Integrated Modeling and Machine Learning of Solid-Electrolyte Interface Reactions of the Si Anode (Si-HPC)

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National Renewable Energy Laboratory

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DOE Vehicle Technologies Program
2021 Annual Merit Review and Peer Evaluation Meeting

Project ID # bat502

Overview

Timeline

- Project start date: 11/1/2019
- Project end date: 9/30/2022
- 50% complete

Budget

- Total project funding: $1,950,000 to NREL
  - DOE share: 100%
- Funding for FY 2020: $650,000
- Funding for FY 2021: $650,000

Barriers

- High-energy-density lithium-ion batteries with silicon (Si) anodes have limited calendar and cycle life.
- Unabated solid-electrolyte interphase (SEI) growth leads to rapid loss of lithium inventory (LLI) on Si as compared to graphite.
- Delineating SEI complexations and strategies for stable growth requires bridging scales from atomistic to continuum.

Partners

- National Renewable Energy Laboratory (lead)
- Lawrence Berkeley National Laboratory
- Oak Ridge National Laboratory
- Colorado School of Mines

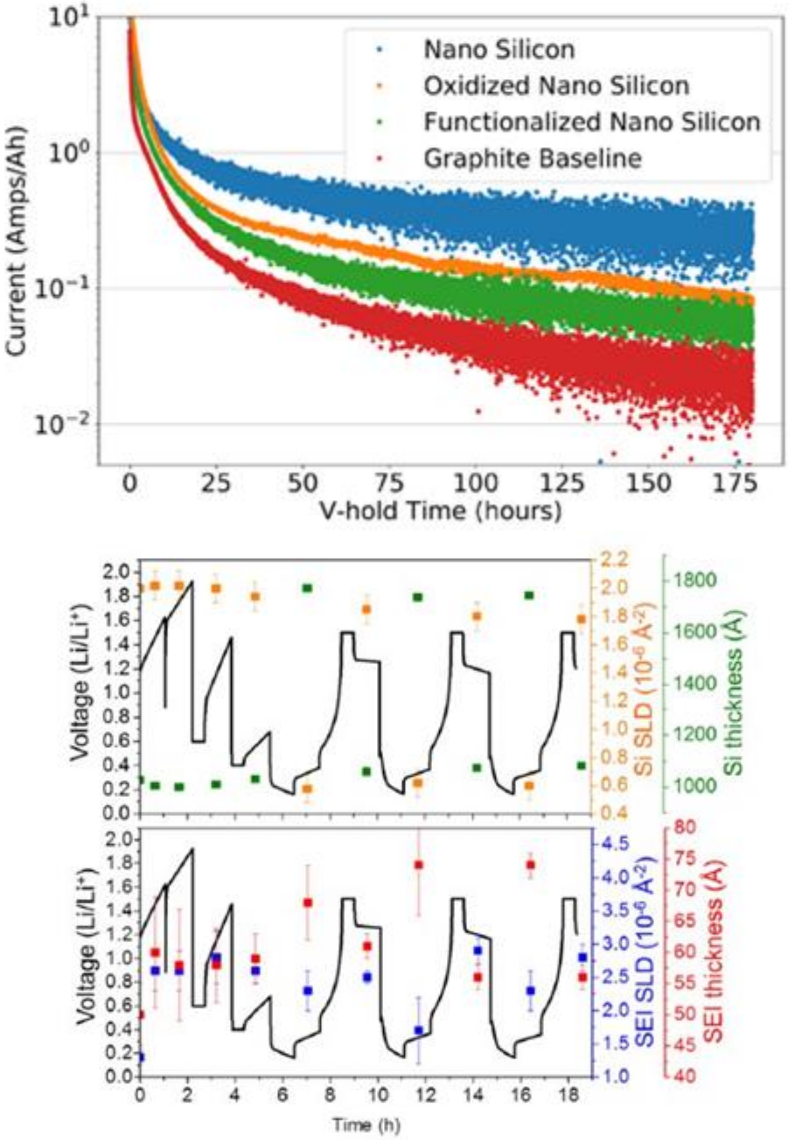
Relevance: Energy and Lifetime Gaps in Silicon Anode Battery Technology

- Silicon/NMC performance targets
  - Cell-level energy density: >350 Wh/kg, 750 Wh/L
  - Calendar life: >5 years
  - Cycle life: >1,000 cycles

- Current Si anodes show severe calendar (1–2 years) and—to a lesser extent—cycle life (1,000–2,000 cycles) limitations

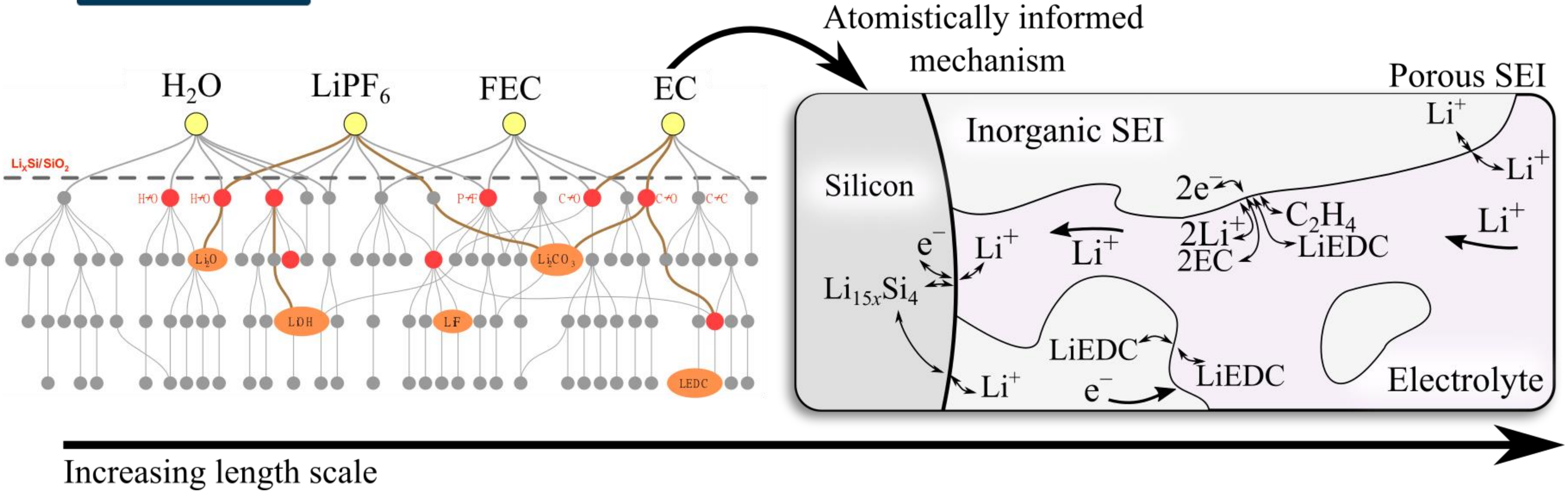
- Parasitic currents due to unabated solid-electrolyte interphase growth from both chemical and mechanical instability to loss of lithium inventory

- SEI film growth mechanisms and composition variations can be determined through coupled computational models bridging atomistic to continuum scales and give insights into novel Si electrolyte formulations for stable film growth.



Silicon Consortium Datasets

Approach: Computational Model Collaboration Bridges Length and Time Scales to Simulate SEI Dynamics



Atomistic modeling combined with machine learning identifies SEI reaction mechanisms and associated thermodynamic and kinetic data sets.

Continuum modeling incorporates atomistically predicted mechanisms and is experimentally validated to identify strategies for stable SEI growth.

Approach: Available Insights from Continuum-Level SEI Model Increases with Reaction Mechanism Complexity

- Goal: Simulate Si anode characteristics
  - High-magnitude parasitic currents under constant voltage calendar holds
  - SEI thickness and compositional changes during cycling, also know as “breathing”
  - SEI sensitivity to electrolyte composition
  - SEI sensitivity to Si surface termination (e.g., oxide, H).

State of the Art

$$2\mathrm{EC} + 2\cdot(\mathrm{Li}^+ + e^-) \rightarrow \mathrm{Li_2EDC} + R$$

$$\mathrm{DMC} + \mathrm{Li}^+ + e^- \rightarrow \mathrm{LiMC} + R$$

$$0.1\mathrm{Li_2EDC} + \mathrm{Li}^+ + e^- \rightarrow \quad 0.6\mathrm{Li_2O} + 0.4\mathrm{C}$$

- Three-reaction mechanism
- Three solid-phase species
- Solvent decomposition
- Solid phase conversion

1) Development

Intermediate

$$2\,\mathrm{Li}^+_{(\mathrm{elyte})} + 2\,\mathrm{EC} + 2\,\mathrm{e}^-_{(\mathrm{SEI})} \leftrightarrow \mathrm{Ethylene} + \mathrm{LEDC}_{(\mathrm{SEI})}$$

$$2\,\mathrm{Li}^+_{(\mathrm{elyte})} + 2\,\mathrm{EC} + 2\,\mathrm{e}^-_{(\mathrm{SEI})} \leftrightarrow \mathrm{Li_2CO}_{3(\mathrm{SEI})} + \mathrm{Ethylene}$$

$$2\,\mathrm{Li}^+_{(\mathrm{elyte})} + \mathrm{Li_2CO}_{3(\mathrm{SEI})} + 2\,\mathrm{e}^-_{(\mathrm{SEI})} \leftrightarrow 2\,\mathrm{Li_2O}_{(\mathrm{SEI})} + \mathrm{CO}$$

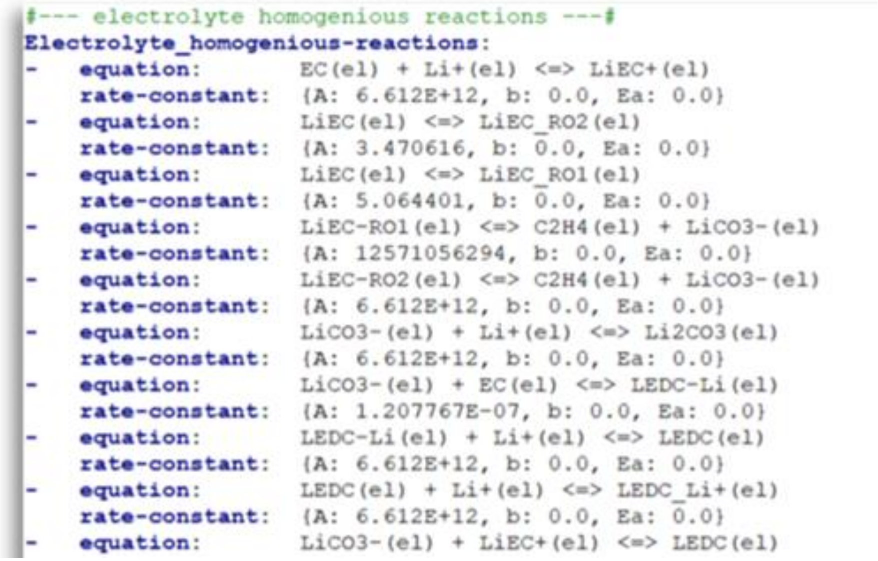
$$\mathrm{LEDC}_{(\mathrm{SEI})} + \mathrm{H_2O}_{(\mathrm{elyte})} \leftrightarrow \mathrm{Li_2CO}_{3(\mathrm{SEI})} + \mathrm{CO_2} + \mathrm{EG}$$

$$\mathrm{DMC} + \mathrm{Li}^+ + e^- \rightarrow \mathrm{LiMC} + R \qquad \ldots$$

- Four- ten reaction mechanism
- Three - six solid-phase species
- Solvent decomposition
- Solid phase conversion

2) Validation

Atomistic-Informed



```
#--- electrolyte homogenious reactions ---#
Electrolyte_homogenious-reactions:
-    equation:          EC(el) + Li+(el) <=> LiEC+(el)
     rate-constant:     {A: 6.612E+12, b: 0.0, Ea: 0.0}
-    equation:          LiEC(el) <=> LiEC_RO2(el)
     rate-constant:     {A: 3.470616, b: 0.0, Ea: 0.0}
-    equation:          LiEC(el) <=> LiEC_RO1(el)
     rate-constant:     {A: 5.064401, b: 0.0, Ea: 0.0}
-    equation:          LiEC-RO1(el) <=> C2H4(el) + LiCO3-(el)
     rate-constant:     {A: 12571056294, b: 0.0, Ea: 0.0}
-    equation:          LiEC-RO2(el) <=> C2H4(el) + LiCO3-(el)
     rate-constant:     {A: 6.612E+12, b: 0.0, Ea: 0.0}
-    equation:          LiCO3-(el) + Li+(el) <=> Li2CO3(el)
     rate-constant:     {A: 6.612E+12, b: 0.0, Ea: 0.0}
-    equation:          LiCO3-(el) + EC(el) <=> LEDC-Li(el)
     rate-constant:     {A: 1.207767E-07, b: 0.0, Ea: 0.0}
-    equation:          LEDC-Li(el) + Li+(el) <=> LEDC(el)
     rate-constant:     {A: 6.612E+12, b: 0.0, Ea: 0.0}
-    equation:          LEDC(el) + Li+(el) <=> LEDC_Li+(el)
     rate-constant:     {A: 6.612E+12, b: 0.0, Ea: 0.0}
-    equation:          LiCO3-(el) + LiEC+(el) <=> LEDC(el)
```

>20 elementary reaction mechanism

3) Prediction

FY 2020 Milestones

Milestone	Date	Status
M1: Data on SEISta silicon are collected from experimental efforts (e.g., carbon coating, particle-size distribution, electrode formulation).	12/31/2019	Complete
M2: Derive conservation equations for multispecies SEI model.	3/31/2020	Complete

FY 2021 Milestones

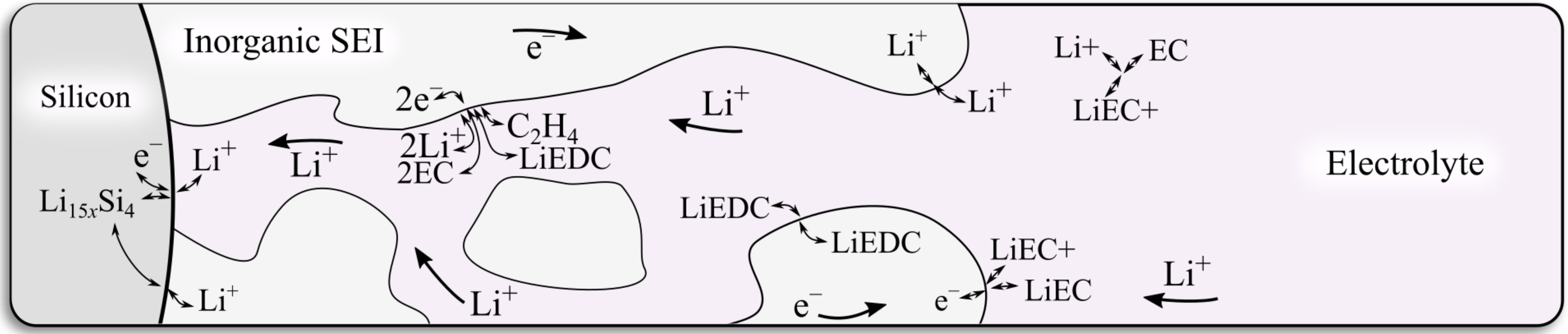
Milestone	Date	Status
M5: Implement multispecies SEI model in planar/stationary surface and report first results	12/31/2020	Complete
M6: Report results from planar, multispecies SEI model that predicts film composition/thickness during cycling at different rates and open-circuit voltage at different states of charge (SOCs)	3/31/2021	Complete
M7: Compare SEI model predictions with capacity fade measured from voltage-hold experiment at multiple SOCs from calendar life subgroup	6/30/2021	On track
M8: Implement SEI model in electrode-scale macro model with large deformation mechanics.	9/30/2021	On track

Approach: Implementation of Si SEI Model

- Solved equations
  - Conservation of charge in the solid-SEI phase and liquid electrolyte phase
  - Conservation of species in Si, SEI, and electrolyte phase
  - Conservation of volume in SEI and electrolyte (i.e., expanding solid SEI due to deposition reactions)
- Key assumptions
  - Constant electrolyte concentration far away from the Si surface
  - Dilute-solution transport of ionic species
  - Isothermal and isobaric
- Numerical implementation
  - Solved using stiff differential-algebraic equation solver in MATLAB
  - Complex reaction mechanism and species production rates handled in Cantera.

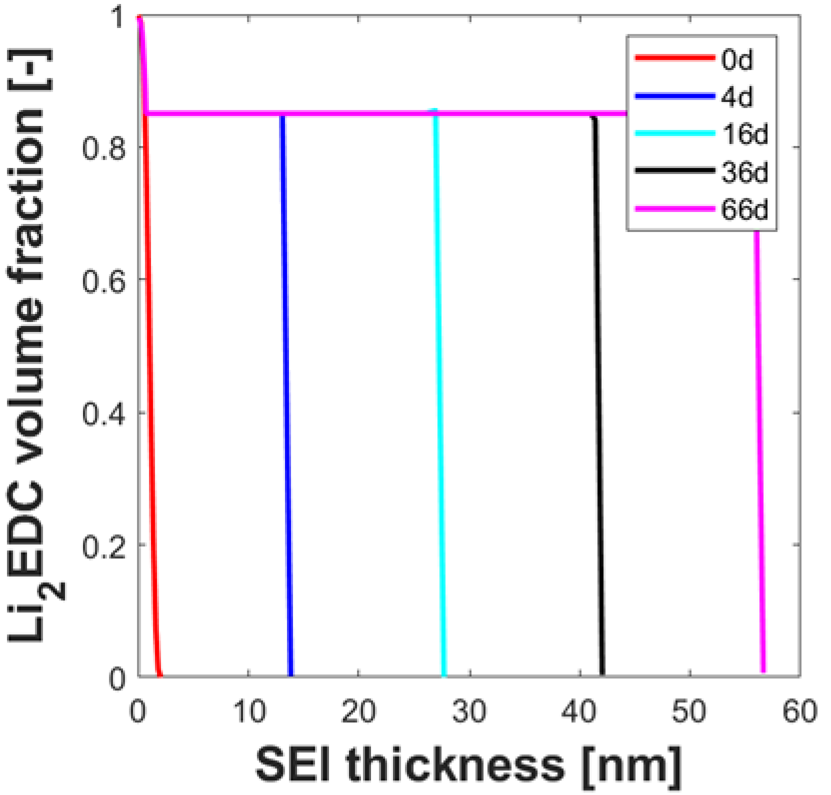
Species conservation

$$\frac{\partial [X_k]}{\partial t} = \nabla \cdot \left(D_k \nabla [X_k] + D_k \frac{z_k F}{RT} [X_k] \nabla \Phi \right)$$

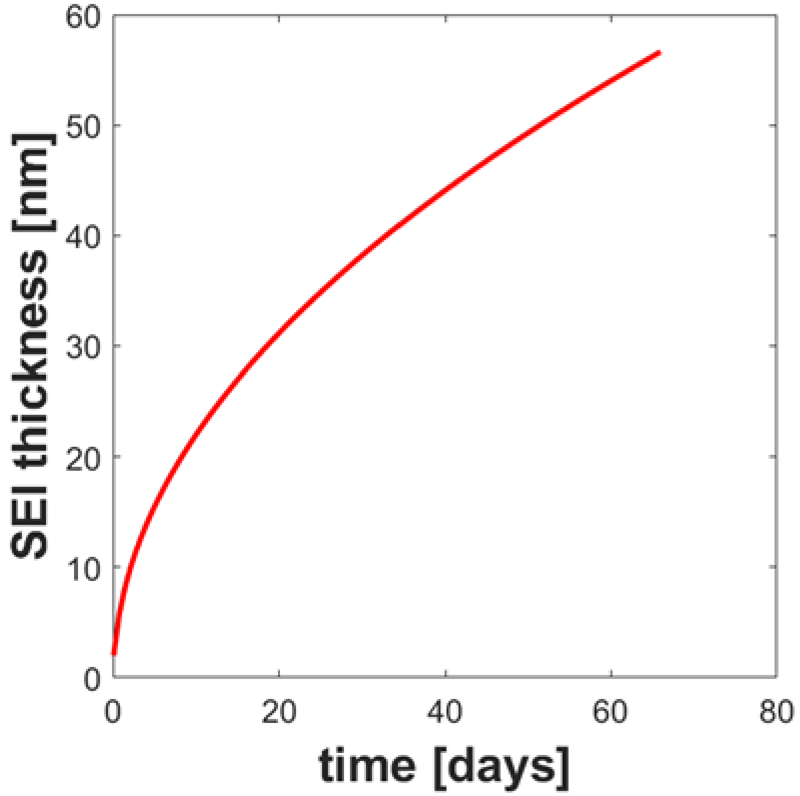


Technical Accomplishments and Progress: Primary Solvent Decomposition Under Calendar Aging Conditions (Voltage hold at 0.1 V))

$$2\mathrm{EC} + 2\cdot(\mathrm{Li}^{+} + e^{-}) \rightarrow \mathrm{Li_2EDC} + R$$



OCP: 0.8 V



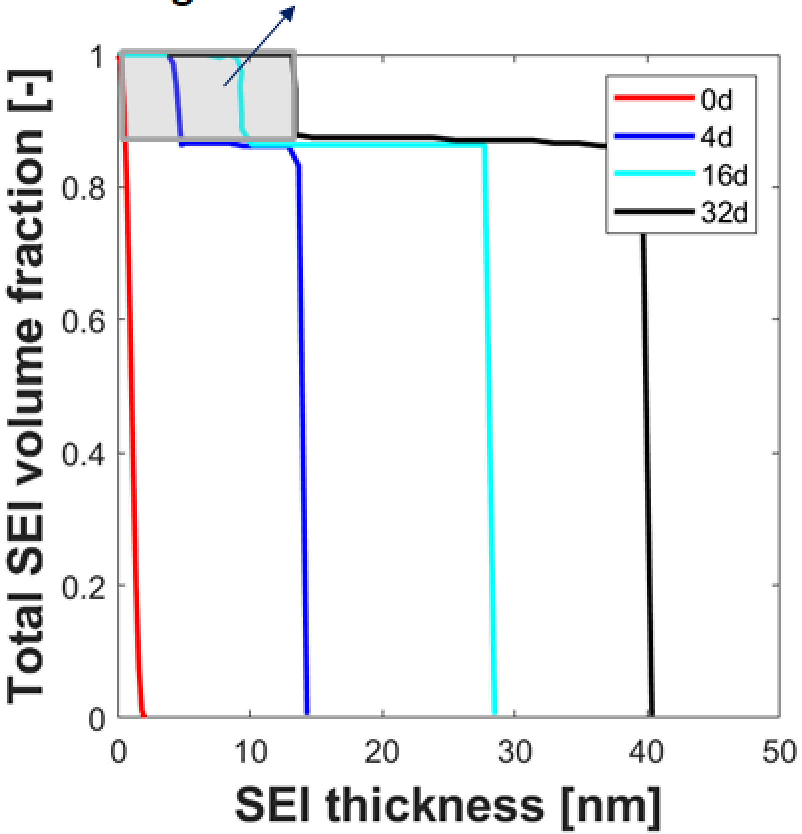
- Here, operating temperature is 30°C, SEI electronic conductivity is 1pS/m and solvent concentration is 4.5 mol/l.
- $\mathrm{Li_2EDC}$ formation continues throughout the SEI leading to the formation of single layer SEI.
- SEI thickness evolution follows square root of time dependence

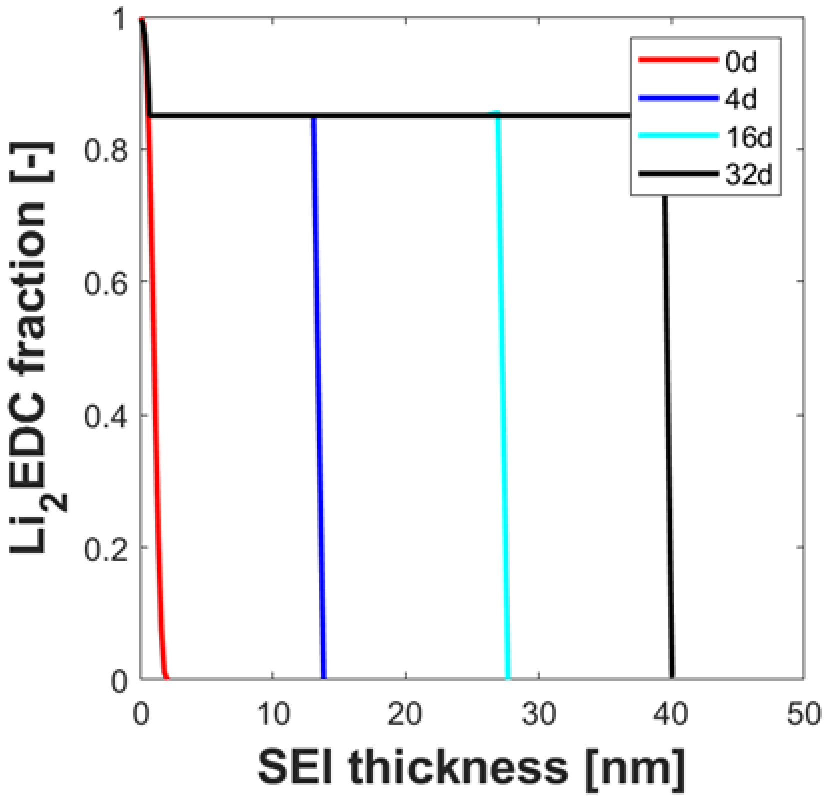
Cosolvent Decomposition Leads to Bi-layer SEI Formation (Voltage hold at 0.1 V)

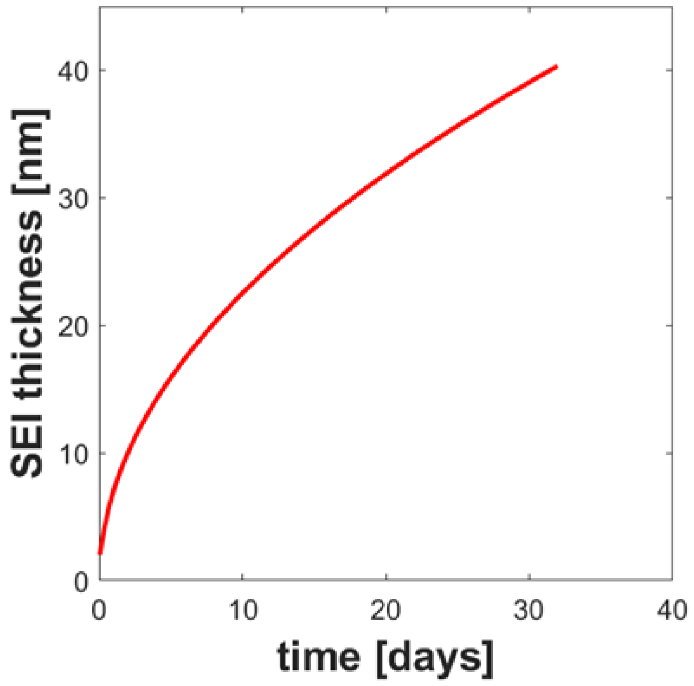
$2\mathrm{EC} + 2 \cdot (\mathrm{Li}^+ + e^-) \rightarrow \mathrm{Li_2EDC} + R$ OCP: 0.8 V

$\mathrm{DMC} + \mathrm{Li}^+ + e^- \rightarrow \mathrm{LiMC} + R$ OCP: 0.3 V

Region of LiMC formation







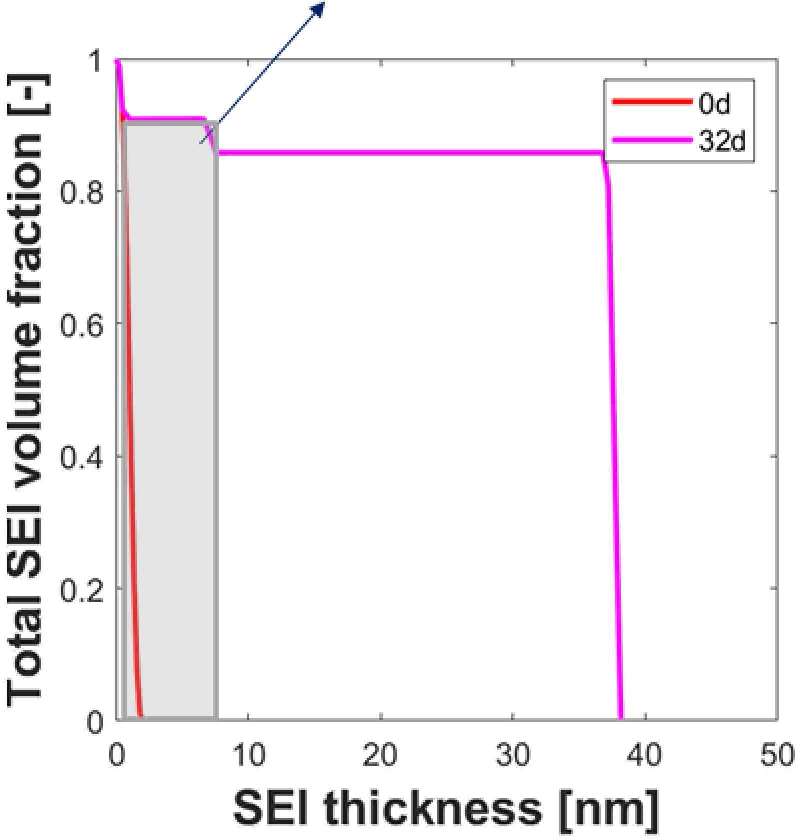
- Here, operating temperature is 30°C, SEI electronic conductivity is 1pS/m and solvent concentrations are 4.5 mol/l.
- Inner layer has both LiMC and LiEDC formation. Outer layer has primarily $\mathrm{Li_2EDC}$ formation.
- SEI thickness evolution follows square root of time dependence

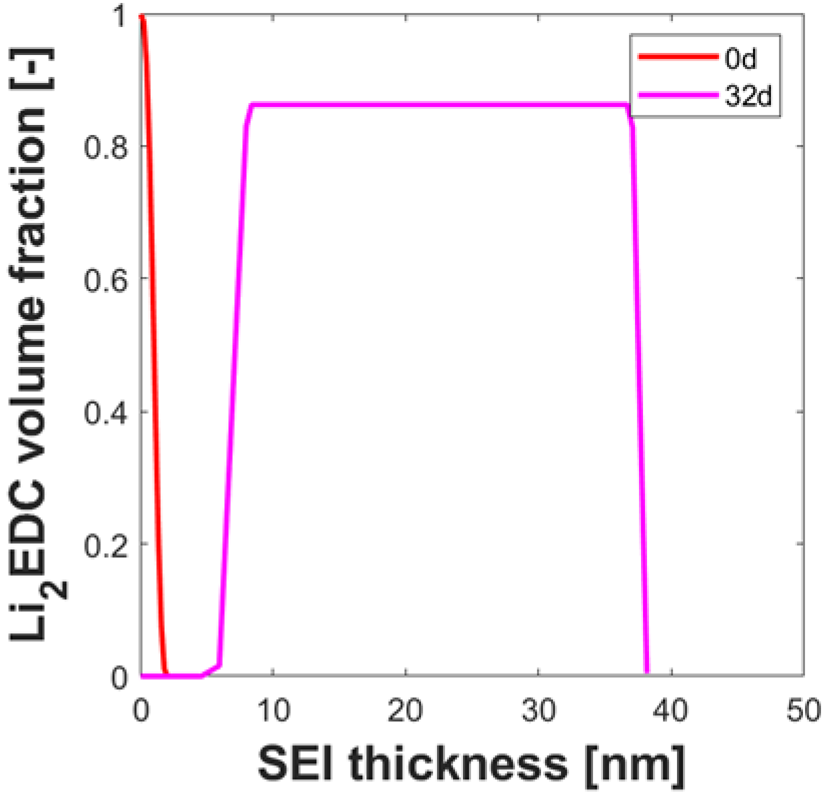
Conversion Reactions Also Lead to Bi-layer SEI Formation (Voltage Hold at 0.1 V)

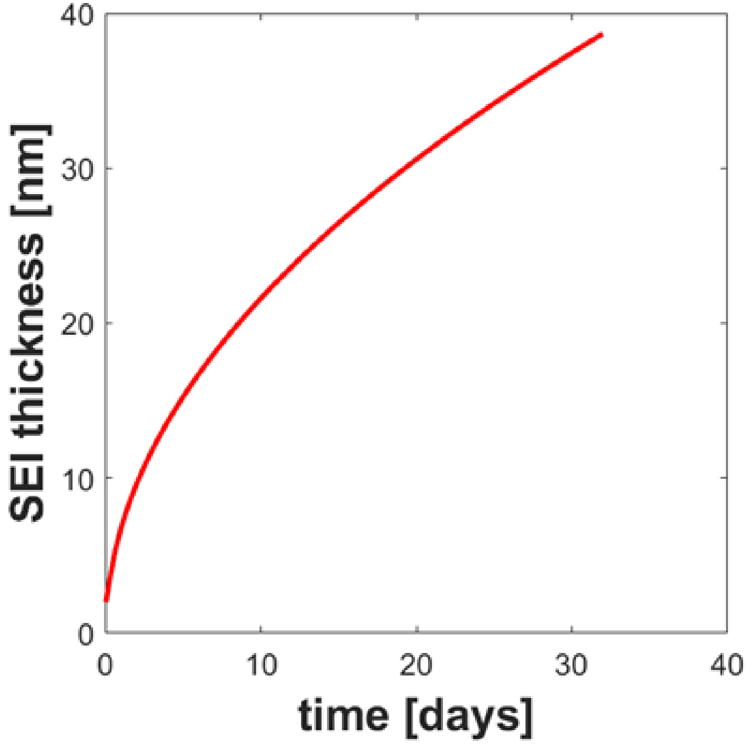
$2\mathrm{EC} + 2 \cdot (\mathrm{Li}^+ + e^-) \rightarrow \mathrm{Li_2EDC} + R$ OCP: 0.8 V

$0.1\mathrm{Li_2EDC} + \mathrm{Li}^+ + e^- \rightarrow 0.6\mathrm{Li_2O} + 0.4\mathrm{C}$ OCP: 0.3 V

Region of Li_2O formation







- Here, operating temperature is 30°C, SEI electronic conductivity is 1pS/m and solvent concentrations are 4.5 mol/l.
- Inner layer has only Li_2O formation, while outer layer comprises of Li_2EDC
- SEI thickness evolution follows square root of time dependence

Kinetic Rates Influence Species Distributions and Breathing Dynamics

10 CV cycles 0.05 – 1.5 V, 10 mV/s
“intermediate” mechanism:

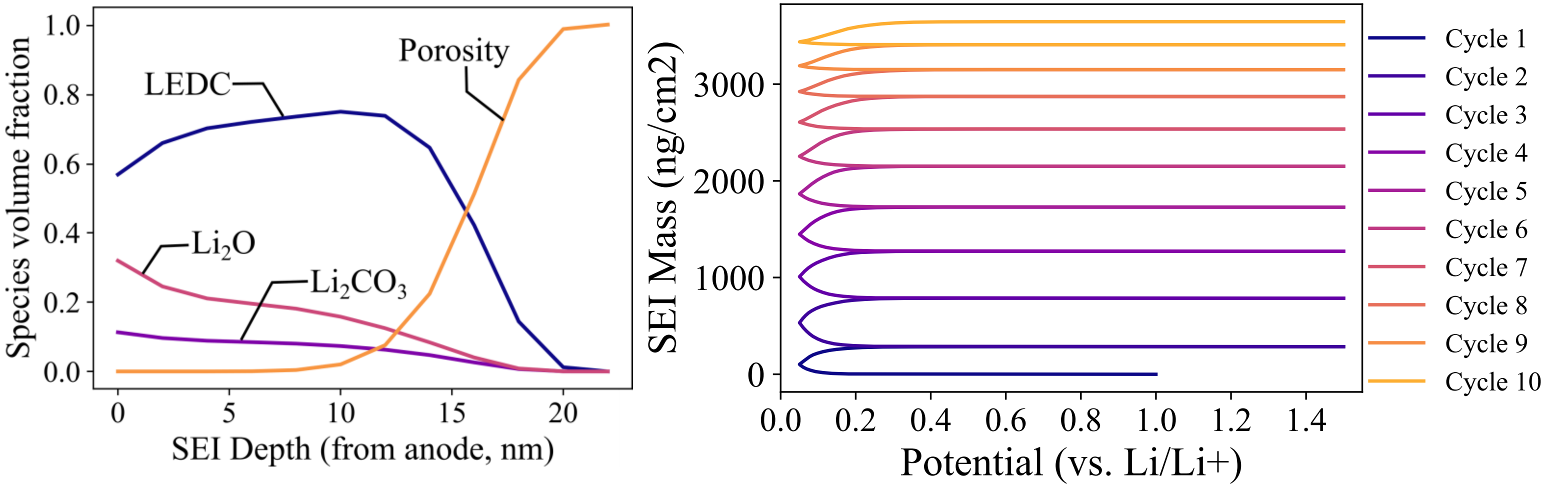
$$2\,\mathrm{Li}^{+}_{(\mathrm{elyte})} + 2\,\mathrm{EC} + 2\,\mathrm{e}^{-}_{(\mathrm{SEI})} \leftrightarrow \mathrm{Ethylene} + \mathrm{LEDC}_{(\mathrm{SEI})}$$

$$2\,\mathrm{Li}^{+}_{(\mathrm{elyte})} + 2\,\mathrm{EC} + 2\,\mathrm{e}^{-}_{(\mathrm{SEI})} \leftrightarrow \mathrm{Li_2CO_{3(SEI)}} + \mathrm{Ethylene}$$

$$2\,\mathrm{Li}^{+}_{(\mathrm{elyte})} + \mathrm{Li_2CO_{3(SEI)}} + 2\,\mathrm{e}^{-}_{(\mathrm{SEI})} \leftrightarrow 2\,\mathrm{Li_2O_{(SEI)}} + \mathrm{CO}$$

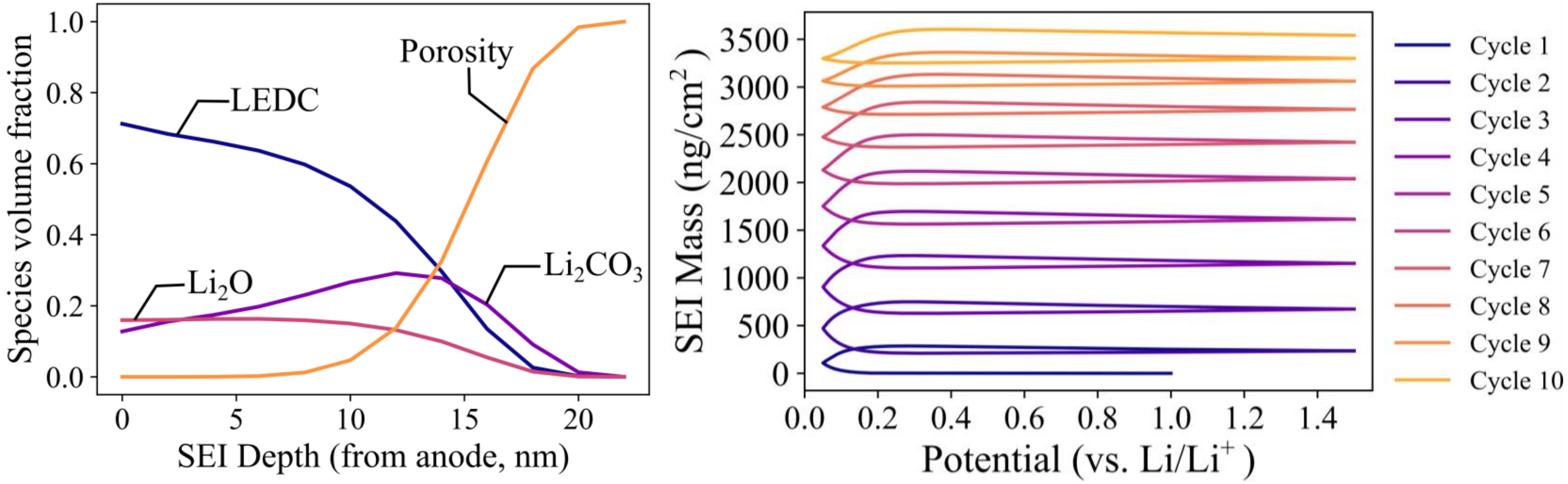
$$\mathrm{LEDC}_{(\mathrm{SEI})} + \mathrm{H_2O}_{(\mathrm{elyte})} \leftrightarrow \mathrm{Li_2CO_{3(SEI)}} + \mathrm{CO_2} + \mathrm{EG}$$

“Baseline” kinetics

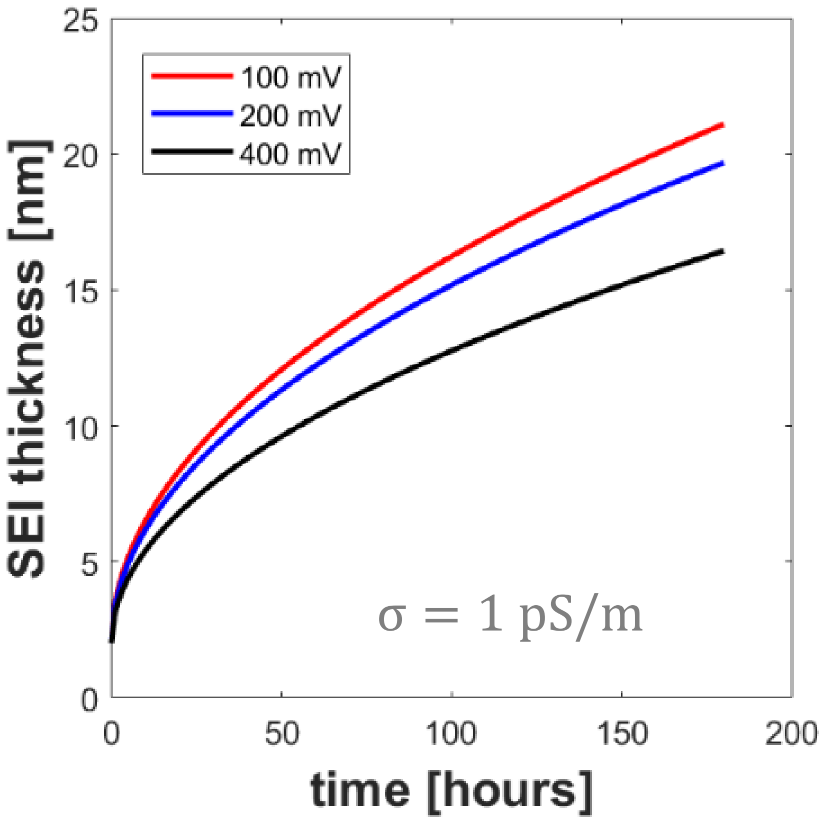


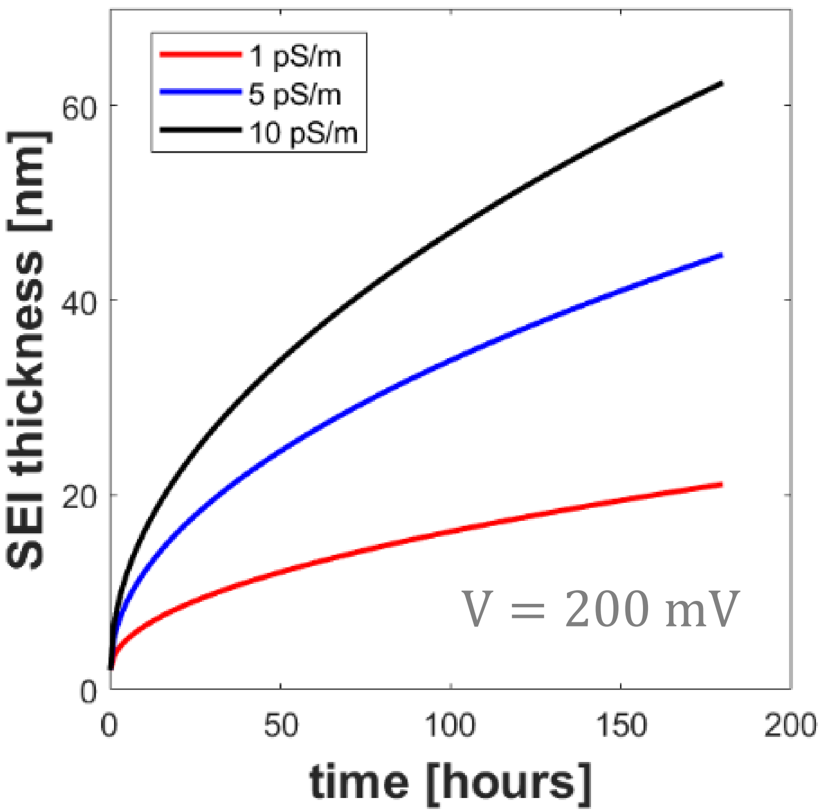
Kinetics shifted to favor Li2CO3, LEDC

- Profiles qualitatively match NR
- Predicted reaction front controlled by volume fraction and electron conduction.
- Passivation: reduced mass uptake with repeated cycling
- Varying kinetic parameters changes the composition, predicts SEI ‘breathing’ (mass uptake *and* loss during cycling)



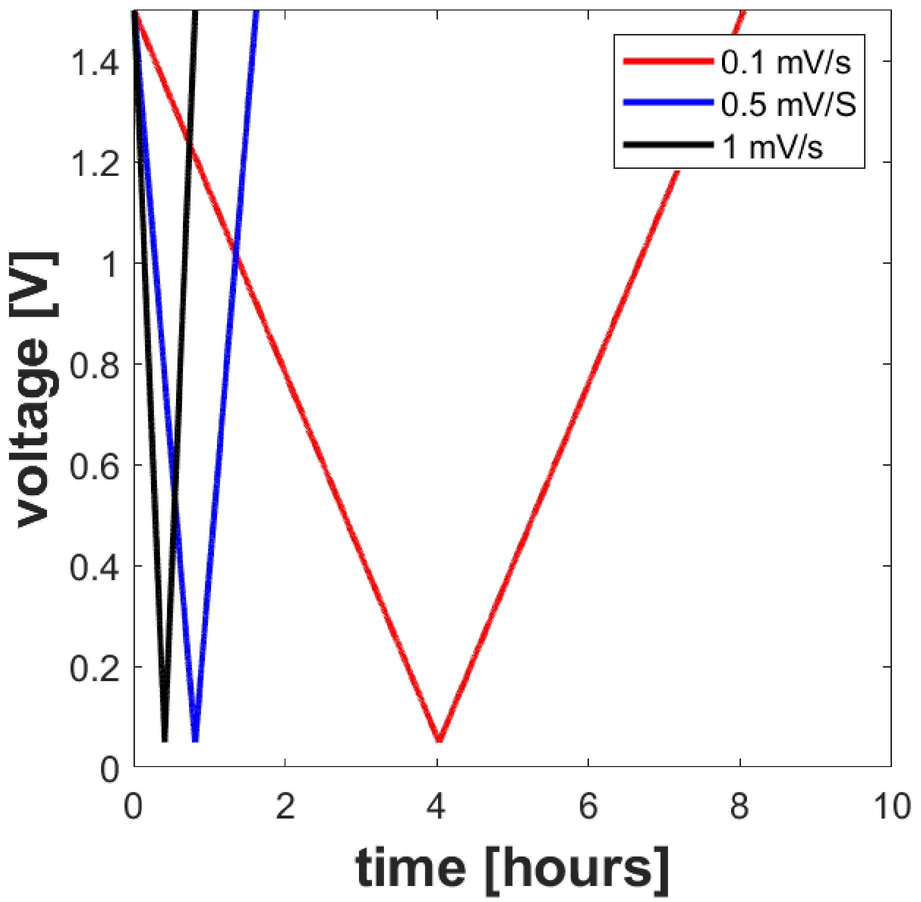
SEI Thickness Varies with Constant Voltage Hold Potential and SEI Conductivity

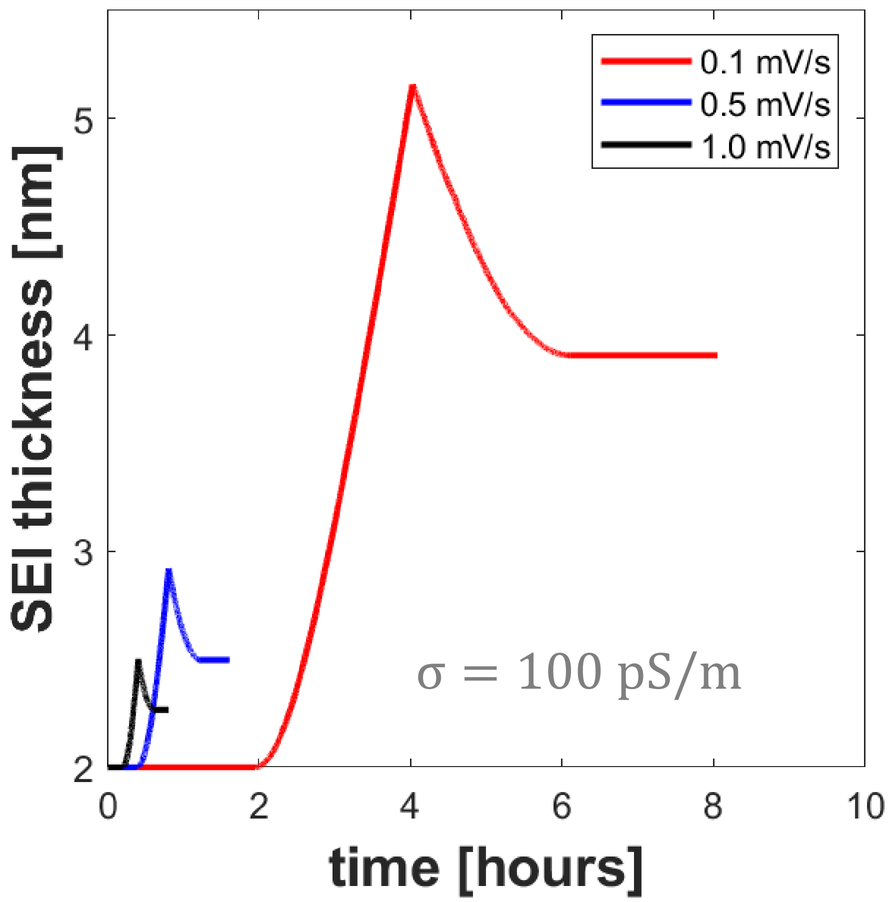




- Four-reaction SEI mechanism is used with electrolyte consisting of Li^+ in EC:EMC (~Gen 2 formulation).
- Low voltage holds (high SOC of Si) result in thicker SEI due to the high driving force for Li_2EDC formation
- Higher electronic conductivity of the SEI exacerbates the electronic current and drives faster SEI formation, which generates thicker SEI.

SEI Thickness Varies with Cycling and Shows Breathing Behavior

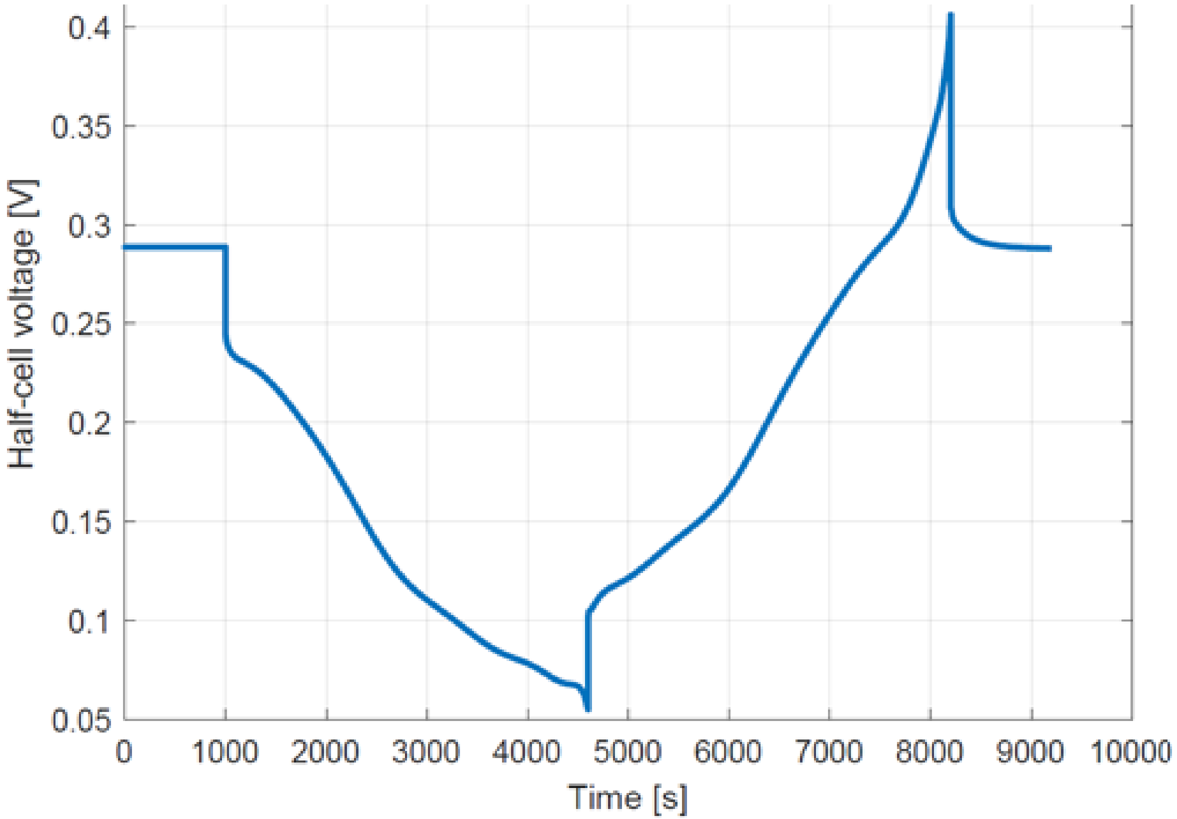




- Voltage scan between 1.5 V and 0.05 V at different scan rates of 0.1, 0.5, and 1 mV/s are simulated
- During charging, the SEI thickens because the electrolyte species reduces to solid-phase components
- Reversible solid-phase conversion reactions (e.g., $Li_2EDC \leftrightharpoons Li_2CO_3$, $Li_2CO_3 \leftrightharpoons Li_2O$) can explain breathing dynamics.

Continuum-Scale Model Using Detailed Atomistic-Scale Mechanism Under Development But Showing Promising Initial Results

Half-cell potential for Si during 1C charging and discharging



Ensuring continuum-scale temporal stability is nontrivial

- Complex reaction-pathway dependence
- Inherently small “radical” concentrations drastically change results
- Requires extremely tight absolute and relative solver tolerances.

Electrolyte reactions

- Homogeneous (primarily)
- Reduction due to free electron

SEI deposition/dissolution reactions

- To be informed by literature
- Propose single-species reactions

$$A(el) \rightleftharpoons A(sei)$$

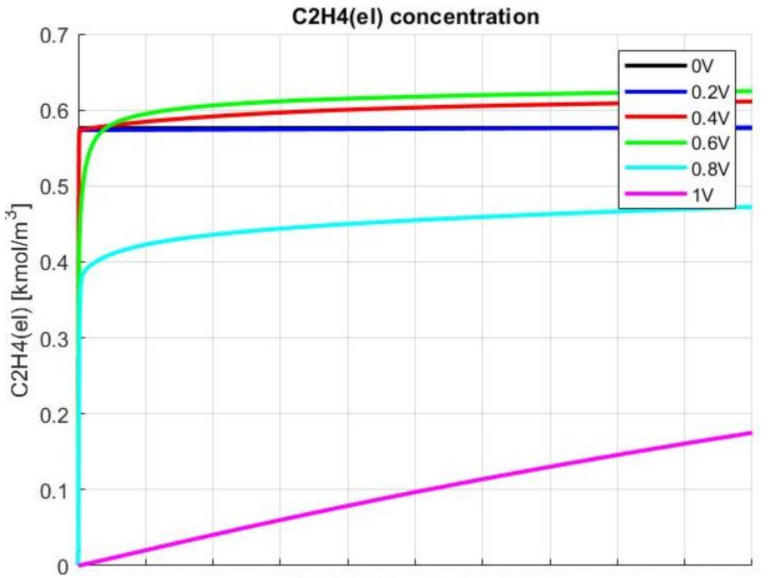
SEI homogeneous reactions

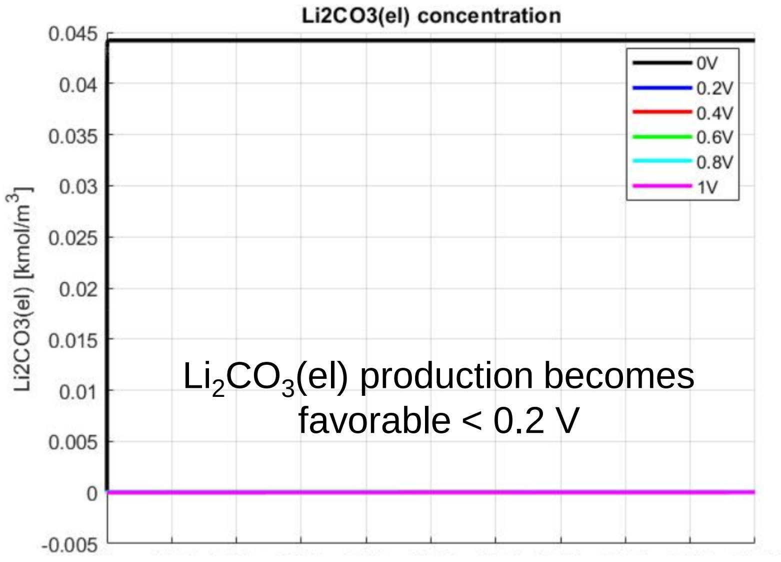
- Can produce SEI “breathing”
- To be informed by literature

Intercalation reactions (Si/electrolyte)

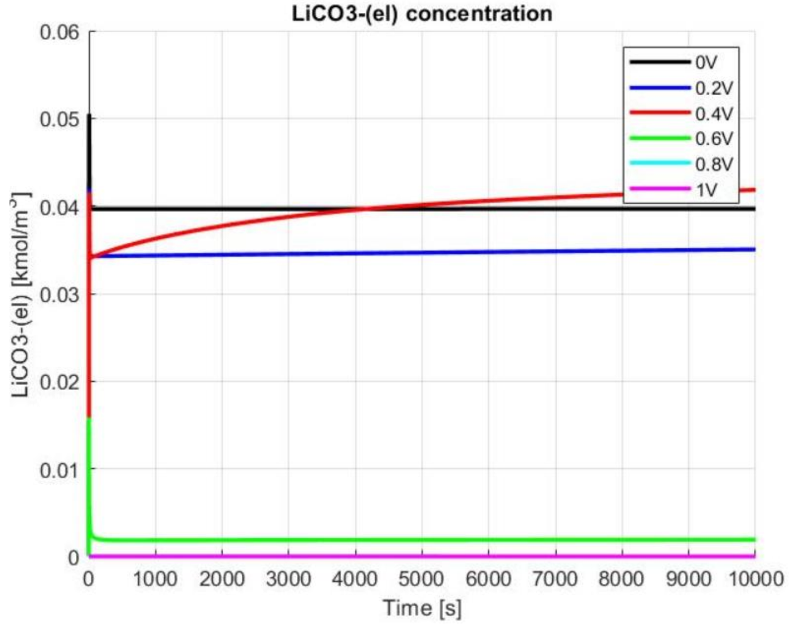
- Nonideal single-step reaction

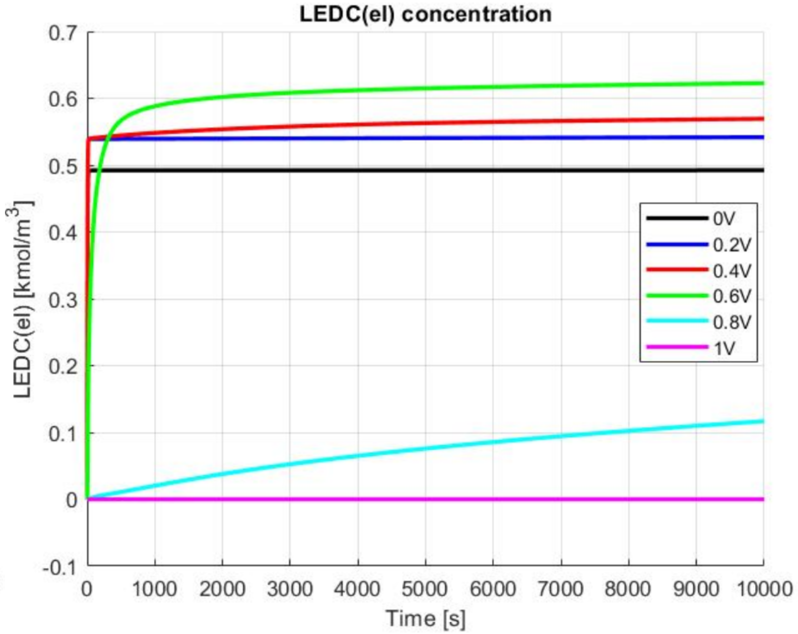
Atomistically Informed Continuum-level Model Predicts Voltage-dependent Electrolyte Decomposition





Li_2CO_3(el) production becomes favorable < 0.2 V





Mechanism description

- 19 species resolved
- 14 reactions
- Homogeneous electrolyte reactions
- Heterogeneous reduction reactions

Electrolyte species concentrations are a result of competing electrochemical and chemical reactions

Next step: Include reactions for deposition/dissolution of solid-phase species

Responses to Previous Year Reviewers' Comments

- Project has not been reviewed previously.

Collaboration and Coordination

Category	Institution	Role
National Laboratories	Lawrence Berkeley National Laboratory	Identify and computationally characterize most important atomistic SEI reaction mechanisms with high-throughput quantum chemistry, machine learning, and reaction network pathfinding
	Oak Ridge National Laboratory	Delineate SEI microstructure evolution and transport dynamics with anode-surface interactions at the atomistic scale
	Entire Si consortium project	The Si-HPC team regularly interacts with the entire Si consortium project to help advance the performance and understanding of Si
University	Colorado School of Mines	Continuum-level SEI model development and validation on non-intercalating anodes.

Remaining Challenges and Barriers

- Improve atomistically informed mechanism numerical stability
- Incorporate additional predominant SEI species to intermediate and atomistically informed mechanism
  - LiF formation, FEC decomposition, and potentially the influence of H_2O
- Include solid-decomposition and deposition/dissolution reactions to the atomistically informed mechanism
  - Example solid-decomposition reaction: $0.1\ \text{LiEDC (sei)} + \text{Li}^+ + e^- \leftrightharpoons 0.6\ \text{Li}_2\text{O(sei)} + 0.4\text{C}$
  - Example deposition/dissolution reaction: $\text{LiEDC(el)} \leftrightharpoons \text{LiEDC(sei)}$
- Experimental validation
  - Parasitic current at different voltage holds from calendar-life subgroup
  - SEI species composition as a function of voltage
- Implement Si-particle chemo-mechanical influences on SEI performance
- Further upscale electro-/chemically complex single-particle model to electrode-level model.

Proposed Future Research

- Incorporate additional predominant solid-phase SEI species and additional electrolyte decomposition
  - LiF(sei) and Li_2O(sei) formulation
  - Implement both literature- and atomistic-informed pathways
  - Incorporate FEC decomposition (atomistic mechanism considers EC decomposition)
- Experimentally validate the intermediate mechanism (simplified four-reaction mechanism)
  - Parasitic current at different voltage holds
  - SEI thickness changes (i.e., breathing) as a function of state of charge
- Experimentally validate the atomistically informed mechanism
  - Parasitic current and SEI thickness at different voltages
  - Relative SEI species concentrations
- Implement Si-particle chemo-mechanical influences on SEI performance
  - Incorporate finite-strain mechanics into SEI model
  - Collaborate with Si consortium mechanics group for model validation
- Develop pseudo-2D electrode-level battery model with chemically complex SEI and finite-strain mechanics.

Any proposed future work is subject to change based on funding levels.

Summary

- A continuum-scale SEI model is developed to understand fundamental Si-SEI passivation dynamics
  - The continuum-scale model is tightly coupled to the atomistic modeling at LBNL and ORNL
  - Three mechanism levels are explored (state-of-the-art, intermediate, and atomistically informed)
- The state-of-the-art mechanism from literature is used to initially validate the continuum-level model
  - Predicts bilayer structure due to LEDC(sei) decomposition reactions
  - Predicts square root of time SEI growth (i.e., no breathing)
- The intermediate mechanism (four reactions with three solid-phase species) predicts important Si-SEI dynamics
  - Predicts that SEI growth depends on voltage, similar to experimental measurements
  - Indicates that SEI growth is highly dependent on SEI conductivity
  - Simulates breathing mechanics due to solid-phase decomposition reactions
- The atomistically informed mechanism is being developed and showing promising initial results
  - Directly upscales atomistically informed reactions
  - Requires tight collaboration with atomistic modeling groups (LBNL and ORNL)
- Future/continuing work
  - Add additional species and couple complex SEI chemistry with finite-strain chemo-mechanics.

Any proposed future work is subject to change based on funding levels.

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Thank You

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Technical Back-Up Slides

The Continuum-Level SEI Model Considers Complex Chemical Reactions and Conserves Charge and Species

- *Species Conservation in Electrolyte Phase*

$$\frac{\partial(\varepsilon c_{e,k})}{\partial t} = \frac{\partial}{\partial x}\left(D_{e,k}^{eff}\left[\frac{\partial c_{e,k}}{\partial x} + \frac{z_{e,k}Fc_{e,k}}{RT}\frac{\partial \phi_e}{\partial x}\right] - c_{e,k}u\right) + a_s\dot{s}_{e,k} + \dot{\omega}_{e,k},\ k = \mathrm{Li}^+, \mathrm{PF}_6^-, \mathrm{EC}, \mathrm{EMC}, \mathrm{FEC}, \mathrm{H}_2 0 \ldots$$

- *Charge Conservation in Electrolyte Phase*

$$\frac{\partial}{\partial x}\sum_{ions}\left(z_{e,k}D_{e,k}^{eff}\left[\frac{\partial c_{e,k}}{\partial x} + \frac{z_{e,k}Fc_{e,k}}{RT}\frac{\partial \phi_e}{\partial x}\right]\right) = -\sum_{ions}\left(z_{e,k}a_s\dot{s}_{e,k}\right)$$

- *Mass Conservation of Solid Phase*

$$\frac{\partial \varepsilon_{s,k}}{\partial t} = V_{s,k}a_s\dot{s}_{s,k} + V_{s,k}\dot{\omega}_{s,k} - \frac{\partial}{\partial x}\left(\varepsilon_{s,k}\nu\right)\ ,\ \varepsilon = 1 - \textstyle\sum_i \varepsilon_{s,k}$$

- *Species Conservation in SEI Solid Phase*

$$\frac{\partial(\varepsilon_s c_{s,k})}{\partial t} = \frac{\partial}{\partial x}\left(D_{s,k}^{eff}\left[\frac{\partial c_{s,k}}{\partial x} + \frac{z_{s,k}Fc_{s,k}}{RT}\frac{\partial \phi_s}{\partial x}\right] - c_{s,k}\nu\right) + a_s\dot{s}_{s,k} + \dot{\omega}_{s,k},\ \ k = \mathrm{Li_2CO_3}, \mathrm{LiF}, \mathrm{LiEDC}, \mathrm{LiF}, \mathrm{Li}^+ \ldots$$

- *Charge Conservation in SEI Solid Phase*

$$\frac{\partial}{\partial x}\sum_{ions}\left(z_{s,k}D_{s,k}^{eff}\left[\frac{\partial c_{s,k}}{\partial x} + \frac{z_{s,k}Fc_{s,k}}{RT}\frac{\partial \phi_s}{\partial x}\right]\right) = -\sum_{ions}\left(z_{s,k}a_s\dot{s}_{s,k}\right)$$

The Continuum-Level SEI Model Considers Complex Chemical Reactions and Conserves Charge and Species

Reaction Kinetics

$$\Delta G^{rxn} = \Delta H^{rxn} - T\Delta S^{rxn}$$

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

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

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

Silicon Anode Species and Charge Conservation

$$\frac{\partial c_{Li}}{\partial t} = \frac{\partial}{\partial x}\left(D_{Li}\frac{\partial c_{Li}}{\partial x}\right), \quad \sigma_{Si}\frac{\partial^2 \phi_S}{\partial x^2} = 0$$

CANTERA is used to handle complex reaction mechanisms

A Continuum-Scale, Pseudo-Perfectly Stirred Reactor Model Determines the Atomistic-Scale Mechanism Stability

Concentration

$$\frac{\partial [X_k]}{\partial t} = \dot{\omega}_k$$

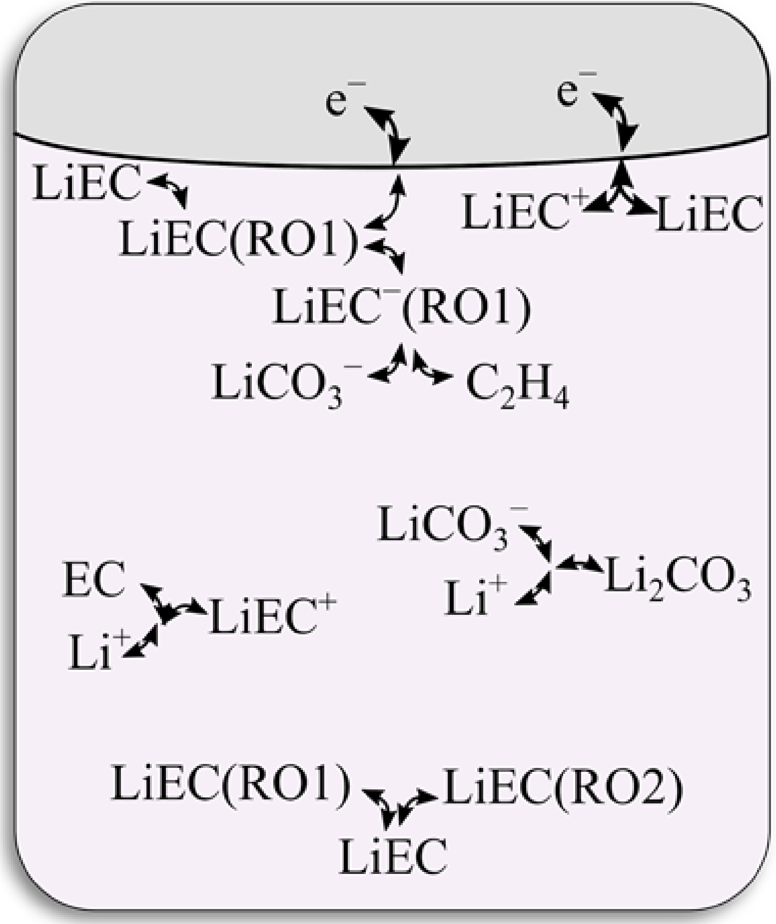
Net production rate

Surface production

$$\dot{\omega}_k = \sum_{i}^{\text{Homo}} \dot{\omega}_{i,k} + \sum_{i}^{\text{Hetero}} \dot{s}_{i,k} A_\text{s}$$

Bulk production

Specific area



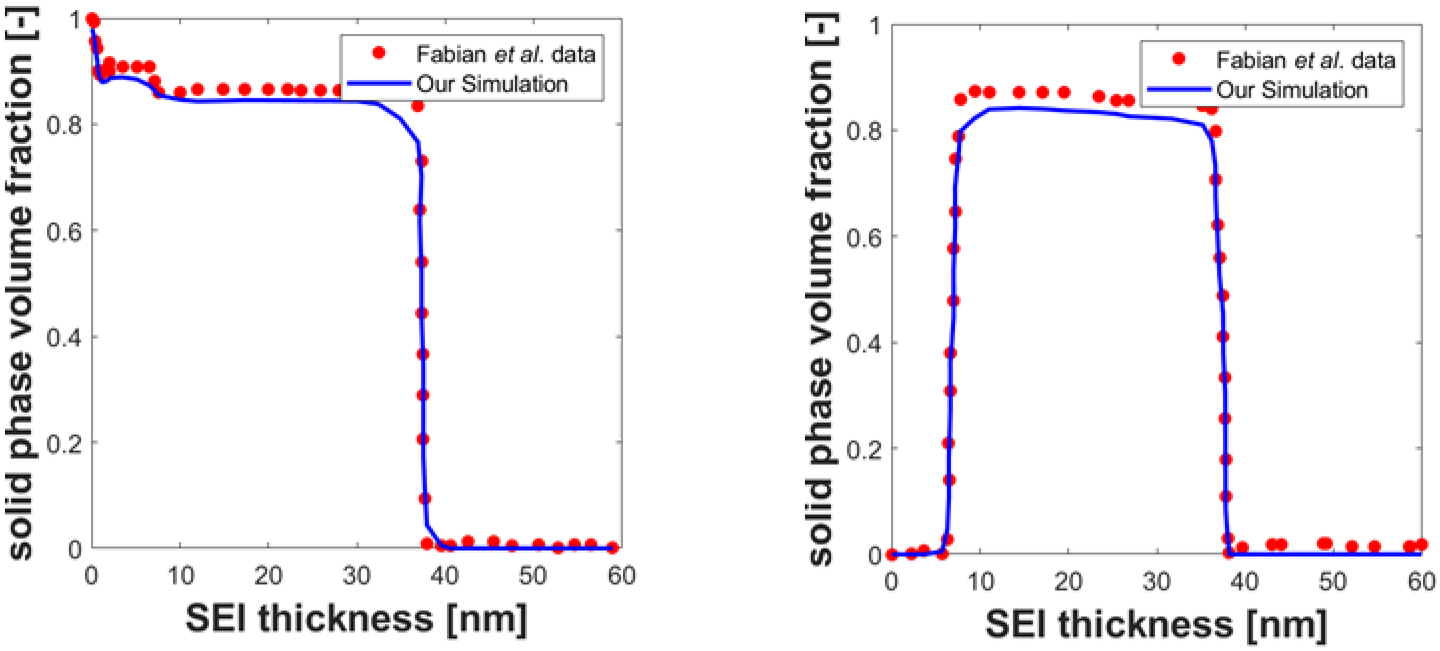
The pseudo-perfectly stirred reactor model tests continuum-level stability before considering transport and SEI deposition/dissolution effects

The Continuum-Level Model Developed at NREL Is Validated Using a Published Mechanism for SEI Growth

Our model is written in a flexible computational framework to allow for much more complicated reaction mechanisms

$$2\mathrm{EC} + 2 \cdot (\mathrm{Li}^+ + e^-) \rightarrow \mathrm{Li_2EDC} + R$$

$$0.1\mathrm{Li_2EDC} + \mathrm{Li}^+ + e^- \rightarrow \quad 0.6\mathrm{Li_2O} + 0.4\mathrm{C}$$



F. Single, et al., *J. Electrochem. Soc.*, 164:E3132-E3145, 2017

The Atomistic Model and Continuum-Level Models Use Different Theory for Electrochemical Reaction Kinetics

Bulk reactions (non-electrochemical reactions)

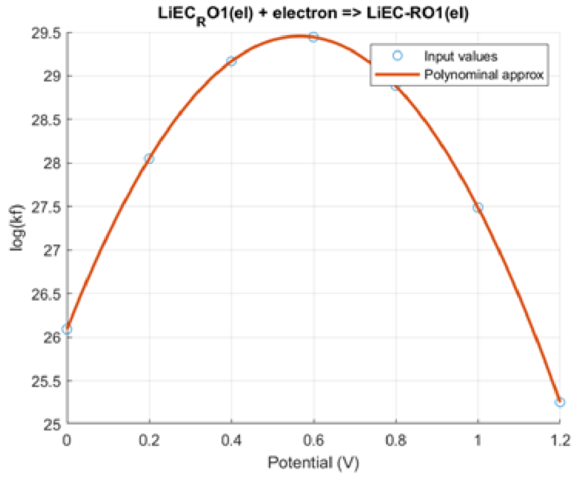
- Implement transition state thermo (currently working and stable at continuum scale)
- Double-checked reverse rates based on microscopic reversibility.

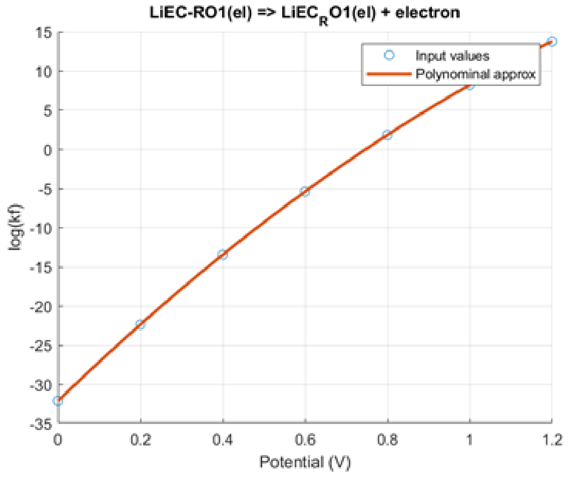
Electrochemical reactions

- Initially not stable at continuum (resulted in realizing difference in theory)
- Atomistic model implements fundamental Marcus theory
  - Incorporates electrostatic potential directly in species thermo

$$k_{\mathrm{f}} = \frac{k_{\mathrm{B}}T}{h}\exp\left(\underbrace{\frac{\lambda}{4}\left(1+\frac{\Delta G}{\lambda}\right)^2}_{\Delta G^{\star}_{\mathrm{eff}}}\frac{1}{k_{\mathrm{B}}T}\right) \qquad k_{\mathrm{f}} = k_{\mathrm{f}}^{\mathrm{t}}\exp\left(-\beta\sum_{k=1}^{K}\frac{\nu_k z_k F\Phi_k}{RT}\right)$$

- Butler—Volmer (native Cantera) is a linear realization of Marcus theory.





Atomistic model forward rates are interpolated using quadratic polynomials

- Continuum-scale model forward rates are overwritten based on polynomials
- Continuum-scale mechanism is stable in homogeneous reactor code!