## **Supporting Information**

Model Systems for Screening and Investigation of Lithium Metal Electrode Chemistry and Dendrite Formation

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For the sake of comparison with the Li cluster reductions, traditional reduction calculations were done with Gaussian. Table S1 shows the reduction energies for common solvent molecules used in lithium battery chemistry with implicit only solvent.

	DME	DOL	EC
Neutral (h)	-308.67	-268.23	-342.32
Reduced (h)	-308.62	-268.20	-342.34
ΔG (eV)	1.42	0.96	0.52
ΔΕ (V)	-1.42	-0.96	-0.52

Table S1: Reduction Calculation and Energies of DME, DOL and EC

The values in the table were calculated by first optimizing each molecule in an implicit solvent field representing the bulk of that solvent. For instance, a DME molecule in a "field" of DME. This optimization is the neutral energy listed. Then the simulation is modified to add an electron to the solvent molecule and then the structure is reoptimized giving the reduced energy. Then the reduced energy is subtracted from the neutral energy providing the Delta G in adding an electron or the reduction energy. This delta G is then transformed into the reduction potential via the Nernst equation. In many publications and reports of the reduction potential, a different calculation method is used known as the thermodynamic cycle. The thermodynamic cycle approach indirectly calculates the same energy but by calculating the difference in structures from the gas phase 1<sup>st</sup> and then adding in the effects of the field. This approach was originally developed to improve the accuracy of calculation due to limitations of the available basis sets. At the time, smaller basis sets which describe the orbitals less accurately were used for the sake of computational resources. The smaller basis sets used in this paper are much larger and more descriptive therefore it is not necessary to utilize the thermodynamic cycle approach to the reduction calculation.

From Table S1, none of the three solvents has a favorable reduction as demonstrated by the negative potential. This means that it is thermodynamically unfavorable for these solvents to be reduced. EC and DOL are respectively more favorable than DME. This has been reported both computationally and experimentally. The results here will be used for comparison later and show that this method of reduction calculation is consistent so far.

Table S2: Li ion reduction with implicit solvent

	DME	DOL
Neutral	-7.41	-7.5
Reduced	-7.48	-7.54
ΔΕ (V)	1.95	1.1

Table S2 shows the implicit solvent reduction results for a lithium ion in DME and DOL. There is  $\sim 0.8$  V difference between the reduction potential for DME and DOL. This gives some indication of how much the implicit solvent field changes the results. The change in reduction potential must be caused by that change since no other modifications are present. DME has a higher dielectric constant which causes the increase in reduction potential for the lone lithium ion.

Table S3: Li+ with 1 explicit DME

Orientation	E (V)	Reduction Location
	1 1.30	) Li
	2 0.70	) Li
	<b>3</b> 0.56	i Li

The next step in implementing the more advanced cluster-continuum solvation model is to introduce explicit solvent molecules into the simulation. The two tables above contain the results for Li+ with DME and DOL along with an implicit solvent. There is a noticeable shift in reduction potential compared to Table 2 for the DME simulations. In each case the potential is lower than in the implicit only simulation. One interesting detail to draw attention to is the difference in reduction energies even though the electron reduced the same location. This difference is caused by the geometry of the optimized simulations and related effects.

Table S4 : FSI reduction with implicit solvent.

	DME	DOL	EC
Neutral	-1351.36	-1351.37	-1351.36
Reduced	-1351.62	-1351.63	-1351.62
ΔΕ (V)	7.18	7.13	7.23

Table S4 contains the implicit solvent reduction results for the FSI anion. In contrast to the results from the Li+ reduction, the FSI ion reduction energy doesn't change much with the different choices of solvent. This result indicates that the larger molecules are less sensitive to the effects of the implicit solvent or that positive ions are more heavily affected by the implicit solvent. Next we explored what the effects of including explicit solvent ions in our previous models.

Table S5 : LiFSI with 1 explicit DME

<b>Explicit Method LiFSI in DME</b>	Gneutral (H)	Greduced (H)	ΔE (V)	ΔE (V)	<b>Reduced Site</b>
				(Li/Li+)	
Orientation 1	-1667.76	-1667.78	0.72	-0.65	solvent
Orientation 2	Same as 1	-	-	-	-
Orientation 3	-1667.76	-1667.78	0.68	-0.69	Li
Orientation 4	Same as 3	-	-	-	-
Orientation 5	-1667.75	-1667.79	0.1	-0.37	Li
Orientation 5	-1667.76	-1667.79	0.9	-0.47	anion
Orientation 6	-1667.75	-1667.75	0.1	-1.27	solvent
Orientation 7	-1667.73	-1667.83	2.72	1.35	anion

In the calculations for table 4. 7 Different geometry configurations were used as initial configurations for the neutral and reduced species. When introducing more than one molecule to the simulation, the initial configuration used will change the final configuration. Unfortunately, most computational chemistry programs are not able to determine the lowest possible energy from any initial configuration so in order to find the true lowest energy configuration multiple unique input configurations must be used. For orientations 3 and 2, the unique input geometry gave the same final geometry as orientation 1 and 3.



Figure S1: Neutral LiFSI with DME optimized geometries.

Figure S1 shows how in some cases the DME molecule closely interacts with the Li+ in the LiFSI but in other cases does not. This is due to the location of the DME in the input geometry thus demonstrating why testing multiple input configurations is important. The reduction for the different cases shows disparity which is mostly due to where the electron actually went in the simulation. Due to how first principles simulations work, the electron for the reduction cannot be directly assigned to a specific location. The simulation will place the electron in the configuration that provides the lowest energy. Based on the location of the DME in the input changed which chemical species was reduced. The localization of the additional electron can be determined by analyzing the spin density. Orientations 1 and 3 which are similar in structure had similar reduction energies and the location of the reduction was the same. The electron was distributed mostly on the lithium ion but some of the electron was localize on the solvent as well. Orientation 6 and 7 have different reduction energies than the other cases due to differences in the reduction site as shown by the table. We can infer that when the DME is interacting with the Li+ ion, the ion is more likely to be reduced. For orientations 6 and 7 where the Li+ is not solvated by DME, the location of reduction is different. This effect is possibly due to stabilization of the Li+ or other species by the solvation of a DME which provides a more energetically favorable environment.

Table S6: LiFSI with explicit DOL

Explicit Method LiFSI in DOL	Gneutral (H)	Greduced (H)	ΔE (V)	ΔE (V)	<b>Reduced Site</b>
				(Li/Li+)	
Orientation 1	-1621.781	-1621.809	0.752	-0.618	

The DME was then replaced with DOL for analogous simulations. Only one orientation was tested due to fewer unique input geometries and that all the different geometries gave the same optimized geometry. The DOL reduction potential determined is similar to the reduction potential for orientations 1 and 3 of the DME explicit results. In these cases, the Li+ ion of the LiFSI molecule was reduced. All the potentials were in the range of 0.6-0.8 eV which is significantly different than the Li+ ion in implicit solvent (Table 2 ). In the EC cases, the reduced site changed in the implicit versus the explicit simulation. The differences in the simulations are the presence of explicit solvent molecules and the FSI anion. The additional molecules have a strong effect on the value of the reduction potential proving that adding more chemical details to the simulations will change the results.

Orientation	E (V)	Reduction Location
1	1.08	Li
2	2.30	Anion (Carbon 12)
3	1.18	Li
4	1.11	Li
5	0.58	Li
6	2.96	Anion (Sulfur 2)

Table S8:	LiTFSI	with	Ex	plicit	DOL

Orientation	E (V)	Reduction Location
1	2.31	Li
2	2.41	Anion (Carbon 12)
3	0.61	Li
4	2.45	Li

Another commonly used lithium salt is LiTFSI. The corresponding reduction calculations are shown in the three tables above. Once again, the effect of different input orientations of the explicit solvent molecules can cause different species to be reduced giving a large disparity in reduction potential (i.e. orientation 1 vs orientation 2) just as with the LiFSI. Even amongst the different Li+ reductions, the potential was not static based on the final geometry of the configuration. Another note is that even in simulations where the Li+ of the LiTFSI was not solvated, Li+ ion reduction was common. This is related to the lower reactivity and reduction potential of the LiTFSI that has been reported previously. In the DME and DOL simulations one of the Li+ has a lower reduction potential than the other Li+. In these simulations, a solvent molecule is closely interacting with the Li+ of the LiTFSI via the solvent molecule's oxygen atom.





Figure S2: Li+ insertion and reduction pathways for Li clusters upto 10 atoms based on thermodynamic calculations

$Li_2 \xrightarrow{1} Li_3$
$Li_3 \xrightarrow{2} Li_4$ $Li_4$
$Li_4 \xrightarrow{4}_{5} \begin{array}{c} \alpha - Li_5 \\ Li_5 \end{array} \xrightarrow{6}_{16} \begin{array}{c} Li_6 \\ Li_6 \end{array}$
$Li_{5} \xrightarrow[10]{8} \stackrel{Q}{\xrightarrow{Q}} \frac{Li_{6}}{\alpha - Li_{6}} \xrightarrow{11} \alpha - Li_{7}$ $Li_{6}$
$Li_{6} \xrightarrow{12} Li_{7} Li_{7} \xrightarrow{Li_{7}} \frac{14}{15} \xrightarrow{\alpha - Li_{8}} \frac{16}{17} \xrightarrow{\alpha - Li_{9}} \frac{21}{22} Li_{10} \xrightarrow{Li_{10}} \frac{14}{15} \xrightarrow{\beta - Li_{8}} \frac{18}{18} Li_{9} 23 \xrightarrow{Li_{9}} Li_{9} \xrightarrow{Li_{9}} Li_{9} \xrightarrow{Li_{9}} Li_{9}$
Li <sub>7</sub> Li <sub>8</sub> Li <sub>8</sub>
Li <sub>8</sub> Li <sub>9</sub> Li <sub>9</sub>
$Li_9 $ $Li_{10}$ $Li_{10}$

Figure S3: Evolution of Li clusters up to 10 atoms based on electrostatic potential based method.

Table S9:



Figure S4: Electrostatic potential for neutral clusters. Orange is negative and Yellow is positive . Isosurface value of 0.008 au



Figure S5: Total Electron Densities for neutral Li Clusters. Isosurface value of 0.008 au



Figure S6: Electrostatic Potentials for Li clusters with 1 additional electron. Orange is negative . Yellow is Positive. Isosurface value of 0.05 au.



Figure S7: Total Electron Densities for Li clusters with 1 additional electron. Isosurface value of 0.05 au.



Figure S8: Geometry , electrostatic potential and total electron density respectively for subset of Li clusters with 1 electron removed. Isosurface value of 0.2 au.



## Li<sub>1</sub> Systems

Li<sub>5</sub> Systems



Li<sub>10</sub> Systems



Li<sub>15</sub> Systems



Li<sub>20</sub> Systems

![](_page_15_Figure_0.jpeg)

Figure S9: Structures, spin densities, reduction or cluster formation energies and HOMO isosurface for all Li reductions. Isosurface values of 0.008 au were used for all systems

![](_page_15_Figure_2.jpeg)

![](_page_16_Figure_0.jpeg)

![](_page_17_Figure_0.jpeg)

Figure S10: Electrostatic potential of Li clusters upto 10 atoms with external field applied. Isosurface values of 0.008,0.008,0.02 respectively.

![](_page_18_Figure_0.jpeg)

Figure S11: Most Acentric Case for  $Li_{1000}$  electrode Model

![](_page_18_Figure_2.jpeg)

Figure S12: Structures of DME, LiFSI and LiTFSI with atom color legend