Comparative Comuptational Study of Solid-solid Interfaces in Liquid- and Solid-electrolyte Based Batteries

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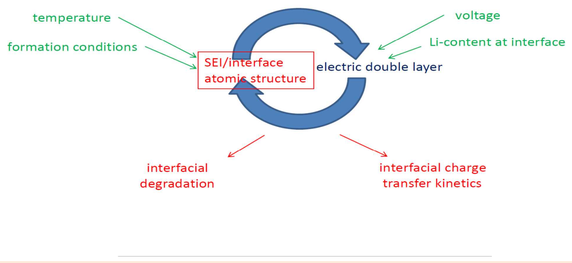
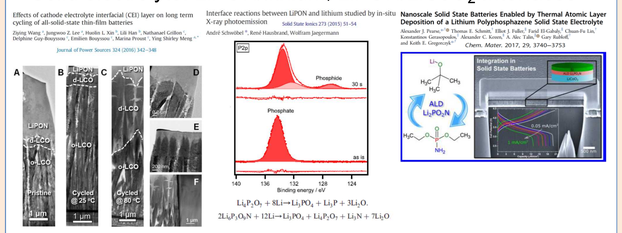
To

- *solid-solid interfaces* are ubiquitous
- present in solid- and liquid-electrolyte-based batteries
- comparative study should be fruitful

Critical to know interfacial structure -> key to many properties



Solid electrolyte: LiPON/lithium, LiPON/$LiCoO_2$ Interfaces



STEM: after cycling, LCO is disordered at LiPON interface, especially at high temperature

XPS: reactions at Li-metal/LiPON interface (deposited, not cycled, but calculations show no voltage dependence)

Despite these reactions, battery cycles well as long as LiPON thickness > 50 nm

Models, methods, and philosophy

- DFT/PBE, DFT+U, optimization and nudged elastic band
- perfect crystal, infinite chain LiPON model by Holzwarth with Li_2PO_2N stoichiometry [Du, Holzwarth, PRB 84, 184106 (2010)]
- recent ALD synthesis attain this stoichiometry [Pearse et al., Chem. Mater. 29, 3740 (2017)]
- Single phase thermodynamics calculations: compare the energies of different phases – each in a different simulation box
  --elegant, efficient, gives final product *if system at equilibrium*
- If system not at equilibrium, needs to calculate reaction barriers (ΔE^*), compare them with thermal energy, to see if reactions occur fast enough. ΔE^* = 0.93 eV ⟷1 hour at T=300 K
- Liquid-electrolyte battery interfaces are seldom at equilibrium. Increasingly, solid-electrolyte batteries also found to be so.

Summary

- single-phase thermodynamics is typically used to model electrode materials and solid electrolyte interfaces
- interfacial kinetics typically used to model liquid state batteries
- Here we use both computational approaches for both battery types
- examples: LiPON, ethylene carbonate, SEI films
- thermodynamics say everything reacts – not too useful
- kinetics – costly but determine what can happen at a certain temperature; indispensable for solid interface studies

Acknowledgement

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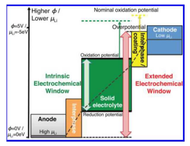
All-solid-state battery example:
LiPON at lithium metal and Li_xCoO2 interfaces

Single phase thermodynamics method (from literature)

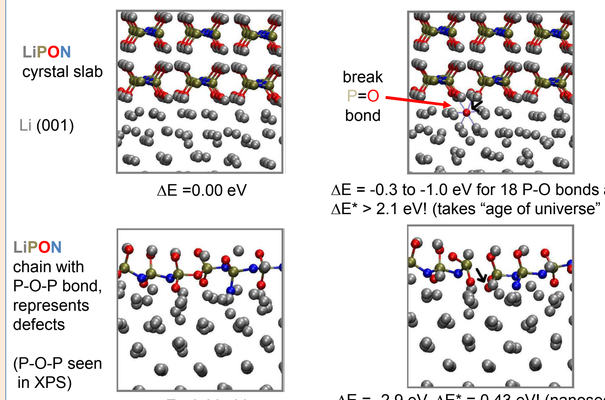
- simple and elegant
- each simulation cell contains one phase
- Find lowest energy phases from single-phase energies
- e.g., 8 Li (s) + Li_2PO_2N $Li_3P + Li_3N + 2\ Li_2O$ -0.66 eV/Li (Zhu et al.)
- no explicit interface; every component in a separate simulation box

Origin of Outstanding Stability in the Lithium Solid Electrolyte Materials: Insights from Thermodynamic Analyses Based on First-Principles Calculations
ACS Appl. Mater. Interfaces 2015, 7, 23685−23693
Yizhou Zhu,† Xingfeng He,† and Yifei Mo*,†,‡



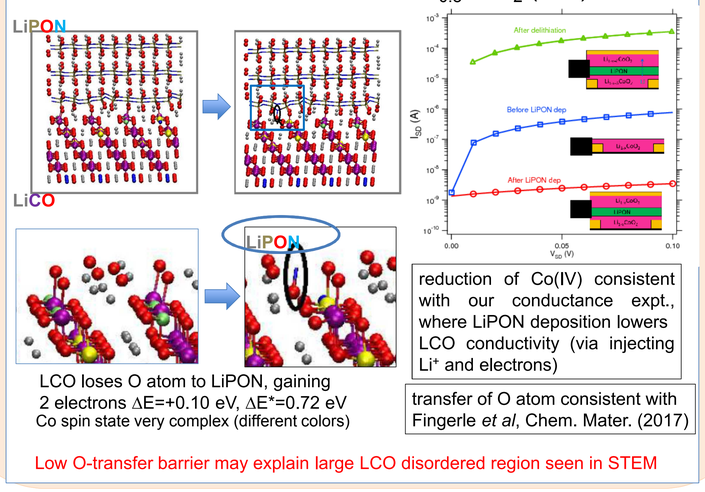
- *assumption: have reached thermodynamic equilibrium*
- reasonable for material synthesis (700-1000°C for 10 hours)
- not a good assumption at interfaces (fabrication at 150-300°C)
- examples of kinetic- (not thermodynamic-) controlled interfacial products exist (e.g., Sang, Haasch, Gewirth, Nuzzo, Chem. Mater. 2017)

Interfacial kinetics slow at LiPON/Li (001) interface (our work)



LiPON stable on Li due to slow reaction kinetics – explains why very little SEI found

Interfacial kinetics faster at LiPON/$Li_{0.8}CoO_2$ (104) interface



reduction of Co(IV) consistent with our conductance expt., where LiPON deposition lowers LCO conductivity (via injecting Li^+ and electrons)

LCO loses O atom to LiPON, gaining 2 electrons ΔE=+0.10 eV, ΔE*=0.72 eV
Co spin state very complex (different colors)

transfer of O atom consistent with Fingerle *et al*, Chem. Mater. (2017)

Low O-transfer barrier may explain large LCO disordered region seen in STEM

Organic liquid electrolyte battery example:
Ethylene Carbonate (EC) and its SEI components

Single phase thermodynamics for liquid electrolytes (our work)

single phase thermodynamics never used for liquid electrolytes – here's why

potential vs. Li⁺/Li(s) (V)

at any voltage,
EC -> CO_2 + C_2H_4O

> 6.0 V:	electrochemical oxidation (glassy carbon)
> 5.0 V:	electrochemical oxidation (Borodin)
< 3.5 V:	EC + $LiMn_2O_4$ -> MnO + Li_2CO_3 (KL)
1.2 V:	thermodynamic instability (KL DFT/PBE0)
0.7-0.8 V:	electrochemical reduction

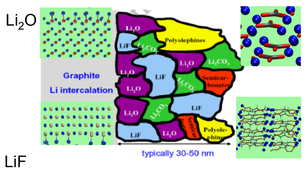
- EC: main solvent
- no instability onset at 4.5-4.7 V, often cited as solvent breakdown in "high voltage" cathode
- 4.5-4.7 V instability onset not due to solvent breakdown?

electrochemical (i.e., observed) stability ≠ thermodynamic stability limit (1.2 – 3.5 V)

- because liquid reactions occur at T~25 °C
- thermodynamic equilibrium is not reached because …
- … reactions governed by kinetics; thermodynamic approach fails

Single Phase Thermodynamics for SEI components

single phase thermodynamics never used for liquid battery SEI – here's why



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†

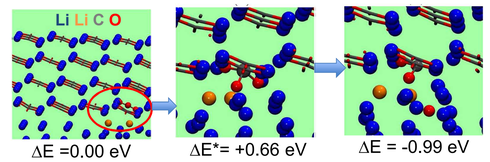
$Li_2CO_3 + 4\ Li \rightarrow 3\ Li_2O + C$ at < 1.29 V vs. Li^+/Li (s)

"LEDC"

$Li_2C_4H_4O_6$ ("LEDC") + 10 Li -> 6 Li_2O + 4 C + 3 H_2
at < 1.22 eV vs. Li^+/Li(s)

- SEI components thermodynamically unstable, except Li_2O and LiF
- Nevertheless, they are found in expt. Thermodynamics fail for SEI films
- But learning from single phase thermodynamics lead to prediction that Li_2O and LiF must be found on Li metal surface (see below)

Interfacial kinetics allows SEI (Li_2CO3) decomposition on Li(s)

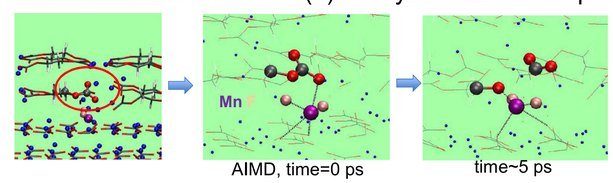


C-O bond-breaking in CO_3^{2-} aided by 2 interstitial Li; they cost only 0.3 eV

Leung *et al*., J. Phys. Chem. C 120: 6302 (2016)

C-O bond breaking barrier surprisingly much lower than P-O cleavage in LiPON!

Interfacial kinetics allows Mn(II) catalyzed SEI decomposition



Mn(II) lodged between inorganic SEI (Li_2CO_3) and organic SEI (LEDC) catalyzes electrochemical reduction of LEDC. [Shkrob et al, J. Phys. Chem. C 120, 15119 (2016)]