LBNL-40741
UC-1500
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Materials Sciences Division

August 1997
Submitted to
Journal of the Electrochemical Society

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This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Transportation Technologies, Office of Advanced Automotive Technologies of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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Abstract

Concentration dependences of a complete set of ionic transport properties are reported for the binary solid polymeric ion-conductor poly(ethylene-oxide) (P(EO)), complexed with NaTFSI, (TFSI= (bis)trifluoromethanesulfonate imide, $(CF_3SO_2)_2N$). Measured transport properties include the ionic conductivity (σ), the differential salt diffusion coefficient (D_S), and the cationic transference number (t_+^0). To measure t_+^0, a recently developed technique based on concentrated solution theory is used. Under this framework no assumptions need to be made concerning ideality of the electrolytic solution. We find that for the $P(EO)_n$-NaTFSI complexes the ionic conductivities and differential salt diffusion coefficients are much higher than those of the previously reported $P(EO)_n$-$NaCF_3SO_3$ system. D_s also varies less with complex composition in concentrated solutions. Interestingly, the cationic transference numbers are found to be negative over a wide concentration range; *i.e.*, t_+^0 decreases with increasing salt concentration and reaches a low of -1.15 ± 0.25 at a composition corresponding to an ether oxygen to sodium ion ratio of 7:1. This implies that the cationic current is mainly carried by complexed ions. Complementary Raman spectroscopic studies directly probing cation-anion and cation-polymer molecular interactions show that extensive inter-ionic interactions occur in this system.

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** Electrochemical Society Active Member.

Introduction

Solid polymer ion-conductors, *i.e. solid polymer electrolytes* (SPEs), are formed by the dissolution of salts in ion-coordinating macromolecules.[1,2] This class of materials has attracted great scientific interest during the last two decades; the driving force in these studies primarily being the prospect of utilizing SPEs in rechargeable, high-energy-density, thin-film batteries, variable transmission "smart" windows, and solid-polymer fuel cells.[2,3] A highly complex chemistry and intriguing ionic transport properties provide further impetus for fundamental studies in this field.

The microscopic mechanisms governing ionic transport processes through a macromolecular polar solvent are considerably different than in liquid organic or aqueous electrolytes, where unconstrained solvent sheaths typically surround solvated ions, creating distinct kinetic entities.[4] In polymer–salt complexes, cations are solvated by polar groups on the polymer chains (ether oxygens in the case of poly(ethylene oxide), PEO), while anions normally interact weakly with the aprotic host.[5] The host matrix is relatively immobile and long-range cationic transport involves the transfer of solvated cations between neighboring coordination sites promoted by local polymer relaxations (referred to as *dynamic bond percolation*[6]), along with migration and diffusion of ionic aggregates weakly coordinated to the polymer solvent. Ionic transport primarily occurs in amorphous regions of the complexes,[7] and segmental motion of the polymer host matrix is critical for long-range charge transport through these systems.[8,9,10]

Due to the relatively low dielectric constants of typical polymer hosts, *e.g.* ε_r~4.7 for poly(propylene glycol)4000,[11] long-range Coulomb forces in general give rise to extensive cation-anion interactions. The extent of such interactions can, for instance, be investigated by analyzing shifts and/or splits of characteristic internal vibrational modes of various polyatomic anions (*e.g.*, $[ClO_4^-]$ or $[CF_3SO_3^-]$) in vibrational spectroscopic studies.[12,13,14,15] It is recognized that cation-anion interactions influence the overall ionic transport properties in polymer electrolyte materials.

Transport phenomena in concentrated electrolytic solutions can be determined using concentrated solution theory.[16] According to Newman, it is necessary to specify n(n-1)/2 independent transport properties, (n refers to the number of independent species in the solution), in order to completely describe ionic transport processes in such systems.[16] For binary polymeric electrolytes, (*i.e.*, n=3), the ionic conductivity σ is frequently the only transport property which is reported in the literature. It is, therefore, essential to consider additional transport properties such as the differential salt diffusion coefficient, D_S, and the cationic transference number, t^0_+. Determinations of t^0_+ in solid

polymer electrolytes are, however, generally experimentally cumbersome (*i.e.*, the Hittorf method)[18] or may inaccurately rely on assumptions concerning the ideality of the solution.[19]

In the present study, we report concentration dependences for the 3 complementary transport properties σ, t^0_+, and D_S in the binary electrolytic system $P(EO)_n$–NaTFSI. To determine t^0_+, we have employed a recently developed electrochemical method requiring no assumptions about the ideality of the electrolyte.[20,21,22,23] These *macroscopic* transport property measurements are complemented by Raman spectroscopic data probing *microscopic* cation-anion and cation-polymer interactions.

Experimental

High-molecular-weight PEO (Aldrich, MW $5 \cdot 10^6$ g/mole) was complexed with NaTFSI salt to produce $P(EO)_n$NaTFSI (P(EO)=poly(ethylene oxide), TFSI=$[(CF_3SO_2)_2N]$) polymer electrolyte films, following procedures described previously.[20,23] The abbreviation O:Na is used throughout the paper to indicate the ratio of $[CH_2CH_2O]$ repeat units to moles of salt.

NaTFSI was prepared by an ion-exchange reaction of LiTFSI with $Na_{0.44}MnO_2$ as described previously[23]. Sodium (Alfa products) was purified as described previously,[20] and rolled into foils approximately 5 mil thick, prior to use in cells.

The densities of the 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.

Symmetrical cells of configuration Na/polymer electrolyte/Na were assembled under an inert atmosphere and equilibrated at the desired operating temperature (85°C) 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 D_s measurements and current interrupt experiments. A Solartron SI 1286 electrochemical interface and 1254 four-channel frequency response analyzer was used to measure ionic conductivities in cells with blocking electrodes. AC-impedance spectra represented as Nyquist plots in the complex plane were extrapolated to determine the bulk sample resistance.

For concentration cell measurements, two polymer electrolyte 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. For concentration cells of the form Na/[electrolyte]$_n$/[electrolyte]$_m$/Na, where [electrolyte]$_{n \text{ or } m}$ represents a polymer–salt solution of composition O:Na= n or m:1, the potential reading is taken to be positive for n>m (O:Na=7:1). Use of a high input impedance electrometer (a Keithley 642) prevents cell polarization during measurement.

In order to obtain D_S, symmetrical cells with non-blocking electrodes (*i.e.*, sodium metal) are polarized galvanostatically. When the current is turned off, the induced salt concentration profile in the cell is allowed to relax. At long times after the current interrupt, the measured cell potential $\Delta\Phi$, which is proportional to the induced concentration difference Δc, relaxes according to equation 1:[20,24,25]

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

where D_S is the differential salt diffusion coefficient, L is the electrolyte thickness and A_1 a constant. Thus, at long observation times a plot of $\ln\Delta\Phi$ vs. time is linear with the slope proportional to D_S.

To calculate transference numbers, the results from three separate experiments are combined, according to equation 2:[20,21,22,23]

$$t_-^0 = 1 - t_+^0 = \frac{mcF(\pi D_S)^{1/2}}{4} \Big/ \left|\frac{dU}{d\ln c}\right| \qquad (2)$$

where c is the molar salt concentration, dU/dlnc is the local slope of concentration cell plots, and m is a slope derived from current interrupt data.[20] It can be shown that the concentration difference Δc across a symmetrical cell after a small perturbation (*i.e.*, galvanostatic polarization with a current density I during time t_i) is proportional to $\xi = It_i^{1/2}$.[20] In equation 2, m is the initial slope of a plot of induced cell potential, $\Delta\Phi$, vs. ξ for small values of ξ. To accurately determine m the potential reading should be taken before significant salt diffusion occurs, but after double layer charging has dissipated. By plotting $\Delta\Phi$ vs. the dimensionless time T:

$$T \equiv \frac{t_i^{1/2}}{t^{1/2} + (t - t_i)^{1/2}} \qquad (3)$$

the potential difference corresponding to the concentration profile at the time of current interrupt can be retained by linear extrapolation back to T=1.[23,26] Reported values are averages of 3-5 experiments.

FT-Raman spectra with a wavenumber resolution of 2 cm^{-1} were recorded at 85ºC ±0.3º C. The spectra were recorded with a Bruker IFS 66 equipped with a Raman module FRA 106 and a continuous Nd:YAG laser (1064 nm) using a 180º back scattering geometry. During measurements, the quartz sample cell was placed in an evacuated thermostat. Samples were equilibrated at the desired temperature for at least 1.5h prior to data acquisition.

Results and Discussion

Figure 1 shows a typical semi-logarithmic plot of the relaxation profile of the cell potential, $\Delta\Phi$, of a symmetrical cell after an initial galvanostatic polarization, used to determine D_s. The theoretical analysis of the method of restricted diffusion for concentrated solutions is well developed.[24,25] According to equation 1, the limiting slope of $\ln\Delta\Phi(t)$ at long observation times is proportional to the differential salt diffusion coefficient. In figure 2, D_S is given as a function of concentration for a range of compositions. It is seen that for O:Na=6–60:1, D_S is about $5x10^{-8}$ cm^2/s, a local minimum is seen at $P(EO)_{120}NaTFSI$ ($D_S=3x10^{-8}$ cm^2/s), and the salt diffusion coefficient increases gradually to about $7.6x10^{-8}$ cm^2/s for very dilute solutions ($P(EO)_{495}NaTFSI$). The values of the diffusion coefficients obtained in this study are similar to those obtained for the analogous $P(EO)_nNaCF_3SO_3$ system, although the variation with composition in the upper concentration range is less pronounced.[20]

Figure 3a shows ionic conductivities as a function of salt concentration at 85°C for the $P(EO)_nNaTFSI$ system. Conductivities as high as ~1 mS/cm are measured for compositions in the range O:Na = 12:1–40:1. Interestingly, the equivalent ionic conductivity, $\Lambda=\sigma/c$, exhibits a concentration dependence roughly resembling that of the differential salt diffusion coefficients, (see Figure 3b). A correlation between the concentration dependence of these two transport properties has previously been reported for polymeric ion-conductors based on the host polymer poly(propylene glycol) of molecular weight 4000 (PPG4000).[15,23,27] In PPG4000-based solutions, Λ typically exhibits a characteristic sharp increase from a minimum in dilute solutions passing through a maximum at intermediate compositions.[15,27,28] Interestingly, for the $LiCF_3SO_3$–PPG4000 system, the close qualitative correlation between the concentration dependencies of D_S and Λ, respectively, was found to be in sharp contrast to the monotonically decreasing trend of the diffusivity of ionic species containing ^{19}F nuclei with increasing salt concentration, determined by ^{19}F pfg-NMR.[29] These results were interpreted in terms of slowly fluctuating salt-rich electrolyte micro-domains in equilibrium with salt–depleted polymer regions and related connectivity effects.[27,29] The very different concentration behavior of D_S

and D(^{19}F), respectively, was attributed to a difference in the time-scale probed in the various experiments.[27,29]

The third transport property, (t_+^0), is calculated from the results of three separate measurements according to equation 2.[20] Figure 4 shows concentration cell data for the $P(EO)_n$–NaTFSI system. 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 cell EMF vs. salt concentration according to equation 4:[30]

$$t_-^0 = \frac{F}{2RT}\left|\frac{dU}{d\ln C}\right| \qquad (4)$$

As seen in figure 4, however, the concentration cell plot deviates markedly from linearity, thus requiring knowledge of the thermodynamic factor (variation of activity with concentration).[19,20] According to equation 2, the resulting transference number is strongly dependent on the value of the local slope of these plots. Therefore, only data points corresponding to high (*i.e.*, O:Na≤12:1) and low (O:Na ≥ 40:1) salt concentrations, respectively, were used because of difficulties in obtaining reliable slopes for intermediate compositions.

Figure 5 shows an example of a plot of cell potential vs. dimensionless time (eqn 3) along with a linear extrapolation back to the time of current interrupt. In figure 6, typical $\Delta\Phi$ vs. ξ data points are given for compositions of O:Na=7:1 and 80:1, respectively. A general trend observed in the present study is that the initial slope (*i.e.*, m) increases with increasing salt concentration, in contrast to the $P(EO)_n$–$NaCF_3SO_3$ system.[20]

By combining results for the differential salt diffusion coefficients with concentration cell data and current-interrupt experiments, t_+^0 is calculated from equation 2. Figure 7 gives t_+^0 as a function of salt concentration. It is clear that t_+^0 is dependent on salt concentration, and is negative over the entire range of compositions investigated. It decreases with increasing salt concentration from –0.27 for O:Na=120:1 to a low of –1.15 for $P(EO)_7$NaTFSI in the most concentrated solution studied.

Few direct measurements of the cationic transference number in solid polymer electrolytes have been reported in the literature.[18,20,31] Because polymer electrolytes, although solid-like, are often sticky, traditional methods for measuring transference numbers, such as the Hittorf method,[17] have met with considerable experimental difficulty. Alternative techniques such as radiotracer,[32] pfg-NMR,[33] concentration cells[34] and potentiostatic polarization have been proposed.[35] Still, it is recognized that these methods typically rely on the assumption of an ideal solution, and the information that is provided must be deconvoluted.[19,31]

Spiro has discussed the distinction between *transport* numbers of individual ionic species and measured *transference* numbers of the ion-constituents in some detail.[17] These distinctions are not always made and have previously been a cause of some confusion in the polymer electrolyte literature. Cameron and Ingram have lucidly reviewed some of the early work.[31] According to Spiro, a transport number can be defined as the fraction of the total current carried by a specific ionic specimen; *e.g.*, determinations of actual transport numbers in systems where cation-anion interactions occur require detailed knowledge of the ionic speciation, as well as the individual ionic mobilities of the species present. This can be a daunting task in non-ideal polymer electrolytes. The transference number, in contrast, is defined as 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, in the absence of concentration gradients.[17] Transference numbers can be measured experimentally whereas transport numbers can only be deduced in special cases.

In a concentrated binary polymer electrolyte, only the transference numbers corresponding to the two ion-constituents (*e.g.*, Na^+ and $(CF_3SO_2)_2N^-$, respectively) are relevant. The only restriction on these numbers is that they, by definition, sum to unity.[17] In contrast, all *transport* numbers relevant to a particular solution must also, by definition, be positive.

A negative value of t_+^0 indicates that solvated "free" cations are relatively immobilized by the polymer 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. Low cationic transference numbers, obtained using pfg-NMR techniques, have previously been reported for PEO-based electrolyte systems incorporating the analogue LiTFSI salt.[33] Lithium ion *transport* numbers nearing 0, obtained using a combination of AC impedance and DC polarization, have also recently been reported for polymeric network structures incorporating LiTFSI salt.[36] These approaches, however, rely on the assumption that cations and anions move independently through the solution (*i.e.*, adherence to the Nernst-Einstein relation), and should strictly only apply in dilute electrolyte systems. Moreover, these assumptions place a limit on the range of possible values of t_+^0; *i.e.*, $t_+^0 \in [0,1]$. In this context, we wish to emphasize that there is ample precedent for negative cationic transference numbers in aqueous electrolytes.[37] Consistently low values of t_+^0 in polymer electrolytes have been reported in investigations based on the Hittorf method or derivatives thereof, which are theoretically rigorous.[18,20,31] One practical consequence of low values of t_+^0 for battery applications is that large, stable, concentration gradients can develop in solid (*i.e.*, non-convective) ion-conductors during

passage of current.[38] This may lead to premature failure of working battery cells through salt precipitation and/or salt depletion in part of the electrolyte.[39]

Turning to the spectroscopic results, we note that vibrational spectroscopic techniques (*i.e.*, Raman and infrared spectroscopies) frequently are used to investigate the local *anionic* environment in various electrolytic systems.[12,13,14] By monitoring spectral shifts and/or splits of characteristic internal vibrational modes of polyatomic anions, the extent of cation-anion interactions in the solution can be determined.

Figure 8 shows the spectral region corresponding to the band envelope of the strong symmetric deformation $\delta_S(CF_3)$ Raman mode at ~741 cm^{-1} of the TFSI anion for a range of salt concentrations. The $\delta_S(CF_3)$ mode (Raman)[40] and also the symmetric stretching $\nu_S(SNS)$ (infrared)[41,42,43] mode at ~740-742 cm^{-1} have previously been used in order to study effects of cation-anion interactions in polymeric electrolytes containing $LiN(CF_3SO_2)_2$ salt. In the present study, no distinct ionic species can be resolved, though the entire $\delta_S(CF_3)$ band shifts slightly towards higher frequencies with increasing concentration. This observation indicates that the extent of cation-anion interactions increases with increasing salt concentration in the solution. For the dry, crystalline NaTFSI salt we find the corresponding band centered at ~748 cm^{-1}.

Microscopic information regarding the local *cationic* environment can be obtained by probing vibrational modes of coordinative polymer-cation bonds, in addition to monitoring internal anionic modes. In particular, Kasatani and Sato have shown that the intensity of a cation-polyether oxygen Raman mode at ~860 cm^{-1} is attributable to a symmetric ring breathing motion of ether oxygens surrounding solvated cations, and can be used as a measure of the degree of complexation in the polymer system.[44] Torell and coworkers have recently used this approach to calculate the fraction of "free" (or solvated) cations in electrolytes based on PEO complexed with MCF_3SO_3 salts (M=Na or Li).[45] Figure 9 shows Raman spectra of the region 700–900 cm^{-1}, including the $\delta_S(CF_3)$ Raman mode at ~741 cm^{-1} and the oxygen-sodium ion (O–Na) ring breathing mode at ~865 cm^{-1}, for polymer salt complexes corresponding to compositions of O:Na=60:1, 15:1 and 7:1, respectively. The spectrum of the pure PEO host matrix is also included. By subtracting the polymer background spectrum from the electrolyte spectra, the ratio between the integrated intensity of the O–Na breathing mode and the intensity of the TFSI $\delta_S(CF_3)$ mode can be calculated. The polymer background spectrum is somewhat affected by the interaction with the solvated salt in the region 800-850 cm^{-1}, as seen in figure 9, which causes slight interference with the spectral subtraction procedure. There are, however, no significant

PEO bands overlapping the two modes of particular interest here. Since the integrated intensity of the $\delta_S(CF_3)$ mode is directly proportional to NaTFSI concentration in the solution, changes in this ratio indicate changes in the relative number of cations solvated by the polymer host matrix.[45] As a result we find that the ratio $I(O\text{-}Na)/I(\delta_S(CF_3))$ decreases montonically with increasing salt concentration from 43% to 28% as the salt concentration is increased from O:Na=60:1 to 6:1. This is consistent with an increasing extent of cation-anion interactions in the electrolyte solution with increasing concentration, as also indicated by the frequency shift of the $\delta_S(CF_3)$ mode seen in figure 8. In view of the negative cationic transference numbers and their decrease with increasing salt concentration, these findings strongly suggest that solvated Na^+ ions are relatively immobilized by coordination to the PEO host, and that larger ionic aggregates are the main cationic carriers in the present system.

Ab initio quantum-chemical studies by Sanchez and coworkers of $[Li^+]-[(CF_3SO_2)_2N^-]$ ion-pair configurations show that the affinity of the TFSI anion for the lithium cation is strong, arising essentially from the electrostatic interaction.[46] It was concluded that bidentate structures involving two oxygen atoms, one from each TFSI SO_2 group, are preferred. Similar optimized structures have also been calculated by Scanlon for the analogue $[Na^+]-[(CF_3SO_2)_2N^-]$ ion-pairs.[47] In view of these observations it seems reasonable that cation-anion interactions in M–TFSI systems may be manifested more markedly as changes in internal anionic vibrational modes with significant SO_2 character, rather than in the $\delta_S(CF_3)$ mode at ~741 cm^{-1}. Recent theoretical work by Lindgren and co-workers shows that a Raman active mode observed at ~400-410 cm^{-1} has a significant SO_2 character.[48] Interestingly, we observe a split band with components at ~398 and 407 cm^{-1} , respectively, see figure 10. The relative intensity of the component at ~407 cm^{-1} increases markedly with increasing temperature, and also somewhat with increasing salt concentration, at the expense of the low frequency component. In the PEO_7–NaTFSI complex, the melting transition occurs at ~58°C so the two spectra shown in figure 10 correspond to a partly crystalline (21°C) and a molten (70°C) solution, respectively.[49] The observed split feature may thus be sensitive to the conformation of the host matrix. Notably, only minute changes were observed in the corresponding $\delta_S(CF_3)$ mode at ~741 cm^{-1}.

We have recently reported a significant lowering in temperature of the melting transition for $P(EO)_n$–NaTFSI complexes;[23] *e.g.*, a eutectic was observed at 46°C for compositions near $P(EO)_{12}$–NaTFSI (pure PEO melts at ~68-70°C)[50]. While these results suggest that practical operating temperatures for SPE-sodium batteries may be substantially lowered from currently used values (85°C)[51], it is, however, not clear how transport properties such as t_+^0 are affected by a decrease in

temperature, nor how potential temperature dependent changes of the solubility of salt[31] in macromolecular solvents may effect the utility of these materials for electrochemical applications.

To summarize, ionic transport phenomena in polymer electrolyte materials are highly complex and, certainly, the microscopic mechanisms governing long-range transportation of cations through the SPEs are not fully understood. In view of the low and even negative cationic transference numbers reported for various SPEs,[18,20,31] it is not obvious that a relatively large number of "free" charge carriers necessarily provides a more effective transference of cations through the solutions.[31] Indeed, the role of complexed ions in the mass transfer in these macromolecular electrolytes remains unclear. Further studies are definitely warranted.

Conclusion

A full set of ionic transport properties are reported for $P(EO)_n$–NaTFSI polymer-salt complexes at 85°C over a range of concentrations. Measured transport properties include the ionic conductivity, σ, the differential salt diffusion coefficient, D_S, and the cationic transference number, t_+^0. We find that σ as well as D_S are enhanced relative to previously reported results for the analogue $P(EO)_n$-$NaCF_3SO_3$ system;[20] the differential salt diffusion coefficient also varies less with complex composition in concentrated solutions. The cationic transference numbers are found to be negative over a wide concentration range, implying that the cationic current mainly is carried by complexed ions. Complementary Raman spectroscopic studies directly probing cation-anion and cation-polymer molecular interactions show that extensive cation-anion interactions occur in this system. In particular, we observe a decrease in the relative abundance of solvated Na^+-ions with increasing salt concentration, as determined from the ratio between the integrated intensity of the O–Na breathing mode at ~865 cm^{-1} and the intensity of the TFSI $\delta_S(CF_3)$ mode at ~741 cm^{-1}. A split Raman mode of the TFSI anion with significant SO_2 character, appearing at ~400-410 cm^{-1}, displays a pronounced temperature and concentration dependence. In view of preliminary theoretical work,[48] this observation supports recent determinations of optimized M–TFSI (M=Li or Na) ion pair configurations.[46,47]

Acknowledgment

This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Transportation Technologies, Office of Advanced Automotive Technologies of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. A. Ferry would like to thank Vattenfall Utveckling AB and Helge Ax:son Johnsons stiftelse for financial support. We would also like to thank Dr. Marc Doyle of DuPont for many helpful discussions.

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Figure Captions

Fig 1.

Typical relaxation of the potential difference across a symmetrical Na/$P(EO)_{12}$–NaTFSI/Na cell after an initial galvanostatic polarization. The slope is taken at long times in order for linear behavior to be observed.[20,24,25] The differential salt diffusion coefficient D_S thus obtained describes average bulk salt motion in response to an initial concentration profile.

Fig 2.

Differential salt diffusion coefficients for the $P(EO)_n$-NaTFSI system at 85°C as a function of salt concentration (O:Na ranging from 6:1 to 495:1, indicated on the top concentration scale).

Fig 3a.

Ionic conductivity as a function of salt concentration for the $P(EO)_n$-NaTFSI system at 85°C.

Fig 3b.

Equivalent ionic conductivity as a function of salt concentration.

Fig 4.

Concentration cell data recorded on cells of the form Na/$[\text{electrolyte}]_n$/$[\text{electrolyte}]_m$/Na, where $[\text{electrolyte}]_{n \text{ or } m}$ represents a polymer–salt solution of composition O:Na = n or m. The potential reading is taken to be positive for n>m (O:Na=7:1).

Fig 5.

Plot of $\Delta\Phi$ vs. dimensionless time T (equation 3) for a typical current interrupt experiment (composition $P(EO)_7$NaTFSI; I= 0.098 mA/cm^2, t_i = 30.55 s). The dashed line shows a linear extrapolation back to T=1, corresponding to the time of current interrupt.

Fig 6.

Typical plots of calculated (figure 5) cell potential $\Delta\Phi$ vs. $It^{1/2}$. The slope at small values of $It^{1/2}$ corresponds to the parameter m in equation 2.

Fig 7.

Sodium ion transference number (t_+^0) as a function of salt concentration. Solid line is drawn as a guide to the eye.

Fig 8.

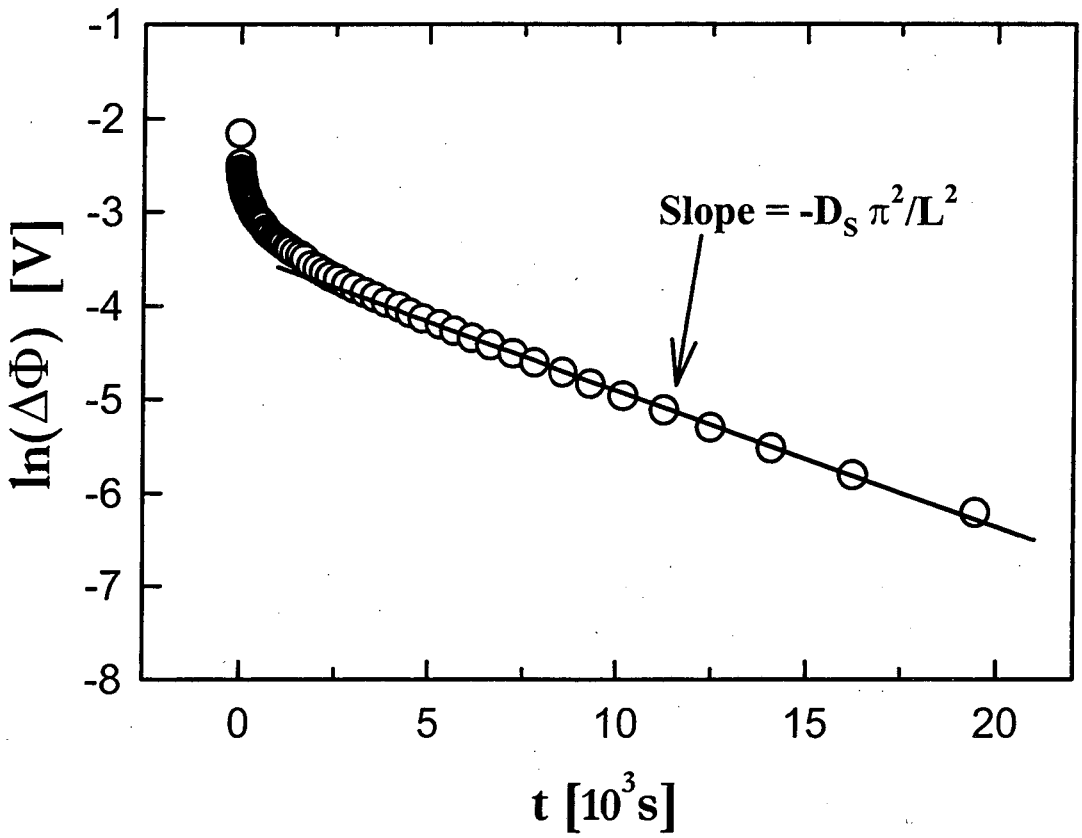
FT-Raman spectra of the spectral region corresponding to the strong $\delta_S(CF_3)$ Raman mode at ~741 cm^{-1} of the TFSI anion for salt concentrations ranging from O:Na=60:1 to 6:1.

Fig 9.

FT-Raman spectra of the region 700–900 cm^{-1}, including the $\delta_S(CF_3)$ Raman mode at ~741 cm^{-1} and the oxygen-sodium ion (O–Na) ring breathing mode at ~865 cm^{-1}, for polymer salt complexes corresponding to compositions of O:Na=60:1, 15:1 and 7:1, respectively. The spectrum of the pure PEO host matrix is also included.

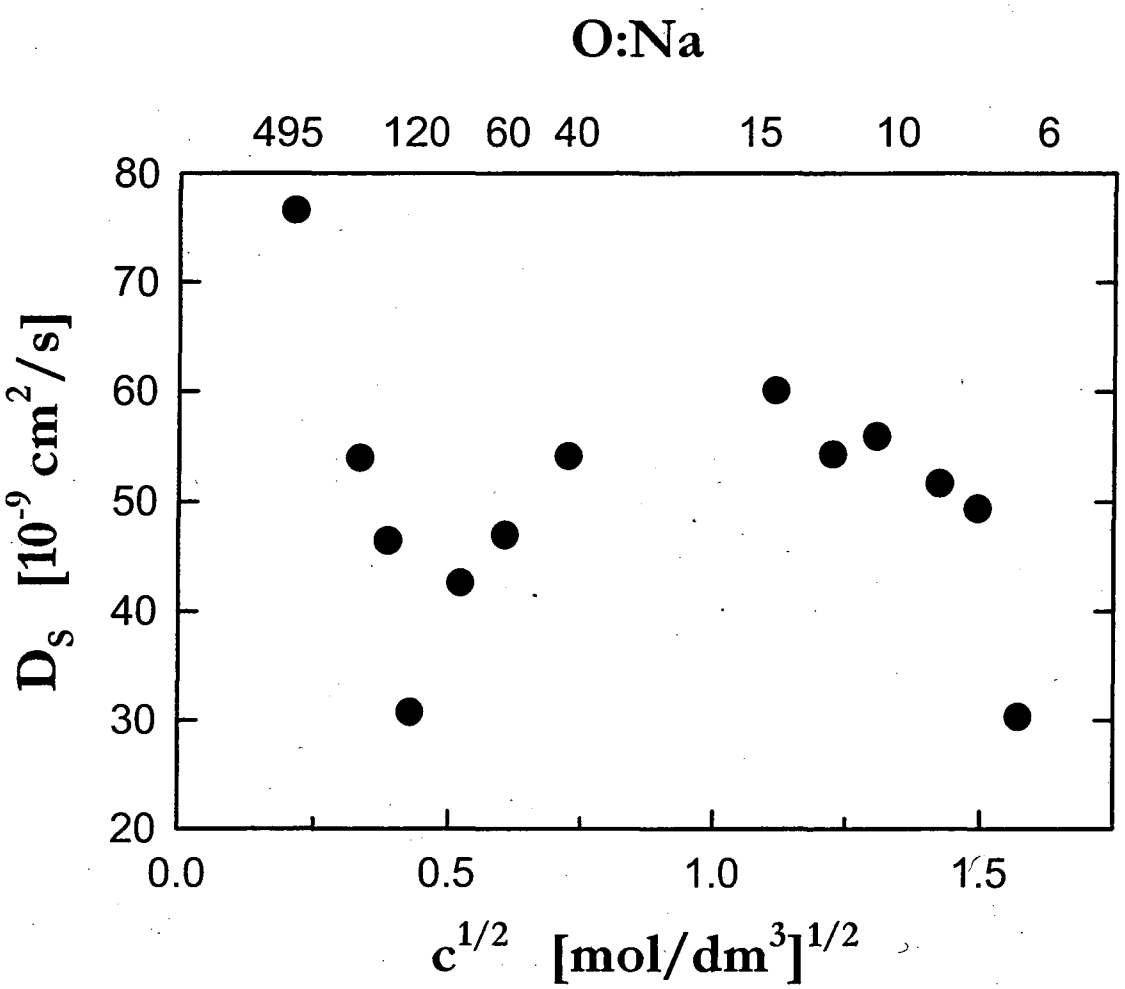
Fig 10.

FT-Raman spectra of the $P(EO)_7$–NaTFSI complex recorded at different temperatures indicated on the figure. A split mode with components at ~398 cm^{-1} and 407 cm^{-1} is observed.



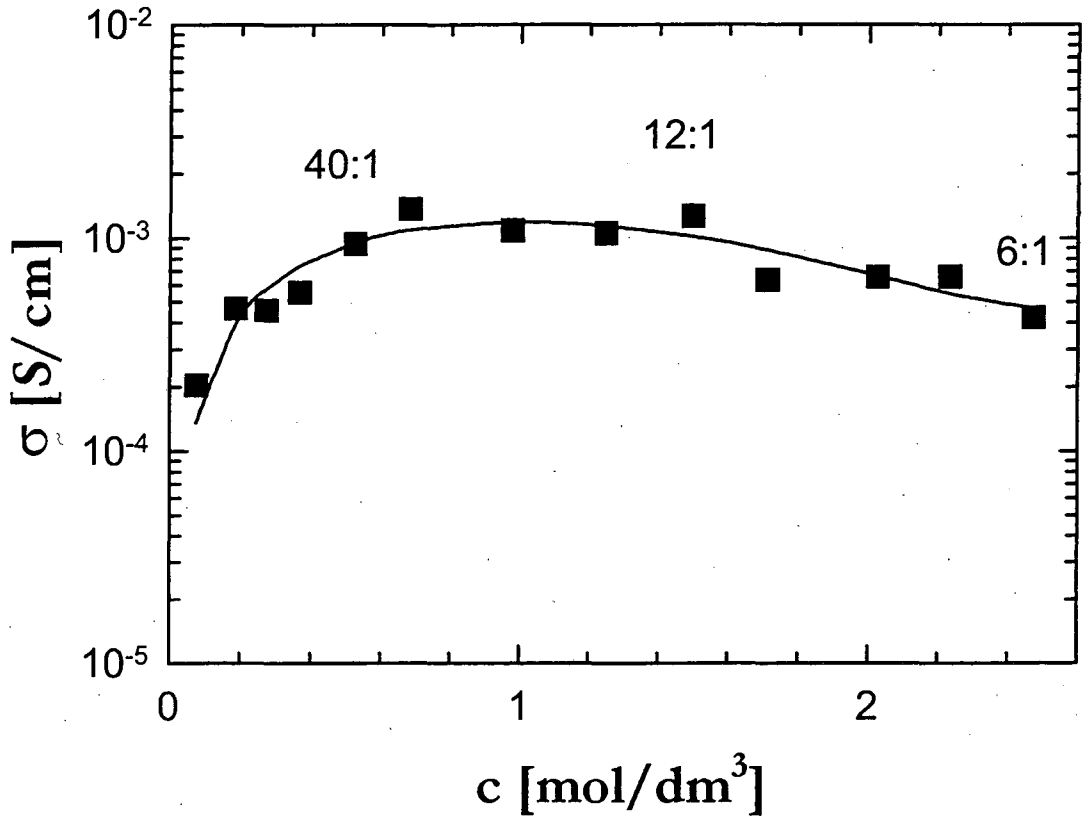
Ferry, Doeff, and De Jonghe, "Transport property and Raman ..."

Fig 1.



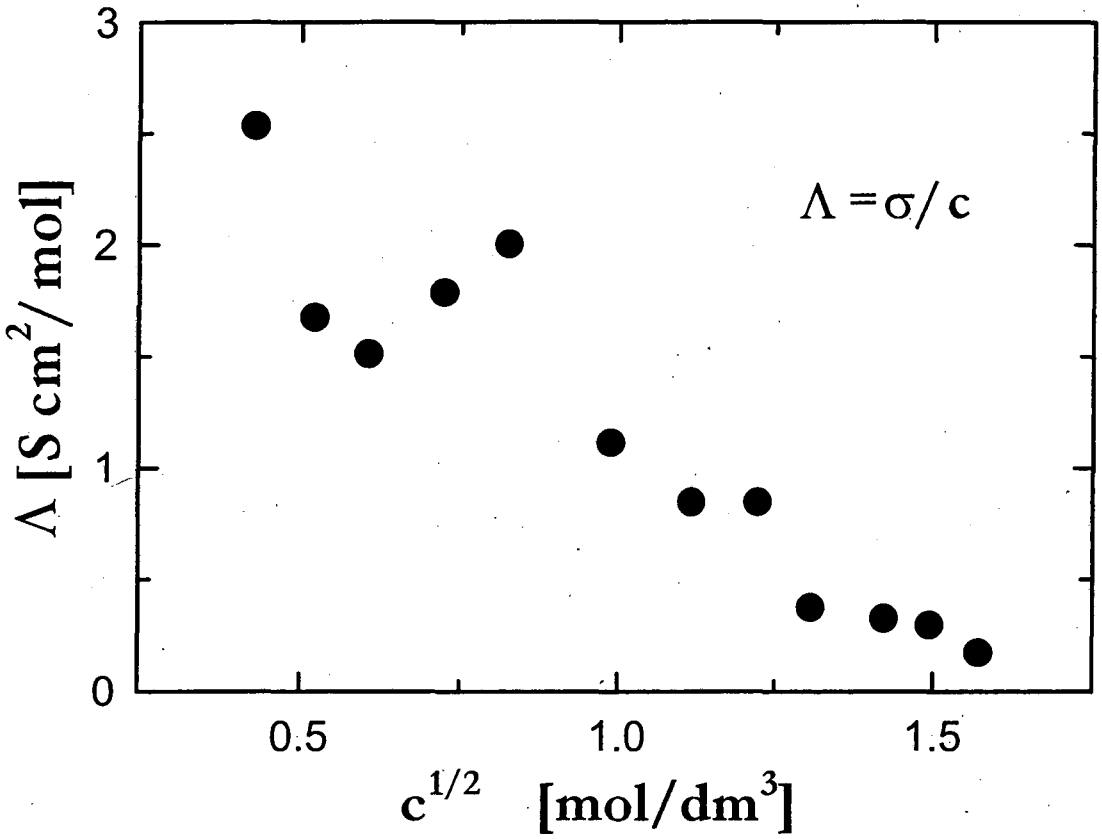
Ferry, Doeff, and De Jonghe, "Transport property and Raman ..."

Fig 2.



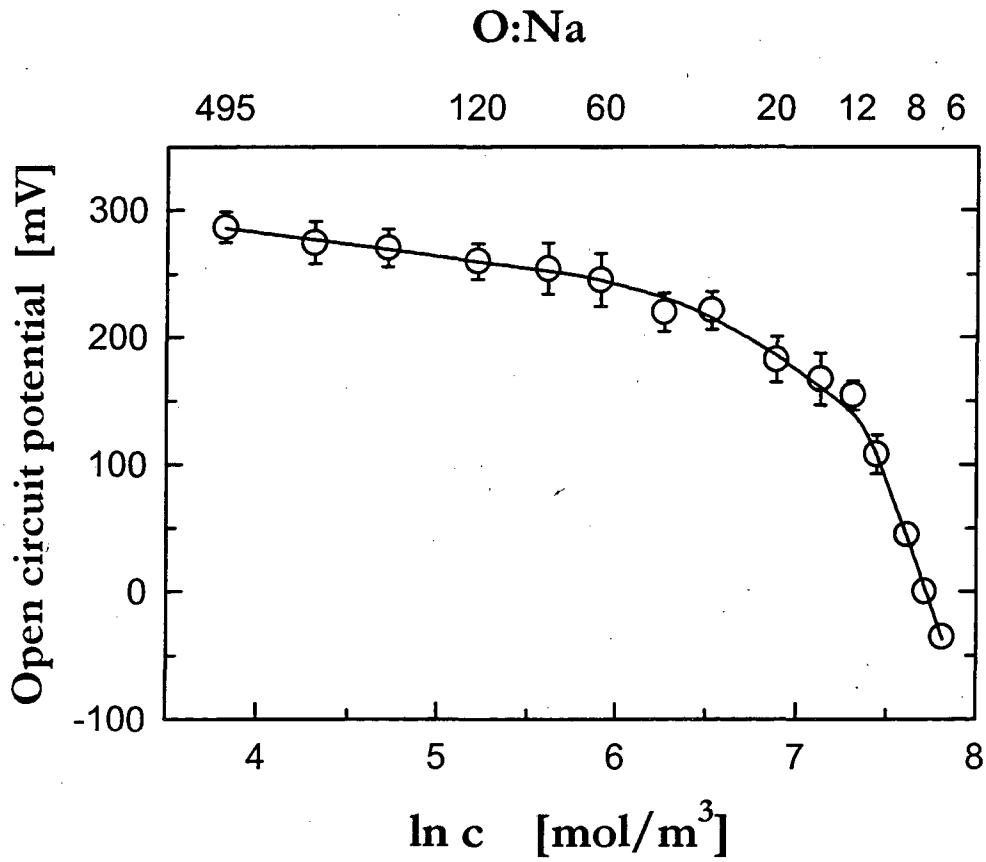
Ferry, Doeff, and De Jonghe "Transport property and Raman ..."

Fig 3a.



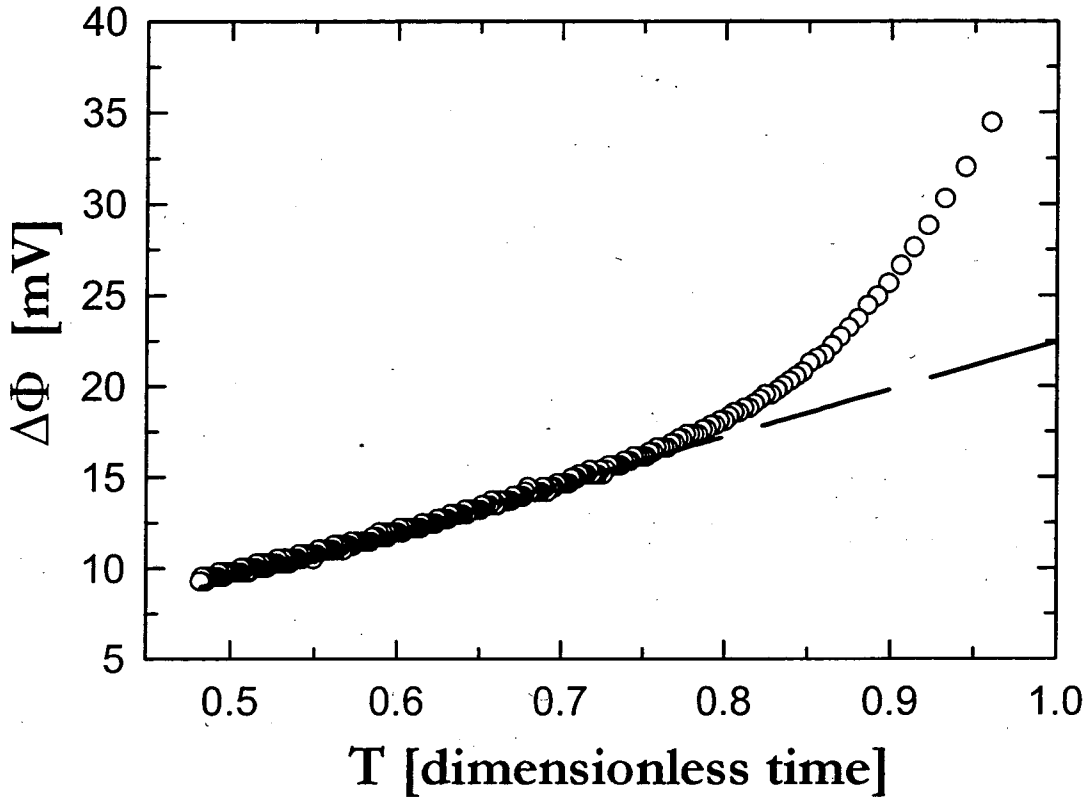
Ferry, Doeff, and De Jonghe, "Transport property and Raman ..."

Fig 3b.



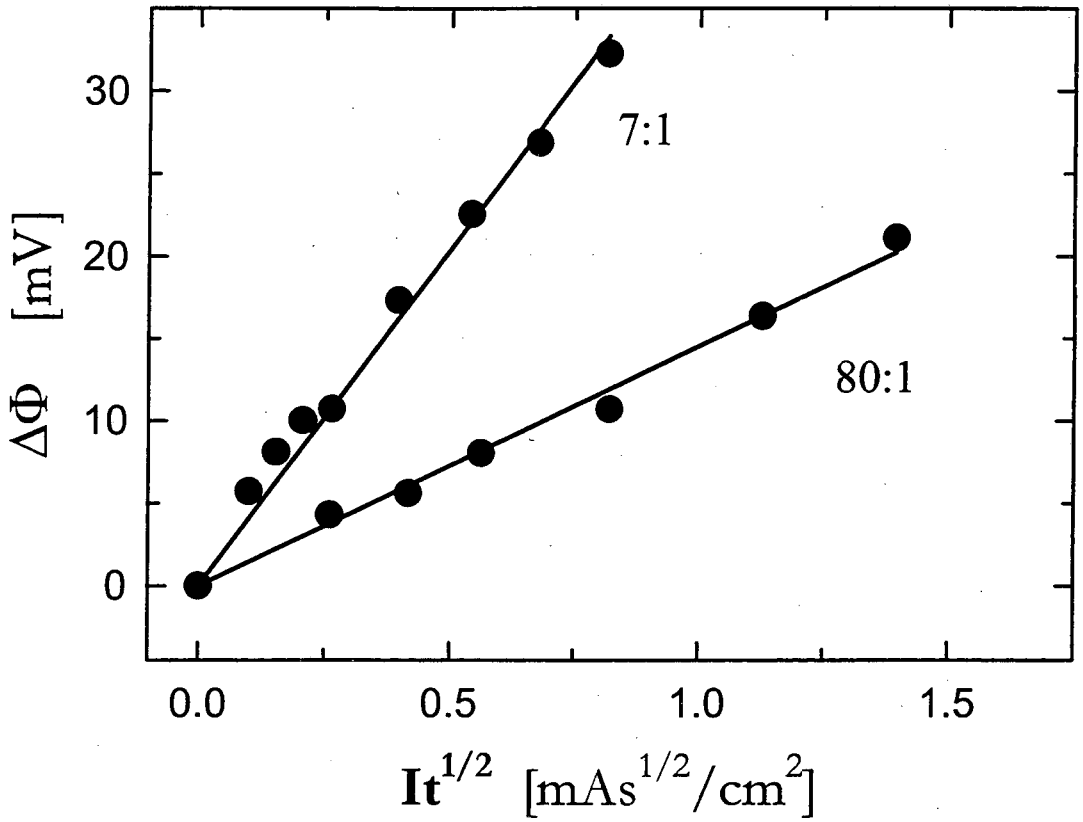
Ferry, Doeff, and De Jonghe "Transport property and Raman ..."

Fig 4.



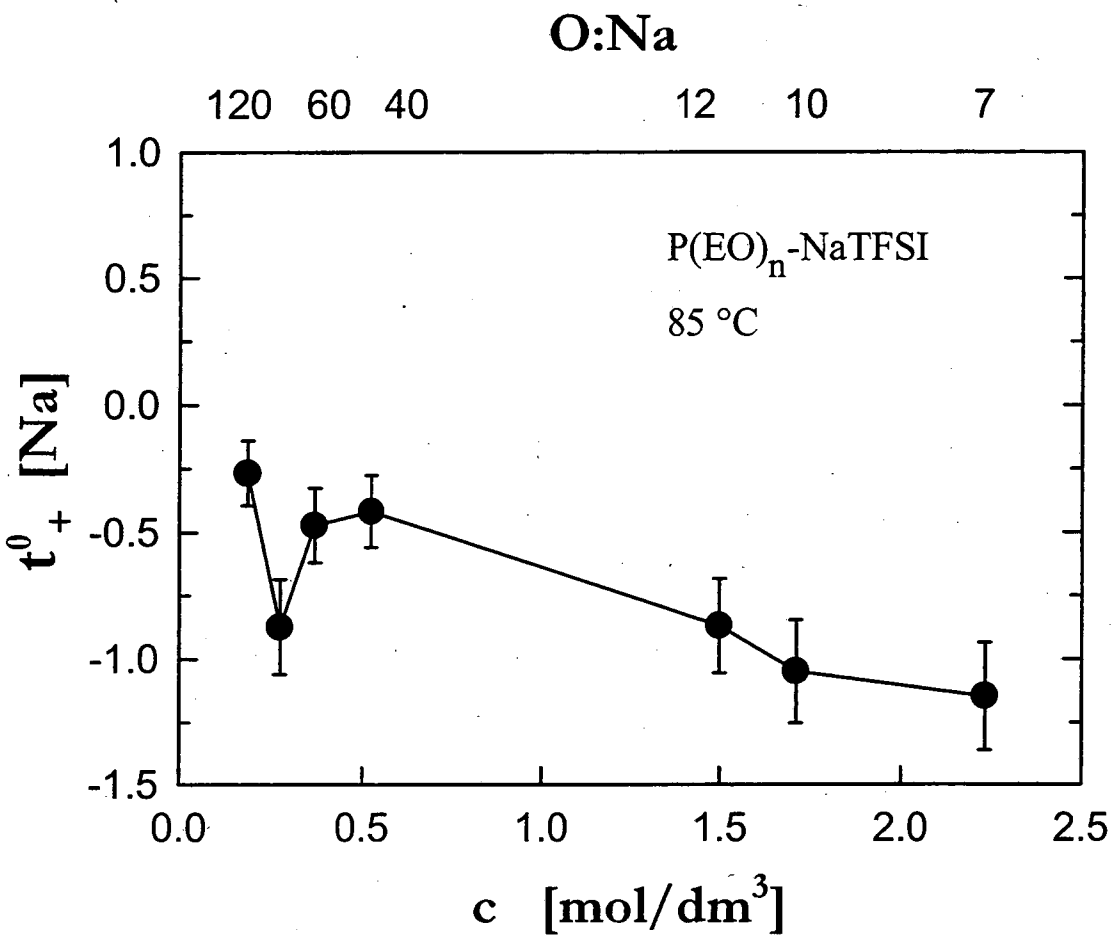
Ferry, Doeff, and De Jonghe "Transport property and Raman ..."

Fig 5.



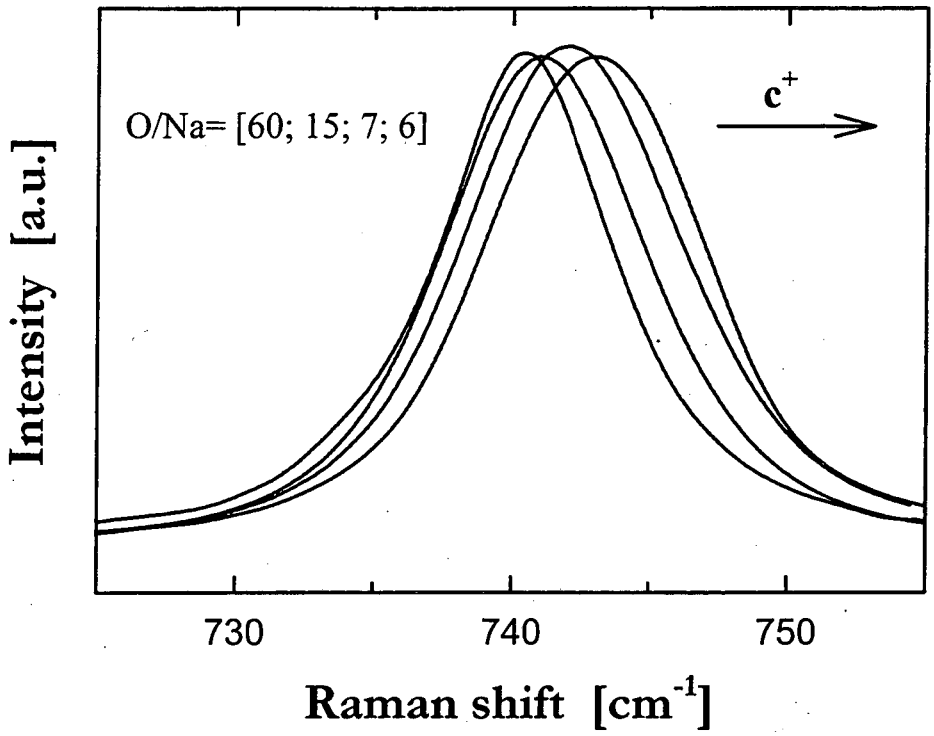
Ferry, Doeff, and De Jonghe "Transport property and Raman ..."

Fig 6.



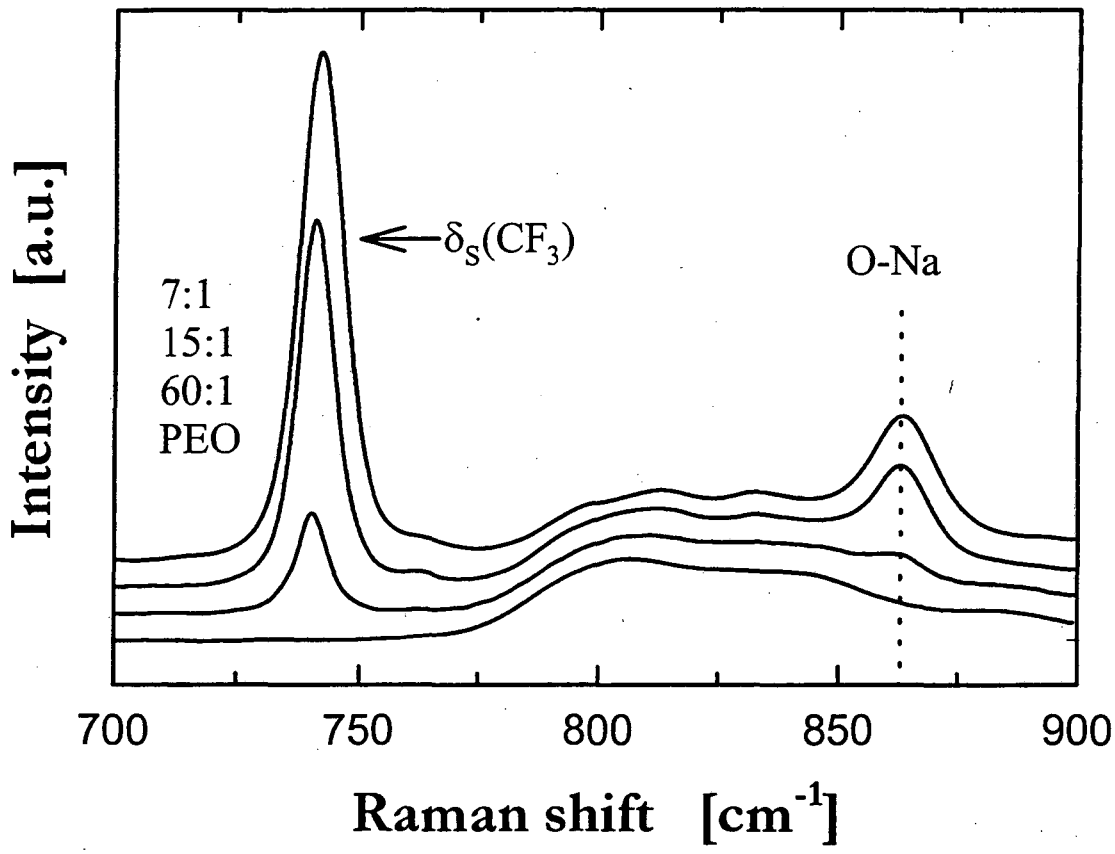
Ferry, Doeff, and De Jonghe "Transport property and Raman ..."

Fig 7.



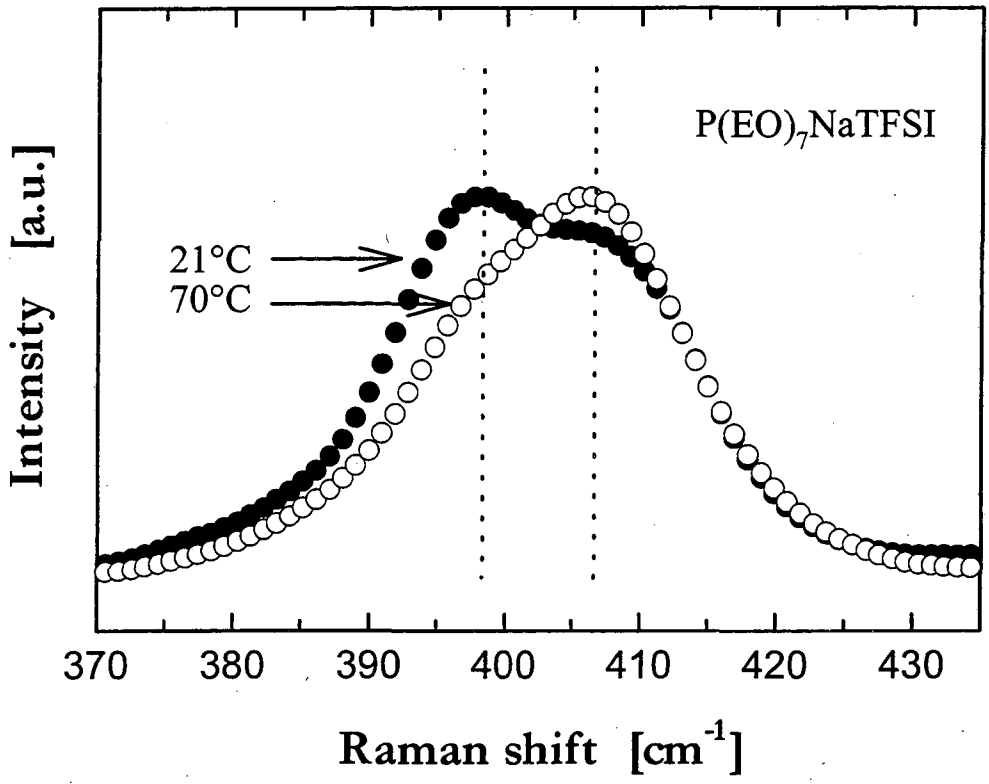
Ferry, Doeff, and De Jonghe "Transport property and Raman ..."

Fig 8.



Ferry, Doeff, and De Jonghe "Transport property and Raman ..."

Fig 9.



Ferry, Doeff, and De Jonghe "Transport property and Raman …"
Fig 10.

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Prepared for the U.S. Department of Energy under Contract No. DE-AC03-76SF00098