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 ($1.28 \times 10^{-3}$ 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-butyllammonium tricyanomethanide (N1134TCM) and PAMPSLi/N, N-dimethyl-N-propyl-N-butyllammonium dicyanamide (N1134DCA) systems showed fairly high conductivity ($6.3 \times 10^{-4}$ S/cm$^{-1}$, $6.0 \times 10^{-4}$ S/cm$^{-1}$). PAMPSLi/Trihexyl (tetradecyl) phosphonium bis (trifluoromethane sulfonyle) amide (P66614TFSA) exhibited low conductivity ($2.22 \times 10^{-5}$ S/cm$^{-1}$) 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. The physical properties of polyelectrolyte based on imidazolium ionic liquid have been extensively studied for their application as electrolyte for batteries and capacitors, fuel cells, dye-sensitive solar cells and actuators. In most of these studies, N, N' dialkyl-imidazolium salt, especially 1-ethyl-3-methylimidazolium salt was focused empirically because of low viscosity and correspondingly high ionic conductivity. The substitution of the methyl group has been shown increasing the electrochemical stability of the imidazolium by over 0.25 V. 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. Tricyanomethanide and dicyanamide is known to afford very low melting point, low viscosity. Bis (trifluoromethane sulfonyle amide 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-...
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 K₂SO₄ initiator (~1 wt%). The polymer product, PAMPSLi was dried under vacuum (~80 torr) at 65°C for at least 48 h. PAMPSLi and ionic liquids (10% polymer + 90% ionic liquid was mixed in ethanol over night and then. The transparent gel samples were obtained

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1. **Results and Discussion**

The thermal trace of PAMPSLi/emIm TCM (a),

\[ \text{Scheme 1. (a) EmIm (b) N} \text{ (c) PAMPSLi/emIm TCM)} \]

\[ \text{1H and } ^13\text{C NMR spectra were recorded on a Bruker} \]

\[ \text{DPX300 spectrometer for solutions in CDCl}_3. \text{ Peaks are noted below only if they were significantly resolved from neighboring peaks and/or the baseline. Tetramethylsilane was used as an internal standard. Positive and negative ion electrospray mass spectra were recorded using a Micromass platform electrospray mass spectrometer on samples dissolved in methanol. NMR data of 5 samples are as follow.} \]

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

\[ ^1\text{Hnmr (CDCl}_3): \text{d} 1.65 (t, 3H, CH}_3, 3.98 (s, 3H, CH), 4.30 (q, 2H, CH₂), 7.38 (d, 2H, CH), 8.88 (s, 1H, CH). ^13\text{Cnmr (CDCl}_3): \text{d} 14.2 (CH}_3, 35.7 (CH}_3, 44.7 (CH₂), 120.4 (CH), 122.0 (CH). \text{ES-MS: ES}^+ \text{m/z 110.6 emIm}^+. \text{ES}^- \text{m/z 89.5 TCM}^- \]

2. **Triethylamine (N\text{134}TCM)**

\[ ^1\text{Hnmr (CH}_3\text{Cl}_2): \text{d} 1.03 (m, 6H, CH), 1.45 (m, 2H, CH), 1.82 (m, 4H, CH), 3.08 (s, 6H, CH), 3.32 (d, 4H, CH), 4.67 (s, CH₂). \text{ES}^+ \text{m/z 144.0 N}134^+. \text{ES}^- \text{m/z 89.7 TCM}^- \]

3. **N,N-dimethyl-N-propyl-N-butylammonium dicyanamide (N\text{1134}DCA)**

\[ ^1\text{Hnmr (CH}_3\text{Cl}_2): \text{d} 1.05 (m, 6H, CH), 1.47 (m, 2H, CH), 1.82 (m, 4H, CH), 3.11 (s, 6H, CH), 3.35 (d, 4H, CH), 4.67 (s, CH₂). \text{ES}^+ \text{m/z 143.9 N}1134^+. \text{ES}^- \text{m/z 65.7 DCA}^- \]

4. **1-ethyl-3-methylimidazolium bis(trifluoromethane sulfonyl amide (emIm TFSA)**

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

5. **Trihexyl (tetradecyl) phosphonium bis (trifluoromethane sulfonyl) amide (P\text{66614}TFSA)**

\[ ^1\text{Hnmr (300MHZ;CCl}_3): \text{d} 2.0-2.3(8H,m,CH}_2), 1.4-1.5 (16H,m,CH), 1.2-1.3(32H, m, CH), 0.79-0.85 (12H, m, CH) ppm. \text{ES-MS: ES}^+ \text{m/z 483[P}66614]+ \text{ES-m/z 279[TFSA]-water content(Karl-Fisher): 141ppm, Cl content:<100ppm} \]
The Tg of pure N1134DCA is not displayed and the emImTFSA 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, N1134TCM and emImTFSA samples have little difference, but the viscosity value of emImTCM is the lowest of all samples.

PAMPSLi/N1134TCM (b), PAMPSLi/N1134DCA(c), PAMPSLi/P66614TFSA (d) are shown in Fig. 1. The T_g of pure N1134DCA 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, N1134TCM and emImTFSA samples have little difference, but the viscosity value of emImTCM is the lowest of all samples.

Fig. 1. DSC thermograms of (a) PAMPSLi/emImTCM (b) PAMPSLi/N1134TCM (c)PAMPSLi/N1134DCA (d) PAMPSLi/P66614TFSA.

Table 1. Properties of polyelectrolyte

<table>
<thead>
<tr>
<th>Property</th>
<th>T_g(°C)</th>
<th>σ (mS/cm)</th>
<th>η (cP)*</th>
<th>σ*</th>
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<tr>
<td>a</td>
<td>-85.49</td>
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<tr>
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<td>0.63</td>
<td>28.6</td>
<td>20</td>
</tr>
<tr>
<td>c</td>
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<td>0.6</td>
<td>287</td>
<td>22</td>
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<tr>
<td>d</td>
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<td>-</td>
<td>39</td>
<td>8.8</td>
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<tr>
<td>e</td>
<td>-71.34</td>
<td>0.022</td>
<td>450</td>
<td>0.2</td>
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</table>

σ* × 10^-4 cm^2 s^-1 is conductivity, η; viscosity σ*: conductivity of Pure IL

Fig. 2. Conductivity of PAMPSLi/emImTCM (a) PAMPSLi/N1134TCM (b) (c) PAMPSLi/N1134DCA (e) PAMPSLi/P66614TFSA(d).
to that of emImTFSA (8.8 m S/cm) and N\textsubscript{1134}TCM (8 m S/cm\textsuperscript{−1}), emImTFSA (8.8 m S/cm\textsuperscript{−1}), P\textsubscript{66614}TFSA (0.89 m S/cm\textsuperscript{−1}) and emImDCA (22 m S/cm\textsuperscript{−1}).

Although there was little difference between the T\textsubscript{g} values of emImTCM, N\textsubscript{1134}TCM and N\textsubscript{1134}DCA, the conductivity of PAMPSLi/emImTCM was found to be fairly higher than that of PAMPSLi/N\textsubscript{1134}TCM and PAMPSLi/N\textsubscript{1134}DCA. The ionic conductivity of N\textsubscript{1134}TCM and N\textsubscript{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.\textsuperscript{(15)} Generally phosphonium ionic liquid showed the lower viscosities and higher conductivities and those of the corresponding phosphonium bis(trifluoromethane sulfonamide) and triethyl(2-methoxyethyl)phosphonium bis(trifluoromethane sulfonamide), exhibited quite low viscosities (35 cP and 44 cP at 25 \degree C, respectively) the viscosity of P\textsubscript{66614}TFSA exhibited the highest value of all samples which leads to a slow rate of diffusion of redox species. P\textsubscript{66614}TFSA are based on relatively large cations derived from Trihexyl(tetradecyl)phosphate and therefore, tend to have high viscosities due to their large molecular weights.\textsuperscript{(14)}

Fig. 3 shows a thermogravimetric trace for emImTCM, emImTFSA and P\textsubscript{66614}TFSA. It was shown that emImTCM and emImTFSA are stable around 300\degree C, but the phosphonium ionic liquid was thermally stable over 400\degree C. Imidazolium cation is somewhat electrochemically unstable in the lithium battery system because the cathodic limiting potential is ca. +1.0 V vs Li/Li\textsuperscript{+}.\textsuperscript{(9)} The Gravimetric decrease of P\textsubscript{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 \times 10\textsuperscript{−3} S/cm\textsuperscript{−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.\textsuperscript{(16)} The PAMPSLi/emImTCM, PAMPSLi/N\textsubscript{1134}TCM and PAMPSLi/N\textsubscript{1134}DCA systems seem to be good electrolytes' materials for secondary lithium battery. PAMPSLi/P\textsubscript{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.

Acknowledgements

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Reference


![Fig. 3. Thermogravimetric trace for emImTCM (a), emImTFSA (b), P\textsubscript{66614}TFSA (c), PAMPSLi/emImTCM (A) and emImTFSA. The PAMPSLi/emImTCM system (A)