Supporting Information

Deciphering Physical Versus Chemical Contributions to the Ionic Conductivity of Functionalized Poly(methacrylate)-based Ionogel Electrolytes

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FTIR Spectroscopy

Fourier transform infrared (FTIR) spectroscopy was used to determine the presence or absence of any unreacted monomer/cross-linker acrylate groups within the ionogel samples, following UV exposure and polymerization/cross-linking. Figure S1 shows representative FTIR spectra of the neat EMI TFSI ionic liquid, three different ionogel types (22 mol% MMA, 23 mol% DMAEMA, and 25 mol% TFEMA), and a 10:1 molar mixture of the scaffold precursors TFEMA and PETA-4 (with 2 wt% HOMPP). Three spectral positions that can be assigned to the unreacted acrylate groups are indicated by vertical dashed lines, highlighting peaks located at wavenumbers of: 810 cm^{-1}, 1410 cm^{-1}, and 1635 cm^{-1} for the 10:1 TFEMA/PETA-4 precursor mixture. These peak positions were consistent for the other two monomers used here (DMAEMA, MMA), as well; only the TFEMA/PETA-4 spectrum is shown for clarity. As evidenced by Fig. S1, no peaks due to unreacted acrylate groups were observed for TFEMA-, DMAEMA-, or MMA-based ionogels. This indicates complete reaction and incorporation of the monomer/cross-linker into the polymer scaffold.

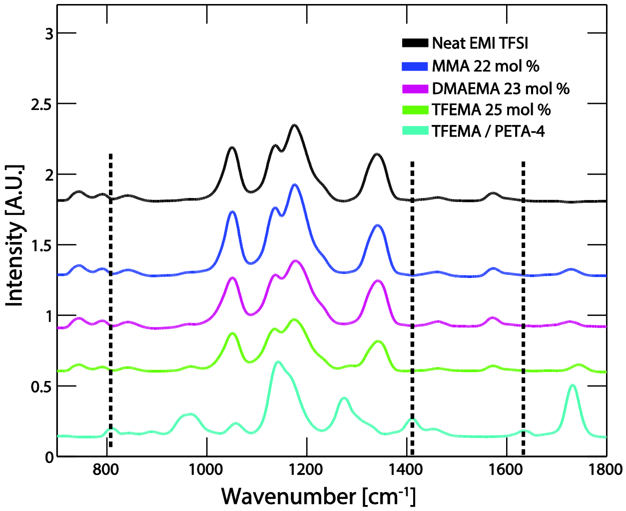

Figure S1. FTIR spectra of neat EMI TFSI, a TFEMA-based (25 mol%) ionogel, a DMAEMA-based (23 mol%) ionogel, a MMA (22 mol%) ionogel, and 10:1 molar mixture of TFEMA/PETA-4 scaffold precursors.

Elastic Modulus Determination

The RSA3 (TA Instruments) dynamic mechanical analyzer was utilized in compression mode to measure applied stress vs. resulting strain for the cylindrical ionogel samples. Figure S2 shows representative stress-strain data recorded for TFEMA-based ionogels with different polymer contents (25-39 mol%). Elastic modulus values were calculated as the slopes of best-fit lines to the data across the 5-10% strain region. The observed increase in the slope, or elastic modulus, indicates a higher cross-link density as polymer content is increased within the ionogel scaffold.

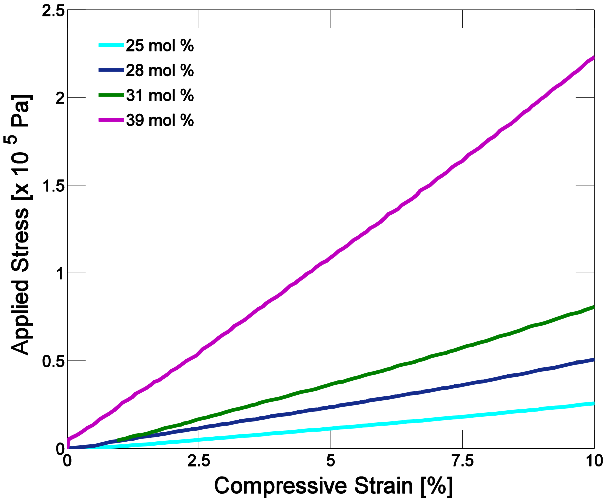

Figure S2. Compressive stress vs. strain data of four representative TFEMA-based ionogel samples with different monomer molar concentrations in the precursor solution (25-39 mol%).

Supplementary Discussion on 'Apparent' vs. 'Effective' vs. 'True' Diffusivity Values and Ionicity vs. Degree of Ionic Dissociation

As noted in several previous PGSE NMR spectroscopy-enabled diffusion studies of ILs or polymer/IL blends,[1-4] the rate of exchange between dissociated ('free') cations/anions and ion pairs (or aggregates) is significantly faster than the time scale of NMR measurements. Therefore, it is essential to recognize that the **apparent diffusivity** values obtained for cations (D_+^{NMR}, from the ^{1}H signal) and anions (D_-^{NMR}, from the ^{19}F signal) via Eq. 1 in the main text reflect the collective motions of *both free and paired ions*. Assuming the majority of associated ions to be neutral pairs, we can follow the framework outlined by Stolwijk et al.[5] and express the experimentally measured apparent diffusivity values as:

$$D_+^{NMR} = D_+^{eff} + D_{pair}^{eff} \qquad \text{Eq. S1}$$

$$D_-^{NMR} = D_-^{eff} + D_{pair}^{eff} \qquad \text{Eq. S2}$$

where one can introduce **effective diffusivity** values for the dissociated cations (D_+^{eff}) and anions (D_-^{eff}), as well as for the neutral pairs (D_{pair}^{eff}). The term 'effective' is employed here because although the steady-state degree of ionic dissociation (or fraction of IL molecules dissociated), denoted as φ, cannot be readily determined experimentally, it follows logically from Eq. S1 and Eq. S2 that the effective diffusivity values must be given by:[5]

$$D_+^{eff} = \varphi D_+ \qquad \text{Eq. S3}$$

$$D_-^{eff} = \varphi D_- \qquad \text{Eq. S4}$$

$$D_{pair}^{eff} = (1-\varphi) D_{pair} \qquad \text{Eq. S5}$$

where D_+, D_-, and D_{pair} represent the (equally experimentally-elusive) **true diffusivity** values of the individual dissociated cations, anions, and ion pairs, respectively.

Next, an important connection can be made via the Nernst-Einstein relation between the true cation/anion diffusivities (discussed up to this point only in the context of PGSE NMR measurements) and the experimentally measured ionic conductivity (via AC impedance spectroscopy), σ_{AC}:

$$\sigma_{AC} = \varphi C_s \frac{e^2}{k_B T}(D_+ + D_-) \qquad \text{Eq. S6}$$

where k_B is Boltzmann's constant, T is absolute temperature, e is the fundamental electron charge, and C_s is the total concentration of IL molecules in the sample. C_s is calculated as the product of the neat IL molar concentration (3894 mol/m^3) and the volume fraction of IL present in the ionogel sample. The volume fraction of IL is found by calculating the volume of each component in the precursor solution (pre-polymerization) from the measured mass and their reported density values, assuming volume additivity.

As described in the main text, one can also define a charge diffusivity term, D_σ, as:

$$D_\sigma = \varphi(D_+ + D_-) = D_+^{eff} + D_-^{eff} = \sigma_{AC} \frac{k_B T}{C_S e^2} \qquad \text{Eq. S7}$$

The expediency of the effective diffusivity terms becomes readily apparent when one sees that they can be solved for directly[5] in terms of the *experimentally measured values* D_+^{NMR}, D_-^{NMR}, and D_σ using Equations S1, S2, and S7:

$$D_+^{eff} = \frac{1}{2}(D_+^{NMR} - D_-^{NMR} + D_\sigma) \qquad \text{Eq. S8}$$

$$D_-^{eff} = \frac{1}{2}(D_-^{NMR} - D_+^{NMR} + D_\sigma) \qquad \text{Eq. S9}$$

$$D_{pair}^{eff} = \frac{1}{2}(D_+^{NMR} + D_-^{NMR} - D_\sigma) \qquad \text{Eq. S10}$$

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Now, while the term 'ionicity' utilized in the literature[1,6-7] is given by the following equation:

$$Ionicity = \frac{D_\sigma}{D_+^{NMR} + D_-^{NMR}} \qquad \text{Eq. S11}$$

by substitution of Equations S1-S5 and S7 into Eq. S11, one may also obtain:

$$Ionicity = \frac{\varphi(D_+ + D_-)}{\varphi(D_+ + D_-) + 2(1-\varphi)D_{pair}} \qquad \text{Eq. S12}$$

It is then straightforward to show using Eq. S12 that the ionicity will be *equal to* the steady-state degree of ionic dissociation, φ, only when the following relationship holds:

$$D_{pair} = \frac{1}{2}(D_+ + D_-) \qquad \text{Eq. S13}$$

Mathematically, this would occur if the true ion pair diffusivity were equal to the average of the true cation and anion diffusivities (including the case where all three values were equal). Although it is not readily apparent from a physical viewpoint why Eq. S13 might be expected to hold true *a priori* in any real IL/ionogel electrolytes, Coulombic interactions experienced by the dissociated ions (but not by neutral pairs) may enable such a relationship in certain samples. Future molecular dynamics studies in these types of systems may be expected to lend additional insights into the expected values of D_+, D_-, and D_{pair}.

References

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