



Mono-and di-cationic Ionic Liquids: Synthesis, Characterization and Applications in Batteries

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Abstract

In this paper, a mono-cationic ionic liquid (MIL) ([BMIM][NTF₂]) and two di-cationic ionic liquids (DILs) ([C₅(MIM)₂][NTF₂]₂ and [C₆(MIM)₂][NTF₂]₂) were synthesized by two-step method, and the conductivity, viscosity and electrochemical stability of the three ionic liquids were systematically studied and analyzed. The results show that the conductivity of MIL is better than that of DILs, while the viscosity and the electrochemical stability of DILs are higher than those of MIL. The viscosity of the DILs decreases with the increasing length of the group within the DILs. Finally, the application of MIL as the electrolyte in the lithium-oxygen battery was studied.

Keywords: Ionic liquids; Conductivity; Viscosity; Electrochemical stability; Lithium-Oxygen Battery

Abbreviations: MIL: Mono-Cationic Ionic Liquid; DILs: Di-Cationic Ionic Liquids; ILs: Ionic Liquids; SCE: Saturated Calomel Electrode; KB: Ketjen Black.

Introduction

Generally, low temperature molten salts with a melting point below 100°C are called ionic liquids (ILs) or room temperature molten salts, which are generally composed of inorganic anions and organic or inorganic cations and have the properties of both liquid and salt [1]. With very low vapor pressure, high electrical conductivity, wide electrochemical window, cryogenic liquid temperature range, strong ability of dissolving and catalytic properties, ILs have a good application prospect in the field of electrochemistry, material preparation, extraction separation, catalytic reaction, and organic synthesis etc [2-6] as compared with the traditional organic solvents. Therefore, ILs have

attracted wide attention and become one of the research hotspots, and gradually moved from laboratory research to industrial applications [7].

At present, the ILs widely studied is mainly single cation ILs. However, in recent years, double cation ILs have attracted the attention of researchers, because they are composed of one double cation and two single anions, and the two cations are connected by linkers. They have the advantages of better thermal stability, higher density, wider liquid range and better physical and chemical controllability and have been used in various fields such as high temperature organic reaction process and dye-sensitized solar cell [8].

In this work, three imidazole based ILs were synthesized, including a mono-cationic IL (MIL) ([BMIM][NTF₂]) and two di-cationic ILs (DIL_s) [C₅(MIM)₂][NTF₂]₂ and [C₆(MIM)₂][NTF₂]₂. Their electrochemical stability, viscosity and

conductivity at different temperatures were measured, and the effects of temperature and IL structure on their properties were also analyzed [9]. Finally, by taking the advantages of high electrochemical stability and conductivity of ILs, [BMIM][NTF₂] was used as the electrolyte in the lithium-oxygen battery.

Experimental

Synthesis of MIL [BMIM][NTF₂]

[BMIM][NTF₂] was synthesized by ion exchange method [10,11]. In a typical procedure, 25mL of lithium trifluoromethanesulfonimide (11.8g) solution was added drop wise to 20mL of [BMIM][Cl] (6.77g) solution, and stirred continuously for 20min. During this process, the solution is gradually stratified. Then, the lower light yellow liquid was extracted with dichloromethane, and the solution was continuously washed with deionized water. The obtained solution was dried with anhydrous magnesium sulfate. The extractant dichloromethane in the product was volatilized in a vacuum drying oven, and the solution was further dried to finally obtain a colorless and viscous IL.

Synthesis of DILs [C₅(MIM)₂][NTF₂]₂ and [C₆(MIM)₂][NTF₂]₂

The two kinds of DILs were synthesized by a similar method [12]. Taking the synthesis of [C₅(MIM)₂][NTF₂]₂ as an example, the synthesis path was divided into the following two steps: 23.0g of 1,5-dibromopentane was firstly added dropwise to 16.4g of N-methylimidazole solution in a round bottom flask. The solution was magnetically stirred at room temperature for 2h to obtain solid [C₅(MIM)₂][Br]₂ bromide salt. Subsequently, the obtained bromine salt was dissolved into 100mL of deionized water, and 50ml of ethyl acetate was added to dissolve the unreacted N-methylimidazole. Finally, the solution was rotary-evaporated at 80°C to remove the solvent to obtain solid [C₅(MIM)₂][Br]₂, which was transferred into a vacuum drying oven and dried at 80°C to remove the remaining trace solvent and water.

Secondly, 19.7g of the [C₅(MIM)₂][Br]₂ and 28.7g of LiNTF₂ were dissolved in deionized water respectively, and were mixed until the solution state was changed. The ion exchange reaction was completely carried out by stirring at room temperature for 12h, and the mixture was allowed to stand until layered. The hydrophobic DIL [C₅(MIM)₂][NTF₂]₂ obtained from the lower layer was washed with deionized water for several times. Finally, the obtained DIL was dried in a vacuum drying oven at 80°C. It was determined by a constant moisture titrator that the water content in the [C₅(MIM)₂][NTF₂]₂ was less than 0.1wt%.

Measurements of Conductivity, Viscosity and Electrochemical Stability

The ILs was placed in the beaker in a constant temperature water bath. The conductivity electrode connected to the conductivity meter was inserted into the beaker and stand still, so that the ILs was naturally cooled to the temperature to be measured in the constant temperature water bath. After stabilizing for five minutes, the conductivity was measured every 5°C. All samples were measured twice and the average value was taken.

The viscosity has a great influence on the mass transfer of ILs, and therefore the viscosity of these ILs at different temperatures was measured by the viscometer (Lovis 2000M, Anton Paar GmbH). The temperature accuracy of the instrument is ±0.01°C, and the uncertainty of the measured viscosity is ±1%.

The electrochemical stability of three different ILs was tested in a three-electrode cell connected to the electrochemical workstation (CHI 660D). Among them, two platinum wires were used as working electrode and auxiliary electrode, respectively, and a saturated calomel electrode (SCE) was used as reference electrode. The scanning rate is 50mV s⁻¹.

Assembly and Charge/Discharge Tests of Lithium-Oxygen Battery

Ketjen black (KB) and polytetrafluoroethylene (PTFE) at the mass ratio of 8:2 were fully dispersed in a certain amount of ethanol. After being stirred to ethanol volatilization, a rubber slurry was formed, which was evenly spread on the foam nickel with a diameter of 12mm and dried for 12h at 80°C to remove residual moisture and solvent. The mass of KB on the electrode is assessed to be 1.1±0.1 mg.

The lithium-oxygen battery was assembled in a glove box filled with argon (H₂O≤1ppm, O₂≤1ppm) [13,14]. Using [BMIM][NTF₂] solvent containing 0.1M LiNTF₂ as electrolyte, the assembly sequence of the battery was: lithium sheet → 50μL electrolyte → diaphragm → absorbent paper → 50μL electrolyte → oxygen electrode sheet, in which the side containing active substance was in contact with the electrolyte. In order to eliminate the influence of other components in the air (especially water and carbon dioxide) on the battery performance, all lithium-oxygen battery tests were tested in a glove box filled with high-purity oxygen (H₂O≤1ppm).

In the oxygen glove box, the galvanostatic charge/discharge performance of the battery is studied, and its

actual specific capacity was calculated. The charge and discharge cut-off voltage was set to 4.5 and 2.0 V, respectively. The charge and discharge tests were conducted by LAND CT2001A charge and discharge instrument.

Results and Discussion

¹H NMR Characterization of the Three ILs

The ¹H NMR spectra of the three ILs were recorded by using a Bruker Avance 500MHz spectrometer (Germany) with deuterated dimethyl sulfoxide (DMSO) as the solvent. The ¹H NMR results of the three ILs are consistent with the target products [10]: [BMIM][NTF₂]: 9.11 (s,1H), 7.77 (t,1H), 7.70 (t,1H), 4.16 (t,2H), 3.85 (s,3H), 1.71 (m,2H), 1.25 (m,2H), 0.91 (t,3H); [C₅(MIM)₂][NTF₂]₂: 9.09 (s,2H), 7.73 (t,2H), 7.70 (t,2H), 4.17 (t,4H), 3.86 (s,6H), 1.83 (m,4H), 1.24 (m,2H); [C₆(MIM)₂][NTF₂]₂: 9.09 (s,2H), 7.73 (t, 2H), 7.70 (t,2H), 4.16 (t,4H), 3.86 (s,6H), 1.80 (m,4H), 1.28 (m,4H), suggesting the high purity of the three ILs.

Conductivity of the Three ILs

The relationship between conductivity (σ) and temperature (T) of the three ILs is shown in Figure 1A. It can be seen that the conductivity of the three ILs increases with increasing temperature, and [BMIM][NTF₂] exhibits the highest conductivity at the same temperature. For the two

kinds of DILs, the conductivity of [C₅(MIM)₂][NTF₂]₂ is higher than that of [C₆(MIM)₂][NTF₂]₂. By comparing the length of the intermediate group between the two kinds of DILs, it can be found that the shorter the intermediate group between the DILs, the higher the conductivity. Because the size of ions in the DILs is larger than that in the MIL, the mobility of the DILs is lower than that of the MIL. Thus, the conductivity of the DILs is slightly lower than that in MIL.

The relationship between the logarithm value of conductivity ($\ln\sigma$) and the reciprocal of temperature ($1/T$) is shown in Figure 1B. It shows a good linear relationship between $\ln\sigma$ and $1/T$. According to Arrhenius formula: $\ln\sigma = \ln\sigma_0 + E_a/RT$, where σ is conductivity (mS cm⁻¹), σ_0 is a constant, E_a is the activation energy of conductivity (kJ mol⁻¹), R is the gas constant (8.314 J mol⁻¹ K⁻¹), and T is thermodynamic temperature (K), the activation energy of conductivity of [BMIM][NTF₂] is calculated to be 13.16 kJ mol⁻¹, which is significantly lower than those of [C₅(MIM)₂][NTF₂]₂ (26.10 kJ mol⁻¹) and [C₆(MIM)₂][NTF₂]₂ (21.77 kJ mol⁻¹). The conductivity of IL is affected by many factors, such as its own density, viscosity, relative molecular weight and ion size [15-17]. The conductivity of the MIL is better than that of the other two DILs, and the E_a of MIL is higher than that of the other two DILs. For the DILs, the length of intermediate group influences the E_a in a degree. The results show that E_a decreases with increasing length of intermediate group.

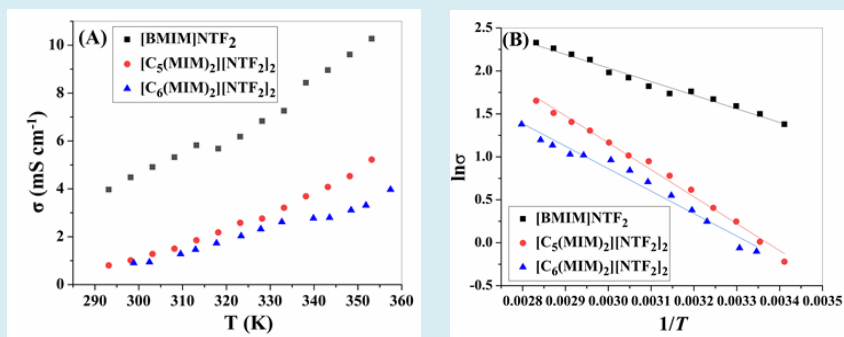


Figure 1: (A) The relationship between conductivity and temperature; (B) The relationship between the logarithm value of conductivity and the reciprocal of temperature.

Viscosity of the Three ILs

Due to the strong interactions between cation and anion of ILs, ILs usually exhibit high viscosity (η) [18,19]. It has been reported that the dynamic properties of ILs are closely related to the binding strength of ion pairs, and the hydrogen bond in ILs can increase the fluidity of ILs [9]. Figure 2 displays the relationship between the logarithm value of viscosity ($\ln\eta$) and the reciprocal of temperature ($1/T$). As can be seen, $\ln\eta$ exhibits a good linear relationship

with $1/T$, conforming to Arrhenius formula: $\ln\eta = \ln\eta_0 + E_\eta/RT$, where η is conductivity, η_0 is a constant, E_η is the viscosity activation energy (kJ mol⁻¹), R is the gas constant (8.314 J mol⁻¹ K⁻¹), and T is thermodynamic temperature (K). The viscosity activation energy (E_η) of [BMIM][NTF₂] (0.40 kJ mol⁻¹) is smaller than those of those of [C₅(MIM)₂][NTF₂]₂ (0.54 kJ mol⁻¹) and [C₆(MIM)₂][NTF₂]₂ (0.52 kJ mol⁻¹), suggesting that the ionic liquid state of the MIL is more easier to be changed than the two DILs. Therefore, MIL is often liquid at room temperature. The ionic liquid state of

the DILs is usually changed under harsh conditions, and they exhibit high viscosity.

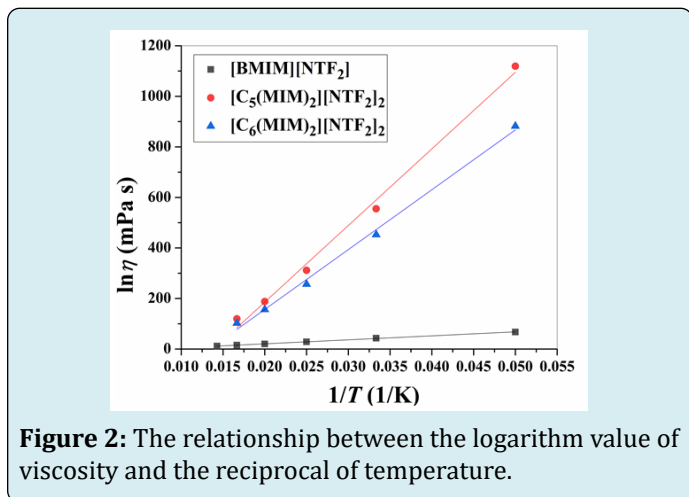


Figure 2: The relationship between the logarithm value of viscosity and the reciprocal of temperature.

Electrochemical Stability of the Three ILs

The electrochemical stability of the three ILs was measured by linear sweep voltammetry (LSV), and the results are presented in Figure 3. The LSV curve of the MIL, [BMIM][NTF₂] is significantly different from those of the other two DILs. When the voltage is less than 2.0 V, the currents of the MIL and the DILs are roughly the same, and there is no significant difference in the stability of the three ILs. However, when the voltage exceeds 2.0 V, the currents of the MIL increase dramatically, suggesting the low stability of the MIL. While the currents of the DILs increase little, which can be ascribed to the relatively high stability of the DILs? Therefore, the electrochemical stability of the DILs is higher than that of the MIL.

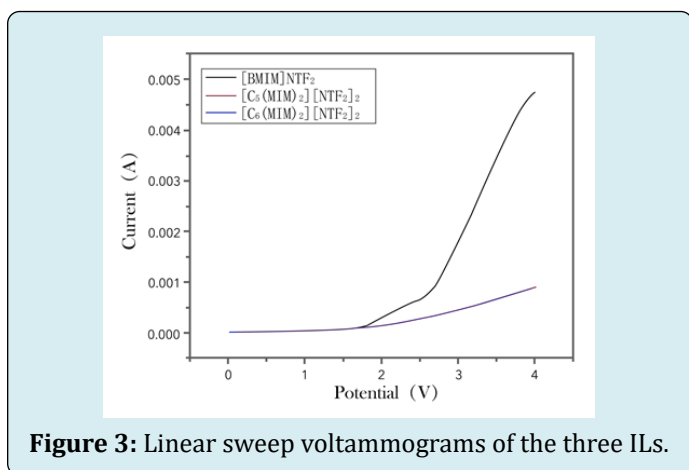


Figure 3: Linear sweep voltammograms of the three ILs.

Application of ILs in Batteries

Based on the good electrochemical stability and conductivity of ILs [20], the MIL of [BMIM][NTF₂] is taken

as the electrolyte of lithium-oxygen battery, and the application of IL in lithium-oxygen battery is investigated by its first cycle of charge/discharge capacity Figure 4. It can be seen that when [BMIM][NTF₂] is used as the electrolyte in lithium-oxygen battery, it exhibits high charge/discharge capacity, and the discharge capacity and charge capacity on the first cycle can reach 4700 mAh g⁻¹ and 2331 mAh g⁻¹, respectively. Therefore, ILs might be a potential candidate as the electrolyte in lithium-oxygen batteries.

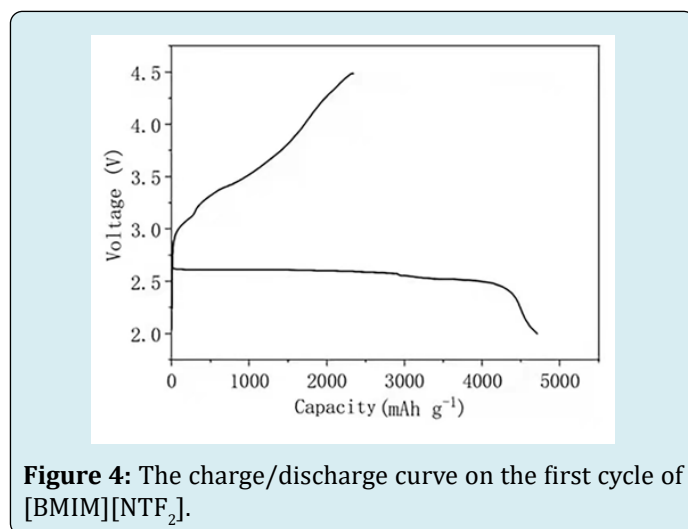


Figure 4: The charge/discharge curve on the first cycle of [BMIM][NTF₂].

Conclusions

In this study, three imidazole based ILs were synthesized, including a MIL [BMIM][NTF₂] and two DILs, [C₅(MIM)₂][NTF₂]₂ and [C₆(MIM)₂][NTF₂]₂. The conductivity, viscosity and electrochemical stability of the three ILs were studied. The conductivity of the three ILs increases with increasing temperature at the same temperature, the conductivity of MIL is better than those of DILs. The viscosity of DILs is higher than that of MIL, and the viscosity of DILs decreases with increasing length of the group within the DILs. The electrochemical stability of DILs is higher than that of MIL. Finally, the MIL is used as the electrolyte in the lithium-oxygen battery, exhibiting high charge/discharge capacity. These findings suggest that the synthesized three imidazole based ILs especially MIL might be potential candidates to be used for lithium-oxygen batteries.

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