Block copolymers of poly(ethylene oxide) materials for polymer electrolytes (transport properties)

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Abstract

The present paper deals with transport properties of polymer electrolytes as mixtures of block copolymers of poly(ethylene oxide) and lithium iodide. By combination of impedance measurements and d.c. polarization methods for a symmetrical cell it was possible to calculate the transport numbers of mobile ions in the system. It has been found that the transport numbers of these electrolytes depend on composition and also on temperature. The electrolyte resistance and the electrode resistance depend in the same way on the content of lithium iodide in the polymer electrolytes. The relation between passivating layers on the electrodes and the shape of impedance plots is discussed in detail.

Introduction

Substitution of poly(ethylene oxide) (PEO) in PEO/LiI systems by block copolymers of PEO in combination with poly(methyl methacrylate) (PMMA) produces polymer electrolytes with higher conductivity and higher transport numbers for Li ions [1]. Donth *et al.* [2] describe the preparation and physical properties of those polymers. For the block copolymers the ability of the PEO block to crystallize decreases if the PEO block is fixed at one or both chain ends by the amorphous poly(alkyl methacrylate) blocks, which is the reason for a higher mobility of the ions, especially in the low-temperature range. We have investigated these polymer electrolytes by a.c. impedance measurements and by d.c. polarization measurements. In this paper, we will discuss some aspects of those measurements for determination of transport numbers and will give a more detailed interpretation of the resulting impedance plots.

Experimental

PEO was used with a molecular weight of 5×10^6. The diblock copolymer (symbol: PMMA–PEO) had a molecular weight of 5400 compared with 4800 for the PEO block. The triblock copolymer had a molecular weight of 80 000 compared with 60 000 for the PEO block in the centre of the polymer chain (symbol: PMMA–PEO–PMMA). LiI was prepared from lithium carbonate and hydroiodic acid. After drying the polymer electrolytes were prepared by a solvent-free method and pressed into tablets. For experimental details, see refs. 1 and 3. A.c. and d.c. data were obtained using a Solartron electrochemical interface 1286 and a Solartron frequency response analyser 1250 controlled by a Hewlett-Packard computer. The samples were sandwiched between

Li electrodes which block against the iodide anion. Ionic conductivity (σ), electrolyte resistance (R_b), and electrode resistance (R_e) were calculated from complex impedance plots before and after the polarization experiment.

The polarization experiments were carried out between Li electrodes with a constant voltage of 50 mV in the same cell as for the a.c. measurements. In all cases the electronic part of the conductivity, measured by d.c. polarization between stainless-steel electrodes, was very low.

Results

For polymer electrolytes such as PEO/LiI both the cations and the anions of the dissolved lithium iodide are mobile. Therefore, in a complex impedance plot three semicircles may be anticipated if the electrolyte is sandwiched between electrodes which are nonblocking towards one of the mobile ions. Bruce [4] has discussed this situation, see Fig.1. The high-frequency semicircle is associated with the bulk electrolyte response (R_b). The second semicircle allows the determination of the electrode resistance (R_e). Figure 1 shows also an impedance diagram for PEO/LiI which is identical with the model of Bruce [4] but without the low-frequency semicircle. We did not investigate our polymer electrolytes in the low-frequency range. Transport numbers for the Li ion were determined by a combination of d.c. polarization experiments and impedance measurements (in all cases between Li electrodes). The transport numbers were calculated with the help of eqn. (1), also mentioned by Evans et al. [5] and Croce et al. [6], because this eqn. considers a change in R_e during the experiment:

$$t_+ = I_\infty (V - I_0 R_{e,0})/I_0 (V - I_\infty R_{e,\infty}) \tag{1}$$

where, V is the constant potential during the polarization experiment, I_0 and $R_{e,0}$ are current and electrode resistance in the initial state, and I_∞ and $R_{e,\infty}$ are current and electrode resistance after the polarization experiment. $R_{e,0}$ and $R_{e,\infty}$ were determined by impedance measurements. Figure 2 shows that during a polarization experiment the electrode resistance increases, and correction for the passivating layer is necessary for precise determination of transport numbers (in Fig. 2 the polarization experiment was interrupted several times by impedance measurements).
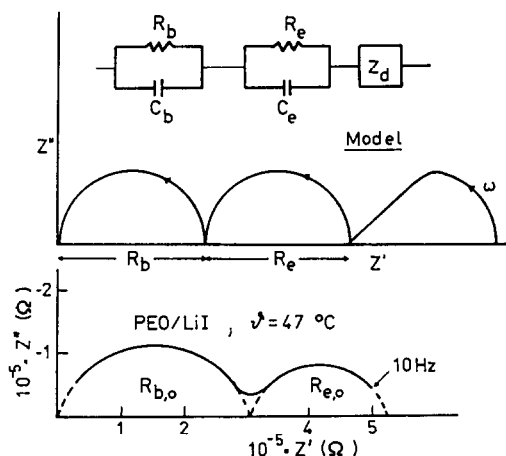

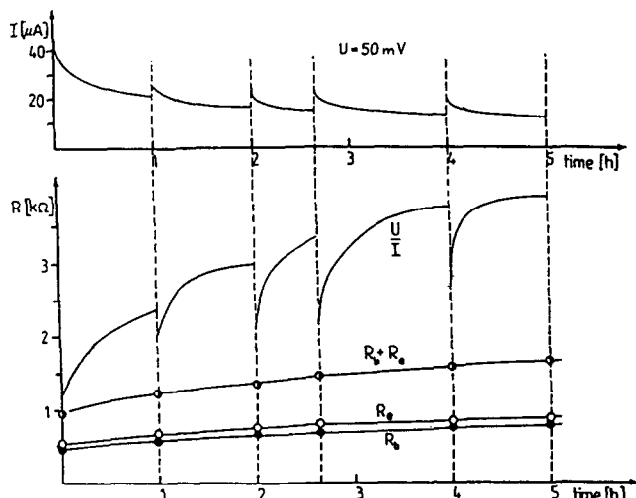Fig. 1. Impedance diagram for PEO/LiI in comparison with a model of Bruce [4].

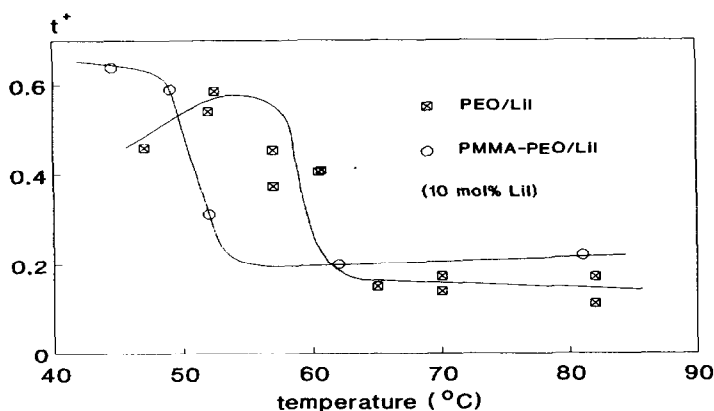Fig. 2. Increase of the electrode resistance (R_e) during a polarization experiment.

Fig. 3. Transport numbers for the systems PEO/LiI and PMMA–PEO/LiI vs. temperature (10 mol% LiI).

Recently, we have reported transport numbers for the Li cation of about 0.1–0.35 [1]. For all systems investigated, the transport number depends on the salt concentration. Figure 3 demonstrates a new aspect. For the systems PEO/LiI and PMMA–PEO/LiI the transport number also depends on the temperature. In the vicinity of phase transition temperature the transport number changes drastically. For temperatures below the phase transition we have calculated transport numbers which are significantly higher than reported before.

From impedance plots we found that the content of LiI in the polymer electrolyte has an effect on R_b and also on R_e. For the systems PEO/LiI and PMMA–PEO–PMMA/LiI the specific resistance ρ (calculated from R_b and the thickness of the probe materials) and R_e depend on the salt content of the polymer electrolyte in the same way, showing

a maximum of conductivity at the same position (see Fig. 4). Watanabe *et al.* [7] reported a constant value for R_e, for cross-linked polymers in combination with $LiClO_4$, independent of the composition of the electrolyte. In our case a linear relationship was observed between ρ and R_e. Small deviations from the linear relationship between ρ and R_e can be explained by the thickness of the electrode layer which must not be a constant value. Additionally, the specific resistance and the electrode resistance show the same temperature dependence.

From these results we conclude that the transport mechanism is influenced by the number of charge carriers for the investigated polymer electrolytes and for the electrode layer (Li as an electrode material) in a similar way.

Partly, we can explain the increasing electrode resistance during a polarization experiment by the shape of the impedance diagram. The impedance diagram gives for R_e a semicircular arc with its centre being displaced below the Z' axis. The resulting angle of depression (α) is not only a fitting parameter but gives a correlation to the electrode roughness or structural inhomogeneities. For the system PEO/LiI, α is independent of the temperature. For the system PMMA–PEO–PMMA/LiI we find a clear difference between the angles of depression before and after the polarization experiments in dependence on the content of LiI (see Fig. 5). Before the polarization experiment this angle should be a result of the surface roughness of the electrodes, but afterwards a result of the electrochemical reaction between the polymer electrolyte and the Li electrodes. The electrode capacity (C_e in Fig. 1), calculated from the complex impedance diagram, depends also on the content of LiI in the polymer electrolyte. We have observed the same dependence on salt content for the capacity as for the conductivity. But the influence of temperature on the electrode capacity is quite different from the temperature dependence of conductivity for a given salt content. In the vicinity of phase transition temperature the (log σ against $1/T$) plots form a knee or bend, but the capacity C_e passes a maximum (see Fig. 6). Hiratani *et al.* [8] reported a similar situation for other polymer electrolytes.

Before and after phase transition a relatively low dielectric constant results for the polymer electrolyte, which favours the formation of ion-ion association. For the system PEO/LiCF$_3$SO$_3$ Jacobsson *et al.* [9] found by Raman scattering experiments ion pairs and higher aggregates besides the 'free ions'. The concentration of ion pairs
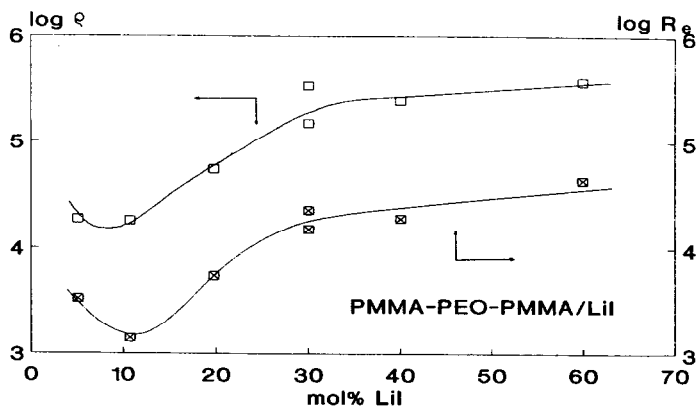

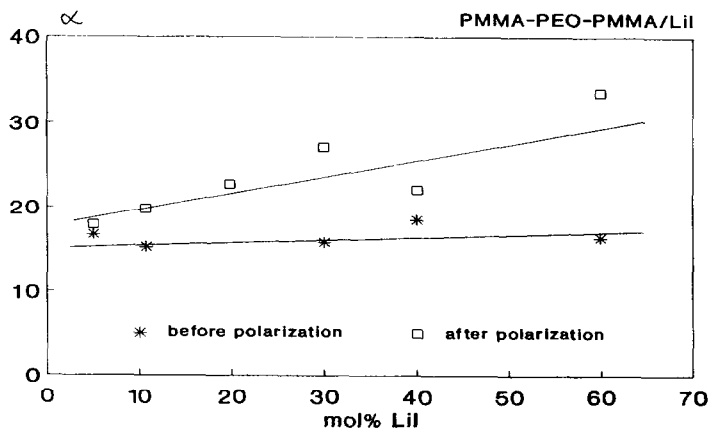Fig. 4. Specific resistance ρ and electrode resistance (R_e) vs. the salt content in the system PMMA–PEO–PMMA/LiI.

Fig. 5. Angle of depression, α, ($*$) before and ($\square$) after polarization for the system PMMA–PEO–PMMA/LiI.
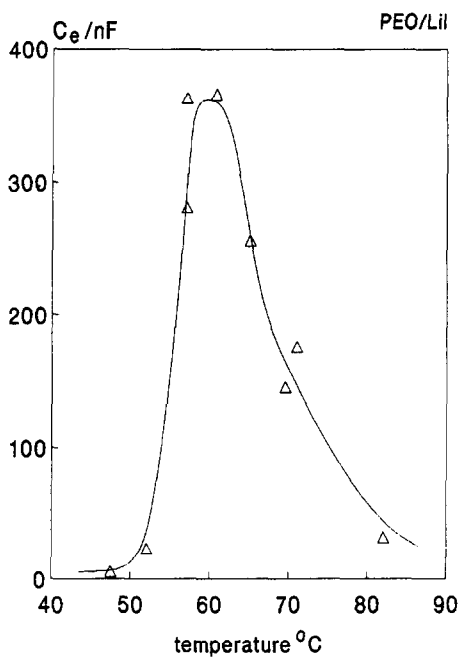

Fig. 6. Electrode capacity C_e vs. temperature.

increases if the temperature increases which can be explained by the lower interaction between the Li ion and the oxygen in the polymer chain. If we assume a lower mobility for ion pairs the relation demonstrated in Fig. 3 is understandable. Lower transport numbers for higher temperatures can be explained by the formation of ion pairs in the polymer electrolyte.

Acknowledgements

References

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