SAND2020-2713C

Determining Potentials Across Solid State Battery Systems

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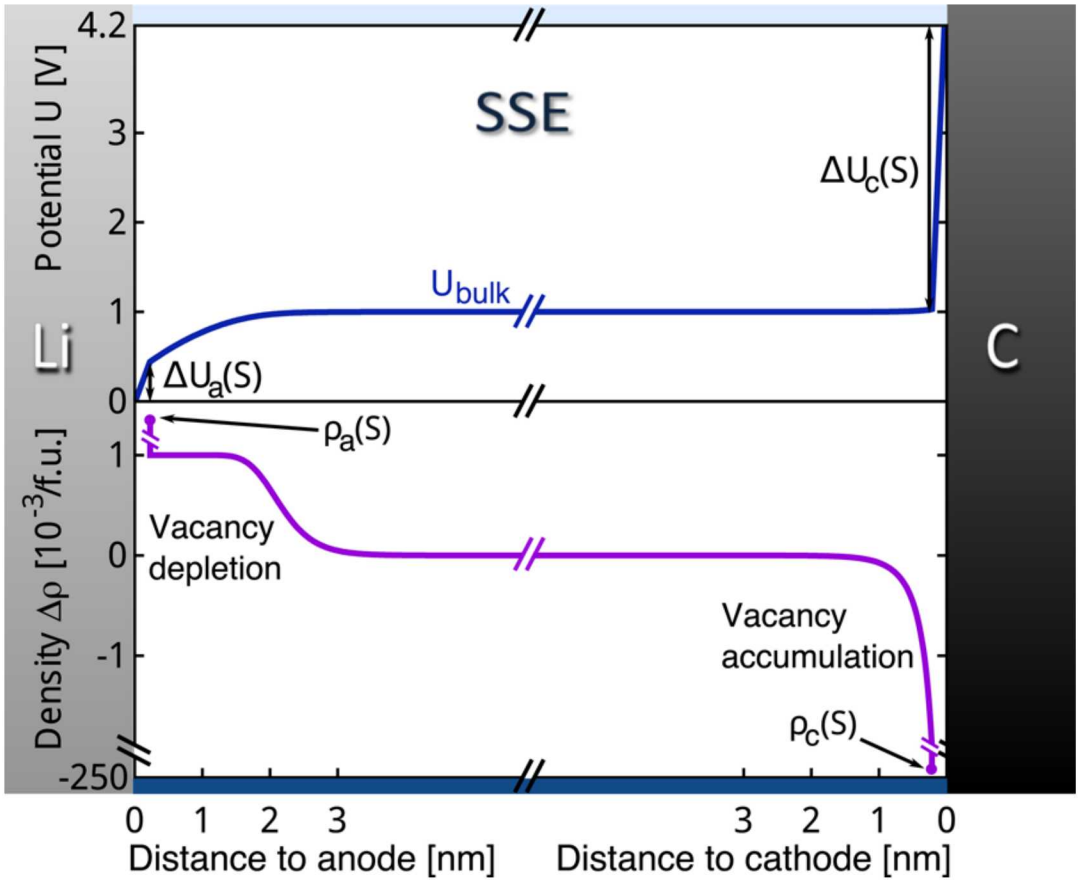
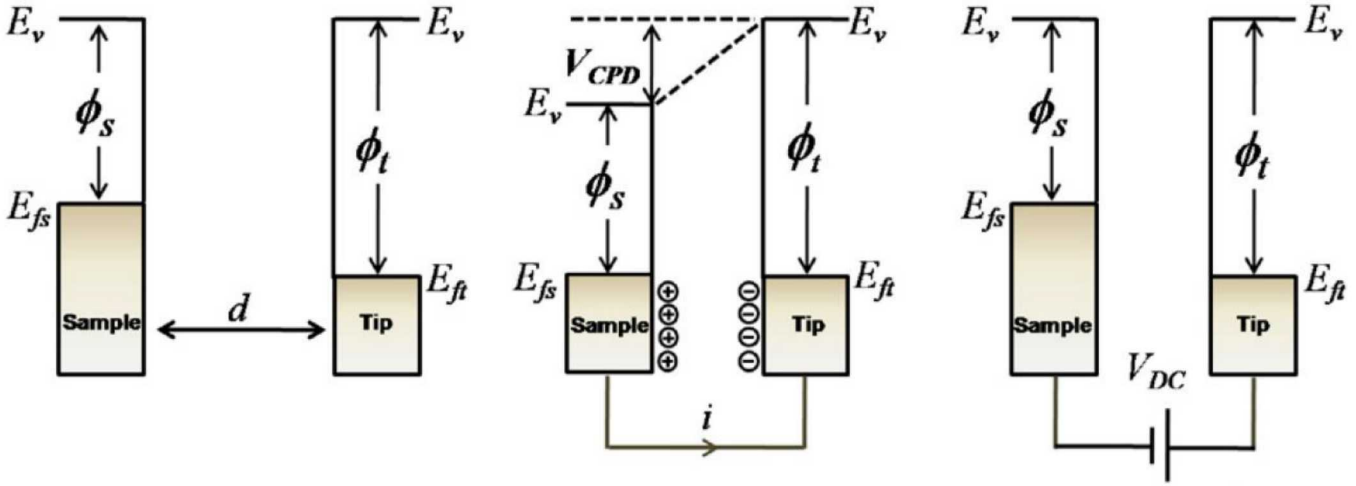
Interface potentials determine stability, performance

…but are generally unknown



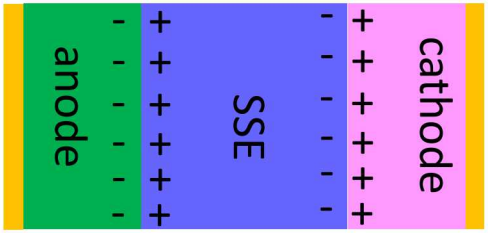
A. C. Luntz, J. Voss, K. Reuter, J. Phys. Chem. Lett. 6, 4599 (2015)

Kelvin Probe Force Microscopy

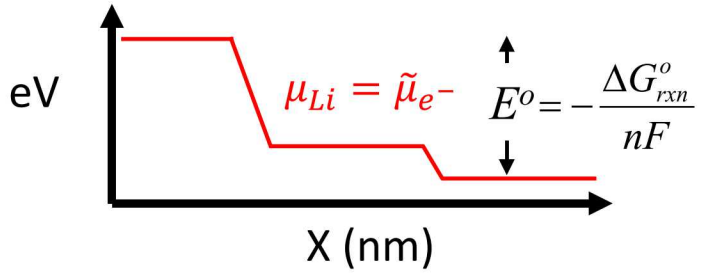


W. Melitz, J. Shena, A. C. Kummel, S. Lee Surf. Sci. Reports 66, 1, 2011

$$V_{CPD} \cong \frac{\tilde{\mu}_{e,tip} - \tilde{\mu}_{e,sample}}{-e}$$

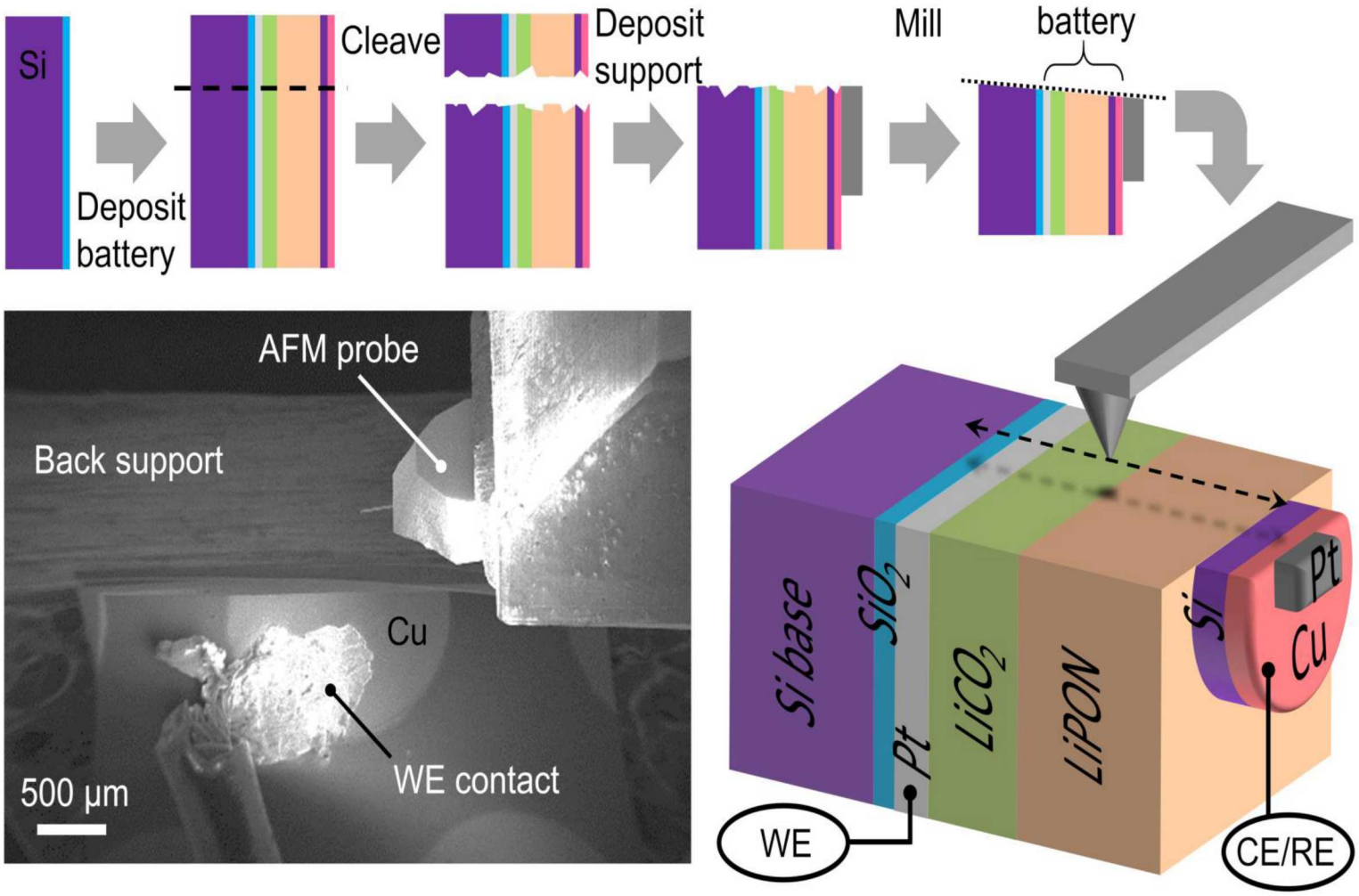


$$\tilde{\mu}_{Li} = \mu_{Li} - \tilde{\mu}_{e^-} = 0$$

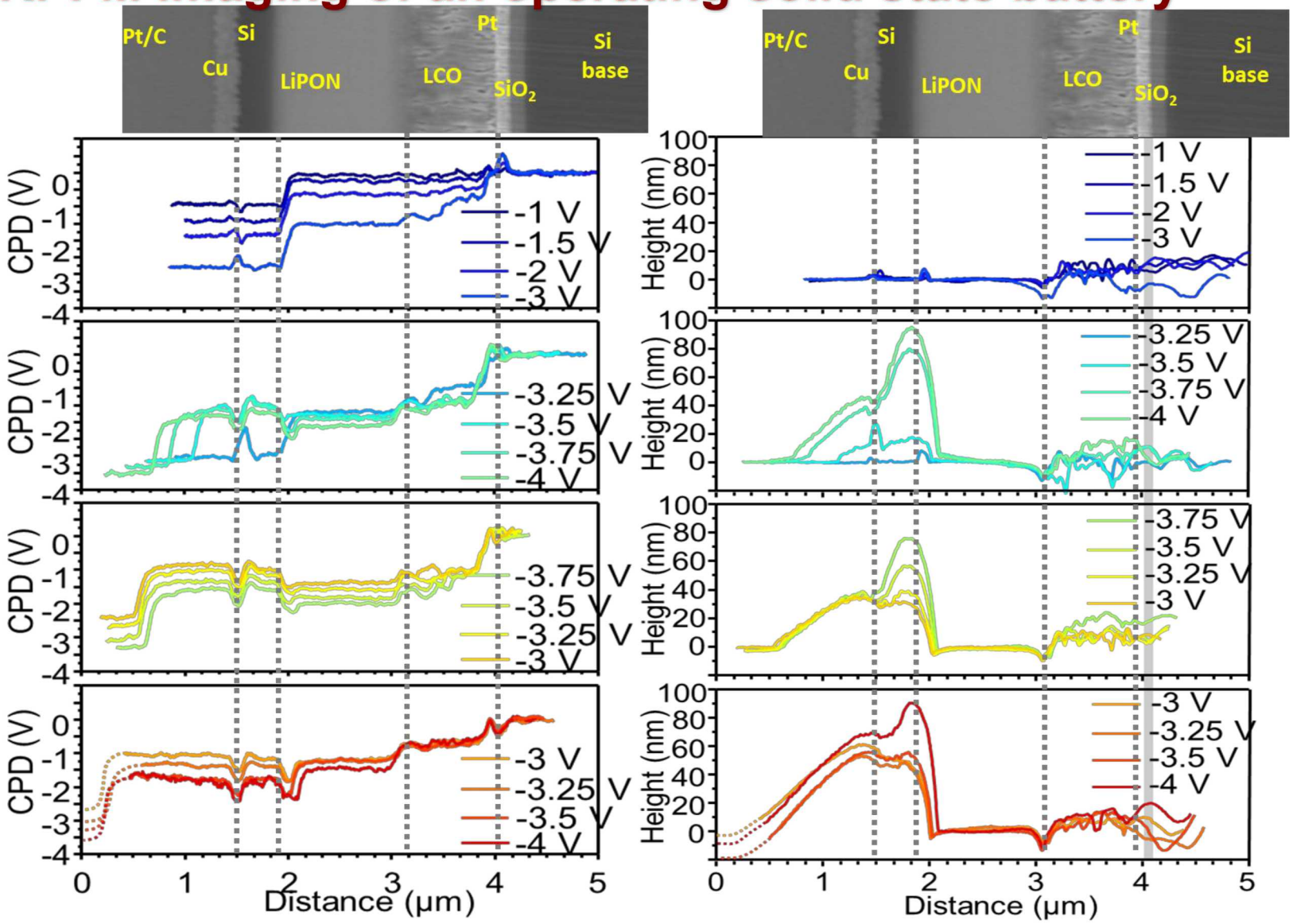


M. W. Swift, Y. Qi, Phys. Rev. Lett. 122, 167701 (2019)

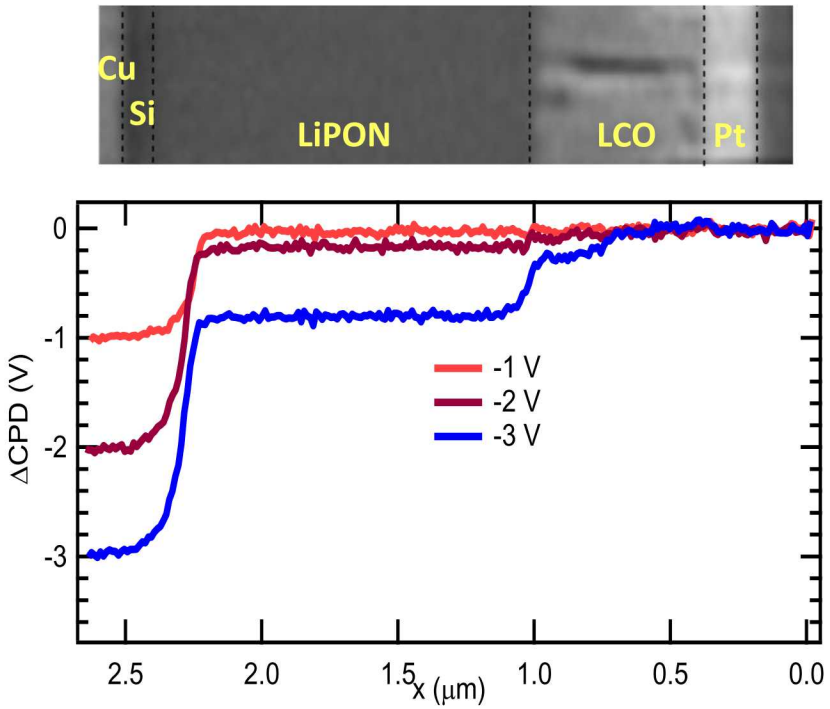
In situ cross section SSLIB to avoid contamination

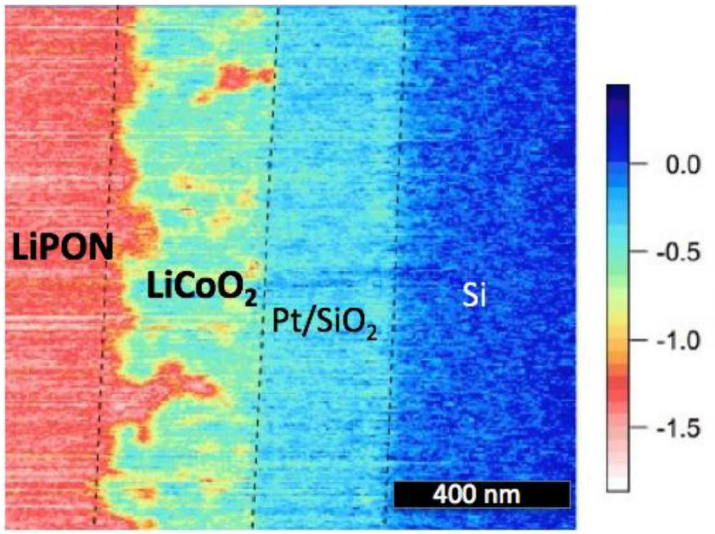


KPFM imaging of an operating solid state battery



KPFM in glovebox; LCO/LiPON interface inhomogeneous





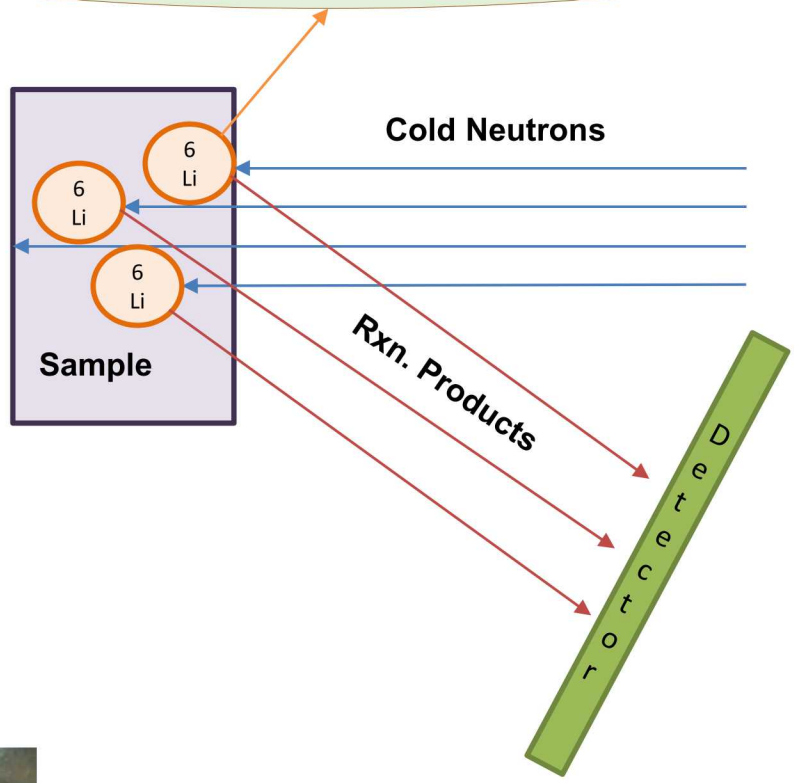
-4V

Neutron Depth Profiling (NDP)

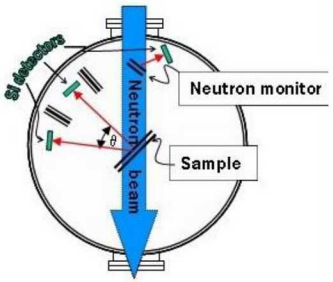
- Provides a concentration profile in the *first few* <u>*μm*</u> of solid materials
- Element and matrix sensitive
- Detects the energy spectra of prompt radiative neutron capture reactions altered by the sample
- Sensitive to ^{6}Li (can detect isotope at natural abundance levels)

^{6}Li NDP Reaction

$$^{6}Li + neutroncold \rightarrow {}^{3}H_{triton,\ 2727\ keV}\ {}_{4}He^{2+}{}_{alpha,\ 2055\ keV}$$

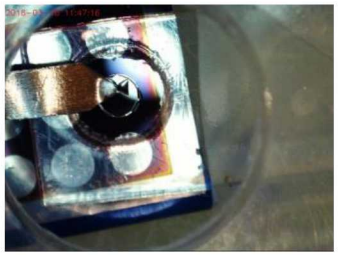


Inside of NIST NDP Chamber

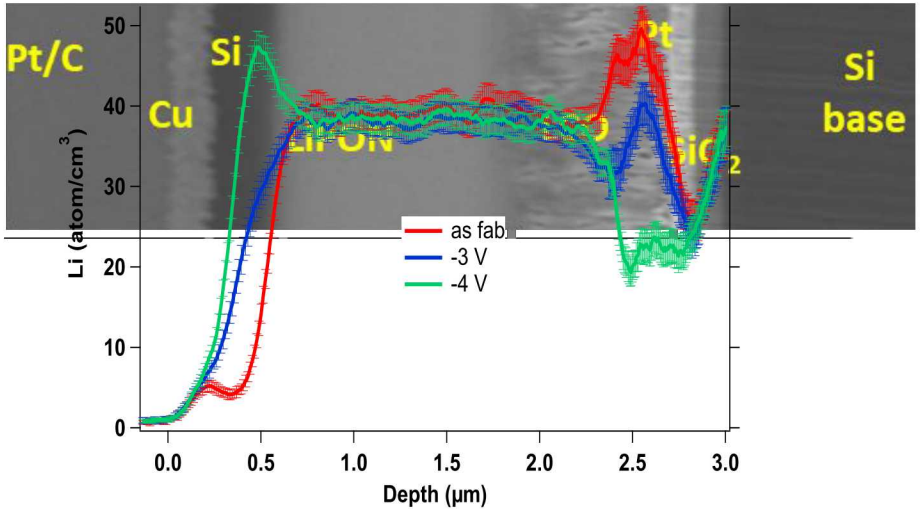


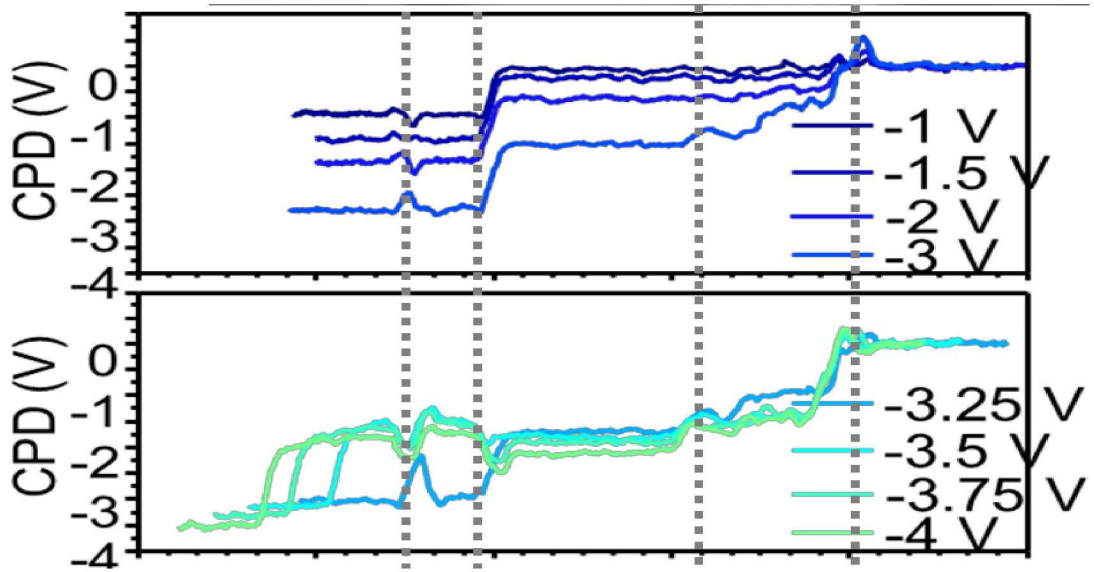
NIST NDP Chamber

In-Situ Cell



NDP [Li] consistent with KPFM μ_{Li}

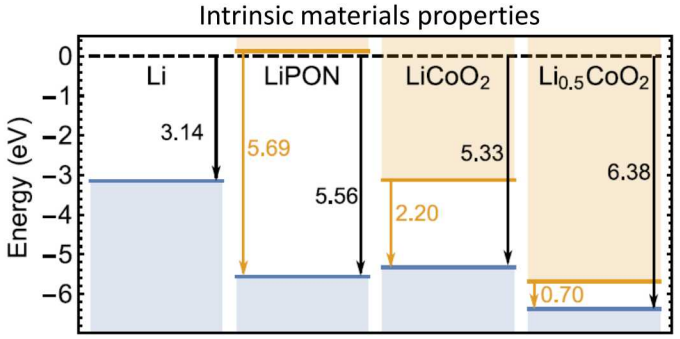


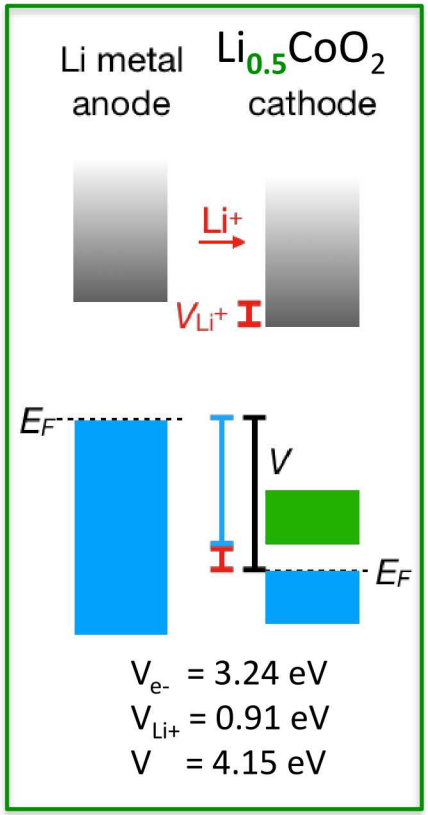


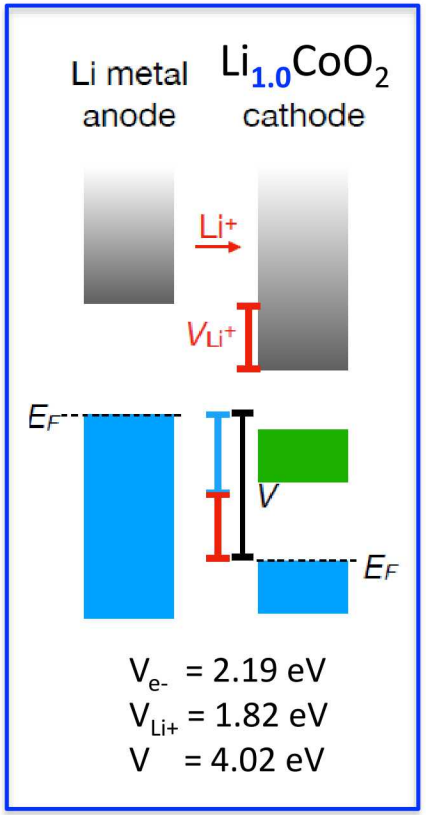
Band Alignment and Open Circuit Voltage

PI-D-1: DECIPHERING POTENTIALS ACROSS SOLID STATE BATTERY CELLS AND INTERFACES

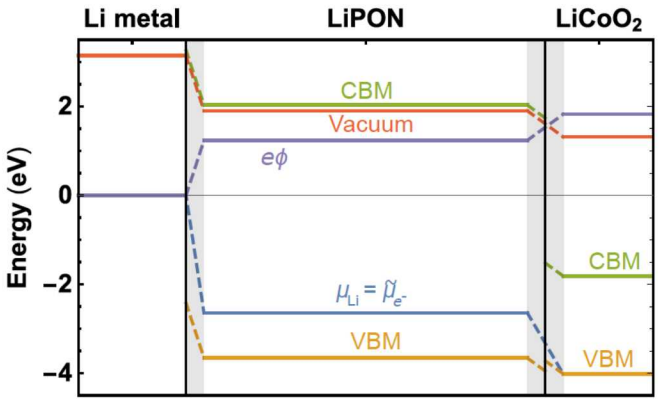
- *Ab initio* framework to calculate thermodynamic driving forces and interface potential drops at open circuit equilibrium
  - Model system Li / LiPON / Li_xCoO_2
- Open circuit voltage V from chemical potential energetics at equilibrium
  - Electronic and ionic components
  - Resulting V consistent with prior DFT and experiment
- Electronic E_F changes and drives battery operation
  - Contrary to behavior in purely electronic systems
- Calculate defect formation energies, electronic band alignments, interface energy barriers

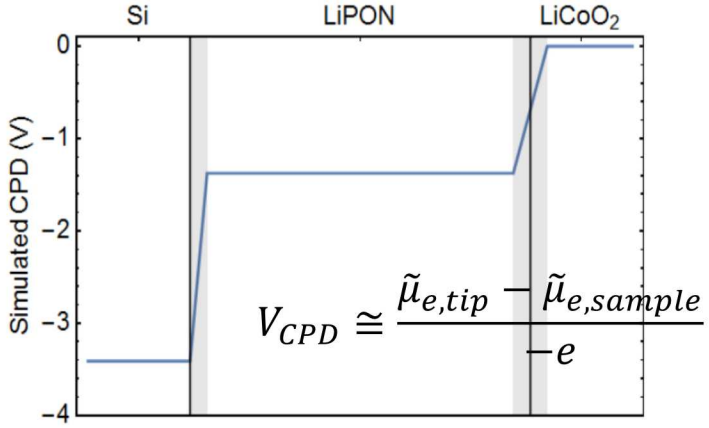


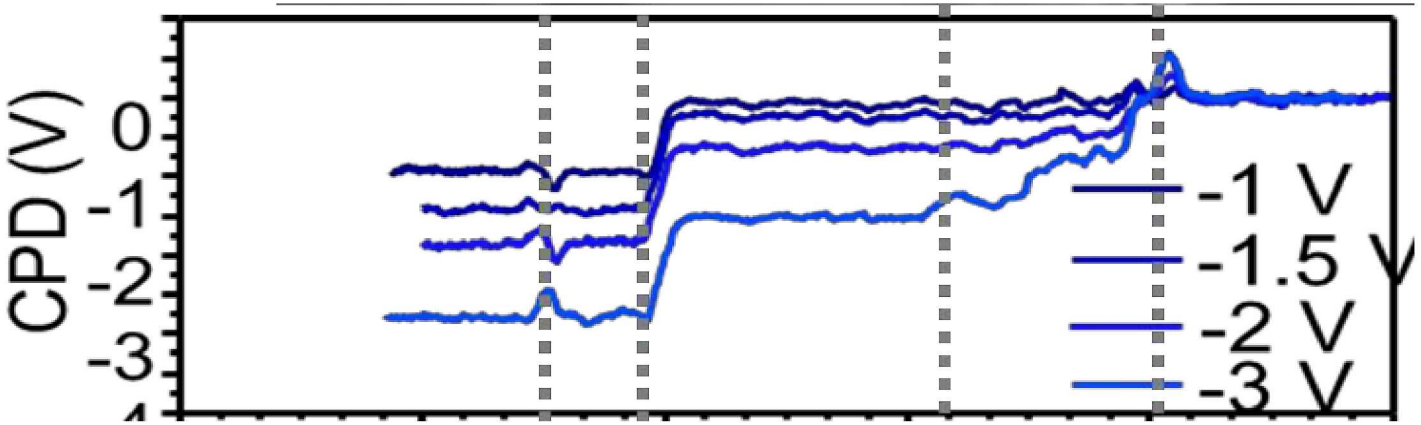




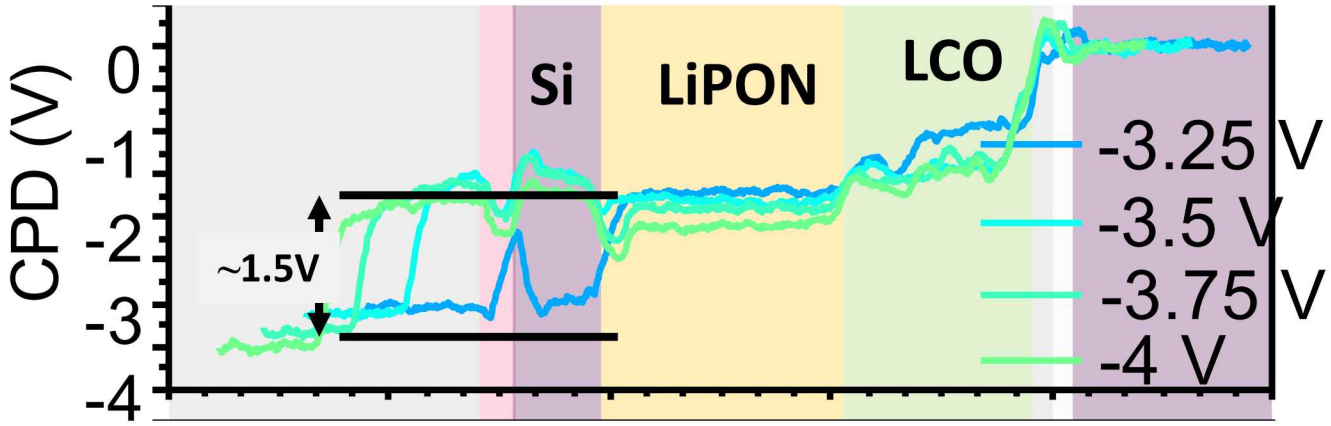
agreement between measured, calculated CPD

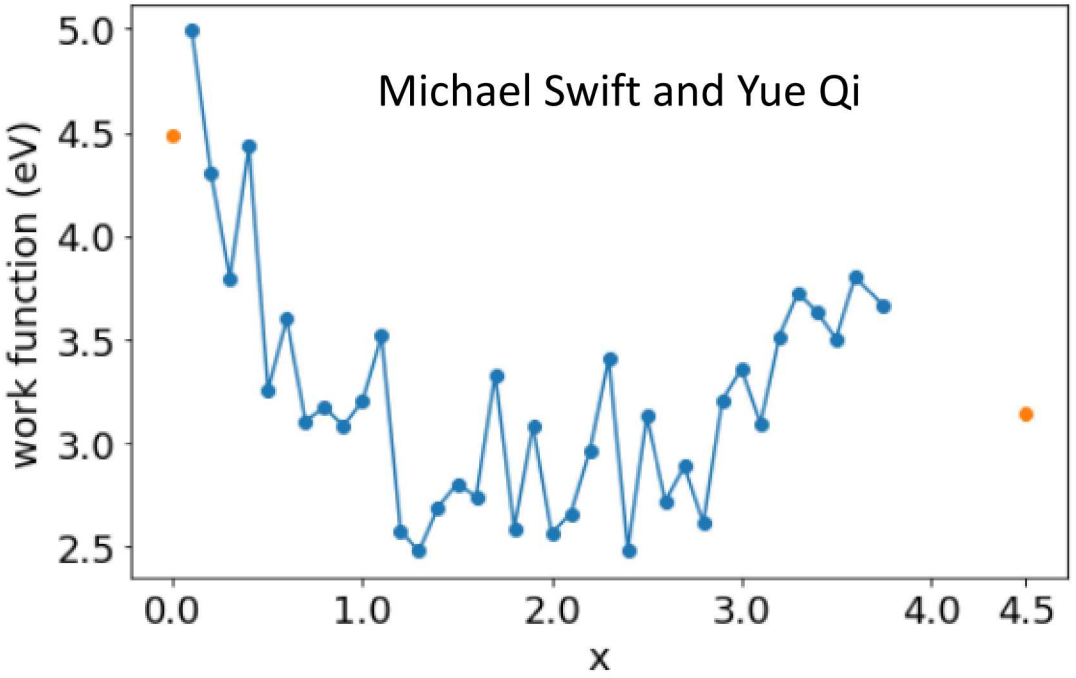






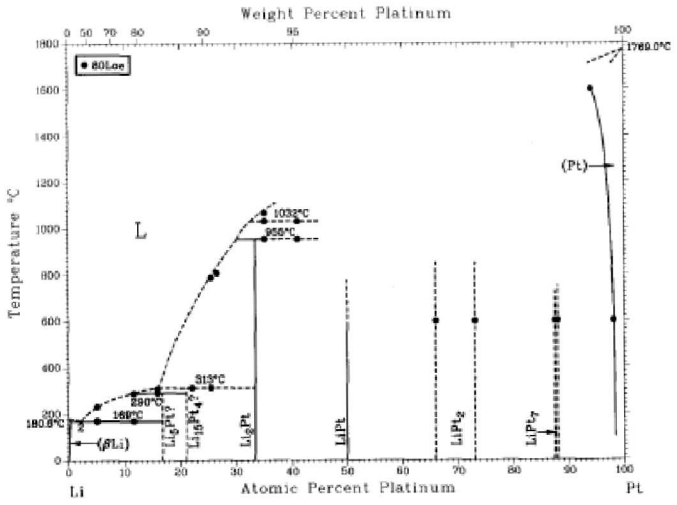
Li induced Δϕ in Si: experiment vs. model

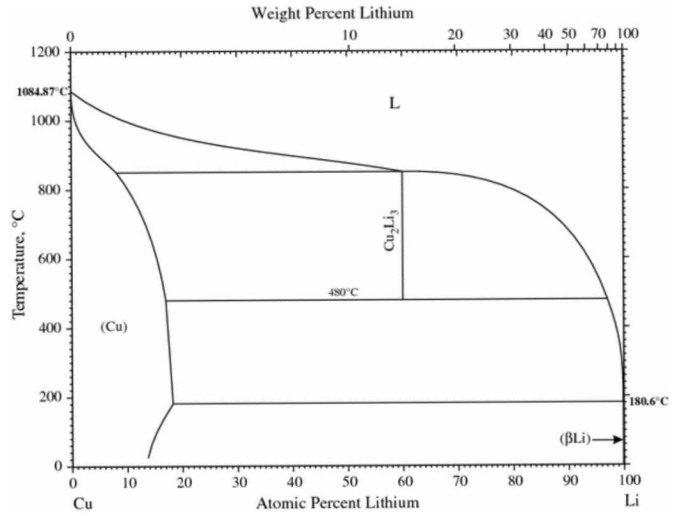




- Caution: based on single amorphous slab calculations
- Some slabs showed a band gap, may be incorrect (GGA)
- HSE work function for Si is 4.10 eV, good agreement with experiment

Li alloying with Pt, Cu explains induced Δϕ



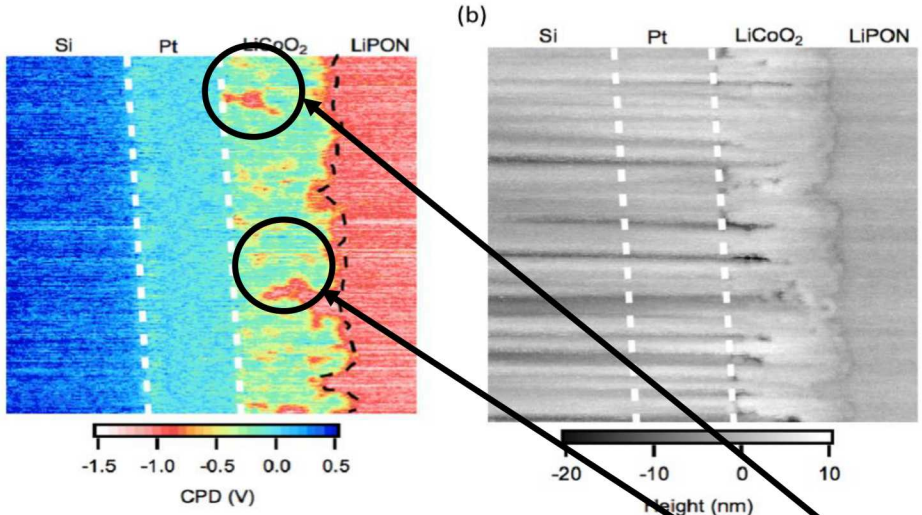


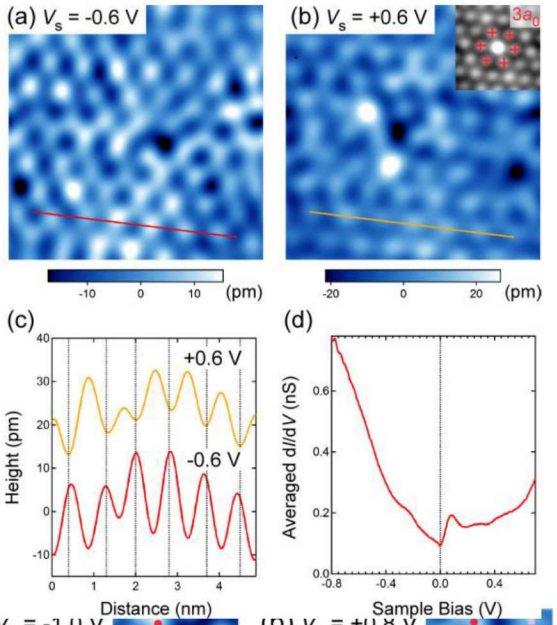
Metal	Open circuit voltage	Voltage immediately after shorting through 1 kohm	Coulombs passed through 1 kohm	Moles of Li alloy based on charge passed (theoretical)	Moles of Li in the alloy from chemical analysis	Coulombic efficiency, %*
Sn	1.99	0.605	338.0	3.49×10^{-3}	3.29×10^{-3}	94
Pb	2.45	1.006	447.0	4.64×10^{-3}	4.69×10^{-3}	101
Al	2.44	0.091	506.0	5.25×10^{-3}	4.84×10^{-3}	92
Au	2.77	0.413	249.0	2.58×10^{-3}	1.90×10^{-3}	74
Pt	2.36	0.432	228.0	2.36×10^{-3}	1.90×10^{-3}	80
Zn	2.44	0.732	119.0	1.23×10^{-3}	0.90×10^{-3}	70
Cd	2.47	1.356	94.0	9.70×10^{-4}	9.01×10^{-4}	93
Ag	3.03	0.410	73.0	7.60×10^{-4}	6.92×10^{-4}	91
Mg	1.25	0.026	43.0	4.40×10^{-4}	4.45×10^{-4}	101
Ti	2.78	0.587	2.4	2.50×10^{-5}	0.50×10^{-5}	20
ST-LF8†	2.58	0.678	2.3	2.40×10^{-5}	0.50×10^{-5}	21
ST-AF12†	2.83	0.410	2.2	2.30×10^{-5}	0.50×10^{-5}	22
Cu	2.95	0.659	1.1	1.18×10^{-5}	0.50×10^{-5}	42
Ni	2.47	0.530	0.9	1.00×10^{-5}	0.50×10^{-5}	50

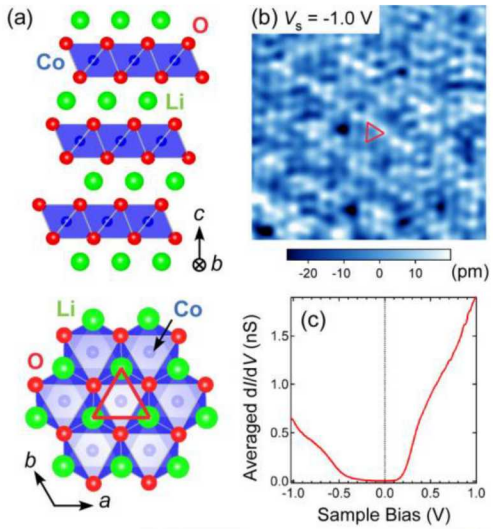
Dey, 1971, doi: 10.1149/1.2407783

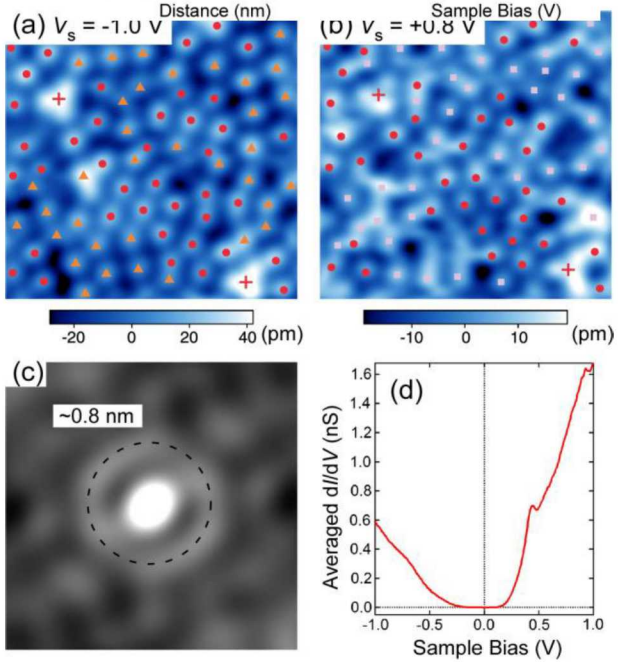
Li alloys with all metals except Mo, Nb and Ta

Origin of inhomogeneous potential at LCO/LiPON interface









Iwaya et al., PRL 111, 126104 (2013)

Summary

- KPFM CPD →map μ_{Li} ($\tilde{\mu}_{e^-}$) across thin film solid state battery
- Ignore surface contributions to CPD
- NDP [Li] consistent with KPFM CPD
- KPFM, NDP qualitative agreement with model
- Large $\Delta\,\mu_{Li}$ at LiPON/Si interface
- Inhomogeneous potential distribution at LiPON/LCO interface
- Li ordering in LCO possible origin of inhomogeneity

What does KPFM measure?

$$F_z^{el} = \frac{\partial W_{el}}{\partial z}$$

$$W_{el} = \frac{1}{2} Q \Delta V = \frac{1}{2} C \Delta V^2$$

ΔV is given by the difference in the electro-chemical potentials of electrons in both objects:

$$\Delta V = \frac{\eta_{e,s} - \eta_{e,t}}{F} = \frac{\varphi_s - F V_s - \varphi_t + F V_t}{F}$$

$$\Delta V = V_t - V_s - V_{CPD}$$

V_t and V_s are Galvani or electrostatic potentials
V_{CPD} is the effective CPD

$$V_t = V_{DCt} + V_{AC} \sin(\omega t)$$

$$F_\omega^{el} = \frac{\partial C}{\partial z} (V_{DCt} - V_{DCs} - V_{CPD}) V_{AC} \sin(\omega t)$$

$$\Delta\omega \propto \frac{\partial F_\omega^{el}}{\partial z} = \left(\frac{\partial^2 C}{\partial z^2} \underbrace{(V_{DCt} - V_{DCs} - V_{CPD})}_{=0} \right) V_{AC}$$

$$V_{DC\ tip} = V_{CPD} + V_{DC\ sample}$$

When $V_{DC\ sample} = 0$, $V_{DC\ tip} = V_{CPD}$

Connection to potential profile

- Neglecting surface terms, the CPD measures the electrons' electrochemical potential difference with the cathode current collector
- Corresponds to $-\tilde{\mu}_{e^-}$ in potential profile model
- Approximations in band alignment calculations are similar to neglecting surface terms in KPFM interpretation

$$\overline{\mu}_e = \mu_e + q_e \cdot \phi$$

$$\begin{aligned} q_e \cdot EMF &= \overline{\mu}_{Li}(CE) - \overline{\mu}_{Li}(WE) \\ &= \mu_{Li}(CE) - \mu_{Li}(WE) \end{aligned}$$

$$EMF = \frac{1}{F}\left(\Delta G^0_{Li}(CE) - \Delta G_{Li}(WE)\right)$$