NEES: Interfaces, Modeling, Synergistic Experiments, and Electrochemistry

SAND2015-9043C

Kevin Leung, Sandia National Laboratories

NEES PI coauthors (alph.): C.T. Harris, Katherine Jungjohann, Sang Bok Lee, Andrew Leenheer, Malachi Noked, Yue Qi, Janice Reutt-Robey, Gary Rubloff, YuHuang Wang, Kevin Zavadil.

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NEES II NANOSTRUCTURES *for* ELECTRICAL ENERGY STORAGE

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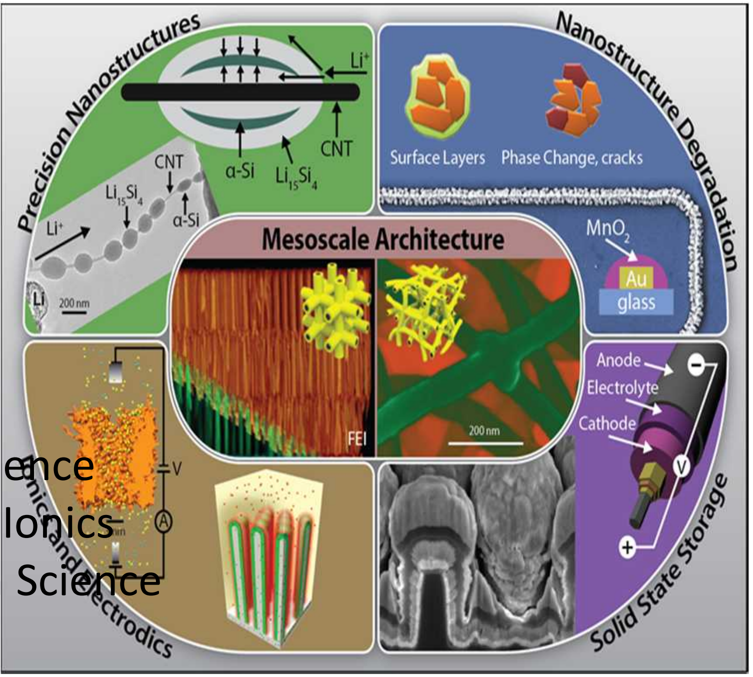
U.S. DEPARTMENT OF ENERGY

Nanostructures for Electrical Energy Storage
A DOE Energy Frontier Research Center



NEES major research areas

☐ Nanostructure Interface Science
☐ Mesoscale Architectures & Ionics
☐ Nanostructure Degradation Science
☐ Solid State Energy Storage

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NEES NANOSTRUCTURES for ELECTRICAL ENERGY STORAGE

TEM postdoctorial position available with Katherine Jung (SNL)

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CALL FOR PAPERS

Abstract Deadline: October 15, 2015

REMINDER: In fairness to all potential authors, late abstracts will not be accepted.

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Symposium EE6: Research Frontiers on Liquid-Solid Interfaces in Electrochemical Energy Storage and Conversion Systems

In batteries, fuel cells, water splitting/oxygen reduction, and other electrochemical energy storage and conversion systems, effectiveness and stability of the solid-liquid interface is directly correlated to the performance and lifetime of an electrochemical device. A mechanistic understanding of the interfacial reactions and processes occurring at the solid and liquid interface is needed to provide the scientific underpinning for the design of next-generation electrochemical energy storage and conversion devices. This requires technique development for characterization of local structures and non-equilibrium dynamics at interfaces at high spatial resolution (down to *nm* scale), time resolution (millisecond or lower) and high chemical sensitivity (spanning from light element H, Li, O to heavy metals). Moreover, the direct comparison of experimental results with modeling of the interfacial chemistry under realistic conditions is a key to the basic understanding of complex interfaces.

The goal of this symposium is to create a forum for fundamental understanding about the charge transfer, ionic transport and heterogeneous reactions at these interfaces and the effect of nano-scale, crystal orientations and other various factors on these phenomena. Similarities and differences between batteries, fuel cells, and other electrochemical systems will be highlighted. Abstracts are particularly encouraged on the development of new sample environment and model electrodes of defined orientations and surface structures that allow the imaging of fundamental phenomena and processes occurring at liquid/solid interfaces *in operando* and permit direct correlation with atomistic modeling.

Topics will include:

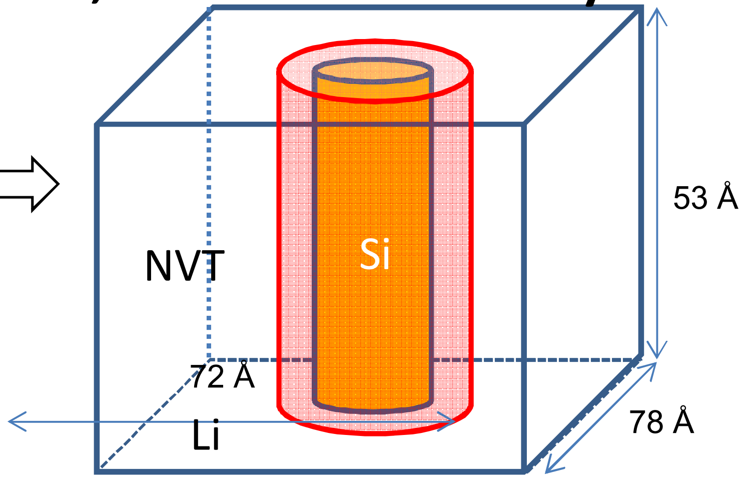
- *In-situ/operando* and other advanced characterization techniques for probing liquid-solid interfaces with high spatial, time resolution and/or chemical sensitivity
- New computational techniques for modeling liquid-solid interfaces
- Fundamental investigation of electrode/electrolyte interfaces in batteries, fuel cells and other electrochemical systems
- Discovery and control of interfacial phenomena, such as ion (de) solvation, transport across liquid-solid interfaces/interphases, and electrodeposition in batteries and other electrochemical systems
- New design of organic/inorganic electrolytes, ionic liquids and liquid-solid interfaces for batteries, fuel cells and other electrochemical systems

Joint sessions are being considered with EE5 - **Next-Generation Electrical Energy Storage Chemistries**.

NEES2 focus: (nano)structures, mechanisms, smart interfaces, degradation, ionics, solid electrolyte

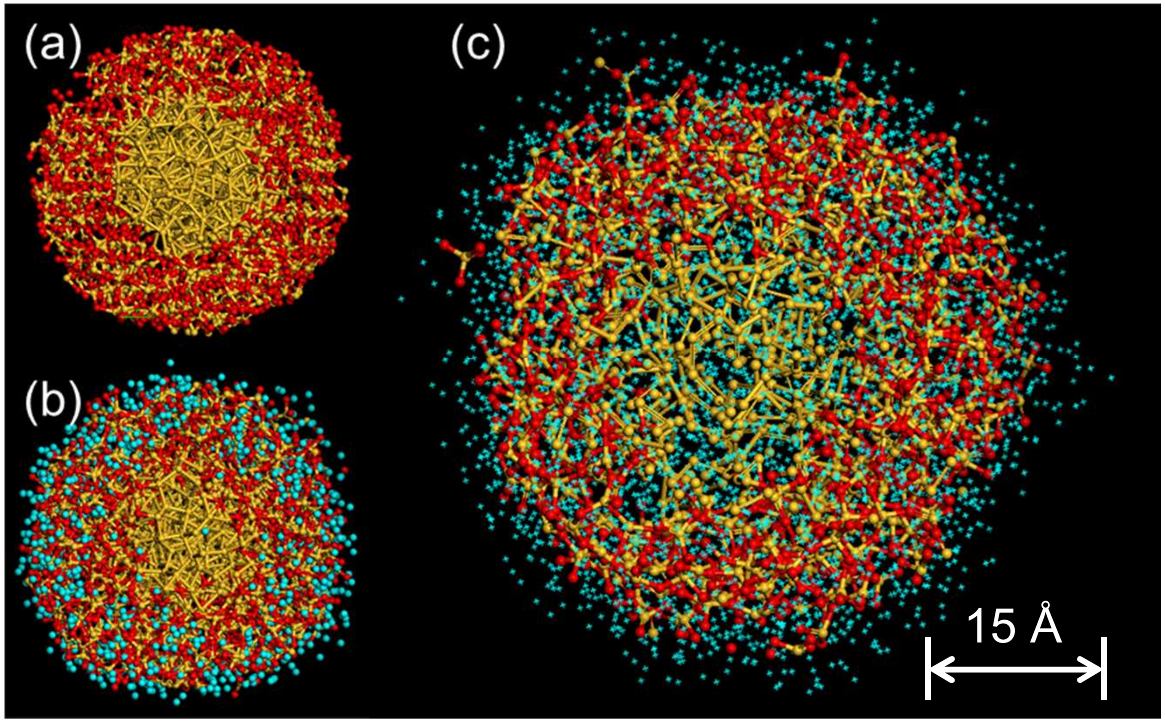
DFT computed
Formation Energies
Diffusion Barriers
Equation of states

ReaxFF
Parameterized
for Li-O-Si-Al



Oxide coating can be lithiated and change its transport and mechanical properties (Kim and Qi, JES 2014)

Lithiation of SiO_2 and Al_2O_3 covered Si nanowires



Compare different shell thickness
2.5 Å
4.5 Å
7.5 Å

Nanostructures

A Beaded-String Silicon Anode

Chuan-Fu Sun,[†,#] Khim Karki,[‡,#] Zheng Jia,[§,#] Hongwei Liao,[†] Yin Zhang,[†,⊥] Teng Li,[§,*] Yue Qi,[¶,*]
John Cumings,[‡,*] Gary W. Rubloff,[‡] and YuHuang Wang[†,*]

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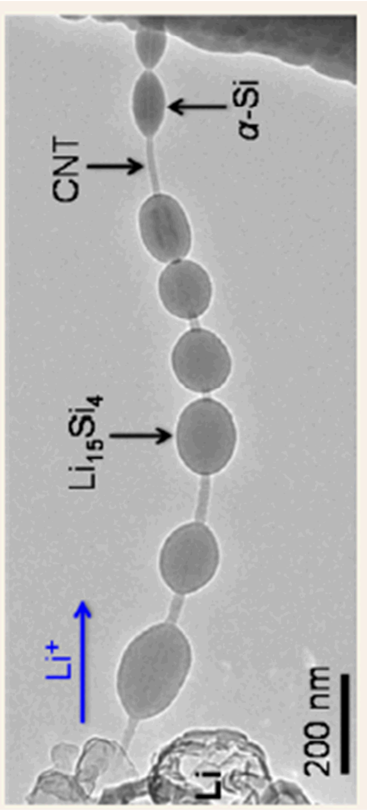
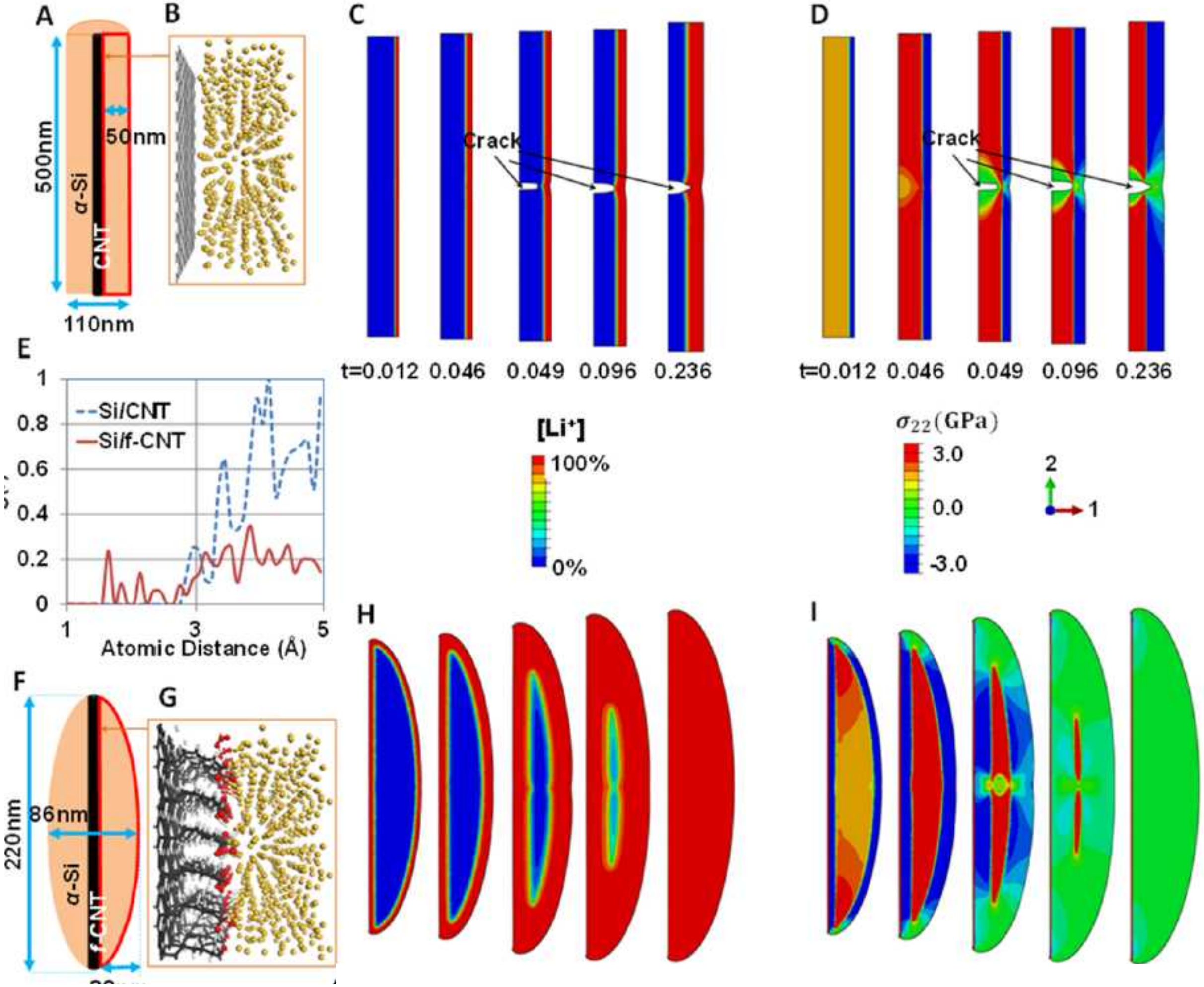
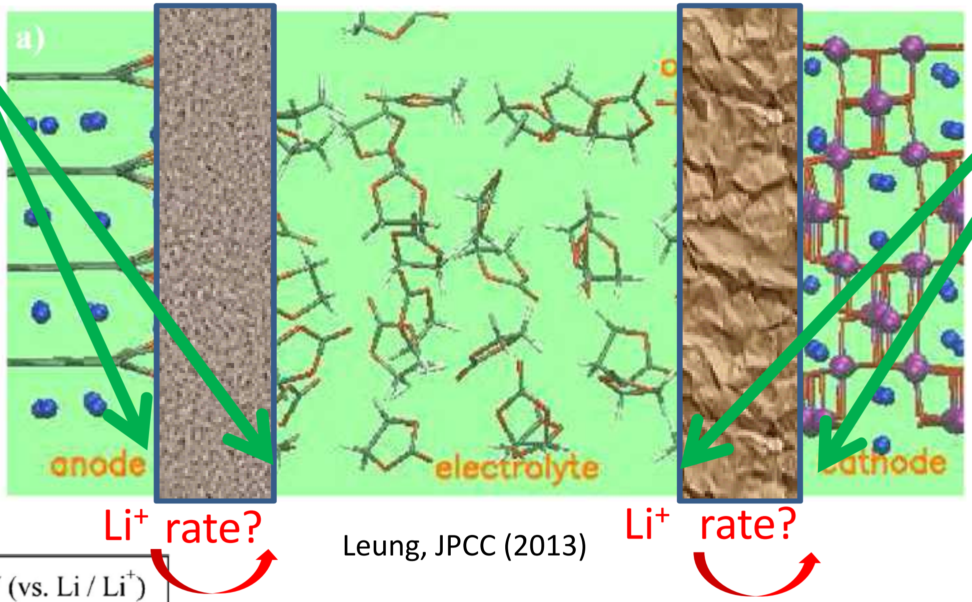




Mechanisms, smart interfaces, degradation, solid electrolyte

Directing Matter and Energy:
Five Challenges for Science and the Imagination

Grand Challenge: How Do We Control Materials Processes at the Level of Electrons?



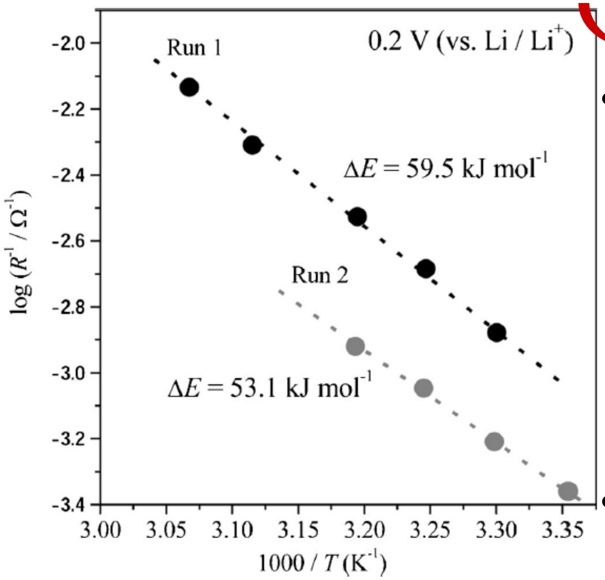
Li^+ transfer (and degradaton) at any of 4 interfaces

Li^+ transfer (and degradaton) at any of 4 interfaces

Li^+ rate?

Li^+ rate?

Leung, JPCC (2013)



- experiments: interfacial charge transfer rate as function of temp., electrolyte, engineered electrode surface …

Solvated Li-Ion Transfer at Interface Between Graphite and Electrolyte JECS 151:A1120 (2004)

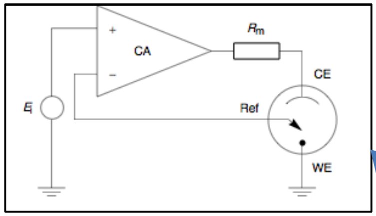
Takeshi Abe,*,z Hideo Fukuda, Yasutoshi Iriyama, and Zempachi Ogumi**

- atomic modeling – not there yet →

Reasons

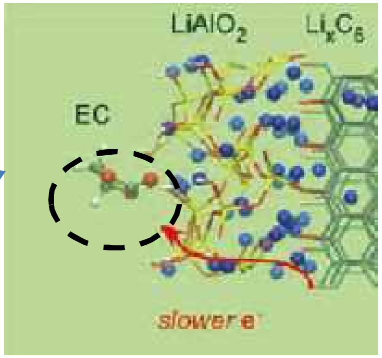
1. thin film, SEI
2. voltage control
3. electrolyte reacts
4. liquid …

Outline



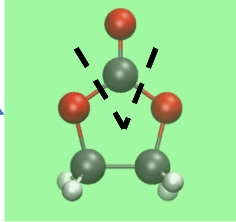
challenges
1. thin film, SEI
2. voltage control
3. electrolyte reacts

(A) Atomic layer deposition (ALD)
modified electrode surfaces

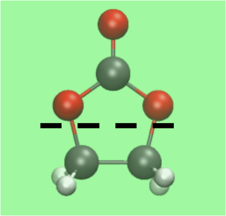


(B) Controlling voltage

(C) Electrolyte stability
(from liquid to solid)



vs.



Main themes

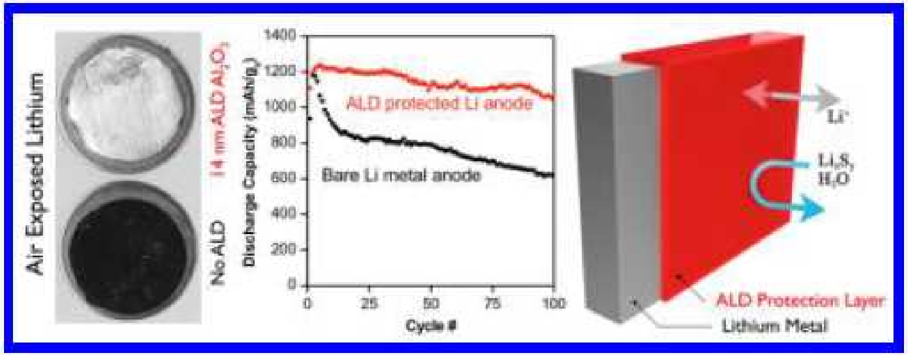
- modeling of solid-liquid and solid-solid interfaces
- fundamental computational electrochemistry
  (e.g., Marcus Theory, potential of zero charge)
- unify different branches of computational electrochemistry

1. Atomic layer deposition (experiments)

conform films with well-contolled uniform thickness, chemistry

Next-Generation Lithium Metal Anode Engineering *via* Atomic Layer Deposition

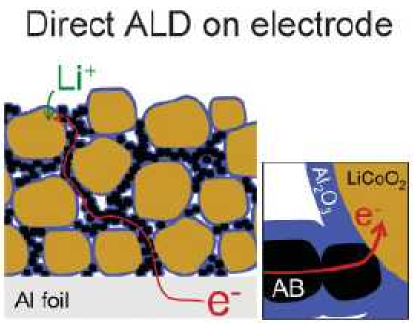
Alexander C. Kozen,[†,‡] Chuan-Fu Lin,[†,‡] Alexander J. Pearse,[†,‡] Marshall A. Schroeder,[†,‡] Xiaogang Han,[†] Liangbing Hu,[†] Sang-Bok Lee,[§] Gary W. Rubloff,[†,‡] and Malachi Noked[*,†,‡,§]

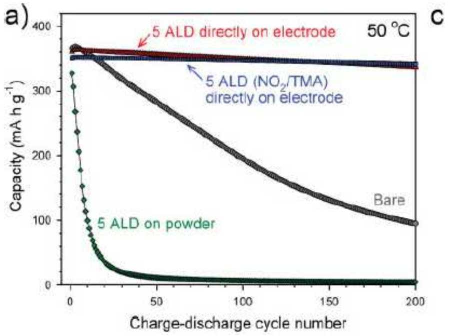


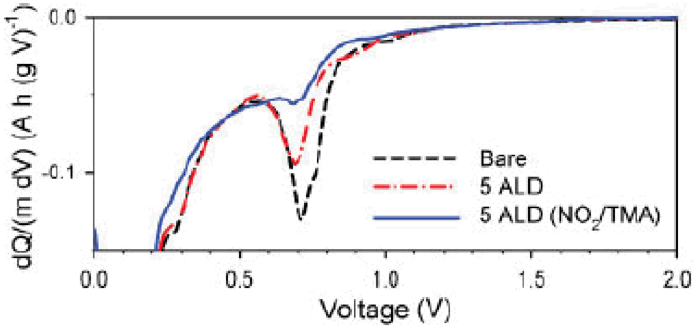
See also Peter Bruce,

Ultrathin Direct Atomic Layer Deposition on Composite Electrodes for Highly Durable and Safe Li-Ion Batteries

By *Yoon Seok Jung, Andrew S. Cavanagh, Leah A. Riley, Sun-Ho Kang, Anne C. Dillon, Markus D. Groner, Steven M. George,* and *Se-Hee Lee**







Modeling e^- transfer to EC from LiC_6 through ALD film to EC molecule

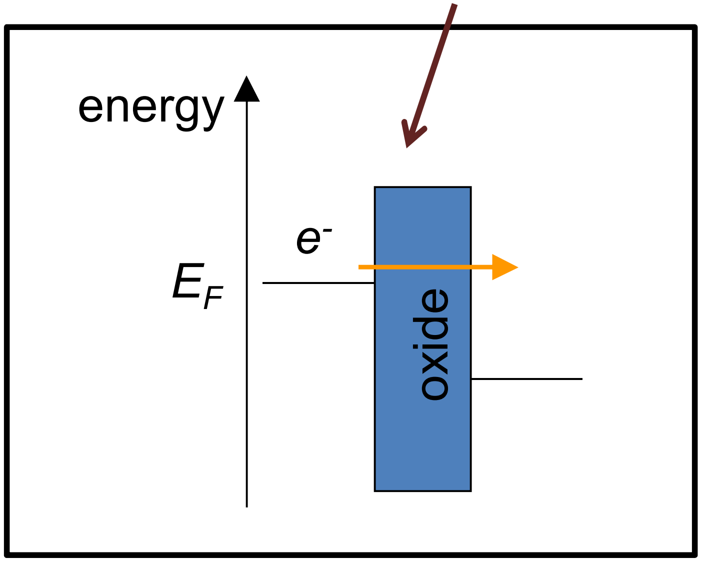
Marcus theory, (non-adiabatic) e^- transfer

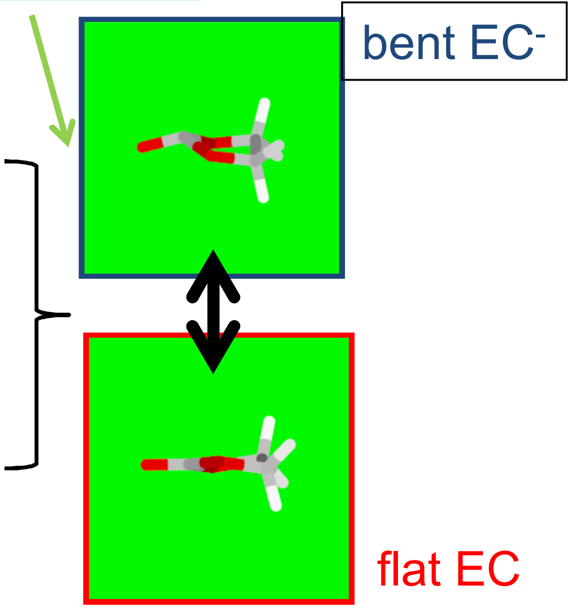
$$k_{\rm et} = \boxed{\frac{2\pi|V_{\rm AB}|^2}{\hbar\sqrt{4\pi\lambda k_{\rm B}T}}}\boxed{\exp\left[-\frac{(\Delta G_o+\lambda)^2}{4\lambda k_{\rm B}T}\right]}$$

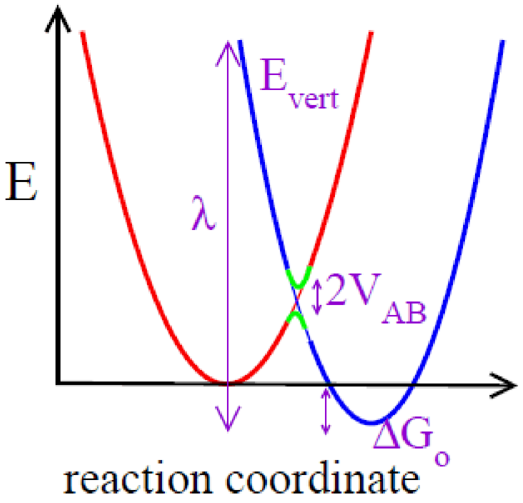
λ: reorganization (free) energy

V_{AB}: tunneling matrix element

ΔG_o: include overpotential







- control charge on EC:

$$W(\mathbf{r}) = V_o[1 - \Pi_i f_i(\mathbf{r})]\,,$$
$$f_i(\mathbf{r}) = 1 - \tanh(\kappa(|\mathbf{r}-\mathbf{r}|_i - w_i)),$$

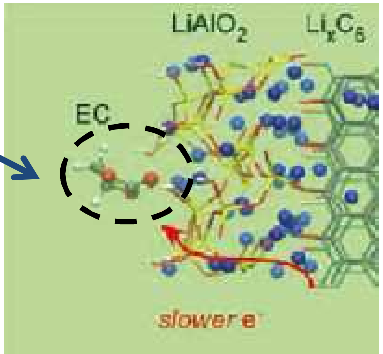
- V_{AB} involves $\langle\Phi_A|\Phi_B\rangle$ and $\langle\Phi_A|\sum_e W(r_e)|\Phi_B\rangle$

use cDFT from photovoltaics

Wu & van Voorhis, JCP 125:164105 (2006)

EC : +0.2|e|

EC-: -0.6|e|



Predictions consistent with microgravimetric expt.

Leung, Qi, Zavadil, Yung, Cavanagh, Dillon, Lee, George, JACS (2010)

Citation here

set to 0 eV, no over potential

$$k_{et} = \boxed{\frac{2\pi}{\hbar}|V_{AB}|^2\frac{1}{\sqrt{4\pi\lambda k_B T}}}\boxed{\exp\left[-\frac{(\Delta G^o+\lambda)^2}{4\lambda k_B T}\right]}$$

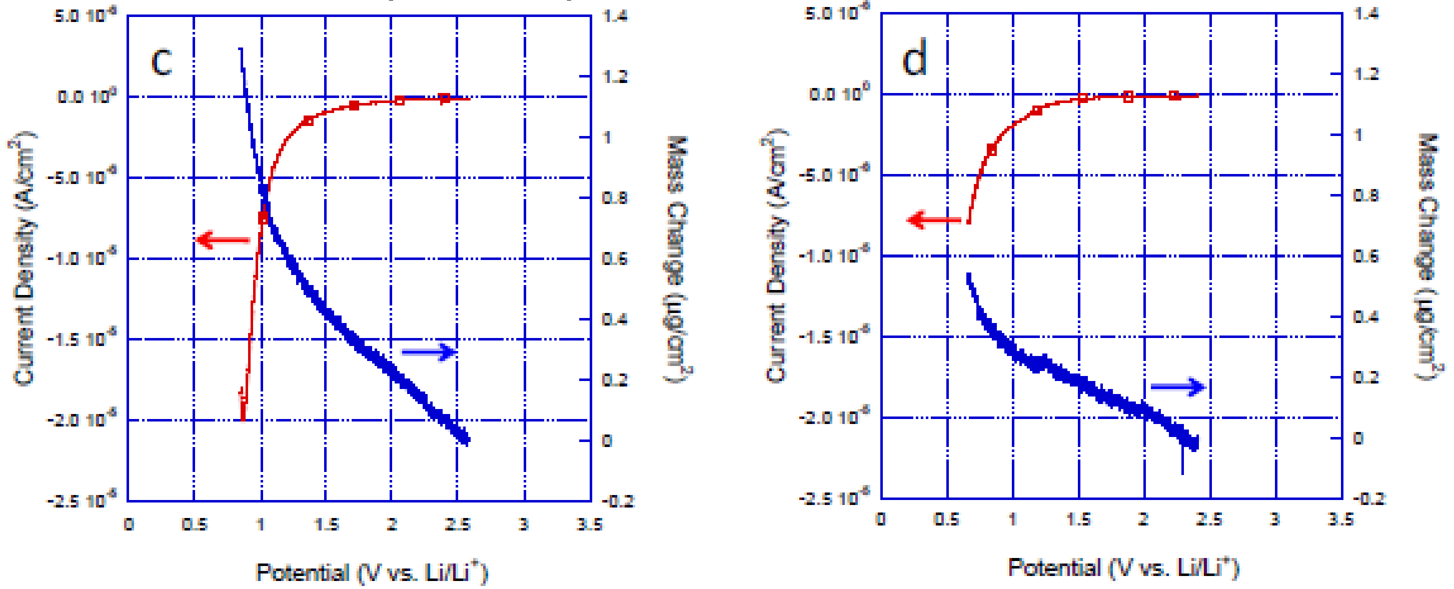
overall

cDFT predictions: 10^{12} /s 10^{-9} ~6 x 10^3/s

(could be overestimated)

Zavadil: some decomposition products; less as oxide thickness increases

5.5 A thick alumina film



11.0 A thick alumina film

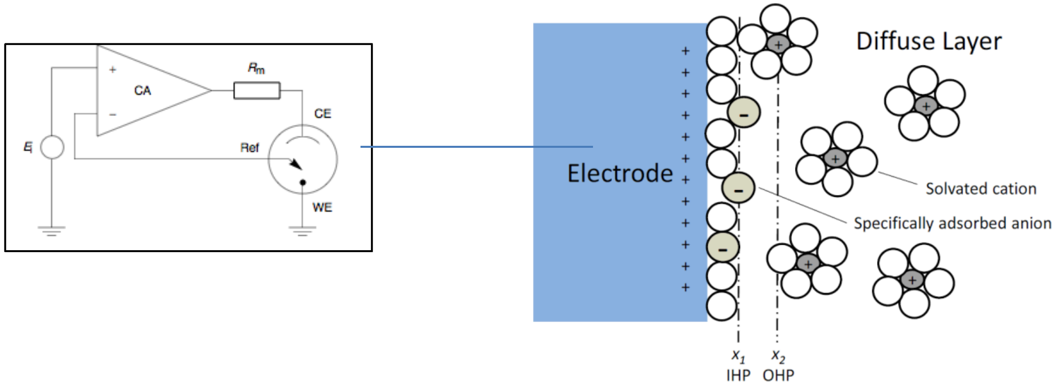
(Yue Qi – WKB estimate of effects of thicker oxide)

Spawned our later work on SEI kinetic phase diagram, Miller/Borodin et al. ….

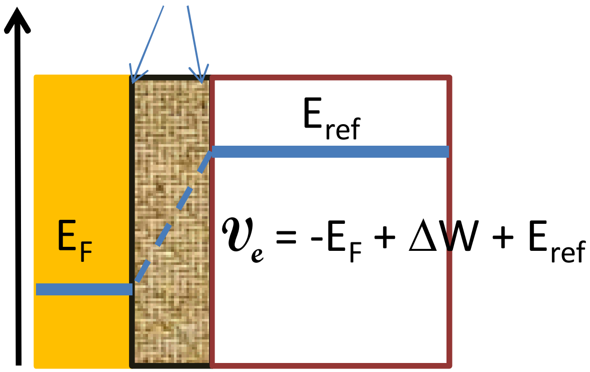
2. What is “voltage”? (at atomic lengthscale)

Expt.: whatever the potentiostat says!
(c.f. Kevin Zavadil’s nano-electrochemistry)

DFT theorist: voltage “=“ Fermi level
+ electric double layer (EDL)

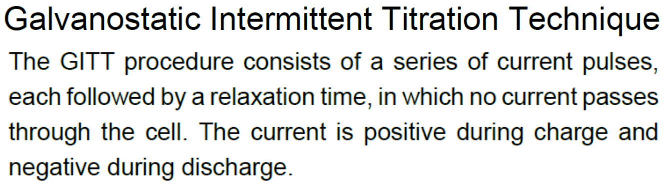


double layer effect



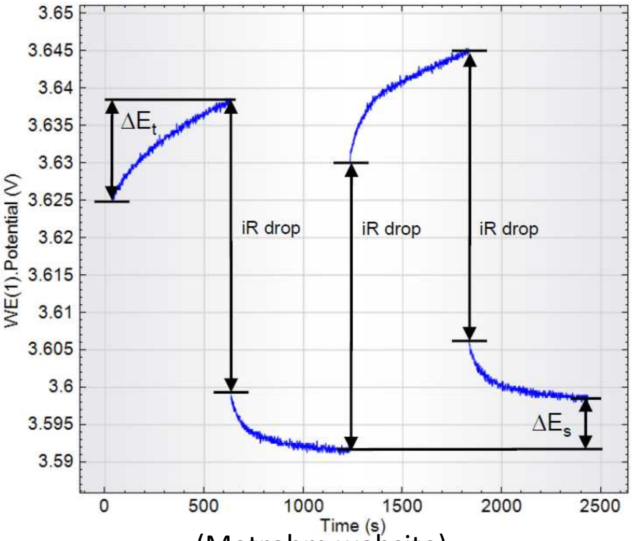
$\mathcal{V}_e = -E_F + \Delta W + E_{ref}$

potentiostat directly controls electrons (fast); Li^+ motion follows, slowly.
true, instantaneous “voltage” is $\mathcal{V}_e$



Galvanostatic Intermittent Titration Technique

The GITT procedure consists of a series of current pulses, each followed by a relaxation time, in which no current passes through the cell. The current is positive during charge and negative during discharge.

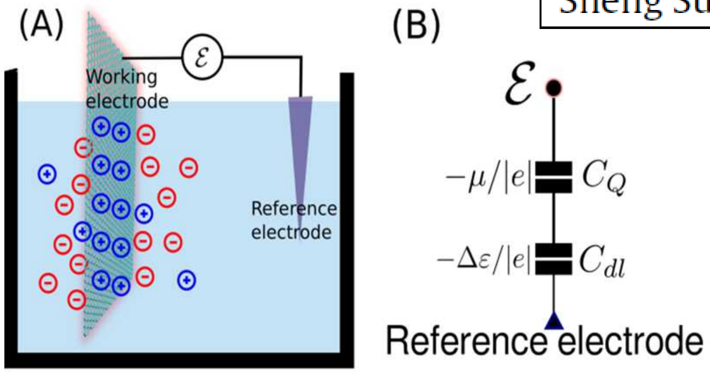


(Metrohm website)

υ_{e} widely-accepted in supercapacitors, catalysis, photovoltaics

e.g., Dissecting graphene capacitance in electrochemical cell --- A Joint DFT calculation

Sheng Sun [a,b], Yue Qi [c], Tong-Yi Zhang [a,*] Electrochimica Acta 163 (2015) 296–302

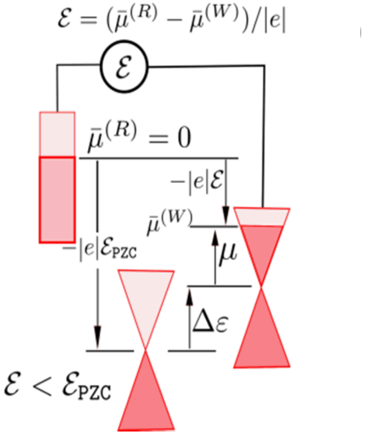


$$\frac{1}{C_{total}} = \frac{1}{C_{dl}} + \frac{1}{C_Q}$$

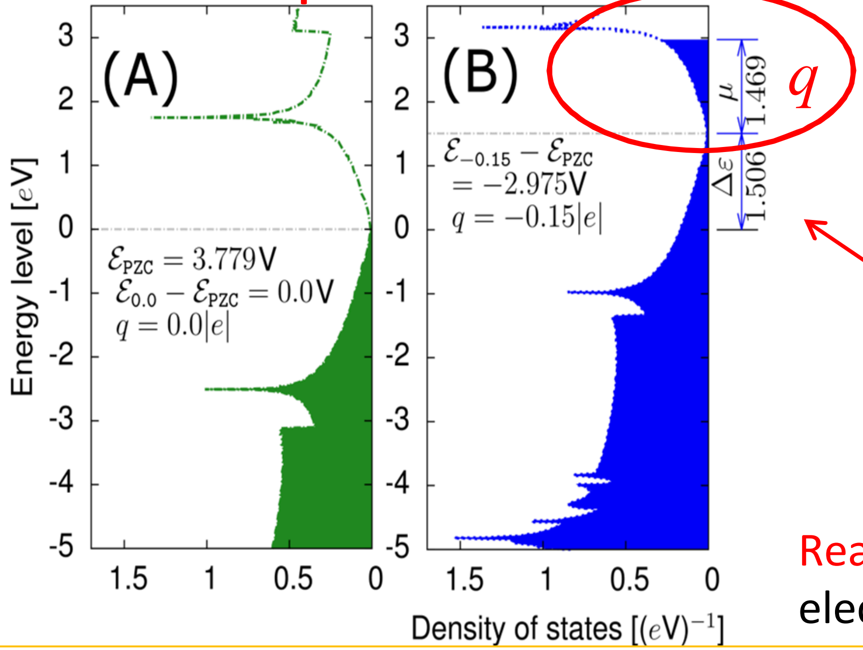
due to electric double layer

quantum capacitance due to the limited states available near the Dirac Point

When measuring with a reference electrode, the electron chemical potential reaches equilibrium



Computed DOS



Excess charge causing the double layers

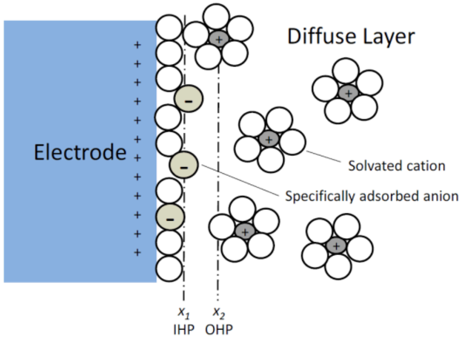
Double layer shifts all electronic energy levels

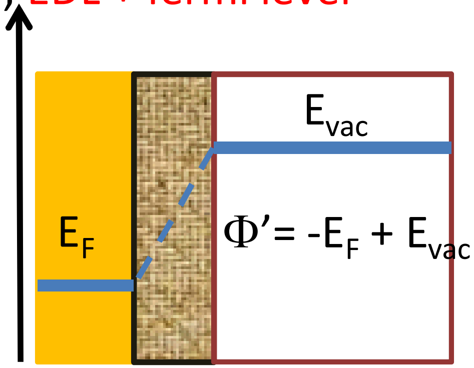
Reaches equilibrium, when electrons stop flowing.

Interfacial, E_F + EDL expressed by Galli, Otani (this p.m.), Jun Cheng, Michiel Sprik

LIB: Two voltage definitions: electronic vs. “ionic” voltage

fuel cell, PV, supercapactiors: “voltage” is electronic, interfacial, EDL + fermi level

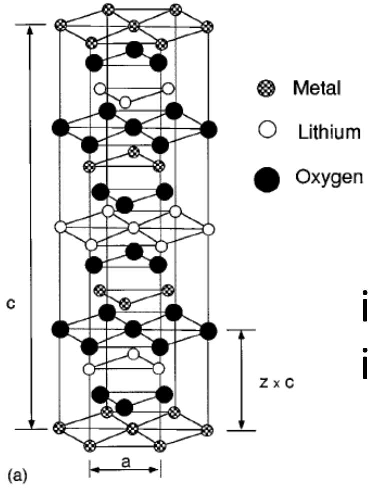




$$\mathcal{V}_e = \Phi'/|e| - 1.37\text{ V}$$

true instantaneous voltage (“potentiostat”)

Battery modeling: voltage is bulk-like, ionic



$$\mathcal{V}_i = -\frac{\mu_{\mathrm{Li}}^{\mathrm{cathode}}(x) - \mu_{\mathrm{Li}}^{\mathrm{anode}}}{zF}$$

$\mathcal{V}_e$ is underfined!

implicitly assume an interface that supports

$\mathcal{V}_i = \mathcal{V}_e$

and system is at equilbrium

Li content slowly responds to $\mathcal{V}_e$

$\mathcal{V}_i = \mathcal{V}_e$ at equilibrium

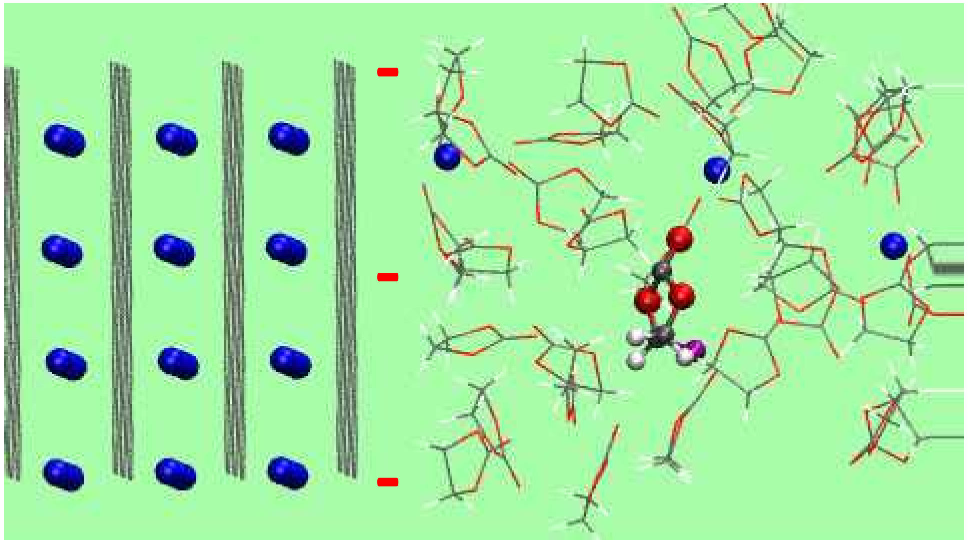
$\mathcal{V}_i > \mathcal{V}_e$ more Li enters electrode if possible*, lowers $\mathcal{V}_i$

$\mathcal{V}_i < \mathcal{V}_e$ some Li leaves electrode if possible, raises $\mathcal{V}_i$

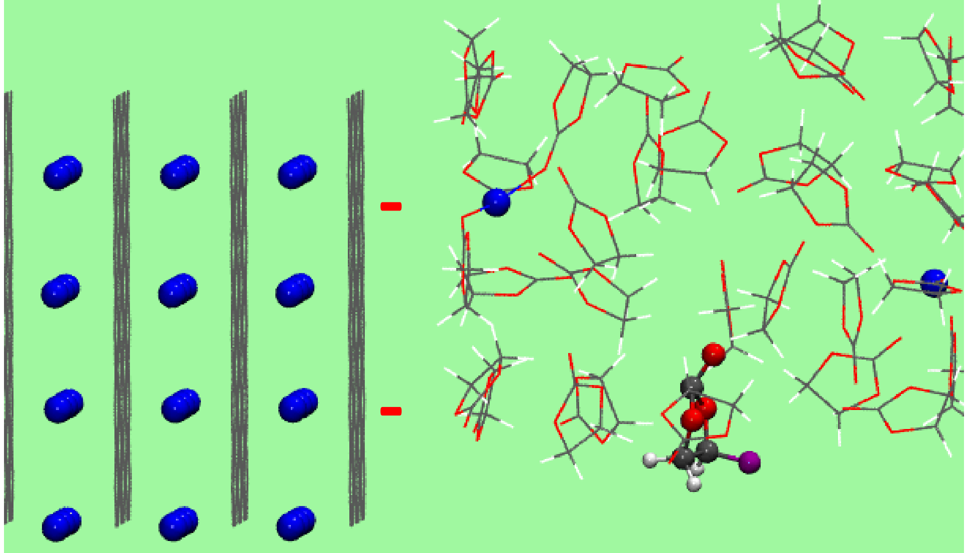
Our voltage-calibrated interface AIMD simulations of FEC reduction shows it is critical to control v_e via surface electronic charge

potential of zero charge of LiC_6 is not at 0.1 V vs. $LIi^+/Li(s)$!

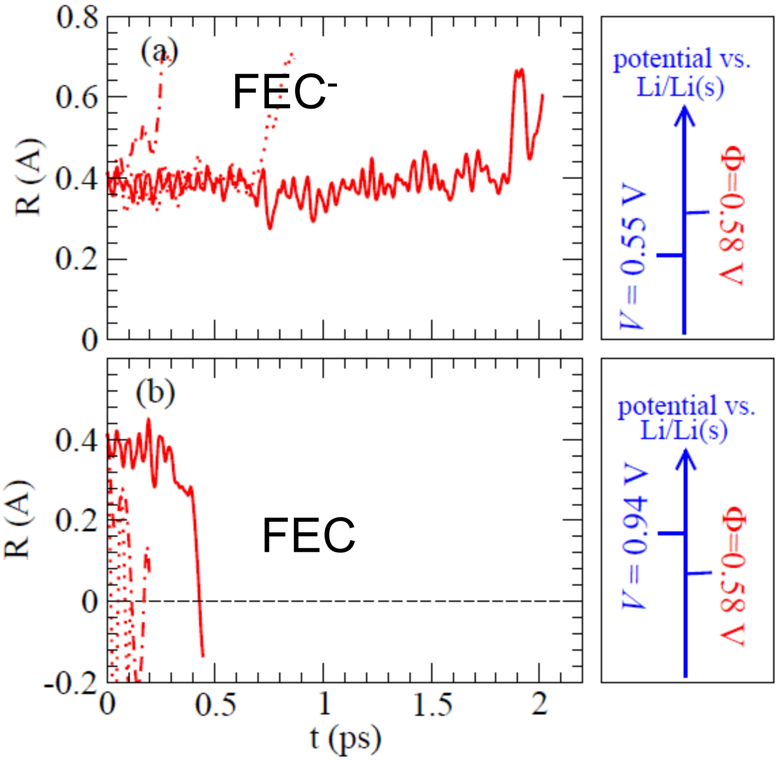
Interface: 0.51 V

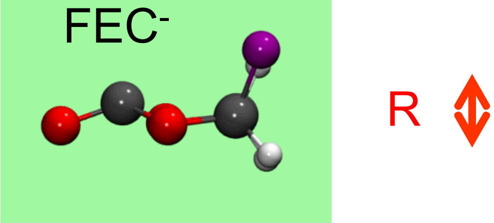


Interface: 0.91 V



G09 "bulk" calculation: 0.58 V threshold

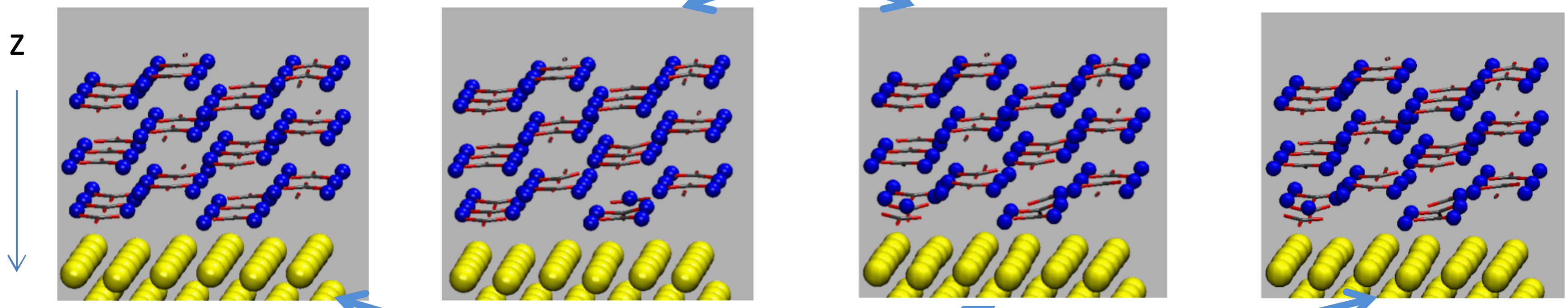


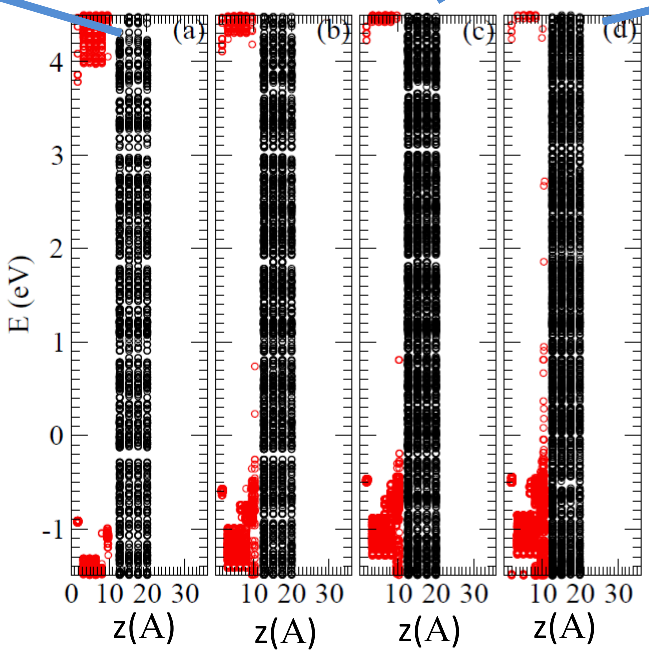


$\mathcal{V}_e$ issue also relevant to solid electrolyte interfaces

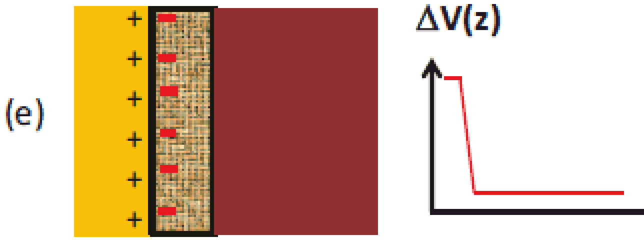
$\Delta N(\mathrm{Li})$	0	-1	-2	-3	-4	-6
$\mathcal{V}_e$	3.56	3.87	4.03	4.03	4.05	4.41
$\mathcal{V}_i$	3.53	3.58	3.26	3.55	NA	

Li_2CO_3 basal plane on Au(111) under UHV conditions





- to "oxidize" Li_2CO_3, remove (e^-, Li^+)
- $|Au^+|V_{Li}^-|$ surface dipole -> raise $\mathcal{V}_e$

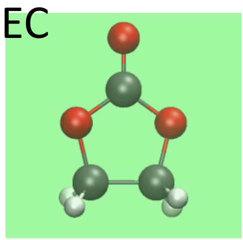


where is voltage drop?
cn lead to new SEI concept

3. Electrolyte stability, decomposition mechanisms

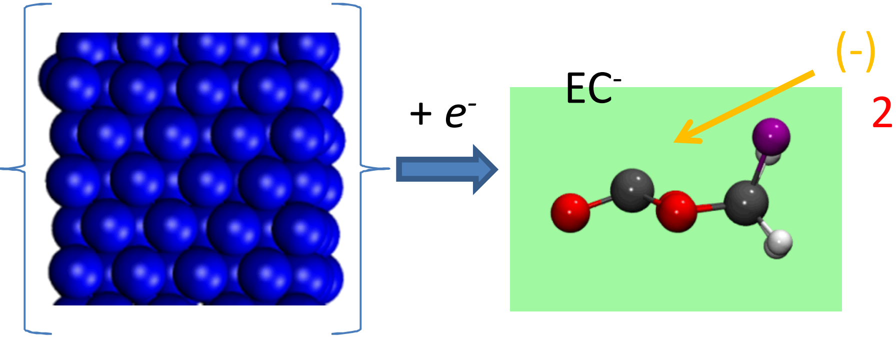
Three possible definitions of instability

1. Thermodynamic
   which phase is most stable?
   (ignores kinetics)

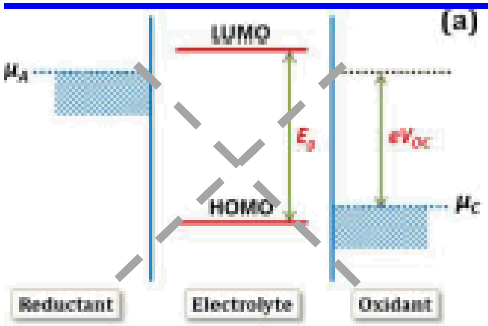


+ Li

Li_2O (s) + C (s) + H_2 (gas)

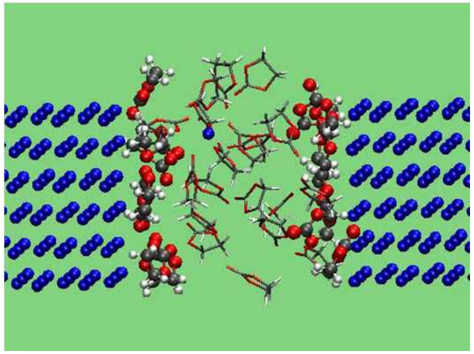


2. Intrinsic electrochemical
   kinetics of e^- transfer
   (break only weak bonds?)



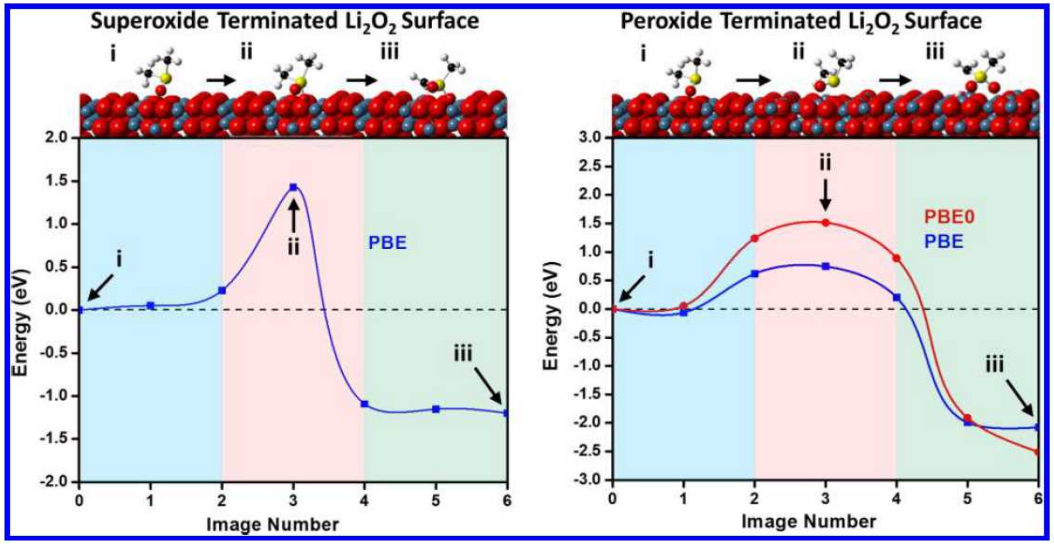
3. Interfacial
   explicitly depends
   on kinetics

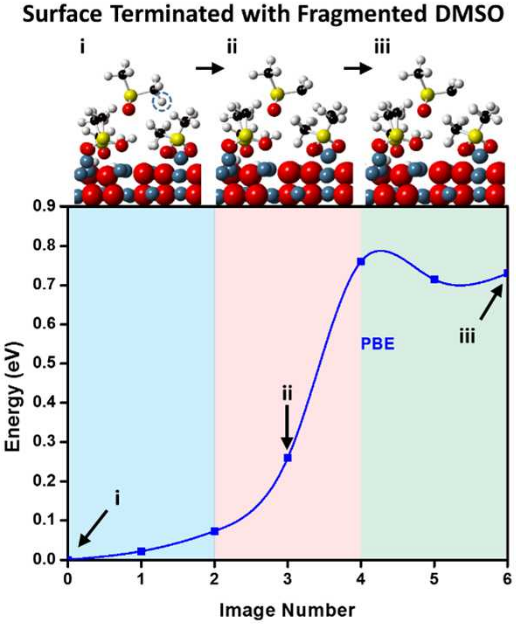
can violate 1 & 2

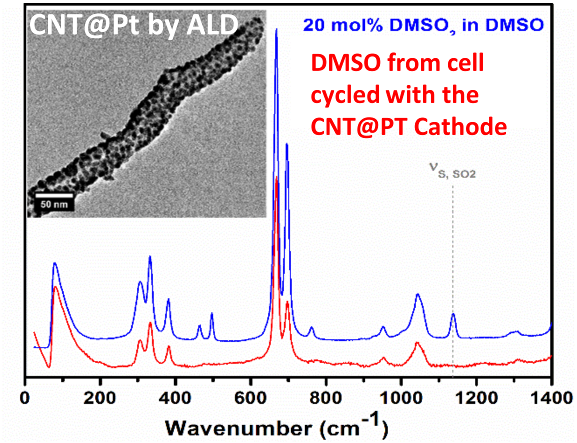


DMSO–Li_2O_2 Interface in the Rechargeable Li–O_2 Battery Cathode: Theoretical and Experimental Perspectives on Stability

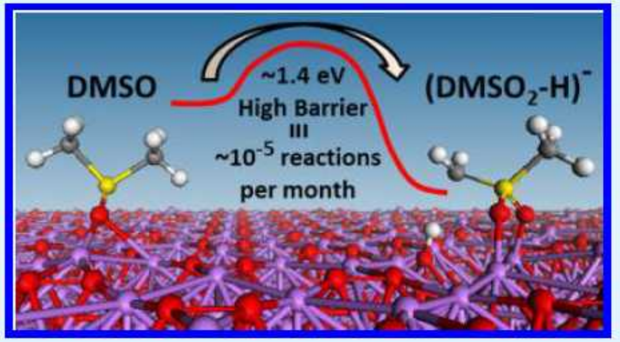
Marshall A. Schroeder,[†] Nitin Kumar,[§,‖] Alexander J. Pearse,[†] Chanyuan Liu,[†] Sang Bok Lee,[‡]
Gary W. Rubloff,[†] Kevin Leung,[§] and Malachi Noked*,[‡]

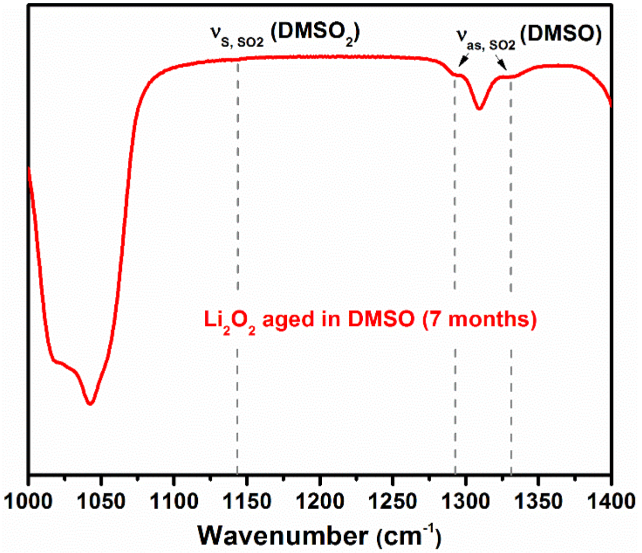






Raman spectrum of electrolyte sample from cycled cell showing no detectable levels of $DMSO_2$



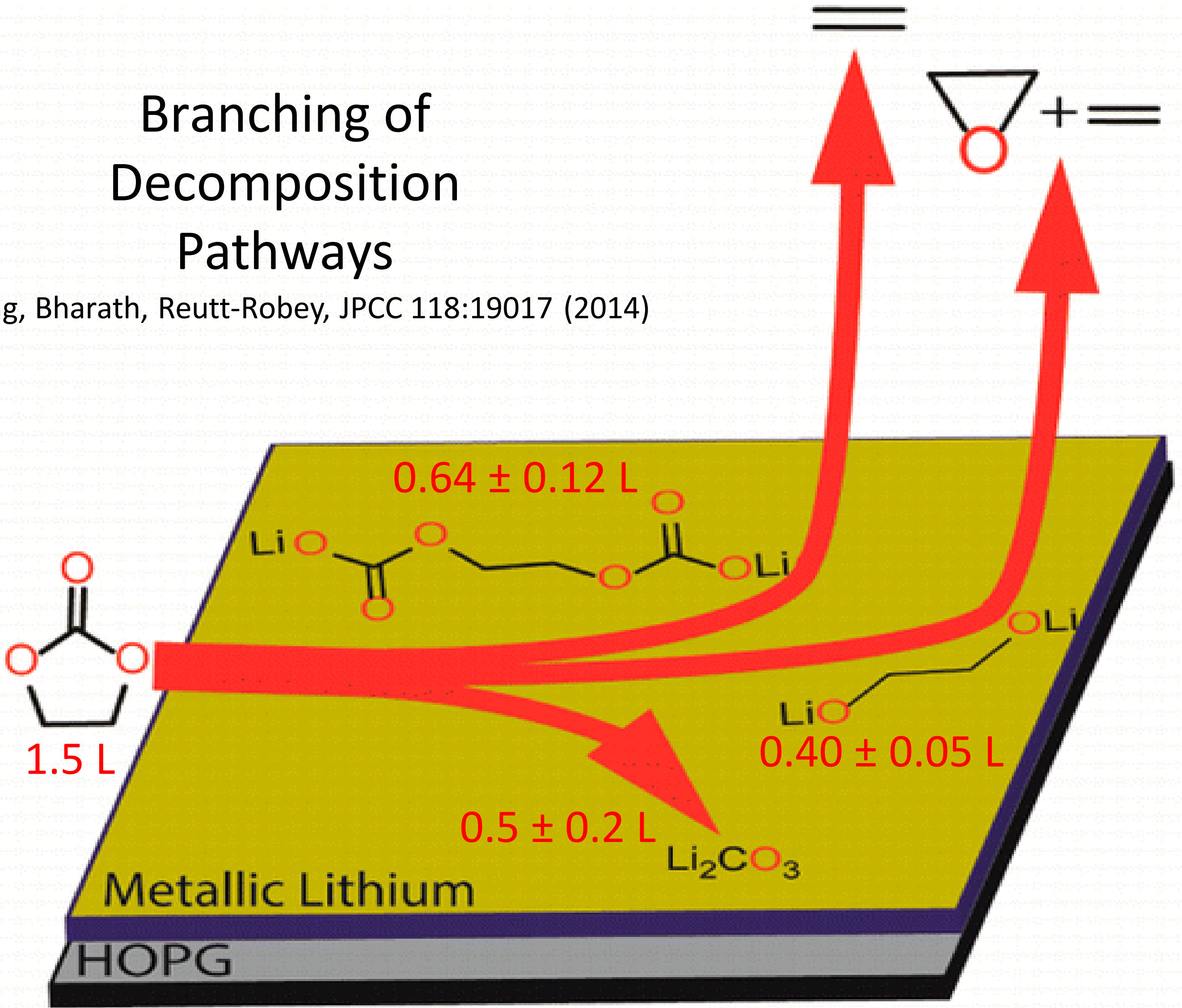


FTIR spectrum of DMSO aged with Li_2O_2, showing no detectable levels of $DMSO_2$

ACS Appl. Mater. Interfaces, **2015**, *7* (21), 11402–11411
DOI: 10.1021/acsami.5b01969

More details in: Thursday, October 15, 2015: 09:00
101-A (Phoenix Convention Center)

EC Reduction and Decomposition Pathways on Metallic Li

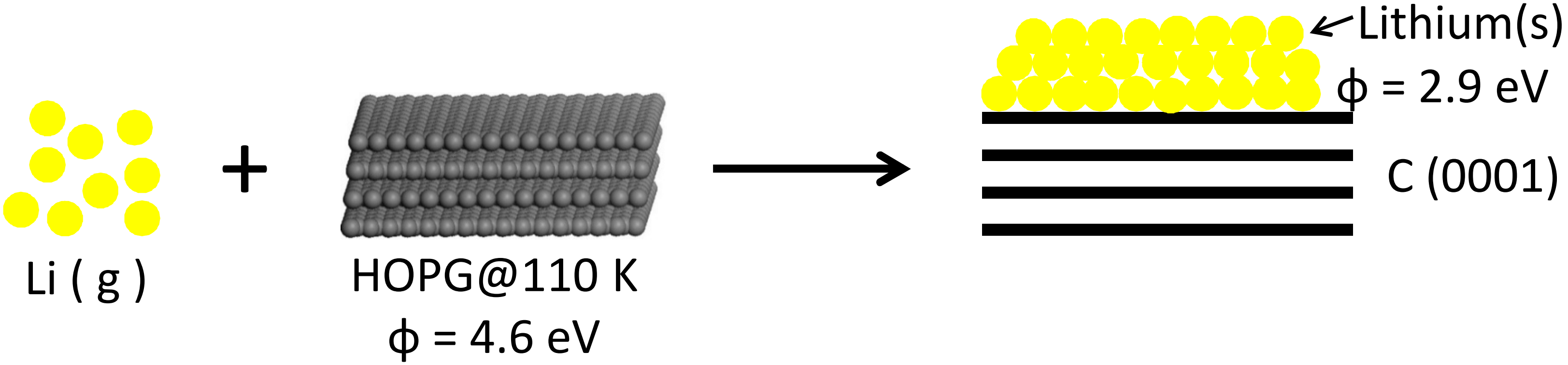


Branching of Decomposition Pathways

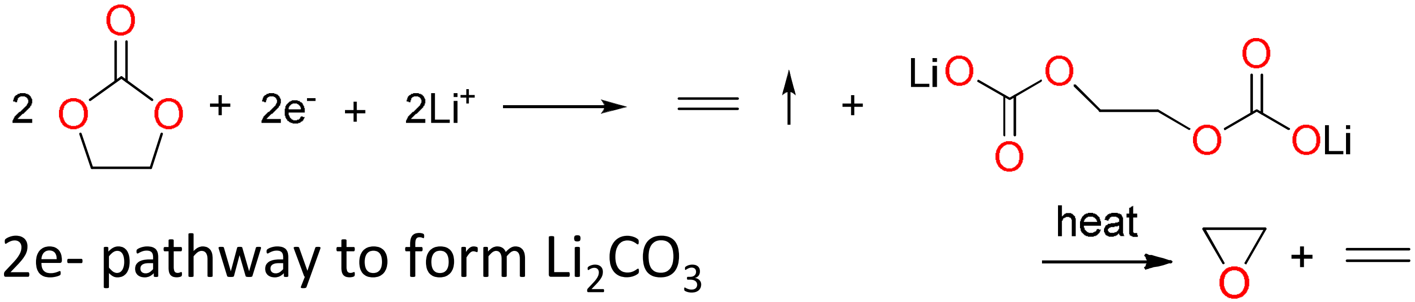
Song, Bharath, Reutt-Robey, JPCC 118:19017 (2014)

organolithium product : inorganic lithium product ≈ 2 : 1

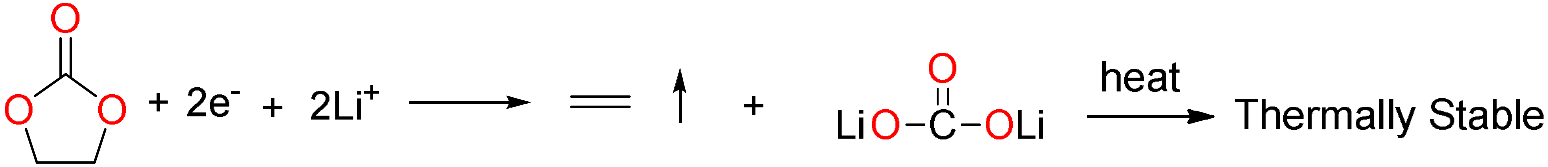
EC Reduction and Decomposition Pathways on Metallic Li



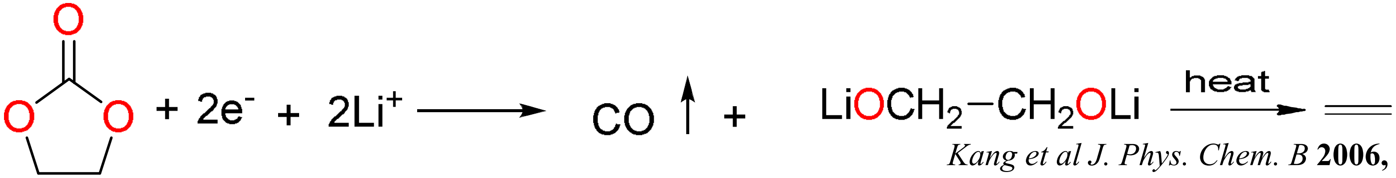
1e- pathway to form lithium ethylene dicarbonate (LEDC)



2e- pathway to form Li_2CO_3



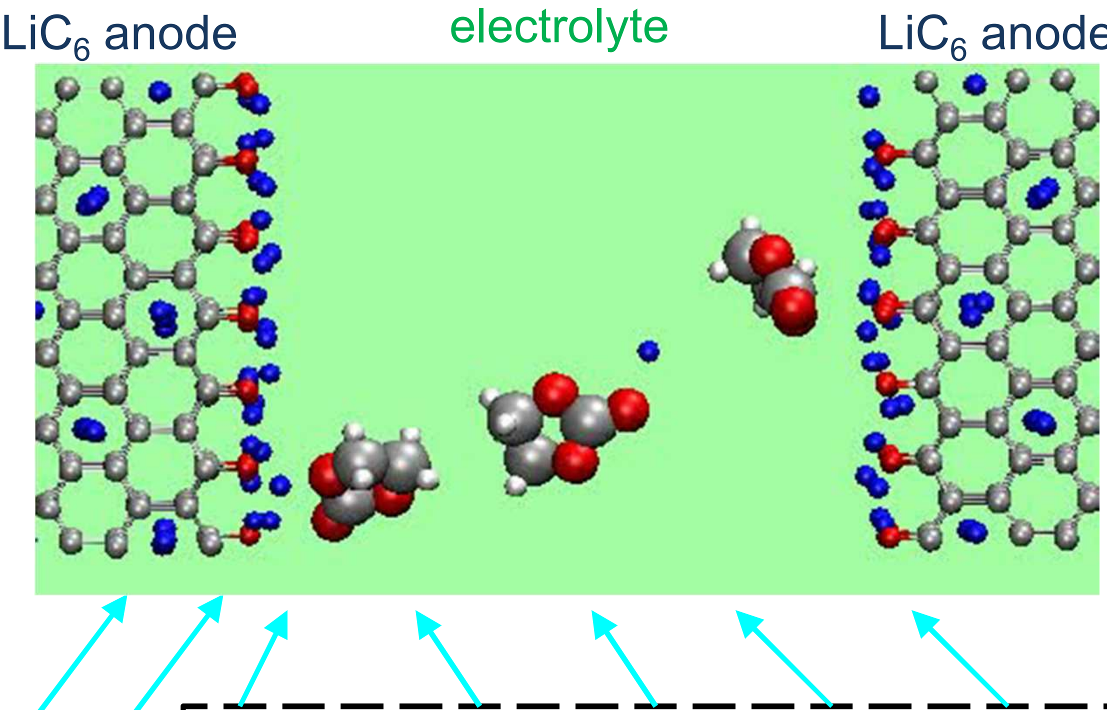
2e- pathway to form lithium ethylene glycol (LEG)



Kang et al J. Phys. Chem. B **2006,** *110,* 7708-7719

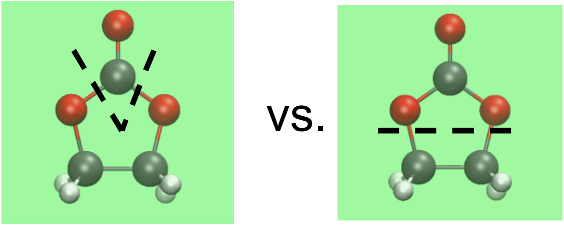
Kevin Private Communication

AIMD modeling: ethylene glycol, CO forms via 2 e^- pathway



Li$^+$ O CO_3^{2-} C_2H_4 $C_2H_4O_2^{2-}$ CO $OC_2H_4OCO^{2-}$ → decomposition products

7 ps AIMD trajectory



Leung, ,Budzien., PCCP 12:6583 (2010)

Experimentally, CO, C_2H_4 in 1:3 ratio, but the CO-route routinely ignored

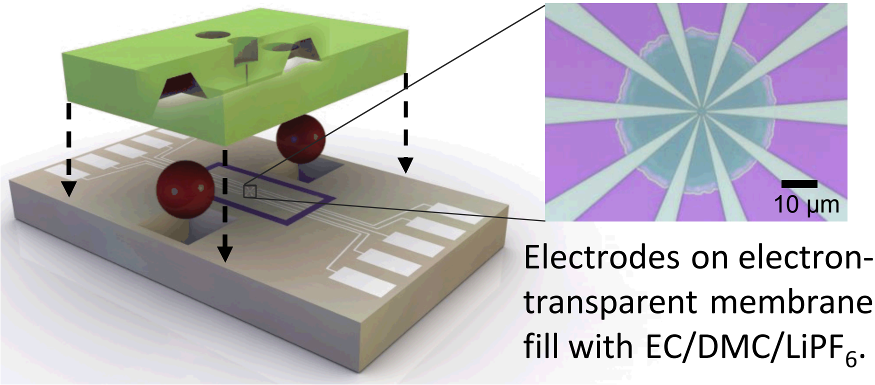
*Onuki et al., JECS 155:A794 (2008)

In this early work the voltage is not well controlled, but only rates, not mechanisms, are affected

A direct view of battery interfaces using *in-situ* TEM

Andrew Leenheer, Tom Harris, and Katherine Jungjohann

Sandia-fabricated TEM liquid cell

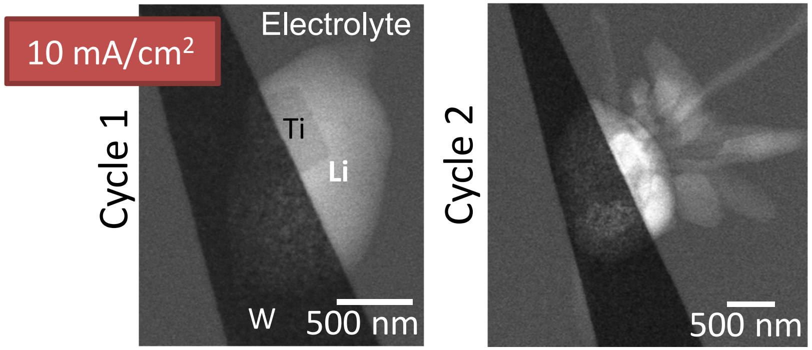


Electrodes on electron-transparent membrane; fill with EC/DMC/$LiPF_6$.

Leenheer *et al.*, *J. Microelectromech. Syst.* **2015**. DOI 10.1109/JMEMS.

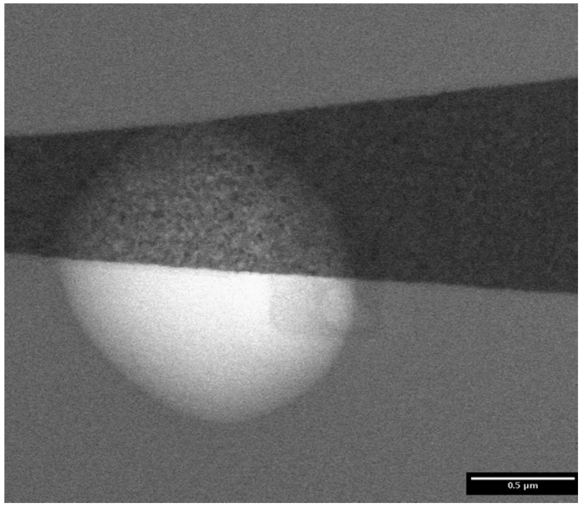
Example application: Li dendrite initiation

Brightfield scanning transmission electron microscopy:



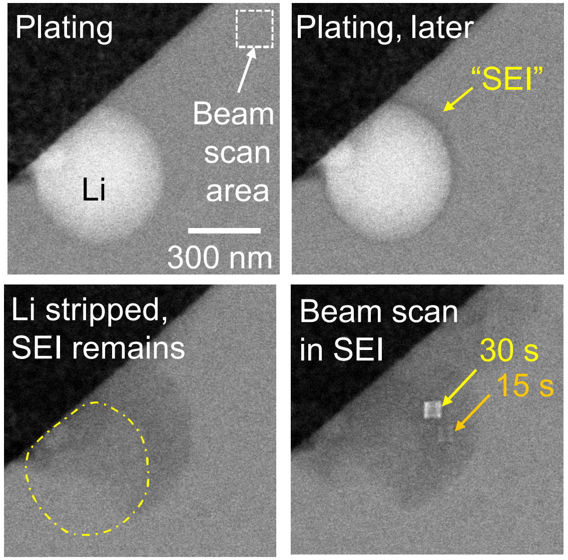
Dendrites formed at high current density and later cycle #.

Operando Li plating and stripping



SEI causes a unique dissolution progression: Li dissolves from isolated defects in SEI.

Electron beam as a probe: create, decompose SEI



Electron beam exposure in the electrolyte accelerates breakdown, forms SEI.

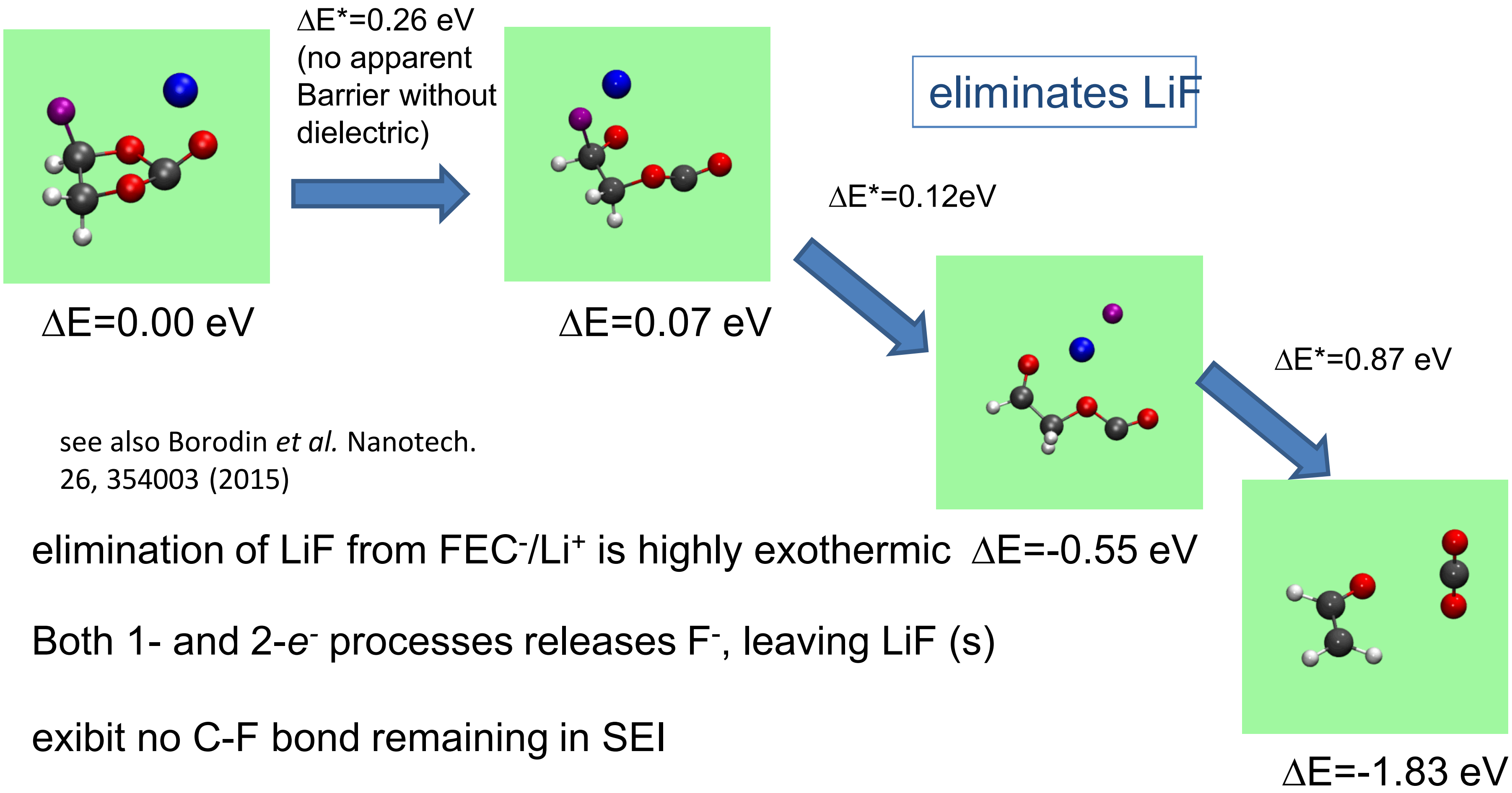
SEI remains after Li stripping.

Beam scanned in SEI reveals light-contrast Li: SEI consisted of Li-containing compounds.

Leenheer *et al.*, *ACS Nano*. **2015**. DOI 10.1021/acsnano.5b00876

Decomposition of FEC^{-}/Li^{+}

fluorethylene carbonate (FEC) a much discussed additive for Si-anode



$\Delta E^{*}=0.26$ eV (no apparent Barrier without dielectric)

$\Delta E=0.00$ eV

$\Delta E=0.07$ eV

eliminates LiF

$\Delta E^{*}=0.12$eV

$\Delta E^{*}=0.87$ eV

$\Delta E=-1.83$ eV

see also Borodin *et al.* Nanotech. 26, 354003 (2015)

- elimination of LiF from FEC^{-}/Li^{+} is highly exothermic $\Delta E=-0.55$ eV
- Both 1- and 2-e^{-} processes releases F^{-}, leaving LiF (s)
- exibit no C-F bond remaining in SEI

confirmed by:

What Makes Fluoroethylene Carbonate Different?

Ilya A. Shkrob,*,† James F. Wishart,‡ and Daniel P. Abrahan

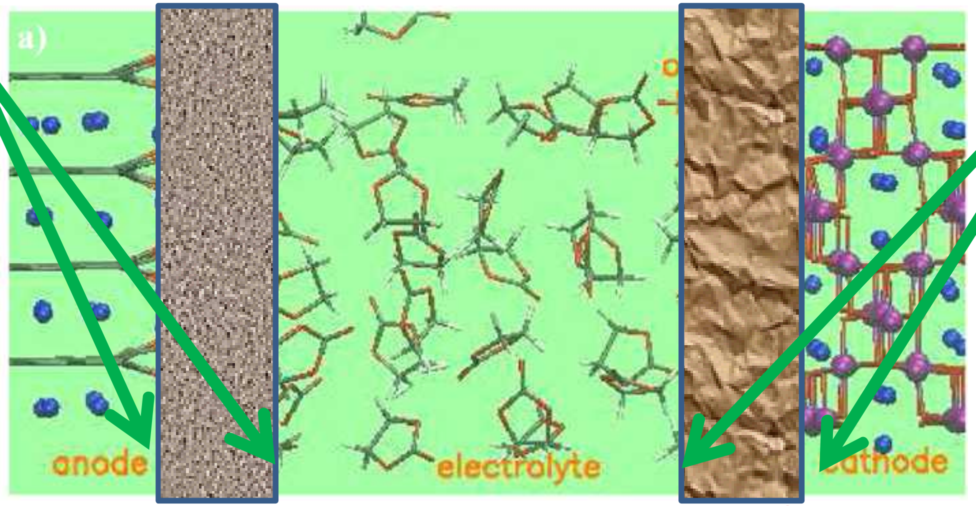
DOI: 10.1021/acs.jpcc.5b03591
J. Phys. Chem. C 2015, 119, 14954−14964

Conclusions + Outlook

- Some accomplishments and challenges
- Computational elecrochemistry needs lots of development (this afternoon)
- LIB interfaces: both electrons and Li+ can move, not pristine electrodes

Directing Matter and Energy:
Five Challenges for Science and the Imagination

Grand Challenge: How Do We Control Materials Processes at the Level of Electrons?



Li$^+$ transfer (and degradaton) at any of 4 interfaces

Li$^+$ transfer (and degradaton) at any of 4 interfaces

Li$^+$ rate?

Li$^+$ rate?

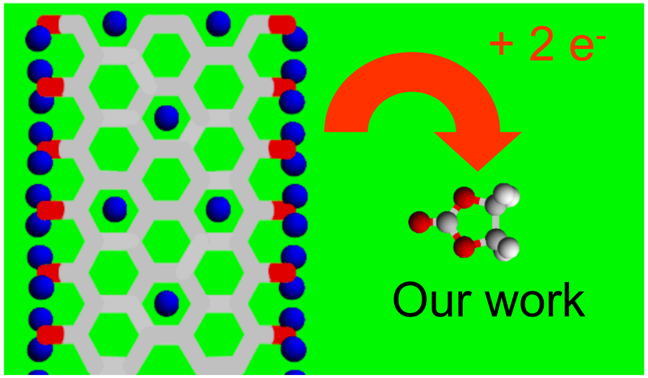
Leung, JPCC (2013)

Please ignore supporting slides after this one

E1

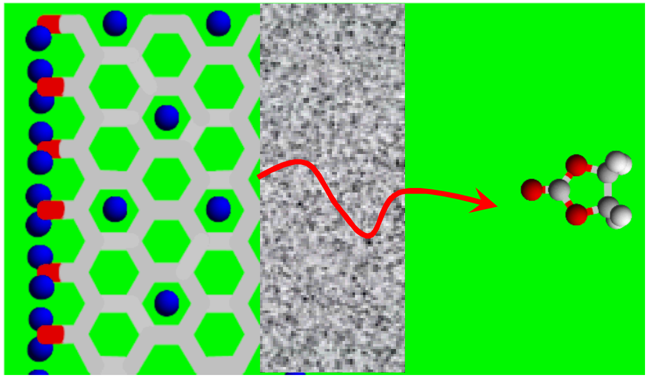
Predictions of anode SEI formation: 2 regimes

No SEI coating



- prediction of two fast mechanisms
- adiabatic (fast electron motion)
- both CO and CO_3^{2-} product channels are barrierless

thin SEI layer (intermediate SEI growth?)



- first “DFT” e^- tunneling rate estimate
- non-adiabatic (slow electron tunneling)
- DFT/PBE overestimates rate, use cDFT

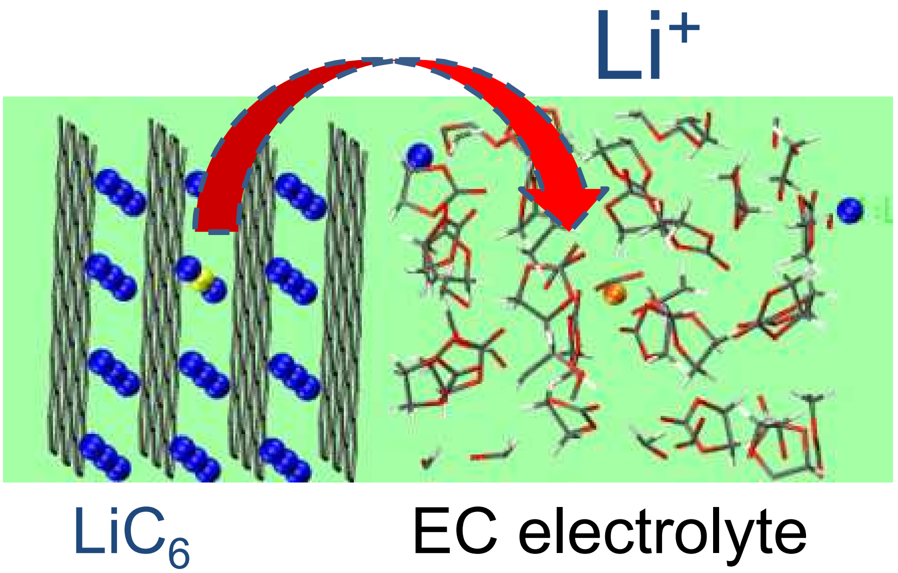
Leung, Qi, Zavadil, Dillon et al., JACS 133:14741 (2011)

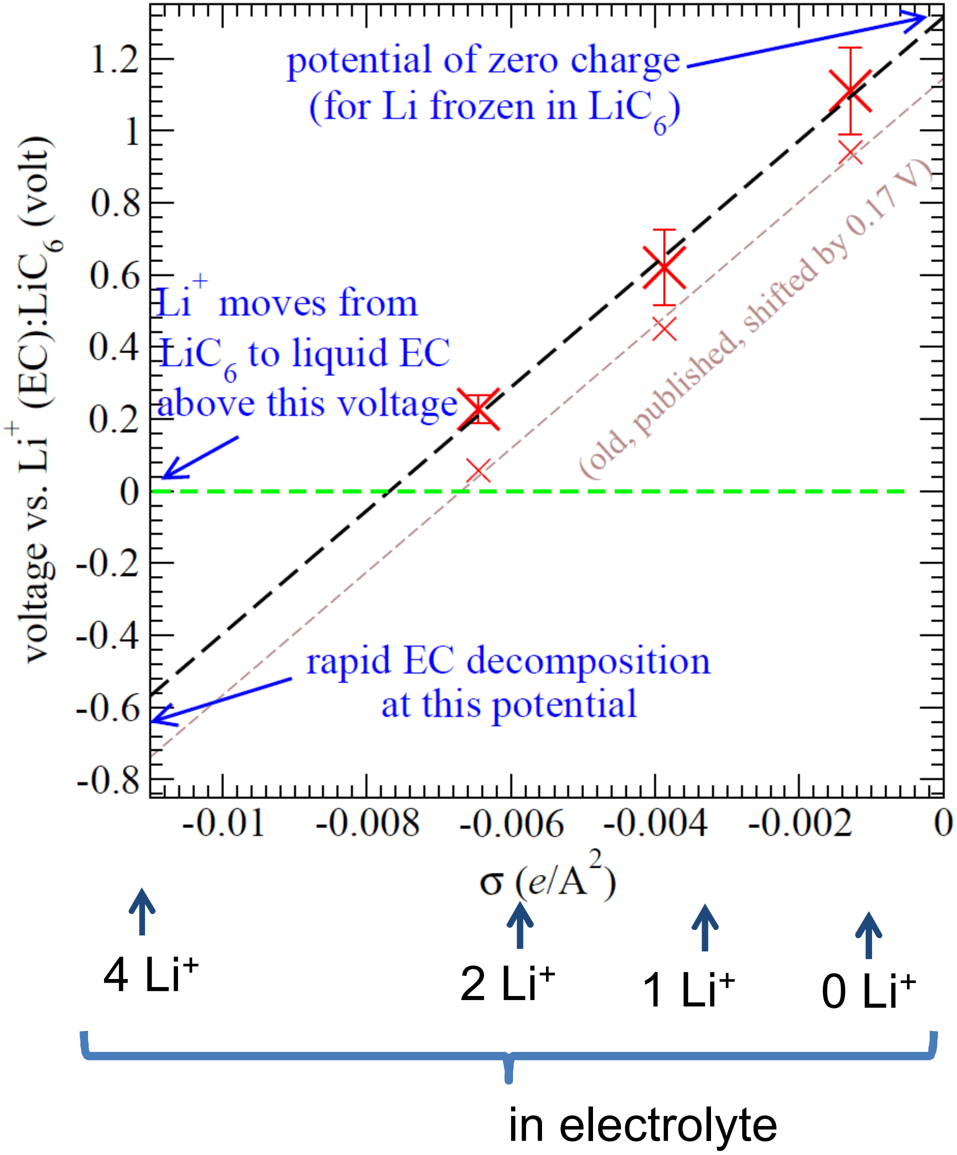
Integrate large scale AIMD simulation predictions of 2-e^- reactions into original cluster-based frame work used by Perla Balbuena *et al.* for 1-e^- reactions [Wang E2 kamura, Ue, Balbuena, JACS 123:11708 (2001)] E3

Slide 25

E1	Changed title font for consistency. Ernie, 2/10/2012
E2	Added footer text. Ernie, 2/10/2012
E3	Changed slide number style for consistency. Ernie, 2/10/2012

“Anode potential” at basal plane/electrolyte interfaces

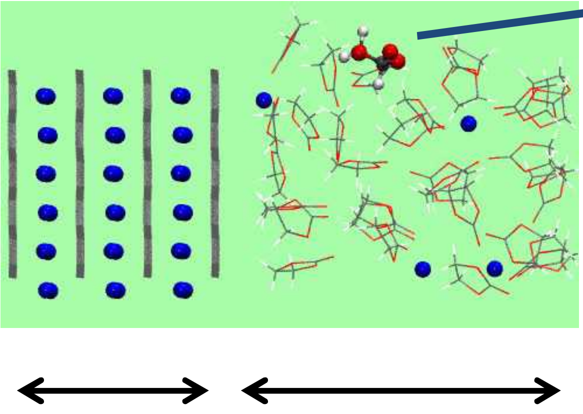




- 0 V vs LiC_6 (y-axis) is ~0.1 V vs $Li^+/Li(s)$
- Net –ve surface charge (σ) exists on basal plane during Li^+ intercalation
- Small cell size -> σ changes during integration ($\Delta G_{\rm hyd} = \int_0^1 d\lambda \left\langle \frac{dH(\lambda)}{d\lambda} \right\rangle_\lambda$). take halfway point for σ value.

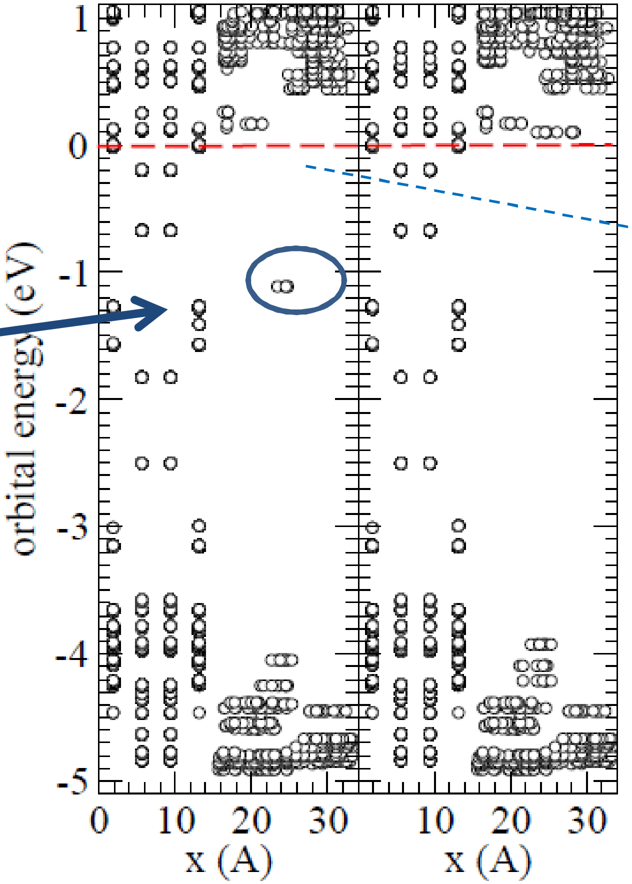
Basal plane work: Leung & Tenney, JPCC 117:24224 (2013)

EC$^-$ and FEC$^-$ form "polaronic" state; *e$^-$ does not* reside in electrolyte LUMO/conduction band



x < 14 A
electrode

x > 14 A
electrolyte



In the literature
you often see:

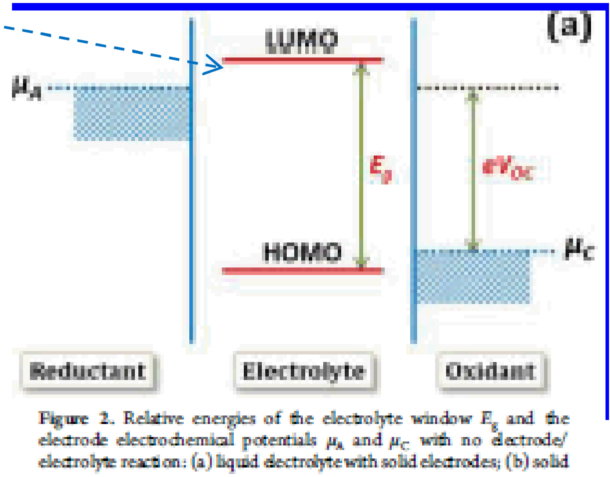


Figure 2. Relative energies of the electrolyte window E_g and the electrode electrochemical potentials μ_A and μ_C with no electrode/ electrolyte reaction: (a) liquid electrolyte with solid electrodes; (b) solid

Goodenough & Park,
JACS 135:1167 (2013)

This is wrong!