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Mechanism of ion transport in perfluoropolyether electrolytes with a lithium salt

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Perfluoropolyethers (PFPEs) are polymer electrolytes with fluorinated carbon backbones that have high flash points and have been shown to exhibit moderate conductivities and high cation transference numbers when mixed with lithium salts. Ion transport in four PFPE electrolytes with different endgroups was characterized by differential scanning calorimetry (DSC), ac impedance, and pulsed-field gradient NMR (PFG-NMR) as a function of salt concentration and temperature. In spite of the chemical similarity of the electrolytes, salt diffusion coefficients measured by PFG-NMR and the glass transition temperature measured by DSC appear to be uncorrelated to ionic conductivity measured by ac impedance. We calculate a non-dimensional parameter, β, that depends on the salt diffusion coefficients and ionic conductivity. We also use the Vogel–Tammann–Fulcher relationship to fit the temperature dependence of conductivity. We present a linear relationship between the prefactor in the VTF fit and β; both parameters vary by four orders of magnitude in our experimental window. Our analysis suggests that transport in electrolytes with low dielectric constants (low β) is dictated by ion hopping between clusters.

Introduction

Perfluoropolyethers are a new class of electrolytes that are promising alternatives to conventional flammable liquid electrolytes used in rechargeable lithium batteries. Due to their high flash points they may be used for intrinsically safer lithium batteries.[1] While previous studies have shown that mixtures of perfluoropolyethers and lithium bis(trifluoromethylsulfonyl)amine (LiTFSI) exhibit reasonable conductivities and high lithium transference numbers that, in some cases, can approach unity, our understanding of the nature of charge carriers in these electrolytes is limited.[2]

The Nernst–Einstein equation is a convenient starting point for discussing the nature of charge carriers. In this equation the ionic conductivity, usually measured by ac impedance, is related to the self-diffusion of dissociated ions, D_{Li} and D_{TFSI}:

$$\sigma = \frac{F^2 c}{RT}(D_{\mathrm{Li}} + D_{\mathrm{TFSI}}) \quad (1)$$

where T is the temperature, R is the gas constant, F is Faraday's constant, c is the molar salt concentration, and D_{Li} and D_{TFSI} are the diffusion coefficients of the lithium and TFSI species, respectively. It is important to note that eqn (1) was developed for dilute solutions and assumes that the dominant charge carriers are individual dissociated ions, not ion clusters. In the dilute limit, D_{Li} and D_{TFSI} correspond to diffusion coefficients of dissociated ions. A popular approach for measuring D_{Li} and D_{TFSI} is pulsed-field gradient NMR (PFG-NMR). It has been recognized that PFG-NMR measurements of diffusion coefficients represent an average over all of the ion-containing species in solution including charged and neutral ion clusters. In such cases, the relationship between σ, D_{Li}, and D_{TFSI} is not well-established. It is convenient to define a dimensionless parameter β as follows,

$$\beta = \frac{\sigma}{\frac{F^2 c}{RT}(D_{\mathrm{Li}} + D_{\mathrm{TFSI}})} \quad (2)$$

In the literature this parameter is sometimes called the ionicity or the inverse of the Haven ratio[3–8] and is related to the extent of salt dissociation. For electrolytes that obey the Nernst–Einstein relationship, β is unity. Incomplete dissociation generally leads to a reduction in β.

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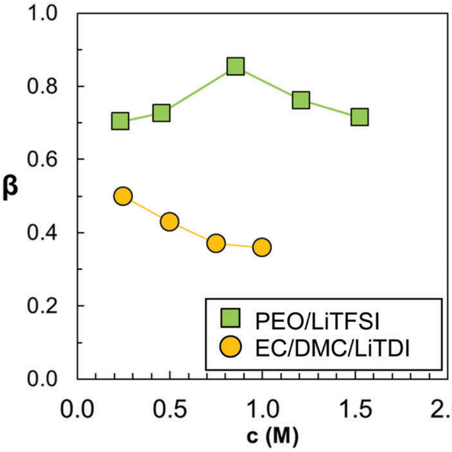


Fig. 1 Values of β calculated for PEO/LiTFSI from Timachova *et al.*[10] and Lascaud *et al.*[11] and EC/DMC/LiTDI from Berhaut *et al.*[9]

In Fig. 1, we show the dependence of β, obtained by combining ac impedance and PFG-NMR, on salt concentration for two well-studied electrolytes: a liquid electrolyte comprising mixtures of alkyl carbonates (EC/DMC) and lithium 4,5-dicyano-2-trifluoromethyl-imidazolide (LiTDI) studied by Berhaut *et al.*, and a polymer electrolyte comprising mixtures of poly(ethylene oxide) (PEO) and LiTFSI studied by Lascaud *et al.* and Timachova *et al.*[9–11] In both cases, β is a weak function of c. The average value of β for the liquid electrolyte is 0.4 while that for the polymer electrolyte is 0.8. One expects the extent of dissociation to be related to the dielectric constant of the solvent, which is 40 for EC/DMC and 7.5 for PEO.[12,13] It is surprising that β obtained in the low dielectric constant solvent is higher than that obtained in the high dielectric constant solvent. The concentration of neutral ion pairs is expected to increase with increasing salt concentration. This implies that β should be a decreasing function of c. Charge screening, described by the Debye–Huckel theory, will also lead to a reduction in β. Data from EC/DMC are consistent with this expectation. To our knowledge, the underpinnings of these observations have not yet been established, indicating that questions regarding the mechanism of charge transport in well-studied systems remain unanswered.

The mechanism of ion transport in polymer electrolytes is the subject of significant current interest. Current studies of ion transport mechanisms are based on a combination of different approaches such as electrochemical measurements, spectroscopy, simulations, as well as more recent work with electrophoretic NMR.[14–16] Electrochemical measurements are usually analyzed using the Vogel–Tamman–Fulcher (VTF) relationship to fit the dependence of ionic conductivity on temperature,

$$\sigma = AT^{-1/2}\exp\left(\frac{-B}{R(T-T_0)}\right), \tag{3}$$

where A is a constant, E_A is a constant often associated with the activation energy for ion motion, R is the gas constant, T is the experimental temperature, and T_0 is the reference temperature taken as 50 degrees below the glass transition temperature, T_g-50. Eqn (3) is used to describe the role of segmental dynamics, dictated by T_g, on ion transport.[17,18] Stolwijk *et al.* and Zugmann *et al.* have used β derived from spectroscopic and electrochemical measurements to estimate the extent of salt dissociation in both liquid and polymer electrolytes.[19,20] Extensive simulations work predicting salt-solvent coordination and ion transport in polymer systems has been done by Borodin and Smith.[21] Hou *et al.* and Gouvernour *et al.* have measured the motion of dissociated ions using electrophoretic NMR.[7,15]

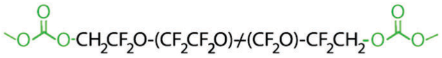
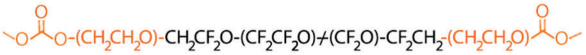
The purpose of this paper is to report values of β measured by combining ac impedance and PFG-NMR in a series of PFPE electrolytes over a salt concentration range similar to Fig. 1. We find that β increases with salt concentration by several orders of magnitude. We also use the Vogel–Tamman–Fulcher (VTF) equation to characterize the temperature dependence of conductivity in PFPE electrolytes. We obtain a surprising correlation between β and A. In addition to organizing the data set, it provides insight into the mechanism of ion transport.

Experimental

Materials

PFPE D10-OH and E10-OH were purchased from Santa Cruz Biotechnology and Solvay, D10-DMC and E10-DMC samples were synthesized as reported previously,[1,22] and LiTFSI salt was purchased from Novolyte. The characteristics of the polymers used in this study are listed in Table 1. Salt was dried at 120 °C and the polymers were dried at room temperature under vacuum for 72 hours before use in an air and water-free Argon environment. LiTFSI salt was mixed directly with the PFPE samples at varying salt concentrations, ranging from 0.3 to 1.7 M (5% to 30% by weight), for 24 h at 60 °C. Electrolyte preparation and

Table 1 Characteristics of polymers used in this study

Polymer	Structure	m	n	q	M (g mol^{-1})
D10-OH	$HO\text{-}CH_2CF_2O\text{-}(CF_2CF_2O)/(CF_2O)\text{-}CF_2CH_2\text{-}OH$	7	3	0	1000
D10-DMC	 $CH_3O\text{-}C(=O)\text{-}O\text{-}CH_2CF_2O\text{-}(CF_2CF_2O)/(CF_2O)\text{-}CF_2CH_2\text{-}O\text{-}C(=O)\text{-}OCH_3$	7	3	0	1116
E10-OH	$HO\text{-}(CH_2CH_2O)\text{-}CH_2CF_2O\text{-}(CF_2CF_2O)/(CF_2O)\text{-}CF_2CH_2\text{-}(CH_2CH_2O)\text{-}H$	5	4	2	1200
E10-DMC	 $CH_3O\text{-}C(=O)\text{-}O\text{-}(CH_2CH_2O)\text{-}CH_2CF_2O\text{-}(CF_2CF_2O)/(CF_2O)\text{-}CF_2CH_2\text{-}(CH_2CH_2O)\text{-}C(=O)\text{-}OCH_3$	5	4	2	1316

m = number of CF_2CF_2O monomers. n = number of CF_2O monomers. q = number of CH_2CH_2O monomers.

conductivity measurements were made in an argon glovebox, with the exception of DSC samples which were prepared in air. Diffusion measurements were performed in NMR tubes sealed with high pressure polyethylene caps.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) thermograms were recorded using a TA Instruments DSC Q200 on PFPE/LiTFSI samples mixed in air over the temperature range from −150 °C to 100 °C using a heat/cool/heat method at a heating and cooling rate of 10 °C min^{-1} and 5 °C min^{-1}, respectively. Glass transition temperatures, T_gs, were determined using the average from the midpoint method on the cooling cycle and second heating cycle thermogram.

Electrochemical measurements

Ionic conductivity was measured using ac impedance spectroscopy on a BioLogic VMP3 potentiostat in homebuilt stainless steel liquid cells. As the electrodes of the cells are asymmetric, the current distributions were modeled using Laplace's equation, and effective cell constants were determined.[23] The complex impedance of the samples was measured over the frequency range 1 MHz to 1 Hz at an applied voltage amplitude of 40 mV. Conductivity was calculated using the in-phase resistance of the complex impedance extracted from a Nyquist plot of the current response.

Pulsed field gradient-NMR (PFG-NMR)

NMR measurements were performed on a Bruker Avance 600 MHz instrument fitted with a Z-gradient direct detection broad-band probe and a variable temperature unit. Measurements were performed on the isotopes of ^{7}Li and ^{19}F to probe the diffusion of lithiated and fluorinated species, respectively. All samples produced peaks around 233 MHz for lithium and 565 MHz for fluorine corresponding to all lithium- and TFSI-containing ion species. The 90° pulse lengths were optimized for each sample to achieve maximum signal amplitude. T1 relaxation times were independently measured for each sample nuclei using inversion-recovery (180–τ–90–acq.) to insure the choice of an appropriate diffusion time interval Δ. A bipolar pulse longitudinal-eddy-current delay sequence was used to measure the diffusion coefficients D. The attenuation of the echo E was fit to,

$$E = \mathrm{e}^{-\gamma^2 g^2 \delta^2 D\left(\Delta - \frac{\delta}{3} - \frac{\tau}{2}\right)} \quad (4)$$

where γ is the gyromagnetic ratio, g is the gradient strength, δ is the duration of the gradient pulse, Δ is the interval between gradient pulses, τ is the separation between pulses, and D is the diffusion coefficient. The diffusion time Δ and gradient pulse length δ were independently varied to confirm that they do not affect the measured value of D. Parameters used for acquisition were diffusion intervals Δ = 0.1–0.5 s (^{7}Li) and 0.05–0.8 s (^{19}F), and pulse lengths δ = 1–10 ms (^{7}Li) and 1–3 ms (^{19}F). For each diffusion measurement, 32 experiments of varying gradient strength up to 0.5 T m^{-1} were performed and the change in amplitude of the attenuated signal was fit to obtain the parameter D. All measured signal attenuations were single exponential decays and the errors in the fits were less than 2%.

Results & discussion

It is generally believed that the conductivity of polymer electrolytes is governed by segmental motion of polymer chains. The glass transition temperature is a convenient parameter that reflects segmental motion. The dependence of T_g measured by DSC on salt concentration in the four electrolytes is shown in Fig. 2. The highest salt concentration in each case reflects the solubility limit. As expected, T_g increases with the addition of salt as increasing interactions between the salt and the polymers slow down segmental motion. The measured viscosities of the electrolytes, previously reported in Olson *et al.*,[22] follow the trend expected from the T_g data presented in Fig. 2. At a given salt concentration, D10-DMC has the lowest T_g while E10-DMC has the highest T_g.

The temperature dependencies of the ionic conductivities at different salt concentrations are shown in Fig. 3 for (a) D10-OH (b) D10-DMC, (c) E10-OH and (d) E10-DMC. As expected, the conductivities increase with increasing temperature following the VTF relationship (eqn (3)). The curves in Fig. 3 are VTF fits through the data. For the D10 electrolytes, increasing salt concentration results in a monotonic increase in conductivity. A more complex, non-monotonic dependence of conductivity on salt concentration is seen in the E10 electrolytes.

The diffusion coefficients of the lithium, D_{Li}, and TFSI, D_{TFSI}, at c = 0.55 M measured by PFG-NMR, are shown as a function of temperature in Fig. 4. D_{Li} and D_{TFSI} increase about two orders of magnitude with increasing temperature over the range 30–90 °C. The diffusion coefficients of Li and TFSI species in E10-OH and E10-DMC are similar. The diffusion coefficients obtained for D10-OH are similar to E10-OH and E10-DMC. Both D_{Li} and D_{TFSI} of D10-DMC are higher than in the other electrolytes.

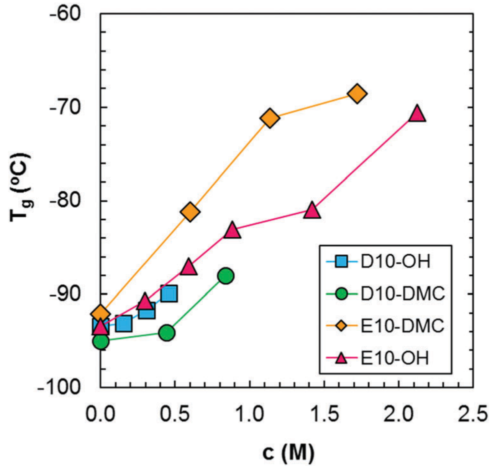


Fig. 2 The glass transition temperature, T_g, measured by differential scanning calorimetry as a function of salt concentration.

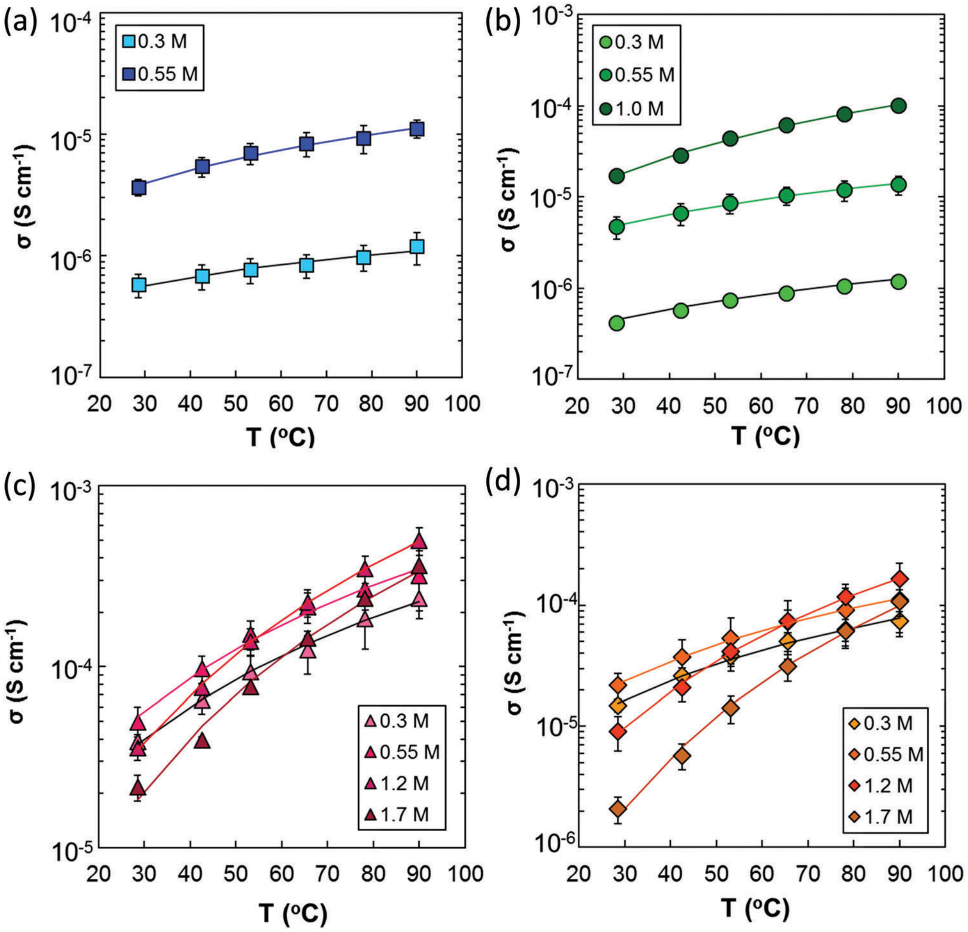


Fig. 3 (a) Ionic conductivity, σ, and as a function of temperature for (a) D10-OH, (b) D10-DMC, (c) E10-OH, and (d) E10-DMC at different salt concentrations, c, up to the maximum solubility in each perfluoropolyether. The solid lines are fits of the data to VTF behavior.

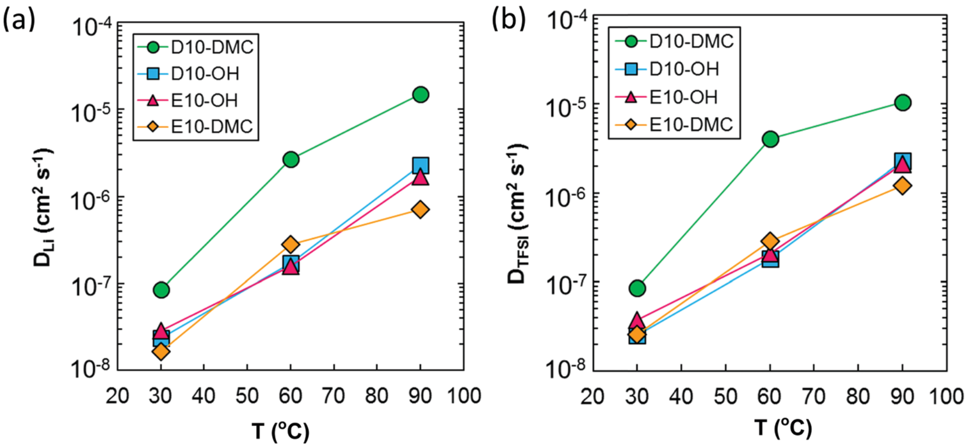


Fig. 4 Diffusion coefficients, (a) D_{Li} and (b) D_{TFSI}, at c = 0.55 M LiTFSI measured by PFG-NMR as a function of temperature (T).

The ionic conductivity, σ, and diffusion coefficients, D_{Li} and D_{TFSI}, are plotted as a function of molar salt concentration, c, in Fig. 5 at a constant temperature of 90 °C up to the solubility limits of the perfluoropolyethers. The ionic conductivity increases for all polymers with the conductivities of the E10-OH and E10-DMC systems reaching maxima around 1.15 M. Both lithium and TFSI diffusion coefficients decrease monotonically with increasing salt concentration. One might expect conductivity and diffusion coefficients to be correlated and exhibit similar trends with respect to the polymer chemistry. The data in Fig. 5 show that this is not the case. The D10 PFPEs show the highest salt diffusivities and the lowest ionic

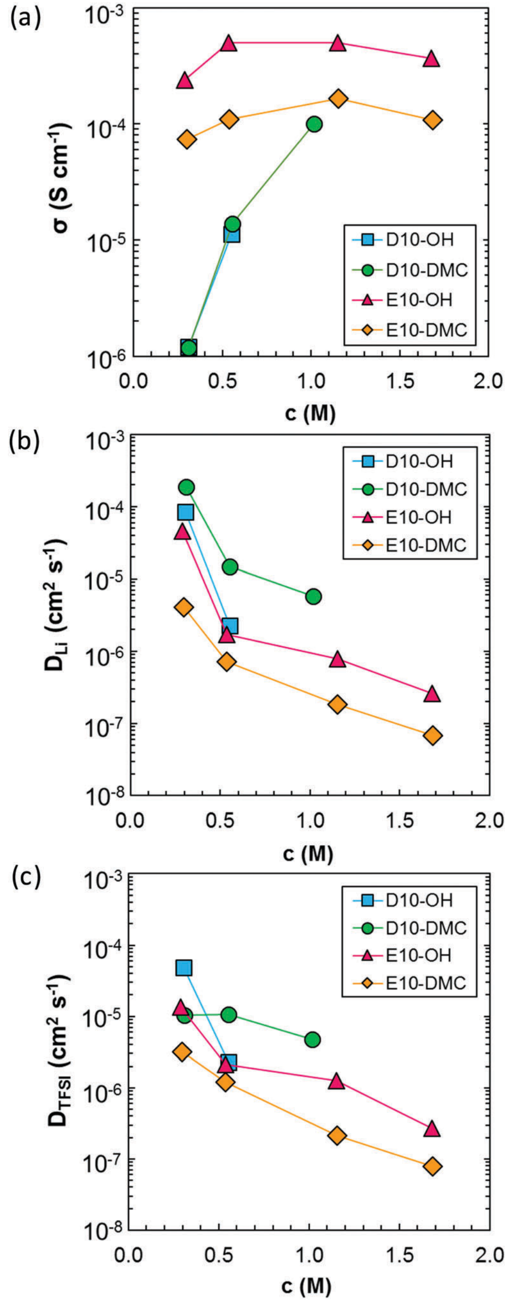


Fig. 5 (a) Ionic conductivity, σ, and diffusion coefficients, (b) D_{Li} and (c) D_{TFSI}, and as a function of salt concentration, c, at 90 °C.

conductivities, while the E10 PFPEs show the lowest diffusivities and the highest ionic conductivities.

Since the major component of all of the polymers in the present study is perfluoropolyether chains, one might expect a simple correlation between T_g, σ, D_{Li}, and D_{TFSI}. In particular, samples with low T_g are expected to exhibit high conductivity and faster diffusion. The results shown in Fig. 2–5 are inconsistent with this expectation. To illustrate this, the properties of the electrolytes at c = 0.55 M and 90 °C are summarized in Table 2. The sample with the lowest T_g is ranked 1 while samples with the highest values of σ, D_{Li}, and D_{TFSI} are ranked 1.

Table 2 Rank ordering of electrolyte properties at 90 °C and 0.55 M

Polymer	T_g	σ	D_{Li}	D_{TFSI}
D10-OH	2	4	2	2
D10-DMC	1	3	1	1
E10-OH	4	1	3	4
E10-DMC	3	2	4	3

T_g is ranked from lowest to highest (1 → 4). σ, D_{Li}, and D_{TFSI} are ranked from highest to lowest (1 → 4).

It is evident that the diffusion coefficients are correlated with T_g. It is also evident that σ is not correlated with either T_g or the diffusion coefficients. While the salt diffusion coefficients are highest in D10-DMC, the conductivity is highest in E10-OH, the sample with the highest T_g. The relationship between conductivity, ion diffusion, and segmental motion is not clear in the data.

In Fig. 6, we plot β, a parameter that depends on both conductivity and the salt diffusion coefficients (eqn (2)) as a function of concentration, c. For the D10-DMC, β increases by two orders of magnitude as c increases from 0.3 to 1.15 M. A similar increase is seen in D10-OH. A more modest increase in β is observed in the E10 systems. It is important to note the qualitative difference between Fig. 1 and 6. In more traditional electrolytes made from PEO and carbonates such as EC/DMC, β either decreases or stays constant with increasing salt concentration (Fig. 1) due to effects such as ion pairing and electrostatic screening. In the E10 PFPEs that contain ethylene oxide endgroups, there is a modest increase in β with salt concentration. Small increases in β have been observed previously in ionic liquid electrolyte systems by Borodin *et al.*[24] In contrast, a dramatic increase in β with salt concentration is seen in the D10 PFPEs that have entirely fluorinated backbones; increasing c by a factor of 3 results in a 500× increase in β.

Given the low dielectric constant of fully-fluorinated D10 PFPEs ($\varepsilon \sim 2.1$), we expect salt ions to be clustered. We propose that ion transport in these PFPE electrolytes only occurs

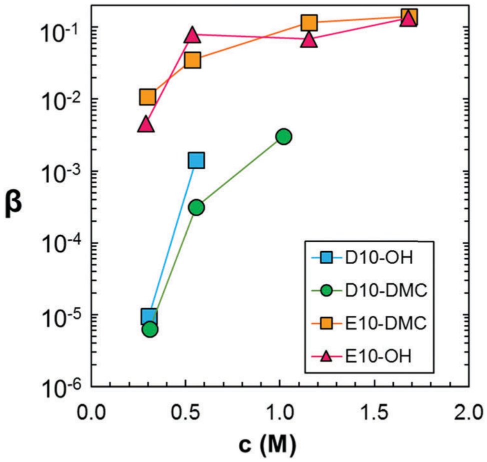


Fig. 6 The effective fraction of salt species available for charge transport, β, obtained from the deviation of the NMR predictions of conductivity at 90 °C based on the Stokes–Einstein relation.

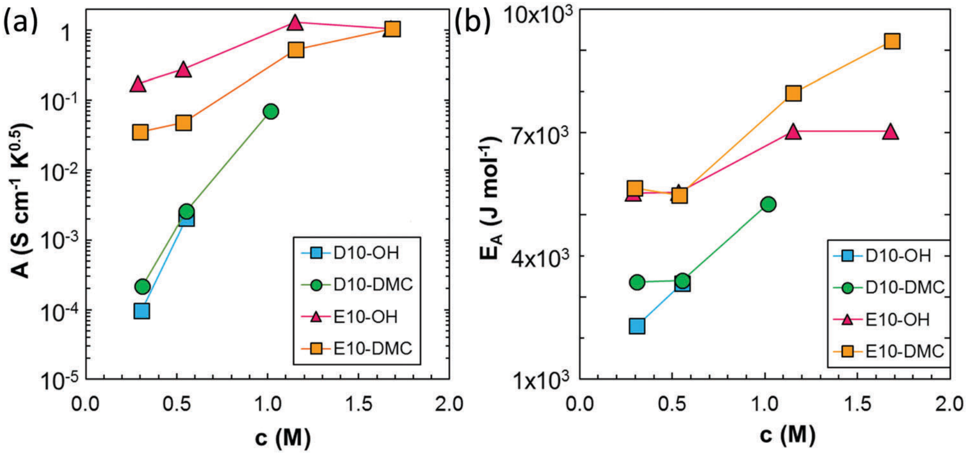


Fig. 7 The VTF fits parameters (a) *A* and (b) E_A from fits of the ionic conductivity as a function of temperature, shown as a function of salt concentration, *c*.

when ion clusters are in close proximity to each other. The characteristic length of LiTFSI is 0.8 nm (calculated from the covalent radii along the longest dimension). If the clusters are predominantly ion pairs, the average distance between LiTFSI molecules at 1 M is ~1.2 nm. At this concentration, we obtain reasonable conductivity ($\beta = 10^{-3}$ and $\sigma = 10^{-4}$ S cm^{-1} in D10-DMC). When the salt concentration is reduced to 0.3 M, the average distance between ion pairs increases to 1.75 nm and this effectively shuts down ion transport ($\beta = 10^{-5}$ and $\sigma = 10^{-6}$ S cm^{-1}). At this juncture, we do not have explicit knowledge about the nature of ion clustering in PFPE electrolytes. If larger clusters exist, then the hopping distances will be longer. For example, if the clusters are predominantly composed of 4 ions then the average hopping distance increases by ~30%. We conclude that inter-cluster hopping is the main mechanism for ions transport in D10 PFPE electrolytes and that appreciable transport is obtained when this distance is commensurate with the size of the anion. The behavior of E10 PFPE electrolytes, which contain ethylene oxide groups, appears to fall in between D10 PFPEs and PEO.

In Fig. 7(a) we plot the VTF parameter *A* as a function of salt concentration, *c*. *A* is a strong function of *c* for the D10 polymers and a weaker function of *c* for the E10 polymers. The similarity of the trends seen in Fig. 6 and 7(a) are obvious. In Fig. 7(b), we plot the VTF parameter E_A as a function of salt concentration, *c*. E_A is a much weaker function of salt concentration and endgroup chemistry for both D10 and E10 polymers. We thus focus on the dependence of *A* on *c*.

In Fig. 8, we plot β as a function of *A* at 90 °C. The data from all of the electrolytes falls on a straight line with $\beta = 0.1$ A. Similar trends are seen at other temperatures. This plot exposes the correlation between conductivity and salt diffusion coefficients in PFPE electrolytes that was not clear from the initial raw diffusion and conductivity data in Fig. 2–5. Comparing Fig. 5 with Fig. 4(a), we see that conductivity has a strong dependence on β and *A*, accounting for the lack of correlation between conductivity, T_g, and diffusivity.

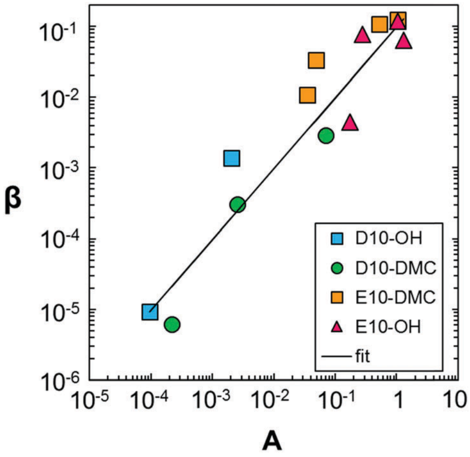


Fig. 8 The effective fraction of salt species available for charge transport, β, *versus* the number of available charge carriers, *A*, as a function of salt concentration at 90 °C. The black line is the fit to $\beta = mA$, where $m = 0.1$.

Conclusions

We have characterized PFPE electrolytes with different endgroup chemistries as a function of salt concentration and temperature by DSC, ac impedance, and PFG-NMR. At a given temperature, the salt diffusivity measured by PFG-NMR decreases with increasing T_g, measured by DSC. In contrast, ionic conductivity measured by ac impedance is highest in the PFPE with the highest T_g. The relationship between conductivity, diffusion, and segmental motion quantified by T_g is thus unclear in these electrolytes. To clarify the relationship between these parameters, we have calculated β from ac impedance and PFG-NMR measurements using eqn (2) and used the VTF equation to fit temperature-dependent conductivity data. We conclude that ion transport in systems with low β is governed by hopping between ion clusters, a distance that decreases with increasing salt concentration. We find a linear correlation between β and the VTF parameter A, which vary by four orders of magnitude over our experimental window.

Author contribution

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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