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Review Article

Ionic Liquid-Based Electrolytes for Aluminum/Magnesium/Sodium-Ion Batteries

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Developing post-lithium-ion battery technology featured with high raw material abundance and low cost is extremely important for the large-scale energy storage applications, especially for the metal-based battery systems such as aluminum, sodium, and magnesium ion batteries. However, their developments are still in early stages, and one of the major challenges is to explore a safe and reliable electrolyte. An ionic liquid-based electrolyte is attractive and promising for developing safe and nonflammable devices with wide temperature ranges owing to their several unique properties such as ultralow volatility, high ionic conductivity, good thermal stability, low flammability, a wide electrochemical window, and tunable polarity and basicity/acidity. In this review, the recent emerging limitations and strategies of ionic liquid-based electrolytes in the above battery systems are summarized. In particular, for aluminum-ion batteries, the interfacial reaction between ionic liquid-based electrolytes and the electrode, the mechanism of aluminum storage, and the optimization of electrolyte composition are fully discussed. Moreover, the strategies to solve the problems of electrolyte corrosion and battery system side reactions are also highlighted. Finally, a general conclusion and a perspective focusing on the current development limitations and directions of ionic liquid-based electrolytes are proposed along with an outlook. In order to develop novel high-performance ionic liquid electrolytes, we need in-depth understanding and research on their fundamentals, paving the way for designing next-generation products.

1. Introduction

The emerging attention to environmental pollution and fossil energy consumption and the rapid promotion and innovation in portable electronic devices have created a surge in demand for more efficient and clean energy storage and conversion devices. This in turn requires the suitable systems to make good use of energy storage in intermittent sources (solar or wind) and the electric or hybrid vehicle power [1]. The rechargeable batteries as efficient energy storage and conversion devices have witnessed the booming development hundreds of years with their intrinsic advantages and greatly advanced and enriched the human event process. Particularly, lithium-ion batteries (LIBs) have attracted considerable attention and dominated the commercial market and academic research in various battery systems in terms of high energy density, high operating voltage, and superior cycle stability [2, 3]. However, the rare lithium sources in the earth's crust of LIBs limit their market share in electronic device applications. In addition, the safety issues caused by thermal runaway also limit their practical application [4].

Fortunately, several new advanced battery chemistries and concepts (not depend on lithium) have emerged in recent years, which opens up new avenues for research. These chemicals come from varieties of different elements (sodium, magnesium, and aluminum), and these materials can be classed as a metal-ion battery concept. Studies of the chemical composition of these new batteries have shown that, although some lessons can be drawn from lithium-based batteries, new insights are needed based on the chemical properties of the elements themselves to develop a commercializable technology [5–7].

Electrolytes are ubiquitous and indispensable in rechargeable batteries [8]. In all cases, an important challenge is to develop electrolytes with good electrochemical properties, contribute to reduce battery aging, enhance battery safety, and allow the system to be charged and discharged electrochemically [2]. Some works have therefore concentrated on the functional electrolyte designs, and different ways are devoted to prepare usable electrolytes with excellent characters or properties, such as high ionic transport ability, excellent chemical/electrochemical stability, nonflammability, low viscosity, and economic cost [9]. Based on the battery concepts described above, ionic liquids have been placed on the electrolyte or electrolyte components. Herein, we make an overview of the development of ionic liquid-based electrolyte in sodium, magnesium, and aluminum batteries, including basic characteristics, interfacial properties, and reaction mechanism. Then, conclusive remarks based on technical difficulties, strategic analysis, and economic aspects are proposed along with an outlook.

2. Basic Principles of Ionic Liquids

Ionic liquids, known as room-temperature molten salts, a unique class of material, consist of organic cations and inorganic/organic anions [10–13]. It is worth mentioning that the electrostatic forces of the ions can be weakened and shielded through the separation of the large molecular ions in an ionic liquid, thus lowering the melting points. Ionic liquids have application value in several areas such as the organic synthesis solvents, chemical sensing, bioscience, green chemistry, and the promising electrical energy storage system (Figure 1). Ionic liquids may be used as solvents in many processes and as electrolytes in electrochemical devices. The widespread investigation and utilization of ionic liquids in an electrical energy storage area are benefited from their desirable properties such as tunable polarity and ionic conductivity, ultralow volatility, good thermal stability, and low flammability [14, 15] (Figure 1). The synergy among the electrostatic, hydrogen bonding, and hydrophobic that exist in ionic liquids provides powerful and tunable solvency properties. Ionic liquids exhibit enhanced safety due to their negligible volatility and low flammability as well as improved feasibility benefited from their wide electrochemical window (ESW) and excellent thermal stability. The coexistences of electrostatic charge, aromatic groups, and alkyl segments in the ionic structure are beneficial to the enhanced affinity of ionic liquids for inorganic and organic materials, which facilitates the preparation of composite cell material, improves interfacial properties, and produces ordered nanostructures [2].

Generally, since an alkyl group is present around the charging center, the cation tends to be large and bulky, and this is subjected to a certain degree of charge protection. Anions generally provide a conformational isomer with close energy and undergo charge delocalization due to the possibility of several resonant structures. We classify some common cations and anions used in batteries (Figure 1). Among the anions, bis(trifluoromethanesulfonyl)imide (TFSI) and bis(oxirosulfonyl)imide (FSI) are probably the most popular along with their high ionic conductivity and stability and good solid electrolyte interface- (SEI-) forming ability. The coordination and combination of ions dominate the ionic liquid characteristics, so ionic liquid can be customized according to the specific application [5]. For example, depending on their composition, ionic liquids have different classes, essentially including aprotic (suitable for lithium batteries and supercapacitors), protic (suitable for fuel cells), and zwitterionic (suitable for ionic-liquid-based membranes) types, each suitable for a particular application (Figure 1). The investigations of various commercial ionic liquids clearly demonstrate the versatility of such material and only represents a small fraction of the theoretically possible numbers of ionic liquids.

3. Advantages of Ionic Liquids as Electrolytes

Electrolyte materials are particularly crucial for the safety and electrochemical performances of advanced battery technologies. The desirable electrolytes are expected to possess several abovementioned outstanding characters. Currently, in most commercial LIBs, the standard electrolyte used is still a mixture of cyclic and linear carbonates, for example, ethylene carbonate (EC)/dimethyl carbonate (DMC) coupled with lithium hexafluorophosphate ($LiPF_6$) [16, 17]. These organic liquid electrolytes (OLEs) generally show high ionic conductivity and good solid electrolyte interphase- (SEI-) forming ability. However, they suffer from significant downfalls particularly owing to their chemical stability and safety. The attractive properties of ionic liquids, especially the high electrochemical stability of some cationic and anionic types, make it suitable for application in high energy electrochemical devices such as lithium batteries. Moreover, the low volatility and flammability properties of ionic liquids can be regarded as their key advantages, thus providing the possibility of enhanced safety and stability.

Despite these advantages, ionic liquid-based battery systems still have some significant drawbacks, primarily high viscosity and cost. Compared to organic electrolytes, relatively high viscosity and thus low ionic conductivity limit the rate performance of ionic liquid-based battery systems. In addition, the current price of ionic liquids is too high, limiting its large-scale application in batteries. But strategies such as extending equipment life and economies of scale can help solve this problem.

In applications requiring long life and increased thermal stability, ionic liquid-based electrolytes are still hoping to overtake OLEs. The performance of the LIB prototype indicates that batteries based on ionic liquid-based electrolytes exhibit good cycle stability and capacity at low rates. In addition, ionic liquids as well as the assembled LIB can adapt to extreme conditions, such as ultrahigh vacuum spaces without heavy reinforced casings, which benefited from the wide available temperature range and low volatility of ionic liquids [5].

In recent years, post-lithium-ion battery technologies have attracted much attention, leading to many different approaches to exploring suitable electrolyte problems. The emerging development of ionic liquid-based electrolytes in aluminum, magnesium, and sodium battery chemistries is worthy to be explored and discussed.

4. Ionic Liquids as Electrolytes for Aluminum Chemistry

According to its lightweight and the three-electron transfer electrode reaction ($Al^{3+}+3e^{-}\leftrightarrow Al$), as summarized in

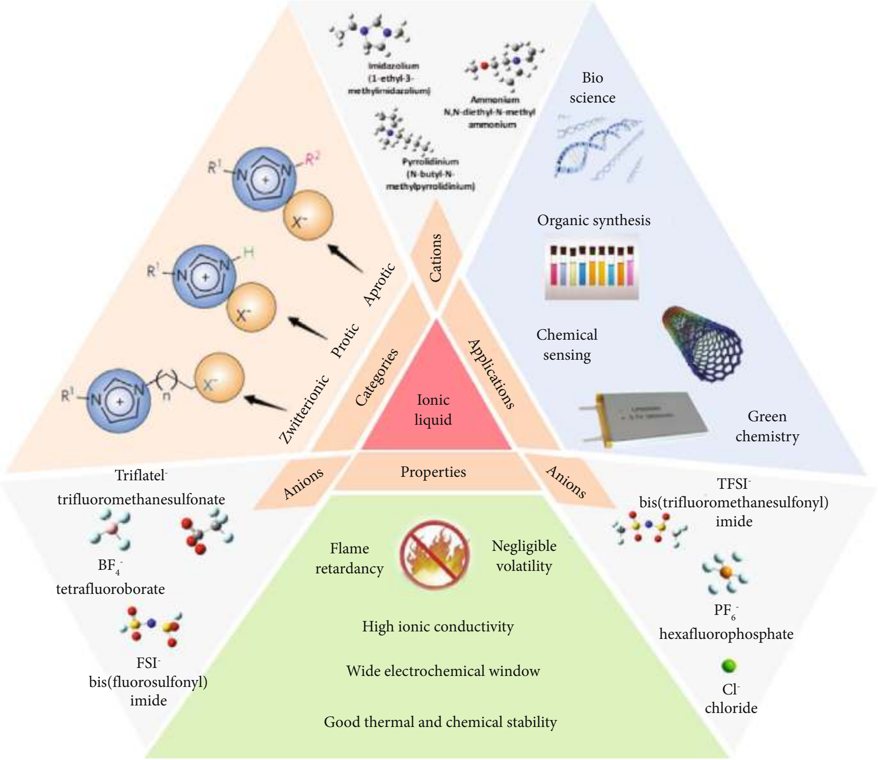


Figure 1: Categories, applications, properties, and compositions of ionic liquids.

Figure 2(a), aluminum metal not only possesses the highest volumetric capacity (8040 mAh g^{-1}) but also the gravimetric capacity (2980 mAh g^{-1}) is comparable to that of lithium metal. Additionally, aluminum metal is honorably certified as the most abundant metal resource in the heart's crust, thus leading to its fairly low price. More importantly, aluminum metal can be exposed to the air, making cell fabrication easier and more convenient and extremely improving the safety of electrochemical storage systems.

4.1. Ionic Liquid-Based Electrolytes for AIBs. For LIBs, organic solvent-based electrolytes are widely used. However, it does not apply for the AIB system. Since aluminum ions carry three positive charges and possess high surface charge density, the Coulombic interaction between cation and anion is enhanced, thereby significantly decreasing the solubility of the Al ion salt in the organic solvent, which is not conducive to the normal ionic transport of the electrolyte. The ether solvents can increase the solubility of Al ion salt with a cation-ether complex under the strong ion-dipole interaction. However, the incidental high electrodeposition polarization can be caused owing to the strong desolvation activation energy [19]. In addition, the common fluorine-containing aluminum salt easily forms a passive layer on the surface of an aluminum anode, thereby inhibiting the reversible electrostripping/deposition in an organic solvent [20, 21]. These problems make it difficult to achieve a viable electrolyte design. Therefore, conventional electrolyte selection strategies used in monovalent battery systems are not suitable for aluminum battery systems.

In fact, at the early stage, an aqueous electrolyte is firstly applied in aluminum battery systems (Al/AgO [22], Al/H_2O_2 [23], and Al/S [24]) due to its low cost, easy to operate, and environment friendly. However, the fatal drawbacks such as passive oxide film formation, hydrogen side reactions, and anode corrosion impede the applications of aluminum battery systems [25]. In order to ensure the reversible plating/stripping of Al, high-temperature molten salts (>100°C, e.g., NaCl-$AlCl_3$) are utilized as electrolyte owing to the fast ion transport under the high temperature [26, 27]. In 1972, a molten salt electrolyte was applied in Al/Cl_2 battery and the carbon cathode was used as the gas diffusion electrode to ensure the solid-liquid-gas interface reaction [28]. Then, in 1980, a high-temperature molten salt electrolyte was introduced to rechargeable battery systems, in which sulfides (such as FeS_2 and Ni_3S_2) were used as cathode materials [29, 30]. The system can be known as the prototypes of AIBs. Unfortunately, high-temperature molten salt batteries require extreme conditions, accompanied by evolution of Cl_2 and disintegration of cathodes, thereby limiting the development of aluminum secondary batteries [31].

Therefore, to make the rechargeable aluminum batteries practical, the design of a suitable electrolyte is crucial. Fortunately, ionic liquids have gained our attention. The attractive properties of ionic liquids, especially the high electrochemical stability of some cationic and anionic types, make it suitable for application in high energy electrochemical devices. The widespread investigation and utilization of ionic liquids in an electrical energy storage area are benefited from their

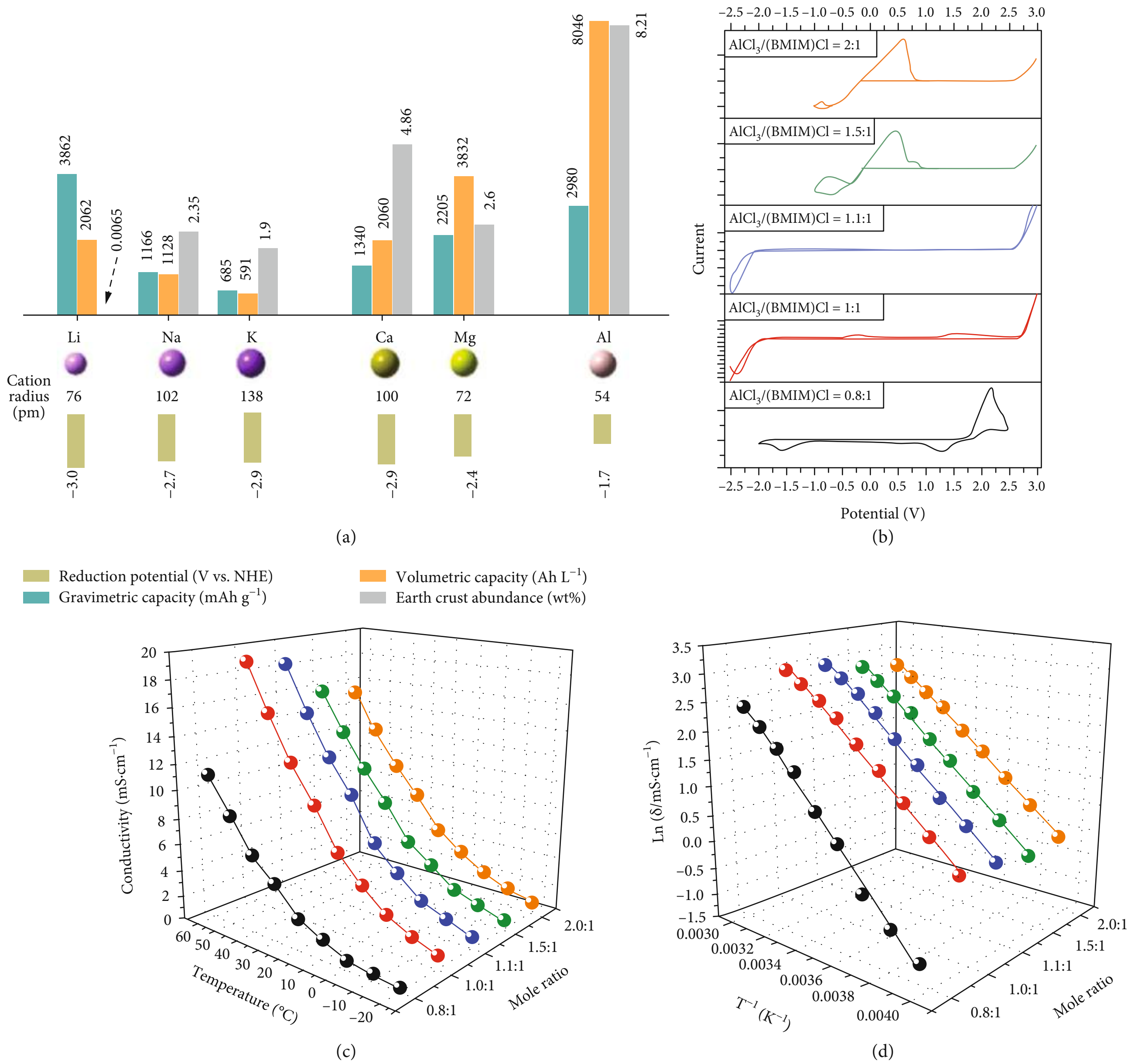


FIGURE 2: Basic properties of aluminum metal and AlCl$_3$/[BMIM]Cl ionic liquid-based electrolyte. (a) Specific capacities, standard reaction potentials, abundances of elements in the Earth's crust, and cation radii for common metal elements in electrochemistry. (b) Cyclic voltammogram, (c) conductivity-temperature (δ-T) curves, and (d) Arrhenius fitted curves of AlCl$_3$/[BMIM]Cl ionic liquid electrolytes [18].

desirable properties such as tunable polarity and ionic conductivity, ultralow volatility, good thermal stability, and low flammability. Moreover, the low volatility and flammability properties of ionic liquids can be regarded as their key advantages, thus providing the possibility of enhanced safety and stability. In addition, the ion-solvent complex formation with low stability promotes the rapid solvation/desolvation of aluminum ion resulting in superior transport properties. The coexistences of electrostatic charge, aromatic groups, and alkyl segments in the ionic structure are beneficial to the enhanced affinity of ionic liquids for inorganic and organic materials, which facilitates the preparation of composite cell material, improves interfacial properties, and produces ordered nanostructures. Thus, the ionic liquid-based electrolyte enables highly reversible stripping/plating of aluminum leading to the increasingly competitive AIB application in secondary batteries [32].

Instead of sodium and potassium cations in high-temperature molten salt, ionic liquid usually concludes long-chain organic substances as cations to decrease melting point. The organic cations can be imidazolium or pyrrolidinium, in particular imidazolium cations bearing various alkyl side chains, such as 1-ethyl-3-methylimidazolium (EMIm) or 1-butyl-3-methylimidazolium (BMIm). The anions can be halogens, like Cl$^-$ (most used in AIBs), Br$^-$, I$^-$, or organic anions. Then, the general ionic liquid electrolytes for AIBs can be obtained by mixing the ionic liquid and AlCl$_3$ [33–38].

A detailed investigation on the various molar ratio $AlCl_3$/[BMIM]Cl has been reported by our group in 2015 [18]. Notably, the molar ratio between the $AlCl_3$ and ionic liquid is the dominant factor governing the electrochemical performance and the whole design of the cell. As the molar ratio of $AlCl_3$ increases, the anions in the ionic liquid electrolytes also undergo a changing process of $Cl^- \rightarrow AlCl_4^- \rightarrow Al_2Cl_7^- \rightarrow Al_3Cl_{10}^-$. It is worth noting that only when the molar ratio of $AlCl_3$ is larger than 1, that is, the ionic liquid electrolyte contains $Al_2Cl_7^-$ anion, the aluminum metal can be reversibly electrostripping/deposition. Because the $Al_2Cl_7^-$ anion possesses an asymmetry structure leading to its high electrochemical activity. As shown in Figure 2(b), the different anions in an ionic liquid electrolyte can also cause the different anode limiting potentials owing to the various corresponding anodic limiting reactions as follows:

$$4AlCl_{4^-} - 2e^- \rightarrow Cl_2 + 2Al_2Cl_{7^-} \tag{1}$$

$$6Al_2Cl_{7^-} - 2e^- \rightarrow Cl_2 + 4Al_3Cl_{10^-} \tag{2}$$

$$2Cl^- - 2e^- \rightarrow Cl_2 \tag{3}$$

Equations (1), (2), and (3) represent the oxidation reactions with a molar ratio equal, higher, or less than 1 : 1. As for cathode limiting reactions, a pair of redox peaks attributed to reversible Al stripping/deposition appears around 0 V when the molar ratio is higher than 1.5 : 1, which reinforces the importance of $Al_2Cl_7^-$ anion. The ionic conductivities of various molar ratio $AlCl_3$/[BMIM]Cl ionic liquid electrolytes are investigated as shown in Figures 2(c) and 2(d). At room temperature, all the ionic liquid electrolytes exhibit the ionic conductivities of 10^{-3} S cm^{-1}, which are adequate for the application in AIBs. The conductivities reach the highest when the $AlCl_3$/[BMIM]Cl molar ratio is 1 : 1 and then decrease with increasing molar ratio [18].

4.2. Ionic Liquid-Based Electrolyte/Electrode Interface Interactions

4.2.1. Ionic Liquid-Based Electrolyte/Cathode Interface Interactions. In an aluminum-ion battery based on chloroaluminate ionic liquid electrolyte, the interfacial reaction between cathode and electrolyte contains three processes, namely:

(1) the dissociation process of polyanions near the surface of the cathode

(2) the migration of dissociated polyanions from an electrolyte to the surface of the cathode

(3) the cathode accepts electrons to form an external circuit

Usually, these three processes are collectively referred to as a charge transfer process. In 2018, Yang et al. studied the effect of dissociation activation energy on the entire electrochemical process in aluminum-sulfur batteries (Figure 3(a)) [39]. In fact, in all multistep electrochemical reactions, the reaction process with the highest activation energy is the rate-determining step (Figure 3(b)). The ease or complexity of the dissociation reaction of anions, as a rate-determining step, does significantly affect the kinetic reaction rate due to the activation energy, which would intuitively determine the charge/discharge performance [37]. The researchers chose two different structures of anions and calculated the activation energy barriers of the two anions. As shown in Figures 3(c)–3(f), the results show that the dissociation activation energy per mole of brominated polyanion $Al_2Cl_6Br^-$ is 71 meV lower than that of $Al_2Cl_7^-$. According to the Arrhenius formula, the dissociation reaction rate of $Al_2Cl_6Br^-$ is also 15 times faster than that of $Al_2Cl_7^-$. This result is also verified by the Tafel equation. In the experiment, the electrolyte system with the anion of $Al_2Cl_6Br^-$ has a higher specific capacity. This work helps us understand the effect of the dissociation process of polyanions on electrochemical kinetics.

4.2.2. Ionic Liquid-Based Electrolyte/Anode Interface Interactions. The surge of AIBs has attracted research into Al metal anode, although cation-type AIBs do not face the urgent need for anode engineering because they have not been able to survive for long time cycles. Several works showed that the anode reaction significantly affected the electrochemical performance of the AIB [40–43]. Usually, there is a dense and Al-ion nonconductive oxide film (Al_2O_3) on the surface of the aluminum metal, which controls the reactions occurred on the interface between Al metal and electrolyte. In 2015, our group reported that a suitable $Al_2Cl_7^-$ concentration would cause slight pitting on the Al metal anode, which helped to properly remove the oxide film on the Al metal anode and improve charge/discharge electrochemical performance [18]. Subsequent in our another study, a noncorrosive and moisture-stable [BMIm]OTF-Al$(OTF)_3$ electrolyte was performed in place of the corrosive [EMIm]Cl-$AlCl_3$ electrolyte, resulting in no electrostripping/deposition activity [44]. However, when the Al metal anode is pretreated in a corrosive [BMIm]Cl-$AlCl_3$ electrolyte, it exhibits electrochemical activity (Figures 4(b) and 4(c)). In fact, the oxide film naturally formed on the surface of the aluminum is so dense that the ionic liquid-based electrolyte is impermeable. However, corrosive $Al_2Cl_7^-$ corrodes and creates cracks in the oxide film, resulting in contact between the electrolyte and the active aluminum, thereby achieving electrostripping/deposition activity, as shown in Figure 4(a). This conclusion is consistent with our previous research.

However, the crystalline structure of the oxide film or the distinct property compared to bulk Al is uncertain. The surface structure of Al_2O_3 is highly defective (oxygen vacancies) and can be modified while immersed in a solution [45]. Thus, the thickness and subtle structure of the oxide film depend on the solution species, greatly affecting the interfacial reaction kinetics [46]. Choi et al. studied the electrochemical properties of Al metal anodes with two different thickness oxide films. The results show that the thinner electropolished aluminum foil surface is more susceptible to erosion by aluminum chloride complexes and shows higher and more stable capacity. This is due to its greater electrochemical reaction area and better contact with active aluminum ions [41]. They

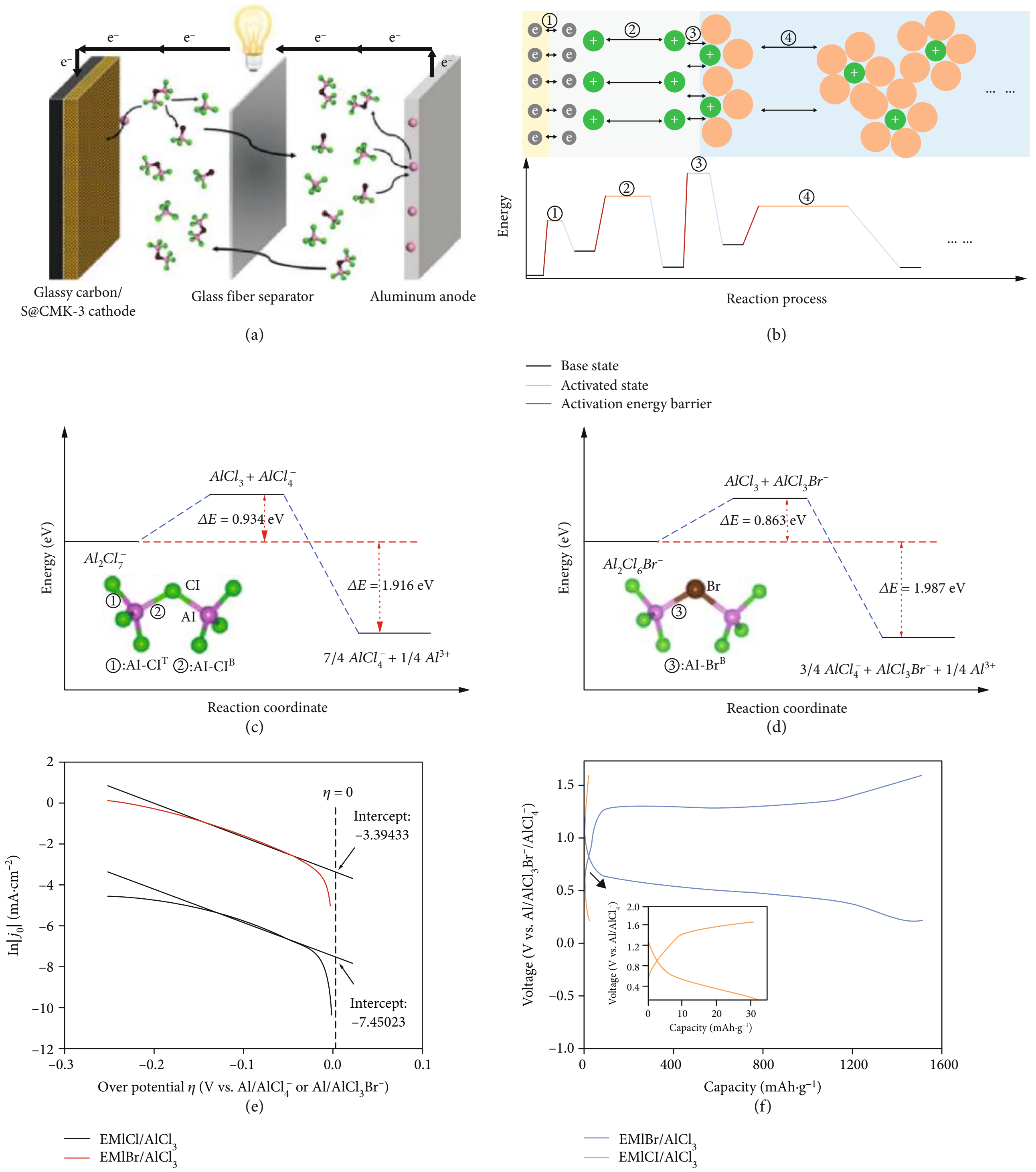
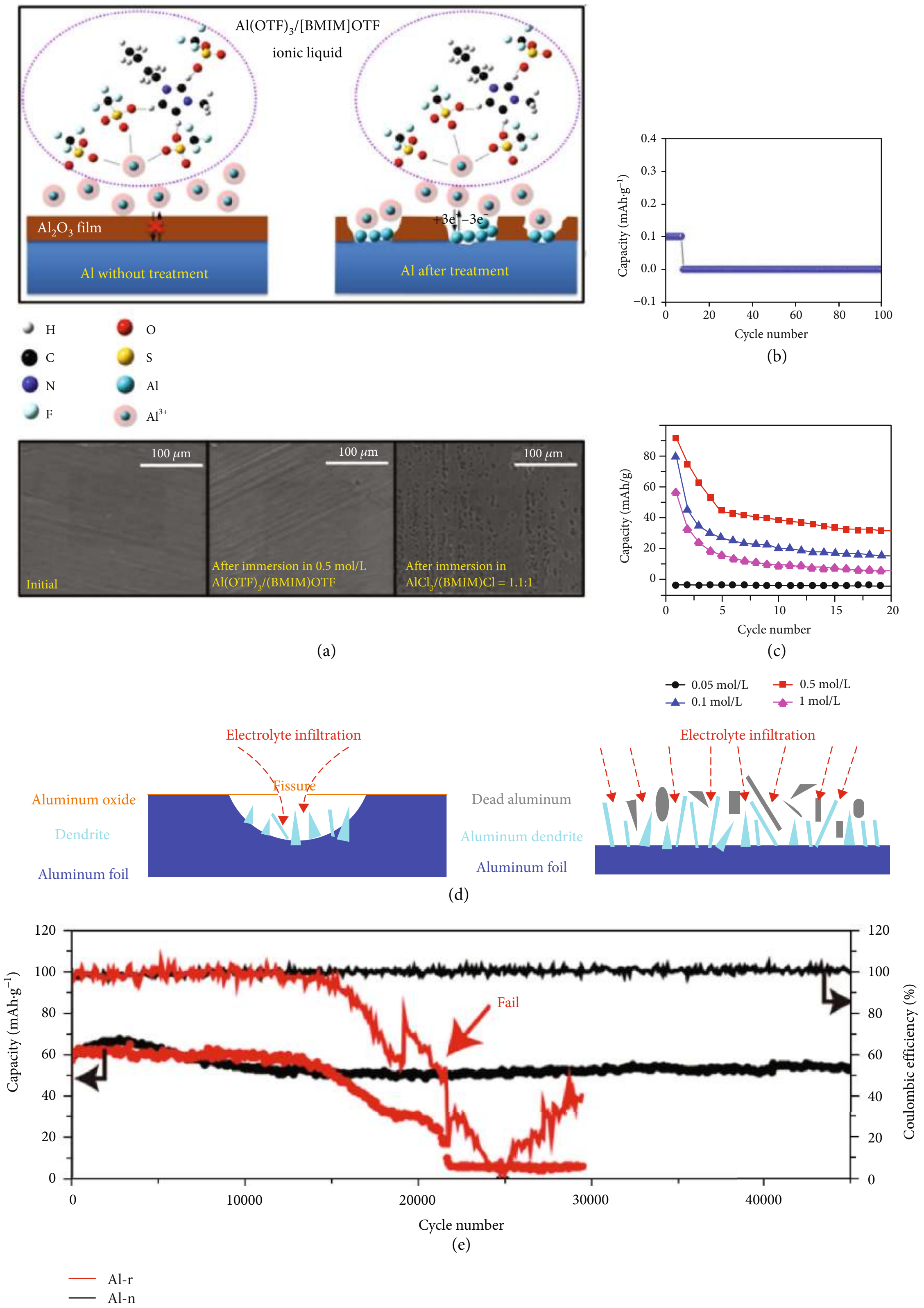


Figure 3: The working mechanism of the Al-S battery with NBMPBr/AlCl$_3$ electrolyte. (a) The discharge process of an Al-S battery with NBMPBr/AlCl$_3$ electrolyte. (b) A representation of the relationship between activation energies and electrochemical process. Process 1: electron transfer/redox reaction; 2: solid diffusion; 3: solvation/desolvation; 4: liquid diffusion. (c) Energy profiles of the dissociation reactions of $Al_2Cl_7^-$ and (d) $Al_2Cl_6Br^-$ anions. The atomic structures of both anions are shown. (e) Tafel plots of Al electrodeposition in [EMIm]Br-AlCl$_3$ and [EMIm]Cl-AlCl$_3$ electrolytes. (f) Charge/discharge curves of Al-S batteries with two electrolytes at 25 mA g^{-1} [39].

also presuppose surface reconstruction theory to explain the important role of oxide film at the anode/electrolyte interface [43]. Surprisingly, the reconstituted Al_2O_3 oxide film no longer blocks the migration of aluminum ion, which will be further explained in the future work. Here, the solid electrolyte interface (SEI) becomes the key factor in the anode reaction and more detailed investigations about its composition and structure need to be further conducted.



(a) (b) (c) (d) (e)

Figure 4: Ionic liquid-based electrolyte/aluminum interface and aluminum dendrites. (a) Above: schematic diagrams of Al deposition/dissolution on the surface of untreated and treated Al anode; below: SEM images of Al foils before and after immersion in 0.5 mol/L Al(OTF)$_3$/[BMIM]OTF and AlCl$_3$/[BMIM]Cl=1.1 : 1 for 24 h. Cycling performance of rechargeable aluminum batteries using Al(OTF)$_3$/[BMIM]OTF ionic liquids (b) using untreated Al anode (c) using treated Al anode [44]. (d) Analysis of the mechanism of the aluminum foil protected by the oxide film. (e) Cycling performance of aluminum-graphene full cells using Al-n or Al-r anodes [38].

Dendrite formation is considered as the most adverse problem for metal anodes, which can produce a short circuit, resulting in the capacity fade and dead cell. However, there are few reports focused on aluminum dendrite formation. Recently, Chen et al. confirmed the existence of aluminum dendrite and proposed that the natural aluminum oxide film on the surface of aluminum anode in AIB can effectively inhibit the growth of aluminum dendrite and stabilize the interface between anode and electrolyte [40]. As shown in Figure 4(d), by limiting the aluminum dendrites below the aluminum oxide protective layer, it is possible to effectively prevent the aluminum anode from disintegrating during the repeated aluminum plating/stripping reaction, thereby obtaining superior cycling performance and an almost complete and flat aluminum foil after cycling (Figure 4(e)).

4.3. Reaction Mechanisms in Ionic Liquid-Based Electrolytes for AIBs. Various materials are performed to realize practical aluminum storage systems based on ionic liquid electrolyte such as carbon materials [47–62], oxide (transition metal oxide) [63–68], transition metal sulfides [69–76], selenides [77–79], conducting polymers [80], Prussian blue analogs [81–83], and sulfur [39, 84–87]. The reaction mechanisms of electron transfer with different types in AIBs based on an ionic liquid-based electrolyte are discussed below. In general, there may be two reversible energy storage mechanisms: intercalation and conversion reactions. Among them, according to the intercalated ions, the intercalation reaction can be further divided into polyanion and Al-ion intercalation.

4.3.1. Intercalation Reactions of Polyanions in Ionic Liquid-Based Electrolyte. The intercalation reaction mechanism in the ionic liquid electrolyte-based AIB means that the movable guest ions (Al-containing cations or polyanions) are reversibly intercalated into the layered host crystal lattice. Moreover, the electrolyte also determines which species can be intercalated into the positive electrode. Instead of intercalating Al^{3+} ions, the polyanion $AlCl_4^-$ complex present in the ionic liquid was intercalated into the positive electrode. The intercalation reaction of polyanion is important and it usually exhibits superior electrochemical performance by assembling an aluminum battery. Depending on the geometry of the intercalation material, the polyanion intercalation reaction is carried out by structural flexibility and free adjustment of the spacing of the host lattice layers. Thus, during the charge/discharge process, this kind of reaction is along with a series of reversible structural changes in the host lattice [25]. Although the anion type AIBs exhibit superior electrochemical performance, their monovalent chemistry undoubtedly hampers the high capacity aluminum battery system design, and most of the research materials only show relatively low capacity. Moreover, large sizes of polyanions cause large volume expansion, which can result in irreversible damage to the battery.

The most commonly used ionic liquid-based electrolyte in AIBs is $[EMIm]Cl–AlCl_3$, which is formed by mixing $AlCl_3$ and [EMIm]Cl with a molar ratio of 1.3 : 1, where the ions present are $[EMIm]^+$, $AlCl_4^-$, and $Al_2Cl_7^-$. Obviously, there is no isolated Al^{3+}, so if the insertion reaction occurs, $AlCl_4^-$ is the most likely reagent because of its smallest ionic radius [88], which results in a lower steric hindrance than the other two ions.

Carbons (graphite, graphene, or amorphous carbon) have acted as intercalation host compounds with $AlCl_4^-$. Taking graphite as an example, as an attractive layered material, graphite has the ability to carry anions besides cations (an acceptor or donor of electrons) [89]. Interestingly, graphite materials can introduce another type of intercalation electrochemistry in the ionic liquid electrolyte-based AIBs. In a conventional AIB system using ionic liquid as an electrolyte, when a graphite material is used as the cathode, the polyanion $AlCl_4^-$ in the electrolyte is inserted into the host structure, and electron holes are generated in the bonded π band, thereby forming an acceptor type graphite intercalation compound (GIC). In addition to carbon materials, conductive polymers are also considered to deintercalate polyanions during charge and discharge. The cathode and anode reactions in carbon materials can be expressed as follows:

$$\text{Cathode}: \mathrm{nC} + \mathrm{AlCl}_{4^-} \leftrightarrow \mathrm{C_n[AlCl_4]} + e^- \tag{4}$$

$$\text{Anode}: 4[\mathrm{Al_2Cl}_{7^-}] + 3e^- \leftrightarrow \mathrm{Al} + 7[\mathrm{AlCl}_{4^-}] \tag{5}$$

4.3.2. Intercalation Reactions of Al-Ions in an Ionic Liquid-Based Electrolyte. Except for polyanions, Al-ions can also be deintercalated by some other certain types of materials. Due to the deintercalation of trivalent aluminum ions in the cathode materials, cation type AIBs theoretically exhibit higher specific capacity, making them attractive for researchers. Recently, vanadium oxide (V_2O_5 [65]), Chevrel phase (Mo_6S_8 [76]), cubic sulfide ($CuTi_2S_4$ [90]), and layered disulfide (TiS_2 [90]) were shown to make reversible deintercalation of aluminum ions. These cathode materials usually feature with large interstitial sites and diffusion path for ion insertion. The proposed intercalation reactions can be summarized as follows:

$$\text{Cathode}: \mathrm{M} + 4\mathrm{n}[\mathrm{Al_2Cl}_{7^-}] + 3\mathrm{n}e^- \leftrightarrow \mathrm{Al_nM} + 7\mathrm{n}[\mathrm{AlCl}_{4^-}] \tag{6}$$

$$\text{Anode}: 4[\mathrm{Al_2Cl}_{7^-}] + 3e^- \leftrightarrow \mathrm{Al} + 7[\mathrm{AlCl}_{4^-}] \tag{7}$$

where M represents the cathode materials.

The schematic illustration of a possible cathode reaction process in the ionic liquid-based electrolyte is proposed in Figure 5. During the charging process of the graphite cathode material, the generation of chlorine gas is also exhibited. As reported by Shi et al., chlorine generation occurs at about 2.4 V versus Al, and in most publications on carbon-based cathode materials, the charge cut-off potential is higher or very close to 2.4 V versus Al. Therefore, it is a reasonable problem that chlorine may be generated during charging on the carbon-based cathode [91]. In fact, in the early study of the use of graphite as a cathode material for rechargeable Al batteries [92], proposals have been made to use chlorine as an intercalation material in graphite. Yang et al. also recently reported the incorporation of chlorine into graphite

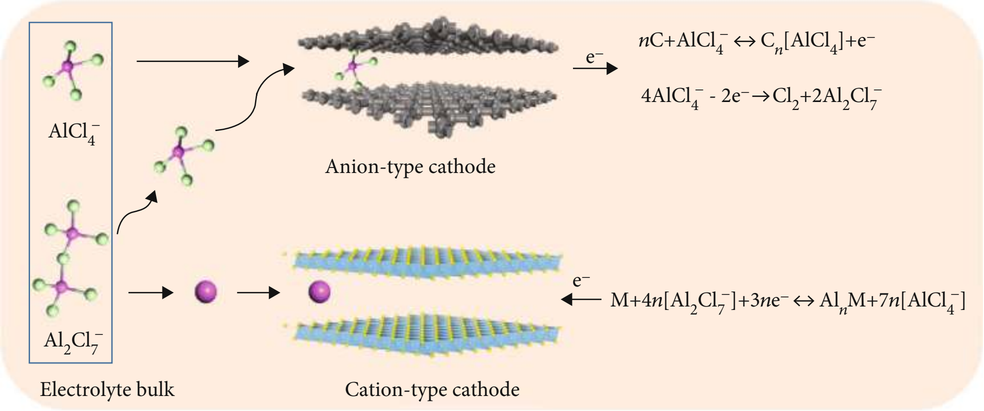


FIGURE 5: Schematic illustration of a possible cathode reaction process in the ionic liquid-based electrolyte.

from chloride-containing electrolytes [93]. Considering that the potential of chlorine generation is closely related to the charge potential, irreversible charge capacity, and severe self-discharge behavior, it is reasonable to assume that chlorine is involved in the intercalation and may not be stably hosted.

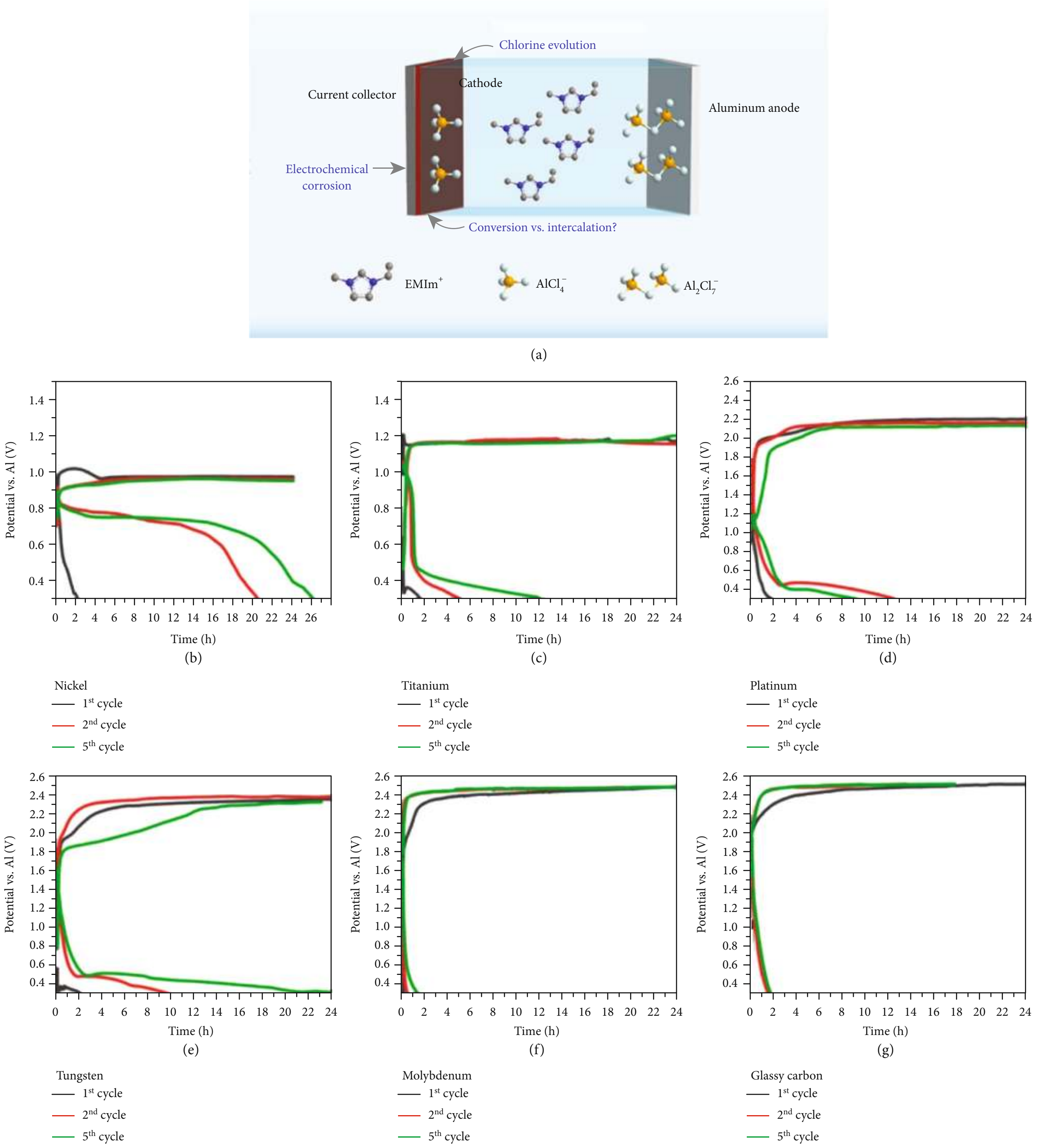
4.4. Challenges of Ionic Liquid-Based Electrolytes for AIBs. Although ionic liquid-based electrolytes show many possibilities in aluminum battery system applications, there are still some problems remaining (Figure 6(a)).

The first obstacle is the reversible/irreversible side reactions that occur on the anodic and cathodic sides, which can seriously affect the battery charge-discharge behaviors.

On the cathode side, it has been reported that the electrophilic element of the VI A group and the nucleophilic C_2 carbon in the imidazole ring in the cation can react with each other, thereby causing a side reaction of the cathodic side [94]. The reactions are present in most aluminum-sulfur batteries [21]. In addition, the reduction of the chloroaluminate-based ionic liquid on the cathode surface may be another nonnegligible potential side reaction. Recently, some studies reported that in the three-electrode system, the reduction potential of the electrolyte on the glassy carbon working electrode reached 0 V (vs. $Al/AlCl_4^-$) [18]. However, during the discharge process, the reduction potential of the electrolyte can be increased due to the catalytic activity of the transition metal oxide/sulfide cathode materials to some extent [95, 96]. That is to say, the side reaction of electrolyte reduction may occur during the discharge process. To date, although no direct evidence confirms that the catalytic activity of the cathodes can contribute to the reduction of electrolyte, the "excess capacity" phenomena have been explored, which may be due to the reduction of electrolyte caused by the cut-off discharge voltage less than 0.1 V [74, 79].

On the anode side, firstly, during the charge and discharge process, side reactions based on chloroaluminate ionic liquid electrolyte are prone to occur. For example, $AlCl_4^-$ will be oxidized by $4AlCl_4^- \rightarrow 2Al_2Cl_7^- + 2e^- + Cl_2$ to form toxic Cl_2, resulting in relatively low Coulombic efficiency for AIBs [18, 97–98]. Secondly, since the chloroaluminate-based ionic liquid electrolyte is extremely corrosive, the cell shells can be eroded, thereby causing side reactions [99, 100]. In 2013, the electrochemical stability of the former electrolyte was reported by Reed and Menke [99]. Interestingly, even if there is no cathode material in the battery, the charge and discharge platforms of the corresponding redox peaks can still be seen. Further analysis indicates that this reversible capacity resulted from the redox reaction of Fe and Cr with $Al_2Cl_7^-$. After that, the stainless steel is to be avoided in AIBs, while the shells are made of polytetrafluoroethylene (PTFE) or pouch cells instead. It has also been suggested to use the expensive molybdenum instead of stainless steel [60, 72, 101, 102]. Thirdly, the selection of current collector is critical to the assembly of the battery, and some usual current collectors can react with the ionic liquid-based electrolyte to produce side reactions. Shi et al. [91] studied the electrochemical stabilities of different current collectors in the electrolyte during charge and discharge. The galvanostatic discharge-charge (reduction-oxidation) curves of various conductive substrates are shown in Figures 6(b)–6(g). The electrochemical oxidation of nickel (Ni) results in a distinct discharge platform at 0.8 V (vs. Al/Al^{3+}) with high apparent capacity and repeatability in subsequent discharges. It is obvious that Ni and Ni-containing alloys are not suitable for use as current collectors for cathode materials. The same applies to titanium (Ti), platinum (Pt), and tungsten (W). However, molybdenum (Mo) and glass carbon (GC) can be stably present in the ionic liquid-based electrolyte without side reactions. Thus, it can be concluded that Mo and GC can be considered as the better current collectors of the cathode materials.

The second obstacle is the compatibility of ionic liquid electrolyte with cathode material and binder. Firstly, the compatibility of cathode material (especially the transition metal oxide/sulfide) with the ionic liquid electrolyte is almost ignored in the current literature reports. But a recent study showed that vanadium pentoxide (V_2O_5), one of the most common cathode materials for AIBs, had been certified to dissolve in Lewis acid ionic liquid electrolyte and form new vanadium compounds [91]. In addition, iron sulfide (FeS_2) is also reported to be soluble in the electrolyte [74]. Based on the above results, we can speculate that there may be the same cases for other cathode materials reported in the



(a)

(b)

(c)

(d)

(e)

(f)

(g)

Figure 6: Potential issues in AIBs. (a) Illustration of the potential issues overlooked in rechargeable aluminum battery research. Galvanostatic discharge-charge (reduction-oxidation) curves of various conductive substrates including (b) nickel, (c) titanium, (d) platinum, (e) tungsten, (f) molybdenum, and (g) glassy carbon versus aluminum under a current of $1.78 * 10^{-2}$ mA cm^{-2} at room temperature [91].

literature. Thereby, in future research, the compatibility between cathode material and electrolyte should be tested in advance. Secondly, our group reported that polymeric binders such as polyvinylidene fluoride (PVDF) were incompatible with chloroaluminate-based ionic liquid electrolyte [18]. The PVDF power is slowly added to the $AlCl_3$/BMIMCl, and the color of the electrolyte changes accordingly, which may be attributed to the reaction of PVDF with $Al_2Cl_7^-$ in the electrolyte.

Finally, the chloroaluminate-based ionic liquid electrolytes are highly hygroscopic, viscous, and expensive, all of which exacerbate their serious limitations as high-efficiency battery electrolytes [103–106]. These shortcomings may hinder the design of high-performance AIBs and suppress the commercial applications of ionic liquid-based electrolytes for AIBs.

4.5. Future Perspective. As mentioned earlier, the side reactions of the Al battery and the compatibility of the electrolyte with the cathode material and the binder are all caused by the unique corrosion of the ionic liquid electrolyte [107]. In order to inhibit the corrosive nature of the electrolyte, the corrosive chloride ions can be replaced by other ions, such as triflate (OTF^-) and bromide (Br^-). Wang et al. used 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([BMIm]OTF) mixing with $Al(OTF)_3$ to obtain a noncorrosive ionic liquid with water stability [44]. After the oxide film is removed by preimmersing the Al anode in the ionic liquids, a noncorrosive electrolyte can also be used in the RAB. Through this research, a new method is proposed. A corrosive $AlCl_3$-based electrolyte is firstly used to create a suitable channel for Al^{3+}, and then, a noncorrosive $Al(OTF)_3$ based electrolyte is used to obtain the stable Al/electrolyte interface. In addition, Br^- has also been used to replace Cl^- to inhibit the corrosion reactions [39]. Surprisingly, the use of Br^- also accelerates the kinetics of the electrochemical process of aluminum-sulfur batteries. Al-S cells have poor reversibility in chloroaluminate-based ionic liquid electrolytes, mainly due to the slow kinetics determined by the decomposition of $Al_2Cl_7^-$ to Al^{3+}. Density functional theory (DFT) calculations show that the dissociation reaction of $Al_2Cl_6Br^-$ is easier than that of $Al_2Cl_7^-$ because the dissociation energy barrier of $Al_2Cl_6Br^-$ is lower. Therefore, a 15 times accelerated dissociation rate can be achieved by replacing all $Al_2Cl_7^-$ with $Al_2Cl_6Br^-$ in the electrolyte. The N-butyl-N-methyl-piperidine ($NBMP^+$) cations instead of EMI^+ also avoid side reactions between EMI^+ and polysulfides. Therefore, the accelerated Al-S battery can be successfully achieved by using $NBMPBr/AlCl_3$ electrolyte. As for the corrosion of the shell by the electrolyte, a new coin-cell-based AIB configuration has been prepared by applying conductive polymer PEDOT coating to prevent corrosion [54].

In addition, we know that in the $AlCl_3$-containing imidazole-based ionic liquid, the dominant $Al_2Cl_7^-$ may be the only active species in aluminum deposition, and at a certain concentration, the passivation film can be appropriately removed, whereas the relative concentration of $Al_2Cl_7^-$ is susceptible to dynamic equilibrium (e.g., $2AlCl_4^- \leftrightarrow Al_2Cl_7^- + Cl^-$ [108], $K \approx 10^{-13}$), which promotes the conversion of $Al_2Cl_7^-$ to $AlCl_4^-$. In turn, the unique behaviors can cause the anodic reaction to be filled with charge and mass transfer entangled with the species. How to control the species is the key to maintaining the anode reaction cycle life. The electrolyte additive toluene is well utilized with the aim to improve the aluminum deposition kinetics [109, 110].

Since the commonly used $AlCl_3$-containing imidazole-based ionic liquid is expensive, corrosive, sensitive to water and air, and features with a narrow electrochemical window, it possesses several difficulties in commercial application for AIBs. Therefore, novel safe, nontoxic, and stable alternative electrolytes are urgently needed and this electrolyte must be able to achieve a fast and efficient aluminum stripping/deposition reaction. In addition, a suitable electrolyte must have appropriate corrosive properties, which can dissolve the Al_2O_3 passivation film on the surface of the aluminum anode, making it electrochemically active, and must also avoid the destructive corrosion for the positive electrode material, current collector, and battery case, thereby suppressing the occurrence of side reactions. The enhancement and advancement of the electrolyte system will contribute a lot to the advanced aluminum battery developments.

5. Ionic Liquids as Electrolytes for Magnesium Chemistry

Magnesium is regarded as a natural choice as an anode material for rechargeable batteries due to its thermodynamic properties. Generally, magnesium has a higher volume energy density compared to other metal (such as Li); this allows the same energy to be stored in smaller batteries, which can be achieved by using magnesium metal anode [5]. Although Mg has a lower gravimetric density than Li (2205 vs. 3860 $mAh\,g^{-1}$), it has a considerably higher volumetric density (3833 vs. 2050 $mAh\,L^{-1}$). In addition, compared to lithium, magnesium is cheaper, environmentally friendly, and higher safety. Currently, the development of magnesium batteries is hampered by two issues [111]. First, due to the chemical activity of magnesium, the ideal electrolytes for use should provide neither protons nor accept protons, thereby inhibiting the electrochemical reaction with the passivated surface layer formation [112–114]. Second, the difficulty of Mg ion insertion in many hosts as well as the nature of the electrolyte limits the choice of cathode material [115]. So the research and process of ideal magnesium electrolytes determine the pace of development of the field.

5.1. Conventional Electrolytes for MIBs. For lithium batteries, we usually dissolve simple salts and anions in carbonate/aprotic solvents to prepare electrolyte solutions, where Li can be reversibly plated and stripped [116]. However, the nature of the mesophase formed at the electrolyte/metal anode interface is quite different, which is one of the most significant differences between the lithium and magnesium battery chemistry. In both cases, the decomposition products will form a layer on the electrode once electrolyte reduction occurs. Generally, the solid electrolyte interface (SEI) on lithium metal contributes to lithium-ion conduction. Unfortunately, this is not the case for magnesium metal. The layer formed on the magnesium metal is passivated, which prevents the transfer of magnesium ions to the electrode [117–119]. Therefore, electrolyte analogs of lithium batteries are generally not considered suitable for magnesium-based systems. Instead of taking advantage of the natural reduction product to prevent further reactions on the metal electrode (like lithium), the ideal electrolyte should possess reduction stability to avoid the unstable interphase layer formation.

The most widely known electrolytes capable of reversible plating/stripping of magnesium ions are based on Grignard reagents or Lewis acid-base pairs dissolved in

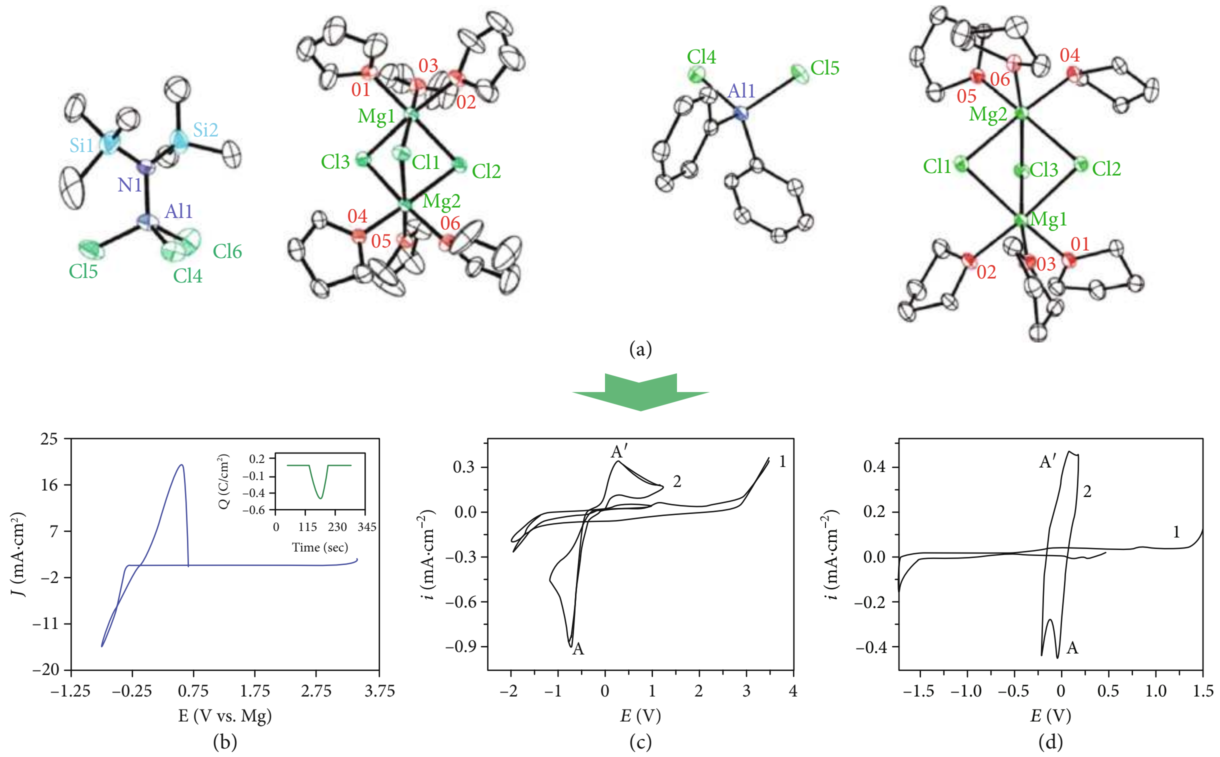


FIGURE 7: Main electrolytes for MIBs. (a) ORTEP plot of (Mg_2 (μ-Cl)$_3$·6THF) ($HMDSAlCl_3$) and (Mg_2 (μ-Cl)$_3$·6THF) (Ph_2AlCl_2). (b) Electrochemical performance of 0.2 M Mg electrolyte (Mg_2 (μ-Cl)$_3$·6THF)($HMDS_nAlCl_{4-n}$) ($n = 1, 2$) [120]. Typical cyclic voltammograms of Mg electrolytes. (c) $BMIBF_4$ without (curve 1) and with 1 M $Mg(CF_3SO_3)_2$ (curve 2) on Pt disk electrode at 50 mV/s [123]. (d) PP13TFSI without (curve a) and with 1 M $Mg(CF_3SO_3)_2$ (curve b, in a steady-state) on silver electrode at 50 mV/s [124].

ether solvents, such as (Mg_2 (μ-Cl)$_3$·6THF) ($HMDSAlCl_3$) and (Mg_2 (μ-Cl)$_3$·6THF) (Ph_2AlCl_2) (Figure 7(a)). For example, as shown in Figure 7(b), magnesium ions can be successfully reversibly plated and stripped from magnesium organohaloaluminates or magnesium organoborate salts containing (Mg_2 (μ-Cl)$_3$·6THF)$^+$ cation dissolved in etheric solvents [120, 121]. The dielectric constant of ether is very low, which limits the magnesium salt solubility. In addition, these electrolytes are confronted with safety risks due to the unstable volatile solvents and salts in the air and/or water. It is expected that the battery electrolyte contains a high concentration of an electroactive salt, thus bringing out fast ion transport [122]. And the desirable electrolyte may as well possess poor volatility and flammability to improve the safety of the battery system. Thereby, ionic liquids are considered as potential solvents for various magnesium salts.

5.2. Ionic Liquid-Based Electrolytes for MIBs.

Ionic liquid can be used not only as a source of cations/anions but also as a nonflammable solvent that dissolves salt cations. In the case of magnesium electrolytes, this advantage is particularly convenient because simple salts of magnesium and conventional solvents (alkyl carbonates, esters, and acetonitrile) can form a passivate layer on the surface of magnesium metal. However, it must be taken seriously whether the ionic liquid has sufficient reducing stability to magnesium.

Research on ionic liquids for magnesium electrochemistry is still on its early stages. A lot of efforts has been made on building efficient magnesium primary batteries, but the development of rechargeable magnesium batteries is still a long way off. The ionic liquid electrolyte containing BF_4^- anion features with high ionic conductivity and low melting point. A mixture of magnesium triflate ($Mg(CF_3SO_3)_2$) and 1-n-butyl-3-methylimidazole tetrafluoroborate ($BMIMBF_4$) was described, which can be considered as one of the earlier reports on magnesium ionic liquid electrolytes [123]. Experimental results show that $BMIMBF_4$ exhibits stability on a platinum working electrode at -1 to 3 V relative to Mg and the plating/stripping process of magnesium with $Mg(CF_3SO_3)_2$ salt occurs at low current, as shown in Figure 7(c). Surprisingly, even with a reported Coulombic efficiency of 100%, the plating/stripping process cannot be repeated for long cycles along with the strong voltage fluctuations. According to EDS analysis, NuLi determines S, F, and Mg in the sediment when depositing at a low charge density. It concludes that even if the $CF_3SO_3^-$ is reduced to form a film, magnesium will still be deposited from the electrolyte system [123]. In Figure 7(d), NuLi also reports the reversible deposition of magnesium from a 1 M solution of 1 M $Mg(CF_3SO_3)_2$ in N-methyl-N-propylpiperidine bis(trifluoromethane)-sulfonimide (PP13TFSI) on a silver working electrode [124]. This is due to the Ag-Mg clusters initially formed, promoting subsequent Mg deposition. Compared with $BMIMBF_4$, the $TFSI^-$ anion has a wider electrochemical window. Subsequent reports describe the use of a mixed ionic liquid made of $BMIMBF_4$ and PP13TFSI, and the same salt

$(Mg(CF_3SO_3)_2)^-$ [125]. Although the aim to use a mixed ionic liquid is to increase ionic conductivity and cathode stability, they also observe that the mixture provides a lower initial deposition/dissolution overpotential than each single ionic liquid system.

However, the most common ionic liquids include anions (such as TFSI), which are usually reductively unstable with magnesium metal. In fact, the TFSI anions in ionic liquids easily form a protective layer on Mg metal-containing Mg and TFSI decomposition products [126]. Early studies mentioned above claimed that Mg can be reversibly plating/-stripping from ionic liquid electrolytes containing ionic magnesium salts [123]. But the results can not be copied [127, 128]. Thus, the satisfactory ionic liquid electrolytes for magnesium-ion batteries require not only wide electrochemical window, high salts solubility, and high ionic conductivity but also interface compatibility and stability. The structure, composition, and ratio of ionic liquid electrolyte were designed to optimize the magnesium/electrolyte interface, so as to find an ideal ionic liquid electrolyte that can effectively deposit and dissolve magnesium reversibly at room temperature. The anode material matched with the electrolytic liquid phase was developed, and the energy was stored and released by the breaking and bonding of the chemical bonds, so as to realize the effective charging and discharging cycle of the battery. It is expected that this basic work will lay a foundation for the in-depth research and extensive application of high-performance rechargeable magnesium batteries.

5.3. Ionic Liquid-Based Polymer Electrolytes. The development of ionic liquid-based polymer electrolytes for magnesium systems has also attracted researchers' attention. The electrolyte can reversibly transport Mg^{2+} ions, in which various Mg salts are coupled with the polymer chain, plasticizer, and/or filler for enhanced ionic conductivity [129].

Morita et al. [130–132] synthesize a solution consisting of poly-(ethylene oxide) PEO-PMA (polymethacrylate) matrix and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI) ionic liquid dissolving $Mg(TFSI)_2$. Then, the ionic conduction as a solid-state electrolyte for magnesium polymer batteries has been studied. They observe that ionic conductivity depends on the content of ionic liquids which contain $Mg(TFSI)_2$ and the highest conductivity of the polymer gel is more than $10^{-4}\,S\,cm^{-1}$. Yoshimoto et al. [133] further report a flexible, self-supporting (medium mechanical strength) transparent polymer electrolyte based on ionic liquids, which contains three components: PEO-PMA polymer matrix, $Mg(TFSI)_2$, and ionic liquid EMITFSI or DEMETFSI. The authors successfully prepare a gel polymer electrolyte using poly(ethylene glycol) monomethacrylate (PEM) and poly(ethylene glycol) diethylacrylate (PED) as prepolymers. An appropriate amount of $Mg(TFSI)_2$ is dissolved in EMITFSI or DEMETFSI at room temperature. In a $Mg(TFSI)_2$/EMITSFI or $Mg(TFSI)_2$/DEMETFSI ionic liquid solution, add a 3 : 1 molar mixture of PEM and PED, which contains a small amount of a photo-induced free radical initiator, and add 2-phenylbenzene acetone. The liquid is cured to an aluminum plate by UV radiation in an Ar atmosphere, and finally, a crosslinked polymer matrix PEO-PMA with salts in an ionic liquid is produced. The ionic conductivity of these polymer electrolytes varies with the content of ionic liquids containing $Mg(TFSI)_2$.

5.4. General Strategies to Develop Ionic Liquid-Based Magnesium Electrolytes. Although ionic liquids can dissolve magnesium salts at high concentrations, they are troubled by the reduced ionic conductivity and electroactive species migration numbers. This is due to its high viscosity, and the additional ions as well as Mg can also migrate when applying an electric field. The addition of tetrahydrofuran (THF) as a cosolvent helps to increase the ionic conductivity with the decreased viscosity. Particularly, Cheek et al. point out that Mg can be reversibly plated/stripped in the 1 M PhMgBr in THF/1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate ($BMPCF_3SO_3$) [134]. Yoshimoto's group report that 1.0 M DEMETFSI has an ionic conductivity of $7.44\,mS\,cm^{-1}$ [135]. The addition of ether into ionic liquid-based electrolytes makes a great significant increase of ionic conductivity and a decrease in viscosity (in both cases an order of magnitude reduction) [136]. The results of spectra [137, 138] and single crystal [139] indicate that the charged Mg substance in the TFSI-based ionic liquid-based electrolyte may be a large anionic complex. On the contrary, when oligomeric ether is added, it shows that Mg is mainly coordinated by ether oxygen. The combined electrochemical and spectroscopy results indicate that the nature of Mg's charge-carrying substance is a crucial ingredient affecting the deposition/dissolution process.

Optimizing the cations in the imidazolium-based ionic liquid using TFSI-anions can further increase the current density [140, 141]. Kakibe et al. prove the magnesium cycle by replacing the alkyl group on the cation (such as $[C_2mim]^+$) to avoid undesired reaction between the magnesium surface and the C_2 proton on the imidazole ring [141]. Interestingly, it also shows that the varied ratio of the $TFSI^-/FSI^-$ anion in a binary ionic liquid mixture can also make a raise in current density. Gao et al. point out that the speciation behavior of Mg^{2+} is crucial for assessing the feasibility of ionic liquid electrolytes in Mg-based batteries [116, 142]. The authors investigate two types of alkoxy-functionalized ionic liquids (one with alkoxy-pyrrolidinium cations and another with alkoxy-ammonium cations) and report better reversibility than the N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (Pyr14TFSI) usually studied. Huie et al. investigate ionic liquids with different cations (pyridine, imidazolium, piperidinium, and pyrrolidinium) in a solution containing Mg $(TFSI)_2$ salt and DPGDME or an acetonitrile cosolvent [143]. A correlation between the high conductivity of ionic liquid with unsaturated rings and short carbon chain lengths can be observed. However, these ionic liquids also exhibit lower oxidative stability. A composition of $Mg(TFSI)_2$ dissolved in 40% 1-ethyl-1-methyl-pyrrolidinium bis(trifluoromethanesulfonyl)imide (EMPTFSI) and 60% acetonitrile exhibits a conductivity of $40\,mS\,cm^{-1}$, and the best performance is obtained, with voltage stability of 5.23 V relative to Mg^0/Mg^{2+}.

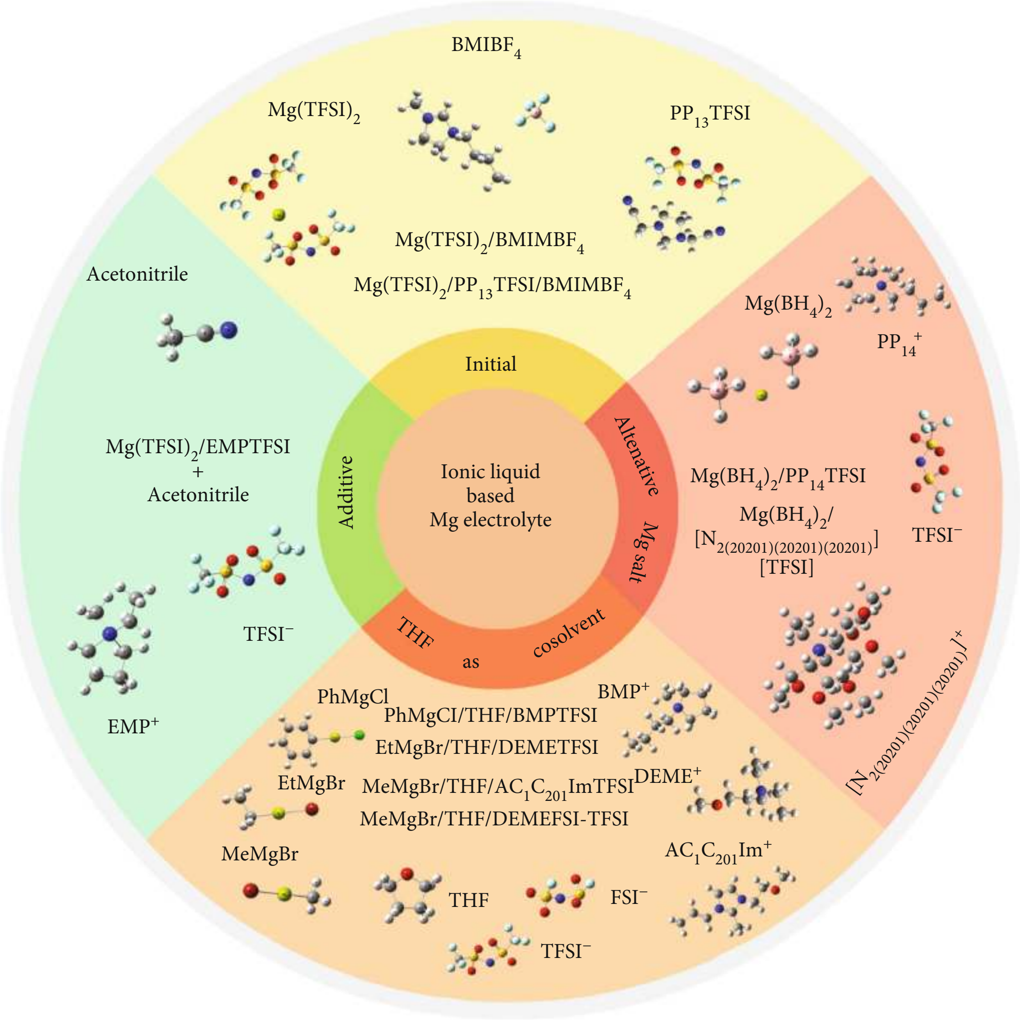


Figure 8: Schematic diagram of Mg^{2+} ionic liquid electrolytes.

In addition to TFSI anion, $Mg(BH_4)_2$ has also been proven to be a salt capable of Mg deposition, and there have been reports of using $Mg(BH_4)_2$ as the source of Mg in ionic liquid electrolytes [144, 145]. And Kar et al. verify the results in an alkoxyammonium-based ionic liquid named $[N_{2\ (20201)\ (20201)\ (20201)}]$ $[NTf_2]$ [144]. Su et al. develop a piperidinium-based ionic liquid-based electrolyte, namely, 1-butyl-1-methylpiperidine bis(trifluoromethanesulfonyl)imide (PP14TFSI). The dissolved magnesium salt is $Mg(BH_4)_2$. The ionic conductivity of the electrolyte ranges from 1 to 3 mS cm^{-1} [145].

The ionic liquids can be regarded as additives to add into magnesium liquid electrolytes, which have made valuable progress [145–147]. Cho et al. find that the addition of 1-allyl-1-methylpyrrolidinium to the Grignard reagent solution can improve its oxidation stability by 1.0 V [146]. Pan et al. develop a new electrolyte by adding DEMETFSI ionic liquid and observe that its ionic conductivity increases linearly with increasing DEMETFSI concentration [147]. Figure 8 provides all kinds of prominent ionic liquid electrolytes used in MIBs.

6. Ionic Liquids as Electrolytes for Sodium Chemistry

Lithium technology powers a lot of our modern devices and is therefore well known. The sodium chemistry shares commonalities. Because of the following reasons, SIBs are expected to meet the requirements for sustainability and performance in various applications [148]. (1) Compared with lithium, sodium has a higher abundance and a wider distribution. The abundance of Na in the earth is about 24000 ppm (20 ppm for Li), which are almost unlimited resources [149]. The price of commonly used Na-containing raw materials (Na_2CO_3) is therefore more than 100 times lower than Li_2CO_3. (2) Although sodium is heavier, subsequent capacity loss (estimated) can be compensated by replacing heavy copper current collectors (which need to be used in LIBs) with lighter aluminum and leading to greatly reduced costs compared to LIBs. (3) Na metal exhibits a low redox potential (2.71 V relative to SHE), resulting in a rather high battery voltage. (4) The ionic radius of Na is larger than that of Li, which causes reduced solvation in

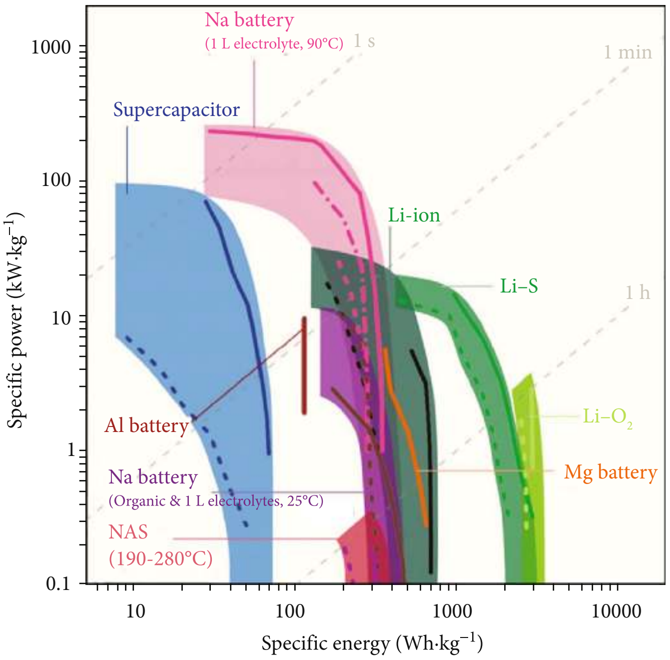


Figure 9: Ragone plot showing sodium secondary batteries with ionic liquid-based electrolytes in comparison with various energy storage systems [148].

polar solvents. It is known that desolvation can control the migration of alkali metals at the interface, so this weaker interaction promotes the insertion of Na^+ [150].

6.1. Motivations for Ionic Liquid-Based Electrolytes for SIBs.

The electrolyte is an essential component of SIBs, and it transfers and balances the charges between the electrodes in the form of ions [17, 151]. The electrolyte is located between the cathode and anode and interacts closely with the electrodes. Therefore, it has been increasingly recognized that the electrolyte will profoundly affect the battery system, not just the transport medium for shuttle ions. Over the past few decades, based on such electrolyte characteristics, the researchers have made great efforts to find the best combination of suitable electrolytes for SIBs. Despite the research on SIBs in the 1980s, the renaissance of SIBs has just begun, so there is currently no perfect "standard" electrolyte. In academic and industrial research and development, carbonate-based electrolyte solutions with sodium salts are regarded as one of the most suitable electrolyte media for SIBs. However, organic electrolytes are flammable and volatile. In the case of battery abuse, the electrolyte may cause the electrolyte to burn. And the internal pressure of the battery may be enlarged by volatilization, which may cause a fire or explosion of the battery [152]. In addition, their high sensitivity to thermal history and temperature fluctuations limit their application in emerging devices [153, 154]. Therefore, it is very urgent to develop a next-generation electrolyte with high safety for SIBs, such as ionic liquid-based electrolytes.

Although ionic liquids are not economical choices due to the high cost, since the amount of electrolyte required in a battery system is very limited, the overall cost of the battery system is not significant [155]. Moreover, with the increasing research on the synthesis and recovery of ionic liquids, their costs are expected to decrease accordingly [156, 157]. It is worth noting that using an ionic liquid as an electrolyte, other functions of the battery, such as enhanced durability and performance/cost ratio, may compensate or eliminate battery cost issues. Figure 9 shows the Ragone diagram of various battery systems [148]. It can be seen from the figure that the sodium-ion battery system using an ionic liquid as the electrolyte has a good specific energy and power at room temperature. Words cannot be reached.

6.2. Cations and Anions for Ionic Liquid-Based Electrolytes.

In this section, different cations and anions of ionic liquids for SIB electrolytes are summarized. It is worth noting that the usual research focuses on cations such as imidazolium, pyrrolidinium, ammonium, and anions of $TFSI^-$, FSI^-, and BF_4^- [158]. The corresponding chemical structures of these anions and cations are listed in Figure 10 and Table 1. In addition, the combination of cations and anions can be freely selected and meet the ideal performance requirements of ionic liquid [159].

Fluoro complex anions (BF_4^-) are widely used to obtain low melting salts previously [160–161]. But their low stability to hydrolysis and high viscosity prevent them from being used as ideal electrolytes in battery systems. Although some works prepared some more stable hydrolysis of BF_4^- in SIBs, based on their hydrophilicity, the synthesis of them is not economical and convenient, so it is not attractive in practical. Sulfonamide-based (also known as sulfonimide-based) ionic liquids are popular due to their ease of synthesis and high ionic conductivity. By expanding its organic framework, the cations in the ionic

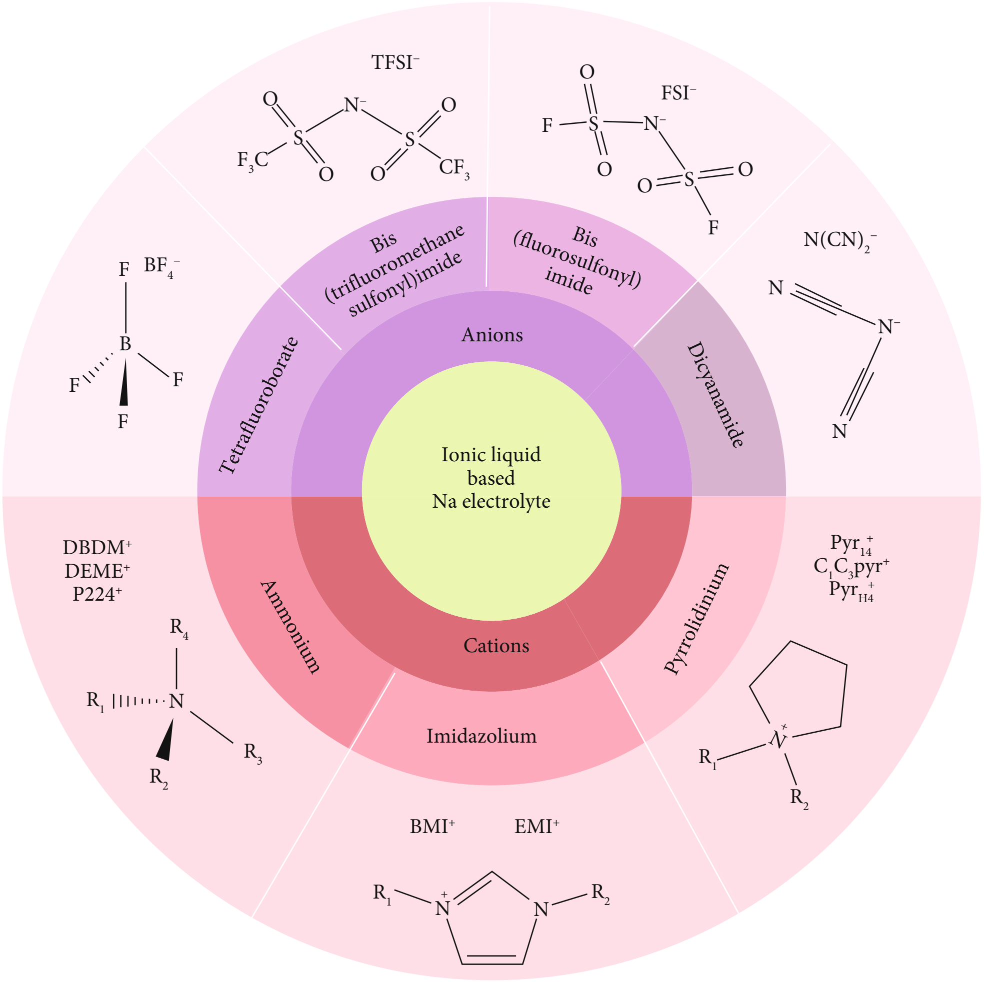


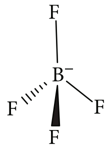
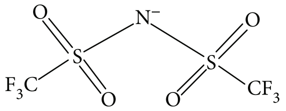
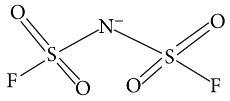
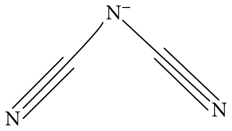
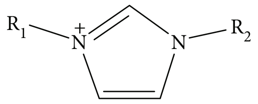
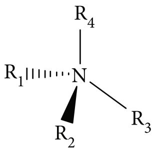
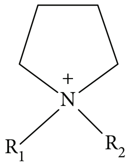
Figure 10: Anions and cations in ionic liquid electrolytes for SIBs.

liquids change more than the anions. Although melting points usually decrease when large or long substituents are introduced, viscosity and ionic conductivity generally increase and decrease, respectively. Therefore, asymmetric cations having a short alkyl chain are generally preferred. Nonaromatic pyrrolidinium cations possess higher reduction stability than imidazolium cations and are therefore widely used in battery systems [162]. In the following review, the research progress and application prospects of three different cationic (imidazolium, pyrrolidinium, and ammonium) ionic liquid-based electrolytes are discussed.

6.3. Imidazolium-Based Ionic Liquid Electrolytes. In practical applications, imidazolium-based ionic liquids, such as 1-ethyl-3-methylimidazolium (EMIm-) and 1-butyl-3-methylimidazolium (BMIm-), have attracted widespread attention because they feature with relatively low viscosity, high ionic conductivity, and high chemical stability [163, 164].

As early as 2005, ionic liquids based on imidazolium cations with trihalides used as anions have been explored [165]. Studies have found that trihalide-based ionic liquids ([Bmim] [Br_3], [Bmim] [ICl_2], and [Bmim] [IBr_2]) provide lower melting point, lower viscosity, and higher density and hydrophobicity, compared to some other common imidazolium ionic liquids, such as chloride, bromide, or iodide. It is worth noting that the size of the anions makes a great influence on the potential for forming ion aggregates. And these aggregates significantly influences the physical-chemical properties of ionic liquids, such as refractive index, electronic polarizability, ion conductivity, and viscosity. Particularly, [Bmim] [IBr_2] exhibits the highest conductivity, $40\,mS\,cm^{-1}$, while the conductivity of [Bmim] [Br_3] and [Bmim] [IBr_2] is lower, and the viscosity is much higher. Subsequently, in early 2010, Plashnitsa et al. have reported an imidazolium-based ionic liquid electrolyte consisting of 1-ethyl-3-methylimidazolium tetrafluoroborate EMIm-BF_4 and 0.4 M $NaBF_4$. And the ionic liquid-based electrolyte is applied to a symmetrical battery with $Na_3V_2(PO_4)_3$ (the cathode and anode are both $Na_3V_2(PO_4)_3$). This battery shows better cycle life due to the lower reactivity of the ionic liquid electrolyte compared to conventional organic electrolytes. In addition, it possesses higher thermal stability at high temperatures. Notably, as shown in Figure 11(a), the $Na_3V_2(PO_4)_3$ electrode coupled with the ionic liquid-based electrolyte still exhibits good thermal stability at temperatures up to 400°C [166]. Recently, Wu et al. also report EMIBF_4-based ionic liquids with different

Table 1: Structures and abbreviations of common ionic liquid anions/cations used in SIBs.

Ion	Abbreviation	Structure
Anions		
Tetrafluoroborate	BF_4^-	
Bis(trifluoromethanesulfonyl)imide	$TFSI^-$	
Bis(fluorosulfonyl)imide	FSI^-	
Dicyanamide	$N(CN)_2^-$	
Cations		
Imidazolium	BMI^+; EMI^+	
Ammonium	$DBDM^+$; $DEME^+$; $P224^+$	
Pyrrolidinium	Pyr_{14}^+; $C_1C_3pyr^+$; Pyr_{H4}^+	

concentrations of $NaBF_4$ as nonflammable electrolytes for SIBs. Particularly, when the concentration of $NaBF_4$ is 0.1 M, the ionic liquid-based electrolyte shows excellent ionic conductivity of 9.833×10^{-3} S cm^{-1} at 20°C. And in the voltage range of 1-5 V, the ionic liquid-based electrolyte remains electrochemically stable. In addition, in Figure 11(b), the electrolyte is proven to possess high thermal stability, and thermal decomposition does not occur until 380°C [167].

Monti et al. investigate the physical and chemical properties of imidazolium-based ionic liquids (1-ethyl-3-methylimidazolium TFSI (EMITFSI)) and 1-butyl-3-methylimidazolium TFSI (BMITFSI) coupled with NaTFSI salts. Taking $Na_{0.1}EMIm_{0.9}TFSI$ (equivalent to 0.4 M NaTFSI) as an example, as shown in Figure 11(c), its ionic conductivity at room temperature is 5.3 mS cm^{-1} and it can maintain thermal stability in the temperature range of -86 to 150°C [168]. By DFT calculation and Raman spectroscopy, it is concluded that the Na charge carrier is the $[Na(TFSI)_3]^{2-}$ complex, which plays a major role in ionic conductivity. Then, the viscosity, diffusion coefficient, and conductivity of the ionic liquid electrolyte based on Emim-TFSI are first calculated by MD simulation [169]. Recently, Wu et al. report $NaPF_6$/BMIm-TFSI electrolytes for SIBs. The self-extinguishing time (SET) and thermogravimetric tests are used to study the flammability and thermal stability of the electrolyte, which are shown in Figures 11(d) and 11(e) [170]. $NaPF_6$/BMImTFSI electrolyte shows a short SET of 25 s g^{-1}, which is much lower than that of the 1.0 M $NaPF_6$/PC electrolyte (210 s g^{-1}). A shorter SET indicates that ionic liquid-based electrolyte is nonflammable. In the TG measurement, the $NaPF_6$/BMIm-TFSI electrolyte does not show significant weight loss until 350°C. In contrast, the

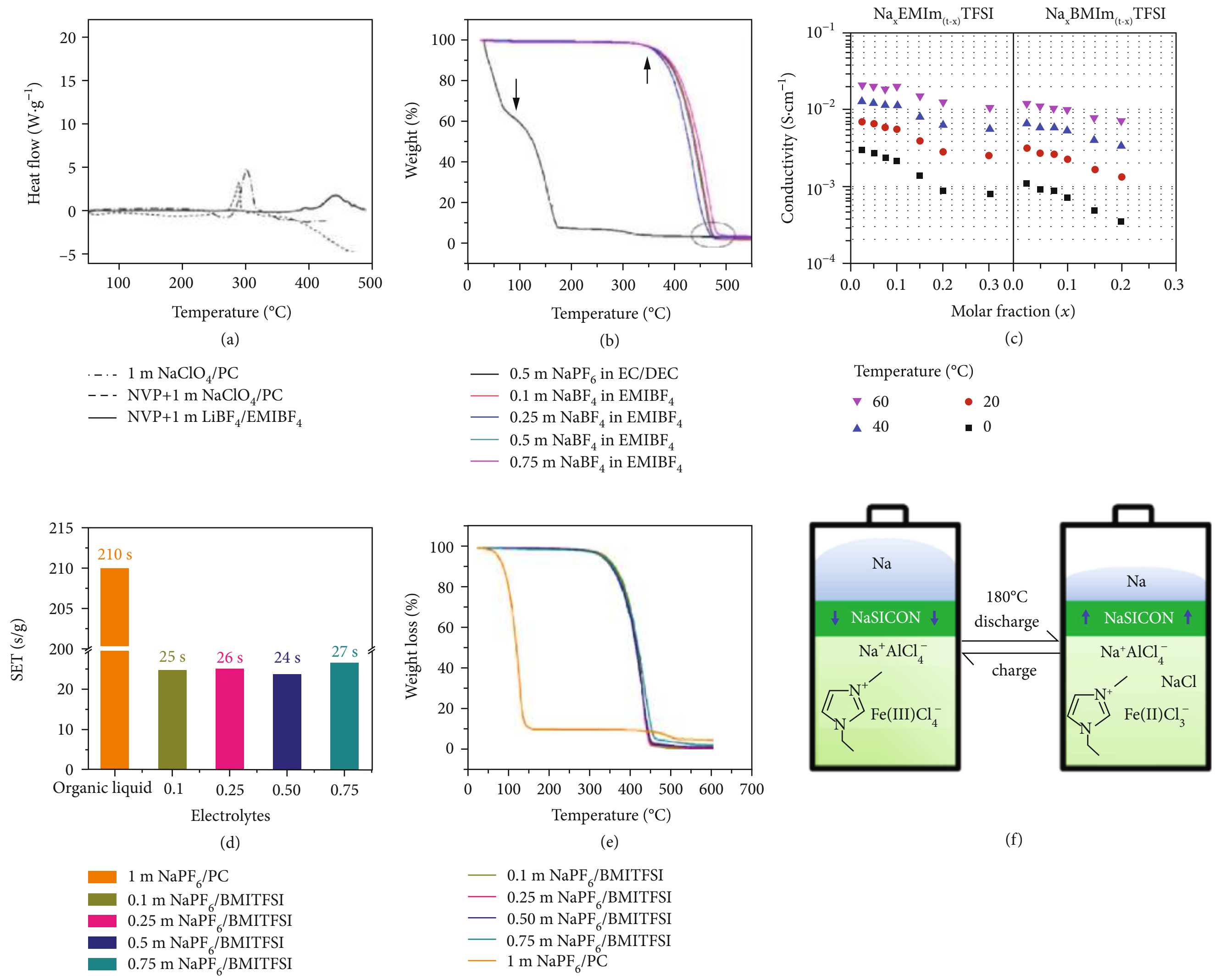


Figure 11: Performances of imidazolium-based IL electrolytes in SIBs. (a) DSC curves for the $Na_3V_2(PO_4)_3$ powder with the organic and ionic liquid-based electrolytes [166]. (b) TGA curves of the organic ($NaPF_6$/EC/DEC) and ionic liquid-based electrolytes ($NaBF_4$/$EMIBF_4$) [167]. (c) Isotherms of conductivity as a function of the molar fraction of $Na_xEMIm_{(1-x)}TFSI$ and $Na_xBMIm_{(1-x)}TFSI$ [168]. (d, e) SETs and TGA curves of 1 M $NaPF_6$/PC and ionic liquid-based electrolytes [170]. (f) Na-Fe (redox) battery using of ionic liquid $EMIFeCl_4$-$NaAlCl_4$ as catholyte [171].

1.0 M $NaPF_6$/PC electrolyte shows a 90% weight loss at 60°C. Therefore, $NaPF_6$/BMIm-TFSI electrolyte shows good thermal stability.

Recently, an energy storage method using an ionic liquid as a combined ion conductive medium and a redox-active catholyte material has been widely concerned [171]. The schematic diagram and working mechanism of the battery are displayed in Figure 11(f). Earth-rich iron ions in the form of a low melting point $NaFeCl_4$ are mixed with the ionic liquid ethylmethylimidazole tetrachloroaluminate as an electrolyte. The electrolyte maintains the highest ionic conductivity. Moreover, the battery with the ionic liquid electrolyte and liquid sodium anode exhibits a high voltage exceeding 3.2 V, and its cyclability is confirmed. When operating at 180°C, it shows a super high energy efficiency. This provides a new insight for ionic liquids as catholytes to further develop high energy density SIBs.

6.4. Pyrrolidinium-Based Ionic Liquid Electrolytes. Pyrrolidinium-based ionic liquid electrolytes including N-propyl N-methylpyrrolidinium (Pyr_{13}-) and N-butyl-N-methylpyrrolidinium (Pyr_{14}- or BMP-) are very attractive for SIB applications [172]. At present, there are mainly two kinds of pyrrolium-based ionic liquid electrolyte systems used in SIBs, namely, NaFSI/Pyr_{13}FSI and NaTFSI/BMPTFSI.

In 2013, Ding et al. investigate the physical and chemical properties of NaFSI/Pyr_{13}FSI ionic liquids that acted as a new electrolyte for SIBs with a wide temperature range [173]. Studies have shown that the viscosity and ionic conductivity of the ionic liquid-based electrolyte as shown in Figure 12(a). This ionic liquid-based electrolyte exhibits a wide electrochemical window, which is shown in Figure 12(b). The battery assembled by using the ionic liquid-based electrolyte with $NaCrO_2$ cathode exhibits a specific capacity of 92 and 106 mAh g^{-1} at 298 and 353 K at 20 mA g^{-1}, respectively. It is

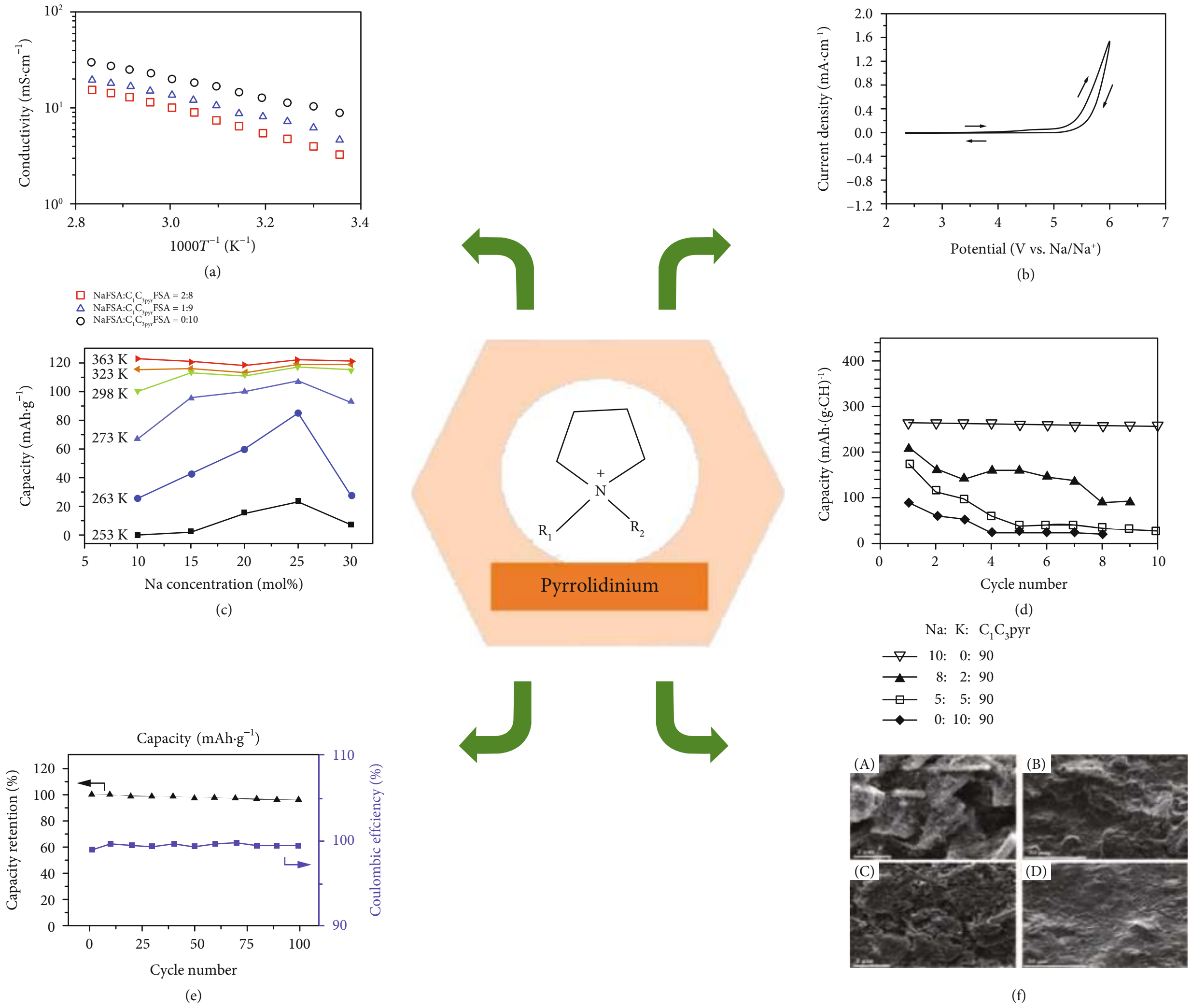


Figure 12: Performances of $Pyr_{13}FSI$-based IL electrolytes in SIBs. (a) Ionic conductivity for NaFSI/$Pyr_{13}FSI$ with various molar ratios [173]. (b) Cyclic voltammogram of a glassy carbon rod electrode in NaFSI/$Pyr_{13}FSI$ ionic liquid at 353 K [173]. (c) Discharge capacities for Na/NaFSI-$Pyr_{13}FSI$/$NaCrO_2$ batteries with various concentrations of NaFSI at 253-363 K [174]. (d) Cyclic dependence of discharge capacity for Na/NaFSI-$Pyr_{13}FSI$/HC batteries [175]. (e) Cyclic stability of $Na_{0.44}MnO_2$/HC full battery in ionic liquid and organic electrolytes [176]. (f) SEM micrographs of (A) and (C) NMO electrodes and (B and D) HC electrodes taken from (A and B) IL and (C and D) organic electrolyte full cells after 100 cycles [172].

verified that NaFSI/$Pyr_{13}FSI$ is a promising electrolyte for SIBs operating in a wide temperature range. Then, the group then investigates the effects of Na ion concentration and operating temperature on the viscosity, ionic conductivity, and charge-discharge performance of Na/NaFSI/$Pyr_{13}FSI$/$NaCrO_2$ batteries. As depicted in Figure 12(c), the optimal concentrations are confirmed for the batteries operating [174].

Subsequently, Fukunaga et al. demonstrate the electrochemical performance of the SIB with NaFSI/$Pyr_{13}FSI$ as the electrolyte and hard carbon (HC) as the anode in Figure 12(d) [175]. This Na/NaFSI-$Pyr_{13}FSI$/HC battery shows a reversible capacity of 260 mAh g^{-1} at the current density of 50 mA g^{-1} at 363 K and remains 95.5% after 50 cycles. The battery also shows a high rate capacity of 211 mAh g^{-1} at the current density of 1000 mA g^{-1}, which is equivalent to a charging rate of about 4C. Therefore, it can be concluded that this combination of HC anode and NaFSI/$Pyr_{13}FSI$ electrolyte can provide a safe, high-rate performance SIB. In addition, Wang et al. report the electrochemical performance of $Na_{0.44}MnO_2$/HC full battery based on NaFSI-$Pyr_{13}FSI$. In Figure 12(e), this battery shows a higher capacity (117 mAh g-1) and higher stability compared to conventional carbonate-based electrolyte because of the SEI layer formed by IL electrolyte on the HC electrode (Figure 12(f)) [176]. Still for the NaFSI/$Pyr_{13}FSI$ electrolyte system, Forsyth et al. find that high concentrations of sodium salts can increase the number of Na^+ transfers in ionic liquids, thereby improving the interfacial characteristics of Na metal anode, achieving low polarization potential and long cycle life [177]. Recently, Kim et al. report a new electrolyte based on a combination of two ionic liquids ($Pyr_{13}FSI$; $Pyr_{13}TFSI$), sodium salts (NaTFSI), and ethylene carbonate (EC) additives for seawater batteries. Adding 5% EC can promote the formation of SEI, then stabilize the

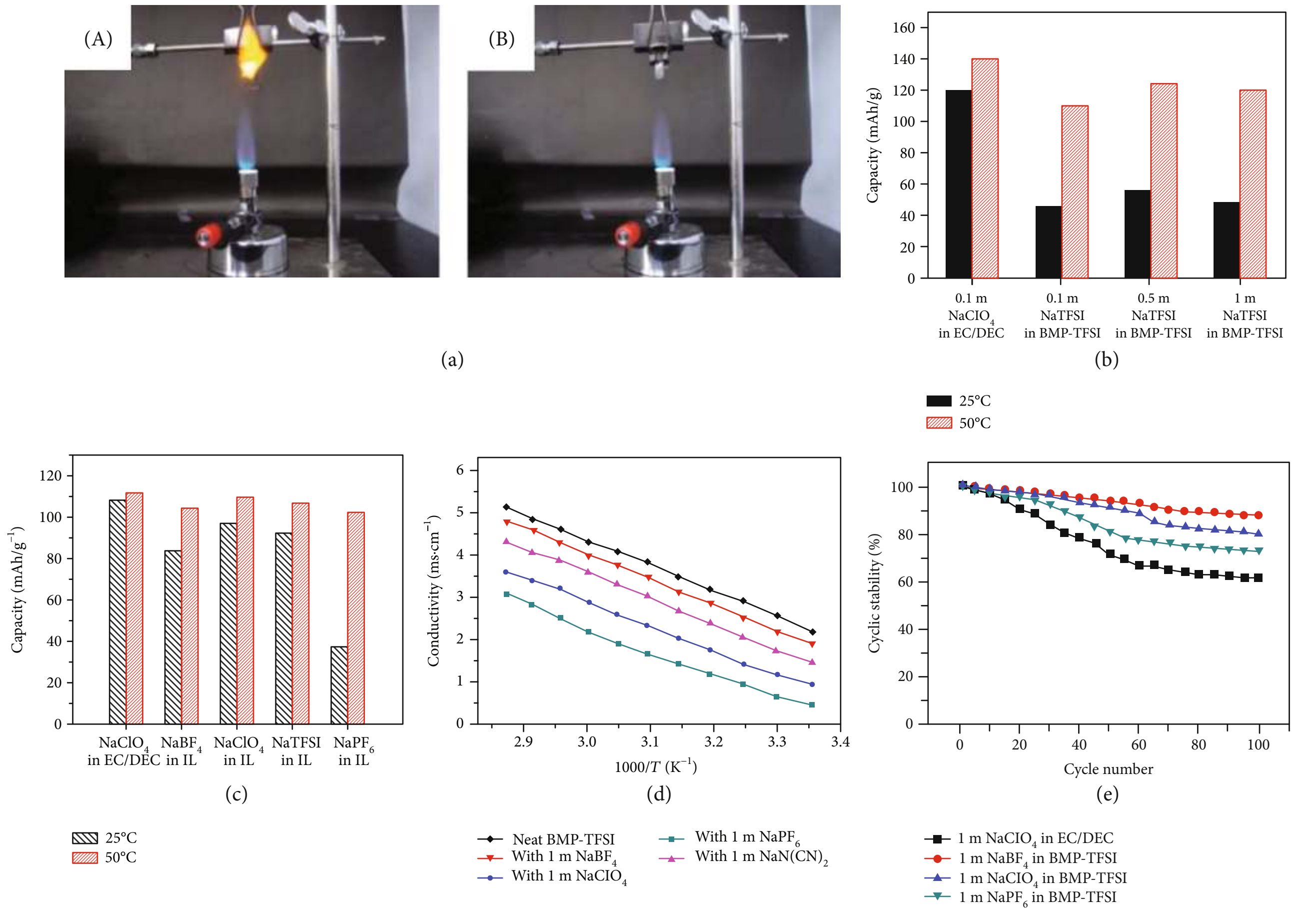


FIGURE 13: Performances of BMPTFSI-based IL electrolytes in SIBs. (a) Flammability tests of (A) conventional organic electrolyte and (B) BMP-TFSI IL electrolyte with 1 M NaTFSI [176]. (b) Comparison of $NaFePO_4$ discharge capacities in various electrolytes at 25°C and 50°C [176]. (c) Comparison of $Na_{0.44}MnO_2$ discharge capacity (at 0.05) in various electrolytes at 25°C and 50°C [177]. (d) Ionic conductivities of BMPTFSI-based electrolytes with various sodium salts [182]. (e) Cyclic stability of Na/$NaFePO_4$ batteries with various sodium salts at 50°C [182].

electrolyte/anode (hard carbon) interface. In addition, this battery shows better energy efficiency (voltage efficiency) and recyclability than conventional organic carbonate-based electrolytes [178].

In addition to NaFSI/Pyr_{13}FSI, there are studies on NaTFSI/BMPTFSI electrolytes in SIBs as early as 2013. Noor et al. conclude that sodium metal can be reversibly plated/-stripped from the ionic liquid-based electrolyte by cyclic voltammetry [179]. And the electrochemical properties, thermal properties, density, viscosity, and conductivity of the electrolyte have been systematically investigated. Surprisingly, the ionic conductivity is up to 8 mS cm^{-1}. Due to the increase in the viscosity and density, their ionic conductivity slowly decreases with the increase of the salt content.

Subsequently, as depicted in Figure 13(b), the effect of NaTFSI concentration on the electrochemical performance of Na/NaTFSI-BMPTFSI/$NaFePO_4$ batteries has been studied [180]. When the NaTFSI concentration is about 0.5 M, a compromise between the number of working ions and the electrolyte conductivity can be achieved to optimize battery capacity and high rate capacity. In addition, the battery also has excellent performance at high temperatures. At 50°C, the Na/NaTFSI-BMPTFSI/$NaFePO_4$ battery capacity in ionic liquid mixed with 0.5 M NaTFSI is 125 mAh g^{-1} (at 0.05 C). Moreover, the nonflammability property of the IL electrolytes is ideal for high-safety batteries (Figure 13(a)).

Not only the concentration of the sodium salt, the composition of the sodium salt also results in different electrolyte performance. Based on the BMPTFSI electrolyte, the effects of different sodium salts (such as $NaBF_4$, $NaClO_4$, NaTFSI, and $NaPF_6$) on the performance of Na/NaTFSI-BMPTFSI/-$Na_{0.44}MnO_2$ batteries are reported [181]. From Figure 13(c), the results indicate that $NaClO_4$ is the most suitable salt for this system. From another perspective, Na/NaTFSI-BMPTFSI/$Na_{0.44}MnO_2$ batteries with different Na salts ($NaBF_4$, $NaClO_4$, $NaPF_6$, and $NaN(CN)_2$) are investigated [182]. In Figures 13(d) and 13(e), $NaBF_4$-based electrolytes exhibit the highest ionic conductivity (1.9 mS cm^{-1} at room temperature), the lowest viscosity, and the most stable cycle performance. Recently, the BMPTFSI-NaTFSI electrolyte is applied in a full battery (P2-$Na_{0.6}Ni_{0.22}Fe_{0.11}Mn_{0.66}O_2$/Sb-C), and the results show a high initial capacity [183].

6.5. Ammonium-Based Ionic Liquid Electrolytes. Ammonium-based ionic liquid electrolytes have also received widespread attention for their high solubility in Na salts. Generally, the increase in sodium salt content can result in high viscosity and glass transition temperature (Tg), as well as low ionic conductivity and diffusion coefficient. To solve this problem, a ternary electrolyte is prepared, in which $NaBF_4$ with poly(ethylene glycol) dimethyl ether (PEGDME) as a ligand dissolved in $DEMEBF_4$ [184]. The ionic conductivity, viscosity, and thermal stability of this new ternary ionic liquid electrolyte are investigated. The highest ionic conductivity of $1.2\,mS\,cm^{-1}$ is obtained at 25°C when the molar ratio of $PEGDME:NaBF_4:DEMEBF_4$ is kept at 8 : 1 : 2. In addition, the ternary electrolyte containing $NaClO_4$, PC, and DEMETFSI has been reported to be used in SIBs [185]. The electrolyte exhibits a highly reversible insertion and extraction behavior of sodium ions with an optimized volume content of 70% DEMETFSI.

To further improve the solubility of ammonium-based ionic liquids for sodium salts, researchers design large volumes of ionic liquids with ether functional groups on quaternary ammonium cations. Because the ether group features with good sodium ion chelating properties, resulting in the excellent solvating ability of the electrolyte, it is reported that the solubility of NaTFSI in the modified ionic liquid electrolyte can be increased to $2.0\,mol\,kg^{-1}$ [186]. A similar phenomenon exists in lithium systems [187].

6.6. Challenges and Benefits of Ionic Liquid-Based Electrolytes for SIBs. For most ionic liquids, cost is undoubtedly a serious issue. Battery-level ionic liquid must be very pure, which can lead to further cost increases. Such pure ionic liquid has not been widely synthesized at the industrial level, and therefore, it is difficult to estimate the price even for lithium-ion batteries. Generally, quaternary ammonium cations are more expensive than that of ternary, as well as fluorine-containing anions are also more expensive than that of non-fluorine-containing. Alkylammonium and alkylphosph are more economical and effective than dialkylimidazolium [188]. In contrast to $TFSI^-$ salt, FSI^- salt can be synthesized without high cost electrofluorination. Therefore, by further improving the synthesis process and mass production in the near future, the price can be potentially reduced [189, 190]. Second, the high viscosity of ionic liquid (especially at low temperatures) can cause many follow-up problems including the porous separators and electrode impregnation [148]. Third, ionic liquids are not always good for the environment, and the decomposition products of some ionic liquids are harmful to the environment [191]. Finally, due to its high thermal stability, compared to traditional organic electrolytes, ionic liquids consume a lot of energy in the disposal process after the use of batteries.

Moreover, the mobility of metal cations in ionic liquid-based electrolytes is lower, which, together with higher viscosities, usually limits the rate performance of Na batteries. A high salt concentration ionic liquid electrolyte (also known as a "solvent in salt") has been made to obtain good rate performance. Na mobility increases significantly with increasing salt concentration (0.3 when the salt content is 50 mol% and <0.1 when it is less than 15 mol%). Despite the higher viscosity, the sodium mobility is still improved [177, 192]. MD simulations show that the key to "unlocking" this conduction mechanism may be related to the coordination of anions with Na cations. These electrolytes make a balance between transference and viscosity, resulting in the perfect performance.

In summary, the imidazolium-based ionic liquids have attracted widespread attention in practical applications, because they feature with relatively low viscosity, high ionic conductivity, and high chemical stability. Pyrrolidinium-based ionic liquid electrolyte, which acted as an emerging system for SIB applications, shows a wide electrochemical window. The assembled batteries exhibit a specific capacity with a wide temperature range. However, the effects of Na ion concentration and operating temperature on the viscosity and their ionic conductivities need in-depth investigations. Moreover, the ammonium-based ionic liquid electrolytes can alleviate the problems of high viscosity and glass transition temperature (Tg), as well as low ionic conductivity and diffusion coefficient due to their high solubility in Na salts. The design of large volumes of ionic liquids with ether functional groups on quaternary ammonium cations is expected. Although there are many problems in the industrial application of ionic liquids, there still exists a great potential in using ionic liquids as SIB electrolytes. First, ionic liquid extends the temperature limit and cut-off voltage range of electrochemical measurements. The test condition flexibility not only facilitates the well-developed material assessment but also helps determine their optimal working environment. Second, ionic liquid-based electrolytes show improved cycling performance among wide range temperatures [170, 182, 193–195]. It is widely recognized that ionic liquid-based electrolytes can provide a uniform and strong SEI layer on active Na metals. In addition, due to the improved interface properties and the ionic conductivity, using ionic liquid at the high temperature can significantly increase the rate capability and power density. Finally, at present, although the use of full battery research to confirm the practical feasibility of SIBs with ionic liquid electrolytes is still in the preliminary stage, there have been several reports on full battery testing of ionic liquids using coin cells [153, 176, 183, 196–198]. There is also a report on prismatic batteries [199].

7. Conclusions and Outlook

Ionic liquids have found applications in almost all "post-lithium" battery chemistry. In this review, we mainly introduce the basic properties of ionic liquid-based electrolyte and discuss their applications in aluminum-ion batteries, magnesium-ion batteries, and sodium-ion batteries. Then, we list the types of ionic liquid-based electrolytes that have been applied and analyze the existing advantages and limitations. In addition, the development directions of ionic liquid-based electrolytes in these three battery systems will be displayed.

In terms of electrolytes, the choice of aluminum ion batteries is very limited. Most studies are focused on ionic liquids containing corrosive and moisture sensitive chloroaluminate. Typical $AlCl_3$-containing imidazolium-based ionic

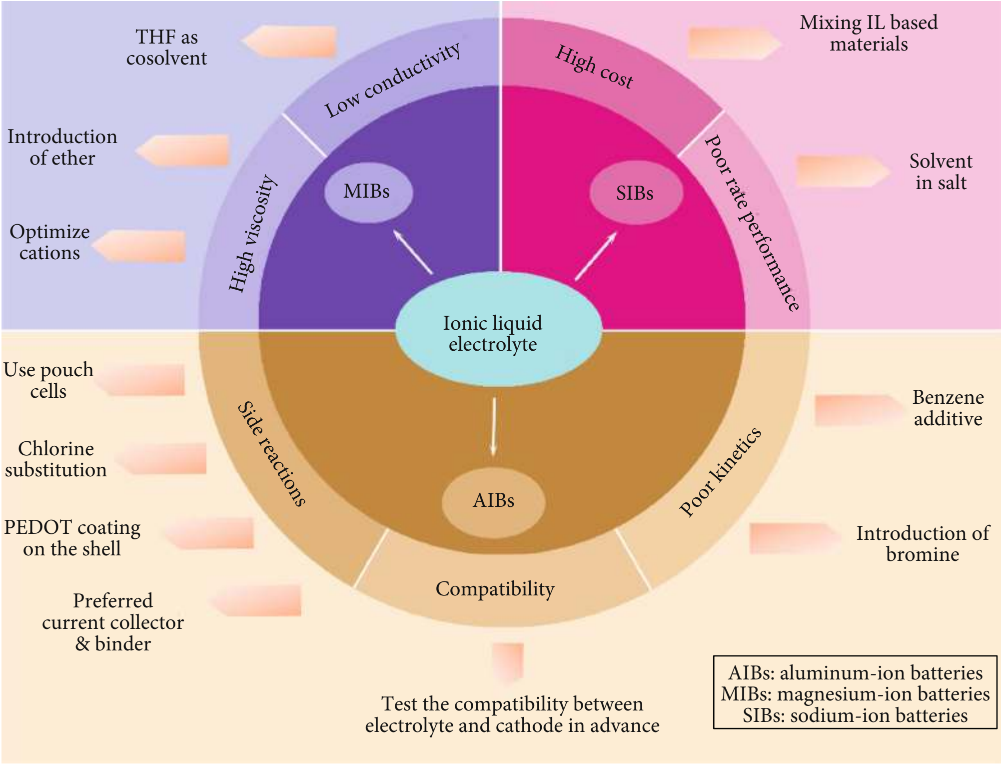


Figure 14: The challenges and strategies of AIBs, MIBs, and SIBs.

liquids are confronted with several problems (expensive, highly corrosive and sensitive, and low electrochemical windows), so they are far from commercial applications. Therefore, considering the practical application of AIBs, it is necessary to develop new, safe, nontoxic, and stable electrolytes. Generally, Al metal is very stable in nature because of its natural oxides. Thus, an ideal electrolyte should both act as a corrosive to dissolve the Al_2O_3 but also a corrosion inhibitor for the anode, polymer binder, current collector, and battery case. The development of advanced aluminum batteries must stem from enhancements and advancements in proper electrolyte systems. The discovery of new cathode materials can certainly be promoted by investigating appropriate electrolytes. So far, much work remains to do to develop the ideal aluminum-ion battery electrolyte.

Although ionic liquid-based electrolytes have also been explored for Mg batteries, the results are still quite limited. In ionic liquid-based electrolyte MIBs, the most commonly used magnesium salt is $Mg(TFSI)_2$. However, the $TFSI^-$ anions are reductively unstable when coordinated with Mg^{2+}. The performance of MIB with $Mg(TFSI)_2$ as magnesium salts is poor. In addition, the layer formed on the Mg metal by the ionic liquid electrolyte decomposition prevents the transmission of Mg ions. However, reversible Mg deposition and dissolution in ionic liquids with $TFSI^-$ anions can be promoted by introducing oligomeric ether additives or using ether-functionalized ionic liquid cations. In these electrolytes, ether oxygen can replace the $TFSI^-$ anion in the Mg^{2+} coordination domain. In addition, in rechargeable magnesium batteries, ionic liquids can be effective additives to improve the electrochemical performance of electrolytes, such as ionic conductivity and anode stability.

At present, there are some ionic liquid-based electrolytes for SIBs with a variety of electrode materials that have been reported to exhibit better capacity, cycle stability, safety, and high-temperature performance than traditional solvent electrolytes. However, there are still many obstacles to realize a commercial SIB coupled with the ionic liquid electrolytes. For example, the high viscosity and density of ionic liquids may cause processing and wetting problems during the manufacturing process and may also decrease the specific energy of the battery. In addition, the battery rate performance must also be improved. We can expect further functionalization of cations and anions to improve the solvation and mobility of charge carriers to overcome above difficulties. Examples include the use of phosphonium systems, functionalized cations, and mixed anion electrolytes. In addition, the rate performance of SIBs can be improved by increasing the salt content to "superconcentrate" (>50 mol%). And the relative required ionic liquid will be greatly reduced leading to lower cost of the electrolyte. On the other hand, mixing ionic liquid-based materials with conventional "cheap" materials is more promising than pure materials to improve economic feasibility or some other disadvantages of ionic liquid. Ionic liquid-molecular solvent mixed electrolytes and ionic gels are all important strategies in this regard. If the economies of scale of these materials can be achieved, then these electrolytes seem to be a viable future technology for medium temperature applications.

The challenges and strategies of the three battery systems are illustrated in Figure 14. The research discussed here demonstrates that it is necessary to think outside the framework established by previous lithium-ion battery research when conducting research on ionic liquid electrolytes for aluminum-ion batteries, magnesium-ion batteries, and sodium-ion batteries, because these different metal elements possess inherent differences in chemical properties. In order to develop novel high-performance ionic liquid electrolytes, we need in-depth understanding and research on their fundamentals, paving the way for designing next-generation products.

Conflicts of Interest

The authors declare no competing financial interest.

Authors' Contributions

Na Zhu and Kun Zhang contributed equally to this work.

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