Controlled Interfacial Phenomena for Extended Battery Life

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Project ID #: bat507

Overview

Timeline

- Start date: October 1, 2017
- End date: September 30, 2021
- Percent complete: 80%

Budget

- Total funding: $1,333,380
  - DOE share: $1,200,000
  - Contractor share: $133,380
- Funding received
  - FY20: $343,000
  - FY21: $171,500

Barriers

- Barriers/targets addressed
  - Loss of available capacity
  - Materials degradation during cycling
  - Lifetime of the cell

Partners

- Interactions/collaborations
  - J. Seminario (TAMU Co-PI)
  - J. Zhang, X. Cao (PNNL collaborators)

- Project lead: TAMU

Relevance and Approach

Impact

Ion transport, redox pathways, and concentration polarization events near and at electrolyte/electrode interfaces influence electrodeposition, degradation behavior, and battery lifetimes

Objective

Evaluate and characterize *electrolyte structure and ion transport mechanisms* in Li-metal batteries using advanced modeling techniques.

Approach

Ionic conductivities and ion transport mechanisms in electrolytes under external applied voltages by ab initio and classical molecular dynamics:

- as a function of salt concentration,
- in localized high concentration electrolytes

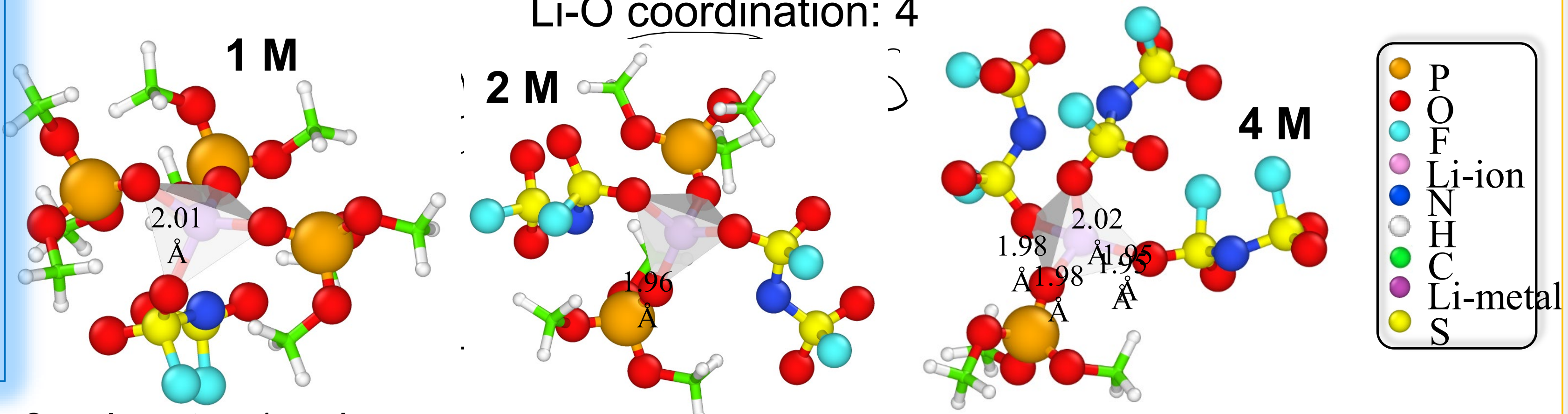
Structural behavior of salt in solution in presence of polysulfide species by ab initio and classical molecular dynamics

Technical Accomplishments: Ionic conductivity analysis-I

Calculated ion-solvent and cation-anion binding reveal very strong interactions that decrease ion conductivities

solvent: 3-methyl phosphate (TMP)
salt: Lithium bis(fluorosulfonyl)imide (LiFSI)

Li-O coordination: 4



3 solvent + 1 anion

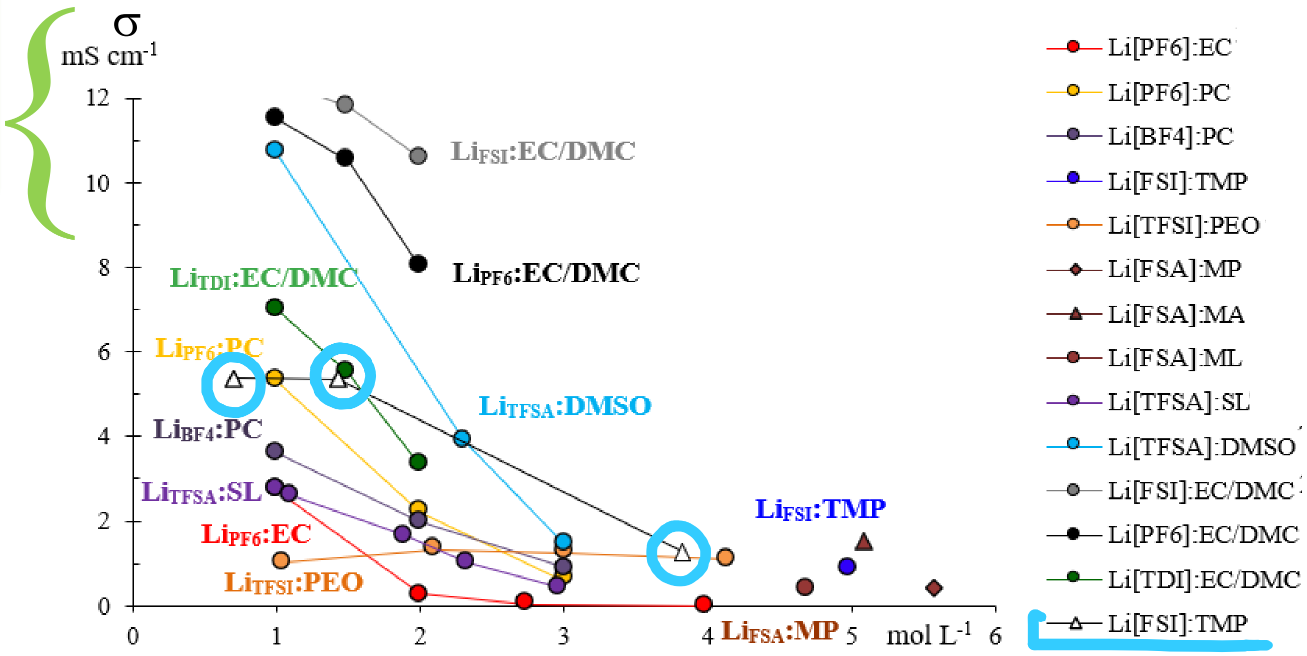
2 solvent + 2 anion

1 solvent + 3 anion

Li- 1st shell analysis as salt concentration increases

This study responds to last year's Reviewer question on ion conductivity: simulations vs. experiments

ion conductivity (σ) desired range



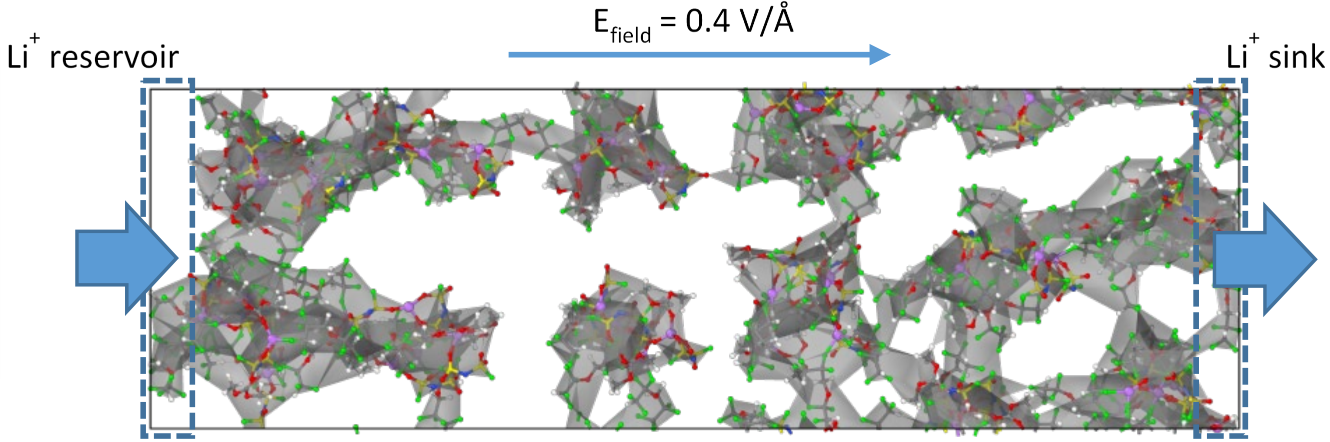
AIMD predicted (blue circles) ion conductivities and reported exp./comp. data

Galvez-Aranda and Seminario, JES, 2021

- the desired range of ion conductivities can be achieved designing weakly bonded ion-solvent complexes
- cation-anion binding can also be tuned
- understanding transport mechanisms needed

Technical Accomplishments: Ionic conductivity analysis-II

Localized high concentration electrolyte (LHCE):
solvent: dimethyl carbonate, DMC
salt:: Lithium bis(fluorosulfonyl)imide, LiFSI
diluent 1, 1, 2, 2-tetrafluoroethyl -2,2,3,3-tetrafluoropropyl ether,TTE

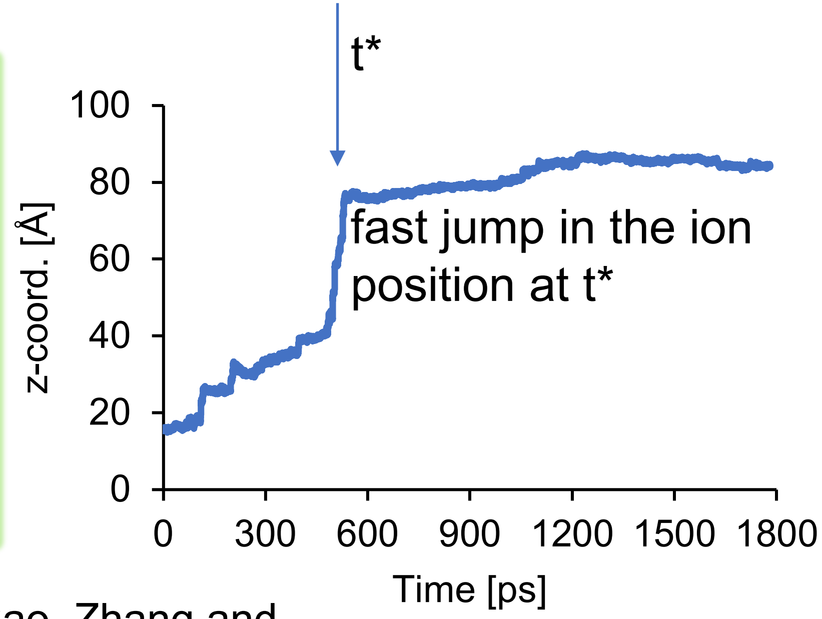


MD simulation setup to follow Li^+ drifting under an applied field

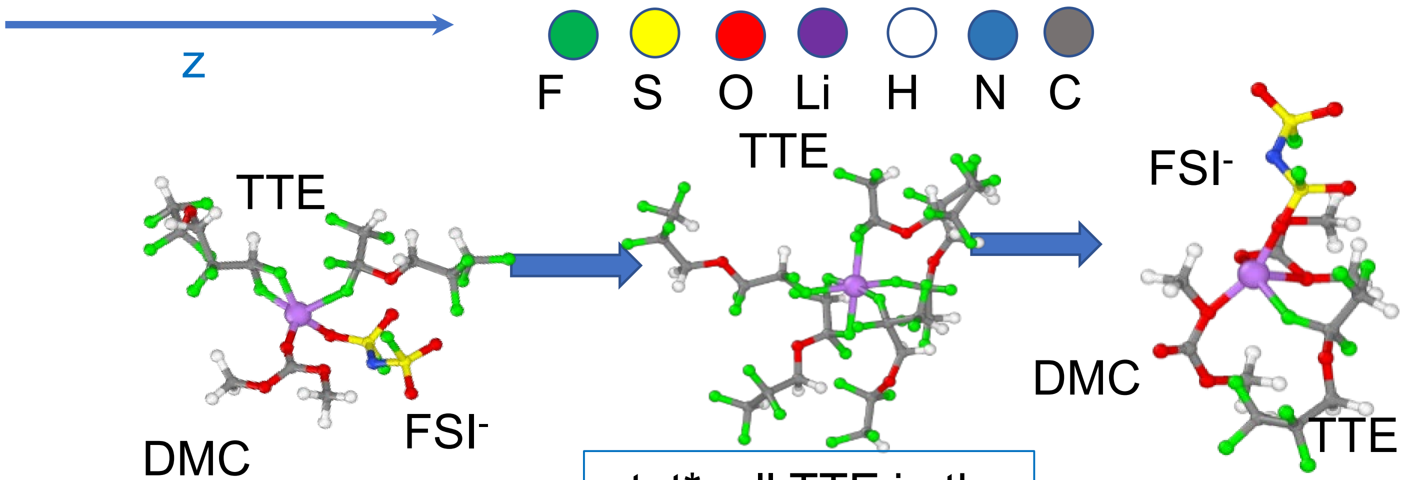
Goal:
Elucidate effect of diluent on Li ion transport mechanism in LHCE

Molar ratio
LiFSI:DMC:TTE
1.00:2.00:5.00

We follow the ion trajectory along the z direction, and examine the reasons of the jump



Perez Beltran, Cao, Zhang and Balbuena, to be submitted



right before t*, two TTE molecules reach solvation shell

at t*, all TTE in the Li^+ solvation shell. **Weak binding Li^+/TTE facilitates the ion jump**

right after t*, Li+ ion moved to stable solvation shell

TTE facilitates ion transport

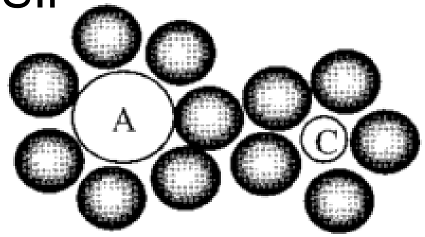
Technical Accomplishments: Ionic conductivity analysis-III

LHCE electrolyte: Salt: Bis(trifluoromethane)sulfonimide, LiTFSI Solvent: 1,2-Dimethoxyethane, DME (solvent), Diluent: 1,2-difluorobenzene, BTFE **and Li_2S_8** (long chain PS)

Goal: elucidate effect of LHCE electrolytes on Polysulfide (PS) solubilities and Li ion conductivity

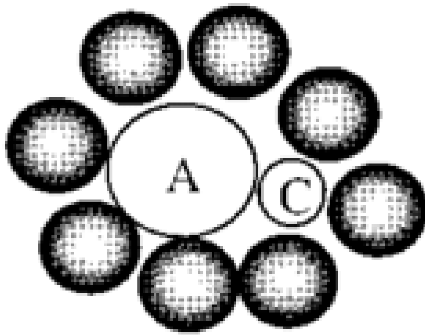
LiTFSI behavior in LHCE solution in presence of PS species

solvent separated ion pair SSIP

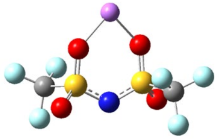


A: anion, C: cation

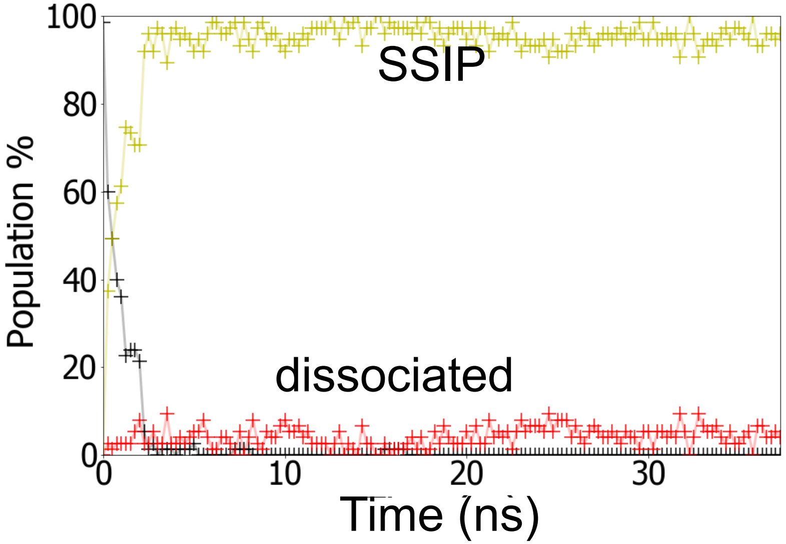
contact ion pair, CIP



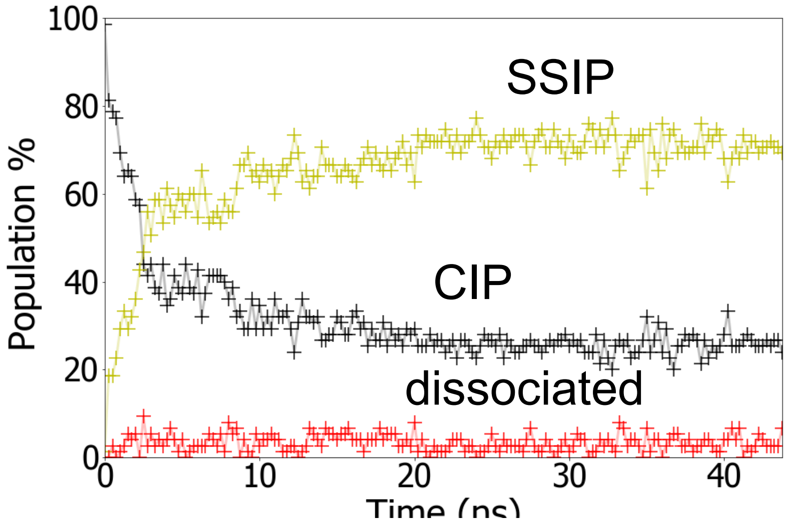
Kamphaus and Balbuena, submitted



low % of BTFE diluent



high % of BTFE diluent



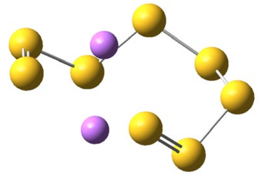
At low % BTFE, LiTFSI salt exists mainly as solvent-separated ion pair (~100%)

At high BTFE, LiTFSI has ~ 30% contact ion pairs, 70% SSIP

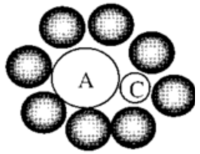
This result implies decrease in ionic conductivity

→ **more LiTFSI association with high diluent concentration (1:2 DME:BTFE)**

Technical Accomplishments:
LHCE effect on polysulfide (PS) solubility

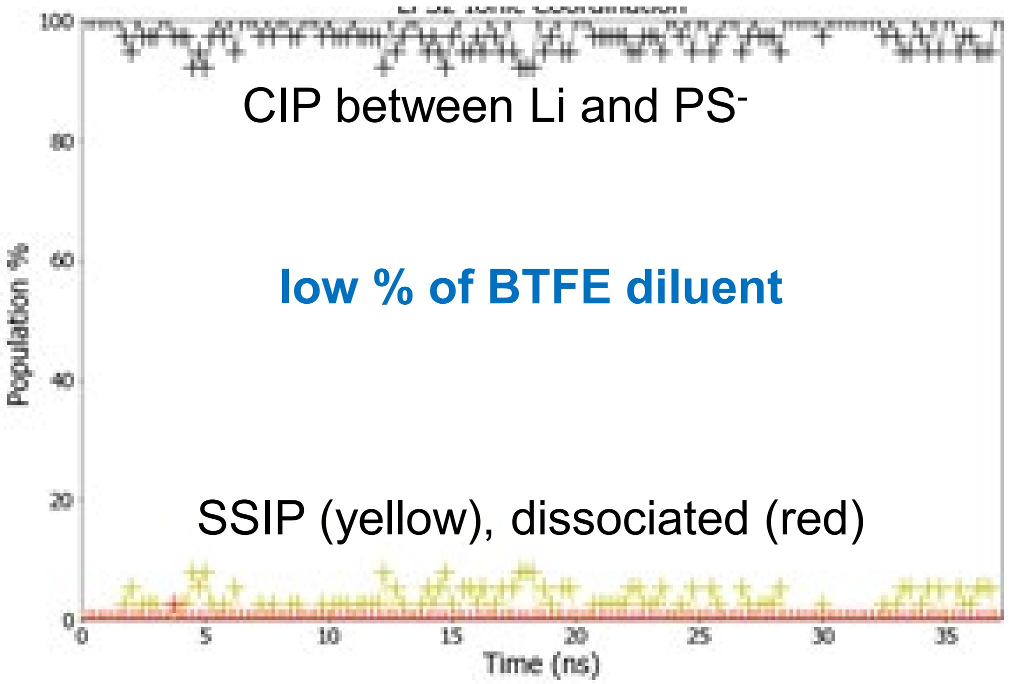


contact ion pair, CIP



LHCE electrolyte:
solvent: DME
salt: LiTFSI
diluent BTFE
PS: Li_2S_8

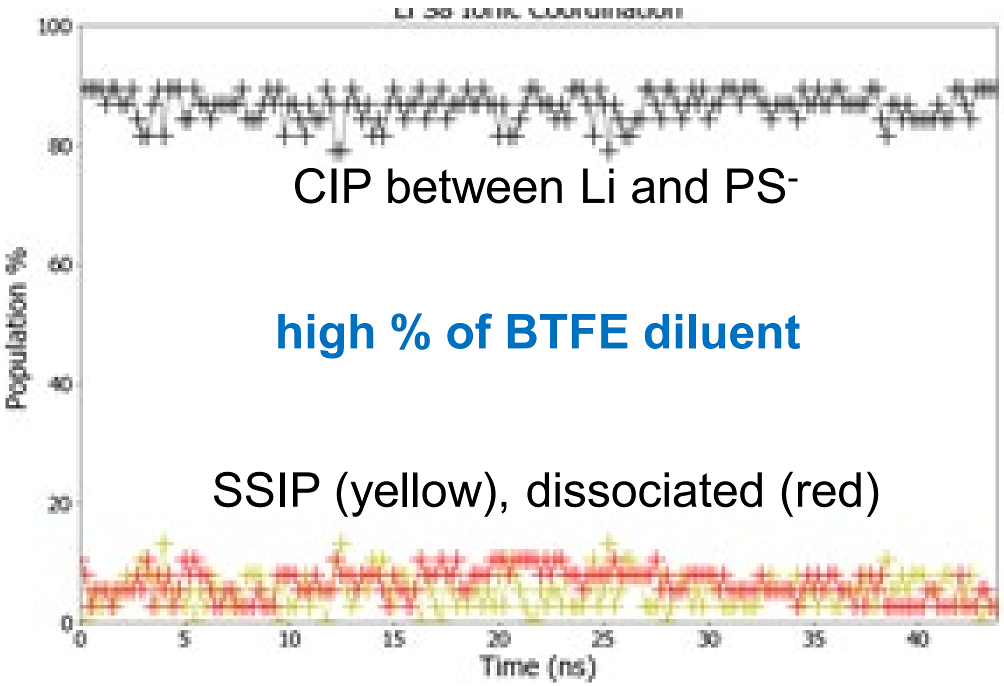
Goal:
Elucidate effect of diluent on PS solubility



CIP between Li and PS^-

low % of BTFE diluent

SSIP (yellow), dissociated (red)



CIP between Li and PS^-

high % of BTFE diluent

SSIP (yellow), dissociated (red)

Kamphaus and Balbuena, submitted

CIP is dominant in PS (~100%), but decreases (85%) when the % of diluent increases

→ LHCE electrolyte (with high % of diluent) favors PS dissolution

Collaboration and Coordination with Other Institutions

We collaborated with the group of Dr. Ji-Guang (Jason) Zhang at PNNL that develops localized high concentration electrolytes (LHCEs). They provided several formulations and their corresponding battery tests. We investigated ion transport mechanisms, and predicted composition of SEI and CEI layers.

Proposed future work

Future work includes:

- Evaluate barriers for ion transport vs. electron transfer forces driving ion deposition for various liquid electrolyte solutions at the Li metal surface
- Evaluate barriers for ion and electron transport through amorphous SEIs.
- Evaluate SEI mechanical properties and effect of external pressure on Li deposition during charge.

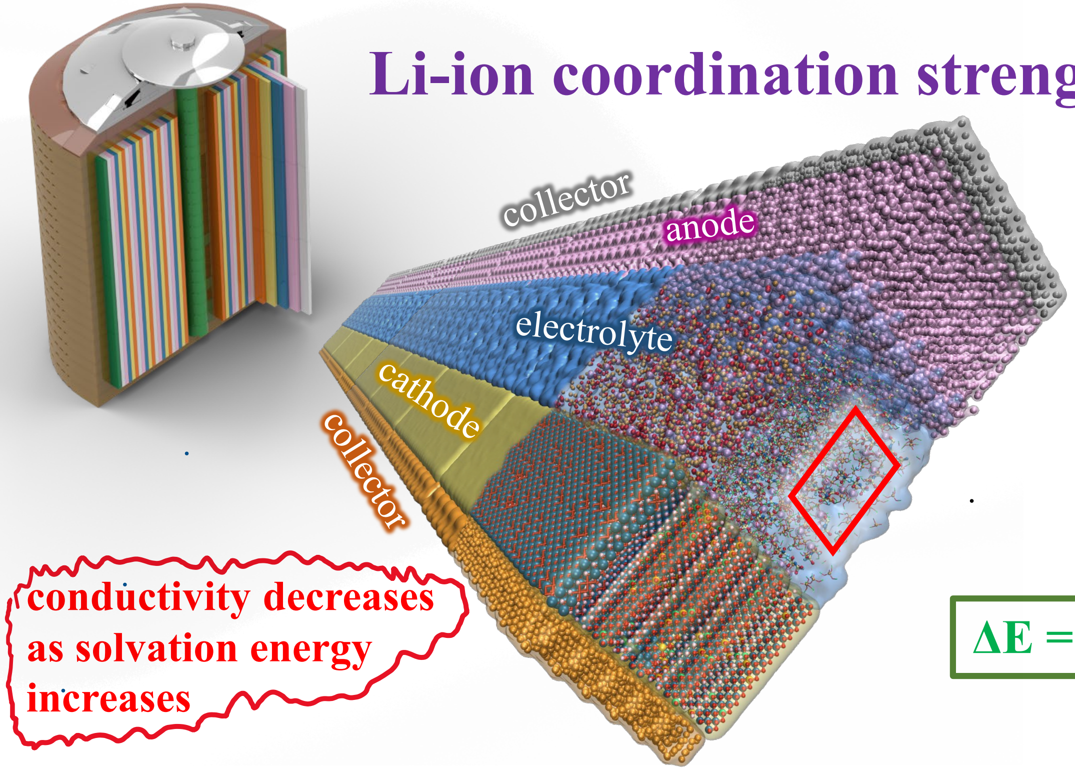
Any proposed future work is subject to change based on funding levels

Summary Slide

- Accomplishments:
  - Electrolyte effects on solution structure and ion transport mechanisms elucidated
- Technical highlights:
  - Salt concentration and Li^+/electrolyte binding strength determine solution structure (ion solvation, salt association) and ionic conductivity.
  - Diluents facilitate ion transport in LHCEs.
  - Diluents may change cation/anion association behavior, thus ion conductivity in presence of polysulfides. This is because both PS and salt compete for Li solvation, causing more ion-pairing in LiTFSI.
  - Due to the salt-PS competition for Li solvation, PS solubility increases slightly in presence of high amounts of diluent.
- Impact to VTO objectives:
  - New insights on ionic conductivity and solution structure impact battery performance and lifetime.

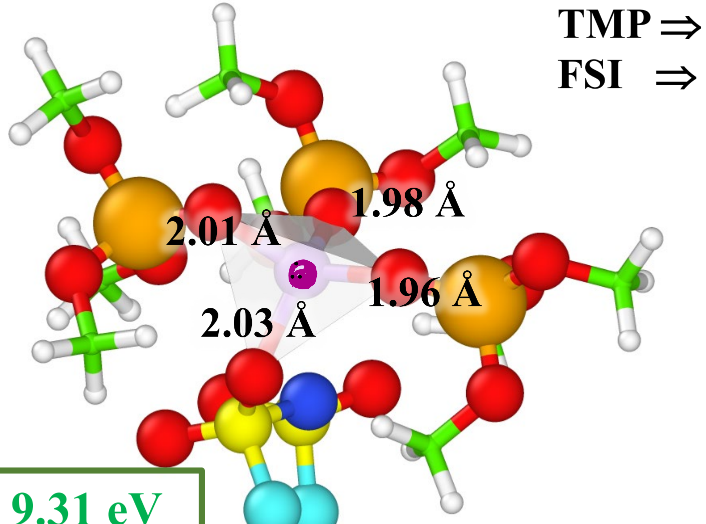
Technical Back Up Slides (maximum 5)

Li-ion coordination strength increases with salt concentration



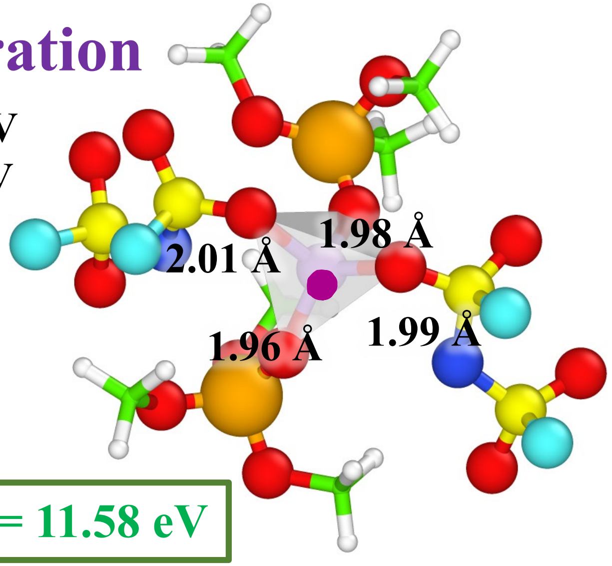
conductivity decreases as solvation energy increases

TMP ⇒ 1.77 eV
FSI ⇒ 2.27 eV



ΔE = 9.31 eV

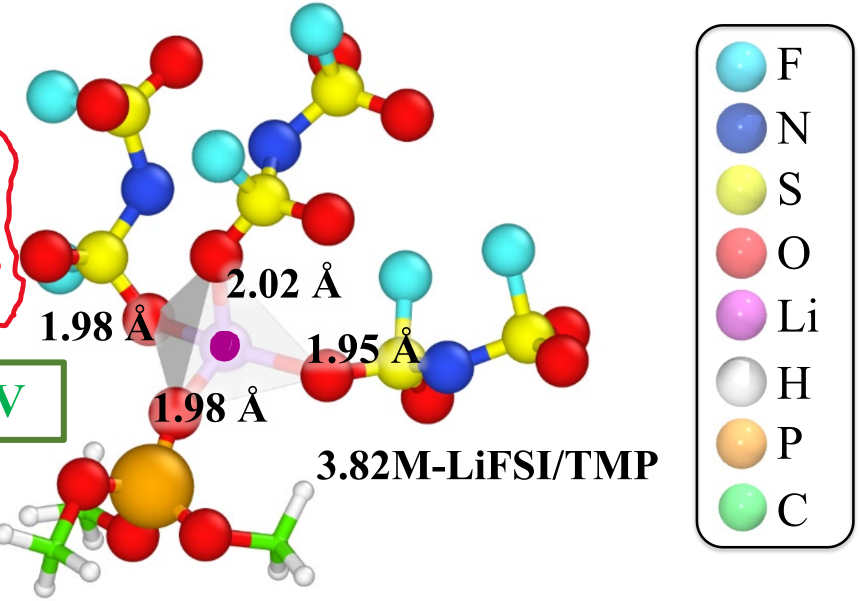
0.70M-LiFSI/TMP



ΔE = 11.58 eV

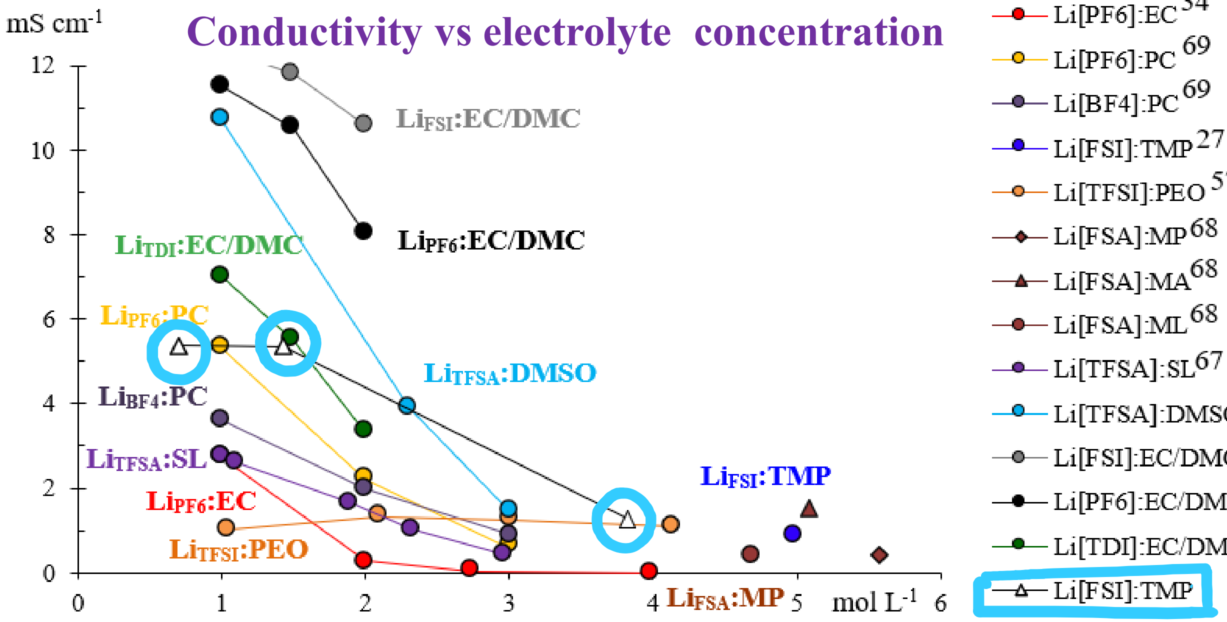
1.43M-LiFSI/TMP

Find electrolytes with much lower binding to the ion, solvent, diluent,…



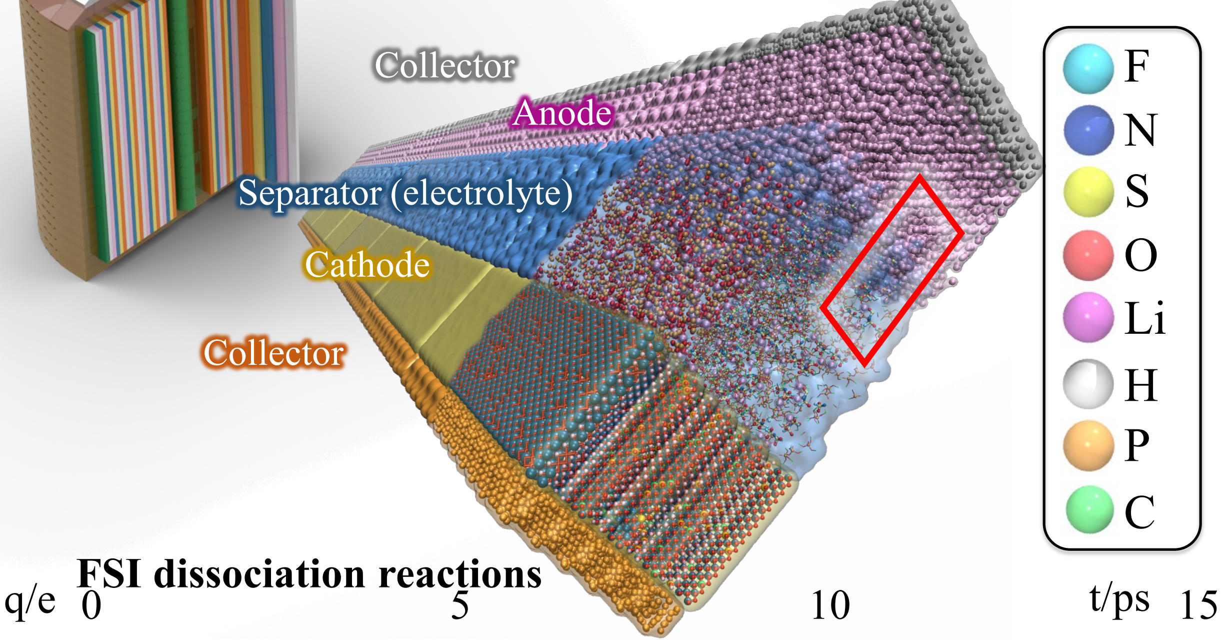
ΔE = 13.88 eV

3.82M-LiFSI/TMP

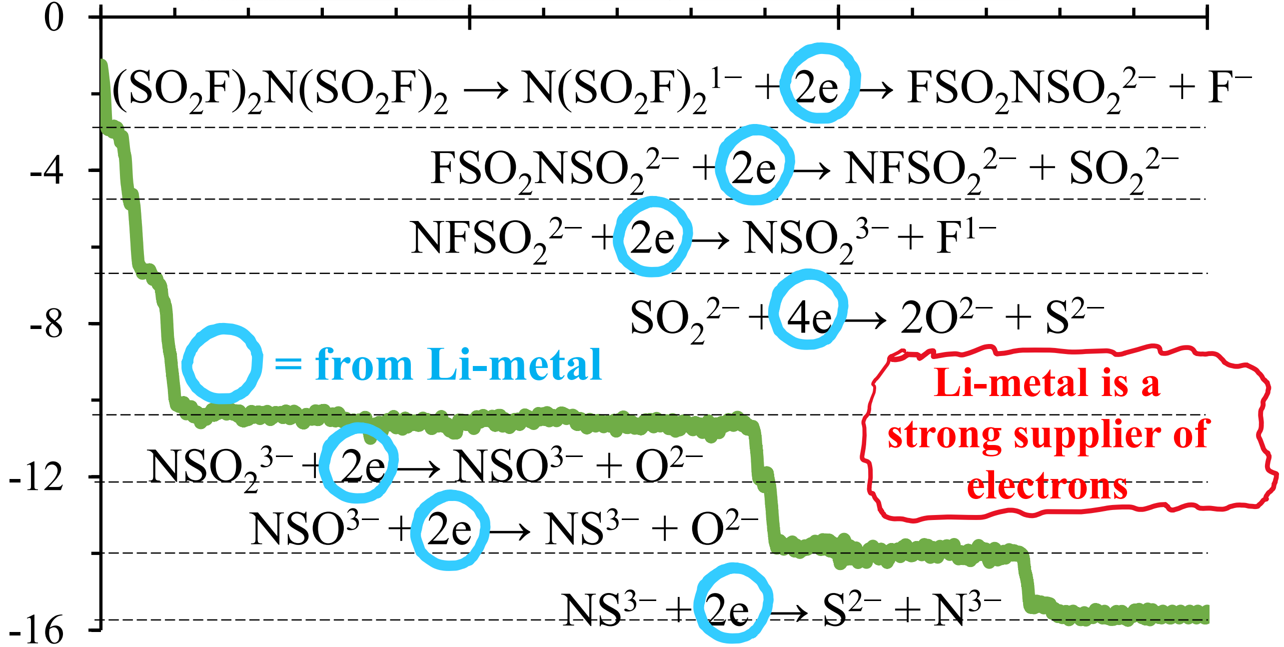

Conductivity vs electrolyte concentration

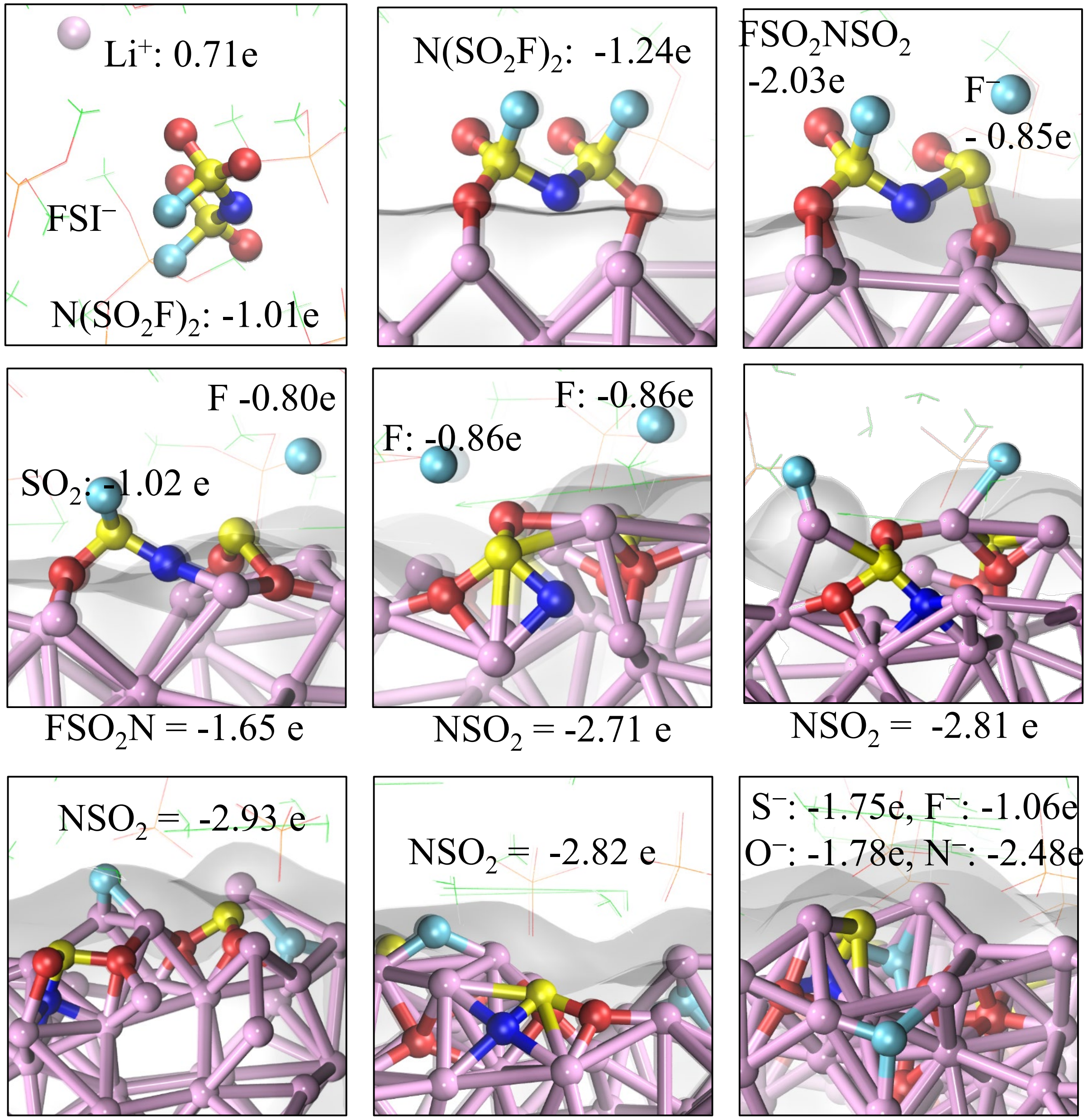
Galvez-Aranda, Seminario; Ion Pairing, Clustering, Transport in LiFSI-TMP Electrolyte as Function of Salt Concentration using MD Simulations,, J. Electrochem. Soc.168 040511, **2021**

Electrochemical stability at the electrolyte/anode interface (1M)



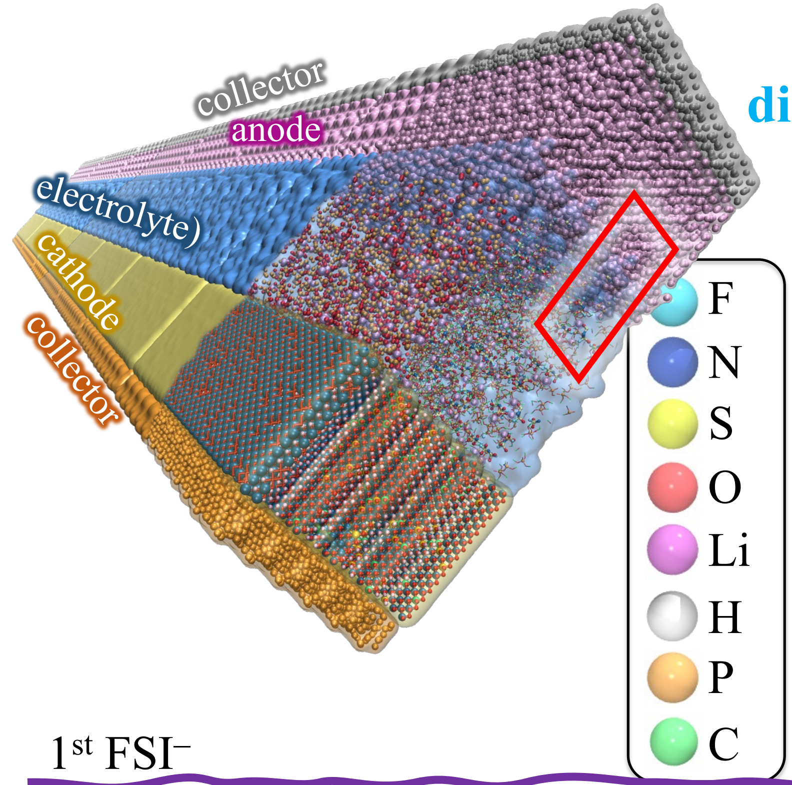
FSI dissociation reactions



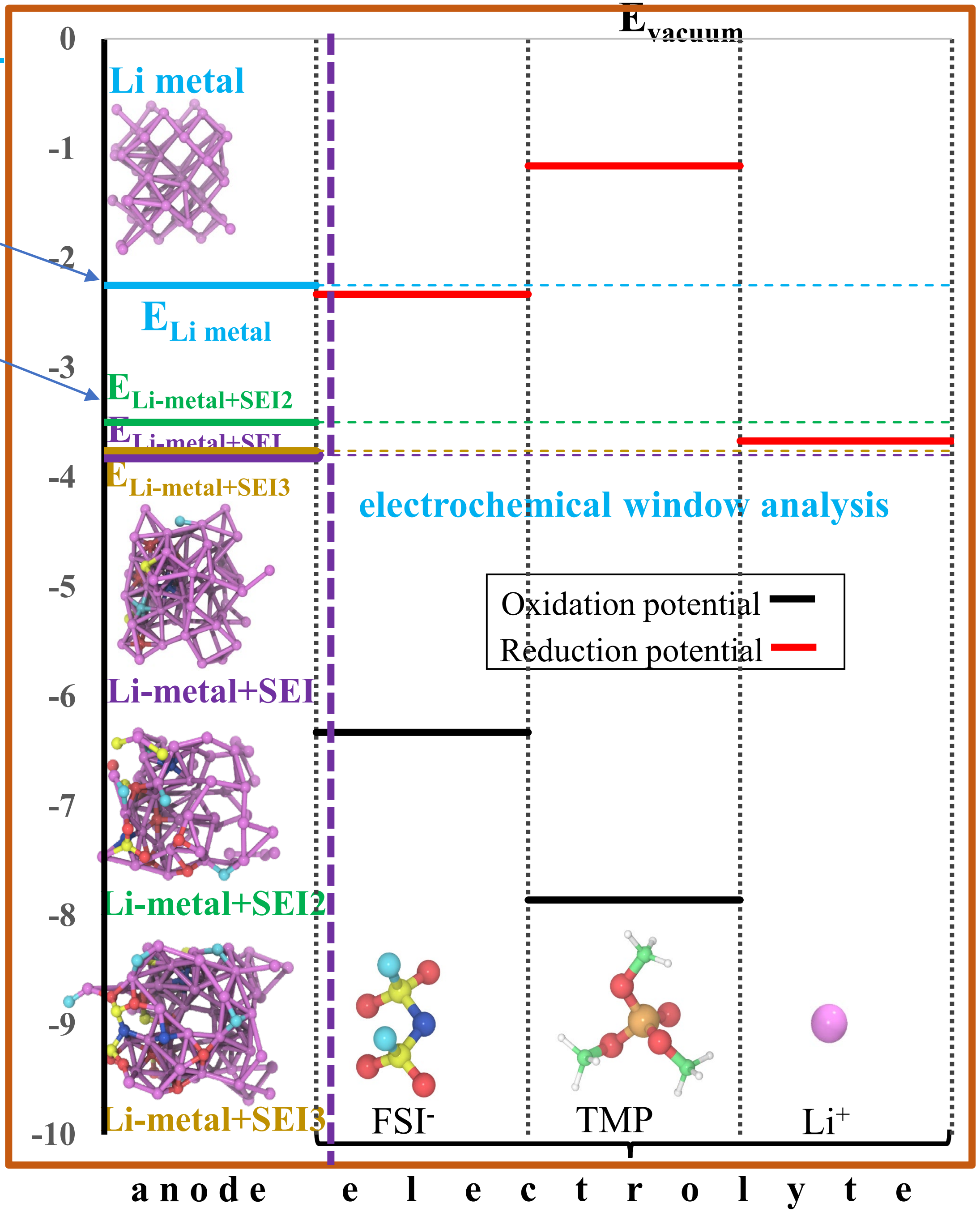


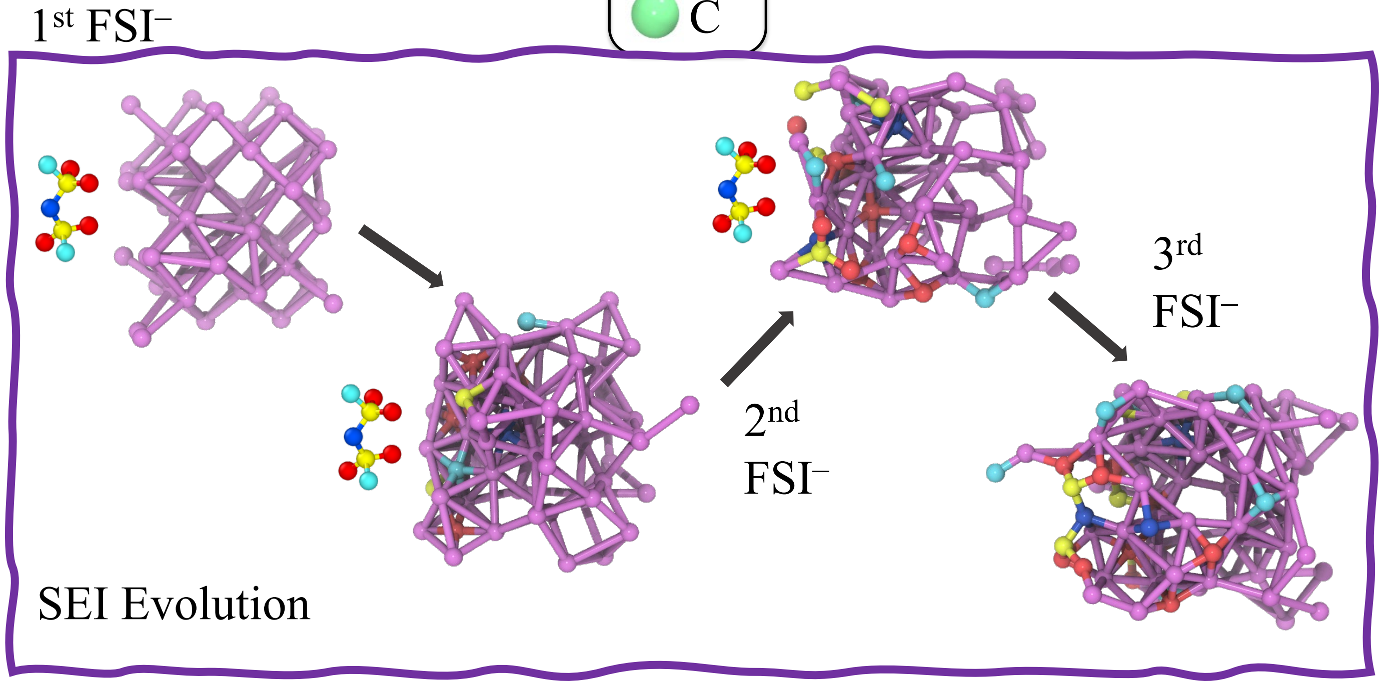
Galvez-Aranda & Seminario; Li-metal anode in dilute electrolyte LiFSI/TMP: electrochemical stability using ab initio MD; J. Phys. Chem. C 124, 21919-34, **2020**

SEI evolution as FSIs dissociate at the electrolyte/Li-metal interface



Fermi level of the Li metal is shifted down due to the anion decomposition and SEI formation that change surface electronic properties. The downshifting of the Fermi level makes electron transfer to the electrolyte more difficult.

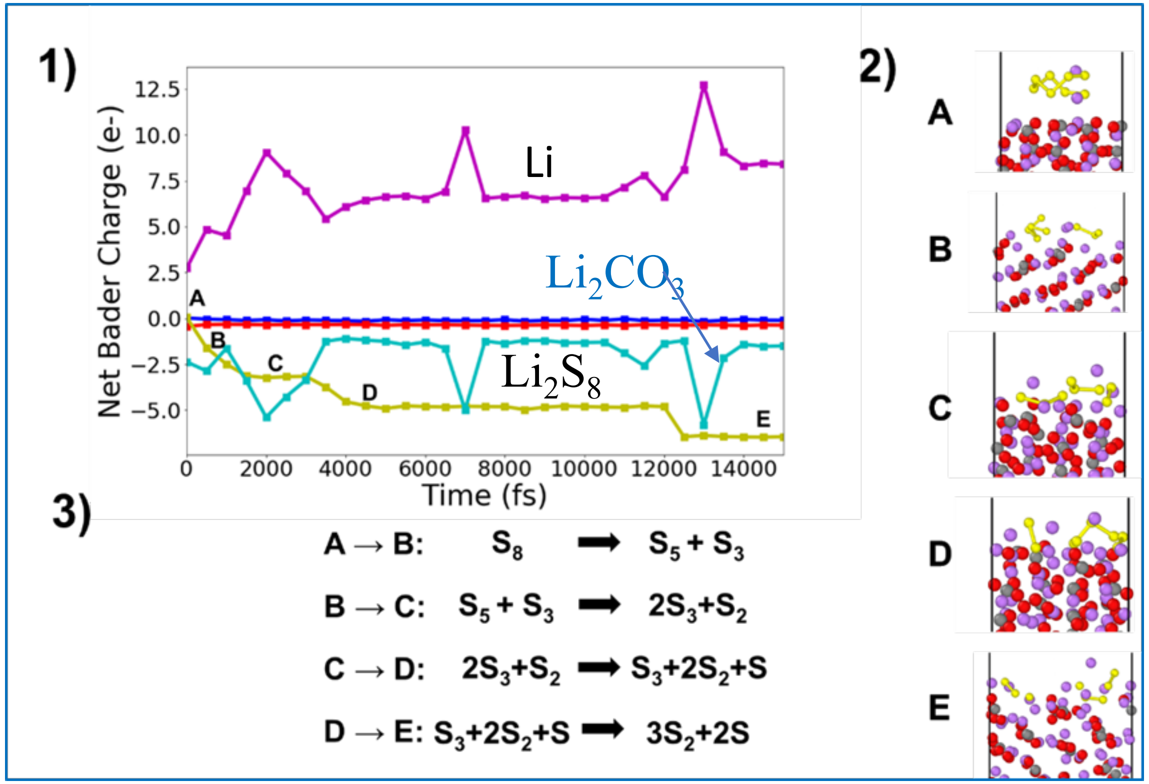




Electronic conductivity through the SEI

Comparison of reactions of a polysulfide Li_2S_8 on a Li metal surface covered by a Li_2CO_3 layer (left), and a Li metal surface covered by a Li_2S film (right). From Kamphaus and Balbuena, J. Power Sources, 2021.

Much faster reaction occurs on the Li_2S film as revealed by the S charge (yellow) as a function of time. Moreover, the Li_2S film does not store charge, in contrast to the Li_2CO_3 film.

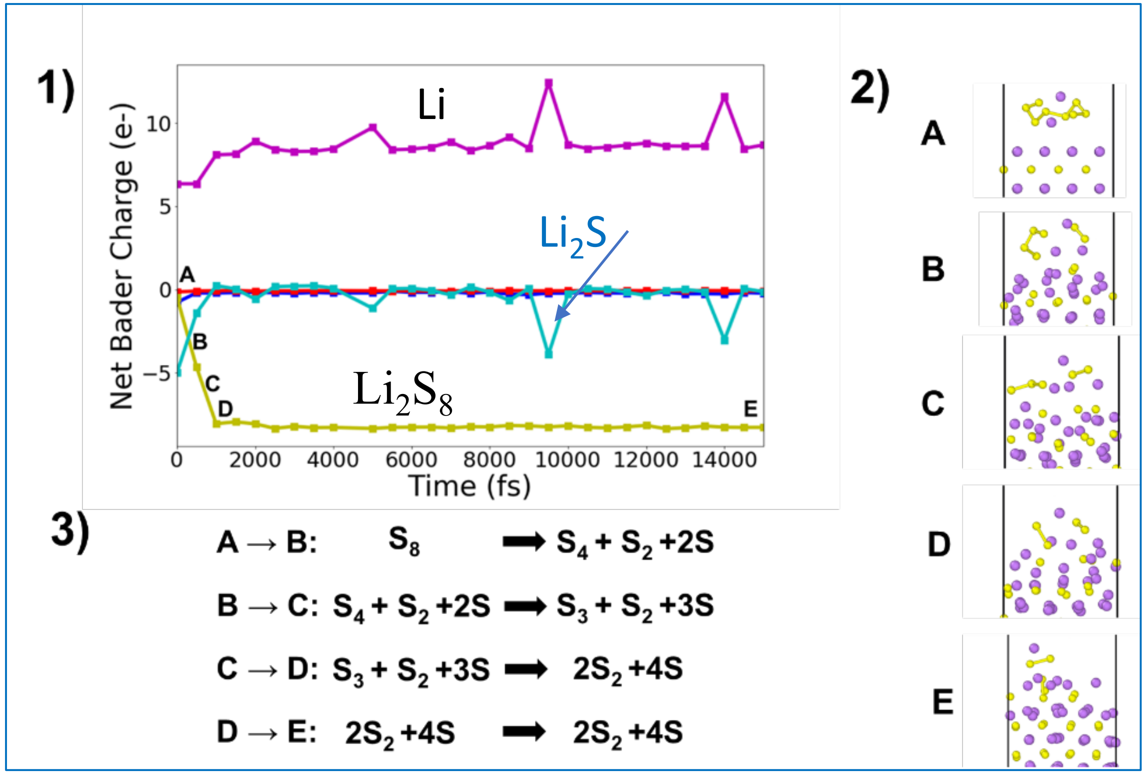


A → B: $S_8 \rightarrow S_5 + S_3$

B → C: $S_5 + S_3 \rightarrow 2S_3 + S_2$

C → D: $2S_3 + S_2 \rightarrow S_3 + 2S_2 + S$

D → E: $S_3 + 2S_2 + S \rightarrow 3S_2 + 2S$



A → B: $S_8 \rightarrow S_4 + S_2 + 2S$

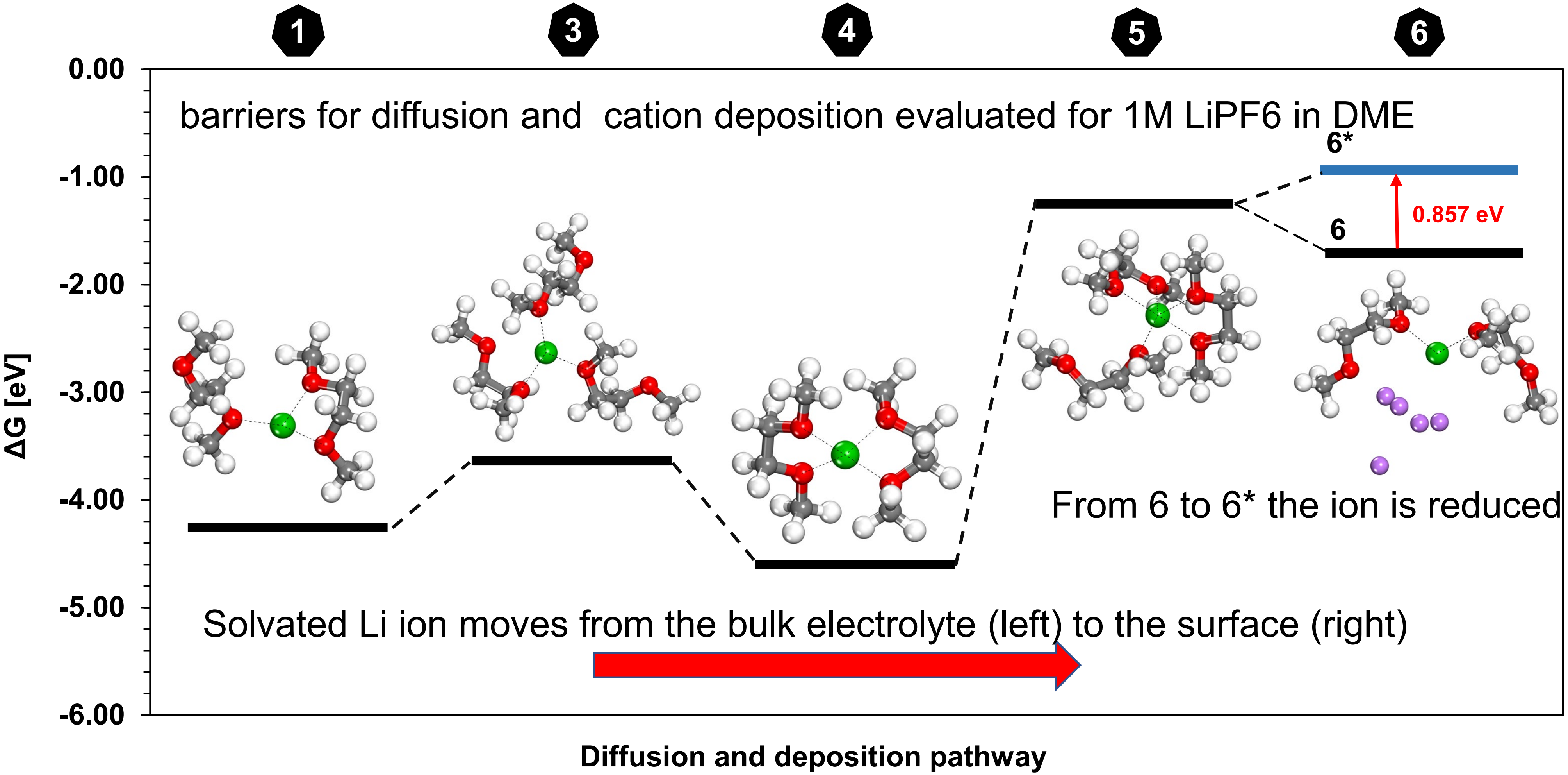
B → C: $S_4 + S_2 + 2S \rightarrow S_3 + S_2 + 3S$

C → D: $S_3 + S_2 + 3S \rightarrow 2S_2 + 4S$

D → E: $2S_2 + 4S \rightarrow 2S_2 + 4S$

$Li/Li_2CO_3/Li_2S_8$ +DME system: 1) Net Bader charges over time of lithium slab; 2) Snapshots of system at labels on charge graph without DME; 3) Reactions for the corresponding snapshots. Color code for atoms: S: yellow; O: red; Li: purple; C: grey.	$Li/Li_2S/Li_2S_8$ +DME system 1) Net Bader charges over time of lithium slab 2) Snapshots of system at labels on charge graph 3) Reactions for the corresponding snapshots. Color code for atoms: Li: purple; S: yellow.

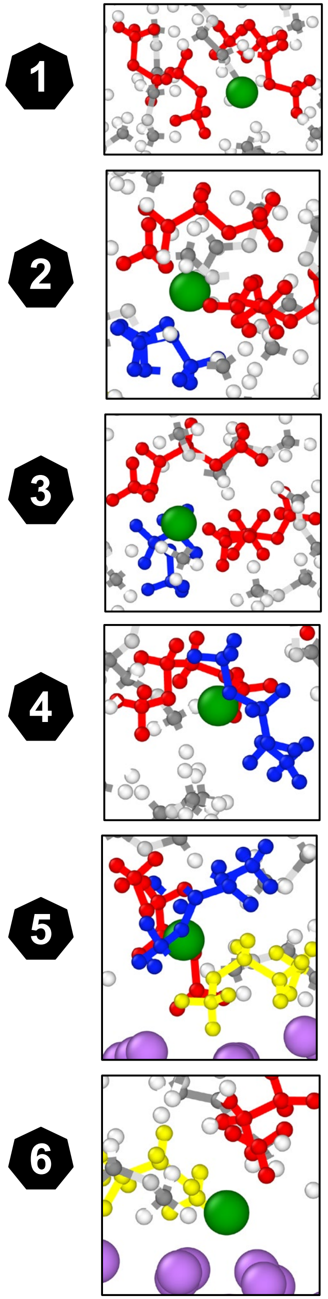
Current/future work: Barriers for Li ion diffusion and deposition



barriers for diffusion and cation deposition evaluated for 1M LiPF6 in DME

From 6 to 6* the ion is reduced

Solvated Li ion moves from the bulk electrolyte (left) to the surface (right)



c-AIMD simulations

🟢 Li+ 🔴 O ⚫ C ⚪ H 🟣 Li

Angarita-Gomez and Balbuena, Chem. Comm. under review