Influence of Water Sorption on Ionic Conductivity in Polyether Electrolytes at Low Hydration

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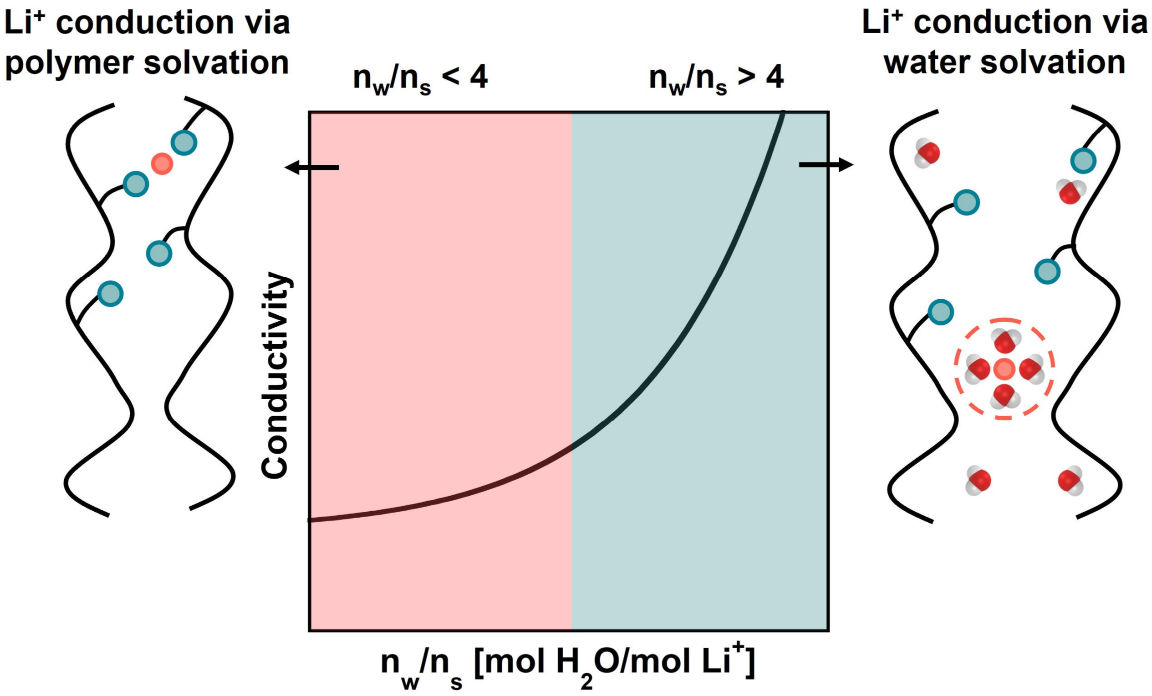

Abstract

Ion-containing polymers are subject to a wide range of hydration conditions across electrochemical and water treatment applications. Significant work on dry polymer electrolytes for batteries and highly swollen membranes for water purification has informed our understanding of ion transport under extreme conditions. However, knowledge of intermediate conditions (*i.e.*, low hydration) is essential to diverse applications (*e.g.*, electrolyzers, fuel cells, and lithium extraction). Ion transport under low levels of hydration is distinct from the extreme conditions typically investigated and the relevant physics cannot be extrapolated from existing knowledge, stifling materials design. In this study, we conducted ion transport measurements in LiTFSI doped polyethers that were systematically hydrated from dry conditions. A semi-automated apparatus that performs parallel measurements of water uptake and ionic conductivity in thin-film polymers under controlled humidity was developed. For the materials and swelling range considered in this study (*i.e.*, < 0.07 g water/g dry polymer electrolyte), ionic conductivity depends non-linearly on water uptake, with the initial sorbed water weakly affecting conductivity. With additional increases in swelling, more significant increases in conductivity were observed. Remarkably, changes in conductivity induced by water sorption were correlated with the number of water molecules per lithium ion, with the normalized molar conductivity of different samples effectively collapsing onto one another until this unit of hydration exceeded the solvation number of lithium-ions under aqueous conditions. These results provide important knowledge regarding the effects of trace water contamination on conductivity measurements in polymer electrolytes and demonstrate that the lithium-ion solvation number marks a key transition point regarding the influence of water on ion transport in ion-containing polymers.

Ion-containing polymers are critical components of electrochemical and water treatment technologies that address the water-energy nexus (*e.g.*, batteries, reverse osmosis, fuel cells, and electrolytic cells)[1-4]. Although these processes require different operating conditions, they each apply similar polymeric materials to regulate ion transport rates. As a result, several communities have studied ion transport in various polymer chemistries and structures[1, 5-9] and at distinct levels of hydration depending on the application of interest. For example, those interested in solid state electrolytes for batteries focus on dry polymers (*i.e.*, approaching 0 wt% water)[1], while those studying water purification membranes explore highly swollen polymers (*ca.* 20 – 60 wt% water)[2]. These disparate and extreme measurement conditions have been emphasized in the literature. Consequently, distinct mechanisms are invoked to describe ion transport that overlook conditions in between these limiting cases, leading to fundamental gaps in our understanding of ion-containing polymers and a lack of comprehensive design rules for such systems.

At the extreme conditions typically explored, hydration is known to profoundly influence penetrant transport in polymers[10], with ion transport rates in highly swollen polymers being significantly higher than those in dry polymers[1, 11-12]. The specific effects of water on the physics of ion transport presumably depend on the extent of hydration and how the water molecules interact with both the polymer and the ions within the polymer. **Figure 1** illustrates such effects across a range of hydration levels for rubbery, amorphous polymer electrolytes, which are commonly studied in dry and wet environments. When such materials are dry, the polymer acts as the solvating medium for the ions[13-14], such that ion transport is largely dictated by polymer segmental dynamics and salt dissociation[1, 4, 13, 15]. In this limit, ionic conductivity is frequently limited by ion solvation[1, 13] and is inversely related to the timescale for polymer segmental relaxation. Accordingly, the Vogel-Tammann-Fulcher equation is commonly used to model the temperature dependence of ionic conductivity in such materials[13, 16].

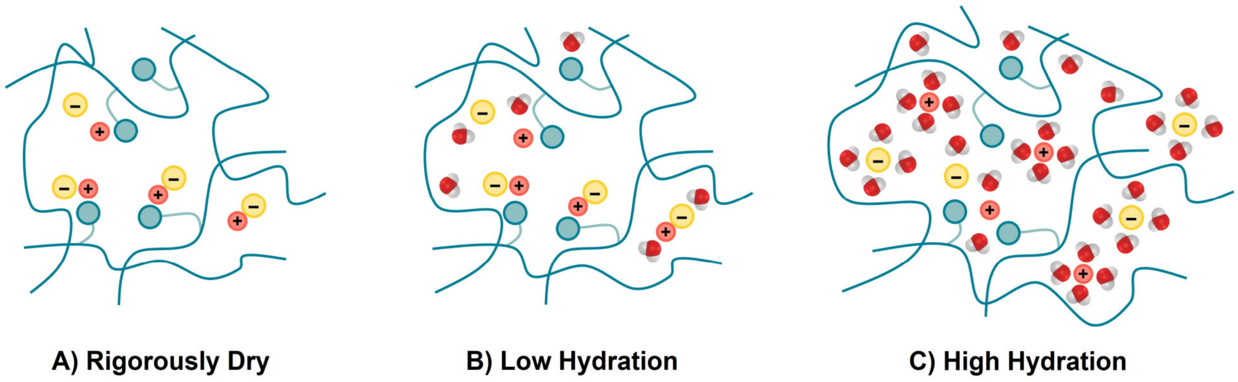

Figure 1. Visual representation of rubbery, amorphous polymer electrolytes across various levels of water content, including, (A) rigorously dry, (B) low hydration, and (C) high hydration. As water content increases, the polymer electrolyte swells and the ions transition from being solvated by the polymer to being solvated by water within the polymer.

Water that has sorbed into a polymer electrolyte presents additional solvation modes for the ions, leading to higher salt dissociation and reducing the coordination of ions to the polymer[14], while also plasticizing the polymer, leading to faster segmental dynamics[17]. These factors increase ionic conductivity in hydrated polymers relative to their dry state. At sufficiently high degrees of hydration, swelling is significant and water molecules cluster and percolate throughout the polymer[14]. For such highly swollen polymers, ion diffusion primarily occurs within water-rich domains of the polymer[10]. In this limit, the concentration of water in the polymer largely governs ion diffusivity and is the main parameter in conventional models used to interpret ion transport in such materials (*e.g.*, the Mackie-Meares[12] and Yasuda models[11]).

While numerous studies focus on understanding ion transport in dry and highly swollen polymers, our basic knowledge regarding the transition between these conditions (*i.e.*, low hydration) is relatively poor. For example, the extent to which water-induced plasticization and ion solvation independently influence ion transport rates in the low hydration regime is unknown. Furthermore, the effective size of an ion is thought to increase upon hydration due to the presence of a hydration shell around the ion[18], yet it is unclear how this impacts ion transport as a function of hydration. Studies directly probing the role of polymer chemistry and ion identity on these physics have not yet been conducted. Such knowledge is of interest in emerging ion selective processes (*e.g.*, lithium extraction), where hydration may have a critical impact on ion specificity[19-20], and in quantifying the performance of solid state electrolytes for batteries, where it is important to understand how trace amounts of water influence conductivity measurements. While the fuel cell community frequently reports polymer electrolyte properties as a function of humidity[5, 21-26], such studies primarily focus on highly heterogeneous and hygroscopic ionomers (*e.g.*, Nafion), and thus, are less generalizable and often do not generate well-resolved datasets in the low hydration regime.

To further explore these physics and provide methodologies for such studies, we report ion transport in lithium-doped polyether electrolytes that were systematically hydrated from dry conditions. An apparatus that simultaneously measures water uptake and ionic conductivity of thin-film polymers as a function of humidity was developed for this purpose. For the initial water partitioning into these materials (*e.g.*, < 1 wt% water), ionic conductivity was weakly dependent on water uptake, though with additional swelling, ionic conductivity increased more significantly. The degree to which conductivity increased with respect to water sorption was described well by the number of water molecules per lithium-ion in the low hydration limit. These results demonstrate that the lithium-ion hydration number characterizes an important transition point regarding the influence of water on ion transport in ion-containing polymers.

In this study, lithium bis(trifluoromethane) sulfonimide (LiTFSI), a commonly used salt in battery electrolytes[1], was blended with poly(allyl glycidyl ether) (PAGE) to prepare model solid polymer electrolytes (SPEs). Ion transport in PAGE has previously been investigated under dry conditions[27-28]. Information regarding its structure and SPE preparation is presented in the SI (**Section S1**). Although poly(ethylene oxide) (PEO) is the prototypical polymer electrolyte[1], it is highly crystalline at room temperature[27], and as a result, its dry conductivity is generally only reported at elevated temperatures (*i.e.*, in the molten state)[13, 29]. PAGE, conversely, is amorphous (*i.e.,* non-crystalline)[27, 30] and less hydrophilic than PEO due to its pendant allyl group[31], which are useful properties for accessing the low hydration regime at ambient conditions under which saturated membranes are generally studied. Furthermore, the allyl group is a reactive handle that can be used to prepare functionalized polyethers[28, 30, 32-33].

Hydration was modulated by equilibrating SPEs under controlled relative humidity (RH) at 25°C. A semi-automated system that produced an active flow of humid N_2 to a chamber containing samples was constructed for this purpose. A schematic of the apparatus is shown in **Figure 2**, with additional details provided in the SI (**Section S2**). The system, as configured in this study, controlled RH in the chamber to set points between 0 and 80 ± 2 % at 25 ± 1 °C. Water sorption and ionic conductivity of SPE samples were measured in parallel while sweeping across RH in this chamber. Thin films are particularly useful for such measurements because the time required for samples to equilibrate under constant RH is related to the timescale for water diffusion through the sample (*i.e.*, l^2/D_w for planar samples of thickness l and mutual water diffusion coefficient D_w)[34]. Thus, to ensure rapid equilibration, thin-film SPEs (*ca.* 100-200 nm) were prepared via spin-coating (SI **Section S3**).

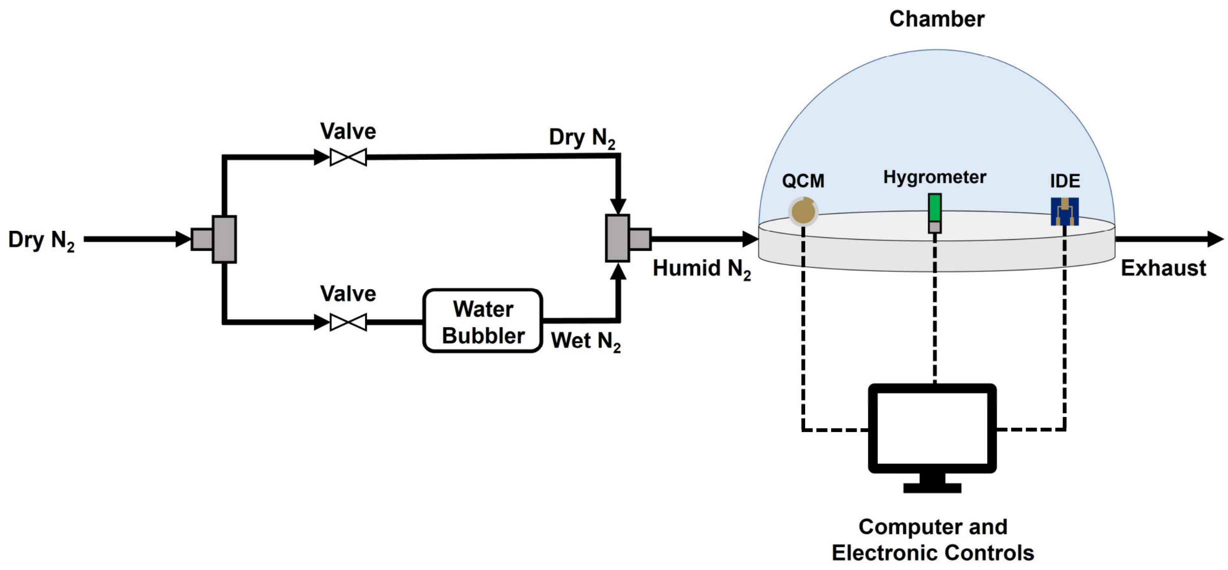

Figure 2. Schematic of the apparatus built to probe ion transport as a function of hydration in polymer electrolytes. Dry and wet N_2 were mixed to generate a stream of humid N_2 directed to a chamber containing samples. RH in the chamber was varied between 0 and 80% at 25 °C using a hygrometer and electronic proportional valves in a PID control scheme. Water sorption and ionic conductivity of thin-film SPEs were concurrently measured using a quartz crystal microbalance (QCM) and interdigitated electrodes (IDE), respectively.

Water content of thin-film SPEs was determined as a function of RH using a quartz crystal microbalance (QCM). By monitoring the change in frequency of a quartz crystal, QCM sensitively determines the associated change in mass of a thin film polymer coated on the crystal[35]. For the experiments conducted in this study, the QCM cell was placed in the humidity-controlled chamber and the Sauerbrey model was used to calculate the change in mass, Δm, based on the measured change in crystal frequency, Δf:

$$\Delta m = \frac{-C\Delta f}{n} \tag{1}$$

where C is the mass sensitivity constant of the crystal and n is the overtone number. By measuring the resonant frequencies of the bare crystal, the coated crystal under dry conditions, and the coated crystal under humid conditions, the mass of dry SPE on the crystal, $m_{dry\,SPE}$, and the mass of water sorbed within the SPE, $m_{sorbed\ water}$, were determined and used to calculate water uptake, w_u:

$$w_u = \frac{m_{sorbed\ water}}{m_{dry\ SPE}} \tag{2}$$

Additional discussion of QCM experiments is included in the SI (**Section S4**).

Ionic conductivity of thin-film SPEs was measured as a function of RH by performing electrochemical impedance spectroscopy (EIS) on custom interdigitated electrodes (IDE) in the humidity-controlled chamber, as this geometry enables sensitive characterization of thin-films[36]. Fabrication of the IDE substrates used in this study is described elsewhere[37] and details regarding EIS experiments are presented in the SI (**Section S5**). Sharon *et al.*[36] explored electrochemical characterization of similar IDEs coated with thin-films (*ca.* 50 nm) of LiTFSI-PEO. Given the similarities with the samples considered in this study, we applied the equivalent circuit analysis reported by Sharon *et al.*[36] to extract the resistance of thin-film SPEs from EIS experiments. For the polyether electrolytes considered in this study, the ionic conductivity of thin-film samples is in quantitative agreement with the ionic conductivity of bulk samples (SI **Section S5**), enabling us to utilize thin-films to study the role of hydration on ion transport, with findings that are relevant to the bulk material. Sharon *et al.* reported a similar observation for LiTFSI-PEO[36], though it is well-known that this is not the case for highly heterogenous materials, such as Nafion[38], where structure changes significantly between thin-film and bulk samples.

For IDE samples, ionic conductivity, σ, can be calculated from electrolyte resistance, R:[36]

$$\sigma = \frac{1}{R}\frac{d}{l(N-1)t} \tag{3}$$

where d is the distance between the teeth of the IDE, l is the length of the teeth, N is the number of teeth, and t is the film thickness. Film thicknesses at a reference condition (*i.e.,* ambient RH, as recorded by a hygrometer) were measured using ellipsometry (SI **Section S6**). This data was combined with swelling measurements from QCM to determine film thicknesses at various RH values, which are required to calculate conductivities from measured resistances. Thickness calculations were based on a polymer mass balance under the assumption that films only swelled in the out-of-plane direction, a common assumption for thin films. **Section S7** in the SI discusses how the EIS, QCM, and RH datasets were compiled and analyzed.

Figure 3 reports the average water uptake and ionic conductivity as a function of RH in PAGE with 10 wt% LiTFSI ($r = 0.045$ mol Li^+/mol monomer). Water uptake increases non-linearly as water activity (*i.e.*, RH) increases, with water partitioning being more pronounced at higher activities. This result is consistent with the Flory-Huggins description of small molecule-polymer phase equilibria[39-40]. Water sorption isotherms exhibiting similar behavior have been reported for non-porous polymers without fixed adsorption sites for penetrant uptake[41-42]. Materials with adsorption sites exhibit distinct sorption isotherms (*e.g.*, Langmuir and dual-mode isotherms) from the behavior observed in this work. Moreover, water uptake in 10 wt% LiTFSI-PAGE is < 0.04 g water/g dry polymer electrolyte for the entire RH range considered, demonstrating that PAGE, even when significantly salt-doped, is far less hydrophilic compared to PEO[31, 43]. Based on recent results from Marioni *et al.*[14], this level of water sorption is within the low hydration regime. These authors reported simulations that show that water forms a percolated network in Li^+ doped PEO when water volume fractions exceed 0.16 to 0.27 (*ca.* a w_u of 0.19 to 0.37 for polymers with densities similar to that of water), which was treated as the transition point to a highly swollen system[14]. The ionic conductivity of 10 wt% LiTFSI-PAGE exhibited a similar trend with respect to RH as the observed water sorption isotherm. Interestingly, ionic conductivities at low water activities (*i.e.,* < 20% RH) are similar to the value determined under rigorously dry conditions, suggesting that PAGE systems, unlike PEO[44-45], can be exposed to a narrow range of humidity before conductivity measurements are significantly affected.

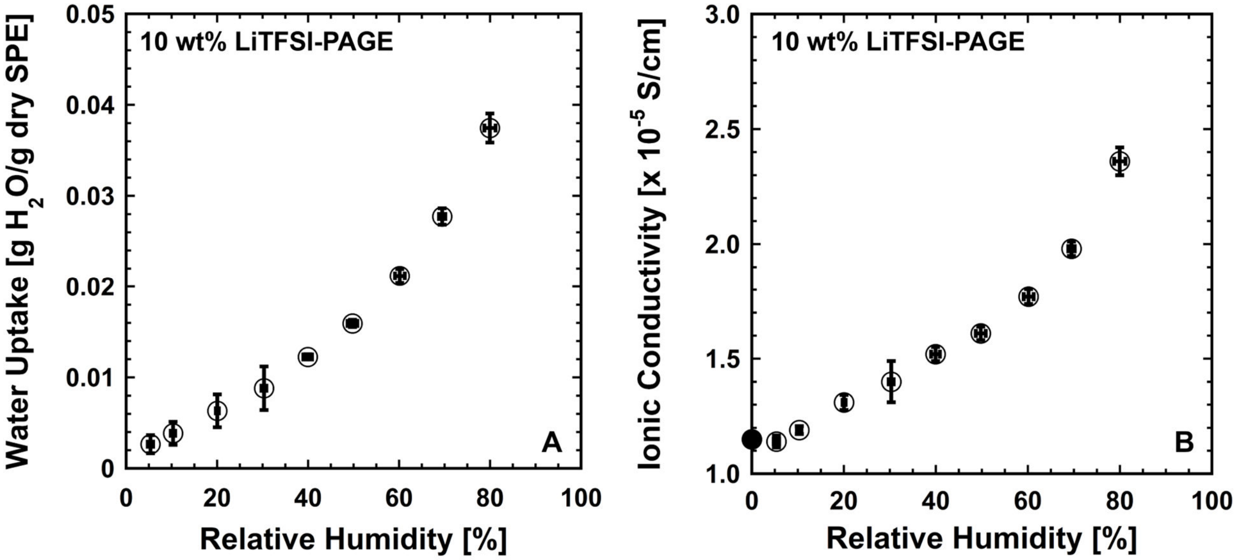

Figure 3. Water uptake (A) and ionic conductivity (B) in 10 wt% LiTFSI-PAGE as a function of RH at 25 ± 1°C. The open circles and error bars represent the averages and standard deviations calculated from measurements taken at ten distinct time windows during a specific RH set-point in a humidity sweep experiment. The filled circle represents the dry ionic conductivity of a bulk sample based on an independent measurement in the literature[27]. Water uptake increases with RH in a manner consistent with the Flory-Huggins model. Ionic conductivity exhibits a similar dependence on RH.

Ionic conductivity is directly reported as a function of water uptake for 10 wt% LiTFSI-PAGE (r = 0.045 mol Li^+/mol monomer) and 20 wt% LiTFSI-PAGE (r = 0.101 mol Li^+/mol monomer) in **Figure 4**. For both salt loadings, the initial water sorbed within LiTFSI-PAGE has a relatively small effect on ionic conductivity, though as water content increases further, conductivity increases more significantly. This non-linear (*e.g.*, roughly exponential) trend is more pronounced for 20 wt% LiTFSI-PAGE than 10 wt% LiTFSI-PAGE. Ionic conductivity in 20 wt% LiTFSI-PAGE appears to slightly decrease relative to dry conditions for $w_u < 0.02$, though the extent of this decrease is less than ~ 10%, which is relatively insignificant within the context of the polymer electrolyte literature. Over the range of water uptake considered, ionic conductivity roughly increased by a factor of two and three in 10 and 20 wt% LiTFSI-PAGE, respectively. Moreover, increases in salt loading increased SPE water content, with 20 wt% LiTFSI-PAGE exhibiting higher water uptake than 10 wt% LiTFSI-PAGE (*i.e.,* $w_u < 0.06$ vs. $w_u < 0.04$) across the entire water activity range considered (SI **Section S8**). This can be explained by LiTFSI being highly hygroscopic, while PAGE is relatively hydrophobic.

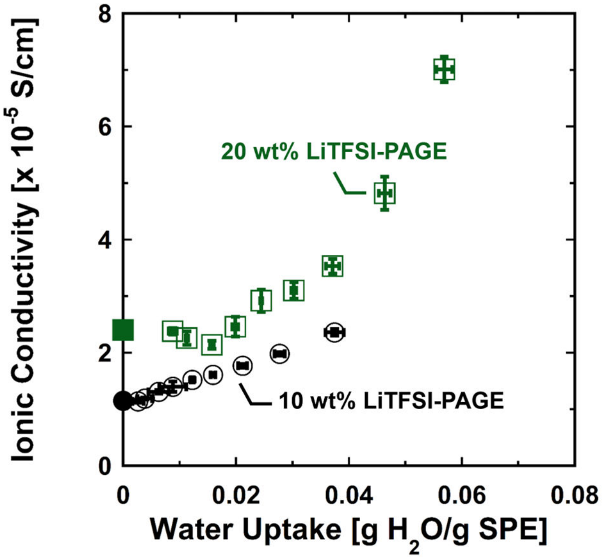

Figure 4. Ionic conductivity as a function of water uptake for 10 wt% LiTFSI-PAGE (black circles) and 20 wt% LiTFSI-PAGE (green squares). The filled symbols at $w_u = 0$ represent dry ionic conductivity data from independent measurements made on bulk samples in the literature[27] and the open symbols represent data determined from humidity sweep experiments using thin-film samples. For both salt loadings, ionic conductivity increases non-linearly with water sorption. Water uptake, ionic conductivity, and the extent to which ionic conductivity increases are all higher for 20 wt% LiTFSI-PAGE compared to 10 wt% LiTFSI-PAGE.

Johansson *et al.* have also reported ion transport measurements in SPEs that were sequentially hydrated at ambient conditions, though to much larger degrees of water content than studied here[46]. These authors dosed lithium triflate-PEO with varying amounts of D_2O and observed that ionic conductivities and ion diffusivities increased well over an order magnitude with increasing D_2O content. Further analysis of their data (SI **Section S9**) shows that most of the samples considered by Johannson *et al.* are beyond the transition point to a highly swollen system[14] and, accordingly, the relatively simple Mackie-Meares model[12] reasonably describes most of their reported Li^+ diffusion coefficients as a function of D_2O content.

The SPEs considered in this study, however, are well below the water percolation threshold. Consequently, the Mackie-Meares model fails to describe ion transport as a function of water uptake in the LiTFSI-PAGE samples of interest (SI **Section S10**), with this model underpredicting ionic conductivity by up to several orders of magnitude for the swelling range considered in this study. Furthermore, the Mackie-Meares model erroneously predicts that the initial water sorbing into such systems strongly increases ion diffusivities from values approaching zero when no water is present. These results demonstrate that many transport models developed for highly swollen polymers are non-physical in the low hydration regime, and that the role of water on ion transport in lowly-hydrated systems fundamentally differs from how water affects ion transport in the highly swollen regime.

The above results focus on an electrolyte system that is less hydrophilic than the more commonly studied PEO, where water contamination has been shown to greatly alter conductivities[45-48]. To probe the generality of our finding that below the percolation threshold, water content non-linearly affects ionic conductivities, we considered another model system: a

P(EO-*co*-AGE) copolymer composed of 24.3 mol% AGE and 75.7 mol% EO. Prior work has shown that this is the minimum amount of AGE required to disrupt PEO crystallinity[27]. For this composition of P(EO-*co*-AGE) doped with 17 wt% LiTFSI (r = 0.045 mol Li^+/mol monomer), water content was within the low hydration regime (*i.e.,* w_u < 0.07) and a similar trend in conductivity with respect to water uptake was observed (SI **Section S11**).

Based on the observed water sorption and ionic conductivity trends, we hypothesize that the extent to which sorbed water initially affects conductivity in the materials considered in this study is related to the solvation of lithium ions by water molecules. In the aqueous solution literature, it is well known that lithium ions are strongly solvated by water and are coordinated to roughly 4 – 6 water molecules in their first hydration shell[18, 49]. To test our hypothesis, we consider the normalized molar conductivity (*i.e.,* wet molar conductivity/dry molar conductivity) as a function of the moles of water per mol of Li^+ (*i.e.,* n_w/n_s) for all three polymer electrolytes discussed, as plotted in **Figure 5**. Molar conductivity, Λ, is calculated as ionic conductivity divided by salt concentration (SI **Section S12**). The experimental data obtained for each sample effectively collapse onto one another when n_w/n_s is < 4, which corresponds remarkably well with the expected hydration number of lithium ions[49]. When n_w/n_s is > 4, differences in the normalized molar conductivity of each sample are observed, suggesting that factors beyond lithium solvation become increasingly important at higher hydration levels. Thus, the lithium-ion hydration number delineates a significant transition point regarding the influence of water on ion transport in the low hydration regime.

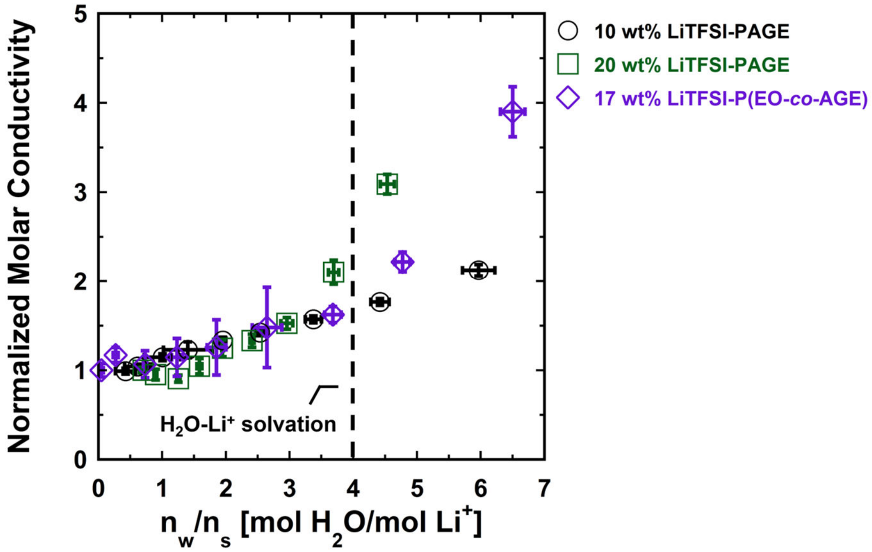

Figure 5. Normalized molar conductivity (*i.e.*, $\Lambda_{Wet}/\Lambda_{Dry}$) plotted against moles of water per mol of Li^+ (n_w/n_s) for 10 wt% LiTFSI-PAGE (black open circles), 20 wt% LiTFSI-PAGE (green open squares), and 17 wt% LiTFSI-P(EO-*co*-AGE) (purple open diamonds). Normalized molar conductivities are similar for each sample when n_w/n_s is < 4, demonstrating that the Li^+ hydration number characterizes how the initial water sorbing into these SPEs affects their conductivity.

Water is expected to play a very different role on the mobility of lithium ions compared to counter anions (*i.e.*, $TFSI^-$) at low hydration, as water can disrupt the strong ether-Li^+ coordination that serves to trap the cation and decrease ionic conductivity and transference number in dry electrolytes[29]. **Figure 6** compares the self-diffusion coefficient of each ion (D_i) in samples of LiTFSI-PAGE prepared dry and those equilibrated at 80% RH as measured using pulsed-field gradient (PFG) NMR spectroscopy. For brevity, details regarding experimental methods and sample preparation are presented in the SI (**Section S13**).

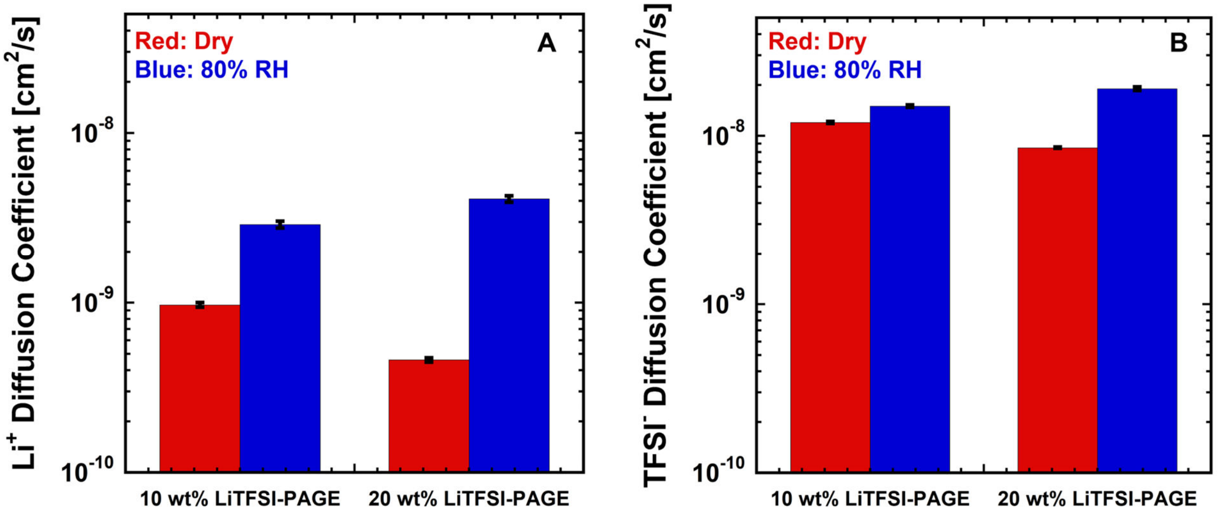

Figure 6. Values of D_{Li} (A) and D_{TFSI} (B) measured in bulk samples of 10 and 20 wt% LiTFSI-PAGE prepared dry and equilibrated under 80% RH. The error bars plotted represent standard errors based on fitting the PFG NMR data to the Stejskal-Tanner equation. Hydration-induced increases in D_{Li} are larger than increases in D_{TFSI}, consistent with the water molecules strongly solvating Li$^+$.

In dry LiTFSI-PAGE, D_{Li} is over an order of magnitude lower than D_{TFSI}, due to strong solvation of lithium ions with ether oxygen groups[27], while the large, organic TFSI ions do not coordinate strongly with groups on the polymer. Under 80% RH, D_{Li} increases by a factor of 3.0 and 8.9 relative to dry conditions in 10 and 20 wt% LiTFSI-PAGE (*i.e.*, $w_u \sim 0.04$ and $w_u \sim 0.06$), respectively. D_{TFSI} also increases with this level of hydration, though to a far lesser extent (*i.e.*, by factors of 1.2 and 2.2 for 10 and 20 wt% LiTFSI-PAGE, respectively). Consequently, the lithium-ion transference number and inverse haven ratio of these PAGE electrolytes increase with hydration (SI **Section S13**). Marioni *et al.* reported similar findings regarding ion diffusion coefficients in Li$^+$ doped PEO at low hydration[14]. These observations are consistent with the hypothesis that the initial water sorbing into LiTFSI-PAGE strongly and preferentially solvates lithium ions, reducing their coordination with ether oxygen groups. As a result, Li$^+$ mobility is far more sensitive to the presence of water than TFSI$^-$ mobility for the relatively low degrees of swelling considered in this study. Further study probing ion diffusion coefficients in PAGE electrolytes, and the distribution of water molecules specifically coordinated with the polymer and the ions, over a broad range of hydration would be of significant interest. Glass transition temperatures (T_g) of these samples were also measured using differential scanning calorimetry (DSC) and were essentially invariant with hydration for the water contents considered in this study (SI **Section S14**). Thus, unlike the dry electrolyte literature, changes in polymer segmental dynamics do not appear to rationalize the observed changes in ionic conductivity with respect to hydration.

In summary, the impact of water on ionic conductivity in polyether electrolytes hydrated from dry conditions was probed by performing parallel QCM and EIS experiments under controlled humidity. For the SPEs considered in this study, ionic conductivity was weakly dependent on water uptake initially, before further increases in water sorption lead to more significant increases in conductivity. Notably, the extent to which molar conductivity increases with hydration was generally found to correlate with the number of water molecules per lithium ion until this unit of hydration exceeds the expected solvation number of lithium-ions in aqueous media. These findings, coupled with PFG-NMR spectroscopy and DSC results, suggest that increases in ionic conductivity due to water sorption in polyethers at low hydration are primarily related to lithium-ion solvation effects.

Supporting Information

Section S1: Materials and preparation of solid polymer electrolytes, Section S2: Humidity controlled chamber and system automation, Section S3: Spincoating procedures, Section S4: QCM experiments, Section S5: EIS experiments, Section S6: Ellipsometer experiments, Section S7: Data analysis for sweep experiments, Section S8: Water sorption isotherms, Section S9-S10: Mackie-Meares analysis, Section S11: RH sweep data in LiTFSI-P(EO-*co*-AGE), Section S12: Calculation of normalized molar conductivity, Section S13-S14: Experimental details for PFG-NMR and DSC measurements in bulk samples.

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