# Operando Observation ~~and Detailed Chemical Modeling~~ of the Bilayer Solid Electrolyte Interphase

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# Acknowledgements


**Collaborators**

**At the NCNR:** Joseph A. Dura, Eric D. Rus, Paul Kienzle

**At Colorado School of Mines:** Christopher H. Lee (MS, 2016), Amy LeBar (MS, 2019), Center for High Performance Computing

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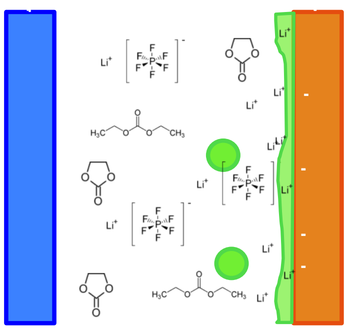
# The Solid Electrolyte Interphase (SEI)



•Because the electrolyte breaks down at the bare anode, LIBs cannot operate without a passivation layer.

-Electrolyte formulations create a passivating film from the decomposition products: <u>Solid Electrolyte Interphase (SEI).</u>

-Electrical and chemical barrier: SEI should 'self-limit.'

-Ion conductivity of SEI allows continued battery operation

•SEI: one of the prevailing technical issues in Li-ion batteries, yet few detailed chemical models exist to explain its growth mechanism.

-Lack of direct, measurements against which to validate

-Materials involved constantly evolving

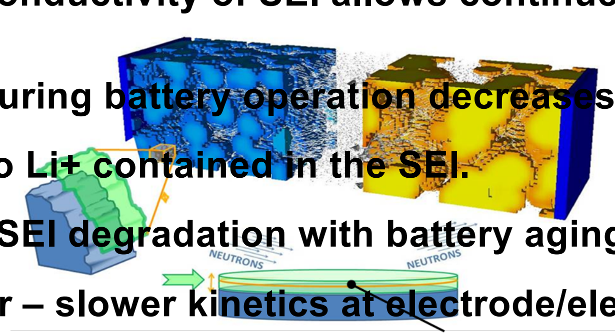
-Chemical modeling tools largely developed 'ad-hoc.'

•In reality, continued SEI growth during battery operation decreases device durability and efficiency

-Long-term capacity fade due to Li+ contained in the SEI.

-Durability and safety issues – SEI degradation with battery aging.

-Higher resistance, lower power – slower kinetics at electrode/electrolyte interface.




Reduce electrolyte on working electrode
(non intercalating) to form SEI

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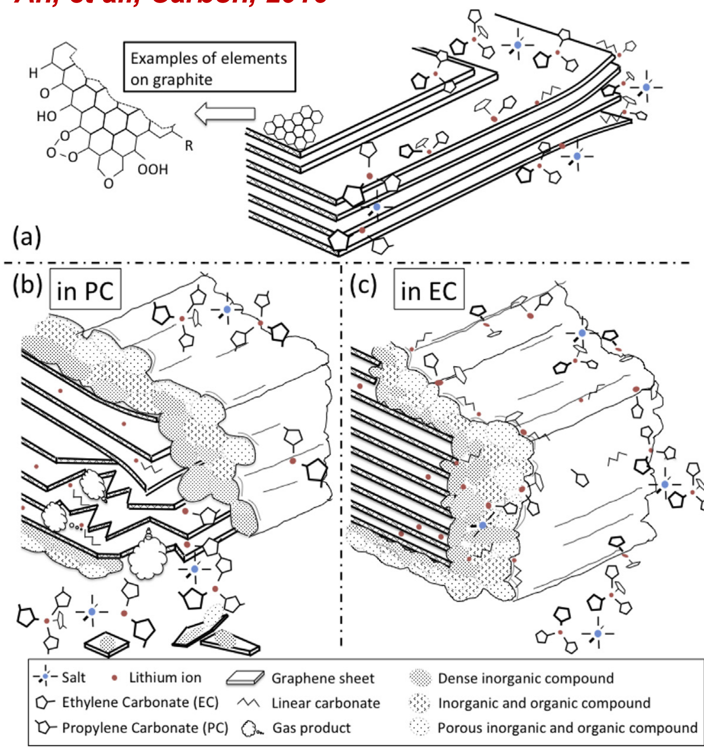
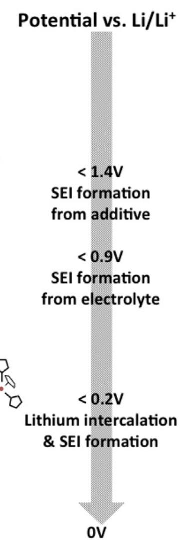
# State of SEI Understanding (1/3): Many reactions are known; few are quantified

*An, et al., Carbon, 2016*



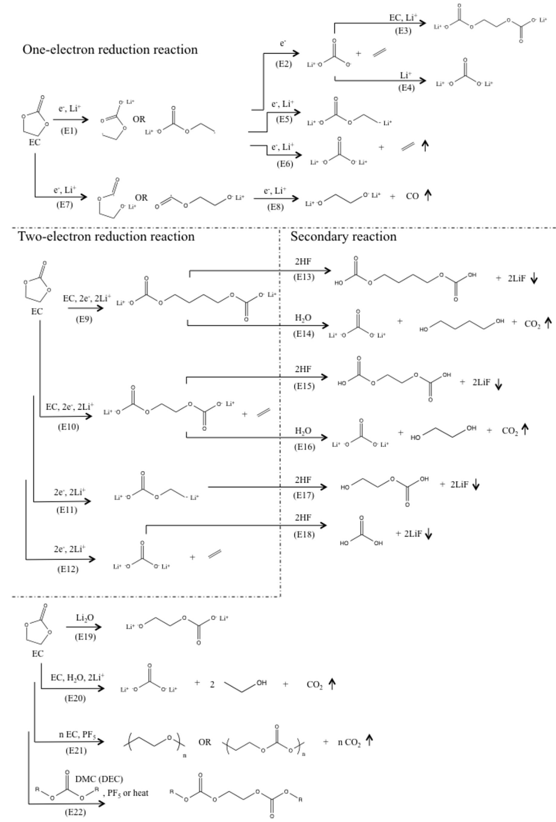




**Fig. 8.** Ethylene carbonate (EC) reduction process (reference groups in parentheses; details are shown in Table 2).

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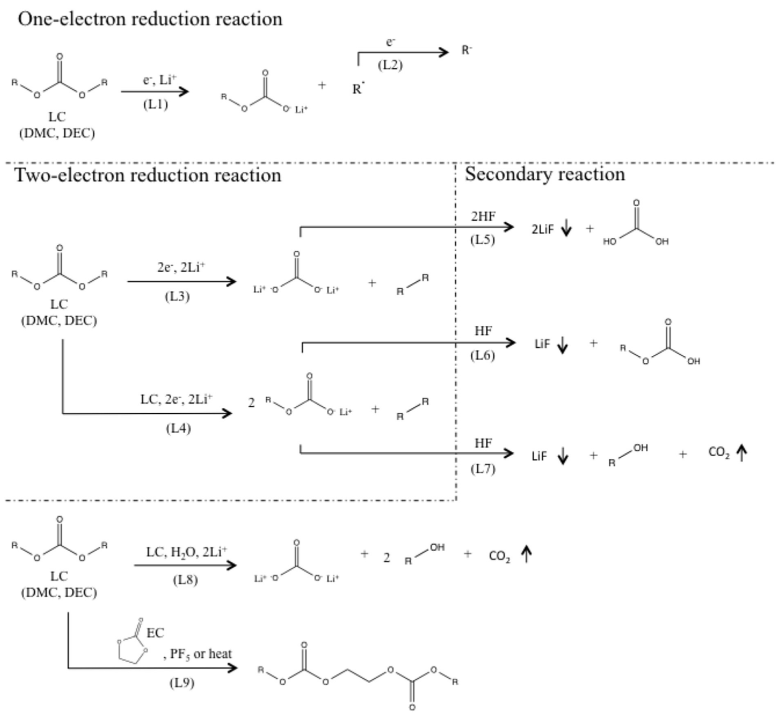
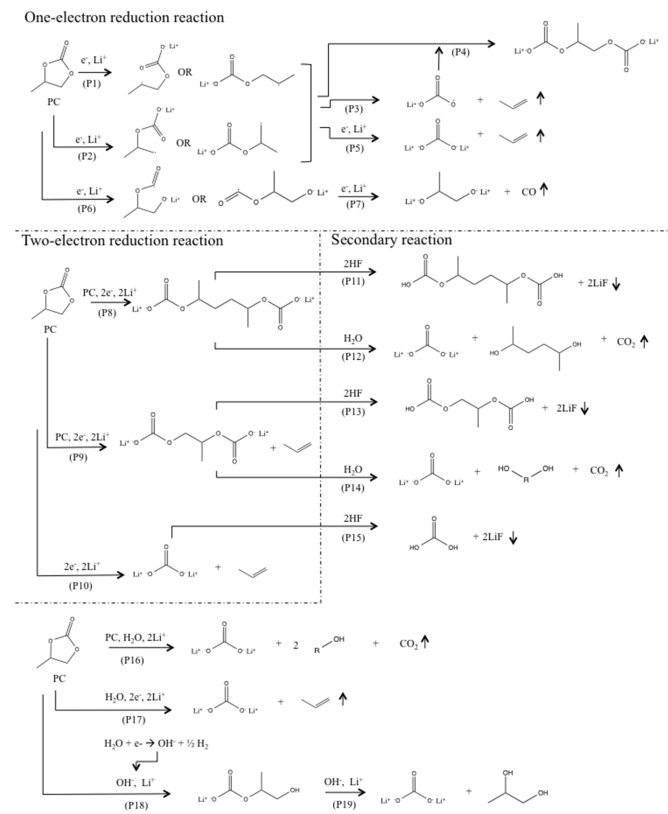
# State of SEI Understanding (2/3): Many reactions are known; few are quantified

*An, et al., Carbon, 2016*

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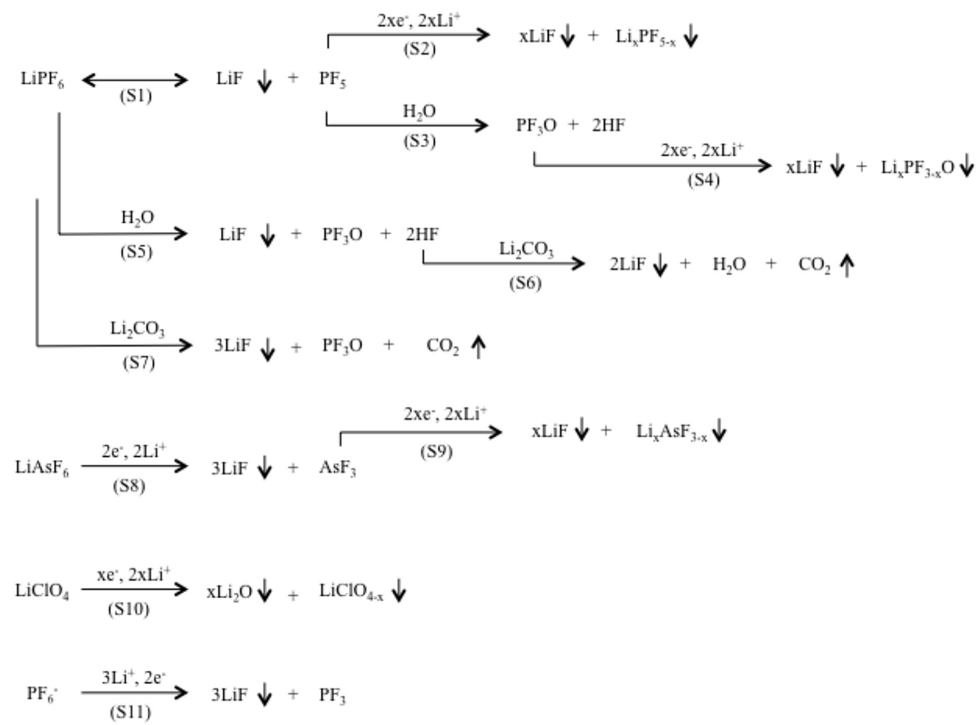
# State of SEI Understanding (3/3): Many reactions are known; few are quantified

*An, et al., Carbon, 2016*

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# There are 2 primary needs, for mechanistic understanding of SEI growth & Evolution

**Need #1: Operando validation data with high spatio-chemical resolution.**

**Need #2: Detailed electrochemical modeling tools, with flexible and robust mechanism implementation**

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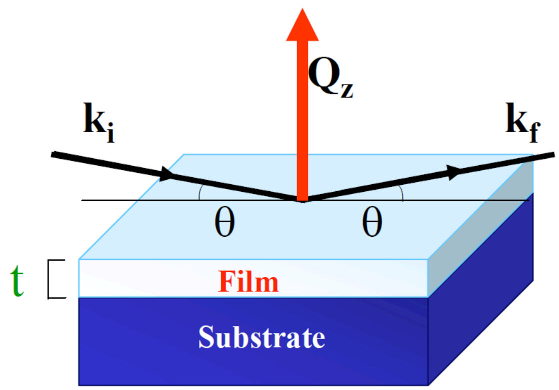
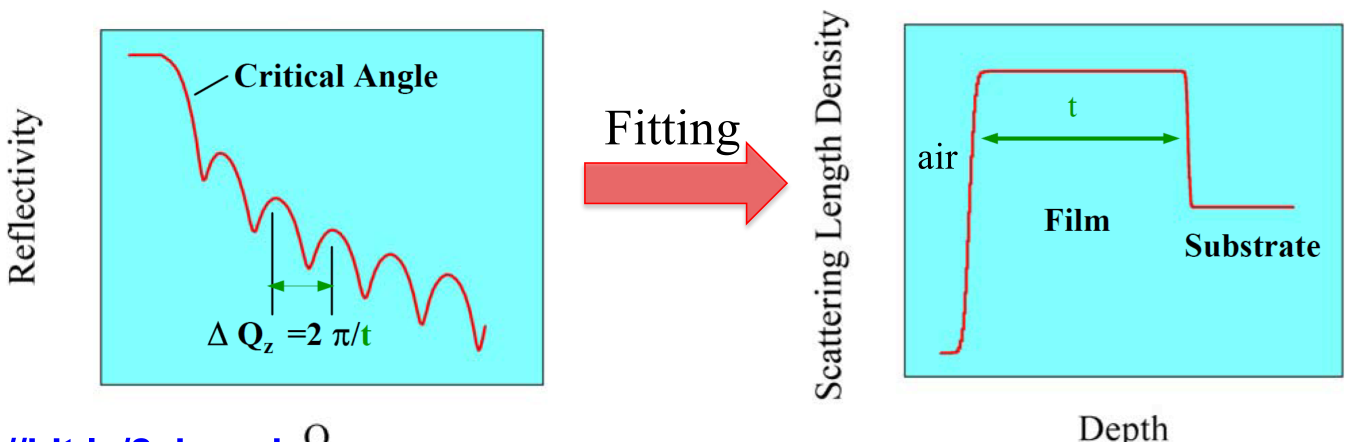
# Neutron Reflectometry Provides Sub-nm Resolution Depth Profiles




- **Measures Reflected Intensity vs. grazing angle θ**
- **Oscillations with period 2π / layer thickness**
- **NR Provides Depth Profile of the SLD**
- **SLD related to Composition:**

$$SLD(z) = \Sigma_j SLD_j\, V_j$$

$$SLD(z) = \Sigma_i b_i\, n_i$$

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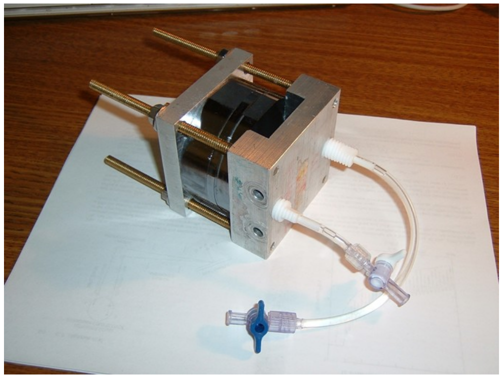
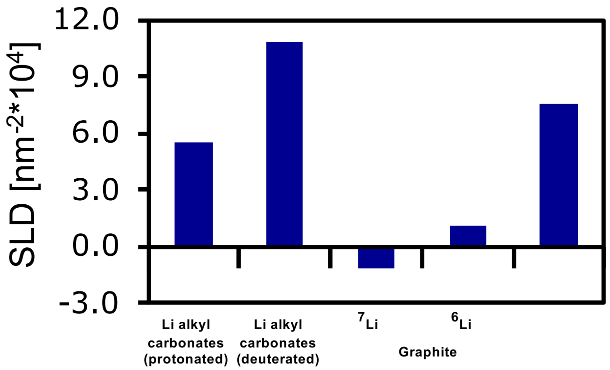
# Neutron Reflectometry: Challenges and Advantages for Electrochemical Interfaces



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NR has several inherent advantages as an *operando* probe for electrochemical systems

- Sensitive to structures with sub-Å resolution.
- Neutrons transmit through many solids with little attenuation - simplifies sample env.
- High SLD contrast for relevant isotopes.

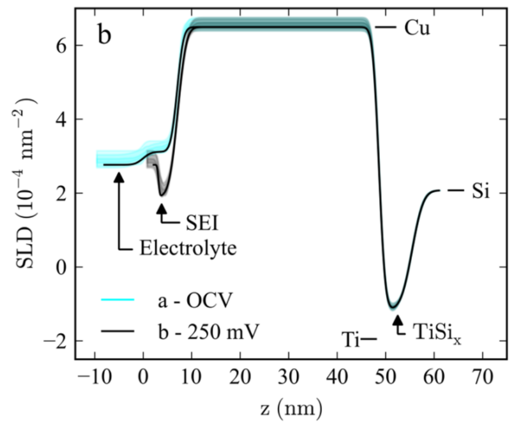
Challenges:

- Requires large, very flat (r < 20 Å) surfaces
- Long collection times (several hours) for best resolution.
- Complicated data fitting/analysis - no unique solution to a single NR spectrum.

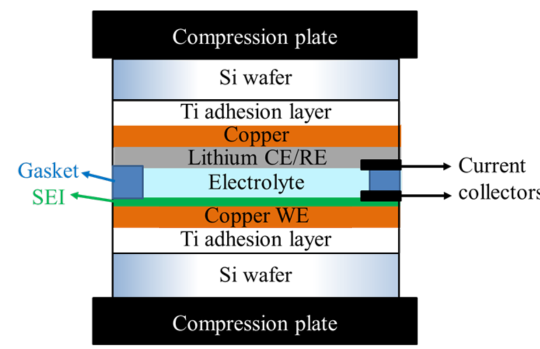
# Experiment 1: NR on Copper Reveals a thin, 4 nm Layer That is Rich in Li

**NR at OCV and 250 mV vs. Li/Li+ fit simultaneously**

- **Constrain substrate, WE parameters.**
- **NR measurements at OCV reveal an initial CuCO3 + Cu(OH)2 layer.**
- **10 initial cycles remove this layer and form an SEI that is 4.0 nm thick at 250 mV vs. Li.**




**The SEI is easily observed via NR, and is rich in Li-containing molecules (low SLD).**




***Owejan, et al., Chem. Mater., 2014***

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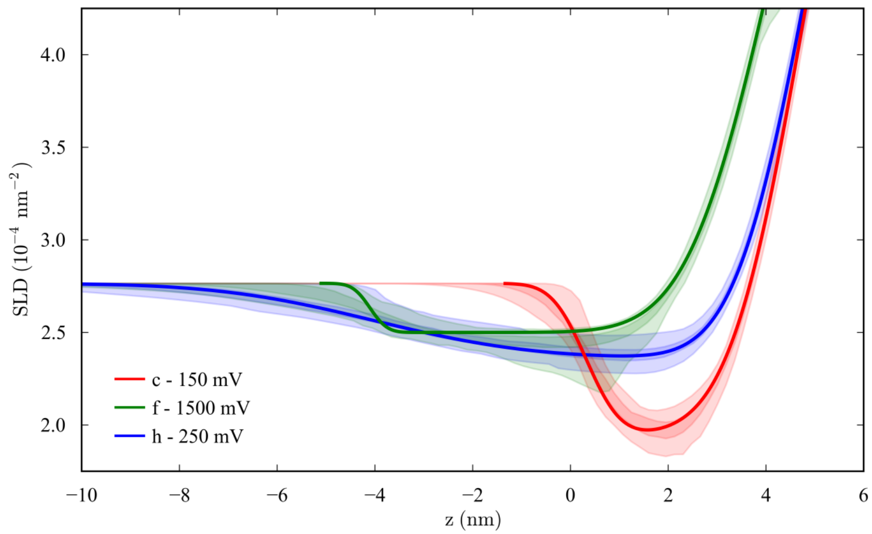
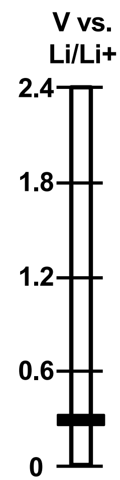
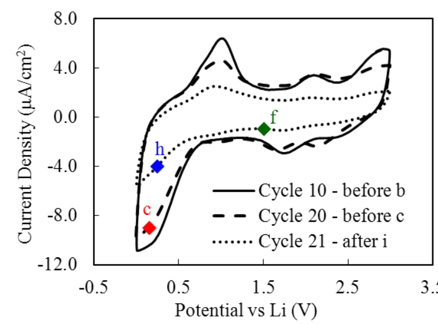
# Electrochemical cycling reveals SEI "Breathing."

**NR results during potentiostatic holds reveal changes to the SEI thickness, composition, and structure with cycling.**

- **-SLD decreases (Li increases) with decreasing WE potential.**
- **-SEI thickness continues to increase with additional processing.**
- **-Some test points show composition gradients; others show mixing.**




***Owejan, et al., Chem. Mater., 2014***

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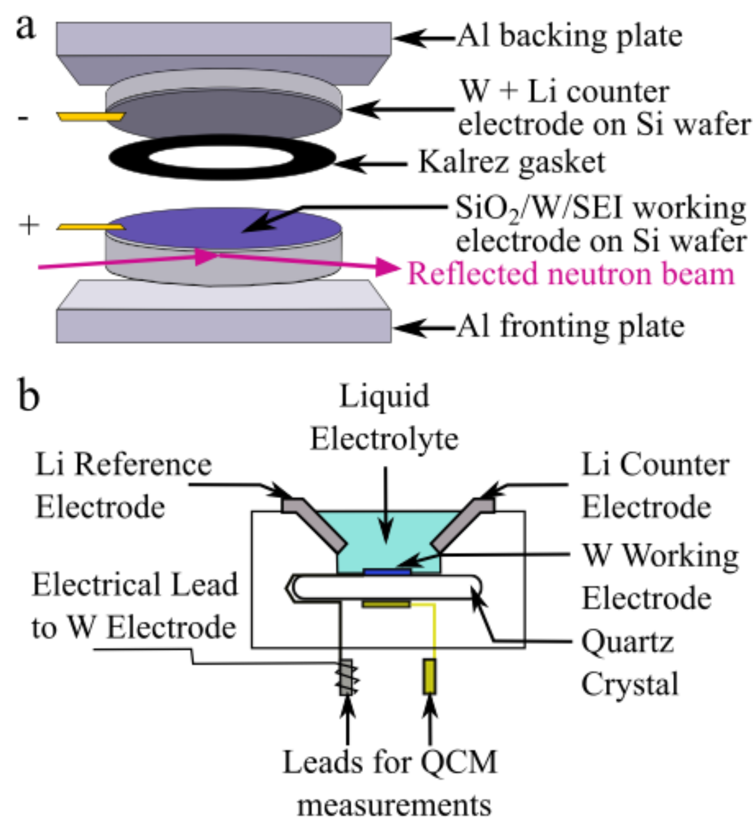
# Experiment 2: W Anode Enhances SEI Sensitivity

**NR Measurements**

- NR in He: structure w/ no SEI
- NR during hold at reducing potential (0.56 V)
- Measure in electrolyte, no electrochemistry

**Electrochemistry + QCM-D**

- Quartz crystal microbalance: highly resoved mass uptake (~2 ng/cm$^2$).
- Simultaneous cyclic voltammetry

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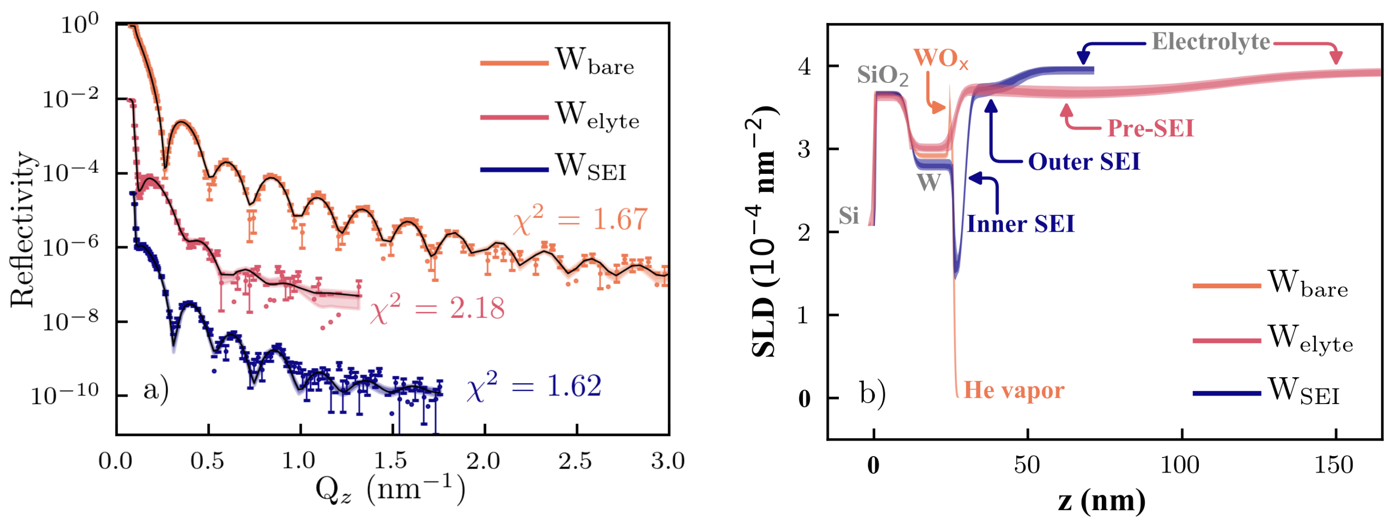
# NR Directly Observed Hypothesized Two-layer SEI

Simultaneously fit NR data in He and after SEI growth

- Constrains substrate layer parameters for greater confidence
- Can be used for element conservation.

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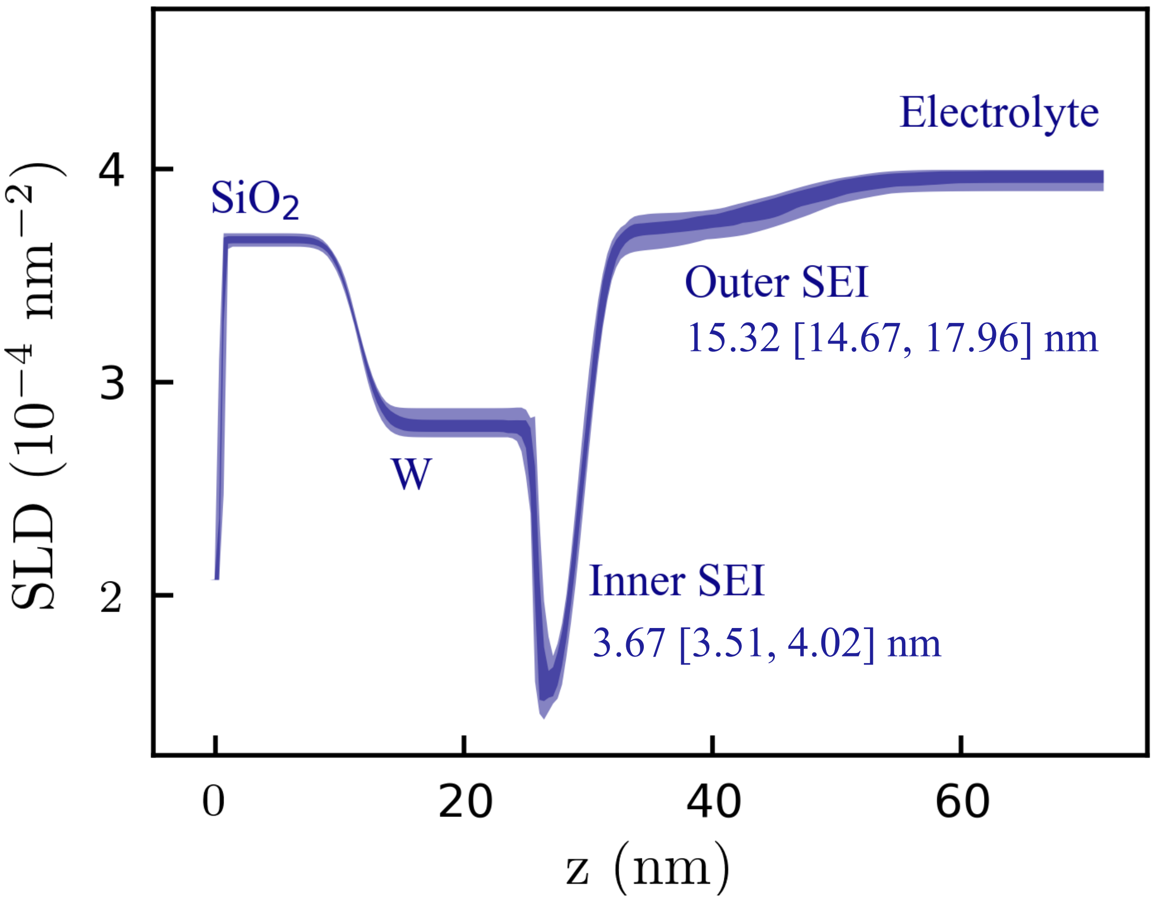
*Lee, et al., J. Power Sources., 2019*

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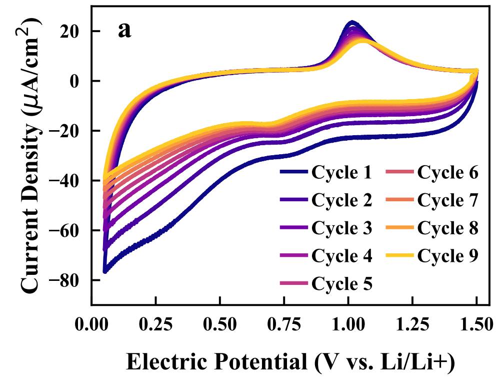
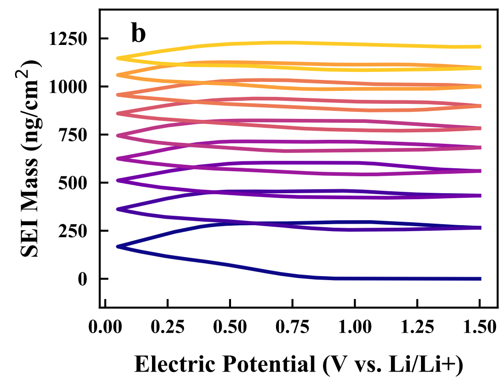
*Lee, et al., J. Power Sources., 2019*

# EQCM-D Shows Growth, Re-dissolution of SEI

- Reduction peaks at 800 mV and 275 mV, vs. $Li/Li^+$.
- Oxidation peak at 1.1 V.
- CV qualitatively similar to that on non-intercalating Cu.
- Current decreases as a function of cycle number, decrease in mass gain per cycle: passivation: SEI passivation
- Mass uptake *and* mass loss during each cycle: SEI breathing




*Lee, et al., J. Power Sources., 2019*

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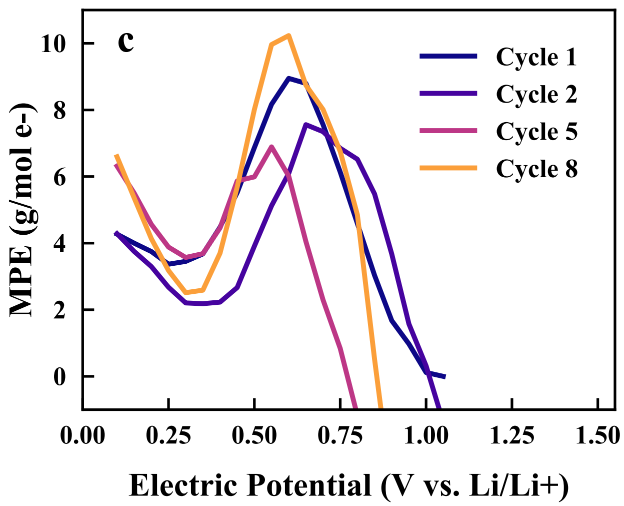
# Mass Per Electron (MPE) Elucidates SEI Chemical Evolution with Cycling

- **Two main processes**
  - **750 mV: higher MPE**
  - **Below 300 mV: lower MPE**
- **Large “extraneous current” prevents quantitative species ID.**

$$m.p.e = \frac{F\Delta m}{\Delta Q}$$




| Compound | m.p.e (g/mol $e^-$) |
|---|---|
| Li | 7 |
| $Li_2O$ | 15 |
| $LiO_2$ | 19 |
| LiOH | 24 |
| LiF | 26 |
| $Li_2CO_3$ | 37 |
| $(CH_2OCO_2Li)_2$ | 81 |

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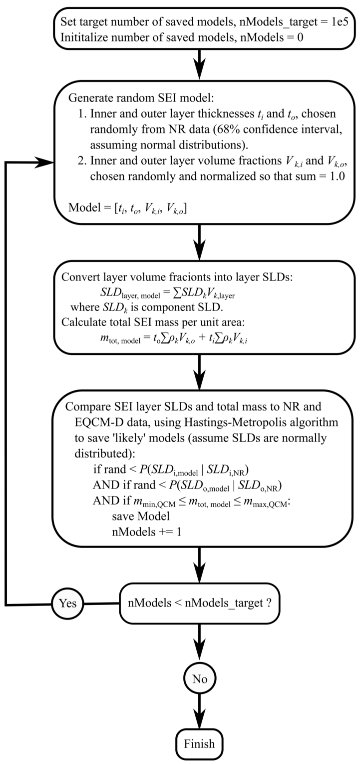
*Lee, et al., J. Power Sources, 2019*

# Monte Carlo Simulations ID Chemical Compositions Consistent with the Data



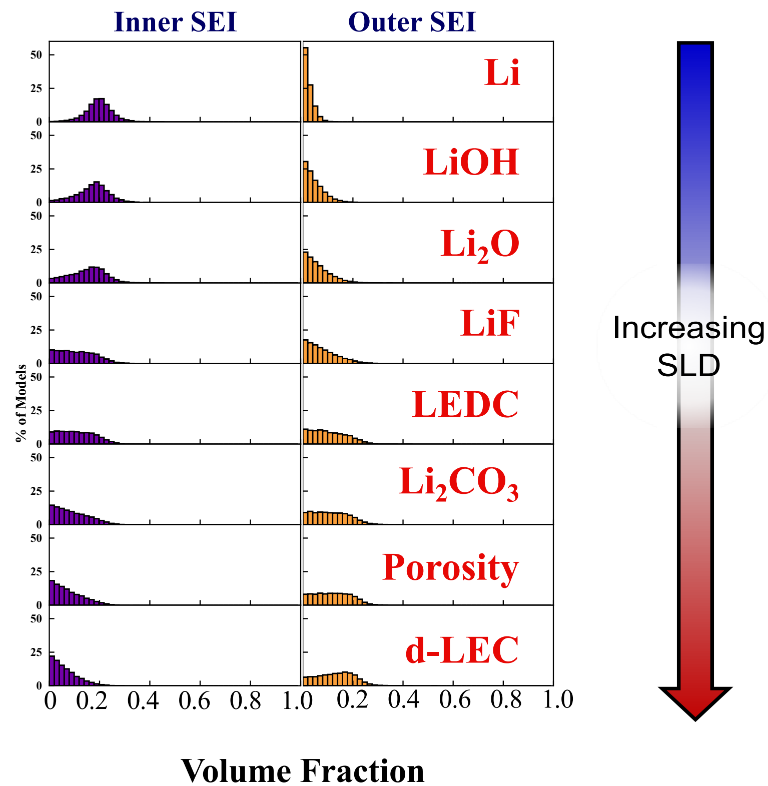

**User Inputs**

**Generate Random Model**
- Layer thicknesses
- Species volume fractions

**Calculate SEI mass and layer SLDs**

**Compare SEI properties to data**
- Screen out “bad” masses
- Calculate probability of observing SLDs
- Metropolis-Hastings algorithm

**Accumulate population of “acceptable” models.**

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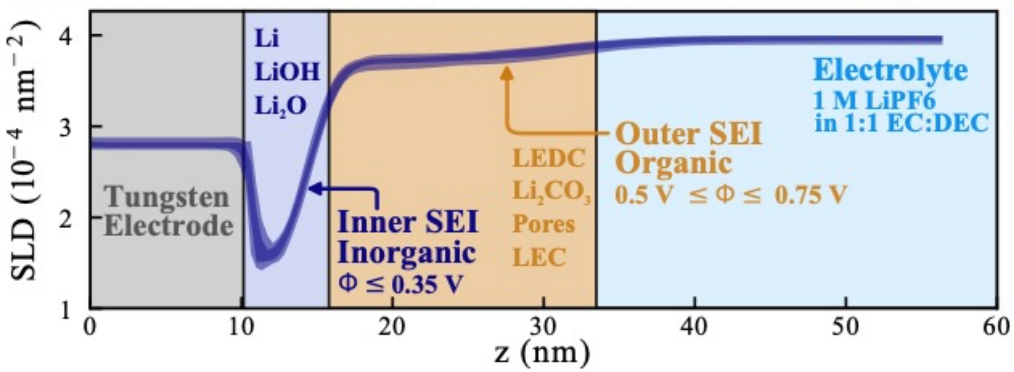
*Lee, et al., J. Power Sources, 2019*

# Conclusions and Outlook

- **Direct, operando observation of two-layer SEI on non-intercalating anode.**
  - Thin, dense inner layer: inorganic, Li-rich compounds
  - Thicker, porous outer layer: organic compounds
  - Outlook: Li-active substrates, interrogate SEI improvement strategies.
- **EQCM-D provides insights into formation mechanisms**
  - Organics deposit at higher potentials; secondary rxns form inorganics at lower potential.
  - Outlook: Operando data as a platform for mode/mechanism validation

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# Thank You

# Preliminary Numerical Simulations