

Short communication

The presence of nanostructured Al₂O₃ in PMMA-based gel electrolytes

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Abstract

Gel polymer electrolytes (GPEs)-based on poly(methyl methacrylate) PMMA and propylene carbonate (PC) with LiClO₄ or NaClO₄ salt are prepared using either the commercial product Superacryl[®] or directly from the monomer and AIBN (2,2'-azobis(isobutyronitrile)) initiator. The nanostructured aluminum oxide is added to the mentioned systems in various ratios. Solutions of liquid PC–perchlorate and polymer electrolytes are compared with focus on ionic conductivity. The ionic conductivity of polymer-based electrolytes is significantly influenced (of almost by one half order of magnitude at room temperature) by the addition of nanosized Al₂O₃. On the contrary, the conductivity of liquid electrolytes is decreased by the addition of alumina in the blend. A slight enhancement of mechanical properties is observed.

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1. Introduction

The role of gel polymer electrolytes (GPE) in the technology of modern batteries [1,2], supercapacitors [3] and electrochromic devices [4–7] has grown steadily recently. For most potential applications, it is desirable that the polymer electrolyte exhibits reasonable conductivity ($\sim 10^{-4}$ S cm⁻¹), high mechanical strength, stability over a wide range of temperature and electrochemical window. The results achieved in poly(methyl methacrylate) (PMMA)-based gel electrolytes prepared by immobilizing an inorganic salt (LiClO₄ and NaClO₄) in an aprotic solvent (propylene carbonate) in a polymer matrix were previously reported [8–10]. However, while our prior research has led to significant improvement, ionic conductivity remained relatively low at ambient temperature.

Various methods have been applied to increase the conductivity of electrolytes. One of the approaches relies upon the addition of nanocomposite sorbents. Recently, the positive influence of inert nanoparticles on either the specific conductivity or mechanical properties of gel electrolytes has been announced [11–13].

In most cases the conductivity measurements were performed in binary polymer (e.g. PMMA and PEO)-based electrolytes with embedded Li ions designated for battery applications [13–15]. In an article by Johansson and Jacobsson [14] the conductivity enhancement in the LiX/PEO-based system was ascribed to specific surface interactions subsequently confirmed by Ahmad et al. on PMMA–LiTf–TiO₂-based electrolytes [15].

In a modern electrochemical cell microporous inorganic fillers such as fumed silica, alumina or titanium oxide are widely used. A large surface area of the sorbent increases the host polymer porosity and enhances electrolyte retention, which results in increased conductivity [17,18].

Our earlier work was dedicated to fundamental electrochemical research of PMMA–PC–salt-based systems [5,9,10]. The polymer matrix is prepared from a mixture of the commercially available PMMA resin Superacryl[®] (SA) and a liquid monomer (MMA). The high ionic conductivity at room temperature (10^{-4} S cm⁻¹) of systems containing dissolved Li and Na ions in an aprotic propylene carbonate was reported [10,16]. An increased ion-movement is due to the heterogeneous nature of the PMMA–PC membrane with a conductive fluid path created by the immobilized solvent in a polymer matrix [8]. In the present work we report the influence of dispersed nanosized Al₂O₃ on the ionic conductivity of PMMA-based GPEs. More-

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over, the GPEs prepared directly from the monomer, thermal polymerization initiator and cross-linking agent were included for comparison. Both, liquid and PMMA-based GPEs containing dissolved Li or Na ions, were studied over a wide temperature range (from -70 to 70 °C).

2. Experimental

2.1. Materials

The aprotic solvent, propylene carbonate (Sigma–Aldrich, >99.7%), was stored under molecular sieves. Lithium and sodium perchlorates (Sigma–Aldrich) were dehydrated in vacuum at 110 °C for 48 h and then stored in a desiccator. The Al_2O_3 filler of the particle size between 40 and 47 nm, purchased from Sigma–Aldrich, was dried at 150 °C for 24 h in an oven. The commercially available oligomeric resin Superacryl[®] was purchased from Spofa-Dental (Prague, Czech Republic) and used without pretreatment. The monomer, methyl methacrylate (MMA), was obtained from Sigma–Aldrich and purified by distillation under reduced pressure. The polymerisation initiator, 2,2'-azobis(isobutyronitrile) (AIBN), was purchased from Fluka and recrystallised from chloroform. Both, the monomer and the initiator, were stored at 4 °C before use. The cross-linking agent, ethylene glycol dimethacrylate (EDMA; Sigma–Aldrich), was used as received.

2.2. Sample preparation

Basically, four sets of samples were prepared using two different PMMA-based structures in combination with embedded Li or Na ions. The first set of samples was prepared from the mixture of PMMA resin Superacryl[®], containing 1 wt.% of dibenzoylperoxide as an initiator of polymerization, and monomeric MMA with addition of nanosized Al_2O_3 and LiClO_4 or NaClO_4 salt dissolved in propylene carbonate (PC) in molar concentration 0.1 mol l^{-1} (further abbreviated as MMA/SA). The mixture of these components in a suitable ratio (1.00 ml PC, 1.50 ml MMA, 0.70 g of SA) was poured in a Petri dish (5 cm in diameter) and heated for 60 min at 90 °C in an oven. The second way of preparation is based on direct polymerization of the monomer (1.75 ml of MMA) and particular additives: nanosized Al_2O_3 and LiClO_4 or NaClO_4 salt dissolved in 1 ml of propylene carbonate (further abbreviated as MMA/AIBN). The stirred solution was cross-linked by the EDMA agent (0.3 mol% of monomer) and thermally polymerized upon addition of 1 mol% AIBN. The whole mixture was bubbled by nitrogen for 8 min and poured into a Petri dish (5 cm in diameter). In this case the polymerization process was finished by warming for 2 h in an oven preheated at 80 °C. Samples prepared in this way were kept in a desiccator. The content of Al_2O_3 in both systems was 0, 3.46, 7.17, 10 and 12 wt.%, respectively.

Liquid electrolytes were prepared from a mixture of LiClO_4 with 20 ml PC in concentration 0.1 mol l^{-1} and a corresponding amount of aluminum oxide (0, 3.46, 7.17 and 10 wt.%). The liquid electrolytes were sonicated to keep the alumina particles evenly distributed in the solution.

2.3. Instrumentation

Ionic conductivity measurements were performed using the impedance module of the potentiostat Autolab 12 (Eco Chemie, The Netherlands) within the frequency range of 100 kHz–1 mHz for lower temperatures and 10 kHz–100 Hz for temperatures above 0 °C. Thin membranes were cut out from Petri dishes and placed between two stainless steel blocking electrodes (1 cm^2) fixed in a nylon holder. The thickness of samples varied from 0.4 to 0.9 mm and was measured using a micrometer screw. The impedance response was measured over the range -70 to 70 °C. For measurement at low temperatures the samples were placed in a cylindrical Dewar flask and cooled using solid carbon dioxide. For measuring at a temperature over 25 °C we used thermostated bath (MEMMERT WB 10, Germany). To avoid direct contact with the cooling or heating medium (distilled water in thermostated bath or ethanol in Dewar flask) the electrodes were placed into a silica glass beaker.

For measuring liquid electrolytes, we used the standard conductivity cell (dimensional constant 0.85 cm^{-1} , Verkon GB) with an integrated temperature sensor.

3. Results and discussion

3.1. Specific conductivity measurements

The ionic conductivity for temperatures above 0 °C was calculated using the resistivity obtained from a Nyquist plot as the intersection of impedance data with the real axis. Fig. 1 shows a typical impedance spectrum of MMA/SA-based membrane with 0.1 M LiClO_4 in PC measured at 60 and 70 °C. The equivalent circuit [19], inserted in the corner (Fig. 1), consists of ohmic resistance (R_1) representing the overall resistance of the membrane in series with the constant phase element (CPE_1). The CPE is a specific circuit element associated with current and potential distribution over an inhomogeneous electrode surface [20].

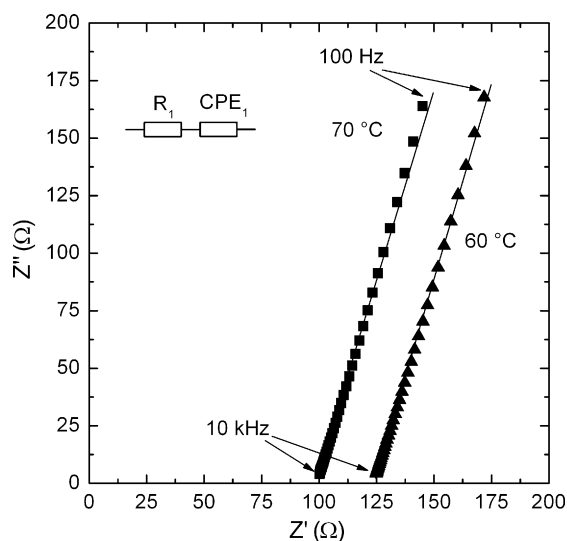


Fig. 1. Nyquist plot of MMA/SA gel containing LiClO_4 in PC with equivalent circuit, frequency range from 10 kHz to 100 Hz, measurement temperature 60 and 70 °C.

For temperatures above 0 °C the overall resistivity decreases due to an increasing content of the free solvent in the polymer matrix. Fig. 2 shows the impedance spectrum of the same sample measured at –60 °C. An equivalent circuit has changed for temperatures below 0 °C into a parallel combination of CPE₂ and R₂ in series with CPE₁ and R₁. The conductivity was then calculated from resistivity R₂ obtained using the FRA2 software (Autolab 12, EcoChemie). When the equivalent circuit is applied to the impedance spectrum in Fig. 2, we received the following values; R₂ = 53.50 kΩ, Q(CPE₂) = 2.18 × 10^{–9} S proportional to ω^{0.82}, Q(CPE₁) = 7.79 × 10^{–6} S and proportional to ω^{0.77}. For temperatures below –40 °C the resistivity increases rapidly, the overall value is driven by the impedance of the parallel combination of R₂ and CPE₂.

Compared to TiO₂ with a relatively high dielectric constant (ε = 180), the Al₂O₃ with ε = 9.8 is expected to be aggravating the solubility of Li salt in PC (ε = 64.5) [18]. Hence, the observed decrease of conductivity values in liquid electrolytes with respect to increasing volume of Al₂O₃ in a blend was in perfect agreement (see Fig. 3). Another reason for resistivity decrease might be mutual interaction of free Li/Na ion and dispersed Al₂O₃ particles.

Fig. 4 demonstrates that the specific conductivity of gels with Li ions in the MMA/SA system increases linearly with increasing the volume of Al₂O₃ up to 7.17 wt.% (0.37 mS cm^{–1}). In case of Na ions the conductivity decreases following the increasing of Al₂O₃ volume up to 7.17 wt.% (0.12 mS cm^{–1}). The overall highest conductivity of 0.39 mS cm^{–1} was surprisingly achieved for the gel containing Na ions at 10 wt.% of Al₂O₃ content, while a further increase of alumina up to 10 and 12 wt.% for both, Li and Na ions containing membranes, means conductivity decrease.

Using specific conductivity values, with respect to Al₂O₃ content, we compared the MMA/SA and MMA/AIBN-based

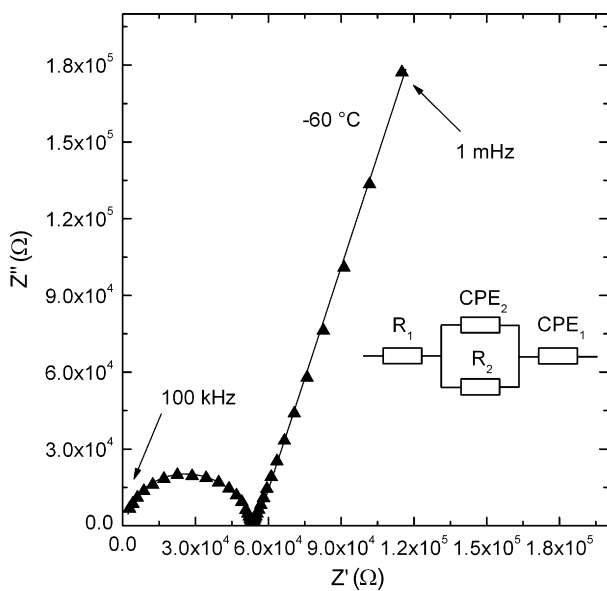


Fig. 2. Nyquist plot of MMA/SA gel containing LiClO₄ in PC with equivalent circuit, frequency range from 100 kHz to 1 mHz, measurement temperature –60 °C.

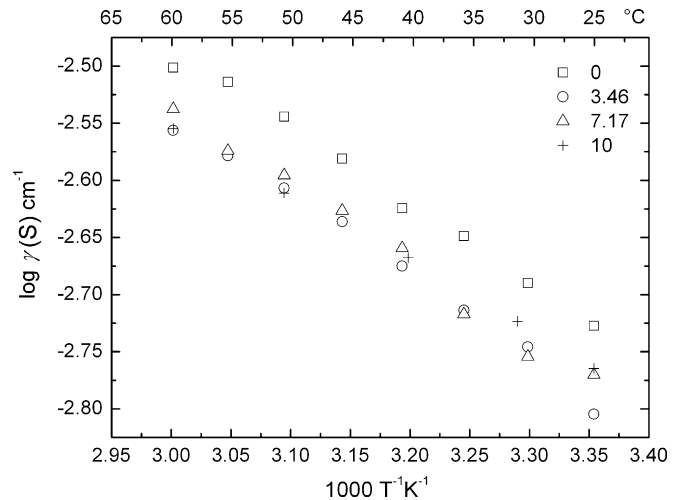


Fig. 3. Arrhenius plot of the specific conductivity of PC–LiClO₄-based liquid electrolytes with corresponding content of Al₂O₃ in wt.%, measurement temperature 25–60 °C.

polymer matrices. Following Fig. 5, we observed a higher dispersion of measured data, over 380% for PMMA–PC–LiClO₄ at 25 °C, resulting in higher conductivity values in case of MMA/SA-based electrolytes. Fig. 5 confirms the presumption of a two-phase colloidal system consisting of a polymeric matrix with immobilized solvent. A similar behavior, though less expressive, was also observed in gels with the MMA/AIBN polymer matrix and Na ions. On the contrary, conductivity values of samples prepared from the MMA/AIBN with dissolved Li ions were not in agreement with values measured in MMA/SA-based membranes. The highest conductivity of 0.03 mS cm^{–1} was achieved for 3.46 wt.% of Al₂O₃.

3.2. Mechanical properties and apparent activation energies of the GPEs with Al₂O₃ sorbents

The GPEs without ceramic sorbent were superficially homogeneous transparent membranes with transmittance over 90%

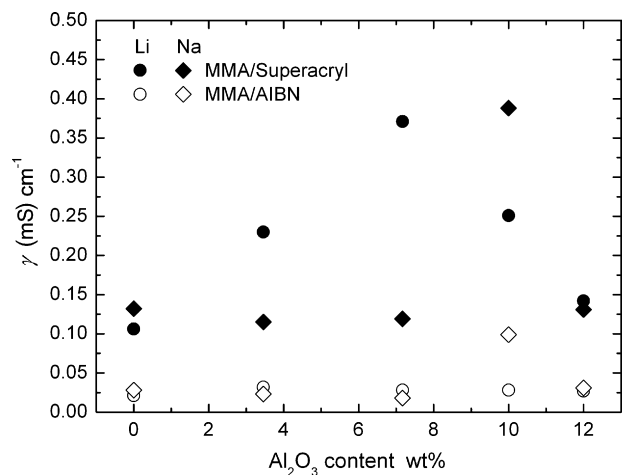


Fig. 4. Specific conductivity versus Al₂O₃ content for MMA/SA and MMA/AIBN-based gel electrolytes containing Li or Na ions, measurement temperature 30 °C.

Table 1
Properties of GPEs based on PMMA–PC–LiClO₄

| Al ₂ O ₃ (wt.%) | A (K) | B | E _{A(0 < ζ < 70 °C)} (kJ mol ⁻¹) | A (K) | B | E _{A(0 < ζ < -70 °C)} (kJ mol ⁻¹) |
|---------------------------------------|--------|-------|---|--------|-------|--|
| 0 | -1.249 | 0.139 | 23.9 | -2.874 | 6.457 | 55.0 |
| 3.46 | -1.045 | 0.156 | 20.0 | -2.607 | 5.93 | 49.9 |
| 7.17 | -1.035 | 0.021 | 19.8 | -2.34 | 5.161 | 44.8 |
| 10 | -0.997 | 0.294 | 19.1 | -2.544 | 5.709 | 48.7 |
| 12 | -0.921 | 0.786 | 17.6 | -2.679 | 6.035 | 51.3 |

Apparent activation energy values E_A obtained from parameter of Arrhenius plot (expressed by parameters A and B) at temperatures ζ between -70 and 70 °C.

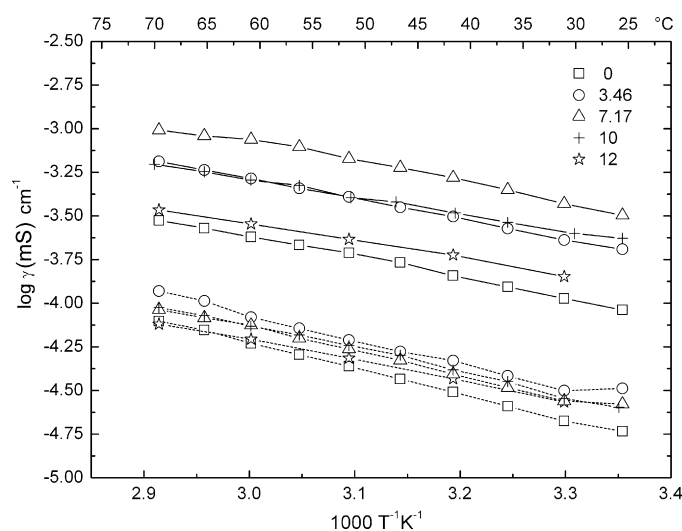


Fig. 5. Arrhenius plot of the specific conductivity of MMA/SA (solid line) and MMA/AIBN (dashed line)-based gel electrolytes containing immobilized Li ions and denoted wt.% of Al₂O₃ sorbent, measurement temperature 25–60 °C.

[16], easy to cut out from the Petri dish. Their transparency strongly depends upon alumina content. Optical observation of the samples revealed that the Al₂O₃ nanopowder was not evenly distributed. In all membranes, prepared from 3.46 wt.% of Al₂O₃, the nanopowder was attracted to both surfaces in comparison to the whole membrane volume. A further increase of alumina over 3.14 wt.% caused that the bulk distribution was fully homogeneous. Increasing the content of Al₂O₃ over 7.17 wt.% we received a deep white, non-transparent membrane with grooved surface suggesting that aluminum clay is not soluble in propylene carbonate.

An example of Arrhenius plot of the specific conductivity of MMA/SA-based GPEs with immobilized Li ions and Al₂O₃ nanoparticles is shown in Fig. 6. The specific conductivity values from Fig. 6 were fitted within a wide temperature range (from -70 to 70 °C) in Arrhenius logarithmic scale. Arrhenius slope A was used to calculate the apparent activation energy derived from equation: $E_A = -2.303AR$. In our previous work, we found the possible application of MMA/SA-based gel electrolytes reasonable at a temperature above -25 °C, the so-called transformation point [16]. At this temperature, disposable changes of polymeric structure, inducing a strong increase of its resistivity, were observed. Fig. 6 shows slight flatter of conductivity curves. Unlike the gel without alumina filler, the transformation point is lowered by Al₂O₃ addition to values below -25 °C, which results in an enhancement of mechanical properties. This expla-

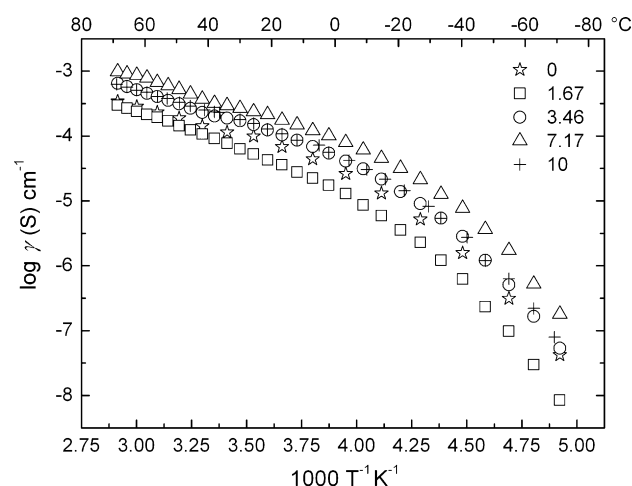


Fig. 6. Arrhenius plot of the specific conductivity of MMA/SA-based gel electrolytes with immobilized Li ions and Al₂O₃ nanoparticles in wt.%, measurement temperature from -70 °C to 70 °C.

nation is supported by apparent activation energy values given in Table 1.

4. Conclusion

We can assume that the conductivity of liquid electrolytes is decreased by the addition of alumina in all Al₂O₃ concentrations. The inhibition of conductivity in liquid electrolytes can be either assigned to increased interactions between free charge carriers and dispersed nanoparticles or inadequate dielectric constant of Al₂O₃ compound.

On the other hand, a remarkable increase of conductivity of almost by one half order of magnitude at room temperature was observed for MMA/SA-based gel electrolytes containing dissolved NaClO₄ in PC. Concerning mechanical properties, a slight enhancement upon addition of Al₂O₃ was achieved.

Moreover, we found an increased content of alumina fillers giving a good contrast to PMMA-based gel electrolytes, hence making them prospective for electrochromic display application.

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