Battery and Time

Leung, Soto, Hankins, Balbuena, Harrison, J. Phys. Chem. C (2016)
Leung & Jungjohann (2017)

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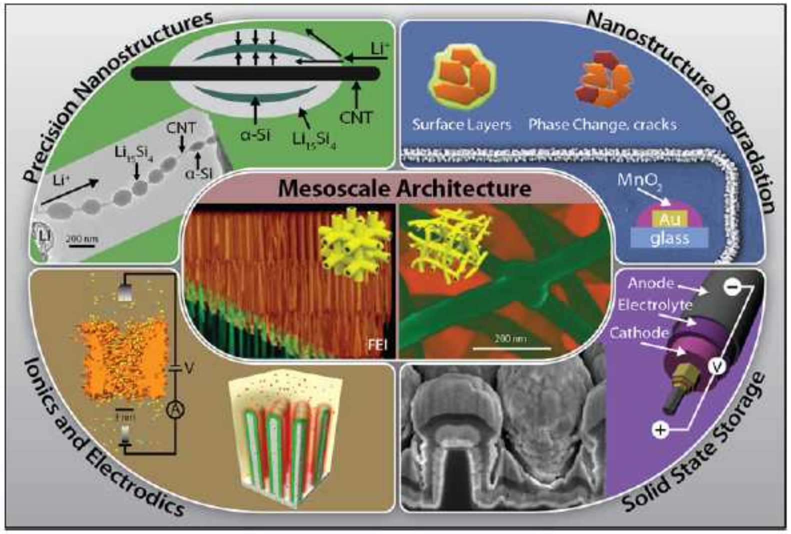
Nanostructures for Electrical Energy Storage
A DOE Energy Frontier Research Center

NEES major research areas

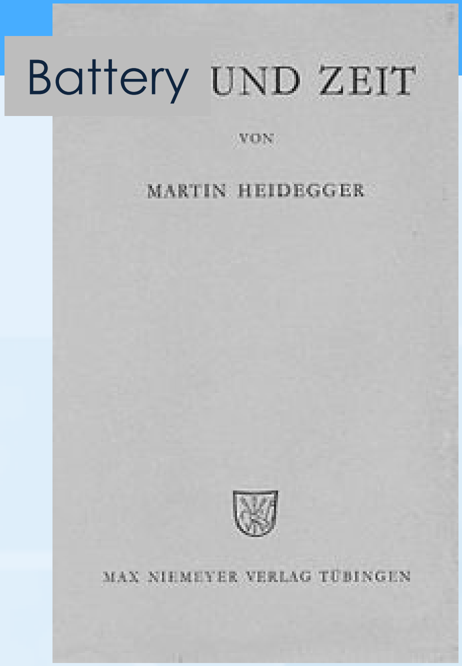
- ☐ Nanostructure Interface Science
- ☐ Mesoscale Architectures & Ionics
- ☐ Nanostructure Degradation Science
- ☐ Solid State Energy Storage



This work was supported as part of the Nanostructures for Electrical Energy Storage (NEES), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science.

U.S. DEPARTMENT OF ENERGY | Office of Science | NEES II NANOSTRUCTURES *for* ELECTRICAL ENERGY STORAGE

Existential Challenges in Energy, Climate Change



Battery UND ZEIT

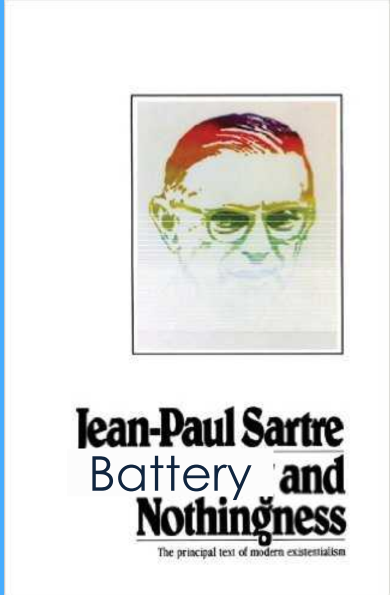
VON

MARTIN HEIDEGGER

MAX NIEMEYER VERLAG TÜBINGEN

- Battery cycle life, charge transfer rate are *time-dependent*
- So are many elements in battery studies not often acknowledged as such
- *Time* could be a unifying theme in battery studies

(In this funding climate, hope we are not left with ->



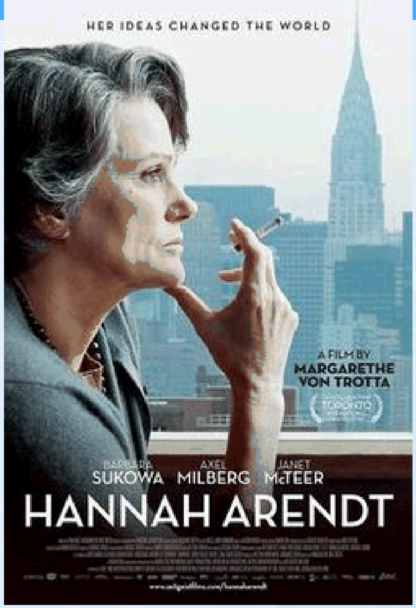
Jean-Paul Sartre

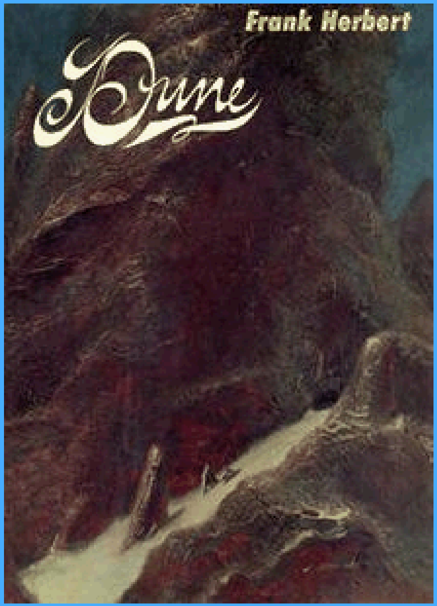
Battery and Nothingness

The principal text of modern existentialism

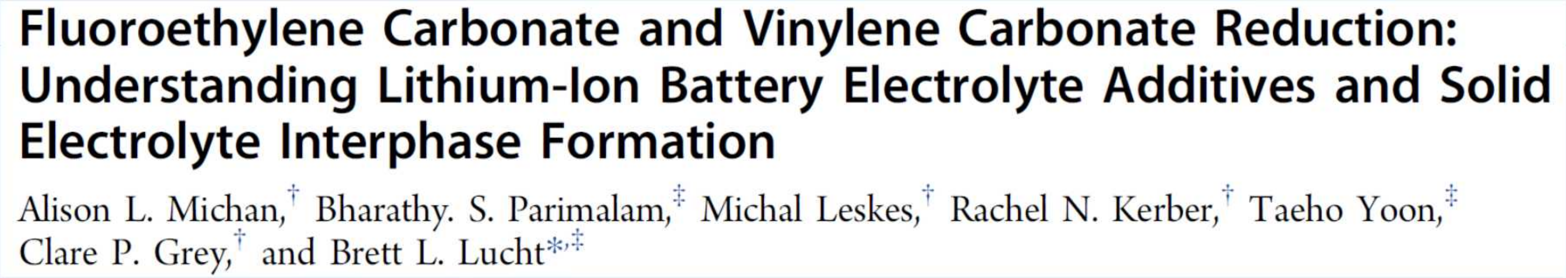
)

Heidegger in popular (& less popular) culture





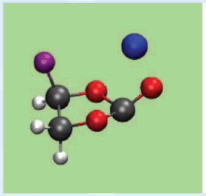
e.g., SEI formation mechanism assigned without regard to time



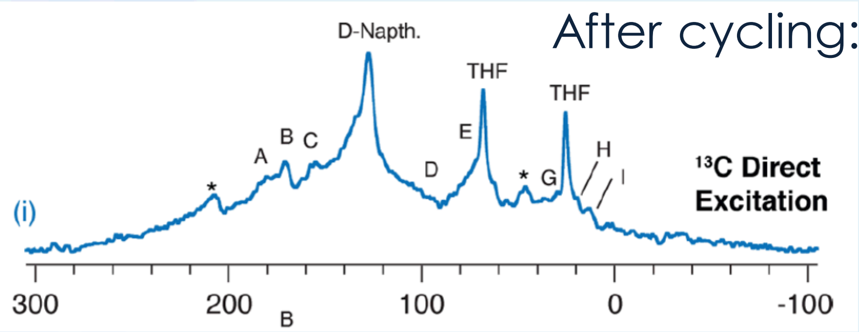
Fluoroethylene Carbonate and Vinylene Carbonate Reduction: Understanding Lithium-Ion Battery Electrolyte Additives and Solid Electrolyte Interphase Formation

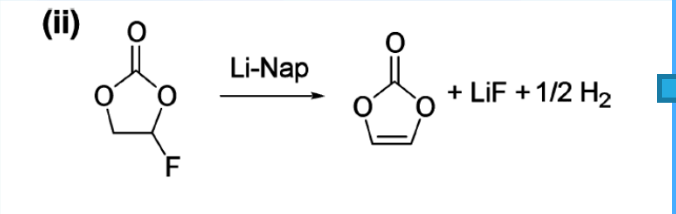
Alison L. Michan,[†] Bharathy. S. Parimalam,[‡] Michal Leskes,[†] Rachel N. Kerber,[†] Taeho Yoon,[‡]
Clare P. Grey,[†] and Brett L. Lucht[*,‡]

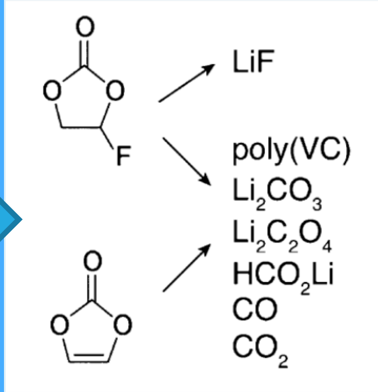
FEC is a popular electrolyte additive makes better SEI



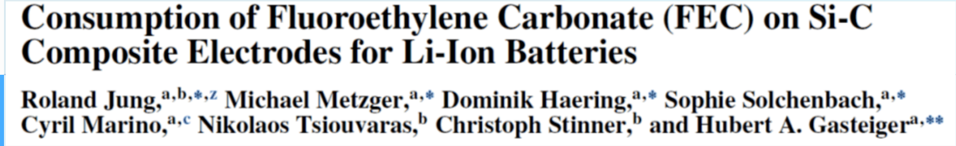
After cycling:







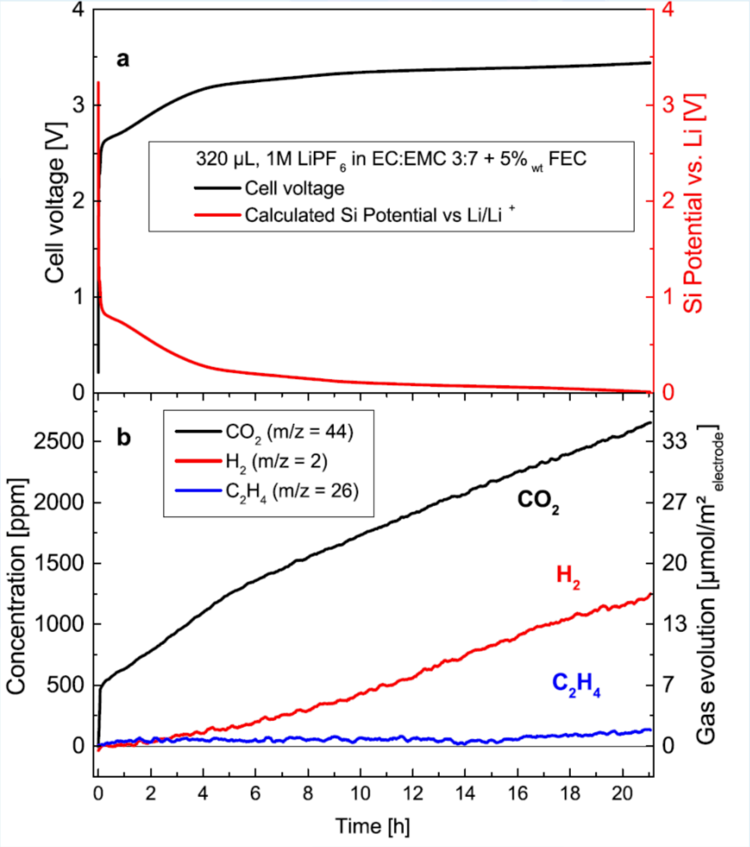
Accounting for time: this mechanism is untenable



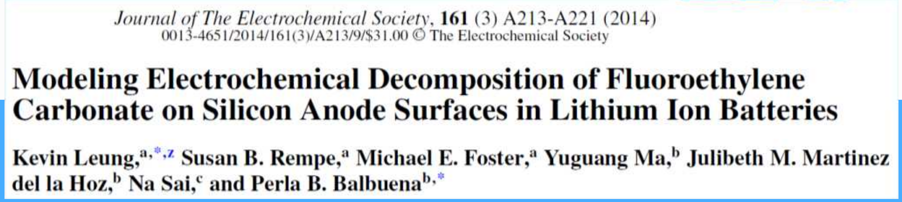
Consumption of Fluoroethylene Carbonate (FEC) on Si-C Composite Electrodes for Li-Ion Batteries

Roland Jung,[a,b,*,z] Michael Metzger,[a,*] Dominik Haering,[a,*] Sophie Solchenbach,[a,*] Cyril Marino,[a,c] Nikolaos Tsiouvaras,[b] Christoph Stinner,[b] and Hubert A. Gasteiger[a,**]

Journal of The Electrochemical Society, **163** (8) A1705-A1716 (2016)



H_2 gas release – 1 hour



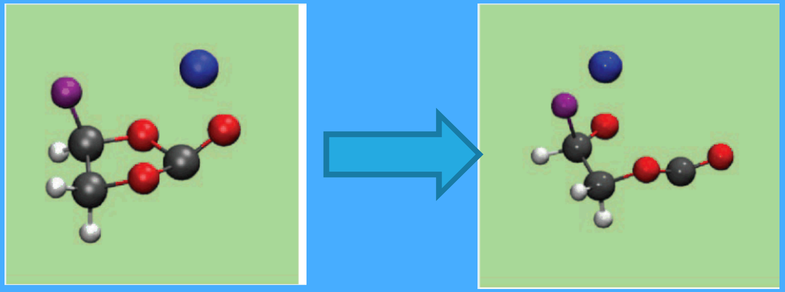
Journal of The Electrochemical Society, **161** (3) A213-A221 (2014)
0013-4651/2014/161(3)/A213/9/$31.00 © The Electrochemical Society

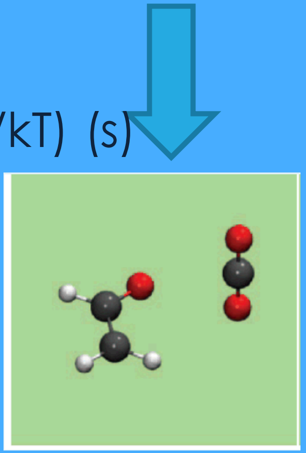
Modeling Electrochemical Decomposition of Fluoroethylene Carbonate on Silicon Anode Surfaces in Lithium Ion Batteries

Kevin Leung,[a,*,z] Susan B. Rempe,[a] Michael E. Foster,[a] Yuguang Ma,[b] Julibeth M. Martinez del la Hoz,[b] Na Sai,[c] and Perla B. Balbuena[b,*]

ring opening pre-empts H_2 release

10^{10} times faster





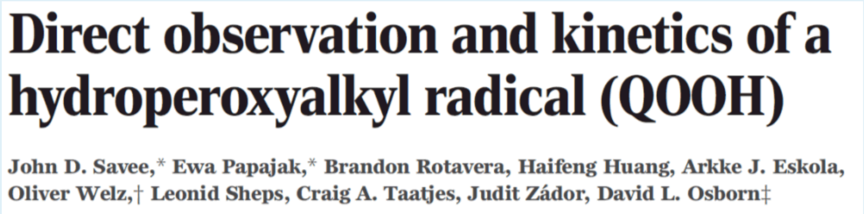
ring opening – $\tau \sim 15$ ns

$1/\tau$ = rate = $10^{12} \exp(-\Delta G^*/kT)$ (s)

$\Delta G^* \sim \Delta E^* \sim<1$ eV
< 1 hour reaction time
"within battery timescale"

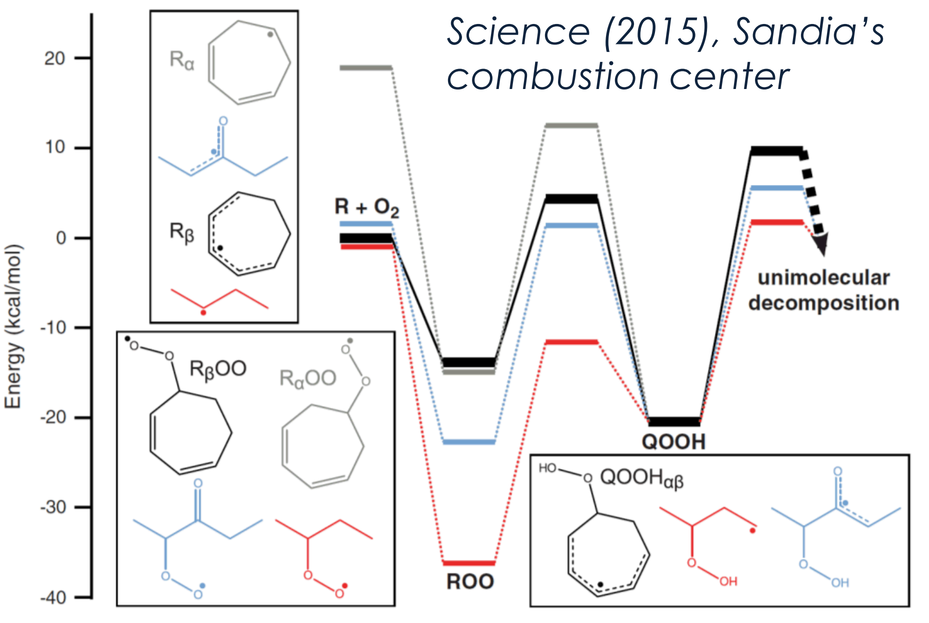
- So, in situ measurement = good
- But experimental platform can seldom span 10^{10} time scales
- Computation really economical at yield reaction time scales

- Screamingly obvious?
- Other scientific communities apply this



Direct observation and kinetics of a hydroperoxyalkyl radical (QOOH)

John D. Savee,* Ewa Papajak,* Brandon Rotavera, Haifeng Huang, Arkke J. Eskola, Oliver Welz,† Leonid Sheps, Craig A. Taatjes, Judit Zádor, David L. Osborn‡



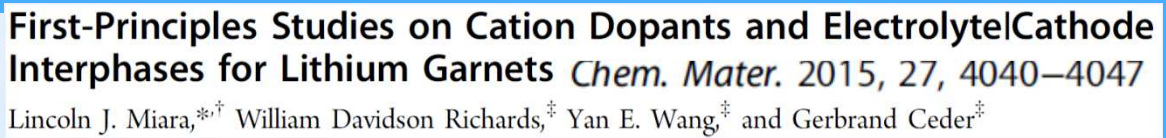
Science (2015), Sandia's combustion center

Fig. 1. Energy landscape for QOOH formation. Computed 0 K stationary point energies relevant to the production of QOOH from R + O_2 for R = 2-butyl (red, derived from *n*-butane) (*25*), 3-oxopent-2-yl (blue, derived from 3-pentanone) (*27*), and 3,5-cycloheptadienyl (gray, R_α) and 2,4-cycloheptadienyl (black, R_β) (both derived from *c*-hpd and calculated in the present work). The different PESs are offset to match at the energy of QOOH. For clarity, slight barriers that may exist in R + O_2 entrance channels are not shown.

- … but battery modeling of ΔG* rare

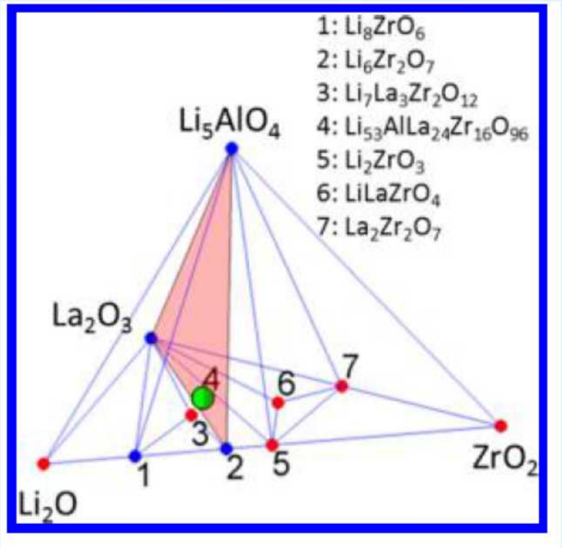
Traditionally battery modeling focuses on materials synthesis

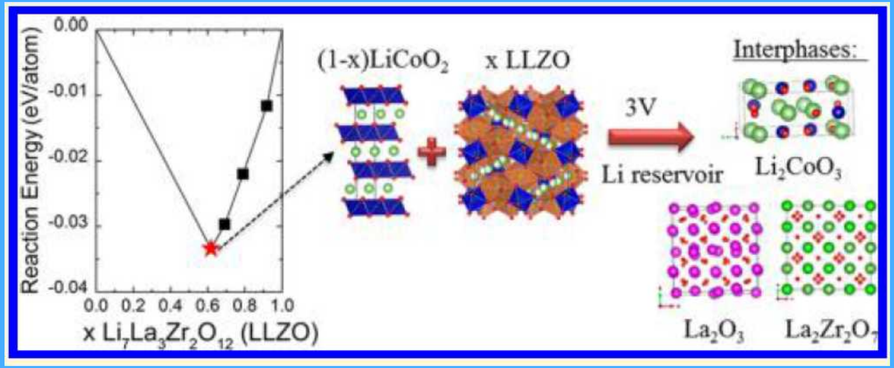
Ceder and coworkers – “materials project, materials genome”



First-Principles Studies on Cation Dopants and Electrolyte|Cathode Interphases for Lithium Garnets *Chem. Mater.* 2015, 27, 4040−4047

Lincoln J. Miara,*[†] William Davidson Richards,[‡] Yan E. Wang,[‡] and Gerbrand Ceder[‡]





Focus is on phase diagrams
(exceptions: Li+ transport, dumbbell defects)

“When tradition thus becomes master, it does so in such a way that what it transmits is made so inaccessible, … it blocks our access to those primordial `sources’ from which the categories and concepts handed down to us have been in part quite genuinely drawn. Indeed it makes us forget that they have had such an origin, and makes us suppose that the necessity of going back to these sources is something which we need not even understand.”

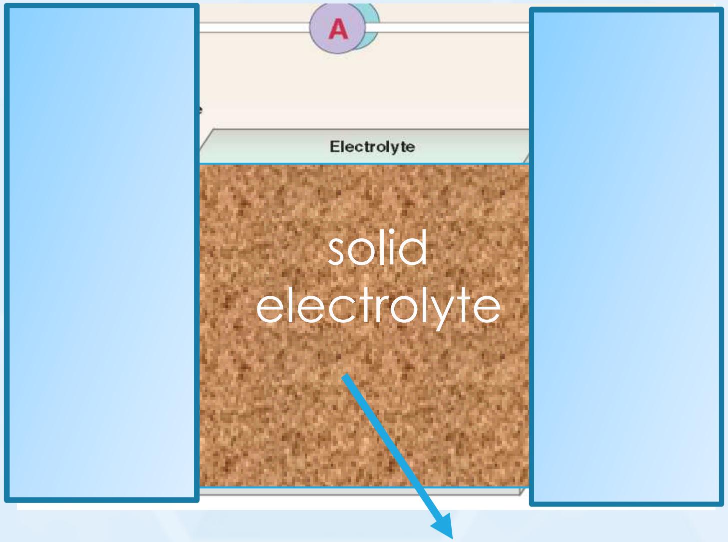
Heidegger, Being and Time (goodread.com)

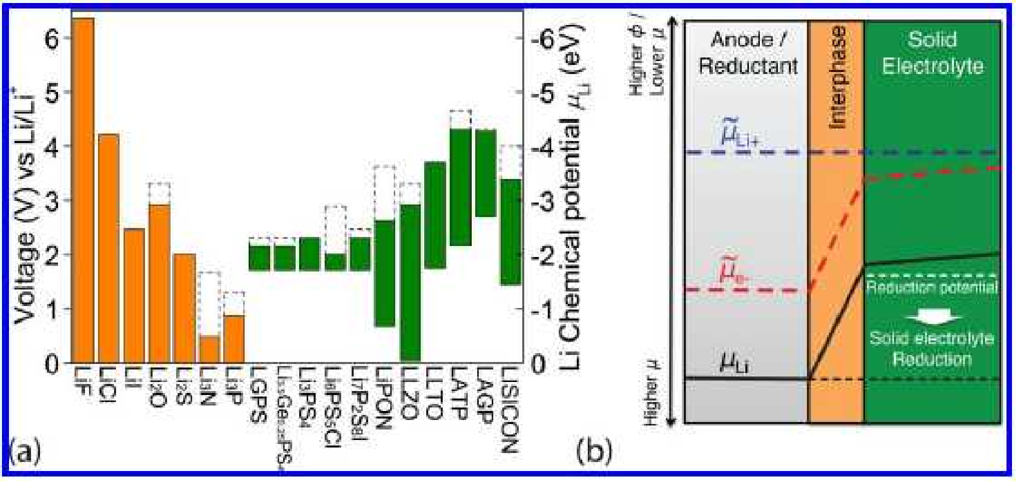
Solid state electrolytes: single phase thermodynamics

Origin of Outstanding Stability in the Lithium Solid Electrolyte Materials: Insights from Thermodynamic Analyses Based on First-Principles Calculations

Yizhou Zhu,† Xingfeng He,† and Yifei Mo*,†,‡

DOI: 10.1021/acsami.5b07517
ACS Appl. Mater. Interfaces 2015, 7, 23685−23693





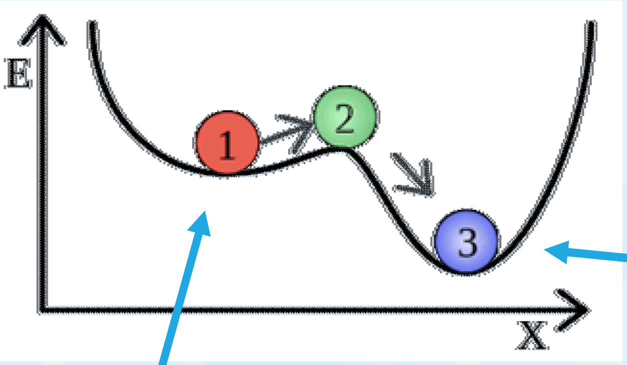
decompose into other phase?

- solid electrolyte stability in all solid state batteries, solid using bulk thermodynamics
- no need to look at explicit interface?
- reasonable because solid interfaces often annealed at high temperature

Reason: materials synthesis occurs at high temperature

e.g., 900 °C for 10 hours

(figure by Georg Wiora)



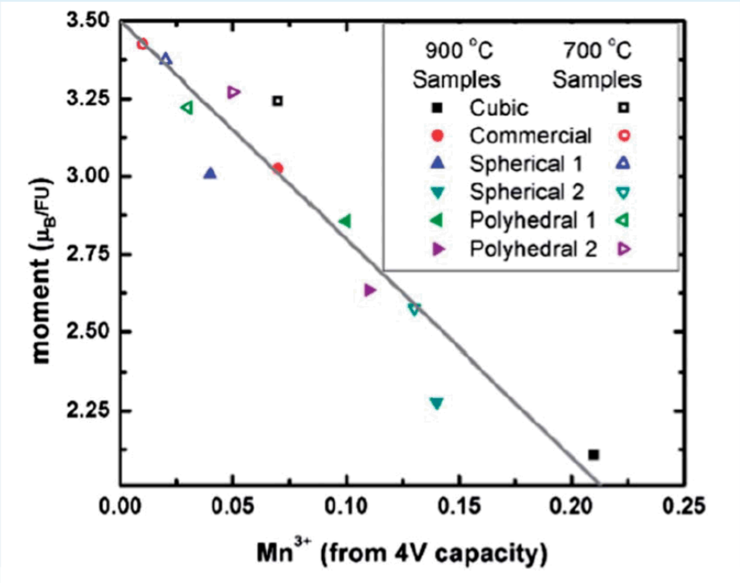
- $1/\tau$ = rate = $10^{12} \exp(-\Delta G^*/kT)$ /s
- If T = 900 °C, 1 hour <-> $\Delta G^* \sim 4$ eV
- Most reactions have barriers << 4 eV
- Reaches most stable phase, thermodynamics rules
- *Time does not exist*

- But even for synthesis, metastability is useful
- Anneal at 700 rather than 900 °C, improves materials

A perspective on the high-voltage $LiMn_{1.5}Ni_{0.5}O_4$ spinel cathode for lithium-ion batteries

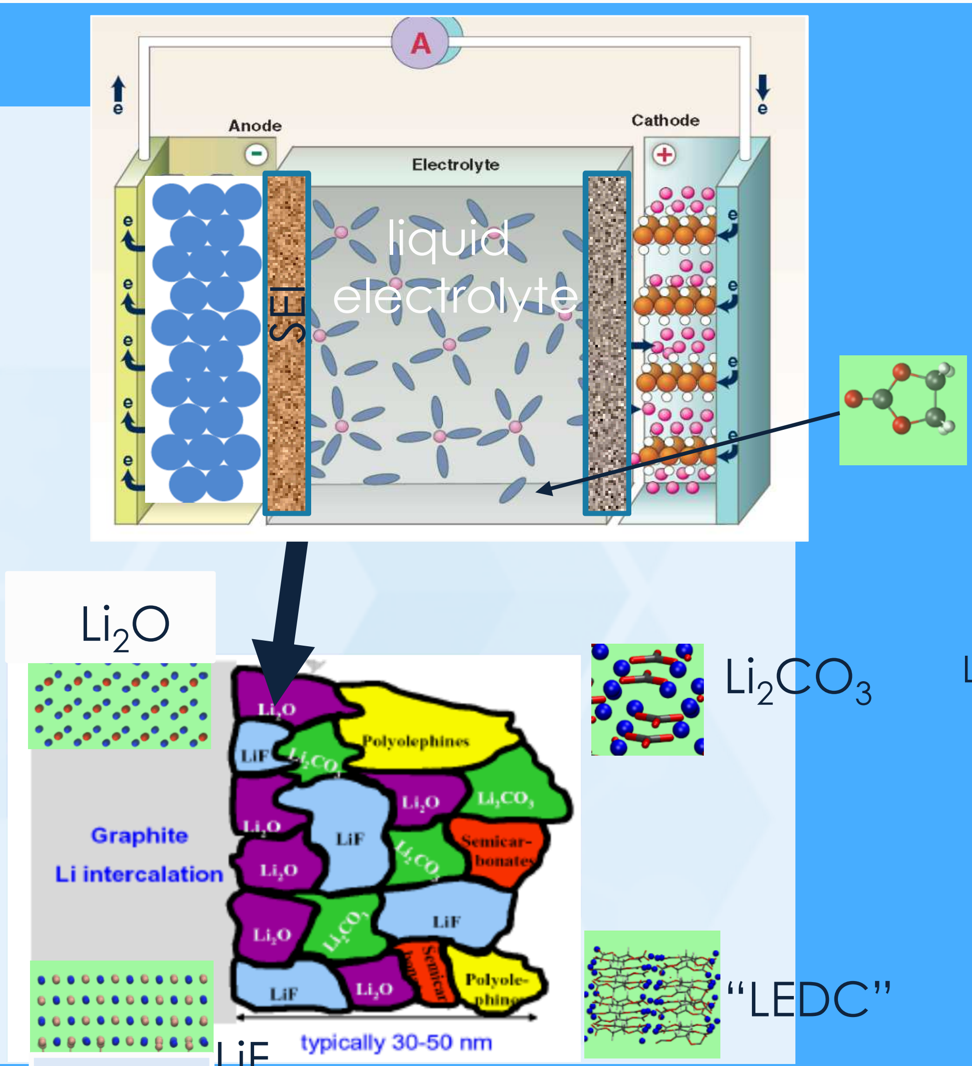
Arumugam Manthiram,* Katharine Chemelewski and Eun-Sung Lee

Energy Environ. Sci., 2014, **7**, 1339–1350



Interface (SEI passivating films) governed by kinetics

inspired by Ceder et al.'s work, did similar calculations for SEI components




Stability of Solid Electrolyte Interphase Components on Lithium Metal and Reactive Anode Material Surfaces

Kevin Leung,*[†] Fernando Soto,[‡] Kie Hankins,[‡] Perla B. Balbuena,[‡] and Katharine L. Harrison[†]

- SEI components thermodynamically unstable, except Li_2O and LiF
- Nevertheless, they are found in expt.
- Thermodynamics fail for SEI films

Li_2CO_3 + 4 Li -> 3 Li_2O + C at < 1.29 V vs. Li^+/Li (s)

reason – C(+IV) right next to Li metal!

$Li_2C_4H_4O_6$ ("LEDC") + 10 Li -> 6 Li_2O + 4 C + 3 H_2

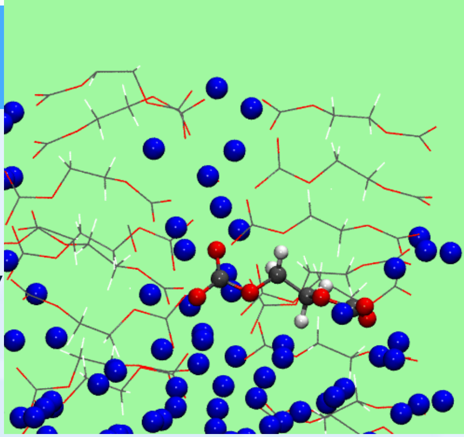
at < 1.22 eV vs. $Li^+/Li(s)$

Hypothesis: instability can manifest itself on reactive anode surfaces

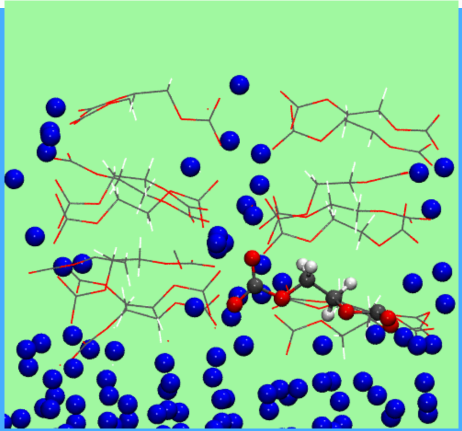
LEDC kinetically unstable at Li (100), a-Si interfaces

3-layer LEDC
on Li

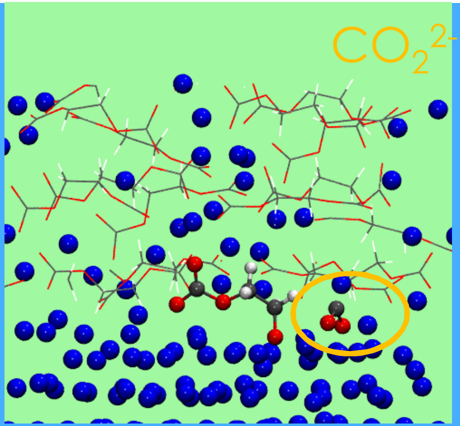
V_e ~ -0.21 V
vs. $Li^+/Li(s)$



$\Delta E = 0.00$ eV



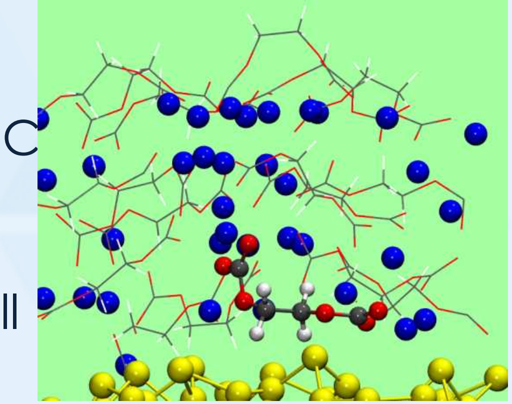
$\Delta E^* = 0.27$ eV



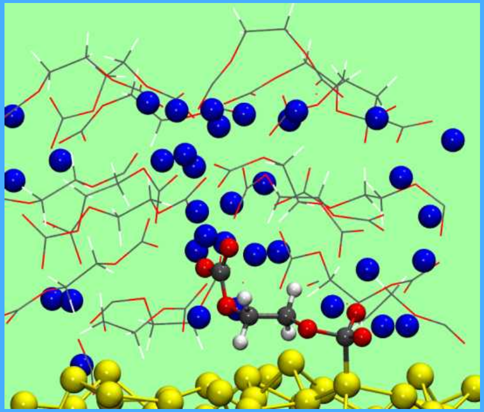
$\Delta E = -2.10$ eV

3-layer LEDC
on a-Si

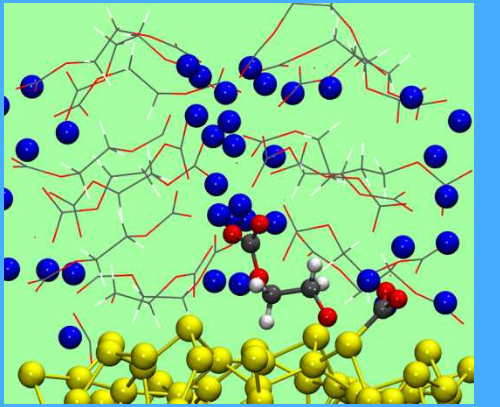
V_e not well
defined



$\Delta E = 0.00$ eV



$\Delta E^* = 0.77$ eV



$\Delta E = -0.18$ eV

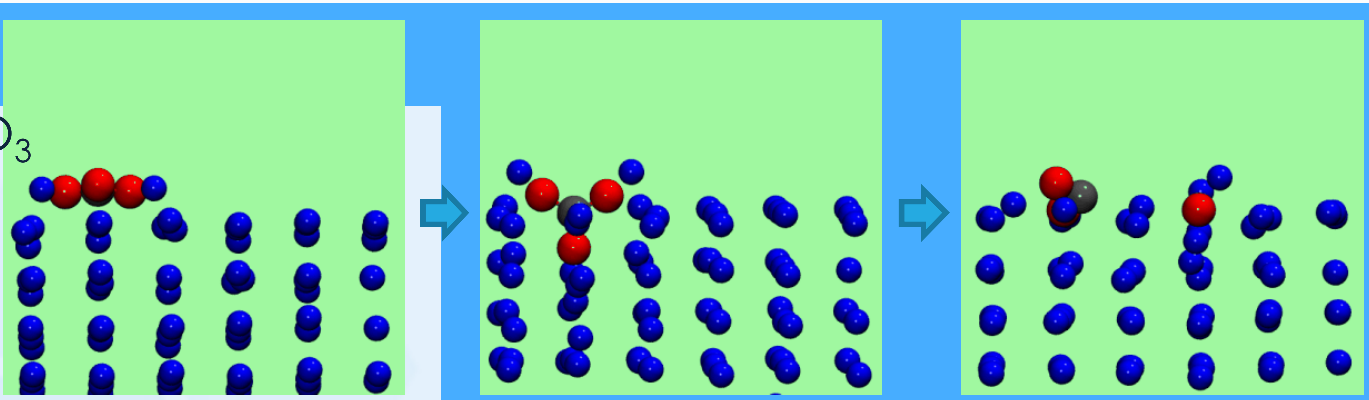
Leung, Soto, Hankins, Balbuena, Harrison, J. Phys. Chem. C (2016)

Li_2CO_3 unstable on Li (100) surface, barrier marginal

- unstable if reaction exothermic and barrier <= 1 eV (< 10 hour reaction time)

single Li_2CO_3

V_e ~ 1.56 V vs. $Li^+/Li(s)$



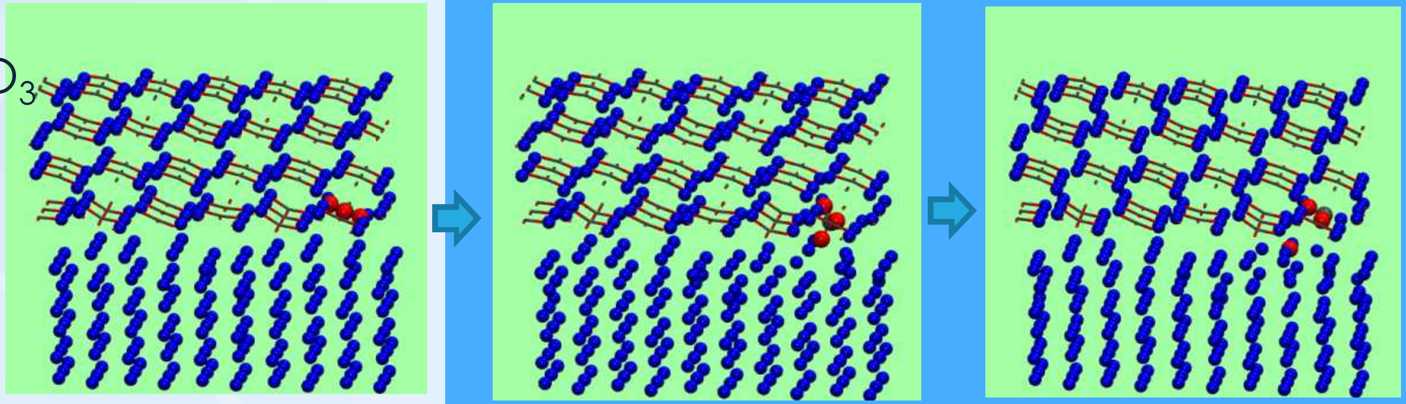
$\Delta E = 0.00$ eV

$\Delta E^* = 1.01$ eV

$\Delta E = -0.64$ eV

4-layer Li_2CO_3

V_e ~ 0.61 V vs. $Li^+/Li(s)$

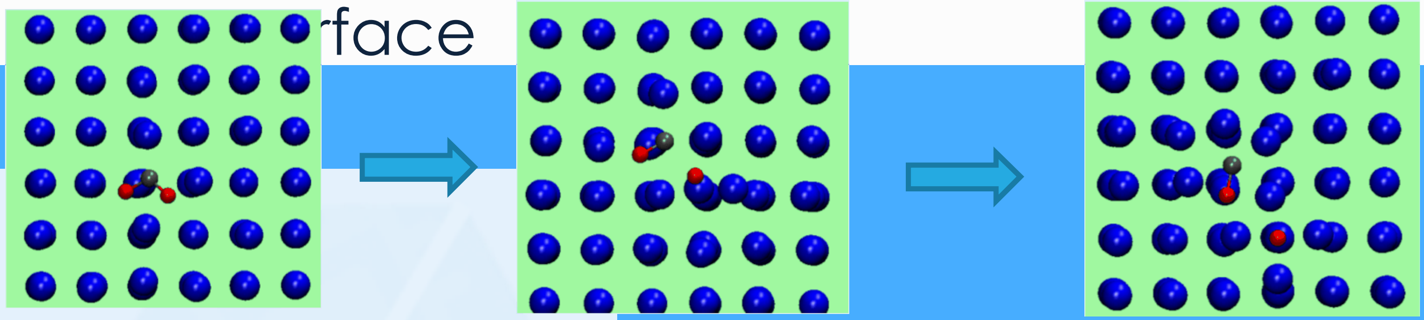


$\Delta E = 0.00$ eV

$\Delta E^* = 0.97$ eV

$\Delta E = -0.99$ eV

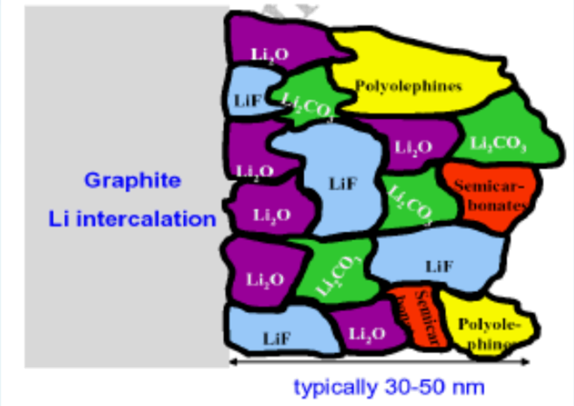
CO$_2$ further decomposes on Li (100) rface

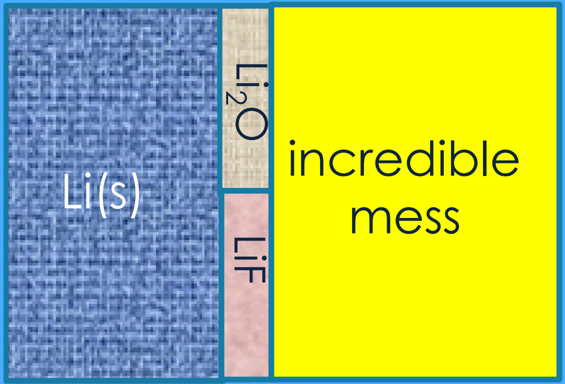


CO$_2$ -> CO: ΔE* = 0.78eV ΔE = -0.97 eV

- Previous AIMD simulations of CO on Li(100) reveal decomposition into C and O
- "C" then forms "Li$_x$C", perhaps ultimately graphite

Destruction of SEI components -> simplification of interface

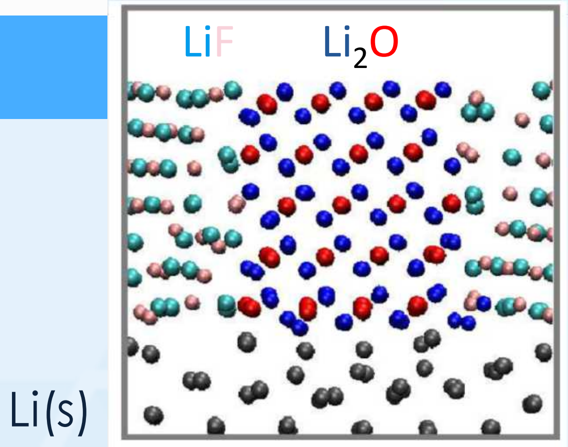


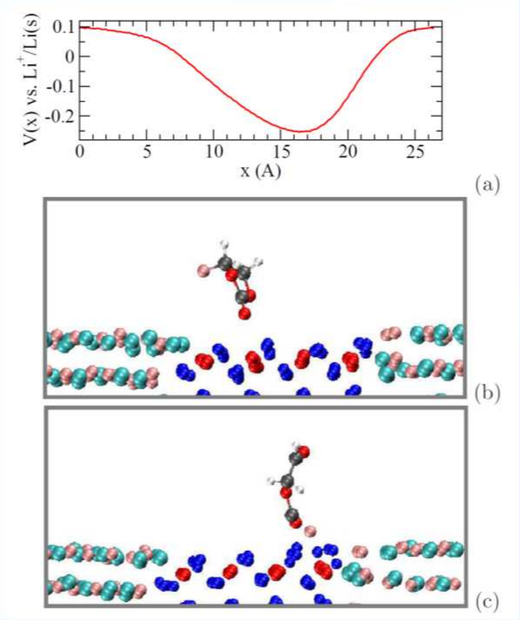


Some clarity in most important interface region

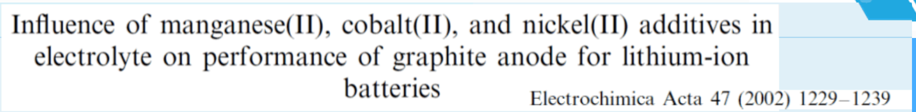
Where this paradigm leads:

hot spots, surface heterogeneities





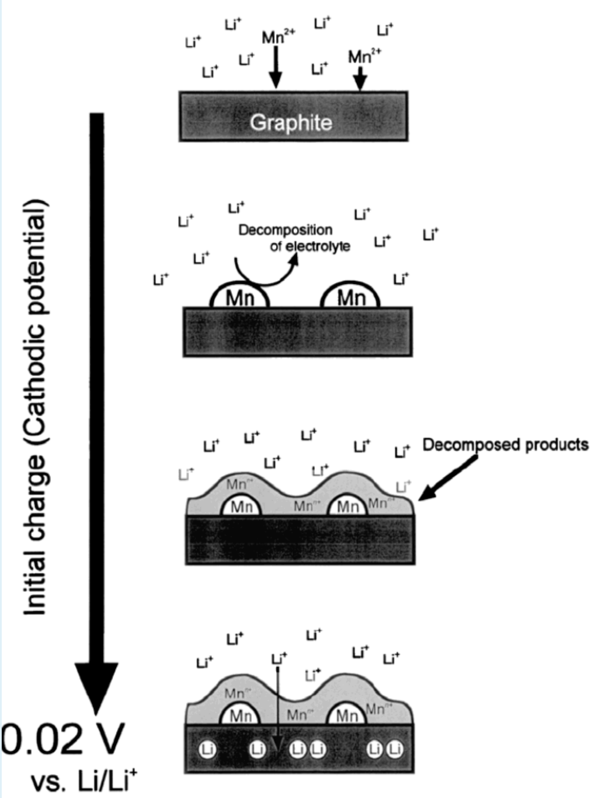
Mn(II) induced SEI disruption

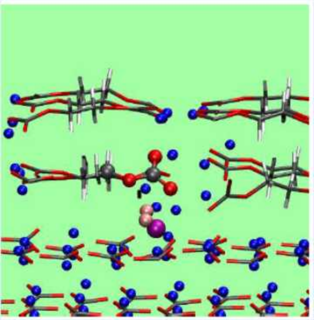


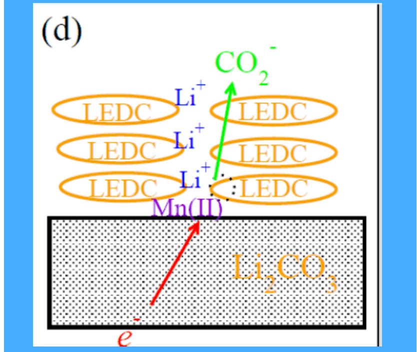
Influence of manganese(II), cobalt(II), and nickel(II) additives in electrolyte on performance of graphite anode for lithium-ion batteries

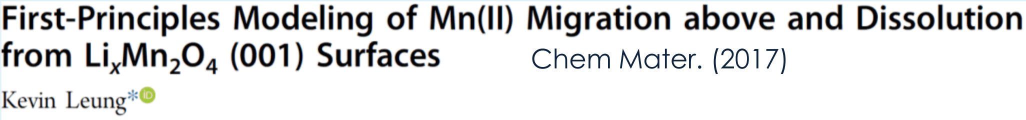
Electrochimica Acta 47 (2002) 1229–1239

(Thanks to Yue for the reference)









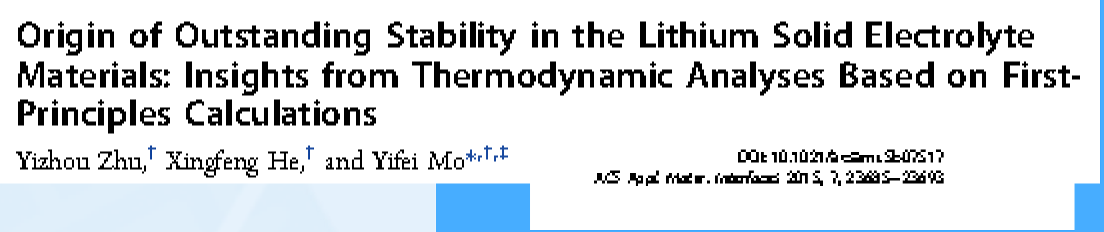
First-Principles Modeling of Mn(II) Migration above and Dissolution from $Li_xMn_2O_4$ (001) Surfaces

Kevin Leung*

Chem Mater. (2017)

the price you pay for metastability

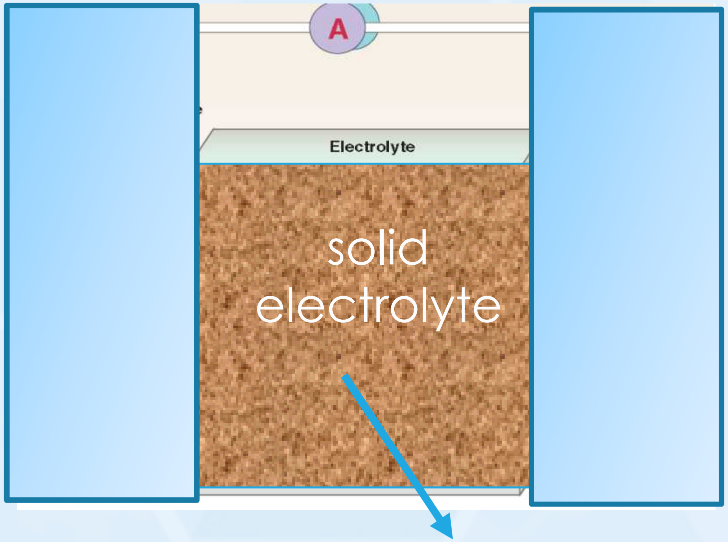
Solid state electrolytes: single phase thermodynamics

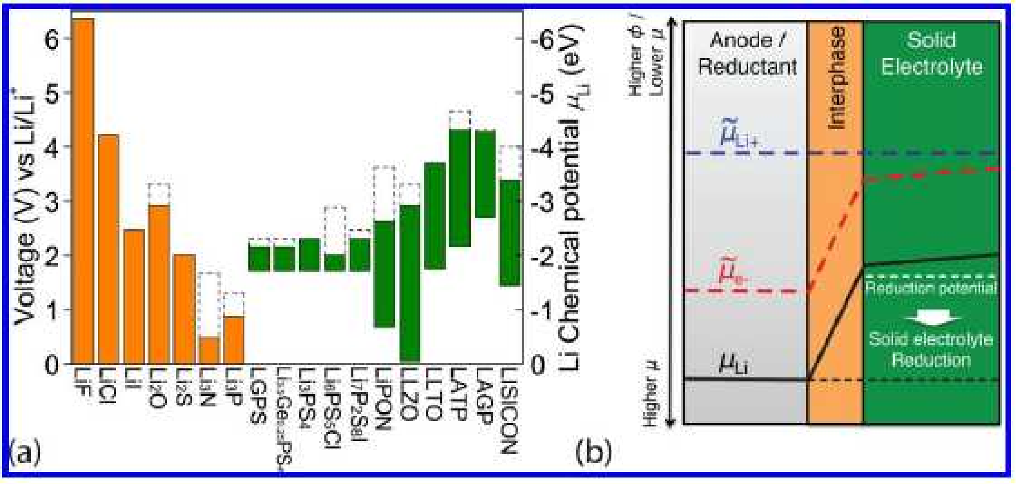


Origin of Outstanding Stability in the Lithium Solid Electrolyte Materials: Insights from Thermodynamic Analyses Based on First-Principles Calculations

Yizhou Zhu,[†] Xingfeng He,[†] and Yifei Mo[*,†,‡]

DOI: 10.1021/acsami.5b07517
ACS Appl. Mater. Interfaces 2015, 7, 23685−23693



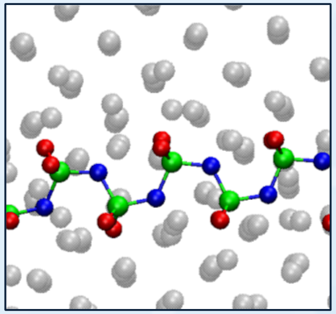


decompose into other phase?

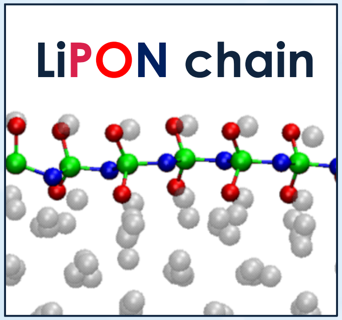
- solid electrolyte stability in all solid state batteries, solid using bulk thermodynamics
- no need to look at explicit interface?
- reasonable because solid interfaces often annealed at high temperature

Going full circle: looking at reaction barriers at solid-solid interfaces

(apply liquid interface techniques to solid electrolyte interfaces)



top view

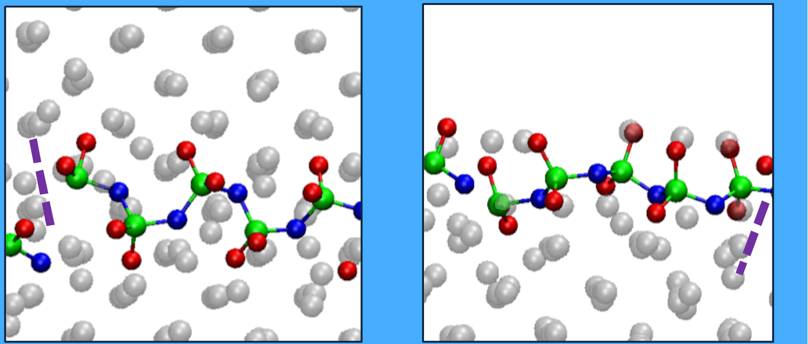


side view

break P-N

ΔE=-1.96 eV

ΔE*=1.37 eV



Some Notes on Electrostatics

Need extreme care when dealing long-range electrostatics
in periodic boundary conditions (PBC) simulation cells

Monopole, dipole, quadrupole corrections

- charged simulation cell:

monopole (+ quadrupole) correction

Periodic boundary conditions in *ab initio* calculations

G. Makov and M. C. Payne

PHYSICAL REVIEW B 51 4014

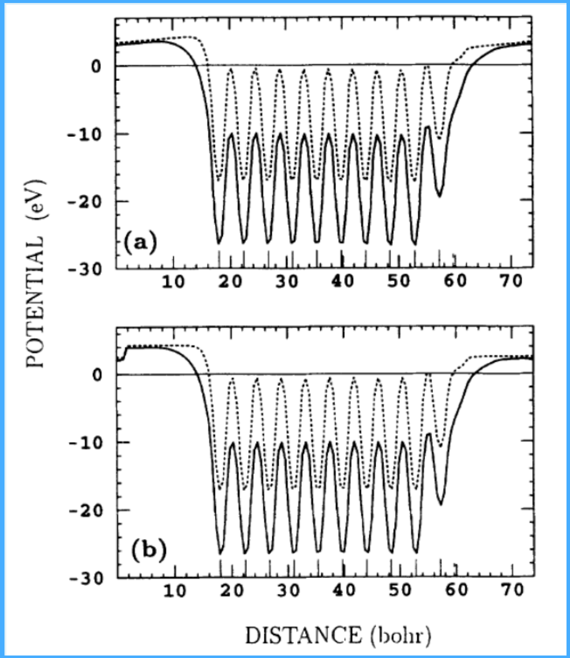
$$E = E_0 - \frac{q^2\alpha}{2L} - \frac{2\pi q Q}{3L^3} + O(L^{-5})$$

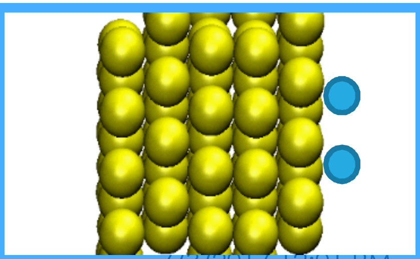
- In chemistry, see L.R. Pratt et al.
- for homogenous systems

Uncharged cell with vacuum layer:

dipole correction for slab geometries

only charge neutral cells





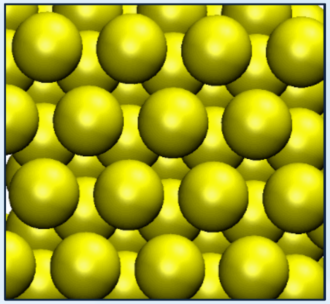
Adsorbate-substrate and adsorbate-adsorbate interactions of Na and K adlayers on Al(111)

Jörg Neugebauer and Matthias Scheffler

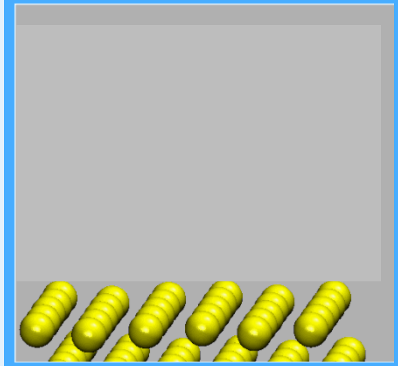
PHYSICAL REVIEW B 46 16 067

Mean electropotential is undefined

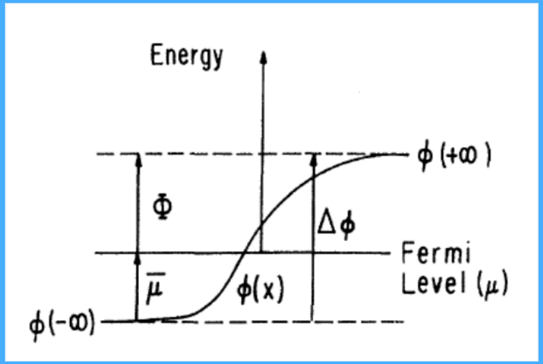
- average electrostatic potential in simulation cell (the **k**=0 contribution to Ewald summation used in PBC DFT), is always set to zero
- So absolute Fermi level E_F in simulation cell is undefined!
- If we have vacuum region, can assign potential in vacuum to zero
- This allow an absolute reference and yields work function, and voltage



bulk crystal simulation cell: E_F, work function are undefined



defined for metals with interfaces



N.D. Lang & W. Kohn, Theory of Metal Surfaces: Work Function PRB 3, 1215 (1971)

- Not really useful for small polaron systems like transition metal oxide

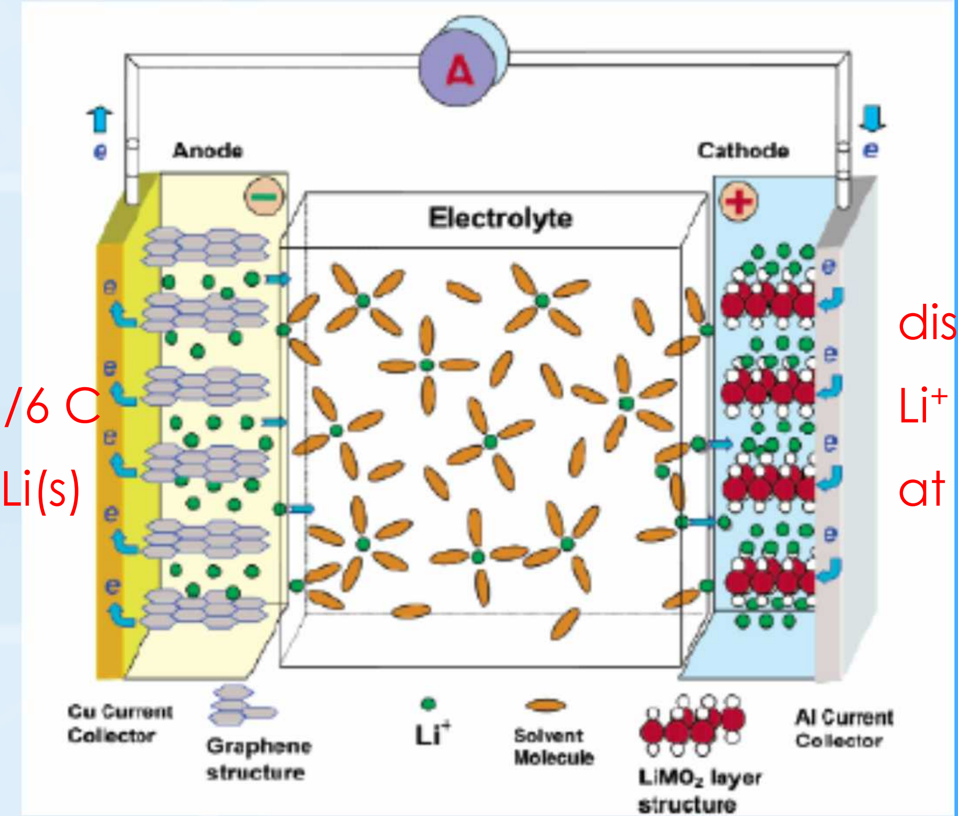
Computing and Controlling Voltages

- At battery interfaces, everything depend on voltage
- So far our ability to model voltage dependences are limited

Leung & Teneny, J. Phys. Chem. C 117:24224 (2013);
Leung, Phys. Chem. Chem. Phys. 17, 1637 (2015)
Leung & Leenheer, J. Phys. Chem. C 119:10234 (2015)

Current lithium current batteries

Anode || electrolyte || cathode



(… also separator membrane,
binders, carbon black …)

discharge:

LiC_6 -> Li^+ + e^- + 1/6 C

at >= 0.1 V vs. $Li_+/Li(s)$

discharge:

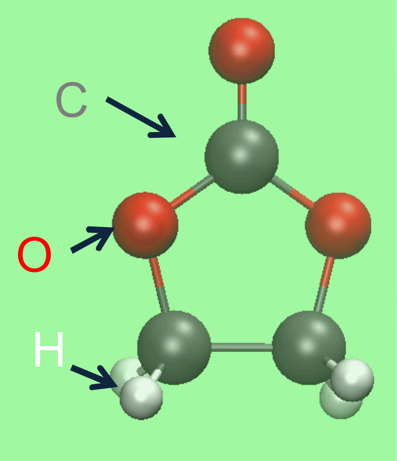
Li^+ + e^- + Li_xCoO_2 -> $LiCoO_2$

at <= 4.0-4.2 V vs. $Li_+/Li(s)$

Battey Interfaces

Li into anode: ~ 0.1 V; Li into cathode: > 3.5 V
EC decomposes: > 4.5 V or 6.6 V(?) (cathode)

- At <0.8 V (vs. $Li^+/Li(s)$), EC-based electrolyte decomposes on anode

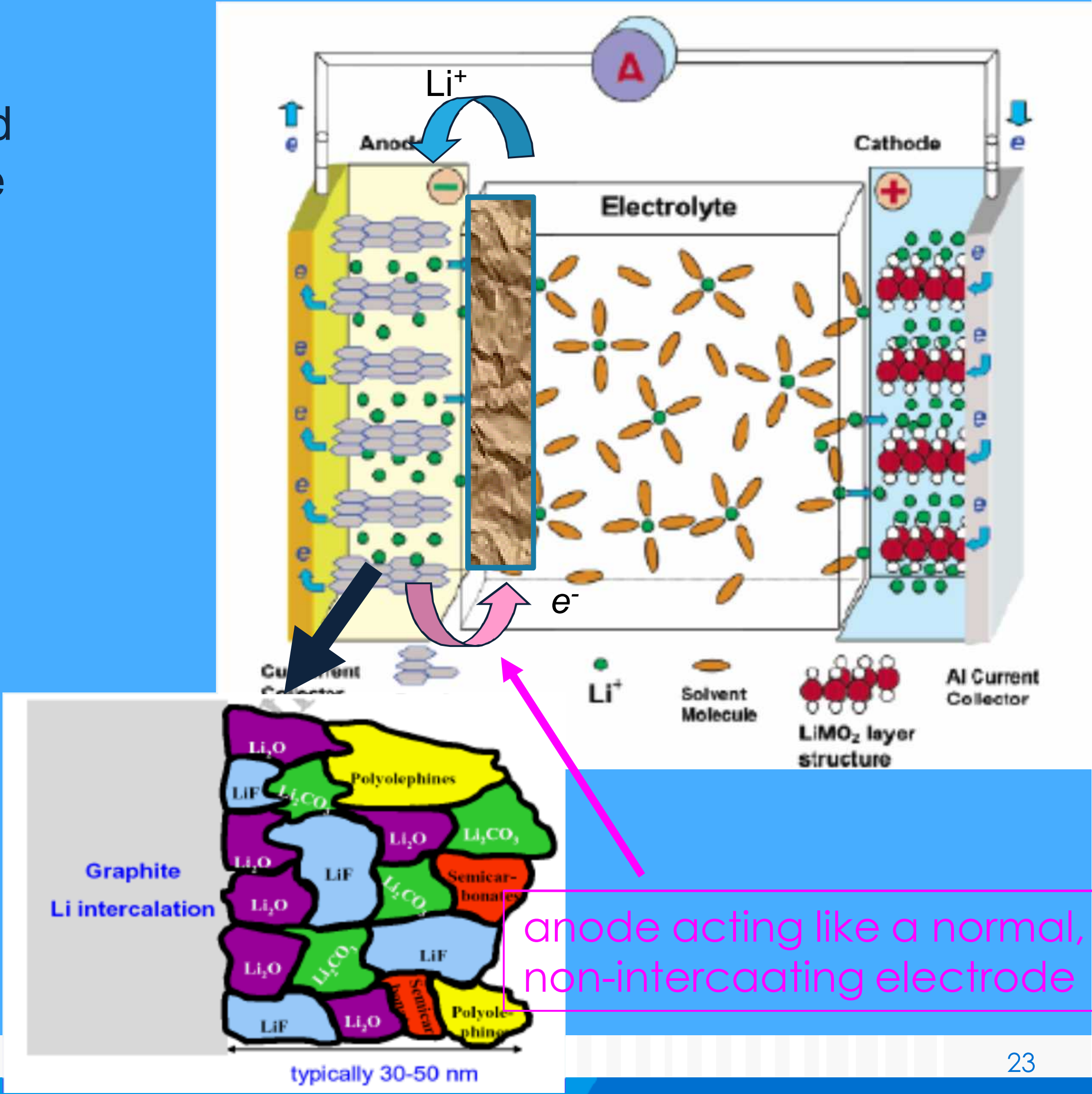


ethylene carbonate (EC)

- self-limiting SEI growth stops further electrolyte breakdown

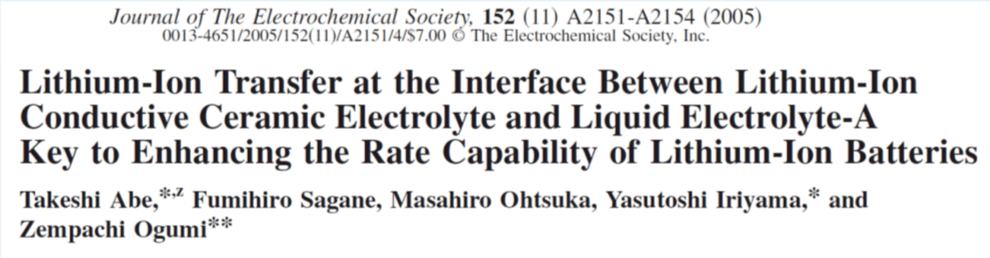
Xu, Chem. Rev. 104:4303 (2004)

- search for alternatives continue



anode acting like a normal, non-intercaating electrode

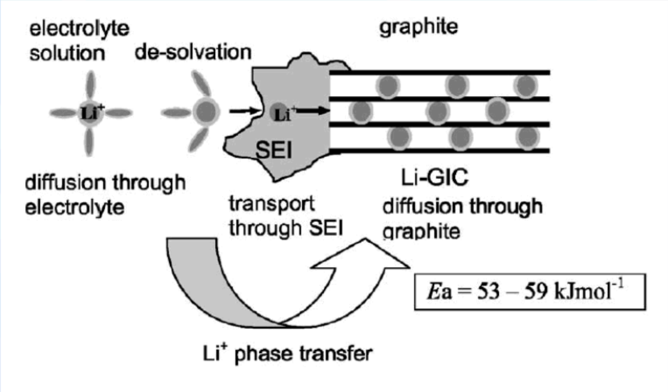
Want to predict Li^+ transfer rate from electrolyte into electrode

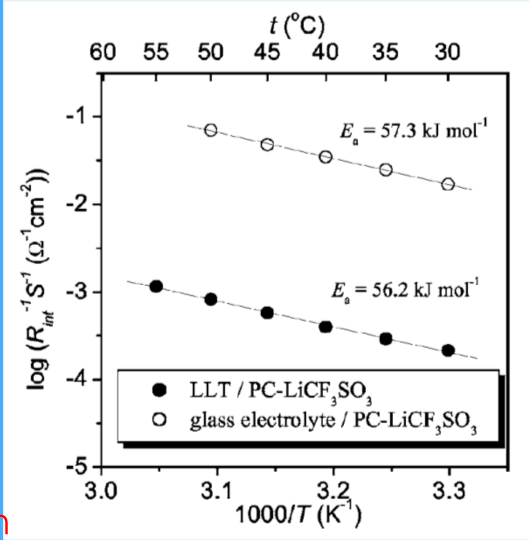


Journal of The Electrochemical Society, **152** (11) A2151-A2154 (2005)
0013-4651/2005/152(11)/A2151/4/$7.00 © The Electrochemical Society, Inc.

Lithium-Ion Transfer at the Interface Between Lithium-Ion Conductive Ceramic Electrolyte and Liquid Electrolyte-A Key to Enhancing the Rate Capability of Lithium-Ion Batteries

Takeshi Abe,*,z Fumihiro Sagane, Masahiro Ohtsuka, Yasutoshi Iriyama,* and Zempachi Ogumi**



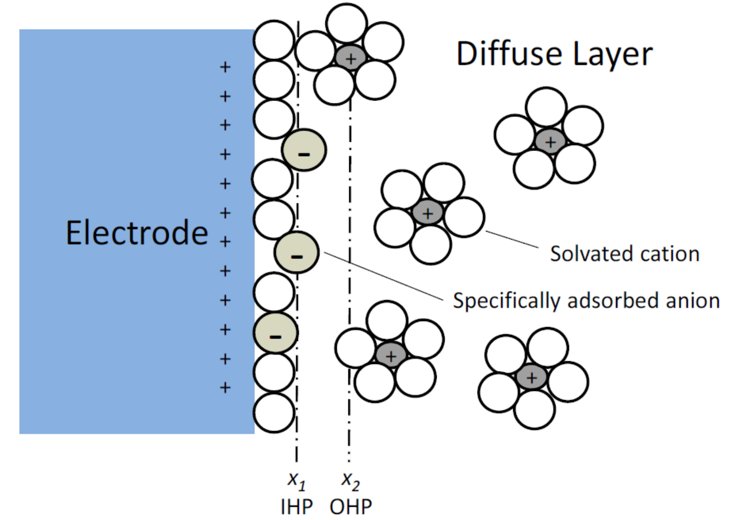


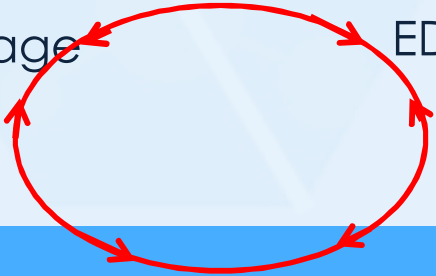
modeling-wise, we are not there yet.

1. electrode surface not pristine; SEI structure not known
2. voltage dependence hard to calibrate

What is “voltage” at atomic lengthscale?

voltage “=“ Fermi level + electric double layer





voltage

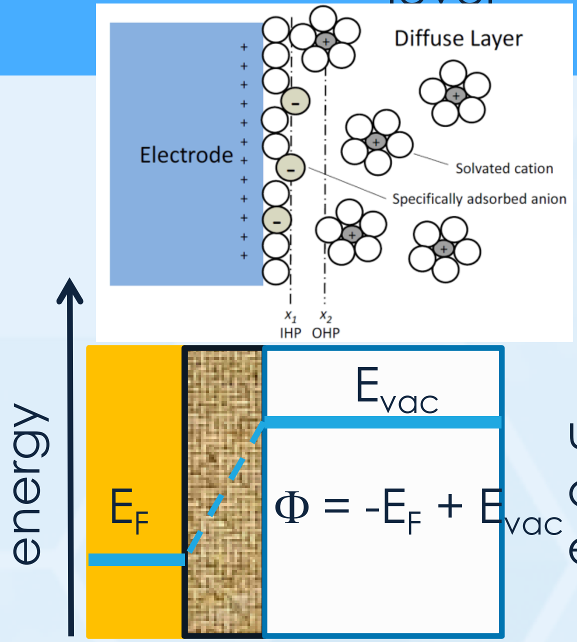
EDL (fancy way of saying there is a dipole layer)

$$\Delta \mathcal{V}_e = -4\pi\delta/(|e|)$$

surface dipole

Voltages: DFT calculations vs. expt.

DFT modeling: one electrode/Fermi level

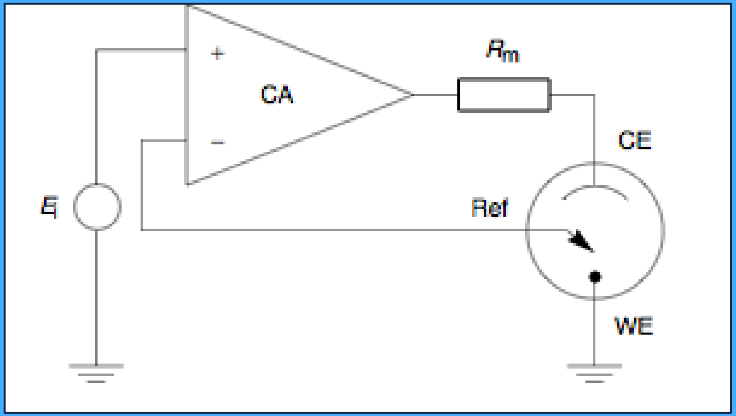


use vacuum as reference electrode

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

(using $Li^+/Li(s)$ reference; for $H^+/H2O$, 4.44 V)

Experiments: >2 electrodes/Fermi levels



Potentiostat controls .electronic voltage $\mathcal{V}_e$

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

In the battery modeling, voltage means something else

PHYSICAL REVIEW B **70**, 235121 (2004)

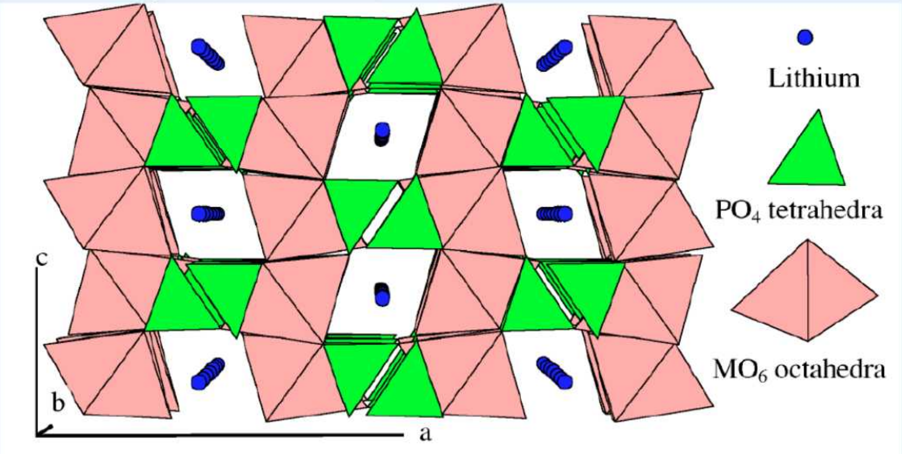
First-principles prediction of redox potentials in transition-metal compounds with LDA+*U*

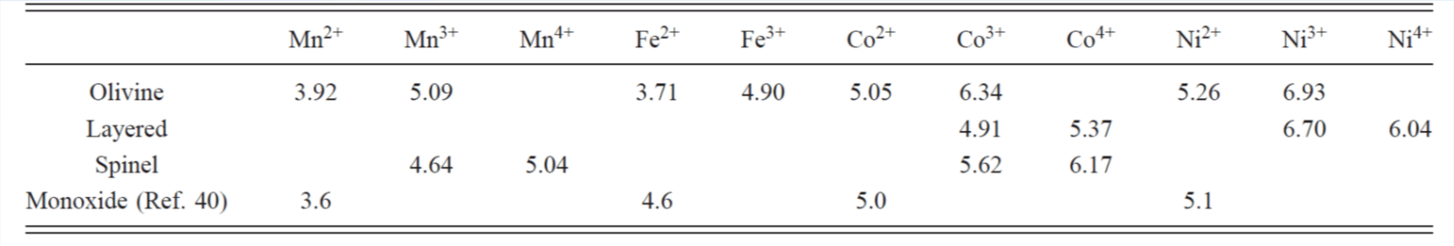
F. Zhou M. Cococcioni, C. A. Marianetti, D. Morgan, and G. Ceder

$$\Delta x\,\mathrm{Li} + \mathrm{Li}_x\mathrm{MO}_y \Leftrightarrow \mathrm{Li}_{x+\Delta x}\mathrm{MO}_y,$$

$$V(x) = -\frac{\mu^{\mathrm{cathode}}_{\mathrm{Li}(x)} - \mu^{\mathrm{anode}}_{\mathrm{Li}}}{F}.$$

$$\langle V\rangle = \frac{-[E(\mathrm{Li}_{x_2}\mathrm{MO}_y) - E(\mathrm{Li}_{x_1}\mathrm{MO}_y) - (x_2 - x_1)E(\mathrm{Li\ metal})]}{(x_2 - x_1)F}$$



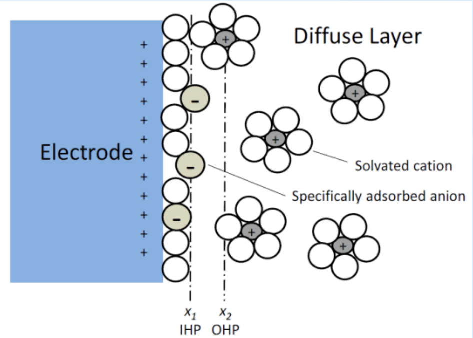


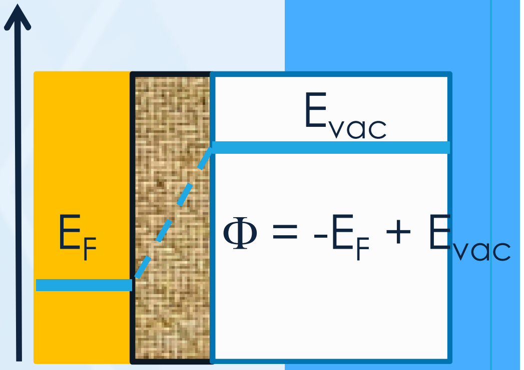
	Mn^{2+}	Mn^{3+}	Mn^{4+}	Fe^{2+}	Fe^{3+}	Co^{2+}	Co^{3+}	Co^{4+}	Ni^{2+}	Ni^{3+}	Ni^{4+}
Olivine	3.92	5.09		3.71	4.90	5.05	6.34		5.26	6.93	
Layered							4.91	5.37		6.70	6.04
Spinel		4.64	5.04				5.62	6.17			
Monoxide (Ref. 40)	3.6			4.6		5.0			5.1		

- Simulation cell has no vacuum level
- Fermi level not defined
- Voltage is here defined via Li chemical potential

LIB: Two voltage definitions: electronic vs. "ionic" voltage (rest of the world vs. battery literature)

fuel cell, PV supercapactiors: voltage is electronic, interfacial

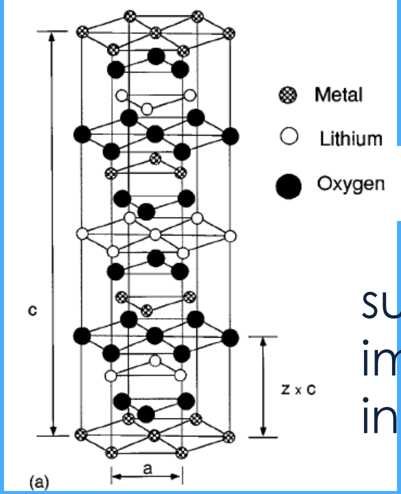




$$\mathcal{V}_e = \Phi/|e| - 1.37\ \mathrm{V}$$

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!

such calculations implicitly assume an interface supporting $\mathcal{V}_i = \mathcal{V}_e$

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

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

An arbitrary DFT interface is not at electrochemical equilibrium

Experimental analogy: Galvanostatic Intermittent Titration (GITT)

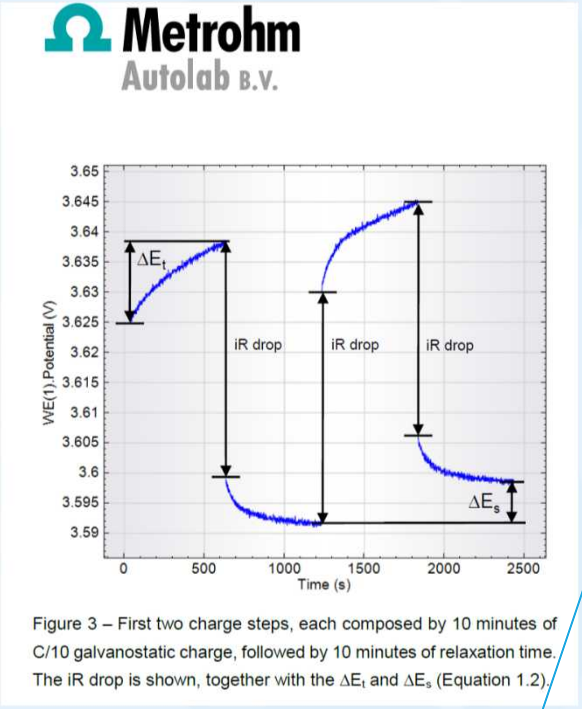


Figure 3 – First two charge steps, each composed by 10 minutes of C/10 galvanostatic charge, followed by 10 minutes of relaxation time. The iR drop is shown, together with the ΔE_t and ΔE_s (Equation 1.2).

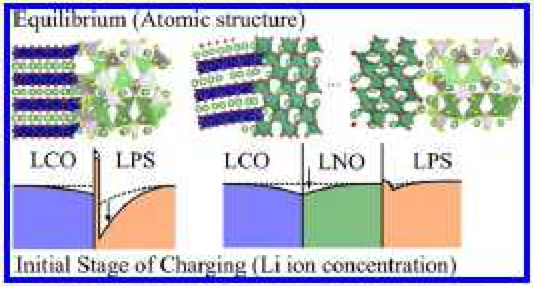
- v_e is the correct instantaneous voltage set by potentiostat
- Li content in solid (or interface) slowly relaxes
- But in DFT calculations, Li hardly move -- little relaxation, system out of equilibrium
- Need to move Li content by hand to make sure we have equilibrium

This confusion about “voltage” occurs in almost all battery interface modeling papers

Space–Charge Layer Effect at Interface between Oxide Cathode and Sulfide Electrolyte in All-Solid-State Lithium-Ion Battery

Jun Haruyama,[†,‡] Keitaro Sodeyama,[†,§] Liyuan Han,[‖,⊥] Kazunori Takada,[†,‡] and Yoshitaka Tateyama*[,†,‡,§,⊥]

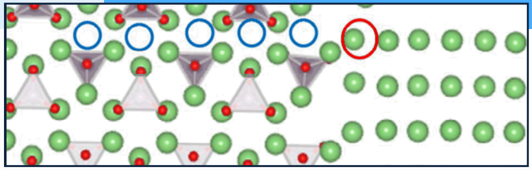
Chem. Mater. 2014, 26, 4248–4255



Electrode-Electrolyte Interface for Solid State Li-Ion Batteries: Point Defects and Mechanical Strain

Santosh KC,[a,z] Roberto C. Longo,[a] Ka Xiong,[a] and Kyeongjae Cho[a,b,*,z]

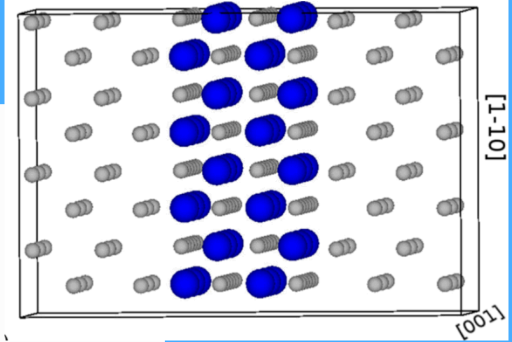
Journal of The Electrochemical Society, **161** (11) F3104-F3110 (2014)



Modeling interfaces between solids: Application to Li battery materials

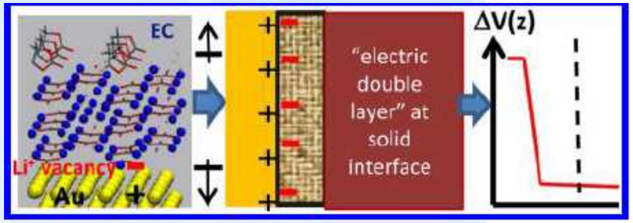
N. D. Lepley and N. A. W. Holzwarth*

PHYSICAL REVIEW B **92**, 214201 (2015)



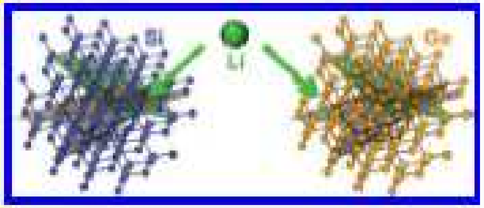
How Voltage Drops Are Manifested by Lithium Ion Configurations at Interfaces and in Thin Films on Battery Electrodes

Kevin Leung* and Andrew Leenheer



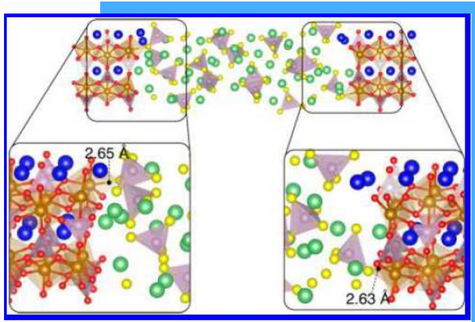
The First-Cycle Electrochemical Lithiation of Crystalline Ge: Dopant and Orientation Dependence and Comparison with Si

Maria K. Y. Chan,[†] Brandon R. Long,[‡] Andrew A. Gewirth,*[,‡] and Jeffrey P. Greeley*[,†]



Charged and Discharged States of Cathode/Sulfide Electrolyte Interfaces in All-Solid-State Lithium Ion Batteries

Masato Sumita,*[,†] Yoshinori Tanaka,[‡] Minoru Ikeda,[†] and Takahisa Ohno*[,†,‡,§]

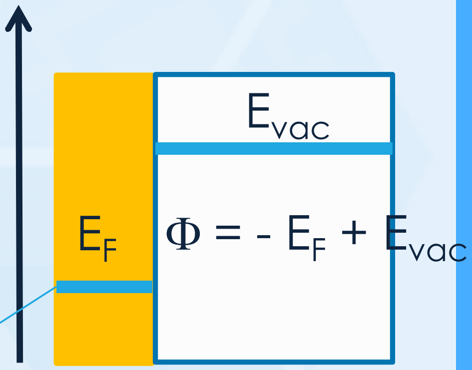


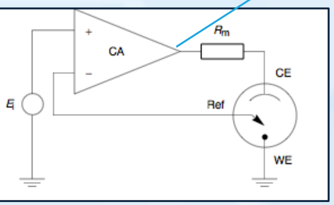
Quiz: what is the "voltage" of Li (100) metal in vacuum?

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

= 1.56 V vs $Li^+/Li(s)$

(Φ = 2.93 eV, CRC handbook)

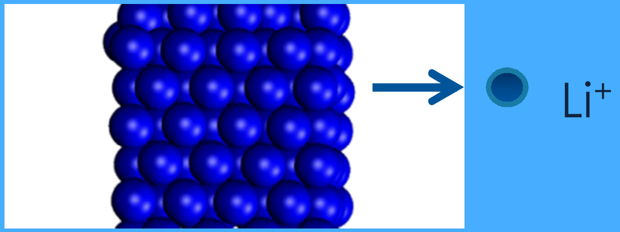




True instantaneous voltage

$$\mathcal{V}_i = (\mu_{\mathrm{Li}} - E_{\mathrm{Li(s)}})/|e|$$

= 0.00 V vs $Li^+/Li(s)$
for $Li(s) \rightarrow Li^+ (solv) + e^-$



Li (100)

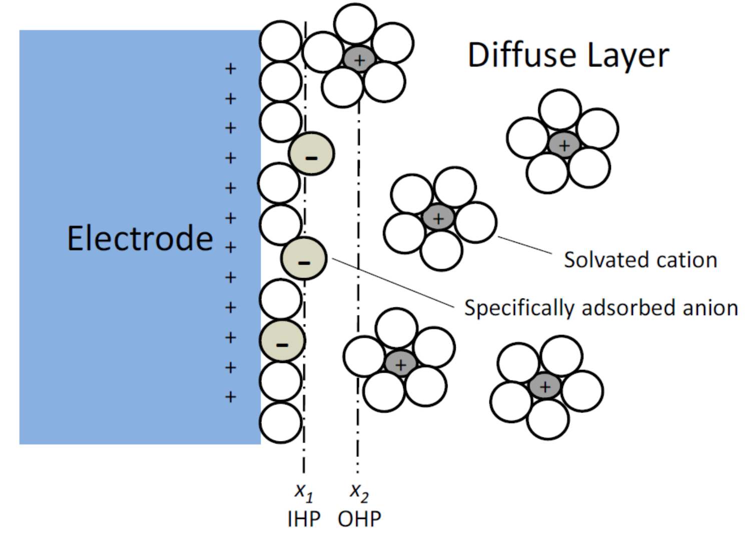
disconnected Li metal is not at electrochemical equilibrium

- $Au^{3+} + 3 e^- \rightarrow Au(s)$ is at 1.52 V vs. SHE
- yet we never assume Au slab is at 1.52 V in DFT calculations
- should not assume Li electrode is always in equilibrium either

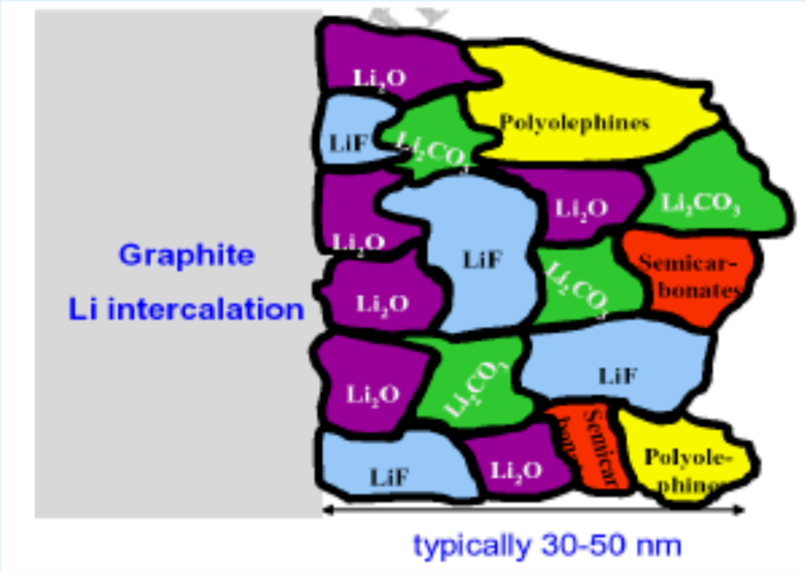
E10

Electric Double Layer (EDL) in lithium ion batteries

pristine electrode
one potential of zero charge (PZC)



LIB electrode
(covered with films)
surface charge? PZC?

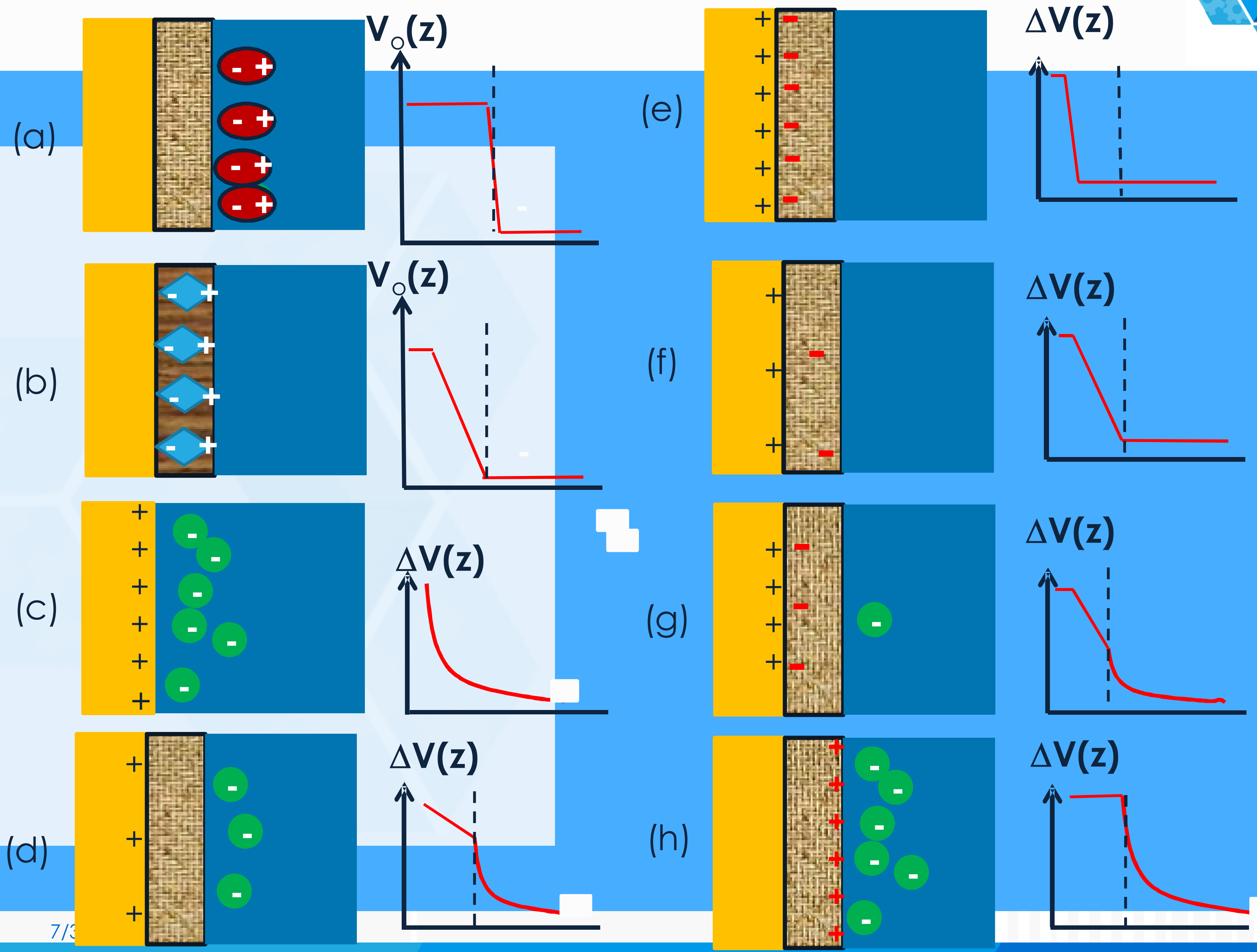


Slide 32

E10 Changed title font for consistency.

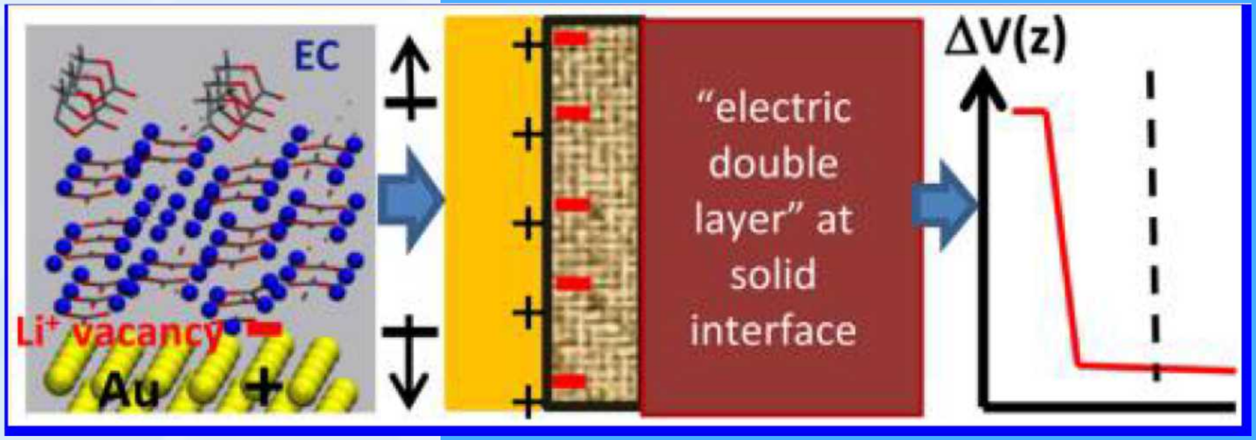
Ernie, 2/10/2012

EDL structures/voltage profiles (liquid outside thin film)



Electrostatic contribution only, ohmic loss not included

(1) Potential drop at solid-solid interfaces

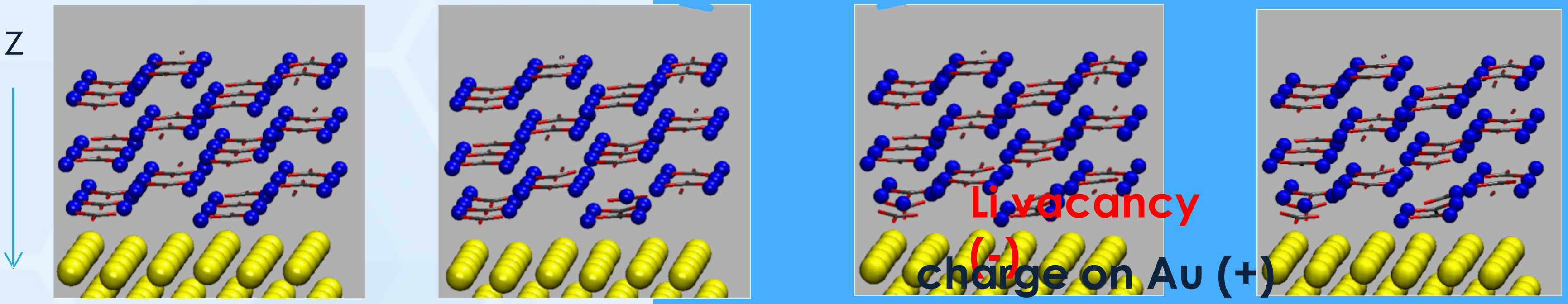


Li_2CO_3 covering Au(111) under UHV conditions

Li_2CO_3 oxidation relevant to Li-air batteries (hysteresis during charging

$\Delta N(\mathrm{Li})$	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	

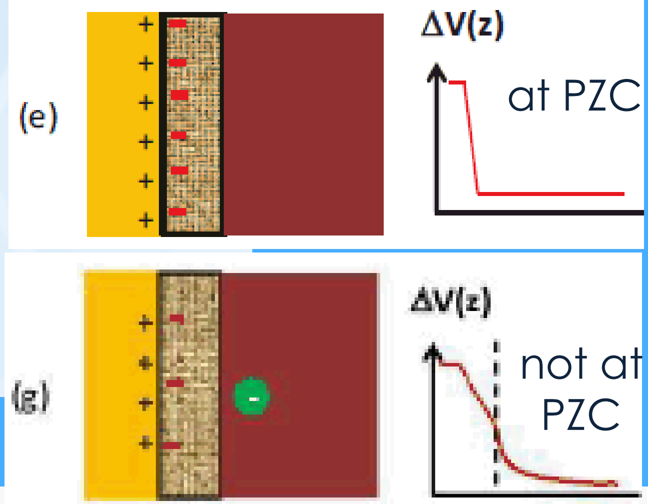
Leung & Tenney, JPCC (to appea



Li vacancy (-)

charge on Au (+)

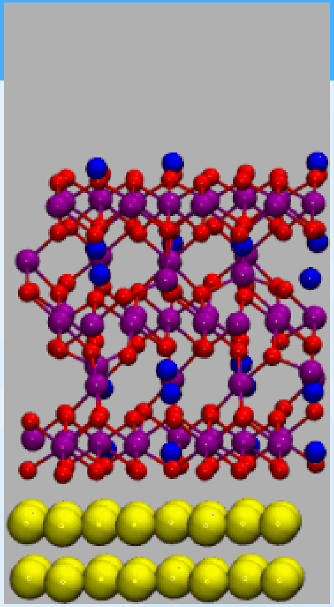
- to "oxidize" Li_2CO_3, remove (e^-, Li^+)
- | Au^+ | V_{Li}^- | surface dipole -> raise $\mathcal{V}_e$
- Only one potential-of-zero-charge at $\mathcal{V}_i = \mathcal{V}_e$



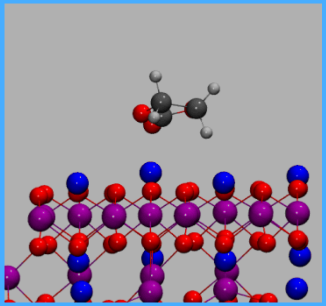
charge separation at interface yields dipole, EDL (c.f. Maier, PRL 2014)

Li vacancies: "space charge" but are mobile (moves to interface) and plentiful

$Li_xMn_2O_4$ (111) on Au(111) “current collector”

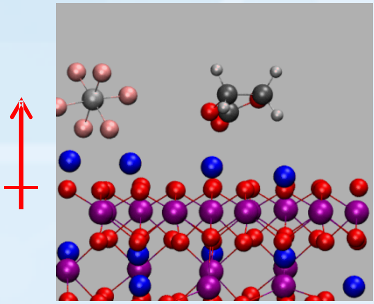


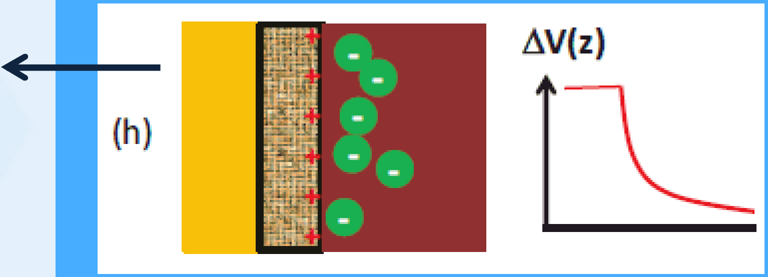
LMO(111) surface: Karim *et al.*, PRB 87:075322 (2013)



In calculations, can mimic expt. with a linear combination of surfaces patches with/without PF_6^-.

V_e = a V’ + (1-a)V’





electronic voltage/Ferm level not so important: LMO is polaronic, not metallic

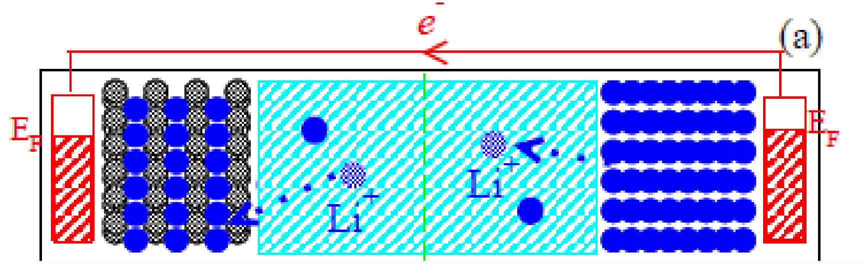
electronic voltage control surface Li-vacancy/anion concentrations, hotspots

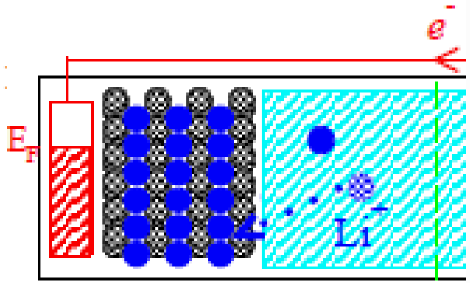
(B) Solid-Liquid Interface

No vacuum! Hard to compute voltage

(pristine electrode, only proof-of-principle)

Our method: Calculating voltage via Li^+ transfer



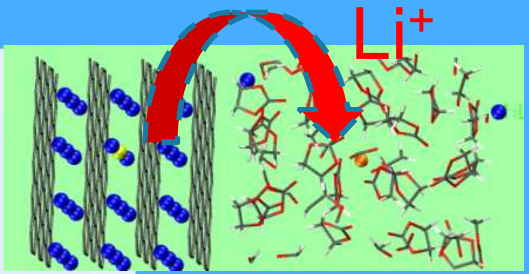


Basal plane work: Leung & Tenney, JPCC 117:24224 (2013)

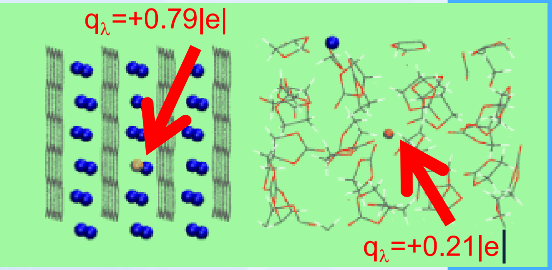
In lithium ion batteries, Li_+ transfer, not just e^- transfer, controls the potential

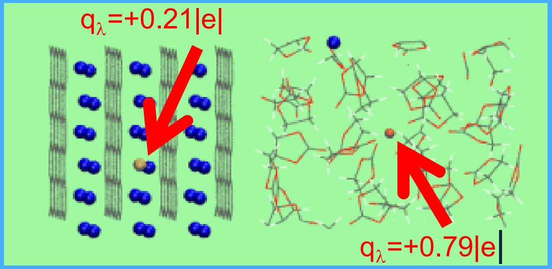
(Our voltage determination method most similar in spirit to Michiel Sprik and coworkers' seminal work for oxide surfaces)

Calculating voltage in lithium ion batteries in charge-neutral cells



$$\Delta G_{\text{hyd}} = \int_0^1 d\lambda \left\langle \frac{dH(\lambda)}{d\lambda} \right\rangle_\lambda$$

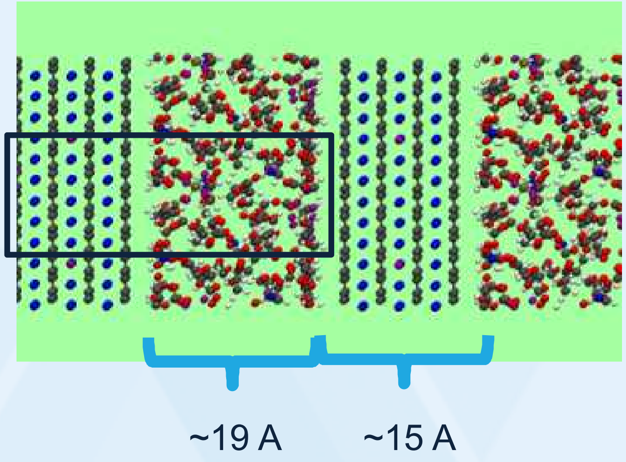




$$\Delta G_t(\text{2 pts}) \sim 0.5 < dH(\lambda)/d\lambda >_{\lambda\,1} + 0.5 < dH(\lambda)/d\lambda >_{\lambda\,2}$$

- moving $Li^{\lambda+}$ into electrolyte leaves λ electron in electrode
- $\Delta G_t = 0$: Li^+ equally likely to be in LiC_6 or in electrolyte (i.e. at ~0.1 V vs Li^+/Li)
- make contact with expt. (don't need vacuum gap for absolute voltage)
- 15-34 ps per simulation window

Nanosized simulation cell details

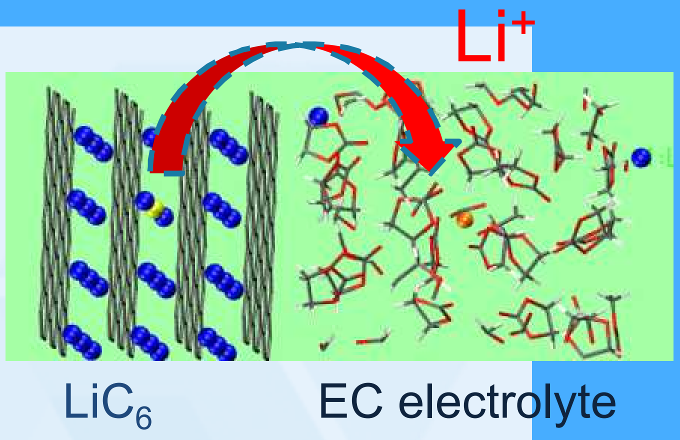


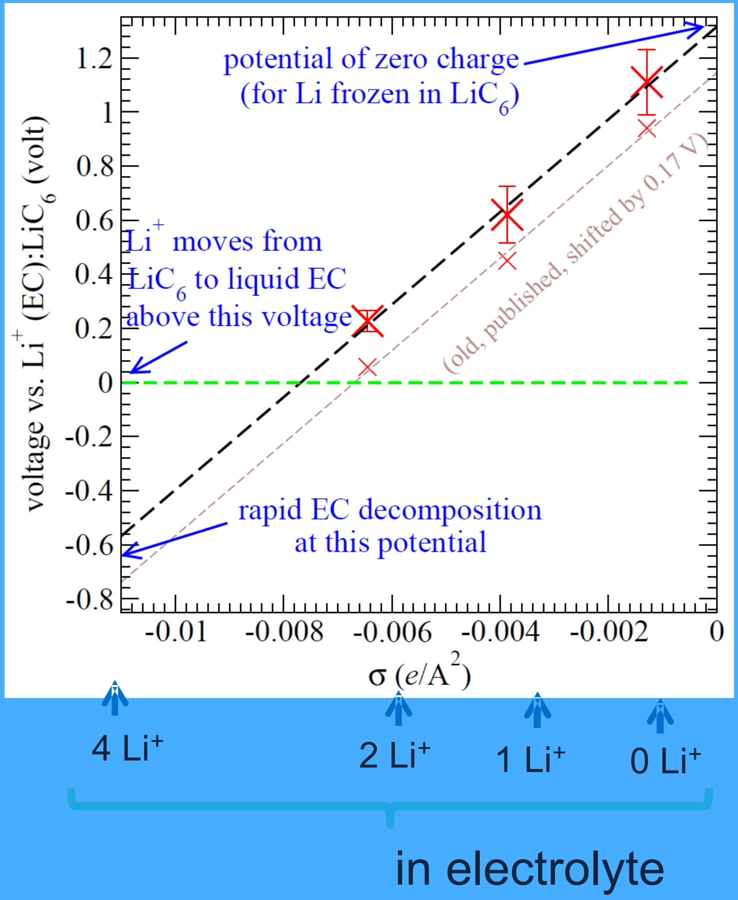
- same simulation cell size to calculate voltage, model electrolyte decomposition
- assume double layer ends at middle of liquid slab (LIB: 1.0 M salt, Debye length ~3 A)
- Method "rigorous" for macroscopic electrochemistry if system size/trajectory length increases

- Put net charge -*n*|*e*| on electrode surfaces, calculate voltages
- *n* excess Li^+ in liquid EC leaves *n* excess e^- in electrode

For aqueous systems, there are alternative methods. See works by Michiel Sprik, Jun Cheng, Giulia Galli, etc.

Calculating voltage drop in batteries via ΔG_t of Li^+ transfer

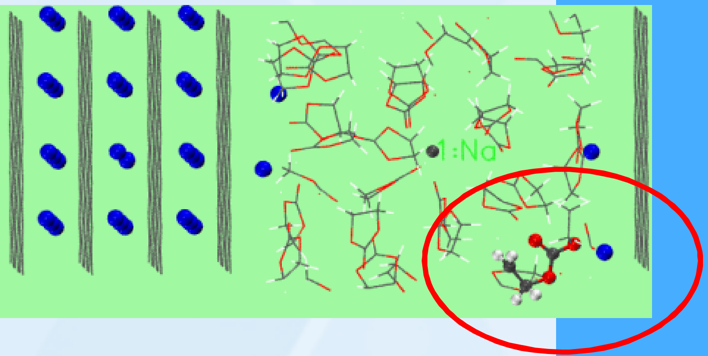


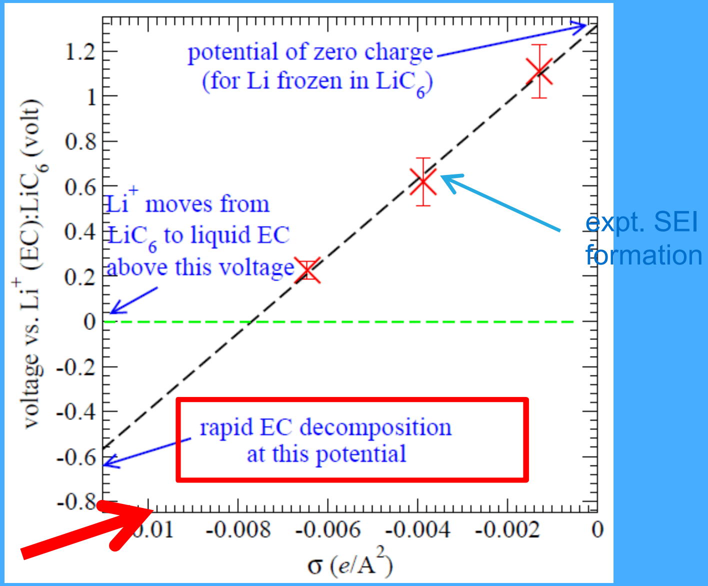


- 0 V vs LiC_6 (y-axis) is ~0.1 V vs $Li^+/Li(s)$
- Net –ve surface charge (σ) exists on basal plane during Li^+ intercalation
- Small cell size -> σ changes during integration ($\Delta G_{hyd} = \int_0^1 d\lambda \left\langle \frac{dH(\lambda)}{d\lambda} \right\rangle_\lambda$). take halfway point for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

EC decomposition seen at very low potentials

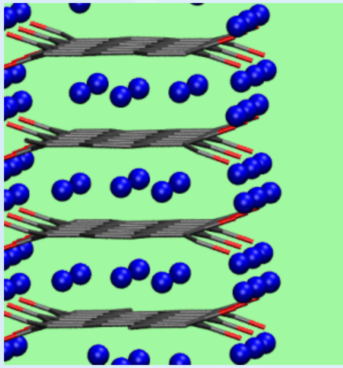
With longer trajectories, should see decomposition at higher voltage

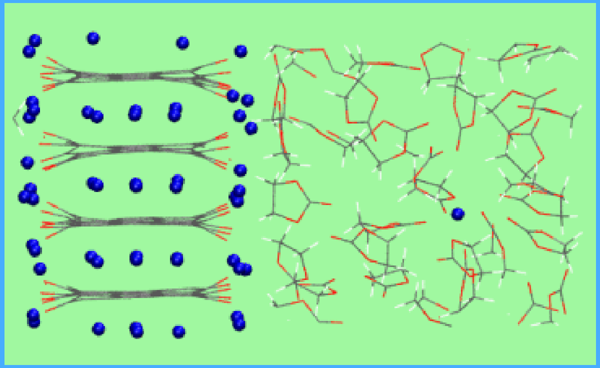




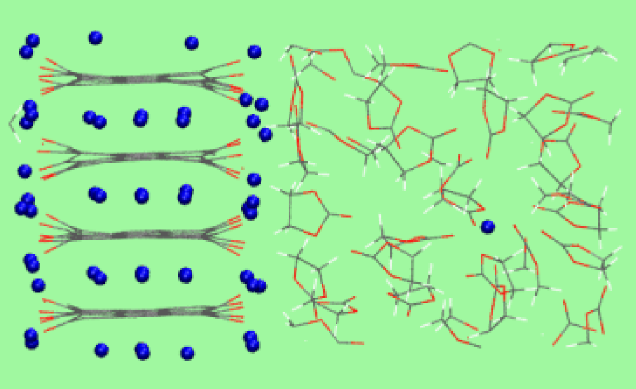
- enough –ve charge (excess e^-) on electrode (compensated by Li^+ in electrolyte for e^- to jump from LiC_6 to EC via a Li^+ bridge at the surface

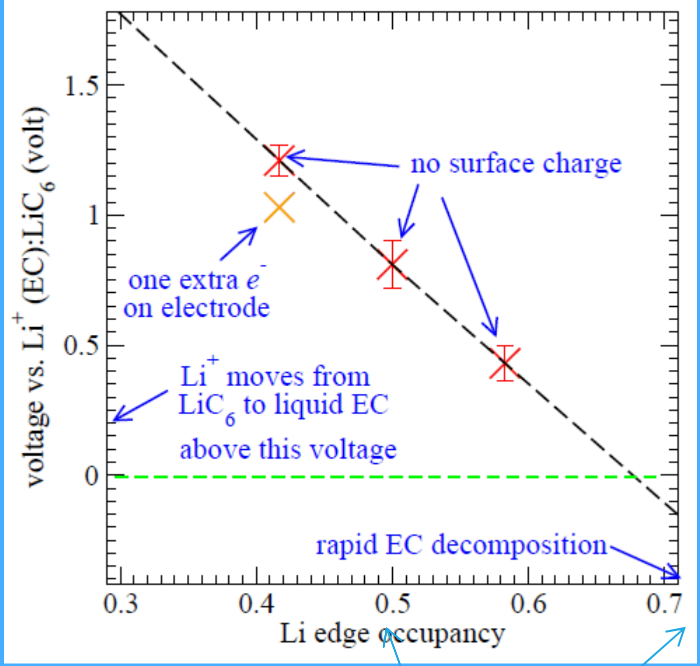
LiC_6 C=O edge planes

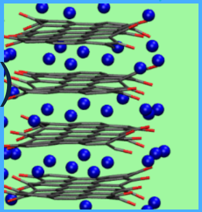


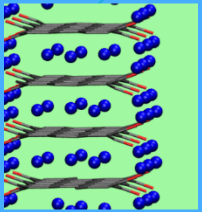


Edge plane: Potential = V(σ, n_{Li}), more complicated!



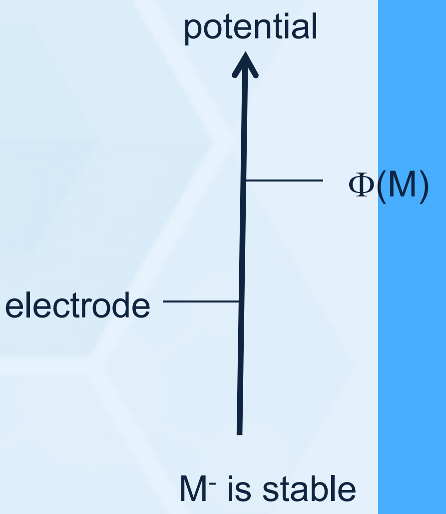






- Focus on σ=0, vary n_{Li} (Li coverage at C=O edge sites)
- ΔG_t = 0 (Li+ intercalation) when n_{Li} = 0.67
- n_{Li} = 1 used previously too low voltage
- If n_{Li} > 0.65, surface should be positively charged (σ > 0)

Validation of potential predictions via e$^-$ transfer

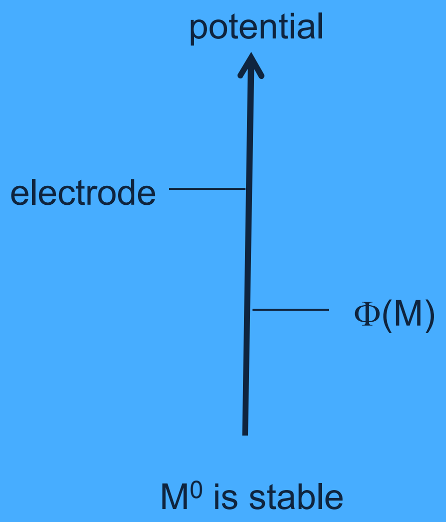


potential

Φ(M)

electrode

M$^-$ is stable



potential

electrode

Φ(M)

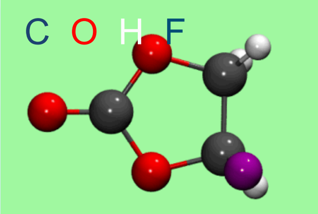
M^0 is stable

Validation of predicted interfacial potentials via e^- transfer to FEC

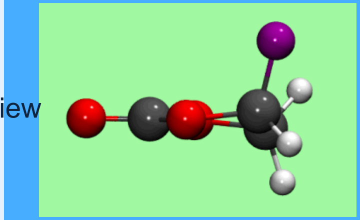
Similar to ferrocene as marker but FEC reduces at low voltages

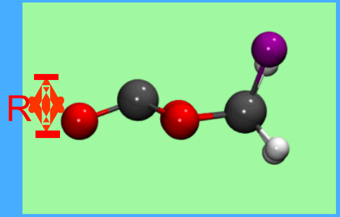
Tang, Lu, Newman, [JECS 159:A1775 (2012)]

top view



side view





FEC$^-$

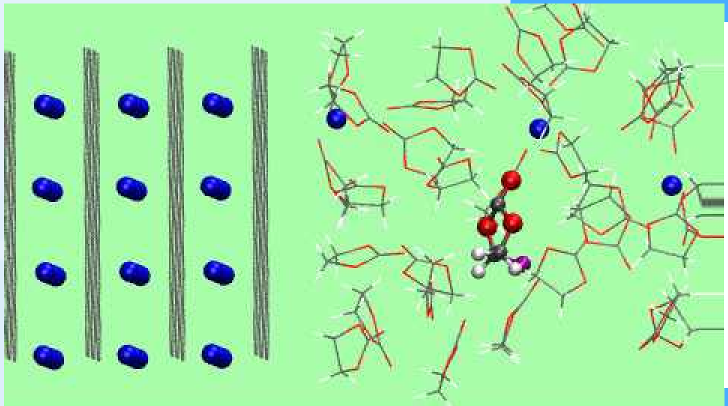
- FEC (fluorethylene carbonate) is a widely used electrolyte additive, gives better SEI
- R ~ 0 for FEC, R ~ 0.4 A for FEC$^-$; thus geometry indicates charge state

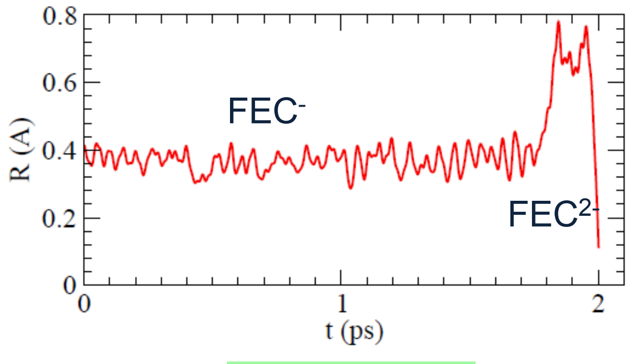
Φ = 0.58 V for FEC not coordinated to Li$^+$, DFT/PBE

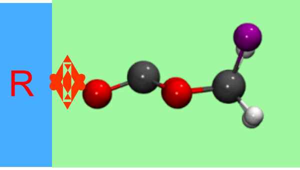
FEC as additivie: , Leung, Rempe, Foster, Ma, Martinez del la Hoz, Sai, and Balbuena, JECS 161:A213 (2014)

AIMD interfacial potential and g09 bulk liquid” calculations agree to within ~0.15 V in FEC reduction threshold

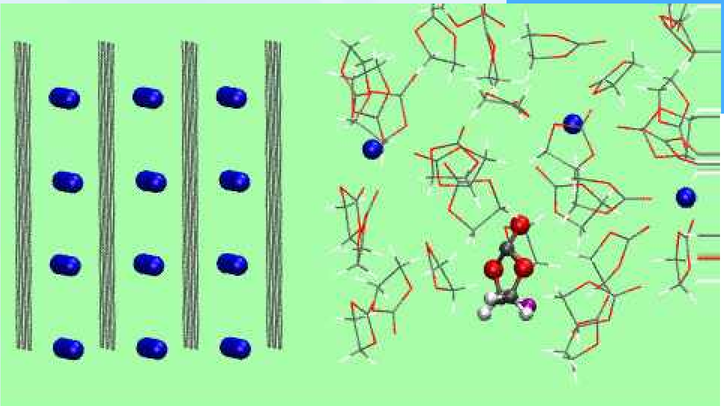
Interface: 0.51 V

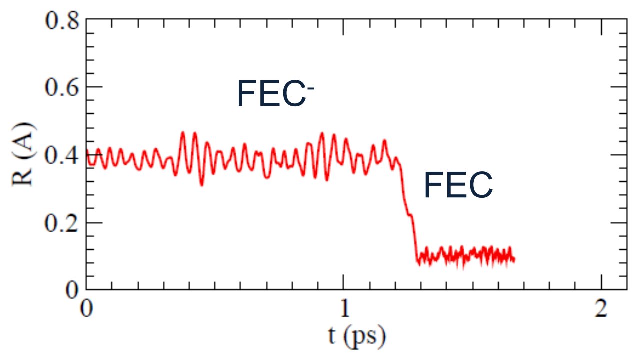






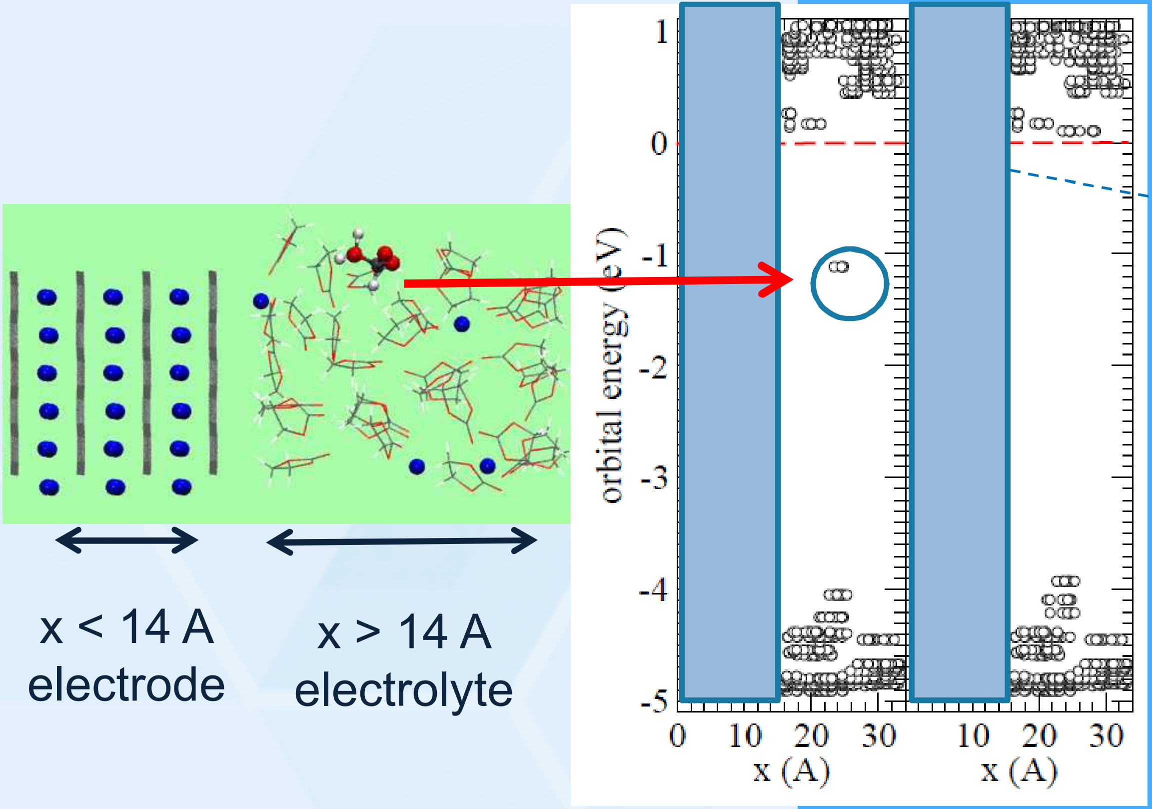
Interface: 0.76 V





G09 “bulk” calculation: 0.58 V threshold

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:

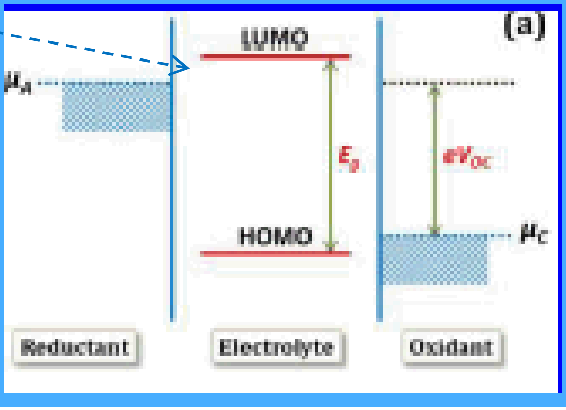
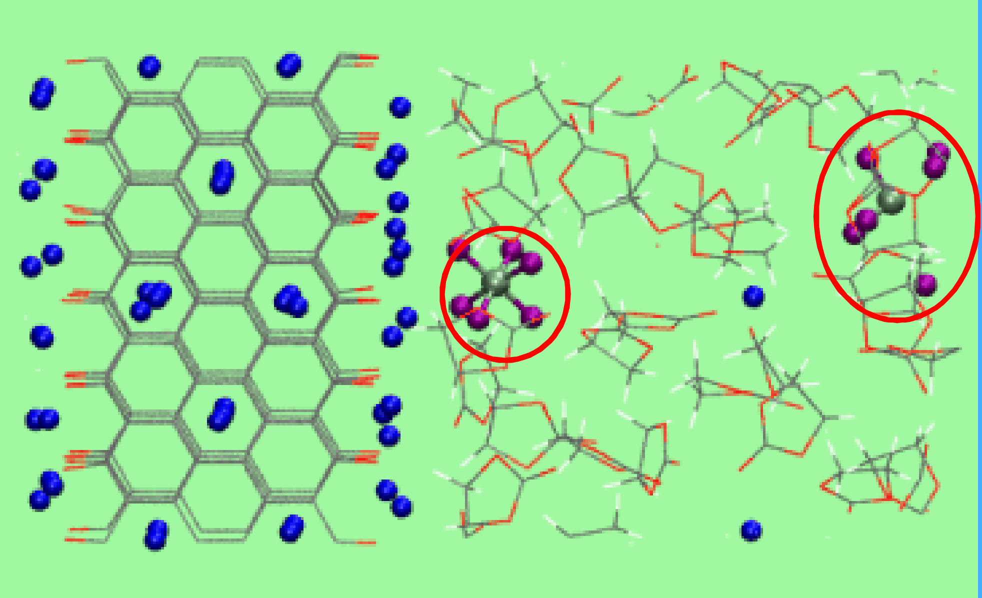


Figure 2. Relative energies of the electrolyte window E_g and the electrode electrochemical potentials μ_A and μ_C with no electrode/electrolyte reaction: (a) liquid electrolyte with solid electrodes; (b) solid

Goodenough & Park,
JACS 135:1167 (2013)

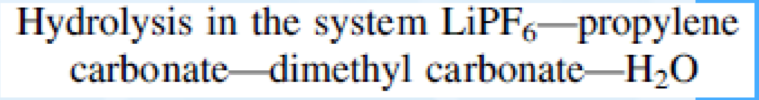
This is wrong!

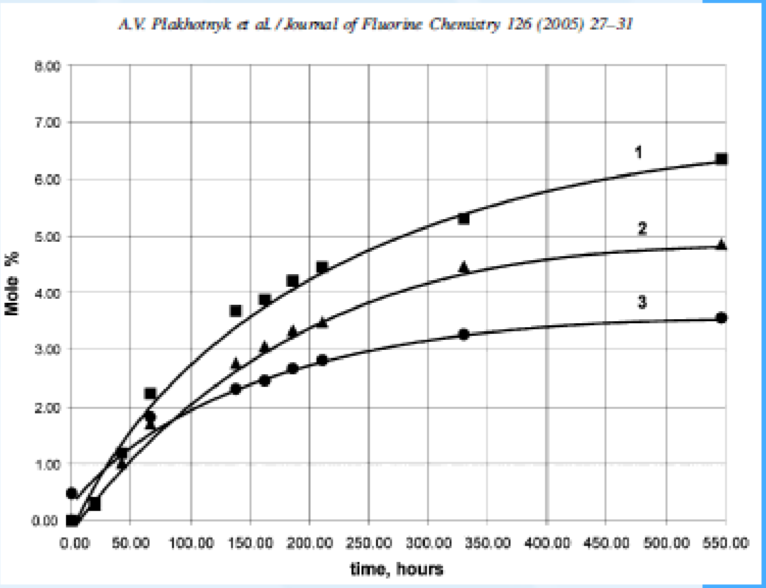
Application: PF_6^- electrochemical reduction on edge plane?



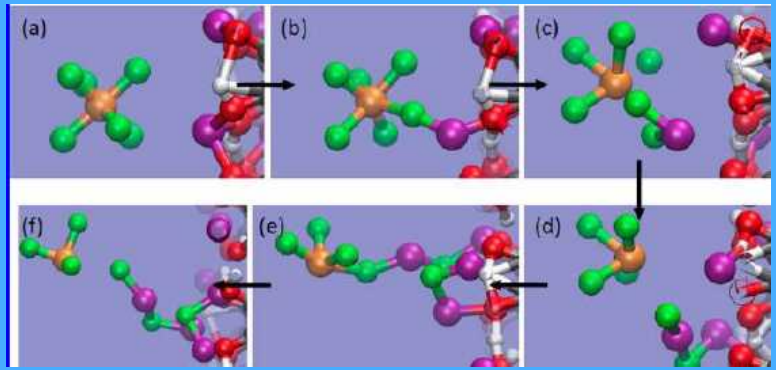
The strange case of PF_6^- degradation

- PF_6^- decomposition, found in SEI, widely accepted to be non-electrochemical
- may be due to thermal/water impurity; indeed, no CV peak for the anion
- But experiments with added water outside batteries show slow reaction


Hydrolysis in the system $LiPF_6$—propylene carbonate—dimethyl carbonate—H_2O


A.V. Plakhotnyk et al. / Journal of Fluorine Chemistry 126 (2005) 27–31

Modeling PF_6^- degradation in the past



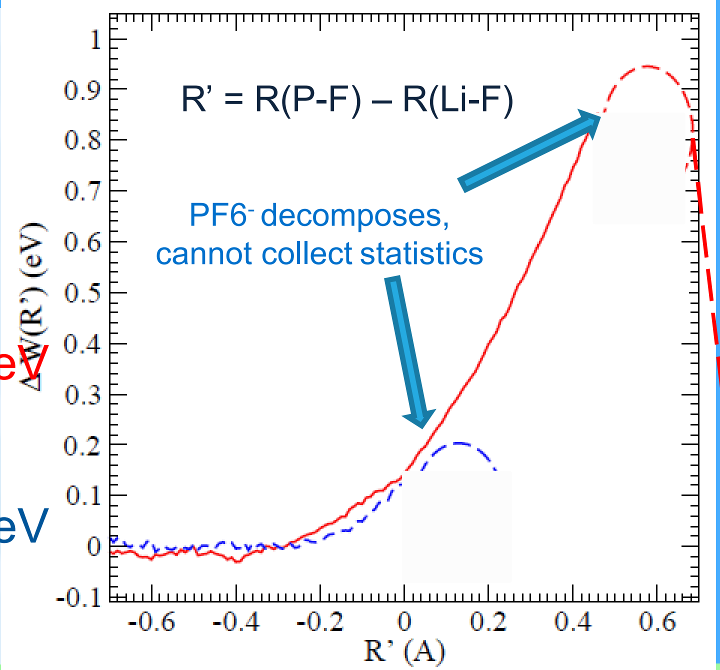
- Previous AIMD study of PF_6- at mixed C=O, C-OH LiC_6 edge finds *barrierless* electrochemical reduction of anion; but voltage-dependence not known

Ganesh, Kent, Jiang, JPCC 116:24476 (2012)

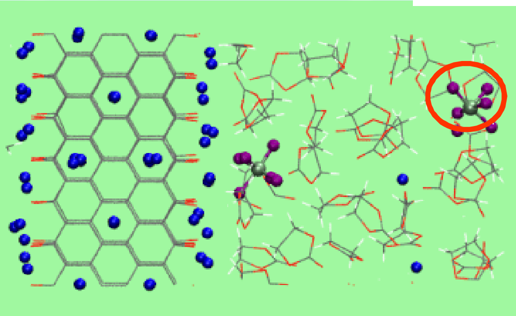
AIMD potential of mean force calculation of P-F bond breaking

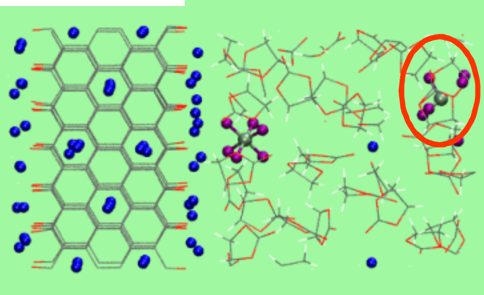
interface: 0.53 V
barrier at least 1.0 eV

interface: -0.35 V
barrier at most 0.2 eV


R' = R(P-F) – R(Li-F)

PF6$^-$ decomposes, cannot collect statistics

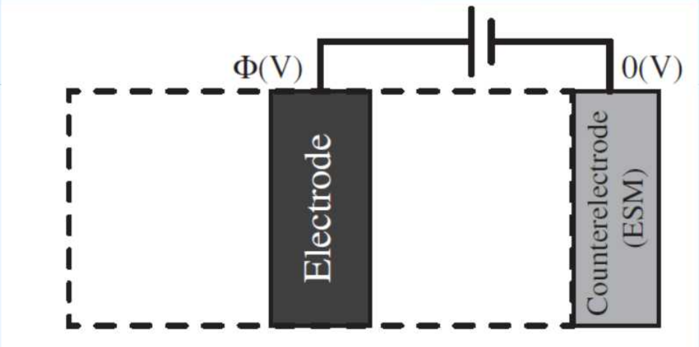




Voltage Calibration: Conclusions

- Devised method for predicting voltage-dependences of liquid/solid interfacial processes
- LiC_6 basal plane negatively charged, edge planes depend on Li content
- PF_6^- reduction on graphite edge incurs high barrier at right potential
- Applications to insulating electrodes, aqueous systems, fuel cells?

Are there easier ways to do this?

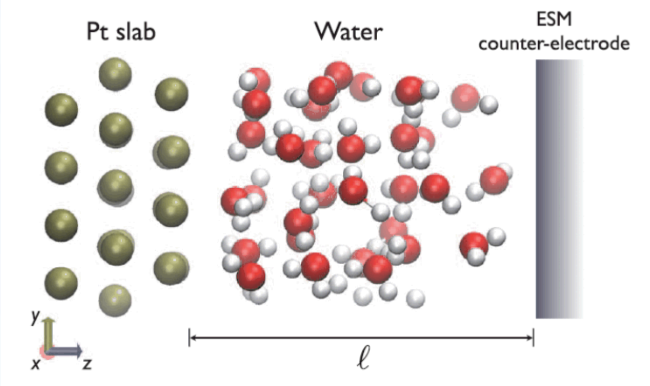


First-Principles Molecular Dynamics at a Constant Electrode Potential

PRL 109, 266101 (2012) PHYSICAL REVIEW LETTERS

Nicéphore Bonnet,[1,2] Tetsuya Morishita,[1] Osamu Sugino,[2] and Minoru Otani[1]

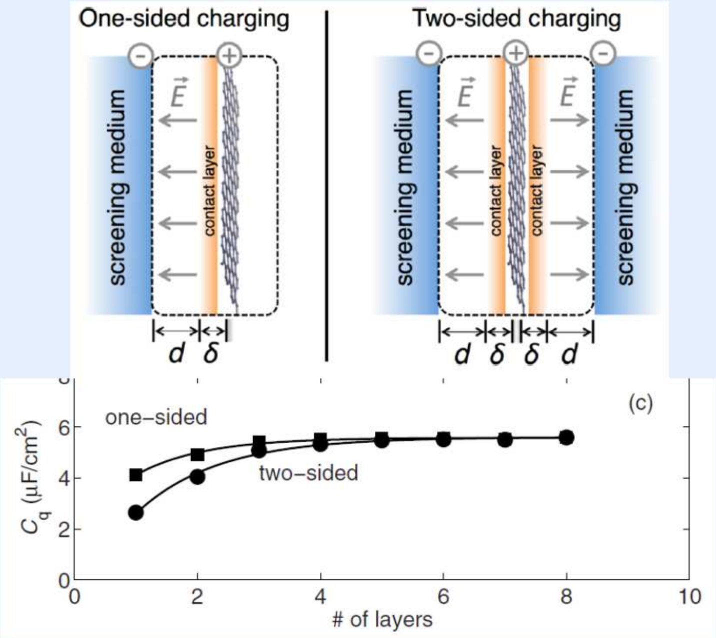
$$\dot{n}_e = \frac{P_{n_e}}{M_{n_e}}, \qquad \dot{P}_{n_e} = F_e = \Phi - \Phi_{\text{pot}},$$



Capacitive charge storage at an electrified interface investigated via direct first-principles simulations

Maxwell D. Radin,[1,*] Tadashi Ogitsu,[2] Juergen Biener,[2] Minoru Otani,[3] and Brandon C. Wood[2,†]

PHYSICAL REVIEW B **91**, 125415 (2015)

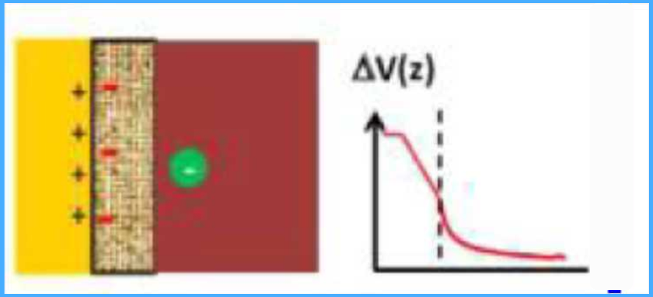


(see also "joint-DFT, which treats the entire liquid as a continuum)

- jDFT not yet calibrated for battery materials/electrolytes
- Li⁺ concentration on/near electrode surfaces – major issues
- main issue: they don't yet include EDL contributions inside solids

Solid-solid interface contribution to Electric Double Layer

- In all-solid batteries, this is all there is
- In liquid electrolyte batteries, there are still solid-solid interfaces (“SEI”)
- How much of the EDC is from solid-solid and solid-liquid interfaces?
- What are the consequences? (SEI evolution, Li^+ transport …)



- we don’t know the answers
- have barely started asking the right questions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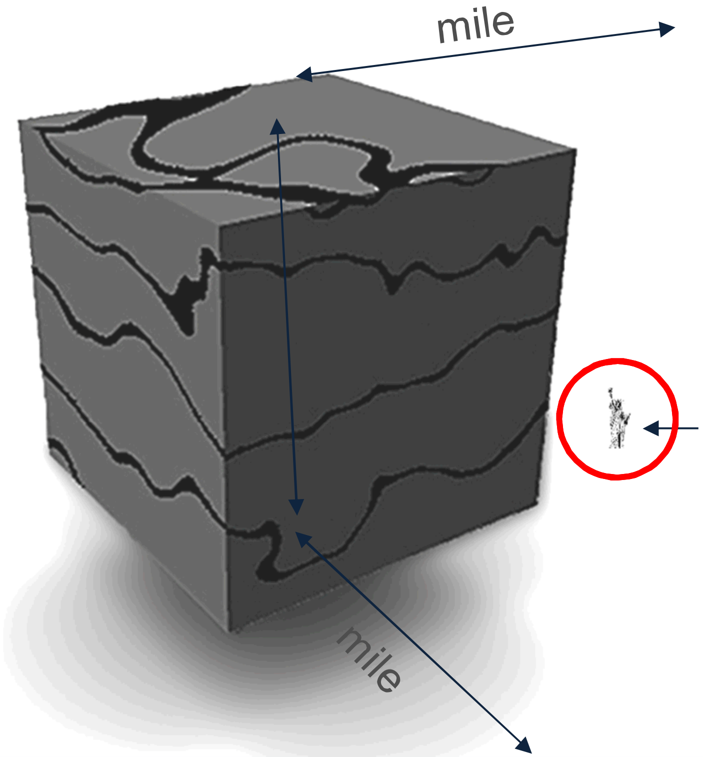
Symposium EN1: Solid-Solid Interfaces in Batteries, Energy Storage and Conversion—Diagnostic and Modeling

Bruce Dunn, Yoshitaka Tateyama, Yue Qi, KL

Energy, climate change, human development



"cubic
mile
of oil"

Backup slides