SAND2018-3095C

Comparing liquid/solid & all-solid interfaces

Towards computational study of LiPON interfaces in all-solid batteries

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Acknowledgement

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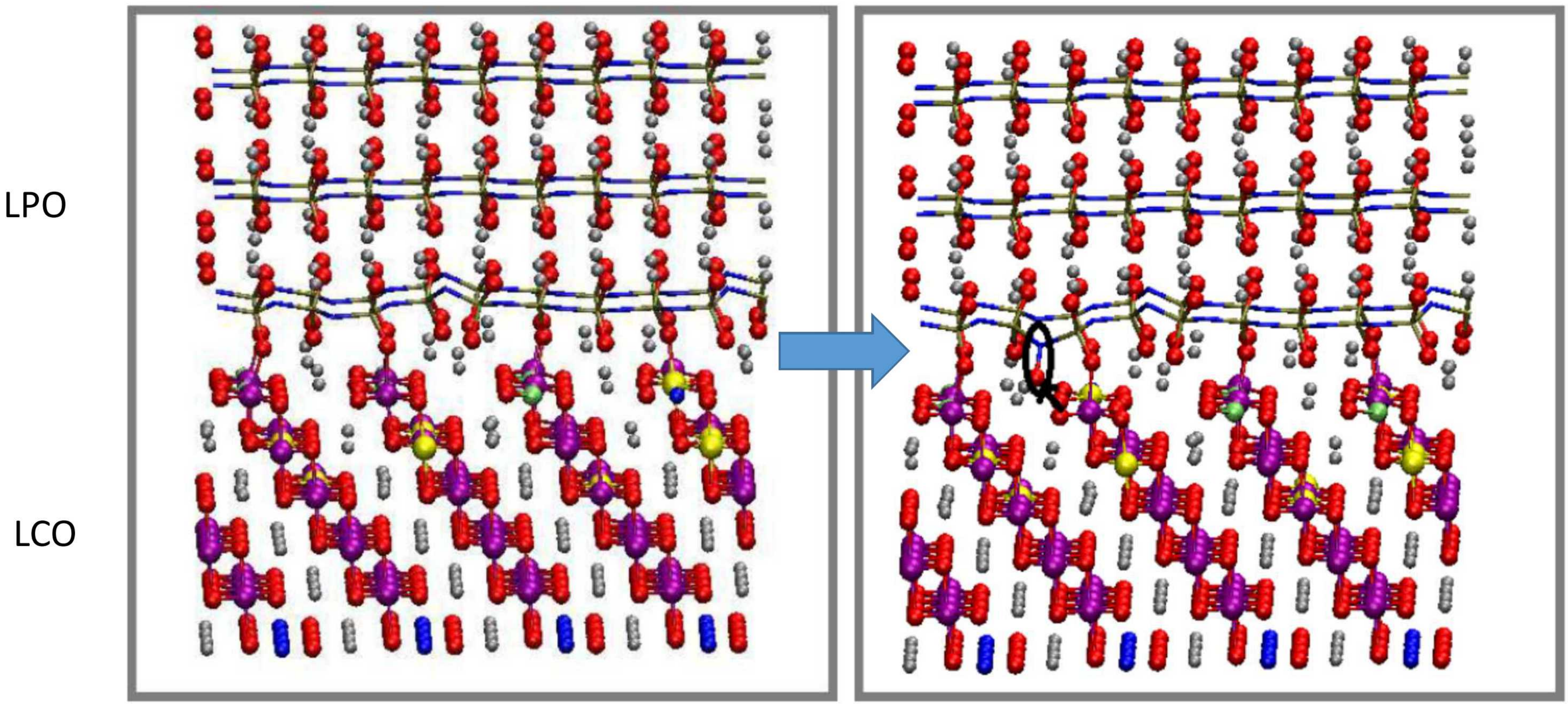
To model interfacial reactions between model LiPON, Li metal & $LiCoO_2$ for interfaces in all-solid-state batteries

… but probably first need a few perspective slides on model techniques



Most interfaces are metastable

Liquid electrolyte

- organic electrolytes – always metastable

EC, key battery solvent, astonishingly unstable

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

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

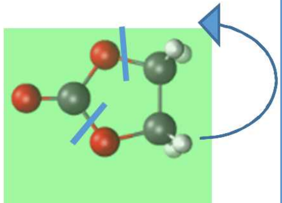
~5.0 V: electrochemical oxidation (Borodin)

~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)

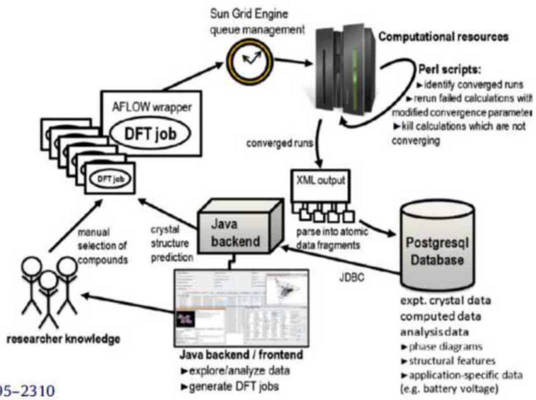
0.7-0.8 V: observed electrochemical reduction



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

solid state materials

- modeling of cathode materials has focused on thermodynamic stability
- expt. synthesis: at 1000 ^oC for 10 hours
- Phase diagram find most stable phase ..



Computational Materials Science 50 (2011) 2295–2310

A high-throughput infrastructure for density functional theory calculations

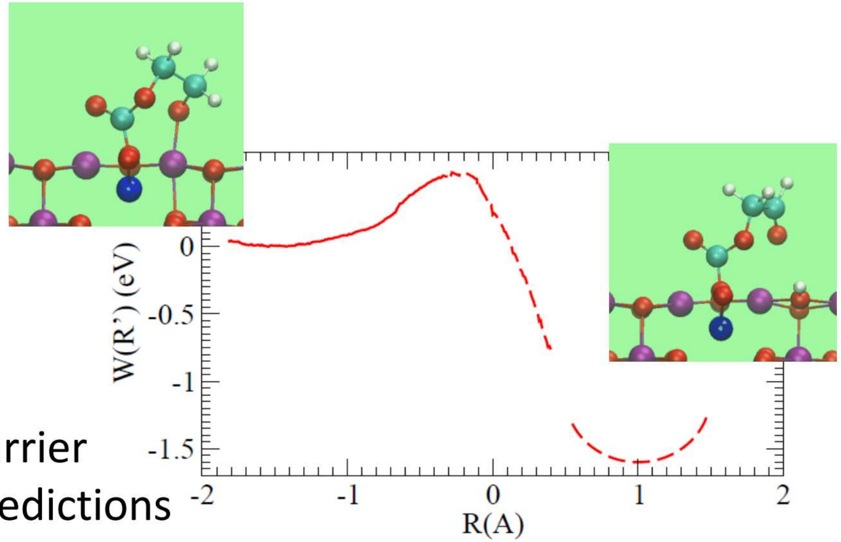
Anubhav Jain, Geoffroy Hautier, Charles J. Moore, Shyue Ping Ong, Christopher C. Fischer, Tim Mueller, Kristin A. Persson, Gerbrand Ceder*

- but interfaces in even all-solid batteries fabricated at << T = 1000 ^oC (e.g., 250 ^oC)
- documented cases that solid interfaces are kinetics-controlled

Need to calculate kinetics at interfaces

Liquid electrolyte

- products not governed by thermodynamics
- always look at reaction rates, barriers



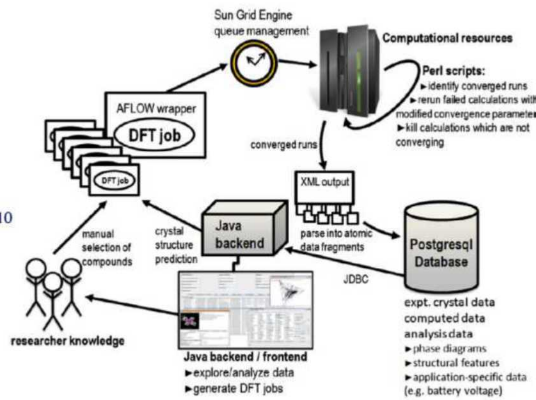
barrier predictions

- Interfacial kinetics calculations messy
- doesn't predict final product
- predict rates of 1st or primary reaction steps

solid state

- modeling of cathode materials has focused on thermodynamic stability
- expt. synthesis: at 1000 °C for 10 hours
- calculations: elegant, efficient

  phase diagram,
  find most
  stable phase …



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- but interfaces in even all-solid batteries fabricated at << T = 1000 °C (e.g., 250 °C)
- documented cases that solid interfaces are kinetics-controlled
- need more "liquid state" type kinetics

Detail: Thermodynamics, kinetics, and driving forces

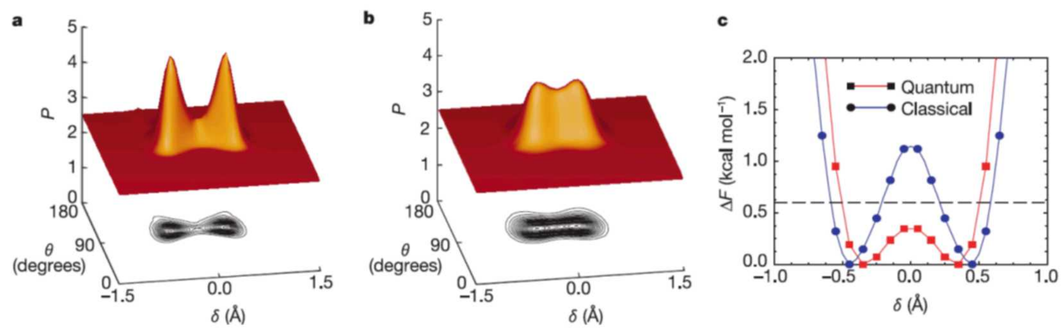
- no *a priori* connection between exothermicity (thermodynamics) and reaction barrier (kinetics)
- For example, H^+ hopping in water ("Grothuss mechanism") is strictly thermoneutral,
- but is lightning fast (~ zero barrier)

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

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

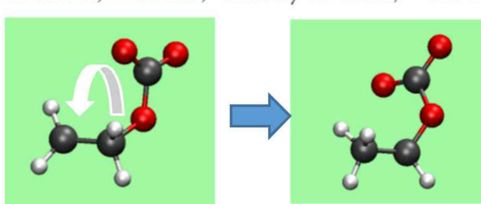


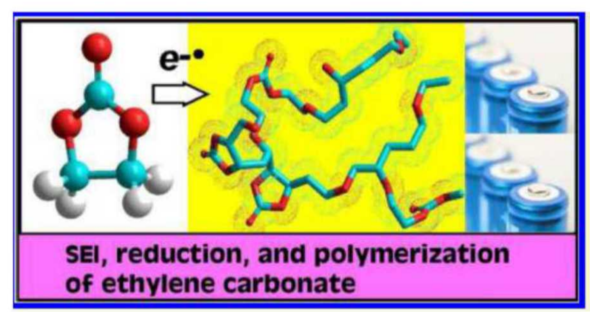
ΔF = -0.0 kJ/mol ΔF^* = +1.20 kJ/mol!

- 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!

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

(unpublished calculations)

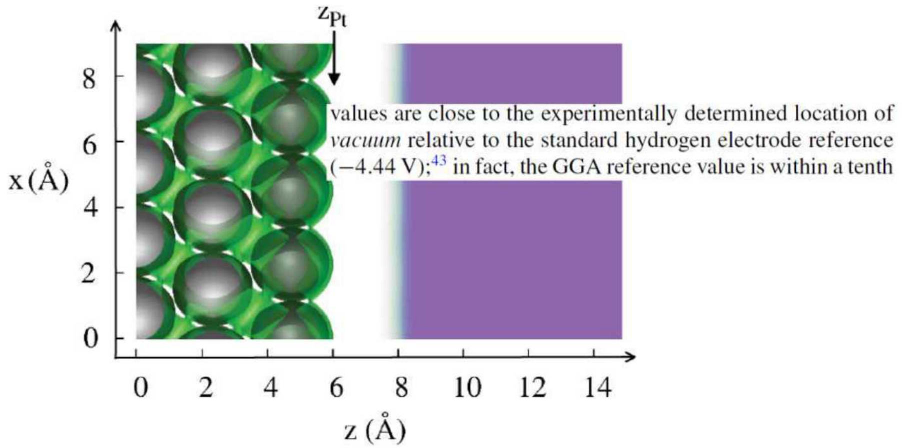
Need instantaneous voltages voltages

Liquid/solid interfaces

- well recognized: voltage <-> Fermi level

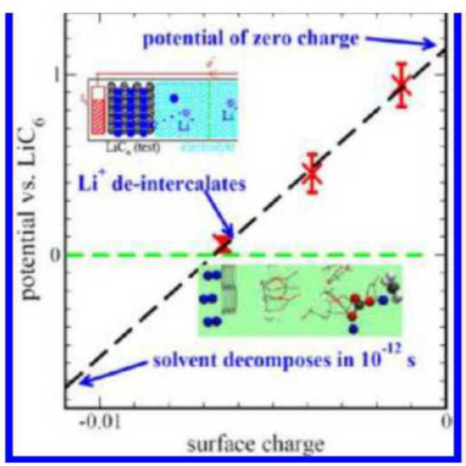
Joint density functional theory of the electrode-electrolyte interface: Application to fixed electrode potentials, interfacial capacitances, and potentials of zero charge

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



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

Kevin Leung* and Craig M. Tenney

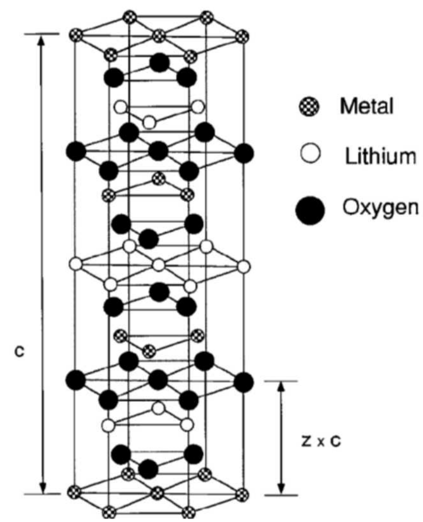


Pure single phase solid state

***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)

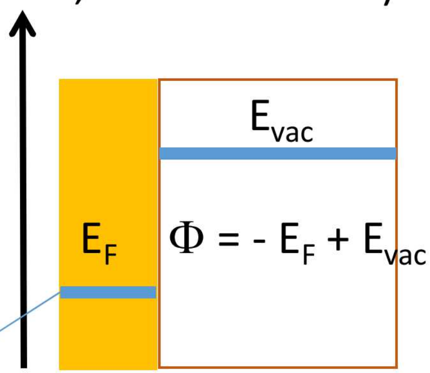
- at interfaces, this doesn't give the actual (instantaneous) voltage
- only reveals whether at overpotential!

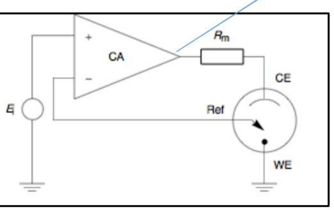
Quiz: what is the "voltage" of Li (100) metal in vacuum?

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

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

(Φ = 2.93 eV, CRC handbook)

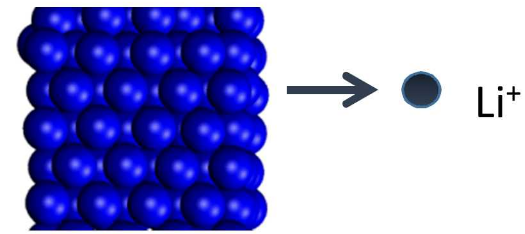




True instantaneous voltage

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

= 0.00 V vs Li^+/Li(s)
for Li(s) -> Li^+ (solv) + e^-



Li (100)

disconnected Li metal is not at electrochemical equilibrium

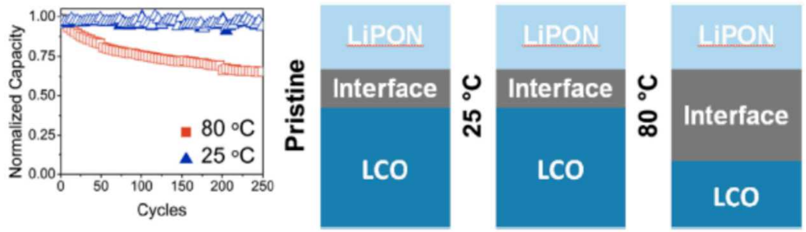
- Au^{3+} + 3 e^- -> Au(s) is at 1.52 V vs. SHE
- yet we never assume Au slab is at 1.52 V in DFT calculations
- should not assume Li electrode is always in equilibrium either

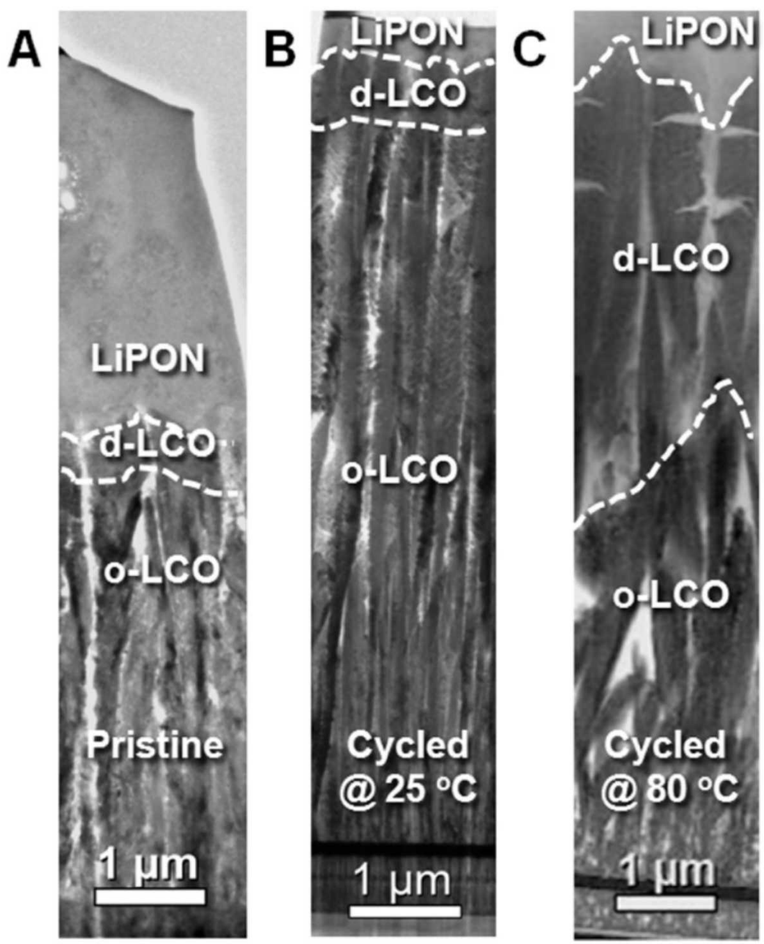
Computational Details:

- PBE functional, DFT+U
- VASP, 400 eV cutoff, 1 fs time step …
- …

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,*]





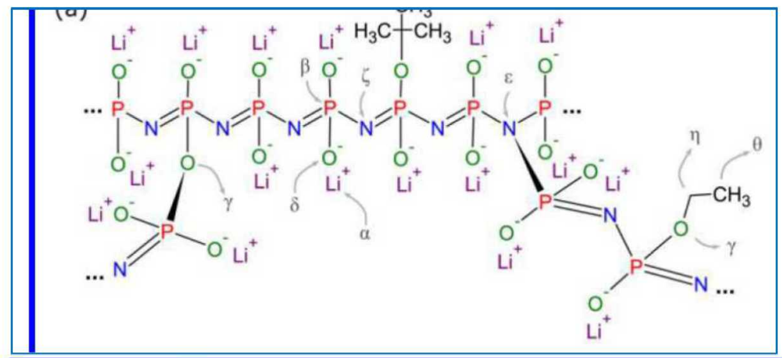
Origin of Outstanding Stability in the Lithium Solid Electrolyte Materials: Insights from Thermodynamic Analyses Based on First-Principles Calculations

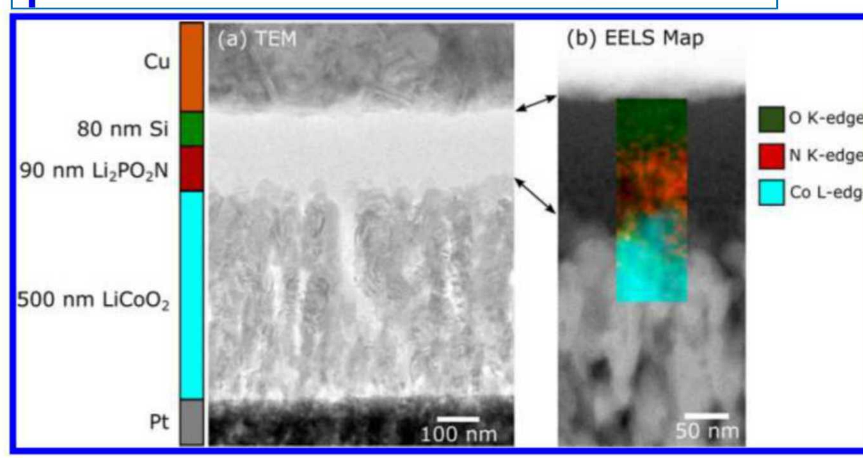
Yizhou Zhu,[†] Xingfeng He,[†] and Yifei Mo*[,†,‡]

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*[,†]



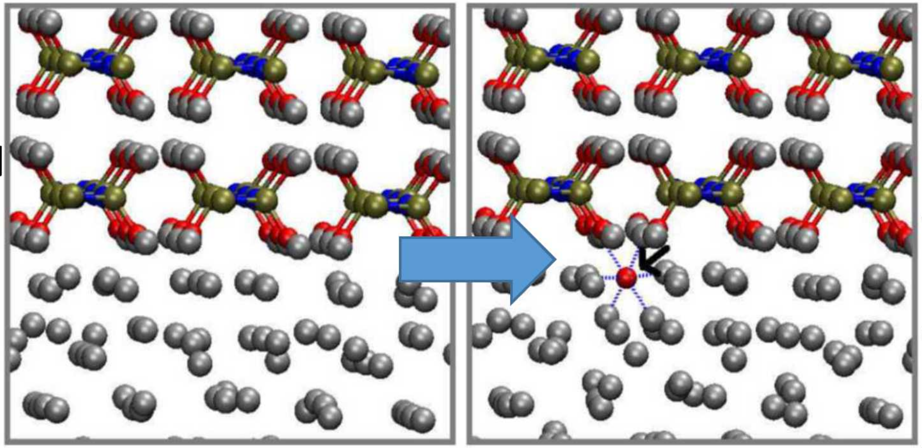


Model LiPON robust on Li metal surface during cycling

slab

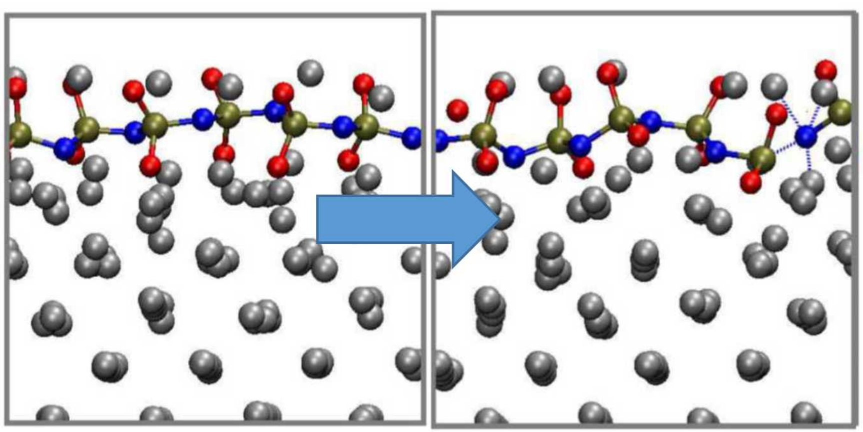
LiPON

Li(s)



- P-O bond breaking exothermic (tried 18)
- 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

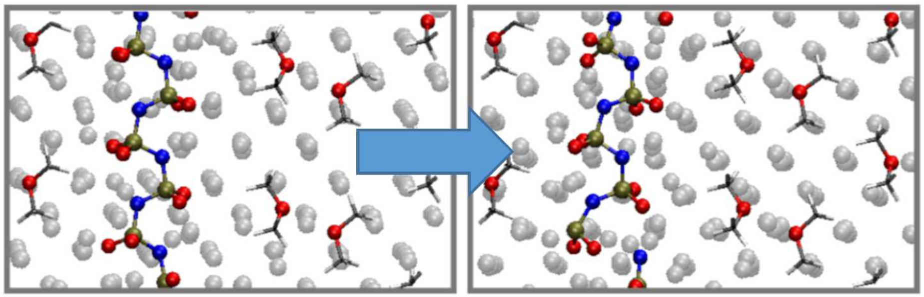
chain



But what about voltage effects?

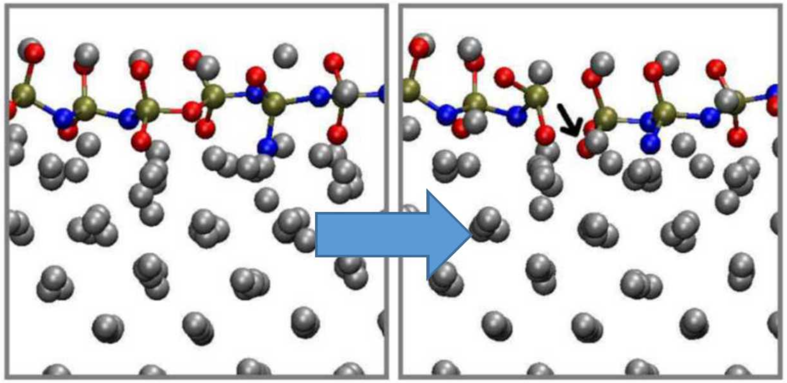
- P-O bond breaking exothermic
- Barrier for P-N breaking is lower
- P-N breaking exothermic (tried 12)
- barrier ~1.5 eV (tried 3)
- “age of universe” at T=300 K

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



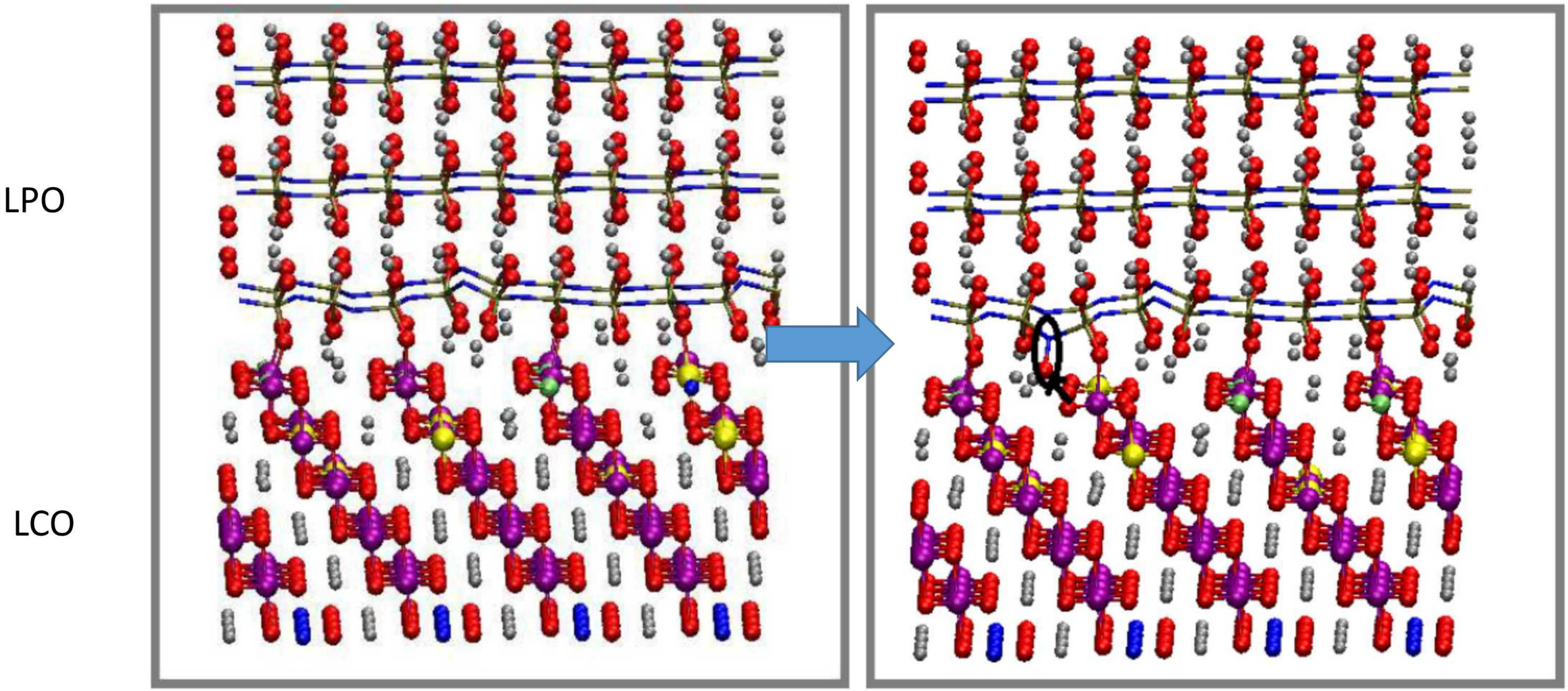
- previous chain calcuations done at ~0.6 V (out of electrochemical equilibrium)
- Shift to ~0.0 V by adding dipolar layer (Li^+ coordinated to ether molecules)
- Little change in barriers or exothermicity
- Reaction is chemical, not electrochemical?

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



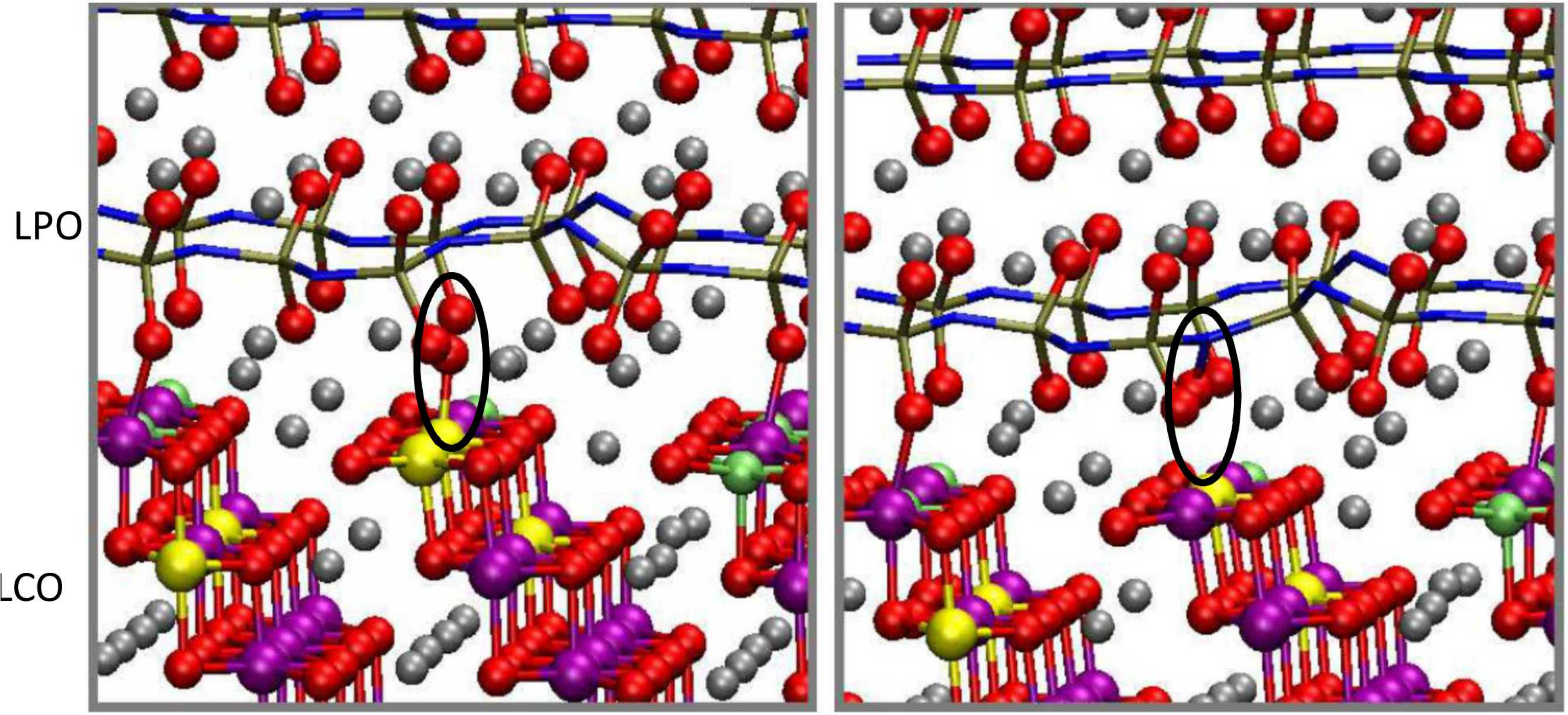
- P-O-P sequence (instead of P-N-P) can break exothermically, with < 1 eV barrier (< 1 hour at T=300 K)
- But subsequent reactions are again slow

Li_xCoO_2 (104) surface can lose oxygen to LiPON at interface, forming N-O bond seen in measurements



- Co(III) high, low, intermediate spins; Co(IV) high & low spins present
- extremely hard to converge DFT orbitals

If surface not flat, has C-O terminations sticking out reacts even faster



Less N near the surface, less reactive

Conclusions for Solid State Electrolytes/LiPON

- thermodynamically, LiPON unstable at both anode (lithium) and Li_xCoO_2 (cathode) interfaces
- kinetically, LiPON reacts slowly with Li-metal, but at 1 hour rate with Li_xCoO_2 at $x<0.8$ (partially charged state)
- in apparent agreement with measurements
- (measurements from Alec Talin, Elliot Fuller, Alex Pearse, Gary Rubloff; happy to discuss those in private)
- Battery modeling community needs to focus more on kinetics and voltage effects at interfaces