Macromol. Symp. **2007**, 249–250, 183–189 DOI: 10.1002/masy.200750330

Electrochemical Properties of PEO-Based Polymer Electrolytes Blended with Different Room Temperature Ionic Liquids

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Summary: Polymer electrolyte (PE) based on poly(ethylene oxide)-lithium bis(trifluoromethane sulfonyl)imide (PEO-LiTFSI) was blended with three room temperature ionic liquids (RTILs), namely 1-butyl-3-methylimidazolium bis(trifluoromethane sulfonyl)imide (BMITFSI), 1-butyl-3-methylimidazolium tetrafluoroborate ($BMIBF_4$) and 1-butyl-3-methylimidazolium trifluoromethanesulfonate ($BMICF_3SO_3$) with a view to enhance the room temperature ionic conductivity to acceptable levels for use in lithium batteries. The incorporation of 80 parts by weight (pbw) of the RTILs in 100 pbw of PEO-LiTFSI resulted in enhanced ionic conductivity, the effect being more pronounced at lower temperatures. Evaluation of electrochemical properties showed that PEs with RTILs exhibit an electrochemical stability window between −1.0 V and 4.5 V *vs* Li/Li^+ and good reversibility of redox reactions on cycling. The optimum results were obtained with the incorporation of BMITFSI in the PE, which exhibited a low and stable interfacial resistance on lithium metal.

Keywords: blending; electrochemistry; ionic liquids; lithium batteries; polymer electrolytes

Introduction

PEs are being intensively studied for use in all-solid-state lithium metal polymer batteries as power source for different types of electronic devices. Since cycling of lithium metal invariably results in deposition of lithium dendrites that decrease cycle life and cause safety concerns, extensive research has been focused on developing suitable electrolytes that can suppress the dendrite growth and improve plating morphology[1] The prototypical solid polymer electrolyte (SPE) is PEO-LiX, prepared by blending PEO with lithium salt of a large anion.[2,3] However, these SPEs generally exhibit low room temperature ionic conductivity (σ, $\leq 10^{-5}$ S/cm) and lithium ion transference number (t_{Li+}), necessitating high operating temperature for successful utilization in practical applications. One promising approach to enhance σ of PEO-LiX electrolytes has been to prepare composite polymer electrolyte by the addition of nanoscale ceramic fillers such as SiO_2 and Al_2O_3[2,4] Although σ and t_{Li+} are improved by these approaches, the enhancement is still not sufficient to consider these electrolytes suitable for practical applications at room temperature.

Recent research efforts have shown that dramatic improvements in the properties of conventional PEO-LiX electrolytes can be achieved by the incorporation of a RTIL.[5–9] RTILs are molten salts having low melting point and exist as liquids at or

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below room temperature and find increasing interest for use as solvents in electrochemical applications in catalysis, fuel cells, solar cells, supercapacitors and lithium batteries due to their unique physical and electrochemical properties.[10] They generally possess high σ, chemical and thermal stability, wide electrochemical window, low toxicity and cause minimal safety concerns being nonflammable and nonvolatile. Different types of RTILs such as those with cations based on imidazolium,[11–13] pyrrolidinium,[5–9] piperidinium, morpholinium and quarternary ammonium are being extensively investigated as electrolyte components for battery/capacitor applications and the results have been highly encouraging. In this paper, we report the evaluation of PEO-LiTFSI electrolyte modified with RTILs having the same organic cation, 1-butyl-3-methyl imidazolium (BMI) and three different anions, namely $(CF_3SO_2)_2N^-$ ($TFSI^-$), BF_4^- and $CF_3SO_3^-$.

Experimental Part

The RTILs used in the study, namely BMITFSI, $BMIBF_4$ and $BMICF_3SO_3$, were prepared by the reaction of 1-butyl-3-methylimidazolium chloride with LiTFSI, $NaBF_4$ and $AgCF_3SO_3$ respectively, in acetone according to the procedure given in literature.[14,15] PEO (Aldrich, $M_w = 2 \times 10^6$) and LiTFSI (Aldrich) were vacuum dried before use. The PEs were prepared following a solvent-free, hot-pressing procedure by blending PEO corresponding to 20 ethylene oxide units with 1 mole of LiTFSI. For preparing PEs containing different RTILs, 100 parts by weight (pbw) of PEO-LiTFSI was blended with 80 pbw of the corresponding RTIL. The ingredients were mechanically mixed at room temperature in a ball mill at 100 rpm for 1 h and the homogenous mixture so obtained was hot-pressed for 30 min at 100 °C under a pressure of ~0.5 MPa. PE films of ~200 μm thickness with good homogeneity and mechanical strength were obtained. All PEs were prepared in an argon-filled glove box with a moisture level <10 ppm.

The σ of the PEs were measured in the temperature range 25–80 °C by the AC impedance method using stainless steel Swagelok cells with an IM6 frequency analyzer, at 10 mV amplitude, over the frequency range 100 mHz to 2 MHz. The interfacial resistance (R_f) between the PE and lithium metal electrode was measured by the impedance response of Li/PE/Li cells over the frequency range 10 mHz to 2 MHz. Cyclic voltammetry (CV) of the PE sandwiched between Li electrodes was measured between –1 and +1 V at a scan rate of 1 mV/s. Electrochemical stability was determined by linear sweep voltammetry (LSV) of Li/PE/SS cells at a scan rate of 1 mV/s, over the range of open circuit voltage to 6 V.

Results and Discussion

The important physical properties and conductivity of the three RTILs used in the study are compiled in Table 1. The incorporation of 80 pbw of $BMIBF_4$ and $BMICF_3SO_3$ in 100 pbw of PEO-LiTFSI

Table 1.
Properties of the RTILs.[10]

Properties	BMITFSI	$BMIBF_4$	$BMICF_3SO_3$
Molecular weight (g/mol)	419	225.8	288
Density (g/cm^3)	$1.429^{(19)}$	$1.210^{(25)}$	$1.290^{(20)}$
Melting point (°C)	−4	−81*	16
Viscosity (cP)	$52^{(20)}$	$180^{(25)}$	$90^{(20)}$
Conductivity (mS/cm)	$3.9^{(20)}$	$3.5^{(25)}$	$3.7^{(20)}$

Superscripts refer to the temperature at which the property is measured.
* Determined in the laboratory.

resulted in free standing films with good handling strength. The film containing the same quantity of BMITFSI was more tacky and difficult to handle. For the fixed weight addition, the molar ratio of BMITFSI: BMIBF$_4$:BMICF$_3$SO$_3$ is 0.69:1.28:1.0. Thus, although BMITFSI is added the least in terms of the number of moles/unit mass, it had the highest adverse influence on the mechanical strength of the PEO-LiTFSI electrolyte because of its much lower viscosity compared to the other two RTILs.

Figure 1(a)–(d) shows the AC impedance response at different temperatures of PEO-LiTFSI and PEs with the three RTILs, respectively. At the lower temperatures the PEs exhibit the typical impedance response of a polymer electrolyte sandwiched between two quasi-blocking electrodes, with a semicircle observed at medium-high frequencies and a straight line inclined with respect to the real axis at lower frequencies. With an increase in temperature to $\geq$60 °C, the ionic resistance of the electrolyte decreases and the semicircles disappear by getting shifted to higher frequencies. PEO-LiTFSI without RTIL showed a much higher resistance when compared to the PEs containing the RTILs. Among the PEs containing RTILs, the one with BMITFSI had the lowest bulk resistance and for this system it was observed that the ionic resistance at 25 °C was also low enough to shift the semicircle to higher frequencies than the range studied.

The temperature dependence of σ of PEO-LiTFSI as such and with the incorporation of RTILs is shown in Figure 2. The incorporation of RTIL results in enhancing σ of PEO-LiTFSI over the entire temperature range investigated and the greatest enhancement occurs at lower temperatures. The effectiveness of the three RTILs in enhancing σ of PEO-LiTFSI electrolyte is in the order BMITFSI >BMIBF$_4$> BMICF$_3$SO$_3$. At 25 °C, the highest σ of 3.2×10^{-4} S/cm was exhibited by the PE containing BMITFSI, which is about two orders higher than that of PEO-LiTFSI

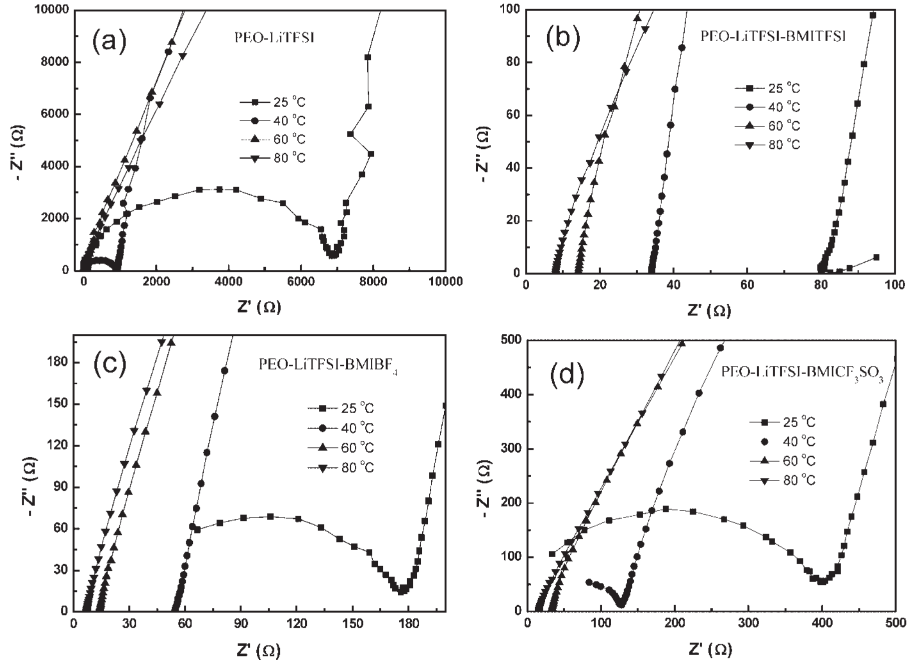

Figure 1.

AC Impedance spectra at different temperatures for the PEs: (a) PEO-LiTFSI; (b) PEO-LiTFSI-BMITFSI; (c) PEO-LiTFSI-BMIBF$_4$; (d) PEO-LiTFSI-BMICF$_3$SO$_3$. Frequency range: 2 MHz – 100 mHz.

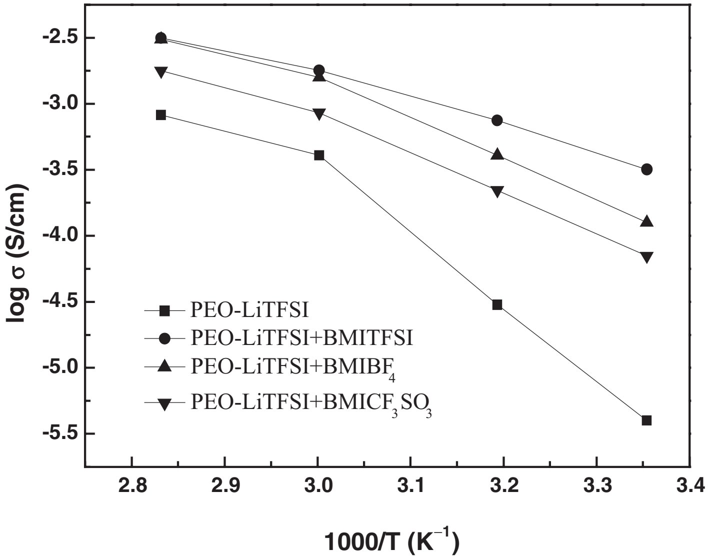

Figure 2.
Variation of ionic conductivity with temperature for the different PEs.

without RTIL (4.0×10^{-6} S/cm). A similar observation of enhanced σ has been reported for PEO-LiTFSI electrolyte by the incorporation of pyrrolidinium based RTIL.[5] The trend in variation of σ with temperature for these PEs shows the typical two-region behavior of PEO-based electrolytes with a change in slope at 60 °C, ascribed to the change in conduction mechanism of the electrolyte associated with the PEO crystalline-amorphous phase transition. This indicates that the Li^+ ions are still interacting with the PEO chains in the PEs containing the RTILs also. However, the change in slope for the curves are considerably lower compared to that of PEO-LiTFSI, and for the highly conducting system based on BMITFSI, the curve is almost a straight line. The higher σ of PE with BMITFSI could be resulting from the combination of low viscosity and high σ of this RTIL. The better compatibility of BMITFSI with PEO-LiTFSI containing the common anion $TFSI^-$ could also be a factor in delivering the highest σ for this PE. The smaller size and faster diffusion of BF_4^- results in a higher σ for PE with $BMIBF_4$ compared to PE with $BMICF_3SO_3$. As reported in earlier studies, the remarkable enhancement in σ results from the formation of the salt-containing amorphous phase at low temperatures in the PEs with RTIL which reduces the overall crystallinity of the system.[8] Shin *et al.* have reported that the presence of an RTIL is able to change the Li^+ ion transport mechanism within the PEO-LiX electrolyte membrane and hence enhance the conductivity to a level that can readily exceed the limits found earlier for "dry" polymer electrolytes.[9] Accordingly, the Li^+ ions that are coordinated with the "O" of PEO amorphous phase segments may become partially or fully coordinated by the anion of RTIL and thus free them to a great extent from the traps of strong polymer EO coordination.

CV data can provide an initial understanding of the behavior of lithium electrode in these PEs, as shown in Figure 3(a). Well-defined processes corresponding to lithium ion deposition and stripping are seen for the PEs containing RTILs. At −1.0 V (*vs* Li/Li^+) that would approximately indicate the cathodic limit for the systems, the reduction current representing

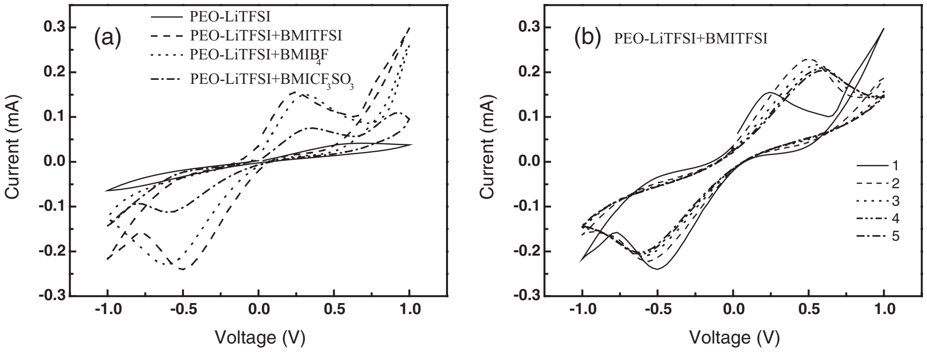

Figure 3.
(a) Comparison of the CV of PEs during the first cycle. (b) CV of PEO-LiTFSI-BMITFSI during cycle numbers 1–5. Li/PE/Li cells, scan rate 1 mV/s, voltage range −1 V to +1 V.

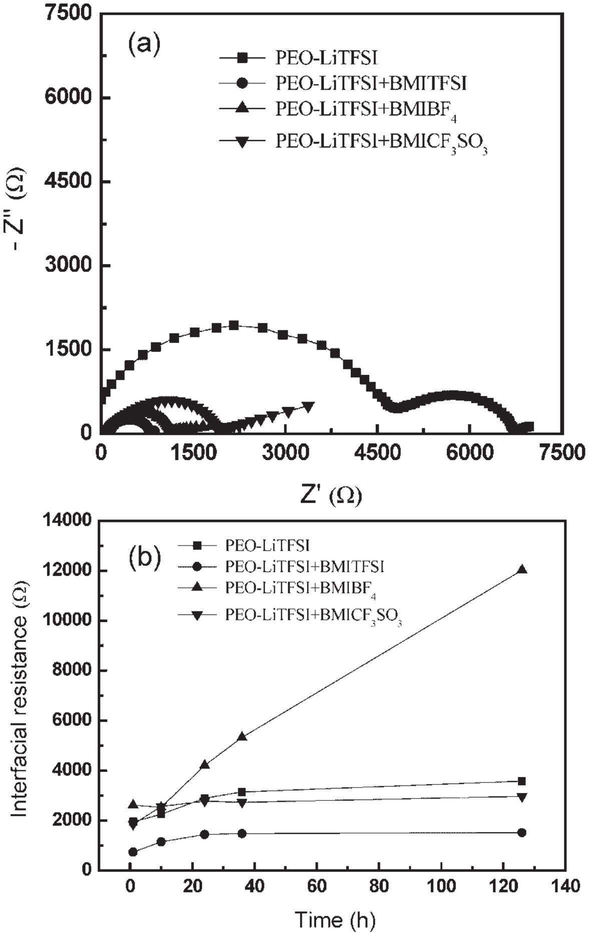

Figure 4.
(a) Comparison of initial R_f of PEs (b) Variation of R_f of PEs with storage time. Li/PE/Li cells, Frequency range: 2 MHz – 10 mHz.

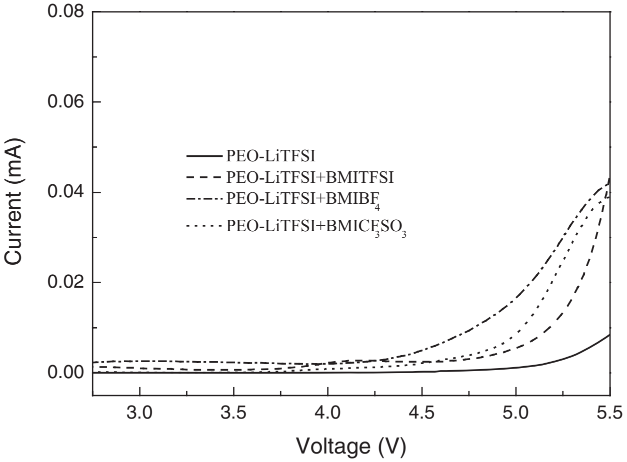

Figure 5.
Comparison of anodic stability of PEs by LSV. Li/PE/Li cells, scan rate: 1 mV/s, voltage range: open circuit voltage to 6 V.

the bulk reduction of RTIL is very low for the 3 samples: in the range of -0.13 to -0.22 mA, thus indicating good cathodic stability. Ethyl-methyl-imidazolium-based RTILs have been reported to be unstable below 1 V *vs* Li/Li$^+$.[12] However, in this study we observed that the PEs containing BMI-based RTILs are able to provide good resolution for the lithium reduction process, occurring at -0.5 to -0.6 V. The presence of LiTFSI salt in the electrolyte could be suppressing the reduction of imidazolium cation effectively, as was observed for pyrrolidinium cation in the presence of LiTFSI.[5] This improvement has been attributed to the formation of a stable passivation layer on the lithium metal surface that can conduct Li$^+$ ion and at the same time prevent further reaction of the RTIL.[1,5] The first cycle oxidation peak occurs at ~0.25 V for all PEs with RTIL. The magnitude of reduction and oxidation currents is lowest for BMICF$_3$SO$_3$. Good reversibility of the redox reactions was observed in the CV during cycling for these PEs, except for BMIBF$_4$ system. Figure 3(b) shows the CV obtained for the PE containing BMITFSI during the first 5 cycles. The improved reversibility observed in cycling could be due to the stability of RTIL to reduction and also the possible formation of a compatible interface on lithium metal.

R$_f$ between the lithium electrode and the electrolyte was determined by the AC impedance technique as a function of storage time. Figure 4(a) shows a comparison of initial R$_f$ of the PEs, and Figure 4(b) provides an overall comparison of R$_f$ of the PEs with storage time. Initial R$_f$ is determined by the properties of the passivation layer spontaneously formed on the surface of lithium metal in contact with the electrolytes. The initial R$_f$ for the PEs containing RTIL were lower than that of PEO-LiTFSI. With advancing time, R$_f$ of PE with BMIBF$_4$ increased substantially, whereas that of PEs with BMITFSI and BMICF$_3$SO$_3$ got stabilized after an initial increase. The exceptional increase in R$_f$ for the PE containing BMIBF$_4$ could be the result of formation of a thick, passivating layer on the lithium electrode by the reaction of F$^-$ ions usually present along with BF$_4^-$ ions. The lowest and stable R$_f$ over the time of study was shown by the PE containing BMITFSI, the values were nearly half of that corresponding to the electrolyte without any RTIL. The formation of a low-resistance interface with lithium metal could contribute to enhancing the cycling properties of the electrolyte as observed in CV.

The anodic limit of the PEs was studied by LSV and the results are shown in Figure 5. Compared to PEO-LiTFSI, the PEs containing RTIL have lower dissociation voltage, but still >4.5 V *vs* Li/Li^+, sufficient to be compatible with most common lithium battery cathode materials. Among the three systems with RTIL, the order of electrochemical stability was BMITFSI (5.2 V) > $BMICF_3SO_3$ (5.1 V) > $BMIBF_4$ (4.8 V). Thus, these electrolytes exhibit a wide electrochemical window of >5.5 V (from −1.0 to >4.5 V), demonstrating their suitability in lithium batteries.

Conclusion

The effect of incorporating 80 pbw of three RTILs namely, BMITFSI, $BMIBF_4$ and $BMICF_3SO_3$ in 100 pbw of the PE based on PEO-LiTFSI was studied for σ and electrochemical properties. Addition of RTILs enhanced σ of PEO-LiTFSI, and the effect was more pronounced at lower temperatures. The PE with BMITFSI exhibited the maximum σ of 3.2×10^{-4} S/cm at 25 °C. The PEs with RTILs exhibit good electrochemical stability, in the range of −1.0 to >4.5 V *vs* Li/Li^+, suitable for lithium battery applications. The PE containing BMITFSI was found to give the optimum results with a low and stable interfacial resistance on lithium metal.

Acknowledgements: This research was supported by the Ministry of Information and Communication (MIC), Korea, under the Information Technology Research Center (ITRC) support program supervised by the Institute of Information Technology Assessment (IITA). Gouri Cheruvally is thankful to the KOFST for the award of Brain Pool Fellowships, and J.W. Choi and Y.H. Kim acknowledge a partial support by the Post Brain Korea 21 Project in 2006.

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