Effects of High and Low Salt Concentration in Electrolytes at Lithium-Metal Anode Surfaces

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Supporting Information

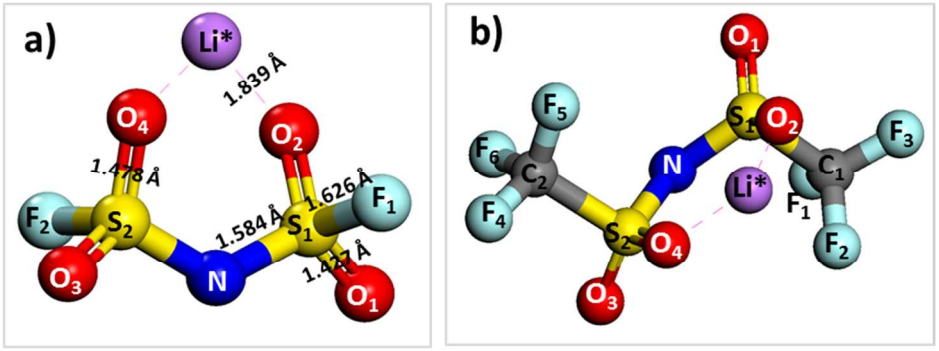

Figure S1. Optimized structures of salt molecules: (a) LiFSI and (b) LiTFSI. Color code as in Figure 1.

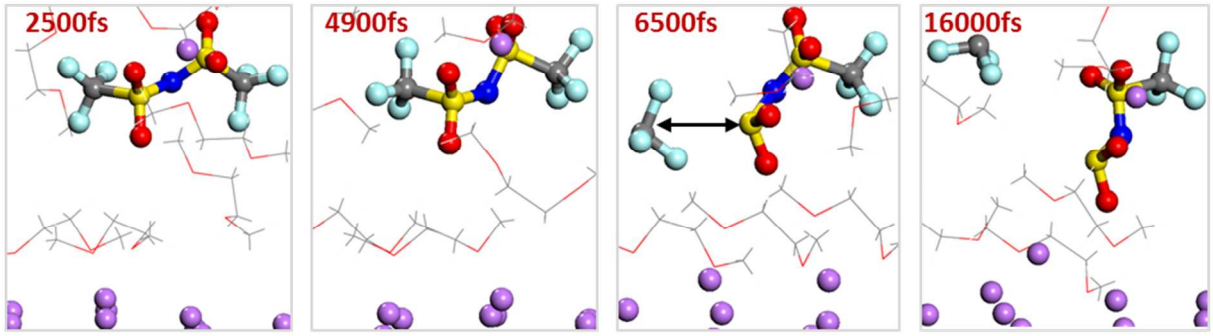

Figure S2. 1M-LiTFSI in DME reduction mechanism. Average charge of Li (form LiTFSI) is 0.88 (±0.01) |e| over the entire simulation time. Color code as in Figure 1.

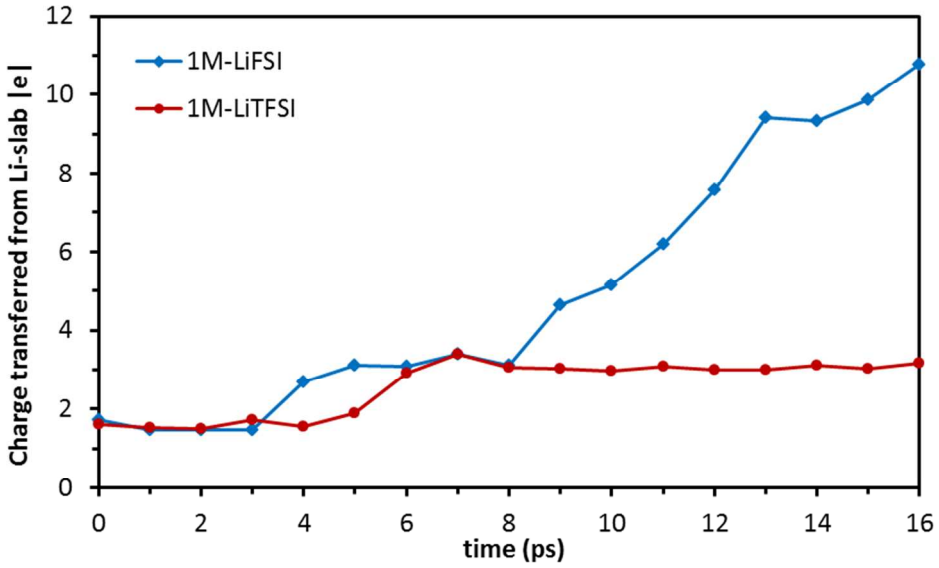

Figure S3. Total charge transfer from the Li anode to the electrolyte in 1M salt in DME. Non-zero initial charge (~2 |e|) is due to solvation/interaction of surface lithium atoms with the electrolyte from the initial model, see example in Figure S10b.

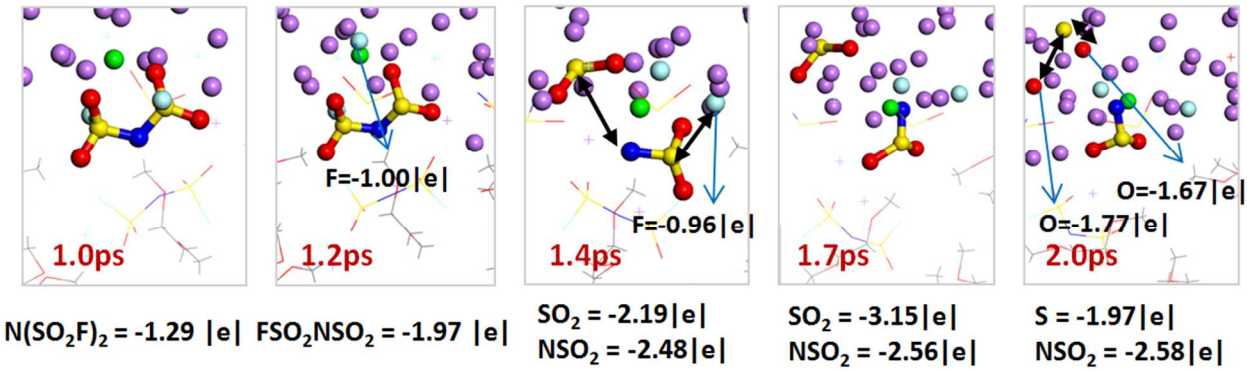

Figure S4. 2-LiFSI reduction mechanism in a 4M-LiFSI/DME solution. Average charge of Li (form LiFSI) 0.83 (±0.04) |e| over the entire simulation time. Color code as in Figure 1.

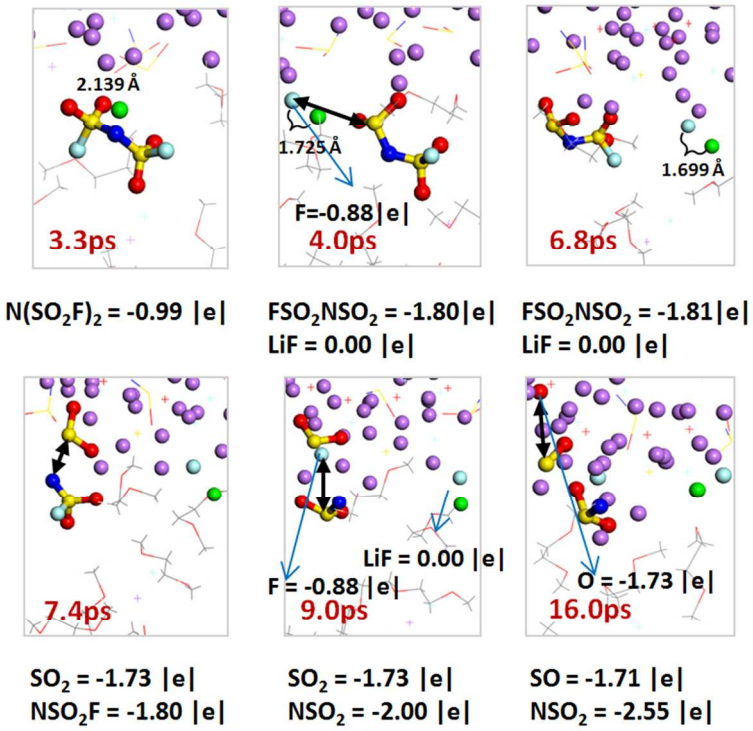

Figure S5. 3-LiFSI reduction mechanism in a 4M-LiFSI/DME solution. Average charge of Li (form LiFSI) 0.88 (±0.01) |e| over the entire simulation time. Color code as in Figure 1.

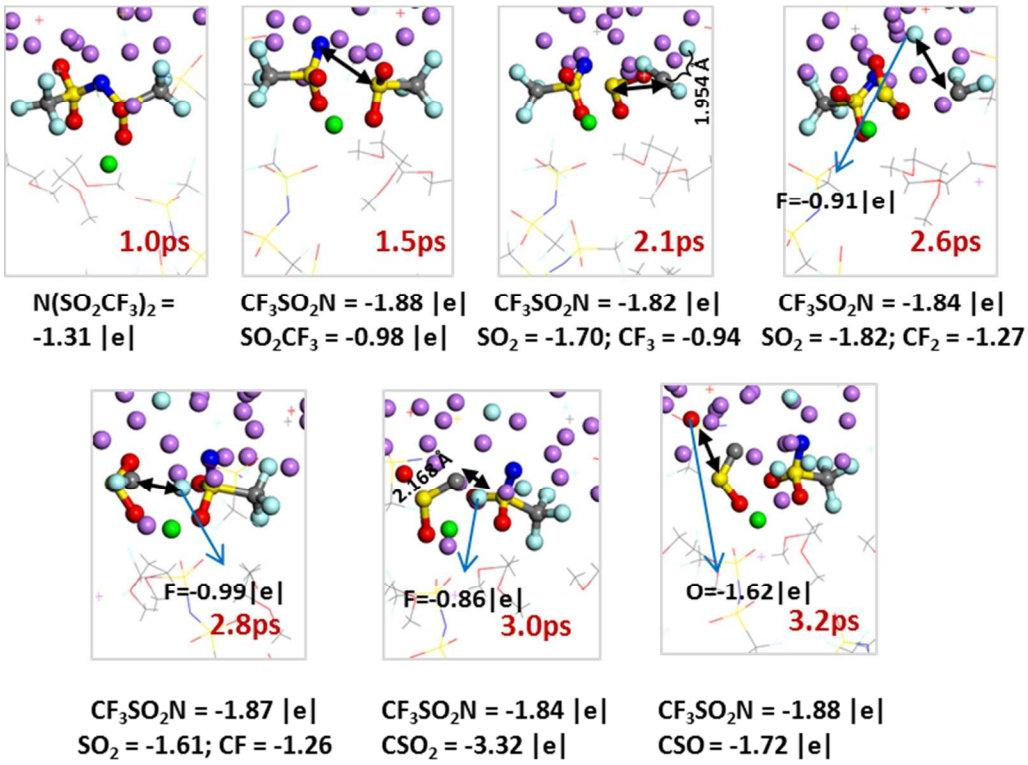

Figure S6. 1-LiTFSI reduction mechanism in a 4M-LiTFSI/DME solution. Average charge of Li (form LiTFSI) 0.88 (±0.01) |e| over the entire simulation time. Color code as in Figure 1.

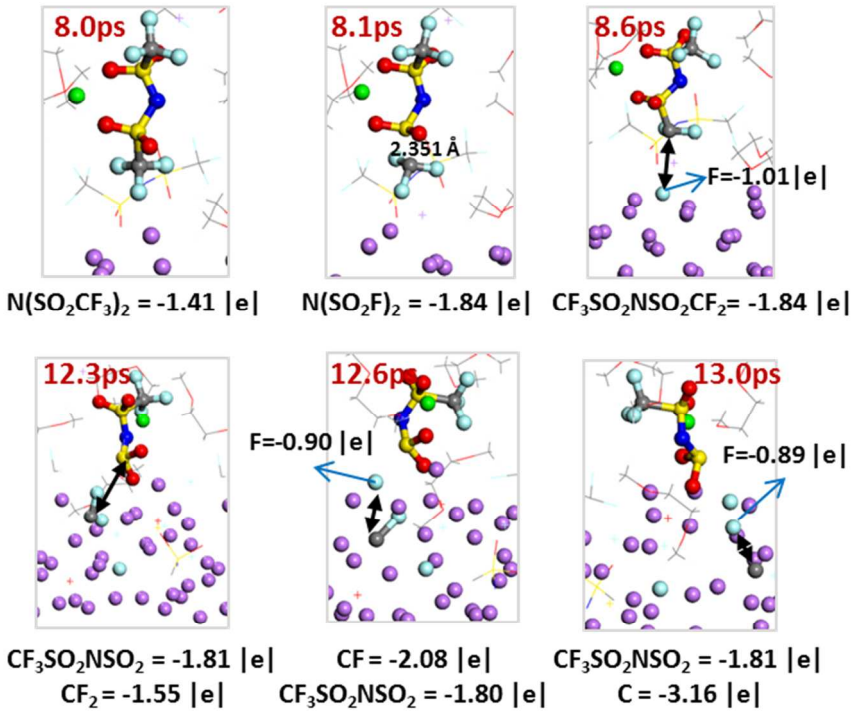

Figure S7. 2-LiTFSI reduction mechanism in a 4M-LiTFSI/DME solution. Average charge of Li (form LiTFSI) 0.88 (±0.01) |e| over the entire simulation time. Color code as in Figure 1.

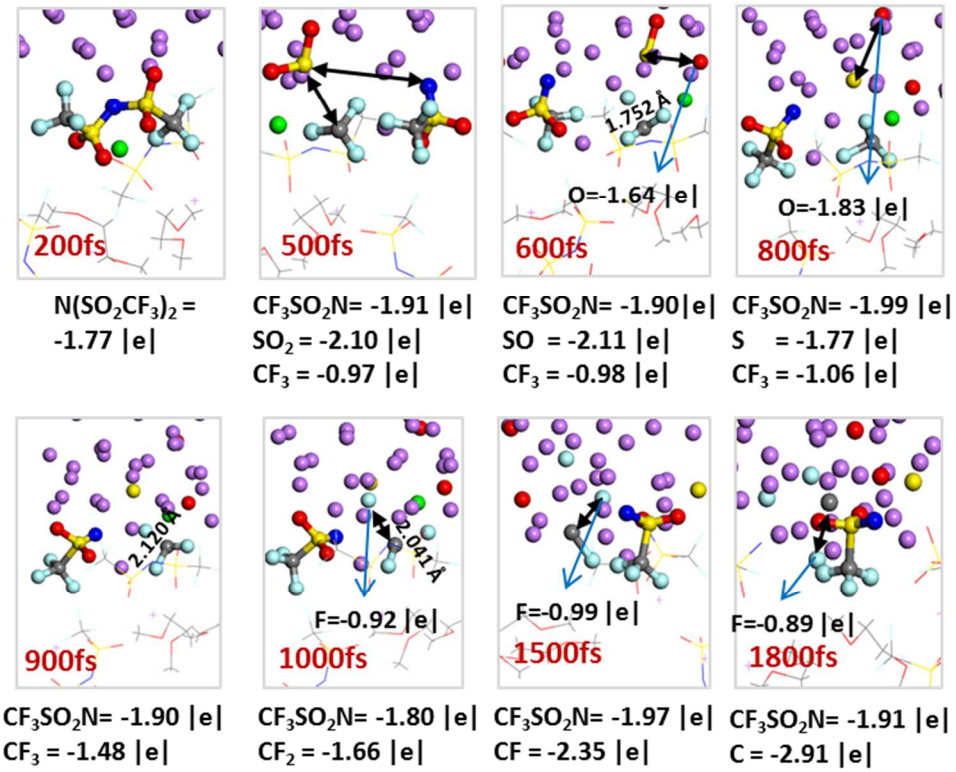

Figure S8. 3-LiTFSI reduction mechanism in a 4M-LiTFSI/DME solution. Average charge of Li (form LiTFSI) 0.85 (±0.01) |e| over the entire simulation time. Color code as in Figure 1.

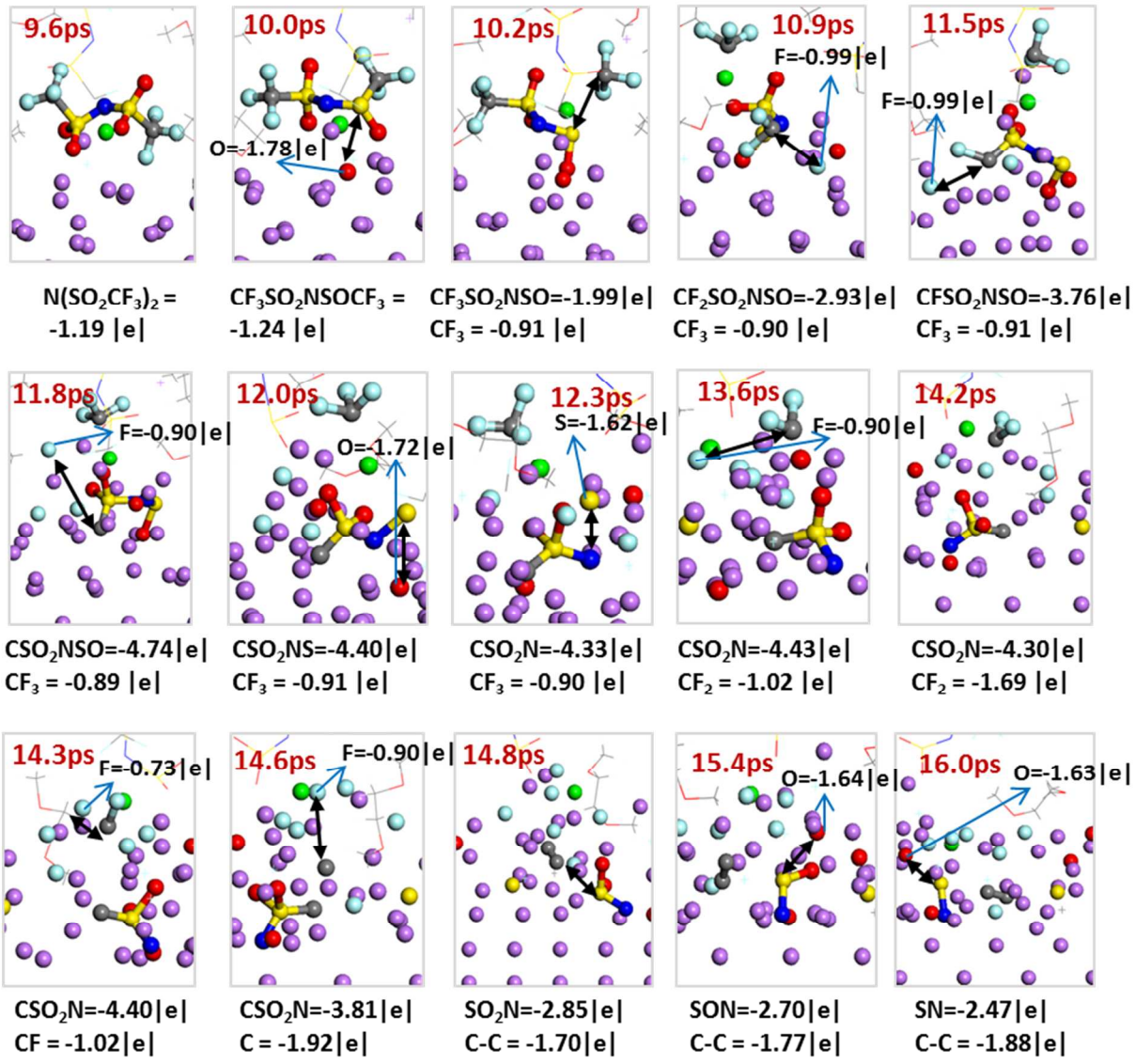

Figure S9. 4-LiTFSI reduction mechanism in a 4M-LiTFSI/DME solution. Average charge of Li (form LiTFSI) 0.87 (±0.03) |e| over the simulation entire time. Color code as in Figure 1.

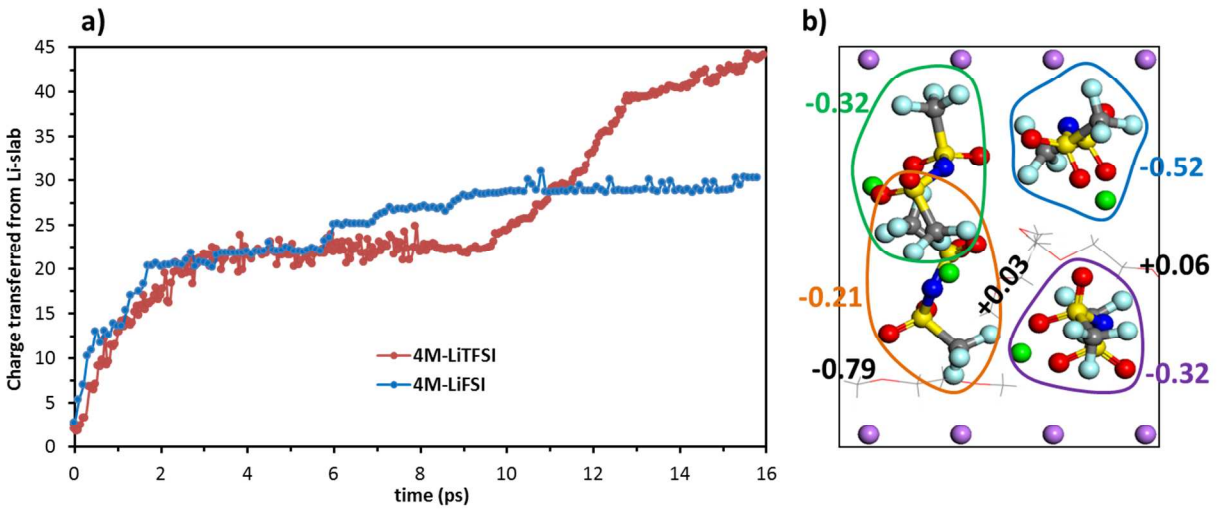

Figure S10. a) Total charge transfer from the Li anode to the electrolyte in 4M salt in DME. Non-zero initial charge (~2 |e|) is due to solvation/interaction between surface lithium atoms with the electrolyte from the initial model. b) Charge distribution (in |e|) of the species forming the electrolyte mixture at time 0 ps. Here the 4M-LiTFSI solution was used as an example to illustrate the non-zero initial charge due to anode/electrolyte interactions for initial configurations as shown in Figures S3 and S10a. Total electrolyte charge at 0 ps is -2.07 |e|. Color code as in Figure 1.

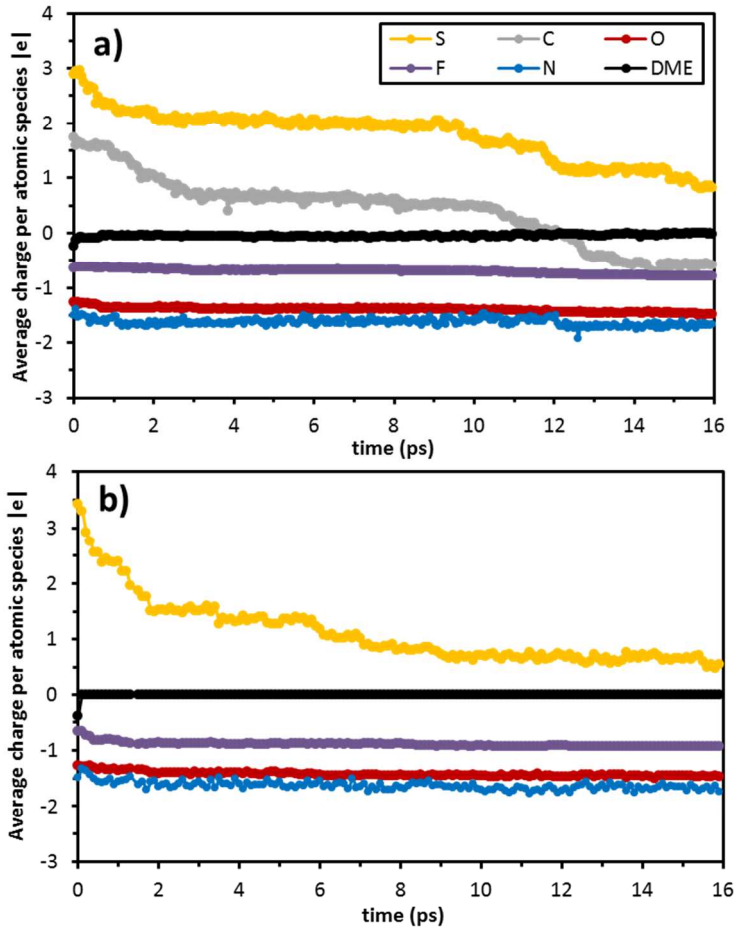

Figure S11. Average charge per atomic species within salts and DME molecules. a) LiTFSI and b) LiFSI

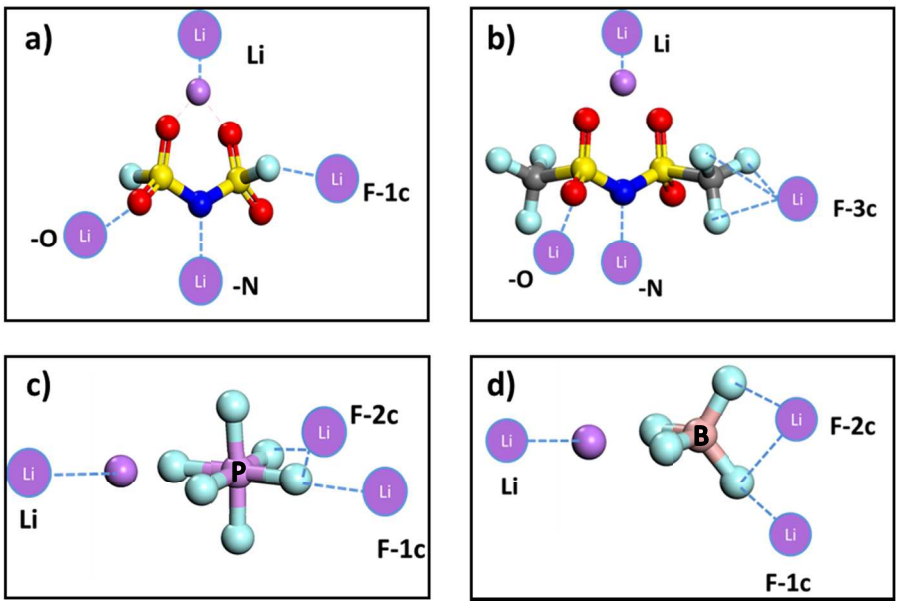

Figure S12. Initial configurations used for study of Li^x (x=0, 1) attack to different salts: a) LiFSI, b) LiTFSI, c) $LiPF_6$, and d) $LiBF_4$. Color code as in Figure 1.

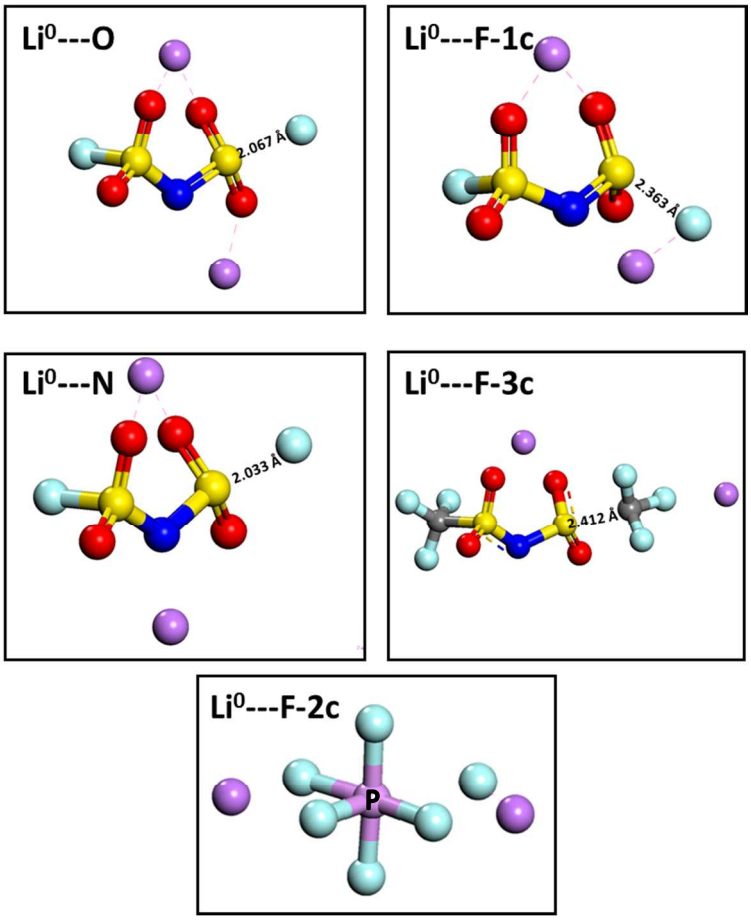

Figure S13. Resulting optimized configurations formed from spontaneous reactions caused by Li^0 radical attack. Color code as in Figure 1.

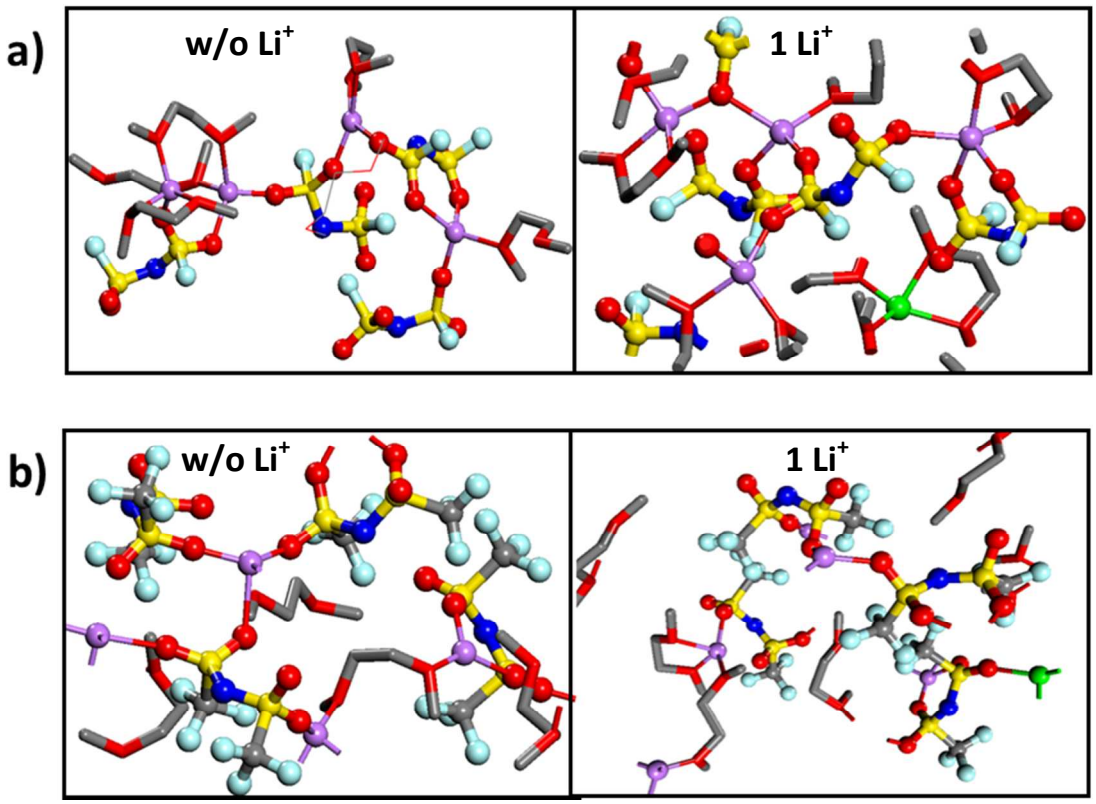

Figure S14. 4M-salt electrolyte solutions after 20ps of simulation time at 330K with different concentration of Li-ions. a) LiFSI and b) LiTFSI, respectively. Color code as in Figure 8. Hydrogen atoms are not shown for clarity.

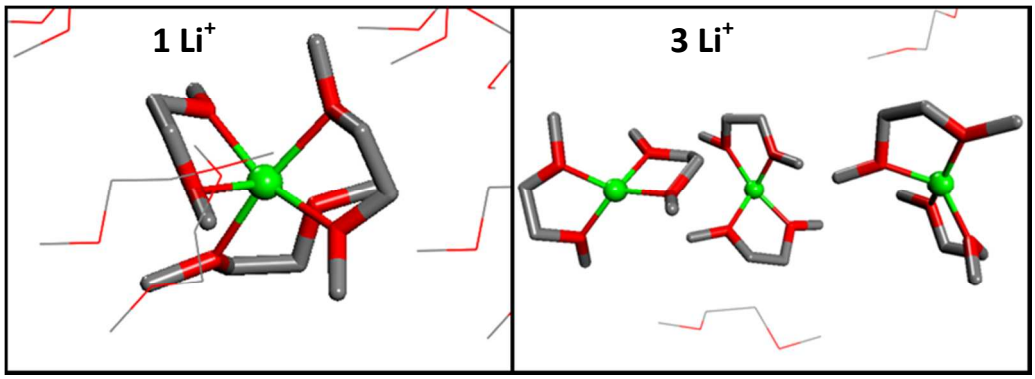

Figure S15. Pure DME after 20ps of simulation time at 330K with different concentration of Li-ions. Color code as in Figure 8. Hydrogen atoms are not shown for clarity.

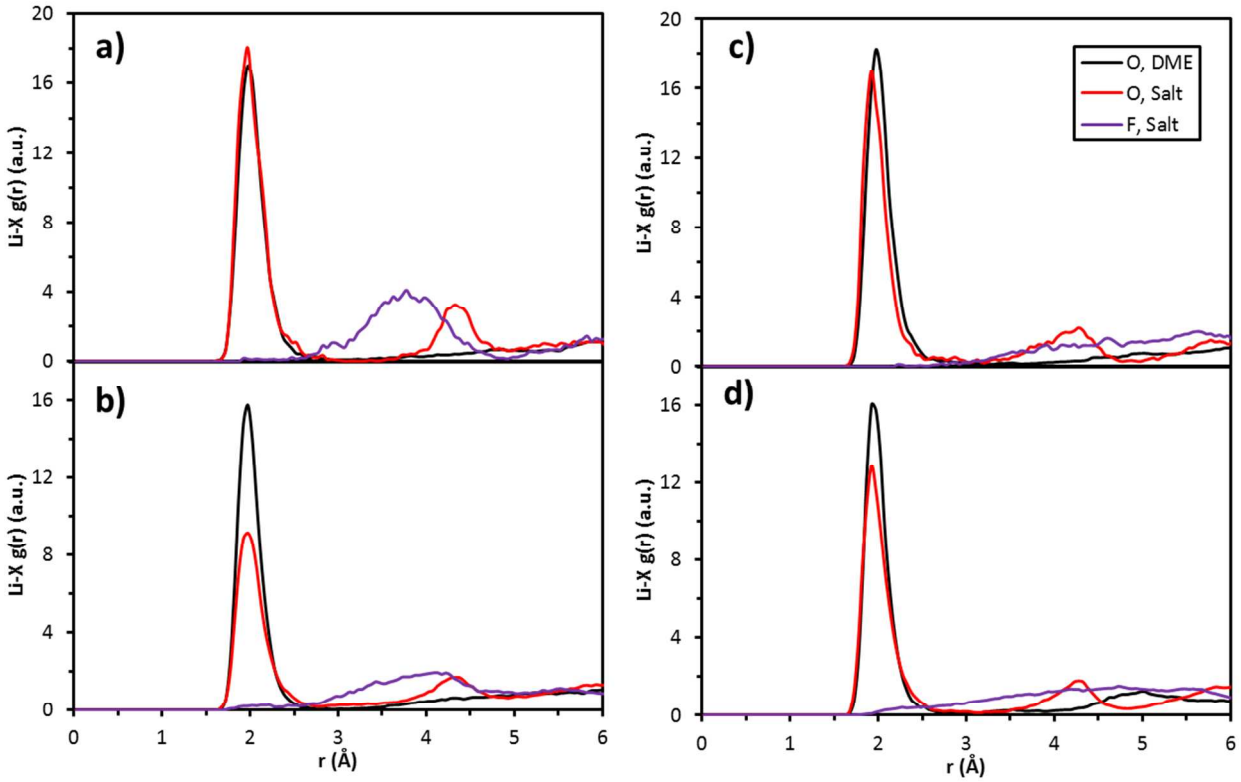

Figure S16. Radial distribution function for Li^+--X (X=O and F atoms) pairs for solutions with one additional cation. a) 1M-LiFSI, b) 4M-LiFSI, c) 1M-LiTFSI, and d) 4M-LiTFSI.

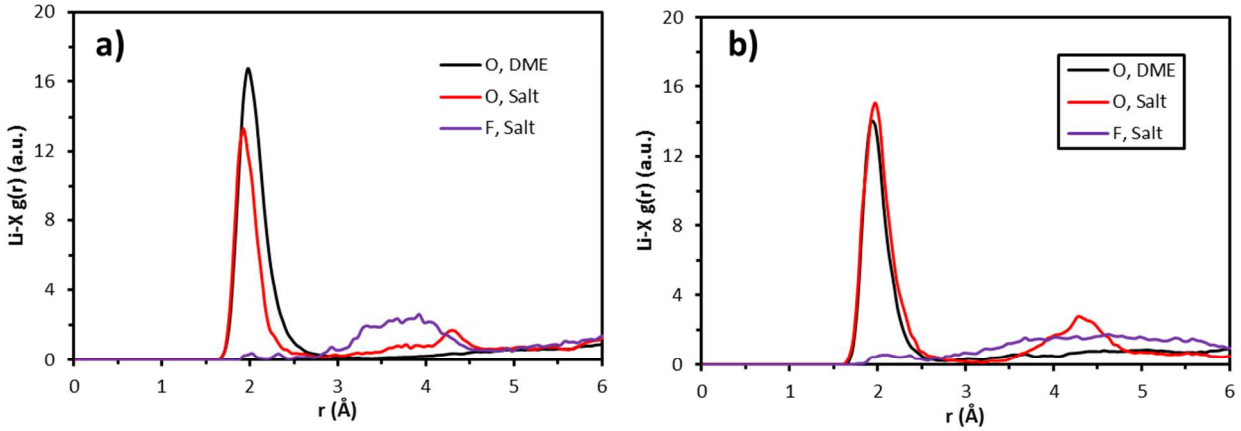

Figure S 17. Radial distribution function for Li^+--X (X=O and F atoms) pairs for solutions with three additional ions. a) 1M-LiFSI, and b) 1M-LiTFSI

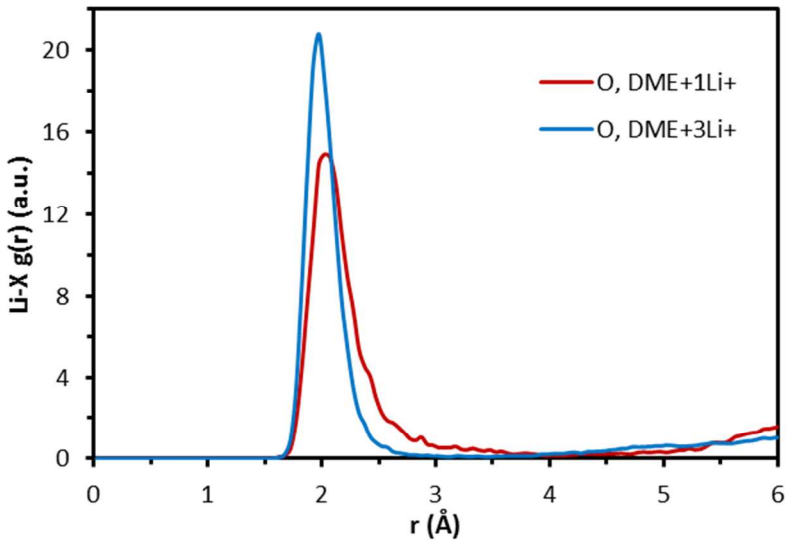

Figure S 18. Radial distribution function for Li^+--X (X=O and F atoms) pairs for pure DME with one and three additional ions.

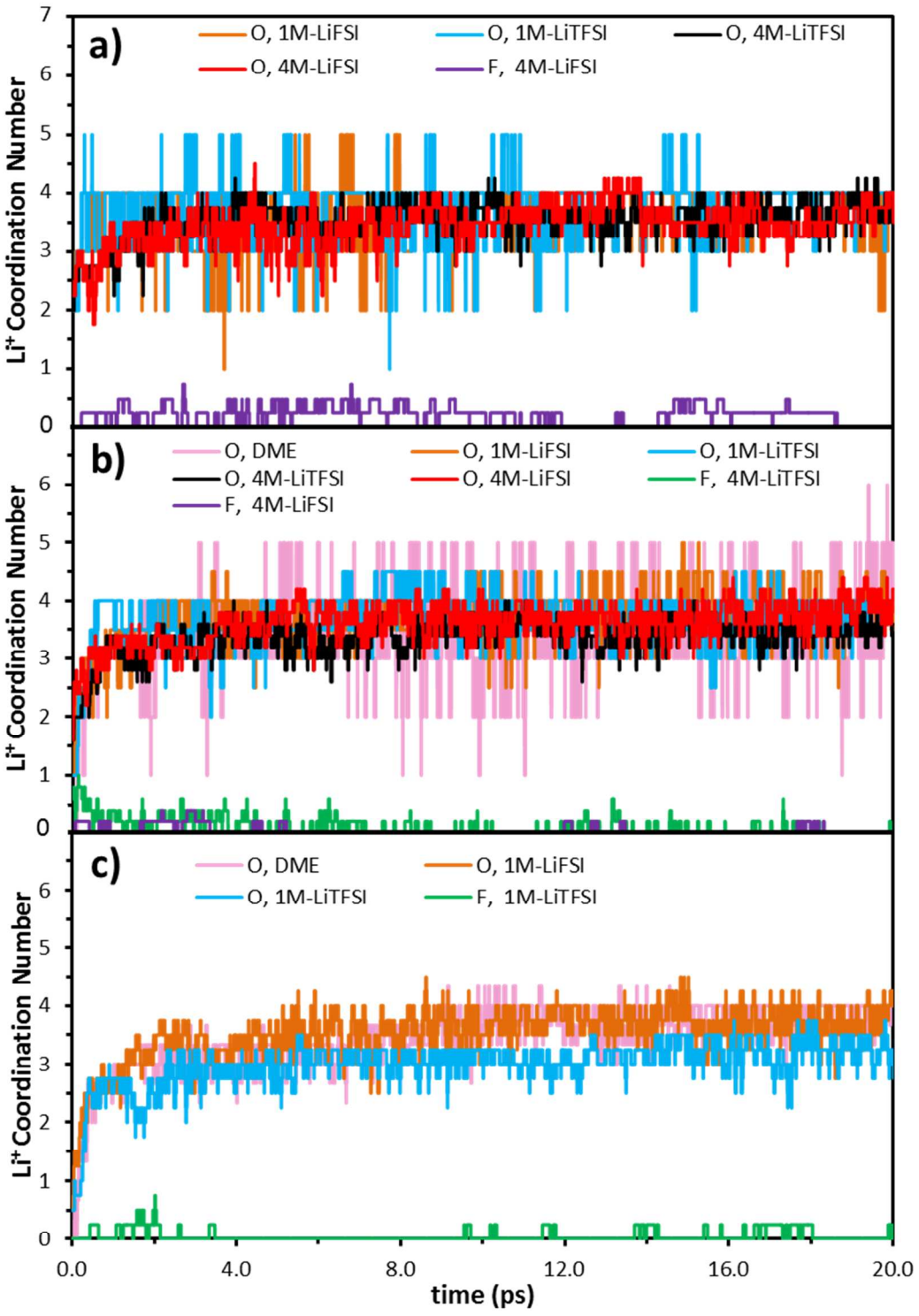

Figure S19. Average coordination numbers calculated as a function of time under different concentrations of lithium ions: a) w/o Li, b) 1 Li^+, and c) 3 Li^+.

Table S1. Calculated bond dissociation energies for LiFSI and LiTFSI from B3PW91/6-311++G(p,d).

Reactions	Dissociation Energies (eV)			
	Gas-phase		in DME	
	ΔE (0K)	ΔG (298K)	ΔE (0K)	ΔG (298K)
$LiFSI \rightarrow Li^+ + FSI^-$	5.77	5.44	0.62	0.31
$LiTFSI \rightarrow Li^+ + TFSI^-$ [ref. 1]	5.96	5.64	0.75	0.43

Table S2. Bond dissociation energies for the FSI^- anion calculated from B3PW91/6-311++G(p,d).

Reactions	Bond Dissociation Energies (eV)	
	in DME	
	ΔE (0K)	ΔG (298K)
$FSI^- \rightarrow F + NS_2O_4F^-$	3.80	3.40
$FSI^- \rightarrow F^- + NS_2O_4F$	2.74	2.38
$FSI^- \rightarrow NSO_2F^- + SO_2F$	3.11	2.53
$FSI^- \rightarrow NSO_2F + SO_2F^-$	3.84	3.29

Table S3. Average coordination numbers for the different solutions over 18 ps (2-20ps). Peak positions from RDF for O—Li and F—Li pairs.

System (in DME)	Average coordination number				RDF for X---Li^+			
	Total	O---Li^+	F---Li^+	% from O	O_Salt (1st)---Li^+	O_Salt (2nd)---Li^+	O_DME---Li^+	F---Li^+
1M-LiFSI	3.77	3.74	0.00	99.2%	1.975	4.225	1.975	4.175
4M-LiFSI	3.79	3.51	0.21	92.8%	1.975	4.325	1.975	1.975 / 4.125
1M-LiTFSI	3.83	3.82	0.00	99.7%	1.975	4.125	1.975	-
4M-LiTFSI	3.70	3.61	0.00	97.6%	1.925	4.275	1.925	-
1Li^+	3.63	3.61	-	99.4%	-	-	2.025	-
1M-LiFSI+1Li^+	3.91	3.85	0.00	98.3%	1.975	4.325	1.975	3.775
4M-LiFSI+1Li^+	3.75	3.67	0.03	98.0%	1.975	4.325	1.975	4.125
1M-LiTFSI+1Li^+	3.81	3.75	0.00	98.5%	1.975	4.275	1.925	-
4M-LiTFSI+1Li^+	3.56	3.45	0.08	96.8%	1.925	4.275	1.925	-
3Li^+	3.62	3.58	-	98.9%	-	-	1.975	-
1M-LiFSI+3Li^+	3.69	3.62	0.00	98.0%	1.975	4.275	1.925	3.925
1M-LiTFSI+3Li^+	3.31	3.08	0.04	93.1%	1.925	4.275	1.975	-

REFERENCES

1. Camacho-Forero, L. E.; Smith, T. W.; Bertolini, S.; Balbuena, P. B., Reactivity at the Lithium–Metal Anode Surface of Lithium–Sulfur Batteries. *The Journal of Physical Chemistry C* **2015**, *119*, 26828-26839.