CTURE INTERFACE SCIENCE

ctional Theory Modeling of Battery Interfaces at Equilibrium and at Overpotentials

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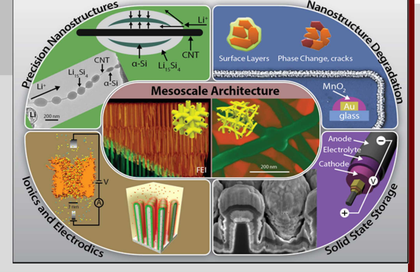

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NANOSTRUCTURES for ELECTR

DOE Energy Frontier R

RESEARCH

Use DFT calculations t
gradient at electrode/e

SCIENCE QU

1. What is the potential landsc
electrolyte interface?
2. What do the time scales for
transfer processes look like
3. What are the chemical and
reactions at all-solid electro

SU contribution

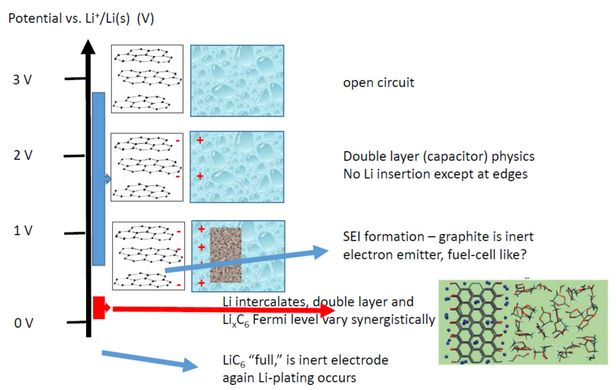
ATIONS & SYNERGY

Leung's Perspectives (hopefully not too pedantic!)

1. Most DFT battery calculations with interfaces in simulation cells are out of electrochemical equilibrium (i.e., are at some overpotential) conditions unless care is taken!
2. Need to take that "care" – otherwise, hard to compare with measurements (e.g., KPFM voltage drop at interface) if DFT calculation has confusion about voltage conditions
3. By "non-equilibrium" I mean the electronic voltage, $\mathcal{V}_e$, does not match ionic voltage, $\mathcal{V}_i$

Two Definitions of Voltages: $\mathcal{V}_e$ and $\mathcal{V}_i$

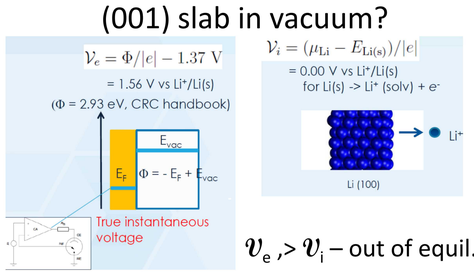
- Unlike other devices, battery electrodes can emit e^- & insert Li atoms – hence 2 "voltages"
- $\mathcal{V}_i$ is familiar to battery theorists: $\mathcal{V}_i = -\frac{\mu_{Li}^{cathode}(x) - \mu_{Li}^{anode}}{zF}$; at interfaces , doesn't govern $\mathcal{V}_e$!
- $\mathcal{V}_e$ is "true" or instantaneous voltage reported in fuel cell/supercapacitor modeling work
  - -- within DFT, most readily calculated via $\mathcal{V}_e$ = (absolute work function) – 4.44 V (vs. S.H.E)
    [S. Trasatti, Pure & Appl. Chem. 58:959 (1986) – cited 700+ times, has a Wikipedia page!]
  - -- seldom reported in battery DFT work because of historical reasons
    -> most battery DFT modeling work are single phase, no interface in simulation cell
    -> without interfaces, absolute electrostatic potential and work functions not well defined
    [de Leeuw, Perram, Smith Proc. Royal Soc. London 373: 27 (1980)]
  - -- but in DFT cells with interfaces, can calculate $\mathcal{V}_e$ via Trasatti relation (-1.37 V vs. $Li^+/Li(s)$)
  - -- critical for NEES3 goal of elucidating spatial voltage profile during charge/discharge
  - -- e.g., graphite anode charging in liquid electrolyte: only red region can be at "equilibrium" ($\mathcal{V}_e = \mathcal{V}_i$)
  - -- blue region governed by EDL (electric double layer) physics
  - -- long-range electron transfer also relevant ("fuel cell"-like)



Leung & Teneny, J. Phys. Chem. C 117:24224 (2013);
Leung, Phys. Chem. Chem. Phys. 17, 1637 (2015)
Leung & Leenheer, J. Phys. Chem. C 119:10234 (2015)

For use of Trasatti relation, see also:
Arais group jDFT (PRB 86, 075140 (2012)
Otani group PR Mater. 2, 095801 (2018)
Rossmeisl group, Sur. Sci. 631: 2 (2015)

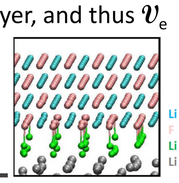
Quiz: what is "voltage" of lithium (001) slab in vacuum?



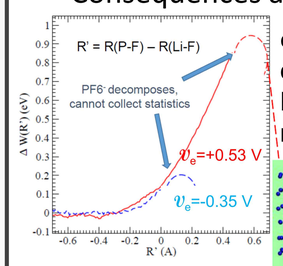
$\mathcal{V}_e$,> $\mathcal{V}_i$ – out of equil.!

- experimentally, equil. takes minutes (GITT)
- DFT – time scale much shorter, expect overpotentials unless interface is adjusted to give correct double layer, and thus $\mathcal{V}_e$
- e.g., coating Li with LiF decreases $\mathcal{V}_e$ by ~2 V!

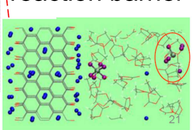
[J. Phys. Chem. C 121:20188 (2017)]



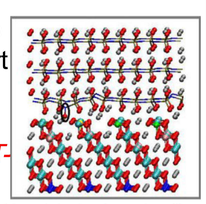
Consequences and Outlook



e.g., $\mathcal{V}_e$ drastically changes parasitic PF_6^- breakdown reaction barrier



- DFT study of voltage effect on Li^+ transport & degradation in all-solid-state battery in its infancy, need *DFT-grand canonical Monte Carlo*



Kinetics-Controlled Degradation Reactions at Crystalline LiPON/Li_2CoO_2 and Crystalline LiPON/Li-Metal Interfaces
Kevin Leung,[a,b] Alexander J. Pearse,[b,c] A. Alec Talin,[c] Elliot J. Fuller,[c] Gary W. Rubloff,[b,c] and Normand A. Modine[a]
ChemSusChem **2018**, *11*, 1956 – 1969

SIGNIFICANCE

A correct interpretation of DFT
overpotential effects, will remo
controversy in the battery mod
correct voltage control, alongsi
Microscopy (KPFM) measurem
effect of voltage gradients at el
interfaces on lithium ion transp
and parasitic reactions. This u
the lifetime and performance o

Acknowledgement

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

upported as part of the Nanostructures for Electrical Energy Storage (NEES), a Energy Frontier Research Center (EFRC) funded by the U.S. Department of Energy, Office of Science.

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