TERNARY POLYMER ELECTROLYTES WITH 1-METHYLIMIDAZOLE BASED IONIC LIQUIDS AND APROTIC SOLVENTS

J. Reiter[1], *J Vondrák*[1], *J Michálek*[2,3]

[1] Institute of Inorganic Chemistry, Academy of Sciences, 250 68 Řež near Prague
[2] Institute of Macromolecular Chemistry, Academy of Sciences, 162 06 Prague
[3] Centre for Cell Therapy and Tissue Repair, Charles University, 150 18 Prague

Corresponding author: Jakub Reiter (reiter@iic.cas.cz)
Phone: +420 266 172 198
Fax: +420 220 941 502

Introduction

Recent technology of modern chemical power sources deals with several limiting factors of further development. Commercialised lithium-ion batteries and supercapacitors usually contain liquid organic compounds and their mixtures, which serve as a solvent for electrolytes (e.g. lithium or alkylammonium salts) [1-3]. This situation brings threat of possible leakage or evaporation of the solvent, what leads not only to decrease of the battery capacity, but is also environmentally hazardous. Therefore a new kind of non-flammable and environmentally friendly solvents is required for large size lithium-ion batteries and supercapacitors possibly used in electric or hybrid vehicles and the room temperature ionic liquids (RTILs, ILs) are promising organic compounds to be used for their excellent properties: high ion content and high conductivity, liquidity in wide temperature range, high thermal stability (up to 400 °C) and low toxicity. Especially for lithium-ion batteries their non-volatility and non-flammability is highly appreciated. They can also serve as conductors in electrochromic devices and organic synthesis [4, 5].

This contribution introduces new conducting polymer electrolytes with embedded ionic liquids. Our work was aimed at development of highly conductive solid electrolyte with suitable properties for electrochemical devices. New, defined way of preparation together with excellent chemical and electrochemical long-term stability of used compounds offers combination of acrylate-based polymer electrolytes with ionic liquids based on 1-methylimidazole. Ternary systems polymer-IL-aprotic solvent (propylene carbonate or mixture of propylene carbonate - ethylene carbonate 50:50 mol. %) and quaternary systems polymer-IL-aprotic solvent-lithium salt ($LiPF_6$ or $LiClO_4$) were prepared and studied. Materials were investigated from the electrochemical point of view as well as they were characterised by using thermogravimetric analysis. Composition of all samples was optimised to obtain samples with sufficient mechanical and electrochemical properties [6].

Experimental

Two ionic liquids were prepared: 1-butyl-3-methylimidazolium tetrafluoroborate ($BMIBF_4$) and 1-butyl-3-methylimidazolium hexafluorophosphate ($BMIPF_6$). Synthetic work followed previously published procedures [7-9]. General method of preparation is based on two-step synthesis, when we modified the published procedures to improve the purity of prepared ionic liquids (the conversion into tetrafluoroborate or hexafluorophosphate with 100% yield is required).

Two solid systems were prepared: ternary system polymer-IL-aprotic solvent and quaternary system polymer-IL-aprotic solvent-lithium salt. These two principal combinations were prepared from particular compounds using thermally initiated polymerisation [10]. The initial mixture was prepared by mixing of these compounds: monomer 2-ethoxyethyl methacrylate (EOEMA), cross-linking ethylene dimethacrylate EDMA (0.3 mol. % of monomer) and the polymerisation initiator 2,2'-azobis(isobutyronitrile) AIBN (1 mol. % of monomers). In the case of ternary systems, pure propylene carbonate or propylene carbonate-ethylene carbonate (50:50 mol. %) mixture was used. For the quaternary systems 0.75 M solutions of $LiClO_4$ or $LiPF_6$ in particular solvent or solvent mixture were used. The polymerisation process was carried out in a preheated oven at 80 °C for 2 h.

Potentiogalvanostat PGSTAT 10 (Eco Chemie, The Netherlands) was used for voltammetrical measurements including FRA-2 (Frequency Response Analyser) module for impedance measurements. Temperature dependent conductivity measurements were performed in the temperature range from -70 to 80 °C using thermostated bath (precision of the temperature ±1 °C). The simultaneous TGA-DTA measurement was taken in air and argon at the heating rate of 5 $°C.min^{-1}$. Experiments were performed with a Simultaneous Thermal Analysis Netzsch STA 409 (Germany).

All potentials in the paper are related to the new solid-state reference electrode based on the PMMA-Cd-Cd^{2+} system ($E(Cd/Cd^{2+}) = 2.66$ V vs. Li/Li^+) – cit. [11].

Results and Discussion

Our previous experiments showed, that 1-ethyl-3-methylimidazolium, 1-propyl-3-methylimidazolium, and 1-butyl-3-methylimidazolium tetrafluoroborates are not compatible with PEOEMA-PC polymer electrolytes, however they are soluble in the EOEMA-PC initial mixture. Phase separation and the ionic liquid exclusion were observed during the polymerisation process.

Systems PEOEMA-PC-$BMIPF_6$ and PEOEMA-PC-EC-$BMIPF_6$ were found to be compatible and prepared samples were transparent to slightly translucent foils of moderate elasticity. The polymer-PC-$BMIPF_6$ samples were somewhat sticky, what can be advantage in an electrochemical device designing, where a good contact between the electrolyte and the electrode is required. However no residual traces were left after the sample removal either from metal electrode or Petri dish glass. No visible changes of

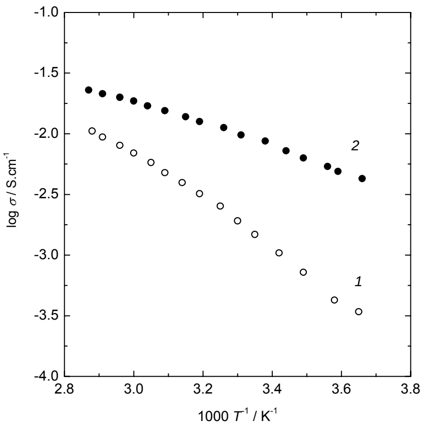
mechanical properties were observed within several weeks, when stored either on air or in inert, nitrogen atmosphere.
The combination of a hydrophobic ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate or tetrafluoroborate with aprotic solvents, propylene and ethylene carbonate strongly increases the ionic conductivity in comparison with the neat ionic liquid.

Figure 1 presents relationship between the ionic conductivity of $BMIPF_6$ and $BMIPF_6$-PC liquids and temperature, when data are plotted in Arrhenius coordinates (specific conductivity is plotted as a decadic logarithm). In both cases linear, simple Arrhenius behaviour over temperature range from 0 to 80 °C can be seen (correlation coefficient $R^2 > 0.995$ in both cases). Solution of $BMIPF_6$ in PC exhibits higher conductivity than the $BMIPF_6$ itself in the whole range of temperatures. Obtained data can be fitted with the Arrhenius equation in logarithmic form:

$$\log_{10}(\sigma) = A / T + B \qquad (1)$$

Similarly, the Arrhenius activation energy for conduction E_A is accessible from the parameter A using the formula (2). The conductivity activation energy corresponds to a slope in the Arrhenius coordinates (see Figure 1) and explains, how the conductivity is influenced by the temperature:

$$E_A = -2.303 \, A \, R \qquad (2)$$



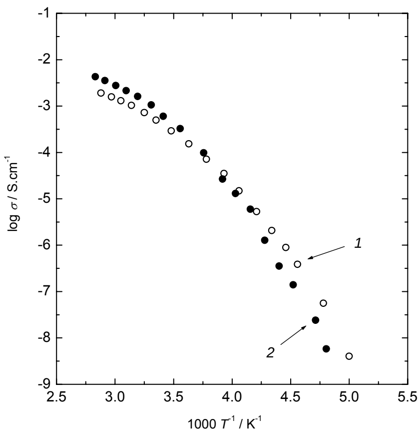


Fig. 1 *(left) Arrhenius plot of ionic conductivities for 1 - neat $BMIPF_6$ and 2 - $BMIPF_6$-PC (20:80 mol. %).*

Fig. 2 *right) Arrhenius plot of ionic conductivities for 1 - PEOEMA-PC-$BMIPF_6$ (50:40:10 mol. %) and 2 - PEOEMA-PC/EC-$BMIPF_6$-$LiPF_6$ (49.2:19.6:19.6:9.8:1.8 mol. %) polymer electrolytes.*

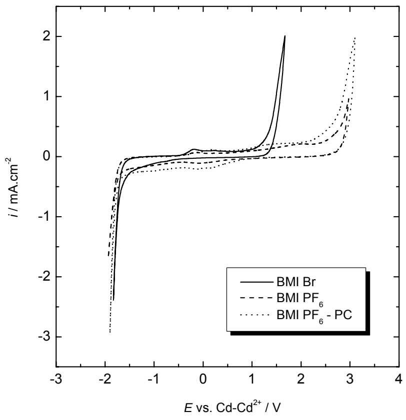
Prepared polymer electrolytes exhibit high ionic conductivity due to the high content of $BMIPF_6$ in the polymer gel structure (up to 19.2 wt. %). Highest conductivity value 0.94 $mS.cm^{-1}$ was reached in the case of PEOEMA-PC/EC-$BMIPF_6$-$LiPF_6$ (49.2 : 19.6 : 19.6 : 9.8 : 1.8 mol. %). The influence of temperature on conductivity is plotted in Fig. 2 and Table 1 includes also the determination of the conductivity activation energies.

Table 1 *Ionic conductivity parameters for the liquid and polymer electrolytes (symbols σ, A, B, and E_A are constants from Eq. 1 and 2)*

Sample	σ (25 °C) [$mS.cm^{-1}$]	A [K]	B	E_A [$kJ.mol^{-1}$]	Source
$BMIPF_6$	1.50	-1980.2	3.78	37.9	[6]
$BMIPF_6$-PC	9.37	-939.8	1.09	18.0	[6]
PEOEMA-PC-$BMIPF_6$	0.50	-1175.5	0.69	22.5	[6]
PEOEMA-PC/EC-$BMIPF_6$-$LiPF_6$	0.94	-1271.6	1.26	24.6	[6]
PEOEMA-PC-$LiClO_4$	0.23	-3043.0	6.21	58.3	[10]

Accessible potential range of the liquid electrolytes $BMIPF_6$-PC and $BMIPF_6$-PC/EC on the glassy carbon was found to be 4.6 - 4.7 V (see Fig. 3). Also the accessible potential window of prepared polymer gel electrolytes based on ionic liquids is wide, 4.3 - 4.4 V.

As it can be seen, the immobilisation of liquid electrolytes in cross-linked PEOEMA polymer does not principally restrict the accessible electrochemical window more than by 0.3 V on the cathodic side due to reduction of oxygen and water moisture absorbed in the gel during the preparation. Impedance measurements done before and after voltammetrical investigation showed in all prepared polymer electrolytes, that no non-conducting layer is formed on the surface of the electrode within several cyclic voltammograms.



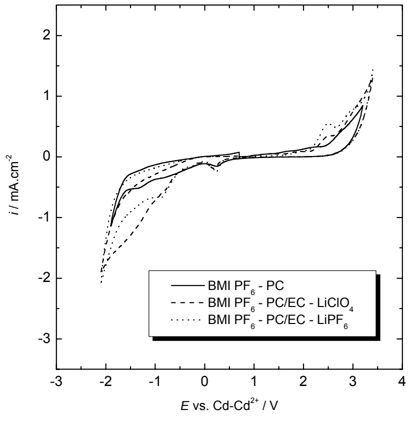


Fig. 3 *(left) Cyclic voltammograms of BMIBr, $BMIPF_6$ and $BMIPF_6$-PC 20-80 mol. % on the glassy carbon electrode (scan rate 50 $mV.s^{-1}$).*

Fig. 4 *(right) Cyclic voltammetry of PEOEMA-PC-$BMIPF_6$, PEOEMA-PC/EC-$BMIPF_6$-$LiClO_4$, and PEOEMA-PC/EC-$BMIPF_6$-$LiPF_6$ polymer electrolytes on the glassy carbon electrode (scan rate 10 $mV.s^{-1}$).*

From the application point of view the thermal stability is another principal question beside the electrochemical and long-term stability and reasonable conductivity. The PEOEMA-PC-$BMIPF_6$ sample exhibits thermal stability up to 150 °C. The weight loss was found less than 0.7 wt. % up to 90 °C and ca. 4.5 wt. % under 150 °C.

Conclusions

New polymer gel electrolytes based on 2-ethoxyethyl methacrylate containing embedded solutions of $BMIPF_6$ in cyclic carbonates (PC and PC/EC) were prepared and characterised by using electrochemical (impedance and voltammetrical) and thermogravimetric techniques. Beside ternary systems PEOEMA-PC-$BMIPF_6$ and PEOEMA-PC/EC-$BMIPF_6$, new materials containing lithium salts $LiClO_4$ or $LiPF_6$ were prepared and studied.

Obtained results allow the application of prepared materials in modern chemical power sources. The quaternary systems containing lithium salts will be studied as solid electrolytes in lithium-ion batteries and the ternary systems will be combined with carbon powders of high surface area to form supercapacitors.

Acknowledgements

This work was supported by the Academy of Sciences (Research Plan AV0Z40320502), Ministry of Education (project MSMT LC523) and Ministry of Environment (project VaV SN/171/05).

References

1. M. Alamgir, K.M. Abraham, in: *Lithium Batteries: New Materials, Developments and Perspectives, Vol. 5* (G. Pistoia, ed.), Elsevier Science, Amsterdam, 1994, Ch. 3.
2. D. Linden, T.B. Reddy (Eds.): *Handbook of Batteries.* McGraw-Hill, New York, 2002.
3. D. Aurbach, Y. Talyosef, B. Markovsky, E. Markevich, E. Zinigrad, L. Asraf, J.S. Gnanaraj, H.J. Kim, Electrochim. Acta 50 (2004) 247.
4. L. Wen, A.G. Fadeev, B. Qi, B.R. Mattes, J. Electrochem. Soc. 151 (2004) 33.
5. L. Wasserscheid, T. Welton, *Ionic Liquids in Synthesis*. Wiley-VCH, Weinheim, 2003.
6. J. Reiter, J. Vondrák, J. Michálek, Z. Mička, Electrochim. Acta, submitted.
7. A. Lewandowski, M. Galiński, J. Phys. Chem. Solids 65 (2004) 281.
8. P. Bonhôte, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Grätzel, Inorg. Chem. 35 (1996) 1168.
9. A. Lewandowski, A. Świderska, Solid State Ionics 169 (2004) 21.
10. J. Reiter, J. Michálek, J. Vondrák, D. Chmelíková, M. Přádný, Z. Mička, J. Power Sources, in press.
11. J. Reiter, J. Vondrák, Z. Mička, Solid State Ionics, submitted.