Electrochemical measurement of transference numbers in polymer electrolytes

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Electrochemical methods for the determination of transference numbers in polymer electrolytes are considered and a new technique which overcomes some of the problems associated with other methods in current use is described. Results are given of measurements of the transference numbers of lithium and trifluoromethanesulphonate ions in poly(ethylene oxide) at 90°C. A mean value of 0.46 ± 0.02 is reported for lithium.

(Keywords: transference number; transport number; polymer electrolyte; poly(ethylene oxide); lithium cell; electrochemistry)

INTRODUCTION

Polymer electrolytes are defined as ionic conductors formed by dissolving salts in suitable high-molecular-weight polymers, such as the polyethers, poly(ethylene oxide) or poly(propylene oxide)[1,2]. True polymer electrolytes contain no low-molecular-weight solvent and have ionic conductivity which is related to the segmental motion in amorphous regions of the polymer host. In recent years there have been numerous studies of the electrical characteristics of such phases, including measurements of the conductivity as a function of salt concentration, host molecular weight, temperature, pressure and the frequency of the electrical perturbation. Theoretical models for the conductivity mechanism have been proposed[3]. Despite this activity it is still unclear what actual species are involved in carrying the electric charge; it has even proved difficult to establish reliably the fractions of current carried by cationic and anionic constituents. Electrochemical methods and measurements of diffusion coefficients (e.g. by pulsed field gradient n.m.r. techniques) have been used to try to answer this question. However, it has been suggested[2] that under certain conditions—such as where the electrolyte contains a significant concentration of ion pairs—these two techniques may provide information that is not directly comparable. In this paper the electrochemical methods so far used to determine transference numbers in polymer electrolytes are briefly reviewed, and a new method is described in detail which gives reproducible and reliable values even at low temperatures where other techniques are difficult to apply.

For an electrolyte which dissociates to give a single cationic and anionic species, the electric transport number, t_+ say, is defined as the number of faradays of charge carried by the cations across a reference plane (fixed relative to the solvent) when a total of one faraday of charge passes across the plane[4], i.e.:

$$t_+ = i_+/(i_+ + i_-) = i_+/i \tag{1}$$

where i_+ and i_- are the partial currents carried by cations and anions respectively, and i is the total current. While such a definition can be generalized to cover the situation where complex ions exist, it is not of any practical value in situations where there is a fast dynamic equilibrium between the complex ions and their constituents.

Consider a salt M^+A^- dissolved in a polymer host of low relative permittivity. Then a series of equilibria are likely to exist in which associated species are formed, e.g.:

$$M^+ + A^- \rightleftharpoons MA \tag{2}$$

$$M^+ + MA \rightleftharpoons M_2A^+ \tag{3}$$

$$A^- + MA \rightleftharpoons MA_2^- \tag{4}$$

Thus the cation constituent M is carried towards the cathode by M^+, M_2A^+, M_3A^{2+}, ..., and towards the anode by A^-, MA_2^-,... The only quantity that can be measured experimentally is the difference between the fluxes of M-containing species directed towards the cathode and anode, i.e. the net number of moles of M being transferred in one direction. The transference number T_+ is defined as the *net* number of faradays of charge carried across the reference plane by the cation constituent in the direction of the cathode, during the passage of one faraday of charge across the plane[4].

In conventional electrolyte solutions, experimental techniques such as the moving-boundary method have been developed to allow almost routine determination of transference numbers with great accuracy. For polymer electrolytes these standard techniques are either inapplicable or usable only with great difficulty, so that a

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number of alternative methods have been studied[5-10]. So far no method has become well established and there is considerable disagreement over the values of transference numbers so far reported. The Tubandt method[11] is the technique most commonly applied to conventional solid electrolytes. It is directly based on Faraday's laws and requires weight variations in the electrolyte regions near the two cell electrodes, caused by the passage of a known amount of charge, to be measured. It is difficult to apply this method to polymer systems because of the requirement to maintain the electrolyte as a series of non-adherent thin sections. Cheradame and coworkers[5] were able to carry out this experiment for highly crosslinked networks where the electrolyte could readily be separated into its component sections after the passage of current. Armand *et al.*[8] developed a technique based on the measurement of the e.m.f. of a concentration cell formed by contacting two previously thermally equilibrated half-cells. This method is experimentally difficult and has the disadvantage of requiring knowledge of the variation of salt activity with concentration. Perhaps the most popular technique for transference number measurements in polymer electrolytes is that developed first by Sørensen and Jacobsen[7] using an analysis of the a.c. impedance of a cell with two electrodes, each non-blocking with respect to the cation. The method is based on the theory for the response of such a cell to a small-signal a.c. perturbation developed by MacDonald[12]. Here it was shown that at low frequencies the current flowing through such a cell is affected by concentration gradients near the electrodes which gave rise to a characteristic feature due to a diffusional impedance in the complex plane. One of the problems of this technique is that it can be applied to polymer electrolytes only at very high temperatures since in general the frequencies required to show the diffusional part of the impedance are too low to be of practical use. There have been further criticisms[13] of this method when used for certain lithium-based polymer electrolytes, where interpretation of the complex impedance plot becomes uncertain.

STEADY-STATE CURRENTS

If a cell of the form

M | MX–polymer host | M

is polarized by the application of a small, constant potential difference between the electrodes, the initial current, the value of which is determined in the absence of electrode effects by the conductivity of the electrolyte, is found to fall with time until a steady-state value is eventually observed. In the simplest case, this fall in current is due to the establishment of a concentration gradient across the cell which is responsible for

(i) reducing and finally stopping net motion of anionic species,

(ii) generating an e.m.f. which acts in the opposite direction to the applied field and thus reduces the migration current of cations and anions, and

(iii) increasing the motion of the cations in the direction of the field to compensate for the reduction in the migration current.

The behaviour of such cells has been analysed in detail by Bruce and Vincent[14], who showed that under defined circumstances,

$$T_+ = I^s/I^0 \tag{5}$$

where I^s and I^0 are the steady-state and initial cell currents respectively. This relationship is only strictly valid for ideal electrolytes in simple cells where there is no convection and where the polarization voltage is vanishingly small. In practice it was demonstrated that useful information can be obtained for real electrolytes, and that the error introduced by using polarization voltages of up to 10 mV was acceptable. It was also shown that equation (5) was invalid where the electrode kinetics were not gast, or when resistive layers were present on the electrode surfaces.

The steady-state current method has been used by Blonsky *et al.*[9] to determine transference numbers in poly(alkoxyphosphasene) polymer electrolytes based on silver and zinc trifluoromethanesulphonate and for a range of lithium and sodium salts in poly(ethylene oxide) and poly(ethylene succinate)[15]. It is not clear whether these workers made any allowance for electrode effects which may significantly affect the potential distribution and the current flowing in such cells and hence significantly affect the determination of the transference number.

We now describe a technique in which a combination of d.c. and a.c. electrical polarizations are used to enable transference numbers of polymer electrolytes to be determined in a straightforward manner, even in circumstances where the diffusion coefficients of the ionic species are low or where precise correction for passivating layers or slow electrode kinetics are required.

EXPERIMENTAL

All operations were carried out in an argon-filled glovebox with water content lower than 2 ppm.

Polymer electrolyte was prepared from poly(ethylene oxide) (PEO) of average molecular weight 4×10^6 (BDH Ltd) and lithium trifluoromethanesulphonate (3M UK Ltd) to give a $-CH_2CH_2O-$ to lithium ratio of 9:1. The solvent-free method previously described[16,17] was used to produce 13.0 mm diameter electrolyte discs of uniform thickness between 150 and 200 μm.

Lithium electrodes 10.7 mm in diameter were punched from ribbon (Alfa Products), and Li | PEO–$LiCF_3SO_3$ (9:1) | Li cells were assembled in the holder shown in *Figure 1a* (an expanded view of the central section, not to scale, is shown in *Figure 1b*). The cell assembly was sealed in a glass tube with tungsten breakthrough contacts and a NiCr/NiAl thermocouple which was located close to the electrolyte. The tube was placed in a miniature oven (Buchi TO-50) which was thermostatted to 90±0.5°C.

Electrochemical measurements were performed using a Solartron 1286 interfaced to a frequency response analyser (Solartron 1250) under the control of a dedicated microcomputer (Hewlett–Packard 9000/216).

RESULTS AND DISCUSSION

Cells were first equilibrated for 3 h at 90°C prior to measurement of the complex impedance as a function of frequency from 1 Hz to 65 kHz using an a.c. signal of

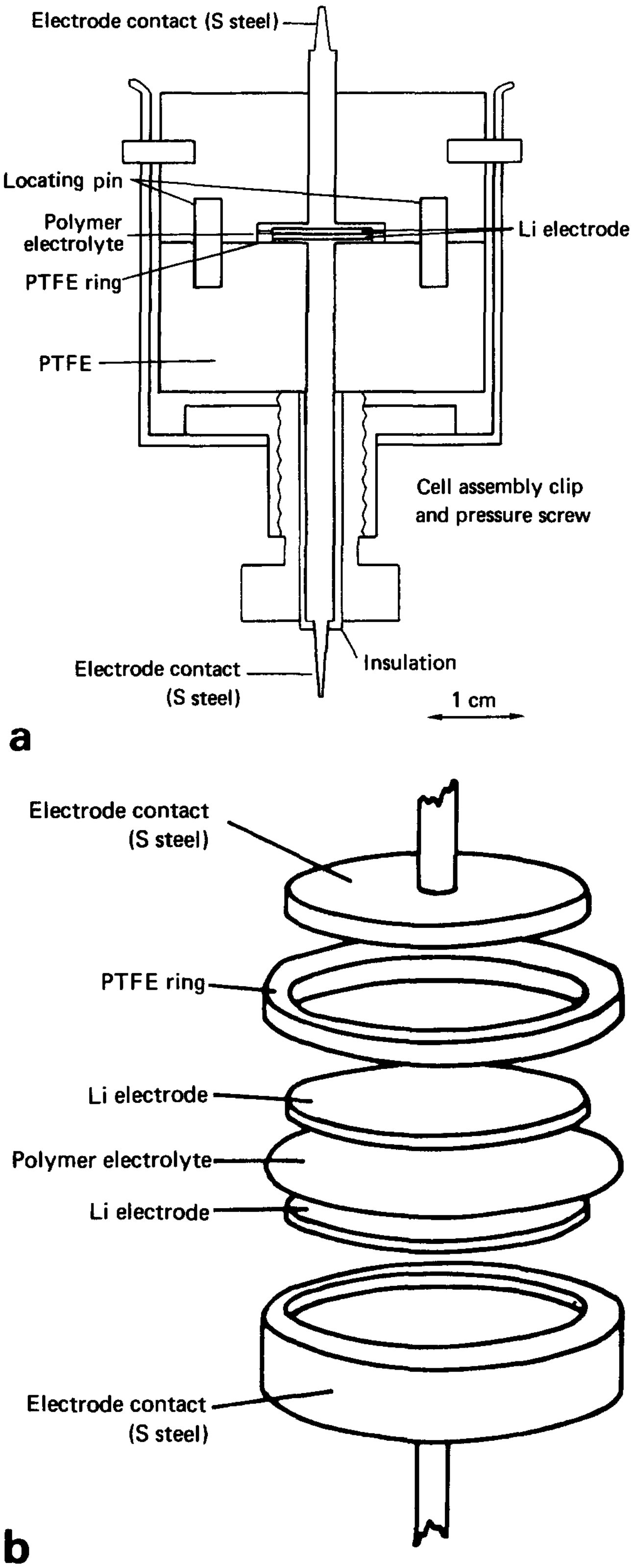

Figure 1 (a) Cross-section of cell assembly. (b) Schematic expansion of central section of cell assembly

10 mV peak-to-peak. The results, when plotted on the complex plane (*Figure 2*), were consistent with the equivalent circuit shown, where R_1 and C_1 are associated with passivating films formed on the electrode (first reported by Fauteux[13]), and R_2 corresponds to the resistance of the electrolyte. A d.c. bias of 10.0 mV was now applied to the cell, and the response of the cell current was monitored with respect to time until a steady-state current was reached (*Figure 3*). In a number of experiments the a.c. impedance was monitored at various times during the course of the d.c. polarization by applying the a.c. perturbation on top of the d.c. level. The a.c. impedance was measured in all experiments when the steady-state current had been reached.

The cells were now left at open circuit for 80–110 h to permit the concentration gradients to disperse, prior to the polarization procedures being repeated to test the method further.

The fall in current from $t = 0$ until the steady-state value was reached is considered to result from two processes:

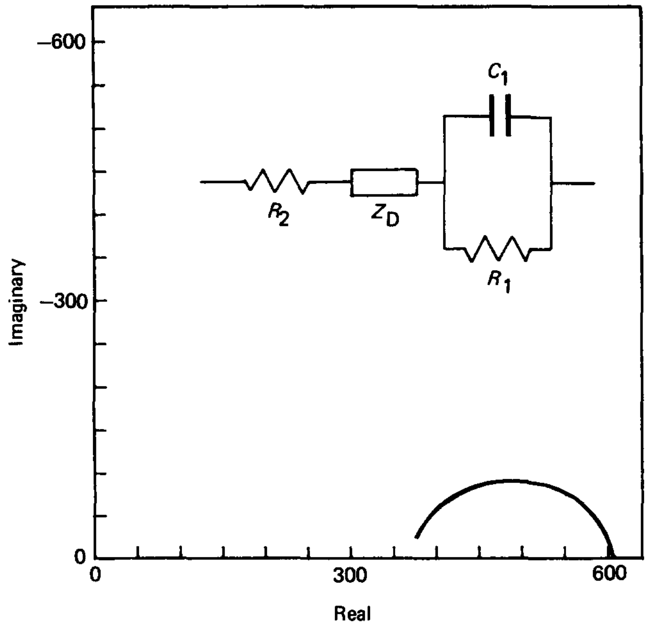

Figure 2 Typical complex-plane plot of the a.c. impedance of a Li | PEO–LiCF$_3$SO$_3$(9:1) | Li cell at 90°C, with inset equivalent circuit. The frequency range of 1 Hz–65 kHz was too high for Z_D to appear on the plot. C_1 = capacitance associated with resistive electrode layer; R_1 = resistance associated with electrode layer; Z_D = diffusion impedance; R_2 = electrolyte impedance

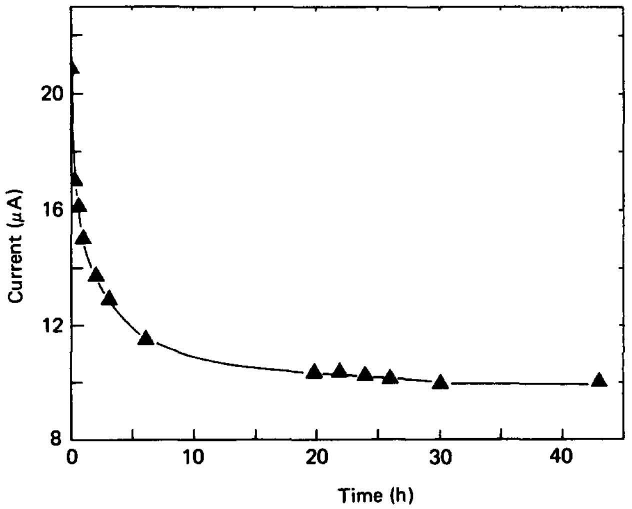

Figure 3 Variation of current with time during polarization of a Li | PEO–LiCF$_3$SO$_3$ (9:1) | Li cell at 90°C, with total applied potential difference of 10 mV

(i) the growth at the electrodes of passivating layers to a limiting thickness (which occurs whether or not a current is flowing), and

(ii) the establishment of a concentration gradient in the electrolyte which affects the motion of the ions.

With the lithium trifluoromethanesulphonate electrolyte the passivating layers were found to increase in resistance over the first 24 h after the cell was assembled and raised to 90°C. The effect of the growth of these layers was seen when the a.c. impedance was monitored intermittently during the d.c. polarization (*Figure 4*). After about 30 h no further significant change with time was found for the a.c. impedance.

Bruce and Vincent[14] showed that for small amounts of polarization, and neglecting ion–ion electrostatic interactions, the initial and steady-state currents are given respectively by

$$I^0 = \Delta V/(R_1^0 + R_2) = \Delta V/(R_1^0 + k/\sigma) \tag{6}$$

and

$$I^s = \Delta V/(R_1^s + k/T_+\sigma) \tag{7}$$

where ΔV is the potential applied across the cell, k is the cell constant, T_+ is the cationic transference number, σ is the (d.c.) conductivity of the electrolyte, R_1^0 and R_1^s are the initial and steady-state resistances of the passivating layers, and I^0 and I^s are the initial and steady-state currents. From equation (6)

$$\sigma = I^0 k/(\Delta V - I^0 R_1^0) \tag{8}$$

Hence from equations (7) and (8)

$$T_+ = \frac{I^s(\Delta V - I^0 R_1^0)}{I^0(\Delta V - I^s R_1^s)} \tag{9}$$

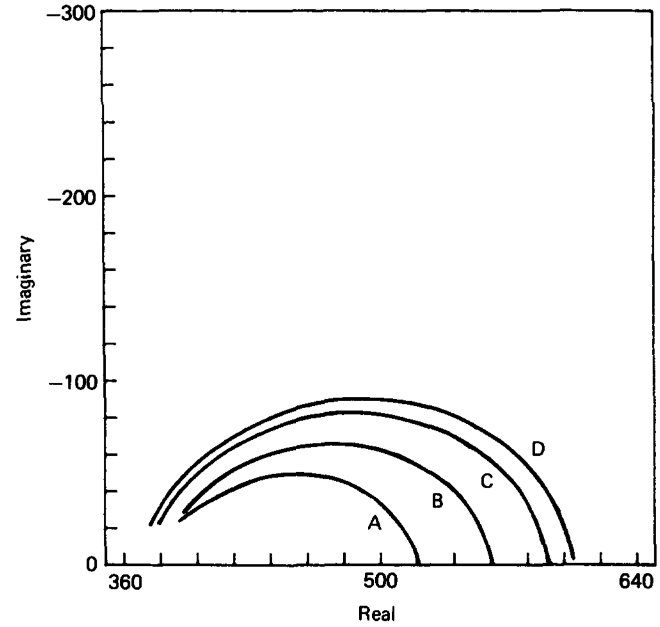

Figure 4 Complex-plane plot (1 Hz–65 kHz) of the a.c. impedance of a Li | PEO–LiCF$_3$SO$_3$ (9:1) | Li cell at 90°C, polarized with a potential difference of 10 mV: curve A, $t=0$ h; B, $t=6$ h; C, $t=20$ h; D, $t=43$ h

The results of six polarization experiments using three different cells are given in *Table 1*. The value of T_+ was found to be 0.46 ± 0.02. Results from subsequent polarizations of the same cell had a deviation of 0.01 or less.

A number of points may be made. First, equating T_+ with I^0/I^s gives rise to a very large and variable error—a value of 0.61 was calculated in one case. Secondly, the method is quite general and may be applied in situations where the electrodes behave differently. For example with LiClO$_4$-based electrolytes we have found that the small impedance associated with a rather different passivating layer shows a decrease in resistance as current is passed. Finally, provided that the passivating layer has been fully established, as in our second polarization experiments, a steady-state current can be established in under 12 h (*Figure 5*). It must be emphasized, however, that even

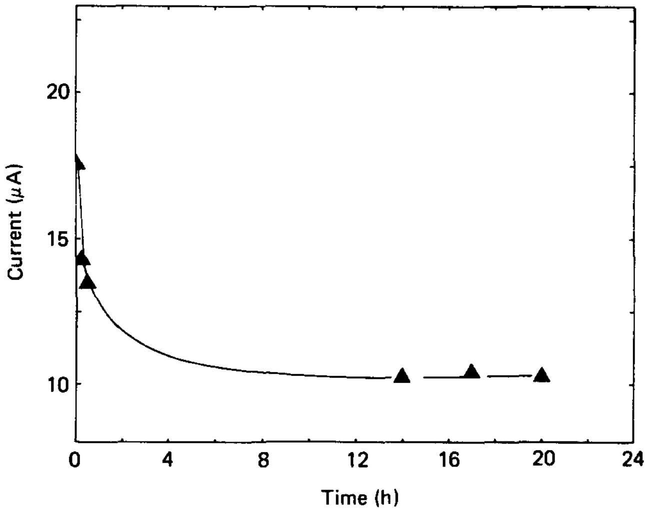

Figure 5 Variation of current with time during polarization of a Li | PEO–LiCF$_3$SO$_3$ (9:1) | Li cell at 90°C, with total applied potential difference of 10 mV, after establishment of invariant resistive electrode layer

Table 1 Calculation of transference numbers from analysis of polarization experiments

Cell	Polarization time (h)	ΔV (mV)	R_1^0 (Ω)	R_1^s (Ω)	I^0 (μA)	I^s (μA)	T_+
1	70	10.0	156	250	20.00	10.15	0.47
1 (after 95 h recovery)	24.5	10.0	243	250	17.54	10.78	0.48
2	43	10.2	150	249	21.00	10.10	0.44
2 (after 112 h recovery)	24	10.2	246	244	17.57	10.18	0.44
3	45	10.2	136	197	19.93	10.42	0.48
3 (after 81 h recovery)	27.5	10.2	209	213	17.51	10.10	0.47

where R_1 does not vary during the experiment, it is still necessary to determine its value from an a.c. analysis in order to calculate T_+.

CONCLUSIONS

By determining the a.c. impedance as a function of frequency of a symmetrical cell of the type

$$\mathrm{M} \mid \mathrm{MX\text{–}polymer\ host} \mid \mathrm{M}$$

before polarization with a small d.c. bias, and after a steady-state current has been reached, it is possible to make allowance for electrode effects and hence make reproducible measurements of the transference number of the polymer electrolyte. The method has been tested with a 9:1 PEO–$LiCF_3SO_3$ electrolyte at 90°C, where T_+ was found to be 0.46 ± 0.02. Further measurements will be reported in which transference numbers have been measured for other electrolytes and under various conditions. We are also currently engaged in a study of transference number as a function of concentration in a completely amorphous polymer electrolyte system.

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