

Supporting Information: Theory of the Double Layer in Water-in-Salt Electrolytes

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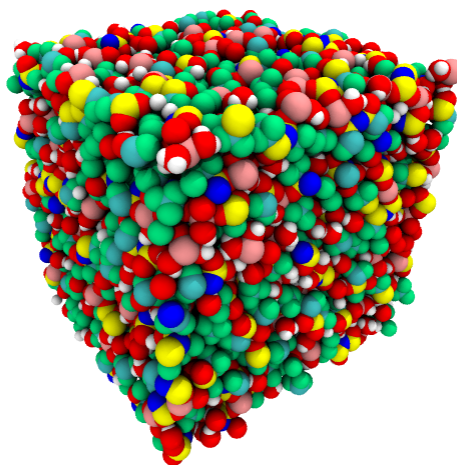
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Molecular Dynamics Simulation Methodology

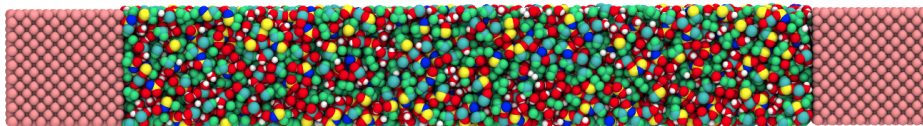
In this study, we performed all-atom classical MD simulations using LAMMPS.¹ We conducted a set of simulations for two different salts: LiTFSI and LiOTF. For each salt we first performed a series of bulk-like, fully periodic simulations at molal concentrations of 7m, 10m, 12m, 15m, and 21m. This yielded bulk densities, ion-water correlation functions, and data for fitting model parameters (p_w and ε_s). Additionally, we conducted MD simulations of the 21m solution in a nano-slit geometry with surface charges of $0, \pm 0.05, \pm 0.1, \pm 0.15$, and ± 0.2 C/m².

Simulation Details: In the periodic geometries, as seen in fig. S1A., we performed simulations containing 1000 water molecules and enough ion pairs for 7m, 10m, 12m, 15m, and 21m solutions. The simulations were carried out at fixed temperature (300 K) and pressure (1 bar), with Nose-Hoover thermostat and barostat until the density of the fluid equilibrated (10 ns with 1 fs time steps). Next, we switched to constant volume simulation box, still with a fixed temperature (300 K) and Nose-Hoover thermostat, and equilibrate for an additional 6 ns. Finally, production runs were performed for an additional 6 ns. In the nano-slit geometries, as seen in fig. S1B., we simulated the system at constant volume and temperature, filling a $33 \times 33 \times 200$ Å³ simulation box, with two $33 \times 33 \times 33$ Å³ electrodes, sandwiching the electrolyte, made up of Lennard Jones (LJ) spheres arranged in an fcc lattice (100) corresponding to gold. We refer to these LJ spheres as ‘gold’ atoms from here on out, although the primary purpose is to hold an applied charge and serve as a hard boundary for the electrolyte. For 21m LiTFSI (LiOTF), the box contained 707 (1096) ion pairs, 1873 (2904) water molecules, and 4096 (4096) ‘gold’ atoms. Surface charges ($0, \pm 0.05, \pm 0.1, \pm 0.15$, and ± 0.2 C/m²) were applied by placing partial charges on the first layer of ‘gold’ atoms. Equilibration runs of about 12 ns (1 fs time steps) were performed initially with no applied potential/charge. Then the surface charge was ramped up from zero, allowing for 12 ns of equilibration and 6 ns of production at each electrode surface charge.

The initial configurations for all simulations were generated using the open-source soft-



(a)



(b)

Figure S1: Snapshots of molecular dynamics simulations in (A) periodic and (B) nano-slit geometries.

ware, PACKMOL.² All MD simulations were visualized using the open-source software, VMD.³

Force Field Details: For all ionic species we employed the CL&P force field, which was developed for ionic liquid simulations, with same functional form as the OPLSAA force field.⁴ Given the dense ionic nature of our systems, we expect the CL&P force field to be appropriate for WiSEs. We note that our model overpredicts the fluid density by 8% (1.804 g/cm^3 vs 1.656 g/cm^3) compared to the APPLE&P many-body polarizable force field used in refs. 5 and 6 for LiTFSI, which is known to compare accurately with experiments of various transport and liquid structure properties. The CL&P force field is known to underestimate electrolyte transport properties such as conductivity and self diffusion coefficients,⁷ but accurate modelling of transport is not of importance for this study. We are more interested

in accurately modelling liquid structure. In particular, the Li^+ solvation structure is vital to our theory. To this end, we plot the coordination number of Lithium as a function of salt concentration in fig. S2A, where we find that the CL&P force field is able to accurately reproduce values obtained in ref. 6. Similarly, we plot the radial distribution functions of various species surrounding Li^+ in 21m LiTFSI in fig. S2. The plots shown almost quantitatively match the radial distribution functions found using the APPLE&P force field in ref. 6. However, in ref. 6, the authors find that Li^+ exhibits a bi-modally distributed solvation shell; some Li^+ is heavily solvated with water ($n_w^{\text{bound}} = 4$) and some is not solvated by any water ($n_w^{\text{bound}} = 0$). The CL&P force field does not predict this phenomena, as seen in fig. S2C. However, we do observe that the average value of $n_w^{\text{bound}} = 2.5$, measured in ref. 6 is recovered by the CL&P force field.

For water, we employed the spc/e force field. Inter-atomic interactions are determined using Lorentz-Berthelot mixing rules. Finally, for nano-slit simulations, we require force fields for the ‘gold’ electrode. We did not explicitly model the dynamics of the electrode, omitting the need for a ‘gold’-‘gold’ force field. The ‘gold’ interacts with the fluid mainly via coulomb interactions, as the surface layer of ‘gold’ atoms are charged. We also include Lennard-Jones interactions, which were made to be the same no matter what atom is interacting with ‘gold’ (LJ well depth: $\varepsilon = 0.001\text{eV}$, LJ well distance: $\sigma = 3\text{\AA}$). We make the Lennard-Jones parameters constant for all species in order to emphasize the role of the electrolyte and obtain conclusions that are not specific to the electrode material. Long range electrostatic interactions were computed using the Particle-Particle Particle-Mesh (PPPM) solver (with a cut-off length of $12\text{\AA}$), which maps particle charge to a 3D mesh for the periodic simulations and a 2D mesh in the transverse direction for the nano-slit simulation.⁸

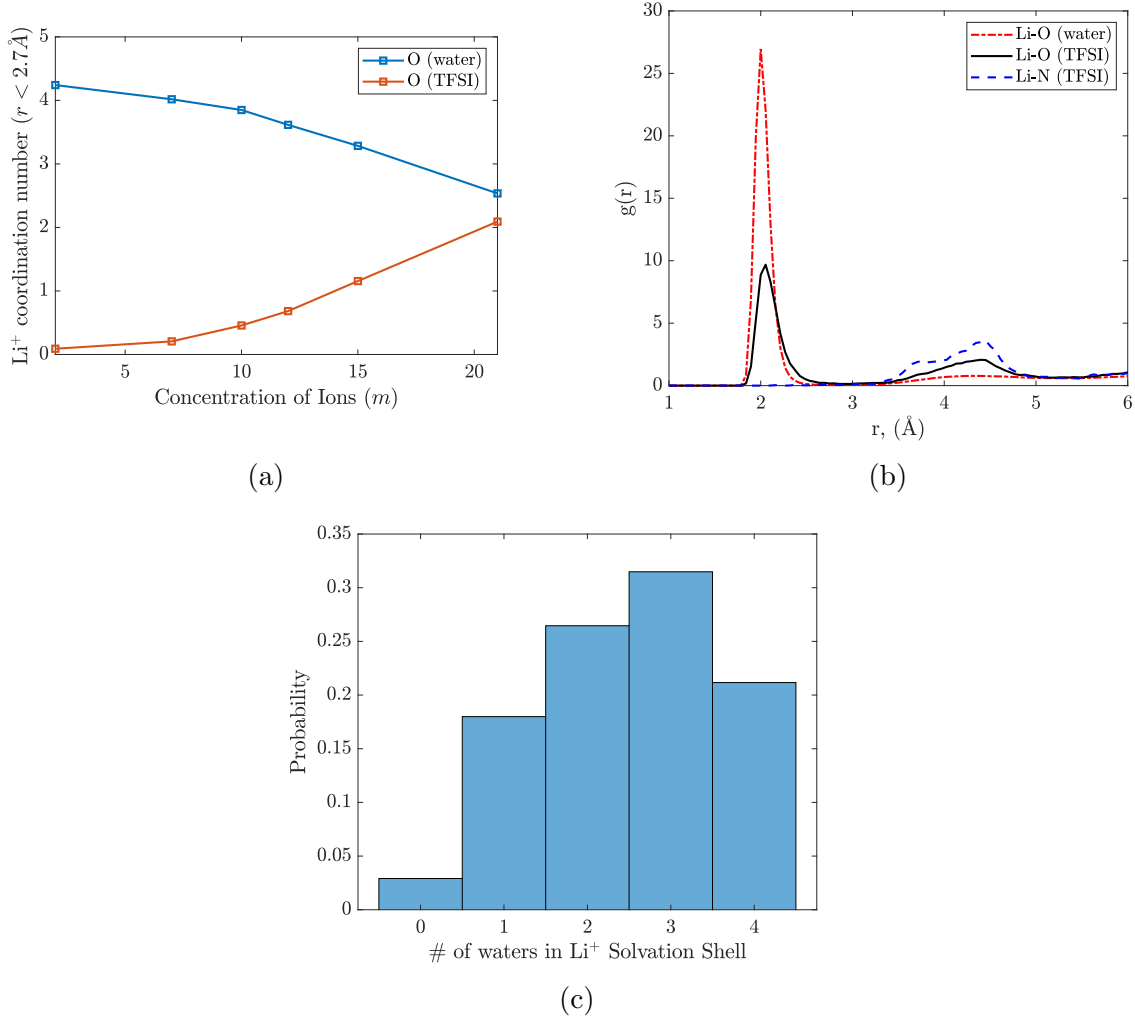


Figure S2: (A) Lithium coordination number as a function of ion concentration. Atoms within $2.7 \text{ \AA}$ of a central Li⁺ is considered to be coordinated to Li⁺. (B) The radial distribution function of various species around a central Li⁺ in 21m LiTFSI electrolyte. (C) A histogram of the number of waters coordinating Li⁺ in 21m LiTFSI electrolyte.

Electrostatic Energy:

We start by writing the displacement field:

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P}_{\text{el}} + \mathbf{P}_{\text{dip}} + \mathbf{P}_{\text{BSK}} \quad (\text{S1})$$

where $\mathbf{E} = -\nabla\phi$ is the electric field and ϕ is the electrostatic potential; ε_0 is vacuum permittivity; $\mathbf{P}_{\text{el}}$ is the local background polarization field of the electrolyte, with major

contributions coming from the electronic polarizability of molecular species which is assumed to be constant; $\mathbf{P}_{\text{dip}}$ is the local dipolar polarization field and is assumed to be a strong function of the concentration of dipoles, c_w ; and $\mathbf{P}_{\text{BSK}}$ is the local polarization field due to the orientation of correlated ions, as described by the Bazant-Storey-Kornyshev (BSK) theory.⁹

Each of the contributions to the polarization field can be written as

$$\mathbf{P}_{\text{el}} = \varepsilon_0(\varepsilon_s - 1)\mathbf{E} \quad (\text{S2})$$

$$\mathbf{P}_{\text{dip}} = c_w \langle p_w \rangle = c_w p_w \mathcal{L}(\beta p_w \mathbf{E}) \quad (\text{S3})$$

$$\mathbf{P}_{\text{BSK}} = -\varepsilon_0 \varepsilon_s l_c^2 \nabla^2 \mathbf{E} \quad (\text{S4})$$

where p_w is the effective dipole moment of free water molecules; $\beta = 1/k_B T$ is inverse thermal energy; $\mathcal{L}(u) = \coth u - 1/u$ is the Langevin function; and l_c is the ionic correlation length.⁹ In reality, $\mathbf{P}_{\text{el}}$ is a function of the local concentrations of all the species in the fluid; this contribution turns out to be roughly constant here. Therefore, in practice, we define ε_s to be the permittivity of the WiSE when there is no free water in the fluid, which is something that we will obtain from fitting MD simulations.

It is convenient to write the displacement field in terms of linear and non-linear contributions:

$$\mathbf{D} = \mathbf{P}_{\text{dip}} + \varepsilon_0 \varepsilon_s (1 - l_c^2 \nabla^2) \mathbf{E} \quad (\text{S5})$$

The differential electrostatic energy, δW_e for a dielectric medium of volume, V , is given

by

$$\delta W_e = \int_V d\mathbf{x} [\mathbf{E} \cdot \delta \mathbf{D}] \quad (\text{S6})$$

where we may write the variation in the displacement field as the following

$$\delta \mathbf{D} = \frac{\delta \mathbf{P}_{\text{dip}}}{\delta \mathbf{E}} \delta \mathbf{E} + \varepsilon_0 \varepsilon_s \delta \mathbf{E} - \varepsilon_0 \varepsilon_s l_c^2 \nabla \delta(\nabla \cdot \mathbf{E}) \quad (\text{S7})$$

where we have used the identity $\nabla \cdot \nabla \mathbf{E} = \nabla \nabla \cdot \mathbf{E}$, when $\nabla \times \mathbf{E} = 0$. We then plug this result into Eq. (S6)

$$\delta W_e = \int_V d\mathbf{x} \left[\frac{\delta \mathbf{P}_{\text{dip}}}{\delta \mathbf{E}} \mathbf{E} \cdot \delta \mathbf{E} + \varepsilon_0 \varepsilon_s \mathbf{E} \cdot \delta \mathbf{E} - \varepsilon_0 \varepsilon_s l_c^2 \mathbf{E} \cdot \nabla \delta(\nabla \cdot \mathbf{E}) \right] \quad (\text{S8})$$

We may then use the vector identity:

$$\mathbf{E} \cdot \nabla \delta(\nabla \cdot \mathbf{E}) = \nabla \cdot (\mathbf{E} \delta(\nabla \cdot \mathbf{E})) - \nabla \cdot \mathbf{E} \delta(\nabla \cdot \mathbf{E}) \quad (\text{S9})$$

and employed the divergence theorem to transform the first term of Eq. (S9) into a surface term, at which the electric field vanishes. Thus

$$\delta W_e = \int_V d\mathbf{x} \left[\frac{\delta \mathbf{P}_{\text{dip}}}{\delta \mathbf{E}} \mathbf{E} \cdot \delta \mathbf{E} + \varepsilon_0 \varepsilon_s \mathbf{E} \cdot \delta \mathbf{E} + \varepsilon_0 \varepsilon_s l_c^2 \nabla \cdot \mathbf{E} \cdot \delta(\nabla \cdot \mathbf{E}) \right] \quad (\text{S10})$$

Integrating δW_e from 0 to W_e , plugging in the definition, $\mathbf{E} = -\nabla \phi$, and enforcing $\nabla \cdot \mathbf{D} = \rho$ with a Lagrange multiplier, λ , obtains:

$$\begin{aligned}
W_e = & \int_V d\mathbf{x} \left[\frac{c_w}{\beta} \left(\beta p_w \nabla \phi \cdot \mathcal{L}(\beta p_w \nabla \phi) - \ln \left(\frac{\sinh(\beta p_w \nabla \phi)}{\beta p_w \nabla \phi} \right) \right) \right] \\
& + \int_V d\mathbf{x} \left[\frac{\varepsilon_s}{2} (|\nabla \phi|^2 + l_c^2 |\nabla^2 \phi|^2) \right] \\
& + \int_V d\mathbf{x} [\lambda (\rho - \nabla \cdot \mathbf{D})]
\end{aligned} \tag{S11}$$

Substituting in Eq. (S1) and integrating by parts shows that $\lambda = \phi$. Hence the electrostatic energy of the WiSE is given by:

$$W_e = \int_V w_e d\mathbf{x} \tag{S12}$$

$$= \int_V d\mathbf{x} \left[\rho \phi - \frac{\varepsilon_0 \varepsilon_s}{2} (|\nabla \phi|^2 + l_c^2 |\nabla^2 \phi|^2) - c_w k_B T \ln \left(\frac{\sinh(\beta p_w |\nabla \phi|)}{\beta p_w |\nabla \phi|} \right) \right] \tag{S13}$$

Pressure Function:

Here we outline a heuristic derivation of the pressure function for a Langmuir model. This allows the form of the pressure function to be derived, without going into too much detail.

The grand canonical partition function for a 3-component system can be seen as:

$$\Xi = \sum_{n_+=0}^{\infty} \sum_{n_-=0}^{\infty} \sum_{n_w=0}^{\infty} e^{\beta \mu_+ n_+} e^{\beta \mu_- n_-} e^{\beta \mu_w n_0} Q(n_+) Q(n_-) Q(n_w) \tag{S14}$$

where $Q(n_j)$ corresponds to the canonical partition function of each species, j , as seen by

$$Q(n_j) = \Omega_j e^{-\beta \epsilon_j n_j} \tag{S15}$$

where the energy is given by $E_j = \epsilon_j n_j$.

In the model of Han *et al.*¹⁰ it was assumed that the lattice is subsequently filled with each species. Hence, the number of configurations for each state is written as if each component, of which there are n_j individual elements, resides on its own ‘individual lattice’ with a total

of N_t available sites,

$$\Omega_j = \frac{N_t!}{n_j!(N_t - n_j)!} \quad (\text{S16})$$

Hence, we have for the partition function

$$\Xi = \sum_{n_w=0}^N \Omega_w e^{\beta \tilde{\mu}_w n_w} \cdot \sum_{n_-=0}^{(N-n_w)/\xi_-} \Omega_- e^{\beta \tilde{\mu}_- n_-} \cdot \sum_{n_+=0}^{(N-n_w-\xi_- n_-)/\xi_+} \Omega_+ e^{\beta \tilde{\mu}_+ n_+} \quad (\text{S17})$$

where $\xi_- = v_-/v_w$ and $\xi_+ = v_+/v_w$, and $\tilde{\mu}_j = \mu_j - \epsilon_j$ has been introduced for convenience.

The sums are evaluated progressively because of the assumption that the lattice is subsequently filled with each component. Using the binomial theorem, we obtain after evaluating the sums

$$\Xi = \left\{ [(1 + e^{\beta \tilde{\mu}_+})^{\xi_-/\xi_+} + e^{\beta \tilde{\mu}_-}]^{1/\xi_-} + e^{\beta \tilde{\mu}_w} \right\}^N \quad (\text{S18})$$

where N is the total number of lattice sites available to free water. In the limit of all components of equal size, we recover the well-known symmetric 3-component Langmuir partition function:

$$\Xi = \left\{ 1 + e^{\beta \tilde{\mu}_+} + e^{\beta \tilde{\mu}_-} + e^{\beta \tilde{\mu}_w} \right\}^N \quad (\text{S19})$$

In the grand canonical ensemble, the partition function is related to the pressure, p , through,

$$pV = k_B T \ln \Xi \quad (\text{S20})$$

Hence, we have for the pressure function,

$$p = \frac{k_B T}{v_w} \ln \{ [(1 + e^{\beta \tilde{\mu}_+})^{\xi_-/\xi_+} + e^{\beta \tilde{\mu}_-}]^{1/\xi_-} + e^{\beta \tilde{\mu}_w} \} \quad (\text{S21})$$

To obtain the pressure function in the main text, we bring a constant out of the chemical potentials:

$$p = \frac{k_B T}{v_w} \ln \{ [(1 + \xi_+ e^{\beta \tilde{\mu}_+})^{\xi_-/\xi_+} + \xi_- e^{\beta \tilde{\mu}_-}]^{1/\xi_-} + e^{\beta \tilde{\mu}_w} \} \quad (\text{S22})$$

It should be evident that this derivation, which is a generalization of the special case of ref. 10, can be further generalized to any number of components of any size.

Concentrations:

The concentrations can be obtained from

$$c_j = \left. \frac{\partial p}{\partial \mu_j} \right|_{T, \mu_{i \neq j}} \quad (\text{S23})$$

Taking these derivatives yields

$$\tilde{c}_w = \frac{2}{\gamma} \frac{e^{\beta(\mu_w + \Psi)}}{[(1 + \xi_+ e^{\beta(\mu_+ - e\phi)})^{\xi_-/\xi_+} + \xi_- e^{\beta(\mu_- + e\phi)}]^{1/\xi_-} + e^{\beta(\mu_w + \Psi)}} \quad (\text{S24})$$

$$\tilde{c}_- = \frac{2}{\gamma} \frac{e^{\beta(\mu_- + e\phi)} [(1 + \xi_+ e^{\beta(\mu_+ - e\phi)})^{\xi_-/\xi_+} + \xi_- e^{\beta(\mu_- + e\phi)}]^{1/\xi_- - 1}}{[(1 + \xi_+ e^{\beta(\mu_+ - e\phi)})^{\xi_-/\xi_+} + \xi_- e^{\beta(\mu_- + e\phi)}]^{1/\xi_-} + e^{\beta(\mu_w + \Psi)}} \quad (\text{S25})$$

$$\tilde{c}_+ = \frac{2}{\gamma} \frac{e^{\beta(\mu_+ - e\phi)} (1 + \xi_+ e^{\beta(\mu_+ - e\phi)})^{\xi_-/\xi_+ - 1} [(1 + \xi_+ e^{\beta(\mu_+ - e\phi)})^{\xi_-/\xi_+} + \xi_- e^{\beta(\mu_- + e\phi)}]^{1/\xi_- - 1}}{[(1 + \xi_+ e^{\beta(\mu_+ - e\phi)})^{\xi_-/\xi_+} + \xi_- e^{\beta(\mu_- + e\phi)}]^{1/\xi_-} + e^{\beta(\mu_w + \Psi)}} \quad (\text{S26})$$

where $\gamma = 2c_{\pm}^{\text{bulk}} v_w$ is the packing parameter for ions in the bulk, and $\tilde{c}_i = c_i/c_{\pm}^{\text{bulk}}$ are non-dimensionalized concentrations. Note that the packing parameter is not equivalent to the typically defined compacity,¹¹ since we have an asymmetric lattice here.

In the limit of $\Psi \gg |e\phi|$ (see main text for definition of the function), $c_w \rightarrow 1/v_w$, while ions are depleted $c_{\pm} \rightarrow 0$. When $e\phi \gg \Psi > -e\phi$, the anions saturate, $c_- \rightarrow 1/\xi_- v_w = 1/v_-$, with all other concentrations tending to zero, $c_{+,w} \rightarrow 0$. For $-e\phi \gg \Psi > e\phi$, the cation concentration reaches a maximum, $c_+ \rightarrow 1/\xi_+ v_w = 1/v_+$, with $c_{-,w} \rightarrow 0$.

The chemical potentials in (S24)-(S26) are determined by the concentrations of species in the bulk reservoir, where the mean-field electrostatic potential is zero. Solving the system of algebraic equations, Eqs. (S24)-(S26), under these conditions yields:

$$\beta\mu_w = \ln \left[\frac{\gamma_w}{1 - \gamma_w} \right] + \frac{1}{\xi_-} \ln \left[\frac{1 - \gamma_w}{1 - \gamma_w - \xi_- \gamma/2} \right] + \frac{1}{\xi_+} \ln \left[\frac{1 - \gamma_w - \xi_- \gamma/2}{1 - \gamma_w - \xi_- \gamma/2 - \xi_+ \gamma/2} \right] \quad (\text{S27})$$

$$\beta\mu_- = \ln \left[\frac{\gamma/2}{1 - \gamma_w - \xi_- \gamma/2} \right] + \frac{1}{\xi_+} \ln \left[\frac{1 - \gamma_w - \xi_- \gamma/2}{1 - \gamma_w - \xi_- \gamma/2 - \xi_+ \gamma/2} \right] \quad (\text{S28})$$

$$\beta\mu_+ = \ln \left[\frac{\gamma/2}{1 - \gamma_w - \xi_- \gamma/2 - \xi_+ \gamma/2} \right] \quad (\text{S29})$$

where $\gamma_w = c_w^{\text{bulk}} v_w$ is the packing parameter of free water molecules in the bulk. Note that $\xi_- \gamma/2$ is the compacity of anions and $\xi_+ \gamma/2$ is the compacity of cations, as they would be defined in a symmetric lattice-gas.¹¹

Model Parameterization:

Our theory is parameterized from molecular dynamics simulations of 21m aqueous solutions of LiTFSI and LiOTF in fully periodic geometries, representing the bulk fluid. The model developed in the main text and Appendix requires the specification of 7 parameters: ξ_+ , ξ_- , γ , γ_w , p_w , ε_s , and l_c . Here, we discuss our procedure for determining these parameters.

In the main text we explained that ξ_+ has a contribution from solvating water molecules.

On the other hand, we made the assumption that ξ_- is only related to the molecular volume of the ‘naked’ TFSI⁻ ions. It can be seen in fig. S3, that cations are much more vigorously solvated than anions. This observation serves as the justification for our assumption that no water is bound to anions.

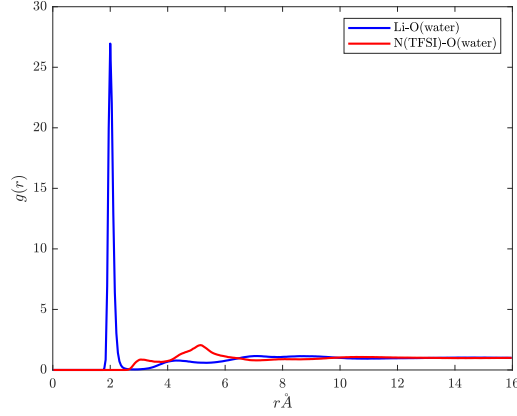


Figure S3: The Li-O(water) and N(TFSI)-O(water) radial distribution functions are plotted to contrast the asymmetry in ion solvation between anions and cations. The correlation functions serve in determining the contribution of ion solvation in the ion size parameters, xi_+ and ξ_- .

We determined the bulk volumetric filling fraction, Φ_B , of the fluid, by fitting it to reproduce the bulk molar concentrations of species observed in MD simulations. For LiTFSI, we found a bulk filling fraction of 0.81. The bulk filling fraction is related to γ and γ_w in the following way:

$$\Phi_B = \gamma_w + \frac{\gamma}{2}(\xi_+ + \xi_-) \quad (\text{S30})$$

where γ and γ_w are related via the molality of the solution, and the number of bound water molecules. We write the equation for the ratio of ion pairs to water molecules:

$$\frac{1 \text{ mol water}}{0.018 \text{ kg}} \times \frac{1 \text{ kg}}{21 \text{ mol ion}} = 2.65 \frac{\text{mol water}}{\text{mol ion}} \quad (\text{S31})$$

We may then write

$$2.65 = \frac{\gamma_w + n_w^{\text{bound}}\gamma/2}{\gamma/2}$$

where n_w^{bound} is the average number of bound water molecules to the cation. Thus, upon determining Φ_B , we specify both γ and γ_w .

We now determine the remaining parameters, p_w and ε_s , from a set of MD simulations with various water concentrations (7m-21m salt concentration) and computing the bulk dielectric constant, using the well-known Kirkwood formula:

$$\varepsilon_{MD} = 1 + \frac{4\pi}{3Vk_BT} (\langle |\mathbf{M}| \rangle^2 - \langle |\mathbf{M}|^2 \rangle) \quad (\text{S32})$$

where $\mathbf{M}$ is the total instantaneous dipole moment of the fluid during a snapshot of the MD simulation.

The model described in the previous section yields the following formula for the permittivity operator:

$$\hat{\varepsilon} = \frac{c_w \beta p_w^2}{\varepsilon_0} \frac{\mathcal{L}(\beta p_w \mathbf{E})}{\beta p_w \mathbf{E}} + \varepsilon_s (1 - l_c^2 \nabla^2) \quad (\text{S33})$$

While parameterizing, the simulations were performed in the absence of an external electric field and averaged over the entire simulation box, so we may take limit of $\hat{\varepsilon}$ as $|\mathbf{E}| \rightarrow 0$ and the limit in which the gradient operators vanish (long wavelength limit):

$$\hat{\varepsilon} \rightarrow \varepsilon = \varepsilon_s + c_w \frac{p_w^2}{3\varepsilon_0 k_B T} \quad (\text{S34})$$

We fit Eq. (S34) to the dielectric constants computed from MD in order to determine p_w and ε_s , as shown in fig. S4. For LiTFSI, we obtained values of $\varepsilon_s = 10.1$ and $p_w = 2.7p_w^0$, where $p_w^0 = 1.85$ Debye is the dipole moment of a water molecule in vacuum.

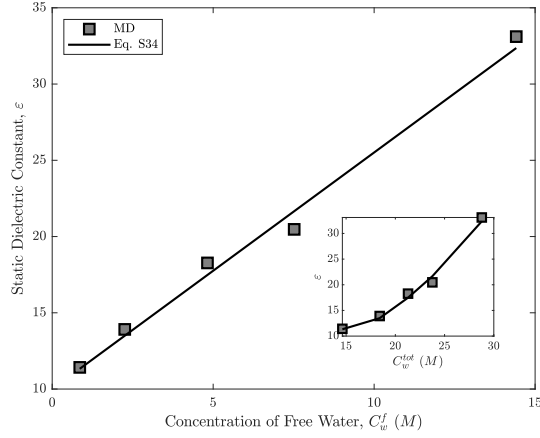


Figure S4: The static dielectric constant computed from MD simulations, as well as with Eq. (S34) is plotted as a function of *free* water concentration. Inset: The dielectric constants are plotted as a function of *total* water concentration.

The last parameter we must specify is l_c , the correlation length, which is perhaps the least well determined parameter in the model. As a modification to the Poisson-Fermi theory for neat ILs, l_c was first introduced by BSK as a parameter which controls the magnitude of electrostatic correlations between charges in an IL.⁹ These electrostatic correlations lead to the "overscreening" phenomena, which manifests as decaying oscillations in density profiles within the EDL. In ref. 9, l_c was taken to be the ionic diameter.

Here we take a similar approach. One complication is that in our system, there is a large asymmetry in the size of cations and anions. MD simulations (see fig. S5, for example) show asymmetric overscreening in positively or negatively charged surfaces. We posit that this observation implies that l_c is a function of the size of the counter-ion attracted to the charged surface. For LiTFSI (and LiOTF), we assumed that l_c is proportional to the counter-ion radii, $a_{\pm}$, with proportionality constant, α . Thus, for $\sigma > 0$, $l_c = \alpha a_-$ and for $\sigma < 0$, $l_c = \alpha a_+$. Interestingly, we find that the LiOTF solution displayed a larger magnitude of overscreening than LiTFSI solution, most likely due to stronger electrostatic correlations between cations and anions. For this reason, we actually needed larger correlation lengths to model the LiOTF electrolyte than for LiTFSI electrolyte, as seen in table S1.

Thus, we have fully parameterized our model from MD simulations. Although we have

outlined the parameterization for LiTFSI, we performed this procedure for LiOTF, as well. The determined parameters are written in table S1.

Table S1: Summary of Model Parameters

Parameter	LiTFSI	LiOTF
Φ_B	0.81	0.83
n_w^{bound}	2.5	2.0
ξ_+	4.68	4.37
ξ_-	14.85	8.02
p_w/p_w^0	2.7	3.0
ε_s	10.1	8.2
α	2.0	4.0
$a_-/\text{\AA}$	3.53	2.87
$a_+/\text{\AA}$	2.41	2.32

Model Results for LiOTF

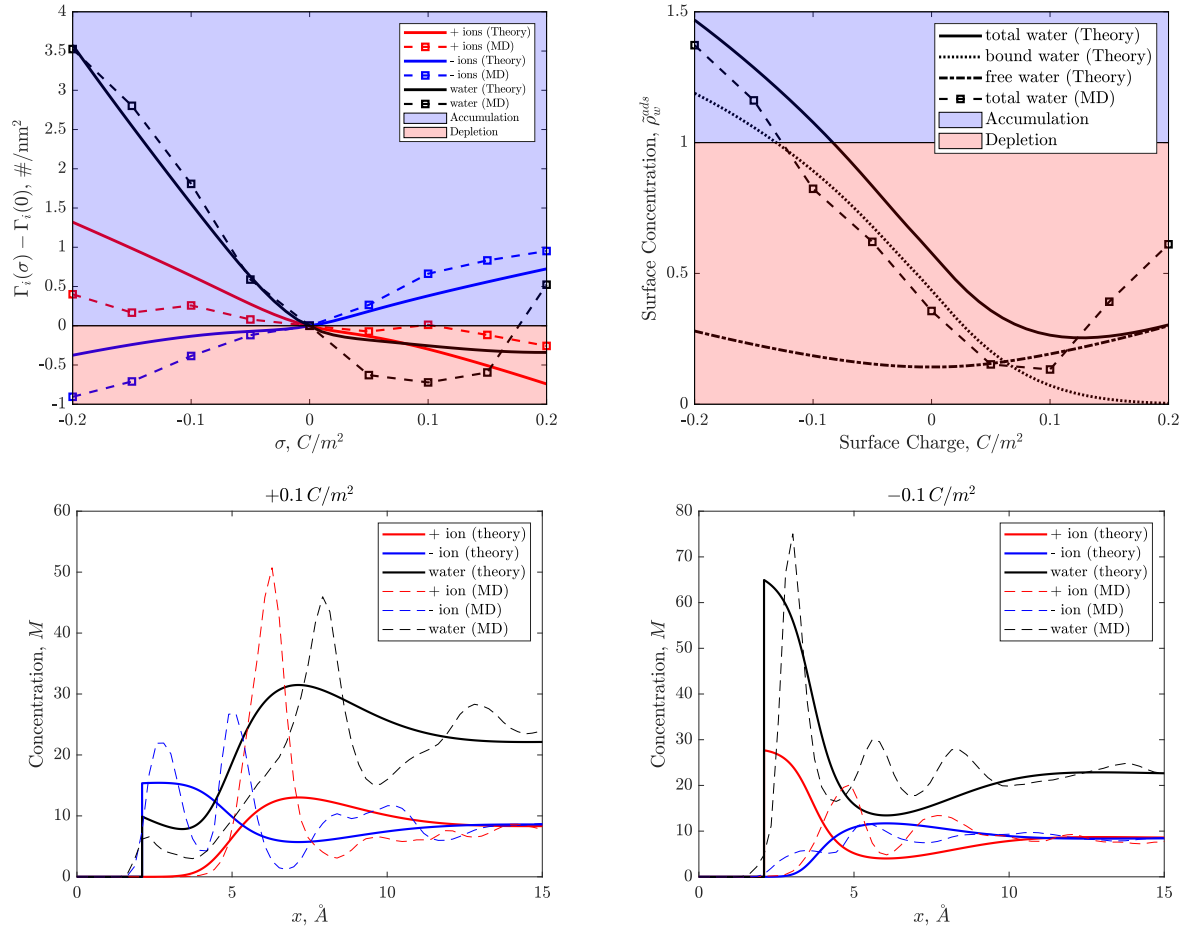


Figure S5: (A) Surface excess concentration isotherms for all species. (B) The interfacial concentration of water integrated within 5 Å of the electrode surface. The concentration profiles of species in 21m LiTFSI next surfaces with charge (C) +0.1C/m² and (D) -0.1C/m²

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