SAND2018-8680C

Modeling solid-solid interfaces in lithium ion batteries

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Acknowledgement

Shen Dillon, Alex Pearse, A. Alec Talin, Elliot Fuller, Gary Rubloff, Normand Modine, Chunsheng Wang, Christine James, Yue Qi

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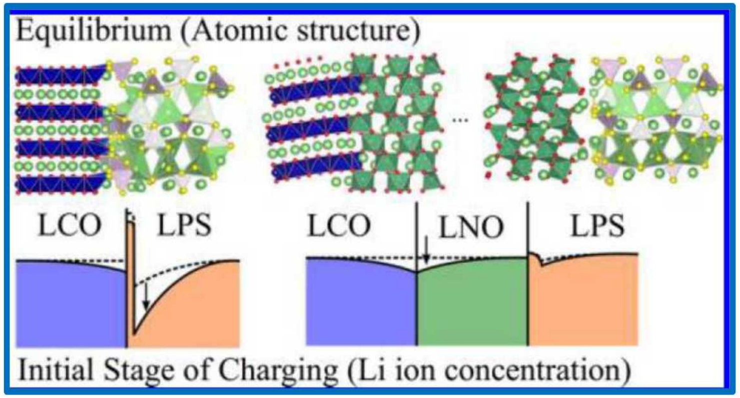
Solid-solid interfaces ubiquitous in Li-ion batteries

- In all-solid-state-batteries: solid electrolyte-electrode interfaces
- In liquid electrolyte-based batteries: SEI (or CEI) film between liquid and electrodes
- almost all battery interfaces are "dirty" – not pristine (like Pt/water or Au/water)

(new challenge but new opportunity, cross-over to other fields)

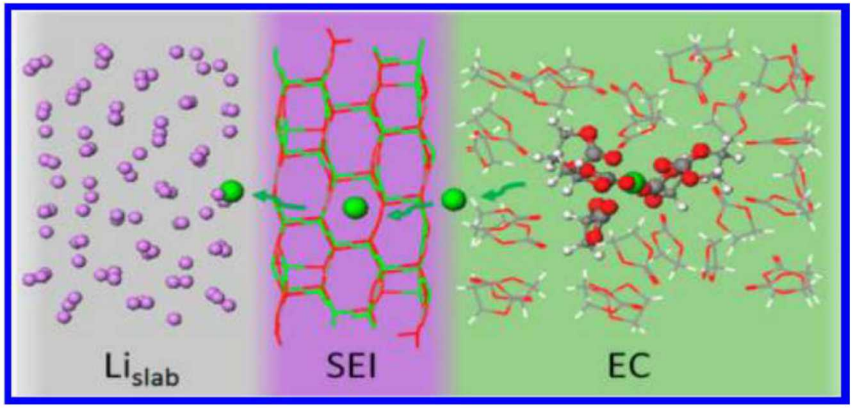


Space–Charge Layer Effect at Interface between Oxide Cathode and Sulfide Electrolyte in All-Solid-State Lithium-Ion Battery

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

Chem. Mater. 2014, 26, 4248–4255

all-solid

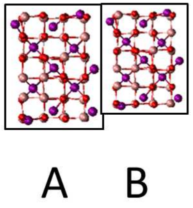


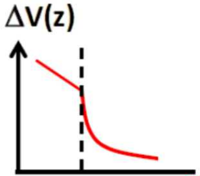
Computational Exploration of the Li-Electrode|Electrolyte Interface in the Presence of a Nanometer Thick Solid-Electrolyte Interphase Layer Yunsong Li,[†] Kevin Leung,[‡] and Yue Qi*[,†] *Acc. Chem. Res.* (2016)

liquid-solid

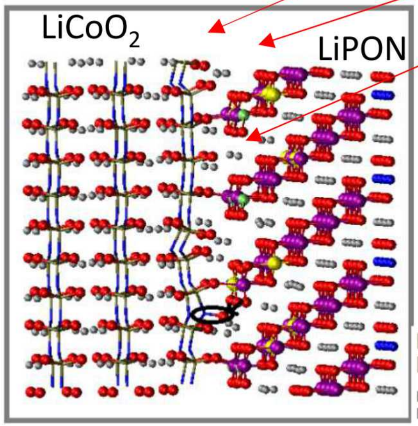
Solid-solid interfaces challenging to simulate

- 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)



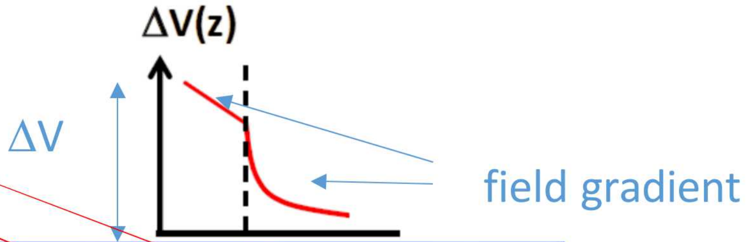


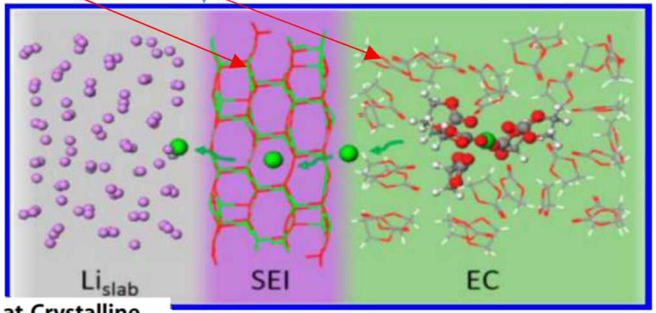
[Li^+] variable everywhere!



$\mu_{Li} = \mu_{Li+} + \mu_{e-}$

So Li content and fermi level are related





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

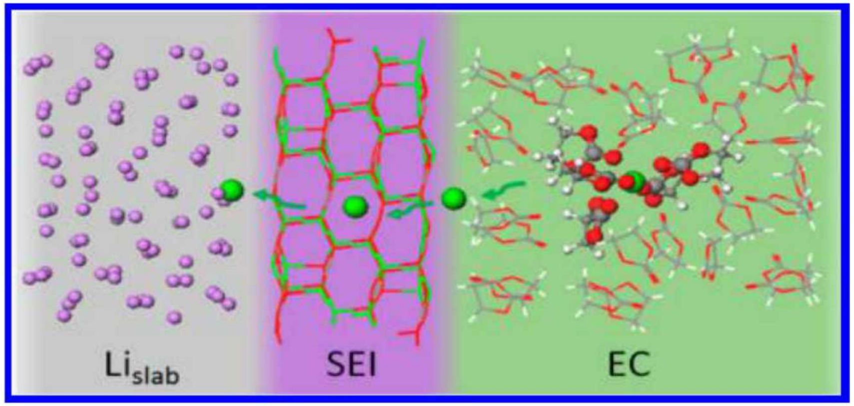
Kevin Leung,*[a] Alexander J. Pearse,[b] A. Alec Talin,[c] Elliot J. Fuller,[c] Gary W. Rubloff,[b] and Normand A. Modine[a]

ChemSusChem **2018**, *11*, 1 – 15

Dirty electrode/liquid interfaces: time-scale mismatch!

Computational Exploration of the Li-Electrode|Electrolyte 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!

In this talk, focus on solid-solid interfaces, T=0 K calculations

- (including electrode/SEI interfaces)
- give 2 examples of interfacial degradation
- Illustrate 2 issues: voltage (Fermi-level) dependence, Li content effect

Solid Interfaces Computational Details

- PBE functional, DFT+U
- VASP, 400 eV cutoff, 1 fs time step …
- Short AIMD trajectories to optimize interfaces
- NEB to calculate reaction barriers
- vacuum region to calculate work function (voltage)
- Ising models for coarse-grained effects
- LiPON model from Du & Holzwarth, PRB 78, 174301 (2008)

(Pearse et al.’s ALD LiPON has N-P-N chain than “regular” LiPON)

Pearse, Schmitt, Fuller, El-Gabaly, …, Rubloff, Gregorczyk Chem. Mater.29, 3740 (2017)

1. Li_2CO_3 oxidation on cathode oxide surfaces

illustrates reaction kinetics, effects of Li content at interface

- Li_2CO_3 coats cathode oxide surface during synthesis (widely, not universally, acknowledged)
- Recent expt. paper by LBL group confirms Li_2CO_3 decomposition on cathode
- modeling this process hints at what happens to SEI on cathode surface ("CEI") at high voltage

JACS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

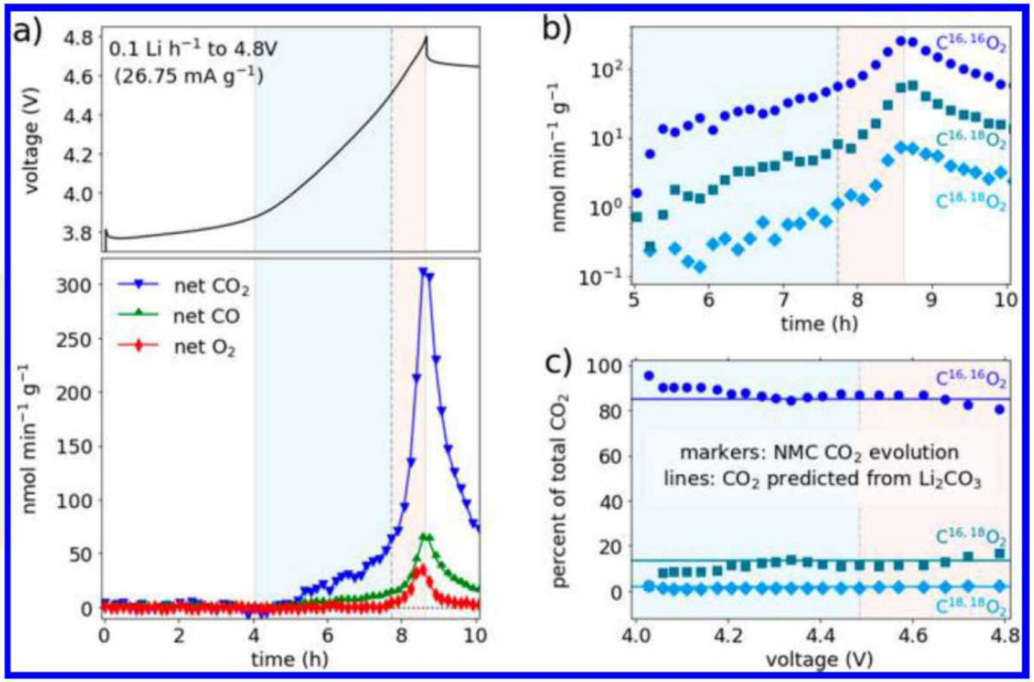
Article

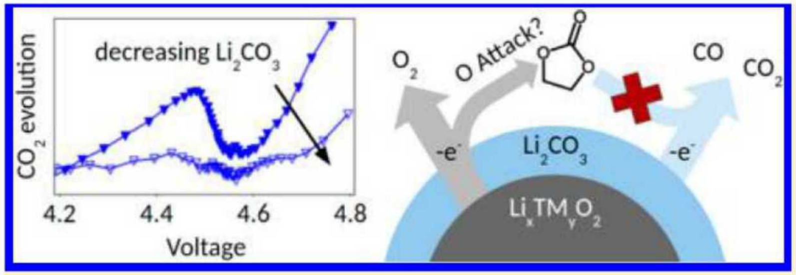
Cite This: *J. Am. Chem. Soc.* 2017, 139, 17853−17860

pubs.acs.org/JACS

Residual Lithium Carbonate Predominantly Accounts for First Cycle CO_2 and CO Outgassing of Li-Stoichiometric and Li-Rich Layered Transition-Metal Oxides

Sara E. Renfrew and Bryan D. McCloskey*

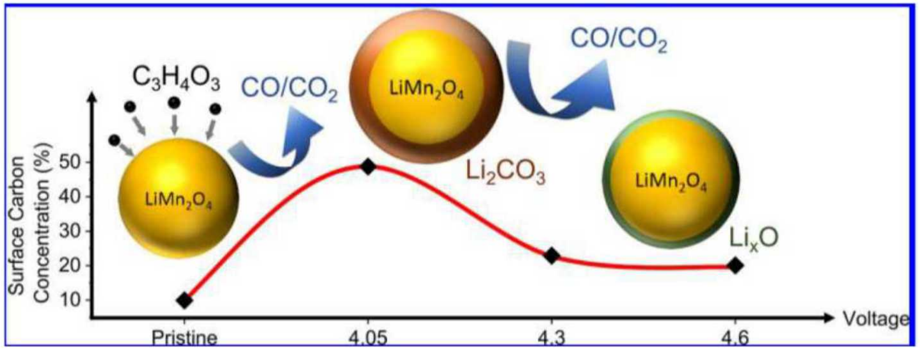




release O_2, CO_2, CO (?)

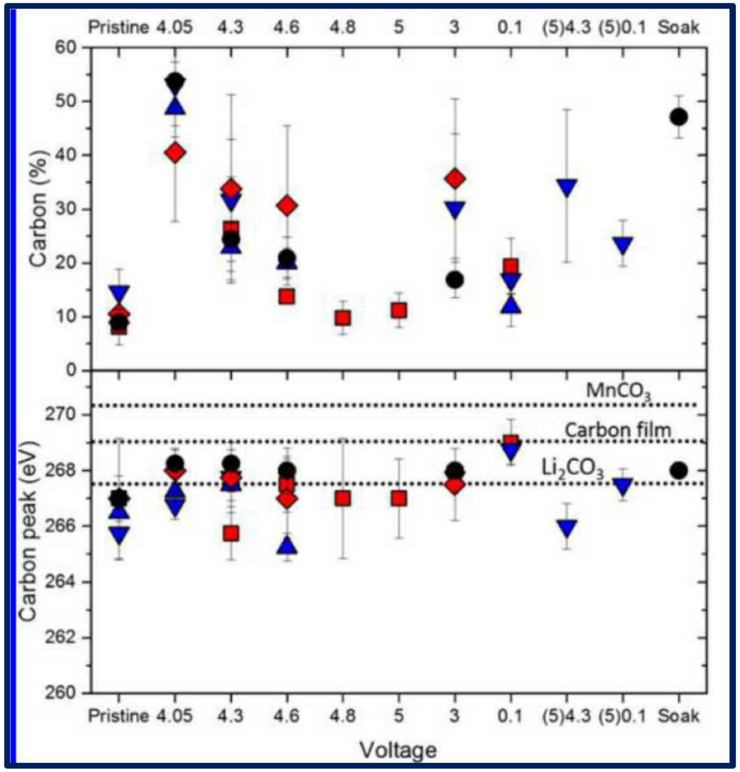
Hypothesis about cathode interfacial films

- oxidation peak at high voltage not due to onset of liquid electrolyte decomposition
- liquid electrolyte decomposes at much lower voltage on oxide surface, passivating it
- instead, the CV oxidation peak due to decomposition of passivating layers on surface (e.g., Li_2CO_3), leading to uncontrolled destruction of liquid electrolyte afterwards



$LiMn_2O_4$ Surface Chemistry Evolution during Cycling Revealed by *in Situ* Auger Electron Spectroscopy and X-ray Photoelectron Spectroscopy *ACS Appl. Mater. Interfaces* 2017, 9, 33968−33978

Ching-Yen Tang,[†] Kevin Leung,[‡] Richard T. Haasch,[§] and Shen J. Dillon*[,†,§]



We should focus more on CEI destruction, not merely liquid electrolyte destruction

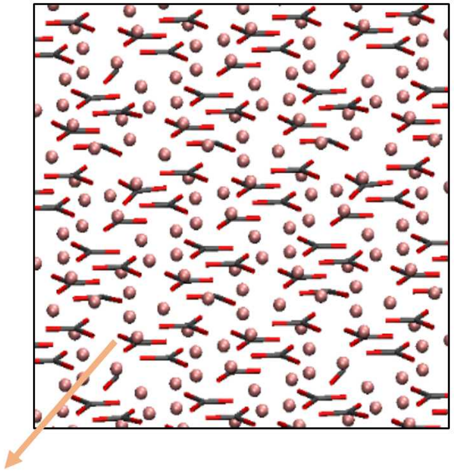
DFT Modeling: Bulk Li_2CO_3 oxidation

Thermodynamics: consistent with McClosky group measurements

Li_2CO_3 -> CO_2 + ½ O_2 + 2 Li(s) : 8.29 eV (4.15 V) (PBE0)
7.56 eV (3.78 V) (PBE)

(although don't see CO ga)

What about mechanism (kinetics)?

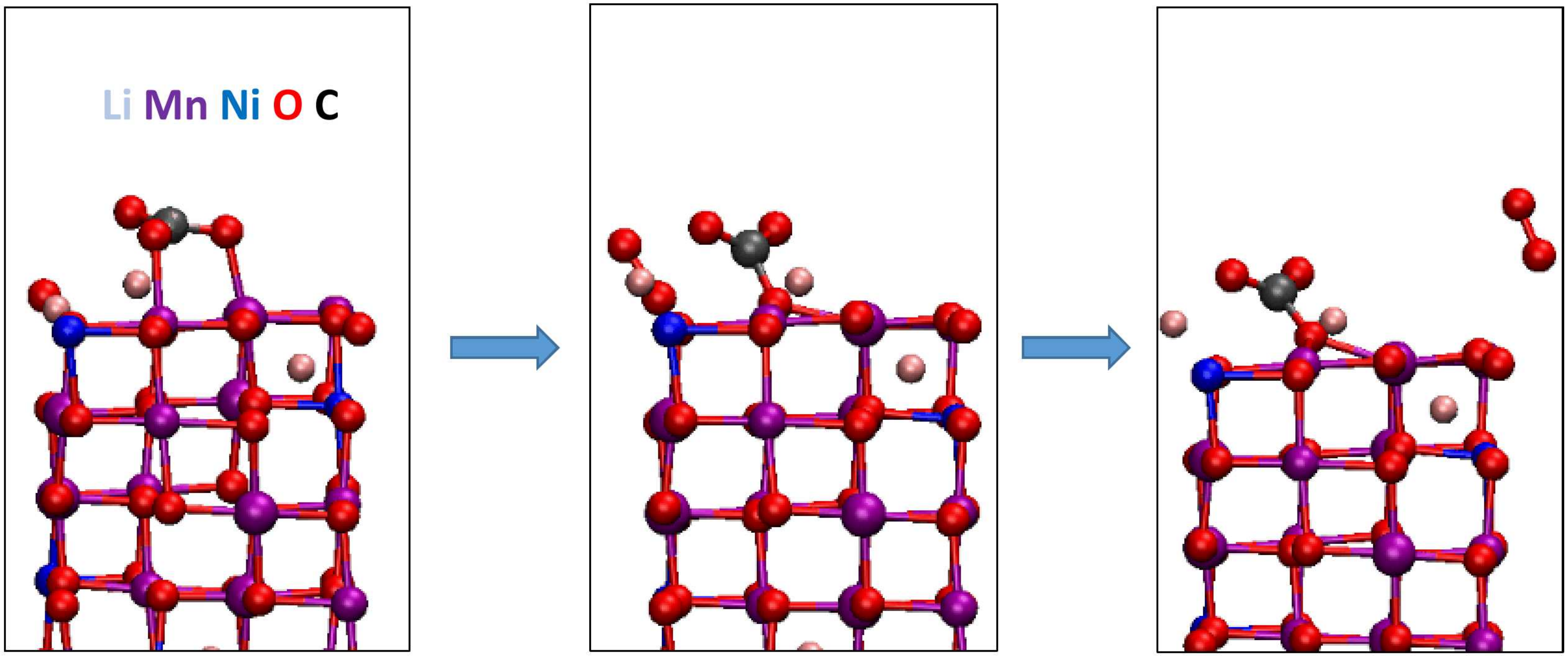


n Li_2CO_3 -> n $Li_{2-1/n}CO_3$ + Li(s) : +5.78 eV (5.78 V) (PBE0)
+4.45 eV (4.45 V) (PBE)

remove Li atom (like in cathode)

- hole is delocalized when using PBE
- expect PBE0 to be more accurate
- so oxidation does not initial in bulk at < 5 V
- *most likely start at interface*

Toy interface: a single Li_2CO_3 unit on $Li_{0.5}Mn_{1.5}Ni_{0.5}O_4$ (100)



PBE+U

Initial, $\Delta E = 0.00$ eV

$\Delta E = -0.30$ eV (exothermic)

CO_3^{2-} loses a O^{2-}, C atom attacks surface oxygen

$\Delta E = -0.23$ eV (endothermic but favored by entropy)

${}^2O_2$ migrates out of surface

PBE0

Initial, $\Delta E = 0.00$ eV

$\Delta E = -0.12$ eV (exothermic)

$\Delta E = -0.37$ eV (more exothermic) (don't see singlet oxygen)

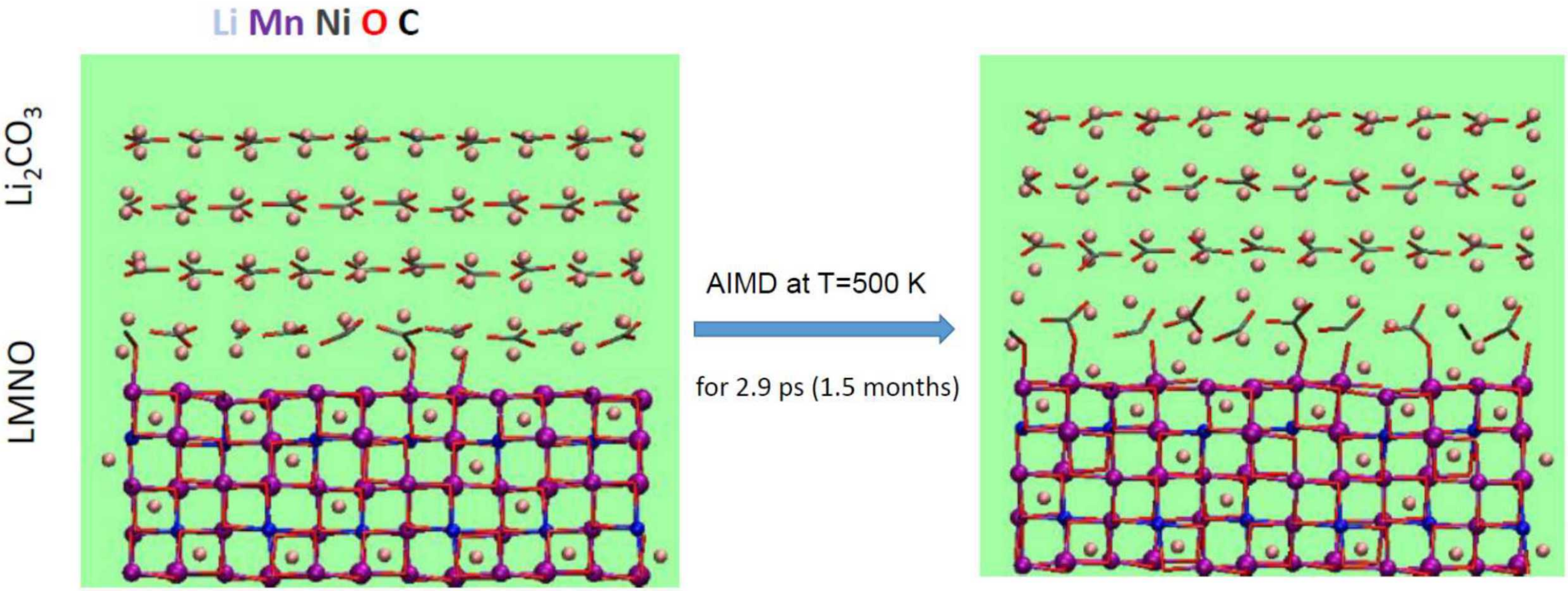
PBE+U

if all Ni replaced by Mn (LMO, regular spinel)

Initial, $\Delta E = 0.00$ eV

$\Delta E = +0.20$ eV (exothermic)

Li_2CO_3 (0001) layer on $Li_xMn_{1.5}Ni_{0.5}O_4$ (100) -- equilibration



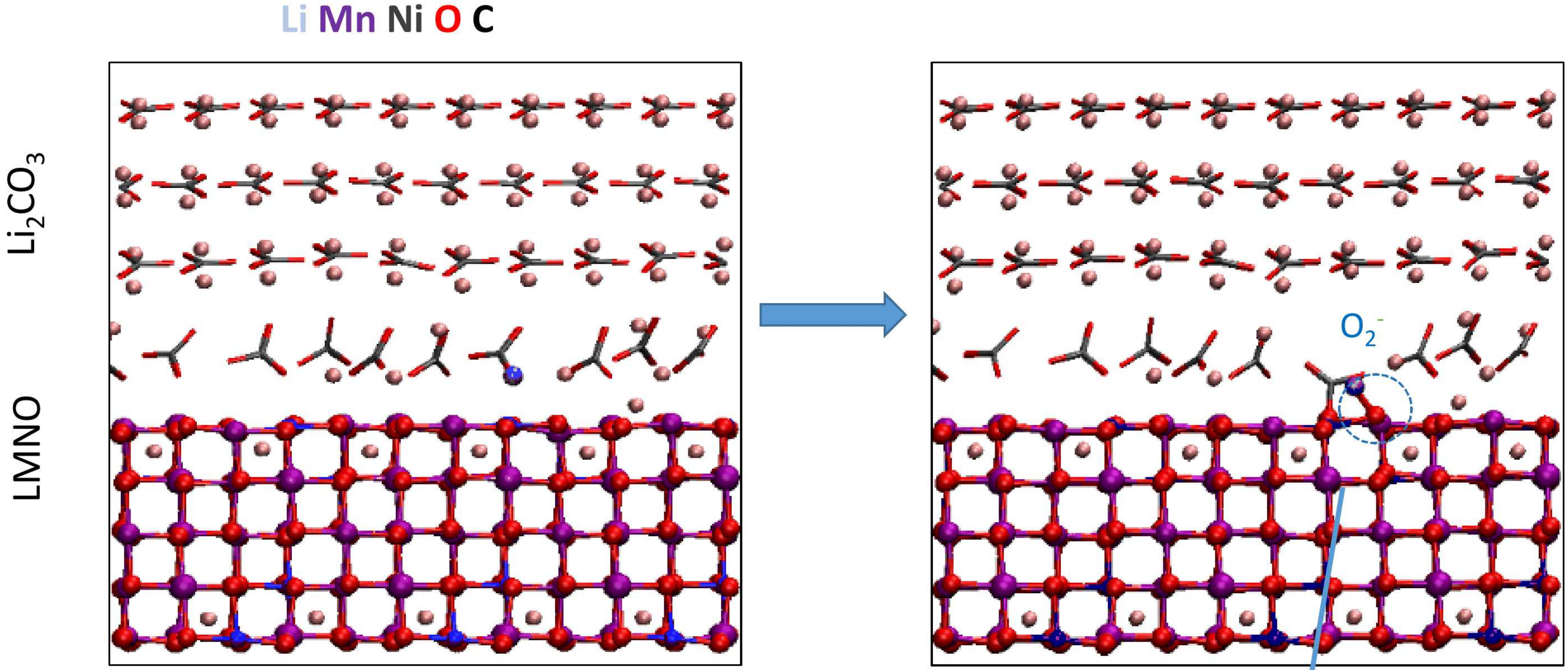
- merge (0001) Li_2CO_3 and (001) LMNO slabs
- optimize configuration
- see minor orientation changes

- run AIMD at T=500 K to accelerate equilibration
- large scale CO_3 re-orientation at interface
- gains 1.1 eV energy

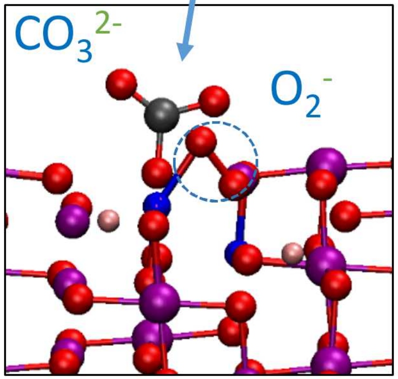
only PBE+U for these large scale models

(I cheated – used a different cut (all Mn termination) for AIMD, switched to partial Ni termination later -- energetically more favorable than Mn termination)

Oxidation of Li_2CO_3 layer on $Li_xMn_{1.5}Ni_{0.5}O_4$ (100)



remove more Li after AIMD*



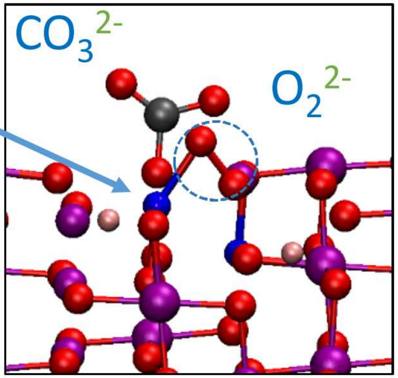
- ΔE = -0.30 eV (exothermic), ΔE^* = 1.08 eV (300 hours)
- most reactive when CO_3^{2-} product coordinates to surface Ni
- tried other CO_3^{2-} sites – endothermic
- electronic voltage ~4.55 V vs Li_+/Li(s)

* x ~ 0.03! removed all 3-coordinated Li in Li_2CO_3 interlayer

Details and further reactions

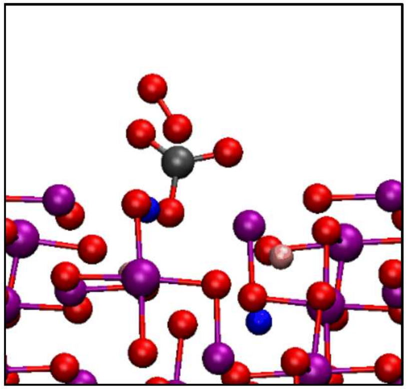
Li Mn Ni O C

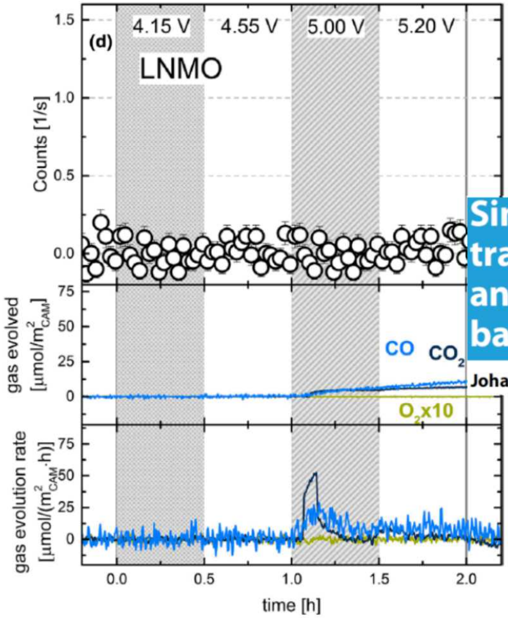
- One Ni(IV) -> Ni(III); “O_2^{2-}” has little magnetic moment
- evolving CO_2 energetically costly (unexplained)
- electronic voltage $\mathcal{V}_e$ ~4.55 V vs Li_+/Li(s)
- $\mathcal{V}_e$ invariant to Li content -- pinned by defect level
- if replace all Ni -> Mn, +0.56 eV instead of -0.30 eV



$^2O_2$ gas evolution

- O_2 gas: ΔE=+0.4 eV at T=0 K
- but entropy (T=300 K) favors gas formation (~0.4-0.5 eV)
- see triplet, not single O_2, which costs an extra 1 eV!





Singlet oxygen evolution from layered transition metal oxide cathode materials and its implications for lithium-ion batteries

Johannes Wandt[†], Anna T.S. Freiberg[*,†], Alexander Ogrodnik, Hubert A. Gasteiger

- once first reaction occurs, O-vacancies, rupture in Li_2CO_3 lattice -> more reactions?

don’t see this in calculations

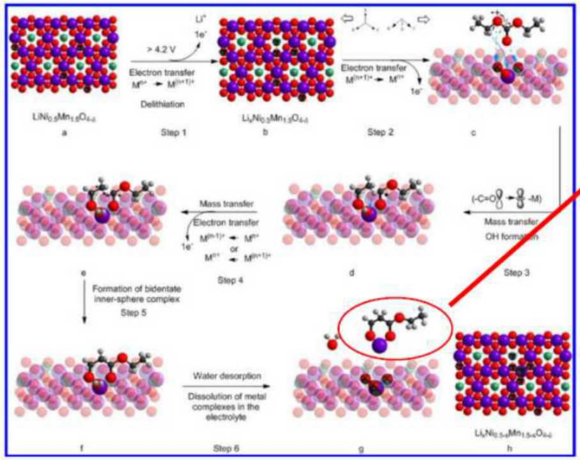
Extrapolating from this idea …

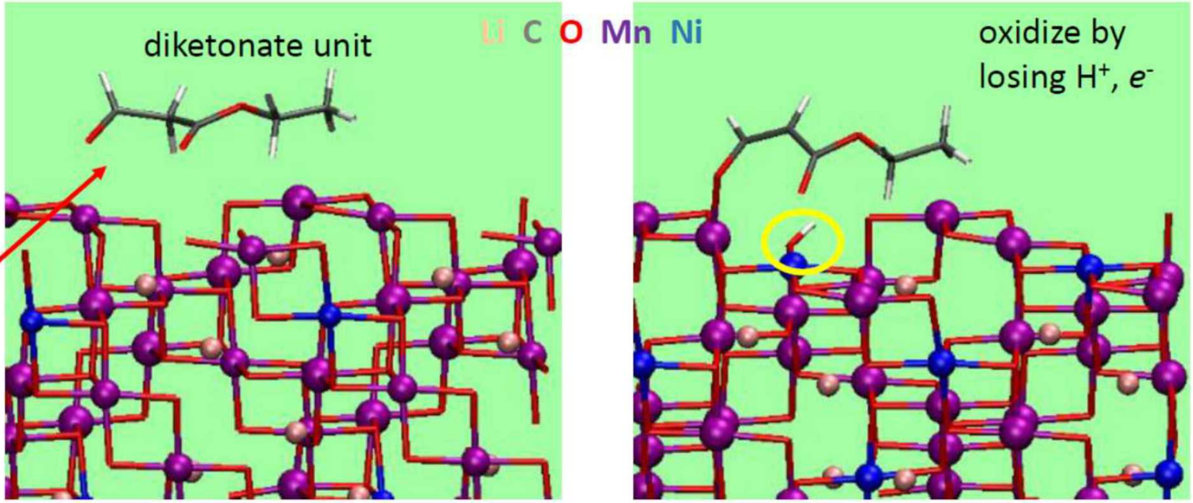
- Li_2CO_3 is a piece of rock, still gets oxidized – what about “CEI” on cathode surfaces?
- unlikely that decomposition product from EC/DMC survive > 4.5 V (unless fluorinated)
- e.g., diketonate proposed by Kostecki group – reacts on high voltage spinel surface too

The Formation Mechanism of Fluorescent Metal Complexes at the $Li_xNi_{0.5}Mn_{1.5}O_{4-\delta}$/Carbonate Ester Electrolyte Interface

Angélique Jarry,[†] Sébastien Gottis,[†] Young-Sang Yu,[‡,§] Josep Roque-Rosell,[‡] Chunjoong Kim,[§] Jordi Cabana,[§] John Kerr,[†] and Robert Kostecki[*,†]

J. Am. Chem. Soc. 2015, 137, 3533–3539





ΔE = 0.0 eV

ΔE = -0.26 eV, favorable

ΔE* = 0.45 eV – very low barrier, 10^{-6} s reaction timescale

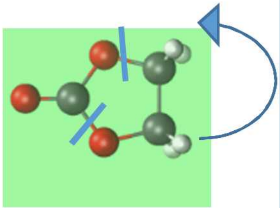
- hypothesis: it is EC/DMC-based CEI which reacts at ~4.5 V, making high-voltage cathode hard to deploy
- the solvent reacts with cathode oxides, decomposes at lower voltages (< 4.5 V)

c.f.: EC-based liquid electrolyte reacts with cathodes at modest voltage

- EC, key battery solvent, more unstable than acknowledged
- reacts on almost fully lithiated cathode oxides

thermodynamics vs **electrochemical**

potential vs. $Li^+/Li(s)$ (V)



at any voltage,
EC -> $CO_2 + C_2H_4O$
is exothermic

>5 V: oxidation (glassy carbon) (Gasteiger group)

~5.0 V: electrochemical oxidation (Borodin)

~4.8 V: reacts with NMC to give CO, CO_2, O_2 (Gasteiger)

< 3.5 V: EC + $LiMn_2O_4$ -> MnO + Li_2CO_3 (KL, thermodynamic)

~1.2 V: thermodynamic instability EC + 6 Li -> 3 Li_2O + 3C +2 H_2 (KL)

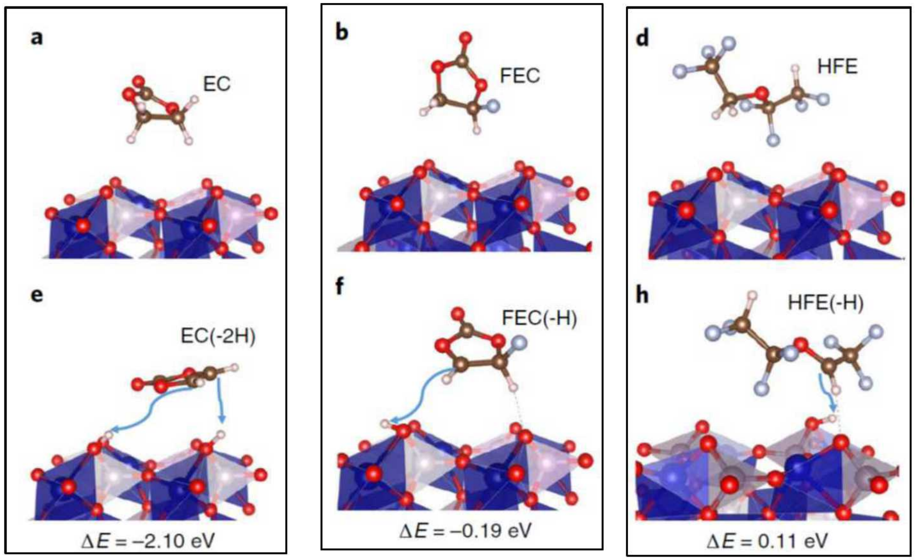
0.7-0.8 V: observed electrochemical reduction

- not denying fluorinated solvents less reactive
- they probably form more stable CEI too!

Non-flammable electrolyte enables Li-metal batteries with aggressive cathode chemistries

Xiulin Fan[1,5], Long Chen[1,5], Oleg Borodin[2], Xiao Ji[1], Ji Chen[1], Singyuk Hou[1], Tao Deng[1], Jing Zheng[1], Chongyin Yang[1], Sz-Chian Liou[3], Khalil Amine[4*], Kang Xu[2*] and Chunsheng Wang[1*]

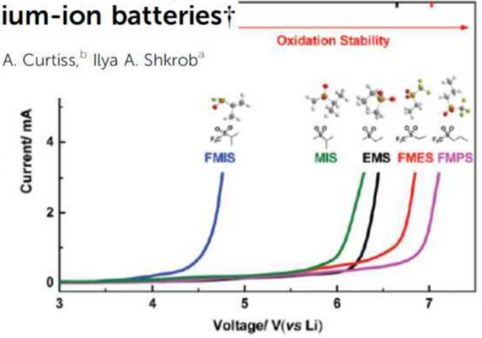
NATURE NANOTECHNOLOGY (2018)



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

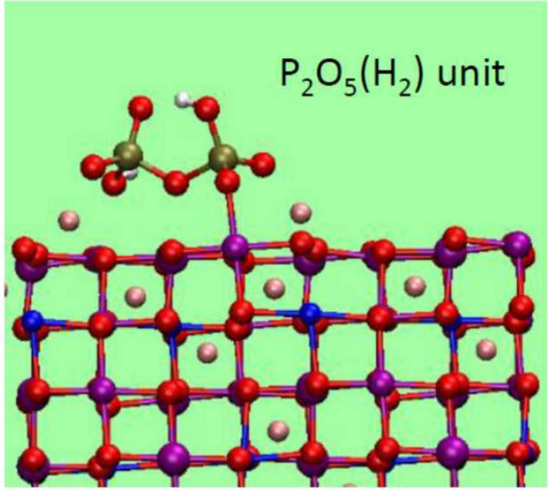
Chi-Cheung Su,[a] Meinan He,[a] Paul C. Redfern,[b] Larry A. Curtiss,[b] Ilya A. Shkrob[a] and Zhengcheng Zhang[*a]

Energy Environ. Sci., 2017, **10**, 900–904



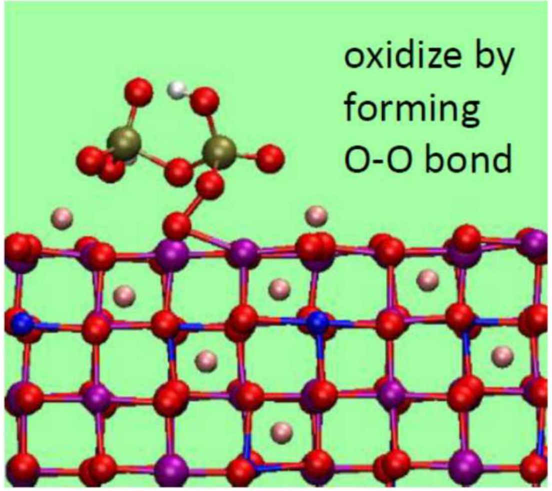
P_xO_y does resist oxidation – robust candidate for cathode SEI (CEI)

- predict that P_2O_5 fragments do not oxidize
- P comes from PF_6^-,
- BO_xF_y from other salts too?



$\Delta E = 0.0$ eV

LMNO
“4.7 V”

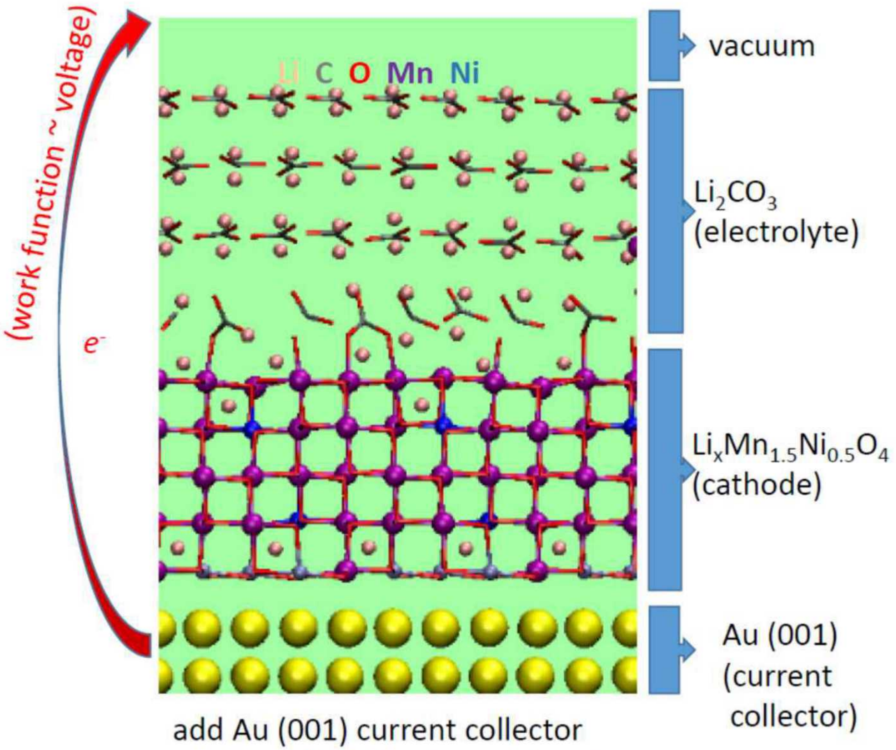


$\Delta E = +1.96$ eV, very unfavorable

Interlude: Computing potential when cathode is polaronic

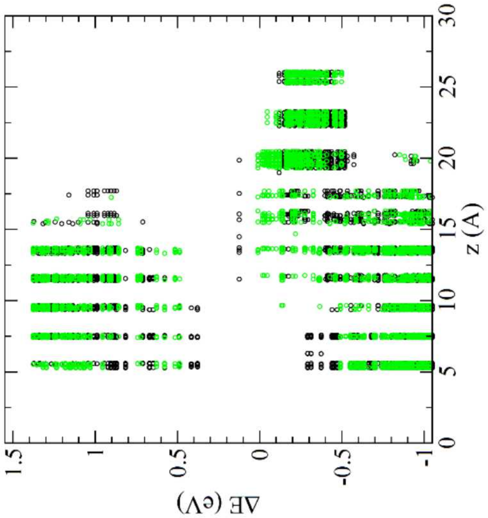
Pure polaronic conducting cathode: Fermi level depends on defects – problematic in calculations

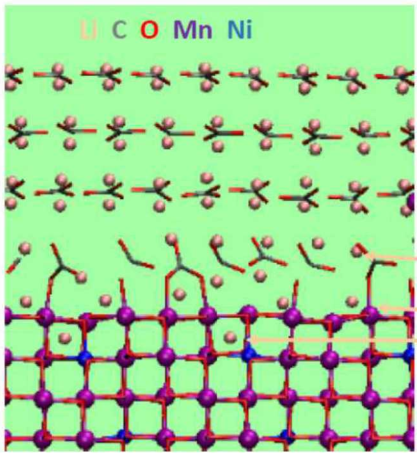
“best” way



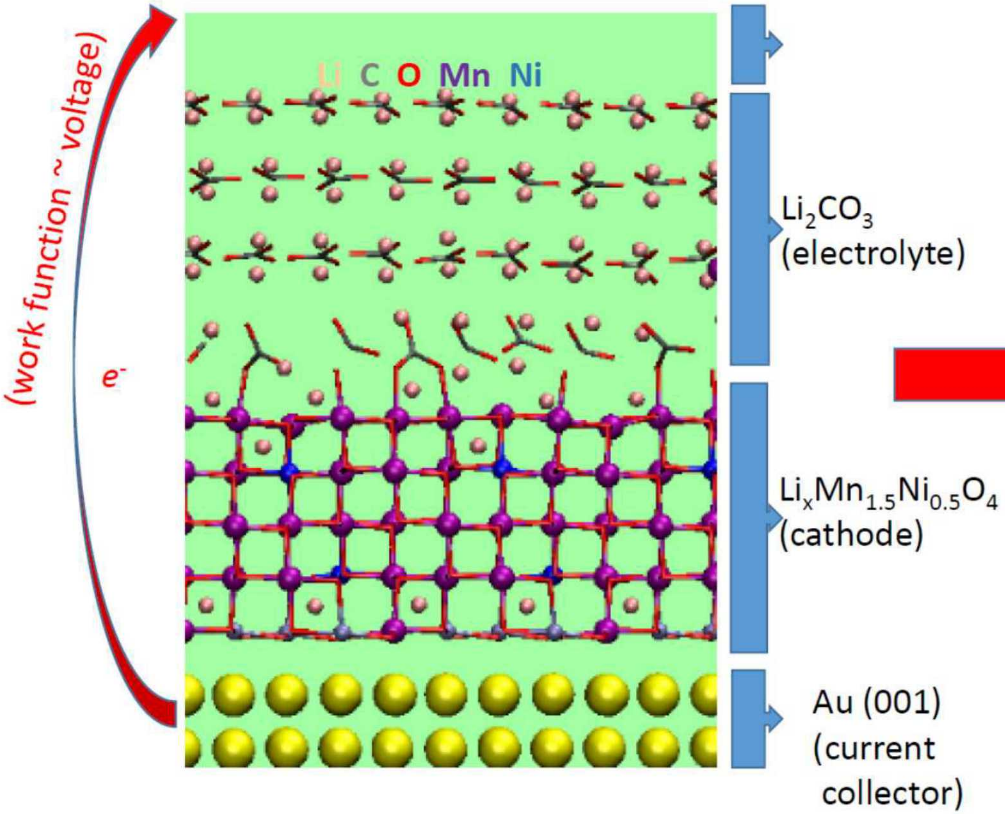
add Au (001) current collector
gives well-defined Fermi level
-> true/instantaneous voltage

- fortuitously in DFT+U calculations, metallic behavior at interface – not poloaronic

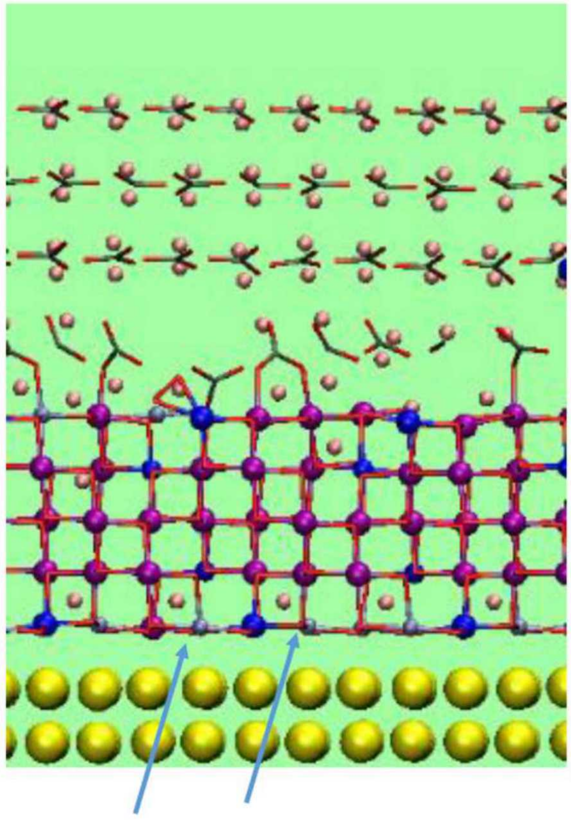




with current collector, ΔE about the same, voltage reasonable



v_e = 4.54 V, not too far from 4.7 for Ni(II)/Ni(III)

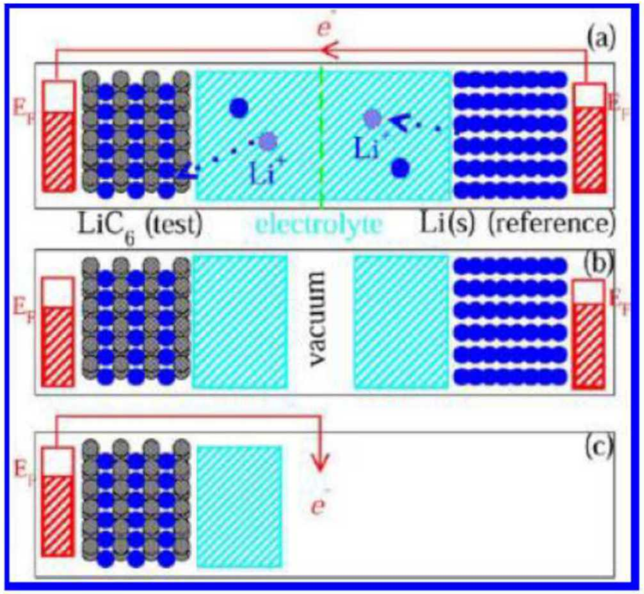


some Mn(IV) reduced at Au interface

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

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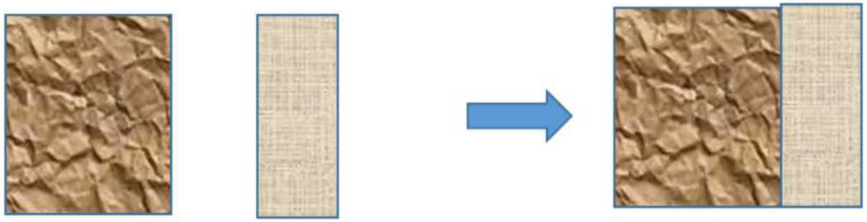
solid electrolytes

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

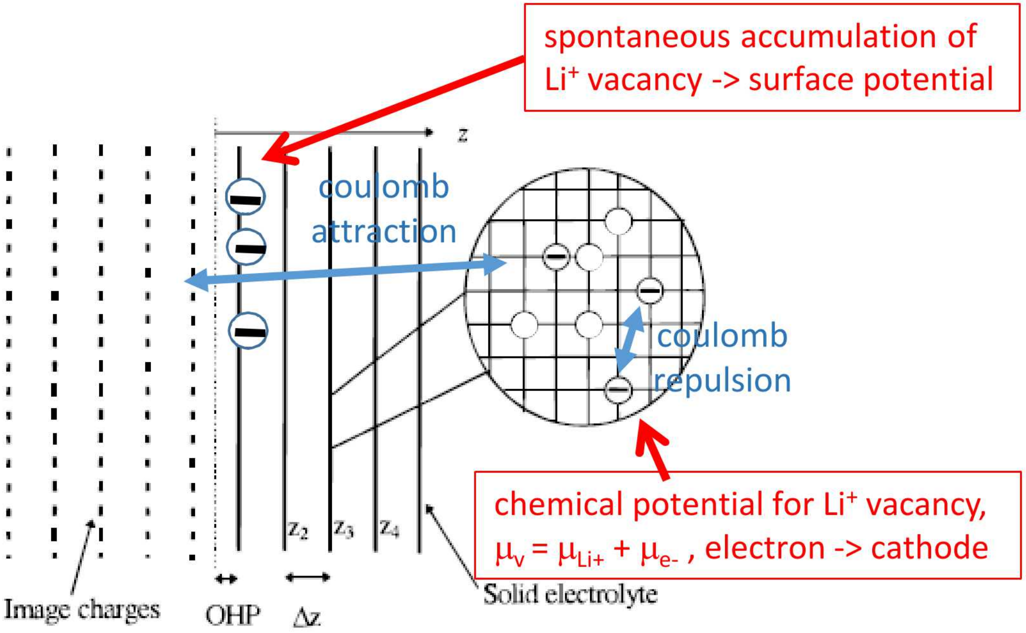


electrode

electrolyte with no net dipole moment (Tasker 2)

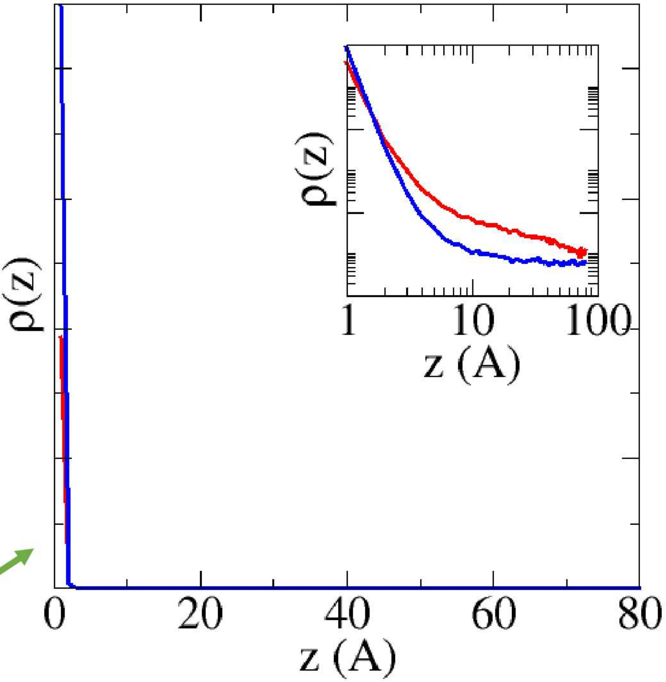
net dipole of system entirely due to interfacial relaxation

Upscale DFT predictions/insight into lattice (“Ising”) model



spontaneous accumulation of Li$^+$ vacancy -> surface potential

chemical potential for Li$^+$ vacancy, $\mu_v = \mu_{Li+} + \mu_{e-}$, electron -> cathode



- very sharp spike in vacancy density at interface
- like in T=0 K DFT calculations
- unlike DFT, can go to T>0 K, longer lengthscale …

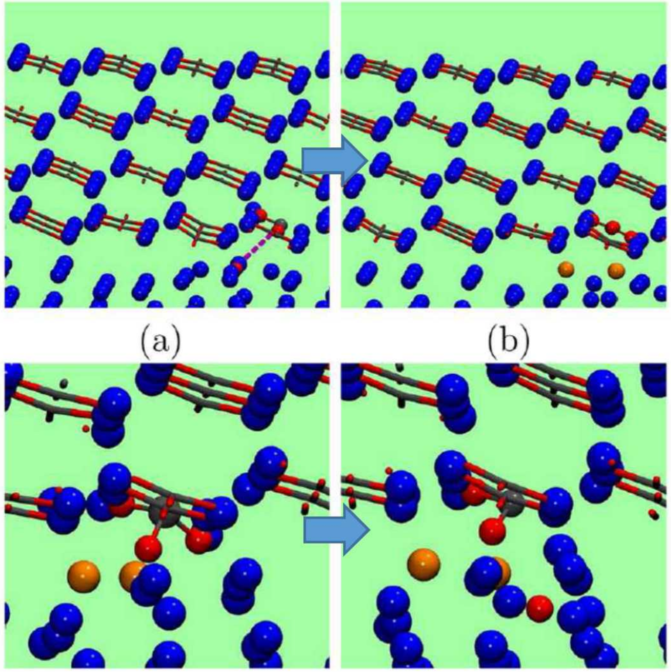
Interlude B. Li_2CO_3 reduction on lithium metal surfaces

(thanks to Chunsheng Wang UMD)

Stability of Solid Electrolyte Interphase Components on Lithium Metal and Reactive Anode Material Surfaces *J. Phys. Chem. C* 2016, 120, 6302−6313

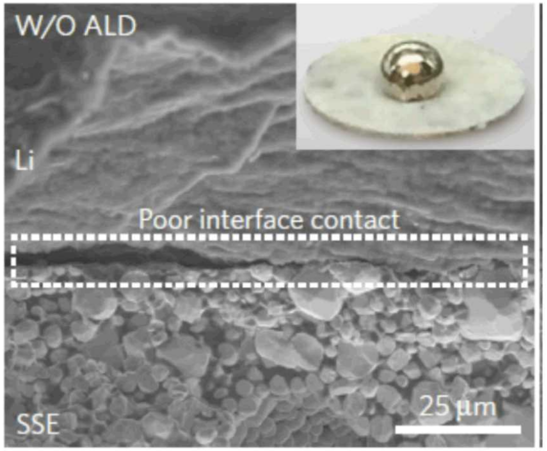
Kevin Leung,*,† Fernando Soto,‡ Kie Hankins,‡ Perla B. Balbuena,‡ and Katharine L. Harrison†

- Predicted: Li_2CO_3 reduction on Li metal thermodynamically + kinetically
- barrier ~1 eV, should be fast at molten Li temperature! (milliseconds)
- (shouldn't happen on graphite)



Negating interfacial impedance in garnet-based solid-state Li metal batteries NATURE MATERIALS | VOL 16 | MAY 2017 |

Xiaogang Han[1†], Yunhui Gong[1†], Kun (Kelvin) Fu[1†], Xingfeng He[1], Gregory T. Hitz[1], Jiaqi Dai[1], Alex Pearse[1,2], Boyang Liu[1], Howard Wang[1], Gary Rubloff[1,2], Yifei Mo[1], Venkataraman Thangadurai[3], Eric D. Wachsman[1]* and Liangbing Hu[1]*

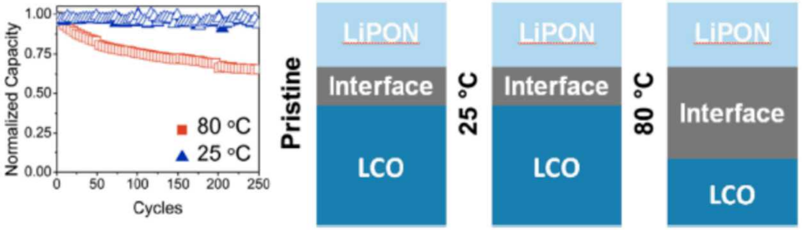


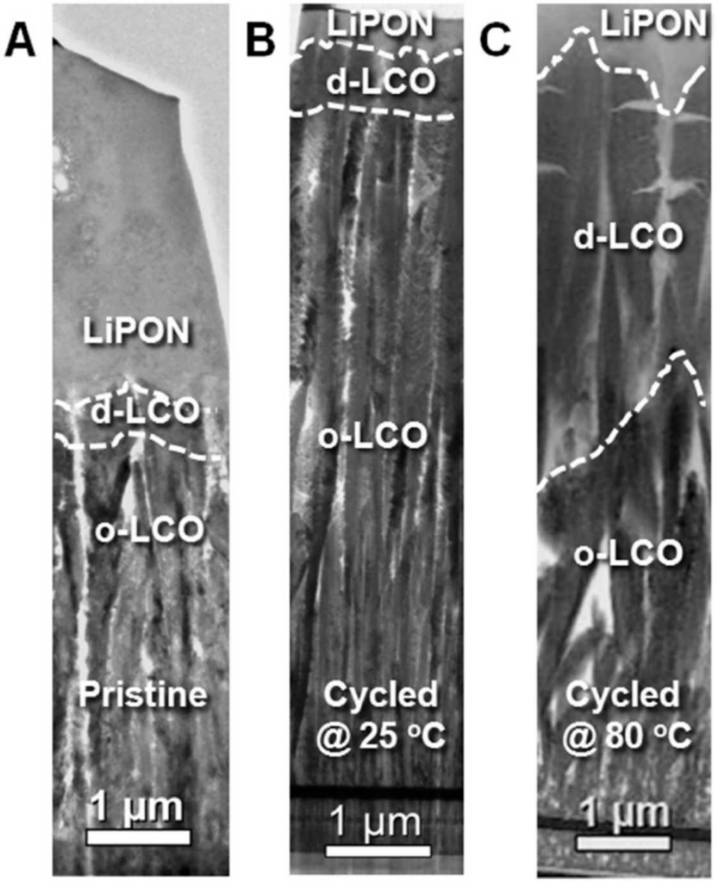
- experimentally, claim is Li bounces off Li_2CO_3, low contact angle
- why no apparent reaction?
- due to carbon formed (bi-product of CO_3^{2-} reduction)?
- encourage experimentalists to re-examine this Li/carbonate interface

2. LiPON reaction with Li-metal surface

Effects of cathode electrolyte interfacial (CEI) layer on long term cycling of all-solid-state thin-film batteries

Ziying Wang [a], Jungwoo Z. Lee [a], Huolin L. Xin [b], Lili Han [b], Nathanael Grillon [c], Delphine Guy-Bouyssou [c], Emilien Bouyssou [c], Marina Proust [c], Ying Shirley Meng [a, *]





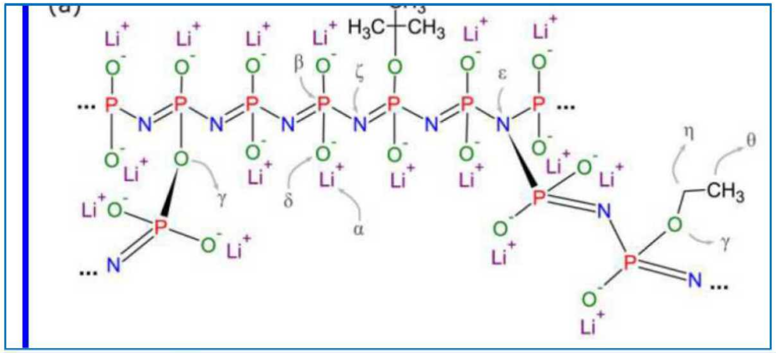
Origin of Outstanding Stability in the Lithium Solid Electrolyte Materials: Insights from Thermodynamic Analyses Based on First-Principles Calculations

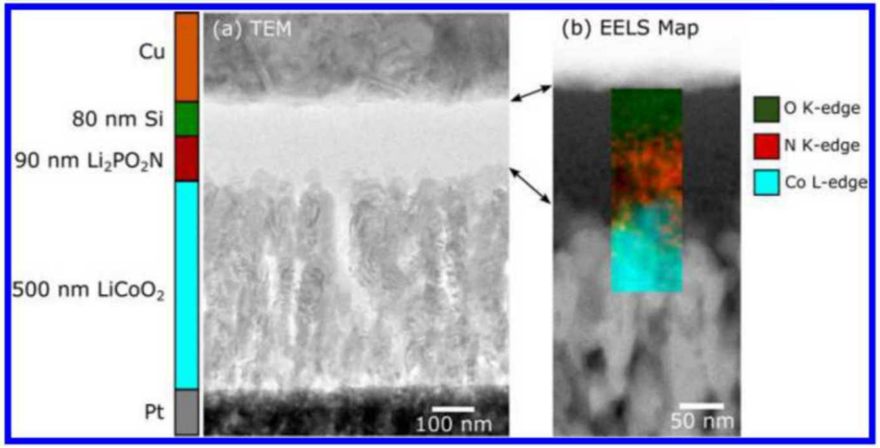
Yizhou Zhu,[†] Xingfeng He,[†] and Yifei Mo*[,†,‡]

LiPON	0.68	Li_3P, $LiPN_2$, Li_2O
	2.63	P_3N_5, $Li_4P_2O_7$, N_2

Nanoscale Solid State Batteries Enabled by Thermal Atomic Layer Deposition of a Lithium Polyphosphazene Solid State Electrolyte

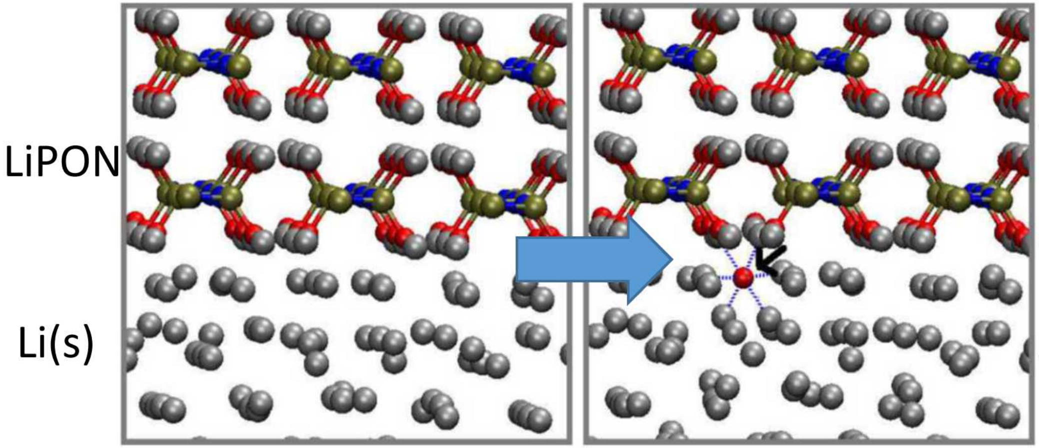
Alexander J. Pearse,*[,†] Thomas E. Schmitt,[†] Elliot J. Fuller,[‖] Farid El-Gabaly,[‖] Chuan-Fu Lin,[†] Konstantinos Gerasopoulos,[‡] Alexander C. Kozen,[§] A. Alec Talin,[‖] Gary Rubloff,[†] and Keith E. Gregorczyk*[,†]





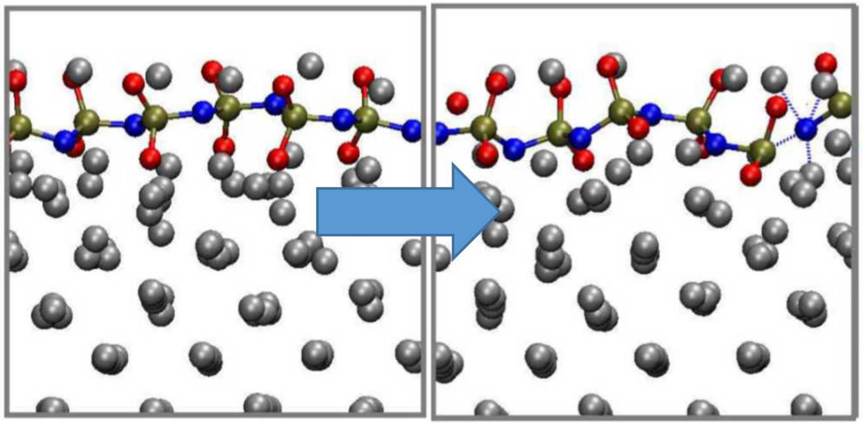
Model LiPON robust on Li metal surface during cycling

slab



- P-O bond breaking exothermic (tried 18) average to -0.53 eV
- barrier ~2 eV (tried 3)
- reacts within 1 hour at T=600 K
- “age of universe” at T=300 K
- P-N bond don’t break at all

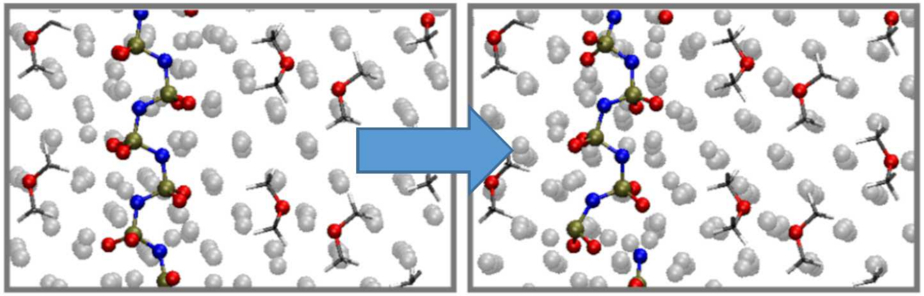
chain



- P-O bond breaking exothermic
- Barrier for P-N breaking is lower
- P-N breaking exothermic (tried 12 average -1.2 eV)
- barrier ~1.5 eV (tried 3)
- “age of universe” at T=300 K

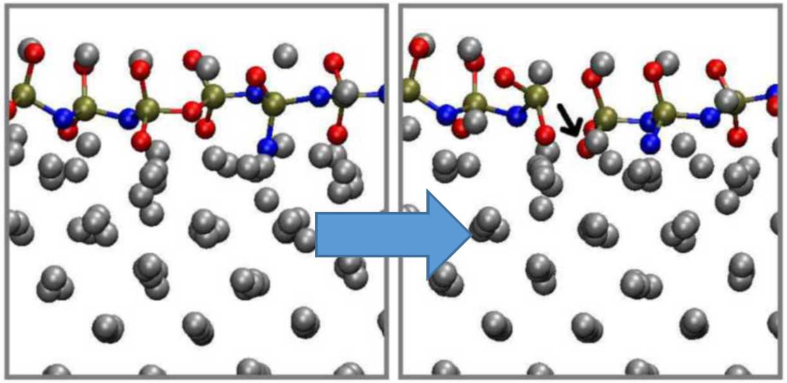
But what about voltage effects?

Is lack of reactivity due to voltage too high? No.



- previous chain calcuations done at ~0.6 V (out of electrochemical equilibrium)
- Shift to ~0.0 V by adding dipolar layer (Li^+ coordinated to ether molecules)
- Little change in barriers or exothermicity
- Reaction is chemical, not electrochemical?
- Cannot use Norskov formulation of voltage

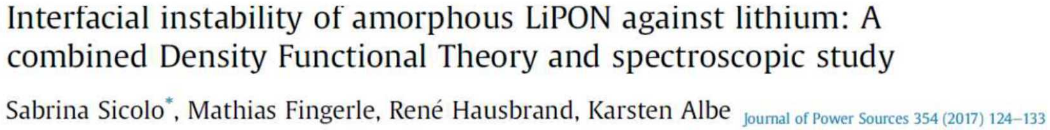
LiPON Backbone Defect (P-O-P) explain some reactions



- P-O-P sequence (instead of P-N-P) can break exothermically, with 0.43-0.9 eV barrier (< 1 hour at T=300 K)
- But subsequent reactions are again slow

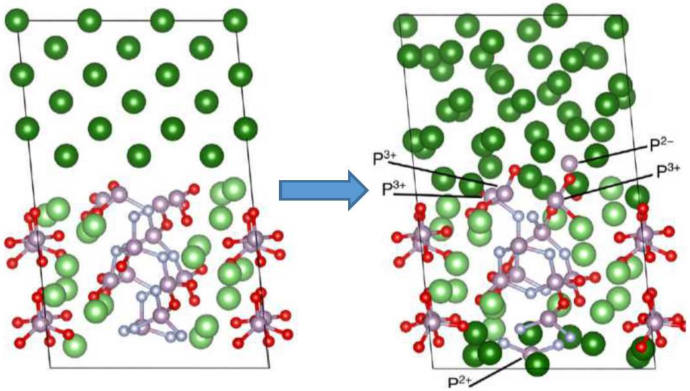
Comparison with measurements, literature

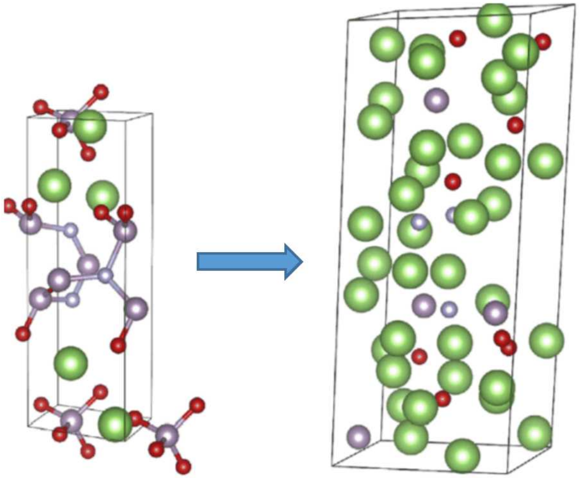
- cannot predict final products, but estimates relevant time scales, mechanisms …
- Schwobel et al. find “SEI” products (Li_3N, Li_3P …), but also decrease of N-P_3 vs. –P-N-P- ratio: -P-N-P- survives? Schwobel, Hausbrand, Jaegerman Solid State Ionics (2015)
- P-O-P breaks on Li surface



Interfacial instability of amorphous LiPON against lithium: A combined Density Functional Theory and spectroscopic study

Sabrina Sicolo*, Mathias Fingerle, René Hausbrand, Karsten Albe Journal of Power Sources 354 (2017) 124–133





- Sicolo *et al*.: opposite starting point, LiPON model with N-P_3 and P-O-P bonds
- Reacts with Li metal rapidly, complimentary to our predictions
- (but in measurements LiPON does not get atomized – not all bonds break)

Conclusions

- Solid-solid interfaces ubiquitous – even in liquid electrolyte batteries
- Should focus on SEI/surface film destruction paradigm, in addition to solvent reaction
- Voltage dependence difficult to capture in pure DFT calculations
- Both electronic and lithium content changes at interfaces as voltage varies
- Need upscaling to (say) Ising model to capture finite temperature space charge

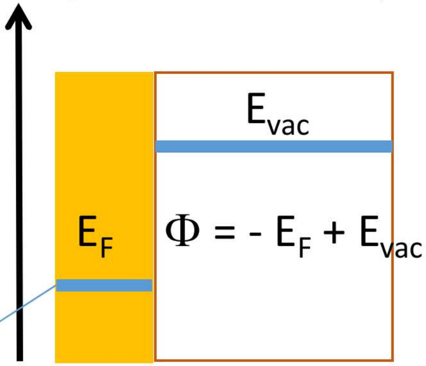
Supporting Slides

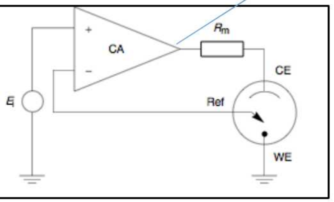
Illustration: what is the “voltage” of Li (100) metal in vacuum?

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

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

(Φ = 2.93 eV, CRC handbook)



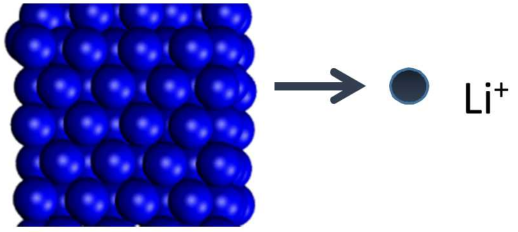


True instantaneous voltage

if electrode=e^- source

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

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



Li (100)

disconnected Li metal is not
at electrochemical equilibrium

if electrode=Li source

- $Au^{3+} + 3 e^- \rightarrow Au(s)$ 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

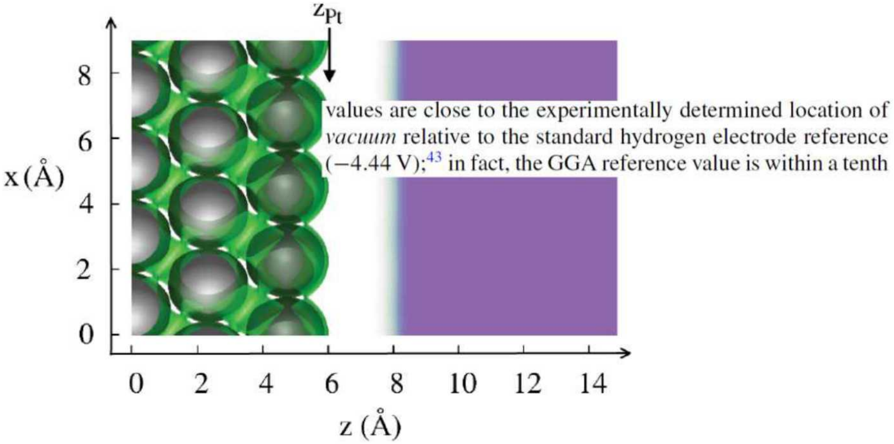
Need to compute instantaneous voltages

Liquid/solid interfaces

- well recognized: voltage <-> Fermi level

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

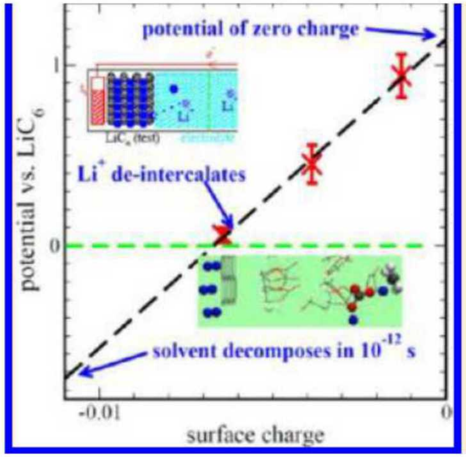
Kendra Letchworth-Weaver and T. A. Arias PHYSICAL REVIEW B **86**, 075140 (2012)



values are close to the experimentally determined location of *vacuum* relative to the standard hydrogen electrode reference (−4.44 V);[43] in fact, the GGA reference value is within a tenth

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

Kevin Leung* and Craig M. Tenney

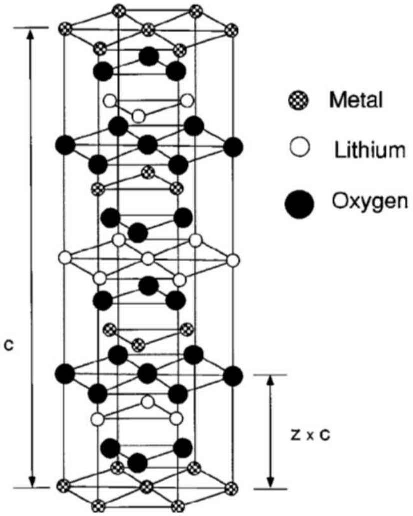


Pure single phase solid state

***Ab initio* study of lithium intercalation in metal oxides and metal dichalcogenides**

M. K. Aydinol, A. F. Kohan, and G. Ceder
K. Cho and J. Joannopoulos
PHYSICAL REVIEW B /97/56(3)/1354

- single phase calculation (no interface)
- "the average voltage is" $\overline{V} = \frac{-\Delta G_r}{(x_2 - x_1)F}$.

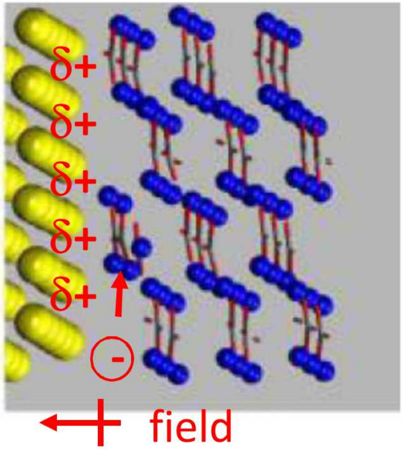


- purely Li chemical potential effect for Li insertion
- no info on absolute Fermi level (no interface)

- at interfaces, this doesn't give the actual (instantaneous) voltage
- only reveals whether at overpotential!

Possible Deficiency of T=0 K DFT interface calculations?

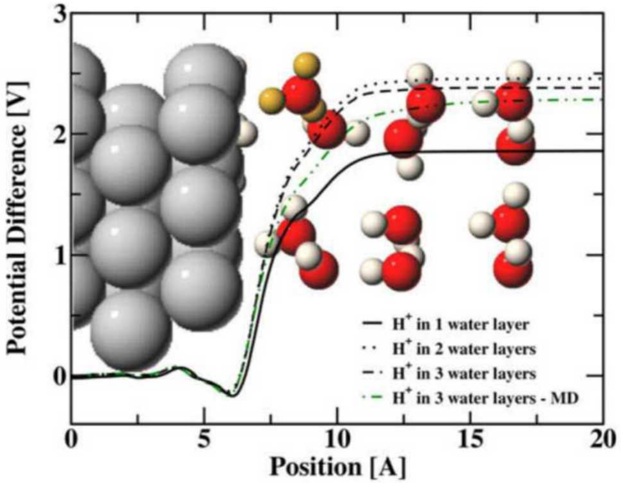
- Predict Li^+ vacancy stuck to Au surface
- field region (EDL) is 1 atomic layer thick
- realistic? Debye length $\lambda_d = (\varepsilon_o k_BT/nq^2)^{0.5}$ -> 0 at T = 0K!
- Is that why EDL is compact?



T=0 K even less forgivable for aqueous electrolytes (fuel cells)

Modeling the electrified solid–liquid interface *J. Rossmeisl et al. / Chemical Physics Letters 466 (2008) 68–71*

Jan Rossmeisl *, Egill Skúlason, Mårten E. Björketun, Vladimir Tripkovic, Jens K. Nørskov



- $\lambda_d = (\varepsilon_o k_BT/nq^2)^{0.5}$

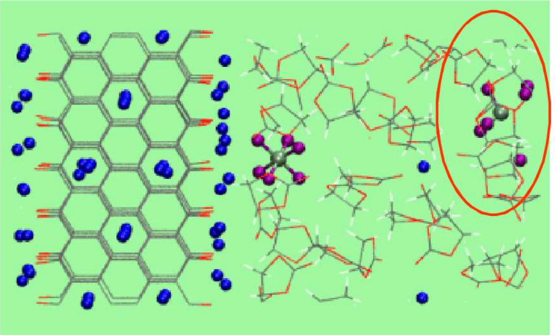
- also predict thin EDL region
- but T= 0 K not adequate for these terms

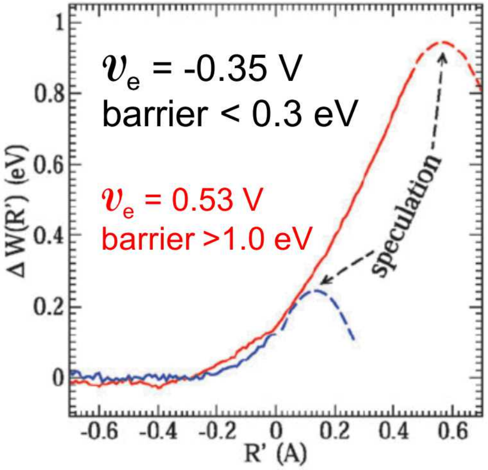
Consequences of interfacial electrochemical effects

SEI creation

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

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



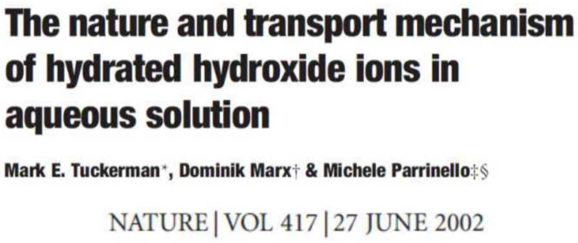


v_e = -0.35 V
barrier < 0.3 eV

v_e = 0.53 V
barrier >1.0 eV

Thermodynamics, kinetics, and driving forces

- 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)

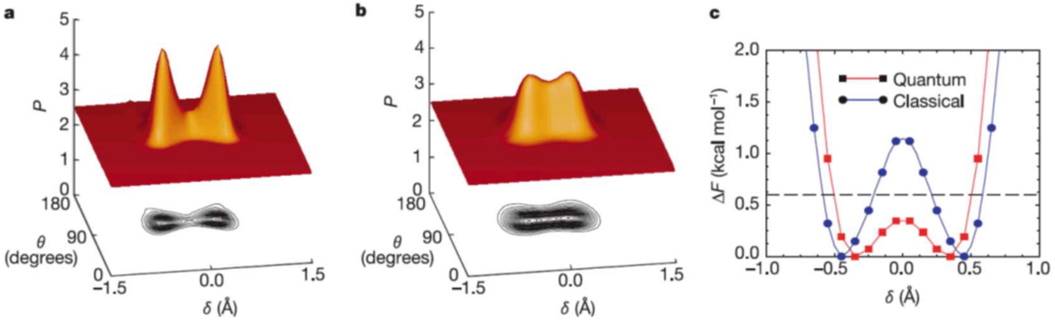


The nature and transport mechanism of hydrated hydroxide ions in aqueous solution

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

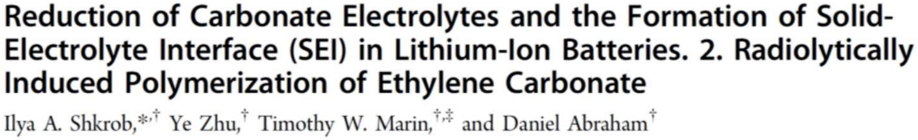
NATURE | VOL 417 | 27 JUNE 2002

$H_2O \ldots OH^- \rightarrow HO^- \ldots H_2O$



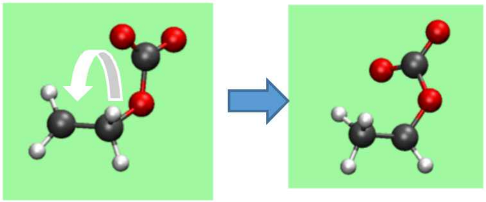
ΔF = -0.0 kJ/mol ΔF* = +1.20 kJ/mol!

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



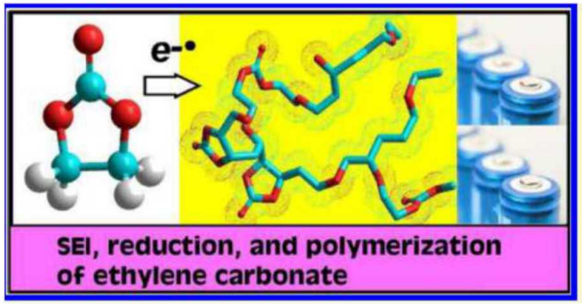
Reduction of Carbonate Electrolytes and the Formation of Solid-Electrolyte Interface (SEI) in Lithium-Ion Batteries. 2. Radiolytically Induced Polymerization of Ethylene Carbonate

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



ΔF = -16.2 kJ/mol ΔF* = +160 kJ/mol!

(unpublished calculations)



SEI, reduction, and polymerization of ethylene carbonate

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