Soild and Liquid Electrolytes for Li-ion Batteries

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Abstract.

Electrolytes are pivotal components of Li-ion batteries. Electrolytes enable ion transport between electrodes. The chemical composition and thermodynamic phase of an electrolyte directly influence performance, safety, and longevity. This chapter discusses challenges and advancements in liquid and solid electrolytes with an accent on their roles in shaping next-generation energy storage systems. Liquid electrolytes, composed of lithium salts dissolved in organic solvents remain the present industry standard, thanks to their desirable ionic conductivity and mature manufacturing infrastructure. Flammability, toxicity, and chemical reactivity under extreme conditions pose risks, such as thermal runaway and fire hazards. In turn, solid electrolytes offer non-flammable alternatives. They exhibit enhanced thermal stability and compatibility with highly energy-dense anodes like lithium metal. Ceramic electrolytes boast promising conductivity and electrochemical stability. Thus far, high production costs and processing challenges hinder the scalability of ceramic alternatives. Polymeric Li-ion electrolytes are flexible and easy to process, yet face limitations, such as relatively low ionic conductivity. Liquid Li-ion electrolytes dominate due to established supply chains and cost-effectiveness. Alternatively, solid electrolytes steadily gain traction amid modern demand for safer and higher-capacity batteries. The synthesis of solid Li-ion electrolytes involves costly processes and requires rare materials. Safety represents a critical driver for solid electrolytes, as they eliminate flammability risks and mitigate lithium dendrite formation. Sustainability and recyclability limitations are common challenges across both electrolyte types. Ionic liquids dissolving lithium salts can be considered to represent the third type of Li-ion electrolyte due to their non-volatility and broad voltage tolerance. Liquid Li-ion

electrolytes contribute harshly to environmental pollution due to toxic solvent leakage, whereas solid electrolytes face obvious hurdles in material recovery. Compatibility with electrode materials and electrochemical stability windows dictate electrolyte selection. Herein, we underscore the need for interdisciplinary innovation to balance performance and safety in electrolyte design for a decarbonized future.

Choice of Electrolytes for Li-Batteries

Electrolytes play a critical role in the operation of Li-ion batteries (Li et al., 2017; Grissa et al., 2018; Falco et al., 2019). Either liquid or solid, they serve as the medium through which lithium ions travel between the anode and cathode during charge and discharge cycles. The ion transport mechanism is the cornerstone for maintaining the electrochemical balance within the battery, thus enabling consequent energy storage and release. The performance, efficiency, and safety of Li-ion batteries are heavily influenced by the properties of the electrolyte. Therefore, an electrolyte represents one of the most crucial components to correctly choose upon battery design (Li et al., 2017; Grissa et al., 2018; Falco et al., 2019; Tröger-Müller and Liedel, 2019; Kim et al., 2020; Pal et al., 2020). Successful electrolytes exhibit high ionic conductivity and relatively low shear viscosity to facilitate rapid ion movement, maintain chemical stability over a wide voltage range, and remain compatible with electrode materials, preventing the degradation upon numerous discharge cycles. Electrolytes must operate effectively under varying temperature conditions, ensuring reliable battery function in diverse practical applications (Bublil et al., 2021).

Two primary types of electrolytes are employed in Li-ion batteries, particularly, liquid and solid electrolytes. Liquid electrolytes are typically composed of lithium salts dissolved in non-aqueous solvents (Alshangiti et al., 2024). They have remained the industry standard since the commercialization of Li-ion batteries in the 1990s. Common formulations include lithium hexafluorophosphate dissolved in mixtures of ethylene carbonate, dimethyl carbonate, and diethyl

carbonate. The above solvents provide high ionic conductivity and good electrochemical stability, allowing for efficient charge transfer. Nevertheless, liquid electrolytes are inherently flammable and pose significant safety concerns. Extreme conditions, such as overcharging, overheating, and mechanical damage, represent a particular peril. These safety concerns drive extensive research into alternative electrolyte materials that enhance safety without compromising the current performance expectations achieved during the last thirty years (Kelchtermans et al., 2024).

Solid electrolytes have emerged somewhat later as a promising alternative to liquid electrolytes (De Klerk and Wagemaker, 2018). Solid electrolytes offer improved thermal stability and reduced flammability. Unlike liquid electrolytes, solid electrolytes do not require separators to prevent direct contact between the anode and cathode. This essential feature simplifies battery architecture and enhances its safety. Solid-state electrolytes are classified into three paramount categories: (1) ceramic-based solid electrolytes, (2) polymer-based solid electrolytes (Figure 1), and (3) glass-based solid electrolytes. Ceramic electrolytes – e.g., lithium lanthanum zirconium oxide and lithium phosphorus sulfide – exhibit high ionic conductivity and noteworthy electrochemical stability. These features make ceramic electrolytes suitable for high-performance applications. Polymer electrolytes – e.g., polyethylene oxide with lithium bis(trifluoromethanesulfonyl)imide – offer flexibility and ease of processing. Yet, polymer electrolytes exhibit, in general, a lower ionic conductivity compared to ceramic materials (Yoon et al., 2023; Yoon and Shin, 2023). Glass-based electrolytes utilize oxide and sulfide glasses. These materials combine high conductivity with mechanical durability. Some challenges related to interfacial resistance and manufacturing scalability persist (Nandan et al., 2022; Asakura et al., 2024).

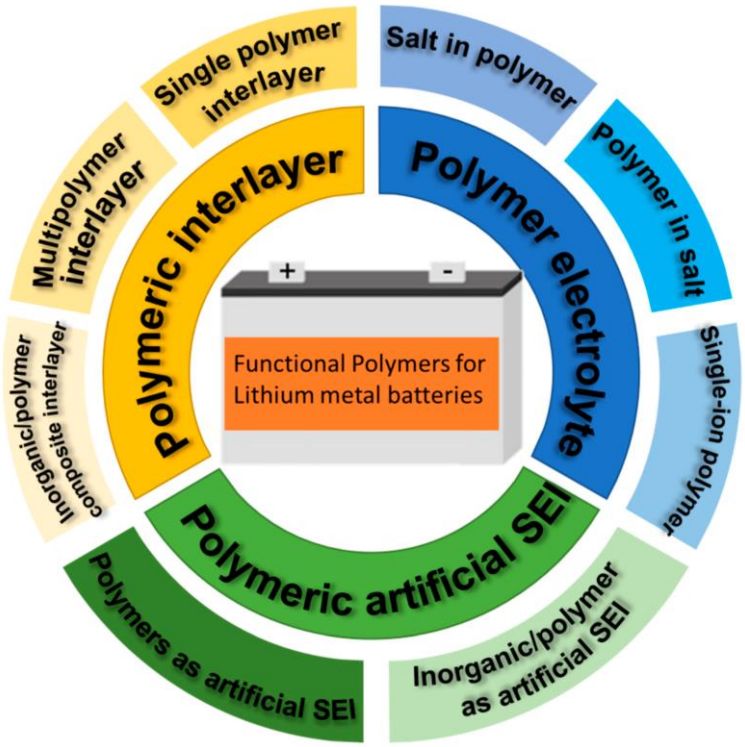

Figure 1. Classification of polymeric materials in modern lithium metal batteries. Reproduced from (Ma et al., 2022). The image is licensed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

The choice of electrolyte significantly influences the aggregate performance (charge/discharge capability), safety, and longevity of modern Li-ion batteries (Figure 2). Liquid electrolytes have enabled the widespread adoption of high-energy-density batteries in consumer electronics, electric vehicles, and renewable energy storage systems (Ramar et al., 2020; Rajendran et al., 2024; Tuul et al., 2024). Their inherent flammability and susceptibility to thermal runaway have fostered research interest in solid-state alternatives that promise safer and more stable operation. As battery technologies continue their evolution, ongoing research is focused on optimizing both liquid and solid electrolytes. It is believed that room for enhancements exists for energy density, reduction of production costs, and improvement of sustainability. In this chapter, we explore the nanoscale architecture, economic considerations, and safety implications of electrolyte types. We provide a comprehensive discussion of their role in shaping the vibrant future of energy storage by means of Li-ion batteries.

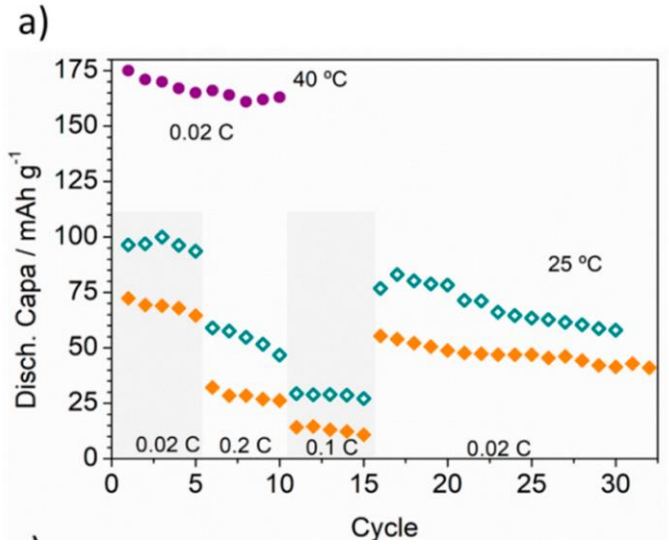

Figure 2. Rate discharge capability of the NMC|Cl-SE|In-Li cell at 25 °C (green dots), 40 °C (purple dots), and of the NMC|I-SE|In-Li cell at 25 °C (orange dots). Reproduced from (Dao et al., 2020). The image is licensed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

Evolution of Electrolytes for Li-Batteries

The evolution of electrolytes in Li-ion batteries continues to be a dynamic journey. It is marked by scientific breakthroughs and technological advancements. The early development of Li-ion technology in the early 1990s laid the groundwork for the commercialization of modern batteries. Various electrolyte systems were explored until organic liquid electrolytes primarily catalyzed the widespread adoption of Li-ion batteries. These electrolytes typically consisted of lithium hexafluorophosphate dissolved in a mixture of lower organic carbonates. This formulation was chosen thanks to its high ionic conductivity and relatively good electrochemical stability. The first commercial Li-ion batteries were introduced by Sony in 1991. They utilized the liquid electrolyte system described above. The Sony's batteries combined a graphite anode and a lithium cobalt oxide $LiCoO_2$ cathode. Sony's innovation marked a significant milestone in battery technology. The first-in-history lightweight, high-energy-density solution for portable electronics emerged (Lee et al., 2021). The success of these early batteries established liquid electrolytes as the industry standard. Continuous improvements aimed at enhancing performance, safety, and

longevity, followed. Electrochemists focused on optimizing solvent mixture compositions and lithium salt concentrations to improve conductivity and reduce viscosity (Zou and Lu, 2021). The inherent flammability of organic solvents had to be attended to simultaneously. The introduction of additives to stabilize the solid-electrolyte interphase layer at the surface of the anode further enhanced battery performance and cycle life.

Despite the advancements in liquid electrolyte technologies (Sirengo et al., 2023), safety concerns persisted owing to the nature of a molecular component of the electrolyte. In particular, they were urgent for high-energy applications in electric vehicles and grid-scale energy storage. The flammability of organic solvents raised the risk of thermal runaway and prompted to exploration of alternative electrolyte designs. The search for safer electrolyte options led to the investigation of solid-state electrolytes (Zhou et al., 2018; Offermann et al., 2024; Yildiz et al., 2024). The latter emerged as a promising alternative to liquid electrolytes in the early 2000s. Early solid-state electrolytes were primarily polymer-based, see polyethylene oxide with lithium salts, which offered flexibility and ease of processing. However, ion conductivity suffered drastically compared to the performance of lower organic carbonates. The breakthrough came with the discovery of ceramic-based solid electrolytes. These exhibited significantly higher ionic conductivities and thermal stabilities. Lithium lanthanum zirconium oxide and lithium phosphorus sulfide demonstrated the potential for solid-state batteries to deliver both high performance and enhanced safety. These ceramic electrolytes were non-flammable and offered the capability to support lithium metal anodes (Yemini and Noked, 2021; Lanjapalli et al., 2022). These advances promised higher energy density compared to conventional graphite anodes. Challenges related to interfacial resistance between the electrolyte and electrodes, as well as manufacturing scalability, hindered their immediate commercialization.

Glass-based solid electrolytes were investigated in parallel. They combined the advantages of high ionic conductivity with mechanical durability (Nagata and Akimoto, 2021). Oxide and sulfide glasses held promise in laboratory settings but faced challenges regarding integration into

commercial battery designs. Nevertheless, the progress in solid-state electrolyte technology laid the foundation for future innovations. Among those, fast-charging applications and designs with enhanced safety must be mentioned.

The historical development of electrolytes in Li-ion batteries reflects a continuous effort to balance performance, safety, and cost-effectiveness. While liquid electrolytes continue to remain the dominant choice due to their established infrastructure and proven performance, the advancements in solid-state electrolytes have opened new avenues for safer and more sustainable energy storage solutions. Nowadays, the demand for high-energy-density batteries steadily increases. Ongoing research into both liquid and solid electrolyte systems plays a crucial role in shaping the next generation of Li-ion batteries (Tron et al., 2017; Oltean et al., 2018; El Kharbachi et al., 2020; Liu et al., 2021; Jiao et al., 2024).

Characterization of Liquid Electrolytes for Li-Ion Batteries

Liquid electrolytes in Li-ion batteries usually employ lithium salts, such as lithium hexafluorophosphate and lithium tetrafluoroborate (Chaban, 2015a; Chaban, 2015b). The composition of these electrolytes is tightly optimized to achieve high ionic conductivity, low viscosity, and adequate electrochemical stability. All of these physicochemical descriptors are essential for efficient battery operation. Yet, despite their widespread use, liquid electrolytes present several technical challenges, which impact battery performance and safety.

Ionic conductivity directly determines the rate at which lithium ions move between the anode and cathode (Chaban and Prezhdo, 2016). High ionic conductivity ensures efficient charge and discharge cycles. It enables fast-charging capabilities and high-power applications. Organic carbonate solvents are commonly used due to their ability to dissolve lithium salts effectively and facilitate rapid ion transport (Chaban and Kalugin, 2009; Chaban and Kalugin, 2010). $LiPF_6$ is the most widely used lithium salt due to its good solubility in carbonates and compatibility with

electrode materials. However, $LiPF_6$ decomposes into hydrofluoric acid HF in the presence of moisture. In turn, HF corrodes battery components and degrades Li-ion battery performance over time. To mitigate this issue, additives, such as vinylene carbonate and fluoroethylene carbonate, are employed. They stabilize the solid-electrolyte interphase layer on the anode, enhance cycling stability, and suppress undesirable side reactions.

Shear viscosity affects ion mobility and diffusion kinetics. Low-viscosity solvents are highly preferable upon designing new electrolytes. Lower organic carbonates enhance ion transport and allow for higher charge-discharge rates. However, excessively low viscosity correlates with increased volatility (Chaban and Prezhdo, 2011). Electrolyte evaporation and gas buildup within the Li-ion battery are undesirable. Solvent blends were developed that optimize the conductivity, viscosity, and electrochemical stability of the electrolyte. A common formulation of such a blend includes a mixture of ethylene carbonate, dimethyl carbonate, and diethyl carbonate. Therein, ethylene carbonate provides a high dielectric constant (Jin et al., 2019). Thus, its presence fosters a higher solubility of $LiPF_6$. In turn, dimethyl and diethyl carbonates contribute to lower viscosity and improved ion mobility.

The electrochemical stability range of organic carbonate electrolytes is a crucial factor that determines their suitability for high-voltage applications. Organic carbonate-based electrolytes exhibit electrochemical stability up to approximately 4.5 V. This limitation restricts the use of high-voltage cathode materials, such as $LiNiMnCoO_2$ and $LiCoO_2$. An extension of the electrochemical stability of liquid electrolytes is possible by fluorinating the hydrocarbon chains of the solvents. Examples are fluoroethylenecarbonate and trifluoropropyl moieties grafted where necessary. By eliminating C…H covalent bonds, these exhibit an enhanced oxidation resistance (Gunnarsdóttir et al., 2020). Additives like lithium difluoro(oxalate)borate and lithium bis(oxalate)borate were recorded to suppress electrolyte decomposition and improve cycling performance under elevated voltages.

Despite obvious improvements during the last three decades, liquid Li-ion electrolytes pose significant safety risks, largely due to their flammability (Murmann et al., 2018). Organic carbonate solvents are highly flammable. In the event of thermal runaway, electrolyte solvents ignite, resulting in a catastrophic failure. Thermal runaway is triggered by overcharging, internal short circuits, and mechanical damage. The enumerated processes generate excessive. Therefore exothermic reactions are readily initiated within the battery. To address these concerns, researchers have developed flame-retardant additives, e.g., triethyl phosphate and trimethyl phosphate. These additives suppress combustion by inhibiting radical chain reactions. These additives simultaneously reduce ionic conductivity and increase viscosity. A careful balance between fire safety and electrochemical performance is urged.

Carbonate electrolytes are susceptible to chemical degradation under high-temperature conditions (Dupré et al., 2017). Prolonged exposure to elevated temperatures accelerates electrolyte decomposition. As a result, the formation of resistive surface films, gas emission, and loss of active lithium ions take place. These degradation processes adversely contribute to the deterioration of capacity and reduced cycle life (Fernandes et al., 2019). Thermal management represents a critical aspect of Li-ion battery design. In electric vehicles and high-power applications, advanced cooling systems, such as liquid cooling and phase-change materials, had to be employed. They assist substantially in regulating battery temperature and minimizing electrolyte degradation. Liquid electrolytes have played a pivotal role in the widespread adoption of Li-ion batteries and the emergence of portable electronics thirty years ago thanks to their high ionic conductivity, compatibility with electrode materials, and established manufacturing infrastructure. However, the characterized above challenges have not been fully addressed thus far. The next section characterizes solid electrolytes, which offer thermal stability and non-flammability.

Characterization of Solid Electrolytes for Li-Ion Batteries

Solid electrolytes may be seen as a promising alternative to conventional liquid electrolytes in Li-ion batteries (Park et al., 2024). They offer enhanced safety for a consumer and compatibility with high-energy-density anode materials, such as those made of Li metal. Solid electrolytes are typically composed of ceramic, polymer, and glass-based materials (Figure 3). Their chemical compositions eliminate the risk of ignition and burning. The outlined fundamental difference makes solid electrolytes to be seen as a compelling solution for next-generation Li-ion batteries that prioritize safety and longer functionality. Despite their advantages, solid electrolytes present unique challenges (Peta et al., 2024). These include lower ionic conductivity compared to organic electrolytes, interface resistance between the electrolyte and the existing electrodes, and manufacturing issues (Quartarone et al., 2023).

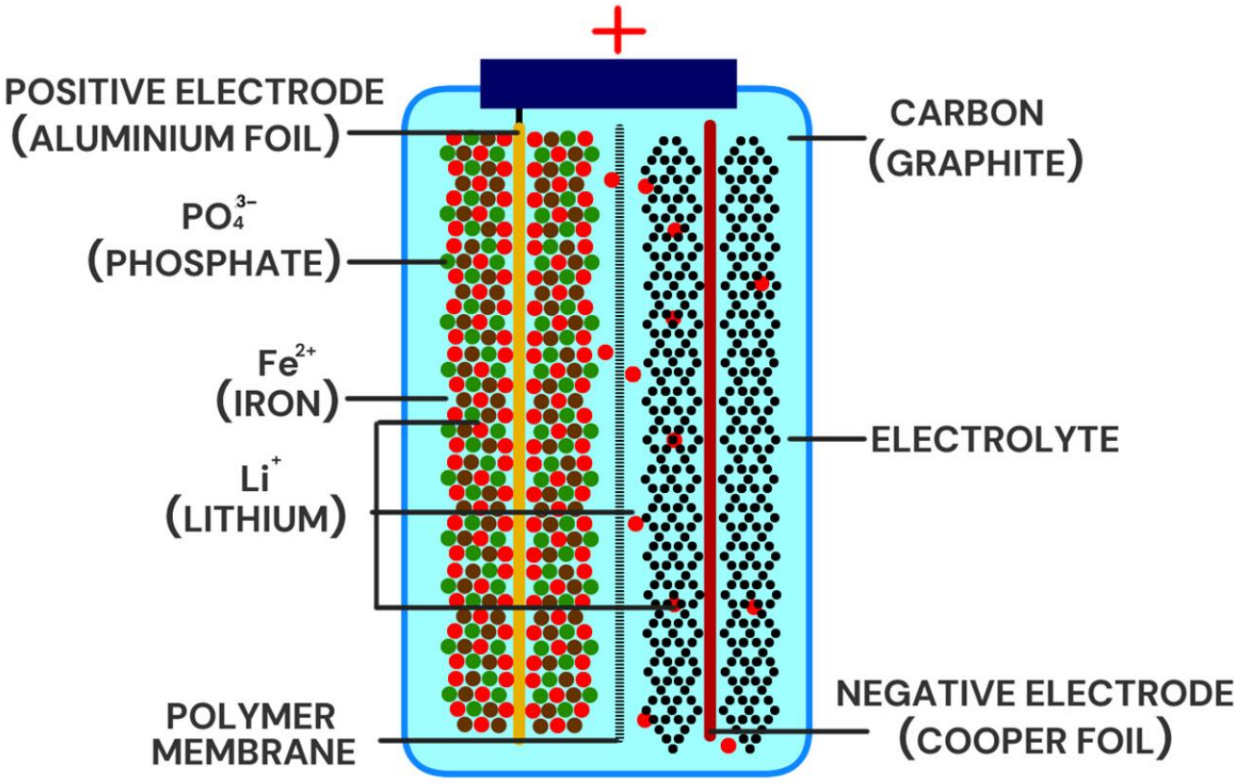

Figure 3. Structural scheme of $LiFePO_4$ Li-ion battery composition. Reproduced from (Köntös and Gyöngyössy, 2024). The image is licensed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

Ceramic-based solid electrolytes are presently among the most studied solid electrolyte materials owing to their high ionic conductivity, wide electrochemical stability window, and mechanical rigidity (Bonizzoni et al., 2019). The latter prevents dendrite formation in lithium metal anodes. Lithium lanthanum zirconium oxide exhibits an unusual room-temperature ionic conductivity exceeding 1 mS/cm (Nguyen et al., 2022; Nguyen et al., 2021; Tian et al., 2022). This ionic conductivity of Li-ion is comparable to the ones in liquid organic electrolytes. Lithium lanthanum zirconium oxide is particularly attractive for high-voltage and high-capacity batteries (Villacis-Segovia et al., 2024). It remains stable over a wide voltage range, allowing for the use of nickel-rich cathodes and lithium metal anodes without significant degradation. Another widely researched ceramic material is lithium phosphorus sulfide. This compound offers exceptional ionic conductivity, up to 25 mS/cm, and low interfacial resistance. Lithium phosphorus sulfide is suitable for fast-charging applications emerging nowadays (Choi et al., 2018; Kim et al., 2021). In the meantime, lithium phosphorus sulfide-based electrolytes are susceptible to moisture. A result of hydrolysis is hydrogen sulfide, which is a toxic gas. H_2S poses safety concerns upon manufacturing and battery assembly.

Ceramic-based solid electrolytes face challenges related to brittleness and poor processability. These flaws of the material complicate their integration into commercial battery designs. The rigid nature of ceramics makes them prone to cracking under mechanical stress. Cracking limits their ability to accommodate volumetric changes in high-capacity electrodes, such as silicon and lithium metal. Achieving uniform and defect-free ceramic electrolyte layers requires high-temperature sintering. Sintering increases production costs and limits scalability. Composite electrolytes are investigated as promising alternatives in this context. Therein, ceramic particles are combined with polymer matrices. The employment of polymer scaffolds fosters the flexibility and manufacturability of Li-ion batteries. The high ionic conductivity of ceramics does not suffer or deteriorate unsubstantially in such setups.

Polymer-based solid electrolytes offer an alternative to ceramic electrolytes. Polymerized matrices provide flexibility, ease of processing, and compatibility with existing Li-ion battery manufacturing techniques. The most commonly studied polymer electrolyte is polyethylene oxide complexed with common lithium salts, particularly lithium bis(trifluoromethanesulfonyl)imide. Polyethylene oxide-based electrolytes are lightweight and non-flammable. They are capable of forming stable interfaces with lithium metal (Figure 4). One of the primary limitations of polymer electrolytes is their inherently low ionic conductivity. The ionic conductivity of Li-ion in such electrolytes typically ranges from 10^{-6} to 10^{-4} S/cm due to steric barriers introduced by the matrix and Li…O electrostatic coupling. These values are significantly lower than those of liquid and ceramic electrolytes. Inappropriately slow ionic transport restricts their use in high-power applications heads to high internal resistance, and slows down charge-discharge rates.

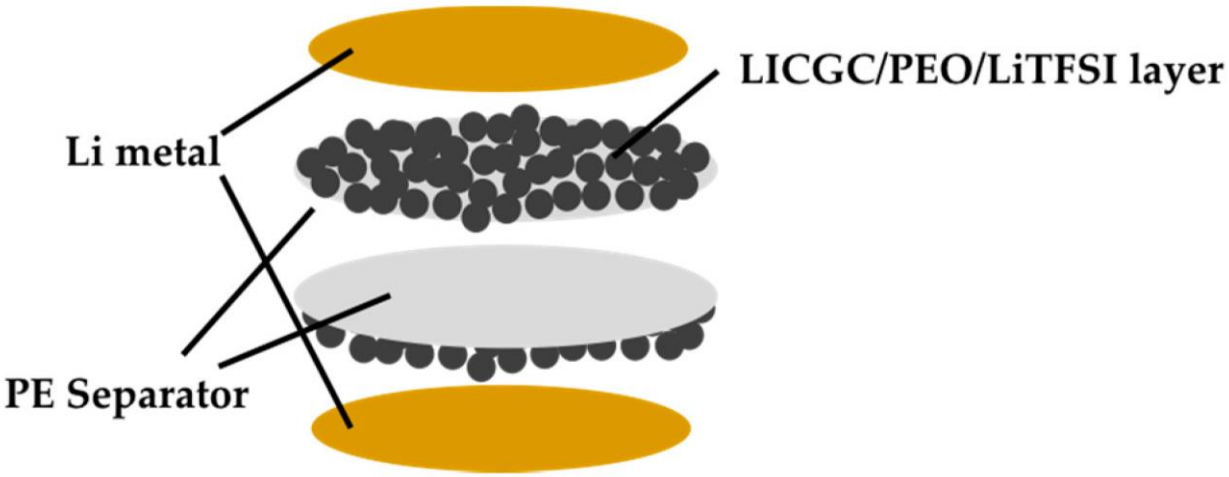

Figure 4. Configuration of the Li/Li symmetric cell using the LICGC/PEO/LiTFSI-PE ceramic separator layer. Reproduced from (Shomura et al., 2022). The image is licensed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

Plasticizers, nanoparticle fillers, and copolymer modifications are added to boost Li-ionic conductivity in polymer-based solid electrolytes. The so-called plasticizers are ethylene carbonate or propylene carbonate. These molecules increase chain segment mobility and strengthen ion diffusion. Inexpensive and stable nanoparticles have also been tried as rather efficient plasticizers.

Silicon and aluminum oxides SiO_2 or Al_2O_3 enhance interfacial stability and reduce crystallinity. The reduced crystallinity is directly linked to the faster Li-ion transport. Despite these essential advancements, polymer electrolytes face challenges related to thermal stability. Most polyethylene oxide-based electrolytes exhibit melting points around 60–70 °C. At higher temperatures, the ionic conductivity of Li-ion drops significantly. Modified polymers, such as cross-linked polymer networks and block copolymers, maintain structural integrity at higher temperatures. Thanks to these architectures, the competitive ionic conductivity can be preserved up to more elevated temperatures.

Oxide and sulfide glasses offer a reasonable balance between high ionic conductivity and mechanical durability. The combination of satisfactory performances makes glass electrolytes attractive candidates for solid-state Li-ion batteries. Lithium borohydride $LiBH_4$ and lithium thiophosphate $Li_7P_3S_{11}$ are considered to be the most promising glass Li-ion electrolytes. The room-temperature ionic conductivities of these glasses exceed 10 mS/cm. These values are almost competitive with those of liquid electrolytes. $Li_7P_3S_{11}$ demonstrates exceptional Li-ion conductivity and low interfacial resistance. These parameters make the $Li_7P_3S_{11}$ electrolyte suitable for high-rate applications. Non-crystalline arrangement of $Li_7P_3S_{11}$ is sensitive to moisture. Humidity must be limited to guarantee a long lifespan of this glass electrolyte without the degradation in the initial conductivity characteristics.

An obvious advantage of glass-based electrolytes in the context of batteries is their amorphous structure. A cation must be able to freely travel throughout the solution supporting thereby the charging and discharging of the battery. Amorphous structure implies the presence of voids and irregularities, which foster ionic mobility via one or more ion transport mechanisms. The higher the degree of amorphicity of the electrolyte material, the faster Li-ion transport must be expected. Glass electrolytes can be processed at relatively low temperatures. This feature reduces manufacturing complexity compared to ceramic electrolytes. Challenges remain in scaling up production and ensuring long-term chemical stability when paired with reactive lithium metal

anodes. Coating techniques and protective interlayers are investigated to improve electrode-electrolyte compatibility and restrict the flow of side chemical reactions.

Compared to liquid electrolytes, solid electrolytes offer superior safety. The utilization of solid electrolytes, instead of volatile and flammable electrolytes, eliminates safety concerns. This makes solid-state electrolyte Li-ion batteries particularly attractive for electric vehicles and grid-scale energy storage. Solid electrolytes enable the use of lithium metal anodes. The latter offers significantly higher energy density than conventional graphite anodes. Solid electrolytes remain inferior to liquid electrolytes in terms of ionic conductivity, manufacturability, and cost-competitiveness. The omnipresent commercialization of solid electrolytes is seen to be premature, considering today's disposition in the market and battery technology today. It is quite realistic that solid electrolytes will never outperform organic carbonate liquids coupled to inorganic fluoride salts based on the current chemical knowledge of the existing systems and their physicochemical properties. Therefore, hybrid electrolyte designs and advanced manufacturing techniques deserve due attention.

Economy of Electrolytes for Li-Ion Batteries

The economic viability of Li-ion batteries is heavily influenced by the cost of materials, manufacturing processes, scalability, and market of chemicals. Among the key components of a Li-ion battery, the electrolyte plays a critical role in determining both the performance of the battery and its final cost. Whereas liquid electrolytes are the industry standard due to their established supply chains and acceptable production costs, solid electrolytes are more expensive. The transition from conventional liquid electrolytes to solid-state alternatives presents significant economic challenges. These include higher material costs and more complex manufacturing requirements as compared to the current industry standard. Understanding the economic landscape of electrolyte technologies is the cornerstone for the responsible assessment of their feasibility in

large-scale commercial applications. Electrocars like Tesla and portable electrons are relevant examples.

The cost of electrolyte materials is at the center. Liquid electrolytes like $LiPF_6$ dissolved in ethylene carbonate, propylene carbonate, dimethyl, and diethyl carbonates benefit from existing established global supply chains and large-scale synthesis methods. These economic factors drive down costs substantially over time. $LiPF_6$ remains the most widely used lithium salt. This source of the Li-ion is relatively cost-effective. Today, the current market price ranges between 15 and 25 USD per kilogram. The cost does depend on purity and slightly on the supplier. Organic carbonates are inexpensive individually, yet contribute to the overall electrolyte cost due to the need for precise blending and quality control to ensure optimal Li-ion conductivity. The inclusion of additives, such as vinylene carbonate and fluoroethylene carbonate, to boost the stability of the solid-electrolyte interphase stability adds marginally to the material cost. These additives are normally used in small quantities.

Solid-state Li-ion electrolytes seem to be significantly more expensive due to the higher material costs, less established market of suppliers, and specialized manufacturing requirements. Ceramic-based solid electrolytes, such as the above-considered lithium lanthanum zirconium oxide and lithium phosphorus sulfide, require high-purity raw materials and energy-intensive chemical processing techniques. These include high-temperature sintering, which drastically increases production expenses. The synthesis involves multiple calcination steps at temperatures exceeding 1,000 °C. Intense energy consumption and high operational costs must be taken into consideration. Similarly, lithium phosphorus sulfide-based electrolytes require processing in an inert atmosphere to prevent moisture-induced decomposition. Polymer-based solid electrolytes, such as polyethylene oxide with lithium bis(trifluoromethanesulfonyl)imide, do not necessitate the application of high processing temperatures. Pristine polyethylene oxide with impregnated lithium salts suffers from lower ionic conductivity. These electrolytes cannot be used “as is” and

necessitate further substantial steps of production. The use of plasticizers or nanoparticle fillers, which are not cheap.

The scalability of electrolyte production is a critical economic consideration. Liquid electrolytes benefit from mature infrastructure. Large-scale production facilities are already in place to meet the demands of the electrical car and consumer electronics industries. The manufacturing process for liquid electrolytes involves mixing lithium salts with solvents under controlled conditions. This fairly straightforward procedure can be easily scaled up using existing battery production lines. Liquid electrolyte filling is a well-established process. It does not look to require essential modifications in response to current battery assembly techniques. To recapitulate, the existing setups are compatible with high-volume production released. Conversely, solid electrolytes face significant challenges in scaling up production due to complex synthesis methods and integration difficulties with existing battery manufacturing workflows. Ceramic electrolytes depend on high-temperature sintering. The procedure is energy-intensive and difficult to implement at industrial scales. Additionally, achieving uniform, defect-free ceramic layers across large battery formats remains a technical hurdle. It limits the commercial viability of solid-state Li-ion batteries. Polymer-based electrolytes offer easier preparation per se. However, additional engineering solutions must be applied to make these products commercially competitive. These are hybrid electrolyte designs that incorporate ceramic nanoparticles. The complexity is thereby added to the manufacturing process. Glass-based electrolytes face scalability challenges. Their amorphous structure requires precise control during synthesis to prevent adverse crystallization, which can degrade the performance of the resulting solid-state Li-ion battery.

Market trends indicate a growing interest in solid-state battery technology. It is driven by the demand for higher energy density and improved safety. Companies, such as Toyota and Panasonic, are known to invest in solid-state battery development. Commercial deployment is expected to take place in the second half of the 2020s. Cost reduction strategies must be explored to make solid electrolytes more economically competitive. One approach is the development of composite

electrolytes. It combines ceramic particles with polymer matrices to leverage the high conductivity of ceramics and maintains the processability of flexible polymers. This hybrid approach can potentially reduce manufacturing costs and preserve acceptable performance levels of Li-ion batteries. An additional strategy involves optimizing synthesis methods to lower energy consumption and raw material waste. The possibilities of sol-gel processing and low-temperature sintering techniques are investigated to reduce the energy required for ceramic electrolyte production. Advancements in thin-film deposition technologies, such as atomic layer deposition and sputtering, can help minimize material usage and improve uniformity in solid electrolyte layers. These innovations bridge the cost gap between liquid and solid electrolytes and, hopefully, make solid-state batteries more competitive in the market of the future.

Considering the steadily growing demand for high-safety batteries in electric aviation, grid-scale energy storage, and wearable electronics, we may hereby expect greater investment in solid electrolyte research. In the longer term, these investments will lead to production cost reductions through economies of scale. As production volumes increase, supply chain efficiencies and improved manufacturing techniques shall reduce the per-unit cost of solid electrolytes. Until the stated advancements reach industrial maturity, liquid electrolytes shall remain the dominant choice for large-scale commercial Li-ion battery applications, especially, in portable electronics.

Safety of Electrolytes for Li-Ion Batteries

Safety remains to be a paramount concern in Li-ion battery design. The chosen electrolyte plays a critical role in determining the risk of thermal runaway, fire hazards, and overall battery sustainability. The industry standard liquid electrolytes, employing lithium salts dissolved in flammable molecular solvents, are susceptible to thermal instability and combustion. These chemical reactions inside the Li-ion battery pose significant safety risks in high-energy electric vehicles, consumer electronics, and grid-scale energy storage systems. In contrast, solid

electrolytes represent a more promising alternative and more expensive option for enhancing safety.

Carbonate electrolytes are inherently flammable because they are based on carbon atoms and hydrogen atoms. Carbonates readily ignite and burn, contributing to battery-related fires and even explosions. When exposed to high temperatures, internal short circuits, or mechanical damage, carbonates propagate thermal runaway. This self-sustaining exothermic reaction leads to rapid temperature increase, gas formation, and potential catastrophic failure. Gas emission creates a peril of bursts. The presence of $LiPF_6$, which is the most widely used source of Li-ion in the electrolyte, exacerbates safety concerns. $LiPF_6$ decomposes into hydrofluoric acid in the presence of moisture, corrodes battery components, and provokes further degradation.

Several mechanisms contribute to fire hazards in liquid electrolytes. At elevated temperatures, organic carbonates evaporate. Internal pressure is hence increased. The likelihood of venting and rupture is increased. During thermal runaway, the decomposition of the electrolyte generates flammable gases, which ignite as soon as access to oxygen appears. Lithium dendrite formations on the anode penetrate the separator. This causes direct contact between the anode and the cathode. Localized heating and rapid energy release into the Li-ion battery leads to fire and explosions. To mitigate these risks, battery manufacturers some safety measures were implemented. For instance, ceramic-coated separators and flame-retardant additives are utilized. The advanced battery management systems monitor temperature and voltage to prevent overcharging and overheating. Such design solutions partially address the inherent flammability of liquid electrolytes at standard exploitation conditions.

Thermal runaway is the most severe safety concern in Li-ion batteries, particularly in high-power applications. This phenomenon occurs when excessive heat generation surpasses the battery's ability to dissipate heat. The emission of excessive heat leads to a self-accelerating reaction that results in cell rupture, fire, and even explosions. The low flash point of organic

carbonates in liquid electrolytes makes them particularly vulnerable to ignition during thermal runaway. If oxygen is released from high-voltage cathode oxide materials $LiNiMnCoO_2$ and $LiNiCoAlO_2$, the battery loses stability and becomes hazardous for consumers.

At temperatures above 120 °C, the solid-electrolyte interphase on the graphite anode starts decomposing. Consequently, it releases heat and reactive molecular species. Next, at 130-150 °C, the polyethylene or polypropylene separator melts. An internal short circuit emerges. The temperature increases. Beyond 200 °C, high-voltage cathodes emit oxygen. The latter reacts with the electrolyte and carbon components. Exothermic reactions further increase the temperature inside the Li-ion battery. As pressure builds up, the battery vents flammable gases. Gases ignite and initiate explosive combustion. The presence of liquid carbonate electrolytes significantly amplifies adverse effects. The electrolyte acts as both a fuel source and a conductive medium for uncontrolled exothermic reactions. Thermal runaway led to numerous incidents involving battery fires in electric vehicles, smartphones, and aircraft. Incidents underscore an urgent need for safer electrolytes in sensitive applications.

Solid electrolytes represent a fundamentally safer alternative to liquid electrolytes. Solid-state electrolytes cannot burn as intensively as carbon-rich solvents, first of all, because of their elemental compositions. Unlike liquid electrolytes, solid electrolytes do not contain volatile organic components. The present designs are resistant to thermal runaway. For instance, ceramic-based solid electrolytes, such as lithium lanthanum zirconium oxide and lithium phosphorus sulfide, exhibit excellent thermal stability. They maintain structural integrity at temperatures exceeding 300 °C. These temperatures are far beyond the operational limits of conventional liquid electrolytes for Li-ion batteries.

In the absence of a separator in solid-state batteries, safety implicitly increases because dendrite-induced internal short circuits, initiating the above-described thermal runaway, are impossible. Solid electrolytes withstand higher temperatures without degradation. This feature

reduces the likelihood of oxygen release from high-voltage cathodes. Mind that exothermic reactions are chemically suppressed in the absence of high concentrations of oxygen.

Sustainability of Electrolytes for Li-Ion Batteries

Lithium is not environmentally benign and must be appropriately processed. The sustainability and recyclability of electrolytes in Li-ion batteries are increasingly important as the global demand for energy storage solutions rises. The environmental impact of battery production, concerning resource extraction, waste generation, and end-of-life management, prompts a re-evaluation of the materials used in battery components. The focus on sustainable practices and recycling technologies is critical for mitigating the ecological footprint of Li-ion batteries. Liquid electrolytes used in Li-ion batteries pose several environmental challenges. The production of $LiPF_6$ involves fluorine-based compounds. These are associated with toxic emissions and environmental contamination during manufacturing. The extraction and processing of Li, Co, and Ni – critical components of both the anode and cathode – raise concerns regarding resource depletion, habitat destruction, and water usage, The Lithium Triangle unites Argentina, Bolivia, and Chile. In this region of the world, lithium extraction significantly affects the well-being of local ecosystems. In turn, organic carbonates belong to volatile organic compounds. They cannot be directly disposed of in the environment because they contribute to air pollution. The disposal of spent Li-ion batteries, containing liquid electrolytes, poses significant risks of the toxicity and flammability of these materials. Undue disposal leads to contamination of soil, water, and atmosphere. Furthermore, it fosters global warming (Figure 5). The potential for leakage and combustion in landfills further complicates the safe disposal of Li-ion batteries. These restrictions emphasize the need for chemically correct recycling and recovery strategies.

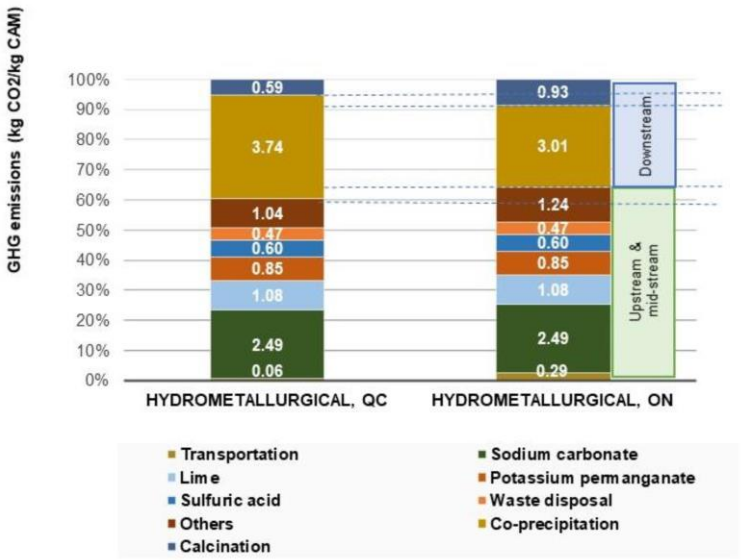

Figure 5. The breakdown of global warming potential of the cathode active materials (CAM), supply chain from recycled battery materials Quebec and Ontario with different electricity carbon intensities. Reproduced from (Gonzales-Calienes et al., 2023). The image is licensed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

The recyclability of liquid electrolytes is complicated by the heterogeneous nature of Li-ion batteries. A battery contains a mix of materials that are not straightforward to separate and recover. Traditional recycling methods are pyrometallurgy and hydrometallurgy. They are often energy-intensive and result in low recovery rates of valuable materials like lithium. In pyrometallurgy, the high-temperature smelting process leads to the destruction of organic components, including the electrolyte. Therefore, waste is generated, whereas the material recovery percentage is marginal. Hydrometallurgical processes, which involve chemical leaching, struggle to effectively recover the lithium salts and organic solvents present in liquid electrolytes. Incomplete recycling and environmental contamination represent two obvious consequences.

Emerging recycling technologies, such as direct recycling, aim to preserve the structure of cathode and anode materials. This allows one for reprocessing and reuse without the need for complete material breakdown. The integration of liquid electrolytes into these processes remains challenging because they can compromise the integrity of the recovered materials if not adequately removed and treated. The development of closed-loop recycling systems, in which useful materials

are recovered and reintegrated into the battery supply chain, is essential for boosting the sustainability of liquid electrolyte use. The implementation of this solution requires not only advanced recycling technologies but also regulatory frameworks that promote the responsible handling and recycling of Li-ion batteries.

Ceramic-based and polymer-based solid-state electrolytes offer a more sustainable alternative to liquid electrolytes due to their non-flammable nature and reduced environmental impact. The absence of volatile organic solvents eliminates the risk of toxic emissions and flammability. Therefore, solid electrolytes are inherently safer for both production and disposal. Longer-term stability of solid electrolytes leads to extended battery lifespans. Longer lifespans inherently reduce the frequency of battery replacements, as well as the associated environmental burden. Yet, the production of solid electrolytes poses environmental challenges. The synthesis of ceramic electrolytes requires energy-intensive procedures. These procedures contribute to greenhouse gas emissions. Next, the use of rare earth elements in some ceramic electrolytes raises concerns about resource scarcity and the environmental impact of mining these materials. While solid electrolytes reduce the need for toxic solvents, they are not inexpensive in production. The energy required for their production must be carefully evaluated to ensure that the overall environmental footprint is minimized.

The recyclability of solid electrolytes presents unique challenges that must be addressed to ensure long-term sustainability. Unlike liquid electrolytes, which can be relatively straightforward to remove from battery cells, solid electrolytes are frequently integrated into the cell structure rigidly. This modern construction makes physical separation from electrodes more complex. For instance, lithium lanthanum zirconium oxide and lithium phosphorus sulfide are typically sintered or pressed into dense layers. These recycling procedures require mechanical grinding or chemical dissolution to recover individual components. This energy-intensive process potentially offsets some of the environmental benefits associated with their non-flammable nature. The presence of rare or exotic elements in some solid electrolytes raises concerns about resource scarcity and

responsible recycling. The current construction of Li-ion batteries does not imply an understandable route for easy recovery of scarce chemical elements at end-of-life.

Polymer-based solid electrolytes are easy to process, yet they face recyclability hurdles. Their organic composition may allow for thermal decomposition or solvent-based extraction, but the low ionic conductivity of many polymer electrolytes necessitates the use of nanoparticle fillers or plasticizers. The removal of these plasticizers complicates the recovery processes. For instance, the presence of nanoscale ceramic particles in composite polymer electrolytes hinders material separation and purification. Advanced recycling methods, e.g., pyrolysis or selective dissolution to isolate individual components, are necessary. Moreover, the low decomposition temperatures of some polymers lead to thermal degradation during recycling. Such a possibility reduces the sustainability of the material recovery.

Glass-based solid electrolytes, such as lithium thiophosphate $Li_7P_3S_{11}$, pose challenges due to their sensitivity to moisture and air exposure. These materials decompose or oxidize when exposed to environmental conditions. The decomposition of the material complicates both its storage and processing during recycling. In turn, the amorphous structure of glass electrolytes requires high-energy mechanical processing to break down the material into reusable components.

Life Cycle of Li-Ion Battery: Liquid/Solid Electrolyte

A comprehensive life-cycle analysis is essential to evaluate the environmental trade-offs between liquid and solid electrolytes. The life-cycle analysis considers the entire lifecycle of a complex product, starting from raw material extraction and manufacturing, considering the exploitation phase until end-of-life management. For liquid electrolytes, the primary environmental concerns include the toxicity of $LiPF_6$, the volatility of organic solvents, and the risks of flammability and leakage. While these issues can be mitigated through additives and improved battery design, the end-of-life challenges – electrolyte recovery and waste treatment –

remain to represent significant barriers to sustainability. On the other hand, solid-state electrolytes exhibit reduced toxicity and flammability risks. However, their higher energy requirements for production and complex recyclability must be carefully weighed against safety upon exploitation. For example, the high-temperature sintering required for ceramic electrolytes contributes to higher energy consumption during manufacturing. This increases the aggregate carbon footprint of solid-state batteries compared to conventional Li-ion systems. Similarly, the use of rare elements in solid electrolytes may exacerbate resource scarcity concerns. Development of the closed-loop recycling systems for solid-state Li-ion batteries is the cornerstone. These systems aim to recover high-purity materials for reuse in new batteries. Therefore, the need for primary resource extraction can be minimized. For instance, solvent-assisted dissolution techniques are developed to selectively separate ceramic electrolytes from electrodes. In turn, mechanical milling and thermal treatments are optimized to break down composite polymer electrolytes without compromising material integrity. On a related note, electrochemical recycling methods, such as reversible intercalation or ion exchange, must be able to regenerate degraded electrolyte materials and extend their usable lifespan.

Final Remarks

Ongoing scientific research is focused on developing novel electrolyte materials and recycling technologies that balance performance, safety, and sustainability. A promising approach is the development of bio-based or aqueous electrolytes with enhanced electrochemical windows, which would eliminate the use of toxic organic solvents and reduce flammability risks. For example, water-in-salt electrolytes demonstrated a reasonably high ionic conductivity and improved safety, though their narrow electrochemical stability windows remain a limitation. Ionic liquids, which are non-volatile and largely non-flammable, are explored as alternatives to

conventional organic solvents. It must be noted that their high production costs and too high shear viscosities currently limit their commercial viability.

In the realm of solid electrolytes, elements and substances abundant in the Earth's crust are tested to replace rare and toxic components. For instance, sodium-based solid electrolytes are developed as a low-cost, sustainable alternative to Li-ion systems. K-ion, Mg-ion, and Ca-ion electrolytes are also investigated as charge carriers to a certain extent. While exhibiting charge carrier characteristics inferior to those of Li-ion, alternative elements are rather cheap and more environmentally friendly. Additionally, oxide-based materials are explored to mitigate the moisture sensitivity of sulfide-based systems. This enhances manufacturability and recyclability.

The development of direct recycling technology steadily gains traction, particularly in the context of solid-state batteries. This approach aims to preserve the structure of electrode materials after the removal of contaminants and degraded components. Thermal treatment and electrochemical rejuvenation techniques restore the performance of aged electrolytes. Modular battery designs, which facilitate easy disassembly and component recovery, enhance the economic viability of recycling solid electrolytes.

The transition to sustainable and recyclable electrolytes assumes coordinated efforts between research institutions, industry stakeholders, and policymakers. Governments and regulatory bodies prioritize battery sustainability through initiatives, such as the European Union's Battery Passport, which mandates transparency in sourcing, performance, and recyclability. In the United States, the Inflation Reduction Act provides financial incentives for domestic battery recycling and ethical sourcing. The act encourages the development of circular supply chains. These frameworks drive the adoption of sustainable practices and ensure that environmental considerations are accounted for upon battery design and production. Industry collaboration advances recycling technologies and standardizing practices. The Battery Recycling Coalition and partnerships between automakers, battery manufacturers, and recycling companies foster the development of scalable

battery recycling solutions. Modern companies Redwood Materials and Li-Cycle were reported to pioneer closed-loop recycling systems that recover lithium, cobalt, and nickel from end-of-life batteries. These practices reduce the need for primary mining and minimize waste generation. As solid-state battery adoption grows, similar collaborations must develop tailored recycling strategies for solid electrolytes.

The future of electrolyte technology hinges on continuous advancements in material science, building cost-efficient recycling infrastructure, and policy support. The development of next-generation electrolytes that combine high ionic conductivity, low shear viscosity, environmental safety, and recyclability represents a critical prerequisite for achieving a sustainable energy storage ecosystem. Hybrid electrolyte systems leverage the advantages of both liquid and solid electrolytes. Gel polymer electrolytes and aqueous hybrid systems balance performance, cost, and eco-friendliness. In parallel, the integration of artificial intelligence and machine learning into battery design and recycling shall accelerate progress. Intelligent models predict optimal material compositions for recyclability and guide process optimization in recycling facilities. Real-time monitoring systems in battery management systems assist in slowing down degradation and enabling adaptive strategies based on current battery health. The sustainability of Li-ion batteries in the future depends on a holistic approach that addresses material sourcing, manufacturing efficiency, and end-of-life management simultaneously. By prioritizing the development of non-toxic, recyclable electrolytes and investing in innovative recycling technologies, the industry moved closer to a circular economy of energy storage. As the global demand for rechargeable batteries continues to increase in response to evading fossil fuels, the integration of sustainability principles into every stage of the battery lifecycle is seen to be essential for minimizing the environmental footprint and ensuring the viability of advanced energy storage solutions.

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