ION-CONDUCTIVE PMMA GEL ELECTROLYTES

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ABSTRACT

Aprotic electrolytes are essential for lithium batteries, electrochromic windows, electrochemical supercapacitors and similar systems. These materials can be also used in the solid-state electrochemical sensors. This paper deals with the basic properties of gel polymer electrolytes based on. propylene carbonate (PC) immobilised by polymethylmethacrylate (PMMA) as a part of their systematic research.

1 INTRODUCTION

This paper deals with research in PMMA gel electrolytes and is a part of systematic investigation of new materials for lithium secondary batteries. Its aim is to find the solid conductive phase with best electrochemical properties.

The research was involved in various PMMA-based gels, which containing four different lithium salts. The investigation was focused on a measurement of gels conductivity or mobility in dependence on a concentration of the salts and a temperature, further on observation of the ageing of gels, monitored by the changes of the specific resistivity of PMMA gels for 95 days till now since preparation (temperature 20 °C).

An Potentiostat Eco Autolab (Eco Chemie,Utrecht, The Netherlands) equipped by FRA-2 impedance module was used for impedance spectra measurements.

The aim of this paper is the description of some electrochemical properties of PMMA-PC gels, which contain lithium salts. Finally this paper brings comparison of electric conductivity of PMMA gels containing various cations.

2 EXPERIMENTAL

2.1. PREPARATION OF GELS

PMMA-based gels were prepared by polymerisation of methylmetacrylate monomer (MMA) with a solution of lithium salts in PC.

The principle of preparation is based on mixture of these components: MMA (99 %), polymeric PMMA resin containing polymerisation initiator dibenzoylperoxide (Superacryl) and optional component. The optional component determines chemical properties of the gel and is realised as a solution of organic and/or inorganic compound in anhydrous PC (99.7%). These gels were prepared by the addition of lithium perchlorate ($LiClO_4$), tetrafluoroborate ($LiBF_4$), hexafluorophosphate $LiPF_6$ and trifluormethansulphonate ($LiCF_3SO_3$) in PC into the MMA and subsequent polymerisation. All lithium salts were dried by vacuum heating at 110 °C overnight. [1]

The mixture is kept for 5 days in a dessicator in the atmosphere of monomer and finally the gel is kept at 90 °C for 60 minutes in order to finish the polymerisation. This procedure guarantees the chemical and mechanical stability of the gel for weeks. The gel is elastic with thickness 0.5 – 1.2 mm, colourless and odourless. Elasticity and consistence is kept for months, required samples can by easily cut out [2]. Gels wre stored partly on air without any decomposition and water absorption and partly in a desiccator under MMA atmosphere. Al measurements were done with all various stored gels, was also monitored their comparison in dependence on gel´s storing.

The gel electrolytes were prepared according to the recommendation of the manufacturer of Superacryl. This method of preparation guarantees good mechanical and optical properties and electrochemical stability for weeks at least.

2.2. CONDUCTIVITY MEASUREMENTS

There were used two kinds of measurement by FRA-2 impedance module. Firstly: investigate impedance spectrum of the gels electrolyte, secondly: influence of temperature on the ionic conductivity was investigated by single potential impedance spectroscopy in the temperature range from -70 °C to 68 °C.

Two stainless steel electrodes with active surface area 4.00 cm^2 were used for conductivity measurements. The thin layer of a gel was inserted between them with constant separation distance. The thickness of the gel was measured by a micrometer. The potentiostat Eco Autolab equipped by FRA-2 impedance module was used for impedance spectra measurements. The ohmic resistance of the gel electrolyte was evaluated from the impedance spectrum at high frequencies by the software FRA-2 [5].

The first experiment of the impedance spectrum was measured using the FRA-2 module with the frequency range from 10 kHz to 100 Hz. The resistance of the sample was then estimated by the linear extrapolation of the Z’-Z’’ plot to horizontal axis, i.e., to the highest frequencies. Fig. 1 presents the spectrum of the gel containing $LiClO_4$. Reproducible results are that the gel containing cation of higher radius has higher conductivity than the gel with smaller cation [5].

The influence of temperature on the specific resistivity was measured by FRA-2 impedance metode using potentiometer for setting and reach the right temperature, the first temperature range was from 20 °C to 68 °C, the second from 20 °C to -70 °C, resistivity was measured with step of 5 degree Celsius.

In Fig. 2, the influence of temperature on the specific resistivity ρ of the lithium gel ($LiClO_4$)in the range between -70 and 68 °C is plotted in coordinates of Arrhenius type (specific resistivity is plotted as decadic logarithm against 1/T). The plot of the specific resistivity consists of two linear parts with different slope. An asymptotic straight line was drawn in the field of temperatures over -25 °C to 68 °C as a tangent to the curve. There should be a point of transformation about -28 °C, where the polymer structure is changed from the elastomeric (less organised) to the crystalline form (more organised). This process is connected with a remarkable increase of the resistivity. At the temperatures above -25 °C the resistivity values were expressed by the Arrhenius formula:

$$\log_{10}(\rho) = A / T + B \qquad [3]\ (1)$$

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

$$E_A = 2.303\ A \,.\, R$$

where R is a constant, R = 8.3143 [$J.K^{-1}.mol^{-1}$] [4] (2)

Obtained values are given in table 1 as well. We see that the gels exhibiting lower conductivity (or higher resistivity) possessed higher apparent activation energy at the same time. Further we see the non-linearity caused by the solidification of the gels.

2.3. AGEING OF PMMA GELS

Structural changes of polymeric network, evaporation of monomer during polymerisation and evaporation of the solvent are the main contributions to the set of processes, which are called the ageing of material. These processes can influence chemical, optical and mechanical properties of the gel. The main contribution in the case of PMMA gel electrolytes prepared by described method is the incomplete polymerisation. Our method of preparation ensures that the process of polymerisation is terminated during the 60-minute warming and the conductivity is stabilised after 5–10 days from preparation. To prevent evaporation of monomer is the Petri dish with the initial mixture placed into the desiccator under MMA atmosphere. With regard to low vapour tension of PC is the evaporation of the solvent insignificant for changes of conductivity [2]. Conductivity measurements in the case of PMMA gels containing $LiClO_4$ and other lithium salts show that no significant structural changes appear in the period of 3 months (see fig. 3). The gels were placed on air at room temperature and the conductivity was measured every 3 – 4 days, twice per week. In the case of PMMA gels at first was observed a rapidly increase of the resistivity in 5-10 day after first measurement day, than drop-off to standard level, than a slightly increase of resistivity was observed after 1 month. This change would not be an obstacle in further application. Mechanical properties of studied materials are not changed within 3 months. Gels keep their reasonable elasticity and they do not disperse or disintegrate. The gels, which were stored in the desiccator, had better mechanical properties and their resistivity was a little bit lower than gel´s resistivity placed on air.

Salt	ρ (Ω.cm), 20°C	A(K)	B	E(kJ.mol^{-1})
$LiClO_4$	$3.3.10^3$	1420	-1.241	27.2
$LiCF_3SO_3$	$1.8.10^4$	1462	-0.685	28.0
$LiBF_4$	$5.2.10^3$	1204	-0.358	23.1
$LiPF_6$	$1.7.10^5$	1404	0.477	26.9

Tab. 1: *Properties of gels containing lithium salts, coefficients A and B were obtained from the Arrhenius equation, E is the apparent activation energy calculated from coefficient A*

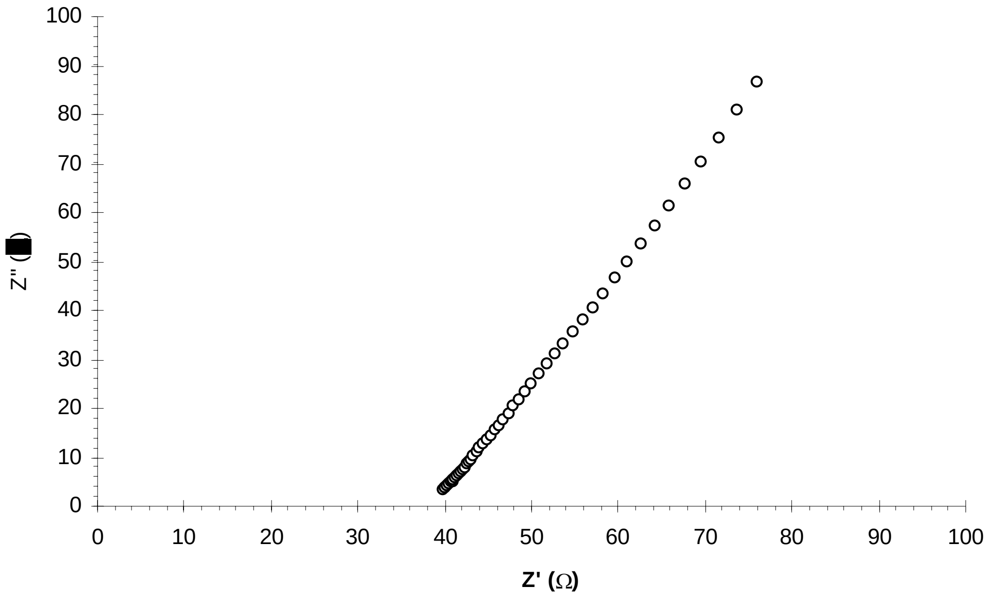

Fig. 1: *The impedance spectrum of the gel electrolyte containing $LiClO_4$ (temperature 20 °C, thickness of gel 0,099cm, electrode surface area 4 cm^2)*

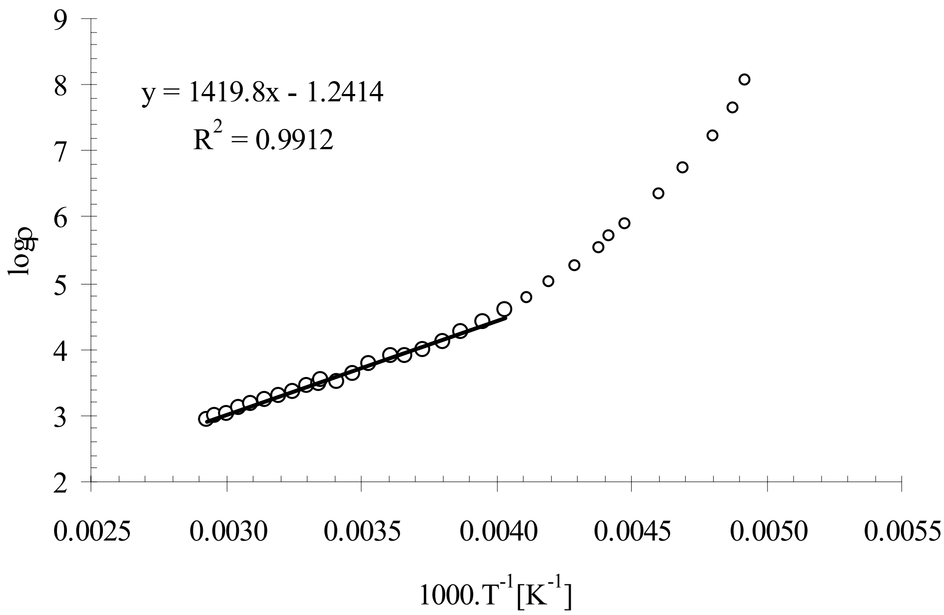

Fig. 2*:* *The influence of temperature on specific resistivity of the $LiClO_4$ gel (in Arrhenius plot, decadic logarithm plotted on vertical axis)*

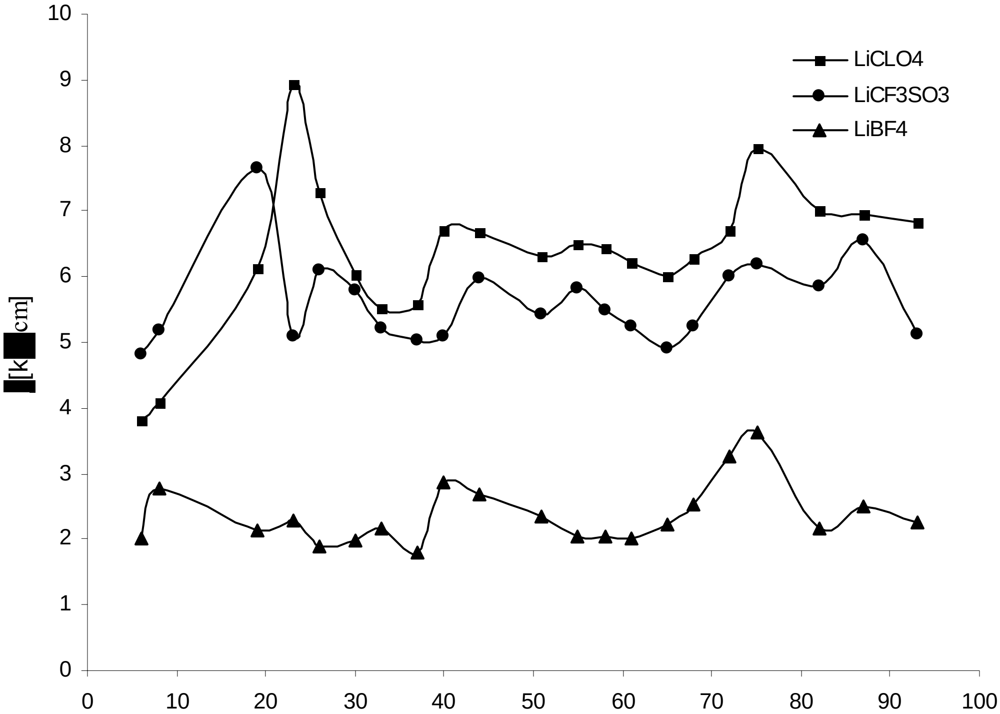

Fig. 3: *Changes of the specific resistivity of PMMA gels containing various lithium salts for 95 days since preparation (temperature 20 °C).*

3 CONCLUSIONS

Due to the low cost, long chemical and mechanical stability and reasonably high conductivity, the PMMA based electrolytes are suitable for various applications in the field of solid state electrochemical devices such as lithium batteries, electrochromic elements and solid-state sensors [2].

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