THE IMPEDANCE OF GLASSY CARBON ELECTRODE IN PMMA-PC GEL POLYMER ELECTROLYTES

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Introduction

The impedance of phase boundary between glassy carbon (GC) and gel polymer electrolytes based on polymethylmethacrylate (PMMA) and propylene carbonate (PC) was studied as a part of extended investigation of gel polymer electrolytes [1-3]. The gels were prepared according to our procedure by polymerization of methyl methacrylate (MMA) to which a salt solution in PC was added. A capacitive impedance was found as a prevailing component of the equivalent circuits in the anodic range of potentials. A marked dependence on potential at 0.1 to 0.3 V vs. Cd-Cd^{2+} pseudo - reference electrode [4] was observed.

Experimental

A sheet of gel was prepared by mixing of the monomer MMA and solution of the salt in PC with the initiator of polymerization SUPERACRYL (Spofa Dental, Inc., Czech republic) in a Petri dish [1-2].

Lithium, sodium, potassium and tetraethylamonium salts were used as perchlorates or tetrafluoroborates (all from Aldrich). Their concentration is given in mole/liter of the solution in PC used for gel preparation.

The impedance spectroscopy and cyclic voltammetry were measured in a three - electrode cell containing glassy carbon counter electrode fig.1 and cadmium pseudo-reference electrode [4]. Both working and counter electrode were fabricated from glassy carbon rods ∅ 0.61 mm (i.e., 0.292 cm^2 of geometric surface area). Potentiogalvanostat PGSTAT 10 (Eco Chemie, The Netherlands) was used for electrochemical measurements including module for impedance measurement FRA21 and Autolab software for impedance spectra analysis.

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Results and discussion

New cell for electrochemical measurements was developed (see Fig. 1).

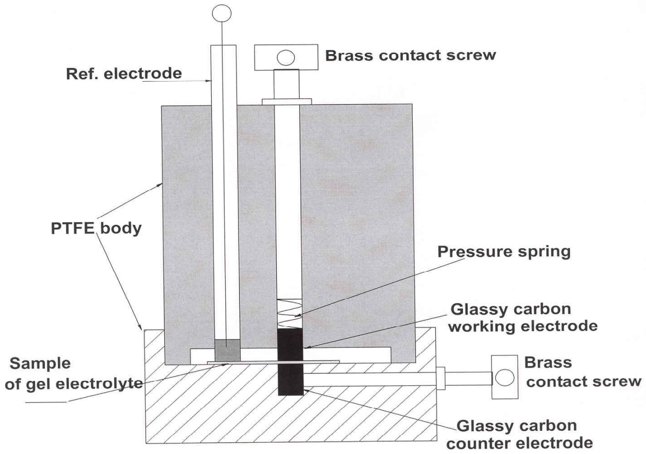


Fig. 1 *Cell for solid-state electrochemical measurements in the medium of polymer gel electrolytes.*

The voltammetric curve of glassy carbon in $LiClO_4$ gel electrolyte is shown in Fig. 2. As we see, some electrochemical process appears at negative potential while the voltammogram does not contain any in the range of positive potentials up to 1.0 to 1.2 V. The process below -0.2 V may be ascribed to the reduction of PMMA-PC either electrolyte itself or of some impurity such as residual water content. Also the reduction of functional groups on the electrode surface might be responsible for that. Hence, we have restricted the impedance measurements to positive potentials only.

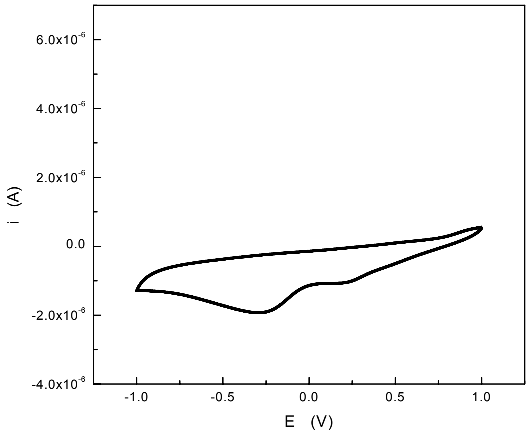
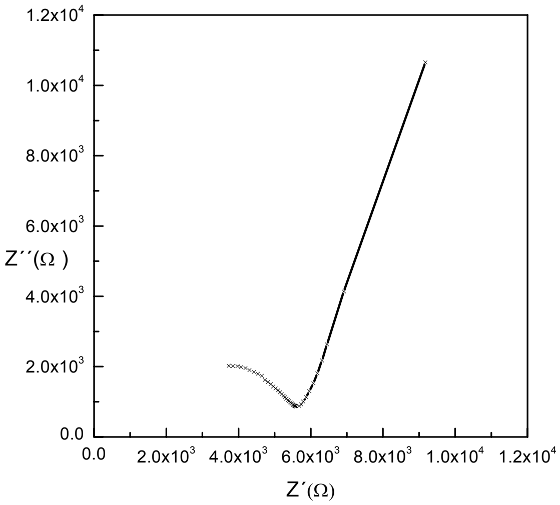


Fig. 2 *Cyclic voltammetry of PMMA-PC gel electrolyte containing lithium perchlorate.*

A typical example of electrode impedance in $LiClO_4$ gel is plotted in Fig. 3 as Cole-Cole plot of impedances and as Bode plot in Fig. 4.

The equivalence circuit was obtained by the software in FRA21 pack. We used a rather complex circuit for the elucidation of data. Aside the high – frequency component R_1 (corresponding to uncompensated residual resistance of the electrolyte, it contains a R_2-C chain, a constant phase element, marked as Q of properties close to those of a pseudocapacitor (phase angle 70° or more). Sometimes a final low-frequency resistance R_3 appears in parallel to the element Q.



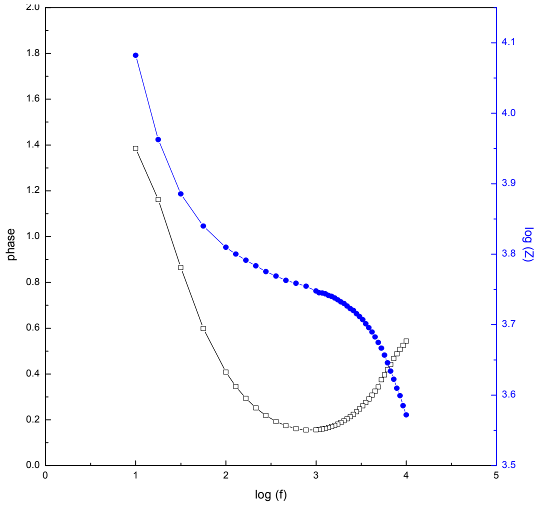


Fig. 3 *(left) Cole-Cole plot of PMMA gel electrolyte containing lithium perchlorate.*
Fig. 4 *(right) Bode plot of PMMA-PC gel electrolyte containing lithium perchlorate.*

The R_2 – C chain is probably connected with some inert film formed on the electrode surface; its properties can be described as a solid electrolyte interface (*s.e.i.*) known generally in the electrochemistry of lithium batteries. The component Q is the capacity of the electrode itself, perhaps that of the double layer. Finally, the R_3 is the residual leakage current by side reactions ion the positively charged electrode.
We can see that the resistance R_1 is much higher in more diluted gels. Contrary to this, the pseudocapacitance Q changes in opposite direction and is the lowest in very diluted gels containing $KClO_4$.

Acknowledgements

This work was supported by the Academy of Sciences (Research Plan AV0Z40320502), Ministry of Education (project MSM 0021630516) and Ministry of Environment (project VaV SN/171/05).

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