SAND2022-10712C

Galvanic Corrosion and Electric Field in Lithium Anode Passivation Films: Effects on Self-Discharge

Kevin Leung, Laura C. Merrill, and Katharine L. Harrison

Sandia National Laboratories

Thanks: Quinn Campbell, Jacob Harvey

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J. Phys. Chem. C 126:8565 (2022)

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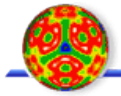


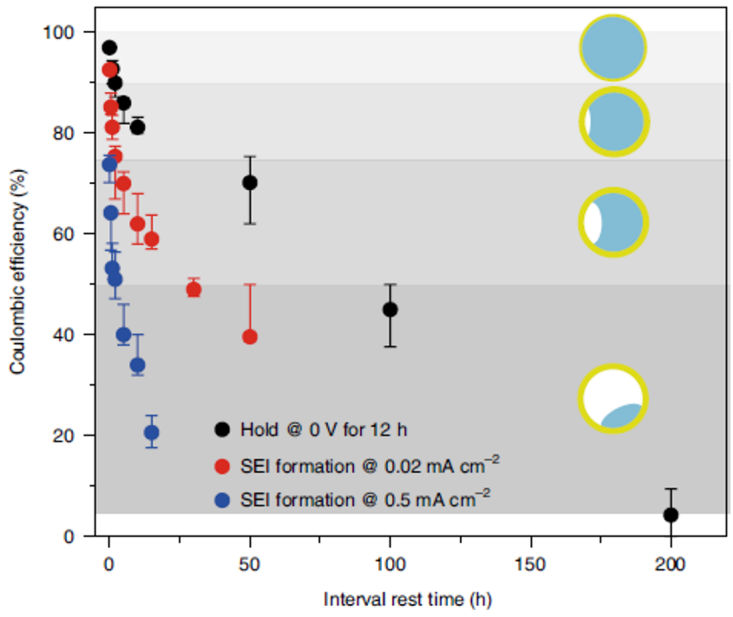
Office of Basic Energy Sciences

DFT interpretation of Galvanic corrosion, overpotentials, contact potentials, & other things you should know

Fast galvanic lithium corrosion involving a Kirkendall-type mechanism

NATURE CHEMISTRY | VOL 11 | APRIL 2019 | 382–389

Dingchang Lin[1,3], Yayuan Liu[1,3], Yanbin Li[1], Yuzhang Li[1], Allen Pei[1], Jin Xie[1], William Huang[1] and Yi Cui[1,2*]

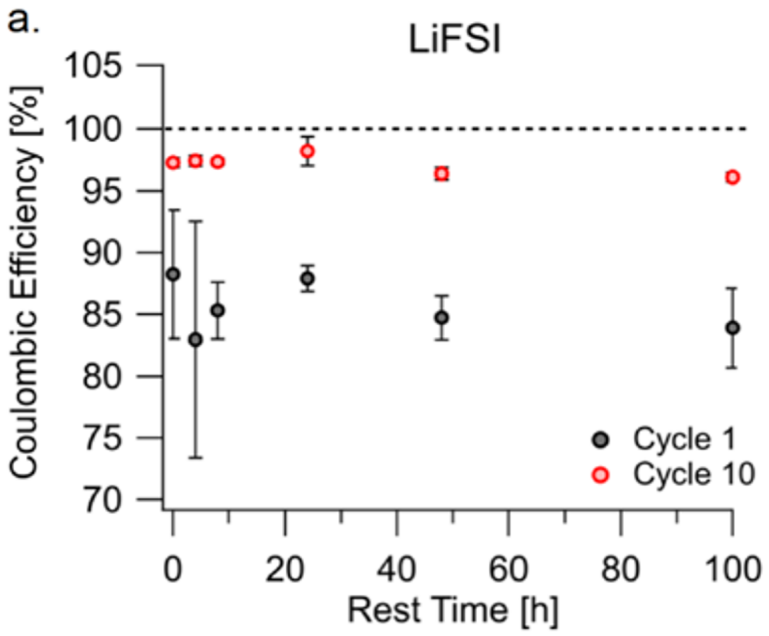


Total charge: 0.05 mAh/cm^2

Uncovering the Relationship between Aging and Cycling on Lithium Metal Battery Self-Discharge

ACS Appl. Energy Mater. XXXX, XXX, XXX–XXX

Laura C. Merrill, Samantha G. Rosenberg, Katherine L. Jungjohann, and Katharine L. Harrison*



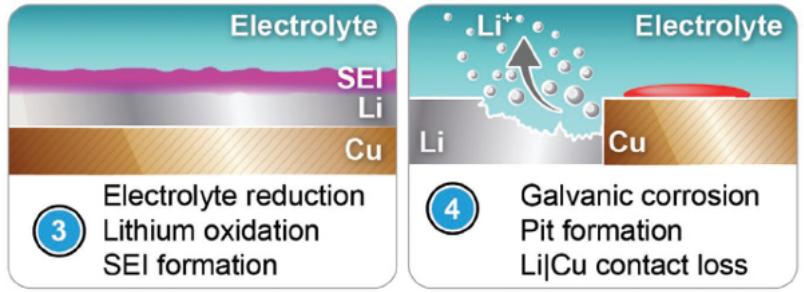
Total charge: 0.5 mAh/cm^2

(see also)

Galvanic Corrosion of Lithium-Powder-Based Electrodes

Aleksei Kolesnikov, Martin Kolek, Jan Frederik Dohmann, Fabian Horsthemke, Markus Börner, Peter Bieker, Martin Winter, and Marian Cristian Stan**

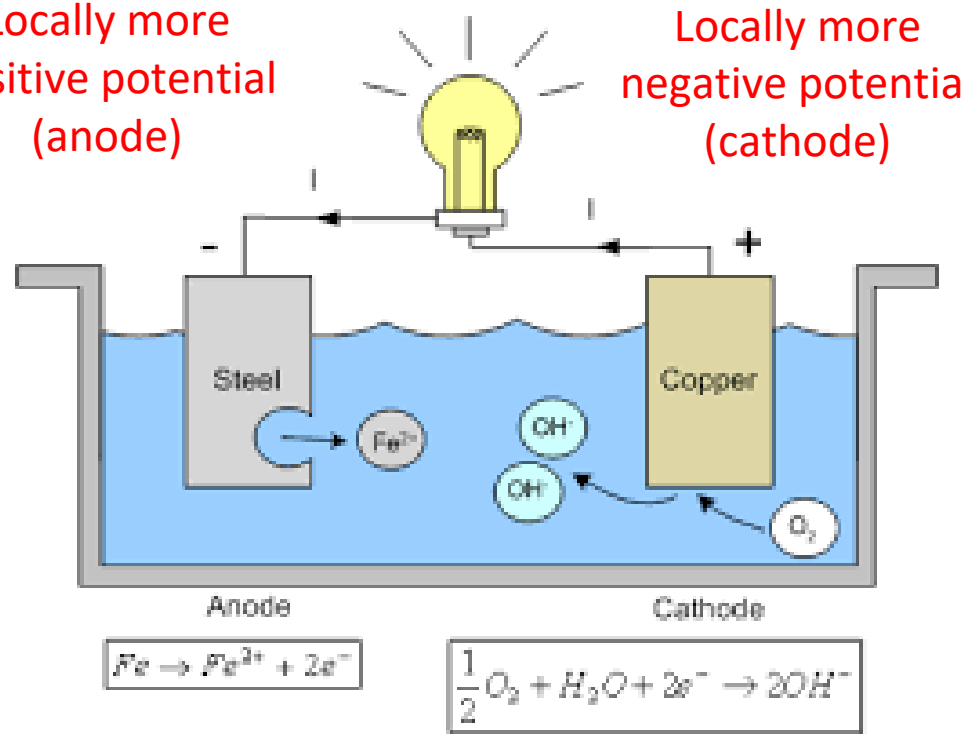
Adv. Energy Mater. **2020**, *10*, 2000017



Pitting corrosion & Galvanic Corrosion for steel, aluminum (canonical)

Locally more positive potential (anode)

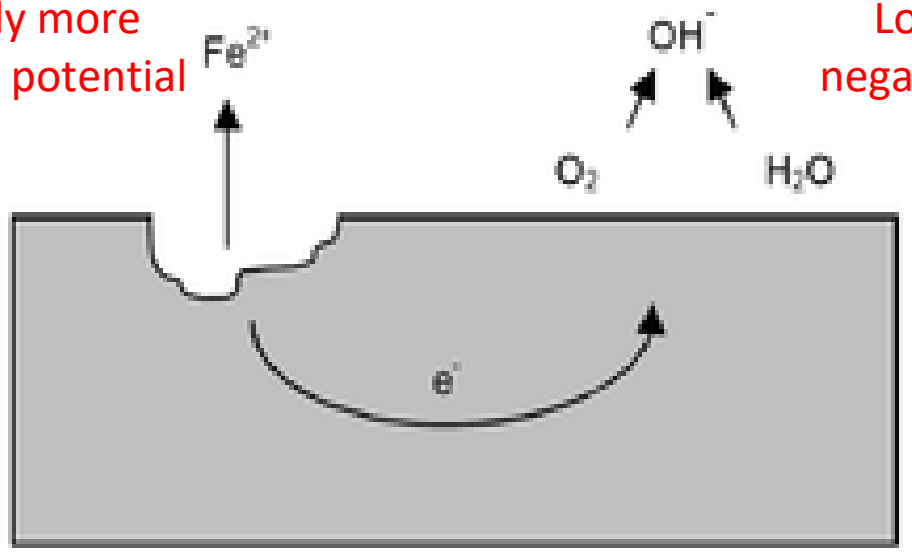
Locally more negative potential (cathode)



Galvanic corrosion, from xapps.xyleminc.com

Locally more positive potential

Locally more negative potential



Non-galvanic From wikipedia

Characteristics

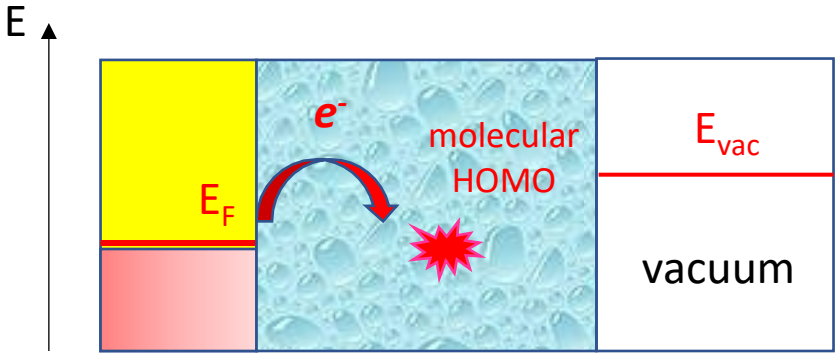
1. Spatial inhomogeneity
2. Overpotential (e.g., Al pitting potential > -0.5 V vs SHE; Al stripping is at -1.66 V vs SHE. > 1.16 V overpotential!)
3. “dirty” (non-pristine) electrode surfaces

Models and Methods

- Usual VASP, DFT/PBE, 400 eV cutoff …
- Will focus on conceptual stuff in the next few slides
- Such as voltage definitions, overpotentials
- To deal with spatial heterogeneity, end up using models with ~3000 atoms

DFT is ground state (one Fermi level, E_F). Electrochemistry (>=2 electrodes) inherent isn't.

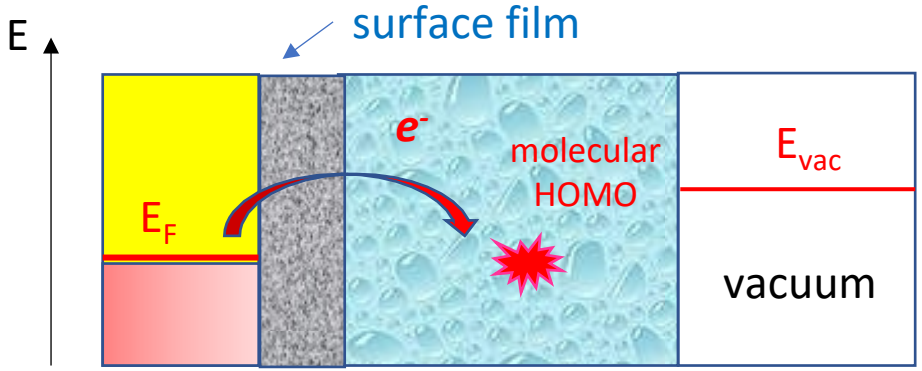
Needs lots of tricks to deal with this. Usually half-cell reactions, with a vacuum as reference electrode



Pristine electrode (mostly Au)

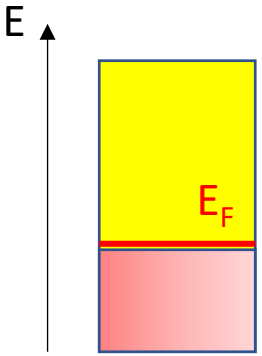
E_{vac} - E_F gives us the absolute voltage via "Trastti relation"

Caveats. 1. Trasatti should be modified for non-aqueous solvents
2. liquid elecrolytes have universal vacuum interfaces.
solid electrolytes have facet dependence. No one has solved this issue.



Non-pristine electrode (already hard to do with DFT)
We do this, as do some battery modeling groups

Equilibrium potential is not adequate at interfaces

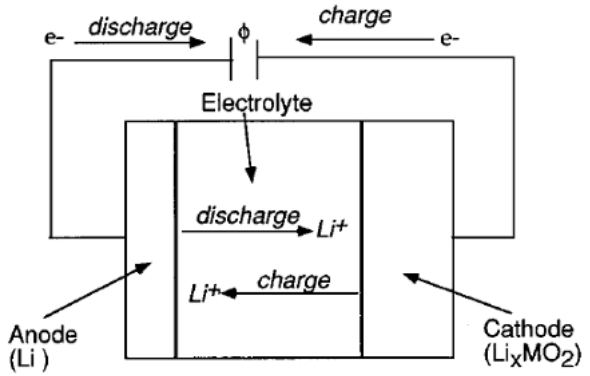


***Ab initio* study of lithium intercalation in metal oxides and metal dichalcogenides**

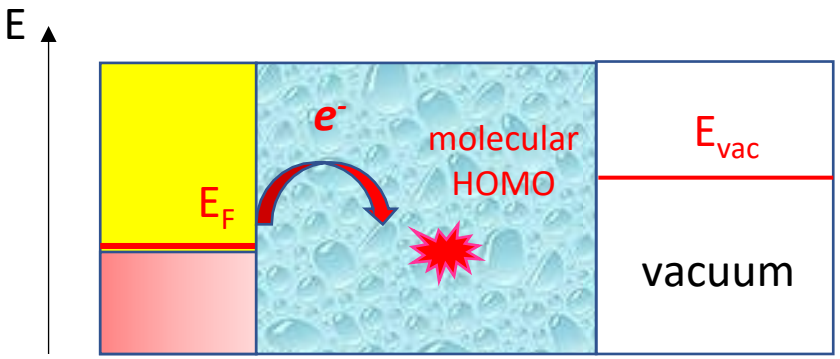
M. K. Aydinol, A. F. Kohan, and G. Ceder
Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

K. Cho and J. Joannopoulos
Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
(Received 31 January 1997)

$$V(x) = -\frac{\mu_{\mathrm{Li}}^{\mathrm{cathode}}(x) - \mu_{\mathrm{Li}}^{\mathrm{anode}}}{zF}.$$



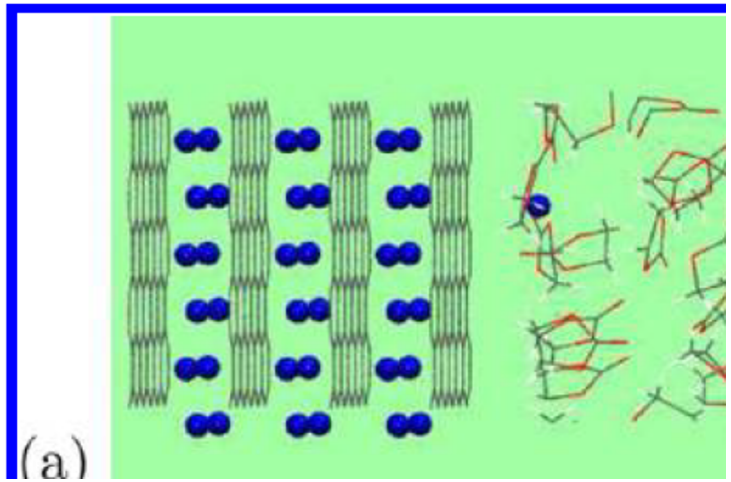
- Historically, battery community consider electrode materials without interfaces
- Completely ignores Fermi level, since without interface the absolute E_F is undefined anyway
- This is the equilibrium potential, not the true (instantaneous) potential
- It assumes existence of an applied potential ϕ_e equals to the equilibrium potential



- But interfacial cells have their own ϕ_e, cannot just assume equilibrium
- Ignoring E_F means you get unintentional overpotentials at interfaces

Corrosion has possible overpotential … DFT can exploit that too

Decouple Φ_e, the potentiostat equilivent, from Φ_i, the Gerd Ceder phase diagram/ equilibrium Li insertion potential



Φ_i = 0.1 V for LiC_6

J. Phys. Chem. C 2013, 117, 24224−24235

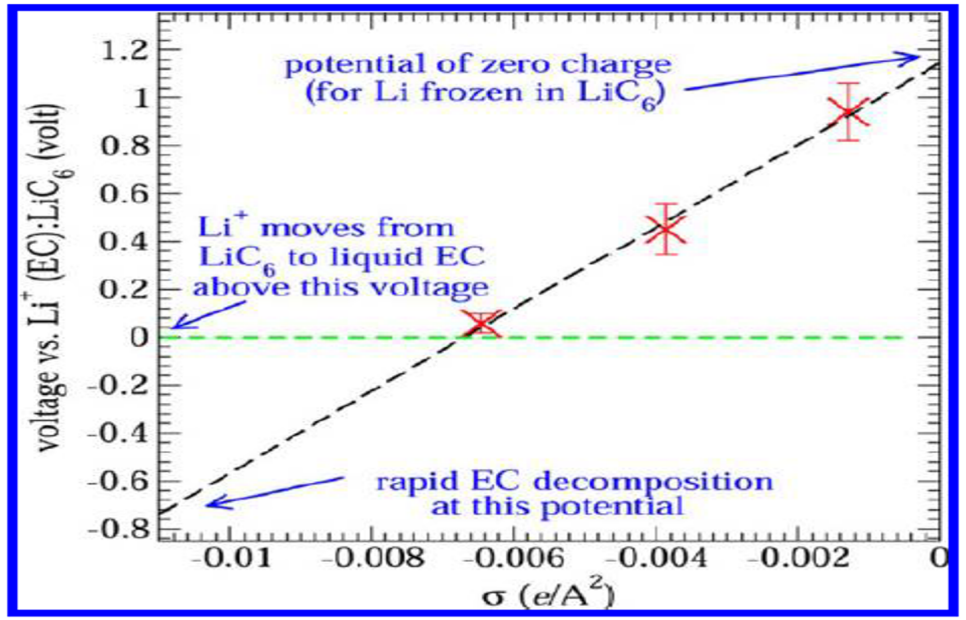


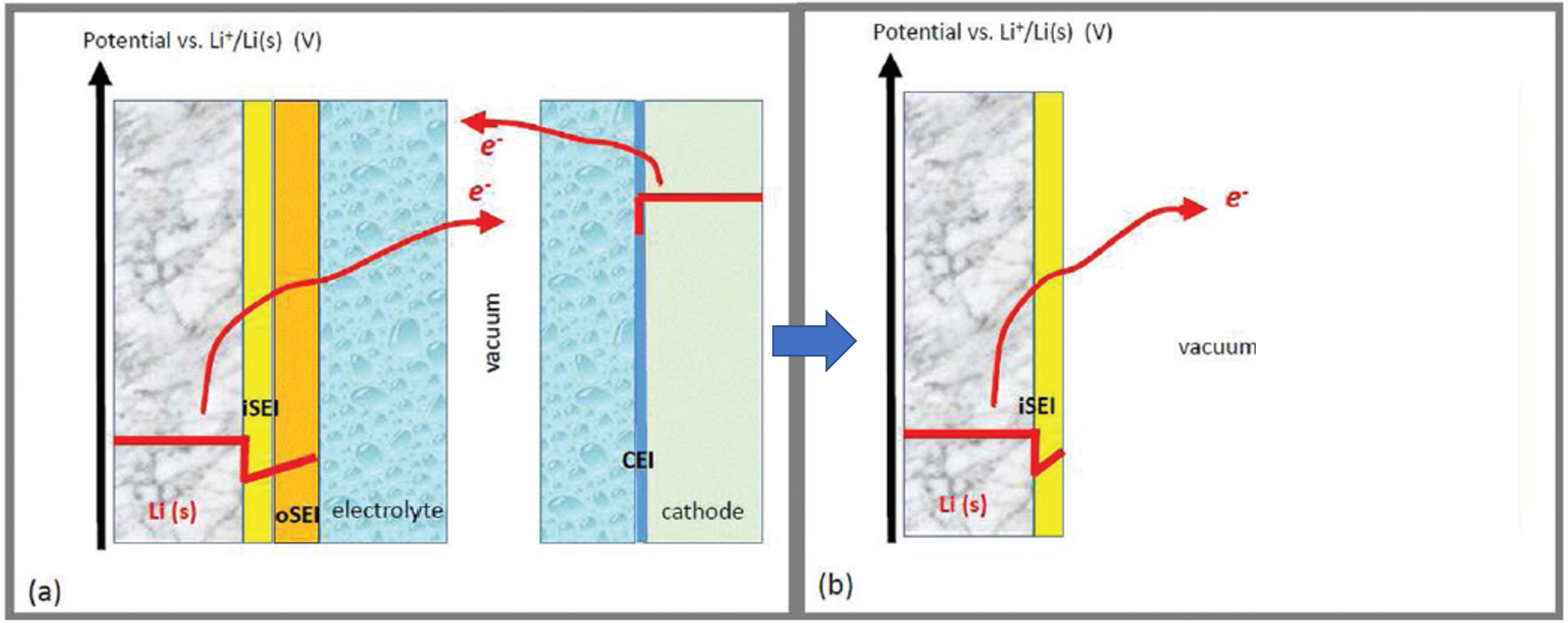
Figure 4. Predicted potential ($-\Delta G_t/|e|$) for virtual Li^+ transfer from the LiC_6 slab to the middle of the liquid EC region as the surface charge (σ) varies. Crosses denote the three data points computed, with 0, 1, and 2 mobile Li^+, respectively. AIMD simulations with 4 mobile Li^+ and no counterions lead to EC decomposition.

Φ_e can be 0.1 V, 0.5 V, or 0.9 V depending on surface charge

- Only basal plane exposed; Li in LiC_6 cannot deintercalated
- Severe kinetic constraint -> one source of overpotential
- We are not at Φ_e = 0.1 V vs. $Li^+/Li(s)$ just because LiC_6 exists!
- It is easier for DFT interface models to be at overpotential than at equilibrium

In this work, calculate *electronic voltage* ϕ_e using work function

ϕ_e, E_F, work function are proportional to each other



exact

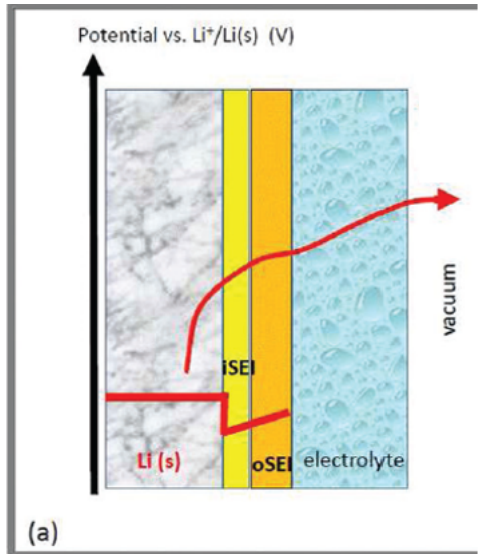
- Approximate, omitting low-dielectric organic SEI (oSEi) and electrolyte
- Assumes all potential drop is in SEI
- Works for LiF, Li_2O, not Li_2CO_3, other coatings … [see also Energy Envir. Sci. 13, 5186 (2020)]

Opportunity to exploit synergy between battery interfaces and corrosion

This talk focuses on lithium metal anodes; Na anodes are similar, but cathodes are not

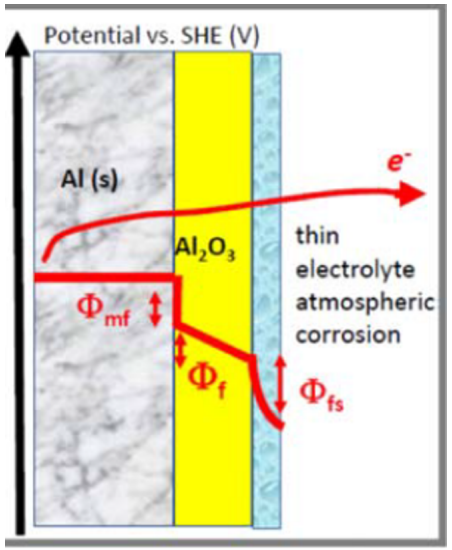
Similarities between lithium passivation and structural metal corrosion

1. Both structural metals and Li anode have passivating films: oxides vs SEI
2. Canonical oxide & (inorganic) SEI thickness ~ 5 nm (WKB theory estimate)
3. Use similar DFT models



Battery anode

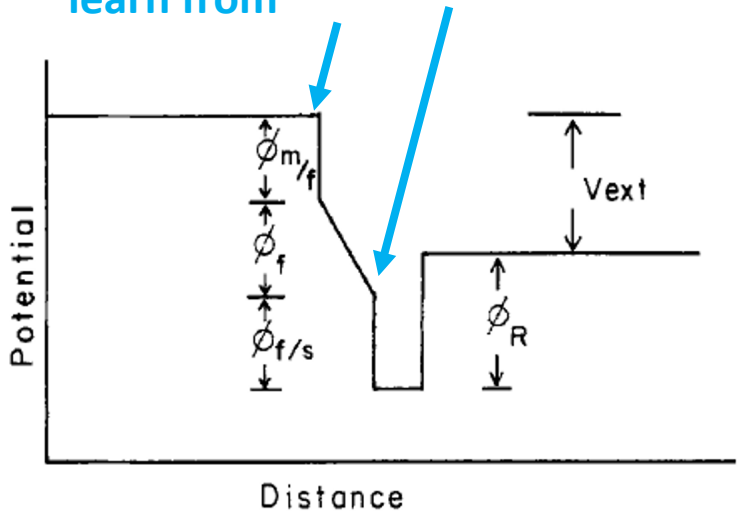
Leung, PCCP 22, 10412 (2020)



corrosion

Leung, JES, 168, 031511 (2021)

Sharp drop: contact potential corrosion experts have known this, battery community can learn from



corrosion ("point defect model")

Chao, Lin, MacDonald, JES, 128, 1187 (1981)

Critical to use “SEI” covered, not pristine, electrode surface

Only Au and Mg (with special electrolytes) are pristine

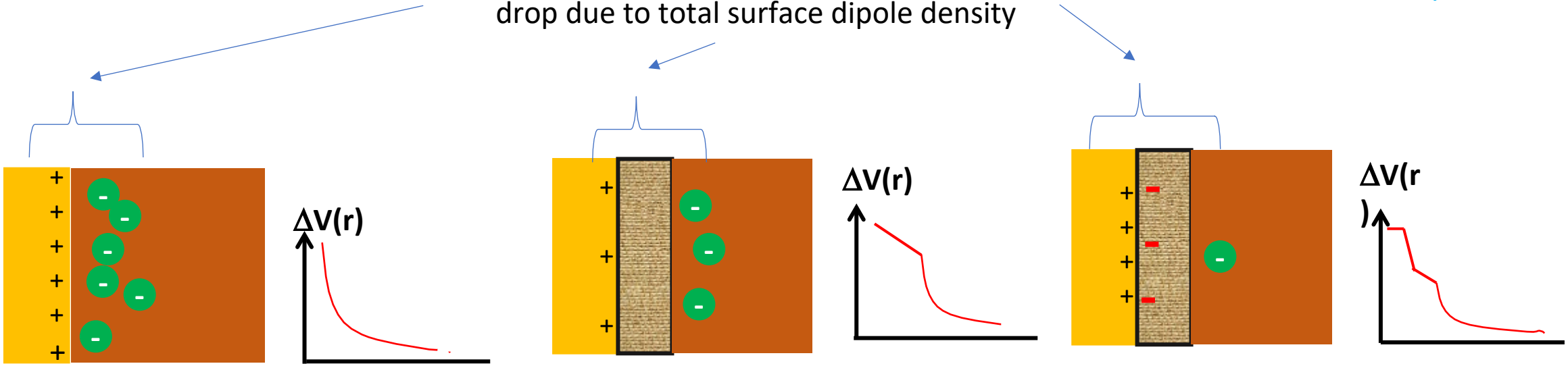
- Dealt with “dirty” electrode surfaces since 2015 this should be frontier of science!

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

Electric double layer (EDL) yields a potential drop due to total surface dipole density → Contact potential



Pristine electrode

Say cathode anion distance is 0.5 nm, need 0.5 nm^{-2} surface anion density for 0.9 V drop

Electrode with insulating coating (e.g., SEI without charged vacancies)

Say SEI thickness is 5 nm, with ε_o=5, need 0.25 nm^{-2} surface anion density for 0.9 V drop

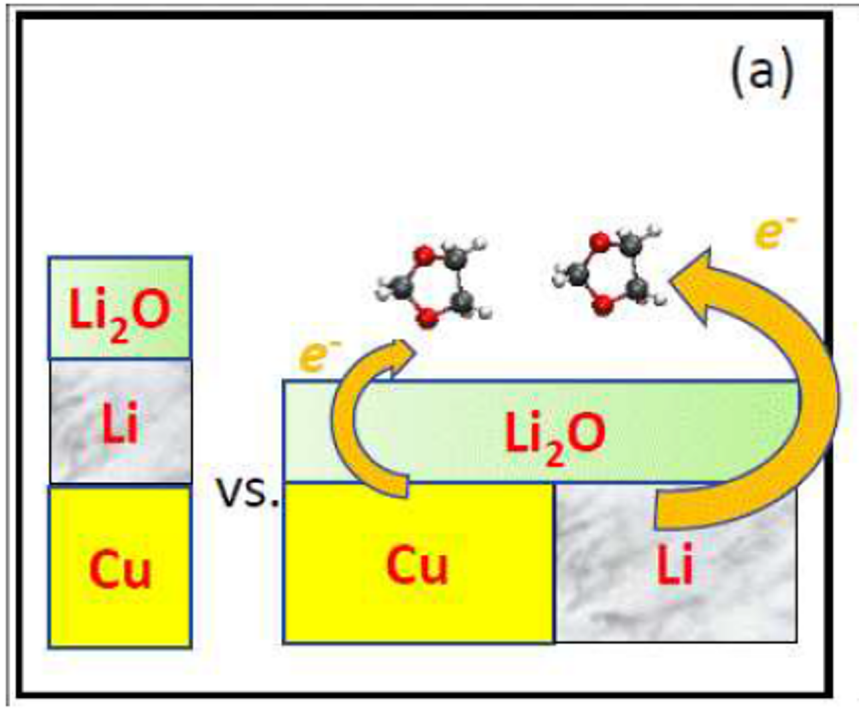
Electrode with coating with charged vacancies

Rui Guo and Betar M. Gallant

Chem. Mater. 2020, 32, 5525−5533

Results

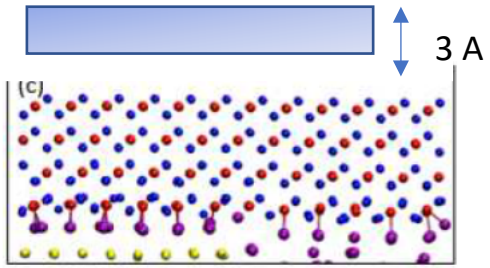
DFT models and results on Li/Cu junction: Li-coverage effects



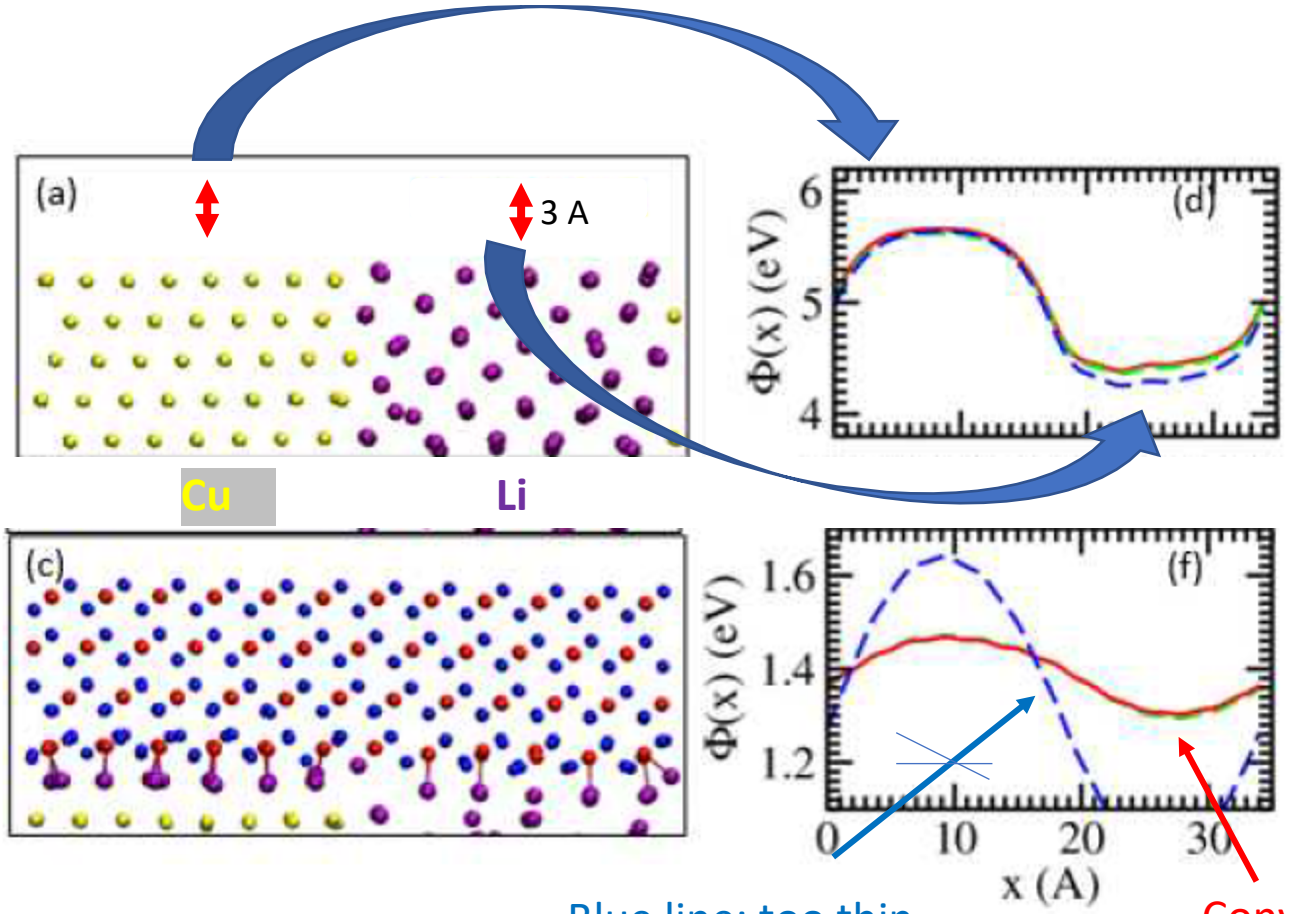
100 % Li coverage: not galvanic
(agree with Merrill et al., ACS Appl. Energy Mater. 2022)

50 % Li coverage: Li -side has galvanic signatures

DFT models and results on Li/Cu junction: “anti-galvanic”



- Φ(x): “local potential” calculated like local work function but only averaged within 3 A of oxide surface – thick vacuum slab needed
- mimics reaction front, not measurable

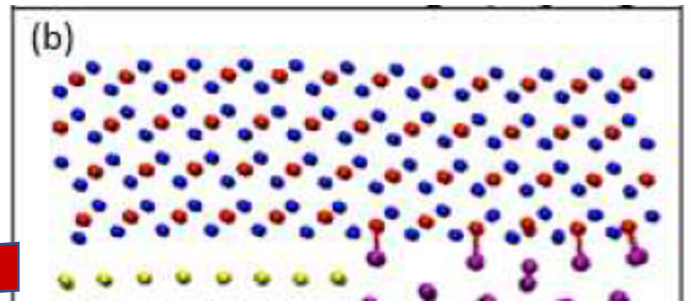


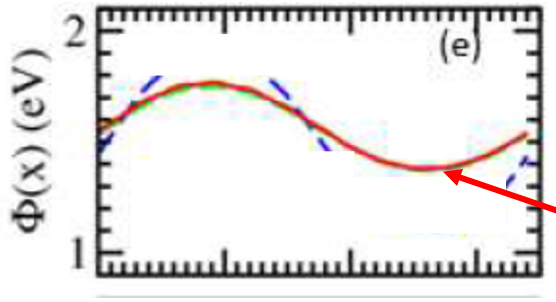
To make "anti-galvanic" argument, knowing the overpotential is crucial

In fact, we have two oxide models

Oxide 1 model: hypothetical, with overpotential, like pitting in Al metal

We lower voltage by 0.84 V by adding interfacial Li metal! *Due to contact potential.*

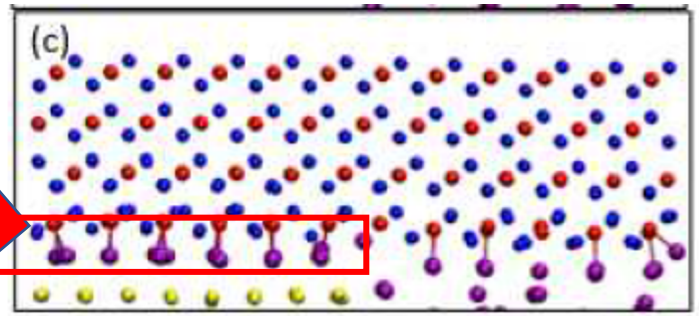


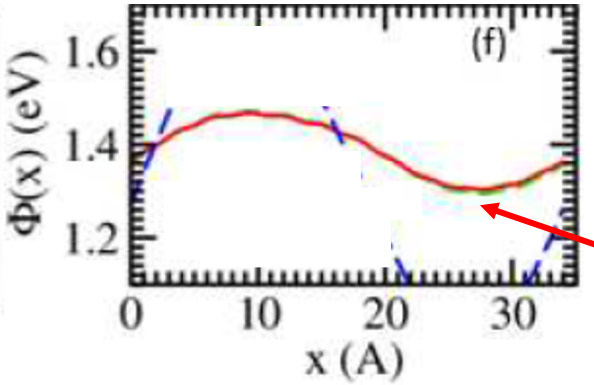


Φ_e = +0.85 V

Li side:
Locally above 0 V, Li can still dissolve
SEI does not form

Oxide 2 model: no overpotential, agree with expt. (see next page)

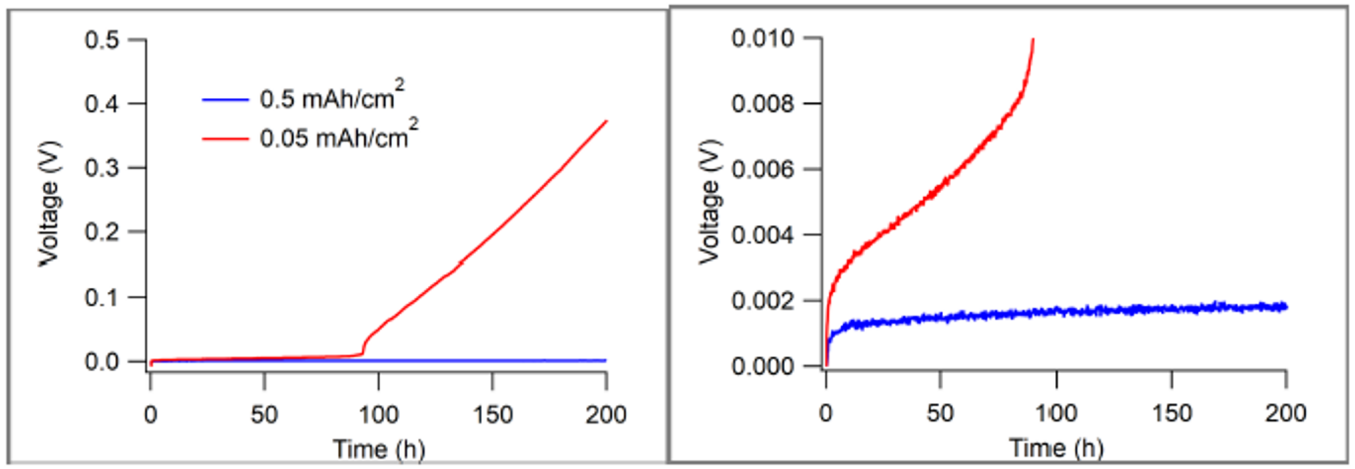




Φ_e = +0.01 V

Li side:
Locally below 0 V, Li cannot dissolve
SEI forms

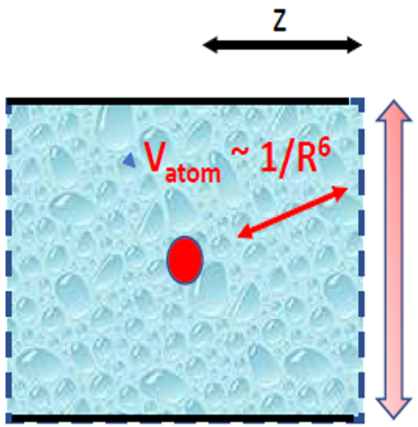
To make “anti-galvanic” argument, measuring overpotential is crucial



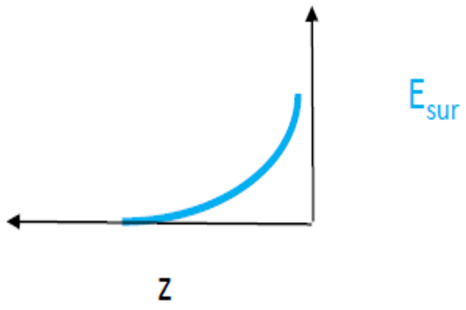
- Merrill and Harrison measured potential during self-discharge: ~ 0.0 V
- Little overpotential until hours passed
- So “oxide 2” corresponds to experimental results (no overpotential at room temperature)
- DFT cannot predict overpotential – time scale too long – but can construct models with overpotential constraints

Contact potential arises from interfacial dipole surface density

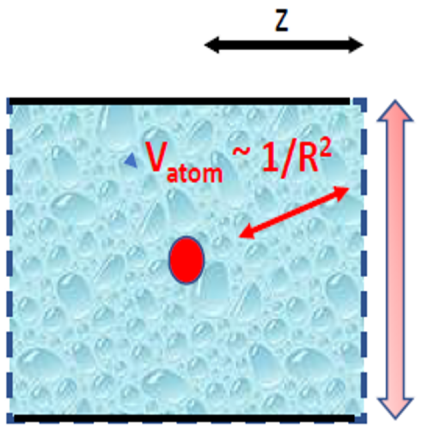
Van der Waal's forces – no surface term



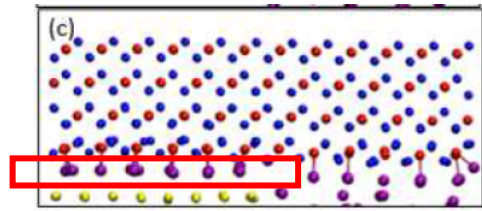
Integrate V_{atom} over surface, E_{sur} ~ $1/z^4$



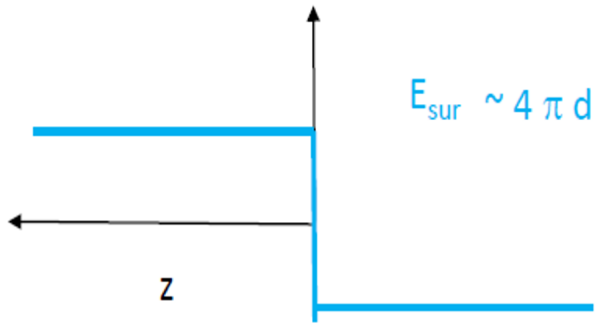
Electrostatic forces – has constant surface term

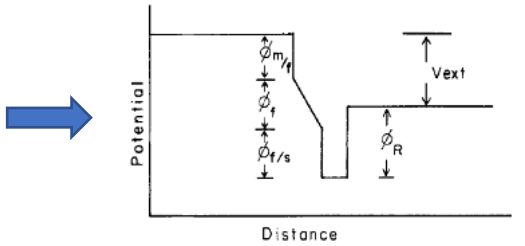


Surface dipole density d



Integrate V_{atom} over surface, E_{sur} ~ log(z)?
Not really – conditionally convergent, surface-sensitive





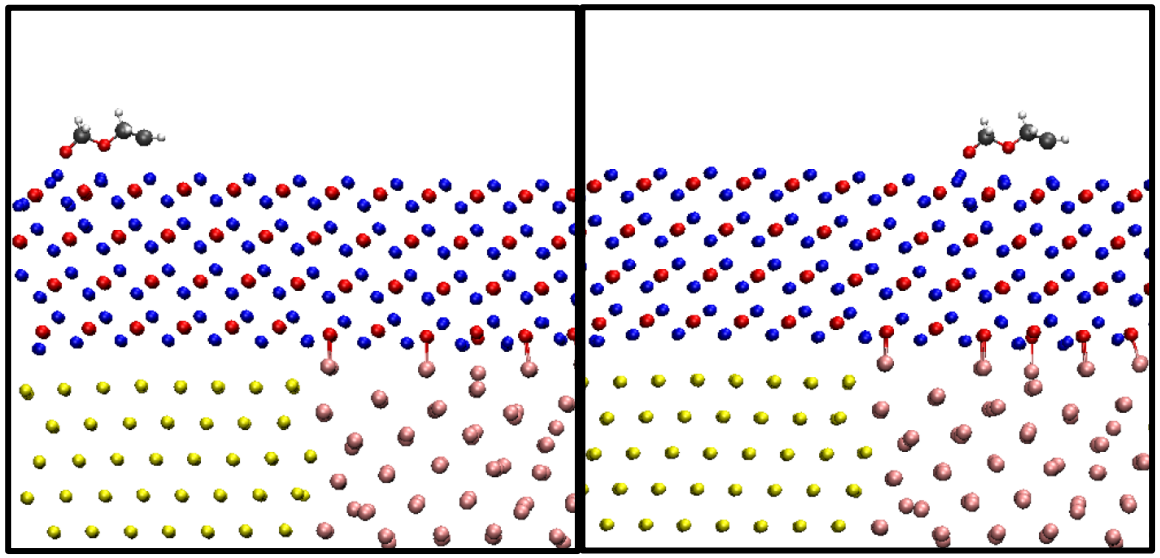
- Interlayer Li provides interfacial dipole sheet – changes contact potential by ~ 1 V!
- Battery researchers somehow hasn't caught on (see Maier however)

- Does not depend on z, neither decays nor diverges
- Due to 1/R interactions in 3 D world

Explicit SEI formation/evolution energetics confirm local overpotentials

Oxide 1 model

ϕ_e = +0.85 V (hypothetical)



ΔE = +0.87 eV

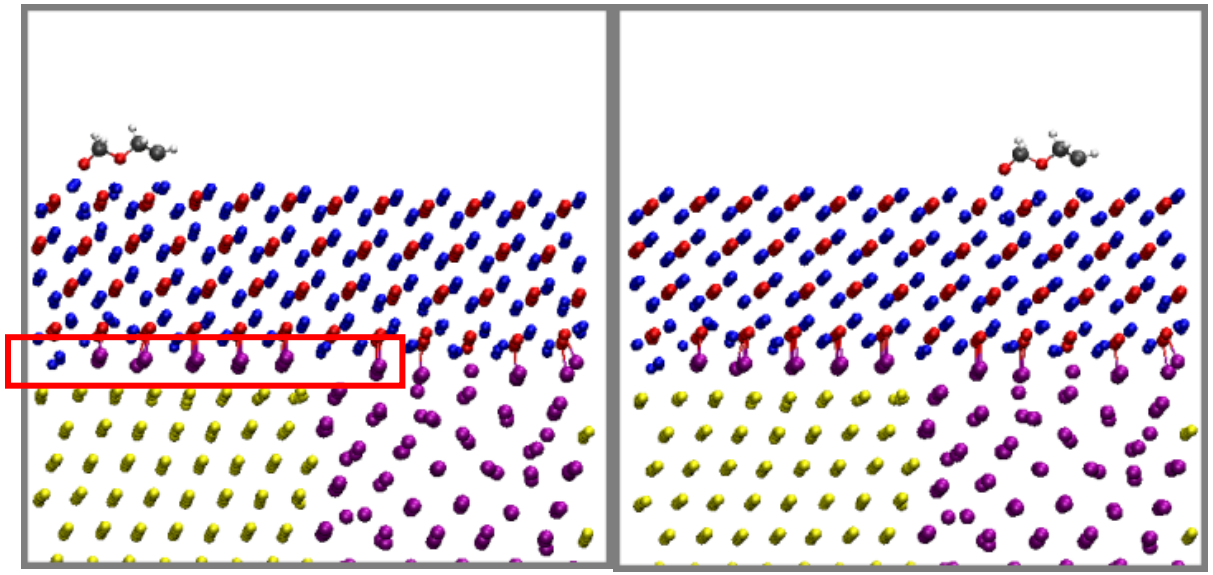
ΔE = +0.31 eV

above 0 V, Li can still dissolve SEI does not form

SEI reactions less unfavorable on Li and Cu sides

Oxide 2 model

ϕ_e = +0.01 V (real at T=300 K)



ΔE = -0.65 eV

ΔE = -1.15 eV

Cu side: locally above 0 V, Li can dissolve, SEI favored

Li side: locally below 0 V, Li cannot dissolve, SEI more favored

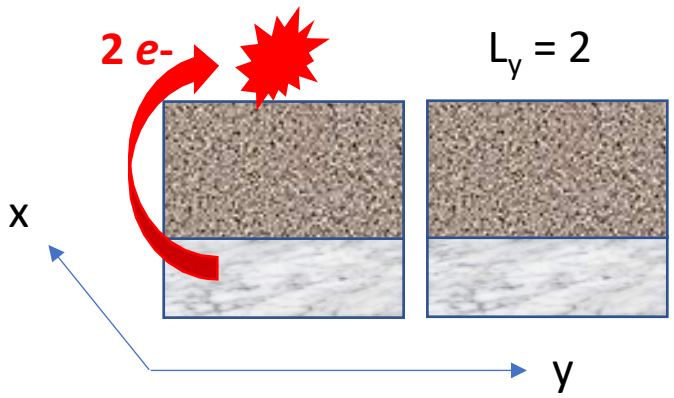
Agree with measurements: SEI 2x thicker on Li side

NATURE CHEMISTRY | VOL 11 | APRIL 2019 | 382–389

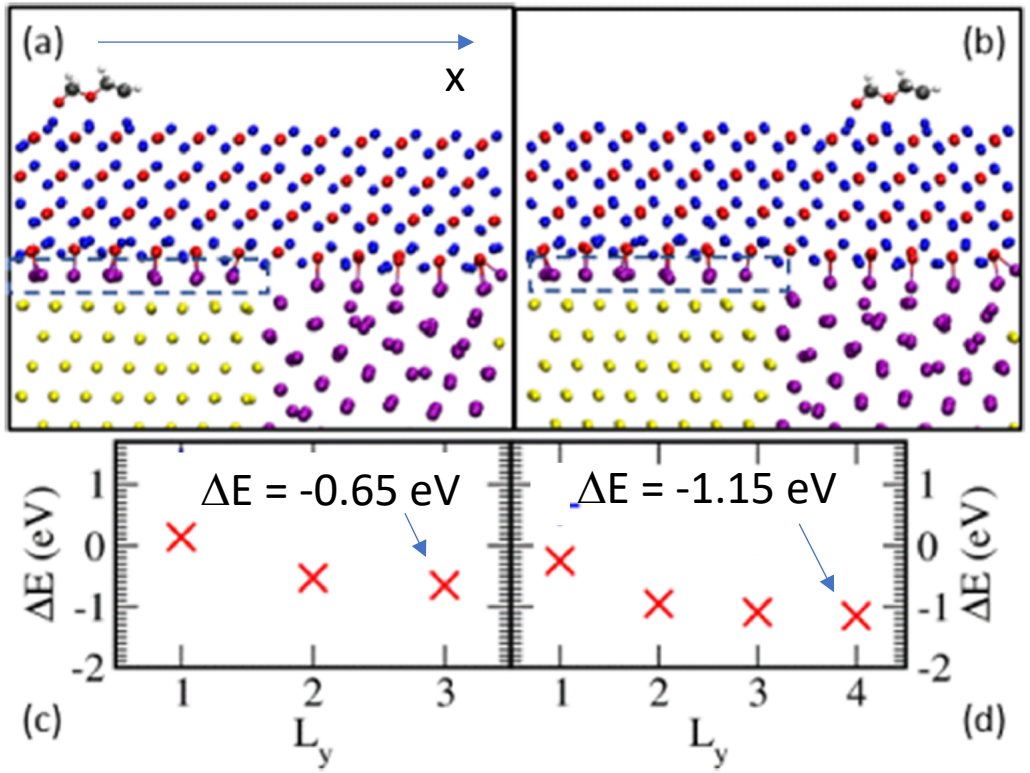
Again, just because Li metal exists in the cell doesn't mean we are automatically at 0.0 V vs. $Li^+/Li(s)$! Due to DFT overpotential.

Two Computational Considerations

- "L_y" (dimension in-plane): need large lateral supercell size because SEI formation involves 2 e^- transfer – forms large dipole moment. Used up to 3000 aoms



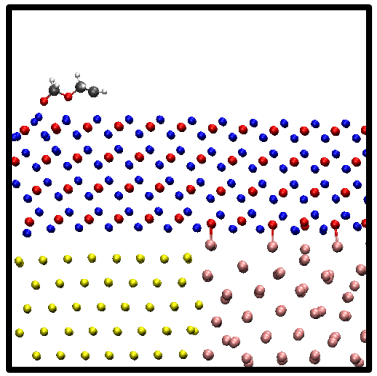
Large dipole moment could be corrected using quantum continuum approx. [Campbell and Dabo, PRB 95, 205308 (2017)]



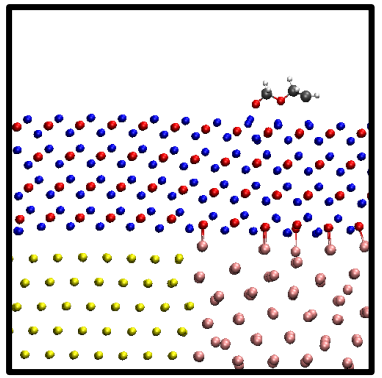
Two Computational Considerations (cont.)

- When doing DFT battery interface calculations, we need to report electronic voltage μ_e! Otherwise you may create an "oxide 1" model and think the coating doesn't form SEI – when the μ_e is simply too high to form SEI.

Oxide 1: μ_e = +0.85 V (hypothetical)



ΔE = +0.87 eV

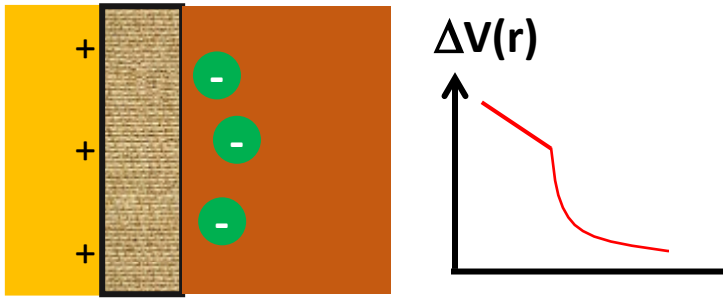


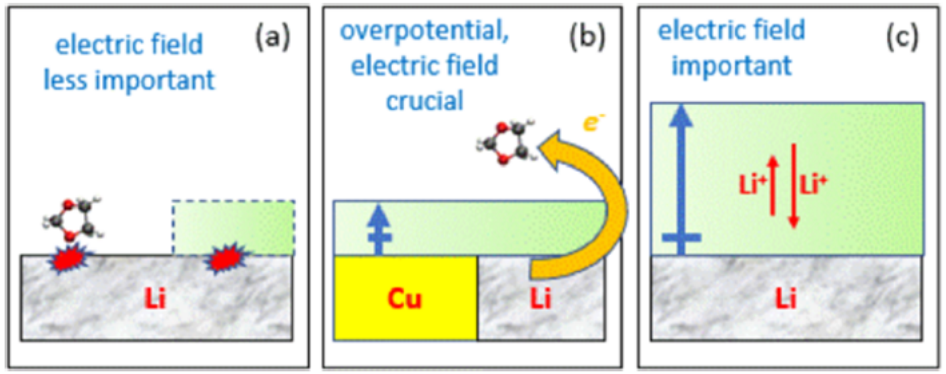
ΔE = +0.31 eV

Discussions/Polemics

Is the field of DFT modeling of battery *interfaces* in a crisis?

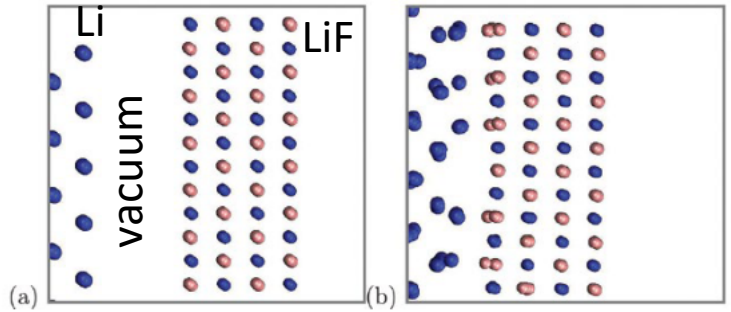
- (almost) every research group working on bulk battery materials use the same methods
- every group working on battery interfaces seem to do something completely different
- Particularly problematic is the handling of potentials (voltage)
- I believe we at Sandia published the first DFT battery anode/liquid-electrolyte interface paper and the first DFT battery cathode/liquid-electrolyte interface paper
- Our early work has some problems/omissions we spent a decade improving upon
- Focusing on anode interfaces, the treatment of voltage is particularly inconsistent in the literature
- Cross-SEI-film electric fields and contact potentials are mostly missing





Recommendations about anode interfaces to theorists

- Always report electronic voltage μ_e (only relevant for *interfaces*)
- Acknowledge possibility of DFT overpotential (often unintentional)
- Electric field across SEI layers, contact potentials cannot be ignored
- E.g., don't assume |Li| vacuum | SEI | is the same as |Li | SEI |



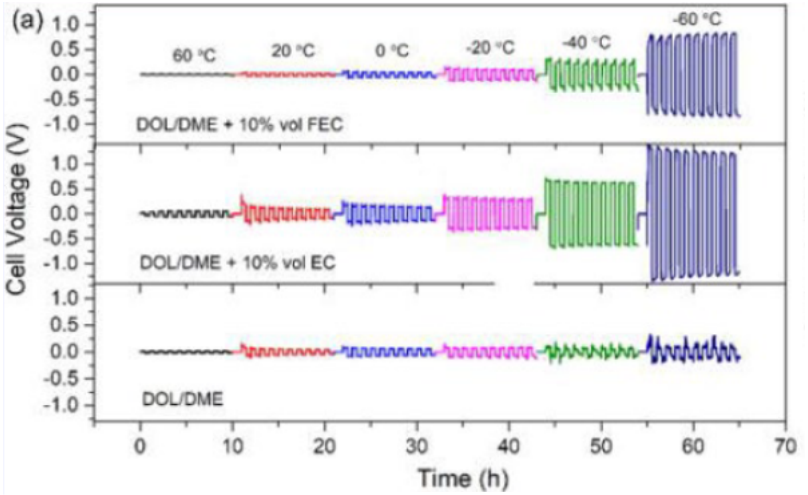
μ_e = 1.65 V μ_e = 0.01 V

DFT modelling of explicit solid–solid interfaces in batteries: methods and challenges

Kevin Leung *Phys. Chem. Chem. Phys.*, 2020, **22**, 10412–10425

- Report key approximations used

- Need experimental potential μ_e as input
- μ_e is a DFT constraint, not a DFT prediction
- T=0 K DFT cannot possibly predict whether there is overpotential, which depends on T!



Efficient Low-Temperature Cycling of Lithium Metal Anodes by Tailoring the Solid-Electrolyte Interphase *ACS Energy Lett.* 2020, 5, 2411–2420

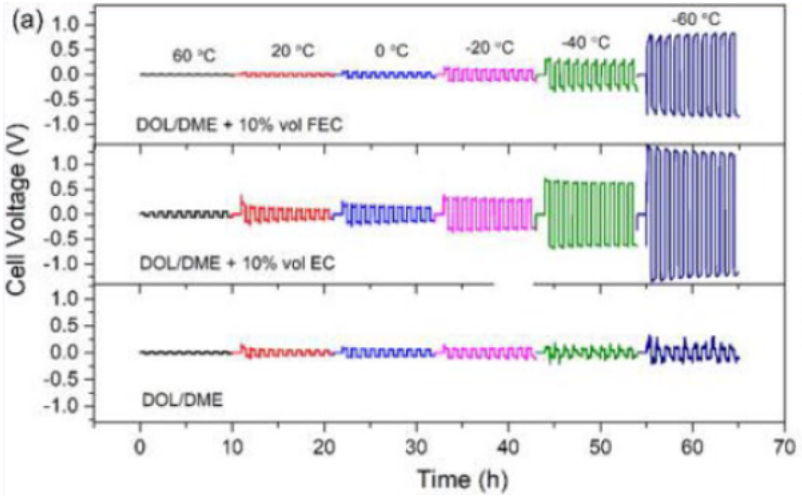
Akila C. Thenuwara, Pralav P. Shetty, Neha Kondekar, Stephanie E. Sandoval, Kelsey Cavallaro, Richard May, Chi-Ta Yang, Lauren E. Marbella, Yue Qi, and Matthew T. McDowell*

(If you don't believe me there is a problem, read this paper, which has at least 3 issues I raised, starting with the title)

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

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

- Electronic voltage is an input, not output
- Cannot assume DFT cell is not at overpotential
- Contact potential, "dirty" electrode interfaces important



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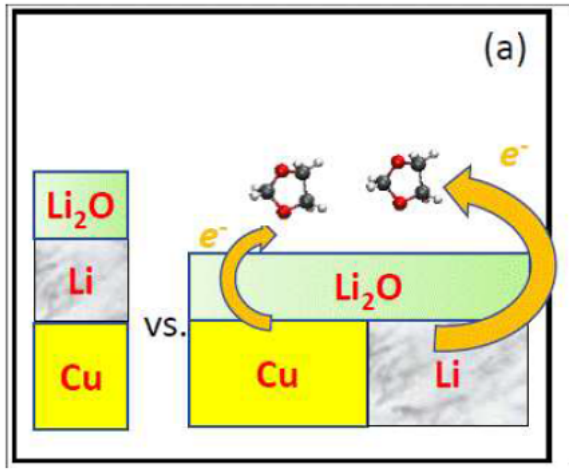
- Experimentalists can help by insisting on knowing the overpotential DFT theorists calculate at anode *interfaces*

Conclusions about Li|Cu Galvanic Corrosion

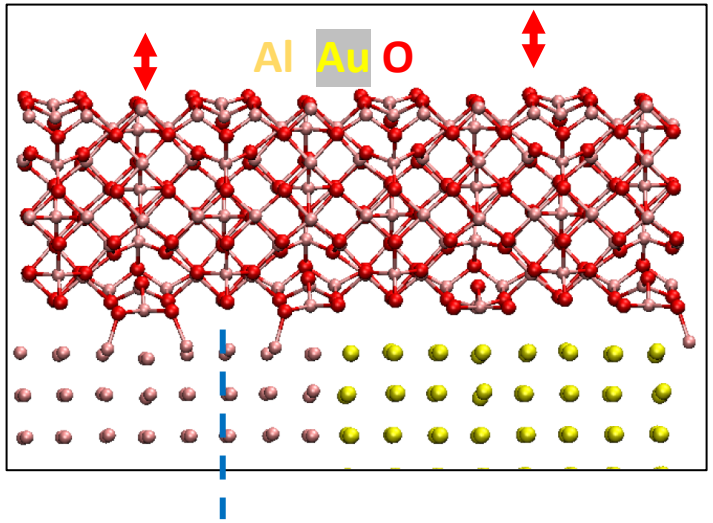
- 100% coverage of Li over Cu – no galvanic effects (agree with Winger group, Merrill and Harrison group)
- No measured overpotential at least at early times
- At 0 V vs. $Li^+/Li(s)$, Li side is actually anode, forms thicker SEI agree with Nat. Chem.)
- Cu side is cathode, Li^+ may dissolve near Li|Cu junction
- Somewhat “anti-galvanic”

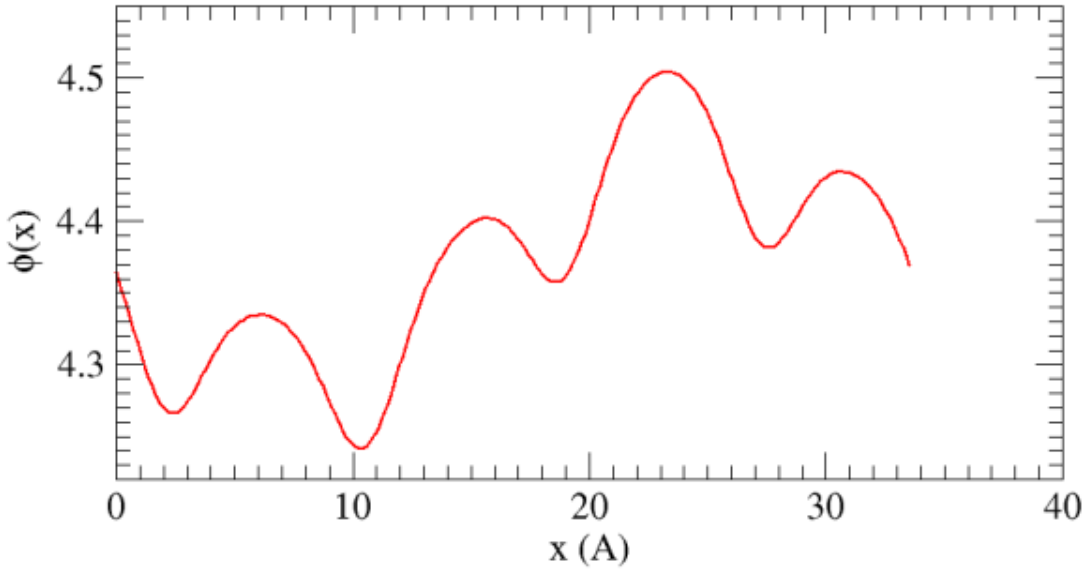


- These analyses can only be made with proper voltage definition (ϕ_e), acknowledgement of DFT overpotential
- Also show that other (non-Li_2O) surface films e.g., $LiAlO_2$, needs explicit cross-film electric field to achieve ϕ_e= 0 V
- Inherent electric field may mean asymmetry in Li-plating and stripping
- LiH is surprisingly kinetically stable in the SEI …

Backup slides

Preliminary DFT models and results for galvanic Al|Au couple



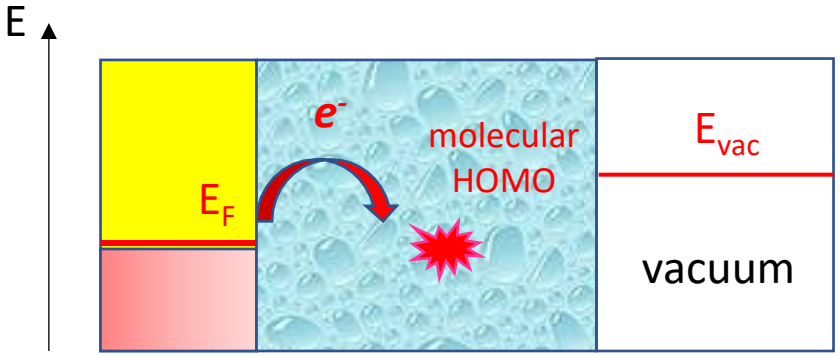


Local potential more ambiguous, but overall Al side remains at higher potential than Al-plating

In other words, coated Al is “Oxide 1”-like model, still galvanic

DFT is ground state (one Fermi level, E_F). Electrochemistry (>=2 electrodes) inherent isn't.

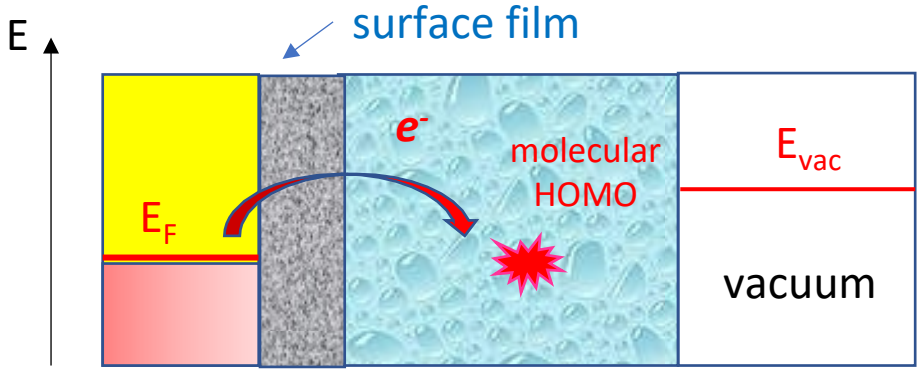
Needs lots of tricks to deal with this. Usually half-cell reactions, with a vacuum as reference electrode



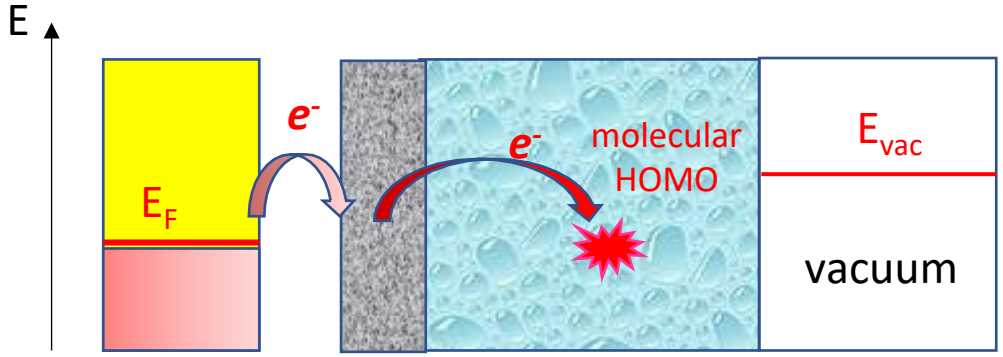
Pristine electrode (mostly Au)

E_{vac} - E_F gives us the absolute voltage via "Trassati relation"

Caveats. 1. Trassati should be modified for non-aqueous solvents
2. liquid elecrolytes have universal vacuum interfaces. solid electrolytes have facet dependence. No one has solved this issue.



Non-pristine electrode (already hard to do with DFT)
We do this, as do some battery modeling groups



Experimental interpretation – often assumes surface oxide is semiconductor-like, with defect levels that pin the Fermi level, ignores the metal