A novel AlCl₃-[EMIM][TF₂N] electrolyte for rechargeable aluminum-ion battery

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Abstract. Owing to the high theoretical capacity, low price, easy availability of aluminum, the rechargeable aluminum-ion battery (AIB) is very suitable as an electrochemical energy storage device for large-scale power storage. High preference of rechargeable AIBs is depended on the suitable electrolytes. In this paper, a kind of novel ionic liquid electrolyte is prepared by mixing aluminum chloride (AlCl₃) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][TF₂N]). This electrolyte possesses high electrical conductivity and a satisfactory oxidation voltage (2.50 V vs. Al/Al³⁺), which are more excellent than conventional AlCl₃-based electrolytes. The Al[1.7AlCl₃-[EMIM][TF₂N] carbon paper battery exhibits a stable discharge specific capacity of ~75 mAh·g⁻¹ at 100 mA·g⁻¹ with a near 100% coulombic efficiency, indicating that AlCl₃-[EMIM][TF₂N] ionic liquid is a promising electrolyte for high-voltage and high-performance aluminum-ion batteries.

1. Introduction

Electrochemical energy storage using rechargeable batteries had become one of the most effective application methods for electrical energy storage [1]. Aluminum was the one of most abundant metal elements in the earth's crust and had high mass and volume theoretical specific capacity [2]. Based on the above advantages, the rechargeable aluminum battery was considered to be a new generation of energy conversion and storage battery systems.

Dymek firstly used aluminum chloride-1-methyl-3-ethylimidazole chloride ionic liquid as the electrolyte to assemble the original aluminum-aluminum cell [3]. Gifford assembled an aluminum-graphite battery using aluminum chloride-iodide 1,2-dimethyl-3-propylimidazolionic liquid as the electrolyte [4]. In 2011, Archer reported the electrochemical behavior of Al-V₂O₅ battery using acidic aluminum chloride-1-ethyl-3-methylimidazole chloride (AlCl₃-[EMIM][Cl]) ionic liquid as the electrolyte [5]. In 2015, Dai reported an aluminum battery with AlCl₃-[EMIM][Cl] ionic liquid as the electrolyte and pyrolytic graphite foam as the cathode [6]. It was found that the preferred molar ratio range of AlCl₃/[EMIM][Cl] is 1.3-1.5. This rechargeable aluminum-ion battery exhibited excellent electrochemical performance. Subsequently, they reported an inexpensive AlCl₃-urea ionic liquid as the electrolyte for aluminum-ion batteries [7]. It exhibited a high specific discharge capacity and cycle stability. AlCl₃-amide-based ionic liquids were considered as the ideal electrolytes because of the low cost and easy synthesis of amides. Thus, Canever prepared AlCl₃-acetamide system which was used as the electrolyte of the aluminum-graphite battery [8]. Although the cost of amide was ten times lower than that of imidazole, the performance of aluminum chloride-amide electrolyte was unsatisfactory, which was related to the composition and physicalchemical properties of the electrolytes. Other aluminum chloride-based electrolytes had been reported, such as aluminum chloride-pyridine chloride...
and aluminum chloride-1-trifluoroacetylpyperidine [9-10]. Aerogel-based electrolytes were developed to avoid the disadvantages of aluminum chloride-based electrolytes [11]. Although they avoided some of the disadvantages of corrosiveness and sensitivity to water, the electrochemical performance of polymers and chlorine-free electrolytes could not meet the requirements of further development of aluminum batteries.

As far, studies on electrolytes were mainly focused on AlCl₃-based room temperature molten salts, which processed outstanding advantage in aluminum-ion batteries. Because of no alternative to the AlCl₃-based electrolytes, it is significant for further study on the AlCl₃-based electrolyte. In this paper, a novel ionic liquid electrolyte was prepared by the anhydrous aluminum chloride (AlCl₃) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][TF₆N]). Its ion composition and physicochemical property were studied. Besides, the electrochemical performance of aluminum-carbon paper battery using AlCl₃-[EMIM][TF₆N] as the electrolyte was evaluated.

2. Experimental

2.1 Synthesis of AlCl₃-[EMIM][TF₆N] electrolyte
The electrolyte was prepared by adding anhydrous aluminum chloride (AlCl₃, 99%, Aladdin) into 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][TF₆N], 99%, Linzhou Keneng Materials Co., Ltd China) with a molar ratio (defined as r) range of 1.1-1.7 to form the light-yellow transparent liquid in the upper layer and pale viscous liquid in the lower layer in a glove box (MBRAUN MB 200B, Germany). The upper liquid was used as the electrolyte.

2.2 Raman spectra measurements of AlCl₃-[EMIM][TF₆N] electrolyte
Raman spectra of AlCl₃-[EMIM][TF₆N] electrolyte were measured by an HR 800 Raman spectrometer (Horiba Jobin Yvon LabRAM) equipped with a He-Cd lasers (20 mW, 325 nm) and an objective lens (10×0.25, Olympus).

2.3 Electrical conductivity measurements of AlCl₃-[EMIM][TF₆N] electrolyte
The electrical conductivity of AlCl₃-[EMIM][TF₆N] electrolyte was measured by the impedance method in a capillary cell in the glove box. The experimental theory and details were described in a previous study.

2.4 Electrochemical behavior measurements of AlCl₃-[EMIM][TF₆N] electrolyte
The electrochemical behavior of AlCl₃-[EMIM][TF₆N] electrolyte was measured on a tungsten electrode at 298 K by cyclic voltammetry (CV) and linear sweep voltammetry (LSV). A high-purity tungsten wire (Φ1 mm, 99.5%) was used as the working electrode, an aluminum wire (Φ0.5 mm, 99.99%) and an aluminum sheet (25×14 mm, 99.99%) were used as the reference and counter electrode, respectively. The scan rate was set as 10 mV·s⁻¹.

2.5 Assembly and testing of Al-carbon paper battery
The pouch cells were prepared using a commercial carbon paper (Φ0.5 mm, Shanghai Hesen) as the cathode and metal aluminum as the anode(99.99%, 15×15 mm), and the glass fiber paper (GF/D, Whatman) was used as the separator. The AlCl₃-[EMIM][TF₆N] ionic liquid was used as the electrolyte. The charged/discharged cut-off voltages were set as 2.5 V and 0.4 V, respectively with a current density of 100 mA·g⁻¹.

2.6 Characterization
The XRD and SEM of the cathode before and after the charge/discharge test were characterized to analyze the phase, morphology, and element distribution of the cathode under fully charged/discharged conditions.
3. Results and discussion

Figure 1. Raman spectra of AlCl\(_3\)-[EMIM][TF\(_2\)N] electrolyte at 298 K.

Raman spectra were performed in AlCl\(_3\)-[EMIM][TF\(_2\)N] ionic liquid to study the ion component in the electrolyte. As shown in figure 1, Two obvious peaks at the Raman shifts of 347 and 310 cm\(^{-1}\) are observed in spectra for AlCl\(_3\)-[EMIM][TF\(_2\)N] electrolytes with different molar ratios, corresponding to [AlCl\(_4\)]\(^-\) and [Al\(_2\)Cl\(_7\)]\(^-\) complexes respectively [12]. The integral area percentage of intensity of [Al\(_2\)Cl\(_7\)]\(^-\) to [AlCl\(_4\)]\(^-\) (I\(_{310}\)/I\(_{347}\)) was analyzed (Table 1). For all systems, the I\(_{310}\)/I\(_{347}\) increases as the molar ratio of AlCl\(_3/[EMIM][TF_2N]\) increases, indicating that the relative concentration of [Al\(_2\)Cl\(_7\)]\(^-\) ions increases as the molar ratio increases.

\[
\begin{align*}
[\text{EMIM}][\text{TF}_2\text{N}]+2\text{AlCl}_3&=2[\text{AlCl}_4]^++[\text{EMIM}]^+ \quad (1) \\
2[\text{AlCl}_3\cdot\text{TF}_2\text{N}]^- &\rightleftharpoons [\text{AlCl}_4]^++[\text{AlCl}_2\cdot\text{TF}_2\text{N}]^- \quad (2) \\
7[\text{AlCl}_4]^++\text{AlCl}_3 &\rightleftharpoons 4[\text{Al}_2\text{Cl}_7]^++3\text{Cl}^- \quad (3)
\end{align*}
\]

After AlCl\(_3\) and [EMIM][TF\(_2\)N] are mixed, [AlCl\(_4\)]\(^-\) is formed through reactions (1) and (2). When more AlCl\(_3\) is added to the liquid, it will react with [AlCl\(_4\)]\(^-\) ions to form [Al\(_2\)Cl\(_7\)]\(^-\) complexes in the form of reaction (3), resulting in an increase of the content of [Al\(_2\)Cl\(_7\)]\(^-\) in the electrolyte as the molar ratio increases.

Table 1 The integral area percentage of intensity of [Al\(_2\)Cl\(_7\)]\(^-\) to [AlCl\(_4\)]\(^-\) (I\(_{310}\)/I\(_{347}\)) was analyzed for AlCl\(_3/[EMIM][TF_2N]\) electrolytes.

| Molar ratio | 1.1 | 1.3 | 1.5 | 1.7 |
|-------------|-----|-----|-----|-----|
| I\(_{310}\)/I\(_{347}\) | 0.8 | 0.8 | 0.24 | 0.44 |

Figure 2 shows the electrical conductivities of AlCl\(_3/[EMIM][TF_2N]\) electrolytes with different molar ratios at different temperatures. The electrical conductivity increases with temperature, which is mainly resulted from the increasing ions movement and charge migration as the temperature increases [13]. Besides, the electrical conductivity decreases as the molar ratio of AlCl\(_3/[EMIM][TF_2N]\) increases, especially at higher temperatures. The electrical conductivity of AlCl\(_3/[EMIM][TF_2N]\) electrolyte decreases as the molar ratio increases because the relative content of [AlCl\(_4\)]\(^-\) ion decreases with increasing the molar ratio which is more conductive than [Al\(_2\)Cl\(_7\)]\(^-\) ion in AlCl\(_3\)-based ionic liquid at the same conditions [13]. With the molar ratio increasing to 1.7, the obvious decrease in electrical conductivity is caused by the lower content of [AlCl\(_4\)]\(^-\) complex, which is still higher than that of aluminum chloride-imidazole-based ionic liquids [13].
Figure 3 (a) linear sweep voltammetry and (b) cyclic voltammetry curves of AlCl$_3$-[EMIM][TF$_2$N] electrolyte at 298 K.

Table 2 The onset reduction potential of aluminum ($E_0$) and anodic limit potential ($E_{lim}$) of AlCl$_3$-[EMIM][TF$_2$N] electrolyte.

| Molar ratio | 1.1 | 1.3 | 1.5 | 1.7 |
|-------------|-----|-----|-----|-----|
| $E_0$ (V)   | -0.30 | -0.30 | -0.25 | -0.20 |
| $E_{lim}$ (V) | 2.20 | 2.30 | 2.50 | 2.50 |

The electrochemical behaviors of AlCl$_3$-[EMIM][TF$_2$N] electrolytes with different molar ratios were studied by linear sweep voltammetry and cyclic voltammetry. The onset reduction potential of aluminum ($E_0$) and anodic limit potential ($E_{lim}$) of all systems obtained from figure 3(a) are listed in table 2. Both the onset reduction and anodic limit potentials move to more positive values as the molar ratio increases, indicating that the aluminum is more easily reduced and AlCl$_3$-[EMIM][TF$_2$N] ionic liquid becomes more stable at higher voltages. Furthermore, the anodic limit potential of those systems with the molar ratio of 1.5 and 1.7 can reach 2.50 V. It reveals that AlCl$_3$-[EMIM][TF$_2$N] system as the electrolyte of aluminum-ion battery may offer a considerable charge voltage, which is higher than that of common electrolytes, such as AlCl$_3$-[EMIM]Cl and AlCl$_3$-amide systems. The effect of the molar ratio on the electrochemical redox process of metal aluminum is further studied. It can be seen from figure 3(b) that the redox peaks are weak when the molar ratio is 1.1 and 1.3, while they increase obviously with increasing the molar ratio to 1.5/1.7. It is caused by the increase of the content of the electroactive species [Al$_2$Cl$_7$]$^-$ ions, which is consistent with the Raman spectra results. Thus, AlCl$_3$-[EMIM][TF$_2$N] system with high molar ratios can be used as an ideal electrolyte for high-performance aluminum-ion batteries.
The electrochemical performances of Al-CP battery: (a) cyclic voltammetry curves at 1 mV·s⁻¹; (b) charge/discharge curves; (c) cycle performance.

The battery using carbon paper as the cathode and aluminum foil as the anode to evaluate the electrochemical performance of AlCl₃-[EMIM][TF₂N] electrolyte for aluminum-ion battery. As shown in figure 4(a), redox peaks observed in cyclic voltammetry curves are resulted from the (de)intercalation reaction of [AlCl₄]⁻ into the cathode [14]. The onset potential of the anode peaks observed in the first cycle becomes more negative as the cycle number increases. It means the better reversibility [14]. Besides, the intensities of redox peaks increase obviously, indicating an increase of (de)intercalation ability of chloroaluminate anions. Figure 4(b) shows the charging/discharging curves for the 1st/50th/100th/180th cycles of the Al||1.7AlCl₃-[EMIM][TF₂N]|CP cell, respectively. There exists only one obvious charging process in the first cycling. Afterward, a new charging stage is observed between 0.75 V and 1.80 V in subsequent cycles. As shown in figures 4(b) and (c), the discharging specific capacity of the Al/CP battery increases in the long-term cycle. The Al||1.7AlCl₃-[EMIM][TF₂N]|CP cell exhibits a stable discharge specific capacity of ~75 mAh·g⁻¹ at 100 mA·g⁻¹ with a near 100% coulombic efficiency after 180 cycles.

Figure 5. SEM and EDS images of cathode for carbon, aluminum and chlorine elements at fully charged/discharged states.
Figure 6. XRD patterns of carbon paper cathode for pristine and discharged state after 100 cycles.

The SEM images of carbon paper cathode under fully charged/discharged states indicate an unchanged morphology of the cathode (Figure 5). Obvious signals of aluminum and chlorine are observed in the fully charged electrode, and the aluminum and chlorine signals of the cathode at discharged state are weaker than that of the cathode at a fully charged state. It indicates the (de)intercalation of the \([\text{AlCl}_4^-]\) ions in the CP cathode. No obvious signal of aluminum and chlorine on carbon fiber indicates that no (de)intercalation reactions take place on the carbon fiber, which is consistent with previous research results [14]. Moreover, the XRD spectrum of the carbon paper cathode after 180 cycles still has a typical (002) peak (\(2\theta = 26.637^\circ\)). The interplanar distance increases from 3.337 Å (pristine, \(2\theta = 26.694^\circ\)) to 3.385 Å (Figure 6), which is still smaller than the size of chloroaluminate anion [14]. The negligible change indicates a good recuperability of the cathode.

4. Conclusions

In summary, a novel \(\text{AlCl}_3\)-[EMIM][TF_2N] ionic liquid is proposed to be used as the electrolyte of the rechargeable aluminum-ion battery. This electrolyte presents high electrical conductivity and a satisfactory oxidation voltage of 2.50 V. The aluminum-carbon paper battery using \(\text{AlCl}_3\)-[EMIM][TF_2N] ionic liquid as the electrolyte exhibits a stable discharge capacity of \(\sim 75\) mAh·g\(^{-1}\) at 100 mA·g\(^{-1}\) with a near 100% coulombic efficiency, indicating that \(\text{AlCl}_3\)-[EMIM][TF_2N] electrolyte is promising for advanced aluminum-ion batteries with high voltage.

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