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Electrochemical Characterization of Lithium Polyelectrolyte Based on Ionic Liquid

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Five novel lithium polyelectrolyte-ionic liquid systems, using poly (lithium 2-acrylamido-2-methyl propanesulfonate; PAMPSLi) were prepared and their electrochemical properties were measured. The ionic conductivity of the PAMPSLi/1-ethyl-3-methylimidazolium tricyano methanide (emImTCM) system was exhibited high conductivity (1.28×10^{-3} S/cm^{-1}). The high conductivity and low viscosity of PAMPSLi/emImTCM system is due to the high flexibility of imidazolium cation and dissociation of lithium cation from the polymer chains. The PAMPSLi/N,N-dimethyl-N-propyl-N-butylammonium tricyanomethanide (N_{1134}TCM) and PAMPSLi/N, N-dimethyl-N-propyl-N-butylammonium dicyanamide (N_{1134}DCA) systems showed fairly high conductivity (6.3×10^{-4} S/cm^{-1}, 6.0×10^{-4} S/cm^{-1}). PAMPSLi/Trihexyl (tetradecyl) phosphonium bis (trifluoromethane sulfonyl) amide (P_{66614}TFSA) exhibited low conductivity (2.22×10^{-5} Scm^{-1}) and thermally stable over 400°C.

Keywords : Conductivity, Imidazolium ionic liquid, Ammonium ionic liquids, Phosphonium ionic liquids, Viscosity

1. Introduction

Ionic liquids which are fascinating materials for a wide range of applications have the properties of large stable liquid range, fairly low viscosity, high conductivity and high thermal and electrochemical stability.[1,2,3] The physical properties of polyelectrolyte based on imidazolium ionic liquid have been extensively studied for their application as electrolyte for batteries and capacitors,[4,5] fuel cells, dye-sensitive solar cells and actuators. In most of these studies, N, N' dialkyl- imidazolium salt, especially 1-ethyl-3-mehyl-imidazolium salt was focused empirically because of low viscosity and correspondingly high ionic conductivity.[6] The substitution of the methyl group has been shown increasing the electrochemical stability of the imidazolium by over 0,25 V.[7,8] In the case of lithium polyelectrolytes based on ionic liquids, the lithium ion transport number is usually significantly small because of ion aggregation and strong association with polymer. The anion species is prefer to have weakly basic and a diffuse charge in order to enhance ionic conductivity and ion dissociation The viscosity of the ILs can be varied replacing different cations and anions with polymer. Quaternary ammonium and phosphonium ILs tend to show somewhat higher viscosity and lower conductivity, but more thermal stability and low cost.[9] Tricyanomethanide and dicyanamide is known to afford very low melting point, low viscosity.[10] Bis (trifluoromethane sulfonyl amide ion is also known to reduced degree of ion interaction its diffuse charge generates.

This paper reports electrochemical properties of lithium polyelectrolyte based on imidazolium, ammonium and phosphonium liquids.

2. Experimental

The monomer, lithium 2-acrylamido-2-methyl-

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propanesulfonate (AMPSLi), was prepared by the reaction of 2 acrylamide-2-methyl propanesulfonic acid (Aldrich) with lithium carbonate (Aldrich) in a water solution placed in an ice bath. The polymer was synthesized by polymerization of AMPSLi at 80°C in presence of K_2SO_8 initiator (~1 wt%). The final polymer product, PAMPSLi was dried under vacuum (~80 torr) at 65°C for at least 48 h.[11)] PAMPSLi and ionic liquids (10%polymer + 90%ionic liquid was mixed in ethanol over night and then. the transparent gel samples were obtained[11)] PAMPSLi/emImTCM (12-14), PAMPSLi/N_{1134} TCM, PAMPSLi/N_{1134}DCA, PAMPSLi/emImTFSA (15), PAMPSLi/P_{66614}TFSA were prepared. (Scheme1).

Thermal analysis of samples was performed using a TA instruments differential scanning calorimeter (DSC Q100) at a scanning rate of 10°C/min over a temperature range of −150°C to 150°C.(But in this paper the data of DSC was displayed from −150°C to 0°C).

Impedance measurements were carried out in a small conductance cell. The samples were loaded and hermetically sealed in the cell using a SI1260 impedance/gain phase analyzer and Solatron 1296 with Solatron impedance measurement software (v.3.2.0). The cell constants were determined before and after measurements at room temperature using 0.01 M KCl solution. Measurements were taken at 10°C increments from 25 to 65°C using the Eurotherm 2240E. Viscosity of the ionic liquids was measured with an AMVn Automated Microviscometer at 25°C, 70°C and the ionic liquids were sealed in the sample tube under a nitrogen atmosphere.

A PerkinElmer thermo gravimetric Analyzer was used to test thermal stability of the ionic liquid and scan rate was 10.0°C/min from room temperature to 800°C.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX300 spectrometer for solutions in $CDCL_3$. Peaks are noted below only if they were significantly resolved from neighboring peaks and/or the baseline. Tetramethylsilane was used as an internal standard. Positive and negative ion electrospray mass spectra were recorded using a Micromass platform electrospray mass spectrometer on samples dissolved in methanol. NMR data of 5 samples are as follow.

1. *1-ethyl-3-methylimidazolium tricyano methanide (emImTCM)*

^{1}Hnmr ($CDCl_3$): d 1.65 (t, 3H, CH_3), 3.98 (s, 3H, CH_3), 4.30 (q, 2H, CH_2), 7.38 (d, 2H, CH), 8.88 (s, 1H, CH). ^{13}Cnmr ($CDCl_3$): d 14.2 (CH_3), 35.7 (CH_3), 44.7 (CH_2), 120.4 (CH), 122.0 (CH). ES-MS: ES^+ m/z 110.6 $emIm^+$. ES^- m/z 89.5 TCM^-.

2. *N,N-dimethyl-N-propyl-N-butylammonium Tricyanomethanide (N_{1134}TCM);*^{1}Hnmr (CH_2Cl_2): d 1.03 (m, 6H, CH_3), 1.45 (m, 2H, CH_2), 1.82 (m, 4H, CH_2), 3.08 (s, 6H, CH_2), 3.32 (d, 4H, CH_2), 4.67 (s, CH_2). ES^+ m/z 144.0 $N_{1134}{}^+$. ES^- m/z 89.7 TCM^-.

3. *N, N-dimethyl-N-propyl-N-butylammonium dicyanamide (N_{1134}DCA)*;^{1}Hnmr (CH_2Cl_2): d 1.05 (m, 6H, CH_3), 1.47 (m, 2H, CH_2), 1.82 (m, 4H, CH_2), 3.11 (s, 6H, CH_2), 3.35 (d, 4H, CH_2), 4.67 (s, CH_2). ES^+ m/z 143.9 $N_{1134}{}^+$. ES^- m/z 65.7 DCA^-.

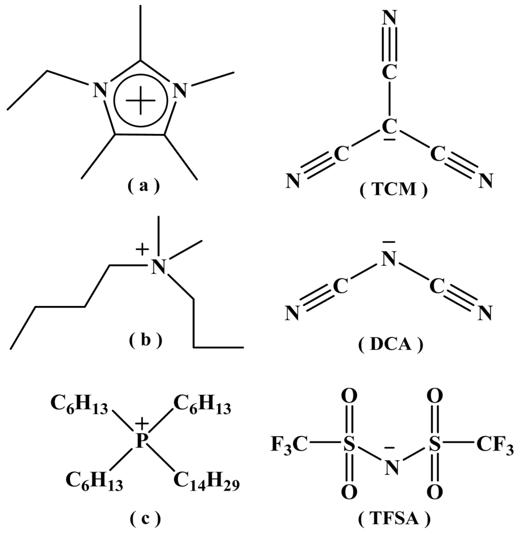
4.*1-ethyl-3-methylimidazolium bis(trifluoro -methane sulfonyl amide(emIm TFSA)*(13)

^{1}Hnmr (400MHZ, DMSO) d 9.09 (s, 1H), 7.77-7.68(m,2H),4.19(q,2H,J=7.3Hz), 3.84(s,3H0,1.42 (t,3H, J=7.3Hz)

5.*Trihexyl (tetradecyl) phosphonium bis (trifluoromethane sulfonyl) amide (P_{66614}TFSA)* ^{1}Hnmr:dH(300MHZ;CCl_3)2.0-2.3(8H,m,CH_2), 1.4-1.5 (16H,m,CH2), 1.2-1.3(32H,m, CH_2), 0.79-0.85 (12H, m, CH3) ppm. ES-MS: ES^+ m/483[P_{66614}]+ ES-m/z 279[TFSA]-water content(Karl-Fisher): 141ppm, Cl ontent:<100ppm

3. Results and Discussion

The thermal trace of PAMPSLi/emImTCM (a),



Scheme1. (a) EmIm (b) N_{1134} (c) P_{66614}

PAMPSLi/N_{1134}TCM (b), PAMPSLi/ N_{1134}DCA(c), PAMPSLi/P_{66614}TFSA (d) are shown in Fig. 1. The T_g of pure N_{1134}DCA is not displayed and the emImTCM did not display any solid-solid transitions. Although the T_g of emImTFSA was measured, The PAMPSLi/emImTFSA system was immiscible, so the T_g could not be shown in Fig. 1. Table 1 shows the glass transition temperature (T_g) and viscosity of, polyelectrolyte based on ionic liquid; As you can see, the T_g value of polyelectrolyte based on emImTCM, N_{1134}TCM and emImTFSA samples have little difference, but the viscosity value of emImTCM is the lowest of all samples.

EmImTCM exhibits the narrower window of electrochemical stability,2) but the charge delocalization occurs stronger and thus, the weaker ion-pairing with the imidazolium cation, providing the emImTCM less viscosity than N_{1134}TCM and P_{66614}TFSA. The viscosity of N_{1134}TCM and N_{1134}DCA is fairly low. An acceptable explanation concerning the ammonium ILs indicates that electron donation from methyl group into cationic center can decrease the positive charge on the nitrogen atom. Hence the electrostatic interaction between the cation and anion is weakened, which results in reducing both the viscosity.16) All polyelectrolyte samples except pure ionic liquids do not have a melting peak from −150°C to 0°C This means that the presence of polymer in ionic liquids hinders the crystallization of the ionic liquid.15) Fig. 3 shows the conductivity of PAMPSLi/emImTCM, PAMPSLi/ N_{1134}TCM, PAMPSLi/ N_{1134}DCA and PAMPSLi/ P_{66614} TFSA(from 25°C to 65°C). The PAMPSLi - emImTFSA system was immiscible, so the conductivity of the PAMPSLi/emImTFSA could not be measured. The conductivity of pure emImTFSA is 8.8×10^{-3} Scm^{-1}. The ionic conductivity of the PAMPSLi/emImTCM system 1that of PAMPSLi/N_{1134}TCM (6.3×10^{-4} S/cm^{-1}), PAMPSLi/N_{1134}DCA (6.0×10^{-4} S/cm^{-1}) and PAMPSLi/ P_{66614}TFSA(2.22×10^{-5} Scm^{-1}). High conductivity and low viscosity of PAMPSLi/emImTCM system is due to high flexibility of imidazolium cation by using the polymerizable anion.17) The lower viscosity of emImTCM (19.56 cP) than that of N_{1134}TCM, and N_{1134}DCA , emImTFSA and P_{66614}TFSA is affected by higher ionic conductivity. Lower viscosity and dissociation of lithium cation from the polymer chains exhibit the higher conductivity. The conductivity of emImTCM is 20 $mScm^{-1}$ at 25°C. This value is superior

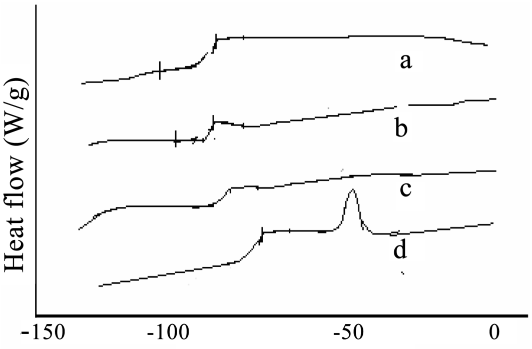


Fig. 1. DSC thermograms of (a) PAMPSLi/emImTCM (b) PAMPSLi/N_{1134}TCM (c)PAMPSLi/N_{1134}DCA (d) PAMPSLi/ P_{66614}TFSA.

Table 1. Properties of polyelectrolyte

	T_g(°C)	σ	η (cP)*	σ*
a	-85.49	1.28	19.56	20
b	-86.63	0.63	28.6	20
c	-	0.6	28.7	22
d	-86.7*	-	39	8.8
e	-71.34	0.022	450	0.2

σ($\times 10^{-4}$ scm^{-1}); conductivity, η; viscosity
σ* : conductivity of Pure IL

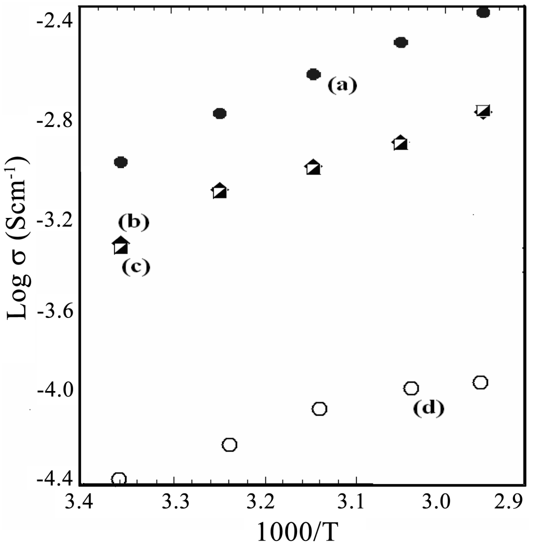


Fig. 2. Conductivity of PAMPSLi/emImTCM (a) PAMPSLi/ N_{1134}TCM (b) (c) PAMPSLi/N_{1134}DCA (c) PAMPSLi/ P_{66614} TFSA(d).

to that of emImTFSA (8.8 mS/cm) and N_{1134}TCM (8 $mScm^{-1}$), emImTFSA (8.8 $mScm^{-1}$), P_{66614}TFSA (0.89 $mScm^{-1}$) and emImDCA (22 $mScm^{-1}$).[2,14] Although there was little difference between the T_g values of emImTCM, N_{1134}TCM and N_{1134}DCA, the conductivity of PAMPSLi/emImTCM was found to be fairly higher than that of PAMPSLi/N_{1134}TCM and PAMPSLi/N_{1134}DCA. The ionic conductivity of N_{1134}TCM and N_{1134}DCA is not as high as that of most other ionic liquids. It is quite viscous by comparison with related ionic liquids (Table 1); this presumably reflects strong electrostatic interactions between ions. The conductivity and viscosity provide the information on the mobility and aggregation of ions and ion-pairing phenomenon. The viscosity of the IL and its hydrophilicity are critical to achieving high conductivity.[15] Generally phosphonium ionic liquid showed the lower viscosities and higher conductivities and those of the corresponding phosphonium bis (trifluoromethane sulfonyl amide) and triethyl (2-methoxyethyl) phosphonium bis (trifluoromethane sulfonyl amide), exhibited quite low viscosities (35 cP and 44 cP at 25°C, respectively) the viscosity of P_{66614}TFSA exhibited the highest value of all samples which leads to a slow rate of diffusion of redox species. P_{66614}TFSA are based on relatively large cations derived from Trihexyl (tetradecyl) phosphine and therefore, tend to have high viscosities due to their large molecular weights.[14]

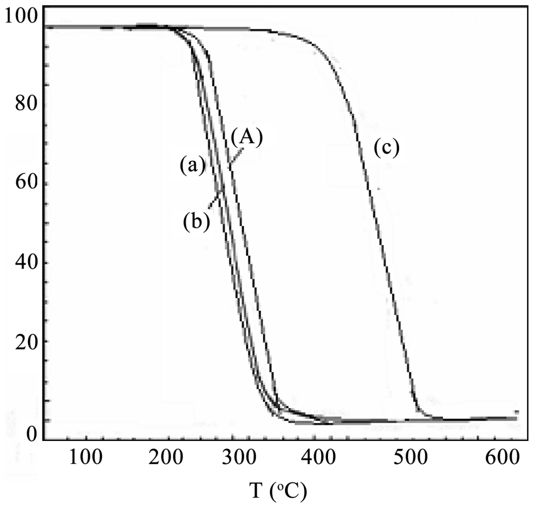


Fig. 3. Thermogravimetri trace for emImTCM (a), emImTFSA (b), P_{66614}TFSA (c), PAMPSLi/ emImTCM (A emImTCM and emImTFSA. The PAMPSLI/emImTCM system (A)

Fig. 3 shows a thermogravimetrc trace for emImTCM. emImTFSA and P_{66614}TFSA. It was shown that emImTCM and emImTFSA are stable around 300°C, but the phosphonium ionic liquid was thermally stable over 400°C. Imidazolium cation is somewhat electrochemically unstable in the lithium battery system because the catholic limiting potential is ca. +1.0 V vs Li/Li+.[9] The Gr avimetric decrease of P_{66614}TFSA was slower than those of exhibited more thermal stability than that of pure ionic liquid (a).

4. Conclusions

The ionic conductivity of the PAMPSLi/emImTCM system was exhibited high conductivity (1.28×10^{-3} Scm^{-1}). PAMPSLI/ emImTCM system exhibited more thermal stability than that of pure ionic liquid. The ammonium ILs which had low viscosity and fairly high conductivity indicates that electron donation from methyl group into cationic center can decrease the positive charge on the nitrogen atom. Hence the electrostatic interaction between the cation and anion is weakened, which results in reducing both the viscosity.[16] The PAMPSLi/emImTCM, PAMPSLi/ N_{1134}TCM and PAMPSLi/N_{1134}DCA systems seem to be good electrolytes' materials for secondary lithium battery. PAMPSLi/P_{66614}TFSA exhibited high viscosity and thermal stability. It is believed that phosphonium types are a good alternative to other ionic liquids and thus deserve further research.

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