Progress in electrolytes for rechargeable aluminium batteries: a review and perspective

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Abstract

The growing demand for safe, sustainable and energy-dense energy storage devices has spurred intensive investigations into post-lithium battery technologies. Rechargeable aluminium batteries are promising candidates for future electrochemical energy storage systems due to the high theoretical volumetric capacity of aluminium and its natural abundance in the Earth's crust, but their practical application is currently hindered by the limitations of presently available electrolytes. In this review, we highlight the key considerations needed to optimise the electrolyte design in relation to the aluminium battery system and critically assess the current state of knowledge and new concepts in liquid and quasi-solid polymer electrolytes, focusing primarily on non-aqueous systems. We then discuss the challenges and approaches in developing polymer electrolytes and finally provide an overview of the opportunities in quasi-solid electrolytes which could pave the way to achieving further improvements in aluminium batteries.

Keywords: aluminium battery; electrolytes; ionic liquids; ionogel; quasi-solid electrolytes

Introduction

Rechargeable electrochemical energy storage technologies have primarily been dominated by the lithium-ion battery system since its commercialisation in the early nineties. However, issues associated with the high cost, resource scarcity and most importantly the flammability of the organic electrolytes used are still key areas of concern. As society becomes more technology-driven, the efforts to reduce the global dependence on fossil fuels and the increase in the utilisation of renewable energy sources have created a growing need for high-performance batteries for electric vehicles, large-scale stationary energy storage and consumer electronics. With the demand for such energy storage devices on the rise, it has become evident that safer, cheaper and more sustainable solutions are needed if these aspirations are to be achieved. The exploration into alternative materials has proliferated in recent years, as researchers seek to utilise more earth-abundant elements in place of lithium, such as sodium, potassium, magnesium, calcium, zinc, sulphur and aluminium. Among these, aluminium is particularly promising due to its availability and accessibility as the third most abundant element on earth. The theoretical specific capacity of an aluminium metal negative electrode (2980 mA h g^{-1}) is about 77% that of lithium (3860 mA h g^{-1}), while its ability to transfer three electrons enables a theoretical volumetric capacity approximately four times that of lithium (8040 mA h cm^{-3} *vs*. 2060 mA h cm^{-3}, respectively)[1]. In addition, the intrinsic safety characteristics of aluminium and the electrolytes used present further advantages which merit the development of aluminium batteries for the next generation of energy storage devices.

Despite the encouraging progress in the development of positive electrode materials for aluminium batteries, several challenges – primarily relating to the electrolyte system – remain unresolved, limiting their presence to laboratory experimental-scale prototypes. In order to harness the full advantages of the high energy density of aluminium, electrolytes which enable fast ion transport and reversible aluminium deposition at the metallic aluminium negative electrode need to be developed. Both aqueous and non-aqueous electrolytes have been investigated for use in rechargeable aluminium batteries, beginning from the initial applications of inorganic molten salts, ionic liquids and organic solvents, to the deep eutectic solvents, water-in-salt and polymer electrolytes of today. A timeline of the various electrolyte classes is shown in Fig. 1 and depicts the progression of electrolytes throughout the history of aluminium battery research.

The most successful prototypes to date are based on chloroaluminate ionic liquids such as Lewis acidic melts of 1-ethyl-3-methylimidazolium chloride-aluminium chloride ($EMImCl-AlCl_3$)[2-4], achieving specific capacities between 60 and 150 mA h g^{-1} when combined with carbon-based positive electrodes. Unfortunately, these imidazolium-based ionic liquids are extremely expensive and hygroscopic, and their Lewis acidity also renders them highly corrosive to conventional battery components. Additional issues of liquid electrolytes, such as leakage and gaseous emissions caused by thermal or electrochemical degradation[5], further complicate their application in practical systems.

The development of electrolyte materials beyond liquids has been a topic of interest across all forms of battery research. Quasi-solid and solid-state electrolytes may assist in enhancing safety and enable flexible battery architectures but are often hindered by reduced ionic conductivity and poor interfacial contact with the electrodes. Improvements in the moisture[6, 7] and electrochemical stabilities[8] of ionic liquid electrolytes by incorporating a polymer matrix have been recently reported, but the application of polymer electrolytes in aluminium batteries is still very much in its infancy and only a limited number of studies in this area presently exist. As such, this review aims to address the development of electrolytes in emerging aluminium batteries with a focus on non-aqueous and quasi-solid polymer (ionogel) electrolytes. First, the key requirements and challenges of the electrolyte system are introduced, followed by an assessment of the current state of knowledge on liquid and polymer electrolytes in the published literature. The core concepts relating to polymer electrolyte design are then discussed in relation to the aluminium battery system to provide an insight into the possible approaches that can be taken to aid further advancements in this area.

The aluminium battery system

During the charge and discharge process of the battery, aluminium is reversibly electrodeposited at the negative electrode whereby the active species involved in this reaction undergoes a three-electron transfer process which contributes to the high theoretical volumetric capacity of metallic aluminium (8040 mA h cm^{-3})[1]. The electrodeposition occurs at -1.66 V *vs*. SHE but may shift slightly to more negative potentials due to the overpotentials of the substrate and as the ions exist in a complex form. In nonaqueous electrolytes, the electroactive species is commonly the $Al_2Cl_7^-$ anion (Eq. 1), although electroplating is also possible from other aluminium complexes, as shown in Eq. 2.

$$4Al_2Cl_7^- + 3e^- \rightleftharpoons Al + 7AlCl_4^- \tag{1}$$

$$2[AlCl_2 \cdot (\text{ligand})_n]^+ + 3e^- \rightleftharpoons Al + AlCl_4^- + 2n(\text{ligand}) \tag{2}$$

At the positive electrode, the mechanisms of ion storage can be broadly divided into three distinct categories depending on the electrode material: inorganic, carbon-based and organic materials. Inorganic compounds such as cheverel phase Mo_6S_8, vanadium oxides[9], sulphides[10], polyanions (e.g. $LiFePO_4$, $Na_3V_2(PO_4)$) and Prussian blue analogues have been reported to intercalate Al^{3+}, while elements (e.g. S, I_2 and O_2) and non-metallic compounds (e.g. CO_2) partake in phase-transfer or conversion reactions with the Al^{3+} ion to form a new chemical phase[11]. The intercalation of Al^{3+} ions in non-aqueous systems requires the dissociation of $Al_2Cl_7^-$ anion at the surface of the positive electrode according to Eq. (3)[10].

$$4Al_2Cl_7^- \rightleftharpoons Al^{3+} + 7AlCl_4^- \tag{3}$$

The intercalation and insertion process of $AlCl_4^-$ ions in graphitic foams, graphite flakes, conductive polymers, and other carbon-based materials is well documented. Although the monovalent intercalation of $AlCl_4^-$ reduces the specific capacity in comparison to Al^{3+} intercalation systems, the low energy barriers to diffusion [12-15] have enabled rapid charge rates of up to 75 C in graphitic foams [2] and correspondingly high specific power[2, 3, 12].

Organic compounds such as quinones[16-20], cyano-organic molecules[21], as well as polyimide-metal organic framework hybrids[22], have recently been explored as potential positive electrode materials for aluminium batteries. Unlike graphitic positive electrode materials, organic electrodes do not involve the intercalation of $AlCl_4^-$, but rather a coordination reaction mechanism, of which a general formula is given in Eq. 4. During discharge, the carbonyl bonds of the organic compound are reduced and interact with the cationic chloroaluminate complex, $AlCl_2^+$. This therefore renders their specific capacities independent of the volume of the electrolyte used and mitigates the challenges of inserting densely charged Al^{3+} ions into inorganic electrode materials.

$$Q \cdot nAlCl_2 + nAlCl_4^- \rightleftharpoons Q + nAl_2Cl_6 + ne^- \tag{4}$$

where *n* is the number of carbonyl groups of an organic compound, Q.

Designing electrolytes for aluminium batteries

The electrolyte of an electrochemical cell provides pathways for ionic transport needed to complete the electrical circuit and plays an important role in controlling the overall chemical reactions within the battery. In an aluminium battery, the electrolyte is required to accommodate the reversible electrodeposition of aluminium during operation. As the electroplating of aluminium takes place from the aluminium-containing species within the electrolyte, the volume of electrolyte used, and the corresponding availability of the electroactive species, effectively serve as capacity-limiting components of the cell. Thus, the electrolyte of an aluminium battery can be considered akin to a liquid anode, or an anolyte, as suggested by Kravchyk et al.[4], and the selection of a suitable electrolyte for aluminium batteries requires the careful consideration of several different influencing factors, listed as follows:

- A wide electrochemical stability window prevents the degradation and decomposition of the electrolyte for long-term cycling stability. To enable aluminium electrodeposition, the stability window needs to be greater than 1.66 V, but much higher potentials (> 4 V) are preferred for battery electrolyte applications to allow a greater range of electrode materials to be used and to increase the specific power and energy of the cell.
- Reversible aluminium electrodeposition with high coulombic efficiency is needed to avoid the loss of electroactive species to side reactions, which would be detrimental to the capacity retention of the battery system. It is essential that the deposits are smooth with no dendritic growth, as rugged and dendritic aluminium deposits may fall off and result in the loss of electroactive material.[23, 24] At the same time, any dendrite formation could potentially lead to contact between the electrodes and subsequent short-circuiting of the battery.
- Efficient ion transport is crucial for reducing the overpotentials due to mass transport limitations and improving the overall performance of the battery system. Ideally, the ionic conductivity of an electrolyte should be greater than 10^{-4} S cm^{-1} for practical applications so that ion mobility can be sustained at high driving currents with a negligible concentration gradient. Most liquid electrolytes have ionic conductivities well beyond this threshold; however, these considerations become particularly important for quasi-solid and solid electrolytes in which ion mobility may be hindered. In addition, the ion transference number of the active ionic species, an indicator of its contribution to the overall current, also needs to be sufficiently high for optimum ion mobility.
- Good adhesion and interfacial contact between the electrode and the electrolyte are necessary to reduce internal resistance. Poor interfacial properties are often the key precursors to cycling instability and cell failure and are exacerbated by volumetric changes during cycling.[25] This is especially important for flexible batteries and solid-state systems, as differences between the expansion and contraction of the electrolyte and electrodes can be detrimental and lead to the fracture of battery components.
- The design of safe, non-flammable and non-toxic electrolytes is critical to the successful implementation of emerging battery systems in their intended applications. In this respect, the consideration of physicochemical properties is necessary to provide resistance against internal and external factors such as gas evolution, mechanical deformation, temperature extremes and radiation, for instance in aerospace applications. Furthermore, when a battery is overcharged, the evolution and accumulation of gas in a small and unvented cell can cause contact loss and battery failure, cell bloating or even venting, which can be quite violent and dangerous. Quasi-solid and solid electrolytes offer an enhanced suppression of gas evolution[7], while liquids with low vapour pressures such as deep eutectic solvents and ionic liquids are also advantageous.
- Other practical factors such as cost, manufacturing, sustainability and recycling are often overlooked in research studies which tend to direct their focus towards electrochemical performance. Realistically, these considerations are, in many instances, the underlying factors which prohibit the commercialisation of alternative battery chemistries on a larger scale and quantity. For example, the chloroaluminate ionic liquids routinely used in aluminium batteries are expensive, sensitive to moisture and react with conventional cell casing materials[26, 27] as well as electrode materials such as vanadium pentoxide[28]; electrolytes that can be safely handled in air are needed to simplify the production process and reduce costs to facilitate large-scale production.

Electrolytes in aluminium batteries

Although imidazolium-based chloroaluminate ionic liquids are currently the most commonly used electrolytes in aluminium battery research, they present several drawbacks, primarily due to their high cost, hygroscopicity and corrosivity. It is therefore paramount to analyse the status and new concepts in electrolyte research so that alternatives and opportunities for further improvements can be identified. Herein, we begin with an overview of rechargeable aqueous systems, followed by a more in-depth discussion of the non-aqueous liquid electrolytes used in aluminium batteries, including organic solvents, inorganic molten salts, deep eutectic solvents and ionic liquids. The electrochemical properties and characteristics of the various electrolyte categories in the existing research are briefly summarised in Table 1.

Aqueous liquid electrolytes

Until recently, the application of aqueous electrolytes in aluminium batteries has largely been limited to primary or secondary batteries which operate at discharge cell potentials below 1.5 V, or do not involve metallic aluminium[29, 30], due to its low standard electrode potential of -1.66 V *vs.* SHE. Although aqueous electrolytes are highly ion-conductive ($\sigma \approx 10^1$-10^2 mS cm^{-1}), relatively inexpensive, non-flammable and usually have a low environmental impact, the very negative potential of aluminium electrodeposition exceeds the narrow electrochemical stability limit of water, resulting in the simultaneous evolution of hydrogen and subsequent decomposition of the electrolyte. Furthermore, the oxide film also introduces a contact resistance of 35 kΩ[31], causing a large reaction overpotential which severely impacts the coulombic efficiency of the cell. While the use of highly basic and acidic electrolytes in accordance with the Pourbaix diagram (pH < 4; pH > 8.6, Fig. 2)[32] can prevent this formation, the simultaneous corrosion of the metallic aluminium anode accompanied with the evolution of hydrogen is problematic. To this end, strategies such as the pre-treatment of the aluminium negative electrode and the use of highly concentrated water-in-salt electrolytes have recently emerged to mitigate these issues and improve battery performance. The pre-treatment of the aluminium electrode by immersion in a Lewis acidic EMImCl-$AlCl_3$ ionic liquid results in the formation of an artificial solid electrolyte interphase, which replaces the passivating oxide film and subsequently improves the reversibility of aluminium deposition in aqueous media. When coupled with manganese oxide positive electrodes, the assembled batteries achieved specific energies exceeding 500 W h kg^{-1}, albeit with low capacity retention[33, 34].

Water-in-salt electrolytes

Water-in-salt electrolytes can be considered as a sub-class of aqueous electrolytes which contain extremely high salt concentrations at or close to the solubility limit. The pronounced interionic interactions suppress hydrogen and oxygen evolution and favour cation transport[35] while allowing the electrolyte to ionic conductivities similar to conventional, less concentrated salt-in-water electrolytes (Fig. 3a)[36]. In a water-in-salt electrolyte consisting of 5 M aluminium trifluoromethanesulphonate [$Al(OTF)_3$], the electrochemical window was widened to 2.65 V (Fig. 3b), while an electrochemical stability window of up to 4 V was recorded in $AlCl_3 \cdot 6H_2O$ (mass ratio of $AlCl_3 \cdot 6H_2O/H_2O = 12$)[37], both of which are significantly wider than that of water. The structure of water-in-salt electrolytes is similar to that of ionic liquids[38], in which the available water molecules form loose and intimate ion clusters (Fig. 3c). The formation of ion clusters is thought to be responsible for suppressing oxygen and hydrogen evolution[36], while the aggregates of water molecules act as conductive channels for fast cation transport[35]. Although the application of water-in-salt electrolytes in aluminium batteries are currently limited, an initial investigation in an aluminium-graphite configuration has demonstrated specific capacities of up to 165 mA h g^{-1} at 500 mA g^{-1}, a high coulombic efficiency exceeding 95% over 1000 cycles, and no dendrite growth observed[37]. The first application of a water-in-salt electrolyte in an aluminium-sulphur battery was recently reported by Hu et al.[39] with an aqueous mixture of 1 M $Al(OTF)_3$, 17 M lithium bis(trifluoromethanesulfonyl)imide and 0.02 M HCl, which had an electrochemical stability window of 3.1 V. The role of HCl was to provide a mildly acidic environment to remove and prevent the formation of the passivating oxide layer of aluminium, allowing the battery to maintain a coulombic efficiency of 97% and a specific capacity of 420 mA h g^{-1} (with respect to the mass of sulphur) after 30 cycles. The substantially lower cost of water-in-salt electrolytes in comparison to traditional EMImCl-$AlCl_3$ ionic liquids[37] make them highly interesting candidates for further investigative research into developing cheaper and safer electrolytes.

Nonaqueous liquid electrolytes

Organic solutions

Given the routine use of non-aqueous electrolytes in the aluminium electroplating industry, it is perhaps unsurprising that much of the existing research in aluminium batteries has been based upon non-aqueous systems. In industrial processes, the electroplating of aluminium is commonly conducted in organic solvents containing aluminium salts, such as alkylaluminium compounds in toluene and $AlCl_3$-$LiAlH_4$ in tetrahydrofuran[40]. Several organic electrolytes have since been proposed[41-43], which produced dendrite-free aluminium deposits. A diglyme electrolyte containing aluminium triflate salts was trialled in a battery with a copper hexacyanoferrate positive electrode[44], which showed very low reversible specific capacities between 5 and 14 mA h g^{-1} and poor capacity retention. Although aluminium deposition from organic electrolytes can produce satisfactory deposits, they often operate above room temperature[45], and the obvious safety issues associated with highly flammable and volatile organic solvents render these electrolytes problematic for use in battery systems. Apart from a limited number of reports, organic electrolytes have been rarely employed in aluminium battery research due to the availability of safer alternatives in inorganic molten salts, ionic liquids and deep eutectic solvents.

Inorganic molten salts

Inorganic molten salts have been shown to readily electrodeposit aluminium at elevated temperatures. Initial investigations in a binary $NaAlCl_4$ mixture at 175°C revealed rapid dendritic growth even at a low current density of 1.4 mA cm^{-2}, although incorporating an $MnCl_2$ additive was found to produce smooth and compact deposits[46,47]. Aluminium-graphite batteries cycled at 120°C with NaCl-$AlCl_3$[48] and $AlCl_3$-NaCl-KCl[49] molten salt electrolytes exhibited no dendritic growth and reached specific capacities of up to 136 mA h g^{-1} at 500 mA g^{-1} and 128 mA h g^{-1} at 100 mA g^{-1} respectively. In a recent study by Wang et al., an aluminium battery with graphite paper as the positive electrode and a ternary inorganic electrolyte of $AlCl_3$-LiCl-KCl was reported to achieve a specific capacity of 107 mA h g^{-1} at 200 mA g^{-1} whilst operating at 99°C with a high coulombic efficiency[50]. By forming ternary inorganic salts, the eutectic point can be reduced to levels below the boiling point of water, which allows for the use of water-based heating systems. Due to the operating conditions required, these electrolytes would be more suited to large-scale energy storage applications at the present stage.

Deep eutectic solvents

The high cost, hygroscopicity and corrosivity of imidazolium-based ionic liquids have incentivised the investigation of alternative electrolytes such as deep eutectic solvents, which are low-cost analogues of ionic liquids containing a mixture of Lewis or Brønsted acids and bases composed of various anions and/or cations[51]. Deep eutectic solvents are commonly formed from Lewis acidic metal salts (in this case, $AlCl_3$) and a hydrogen bond donor or Lewis basic ligand, such as urea or acetamide (Eq. 5).

$$2AlCl_3 + n(\text{ligand}) \rightleftharpoons [AlCl_2 \cdot n(\text{ligand})]^+ + [AlCl_4]^- \qquad (5)$$

Deep eutectic solvents share many similar physical properties with ionic liquids, including having low vapour pressures, a relatively wide liquidus range and non-flammability, making them suitable for battery applications. The use of eutectic mixtures such as $AlCl_3$-urea[52-54] and $AlCl_3$-acetamide[55] in aluminium-graphite batteries have demonstrated coulombic efficiencies above 95%, but the specific discharge capacities reported remain relatively low, ranging between 30 to 75 mA h g^{-1} due to their viscosity and low ionic conductivity at room temperature[54]. Forming electrolytes based on urea derivatives such as N-ethyl urea and N-methyl urea with $AlCl_3$ result in mixtures with drastically lower viscosities than urea-based eutectic solvents (η = 45 and 67 cP respectively for $AlCl_3$-N-ethyl urea and $AlCl_3$-N-methyl urea, *vs.* 133 cP for $AlCl_3$-urea at 25°C, at a 1.4 $AlCl_3$/[urea derivative] ratio). Similarly, higher conductivities were observed for the urea derivative electrolytes, as well as higher intrinsic discharge potentials. This is anticipated to be a result of the greater concentration of electroactive $Al_2Cl_7^-$ anions over other aluminium complexes present in the urea derivative systems. Additionally, acetamide- and urea-based deep eutectic solvents have also been shown to be promising for improving the cell cycling stability and cycle life in aluminium-sulphur batteries, maintaining specific capacities of 500 mA h g^{-1}, for 60 and 100 cycles, respectively.[56, 57] In contrast, Al-S batteries with an EMImCl-$AlCl_3$ electrolyte exhibit a rather short cycle life of approximately 20 cycles[58], owing to the poor chemical stability of sulphur in EMIm-based electrolytes.

Ionic liquids

Room-temperature ionic liquids are broadly defined as organic salts made up of weakly coordinated complex ions which exist in the liquid state at room temperature. Due to their thermal stability, non-flammability, low volatility and negligible vapour pressures,[59] ionic liquids have been extensively investigated for use in electrochemical energy storage devices. Ionic liquids used in aluminium batteries are generally Lewis acidic melts of aluminium chloride and an organic salt in the form R^+X^-, where R^+ is an organic cation such as imidazolium, pyridinium or pyrrolidinium, and X^- is a halide anion, usually chloride. Electrolytes containing alkyl imidazolium cations such as 1-ethyl-3-methylimidazolium, $[EMIm]^+$, and 1-butyl-3-methylimidazolium, $[BMIm]^+$, make up the vast majority of ionic liquid-based aluminium battery systems in the published literature, due to the ease of obtaining relatively dense and crystalline aluminium deposits at moderate current densities (≤ ca. 40 mA cm^{-2}), and close to 100% coulombic efficiency.[60]

Chloroaluminate ionic liquids offer relatively wide electrochemical stability windows of up to 4 V,[61] with ionic conductivities in the range of 10-25 mS cm^{-1}, which is in the same order of magnitude as that of aqueous electrolytes (10-50 mS cm^{-1}).[33] However, they are also hygroscopic in nature and exposure to moisture leads to a rapid exothermic reaction, generating hydrochloric acid and other oxide- and proton-containing species.[62]

The Lewis acidity of chloroaluminate ionic liquids refers to the molar ratio (r) of $AlCl_3$ to the organic salt, which determines the corresponding speciation and its physical and electrochemical properties. In Lewis acidic compositions ($1 < r < 2$), aluminium exists primarily in the form of $AlCl_4^-$ and $Al_2Cl_7^-$ anions, of which the latter is considered a Lewis acid due to its ability to accept electron pairs. Oligomeric $Al_3Cl_{10}^-$ anions are also formed in very acidic melts ($r > 1.5$)[62, 63] and $AlCl_3$ is not soluble in molar ratios exceeding $r = 2$. Both $AlCl_4^-$ and uncoordinated chloride ions, which serve as electron-pair donors, are present in Lewis basic ionic liquids ($r < 1$), while equimolar mixtures contain mostly neutral $AlCl_4^-$ anions.

Since the reduction of $AlCl_4^-$ takes place at a lower electrode potential than the organic cation of the ionic liquid, it is typically not possible to electrodeposit aluminium from neutral and basic ionic liquids as the electrolyte decomposes before electroplating can occur. Thus, the application of chloroaluminate ionic liquids in aluminium batteries is almost exclusively limited to Lewis acidic melts which contain $Al_2Cl_7^-$ anions. However, it has been recently shown that if the electrochemical stability of the organic cation can be widened sufficiently, such as by forming an ionic liquid gel, or ionogel, it is possible to electroplate aluminium from tetrachloroaluminate anions in Lewis neutral ionogels, albeit at coulombic efficiencies below 60%. The low efficiency can be attributed to the increased viscosity and reduced ionic mobility and conductivity of the ionogel[8]. For comparison, the coulombic efficiency of aluminium electrodeposition in a Lewis acidic EMImCl-$AlCl_3$ gel electrolyte was approximately 80% at 50°C,[6] while a triethylamine hydrochloride (Et_3NHCl-$AlCl_3$) gel was reported to achieve efficiencies over 90%. The formation, characteristics and application of ionogels in aluminium batteries are discussed in greater detail in the next section.

In theory, the anodic specific capacity of the battery increases with the Lewis acidity of the ionic liquid owing to the greater concentration of $Al_2Cl_7^-$ anions from which aluminium can be electrodeposited during the charging process. Empirically, this was found to be true only at low specific currents (ca. 20 mA g^{-1})[65], due to the limitations on the rate of diffusion which cause a localised depletion of $Al_2Cl_7^-$ anions and thus Lewis acidity at the electrode surface. In battery applications, the best charge and discharge behaviour is observed in ionic liquid electrolytes with low to moderate acidity (r = 1.1 to 1.3), owing to the reduced corrosion of the aluminium negative electrode and the higher ionic conductivities of less acidic compositions[66, 67]. Additionally, the mildly corrosive properties of slightly acidic melts have been suggested to aid the removal of the oxide film on the aluminium anode surface[66]. While the formation of the passivation film should not present an issue when materials are handled in an inert atmosphere, this “self-cleaning” ability would be beneficial for removing any remaining oxide residue introduced during the manufacturing process.

Although aluminium electrodeposition from acidic chloroaluminate ionic liquids takes place at high coulombic efficiency, the morphology of the deposited layer appears to be highly dependent on the composition of the solution, the current density and the operating conditions[23, 68], as well as the coordination chemistry of the electrolyte and the nucleation and growth mechanisms during electroplating.[27] The cyclic electrodeposition of aluminium in EMImCl–$AlCl_3$ electrolytes has also been reported to lead to the roughening of the aluminium electrode, albeit with no dendrite growth.[1] This increase in surface roughness may result in the loss of electroactive species if the deposits fall off, reducing the capacity of the cell. Plating aluminium from EMImCl-$AlCl_3$ at low current densities below 40 mA cm^{-2} generally produces dense and adherent deposits, while poorly attached, dendritic deposits have been observed at higher current densities.[68, 69] Long et al.[24] recently demonstrated that the use of porous aluminium negative electrodes can effectively suppress dendrite growth, which was observed on planar aluminium electrodes during both galvanostatic electrodeposition and cycling in an EMImCl-$AlCl_3$ electrolyte. The increased surface area of the porous electrode contributes to reducing the local current density, allowing homogeneous deposits to be formed and subsequently enhancing the cycling stability of the cell to over 18,000 cycles. Dendrite growth in aluminium-metal batteries is rarely reported in the existing literature; however, the results of Ref. [24] suggest that this issue may have been overlooked. Thus, further investigative studies into the metal growth mechanisms during battery cycling would certainly be beneficial for developing long-life rechargeable aluminium batteries.

It is noted that ionic liquid electrolytes are not limited to imidazolium-based ionic liquids. The high cost and hygroscopicity of these mixtures have incentivised the investigation of ionic liquids formed from alternative organic salts such as trimethylamine (TMAHCl-$AlCl_3$)[70], and Et_3NHCl, which is reported to be 20 to 30 times cheaper than EMImCl.[71, 72] When paired with graphene-based positive electrodes, aluminium-metal batteries with TMAHCl-$AlCl_3$[70] and Et_3NHCl electrolytes exhibit excellent cycling stability during prolonged cycling[70, 72]. Furthermore, the replacement of chloroaluminate ions with neutral pyridine-based ligands[27, 73] can mitigate the problematic corrosion caused by traditional chloroaluminate ionic liquids.

Tuning ionic liquids for battery applications

Improvements in the electrochemical properties of ionic liquids can be achieved by altering their constituent cations and anions, or by introducing additives such as dichloromethane to reduce the viscosity and subsequently improve the conductivity and specific capacity of the electrolyte.[74] However, the addition of organic solvents may inherently have a negative impact on the safety and environmental-friendliness of the resulting electrolyte.

The effects of different organic cations on the electrodeposition of aluminium in ionic liquids have been studied by several groups.[75-77] The physical and electrochemical characteristics of 1-methyl-1-

propylpyrrolidinium chloride-aluminium chloride (Py1,3Cl-$AlCl_3$) were compared with those of EMImCl-$AlCl_3$ by Zhu et al.[76] The Py1,3Cl-$AlCl_3$ ionic liquid exhibited a lower specific energy in an aluminium-graphite battery, as well as a higher viscosity and lower conductivity than EMImCl-$AlCl_3$. These differences in properties were attributed to the larger size of the $[Py1,3]^+$ cation (142 Å^3, *vs.* 118 Å^3 for $[EMIm^+]$)[76], which helps to stabilise and favour the formation of larger $(AlCl_3)_n$ anions, lowering the overall concentrations of the electrochemically active $AlCl_4^-$ and $Al_2Cl_7^-$ species. In turn, this results in an increase in viscosity, reduced ionic mobility and higher overpotentials during battery charge and discharge cycles. In addition to the cation size, the intermolecular forces between organic cations and chloroaluminate anions also play a crucial role in the reversibility of aluminium electrodeposition/dissolution. Weaker cation-anion interactions have been shown to improve the morphology of aluminium deposits, giving smooth and compact coatings[75], as well as increase the efficiency of electrodeposition and the reversibility of $AlCl_4^-$ intercalation and deintercalation in graphite positive electrodes.[77] Thus, smaller organic cations and weaker intermolecular interactions between cations and anions are favoured in the synthesis of new ionic liquids for electrolyte applications.[75, 77]

Computational and theoretical approaches

While the majority of the existing research on aluminium batteries has been conducted experimentally, computational and theoretical studies can provide a deeper understanding of the underlying mechanisms, and serve as useful tools for predicting the electrochemical properties of different electrolytes. A good understanding of the factors that determine the performance of the electrolyte in an aluminium battery is crucial to developing and identifying the appropriate electrolyte for the intended application.

The electrochemical stability window of ionic liquids is bounded by the reduction and oxidation potential of the organic cation and the aluminum anion[66], respectively, and the formation of a stable battery system requires that the anode and cathode Fermi energy levels fall within the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the electrolyte.[78] A computational analysis of several different ionic liquids, confirmed the stability and suitability of imidazolium-based chloroaluminate ionic liquids in aluminium-graphite batteries. Of the ionic liquids investigated, 1-propyl-3-methyl imidazolium chloride (PMImCl-$AlCl_3$) and EMImCl-$AlCl_3$ exhibited the widest electrochemical stability windows (4.7 and 4.34 V, respectively) and highest ionic conductivities (12.4 and 14.1 mS cm^{-1}, respectively). The ionic conductivity of the imidazolium-based ionic liquids was shown to decrease with longer cation alkyl chain lengths, due to the increase in cation size. These results suggest that, in addition to the commonly used EMImCl-$AlCl_3$ ionic liquid, PMImCl-$AlCl_3$ may be a suitable electrolyte for aluminium-graphite batteries.

Quasi-solid electrolytes

There is no doubt that the high ionic conductivity and excellent interfacial contact offered by liquid electrolytes have often made them a simple and straightforward means of testing new concepts in battery research. In certain applications, however, where safety, weight and volume are crucial, the physical attributes of quasi-solid and solid materials may provide greater advantages over liquid systems.

From a materials standpoint, quasi-solid electrolytes attempt to combine the merits of solid-state and liquid electrolytes by providing enhanced mechanical stability and a reduced risk of electrolyte leakage over liquids, while retaining higher ionic conductivity and better contact with the electrodes in contrast to solid materials. The gaseous emission at the electrodes can be suppressed[7], and depending on its dimensional stability, quasi-solid materials may restrict the growth of dendrites and eliminate the need for a porous separator between the electrodes while enabling flexible battery architectures. This, in turn, enables shorter ion transfer paths and a lower potential drop, as well as reductions in mass and volume. However, as a consequence of these enhanced physical properties, the resulting ionic conductivity often suffers. Electrochemically, the confinement of ionic liquids in a polymer matrix to form ionogels has not only been demonstrated to improve the thermal[79] and moisture sensitivities[6, 7], but also extend their electrochemical stability window[8, 80]. These improvements are particularly relevant to aluminium batteries due to the hygroscopic nature of chloroaluminate ionic liquid electrolytes.

The class of quasi-solid electrolytes spans broadly both in terms of physical properties, encompassing viscous liquids and gels to rubbery elastomers and self-standing membranes, as well as in the methods used to synthesise them. Typically, quasi-solid electrolytes comprise a liquid component confined within a solid inorganic or polymer host, or a combination of both, which are commonly referred to as hybrid electrolytes. The appropriate combination of solid and liquid phases gives rise to properties that can be tuned as required. To our knowledge, research on quasi-solid electrolytes for aluminium batteries is presently limited to polymer-based ionogels and eutectogels, although many other possibilities exist, which have been shown to work in other battery chemistries. The terms “ionogel” and “eutectogel” refer to gels derived from ionic liquids and deep eutectic solvents, respectively.

Polymer electrolytes

The initial application of polymer materials in electrochemical cells were in lithium batteries, which can be dated back to the pioneering work of Armand in the late 1970s, following the initial discovery of ionic conductivity in sodium and potassium complexes of polyethylene oxide (PEO) by Fenton, Parker and Wright a few years earlier.[81] Since then, research into polymer electrolytes has expanded across a multitude of fields in energy storage and conversion, including fuel cells, supercapacitors, solar cells, electrochromic devices, as well as batteries based on alternative metals. However, despite the extensive research surrounding polymer electrolytes in lithium batteries, this knowledge cannot be directly translated to aluminium battery systems due to the fundamental differences in the charge storage mechanisms. As outlined previously, the charge storage mechanism at the negative electrode in non-aqueous batteries usually relies on the electrodeposition of aluminium from $Al_2Cl_7^-$ ions within the electrolyte. Unfortunately, herein lie the challenges in selecting compatible polymers and solvents which do not produce side reactions. Commonly used polymer hosts for alkali metal salts such as PEO, polyacrylonitrile (PAN), polymethyl methacrylate (PMMA) and polyvinylidene fluoride (PVDF) are not optimal in Lewis acidic chloroaluminate ionic liquids, as their lone electron-bearing functional groups serve as Lewis bases and form complexes with the electrophilic $Al_2Cl_7^-$ ions. As a result, fewer $Al_2Cl_7^-$ ions are available for electrodeposition and the electrochemical activity of the electrolyte is reduced. These acid-base interactions are corroborated by several studies[6, 9, 82], notably in Ref. [82], where no electrochemical activity was observed in a PEO-based hybrid polymer electrolyte. It is worth mentioning that the use of acetone as a solvent in the mechanochemical route of synthesis is likely to have caused the additional consumption of the electroactive species due to its lone electron pairs. Separately, the use of PVDF as a polymer binder in positive electrodes has also been proven to be incompatible with acidic chloroaluminate ionic liquids.

Gel formation

While numerous methods can be used to synthesise gel electrolytes, many of these processes, such as solution casting and *in situ* polymerisation frequently involve the use of solvents to homogenise the liquid and solid components. In this regard, the selection of solvents for use in these procedures also requires careful consideration. The interactions between chloroaluminate ionic liquids and frequently used solvents have been investigated by Sun et al.[6] The addition of acetone, acetonitrile and tetrahydrofuran to an EMImCl-$AlCl_3$ ionic liquid were found to severely hinder its ability to electrodeposit and strip aluminium, which is expected given the presence of lone electron pairs in these solvents. Interestingly, cyclic voltammetry measurements showed an increase in the peak current density of EMImCl-$AlCl_3$ electrolyte solutions containing toluene and dichloromethane, likely due to improvements in the ionic conductivity and mobility. Building on these findings, dichloromethane has been used as a solvent for the polymerisation of acrylamide monomers (Fig. 4a) in the presence of EMImCl-$AlCl_3$[6] and Et_3NHCl-$AlCl_3$[7, 80] to produce self-standing polymer membranes suitable for aluminium batteries. Both gels showed improved resistance to moisture, while the Et_3NHCl-$AlCl_3$ gel was also shown to operate well at low temperatures, with over 60% capacity retention at -10°C.[7] In an aluminium-graphite battery, the Et_3NHCl-$AlCl_3$ gel electrolyte delivered an initial capacity of 120 mA h g^{-1} and was able to retain a specific capacity of over 100 mA h g^{-1} after 100 cycles, at a current density of 60 mA g^{-1}.

One strategy to avoid unwanted solvent-electrolyte interactions is to omit the solvent completely, as quasi-solid gel electrolytes can be synthesised relatively easily by facile, solvent-free methods. PEO-based EMImCl-$AlCl_3$ ionogels have been synthesised by the direct addition of PEO to the ionic liquid under inert conditions[8, 83]. In lieu of a solvent, the PEO-ionic liquid mixture was stirred and heated to temperatures below 80°C to melt the polymer and to combine the components into a single phase, as shown in Fig. 4b. A similar procedure was used by Miguel et al.[84], instead using a deep eutectic solvent, urea-$AlCl_3$, as the liquid component. The simplicity of these methods presents significant advantages in manufacturing, while the omission of organic solvents improves the environmental friendliness of the process.

The molecular weight and chain length of the polymer host have several profound impacts on the physical and electrochemical characteristics of the gel electrolytes. The consistency of the gels differs substantially depending on the chain length of the polymer host, ranging from viscous liquids for gels made with PEO of 1×10^5 g mol^{-1} molecular weight, to rubbery elastomers (molecular weight up to 5×10^6 g mol^{-1}).[84] When high molecular weight polymers are used, gels can often be formed with a lower ratio of polymer to liquid, which could indeed be beneficial in retaining the electrochemical properties of the liquid component. Polyethylene glycol of 800 and 1000 g mol^{-1} molecular weight forms stable self-assembled complexes with alkyl imidazolium and alkyl pyridinium ionic liquids via ion-dipole interactions, which are understood to originate from the suitability of the chain lengths to wrap around the imidazolium and pyridinium rings, as illustrated in Fig. 5.[85] Although this self-assembly behaviour would appear to aid in providing greater electrochemical stability to the ionogels, the low molecular weight of polyethylene glycol and correspondingly higher amounts of polymer needed to solidify the electrolyte is likely to increase the internal resistance and restrict ion mobility. A balance between the physical and electrochemical characteristics therefore needs to be maintained and it may be worth investigating a blend of low and high molecular weight polymers to benefit from the attributes of both polymers.

Future prospects of quasi-solid electrolytes

The incorporation of semi-crystalline polymer matrices such as PEO inherently impacts the ion mobility and conductivity of the resulting polymer electrolyte. The addition of just 2.5 wt.% PEO to a urea-$AlCl_3$ deep eutectic solvent reduced its ionic conductivity by 46%,[84] while the diffusion coefficient of a 10 wt.% PEO-EMImCl-$AlCl_4$ ionogel was reported to be eight orders of magnitude lower than that of the neat ionic liquid.[8] As it is generally agreed that ionic movement in polymers takes place in the amorphous phase, reducing the crystallinity of polymer electrolytes by adding plasticisers or selecting amorphous polymers with low glass transition temperatures can promote better ionic conductivity in such electrolytes.[86-88] Additionally, plasticisers can also increase the ductility and flexibility of the electrolyte, which is particularly useful in flexible battery designs. Hybrid electrolytes are formed when inorganic plasticisers such as ceramic nanoparticles are added polymer-based electrolytes. The inorganic particles act as fillers which disrupt the polymer chain crystallinity and prevent the recrystallisation of the polymer chains. As a result, this aids in promoting the amorphicity of the electrolyte without compromising its mechanical stability. Apart from polymer-based electrolytes, inorganic nanoparticles such as SiO_2, TiO_2, Al_2O_3, ZnO_2 and carbon nanotubes can be used to form ionogels[89, 90] and inorganic quasi-solid electrolytes. While these approaches are commonly applied to polymer electrolytes of lithium-ion and multivalent metal-ion batteries, the effectiveness of these strategies in aluminium batteries remains to be seen.

Conclusions and outlook

The growing demand for safe, sustainable and high-performance batteries in transportation applications, electronic devices and large-scale grid storage has led to a rapid rise in the development of electrochemical energy storage based on naturally earth-abundant elements. Aluminium-based batteries are highly promising candidates, but many of the prevailing issues in currently available electrolytes render their practical application unfeasible. For optimum performance, the development of electrolytes with a wide electrochemical stability window from which aluminium can be efficiently and reversibly electroplated without dendritic growth is crucial. While a survey of the existing literature indicates that Lewis acidic chloroaluminate ionic liquids such as EMImCl-$AlCl_3$ show the best electrochemical performance of all currently available electrolytes, their high cost, hygroscopicity and corrosive nature are problematic. Developing new ionic liquids, water-in-salt electrolytes, and deep eutectic solvents to mitigate these issues will certainly aid in advancing aluminium battery technologies for future energy storage devices.

Besides electrochemical performance, the development of batteries should fundamentally focus on the safety, cost and practical implications of the battery system. Tuning the physical properties of electrolytes to form quasi-solid electrolytes can mitigate the risk of electrolyte leakage, suppress dendrite growth and enable the development of lightweight, flexible and bendable batteries. Although initial investigations into ionogels have shown to be effective in improving the moisture sensitivity and electrochemical stability of ionic liquid-based electrolytes, the low coulombic efficiencies and poor ionic conductivity necessitate further research into this concept. To improve the performance of these electrolytes, polymers that do not interact with $Al_2Cl_7^-$ ions need to be identified; alternatively, the omission of heptadichloroaluminate anions is a means of avoiding unwanted side reactions and corrosion of battery components.

Evidence from lithium and other metal-ion batteries suggests that the ionic conductivity of polymer electrolytes can be improved by adding plasticisers and inorganic nanoparticles. However, these approaches are currently unexplored in aluminium batteries and cannot simply be transferred due to the distinct differences between the electrochemistry of aluminium and lithium batteries. New opportunities may be found in inorganic and hybrid quasi-solid electrolytes, suggesting interesting avenues for further investigation.

Acknowledgements

We gratefully acknowledge funding from the International Consortium of Nanotechnology of the Lloyd's Register Foundation (LRF-ICON) and the Zepler Institute for Photonics and Nanoelectronics at the University of Southampton.

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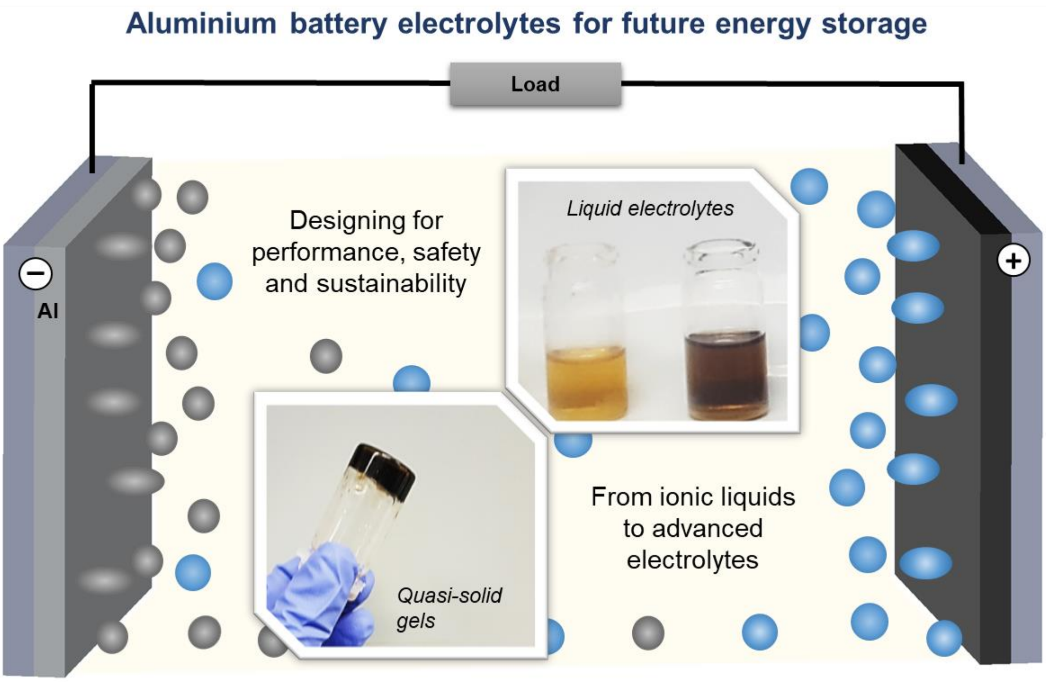
Figures and Tables



Graphical abstract

Table 1 Electrochemical properties and limitations of various liquid and quasi-solid electrolytes in the published literature.

	Electrolyte category							
Electrolyte properties	**Aqueous**	**Water-in-salt**	**Organic solvents**	**Inorganic molten salts**	**Chloro-aluminate ionic liquids**	**Deep eutectic solvents**	**Polyethylene oxide-based gels**	**Acrylamide polymerised in ionic liquids**
Electrochemical stability / V	1.23	< 4	3.5	~2	~4	~3	< 5	< 3
Coulombic efficiency of Al deposition/ dissolution / %	> 85%	> 95%	> 85%	> 99%	> 99%	> 99%	< 60%	80-95%
Ion conductivity at 25°C / mS cm^{-1}	10^1-10^2	~25	5-25	> 100 at 120°C	10-25	1-1.5	0.2-0.62	1.66-5.77
Limitations	Narrow electrochemical window	Low discharge potential	Flammable; poor capacity retention	Working temperature > 95°C	Corrosive; expensive	Low conductivity and specific capacity	Low coulombic efficiency, conductivity	Modest specific capacity
References	[30]	[36]	[43, 91, 92]	[48-50]	[60, 93]	[52, 54, 55]	[8, 84]	[6, 7, 80]

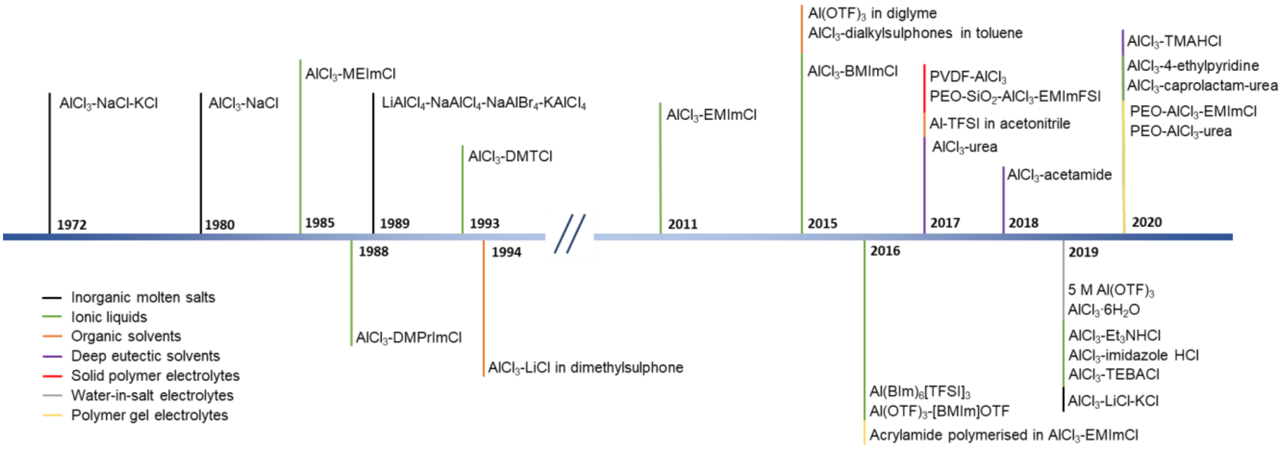


Fig.1 Timeline showing an overview of the key aqueous and non-aqueous electrolytes used in aluminium batteries.[6, 8, 27, 36, 37, 41-43, 50, 52, 53, 55, 66, 71, 72, 80, 82, 84, 91, 92, 94-108] DMPImCl, 1,2-dimethyl-3-propylimidazolium chloride; MEImCl, 1-methyl-3-ethylimidazolium chloride; DMTCl, 1,4-dimethyl-l,2,4-triazolium chloride; BIm, 1-butylimidazolium; BMImCl, 1-butyl-3-methylimidazolium chloride; TFSI, bis(trifluoromethanesulphonyl)imide; OTF, trifluoromethanesulfonate; Et_3NHCl, triethylamine hydrochloride; TEBACl, benzyltriethylammonium chloride; TMAHCl, trimethylamine hydrochloride.

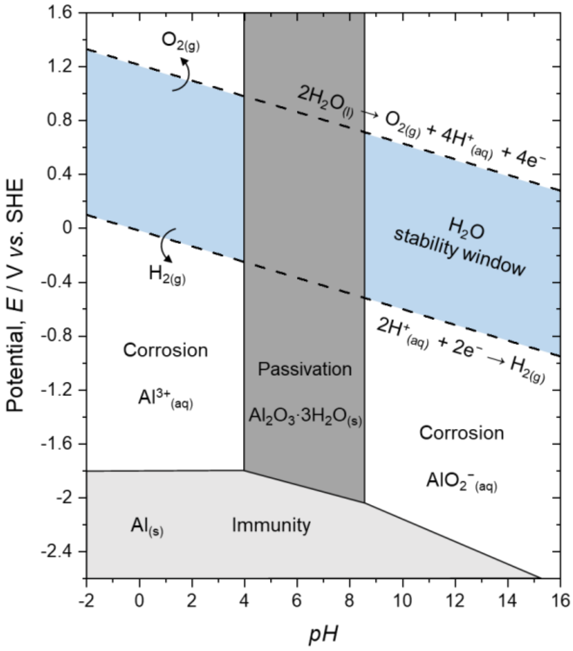


Fig. 2 Pourbaix diagram for aluminium in water at 25°C, showing the stability limits of water (shaded blue). Redrawn and adapted from Detombe and Pourbaix.[32]

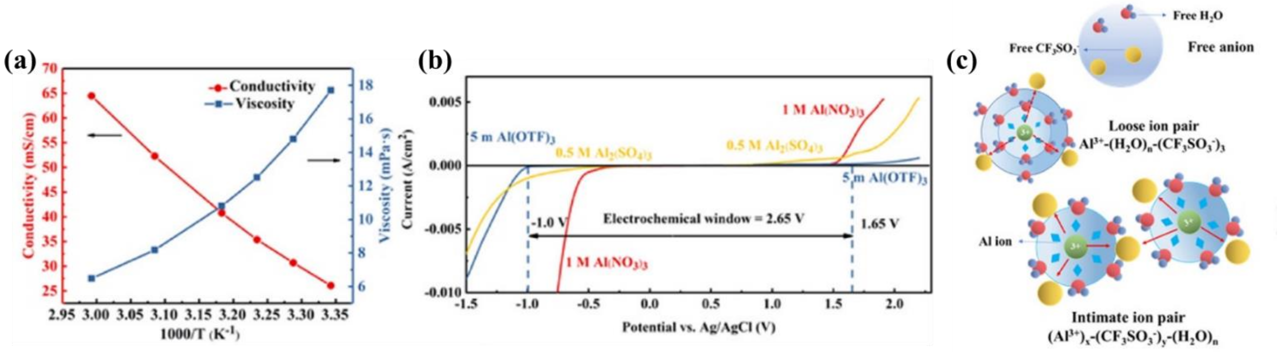


Fig. 3 (a) Variation of conductivity and viscosity of a 5 M $Al(OTF)_3$ water-in-salt electrolyte as a function of temperature between 25 and 60°C. (b) Linear sweep voltammograms of 5 M $Al(OTF)_3$, 1 M $Al(NO_3)_3$, and 0.5 M $Al_2(SO_4)_3$ electrolytes on titanium mesh in a three-electrode system swept at 10 mV s^{-1}. (c) A schematic diagram showing the solvation structure of the water-in-salt electrolyte. Diagrams reproduced and adapted with permission from Ref. [36]. Copyright 2019, American Chemical Society.

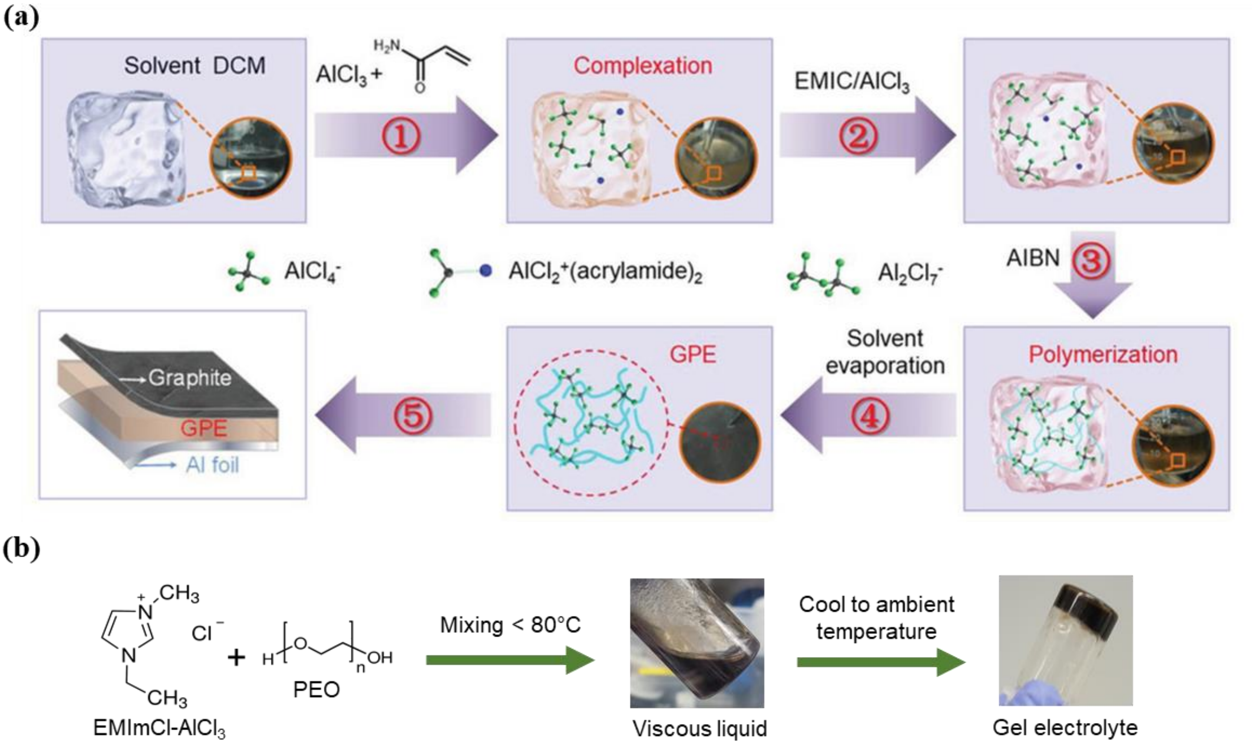


Fig. 4 (a) Preparation process of a gel polymer electrolyte (GPE) via the complexation of acrylamide and $AlCl_3$ in the presence of an EMImCl-$AlCl_3$ ionic liquid. Adapted with permission from Ref. [7]. Copyright 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) Solvent-free preparation of the PEO-EMImCl-$AlCl_3$ ionogel electrolyte reported in Ref. [8].

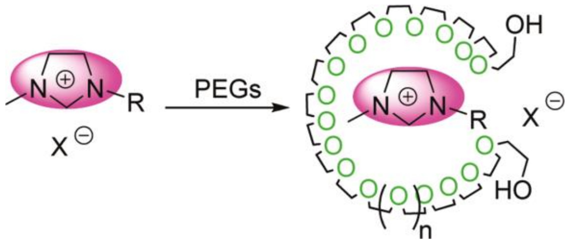


Fig. 5 A schematic diagram of the self-assembly interaction between an alkyl imidazolium ionic liquid and polyethylene glycol (PEG), where X^- represents an inorganic anion and R is an alkyl group. Reprinted with permission from Ref. [85]. Copyright 2010, American Chemical Society.