve accuracy but also lead to the autonomous development of more efficient models [323]. Last but not least, Virtual Reality and Mixed Reality technology give the promise to facilitate the interaction between the humans and the digital twins, in order to exploit the full potential of the latter (figure 23) [324].

Concluding remarks

As shown in previous sections of this roadmap, more sustainable battery chemistries and manufacturing methods are on the R&D pipeline. To accelerate the transition to production scale, full digitalization in battery manufacturing is necessary, yet two major challenges have to be addressed. First, existing physics-based models must be made more efficient to allow for real-time integration with the prototyping/pilot line and/or factory. A tight integration of these models with ML tools can achieve this. Second, the scarcity and lack of organization of experimental data can hinder its use for supervised ML training. To overcome this, efforts should focus on standardizing experimental methods and reporting, as well as developing smart autonomous data aggregation tools. The usefulness of ML is evident in addressing these challenges. With the growing demand for efficient and sustainable manufacturing, and escalating competition in the field of generative Artificial Intelligence tools such as Large Language Models, manufacturing automation developments are expected to accelerate. Though the details of how to attain the goal of full holistic automation in the optimization of battery manufacturing remain unknown due to the rapid pace in improvement of these tools, it is certain that exciting and potentially disruptive changes lie ahead in the field.

Acknowledgments

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16. Sustainable recycling processes for end-of-life batteries

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Status

The world is in the midst of a climate crisis characterized by an unprecedented sharp increase in global temperature, resulting in a growing risk of food and water insecurity, and an alarming rise in the frequency of devastating weather events. A climate-neutral, zero-polluting, and competitive economy for Europe is defined in the European Green Deal for 2030 and 2050, which implies an electrification scenario to minimize fossil fuel consumption. A decarbonized economy and an energetic transition leverage the development of energy storage devices to deploy new strategies in the transport and energy sectors, where electrochemical energy storage plays a crucial role. The raw materials required by the battery manufacturing industry represent a significant part of its costs as well as its carbon footprint. For this reason, Battery Regulation, launched by the European Commission on 10 December 2020 [325] and the European Raw Materials Act on 16 March 2023 [326], will regulate over the exponential growth of the battery market to reduce strategic dependencies on raw materials.

The competitiveness and sustainability of the European battery business require an efficient waste management strategy throughout the battery value chain. Examples from legacy technology, such as lead acid batteries, have demonstrated that besides reaching high recyclability rates is possible, it is also fundamental to consider factors like CO_2 emissions and energy expenses in the recycling process. In the case of lithium-ion battery (LIB), alternative recycling approaches are needed, not only to allow the recycling of valuable metals (Ni, Co, Mn, Li, Cu, Al, etc) but also that of non-metallic components (graphite, binders, separators, etc) to meet the growing battery demand effectively. Because of this, it is necessary to develop a holistic approach to battery and supercapacitor recycling, encompassing social, economic, and environmental aspects. These integrated approaches are fundamental in fostering a circular economy, diverging from conventional recycling practices that often entail the indiscriminate incineration of waste battery systems to novel approaches that represent new sources of raw materials. Global demand for batteries (in GWh/y) is expected to increase exponentially in the coming years, with a changing evolution of its own market share due to the continuous improvement and development of electrochemical energy storage (EES) technologies (figure 24(a)). LIBs will dominate the market with a share of close to 90% until 2030, when the new generation of battery technologies (including Solid-State Batteries (SSB) and Sodium-ion Batteries (NIBs) among others) will start gaining the market quickly. Due to the exponential increase in the demand for batteries and their lifespan, the electrode manufacturing scraps will represent the main source of materials to be recycled during the first wave of recycling. In contrast, in the coming years, end-of-life (EoL) batteries are expected to dominate the waste stream of materials to be recycled. A major concern in this regard is the collection logistics of these spent/used batteries; recyclers have to deal with these residues three years after the manufacture of electronic devices, e-bikes, etc. and at best 8–10 years for electric vehicles (EVs). As a result, current battery recycling actions and challenges primary target LIBs to increase the strength of the supply chain and promote circularity in the battery industry. This underscores the need for adopting conventions, such as design for recycling, to ensure straightforward recyclability across the battery lifecycle.

Due to the large number of battery chemistries (Lithium nickel manganese cobalt oxide (NMC), lithium nickel cobalt aluminium oxide (NCA), lithium iron phosphate (LFP), lithium manganese oxide (LMO), etc), the composition of the waste stream of the EoL batteries has an important impact on the technical, economic, and environmental feasibility of recycling processes (figure 24(b)). Some of the future upcoming recycling feeds contain economically low-value materials (e.g. LFP), which require innovative recycling solutions to close the profitability gap of these battery chemistries in order to ensure a competitive and environmentally friendly European Battery Business. In addition to the recovery of the active materials, the approach to the recycling of spent batteries should also address the treatment and recycling for reuse of the lower-value constituents of the battery: electrolytes, binders, plastics, separators, and so on.

Hence, the first crucial step in the recycling chain is the safe, cost-effective, and environmentally friendly collection, discharge, sorting, and dismantling of EoL batteries.

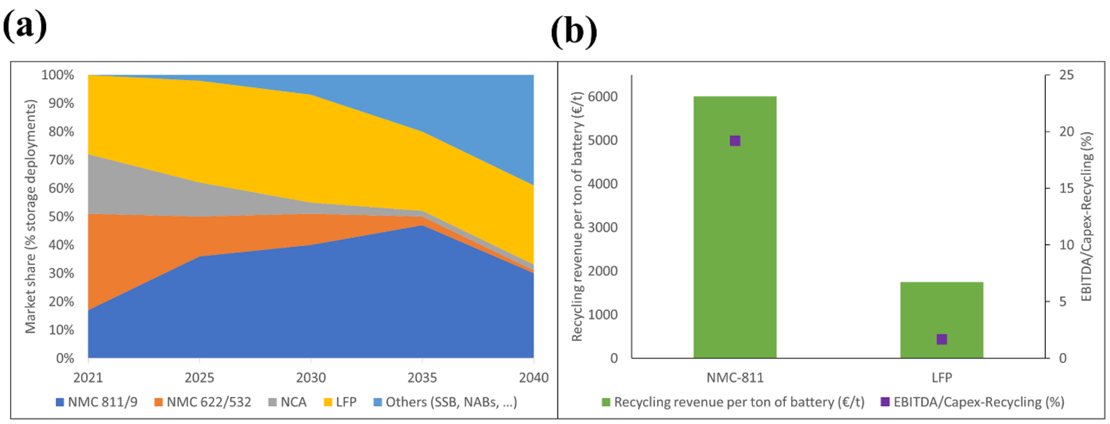

Figure 24. (a) EV battery chemistry market share forecast, and (b) The recycling revenues, Repoduced with permission [327], copyright (2022) Goldman Sachs Investment Research.

Battery pretreatment (pre-processing and separation)

Effective liberation of the enclosed materials in the battery is required to enable high recovery yields of all components to meet the zero-waste concept, thus establishing a circular economy for the battery business. According to the legislation [328], spent batteries are a hazardous, explosive, and corrosive waste, containing toxic chemicals and a residual electrical charge with a large variety of compositions and geometries. Much research effort is currently focused on automating the collection and sorting by battery chemistry, the discharge of the batteries as well as their dismantling, to increase the safety of the disassembly and shredding operations while increasing production capacity and subsequent recycling efficiency [329, 330]. In addition, new mechanical liberation technologies for these spent batteries are being thoroughly researched, due to the presence of alkali metals (lithium and sodium) and volatile and toxic solvents and/or polymers. These new approaches encompass wet shredding (electrohydraulic fragmentation), crushing under inert atmosphere (vacuum, nitrogen or CO_2), etc [331, 332].

All of these pre-processing steps are expected to significantly increase the recovery yield of the elements contained in a battery after the end of its useful life, ensuring a sustainable and cost-effective approach. Additionally, the disruptive developments in EoL battery pre-treatments driven by advanced characterization techniques, artificial intelligence, and automation technologies are fully linked with the performance of downstream recycling alternatives.

Battery recycling routes

Future battery recycling plants should extend their focus beyond the recovery of strategic raw materials to also include non-metallic elements (electrolyte salts, solvents, binders, graphite, and plastics). From a circular economy perspective, the battery recycling aims to recover materials suitable for manufacturing new batteries from spent batteries, thus bringing economic, environmental health, and social benefits to the battery industry [333]. Different routes and methodologies have been developed (figure 25) to meet the challenge of increasing the recovery yield of as many battery constituents as possible for reintroduction into a new battery.

- **Pyrometallurgical route:** the high temperatures employed in pyrometallurgical processes allow the battery to be deactivated, eliminating the risk of exploitation and electric shock, which is crucial for worker safety [334]. Pyrometallurgical methods are based on high-temperature melting and reduction processes of the battery and aim to produce mixed alloys, focussing on the recovery of valuable metals (mainly nickel, cobalt, and manganese) with substantial losses of lithium. Moreover, the use of high temperatures prevents the recovery of many of the constituents of the battery, such as lithium (salts), binders, solvents, separators, and graphite, among others, thus compromising the circularity of the recycling process. In addition, the high energy consumption and flue gas treatment make this route the least environmentally friendly option [335].
- **Hydrometallurgical route:** According to the European directive [325], the hydrometallurgical process currently appears to be the most promising alternative to meet the agreed battery recycling objectives. It is based on a pre-treatment step to facilitate the element's recovery and impurity removal, followed by leaching and purification stages [336]. The choice of leaching agents and conditions, the minimization of water and energy consumption, and the valorisation of the generated by-products must be carefully studied in order to find the most environmentally friendly and profitable way to close the battery life cycle. Several

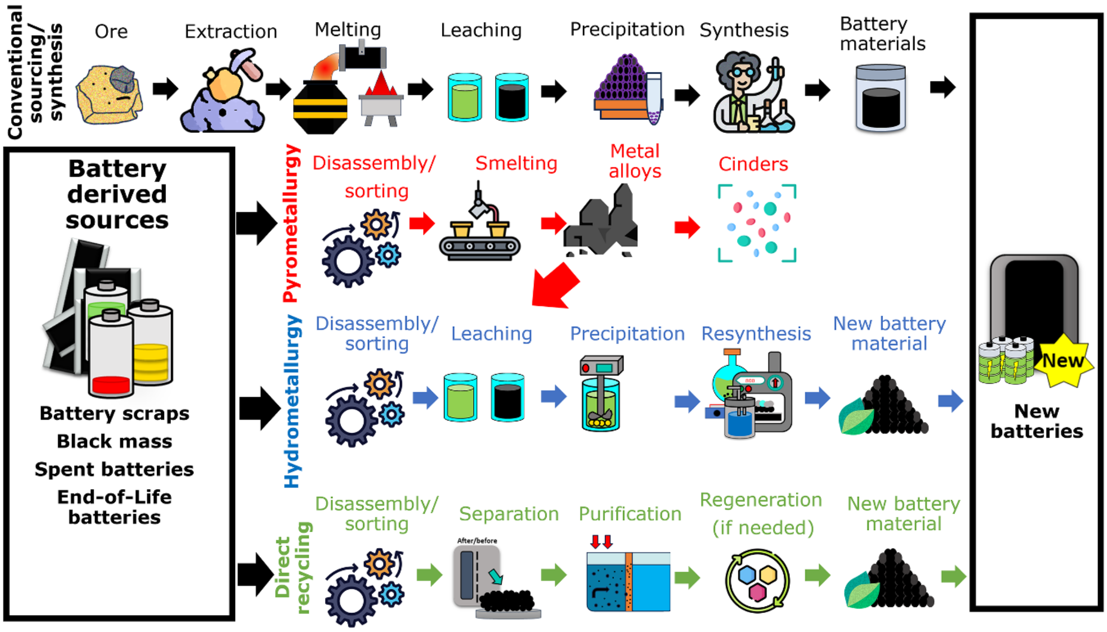

Figure 25. Simplified block flowsheet comparing pyrometallurgical, hydrometallurgical, and direct recycling routes of battery-derived recycling processes compared to conventional battery manufacturing processes from primary sources.

efforts are focused on improving the selective dissolution (inorganic and organic acids, redox conditions, etc) and the process efficiency (purification steps, microwaves-assisted reactors, etc) in order to maximize the recovery yield and the purity of the target products (battery grade materials) [337].

- **Direct recycling route:** Unlike the recycling techniques described above, direct recycling involves the recovery and refurbishment of degraded or scrap electrodes to achieve equal or better performance without altering the material's inherent structure and returning it to the battery supply chain with little or no additional processing [338]. In some cases, further steps involving the material structure's purification, relithiation, and/or restoration may be necessary to recover its original performance. Effective sorting of the harvested materials is essential for successful electrode recycling and potential upcycling and requires methods tailored to the electrode's binder, chemistry, and state of life [339]. Once the batteries have been classified, the cells are disassembled, components are separated and consequently delaminated using several methodologies that exploit differences in conductivity, density, solubility, binding ability, or other properties, allowing the recovery of the active material of interest, and also, of the metallic current collector. To date, approaches like mechanical [340], chemical [341], or thermal separation [342] are the ones most reported. After the separation step, additional steps such as filtration, centrifugation, or temperature treatments can be required to remove the non-desired residues.

Despite advances in the field, challenges to the large-scale implementation of direct recycling remain, particularly in sorting, delamination, study of degradation mechanisms, and regeneration, due to the complexity and associated costs of the processes [343]. Initiatives such as the implementation of the battery passport, the automation of cell opening, and the streamlining of the disassembly procedures show promise in reducing costs and promoting the feasibility of direct recycling approaches [344, 345]. It is also essential that the proposed methodologies are applied in realistic cases since most of today's works rely solely upon laboratory scale or ideal scenarios, and manufacturers may be reluctant to purchase recycled compounds if a performance equivalent to virgin material is not guaranteed.

Current and future challenges

EoL battery recycling will play a crucial role in the green and digital energy transition due to its impact on raw material dependency, sustainability, and profitability of the battery business. The current challenges focus on increasing the level of automation of the recycling process, the recovery and purity yields of the products obtained, their reintegration into new cells, and the cost-effectiveness while simultaneously decreasing the safety risks and environmental impact for LIBs. In the future, the most challenging issue will be the adaptability of the developed and optimized recycling alternatives to new generation battery technologies. These future processes will deal with new chemistries of active materials (NIBs, LIBs with Si/C or Silicon anodes, etc), the presence of solid electrolytes (polymeric, ceramic, hybrid), and lithium metal anodes in solid-state batteries, among others.

Concluding remarks

The development of appropriate recycling processes will ensure a resilient supply chain of battery raw materials, minimal environmental footprint, circularity, and competitiveness of the battery business. Flexible, robust and efficient battery recycling processes would overcome these challenges and drive the growth of more sustainable battery technologies. The complex challenges ahead require an interdisciplinary approach, advances in science and technology, and closer collaboration between academia and industry throughout the entire battery value chain (design, raw materials, components, cells, and packs manufacturing and recycling).

Data availability statement

No new data were created or analysed in this study.

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