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Enhanced Li$^+$ Conduction within Single-Ion Conducting Polymer Gel Electrolytes via Reduced Cation–Polymer Interaction

Hunter O. Ford, Bumjun Park, Jizhou Jiang, Morgan E. Seidler, and Jennifer L. Schaefer*

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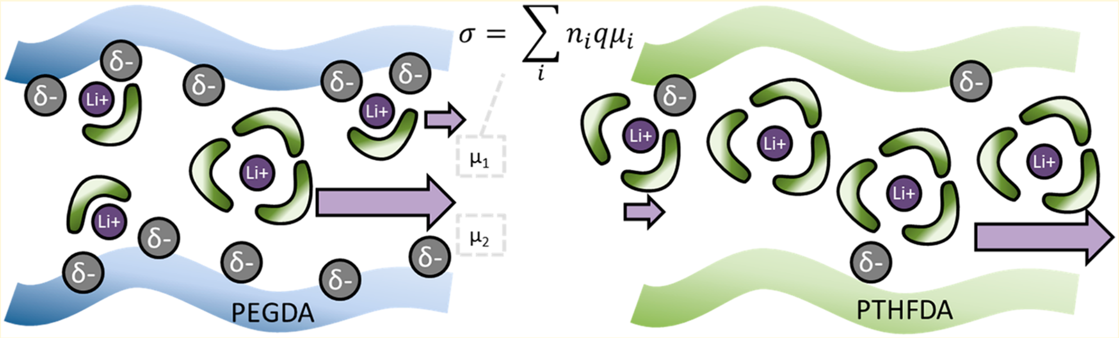

ABSTRACT: **The development of advanced electrolytes compatible with lithium metal and lithium-ion batteries is crucial for meeting ever growing energy storage demands. One such class of materials, single-ion conducting polymer electrolytes (SIPEs), prevents the formation of ion concentration gradients and buildup of anions at the electrode surface, improving performance. One of the ongoing challenges for SIPEs is the development of materials that are conductive enough to compete with liquid electrolytes. Presented herein is a class of gel SIPEs based on crosslinked poly(tetrahydrofuran) diacrylate that present enhanced room temperature conductivities of 3.5 × 10^{-5} S/cm when gelled with lithium metal relevant 1,3-dioxolane/dimethoxyethane, 2.5 × 10^{-4} S/cm with carbonate solutions, and approaching 10^{-3} S/cm with dimethyl sulfoxide. Remarkably, these materials also demonstrate high ionic conductivity at low temperatures, 1.8 × 10^{-5} S/cm at −20 °C in certain solvents. Most importantly, however, when contrasted with identical SIPEs formulated with poly(ethylene glycol) diacrylate, the mechanisms responsible for the enhanced conductivity are elucidated: decreasing Li$^+$−polymer interactions and gel solvent−polymer interactions leads to an increase in Li$^+$ mobility. These findings are generalizable to various SIPE chemistries and can therefore be seen as an additional set of design parameters for developing future high conductivity SIPEs.**

To avoid the most catastrophic effects of fossil fuel driven climate change, a widespread shift towards renewable energy sources must be adopted. Of particular interest from the perspective of electrified transportation are so-called "beyond lithium-ion" batteries. Such systems have potential to enable improved battery energy density, life-span, and safety. A major focus of developing beyond lithium-ion batteries is the formulation of an electrolyte that can support these desired characteristics. A common challenge facing liquid and polymer electrolytes that contain dissolved salts is low cation transference numbers, t_+. In systems where the cation and anion are both freely dissolved in the electrolyte, typically far less than half of the observed conductivity for the electrolyte comes from the motion of the active cationic species.[1,2] As t_+ approaches unity (i.e., all observed ion conduction is attributed to the active cation), ion concentration gradients in the bulk and anion accumulation at the electrode interface are greatly reduced. Tangible systems benefits of these effects include reduced side reactions, faster rate cycling, reduced tendency to form Li dendrites, and extended cell life span.[2−5] In an effort to enhance t_+, a specific class of polymer electrolytes known as single-ion conducting polymer electrolytes (SIPEs) has received great attention. SIPEs contain covalently anchored anions throughout the

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polymer. With anchored anions, theoretically all the long-range ion transport observed within such electrolytes can be attributed to the active cationic species, meaning t_+ approaches unity. One of the ongoing challenges however has been designing SIPEs that exhibit active ion conductivities on par with conventional liquid electrolytes at room temperature.

State of the art dry SIPEs exhibit ionic conductivities on the order of 10^{-6} S/cm with near unity t_+.[6−8] Introduction of solvent into the polymer markedly increases ionic conductivity.[4] Solvent molecules can plasticize the polymer, enhancing polymer chain segmental motion, increase ion pair dissociation, and offer another transport mechanism for cationic species by facilitating vehicular transport of the solvated cation. Although incorporating solvent into SIPEs increases flammability, relative to conventional liquid electrolytes, the overall safety may still be improved.[9] A number of highly conductive gel SIPEs have recently been demonstrated. Nguyen and colleagues describe a multi-block copolymer with a highly delocalized tethered anion and partially fluorinated arylene backbone that when swelled in ethylene carbonate (EC) displays ionic conductivity on the order of 10^{-3} S/cm above 30 °C.[9] Similarly, Oh and colleagues demonstrated a poly(arylene ether) backbone SIPE with the same order of magnitude conductivity when swelled with carbonate solutions.[10] Quite recently, Borzutzki and colleagues developed an SIPE with the ionic monomer incorporated within the fluorinated arylene backbone.[11] This material exhibited an ionic conductivity of 5×10^{-4} S/cm when swelled in a mixture of propylene carbonate (PC) and EC.

Using popular poly(ethylene glycol) (PEG)-based mono- and di-functional acrylate monomers along with a delocalizing methacrylate ionic monomer, Porcarelli and coworkers demonstrated a crosslinked network with an impressive 10^{-4} S/cm ionic conductivity when swelled with PC.[12] A similar acrylated PEG network with the ionic monomer 4-styrenesulfonyl (trifluoromethylsulfonyl)imide (STFSI) was demonstrated by Luo and colleagues, displaying an ionic conductivity of 1.8×10^{-4} S/cm at 30 °C when swelled with EC.[13]

While the progress in SIPE development has been substantial, due to the widely varied polymer chemistries, solvent systems, and testing conditions across the SIPE literature, direct comparison of SIPEs in an effort to gain fundamental material insights is limited. With the goal of gaining explicit fundamental understanding that can be used to guide future materials development, we herein present a simple crosslinked SIPE system that allows us to facilely investigate the effect of polymer chain chemistry on ion transport in gel SIPEs. We identify a polymer chemistry that improves lithium ion conduction, and more importantly, we describe the underlying mechanism responsible for the improvement.

Recently, poly(tetrahydrofuran) (PTHF)-based polymer electrolytes have received renewed attention for their loose cation coordination leading to enhanced ionic conductivity.[14−17] To our knowledge, we herein present the first SIPE based on PTHF chemistry, and by comparing with a PEG SIPE analog demonstrate the importance of loose Li^+ coordination in systems that do not contain free salt. We demonstrate that by tuning the polymer chemistry, cation−polymer coordination is reduced and solvent−polymer interactions are altered, enhancing Li^+ mobility. The former observation is corroborated by recent reports in the literature, while the latter is the first description of the importance of solvent−network interactions for PTHF systems. With this promising polymer chemistry, by screening molecular weight, charge density, and swelling solvent, we demonstrate high ionic conductivity room temperature (25 °C) SIPEs. The best performing materials display lithium conductivities of 3.5×10^{-5} S/cm when swelled with lithium metal relevant ethereal solvents such as 1,3-dioxolane/dimethoxyethane (DOL/DME), 2.5×10^{-4} S/cm with carbonate solutions, and approaching 10^{-3} S/cm with dimethyl sulfoxide (DMSO). Low temperature ionic conductivity is observed to be as high as 1.8×10^{-5} S/cm at −20 °C with select solvents. Furthermore, at room temperature, the self-supported gel SIPEs support limiting currents up to 1.0 mA/cm^2 and enable cycling of the $LiFePO_4$ cathode. The underlying principles leading to the enhanced Li^+ conduction in the PTHF-based SIPEs are generalizable to a broad selection of polymer electrolytes and therefore can be seen as important design characteristics for the engineering of next generation materials.

Polymer Synthesis and Composition. The SIPE system investigated here is composed of diacrylated crosslinking macromonomers of varying chemistry and molecular weight copolymerized with STFSI (styrene-$SO_2NSO_2CF_3^-$) ionic monomers, the structures of which are shown in Figure S1. The difunctional crosslinkers result in a freestanding permanently crosslinked SIPE containing anchored ionic units and no free-salt. Two distinct polymer chemistries are explored, poly(ethylene glycol) diacrylate (PEGDA) and poly(tetrahydrofuran) diacrylate (PTHFDA). PEGDA contains an oxygen and two CH_2 groups per repeat unit $(-(OCH_2CH_2)_n-)$, whereas PTHFDA has an oxygen and four CH_2 groups per repeat unit $(-(OCH_2CH_2CH_2CH_2)_n-)$. By matching the crosslinker molecular weights and charge density, two SIPEs identical in every feature (acrylate content, ionic monomer content, degree of crosslinking, etc.) aside from oxygen density can be directly compared, thus elucidating the impact of polymer chain repeat unit chemistry on ion conduction. Full synthesis protocols for the PTHFDA and STFSI monomers as well as the crosslinked polymers and additional characterization are described in the Supporting Information and in the literature.[18]

As a starting point, we define our control SIPE as a polymer containing the widely available PEGDA of molecular weight 700 g/mol, with LiSTFSI ionic units at an ether oxygen:charge ratio (EO:Ch) of 20. This system is denoted PEG$_{700}$DA20. For comparison, an SIPE containing PTHFDA of nominal molecular weight 700 g/mol and the same charge density (mole of charge per gram of dry polymer) as PEG$_{700}$DA20 was synthesized and denoted PTHF$_{700}$DA20. Note, the EO:Ch for PTHFDA and PEGDA at matching charge densities is necessarily different due to the different network oxygen contents. All composition denotations, charge densities, and associated EO:Ch are shown in Table S1. Considering eq 1,

$$\sigma = nq\mu \tag{1}$$

where σ is conductivity, n is the number density of ions, q is the charge on an ion, and μ is the ion mobility, matching the charge density and crosslinker molecular weight between SIPEs ensures that, to the best of our abilities, any differences in conductivity between the networks arise from the chain chemistry.

Conductivity Comparison of SIPEs. The ionic conductivities of PEG$_{700}$DA20 and PTHF$_{700}$DA20 in the as-synthesized dry state and in the gel states when swollen with a

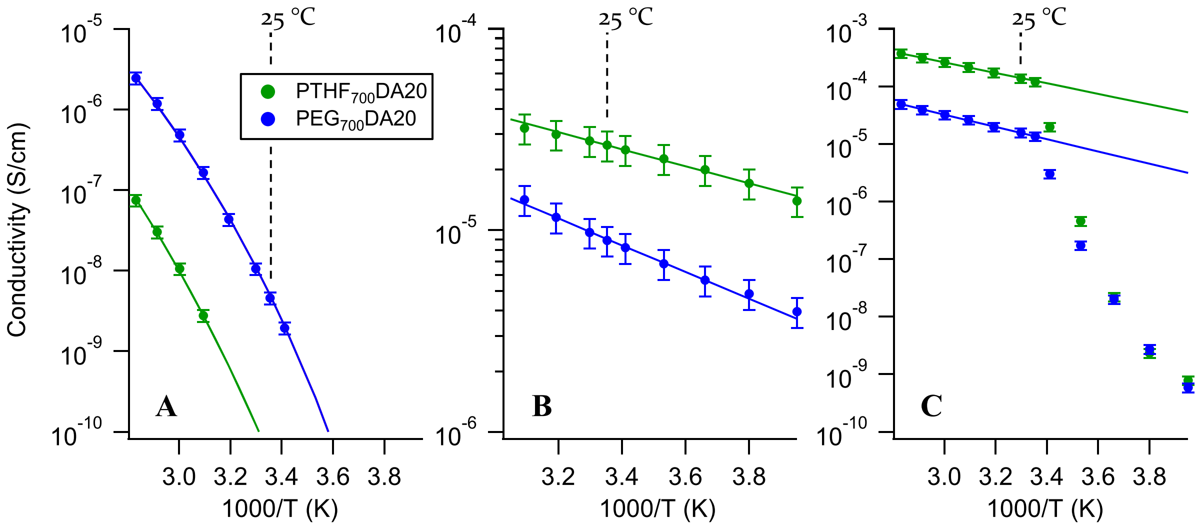

Figure 1. Ionic conductivity of PTHF$_{700}$DA20 and PEG$_{700}$DA20 SIPEs in (A) dry state from −20 °C to 80 °C, (B) DOL/DME swollen state from −20 °C to 50 °C, and (C) EC/DEC swollen state from −20 °C to 80 °C. Note the approximate melting temperature of the EC/DEC mixture is around 20 °C. Markers are experimentally measured values and lines are (A) VFT or (B,C) Arrhenius fits, with extrapolation.

salt-free 1:1 mixture of DOL/DME or 1:1 ethylene carbonate and diethyl carbonate (EC/DEC) are presented in Figure 1. The dry PEG$_{700}$DA20 network is notably more conductive than the PTHF$_{700}$DA20 analog, 1.7×10^{-7} S/cm compared with 2.8×10^{-9} S/cm at 50 °C, as evident from Figure 1A. This is despite PTHF$_{700}$DA20 having a lower T_g (−58.2 °C) than PEG$_{700}$DA20 (−35.0 °C, Figure S3). Generally, for polymer electrolytes, lower T_g correlates to higher conductivity at a given temperature, indicating another phenomenon besides just polymer segmental dynamics is at play.[19] It is well known from the polymer electrolyte work with poly(ethylene oxide) that the mechanism of ion conduction in these dry systems is dependent on ether oxygen−cation interaction.[20] The cation is coordinated by ether oxygens on the polymer chains, and exchanges between coordination sites occur at a rate dependent on the polymer segmental dynamics. The higher density of oxygens in the PEG$_{700}$DA20 SIPE compared to the PTHF$_{700}$DA20 SIPE in the dry state accounts for the former's higher conductivity; the exchange rate of Li^+ between the available coordination sites in PEG is more facile than PTHF, and the dissociation of Li^+ from the anion may be increased due to the increase in density and interconnectivity of solvation sites.[21−23] In Figure 1B and C, the ionic conductivity relationship is reversed, where now the gel PTHF$_{700}$DA20 is the more conductive SIPE. In DOL/DME at 25 °C, the PEG$_{700}$DA20 displays $\sigma = 8.9 \times 10^{-6}$ S/cm and PTHF$_{700}$DA20 displays $\sigma = 2.7 \times 10^{-5}$, a 200 % difference in conductivity. In EC/DEC at 25 °C, the PEG$_{700}$DA20 exhibits $\sigma = 1.4 \times 10^{-5}$ S/cm and PTHF$_{700}$DA20 exhibits $\sigma = 1.2 \times 10^{-4}$, a 760 % difference in conductivity. For completeness, Figure S11 in the SI displays conductivity comparison for SIPEs containing equivalent EO:Ch ratios; the results are qualitatively analogous to those shown here for equivalent charge density.

The data in Figure 1A are fit with the Vincent−Fulcher−Tamman equation, indicating that ion transport in the dry SIPEs is coupled to polymer dynamics. In both gelled states (Figure 1B,C), the temperature versus ionic conductivity relationship can be described as pure Arrhenius behavior, indicating ion transport largely decoupled from polymer dynamics. For each fit, the (pseudo)activation energies are extracted and compared. The ion transport activation energy for PTHF$_{700}$DA20 is higher than that of PEG$_{700}$DA20 in the dry case, whereas the opposite is true of both gelled cases. These results suggest that ion conduction is more facile in the PEG polymer when the primary conduction mechanism is dictated by polymer dynamics and more facile in the PTHF polymer when the transport mechanism is decoupled from polymer dynamics. All fitting parameters and further discussion can be found in the SI, Table S2.

Enhanced Ion Transport: Interactions between Cation, Polymer, and Solvent. The difference in conductivity between the gel SIPEs is a result of differing interactions between lithium cations, solvent molecules, and polymer chains. Within the gel SIPE, a lithium cation can have its coordination sites filled by either solvent molecules, bound anion functionality, or polymer chain segments. Different cation coordination states (coordinated purely by solvent, polymer, or a combination) give rise to different ion mobilities. Ions that are purely solvent coordinated have a greater mobility than those that are coordinated with oxygens on the polymer chain, as the chain dynamics are slower than the vehicular motion of the small molecule solvated cation.[24] A cartoon representation of this proposed phenomenon can be seen in the TOC image. Considering eq 2, the observed ionic conductivity is therefore the sum of the number density of ions existing in the different coordination states:

$$\sigma = \sum_i n_i q \mu_i \tag{2}$$

The distribution of ion coordination states within an SIPE is driven by the likelihood that a solvent molecule will exchange with a polymer chain segment within a lithium coordination site. The likelihood of exchange is a function of the interactions between cations, polymer chains, and solvent molecules. For the sake of discussion, we loosely define a so-called "interaction parameter" that consists of considerations such as dielectric constant/Gutmann donor number, sterics/geometry, and dynamics. For example, the interaction parameter between a lithium cation and a solvent molecule will be generally

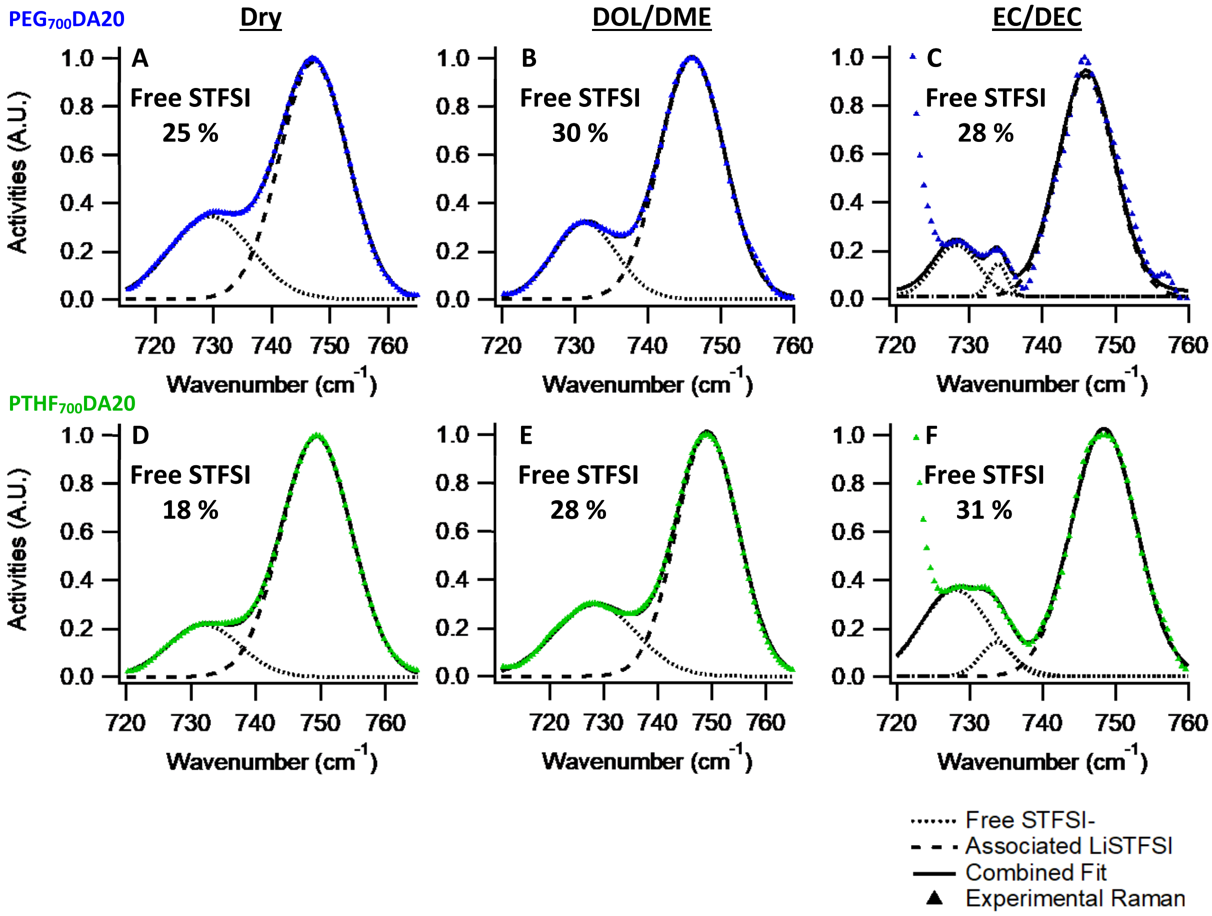

Figure 2. Experimental and fit Raman spectra of PEG$_{700}$DA20 and PTHF$_{700}$DA20 SIPEs in various swelling conditions.

enhanced as the dielectric constant/donor number of the solvent is increased. The same holds true for the lithium−polymer interaction parameter, with the additional caveat that by changing oxygen density and distribution throughout, the polymer geometric differences are also introduced, that is, Li$^+$ solvation sites are changed.[21−23] In a system with a strong cation−solvent interaction and a weak cation−polymer interaction, the likelihood of exchange from a solvent coordinated state to polymer coordinated state is low.

The third interaction, between solvent and polymer, is generally less considered but is in fact of importance. In the case of greatly different dielectric constants or molecular geometry between solvent and polymer, the solvent−polymer interaction parameter is decreased. Decreasing the solvent−polymer interaction parameter decreases the probability that a cation coordination exchange will take place, as the polymer segment and solvent molecule are less likely to come into close enough proximity for the exchange to occur. An extreme example of this phenomenon is the formation of water channels in Nafion; the fluorinated Nafion backbone and water are so dissimilar that there is little interaction between the two.[25] Decreasing the solvent−polymer interaction therefore results in a greater portion of solvent coordinated lithium cations in that solvent coordinated cations are prevented from interacting with the polymer chain.

The framework of interaction strength fully explains the observed conductivity data. When the solvent−polymer polarity difference is small, such as in the case of the DOL/DME swelled SIPEs ($\varepsilon_{\mathrm{PEG}} = 7.4$, $\varepsilon_{\mathrm{PTHF}} = 5.5$, $\varepsilon_{\mathrm{DOL/DME}} = 7.1$), the difference in ionic conductivity is primarily due to the difference in cation−polymer interactions. PTHF has a lower oxygen density and therefore fewer and less interconnected Li$^+$ coordination sites than PEG. We observe that the dielectric constant of the PTHF SIPE is lower than the PEG analog in all swelling conditions (Figure S5), suggesting that the PTHF polymer would interact less with Li$^+$. The less lithium interacts with the polymer, the more mobile it is and the greater the conductivity. When the solvent−polymer dielectric difference is large, such as in the case of EC/DEC, there is the additional effect of the decreased solvent−polymer interactions, which further ensures the lithium cation remains solvent coordinated. This is why the difference in ionic conductivity between the SIPEs is greater in EC/DEC than DOL/DME; hence, the importance of the solvent−polymer interaction cannot be overlooked.

We propose that tuning the cation−polymer and solvent−polymer interaction parameters, accomplished here by decreasing polymer oxygen density, is a useful method for improving Li$^+$ conductivity. Up to this point, however, only the impact of polymer chemistry on ion mobility has been considered. It is possible that the SIPEs contain a different number of dissociated ionic groups as a result of differing oxygen density. With the use of Raman spectroscopy, the degree of ion dissociation in each SIPE is probed, helping to determine if it is truly a difference in ion mobility or simply a difference in charge carrier density that gives rise to the enhanced PTHF$_{700}$DA20 ionic conductivity.

Raman Spectroscopy of SIPEs. The use of Raman spectroscopy is particularly useful for comparing ion dissociation within these SIPEs owing to the strong unique stretch associated with the STFSI anion expansion/contraction.[26] We have demonstrated previously with DFT calculations validated with Raman experiments that the stretch associated with the STFSI anion is observed at a different wavenumbers when the anion is associated or dissociated.[27] The dissociated anion stretch is observed around 730 cm^{-1}, and the associated anion stretch is around 748 cm^{-1}. Similar analyses have been performed for liquid and ionic liquid mixtures containing conventional TFSI anions.[26,28−34] By this method, we can compare the STFSI dissociation between PEG$_{700}$DA and PTHF$_{700}$DA SIPEs, gauging the concentration of charge carriers present in each system by comparing the peak areas of the different anion stretches. Figure 2A−F display experimental and fit Raman spectra for each SIPE in the dry, DOL/DME swollen, and EC/DEC swollen states.

The Raman spectra are fit such that peak area comparison provides a quantitative estimate to the percent of dissociated STFSI anions and therefore percent of Li^{+} not associated with STFSI. In the case of the dry SIPEs, PEG$_{700}$DA20 has a greater degree of STFSI dissociation than PTHF$_{700}$DA20. This is consistent with the conductivity data, and with the notion that in the absence of solvent, network ether oxygens are responsible for dissociating the ionic groups. In the case of the DOL/DME swelled SIPEs, the proportion of dissociated ionic groups is similar between SIPEs, indicating that in DOL/DME the difference in ionic conductivity does not come from a difference in ion dissociation and therefore must come from a difference in average ion mobility.

In EC/DEC, the analysis is less straightforward. Firstly, there appear to be three distinct peaks that make up the anion stretch. We attribute the two around 728 cm^{-1} and 735 cm^{-1} to the dissociated anion stretch. Some literature suggests that the lower the wavenumber, the closer the anion is to being fully dissociated.[35] We tentatively assign the stretch at 728 cm^{-1} to a fully dissociated anion, and the stretch at 735 cm^{-1} to an anion that is in the secondary solvation shell of a Li^{+} cation, whereby the anion is dissociated but still influenced by the Li^{+} in its local environment. A further complication is the presence of a large peak at 717 cm^{-1} that is due to a ring breathing mode of EC, making accurate fitting of the peaks difficult.[29] Because of the error in the Raman fitting that comes from the solvent peak interference, the quantitative results should not be over analyzed. Qualitatively, the EC/DEC gelled PEG$_{700}$DA20 and PTHF$_{700}$DA20 spectra are similar; both contain the two different dissociated anion stretches, and the areas corresponding to the total dissociated ions are similar. Accordingly, we believe the difference in conductivity observed in the case of the EC/DEC swollen SIPEs cannot be explained solely by a difference in dissociation degree and must therefore be primarily a function of ion mobility. We conclude that by decreasing the oxygen density within the SIPE network, more of the Li^{+} cations are solvent coordinated as opposed to network coordinated, which improves the SIPE ionic conductivity via increased ion mobility.

PTHFDA: Varying Molecular Weight, Charge Density, and Swelling Solvents. With the enhanced conductivity mechanism demonstrated, the molecular weight of the PTHF crosslinker, the charge density of the network, and the swelling solvent were then systematically varied to ascertain the limits of conductivity with PTHF-based SIPEs. As can be seen in Figure S7, it was found that ionic conductivity was not altered when molecular weight of the crosslinker was changed, so long as the materials were mechanically similar, further indicating that ion transport in the PTHF-based SIPEs is greatly decoupled from polymer segmental dynamics.[36] To assess the impact of charge density on conductivity, a series of PTHF$_{700}$DA SIPEs with varying charge density (mole of charge per gram of dry polymer) was synthesized. The ionic conductivity of each varying charge density PTHF SIPEs at 25 °C in DOL/DME and EC/DEC is presented in Figures S9 and S10. For EC/DEC, the maximum observed was for PTHF$_{700}$DA8, the highest charge density material studied, with $\sigma = 2.5 \times 10^{-4}$ S/cm. For DOL/DME, the maximum was observed for PTHF$_{700}$DA12, the second highest charge density material studied, with $\sigma = 3.5 \times 10^{-5}$ S/cm. Refer to Table S1 for exact composition of these samples. PTHF$_{700}$DA12 was chosen as the SIPE for the remaining investigations as it has the highest conductivity in lower dielectric/donor number ether-based solvents and the second highest conductivity in the higher dielectric/donor number carbonate solution.

Besides DOL/DME and EC/DEC, there are many solvents relevant for SIPEs. Higher order glymes such as diglyme and tetraglyme offer increased thermal stability and chelating effects, PC is another common carbonate solution, mixtures of DME and sulfolane have been investigated for use in lithium−sulfur systems, and DMSO is a high dielectric/high donor number organic solvent.[37] Ionic conductivity of PTHF$_{700}$DA12 swelled in each of these solvents is presented in Figure 3. Largely, the results follow expectation. DMSO, known for its solvation strength, yields the highest conductivity due to increased ion dissociation.[24,38] PC is nearly identical to EC/

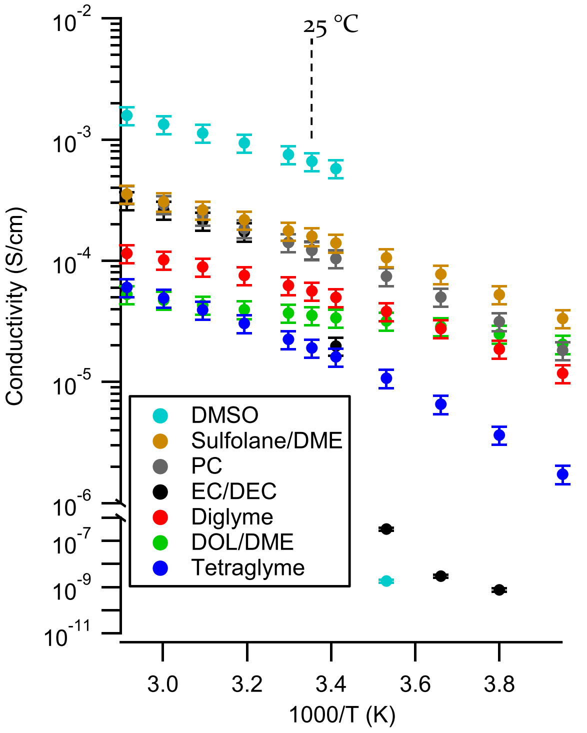

Figure 3. Ionic conductivity of PTHF$_{700}$DA12 swelled to equilibrium in a variety of organic solvents. All mixtures are 1:1 by volume.

DEC, with the exception that the PC swollen SIPE maintains an impressive conductivity of 1.8×10^{-5} S/cm even at −20 °C. The ethers likewise follow chemical intuition. As the order of the glyme increases, there is an increase in the chelation strength of the solvent molecule, which can enhance ion dissociation, increasing conductivity. This effect however is offset by an increase in viscosity with glyme order, which decreases ion mobility. Diglyme outperforms DOL/DME, likely due to the chelation effect yet fairly low viscosity of diglyme. Tetraglyme, while having the highest chelation strength, presents a lower conductivity, likely due to the solvent viscosity. The conductivity of the sulfolane/DME mixture is high, even at low temperatures. We have demonstrated previously that as little as 10% by volume of a high dielectric solvent/donor number dissolved in a low dielectric solvent yields conductivity on par with that of the pure high dielectric solvent, which could explain these results.[24] Overall, the high conductivity in a variety of solvents demonstrates the versatility of the PTHF-based SIPEs.

Coin Cell Measurements. Limiting current measurements were performed on Li symmetric cells containing the freestanding $\mathrm{PTHF_{700}DA12}$ gel electrolytes swelled in DOL/DME or EC/DEC. This was accomplished by application of a galvanostatic current that was sequentially increased after a period of 1 h until cell failure. Despite the chemical incompatibility of EC/DEC with lithium metal, the limiting current supported by the EC/DEC gel was nevertheless examined due to its relevance for Li-ion systems. The results are presented in Figure 4. Self-supported $\mathrm{PTHF_{700}DA12}$-based SIPE films enable rates of at least 0.5 mA/cm^2 in DOL/DME and at least 1.0 mA/cm^2 in EC/DEC at room temperature. At each current density, the potential of the EC/DEC SIPE is lower than that of the DOL/DME, which should be expected from the conductivity results.

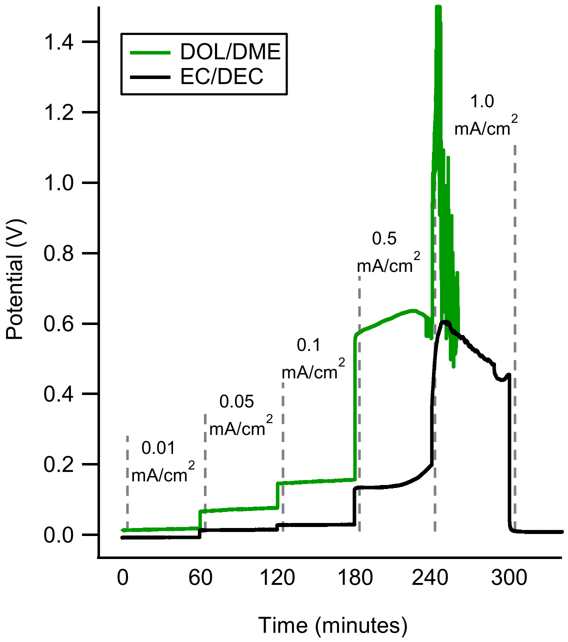

Figure 4. Results of limiting current tests for Li|gel PTHF-based SIPE|Li cells.

With the use of impedance spectroscopy shown in Figure S13, it was observed that the resistance associated with the bulk polymer electrolyte (165 μm thick) was about 80 Ω and 570 Ω for the EC/DEC and DOL/DME SIPEs, respectively. With the same material but at a thickness of a commercial separator (25 μm), this would translate to a bulk resistance of roughly 12 Ω and 86 Ω, respectively, a significant reduction that would enable even higher rate capabilities. $t_{\mathrm{LI+}}$ was measured for $\mathrm{PTHF_{700}DA12}$ polymers gelled with DOL/DME and EC/DEC with the use of impedance spectroscopy on Li symmetric cells. For the DOL/DME gelled case, $t_{\mathrm{LI+}} = 0.84$ and for the EC/DEC gelled case, $t_{\mathrm{LI+}} = 0.66$. The deviations from non-unity may be a result of non-valid assumptions inherent in applying the Bruce-Vincent method to these gel SIPE systems including the continual reactivity of the solvent with Li metal. Additional details are in the SI.

Li symmetric cell cyclings of DOL/DME and EC/DEC swelled $\mathrm{PTHF_{700}DA12}$ (Figure S15) show that the gel SIPEs are capable of reversible Li electrodeposition/dissolution for extended periods despite solvent decomposition on the lithium anode. Finally, an EC/DEC gelled $\mathrm{PTHF_{700}DA12}$ SIPE was tested in a full cell configuration, with a lithium metal anode and $\mathrm{LiFePO_4}$-based cathode with no free-salt, as a proof of concept (Figures S16 and S17). After a few activation cycles, the cell exhibited a capacity of 121 mAh/g $\mathrm{LiFePO_4}$ with near 100% efficiency, demonstrating that this SIPE is capable of facilitating reversible energy storage in a Li/$\mathrm{LiFePO_4}$ cell.

■ CONCLUSIONS

The impact of polymer chemistry on ion transport within gel SIPEs was characterized. It was found that decreasing the oxygen content within the polymer reduces $\mathrm{Li^+}$−polymer coordination and modulates how solvent−cation complexes interact with the SIPE, overall improving $\mathrm{Li^+}$ mobility. PTHF-based ionic networks, having lower oxygen content than their PEG-based analogs, were explored over a variety of crosslinker molecular weights, charge densities, and swelling solvents to better understand PTHF as an SIPE material and probe the limits of achievable conductivity. High room temperature lithium conductivities with lithium metal and lithium-ion relevant solvents were observed, and the best performing PTHF-based gel SIPEs demonstrated relevant limiting currents and compatibility with $\mathrm{LiFePO_4}$ cathodes. These results demonstrate the importance of considering the impact of polymer chain chemistry on ion transport in gels and highlight that slightly tuning relationships that influence transport can have a large impact on performance.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmaterialslett.9b00510.

> Experimental procedures, chemical structures, polymer compositions, FTIR, DSC, photographs of SIPEs, fitting parameters, solvent uptake, polymer permittivity, conductivity as function of swelling %, chain length, and charge density, temperature conductivity data, molar conductivity data, additional Raman spectroscopy on DMSO swelled polymers, impedance spectroscopy, scanning electron microscopy, lithium symmetric cycling, lithium-$\mathrm{LiFePO_4}$ cell performance, solvent properties, NMR spectroscopy (PDF)

AUTHOR INFORMATION

Corresponding Author

Jennifer L. Schaefer − *Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, Indiana 46556, United States;* orcid.org/0000-0003-4293-6328; Phone: (574)-631-5114; Email: Jennifer.L.Schaefer.43@nd.edu

Authors

Hunter O. Ford − *Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, Indiana 46556, United States*

Bumjun Park − *Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, Indiana 46556, United States;* orcid.org/0000-0002-3779-1315

Jizhou Jiang − *Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, Indiana 46556, United States*

Morgan E. Seidler − *Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, Indiana 46556, United States*

Complete contact information is available at:
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Notes

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