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Measurement of Li^+ Ion Transport Numbers in Poly(ethylene oxide)–LiX Complexes

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ABSTRACT: The transport number for Li^+ ions in Poly(ethylene oxide)–LiX complexes was measured using a potentiostatic polarization technique. The results indicate that the Li^+ ion transport is strongly influenced by the salt concentration and the type of counter ions.

KEY WORDS Transport Number / Poly(ethylene oxide) / Salt / Polarization / Lithium /

Lithium ion conducting polymer materials are being intensively investigated in a number of research laboratories because of their potential use as solid electrolytes in high energy density solid state lithium batteries. The most widely used polymer has been based on poly(ethylene oxide) (PEO). The conduction mechanism in these polymer electrolytes has generally been assumed to be due to Li^+ ion transport from one lone pair site to another along the helical PEO strands. However, recent studies have shown that the Li^+ transport number is less than unity.[1-7]

The mechanism of ion transport in these polymer electrolytes remains an important issue and despite numerous studies its modus operandi therein is not well understood.

In a previous study,[8] it was found that the ionic conductivity of the PEO–LiX system was strongly influenced by the salt concentration and anion type. A model was proposed whereby the decrease in the ionic conductivity with increasing salt concentration was due to ion-pair formation. In addition, there was an empirical relationship between the anion size and conductivity. The present study involving the measurement of transport numbers of the cations and anions in these polymer electrolytes was undertaken to clarify some of the addressed issues.

A number of methods have been used to measure the transport number of Li^+ ions in polymer electrolytes with quite diverse results. This may be due to the technique not being sound for this type of electrolyte. The transport of cations and anions through the electrolyte involves a number of parameter changes, *viz*, ionic mobility of cations and anions, conductivity of electrolyte, cation–anion interactions, and motions of PEO molecules in the electrolyte. These parameters vary for different salt concentrations, temperature and molecular weight of the PEO electrolyte. Hence it is not surprising to find that conventional methods of measuring transport numbers in such polymer electrolytes appear to be inapplicable. The use of dilute solution theory to explain ion transport phenomena is inadequate for such complex systems. In addition, concentrated solution theory is not well developed for polymer electrolytes. Until these phenomena are better understood, a compromise has to be made on the measurement techniques.

Clearly the classical Tubandt method is unsuitable because at elevated temperatures, the electrolyte layers fuse to one another. More recently, a.c. impedance techniques have been used to determine the transport number of the lithium cation in polymer electrolytes. This is carried out in the diffusion region at very low frequencies (<1 Hz). At such low frequencies, the techniques reduce to one involving potentiostatic polarization described by Shriver *et al.*[9] It is not unreasonable, thus, to obtain comparable results using the two techniques.[10] The method developed by Shriver relies solely on the initial and final state and any intermediate state is ignored.

This technique was used in this paper to determine the transport number of lithium ions in PEO–LiX electrolytes and the results discussed in relation to ion transport phenomena.

EXPERIMENTAL

The preparation of the polymer electrolyte films using five different salts and six different PEO–LiX compositions have been described elsewhere.[8] The salts under study were $LiCF_3SO_3$, $LiAlCl_4$, $LiAsF_6$, $LiBF_4$, and $LiPF_6$ and the PEO–LiX concentrations were 50:1, 25:1, 8:1, 4:1, 2:1, and 1:1. All subsequent handling of the films and cell manipulation were carried out in the glove-box.

A two electrode cell, reversible to one of the ions in the electrolyte (namely Li) was used to determine the transport number (Figure 1). A constant voltage of 50 mV was applied across the cell and the current flow measured as a function of time. Under the applied load, cations migrate to the negative electrode and anions to the counter electrode. This leads to a salt concentration gradient across the electrolyte. As the cell polarizes, a depletion of salt concentration results near the negative electrode with concurrent increase near the positive electrode. The current decreases to a steady state when the back emf created by the concentration gradient exactly opposes the applied potential. A plateau results in the I-t curve since cations are now the only species carrying the current. The ratio of the steady state current to the initial current gives the transport number for the cation. The initial current was calculated from the total cell impedance determined by a.c. methods (using stainless steel blocking electrodes) and the applied d.c. potential. It is important that blocking electrodes are used to obtain the electrolyte impedance since the use of lithium non-blocking electrodes may very well lead to the formation of a passive film *via* the a.c. perturbation signal. This passive film may ultimately interfere with the subsequent transport number measurement. In some cases measurements were made using three different thicknesses of electrolytes to determine the variability in the result. The temperature range studied was 70—120°C.

RESULTS AND DISCUSSION

A typical variation in the cell current with time under an applied d.c. potential is shown in Figure 2. At high potentials (100 mV—1 V) current values were not "steady" probably

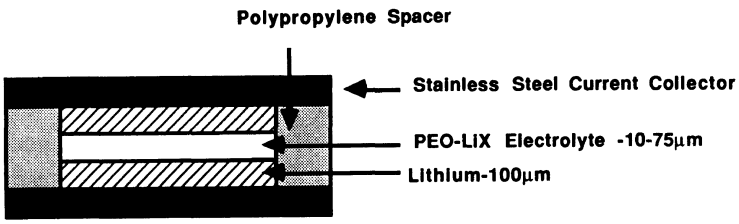

Figure 1. Schematic of the polarization cell.

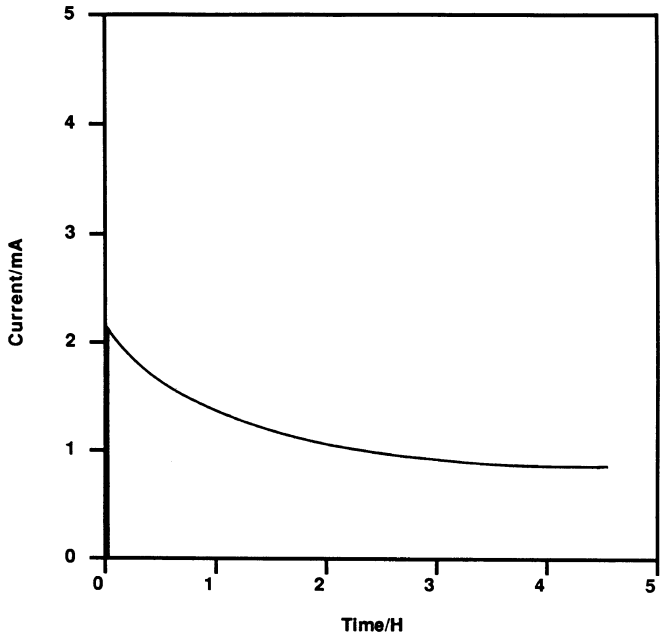

Figure 2. Typical variation in the cell current with time; *e.g.*, 8 : 1 PEO–$LiCF_3SO_3$ at 100°C.

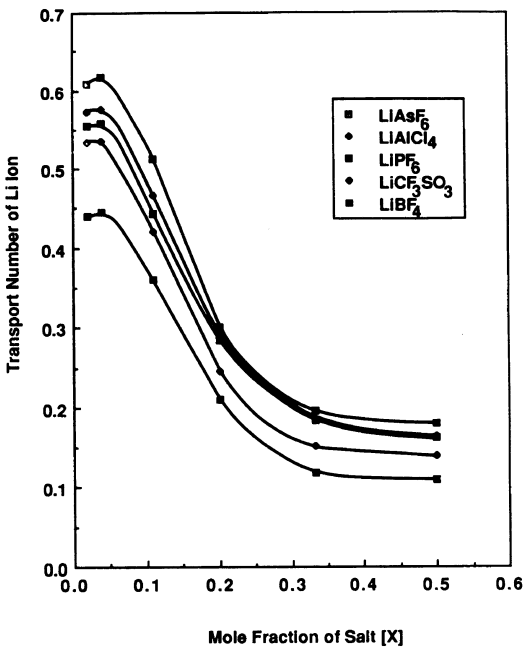

Figure 3. Variation in the Li transport number with mole fraction of salt.

because concentration polarization prevailed over steady state.

Figure 3 shows the variation in the transport number of the Li^+ cation against concentration of various lithium salts in PEO at 100°C. As shown, the transport number changes dramatically with composition. During the potentiostatic polarization, the composition gradient means that the transport number across the cell varies. We observe an "averaged" value. At low salt concentration, the transport number values are high indicating a high degree of solvation of the Li^+ cation by the oxygen lone pairs of electrons from the PEO. As the salt concentration in PEO increases, the number of lithium ions occupying the lone pairs increases until saturation is reached. This corresponds to an increase in the transport number value indicated by a maximum on the curve. Further increase in salt concentration results in a decrease in transport number. This suggests the formation of ion-pairs. As the number of free PEO segments decreases, the subsequent formation of ion-

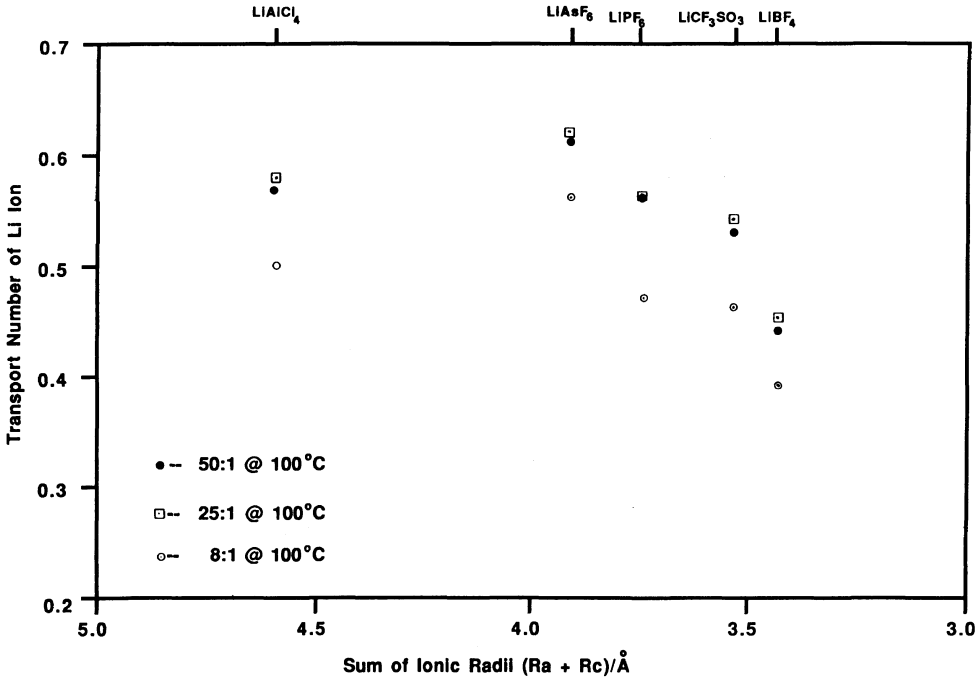

Figure 4. Variation of Li transport number with ionic radius of salts.

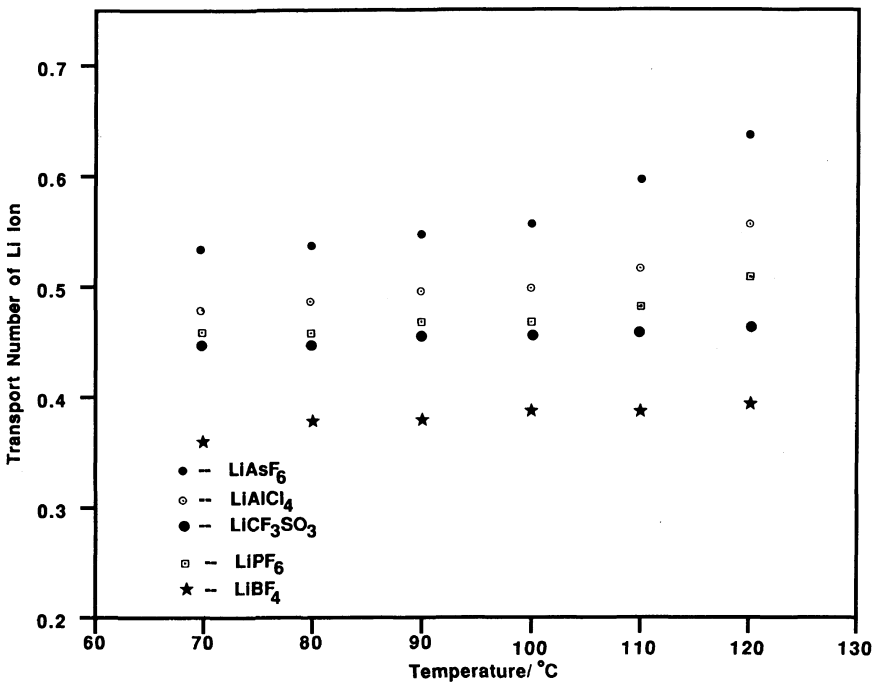

Figure 5. Variation of Li transport number with temperature for PEO–LiX system.

pairs hinders the motion of Li^+ ions, resulting in a decrease in the ionic mobility of Li^+. These results are in excellent confirmation with the a.c. conductivity data which suggest a decrease in the ionic conductivity of the polymer electrolyte with increasing salt concentration. Furthermore, the presence of a crystalline phase in the PEO–LiX salt systems significantly interferes with the evaluation of the glass transition temperature and so its effect on the conductivity cannot be assessed accurately. The constancy in the values of the transport number at the higher salt concentration range suggest the formation of multiplets.

Figure 4 shows the variation in the transport number of the Li^+ ion *versus* the sum of the ionic radius[8] of the cations and anions for the various salts under study at 100°C. The trend is as expected with the transport number value being highest for the $LiAsF_6$ salt. Since the energy required to separate the ions is proportional to the inverse of their ionic radii, considerably less ionic interaction takes place in the case of the larger AsF_6^- anion. Beyond this size, it is believed that steric hindrance dominates which introduces strong electrostatic repulsive forces among the Li^+ ions thus reducing its mobility.

Figure 5 shows the variation of Li^+ transport number with temperature in various PEO–LiX electrolytes at a fixed O : Li concentration of 8 : 1. In the case of the PEO–$LiAlCl_4$, PEO–$LiAsF_6$ and PEO–$LiPF_6$ system, the transport number was found to increase somewhat with temperature. In the other two systems investigated the transport number was found to be temperature independent. The dependence on temperature suggests that the activation energy for cation transport is greater than for anion transport. This probably results because the cation-anion interaction is considerably less due to the larger anion size. It follows that the mobility of the cation is relatively higher than that of the anion.

In the case of smaller anions such as $CF_3SO_3^-$ and BF_4^-, the cation-anion interaction is much larger and the mobility of the cation approaches that of the anion. This suggests that the activation energy for cation and anion transport are about the same. This leads to a curve which is temperature independent.

Table I. Variation in the transport number of Li^+ against electrolyte thickness

System		Electrolyte thickness/μm	Transport number at 100°C
8 : 1	PEO–$LiAlCl_4$	15	0.50
8 : 1	PEO–$LiAlCl_4$	32	0.49
8 : 1	PEO–$LiAlCl_4$	60	0.50
8 : 1	PEO–$LiAsF_6$	18	0.56
8 : 1	PEO–$LiAsF_6$	33	0.54
8 : 1	PEO–$LiAsF_6$	49	0.54
8 : 1	PEO–$LiPF_6$	12	0.47
8 : 1	PEO–$LiPF_6$	16	0.47
8 : 1	PEO–$LiPF_6$	37	0.48
8 : 1	PEO–$LiCF_3SO_3$	8	0.46
8 : 1	PEO–$LiCF_3SO_3$	23	0.45
8 : 1	PEO–$LiCF_3SO_3$	56	0.46
8 : 1	PEO–$LiBF_4$	7	0.38
8 : 1	PEO–$LiBF_4$	19	0.37
8 : 1	PEO–$LiBF_4$	28	0.40

The above observations are consistent with the model proposed in an earlier study. The transport number of the Li^+ ion was also determined using three electrolyte thickness. The results shown in Table I suggest that in the range studied, the transport number is independent of thickness.

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