# Ionic Liquids at Electrified Interfaces

## *From Double Layers to Decomposition*


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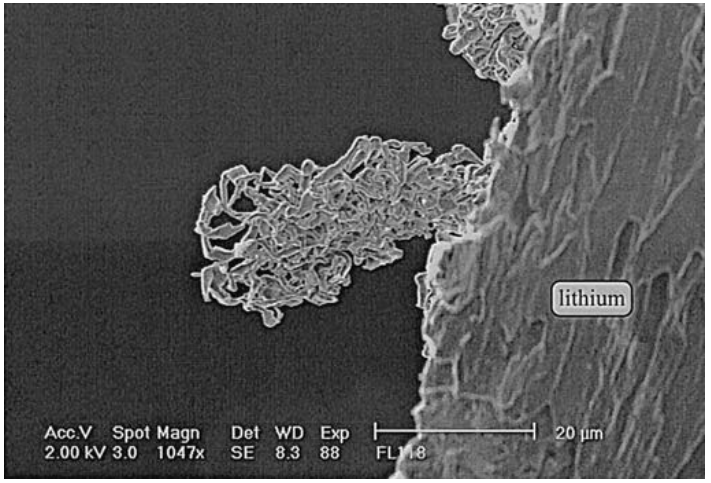
# Ionic Liquids for Electrochemical Applications

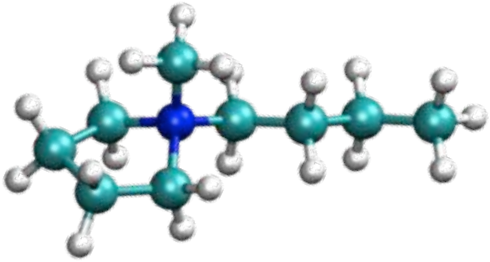
- **Advanced electrodes**: help stabilize cycling against Li-metal
- **Li-ion batteries**: possible safer alternative to organic electrolytes
- **Supercapacitors:** double layer capacitor electrolyte
- **Electrodeposition**: wide electrochemical window solvent
- **Biofuel cells**: replace water as more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



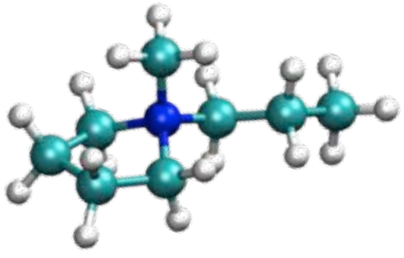

F. Orsini et al., J. Power Sources 76, 19-29 (1998)

NASA Electric Aircraft

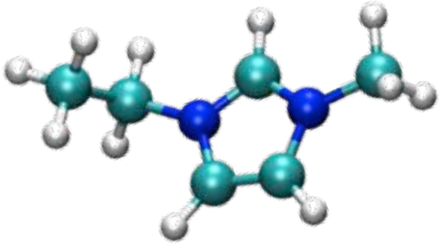
# Ionic Liquids



[pyr14][TFSI]



[pyr13][FSI]

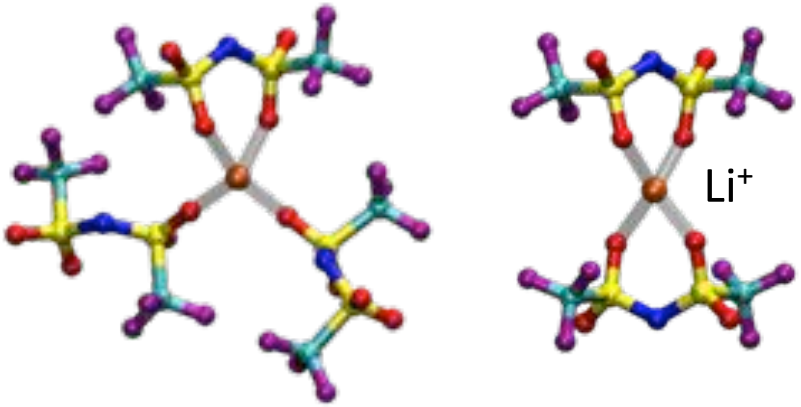


[EMIM][$BF_4$]

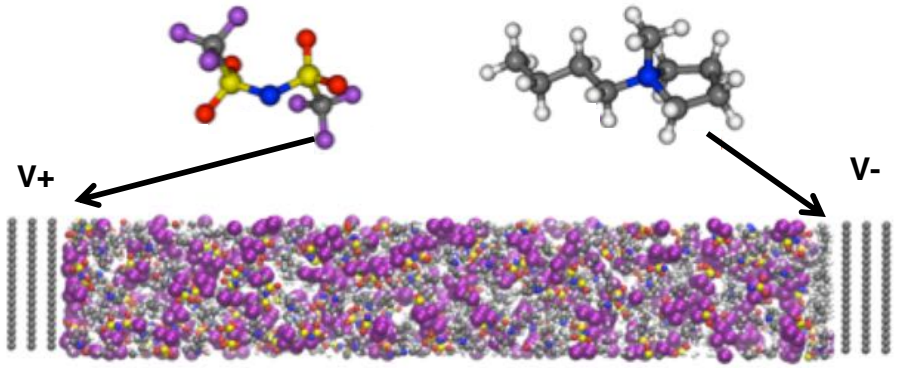
Chosen for suppression of dendrites on $Li^+$ metal anodes*

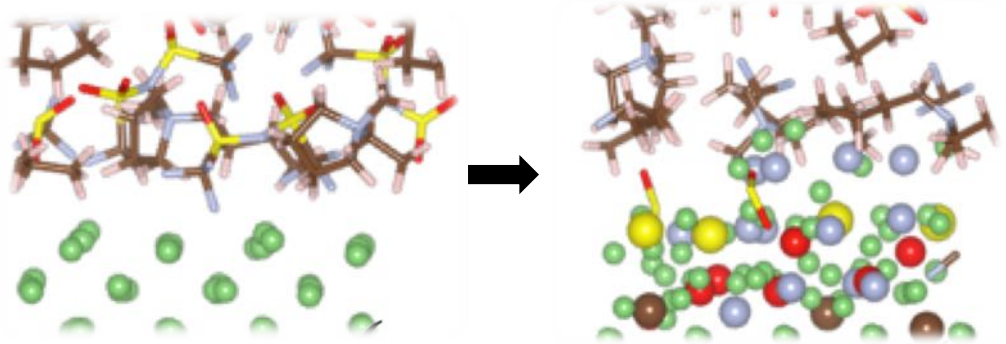
Bhattacharyya et al., Nature Mater. (2010)
Basile, et al., Elechem. Commun. (2013)

## 1) $Li^+$ Solvation and Transport




## 2) Behavior at Charged Interfaces



## 3) Behavior at Reactive Interfaces

# Computational Techniques

**Quantum Chemistry:**

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

**Polarizable Molecular Dynamics (MD):**

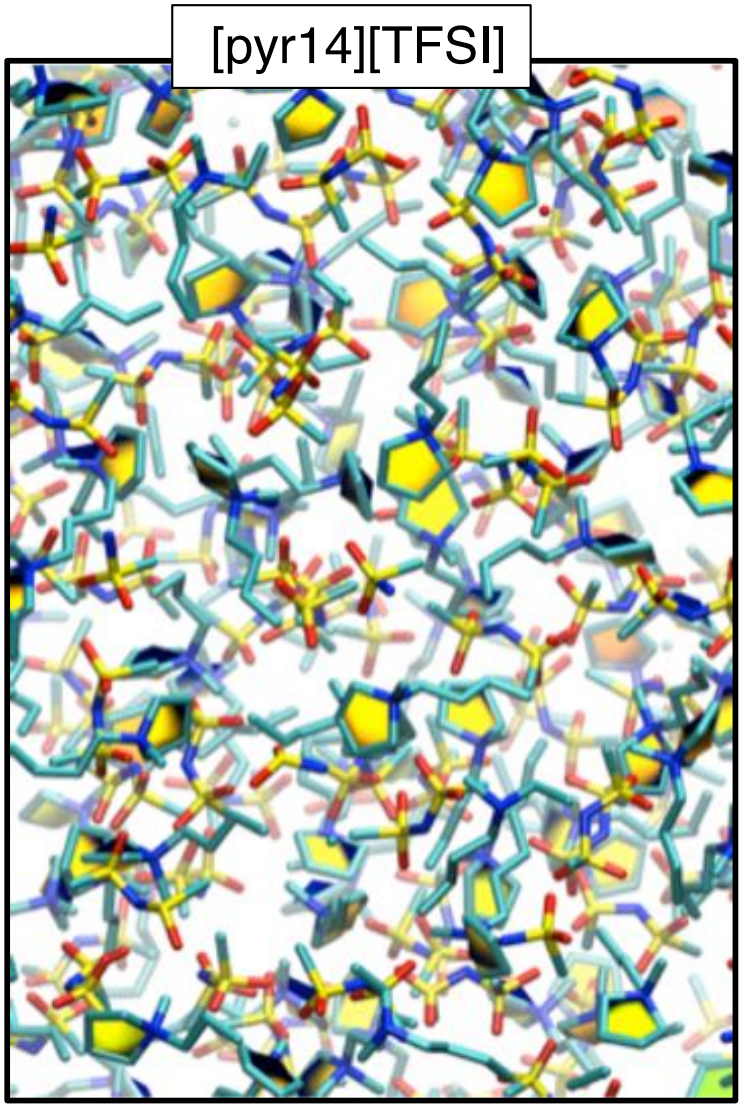
- APPLE&P
- Large-scale $Li^+$ solvation structures
- Physical properties

**Constant Potential MD:**

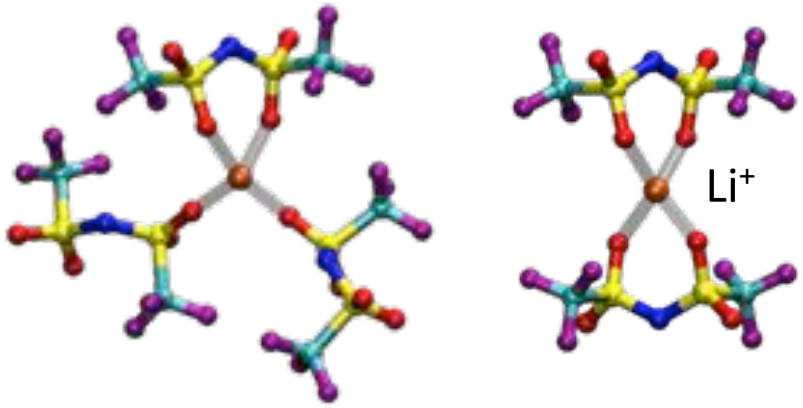
- Double layer structure
- Capacitance

**Density Functional Theory MD:**

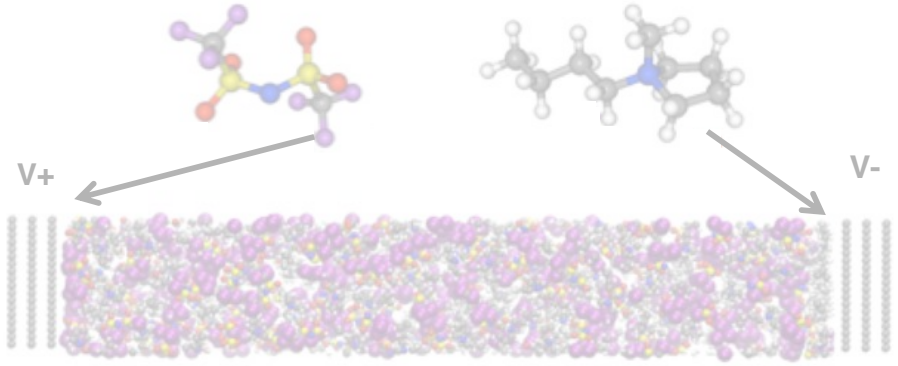
- Electrochemical window
- Reactions

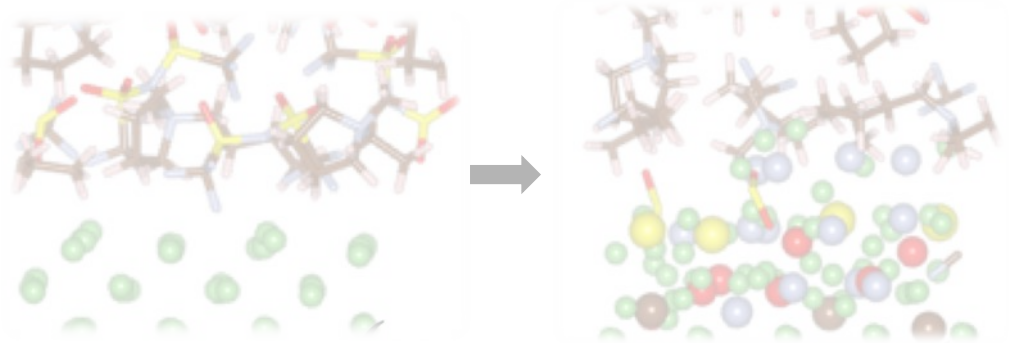


## 1) $Li^+$ Transport and Solvation



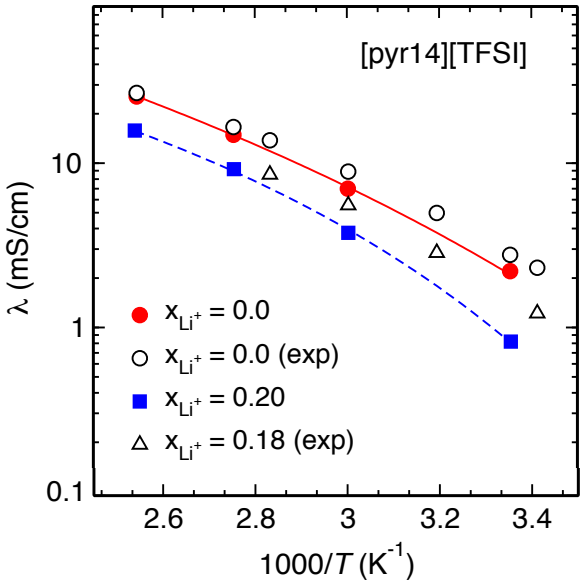

## 2) Behavior at Charged Interfaces

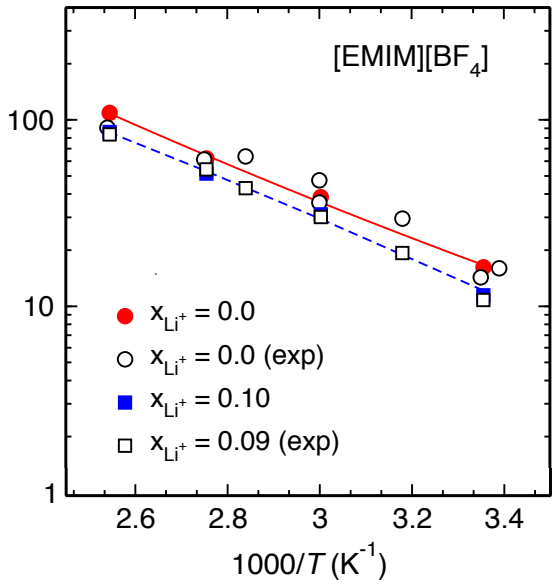


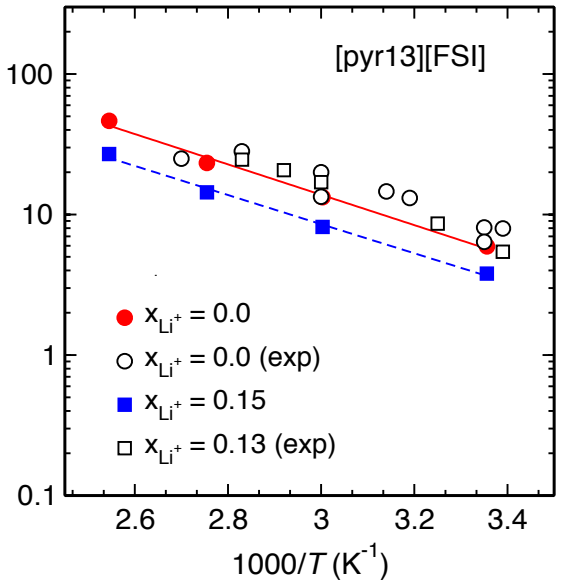



## 3) Behavior at Reactive Interfaces

# Ionic Conductivity

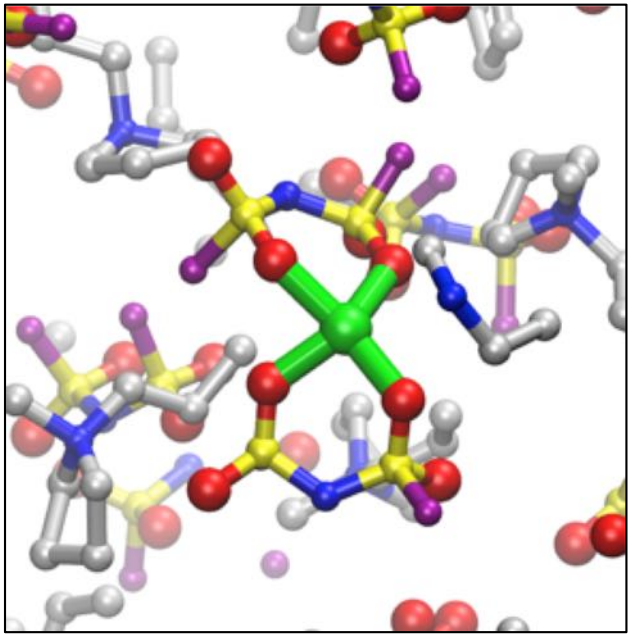


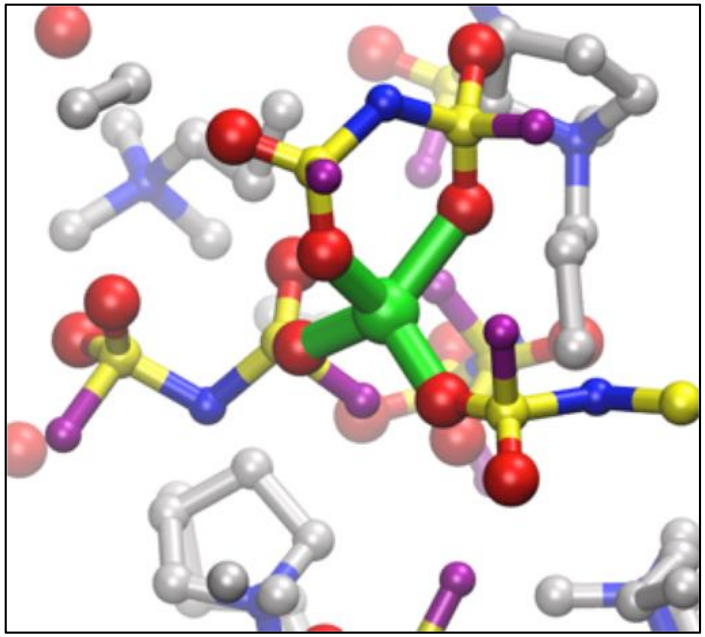




Conductivity decreases with anion size: TFSI < FSI < $BF_4$
Li-doping suppresses conductivity of all systems

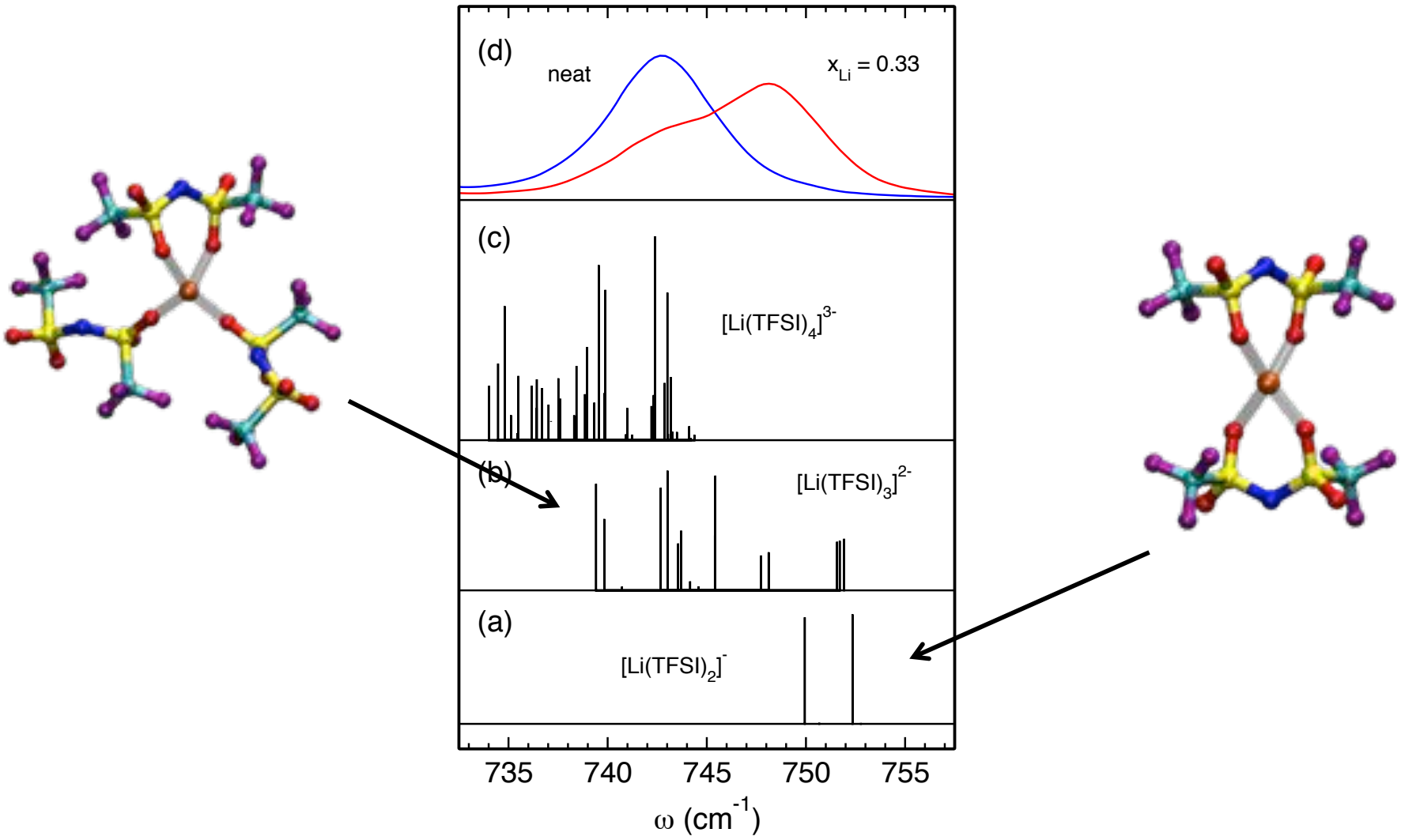
# Solvation Structure in Bulk Liquid





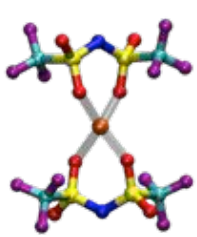
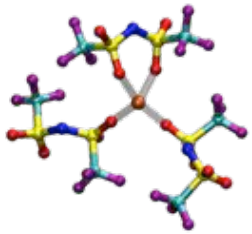
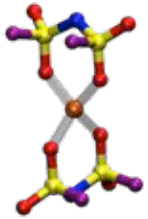
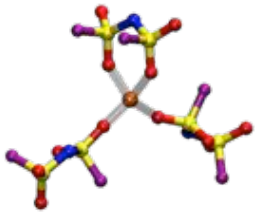
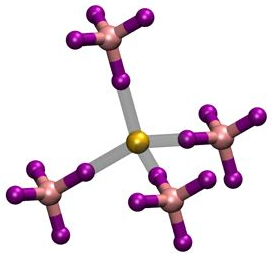
Highly unfavorable configurations exchange anions

# Raman Analysis of Li[TFSI]



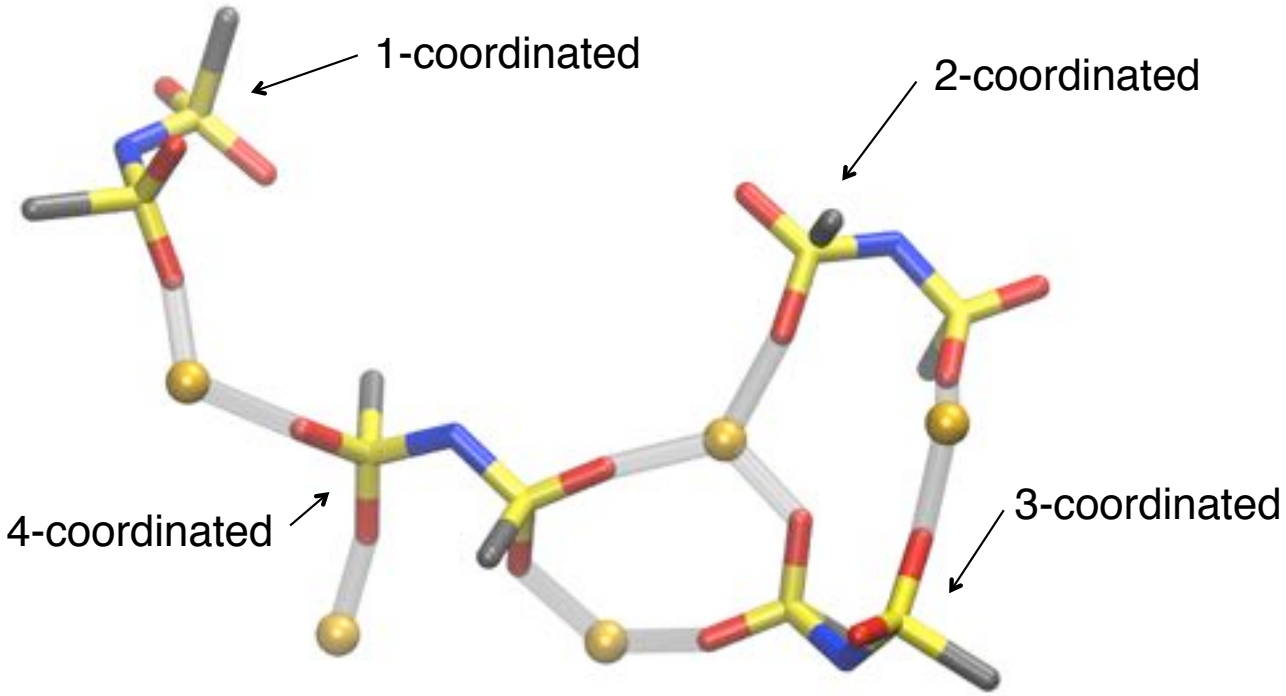

2 [TFSI] coordination dominant, 3 [TFSI] possible

# Solvation Shells of $Li^+$

| | 2-anion | 3-anion | 4-anion |
|---|---|---|---|
| $[TFSI]^-$ |  |  |  |
| $[FSI]^-$ |  |  |  |
| $[BF_4]^-$ |  |  |  |

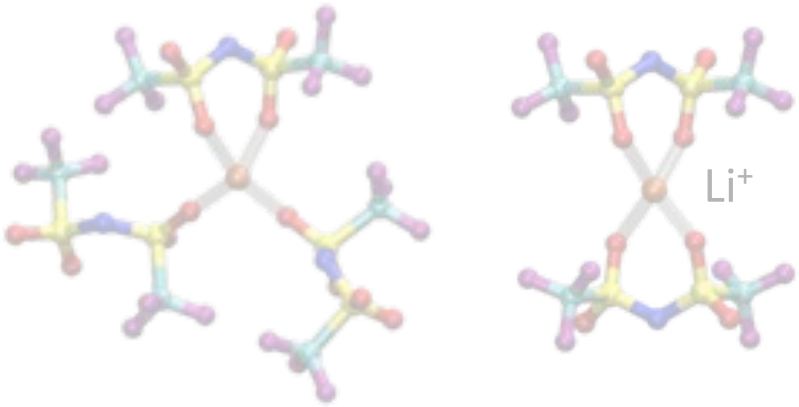
2, 3 anion $Li^+$ solvation shells for TFSI/FSI
4 anion $Li^+$ solvation shell for $BF_4$

# $Li^+ \ldots Li^+$ Networks

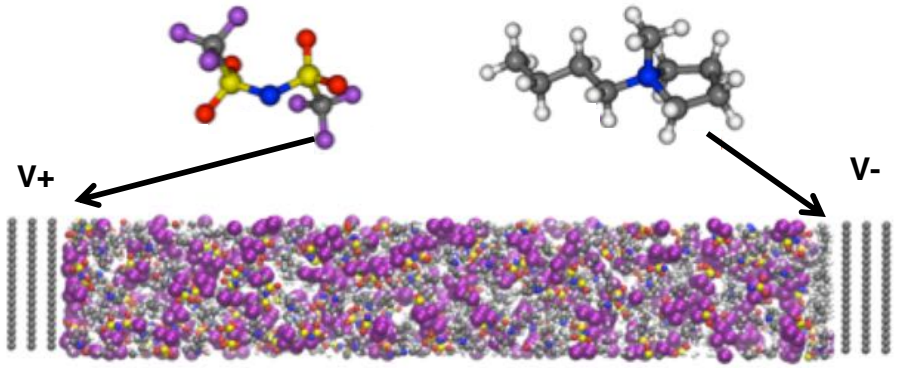


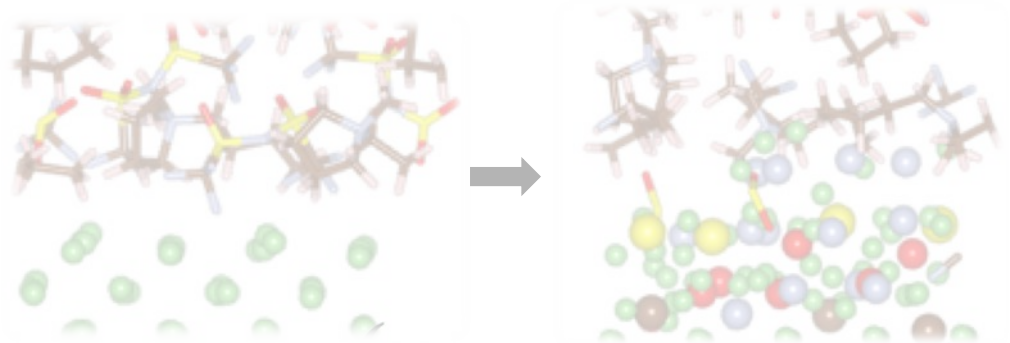

Networks of $Li^+$ prevalent in ionic liquids

1) $Li^+$ Transport and Solvation



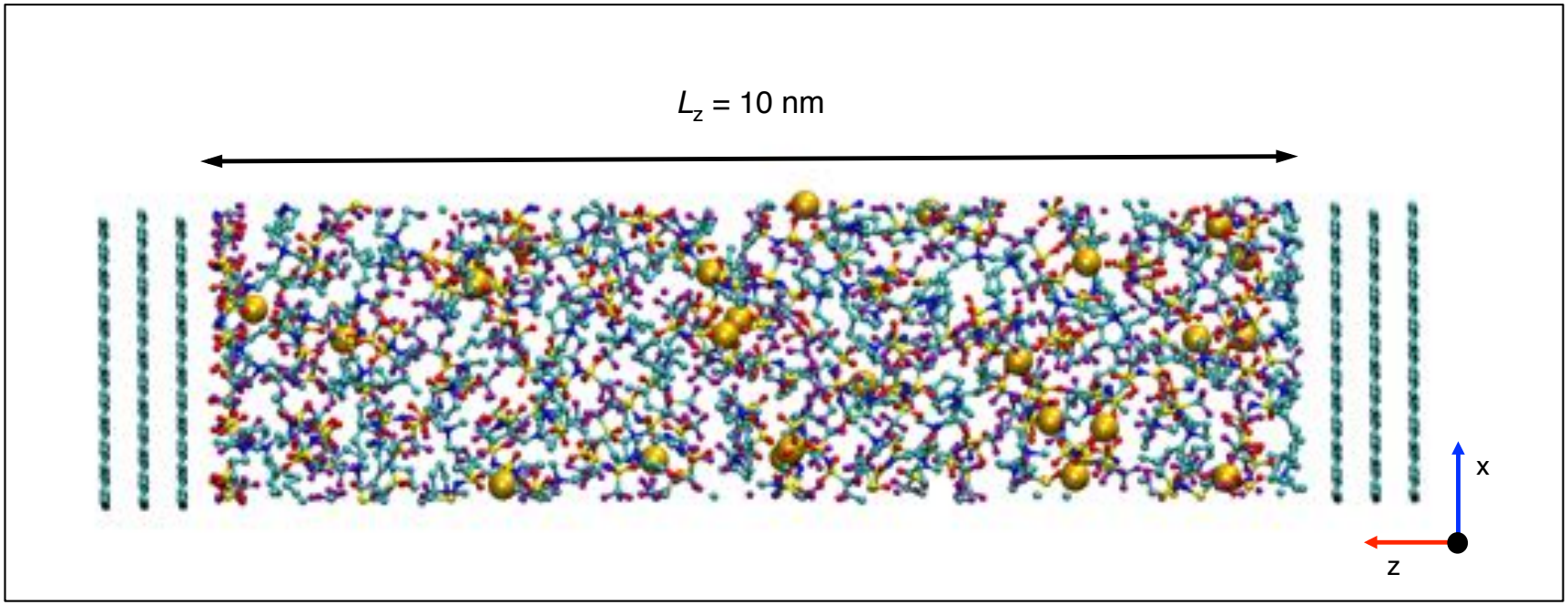

**2) Behavior at Charged Interfaces**



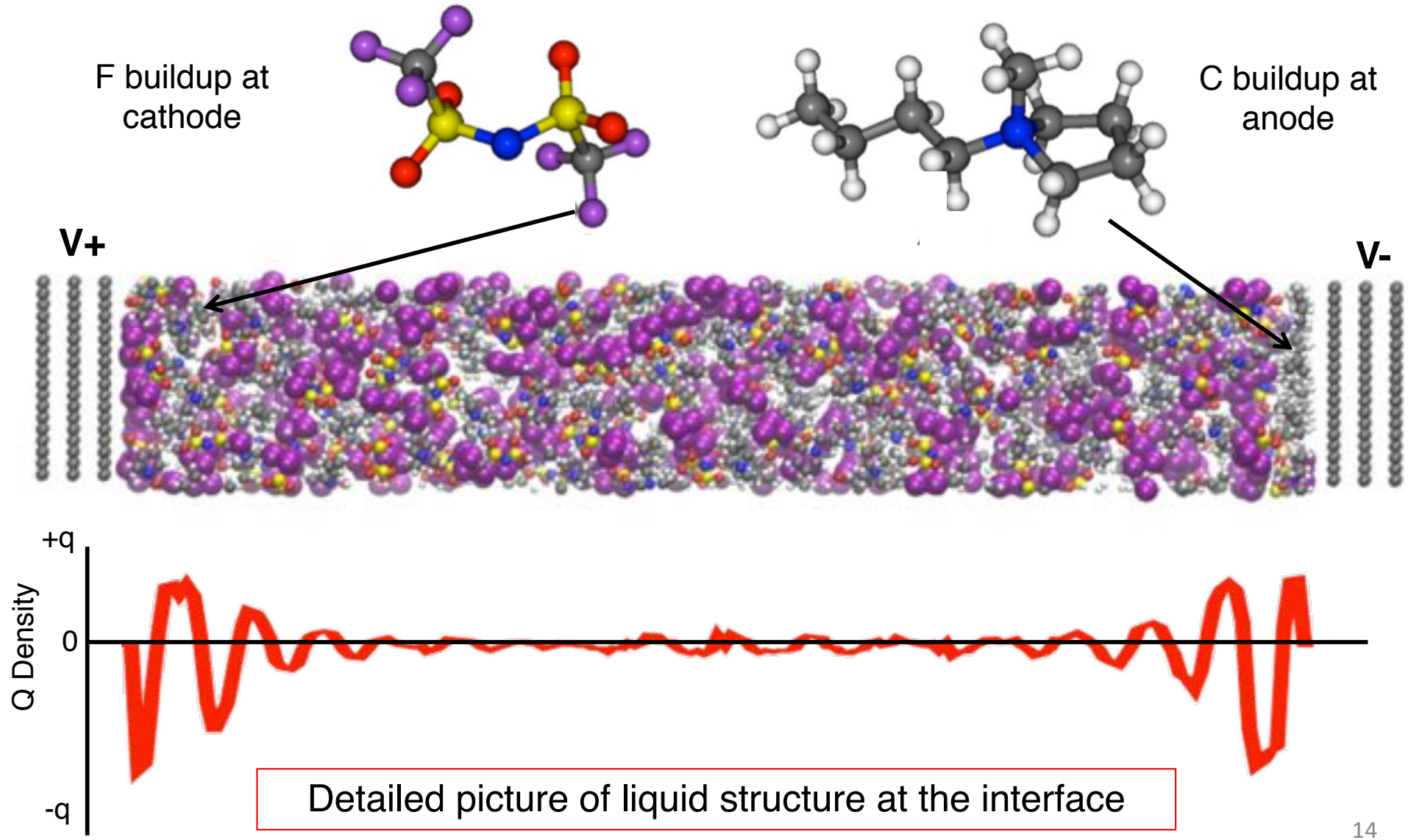
3) Behavior at Reactive Interfaces

# Ionic Liquids at Electrified Interfaces



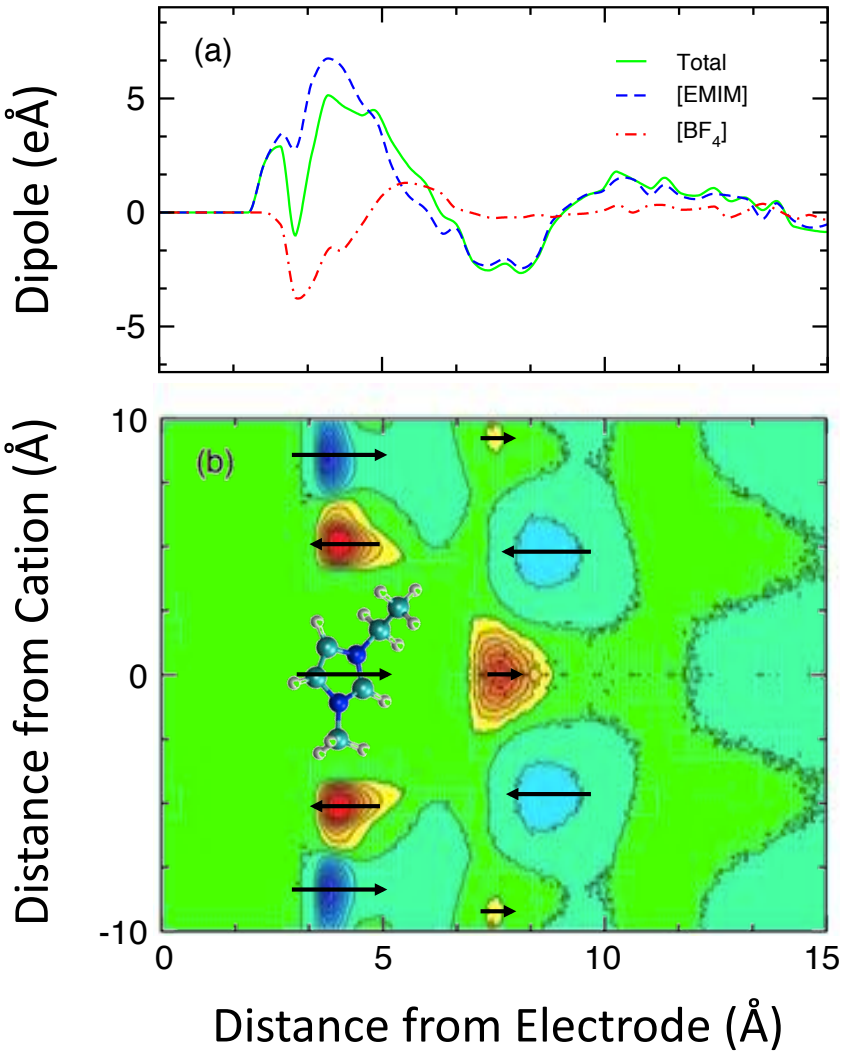

Two electrode simulations performed as a function of electrode voltage drop

# Electric Double Layer (EDL)



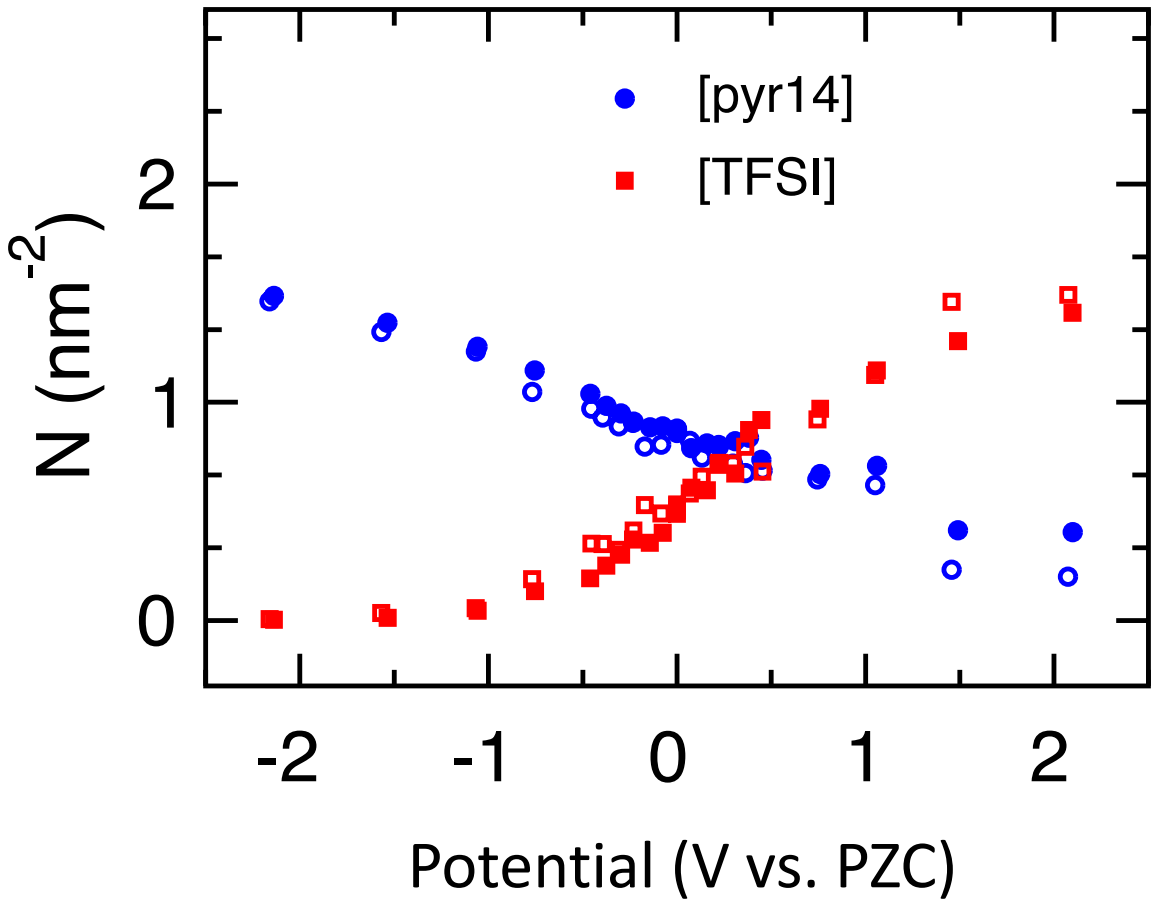

Detailed picture of liquid structure at the interface

# Influence of Atomic Polarization on EDL



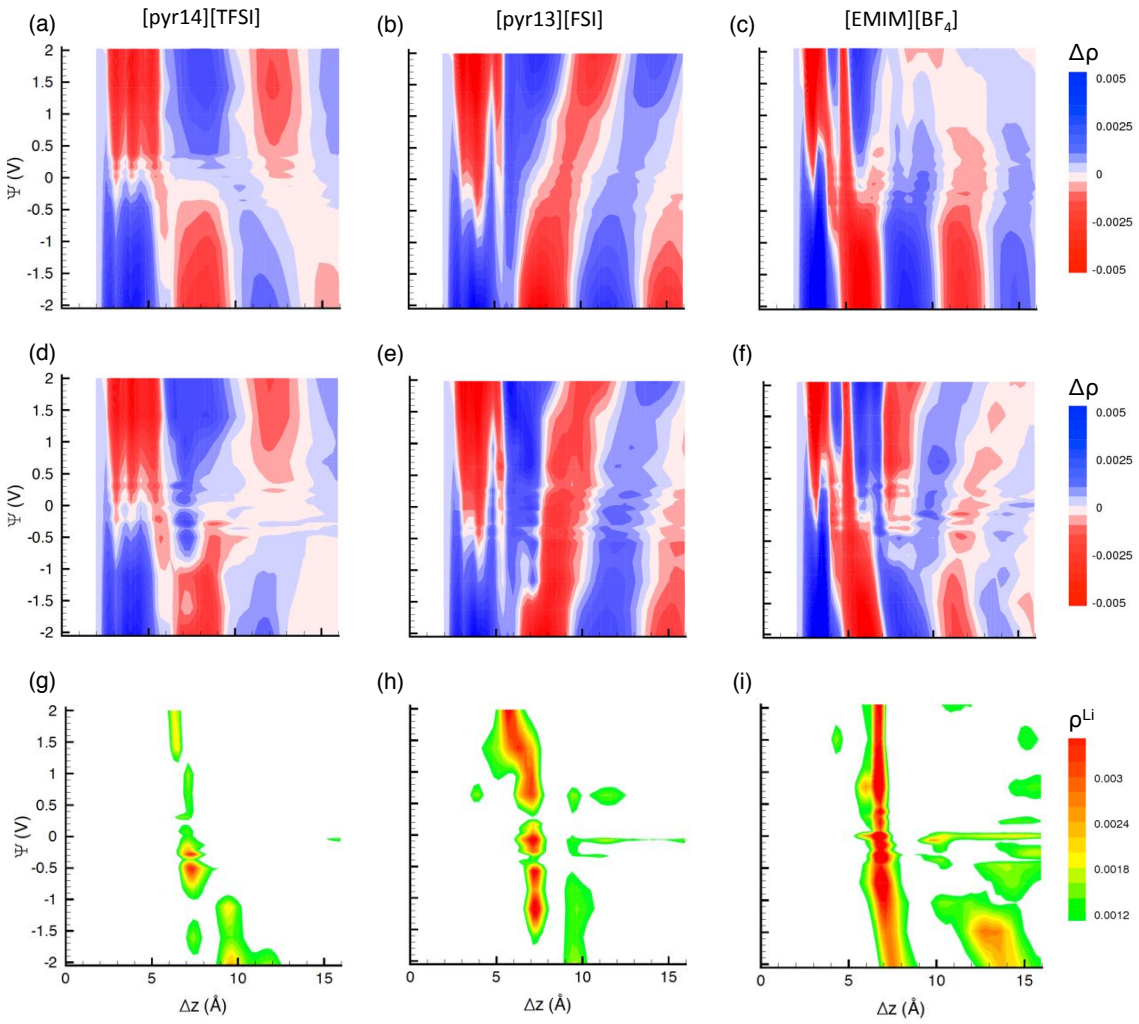

Polarization opposes formation of the EDL

# Ion Accumulation at the Interface




Interface is enriched in cations or anions

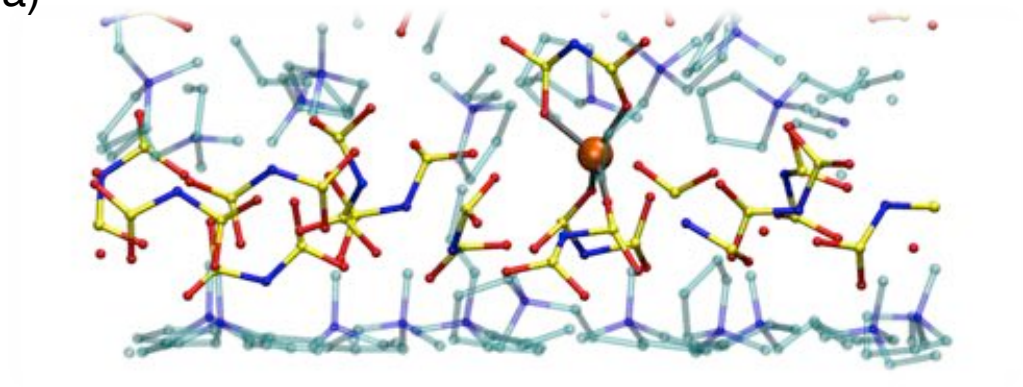
# $Li^+$ in the EDL



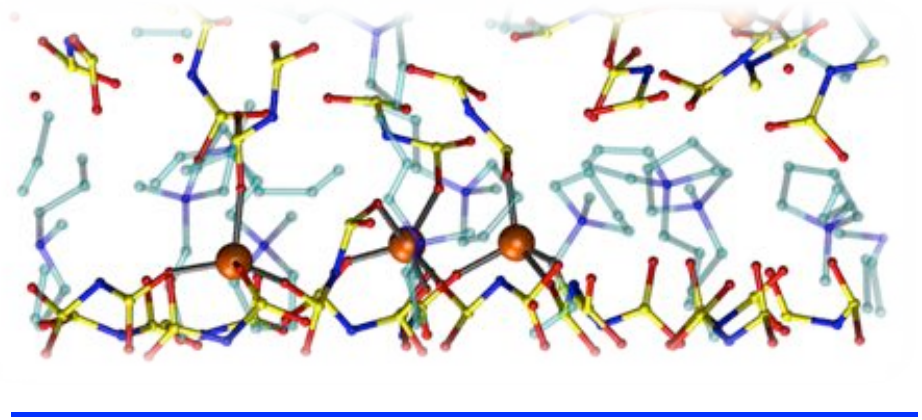

$Li^+$ disrupts the EDL and accumulates near the surface

# $Li^+$ Binding in the EDL

(a)

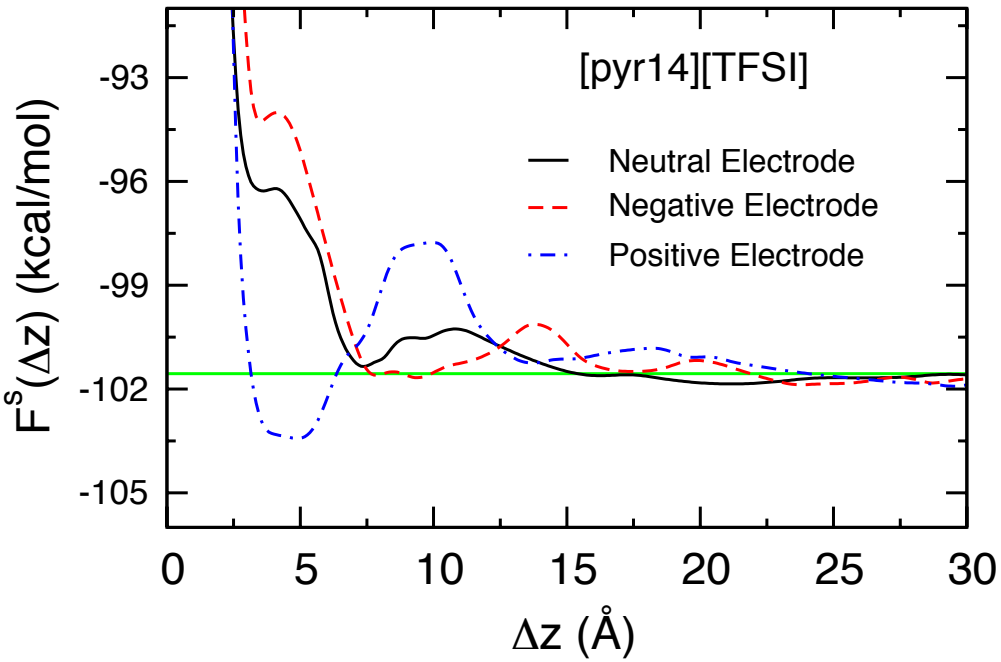


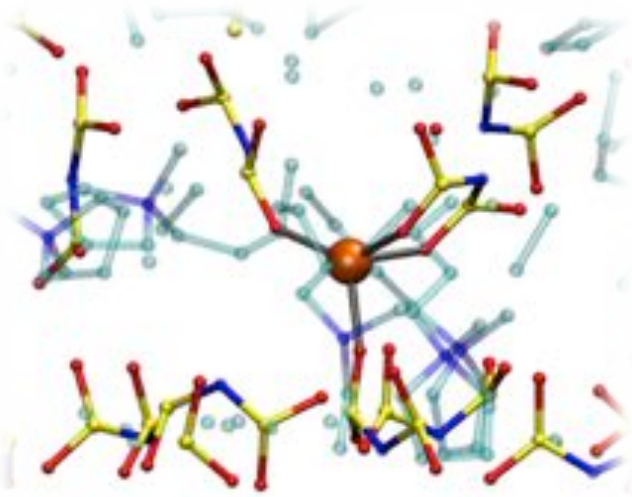
(b)



$Li^+$ accumulates in the second molecular layer

# Free Energy Barrier to $Li^+$ Intercalation

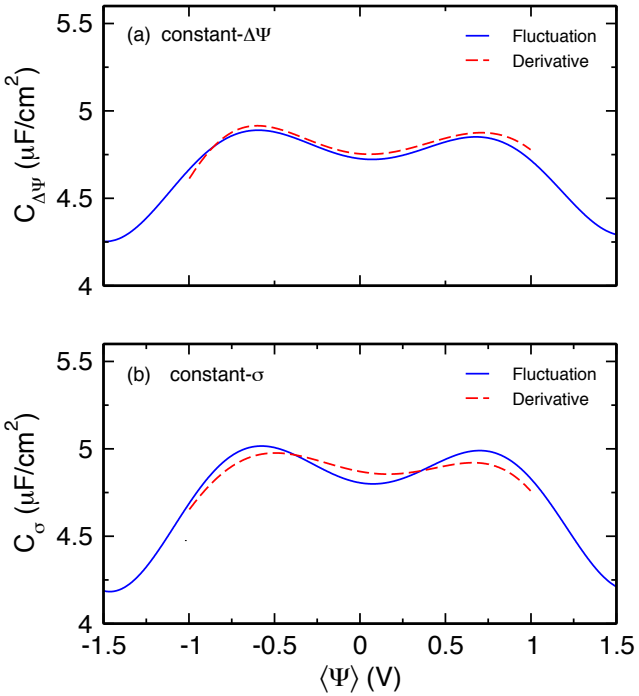


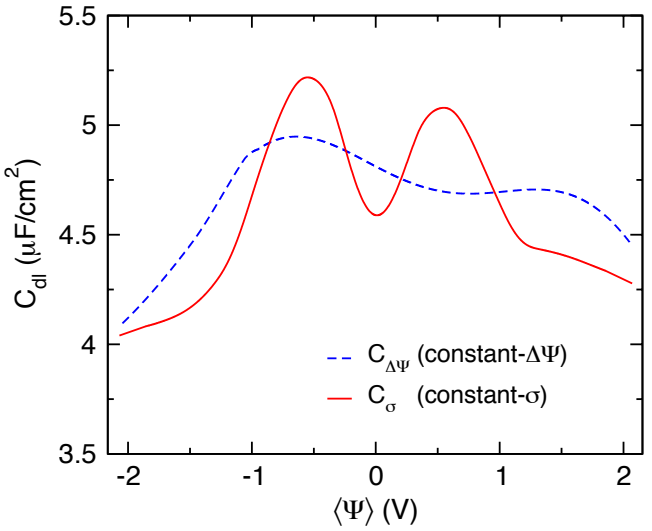



Large energy to move $Li^+$ to the surface

# Capacitance from Fluctuations

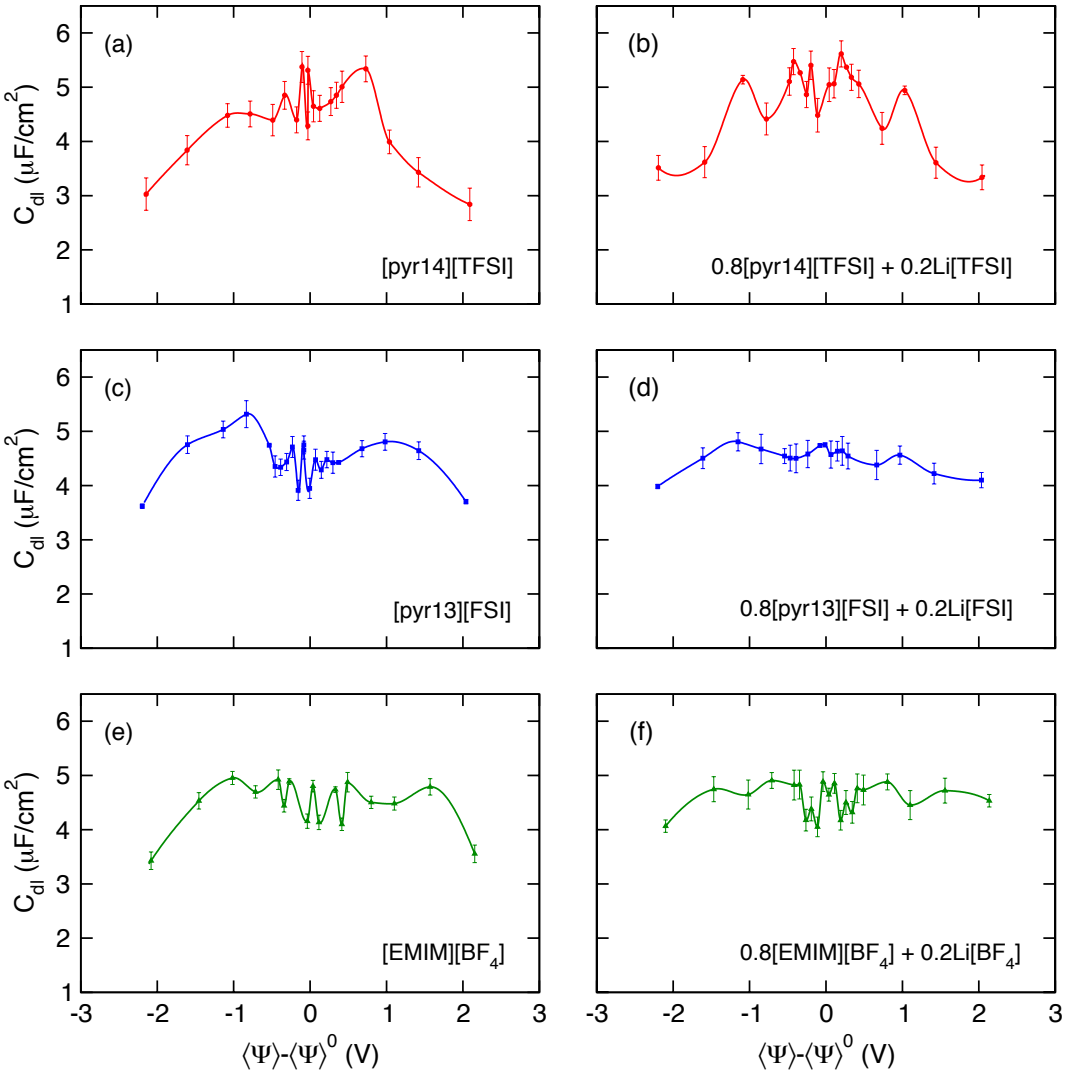
$$C_{\Delta\Psi} = \frac{\partial\langle\sigma\rangle}{\partial\langle\Psi\rangle} = \left[\beta A\,\langle|\sigma|\delta\sigma\rangle + \left\langle\frac{\partial\sigma}{\partial\Delta\Psi}\right\rangle\right]\left[\beta A\,\langle|\sigma|\delta\Psi\rangle + \left\langle\frac{\partial\Psi}{\partial\Delta\Psi}\right\rangle\right]^{-1}$$




Validated fluctuation formulas for capacitance
Electrode surface subtly influences capacitance

# Capacitance

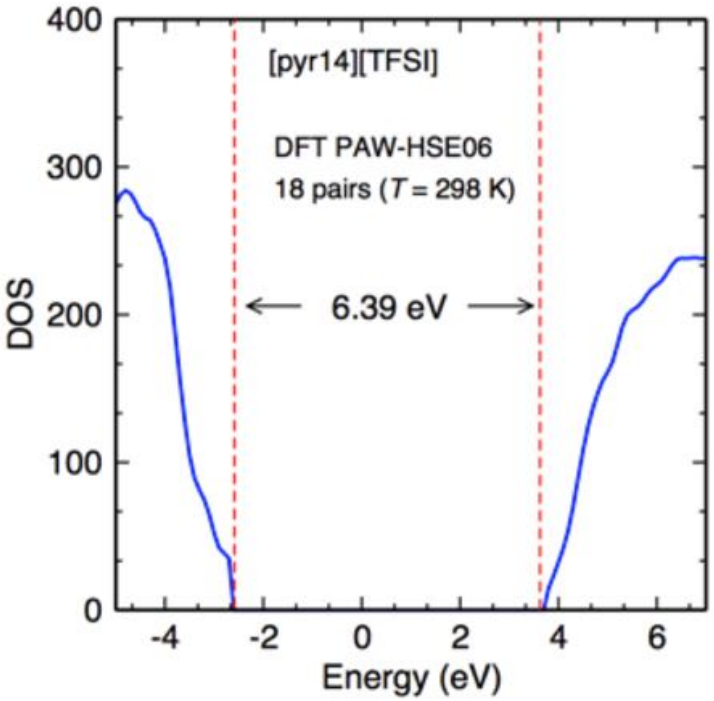



Li⁺ suppresses features in the capacitance profile

# Electrochemical Windows

Occupied Molecular Level

Unoccupied Molecular Levels




| | 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

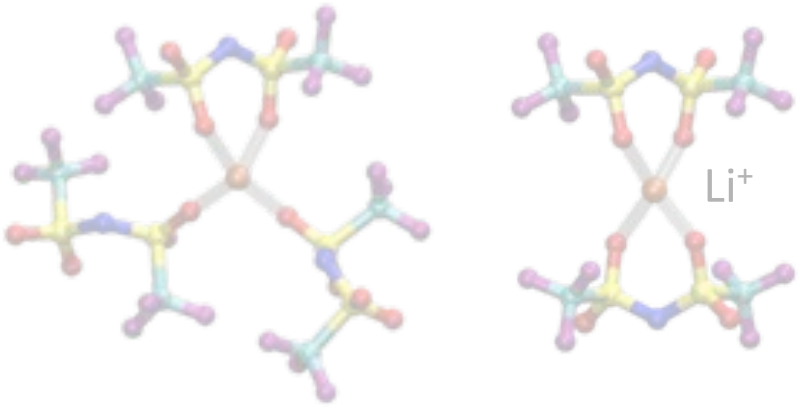
# Specific Energy Estimates

| | | 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 |

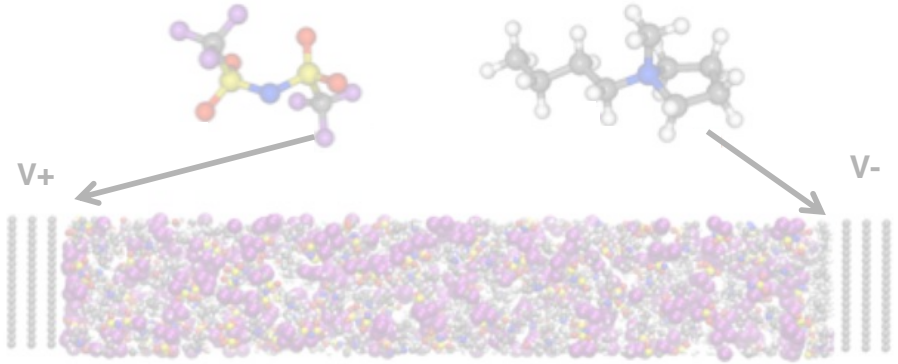
Assume specific surface area 1074 m$^2$/g

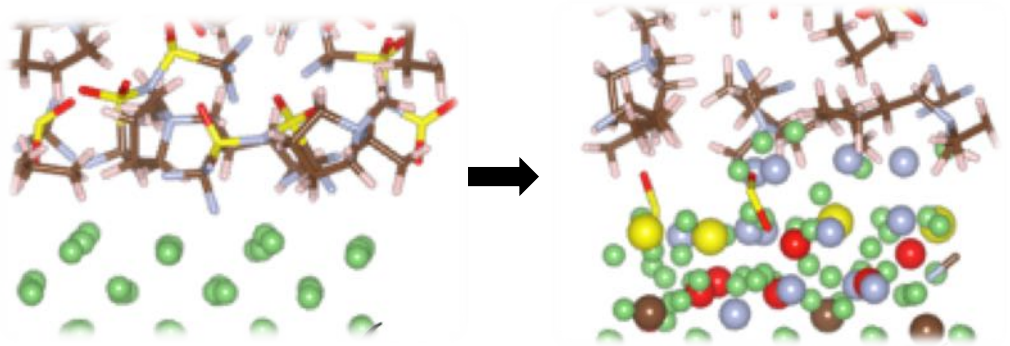
[pyr13][FSI] highest energy from both experiment and theory

1) $Li^+$ Transport and Solvation




2) Behavior at Charged Interfaces

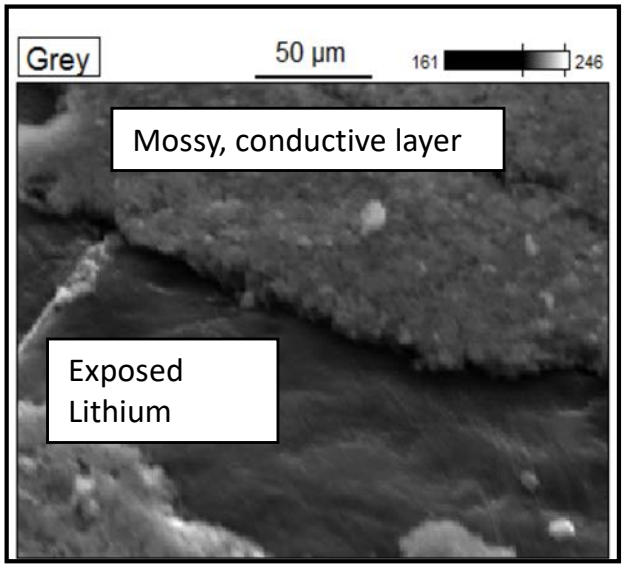


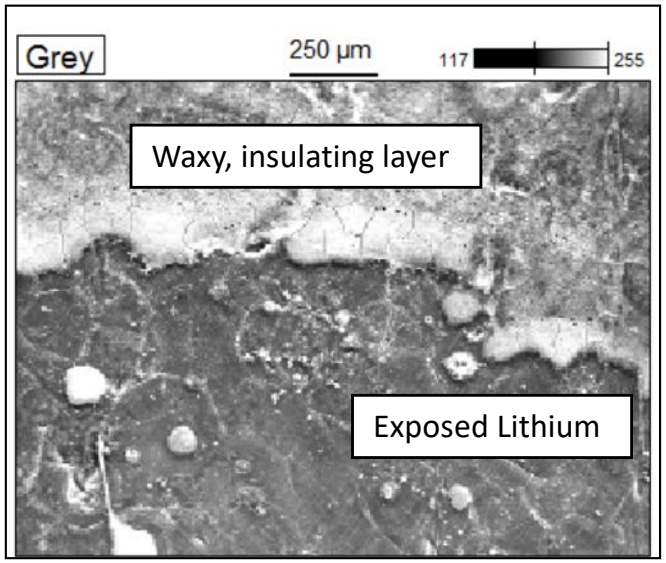
**3) Behavior at Reactive Interfaces**

# Evaluation of Decomposition

**[pyr14][TFSI]**

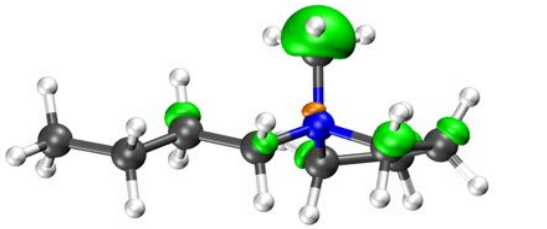


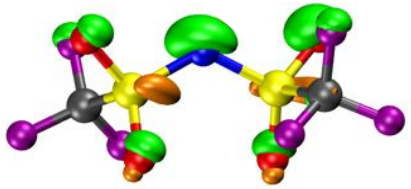

**[EMIM][BF4]**

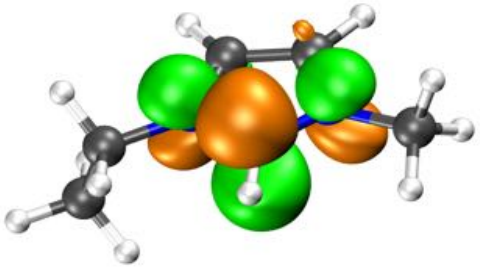


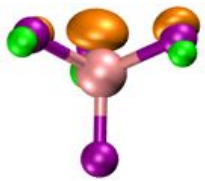

Surface layers (*mossy* vs *waxy*) have dramatic effect on cycling performance

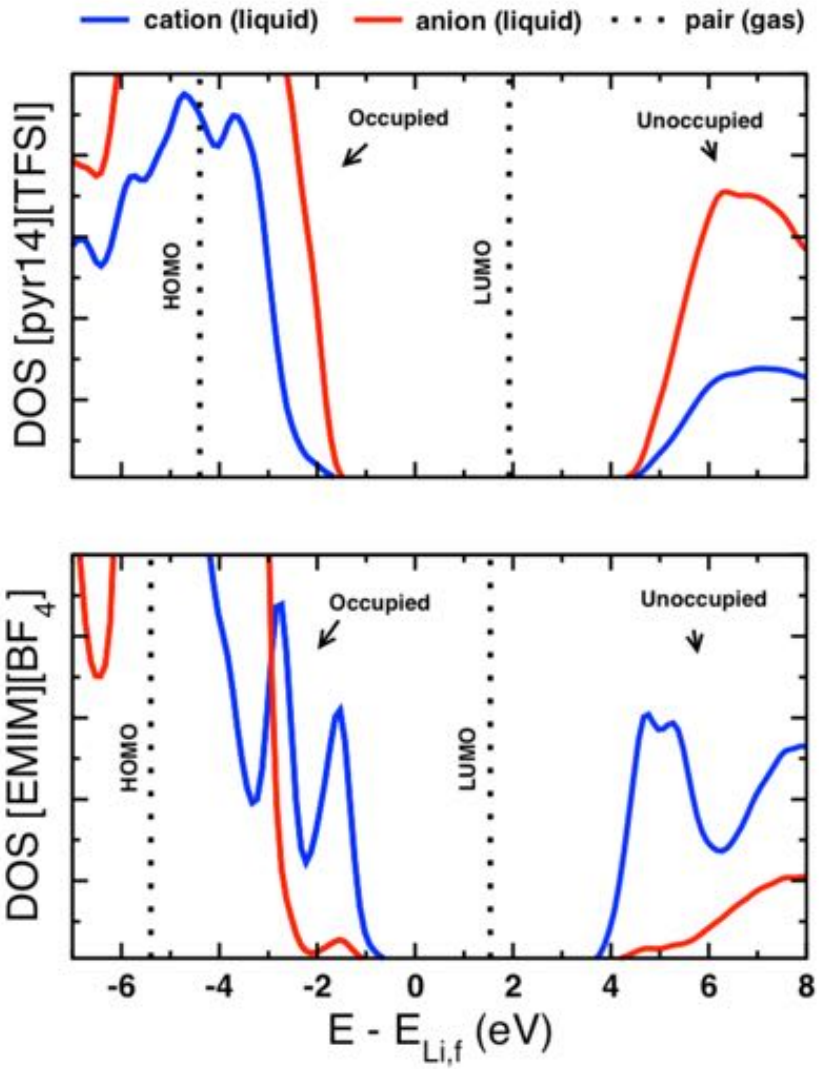
# Level Alignment: Vacuum Levels





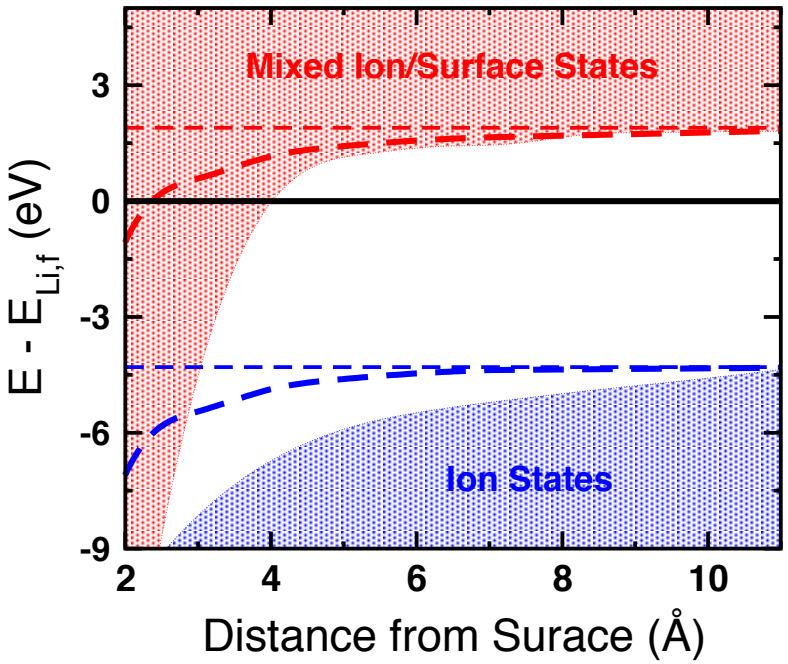


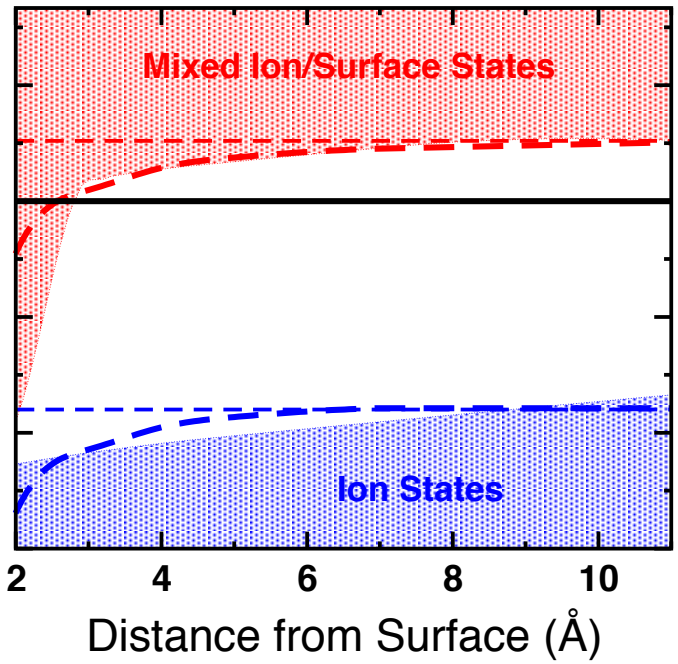


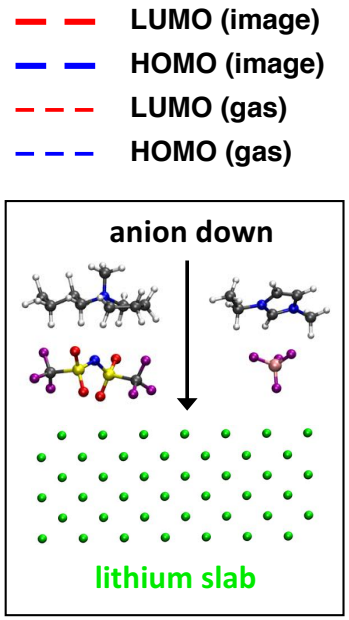



LUMO level is shared by both anions of the ionic liquid pair
Vacuum level alignment indicates the liquids are stable

# Level Alignment: Explicit Computation



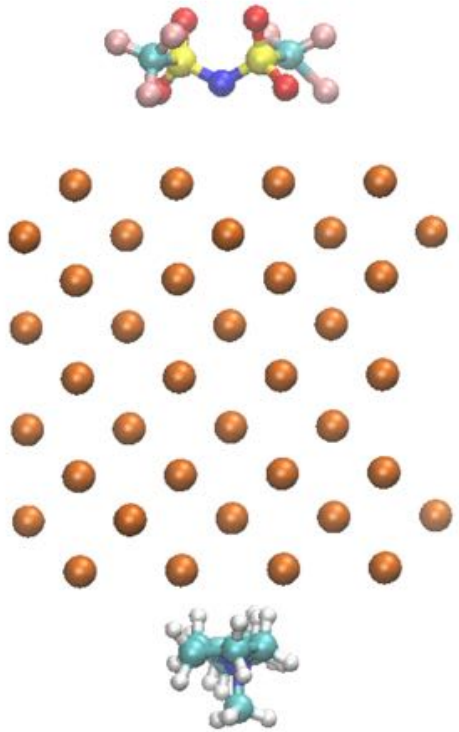



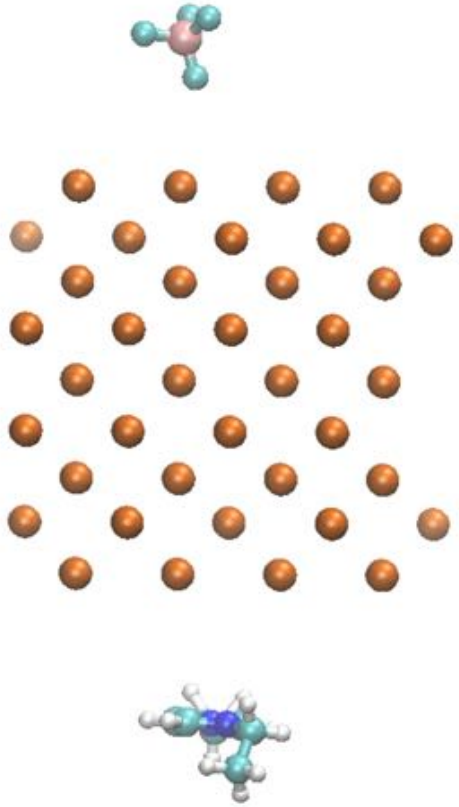

Ion levels mix with surface levels when near the surface

# Ion Pair Decomposition

Lithium Metal Surface



[pyr14]$^{+}$[TFSI]$^{-}$

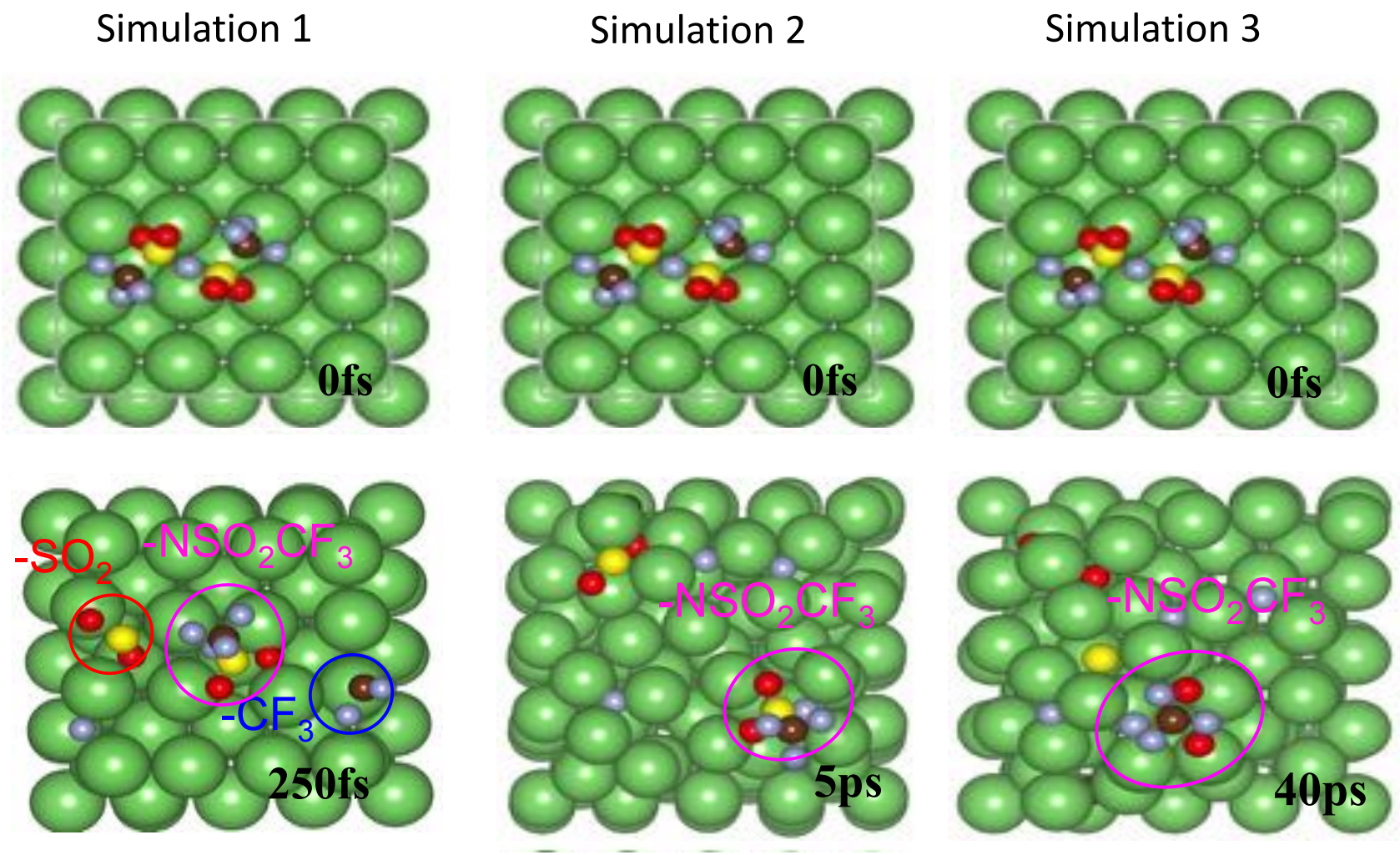


[emim]$^{+}$[$BF_4$]$^{-}$

Lithium Metal Surface

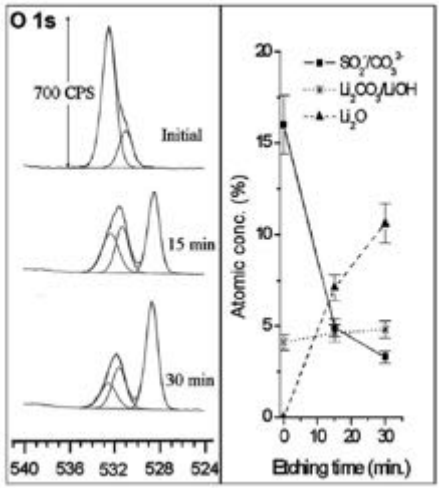
Dynamics show that [TFSI]$^{-}$ readily decomposes

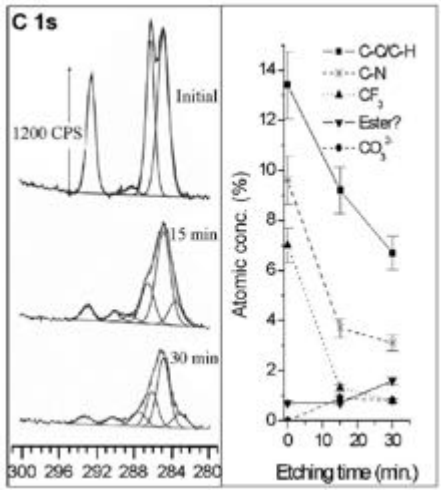
# [TFSI]$^-$ Decomposition Products

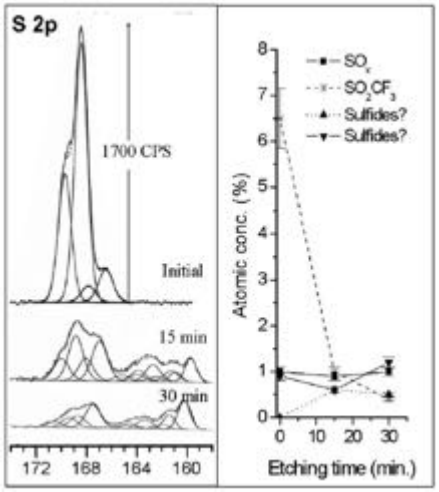


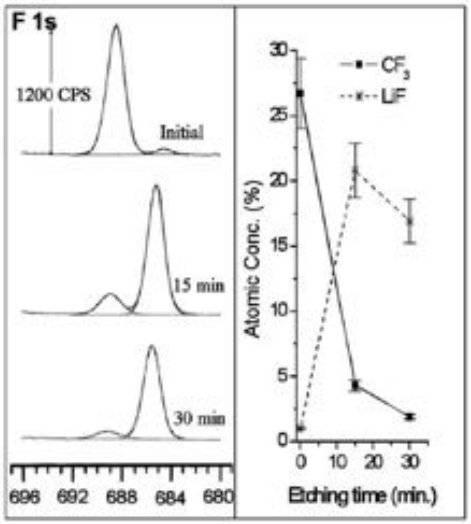

LiF, $Li_2O$, $-CF_3$, $-SO_2$, and $-NSO_2CF_3$ groups are generated

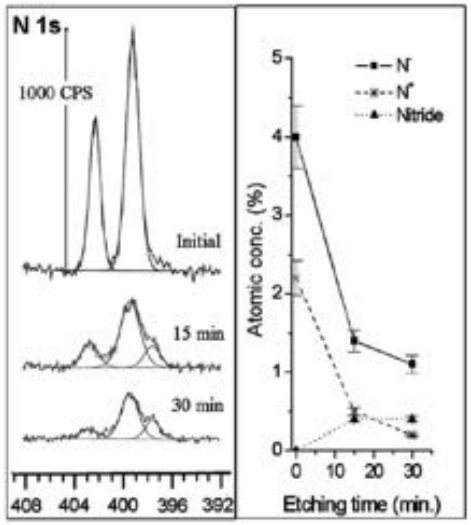
# XPS Analysis of Etched Surface Layer



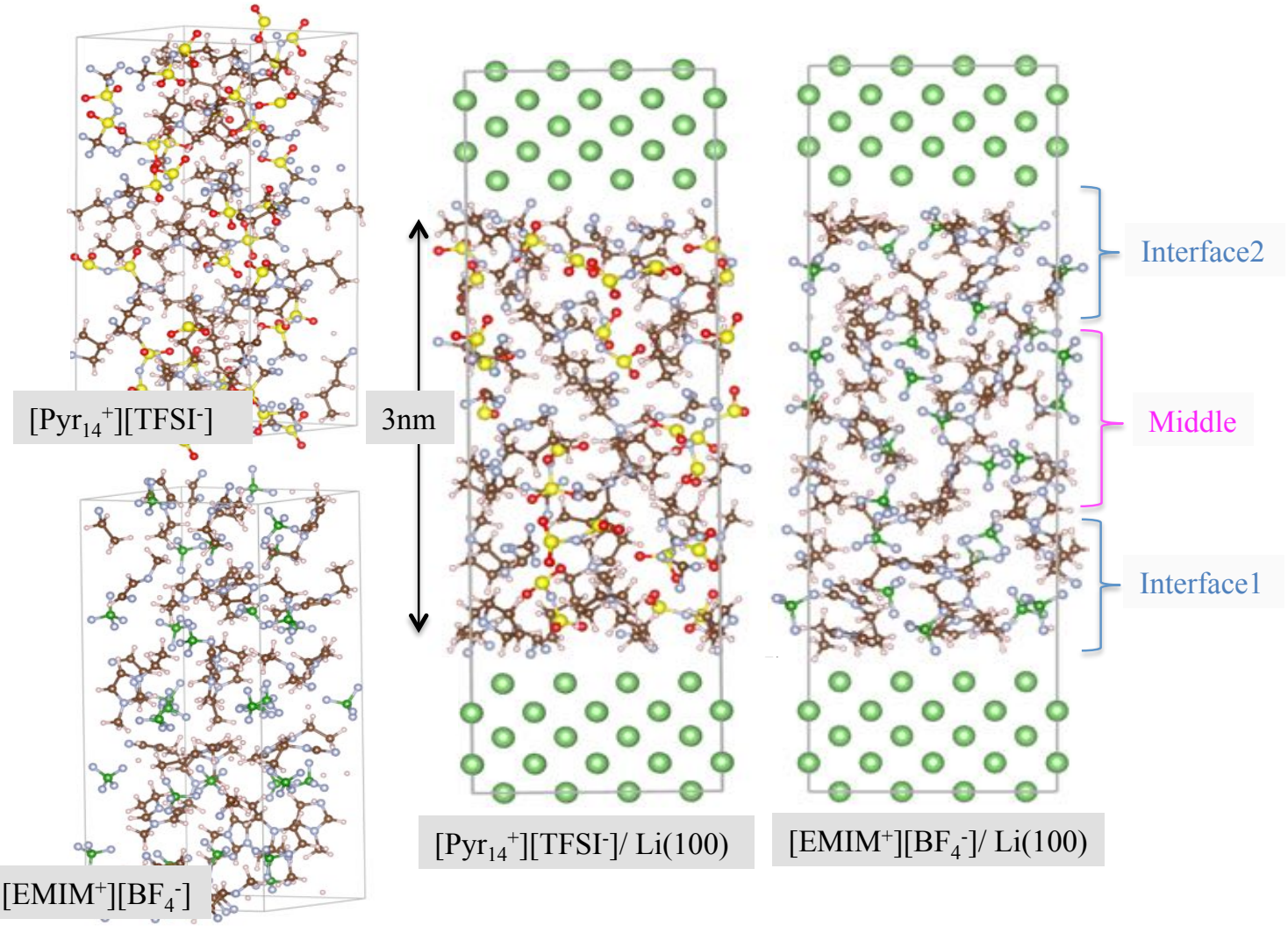




LiF, $Li_2O$, -$CF_3$, -$SO_2$, and –$NSO_2CF_3$ products match XPS results

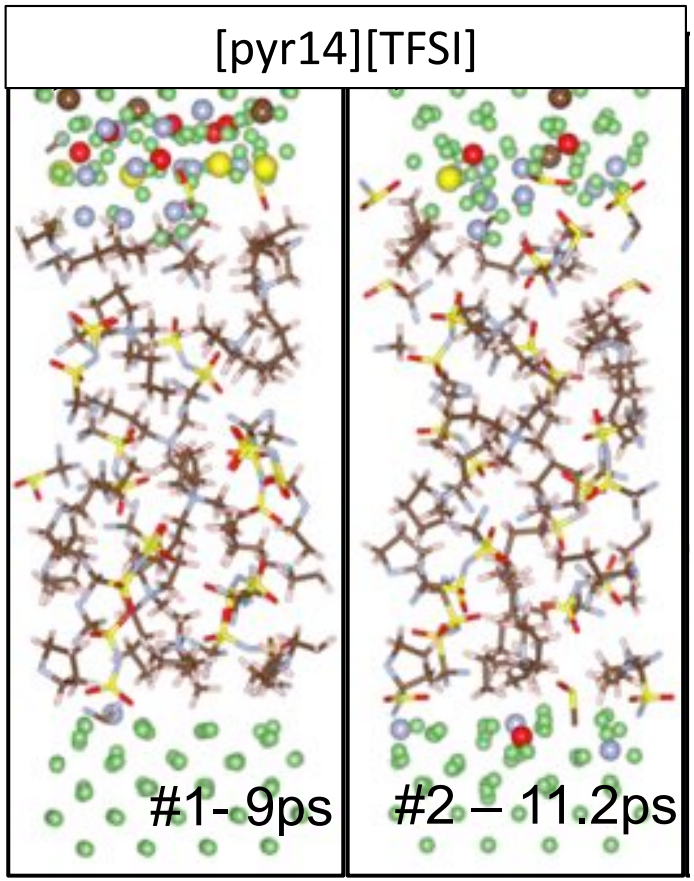
Howlett, Z. Phys. Chem. 220, 1483 (2006)

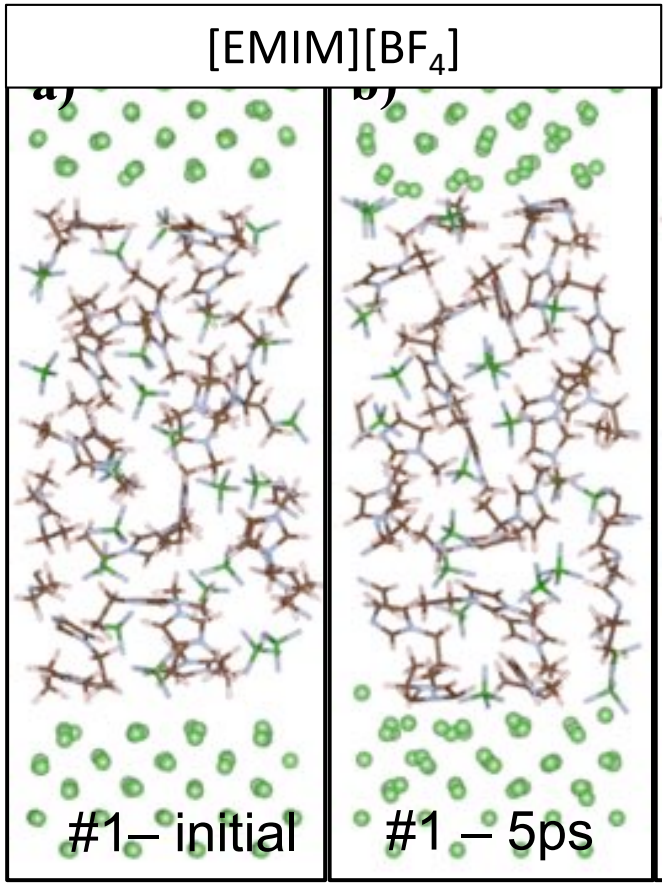
# Bulk Interface Reactions




Bulk systems examined to examine other possible reactions

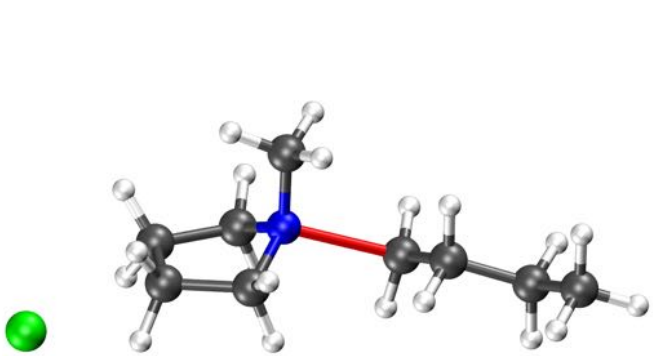
# Bulk Interface Reactions



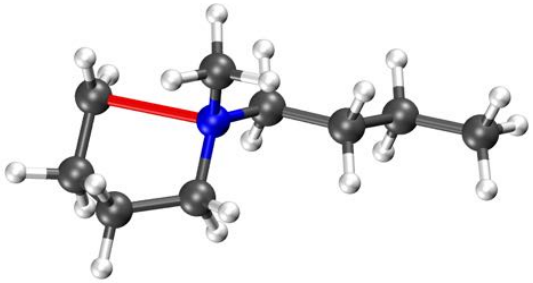




Product profile similar to single pair simulations

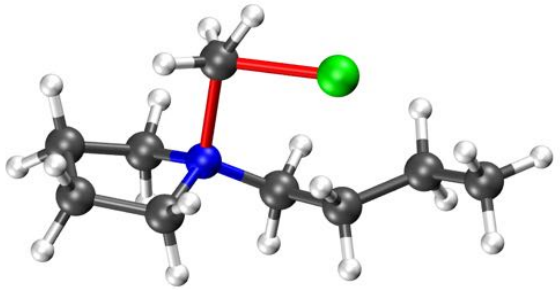
# Cation Decomposition Barriers



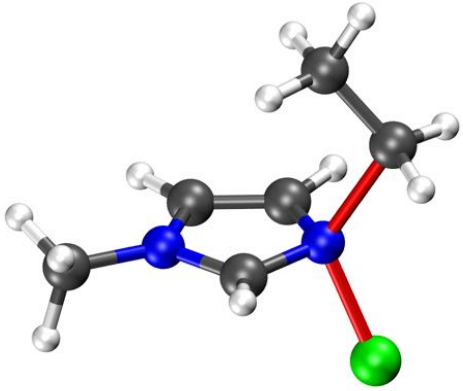
ΔG = -22.7
ΔG*= 26.6



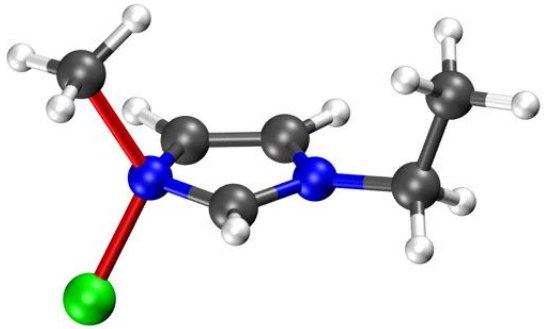
ΔG = -22.5
ΔG*= 24.6



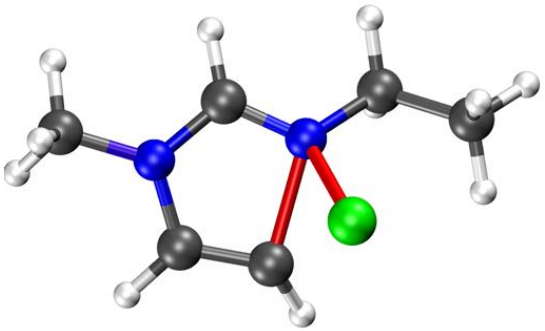
ΔG = -23.7
ΔG*= 30.2



ΔG = -25.6
ΔG*= 11.7



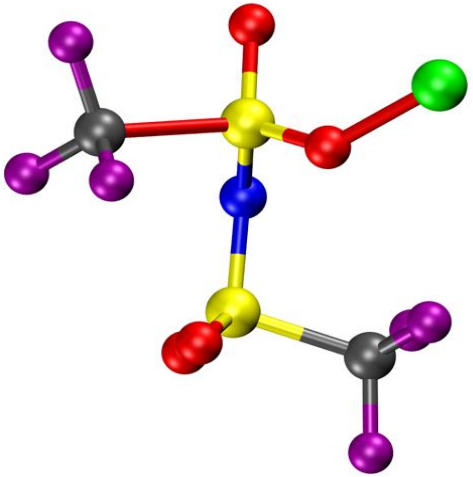
ΔG = -24.0
ΔG*= 13.6



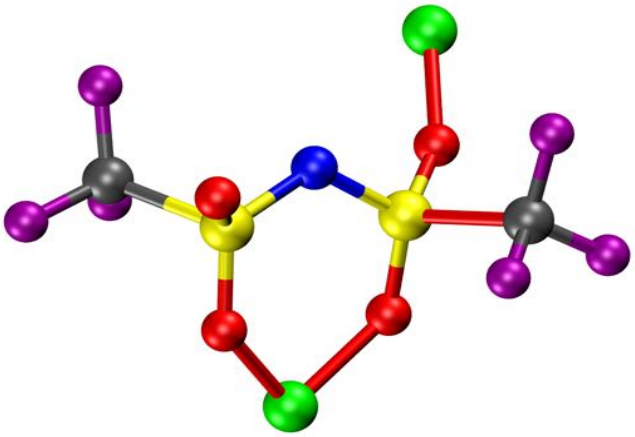
ΔG = 8.1
ΔG*= 23.3

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

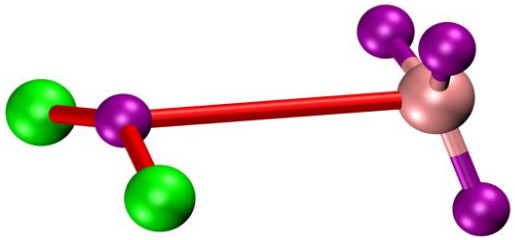
# Anion Decomposition Barriers



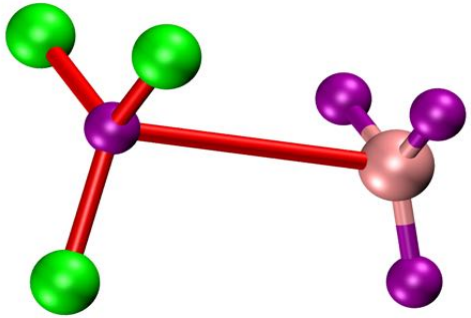
ΔG = -87.4
ΔG*= 10.1



ΔG = -97.2
ΔG*= 0.2



ΔG = -5.3
ΔG*= 18.0



ΔG = -14.0
ΔG*= 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)

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Yildirim, et al., *JPCC* **121**, 28214 (2017)