ROOM TEMPERATURE IONIC LIQUID MIXTURES AS EDLC ELECTROLYTES

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Introduction

Room temperature ionic liquids (RTILs) are potential alternative electrolytes for carbon based electrochemical double layer capacitors (EDLCs). Commercial electrolytes are generally alkylammonium salts dissolved in an organic solvent which have high volatility, flammability and toxicity [1]. In order to obtain safer, reliable and higher energy density devices, RTILs are being investigated due to their low-volatility, high flame resistance and wide electrochemical window. Currently, their main limitation is their relatively high viscosity [2,3] which limits low temperature performance and the internal resistance of the cell.

Several approaches have been undertaken in order to improve the ionic conductivity of RTILs (e.g. salt addition, IL blending [4,5]). The aim of this work is to improve the conductivity of RTILs by preparing a number of binary IL-solvent mixtures (from 0- 100 wt.% IL). The physical and electrochemical properties of the RTIL-solvent blends were examined.

Experimental

N-butyl-n-methylpyrrolidinium bis(trifluoromethane sulfonyl)imide (PYR$_{14}$TFSI) supplied by *Merck Chemicals* was selected based on its wide electrochemical window, ~ 6 V (glassy carbon working electrode and Ag|Ag$^+$, 10 mM silver trifluoromethanesulfonate in PYR$_{14}$TFSI, reference electrode).

The ionic conductivity of the neat IL and its mixtures was evaluated with a Mettler Toledo conductimeter system inside a N$_2$-purged glove box. Dynamic viscosity was determined using an Anton Paar viscosimeter at various temperatures (20, 40, 60 and 80°C). Two electrode EDLC devices were assembled in laminated pouch-type cells (2.5 cm x 2.5 cm electrode dimensions). Carbon coated aluminium collectors (30 µm thick) were utilized as electrodes. The composition of the carbon coating was: activated carbon (supplied by *Maxsorb*), carbon black and carboxymethylcellulose in a proportion 1 : 0.2 : 0.1. A 25 µm thick polypropylene separator was used as a separator. Neat ionic liquids and their mixtures were used as electrolytes. For comparative purposes a conventional organic electrolyte, 1M TEABF$_4$-ACN, was also evaluated. Electrochemical testing was performed at varying temperatures (25, 50, 80 and -20°C).

Results and Discussion

Table 1 summarizes the physical properties of PYR$_{14}$TFSI. An interesting feature of this IL is its high electrochemical window (6 V). However, its conductivity is relatively poor (2.48 mS/cm) and in order to improve this property a series of solvents were mixed with the IL in various proportions. Figure 1 shows the conductivity of the PYR$_{14}$TFSI mixtures with various solvent concentrations obtained for a series of nitriles: acetonitrile (ACN), butyronitrile (buCN), benzonitrile (BenzoCN) and benzyl cyanide (BzCN). Initially an increase in the ionic conductivity with the increasing amount of solvent is observed, then it reaches a maximum and decreases down to the specific conductivity of the solvent. This trend indicates that the IL mixtures behave like simple solutions of salts in molecular solvents.

At the point of maximum conductivity (corresponding to ~ 50 wt. % solvent concentration) the conductivities of the IL-solvent mixtures are between 3-20 times higher than that of the neat IL, depending on the solvent used. Conductivity values of 8 - 45 mS/cm were obtained (Table 2). Acetonitrile solvent showed the most dramatic increase in conductivity which is consistent with his low molecular weight and density (Table 2).

Table 1. Physical properties of PYR$_{14}$TFSI.

M(g/mol)	ρ(g/cc)	σ(mS/cm)	η(cP)	MP(ºC)	EW(V)
422	1.41	2.48	85	-18	6

Molecular weight (M), density (ρ), measured ionic conductivity at 25°C (σ), measured dynamic viscosity at 20°C (η), Melting point (MP), electrochemical window (EW).
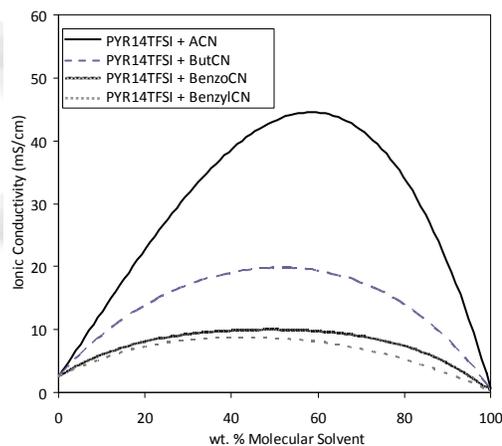

Fig. 1. Ionic conductivity of IL mixtures with several nitriles. Room temperature.

The viscosity of the IL is also reduced by the addition of molecular solvents; from the initial 100 cP shown by the neat IL (at 20°C), down to 1.6-6.7 cP depending on the solvent (Table 2). In all of the solvent –IL systems investigated, an Arrhenius-*like* behaviour was obtained from the temperature dependence of the viscosity.

In addition to the nitrile-based solvents, other solvents were also evaluated including: propylene carbonate (PC), butylene carbonate (BC), Dimtheyl carbonate (CMC), Formamide (FA) and dimethylformamide (DMFA). A summary of the results is shown in Table 2. Among the carbonates, the DMC-IL mixture shows the highest increase in

conductivity (6 times that of the neat IL). DMFA increases the conductivity of the neat IL by 10 times, whereas, FA increases the conductivity by 3.5. Figure 2 shows the dependence of the ionic conductivity value of the IL mixtures as a function of the molecular weight of the solvent used in the mixture. In general, these two properties are inversely related. However, FA clearly stands out from the linear trend.
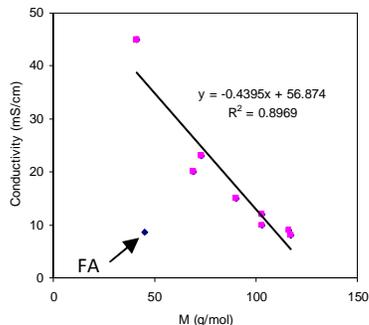

Fig. 2. IL mixtures conductivity as a function of the molecular weight of the solvent.

Table 2. Physical properties of solvents and IL mixtures.

Solvent	M(g/mol)	ρ(g/cc)	BP(ºC)	σ*(mS/cm)	η*(cP)
ACN	41	0.78	82	45	1.6
BuCN	69	0.79	117	20	2.3
BenzoCN	103	1.00	191	10	4.3
BzCN	117	1.02	233	8	6.7
DMC	90	1.07	90	15	3.5
PC	103	1.21	240	12	6.2
BC	116	1.14	250	9	-
FA	45.04	1.133	210	8.63	-
DMFA	73.09	0.944	153	23	-

Molecular weight (M), density (ρ), Boiling point (BP), measured ionic conductivity at 25°C (σ), measured dynamic viscosity at 20°C (η). * indicates that the measurement corresponds to the mixture.

The electrochemical performance of the neat IL and the IL mixture with one of the solvents, BuCN is shown in Fig. 3. The *conventional* organic electrolyte is also included for comparison. At sub-zero temperature, the neat IL does not function, as it is below its melting point (-18 °C). The other two electrolytes (IL-BuCN and TEABF$_4$-ACN) show a very pronounced reduction of capacitance values with an increase in current density due to the high resistance of the system at low temperature (e.g. low ionic conductivity). When the temperature is increased, the capacitance values become more stable with the applied current density. At +25 °C the neat IL has poor performance and requires heating to 50 °C in order to provide comparable capacitance values to the other two electrolyte media. When the neat IL is tested at 80°C, it records a better capacitance than the other electrolytes; thereby highlighting the advantages of using neat ionic liquids under favourable conditions.

The IL-BuCN mixture provides higher capacitance values than TEABF$_4$-ACN and that the neat IL not only at –20 °C but also at 25 and 50 °C. More importantly, it can operate at 80 °C, where the conventional EDLCs are limited by the low boiling point of acetonitrile.
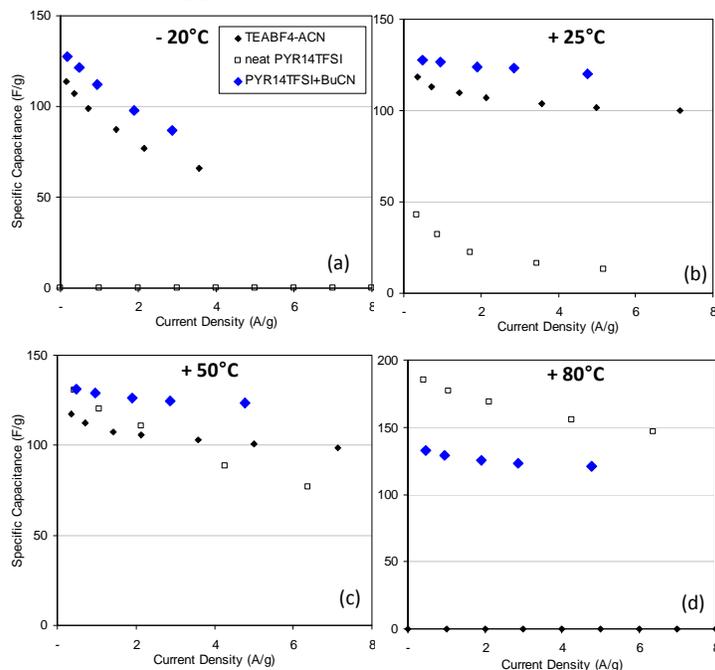

Fig. 3. Capacitance values for the EDLCs at different temperatures.

Conclusions

The conductivity of the selected PYR$_{14}$TFSI-solvent mixtures was found to be **3**-**20 times** higher than for the neat IL.

The performance of the mixture PYR$_{14}$TFSI- butyronitrile mixture in a carbon based EDLC showed enhanced capacitance relative to neat IL and the conventional TEABF$_4$-ACN electrolyte. Moreover, it was possible to operate EDLCs containing ILs mixtures in a wide temperature range, from -20 to 80°C, where neat ILs and conventional organic electrolytes fail to operate.

References

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