First-Principles Computations of Reactions at the Electrode/Electrolyte Interface

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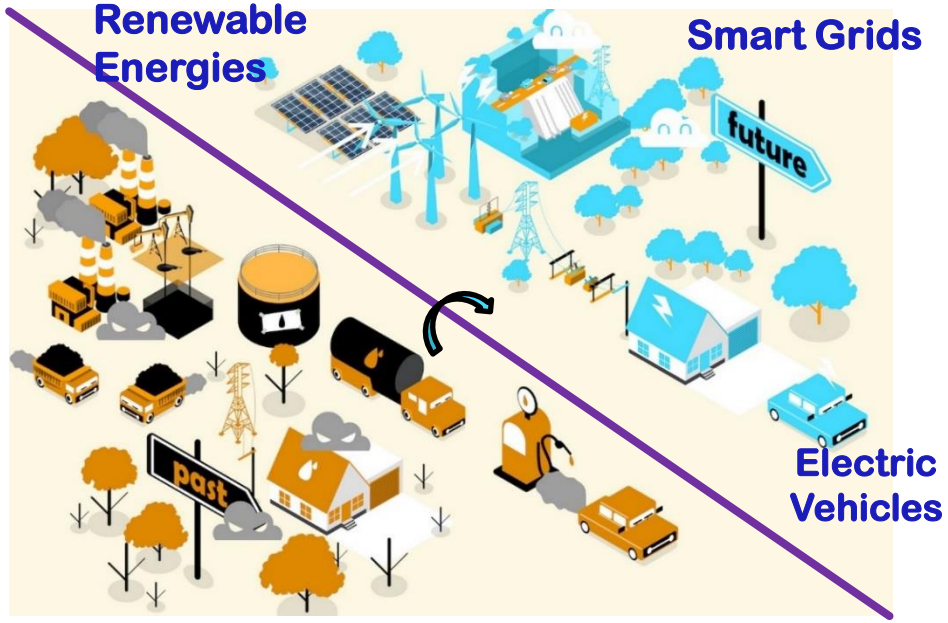
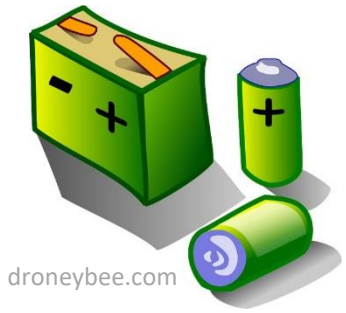
Motivation

Shift in energy sources

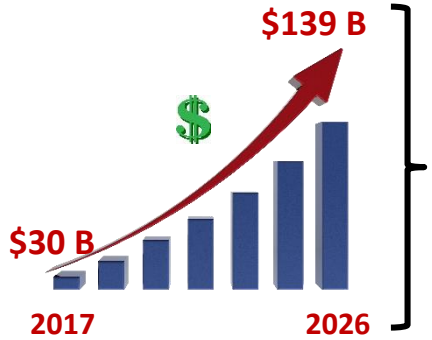


Source: memoori.com

Increasing demand for energy storage



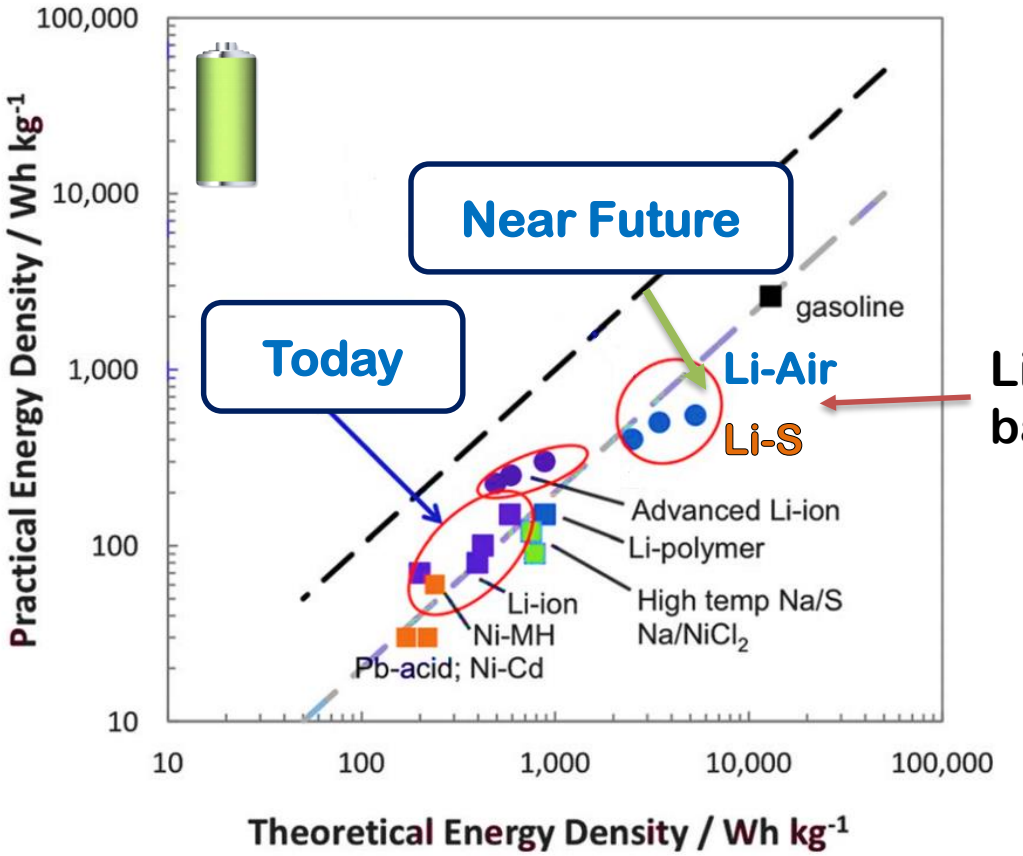
droneybee.com



Li-ion Battery Global Market

Battery Technology

- Li-ion acceptable for small electronic devices
- Does not meet long-term performance EVs

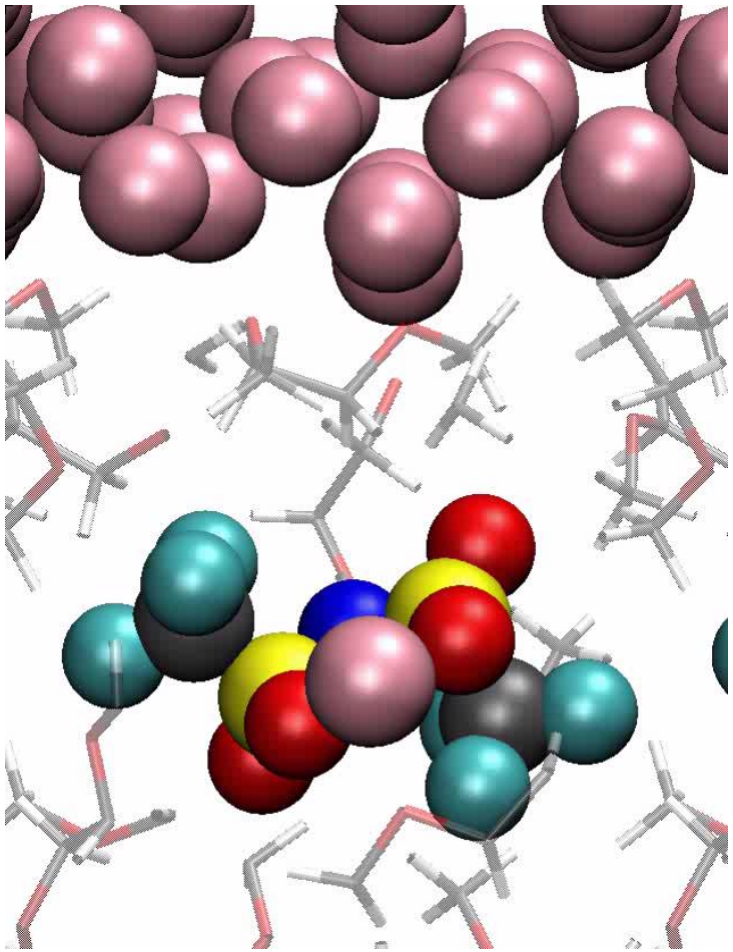


Thackeray *et al.*, Energy Environ. Sci., **2012**, 5, 7854

TeamViewer.com

Reactivity: Solvent/LiTFSI

1M-LiTFSI/DME



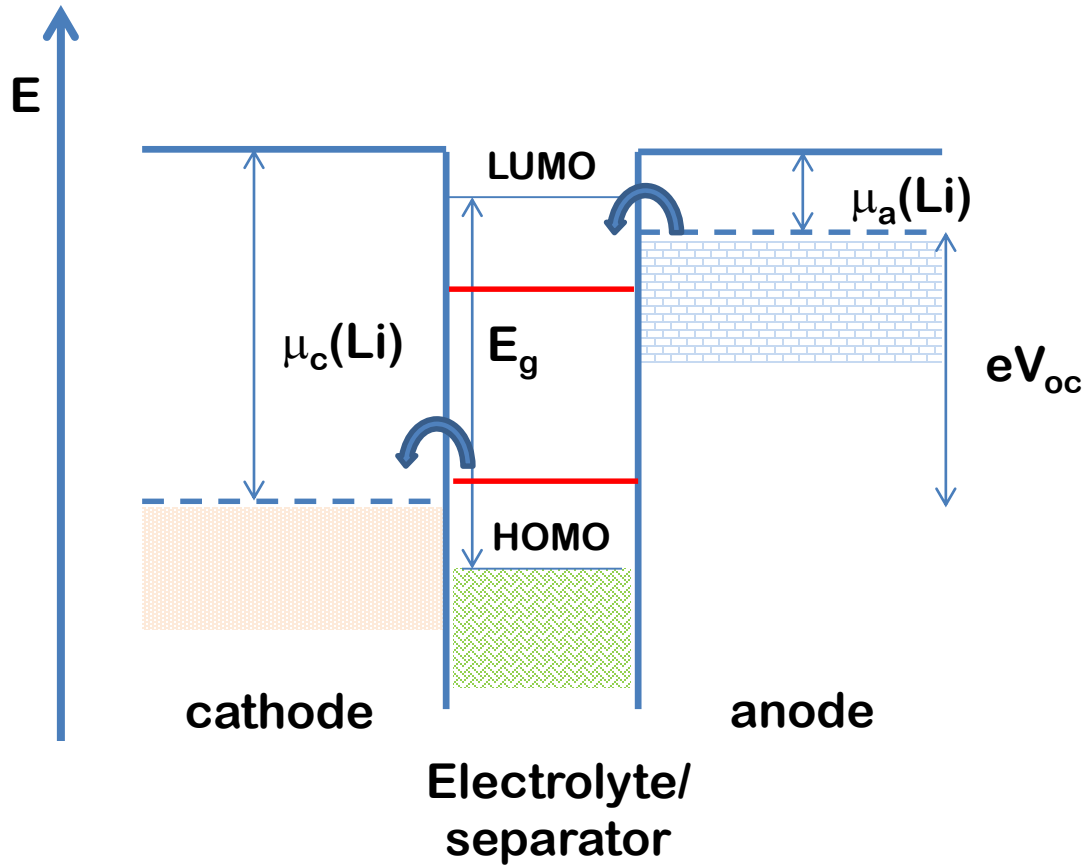
Li metal reactivity: AIMD simulations show anion reduction due to electron transfer from the surface

first principles calculations

- Methods of computational surface science/electrochemistry:
  - DFT, high level ab initio methods
  - DFT-MD
  - DFT-MD + free energy calculations
- Effect of electrode potential

Electrochemical stability

Condition: $eV_{oc} \leq E_g$



Otherwise: electron transfer from electrode to electrolyte (or vice versa) may occur

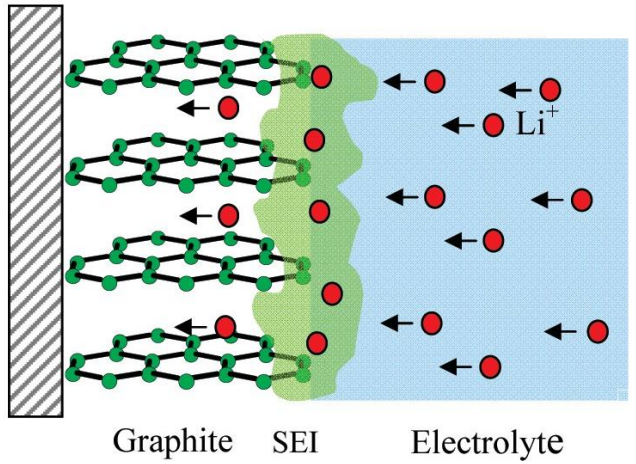
Materials design is crucial

First-principles computational analyses -- understand and predict complex phenomena

Solid-Electrolyte-Interphase layer

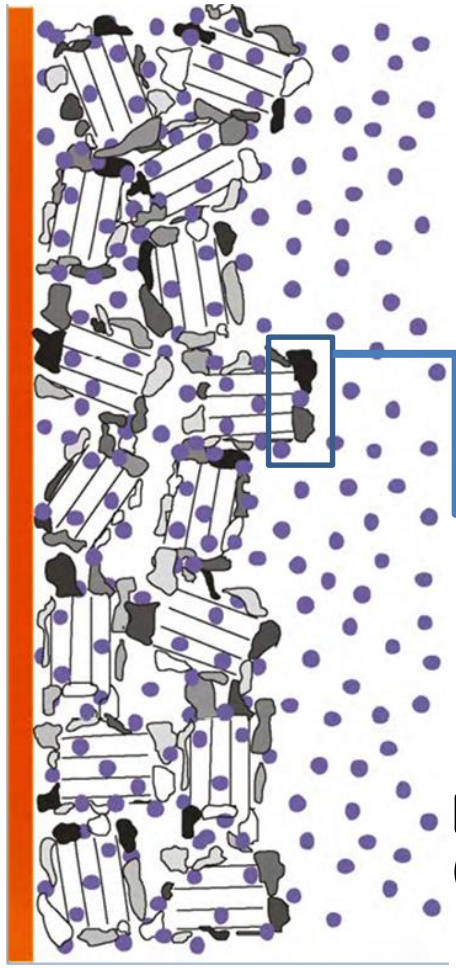
- SEI--surface film formed at anode and cathode surfaces

- Due to electrolyte decomposition (reduction or oxidation)

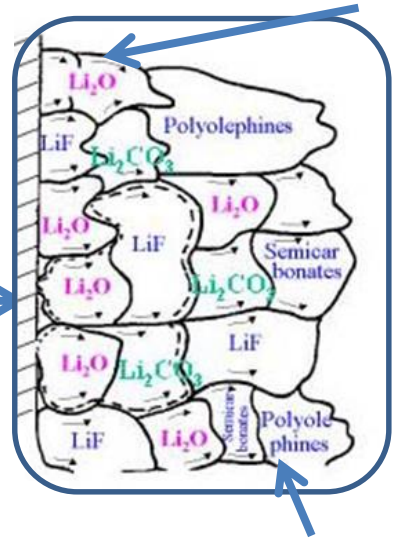


- May protect and stabilize anodes (carbon, Li metal); be unstable (metal-oxide cathodes; silicon anodes)

SEI “mosaic” composition



dense inorganic layer
(from salt decomposition)



porous organic layer
(from solvent decomposition)

yes, there are other interfaces in life… any similarity is pure coincidence !!

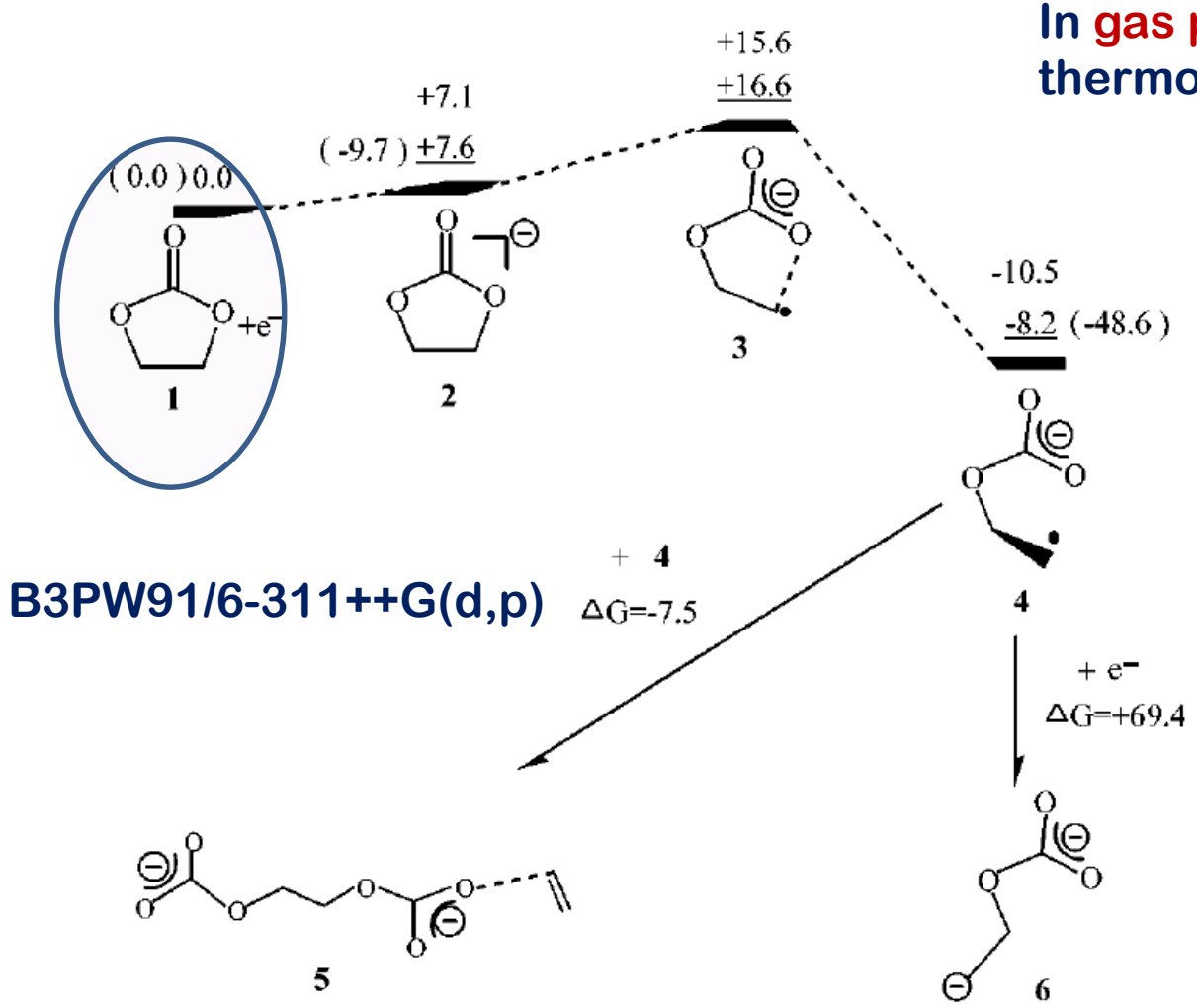
Verma, Maire, Novak, EC Acta 2010

Thickness: from a few Å to tens or hundreds of Å

How is the SEI layer formed at the anode/electrolyte interface?

Electrolyte:
solvent (cyclic and linear carbonates)
+ salt (e.g. $LiPF_6$)
+ additives

EC reductive dissociation



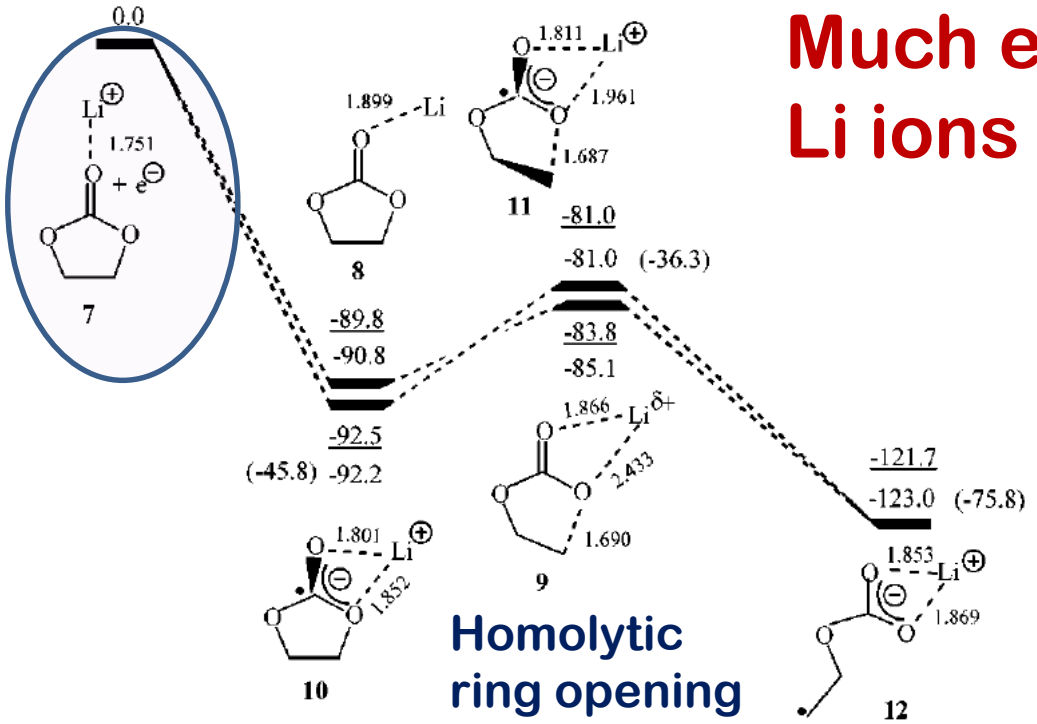
In gas phase:
thermodynamically forbidden

In solvent:
1 and 2 e^- reductions are possible

B3PW91/6-311++G(d,p)

Wang, Nakamura, Ue, Balbuena, JACS, 123, 11708-11718, (2001)

Li^+(EC) reductive dissociation



Much easier !!!
Li ions facilitate the reaction

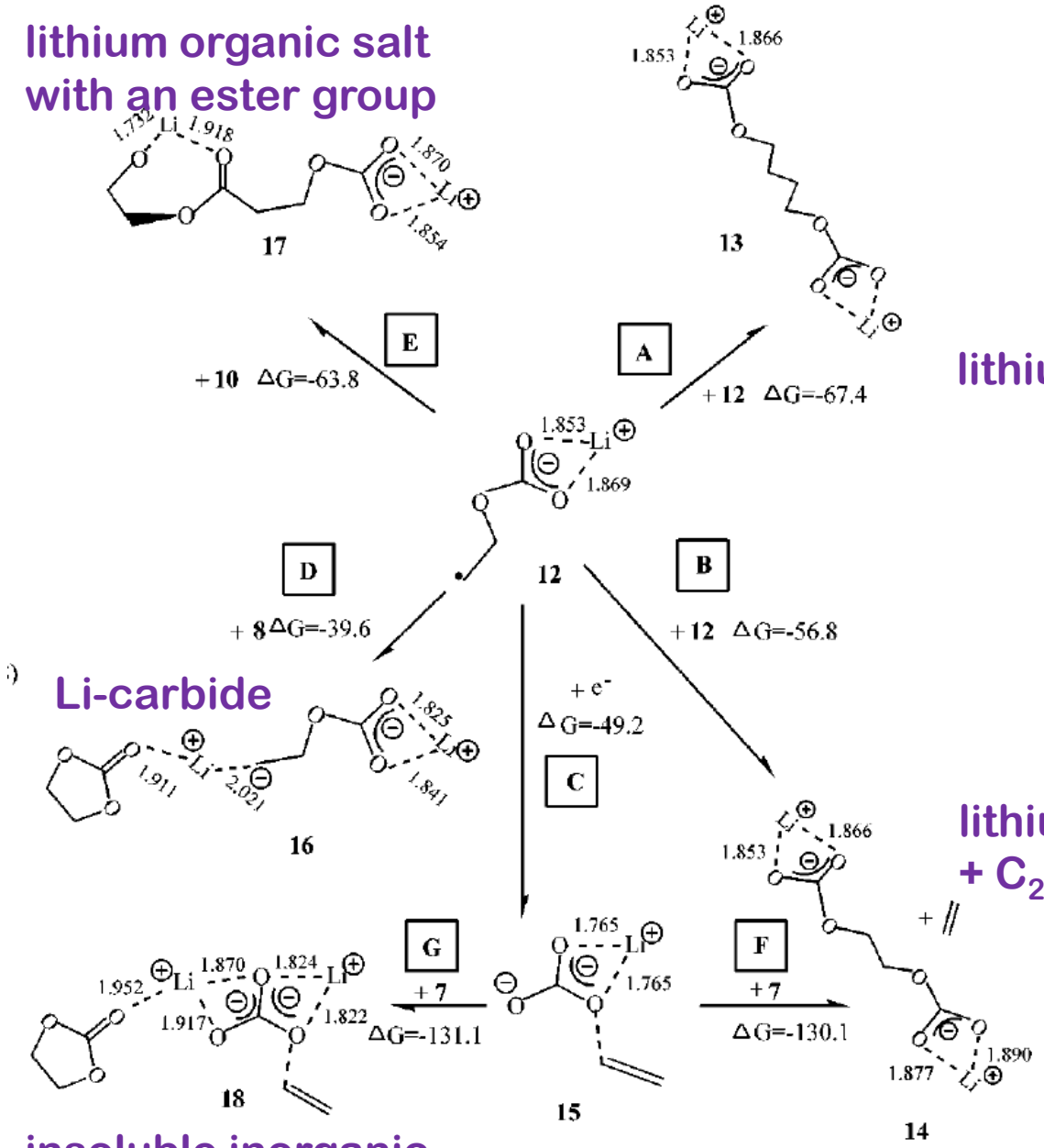
Homolytic ring opening

Ion-pair intermediate; e^- is transferred to EC

Radical anion

Termination reactions

lithium organic salt with an ester group



lithium butylene dicarbonate

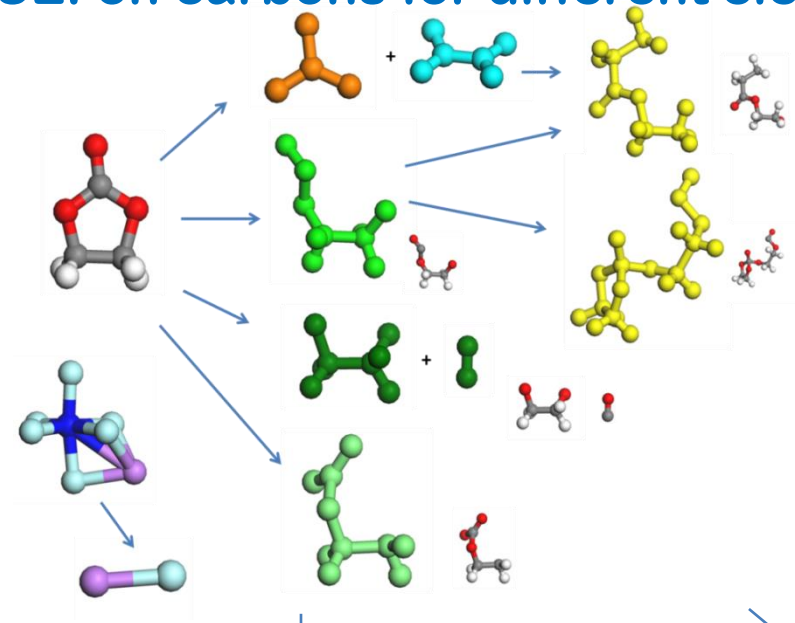
Li-carbide

lithium ethylene dicarbonate + C_2H_2

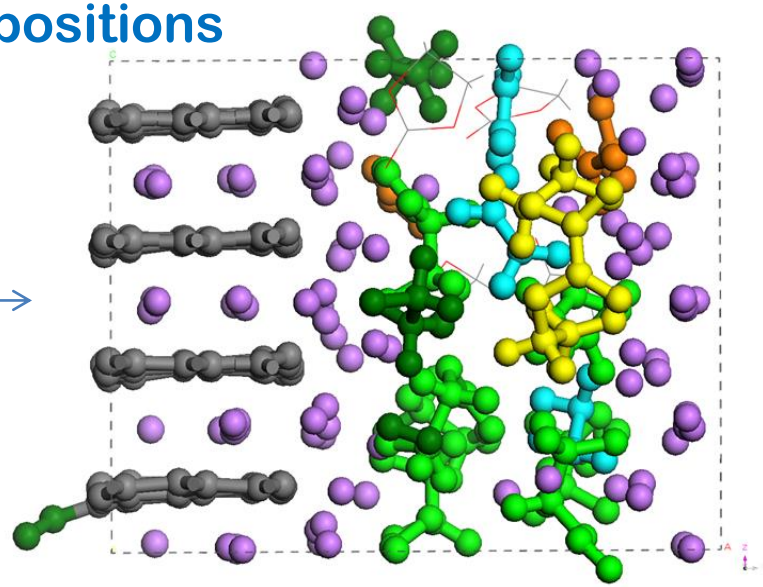
insoluble inorganic Lithium carbonate

Another e^- transfer

SEI on carbons for different electrolyte compositions

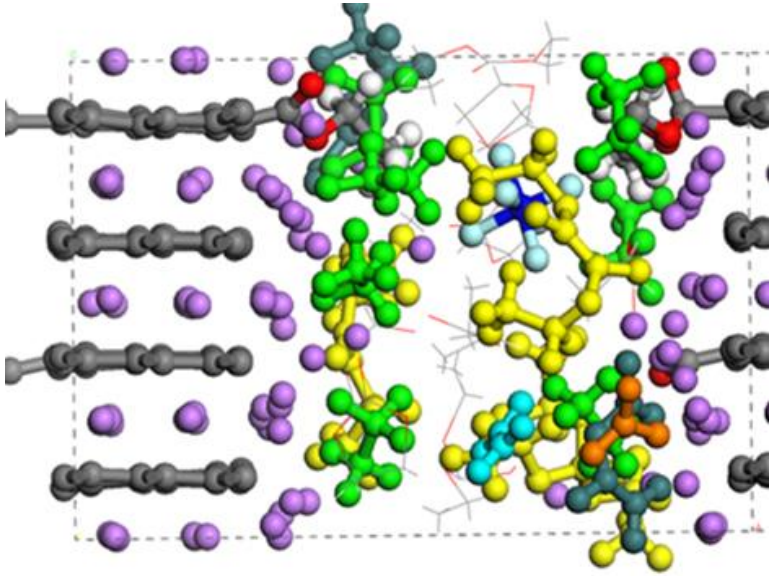


EC

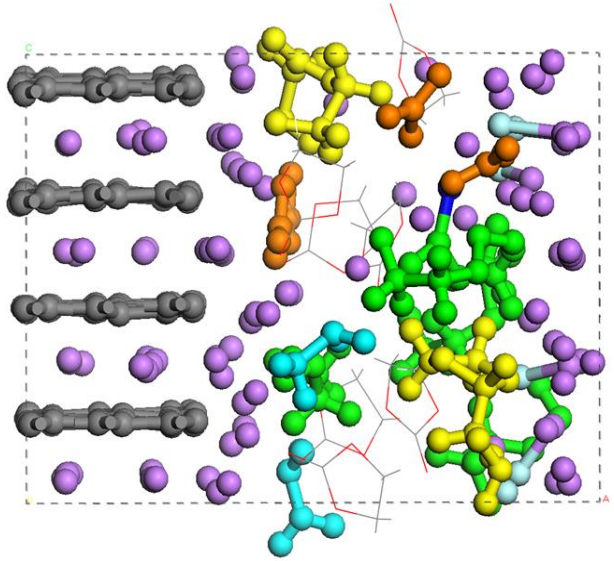


Very different SEI composition and product distribution

$EC + DEC + LiPF_6$

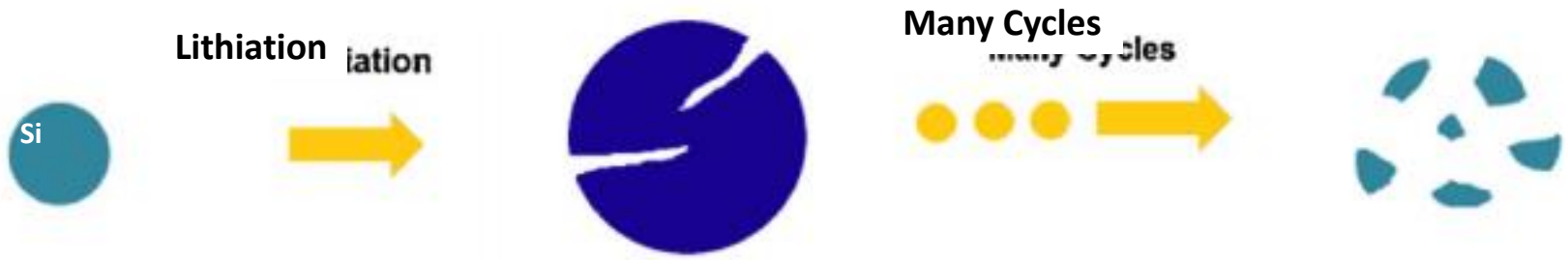


$EC + LiPF_6$

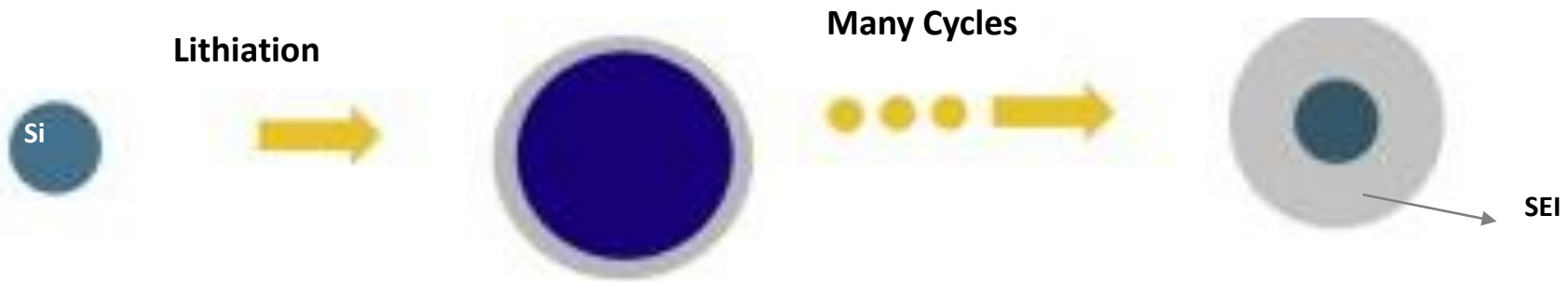


G. Ramos Sanchez, A. Harutyunyan, P. B. Balbuena, JES, 2015

Improving the anode capacity: The Si electrode (capacity: one order of magnitude > carbon)



SEI layer formation

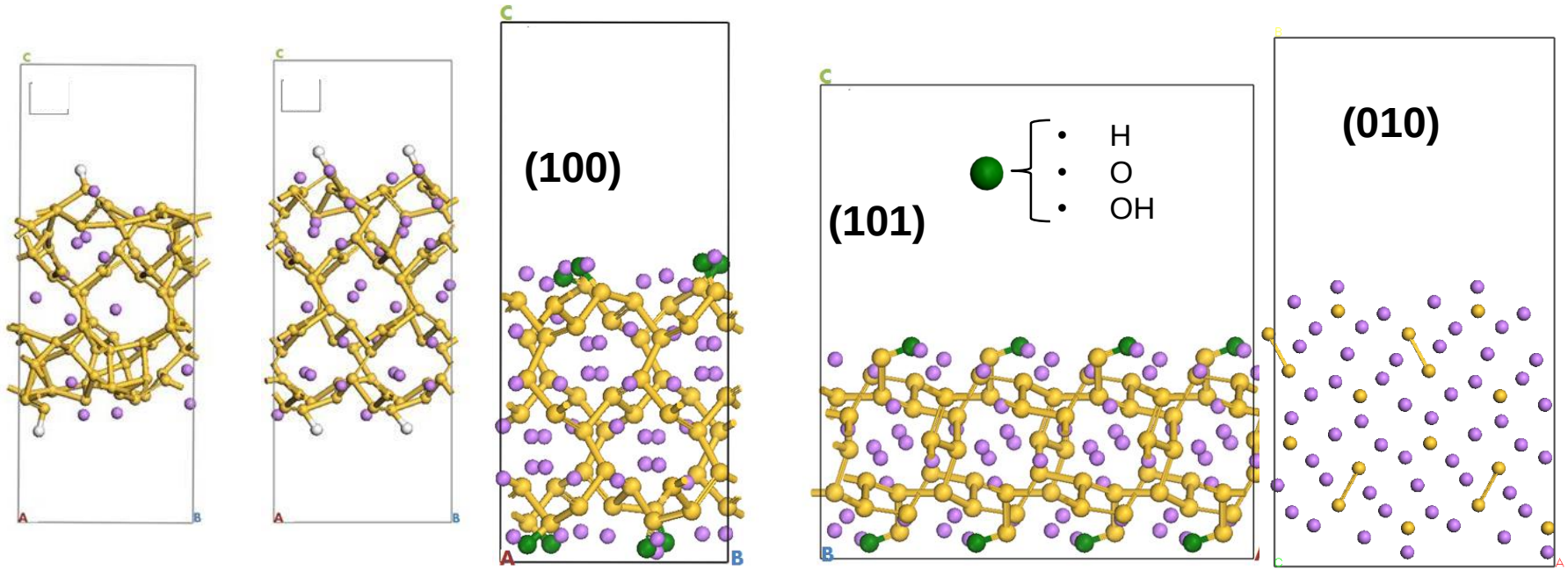


Nano Today, Volume 7, Issue 5, October 2012, 414-429

Voltage range (relative to Li/Li^+)

0.8 to~0.4 V → ~0.2 V

$LiSi_{15}$ $LiSi_4$ $LiSi_2$ LiSi $Li_{13}Si_4$



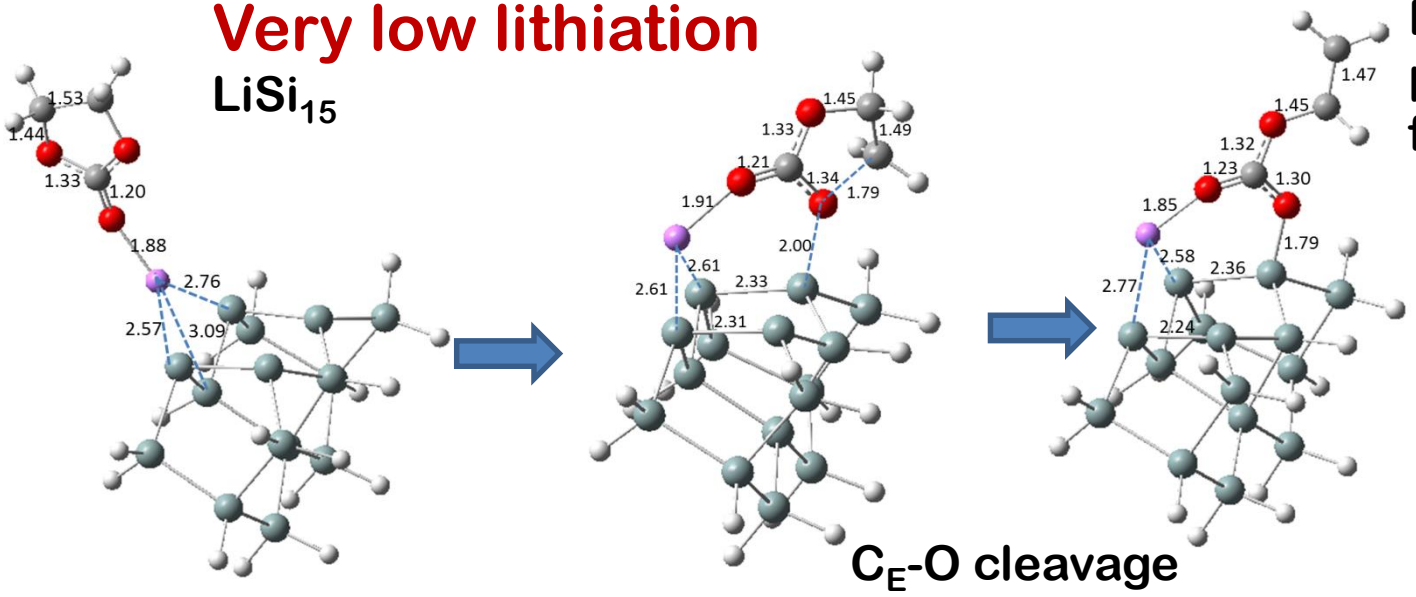
Early stages of lithiation

Highly lithiated

Extent of lithiation: Effect on EC reduction mechanisms

Very low lithiation

$LiSi_{15}$



C_E-O cleavage

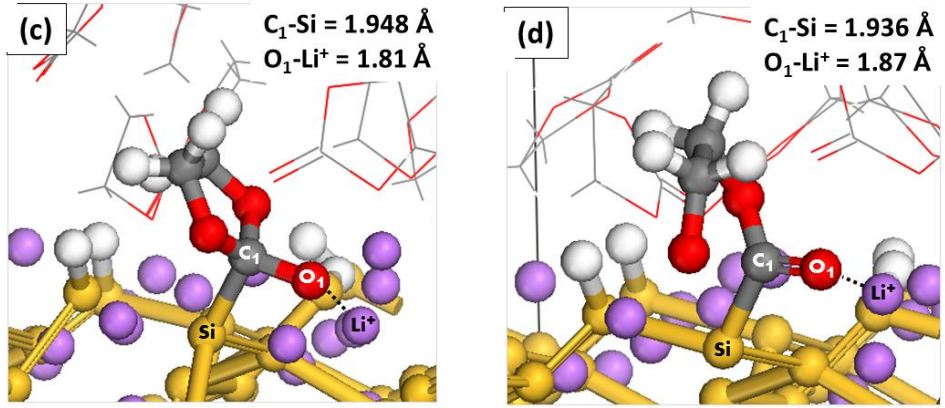
Li over the surface plane; Si-O_E bonds formed

1 and 2-e^- mech. can coexist based on calculated activation energies

Ma and Balbuena JES, 2014

Intermediate to high lithiation

Li on the surface plane or in the subsurface: Si-C bonds are formed

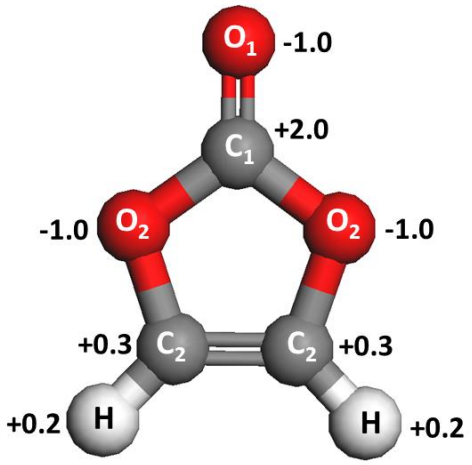


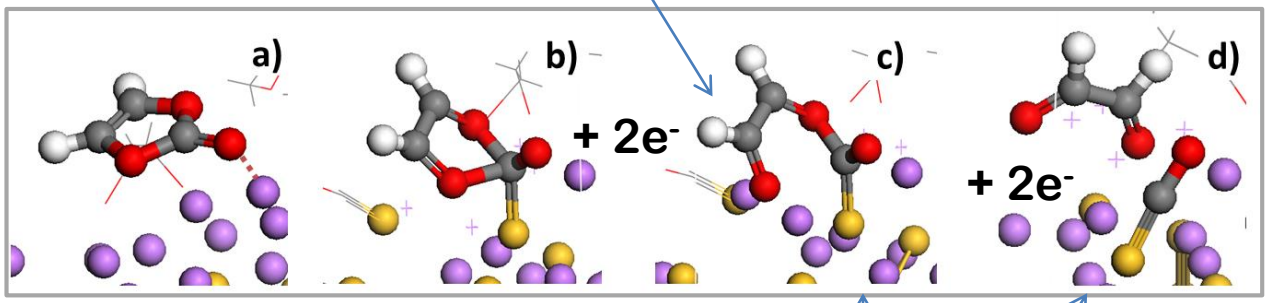
2-e^- mech. preferred; at higher lithiation 4 e^- mech. observed

JM Martinez de la Hoz, K Leung and P B Balbuena, ACS Appl. Mat. and Interfaces, 2013

VC reduction on lithiated Si anodes

Cleavage of C1O2 bond: $VC_{(ads)} + 2e^- \rightarrow \cdot OC_2H_2OCO^{2-}{}_{(ads)}$





All surfaces

a) Li-O interaction
b) Formation of C-Si bond
c) Ring opening (open VC^{2-})
d) Cleavage of a 2nd C1O2 bond — Higher lithiated

CO_2 formation results from: $VC + CO_3^{2-} \rightarrow \cdot OC_2H_2OCO_2^{2-} + CO_2$

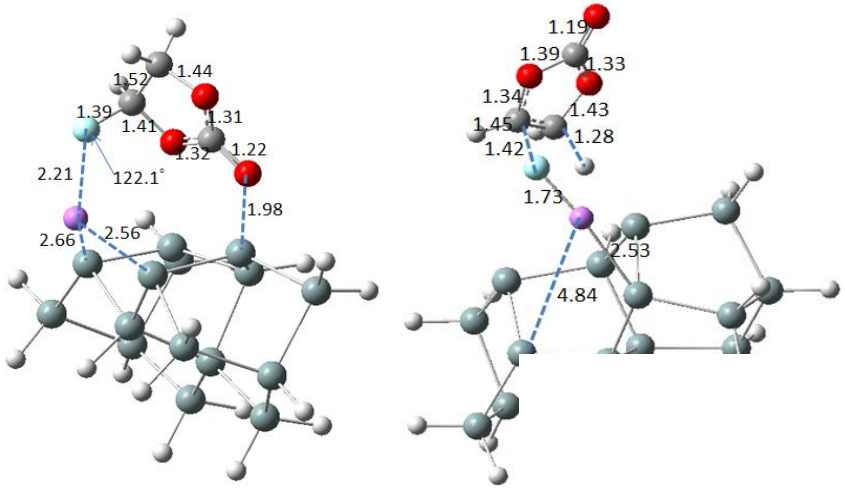
CO_3^{2-} is a product of EC and oligomers decomposition (alternative mechanism to Ushirogata et al, JACS 2013)

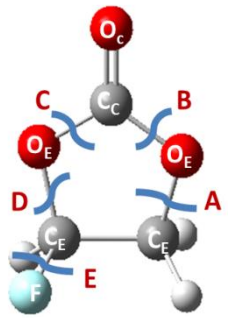
VC products: open VC^{2-}, $OC_2H_2O^{2-}$, $OC_2H_2OCO_2^{2-}$, CO, CO_2

C=C containing species

J. M. Martinez de la Hoz and P. B. Balbuena, PCCP, 16 (32), 17091-17098 (2014)

Effect of degree of lithiation on additives





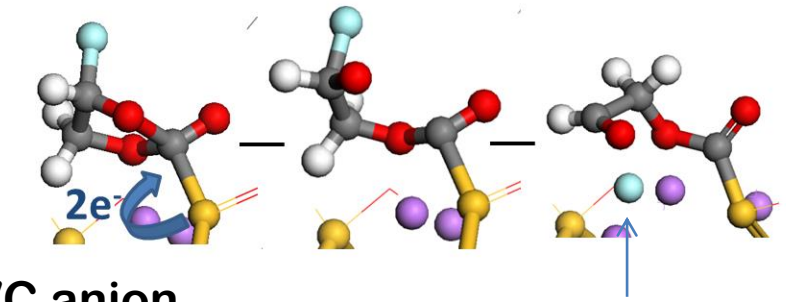
very low lithiation

FEC: 2 e⁻ mechanism preferred;
C_C-O_E and C_c-F bond cleavages: low/moderate barriers

Ma and Balbuena
JES, 2014

multi-electron reactions on highly lithiated surfaces

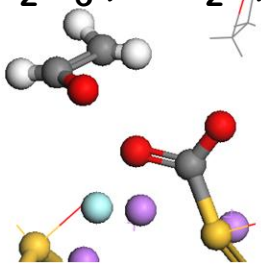
2 e⁻ transfer to FEC → **ring opening**



C-F bond breaking

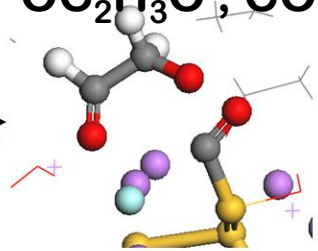
$\cdot OC_2H_3^-$, CO_2^{2-}, F^-

(I) + 2e⁻

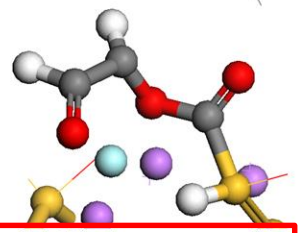


$\cdot OC_2H_3O^-$, CO^{2-}, F^-

(II) + 2e⁻



(III) + 1e⁻



$\cdot OCOC_2H_2O^{2-}$, CO_2^{2-}, H, F^-

open VC^{2-}

FEC can yield open VC anion (path III) and therefore all VC-derived products , in addition to other specific FEC products (paths I, II, and III)

J. M. Martinez de la Hoz and P. B. Balbuena, PCCP, 16, 17091-17098 (2014)

Effects of electrolyte composition

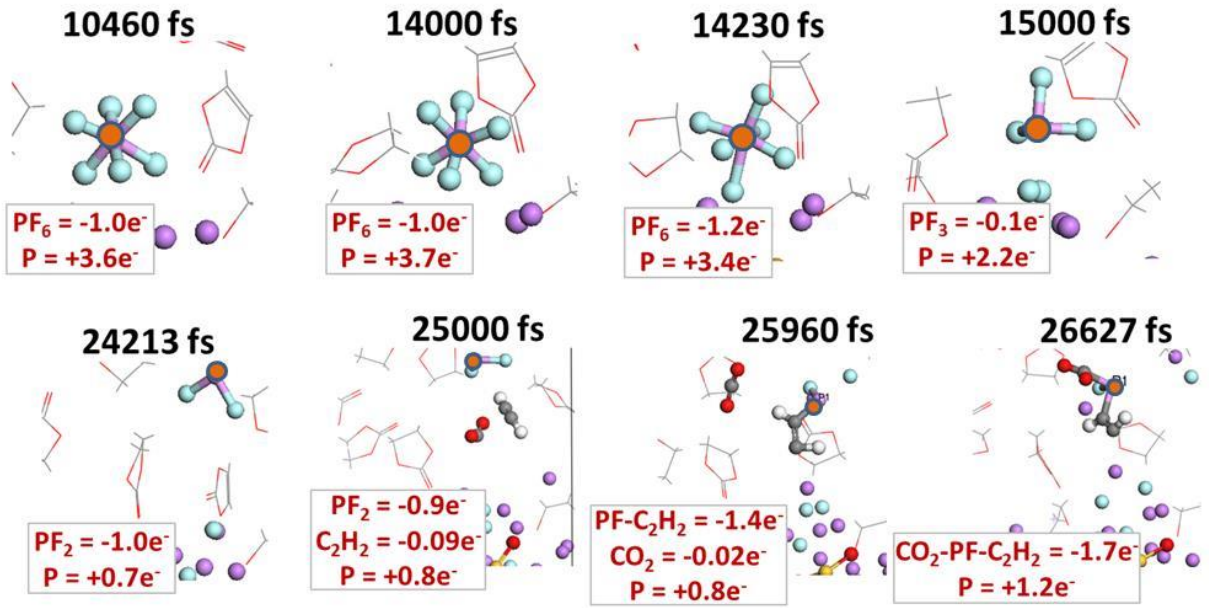
Mixture	Number of molecules					% wt.
	EC	VC	FEC	DEC	$LiPF_6$	
1	13	0	0	0	1	100 (EC)
2	12	1	0	0	1	7.5 (VC)
3	11	2	0	0	1	15 (VC)
4	7	6	0	0	1	46 (VC)
5	12	0	1	0	1	9.1 (FEC)
6	11	0	2	0	1	18 (FEC)
7	7	0	6	0	1	50 (FEC)
8	2	0	0	7	1	71.6 (DEC)

AIMD simulations of mixtures of various compositions

Salt produces LiF and other fragments interact with solvent products

Illustration:

mixture 3
15% wt VC



JM Martinez de la Hoz, FA Soto and PB Balbuena, JPCC, 2015

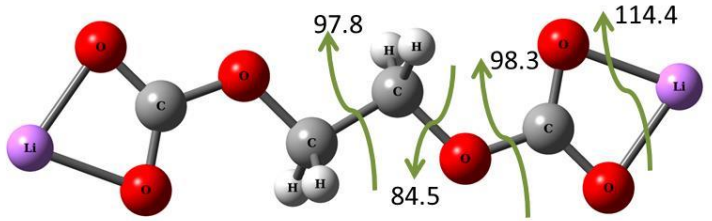
How is the ionic/electronic transport through the various SEI components:

- LiF (from salt or solvent)
  Li_2O (from further reactions among products), Li_2CO_3,
  organic oligomers, polymers??
- How are “good” and “bad” SEI layers characterized?
- How does the SEI layer grow beyond the e^- tunneling regime?

Electron transfer through growing SEI

We examined oligomers:

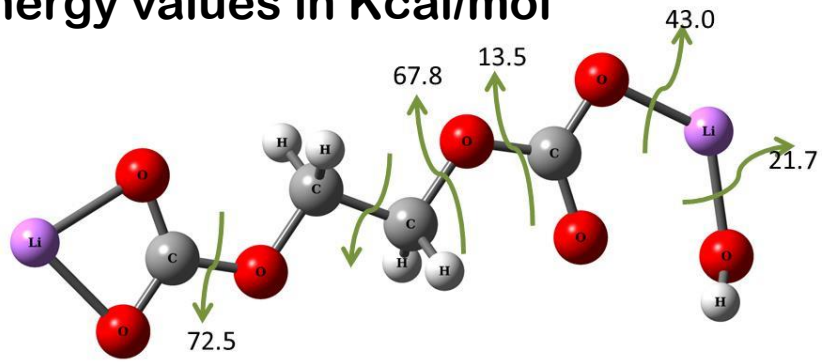
Li_2EDC, Li_2VDC



+ OH•

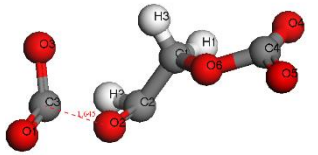
0.0 kcal/mol

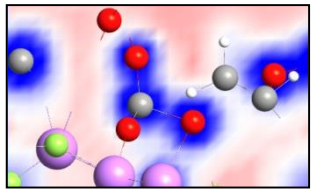
energy values in Kcal/mol



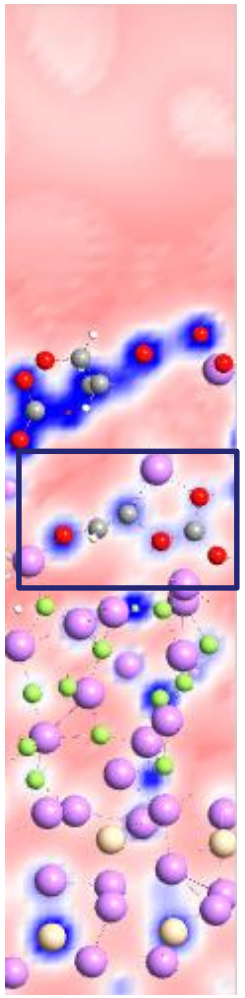
-21.7 kcal/mol

CO bond breaking



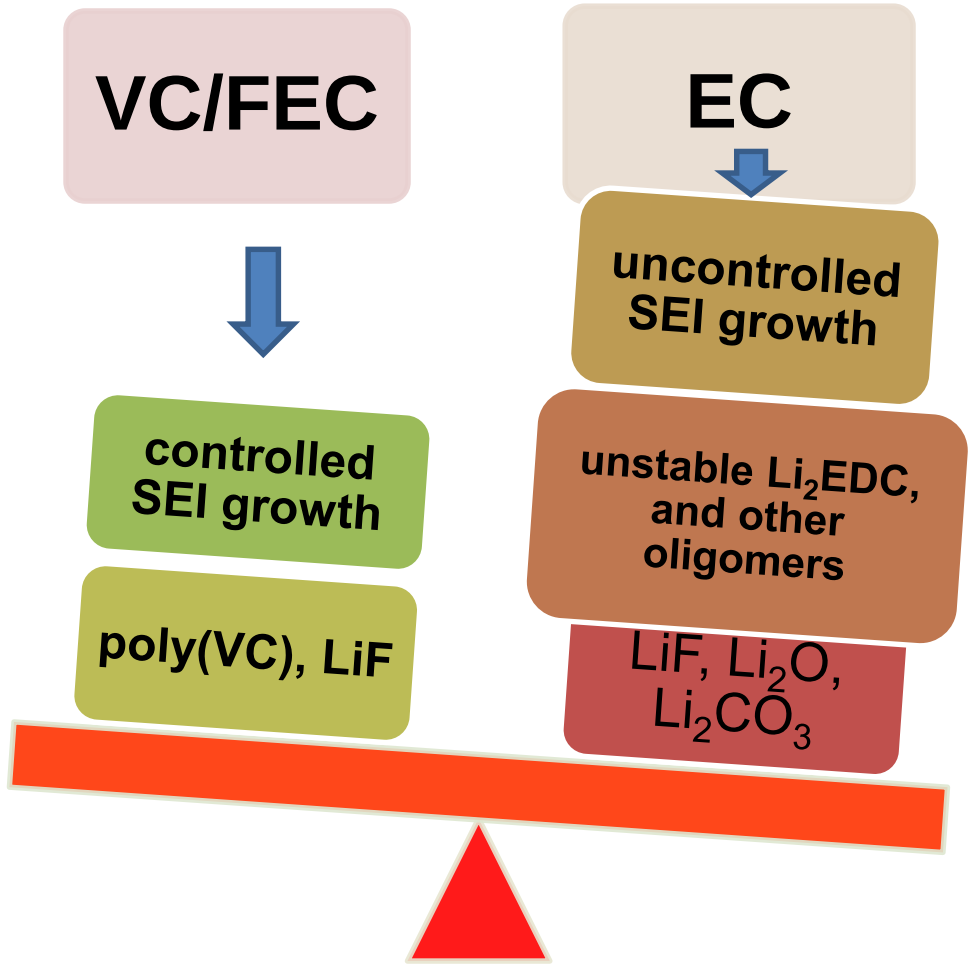


new radicals are formed; electron transfer shown by blue regions



Attack of Li_2EDC by radical species debilitates its bonds causing fast decomposition. Same for Li_2VDC

SEI from VC/FEC ("good") vs. EC ("bad")



oligomers (formed from Li_2EDC, Li_2VDC and others) decompose by radical attack; generate more radicals→ SEI uncontrolled growth

best additives control excessive radical formation

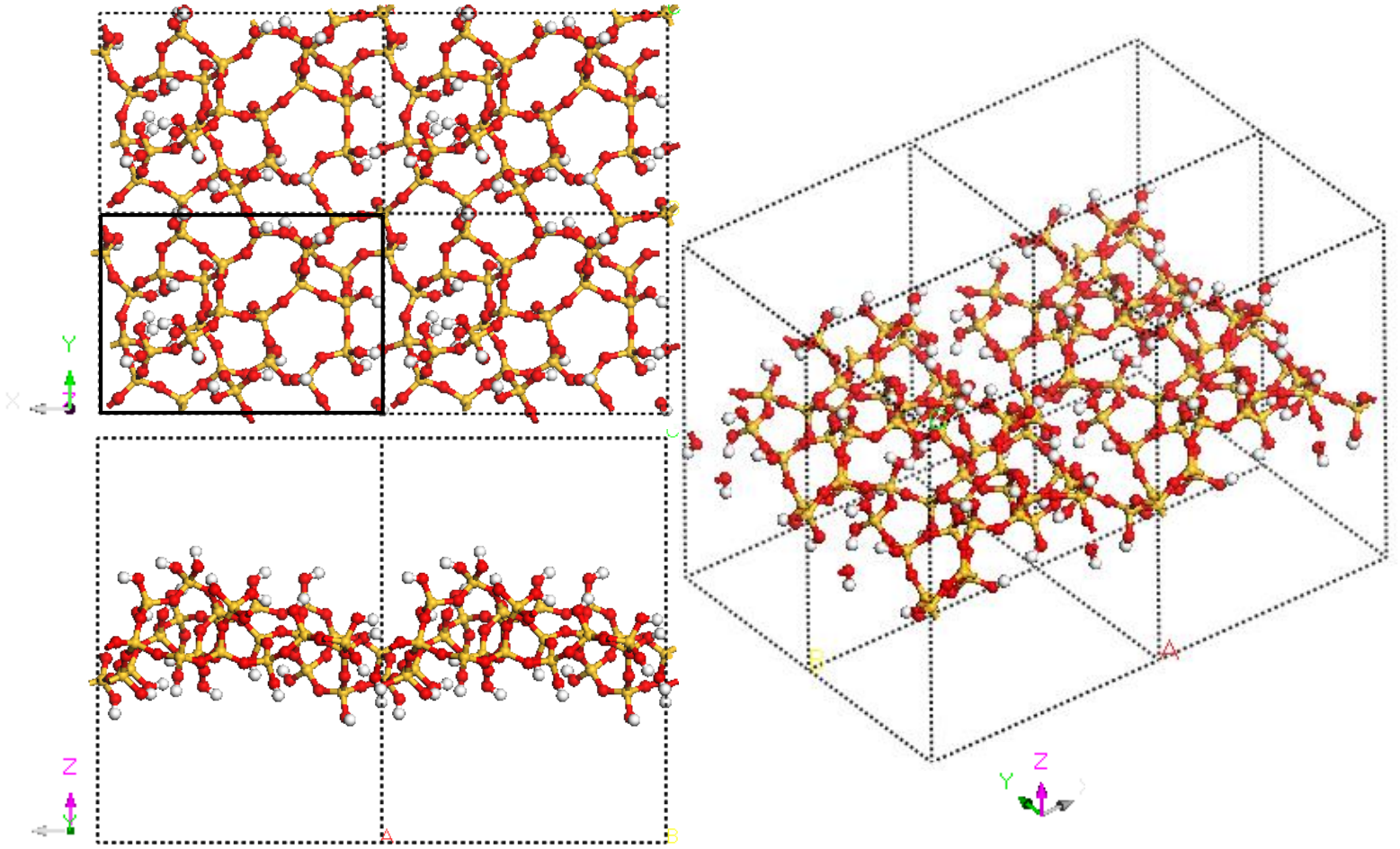
Soto, Martinez, Ma, Seminario, Balbuena, Chem. Mater. 2015

surface structure and
electrolyte chemistry play important roles;

how does the surface chemistry matter?

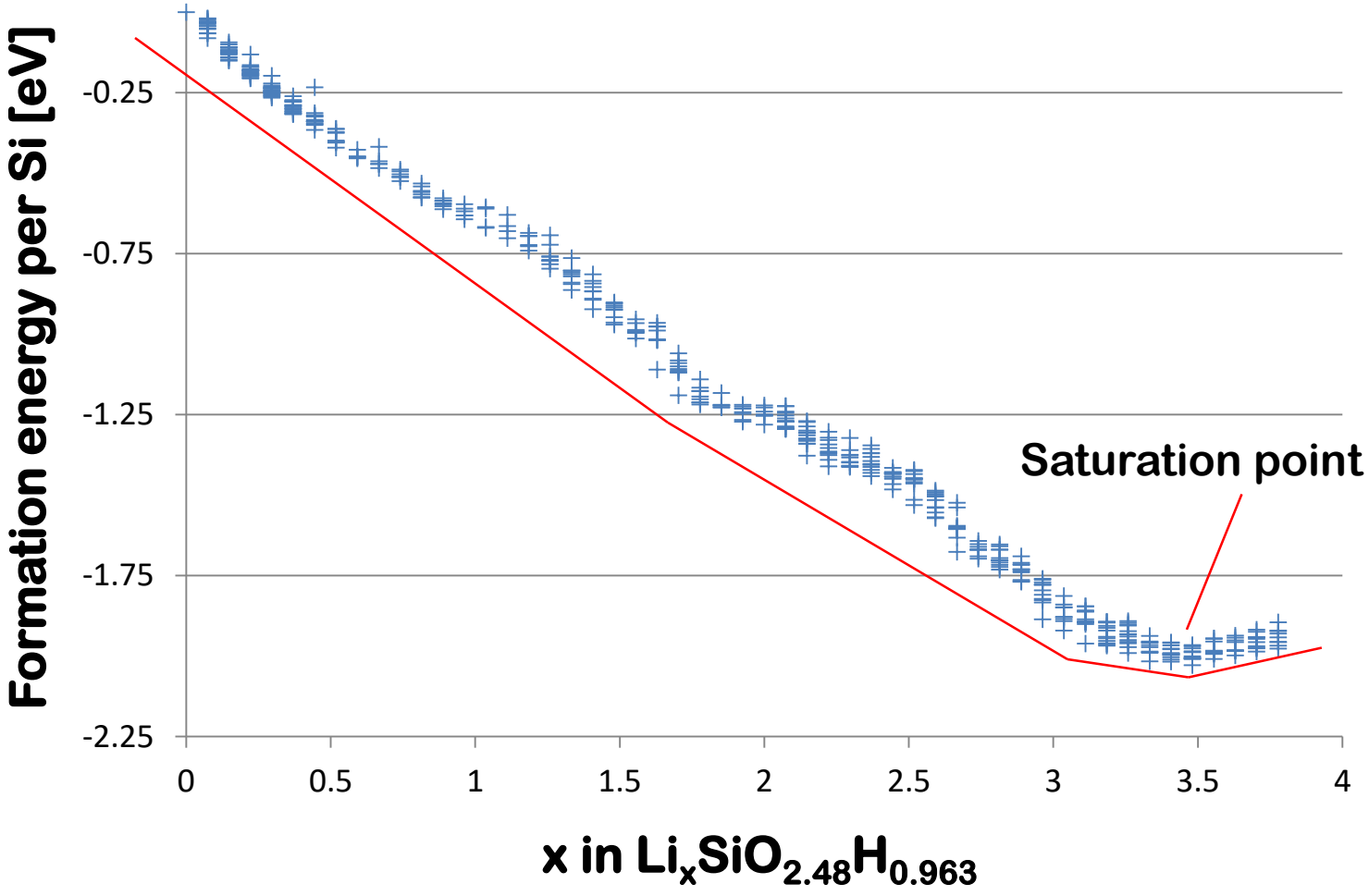
-native oxides
-artificial coating

SiO_2 : lithiation and reactivity



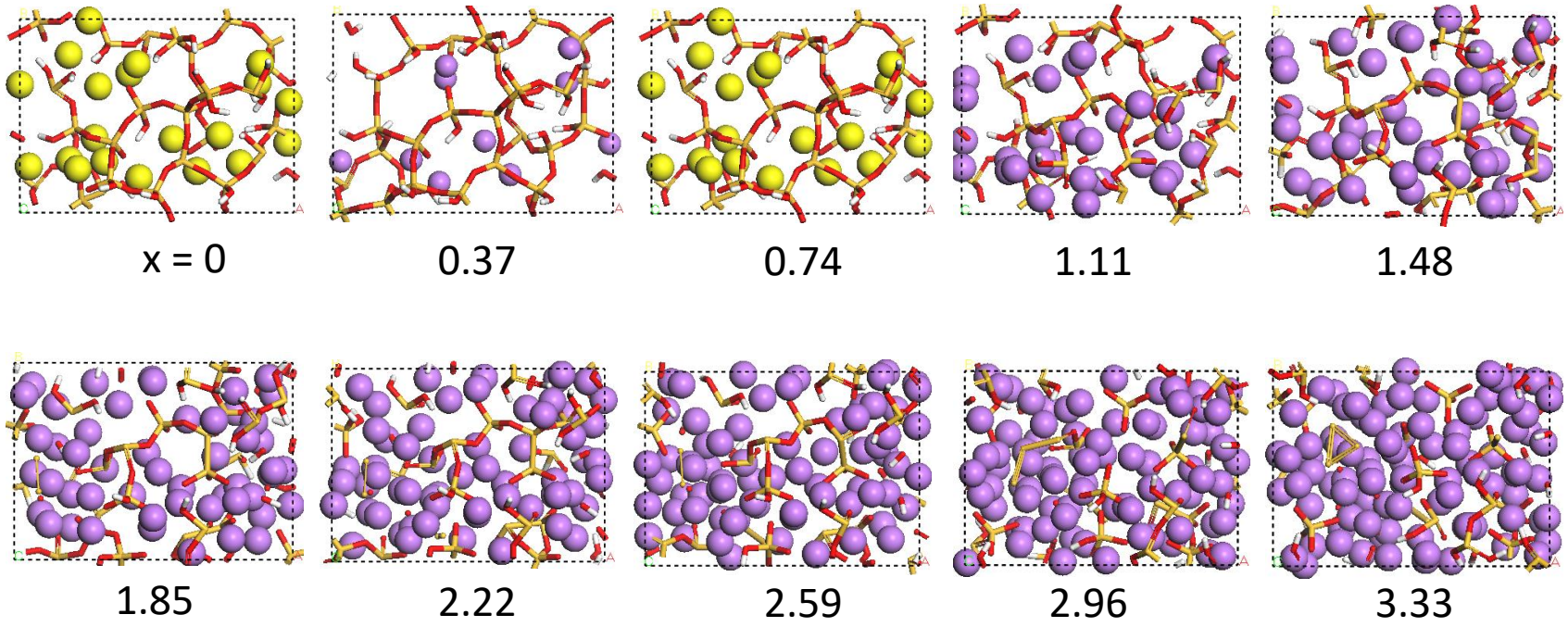
hydroxylated amorphous Si surface

Lithiation formation energy



$$\Delta E(x) = [E(Li_xSurface) - x\,E(Li_{metallic}) - E(Surface)] / N$$

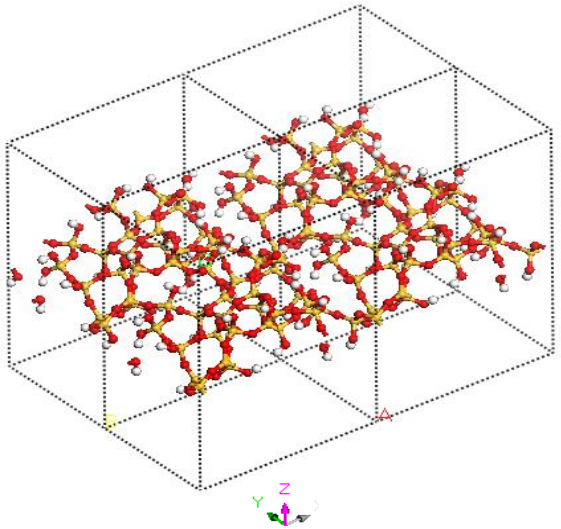
Structural evolution

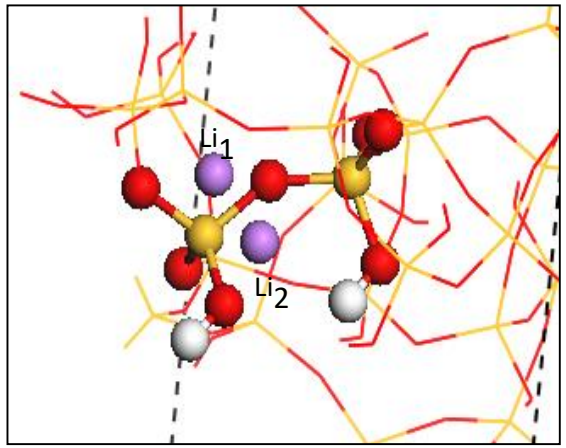


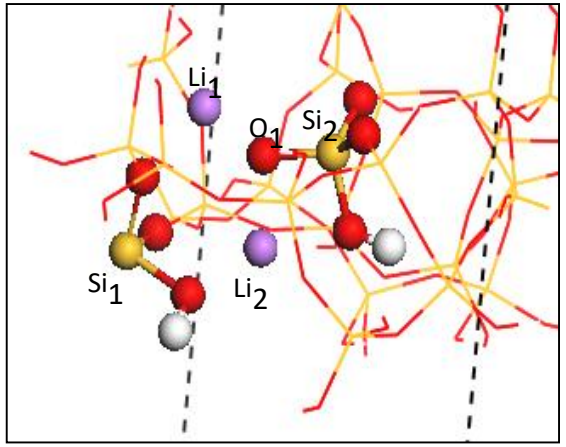
x in $Li_xSiO_{2.48}H_{0.963}$

S. Perez Beltran, G. E. Ramirez-Caballero, and PB Balbuena, JPCC, 2015

Lithiation mechanisms in native oxides

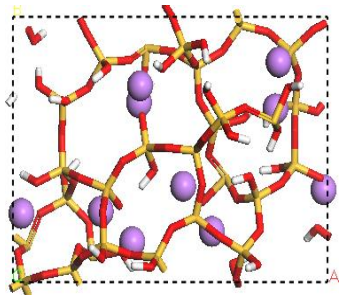




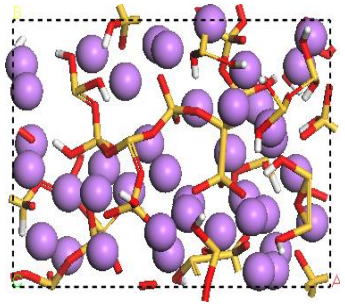


Si-O broken, Si-Si formed, Li_6O complexes formed

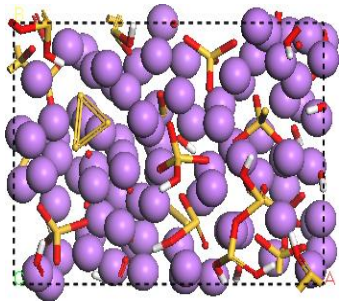
hydroxylated amorphous film $Li_xSiO_{2.48}H_{0.97}$



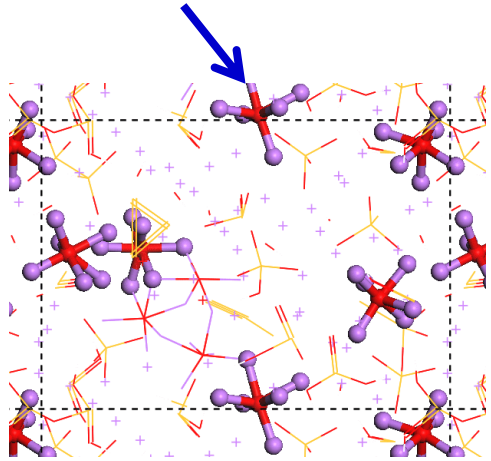
x = 0.37



x = 1.48

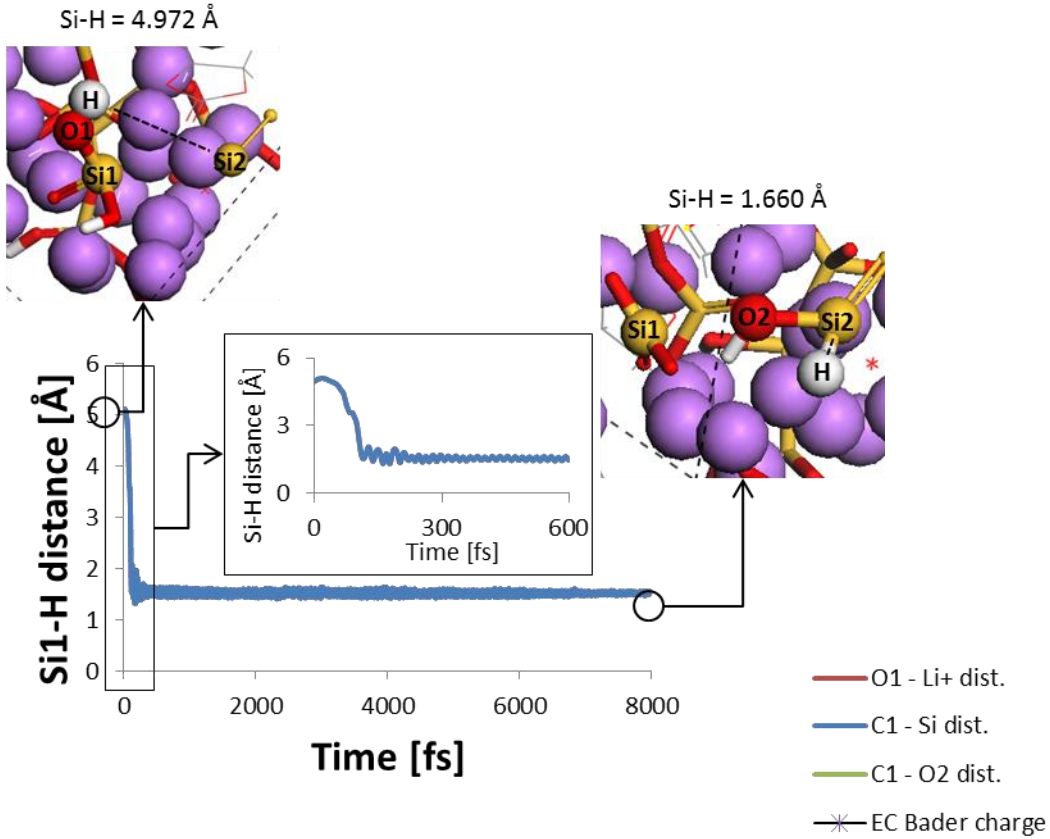


x = 3.33

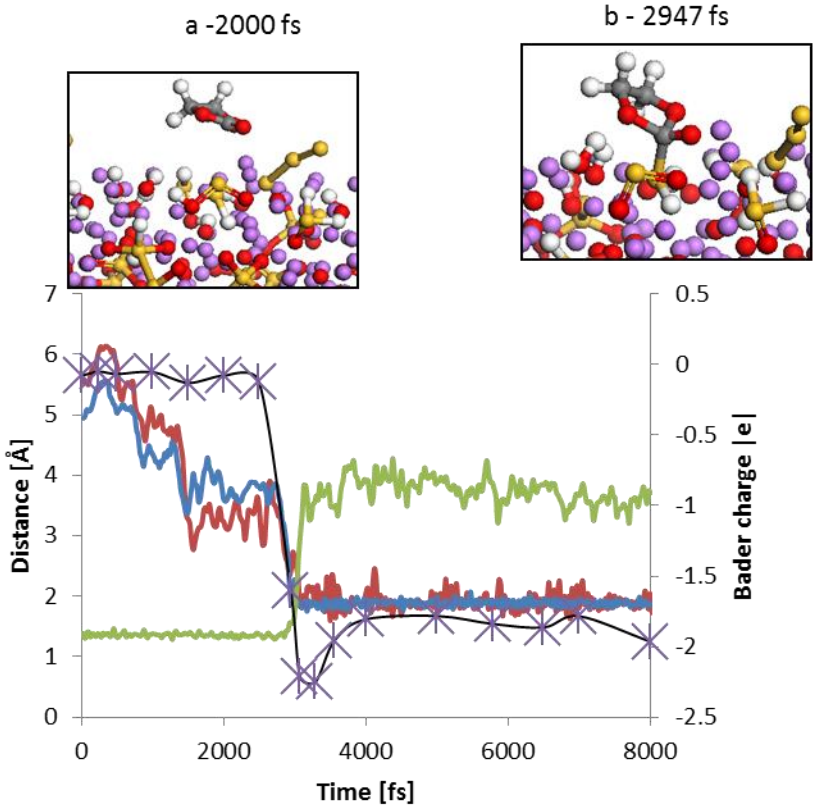


Perez-Beltran Ramirez-Caballero & Balbuena, JPCC 2015

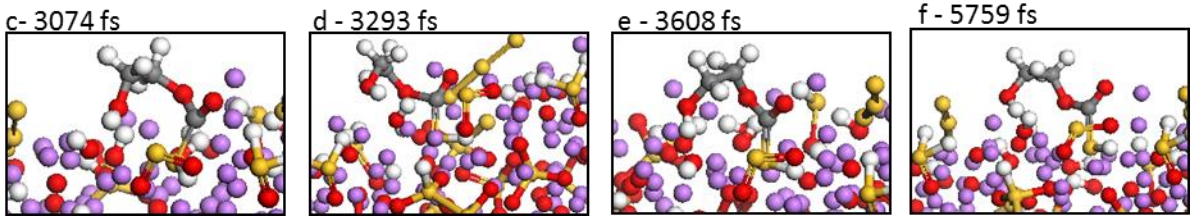
Lower reactivity of the hydroxylated surface



2 e⁻ reduction of EC



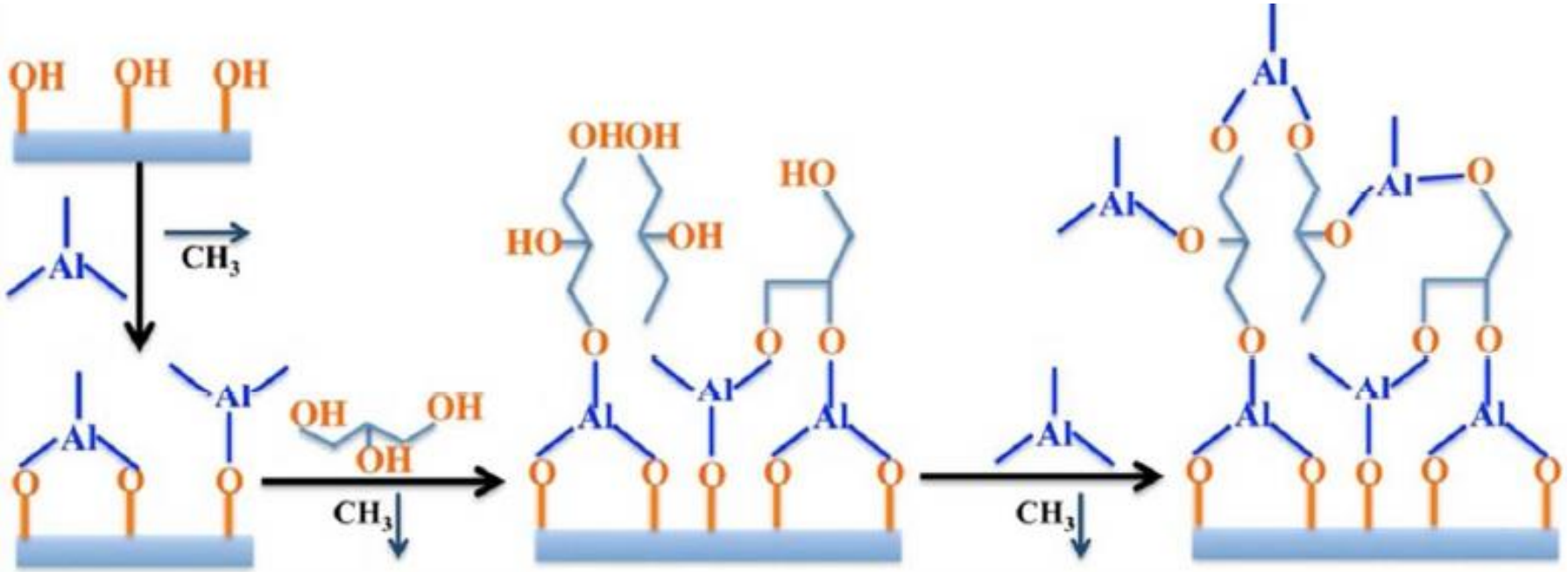
decomposition of OH groups and formation of SiH bonds



$$EC_{(ac)} + 2e^- \rightarrow O(C_2H_4)OCO^{2-}{}_{(ads)}$$

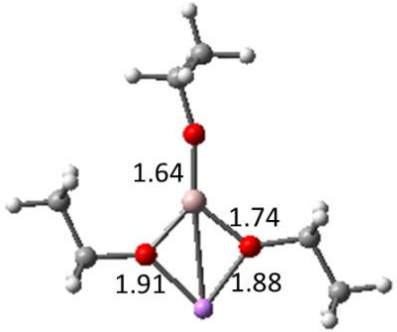
Aluminum alcoxide (alucone) coating

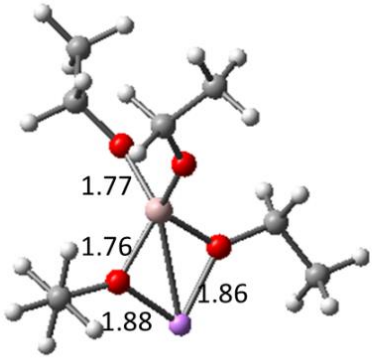
- Collaboration with Chunmei Ban (NREL)

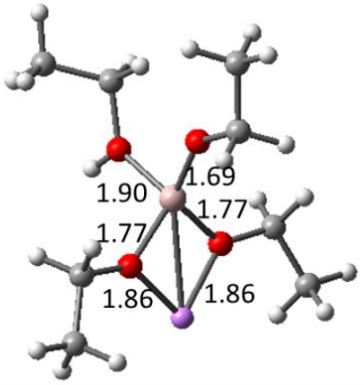


film formation, lithiation, reactivity

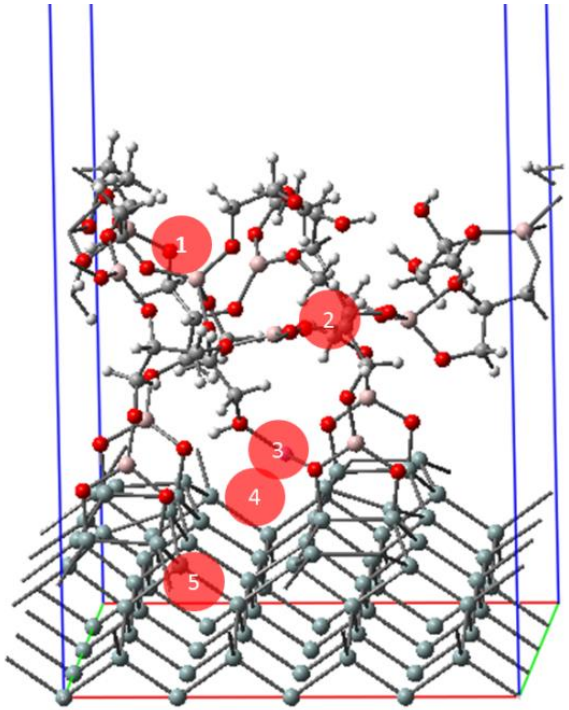
Film lithiation







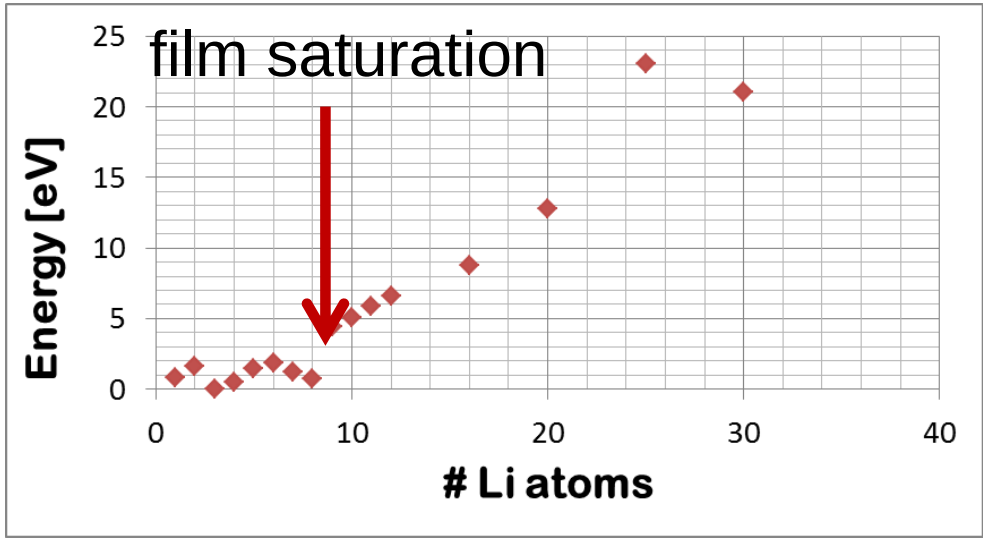
-2.63 eV; -3.15 eV; -3.3 eV

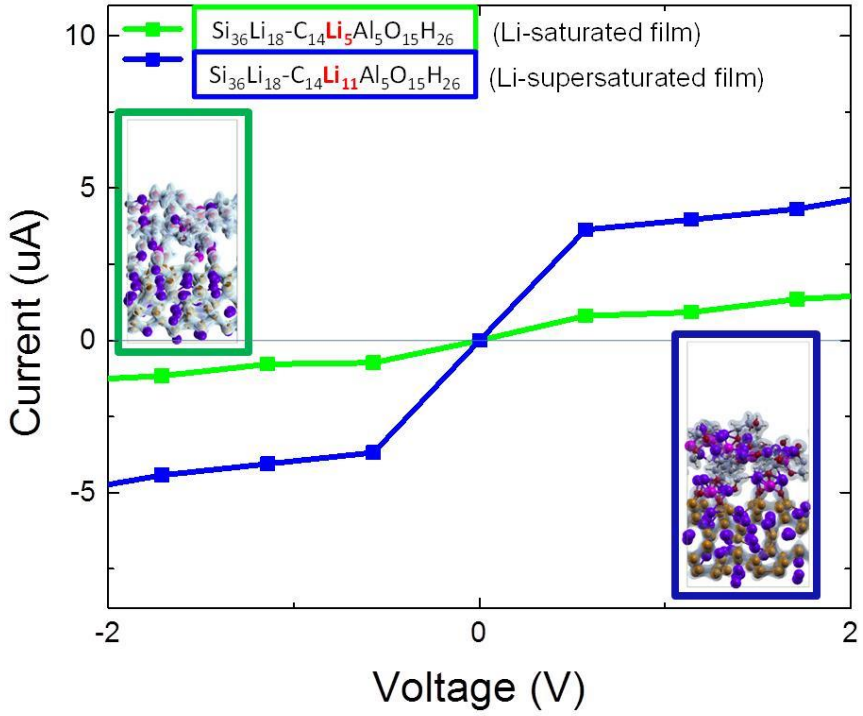


agreement with experiment: fast film lithiation

binding to the film stronger than to Si

Electronic conductivity in alucone film





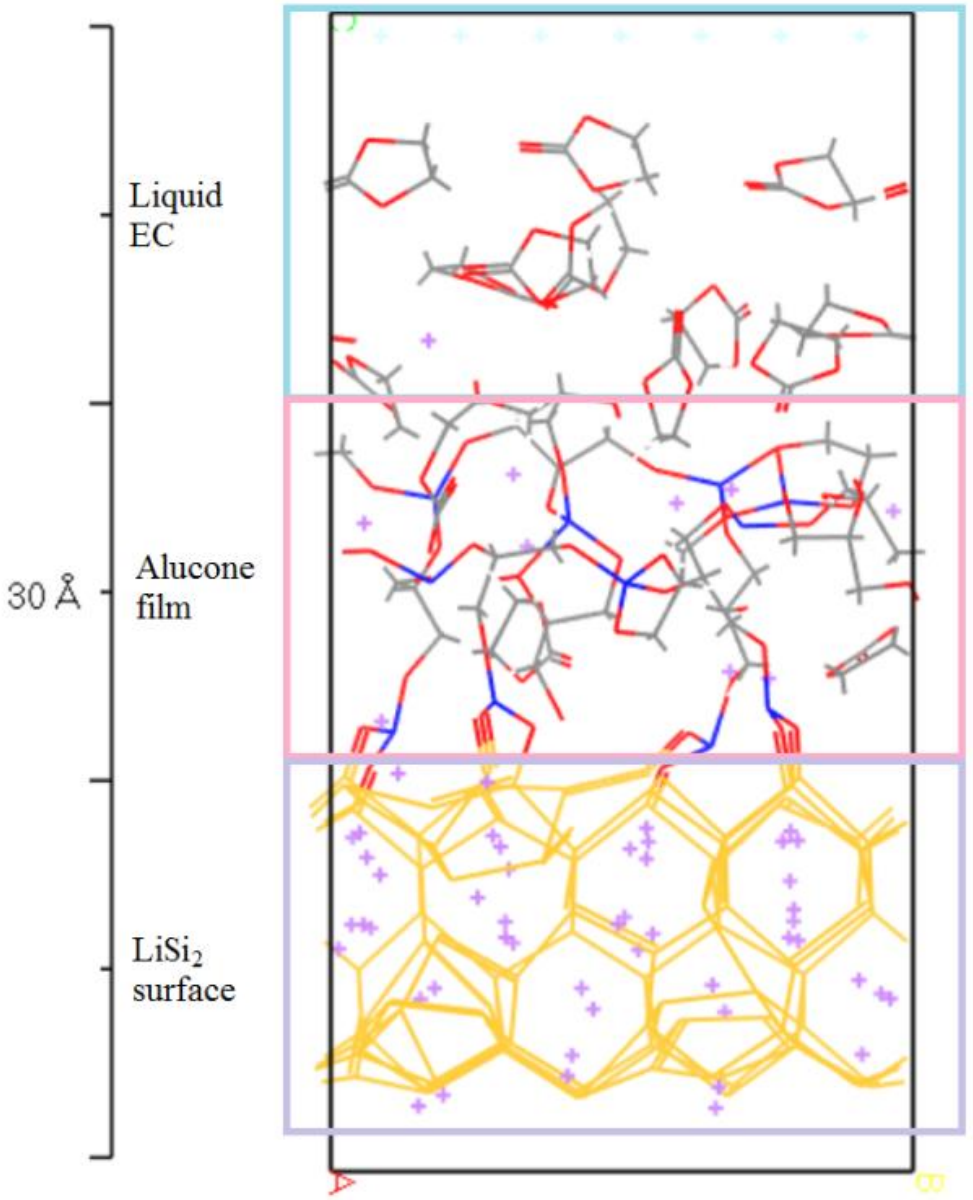
once the film is saturated with Li,
it becomes electronically conductive;
SEI reactions observed

Collaboration with C. Ban (NREL)

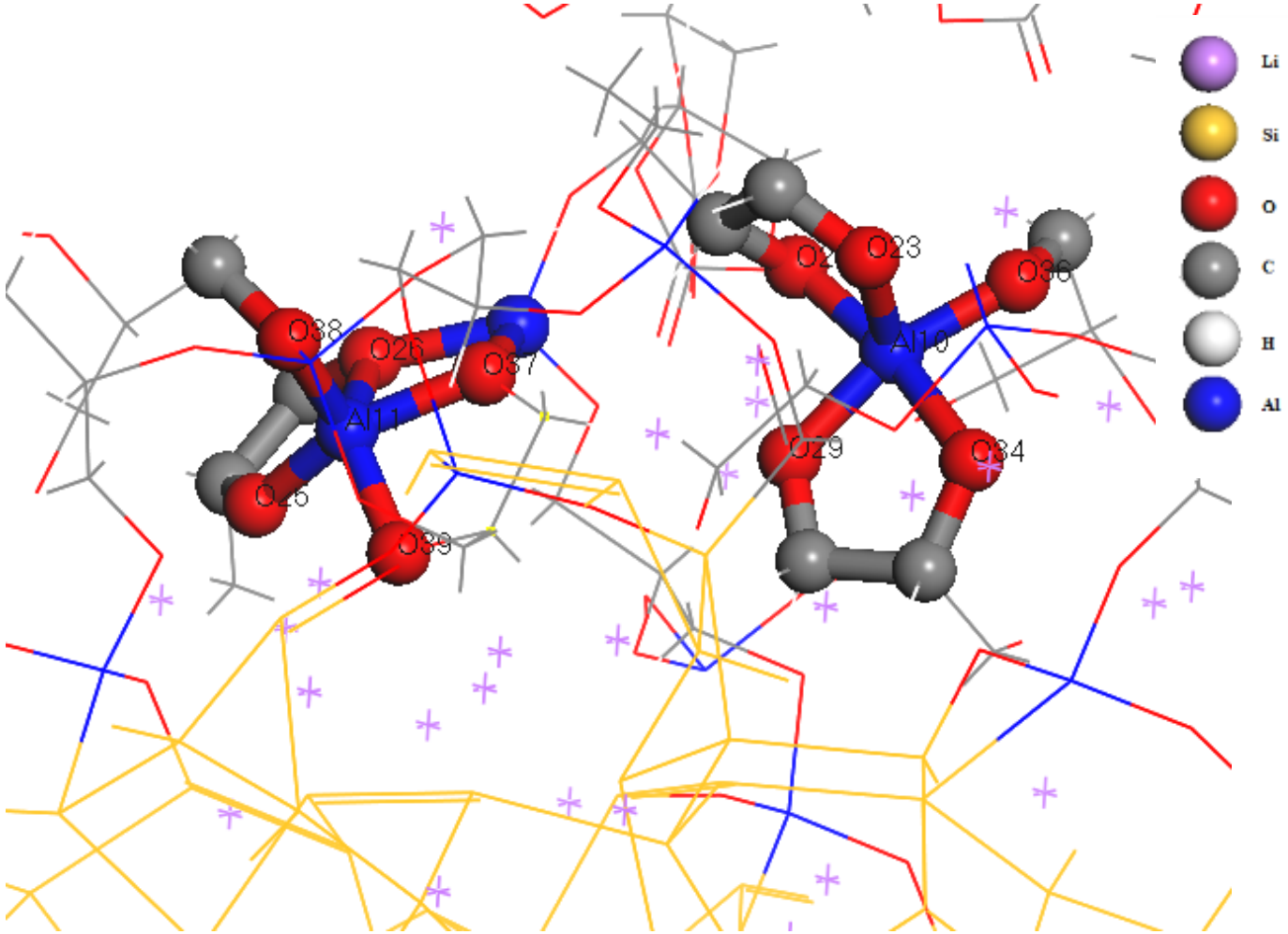
Balbuena, Seminario, C.H. Ban et al, ACS Appl. Mater. Inter., 7, 11948, (2015)

what type of SEI layer could be formed over alucone-covered Si?

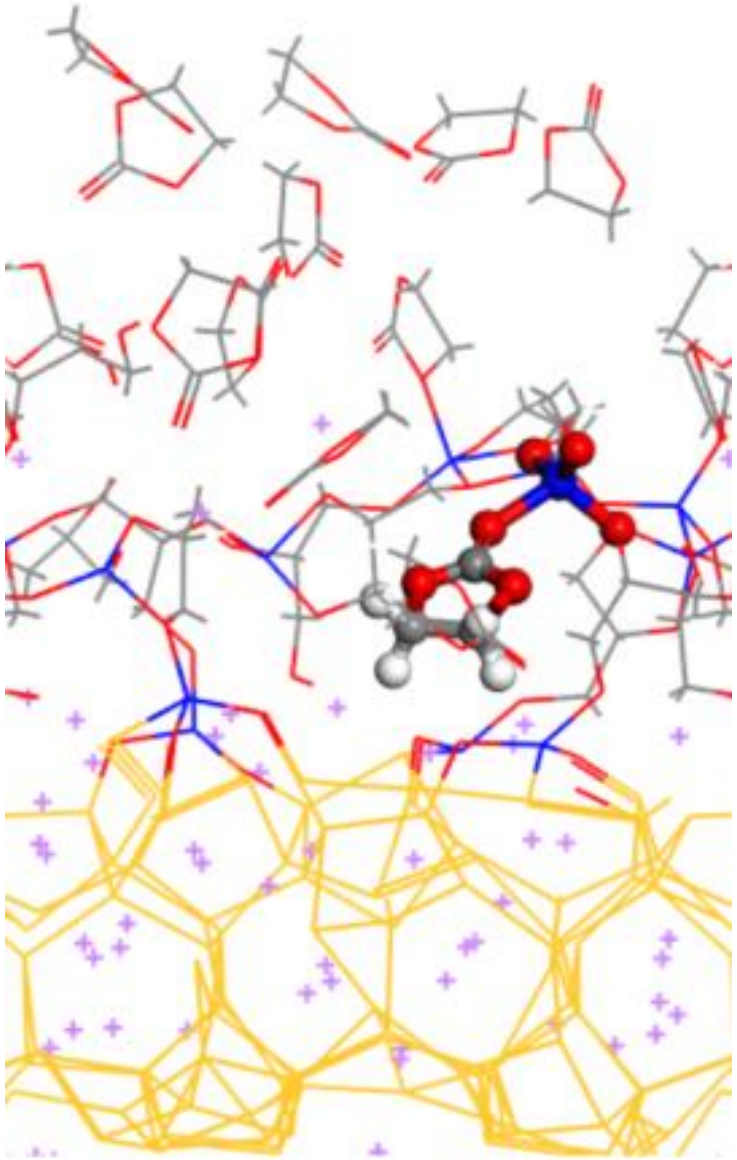
Simulation setting



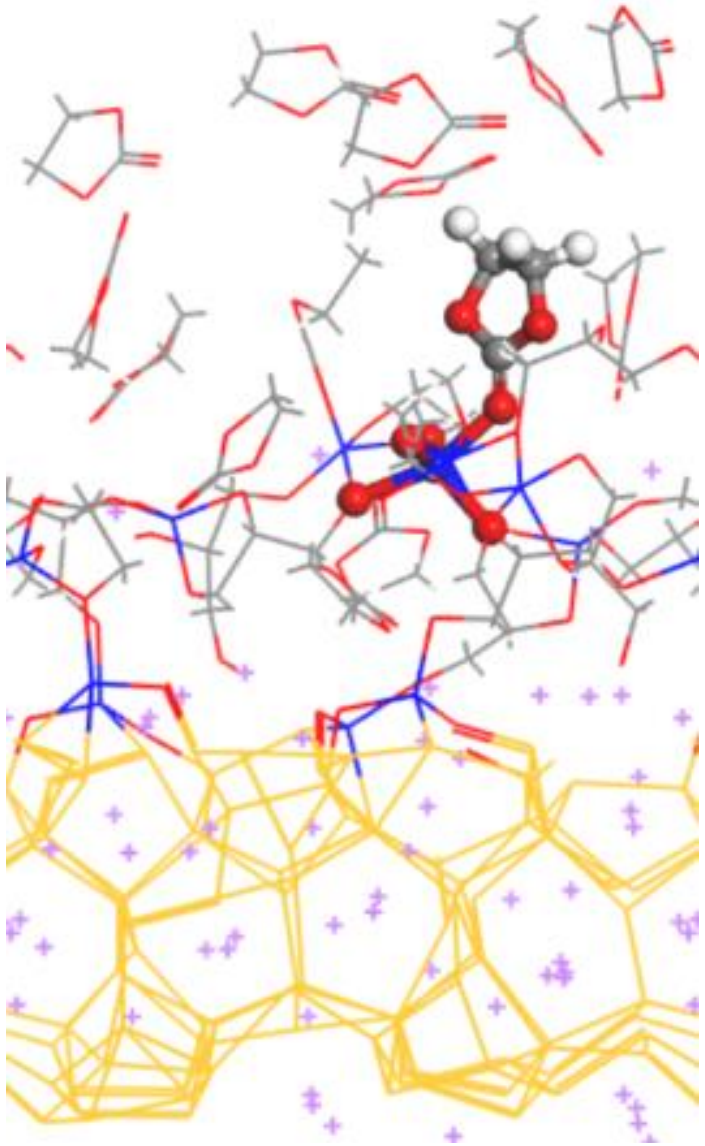
film restructuring; Al coord. # 5

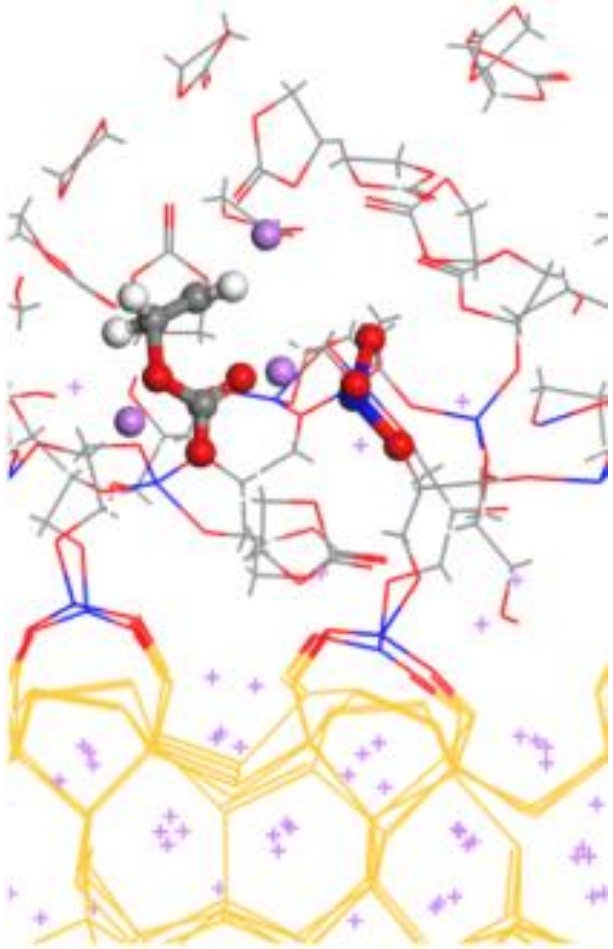


EC molecule bonding to AlOx groups



inside the film or at the interface





2 e^- reduction of EC at the alucone/electrolyte interface

Gomez-Ballesteros and Balbuena,
JPC Lett 2017

Artificial layer modified & covered by a natural SEI

-Solvent and its decomposition products able to penetrate the film

-The alucone film is modified because SEI decomposition products form complexes with AlOx groups inside the film or at the interfaces

-Reactions may take place at the film/electrolyte interface or at the anode/film interface

Li metal issues:

extremely high reactivity → uncontrolled electrodeposition and dendritic growth

Most strategies are based on:

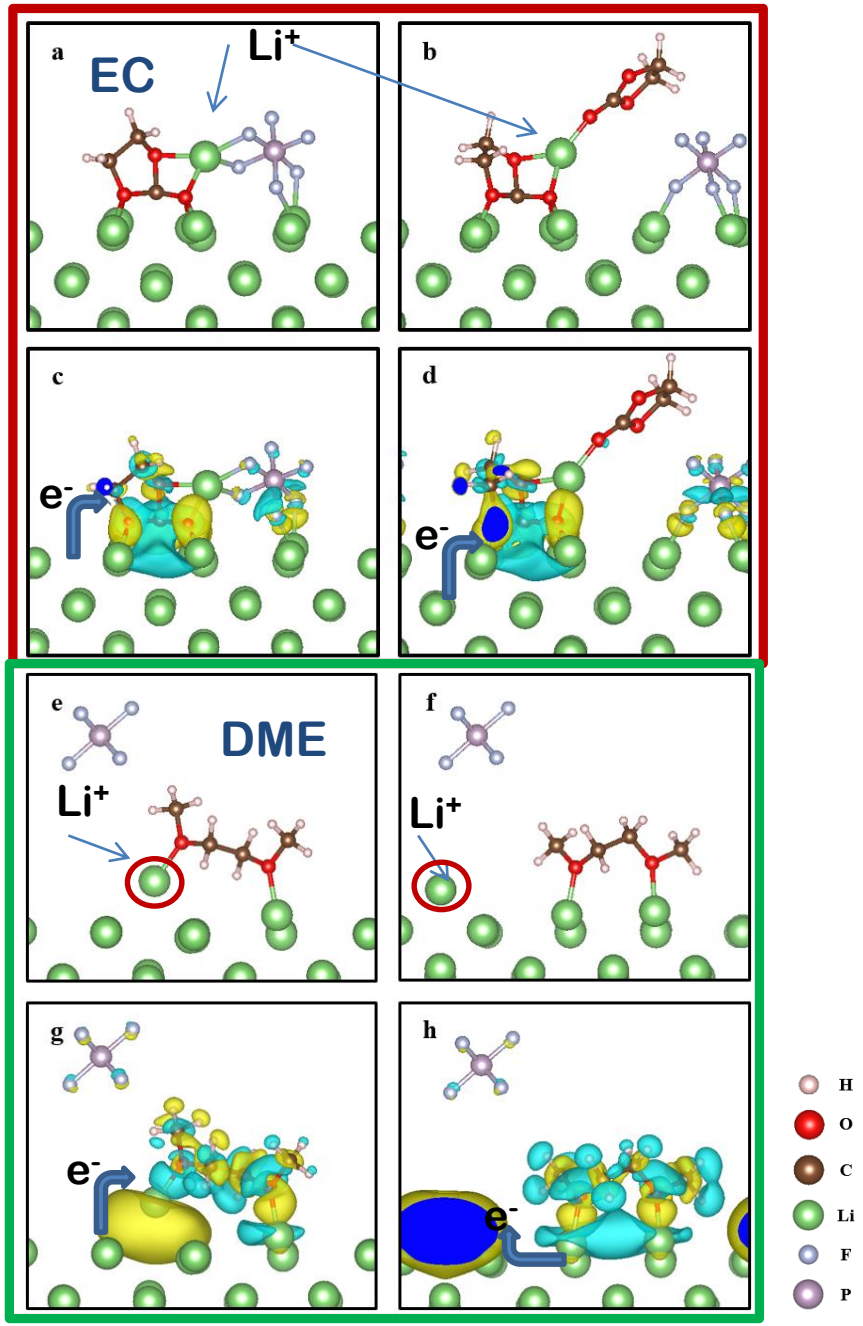
a) mechanically stopping or reducing the growing dendrite structure (solid electrolytes, coatings);

b) reducing the ionic current (high salt concentration)

It is crucial to understand,

- Is there a chemical origin of the dendrite growth?
- How does the surrounding environment modify the intrinsic Li reactivity?

Understanding charge transfer from the surface



Solvent + salt $Li^+ PF_6^-$) on Li-metal surface

large charge transfer from the surface to EC (-1.84 e) in presence of a Li ion; EC is reduced; Li^+ is not reduced (+0.87 e)

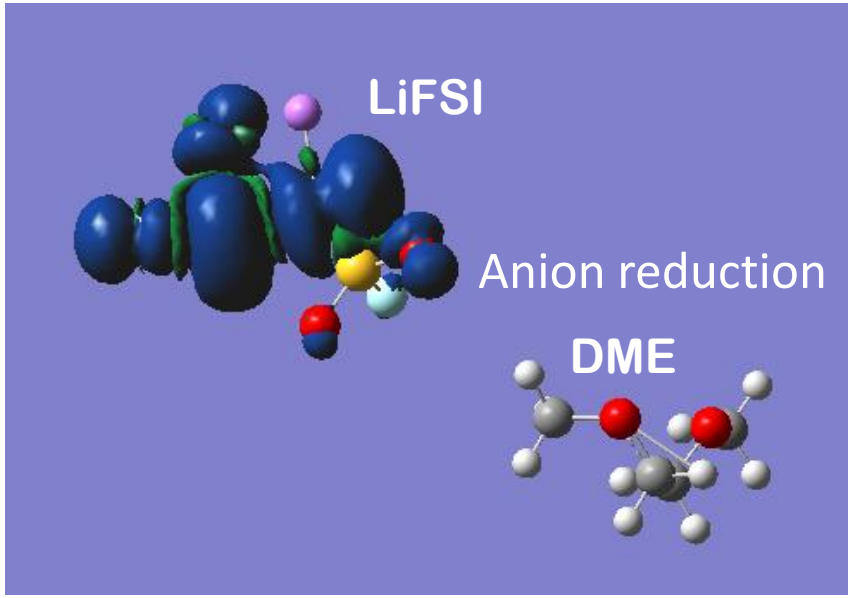
solvent electron affinities and solvation properties decide whether the solvent or the Li ion are reduced

small charge transfer from the surface to DME (-0.15 e) in presence of a Li ion; DME is not reduced; Li^+ is reduced; large electron accumulation on the surface

yellow: e- accumulation
blue: e- depletion

Qin, Shao, Balbuena
EC Acta 2018

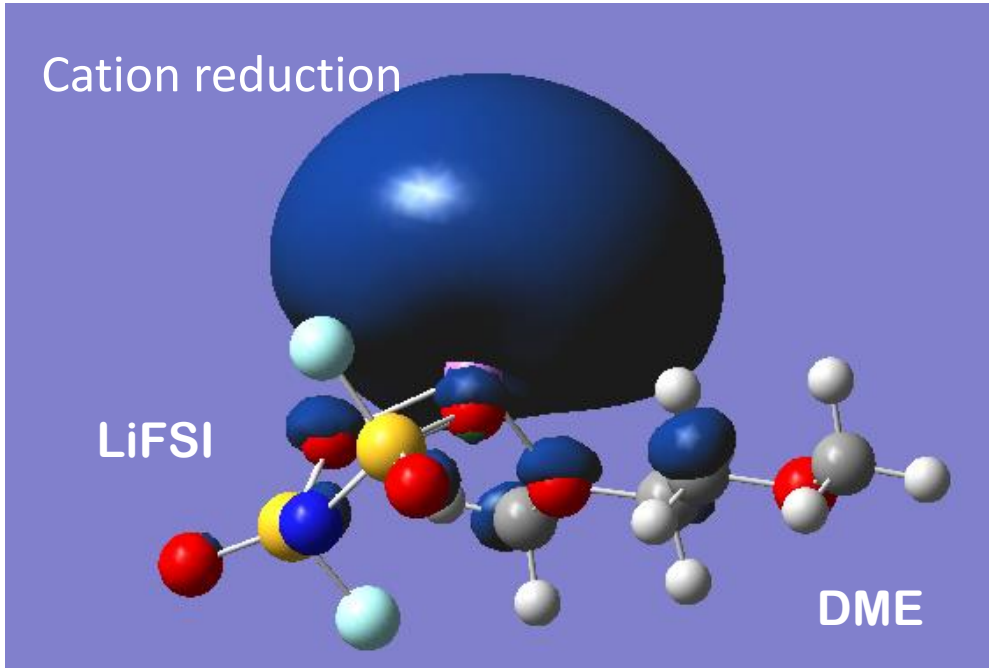
How do these structures reduce?



Weak interaction salt/DME;
Weak interaction anion-cation

DFT calculations of reduction potential salt + solvent complexes

Blue region shows localization of spin density



Strong interaction salt/DME

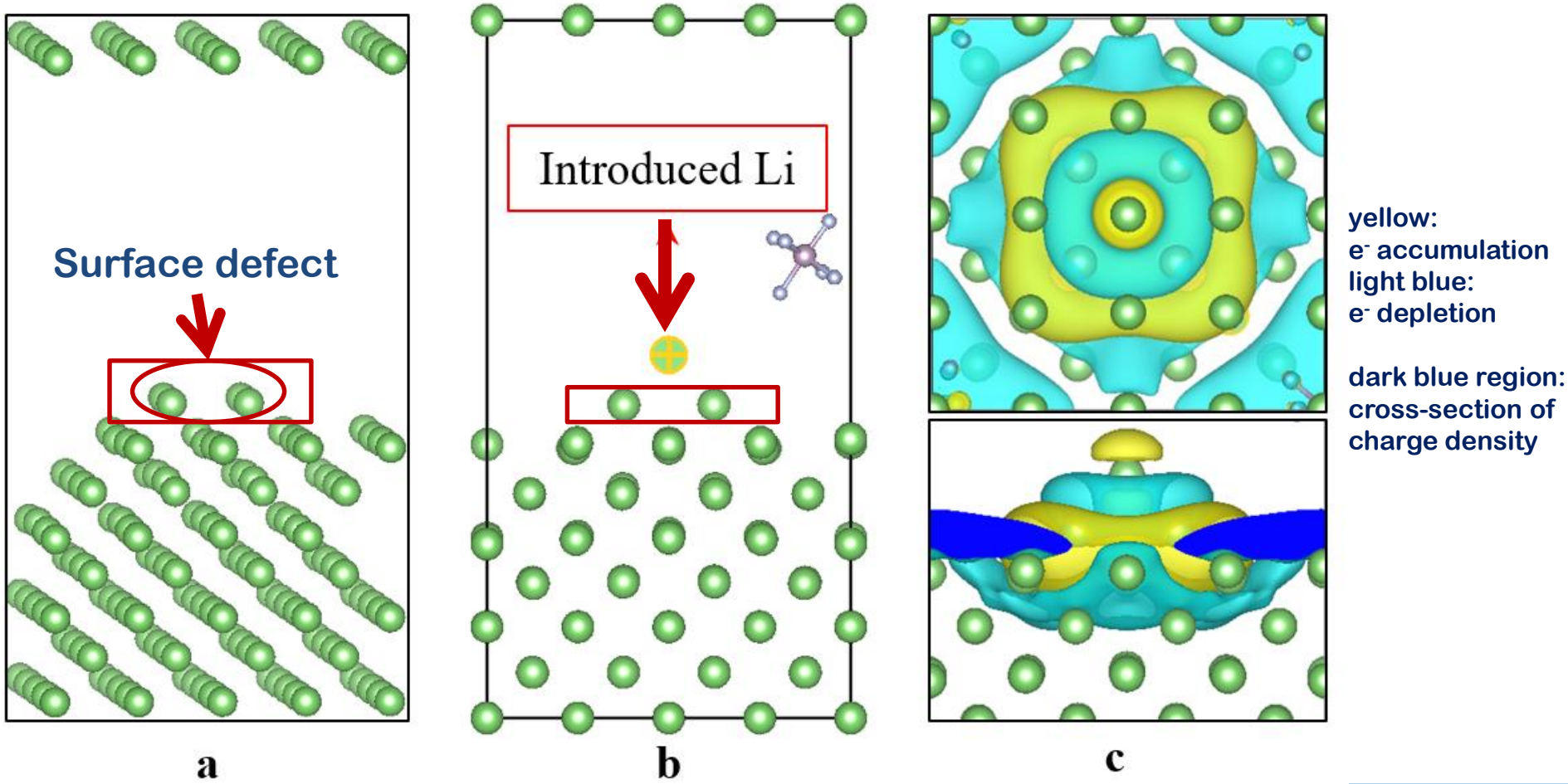
Effect of local environment dominates

Strong interaction anion-cation

Karoline Hight, Micah Dermott, Ethan Kamphaus, work in progress

Understanding Li plating: $Li^+ + e^- \rightarrow Li^0$

Li^+ reduced over a defect



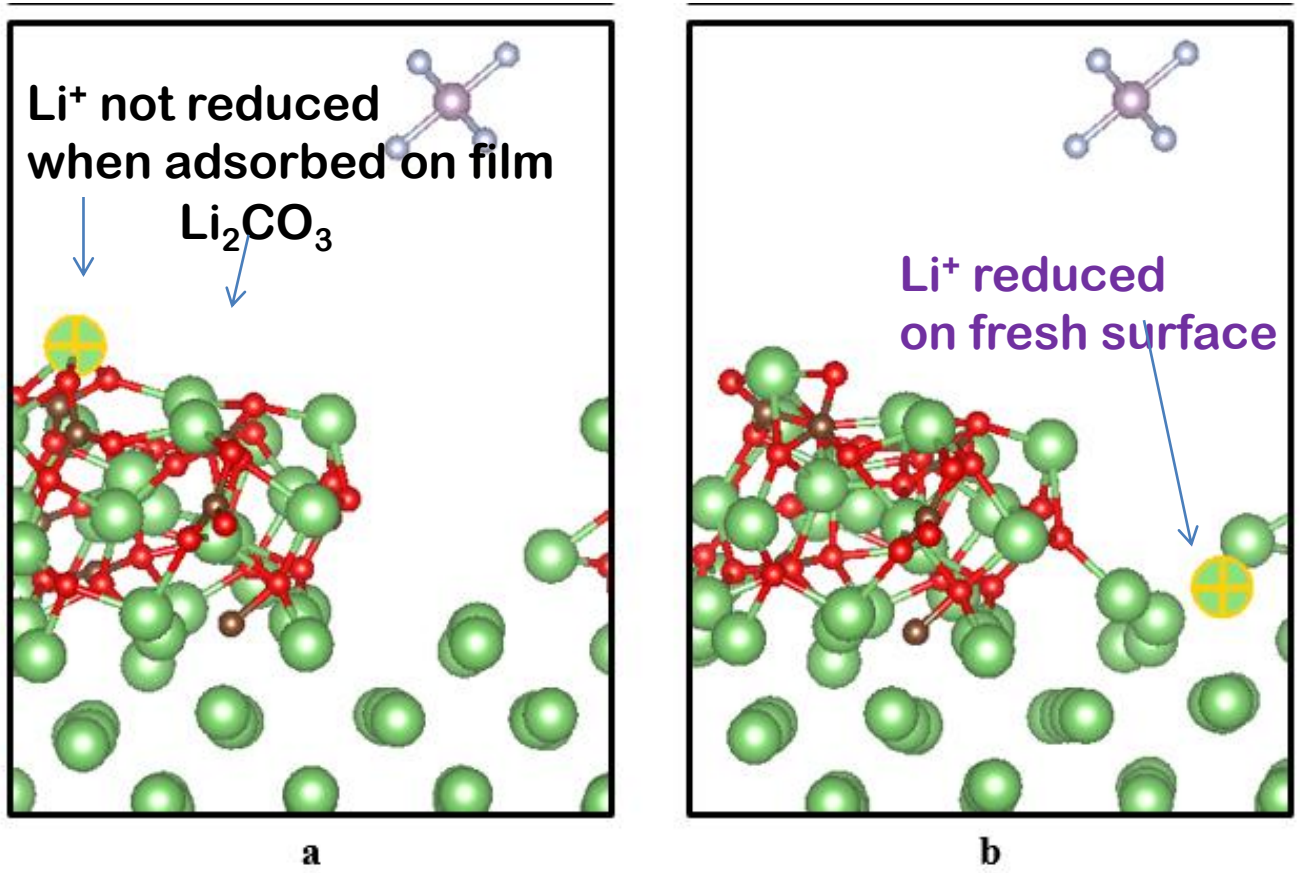
yellow:
e^- accumulation
light blue:
e^- depletion

dark blue region:
cross-section of
charge density

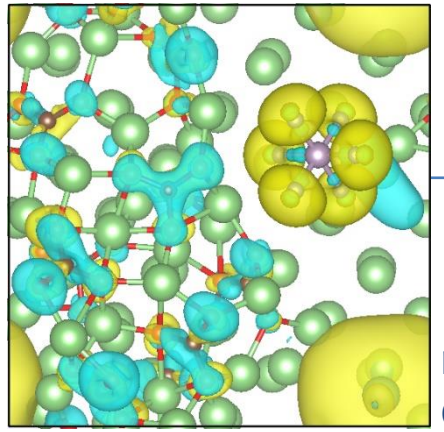
Li^+ is reduced; large electron accumulation region near reduced Li:
It may attract and reduce further Li cations (needle growth) and electrolyte (SEI)

Understanding Li plating

Li_2CO_3 partially covered surface



top view showing
e accumulation (yellow)



X. Qin, M. Zhao, and P. B. Balbuena, EC Acta,2018

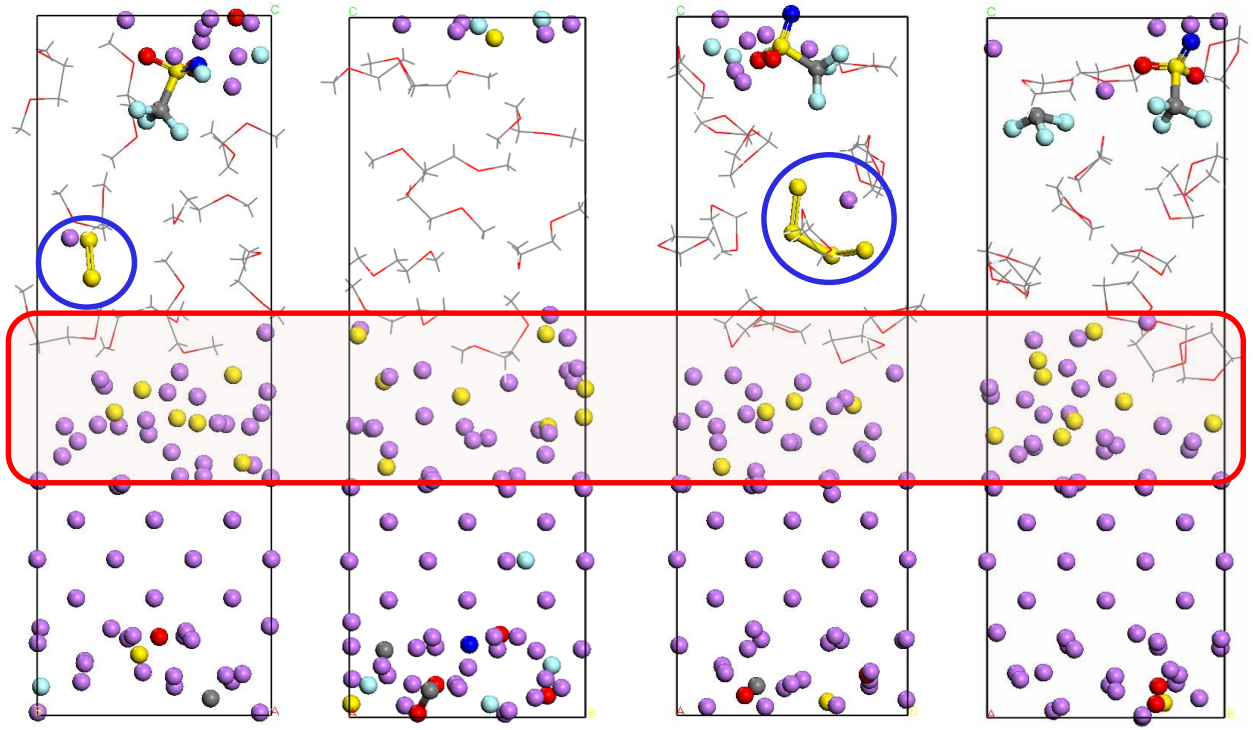
Li deposition generates an uneven distribution of charges
near the reduction site; such large e^- accumulation can attract more Li cations
→ favoring further plating on localized regions instead of smooth deposition

(i) Stability of Electrolyte Components

Solvent: DME and DOL

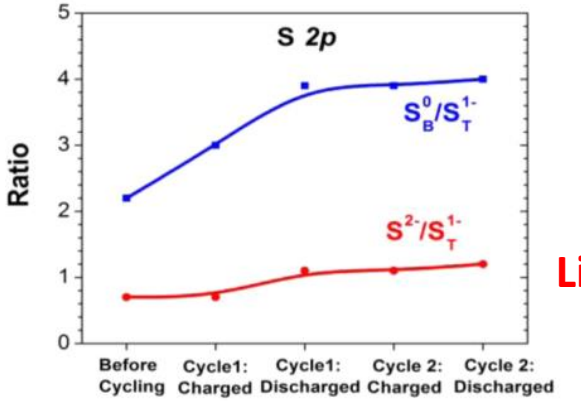
AIMD @ 20 ps

Polysulfides?



PS highly reactive on Li-anode
Initial stage of Li_2S formation

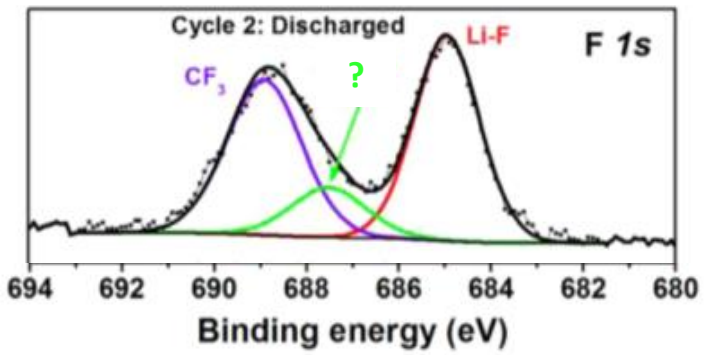
In Situ XPS (PNNL)



Li_2S

Luis Camacho-Forero

Information from simulations critical to decipher XPS spectra



Bonding pattern including the F atom	Average charge on the F atom, |e|
F-Li-S	-0.95
F-Li-C	-0.92
F-Li-O	-0.92
F-Li-F	-0.93
F-Li-N	-0.97
F-C-S	-0.61
F-C	-0.67

CF_x

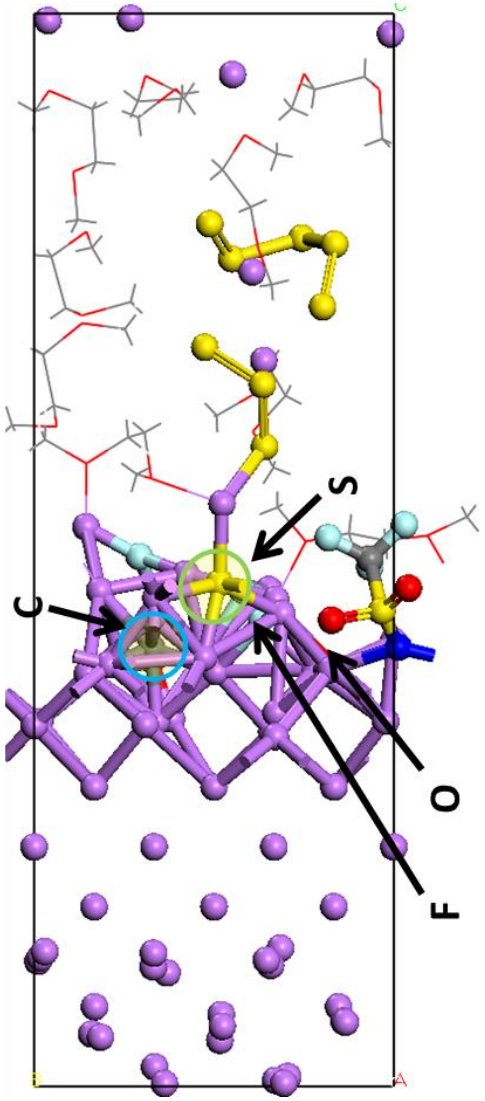
F-X

JPCC, **2015**, 119 (48), 26828–26839; ACS Appl. Mater. Interf. **2016**, 8, (7), 4700-4708,

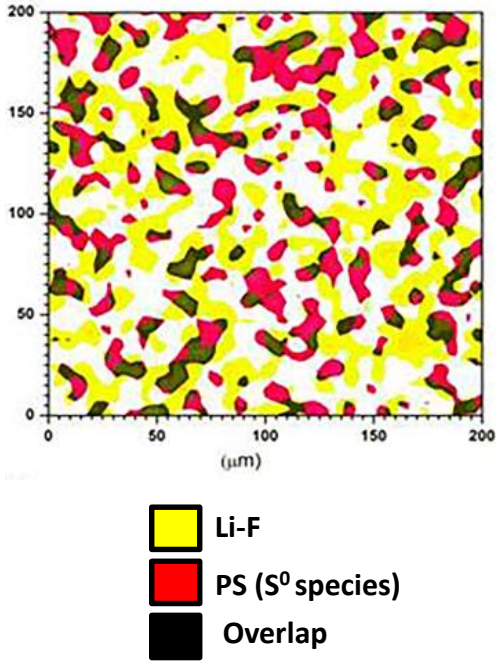
(i) Stability of Electrolyte Components

Solvent: DME and DOL

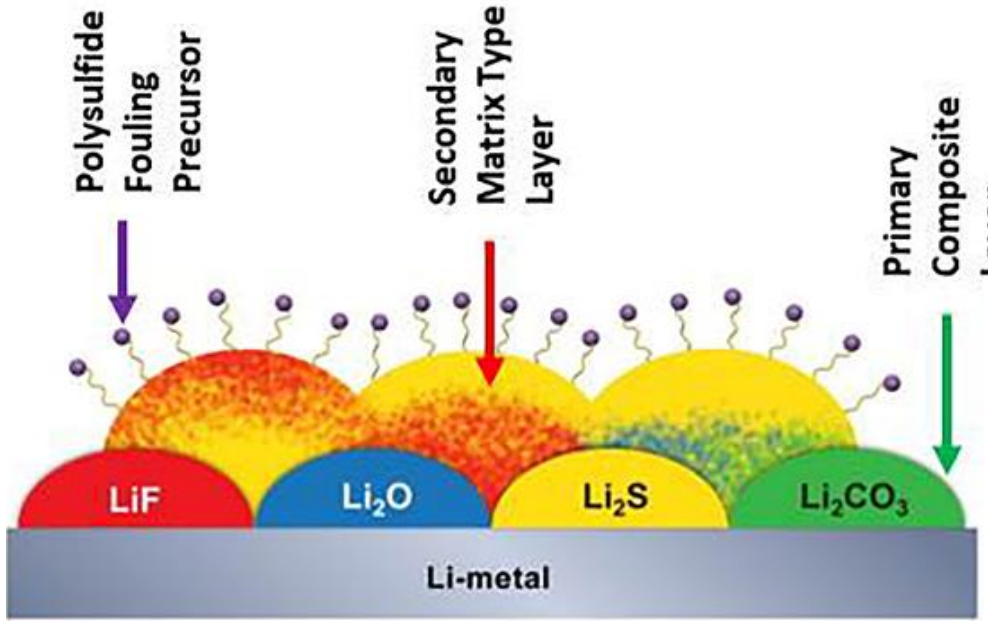
AIMD and *In Situ* XPS Imaging



+



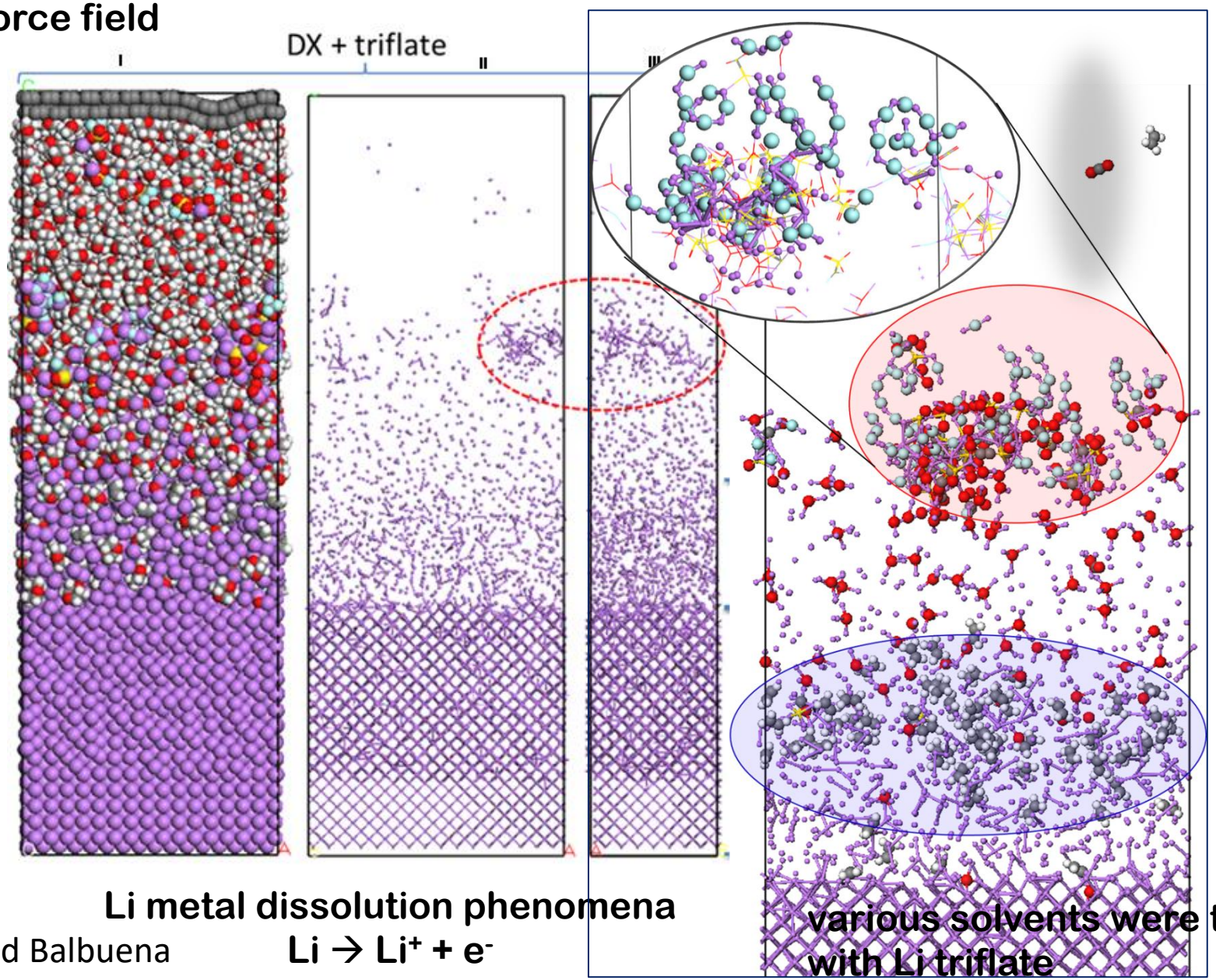
SEI Layer Growth

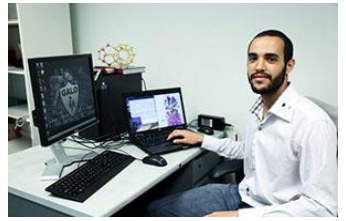


Important point:
presence of SEI blocks that are
not mono-components
but multi-components

Li dissolution in contact with electrolyte

Classical MD;
Reactive force field





Samuel Bertolini

← **Li oxidized**

Nucleation of SEI products observed

←**Li neutral**

Li metal dissolution phenomena

$Li \rightarrow Li^+ + e^-$

various solvents were tested with Li triflate

Bertolini and Balbuena
JPCC 2018

Basis of the AIMD/ESM method

Otani and Sugino, PRB 73, 115407 (2006)

Total energy functional

$$E[\rho] = T[\rho] + E_{\mathrm{xc}}[\rho] + \frac{1}{2}\iint d\boldsymbol{r}d\boldsymbol{r}'\frac{\rho(\boldsymbol{r})\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} + \int d\boldsymbol{r}v_{\mathrm{ext}}(\boldsymbol{r})\rho(\boldsymbol{r}) + E_{\mathrm{ion}}$$

V ➠ variable

$$E[\rho_{\mathrm{e}}, V] = T[\rho_{\mathrm{e}}] + E_{\mathrm{xc}}[\rho_{\mathrm{e}}] + \int d\boldsymbol{r}\left[+\frac{\epsilon(\boldsymbol{r})}{8\pi}|\nabla V(\boldsymbol{r})|^2 + \rho_{\mathrm{tot}}(\boldsymbol{r})V(\boldsymbol{r})\right]$$

$\frac{\delta E}{\delta V} = 0$ → Poisson equation

$$\nabla[\epsilon(\boldsymbol{r})\nabla]V(\boldsymbol{r}) = -4\pi\rho_{\mathrm{tot}}(\boldsymbol{r})$$

conventional

$$\epsilon(\boldsymbol{r}) = 1$$

$$V(\boldsymbol{r}) = \int \mathrm{d}\boldsymbol{r}\frac{\rho_{\mathrm{tot}}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}$$

ESM

$\epsilon(\boldsymbol{r})$: model dependent

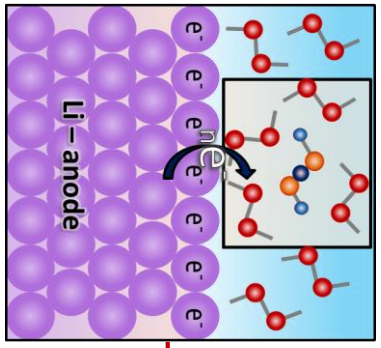
$$V(\boldsymbol{r}) = \int \mathrm{d}\boldsymbol{r}G(\boldsymbol{r},\boldsymbol{r}')\rho_{\mathrm{tot}}(\boldsymbol{r}')$$

$\frac{\delta E}{\delta \rho_{\mathrm{e}}} = 0$ → Kohn-Sham equation

$$\left[-\frac{1}{2}\nabla^2 + V(\boldsymbol{r}) + \hat{V}_{\mathrm{NL}} + V_{\mathrm{xc}}(\boldsymbol{r})\right]\psi_i(\boldsymbol{r}) = \varepsilon_i\psi_i(\boldsymbol{r})$$

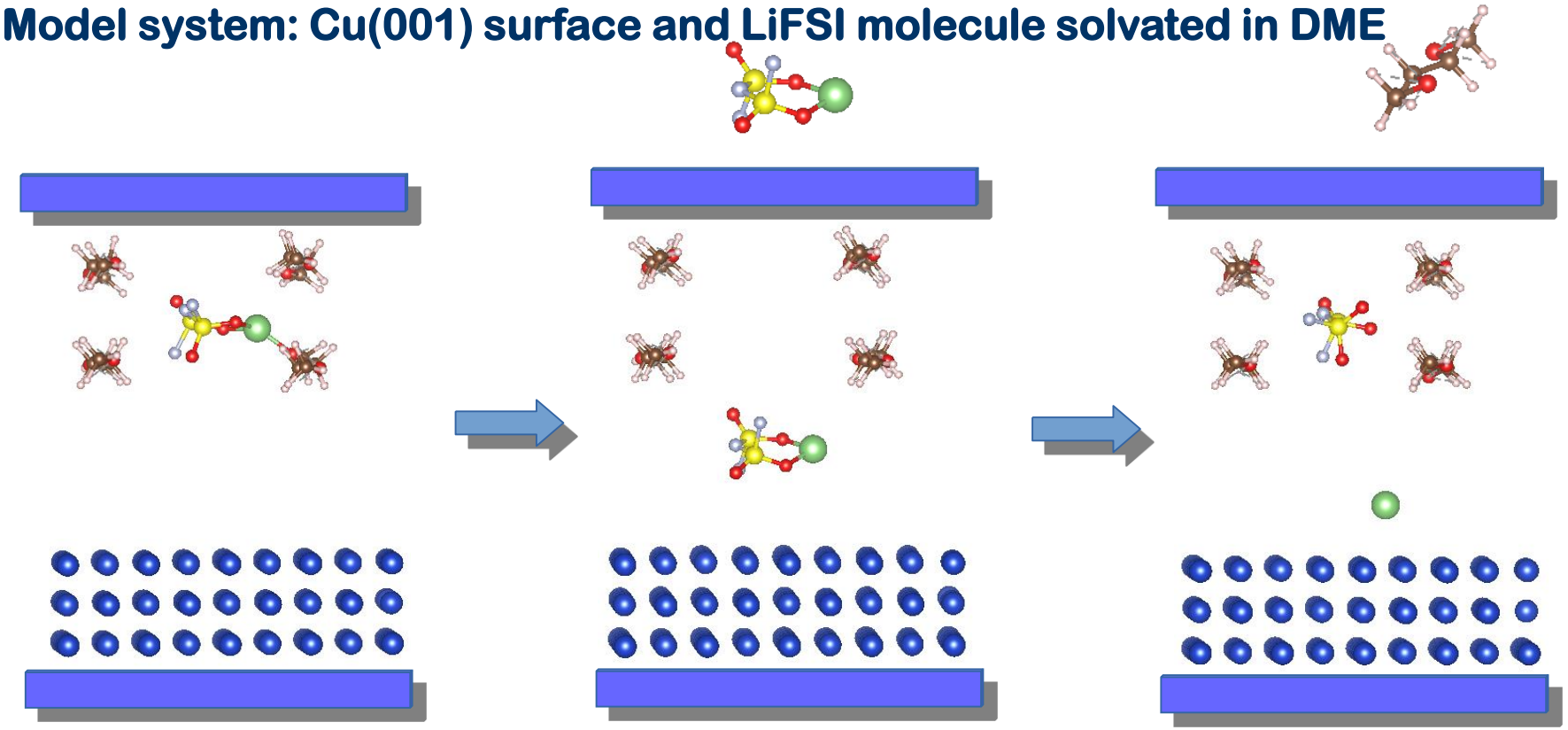
Uses open boundary conditions in the direction perpendicular to the slab to avoid discontinuities of the electric field. V(r) is solved analytically from Poisson equation and is used in the Kohn Sham formalism of DFT

Electrode/electrolyte interface


Li – anode
e⁻
e⁻
e⁻

Effective screening medium method

Model system: Cu(001) surface and LiFSI molecule solvated in DME

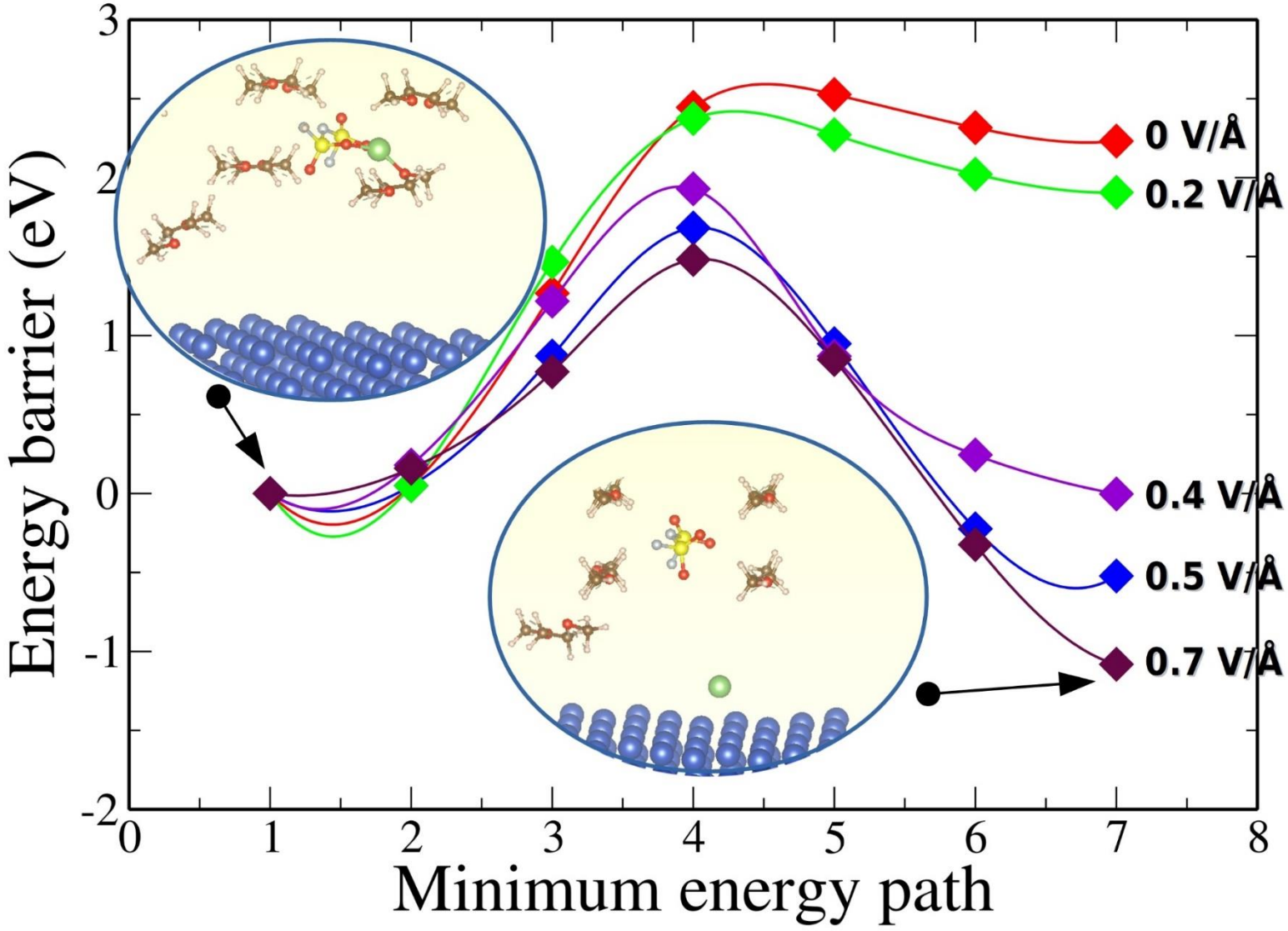


i) At E=0 V/Å, the deposition of a Li adatom is a highly endothermic process, ΔE=2.23 eV

ii) In the presence of E, the surface is polarized. Can this trend be reverted? Is it a kinetically viable process?

Effects of applied potential

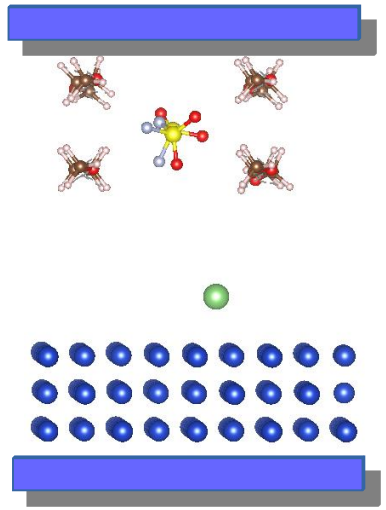
At E=0.4 V/Å, Li^+ deposition becomes exothermic, with a LiFSI dissociation energy barrier of 1.92 eV

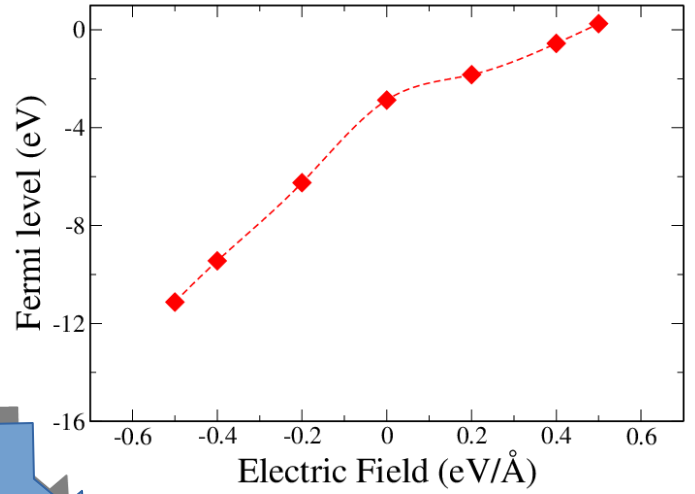


Longo, Camacho, Balbuena, J. Mater. Chem. A, 2019

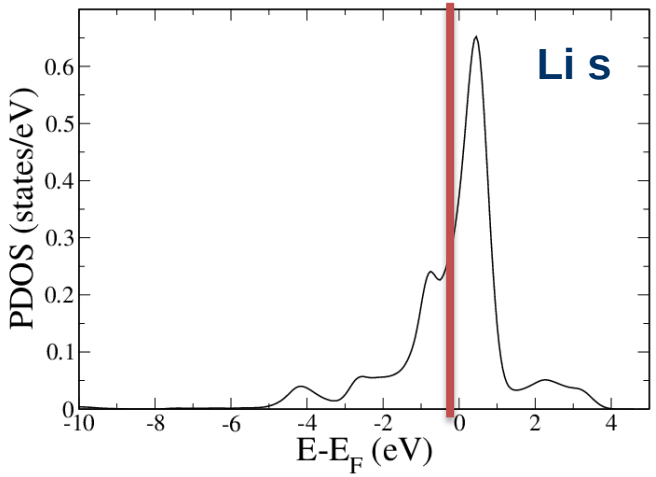
Effective screening medium method

Even though Cu is a noble metal, the EF polarizes the surface, increasing the "capacity" of the Li ion to be reduced, i.e., the Fermi level "shifts" to the right

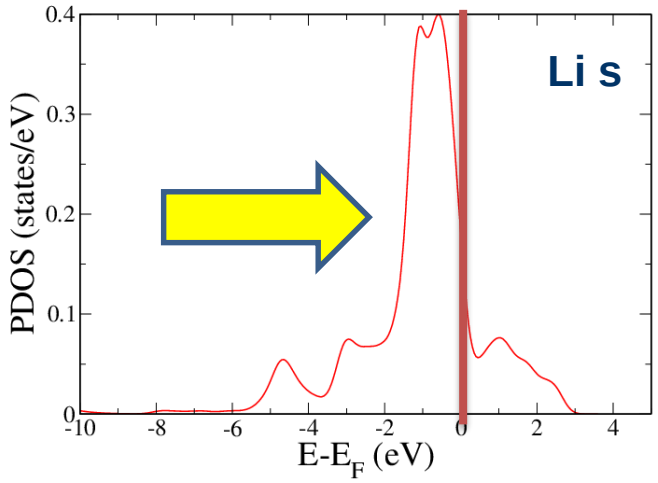




E=0 eV/Å

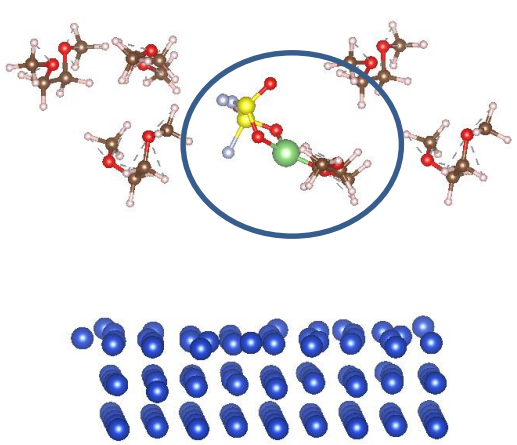


E=0.5 V/Å

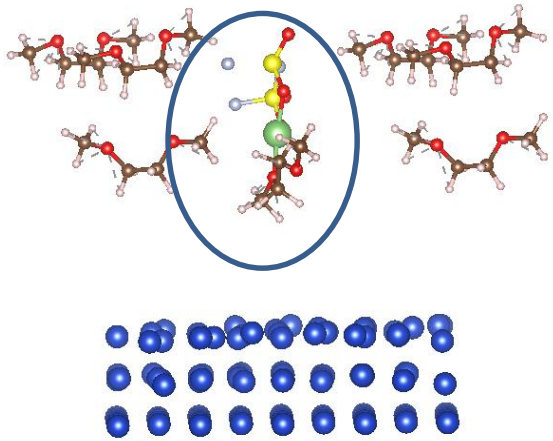


Effective screening medium method

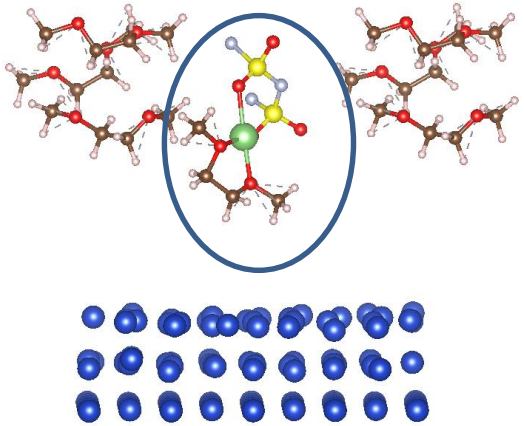
MD modeling of the Li deposition process, for E=0.5 V/Å (electrodes not shown)



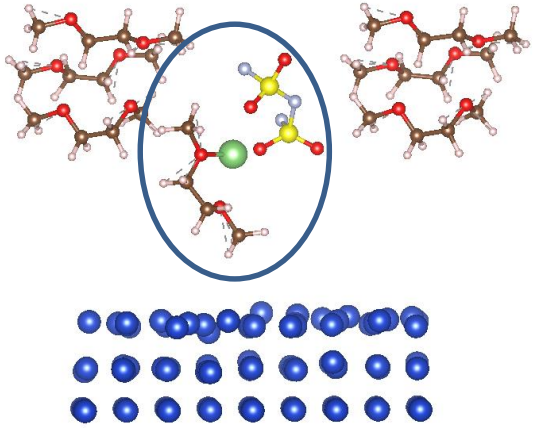
t=0.5 ps



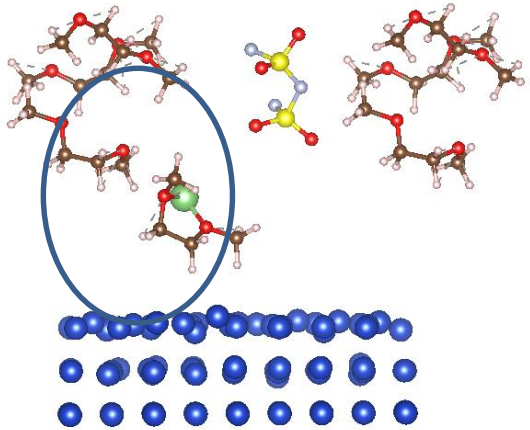
t=2 ps



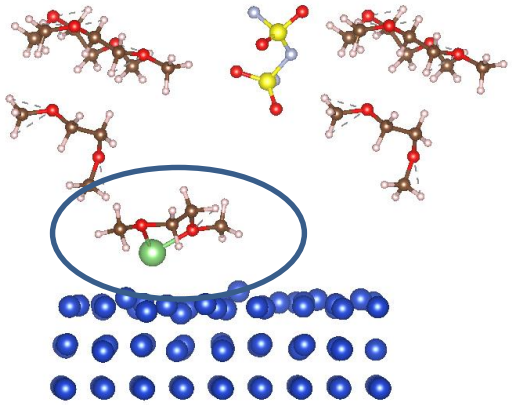
t=4 ps



t=5.2 ps



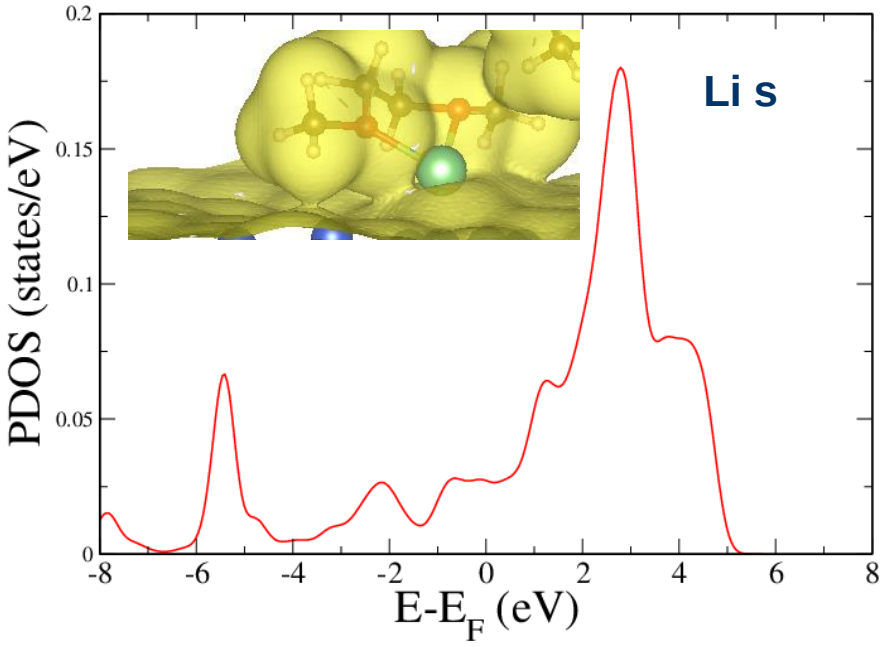
t=6 ps



t=7.5 ps

Effective screening medium method

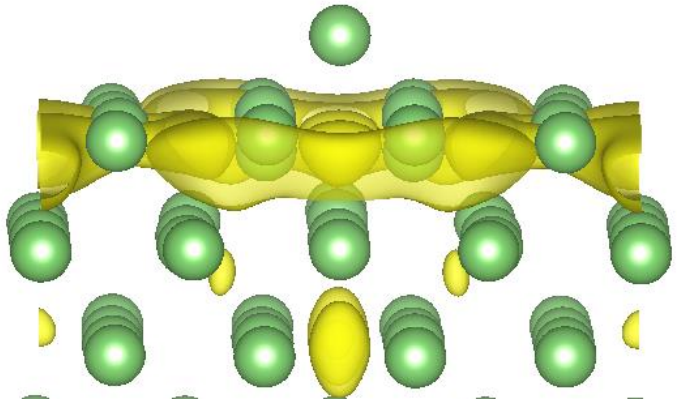
After 7.5 ps of MD, a Li-DME composite adsorbed on Cu(001) is obtained:



i) The Li ion is only partially reduced: Δq=0.37e$^-$

ii) Cu is noble metal. As such, it is very resistant towards corrosion and oxidation

Iii) Other substrates, like Li itself, would accelerate the reduction of the Li ion, at the cost of surface stability.



Li(001) surface polarization orbitals created by a E=0.5 V/Å. These orbitals do not exist for Cu(001).

Conclusions

- Interfaces are very complex
- First principles methods help in the understanding of the complexity
- Understanding the physics and chemistry of the problem essential to decide on the computational model

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