

## Ionic Liquid-Lithium Salt Electrolyte Mixtures: Phase Behavior and Electrochemical Characteristics

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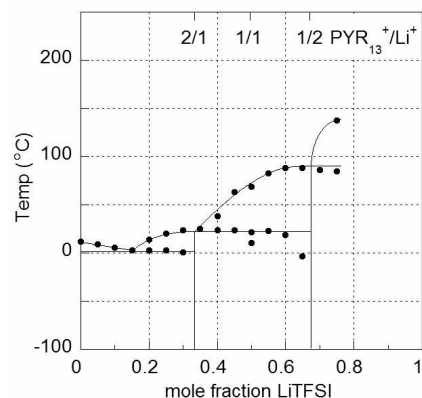
Room temperature ionic liquids (RTILs) are rapidly gaining notoriety as replacements for conventional solvents (and perhaps salts) for electrolyte applications. Work with RTILs (or molten salts) for battery electrolytes began in the early 1960s at the U.S. Air Force Academy (1,2). The imidazolium chloride/ $\text{AlCl}_3$  salts used were difficult to handle, however, due to reactivity with water. The development of ILs with air- and water-stable anions (3) has resulted in an increased interest in these novel materials.

RTILs with imidazolium cations are the most widely used, but the acidic protons on these cations limit the cathodic electrochemical stability of the RTILs. The use of cations without acidic protons greatly increases the cathodic stability (4,5). One category of such RTILs is the *N*-methyl-*N*-alkylpyrrolidinium bis(trifluoromethanesulfonyl)imide ( $\text{PYR}_{1R}\text{TFSI}$ ) salts. The physical properties of these RTILs and plastic crystalline salts have been reported (6). Mixtures of the  $\text{PYR}_{1R}\text{TFSI}$  salts with LiTFSI have been suggested for electrolyte applications (4,7). Further research on RTIL-LiX properties must be done, however, since the formation of a crystalline solid in a liquid  $(1-x)\text{N}_{1113}\text{TFSI}(x)\text{LiTFSI}$  ( $x = 0.12$ ) ( $\text{N}_{1113}$  = trimethylpropylammonium) electrolyte mixture was found to be very detrimental to the performance of Li/electrolyte/LiCoO<sub>2</sub> batteries (4).

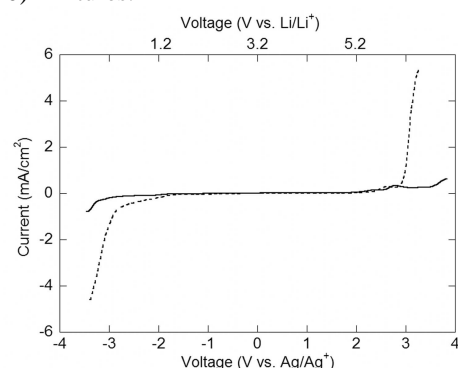
Phase diagrams have been prepared for  $(1-x)\text{PYR}_{1R}\text{TFSI}(x)\text{LiTFSI}$  mixtures with  $R = 2-4$  (ethyl-butyl). Numerous mixed salt crystalline phases form. For the  $\text{PYR}_{13}\text{TFSI}(x)\text{LiTFSI}$  mixtures, crystalline  $x = 0.33$  and  $x = 0.66$  phase are found corresponding to 2/1 and 1/2  $\text{PYR}_{13}\text{TFSI}/\text{LiTFSI}$  ratios, respectively (Figure 1). A 1/1 metastable phase ( $x = 0.50$ ) may also form under certain conditions. A eutectic appears to be present near  $x = 0.15$ . The addition of even small amounts of LiTFSI to the  $\text{PYR}_{1R}\text{TFSI}$  salts dramatically improves the cathodic electrochemical stability (Figure 2). The cathodic current near 0 V vs.  $\text{Li}/\text{Li}^+$  may be due to the plating of Li metal rather than degradation of the organic cations. The temperature dependence of the ionic conductivity for  $\text{PYR}_{13}\text{TFSI}(x)\text{LiTFSI}$  mixtures is reported in Figure 3. The pure  $\text{PYR}_{13}\text{TFSI}$  salt has a low conductivity of  $4 \times 10^{-9}$  S/cm (near the measurement limit) at  $-20^\circ\text{C}$ . This rapidly increase just before the  $T_m$  at  $11^\circ\text{C}$  rising to  $3 \times 10^{-3}$  S/cm just after melting. A similar low conductivity is found for mixtures containing LiTFSI (both near the eutectic and for the pure 2/1 phase) below the  $T_m$ s of these mixtures. The conductivity again rises rapidly as these melt. The conductivity of the  $x = 0.33$  mixture in the melt is noticeably lower than for the pure  $\text{PYR}_{13}\text{TFSI}$  salt and  $x = 0.10$  mixture. This may be due to a much higher viscosity from strong  $\text{Li}^+\dots\text{TFSI}$  interactions. Polarization measurements are in progress to determine the  $\text{Li}^+$  cation contribution to the overall ionic conductivity.

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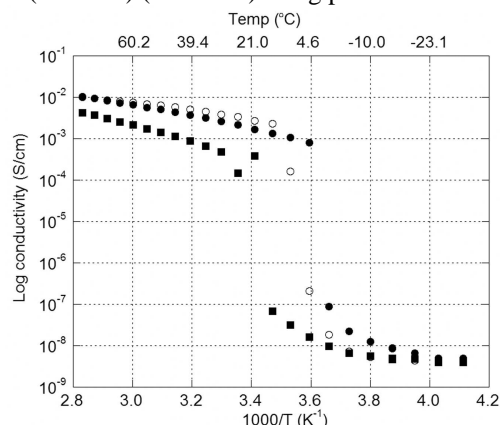
Italian Foreign Ministry and the NSF International Research Fellowship Program (IRFP 0202620), respectively.



**Figure 1.** Phase diagram of  $(1-x)\text{PYR}_{13}\text{TFSI}(x)\text{LiTFSI}$  ( $x = 0.10$ ) mixtures.



**Figure 2.** Linear sweep voltammetry (10 mV/s) of  $\text{PYR}_{13}\text{TFSI}$  (dashed line) and  $(1-x)\text{PYR}_{13}\text{TFSI}(x)\text{LiTFSI}$  ( $x = 0.10$ ) (solid line) using platinum electrodes.



**Figure 3.** Conductivity vs. temperature for  $\text{PYR}_{13}\text{TFSI}$  (open circles) and  $(1-x)\text{PYR}_{13}\text{TFSI}(x)\text{LiTFSI}$  ( $x = 0.10$  - filled circles and  $x = 0.33$  - filled squares).

### References:

- Gale, R. J.; Gilbert, B.; Osteryoung, R. A. *Inorg. Chem.*, **17** (1978) 2728.
- Wilkes, J. S.; Levisky, J. A.; Wilson, R. A.; Hussey, C. L. *Inorg. Chem.*, **21** (1982) 1263.
- Wilkes, J. S.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.*, (1992) 965.
- Sakaebe, H. and Matsumoto, H. *Electrochem. Commun.*, **5** (2003) 594.
- Oldham Jr., W. J.; Costa, D. A.; Smyth, W. H. in *Ionic Liquids: Industrial Applications to Green Chemistry*, Rogers, R. D. and Seddon, K. R., Eds. (Oxford Univ. Press, 2002) p. 188.
- MacFarlane, D. R.; Meakin, P.; Sun, J.; Amini, N.; Forsyth, M. *J. Phys. Chem. B*, **103** (1999) 4164.
- MacFarlane, D. R.; Huang, J.; Forsyth, M. *Nature*, **402** (1999) 792.