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Rechargeable aluminum batteries utilizing a chloroaluminate inorganic ionic liquid electrolyte†

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Rechargeable aluminum batteries composed of an aluminum anode, an expanded graphite cathode, and an inorganic chloroaluminate ionic liquid electrolyte show remarkably improved capacity, reversibility, and rate capability at 393 K compared to cells based on a common organic salt based ionic liquid, AlCl₃–1-ethyl-3-methylimidazolium chloride.

Electrochemical energy storage is a key enabler of the future smart grid. Besides lithium ion batteries (LIBs), which dominate the field of portable electronic devices and automotive applications, new battery systems in which earth-abundant elements, e.g., Na, K, Mg, Ca, Zn, etc., serve as charge carriers and/or electrodes are attracting considerable interest on account of their low cost and sustainability benefits. This is especially true for large-scale stationary energy storage and industrial applications.^{1–3} Against this background, batteries employing metallic aluminum (Al) as the anode material warrant special attention because they offer many unique advantages, including high volumetric energy density, cost-effectiveness, and outstanding safety characteristics. This is because of the trivalent nature of Al, its rich abundance, and, its stability under atmospheric conditions. Furthermore, its low reactivity and ease of handling are a great benefit during the battery manufacturing process.⁴

However, the development of rechargeable Al batteries faces two scientific challenges. Like other emerging multivalent metal-based batteries, there is a lack of high-performance cathode materials and suitable electrolytes that support reversible metal deposition/stripping. The former is derived from the extremely high charge density of Al³⁺ cations that induces strong intercalation with host materials, leading to sluggish Al³⁺

diffusion and inhibiting intercalation on practical timescales.⁴ With respect to the latter issue, the formation of a passive film on the Al surface creates a large reaction overpotential, and consequently, a decreased cell potential, both of which are detrimental to battery performance.⁵ In an attempt to overcome these issues, room-temperature ionic liquids (RTILs) have been investigated.^{6–8} It is acknowledged that haloaluminate RTILs, composed of aluminium halides combined with organic halide salts, constitute an important class of ILs, in which the Al plating/stripping process proceeds at a satisfactory coulombic efficiency.^{5,9} Furthermore, the active Al-containing species in these ILs are haloaluminate complex ions such as [AlX₄][−] and/or the Lewis acidic species, [Al₂X₇][−] (X = Cl, Br). Such singly-charged complex anions can be more readily intercalated into graphitic hosts by using electrochemical methods.^{10,11} As a result, the target working potential has been achieved, and exceptional cycling stability has been observed. However, the modest cathodic capacity (typically 60–80 mAh g^{−1}) and the inadequate rate capability must still be improved.

Of particular importance is the fact that the haloaluminate RTIL electrolyte itself is actively involved in redox reactions at both the cathode and anode, causing the electrolyte composition to vary continuously during operation.^{12,13} This is fundamentally distinct from the rocking-chair LIBs, in which electrolyte is the transport medium for the intercalation processes. As a consequence, the choice of an appropriate electrolyte for Al batteries may strikingly influence the overall cell characteristics.

In this work, we explore the feasibility of the ternary chloroaluminate inorganic IL, AlCl₃–NaCl–KCl (eutectic point ≤ 373 K), as the electrolyte for rechargeable Al batteries. The inorganic halide melt is known as low-temperature molten salt, which contains exclusively abundant elements and is much cheaper to prepare and purify than electrolyte systems based on organic RTILs. The high intrinsic ionic conductivity of chloroaluminate inorganic ILs and the elevated operating temperature are expected to facilitate intercalation/deintercalation and deposition/dissolution kinetics at the cathode and anode, respectively. Control experiments using the most

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extensively employed chloroaluminate RTIL, AlCl_3 -1-ethyl-3-methylimidazolium chloride ($[\text{C}_2\text{mim}]\text{Cl}$), highlights the unique properties of its inorganic chloroaluminate cousin.

Investigations about inorganic salt-based chloroaluminate ILs have a long history covering both fundamental research as well as practical applications.¹⁴ In addition to their useful roles as ionic solvents for electrowinning, they have been recognized as electrolytes for primary thermal batteries and secondary (rechargeable) batteries since the early 1960s.¹⁴

The ternary AlCl_3 - NaCl - KCl melt in a molar ratio of 61:26:13 or 61-26-13 percent mol fraction (mol%) that was used in this study is a eutectic mixture and exhibits a relatively low melting point of 366 K. Contrast this with the AlCl_3 - NaCl and AlCl_3 - KCl systems which melt at > 381 and > 401 K, respectively, depending on the composition.^{15,16} The ionic conductivity of the AlCl_3 - NaCl - KCl melt as a function of temperature is shown in Fig. S1 (ESI[†]), along with the values reported for some other binary AlCl_3 -alkali metal chloride molten salts. Notably, inorganic systems display a higher conductivity than the AlCl_3 - $[\text{C}_2\text{mim}]\text{Cl}$ RTIL due to the smaller cation size and larger population of mobile ions. A conductivity greater than 100 mS cm^{-1} is observed for AlCl_3 - NaCl - KCl at 393 K.

To investigate the effectiveness of AlCl_3 - NaCl - KCl as an electrolyte, a unique form of graphite called Grafoil[®] made from the thermal expansion of chemically treated natural graphite flakes was used as the active cathode material. Its highly aligned

structure and crystallinity meet the prerequisite for the efficient uptake of anionic intercalation materials.¹⁷ The electrochemical properties of the Grafoil[®] cathode was evaluated using a two-electrode cell with pure Al as the anode (Fig. S2, ESI[†]).

Cyclic voltammograms (CVs) recorded at a scan rate of 0.5 mV s^{-1} using the Al/Grafoil[®] cells with 61-26-13 mol% AlCl_3 - NaCl - KCl and 60-40 mol% AlCl_3 - $[\text{C}_2\text{mim}]\text{Cl}$ electrolytes are illustrated in Fig. 1a. The Grafoil[®] electrode underwent $[\text{AlCl}_4]^-$ anion intercalation during the forward scan and deintercalation in the reverse scan as evidenced by pairs of redox peaks that are observed in each CV profile.¹⁰ The pronounced peak separation and obvious current peaks in the AlCl_3 - NaCl - KCl voltammogram imply that the intercalation process is more favorable in the chloroaluminate inorganic IL at 393 K than in the lower temperature system. Furthermore, the onset potential for anion uptake is much lower in the AlCl_3 - NaCl - KCl melt compared to the AlCl_3 - $[\text{C}_2\text{mim}]\text{Cl}$ ionic liquid, highlighting the influence of the electrolyte chemistry on intercalation behavior. As shown in Fig. 1b, the charge-discharge curve in the inorganic IL is distinct from that in the organic RTIL because it involves a staircase voltage profile with three well-defined plateaus appearing at ca. 1.5, 1.8, and 2.2 V. This represents structural rearrangement of the graphite film upon intercalation.^{6,7} A reversible capacity of 128 mAh g^{-1} is obtained in the AlCl_3 - NaCl - KCl melt at a discharge rate of 100 mA g^{-1} . This capacity is approximately 1.5 times higher than that obtained in AlCl_3 - $[\text{C}_2\text{mim}]\text{Cl}$ at 298 K. It is reasonable to postulate that the high onset voltage for anion uptake by the Grafoil[®] in the organic salt-based electrolyte precludes the upper charging plateau and consequently limits the achievable capacity. Interestingly,

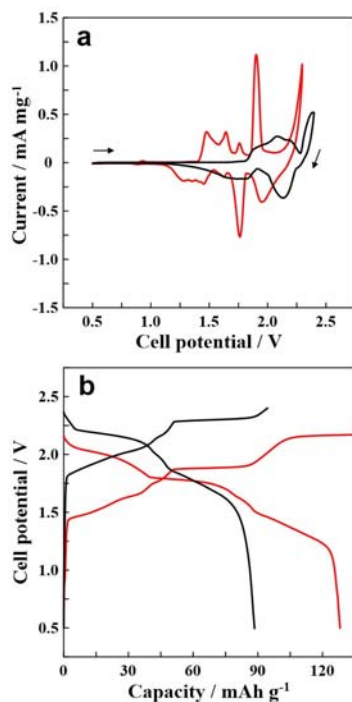


Fig. 1 (a) Cyclic voltammograms and (b) galvanostatic charge-discharge curves obtained from Al/Grafoil[®] cells with 61-26-13 mol% AlCl_3 - NaCl - KCl at 393 K (red line) and 60-40 mol% AlCl_3 - $[\text{C}_2\text{mim}]\text{Cl}$ at 298 K (black line). The scan rate and current density for each measurement was 0.5 mV s^{-1} and 100 mA g^{-1} , respectively.

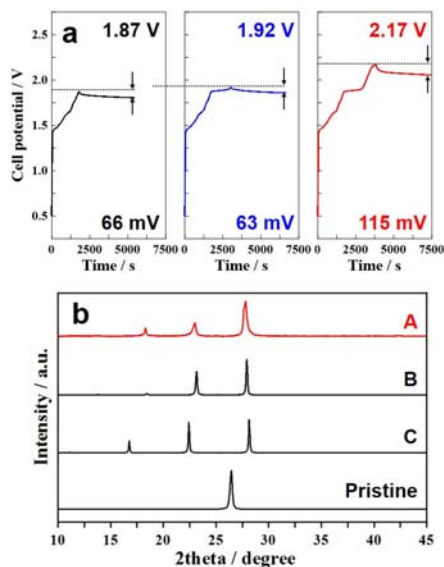


Fig. 2 (a) Open circuit potential variation of the Al/Grafoil[®] cells with an inorganic 61-26-13 mol% AlCl_3 - NaCl - KCl IL charged to different cut-off potentials (1.87, 1.92, and 2.17 V) at 393 K. The potential drops after one h at each condition are 66, 63, and 115 mV, respectively. (b) XRD patterns of the Grafoil[®] electrode charged under different conditions, (A) in the inorganic IL at 393 K, in the RTIL at (B) 393 K and (C) 298 K.

neither enhancement of the reversible capacity nor reduced onset voltage for intercalation is observed for Grafoil[®] examined in AlCl₃-[C₂mim]Cl at elevated temperatures (over 353–393 K), indicating the intercalation ability is enhanced in the inorganic IL electrolyte and that is not simply a thermal effect (Fig. S3, ESI[†]). It is also found that the oxidative decomposition of [C₂mim]⁺ becomes noticeable at temperatures greater than 363 K on the cathode, which leads to a decreased discharge capacity.

To investigate the reaction mechanism of the Grafoil[®] cathode in the inorganic IL electrolyte, self-discharge tests were conducted. It was found that the open circuit potential of the charged Al/Grafoil[®] cell varies to only a small extent after a one hour period, providing evidence that the cathodic capacity does not originate from ion adsorption/desorption onto the surface of electrode (Fig. 2a). The stability of the graphite intercalation compounds (GICs) allows us to perform ex situ XRD measurements without experimental difficulty. The (002) peak of pristine Grafoil[®] located at 2 theta = 26.46° completely vanished and split into new peaks upon charging, indicating that the Grafoil[®] undergoes oxidative intercalation by chloroaluminate anions and leads to strained graphene stacks (Fig. 2b).⁶ Most importantly, the full-width at half-maximum (FWHM) of the diffraction peaks for Grafoil[®] charged in the inorganic IL is found to be much broader than those charged in the organic RTIL. This result suggests that the inorganic IL facilitates anion penetration into the van der Waals gaps between the graphite interlayers, leading to a higher degree of exfoliation and an efficient storage. An additional intriguing finding is that Grafoil[®] charged in the inorganic melt with higher

concentrations of intercalants actually has a smaller interlayer spacing (see patterns A and C, calculated in accordance with previous publications).^{6,17} This phenomenon has also been observed for [PF₆]⁻ intercalated graphite,¹⁷ and it is speculated that it is caused by a closer packing and/or distorted conformation of intercalants.^{6,13,17}

A strong trade-off between accessible capacity and applied current is found for Grafoil[®] in the organic RTIL at 298 K (Fig. S4, ESI[†]). Similar kinetic limitations are known for a wide range of cathode materials in Al batteries and have been ascribed to the large ionic radius of [AlCl₄]⁻ ion (~5.28 Å) and its slow solid state diffusivity.^{6,7,18,19} To circumvent this problem, materials engineering is employed to tailor the nanostructure of the Grafoil[®] and/or to introduce macroscopic voids to improve its reversible capacity and rate performance.^{6,20–22} These strategies effectively enhance the accessibility of the electrolyte as well as decrease the diffusion distance of guest species, leading to a better electrochemical properties. However, it should be realized that any improvements in gravimetric energy and power densities by these ultralow-density nanomaterials (e.g. 5 mg cm⁻³ as reported elsewhere²³) are usually accompanied by a loss in volumetric ones.²⁴ As shown in Fig. 3, the use of the inorganic IL electrolyte is also advantageous. It can be seen that polarization is considerably alleviated in the inorganic melt compared to the organic salt under the same conditions. The high-rate performance is therefore far superior to that measured in the organic RTIL. The Al/Grafoil[®] cell with the inorganic melt delivers capacities of 124, 97, 90, and 63 mAh g⁻¹ at rates of 1000, 2000, 4000, and 8000 mA g⁻¹, respectively (Fig. 3a). Most importantly, this rate capability is achievable by an electrode of high bulk density (ca. 1.12 g cm⁻³), suggesting that the inorganic IL electrolyte has a greater ability to maximize graphitic cathode properties. This result also implies that anion intercalation is not the only deciding factor for kinetic properties at elevated

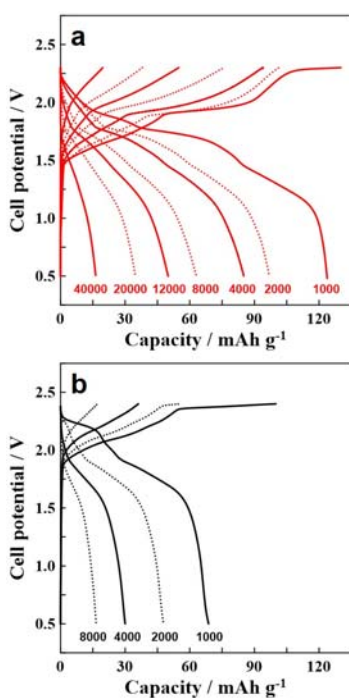


Fig. 3 Rate performance of the Al/Grafoil[®] cells with (a) the inorganic IL and (b) the RTIL at 393 K. Current density unit: mA g⁻¹.

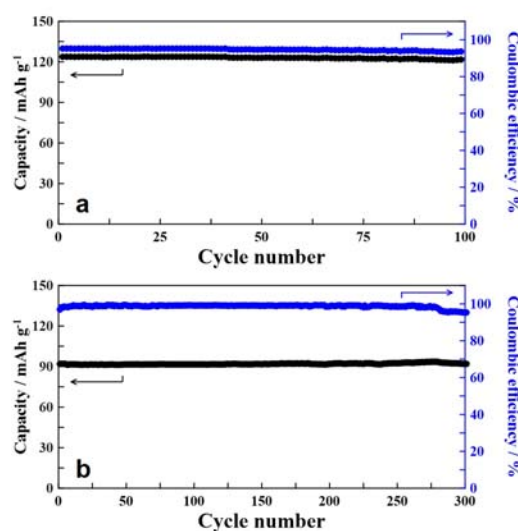


Fig. 4 Cycling performance and coulombic efficiency of the Al/Grafoil[®] cell measured in the inorganic IL at 393 K at current densities of (a) 1000 and (b) 4000 mA g⁻¹.

temperatures because the cathode performance totally depends on the electrolyte species, not on the temperature. Electrochemical impedance spectroscopy (EIS) results point out that the anode charge transfer contributes largely to the overall impedance as tested in the organic RTIL electrolyte at 298 K (Fig. S5, ESI†). This finding is consistent with previous studies on rechargeable batteries utilizing multivalent metal anodes.^{25,26} On the contrary, the low impedance observed in the inorganic electrolyte supports the results of the enhanced rate performance. As shown in Fig. 4, the Al/Grafoil® cell employing the inorganic IL electrolyte is suitable for continuous high-rate operation at 393 K. A stable capacity of 120 mAh g⁻¹ is retained after cycling at 1000 mA g⁻¹ over 100 cycles. Furthermore, a good cyclability with negligible capacity decay is observed at rates up to 4000 mA g⁻¹ over 300 cycles, with an average coulombic efficiency higher than 99% (see Fig. S6 for corresponding charge-discharge curves, ESI†).

All of the results obtained in this research show that the inorganic IL electrolyte offers opportunities to improve the characteristics of graphitic cathode materials. It is known that the electrode reactions in the Al/chloroaluminate IL/graphite cell are based on [AlCl₄]⁻ anion intercalation/deintercalation into the cathode ($C_n + [AlCl_4]^- \rightleftharpoons C_n[AlCl_4] + e^-$) and Al deposition/stripping ($4[Al_2Cl_7]^- + 3e^- \rightleftharpoons Al + 7[AlCl_4]^-$) at the anode.^{6,7} It is worth emphasizing that the electrolyte composition constantly varies during battery operation. The change in the Lewis acidity likely affects the overpotential for the electrode reaction especially in the vicinity of the anode. Recent experimental results support this idea.^{6,12} Compared with the RTIL (3.89 M for 60-40 mol% AlCl₃-[C₂mim]Cl at 298 K),²⁷ the inorganic IL is a much more concentrated system (6.56 M for 60-30-10 mol% AlCl₃-NaCl-KCl at 423 K (please see the ESI† for the method used to calculate the molar concentration of the two systems)).^{27,28} Therefore, the variation of the Lewis acidity during charge-discharge is more easily accommodated by the inorganic system. Also, the lower viscosity of the inorganic IL contributes positively to the decrease in the overpotential.

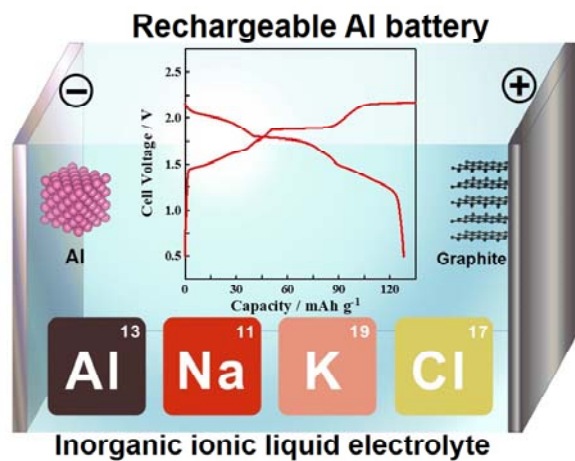
In conclusion, rechargeable Al batteries comprising inexpensive components based on abundant elements have been constructed based on an Al anode, graphitic carbon cathode, and an inorganic AlCl₃-NaCl-KCl IL electrolyte. The batteries exhibit a high capacity (128 mAh g⁻¹), outstanding rate capability (63 mAh g⁻¹ at 8000 mA g⁻¹) as well as stable cyclability at 393 K, which cannot be achieved in the commonly used AlCl₃-[C₂mim]Cl RTIL electrolyte. The excellent cost-performance makes this battery a competitive option for large-scale energy storage applications.

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Chloroaluminate inorganic ionic liquid electrolyte can boost the electrochemical activity of a graphitic carbon cathode for rechargeable Al batteries.