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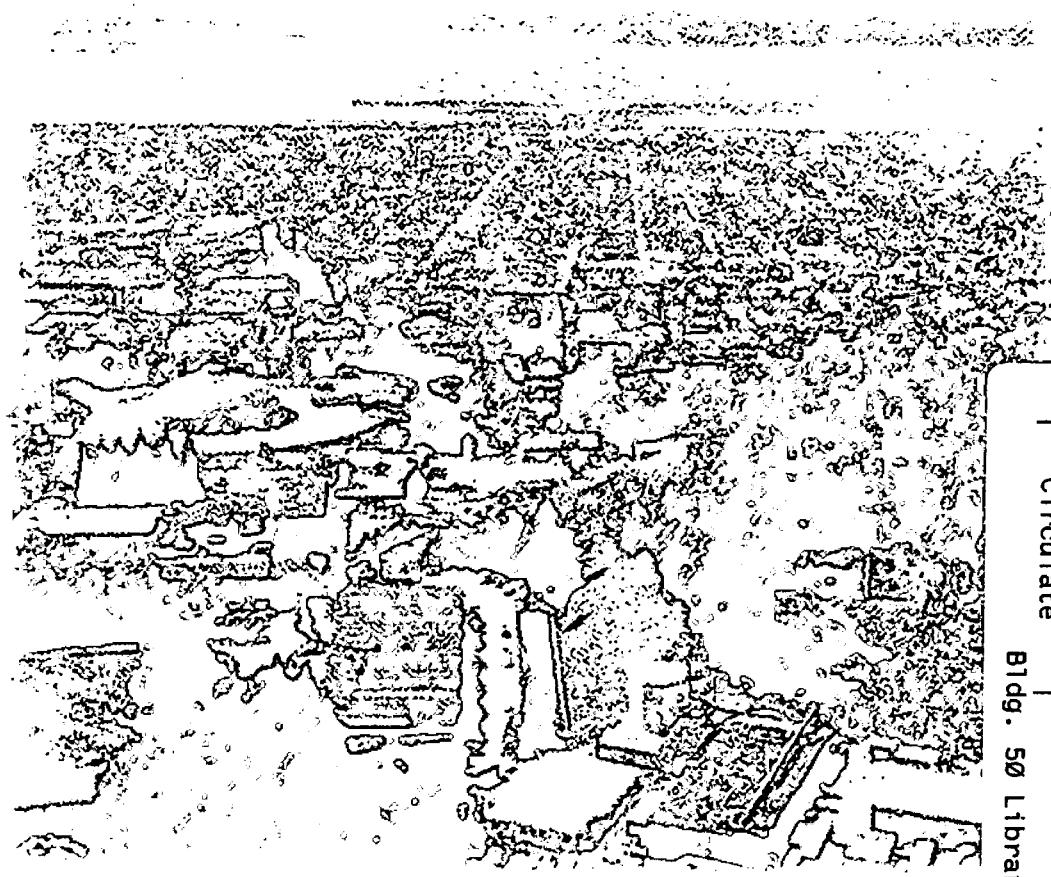

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Abstract

Straightforward electrochemical methods for determining the transport properties (bulk ionic conductivity, salt diffusion coefficient, and cation transference number) of polymer electrolytes are described herein. The new technique for measuring t_+^0 is based on concentrated solution theory, and requires no assumptions to be made concerning ideality of the solution. The experimental methods are described and results on representative polymer electrolyte systems are presented in this paper. Cation transference numbers are found to be salt-concentration dependent and considerably less than unity or even negative over a wide concentration range. This implies that the cationic current is mainly carried by complexed ions. The presence of associated ionic species in polymer electrolytes is confirmed by Raman spectroscopic evidence. Finally, the practical effects of a negative t_+^0 on cell operation and implications for device design are discussed.

Key words: polymer electrolyte, transport properties, transference number, Raman spectroscopy, diffusion

Introduction

Operation of electrochemical devices utilizing polymer electrolytes requires the passage of ionic current. Insight into the nature and mobility of the current-carrying species is, therefore, essential to the successful design and utilization of polymer electrolyte materials in such devices. Three transport properties are needed for the full description of a binary salt/polymer solvent system [1]; these can be chosen to be ionic conductivity, the salt diffusion coefficient and the cationic transference number (t_+^0). By definition, a transference number is the net number of moles of an ion constituent that crosses a reference plane fixed with respect to the solvent when one Faraday of current is passed through the fixed plane. Measurement of the last has either proven to be difficult experimentally (e.g., the Hittorf method) or requires assumptions to be made about the ideality of the polymer solutions [2].

We have recently developed simple electrochemical methods to determine the transport properties of non-ideal binary salt/polymer solutions, including t_+^0, based on concentrated solution theory [3]. The transport properties calculated from these measurements are based on a macroscopic model and are, therefore, independent of speciation (e.g., t_+^0 includes cations in both the free and complexed states). There is no need for detailed knowledge concerning the formation of ion pairs, triplets or higher order aggregates to gain a thorough understanding about ionic transport in the polymer electrolyte relevant to device operation.

Ionic conductivity is measured as a function of salt concentration at the temperature of interest, using the AC impedance method. Salt diffusion coefficients are determined from the relaxation of symmetrical cells galvanostatically polarized for short times. Data from the diffusion coefficient experiments, concentration cells and current interrupts are used to calculate t_+^0 as a function of salt concentration for the polymer system of interest. Finally, the complete set

of data may be used to calculate the thermodynamic factor (variation of the activity coefficient with salt concentration). While no specific information is provided regarding the types of species present in the polymer solution, the degree of non-ideality of the system can be determined. In contrast, Raman spectroscopy can be used to observe microscopic speciation directly [4, 5], and thus is complementary to the methods described herein.

Experimental

P(EO)NaX (P(EO) = poly(ethylene oxide), X= $CF_3SO_3^-$ or $N(CF_3SO_2)_2)^-$) polymer films were prepared as described previously [3]. Poly(propylene oxide) (PPO, average MW 4000, Aldrich) was carefully freeze dried using repeated pump-thaw cycles; dried salt was dissolved directly into the polymer using a magnetic stirrer and small amounts of acetonitrile. Acetonitrile was removed from the solution by further drying under vacuum at 100 °C for 100 h. The abbreviation O:M is used throughout the paper to indicate the ratio of CH_2CH_2O or $CH_2CH_2CH_2O$ groups to moles of salt (M indicates either Li or Na).

LiTFSI (TFSI=(bis)trifluoromethanesulfonate imide, $N(CF_3SO_2)_2$) was a gift from 3M Company. NaTFSI was prepared by an ion-exchange reaction of LiTFSI with $Na_{0.44}MnO_2$. LiTFSI was dissolved in acetonitrile and excess $Na_{0.44}MnO_2$ added. The solution was stirred for twenty-four hours and then filtered. The process was then repeated. Acetonitrile was removed from the solution by rotary evaporation, and the salt dried thoroughly in air and under vacuum. No lithium was detected in the elemental analysis of the resultant product (University of California Micro-analytical Laboratory, Berkeley, CA).

Sodium (Alfa products) was purified as described previously [3], and rolled into foils approximately 5 mil thick, prior to use in cells. Lithium foils 5 mil thick from Cyprus-Foote Mineral Company were used as provided.

The densities of the PEO based polymer electrolytes were measured by placing weighed films in 10 mL specific gravity bottles filled with cyclohexane. The weight of the bottle before and after displacement of the liquid then allows the volume of the electrolyte to be calculated.

Thermal characterization of PEO electrolytes was carried out using a Perkin-Elmer DSC-7 differential scanning calorimeter, and by measuring AC conductivity as a function of temperature.

Cells of configuration Na/polymer electrolyte/Na or Li/polymer electrolyte + Celgard 2500/Li were assembled under an inert atmosphere and equilibrated at the desired operating temperature (85 °C for the former, 25 °C for the latter) for several hours prior to testing. A computer-controlled MacPile II (Bio-logic, Claix, France) or PAR 173 potentiostat/galvanostat (EG&G) was used for the diffusion coefficient measurements and current interrupt experiments.

For concentration cell measurements, two polymer films of different compositions were overlapped edgewise, and sodium electrodes placed at the ends, to provide a diffusion pathway of several cm. This is to prevent rapid relaxation of the salt concentration gradient and ensures that an accurate potential difference is obtained. Use of a high input impedance electrometer (a Keithley 642) prevents cell polarization during measurement. A cell holder with a removable separator was used for the PPO concentration cells; the potential difference was determined immediately upon removal of the device separating two polymer solutions of differing compositions.

A Solartron SI 1286 electrochemical interface and 1254 four-channel frequency response analyzer was used to measure conductivities of polymer electrolytes in cells with blocking electrodes.

FT-Raman spectra with a wavenumber resolution of 2 cm^{-1} were recorded at 85 °C with the temperature stability in the sample estimated to be ±0.3 °C. The spectra were recorded with a Bruker IFS 66 with a Raman module FRA 106 and a continuous Nd:YAG laser (1064 nm) using a 180° back scattering geometry. During measurements, the sample cell was placed in an evacuated thermostat. To compensate for differences in overall signal intensity due to varying sample thickness and sample composition, all spectra were normalized to the characteristic CH_2 region at ~2700-3100 cm^{-1}, which was not affected by the introduction of lithium salt into the polymer matrix.

Results and Discussion

The methods described herein are best applied to true binary salt/polymer or liquid systems since concentrated solution theory dictates that n(n-1)/2 independent transport properties are needed to describe a system of n components [1]. Thus, the presence of low molecular weight additives in gelled polymer systems requires determination of additional transport properties (e. g., additional transference numbers and pairwise interaction parameters). In practice, these may be extremely difficult to obtain. These complications arise from the microscopic interactions among polymer, solvent and salt.

Devices utilizing liquid electrolytes (e.g., $LiClO_4$ in propylene carbonate) commonly have a porous separator such as a polypropylene film between electrodes. Although the solvent-saturated separator resembles a gelled or plasticized polymer electrolyte in certain respects, the pores in the polymeric separator are much larger than those in the gelled systems [6]. The

separator is, therefore, essentially inert, and may be regarded simply as a barrier reducing the effective cell area. Appropriate corrections should be made for pore volume fraction and tortuosity, but otherwise, the system may be considered a true binary salt solution, and the methods described herein are applicable. It should be noted, however, that rapid diffusional processes in low viscosity solvents may, in practice, be difficult to follow experimentally.

Ionic transport occurs predominantly in amorphous (molten) regions of the polymer-salt complexes [7]. Therefore, the presence of crystalline polymer/salt complexes in some solutions at or near the operating temperature is a complicating factor in determining diffusion coefficients and t_+^0. This is of particular concern in the case of PEO based electrolytes, which are frequently partially or fully crystalline at room temperature [8]. In some cases, the electrolyte is two-phase at the operating temperature, consisting of a poorly conducting crystalline phase dispersed in a molten conducting phase with a different stoichiometry than that of the original polymer-salt mixture [9]. Any attempt to correlate transport properties with the salt concentration of the bulk polymer electrolyte will then lead to erroneous results, although some useful information may still be obtained. For this reason, thermal characterization of the polymer-salt system prior to obtaining transport properties is desirable. We note that the thermal history of PEO based electrolytes may be of importance in these studies, due to the slow kinetics of recrystallization for high molecular weight systems [10]. Phase diagrams of some polymer-salt systems are available in the literature (see, e.g., reference 9 and papers cited therein). If possible, temperature and salt concentration ranges should be chosen so that two-phase regions are avoided.

Figure 1 shows conductivity as a function of temperature for $P(EO)_{15}NaTFSI$, as well as differential scanning calorimetry data. The conductivity shows a changeover from Arrhenius behavior to the predicted Vogel-Tammann-Fulcher behavior [11] at about 50°C, close to the

melting transition observed in the DSC scan. A eutectic was observed at 46°C for compositions near $P(EO)_{12}NaTFSI$. No melting transitions above 68°C were observed over the concentration range used in this study (O:M=6-500). Prud'homme and coworkers [12] obtained similar results on the PEO/NaTFSI system, with slight differences ascribable to their use of polymers with lower molecular weights than in this work. While these results suggest that the operating temperature of sodium batteries may be substantially lowered from the currently used 85 °C [13], we chose to make measurements at this temperature to avoid any possible complications from the presence of two-phase mixtures in the salt-rich region of the phase diagram.

The first transport property to be measured is the bulk ionic conductivity at the temperature of interest. This is most conveniently done using AC impedance techniques and cells with either blocking or non-blocking electrodes. In the latter case, the interfacial impedance may be determined in addition to the bulk electrolyte conductivity. It is well-known that the interfaces between polymer electrolytes and alkali metals are composed of either a corrosion layer (for sodium) [14] or a solid electrolyte interphase region (SEI) [15] for lithium. Ion transport phenomena in the interfacial regions can generally be observed separately from analogous processes in the polymer electrolyte and, therefore, do not interfere with the transport property measurements. A possible exception is for t_+^0 and will be discussed below.

Results for the $P(EO)_nNaCF_3SO_3$ and $P(EO)_nNaTFSI$ systems are shown in Figure 2. $P(EO)_nNaTFSI$ is generally more conductive than $P(EO)_nNaCF_3SO_3$ over the entire composition range, but both systems have values comparable to, or somewhat greater than the lithium analogs. A maximum is seen at intermediate salt concentrations (at O:M = 20, in both cases). At low salt concentrations, conductivity decreases due to low numbers of charge carriers, whereas at high salt

concentrations, the polymer segmental mobility is restricted by large densities of ionic crosslinks that reduce the ionic mobility.

PPO(4000) is fully amorphous at room temperature; however, Prud'homme and coworkers [16] have interpreted glass transition anomalies in terms of a micro-phase separation occurring in complexes of PPO-$LiClO_4$. No such observations have been reported in the literature for PPO complexed with the imide salts and in the present study we treat the PPO-LiTFSI system as a single phase binary electrolyte. At any rate, microscopic phase separation is unlikely to influence the measurement of macroscopic properties such as salt diffusion coefficients unless the phases have very different conductivities and the domain sizes are relatively large or exist for long times relative to the diffusion phenomena.

For the $P(PO)_nLiTFSI$ system, conductivities of about 1 x 10^{-5} S/cm are seen for moderately concentrated solutions (n = 15-50) at 25 °C. The molar conductivity (ionic conductivity normalized to salt concentration) exhibits the characteristic concentration dependency generally found in PPO based electrolytes [17-19]; a rapid increase from a minimum in dilute solutions passing through a maximum at an O:M ratio of about 40:1. Notably, the maximum conductivity is approximately an order of magnitude higher compared to PPO(4000) complexed with $LiCF_3SO_3$ [17].

In order to obtain salt diffusion coefficients, D_S, symmetrical cells with non-blocking electrodes are polarized galvanostatically for short periods of time. When the current is turned off, the induced concentration profile in the cell is allowed to relax. At long times after the current interrupt, the following equation holds true [3]:

$$\ln \Delta\Phi = \frac{\pi^2 D_S}{L^2} t + A_1 \qquad (1)$$

Where $\Delta\Phi$ is the measured cell potential, D_S is the salt diffusion coefficient, L is the electrolyte thickness and A_1 a constant. A plot of $\ln\Delta\Phi$ vs. time is linear and the slope is proportional to D_S.

For the $PEO/NaCF_3SO_3$ system [3] at 85°C, D_S decreases over nearly an order of magnitude as the salt concentration increases, ranging from about 8 x 10^{-8} cm^2/sec for dilute solutions to about 1.2 x 10^{-8} cm^2/sec for $P(EO)_8NaCF_3SO_3$. A small local minimum is seen at $P(EO)_{80}NaCF_3SO_3$ for which D_S is about 5 x 10^{-8} cm^2/sec. For PEO/NaTFSI, there is less variation with salt concentration for the higher ratios; for O:M=6-60, D_S is about 5 x 10^{-8} cm^2/sec, a local minimum is seen at $P(EO)_{120}NaTFSI$ (D_S= 3 x 10^{-8} cm^2/sec), and the diffusion coefficient increases gradually to about 7.6 x 10^{-8} cm^2/sec for very dilute solutions ($P(EO)_{495}NaTFSI$). For $P(PO)_nLiTFSI$ electrolytes at 25°C, D_S increases with increasing concentration from n=300 (D_S ~0.7 x 10^{-9} cm^2/s), passing through a maximum of about 2.8 x 10^{-9} cm^2/sec for a composition of $P(PO)_{70}LiTFSI$. The observed increase closely resembles the concentration behavior of the molar conductivity. A relatively large number of hydroxyl terminal groups (O:OH ~35:1) are present; solvated lithium ions may be preferentially coordinated to such polar moieties at low salt concentrations [19, 20, 21].

It is important to stress that the salt diffusion coefficients measured by this method, by definition, do not differentiate among species; diffusion due to all free ions, ion-pairs and aggregates are included in these values. The complexation reactions of ions in highly non-ideal polymer electrolytes may involve multiple concurrent equilibria yielding species that vary greatly in their diffusivity; therefore, no simple relationships between salt diffusion coefficients and composition are to be expected. Rather, the variation between salt diffusion coefficient and concentration will be highly system specific and should be determined separately for each

electrolyte and set of conditions. The variation of D_S with polymer composition is useful for determining the effect of concentration gradients upon the operation of working devices; large variations in D_S (and conductivity) with composition may promote premature failure of cells due to insufficient ionic mobility in part of the electrolyte layer, or composite electrode.

As with D_S, t_+^0 is a macroscopic quantity in this treatment and includes transference due to all cation-carrying species; i.e., ion-pairs, triplets and higher order aggregates. For the purpose of evaluating device performance, it is not necessary to know the details of speciation, although these may be of considerable interest to the polymer electrolyte scientist. It should also be noted that t_+^0 is defined in the absence of concentration gradients; although small gradients must be induced in experimental cells to make measurements, care should be taken to minimize perturbation of the system.

To calculate transference numbers, the results from three separate experiments are combined, according to equation 2 [3]:

$$t_-^0 = \frac{mc_\infty F(\pi D)^{1/2}}{4}\left(\frac{d\ln c}{dU}\right) \qquad (2)$$

D_S is the salt diffusion coefficient from the restricted diffusion experiment, c_∞ is the molar salt concentration, dlnc/dU is the reciprocal of the local slope of concentration cell plots, and m is a slope derived from current interrupt data. The means for obtaining the latter two values are described below.

Concentration cells of the form M/[electrolyte]$_n$/[electrolyte]$_m$/M are constructed, where M represents an alkali metal electrode and [electrolyte]$_{n\ or\ m}$ represents the polymer solution with salt concentration, n or m. Most conveniently, m is held constant, and n is varied; c refers to the concentration of [electrolyte]$_n$ and the potential reading is taken to be positive for n>m.

If the polymer/salt solution is ideal (activities equal to salt concentrations), the transference number can be determined from the slope of a plot of the salt concentration vs. cell EMF according to equation 3 [22]:

$$t_{-}^{0} = \frac{F}{2RT}\frac{dU}{d\ln C} \qquad (3)$$

These plots, however, deviate markedly from linearity, requiring knowledge of the thermodynamic factor (variation of activity with concentration). A second experiment is necessary to obtain sufficient information for the transference number calculation.

For this, symmetrical cells are assembled and galvanostatically polarized by applying a current i for a time t_i. Again, conditions are chosen so that there is minimal perturbation, sufficient to establish concentration gradients at the electrodes, but not at the center of the cell. A potential reading taken shortly after the current is interrupted can then be correlated with the data from the concentration cell. Thus, the amount of salt in one segment of the polymer film can be directly determined, as in the Hittorf method, without the need for sectioning and weighing the electrolyte film. In equation 2, m is the initial slope of the cell potential vs. $it_i^{1/2}$ from several experiments in which i and/or t_i is varied.

The potential reading $\Delta\Phi$ should be taken before significant salt diffusion occurs, but after double layer charging has dissipated. The latter is usually rapid (on the order of milliseconds) and the former slow (minutes to hours for polymer electrolytes). By plotting $\Delta\Phi$ vs. the dimensionless time T:

$$T = \frac{t_i^{1/2}}{t^{1/2} + \left(t - t_i\right)^{1/2}} \qquad (4)$$

the potential difference corresponding to the concentration profile at the time of current interrupt can be retained by linear extrapolation back to T=1 [23]. Figure 3 shows an example of this calculation.

Obviously, it may be difficult to determine t^0_+ accurately if the overpotential in the cell is dominated by the SEI or corrosion layer, and relaxation processes are on similar time scales as that of the polymer electrolyte. Some information regarding this may be obtained from AC impedance measurements on cells with non-blocking electrodes. The usual precautions with regards to purity and dryness should, of course, be taken prior to cell assembly. The systems used in this study were generally well-behaved, and no unusual difficulties were encountered. If high interfacial impedance is a persistent problem, less strongly reducing electrode materials may be used in place of metallic lithium or sodium, e.g., two phase Li or Na alloys [24-26]. Care should be taken to avoid changing the composition of these electrodes, as will occur if a substantial current is passed for a long time.

Cationic transference numbers for all of the polymer systems in this study were strongly composition dependent. For the $P(EO)_nNaCF_3SO_3$ system, t_+^0 values close to 0 were found for n=40-120; for compositions more salt-rich than $P(EO)_{40}NaCF_3SO_3$ t_+^0 becomes negative [3]. For the PEO/NaTFSI system t_+^0 is negative over the entire range investigated, O:M=120-7:1, decreasing slightly with increasing concentration and reaching a low of t_+^0 = -1.15 for $P(EO)_7NaTFSI$ in the most concentrated solution studied.

A more complex relationship between t_+^0 and salt concentration is seen for the PPO-LiTFSI system. The lithium ion transference number is negative for compositions O:M=30-200, nearing 0 for the most dilute solutions, but reaches a minimum of -2.3 at O:M=70. Interestingly,

this matches the point at which the salt diffusion coefficient is at a maximum and roughly corresponds to the observed maximum in molar conductivity.

The consistent observation of negative t_+^0 values for polymer electrolytes in all but the most dilute solutions may, at first glance, seem surprising. There is, however, ample precedence for negative transference numbers in aqueous electrolytes [27]. This is best understood in terms of the deviation of the solution from ideality caused by ion complexation reactions. This may be further quantified by relating the transference numbers to the thermodynamic factor [3].

Since t_+^0 is a macroscopic quantity, all cations, whether free or complexed, are included. Thus, a negative t_+^0 indicates that solvated "free" cations are relatively immobilized by the host matrix and that long range cationic transport predominantly involves correlated motions of cations and anions in the form of negatively charged aggregates of ions. In concentrated solutions, (like those typically used in devices) the separation between ions may be only about 10Å, and interchange among sites (ion pairs, triplets, aggregates, ions complexed by polymer, etc.) occurs rapidly. Thus, to interpret ion transport processes in terms of discrete species is undoubtedly an oversimplification. However, the notion that distinct associations of ions exist, at least over short time scales, is supported by extensive spectroscopic evidence [4, 5, 28]. For instance, in figure 4, the multi-component nature of the Raman active $\nu_S(SO_3)$ mode reveals that the anions experience several different potential energy environments in the $P(EO)_nNaCF_3SO_3$ solutions. Components at 1033, 1037 and 1047 cm^{-1} have been attributed to "free" anions, $NaCF_3SO_3$ pairs and negatively charged triple ions, and positively charged $Na_2CF_3SO_3$ triplets respectively [28]. The feature at around 1058 cm^{-1} has been assigned to larger aggregations of ions [28], possibly precursors to salt precipitation, and is only observed at higher concentrations in the present study (O:M<55:1). We note that the existence of negatively charged ionic

aggregates has been inferred from spectroscopic data in an endo-methylated PPO(4000)-$LiCF_3SO_3$ system by one of us [19].

It has been pointed out that a lithium battery can operate successfully even when $t_+^0 = 0$ [29], provided that ion pairs are mobile and anions can migrate in a direction opposite that of the ion pair diffusion. A similar logic applies when t_+^0 is negative. The lower the cationic transference number, however, the stronger the tendency towards development of concentration gradients in the cell. The steady-state concentration gradient during discharge is given by equation 5 [30]:

$$\frac{\Delta c}{L} \approx \frac{I\left(1 - t_+^0\right)}{FD_S} \qquad (5)$$

where L is the thickness of the electrolyte. If local regions of the electrolyte have compositions that exhibit poor transport properties, premature failure will occur. Computer simulations of $Na/P(EO)_{12}NaCF_3SO_3/Na$ cells show that a steeper concentration profile is generated at the anode than at the cathode [31] upon passage of current. Because the transference number and salt diffusion coefficient decrease with increasing salt concentration for this system, precipitation at the anode will occur before a limiting current at the cathode is reached. Although it is a common practice to use highly concentrated electrolytes to prevent salt depletion, these results indicate that better cell performance will be obtained with less highly concentrated solutions. Markedly better rate capability is indeed seen for $Na/P(EO)_{20}NaCF_3SO_3/P2\ Na_xCoO_2$ cells than for $Na/P(EO)_8NaCF_3SO_3/P2\ Na_xCoO_2$ analogs [13].

Conclusions

Electrochemical techniques for determining the three transport properties necessary for describing the behavior of a single phase, binary salt/polymer electrolyte are discussed. These are 1) ionic conductivity, 2) salt diffusion coefficient, and 3) cationic transference number, t_+^0. A new, theoretically rigorous method for determining t_+^0 is presented, which has the advantage of experimental ease. Possible complications arising from the presence of solid electrolyte inter-phases, crystalline phases in the polymer/salt mix and liquid additives such as those used in gelled electrolytes are noted. It is found that the cationic transference number varies with the salt concentration in the polymer, and is often negative, especially for concentrated solutions. This is a direct result of the marked non-ideality of the polymer electrolytes, and indicates that cationic transport takes place primarily in the form of migration and diffusion of complexed ions. This may cause large concentration gradients to develop in working cells, leading to premature failure. For devices containing concentrated PEO/$NaCF_3SO_3$ electrolytes, salt precipitation occurs at the anode, and better rate capability is obtained when less concentrated electrolyte solutions are used.

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References

1. J. Newman, *Electrochemical Systems* Prentice-Hall, Englewood Cliffs, NJ (1991).

2. See M. Doyle and J. Newman, *J. Electrochem. Soc.* **142**, 3465 (1995) and references therein.

3. Y. Ma, M. Doyle, T. Fuller, M. M. Doeff, L. C. De Jonghe and J. Newman, *J. Electrochem. Soc.* **142**, 1859 (1995).

4. S. Schantz, L. M. Torell, J. R. Stevens, *J. Chem. Phys.* **94**, 6862 (1991)

5. W. Huang, R. Frech and R. A. Wheeler, *J. Phys. Chem.* **98**, 100 (1994)

6. M. Doyle, J. Newman, A. S. Godz, C. N. Schmutz, and J.-M. Tarascon, *J. Electrochem. Soc.* **143**, 1890 (1996).

7. C. Berthier, W. Gorecki, M. Minier, M. B. Armand, J. M. Chabagno and P. Rigaud, *Solid State Ionics*, **11**, 91 (1983).

8. P. V. Wright, in *Polymer Electrolyte Reviews-1,* (Edited by J. R. MacCallum and C. A. Vincent), p. 61. Elsevier Applied Science, London (1987).

9. D. Fauteux, in *Polymer Electrolyte Reviews-1,* (Edited by J. R. MacCallum and C. A. Vincent), p. 121. Elsevier Applied Science, London (1987).

10. P. Ferloni, G. Chiodelli, A. Magistris and M. Sanesi, *Solid State Ionics*, **18&19**, 265 (1986).

11. M. A. Ratner, *Mat. Forum*, **15**, 1 (1991).

12. M. Perrier, S. Besner, C. Paquette, A. Vallee, S. Lascaud and J. Prud'homme, *Electrochim. Acta*, **40**, 2123 (1995).

13. M. Doeff, S. J. Visco, Y. Ma, M. Peng, L. Ding and L. C. De Jonghe, *Electrochim. Acta*, **40**, 2205 (1995).

14. K. West, B. Zachau-Christiansen, T. Jacobsen, E. Hiort-Lorenzen and S. Skaarup, *Brit. Polymer J.*, **20**, 243 (1988).

15. D. Fauteux, *J. Electrochem. Soc.*, **135**, 2231 (1988).

16. C. Vachon, M. Vasco, M. Perrier, and J. Prud'homme, *Macromolecules* **26**, 4023 (1993).

17. I. Albinsson, B.-E. Mellander and J. R. Stevens, *J. Chem. Phys.* **96**, 681 (1992).

18. I. Albinsson, B.-E. Mellander and J. R. Stevens, *Solid State Ionics* **72**, 177 (1994).

19. A. Ferry, *J. Phys. Chem.*, to be published.

20. J. Manning, R. Frech and W. Huang, *Polymer* **31**, 2245 (1990).

21. A. Bernson and J. Lindgren, *Polymer* **35**, 4842 (1994).

22. A. Bouridah, F. Dalard, D. Deroo, M. Armand, *J. Applied Electrochem.*, **17**, 625 (1987).

23. J. Newman, personal communication.

24. J. O. Besenhard, M. Hess and P. Komenda, *Solid State Ionics*, **40/41**, 525 (1990).

25. J. O. Besenhard, P. Komenda, A. Paxinos and E. Wudy, *Solid State Ionics,* **18&19**, 823 (1986).

26. B. A. Boukamp, G. C. Lesh, and R. A. Huggins, *J. Electrochem. Soc.*, **128**, 725 (1981).

27. R.A. Robinson and R. H. Stokes, *Electrolyte Solutions,* 2nd edition., p. 161. Butterworths, London (1959).

28. P. Jaconsson, I. Albinsson, B.-E. Mellander and J. R. Stevens, *Polymer*, **33**, 2778 (1992).

29. G. G. Cameron, J. L. Harvie and M. D. Ingram, *Solid State Ionics,* **34**, 65 (1989).

30. M. Doyle, T. F. Fuller and J. Newman, *Electrochim. Acta*, **39**, 2073 (1994)

31. Y. Ma, *Ph.D Thesis*, University of California at Berkeley, 1996.

Figure Captions

1. Conductivity as a function of temperature for an electrolyte of composition $P(EO)_{15}NaTFSI$. The differential scanning calorimetry data is included and shows good agreement with the conductivity measurements.

2. Conductivities of $P(EO)_nNaCF_3SO_3$ (O) and $P(EO)_nNaTFSI$ (■) electrolytes at 85 °C as a function of salt concentration. Data on $P(EO)_nNaCF_3SO_3$ is taken from reference 3.

3. Plot of $\Delta\Phi$ vs dimensionless time T (equation 4) for a typical current interrupt experiment (composition $P(EO)_7NaTFSI$; i= 0.073 mA/cm^2, t_i = 30.35 s). The dashed line shows a linear extrapolation back to T=1, corresponding to the time of current interrupt.

4. Raman spectra, $\nu_S(SO_3)$ region, of $P(EO)_nNaCF_3SO_3$ electrolytes at 85°C. Components at 1033, 1037 and 1058 cm^{-1} are indicated by dotted lines. (Assignments in the text are taken from in reference 28.)

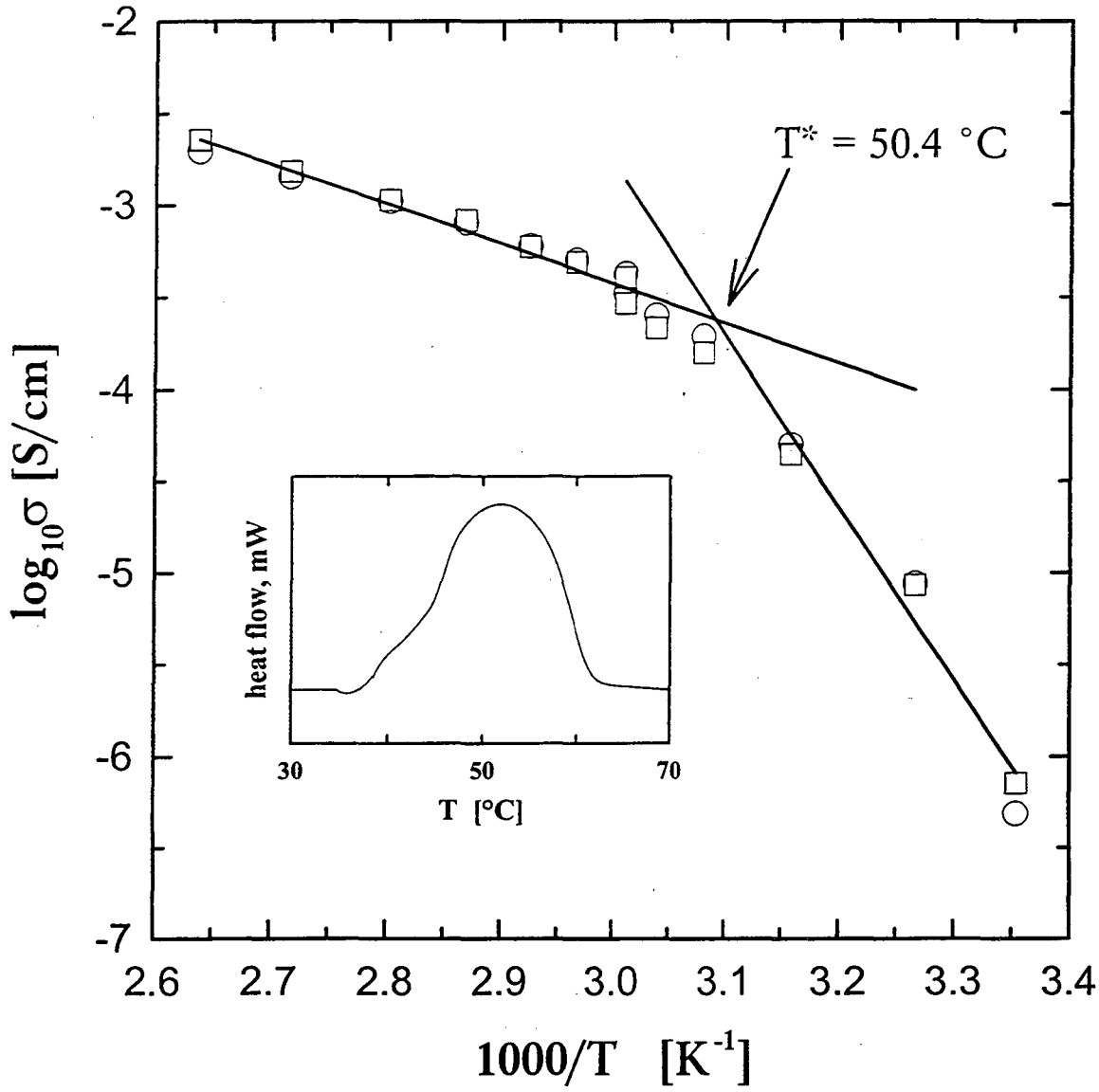
T* = 50.4 °C
log10σ [S/cm]
1000/T [K-1]
-2
-3
-4
-5
-6
-7
2.6
2.7
2.8
2.9
3.0
3.1
3.2
3.3
3.4
heat flow, mW
30
50
70
T [°C]

Figure 1

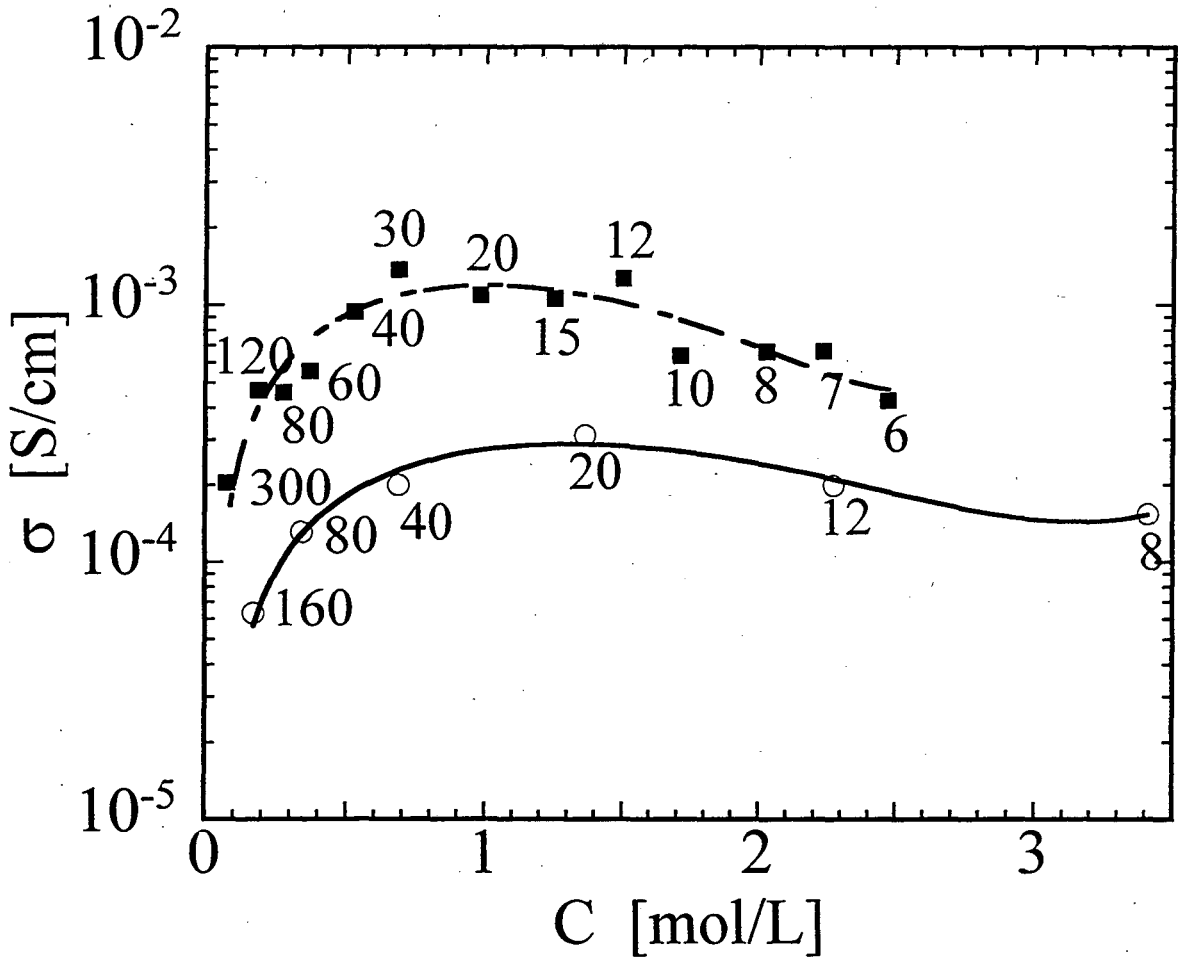
10-2
10-3
10-4
10-5
σ [S/cm]
0
1
2
3
C [mol/L]
30
20
12
40
15
120
60
10
8
7
80
6
300
20
40
12
80
8
160

Fig. 2

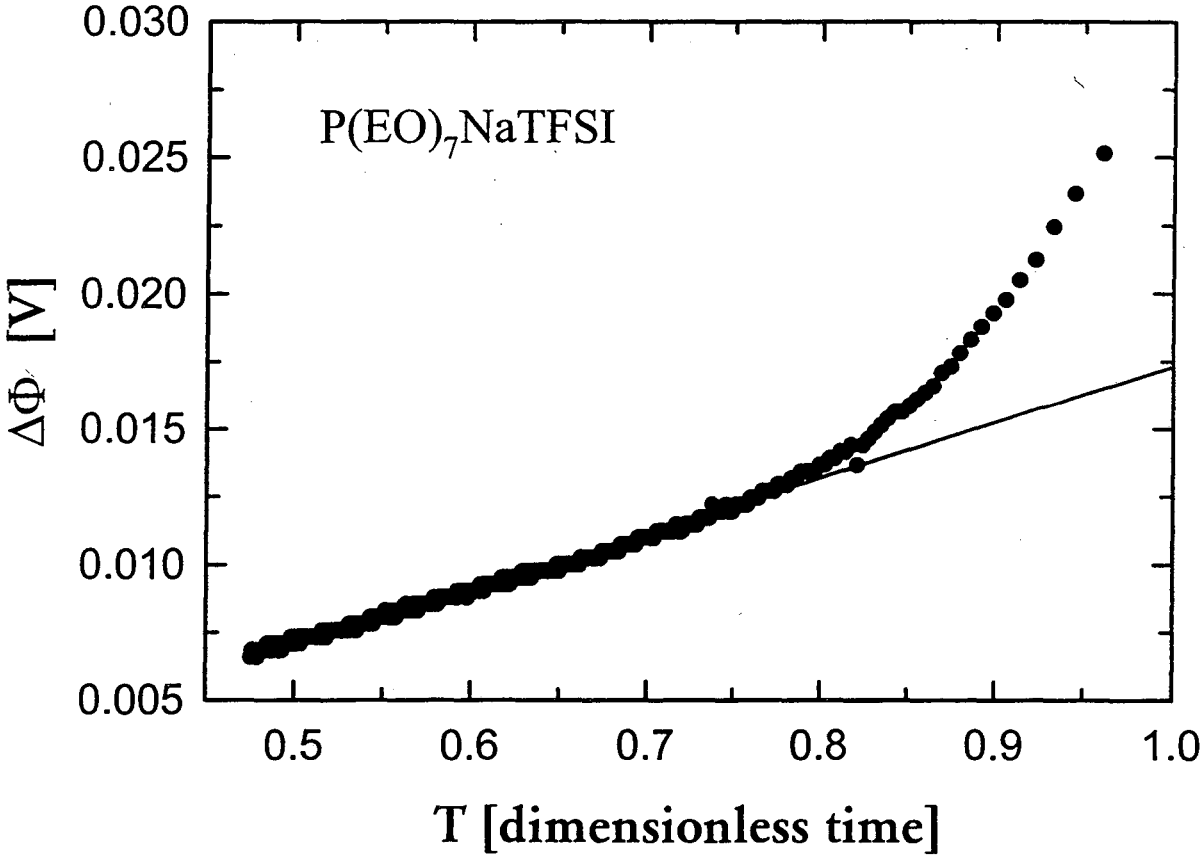
P(EO)7NaTFSI
0.030
0.025
0.020
0.015
0.010
0.005
ΔΦ [V]
0.5
0.6
0.7
0.8
0.9
1.0
T [dimensionless time]

Fig 3

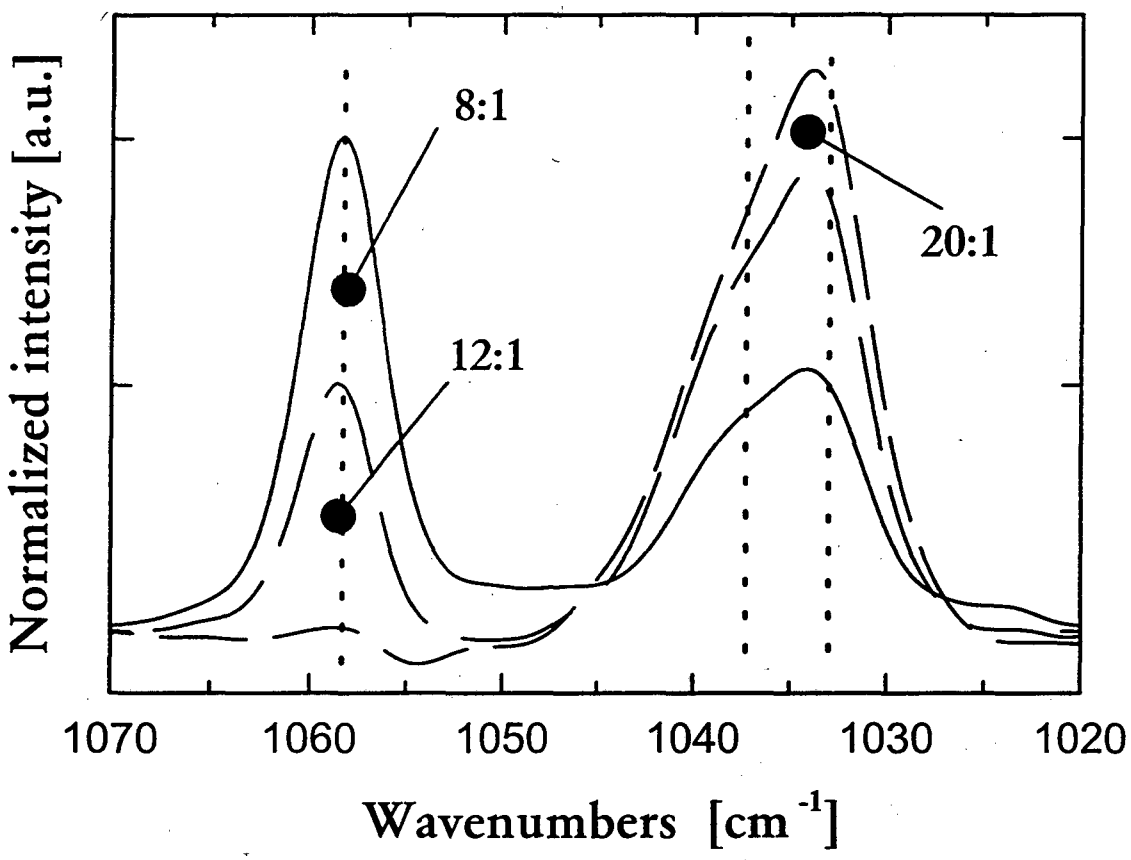
Normalized intensity [a.u.]
8:1
12:1
20:1
1070
1060
1050
1040
1030
1020
Wavenumbers [cm -1]

Figure 4

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