IONIC CONDUCTANCE OF LITHIUM SALTS IN PMMA GEL ELECTROLYTES

M. Tretera[1], J. Reiter[2], J. Vondrák[1], M. Sedlaříková[2]

[1] Institute of Electrotechnology, Technical University of Brno, 602 00 Brno
[2] Institute of Inorganic Chemistry AS CR, 250 68 Řež near Prague

Introduction

Polymer gel electrolytes have been intensively investigated since their introduction by M. Armand [1-4]. Our recent research is mainly aimed at conductivity measurements of polymethylmethacrylate – propylene carbonate (PMMA-PC) gel electrolytes containing various lithium salts commonly used in the technology of electrochromic devices and lithium batteries (see Fig. 1). Relationships between conductivity and salt concentration, temperature and solvent composition were studied [5].

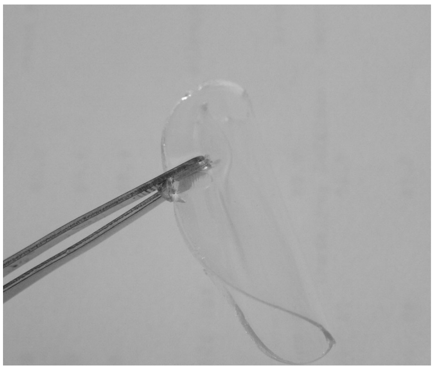

Fig. 1 *PMMA-PC gel electrolyte containing lithium perchlorate*

Experimental

Preparation of polymer gel electrolytes was described in our previous papers [3, 4] and is based on forming gel from three components: monomeric methylmethacrylate (Sigma-Aldrich), polymeric PMMA resin containing polymerisation initiator (dibenzoylperoxide, 1 wt. %) – commercially produced material Superacryl (Spofa-Dental Prague, Czech Republic) and an optional component. As the optional component figures a solution of an organic and/or inorganic compound in an aprotic anhydrous solvent – propylene carbonate. Mixture of these three parts in suitable ratio (1.50 ml MMA, 1.00 ml PC solution, 0.70 g PMMA) is placed in a Petri dish (5 cm diameter) and kept for 5 days at the room temperature in a desiccator. Polymerisation process is than finished by warming at 90°C for 60 minutes. The method of preparation guarantees good mechanical properties and electrochemical stability for weeks. The gel is elastic and odourless material, required

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Corresponding author: Jakub Reiter
E-mail: reiter@iic.cas.cz
Phone: +420 266 172 198, Fax: +420 220 941 502

foils can by easily cut out.
The composition of the optional part is following further application of the gel. 0.25 - 1.25M solutions of anhydrous lithium salts – perchlorate, tetrafluoroborate, hexafluorophosphate and trifluormethansulfonate (all Sigma-Aldrich) were immobilised in the gel. Salts were dried at 110°C under vacuum overnight and dissolved in anhydrous propylene carbonate (Sigma-Aldrich, 99.7%, water content under 0.005%, stored under molecular sieves).

Beside pure propylene carbonate solvent mixtures were used as the optional part: dimethyl carbonate – propylene carbonate (DMC-PC 7:3 wt.) and ethylene carbonate – propylene carbonate (EC-PC 6:4 wt.) previously used by with the aim to improve either conductivity or electrochemical stability [6].

Potentiogalvanostat PGSTAT 10 (Eco Chemie, The Netherlands) was used for electrochemical measurements including FRA-2 (Frequency Response Analyser) module used for impedance measurement. For the conductivity measurements a slide of gel was placed between two parallel stainless steel electrodes (2 × 2 cm). The impedance spectra were measured in the range from 100 kHz to 100 Hz and analysed by the Eco Autolab software producing the values of the equivalent circuit elements. The evaluated value of ohmic resistance was converted in the value of specific resistivity or conductivity. Temperature dependence of resistivity was measured in the range from -70 to 70°C using thermostated bath.

Results and Discussion

Impedance measurements using the FRA-2 module with the frequency range from 10 kHz to 100 Hz. Fig. 2 presents the spectra measured at different temperatures for the gel containing 1M $LiClO_4$ solution. Proposed equivalent circuit for temperatures above -25°C can be expressed as a resistance R in the serial connection with the constant phase element Q (see Fig. 2).

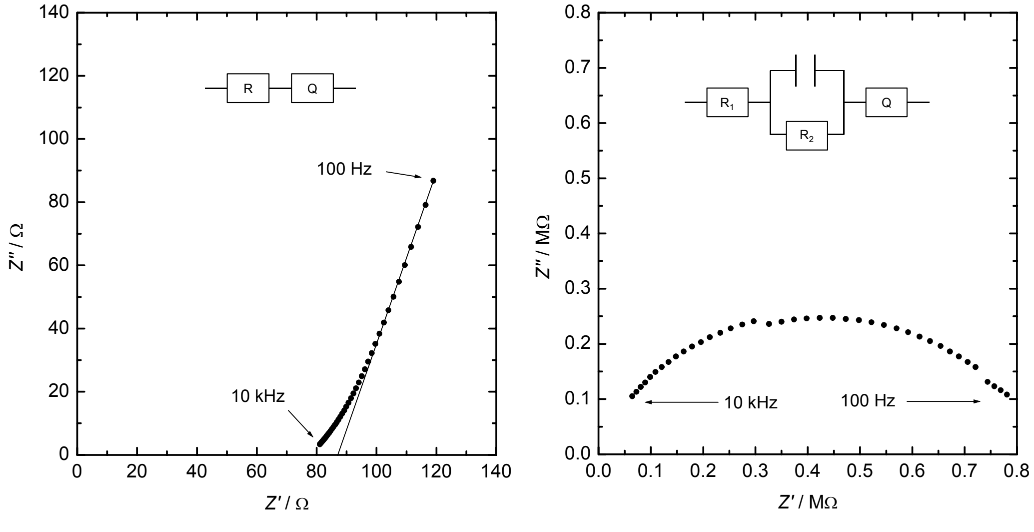

***Fig. 2** (left) and **3** (right) Nyquist plots measured at 20°C (left) and -60°C (right).*

At low temperatures the RQ equivalent circuit is changed to $R_1(R_2C)Q$ according to the Boucamp notation. Beside the increase of the resistance R_1 and R_2, a new parameter C is proposed describing dielectric behaviour of non-conducting phase of the gel (see Fig. 3).

Reproducible results are that the gel containing cation of higher radius has higher conductivity than the gel with smaller cation [3]. This effect is remarkable for the pair lithium - sodium, when the mobility of smaller lithium cation is strongly limited by the interaction with polymeric network.

The influence of temperature in the range from -70°C to +70°C on the specific resistivity of the PEMA gel is plotted in Fig. 4 in the Arrhenius coordinates (specific resistivity is plotted as a decadic logarithm) similarly to our previous work [3, 4].

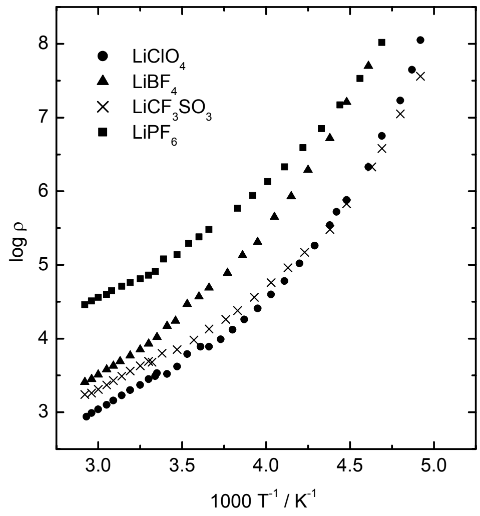

Fig. 4 *Arrhenius plot for PMMA-PC gel electrolytes containing 1M lithium salts.*

In the case of acrylate-based polymer electrolytes the plot of the specific resistivity consists of two linear parts with different slope. The point of transformation occurs in the temperature range from -25° to -30°C, where the polymer structure is changed from the elastomeric (less organised) to the crystalline form (more organised). This process is associated with remarkable increase of resistivity. At temperatures above 0°C the resistivity values were expressed by the Arrhenius formula:

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

Similarly, the apparent activation energy E_A was evaluated from the parameter A using the formula:

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

Table 1 summarises the room temperature conductivity of methacrylate based electrolytes including apparent activation energy values.

PMMA-PC electrolytes containing lithium hexafluorophosphate exhibit higher resistivity than the samples with other lithium salts especially at temperatures above -30°C, when different behaviour was observed (see Table 1). It is probably caused by hydrolysis of the salt during the polymerisation process. Other results of conductivity measurements are corresponding with experiments done by Rajendran [7] in the case of PVA solid polymer electrolytes.

***Table 1** Properties of methacrylate (MMA) based gel electrolytes containing 0.5M lithium salt in PC (the symbols ρ, A, B, and E_A are constants from Eq. 1 and 2).*

Salt	ρ (20°C) (Ω.cm)	A (K)	B	E_A (kJ.mol^{-1})
$LiCF_3SO_3$	4.9×10^3	1 399	-0.69	26.8
$LiBF_4$	1.5×10^4	1 242	-0.41	23.8
$LiPF_6$	1.2×10^5	1 053	+1.40	20.2
$LiClO_4$	3.3×10^3	1 353	-1.02	25.9

However propylene carbonate is a low-volatile solvent with low vapour pressure, slight evaporation was observed after ca. 90th day since preparation (see Fig. 5) in the case of PMMA gel electrolytes containing lithium salts of lower concentration. The solvent escape was remarkable in the case of gel electrolytes containing DMC-PC mixtures. Escape of the solvent is causing decrease of the ionic conductivity, when the aprotic solvent phase in the only conductive phase in the structure of the gel. If the polymer electrolyte is encapsulated, the evaporation of solvent was not observed and the material conductivity is kept constant [8].

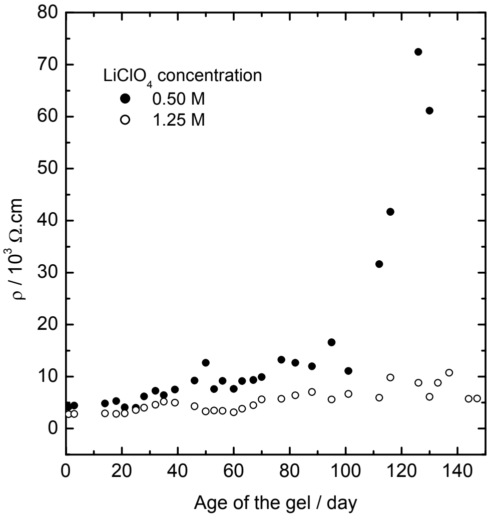

***Fig. 5** Ageing of the PMMA-PC gel electrolyte containing lithium perchlorate.*

Conclusions

PMMA based electrolytes can embed highly concentrated solutions of lithium salts in aprotic solvent. Conductivity measurements showed high ionic conductivity of prepared electrolytes except the samples containing lithium hexafluorophosphate. After ca. 3 months from preparation a remarkable decrease of conductivity was observed due to the

solvent evaporation. If encapsulated, the electrolytes keep their electrochemical properties stable for months.
Estimation of lithium ion transference numbers will follow together with investigation of dielectric properties of prepared materials.

Acknowledgements

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