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The 2021 battery technology roadmap

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Roadmap

The 2021 battery technology roadmap

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Abstract

Sun, wind and tides have huge potential in providing us electricity in an environmental-friendly way. However, its intermittency and non-dispatchability are major reasons preventing full-scale adoption of renewable energy generation. Energy storage will enable this adoption by enabling a constant and high-quality electricity supply from these systems. But which storage technology should be considered is one of important issues. Nowadays, great effort has been focused on various kinds of batteries to store energy, lithium-related batteries, sodium-related batteries, zinc-related batteries, aluminum-related batteries and so on. Some cathodes can be used for these batteries, such as sulfur, oxygen, layered compounds. In addition, the construction of these batteries can be changed into flexible, flow or solid-state types. There are many challenges in electrode materials, electrolytes and construction of these batteries and research related to the battery systems for energy storage is extremely active. With the myriad of technologies and their associated technological challenges, we were motivated to assemble this 2020 battery technology roadmap.

Keywords: lithium batteries, sodium batteries, potassium batteries, metal–air batteries, energy-storage devices

(Some figures may appear in color only in the online journal)

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1. Introduction

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Vast consumption of fossil fuels and increased greenhouse gas emissions bring about drastic environmental impacts that have led to an increased global demand for developing methods of harvesting and storing energy sustainably [1]. Renewable energy sources, such as solar, hydro, and wind energy are the most promising solutions for addressing these concerns [2]. However, electricity produced from these sources must be efficiently stored to supply the world with energy on demand [3]. Among the various energy-storage devices, secondary batteries, currently used in consumer electronics, represent the leading electrochemical energy-storage (EES) technology due to their high energy densities (figure 1) [4] and their accessible range of chemical potentials [5].

Figure 2 shows the number of the papers published each year, from 2000 to 2019, relevant to batteries. In the last 20 years, more than 170 000 papers have been published. It is worth noting that the dominance of lithium-ion batteries (LIBs) in the energy-storage market is related to their maturity as well as the intricate understanding of the associated commercial scale manufacturing processes of their cathode/anode materials. Although the LIB has enabled tremendous technological advancements, their low energy density restrict their ability to meet growing demand [6]. Great effort has been

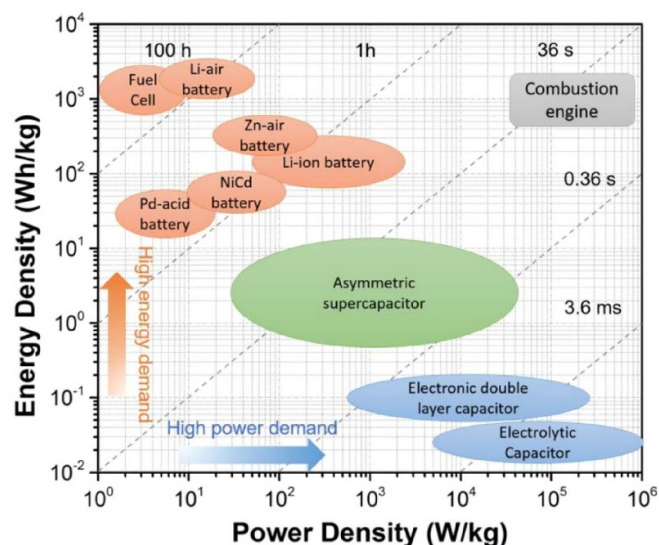


Figure 1. Ragone plot illustrating the performances of specific power vs specific energy for different electrical energy-storage technologies. Times shown in the plot are the discharge time, obtained by dividing the energy density by the power density. Reproduced from [4].

focused on alternative battery chemistries, such as lithium-sulfur (Li-S) batteries, sodium-related batteries, zinc-related batteries, and aluminum-related batteries. Particularly, Li-S batteries have developed rapidly in the past 5 years due to their high energy density and low-cost materials (inset of figure 2) [7, 8]. Solid-state LIBs have become a new research hotspot for high safety and high energy-density batteries [9, 10]. Even with all of the recent work and development, the concept of

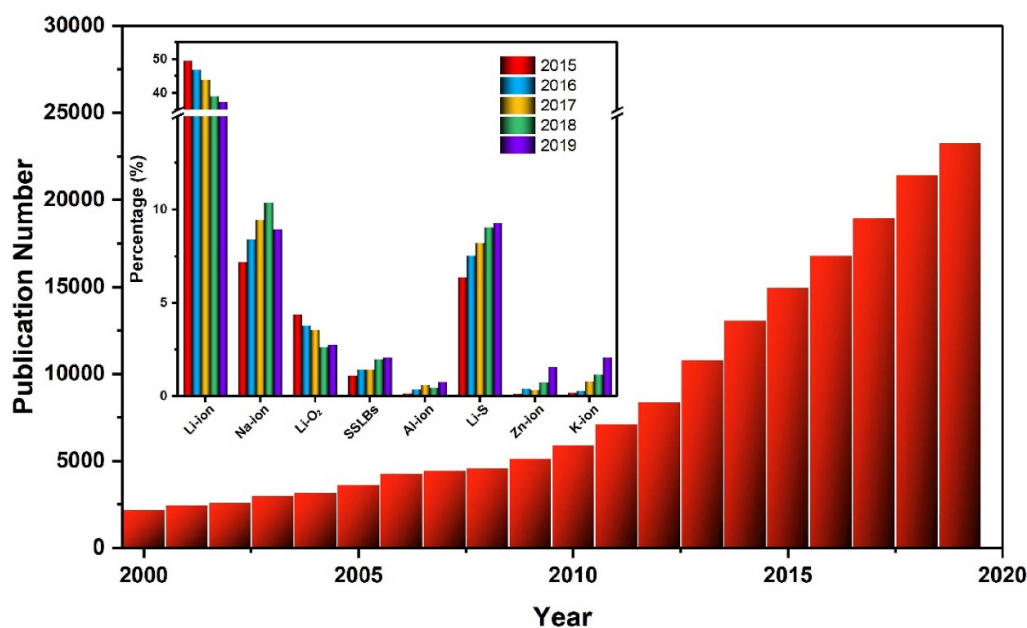


Figure 2. The number of papers published each year relevant to batteries from 2000 to 2019. The inset displays the percentage of papers published for different batteries from 2015 to 2019. Here, the papers searched from the web of science refined by 'topic = Batter*' and document types = articles' on 16 January 2020 (SSLBs: solid-state lithium-ion batteries).

designing new electrode materials and battery technology is still relatively new, with enormous potential for further expansion and impact.

This roadmap presents an overview of the current state of various kinds of batteries, such as the Li/Na/Zn/Al/K-ion battery, Li-S battery, Li-O₂ battery, and flow battery. Each discussion focuses on current work being done on a particular battery type, comparing the advantages and disadvantages of certain approaches to scientific and technological advancement towards maximizing the potential of the respective battery chemistry. Additionally, current and future challenges that must be addressed to improve the electrochemical

performance of batteries is discussed. We have asked leading researchers in each area of batteries to weigh in on these issues, providing their perspectives and visions for advancement in their respective battery field. We hope this roadmap will provide a concise yet comprehensive review and a reasonable development strategy for the fast-growing field of battery technology.

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2. Li-ion batteries

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2.1. Status

In the 1960s, Jean Rouxel in France and Robert Schroeder in Germany investigated the reversible insertion/extraction of Li^+ into the van der Waals gap between MS_2 layers having M as a transition-metal with an accessible redox couple. Whittingham later performed more extensive studies on Li^+ intercalation into layered TiS_2 , showing rapid and reversible intercalation without structural degradation of the material [11].

The chemical reaction in a rechargeable battery requires a reversible reaction between the two electrodes, and the concept of intercalation of Li^+ in a layered compound became an obvious strategy for the electrode of a rechargeable battery. In order to have a cell providing a large open-circuit voltage, Goodenough and co-workers investigated how much Li^+ can be extracted reversibly from the layered oxide LiCoO_2 and reported that over half of the Li can be extracted before the structure changes [12]. This observation led to the development of a cell with a discharged cathode, LiCoO_2 . Although the open-circuit voltage versus a lithium anode of a LiCoO_2 cathode was about 4.0 V, the battery manufacturers dismissed the idea of manufacturing a discharged cell; but Rachid Yazami previously recognized that intercalation of Li^+ into a graphitic carbon anode could be dendrite-free. Akira Yoshino then constructed the first discharged Li-ion cell consisting of a carbon anode and LiCoO_2 as the cathode. Workers at the SONY corporation then licensed the technology and did the technical development of a commercial LIB having a carbon anode and an LiCoO_2 cathode. They used this LIB to launch the wireless revolution.

This LIB is plagued by three defects: (a) too fast a charge plates metallic lithium on the carbon anode, (b) removal of too much Li from the cathode during charge results in O_2 evolution from the cathode into a closed space, and (c) the electrolyte is flammable and is ignited if a lithium dendrite grows to the cathode to create a short circuit that heats the cell. Nevertheless, the LIB will remain the best portable electric-power storage device for another few years.

2.2. Current and future challenges

A commercial LIB is assembled in the discharged state (figure 3). As the cell is charged, an electron is removed from the cathode and transported to the anode. To balance charge, a Li-ion is extracted from the cathode and inserted into the anode. Some lithium ions are consumed in the formation of a solid–electrolyte interphase (SEI) on the anode as the electrochemical potential of the graphite begins to exceed the lowest unoccupied molecular orbital (LUMO) of the organic-liquid electrolyte when lithiation begins (figure 4). If the growth of

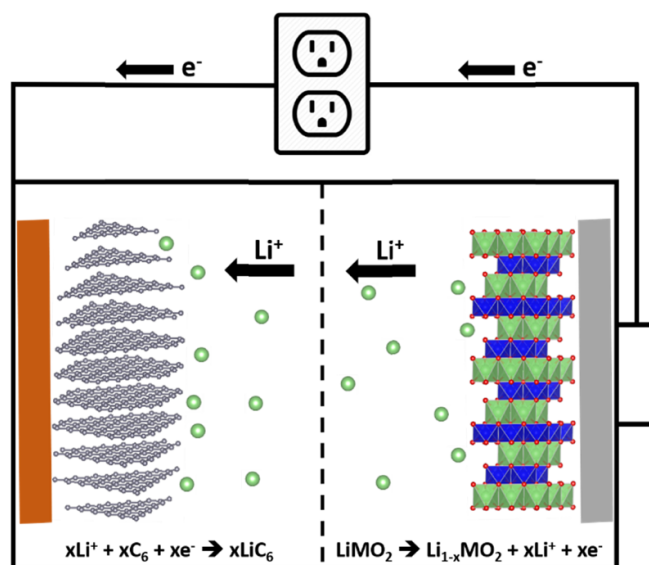


Figure 3. Schematic of the lithium-ion battery comprised of a layered transition-metal oxide cathode with an aluminum current collector against a graphite anode with a copper current collector. The half reactions for each electrode during charge are shown. The dashed line represents a separator. An organic-liquid solvent with a lithium conducting salt is used as the electrolyte.

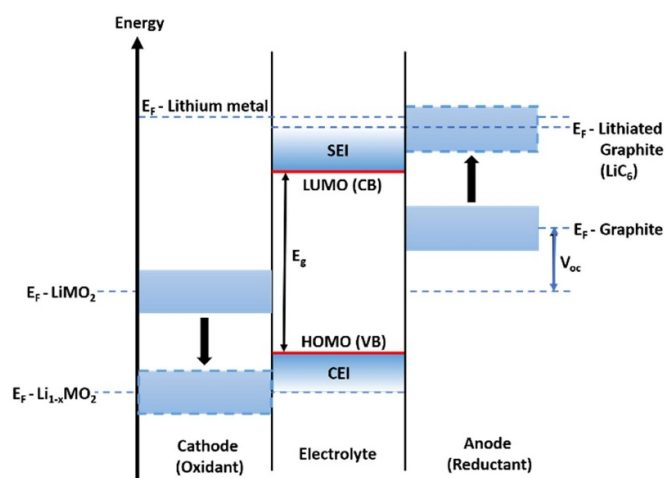


Figure 4. Energy diagram of a lithium-ion battery. Boxes with dashed borders indicate energy levels of electrodes in the charged state. Boxes without dashed border indicate energy levels electrodes in the as-prepared state.

this interphase is performed in a controlled manner with slow charging, stable cycling of the cell can be achieved. The cathode begins to form a cathode–electrolyte interphase (CEI) as the Fermi level of the layered transition-metal oxide begins to dip below the highest occupied molecular orbital (HOMO) of the electrolyte. The growth of the CEI is harder to control than the SEI and the composition of each interphase is still not well understood. Upon cycling, these interphases become problematic as volume expansion/contraction leads to cracking of the particles, requiring additional consumption of chemical species within the cell for new interphases to grow.

A lithium metal anode with a higher theoretical capacity than that of graphite would allow for an electrochemical cell with less anode material for the same amount of total energy, increasing the energy density of the cell. However, lithium metal has a greater propensity than graphite to form dendrites upon deposition that can ultimately grow across the cell and cause an electrical short. To increase energy density from the cathode side, one is relegated to increasing the voltage of their material by tailoring the potential of the transition-metal redox couple(s) within their structure, using multivalent transition-metal ions, or optimizing a material to maximize the reversible specific capacity via doping to obtain structural stability at high amounts of delithiation. Increasing the voltage of active materials is difficult owing to the limited electrochemical stability of the organic-liquid electrolyte. The flammability of the organic-liquid electrolyte along with the cost and toxicity of cobalt in current cathode active material provide additional concerns.

2.3. Advances in science and technology to meet challenges

Electrolyte additives are an effective strategy to manipulate the properties of the organic-liquid electrolyte. Recent reports have shown stable lithium plating with a dual-salt approach, removing the issue of dendrite growth from the lithium surface [13]. Another strategy is to engineer the surface chemistry of lithium metal to make uniform plating/stripping more favorable. Several different coatings and protective layers have been investigated, showing stable plating/stripping of lithium metal. These strategies are thought provoking towards developing artificial SEIs for lithium metal batteries with a liquid electrolyte that would normally get reduced, but they have yet to catch on commercially [14–16]. Additionally, new separator strategies have emerged that may allow for plating of metallic lithium in an electrochemical cell [17].

Solid-state ionic conductors provide a promising avenue to improve the safety and energy density of LIBs by removing the flammable liquid electrolyte. However, achieving values of ionic conductivity that are comparable to liquid lithium electrolytes is challenging in a solid. Sulfide-based solid electrolytes display the highest values of conductivity, but suffer from poor thermodynamic and kinetic stability, drastically hindering their applicability to electrochemical cells with an attractive working voltage [18]. Some of these materials

can form ionically conducting interfacial layers with lithium metal, but their electrochemical stability as well as mechanical stability against the cathode remain a struggle. Different cathode particle coating compounds and electrolyte/electrode interfacial layers are being explored to resolve these issues, but this strategy is in its infancy and has yet to yield results promising enough to conclude they are a reasonable solution.

Research and development of new cathode materials and structures that are optimal for solid-state batteries seems to be an area of research that is lacking. With most current efforts pushing to retrofit the layered oxides of traditional LIBs to the schematic of an all-solid-state design, we are left with more problems than we started with. The development of strain-free cathodes would circumvent the mechanical contact issue of the cathode-solid electrolyte interface that lose contact upon cycling. Although these contact issues could potentially be solved with a pressurized cell, engineering this for commercial application and consumer safety would be challenging.

2.4. Concluding remarks

LIBs have changed the way we view energy storage. However, after pushing the chemistry of the traditional LIB to its limits, it has been found wanting in terms of delivering competitive large-scale devices such as an all-electric vehicle (EV) that can drive extended distances on a single charge. All types of batteries and combinations thereof will be necessary to ensure that modern civilization leads a sustainable existence.

Research towards novel materials and structures for applications as electrode and electrolyte materials in LIBs should continue in order to spark innovation. As tremendous effort is being poured into making the materials that have previously been discovered viable for commercial application, equal effort should be dedicated to finding materials that do not have these issues to begin with, such as electrochemical stability issues for solid electrolytes or volume expansion and particle cracking issues for layered oxide cathode materials.

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3. Lithium–oxygen batteries

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3.1. Status

In the context of global environmental protection for sustainable development of human society, the electrification of road transportation using EVs has been deemed to be one of the major measures. Current EVs are propelled mainly by LIB-based power sources. Operation of the LIB relies on the intercalation/deintercalation of Li⁺ ions into/out of the host electrode materials having distinct voltages [19]. After decades of optimization, the specific energy or energy density of the LIBs will soon approach their theoretical limit due to their intrinsic intercalation chemistry, and may not meet the driving range requirement (typically 500 km per charge), expected for future EVs.

To address this driving range problem, radically new battery chemistries (e.g. Li–S, Li–O₂, multivalent ion, etc), sometimes called ‘beyond Li-ion’, have been proposed, among which the rechargeable Li–O₂ battery having an unrivaled theoretical specific energy 3500 Wh kg^{−1} and attracting much attention [20]. The Li–O₂ battery consists of two challenging electrodes, i.e. Li and O₂. Its operation depends on the stripping/plating of lithium on the negative electrode and formation/decomposition of Li₂O₂ on the positive electrode. In 1996, Abraham *et al* reported a prototype Li–O₂ cell that cycled a few times and this work is often thought to be the birth of the aprotic Li–O₂ batteries [21] despite pioneering work had been conducted as early as in 1966 [22]. In 2006, Bruce *et al* who were armed with differential electrochemical mass spectrometry, successfully oxidized Li₂O₂ to O₂ and proved that Li–O₂ battery is, in principle, rechargeable [23]. This work ignites the world wide enthusiasm pursuing Li–O₂ batteries in the following decades. However, formidable challenges remain on the road to practical Li–O₂ cells.

3.2. Current and future challenges

Despite alluring prospects, the Li–O₂ battery is still in its infancy stage. Numerous scientific and technological challenges must be addressed before a practical device could be developed. These challenges are summarized in figure 5, including, but not limited to, elucidation of reaction mechanisms, chemical and electrochemical stability of

cell components in open surroundings, and improvement of energy-storage efficiency and lifetime by catalyst design [20].

The challenges on the O₂ cathode arguably originate from the solid and insulative discharge product Li₂O₂ on the cathode surface. During charging of Li–O₂ batteries, a high overpotential is often observed, which leads to not only a low Coulombic efficiency but also oxidative degradation of cell components (e.g. electrolytes and cathode materials). One notorious side-reaction product is Li₂CO₃, which is hard to decompose even at a high voltage and can accumulate at the cathode–electrolyte interface upon cycling. As a result, an ever-growing charging potential is frequently observed, which in turn induces further decomposition of the cell components (electrolyte, cathode, catalyst, binder, etc) [24].

The challenges on the lithium metal anode (e.g. low Coulombic efficiency and poor cycle life) has been intensively but vainly studied for decades. In the context of the Li–O₂ battery, a new vexing player, the O₂ from the cathode compartment, could exacerbate the side reactions and possibly the dendrite growth of the metallic lithium anode [20].

3.3. Advances in science and technology to meet challenges

In the last decade, a great deal of research efforts have been devoted to the aforementioned challenges. Significant progress has been made on the understanding of the chemistry and electrochemistry of the discharge reaction, i.e. O₂ reduction to Li₂O₂ [20, 25]. Two distinct pathways of Li₂O₂ formation, i.e. the solution-mediated and surface-mediated routes, were identified by using various advanced characterization techniques [20]. The reaction pathway determines the morphology and properties of the discharge product Li₂O₂, and the discharge capacity, and charge overpotential. When the discharge reaction follows the surface route, Li₂O₂ continuously deposits on the surface of electrode as a Li₂O₂ film. The film-like Li₂O₂ eventually passivates the electrode surface and blocks the diffusion of Li⁺ and O₂, so that the discharge process rapidly terminates [26]. The solution route of Li₂O₂ formation mitigates the electrode passivation and is beneficial to a high discharge capacity. To pursue a higher discharge capacity, organic solvents with high solvating ability, i.e. higher donor number (DN), are desired, because high DN solvents can induce Li₂O₂ to form via the solution pathway by improving the solvation of LiO₂ intermediate [27]. For the charging of Li–O₂ batteries, mitigation of side reactions and charging overpotential is of crucial importance. Researchers have tried to replace the unstable carbon cathode with more stable non-carbon materials (e.g. nanoporous gold, metal oxides, perovskite, etc), the unstable organic carbonate electrolyte with more stable non-carbonate electrolyte (e.g. ether, sulfone, ionic liquid (IL), etc), with the aim of building better Li–O₂ batteries [28].

Reversible formation and decomposition of Li₂O₂ with high O₂ recovery efficiency has been demonstrated in Li–O₂ battery containing DMSO solvent (high DN) [25]. However, later studies showed that the life-span of superoxide species in high DN solvents are prolonged and it is likely to cause more solvent decomposition in high DN solvents than in low

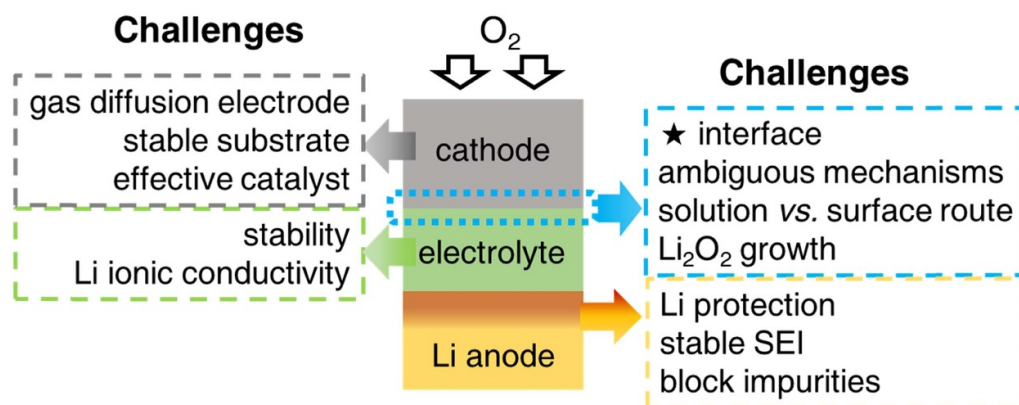


Figure 5. Schematics of challenges remained in Li–O₂ batteries.

DN solvents. The solvent decomposition can be suppressed either by using a more stable electrolyte solvent or by inhibiting the reactivity of superoxide intermediates. For instance, new organic solvents are designed and synthesized, which own significantly improved chemical stability without sacrificing the DN, reserving their ability to promote Li₂O₂ formation in electrolyte solution [29]. Another notable strategy to achieve Li₂O₂ formation in solution with less side reaction has been achieved by introducing a reduction mediator (RM_{disch}). RM_{disch} is a soluble molecule that transfers electrons from electrode to O₂ and forms a LiO₂–RM_{disch} complex as a new soluble intermediate. By replacing the aggressive LiO₂ intermediate with a mild LiO₂–RM_{disch} complex, the side reactions such as electrolyte and electrode decomposition are inhibited and the yield of Li₂O₂ upon discharge is increased [30]. Additionally, by using RM_{disch}, the reaction region at the cathode–electrolyte interface is expanded and the solution route proceeds even in solvents with moderate and even low DN solvents, which otherwise deliver a low discharge capacity because of their limited solubility towards LiO₂ and Li₂O₂.

Catalysts, either in the form of solid or molecular state, have dramatic effects on the discharge and charge processes of the Li–O₂ batteries. More radically, solid-state electrolytes, either organic or inorganic or hybrid, have been invoked, although intrinsically low charge transport capability and interfacial instability problems remain [31]. For the discharging process, the significant challenge is how to enhance the kinetics of O₂ reduction without passivating the active sites of catalysts by insulating Li₂O₂ and side-reaction products. This challenge makes the catalyst design for Li–O₂ batteries more complicated and difficult than that for fuel cells. For the charging process, a great barrier is the poor contact between the positive electrode surface and Li₂O₂, which leads to a large overpotential even at a moderate rate of charging. There are very limited studies on the charging mechanisms of Li–O₂ batteries, and so far it has not been clearly understood yet. Although certain theoretical studies have been conducted a decade ago, it is still lack of solid evidence to confirm the proposed mechanism. A promising strategy to overcome the poor contact between the positive electrode and Li₂O₂ is to use an oxidation mediator (RM_{charge}) to transfer electron between the electrode and Li₂O₂ [30].

In spite of the high specific energy of lithium metal anode, its poor safety issue when used in commercial battery will rise great concern and hence alternate negative electrode materials, i.e. silicon, tin, their compounds, have been explored to replace the metallic Li [32, 33]. However, the low operational potential of these negative electrode materials is unlikely to avoid the side reactions of electrolyte at anode unless a high-quality SEI layer is formed to inhibit the continuous side reactions. Therefore, electrolytes and additives that have the ability to form a high-quality SEI are preferred. For instance, polymeric IL electrolyte can produce stable electrode–electrolyte interfaces at both cathode and anode [34]. Dahn *et al* extended the lifespan of anode-free cells to 200 cycles by forming a high-quality SEI with a dual-salt carbonate electrolyte in LIBs [35].

Protection of lithium metal anode from electrolyte and impurities from ambient air, i.e. H₂O, CO₂, etc, has been carried out. Modified separator, such as solid-state electrolyte and quasi-solid-state electrolyte has been used to block H₂O and CO₂. Membranes with proper pore size, e.g. metal organic frameworks (MOFs)-based separator, selectively allows Li⁺ ion to transport through and effectively blocks other electrolyte components. By using this type of membrane two completely different types of electrolytes, e.g. water-in-salt electrolyte and aprotic electrolyte, have been employed to build Li–O₂ batteries [36].

3.4. Conclusions and remarks

Li–O₂ battery has a high theoretical specific energy, yet formidable challenges remain on its road to a practical technology. To address these challenges, a wide range of advanced *in situ* characterization techniques (e.g. *in situ* NMR, XPS, XAFS, XRD, TEM, Raman, DEMS, etc) have been developed, with the aim of a profound understanding of the reactions and processes underpinning the operation of Li–O₂ batteries. With the aids from material science and chemical/electrochemical engineering, stable electrolyte, efficient catalyst, and rational-designed electrode structure will hopefully be developed to bring Li–O₂ batteries close to reality.

4. Lithium–sulfur batteries

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4.1. Status

Built with the insertion-compound-based electrodes, conventional LIBs are approaching their theoretical energy-density limitations. To meet the ever-increasing demands for the energy-storage systems with high energy density and low cost, more and more researchers have shifted their forces to battery systems using high-capacity metal anodes (Such as Li, Na, and Zn) and chalcogen cathodes (Such as O₂, S, and Se), the Li–S battery is regarded as the most promising one. Based on the conversion reaction between Li and S ($\text{Li} + \text{S} \leftrightarrow \text{Li}_2\text{S}$), the Li–S system could deliver a high theoretical energy density of 2600 Wh kg⁻¹, which is five times that of LIBs. Besides, sulfur is abundant, cost-effective, and environmentally friendly. All these features make Li–S batteries attractive for the applications in both stationary energy storage and EVs.

Sulfur was firstly applied to batteries as a cathode material in dry cells by Herbet and Ulam in 1962 [37]. The years after the invention of Li–S batteries, the main research effects were devoted to finding suitable organic electrolyte to improve their electrochemical performances, with the introduction of ether into the electrolyte in 1989, a rechargeable Li–S cell with an average discharge voltage of 2.1 V and an energy density of ~80 Wh kg⁻¹ was obtained [38]. However, the research activity on Li–S batteries did not burst until the early 2000s, when lithium nitrate (LiNO₃) additive and the composition of sulfur with porous carbon were found to be effective in suppressing the ‘shuttle’ of lithium polysulfides and stabilizing the cycling performances [39, 40]. In the last decade, more than 3400 research papers have been published, and inspiring improvements are achieved in the lab.

Although Li–S batteries successfully powered a solar plane's flight for 3 d in 2008 and OXIS energy has already released 400 Wh kg⁻¹ Li–S batteries with the cycle life of 60–100 cycles, the practical applications of Li–S batteries are still restricted to limited fields. In this roadmap, we will first categorize the research area for the 3461 published papers relevant to Li–S batteries in the last 10 years, and then we will try to identify the gaps between academic research and industry requirements and discuss possible solutions to speed up the development of Li–S batteries with competitive performances.

4.2. Current and future challenges

Many challenges are slowing down the development of Li–S batteries. From the academic view: (a) to guarantee the fast conversion between electric/ionic insulating S and its discharge products (Li₂S), a large ratio of the conductive matrix such as porous carbons or conductive polymers are always needed to confine or disperse the active materials; (b) there

is a significant volume expansion (80%) during the lithiation of S to Li₂S, the expansion leads to structural collapse of S electrodes and makes the development of high-density S electrodes difficult; (c) the use of ether-based electrolyte, the most-utilized electrolyte system for Li–S batteries, in which the intermediate discharge products (Li₂S_n, 4 ≤ n ≤ 8, Li₂S_n) could dissolve in, could significantly promote the conversion between S and Li₂S. However, known as ‘shuttle effect’, the dissolution of the Li₂S_n(LPS) leads to chemical instead of the electrochemical reaction of active species with Li [41], resulting in irreversible consumption of both Li and S accompanied by the polarization increase and electrolyte decomposition.

To make the Li–S batteries commercially competitive, the industry is facing more challenges (figure 6): (a) there are several fatal barriers squeeze the practical gravimetric and volumetric energy densities, such as the high electrolyte to sulfur E/S ratio, the high anode-to-cathode capacity ratio (N/P), the low areal loading of the cathodes, and the use of high-content porous carbons in the cathodes. How to reduce the use of excessive carbon, electrolyte, and lithium anode without sacrificing the electrochemical performances is the biggest challenge to make Li–S batteries competitive in energy density. (b) Production challenges. The manufacture of high-loading sulfur cathodes with low porosity and the use of Li-metal anode requires new production technologies that could be easily scaled up to industry level at a reasonable cost. (c) Safety concerns. The use of flammable and volatile ether-based electrolytes, gas-produce LiNO₃, and the high-active lithium anode of Li–S batteries intrinsically raise safety problems, which need to be adequately addressed before the broad applications of Li–S batteries.

Unfortunately, although the Li–S papers published have reached to 800 in 2018 (figure 7), most of the studies were focused on novel material designs to improve the conductivity of the cathodes or suppress the ‘shuttle effect’, and excessive conductive additives, electrolyte, and lithium metal anode were always used to guarantee the ‘nice-looking’ electrochemical performances. In contrast, few studies were performed under a real application condition (high-active materials loading, lean electrolyte, and limited lithium supply), which makes the conversion from the academic results to commercially viable cells difficult.

4.3. Advances in science and technology to meet challenges

With extensive investigations in the last decade, significant progress has been achieved in the Li–S community. On the cathode side, the introduction of porous carbons into the sulfur electrodes is effective in improving the conductivity and suppressing the ‘shuttle effect’, but significantly reduce the density of the electrode. Besides, the non-polar carbon hosts mainly absorb LPS physically, which is insufficient when the sulfur content or areal sulfur loading in the electrode increases. In the recent 5 years, more and more efforts have been devoted to creating LPS chemical anchoring or catalytic sites by introducing heteroatoms or transition-metal compounds into the carbon hosts. Such an approach is capable to further suppress the ‘shuttle effect’ and promote the conversion reaction between

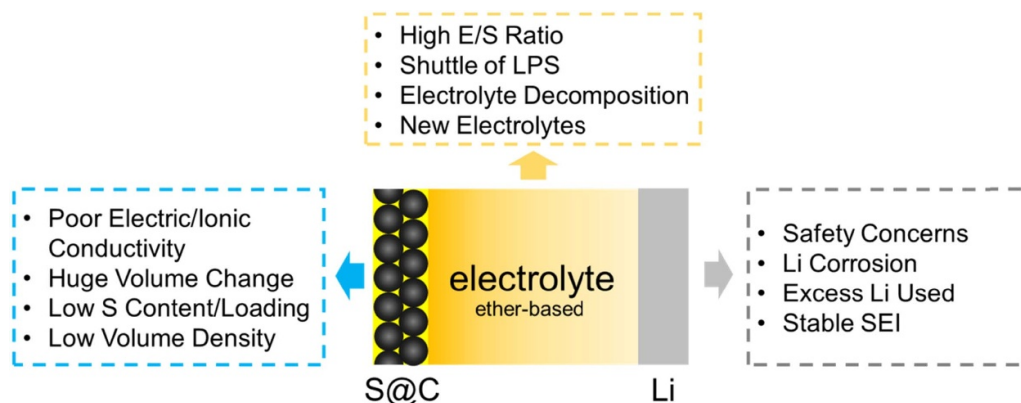


Figure 6. Schematics of challenges remained in Li-S batteries.

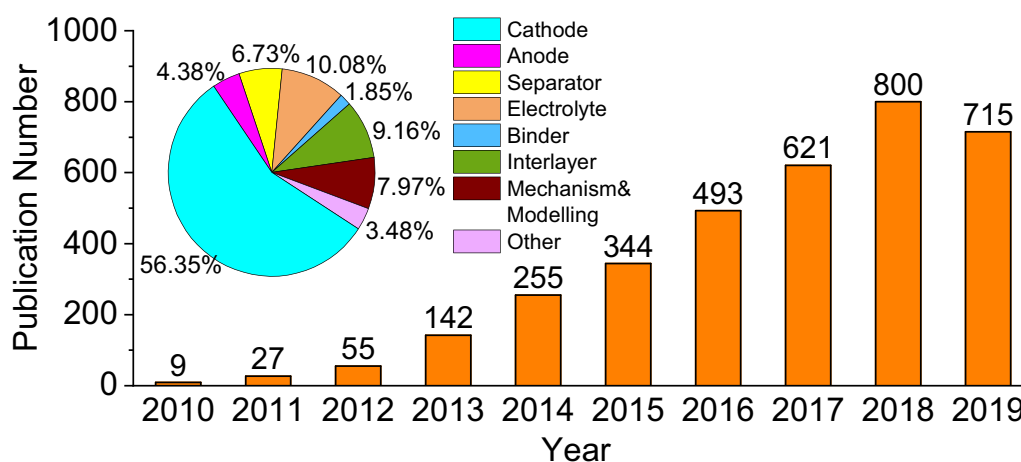


Figure 7. The numbers of the papers published each year relevant to Li-S batteries from 2010 to 2019 with the inset displaying the distribution of each research topic to all the 3461 papers. Here, the papers were selected from web of science refined by 'topic = Li-S batteries and document types = article' on 21 October 2019. To categorize the papers, the abstracts of all the papers were reviewed carefully and one paper may cover multiple topics.

S and Li_2S [42]. On the other side, the structure of carbon hosts and sulfur dispersion state directly impact sulfur utilization and electrochemical dynamics. The further optimization of the cathode microstructure with a hierarchical or aligned pore structure might be another way to reduce the porosity of sulfur electrodes. For the anode, the use of Li-metal anode not only brings safety concerns but also leads to the loss of the active materials due to the 'shuttle effect'. Therefore, protected Li anodes with effective solid electrolyte interfaces or protective coating are essential to achieve safer and more economical Li-S batteries, which are extensively investigated and make considerable progress. Building a lithium metal-free system might be another direction for the next-generation Li-S batteries.

The high electrolyte-to-sulfur ratio (E/S) and 'shuttle effect', which are mainly due to the unique solid-liquid-solid reaction mechanism in the ether-based electrolyte, significantly reduce the practical energy density and cycling life of Li-S batteries. To develop Li-S batteries with competitive performances, it is critical to developing new Li-S systems without the dissolution of LPS. By confining small sulfur molecules (S_{2-4}) into a conductive microporous

(0.5 nm) carbon matrix or covalently immobilizing sulfur onto polymeric chains (sulfurized polyacrylonitrile), Xin *et al* and Wang *et al* have successfully developed high-performance sulfur electrodes compatible to carbonate-based electrolytes [43, 44]. New sparingly solvating electrolytes based super-concentrated solutions and solid electrolytes based on sulfide glasses ($\text{Li}_2\text{S}-\text{SiS}_2$ and $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$) [45, 46], in which sulfur undergoes a solid conversion pathway without LPS solvating, are also promising to reduce E/S, eliminate the 'shuttle effect', and thus enhance the practical energy density of Li-S batteries.

Besides the research from the material level, new technologies on cell design, cell production, and so on are also highly desired to develop Li-S batteries for real-world applications.

4.4. Concluding remarks

In conclusion, although Li-S batteries with high capacity and long cycle life have been widely reported, there is still a long way to go to realize the broad applications of Li-S batteries. To

bridge the gap between the academic research and commercial needs, continuous research on advanced sulfur cathode materials with high-density and high sulfur loading, high-efficient electrolytes, safe and stable Li anodes, functional separators and high-efficient binders are necessary. In addition, in-depth studies are needed to excavate and further understand the conversion mechanisms of Li-S batteries in different electrolytes under low E/S conditions. Above all, further works are supposed to focus on meeting the necessary practical parameters, creating safe, low-cost, facile, and high-performance Li-sulfur

pouch cells, ultimately promoting the commercialization of Li-S batteries.

Acknowledgments

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5. Solid state lithium battery

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5.1. Status

The liquid organic electrolytes in commercial rechargeable LIBs have high Li^+ conductivities and small electrolyte/electrode interfacial resistances. However, these flammable and volatile liquid electrolytes have limited electrochemical window and cannot suppress the lithium-dendrite growth at a high current density during charge.

Recently, the rapid developed electrical vehicles are anxious for safe batteries with high energy density. By replacing the flammable liquid electrolytes with solid-state Li^+ conductors, all-solid-state lithium batteries are considered as one of the most promising candidates for next-generation energy storage. Solid electrolytes enabled lithium metal battery has both high energy density and good safety, thus arousing much interest in this field. However, to replace the liquid electrolyte, solid electrolytes have a long way to go. Though the conductivities of solid electrolytes have been increased during the past decade, even some of them are comparable with liquid electrolytes, the room-temperature conductivities of most electrolytes are relatively low, making most of all-solid-state batteries must be run at elevated temperature. Some solid electrolytes are not stable in the moist air. Besides, the interfaces between solid electrolytes and electrodes have become the big problems. Many efforts have been made to improve the interfacial contact and the electrochemical stability between the solid electrolytes and the electrodes. The dynamic interfaces between the solid electrolyte and lithium metal anode, which is related to the failure of solid lithium metal batteries, are being carefully studied. In addition, the manufacturing cost of solid electrolytes is still high at present.

Once the above problems of the solid electrolytes, the interfaces and the electrodes are conquered and the all-solid-state batteries are made with low-cost, batteries with energy density about 500 Wh kg^{-1} will be possible and the world will be changed. The vehicles will be driven by solid-state power, getting rid of mileage anxiety and safety issues. The society will be less relied on the fossil energy and the environment will become more suitable.

5.2. Current and future challenges

Solid electrolytes in all-solid-state lithium batteries mainly include oxide, sulfide and polymer electrolytes. The oxide electrolytes (e.g. Ta/Ga/Nb-doped garnet $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$

(LLZO)) have a room-temperature Li^+ conductivity of $10^{-3} \text{ S cm}^{-1}$ and high mechanical strength. However, the poor wettability between Li metal and the oxides leads to large interfacial resistance in all-solid-state lithium batteries. The brittleness nature of oxide electrolytes makes them unreliable. The electrochemical window and chemical stability of oxide electrolytes are also the main challenges. Some electrolytes (e.g. Li_3OCl , LLZO) are unstable in water or in moist air. Some electrolytes, e.g. $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ (LATP) and LLTO, containing variable-valence elements (e.g. Ti^{4+}) could be easily reduced by lithium metal at low voltages [47]. The sulfide electrolytes exhibit high ionic conductivities ($10^{-2} \text{ S cm}^{-1}$) at room temperature but with poor electrochemical stability and interface stability in batteries; the instability of sulfides in air also limits their large-scale application. The polymer electrolytes are flexible and facile to process, but the low room-temperature conductivity, narrow electrochemical window, and poor thermal stability restrict their application in batteries [48]. Figure 8 shows ionic conductivities with temperature ($\log \sigma \sim 1/T$) of many kind of solid electrolyte [49, 50].

Metallic lithium anode has the highest theoretical capacity (3860 mAh g^{-1}) and the lowest potential ($-3.04 \text{ V vs H}^+/\text{H}$), thus batteries with lithium anode have the highest energy density. The main challenges between the lithium anode and solid electrolytes are: (a) short circuit caused by lithium dendrite; (b) the wettability between lithium metal and solid electrolyte; and (c) the lithium surface morphology and volume change during charge and discharge. The rough surface morphology and large volume change of Li anode during cycling would form gaps in the interface of Li/electrolyte and further deteriorate the interfacial contact increasing the interfacial resistance [51].

Currently, the widely used cathode materials (e.g. LiFePO_4) with low energy density could not satisfy the requirements of EVs. The high-voltage cathode materials, e.g. $\text{Li}[\text{Ni}_x\text{Co}_y\text{Al}_{1-x-y}]\text{O}_2$ (NCA) and $\text{Li}[\text{Ni}_x\text{Co}_y\text{Mn}_{1-x-y}]\text{O}_2$ (NCM), have advantages in energy density but need to address the problems of cycle life, rate performance, voltage attenuation and interface compatibility with solid electrolytes [52].

5.3. Advances in science and technology to meet challenges

Some effective strategies have been made to address the above challenges, as shown in figure 9.

For oxide solid electrolytes, the ionic conductivity and phase stability can be effectively improved through element substitution, suitable sintering methods, and techniques processes. Moreover, surface modification, nanostructure design and incorporated polymer buffer layer can significantly lower the interfacial resistance and improve the stability between solid oxide electrolytes and lithium metal anode. This surface layer could be a Li-ion conducting polymer or an *in situ*-formed Li-alloy layer [53]. For example, the interface between Li metal and solid oxide electrolyte can be wetted by introducing a thin metal (e.g. Au) or oxide (e.g. Al_2O_3) layer on the surface of the solid oxide electrolyte. However, this alloy layer may disappear after a long-time cycling, and with a large

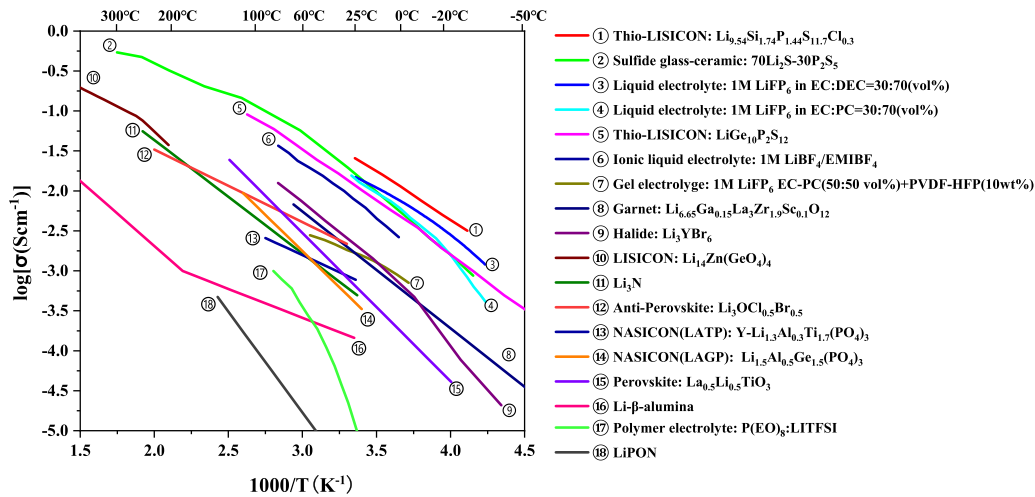


Figure 8. Ionic conductivities with temperature ($\log \sigma \sim 1/T$) of many kind of solid electrolytes.

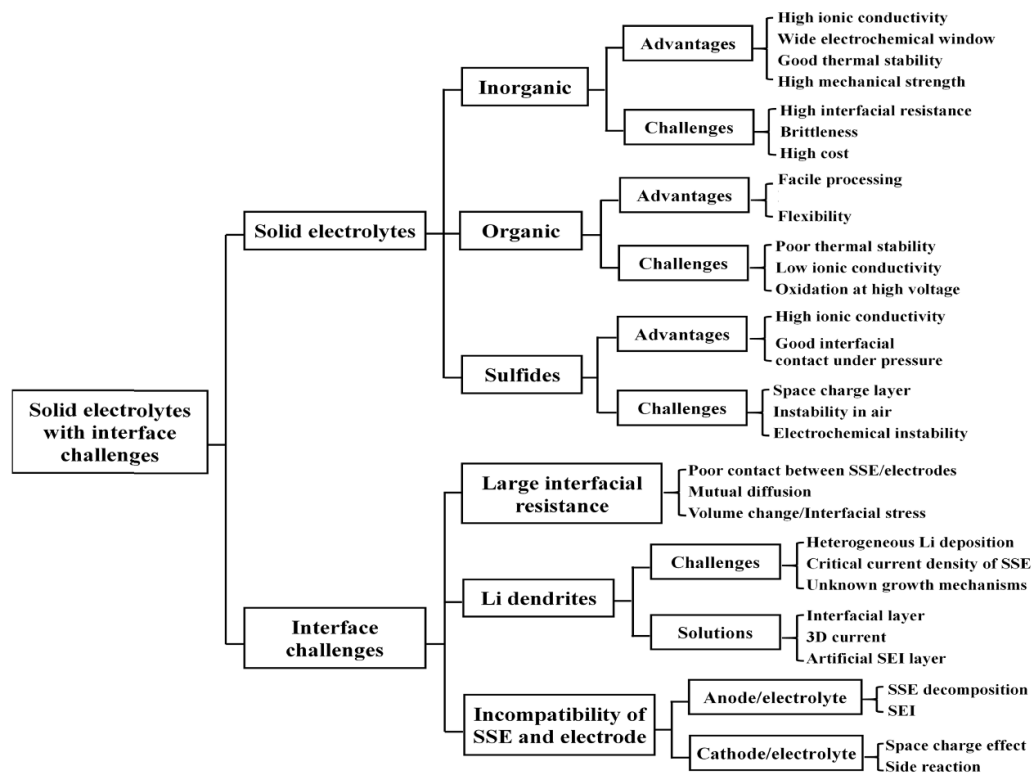


Figure 9. Solid–electrolyte and electrode/electrolyte interface challenges in all-solid-state battery.

amount of lithium plating, the lithium dendrites may form and grow again after the alloy (e.g. Si, Al) is fully lithiated.

For sulfide-based solid electrolytes, pursuits to reach higher range of conductivities of the glass sulfide-based solid electrolytes (e.g. $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$) have included the doping of a small amount of oxide or halide salts as well as the adoption of pressurization to improve contact and reduce the presence of voids. The sulfide-based solid electrolytes (e.g. $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, $\text{Li}_{10}\text{SiP}_2\text{S}_{12}$) can be reduced by lithium, both isovalent and aliovalent-doping, surface coating and adding phosphate as well as lithiation/delithiation could improve the electrochemical window [54]. To date, the

advanced development in application of the sulfide prototypes are demonstrated by Toyota in the Concept-i-ride with $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$ and $\text{Li}_{11}\text{Si}_2\text{PS}_{12}$ as electrolytes.

For polymer electrolytes with poor room-temperature conductivity, by adding inorganic fillers (either ionic conducting or non-ionic conducting) to a polymer matrix, the Li-ion conductivity, mechanical properties and thermal stability of the composite electrolyte can be enhanced, which allows them to serve as a thin and robust SEI membrane with a small interfacial resistance [55]. Another strategy is to design a 3D nanostructured hydrogel-derived solid–electrolyte framework, which was used as a 3D nanofiller for composite polymer

lithium-ion electrolyte [56]. However, facing the great challenge to suppress dendrite growth in the solid lithium batteries, elaborately designing the structure, modifying the solid electrolyte and its interface can minimize dendrite growth in solid lithium batteries.

In general, the performance of LIBs strongly depends on the cathode materials. Usually, cations doping and particles coating are the main methods to improve the intrinsic properties of the cathode materials, e.g. 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].

5.4. Concluding remarks

The goal of all-solid-state batteries with high safety and high energy density (500 Wh kg^{-1}) could be achieved from the following aspects: (a) currently, perfect solid electrolyte has not been synthesized to completely replace liquid electrolyte, so it is necessary to develop new material systems, such as

amorphous solid electrolyte without grain boundaries. For several widely studied electrolytes, surface engineering, organic-inorganic composites and mechanism exploration may be the main research directions for solid-state electrolytes. (b) The Li-metal anode is considered as the 'Holy Grail' in lithium batteries. However, in a short period, the artificial SEI film on Li anode, anode pre-lithiation and Li-C, Li-Si anodes are expected to be first realized on a large scale. (c) High-Ni-content ternary cathode and Li-rich oxides cathode are the mainstream choices in the future. The specific discharge capacity, cycling and rate performance need to be improved further based on the guarantee of safety.

Acknowledgments

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6. Sodium-ion batteries

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6.1. Status

Rapid growth in the demand of the energy-storage technologies, from portable electronic devices to electrical vehicles and smart grids, makes the development of the alternative battery technologies beyond the LIBs. Due to the natural abundance and low-cost of sodium resources, sodium-ion batteries (SIBs) are becoming one of the most promising alternative battery systems to LIBs. The early studies of SIBs can be traced back to the 1970s and 1980s [12, 57], almost the same age with the LIBs. Around 1990s, the largely suppressed development on SIBs could be ascribed to the pursuit of the high energy density for catering the portable electronic devices and electrical vehicles markets, therefore, LIBs become the mainstream of research due to their competitive volumetric and gravimetric energy densities. Over the past decade, along with the successful commercialization of LIBs, materials, techniques, and methodologies have been largely developed, which benefits the renaissance of SIBs owing to the similar physical and chemical properties between Li- and Na-containing compounds. Meanwhile, it has shifted from simply pursuing energy density to studying different battery systems for different applications. Although SIBs do not show the dominant energy density and almost cannot occupy the portable electronics and EVs markets, they still provide a scalable solution for large-scale energy storage with high adaptability and high energy efficiency. As a promising choice for large-scale electrical energy storage and conversion due to the low-cost, abundant supply and considering the scarcity of Li resources, SIBs hold a great chance in case their electrochemical performance is enormously improved. Even though the larger size of the sodium (Na) ion as a charge carrier is believed to be an unavoidable disadvantage compared with the smaller lithium (Li) ion, tremendous research efforts over the past few years led to considerable progress in SIB electrode materials. Furthermore, the knowledge and experience gained from LIBs is directly applicable to SIBs, which greatly accelerates the progress of SIB research. It has shown that the SIB electrodes could deliver a specific capacity comparable to or even higher than their corresponding LIB counterparts and they also demonstrated impressive ultra-long cycle performance [58]. These achievements provide hope for developing satisfactory SIBs for use in grid-scale energy-storage applications.

6.2. Current and future challenges

Of course, there are challenges for the development of SIBs, especially in electrodes, due to the higher ionization potential and larger ionic diameter of Na (1.02 Å) vs Li (0.76 Å). There

remains a lack of appropriate cathode materials with sufficiently large interstitial space within their crystallographic structure to host Na ions and present a satisfactory electrochemical performance. The biggest challenge faced by anode materials of SIBs is that the Na ions are subject to high diffusion barriers due to the large size of the Na ion. With regards to the structural preference, it is evident that the ability of the crystal structure to accommodate the significantly larger Na ion is an important factor [59]. The larger ionic radius presents a steric limitation in numerous host structures, leading to a low diffusion rate and higher volume expansion upon cycling [60]. It has been found that the large Na ion and its higher ionization potential require a more open framework and high surface energy anode materials in order to move reversibly with an acceptable mobility [61]. So far much progress has been made on framework cathode materials. For example, a specific capacity of 147 mA h g⁻¹ with olivine NaFePO₄ has been obtained [62], but its reversibility is poor (only 50.6 mA h g⁻¹ in the second cycle). Fluoride-based cathode materials, e.g. NaMF₃ (M=Fe, Mn, V and Ni), have been prepared with specific capacities ranging from 30 to 170 mA h g⁻¹ [63]. Moreover, layered transition-metal oxides, such as P2-Na_xCoO₂ and Na_{2/3}[Fe_{1/2}Mn_{1/2}]O₂, also presented the limited capacities. For anode materials, it is hard to find a suitable material for insertion of Na ions at low potential. The common anodes for LIBs, such as soft carbons, based on the intercalation mechanism (figure 10(a)), are not suitable for SIBs. Instead, recent studies have highlighted the potential of novel forms of hard carbons, even though hard carbons cannot contribute high capacity (less than 300 mA h g⁻¹). Alternative oxide anodes based on the conversion reaction with Na ions (figure 10(b)), such as Na₂Ti₃O₇ [64] have been investigated, but so far attain less than 300 mA h g⁻¹ capacity. Metal alloys, which work by alloying/de-alloying with Na ions, can dramatically improve sodium storage capacity [65], but the huge volume expansion and constriction of the anode materials result in bad cycling performance (figure 10(c)). Therefore, finding and optimizing suitable materials are crucial for the development of SIBs.

6.3. Advances in science and technology to meet challenges

Investigations on electrode materials with controlled crystal habits have found that, for the intercalation-based cathode materials, the surface structure for alkali cations transportation is critical to the diffusion rate, because the electrode materials are generally bounded by closest-packed facets, which intrinsically present difficulties in furnishing suitable channels for fast transportation of alkali cations. As demonstrated by figure 10(a), if electrode crystals can be terminated by facets that expose a tunnel structure, then intercalation of Na ions will be facilitated. Furthermore, it has been proved through both theoretical and experimental investigations that different crystalline facets present significant lithiation or sodiation anisotropy for the case of electrode materials based on the alloying/de-alloying [61]. This indicates that the various crystal planes have quite different electrochemical properties. For

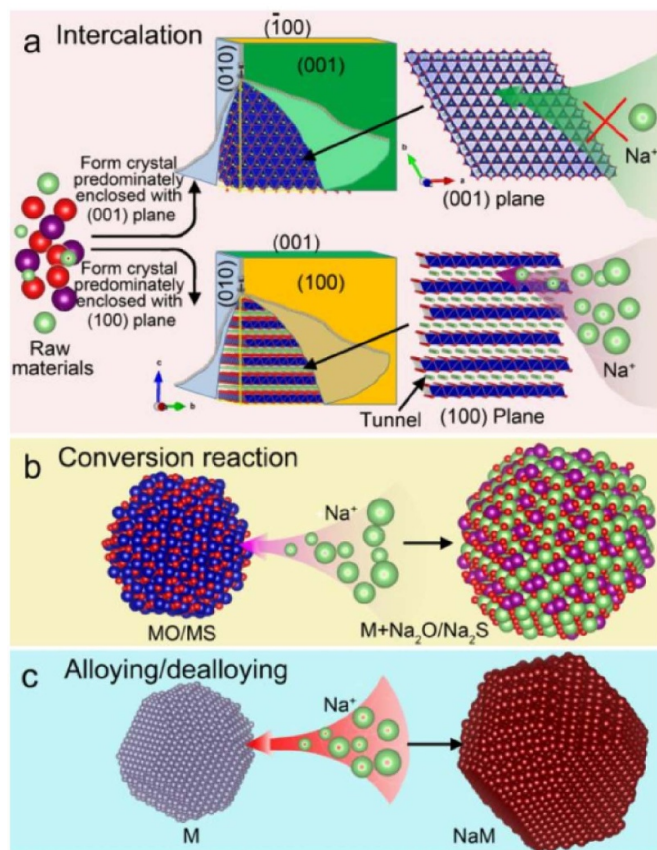


Figure 10. Schematic illustration of the reaction mechanisms ((a) intercalation, (b) conversion reaction, (c) alloying/de-alloying) of electrode materials with Na ions in sodium-ion batteries.

instance, the graphite, the most common anode for commercial LIBs, has been reported to have a very low capacity as an anode for SIBs. But after expanding the interlayer lattice distance of 4.3 Å within the graphite through a process of oxidation and partial reduction on graphite, it can deliver a high reversible capacity of 284 mA h g⁻¹ at a current density of 20 mA g⁻¹, maintain a capacity of 184 mA h g⁻¹ at 100 mA g⁻¹, and retain 73.92% of its capacity after 2000 cycles [66].

The nature of the exposed crystal planes of the electrode materials are crucial for their electrochemical performances irrespective of whether the electrode is based on intercalation, conversion reaction or alloying/de-alloying processes (figure 10). Therefore, the nanostructured electrode materials with controlled crystal facets will bring significant advantages relative to bulk materials of random crystalline texture. Furthermore, for practical application in electricity storage system of the SIBs, electrode materials design for improving the power density is more crucial than the energy density. Because the grid-scale energy-storage from renewable energy sources (wind, solar, tide, etc) requires the general function for smoothing out the fluctuations and tolerate frequency regulation by delivering active power for grid frequency dropping or above certain thresholds. Power capability of SIBs for

their practical applications in electricity storage system highly depends on the speed at which Na ions and electrons migrate through the electrolyte and electrode, namely again, the diffusion rate barrier issues. Therefore, by developing nanostructured electrode materials in which Na ions have improved mobility is also the critical factors to tackle the challenge for practical power density improvement of SIBs. For instance, the typical layered cathodes materials, NaCrO₂ demonstrated the high capacity in spite of the same polymorph and transition metal with its Li-ion counterpart LiCrO₂, which is electroinactive. The contradictory activity was ascribed to the difference of the bond length in unit cell of LiCrO₂ and NaCrO₂ [67]. In both LiCrO₂ and NaCrO₂, chromium is trivalent with $t_{2g}^3 e_g^0$ configuration in (CrO₆) octahedral coordination. During the initial charge process, partial Cr(III) will be oxidized because of the loss of electron and forming of the less stable Cr(IV) with $t_{2g}^2 e_g^0$ configuration. After the initial charge process, the less stable Cr(IV) has a tendency to be disproportionated into 2/3 Cr(III) and 1/3 Cr(VI) having the stable configuration of d3 and d0, respectively. However, the Cr(VI) d0 is stable at tetrahedral four-oxygen coordination because of its smaller ionic size, resulting the migration of chromium from the original octahedral site to the interstitial tetrahedral site in the inter slab space with the 2.69 Å O–O bond length and 2.47 Å tetrahedron height [68]. The interstitial tetrahedron in LiCrO₂ (2.89 Å in O–O bond length and 2.56 Å in CrO₂ slab distance) matches better with the tetrahedron Cr(VI)O₄, while the much larger O–O bond length (2.97 Å) and tetrahedron height (3.15 Å) of interstitial tetrahedron in NaCrO₂ could not be possible for Cr(VI) in octahedral site to migrate into the interstitial tetrahedral site. Therefore, sodium intercalation of NaCrO₂ materials demonstrated the attractive electrochemical properties as cathode for SIBs. Furthermore, some polyanion framework cathode materials attract much wide attention because they are applied as positive electrode materials of practical SIBs, such as the Na₃V₂(PO₄)₃ [69]. For Na₃V₂(PO₄)₃, consisted by the (V₂(PO₄)₃) ribbons in an open 3D framework structure, each VO₆ octahedron corner-shares with three PO₄ tetrahedrons, and the Na⁺ ions occupying in the octahedral sites (between two adjacent (V₂(PO₄)₃) units in the same (V₂(PO₄)₃) ribbon) and tetrahedral sites (between adjacent (V₂(PO₄)₃) ribbons) of the interstitial sites with different occupancy [70]. A high capacity (118 mA h g⁻¹ at 0.5 °C attaining the theoretical value), a superior rate capability (73 mA h g⁻¹ at 100 °C and even up to 41 mA h g⁻¹ at 200 °C), ultralong cyclability (70.0% capacity retention after 15 000 cycles at 50 °C) at both low and high operating temperatures can be achieved by the Na₃V₂(PO₄)₃ cathode materials. For the anode side, antimony-based materials are promising candidates due to their high theoretical capacity of 660 mA h g⁻¹ [71]. Furthermore, with newly developed strategies (e.g. Sb-carbon composite and Sb₂X₃ (X=O, and S)), the common problem of volume expansion by forming the Na₃Sb has been tackled a lot, all leading to renewed interest in antimony-based SIBs materials. The carbon-based anode materials and their composites with alloy metals were also reported as the promising candidates for SIBs [72].

6.4. Concluding remarks

Benefiting from the abundance of sodium in the interior of the earth, the SIBs are competitive in the future grid-scale energy-storage market, which shows the unique market superiority than LIBs counterpart. Meanwhile, the advantage of the similarity between the lithium and sodium chemistries makes the rapid progress of materials and technologies of SIBs. The development of superior electrode materials is the best way to achieve a breakthrough in SIBs. Of course, controlling the surface crystal structure is an efficient way to alter the kinetics of diffusion of the sodium in and out of the electrodes. Investigation of electrochemical sodiation/desodiation anisotropy on electrode crystalline facets will generate insights that can help to overcome the fundamental challenge of low diffusion rates

across electrode surfaces, demonstrating the feasibility of grid-scale SIBs deployment. However, we should also bear in mind that there is still a long way for practical large-scale application of SIBs.

Acknowledgments

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7. Zinc–air batteries

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7.1. Status

Zinc–air battery with high energy density, low-cost, and long-lasting rechargeable ability has attracted great attention and received increasing research efforts in recent years. A typical zinc–air battery is composed of a zinc anode, an oxygen-permeable cathode, a separator, and the caustic alkaline electrolyte (figure 11) [73]. Zinc, owing to its low-cost, stability, high theoretical specific energy (1218 Wh kg^{-1}) and promising volumetric energy density (6136 Wh l^{-1}), has been considered as the most promising anode material among various metal–air batteries [74]. Furthermore, from a safety perspective, the aqueous electrolyte used in zinc–air battery is relatively safe and can reduce the fire hazard. Primary zinc–air battery has been commercialized in the 1930s, while the rechargeable zinc–air battery has been studied since the 1970s and the development of practically viable rechargeable zinc–air battery remains a challenge [75]. Recently, the lowest price point of zinc–air battery for energy systems has been projected to be $160\text{--}200 \text{ US\$ kW h}^{-1}$, and is forecast to further reduce to $70 \text{ US\$ kW h}^{-1}$, which is much lower than the acceptable cost ($150 \text{ US\$ kW h}^{-1}$) for EVs to be economically competitive [76]. Thus, zinc–air battery is supposed to be a promising energy-storage system for EVs, electrical grid regulation, and portable electronic devices. Nevertheless, in comparison with its theoretically high performances and economic potential, the development of practically viable rechargeable zinc–air battery is still a challenge, which is related to the zinc irreversibility, electrocatalytic activation for oxygen reduction and evolution reactions, and integrated technology. The current zinc anode suffers from severe shortcomings (i.e. the formation of zinc dendrite and zinc oxide passivation), while oxygen-permeable cathode need to be further improved in electrocatalytic performances, corrosion resistance and cost concerns. Therefore, the development of zinc–air battery is quite meaningful and full of opportunities and challenges.

7.2. Current and future challenges

Although significant progress in developing rechargeable zinc–air battery have made in recent years, it still suffers from numerous challenges for commercialization and large-scale application. On one hand, zinc anode faces a severe problem (i.e. irreversibility of zinc), which is attributed to the formation of zinc dendrite, undesired relocation and zinc oxide passivation. Although zinc anode with special structure and morphologies have been designed to settle down zinc irreversibility problems, it is still difficult to realize high

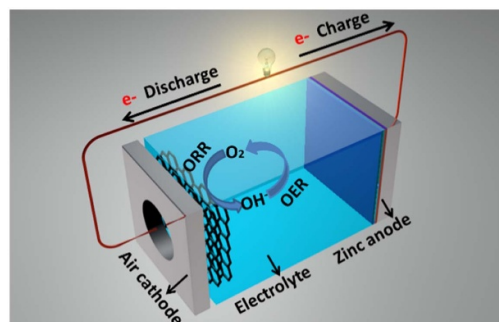


Figure 11. A schematic illustration of a zinc–air battery.

energy density, excellent cycling stability, and high zinc utilization simultaneously [73]. On the other hand, since oxygen reduction reactions (ORRs) and oxygen evolution reactions (OERs) are fundamental reactions for the rechargeable zinc–air battery, high-performance bifunctional oxygen catalysts can significantly minimize the overpotentials of these reactions. However, as typical catalysts, noble metals and their oxides are highly active but suffer from some drawbacks, such as high cost, scarcity and limited stability. In the past decade, numerous efforts have been made to design low-cost and advanced non-noble metal catalysts. Notable progress has been made in engineering active non-noble metal catalysts, but there is still much space for electrochemical improvement, and other problems (e.g. increasing cost concerns and complex synthetic strategies) also come along and remain unsettled. Meanwhile, although carbon-based catalysts are widely investigated, they are readily corroded (oxidized) in alkaline electrolytes during repetitive charging and discharging [77]. Furthermore, the mechanisms behind bifunctional active sites are not clear and should be given more attention in order to guide the rational design of high-performance catalysts.

Apart from the above challenges, zinc–air battery also suffers from other problems associated with electrolyte, separator, integration of air electrodes, and battery-performance evaluation. For instance, there is no standard parameter in evaluating the performances of zinc–air battery, and the testing conditions are not specific. For electrolyte, many non-aqueous electrolytes have been developed recently, but the performances of the battery are still unsatisfied owing to the relatively low ionic conductivity. Furthermore, integrated air electrodes and flexible zinc–air battery have attracted increasing attention owing to the rapid development of smart wearable devices and wireless communication. However, the ‘solidification’ of the electrolytes is a thorny problem, and the mechanically performances of electrodes and support materials, energy density and cycling stability of the battery are unsatisfied for commercial application.

7.3. Advances in science and technology to meet challenges

To overcome the above challenges, some promising specific approaches have been proposed and under investigation (figure 12).

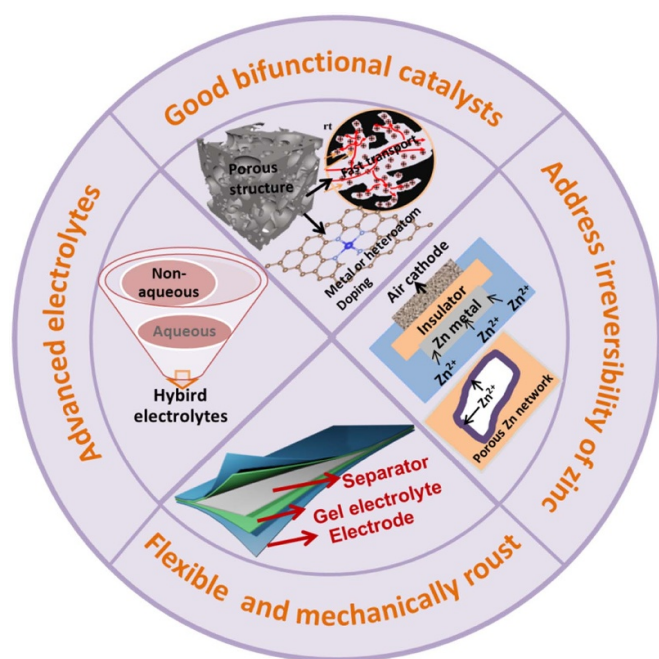


Figure 12. The promising specific approaches proposed for developing high-performance zinc–air battery, including fabricating outstanding bifunctional catalysts, addressing irreversibility of zinc, enhancing the flexibility and mechanical performances, and developing advanced electrolyte.

Since bifunctional catalysts are critical for zinc–air battery, many practical and effective methods have been proposed to improve their electrochemical performances. For instance, by combining computational simulation and high-throughput screening, catalysts with relatively high intrinsic catalytic activities have been developed [77]. Researches also demonstrate many methods about controllable structure design of catalysts to expose more active site and improve mass transfer [74]. Moreover, by replacing the carbon-based gas diffusion or catalyst substrates with materials having high corrosion resistance, the cycling stability can be significantly improved [73]. To enhance the zinc anode performances, many effective strategies have been proposed, such as constructing porous

structures with high surface area, adoption of 3D conductive host materials, and physical inhibition/suppression [78, 79]. Furthermore, hybrid electrolytes combining the advantages of aqueous and non-aqueous have been investigated, which can not only manage operating environmental parameters, but also improve the cycling durability of the battery [80]. For flexible zinc–air battery, *in situ* characterizations have been used to correlate its microscopic structure with the electrochemical and mechanical performances. In addition, multi-scale modeling and simulation are employed to better understand the mechanisms and theories of catalysis process.

7.4. Concluding remarks

The high theoretical energy density, inherent safety, and cost merits of rechargeable zinc–air battery make it a promising candidate for emerging mobile and electronic application. Although numerous researches have been proposed and remarkable progress has been made in recent years, there are still unsettled challenges before its commercialization, such as the low energy efficiency and relatively short cycle life. To further improve the performances of rechargeable zinc–air battery and realize its wide spread application, more efforts are necessary and should be focused on the following aspects: (a) developing new zinc electrodes to restrain dendrite formation and surface passivation; (b) synthesizing electrocatalysts with enhanced electrochemical performances; (c) further investigating and understanding the mechanisms and theories of the catalysis process; and (d) optimizing electrolyte compositions and simplifying preparation process. In conclusion, the technology of fabricating rechargeable zinc–air battery is not mature, and more efforts should be made to promote its electrochemical performances and realize its widespread application.

Acknowledgments

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8. Aluminum-ion batteries

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8.1. Status

EES technology is important for the reliability of the electric grid systems. Currently, despite the successful commercialization of LIBs, the limited lithium resources and safety problems are hard to meet the increasing energy-storage requirements in the further [81]. Thus, alternative metal ion rechargeable batteries, including SIBs, magnesium-ion batteries and aluminum-ion batteries (AIBs), are attracting much recent research interest. Among these new type of batteries, AIBs have been considered as promising candidates for large-scale application due to rich abundance (8.2 wt% in earth crust) and lower price of Al metal (figure 13(a)) [82]. The Al metal anode can exchange three electrons during the electrochemical process and thus delivers superior theoretical specific volumetric capacity and gravimetric capacity (8040 mAh cm⁻³ and 2980 mAh g⁻¹, respectively) [83]. In addition, the ease of operation for Al metal in the ambient environment significantly enhances the safety of AIBs systems. Therefore, AIBs are able to become a competitive and attractive choice for large-scale energy-storage systems after extensive research (figure 13(b)).

Figure 14 displays the development of AIBs. Aluminum served as a battery electrode can date back to the 1850s, when Hulot described a primary cell with Zn/H₂SO₄/Al configuration. In despite of the Leclanche-type dry cells Al/MnO₂ batteries have been realized in 1951, these AIBs with aqueous electrolyte are still not rechargeable. When an Al/Cl₂ battery with high-temperature NaCl–KCl–AlCl₃ molten salt electrolyte was disclosed, serious efforts were made on the utilization of molten salt electrolyte in plating/stripping of Al metal [84]. However, owing to the severe working condition of the molten salt electrolyte, researchers were urgent to search other suitable electrolyte for rechargeable AIBs (RAIBs). In 1985, the room-temperature IL was first employed as electrolyte in RAIBs, which successfully achieved the stripping/plating of Al together with the removal of passive Al₂O₃ film [85]. Later, Archer *et al* demonstrated a Al/V₂O₅ system in AlCl₃/1-ethyl-3-methylimidazolium chloride (EMIC) IL electrolyte for RAIBs in 2011 [86]. By introducing this IL electrolyte, graphite materials were conducted to show its outstanding stability for RAIBs in 2015 [82]. Since then, the RAIBs have stimulated plentiful studies especially in seeking low-cost electrolyte (AlCl₃/urea, AlCl₃/acetamide and Al trifluoromethanesulfonat (Al(OTF)₃)) as well as new RAIB systems (Al/S and Al/Se) [87–91].

8.2. Current and future challenges

The configuration of RAIBs mainly involves cathode, anode and electrolyte, all of which must be considered and optimized in practical application. Although various strategies have been employed to improve the electrochemical performance of RAIBs, it still suffers from the poor electrochemical performance (figure 14).

- As for cathode, a series of materials have been explored recently, such as graphite materials, transition-metal sulfide, transition-metal oxide and Prussian blue analogues. Despite the graphite materials with AlCl₄⁻ intercalation process delivered a super stability, it was still hindered by the low specific capacity. While the high-capacity transition-metal sulfide and oxide materials have poor kinetics and inferior cycling stability. Additionally, the electrochemical reaction mechanism in IL-based RAIBs still need to be further investigated especially in the intercalation ion species (AlCl₄⁻ or Al³⁺), due to the overlapped signals of chlorine element from the electrolyte.
- In the aspect of electrolyte, the costly and air sensitive IL electrolytes could restrict the application of economic friendly RAIBs. Moreover, the extremely strong corrosivity of chloroaluminate species greatly restricts the choices for current collector, polymer binder and also battery assembling cans. For example, stainless steels are extremely instable in IL electrolyte, hindering the utilization of widely used coin cells [81].
- Finally, the electrochemical property of Al anode must be considered, particularly the dendrite growth and passivating Al₂O₃ film of Al anode, both of which would impede the reversible stripping/plating of Al metal. However, the modification of Al anode is still lacking in RAIBs so far. Strategies for designing superior performance and stable Al anode for RAIBs demand a deeper understanding of the Al dissolution/deposition process.

All of these drawbacks lead to poor electrochemical performance and could jeopardize the commercial application of high-energy-density RAIBs. Thus, searching for the suitable cathode materials with high energy density and good stability, an electrolyte with low corrosion and low-cost, as well as an Al anode with appropriate morphology and proper thickness of passivating Al₂O₃ film will be a crucial challenge.

8.3. Advances in science and technology to meet challenges

Here, we give some short examples of recent advances in the RAIBs that may help to address the challenges (figure 14).

- For graphite materials, it has been reported that the capacity increase from 70 to 105 mAh g⁻¹ when decreasing the intercalation staging state from stage-4 to stage-3 [83]. Thus, the strategies to decrease the AlCl₄⁻ intercalation staging state are significantly crucial for

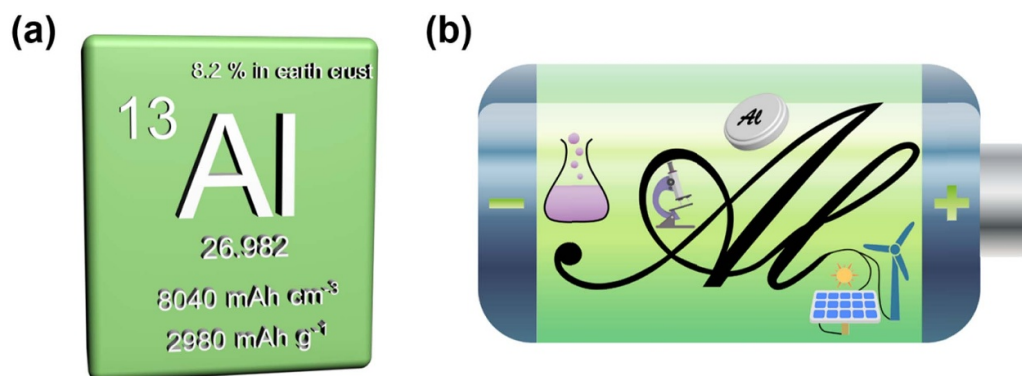


Figure 13. (a) Important indicators of Al metal electrode. (b) Schematic illustration of the RAIBs research.

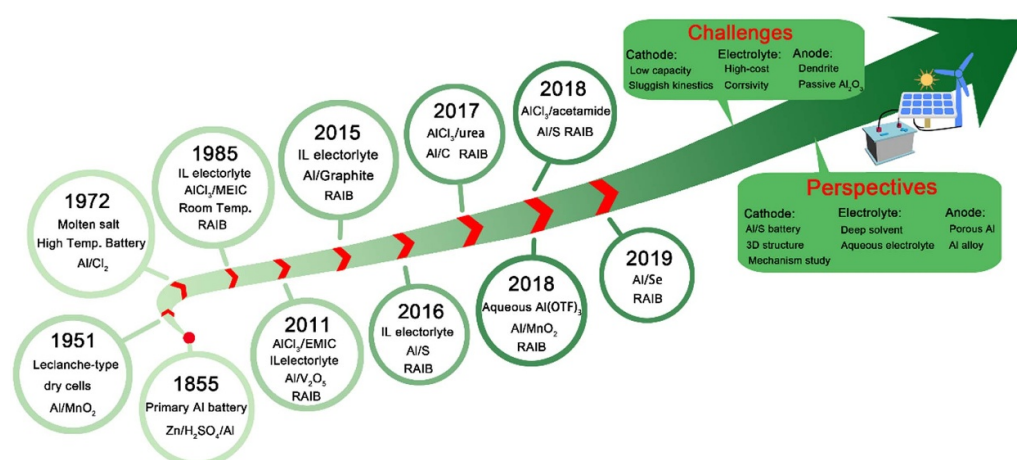


Figure 14. The development, challenges and perspectives of AIBs.

increasing the capacity of graphite materials. Sulfur as a cathode for RAIBs displays a remarkable capacity, which also provides an effective solution to enhance RAIBs systems [81]. Moreover, metal sulfide/oxide with three-dimensional structure or composited with carbon materials are preferable, which can improve the ion diffusion kinetics. New materials, such as Mxenes, polyanion-type materials or organic materials, are also considerable for advanced RAIBs. New characterization methods, such as *in situ* techniques, are requisite for further investigating the reaction mechanism of cathode materials.

- (b) The ionic structure of the haloid aluminate can be modified by tuning the functional group and anion species of IL electrolyte precursors, which can accelerate electrochemical kinetics. For example, the utilization of 1-ethyl-3-methyl-imidazolium bromide (EMIBr) precursor can enhance the charge/discharge kinetics [92]. Furthermore, deep eutectic solvent electrolytes, including AlCl₃/urea and AlCl₃/acetamide, have been successfully employed in RAIBs [87, 88]. The low-cost and good stability features suggest their potential application as suitable electrolytes in RAIBs to alternate the IL electrolyte. However, the strong corrosivity of chloroaluminate species in these IL

and deep eutectic electrolytes still restricts the practical application of RAIBs. Several strategies can be applied to avoid the corrosion in RAIBs, such as using a noble cap to prevent the contact between electrolyte and stainless-steel shell, employing freestanding electrode or carbon-based current collector, replacing the unstable binder with polytetrafluoroethylene (PTFE). Aqueous electrolytes, such as aqueous Al(OTF)₃ solution and ‘water-in-salt’ electrolyte, can offer RAIBs with many advantages including the higher safety, lower cost, H₂O/O₂ insensitivity, which can also serve as alternative electrolytes for RAIBs [93].

- (c) The Al anode with surface protection would retard the dendrite growth on the surface or coating on separator, similar to a phenomenon observed in Li anodes of LIBs [83]. In addition, porous Al or Al foam anode can provide fast kinetics for reversible stripping/plating of Al. Pre-treating the Al anode with chloroaluminate or physical polishing can tune the properties of passivating Al₂O₃ film on Al anode, which also effect the chemical performance of anode. The alloy Al anode with different alloying elements is effective to increase the discharge platforms of RAIBs owing to the standard electrode potential changing of the Al alloy.

8.4. Concluding remarks

In summary, the promising combination of safety, low-cost and high energy density should allow RAIBs to become one of the candidates for energy-storage technology. To promote the commercial application of RAIBs, attentions must be paid to cathode design, electrolyte exploitation and anode research. Various strategies for cathode materials need to be further researched to understand and overcome the challenges. Taking the practical application of the RAIBs into consideration, low-cost electrolytes without assembling limitation are urgently need. Once these electrolyte systems have been introduced, the passivation caused by Al_2O_3 and the dendrite growth needs to be concerned. Although the RAIBs are still in its infancy and

needs further investigation, the mature RAIBs technology is a potential candidate for providing requisite solutions to the energy demand.

Acknowledgments

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9. Aluminum–air batteries

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9.1. Status

The growing energy crisis and increasingly serious environmental pollution caused by the fast consumption of fossil fuels stimulate rapid development of green and renewable energy-storage and conversion systems. LIBs have dominated battery market for decades. However, the unsatisfied energy density ($150\text{--}250\text{ Wh kg}^{-1}$) of state-of-the-art LIBs cannot fulfill customer demands for EVs and smart-grid-scale storage systems. Additionally, the excessive consumption of expensive Li and Co minerals further raise the cost of LIBs. Therefore, tremendous research efforts have been devoted to exploring novel non-lithium batteries for future applications [94]. Metal–air batteries have received great interests due to the low-cost and high theoretical energy densities (2–10 folds higher than that of LIBs). Among various metal–air systems, aluminum–air batteries stand out with the feature of high specific energy (8.1 kWh kg^{-1} or 8.04 Ah cm^{-3}), low-cost and lightweight of Al anodes. More interestingly, Al can be recovered from the combination of recycling electrolyte and electrolyzing Al by the power from solar or wind energy (figure 15).

Al–air battery is composed of an Al anode and an air cathode with an aqueous electrolyte, generating power through the oxidation of Al by oxygen from the air. Al–air battery was firstly proposed by Zaromb in 1960s [95]. Subsequently, extensive studies have been put into this area to boost the performance. A variety of Al alloy anodes by adding various alloy elements are prepared to minimize the self-corrosion in order to boost the energy density, while a series of non-Pt-based catalysts for cathodes are synthesized to replace Pt-based catalysts in order to reduce cost [96]. Meanwhile, many institutes and enterprise have investigated and demonstrated different applications of Al–air systems, such as military communications, reserve power unit, underwater vehicle and EVs. Alcoa–Phinergy demonstrated an electric car equipped with an Al–air battery system in 2014, and a mileage of 1600 km was claimed. The continues progress in Al–air batteries encourages scientists and engineers to further optimize and commercialize this technology, and it is expected that the practical energy density of Al–air batteries can surpass 1000 Wh kg^{-1} and the power density can compete that of LIBs.

9.2. Current and future challenges

Despite many significant achievements, there are still some challenges that hinder the deployment of aluminum–air batteries on a commercial scale. One main obstacle is the self-corrosion rate of Al anodes. Generally, the electrolytes for Al–air batteries are either alkaline solutions or neutral solution, and Al anode, typically a highly active metal with a

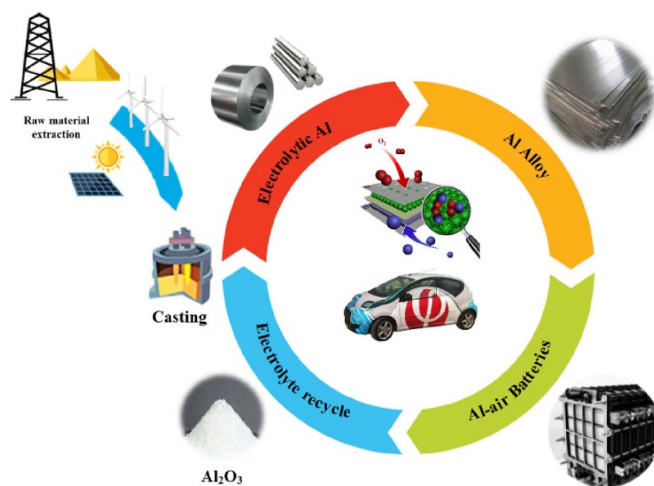


Figure 15. Schematic illustration of the Al cycle for energy storage.

negative standard potential of -2.33 V vs standard hydrogen electrode (SHE), can chemically react with electrolytes to generate hydrogen. Such unavoidable side reaction sacrifices the anode utilization and reduces shelf life, which cause the practical energy density is far away from its theoretical value. In addition, the formation of a compact oxide layer of $\text{Al}(\text{OH})_3$ or Al_2O_3 on Al surface during discharge can lower the battery's working voltage, especially in neutral electrolytes. The other main obstacle is the sluggish kinetics of cathodic ORR, which limits the power density of Al–air batteries. Therefore, ORR electrocatalysts, playing an important role in determining the rate capability, are indispensable in air cathodes. Pt-based precious metals are well-recognized highly active ORR electrocatalysts. However, the high cost and limited resource make Pt-based precious metals practically infeasible to be used in commercial Al–air batteries. Therefore, extensive efforts are needed to explore non-precious-metal electrocatalysts without any compromise of performance. There are also technique issues in operation. One issue is that the remaining electrolyte and by-products (e.g. $\text{Al}(\text{OH})_3$ precipitates) clings to both cathode and anode after shutdown needs to be carefully cleaned with pH-neutralizing agents and water, which unfortunately may require an additional ringing system. There is the other issue. Al–air batteries cannot be electrically recharged as the reduction of aluminum hydroxide is not thermodynamically favorable in aqueous solutions, Therefore, the continuous discharge can only be achieved by replacing the Al anodes (called mechanically recharge), which may need extra professionals. Furthermore, similar to LIBs, the battery management systems for Al–air batteries are also essential for practical application in different fields, unfortunately, such research is missed in literature.

9.3. Advances in science and technology to meet challenges

To date, extensive efforts have been devoted to addressing the above challenges (figure 16). On the anode side, various

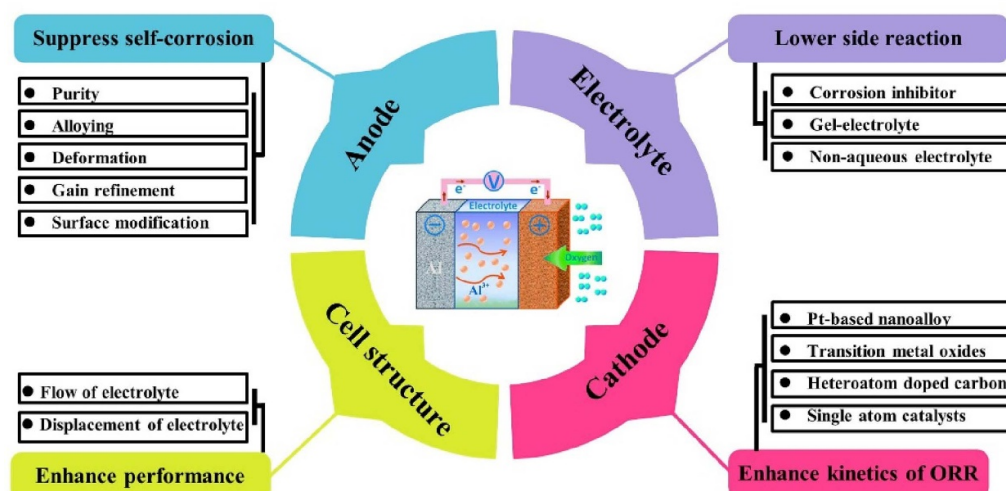


Figure 16. Classification of various strategies to enhance the performance of Al-air batteries.

strategies including anode alloying, grain refinement, and surface modification have been introduced to suppress the self-corrosion. Al alloying is the research mainstream to achieve a high Al utilization, and generally high purity Al (99.99%) alloyed with a variety of elements (Mg, Bi, Sn, In, Ga, Mn) combined with appropriate post heat-treatment can effectively lower the parasitic hydrogen evolution and also eliminated the oxide layer [97]. Meanwhile, electrolytes with an addition of corrosion inhibitors including organic and inorganic additives have also been investigated to minimize self-corrosion reaction of Al anodes. Organic additives such as polyethylene glycol, cetyltrimethylammonium bromide and imidazole derivatives can increase the hydrogen evolution overpotential by surface adsorption. Organic additives such as ZnO, Na₂SnO₃, In(OH)₃ can not only reduce self-corrosion but also activate the Al surface. Investigation on gel and non-aqueous electrolytes is also a direction to suppress the self-corrosion reaction, but this strategy will compromise the energy and high densities of Al-air batteries. The structure design of Al-air cells is an alternative to boost anode utilization. Flow of electrolytes can lower self-corrosion reaction [98], and also a novel strategy of displacing electrolyte from the anode surface with a non-conducting oil during battery standby was proposed to achieve a 420% increase in energy density [99].

On the cathode side, the exploring of ORR electrocatalysts with Pt-comparable performance and low-cost is continuously a hot topic. ORR electrocatalysts can be categorized into precious metal and non-precious metal materials. Researchers tend to alloying precious metals with a proper transition metal (Ni, Co, Mo, V, Cu), which can not only lower the dosage to reduce cost, but also boost the electrocatalytic activity. The activity of alloy electrocatalysts can be regulated by morphology and composition [100]. More efforts focus on non-precious metal electrocatalysts. Transition-metal oxides

were first intensively studied, although the electrocatalytic performance is unsatisfied. Heteroatom doped carbon is a big family with superior ORR performance due to the various N species and carbon edges/defects [101]. Recently, studies move to atomically dispersed metal catalysts on conductive matrix, which can beat Pt-based electrocatalysts in terms of ORR performance, and the catalytic mechanisms of these so-called single-atom catalysts have been well discussed [102].

9.4. Concluding remarks

Al-air batteries have been proven to be an attractive energy-storage system with the features of low-cost, high energy density and environmental benign that can meet the basic requirements from portable devices to large power delivery. However, both fundamental and applied research is still needed to address the above mentioned issues and challenges in order to facilitate the commercialization of Al-air batteries. Each part of Al-air system offers its own opportunity and challenge. Especially, the cell design and optimization, which are currently more or less neglected, need more attention for the sake of practical application. Additionally, it is also of great value to take into account the electrolyte recycling. Therefore, there are still many opportunities to develop more cost-effective Al-air batteries for commercialization. It is believed that Al-air battery systems have a promising potential for next-generation power supply.

Acknowledgment

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10. Potassium-ion batteries

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10.1. Status

Stationary rechargeable batteries have been considered as one of the most promising solutions for the utilization of intermittent renewable power and reduction of greenhouse gas emissions [5, 103]. Rechargeable LIBs launched in 1991 by the SONY Corporation currently dominate the market for portable devices and electric cars and drives modern civilization. However, the scarcity (~ 0.0017 wt% in the Earth's crust) and continuously increased consumption of lithium resources make Li-ion technology nearly impossible to meet the 'low-cost' and 'large-scale' characteristics of stationary energy storage. Therefore, alternative battery chemistry constructed by earth-abundant and inexpensive elements has evoked widespread attention, including Na/K/Zn/Al-ion batteries [103, 104]. Among them, rechargeable K-ion batteries first invented by Ali Eftekhari in 2004 stand out because of their significant advantages (figure 17) [104–109]: (a) high abundance (2.09 wt% in the Earth's crust) and low-cost of potassium; (b) exceptionally low potential of the K/K^+ redox couple in non-aqueous electrolytes (even lower than that of Li/Li^+ in certain solvents) favors the achievement of high battery voltage and energy density; (c) comparing to Li and Na ions, K ions form smaller solvated ions in liquid electrolytes due to their weaker Lewis acidity, resulting in faster ion diffusion kinetics and lower ion desolvation energy; (d) potassium does not alloy with Al, eliminating the use of expensive Cu current collector; (e) K ions readily intercalate into graphite electrochemically with a relatively high K-ion storage capacity of 279 mAh g^{-1} [106]. This graphite intercalation chemistry indicates that the mature graphite manufacture industry in LIBs may be easily integrated into K-ion batteries, representing a major advance beyond SIBs; (f) solution-processable Prussian blue analogs provide material of choice for low-cost and long lifespan cathodes [108, 109]. In theory, K-ion batteries constructed with graphite anodes and Prussian blue cathodes are capable of delivering a full-cell voltage of $>3.5 \text{ V}$ and an energy density of $>120 \text{ Wh kg}^{-1}$ at the punch-cell level. This specific energy is much higher than those of lead–acid and nickel–metal hydride (Ni–MH) battery systems, and even comparable to that of first-generation LIBs, demonstrating tremendous prospect and potential.

10.2. Current and future challenges

Although breakthrough results have been achieved, K-ion batteries are still in the very early stage and lag behind the Li-ion and Na-ion counterparts because of the unsatisfied

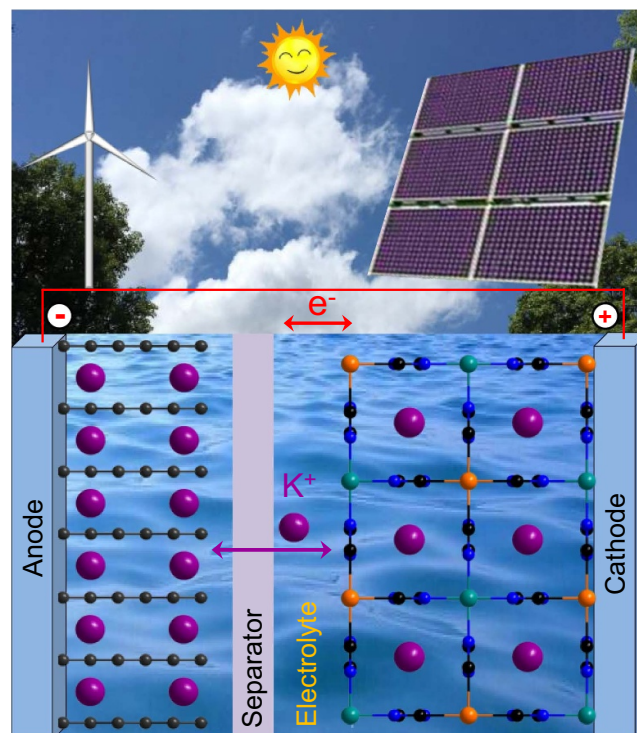


Figure 17. Schematics depicting the operation of K-ion batteries for stationary storage of electricity generated from renewable power.

performance of both the electrode and electrolyte materials [107]. On the electrode side, the (de)insertion of large-ionic-size K ions (1.38 \AA versus 0.68 \AA for Li-ion) typically results in high lattice strain, irreversible structural degradation, and sluggish reaction kinetics to the host materials. For instance, the most promising graphite anode presents a large volume change of $\sim 60\%$ and short cycle life of <50 cycles in the conventional carbonate ester electrolyte [106]. Prussian blue cathodes exhibit high structural stability and long lifespan; however, their nanocrystal-growth habit causes low tap density and volumetric energy density. The growth of their micro-size crystals is of importance and necessity but remains a big challenge [108, 109]. Organic cathodes, including small molecules and polymers, demonstrate relatively high structural stability. However, the absence of K-ion and the low redox potential ($<3.0 \text{ V}$ versus K/K^+) set up formidable obstacles to overcome [110]. On the electrolyte side, the conventional carbonate ester electrolyte fails to construct robust solid electrode–electrolyte interphases at high voltages on the cathode and low voltages on the anode surface, consequently leading to continuous consumption of electrolyte and inferior lifespan [106]. Aqueous electrolytes enable fast chargeability but provide significantly narrowed battery voltages [108, 109]. Also, how a single K-ion interacts with solvent molecules and how the interaction dictates the structuring of electrode–electrolyte interphase remain largely elusive in both aqueous and non-aqueous electrolytes. In a word, the key challenges lie in the exploration of (a) revolutionary solutions to resolve the long-standing issues facing the most promising graphite anode and Prussian blue cathode; (b) low-cost and low-strain hosts that can

reversibly store a large amount of K ions at appropriate operation potential while exhibiting fast electrochemical reaction kinetics; (c) advanced aqueous and non-aqueous electrolytes that can conduct K ions and passivate electrode efficiently in wide voltage and temperature windows.

10.3. Advances in science and technology to meet challenges

Materials morphology regulation, such as nanostructure design and surface coating, represents an effective approach to shorten the K-ion diffusion pathway for improved reaction kinetics and buffer mechanical stress for high structural stability. In the extremity of thickness, two-layer graphite undergoes a lattice expansion of ~ 0.2 nm upon full K-ion intercalation, which unlikely degrades the structural integrity of the SEI (typically 2 nm to tens of nanometers in thickness). High-performance graphite anode could be achieved with a reasonable balance between electrochemical performance and volumetric energy density, especially when a robust SEI layer is structured with advanced electrolytes. More essentially, elemental doping and lattice vacancy could be applied to regulate materials' intrinsic characteristics, including electronic structure, K-ion conduction, and crystal structure, etc for achieving radically enhanced battery performance without compromising volumetric energy (figure 18). Moreover, crystal engineering, together with high-throughput computations, will provide important insights and guide the design of new advanced electrode materials. For example, KTiOPO_4 -type inorganic-open frameworks are recently evaluated as promising electrode materials [111]. Their fast reaction kinetics and low-strain characteristics may enable the use of micrometer-sized materials and thus tackle the key issues facing Prussian blue cathodes and graphite anode as well.

Electrolytes not only conduct the K ions between the cathode and anode but also dictate the electrolyte-electrode interfacial electrochemistry and even electrode redox reactions [5]. Atomic/molecular-level understanding of how K ions interact with solvent and how the solvation structures interact with electrode materials, using advanced characterization techniques and computations, could provide design principles for regulating electrolyte components to the achievement of high battery performance. Through regulation of salts, solvents, ion solvation structures and their redox behavior, robust and fast K-ion conducting SEIs can be structured on both anode and cathode sides, enabling wide voltage windows, long battery lifespan, fast-charging ability, and high-temperature performance for both non-aqueous and aqueous K-ion batteries (figure 18). Also, the adoption of low melting-point solvents could enable the construction of K-ion batteries operating in extremely cold conditions, while appropriate electrolytes and

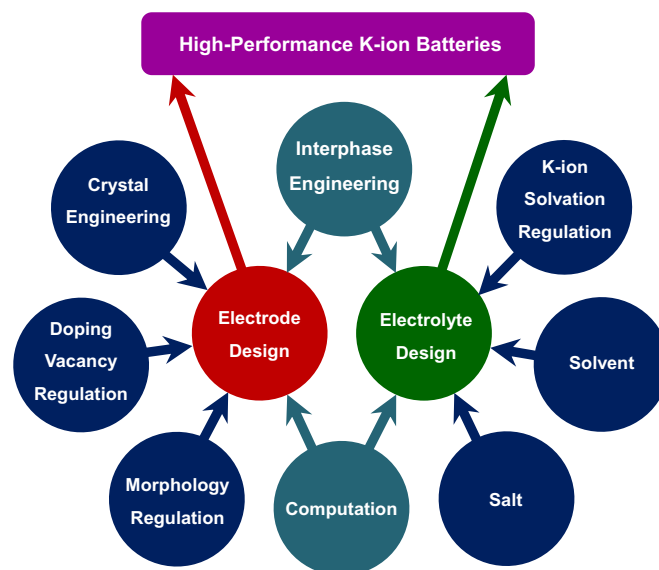


Figure 18. Strategies for achieving low-cost and high-performance K-ion batteries.

electrodes could build high safety and fast-charging aqueous and solid-state K-ion batteries.

10.4. Concluding remarks

Low-cost rechargeable K-ion batteries sharing a similar operation mechanism with LIBs have shown tremendous potentials and will play critical roles in the utilization of clean, renewable energy sources. To this end, innovative solutions and collaborations from diverse research fields, including chemistry, material science, computation, battery community, and industry, are needed to overcome the remaining challenges and promote the realization of rechargeable K-ion batteries at full-cell scale. Looking to the future, aqueous K-ion batteries could provide superior safety, ultrafast-charging rate, and extremely long cycle life, while non-aqueous counterparts could be utilized to meet the demand of high energy density with a similarly long cycle life and relatively fast chargeability. Though many difficulties lay in the way, it is undoubted that K-ion batteries are rapidly in development and could bring actual advances in grid-scale energy storage in the near future.

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11. Dual-ion batteries

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11.1. Status

The energy conversion and storage devices are indispensable to accommodate renewable energy like solar, wind, and tide, where the conventional 'rocking-chair' rechargeable LIBs as an efficient device have been widely utilized for consumer electronics, and represented potency to apply for EVs and grid-scale energy stations [112]. However, the price of cathode raw materials composed of Li, Co and Ni is raising owing to diminished reserves, which restricts applications of LIBs in future [113]. Consequently, the inexpensive battery systems with glorious performance including excellent energy and power densities, prominent rate capability and ultra-long cycle life are future trends to satisfy social development challenges.

Herein, dual-ion batteries (DIBs) are one of the most potential representatives. The working mechanism of DIBs is different from that of traditional LIBs, where cations and anions both participate in the intercalation and deintercalation processes with the low-cost graphite as both cathode and anode materials [114]. As illustrated in figure 19, cations (e.g. Li^+) and anions (e.g. PF_6^-) are intercalated/deintercalated into the anode and cathode during the charge/discharge process, respectively [114, 115]. According to the working principle, the intercalation and deintercalation of anions on the graphitic cathode endows DIBs with a high cut-off voltage over 4.5 V, which tends to achieve relatively high energy density [116]. Additionally, electrolytes with high concentrations can also promote energy density of DIBs because anions from electrolytes are also active substances [116]. Furthermore, the graphite as a cathode instead of high-cost lithium-containing metal oxides can efficiently decrease the battery cost and relieve environmental pollutions.

In this perspective, we will outline current and future challenges on DIBs from aspects of electrolyte and electrodes, respectively, propose corresponding advances in science and technology to meet challenges, and outlook prospects.

11.2. Current and future challenges

The poor rate capability, limited specific capacity and poor cycling life are critical challenges to DIBs due to the decomposition of electrolyte, and sluggish reaction kinetics of anions and cations. Herein, we will summarize challenges to restrict the performance of DIBs from the electrolyte and electrodes.

11.2.1. Electrolytes. Organic liquid electrolytes and ion liquid electrolytes are commonly utilized for DIBs due to the intimate contact between the electrolyte and electrodes. The energy gap of electrolyte (i.e. the potential window, E_g)

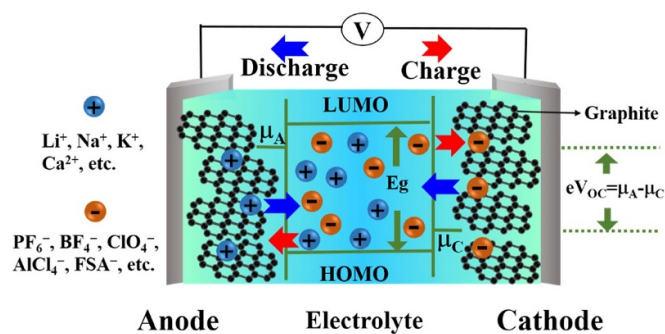


Figure 19. Schematic diagram of the charge/discharge mechanism of a DIB with graphite as both of the anode and cathode.

could be determined by the difference between the HOMO and the LUMO, where electrochemical potentials (i.e. Fermi levels) of cathode (μ_C) and anode (μ_A) should be located above the HOMO and below the LUMO of electrolyte, respectively, to block the oxidation or reduction of electrolyte [114], as the open-circuit potential $eV_{OC} = \mu_A - \mu_C$ displayed in figure 19. Nevertheless, electrolytes are still restricted to the severe decomposition at the charge/discharging process, resulting in low Coulombic efficiency and poor cycling stability of DIBs [116].

11.2.2. Electrodes. In DIBs, the graphite can act as both of cathode and anode materials to decrease the cost. During the charge process, anions and cations would intercalate into the graphite cathode and graphite anode, respectively. Thus graphite electrodes are plagued by the ineluctable volume expansion from large intercalation ions and the co-intercalation of solvent, resulting in the exfoliation of graphite and shrunken capacity of DIBs [117]. Furthermore, the graphite displays finite active sites and specific surface areas, which cannot reach the anticipated capacity. Thus, searching for novel materials with more intercalation sites or redox active sites is competitive to surmount the conventional intercalation mechanism and obtain promotional energy densities.

11.3. Advances in science and technology to meet challenges

Considering aforementioned challenges, we sum up and present several solutions as follows:

11.3.1. Electrolyte. In terms of electrolytes of DIBs, the electrolytes require great compatibility with electrodes and redox stability at the relatively high voltage to avoid the decomposition. Carbonates (e.g. ethylene carbonate (EC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), diethyl carbonate (DEC), etc) with relatively high ion conductivity, small electronic conductivity and low viscosity are one of the most promising organic-liquid electrolytes to dissolve anions and cations, which have a wide potential window and induce a low activation energy for ion diffusion [116]. In addition, the reversible capacity and rate capability of DIBs can be

also optimized by electrolyte formulations including the type and concentration of solvents, salts, and additives, which can strongly affect the behavior for the ion storage in a certain electrode material, where the common ionic salts comprise anions (e.g. PF_6^- , BF_4^- , ClO_4^- , AlCl_4^- , amide-based anions (FSA^- , TFSI^-), etc) and cations (e.g. Li^+ , Na^+ , K^+ , Ca^{2+} , etc). It is noticeable that fluorinated components in the electrolyte with high oxidation potentials can reinforce the oxidative stability. Furthermore, ion liquid-based electrolytes and highly concentrated electrolytes are promising options to reach a high reversibility and long-term cycle stability of DIBs [116].

11.3.2. Electrode materials. To boost the performance of DIBs, it is indispensable to modify graphite-based electrodes [117, 118]. Firstly, the graphitization degree of electrode materials could improve electronic conductivity, ion diffusion rate and structural stability, which are correlative with intercalation/deintercalation kinetics of ions. Generally, an enhanced graphitization degree could induce the improved Coulombic efficiency and voltage efficiency, with an enhanced ion storage capability and decreased polarization. Secondly, the nanostructure construction of electrode materials provides large specific surface areas with increased intercalation sites and short diffusion paths with the enhanced ion transport, which also can effectively tolerate the volume expansion from the intercalation of ions, thus improving the robust cycling stability and glorious rate capability of DIBs. Thirdly, appropriate dopants and defects in electrode materials can enhance their electronic conductivity, generate abundant active sites and decrease energy barriers of the ion diffusion, which lead to the fast intercalation kinetics of ions and high specific capacity of DIBs.

In addition of graphite-based materials, several novel materials [119, 120] such as intercalation materials (e.g. MXenes), organic materials (e.g. polymers, MOFs, covalent organic frameworks, etc) could also be selected as electrodes. Whereas for anode materials, metals (e.g. Li, Na, K, etc), intercalation materials (e.g. layered metal chalcogenide etc), alloying materials (e.g. Si, Sn, etc) are also

competitive candidates. Among them, novel organic materials are attractive research focuses due to their superiority of flexibility in structure and various active sites, which make them with the large theoretical capacity [121]. Especially, organics can store large size ions by abundant redox functional groups without the structural smash, indicative of the great stability. Moreover, alloying and conversion reaction mechanism has attracted plentiful attentions as anode materials. Further, the nanostructural design and interface modification by nanostructure design and carbon coating layered introduced into anode materials are efficient strategies to increase the theoretical capacity, to promote intercalation reaction kinetics of anode and to enhance the robustness of DIBs.

11.4. Concluding remarks

In brief, DIBs as a novel battery device other than the state-of-the-art LIBs are still in their infancy. In this perspective, current challenges and recent investigation strategies on electrolytes and electrode materials have been overviewed including the optimization of electrolyte formulations, the structural engineering and interface modification of electrode materials to boost the energy and power densities, to improve the rate capability and to reinforce cycle stability of low-cost DIBs. Although DIBs has attracted considerable attention, they still leave much space for researchers to acquire further fundamental understanding and technical improvements. With advancing evolution in the energy density and cycle life to overcome pivotal bottlenecks, DIBs might be a competitive option for the practical application on sustainable stationary energy storage in future.

Acknowledgments

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12. Flow batteries

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12.1. Status

Large-scale energy-storage technologies are vital to realize the wide utilization of renewable energy sources since they can effectively solve the intermittence, uncontrollability and instability of the electricity generated by renewable energy sources [122]. The technologies proper for large-scale energy storage should possess the features of high economy, long lifespan, high safety and low environmental load. Accordingly, the flow battery energy-storage technology, which owns high safety with aqueous electrolytes, long cycling life, recyclable electrolytes and excellent environmental benignity (figure 20) [122, 123], becomes one of the most suitable candidates. Different from traditional solid batteries, the electrolytes of flow batteries are stored in the external tanks. The electrolyte flows through its corresponding electrode circularly by the pump, and redox reaction of active materials in the electrolyte occurs on the electrode (figure 20). The conversion between the chemical energy and electric energy is thus achieved. In principle, ions pairs with the valence state change can all serve as the redox couples (namely active materials in electrolytes) for flow batteries. Therefore, the power and energy of flow batteries can be independently tuned. Among various flow batteries, vanadium flow batteries (VFBs) and zinc-based flow batteries (ZFBs), where aqueous solutions serve as the electrolytes, are currently at the demonstration stage [122, 124, 125]. For example, a 5 MW/10 MWh VFB energy-storage system has been implemented in 2012 and ran stably for more than 7 years [122]. And nowadays, many commercial organizations, such as Redflow (Austria), Sumitomo (Japan), Vanadis Power (Germany), EnSync (United States) and VnZn (United States) are all devoting to the successful commercialization of flow batteries. However, the hydrogen evolution and oxygen evolution often occurring in aqueous solutions restrict the improvement in the voltage and further energy density of flow batteries [126]. Therefore, to improve the energy density and reduce the cost are the key measures for commercialization and industrialization of flow batteries.

12.2. Current and future challenges

Even though flow batteries are very promising for large-scale energy storage, the energy density and power density of flow batteries are still need to be further improved. Among various flow batteries, VFBs and ZFBs are currently the most mature technologies for the industrial and commercial application. As we mentioned, a 5 MW/10 MWh VFB energy-storage system assembled by Rongke Power Co. Ltd has been successfully constructed and has ran stably for more than 7 years.

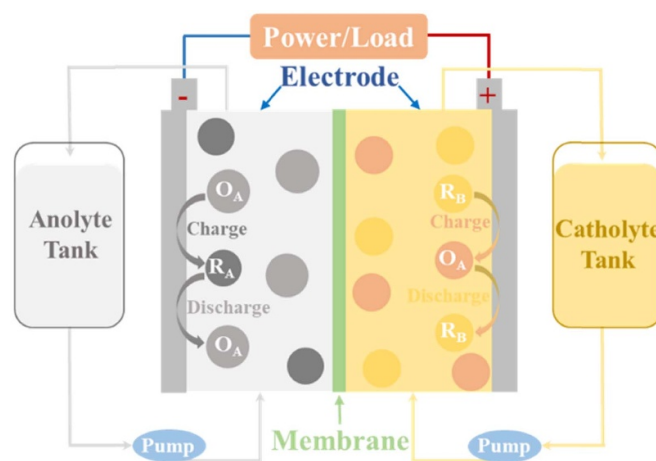


Figure 20. The schematic diagram of a typical flow battery.

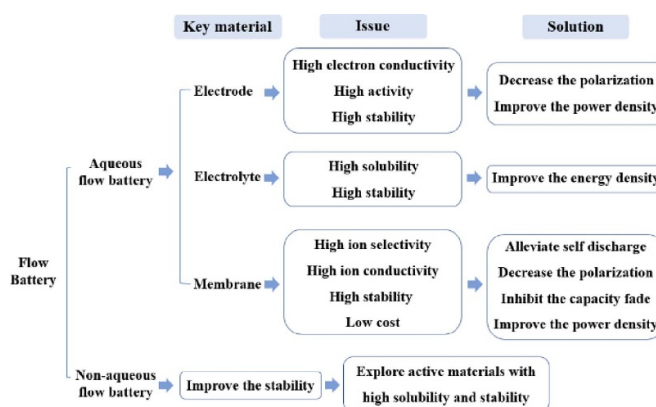


Figure 21. The challenges and countermeasures of the industrialization and commercialization of flow battery energy-storage technologies.

And more than 30 VFB systems with different scales have been demonstrated. Besides, several ZFB systems have been assembled and applied in different fields as well. Nevertheless, the VFBs still confronts the challenges of relatively low energy density and high cost (Around 400 \$ kWh⁻¹). Quite recently, new flow batteries with lower cost and high energy density were widely investigated, which are mainly divided into aqueous and non-aqueous systems. Non-aqueous flow battery systems, which utilize organic solvents as the supporting electrolytes, possess wider voltage window and higher theoretical energy density due to the lack of hydrogen evolution reaction (HER) and OER. However, their power density is very limited due to the low conductivity of ions under organic solvent medium. And the as-used organic solvents are commonly flammable. Up to now, although many high-quality papers with regard to non-aqueous flow battery systems together with novel aqueous flow battery systems apart from VFBs and ZFBs have been reported in recent years, they are still meet a lot of challenges like stability, low power density etc for practical applications [122, 127–129].

12.3. Advances in science and technology to meet challenges

As mentioned above, aqueous flow battery systems, especially VFBs and ZFBs, still are the research focus in the research field of flow battery energy-storage technologies. As for aqueous flow battery systems, the improvement in power density and energy density are the key for their industrialization. Thus the structure design and performance optimization of key materials of aqueous flow batteries are significantly important. The key materials of flow batteries mainly include the electrode, the electrolyte and the membrane. The properties of electrode materials are closely relevant with the battery polarization, that is to say the power density of batteries. Consequently, to develop electrode materials with high electron conductivity, high activity to redox couples, high chemical and electrochemical stability is significant for reducing the battery polarization and increasing power density (figure 21). In general, the concentration and volume of the electrolyte determine the energy density of flow batteries. Accordingly, how to improve the solubility of active materials in electrolytes, and to improve the stability of electrolytes are the key to develop high-performance and highly stable electrolytes (figure 21). As for the membrane, its properties and price directly affect the performance and cost of flow battery systems. As a consequence, ideal membrane materials should own high ion selectivity, high ion conductivity, high stability and low-cost at the same time (figure 21). The improvement in membrane performance can efficiently alleviate the self-discharge along with capacity fade, and increase the power density and energy density of batteries. Based on the high-performance and low-cost key materials, flow battery stacks with high power density and energy density can be designed and manufactured, further facilitating the indus-

trialization and commercialization of aqueous flow battery systems. Different from aqueous flow battery systems, the primary issue that non-aqueous flow battery systems need to address lies in to explore more stably active materials and supporting electrolytes. To exploit novel non-aqueous flow battery systems with higher stability is of great importance (figure 21) [122, 127–129].

12.4. Concluding remarks

In summary, accelerating the research and development of flow battery energy-storage technologies is the key of the widespread utilization of green and clean renewable energy sources. Up to now, aqueous flow battery systems show great potential in industrial application. Thereby, the design and optimization of key materials for aqueous flow battery systems need to be enhanced to improve their performance and decrease their cost. And the design and assemble of high power density battery stacks are also very important. As for non-aqueous flow battery systems, the optimization of electrolytes, including the research and development of active materials with high solubility and stability, is the most important issue. In other words, the exploration of innovatively stable non-aqueous flow battery systems still needs to be carried out. In short, the research emphasis should be still concentrated on aqueous flow battery systems, particularly VFBs and ZFBs which have been in the demonstration stage.

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13. Aqueous batteries

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13.1. Status

Most battery types employ aqueous electrolytes since the invention of Voltaic piles in the late 18th century. To date, two battery technologies dominate nearly the entire market of batteries; they are lead–acid batteries and LIBs. The climate crisis insinuated by the recent record-breaking extreme weather calls upon the revolutionary transformation of our energy industry based on fossil fuels to focusing on renewables such as solar and wind. However, a high percentage of electricity from renewables demand the massive installation of energy-storage capacity. It is predicted by BloombergNEF that the global storage capacity excluding pumped hydro storage (PHS) will increase from 9 GW currently to more than 1095 GW by 2040. To date, 94% of the storage is undertaken by PHS, which is geographically limited. It is a grand challenge of our time to create new storage solutions. One most promising approach is to install gigantic battery facilities. Albeit the most successful battery technology to date is LIBs, any non-aqueous batteries are not suitable for large-scale storage purposes for the safety reasons. Furthermore, any lithium-related batteries may face the limits of lithium resources and their price volatility. Therefore, it is pivotal for the battery community to invent new aqueous battery technologies that address the shortcomings of lead–acid batteries, i.e. low energy density and short cycle life, and of Ni–MH batteries, i.e. the reliance on rare earth elements. For aqueous batteries, there are three strategies of device configurations: rocking-chair ion batteries, rocking-chair metal batteries, and DIBs. The difference between the first two types resembles that between LIBs and Li-metal batteries. DIBs are an emerging category, where the two electrodes operate on hosting cations and anions, respectively, and such batteries can use a metal anode as well. In order to exhibit much higher energy density than lead–acid batteries, it appears that the usage of metal anode represents the most viable pathway forward.

13.2. Current and future challenges

The reactivity of water molecules defines the future of aqueous batteries in the electrolyte. When the potential is low on the anode side, water is reduced, causing HER; when the potential is very high on the cathode, water can be oxidized, thus leading to OER. HER and OER are associated with a series of long-standing challenges of aqueous batteries: (a) safety concern, (b) poor cycling life, (c) self-discharge, and (d) limited

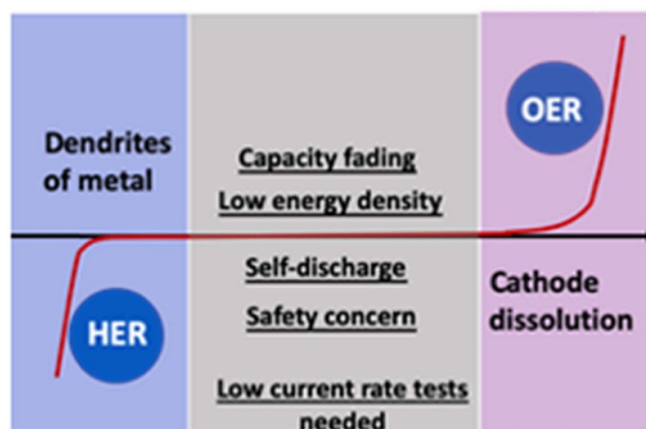


Figure 22. Challenges of aqueous metal batteries.

energy density. A battery may be commercially viable with a low energy density; however, any one of the three former challenges could jeopardize the legitimacy of a commercial battery technology. I will use aqueous metal batteries, particularly, rechargeable Zn-metal batteries (ZMB), to expand this thread of discussion. ZMB is a very promising next-generation battery technology for energy storage because the usage of zinc metal anode (ZMA) renders ZMB a good energy density. However, ZMBs have yet to be commercialized on a large scale due to the first three challenges listed above. The limited cycling life of ZMB originates from both cathode and anode. Cathode materials of ZMBs, typically, metal oxides, fade rapidly when hosting Zn^{2+} ions because these metal oxide electrodes often slowly dissolve into the electrolytes. The co-insertion of water may take place. We recently reported that the dynamic transport of water during (de)insertion of protons in a metal oxide electrode, and interestingly the water transport plays a tremendous role in the electrochemical properties of the electrode [130]. The ZMA anode suffers poor reversibility: i.e. the charges used to plate ZMA mass from battery charge cannot be claimed during the battery discharge. For ZMA, there are three aspects of challenges: (a) the hydrogen evolution of water, which pertains to water's cathodic reactivity, (b) the stability of ZMA, which is about the anodic stability of ZMA, and (c) the dendritic formation of ZMA over plating. To date, the battery community has been tackling the dendrite formation issue [79, 131] but the reactivity of water and ZMA has yet to be controlled. Figure 22 summarizes the challenges of aqueous metal batteries.

13.3. Advances in science and technology to meet challenges

For cathode in aqueous batteries, progress has been made on the electrode structures [132, 133]. Certain structures of metal oxides exhibit better cycling in aqueous environments. Nevertheless, the root-solution may be from the electrolytes, in particular about an emerging research area—water-in-salt (WiS) electrolytes. Xu, Wang, and co-workers first reported a

21 m (moles of solute in kilogram of solvent) LiTFSI electrolyte that transformed the properties of cation-insertion electrodes [134]. There are several consequences of WiS electrolytes (a) widened electrochemical stable window of water, (b) shifted potentials of ion insertion in electrodes, and (c) shifted potentials of metal plating. For the widened electrolyte potential window, the understanding of the community is still elusive. Evidence indicates that solid–electrolyte interphase (SEI) can be formed by decomposing electrolyte salts on the surface of the anode. On the other hand, Raman and Fourier transform infrared spectroscopy results reveal that in WiS electrolytes, the O–H covalent bonds in water molecules are strengthened [135]. For the potential shifting, it goes to a higher potential in WiS electrolytes for electrodes that host cations, which was widely observed. We first reported that the potential declines for electrodes hosting anions from more concentrated electrolytes [136]. Such potential shifts for cation or anion accommodation can be understood from the point of view of the Nernst equation and the large impacts of concentration on the activity coefficients of ions. When the anion hosting occurs at a sufficiently low potential, such an electrode can serve as an anode for a DIB, where a cation-deficient cathode is solicited for a full-cell configuration. Thus, this is operating in a reverse manner compared to the conventional

DIBs, and we name this battery configuration as reverse DIBs [136].

13.4. Concluding remarks

For storage batteries, it is pivotal for the community to identify the roadmap that encompasses holistic considerations. I recently propose five-dimensional considerations from a perspective of designing a synthetic reaction, where the electrodes and ion charge carriers are reactants, electrolytes offer the reaction media, battery configurations define the reactors, and electrode-ion chemical bonding is the descriptor of the nature of a reaction [137]. The ultimate evaluation of a battery technology is the market based on the levelized energy cost. For the design of new battery chemistries for storage, safety is the first consideration, and the field works on how to promote the performance and lower the cost. The inherent challenges of aqueous batteries pertain to the lack of inertness of water as the electrolyte solvent.

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14. Flexible batteries

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14.1. Status

The market for portable, ultrathin/lightweight and flexible electronics and devices is growing quickly, such as roll-up displays, touch screens, active radio-frequency identification tags, smart electronics, flexible solar panels, wearable sensors and implantable medical devices. In this case, it is urgent to develop flexible batteries that can continuously provide and store energy for them under various mechanical deformations [138]. The conventional batteries incline to structure damage, power supply interruption and safety issues when they are subject to bending, twisting, folding, and stretching, etc. In detail, the original intimate interface including electrode/substrate (such as current collector), electrode/electrolyte and active material/conductor additive is deteriorated and even destroyed, which blocks the ionic and/or electronic transfer channel. At the other extreme, the internal direct electronic conduction derived by mechanical deformation leads to short circuit and severe side reaction of the batteries. Therefore, novel strategy for material, electrode and deformable architecture designs are required to enable batteries bendable, implantable and wearable. Usually high flexibility of batteries is achieved by introducing redundancy in volume to release strain, so improving energy density without compromise of flexibility is one of challenging requirements for batteries [139]. Meanwhile, high safety, long lifespan and high power density are also simultaneously criterion for ideal flexible batteries. Moreover, flexible batteries possessing multiple functionalities such as optical transparency and stretchability are more and more attractive to cope with the development of future electronic devices. In this perspective, some recent research progress on flexible batteries is reviewed, covering advances in key components including electrolyte/separator, electrode/current collector, and in battery structure designs as shown in figure 23. Moreover, the challenges in development and commercialization of flexible batteries are discussed.

14.2. Current and future challenges

Continuous ion-conductive path is believed to be one of the most important factors for building flexible batteries as mentioned above. Liquid electrolyte wets the interface and transports Li ions between cathode and anode via penetrating the porous electrode and tortuous holes in the separator, but the fluidic properties of liquid electrolytes also restrict the shape and size design of a flexible battery. So, plastic and rubbery ion-conductive material is considered to replace the liquid electrolyte in flexible batteries [140], where gel polymer electrolytes are good candidates to integrate with a separator. Meanwhile, plastic crystal electrolytes incorporated with a

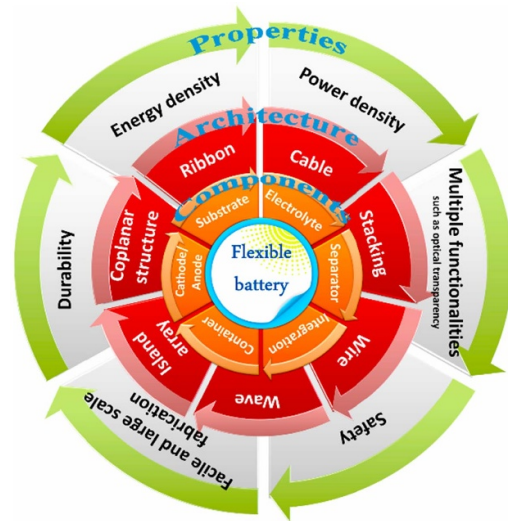


Figure 23. The components, architecture and application requirements of flexible battery.

polymer matrix as a mechanical framework are also focused due to a high ionic conductivity, excellent thermal stability and further improved mechanical properties. Moreover, the composite solid polymer electrolytes (SPEs) consisting of polymer matrix (such as polyethylene oxide (PEO), polyacrylonitrile (PAN), polymethyl methacrylate (PMMA), polyvinylidene fluoride (PVDF)) and Li salt have been employed to avoid the liquid electrolyte extrusion, additionally ceramic nanoparticles as fillers and/or ion conductors are also introduced to inhibit crystallization of polymers and further enhance the ionic conductivity [141]. Although solid-state electrolytes are an ideal ion transport medium and can be easily shaped, patterned and integrated, the development of solid electrolyte for flexible batteries is facing some challenges, including keeping intimate contact with active material and suppressing serious interfacial passivation.

Moreover, flexible electrode is another of the most important components of flexible batteries, in which substrates for the electrode are critical for achieving flexibility and conductivity simultaneously [142]. The typical substrates for LIBs, named as current collectors are aluminum and copper foils. As known, the tensile fracture strains Cu and Al of foils are roughly 2.7% and 4.5%, let alone that their yield strains are only 0.9% and 1.2%, respectively. Therefore, it is difficult for the electrode obtained from the conventional coating slurry on the foils to keep integrity under repetitive deformations [143]. So far the stacking cell configuration of the conventional batteries is widely applied in most of the flexible systems. Though there is no problem to maintain good flexibility for a thin battery, the stacking thick cell exist dramatically deteriorated flexibility and elimination.

14.3. Advances in science and technology to meet challenges

14.3.1. Electrolyte/separator. In lithium metal batteries, SPEs integrated with separator play important role to

smooth Li-metal electrochemical behaviors and achieve the more disciplined Li plating/stripping. Some novel SPE with self-healing ability has been proposed via supra-molecular design such as encapsulating healing agents or incorporating reversible covalent bonds or non-covalent interactions into a polymer matrix [144]. Taking advantage of the dynamic reversibility of bonds or interactions in SPEs, the interface between electrolyte and electrode can spontaneously repair damage when wounded, which contributes to superior cycling stability and freely bending flexibility of the batteries, moreover the safety issues concerning the lithium metal batteries could be solved ultimately.

14.3.2. Electrode/current collector. The highly conductive flexible substrate including carbon materials and conductive polymers has been proposed to avoid exfoliation of active material and alleviate interfacial stress with current collectors [145]. Applying carbon nanotubes, grapheme, carbon nanofibers and carbon cloth/textiles as the substrates for constructing the membrane/paper-like carbon-based electrodes becomes a common strategy, owing to their porous network, high surface area, excellent electrical conductivity, good mechanical and chemical properties [146]. Dimensional carbon-based collector can accommodate and release various kinds of stresses, enabling high flexibility of the electrode. Moreover, the carbon-based collector possesses light weight to improve the gravimetric energy density, high surface area to support active materials and interconnected charge transfer channels to lower the interfacial resistance [147].

14.3.3. Architecture. The integration of all battery components innovation in battery structures can overcome conventional-design constraints and cope with diversified demand of batteries for flexible devices [148]. Building novel battery architecture such as wire-, cable-, wave-shaped, paves a way to remarkably enhance flexibility. For instance,

wire-like cells can be easily woven into textiles or twisted to various shapes without any restrictions in shape, size, length, etc. Moreover, the flexible batteries in cable/wire type can reconcile the demands of energy density and power density simultaneously of the batteries. The progress in architecture design provides a platform for the development of high-performance flexible batteries with excellent shape-compliance [149].

And above all, the flexible energy-storage and transformation devices must be considered as a whole system including their electrode/electrolyte selectivity, structural design and suitable packaging.

14.4. Concluding remarks

During the past decades, LIBs, lithium-sulfur batteries, lithium-air/oxygen batteries and SIBs have been designed to be bendable, implantable, and wearable. First, the safety and sturdiness of battery should be ensured during the complex deformation process. Additionally, the degradation of charge transfer channel in batteries over a prolonged period of operation should be addressed to avoid increased overpotential, reduced capacity retention and energy conversion efficiency. So far, the significant progress has been made in material chemistry for flexible batteries, the integration of all battery components including layout of electrode materials, architecture, assembly and packaging are central issues in developing high-performance flexible batteries. Moreover, the development of facile and large-scale fabrication technique for flexible electrodes, electrolytes and packages is urgently required to realize low-cost production and broaden the applications of flexible batteries.

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15. Biodegradable batteries

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15.1. Status

The need for transient implantable medical devices (TIMDs) for monitoring to enable a stimulation for treatment of diseases is growing [150]. Such devices have a short time operational window and can be used for wound healing, bone regeneration and monitoring for diagnosis. The current available power sources (e.g. remote wireless power, lithium batteries) require surgical retrieval after usage. On-board transient power sources that can provide the required energy with a controllable degradation profile is ideal.

The concept of a bioelectric battery that could be directly implanted into the body with body fluid as electrolyte has existed since the 1970s [151], as body fluids contain various ions suitable for use as electrolyte. The first biodegradable battery with bioresorbable metallic electrodes was reported by Rogers' group in 2014 [152]. The Mg/Mo system delivered a stable voltage output of 1.5–1.6 V for up to 6 h, and electrodes were partially degraded after 11 d in phosphate-buffered saline (PBS) at 37°. In 2017, our group reported a solid-state Mg–Au battery with silk-ionic liquid polymer electrolyte that was almost completely decomposed after 45 d in protease solution (figure 24(A)) [153], and could generate a voltage of ~1.3 V. In 2018, Yin's group reported a Mg–MoO₃ battery system that offered a high capacity of 6.5 mAh cm⁻² with a voltage of 1.6 V and a prolonged lifetime of 13 d [154]. They performed *in vitro* and *in vivo* degradation tests where the latter revealed the complete disappearance of a battery implanted in the subdermal region of a rat after 4 weeks (figure 24(B)). The power from these biodegradable batteries can drive medical devices with low power requirements such as sensors or monitors [155].

15.2. Current and future challenges

Being a power source for use to drive transient biomedical devices, biodegradable batteries should first meet the requirements of nontoxicity, reliability, high energy density and predictability of performance [156]. They should also possess the characteristic of controllable biodegradability in that they can be gradually dissolved or decomposed in a controlled way, then absorbed or excreted by the body without inducing any adverse effects. These requirements place strict conditions on materials which can be

used, thus limiting the development of biodegradable batteries. Moreover, there exists a tradeoff between electrochemical performance and the biodegradation profile for electrodes. Matching of energy-storage performance with the specific function (monitoring or stimulation) at hand is an ongoing challenge.

Current research mainly focuses on characterizing the properties (e.g. electrochemical performance, biodegradation profile) of individual components in PBS prior to the discharge process. Evaluation of performance during biodegradation is essential in simulated body fluid. In addition, the cytocompatibility using relevant cells should be evaluated (*in vitro*) during discharge.

15.3. Advances in science and technology to meet challenges

Materials hold the key to the development of current biodegradable primary batteries, or even future secondary batteries. Expanding the materials inventory will promote the development of biodegradable batteries to enable realization of practical applications. The machine-learning techniques are capable of considerably speeding up both fundamental and applied research from materials prediction to chemical reactivity optimization [157]. It is expected to assist in the discovery of new materials without conducting costly experiments, thus greatly promoting development. A deep understanding of the electrochemical processes and structural changes of materials during the discharge and biodegradation processes using *in situ* microscopic/spectroscopic techniques will provide further information for guiding the design and synthesis of new materials.

Seamless integration with various TIMDs and the need for development of miniaturized biodegradable batteries in different and/or complicated configurations needs to be addressed. 3D printing techniques can make a significant contribution to this area. It is a powerful tool for creating free-form 2D and 3D structures with pre-designed patterns for batteries [158], especially powerful for the development of micro-sized electrodes in complicated configurations.

15.4. Concluding remarks

Research on biodegradable batteries is still in the very early stages of development but will be accelerated by new emerging technologies and techniques. The ultimate goal is to realize the practical application of biodegradable batteries as on-board power source for TIMDs. As different TIMDs perform different functionality, the current research on biodegradable batteries should target a specific application that meet all the requirements. Its development involves materials discovery and optimization, battery technology, device design, manufacturing methods, degradation profile control, as well as the implantation in the body. To achieve the ultimate

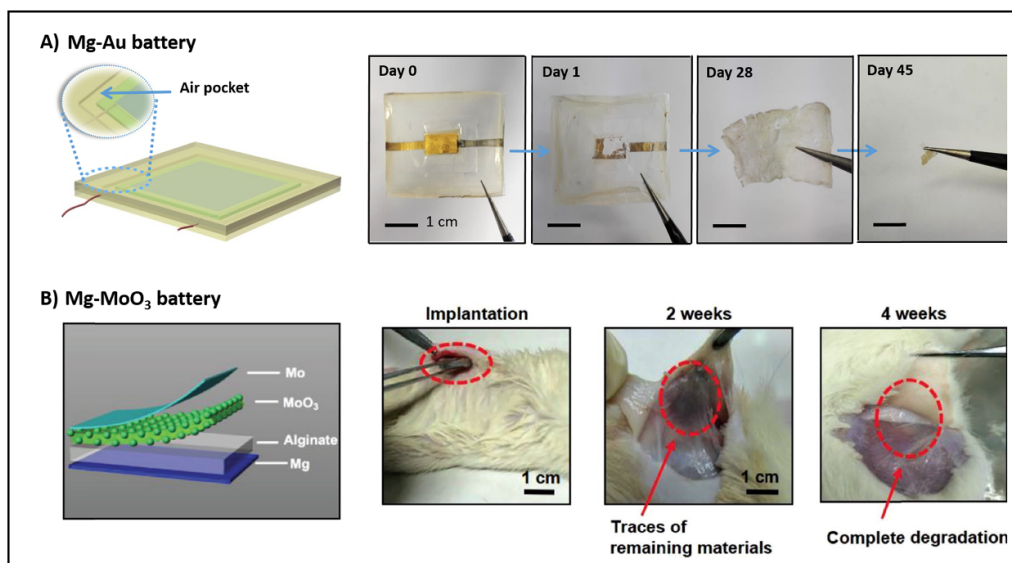


Figure 24. Device structure and biodegradation profile of biodegradable Mg-based primary batteries. (A) A Mg–Au thin film battery and representative photos showing its biodegradation in buffered protease solution at 37 °C (reproduced with permission from [4]. © 2017 ACS Publications). (B) A Mg–MoO₃ battery and the *in vivo* degradation evaluation in the subdermal region of a SD rat (reproduced with permission from [5]. © 2018 Wiley-VCH Verlag GmbH & Co. KGaA).

goal, namely translating emerging technology into clinical practice, requires close collaboration involving materials scientists and engineers, mechatronic engineers, biologists and clinical practitioners.

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16. Recycling of spent lithium-ion batteries

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16.1. Status

Since 1991, the LIBs have served people's daily life and related industries for almost 30 years, first in consumer electronics, and then in EVs and grids [159]. Particularly, the market demand for LIBs has witnessed rapid growth in the last decade. However, like other electrochemical power sources, the LIBs have limited operational lifespans. For example, the LIBs used in laptops, cell phones and other electronic devices are expected to last for 1–2 years (*ca.* 500–800 discharge–charge cycles), and the ones served in electric cars are expected to last for 5–8 years (*ca.* 100–150 k km). As a result, the continuous growth of production of commercial LIBs leads to a raising number of retired batteries per year (figure 25) [160]. The spent LIBs usually show aggravated chemical conditions compared with the new ones, which, if not disposed properly, could lead to the life-threatening safety hazards (e.g. fire or explosion due to internal short circuit and thermal runaway) and the pollution of living environment (e.g. leakage of organic electrolyte and discharge of heavy metals). In addition, the manufacture of the LIBs strongly relies on the steady supply of various rare metals, for example, lithium and transition metals including cobalt, nickel and manganese. The drastic fluctuation of rare metal prices on the international market significantly influences the basic manufacture cost of the LIBs. On the other hand, the gradual depletion of metal reserves raises concerns on the long-term economic sustainability of the LIBs. The spent LIBs have much higher contents and purity of rare metals than the natural ores, and can be considered as high-quality minerals. Recycling of the spent LIBs turns the hazardous industrial wastes into the precious 'urban mines', which helps to reduce the safety risks and environmental impacts of the discarded batteries, alleviate the resource anxiety on the rare metals, and stabilize the production cost of the new batteries [161]. In this way, the technology is expected to insert the last piece of the jigsaw puzzle to complete the industrial chain of LIB manufacture.

16.2. Current and future challenges

Although the recycling of spent LIBs is important, challenges remain on the way from the lab study to the industrial application. Before recycling, retired LIBs packs/modules should be evaluated first for its vital performance metrics, such as

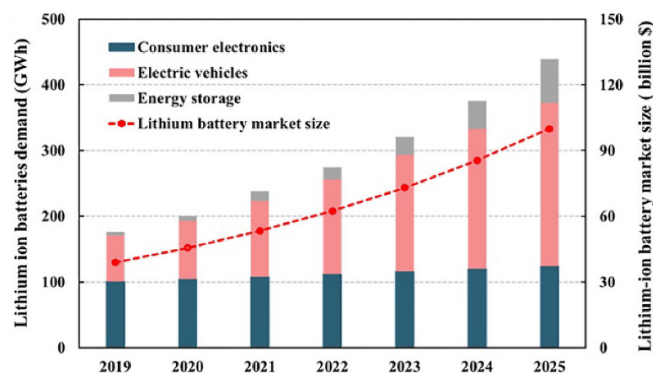


Figure 25. The ascending numbers of commercial LIBs in consumer electronics, EVs and energy storage, and its market size forecast from 2019 to 2025. Reproduced with permission from [160]. Copyright 2020 American Chemical Society.

capacity retention, energy efficiency, structural integrity, and most important, safety. The results of evaluation determine the two outcomes of the spent LIBs, i.e. cascade utilization and materials recycling. However, no standard method has been established for battery evaluation. The spent LIBs usually show poor performance consistency, making it hard for cascade utilization. To enable stable operation at pack level, high-performance battery management system which precisely monitors and controls each single cell is desired, yet it may increase the cost of the storage device. Since the spent LIBs are hazardous wastes, there are always safety concerns accompanied with the storage, transportation and disassembly. Unfortunately, there is no good practice or procedures identified for safe recycling of LIBs at present. The compositions of the LIBs are complex and vary from one to another. Therefore, the recycling process usually involves complicated separation and purification process, which leads to increased consumption of energy and materials cost. As most of the recycling procedures involve wet chemistry or pyrogenic reactions, the secondary pollution (e.g. generation of toxic gases or discharge of wastewater) and carbon emissions that related with the battery recycling should not be ignored. Last, like other relevant industries, the recycling of LIBs is a profit-driven business. Strict control of the manufacture costs (e.g. materials and labor) and process, and the quality of products is crucial for guaranteeing the immediate and short-term economic profits. In the long term, one may refer to the environmental benefits of the recycling industry. Also, sustainable development of the recycling market may play as a game-changing chip in the international trade if one looks into the function of rare metals as strategic reserves. To stimulate healthy growth of the recycling market, joint efforts are required from the government, the companies and the consumers. However, it still takes time for all of parties to reach a consensus on the profit-making model and protect the industry with a complete set of policies and regulations.

16.3. Recent advancements in spent LIB recycling

The recycling of spent LIBs is at its infancy stage, and most of the recent proceedings are enabled in the lab research.

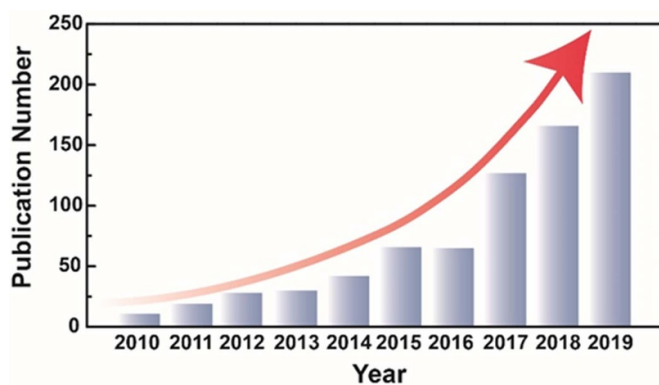


Figure 26. The number of articles published per year under the theme ‘spent LIBs recycling’ from 2010 to 2019. The results were obtained from the web of science on 1 July 2020, refined by ‘topic = recycle lithium-ion batteries’.

Intuitively, the number of publications per year has shown a rapid growth during the past decade (figure 26).

For the retired EV batteries, ‘re-use’ has been given a higher priority over ‘recycling’ [161]. In that case, the spent LIBs with considerable residue energy and no safety problem are directly used to power lower-level applications such as stationary storage power station and low-speed EVs. In the previous studies, diagnosis of internal conditions and potential failure of battery packs, modules and cells were emphasized for improving the safety of cascade utilization. The LIBs with diagnosis of ‘total failure’ are subject to recycling. The typical recycling process consists of two crucial steps: disassembly of LIB packs/modules and materials recycling at single-cell level. Disassembly of battery packs/modules with the aid of artificial intelligence is expected to minimize the risk of on-site human exposure and personal injury, while is also expected to reduce the labor cost. Nevertheless, due to the diversified battery configuration, it is unlikely to realize fully automatic battery disassembly in the near term. New methods and technologies on the cell-level materials recycling are equally important. The cathode holds the largest share of cost among all the components of a commercial LIB (figure 27), and is therefore of the highest value for recycling. During the cathode recycling process, rare metals are extracted from the cathode active materials via the pyro-/hydro-/bio-/electrometallurgical route [162], and are purified and collected in their salt forms. While pyrometallurgy and hydrometallurgy methods are commonly adopted for 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, were proposed based on the intrinsic properties and (electro)chemical degradation mechanism of the spent LIBs [163, 164]. Different from the traditional metallurgy approaches, the new strategies target specifically at recovery of cathode performance or restoration of cathode structures, which could show advantages over the traditional approaches in terms of cost and efficiency. To maximize the recovery value of the spent LIBs, recycling of other battery components was also claimed. For instance, it has been reported that the spent graphite anode can

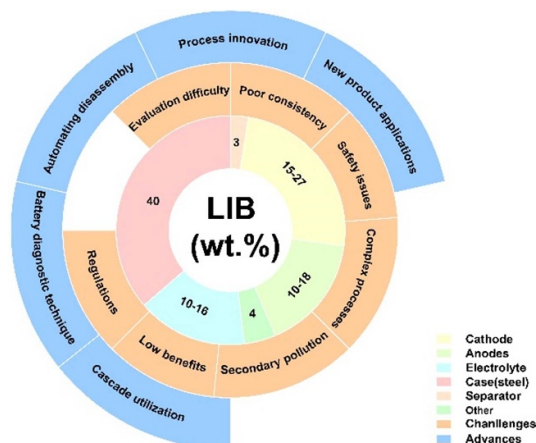


Figure 27. A schematic illustration that shows the composition by weight of a typical spent LIB, and challenges and advances regarding its recycling.

be recycled to manufacture high-performance Li-ion capacitors after calcination [165]. In addition, the electrolytes in the spent LIBs were extracted by supercritical CO₂ and reused in the LIBs production [166]. Innovations were also made to address the challenges in other crucial steps of the recycling process, for example, using deep eutectic solvents for separation of active materials from the metal collector foil during the pretreatment [167]. Finally, good quality control of the products are equally important for building long-term profitable recycling industry. Efforts have been made to broaden the market of recycling products, which includes introduction of more purification steps at an affordable cost, and finding of new applications that are not promptly demanding [168].

16.4. Concluding remarks

The recycling of spent LIBs, as an emerging field of study, has attracted considerable attentions owing to its necessity and urgency for enabling sustainable LIB manufacture. In determining the best route for LIB recycling, cost, economic benefits and environmental impacts must be taken into consideration (figure 27). Endeavors should be made on the innovation of current recycling technology and improvement of critical steps of the recycling process, for example, battery recovery, and remanufacture of key materials and modules/packs. Future research on LIB recycling is encouraged to be consistent with the development of the LIB technology, so that one can customize strategies for solving issues in specific battery systems. Finally, the government, the companies and even the consumers should work together to monitor the LIBs in their whole life cycle, so that the recycling of the spent LIBs can proceed in a more efficient way.

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