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New polymerized ionic liquid (PIL) gel electrolyte membranes based on tetraalkylammonium cations for lithium ion batteries

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ABSTRACT

New polymerized ionic liquids (PILs) based on tetraalkylammonium cations with $N(CF_3SO_2)_2^-$ ($TFSI^-$) anions are synthesized by homopolymerization and anion exchange reaction. Furthermore, a gel polymer electrolyte membrane based on the PILs as polymer host is prepared incorporating a tetraalkylammonium ionic liquid, LiTFSI salt and nano-size SiO_2. The gel polymer electrolyte membranes show exceptional thermal and electrochemical properties. They are found to be thermally stable up to 336 °C. With the increase of the IL, T_g of the PIL-based electrolyte samples decreases obviously. When the IL concentration is 25 wt%, the ionic conductivity of the electrolytes reaches 4.9×10^{-4} S cm^{-1} at 60 °C. After 130 cycles, the Li/$LiFePO_4$ battery with the gel polymer electrolyte membranes at 60 °C has discharge capacity of 122 mA h g^{-1} at 0.1 current rates.

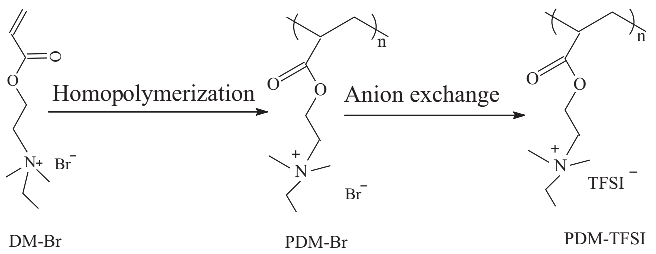
1. Introduction

Polymerized ionic liquids (PILs) combining the merits of ionic liquids (e.g., negligible vapor pressure, non-flammability, high ionic conductivity, and wide electrochemical window) and the general properties of polymers especially film-forming ability have attracted great interest in recent years [1–3], and also for application in a variety of fields such as CO_2 separations [4], ionic conductors [5], fuel cells [6] and polymer electrolytes [7,8]. The exceptional properties of PILs membranes particularly high ionic conductivity draw increased attention in view of the application as polymer electrolytes for lithium ion batteries.

Recently, a series of PILs electrolytes with high ionic conductivity based on immidazolium cations have been synthesized and systematically characterized [9–13]. An immidazolium-based PIL single ion conductor was prepared [11]. The authors investigated the isolated effect of anion type on the chemical, thermal, and conductive properties of the PIL. They suggested that the ion transport was influenced by some factors, including the size and symmetry of the anion and dissociation energy of the ion pair. New anionic PILs based-immidazolium cations with high charge delocalization were synthesized [13]. The conductive behaviors of the PILs electrolytes were thoroughly investigated. The researchers found the increase in ionic conductivity is as high as three orders of magnitude depending on the size of the attached anion.

Although the high ionic conductivity of the PILs were obtained, very few applications of the PILs as electrolytes in lithium batteries have been reported, so far [14]. The cause lies in the fact that the interfacial resistance between the solid PILs electrolytes and the electrode materials in lithium ion batteries is enormous and their compatibility is not good, which results in that the batteries cannot normally charge and discharge. In addition, the PILs based on the other cations such as tetraalkylammonium, pyrrolidinium, and piperidine have been rarely reported [15].

In this study, a new kind of PIL based on tetraalkylammonium cations was synthesized by homopolymerization and anion exchange reaction (see Scheme 1). To improve the interfacial compatibility between the PIL electrolyte and the electrodes in lithium ion batteries,



Scheme 1. Illustration for the synthesis of the PILs.

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a gel PIL electrolyte was prepared by adding a tetraalkylammonium ionic liquid (DEME-TFSI). Furthermore, nano-silica was also added in the electrolytes to increase the mechanical strength of the electrolyte membrane. The gel polymer electrolyte membranes were used in Li/$LiFePO_4$ cells and showed good performances at current rates of 0.1C and 50 °C.

2. Experimental

2.1. Reagents and materials

N-ethyl-*N*-methyl-*N*-(2-methoxyethyl) ammonium, 2-(dimethylamino)ethyl methacrylate and ethylbromide were purchased from Alfa Aesar. Lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) was kindly provided by Morita Chemical Industries Co., Ltd. and used as received. Nano-silica (fine reagent grade) with average diameter 30 nm was purchased from Aladdin Co., Ltd. All the other chemicals used in this work were of A.R. grade.

2.2. Synthesis of the monomer

2-(Dimethylamino)ethyl methacrylate was treated with 1.2 equiv. of ethylbromide in tetrahydrofuran and stirred for 48 h. The solution was washed with lots of diethyl ether. The precipitate obtained was filtered off and recrystallized in tetrahydrofuran–ethanol solvent. The structure was confirmed by ^{1}H NMR and IR.

2-(Dimethylethylamino)ethyl methacrylate bromide (DM-Br), ^{1}H NMR (400 M Hz, $CDCl_3$), δ (TMS, ppm): δ=6.49 (m, 1H), 6.13 (m, 1H), 5.95 (m, 1H), 4.46, (m, 2H) 3.56 (m, 2H), 3.45 (t, 2H), 3.05 (s, 6H), 1.75 (t, 3H).

Infrared spectra, methacryl group (1680 and 1720 cm^{-1}).

2.3. Synthesis of the PIL with TFSI anions

The synthesis route of the PIL with TFSI anions is illustrated in Scheme 1. 2-(Dimethylethylamino)ethyl methacrylate bromide (DM-Br) (2 g), acetonitrile (14 mL) and 2, 2′-azobis (2-methylpropionitrile) (AIBN, 0.01 g), at a ratio of 0.5 wt% to the amount of methacryl groups present in the DM-Br, were mixed until they became homogeneous. The mixture was degassed in vacuum at 40 °C, and kept standing at 60 °C for 12 h. After polymerization, the obtained polymers were dried at 80 °C for 6 h, then rinsed with large amounts of deionized water. The obtained polymer was denoted as PDM-Br, 1.5 g, 75% yield. Then, after a simple ion-exchange reaction PIL with TFSI anions was obtained, as follows.

1.2 g of PDM-Br was dissolved in 5 mL acetone, stirred for 2 h, and then lithium salts (LiTFSI) of which amount is 0.63 g was added into the solution, and was stirred for another 4 h. After the ion-exchange reaction finished, the solution was poured into Teflon dishes and air-dried at 80 °C for 4 h. Then the obtained PILs were immersed in deionized water at 40 °C for 1 h, and rinsed with large amounts of deionized water. The process of immersion and rinse was repeated twice so as to remove the superfluous lithium salts. After that, the polymer denoted as PDM-TFSI was dried in vacuum at 80 °C for 24 h and the pure product was obtained.

2.4. Preparation of the IL, DEME-TFSI

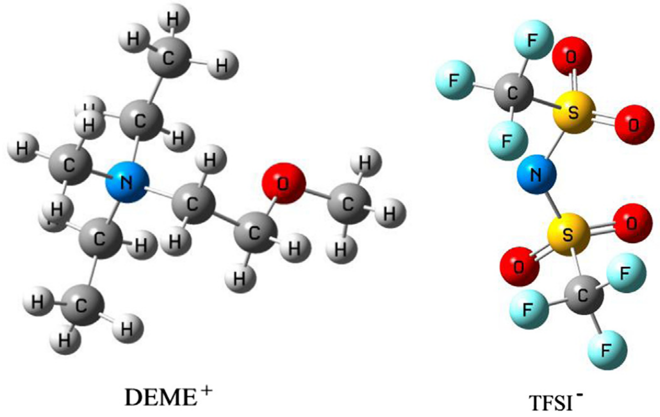
The IL, *N*,*N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)imide (DEME-TFSI) was synthesized according to the methods in Refs. [16,17]. *N*-ethyl-*N*-methyl-*N*-(2-methoxyethyl) ammonium was treated with 1.2 equiv. of ethylbromide in tetrahydrofuran and stirred for 48 h. The solution was washed with lots of diethyl ether. The precipitate was filtered off and recrystallized in tetrahydrofuran–ethanol solvent. Then the pure *N*,*N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl) ammonium bromide was obtained. Recrystallized *N*,*N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl) ammonium bromide was treated with exactly 1.0 equiv. of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in water for 5 h. After the reaction, the mixture was separated in two phases, bottom phase being DEME-TFSI. The ionic liquid was extracted twice with chloroform, and combined organic solution was washed twice with deionized water. It was then concentrated by rotary evaporation in vacuum. After being dried in vacuum at 110 °C for 12 h, the pure DEME-TFSI (see Scheme 2) was obtained.

2.5. Preparation of the polymer gel electrolytes

The polymer gel electrolytes were prepared by separately dissolving the PDM-TFSI, DEME-TFSI, LiTFSI and nano-scale SiO_2 in acetone at 40 °C for 5 h, and then mixed in three different proportions (see Table 1). The solution was casted onto PTFE slides to prepare the electrolyte films. Then the film was dried in the nitrogen atmosphere at room temperature for 12 h and subsequently dried at 80 °C under vacuum for another 12 h.

2.6. Preparation of batteries

Lithium foil (battery grade) was used as a negative electrode. And positive electrode was fabricated by spreading the mixture of $LiFePO_4$, acetylene black and PVdF (initially dissolved in N-methyl-2-pyrrolidone) with a weight ratio of 8:1:1 onto Al current collector (battery use). Loading of active material was about 2.5 mg cm^{-2} corresponding to 0.4 mAh cm^{-2} and this thinner electrode was directly used without pressing. Li/$LiFePO_4$ polymer batteries were fabricated (in an argon-filled glove box) by laminating the lithium foil, a PIL–(DEME-TFSI)–LiTFSI–SiO_2 polymer electrolyte membrane and a $LiFePO_4$ cathode tape.



Scheme 2. Molecular structure of conformer of the IL, DEME$^+$TFSI$^-$ for density functional theory (DFT) calculations.

Table 1
Composition of PIL–IL–LiTFSI–SiO_2 gel polymer electrolytes.

Sample name	Weight (g)				DEME-TFSI/PIL ratio
	PIL	LiTFSI	Nano-scale SiO_2	DEME-TFSI	wt/wt
PDM-IL-0.15	0.6	0.12	0.06	0.09	0.15
PDM-IL-0.20	0.6	0.12	0.06	0.12	0.20
PDM-IL-0.25	0.6	0.12	0.06	0.15	0.25