

Transport Properties of the Solid Polymer Electrolyte System P(EO)_nLiTFSILudvig Edman,^{*,†} Marca M. Doeff,[†] Anders Ferry,[‡] John Kerr,[§] and Lutgard C. De Jonghe[†]*Lawrence Berkeley National Laboratory, Materials Science Division and Environmental Energy Technology Division, University of California, Berkeley, California 94720, and Department of Materials Engineering, Monash University, Clayton, 3168 VIC, Australia**Received: November 4, 1999; In Final Form: January 11, 2000*

Values for the lithium ion transference number (t_+^0) are reported for the solid polymer electrolyte system poly(ethylene oxide) (PEO) complexed with Li(CF₃SO₂)₂N (LiTFSI). t_+^0 ranges from 0.17 ± 0.17 to 0.60 ± 0.03 in the salt concentration (c) region of 742 to 2982 mol/m³ at 85 °C. The concentration dependence of t_+^0 and the molar ionic conductivity (Λ) are shown to be in good agreement with a free volume approach over the salt-rich composition range investigated. The present t_+^0 results were obtained using an electrochemical technique based on concentrated solution theory. This experimentally straightforward method is herein demonstrated to give accurate results for a highly concentrated SPE system, without relying on any dubious simplifications regarding the state of the electrolyte.

Introduction

The concept of dissolving the salt of an alkaline metal in a polar macromolecule and thus creating an ion-conducting solid material, also called a solid polymer electrolyte (SPE), was initially proposed by Wright and coworkers more than two decades ago.¹ Armand et al. subsequently proposed their use in electrochemical devices such as rechargeable lithium batteries.² Much research effort has since then been directed toward understanding the complex chemistry and ionic transport properties of these technologically important materials.³ A few years following Armand's proposal, it was established that phase diagrams of SPEs constitute so-called eutectic systems of one or more intermediate crystalline compounds with melting points well above room temperature.^{4,5} Concurrently, it was recognized that significant long range ionic transport only takes place through amorphous regions,⁶ restricting use of SPEs based on, for instance, poly(ethylene oxide) (PEO) to moderately elevated temperatures. Several routes to suppress the formation of crystalline domains have since been explored, e.g., the inclusion of nano- or micrometer sized fillers, such as fullerenes⁷ and ceramic powders,^{8–11} as well as the incorporation of low molecular weight solvents.¹² Another interesting avenue involves the development of novel salts with bulky anions such as Li(CF₃SO₂)₂N [(lithium (bis)trifluoromethanesulfonate imide, LiTFSI)],¹³ which are reported to act as plasticizers when complexed with PEO.¹⁴ Later reports have, however, shown that a crystalline eutectic system is the favored thermodynamic state for this system as well, at least for high molecular weight polymers,¹⁵ though the recrystallization kinetics are extremely slow.¹⁶

For the effective design of SPEs for advanced rechargeable batteries and other applications, the ionic transport properties

must be thoroughly understood. In spite of extensive research efforts, however, it is often only the bulk ionic conductivity (i.e., related to motion of *both* cations and anions) which is reported. This is somewhat surprising since it is *only the cations* that are electroactive towards the electrodes in a typical lithium polymer battery; hence, the relative transfer of charge of this ion-constituent, the cationic transference number (t_+^0), is a parameter of fundamental significance.¹⁷ 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 in the absence of concentration gradients.¹⁸

Although some measurements of transference numbers in SPEs have been obtained, the results are inconsistent,¹⁹ most probably due to invalid simplifying assumptions regarding the ideality of the electrolyte.²⁰ In particular, the so-called "steady state current method"²¹ is still frequently applied, despite theoretical shortcomings apparent when dealing with concentrated solutions.²⁰ The proliferation of papers in the literature reporting (invalid) data, with analyses relying on the "ideal" Nernst–Einstein relation, can be traced back to the inherent sticky and solid nature of SPEs, which largely precludes use of the classical Hittorf method (in which the electrolyte layer is sectioned and weighed after passage of current).²²

To overcome these difficulties, a new electrochemical Hittorf method, general in nature but especially useful for solid-like materials such as SPEs, was recently developed by Newman and coworkers.²³ It is based on concentrated solution theory and allows calculation of the cationic transference number from the results of three different electrochemical measurements; i.e., concentration cell, restricted diffusion, and current interrupt experiments.^{3b,23,24}

In this paper, we present results from these electrochemical measurements with the calculated lithium ion transference numbers and molar ionic conductivities as a function of salt concentration for LiTFSI dissolved in PEO. All results were obtained at 85 °C to ensure that samples with ether oxygen to lithium ratios (from hereon referred to as n) equal to or greater than 5 were single-phase. This also facilitated a comparison with

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previously published data on related systems.^{23,25–28} Since the calculation of the cationic transference number is dependent on three different experimental parameters, we found it important to include a careful error analysis.

Experimental

High molecular weight PEO (Aldrich, $M_w = 5 \times 10^6$ g/mol) was dissolved in acetone and recrystallized in order to remove the butylhydroxytoluene (BHT) stabilizer. LiTFSI, a gift from the 3M Company, was dried at 180 °C for at least 12 h under vacuum. The P(EO)_nLiTFSI electrolytes were synthesized in a glove box under helium ($O_2 < 1$ ppm) by dissolving pre-weighed amounts of polymer and salt in acetonitrile. The clear solutions were stirred and then cast into glass rings on Teflon-coated plates. Further drying took place for at least 24 h under vacuum in order to remove the solvent. During this process, care was taken not to heat the electrolytes.

The bulk molar salt concentration (c) as a function of n was measured by placing weighed electrolytes in pycnometric flasks of known volume (10 cm³) filled with n -heptane. The weight of the flask before and after displacement of the liquid allowed densities and, subsequently, c values to be calculated for each electrolyte. n values from 3 to 100 corresponded to salt concentrations covering the 3970–255 mol/m³ range.

Concentration cells of the configuration Li/P(EO)_mLiTFSI/P(EO)_nLiTFSI/Li were assembled on glass substrates under an inert helium atmosphere, with m kept constant at 12 while n was varied between 5 and 50. All interfaces were established through edgewise overlap of the lithium and/or SPE films, respectively, thereby providing for diffusion pathways of several centimeters in each phase. This was done to prevent a relaxation of the induced concentration gradients on the time scale of the experiment.^{23,24} A high input impedance electrometer (Keithley 642) was used for data acquisition in order to eliminate effects of cell polarization not stemming from the pre-set concentration gradient. A mathematical relation between the cell potential and the concentration gradient in the form of $dU/d \ln c$ was achieved using a 4th order polynomial fit of the measurement data using Origin software.

For restricted diffusion and current interrupt measurements, symmetrical cells with lithium electrodes, the electrolyte, and a 76 μm thick polypropylene spacer were assembled in the glove box. The whole “cell sandwich” was put into airtight Swagelok cells before being transferred to a convection oven (estimated temperature stability of ±0.5 °C) for a 24-h thickness equilibration at 85 °C. A computer-controlled Arbin multichannel potentiostat/galvanostat was used for the galvanostatic polarizations required for both experimental quantities. To obtain values for the salt diffusion coefficient (D_s), the method of restricted diffusion was used, which also provides values of high accuracy for concentrated solutions.²⁹ Following an initial polarization, the relaxation of the potential ($\Delta\Phi$) towards equilibrium for a SPE of known thickness (L) was monitored. At long times, the following relationship, in which C_1 is a constant, holds true:

$$\ln(\Delta\Phi) = -\pi^2 D_s t / L^2 + C_1 \quad (1)$$

The aim of the current interrupt experiments is to establish concentration gradients at the electrode surfaces without allowing the concentration boundary layers to propagate to the center of the cell. In order to fulfill this requirement, the upper limit for the polarization time (t_i) is set by the condition:²³

$$t_i \ll L^2 / D_s \quad (2)$$

With this requirement fulfilled, the established salt concentration gradient (Δc) over the full cell is directly proportional to the anionic transference number (t_-^0), in accordance with eq 3, where I is the current density and F represents Faraday's constant. For a thorough derivation of this key equation, the original work should be consulted.²³

$$\Delta c = 4t_-^0 (It_i)^{1/2} / F(\pi D_s)^{1/2} \quad (3)$$

By using the relationship between the cationic and anionic transference number,¹⁸ as described in eq 4, it is mathematically relatively straightforward to rewrite the above equation to obtain t_+^0 as a function of three parameters accessible from previously described experiments. In order to make this equation more compact, the parameter m has been made to represent the initial slope of a plot of cell potential vs ($It_i^{1/2}$).

$$t_+^0(m, D_s, dU/d \ln c) = 1 - t_-^0 = 1 - (mcF(\pi D_s)^{1/2} / (4dU/d \ln c)) \quad (4)$$

For the AC conductivity measurements, preparations were identical to those of the current interrupt experiments with the notable exception that blocking stainless steel electrodes were used instead of lithium electrodes. The impedance of an electrolyte was determined for a frequency range of 65 kHz to 1 Hz, with a Solartron SI 1254 four-channel frequency response analyzer coupled to a 1286 electrochemical interface, with the bulk resistance taken as the touchdown point of the semi-circle or spur on the Z' -axis of a Nyquist plot.

The Gauss approximation formula was used to estimate the accuracy of our data (error bars included in Figure 5).³⁰ For m and D_s the standard deviation calculated at each discrete salt concentration was used for the error, while the error in c was set to zero considering its comparatively small size. For the error in the quantity $dU/d \ln c$, we chose to calculate the maximum difference between the derivative of the fit presented in eq 5 and the slope of a straight line connecting two adjacent potential readings as presented in Figure 4. This approach probably overestimates the error, especially at low salt concentrations, but the trend showing an increasing t_+^0 value with increasing salt content is still significant.

Results and Discussion

The first quantity needed for the determination of t_+^0 is m , i.e., the initial slope in a plot of potential vs ($It_i^{1/2}$), obtained from current interrupt experiments; this subsequently required a whole set of independent experiments to be performed for each salt concentration. A notable problem in obtaining these data points originated in the occurrence of two superimposed effects—a concentration potential and a “double layer” potential—resulting from the galvanostatic polarization. One way to deconvolute the former is to make use of the comparatively long time scale on which it dissipates as compared to the latter (minutes vs milliseconds),²⁴ and to plot the potential vs the dimensionless time ($T = t_i^{1/2} / (t^{1/2} + (t - t_i)^{1/2})$; t_i = polarization time).³¹ A linear extrapolation of the potential at long times ($T < 1$) back to the time of the current interrupt ($T = 1$) then allows the concentration potential at the time of the current interrupt ($\Delta\Phi_0$) to be determined. This concept is visualized in Figure 1 for P(EO)₁₂LiTFSI, which initially had been galvanostatically polarized at 150 μA/cm² for 34.29 s. This polarization time fulfills the requirement set by eq 2, since the characteristic values of this study of $L = 76 \times 10^{-6}$ m and $D_s < 6 \times 10^{-12}$ m²/s leads to $t_i \ll 1000$ s. Three of the data sets used for the m

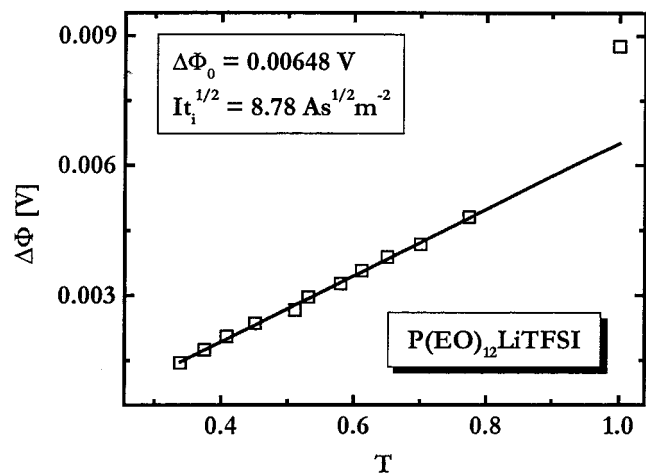


Figure 1. Plot of the relaxation of potential ($\Delta\Phi$) vs the dimensionless time (T) for P(EO)₁₂LiTFSI at 85 °C after a galvanostatic polarization ($I = 150 \mu\text{A}/\text{cm}^2$; $t_i = 34.29 \text{ s}$). The solid line represents a linear extrapolation back to time of the current interrupt ($T = 1$) allowing the initial concentration potential, $\Delta\Phi_0$, to be determined.

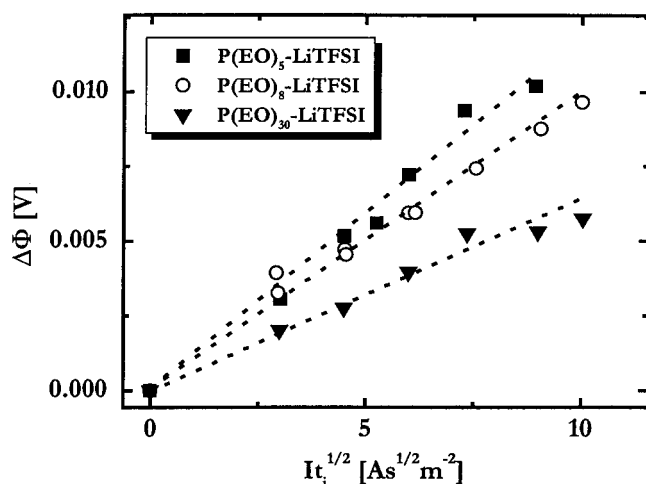


Figure 2. Current interrupt data taken for representative P(EO)_{*n*}LiTFSI electrolytes at 85 °C. The initial slope, i.e., when $It_i^{1/2} \rightarrow 0$, is used as the m value in eq 4.

calculation are presented in Figure 2. The SPE systems PEO–NaCF₃SO₃²³ and PPO–LiCF₃SO₃²⁵ (PPO = poly(propylene oxide)) showed a negative dependence on m with c in contrast to PEO–NaTFSI,²⁶ but for the PEO–LiTFSI system no monotonic relationship was observed.

In Figure 3, a plot of the natural logarithm of potential vs time for the relaxation of the galvanostatically polarized electrolyte P(EO)₁₂LiTFSI is shown. The slope of this plot at long times, i.e., when the cell is recovering its initial undisturbed condition, is directly proportional to the salt diffusion coefficient in accordance with eq 1. To get reliable data on this slope and hence D_s , it was necessary to polarize the cell substantially; for the measurement described in Figure 3, a current density of 250 $\mu\text{A}/\text{cm}^2$ was used for 300 s. In comparison, the salt diffusion coefficients for PEO–LiTFSI are of the same magnitude as those of the PEO–NaTFSI²⁶ and PEO–NaTf²³ systems, but are significantly larger than those of the PPO–LiTf system.²⁵

The dependence of potential on the logarithm of salt concentration, i.e., a concentration cell plot, is shown in Figure 4. For each concentration at least four independent measurements were performed since the property $dU/d \ln c$, on which t_+^0 is dependent, is extremely sensitive to small experimental errors. The maximum deviation between the calculated mean

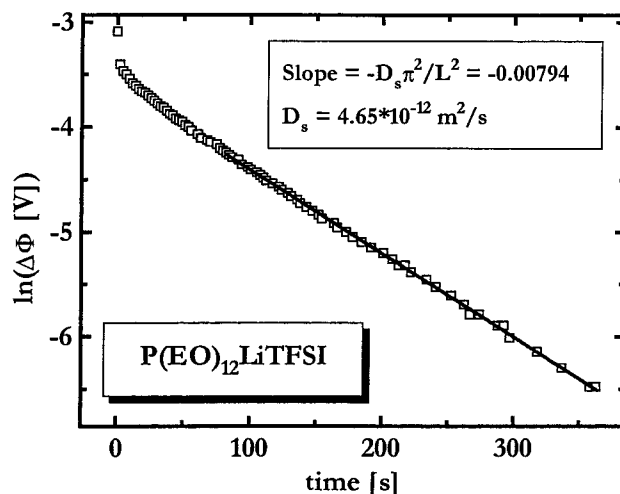


Figure 3. Semi-logarithmic plot of potential ($\ln(\Delta\Phi)$) vs time (t) for a galvanostatically polarized P(EO)₁₂LiTFSI electrolyte at 85 °C. The solid line represents a linear fit to data at long times after the current interrupt, for determination of the salt diffusion coefficient (D_s) (see eq 1).²⁹

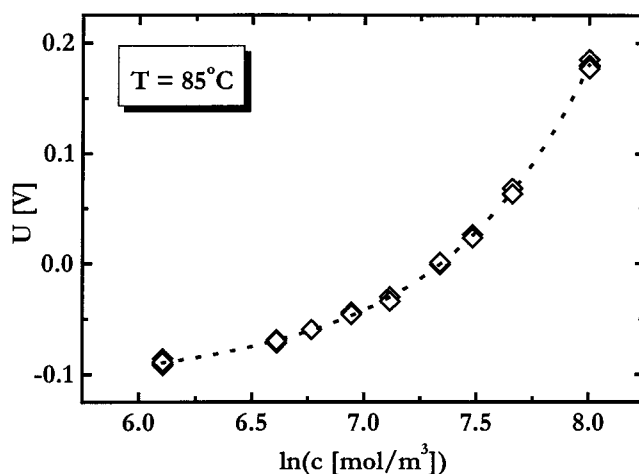


Figure 4. Concentration cell data for Li/P(EO)_{*n*}LiTFSI/P(EO)_{*n*}LiTFSI/Li cells at 85 °C. c (and n) represents the salt concentration of the latter electrolyte, whereas m is kept constant at a value of 12, corresponding to a salt concentration of 1537 mol/m^3 . The dashed line represents the polynomial fit described in eq 5.

value and a data point was 5 mV corresponding to a relative error of 2.6%. All data points were used for the 4th order polynomial fit presented below.

$$U(\ln c) = 22.275632 - 14.143573 \times \ln c + 3.3606198 \times (\ln c)^2 - 0.35640522 \times (\ln c)^3 + 0.014270731 \times (\ln c)^4 \quad (5)$$

By differentiating eq 5, all variables included in eq 4 are available. Figure 5 shows the transference number of the lithium ion as a function of bulk molar concentration in the salt-rich region. As can be seen, t_+^0 is positive over the entire concentration range with a small positive dependence on c . Our results readily reproduce and extend recent independent studies by Rey and coworkers (using confocal Raman spectroscopy) in which a t_+^0 value of 0.29 ± 0.08 for $n = 20$ was obtained at 80 °C,²⁷ as well as the single data point ($t_+^0 \approx 0.57$ for $n = 8$ at 67 °C; electrophoretic NMR) reported by Gorecki and coworkers.²⁸ Another study on transference numbers of the PEO–LiTFSI system has also been reported using pulsed-field-gradient-NMR

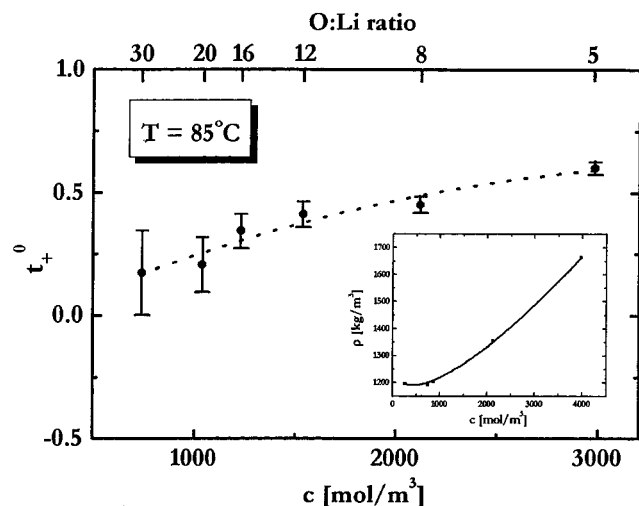


Figure 5. Lithium transference number (t_+^0) as a function of salt concentration (c) at 85 °C. The dashed line is a fit to the t_+^0 data, and the error bars are calculated as described in the text. The density (ρ) as a function of c is also included.

diffusion methods;³² however, since such analyses rely on the Nernst–Einstein equation, any experimentally reliable results would only be valid for “ideal” solutions.^{20,33}

Our high values for t_+^0 are somewhat remarkable, especially considering previously studied SPE systems in which t_+^0 exhibited a negative dependence on c , with very negative values for high salt concentrations.^{23,25,26} Although it has been shown that a battery can function despite very low or even negative values of t_+^0 ,³⁴ this is strongly coupled to detrimental effects such as salt depletion or precipitation. These negative events are related to the formation of a severe concentration gradient over the electrolyte during charge/discharge in agreement with the following relationship:^{17,23}

$$\Delta c \approx I(1 - t_+^0)L/FD_s \quad (6)$$

It is therefore desirable to develop and accurately identify SPEs with the highest possible cationic transference numbers. Unfortunately, other SPE systems with positive t_+^0 values^{25,35} have low ionic conductivities, indicating that anions and anionic complexes become relatively immobile, rather than that the mobility of the cations is improved. No such compromise is, however, seen in the PEO–LiTFSI system. Thus, our observation of positive values for the PEO–LiTFSI system is indeed very promising. Another attractive characteristic of this electrolyte system is the relative insensitivity of t_+^0 to changes in c (see Figure 5) which prevents a “snowball effect” in the Δc and t_+^0 values during cell operation in accordance with eq 6. The “snowball effect” refers to a situation in which transport properties become markedly less favorable as the salt concentration increases on one side of operating cells, causing premature shutdown.

Figure 6 shows a plot of the molar ionic conductivity (Λ) as a function of salt concentration, calculated from data obtained in this laboratory. There is a good qualitative agreement with previously published results although somewhat lower absolute values are observed, possibly due to the higher molecular weight of the polymer used in this study as compared to that used by Prud’homme and coworkers (5×10^6 vs 3.9×10^3).^{14,36,37} For c values ranging from 500 to 3000 mol/m³, there is a decrease in Λ with increasing salt concentration at 85 °C. This trend, regularly seen in SPEs at salt-rich compositions, can be

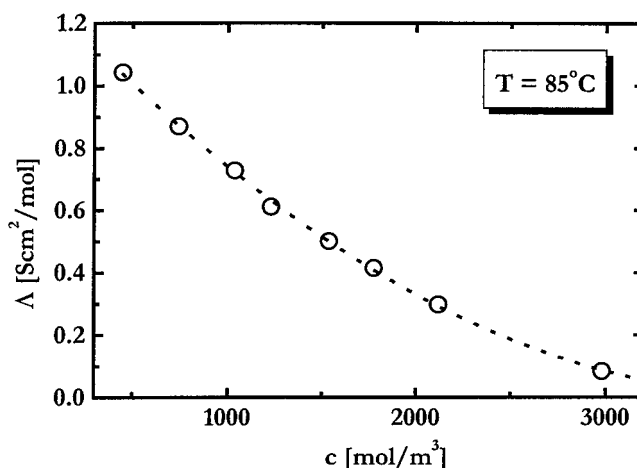


Figure 6. Molar ionic conductivity (Λ) for the P(EO)_nLiTFSI system as a function of salt concentration (c) at 85 °C. The dashed line is a polynomial fit to experimental data.

explained in the context of different modes of ionic motion. According to Bruce et al. the cationic motion can be “visualized as the making and breaking of coordinate bonds with motion between coordinating sites, while anion motion is regarded as hopping between an occupied site and a void which is large enough to contain the ion”.³⁸ Both these modes will be negatively affected by an increase in c , with the cationic motion being restricted by a decrease in the polymer segmental motion (manifested as an increase in the glass transition temperature) and the anionic motion being limited by the diminishing of suitable voids with increasing density (ρ). It has also been concluded from vibrational spectroscopy that there is negligible ionic association even at concentrated solutions for this particular system,^{39,40} in sharp contrast to other SPEs such as PEO–LiCF₃SO₃.^{41–43} In fact, Rey et al. could not detect any signs of ion pairs or larger aggregates at 80 °C, even in such a concentrated solution as P(EO)₈LiTFSI.³⁹

Following Bruce et al.,³⁸ and in view of vibrational spectroscopic results,^{39,40,44} we propose that the increase in t_+^0 with c (see Figure 5) for this specific system is largely attributable to a decrease in mobility of the anions due to a decrease in free volume with increasing density (ρ increases from 1192 to 1663 kg/m³ for n ratios going from 30 to 3), and that the cationic mobility (and the relative carrier concentrations) are static variables in c in comparison. If the contrary was true, and the mobility of the cations had a stronger negative dependence on c than the anions, then the opposite trend with a decreasing t_+^0 value with c would have been expected. A concentration independence for the lithium diffusion coefficient in the salt-rich regime in a SPE containing another bulky anion, PF₆[−], has also been reported by Vincent and coworkers.⁴⁵ Interesting to note is that Johansson et al. recently presented a simulation of anion-independent Li⁺-transport in a PEO matrix in this journal.⁴⁶ The model also fits the data presented in Figure 6, in which the decrease in Λ with c consequently is attributed to a decrease in the anionic mobility. It is interesting to see that a relatively large positive dependence of t_+^0 with c at low c values ($750 \text{ mol/m}^3 < c < 1500 \text{ mol/m}^3$) coincides with a stronger dependence of Λ with c in the same salt concentration range. To further elucidate these issues, we will initiate complementary pulsed-field gradient NMR diffusion studies (both anion and cation) of this particular system, as well as other representative SPEs, to be correlated with accurate t_+^0 determinations, as described herein.

Clearly, in order to experimentally distinguish different modes of ion-transport in concentrated (non-ideal) SPE systems, and thus provide a deeper understanding of the underlying physics of ion-transport in general, it is essential that a reliable and readily accessible method be available for the measurement of ionic transference numbers. This is naturally especially important for the development and evaluation of novel, more efficient materials to be used in actual applications.

Conclusions

A recently developed electrochemical technique based on concentrated solution theory has been used to obtain the cationic transference number as a function of salt concentration at 85 °C for the system PEO–LiTFSI. The high t_+^0 values (e.g., $t_+^0 = 0.60 \pm 0.03$ for O:Li = 5) with a positive dependence on c reported are in contrast with previous studies on other SPEs, but readily reproduce and extend recent independent studies based on the confocal Raman method, as well as electrophoretic NMR on the same system. Thus, we have shown that the very straightforward electrochemical method developed by Newman and coworkers yields accurate and reliable results, without relying on erroneous assumptions or special dedicated equipment. In addition, we report that the ionic conductivity is not compromised by the high t_+^0 values, in contrast to other SPE systems with this feature. We also suggest that the concentration dependences of t_+^0 and Λ in PEO–LiTFSI are attributable to a decrease in anion mobility with decreasing free volume.

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