Recent Trends in Electrode and Electrolyte Design for Aluminum Batteries

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ABSTRACT: Due to the drawbacks in commercially known lithium-ion batteries (LIB) such as safety, availability, and cost issues, aluminum batteries are being hotly pursued in the research field of energy storage. Al being abundant, stable, and possessing high volumetric capacity has been found to be attractive among the next generation secondary batteries. Various unwanted side reactions in the case of aqueous electrolytes have shifted the attention toward nonaqueous electrolytes for Al batteries. Unlike LIBs, Al batteries are based on intercalation/deintercalation of ions on the cathode side and deposition/stripping of Al on the anodic side during the charge/discharge cycle of the battery. Hence, to provide a clear understanding of the recent developments in Al batteries, we have presented an overview concentrating on the choice of suitable cathodes and electrolytes involving aluminum chloride derived ions (AlCl$_4$$^-$, AlCl$_2$$^+$, AlCl$_3$$^+$, etc.). We elaborate the importance of innovation in terms of structure and morphology to improve the cathode materials as well as the necessary properties to look for in a suitable nonaqueous electrolyte. The significance of computational modeling is also discussed. The future perspectives are discussed which can improve the performance and reduce the manufacturing cost simultaneously to conceive Al batteries for a wide range of applications.

1. INTRODUCTION

Though, in the current scenario, nonrenewable energy sources help in meeting a large proportion of the energy demands, overdependence on these energy sources, like coal and oil, is not recommended, keeping an eye on sustainability for the future. The energy sources which are in the forefront today are bound to be exhausted, and hence, attention is shifted toward tapping abundant natural resources such as solar, water, and wind to meet the ever-increasing energy requirements. A major shortcoming of renewable sources of energy is their intermittent nature which ushers in the need for efficient energy storage systems, such as batteries and supercapacitors. In the past decade or so, lithium-ion batteries (LIBs) boasting high discharge voltage and storage capacities have become the go-to solution for energy storage technologies. As a result, other metal-ion batteries are being explored nowadays, out of which Al batteries have been earmarked as highly prospective next generation secondary batteries. Al is highly abundant in the earth’s crust and is chemically very stable. Al also possesses high gravimetric capacity (2980 mAh/g) and volumetric capacity (8046 mAh/cm$^3$), 4 times that of Li due to its three-electron reduction ability. However, Al batteries based on a rocking chair mechanism like LIBs face hardships to intercalate Al$^{3+}$ species. Al$^{3+}$ cations are difficult to reversibly intercalate/deintercalate from host materials, thus leading to poor ion diffusivity in the battery. Due to the +3 positive charge, the electrode material has to accept three electrons in order to bind a single cation, thus making the process much more challenging in a real scenario where the electrode is required to reversibly bind multiple cations. The aqueous electrolytes are not suitable in this case as its narrow electrochemical window combined with low standard electrode potential of Al (−1.66 V) leads to various side reactions and formation of Al$_2$O$_3$. The evolution of H$_2$ gas is also a major concern (2Al + 6H$_2$O → 2Al(OH)$_3$ + 3H$_2$). As a result, the battery has long-term stability issues. In 2011, Archer and co-workers achieved breakthrough by designing an Al battery with nonaqueous ionic liquid electrolyte (1-ethyl 3-methylimidazolium chloride/AlCl$_3$) and vanadium pentoxide as the cathode. In 2015, Dai and co-
workers designed a battery exhibiting a discharge voltage of \( \sim 2.0 \) V at 70 mAh/g specific capacity with ultrafast charge/discharge rate, as represented in Figure 1a.\(^\text{10}\) Here, a similar electrolyte was used with a graphitic foam cathode. The uniqueness in these battery systems was the involvement of AlCl\(_4^–\) ions rather than Al\(^{3+}\) in the cell reactions. Intercalation/deintercalation of AlCl\(_4^–\) at the cathode and electrodeposition/stripping of Al at the anode takes place during charge/discharge cycles of the battery. Monovalent AlCl\(_4^–\) facilitates easier reversible intercalation/deintercalation into the cathode material. These findings gave a new impetus to the research in the field of Al batteries since 2015, which was significantly stagnant previously due to the inability in dealing with Al\(^{3+}\) ions. Enormous research has been carried out since then to identify suitable cathode materials and compatible electrolytes both experimentally as well as computationally.\(^\text{11}\)

In this review, we have elaborated on the recent developments in the field of Al batteries, as represented in Scheme 1, brought about by the use of various aluminum chloride derived ions (such as AlCl\(_4^–\), AlCl\(_2^+\), and AlCl\(_2^{2+}\)). We discuss how the intercalation or binding properties of these ions with cathode material can determine the overall performance of batteries, taking examples from theoretical as well as experimental reports. We also demonstrate the major role played by various electrolytes in these batteries via the participating ions. Lastly, we suggest some probable ways on which further research may be directed to realize Al batteries with widespread applications in the energy storage technologies.

2. CATHODE MATERIALS

In this section, we discuss about the various classes of materials which have been successfully used as hosts to intercalate/deintercalate ions from the electrolyte during the working of Al-based batteries. Discussion on the various cathode materials starting from graphite to structurally similar materials is necessary to understand the intricate relationship between electrodes and ions from the electrolyte, which determines the electrochemical performance of the overall battery.

2.1. Three-Dimensional Graphite and Its Forms. Lin et al. brought about the breakthrough in the field of Al-ion batteries by utilizing 3D graphitic foam as the cathode material and Al metal as the anode, as shown in Figure 1a.\(^\text{10}\) Ionic liquid electrolyte, 1-ethyl 3-methylimidazolium chloride ([EMIM]-Cl) along with AlCl\(_4^–\) in a ratio of 1:1.3, was utilized to generate
Al$_2$Cl$_7^-$ ions in the electrolyte. During discharging of the battery, AlCl$_4^-$ can react with Al to form Al$_2$Cl$_7^-$ on the anodic side, leading to dissolution of Al metal. Simultaneously, the AlCl$_4^-$ gets deintercalated from the graphite (C$_n$) layers at the cathodic side. The reverse processes take place during the charging of the battery. Cell reactions can be given as

anode: $\text{Al} + 7\text{AlCl}_4^- \rightleftharpoons 4\text{AlCl}_7^- + 3e^-$

cathode: $\text{C}_n[\text{AlCl}_4] + e^- \rightleftharpoons \text{C}_n + \text{AlCl}_4^-$

This battery could give a discharge voltage of \(\sim 2\) V at a specific capacity of 70 mAh/g with an ultrafast discharge rate, as shown in Figure 1b, c. The cutoff charging voltage was determined to be 2.45 V, which is the limit of the electrochemical stability window for the considered ionic liquid electrolyte. After this potential, the AlCl$_4^-$ anion oxidizes to gaseous chlorine. However, the reason behind the charging/discharging rate was not clear. Also, the geometry of intercalating AlCl$_4$ and the perceived staging mechanism of intercalation had still not been explained. Hence, theoretical studies were carried out by our group and a few others, which provide meaningful insights...
about these batteries.\textsuperscript{12} The graphite layers are found to expand from 3.34 Å initially to more than 8 Å upon full intercalation.\textsuperscript{12a,b} The AlCl$_4^-$ maintains its tetrahedral geometry and due to the expanded gallery height can diffuse very easily, which is the reason behind an ultrafast charging rate. Initial intercalation was found to be energetically demanding due to the need to overcome the van der Waals interactions between graphite layers, and hence, a high concentration of AlCl$_4^-$ in the electrolyte is required.\textsuperscript{12b} In another work, the X-ray diffraction pattern of an AlCl$_4^-$-intercalated graphite system was simulated using density functional theory (DFT), which showed that, at low AlCl$_4^-$ concentration, the gallery height could not be expanded.\textsuperscript{13} However, with increasing density of AlCl$_4^-$, the gallery height opens up to allow further anion binding. Another important insight obtained was that, in order to obtain a high output voltage, the AlCl$_4^-$-intercalated graphite systems should be less stable to maintain the reversibility during charging/discharging processes.\textsuperscript{12e} This has also been demonstrated by considering the BC$_3$ system, which could yield a higher voltage due to AlCl$_4^-$ binding weaker than that in the graphite system.\textsuperscript{13e} This led to further experiments with other forms of graphite.\textsuperscript{11b,c,d} One such work used natural pristine graphite contrary to the pyrolytic graphite mentioned previously.\textsuperscript{11b} C–Cl bonds could be detected between the AlCl$_4^-$ anions and graphite edges, which leads to improvement in the storage capacity up to 110 mAh/g. With the idea that expanding the interlayer spaces of graphite can help with easier intercalation and diffusion of AlCl$_4^-$, Wu et al. prepared expanded graphite foam and oriented them perpendicular to the current collector, as represented in Figure 2a.\textsuperscript{11c} This led to higher rate capability as the diffusion of anions depends largely on the path length and, hence, could exhibit a discharge capacity of $\sim 60$ mAh/g at a high current density up to 12000 mA/g, stably cycled over 4000 cycles. Another form of highly crystalline graphite, namely, kish graphite flakes, has been used to further improve the capacity up to 142 mAh/g at an average discharge voltage of 1.79 V (Figure 2b), the idea being the availability of defect-free crystalline structure as well as crater-like morphology accommodating AlCl$_4^-$ anions easily as well as reversibly.\textsuperscript{11d}

Further, Jung et al. had theoretically studied the intercalation behavior using DFT by varying the number of graphite layers and found that decreasing layer of graphite flakes can dramatically increase the diffusivity of anions (Figure 2d) and, hence, the ultrafast charging behavior.\textsuperscript{14c} Few-layered graphite systems have higher elasticity and can allow diffusion by increasing the gallery height quite easily. Taking such theoretical findings into account, large-sized few-layered graphite as well as graphene have been investigated as cathode materials to perceive an ultrafast charging Al battery.\textsuperscript{14b} Whereas on one hand, this work further verified the decrease in layers directly contributing to fast kinetics of ion diffusion, on
the other hand, it also illustrated that the large size of the material in the horizontal direction can enhance the stability and maintain a longer life, as shown in Figure 2e. Gao et al. designed a graphite cathode, namely, trihigh tricontinuous (3H3C) graphite (Figure 2c), which shows further improved features. 14 With high temperature annealing combined with gas pressure effect, they were able to make highly crystallized defect-free graphite with readymade interconnected channels for trouble-free diffusion of AlCl4 during the functioning of the battery. With the help of such innovative design, specific capacities of ~120 mAh/g at a current density of 400 A/g with 91.7% retention after 250000 cycles was obtained, which is unprecedented in terms of longevity.

2.2. Low-Dimensional Graphite and Analogous Materials. Low-dimensional materials composed of carbon or other carbonaceous materials have also been used as cathodes in recent years. 15 These materials such as nanotubes, nanorods, nanoribbons, or 2D materials possess various kinds of binding sites as well as large surface area, thus making the intercalation process easier. Various theoretical insights can be gained from our works regarding such reduced dimensional materials. 11f,16 One such work demonstrated the applicability of single-walled carbon nanotubes as the cathode material. 16a Due to the availability of hollow spaces and porous nature, it can intercalate anions without interlayer expansion unlike 3D graphite. The predicted theoretical voltage was as high as 1.96 V at a specific capacity of 275 mAh/g along with trouble-free diffusion through the inner walls of the nanotubes. Another study involving graphite-like material, C3N, explained the benefits of using 1D nanotubes and a 2D bilayer over a 3D bulk structure. 11b Though the higher electron-donating ability of C3N leads to stronger binding of AlCl4 and hence lower voltage, decreasing the dimension can be a strategy for increasing the output characteristics. With stable AlCl4 intercalation, 1D and 2D systems have lower diffusion barriers (Figure 3a) as well as feature higher storage capacity. Yu et al. synthesized graphene nanoribbons on porous 3D graphene as represented in Figure 3b, whereby incorporating nanovoids, the surface area, mechanical strength, and conductivity of the cathode were improved. 15a As a result, the material performs with high specific capacity and cyclability over a wide range of temperatures. In a similar work, a flexible unzipped multiwalled carbon nanotube film was synthesized consisting of graphene nanoribbons and a carbon nanotube backbone, as represented in Figure 3c. 15b The unzipped nanotubes provide AlCl4 binding sites, whereas the nanotube backbone facilitates quick ion diffusion to deliver specific capacity of ~100 mAh/g and cycle life of 5600 cycles. One of the attractive innovations in this field has been development of carbon nanoscroll cathodes (Figure 3d) by Liu et al. 15c Few-layered graphene rolled into scrolls with an interlamellar spacing of 3.77 Å exhibits a specific capacity of 101.24 mAh/g at an ultrafast rate of 50000 mAh/g with 100% capacity retention even after 55000 cycles. The cathode material can function well enough across a wide temperature range (~25 to 80 °C). The stability and superior performance can be attributed to its ability to expand and intercalate AlCl4 reversibly in an easier manner compared to layered graphite structure. A 0D system, such as the carbon@graphene microstructure, was also adopted as cathode to deliver an average discharge voltage of 1.6 V at a specific capacity of 99 mAh/g. 15d It is noteworthy to mention various theoretical reports on low-dimensional materials of carbon-like systems for Al batteries, as well. These include monolayers such as that of phosphorene or heterostructures of graphite and h-BN, which has a similar geometry with minimum lattice mismatch. 16b,c

2.3. Organic Cathodes and Polymers. In recent years, some organic materials and their conducting polymers have also attracted interest. 11a,17 These materials generally show p-type redox activity, which means they can get oxidized to +1 or other oxidation states, in turn intercalating AlCl4− during the charging process. Though the conductivity in the case of such materials is a concern, they feature voids for AlCl4 adsorption and hence can attain higher storage capacity. One of the pioneering works on Al organic batteries was carried out by Hudak, where polypyrrole and polypthiophene were used as positive electrodes with the ability to bind AlCl4 anions. 15a However, as the Coulombic efficiency decreases at higher voltage, these electrodes could reach a specific capacity of ~100 mAh/g with an energy density of 44 Wh/kg, which is comparable to those of standard battery chemistries. A polythiophene/graphite composite prepared by keeping the ratio 1:1 has been able to show good electrochemical performance by delivering a high capacity of 152.5 mAh/g at a current density of 500 mA/g. 17a Another work involving poly(nitropyrene-co-pyrrole) as the cathode material demonstrated the benefits of using polymers of organic molecules rather than lightweight organic materials such as polycyclic aromatic hydrocarbons. 17b By virtue of their unique geometry, these materials can bind AlCl4 at their edge sites, maintaining high capacities, but suffer from low conductivity which can be improved by adopting longer chain polymers. As a result, this innovative cathode material could maintain a capacity of ~100 mAh/g with a discharge voltage of 1.7 V at a current density of 200 mA/g after 100 cycles. Some recent reports have also demonstrated the use of n-type redox material in Al batteries, which involves participation of AlCl4− or AlCl2+ ions. 18 Anthraquinone has been used as cathode material, which can reduce to −2 oxidation state and hence bind AlCl2+ cations. 18a However, a rather low discharge voltage of 1.1 V was obtained. Stoddart and co-workers developed a layered structure of the phanthenrenequinone-based macroyclic compound, which can bind three AlCl4− per macrocycle at a time, delivering ~1.5 V at a high capacity of 110 mAh/g for up to 5000 cycles. 18b Further, blending of the macrocycles with graphite flakes resulted in bipolar storage of anions (AlCl4−) and cations (AlCl2+) and hence could deliver up to 2.15 V at a higher capacity (140 mAh/g) and better conductivity. 2,3,5,6-Tetraphthalimido-1,4-benzoquinone has also been used as a cathode material for urcha-based electrolyte systems in Al batteries, which could deliver a capacity as high as 175 mAh/g for 250 cycles. 18c Hence, further research can be carried out to realize Al organic batteries on par with graphitic cathode materials.

2.4. Other Cathode Materials. Some other cathode materials, such as those based on transition metal or using porous structures like metal—organic frameworks, are also worth discussion. 19 As zeolites are known to have a porous structure with a large surface area, carbon templated on zeolite has been used as a cathode material by Kovalenko and co-workers. 19a The charge storage is a surface-based phenomenon here and, hence, facilitates fast ion diffusion, as well. With a conductive network of channels as wide as 12 Å, it can deliver ~2.2 V with volumetric and gravimetric performance better than that of crystalline graphitic foams. Xing and co-workers have put forward various Co-based competitive cathode
systems. One of them is carbon-encapsulated CoSe nanoparticles, developed from metal–organic frameworks featuring well-defined nanostructure which delivers a notable specific capacity of 427 mAh/g with two discharge plateaus at 1.0 and 1.9 V. Another recent work involving nanofibers of carbon covered with V₂O₅ has been found to intercalate AlCl₄⁻ and Al³⁺, alternately during the charge/discharge cycle, delivering voltage peaks of 2.4 and 1.5 V. Even though the battery has a very poor cycle life and disintegrates in just five cycles, further work can be done on such systems.

Figure 4 represents the electrochemical properties of the noteworthy representative cathode materials from all of the subsections discussed until now. Though the output voltage has remained close to 2 V in all of the materials, improvements in specific capacity can be seen due to the improvisations in morphology of the cathode material.

3. ELECTROLYTES

Electrolytes are a major component of battery technology beyond the cathode and anode, which plays a crucial role in increasing the battery efficiency. Fast ion mobility is a fundamental criterion in storage devices, which typically depends upon the choice of electrolyte. The development of nonaqueous electrolyte systems is of paramount importance so that the battery reactions with the cathode and Al anode can happen without formation of any side product. Some of the prerequisites of a suitable electrolyte should be its electrochemical stability and electronically insulating but ionically conducting nature, as presented in Scheme 2. The electrolytes should have a fixed electrochemical window (ECW) value such that it does not take part in any undesirable redox reactions. Electrolytes should have less viscosity and high mobility to ensure good conductivity. They should also be less corrosive in nature, so that the Al stripping/deposition on the anode can happen in a synchronized way. To maintain electrochemical stability of an electrolyte, as shown in Scheme 2, the cathodic reduction limit (Vₐₜ) should be positioned above the Fermi level of the cathode (μₐ) and the anodic oxidation limit (Vₐ) should be positioned below the Fermi level of the anode (μₐ) to avoid undesirable redox reactions. However, in a practical scenario, none of the developed electrolytes behaves as an ideal electrolyte due to in situ chemical reactions. Hence, a discussion on the developments of nonaqueous electrolytes for Al batteries is essential.

3.1. Ionic Liquids as an Electrolyte. In current scenario, the standard electrolytes for Al batteries are the various ionic liquid electrolytes. Ionic liquids (ILs) are a special class of electrolytes due to desirable properties such as good thermal and chemical stability, low melting point, negligible volatility (thus low flammability), high ionic conductivity, polarity, lower vapor pressure, and moderate viscosity. Though they are salts, they exist in a liquid state at room temperature because of weak electrostatic attraction between cations and anions and hence are called room temperature ionic liquid (RTILs). In general, the cation size is large and bulky due to the presence of long-chain alkyl groups that can protect the charge on organic moieties. Commonly used cation-based ionic liquids are imidazolium, pyridinium, pyrrolydinium, ammonium, and phosphonium salt. The counterpart anions are generally one of bis(trifluoromethanesulfonyl)imide (TFSI), bis(fluorosulfonyl)imide (FSI), chloroaluminate (AlCl₄⁻), BF₄⁻, and Cl⁻. In Al batteries, AlCl₄⁻ and Al₂Cl₇⁻ ions participate in intercalation or deintercalation and dissolution/electrodeposition processes, respectively. Imidazolium cation-based ionic liquids are the most studied electrolyte in modern battery technology. They can be easily synthesized through the alkylation of an N-alkylimidazole and subsequent anion metathesis to incorporate the desired anion. The most common modifications are carried out by alkyl group addition on 1 N and 2 C of the aromatic imidazolium ring, as shown in Scheme 2. The physical

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property of imidazolium ionic liquids can be varied by addition of different alkyl carbon chains on these positions of the imidazolium ring. Because of this flexibility, the imidazolium cation-based ionic liquids are mostly used as electrolytes in battery technology.

To understand the substituent effect of the imidazolium cation ring, our previous report considered a series of imidazolium-based RTILs with varied alkyl groups, such as 1-ethyl-3-methylimidazolium chloride ([EMIM][Cl]), 1-propyl-3-methylimidazolium chloride ([PMIM][Cl]), 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]), 1,2-dimethyl-3-propylimidazolium chloride ([DMP][Cl]), N-buty-1-N-methylpyrroldinium chloride ([BMP][Cl]), 1-hexyl-3-methylimidazolium chloride ([HMIM][Cl]), and 1-methyl-3-octylimidazolium chloride ([OMIM][Cl]) with AlCl3, as shown in Figure 5. Reprinted with permission from ref 20. Copyright 2020 Royal Society of Chemistry.

g. Yang et al. have studied some other RTILs, such as 1-AlCl4.20 Reprinted with permission from ref 20. Copyright 2020

From the investigated electrochemical properties, dimethyl-3-butylimidazolium chloride ([DMBIM][Cl]) with isopropyl-3-methylimidazolium chloride ([MIPIM][Cl]) or 1,2-dimethyl-3-propylimidazolium chloride ([DMP][Cl]), N-buty-1-N-methylpyrroldinium chloride ([BMP][Cl]), 1-hexyl-3-methylimidazolium chloride ([HMIM][Cl]), and 1-methyl-3-octylimidazolium chloride ([OMIM][Cl]) with AlCl3, as shown in Figure 5a–g. From the investigated electrochemical properties, it was concluded that, with increasing substituent alkyl chain, the cation-based ionic liquids are mostly used as electrolytes in battery technology.

Table 1. Experimental Density, Viscosity, Conductivity, and Average Voltage for a Series of Imidazolium-Based Ionic Liquids

| Ionic Liquid | Viscosity (P) | Density (kg/m³) | Conductivity (mS/cm) | Average Voltage (V) |
|--------------|---------------|-----------------|----------------------|---------------------|
| EMIM-AlCl4   | 0.18±0.01     | 1294±25a        | 14.1±0.6             | 2.25–2.0          |
| PMIM-AlCl4   | 0.15±0.01     | 1262±25b        | 12.4±0.7             | 2.1–1.98           |
| BMIM-AlCl4   | 0.24±0.02     | 1238±25a        | 8.9±0.5              | 2.0–1.7±0         |
| DMP-AlCl4    | 0.32±0.03     | 1170±25a        | 6.6±0.2              | 2.0               |
| MIPIM-AlCl4  | 0.40±0.04     | 1195±25a        | 4.6±0.1              | 2.0               |
| OMIM-AlCl4   | 0.42±0.05     | 1193±25a        | 4.1±0.1              | 2.0               |
| DMBIM-AlCl4  | 0.27±0.02     | 1230±25a        | 6.0±0.2              | 2.0               |

Table 1. Experimental average voltages were calculated by varying the imidazolium electrolytes in graphite cathode and Al anode systems. Hence it is evident why the imidazolium-based ionic liquids have been commonly used as an electrolyte, especially EMIM-AlCl4, due to the high ionic conductivity, moderate discharge voltage, and high ECW value (4.34 V). PMIM-AlCl4 can also be used as second generation ionic liquid electrolyte, beyond the EMIM-AlCl4 electrolyte system.20 Other than imidazolium cation-based electrolytes, very few cations have been studied as Al battery electrolytes, such as, N-buty-1-N-methylpyrroldinium chloride (BMP) (Figure 5e) and N-propyl-N-methylpyrroldinium chloride with AlCl3.24a However, due to lower ionic conductivity and narrow ECW potential value (~0.25 V), these electrolytes are not considered as good as the EMIM-AlCl4 electrolyte.24b

3.2. Molten Salt Electrolytes. Molten salt electrolytes have emerged as an area of research in the limited field of Al battery electrolytes to replace the costly imidazolium-based ionic liquids. Molten salt electrolytes operate at higher temperature (~180 °C). Mostly, the NaCl-AlCl3 binary and, later, the KCl-NaCl-AlCl3 trinary system have been used with partial success. The major concerns are small size and high polarizing power of generated cations (Na+ and K+) due to which the intercalation/deintercalation process becomes irreversible to some extent. Also, its higher operating temperature may not be suitable for practical battery systems. As a result, small cations are replaced by the long-chain organic cations such as amide and urea derivatives featuring optimum size and moderate ionic conductivity.

Various amide-based molten salt ionic liquids such as urea, acetamide, propionamide, and butyramide can also be considered as Al battery electrolytes based on the properties such as density, viscosity, and ionic conductivity. The density of AlCl3-amide ionic liquid analogues follow the order: AlCl3-urea (AlCl3−UR) > AlCl3-acetamide (AlCl3-AA) > AlCl3-propionamide (AlCl3−PA) > AlCl3-butyramide (AlCl3−BA), as shown in Figure 6a,b.20

Similarly, the viscosity trend follows the order: butyramide < propionamide < acetamide < urea at the same molar ratio of AlCl3/amide, as shown in Figure 6c. This could be due to the increasing hydrogen bonding between amide and Al complexes. In the case of urea, three possible donor atoms (one O atom and two N atoms) exist, whereas in amide, two possible donor atoms (one N and one O atom) are present. The stable isomerase forms of urea and acetamide are [AlCl3(U)2][AlCl4]− and [AlCl3(ACAm)2][AlCl4]−, respectively, as shown in Figure 6h,i.

Among all amide-based molten salts, researchers have chosen the urea/AlCl3 molten salt as the suitable electrolyte due to higher conductivity (7.9 mS/cm), higher ECW value (3.1 V), and moderate discharge voltage (2.3 V) compared to those of acetamide.20 Recently, Angell et al. considered N-methyl urea, N-ethyl urea, and urea as electrolytes with AlCl3 salt for Al batteries.25b These electrolytes have significantly lower viscosity (45, 67, and 133 cP for urea, and urea, respectively) compared to 1.95 V obtained for a pure urea electrolyte system. In these systems, the Al deposition can occur in two pathways, first from AlCl3− (similar as ionic liquid electrolytes) and second from the.
In this review, we have covered the recent developments in the field of Al batteries particularly based on aluminum chloride derived ions (AlCl4−, AlCl32+, AlCl53+). In these last 5–6 years, due to incredible research, Al batteries have come up as one of the suitable secondary battery mechanisms with prospects to compete with commercially prevalent lithium-ion batteries. Al batteries in comparison to Li-ion batteries are perceived to be much safer and boast attractive features like high abundance and volumetric capacity. However, careful research and clear understanding of Al batteries is required to commercialize them in the future. Though some interesting results have been obtained in a short period of time, the properties, such as discharge voltage, cycle life, and Coulombic efficiency, still are not up to the mark. The key to improving these properties lies in the proper structural consideration of the cathode material adopted. Chloroaluminate ions being bulky require host materials with enough structural flexibility or readymade space to accommodate them. Hence, using low-dimensional materials with different morphologies according to the requirements can be beneficial in this respect. Another idea can be to have defect-free forms of the available cathode materials. To have a commercial battery, its cost evaluation is important for which whatever synthetic methods are adopted for cathode materials should be cost-effective. Computational modeling of electrodes has also been able to predict the electrochemical properties such as voltage, capacity, and diffusion rate of the cathode materials and hence should be extensively used to explore new materials. Cheap organic cathode materials and bipolar ion storage systems also have bright prospects. By virtue of involving both cation and anion, the capacity and voltage can be greatly improved as has been seen in a few available reports. However, further exploration is necessary, as research in this direction is still in the infancy stage. Composite structures of redox-active materials with graphite can also be considered to increase overall conductivity of the cathode materials. Taking inspiration from the new advancements in dual-ion batteries, such as LiPF6 or Li[TFSI] batteries, dual-ion batteries of Al with intercalation-type anode materials can also be looked into. In such batteries, the AlCl4 anions as well as ionic liquid-based cations can participate in intercalation/deintercalation toward the cathode and anode, thus leading to higher voltage and specific capacity. Hence, connecting the concepts of dual-ion batteries with Al-based nonaqueous electrolytes can be a solution for future Al batteries with optimum electrochemical performance. The ionic liquids being expensive and corrosive in nature also...

Figure 6. (a) Temperature dependence on density of AlCl3-amide IL analogues, AlCl3/amide = 1.3. (b) AlCl3/amide molar ratio dependence on density of AlCl3-amide IL analogues, T = 333 K. (c) Temperature dependence on the viscosity of AlCl3-amide IL analogues. Reprinted with permission from ref 25a. Copyright 2017 Elsevier.

$[\text{AlCl}_2(\text{U})_2]^+$ cation. So, the negative electrode reactions are as follows, where the aluminum deposition would likely occur dominantly from cation species (path 2).25e

path1: $4\text{AlCl}_2^- + 3e \leftrightarrow \text{Al} + 7\text{AlCl}_4^-$

path2: $2[\text{AlCl}_2(\text{U})_2]^+ + 3e \leftrightarrow \text{Al} + 2\text{AlCl}_4^- + 4\text{U}$

From the perspective of battery performance rate, pure urea and urea derivative salts are a better choice as an electrolyte in Al battery systems compared to very costly imidazolium-based ionic liquids, and hence more investigation and understanding of these electrolytes can help to improve the electrochemical properties in Al batteries.

### 3.3. Other Electrolytes

Nonaqueous electrolytes containing AlCl3-derived ions have a hygroscopic nature due to which the electroplating process needs to be performed in an inert gas atmosphere. As a result, researchers have also developed polymer gel electrolytes for Al batteries that are more user-friendly. In the case of polymer gel electrolytes, solvent plays a critical role as the ionic liquids and monomers need to be soluble in it, and at the same time, there should not be any reaction between the solvent and gel polymer. Gel electrolyte was first adopted for Al batteries by Sun et al., where AlCl3-complexed acrylamide as a functional monomer along with acidic ionic liquid of [EMIM]Cl-AlCl3 (1–1.5, in molar ratio) as a plasticizer were used. By achieving Al deposition, the applicability of this electrolyte for rechargeable Al batteries has been verified.25d,e A high-rated quasi-solid-state Al battery has been prepared using a Et3NHCl/AlCl3-based polymer gel electrolyte, which possesses higher decomposition voltage of 2.9 V. A more robust electrode–electrolyte interface has been constructed upon using this electrolyte, which has been able to enhance the mechanical stability of Al batteries.25f

Few hybrid electrolyte-based dual-ion batteries have also been reported to overcome the limited choices of cathode material for Al batteries. Sun et al. chose LiFePO4 as a cathode material with the hybrid electrolyte LiAlCl4 + [EMIM]Cl, where Li participates in intercalation/deintercalation at the LiFePO4 cathodic side while regular Al deposition/stripping occurs at the Al anodic side.25g

### 4. CONCLUSION AND FUTURE PERSPECTIVES

In this review, we have covered the recent developments in the field of Al batteries particularly based on aluminum chloride
require improvements. Overall, we have reviewed all of the possible electrolytes, including different cation-based room temperature ionic liquids and molten salt electrolytes for Al battery systems. As of now, imidazolium-based ionic liquid electrolytes, specially EMIM-\(\text{AlCl}_4\), have been preferred. These expensive electrolytes may be substituted with newly discovered urea-based molten salt electrolytes, which are less expensive. More research needs to be carried out on various aspects to understand properties such as electrochemical window and redox reactions to develop suitable electrolytes with minimal side reactions. Less corrosive electrolytes generating chloroaluminate ions can also be tested further and optimized. Adopting solid electrolytes can be a good choice in developing safer batteries with easier operation in a noninert atmosphere. Polymer gel electrolytes may be considered for quasi-solid- or solid-state batteries, opening a wide application range. Proper investigation is required to identify suitable organic solvents, which can improve the monomer to polymer conversion process. Some other necessary parts of the battery such as current collectors should also be given importance. Due to corrosive nature of ionic liquids and stability issues, only a few binders and current collectors, such as Mo and W, have been found to be suitable. Hence, other current collectors can be investigated to ensure proper distribution of current to improve the battery. To summarize, thoughtful consideration of structure and morphology of cathode materials, developing composite materials, and comprehending new Al dual-ion battery systems can enhance the electrochemical properties of Al batteries. Similarly, adopting much safer and handier molten salt electrolytes and solid electrolyte systems can cut the production costs while maintaining the stability of these batteries. With thoughtful innovations from both experimental and computational perspective, Al batteries can fulfill the needs for grid-scale applications in a world of increasing energy demands.

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