



Ion Transport in Silica Nanocomposite Electrolytes

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The ion-transport properties of composite electrolytes composed of oligomers of poly(ethylene glycol) dimethyl ether, hydrophobic fumed silica, and $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ (LiTFSI) are investigated using nuclear magnetic resonance (NMR), electrophoretic NMR (ENMR), ac impedance spectroscopy, and rheology. The effects of fumed silica and salt concentration on ionic conductivity, diffusivity of ions and oligomers, and lithium transference number (T_{Li}) are examined at 30°C. The fumed silica forms a self-supporting network with large pores such that the network, regardless of silica concentration, has little effect on ion-transport characteristics. Examination of the effect of salt on ion transport reveals a maximum ionic conductivity at around 1.06 M, which is attributed to a tradeoff of adding more charge carriers balanced against increased ion-ion interactions and reduced mobilities. T_{Li} with respect to salt concentration surprisingly passes through a minimum around 0.35 M. The increase in T_{Li} at higher concentrations is attributed to the mobilities of cations, anions, and solvating oligomer becoming constrained to the same value due to "loss of free volume." The values of T_{Li} at low salt concentrations (<0.35 M) are attributed to the ions existing in either a fully dissociated state or primarily as charged complexes. Results of T_{Li} from ENMR and from estimation via pulse field gradient NMR (pfg-NMR) are compared showing that pfg-NMR consistently overestimates T_{Li} . Finally, a comparison is presented of measured conductivity with that calculated from the Nernst-Einstein equation and diffusivities found from pfg-NMR measurement; we discuss possible reasons why it is inappropriate to estimate ion-pair formation by this comparison.

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Introduction

An impediment to the use of polyethylene oxide-(PEO) based polymer electrolytes in electrochemical devices (batteries, actuators, etc.) is obtaining both high ionic conductivity ($\sigma > 10^{-3}$ S/cm) and mechanical stability below 70°C.¹⁻³ Several approaches have been undertaken to alleviate this problem, including addition of plasticizers and development of gel-polymer electrolytes.³⁻⁵ The use of plasticizers increases room-temperature conductivity but also results in a corresponding decrease in mechanical properties and loss in interfacial stability with lithium metal.^{4,5} Gel electrolytes also exhibit higher conductivities than standard PEO electrolytes but at the expense of mechanical stability. One promising technique in this regard is the addition of inorganic filler particles to high-molecular weight PEO to form composite polymer electrolytes (CPEs). CPEs exhibit mechanical stability and show enhancement in conductivity, primarily through decrease in the crystallinity of the high-molecular-weight PEO.^{6,7}

We have taken a fundamentally different approach to the use of fillers in formulating CPEs with surface-modified fumed silica particulates in low-molecular-weight end-capped PEO [i.e., poly(ethylene glycol) dimethyl ether, PEGdm] in the presence of lithium salts (e.g., $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$, LiTFSI). These electrolytes exhibit mechanical characteristics of a solid, yet have the processability of liquids, and achieve room-temperature conductivities exceeding 10^{-3} S/cm.⁸⁻¹⁰ These characteristics are the direct consequence of the unique properties of the nanosized fumed silica filler. Its branched, primary structure consisting of fused SiO_2 spheroids favors formation of open-network structures, and the ability to tailor its surface functional groups enables control over network formation. These features contrast with those of conventional fillers (e.g., Al_2O_3) that disperse in electrolytes without network formation.

Previous work on fumed-silica based electrolytes have utilized silica with various surface chemistries, including silanol (Si-OH) and octyl (C_8H_{17}) groups, and focused on investigating their rheology,^{8,10} conductivity,^{9,11} and interfacial stability with lithium metal.^{9,12} However, no comprehensive study of the various transport

properties, including ionic conductivity, ion and PEGdm self-diffusion coefficients, and lithium transference number, has been undertaken. The effects of fumed silica content and lithium salt concentration on these ion-transport properties is also missing. In addition, the mechanism of ion transport and how it is affected by fumed silica microstructure and/or solvent viscosity remains to be seen. In this study, we examine these issues using the techniques of electrophoretic nuclear magnetic resonance (ENMR) spectroscopy, pulse-field-gradient NMR (pfg-NMR), ac impedance spectroscopy, and rheometry.

Experimental

Materials and sample preparation.—Lithium bis(trifluoromethanesulfonyl)imide [$\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$] (LiTFSI, 3 M) was dried at 80°C under vacuum ($\sim 10^{-4}$ Torr) for 2 days before use. PEGdm (250 M_n , Aldrich) was dried over 4 Å molecular sieves for 1 week. Hydrophobic fumed silica (Aerosil R805, Degussa) was dried at 120°C under vacuum for 3-5 days. R805 fumed silica has octyl [C_8H_{17}] groups attached to its native Si-OH surface at a surface coverage of 50% C_8H_{17} .¹³

The composite electrolytes were prepared by dissolving a suitable amount of lithium salt in PEGdm in an argon-filled glove box (moisture content <5 ppm). The amount of salt added was determined by the target ratio of oxygen in the PEGdm to lithium in the salt (O:Li). Aerosil R805 was then added to the PEGdm and dispersed into the electrolyte with a high-shear mixer (Powergen 500 mixer, Fisher) in the dry box. The sample was then degassed at ambient temperature under vacuum ($\sim 10^{-4}$ Torr) for several hours to remove bubbles. The maximum moisture content of the composite electrolyte, as determined by a Karl-Fischer titration, was <50 ppm.

Proper determination of molar concentration (moles of lithium salt per volume of electrolyte) requires knowledge of the density of the electrolyte as a function of salt content. The density of the liquid electrolyte (PEGdm and Li salt) was measured at ambient temperature for ten different compositions. Density was estimated by weighing a known volume of electrolyte on the analytical balance in the dry box. This measurement was done 7-10 times and averaged at each salt composition. A relationship was then developed between the density of the liquid electrolyte and the moles of salt added per total mass of electrolyte.

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NMR.—Measurements of the self-diffusion coefficient of lithium cation (D_{Li} , via 7Li observation), salt anion (D_F , via ^{19}F observation), and the PEGdm oligomer (D_H , via 1H observation) were done via pfg-NMR employing the stimulated echo technique of Stejskal-Tanner.¹⁴ Diffusivities of cation and anion in the composite electrolytes, used in ENMR experiments, were determined on a Bruker AMX400 NMR spectrometer (Los Alamos National Laboratory, LANL) using either 12 or 7.5 mm NMR glass tubes. Measurements of cation and oligomer diffusion coefficients were done on a Bruker DRX500 NMR spectrometer (North Carolina State University) using 5 mm NMR glass tubes. Spin lattice (T_1) relaxation experiments were done on the DRX500 using the inversion-recovery technique as described in standard texts.¹⁴

ENMR.—The ENMR technique was used to determine transference numbers. Details of this technique are described by Dai and Zawodzinski^{15,16} and Dai.¹⁷ The composite electrolyte samples were placed in either 12 or 7.5 mm NMR glass tubes and sandwiched between polished lithium foil electrodes cold-pressed to platinum mesh current collectors. More concentrated samples (above 0.5 M LiTFSI) were prone to incomplete excitation of nuclei across the entire cross section of the sample as a result of radio frequency rf field energy loss in the sample.¹⁴ This was detected as loss of a distinct $\pi/2$ pulse and poor reproducibility of the spin echoes in the concentrated, large cross-section samples. In these cases, the smaller diameter glass was used to mitigate the rf field energy loss. The use of lithium foil electrodes allows for signal averaging without significant composition changes in the electrolyte during the measurement. A homemade 7Li or ^{19}F NMR coil was used to collect spectra on a Bruker AMX400 NMR spectrometer at LANL. The current was applied in the range of ± 10 mA with a Keithley 137 source-measure unit (which allows a maximum of 110 V).

The lithium transference numbers (T_{Li}) were not measured directly but rather were determined from measurement of the anion transference number via observation of the ^{19}F in the anion. The lithium transference number was calculated as $T_+ = 1 - T_-$; Walls and Zawodzinski¹⁸ demonstrated that to within experimental error, independent measurement of the cation (T_+) and the anion (T_-) transference numbers via ENMR satisfies the relationship $T_+ + T_- = 1$.

Conductivity.—Conductivity was measured using ac impedance spectroscopy. An EG&G Princeton Applied Research 273 potentiostat and an EG&G 5210 lock-in amplifier were used and controlled by the EG&G PAR M398 impedance software. The temperature was controlled to $\pm 0.5^\circ C$ using an Isotemp 1016S (Fisher) circulating water bath. The conductivity cells with platinum electrodes are described elsewhere.⁹

Rheology.—The viscosity of the liquid electrolyte (PEGdm with LiTFSI) was measured using a Rheometrics DSR-II equipped with a circulating water bath for temperature control. A couette (concentric cylinder) or parallel-plate geometry was used to measure the viscosity. A glove bag (Instruments for Research and Industry) was modified to fit over the rheometer and a dry nitrogen atmosphere used to minimize any possible effect of moisture.

Transmission electron microscopy (TEM).—Due to the deformable nature of the composite electrolytes generated here, a homologous sample was prepared for transmission electron microscopy (TEM) in which PEGdm was substituted partially by PEG diacrylate (PEGda) from Aldrich Chemicals. The PEGda was chemically cross-linked in the presence of 2,2-azobisisobutyronitrile (AIBN, Aldrich) at $80^\circ C$ to form a material possessing greater solid-like character. The fumed silica composite contained 10 wt % Aerosil R711 (Degussa), which possesses cross-linkable methacrylate surface groups but the same primary particle size and surface area as R805. The cross-linked materials were sectioned at $-100^\circ C$ in a Reichert-Jung cryo-ultramicrotome, and the electron-transparent

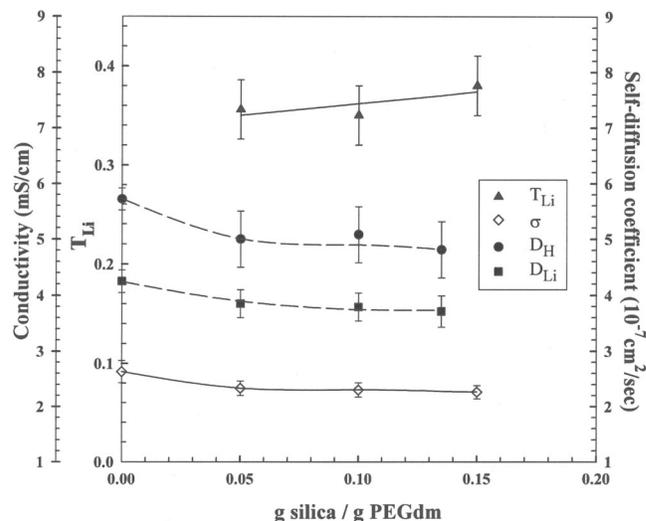


Figure 1. Ion-transport properties of composite electrolyte as a function of the mass ratio of silica filler to PEGdm oligomer. The samples are PEGdm, 1.06 M LiTFSI (O:Li = 20:1), and R805 fumed silica at $30^\circ C$. Lithium transference number (T_{Li}), oligomer self-diffusion coefficient (D_H), cation self-diffusion coefficient (D_{Li}), and specific ionic conductivity (σ) are reported. Lines are to guide the eyes.

sections were imaged at 80 kV and various energy-loss (ΔE) settings with a Zeiss EM902 electron spectroscopic microscope.

Results

Effect of fumed silica on ion transport.—Figure 1 presents the effect of fumed-silica content on various ion-transport properties at $30^\circ C$: conductivity, lithium transference number, and diffusion coefficients of the lithium anion and solvating oligomer. There is a slight attenuation of the conductivity (σ), up to a maximum of 14%, with the addition of silica to 0.15 g silica per gram of PEGdm. These results are consistent with the work of Fan and Fedkiw,⁹ who first studied ionic conductivity in fumed silica systems and reported a weak effect of fumed-silica content. The self-diffusion coefficient of both the lithium cation (D_{Li}) and solvating oligomer (D_H) (in Fig. 1) show a corresponding decrease with addition of fumed silica. The lithium transference number exhibits a minor increase with fumed silica content but in general follows this trend of little change with addition of fumed silica. Determination of T_{Li} in the liquid electrolyte (*i.e.*, in the absence of fumed silica) was not possible as convection currents form during the ENMR measurement, which invalidates an underlying assumption in the data analysis.¹⁵

The diffusion-length scale in a pfg-NMR measurement is a function of the diffusion coefficient of the observed nucleus, gradient strength, and experimental diffusion time (Δ).^{14,17} In some systems the self-diffusion coefficient may be a function of Δ , indicating different apparent diffusion rates at different length scales. Such restricted diffusion indicates that the probed species encounters an obstruction preventing free diffusion in the bulk on the experimental time scale, limiting the extent of evolution of the magnetization phase.^{14,19}

NMR signals from lithium and PEGdm were used to test for restricted diffusion in our composite electrolytes. This test was done by varying Δ in a sample composed of 10 wt % fumed silica, PEGdm, and 1.06 M LiTFSI. For 1H observation, Δ was varied from 0.082 to 0.322 s with no statistically significant change observed in the diffusion coefficient. For 7Li observation, Δ was varied from 0.042 to 0.42 s and again no statistically significant change in the diffusion coefficient was seen.

To further explore the possibility of the lithium cation interacting with the silica filler, a spin lattice (T_1) relaxation study was done on

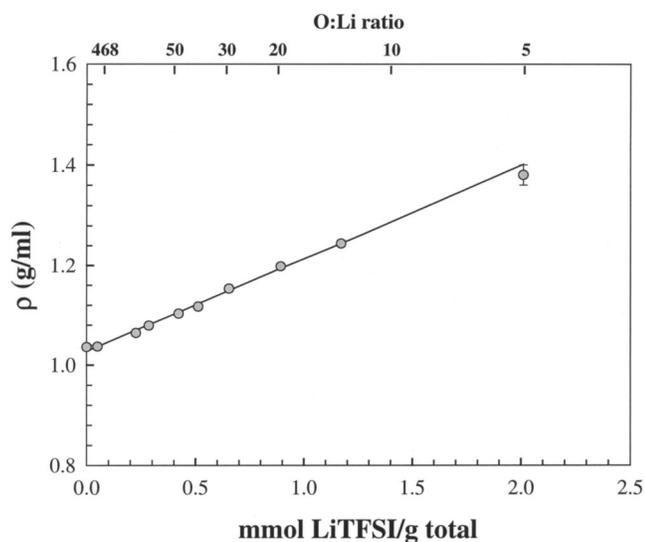


Figure 2. Density of liquid electrolyte (PEGdm and LiTFSI) as a function of salt content at room temperature. Typically, data points obscure the error bars.

^7Li as a function of R805 fumed silica content. The study showed that the T_1 relaxation for ^7Li is 526 ± 30 ms for a 1.06 M solution regardless of the filler content from 0 to 15 wt % silica.

Effect of lithium salt concentration on ion transport.—The study of salt-concentration effect on ion transport requires a reasonable estimation of the molar concentration of the salt. Addition of salt to the solvent (especially above 0.2 M) results in a significant change in the density of the electrolyte, thus invalidating the simple assumption that moles of solute per volume of solvent is a good approximation of moles of solute per total mixture volume. Therefore, we measured the density of the liquid electrolyte (PEGdm and LiTFSI) at ten different concentrations. These results are shown in Fig. 2 and were used in calculating the molar concentrations reported in this paper. If the density change with concentration is not properly taken into account, then the calculated molar concentration is overestimated. For example, for a solution of O:Li = 20, an $\sim 17\%$ error occurs, while at the high concentrations errors exceed 30%. Typically, O:Li ranges from 20 to 5 for studies on ion transport in PEO-based electrolytes.^{3,19-21}

Figure 3a displays the specific ionic conductivity (σ) and molar conductivity ($\Lambda = \sigma/c$) of the liquid electrolyte as a function of LiTFSI concentration at 30°C. The conductivity increases rapidly with salt concentration and passes through a maximum of 2.2 mS cm^{-1} at around 1.06 M (O:Li = 20). A ratio of O:Li = 20:1 corresponds to about four PEGdm chains to one LiTFSI (with a M_n of 250 g/mol). The largest concentration used was about 2.8 M or a ratio of O:Li $\sim 5:1$. This ratio of O:Li corresponds to about one oligomer chain per LiTFSI. The molar conductivity curve exhibits a local maximum of 3.4 S $\text{cm}^2 \text{mol}^{-1}$ at about 0.30 M (O:Li ~ 80). The concentration dependence of the molar conductivity is more clearly shown in Fig. 3b, where Λ is plotted as a function of concentration to the $\frac{1}{2}$ power. The data indicate the molar conductivity at infinite dilution is about 7 S $\text{cm}^2 \text{mol}^{-1}$.

The effect of LiTFSI concentration on the self-diffusion coefficients of cation (D_{Li}) and oligomer (D_{H}), and Newtonian viscosity (η) of the liquid electrolyte is shown in Fig. 4. The diffusivity of both the oligomer and cation decrease with increasing LiTFSI concentration until they appear to converge to a single value at a concentration of approximately 2.8 M. The viscosity monotonically increases with addition of lithium salt. A plot of D_{Li} vs. η^{-1} (not shown) yields a straight line with a slope of $6.83 \pm 0.42 \times 10^{-6}$

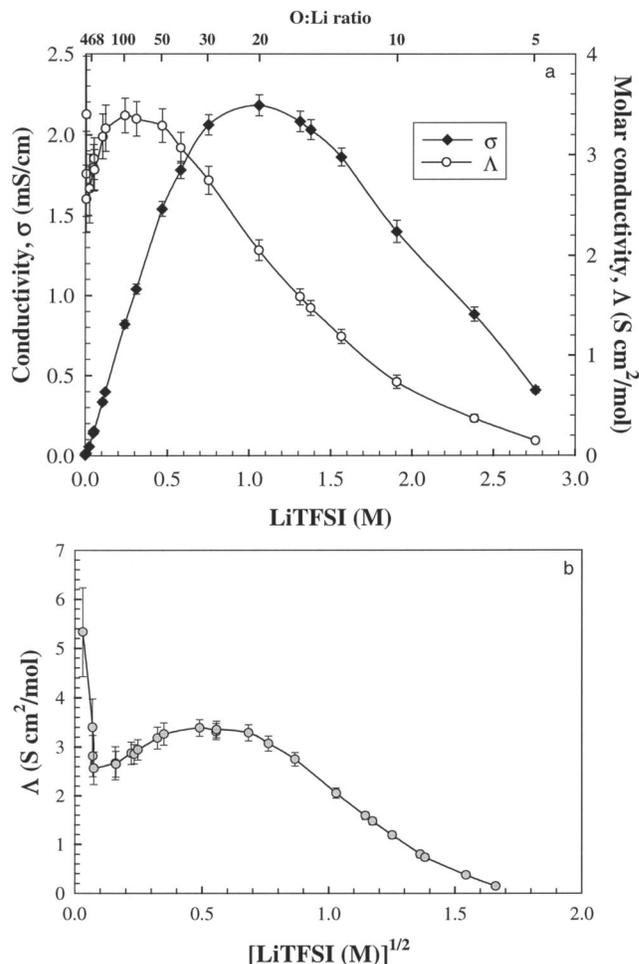


Figure 3. (a) Effect of lithium salt concentration on specific ionic conductivity (σ) and molar conductivity ($\Lambda = \sigma/c$) of liquid electrolyte. The samples are PEGdm and LiTFSI (*i.e.*, no silica filler) at 30°C. (b) Expanded scale to illustrate behavior in Λ at low concentration.

$\text{cm}^2 \text{ s}^{-1} \text{ cP}^{-1}$ with an intercept not statistically different from zero and an R -squared value of 0.97.

The self-diffusion coefficients of anion and cation were measured as a function of salt concentration for a CPE of 0.05 g silica/g PEGdm and are shown in Fig. 5. These data show some peculiar features. From 0.58 M (O:Li ~ 40) to higher concentrations, the self-diffusion coefficients converge. For the 1.85 and 2.75 M concentrations, the cation and anion self-diffusion coefficients are statistically the same. From 0.58 M to lower concentrations, the trend in the ratio of anion-to-cation diffusivity decreases with decreasing concentration. The data shown in Fig. 5 are average values of 2-5 separate measurements and are reproducible.

The lithium transference number (T_{Li}) as a function of LiTFSI concentration is shown in Fig. 6. Some interesting features are observed in the data. A minimum in T_{Li} occurs at around 0.35 M. For concentrations below the minimum, T_{Li} rapidly increases. Measurement of a transference number below 0.24 M, however, becomes difficult because of the unacceptable signal-to-noise ratio resulting from the dilute concentration. At salt concentrations above 0.47 M, T_{Li} increases appearing to approach 0.5. Measurement of T_{Li} at high concentrations becomes difficult as the mobility of the ion becomes quite small ($D < 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, Fig. 4), which results in too low of a signal-to-noise ratio in the spin-echo signal for the determination of a transference number.

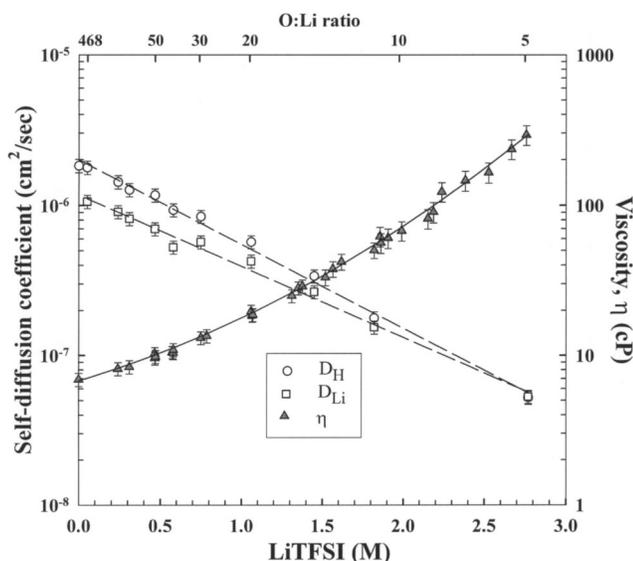


Figure 4. Effect of lithium salt concentration on diffusivity and viscosity of liquid electrolyte. The samples are PEGdm and LiTFSI (*i.e.*, no silica filler) at 30°C. Self-diffusion coefficient of PEGdm oligomer (D_H), cation (D_{Li}), and Newtonian viscosity (η) are reported.

Discussion

Ion transport through fumed-silica networks.—The minimal effect of fumed silica on transport can best be explained in terms of the 3D network it forms. Fumed silica dispersed in a solvent forms a network structure if there is sufficient silica (*i.e.*, achieves percolation) and a large enough mismatch between the solubility parameter of the solvent and the surface groups attached to the silica.¹³ The Aerosil R805 fumed silica forms a network due to the alkyl C_8H_{17} chains of the silica surface preferring to interact with each other *vs.* the polar PEGdm/LiTFSI medium the particles are dis-

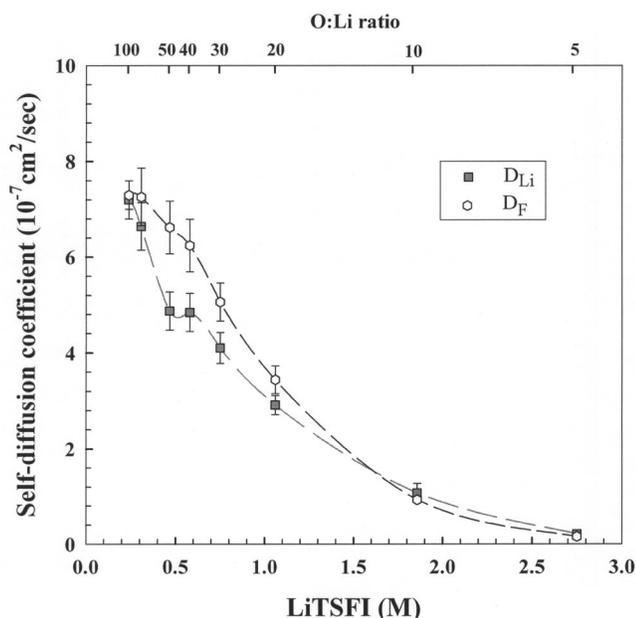


Figure 5. Effect of lithium salt concentration on diffusivity of composite electrolyte. The samples are PEGdm, LiTFSI, and 0.05 g silica/g PEGdm at 30°C. Self-diffusion coefficient of cation (D_{Li}) and anion (D_F) are reported.

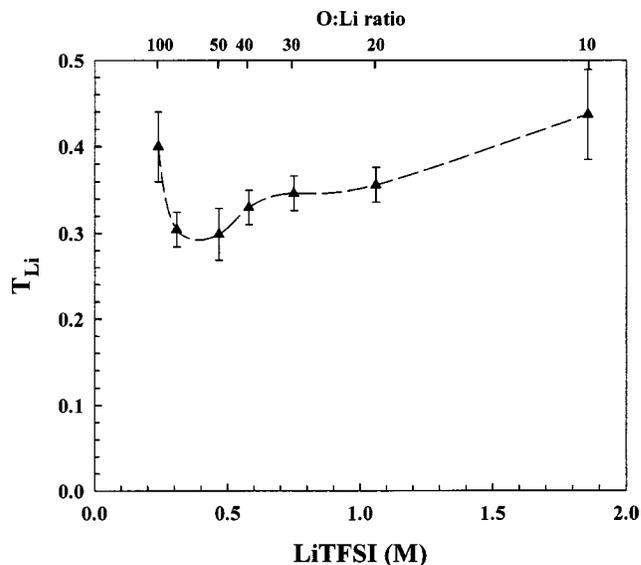


Figure 6. Effect of lithium salt concentration on lithium transference number (T_{Li}) of composite electrolyte. The samples are PEGdm, LiTFSI, and 0.05 g silica per g PEGdm at 30°C.

persed in. The structures formed by these silica networks are relatively strong with an elastic modulus exceeding 10^4 Pa, despite their open structure.^{8,10}

The type of network structure formed by fumed silica particles is illustrated in Fig. 7. The TEM shown is of a fumed silica with methacrylate surface groups (Aerosil R711) dispersed in a mixture of 66 wt % PEGdm and 33 wt % PEGdm. The difficulty of obtaining TEMs of Aerosil R805 and PEGdm systems led us to use this cross-linkable analog. The elongated-branched fumed silica particles associate with each other and form fractal-like structures (shown in white) with large open spaces filled with the liquid medium (shown in dark). The size of the pores (dark spaces) in the fumed silica network is on the order of $0.4 \mu\text{m}$. A much more detailed discussion of the morphology of these composite electrolytes is given elsewhere.²²

Further exploration of the length scale of the silica network and the length scale of structures and motions in the liquid electrolyte phase (oligomers of PEGdm and salt) can be done using our diffusion data and information from the literature.

The diffusion coefficient and pfg-NMR experimental observation time Δ can be used to estimate a length scale of diffusion. The Einstein-Smoluchowski equation provides one such estimate via the random walk distance $\langle x^2 \rangle$ ²³

$$\langle x^2 \rangle = 2Dt \quad [1]$$

where D is the self-diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$) and t time (s). The test for restricted diffusion, done by varying Δ , explored length scales of diffusion from 2 to $7 \mu\text{m}$, as calculated using Eq. 1. Over these length scales no change in the self-diffusion coefficient is observed. Smaller length scales were not experimentally accessible given the 61.5 G cm^{-1} maximum gradient possible with the Nalorac microimaging probe used in our DRX500. There are two main conclusions drawn from this data. First, the data in Fig. 4 and 5 are bulk diffusion coefficients. Second, the measured diffusion coefficients are not a function of experimental time, unlike the cross-linked poly(ethyleneoxide-propyleneoxide) electrolytes of Hayamizu *et al.*;¹⁹ thus, the fumed silica network does not significantly impede diffusion over the length scales studied. Note that this does not rule out more local influences on the transport. For example, the presence of Si-OH surface groups may lead to speculation about possible interaction with lithium. The coverage of the fumed silica surface with

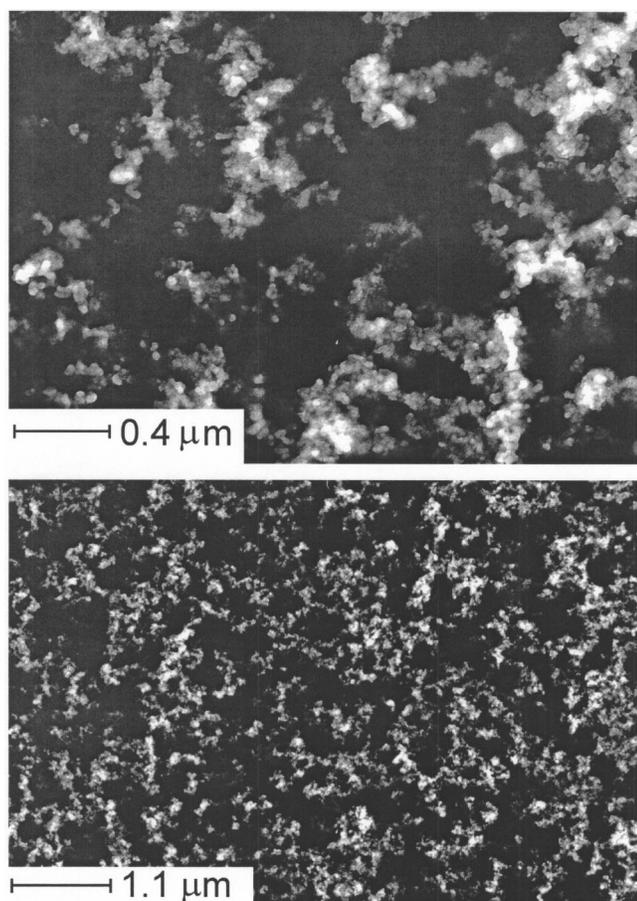


Figure 7. TEM of typical network structure formed by fumed silica. This is an inverse image where the white represents energy reflected by the fumed-silica particles and the dark areas represent absence of silica. The material is Aerosil R711 fumed silica dispersed in poly(ethylene glycol) dimethacrylate and then cross-linked.

C_8H_{17} groups is only 50%, leaving the balance as native Si-OH groups. However, the lack of change in 7Li spin-lattice relaxation (T_1) and little change in T_{Li} with increasing fumed-silica content suggests that there is no significant interaction between the lithium and silanol groups.

The size of the PEGdm oligomers may be estimated using small angle neutron scattering (SANS). Branca and co-workers used SANS to determine the radius of gyration (R_g) of low-molecular-weight PEO in water.²⁴ They found that for concentrated solutions (approaching the melt) of 3400 M_n PEO, the R_g is on the order of 10 Å.²⁴

Diffusion and viscosity data can be used to estimate the hydrodynamic radius (R_H) of a polymer. The R_H is defined as²⁵

$$R_H = \frac{k_b T}{6\pi\eta D} \quad [2]$$

where k_b is Boltzmann's constant ($J K^{-1}$), T is the temperature (K), and η is the viscosity (P). Using the data in Fig. 3 for pure PEGdm and Eq. 2, R_H for 250 M_n PEGdm is ~ 12 Å.

These two values for the size of the oligomer suggest that a characteristic length scale for reorientation of the oligomer is on the order of 10 Å. Examination of Fig. 1 and 7 shows that structures and motions on the length scale of the oligomer/salt are much smaller than those of the self-supporting fumed silica network. In short, the

ion transport of the liquid electrolyte incurs minimal impediment due to the supporting physical network of fumed silica.

Ionic conductivity in electrolytes composed of oligomers of ethylene oxide and LiTFSI salt.—For a dilute ideal electrolyte, the ionic conductivity σ ($S cm^{-1}$) can be expressed as^{23,26}

$$\sigma = F^2 \sum_i z_i^2 u_i c_i \quad [3]$$

where F is Faraday's constant, z_i is the valence of species i , u_i is the mobility ($cm^2 mol^{-1} s^{-1}$), and c_i ($mol cm^{-3}$) the species concentration. At infinite dilution, the diffusion coefficient may be related to the mobility via the Nernst-Einstein equation^{23,26}

$$D_i = u_i RT \quad [4]$$

These two equations are valid for dilute, unassociated electrolytes.^{23,26} Nevertheless, they are easy to work with and describe general trends in electrolytes.^{23,27}

The ionic conductivity (Fig. 3) initially increases with salt content due to addition of charge carriers to the electrolyte as represented by Eq. 3. Above 1.06 M, however, the conductivity decreases as other effects exceed that of adding charge carriers to the electrolyte. One major factor is decreasing mobility of the charge carriers. The mobility of the ions may be estimated via the diffusion coefficient (Eq. 4). Figure 4 shows that viscosity is rapidly increasing while the diffusivities are decreasing. Also, recall that a plot of D_{Li} vs. η^{-1} yielded a positive linear relationship. Thus, we can expect that an impediment to charge transport is the decreasing ion mobility due to increasing electrolyte viscosity. However, a plot of $\Lambda\eta$ vs. concentration (Walden's rule)²³ is neither a constant nor a linear relationship, suggesting that increasing viscosity alone is insufficient to explain the decreasing conductivity. The unaccounted effects are ion-ion interactions and the formation of ion pairs or higher aggregates.

Molar conductivity has traditionally been used as a tool in detecting ion-ion interactions and ion-pair formation.²⁸ The Λ data shown in Fig. 3 exhibits a local maximum. Local maxima in Λ , as a function of salt, for polymer electrolytes have been attributed to both redissociation of the salt^{29,30} and formation of charged triplets.^{31,32} Gray³ compares Raman spectroscopy and molar conductivity data for lithium triflate ($LiCF_3SO_3$) in poly(propylene glycol) showing that a local maximum in Λ occurs with the appearance of triple ions. It is interesting to note that our PEGdm/LiTFSI electrolyte exhibits a local maximum in Λ , despite recent results suggesting that low-lattice energy salts such as LiTFSI in PEO form few, if any, ion pairs and ion aggregates.³³⁻³⁵ However, the evidence presented for complete dissociation tends to be weak and negative. The absence of ion pairs is often inferred from the lack of ion-pair bands in vibrational spectra, but the absence of a perturbed band does not absolutely imply that *no* interaction takes place, only that the interaction is too weak or delocalized to yield a substantial change in band structure. Furthermore, for some anions bandshifts are not observed spectroscopically despite the fact that it is likely that ion pair formation is present. This is a situation of *no information*, not one of *no interaction*.

The local maximum in molar conductivity is unexpected for dilute electrolytes that are completely dissociated. Moreover, increased ion pairing only can be expected to reduce the molar conductivity. Let us examine the assumption that in such low-dielectric-constant media, ion-ion interaction is rampant at all concentrations studied here. It may then be possible that the local maximum in molar conductivity is caused by increased numbers of charge carriers as salt is added, as the medium dielectric constant increases slightly upon the first additions of salt.³⁶ This is eventually counterbalanced, by the limited solvating power of the medium toward ionic species, leading to a rapid decrease in Λ after the local maxi-

mum. The decrease is then due to increased ion-ion interactions, leading to the formation of neutral pairs and larger, less mobile aggregates.^{28,37}

Transference numbers.—Both high conductivity and lithium transference number are desired for electrolytes.^{3,38} Comparing Fig. 3a and 6 shows that the maximum in σ does not coincide with a maximum in T_{Li} . Thus, both conductivity and lithium transference number must be considered when designing or optimizing an electrolyte.

The transport number (t_i) is the fraction of current carried by a particular charged species in the absence of a concentration gradient.³⁷ The cation transport number (t_{M}^+) is measurable only if complete dissociation of the salt occurs such that only M^+ and A^- species are present. Suppose a salt MA dissolved in a solvent forms the equilibrium species M^+ , A^- , $[\text{MA}]^0$, $[\text{M}_2\text{A}]^+$, and $[\text{MA}_2]^-$. In principle there will exist a transport number for each of the charged species. However, to measure each of these numbers would require a means of distinguishing each species and determining its mobility in a field on a time scale shorter than the lifetime of the species. Thus, we rely on a measurable, weighted average transport number to describe the electrolyte. The cation transference number is defined as the net number of faradays carried by the cations from anode to cathode upon the passage of 1 F of charge through the cell.^{3,39} The anion transference number is similar with the direction of migration switched, *i.e.*, cathode to anode. Thus, the cation transference number is related to the transport numbers in our example by

$$T_+ = t_{\text{M}^+} + 2t_{\text{M}_2\text{A}^+} - t_{\text{MA}_2^-} \quad [5]$$

For a dilute fully dissociated electrolyte, the transport number may be related to the self-diffusion coefficient through application of Eq. 4³

$$t_{\text{M}^+} = \frac{D_{\text{M}^+}}{D_{\text{M}^+} + D_{\text{A}^-}} \quad [6]$$

The observation of a local minimum in the lithium transference number (Fig. 6) is unusual and merits some discussion. First, consider the diffusivities (Fig. 5) and molar conductivities (Fig. 3) in the concentration range from 0.23 to 0.47 M LiTFSI. A maximum in Λ occurs at about 0.24 M (O:Li \sim 100) and at that concentration D_{Li} and D_{F} are similar in value. The similarity of the self-diffusion coefficients suggests that the mobilities of the cation and anion are nearly equal, which should tend to make T_{Li} take on a value of 0.5 (Eq. 6) in the absence of ion pairs and ion-ion interactions.

The corresponding local maximum in Λ , similar diffusivity of cation and anion, and $T_{\text{Li}} > 0.4$ suggests that charge transport in the electrolyte is tending to one type of charge carrier such as charged triplets (*i.e.*, only $[\text{Li}_2\text{A}]^+$ and $[\text{LiA}_2]^-$). As concentration increases from 0.23 to 0.5 M, ion-ion interactions^{28,37} or formation of ion aggregates causes T_{Li} to decrease (Eq. 5). For dissociated, 1:1 valency, aqueous electrolytes, if T_+ at infinite dilution is less than 0.5 then T_+ will decrease with increasing salt, which is ascribed to ion-ion interactions via the electrophoretic effect.³⁷ Decreasing T_{Li} with increasing LiCF_3SO_3 concentration has been observed in gel electrolytes composed of propylene carbonate in a copolymer of poly(vinylidene fluoride) and hexafluoropropylene, and was attributed, in part, to the electrophoretic effect (*i.e.*, ion-ion interactions).¹⁶

Another interesting feature over the range 0.23-0.58 M is that D_{F} decreases more slowly than D_{Li} , suggesting that the anions are becoming relatively more mobile. In the absence of ion complexes, this trend alone would result in a decrease in T_{Li} (Eq. 6). The decrease in T_{Li} from 0.23 to 0.58 M is likely a combination of ion-ion interactions and a change in the electrolyte structure (formation of ion complexes and association between the solvating PEGdm and

charged complexes). Currently, we can only speculate as to the source of features in the T_{Li} data over the range 0.23-0.58 M LiTFSI.

Now consider the increase in T_{Li} with concentrations above 0.58 M. Figure 5 shows that the diffusivities of the cation and anion converge toward a single value. In Fig. 4 the diffusivity of the PEGdm and cation also appear to converge and are identical at the extreme concentration of one cation per oligomer of PEGdm (\sim 2.8 M). In other words, the mobilities of all species in the electrolyte are converging. We argue that we can make use of the data in Fig. 4 (no fumed silica) due to the lack of influence fumed silica has on ion transport (*cf.* Fig. 1). In the absence of ion pairing and ignoring ion-ion interactions, T_{Li} would tend toward 0.5 via Eq. 6. Edman and co-workers have studied high-molecular weight PEO and LiTFSI at 85°C and found the same behavior of the lithium transference number tending toward 0.5 for an O:Li ratio of 5.²⁰ They attribute the increase in T_{Li} with concentration to the mobility of the anions in the spaces between the polymer chains decreasing and becoming similar to the mobility of the cations. We are not aware of any studies of the ion-transport properties of LiTFSI-PEO electrolytes at the low concentrations where we observed the anomalous behavior in T_{Li} and Λ .

The T_{Li} behavior as a function of LiTFSI shown in Fig. 6 is a combination of effects. At the lowest concentration, a single type of charge carrier dominates with high molar conductivity (Λ). Based on research of polymer electrolytes with lithium salts in PEO or poly(propylene glycol) where ion complexes are more easily observed (*e.g.*, LiClO_4 and LiCF_3SO_3), charged triplets (*i.e.*, $[\text{M}_2\text{A}]^+$ and $[\text{MA}_2]^-$) are expected to be the dominate charged aggregate when aggregation occurs.³ As concentration increases, ion-ion interactions cause T_{Li} to decrease and the structure of the electrolyte changes such that anions are relatively more mobile than cations. Above 0.58 M LiTFSI, however, the relative mobilities of the cations and anions converge such that charge transport is more evenly shared by positively and negatively charged species.

Comparison of ENMR measured transference numbers and those calculated from pfg-NMR measured diffusivities and the Nernst-Einstein equation.—Measurement of lithium transference numbers has been a difficult and somewhat controversial issue in the area of polymer electrolytes.³⁹⁻⁴³ Fritz and Kuhn⁴⁰ measured the transference number of an electrolyte composed of LiClO_4 , propylene carbonate, and fumed silica by four methods: (i) ac impedance spectroscopy, (ii) isothermal transient ionic current, (iii) steady-state current, and (iv) Tubandt-Hittorf. Their study yielded results that varied by as much as a factor of 2; hence, the reported transference number is a function of the measurement method. This was, in part, the motivation for the development of the ENMR technique for lithium transference number measurement, the validity of which has been previously demonstrated.¹⁵⁻¹⁸

A common and fairly simple way to determine transference numbers is to use pfg-NMR to find the self-diffusion coefficients of the cation and anion and then calculate the transference number using Eq. 6.^{3,21,39,42} The implicit assumption is that the transport and transference numbers are equal.

Figure 8 compares the lithium transference number results obtained via ENMR and those calculated from Eq. 6 using the self-diffusion coefficients determined via pfg-NMR (Fig. 5), with the latter consistently overestimating the former. Two factors contribute to this overestimation. The first is that Eq. 6 depends upon the electrolyte being dilute and that ion-ion electrostatic interactions are unimportant. This clearly is not the case for these electrolytes, since dilute ideal electrolytes are typically 0.01 M or less, fully dissociated salts in high-dielectric solvents.²³ The existence of ion-ion interactions causes mobilities based on pfg-NMR measured self-diffusion coefficients to be overestimated. The inherent problem is that nondilute electrolytes behave differently in the presence of an external field (*e.g.*, during ENMR and hence the electrophoretic ef-

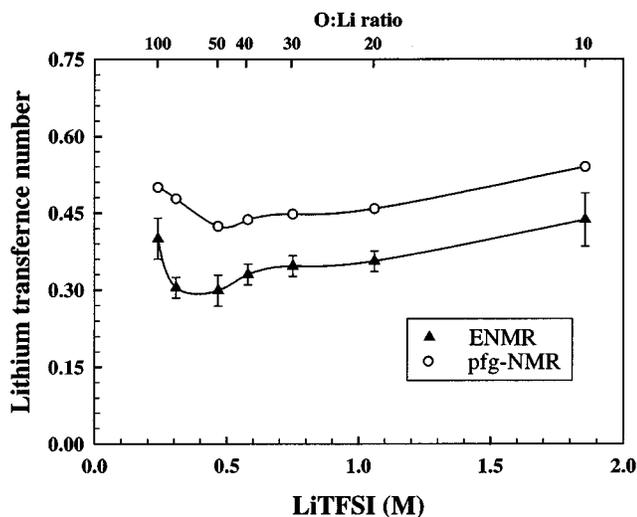


Figure 8. Comparison of lithium transference numbers measured via ENMR and estimated from pfg-NMR measured ion self-diffusion coefficients and Eq. 6. Samples are those of Fig. 5.

fect is important) than in the absence of an external field (*e.g.*, during pfg-NMR).

The second factor contributing to overestimation is that pfg-NMR gives an ensemble average over all species present,¹⁴ pfg-NMR does not discriminate between single ions, neutral pairs, and aggregates of ions. This leads to an overestimation of the mobilities of the charged species, assuming ion pairs (which are neutral) have higher mobilities based on their reduced interaction with solvent and charged species.

Overall, this discussion of the results in Fig. 8 is consistent with our claim that the concentrations used here are outside the dilute limit, and thus substantial ion-ion interaction occurs over the full range of concentration. In a neutral ion pair, the average anion and cation mobilities are equal. However, the mobility of a solvated “free” uncomplexed lithium ion is apparently lower than that of the “free” anion. The transference number deduced from pfg-NMR by inclusion of ion pairs in the averaging tends to raise the lithium transference number toward 0.5. Thus, the consistent overestimation of T_{Li} by pfg-NMR relative to that derived from ENMR is an indication that neutral ion pairs contribute to the T_{Li} as measured by pfg-NMR. As noted previously, the prevalence of ion complexes also contributes to the nonideal behavior of the molar conductivity.

T_{Li} , as determined via ENMR, does not require any assumptions about dilute solutions, complete dissociation of salt, or relationship between self-diffusion coefficient and electrophoretic mobility of ions.^{15,17,18} ENMR observes the migration of all charged species in the electric field and from this T_{Li} is calculated. As detailed by Dai and Zawodzinski¹⁵ and Walls and Zawodzinski,¹⁸ T_{Li} determination via ENMR is thus a direct and accurate measurement not subject to assumptions.

The Nernst-Einstein equation is often used in the literature to write the conductivity as^{23,44-46}

$$\sigma = \frac{z^2 F^2}{RT} c(D_+ + D_-) \quad \text{or} \quad \Lambda = \frac{F^2}{RT} (D_+ + D_-) \quad [7]$$

The utility of this equation is the simple relation between conductivity and measurable diffusion coefficients. However, the Nernst-Einstein equation does not account for ion-ion interactions. A number of investigators compare conductivity as calculated via Eq. 7 from pfg-NMR-determined self-diffusion coefficients to conductivity

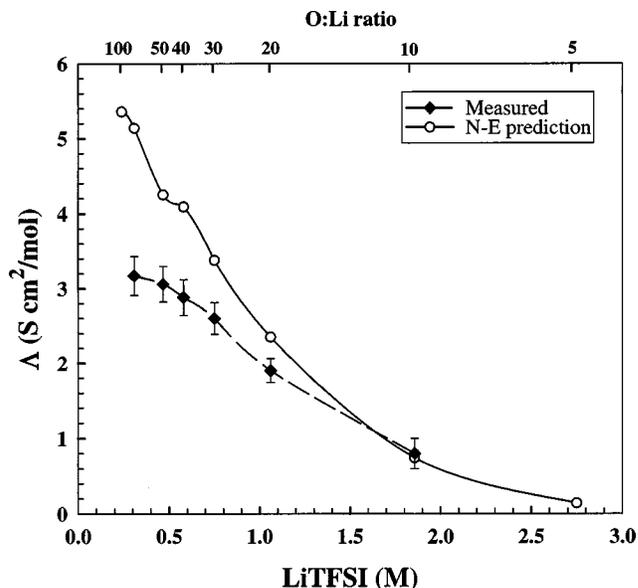


Figure 9. Comparison of measured molar conductivity and that calculated from the Nernst-Einstein (N-E) equation using data from Fig. 5.

ity determined via ac impedance spectroscopy. They then relate the difference in Eq. 7-determined conductivity and the experimentally determined conductivity to ion pairing.⁴⁴⁻⁴⁸

The insufficiency of the Nernst-Einstein equation (Eq. 7) for describing conductivity in polymer electrolytes is demonstrated in Fig. 9. Here Λ , as determined from ac impedance spectroscopy, is compared with the value calculated via Eq. 7 and the pfg-NMR-determined self-diffusion coefficients given in Fig. 5. At low concentrations, Eq. 7 overestimates Λ . However, at higher concentrations the calculated and measured values for Λ converge. Several researchers have seen this phenomenon in polymer electrolytes and attribute it to increased dissociation of the lithium salt with increasing concentration.⁴⁴⁻⁴⁷ This goes against conventional electrolyte theory, which states that ion association and ion-ion interactions increase with concentration, especially in low-dielectric solvents.^{28,37} We suggest that this convergence is not an indication of the electrolyte becoming more dissociated and more ideal (*i.e.*, an increase in the validity of Eq. 7 with increasing concentration) but rather is an artifact of the mobilities of all charged species converging to the same value because of increased aggregation. As mentioned before, pfg-NMR cannot discriminate the different charged species present but if all species of charged ions and neutral pairs have the same mobility, then their diffusivities converge to a single value and the Nernst-Einstein equation will coincidentally better predicts Λ .

The T_{Li} determined by ENMR and the conductivity determined by ac impedance are independent quantities. For both transport properties, application of the Nernst-Einstein equation overestimates the observed results as a function of the salt concentration. The problem is that the Nernst-Einstein equation does not account for ion-ion interactions and assumes completely dissociated salt with only two ionic species present (single cations and single anions). Nevertheless, the qualitative trends of both conductivity and lithium-transference-number dependence on LiTFSI concentration are captured by the rather simple Nernst-Einstein equation.

Structure of PEO-LiA electrolytes.—Extensive effort has been put forth to elucidate the structure of polymer electrolytes based on PEO and LiA (where A is some anion; *e.g.*, TFSI, AsF₆, etc.).^{33-35,49-53} Most of these studies used X-ray and neutron scattering from crystalline electrolytes. Some of the key phenomena to understand are coordination of Li⁺ by ether oxygens, conformation

of PEO chains solvating the lithium ions, and location of anions. The lithium cations are typically coordinated by oxygens on PEO chains with the chain coiled about the cations. The anions typically occupy the interchain spaces between PEO-Li⁺ complexes. A number of researchers have determined that lithium ions coordinate five to six oxygens when possible.^{33,49-52,54} If we designate the mole ratio of ether oxygens to lithium as $n:1$, then any system with $n \geq 6$ should form lithium-polymer complexes with five to six oxygens. It is essential to note, however, that conduction in typical polymer electrolytes most likely does not occur through the crystalline phases but rather through amorphous phases.^{2,3,5,32,55} We must be cautious in drawing conclusions from this structural work. However, recently Gadjourova *et al.*⁵⁶ have demonstrated that highly ordered crystalline PEO can yield higher conductivity than amorphous PEO. Nonetheless, this is not the typical system studied.

The work of Bruce and co-workers suggests that for crystalline PEO electrolytes, two polymer chains provide the coordinating oxygens for $n \geq 6$.^{33,50} Gadjourova *et al.*⁵⁰ and Johansson⁵³ both argue that two PEO chains coordinate a lithium ion, since wrapping a single PEO chain around a lithium ion to provide six oxygens "would impose an undue strain on the PEO chain."⁵⁰ If n is less than six, then the conformations change and only one PEO chain provides three coordinating oxygens and the remaining two coordinations are provided by anions.³³ A few things should be noted about these studies *vs.* our electrolyte: (i) high-molecular-weight PEO was used *vs.* our short oligomers (which contain only five to six oxygens per chain); (ii) highly crystalline PEO-LiA samples were used *vs.* our liquid/amorphous electrolyte; (iii) detailed structures were obtained for salts other than LiTFSI; and (iv) n was never more than six for the detailed structure studies.

Crystal structure studies (mentioned previously) along with Raman and Fourier transform infrared (FTIR) spectroscopy studies have been conducted to understand the extent and type of ion pairing and ion interactions that occur in PEO electrolytes.^{33-35,57,58} In crystalline PEO electrolytes with low-lattice energy anions such as AsF₆⁻ and $n \geq 6$, there is little evidence of ion pairing between the cation and anion.³³ Spectroscopy studies of PEO₆-LiAsF₆ support the conclusion that neutral ion pairs are not present in any appreciable amount.⁵⁸ Rey *et al.*³⁵ and Edman³⁴ did Raman and FTIR spectroscopy studies on PEO-LiTFSI electrolytes, both crystalline and amorphous forms, and also claimed that ion pairing was small when $n \geq 6$. Edman found that for $n = 20$ only 4-7% of the salt existed as ion pairs.³⁴ However, Edman also claimed that ion pairing was more common in the amorphous phase than in the crystalline phase. He also found that ion pairing increases as n decreases from 20 to 6 and changed with sample history (temperature treatment and age). Once again there are some importance differences between these systems and ours in that the PEO oligomers are much shorter and not subject to crystallization. We also reiterate our aforementioned concern with attempting to draw quantitative conclusions regarding the extent of ion pairing from such vibrational studies.

Given this previous work and our experimental data, we can envision a qualitative model for the molecular structure of our electrolyte. For all concentrations tested, there were at least five oxygens available to coordinate a lithium cation. We also know that a single PEGdm chain contains only five to six oxygens and is much freer to obtain conformations where the chain ends are closer together than that of high-molecular-weight PEO. That is, the end-to-end distance in PEGdm (250 M_n) is much smaller than PEO of 1000 and greater M_n used in the studies cited. So it is quite feasible for a single chain of five to six ethylene-oxide units to coordinate a single lithium cation. The low viscosity and small chain length of our system implies much more flexibility than exhibited by the higher molecular weight PEO electrolytes (also seen in the higher conductivity of our composite electrolyte). Given this scenario and that Edman³⁴ did observe more ion-pair formation in the amorphous phase of his polymer electrolyte, we hypothesize that ion complexes form, as indicated by the local maximum in the Λ curve in Fig. 3. Given that

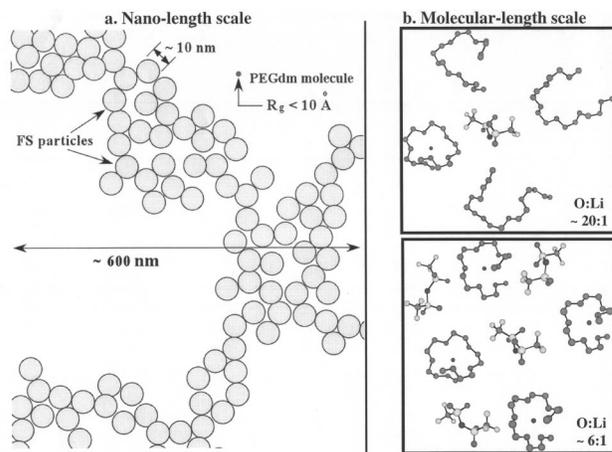


Figure 10. Qualitative structure of composite polymer electrolyte: (a) At the nanometer-length scale, fumed silica (FS) particles associate to form a volume-spanning network with large pores. The PEGdm oligomers occupy these large pores with little impediment of chain motion due to FS network. R_g is the radius of gyration of an oligomer of PEO. (b) At the molecular-length scale, the oligomer chains solvate the cations while the large anions occupy the void spaces in the solvent matrix. Loading of matrix by Li⁺ cations and TFSI⁻ anions is indicated at the maximum in conductivity (O:Li ~ 20:1; top) and at a very high concentration (O:Li ~ 6:1; bottom).

anion diffusivity was typically higher than cation diffusivity (Fig. 5) and that the cation transference number was always less than 0.5 (Fig. 6), we can state that charge transport due to anions is higher than that due to cations. All this information and our data lead to a suggestion of the structure of our composite electrolytes.

Graphic representation.—The ChemOffice software suite (Cambridge Soft), with its tools in 3D modeling and simple *ab initio* and molecular dynamics calculations, was used to generate some plausible (but not quantitative) structures shown in Fig. 10b. Figure 10 summarizes pictorially some of our findings. In Fig. 10a the composite electrolyte is shown at the nanometer-length scale. The nanoparticles of fumed silica assemble into a volume-spanning network that provides for mechanical strength. The network contains large open pores that are filled with the oligomers of PEGdm and solvated lithium salt. The radius of gyration of the oligomers is on the order of 1 nm, while the pores in the silica network are on the order of 400 nm. This large disparity in length scale allows free movement of the oligomers, and the structures of the fumed silica network have little influence on the structures of the liquid electrolyte phase.

Figure 10b shows the electrolyte at the molecular-length scale with the oligomers of PEGdm solvating the cations and the anions occupying the interchain space in the solvent matrix. These are qualitative figures which do not attempt to capture the features of ion complexes. Two salt concentrations of interest are represented pictorially, O:Li ~ 20:1 and O:Li ~ 6:1. Recalling that the maximum in conductivity occurs at 1.06 M (O:Li ~ 20), we see that even though charge carriers are present, the solvent matrix is only partially occupied. This could be interpreted as a presence of free volume, which allows easy movement of an anion from one interchain space to another or, for movement of a cation or cation/PEGdm complex, from one location to another. At the highest concentrations studied, which corresponds with low conductivity and T_{Li} approaching 0.5, the solvent matrix is more fully occupied, thus constraining the mobilities of all species present to the same value. Table I tabulates properties of the liquid electrolyte at three concentrations. For 1.06 M LiTFSI the viscosity and density are low and the cation diffusivity is high; thus, a high-molar conductivity occurs given there are plenty of charge carriers present (one per every four oligomers). As the concentration increases, providing for a repletion of charge carriers, free volume is lost and the system becomes too

Table I. Properties of PEGdm/LiTFSI electrolytes for three concentrations at 30°C.

O:Li	<i>c</i> (M)	ρ (g mL ⁻¹)	η (cP)	D_{Li} (cm ² s ⁻¹)	$D_{\text{Li}}/D_{\text{F}}$	T_{Li}	σ (mS cm ⁻¹)
20	1.06	1.2	19	4.2×10^{-7}	0.85	0.36	2.2
9.8	1.86	1.3	58	1.5×10^{-7}	~1	0.44	1.5
5.3	2.75	1.4	292	5.3×10^{-8}	~1	Not measured	0.44

viscous; thus, a marked loss in ion mobility occurs. However, as the mobility of the anion becomes restricted, the relative mobility of the cation increases, yielding a lithium transference number approaching 0.5.

Turning to a simple model describing the electrolyte in broad brushstrokes, we suggest that the data support an orderly increase in the extent of aggregation of ions as salt concentration increases. At about 0.24 M (O:Li ~ 100:1), the electrolyte most likely consists of loose ion triplets (rapidly exchanged) with a smaller population of free ions. As the concentration is increased, the ion-ion aggregation increases, leading to a broad decrease in mobility of the ions, culminating in a highly aggregated system in which the anion and cation motions are closely coupled.

Conclusions

In this study, we examine the effects of fumed silica concentration on ion transport in a composite electrolyte comprised of hydrophobic fumed silica, low-molecular-weight end-capped PEG, and lithium salts. The addition of fumed silica has a minimal effect on ionic conductivity and on the diffusivity of cations and PEGdm oligomers. These results are consistent with the microstructure of the electrolyte, which reveal fumed silica forms a network structure with large open pores that would offer negligible impediment to the motion of the ions and solvating oligomers. Measurements of lithium transference number (T_{Li}) and spin-lattice relaxation (T_1) of ⁷Li as a function of silica content also indicate little interaction between the lithium ions and fumed silica particles.

The effect of salt content on ion transport reveals a maximum in conductivity at 1.06 M LiTFSI (O:Li = 20). Corresponding studies on the effect of salt on electrolyte viscosity and diffusivity of cation and solvating oligomer suggest that at about 1.06 M a trade-off of adding more charge carriers is balanced against the deleterious effects of decreasing mobilities and increased ion-ion interactions. Measurement of lithium transference numbers indicates that T_{Li} approaches 0.5 as all the PEO chains complex positively charged ionic species (*i.e.*, the solvent matrix becomes more fully loaded); hence, the electrophoretic mobilities of cations and anions are constrained to have the same value. At low concentrations of 0.23 M or less, some interesting features are observed with T_{Li} drastically increasing and Λ reaching a local maximum. This is suggestive of an electrolyte that consists primarily of fully dissociated ions or of charged complexes, with triplets (*i.e.*, [M₂A]⁺ and [MA₂]⁻) being most likely.

Finally, we explore the validity of the Nernst-Einstein equation in describing ion transport in polymer electrolytes and its application with pfg-NMR to determine transference numbers. We show that transference numbers determined via the use of pfg-NMR are consistently higher than those accurately measured via ENMR. However, the same trends in salt content are observed by both methods. At low concentrations (less than 1 M), the Nernst-Einstein equation overpredicts Λ compared to those obtained from ac impedance spectroscopy measurements. At higher concentrations, the calculated Λ values converge to the measured values. We argue that this convergence is not due to an increase in the validity of the Nernst-Einstein equation at higher concentrations (*i.e.*, reduction in ion complexes) but rather is an artifact of the mobilities converging to a single value. Therefore, comparing Λ calculated from the Nernst-Einstein equation to that determined from ac impedance spectroscopy is not an appropriate method of estimating the extent of dissociation of a lithium salt in the polymer solvent.

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