

Electronic Supporting Information for

Increased Donnan Exclusion at High Salt Concentrations

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Materials. (PSLiTFSI)_{10k}-*b*-(PE)_{50k}-*b*-(PSLiTFSI)_{10k} triblock copolymer was used in this study. Cyclooctadiene was first polymerized by ring-opening metathesis polymerization to give a prepolymer with nitroxide end groups. Styrenesulfonyllithium(trifluoromethylsulfonyl)imide monomer was then polymerized at the chain ends using nitroxide-mediated polymerization. In the final step, the unsaturated polymer was hydrogenated using Wilkinson catalyst. End group analysis on ¹H NMR spectrum of the prepolymer and elemental analysis of the final polymer were used to determine the average chain lengths of the blocks. A polydispersity index of 2 was determined via gel permeation chromatography on the prepolymer. More detailed synthetic procedure and characterization details of (PSLiTFSI)_{10k}-*b*-(PE)_{50k}-*b*-(PSLiTFSI)_{10k} were described in ref. 1.

Measurement of Electrolyte Uptake and Salt Partitioning. The ionic separator was placed in solutions of EC/DMC (50/50 wt%) with varying amounts of LiTFSI. After 24 hours, the separator was removed from solution and all residual solution on the surface was wiped away. The swollen membrane was weighed to determine the uptake mass. The swollen membrane was then placed into 1 gram of EC/DMC (50/50 wt%) solvent. After 24 hours, 500 μL of the extracted solution was mixed with 50 μL of trifluoromethanesulfonamide (CF₃SO₂NH₂) solution in EC/DMC (10 mg/g) as the internal standard and subjected to ¹⁹F NMR experiments. These experiments were conducted at room temperature (22 °C). The moles of salt uptake, n_{LiTFSI} , and

the electrolyte partitioning as quantified by $\frac{\phi_-}{\phi^e_-}$, can then be calculated from the following equations:

$$n_{LiTFSI} = \frac{10 \frac{mg}{g}}{M_{CH_3SO_2NH_2}} \times \frac{\frac{P_{LiTFSI}}{6}}{\frac{P_{CF_3SO_2NH_2}}{3}} \times \frac{50}{500} \times 1 g \quad \#(S1)$$

$$\frac{\phi_-}{\phi_-^e} = \frac{n_{LiTFSI}}{W_u - n_{LiTFSI} M_{LiTFSI}} \times \frac{1}{m_{ext}} \quad \#(S2)$$

where M_i is the molecular weight, P_i is the peak integration in the NMR spectra, W_u is the weight of total uptake, and m_{ext} is the molality of the external solution.

Flory-Huggins interaction parameter. We use a lumped Flory-Huggins parameter, χ , to capture the individual interaction parameters between the solvent and ions, polymer and solvent, and polymer and ions. This lumped Flory-Huggins parameter can be expressed as the following:

$$\chi = \frac{\chi_{ions,p}(\phi_+ + \phi_-)\phi_p + \chi_{s,p}\phi_s\phi_p + \chi_{ions,s}(\phi_+ + \phi_-)\phi_s}{\phi_p(1 - \phi_p)}, \quad \#(S1)$$

where $\chi_{ions,p}$ is the interaction parameter between ions and polymer, $\chi_{s,p}$ is the interaction parameter between solvent and polymer, and $\chi_{ions,s}$ is the interaction parameter between ions and solvent.

Volume fraction of bound negative ions in the gel phase. We show the dependence of the volume fraction of bound negative ions in the gel phase, $\phi_{-,b}$, on the volume fraction of anions in the external solution, ϕ_-^e . Recall that $\phi_{-,b} = f\phi_p$. Figures S3-S7 show the predicted behavior from using the original quadratic Donnan exclusion expression (see Equation 1 and Figure 9 in the main text).

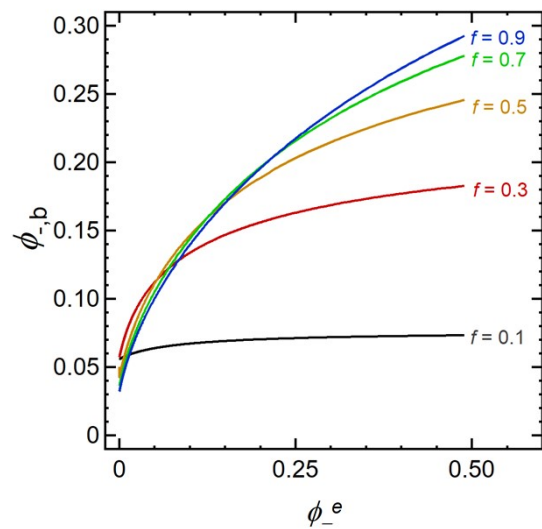


Figure S1. Dependence of the volume fraction of bound negative ions in the gel phase, $\phi_{-,b}$, on the volume fraction of anions in the external solution, $\phi_{-,}^e$. Curves are shown for selected values of the fraction of charged monomers on the polymer strands, f . Parameters held fixed: $z_+ = -z_-$, $N = 10$, and $\chi = 1$.

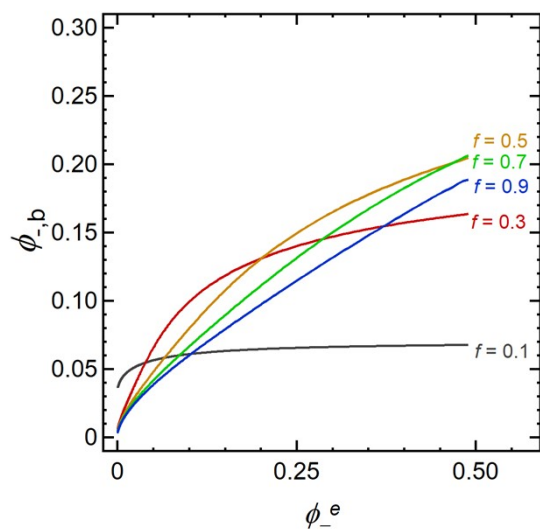


Figure S2. Dependence of the volume fraction of bound negative ions in the gel phase, $\phi_{-,b}$, on the volume fraction of anions in the external solution, ϕ_-^e . Curves are shown for selected values of the fraction of charged monomers on the polymer strands, f . Parameters held fixed: $z_+ = -z_-$, $N = 50$, and $\chi = 1$.

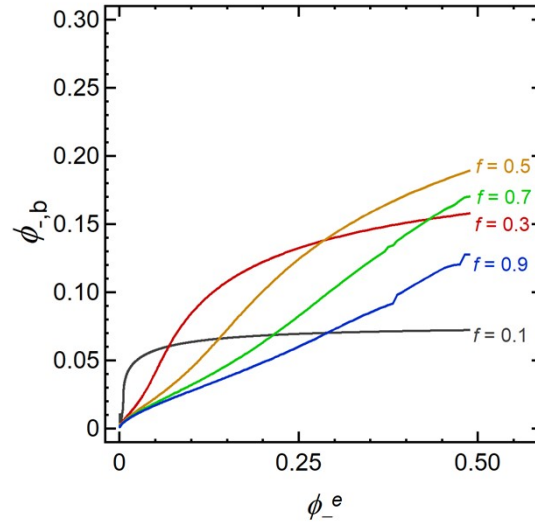


Figure S3. Dependence of the volume fraction of bound negative ions in the gel phase, $\phi_{-,b}$, on the volume fraction of anions in the external solution, ϕ_-^e . Curves are shown for selected values of the fraction of charged monomers on the polymer strands, f . Parameters held fixed: $z_+ = -z_-$, $N = 200$, and $\chi = 1$.

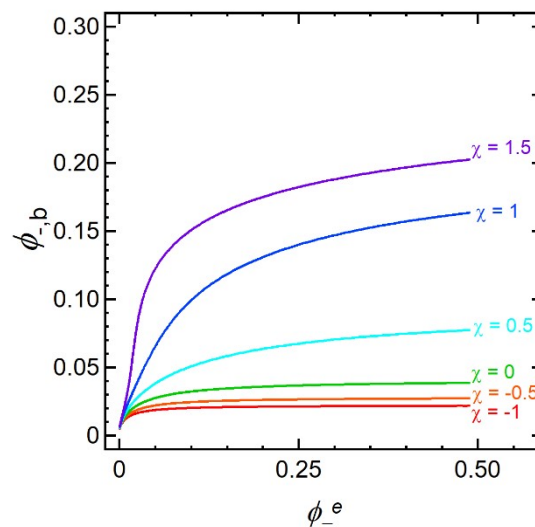


Figure S4. Dependence of the volume fraction of bound negative ions in the gel phase, $\phi_{-,b}$, on the volume fraction of anions in the external solution, $\phi_{-,}^e$. Curves are shown for selected values of χ . Parameters held fixed: $z_+ = -z_-$, $N = 50$ and $f = 0.3$.

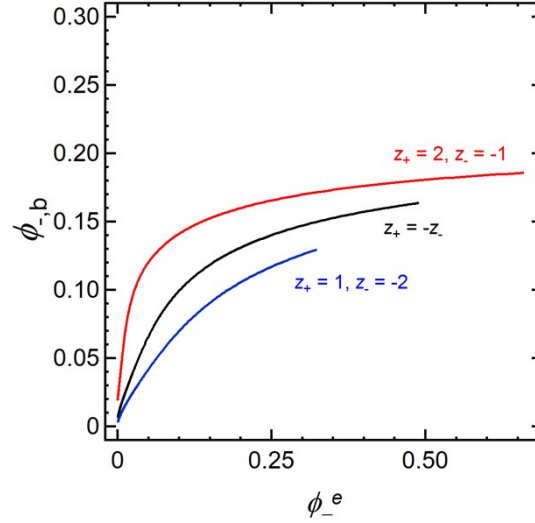


Figure S5. Dependence of the volume fraction of bound negative ions in the gel phase, $\phi_{-,b}$, on the volume fraction of anions in the external solution, $\phi_{-,}^e$. Curves are shown for selected values of the charge numbers, z_+ and z_- . Parameters held fixed: $N = 50$, $\chi = 1$, and $f = 0.3$.

Comparing Experimental Donnan exclusion data with theoretical predictions. We show the exclusion of ions in the gel; the dependence of the ratio of concentration of anions in the gel to that in the external solution, C_{in}/C_e , on C_e , the concentration of ions in the external solution, which has units of moles of ions per liter of solvent. We also show the dependence of the concentration of ions in the gel, C_{in} , to that in the external solution, C_e . Figure S6 and Figure S7 recast Figure 10b and Figure 11b from the main text from volume fractions into units of concentration. For Figure S6, to calculate the theoretical values of C_e from volume fraction, we

use Equation 26 to solve for m , the molality of the external solution, given ϕ_-^e , the volume fraction of anions in the external solution. C_e is then obtained from m by multiplying by the density of the solvent. C_{in} is obtained by assuming that the ratio C_{in}/C_e is equal to ϕ_-/ϕ_-^e . For Figure S7, to calculate the theoretical values of C_e from volume fraction, we use Equation 29. C_{in} is obtained by using Equation 28 to solve for C . ($C = C_{in}$). We use interpolated values of the water uptake, W_u , and C_+ , the moles of the counterion per liter of solvent, from the experimental data from ref. 2, for a given value of ϕ_-^e .

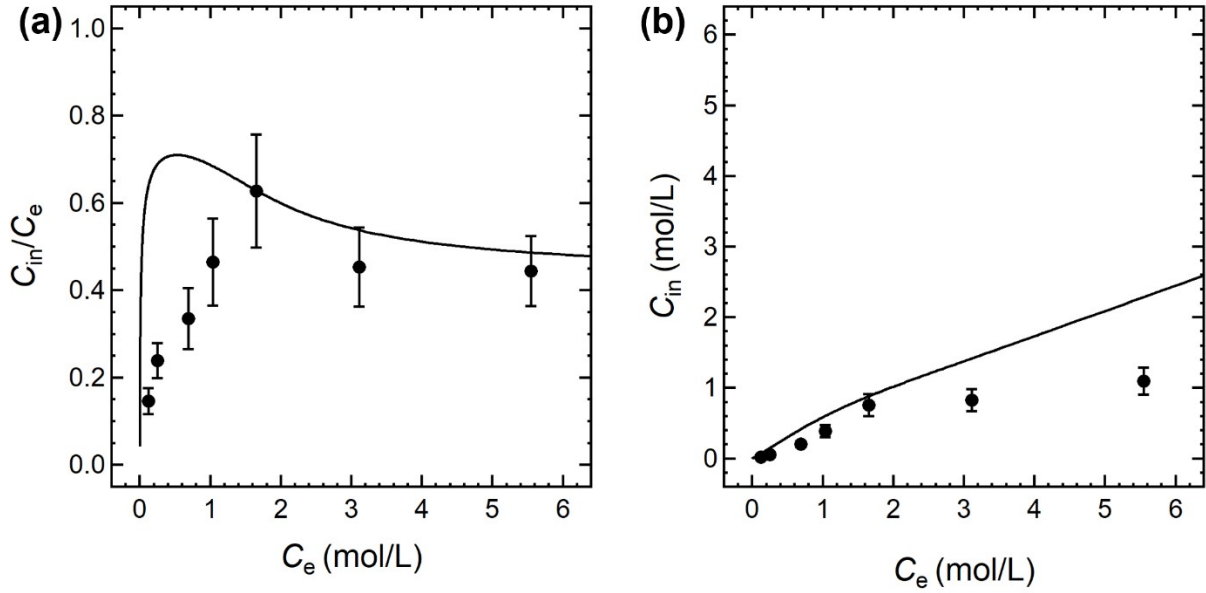


Figure S6. Experimental data for the swelling and salt partitioning between a PSLiTFSI-*b*-PE-*b*-PSLiTFSI triblock copolymer membrane and external solutions of LiTFSI in an EC/DMC mixture. (a) Exclusion of ions in the gel: dependence of the ratio of ion concentration in the gel to the concentration of ions in the external solution, C_{in}/C_e , on C_e . (b) Dependence of ion concentration in the gel, C_{in} , on the concentration of ions in the external solution, C_e . We give the concentration as the moles of ions per liter

of solvent. Curves are the comparison to theory and were calculated using $\chi = 0.85$, $z_+ = -z_-$, $N = 250$ and $f = 0.3$. See Figure 10 in the main text for more details.

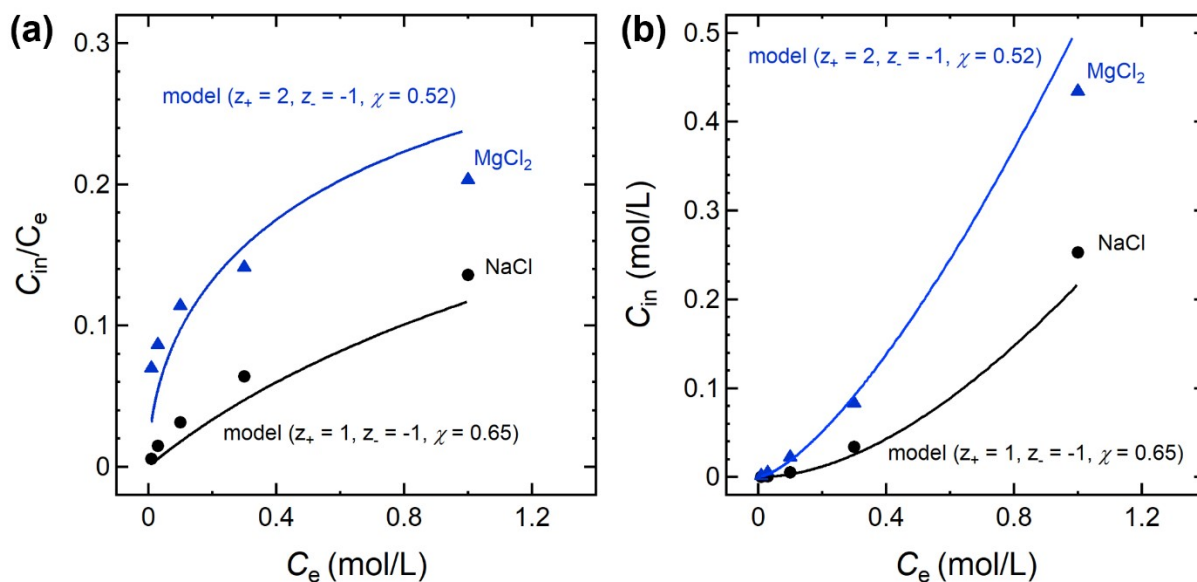


Figure S7. Comparing experimental data from ref. 2 with theoretical predictions. Data points represent partitioning of NaCl and MgCl₂ from an aqueous solution into an acrylamide-based polymeric gel with sulfonic acid groups. (a) Exclusion of ions in the gel: dependence of the ratio of ion concentration in the gel to the concentration of ions in the external solution, C_{in}/C_e , on C_e . (b) Dependence of ion concentration in the gel, C_{in} , on the concentration of ions in the external solution, C_e . We give the concentration as the moles of ions per liter of solvent. Curves are the comparison to theory and were calculated using $\chi = 0.65$ and $z_+ = -z_-$ for comparisons with the NaCl data, and $\chi = 0.52$, $z_+ = 2$ and $z_- = -1$ for comparisons with the MgCl₂ data. Parameters held fixed: $N = 9$ and $f = 0.1$. See Figure 11 in the main text for more details.

References:

1. X. Yu, X. Jiang, M. E. Seidler, N. J. Shah, K. W. Gao, S. Chakraborty, I. Villaluenga, N. P. Balsara, "Ionic separator formed by block copolymer microphase separation: a gateway for alleviating concentration polarization in batteries." *Submitted*.
2. J. Kamcev, D. R. Paul, B. D. Freeman. "Equilibrium ion partitioning between aqueous salt solutions and inhomogeneous ion exchange membranes." *Desalination*. 2018, 446, 31-41.