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The Effect of Low-Molecular-Weight Poly(ethylene glycol) (PEG) Plasticizers on the Transport Properties of Lithium Fluorosulfonimide Ionic Melt Electrolytes

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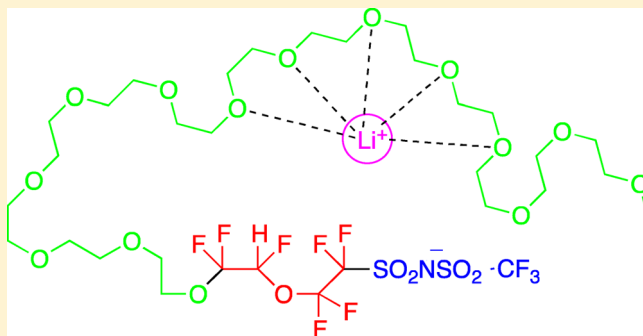
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ABSTRACT: The influence of low-molecular-weight poly(ethylene glycol) (PEG, $M_w \approx 550$ Da) plasticizers on the rheology and ion-transport properties of fluorosulfonimide-based polyether ionic melt (IM) electrolytes has been investigated experimentally and via molecular dynamics (MD) simulations. Addition of PEG plasticizer to samples of IM electrolytes caused a decrease in electrolyte viscosity coupled to an increase in ionic conductivity. MD simulations revealed that addition of plasticizer increased self-diffusion coefficients for both cations and anions with the plasticizer being the fastest diffusing species. Application of a VTF model to fit variable-temperature conductivity and fluidity data shows that plasticization decreases the apparent activation energy (E_a) and pre-exponential factor A for ion transport and also for viscous flow. Increased ionic conductivity with plasticization is thought to reflect a combination of factors including lower viscosity and faster polyether chain segmental dynamics in the electrolyte, coupled with a change in the ion transport mechanism to favor ion solvation and transport by polyethers derived from the plasticizer. Current interrupt experiments with Li/electrolyte/Li cells revealed evidence for salt concentration polarization in electrolytes containing large amounts of plasticizer but not in electrolytes without added plasticizer.



INTRODUCTION

Ion transport in a lithium-ion battery strongly influences its performance. It is important for the electrolyte in the battery to have both high ionic conductivity and high lithium transference number. Such desirable properties allow for high power density which is critical in EV and HEV applications.^{1,2} Moreover, lithium ion batteries offer 2–4 times higher energy densities than the Ni–MH and Ni–Cd batteries.^{3,4} In previous work,^{5–7} we reported the synthesis, characterization, and molecular dynamics (MD) simulations of novel ionic melt electrolytes (which in fact are ionic liquids too, ILs) with the structure oligoether–anion[−]/Li⁺ with the anion covalently bound to a polyether chain that can solvate a lithium ion. These electrolytes are special insofar as they do not allow for salt concentration polarization to occur when they are used in cells with electrodes that are nonblocking for lithium. Salt concentration polarization is undesirable in lithium batteries because it can cause voltage losses and limit currents in the cells.^{8,9} These IM/IL electrolytes are lithium fluorosulfonimide salts (lithium fluorosulfonimide = fluoroalkyl–SO₂N(Li)SO₂–fluoroalkyl[′]) that provide a high degree of Li⁺/anion dissociation and, therefore, improved conductivity compared

to other polyether-based ionic liquids with sulfonate anion¹⁰ or sulfate ester anion¹¹ attached to oligoethers. The oligoether solvating host also provides better salt dissociation and lithium transport compared to oligo(propylene oxide) used in other previous studies of ionic liquids with the anion attached to a solvating polyether host.^{10,12} The structure of the fluorosulfonimide anion used in our studies is also different from that of fluorosulfonamides (fluorosulfonamide = fluoroalkyl–NH–SO₂CF₃, with only one sulfonyl group bound to nitrogen) that have been used in previous studies.^{12–15}

It is desirable to increase the ionic conductivity of lithium-containing electrolytes while maintaining a relatively high lithium-transference number in order for such materials to be useful in lithium battery applications.¹⁶ The most common approach to improving polymer electrolyte ionic conductivities, especially at ambient temperature, is plasticization.^{17–19} In this paper, we report a plasticizing effect on the transport properties, including rheological properties, of the previously

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Table 1. Materials and Their Abbreviations

material	composition (experimental)
IM550 ($M_w = 965$ Da)	$\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_{11.8}-\text{CF}_2\text{CFHOCF}_2\text{CF}_2\text{SO}_2\text{N}^-\text{SO}_2\text{CF}_3/\text{Li}^+$
IM550_Gel2 ($M_w = 887$ Da)	IM550 + 20 wt % PEGME550 (or PEGDME500)
IM550_Gel1 ($M_w = 811$ Da)	IM550 + 50 wt % PEGME550 (or PEGDME500)
material	composition (simulation)
IM516 ($M_w = 797$ Da)	$\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_{11}-\text{CH}_2\text{CF}_2\text{SO}_2\text{N}^-\text{SO}_2\text{CF}_3/\text{Li}^+$ ($\text{EO}_{12}\text{TFSI}^-/\text{Li}^+$)
IM516_Gel1	IM516 + 40 wt % PEG530

reported ionic liquids of the structure oligoether–anion/ Li^+ .⁶ We have used low-molecular-weight PEG oligomers to increase ionic conductivity by a plasticization mechanism.^{20,21} Low-molecular-weight oligoethers have high boiling points and low vapor pressure, and their ethylene oxide (EO) units have a high donor number for Li^+ and, also, a high chain flexibility, all of which are important for promoting rapid ion transport.²² We report here on the preparation and characterization, including by MD simulation methods, of these plasticized ionic melt electrolytes. We also report on the possible negative consequences of plasticization relating to salt concentration polarization in cells, which could potentially offset the advantages of plasticization for improving conductivity.

EXPERIMENTAL SECTION

Chemicals. The ionic melt IM550 having the chemical formula $\text{CH}_3\text{O}-(\text{CH}_2\text{CH}_2\text{O})_{11.8}-\text{CF}_2\text{CFHOCF}_2\text{CF}_2\text{SO}_2\text{N}^-(\text{Li})\text{SO}_2\text{CF}_3$ was prepared as described previously.⁶ Note that the designation of 11.8 EO units per polymer chain for IM550 is an average value. Obviously, the sample is a mixture with each polymer molecule in the mixture having an integral number of EO units in the chain. The melt electrolyte was kept under dry conditions in an argon-filled glovebag prior to use. Both poly(ethylene glycol) monomethyl ether (PEGME) of $M_w \approx 550$ Da and poly(ethylene glycol) dimethyl ether (PEGDME) of $M_w \approx 500$ Da were purchased from Aldrich and were dried under a dynamic vacuum before use. Acetonitrile (ACN), HPLC grade, was dried by refluxing it over P_2O_5 for more than 24 h. A lithium ribbon of 0.75 mm thickness and 20 mm width was purchased from Aldrich and was stored in a glass jar placed in an argon filled drybox.

Electrolyte Preparation. Plasticized electrolytes consisting of IM550 with 50 and 20 wt % PEGME550 (or PEGDME500 used only for the galvanostatic polarization experiments) denoted as IM550_Gel1 and IM550_Gel2, respectively, were prepared by mixing IM550 and PEGME550/PEGDME500 in a round-bottom flask. The mixture was well-stirred, using a magnetic stir bar, in 20 mL of dry ACN and was homogenized at room temperature for 5 h. The solvent was then evaporated, and the electrolyte was dried under a dynamic vacuum. The ^1H NMR spectrum confirmed the absence of residual solvent.

Measurements. Ionic Conductivities. Electrochemical impedance spectroscopy (EIS) was used to measure the electrolyte resistance. Measurements were done similarly to what has been previously described²³ using a Solartron SI 1287 electrochemical interface and a Solartron SI 1260 frequency response analyzer. The electrolyte samples were sandwiched between two nickel blocking electrodes separated by an annular ring spacer of 0.1 in. thickness and 0.9 in. diameter. Analysis was performed upon cooling from 150 °C down to 20 °C in a Tenney Jr. thermal chamber, acquiring spectra every 10 °C decrement in the frequency range from 0.1 Hz to 1 MHz. The real impedance of the electrolyte was obtained from the

complex-plane impedance plot,^{24–26} and the ionic conductivity was determined accordingly.

Calorimetric Measurements. DSC measurements were performed using a Mettler-Toledo 820 differential scanning calorimeter. The samples were sealed in aluminum pans and scanned from –150 to 150 °C at a rate of 10 °C/min.

Rheological Experiments. An ARES-LS type rheometer from Rheometric Scientific was used for the rheological studies. A cone-and-plate geometry was used, whereby a circular plate and a linearly concentric cone are rotated relative to each other. The cone-and-plate geometry produces a flow in which the shear rate is very nearly uniform.²⁷ The melt electrolyte was placed in the gap between the plate and the cone under a dry nitrogen atmosphere in order to avoid any moisture interference. For determining the viscosity as a function of shear rate or shear stress, steady-shear experiments were performed at room temperature. The shear viscosity can be calculated by dividing the shear stress to the shear rate.²⁸ The shear rate applied was in the range 0.01–100 s^{-1} . It should be noted that the shear rate can be used synonymously with the rate of strain or velocity gradient. Also, dynamic rheology measurements were acquired at variable oscillation frequency and fixed amplitude at room temperature. From dynamic rheology, the elastic (storage) modulus G' (Pa) and the viscous (loss) modulus G'' (Pa) can be obtained as functions of the oscillation frequency ω (rad/s).

Galvanostatic DC Polarization/Current Interruption Experiments. Only for this type of experiment, PEGDME500 (no –OH groups in contact with Li metal) was used as plasticizer instead of PEGME550 to account for voltage losses within the electrochemical cell subjected to galvanostatic polarization performed at room temperature. The symmetric cell consisted of the electrolyte sandwiched between two lithium electrodes that were separated by a Teflon spacer of thickness 3 mm. Two square-wave current steps of magnitude 10 and 50 μA , respectively, were applied for 1 h each, and cell voltage was monitored. A current of 0 A was applied at the beginning of the experiment and after each current step for 0.5 h.

Molecular Dynamics Simulation Methodology. Polarizable versions of the MD simulation code Lucretius were used for all MD simulations. A previously developed many-body polarizable force field⁵ was used. The compositions of simulated electrolytes are summarized in Table 1. The simulated compositions are close to experimental ones but do not match them exactly because MD simulations and experimental efforts were coordinated only at later stages of the project. MD simulation cells for IM550 consisted of 32 molecules of IM516, while IM516_Gel1 consisted of 16 IM516 and 16 PEG530DME ($\text{H}(\text{CH}_2\text{OCH}_2)_{12}\text{H}$) plasticizer molecules, respectively. Periodic boundary conditions were utilized in all simulations. Simulations were performed with bond lengths constrained using the Shake algorithm²⁹ in order to utilize a larger time step. The Ewald summation method was

Table 2. Length of MD Simulations, Fractions of Free Ions α_s ($r_{\text{Li-N}} > 5 \text{ \AA}$), Degree of Ion Uncorrelated Motion (α_d), and Number of Ether Oxygen Atoms in the Li^+ First Coordination Shell ($n_{\text{Li}^+/\text{EO}}$)

temperature (K)	equilibration run length (ns)	production run length (ns)	density (kg/m ³)	fraction of separated ions (α_s)	$n_{\text{Li}^+/\text{EO}}^a$	
					anion	plasticizer
EO ₁₂ TFSI [−] /Li ⁺ (IM516)						
423	3	25	1209	0.78	4.2	
393	2	8	1231	0.82	4.3	
363	2	15	1257	0.84	4.3	
333	2	27	1285	0.85	4.3	
IM516 + 40 wt % PEG530						
423	3	32	1100	0.84	2.1	2.2
393	2	12	1122	0.86	2.5	1.8
363	2	15.3	1144	0.87	2.5	1.8
333	2	11	1172	0.86	2.4	1.7

^aAn average number of etheric oxygen atoms within a radius of 2.8 Å of a Li^+ cation.

used for treatment of long-range electrostatic forces between partial charges and between partial charges and induced dipoles ($k = 6^3$ number of reciprocal vectors have been used, $\alpha = 7.5\text{--}8 \text{ \AA}$). A tapering function was used to drive the induced dipole–induced dipole interactions to zero at a cutoff of 10 Å, with scaling starting at 9 Å. A reversible reference system with a multiple time step and a propagator algorithm was employed,³⁰ with the following time steps having been utilized: 0.5 fs for bonding, bending, and torsional motions, 1.5 fs for nonbonded interactions within a 6.5 Å sphere, and 3.0 fs for nonbonded interactions between 6.5 and 10.0 Å and the reciprocal space part of the Ewald summation.²⁹ Dispersion interactions were truncated at 10.0 Å.

A Nosé–Hoover thermostat and barostat were used to control the temperature and pressure with the associated frequencies of 10^{-2} and 10^{-3} fs^{-1} . Simulation cells for liquid simulations were created at low density with an initial periodic cell (box) size of 100 Å. The density was then increased in simulations using a Brownian dynamics algorithm²⁹ over a period of 0.5 ns at constant temperature (423 K) in order to yield estimated liquid densities. Simulations were first performed at 423 K in the NPT ensemble at 1 atm pressure. After generating approximately 40–60% of the trajectory at 423 K, the temperature was decreased to 393 K. The same procedure was repeated at 363 K and again at 333 K. Table 2 summarizes the length of production and equilibration runs performed using NVT and NPT ensembles, respectively.

RESULTS AND DISCUSSION

Ionic Conductivity. Figure 1 presents Arrhenius plots of the ionic conductivities of the previously reported IM550 lithium fluorosulfonimide ionic melt electrolyte along with those of the plasticized IM550 samples with 20 and 50 wt % PEGME550 plasticizer (IM550_Gel2 and IM550_Gel1, respectively) added. All of the Arrhenius plots show convex curvature, indicating that ion transport is coupled to polymer dynamics that have non-Arrhenius behavior and exhibit a glass transition. A large increase in ionic conductivity is observed, particularly at the lower temperatures, by increasing the wt % of polyether plasticizer added to the sample. For example, the ambient-temperature conductivity of the IM550_Gel1 is more than 20 times higher than that of the IM550 without plasticizer. Such a considerable increase is attributed largely to the decrease in mixture viscosity by an order of magnitude as a result of the plasticizing effect which will later be revealed and discussed in the section on rheological studies. Additionally, as the

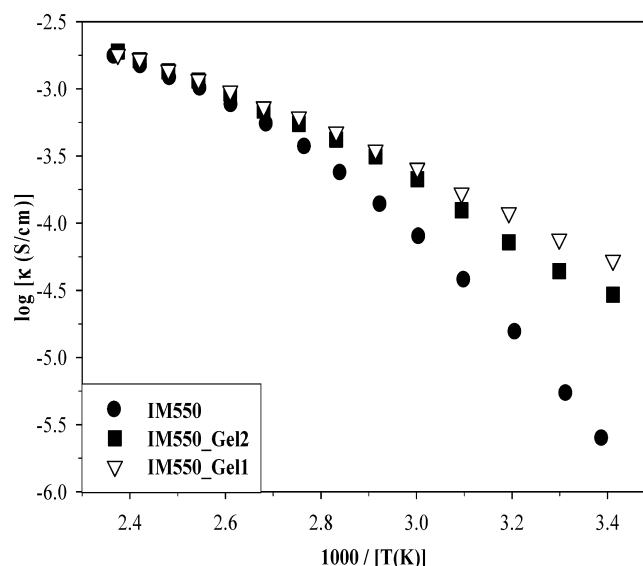


Figure 1. Arrhenius plots for the ionic conductivities of the pure ionic melt (IM550) compared to those that are plasticized with unmodified polyether oligomers (IM550_Gel1 and IM550_Gel2) in the temperature range RT–150 °C.

concentration of EO units increases upon plasticization, additional etheric oxygen coordination sites become available to aid in transport of lithium cations. This effect results in formation of the EO-separated Li^+ cation from anionic groups and a modification of the transport mechanism for Li^+ as revealed by MD simulations discussed below.

Data Fitting and VTF Parameters. We fit the ionic conductivity data shown in Figure 1 by using the Vogel–Tamman–Fulcher (VTF) equation^{31,32}

$$\kappa = A \cdot T^{-1/2} \exp \left[\frac{-E_a}{R \cdot (T - T_0)} \right] \quad (1)$$

where A is a preexponential constant proportional to the concentration of ionic charge carriers, E_a is the effective activation energy for ion conduction, and T_0 is the ideal glass transition temperature (at which the ionic conduction is completely frozen). The ideal glass transition temperature (T_0) was taken to be equal to 25 K lower than the experimental DSC glass transition temperature (T_g).⁷ The data fitting was done using the least-squares method over three different temperature ranges: from ambient temperature to 60 °C, where the ionic

conductivities between the three electrolytes displayed significant changes, from 60 to 150 °C, which corresponds to the range for which MD simulations were performed, and for the overall temperature range of ambient to 150 °C. The graph for the VTF model, applied for a temperature range between ambient and 90 °C where the ionic conductivities between the three materials start to display significant changes, is displayed in Figure 2 as a plot of $\ln(\kappa \cdot T^{1/2})$ vs $1000/(T - T_0)$, and it is

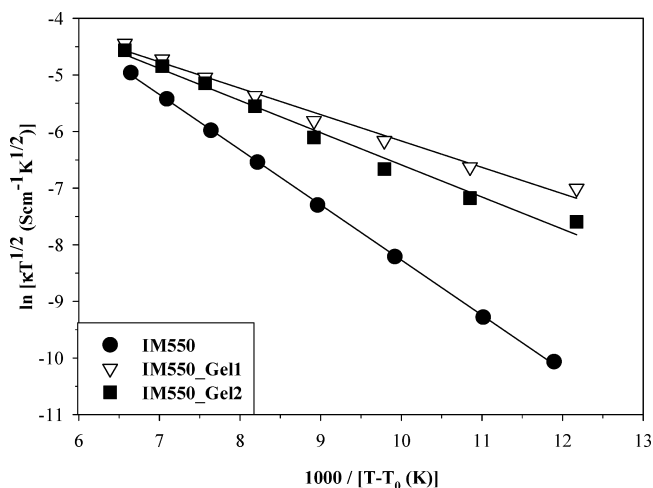


Figure 2. VTF plots for the ionic conductivities of the pure ionic melt (IM550) compared to those that are plasticized with unmodified polyether oligomers (IM550_Gel1 and IM550_Gel2) in the temperature range RT–90 °C.

linear for all three electrolytes, validating the use of this semiempirical correlation for these electrolytes. The values for the parameters of the VTF equation, A and E_a , obtained from linear curve fitting are summarized in Table 3 as a function of

Table 3. Values for the Parameters of the VTF Equation Obtained from Ionic Conductivity Data Fitting for Different Temperature Ranges (A in $S/cm \cdot K^{1/2}$ and E_a in kJ/mol), Where $T_0 = T_g - 25$ K

material	T_0 (K)	RT–60 °C		60–150 °C		RT–150 °C	
		A	E_a	A	E_a	A	E_a
IM550	210.7	7.8	8.9	4.3	8.2	5.3	8.5
IM550_Gel2	199.0	1.0	6.3	1.5	7.0	1.3	6.6
IM550_Gel1	188.0	0.6	6.0	1.4	6.8	1.1	6.5

the temperature range. These values offer insight into the ionic conductivity trends shown in Figure 1. It is observed that A , E_a , and T_0 values for IM550_Gel1 are all lower than the corresponding values for IM550_Gel2. The trend could be explained by the fact that the former consists of a higher concentration of polyether oligomers (50 vs 20 wt %) that contributes to a lower charge carrier concentration (A). Also, the more plasticized electrolyte (IM550_Gel1) would be expected to exhibit faster segmental motion associated with a lower activation energy that would translate to faster/lower activation energy for Li^+ motion. Finally, the lower T_g value for IM550_Gel1 than the other two electrolytes furthermore contributes to its higher ionic conductivity.

Thermal Analysis. The DSC results shown in Figure 3 provide further insight regarding the increase in ionic conductivity upon the addition of plasticizer PEGME550.

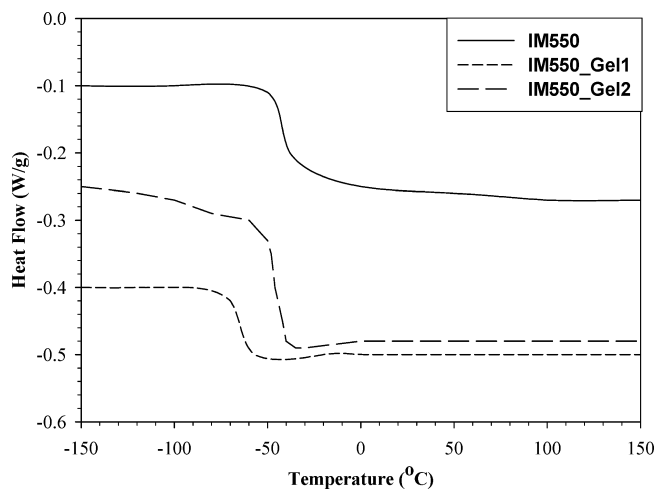


Figure 3. DSC curves of the pure ionic melt compared to those that are plasticized with unmodified polyether oligomers displaying the glass transition temperatures.

The glass transition temperature (T_g) for IM550 is -37.3 °C as compared to those of -49.0 and -60.0 °C for IM550_Gel2 and IM550_Gel1, respectively. For polymer electrolytes, T_g is generally correlated with the transport of the ionic species through the segmental motion of the EO chains in the polyether oligomer. A decrease in the T_g value due to the increase in the polymer chain mobility due to addition of a plasticizer can be expected to result in increased ionic conductivity as long as the plasticizer does not interfere with Li^+ solvation. Interestingly, none of the DSC thermograms reveals any sharp endotherms or exotherms, as would be expected from melting/freezing of crystalline phases. This finding explains why the ionic conductivity profiles do not show any steep drop at a particular temperature which is commonly observed for PEG-based polymer electrolytes due to partial crystallization of the polymer at around 60 °C.

Rheological Studies. Rheological studies seek to achieve understanding of the flow and deformation of materials. Particularly, for lithium battery applications, it is informative to investigate electrolyte materials with respect to shear stress and flow, since these material properties are not only connected to ionic conductivity but are also critical during battery fabrication and packaging. Moreover, rheological studies provide insight into the mechanical properties of the material with respect to viscosity and elasticity.

Figure 4 represents the plots of shear stress, τ in Pa, versus shear rate, dy/dt in s^{-1} , for all three electrolytes at 25 °C. The plots are linear, which indicates that the slope is constant (which means that steady-state viscosity, μ in Pa·s, is constant), and therefore, all three electrolytes behave as simple Newtonian fluids over the range of shear rates investigated.³³ From the slopes of these plots, we obtain room-temperature viscosity values of 5.8 Pa·s (5800 cP, $R^2 = 1.000$) for IM550, 0.60 Pa·s (600 cP, $R^2 = 1.000$) upon the addition of 20 wt % PEGME550, and 0.29 Pa·s (290 cP, $R^2 = 1.000$) when 50 wt % PEGME550 is added.

The Arrhenius plots for fluidities (reciprocal of dynamic viscosities) of all three electrolytes, Figure 5, reveal positively curved profiles that are similar to those for Arrhenius plots of conductivity. These data may also be interpreted using the Vogel–Tamman–Fulcher (VTF) equation applied this time to fluidity data

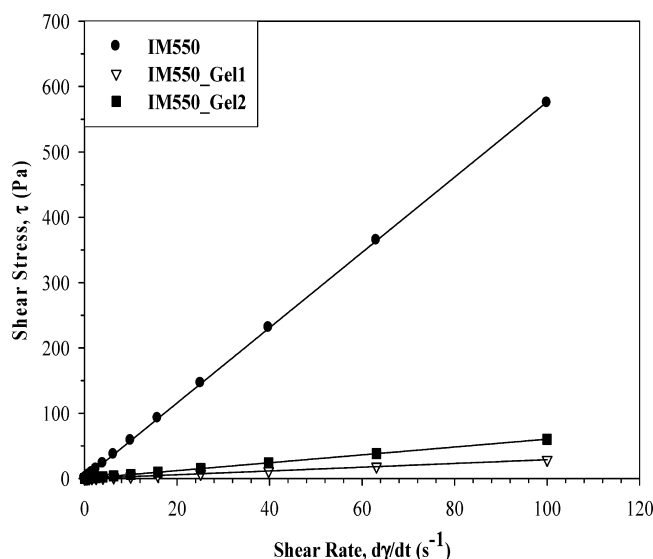


Figure 4. Plot showing Newtonian behavior for both pure ionic melt (IM550) and the electrolytes plasticized with unmodified polyether oligomers (IM550_Gel1 and IM550_Gel2) at 25 °C.

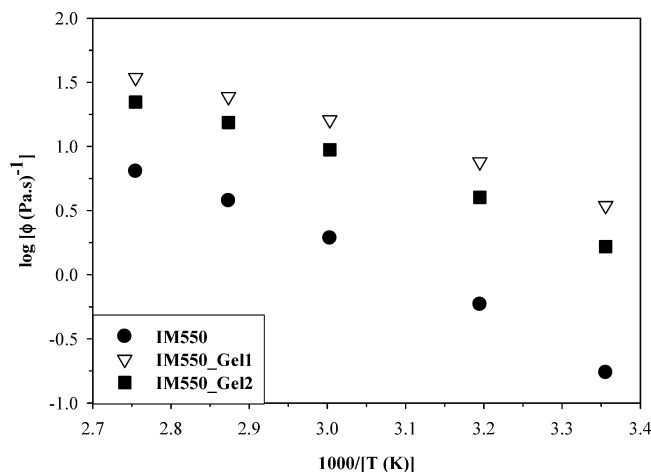


Figure 5. Arrhenius plots for the fluidity of the pure ionic melt (IM550) compared to those that are plasticized with unmodified polyether oligomers (IM550_Gel1 and IM550_Gel2) in the temperature range RT–90 °C.

$$\Phi = A' \cdot T^{-1/2} \exp \left[\frac{-E'_a}{R \cdot (T - T'_0)} \right] \quad (2)$$

where A' is a preexponential constant and E'_a is the effective activation energy for viscous flow, and T'_0 has the same meaning as for ionic conduction, the ideal glass transition temperature (at which the flow is completely frozen). Due to the relaxation nature of the two transport properties, ionic conductivity and viscous flow, the ideal glass transition temperature (T'_0) used for interpreting fluidity data was taken to be equal to that used for interpreting ionic conductivity data, which is 25 K lower than the experimental DSC glass transition temperature (T_g). The data fitting was done over a temperature range of 25–90 °C for all three electrolytes. The graph for the VTF model, applied for a temperature range between 25 and 90 °C where the ionic conductivities of the three materials start to display significant changes, is displayed in Figure 6 as a plot of $\ln(\Phi \cdot T^{1/2})$ vs $1000/(T - T_0)$ and it is linear for all three electrolytes,

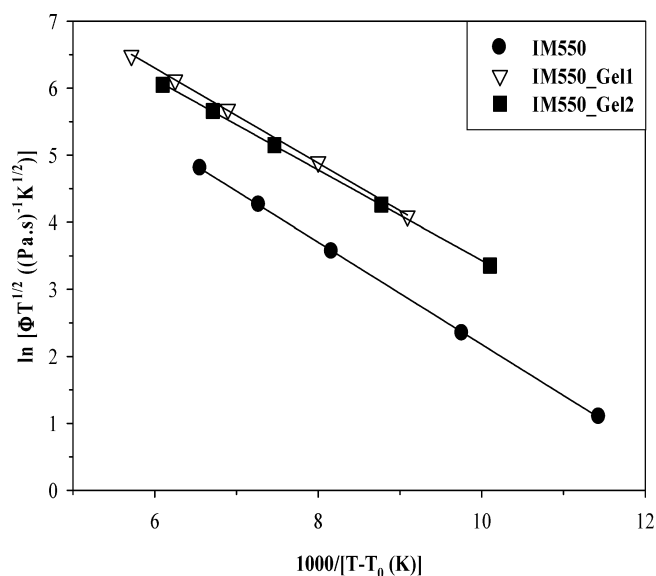


Figure 6. VTF plots for the fluidities of the pure ionic melt (IM550) compared to those that are plasticized with unmodified polyether oligomers (IM550_Gel1 and IM550_Gel2) in the temperature range 25–90 °C.

validating the use of this semiempirical correlation for interpreting fluidity data for these electrolytes.

Then, to refine even more the interpretation of the experimental data, the values for all the parameters of the VTF equation, for both ionic conductivity data (A , E_a , and T_0 from eq 1) and fluidity data (A' , E'_a , and T'_0 from eq 2) were obtained for the ambient temperature to 90 °C range using a nonlinear least-squares method (Levenberg–Marquardt algorithm aka the damped least-squares method), and these values are summarized in Table 4. From these data, we see, as expected, a monotonic decrease in A , E_a , and T_0 values with the increased addition of unmodified polyether oligomer while the calculated equilibrium glass transition temperatures (T_0) compare well with those determined from the glass transition temperature ($T_{0,DSC}$). The same trend can be observed for A' and E'_a as we move from IM550 to IM550_Gel 2 (with 20 wt % PEGME550) to IM550_Gel1 (with 50 wt % PEGME550), and the calculated equilibrium temperatures from rheology (T'_0) are all closer to each other. This tendency could be explained by the fact that the diluted electrolytes consist of a higher concentration of polyether oligomers that contributes to a lower charge carrier concentration (A), while, at the same time, they exhibit a more intense segmental motion providing lower activation energy both for lithium ion transport (E_a) and for momentum transfer (E'_a).

The Walden Plot. The relationship between ionic conductivity (κ) and dynamic viscosity (μ) may be further examined using the Walden plot formalism, which was initially developed for the study of aqueous solutions of strong electrolytes.³⁴ The plot links the conductivity per mole of charge (molar conductivity, $\Lambda = \kappa \cdot V_E$ in S·cm²/mol, where V_E is the molar volume containing one Faraday of positive charge) and the fluidity (which is the reciprocal dynamic viscosity, $1/\mu$ in Poise^{−1}) according to the following equation:

$$\Lambda \cdot \eta = \text{const.} = C \quad (3)$$

or

Table 4. Values for the Parameters of the VTF Equation Obtained from Ionic Conductivity and Fluidity Data Fitting for the RT to 90 °C Temperature Range

material	$T_{0,DSC}$ (K)	$\ln A$ (S/cm·K ^{1/2})	$\ln A'$ [(Pa·s) ⁻¹ ·K ^{1/2}]	E_a (kJ/mol)	E_a' (kJ/mol)	T_0 (K)	T_0' (K)
IM550	210.7	2.0 ± 0.3	10.1 ± 1.1	9.1 ± 0.5	7.0 ± 0.2	208.1 ± 3.2	205.4 ± 1.7
IM550_Gel2	199.0	1.2 ± 0.1	9.9 ± 1.1	7.8 ± 0.1	5.0 ± 0.3	191.3 ± 0.9	206.0 ± 3.0
IM550_Gel1	188.0	0.6 ± 0.1	9.9 ± 1.1	6.6 ± 0.2	4.5 ± 0.2	188.6 ± 2.4	204.9 ± 2.1

$$\ln(\Lambda) = \ln C + \ln(\eta^{-1}) \quad (4)$$

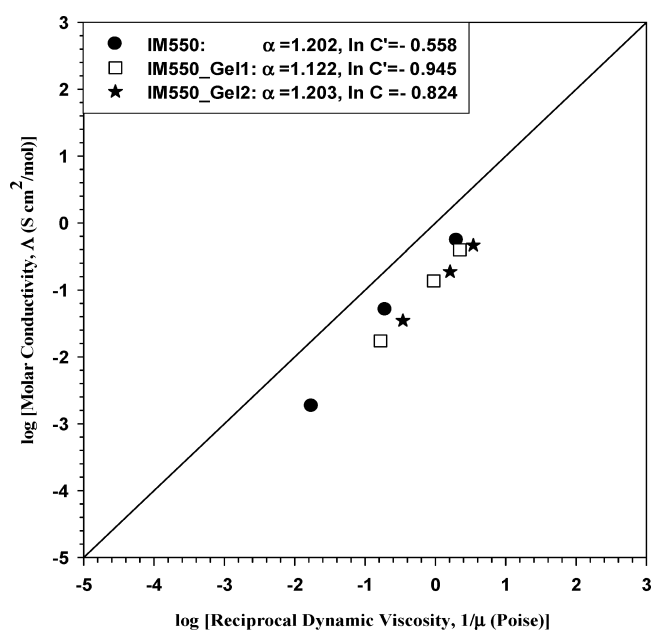
Different electrolytes of course do not necessarily need to fall on the same line, as their C value depends on their Stokes radii for cation and anion, respectively. By introducing an additional exponent “ α ” to the viscosity in eq 3, one can obtain a fractional Walden rule³⁵ that allows the slope to vary in the corresponding Walden plot, and by linear data fitting, the exponent is gathered together with the graph’s intercept, $\ln C'$:

$$\Lambda \cdot \eta^\alpha = \text{const.} = C' \quad (5)$$

or

$$\ln(\Lambda) = \ln C' + \alpha \ln(\eta^{-1}) \quad (6)$$

Conductivity and viscosity data acquired at different temperatures may be correlated in the Walden plot in the same manner as for electrolyte solutions, as can be seen in Figure 7,

**Figure 7.** Walden plot for the three electrolytes at 25, 60, and 90 °C (in this order from left to right).

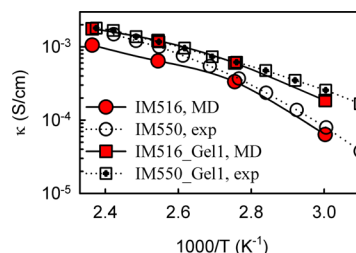
for each of the three IMs at three different temperatures (25, 60, and 90 °C). The Walden plot has been used increasingly in the past several years to illustrate the conductivity–viscosity relationship of pure ionic liquids (ILs) and IL–solvent mixtures in order to draw conclusions on the extent of “ionicity” (i.e., the effective fraction of ions available for participation in ionic conduction) by comparing results to the so-called ideal electrolyte solution, typically a 0.01 M aqueous KCl solution.^{36–42} On this log–log plot, an “ideal” line is constructed by using data for dilute aqueous KCl solutions as the standard of an almost ideal electrolyte behavior and placing a line with slope 1 through this data, as suggested by the

Walden equation. The diagonal represents the “ideal” Walden line corresponding to dilute aqueous KCl solutions which are known to be fully dissociated and to have ions of similar mobility.³⁹

First, we should note that, for ILs, the most favorable systems will have their ambient temperature values located in the top right-hand corner of the diagram. These will be ionic melts in which low viscosities are combined with high ionic conductivities.³⁹ Also, under the diagonal will be located the poor ionic liquids, while over the diagonal will be placed the superionic liquids.

In our case, the exponent “ α ” has a singular value between 1.12 and 1.20 for all three IMs which according to Angell et al.^{39,40} is to be expected for ionic liquids for which the activation energies opposing Li^+ motion (E_a) are not smaller than those for viscous flow (E_a'), as is the case for our materials as evidenced by the data in Table 4. The corresponding Walden lines for all three IMs are just below the ideal Walden line and thus represent a behavior near what Angell et al. describe as “good ionic liquids”. The C' value decreases from 0.57 to 0.44 to 0.39 with increasing polymeric plasticizer content in the ionic melt from 0 to 20 to 50 wt %, respectively, which most probably translates into a change in the average Stokes radii of cation and/or anion. Such a variation could be caused only by a change in the transport mechanism of Li^+ due to the addition of the plasticizer which can be observed from the decrease in the concentration of participating charge carriers (A values in Table 3) and apparent activation energy (E_a values in Table 3) especially in the low temperature range (RT–60 °C) and which cannot be accounted for only by the dilution of IM550 by the polymeric plasticizer PEGME550.

Molecular Dynamics Simulations. MD simulations have been performed to provide a better understanding of changes in the Li^+ transport with addition of plasticizer. Ion self-diffusion coefficients and electrolyte conductivity were calculated using a previously described methodology.⁴³ Figure 8 compares

**Figure 8.** Comparison of ionic conductivity data from experiments and MD simulations over the 60–150 °C temperature range.

conductivity from MD simulations with experimental data. It demonstrates for the most part that simulations accurately predict ion transport in ionic liquids and Gel 1 electrolyte. Adequate conductivity predictions together with our previous extensive validations on polymeric and liquid electrolytes^{5,43–49} give us confidence that simulations effectively reflect structural

and dynamic properties of ionic liquids and gels and could be utilized to glean additional insight into the Li^+ coordination and transport mechanism.

In the first step, we analyzed the degree of Li^+ cation dissociation from the TFSI[−] part of anions attached to oligoethers, as shown in Table 2. We observed a rather high degree of the Li^+ separated from TFSI[−] by oligoether groups for both ionic liquid IM516 and gel IM516_Gel1 indicating that the addition of oligoether plasticizer only slightly increases Li^+ dissociation from the TFSI[−] part of anions. This behavior is expected, as both the plasticizer and the anions are composed of the same solvating host, namely, oligoether. The simulation results reveal a general trend toward a diminished degree of ion separation with increasing temperature. The polyether chains have sufficiently high molecular weight that an entropic conformational penalty prevents them from being effectively wrapped around a Li^+ cation. A less effective Li^+ –oligoether coordination at high temperature results in formation of ion pairs and aggregates at high temperature. This behavior was very pronounced for polymer electrolytes and is less pronounced for $(\text{EO})_{12}$ –TFSI[−]/ Li^+ ionic liquids, as was discussed previously.⁵

Table 2 shows that on average a Li^+ is coordinated by the same number of etheric oxygens from anion and from the plasticizer for IM516_Gel1. Further analysis indicates that there is an almost equal probability for a Li^+ to be coordinated by one oligoether chain (either from plasticizer or from anion) or by two chains that contribute at least two ether oxygen atoms each to the Li^+ coordination shell. This coordination is similar to the behavior observed in oligoethers doped with binary lithium salts.^{43,50,51} Finally, we estimated that approximately 30% of the plasticizer and anions are not contributing atoms to the Li^+ first coordination shell.

Analysis of ion self-diffusion coefficients shown in Figure 9 indicates that addition of plasticizer increases self-diffusion

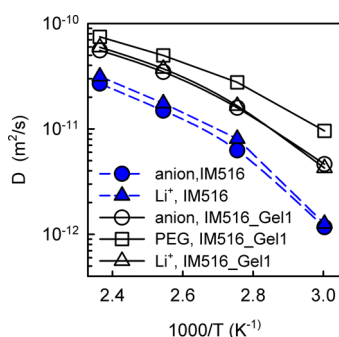


Figure 9. Ion self-diffusion coefficients from MD simulations.

coefficients of both anions and cations with the plasticizer being the fastest diffusing species in the electrolyte. Faster diffusion of the plasticizer compared to anion is attributed both to its lower molecular weight (530 Da) compared to anion (790 Da) and to the absence of relatively strong Coulomb interactions that are present between the TFSI[−] part of the IM516 anion and the Li^+ cation. Because the fastest moving species in the IM516_Gel1 is the uncharged plasticizer, we expect that a further increase of the plasticizer will decrease IM516 viscosity to a larger extent than it increases its molar conductivity. This behavior is consistent with the decrease of ionicity with addition of the plasticizer extracted from the experimental Walden plots above.

In the next step, we explored the Li^+ transport mechanism. In our previous studies,^{5,52} we found that about 90% of the lithium transport in a binary PEG ($M_w = 530$ Da)/LiTFSI electrolyte comes from the Li^+ motion together with an oligoether (vehicular motion) and only 10% comes from the exchange of oligoether solvating hosts (structural diffusion by interchain hopping). In contrast to this, in the IM516 ionic melt, Li^+ transport occurred by approximately equal contributions due to the Li^+ motion with EO_{12} TFSI[−] anion (vehicular motion) and the Li^+ exchange of solvating hosts (structural diffusion). Only the interchain hopping contributes to the charge transport in IMs, because the vehicular motion results in transport of a net-neutral species and does not contribute to conductivity. In IM516_Gel1 electrolyte, we found that the most mobile lithium cations are coordinated by the plasticizer only and move together with it, while the slower lithium cations are coordinated by the oligoetheric parts of two polymeric anions. This picture correlates well with our previous findings⁴³ for PEG/LiTFSI binary electrolyte, indicating that the lithium cations coordinated by two segments exhibit the slowest mobility. We estimate that the Li^+ coordinated only by the oligoetheric plasticizer (~30% of all lithium) makes the dominating contribution for Li^+ transport in the IM516_Gel1 electrolyte. Consequently, we observe that plasticization of IM516 with oligoether changes the primary Li^+ transport mechanism from the interchain hopping in IM516 to the vehicular motion of a Li^+ solvated by the plasticizer in the IM516-Gel1. We suggest that the change in the Li^+ transport mechanism is largely responsible for lowering the activation energy of the ionic conductivity vs temperature profiles for gels as compared to the ionic melt alone (IM550), as shown in Figures 8 and 9.

Galvanostatic DC Polarization/Current Interruption.

Salt concentration polarization can occur in a lithium electrolyte between two electrodes when high currents are passed through the electrolyte accompanied by lithium reduction/oxidation (or insertion/deinsertion) at the electrodes. Electrolyte anions move in response to the applied electric field, and because they are not discharged at the electrodes, they tend to accumulate at one electrode and become depleted at the other. Salt concentration polarization is undesirable in a battery electrolyte because it can limit the current that can flow for charging or discharging the battery. Lithium-electrolyte salt concentration polarization may be detected via a current interrupt experiment in which a relatively large current is passed for a relatively long time between electrodes that are nonblocking for lithium (often two lithium metal electrodes).⁵³ Upon current interruption, the cell potential is then monitored as a function of time. If salt concentration polarization has *not* occurred, the cell potential will immediately drop to zero and remain there. If however the salt concentration is higher at one electrode than at the other, the cell potential will drop to a nonzero value following current interruption and will slowly trend toward zero as salt diffusion occurs and the concentration polarization relaxes.

We have used the current interrupt technique to study salt concentration polarization in PEG-plasticized IL/IM electrolytes. Figure 10 presents results from galvanostatic DC polarization/current interrupt experiments on the ionic melt electrolyte without plasticization (IM550, top), with 20% PEGDME plasticizer added (IM550_Gel2, middle), and with 50 wt % PEGDME plasticizer added (IM550_Gel1, bottom). The areas inside the dark circles contain the critical data. For

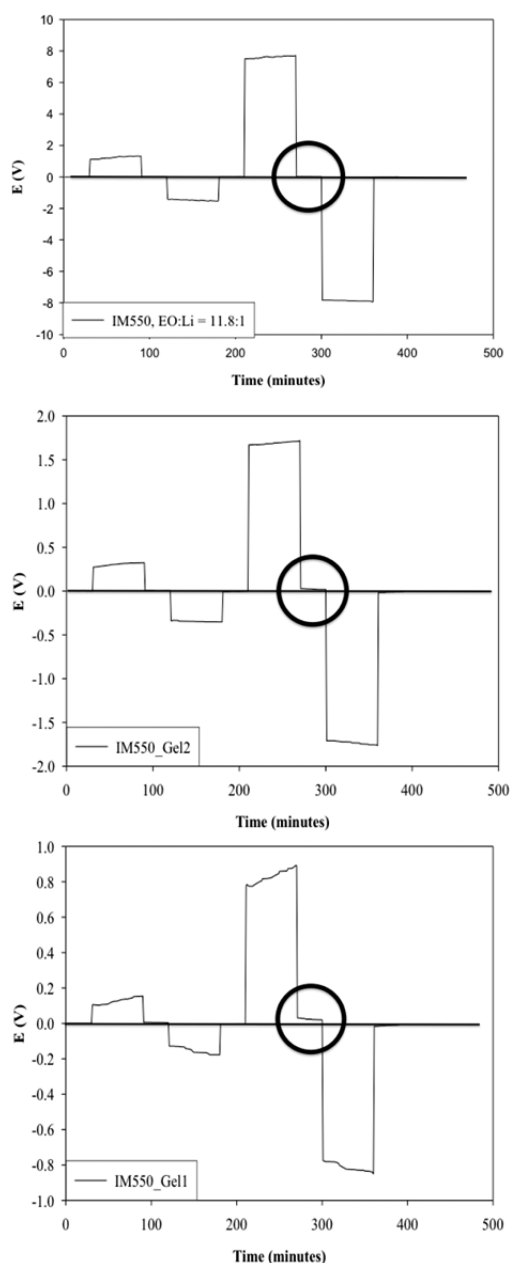


Figure 10. Potential–time plots from DC-galvanostatic polarization/current interrupt experiments performed in symmetric Li/electrolyte/Li cells. The currents for the first and second steps are 10 and 50 μA for a duration of 1 h each. Top, IM550; middle, IM550_Gel2; bottom, IM550_Gel1.

the IM 550 electrolyte, the cell potential following interruption of current drops promptly back to a value very near zero, indicating that salt concentration polarization has not occurred, as expected since this electrolyte contains only ions and salt concentration is constant.

In contrast, for the two plasticized electrolytes, following current interruption, the cell potential drops promptly to 27 mV for IM550_Gel2 and 37 mV for IM550_Gel1, followed by a further slow decrease toward zero. This behavior provides strong evidence that adding large amounts of plasticizer to these ionic-melt electrolytes changes their character from ionic liquids in which all the components are ions into more conventional salt-in-solvent electrolytes in which salt concen-

tration polarization can occur, and can limit battery performance.

CONCLUSIONS

The transport and rheological properties of the novel plasticized ionic melts were studied. Upon the addition of oligomeric polyether plasticizers, the ionic conductivities showed a dramatic improvement, especially near ambient temperature where it increased more than an order of magnitude when 50 wt % unmodified polyether was used. Improved segmental and chain dynamics, due to a decrease in viscosity, and the change in the transport mechanism are largely responsible for the improvement of ionic conductivity in gels compared to IMs, as demonstrated by MD simulations and DSC and rheological measurements, showing both lower glass transition temperature and lower viscosity values for gels when compared to IMs. We also found by MD simulations that the fraction of the $\text{Li}^+/\text{TFSI}^-$ contact pairs did change with addition of plasticizer to the IM, while addition of the ideally dissociated electrolyte in the Walden plot. This deviation from the ideal line in the Walden plot is consistent with the larger drop of the solution viscosity compared to the improvement of conductivity observed with the addition of plasticizer, which is associated with the change of the Li^+ transport mechanism from the exchange of anions in pure IMs to the largely vehicular motion of a Li^+ solvated by the plasticizer and not with the decrease of the $\text{Li}^+/\text{TFSI}^-$ contacts. In fact, MD simulations predicted that the fraction of the separated $\text{Li}^+/\text{TFSI}^-$ did not significantly change upon addition of plasticizer.

DC-galvanostatic polarization experiments showed that the improvement in ionic conductivities for gels was compromised by voltage losses due to salt concentration polarization in cells following large passage of current.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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