

Ionic Liquids at Electrified Interfaces

From Double Layers to Decomposition



Justin B. Haskins¹, John W. Lawson²

¹AMA, Inc., NASA Ames Research Center

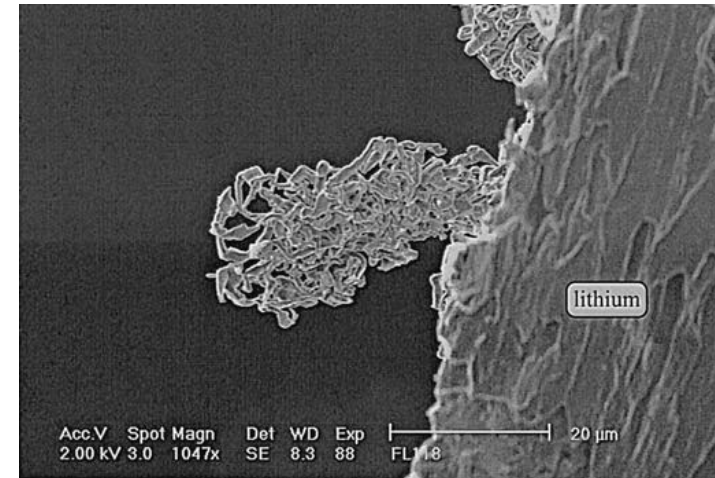
²NASA Ames Research Center



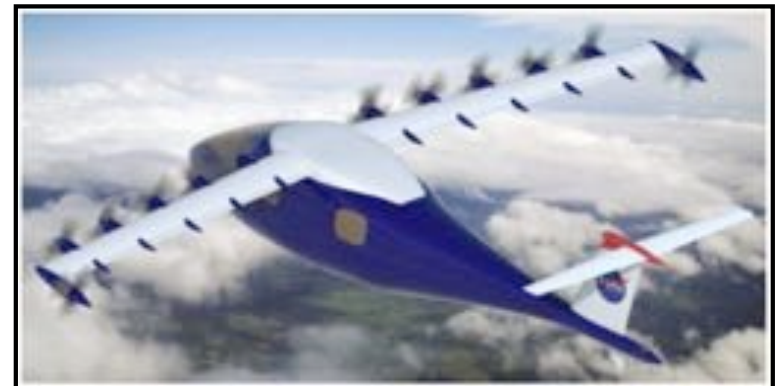
Ionic Liquids for Electrochemical Applications



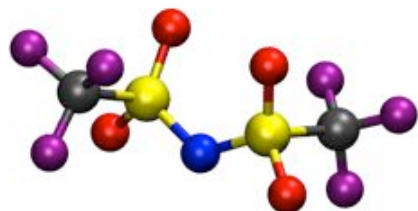
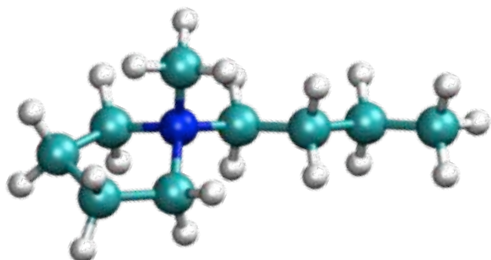
- **Advanced electrodes:** help stabilize cycling against Li-metal
- **Li-ion batteries:** possible safer alternative to organic electrolytes
- **Supercapacitors:** double layer capacitor electrolyte
- **Electrodeposition:** wide electrochemical window solvent
- **Biofuel cells:** replace water as more stable solvent



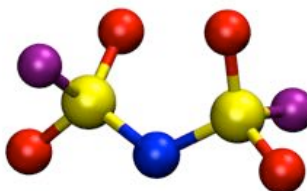
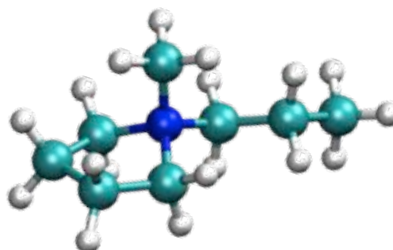
F. Orsini et al., J. Power Sources 76, 19-29 (1998)



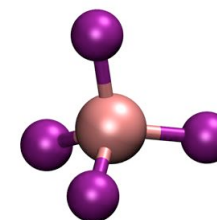
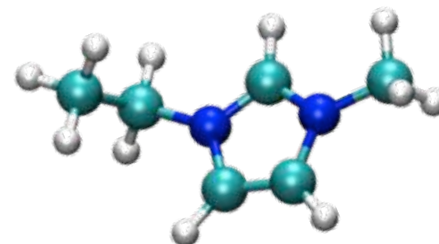
NASA Electric Aircraft



[pyr14][TFSI]



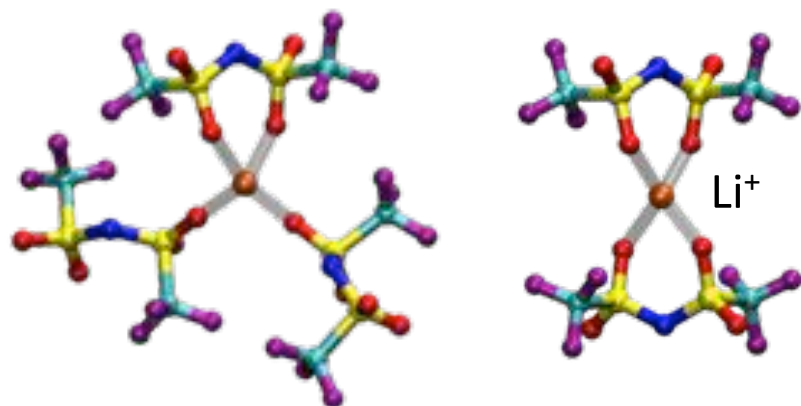
[pyr13][FSI]



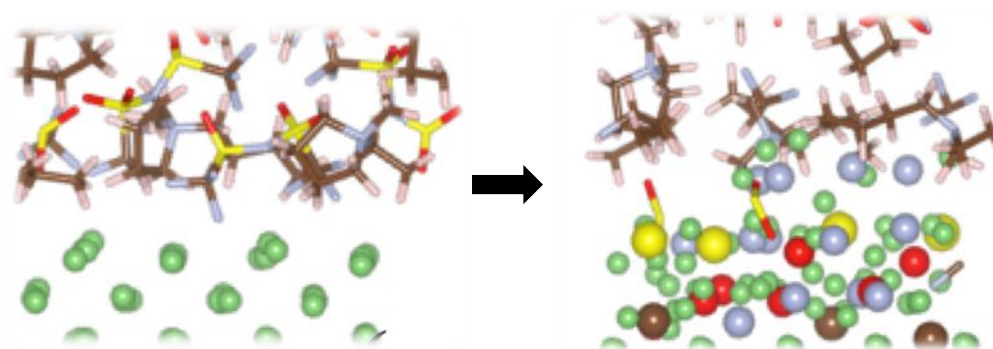
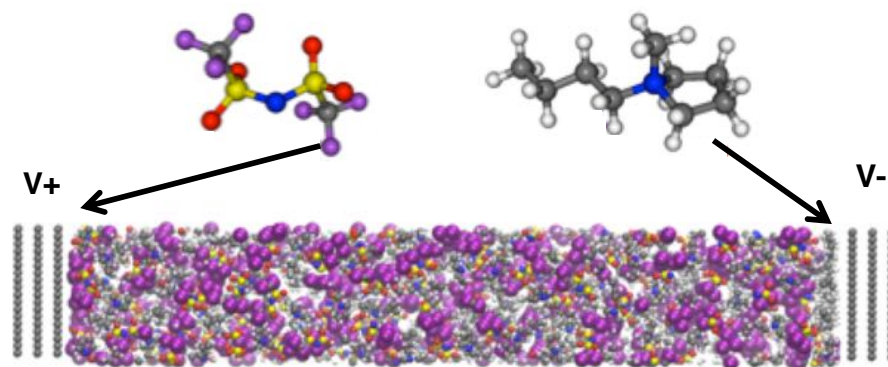
[EMIM][BF₄]

Chosen for suppression of dendrites on Li⁺ metal anodes*

1) Li^+ Solvation and Transport



2) Behavior at Charged Interfaces



3) Behavior at Reactive Interfaces

Quantum Chemistry:

- Single Li^+ solvation structures
- Electrochemical windows
- Reaction barriers

Polarizable Molecular Dynamics (MD):

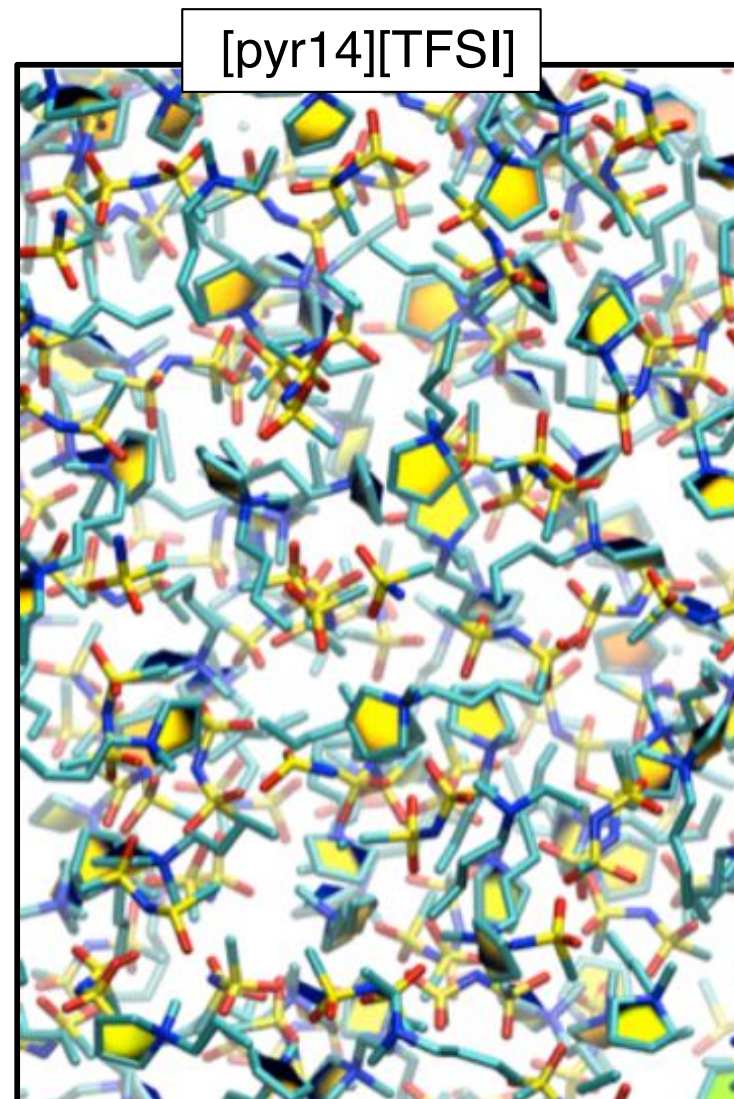
- APPLE&P
- Large-scale Li^+ solvation structures
- Physical properties

Constant Potential Molecular Dynamics:

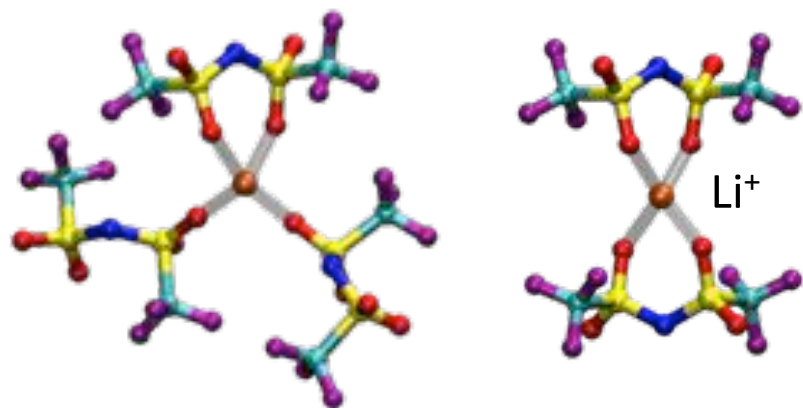
- Double layer structure
- Capacitance

Ab Initio Molecular Dynamics:

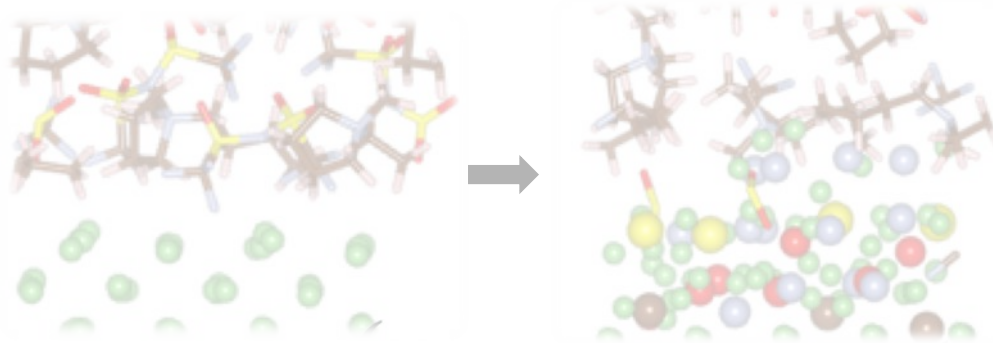
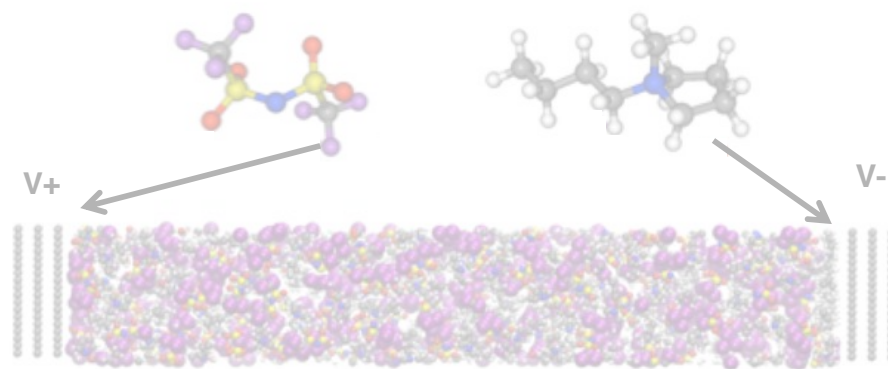
- Electrochemical window
- Reactions



1) Li^+ Transport and Solvation



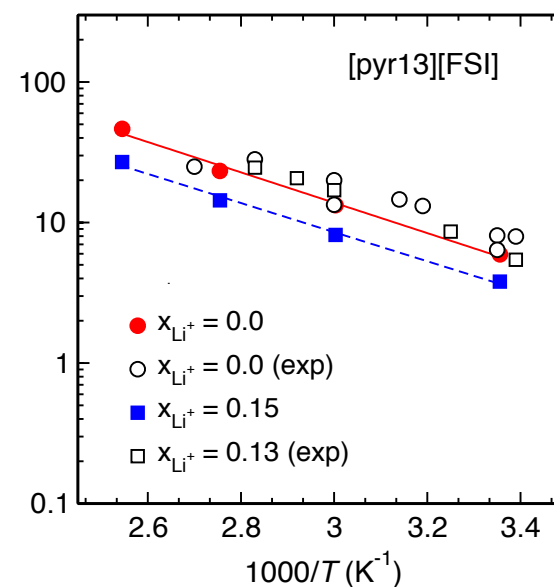
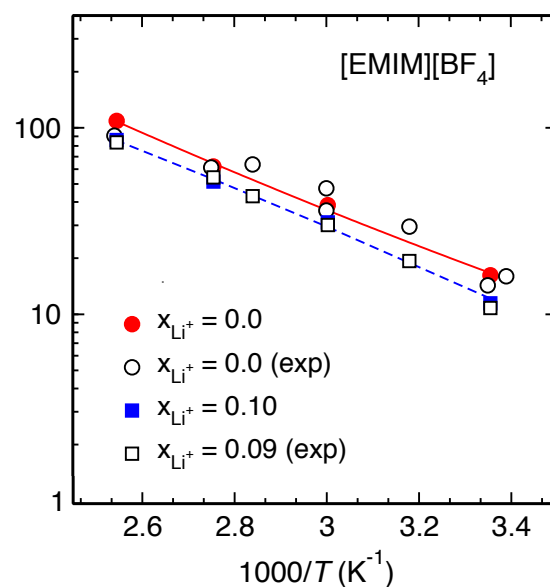
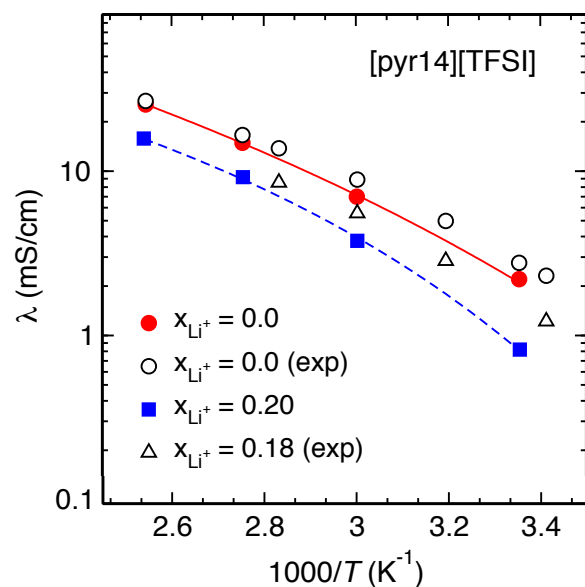
2) Behavior at Charged Interfaces



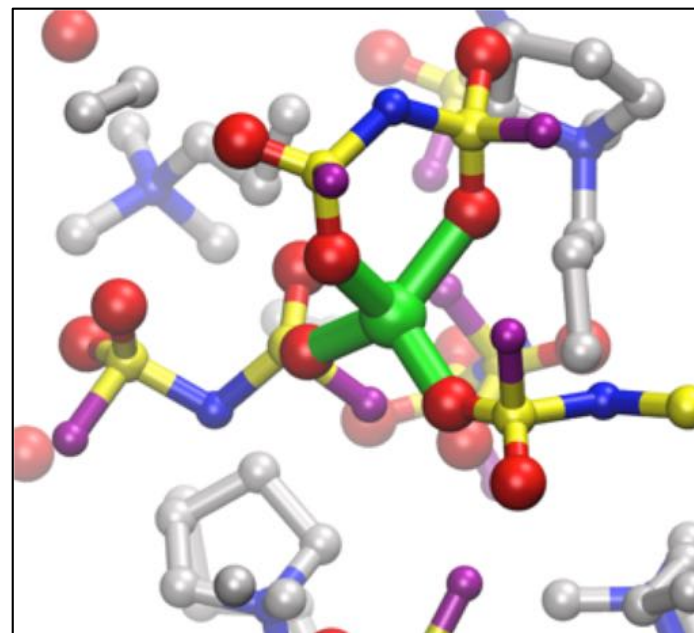
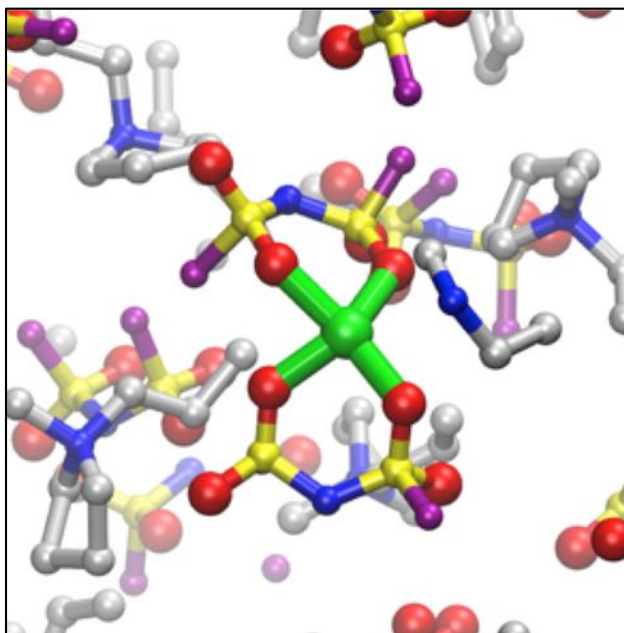
3) Behavior at Reactive Interfaces



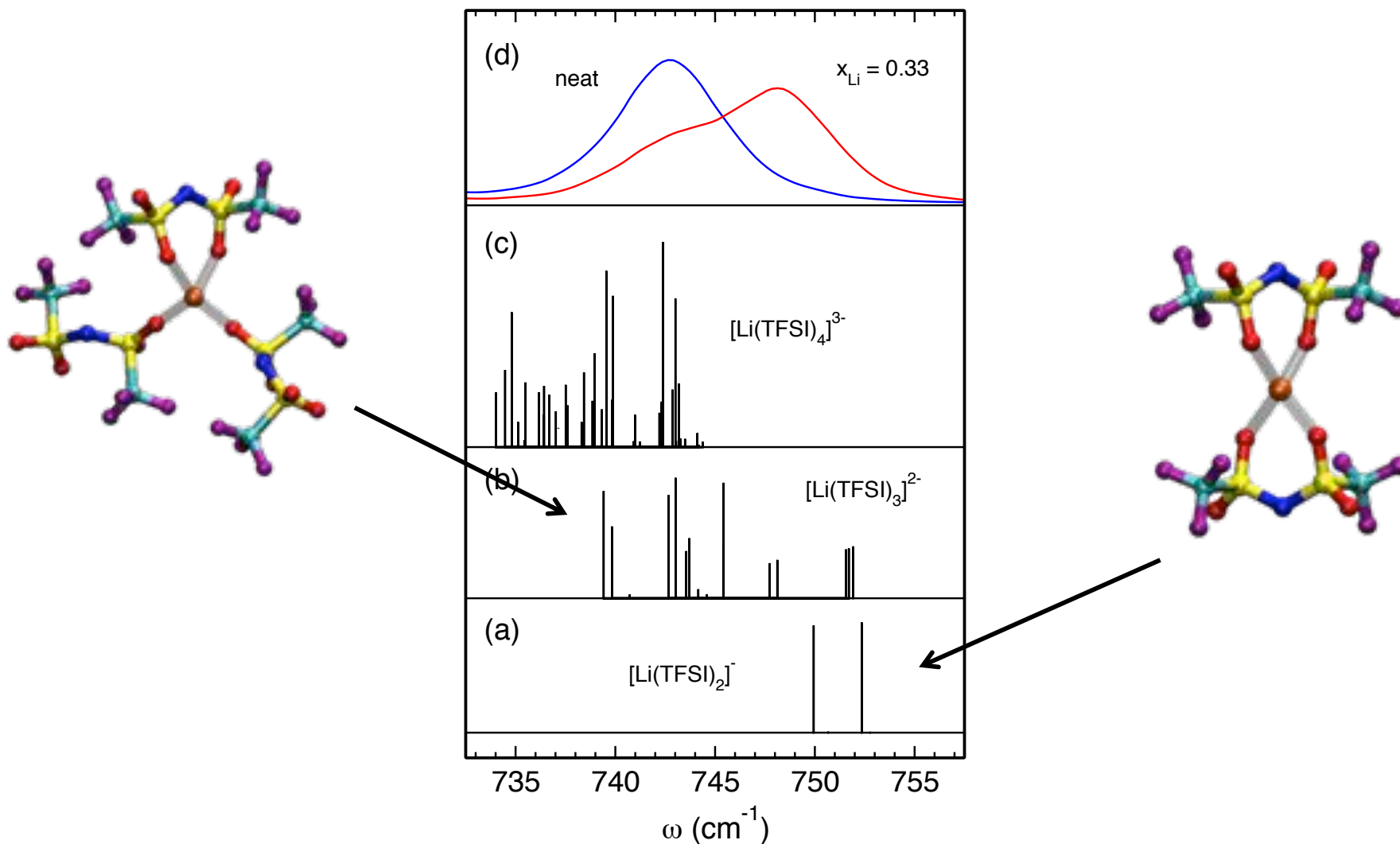
Ionic Conductivity



Conductivity decreases with anion size: TFSI < FSI < BF₄
Li-doping suppresses conductivity of all systems

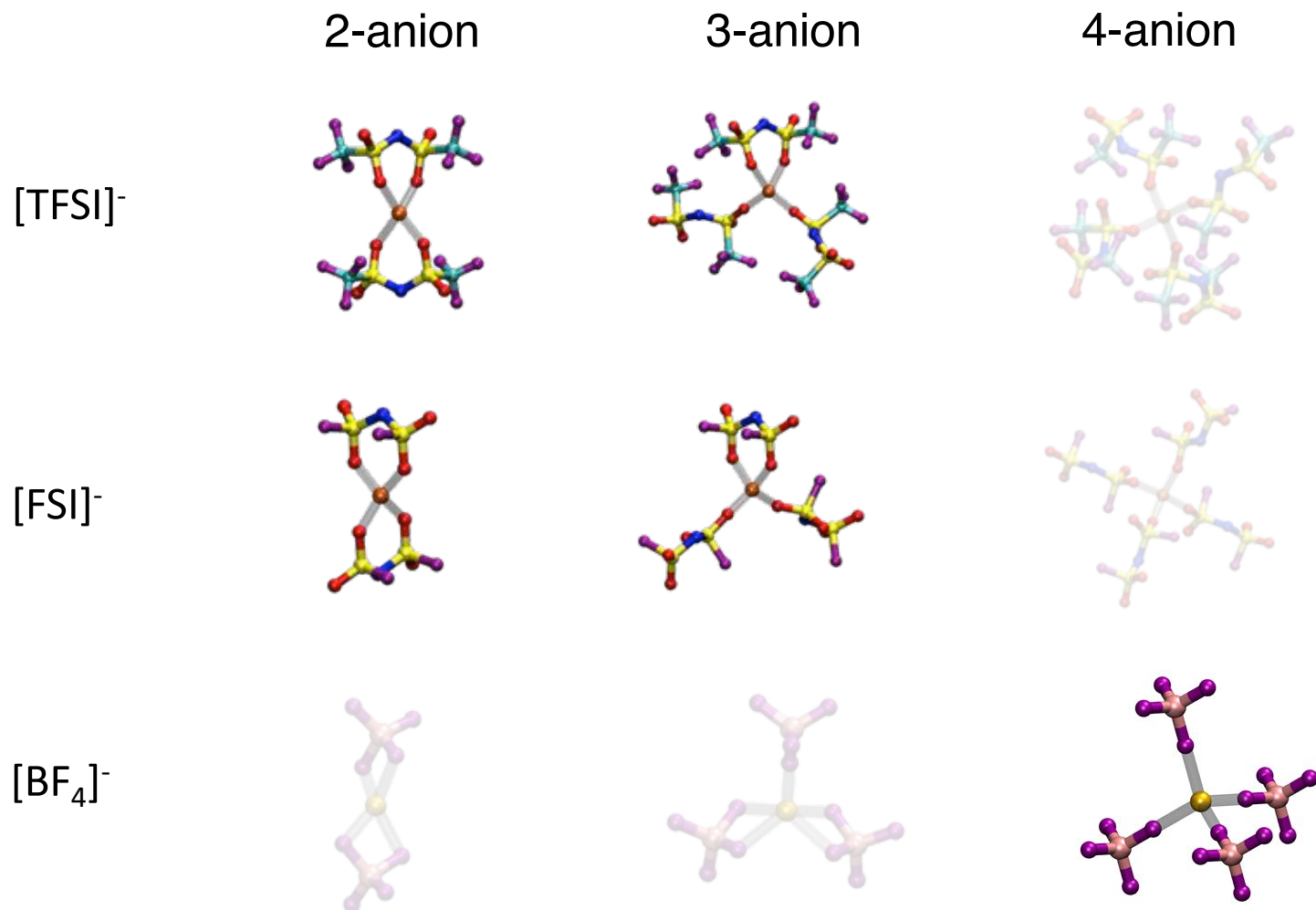


Highly unfavorable configurations exchange anions

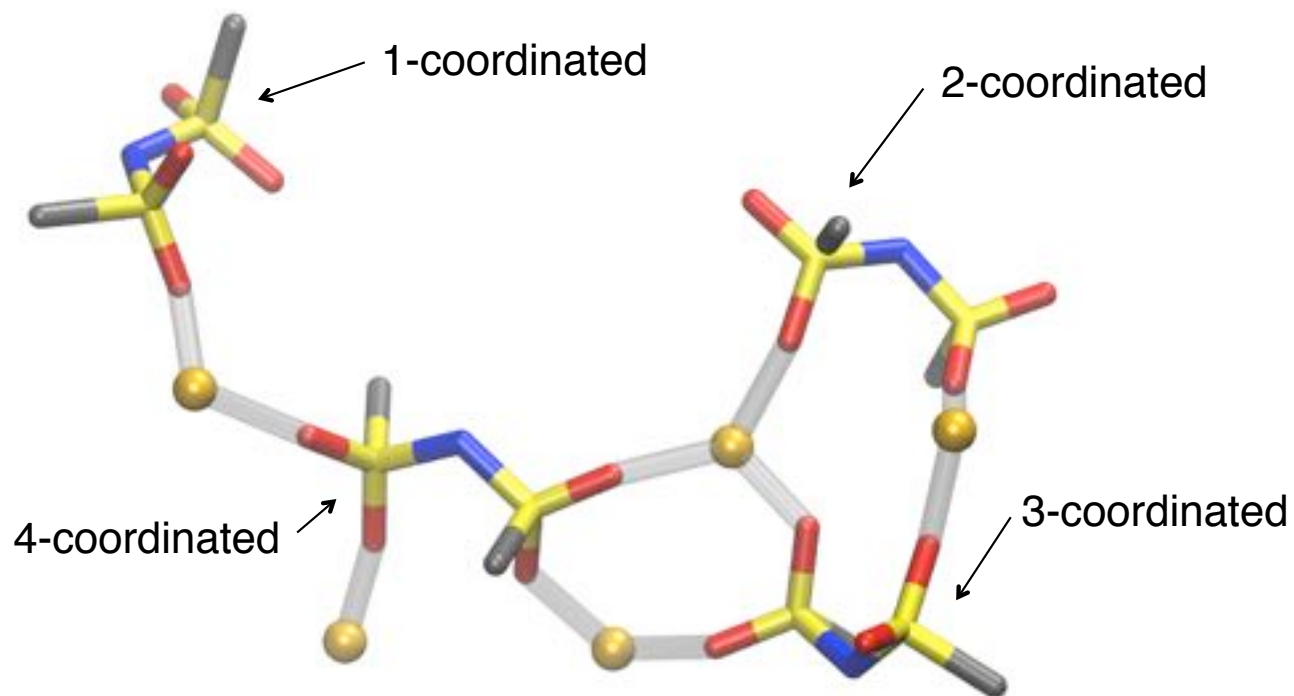


2 [TFSI] coordination dominant, 3 [TFSI] possible

Solvation Shells of Li^+

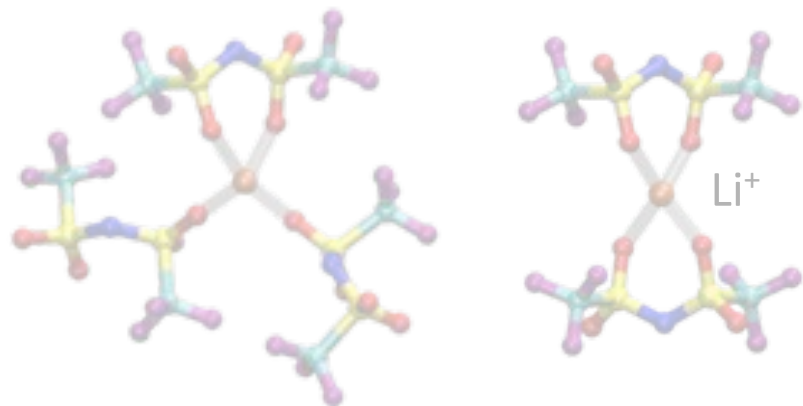


2, 3 anion Li^+ solvation shells for TFSI/FSI
4 anion Li^+ solvation shell for BF_4

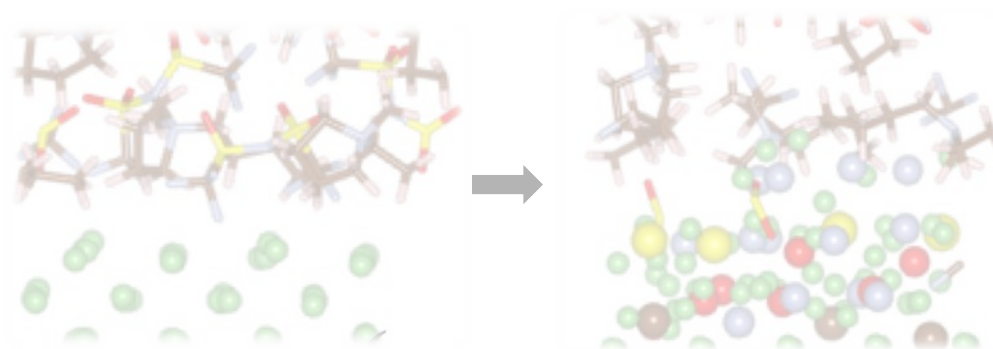
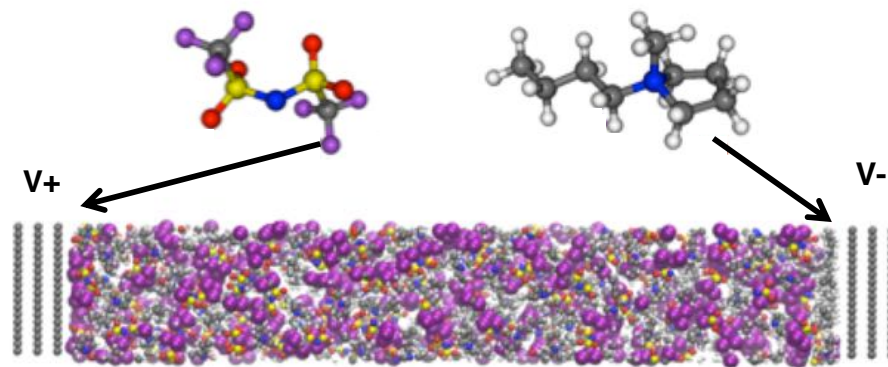


Networks of Li⁺ prevalent in ionic liquids

1) Li⁺ Transport and Solvation



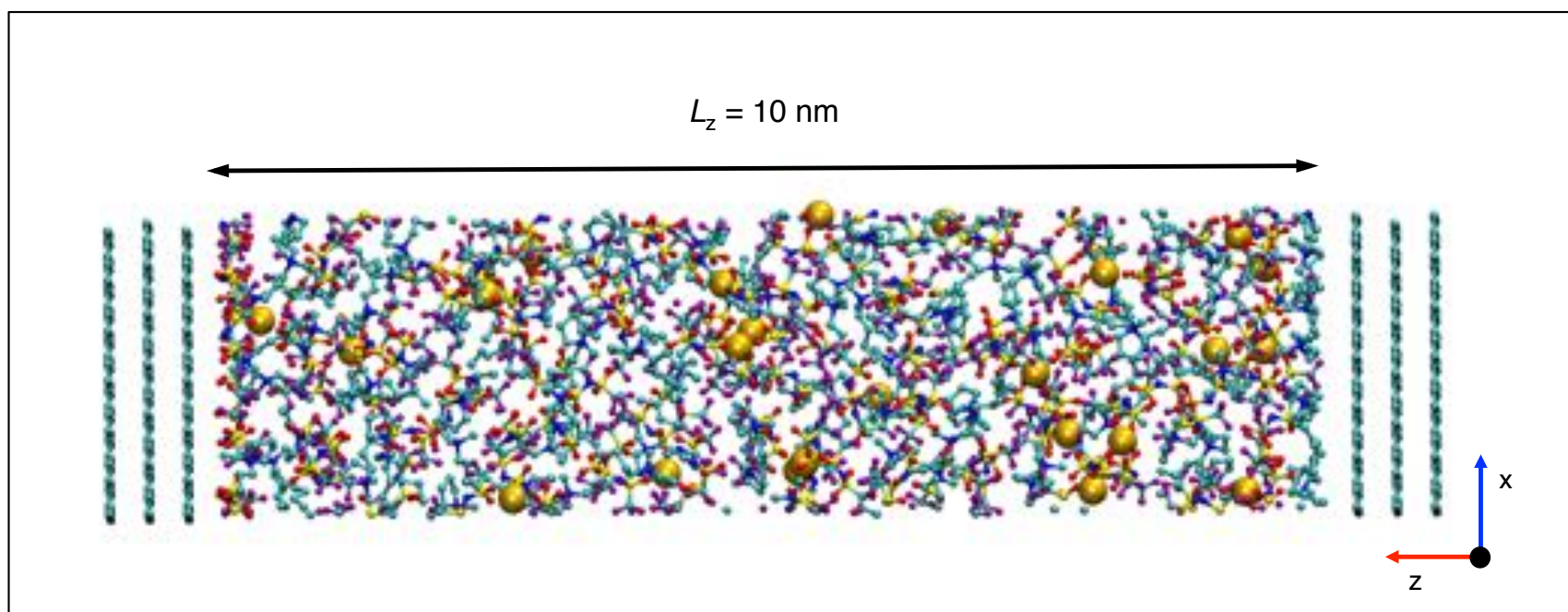
2) Behavior at Charged Interfaces



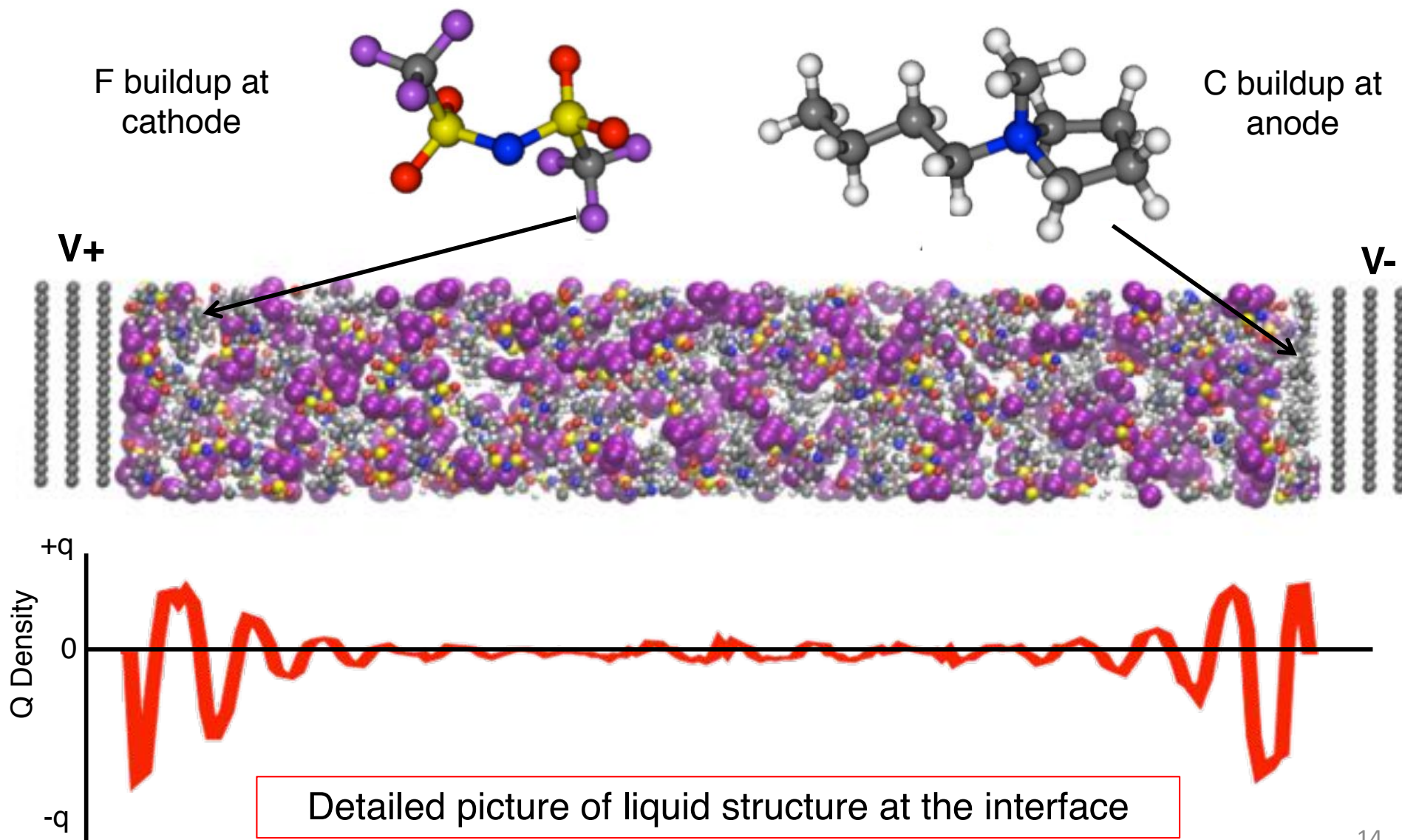
3) Behavior at Reactive Interfaces



Ionic Liquids at Electrified Interfaces

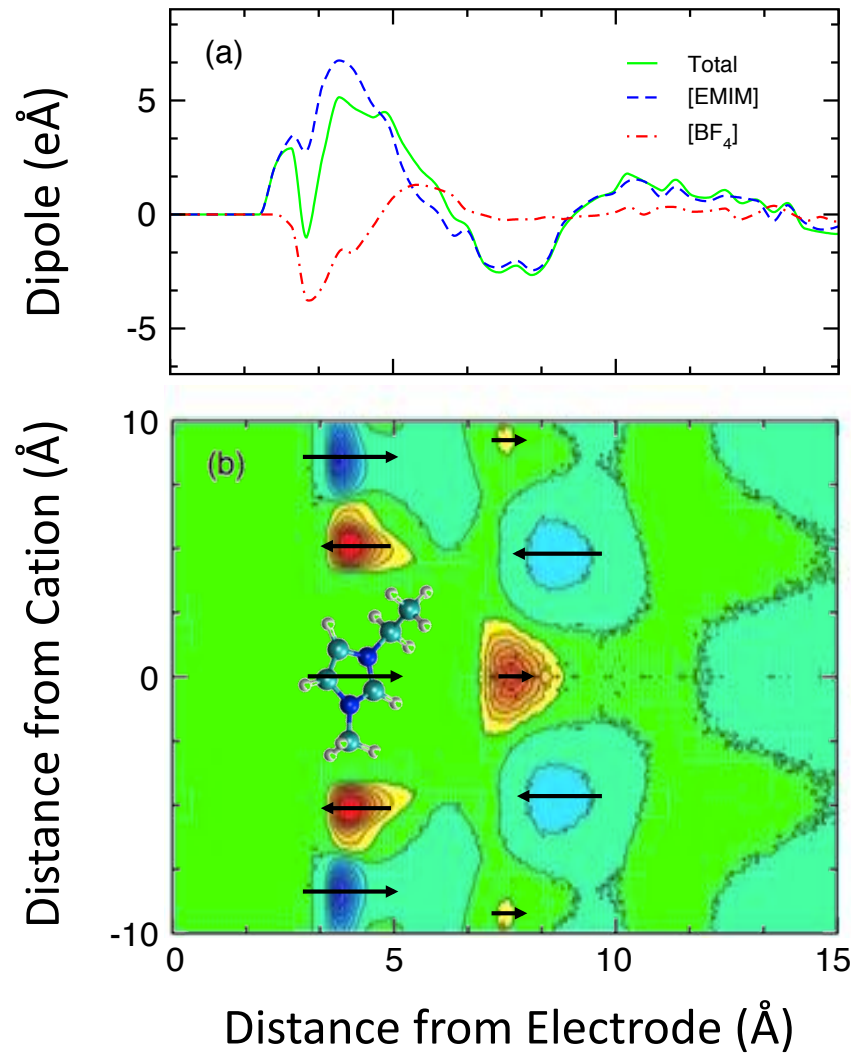


Two electrode simulations performed as a function of electrode voltage drop





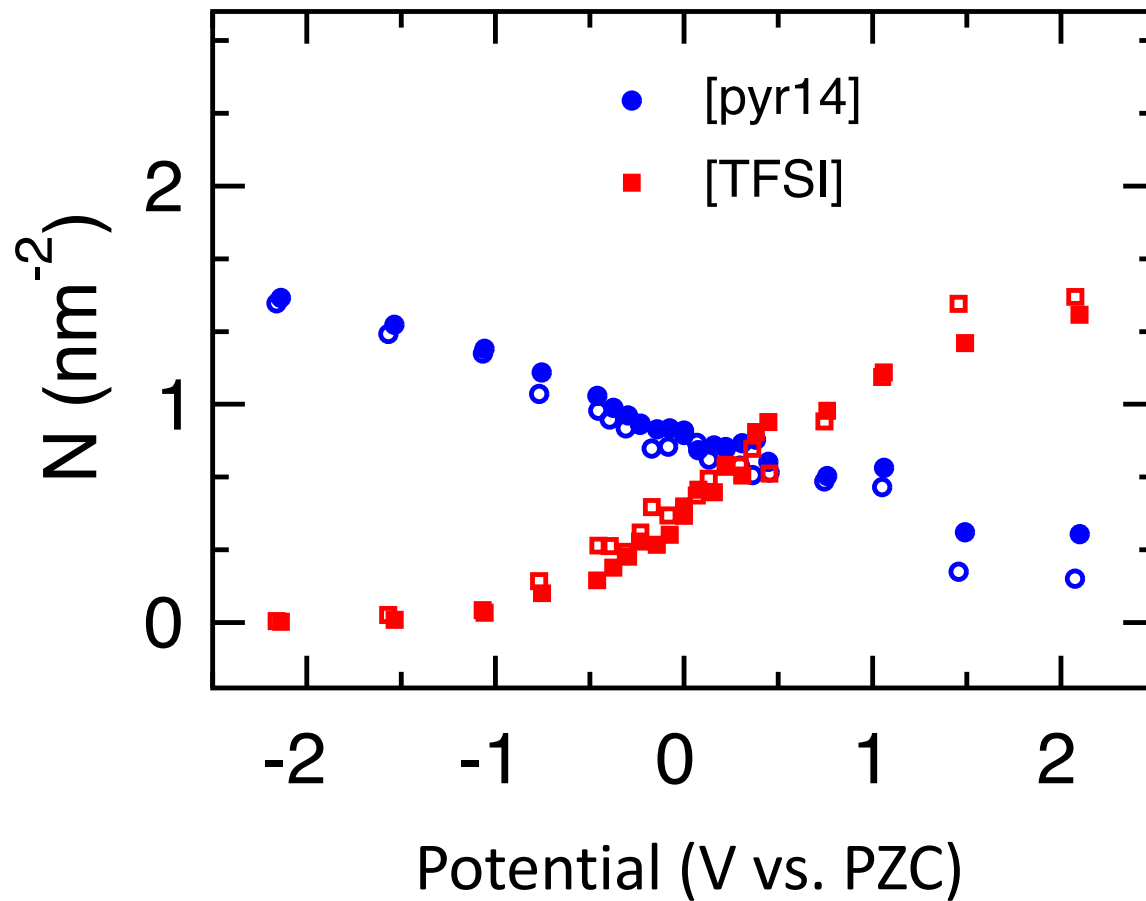
Influence of Atomic Polarization on EDL



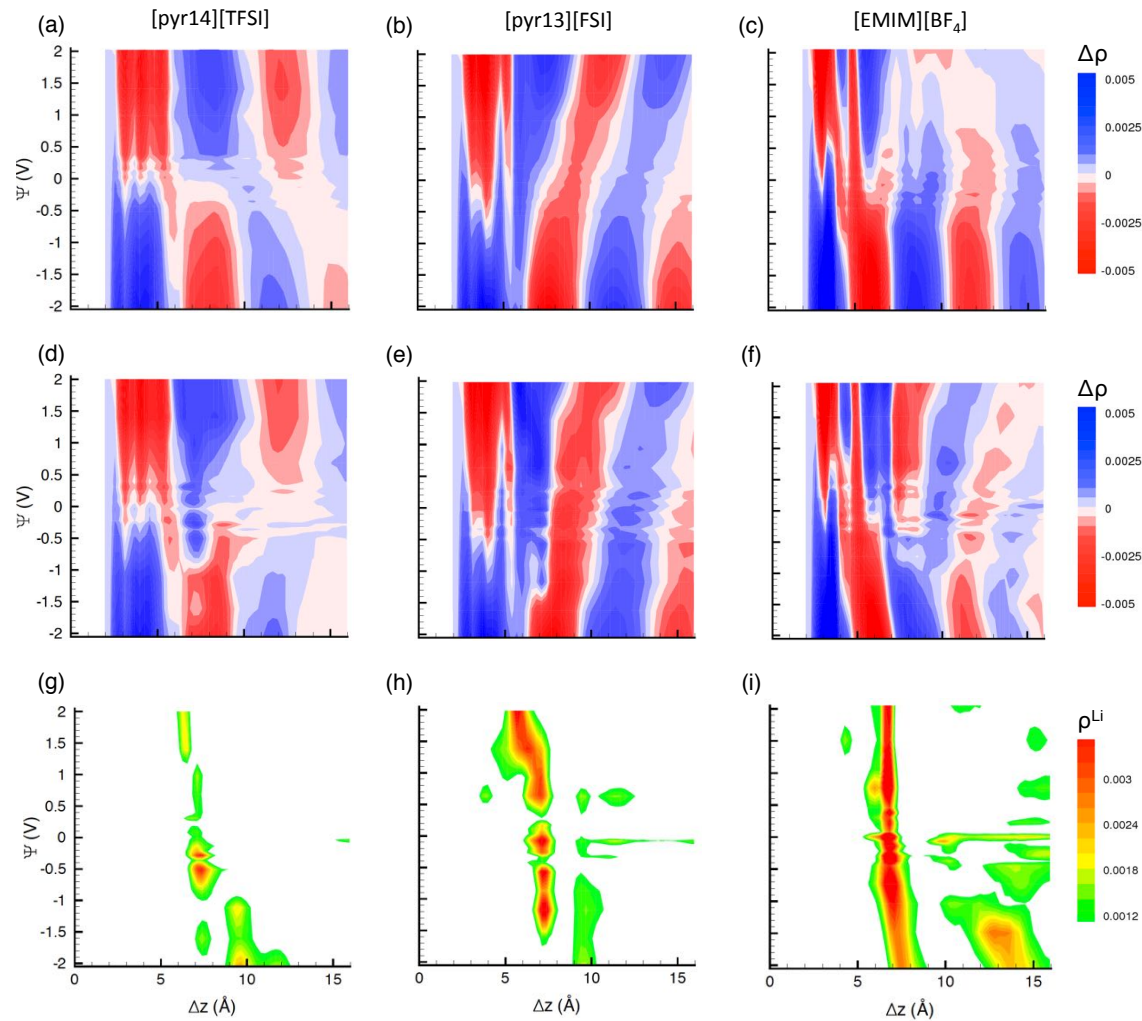
Polarization opposes formation of the EDL



Ion Accumulation at the Interface



Interface is enriched in cations or anions

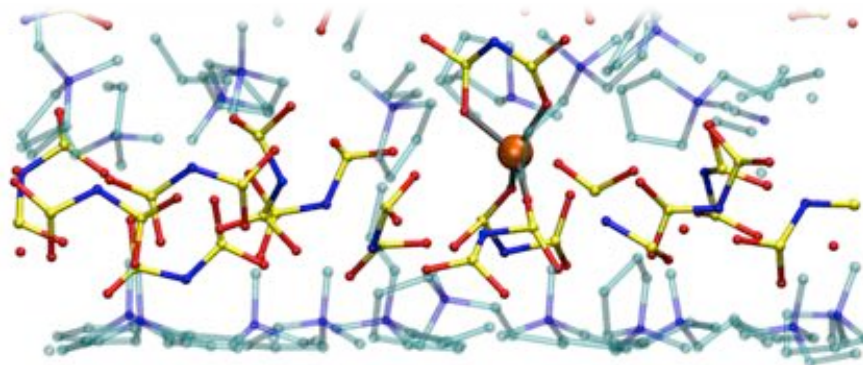


Li⁺ disrupts the EDL and accumulates near the surface

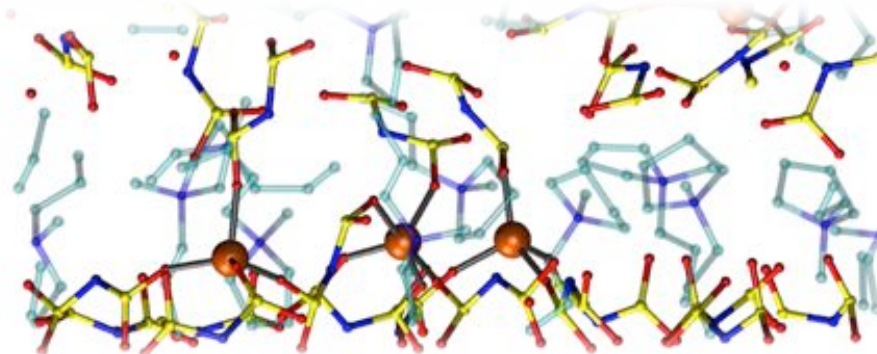
Li⁺ Binding in the EDL



(a)



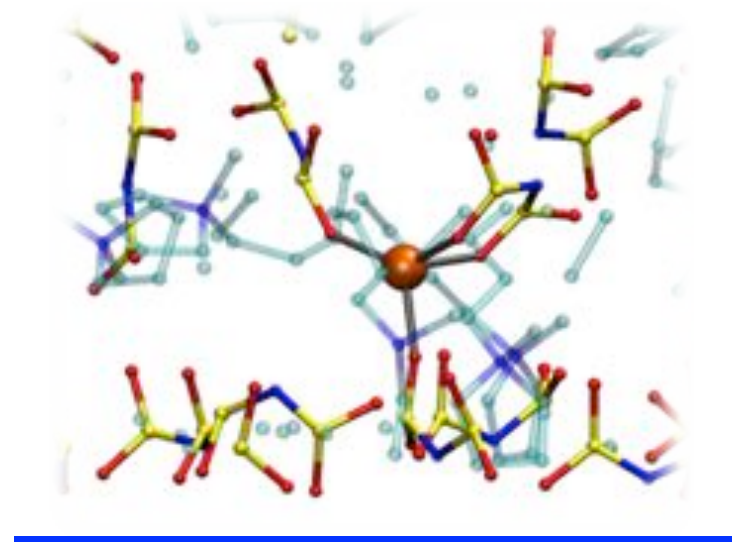
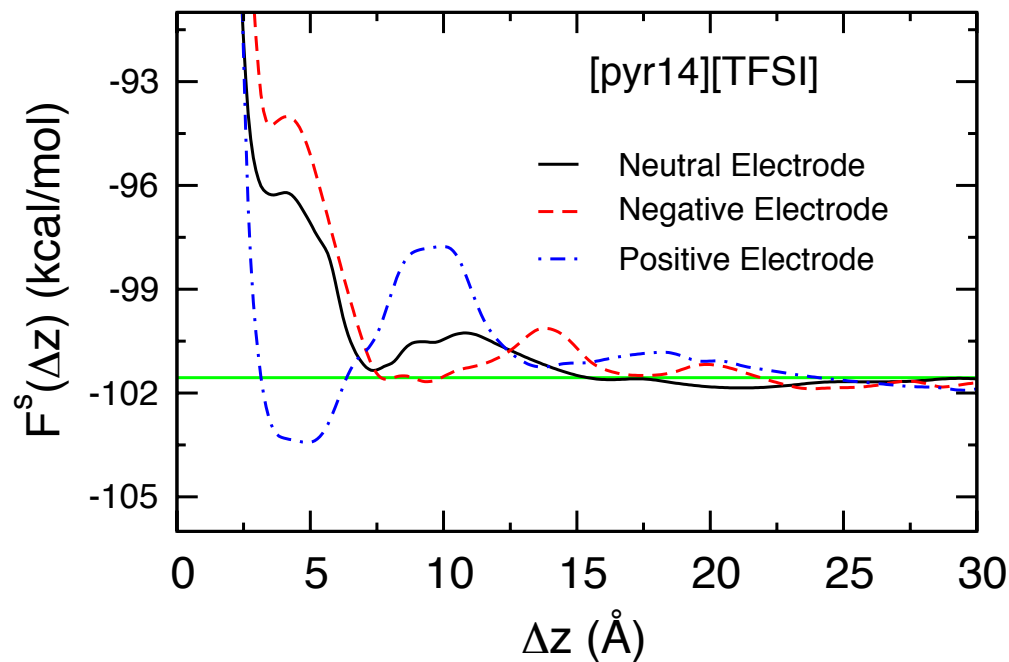
(b)



Li⁺ accumulates in the second molecular layer



Free Energy Barrier to Li^+ Intercalation



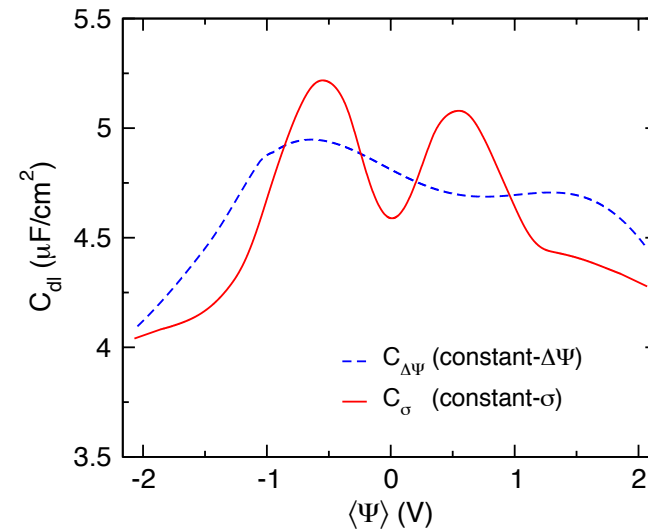
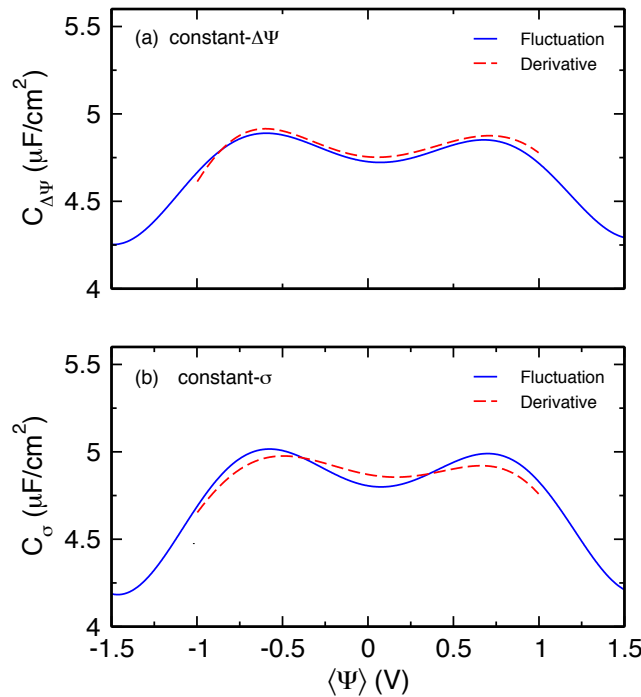
Large energy to move Li^+ to the surface



Capacitance from Fluctuations



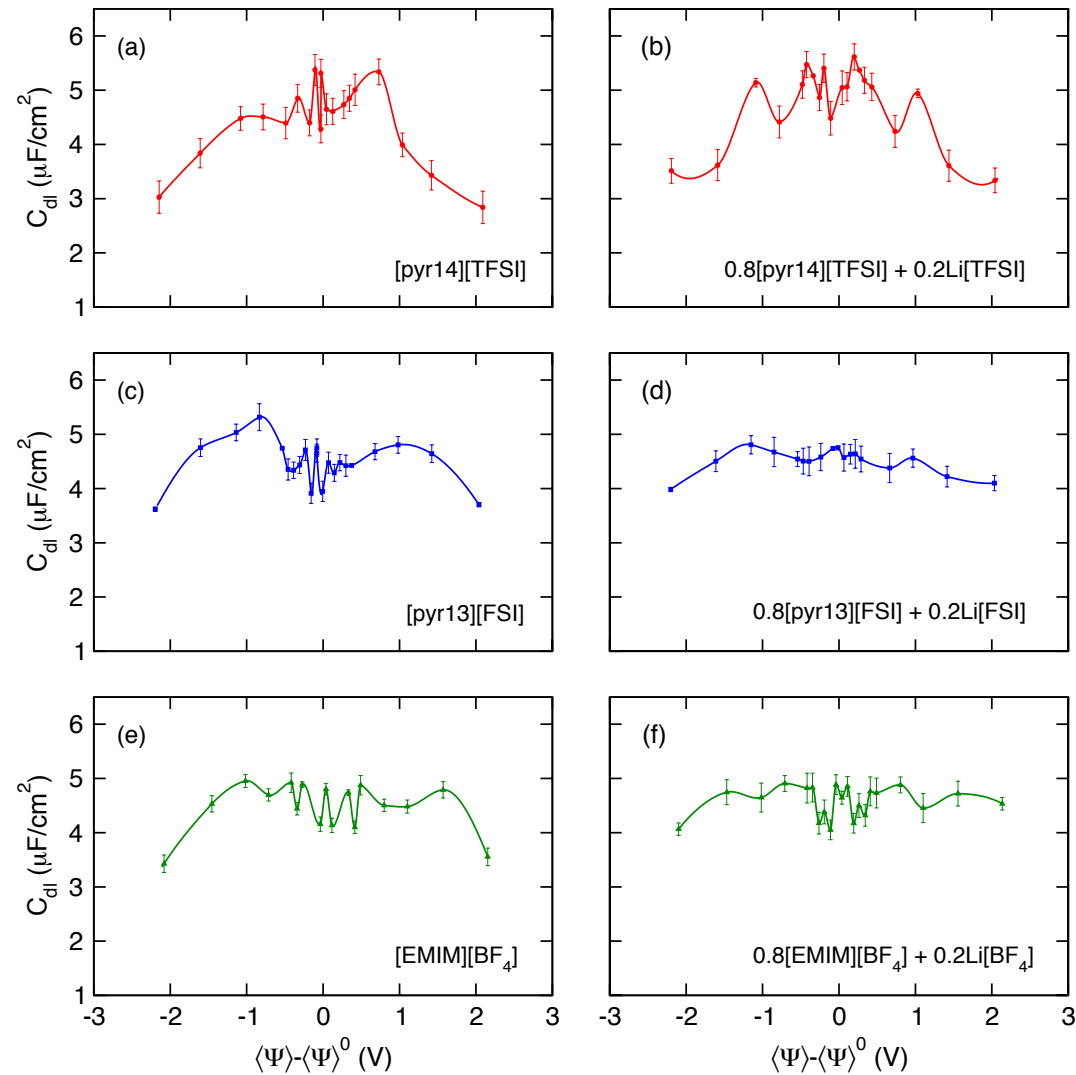
$$C_{\Delta\Psi} = \frac{\partial\langle\sigma\rangle}{\partial\langle\Psi\rangle} = \left[\beta A \langle|\sigma|\delta\sigma\rangle + \left\langle \frac{\partial\sigma}{\partial\Delta\Psi} \right\rangle \right] \left[\beta A \langle|\sigma|\delta\Psi\rangle + \left\langle \frac{\partial\Psi}{\partial\Delta\Psi} \right\rangle \right]^{-1}$$



Validated fluctuation formulas for capacitance
Electrode surface subtly influences capacitance



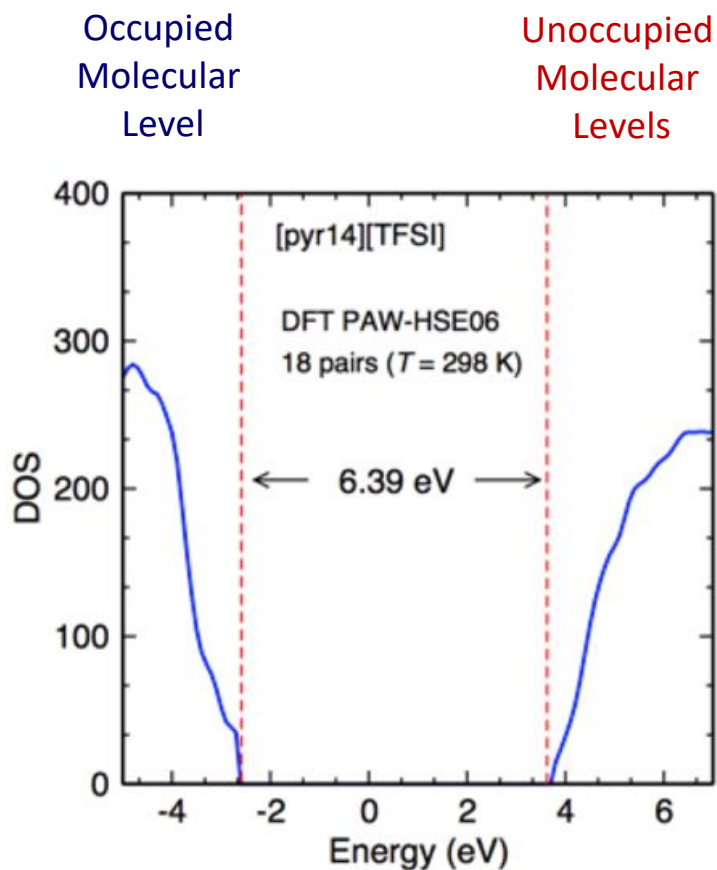
Capacitance



Li⁺ suppresses features in the capacitance profile



Electrochemical Windows



	E-window	Exp.
[pyr14][TFSI]	4.6-6.5 eV	6 eV
[EMIM][BF ₄]	3.9-5.4 eV	4.3 eV
[pyr13][FSI]	4.7-6.7 eV	4.3-6 eV

Bound the electrochemical window of liquids with pure and hybrid functionals



Specific Energy Estimates

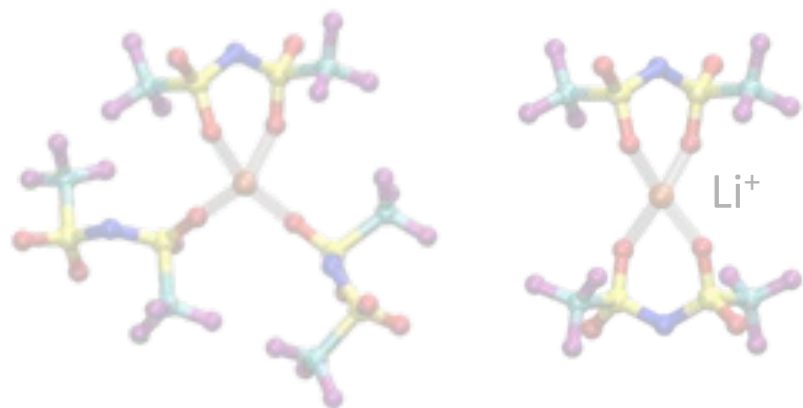


		E (Wh/m ²)	E (Wh/kg)
[pyr14][TFSI]	Theory	0.7-1.3	0.8-1.4
	Exp.	1.4-3.5	1.5-3.8
[pyr13][FSI]	Theory	0.7-1.4	0.8-1.5
	Exp.	3.5-6.8	3.8-7.3
[EMIM][BF ₄]	Theory	0.5-0.9	0.5-1.0
	Exp.	1.3-1.5	1.4-1.6

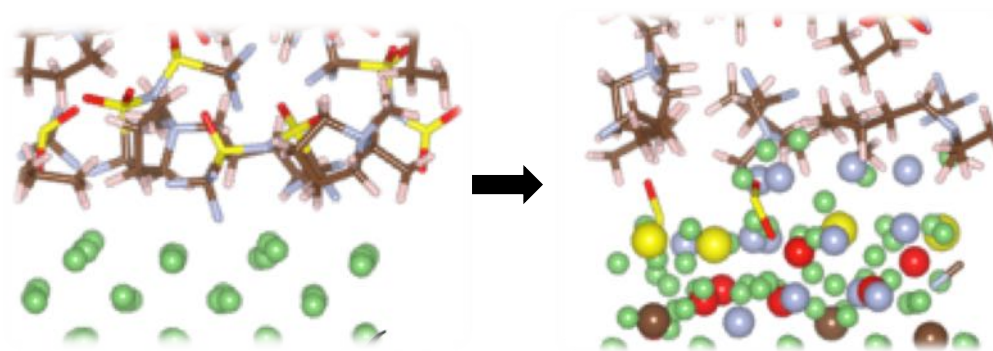
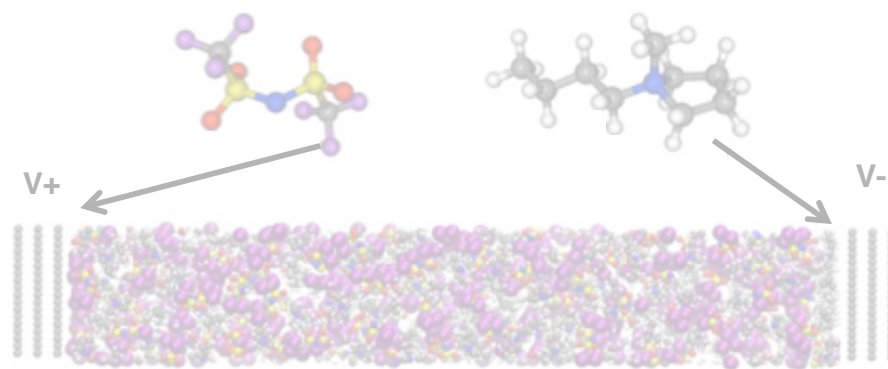
Assume specific surface area 1074 m²/g

[pyr13][FSI] highest energy from both experiment and theory

1) Li⁺ Transport and Solvation

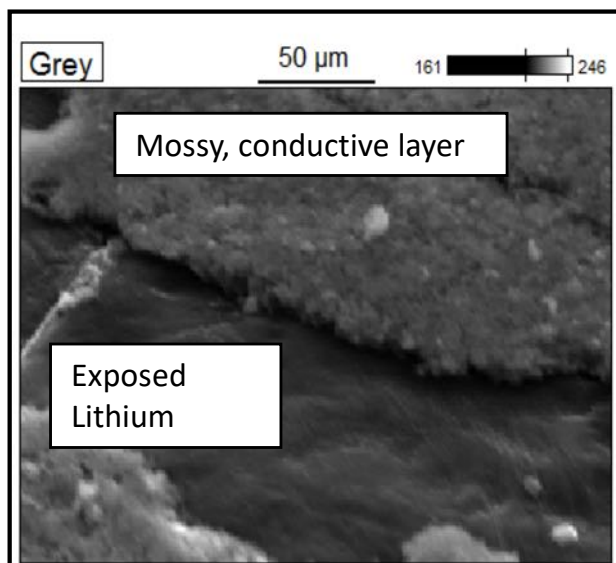


2) Behavior at Charged Interfaces

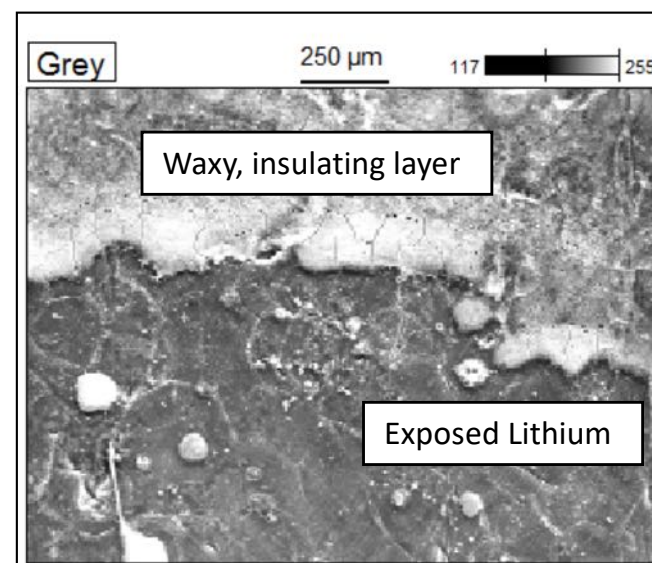


3) Behavior at Reactive Interfaces

[pyr14][TFSI]

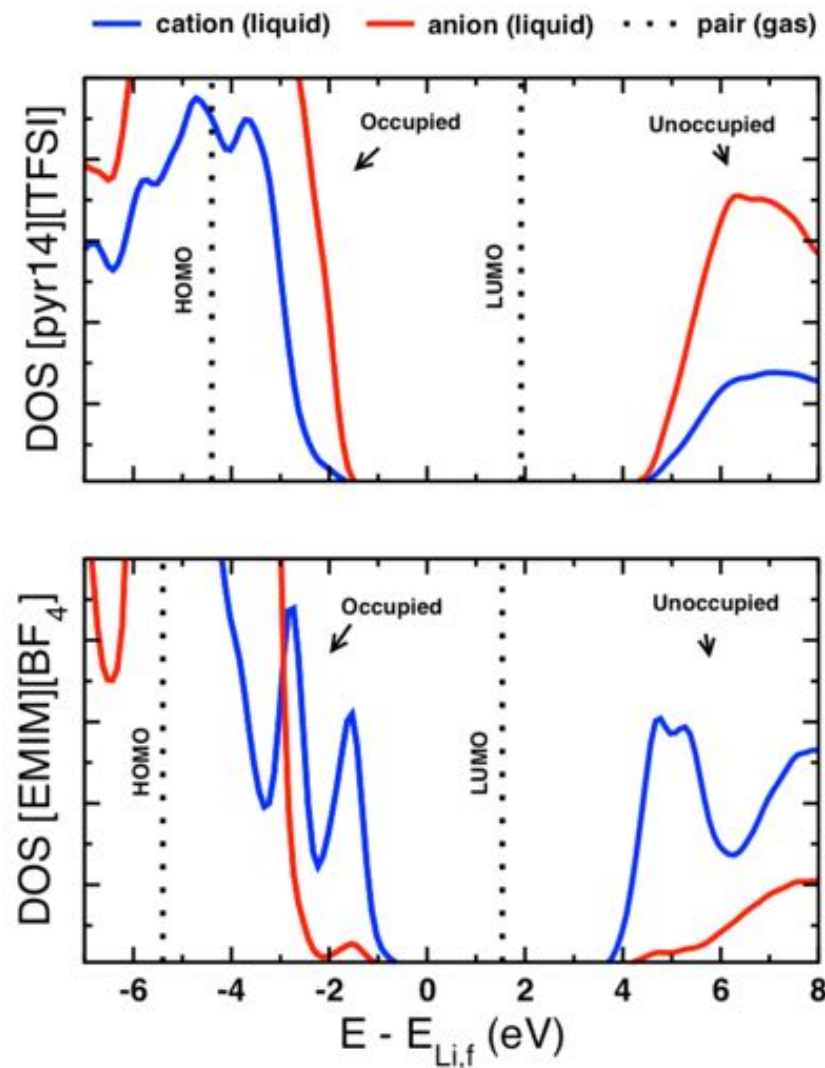
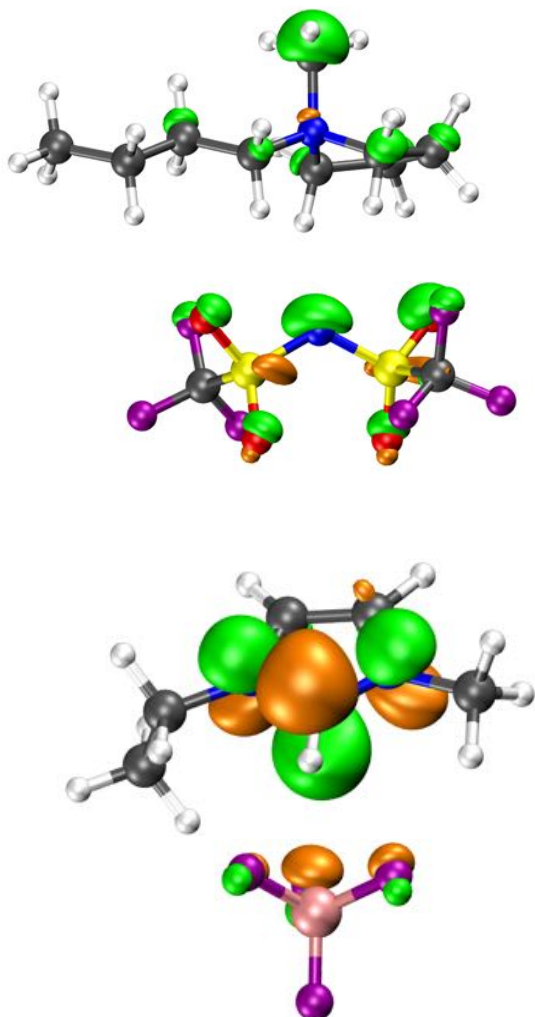


[EMIM][BF4]



Surface layers (mossy vs waxy) have dramatic effect on cycling performance

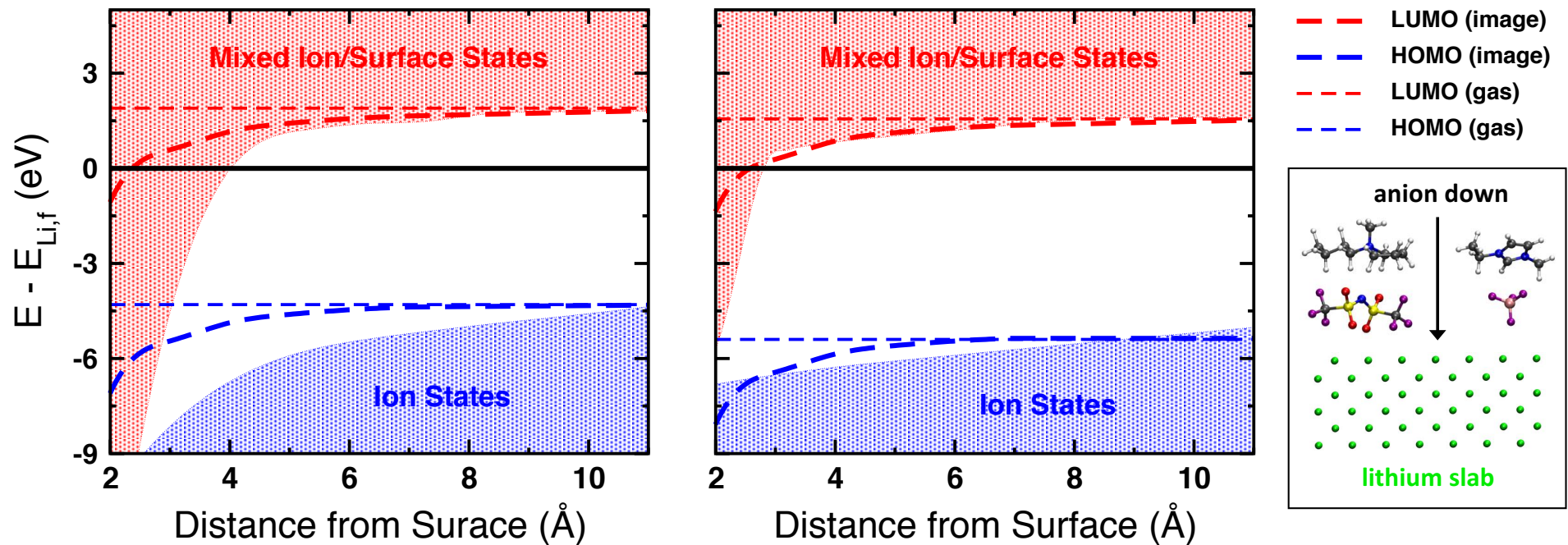
Level Alignment: Vacuum Levels



LUMO level is shared by both anions of the ionic liquid pair
Vacuum level alignment indicates the liquids are stable



Level Alignment: Explicit Computation

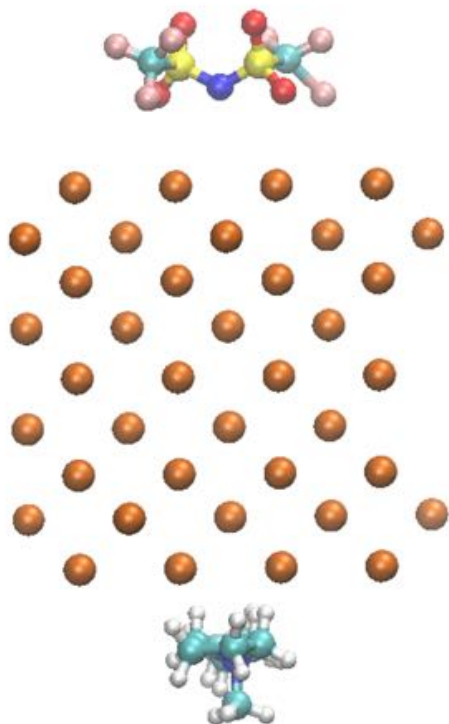


Ion levels mix with surface levels when near the surface

Ion Pair Decomposition

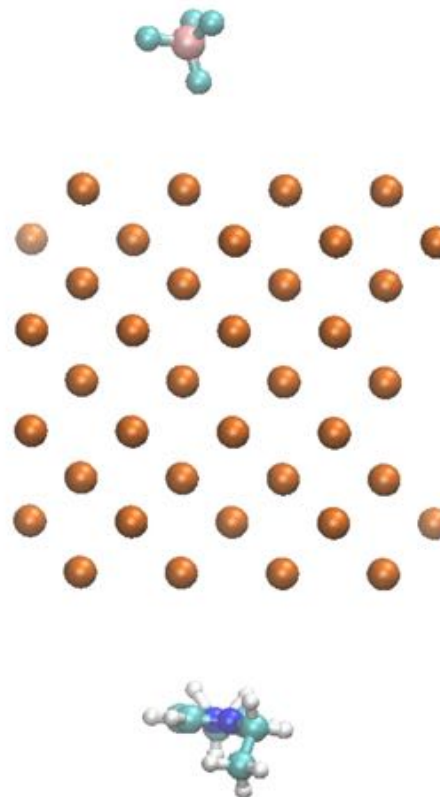


Lithium Metal Surface



[pyr14]⁺[TFSI]⁻

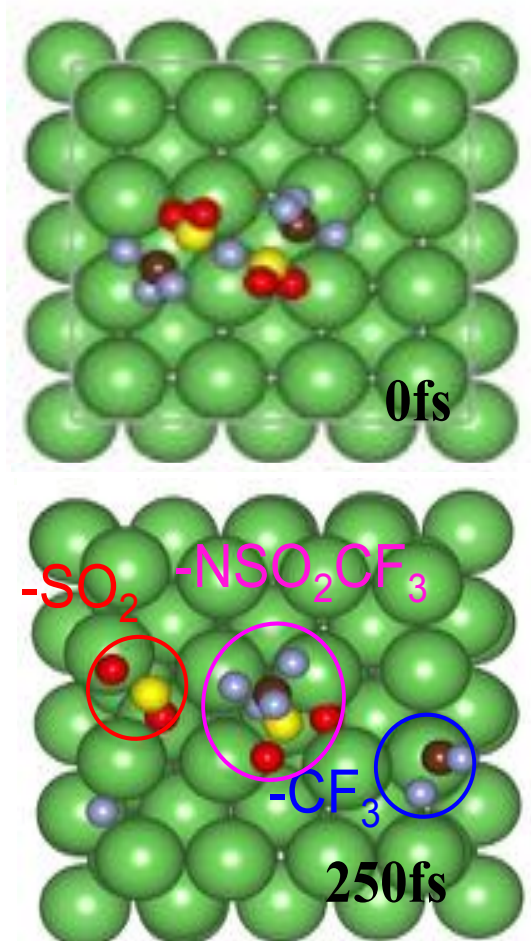
Lithium Metal Surface



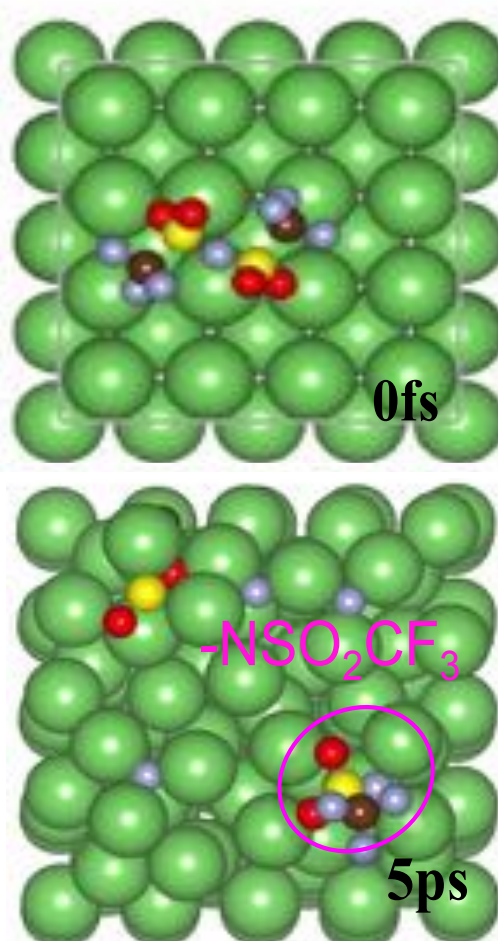
[emim]⁺[BF₄]⁻

Dynamics show that [TFSI]⁻ readily decomposes

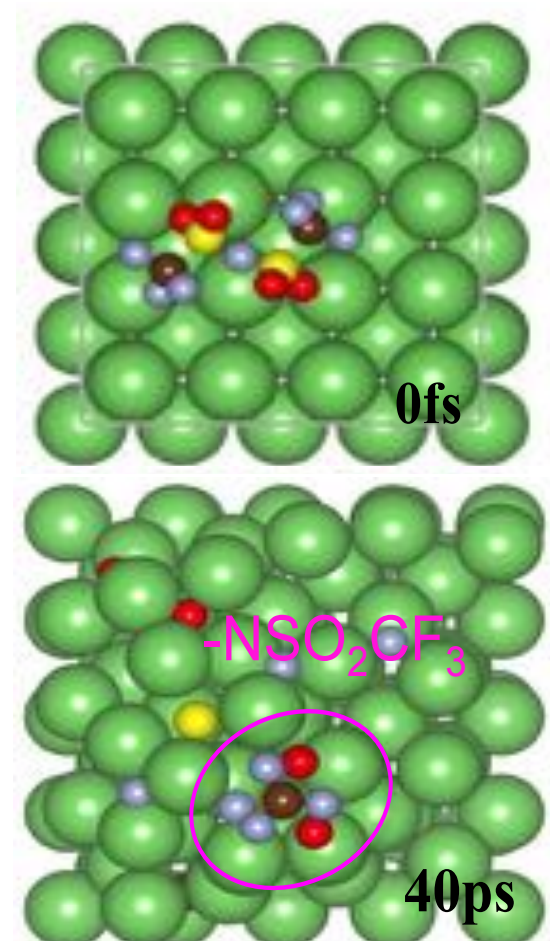
Simulation 1



Simulation 2



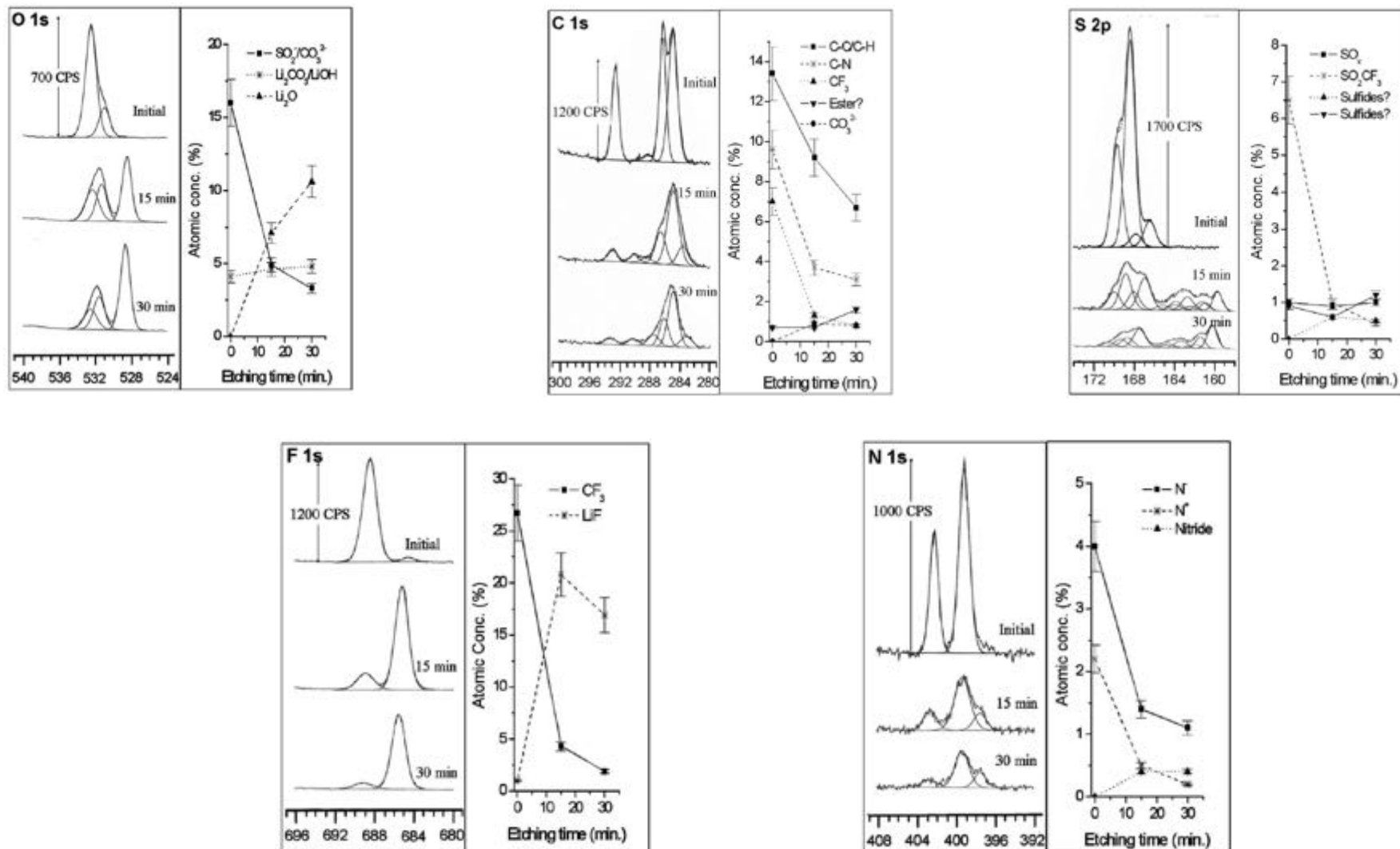
Simulation 3



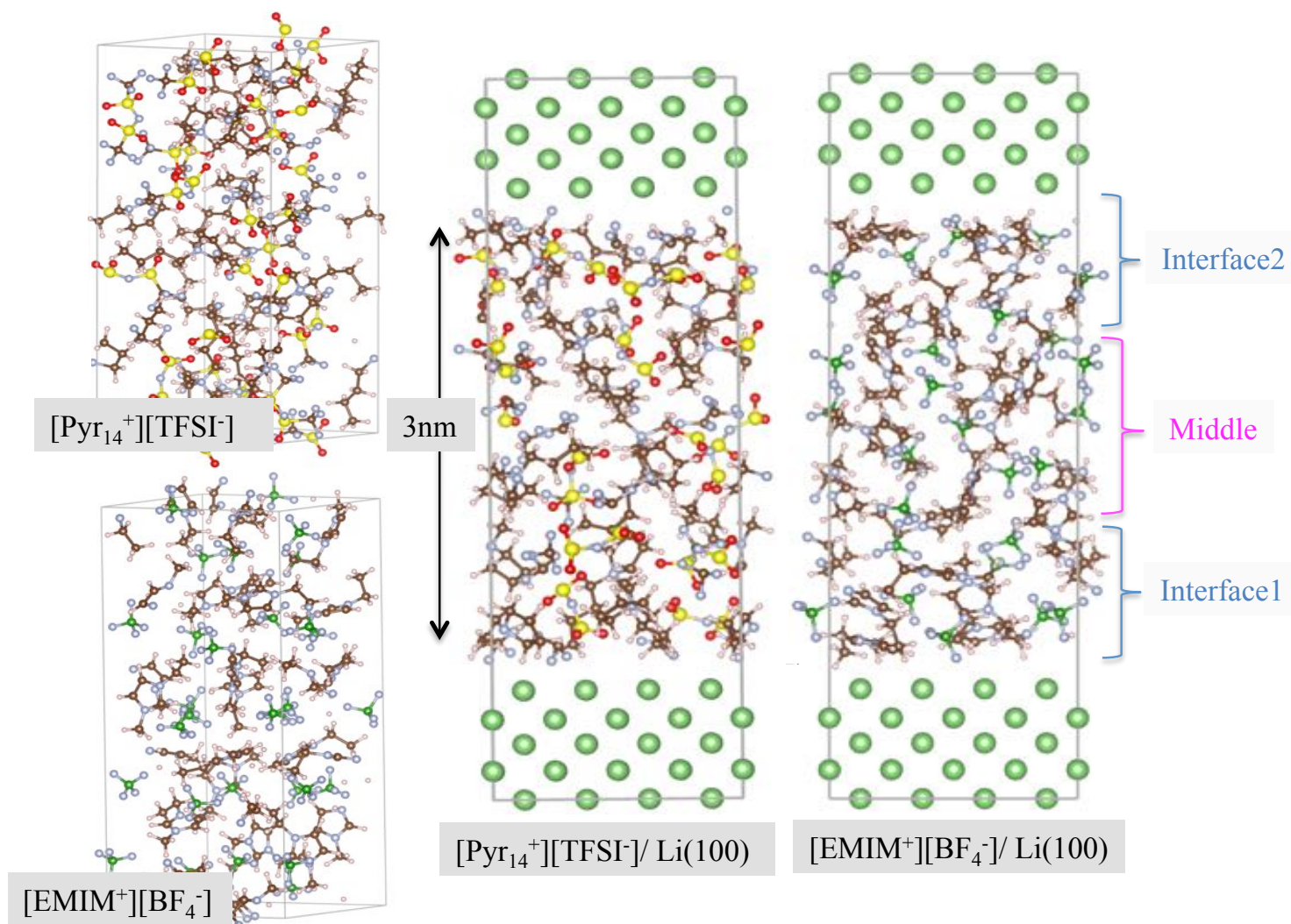
LiF, Li_2O , $-\text{CF}_3$, $-\text{SO}_2$, and $-\text{NSO}_2\text{CF}_3$ groups are generated



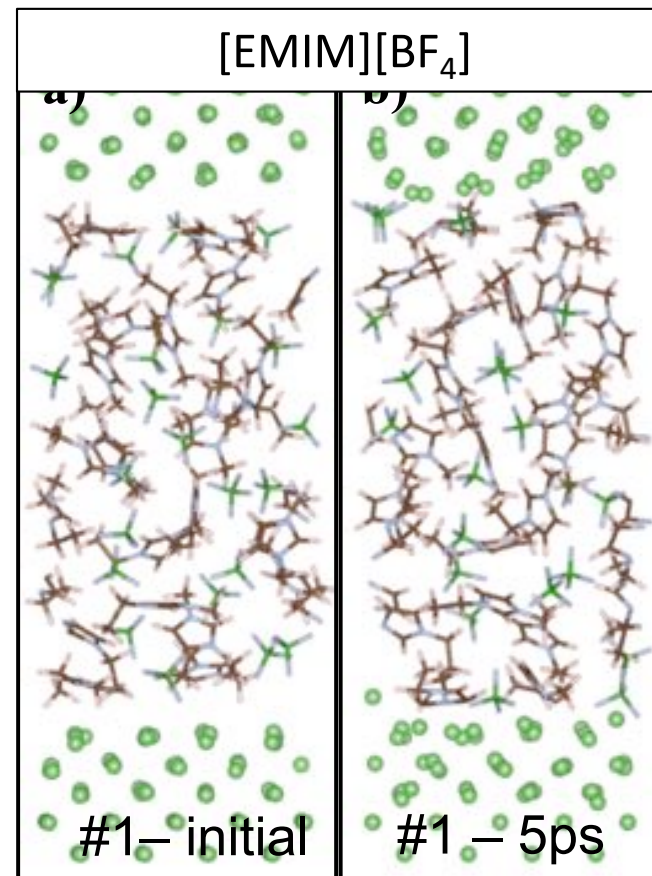
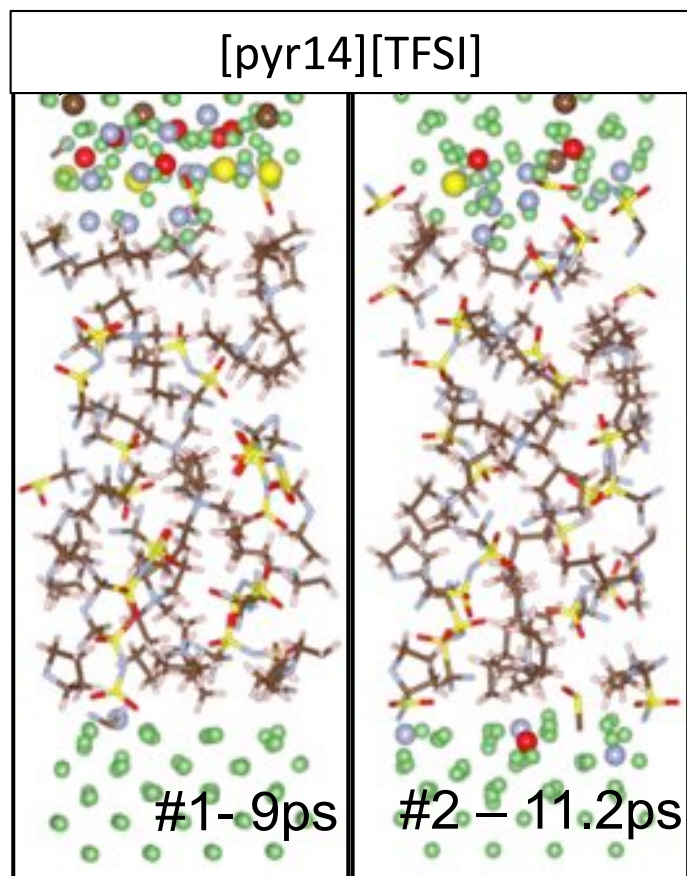
XPS Analysis of Etched Surface Layer



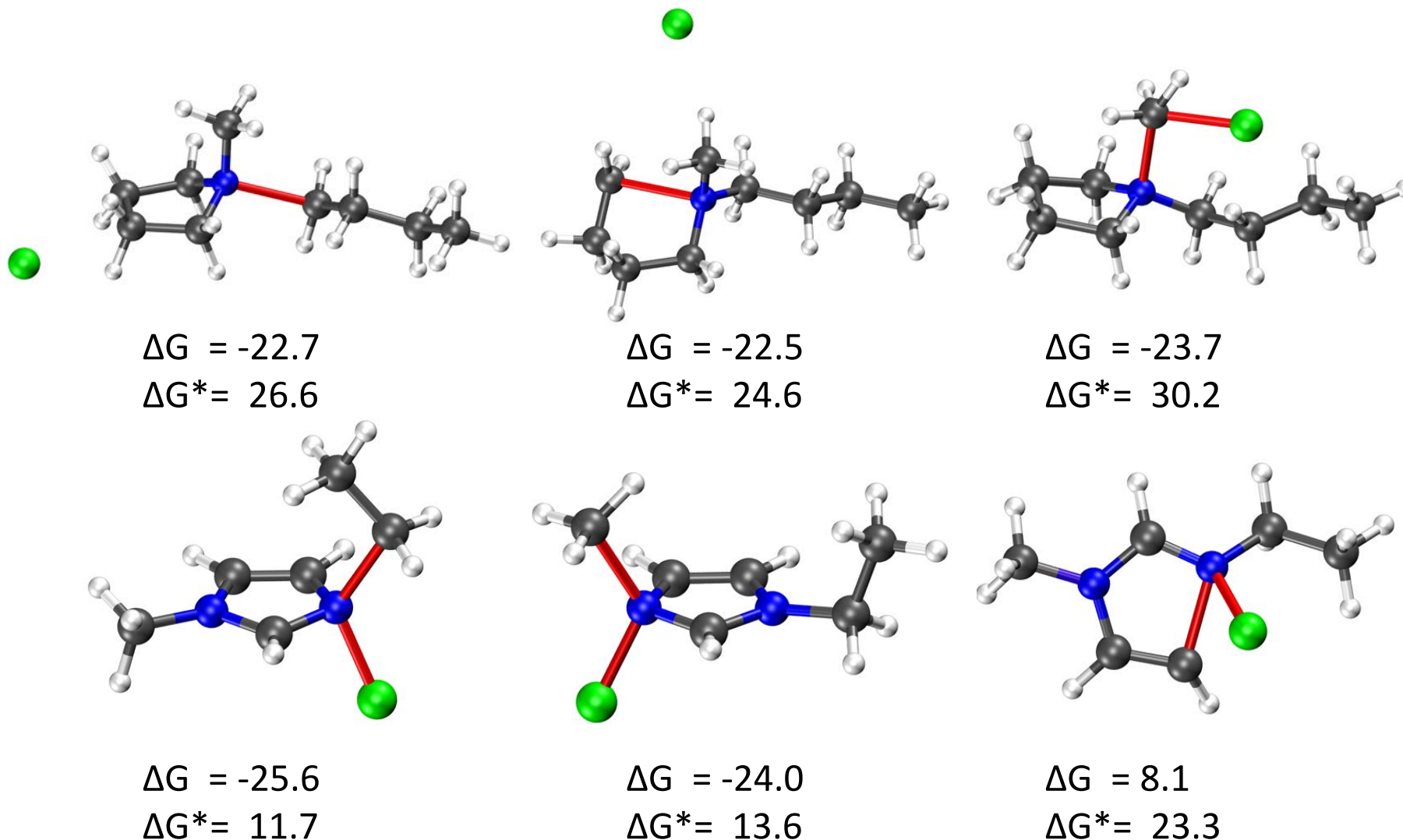
LiF, Li_2O , $-\text{CF}_3$, $-\text{SO}_2$, and $-\text{NSO}_2\text{CF}_3$ products match XPS results



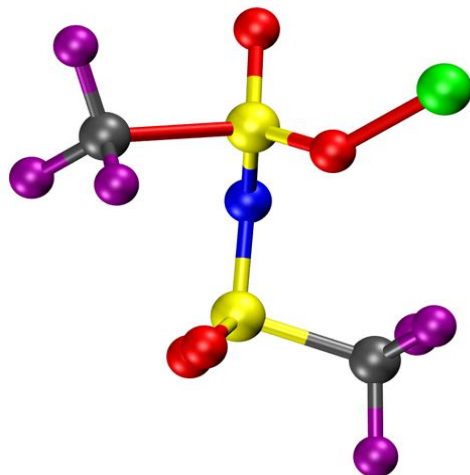
Bulk systems examined to examine other possible reactions



Product profile similar to single pair simulations

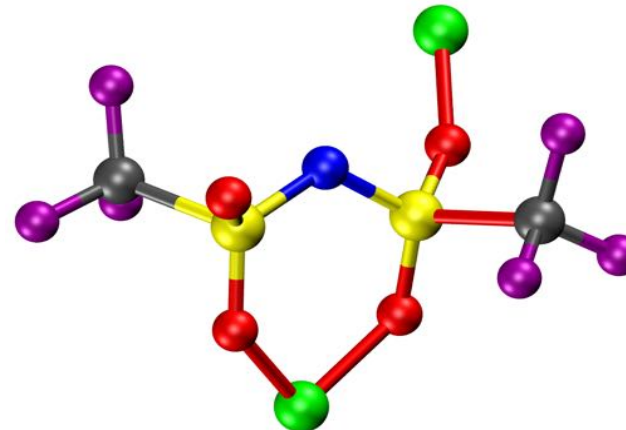


All examined decompositions favorable except aromatic ring breaking in [EMIM]



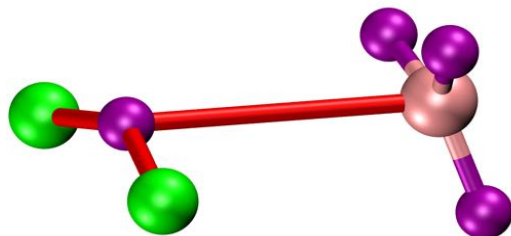
$$\Delta G = -87.4$$

$$\Delta G^* = 10.1$$



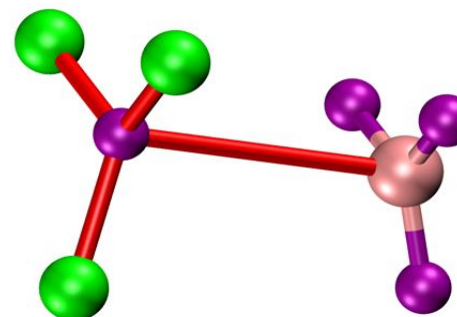
$$\Delta G = -97.2$$

$$\Delta G^* = 0.2$$



$$\Delta G = -5.3$$

$$\Delta G^* = 18.0$$



$$\Delta G = -14.0$$

$$\Delta G^* = 16.7$$

All reactions favorable, more Li^+ reduce the reaction barrier



Conclusions



- **Ionic conductivity a direct function of Li^+ solvation structure and network formation**
- **Capacitor energetics governed primarily by voltage window**
- **Electric double layer impedes Li^+ diffusion to the electrode surface**
- **All ions are found to decompose in the presence of Li-metal in reductive processes**
- **Differences in the solid electrolyte interphases can be traced to the reactants**
 - Haskins, et al., *JPCB* **118**, 11295 (2014)
 - Bauschlicher, et al., *JPCB* **118**, 10785 (2014)
 - Haskins, et al., *JPCB* **119**, 14705 (2015)
 - Haskins, et al., *JCP* **114**, 184707 (2016)
 - Haskins, et al., *JPCC* **120**, 11993 (2016)
 - Haskins, et al., *JPCC* **121**, 28235 (2017)
 - Yildirim, et al., *JPCC* **121**, 28214 (2017)

Acknowledgements



NASA Ames Research Center
Handan Yildirim
Charles W. Bauschlicher
Josh D. Monk



NASA Glenn Research Center
James J. Wu
Dionne M. Hernandez
William R. Bennett
Vadim Lvovich



Army Research Center
Oleg Borodin

Haskins, et al., *JPCB* **118**, 11295 (2014)
Bauschlicher, et al., *JPCB* **118**, 10785 (2014)
Haskins, et al., *JPCB* **119**, 14705 (2015)
Haskins, et al., *JCP* **114**, 184707 (2016)
Haskins, et al., *JPCC* **120**, 11993 (2016)
Haskins, et al., *JPCC* **121**, 28235 (2017)
Yildirim, et al., *JPCC* **121**, 28214 (2017)