



Recent developments of lithium and zinc ion batteries

Rahul Roy¹

Department of Chemical Engineering, National Institute of Technology Agartala, Tripura 799046, India

Abstract

Batteries are the most widely used electrochemical energy storage technology due to their high energy densities. The most current advancements in lithium-ion (LIB) and zinc-ion (ZIB) battery technology are thoroughly reviewed in this study. Both battery technologies have potential and challenges, including problems with materials, performance, safety, and recycling. The discovery of novel cathode materials, solid-state electrolytes, and silicon anodes, as well as other advancements in the field of lithium-ion batteries, are highlighted in the study. It also discusses the newly developing field of zinc-ion batteries, which has a lot of potential because of the inexpensive and plentiful availability of zinc, their high energy density, and their environmental friendliness. The evaluation also touches on the need for more ecological practises and the existing difficulties with recycling of used batteries. Overall, this paper provides a valuable reference for researchers and industry practitioners seeking to understand the recent developments and challenges in the field of advanced battery technologies.

1. Introduction

Renewable energy sources are increasingly in demand due to the detrimental environmental effects of fossil fuel usage and rising greenhouse gas emissions [1]. Solar, hydro, and wind energy are the most promising solutions to these issues [2], but efficient energy storage methods are required to meet global energy demands [3]. Currently, batteries are the most widely used electrochemical energy storage technology due to their high energy densities [4]. The development of new electrode materials and battery technology is still in its early stages and holds great potential for further expansion and impact (Figure 1) [4]. Over 170,000

papers related to batteries have been published in the last two decades [5]. Lithium-ion batteries (LIBs) are dominant due to their commercial viability and material availability, but alternative chemistries such as lithium-sulfur (Li-S), and zinc batteries are being explored [6, 7, 8]. Solid-state LIBs have emerged as a new research area due to their high safety and energy density [9, 10]. This paper provides a brief overview of Li ion and zinc ion battery types. It discusses the current state of research, compares different approaches to maximize the potential of each battery chemistry, and highlights the challenges that need to be addressed to improve battery performance. Leading researchers in each area share their perspectives and visions for advancement in their respective fields. This study aims to offer a concise yet comprehensive review and development strategy for the growing field of battery technology.

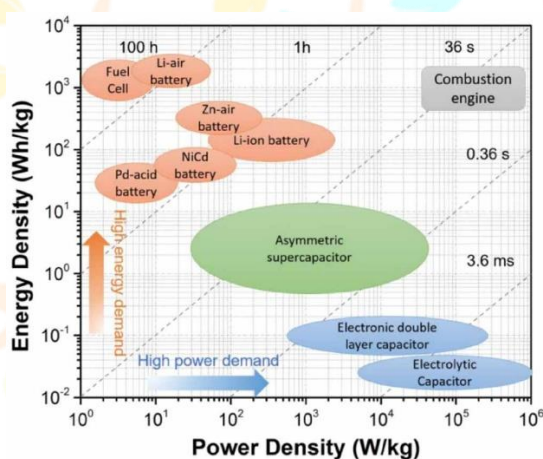


Figure 1. The figure displayed is a Ragone plot, which depicts the performance characteristics of various electrical energy-storage technologies based on their specific power and specific energy. The time scale represented on the graph is the discharge time, calculated by dividing the energy density by the power density. This figure has been reproduced from reference [4].

2. Li-ion batteries

The use of intercalation of Li^+ in a layered compound became a viable strategy for rechargeable battery electrodes, thanks to the work of Rouxel, Schroeder, and Whittingham in the 1960s [11]. Goodenough and colleagues later investigated the reversible extraction of Li^+ from LiCoO_2 , leading to the development of a cell with a discharged cathode. Despite initial resistance from battery manufacturers, Yazami and Yoshino's work on intercalation of Li^+ into a carbon anode and LiCoO_2 cathode led to the first commercially successful lithium-ion battery (LIB) at SONY [11]. However, the LIB still has drawbacks such as metallic

lithium plating on the carbon anode during fast charging, O₂ evolution from the cathode during charge, and the flammable electrolyte causing ignition if a lithium dendrite causes a short circuit [11]. Nevertheless, the LIB remains the best portable electric-power storage device for the near future.

2.2. Challenges in the Li-ion batteries

In a commercial lithium-ion battery (LIB), the cell is initially assembled in a discharged state. As the cell is charged, an electron is removed from the cathode, and a lithium-ion is extracted from the cathode and inserted into the anode to balance the charge (Fig. 2). The graphite anode undergoes the formation of a solid-electrolyte interphase (SEI), which consumes some lithium ions, especially during lithiation (Fig. 3). Controlled growth of the SEI during slow charging can ensure stable cycling of the cell. On the other hand, the cathode forms a cathode-electrolyte interphase (CEI) as the Fermi level of the transition-metal oxide layer dips below the highest occupied molecular orbital of the electrolyte. However, controlling the growth of the CEI is harder than the SEI, and their compositions are not yet fully understood. Cycling leads to volume expansion and contraction, resulting in interphase cracking, which necessitates the consumption of chemical species for new interphases to grow. Using lithium metal instead of graphite as the anode material can increase the energy density of the cell due to its higher theoretical capacity. However, lithium metal is prone to dendrite formation, which can cause a short circuit. Increasing the voltage of active materials to enhance the energy density is challenging due to the limited electrochemical stability of the organic-liquid electrolyte. Additionally, concerns regarding the cost, toxicity, and flammability of the cathode active material (cobalt) and electrolyte persist.

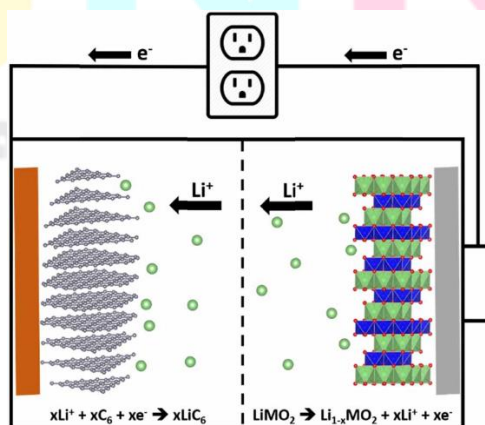


Figure 2. This passage describes a diagram showing the structure of a lithium-ion battery. The battery includes a cathode made of layered transition-metal oxide with an aluminum current collector, and an anode

made of graphite with a copper current collector. The half reactions that occur during the charging process are depicted for each electrode. A separator is represented by a dashed line, and the battery's electrolyte is an organic-liquid solvent containing a lithium conducting salt. [12].

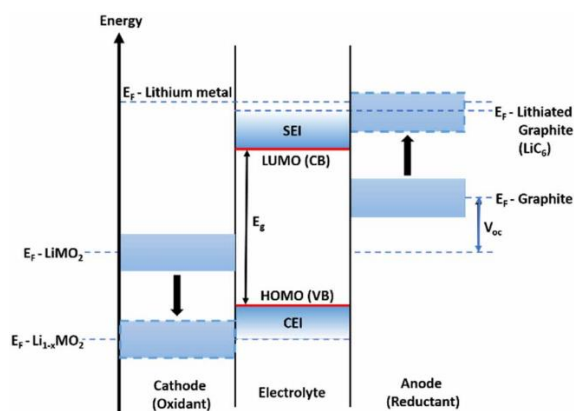


Figure 3. This is a description of an energy diagram for a lithium-ion battery. The diagram includes boxes with dashed borders, which represent the energy levels of electrodes when the battery is charged. It also includes boxes without dashed borders, which represent the energy levels of the electrodes in their original state before charging. [12].

2.3. Advances in technology to minimize challenges

Recent studies have explored various strategies to improve the properties and safety of lithium-ion batteries (LIBs). One such approach involves using electrolyte additives to manipulate the properties of the organic-liquid electrolyte. Dual-salt approaches have shown stable lithium plating, eliminating dendrite growth from the lithium surface [13]. Coatings and protective layers on the surface of lithium metal can also promote uniform plating and stripping [14-16]. In addition, new separator strategies have emerged that may allow for plating of metallic lithium [17].

Another promising approach is the use of solid-state ionic conductors to remove the flammable liquid electrolyte and improve safety and energy density. However, achieving comparable levels of ionic conductivity to liquid lithium electrolytes in solids is challenging. Sulfide-based solid electrolytes have high conductivity but suffer from poor thermodynamic and kinetic stability [18]. Coating compounds and interfacial layers between the cathode and electrolyte are being explored to improve stability, but this strategy is still in its early stages.

One area lacking in research is the development of cathode materials and structures optimized for solid-state batteries. Retrofitting traditional LIBs to all-solid-state designs has created new challenges, such as mechanical contact issues at the cathode-solid electrolyte interface. Strain-free cathodes could resolve this issue, but engineering this for commercial use and safety would be challenging.

3. Lithium–oxygen batteries

3.1 Status

In the pursuit of global environmental protection and sustainable development, the electrification of road transportation using electric vehicles (EVs) is seen as a significant measure. The current technology used in EVs mainly relies on lithium-ion batteries (LIBs) for power. The operation of LIBs is based on the intercalation/deintercalation of Li^+ ions into/out of host electrode materials with distinct voltages [19]. However, the specific energy or energy density of LIBs will soon reach their theoretical limit, and they may not meet the driving range requirement (typically 500 km per charge) expected for future EVs.

To address the driving range problem, new battery chemistries beyond Li-ion, such as Li–S, Li– O_2 , and multivalent ion batteries, have been proposed. Among these, the rechargeable Li– O_2 battery has an unrivaled theoretical specific energy of 3500 Wh kg^{-1} , and it is receiving significant attention [20]. However, the Li– O_2 battery has two challenging electrodes: Li and O_2 . Its operation depends on the stripping/plating of lithium on the negative electrode and the formation/decomposition of Li_2O_2 on the positive electrode. The prototype Li– O_2 cell was first reported in 1996 by Abraham et al [21], and it is considered the birth of aprotic Li– O_2 batteries, although pioneering work was conducted as early as 1966 [22]. In 2006, Bruce et al successfully oxidized Li_2O_2 to O_2 , proving that Li– O_2 batteries are rechargeable [23]. This work has ignited worldwide enthusiasm for Li– O_2 batteries, but significant challenges remain in developing practical Li– O_2 cells.

3.2. Challenges in the Lithium–oxygen batteries

The Li– O_2 battery holds great promise as an energy-storage device but is still in its early stages of development. Numerous scientific and technological challenges must be addressed before a practical device can be created, including understanding reaction mechanisms, ensuring the chemical and electrochemical

stability of cell components in open surroundings, and improving energy-storage efficiency and lifetime by catalyst design. These challenges are summarized in Figure 4 [20].

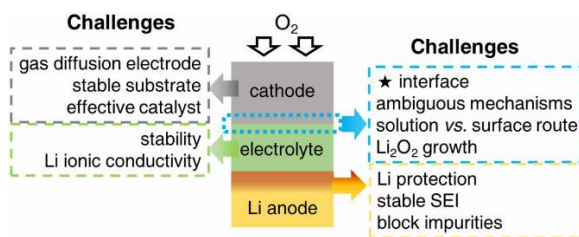


Figure 4. Schematics of challenges regarding Li–O₂ batteries [12].

One of the main challenges with the Li-O₂ battery is the solid and insulative discharge product Li₂O₂ on the cathode surface, which can lead to high overpotential during charging. This results in low Coulombic efficiency, oxidative degradation of cell components (e.g. electrolytes and cathode materials), and the formation of the hard-to-decompose side-reaction product Li₂CO₃, which accumulates at the cathode-electrolyte interface upon cycling. This accumulation results in an ever-growing charging potential, inducing further decomposition of the cell components [24,25].

The lithium metal anode also presents significant challenges, including low Coulombic efficiency and poor cycle life. These challenges have been studied for decades, but the introduction of O₂ from the cathode compartment in Li-O₂ batteries could exacerbate side reactions and dendrite growth of the metallic lithium anode [20].

3.3. Advances in technology to minimize challenges

Significant progress has been made in the last decade towards addressing the challenges of Li-O₂ batteries. Researchers have identified two pathways for Li₂O₂ formation: solution-mediated and surface-mediated routes, which determine the discharge product's morphology and properties, discharge capacity, and charge overpotential [20]. High DN solvents can induce Li₂O₂ to form via the solution pathway, leading to a higher discharge capacity [26, 27]. To mitigate side reactions and charging overpotential, researchers have explored replacing unstable components, such as carbon cathodes and organic carbonate electrolytes, with more stable materials [28].

Recent studies have demonstrated reversible Li_2O_2 formation and decomposition with high O_2 recovery efficiency in Li- O_2 batteries containing DMSO solvent (high DN) [25]. However, prolonged lifespans of superoxide species in high DN solvents can lead to more solvent decomposition than in low DN solvents. To suppress solvent decomposition, researchers have designed and synthesized new organic solvents with improved chemical stability without sacrificing DN [29]. Another strategy involves introducing a reduction mediator (RMdisch), which inhibits side reactions and increases Li_2O_2 yield by forming a LiO_2 -RMdisch complex as a new soluble intermediate [30]. RMdisch can also expand the reaction region and enable the solution route in solvents with limited solubility towards LiO_2 and Li_2O_2 .

Li- O_2 batteries pose several challenges for both the discharge and charge processes. Catalysts, in solid or molecular form, have a significant impact on the battery's performance [31]. However, designing effective catalysts is more complicated for Li- O_2 batteries than for fuel cells because of the challenge of enhancing O_2 reduction kinetics without passivating active sites. Another significant challenge is the poor contact between the positive electrode surface and Li_2O_2 , leading to a large overpotential during charging [30]. The mechanisms of charging in Li- O_2 batteries are not yet fully understood, although using an oxidation mediator shows promise.

Lithium metal anodes have high specific energy but pose safety concerns, so alternate negative electrode materials such as silicon and tin compounds have been explored [32, 33]. However, these materials have low operational potential, making it difficult to avoid side reactions with the electrolyte. Thus, electrolytes and additives that can form a high-quality solid electrolyte interphase (SEI) layer are preferred [34, 35]. Modified separators, such as solid-state electrolytes and quasi-solid-state electrolytes, have been used to block impurities from the ambient environment [36]. Metal organic frameworks (MOFs)-based separators with proper pore sizes selectively allow Li^+ ions to transport while blocking other electrolyte components. Using such membranes, Li- O_2 batteries have been built with two different types of electrolytes, including water-in-salt and aprotic electrolytes.

4. Lithium–sulfur batteries

Li-S batteries have become a promising alternative to conventional lithium-ion batteries due to their potential for high energy density and low cost, using high-capacity metal anodes and chalcogen cathodes.

The Li-S system operates through the conversion reaction between Li and S, delivering a theoretical energy density of 2600 Wh kg⁻¹, which is five times that of LIBs. Sulfur is abundant, cost-effective, and environmentally friendly, making Li-S batteries attractive for use in stationary energy storage and electric vehicles [37].

Early research on Li-S batteries focused on finding suitable organic electrolytes to improve their electrochemical performance. In 1989, an average discharge voltage of 2.1 V and an energy density of ~80 Wh kg⁻¹ were achieved by introducing ether into the electrolyte [38]. However, significant progress was not made until the early 2000s when the addition of lithium nitrate (LiNO₃) and the use of sulfur compositions with porous carbon were found to be effective in stabilizing cycling performance and suppressing the "shuttle" of lithium polysulfides [39, 40]. In the last decade, over 3400 research papers have been published, and significant improvements have been made in the lab.

While Li-S batteries have been used to power a solar plane's flight and have been developed with a cycle life of 60-100 cycles, their practical applications are still limited. This roadmap categorizes the research areas covered by the 3461 published papers on Li-S batteries in the last decade, identifies gaps between academic research and industry requirements, and discusses possible solutions to speed up the development of Li-S batteries with competitive performance [37].

4.1. Challenges in Lithium-sulfur batteries

The development of Li-S batteries faces various challenges that need to be addressed for practical applications (figure 5). From an academic perspective, several issues include the need for a conductive matrix to ensure fast conversion between insulating S and its discharge products, significant volume expansion during lithiation, and the shuttle effect caused by the dissolution of intermediate discharge products in ether-based electrolytes. On the other hand, the industry faces more challenges, such as the high E/S ratio, high N/P ratio, low cathode areal loading, and the use of high-content porous carbons, that squeeze the practical energy densities. Production challenges and safety concerns are other issues that need to be resolved. Although many studies have been published on Li-S batteries, most of them focus on improving conductivity or suppressing the shuttle effect, and few studies have been conducted under real

application conditions. This limits the conversion of academic results into practical, commercially viable cells. [41][42][43]

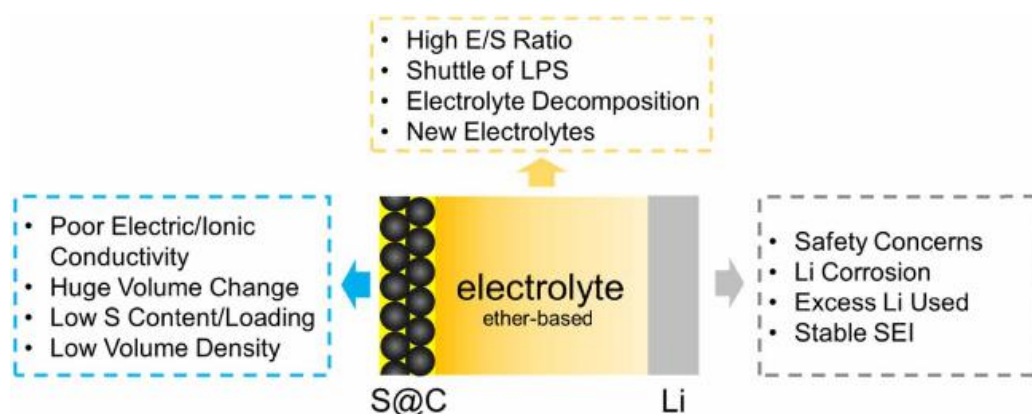


Figure 5. Schematics of challenges regarding Li-S batteries [12].

4.2. Advances in technology to minimize challenges

The development of lithium-sulfur (Li-S) batteries faces several challenges such as low energy density, poor cycling life, safety concerns, and the need for new production technologies that can be scaled up at a reasonable cost. Safety concerns arise from the use of flammable and volatile ether-based electrolytes, gas-producing LiNO_3 , and the high-active lithium anode of Li-S batteries. While research in the Li-S community has made significant progress in improving the conductivity of cathodes and suppressing the 'shuttle effect', most studies have focused on novel material designs rather than addressing real-world application conditions. Extensive investigations have been devoted to creating LPS chemical anchoring or catalytic sites by introducing heteroatoms or transition-metal compounds into the carbon hosts. Efforts have also been made to optimize the cathode microstructure and use protected Li anodes with effective solid electrolyte interfaces or protective coatings. High electrolyte-to-sulfur ratios and the 'shuttle effect' are also major obstacles to achieving practical energy density and cycling life. Researchers have successfully developed high-performance sulfur electrodes compatible with carbonate-based electrolytes by confining small sulfur molecules into a conductive microporous carbon matrix or covalently immobilizing sulfur onto polymeric chains. New sparingly solvating electrolytes based on super-concentrated solutions and solid electrolytes based on sulfide glasses are also promising to reduce E/S, eliminate the 'shuttle effect', and enhance the practical energy density of Li-S batteries. Furthermore, new technologies in cell design and production are necessary to develop Li-S batteries for real-world applications [42-46].

5. Solid state lithium battery

Current rechargeable lithium-ion batteries (LIBs) use flammable liquid organic electrolytes with high Li⁺ conductivities and small electrolyte/electrode interfacial resistances, but these electrolytes have limited electrochemical windows and cannot suppress dendrite growth at high charge rates. To address this issue, all-solid-state lithium batteries have emerged as promising candidates for high-energy-density, safe energy storage by replacing liquid electrolytes with solid-state Li⁺ conductors. While solid electrolytes have improved in conductivity over the past decade, most still have low room-temperature conductivities, require elevated temperatures to function, and may not be stable in moist air. Additionally, the interfaces between solid electrolytes and electrodes present significant challenges, including improving interfacial contact and electrochemical stability. Furthermore, the dynamic interfaces between solid electrolytes and lithium metal anodes have been identified as a factor in the failure of solid lithium metal batteries and are being studied. Despite these challenges, efforts are ongoing to reduce the high manufacturing costs of solid electrolytes. Successful solutions to these issues will enable the development of all-solid-state batteries with an energy density of about 500 Wh kg⁻¹, revolutionizing the world by reducing reliance on fossil fuels and enabling safer, more efficient energy storage for vehicles.

Solid electrolytes are an important component of all-solid-state lithium batteries, and they are typically classified into three categories: oxide, sulfide, and polymer electrolytes. Oxide electrolytes, such as Li₇La₃Zr₂O₁₂ (LLZO) doped with Ta, Ga, or Nb, offer high room-temperature Li⁺ conductivity of 10⁻³ S cm⁻¹ and excellent mechanical strength. However, the poor wettability between Li metal and oxide electrolytes leads to high interfacial resistance, and their brittle nature makes them unreliable. The electrochemical window and chemical stability of oxide electrolytes are also major challenges, as some electrolytes are unstable in water or moist air, and some containing variable-valence elements can be easily reduced by lithium metal at low voltages [47].

Sulfide electrolytes, on the other hand, offer high ionic conductivities of 10⁻² S cm⁻¹ at room temperature, but they suffer from poor electrochemical and interface stability in batteries, as well as instability in air, which limits their large-scale application. Finally, polymer electrolytes are flexible and easy to process, but they exhibit low room-temperature conductivity, narrow electrochemical window, and poor thermal stability,

which restrict their use in batteries [48]. Figure 6 illustrates the ionic conductivities of different types of solid electrolytes at varying temperatures [49, 50].

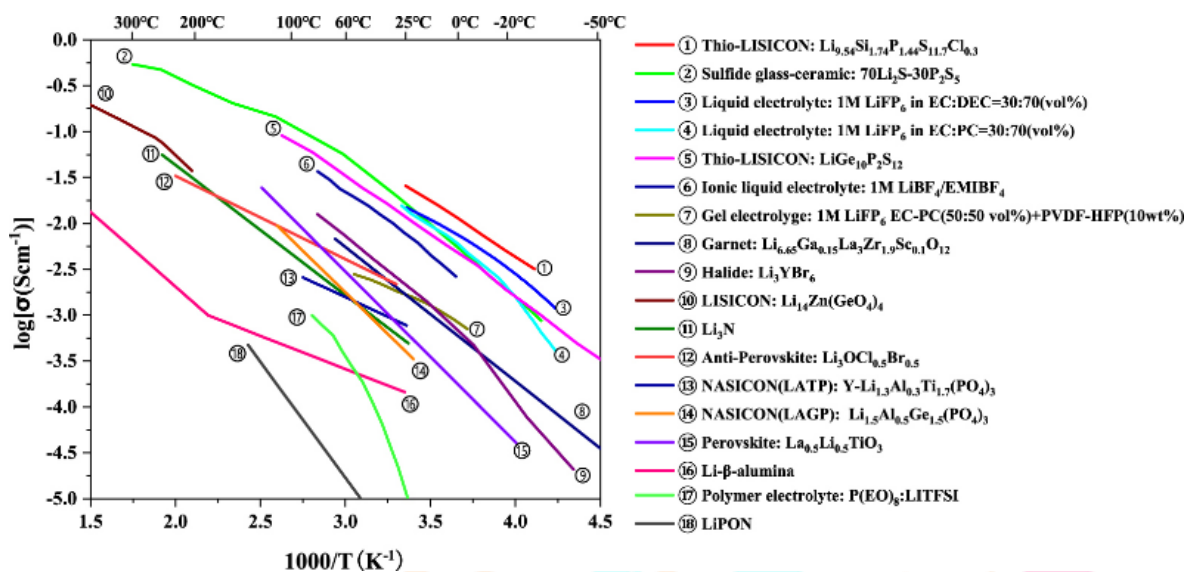


Figure 6. Ionic conductivities with temperature ($\log \sigma \sim 1/T$) of different types of solid electrolytes [12].

Batteries with a metallic lithium anode have the highest energy density due to its high theoretical capacity (3860 mAh g^{-1}) and low potential ($-3.04 \text{ V vs H}^+/\text{H}$). However, the use of a lithium anode in solid electrolytes faces challenges such as the formation of short circuits caused by lithium dendrite, poor wettability between the lithium metal and solid electrolyte, and changes in the lithium surface morphology and volume during cycling. The rough surface morphology and volume changes of the Li anode during cycling can result in the formation of gaps in the Li/electrolyte interface, leading to an increase in interfacial resistance [51].

Although cathode materials like LiFePO_4 have been widely used, they have low energy density and are unable to meet the demands of electric vehicles. High-voltage cathode materials such as $\text{Li}[\text{Ni}_x\text{Co}_y\text{Al}_{1-x-y}]\text{O}_2$ (NCA) and $\text{Li}[\text{Ni}_x\text{Co}_y\text{Mn}_{1-x-y}]\text{O}_2$ (NCM) have higher energy density but must address issues such as cycle life, rate performance, voltage attenuation, and interface compatibility with solid electrolytes [52].

Improving the ionic conductivity and phase stability of oxide solid electrolytes can be achieved through techniques such as element substitution, suitable sintering methods, and surface modification. Additionally, nanostructure design and incorporating a polymer buffer layer can lower interfacial resistance and improve

stability between solid oxide electrolytes and lithium metal anodes [53]. For sulfide-based solid electrolytes, doping with oxide or halide salts, pressurization, surface coating, and adding phosphate can improve conductivity and the electrochemical window [54]. In polymer electrolytes with poor room-temperature conductivity, adding inorganic fillers or designing a 3D nanostructured hydrogel-derived solid–electrolyte framework can enhance Li-ion conductivity, mechanical properties, and thermal stability [55][56]. To improve the performance of LIBs, cations doping and particles coating are the main methods used, such as in Ni-rich $\text{Li}[\text{Ni}_x \text{Co}_y \text{Al}_{1-x-y}] \text{O}_2$ (NCA) and $\text{Li}[\text{Ni}_x \text{Co}_y \text{Mn}_{1-x-y}] \text{O}_2$ (NCM) [52]. In order to suppress dendrite growth in solid lithium batteries, the structure of the solid electrolyte and its interface must be elaborately designed and modified [53][54][56].

6. Zinc–air batteries

In recent years, there has been growing interest in the development of zinc–air batteries due to their high energy density, long-lasting rechargeable ability, and low cost [57]. A typical zinc–air battery consists of a zinc anode, an oxygen-permeable cathode, a separator, and a caustic alkaline electrolyte (Figure 7). Zinc is an attractive anode material for metal–air batteries due to its low cost, stability, high theoretical specific energy (1218 Wh kg^{-1}), and promising volumetric energy density (6136 Wh l^{-1}) [58]. Additionally, the use of an aqueous electrolyte in zinc–air batteries increases safety and reduces fire hazards.

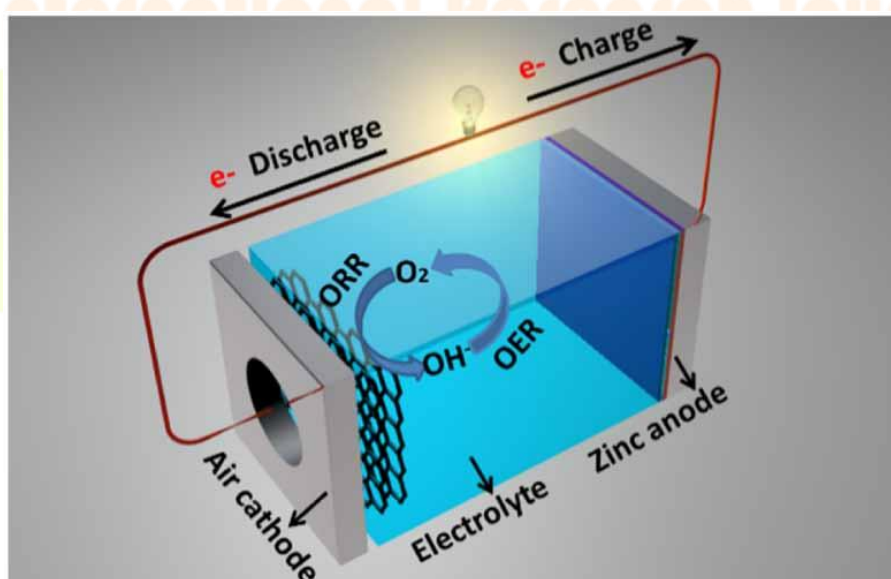


Figure 7: A schematic diagram of a zinc–air battery [12].

Although primary zinc-air batteries were commercialized in the 1930s, the development of rechargeable zinc-air batteries has been a challenge since the 1970s [59]. Recently, the cost of zinc-air batteries for energy systems has been projected to decrease to 70 US\$ kW h⁻¹, which is lower than the acceptable cost (150 US\$ kW h⁻¹) for electric vehicles to be economically competitive [60]. Therefore, zinc-air batteries have the potential to be used in various energy storage applications, including electric vehicles, electrical grid regulation, and portable electronic devices.

Despite the promising properties of zinc-air batteries, the development of practically viable rechargeable zinc-air batteries remains a challenge due to issues such as zinc irreversibility, electrocatalytic activation for oxygen reduction and evolution reactions, and integrated technology. The current zinc anode suffers from limitations such as the formation of zinc dendrites and zinc oxide passivation, while the oxygen-permeable cathode needs further improvement in electrocatalytic performances, corrosion resistance, and cost concerns [57]. Therefore, the development of zinc-air batteries presents both opportunities and challenges [57].

Despite the significant progress made in developing rechargeable zinc-air batteries in recent years, there are still numerous challenges that need to be overcome for commercialization and large-scale application. One major problem is the irreversibility of zinc anodes, which is caused by the formation of zinc dendrites, undesired relocation, and zinc oxide passivation. Although various zinc anodes with special structures and morphologies have been designed to address this issue, achieving high energy density, excellent cycling stability, and high zinc utilization simultaneously is still difficult [57]. Another challenge is the need for high-performance bifunctional oxygen catalysts to minimize the overpotentials of the oxygen reduction and evolution reactions, which are fundamental reactions in rechargeable zinc-air batteries. However, noble metal catalysts suffer from high cost, scarcity, and limited stability, while non-noble metal catalysts still have room for electrochemical improvement and pose problems such as increasing cost concerns and complex synthetic strategies [57][61]. Moreover, carbon-based catalysts are readily corroded in alkaline electrolytes during repetitive charging and discharging [61]. The mechanisms behind bifunctional active sites also need to be better understood to guide the rational design of high-performance catalysts.

Apart from these challenges, zinc-air batteries also face other issues associated with electrolyte, separator, integration of air electrodes, and battery-performance evaluation. For example, there is no standard

parameter for evaluating the performances of zinc–air batteries, and the testing conditions are not specific. Although many non-aqueous electrolytes have been developed recently, the performances of the battery are still unsatisfactory due to the relatively low ionic conductivity. Additionally, integrated air electrodes and flexible zinc–air batteries have attracted increasing attention, but the solidification of the electrolytes is a thorny problem, and the mechanical performances of electrodes and support materials, energy density, and cycling stability of the battery are unsatisfactory for commercial application [57].

To address the challenges faced by zinc-air batteries, several promising approaches are being investigated (Figure 8).

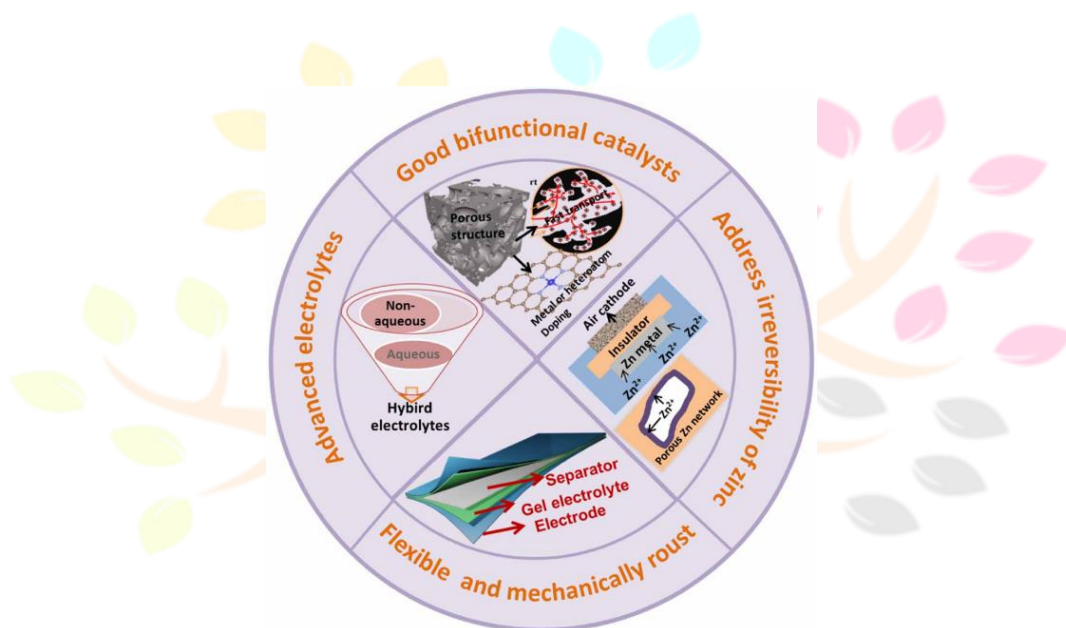


Figure 8: In order to develop high-performance zinc-air batteries, several specific approaches have been proposed. These include the fabrication of exceptional bifunctional catalysts, finding solutions for the irreversibility of zinc, improving the flexibility and mechanical properties of the battery, and developing advanced electrolytes [12].

Bifunctional catalysts play a critical role in the performance of zinc-air batteries, and several practical and effective methods have been proposed to improve their electrochemical performance. For example, by using computational simulation and high-throughput screening, catalysts with high intrinsic catalytic activity have been developed [61]. Other methods include controllable structure design of catalysts to expose more active sites and improve mass transfer [58], and replacing the carbon-based gas diffusion or catalyst substrates with materials having high corrosion resistance to improve cycling stability [57]. To enhance the performance of the zinc anode, effective strategies such as constructing porous structures with high surface

area, adopting 3D conductive host materials, and physical inhibition/suppression have been proposed [62, 63]. Hybrid electrolytes that combine the advantages of aqueous and non-aqueous systems have also been investigated, which can manage operating environmental parameters and improve the cycling durability of the battery [64]. For flexible zinc-air batteries, in-situ characterizations have been used to correlate the microscopic structure with the electrochemical and mechanical performance, while multi-scale modeling and simulation are employed to better understand the mechanisms and theories of the catalysis process [57, 61-64].

In a study by Alfaruqi et al., the phase transformation of a mesoporous γ -MnO₂ material during the intercalation of zinc ions was investigated using in situ Synchrotron XANES and XRD [65]. The results showed that as zinc ions were intercalated, the tunnel-type γ -MnO₂ gradually transformed into spinel-type ZnMn₂O₄, as well as two new intermediary Mn(II) phases, namely tunnel-type γ -Zn_xMnO₂ and layered-type L-Zn_yMnO₂. Upon the extraction of zinc ions, most of these phases returned back to the γ -MnO₂ phase, indicating a reversible phase transformation during the electrochemical reaction (Fig 9). At a current density of 0.05 mA cm⁻², the mesoporous γ -MnO₂ cathode demonstrated an initial discharge capacity of 285 mAh cm⁻².

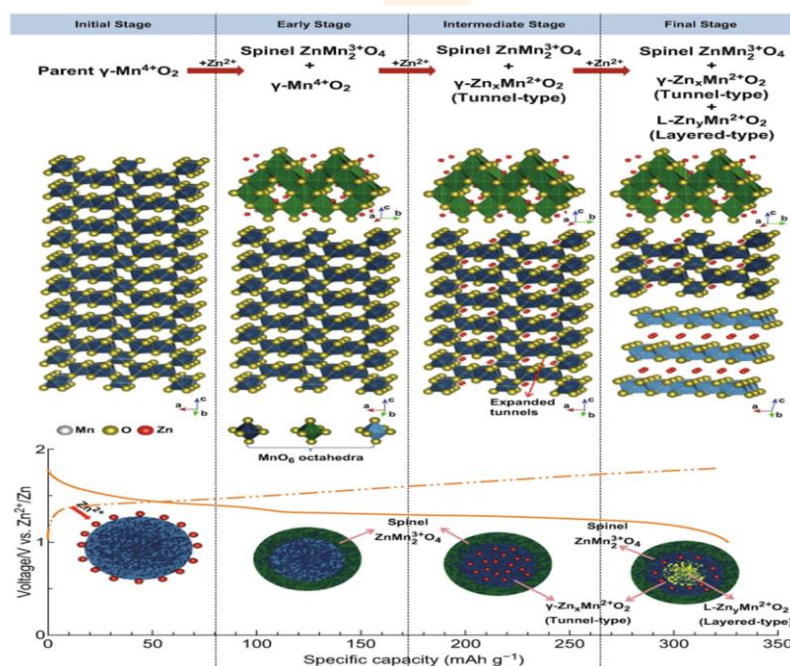


Figure 9: Schematic illustration of the transformation process of γ -MnO₂ cathode with Zn²⁺ ion insertion [65].

A recent study by Li et al. reports on a 2D layered V₂CT_x MXene cathode for AZIBs that exhibits a Zn²⁺/Li⁺ hybrid intercalation mechanism in a WISE electrolyte containing 21 M LiTFSI and 1 M Zn(OTf)₂. The cathode shows a high capacity of 508 mAh g⁻¹ at 0.2 A g⁻¹ and a durable cycle life of up to 18000 cycles at 10 A g⁻¹. The use of WISE leads to a wide voltage range of 0.1-2 V and a dendrite-free plating/stripping process in the Zn anode. The exceptional capacity enhancement is attributed to the continuously delaminated V₂CT_x, which provides more active sites to accommodate Zn²⁺ ions, and an unusual phase transition that takes place during the prolonged cycle to form the V₂CT_x/V₂O₅/C composite, which can synergistically contribute to the capacity. The high energy density of 386.2 Wh kg⁻¹ is achieved relying on the increased capacity and working voltages, making V₂CT_x MXene a promising alternative for stationary grid-scale Zn-ion storage. Fig 10 a,b shows the cyclic voltammogram and the galvanostatic charge/discharge curves of the V₂AIC cathode in the WISE electrolyte, respectively. Figure 10 c shows the variation of the valence state of V species during the cycling process [66,67].

(Fig 10 d) shows the improved hydrophilicity and the 3.3 Å distance increment of interlayer spacing in the engineered MoS₂ host cathode. (Fig 10 e) displays the high capacity achieved by the MoS₂ cathode, while (Fig 10 f) shows the reversible phase transition from 2H to 1T MoS₂ during the discharge/charge process. Finally, (Fig 10 g) shows the Mo 3d regions of ex situ XPS spectra, confirming the reversible phase transition [68].

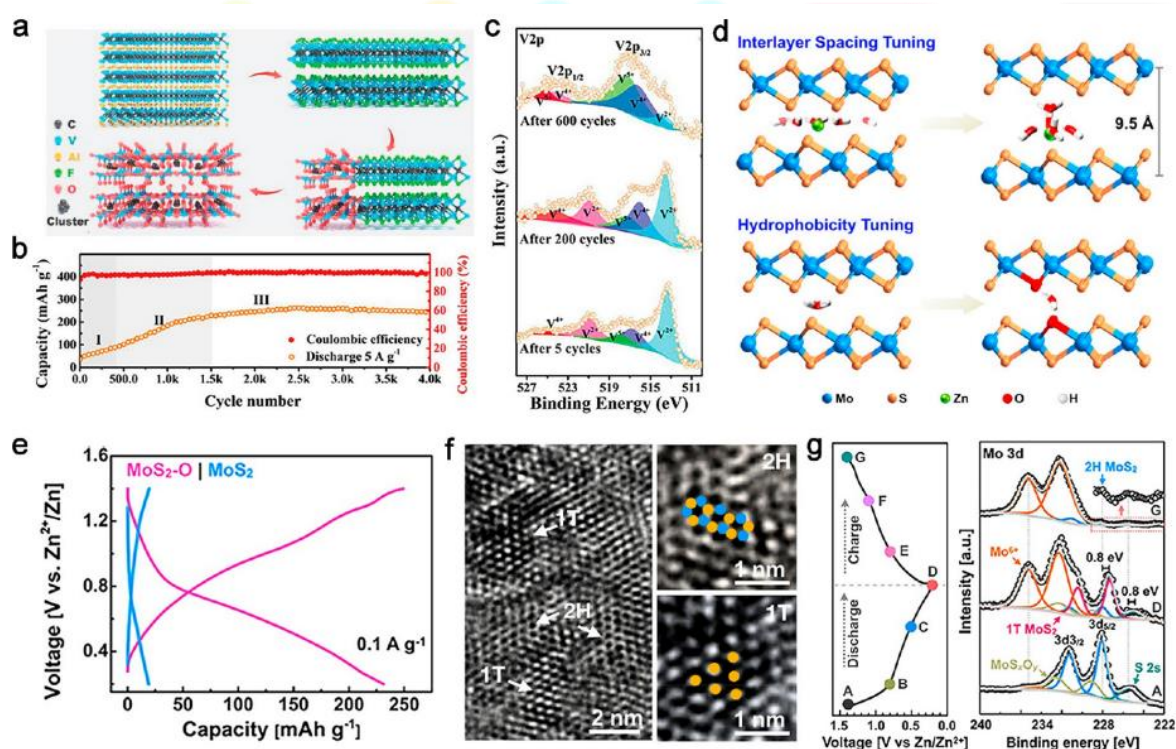


Fig 10. Charge storage chemistries in layered V_2AlC Mxene and MoS_2-O cathodes. (a,b) Illustration of phase and structure transition of V_2AlC cathode during the whole cycle and corresponding cycling performance at $5 A g^{-1}$. (c) XPS spectra of V 2p regions in the V_2AlC cathode after 5, 200, and 600 cycles at $5 A g^{-1}$ (d) Interlayer spacing and hydrophilicity tuning in a MoS_2-O cathode. (e) Comparison of discharge/charge profiles at $0.1 A g^{-1}$ in MoS_2-O and MoS_2 cathodes. (f) High-resolution transmission electron microscopy images of MoS_2-O after the discharge process ($100 mA g^{-1}$). (g) Charge/discharge profile at $100 mA g^{-1}$ and corresponding XPS spectra of Mo 3d regions in a MoS_2-O cathode. Reprinted from [69]

Various strategies have been investigated to tackle the issue of complex structural changes in Mn-based oxides during battery cycling. One approach is pre-adding Mn^{2+} salt to achieve a balance between dissolution and reoxidation, leading to a stable electrode. Another method is to create a protective layer on the MnO_2 cathode's surface, such as graphene scrolls, PEDOT, PPy, or PF. A solid electrolyte interface (SEI) layer can also be formed via an in situ electrochemically charging process in a Ca_2MnO_4 (CMO) cathode to inhibit Mn^{2+} dissolution. Pre-intercalated ions can create a stable architecture with strong ionic and covalent bonds between the oxide matrix. For instance, α - MnO_2 cathodes stabilized by K^+ incorporation showed reduced Mn^{2+} dissolution behavior. Vanadium oxide cathodes face similar issues, but an ultrathin, inactive HfO_2 film has been coated onto $Zn_3V_2O_7(OH)_2 \cdot 2H_2O$ (ZVO) cathodes via atomic layer deposition (ALD) to suppress ZVO dissolution and ZHS LDH precipitates, resulting in higher capacity and stable cycles. Intrinsically stable vanadium oxides with robust architectures created by more stable V–O bonds are a promising approach for future development.

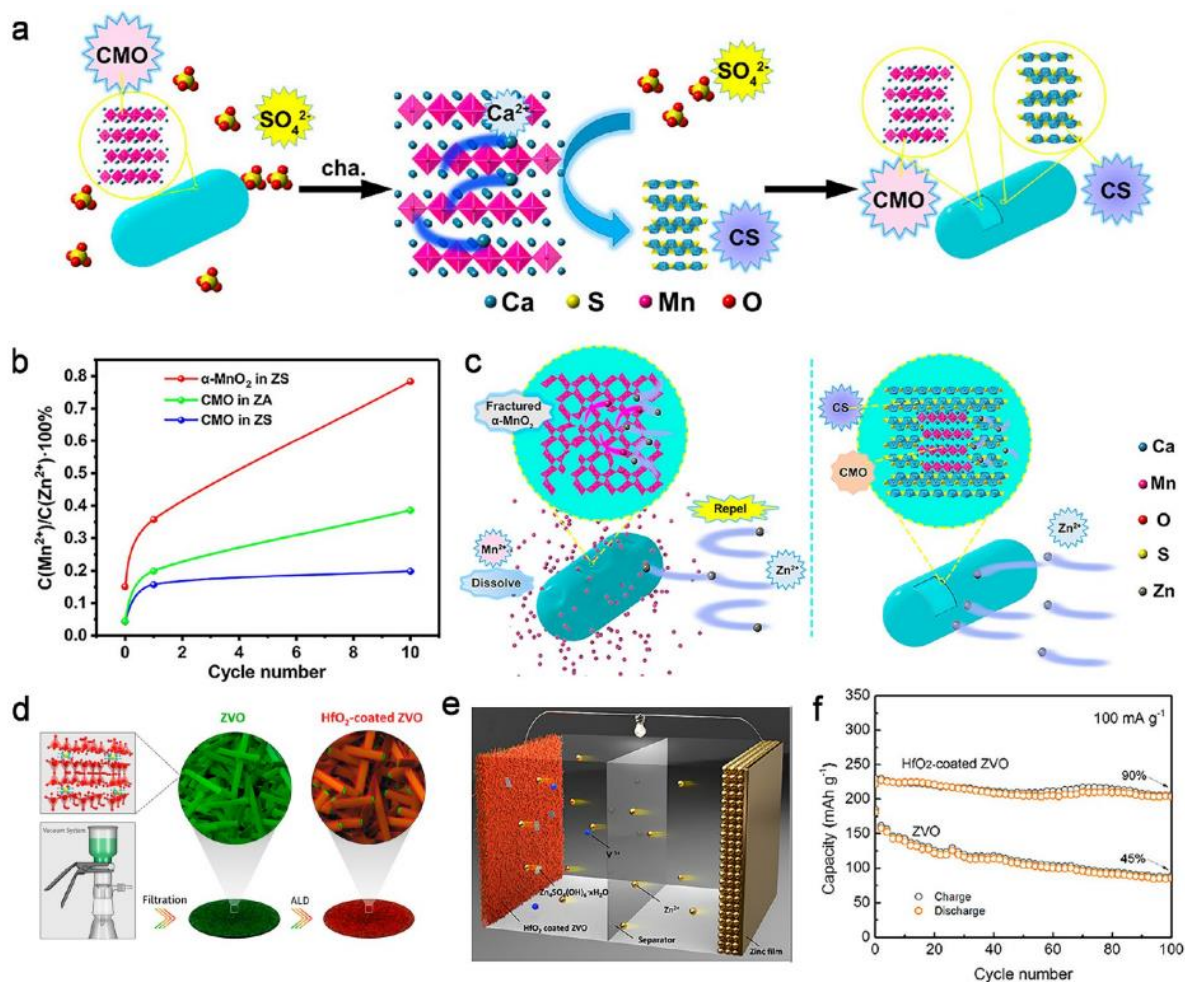


Fig 10. Cases of suppressing cathode dissolution in manganese and vanadium oxides. (a) Formation mechanism of CS SEI layer-coated CMO structure. (b) Comparison of manganese dissolution rate of $\alpha\text{-MnO}_2$ and CMO in different electrolytes (“2 M ZnSO_4 ” (ZS) and “1 M $\text{Zn}(\text{CH}_3\text{COO})_2$ ” (ZA) electrolyte). (c) Battery reaction mechanism schematic diagram of $\alpha\text{-MnO}_2$ and CMO [70]. (d) Schematic illustration of the fabrication process of a pristine ZVO cathode and the HfO₂-coated ZVO by atomic layer deposition. (e) Schematic illustration of charge storage mechanism in the HfO₂-coated ZVO cathodes. Colors: blue, dissolved V ions; gold, Zn. (f) Comparison of cycling performance at 100 mA g⁻¹ in the ZVO and the HfO₂-coated ZVO cathodes [71].

7. Recycling of spent lithium-ion batteries

LIBs have been widely used in consumer electronics, EVs, and grids for nearly 30 years, and their demand has rapidly grown in the past decade [72]. However, these batteries have limited operational lifespans, and retired batteries are increasing in number each year (figure 11) [73]. These retired batteries can pose a significant threat to the environment and human health due to their chemical conditions, which are

aggravated compared to new batteries. The manufacture of LIBs also heavily depends on rare metals such as lithium, cobalt, nickel, and manganese, which experience drastic price fluctuations, making the manufacture cost unstable. Furthermore, the gradual depletion of metal reserves raises concerns about the long-term economic sustainability of LIBs. To address these issues, recycling spent LIBs can turn them into high-quality minerals and 'urban mines,' which can reduce safety risks, environmental impacts, and resource anxiety on rare metals, and stabilize the production cost of new batteries [74]. Therefore, recycling technology is considered a crucial component in completing the industrial chain of LIB manufacture.

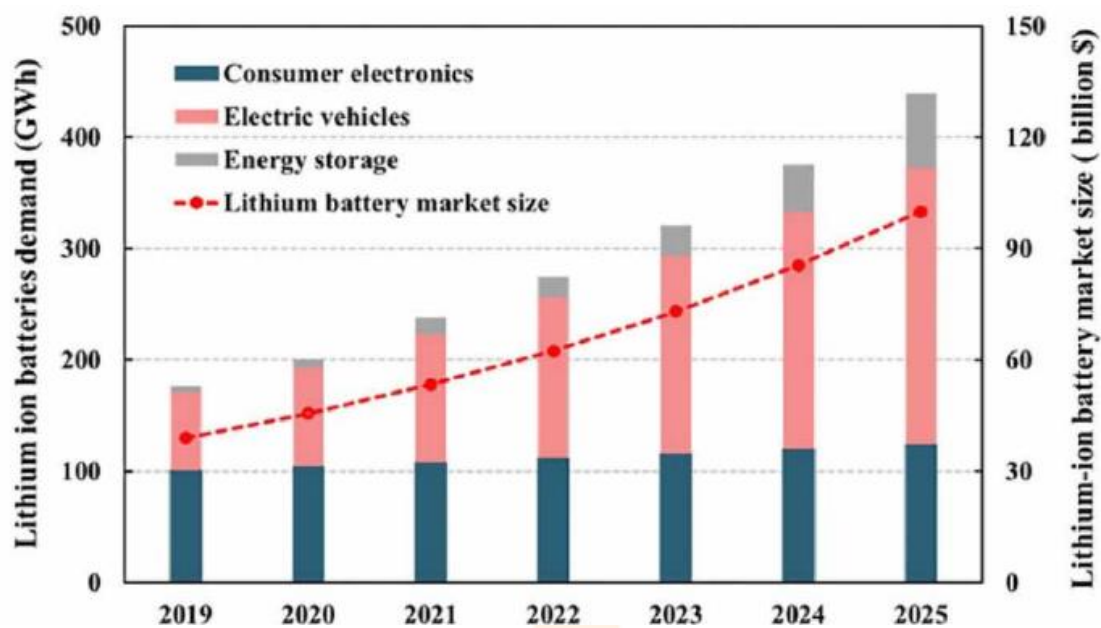


Figure 11: The usage of commercial lithium-ion batteries (LIBs) in consumer electronics, electric vehicles (EVs), and energy storage is steadily increasing, and market predictions indicate that it will continue to grow from 2019 to 2025 [73].

The recycling of spent lithium-ion batteries (LIBs) is important, but there are several challenges that need to be addressed before it can be implemented on an industrial scale. Before recycling, the performance metrics of retired LIBs packs/modules, including capacity retention, energy efficiency, structural integrity, and safety, should be evaluated. The results of the evaluation determine whether the spent LIBs can be cascaded or recycled for materials. However, there is currently no standard method for battery evaluation, and the poor performance consistency of spent LIBs makes cascade utilization difficult. A high-performance battery management system is desired to enable stable operation at the pack level, but it may increase the cost of the storage device. Additionally, spent LIBs are hazardous wastes, and there are safety concerns related to their

storage, transportation, and disassembly. Furthermore, the complex and varying compositions of LIBs make the recycling process complicated, leading to increased energy and materials costs. Recycling procedures often involve wet chemistry or pyrogenic reactions, which can lead to secondary pollution and carbon emissions. Moreover, the recycling of LIBs is a profit-driven business, which requires strict control of manufacturing costs, processes, and product quality. While the recycling market may have environmental benefits and play a significant role in the international trade of rare metals, it will take time for all parties to reach a consensus on the profit-making model and establish a complete set of policies and regulations to protect the industry. To achieve healthy growth of the recycling market, joint efforts are required from the government, companies, and consumers. Reference sources are not necessary as this is general knowledge. It has been found that for retired electric vehicle (EV) batteries, re-use is preferred over recycling [74]. Spent lithium-ion batteries (LIBs) with residual energy and no safety issues can be directly used for lower-level applications such as stationary storage power stations and low-speed EVs. Prior studies have emphasized the diagnosis of internal conditions and potential failure of battery packs, modules, and cells to improve the safety of cascade utilization. LIBs diagnosed with total failure are subjected to recycling. The recycling process involves disassembling battery packs/modules and materials recycling at the single-cell level. The disassembly of battery packs/modules is aided by artificial intelligence to minimize the risk of human exposure and reduce labor costs. However, due to the diverse battery configurations, fully automatic battery disassembly is unlikely in the near term. New methods and technologies for cell-level materials recycling are equally important. Among all the components of a commercial LIB, the cathode holds the largest share of cost and is, therefore, of the highest value for recycling. Rare metals are extracted from the cathode active materials through pyro-/hydro-/bio-/electrometallurgical routes [75], and are purified and collected in their salt forms. While pyrometallurgy and hydrometallurgy methods are commonly adopted by the industry due to their advantages in cost and technical maturity, new methods and technologies keep emerging in the lab. For example, closed-loop recycling and direct regeneration of cathode materials have been proposed based on the intrinsic properties and (electro)chemical degradation mechanism of spent LIBs [76, 77]. These strategies target the recovery of cathode performance or restoration of cathode structures, which could show advantages over traditional approaches in terms of cost and efficiency. To maximize the recovery value of spent LIBs, recycling of other battery components was also suggested. For instance, the

spent graphite anode can be recycled to manufacture high-performance Li-ion capacitors after calcination [78]. The electrolytes in spent LIBs were extracted by supercritical CO₂ and reused in the production of LIBs [79]. Innovations have been made to address the challenges in other crucial steps of the recycling process, such as using deep eutectic solvents for the separation of active materials from the metal collector foil during pre-treatment [80]. Finally, good quality control of the products is equally important for building a long-term profitable recycling industry. Efforts have been made to broaden the market of recycling products, which includes introducing more purification steps at an affordable cost and finding new applications that are not immediately demanding [81].

The recycling of used LIBs has become a growing area of interest due to the need for sustainable battery production. To determine the best approach for recycling LIBs, economic benefits, cost, and environmental impacts must all be taken into consideration (figure 12). Current recycling methods should be improved and innovative techniques developed to address key steps in the recycling process such as battery recovery and remanufacturing of important materials and modules/packs. Future research in LIB recycling should align with advancements in LIB technology to develop tailored strategies for resolving specific battery system issues. To achieve efficient LIB recycling, collaboration between government, companies, and consumers is necessary to monitor the complete lifecycle of LIBs.

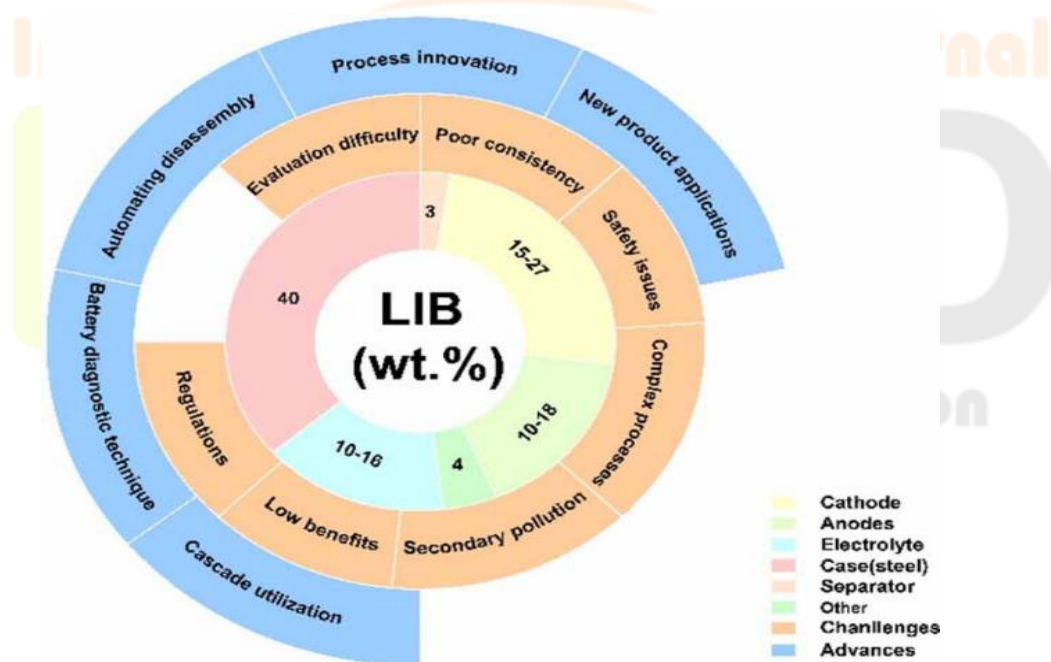


Figure 12. This schematic diagram depicts the weight composition of a common spent lithium-ion battery (LIB) and the advancements and obstacles in its recycling process [12].

8. Conclusions

In conclusion, this paper presents a comprehensive review of the recent developments in lithium-ion and zinc-ion battery technologies. The research focuses on the main challenges and opportunities in both battery technologies, including the issues related to their materials, performance, safety, and recycling. The paper highlights the significant progress made in the field of lithium-ion batteries, such as the development of new cathode materials, solid-state electrolytes, and silicon anodes. Additionally, it discusses the emerging field of zinc-ion batteries, which offers great potential due to the abundance and low cost of zinc, along with its high energy density and environmental friendliness. The review also sheds light on the current challenges facing the recycling of spent batteries and the need for more sustainable and cost-effective recycling methods. Overall, this paper provides a useful reference for researchers and industry practitioners seeking to understand the recent developments and challenges in the field of advanced battery technologies.

Abbreviations:

AOPs	: Advanced oxidation processes
BOD	: Biological oxygen demand
LIP	: Lithium-ion battery
CIP	: Clean in place
COD	: Chemical oxygen demand
DO	: Dissolved oxygen
EF	: Electro-Fenton
GMP	: Good manufacturing practises
MW-PS	: Microwave-persulfate
MWCNT	: Multi-walled carbon nano tube
NTU	: Nephelometric turbidity
PS	: Persulfate
RDW	: Real dairy wastewater
SCMFC	: Single chamber microbial fuel cell
US	: Ultrasound
UV	: Ultraviolet

Symbols:

C_i	: Initial COD of wastewater
C_f	: Final COD of wastewater
k_1	: Rate constant of first order kinetic model
k_2	: Rate constant of pseudo-second order kinetic model
k_3	: Rate constant of second order kinetic model

Acknowledgments

Ministry of Human Resources and Development (MHRD), India is thankfully acknowledged for funding this experimental study through institute funding for research facilities.

Funding

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Declaration of interest of statements

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

- [1] Lashof D A and Ahuja D R 1990 Relative contributions of greenhouse gas emissions to global warming Nature 344 529–531
- [2] Kondratenko E V, Mul G, Baltrusaitis J, Larrazábal G O and Pérez-Ramírez J 2013 Status and perspectives of CO₂ conversion into fuels and chemicals by catalytic, photocatalytic and electrocatalytic processes Energy Environ. Sci. 6 3112–35
- [3] Yang Z, Zhang J, Kintner-Meyer M C, Lu X, Choi D, Lemmon J P and Liu J 2011 Electrochemical energy storage for green grid Chem. Rev. 111 3577–613
- [4] Shao Y, El-Kady M F, Sun J, Li Y, Zhang Q, Zhu M, Wang H, Dunn B and Kaner R B 2018 Design and mechanisms of asymmetric supercapacitors Chem. Rev. 118 9233–80

- [5]Dunn B, Kamath H and Tarascon J-M 2011 Electrical energy storage for the grid: a battery of choices Science 334 928
- [6]Tarascon J M and Armand M 2010 Issues and challenges facing rechargeable lithium batteries Nature 414 359–67
- [7]Xu R, Lu J and Amine K 2015 Progress in mechanistic understanding and characterization techniques of Li–S batteries Adv. Energy Mater. 5 1500408
- [8]Bruce P G, Freunberger S A, Hardwick L J and Tarascon J M 2011 Li–O₂ and Li–S batteries with high energy storage Nat. Mater. 11 19–29
- [9]Quartarone E and Mustarelli P 2011 Electrolytes for solid-state lithium rechargeable batteries: recent advances and perspectives Chem. Soc. Rev. 40 2525–40
- [10]Gao Z, Sun H, Fu L, Ye F, Zhang Y, Luo W and Huang Y 2018 Promises, challenges, and recent progress of inorganic solid-state electrolytes for all-solid-state lithium batteries Adv. Mater. 30 e1705702
- [11]Whittingham M S 2004 Lithium batteries and cathode materials Chem. Rev. 104 4271–302
- [12] (Jianmin Ma et al. The 2021 battery technology roadmap, J. Phys. D: Appl. Phys. 54, 2021, DOI 10.1088/1361-6463/abd353)
- [13]Weber R, Genovese M, Louli A J, Hames S, Martin C, Hill I G and Dahn J R 2019 Long cycle life and dendrite-free lithium morphology in anode-free lithium pouch cells enabled by a dual-salt liquid electrolyte Nat. Energy 4 683–9
- [14]Pang Q, Liang X, Kochetkov I R, Hartmann P and Nazar L F 2018 Stabilizing lithium plating by a biphasic surface layer formed in situ Angew. Chem., Int. Ed. Engl. 57 9795–8
- [15]Shen X, Li Y, Qian T, Liu J, Zhou J, Yan C and Goodenough J B 2019 Lithium anode stable in air for low-cost fabrication of a dendrite-free lithium battery Nat. Commun. 10 900
- [16]Park K and Goodenough J B 2017 Dendrite-suppressed lithium plating from a liquid electrolyte via wetting of Li₃N Adv. Energy Mater. 7 1700732

- [17]Grundish N S, Amos C D, Agrawal A, Khani H and Goodenough J B 2019 Low-cost self-assembled oxide separator for rechargeable batteries *Adv. Funct. Mater.* 29 1903550
- [18]Hayashi A, Sakuda A and Tatsumisago M 2016 Development of sulfide solid electrolytes and interface formation processes for bulk-type all-solid-state Li and Na batteries *Front. Energy Res.* 4 25
- [19]Armstrong A R, Lyness C, Panchmatia P M, Islam M S and Bruce P G 2011 The lithium intercalation process in the low-voltage lithium battery anode $\text{Li}(1+x\text{V}(1-x)\text{O}_2$ *Nat. Mater.* 10 223–9
- [20]Aurbach D, McCloskey B D, Nazar L F and Bruce P G 2016 Advances in understanding mechanisms underpinning lithium–air batteries *Nat. Energy* 1 16128
- [21]Abraham K M and Jiang Z 1996 A polymer electrolyte-based rechargeable lithium/oxygen battery *J. Electrochem. Soc.* 143 1–5
- [22]Toni J E A, McDonald G D and Elliott W E 1966 Lithium–moist air battery Semiannual Report No. 1 (Milwaukee, WI: Globe-Union, Inc.) Medium: X 94
- [23]Lilley S J, Andreev Y G and Bruce P G 2006 Ionic conductivity in crystalline PEO6: $\text{Li}(\text{AsF}_6)_{1-x}(\text{SbF}_6)_x$ *J. Am. Chem. Soc.* 128 12036–7
- [24]Zhao Z, Huang J and Peng Z 2018 Achilles' heel of lithium–air batteries: lithium carbonate *Angew. Chem., Int. Ed. Engl.* 57 3874–86
- [25]Peng Z, Freunberger S A, Chen Y and Bruce P G 2012 A reversible and higher-rate Li–O₂ battery *Science* 337 563–6
- [26]Johnson L, Li C, Liu Z, Chen Y, Freunberger S A, Ashok P C, Praveen B B, Dholakia K, Tarascon J M and Bruce P G 2014 The role of LiO₂ solubility in O₂ reduction in aprotic solvents and its consequences for Li–O₂ batteries *Nat. Chem.* 6 1091–9
- [27]Zhang Y, Zhang X, Wang J, McKee W C, Xu Y and Peng Z 2016 Potential-dependent generation of O₂ – and LiO₂ and their critical roles in O₂ reduction to Li₂O₂ in aprotic Li–O₂ batteries *J. Phys. Chem. C* 120 3690–8

- [28]Wang L, Zhang Y, Liu Z, Guo L and Peng Z 2017 Understanding oxygen electrochemistry in aprotic LiO₂ batteries Green Energy Environ. 2 186–203
- [29]Feng S, Huang M, Lamb J R, Zhang W, Tatara R, Zhang Y, Zhu Y G, Perkinson C F, Johnson J A and Shao-Horn Y 2019 Molecular design of stable sulfamide- and sulfonamide-based electrolytes for aprotic Li–O₂ batteries Chem 5 2630–41
- [30]Shen X, Zhang S, Wu Y and Chen Y 2019 Promoting Li–O₂ batteries with redox mediators ChemSusChem 12 104–14
- [31]Liu Y, He P and Zhou H 2018 Rechargeable solid-state Li–air and Li–S batteries: materials, construction, and challenges Adv. Energy Mater. 8 1701602
- [32]Kwak W-J, Shin H-J, Reiter J, Tsiouvaras N, Hassoun J, Passerini S, Scrosati B and Sun Y-K 2016 Understanding problems of lithiated anodes in lithium oxygen full-cells J. Mater. Chem. A 4 10467–71
- [33]Zhang X, Xie Z and Zhou Z 2019 Recent progress in protecting lithium anodes for Li–O₂ batteries ChemElectroChem 6 1969–77
- [34]Liu Z et al 2019 Taming interfacial instability in lithium–oxygen batteries: a polymeric ionic liquid electrolyte solution Adv. Energy Mater. 9 1901967
- [35]Louli A J et al 2020 Diagnosing and correcting anode-free cell failure via electrolyte and morphological analysis Nat. Energy 5 693–702
- [36]Qiao Y, Wang Q, Mu X, Deng H, He P, Yu J and Zhou H 2019 Advanced hybrid electrolyte Li–O₂ battery realized by dual superlyophobic membrane Joule 3 2986–3001
- [37]Danuta H and Juliusz U 1962 Electric dry cells and storage batteries United States Patent No. US3043896A
- [38]Peled E, Gorenshstein A, Segal M and Sternberg Y 1989 Rechargeable lithium–sulfur battery J. Power Sources 26 269–71
- [39]Mikhaylik Y V 2008 Electrolytes for lithium sulfur cells United States Patent No. US7354680B2

- [40] Ji X, Lee K T and Nazar L F 2009 A highly ordered nanostructured carbon-sulphur cathode for lithium-sulphur batteries *Nat. Mater.* 8 500–6
- [41] Mikhaylik Y V and Akridge J R 2004 Polysulfide shuttle study in the Li/S battery system *J. Electrochem. Soc.* 151 1969–76
- [42] Song Y, Cai W, Kong L, Cai J, Zhang Q and Sun J 2019 Rationalizing electrocatalysis of Li–S chemistry by mediator design: progress and prospects *Adv. Energy Mater.* 10 1901075
- [43] Xin S, Gu L, Zhao N H, Yin Y X, Zhou L J, Guo Y G and Wan L J 2012 Smaller sulfur molecules promise better lithium-sulfur batteries *J. Am. Chem. Soc.* 134 18510–3
- [44] Wang J, Yang J, Xie J and Xu N 2002 A novel conductive polymer-sulfur composite cathode material for rechargeable lithium batteries *Adv. Mater.* 14 963–5
- [45] Cheng L, Curtiss L A, Zavadil K R, Gewirth A A, Shao Y and Gallagher K G 2016 Springily solvating electrolytes for high energy density lithium-sulfur batteries *ACS Energy Lett.* 1 503–9
- [46] Hayashi A, Ohtomo T, Mizuno F, Tadanaga K and Tatsumisago M 2003 All-solid-state Li/S batteries with highly conductive glass-ceramic electrolytes *Electrochem. Commun.* 5 701–5
- [47] Manthiram A, Yu X and Wang S 2017 Lithium battery chemistries enabled by solid-state electrolytes *Nat. Rev. Mater.* 2 16103
- [48] Yue J, Yan M, Yin Y-X and Guo Y-G 2018 Progress of the interface design in all-solid-state Li-S batteries *Adv. Funct. Mater.* 28 1707533
- [49] Kamaya N et al 2011 A lithium superionic conductor *Nat. Mater.* 10 682–6
- [50] Fan L, Wei S, Li S, Li Q and Lu Y 2018 Recent progress of the solid-state electrolytes for high-energy metal-based batteries *Adv. Energy Mater.* 8 1702657
- [51] Cheng X-B, Zhao C-Z, Yao Y-X, Liu H and Zhang Q 2019 Recent advances in energy chemistry between solid-state electrolyte and safe lithium-metal anodes *Chem* 5 74–96
- [52] Maleki Kheimeh Sari H and Li X 2019 Controllable cathode-electrolyte interface of Li[Ni_{0.8}Co_{0.1}Mn_{0.1}]O₂ for lithium ion batteries: a review *Adv. Energy Mater.* 9 1901597

- [53]Li Y, Chen X, Dolocan A, Cui Z, Xin S, Xue L, Xu H, Park K and Goodenough J B 2018 Garnet electrolyte with an ultralow interfacial resistance for Li-metal batteries *J. Am. Chem. Soc.* 140 6448–55
- [54]Fitzhugh W, Ye L and Li X 2019 The effects of mechanical constriction on the operation of sulfide based solid-state batteries *J. Mater. Chem. A* 7 23604–27
- [55]Huang Z, Pang W, Liang P, Jin Z, Grundish N, Li Y and Wang C-A 2019 A dopamine modified Li_{6.4}La₃Zr_{1.4}Ta_{0.6}O₁₂/PEO solid-state electrolyte: enhanced thermal and electrochemical properties *J. Mater. Chem. A* 7 16425–36
- [56]Bae J, Li Y, Zhang J, Zhou X, Zhao F, Shi Y, Goodenough J B and Yu G 2018 A 3D nanostructured hydrogel-framework-derived high-performance composite polymer lithium-ion electrolyte *Angew. Chem., Int. Ed. Engl.* 57 2096–100
- [57]Fu J, Liang R, Liu G, Yu A, Bai Z, Yang L and Chen Z 2019 Recent progress in electrically rechargeable zinc–air batteries *Adv. Mater.* 31 e1805230
- [58]Fu J, Cano Z P, Park M G, Yu A, Fowler M and Chen Z 2017 Electrically rechargeable zinc–air batteries: progress, challenges, and perspectives *Adv. Mater.* 29 1604685
- [59]Cano Z P, Banham D, Ye S, Hintennach A, Lu J, Fowler M and Chen Z 2018 Batteries and fuel cells for emerging electric vehicle markets *Nat. Energy* 3 279–89
- [60]Nykqvist B and Nilsson M 2015 Rapidly falling costs of battery packs for electric vehicles *Nat. Clim. Change* 5 329–32
- [61]Meng F L, Liu K H, Zhang Y, Shi M M, Zhang X B, Yan J M and Jiang Q 2018 Recent advances toward the rational design of efficient bifunctional air electrodes for rechargeable Zn–air batteries *Small* 14 e1703843
- [62]Higashi S, Lee S W, Lee J S, Takechi K and Cui Y 2016 Avoiding short circuits from zinc metal dendrites in anode by backside-plating configuration *Nat. Commun.* 7 11801
- [63]Parker J F, Chervin C N, Pala I R, Machler M, Burz M F, Long J W and Rolison D R 2017 Rechargeable nickel–3D zinc batteries: an energy-dense, safer alternative to lithium-ion *Science* 356 415–8

- [64] Mainar A R, Iruin E, Colmenares L C, Kvasha A, de Meatza I, Bengoechea M, Leonet O, Boyano I, Zhang Z and Blazquez J A 2018 An overview of progress in electrolytes for secondary zinc–air batteries and other storage systems based on zinc *J. Energy Storage* 15 304–28
- [65] M. Alfaruqi, V. Mathew, J. Gim, S. Kim, J. Song, J.P. Baboo, S.H. Choi, J. Kim, Electrochemically induced structural transformation in a γ -MnO₂ cathode of a high capacity zinc-ion battery system. *Chem. Mater.* 27(10), 3609–3620 (2015). <https://doi.org/10.1021/cm504717p>
- [66] Li, X.; Li, M.; Yang, Q.; Li, H.; Xu, H.; Chai, Z.; Chen, K.; Liu, Z.; Tang, Z.; Ma, L.; Huang, Z.; Dong, B.; Yin, X.; Huang, Q.; Zhi, C. Phase Transition Induced Unusual Electrochemical Performance of V₂CTX MXene for Aqueous Zinc Hybrid-Ion Battery. *ACS Nano* 2020, 14, 541–551.
- [67] Li, X.; Li, M.; Yang, Q.; Liang, G.; Huang, Z.; Ma, L.; Wang, D.; Mo, F.; Dong, B.; Huang, Q.; Zhi, C. In Situ Electrochemical Synthesis of MXenes without Acid/Alkali Usage in/for an Aqueous Zinc Ion Battery. *Adv. Energy Mater.* 2020, 10, 2001791.
- [68] Hu, Z.; Liu, Q.; Chou, S.; Dou, S. Advances and Challenges in Metal Sulfides/Selenides for Next-Generation Rechargeable Sodium Ion Batteries. *Adv. Mater.* 2017, 29, 1700606.
- [69] Liang, H.; Cao, Z.; Ming, F.; Zhang, W.; Anjum, D. H.; Cui, Y.; Cavallo, L.; Alshareef, H. N. Aqueous Zinc-Ion Storage in MoS₂ by Tuning the Intercalation Energy. *Nano Lett.* 2019, 19, 3199–3206.
- [70] Guo, S.; Liang, S.; Zhang, B.; Fang, G.; Ma, D.; Zhou, J. Cathode Interfacial Layer Formation via in Situ Electrochemically Charging in Aqueous Zinc-Ion Battery. *ACS Nano* 2019, 13, 13456–13464.
- [71] Guo, J.; Ming, J.; Lei, Y.; Zhang, W.; Xia, C.; Cui, Y.; Alshareef, H. N. Artificial Solid Electrolyte Interphase for Suppressing Surface Reactions and Cathode Dissolution in Aqueous Zinc Ion Batteries. *ACS Energy Lett.* 2019, 4, 2776–2781.
- [72] Etacheri V, Marom R, Elazari R, Salitra G and Aurbach D 2011 Challenges in the development of advanced Li-ion batteries: a review *Energy Environ. Sci.* 4 3243
- [73] Fan E, Li L, Wang Z, Lin J, Huang Y, Yao Y, Chen R and Wu F 2020 Sustainable recycling technology for Li-ion batteries and beyond: challenges and future prospects *Chem. Rev.* 120 7020–63

- [74]Harper G et al 2019 Recycling lithium-ion batteries from electric vehicles *Nature* 575 75–86
- [75]Zhang X, Li L, Fan E, Xue Q, Bian Y, Wu F and Chen R 2018 Toward sustainable and systematic recycling of spent rechargeable batteries *Chem. Soc. Rev.* 47 7239–302
- [76]Shi Y, Chen G, Liu F, Yue X and Chen Z 2018 Resolving the compositional and structural defects of degraded $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ particles to directly regenerate high-performance lithium-ion battery cathodes *ACS Energy Lett.* 3 1683–92
- [77]Wang T, Yu X, Fan M, Meng Q, Xiao Y, Yin Y X, Li H and Guo Y G 2019 Direct regeneration of spent LiFePO_4 via a graphite prelithiation strategy *Chem. Commun.* 56 245–8
- [78]Divya M L, Natarajan S, Lee Y-S and Aravindan V 2020 Achieving high-energy dual carbon Li-ion capacitors with unique low- and high-temperature performance from spent Li-ion batteries *J. Mater. Chem. A* 8 4950–9
- [79]Liu Y, Mu D, Li R, Ma Q, Zheng R and Dai C 2017 Purification and characterization of reclaimed electrolytes from spent lithium-ion batteries *J. Phys. Chem. C* 121 4181–7
- [80]Wang M, Tan Q, Liu L and Li J 2019 A low-toxicity and high-efficiency deep eutectic solvent for the separation of aluminum foil and cathode materials from spent lithium-ion batteries *J. Hazard. Mater.* 380 120846
- [81]Natarajan S and Aravindan V 2018 Burgeoning prospects of spent lithium-ion batteries in multifarious applications *Adv. Energy Mater.* 8 1802303
- [1] D.A. Lashof, D.R. Ahuja, Relative contributions of greenhouse gas emissions to global warming, *Nature* 344(6266) (1990) 529-531. <https://doi.org/10.1038/344529a0>.
- [2] E.V. Kondratenko, G. Mul, J. Baltrusaitis, G.O. Larrazábal, J. Pérez-Ramírez, Status and perspectives of CO₂ conversion into fuels and chemicals by catalytic, photocatalytic and electrocatalytic processes, *Energy & Environmental Science* 6(11) (2013) 3112-3135. <https://doi.org/10.1039/C3EE41272E>.