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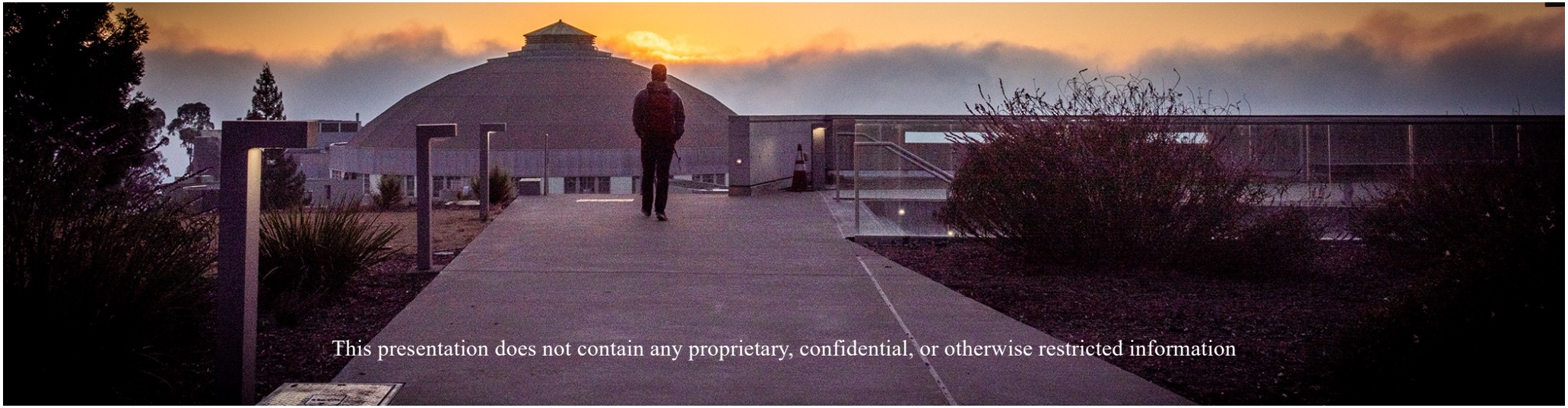
Integrated Modeling and Machine Learning of Solid-Electrolyte Interface Reactions of the Si Anode

Principal Investigator: Kristin A. Persson

Principal Investigator, Project ID BAT501

The Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California 94720



This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- November 1st 2019 - September 30st 2022.
- Percent complete: **90%**

Barriers

- Silicon (Si) has limited lifetime, preventing commercialization.
- Solid electrolyte interface (SEI) growth leads to loss of lithium inventory.
- Engineering Si SEI formation and properties via novel electrolytes requires understanding the SEI reaction mechanisms

Budget

- Funding for FY 20: $650K
- Funding for FY 21: $650K
- **Funding for FY 22: $650K**

Partners

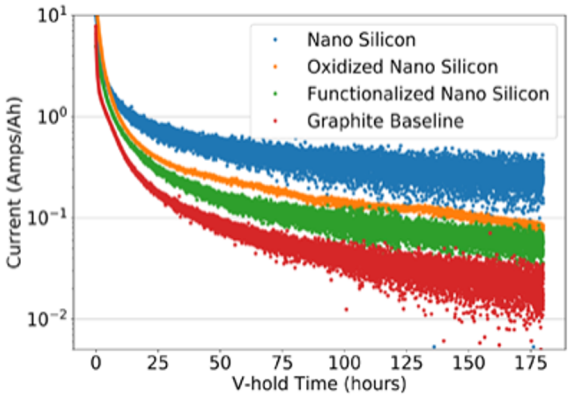
- Oak Ridge National Laboratory
- National Renewable Energy Laboratory
- Colorado School of Mines

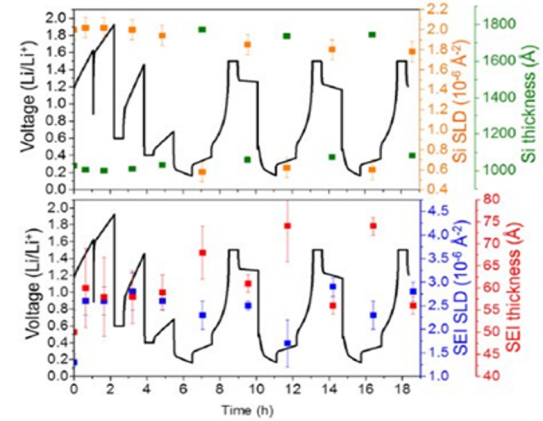
Support for this work from the Office of Vehicle Technologies, DOE-EERE, is gratefully acknowledged – Brian Cunningham

Relevance

- Silicon/NMC Performance Targets
  - Cell Level Energy Density: >350 Wh/kg, 750 Wh/L
  - Calendar Life: >5 years
  - Cycle Life: >1000 cycles
- Current Si anodes show calendar and to a lesser extent cycle life (1000-2000 cycles) limitations.
- Parasitic currents due to unabated SEI growth **from both chemical and mechanical instability lead to loss of lithium inventory**.

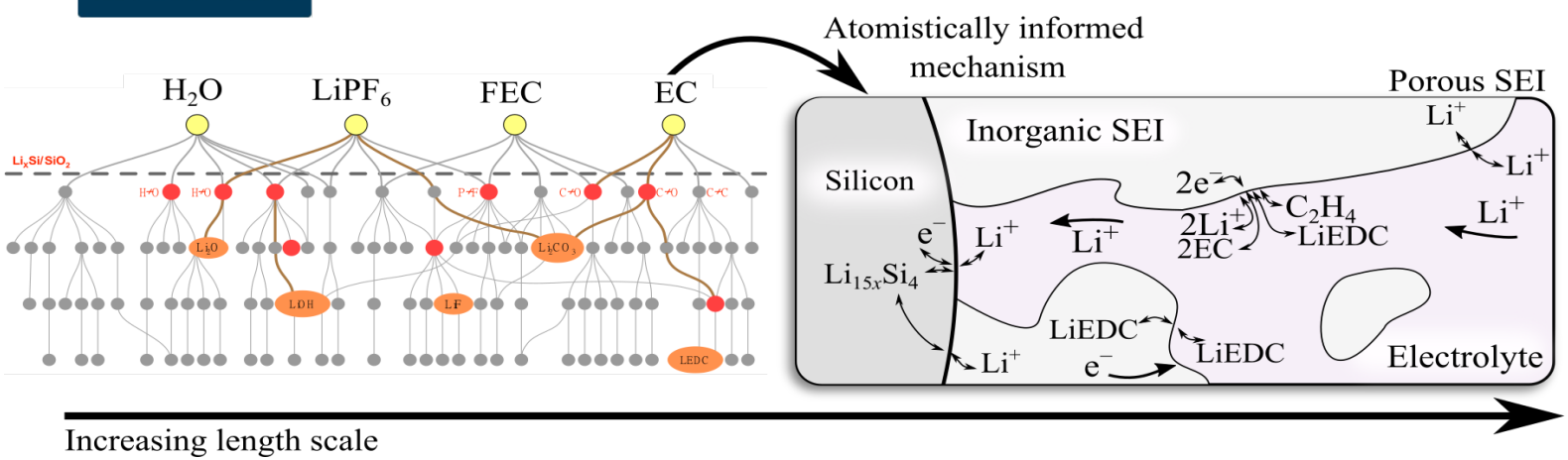
SEI film growth mechanisms and composition variations can be determined through coupled computational models bridging atomistic to continuum scales and give insights into novel Si electrolyte formulations for stable film growth.





Silicon Consortium Datasets

Computational model collaboration bridges length and time scales to simulate SEI dynamics

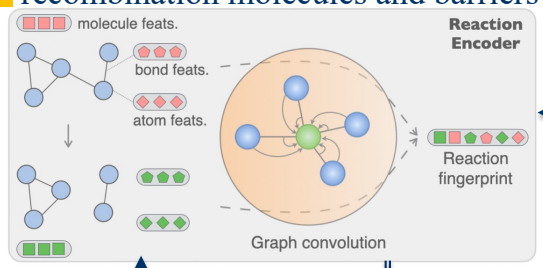


Atomistic simulations, machine learning, and reaction networks identify and characterize the paths and mechanisms that form key SEI species

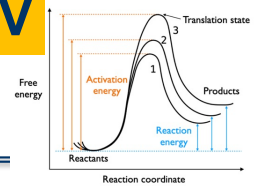
Continuum modeling incorporates atomistically predicted mechanisms and is experimentally validated to identify strategies for stable SEI growth

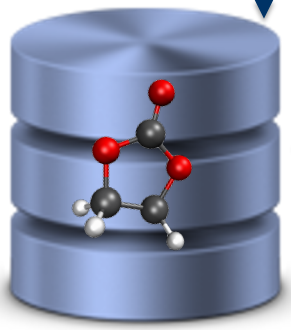
A Massive Framework to automatically explore millions of possible SEI reactions

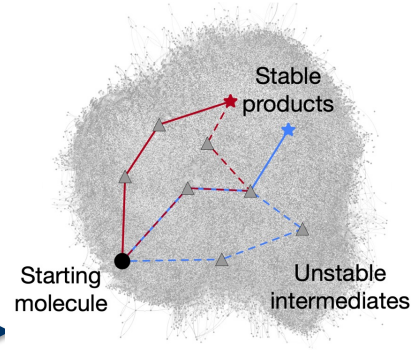
II ML to reduce target fragments, recombination molecules and barriers

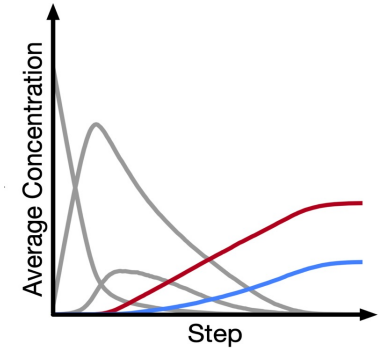


IV Transition states (Schrodinger Inc.)

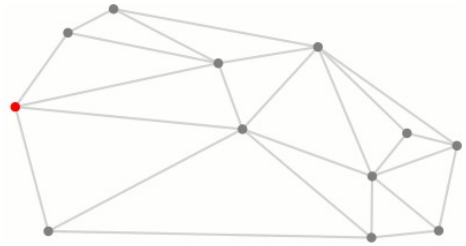




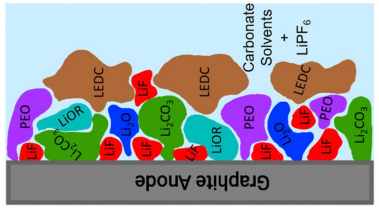




I High-performance computing



III Analyses of reaction network



V Microkinetic models

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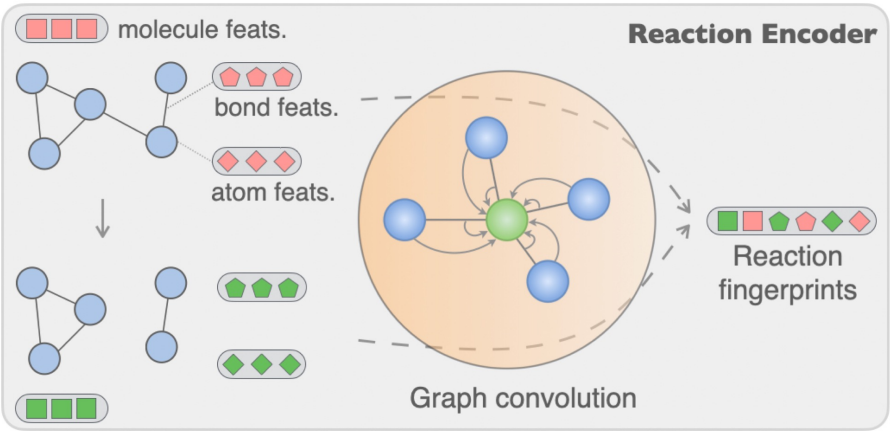
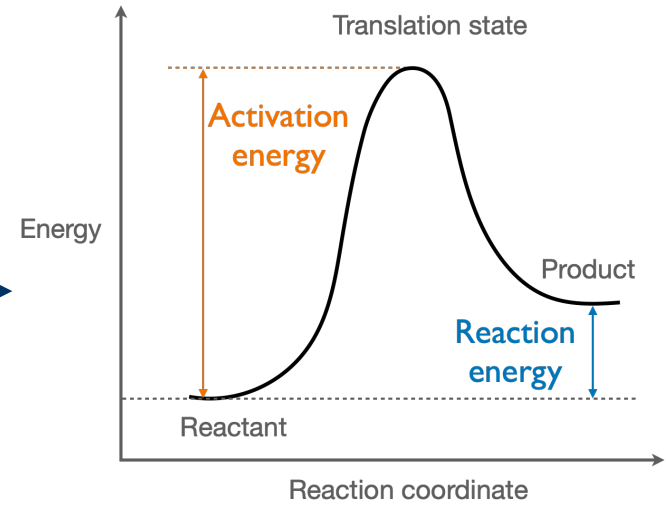
Accelerating discovery of reaction mechanisms via machine learning

- Goal: leverage machine learning surrogate models to pinpoint the chemical reaction space that needs further investigation
  - ✓ Rapid estimation of reaction thermodynamic and kinetic properties
  - ✓ Identifying thermodynamically and kinetically favorable molecules formed via recombination



Chemical reaction 'fingerprinting' using a graph convolutional neural network that maps a reaction energy to its fingerprints.

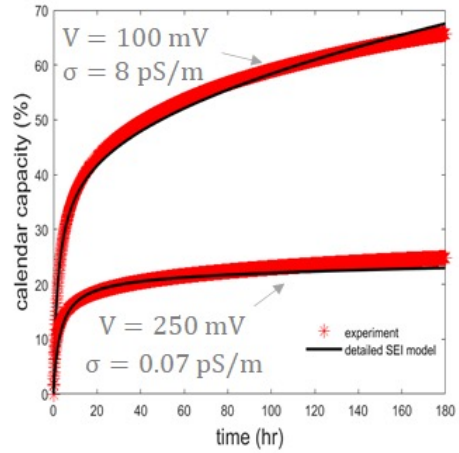


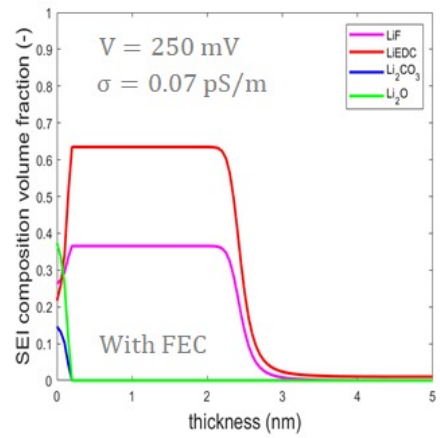
Approximation of chemical reaction properties – reaction energy and activation energy – from fingerprints.

Global and atomistic reaction mechanisms to simulate SEI formation at the continuum scale

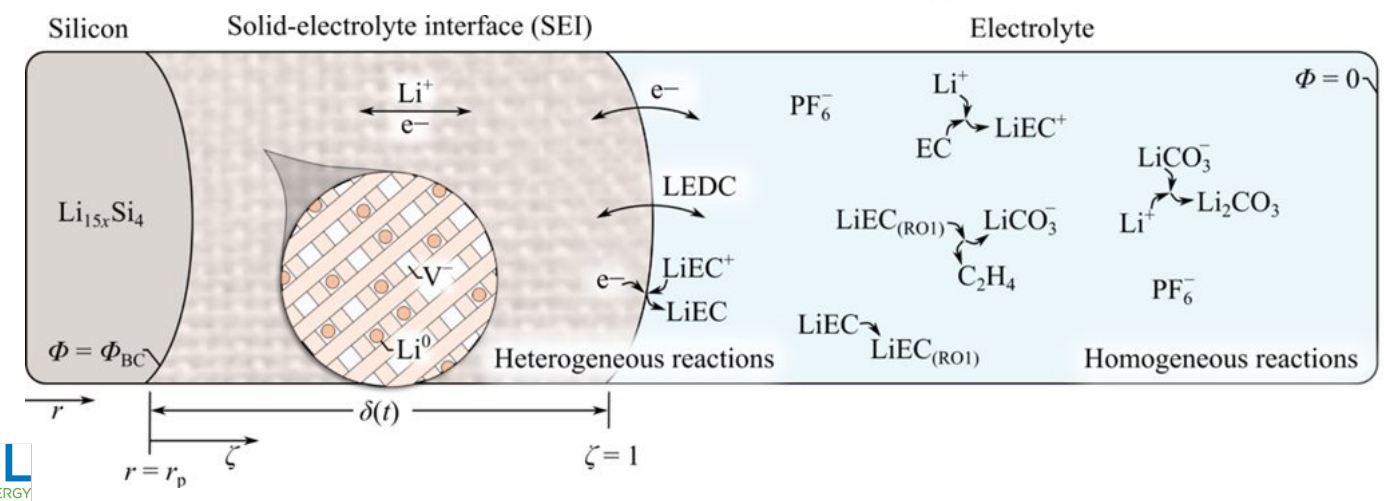
Global Reaction Pathway

1. $2EC + 2(Li^+ + e^-) \leftrightarrow LEDC + C_2H_4(g)$
2. $EC + 2(Li^+ + e^-) \leftrightarrow Li_2CO_3 + C_2H_4(g)$
3. $0.1Li_2EDC + (Li^+ + e^-) \leftrightarrow$
   $0.6Li_2O + 0.2C + 0.1C_2H_4$
4. $Li_2CO_3 + 2(Li^+ + e^-) \leftrightarrow 2Li_2O + CO$
5. $FEC + (Li^+ + e^-) \leftrightarrow LiF + VC + 0.5H_2$



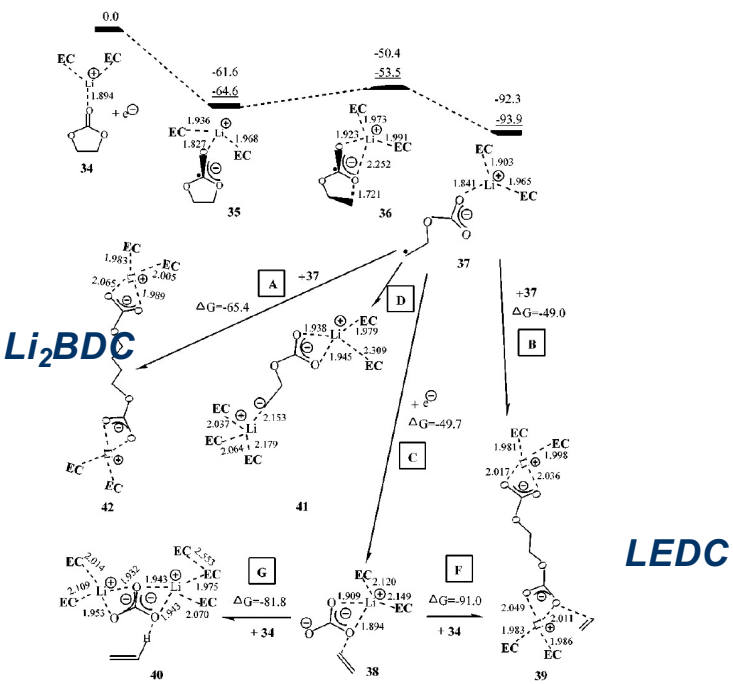


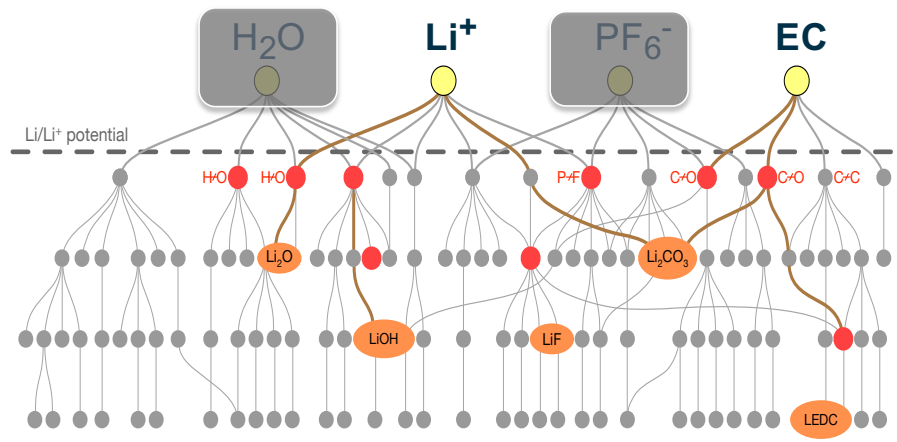
Atomistic Reaction Pathway



Predicts SEI species composition, film thickness, leakage currents

Automatic retrieval of electrochemical reduction pathways of Li^+-EC to LEDC





Constructed network with ***6000 species, 4.5 mil. Reactions***

First electrochemical reaction network

By far the largest electrochemical network ever reported

Li, T. & Balbuena, P. B. Theoretical studies of the reduction of ethylene carbonate. Chem. Phys. Lett. 317, 421–429 (2000).; Wang, Y. X., Nakamura, S., Ue, M. & Balbuena, P. B. Theoretical studies to understand surface chemistry on carbon anodes for lithium-ion batteries: reduction mechanisms of ethylene carbonate. J. Am. Chem. Soc. 123, 11708–11718 (2001).

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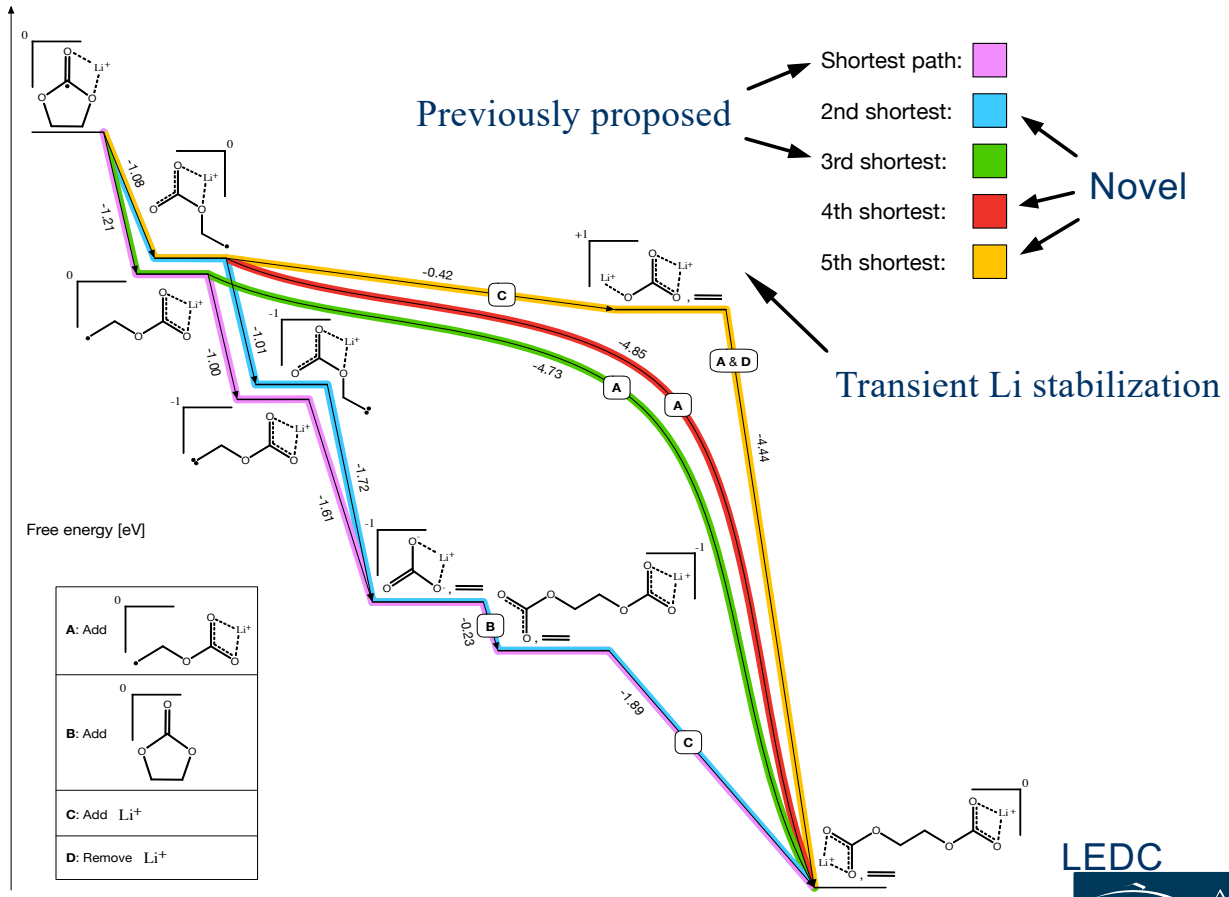
Automatic retrieval of electrochemical reduction pathways of Li^+-EC to LEDC

- Identified pathways to well-studied SEI product lithium ethylene dicarbonate (LEDC)
- Recovered expert-proposed pathways
- Proposed novel but chemically reasonable paths



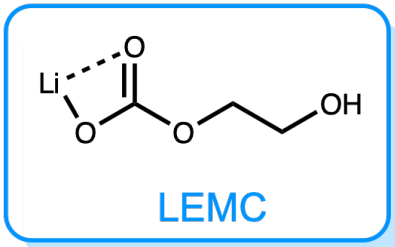
Balbuena 2001 JACS ; Balbuena 2000 Chem Phys Lett paper, 1997 J Phys Chem B paper Alex Schechter ; 2017 Stephen E. Burkhardt; J. Electrochem. Soc. and Blau, **K. A. Persson** et al., *Chem. Sci.*, 2021

Major SEI organic component LEDC questioned

nature chemistry
ARTICLES
https://doi.org/10.1038/s41557-019-0304-z

Identifying the components of the solid-electrolyte interphase in Li-ion batteries

Luning Wang[1], Anjali Menakath[2], Fudong Han[3], Yi Wang[1], Peter Y. Zavalij[1], Karen J. Gaskell[1], Oleg Borodin[4], Dinu Iuga[2], Steven P. Brown[2], Chunsheng Wang[1,3]*, Kang Xu[4]* and Bryan W. Eichhorn[1]*



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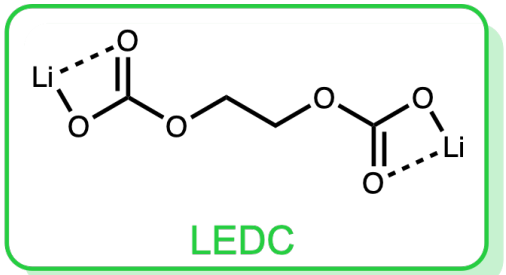
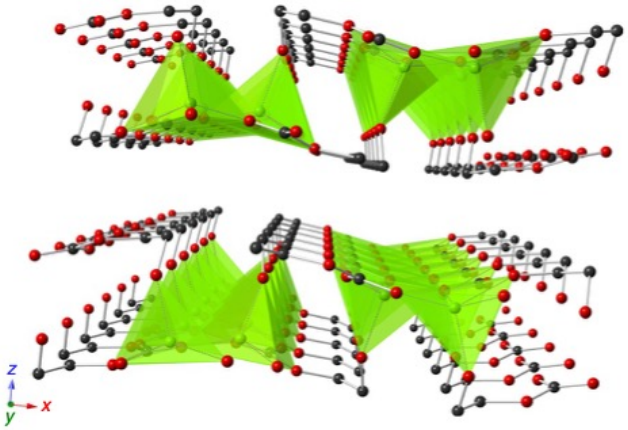


Despite decades of work, the identity of the major organic component of the Li-anode SEI is still controversial

…synthesis and structural and spectroscopic characterizations of authentic LEDC and lithium ethylene mono-carbonate (LEMC)

FTIR, 1D and 2D solution and solid-state NMR spectroscopy suggest that common LEDC standards are composed of lithium ethylene monocarbonate (LEMC).



Nature Chem., **2019**, 11, 789-796

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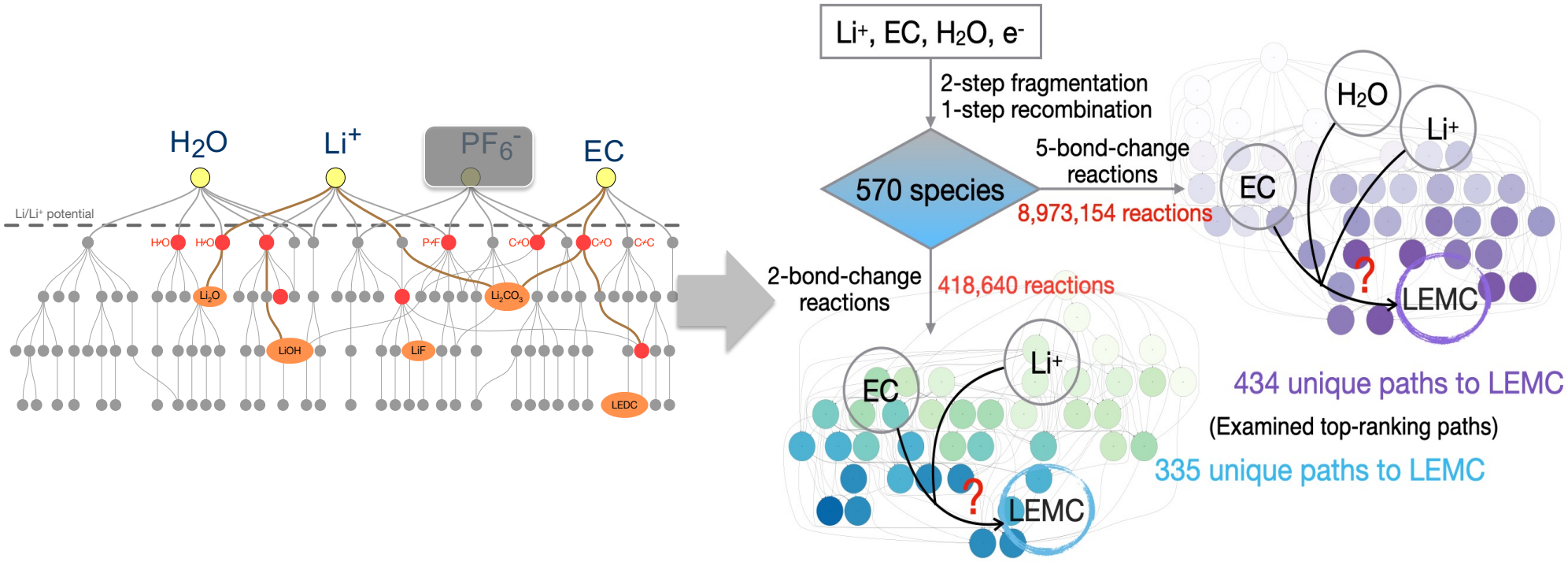
Using the Data-Driven First-principles Framework to track all reactions to LEMC

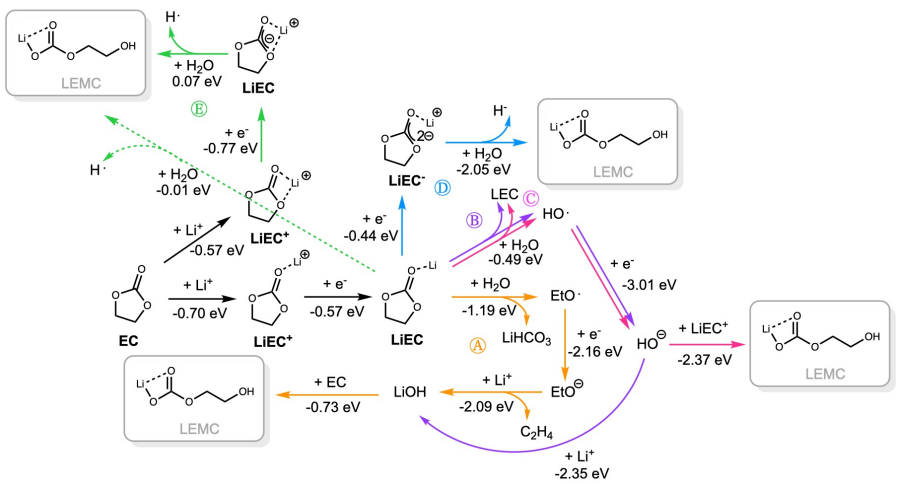


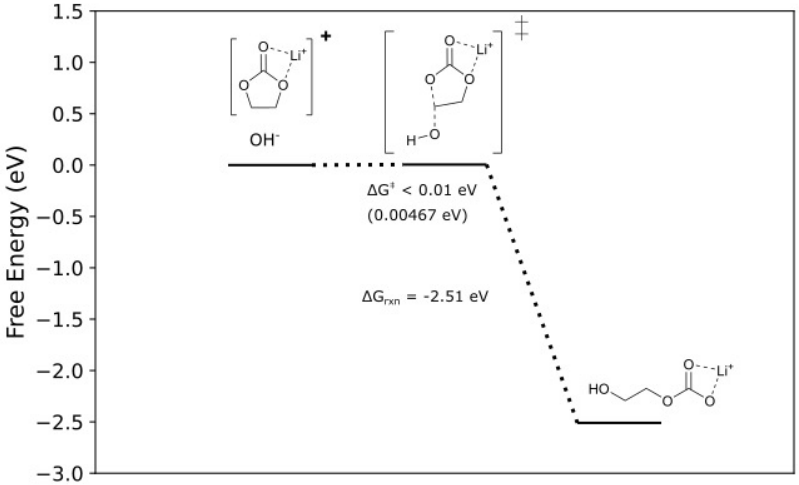
Xiaowei Xie, Evan Walter Clark Spotte-Smith, Mingjian Wen, Hetal D. Patel, Samuel M. Blau, and Kristin A. Persson, **JACS 2021** *143* (33), 13245-13258, DOI: 10.1021/jacs.1c05807

Overwhelming majority of reaction pathways to LEMC involve *water*

LEMC:

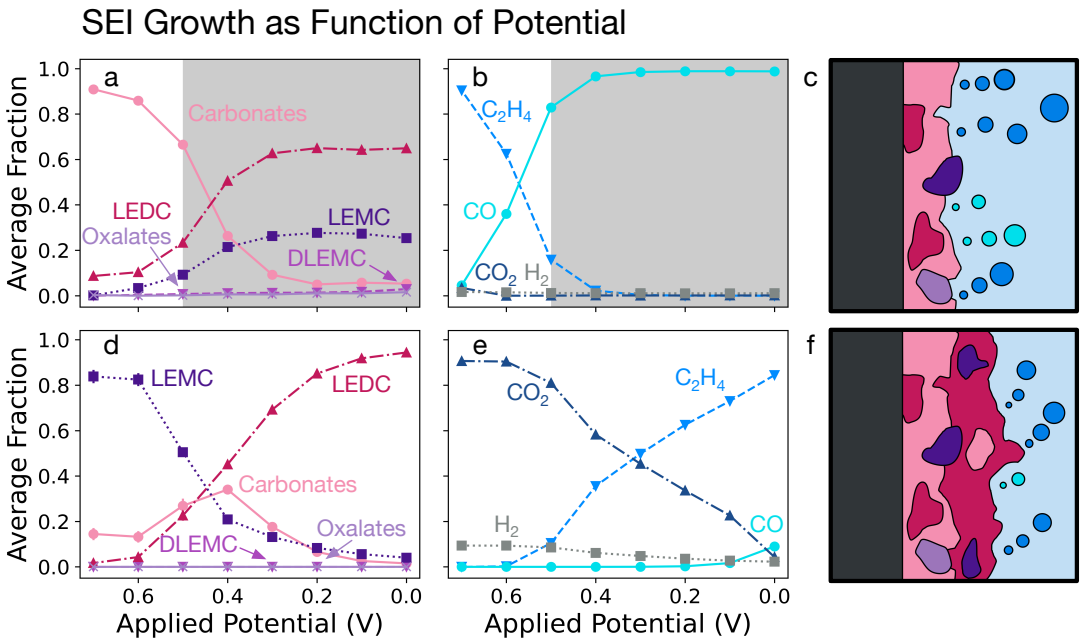
- Thermodynamically feasible, possible product in SEI
- Mechanistic explanations (confirming hypotheses from Nat. Chem paper) but also novel pathways
- Over 400 unique pathways identified but all but 8 involve hydrolysis hence water was found to be essential for LEMC formation and/or conversion of LEDC.



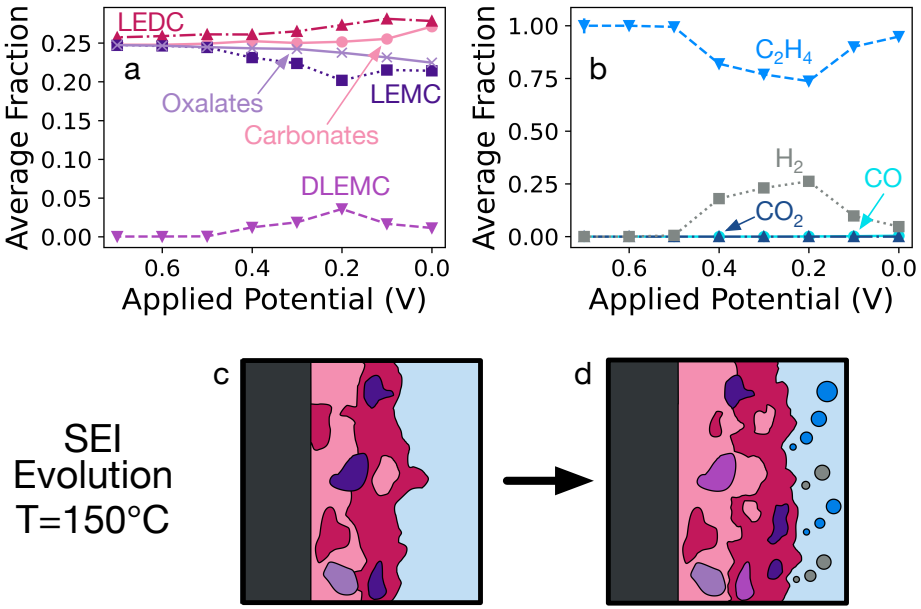


Xiaowei Xie, Evan Walter Clark Spotte-Smith, Mingjian Wen, Hetal D. Patel, Samuel M. Blau, and Kristin A. Persson, **JACS 2021** *143* (33), 13245-13258, DOI: 10.1021/jacs.1c05807

Recovers Peled Bilayer SEI Model without any Fitted Parameters



Recovers and explains the Peled bilayer structure of the SEI without any fitted parameters



Using accelerated simulations at elevated temperature, observe electrochemical instability and decomposition of lithium ethylene dicarbonate (LEDC), lithium ethylene monocarbonate (LEMC)

Spotte-Smith, E.W.C., Kam, R.L., Barter, D., Xie, X., Hou, T., Dwaraknath, S., Blau, S.M., **Persson, K.A.**, *ACS Energy Letters*, **2022.**

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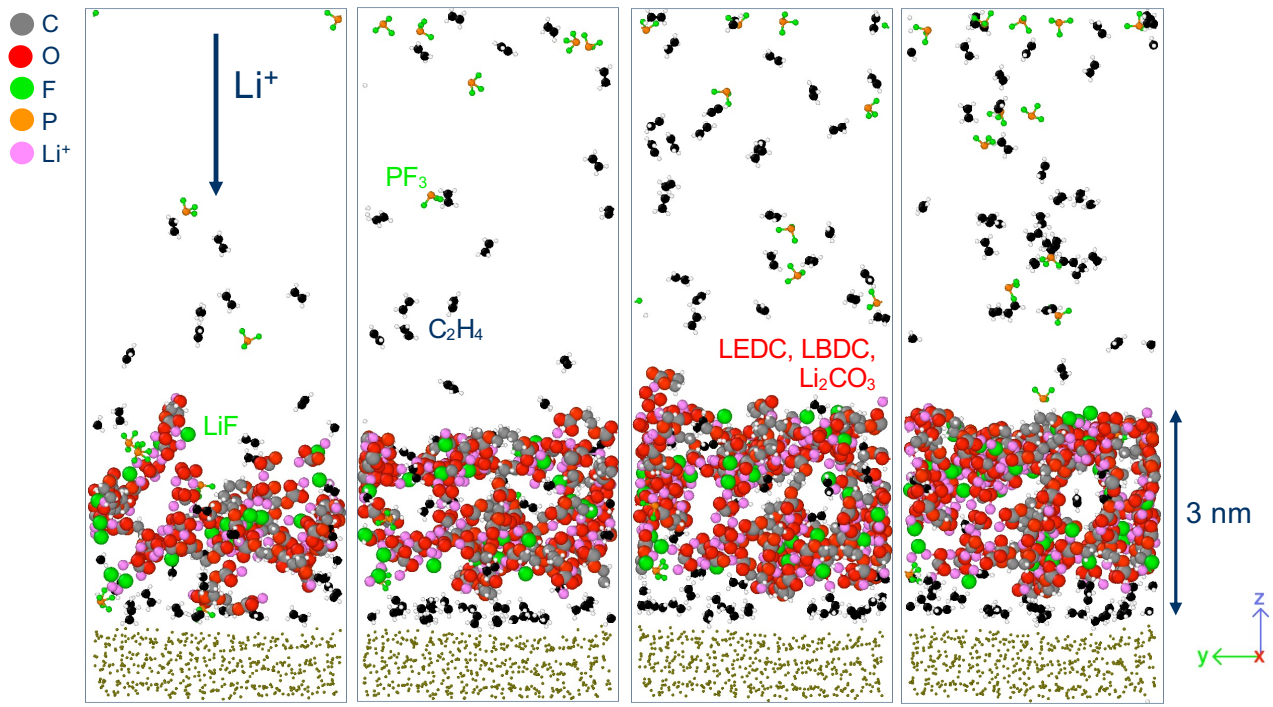
Accelerated molecular dynamics (MD) with reactions enables observation of SEI formation

- Classical MD + templates describing each reaction (pre and post topologies), as implemented in LAMMPS
- Force-field information is updated when a reaction happens: geometries, bonds, charges and non-bonded parameters
- Take solvation and residence times into account.
- Rates are accelerated



- Model: liquid mixture of 1M $LiPF_6$/EC + amorphous silicon anode
- 12 reactions (9 for EC, 3 for PF_6 decomposition)

OAK RIDGE National Laboratory

L. Alzate-Vargas, S.M. Blau, E.W.C. Spotte-Smith, S. Allu, K.A. Persson, and J.-L. Fattebert, The Journal of Physical Chemistry C (2021)

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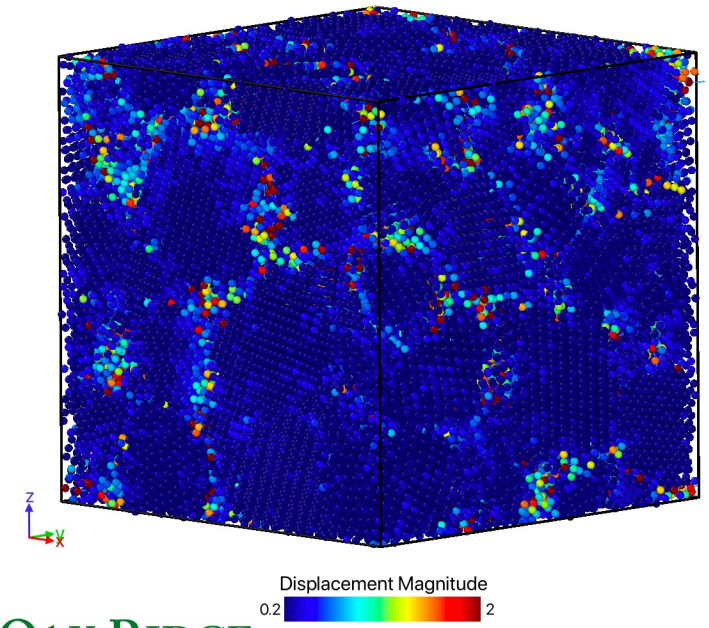
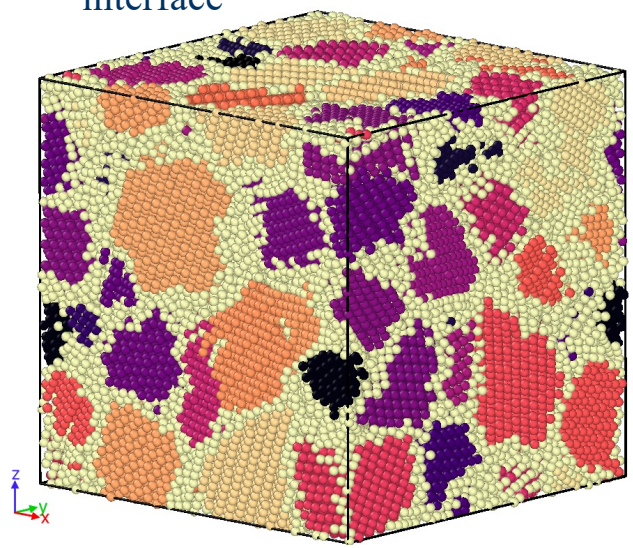
Modeling diffusion and ionic conduction in SEI using polycrystalline LiF surrogate

Displacement magnitude of lithium ions after 10 ns



Grain boundaries vs. bulk using local measure of ordering: Atoms in light yellow are boundaries or interface



Atoms with larger displacement are at grain boundaries

Size (nm)	Number of grains	D_{Li} (m^2/s)	σ_{Li} (S/cm)
10	8	6.1×10^{-15}	2.1×10^{-5}
10	64	1.1×10^{-14}	3.7×10^{-5}
15	8	3.3×10^{-15}	1.2×10^{-5}

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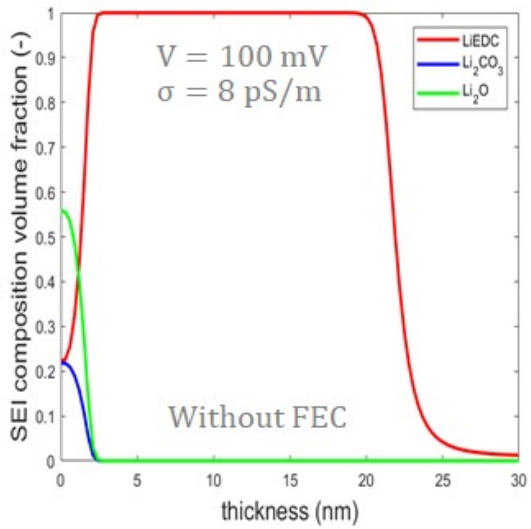
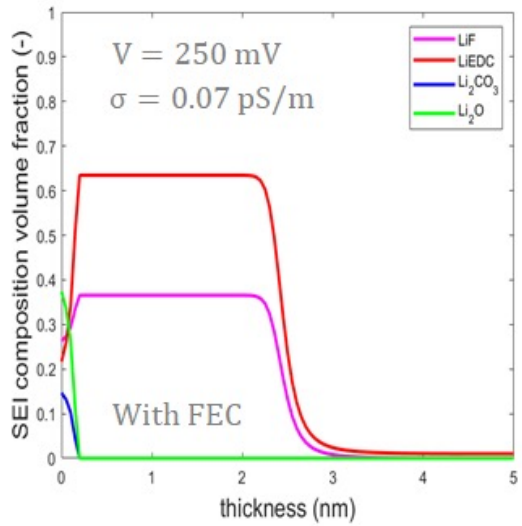
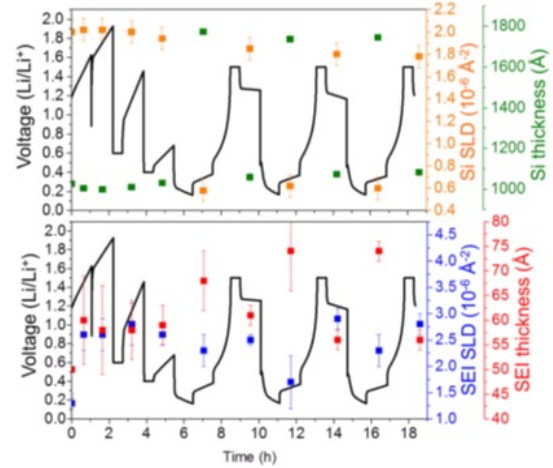
A global reaction mechanism captures depth-dependent SEI species and thickness changes in time



Gen 2: 100 mV



Gen 2F: 250 mV

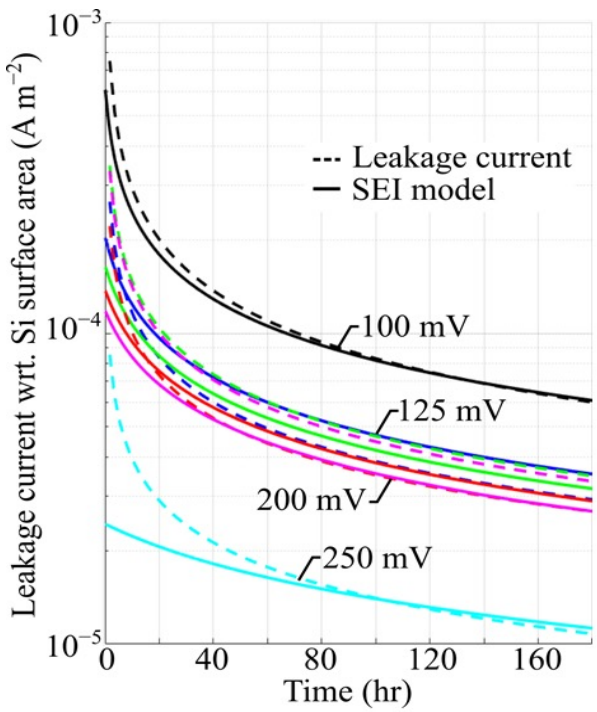


Veith *et al.* Sci. Rep. **7** (1), 1 (2017)

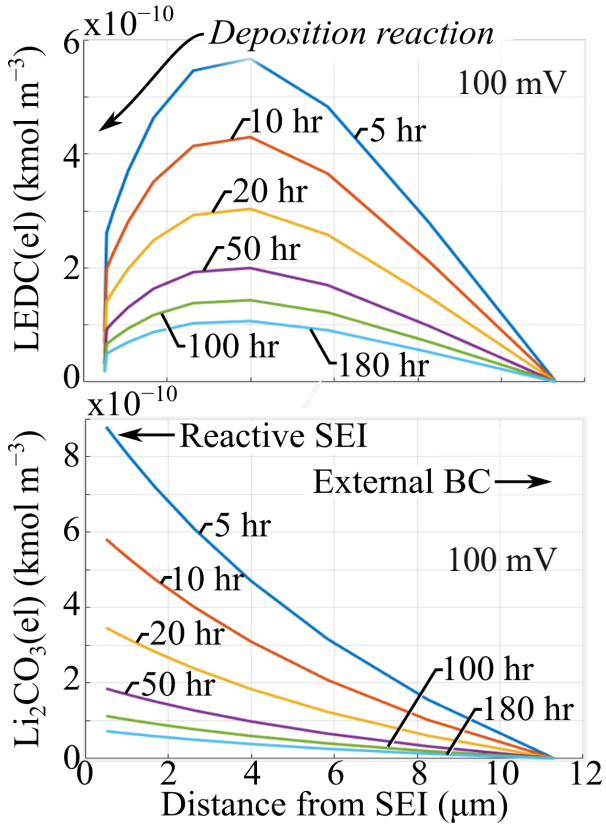
Inorganic/organic solid phase SEI species consisting of Li_2O, Li_2CO_3, LiF, LEDC is produced by the global reaction mechanism with gas phase species C_2H_4, CO and H_2.

Experimentally, SEI thickness, solid-phase composition datasets via neutron reflectometry, and XPS measurements are available in the consortium.

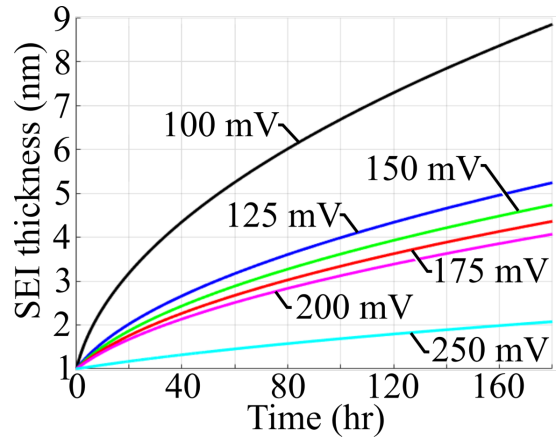
The atomistically informed mechanism is validated against deconvoluted leakage currents in voltage-hold experiments



Leakage current is highly dependent on the e-(sei) diffusion coefficient, i.e., the SEI conductivity



- Predict electrolyte composition changes
- Quantify species production from side reactions



Leakage current
- Taken from potential-hold experiments
- Interpreted as "irreversible" component
- Decreases with increasing voltage hold
- Diffusion-limited response

SEI atomistically informed model
- Captures leakage current dynamics
- Predicts the correct voltage dependence
- Models rate-limiting e-(sei) transport

Responses to Previous Year Reviewers' Comments

Project has not been reviewed previously

Acknowledgments

Supported by DOE VTO
– Brian Cunningham, Program Manager (reactions relevant for Si anodes)
– Tien Duong (reactions relevant for Li metal anodes)

Collaboration and Coordination

Category	Institution	Role
National Laboratories	Lawrence Berkeley National Laboratory	First-principles high-throughput quantum mechanical calculations, machine learning and reaction network framework to automatically predict feasible SEI formation mechanisms.
	National Renewable Energy Laboratory	Continuum-level SEI model development on intercalating anodes with multiple levels of mechanistic complexity.
	Oak Ridge National Lab	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 on non-intercalating anodes.

Remaining Challenges and Barriers

Improving species generation to efficiently develop reaction networks with novel additives

- Calculations to construct a reaction network in a new chemical space can cost tens of millions of CPU-hours
- Many calculations related to species that are not likely to form in SEI, creating severe inefficiency
- Use network products, machine learning to automatically identify most important species based only on initial electrolyte components

Machine learning solution-phase energy barriers for kinetically-informed reaction networks

- Kinetic barriers are essential to accurately identifying the most important SEI formation pathways
- Calculating barriers from first principles is very costly and difficult to automate
- Train equivariant graph neural network to predict energy barriers based on dataset of ~10,000 reactions

Accurate prediction of charge transfer rates

- SEI growth critically depends on conductivity
- Charge transfer mechanism through SEI poorly understood, especially due to limiting atomistic and mesoscale models
- Employ charge-constrained quantum chemistry to predict effective conduction rates from first principles

Proposed Future Research

Explore electrolyte oligomerization mechanisms

- Polymers believed to be important to Si SEI due in part to mechanical stability
- Identify expected oligomeric structures, formation mechanisms

- **Determining mass transport mechanisms through the SEI**
  - High ionic conductivity critical to enable rapid charging and discharging at low overpotential
  - Develop machine learning interatomic potentials to accurately model interactions in complex SEI layers
  - Determine main transport modes, as well as variation in Li^+ transport as function of SEI composition

Upscale additional reaction pathways to chemically relevant species measured in the Si consortium

- Simulate pathways that correspond to FEC decomposition, and subsequent LiF formation
- Determine additional pathways to common gas-phase species (e.g., H_2, CO, CO_2, CH_4)

Validate the atomistic-scale informed and global reaction mechanism model on new experiments

- Capture irreversible capacity fade due to SEI reactions measured in reference performance tests
- Predict the measured gas-phase species concentrations as a function of voltage-hold and time
- Simulate predominate SEI species that correspond to measured XRD and SLD profiles

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

Summary

First-principles chemical reaction networks

Stochastic approach to network analysis automatically reveals SEI products

Microkinetic modeling based on network pathways explain observed trends in SEI formation and evolution

Designing methods to improve computational efficiency of network generation for more rapid deployment

Expanding network analysis to oligomerization of solvents and additives

Molecular dynamics of the SEI

Observed SEI growth by combining classical MD with accelerated chemical reaction mechanisms

Predicted lithium transport mechanism through polycrystalline LiF

Machine learning of electrochemical reactivity

Designed pretraining method that greatly improves model performance on small reaction datasets

Actively working on equivariant neural network model to predict solution-phase energy barriers

Opportunities for ML to improve understanding of transport through SEI

Continuum-level modeling

Two continuum-level SEI models are developed to predict complex SEI formation and determine source of measured leakage current.

Both models indicate that electron transport is a key feature that determines leakage current magnitudes.

Continuum-level models resolve spatial and temporal electrolyte and SEI species evolutions.

Future work includes extending models to validate on additional measurements and ensure model fidelity.

Critical Assumptions and Issues

- Electrolyte stability insights, SEI phase evolution, microstructure and spectroscopy data will provide valuable data for feedback and close integration with the existing DOE SCP program to ultimately advance our understanding of the Si anode reactivity and develop novel Si electrolyte formulations.

The lack of understanding of the range of viable electrochemical reaction mechanisms that may participate in the electrochemical reaction cascade responsible for the formation of the SEI necessitates a minimally biased data-driven approach to identify the critical reaction pathways that could be targeted for suppression or enhancement to obtain desirable SEI properties with a novel Si electrolyte formulation.

Such a data-driven approach should be able to leverage the power of machine learning/AI in order to tractably describe the inherent complexity of the SEI formation reaction cascade.

First-principles density functional theory (DFT) calculations with an implicit solvent environment, no explicit surface, and a robust description of the underlying electronic structure via a large basis set and advanced modern density functional are a sufficiently accurate foundation for our data-driven approach.

The shortest paths of a thermodynamic reaction network leading to a given SEI components are very likely to include all important reaction paths responsible for the formation of that species in a real battery cell SEI.

Kinetic refinement via the first principles calculations of reaction barriers and stochastic time propagation that captures pathway competition is necessary for quantitative identification of the dominant pathways responsible for the formation of individual SEI components.

Key reactions identified by the LBNL team are reliable inputs to the multiscale models of ORNL, NREL, and CSM.

Publications

Publications

Alzate-Vargas, L., Blau, S.M., Spotte-Smith, E.W.C., Allu, S., Persson, K.A., Fattebert, J.-L., "Insight into SEI growth in Li-ion batteries using molecular dynamics and accelerated chemical reactions", *Journal of Physical Chemistry C* **125**(34), 2021.

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