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Potentiometric measurements of ionic transport parameters in poly(ethylene oxide)–LiX electrolytes

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An electrochemical technique based on concentration cell e.m.f. measurements is used to determine the lithium transference number and diffusion coefficient in poly(ethylene oxide)–lithium salt complexes. Measurements were carried out at 90° C on PEO–LiI, PEO–$LiClO_4$ and PEO–$LiCF_3SO_3$ electrolytes. According to the phase diagram of the PEO–lithium salt system these complexes are fully amorphous at 90° C. Accurate determination of t_{Li^+} by the e.m.f. concentration cell method generally requires knowledge of the mean salt activity coefficients. However, this becomes unnecessary when the two electrolyte concentrations differ only slightly. As a first step the mean salt activity coefficient was estimated using a galvanic cell of the lithium/PEO–LiX/MX_n/M type with $M^{n+} = Ag^+$ or Pb^{2+} and $X^- = I^-$ or $CF_3SO_3^-$. The resulting lithium transference numbers are 0.34 for the PEO–LiI complex and 0.7 for PEO–$LiCF_3SO_3$. Discrepancies between the t_{Li^+} values can be explained by the formation of triplets in the PEO–$LiCF_3SO_3$ electrolyte. By recording concentration cell potential versus time and comparing with theoretical curves, the salt lithium diffusion coefficient was obtained. D_{LiI} was found to be around $4 \times 10^{-8}\,cm^2\,s^{-1}$ in PEO–LiI and $8 \times 10^{-8}\,cm^2\,s^{-1}$ in PEO–$LiCF_3SO_3$ at 90° C. These results suggest a liquid-like behaviour for the microscopic transport mechanism.

1. Introduction

Poly(ethylene oxide)–alkali metal salt complexes are at present considered as promising electrolytes in advanced, high specific energy batteries. The feasibility of solid state cells involving thin polymer films has been demonstrated [1–3]. Much effort is now devoted to the determination of the respective cation and anion mobilities of these electrolytes. It is accepted that PEO complexes are pure ionic conductors, based on work by Rigaud [4] and Dupon *et al.* [5] indicating that electronic conductivity is negligible. The existence of an oxidation wall on cyclic voltammograms of PEO complexes [6] in earlier studies suggested an anionic mobility. This result was much clearer in radioactive tracer diffusion experiments [7]. A quantitative determination of the cationic transference number is, however, difficult due to the visco-elastic nature of these materials. This explains the wide variety of methods used over recent years, as shown in Table 1.

Quoted values of the cationic transference number vary widely for the same complex. These discrepancies are probably related to validity problems and limitations concerning the various methods, a subject which has not been adequately discussed. The first t_{Li^+} determination was that of Chabagno [6]. This was based on NMR T_2 relaxation time measurements and was calculated from the Nernst–Einstein relation. This is theoretically valid if the mobile species are independent and not interrelated by a chemical equilibrium. Furthermore, as shown later, the complex is not fully single-phase at this temperature.

An a.c. complex impedance analysis [8, 9] may also be used with a homogeneous electrolyte. However, at low frequencies a salt concentration arises involving the nucleation of a non-conducting crystalline complex in the vicinity of

Table 1. Extended lithium transference number in PEO–lithium salt complexes published in the literature

PEO nature[9]	*Salt*	*O/Li range*	*Method*	*Temperature range (°C)*	t_{Li^+} *range*	*Reference*
L	$LiCF_3SO_3$	4.5	NMR lithium	25	0.87	[6]
L	LiSCN	4.5	a.c. complex impedance analysis	20–170	0.54	[8]
L	$LiClO_4$	8	a.c. complex impedance analysis	110–130	0.25	[9]
L	$LiCF_3SO_3$	16	Chronoamperometry	85–125	0.1–0.35	[10]
C	$LiClO_4$	8.59	Tubandt	70–120	0.19–0.37	[11]
L	$LiCF_3SO_3$	4	d.c. polarization	100	0.56	[12]
C	$LiClO_4$	10–100	d.c. polarization	50	0.5	[13]
L	$LiClO_4$	6, 8, 20	Pulsed magnetic field gradient	50–120	0.17–0.29	[14]
L	$LiCF_3SO_3$	8	Pulsed magnetic field gradient	155–175	0.34–0.40	[15]

[a] L = High molecular linear poly(ethylene oxide); C = low molecular cross-linked poly(ethylene oxide).

the anode. The equivalent circuit model proposed by Sorensen and Jacobsen does not take this into account. In addition the model does not include the so-called solid electrolyte interphase recently shown with PEO–LiX electrolytes [15].

Tubandt's method cannot be applied easily to uncross-linked high molecular PEO electrolytes because of difficulties in separating the films after experiments. Cross-linked, PEO-based electrolytes do not adhere to one another. Tubandt's method is therefore of value [11] if the nature of the electrode reactions and the charge carriers has been clearly determined.

Chronoamperometry [10] and d.c. polarization [12] methods also suffer from the phase heterogeneity of PEO complexes, so that diffusion equations may not easily be used.

The method proposed by Watanabe *et al.* [13] is based on d.c. polarization of a lithium polymeric solid electrolyte/stainless steel cell. The ratio between the amount of lithium deposited and the total charge passed through the cell supposedly leads to the apparent transport number of the lithium ion. We do not, however, agree with this principle for t_{Li^+} measurements. An ionic transference number refers to the number of farads carried by an ion across a fixed reference plane when one farad passes through this plane. The determination of t_{Li^+} therefore requires the measurement of intrinsic electrolyte properties such as ionic conductances, ionic diffusion coefficients or ionic concentration variations. The amount of lithium deposited on the cathode does not represent the charge carried by lithium ions; it simply verifies Faraday's law. The t_{Li^+} result should therefore always be unity with this method. We interpret the discrepancies in t_{Li^+} values as being due to the nature of the cathode which is not a real ion blocking electrode or to residual water or solvent in the electrolyte.

The pulsed field magnetic gradient (PFMG) method [14, 15] is very attractive. This technique accounts for the nuclei of both ions and neutral species, since the magnitude of all nuclear spin echoes is measured. Therefore, the diffusion coefficient measured has a global significance.

In summary these methods may be classified as either 'perturbing' and 'non-perturbing' methods according to the magnitude of the perturbation energy as compared to the thermal activation energy. The 'perturbing' approaches include d.c. polarization, chronoamperometry, a.c. complex impedance analysis and Tubandt's method. In these methods a concentration gradient is created by the ion balance, leading to the mean t_{Li^+} value. The 'non-perturbing' methods are based on diffusion measurements either with labelled ions [16] or by the PFMG technique. Since the diffusion coefficients measured describe the ionic free diffusion in a homogeneous medium, comparison with other results from the so-called perturbing methods is possible provided the thermodynamic factor is unity and no ion–ion interactions occur.

This paper reports measurements of e.m.f. concentration cells in order to determine the lithium transference number and the salt diffusion coefficient in PEO–LiX electrolytes.

2. Theory

The following concentration cells with PEO electrolytes were used:

$$\mathrm{Li/PEO}_m\text{–LiX/PEO}_n\text{–LiX/Li} \quad \text{(type 1)}$$

where m and n represent the conventional O/Li ratio. Hereafter, m is assumed higher than n.

The cell potential depends on the junction potential created when the two electrolytes are in contact [17]. This potential arises from the unequal cation and anion mobilities. The expression of the steady-state junction potential between regions of two different activities can be obtained either by a classical thermodynamic procedure [18] or by irreversible linear process thermodynamics [19].

In the present case, if only two ionic species are assumed to be mobile, the steady-state junction potential is expressed by

$$E_\mathrm{j} = \frac{RT}{F}\int_{a(m)}^{a(n)} (1 - 2t^-)\mathrm{dln}\, a\pm \qquad (1)$$

where $a\pm$ is the mean salt activity, $a(m)$ and $a(n)$ are the mean salt activities in PEO_m–LiX and PEO_n–LiX, respectively, and t^- is the anionic transference number.

As the ionic diffusion coefficient is in the range 10^{-7} to $10^{-9}\,\mathrm{cm^2\,s^{-1}}$ in the amorphous region [7, 19, 20], it is reasonable to assume that the steady-state starting potential is equal to the cell e.m.f. as long as the experimental set-up is correctly designed (see Experimental section). This e.m.f. is then of the following form:

$$E_\mathrm{cell} = \frac{2RT}{F}\int_{a(m)}^{a(n)} t^-\,\mathrm{dln}\, a\pm \qquad (2)$$

and consequently

$$t^- = \frac{F}{2RT}\frac{\mathrm{d}E_\mathrm{cell}}{\mathrm{dln}\, a\pm} \qquad (3)$$

Thus, calculation of t^- requires measurements of both the concentration cell e.m.f. and the mean salt activity under the same conditions. However, if PEO–LiX is assumed to behave ideally, the mean salt activity coefficient can be neglected and t^- is given by the relation

$$t^- = \frac{F}{2RT}\frac{(E_1 - E_2)}{\ln (M_1/M_2)} \qquad (4)$$

where M is the salt molality and the indices refer to two different salt concentrations.

3. Experiment details

3.1. *Materials*

All experiments and polymer film preparations were performed in an argon dry box. Poly(ethylene oxide) with an average molecular weight of 5 000 000 was obtained from Aldrich. Lithium iodide (Merck) was ground and dried in a vacuum (1 Pa) at 200° C for 2 days. Lithium perchlorate (F. Smith) was vacuum dried at 140° C for 24 h. Lithium trifluoromethane sulphonate was prepared by a stoichiometric reaction between $\mathrm{HCF_3SO_3}$ (Merck) and $\mathrm{Li_2CO_3}$ (Merck), then recrystallized twice in acetone and vacuum dried at 140° C.

Lead trifluoromethane sulphonate was prepared similarly. Silver/silver iodide and lead/lead iodide electrodes were obtained by the usual electrolysis in a slightly acidified 0.1 sodium iodide solution. The lead/lead trifluoromethane sulphonate electrode was prepared as follows. A suspension of lead powder was prepared in an acetonitrile solution of lead trifluomethane sulphonate and PEO. A small amount of acetylene black was added to enhance the percolation effect. After homogenization the viscous solution was deposited on a clean lead electrode. Traces of solvent were removed by heating in a vacuum. For a given O/Li ratio, required amounts of PEO and lithium salt were dissolved in acetonitrile (Merck) to give approximately 5% solutions by weight. Once homogeneous, the solution was cast in PTFE plates. Solvent evaporation was carried out in a closed-circuit apparatus through a molecular sieve column (13X) with argon as a carrier gas. The thin films were then vacuum-dried in a Buchi TO 50 oven

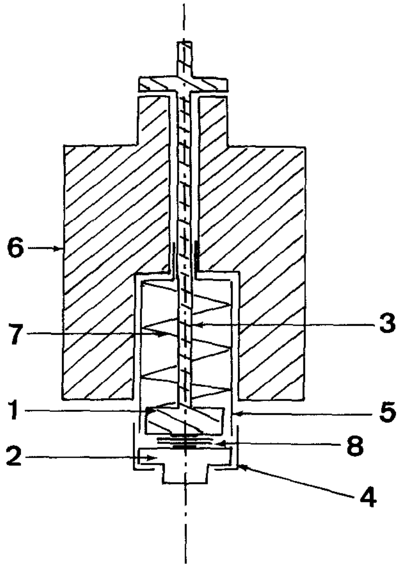

Fig. 1. Experimental concentration cell device. 1 and 2, stainless steel electrodes; 3, rod; 4, screw cap; 5, glass tube; 6, nylon sheath; 7, spring; 8, Li/polymer, electrolyte 1/polymer, electrolyte 2/Li.

at 140° C for 1 day and finally stored in the glove box. Concentrations are expressed hereafter as O/Li ratios or in mol kg^{-1} (molality).

3.2. *Device for measurement of e.m.f.*

The concentration cell assembly is shown schematically in Fig. 1. A lithium disc and a polymer sample were set on each stainless steel electrode. The lithium disc was held on the metallic substrate by cold pressing and the polymer sample adhered to the lithium after melting. The upper electrode was guided into the rest or working position by a rod. The lower electrode was supported by a screw cap fitted to a threaded glass tube. The assembly was surrounded by a nylon sheath. A spring ensured good contact between the two electrolytes.

The assembly was heated in a Buchi TO 50 oven and the inner cell temperature was always 90 ± 1° C. The cell was allowed to stand at thermal equilibrium for at least 6 h before each experiment. The electrodes were then moved into working position and the potential was recorded with a Solea Minisis 6000 voltmeter (Input impedance $> 10^{12}\,\Omega$).

4. Results and discussion

4.1. *Measurements of e.m.f.*

Salts were chosen according to the suitability of the corresponding electrolytes for use in solid-state batteries. As mentioned above, PEO–$LiClO_4$ and PEO–$LiCF_3SO_3$ complexes have already proved to be suitable electrolytes; PEO–LiI complexes were also used.

Complexes, however, are not always single-phase systems over the entire range of temperature and composition considered. This was originally suggested by conductivity–temperature behaviour [6]. By differential scanning calorimetry measurements, Sorensen and Jacobsen [20] and Berthier *et al.* [21] have investigated PEO–$LiCF_3SO_3$ complexes. PEO–LiI and PEO–$LiClO_4$ complexes have been studied by various techniques, including DSC, by Robitaille and Fauteux [22]. Measurements were carried out at 90° C for each complex in order to have a large concentration range in the amorphous domain.

Thus in the type 1 cell, the following O/Li ratios were used: $-m = 8$ and n varying from 8 to 120 for PEO–$LiClO_4$ and PEO–LiI; $-m = 30$ and n varying from 30 to 120 for PEO–$LiCF_3SO_3$. The half cell involving the constant molality electrolyte could be regarded as a reference electrode. Plots of e.m.f. of the type 1 cell are reported in Fig. 2. The PEO–LiI and PEO–$LiClO_4$ cell e.m.f. plots show a similar variation. However, no linear dependence is

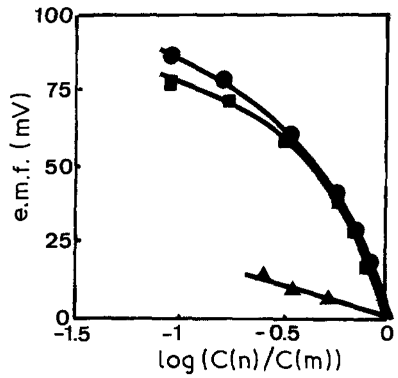

Fig. 2. Concentration cell e.m.f. plots versus salt molality ratio at 90° C. ●, PEO–$LiClO_4$; ■, PEO–LiI; ▲, PEO–$LiCF_3SO_3$.

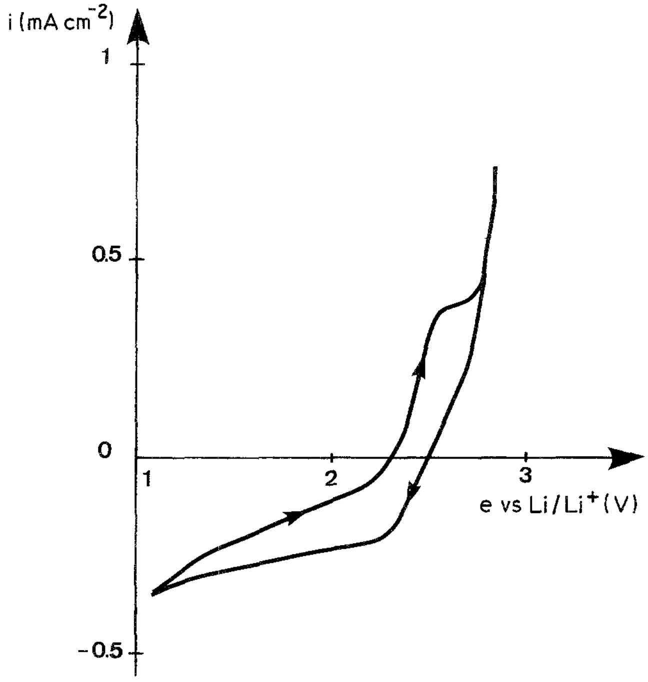

Fig. 3. Cyclic voltammogramm of Ag/AgI electrode in PEO_{16}–LiI complex. Temperature, 90° C; scan rate, 1 mV s^{-1}.

observed, so Equation 4 is not valid over the whole range of molalities.

For the PEO–$LiCF_3SO_3$ cell, e.m.f. values are low and are linear versus the molality ratio in the range studied. A preliminary calculation leads to $t_{Li^+} = 0.8$ by neglecting the mean salt activity coefficient. This value is not reliable with respect to the cyclic voltammetry [4] and tracer diffusion experiments [7]. Salt activities are needed.

4.2. *Mean salt activities*

For the PEO–LiI and PEO–$LiClO_4$ curves, departure from linearity is interpreted in terms of ion interaction. According to Equation 3, calculation of the lithium transference number requires knowledge of the variation of the mean salt activity with concentration. Assuming conduction by two ionic species, mean salt activities are obtained from the following cell:

$$\text{Li/PEO}_n\text{–LiX/electrode reversible to X}^- \quad \text{(type 2)}$$

The main difficulty arises in finding a suitable anionic electrode. This electrode must be insoluble, reversible and non-polarizable. By similarity with liquid electrolytes, the Ag/AgI electrode was considered as a possible iodide reversible electrode. AgI is insoluble in salt-free PEO [23].

Fig. 3 shows a cyclic voltammogram of the Ag/AgI electrode in PEO_{16}–LiI electrolyte at 90° C. The reference system is the Li/Li$^+$ couple. A peak is observed at +2.5 V (versus Li/Li$^+$) as well as a plateau during the cathodic sweep. Comparison of cathodic and anodic coulombic areas suggests that the oxidation product is not entirely reducible. These results are attributed to silver iodide dissolution due to its solvation by lithium iodide. Furthermore, the cell open-circuit voltage of various Li/PEO_X–LiI/AgI/Ag cells was observed to decrease with time. Such solvation of AgI by alkali iodide salts has been reported in various organic electrolytes [24]. The present results are consistent with those of Stevens and Mellander [25] who have prepared $LiAg_4I_5$ crystals in PEO. Ag/AgI was therefore rejected as an iodide reversible electrode in PEO–LiI complexes. As a consequence, another electrode of the second type was investigated, involving a divalent cation as a possible iodide reversible electrode, namely Pb/PbI_2.

Fig. 4 shows a cyclic voltammogram of Pb/PbI_2 under the same conditions. Negligible change was recorded on the overall scan over several hours. Anodic and cathodic peaks are

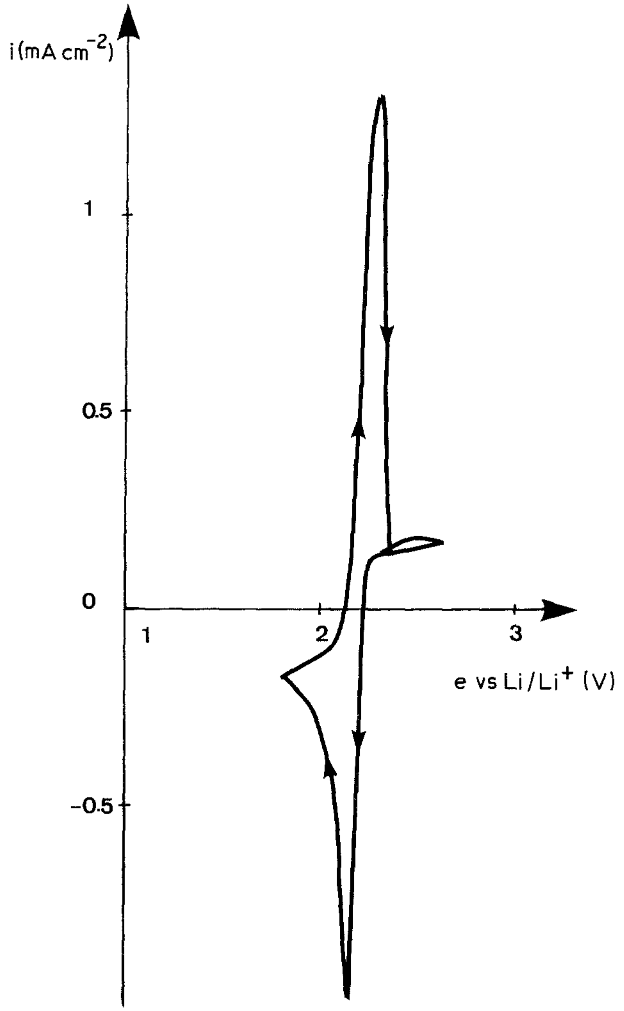

Fig. 4. Cyclic voltammogramm of Pb/PbI_2 electrode in PEO_{16}–LiI complex. Temperature, 90° C; scan rate, 1 mV s^{-1}.

sharp and have similar coulombic areas (more than 85% recovery). PbI_2 seems to have negligible solubility in the PEO–LiI complex, an aspect which will be detailed in a future paper. Consequently, Pb/PbI_2 can be used as the iodide reversible electrode.

4.3. *Determination of* t_{Li+}

Fig. 5 plots e.m.f. values for the chosen PEO–LiI type 1 cell against activities at 90° C. PEO_8–LiI at 90° C was used as the reference state. The type 1 e.m.f. data versus salt activities for PEO–LiI complexes suggest a linear dependence. Assuming negligible variation with concentration, t_{Li+} can be calculated by linear regression. It follows that at 90° C,

$$t_{Li^+/LiI} = 0.34 \pm 0.06$$

In the absence of a specific perchlorate reversible electrode it is assumed that LiI and $LiClO_4$ have similar activities at the same molalities. This hypothesis appears reasonable considering that both electrolytes give similar type 1 cell e.m.f. and salt diffusion coefficient values, as will be shown below. Accordingly,

$$t_{Li^+/LiClO_4} = 0.25 \pm 0.07$$

Since junction potentials are additive, the type 1 cell e.m.f. values for the PEO–LiI complex were calculated within narrower molality ranges, i.e. m differing only slightly from n. Calculation of

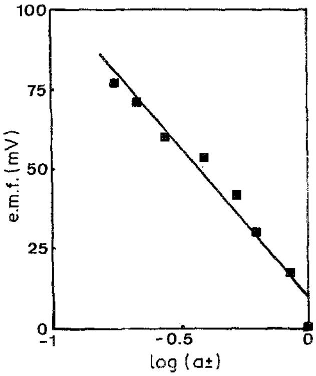

Fig. 5. Plots of e.m.f. versus mean salt activities for PEO$_X$–LiI complexes where 120 $\leqslant X \leqslant$ 8. Temperature, 90° C.

t_{Li^+} gives values varying between 0.3 and 0.5 within all these molality ranges.

These t_{Li^+} values and their slow variation with concentration show a similarity in the ionic transport mechanism of PEO electrolytes and liquid organic solvents containing lithium perchlorate such as propylene carbonate or acetonitrile [26].

Fig. 6 reports a cyclic voltammogram of a Pb/Pb$(CF_3SO_3)_2$ electrode in a PEO$_{30}$–LiCF$_3$SO$_3$ complex. The Pb/Pb$(CF_3SO_3)_2$ electrode is not a true electrode of the second kind as described in the experimental section, since the Pb$(CF_3SO_3)_2$ phase is a complex with PEO. The observed scan is stable over more than 20 cycles. The sharp cathodic and anodic peaks seem to indicate rapid electron transfer. Thus PEO–Pb$(CF_3SO_3)_2$ behaves as an electrode of the second kind, probably due to a very low transference number for the divalent cation. Preliminary measurements carried out on type 2 cells with this electrode showed stable e.m.f. values over 1 h. Mean salt activity calculations for PEO–LiCF$_3$SO$_3$ showed quite reproducible e.m.f. values, with standard errors lower than 0.8% except for dilute molalities (O/Li < 90). Accounting for the mean LiCF$_3$SO$_3$ activities, the corrected t_{Li^+} at 90° C would be

$$t_{Li^+} = 0.7 \pm 0.1$$

This value is surprising compared to t_{Li^+} in PEO–LiI complexes. It seems that the Li$^+$ molality in PEO–LiCF$_3$SO$_3$ is twice as high as in PEO–LiI. A further anomaly concerning PEO–LiCF$_3$SO$_3$ was mentioned by Gorecki *et al.* [14]. In fact, one must be cautious when dealing with ionic transference numbers, specifying clearly whether the single ionic transference number or the total transference number is concerned. Spiro [27] emphasized that the ionic transference number should be calculated rigorously only with strong electrolytes. Outside this case an 'ion constituent' or 'total' transference number, i.e. the fraction of current carried by an ion either single or in ionic association, can be measured experimentally. Since PEO–LiX complexes are media of low dielectric constants [28], and since only the elastomeric phase is responsible for the ionic motion [21], it is reasonable to expect that ions pairs and/or multiplets exist. Le Nest [29] suggested that ionic transport in cross-linked electrolytes occurs in two steps: dipole motion

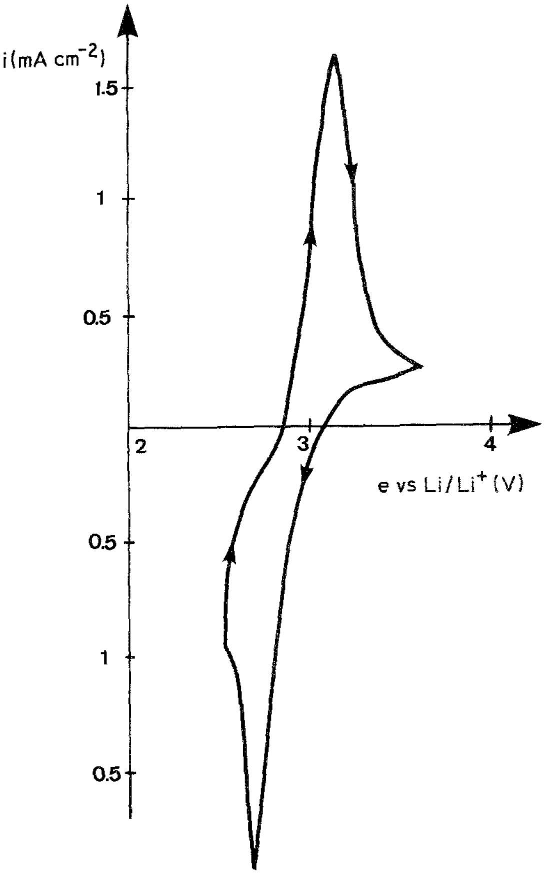

Fig. 6. Cyclic voltammogramm of the electrode Pb/Pb–Pb$(CF_3SO_3)_2$–PEO in PEO$_{30}$–LiCF$_3$SO$_3$ complex. Temperature, 90° C; scan rate, 1 mV s^{-1}.

leading to cluster formation, then charge transfer. Ion pairing in PEO electrolytes was pointed out in crystalline PEO complexes [30, 31]. In such media, electrochemical methods such as Tubandt's or the e.m.f. method give the total transference number. In light of this motion, the transference number discrepancy between $LiCF_3SO_3$ and LiI could be interpreted in terms of the different nature of the mobile species.

As mentioned in Table 1, Gorecki *et al.* [14] found a t_{Li^+} range of 0.16 to 0.22 for PEO–$LiClO_4$ complexes at 90° C, assuming that neither ion pairs nor multiplets were diffusing. Since a total transference number is measured by the present method, its similarity with the value for PEO–$LiClO_4$ complexes in [14] implies that Li^+ and ClO_4^- are the only charge carriers.

For PEO–$LiCF_3SO_3$, neither the total lithium transference number nor the lithium diffusion coefficient agree with the present PEO–LiI and PEO–$LiClO_4$ values. The only explanation proposed at present for the high transference number is the transport of anions associated with one mole of salt; however, this assumption needs to be checked. In calculating the mass balance on Li^+ and $CF_3SO_3^-$ associated with charge transport, the lithium transference number is comparable to that of LiI or $LiClO_4$, assuming that the main charge carriers are Li^+ and $Li(CF_3SO_3)_2^-$. Nevertheless, the $LiCF_3SO_3$ salt diffusion coefficient value is consistent with the results of other authors, as shown below.

4.4 *Salt diffusion coefficient*

An estimate of D_{LiI} can be obtained by recording the whole experimental potential versus time curve for the type 1 cell. Theoretical curves are obtained by solving the modified second Fick's law for the one-dimensional case, assuming a concentration-independent value of D_{LiI}

$$\frac{\partial C}{\partial t} = -D_{LiI}\left(\frac{\partial^2 C}{\partial x^2}\right) \qquad (5)$$

Initial conditions are as follows.

Electrolyte 1: $0 \leqslant x \leqslant l_1$; $C(x, 0) = C^\circ_1$.

Electrolyte 2: $l_1 \leqslant x \leqslant l_2$; $C(x, 0) = C^\circ_2$.

Boundary conditions: $t > 0$, and

$$\left(\frac{\partial C}{\partial x}\right)_{x=0} = \left(\frac{\partial C}{\partial x}\right)_{x=l} = 0$$

Equation 5 can be solved either by an explicit finite difference method [32] or by an analytical procedure [33]. For the sake of accuracy, the latter method is chosen here. The solution is then

$$C(x, t) - C^\circ_2 = (C^\circ_1 - C^\circ_2)\frac{l_1}{l_2} + \frac{2}{\pi}\sum_{n=1} \sin\left(\frac{nl_1}{l_2}\right)\cos(n\pi x)\exp(-n^2\pi^2 T) \qquad (5)$$

with $X = x/l_2$

$$T = \frac{Dt}{(l_1 + l_2)}$$

Using the experimental values of temperature, film thickness and diffusion coefficient, the concentrations are easily calculated. In order to achieve better accuracy, the Taylor series was calculated until the convergence criterion was lower than 10^{-3}. Electrolyte concentration profiles can be simulated for any time.

This procedure was used on the following type 1 cell:

$$\text{Li/PEO}_{30}\text{–LiI/PEO}_{60}\text{–LiI/Li} \qquad \text{(A)}$$

The concentration profiles in the two electrolytes are presented in Fig. 7. The final O/Li ratio is 41.

Knowing the salt activities of PEO_{30}–LiI and

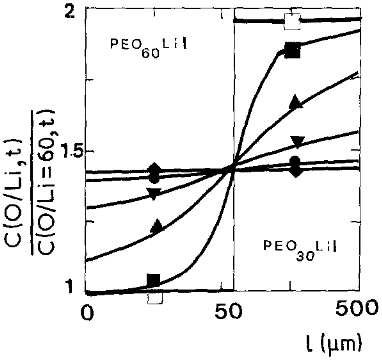

Fig. 7. Lithium concentration versus time profiles in PEO_{60}–LiI/PEO_{30}–LiI electrolytes at 90° C. Percentage of total homogenization time (at e.m.f. 1 mV): □, ○; ■, 1.5; ▲, 10; ▼, 25; ●, 50; ◆, 100.

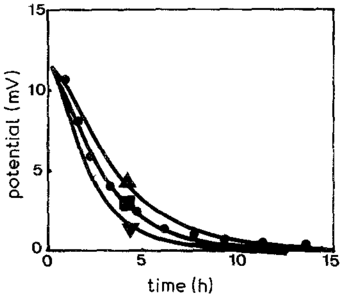

Fig. 8. Potential versus time profiles for the concentration cell Li/PEO_{30}–LiI/PEO_{60}–LiI/Li at 90° C. Values of D obtained experimentally ($cm^2 s^{-1}$): ▲, 3×10^{-8}; ■, 4×10^{-8}; ▼, 5×10^{-8}. Solid lines show the calculated curves.

PEO_{60}–LiI, the previous procedure can be used to simulate the potential versus time curve. Assuming a linear interpolation of $a \pm$ (LiI) between O/Li = 30 and O/Li = 60, the type 1 cell potential is calculated for each time. Fig. 8 shows that the experimental plots are well fitted with the theoretical curve calculated using $D_{LiI} = 4 \times 10^{-8} cm^2 s^{-1}$.

Fig. 9 gives the same kind of curves for cell B defined below:

$$Li/PEO_{30}\text{–}LiCF_3SO_3/PEO_{60}\text{–}LiCF_3SO_3/Li \quad (B)$$

The best fit is for $D_{LiCF_3SO_3}$ ranging between 7 and $8 \times 10^{-8} cm^2 s^{-1}$. This is twice as high as for PEO_x–LiI. Ratios of this order of magnitude were observed in simulations based on other concentration cells.

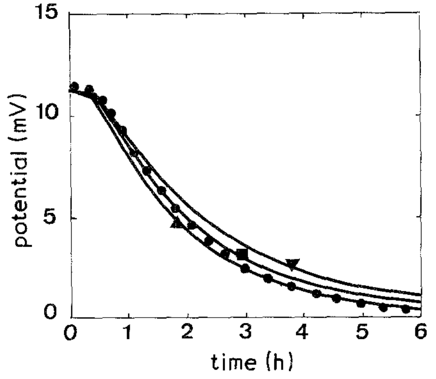

Fig. 9. Potential versus time profiles for the concentration cell Li/PEO_{30}–$LiCF_3SO_3$/PEO_{60}–$LiCF_3SO_3$/Li at 90° C. Values of D obtained experimentally ($cm^2 s^{-1}$): ▼, 7×10^{-8}; ■, 8×10^{-8}; ▲, 9×10^{-8}. Solid lines show the calculated curves.

5. Conclusion

E.m.f. measurements have been applied to fully amorphous PEO–lithium salt complexes. Concentration cells are easy to set up due to the slow salt diffusion, and no special experimental devices are required as with liquid electrolytes. This method enables estimation of both the lithium transference number and the lithium diffusion coefficient subject to certain assumptions. Since the ion nature of the electrolyte is unknown in such complexes, it is more convenient to use the notion of total ionic transference number. Assuming negligible variation with concentration, total lithium transference number measurements at 90° C give values of 0.34 for PEO–LiI and 0.7 for PEO–$LiCF_3SO_3$. A discrepancy is observed at 90° C for the lithium diffusion coefficient, with values around $4 \times 10^{-8} cm^2 s^{-1}$ in PEO–LiI and $8 \times 10^{-8} cm^2 s^{-1}$ in PEO–$LiCF_3SO_3$. Consequently, much attention will be focused on PEO–$LiCF_3SO_3$ since this singular behaviour, if confirmed, indicates that multiplet ions should diffuse. This might explain the lower performances of PEO–$LiCF_3SO_3$ compared with PEO–$LiClO_4$ batteries [2]. No further speculation can be made concerning ionic association in these electrolytes, since such an investigation generally requires the combination of both electrochemical and spectroscopic methods. The main feature of PEO–LiX complexes revealed by this transport phenomena study is their microscopic scale similarity with liquid organic electrolytes, an observation corroborated by the results of other authors [14, 15].

Acknowledgements

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