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Effects of Ion Pairs on Mass and Charge Transport in a Crosslinked Amorphous Polymer Electrolyte

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1. Introduction

Polymer electrolytes are solutions of salts in polymers with great potential for application in batteries and chemical sensors. Despite numerous studies related to ionic transport in polymer electrolytes the understanding of the underlying mechanisms is still not very satisfactory. In a recent study [1,2] by our group we showed that successful modeling of ionic migration processes requires not only the overall ionic conductivity resulting from electrical impedance measurements but also the tracer diffusivity of cations and anions individually. The present paper focuses on NaI dissolved in crosslinked PolyG 83-48 (Arch Chemicals) which is a trifunctional 4:1 EO/PO random co-polymer and fully amorphous at room temperature. Specifically, for $\mathrm{PolyG_{20}NaI}$ with an O-to-Na ratio of 20 the diffusivities of $^{22}\mathrm{Na}$ and $^{125}\mathrm{I}$ are compared with the ionic conductivity over a wide temperature range. It will be shown that neutral ion pairs play a major role in describing the significant features of the experimental data.

2. Experiments

Depth profiles of $^{22}\mathrm{Na}$ and $^{125}\mathrm{I}$ were measured by means of microtome sectioning after isothermal diffusion annealing in the temperature range from 23 to 120 °C, in which $\mathrm{PolyG_{20}NaI}$ is fully amorphous. Additional information was obtained by measurements of the dc electrical conductivity using impedance spectroscopy. To this aim the frequency-dependent impedance of $\mathrm{PolyG_{20}NaI}$ samples was recorded between –30 and 120°C using stainless steel electrodes.

3. Results and Discussion

Tracer diffusion coefficients of Na and I were obtained from Gaussian or erfc-type penetration profiles. Iodine was found to be faster than sodium by a factor of 9 to 4 upon going from low to high temperatures. The charge diffusivity deduced from the dc conductivity appeared to be close to the anion diffusivity. All individual sets of data reveal a pronounced Vogel-Tamann-Fulcher (VTF) behavior. It is further significant that the sum of the ion diffusivities exceeds the charge diffusivity. This feature can be explained by the occurrence of neutral ion pairs which contribute to mass transport but not to charge transport [3]. In particular, we are able to reproduce the experimental data within an ion migration model [1,2] which is based both on the formation of ion pairs and on the tight coupling of the ion mobility with the motion of the polymer segments. The latter property is reflected by the circumstance that the true diffusivity of all mobile species can be described by the same VTF parameters B and T_0. Specifically, we find that the diffusivity of single cations in $\mathrm{PolyG_{20}NaI}$ is very low, so that Na transport is effectively due to ion pairs only. On the other hand, charge transport is dominated by the single iodine ions.

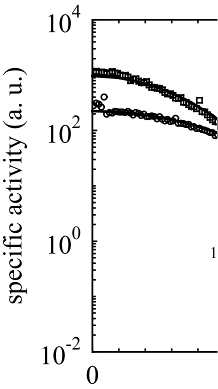

Fig. 1: Typical diffusion profiles of sodium and iodine resulting from radiotracer experiments.

3. Conclusions

This work contributes to the understanding of ion transport in polymer electrolytes. For PolyG$_{20}$NaI the results can be summarized as follows:

(i) Neutral cation-anion pairs contribute to mass transport but not to charge transport.

(ii) The diffusivities of ion pairs and single ions obey the same VTF temperature dependence.

(iii) Cation transport almost exclusively takes place in the highly mobile ion-pair configuration.

(iv) The true cation transference number is as low as 0.02 and independent of temperature.

(v) The fraction of ion pairs increases with increasing temperature according to a pair formation enthalpy of about 0.1 eV.

References

[1] N.A. Stolwijk, Sh. Obeidi, Phys. Rev. Lett., 93 (2004) 125901.
[2] Sh. Obeidi, B. Zazoum, N.A. Stolwijk, Solid State Ionics, 173 (2004) 77.
[3] P.G. Bruce, C.A. Vincent, Solid State Ionics, 40-41 (1990) 607.