Electronic Supplementary Material (ESI) for Materials Advances.

Supplemental Information

Ion Mobility and Solvation Complexes at Liquid-Solid Interfaces in Dilute, High Concentrated, and Localized High Concentrated Electrolytes

Stefany Angarita-Gomez and Perla B. Balbuena*

Department of Chemical Engineering,

Texas A&M University, College Station, TX 77843

*e-mail: balbuena@tamu.edu

Table S1. Electrolyte composition and formulations. Full description of these formulations can be found in the reference (S. Perez Beltran et al. Chem. Mater. 2020, 32, 14, 5973–5984)

Type of electrolyte	Molarity [mol/L]	Molar Ratio LiFSI:DMC:BTFE	Density [g/cm^3]	Total number of molecules in electrolyte LiFSI:DMC:BTFE
LCE	1.21	1.00:9.00:0.00	1.21	3:29:0
HCE	3.74	1.00:2.00:0.00	1.37	11:22:0
LHCE	1.77	0.64:1.10:1.65	1.44	5:8:14

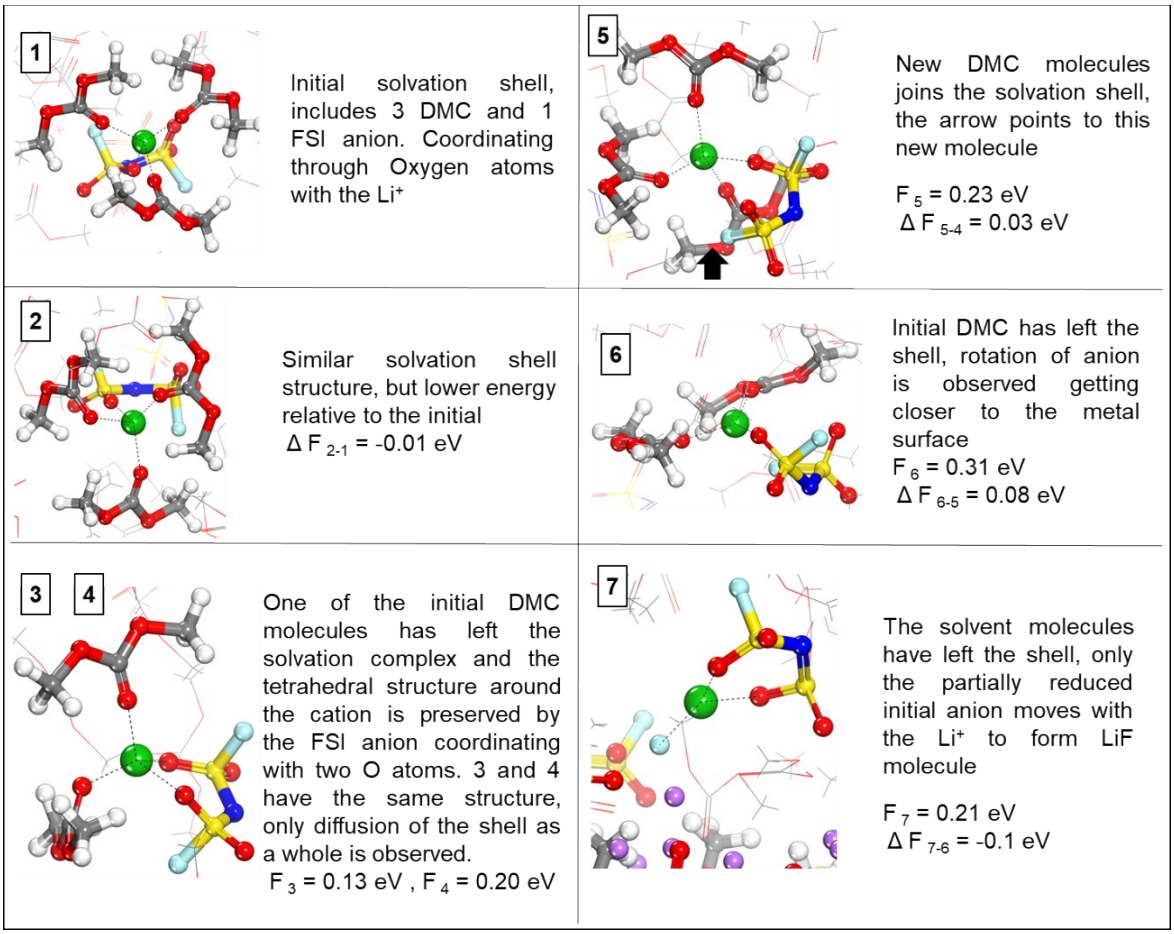

Figure S1. Summary and energy barriers description of the diffusion and deposition pathway of a Li^+ in Low Concentration Electrolyte (LCE)

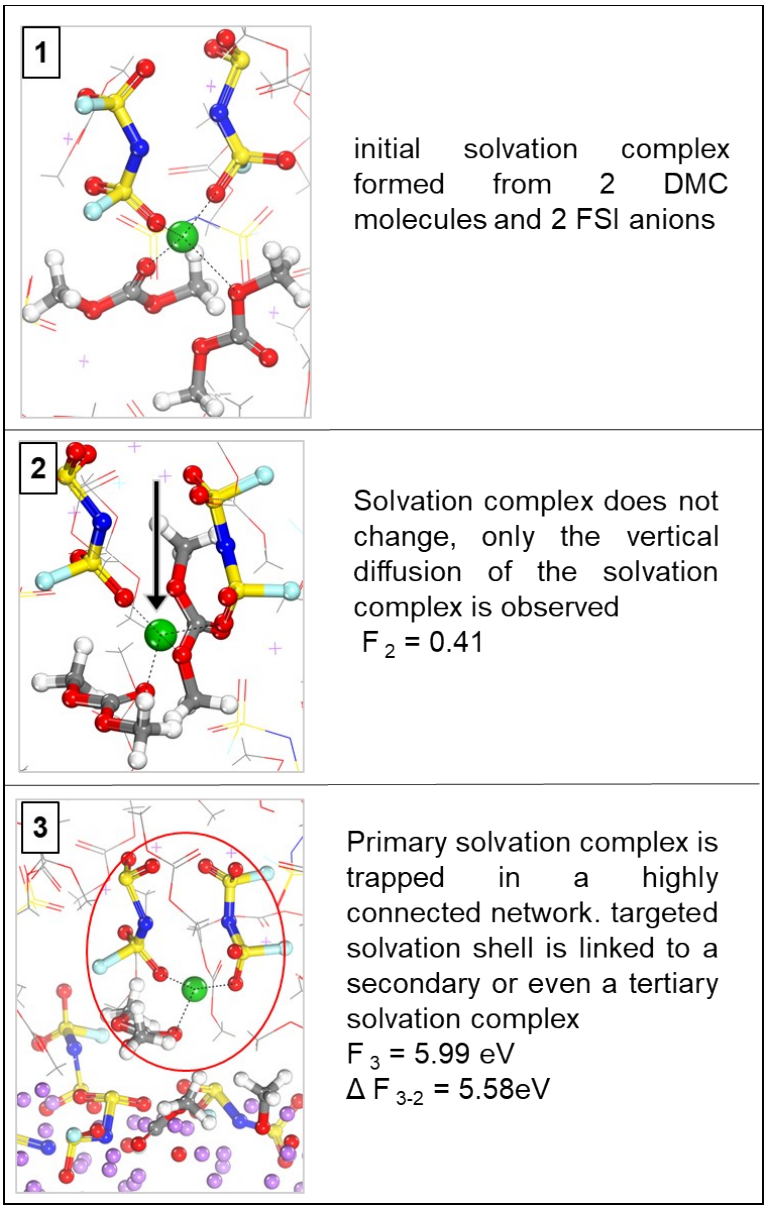

Figure S2. Summary and energy barrier's description of the diffusion and deposition pathway of a Li^+ on High Concentration Electrolyte (HCE)

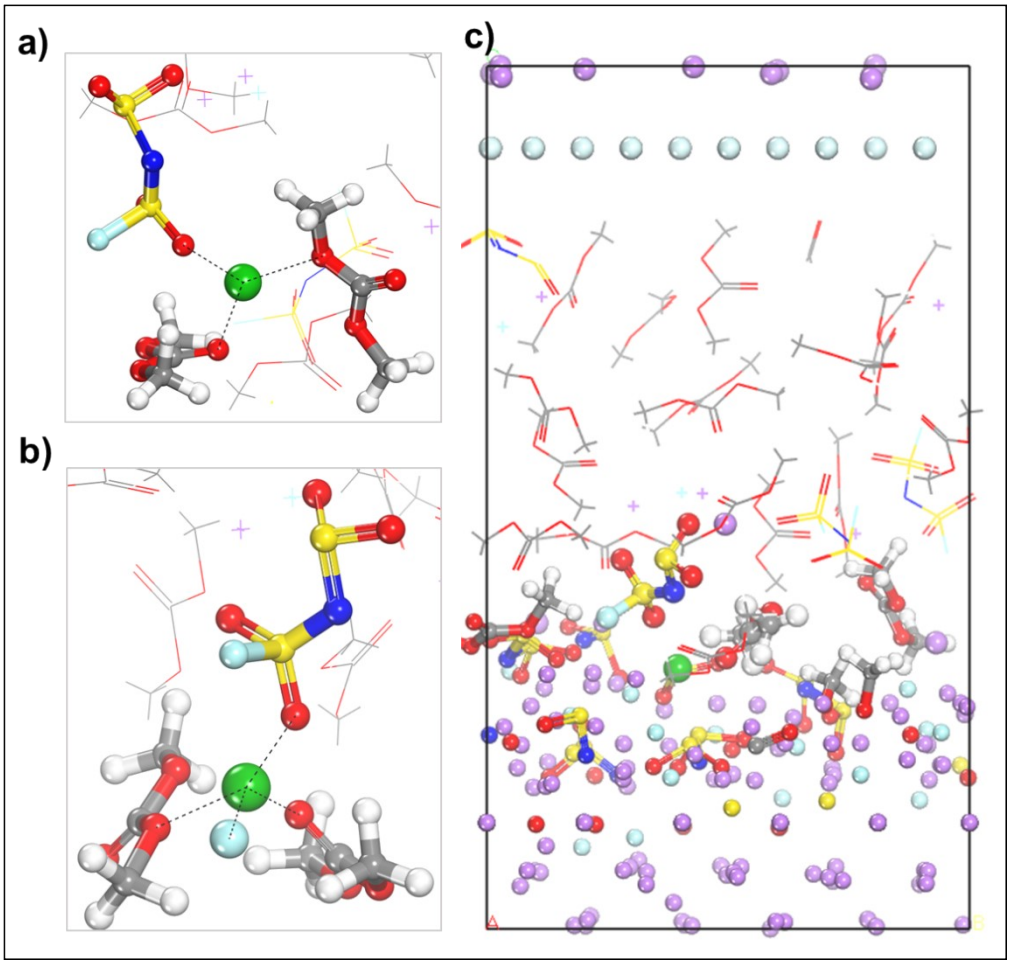

Figure S3. Continuation of HCE structure (Figure 3 Mark 3) by adding additional lithium layers to the lithium metal slab. a) Solvation complex continuation b) partial reduction of anion and F atom c) zoom out of the cell structure. Color code as Figure 1.

Due to the large number of interfacial reactions, the electrons available in the Lithium metal slab were mostly depleted in Figure 3 Mark 3. Thus, to continue the analysis, additional lithium layers were added to the structure and the results are shown in Figure S3. The solvation shell form in Figure S3a showcases one anion and 2 solvent molecules as part of the primary solvation complex this leads to a partially reduced anion and a Fluorine atom that joins said solvation structure (Figure S3b). Toward the end, the Li

cation is part of a complex SEI formed by the reduction of electrolyte molecules including solvent molecules and anions.

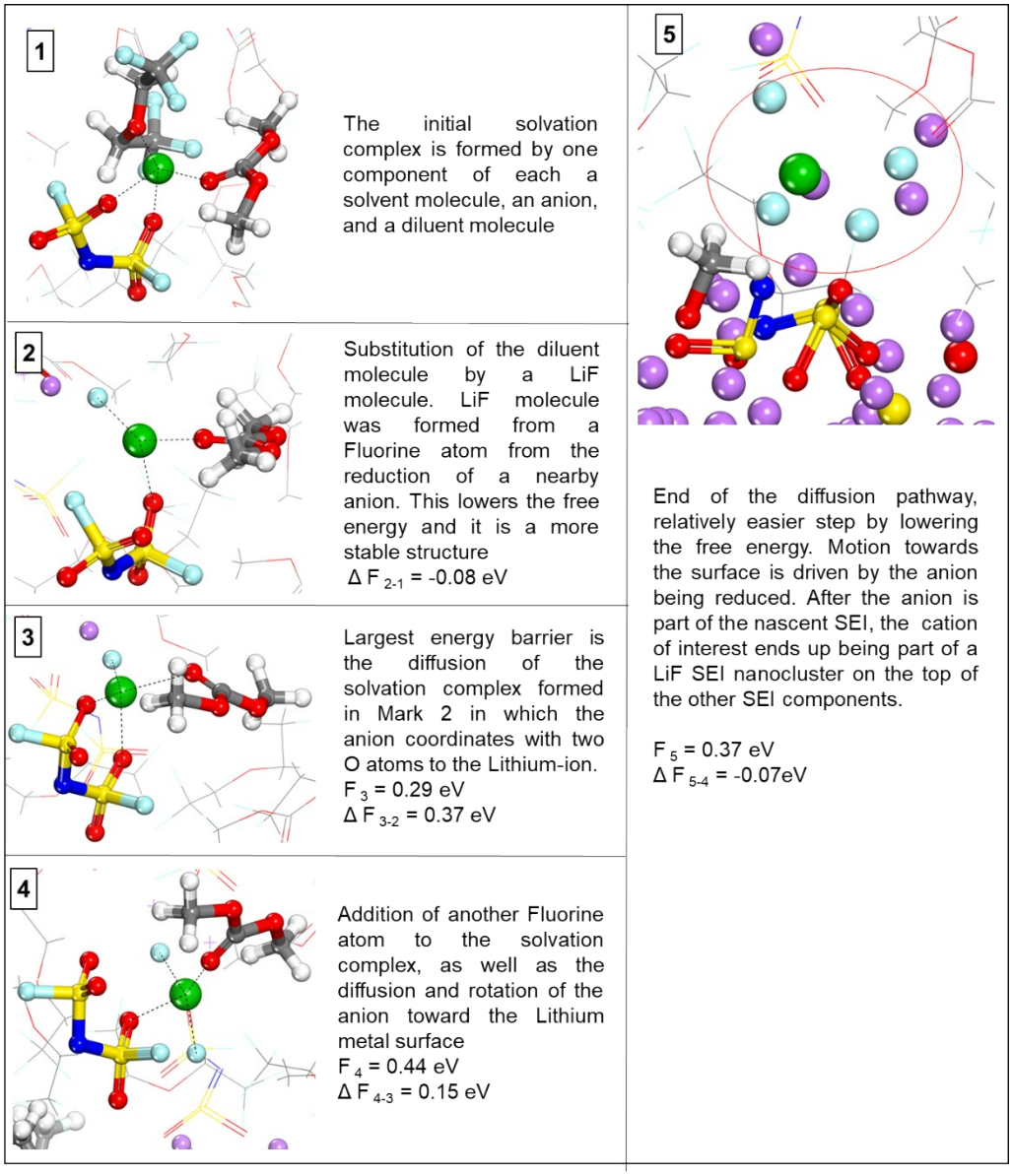

Figure S4. Summary and energy barrier's description of the diffusion and deposition pathway of a Li^+ on Localized High Concentration Electrolyte (LHCE) Shell 1.

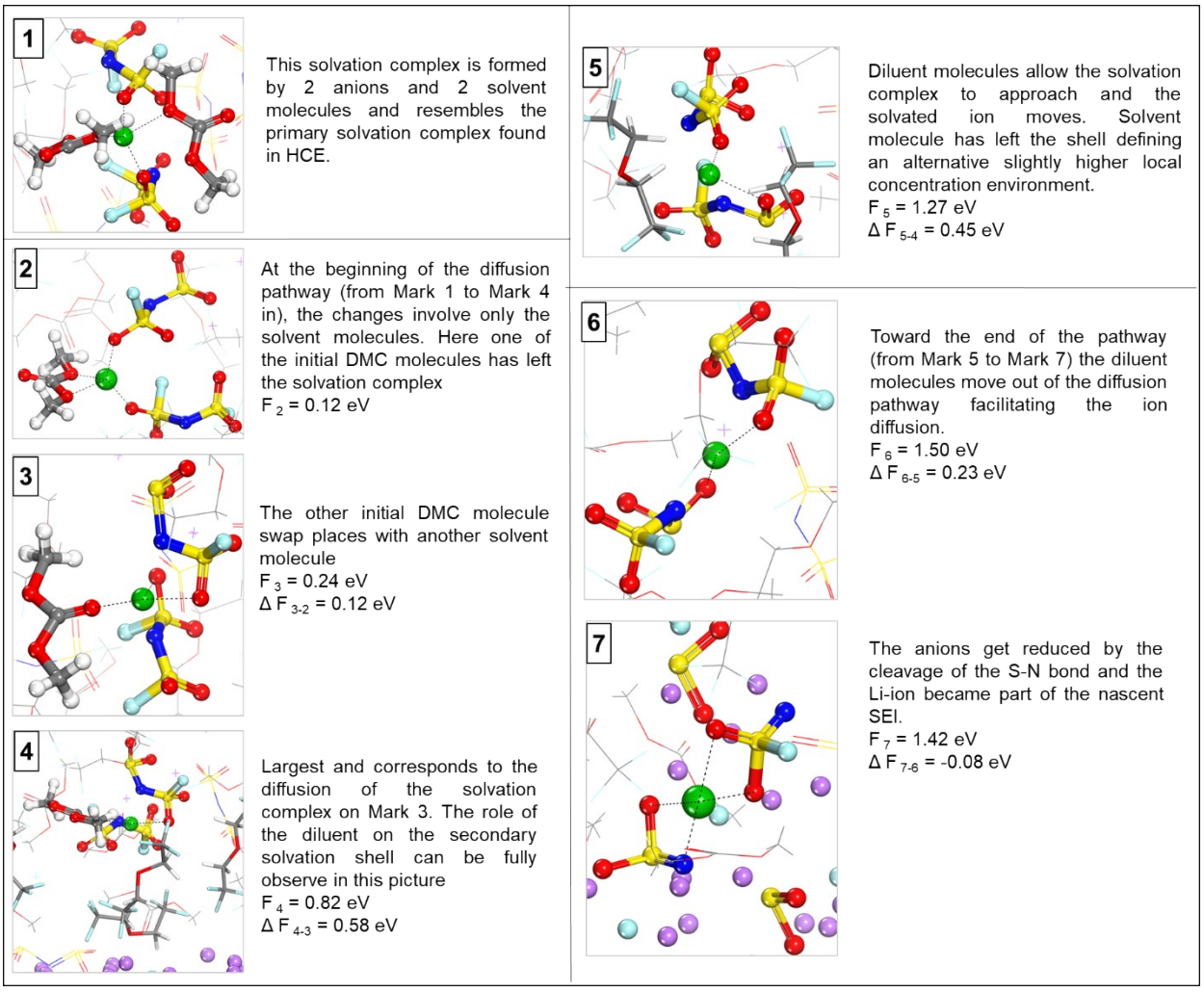

Figure S5. Summary and energy barrier's description of the diffusion and deposition pathway of a Li^+ on Localized High Concentration Electrolyte (LHCE) Shell 4.

Standard errors were determined using the block averaging method, by running 2ps (2000 steps) of simulation at each of the highlighted frames in LCE (at a reduced step size $8x10^{-6}$Å), discarding 300 steps and doing the block average method. The average force error shows values of 0.016 eV/Å.