

## Supplementary Information

### Predicting the Ion Desolvation Pathway of Lithium Electrolytes and Their Dependence on Chemistry and Temperature

John Holoubek<sup>a</sup>, Artem Baskin<sup>b,\*</sup>, John W. Lawson<sup>b</sup>, Hridayanand Khemchandani<sup>a</sup>, Tod A. Pascal<sup>a,c,d,e</sup>, Ping Liu<sup>a,c,d,e\*</sup>, Zheng Chen<sup>a,c,d,e\*</sup>

<sup>a</sup>*Department of NanoEngineering, University of California, San Diego, La Jolla, CA 92093, USA*

<sup>b</sup>*NASA Ames Research Center, Moffett Field, CA 94035, USA*

<sup>c</sup>*Program of Chemical Engineering, University of California, San Diego, La Jolla, CA 92093, USA*

<sup>d</sup>*Program of Materials Science and Engineering, University of California, San Diego, La Jolla, CA 92093, USA*

<sup>e</sup>*Sustainable Power and Energy Center, University of California, San Diego, La Jolla, CA 92093, USA*

#### Corresponding Authors

\*(A.B.) E-mail: abaskin@lbl.gov

\*(P.L.) E-mail: piliu@eng.ucsd.edu

\*(Z.C.) E-mail: zhengchen@eng.ucsd.edu

#### Experimental Methods

##### *Equilibration MD Simulations*

Classical, fixed-charge Molecular Dynamics (MD) simulations were performed in LAMMPS using the OPLS-AA forcefield<sup>[1]</sup> for solvents and Li<sup>+</sup> with the anion described with the potentials of Gaouveia et al.<sup>[2]</sup> Liquid simulation boxes were constructed from random distributions of the molecules, with compositions described in Table S1. For electrolyte cells in contact with graphene, a hexagonal graphene sheet was fixed in place (at  $z = 0$ ) with interactions described by Pascal et al.<sup>[3]</sup> For charged graphene simulations, a fixed negative charge was uniformly applied to each atom and overall neutrality was maintained by adding 5 additional Li<sup>+</sup> atoms. In all cases the charges of the Li<sup>+</sup> and FSI<sup>-</sup> molecules were scaled to the high-frequency dielectric properties of the solvents present in the system according to the method employed by Park *et al.*<sup>[4]</sup> which is 0.73 for DOL/DME and 0.74 for DEE. Periodic boundary conditions were applied in all directions.

For each system, an initial energy minimization at 0 K (energy and force tolerances of  $10^{-4}$ ) was performed to obtain the ground-state structure. After this, the system was slowly heated from 0 K to room temperature at constant volume over 0.01 ns using a Langevin thermostat, with a damping parameter of 100 ps. The system was then subjected to 5 cycles of quench-annealing dynamics in order to eliminate the persistence of any meta-stable states, where the temperature was slowly cycled between 298 K and 894 or 213 and 639 K with a ramp period 0.025 ns followed by 0.1 ns of dynamics at either temperature extreme. All 5 anneal cycles thus take 1.25 ns total. After annealing, the system was equilibrated in the constant temperature (Table S1), constant pressure (1bar) (NpT ensemble) for 1.5 ns. We resolved stresses in the system isotropically using the Andersen barostat (pressure relaxation constant of 1 ps). We used the Shinoda et al.<sup>[5]</sup> equations of motion which combine the hydrostatic equations of Martyna et al.<sup>[6]</sup> with the strain energy proposed by Parrinello and Rahman<sup>[7]</sup>. The time integration schemes closely follow the time-reversible measure-preserving Verlet integrators derived by Tuckerman et al.<sup>[8]</sup> Finally, we performed 10 ns of constant volume, constant temperature (NVT) production dynamics at the temperatures indicated in table S1. Radial distribution functions and density profiles were obtained using the Visual Molecular Dynamics (VMD) software. Pictures of the various solvation shells, sampled from the simulation trajectory, were also obtained using VMD. The stepsize for all simulations was 1 fs.

**Table S1.** MD simulation system parameters

Temperature	Simulation	# Molecules in box	Equilibrated box dimensions (Å)
298 K	1 M LiFSI DOL/DME (Bulk)	20 Li <sup>+</sup> , 20 FSI <sup>-</sup> , 143 DOL, 96 DME	33.252 x 33.252 x 33.252
298 K	1 M LiFSI DEE (Bulk)	20 Li <sup>+</sup> , 20 FSI <sup>-</sup> , 192 DEE	33.106 x 33.106 x 33.106
298 K	1 M LiFSI DOL/DME in contact with neutral graphene	192 C (Graphene), 12 Li <sup>+</sup> , 12 FSI <sup>-</sup> , 86 DOL, 62 DME	25.533 x 19.654 x 50.631
298 K	1 M LiFSI DEE in contact with neutral graphene	192 C (Graphene), 13 Li <sup>+</sup> , 13 FSI <sup>-</sup> , 127 DEE	25.533 x 19.654 x 54.603
298 K	1 M LiFSI DOL/DME in contact with charged graphene	192 C (Graphene, q = -0.0190 per atom), 17 Li <sup>+</sup> , 12 FSI <sup>-</sup> , 86 DOL, 62 DME	25.533 x 19.654 x 49.727

298 K	1 M LiFSI DEE in contact with charged graphene	192 C (Graphene, $q = -0.0193$ per atom), 18 Li <sup>+</sup> , 13 FSI <sup>-</sup> , 127 DEE	25.533 x 19.654 x 53.586
213 K	1 M LiFSI DOL/DME (Bulk)	20 Li <sup>+</sup> , 20 FSI <sup>-</sup> , 143 DOL, 96 DME	32.200 x 32.200 x 32.200 x
213 K	1 M LiFSI DEE (Bulk)	20 Li <sup>+</sup> , 20 FSI <sup>-</sup> , 192 DEE	31.666 x 31.666 x 31.666
213 K	1 M LiFSI DOL/DME in contact with neutral graphene	192 C (Graphene), 12 Li <sup>+</sup> , 12 FSI <sup>-</sup> , 86 DOL, 62 DME	25.533 x 19.654 x 45.620
213 K	1 M LiFSI DEE in contact with neutral graphene	192 C (Graphene), 13 Li <sup>+</sup> , 13 FSI <sup>-</sup> , 127 DEE	25.533 x 19.654 x 47.166
213 K	1 M LiFSI DOL/DME in contact with charged graphene	192 C (Graphene, $q = -0.0190$ per atom), 17 Li <sup>+</sup> , 12 FSI <sup>-</sup> , 86 DOL, 62 DME	25.533 x 19.654 x 46.860
213 K	1 M LiFSI DEE in contact with charged graphene	192 C (Graphene, $q = -0.0193$ per atom), 18 Li <sup>+</sup> , 13 FSI <sup>-</sup> , 127 DEE	25.533 x 19.654 x 45.280

### Free Energy Calculations

We performed classical free energy sampling on equilibrated MD cells to evaluate the free energy profiles along the following collective variables (CVs): **1)** The Li<sup>+</sup>/solvent coordination number (CN) in the first solvation sphere, **2)** The Li<sup>+</sup>/Solvent + FSI<sup>-</sup> CN in the first solvation sphere, and **3)** the distance between Li<sup>+</sup> and the graphene plane. Specifically, we use the metadynamics protocol to evaluate the potential of mean force along the collective variables.<sup>[9,10]</sup> The simulations were carried out using the Colvars module in LAMMPS.<sup>[11]</sup>

We use the following definition of CN:

$$\sum_{i=1}^N \frac{1 - \left(\frac{r_i}{r_0}\right)^p}{1 - \left(\frac{r_i}{r_0}\right)^q}$$

where  $p=6$  and  $q=12$ .  $r_i$  is the distance between Li<sup>+</sup> and the  $i$ -th coordinating atom. In this case only the solvent and FSI<sup>-</sup> oxygens were considered as coordinating species, as nitrogen was not determined to coordinate directly with Li<sup>+</sup> from equilibration simulations.  $r_0$  is the cut-off radius that defines atoms as inside or outside of the first solvation sphere, where  $i$  runs over the range that includes all possible coordinating atoms (e.g., all oxygen atoms in the simulation box). The applied cut-off radius was 3.07 Angstroms, similar to previous work with comparable ether solvents.<sup>[12]</sup>

## MD Metadynamics Protocol

MD simulation boxes (Table S1) after equilibration (Equilibration MD section) were used as initial configuration for the free energy sampling with the metadynamics protocol. This protocol was applied in either a 1-D or 2-D fashion depending on the purpose of the simulation. Typically, free energy sampling was determined to be converged when both of the following conditions were met: **1)** The phase space of interest for the simulation was entirely elucidated (i.e., all relevant solvation/electrode distance states were visible in the profile), and **2)** the trajectory was determined to be diffusive within the aforementioned phase space from examination of the trajectory profiles along the relevant CVs. In Table S2 we summarize the parameters of the metadynamics free energy sampling for various simulations: height of the Gaussian hills (kcal/mol), frequency of hill creation (steps), width of hills in Å for electrode distance or unitless for CN, and simulation time in ns.

**Table S2.** Metadynamics parameters for each simulation of interest.

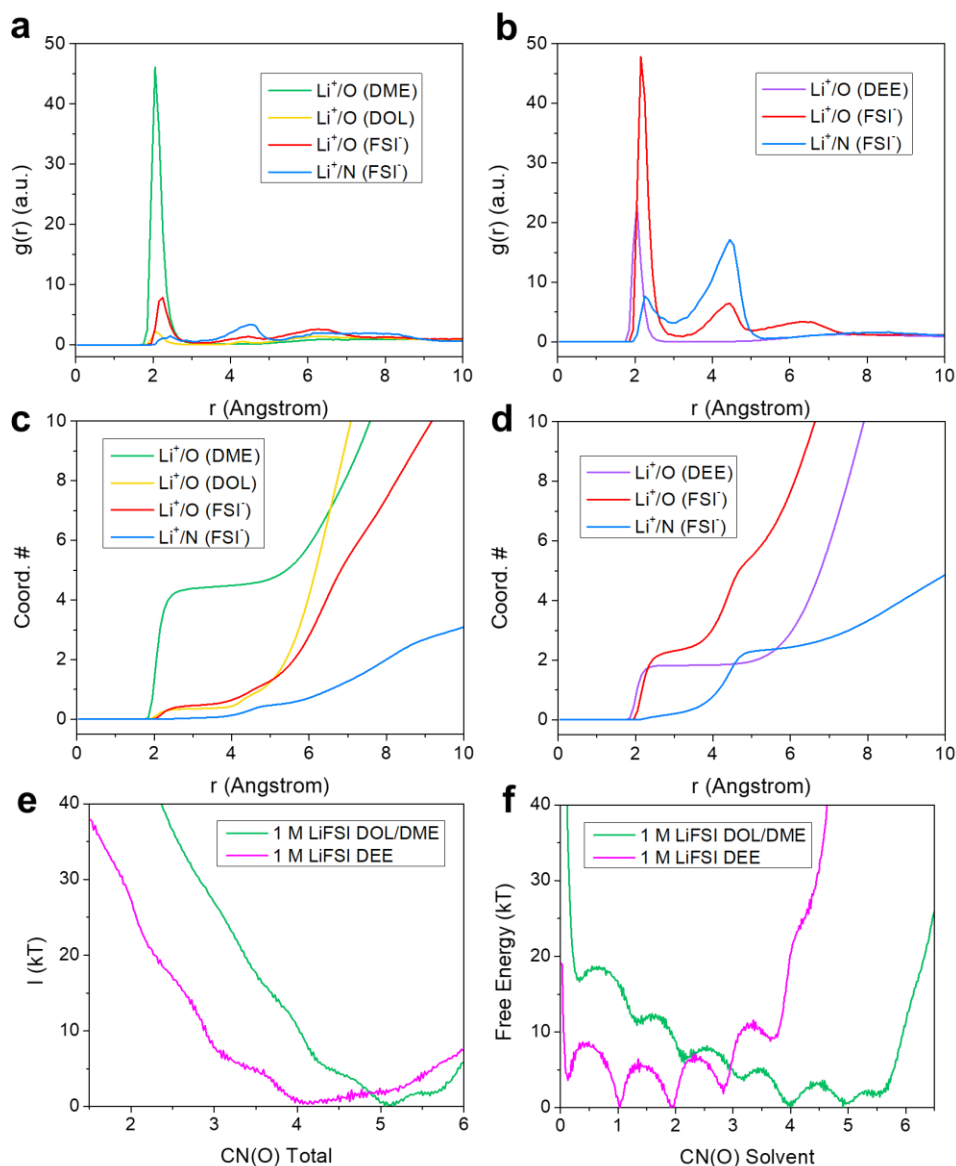
<b>Simulation</b>	<b>Hill Height (kCal mol<sup>-1</sup>)</b>	<b>Hill Width (kCal mol<sup>-1</sup>)</b>	<b>Hill Creation Freq. (fs)</b>	<b>Simul. Time (ns)</b>
1 M LiFSI DOL/DME Bulk <b>1-D, 298 K</b> Fig. S1e & S2a: Li <sup>+</sup> /total CN (0 – 6) Fig. S1f & 4a: Li <sup>+</sup> /solvent CN (0 – 6)	0.02	0.05	500	~ 500
1 M LiFSI DEE Bulk <b>1-D, 298 K</b> Fig. S1e & S2b: Li <sup>+</sup> /total CN (0 – 6) Fig. S1f & 4b: Li <sup>+</sup> /solvent CN (0 – 6)	0.02	0.05	500	~ 500
1 M LiFSI DOL/DME Bulk <b>1-D, 213 K</b> Fig. S2a: Li <sup>+</sup> /total CN (0 – 6) Fig. 4a: Li <sup>+</sup> /solvent CN (0 – 6)	0.01	0.025	1000	~ 700

<p>1 M LiFSI DEE Bulk <b>1-D, 213 K</b> Fig. S2b: Li<sup>+</sup>/total CN (0 – 6) Fig. S4b: Li<sup>+</sup>/solvent CN (0 – 6)</p>	0.01	0.025	1000	~ 700
<p>1 M LiFSI DOL/DME Neutral graphene <b>1-D, 298 K</b> Li<sup>+</sup>/electrode distance (1.5-15 Å) Fig. 1c</p>	0.02	0.05	200	~ 500
<p>1 M LiFSI DEE Neutral graphene <b>1-D, 298 K</b> Li<sup>+</sup>/electrode distance (1.5-15 Å) Fig. 1d</p>	0.02	0.05	200	~ 500
<p>1 M LiFSI DOL/DME Neutral graphene (Fig. 2a) <i>or</i> 11.5 μC cm<sup>-2</sup> graphene (Fig. 2b) <b>2-D, 298 K</b> Li<sup>+</sup>/electrode distance (1.5-15 Å) Li<sup>+</sup>/solvent CN (0 – 6.0)</p>	0.02	0.05	200	~ 600
<p>1 M LiFSI DOL/DME Neutral graphene (Fig. 2a) <i>or</i> 11.5 μC cm<sup>-2</sup> graphene (Fig. 2b) <b>2-D, 298 K</b> Li<sup>+</sup>/electrode distance (1.5-15 Å) Li<sup>+</sup>/solvent + anion CN (0 – 6.0)</p>	0.02	0.05	200	~ 500
<p>1 M LiFSI DEE Neutral graphene (Fig. 3a) <i>or</i> 11.7 μC cm<sup>-2</sup> graphene (Fig. 3b) <b>2-D, 298 K</b> Li<sup>+</sup>/electrode distance (1.5-15 Å) Li<sup>+</sup>/solvent CN (0 – 6.0)</p>	0.02	0.05	200	~ 600

<p>1 M LiFSI DEE Neutral graphene (Fig. 3a) <i>or</i> 11.7 <math>\mu\text{C cm}^{-2}</math> graphene (Fig. 3b) <b>2-D, 298 K</b> Li<sup>+</sup>/electrode distance (1.5-15 Å) Li<sup>+</sup>/solvent + anion CN (0 – 6.0)</p>	0.02	0.05	200	~ 500
<p>1 M LiFSI DOL/DME Neutral graphene <b>2-D, 213 K</b> Li<sup>+</sup>/electrode distance (1.5-12 Å) Li<sup>+</sup>/solvent CN (1.0 – 6.0) Fig. S3a</p>	0.01	0.025	1000	~ 2000
<p>1 M LiFSI DOL/DME Neutral graphene <b>2-D, 213 K</b> Li<sup>+</sup>/electrode distance (1.5-12 Å) Li<sup>+</sup>/solvent + anion CN (1.5 – 6.0) Fig. S3c</p>	0.01	0.025	1000	~ 1400
<p>1 M LiFSI DEE Neutral graphene <b>2-D, 213 K</b> Li<sup>+</sup>/electrode distance (1.5-12 Å) Li<sup>+</sup>/solvent CN (1.0 – 6.0) Fig. S3b</p>	0.01	0.025	1000	~ 2000
<p>1 M LiFSI DEE Neutral graphene <b>2-D, 213 K</b> Li<sup>+</sup>/electrode distance (1.5-12 Å) Li<sup>+</sup>/solvent + anion CN (1.5 – 6.0) Fig. S3d</p>	0.01	0.025	1000	~ 1400
<p>1 M LiFSI DOL/DME 11.5 <math>\mu\text{C cm}^{-2}</math> graphene <b>2-D, 213 K</b> Li<sup>+</sup>/electrode distance (1.5-7 Å) Li<sup>+</sup>/solvent CN (1.0 – 6.0) Fig. 4c</p>	0.01	0.025	1000	~ 2000

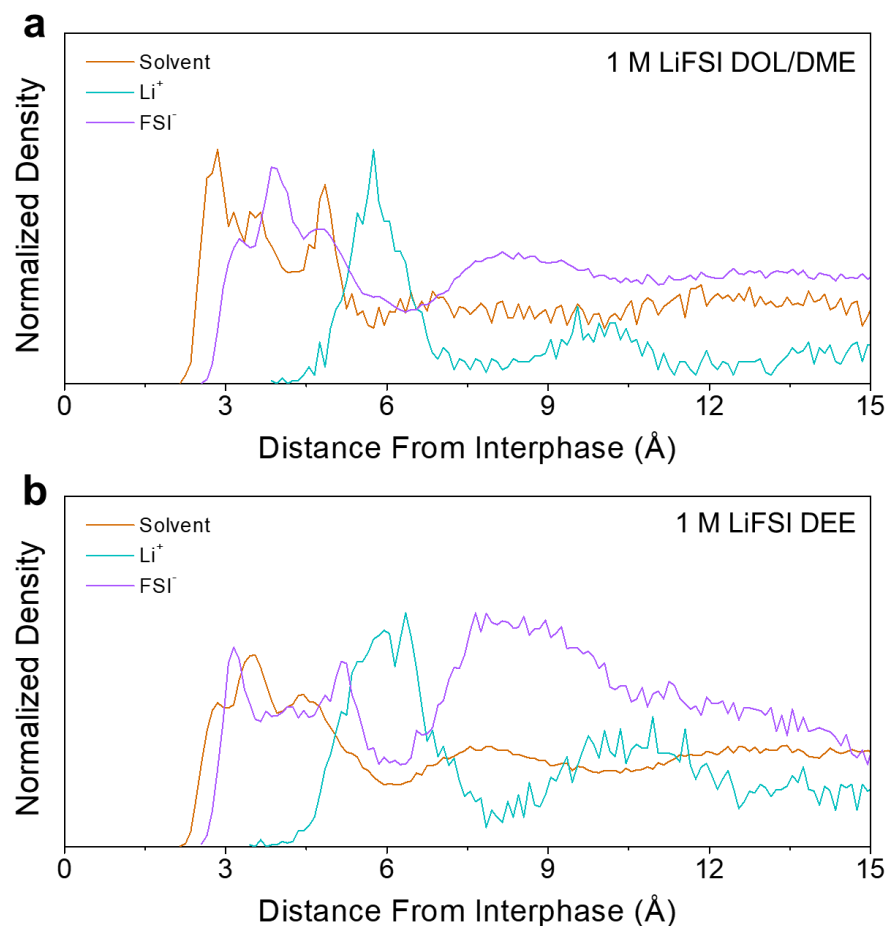
1 M LiFSI DOL/DME 11.5 $\mu\text{C cm}^{-2}$ graphene <b>2-D, 213 K</b> Li <sup>+</sup> /electrode distance (1.5-7 Å) Li <sup>+</sup> /solvent + anion CN (1.5 – 6.0) Fig. S4b	0.01	0.025	1000	~ 1400
1 M LiFSI DEE 11.7 $\mu\text{C cm}^{-2}$ graphene <b>2-D, 213 K</b> Li <sup>+</sup> /electrode distance (1.5-7 Å) Li <sup>+</sup> /solvent CN (0 – 5.0) Fig. 4d	0.01	0.025	1000	~ 2000
1 M LiFSI DEE 11.7 $\mu\text{C cm}^{-2}$ graphene <b>2-D, 213 K</b> Li <sup>+</sup> /electrode distance (1.5-7 Å) Li <sup>+</sup> /solvent + anion CN (1.5 – 6.0) Fig. S4b	0.01	0.025	1000	~ 1400

The free energy profiles shown in this work were averaged over the last 100 ns for 298 K simulations, and the last 200 ns for 213 K simulations. 1-D profiles were generated in Origin Pro, whereas 2-D profiles were generated in gnuplot. Averaged plots and integrated 1-D slices from the 2-D plots shown in figures 2, 3, and 4 were calculated using Python.

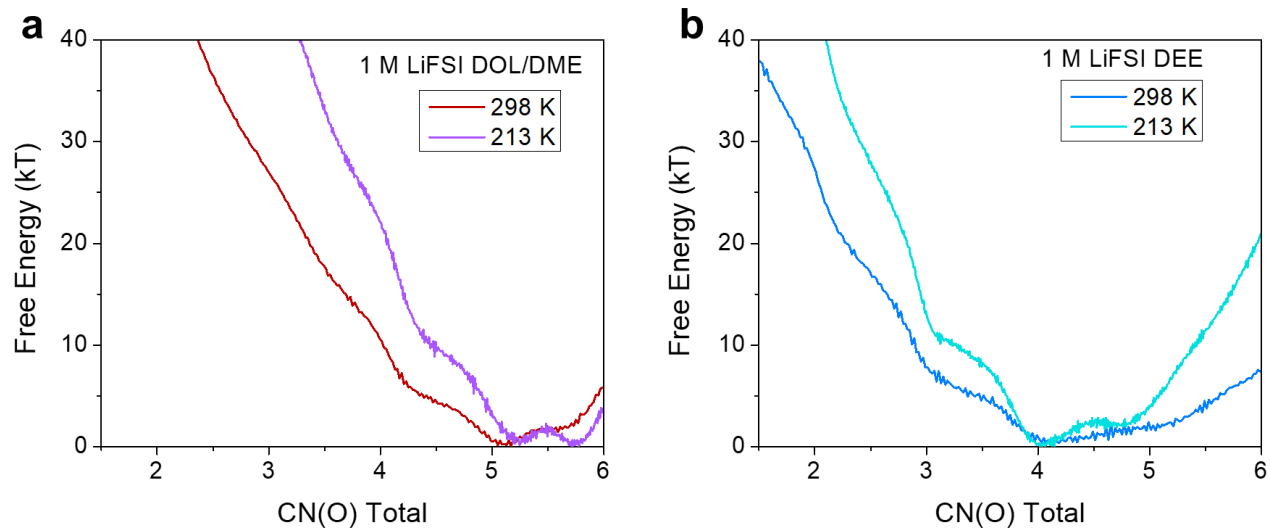


**Figure S1.** Solvation structure analysis of selected electrolytes in bulk MD simulations without an interphase at 298 K.  $\text{Li}^+$  radial distribution function of **a)** 1 M LiFSI DOL/DME, and **b)** 1 M LiFSI DEE extracted from production dynamics post-equilibration.  $\text{Li}^+$  coordination number analysis of **c)** 1 M LiFSI DOL/DME, and **d)** 1 M LiFSI DEE extracted from production dynamics post-equilibration. 1D free energy profiles of bulk electrolytes at 298 K as a function of **e)** total coordination number (FSI and all solvents), and **f)** solvent coordination number.

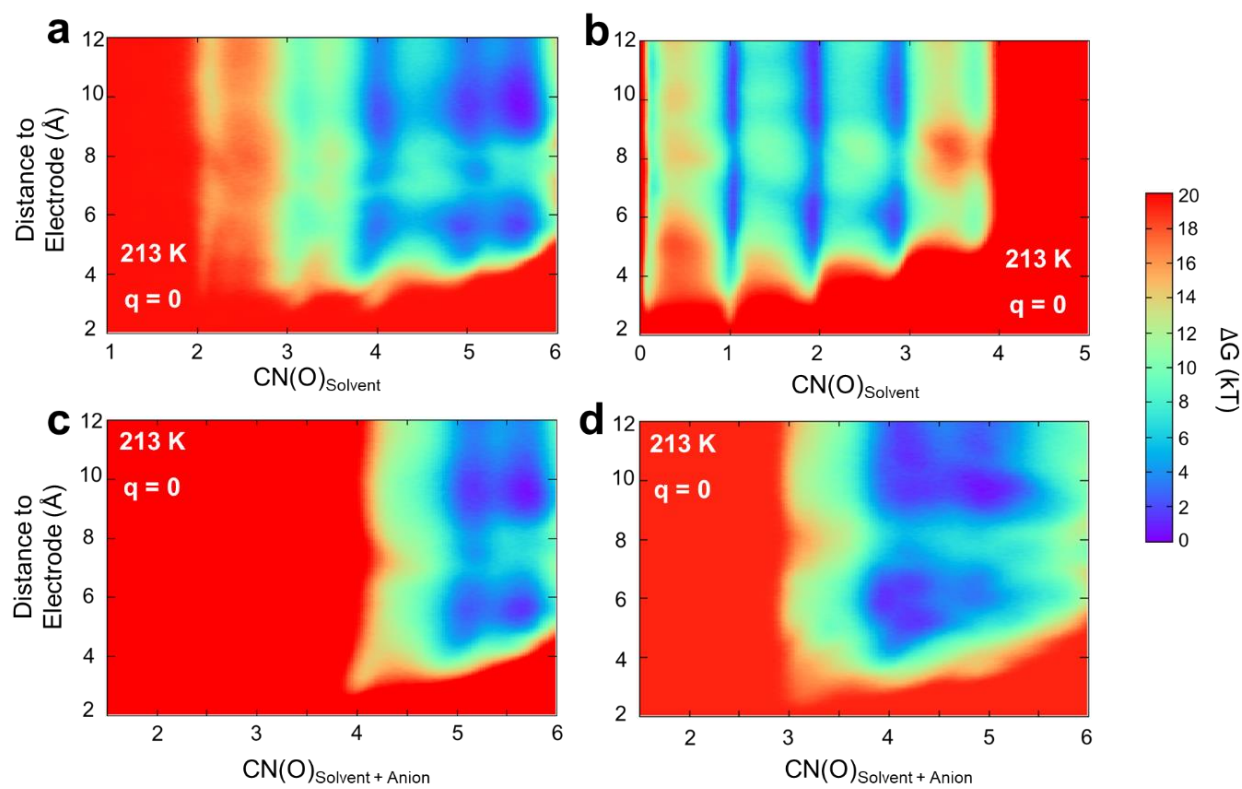




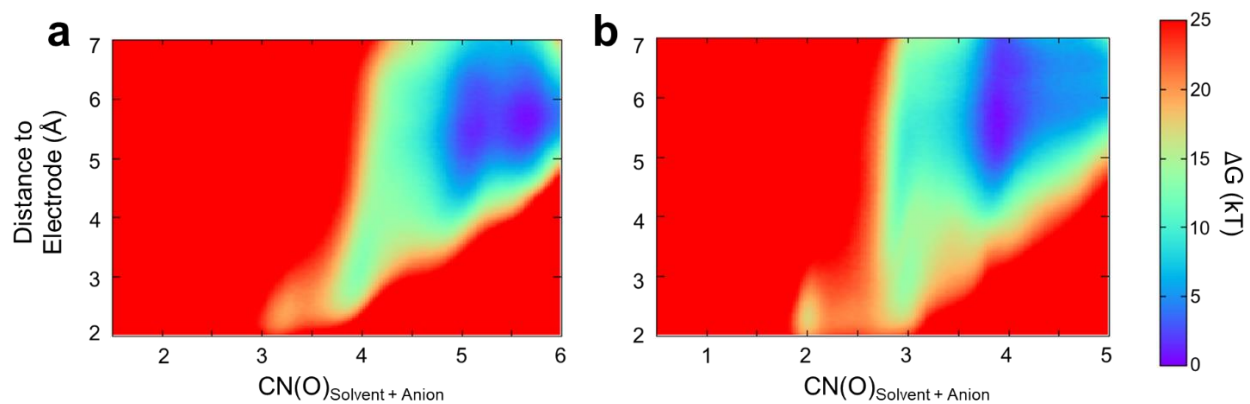
**Figure S2.** Normalized number density profiles from the interphasial regions of equilibration MD runs employing **a)** 1 M LiFSI DOL/DME, and **b)** 1 M LiFSI DEE in contact with graphene averaged over the production portion of equilibration dynamics. The total number density profiles are shown in Figures 2e and 2f.



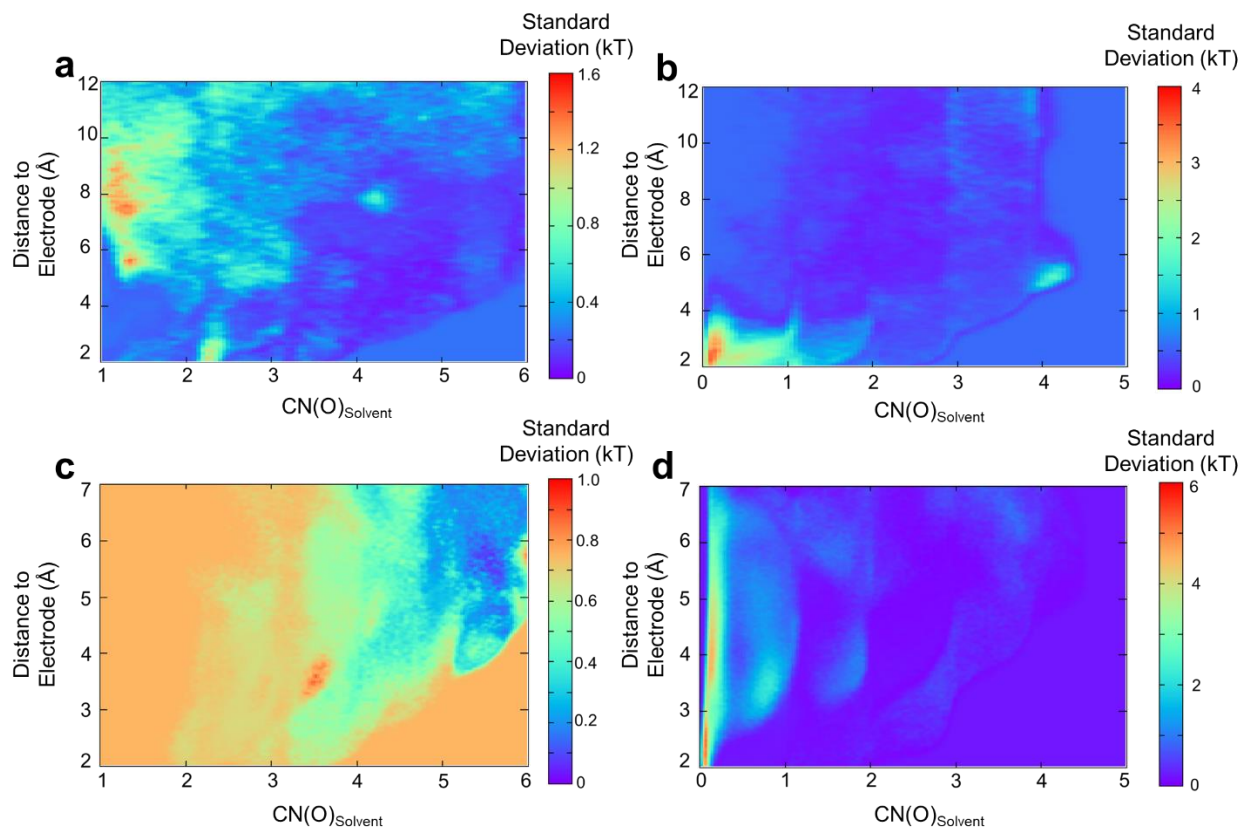
**Figure S3.** 1D Free energy profiles as a function of total Li<sup>+</sup>/oxygen coordination number (solvent & anion) in **a)** 1 M LiFSI DOL/DME, and **b)** 1 M LiFSI DEE.



**Figure S4.** 2D Free energy profiles of electrolyte/graphene cells with a neutral charge at 213 K as a function of  $\text{Li}^+$ /graphene distance. Profiles with respect to  $\text{Li}^+$ /solvent oxygen coordination number in **a)** 1 M LiFSI DOL/DME, and **b)** 1 M LiFSI DEE. Profiles with respect to  $\text{Li}^+$ /solvent and anion oxygen coordination number in **c)** 1 M LiFSI DOL/DME, and **d)** 1 M LiFSI DEE.



**Figure S5.** 2D Free energy profiles of electrolyte/charged graphene cells at 213 K as a function of  $\text{Li}^+$ /graphene distance. Profiles with respect to  $\text{Li}^+$ /solvent and anion oxygen coordination number in **a**) 1 M LiFSI DOL/DME, and **b**) 1 M LiFSI DEE.



**Figure S6.** Standard deviation of averaged profiles utilizing charged graphene electrodes and 1 M LiFSI DOL/DME and 1 M LiFSI DEE. Statistics corresponding to **a)** Figure 2b, **b)** Figure 3b, **c)** Figure 4c, and **d)** Figure 4d.

## References

- [1] Kaminski, G. A.; Friesner, R. A.; Tirado-Rives, J.; Jorgensen, W. L. Evaluation and Reparametrization of the OPLS-AA Force Field for Proteins via Comparison with Accurate Quantum Chemical Calculations on Peptides. *J. Phys. Chem. B* **2001**, *105* (28), 6474–6487.
- [2] L. Gouveia, A. S.; S. Bernardes, C. E.; C. Tomé, L.; I. Lozinskaya, E.; S. Vygodskii, Y.; S. Shaplov, A.; Canongia Lopes, J. N.; M. Marrucho, I. Ionic Liquids with Anions Based on Fluorosulfonyl Derivatives: From Asymmetrical Substitutions to a Consistent Force Field Model. *Physical Chemistry Chemical Physics* **2017**, *19* (43), 29617–29624.
- [3] Pascal, T. A.; Karasawa, N.; Goddard, W. A. Quantum Mechanics Based Force Field for Carbon (QMFF-Cx) Validated to Reproduce the Mechanical and Thermodynamics Properties of Graphite. *J. Chem. Phys.* **2010**, *133* (13), 134114.
- [4] Park, C.; Kanduč, M.; Chudoba, R.; Ronneburg, A.; Risse, S.; Ballauff, M.; Dzubiella, J. Molecular Simulations of Electrolyte Structure and Dynamics in Lithium–Sulfur Battery Solvents. *Journal of Power Sources* **2018**, *373*, 70–78.
- [5] W. Shinoda, M. Shiga, M. Mikami, Rapid estimation of elastic constants by molecular dynamics simulation under constant stress, *Physical Review B* **69** (2004) 134103.
- [6] G.J. Martyna, D.J. Tobias, M.L. Klein, Constant pressure molecular dynamics algorithms, *J. Chem. Phys.* **101** (1994) 4177-4189.
- [7] M. Parrinello, A. Rahman, Polymorphic transitions in single crystals: A new molecular dynamics method, *J. Appl. Phys.* **52** (1981) 7182-7190.
- [8] M.E. Tuckerman, J. Alejandre, R. López-Rendón, A.L. Jochim, G.J. Martyna, A Liouville-operator derived measure-preserving integrator for molecular dynamics simulations in the isothermal–isobaric ensemble, *J. Phys. A: Math. Gen.* **39** (2006) 5629.
- [9] Laio, A.; Gervasio, F. L. Metadynamics: A Method to Simulate Rare Events and Reconstruct the Free Energy in Biophysics, Chemistry and Material Science. *Rep. Prog. Phys.* **2008**, *71* (12), 126601.
- [10] Barducci, A.; Bonomi, M.; Parrinello, M. Metadynamics. *WIREs Computational Molecular Science* **2011**, *1* (5), 826–843.
- [11] Giacomo Fiorin, Michael L. Klein, and Jérôme Hénin. Using collective variables to drive molecular dynamics simulations. *Mol. Phys.*, **111**(22-23):3345--3362, 2013.
- [12] Baskin, A.; Prendergast, D. “Ion Solvation Spectra”: Free Energy Analysis of Solvation Structures of Multivalent Cations in Aprotic Solvents. *J. Phys. Chem. Lett.* **2019**, *10* (17), 4920–4928.