SPECIFIC CONDUCTIVITY MEASUREMENTS OF THE PMMA BASED ELECTROLYTES CONTAINING Al_2O_3 NANOPARTICLES

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Introduction

Ion conductive polymeric electrolytes are widely investigated because of their potential applications in a variety of electrochemical devices like solid state batteries, gass sensors, electrochromic windows, supercapacitors, fuel cells, etc. The PMMA (Poly-methyl methacrylate) based gel polymer electrolytes prepared by immobilizing an inorganic salt (Li and Na) in an aprotic solvent (propylene carbonate) in a polymer matrix were previously examinated [1, 2].

For most potential applications, it is desirable that the polymer electrolytes exhibit resonable conductivity (~10^{-4} $S.cm^{-1}$) and stability over wide operational temperature and electrochemical window. However, our prior research have lead to significant improvement, the ionic conductivity still remains relatively low at ambient temperatures.

Various methods have been applied to increase the ionic conductivity of the electrolyte. One of the approaches relies on the addition of nanocomposite sorbents. In present work we have investigated the influence of PMMA based gel polymer electrolytes with dissolved Li and Na salts and different content of embedded nanosized Al_2O_3 on specific conductivity measured at temperature rage from -70 to 70 °C.

Experimental

Preparation of polymer gel electrolytes was based on mixture of these componens: PMMA resine containing polymerization initiator (dibenzoilperoxide, 1 wt. %) – commercialy produced material Superacryl (Spofa-Dental Prague, Czech Republic) and an optional component. The optional component was represented by Li and Na perchlorates dissolved in an aprotic solvent (PC) in concentration of 0.1 $mol.l^{-1}$. The ceramic filler (white powder) with particle sizes between 40 and 47 nm, purchased from Sigma-Aldrich, was dried at 150 °C for 24 hours. Mixture of these components in suitable ratio was than placed in a Petri dish (4 cm diameter) and kept for 5 days in a dessicator. The polymerization process is than finished by 60 minute warming at 90 °C in an oven. Ceramic Al_2O_3 was represented in following weight ratios: 0, 1.67, 3.14 and 7.17 wt. % for gels containing $LiClO_4$ and 0, 7.17 wt. % for $NaClO_4$.

Ionic conductivity measurements were conducted on a Autolab (Eco Chemie, The Netherlands) within the frequency range from 100 Hz to 10 kHz. Thin membranes were cut and placed between two stainless steel electrodes (1 cm squared) fixed in a nylon holder.

The samples thickness varied from 0.2 to 0.5 mm and the impedance response was measured over the range from -70 to 70 °C. For measuring at low temperatures the samples were placed in a sferical Dewar flask and cooled using solid carbon dioxide. For measuring in temperature region over 25 °C we used thermostated bath (MEMMERT WB 10, Germany) with modulated temperature step. In order to avoid direct contact with cooling/heating medium (distilled water in thermostated bath and ethanol in Dewar flask) the electrodes were fixed into a siliceous beaker.

Results and discussion

The gels without ceramic sorbent were slide transparet membranes, easy to cut out from Petri dish. The transparency depends on volume of added Al_2O_3 nanopowder. Optical observation of the samples containing ceramic sorbents revealed that the distribution of Al_2O_3 content was not uniformed. In the membrane prepared from 1.67 wt. % of Al_2O_3, the nanopowder was sedimented to the both surfaces with respect to the whole membrane volume. Further increase of Al_2O_3 content occured that the distribution was homogeneous in the whole membrane volume.

The ionic conductivity was calculated using a resistivity obtained from a Nyquist plot as the intersection of the impedance data with the real part of the axis at the high frequency.

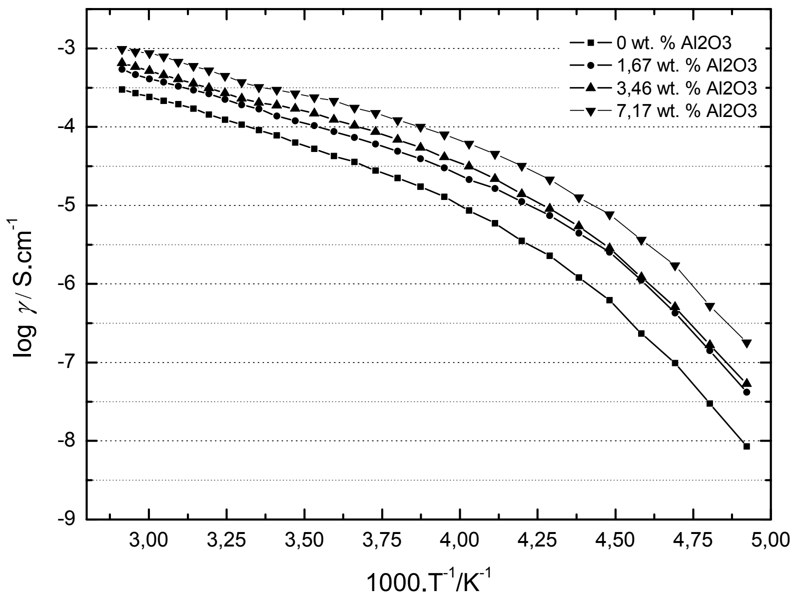

Fig. 1 *Arrhenius plot of the specific conductivity vs. reciprocal temperature of PMMA/PC/$LiClO_4$ gels with different content of Al_2O_3 nanopowder (-70~70 °C).*

Fig. 1 shows the conductivity of PMMA/PC/$LiClO_4$ gels increases with increasing content of Al_2O_3. The conductivity of the gel without ceramic filler was 0.09 $mS.cm^{-1}$ while the conductivity of the same membrane containing 7.17 wt. % of Al_2O_3 was 0.32 $mS.cm^{-1}$ at ambient temperature.

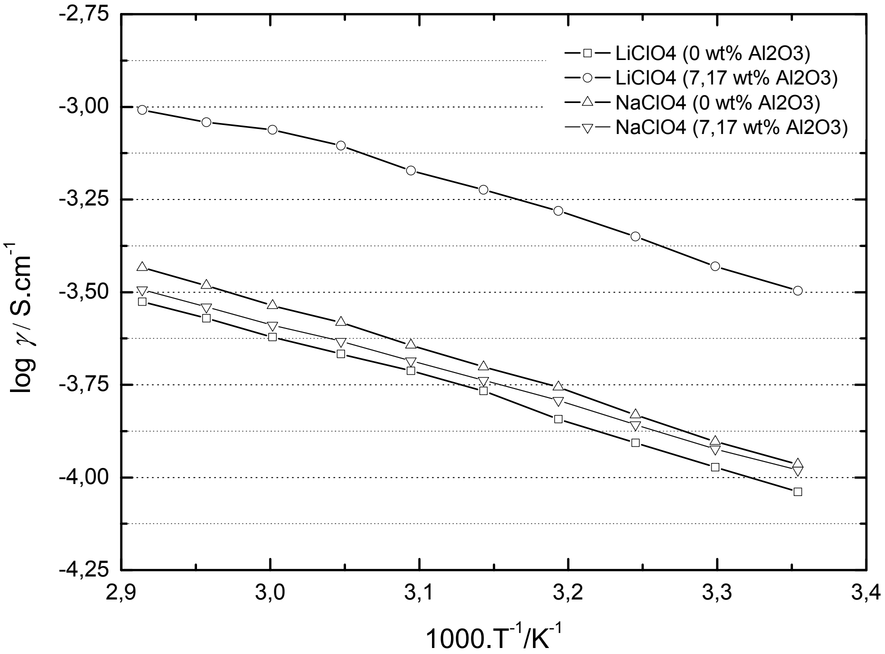

Fig. 2 *Arrhenius plot of the specific conductivity vs. reciprocal temperature of PMMA/PC/$LiClO_4$ and PMMA/PC/$NaClO_4$ gels with different content of Al_2O_3 nanopowder (25~70 °C).*

The previous research on PMMA based polymer electrolytes containing Li and Na salts revealed that the conductivity of sodium is higher that in case of lithium ions (seen Fig. 2). Unlike PMMA/PC/$LiClO_4$ gels containing Al_2O_3, the slight decrease of the specific conductivity of PMMA/PC/$NaClO_4$ gel with 7.17 wt. % of Al_2O_3 was observed. The conductivity of PMMA/PC/$NaClO_4$ gel without ceramic filler was 0.11 $mS.cm^{-1}$ while the conductivity of the PMMA/PC/$LiClO_4$ membrane containing 7.17 wt. % of Al_2O_3 was 0.32 $mS.cm^{-1}$ at ambient temperature.

Acknowledgements

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References

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