Detailed Chemistry Modeling via Cantera: A Pathway to Understand Li-ion Battery Degradation

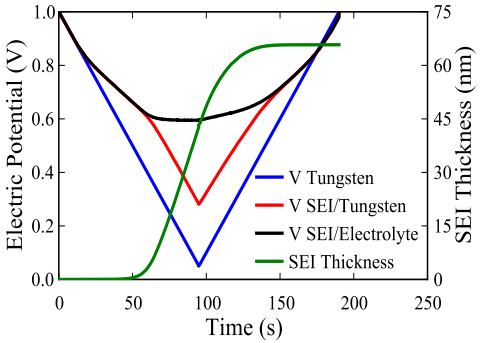
$$2\,EC_{elyte} + 2\,Li^{+}_{elyte} + 2\,e^{-} \leftrightarrow LEDC_{SEI} + 3\,Li_2O_{SEI}$$

$$EC_{elyte} + 2\,Li^{+}_{elyte} + 2\,e^{-} \leftrightarrow Ethylene_{g} + Li_2CO_{3,SEI}$$

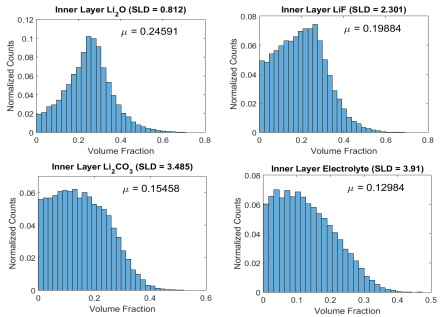
$$Li_2CO_{3,SEI} + 2\,Li^{+}_{elyte} + 2\,e^{-} \leftrightarrow 2\,Li_2O_{SEI} + CO_{g}$$

$$LEDC_{SEI} + H_2O_{elyte} \rightarrow Li_2CO_{3,SEI} + CO_{2,g} + (CH_2OH)_{2,elyte}$$

Detailed SEI Chemistry



Numerical Simulation



Validation

SEI Chemical Composition

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Presented at ECS Data Science Showcase
Monday, 01 October, 2018

MINES

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- Paul Kienzle – Refl1D Fitting software

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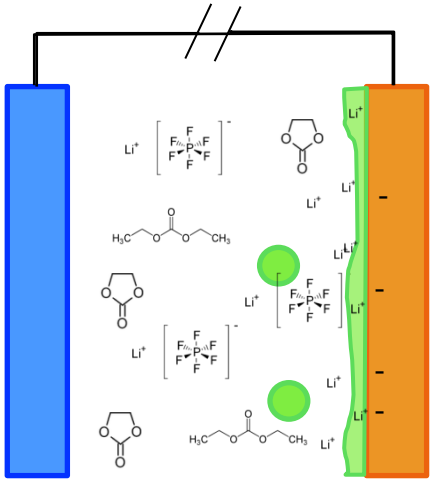
- **State of Colorado Energy Research Collaboratory, Seed Grant (Program contact: Maury Dobbie)**

Lithium batteries: promise, challenges, and the SEI (2)



•**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: Solid Electrolyte Interphase (SEI).

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

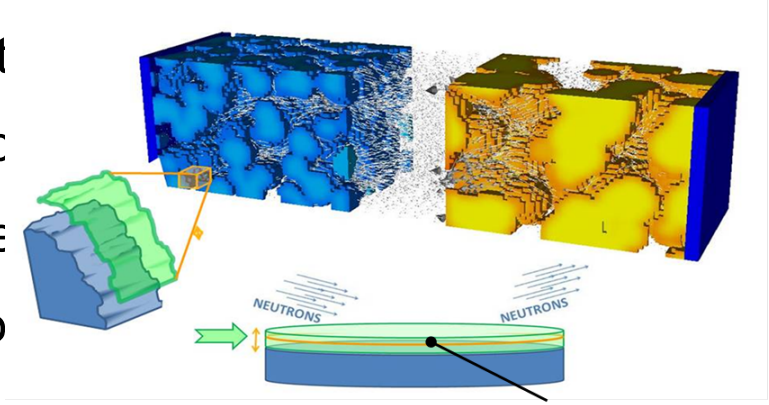
-Ion conductivit

-Long-term capacity fade due to Li+ c

-Durability and safety issues – SEI de

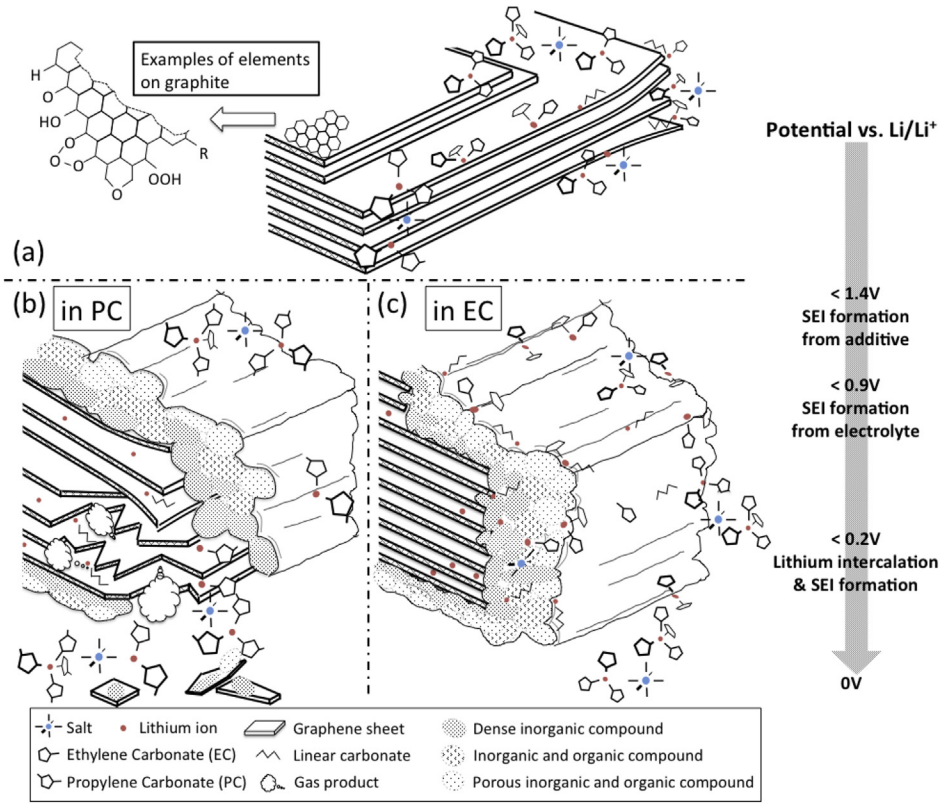
-Higher resistance, lower power – slo

interface.



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

State of SEI Understanding (1)



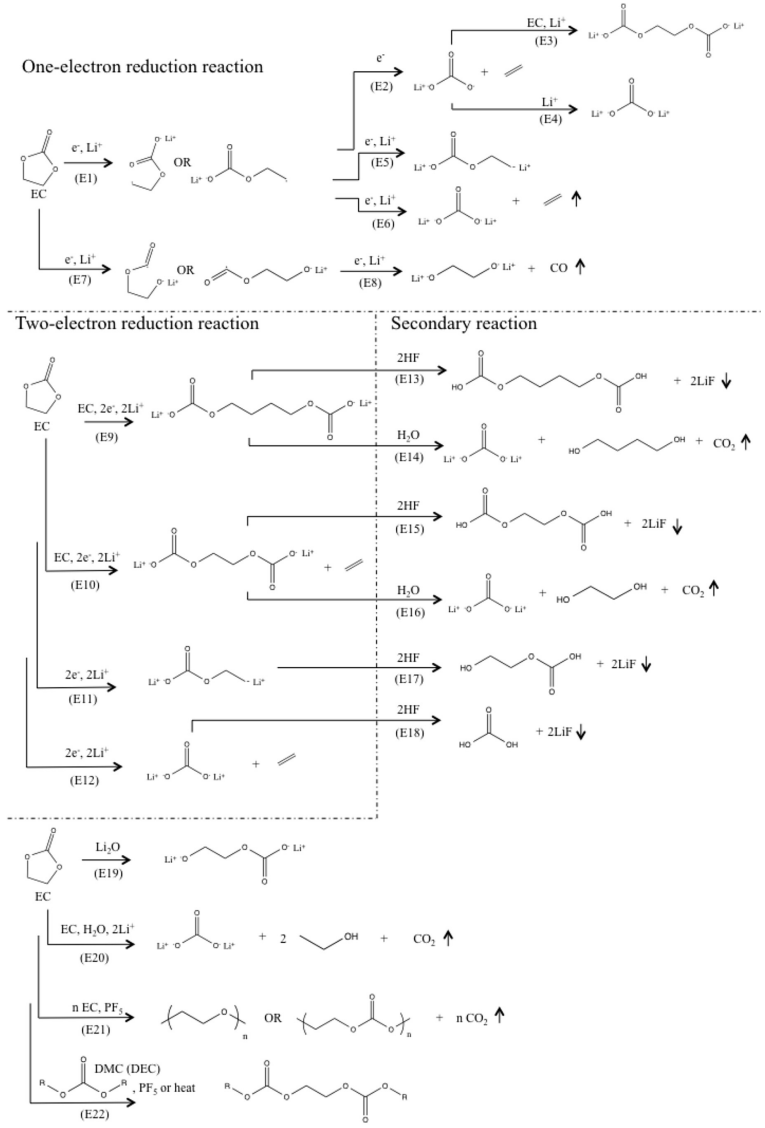
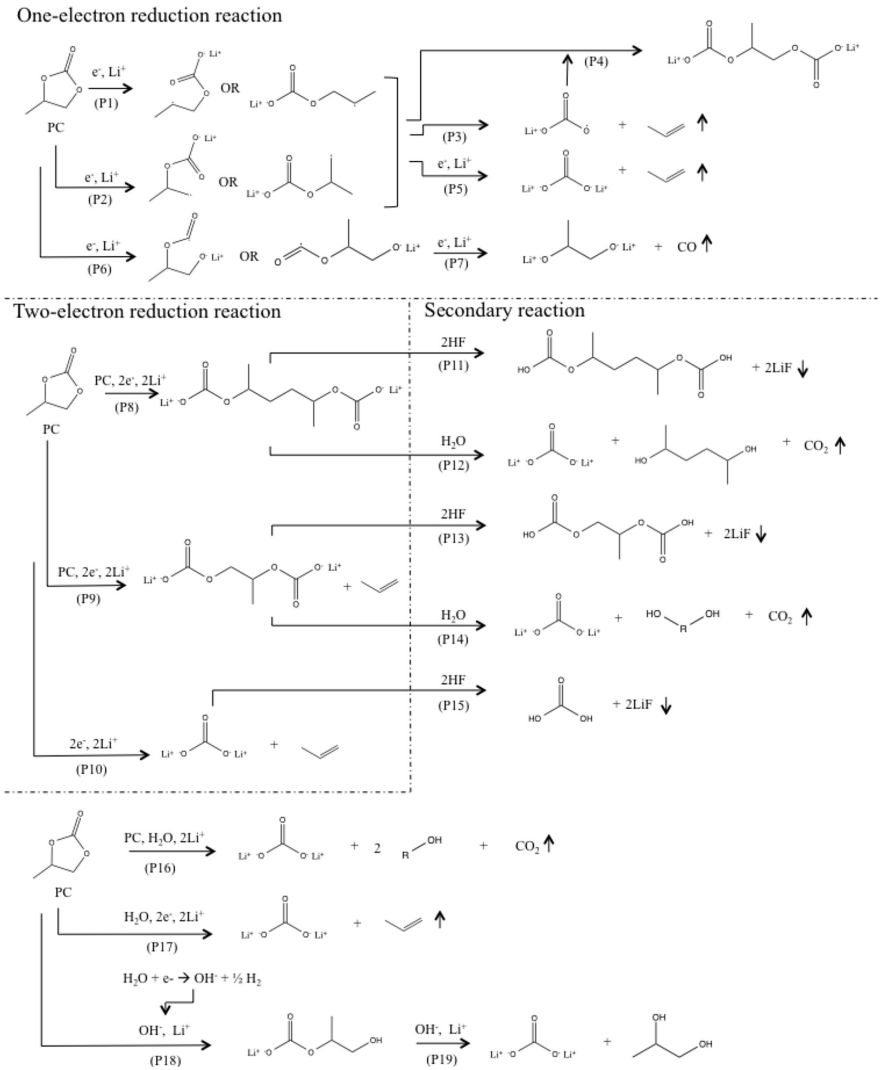
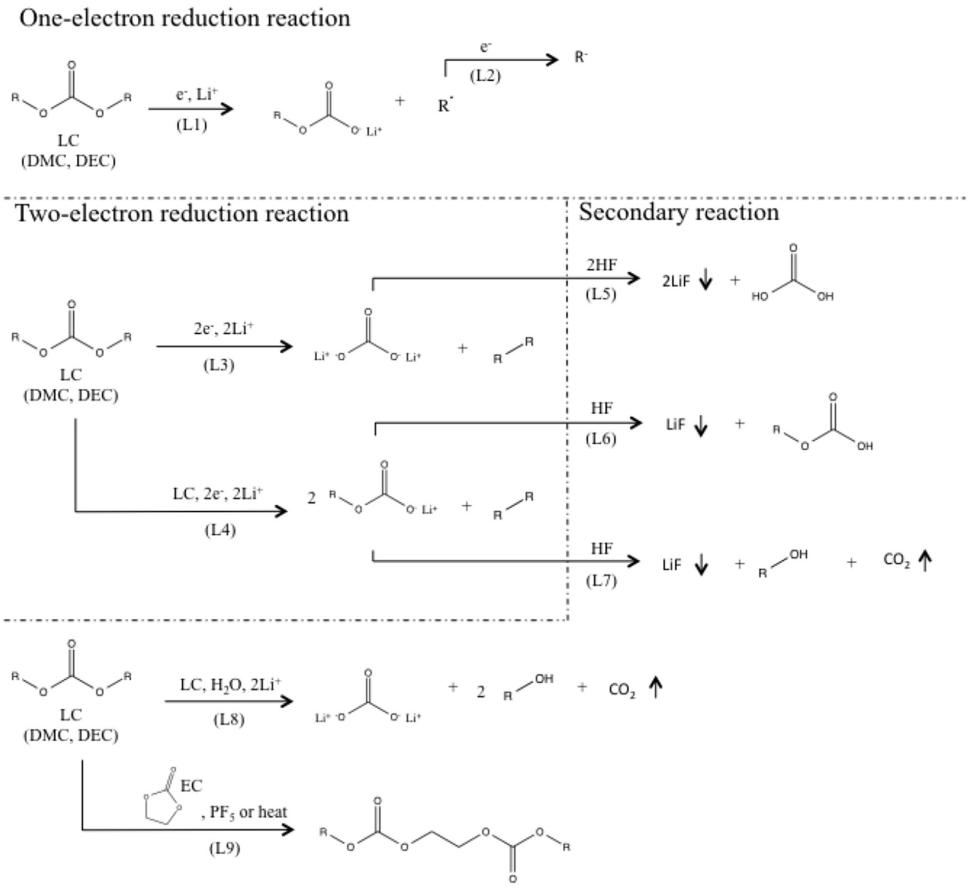


Fig. 8. Ethylene carbonate (EC) reduction process (reference groups in parentheses; details are shown in Table 2).

An, et al., *Carbon* (2016)

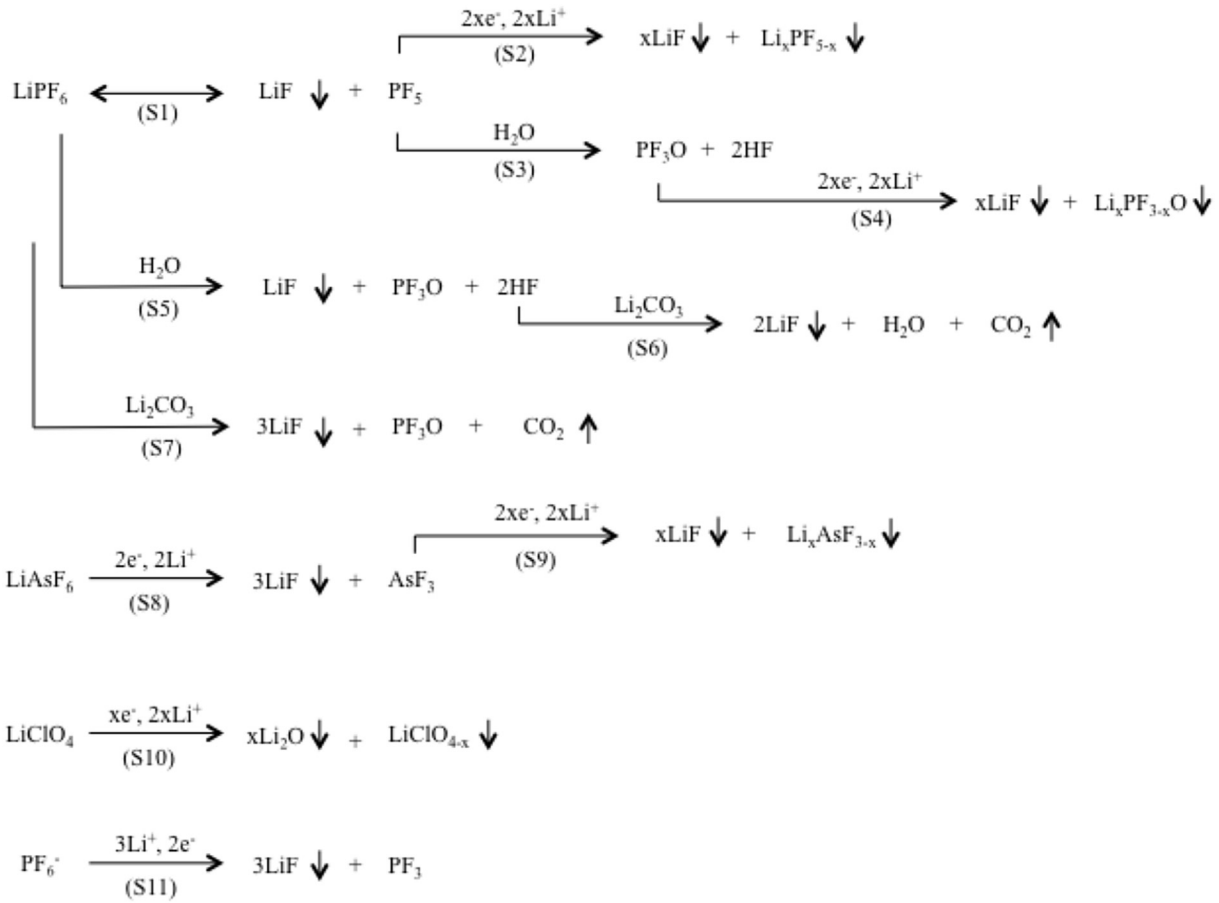
State of SEI Understanding (2)





An, et al., *Carbon* (2016)

State of SEI Understanding (3)



An, et al., *Carbon* (2016)

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Tanaka and Bessler

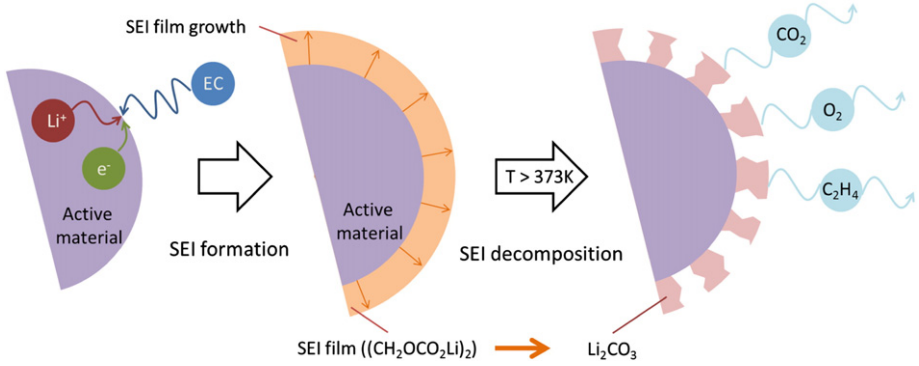
(Solid State Ionics, 2014)

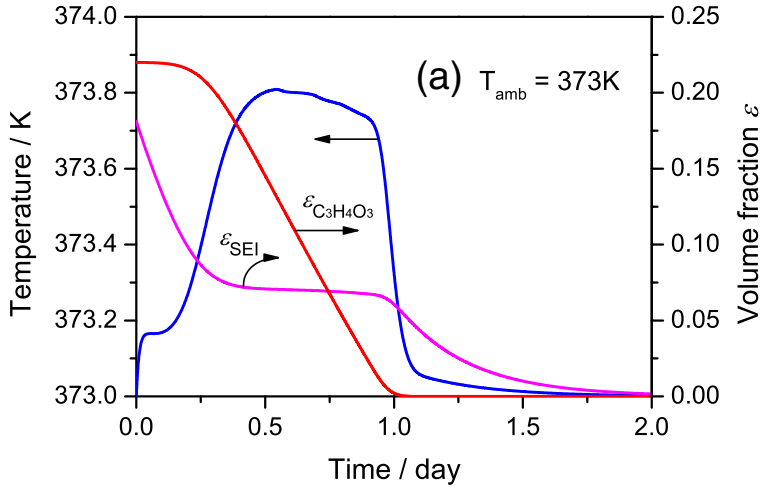
SEI Growth:

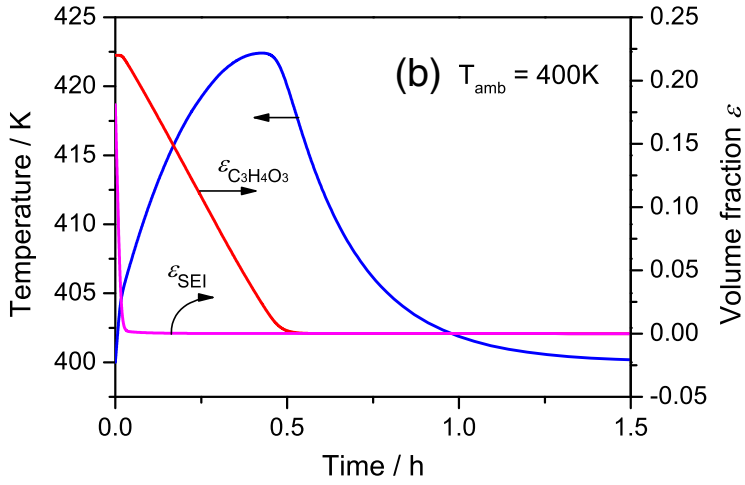
$$2C_3H_4O_3 + 2Li^+ + 2e^- \rightarrow (CH_2OCO_2Li)_2 + C_2H_4\uparrow.$$

SEI Decomposition:

$$(CH_2OCO_2Li)_2 \rightarrow Li_2CO_3 + C_2H_4\uparrow + CO_2\uparrow + \frac{1}{2}O_2\uparrow.$$



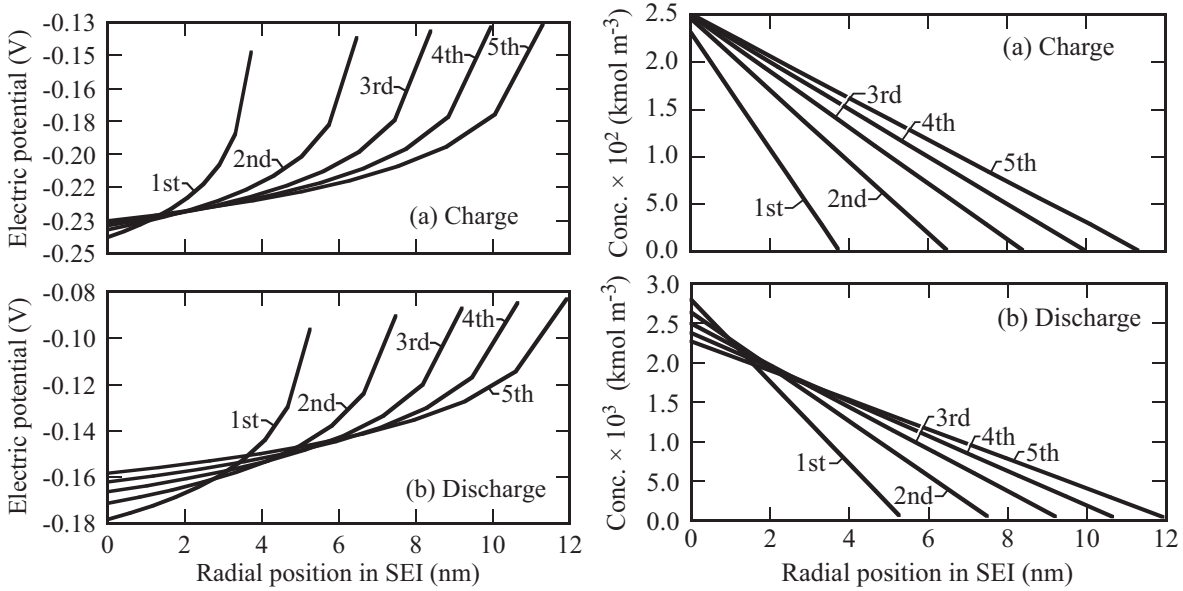




Colclasure, Smith, Kee

(Electrochmica Acta, 2011)

	Reaction
SEI–electrolyte interface	
1	$C_3H_4O_3(E)+(S^s)\rightleftharpoons C_3H_4O_3(S^s)$
2	$Li^+(S^s)\rightleftharpoons Li^+(E)+(S^s)$
3	$C_2H_4(E)+2(S^s)\rightleftharpoons C_2H_4(S^s)$
4	$C_3H_4O_3^-(S^s)\rightleftharpoons C_3H_4O_3(S^s)+e^-_{S^b}$
5	$C_2H_4(S^s)+CO_3^{2-}(S^s)\rightleftharpoons C_3H_4O_3^-(S^s)+e^-_{S^b}+2(S^s)$
6	$CO_3^{2-}(S^s)+2Li^+(S^s)+(S^b)\rightleftharpoons Li_2CO_3(S^b)+3(S^s)$
7	$Li(S^b)+(S^s)\rightleftharpoons V^-(S^b)+Li^+(S^s)$
8	$Li^+_{S^b}+(S^s)\rightleftharpoons Li^+(S^s)$
Graphite–SEI interface	
9	$e^-_{S^b}\rightleftharpoons e^-_{C_6}$
10	$Li(C_6)+V^-(S^b)\rightleftharpoons Li(S^b)+e^-_{C_6}+(C_6)$
11	$Li(C_6)\rightleftharpoons Li^+_{S^b}+e^-_{C_6}+(C_6)$



Kupper and Bessler, JECS 2017

Layer	Phase	Initial volume fraction ε	Density ρ/kg · m^{-3}	Species (initial mole fraction X)
Cathode	Cathode active material	0.67[101]	1510[101]	Li[LFP] (0.01), V[LFP] (0.99)
	Electrolyte	0.28**[101]	1130[101]	$C_3H_4O_3$(l) (0.6), $C_4H_6O_3$ (0.2), Li^+(solv) (0.1), PF_6^-(solv) (0.1)
	Gas phase cathode	0.05**	1.14[104]	N_2 (0.999), $C_3H_4O_3$(g) ($1.0 \cdot 10^{-8}$), C_2H_4 ($1.0 \cdot 10^{-8}$), O_2 ($1.0 \cdot 10^{-8}$), CO_2 ($1.0 \cdot 10^{-8}$), H_2O ($1.0 \cdot 10^{-8}$), H_2 ($1.0 \cdot 10^{-8}$)
Separator	Separator	0.5[105]	200[106]	Separator (1.0)
	Electrolyte	0.5[105]	1130[101]	$C_3H_4O_3$(l) (0.6), $C_4H_6O_3$ (0.2), Li^+(solv) (0.1), PF_6^-(solv) (0.1)
Anode	Anode active material	0.72[101]	2540[101]	Li[C_6] (0.57), V[C_6] (0.43)
	Electrolyte	0.22**[101]	1130[101]	$C_3H_4O_3$(l) (0.6), $C_4H_6O_3$ (0.2), Li^+(solv) (0.1), PF_6^-(solv) (0.1)
	SEI	0.01*	1300[107]	$(CH_2OCO_2Li)_2$ (1.0)
	Gas phase anode	0.05**	1.14[104]	N_2 (0.999), $C_3H_4O_3$(g) ($1.0 \cdot 10^{-8}$), C_2H_4 ($1.0 \cdot 10^{-8}$), O_2 ($1.0 \cdot 10^{-8}$), CO_2 ($1.0 \cdot 10^{-8}$), H_2O ($1.0 \cdot 10^{-8}$), H_2 ($1.0 \cdot 10^{-8}$)

Liu, et al., J Power Sources, 2014

$$EC + e^-(\text{graphite}) \rightarrow EC^- \quad (1)$$

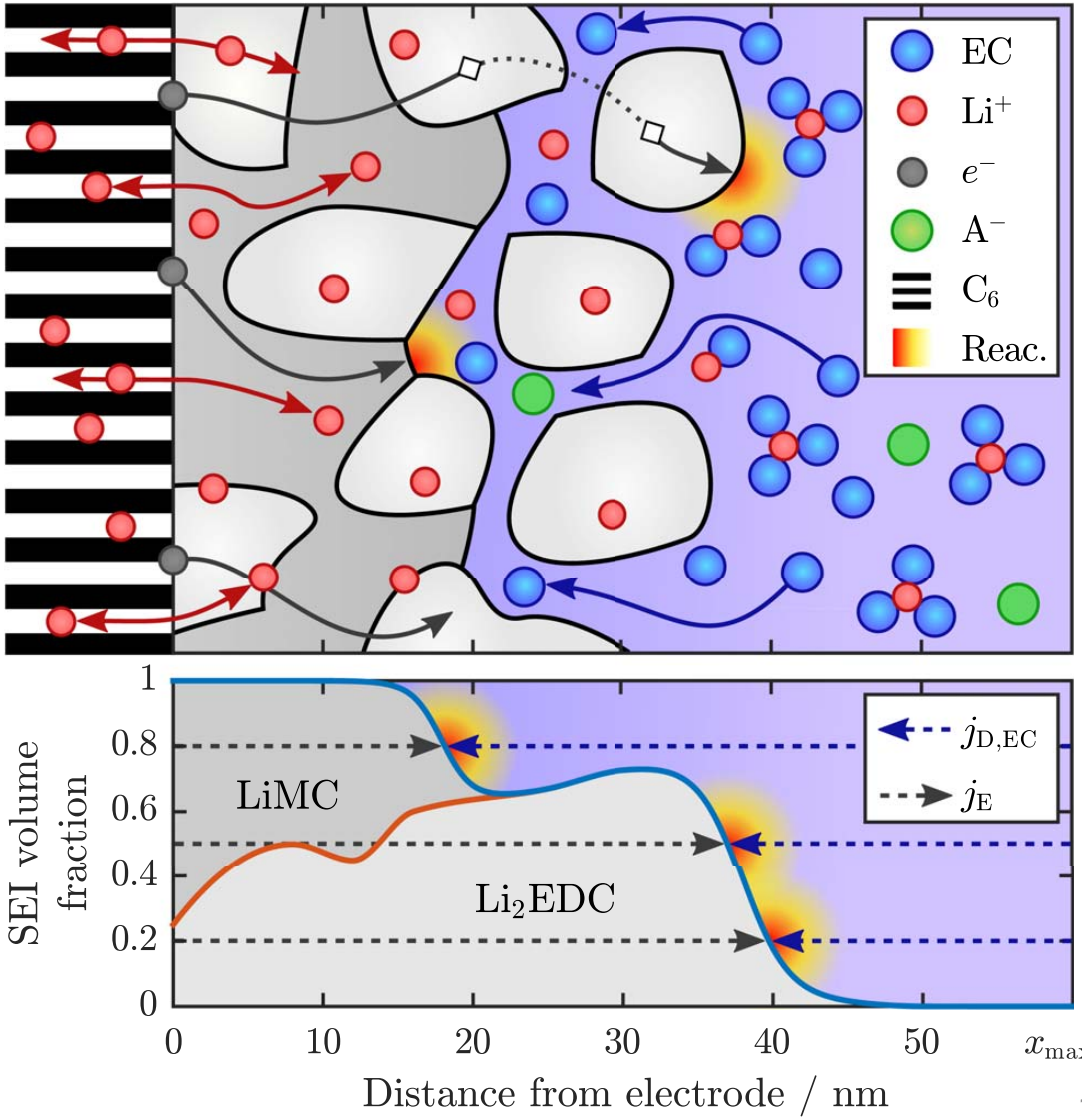
$$EC^- + EC^- \rightarrow (O_2CO)^-(CH_2)_2(O_2CO)^- + C_2H_4\uparrow \quad (2)$$

$$EC^- + EC + e^-(\text{graphite}) \rightarrow (O_2CO)^-(CH_2)_2(O_2CO)^- + C_2H_4\uparrow \quad (3)$$

$$(O_2CO)^-(CH_2)_2(O_2CO)^- + 2Li^+ \rightarrow Li^+(O_2CO)^-(CH_2)_2(O_2CO)^-Li^+ \quad (4)$$

Single, Horstmann, Latz,

J. Electrochem. Soc. (2017)



SEI Chemistry Models

- **Compared to other fields, "large" SEI mechanisms are small, do not yet reflect the considerable chemical, structural complexity.**

- **Limited development of detailed chemistry is understandable.**
  - **Materials constantly evolving**
  - **Computational tools not widely adopted; each new model must "reinvent the wheel."**
  - **Limited *in situ / in operando* chemical data available for validation of simulation results.**

Outline

- Introduction: Current understanding of the SEI
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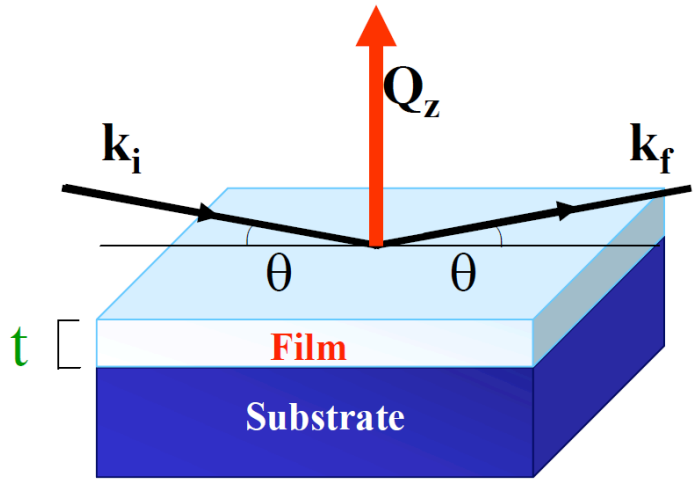
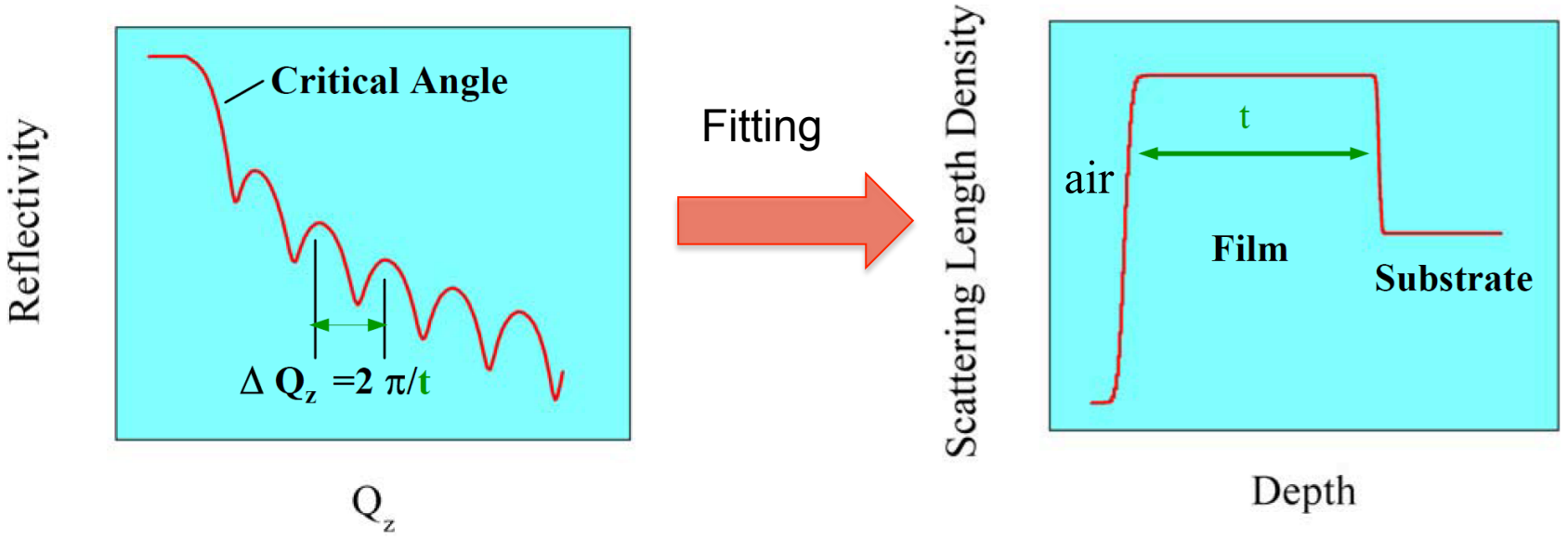
Neutron Reflectometry Overview



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

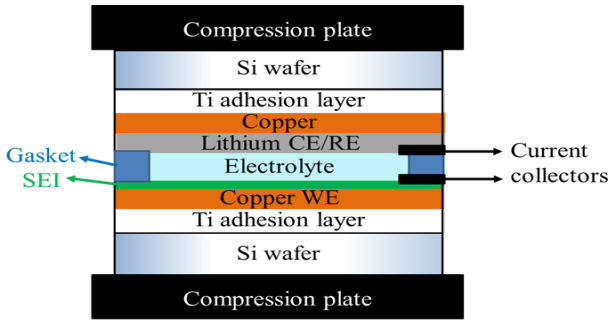
$$SLD(z) = \Sigma_j SLD_j V_j$$

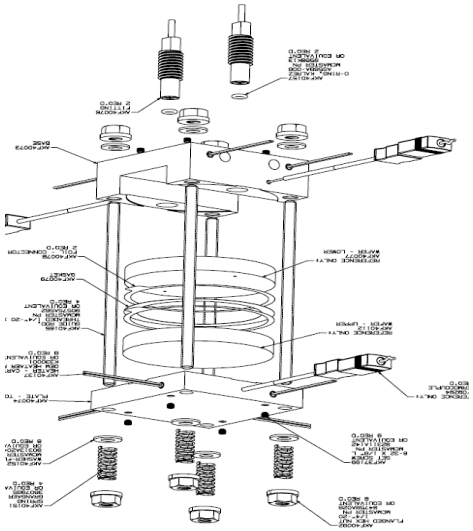
$$SLD(z) = \Sigma_i b_i n_i$$



Cell Fabrication

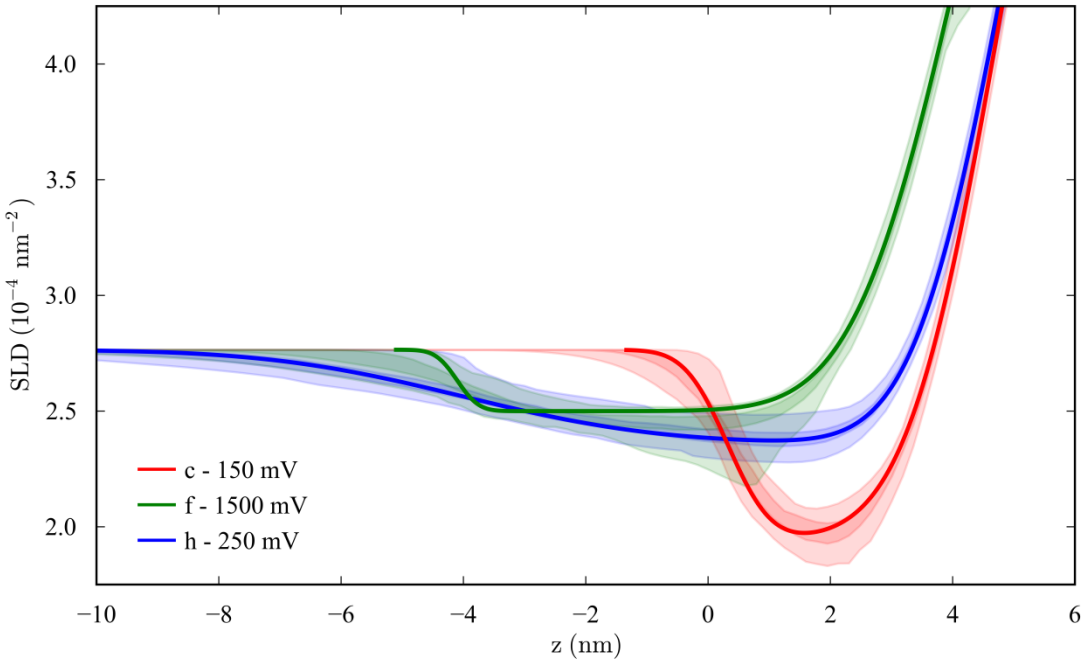
- **Non-intercalating working electrode (WE)**
  - -All charge attributed to SEI chemistry.
  - -Minimal WE change during experiments.
- **Li metal counter/reference electrode.**
- **Substrate: 5 mm thick polished Si.**
- **Thick (100-500 μm) liquid electrolyte reservoir:**
  - -Deuteration increases SLD, better contrast with lithiated compounds in SEI.

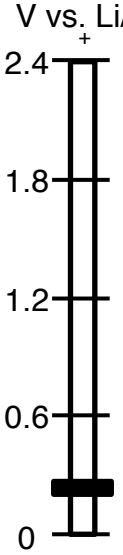


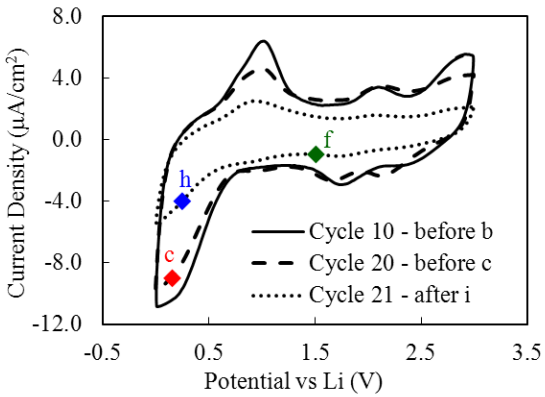


NR of SEI on Cu at Varying Potentials

- 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 of SEI assumptions from *ex situ* data.

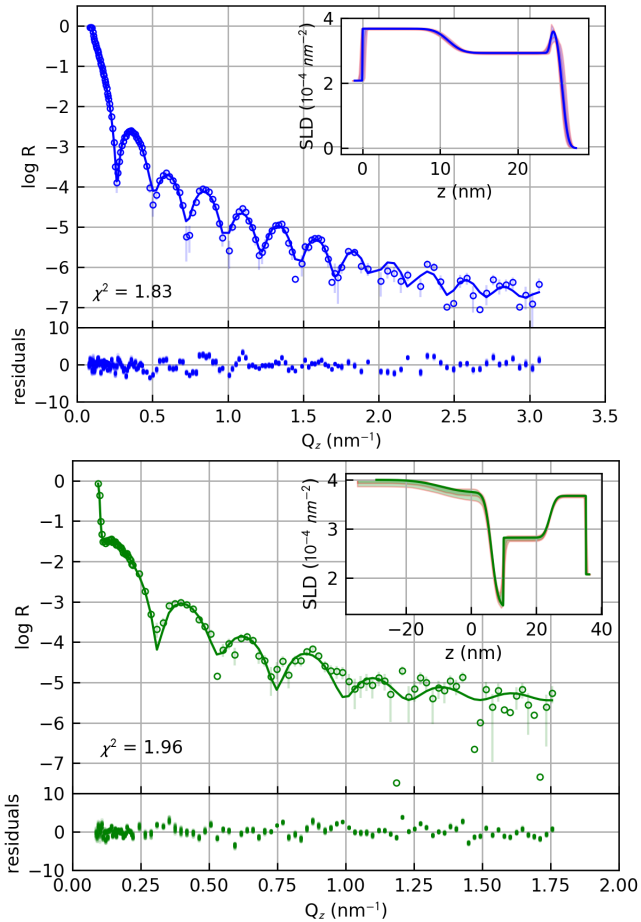


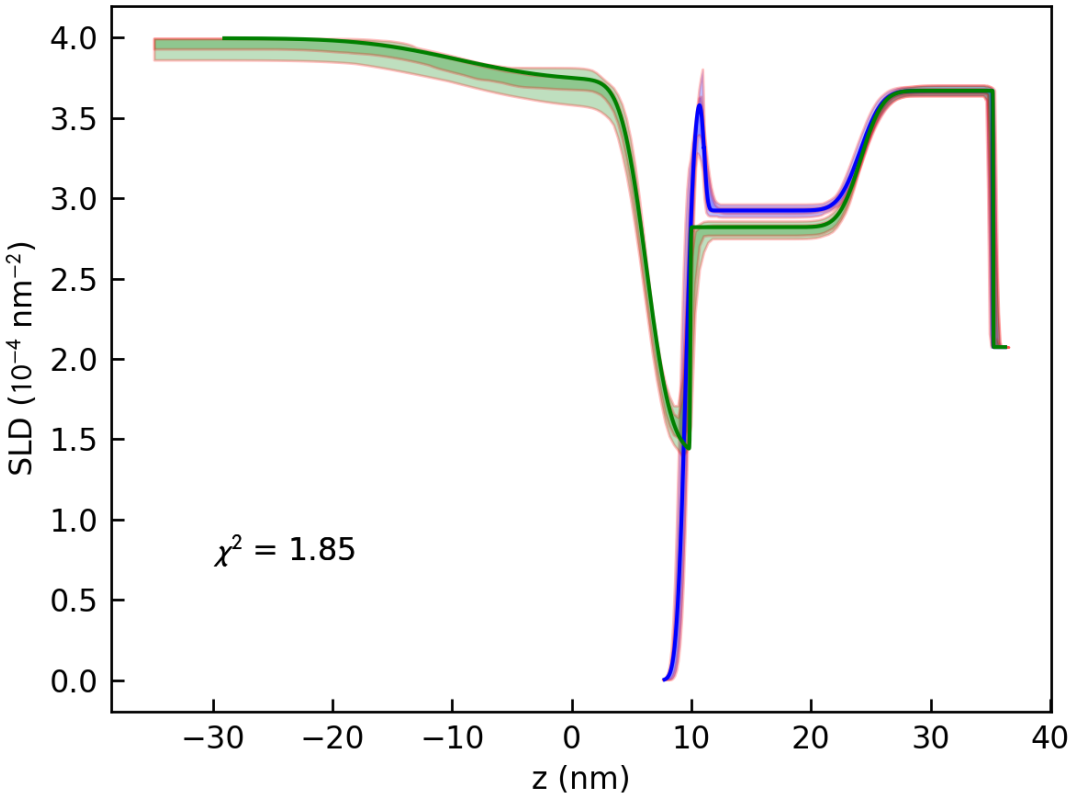




NR of SEI on Tungsten Directly Reveals Hypothesized Two-layer Structure

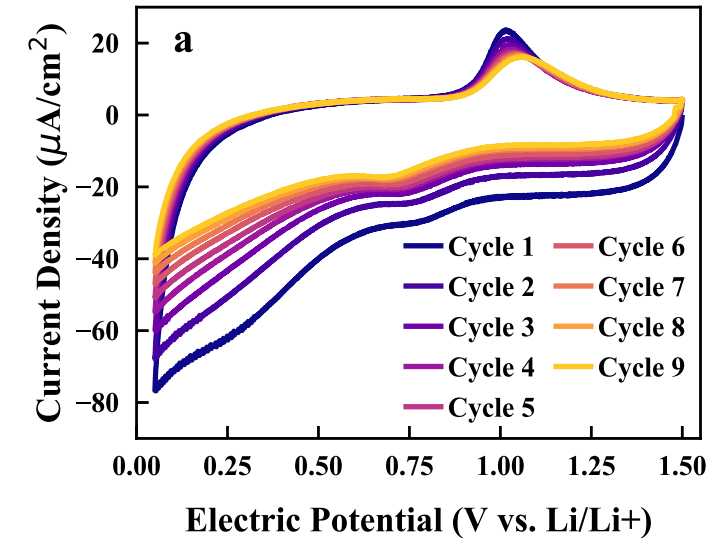
- **Two layer SEI structure**
  - **Denser "inner" SEI – 3.7 nm**
  - **Porous "outer" SEI – 15.3 nm**

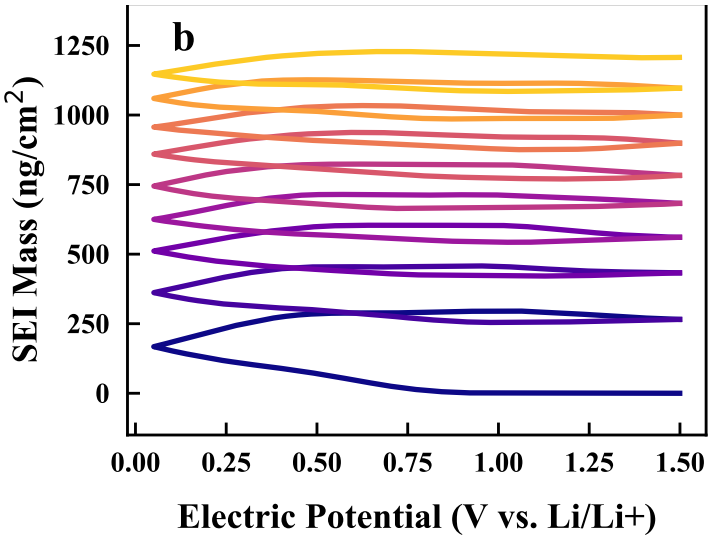




EQCM-D Shows Growth, Re-dissolution of SEI

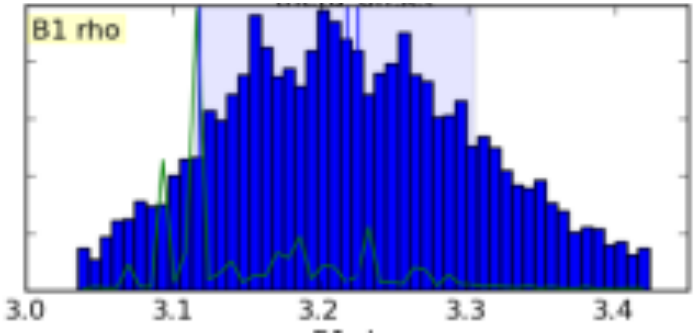
- Reduction peak at 800 mV: electrolyte decomposition
- Reduction peak at 275 mV, oxidation peak at 1.1 V: lithium underpotential deposition, stripping
- Decrease in mass gain per cycle – passivation and partial SEI dissolution





NR + QCM Provides Detailed Look at SEI Chemistry

- NR gives thickness and SLD



- EQCM-D determines SEI mass

- Monte Carlo model of SEI chemical composition
  - Randomly generate mole fractions, choose thickness from fitted distribution
  - Calculate SLD and Mass for the generated composition and thicknesses (inner & outer layer).
  - Mass must fall within uncertainty window of QCM data
  - Compare SLD values to probability distribution function from NR, use Metropolis Algorithm to choose “likely” models.

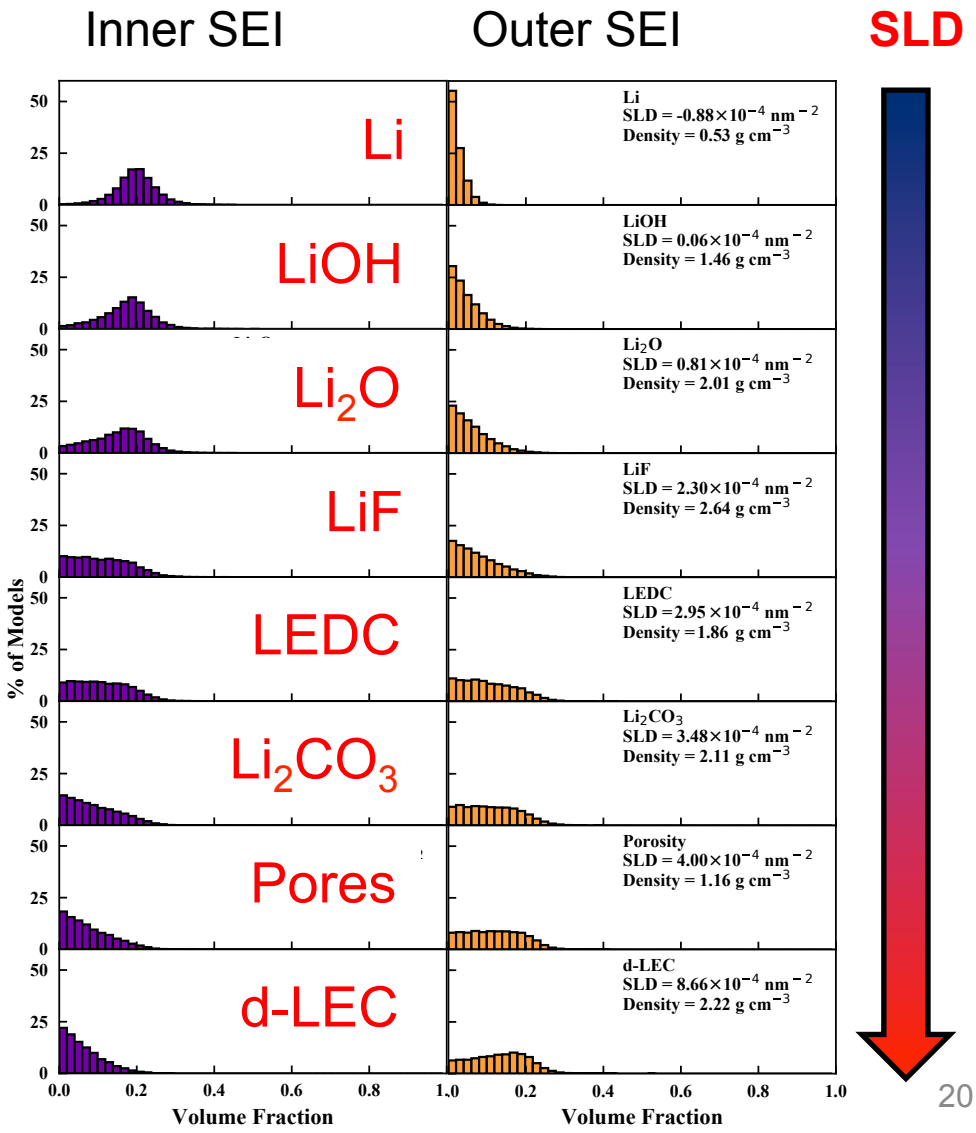
SEI Chemistry

Inner SEI:
Low-SLD components most prominent
Li, LiOH, Li2O, but all below 30%.

Outer SEI:
High-SLD components most prominent
Li Ethyl Carbonate, Electrolyte/ pores

Intermediate SLD components: not really discriminated

Lower noise in QCM-D needed to determine composition with greater resolution.



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Numerical Simulation of SEI Growth

- **Growth of SEI modeled via elementary electrochemistry:**

$$\dot{q}_i = k_{\text{fwd}} \prod_j a_j^{v_{j,i,\text{fwd}}} - k_{\text{rev}} \prod_j a_j^{v_{j,i,\text{rev}}}$$

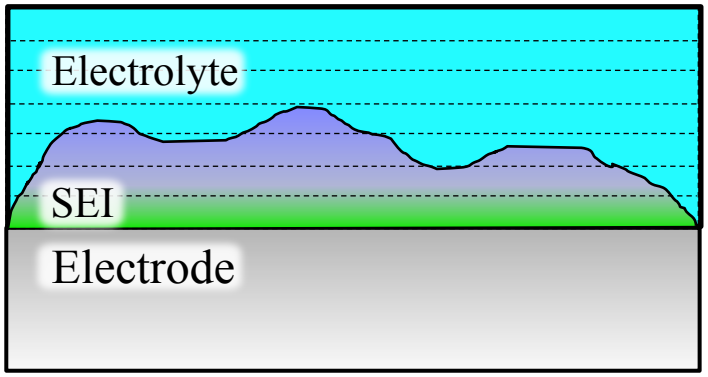
where:

$$k_{\text{fwd}} = k_{\text{fwd}}^{\circ} \exp\left(\frac{nF\beta\Delta\phi}{RT}\right)$$

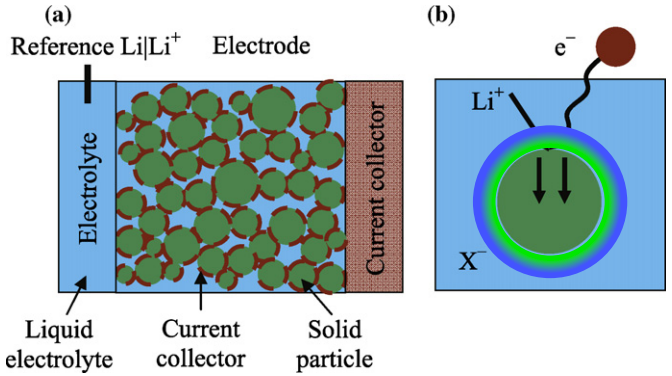
$$k_{\text{rev}} = k_{\text{rev}}^{\circ} \exp\left(\frac{nF(1-\beta)\Delta\phi}{RT}\right)$$

- **Initial model: planar, non-intercalating "model" electrode**
- **Depth profiling enabled by dividing electrolyte at electrode surface into volumes.**

Step 1: Model electrode



Step 2: Newman-type model



W. Lai, F. Ciucci, Electrochimica Acta, 2011

Simulation Approach

- **Simple SEI chemistry:**

$$2\,EC_{elyte} + 2\,Li^{+}_{elyte} + 2\,e^{-} \leftrightarrow LEDC_{SEI} + 3\,Li_2O_{SEI}$$

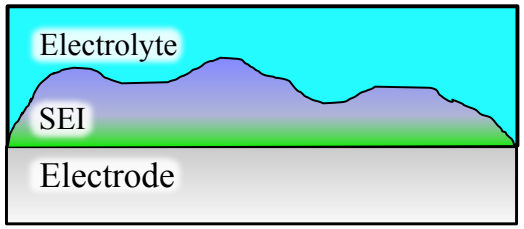
$$EC_{elyte} + 2\,Li^{+}_{elyte} + 2\,e^{-} \leftrightarrow Ethylene_{g} + Li_2CO_{3,SEI}$$

$$Li_2CO_{3,SEI} + 2\,Li^{+}_{elyte} + 2\,e^{-} \leftrightarrow 2\,Li_2O_{SEI} + CO_{g}$$

$$LEDC_{SEI} + H_2O_{elyte} \rightarrow Li_2CO_{3,SEI} + CO_{2,g} + (CH_2OH)_{2,elyte}$$

- **Charge transfer capacitance, (electro)chemical reaction rates, SEI resistance all are tunable parameters.**

- **Simulate a simple CV curve between 1.0 V and 0.05 V, at a scan rate of 10 mV/s.**



SEI Growth Rate:

$$\frac{\partial \phi_{SEI}}{\partial t} = \sum_{k,SEI} \frac{W_k}{\rho_k \Delta z} \dot{s}_k$$

Charge Transfer:

SEI / W anode:

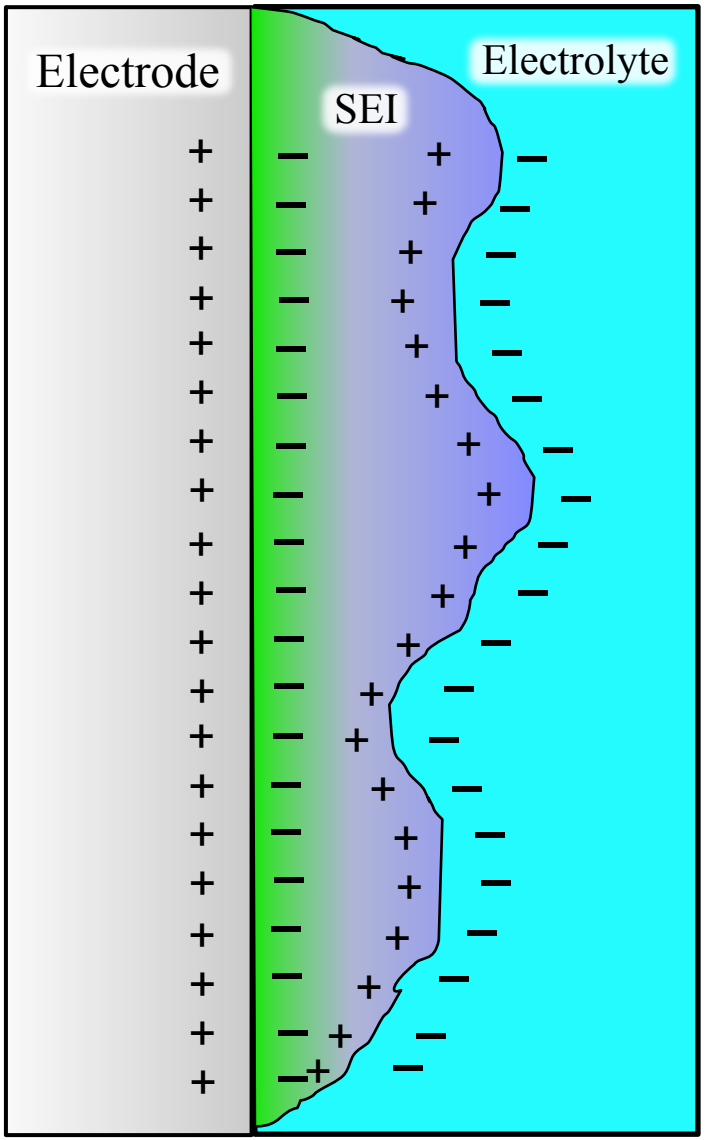
$$\dot{q}_{SEI/W} = k_{fwd} \prod_j a_j^{v_{jSEI/Wi,fwd}} - k_{rev} \prod_j a_j^{v_{j,SEI/W,rev}}$$

SEI / Electrolyte

$$\dot{q}_{SEI/elyte} = k_{fwd} \prod_j a_j^{v_{j,SEI/elyte,fwd}} - k_{rev} \prod_j a_j^{v_{j,SEI/elyte,rev}}$$

Finite electronic conductivity.

Simulation Approach



Charge neutrality:

$$i_{\text{SEI,elyte}} = i_{\text{SEI,cond}} = i_{\text{SEI,W}}$$

$$i_{\text{SEI, elyte}} = \sum_{k,SEI} z_k F v_{k,\text{SEI/elyte}} \dot{q}_{\text{SEI/elyte}}$$

$$i_{\text{SEI, cond}} = \frac{R_{\text{SEI}}}{\Delta\phi_{\text{SEI}}}$$

$$i_{\text{SEI, W}} = -\sum_{k,SEI} z_k F v_{k,\text{SEI/W}} \dot{q}_{\text{SEI/W}}$$

$$\phi_{\text{W}} - \phi_{\text{SEI}} = \Delta\phi_{\text{W/SEI}} + \Delta\phi_{\text{SEI}} + \Delta\phi_{\text{SEI/elyte}}$$

Outline

- Introduction: Current understanding of the SEI
- Chemical models of SEI growth
- Experimental data for validation
- Numerical Simulation of SEI Chemistry (1)
- **Interlude: Cantera**
- **Numerical Simulation of SEI Chemistry (2)**
- **Conclusions and Next Steps**

Cantera: Chemical Kinetics, Thermodynamics, Transport

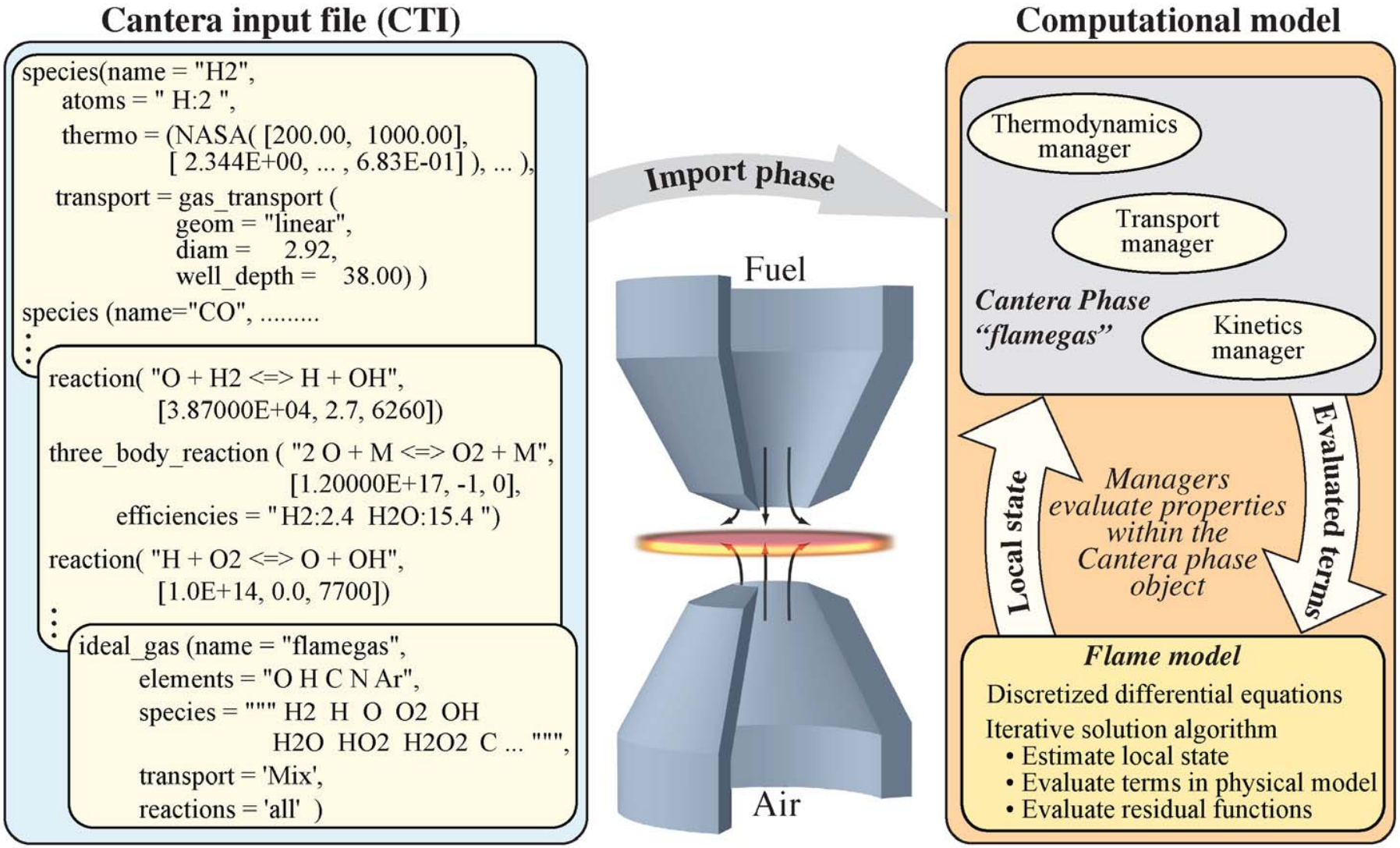


Image courtesy R. J. Kee, Colorado School of Mines

Cantera: Chemical Kinetics, Thermodynamics, Transport

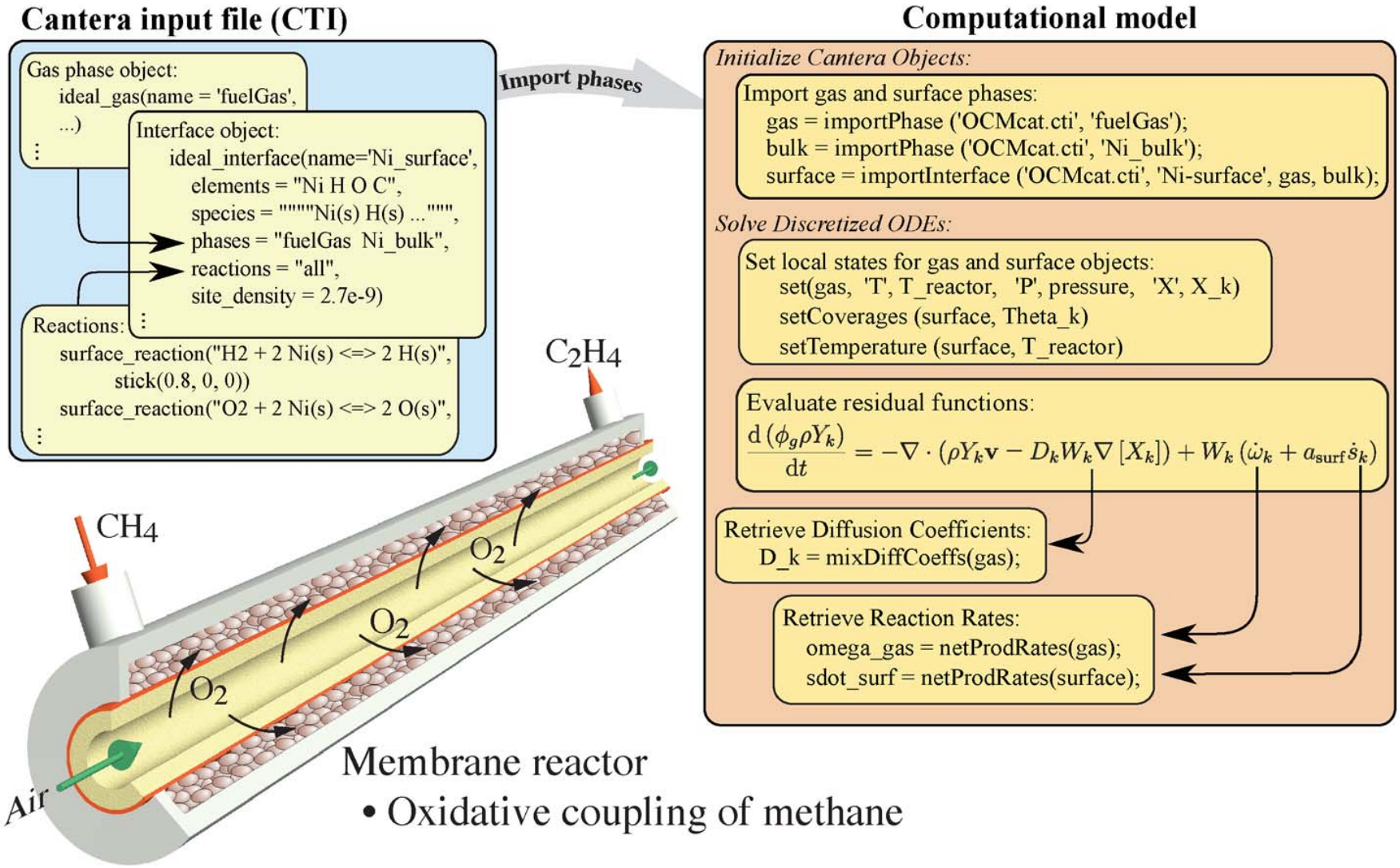


Image courtesy R. J. Kee, Colorado School of Mines

Cantera website: cantera.org

Repository on GitHub: https://github.com/cantera

Users' Group: https://groups.google.com/forum/#!forum/cantera-users

Demonstration: https://github.com/decaluwe/ECS_2018_materials/blob/master/ECS_2018.ipynb

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On the Fundamental and Practical Aspects of Modeling Complex Electrochemical Kinetics and Transport

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Numerous technologies, such as batteries and fuel cells, depend on electrochemical kinetics. In some cases, the responsible electrochemistry and charged-species transport is complex. However, to date, there are essentially no general-purpose modeling capabilities that facilitate the incorporation of thermodynamic, kinetic, and transport complexities into the simulation of electrochemical processes. A vast majority of the modeling literature uses only a few (often only one) global charge-transfer reactions, with the rates expressed using Butler–Volmer approximations. The objective of the present paper is to identify common aspects of electrochemistry, seeking a foundational basis for designing and implementing software with general applicability across a wide range of materials sets and applications. The development of new technologies should be accelerated and improved by enabling the incorporation of electrochemical complexity (e.g., multi-step, elementary charge-transfer reactions and as well as supporting ionic and electronic transport) into the analysis and interpretation of scientific results. The spirit of the approach is analogous to the role that Chemkin has played in homogeneous chemistry modeling, especially combustion. The Cantera software, which already has some electrochemistry capabilities, forms the foundation for future capabilities expansion.
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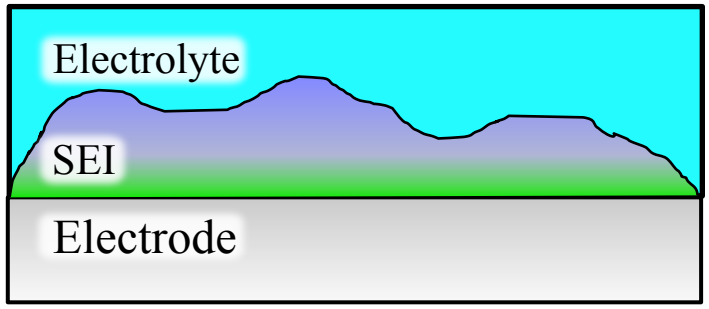
Preliminary Simulation Results

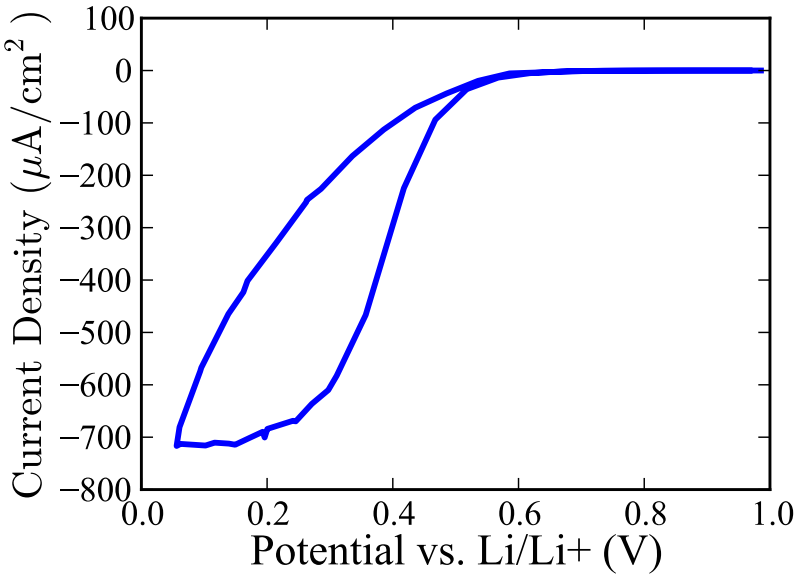
- **Simple SEI chemistry:**

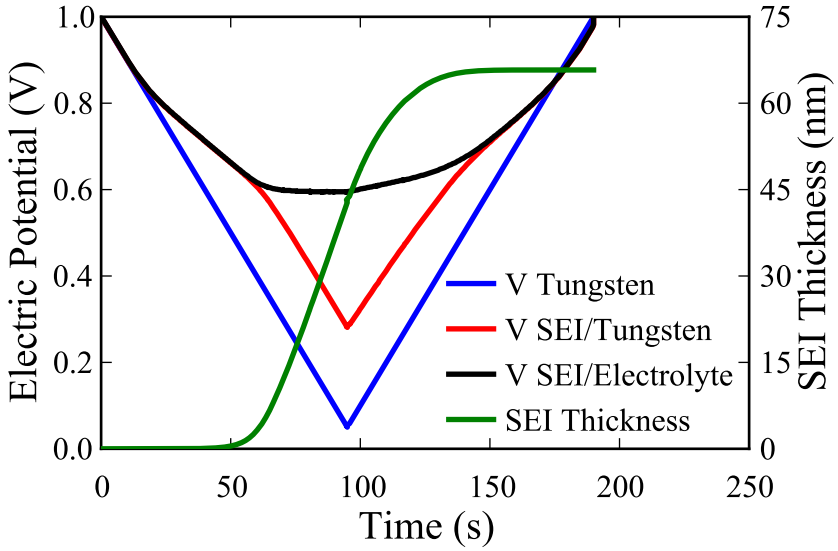
$$EC_{elyte} + 2\,Li^{+}_{elyte} + 2\,e^{-} \leftrightarrow Ethylene_{g} + Li_2CO_{3,SEI}$$

- **Charge transfer capacitance, (electro)chemical reaction rates, SEI resistance all are tunable parameters.**

- **Simulate a simple CV curve between 1.0 V and 0.05 V, at a scan rate of 10 mV/s.**







Preliminary Simulation Results

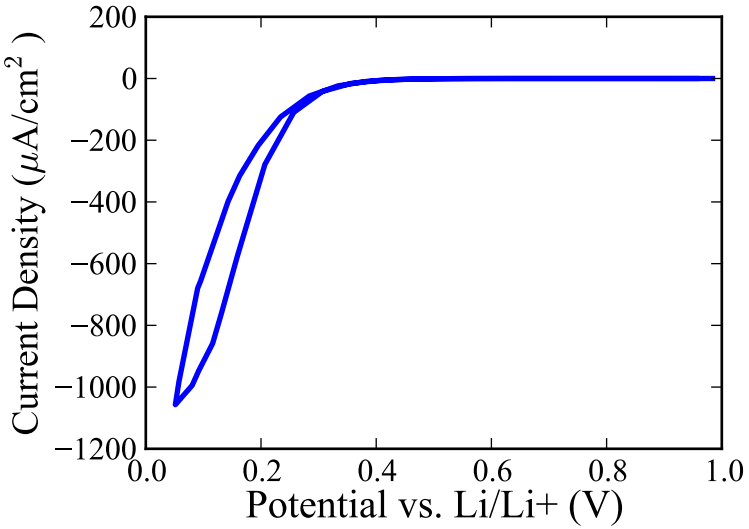
- **"Complex" SEI chemistry:**

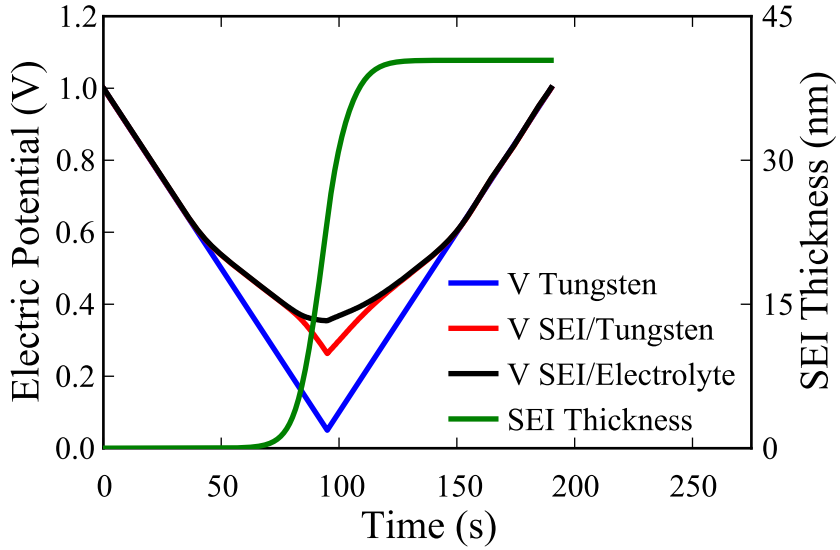
$$2\ EC_{elyte} + 2\ Li^{+}_{elyte} + 2\ e^{-} \leftrightarrow LEDC_{SEI} + 3\ Li_2O_{SEI}$$

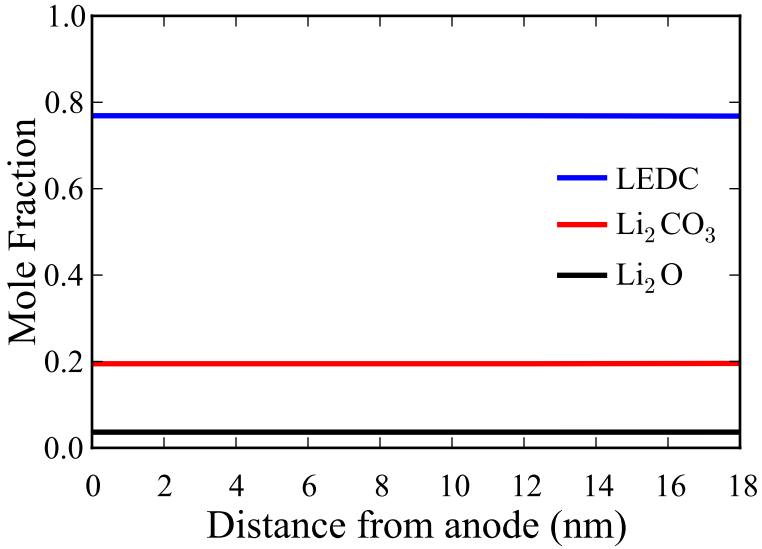
$$EC_{elyte} + 2\ Li^{+}_{elyte} + 2\ e^{-} \leftrightarrow Ethylene_{g} + Li_2CO_{3,SEI}$$

$$Li_2CO_{3,SEI} + 2\ Li^{+}_{elyte} + 2\ e^{-} \leftrightarrow 2\ Li_2O_{SEI} + CO_{g}$$

$$LEDC_{SEI} + H_2O_{elyte} \rightarrow Li_2CO_{3,SEI} + CO_{2,g} + (CH_2OH)_{2,elyte}$$







Conclusions, Outlook

- More NR and EQCM-D
  - More realistic substrates (carbon)
  - Verify SEI mitigation / improvement strategies: additives, growth conditions.

- Additional physics for SEI growth model
  - Porosity and roughness
  - Discretized SEI electric potential
  - Local resistance function of composition
  - Ion transport in SEI – solid diffusion and diffusion in electrolyte-filled pores

Thank You.