SAND2019-7767C

Modeling solid-solid & solid-liquid interfaces in lithium batteries

Kevin Leung

(just moved into geochemistry department!)

Sandia National Laboratories

Acknowledgement

Katherine Jungjohann, Katharine Harrison, Shen Dillon, Angelique Jarry, Jacob Harvey, Maureen Tang, Ilya Shkrob, Michiel Sprik ...

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NANOSTRUCTURES for ELECTRICAL ENERGY STORAGE

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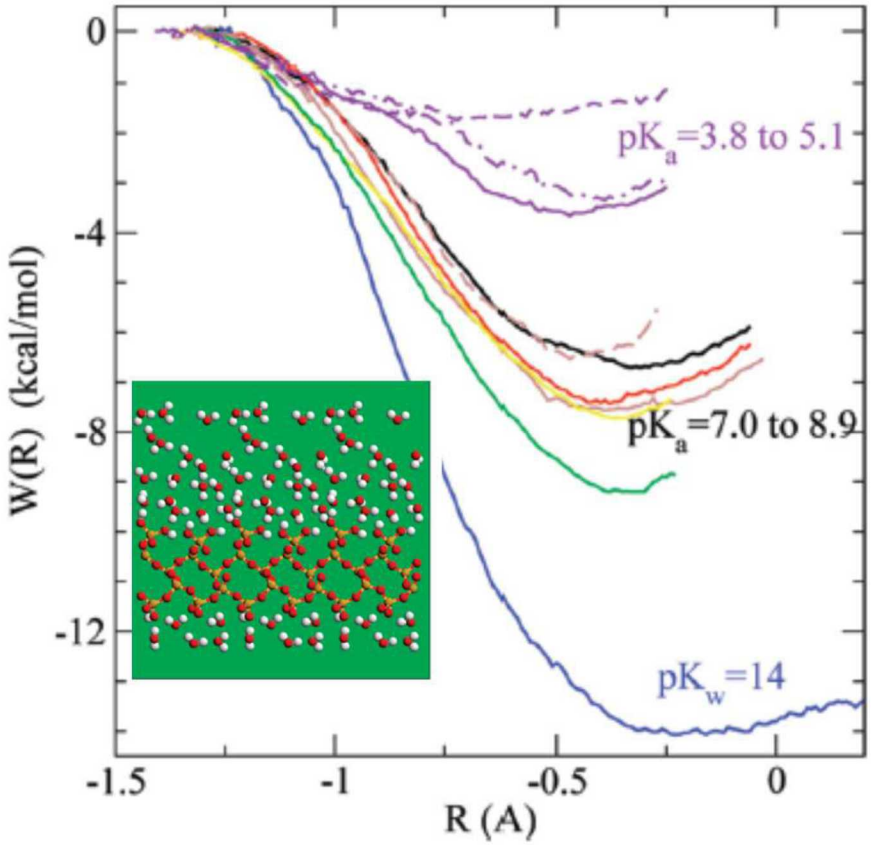
U.S. DEPARTMENT OF ENERGY

I am very interested in liquid-solid interfaces, e.g., water-silica

Elucidating the Bimodal Acid–Base Behavior of the Water–Silica Interface from First Principles

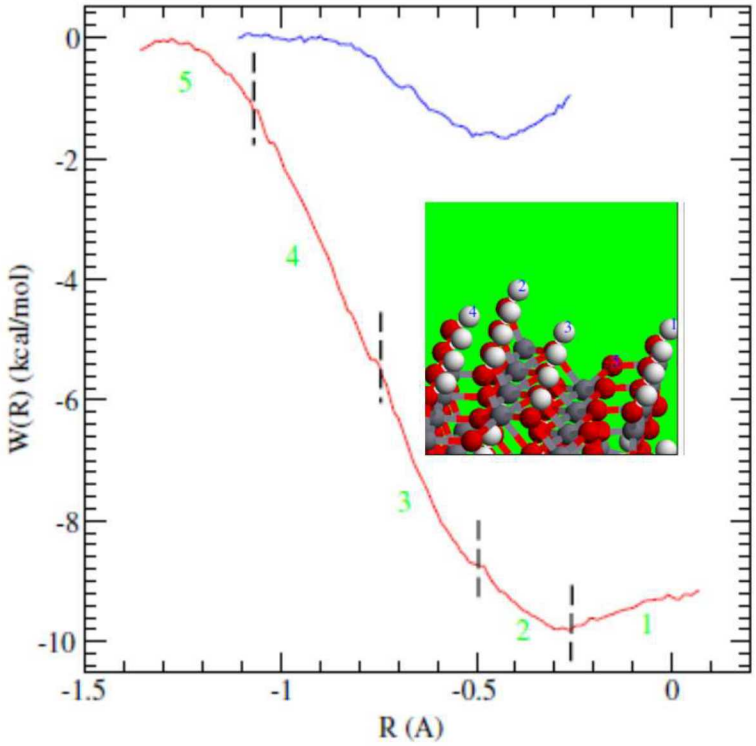
Kevin Leung,*,† Ida M. B. Nielsen,‡ and Louise J. Criscenti†

Sandia National Laboratories, MS 1415 and 1322, Albuquerque, New Mexico 87185 and Sandia National Laboratories, MS 9158, Livermore, California 94551



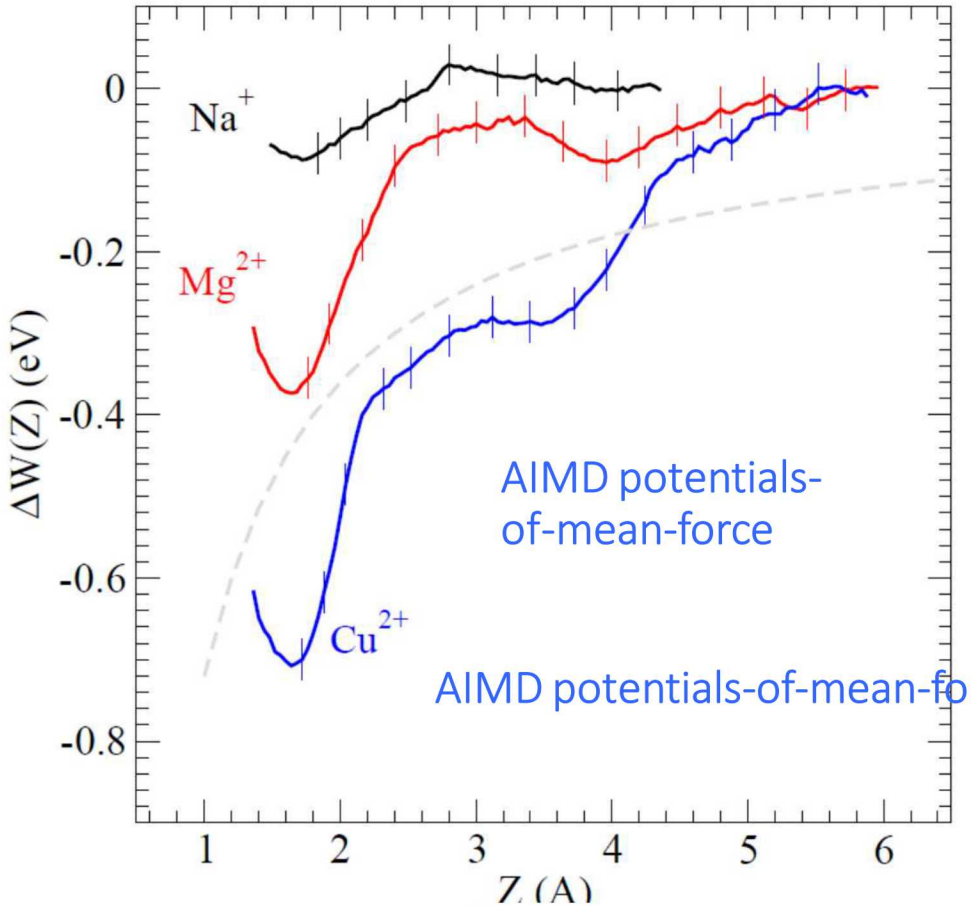
Predicting the acidity constant of a goethite hydroxyl group from first principles Kevin Leung and Louise J Criscenti

J. Phys.: Condens. Matter **24** (2012) 124105 (9pp)



Concerted Metal Cation Desorption and Proton Transfer on Deprotonated Silica Surfaces

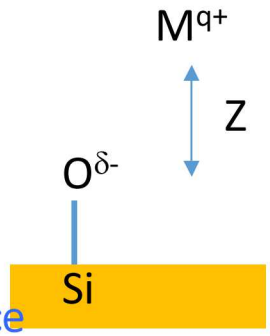
Kevin Leung,* Louise J. Criscenti, Andrew W. Knight, Anastasia G. Ilgen, Tuan A. Ho, and Jeffery A. Greathouse



AIMD potentials-of-mean-force

AIMD potentials-of-mean-force

weak lateral harmonic potential



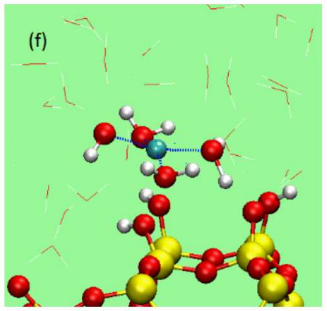
$$\Delta G_{\mathrm{ads}}/k_{\mathrm{B}}T = -\log\{\int_{\Omega} d\Omega \exp[-\Delta W(Z)/k_{\mathrm{B}}T]/(V_o)\}$$

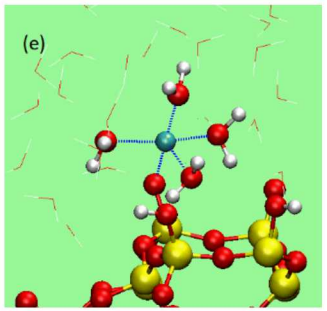
Na^+ : +0.13 +/- 0.03 eV (unbound)

Mg^{2+}: -0.14 +/- 0.05 eV

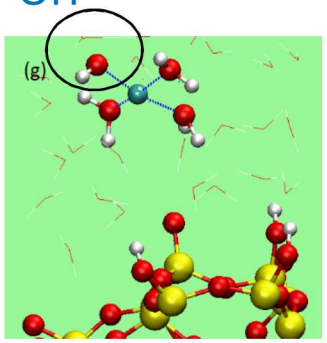
Cu^{2+}: -0.47 +/- 0.07 eV

Cu desorbs as $Cu^{2+}(H_2O)_3$ (OH^-) complex! Because Of SiOH pKa





OH^-



… but increasingly recognize importance of solid-solid interfaces in battery lifetime, corrosion, problems with realistic electrodes

e.g., DFT work that has “dirty electrode” (metal|oxide|liquid|) flavor

Combining the Physics of Metal/Oxide Heterostructure, Interface Dipole, Band Bending, Crystallography, and Surface State to Understand Heterogeneity Contrast in Oxidation and Corrosion

Xiao-xiang Yu‡, and Laurence D. Marks**

CORROSIONJOURNAL.ORG

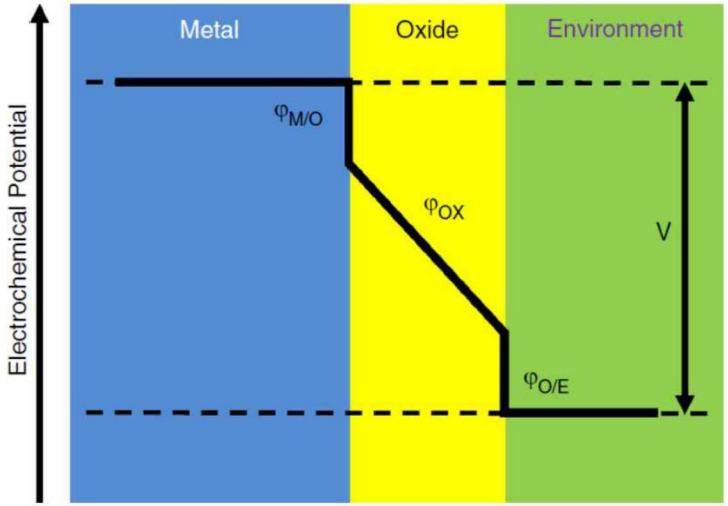
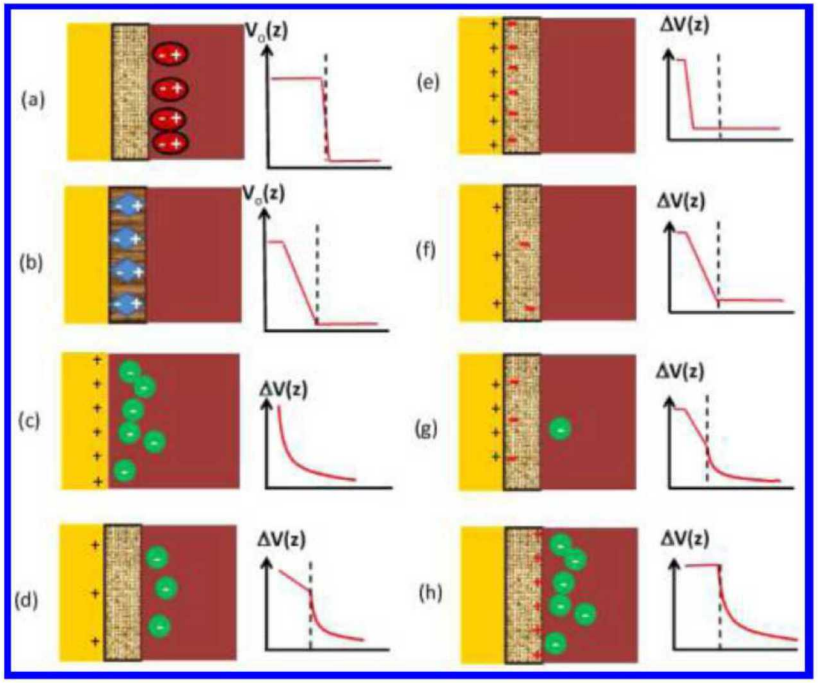


FIGURE 1. *The classic description of the electrochemical potential change in the metal/oxide/environment system.*

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

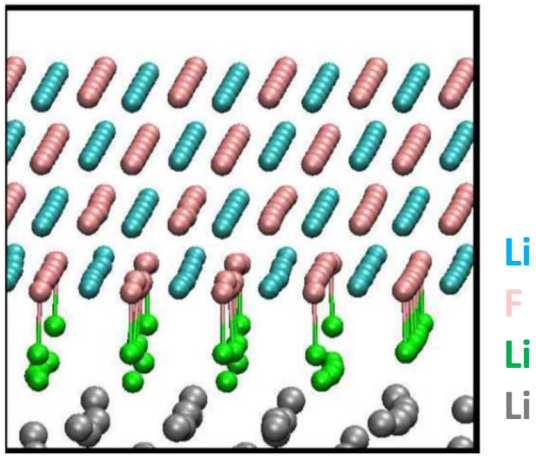
Kevin Leung* and Andrew Leenheer *J. Phys. Chem. C* 2015, 119, 10234–10246



DFT work that has |metal|oxide|vacuum| flavor

Spatial Heterogeneities and Onset of Passivation Breakdown at Lithium Anode Interfaces

Kevin Leung*,† and Katherine L. Jungjohann‡



Li(001)/LiF (001) work function shift is -1.69 V compared with bare Li metal (001)

Combining the Physics of Metal/Oxide Heterostructure, Interface Dipole, Band Bending, Crystallography, and Surface State to Understand Heterogeneity Contrast in Oxidation and Corrosion

Xiao-xiang Yu‡, and Laurence D. Marks**

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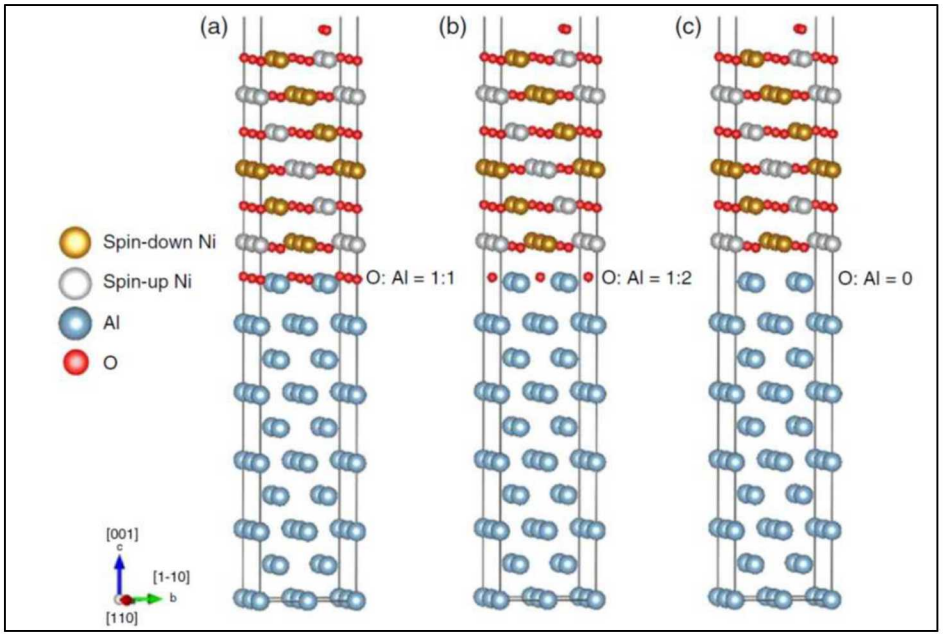


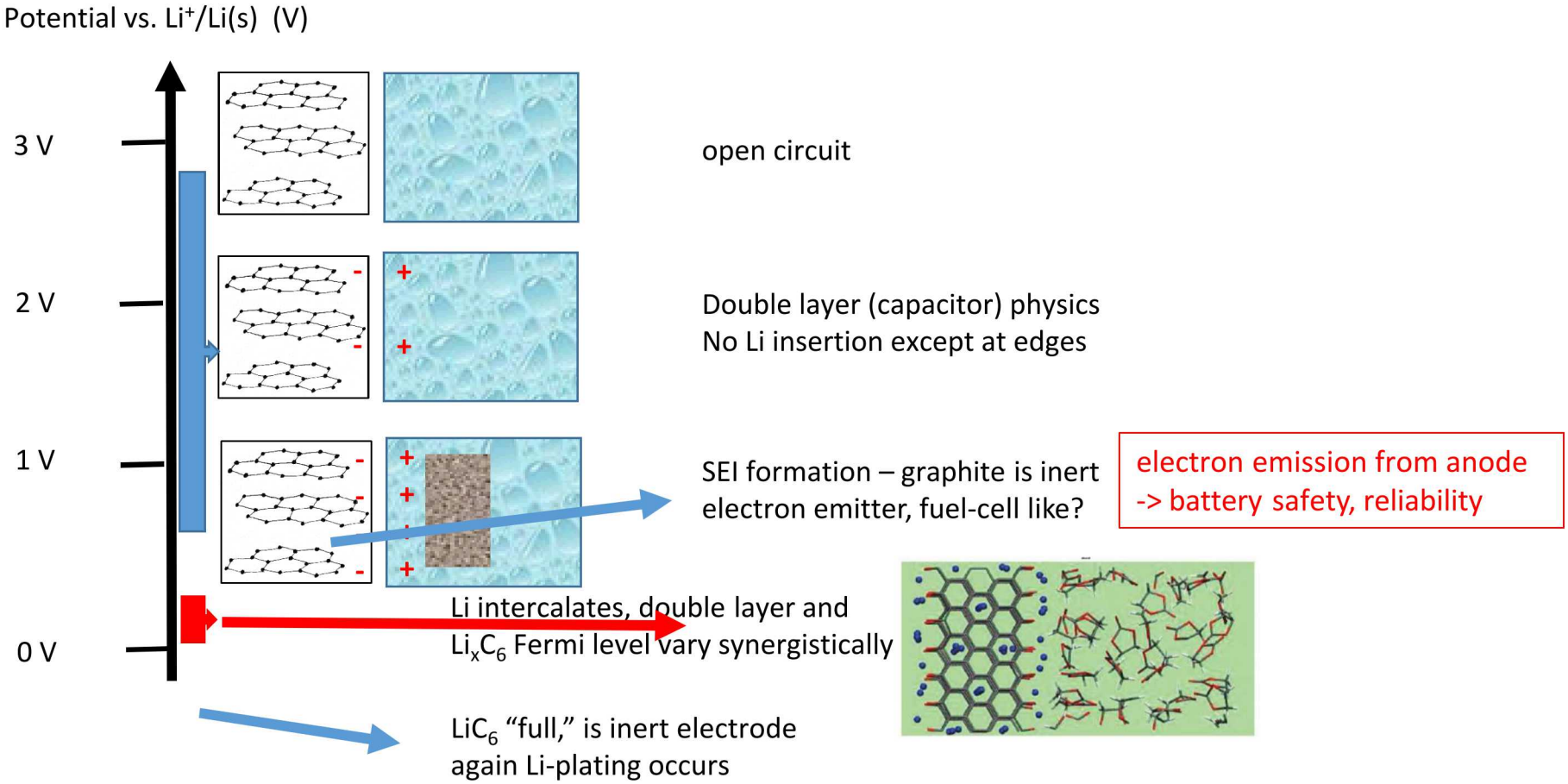
Table 3. *Summary of the Type of Oxide, Surface and Interfacial States, Contact and Dipole Direction in Different Metal/Oxide Junctions*[(A)]

	NiO/Al	NiO/Al	NiO/Ni	MgO/Al	MgO/Li	MgO/Li	MgO/Ag	MgO/Ta	MgO/Ta
Work function changes (eV) $\Delta\Phi = \Phi_{O/M} - \Phi_M$	−1.57	−0.87	−1.08	−0.9	+2.01	−1.27	−0.68	−2.74	−3.04

A main goal: to unify computational electrochemistry

e.g. little acknowledged fact among battery theorists: double layer capacitor physics dominates during much of battery charging, such as on graphite

- If no explicit interface (EDL) in theory, cannot account for battery charging



Electronic voltage rarely addressed in DFT battery interfacial modeling

Some challenges in modeling battery interfaces

"God made the bulk; surfaces were invented by the devil."

Wolfgang Pauli

- Pauli clearly never dealt with electrified interfaces on battery electrode surfaces!
- 3 reasons battery interfaces are particularly hard to model (in addition to the usual problem with buried interfaces, hard to measure atomic positions etc.):

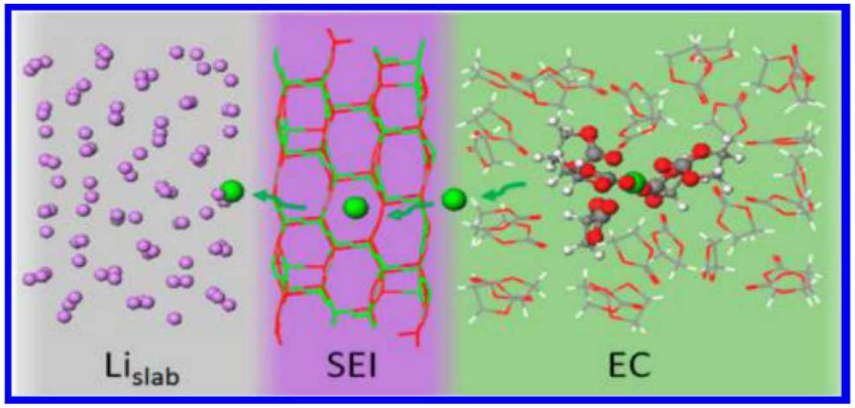
1. Electrode surfaces are dirty, covered in solid electrolyte interphase (SEI/CEI)
2. Need to deal with both instantaneous and equilibrium voltages
3. Processes/structures are kinetically (not thermodynamically controlled)

1. Electrode Interfaces are Dirty

modeling time-scale mismatch!

Computational Exploration of the Li-ElectrodelElectrolyte Interface in the Presence of a Nanometer Thick Solid-Electrolyte Interphase Layer

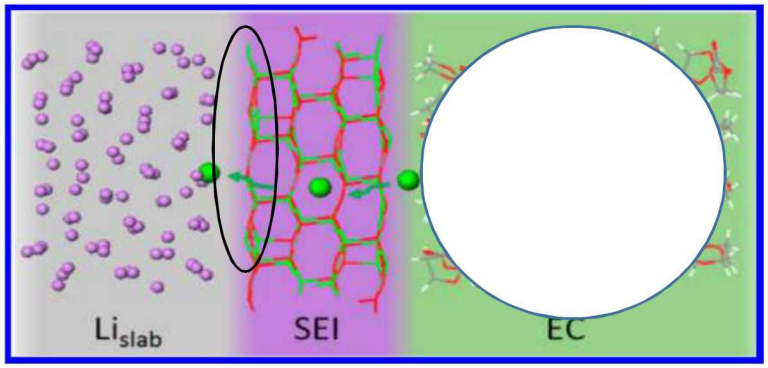
Yunsong Li,[†] Kevin Leung,[‡] and Yue Qi*[,†] *Acc. Chem. Res.* (2016)



- "coated electrode" paradigm (Al Bard, see also Maureen Tang)
- as Li^+ moves from liquid to SEI, it sees very different diffusion barriers
- AIMD simulations ineffective
- DFTB-based MD by Yue Qi's group
- AIMD with GCMC would help!

focus either on solid-solid interfaces, T=0 K calculations …

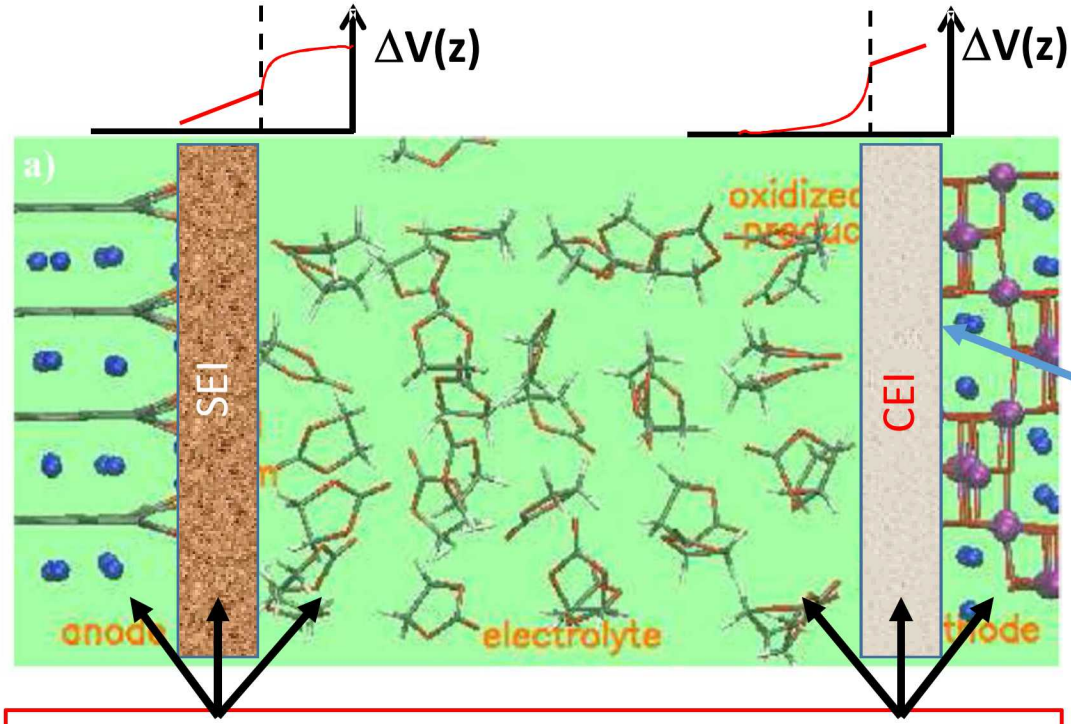
- (including electrode/SEI interfaces)
- give 2 examples of interfacial degradation
- Illustrate 2 issues: Li content effect, highlights kinetics



… or on liquid/solid interfaces, T>0 K, omit SEI film

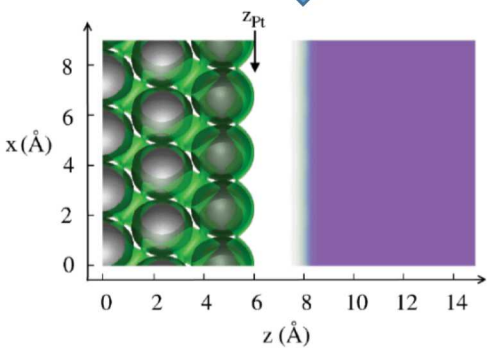
2. Both electronic and lithium ion “voltages” needed

- Battery electrodes are both electron- and Li^+ emitters, forming SEI and storing Li



local Li^+ conc.? charge/dipole surface density? voltage drop?

Fermi level?



Direct coupling of first-principles calculations with replica exchange Monte Carlo sampling of ion disorder in solids

Shusuke Kasamatsu Osamu Sugino

(finite temperature Grand Canonical Monte Carlo of Li content with DFT)

+

PHYSICAL REVIEW B **86**, 075140 (2012)

Joint density functional theory of the electrode-electrolyte interface: Application to fixed electrode potentials, interfacial capacitances, and potentials of zero charge

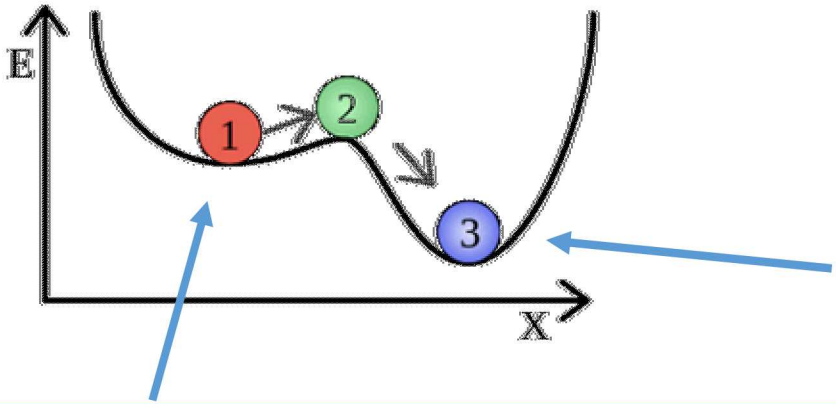
Kendra Letchworth-Weaver and T. A. Arias

3. Interface structures governed by kinetics not thermodynamics

Materials synthesis occurs at high temperature -> thermodynamics

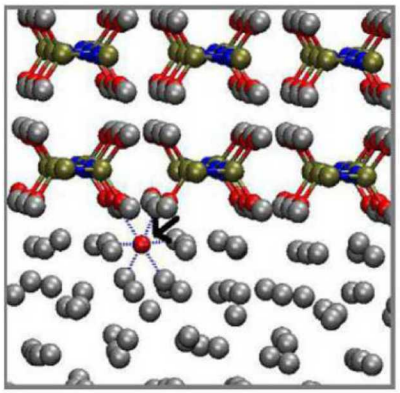
e.g., 900 °C for 10 hours

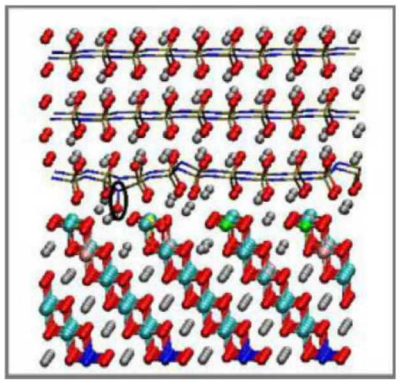
(figure by Georg Wiora)



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

- In contrast, in organic liquid electrolyte-based batteries, SEI are formed at room temperature
- Thermodynamics is irrelevant; in fact all organic molecules are metastable (reacts slowly)
- in all-solid state batteries, interfaces are fabricated at < 250 °C; kinetics must be considered





Kinetics-Controlled Degradation Reactions at Crystalline LiPON/Li_xCoO_2 and Crystalline LiPON/Li-Metal Interfaces

Kevin Leung,*[a] Alexander J. Pearse,[b] A. Alec Talin,[c] Elliot J. Fuller,[c] Gary W. Rubloff,[b] and Normand A. Modine[a]

ChemSusChem **2018**, *11*, 1956 – 1969

thermodynamic driving force yields fast reactions? incorrect

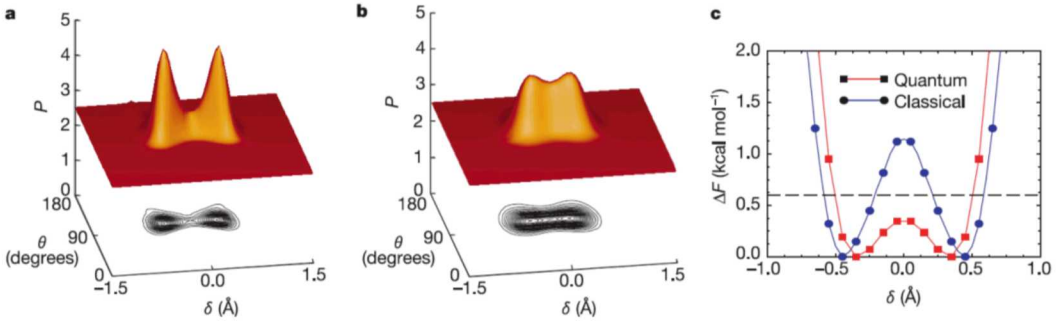
- Interfaces governed by moderate temperatures (< 250°C for solid electrolytes, 25°C liquids)
- Kinetics and thermodynamics (exothermicities) not always correlated
  - no *a priori* connection between exothermicity (thermodynamics) and reaction barrier (kinetics)
  - For example, H^+ hopping in water ("Grothuss mechanism") is strictly thermoneutral,
  - but is lightning fast (~ zero barrier)

The nature and transport mechanism of hydrated hydroxide ions in aqueous solution

Mark E. Tuckerman*, Dominik Marx† & Michele Parrinello‡§

NATURE | VOL 417 | 27 JUNE 2002

H_2O … OH^- → HO^-…H_2O

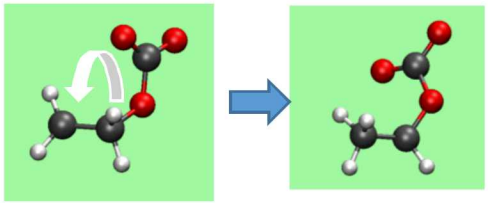


ΔF = -0.0 kJ/mol ΔF* = +1.20 kJ/mol!

- Yet H^+ migration from one C atom to another in a molecule (radical anion) is *exothermic but slow*

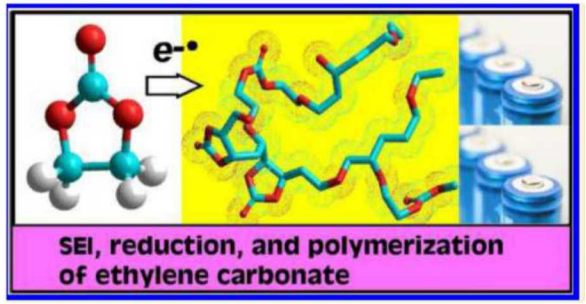
Reduction of Carbonate Electrolytes and the Formation of Solid-Electrolyte Interface (SEI) in Lithium-Ion Batteries. 2. Radiolytically Induced Polymerization of Ethylene Carbonate

Ilya A. Shkrob,*,† Ye Zhu,† Timothy W. Marin,†,‡ and Daniel Abraham†



ΔF = -16.2 kJ/mol ΔF* = +160 kJ/mol!

(unpublished calculations)



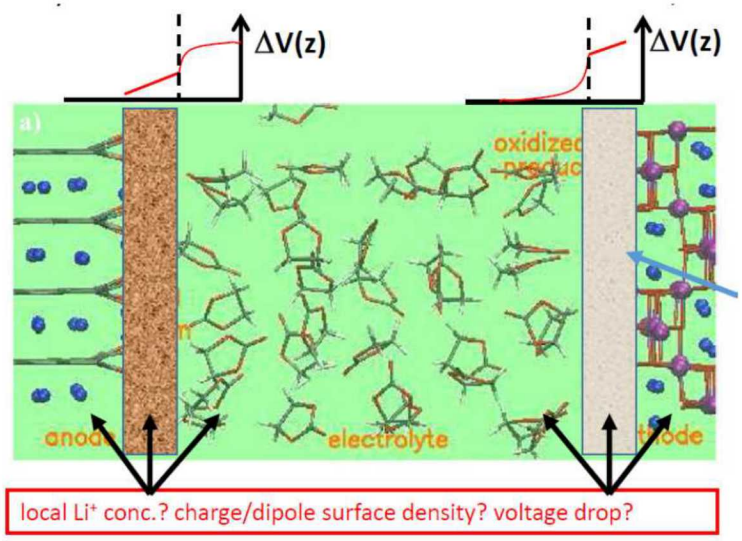
J. Phys. Chem. C 2013, 117, 19270–19279

Computational Details:

- PBE functional, DFT+U, U-J = 4.85 and 6.95 eV for Mn, Ni
- VASP, 400 eV cutoff …
- PBE0 for more accurate barrier predictions (100x costlier than DFT+U)
- Nudged elastic band for barrier calculations (solid)
- AIMD potential of mean force, thermodynamic intergration … (liquid)
- Use Trasatti relation to estimate voltage: v_e = (work function) – 1.37 V
  (-4.44 V vs. S.H.E.)

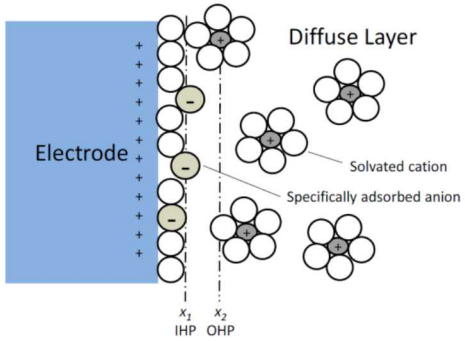
1. Calibrating voltage at model (i.e., clean) liquid-solid interfaces

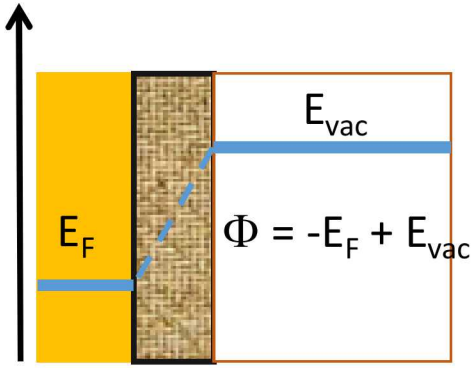
"Unification of different branches of computational electrochemistry"



LIB: Two voltage definitions: electronic vs. “ionic” voltage (interfaces vs. bulk crystal)

fuel cell, PV supercapactiors: voltage is electronic, interfacial

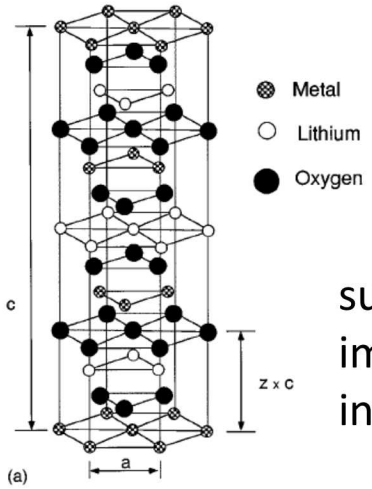




$$\mathcal{V}_e = \Phi/|e| - 1.37\ \mathrm{V}$$

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 without interfaces!

such calculations implicitly assume an interface supporting

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

“Lithium cohesive energy approach”

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 $\mathcal{V}_i$

Counter example that I don't agree with

First-Principles Prediction of Potentials and Space-Charge Layers in All-Solid-State Batteries

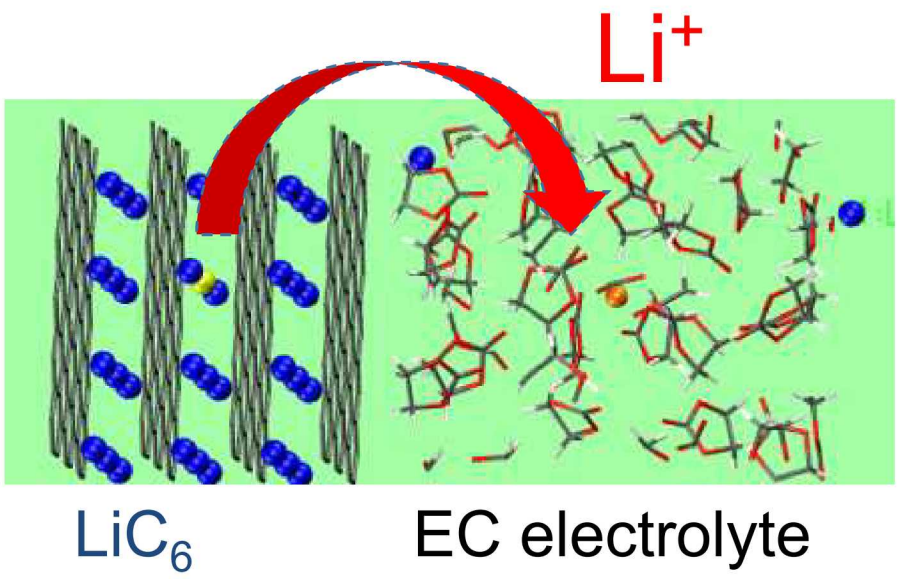
Michael W. Swift* and Yue Qi†

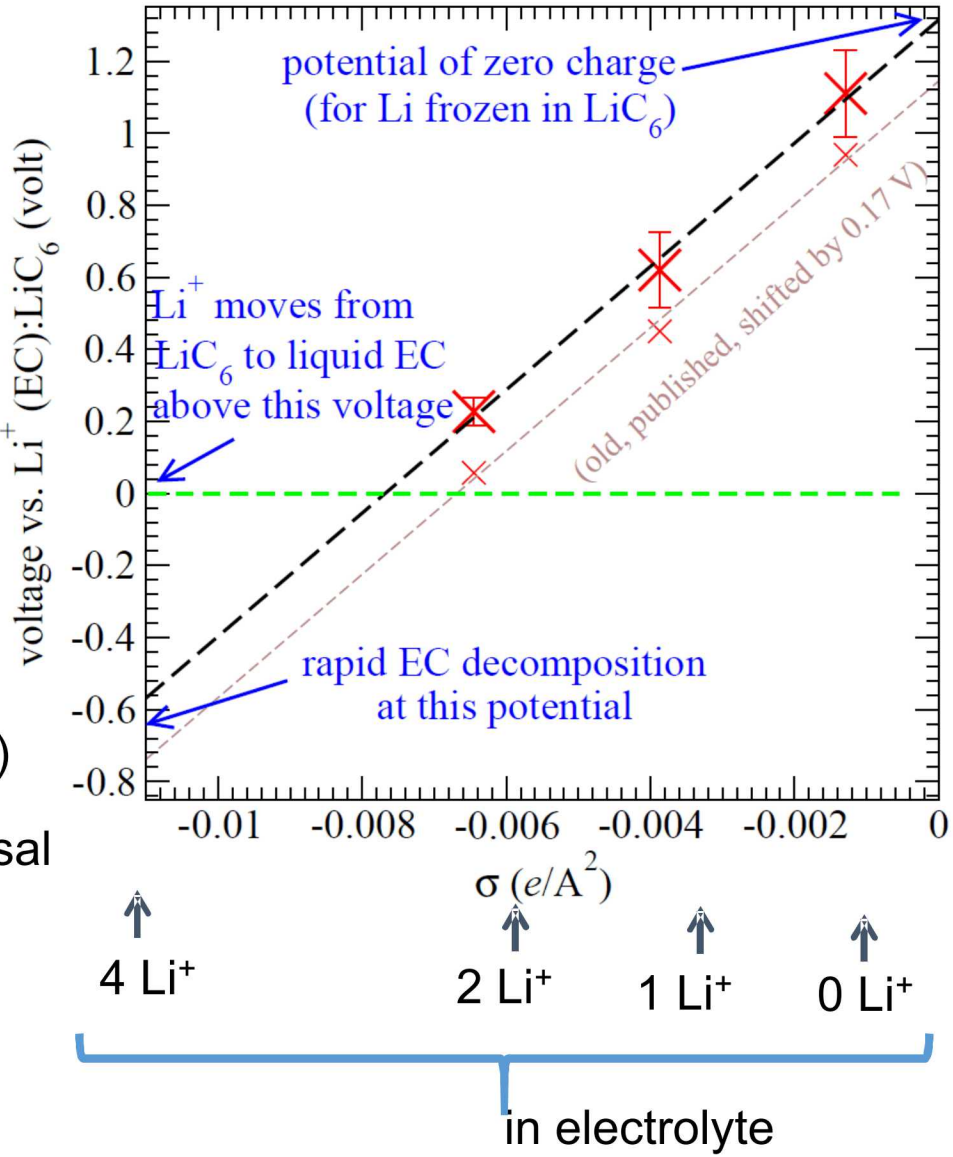
PHYSICAL REVIEW LETTERS **122,** 167701 (2019)

	E_F	IP	$\tilde{\mu}_{e^-}$	V_{e^-}	V_I
Li metal	0	3.14	0		

- assumes Li metal in vacuum at 0 V vs. $Li^+/Li(s)$?
  violates Trasatti relation
- system never at overpotential conditions
- no explicit Li-metal/electrolyte interface
- I disagree with all these!

“Anode potential” at basal plane/electrolyte interfaces



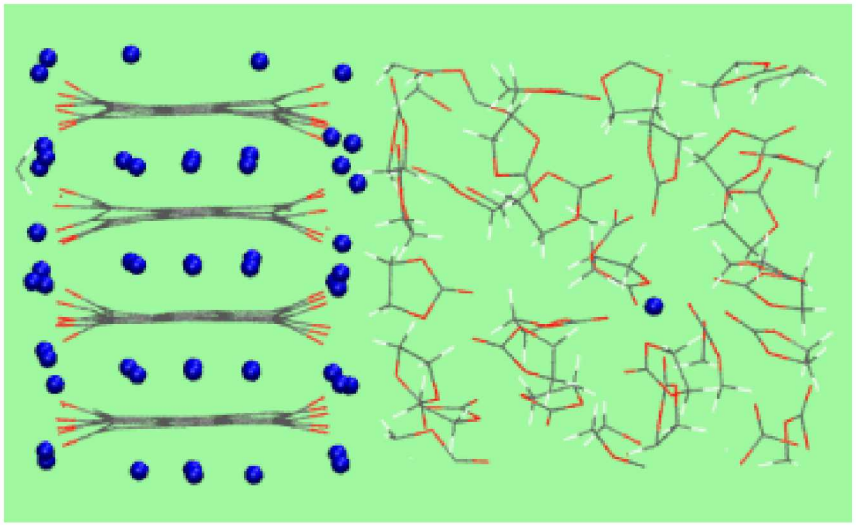


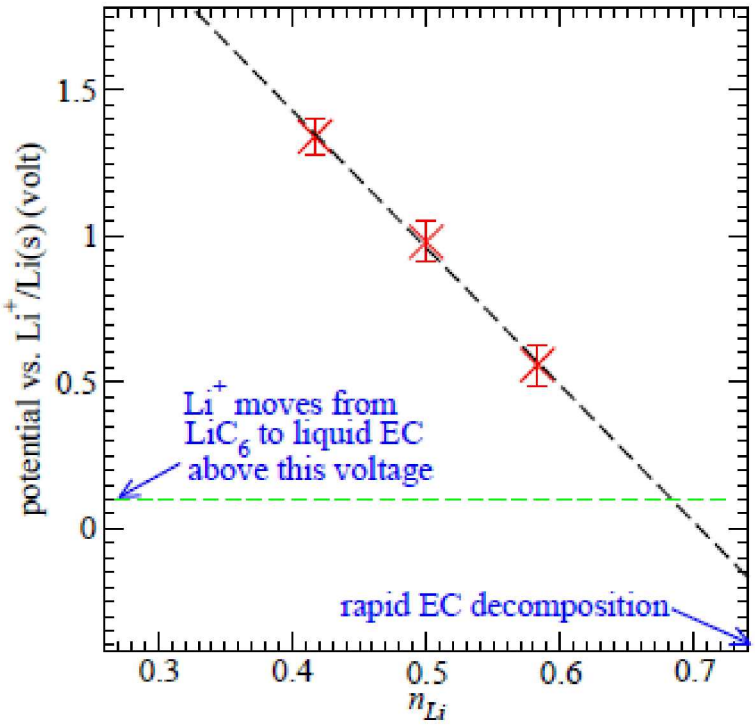
- 0 V vs LiC_6 (y-axis) is ~0.1 V vs $Li^+/Li(s)$
- Net –ve surface charge (σ) exists on basal plane during Li^+ intercalation
- Small cell size -> σ changes during integration ($\Delta G_{hyd} = \int_0^1 d\lambda \left\langle \frac{dH(\lambda)}{d\lambda} \right\rangle_\lambda$). take halfway point for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

Toward First Principles Prediction of Voltage Dependences of Electrolyte/Electrolyte Interfacial Processes in Lithium Ion Batteries

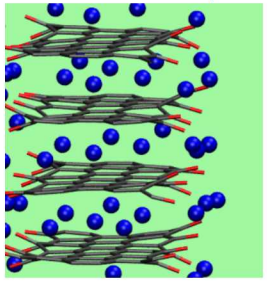
Kevin Leung* and Craig M. Tenney *J. Phys. Chem. C* 2013, 117, 24224–24235

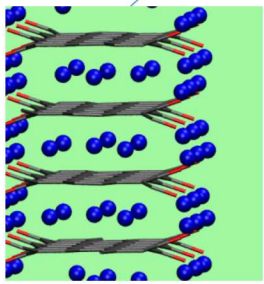
Edge plane: Potential = V(σ, n_{Li}), more complicated!





- 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)



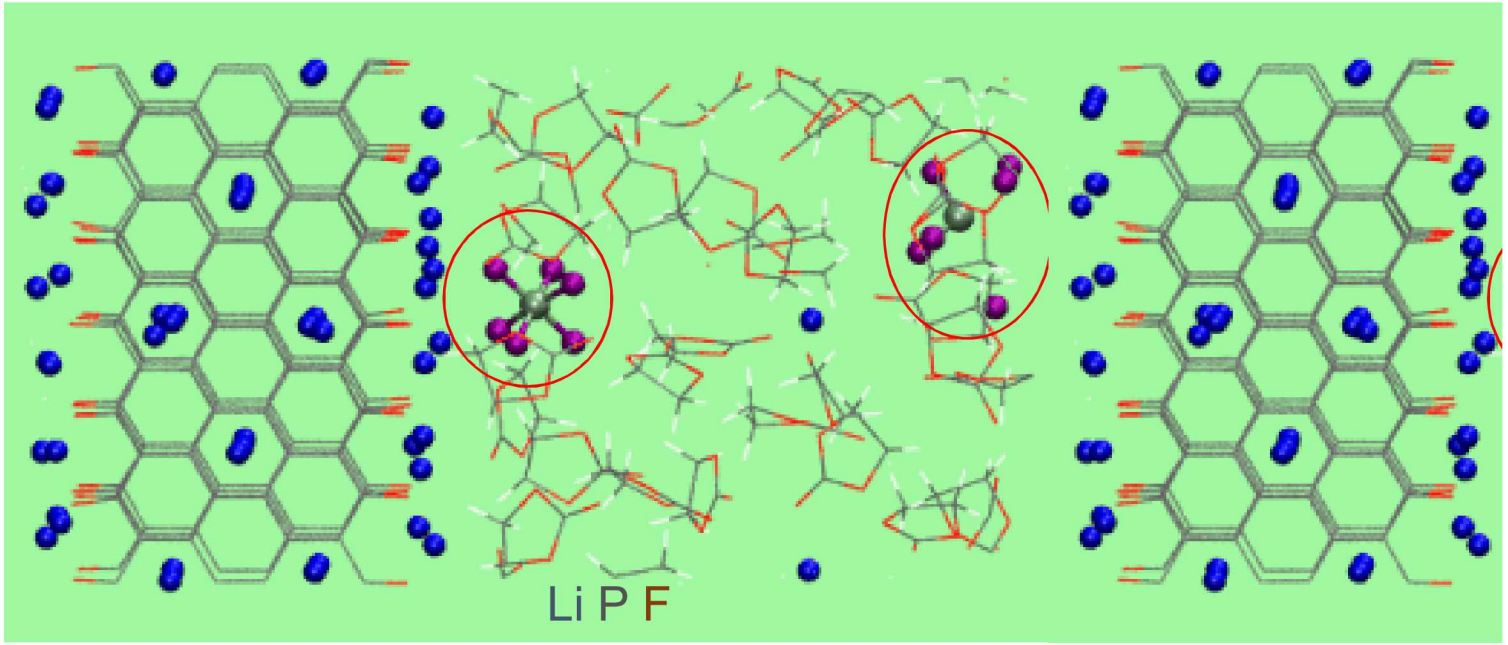


Predicting the voltage dependence of interfacial electrochemical processes at lithium-intercalated graphite edge planes†

Phys. Chem. Chem. Phys., 2015, **17**, 1637–1643

Kevin Leung

2. The strange case of PF_6^- electrochemical reduction

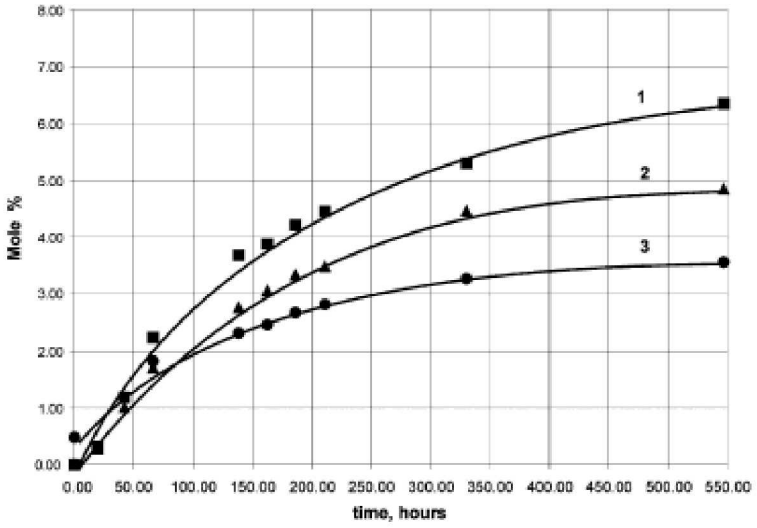


The strange case of PF_6^- degradation

- 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

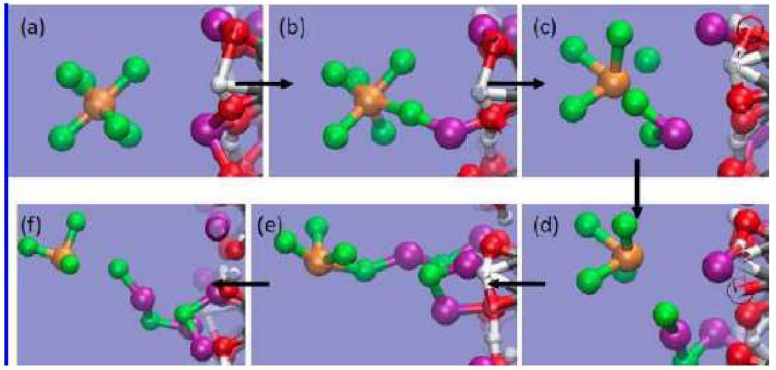
Hydrolysis in the system $LiPF_6$—propylene carbonate—dimethyl carbonate—H_2O

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



See however Delp, Borodin, Olguin, Eisner, Allen, Jow, Electrochim Acta 209:98 (2016)

Modeling PF_6^- degradation in the past



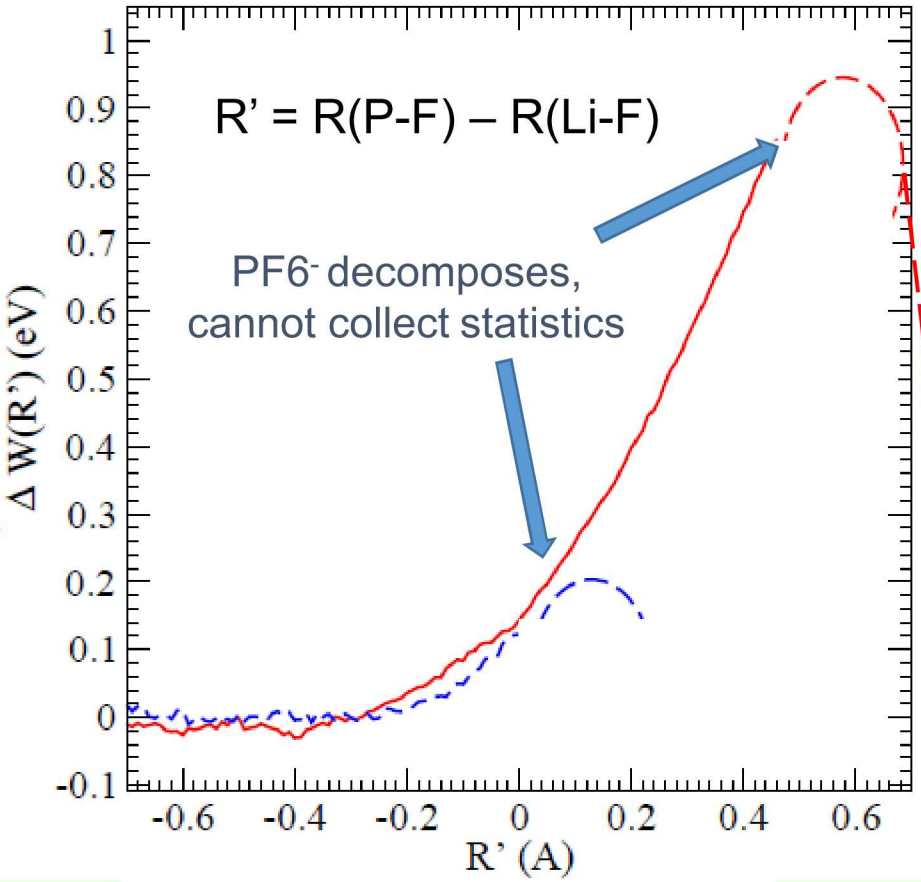
- Previous AIMD study of PF_6- at mixed C=O, C-OH LiC_6 edge finds *barrierless* electrochemical reduction of anion; but voltage-dependence not known

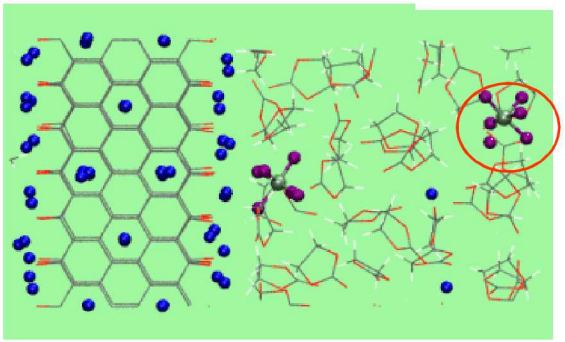
Ganesh, Kent, Jiang, JPCC 116:24476 (2012)

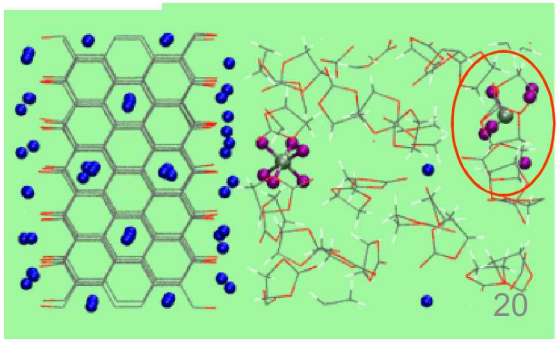
AIMD potential of mean force calculation of P-F bond breaking

interface: 0.53 V
barrier at least 1.0 eV

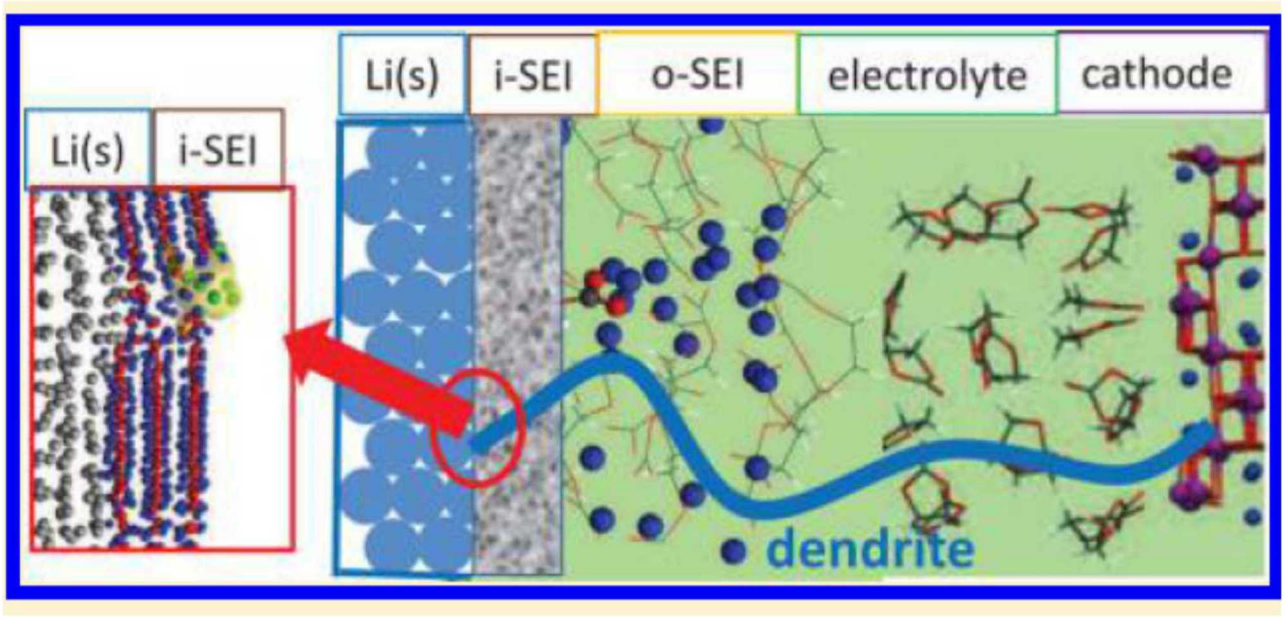
interface: -0.35 V
barrier at most 0.2 eV





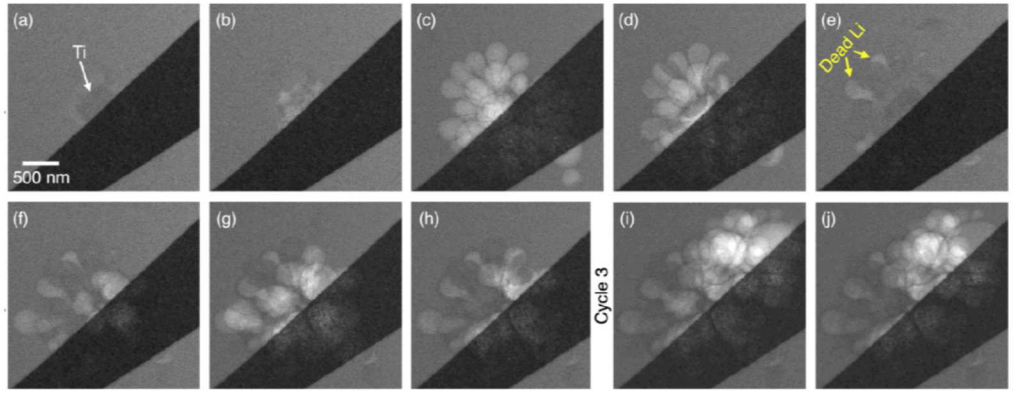


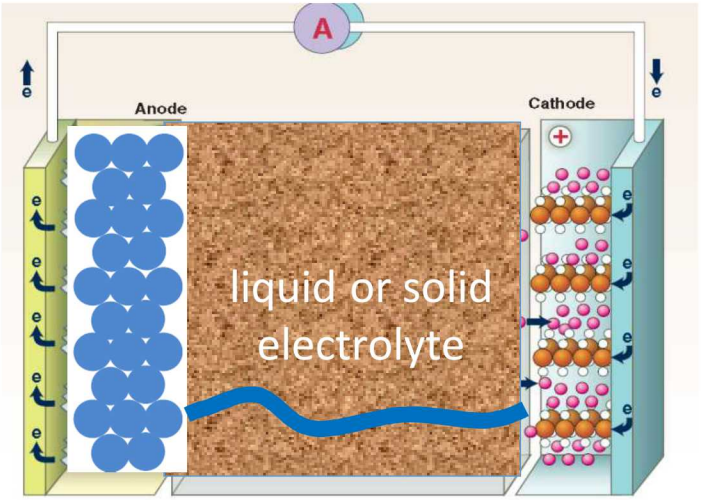
3. Modeling Electron Leakage, Incipient Dendrites in Li metal anode SEI



Electron leaks, dendrites initiate at heterogeneities in SEI

- Lithium metal anode gravimetrically favorable for next generation lithium batteries (LIB)
- risk of dendrite formation – reliability, safety risk
- new imaging evidence emphasizes heterogeneities





Lithium Electrodeposition Dynamics in Aprotic Electrolyte Observed *in Situ via* Transmission Electron Microscopy

Leenheer, Jungjohann, Zavadil, Sullivan, Harris, ACS Nano 9:4379 (2015)

Solid state electrolytes dendrites: role of grain boundaries

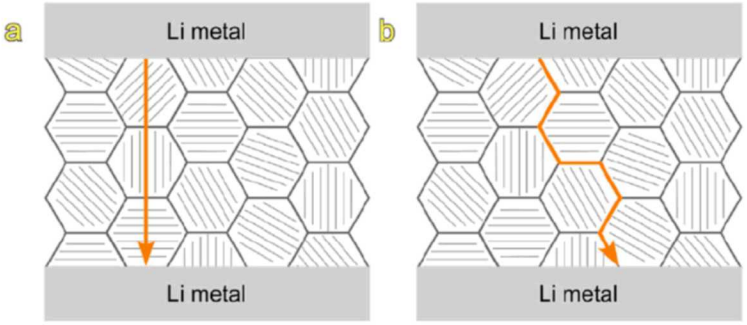


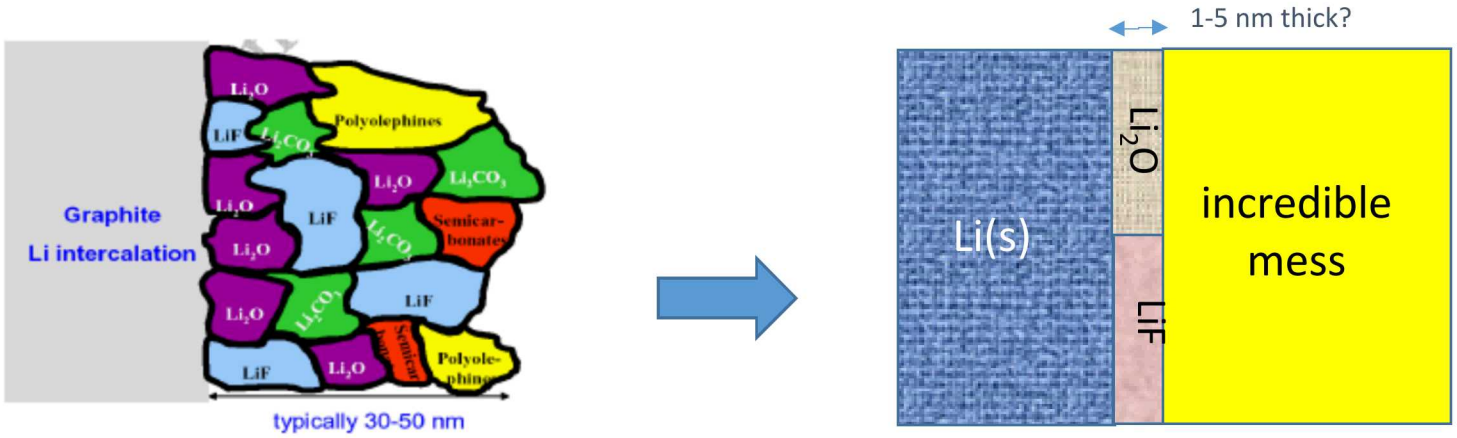
Fig. 1. Illustration of Li metal plating through polycrystalline LLZO solid electrolyte (a) transgranular, (b) intergranular.

Intergranular Li metal propagation through polycrystalline $Li_{6.25}Al_{0.25}La_3Zr_2O_{12}$ ceramic electrolyte

Eric Jianfeng Cheng, Asma Sharafi, Jeff Sakamoto*
Electrochimica Acta 223 (2017) 85–91

Hypothesis

- dendrites in organic electrolyte lithium batteries also initiate at grain boundaries/cracks in the SEI film
- particular in inorganic SEI components on Li metal surfaces
- Use LiF and Li_2O on Li metal as SEI models

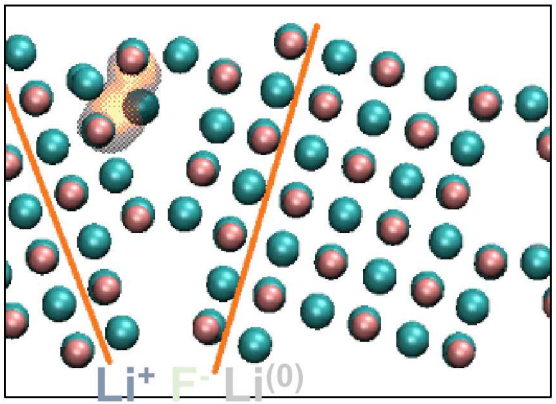


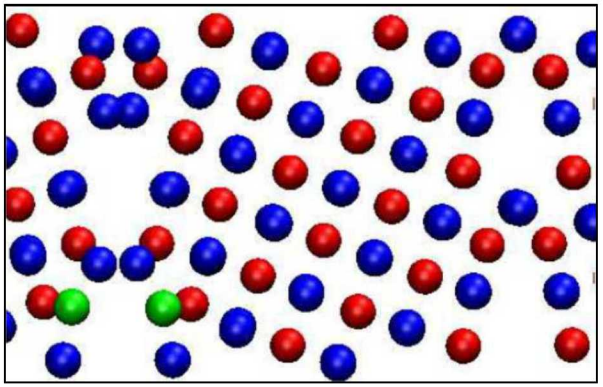
Stability of Solid Electrolyte Interphase Components on Lithium Metal and Reactive Anode Material Surfaces

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

Four trial grain boundaries in LiF & Li_2O

grain boundary 1: "Σ_5" by rotating two (001) slabs by 18.4° (310 facet)





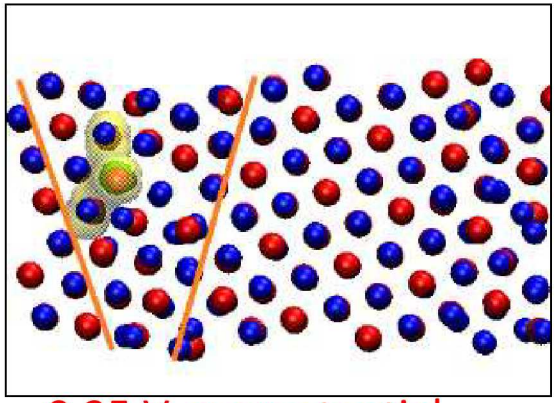
prefered for LiF because
LiF (001) is stable facet

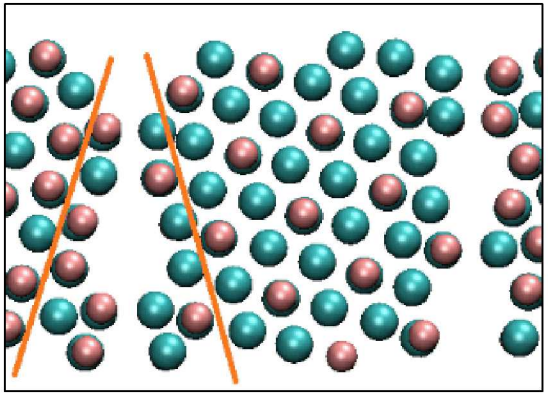
overpotential = $\mu_{Li} - \mu_{Li}$(metal) divided by |e|. Later on we focus on electronic voltage

1.41 V overpotential

1.06 V overpotential for inserting $Li^{(0)}$

grain boundary 2: "16°" by rotating two (111) slabs by 16.1°





prefered for Li_2O because
Li_2O (111) is stable facet

details about constructing GB simulation cell – please ask questions later

0.25 V overpotential
0.03 V for1.7% strain

1.36 V overpotential for inserting $Li^{(0)}$

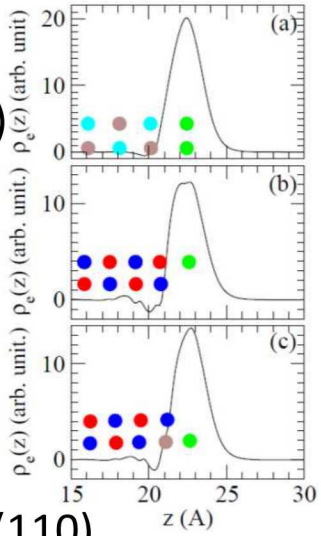
Why the 16° GB in Li_2O can accommodate $Li^{(0)}$?

1. material: LiF is a negative electron affinity material
   Li_2O can support surface electronic states

Electron-trapping polycrystalline materials with negative electron affinity

KEITH P. McKENNA* AND ALEXANDER L. SHLUGER

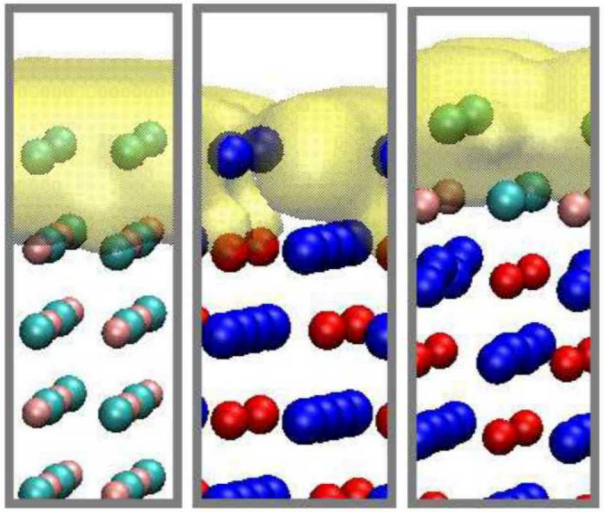
nature materials | VOL 7 | NOVEMBER 2008 | www.nature.com/naturematerials



LiF (001)

Li_2O (110)

Li_2O (110) w/LiF layer



	LiF (001)	Li_2O (110)	Li_2O (110) w/LiF layer
overpotential	0.45 V	0.23 V	0.64 V

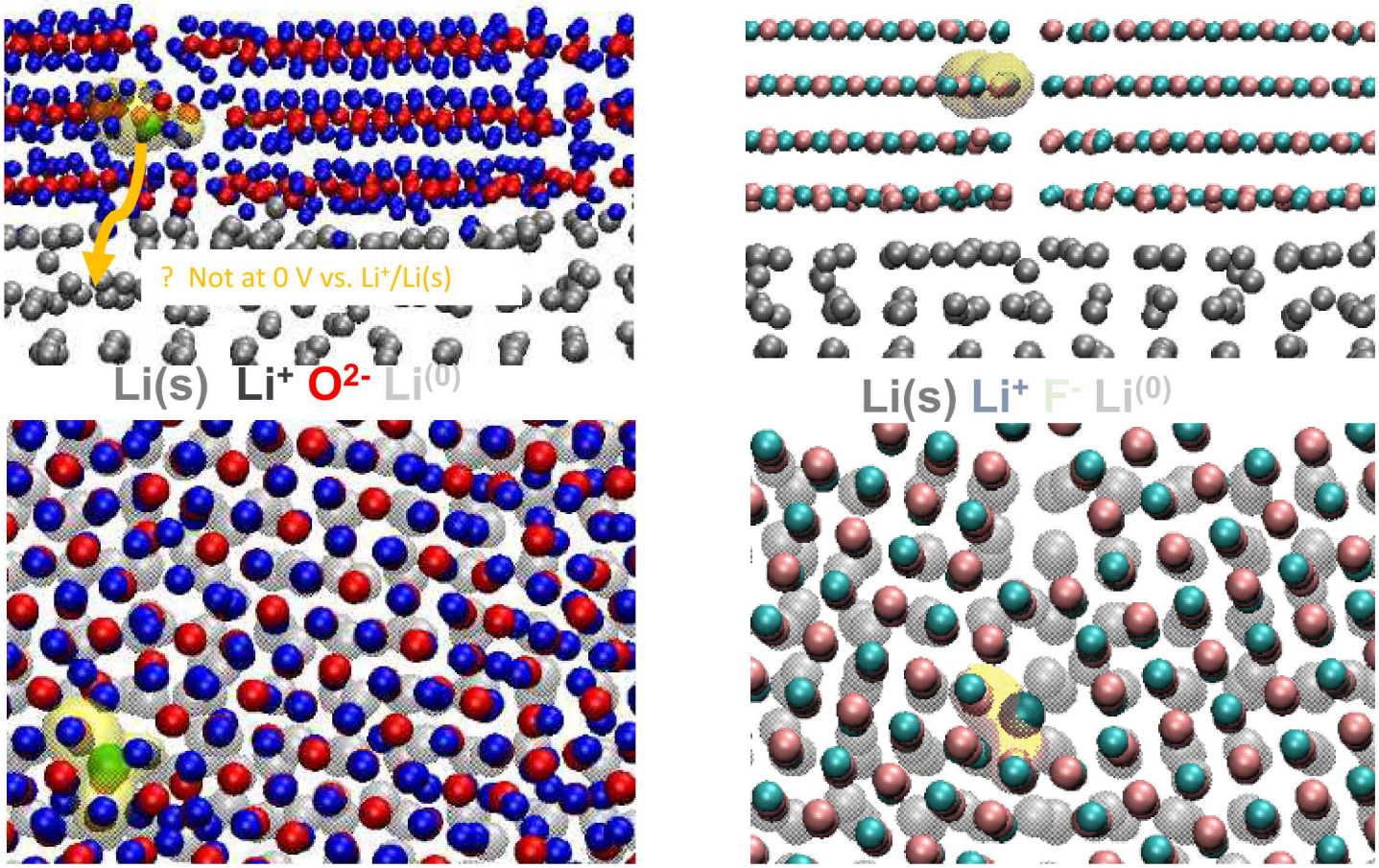
other Li_2O facets even more favorable to Li monolayer

facet	(111)	(310)	$(\bar{1}10)$	"16°"
sur. energy	0.54	1.11	0.94	1.06
Li monolayer	−0.346	0.028	−0.228	0.036

there is only one Li_2O (111) facet: others facets inevitably exposed in GB

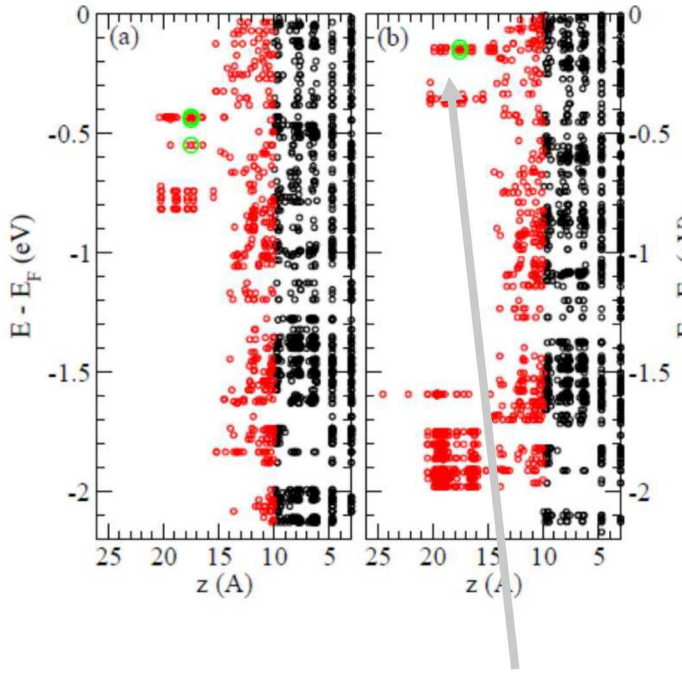
2. distance between added Li to O ions: 1.85, 1.88, 1.95 A for 16° Li_2O GB
   1.88, 1.89, 2.25 A for Σ_5 Li_2O GB

$Li^{(0)}$ are supported even when Li metal present

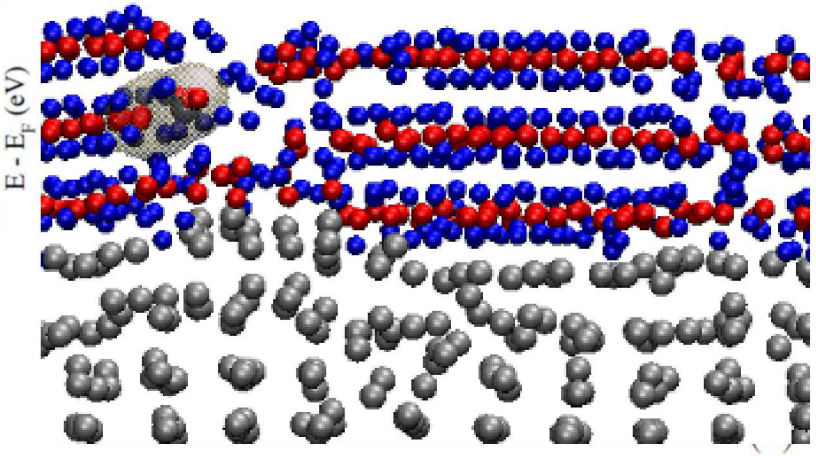


- simulation cells at about $\mathscr{V}_e$ = 0.05 V vs. $Li^+/Li(s)$
- excess e^- cloud does not leak into Li(s)

Band alignment of excess e^- inside Li_2O film



12% tensile strain



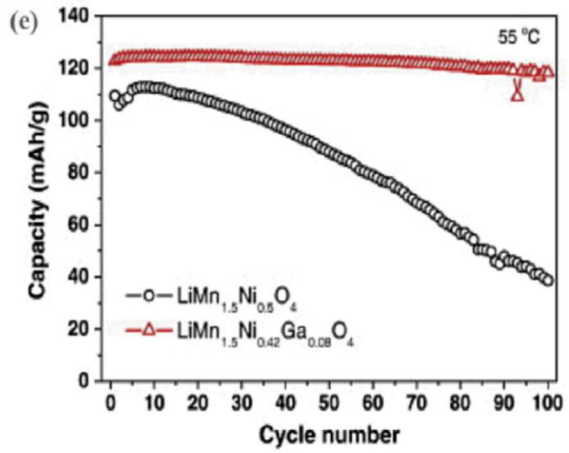
- without strain, excess e^- is almost at Fermi level (barely localized)
- A strain of just 2% drops it into the valence band
- At 12% strain drops it further to -0.5 eV level
- 0.03 V over potential when graind boundary is strained strained

Conclusions on incipient dendrites

- dendrite initiation at heterogeneity confirmed by modeling
- SEI grain boundaries which has sufficient void space facilitate passivation breakdown via $Li^{(0)}$ insertion at low overpotential
- applying strain makes such localized states even more favorable
- incipient Li metal nanoplates can grow in SEI crack
- Li_2O much more permissive of Li metal growth than LiF
- suggest experimental confirmation

4. Interfacial electrolyte reactions on high voltage spinel surfaces

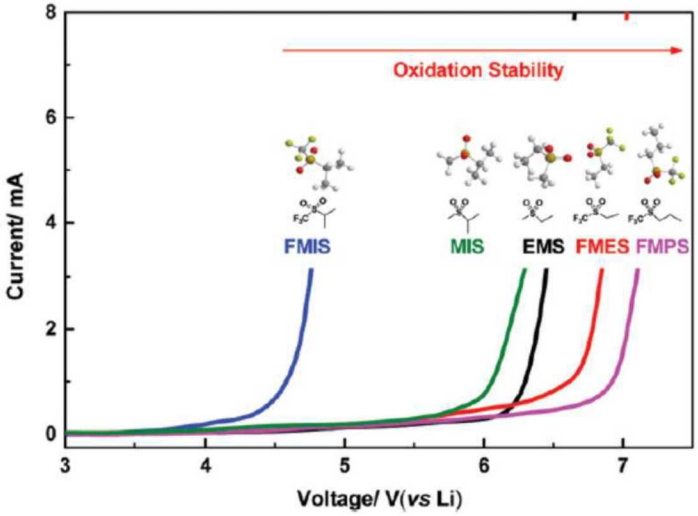
Electrolyte oxidative instability with high voltage cathodes(?)



Key strategies for enhancing the cycling stability and rate capacity of $LiNi_{0.5}Mn_{1.5}O_4$ as high-voltage cathode materials for high power lithium-ion batteries

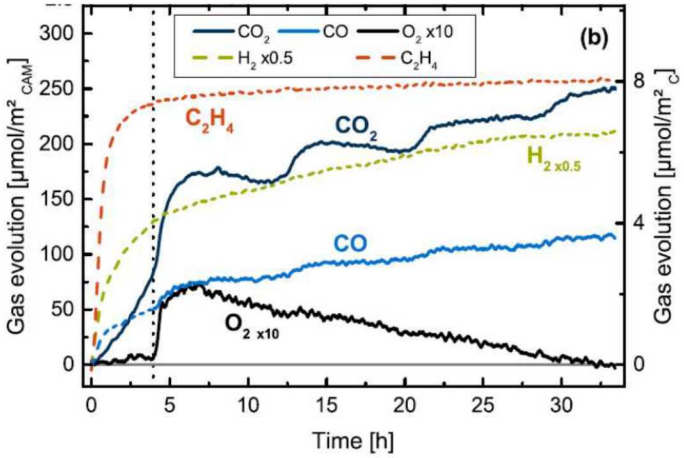
Journal of Power Sources 316 (2016) 85–105

Ting-Feng Yi*, Jie Mei, Yan-Rong Zhu



Oxidatively stable fluorinated sulfone electrolytes for high voltage high energy lithium-ion batteries†

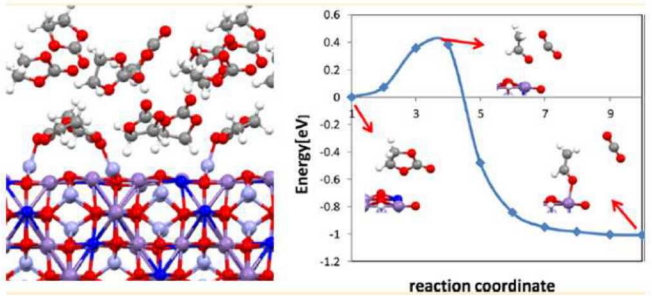
Chi-Cheung Su,[a] Meinan He,[a] Paul C. Redfern,[b] Larry A. Curtiss,[b] Ilya A. Shkrob[a] and Zhengcheng Zhang[a]* *Energy Environ. Sci.*, 2017, **10**, 900–904



Oxygen Release and Its Effect on the Cycling Stability of $LiNi_xMn_yCo_zO_2$ (NMC) Cathode Materials for Li-Ion Batteries

Roland Jung,[a,b,*,z] Michael Metzger,[a,*] Filippo Maglia,[b] Christoph Stinner,[b] and Hubert A. Gasteiger[a,**]

Journal of The Electrochemical Society, **164** (7) A1361-A1377 (2017)



Structures, Electronic States, and Reactions at Interfaces between $LiNi_{0.5}Mn_{1.5}O_4$ Cathode and Ethylene Carbonate Electrolyte: A First-Principles Study

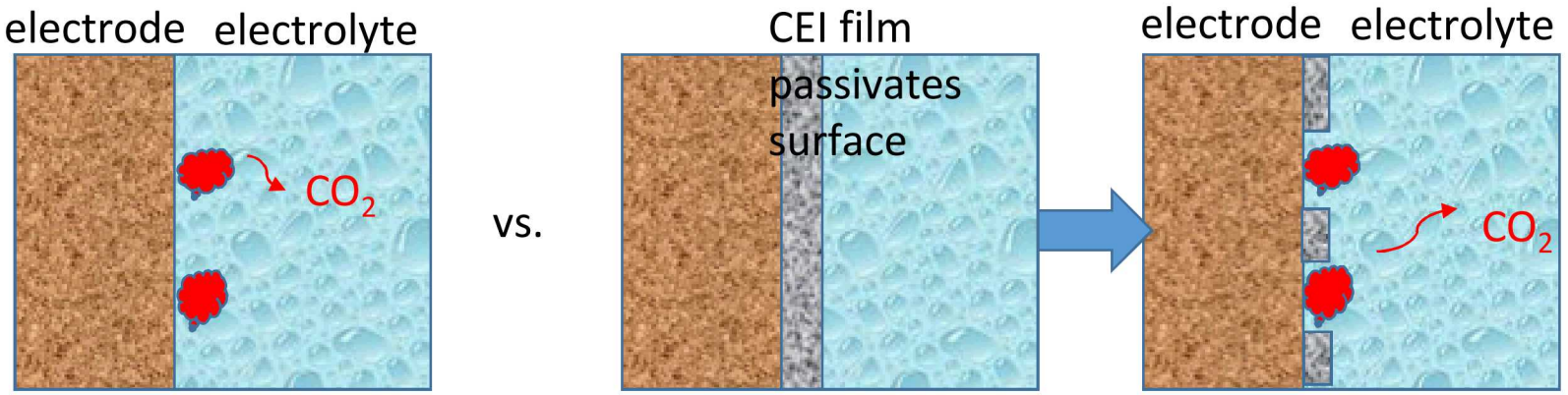
Yukihiro Okuno,[*,†,‡] Keisuke Ushirogata,[†,‡] Keitaro Sodeyama,[§,∥,⊥] Ganes Shukri,[‡,∥] and Yoshitaka Tateyama[*,‡,§,∥]

J. Phys. Chem. C XXXX, XXX, XXX–XXX

My Hypothesis

- capacity fade at high voltage not (all) due to onset of liquid electrolyte decomposition
- liquid electrolyte decomposes at lower voltage on oxide surface, CEI covers catalytic sites
- instead, the oxidation signature > 4.5 V due to decomposition of passivating layers on surface (e.g., organic residues and Li_2CO_3) ->uncontrolled destruction of liquid electrolyte

- should focus more on CEI destruction, not only liquid electrolyte destruction
- kinetic stability of CEI/SEI films clarifies what should happen at the interface



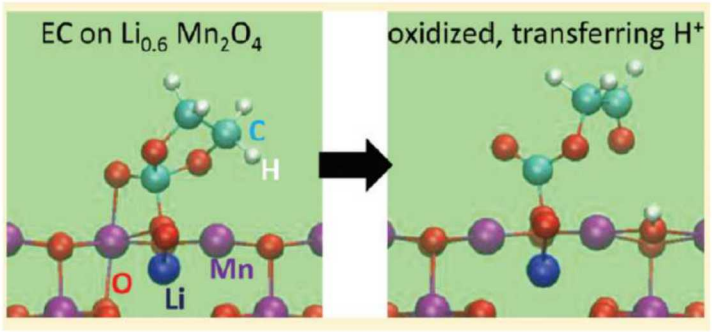
low voltage: clean electrode surface
high voltage: electrolyte breakdown

low voltage: clean electrode
Intermediate voltage: CEI

high voltage: CEI
breaks down

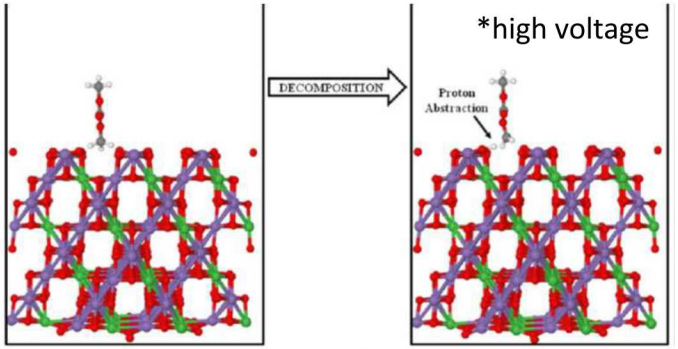
EC-based liquid electrolyte reacts with cathodes at modest voltage

- Bulk thermodynamics:EC oxidizes < 3.8 V: EC + $LiMn_2O_4$ -> MnO + Li_2CO_3 , ~ -1 eV! (PBE0)



ΔE = -2.1 eV
(exothermic)

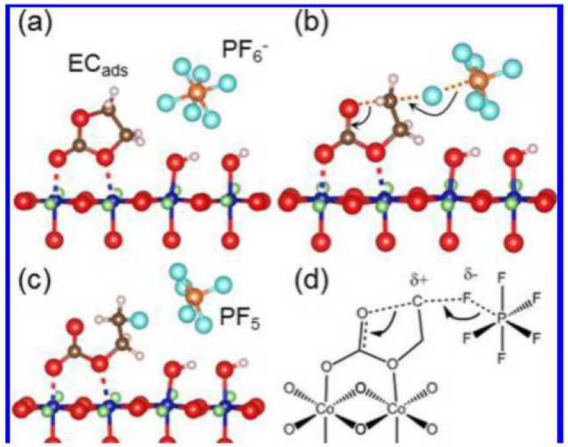
barrier 0.6 eV



First-Principles Modeling of the Initial Stages of Organic Solvent Decomposition on $Li_xMn_2O_4$(100) Surfaces

Kevin Leung* *J. Phys. Chem. C* 2012, 116, 9852–9861

*1.28 eV barrier
but fully lithiated
(low voltage)



Degradation of Ethylene Carbonate Electrolytes of Lithium Ion Batteries via Ring Opening Activated by $LiCoO_2$ Cathode Surfaces and Electrolyte Species

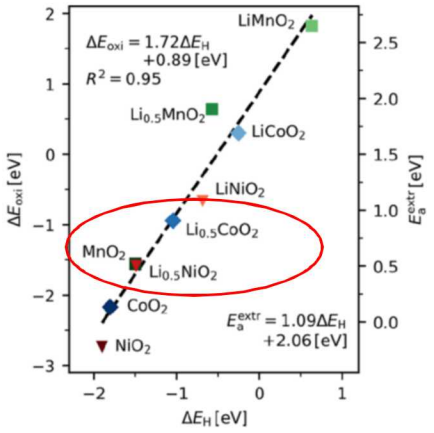
ACS Appl. Mater. Interfaces 2016, 8, 26664–26674

Jonathon L. Tebbe,† Thomas F. Fuerst,† and Charles B. Musgrave*,†,‡

Towards high throughput screening of electrochemical stability of battery electrolytes

Nanotechnology **26** (2015) 354003

Oleg Borodin[1], Marco Olguin[1], Carrie E Spear[2], Kenneth W Leiter[2] and Jaroslaw Knap[2]



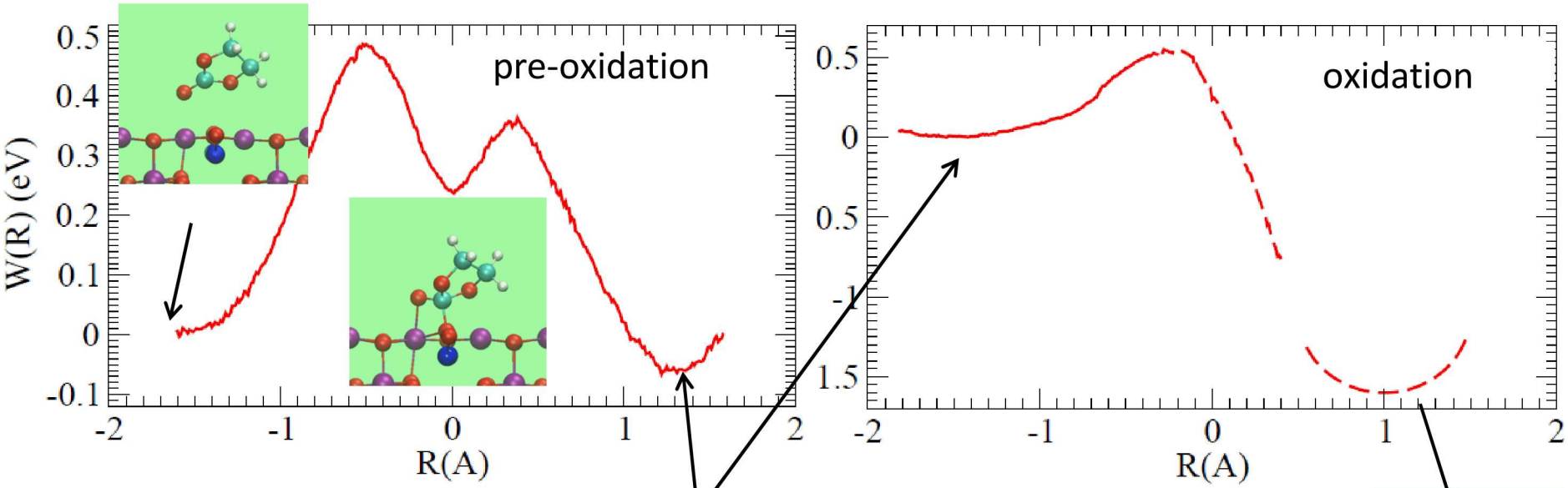
Oxidation of Ethylene Carbonate on Li Metal Oxide Surfaces

Thomas M. Østergaard,† Livia Giordano,‡,§ Ivano E. Castelli,∥,† Filippo Maglia,⊥ Byron K. Antonopoulos,⊥ Yang Shao-Horn,‡,#,∇ and Jan Rossmeisl*,†

J. Phys. Chem. C 2018, 122, 10442–10449

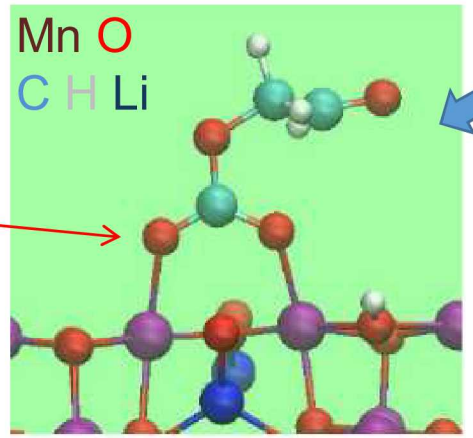
- Partially delithated cathode oxide surfaces reacts with EC at modest equilibrium voltage
- barrier < 1 eV (faster than 1 hour) -> electrolytes already degrade, don't need high voltage

EC decomposition at liquid/$Li_{0.6}Mn_2O_4$ interface



(only showing decomposed EC)

If the (100) facet exhibits modest barriers, step edges/defect sites even more likely to react this way.

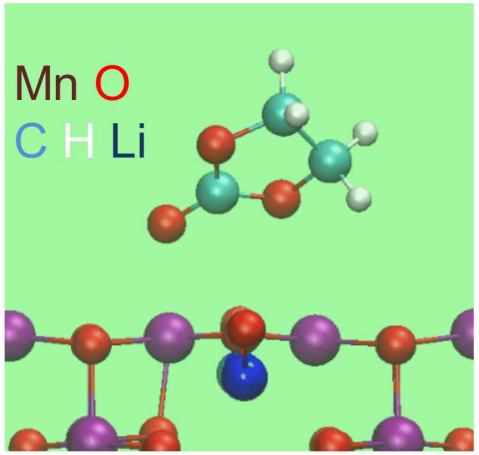


AIMD simulations:
energetics similar to UHV
But a surface O yanked out

1 eV barrier <-> 1 hour reaction time at T=300 K
If barrier (ΔE^*) > 1 eV, assume reaction too slow

EC decomposition on $Li_{0.6}Mn_2O_4$ (100): UHV, T=0K similar

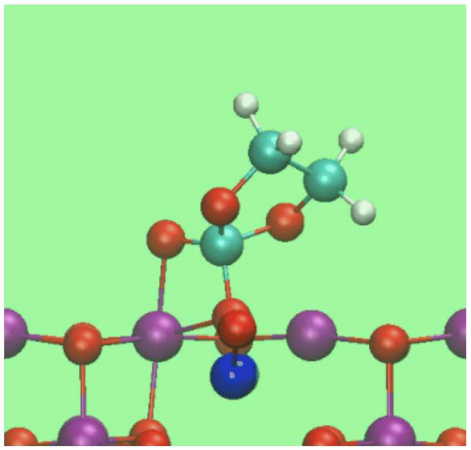
Leung, JPCC 116:9852 (2012)



physisorb

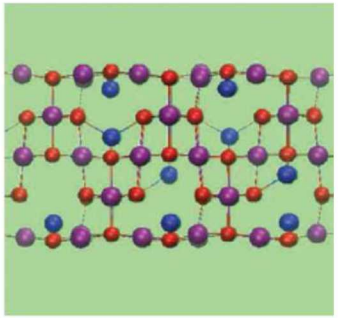
ΔE = -0.01 eV
ΔE^* = 0.24 eV

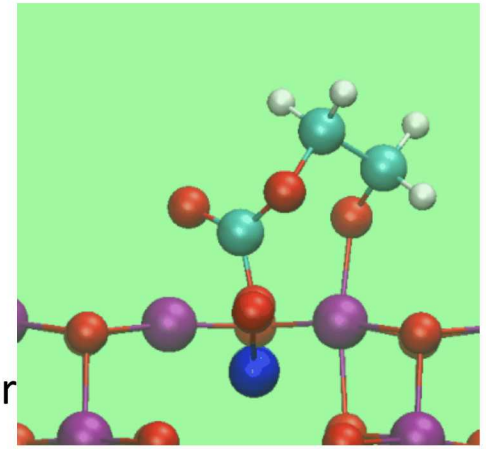
1 eV barrier ~ 1 hour reaction time, attainable



chemisorb

ΔE = -0.10 eV
ΔE^* very low

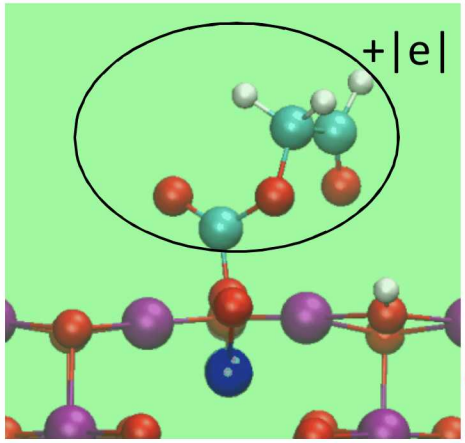




bond-breaking

ΔE = -2.06 eV
ΔE^* = 0.62 eV

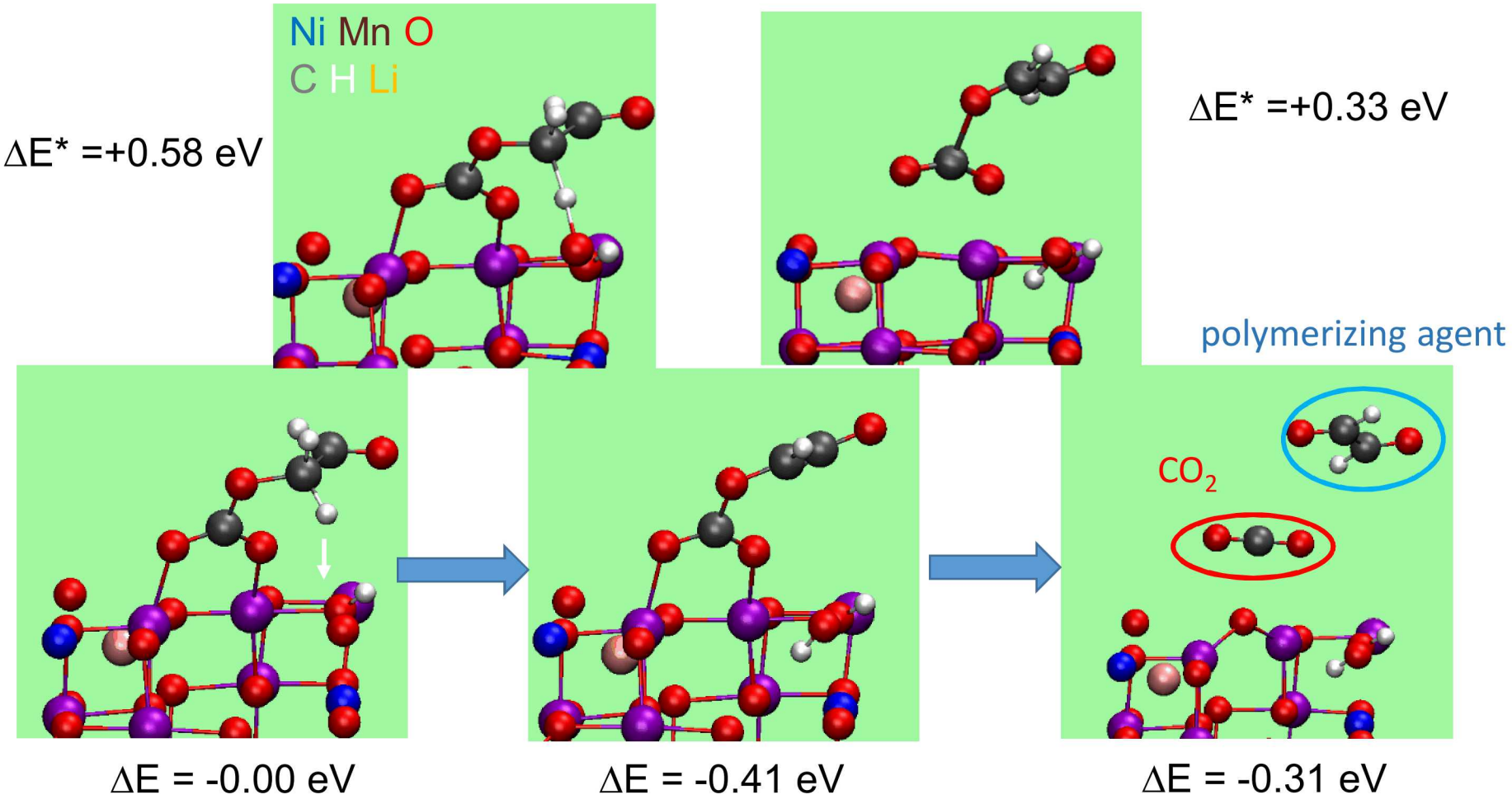
surface-assisted oxidation + H^+ transfer



oxidation + H^+ transfer

Next steps in oxidative degradation? (DFT+U)

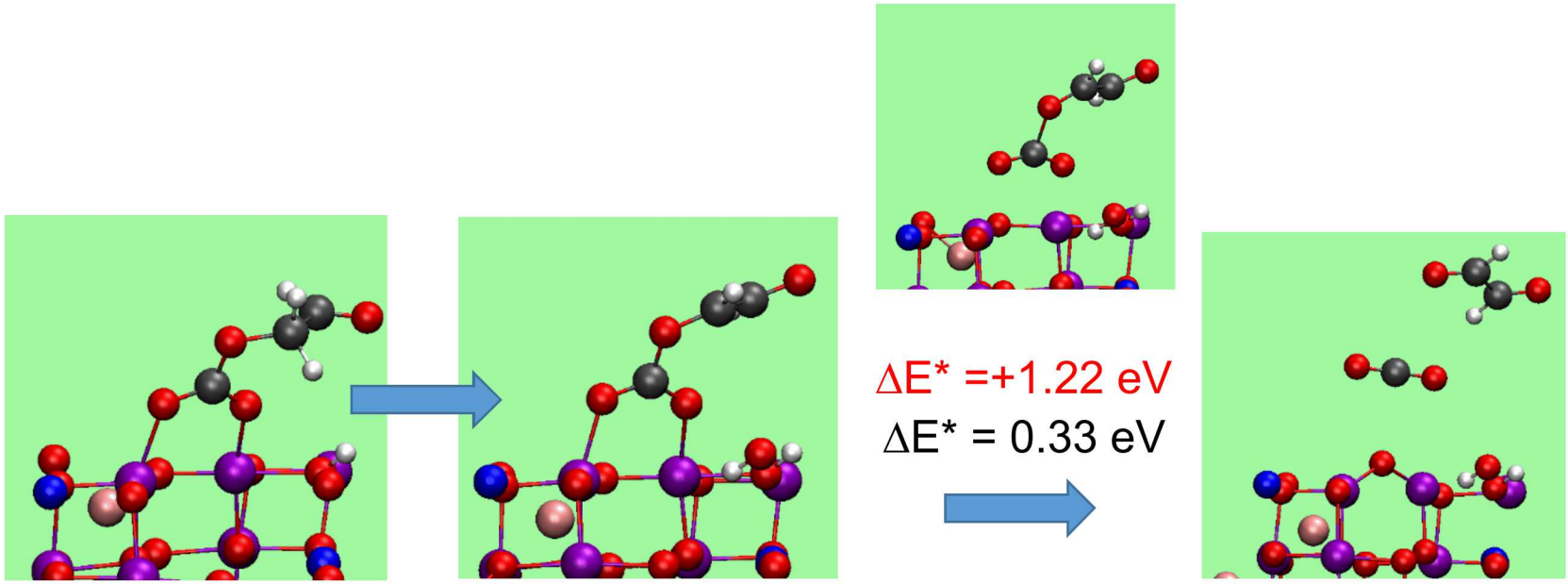
- Low voltages: initial EC decomposition on LNMO (001) surface just like on LMO (001)
- EC fragment adsorbs and block reaction sites
- high voltages these fragments further oxidizes, release CO_2 and catalytic sites – more reactions



- Predict all steps exothermic (downhill), all barriers < 1 eV, release CO2 – success?

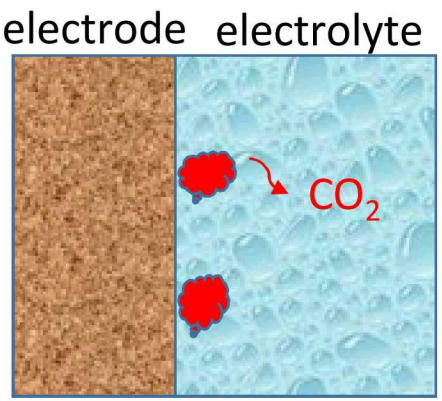
Story doesn't end here …

- Showed that for cathode chemical reaction at interphase, electronic voltage less important
- But DFT functional more delicate
- With DFT+U, cannot distinguish between LNMO (high voltage) and LMO (non-high voltge)
- Have to switch to PBE0 hybrid functional – 100 x more costly

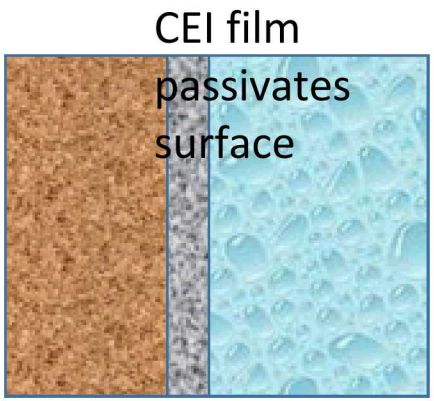


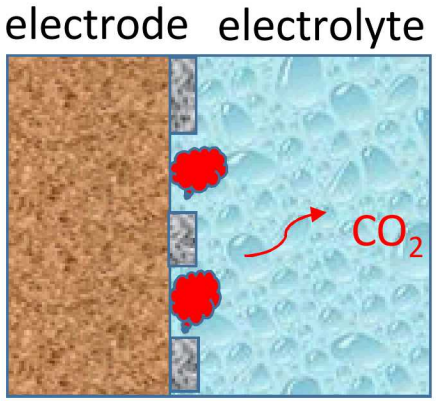
Conclusions

- Two step process hypothesis of electrolyte oxidation on high voltage spin (001) surfaces demonstrated computationally
- EC molecules decompose on both $Li_xMn_2O_4$ and high voltage LNMO (001) at modest potentials ($x > 0.5$)
- Partially decomposed EC fragments further oxidize to form CO_2, at higher potentials
- this clears the surface for more reactions, on LNMO surfaces at higher voltage, not on LMO
- Use of hybrid DFT functional (PBE0) crucial to differentiate LMO and LNMO



vs.





low voltage: clean electrode surface
high voltage: electrolyte breakdown

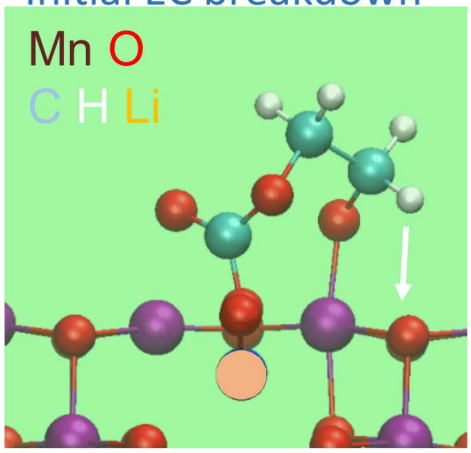
low voltage: clean electrode
Intermediate voltage: CEI

high voltage: CEI
breaks down

Backup Slides

Re-examine interfacial reactions on LMO (001) with DFT/PBE0

Initial EC breakdown



DFT+U (old)

ΔE = -2.06 eV

ΔE^* = 0.62 eV

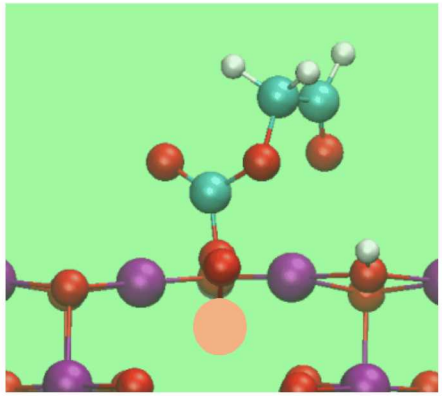
PBE0 (new)

ΔE = -1.75 eV

ΔE^* = 1.05 eV

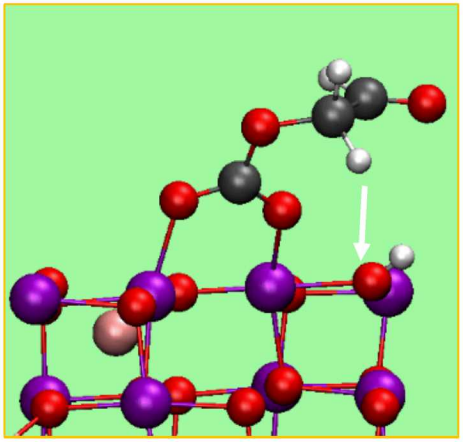
First-Principles Modeling of the Initial Stages of Organic Solvent Decomposition on $Li_xMn_2O_4$(100) Surfaces

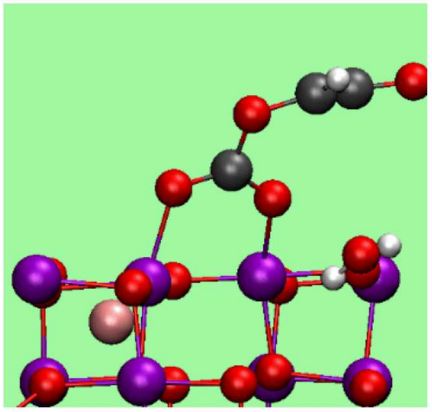
Kevin Leung* *J. Phys. Chem. C* 2012, 116, 9852–9861



- ΔE^* 60% higher!
- zero-point energy brings ΔE^* below 1 eV, within 1 hour

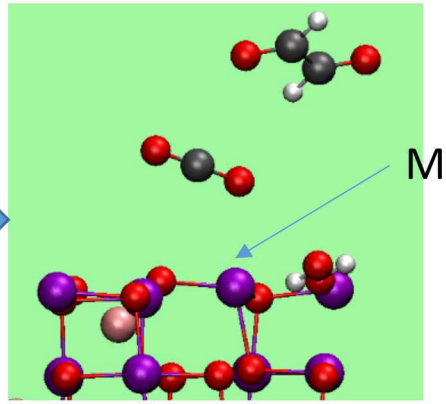
Subsequent EC breakdown on LMO (001)





ΔE = -0.45 eV

ΔE = -0.62 eV



ΔE = -0.15 eV

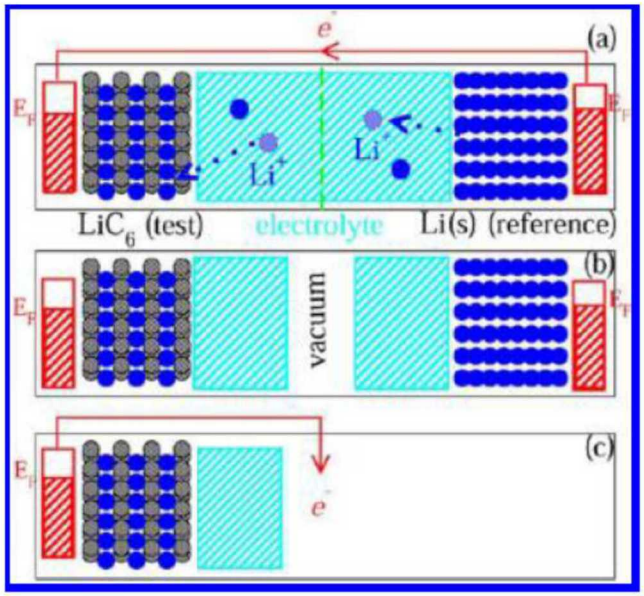
ΔE = +0.62 eV!

- PBE0 (unlike DFT+U) predicts CO_2 release is unfavorable (even counting gas entropy)
- PBE0 predicts first EC oxidation step is still kinetically favorable (barely)

should re-examine voltage calculations (and measurements)

liquid electrolytes

- DFT – only one electrode (one E_F)
- on clean liquid/electrode interface, can open up gap in liquid, compute work function -> absolute voltage
- liquid-air interfacial contributions cancel when adding other electrode

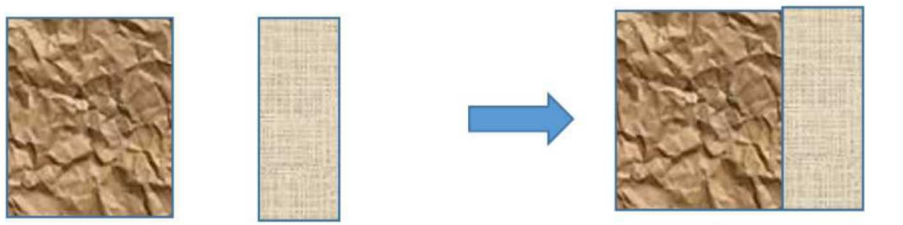


Toward First Principles Prediction of Voltage Dependences of Electrolyte/Electrolyte Interfacial Processes in Lithium Ion Batteries

Kevin Leung* and Craig M. Tenney *J. Phys. Chem. C* 2013, 117, 24224–24235

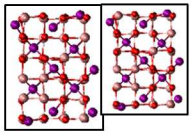
solid electrolytes

- similar with solid-solid interfaces (?)
- Indeed, this is basis of Kelvin probe force microscopy (KPFM voltage measurements
- but no universal solid-air for solids – KPFM should be facet dependent!
- one assumption in DFT calculations – no long-range space charge

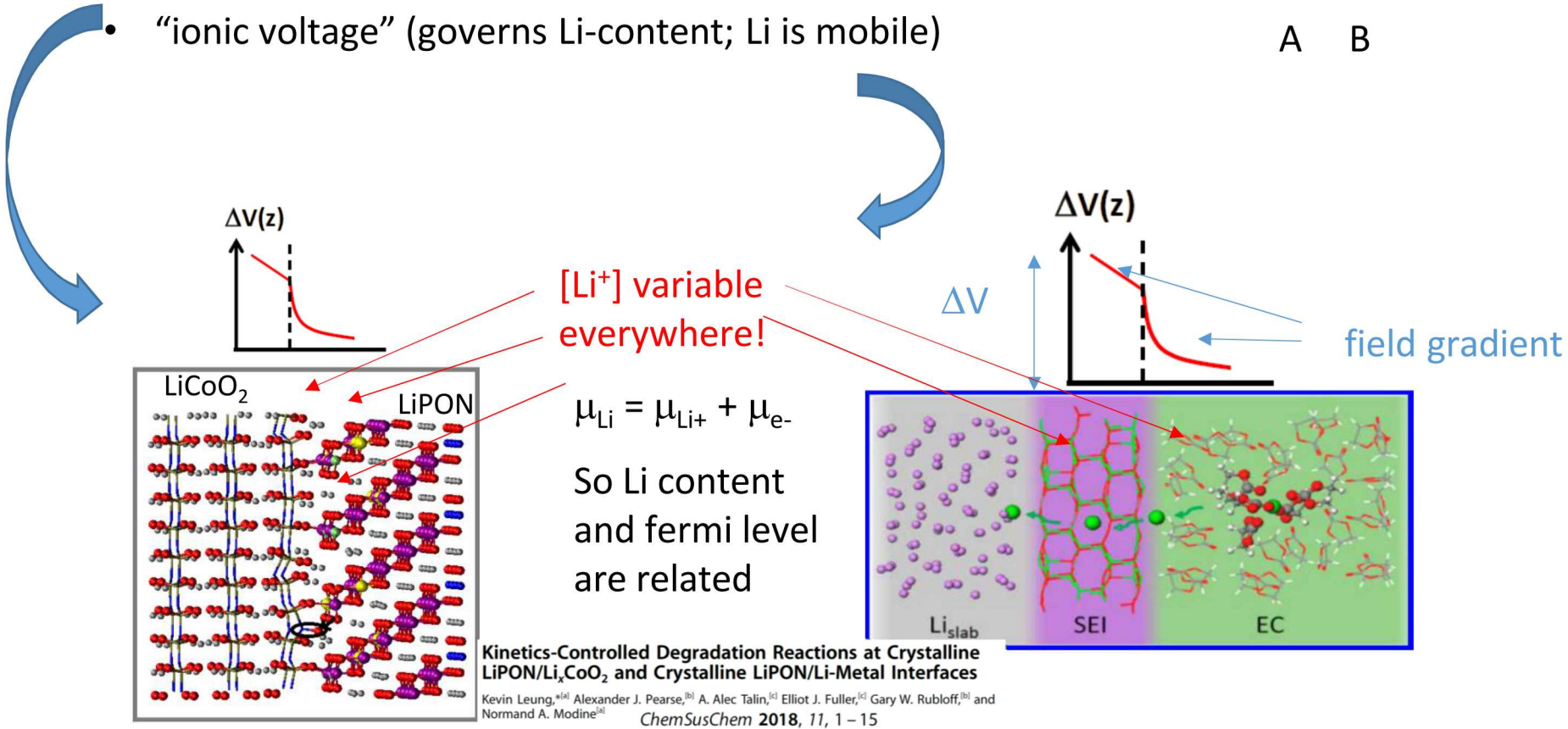


Solid-solid interfaces challenging to simulate

- Interfacial reactions -> interfacial structures -> function
- In general, solid-solid interfaces hard to model
- lattice registry between A & B phases, lack of atomic-resolution experimental input
- In electrochemical interfaces: voltage dependence too:
- electronic voltage (~ Fermi level)
- "ionic voltage" (governs Li-content; Li is mobile)



A B



Kinetics-Controlled Degradation Reactions at Crystalline LiPON/Li_xCoO_2 and Crystalline LiPON/Li-Metal Interfaces

Kevin Leung,*[a] Alexander J. Pearse,[b] A. Alec Talin,[c] Elliot J. Fuller,[c] Gary W. Rubloff,[b] and Normand A. Modine[a]

ChemSusChem **2018**, *11*, 1 – 15

Experimental analogy: Galvanostatic Intermittent Titration (GITT)

Metrohm Autolab B.V.

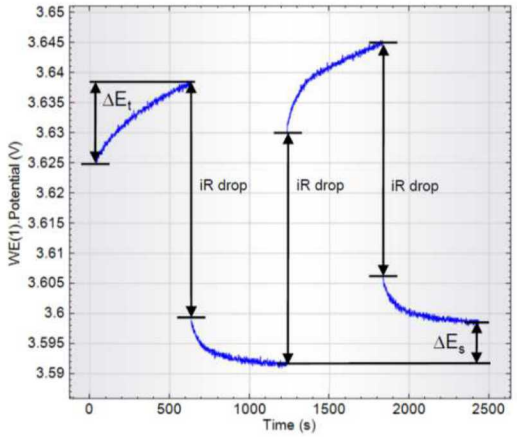
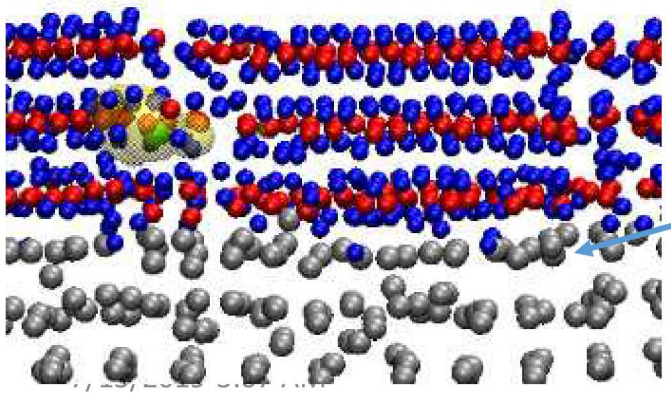
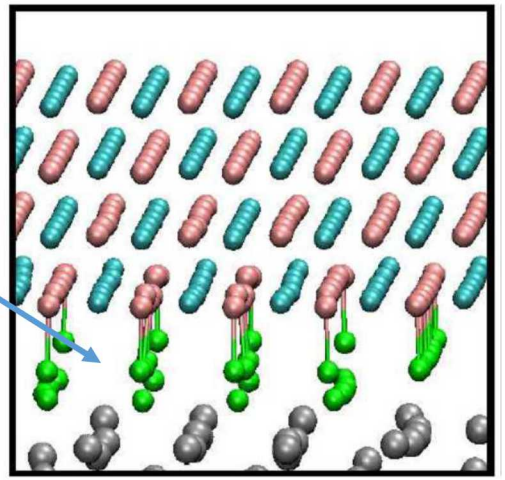


Figure 3 – First two charge steps, each composed by 10 minutes of C/10 galvanostatic charge, followed by 10 minutes of relaxation time. The iR drop is shown, together with the ΔE_t and ΔE_s (Equation 1.2).

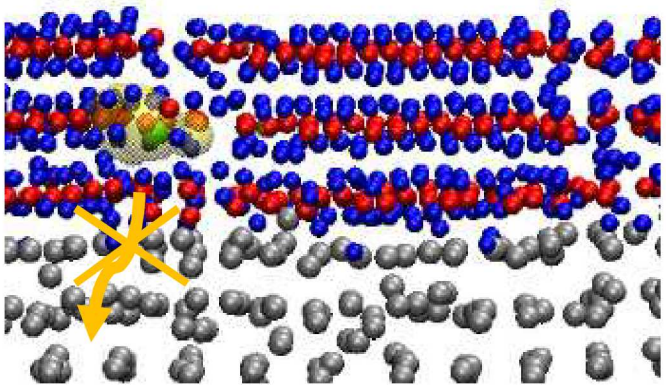
- v_e is the correct instantaneous voltage set by potentiostat
- Li content in solid (or interface) slowly relaxes
- But in DFT calculations, Li hardly move
  -- little relaxation, system out of equilibrium
- Need to move Li content by hand to make sure we have equilibrium



voltage and Fermi level controlled by “interlayer” of partially charged Li



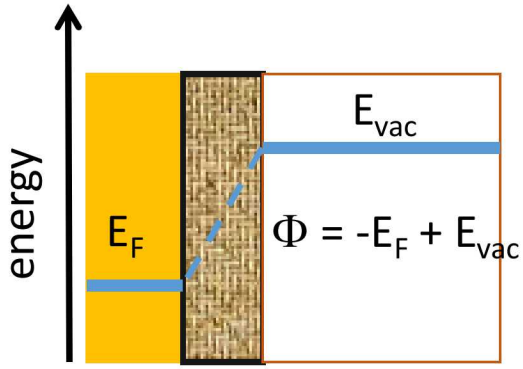
Must use correct definition of voltage



To show this, need a detour into the proper definition of "voltage"

(confusion in battery community)

- previous voltage definition in this talk: "equilibrium" or "ionic voltage", μ_{Li}
- true (electronic) voltage $\mathcal{V}_e$: fermi level referenced to vacuum, minus 1.37 V
- can only talk about $\mathcal{V}_e$, if simulation cell has an interface
- at equilibrium, this definition ($\mathcal{V}_e$) must coincide with "ionic voltage" (μ_{Li})



use vacuum as reference electrode

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

A High-Capacity Lithium–Gas Battery Based on Sulfur Fluoride Conversion

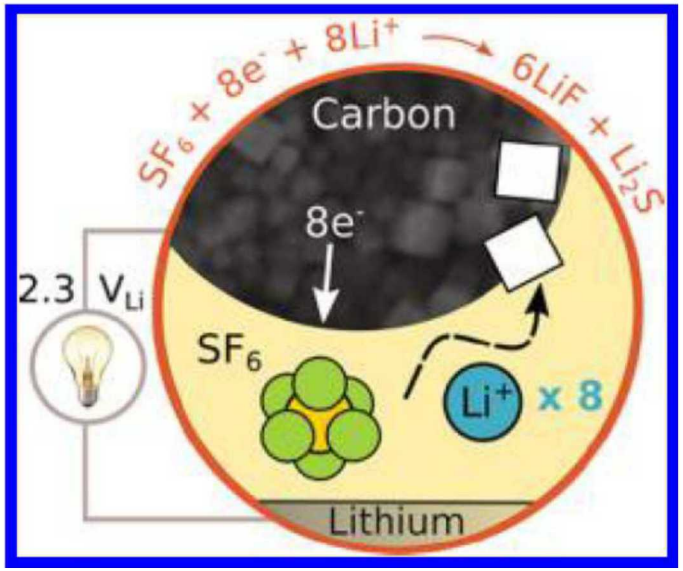
J. Phys. Chem. C 2018, 122, 7128–7138

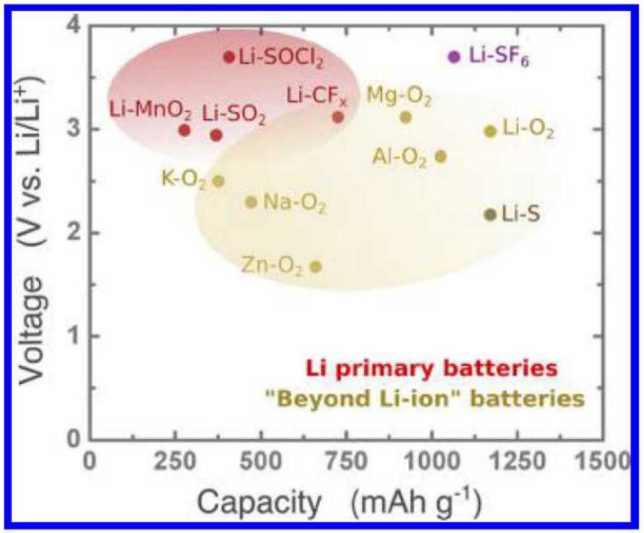
Yuanda Li, Aliza Khurram, and Betar M. Gallant*

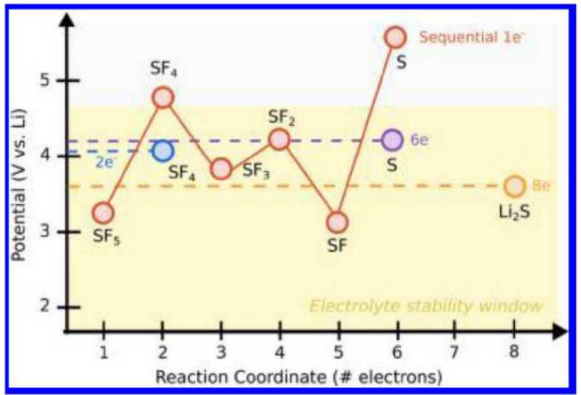
Anode: $8Li \rightarrow 8Li^+ + 8e^-$

Cathode: $SF_6(g) + 8e^- + 8Li^+ \rightarrow 6LiF(s) + Li_2S(s)$

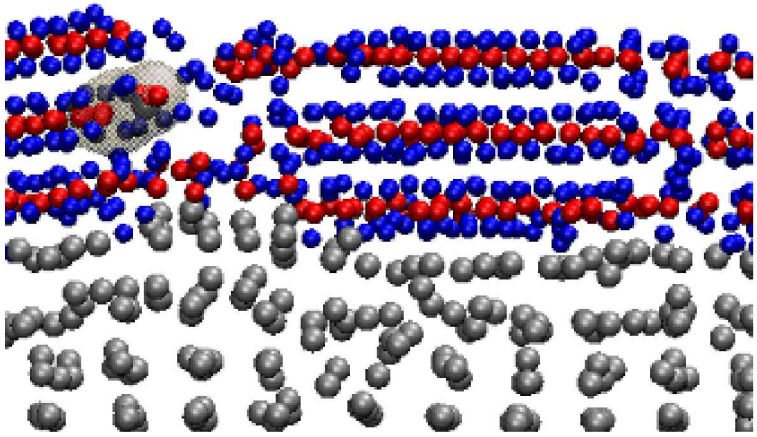
It is reasonable to hypothesize that the high overpotentials originate from weak attraction and interactions of SF_6 with the carbon surface and/or to intrinsically slow kinetics of S–F bond breaking, both of which could give rise to sluggish electron transfer. The CV results show that even highly convective conditions do not modify the reaction rate at any potential during the reduction scan.



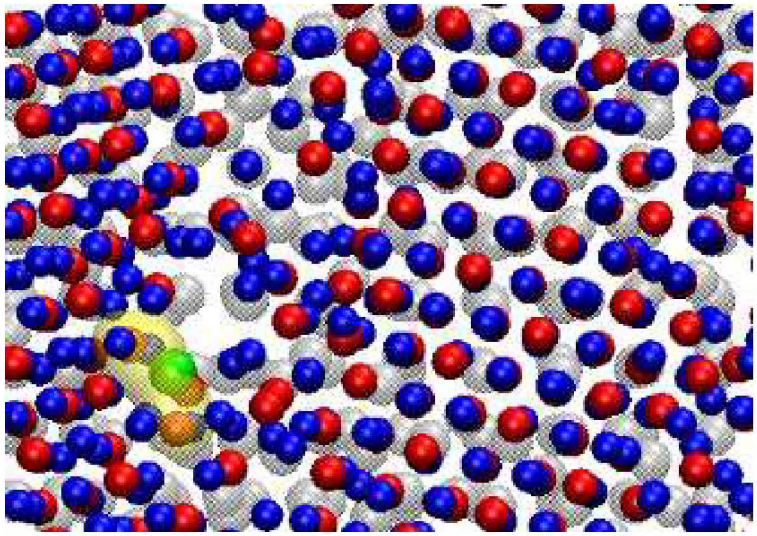




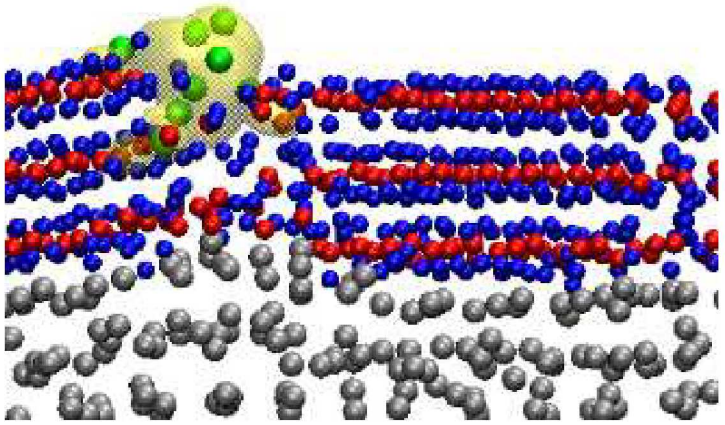
Stretch simulation cell 12%, mimic SEI curvature



Li(s) Li^+ O^{2-} $Li^{(0)}$



- LiF Σ_5 GB – not much happens
- Li_2O 16° GB – broken Li-O bonds, crack at surface
- adding 9 Li to crack region costs no overpotential



DFT functional problem?

Insights into Current Limitations of Density Functional Theory

Aron J. Cohen, Paula Mori-Sánchez, Weitao Yang*

8 AUGUST 2008 VOL 321 SCIENCE

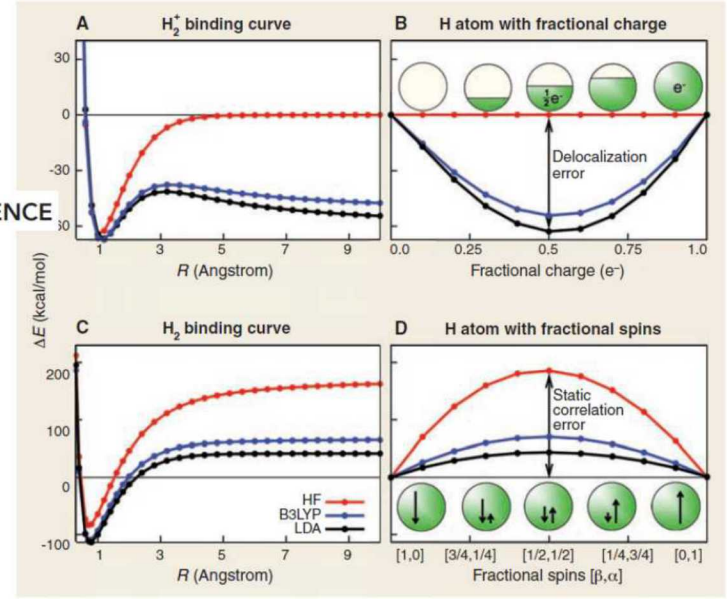
Energetic Study of Clusters and Reaction Barrier Heights from Efficient Semilocal Density Functionals

Guocai Tian [1,2,*], Yuxiang Mo [2] and Jianmin Tao [2,*]

Computation **2017**, 5, 27

Method	LSDA	PBE	TPSS	TM	TMTPSS	B3LYP	M06L	PBE0	SCAN
ME	−14.78	−8.66	−8.14	−7.08	−6.86	−4.15	−3.9	−3.68	−7.7
MAE	14.88	8.71	8.17	7.08	6.86	4.28	4.1	3.99	7.7

Table 3. Summary of deviations of the calculated reaction barrier heights from best values [41] for the BH76 test set. Results are taken from Reference [42] for M06L, Reference [8] for SCAN, and Reference [41] for local spin-density approximation (LSDA), PBE, TPSS, B3LYP, and PBE0. All values are in kcal/mol. ME = theory − best values from Reference [41].

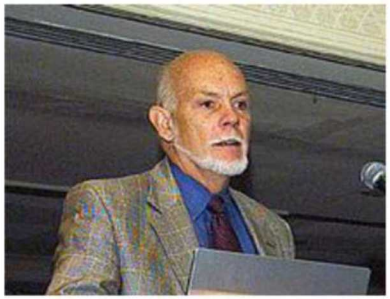


- barriers (ΔE*) more accurate with PBE0
- but PBE0 100x costlier than DFT+U

- "+U" augmentation also less accurate than PBE0 for Mn localized electrons in d-orbitals

One Nobel Laureate's View

Humanity's Top 10 Problems for Next 50 Years



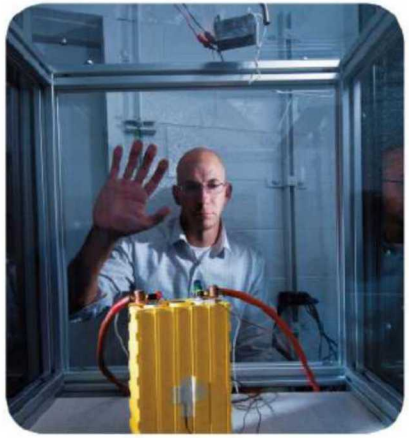
Richard E. Smalley, "Our Energy Challenge"

https://www.youtube.com/watch?v=CpYTVMhPUzc

1. **Energy**
2. **Water**
3. **Food**
4. **Environment**
5. **Poverty**
6. **Terrorism and War**
7. **Disease**
8. **Education**
9. **Democracy**
10. **Population**

Lifetime/safey/reliability critical

http://www.popularmechanics.com/cars/news/pictures/Chevy_Volt_Slideshow



A Sandia researcher prepares to test a battery to determine its response under abuse conditions.

Vehicle batteries are not laptop batteries.

- 16 KWh Li-ion battery pack for the Chevy Volt (175 kg)
- expensive (~$10K?)
- requirement: > 8 year life