POLY(ETHYL METHACRYLATE) AND POLY(2-ETHOXYETHYL METHACRYLATE) BASED POLYMER GEL ELECTROLYTES FOR LITHIUM-ION BATTERIES

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Introduction

Electrochemical and mechanical properties of polymer gel electrolytes have been intensively investigated since the introduction of the 1st generation of solid polymer electrolytes by M. Armand [1]. Wide application of the gel polymer electrolytes in secondary lithium batteries, supercapacitors, and electrochromic devices is allowed due to the higher ionic conductivity compared with solid polymer electrolytes and due to the higher safety properties in comparison with common liquid electrolytes. Organic acrylate based polymer are perspective materials for their low toxicity both of monomer and polymer form, when methyl methacrylate (MMA) is widely used in the dental praxis.

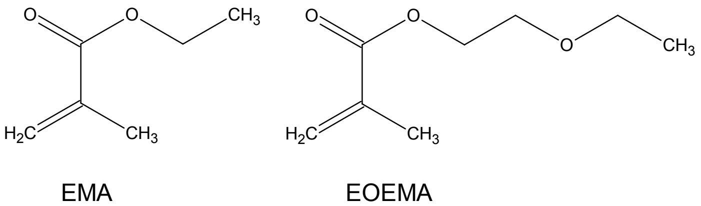

Fig. 1 *Formulas of two mainly used monomers EMA and EOEMA.*

The PMMA based gels prepared by thermal polymerisation were already investigated in our laboratories and were described elsewhere [2, 3]. Our latest research was aimed at different acrylate based polymer gel electrolytes, ethyl methacrylate (EMA) and 2-ethoxyethyl methacrylate (EOEMA; structures are drawn in Fig. 1), when several parameters of the preparation were changed with the aim to study the changes of electrochemical properties [4]. The main difference is in polarity of the monomers, on the contrary to EMA the 2-ethoxyethyl methacrylate dissolves inorganic salts itself and allows preparation of polymer electrolytes with higher salt content.

Changing of parameters was allowed due to applied UV photoinitiated free-radical polymerisation method of liquid mixture of initial components. The parameters included the carbon chain length of used monomer, type and concentration of used cross-linking agent, concentration of used inorganic perchlorate, and composition of the gel with the stress on monomer-PC volume ratio [4].

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Experimental

Samples of PEMA and PEOEMA gel electrolytes were prepared by direct UV light initiated polymerization of a liquid mixture of freshly distilled monomer and solution of lithium perchlorate in anhydrous propylene carbonate. Benzoine ethyl ether was used as a polymerization initiator. Obtained samples, the foils with an area 5 × 5 cm and thickness ca. 0.8 - 1 mm, were less or more elastic in dependence on solvent content and mostly transparent. This method of preparation disallows evaporation of the volatile monomer. The composition of the gel is expressed in molar percentage ratio - monomer/PC/salt.

Potentiogalvanostat PGSTAT 10 (Eco Chemie, The Netherlands) was used for electrochemical measurements including module for impedance measurement. New cell for solid-state electrochemical measurements was developed [5] with glassy carbon as the working and auxiliary electrodes (both $\varnothing = 3$ mm) and PMMA-Cd-Cd^{2+} solid-state reference electrode [5]. All potentials are related to this Cd/Cd^{2+} system ($E(Cd/Cd^{2+}) = 2.66$ V vs. Li/Li^+).

Results and Discussion

1. PEMA gel electrolytes - conductivity measurements

First experiments were done with different monomers (methyl MMA, ethyl EMA, butyl BUMA and hexyl HMA methacrylate) to study the influence of the side chain length on the mechanical properties and conductivity of prepared gels. Measurements showed low conductivity at the room temperature in the case of butyl and hexyl methacrylate. Poly(ethyl methacrylate) based electrolytes were further studied due to their optimal mechanical and electrochemical properties.

Cross-linkage of the polymer network has a positive influence on the ionic conductivity of prepared samples, when the suitable agent concentration was found 0.3 mol. %. However, further increase of the cross-linking agent concentration caused slight increase of the resistivity values. Generally the non-linked polymer gels exhibited higher resistivity in comparison with moderately cross-linked samples.

Two sets of PEMA gel electrolytes with different initial monomer/PC ratio were prepared - 60/40 or 53/47 mol. %. In both cases the impedance spectroscopy measurements showed, that almost three-order decrease of resistivity can be caused by addition of lithium perchlorate solution in comparison to the samples with pure PC only. The highest specific conductivity, 0.23 $mS.cm^{-1}$ was reached with the gel electrolytes of the composition EMA/PC/$LiClO_4$ = 50.5/44.7/4.8 mol. %, when high concentration of the lithium ions is required in the technology of secondary lithium batteries ($LiClO_4$ concentration in PC was 1.25M). Previously reported PMMA gel electrolytes with 0.5M $LiClO_4$ solution exhibited specific conductivity around 0.13 $mS.cm^{-1}$ [2, 3].

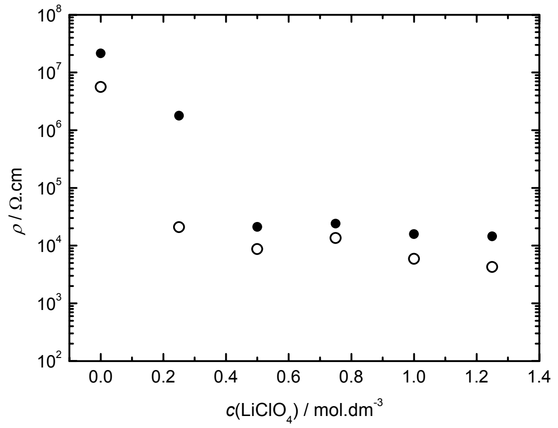


***Fig. 2** Dependence of the specific resistivity of PEMA gel electrolytes on the concentration of $LiClO_4$ in PC. Initial composition was EMA/PC = 60/40 (empty dot) or 53/47 mol. % (full dot).*

2. PEOEMA gel electrolytes - conductivity measurements

The 2-ethoxyethyl methacrylate monomer was chosen for further synthesis due to its higher polarity caused by higher content of oxygen in the structure. This modification allowed dissolution of $LiClO_4$ in the monomer itself. PEOEMA containing inorganic salt only exhibited very low conductivity 4×10^{-7} $S.cm^{-1}$, when the motion of ions in strongly restricted due to the absence of conductive liquid phase. This result shows, that the contribution of the polymer phase to the conductivity of material is very low.

Two series of EOEMA gel electrolytes were prepared with the initial composition EOEMA/PC/$LiClO_4$ = 90.5/0/9.5 and 65.5/0/34.5 mol. %. Addition of propylene carbonate to the initial $LiClO_4$ solution in EOEMA strongly increased the mobility of the ions in prepared gel. Fig. 3 shows significant decrease of the specific resistivity values with increasing volume of PC incorporated in the structure of the polymer. The increase of the conductive liquid phase is also connected with decreasing association of the ions and both factors lead to an increase of the material ionic conductivity.

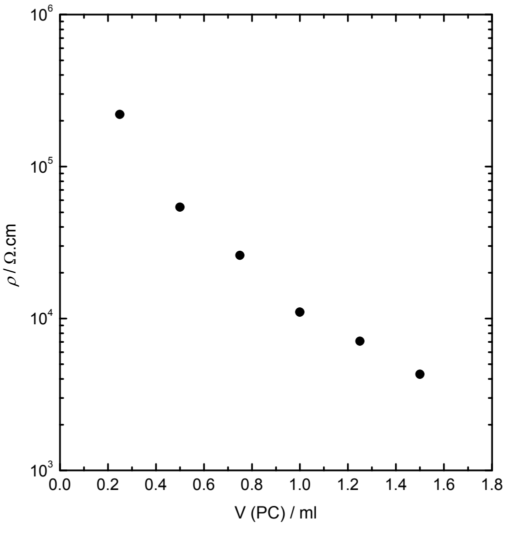


***Fig. 3** Dependence of the specific resistivity of PEOEMA gel with $LiClO_4$ on the amount of added PC. Initial composition EOEMA/PC/$LiClO_4$ = 65.5/0/34.5 mol. %.*

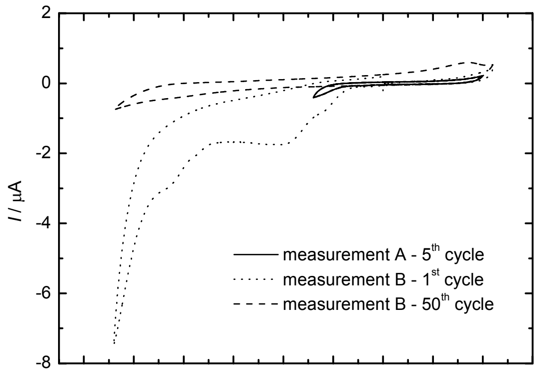
The highest conductivity values ca. 0.23 mS.cm^{-1} were reached with the composition EOEMA/PC/$LiClO_4$ = 58.2/35.7/6.1 and 49.3/45.5/5.2 mol. %, where the highest degree of the salt dissociation occurs.

3. Electrochemical behaviour of PEMA and PEOEMA gel electrolytes

Initial voltammetry measurements did not show any electrochemical reaction in the potential range from 0.1 to 1.5 V vs. Cd/Cd^{2+} (measurement A on Fig. 4 and 5) in agreement with investigation of PMMA gel electrolytes [3]. No change of conductivity was observed by the impedance measurements before and after each voltammogram, what concludes that no non-conductive layer is electrochemically created by redox reaction of present propylene carbonate, lithium perchlorate or polymer.

The potential limit at the positive side (over 1.5 V) was assigned to the oxidation of propylene carbonate [6]. If the potential range was enlarged down to -2.2 V, an irreversible cathodic wave appeared at the potential ca. -0.5 V during the first cycle (measurement B - 1st cycle). Further cycling caused rapid decrease of the wave and it almost disappeared within 3 - 5 cycles. The voltammograms did not change during the further cycling (measurement B - 50th scan presented in Fig. 4 and 5). This process was already described by Aurbach and Pletcher, when the irreversible wave appearing at the same potential was attributed to the oxygen reduction [6, 7]. This wave is greatly reduced in the second and subsequent scans due to the LiO_2 and Li_2O_2 film creation. Formed layer protects the electrode against further oxygen reduction and also suppresses other reduction processes such as water and solvent reduction. The wave of the irreversible reduction of water was also observed at ca. -1.7 V in both PEMA and PEOEMA gel electrolytes (see Fig. 4 and 5) and the wave was also strongly reduced within 3 - 5 cycles.

Fig. 4 (left) Cyclic voltammograms of PEMA gel electrolyte (5 mV.s^{-1} scan rate).



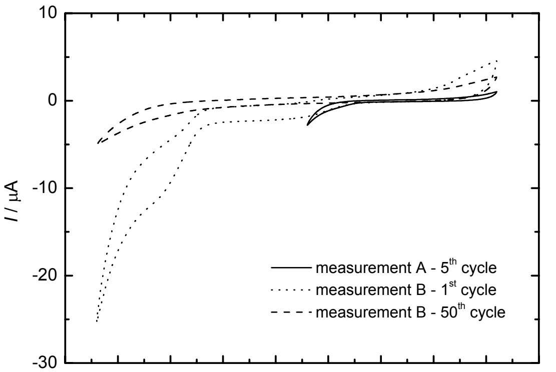


***Fig. 5** (right) Cyclic voltammograms of PEOEMA gel electrolyte (5 mV.s^{-1} scan rate).*

Impedance measurement showed that no non-conducting layer is formed on the working electrode, when the ohmic resistivity of the material is not significantly changed during voltammetrical measurements either in narrow or large potential range.

Conclusions

New poly(ethyl methacrylate) and poly(2-ethoxyethyl methacrylate) gel electrolytes prepared by UV radical polymerisation and their electrochemical properties were examined. Developed method of preparation allows production of materials with uniform chemical structure and reproducible electrochemical and mechanical properties.

The composition of the material was fluently optimised and the best samples exhibited high ionic conductivity ca. 0.23 $mS.cm^{-1}$ at 20^oC. The high ionic conductivity was caused by high content of the $LiClO_4$ solution incorporated in the structure of polymer. However the mechanical properties were kept suitable for the application in lithium-ion batteries or electrochromic devices.

Voltammetrical measurements showed broad accessible potential window, from -2.1 to +1.5 V vs. Cd/Cd^{2+}.

In comparison with previously reported PMMA gel electrolytes [2, 3, 5] the PEMA and PEOEMA gel electrolytes have higher ionic conductivity above -20^oC and broader potential window.

Acknowledgements

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