

Enhancement of the ionic conductivity and the amorphous state of solid polymer electrolytes for rechargeable lithium batteries

H. Bischoff, D. Rahner and K. Wiesener

Dresden University of Technology, Institute of Physical Chemistry and Electrochemistry, Mommsenstraße 13, D-8027 Dresden (Germany)

T. Steurich and R. Sandner

Merseburg University, Institute of Macromolecular Chemistry, Otto-Nuschke-Straße, D-4200 Merseburg (Germany)

Abstract

Complexes of LiCF_3SO_3 and a polymer obtained by polymerization of triethylene glycol dimethacrylate (TRGDMA) and its copolymerization with acrylonitrile (AN) at molar ratios of 0.67, 2.0 and 4.0, both in the presence of poly(ethylene glycol) dimethylether as a plasticizer, provides a.c. conductivities in the range between 10^{-5} and 10^{-4} S/cm at ambient temperature. An increase of conductivities has been found at growing ratios of AN:TRGDMA from 0 to 2.0 and molar ratios of ethylene oxide (EO) units: LiCF_3SO_3 , ranging from 12 to about 26. The conductivity is nearly independent of the content of AN at $\text{EO}:\text{Li}^+ = 52$. Impedance measurements of cells modified with these solid electrolytes show that the electrochemical behaviour of the composite lithium/PEO-lithium salt-complex is determined by the properties of the phase boundary metal/solid electrolyte. The mechanical stability of the polymer, acting simultaneously as a separator between the active electrodes, determines the cycle life.

Introduction

In order to develop a secondary all-solid-state lithium battery on the basis of solid polymer electrolytes working at ambient temperature it is necessary to find an electrolyte of high stability and ionic conductivity.

At room temperature the ionic conductivity of the most used polyethylene oxide (PEO)-lithium salt complexes is too low for an application in battery systems. By means of chemical modification one is able to decrease the crystalline part and to increase the Li ion conductivity above 10^{-5} S/cm [1].

In our investigations we changed the ionic conductivity of the polymer electrolyte by chemical modification of the polymer using a polymer host obtained by cross-linking homo- and copolymerization of triethylene glycol dimethacrylate (TRGDMA) in the presence of polyethylene glycol dimethylether as plasticizer and LiCF_3SO_3 as lithium salt. The influence of the additional polarity of the polymer host on the ionic conductivity in the presence and absence of acrylonitrile (AN) has been studied.

Experimental

Materials

Poly(ethylene glycol)dimethylether (PEGDME, mol. wt. = 500, Merck-Schuchardt) and triethylene glycol dimethacrylate (TRGDMA, Aldrich Co.) were dried prior to use over a molecular sieve type 4A. Anhydrous lithium trifluoromethane sulfonate (LiCF_3SO_3 , Fluka) was treated under reduced pressure at 130 °C for 12 h. Inhibitor-free acrylonitrile (AN) was distilled from calcium hydride.

Film preparation

Films of 100 to 300 μm thickness were prepared by cross-linking homopolymerization of TRGDMA and copolymerization of TRDGMA and AN in the presence of PEGDME and LiCF_3SO_3 . The composition of the films is described in ref. 2.

Impedance measurements

The measurements in the frequency range of 0.1 Hz to 100 kHz were performed from ambient temperature to approximately 348 K using a transfer-function analyser (Schlumberger, SI 1255). The impedance of the working electrode was determined at its equilibrium potential by means of a potentiostat-galvanostat (EG&G Princeton Applied Research, PAR 273). The working and counter electrode area of the two electrode Li cells built for electrochemical experiments was 2 cm^2 .

Cycling experiments

Cycling experiments were carried out under galvanostatic conditions in two electrode Li cells ($i_{\text{discharge}} = i_{\text{charge}} = 0.03 \text{ mA/cm}^2$).

Results and discussion

Conductivity σ

Conductivity measurements have been performed by a.c. impedance spectroscopy. The temperature dependence of the conductivity of linear polymer chains of PEO shows a classical Arrhenius plot, where (Fig. 1):

$$\sigma = A \exp(-E_A/kT) \quad (1)$$

The activation energy for conduction below 343 K is very high (145 kJ/mol). At these temperatures, PEO-lithium salt complexes have a great ability to crystallize. The activation energy for conduction above 343 K is 54 kJ/mol.

Redox-initiated, solvent-free preparation of LiCF_3SO_3 -doped network structures provides yellowish-transparent and homogeneous films of sufficient mechanical stability. The plasticized networks (Figs. 1, 2) show a high conductivity at room temperature. The activation energy exhibits a value of 23.6 kJ/mol. The temperature dependence of σ (related to the glass temperature T_g) is described according to the Vogel-Tamman-Fulcher (VTF) law given by:

$$\sigma = BT^{-1/2} \exp(-E_A/k(T - T_g)) \quad (2)$$

In the whole area of temperature these cross-linked networks show amorphous behaviour.

The plots of conductivity, σ , versus the EO/ LiCF_3SO_3 show a dependence on the content of AN (Fig. 3). A maximum is observed at a EO: LiCF_3SO_3 ratio of approximately

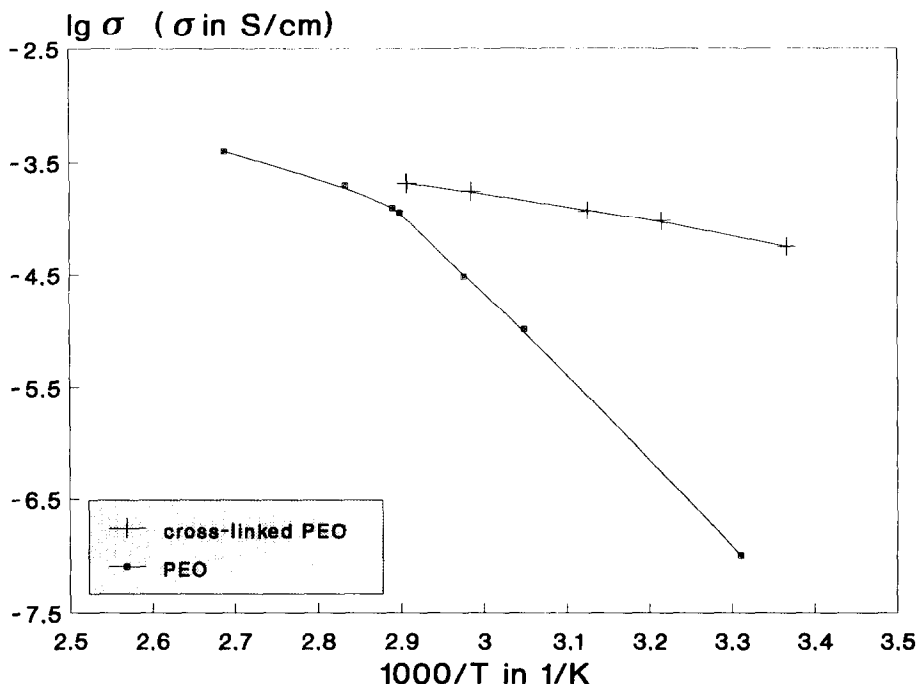


Fig. 1. Arrhenius plot of the conductivity from polymer chains of PEO/LiClO₄ (EO:Li⁺ = 8) and cross-linked PEO/LiCF₃SO₃ (EO:Li⁺ = 25.8 and AN:TRGDMA = 2).

26 in the cases of AN:TRGDMA = 0, 0.67 and 2, whereas a maximum of conductivity for AN:TRGDMA = 4 is found in the range between 15 and 17. A shift in the conductivity maximum has already been pointed out in a flatter slope of the curve by AN:TRGDMA = 2 in the range of high salt concentrations. The appearance of a conductivity maximum is not surprising and extensively discussed in literature [3–5]. In the range of low salt concentration (EO:LiCF₃SO₃ = 52–55), the conductivity is nearly independent of the content of AN, and it is relatively good in accordance with measurements of Hu and Wright [6] for unsaturated polyester networks.

Furthermore, Fig. 3 illustrates that the conductivities are increased when the cross-linking monomer TRGDMA is replaced by the comonomer AN in the ratio range of AN:TRGDMA from 0 to 1 and EO:LiCF₃SO₃ from 12 to about 26. These results are suitable to confirm the supposition that ion conduction in a polymer, which contains a relatively great part of strongly polar units in addition to EO-sequences, is promoted by an improved salt dissociation. In fact, an intense interaction between the nitrile group of AN and LiCF₃SO₃ has been evidenced by IR spectroscopy [7]. On the other hand, it has to be noted that this kind of association may contribute to a restricted movement of the charge carriers. The anions should be preferably solvated by the nitrile monomer units. The balance in polymer-ion interaction in the complexes investigated seems to appear in the films prepared with a molar ratio AN:TRGDMA = 2.00. Films prepared at this composition showed the highest values of conductivity reaching 6.3×10^{-5} S/cm at ambient temperature.

In comparison with the copolymer films the complexes prepared without AN exhibit somewhat lower conductivities. It should be added that these materials are

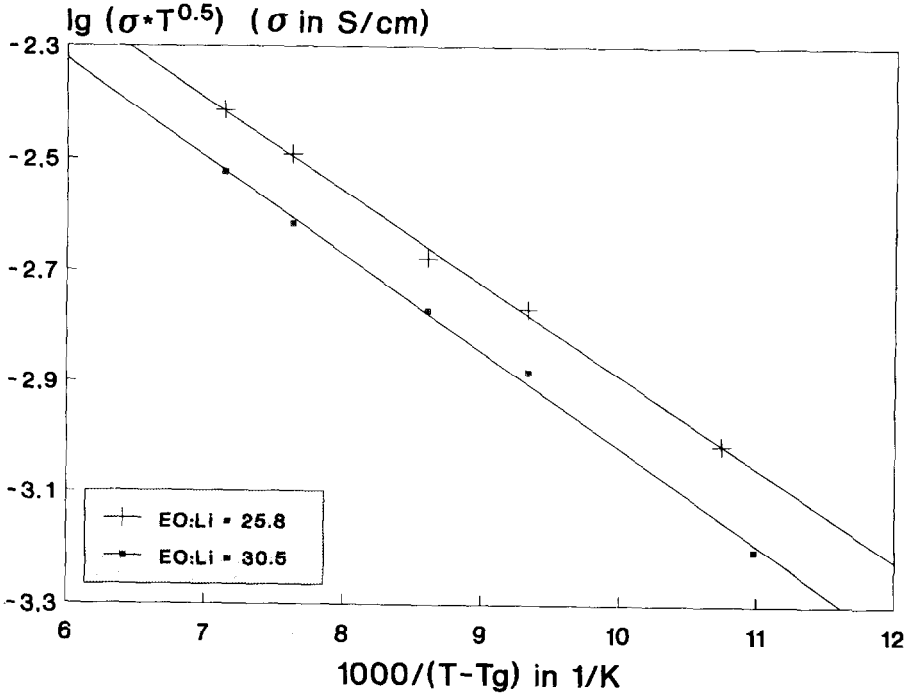


Fig. 2. Vogel-Tamman-Fulcher plots of the conductivity for cross-linked films of AN:TRGDMA = 2 and $LiCF_3SO_3$ at $EO:Li^+ = 25.8$ and 30.6.

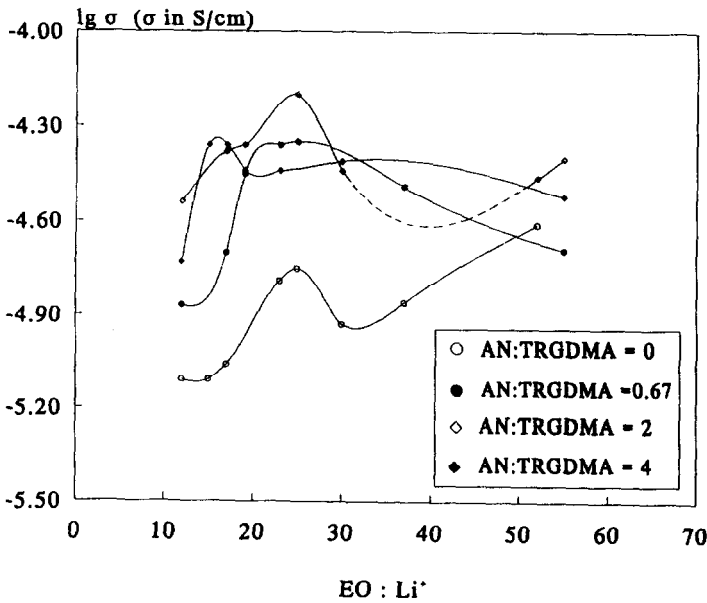


Fig. 3. $\lg \sigma$ vs. $EO:Li^+$ for plasticized networks at various contents of AN at ambient temperature

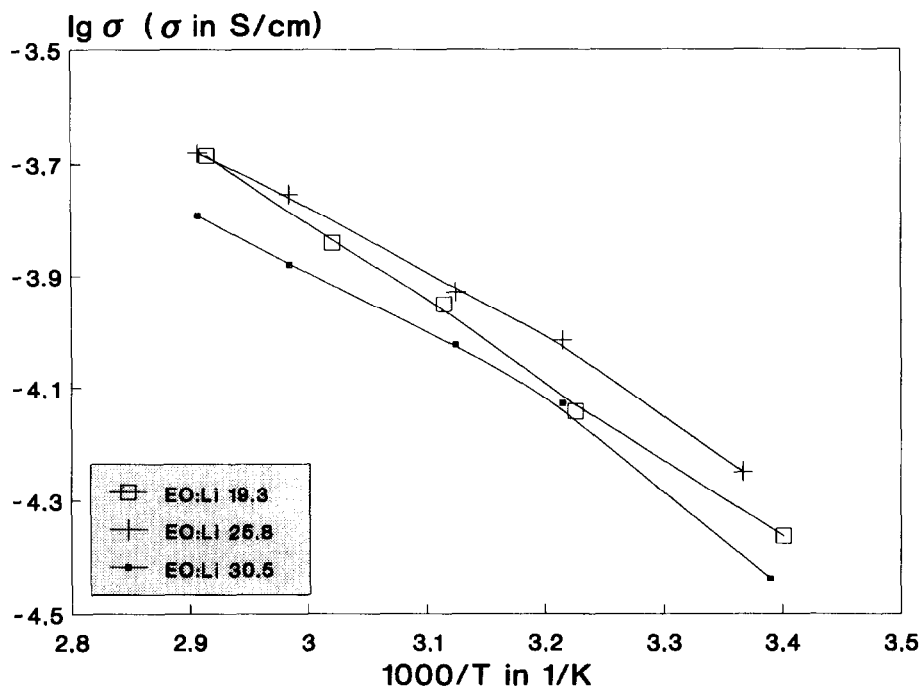


Fig. 4. Temperature vs. conductivity for cross-linked complexes of AN:TRGDMA = 2 and LiCF_3SO_3 at $\text{EO}:\text{Li}^+ = 19.3, 25.8$ and 30.5 .

expected to show the highest degree of cross-linking because of the absence of AN which decreases the cross-linking density.

Figure 4 presents related curves for the films with a ratio AN:TRGDMA = 2 at three selected salt contents. A typical Arrhenius-type behaviour ($E_A = 30.6$ kJ/mol) can only be ascertained at the highest salt concentration ($\text{EO}:\text{Li}^+ = 19.3$). It may be attributable to a crystalline phase structure [6], probably due to increased interionic interactions.

A similar feature is given in Fig. 5 depicting the temperature dependence of all complexes studied at the optimum composition in relation to conductivity. Cross-linked copolymer films with the highest content of AN show a nearly Arrhenius-type relationship ($E_A = 21\text{--}35$ kJ/mol) which can be derived over the complete range of salt concentration considered. That seems to be connected with their most probable tendency to form microcrystalline domains by a favoured association with the salt caused by the nitrile groups.

Cycling behaviour

For an application in Li batteries a high stability of the electrolyte is necessary. The sample (AN:TRGDMA = 2; $\text{EO}:\text{Li}^+ = 25.8$) with the best conductivity shows a good cycling behaviour (Fig. 6). The test cells are working since 50 days and have been cycled till now about 300 cycles. With growing cycling time the overpotential increases. This is in agreement with a rising polarization resistance shown in the impedance plot (Fig. 7).

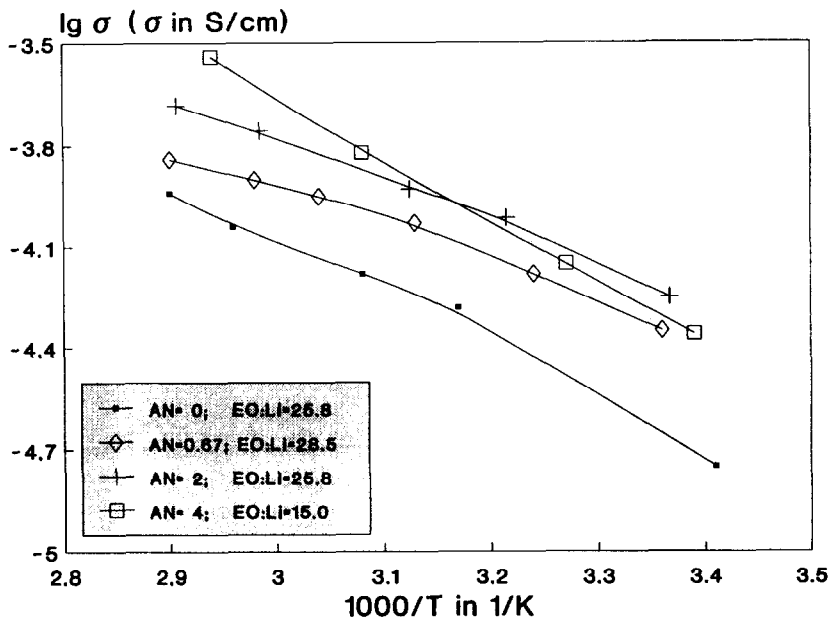


Fig. 5. Temperature vs. conductivity for cross-linked complexes at the optimum of salt concentration.

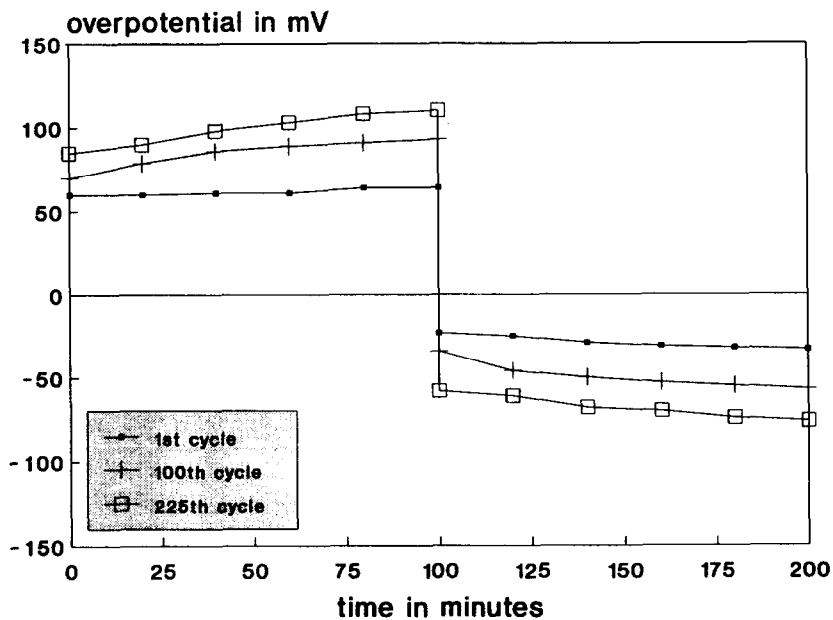


Fig. 6. Cycling curves for the cell Li/solid electrolyte/Li at room temperature (AN:TRGDMA=2 and EO:Li⁺=25.8); $i=0.015$ mA/cm², $q=0.1$ C/cm².

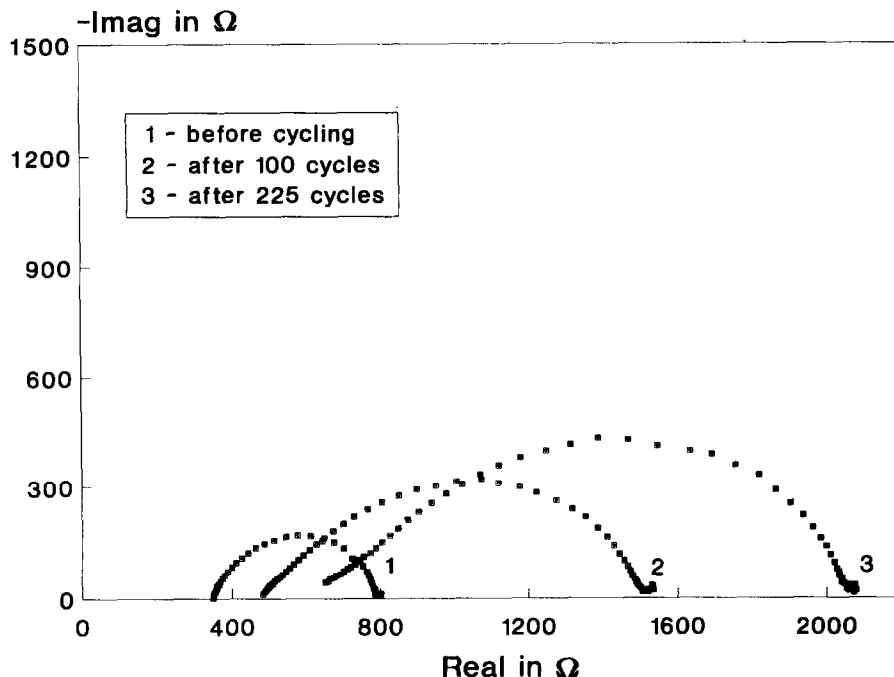


Fig. 7. Complex impedance plot for the cell Li/solid electrolyte/Li at room temperature (AN:TRGDMA=2 and EO:Li⁺ = 25.8).

Conclusions

The insertion of the highly polar AN into polyether-based network structures plasticized with PEGDME was found to enhance the conductivities of their complexes with LiCF₃SO₃ depending on the molar ratio of cross-linker to comonomer. However, one can imagine that the external plasticizer providing a liquid-like phase behaviour plays the main part in solvating the salt in the systems described in this paper.

References

- 1 D. Fish, I. M. Khan and J. Smid, *Macromol. Chem., Rapid Commun.*, **7** (1986) 115.
- 2 T. Steurich, H. Bischoff, B. Sandner and K. Wiesener, *Polym. Bull.*, **28** (1992) 355.
- 3 A. Killis, J. F. Le Nest, H. Cheradame and A. Gandini, *Macromol. Chem.*, **183** (1982) 2835.
- 4 R. Dupon, B. L. Papke, M. A. Ratner and D. F. Shriver, *J. Electrochem. Soc.*, **131** (1984) 586.
- 5 J. R. Mac Callum, A. S. Tomlin and C. A. Vincent, *Eur. Polym. J.*, **22** (1986) 787.
- 6 C. P. Hu and P. V. Wright, *B. Polym.*, **21** (1989) 421.
- 7 S. Rudolph, *Thesis*, Technical University of Merseburg, Germany, 1991, p. 16.