

First Principles Modeling of SEI Formation on Bare and Surface/Additive Modified Silicon Anodes

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**Project ID #:
ES214**

Overview

Timeline

- Start date: April 1, 2013
- End date: March 31, 2017
- Percent complete: 25%

Budget

- Total funding: \$714,128
 - DOE share: \$714,128
 - Contractor share: Personnel
- Funding received
 - FY13: \$186,500
 - FY 14: \$157,500

Barriers

- Barriers/targets addressed
 - Loss of available capacity
 - Materials evolution during cycling
 - Lifetime of the cell

Partners

- Interactions/ collaborations
 - Sandia National Lab (Leung, Rempe)
 - NREL (Chunmei Ban)
 - Univ. of Rhode Island (B. Lucht)
- Project lead: TAMU

Relevance/Objectives

- **Objective:** Develop fundamental understanding of the molecular processes that lead to the formation of a solid electrolyte interphase (SEI) layer due to electrolyte decomposition on Si anodes.
- **FY 2013 goals:** Identify SEI reduction mechanisms and initial products; characterize electron transfer through model film.
- **Addressing targets and barriers:**
 - Elucidating how SEI forms *during initial cycles* and leads to anode *capacity losses* as functions of anode lithiation, and surface and electrolyte chemistries.
- **Impact:**
 - Practical implementation of *high energy* Si anodes depends on *structural evolution* during battery operation. Understanding SEI reactions will allow rational electrolyte and electrode design.

Relevance/Milestones

- a) Identification of most favorable surfaces of bare Li_xSi_y periodic structures and characterize their reactivity. (Jun. 13) **Completed**
- b) Develop preliminary model to estimate SEI layer thickness for electron transfer in model SEI films. (Jun. 13). **Completed.**
- c) Characterize surface effects on EC, VC, FEC decomposition using cluster models of bare Li_xSi_y structures. (Sept. 13). **Completed.**
- d) Identification of reaction pathways and activation energies for EC and FEC reduction on lithiated Si surfaces. (Dec-13) **Completed**
- e) Quantify electron transfer from a lithiated Si surface covered by a model SEI layer to the electrolyte; develop theory/algorithms accounting for voltage effect on electrolyte reduction reactions. (Mar-14)- **Ongoing**
- f) Characterize reactivity of additives; identify reaction pathways and interactions of reaction products with electrolyte components; assess aggregation effects. (Jun-14)- **Ongoing**
- g) Go/No-Go Decision: Development of a coarse-grained Kinetic Monte-Carlo approaching approach for assessing long-time evolution (order of days) of SEI films. (Sep-14)- **Ongoing**

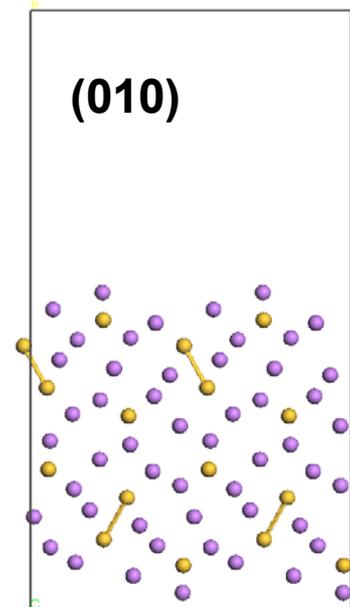
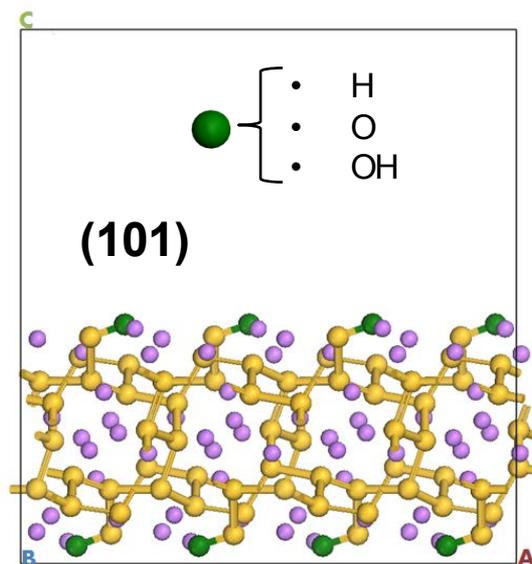
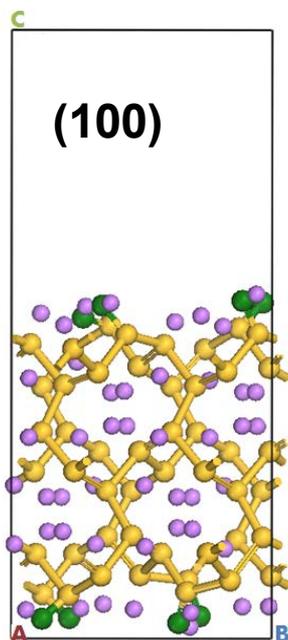
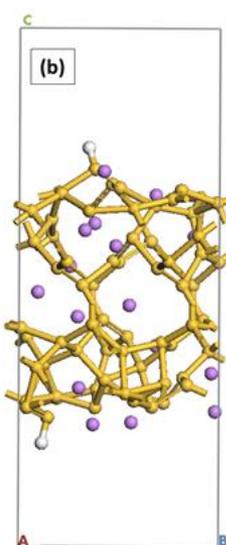
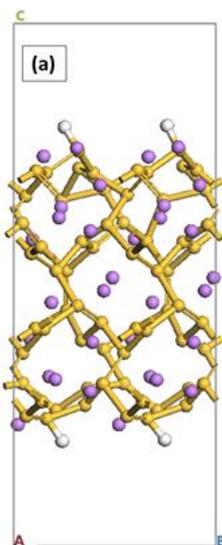
Approach/Strategy

- **Overall technical Approach/Strategy:**
 - Reduction of solvents, additives, and salts evaluated on Li_xSi_y surfaces with increasing extent of lithiation. Effects of surface functionalization, surface structure, and surface oxide films investigated.
 - Once the main initial products are identified, electron conductivity through a surface covered by a thin SEI film evaluated as a function of film thickness and porosity.
 - Addresses technical barriers/targets: Various stages of lithiation represent *surface evolution during first cycle*. SEI product identification and assessment of electron transfer through film elucidate *anode capacity loss*.
 - Electrolyte reduction studies complement experiments from U. of Rhode Island; analysis of coating effects complement NREL experimental studies.
- **Progress towards FY13 and FY14 milestones and Go/No Go decisions:** Product aggregation and electron conductivity studies build basis for planned mesoscopic scale model.

Technical Accomplishments: Barriers Addressed

- **Loss of available capacity**
 - *Identified specific SEI products* allow evaluation of the Li retention capacity of the film.
- **Materials evolution during cycling**
 - Study reveals changes *in reduction mechanisms, SEI products, and film properties* as the surface lithiates due to cycling and/or due to the presence of additives.
- **Lifetime of the cell**
 - *Characterized electron conductivity* through SEI –driving SEI growth- shown to depend on nature, thickness, and packing properties of the film. SEI protective properties influence cell lifetime.

Technical Accomplishments: Characterization of Lithiated Si Surfaces

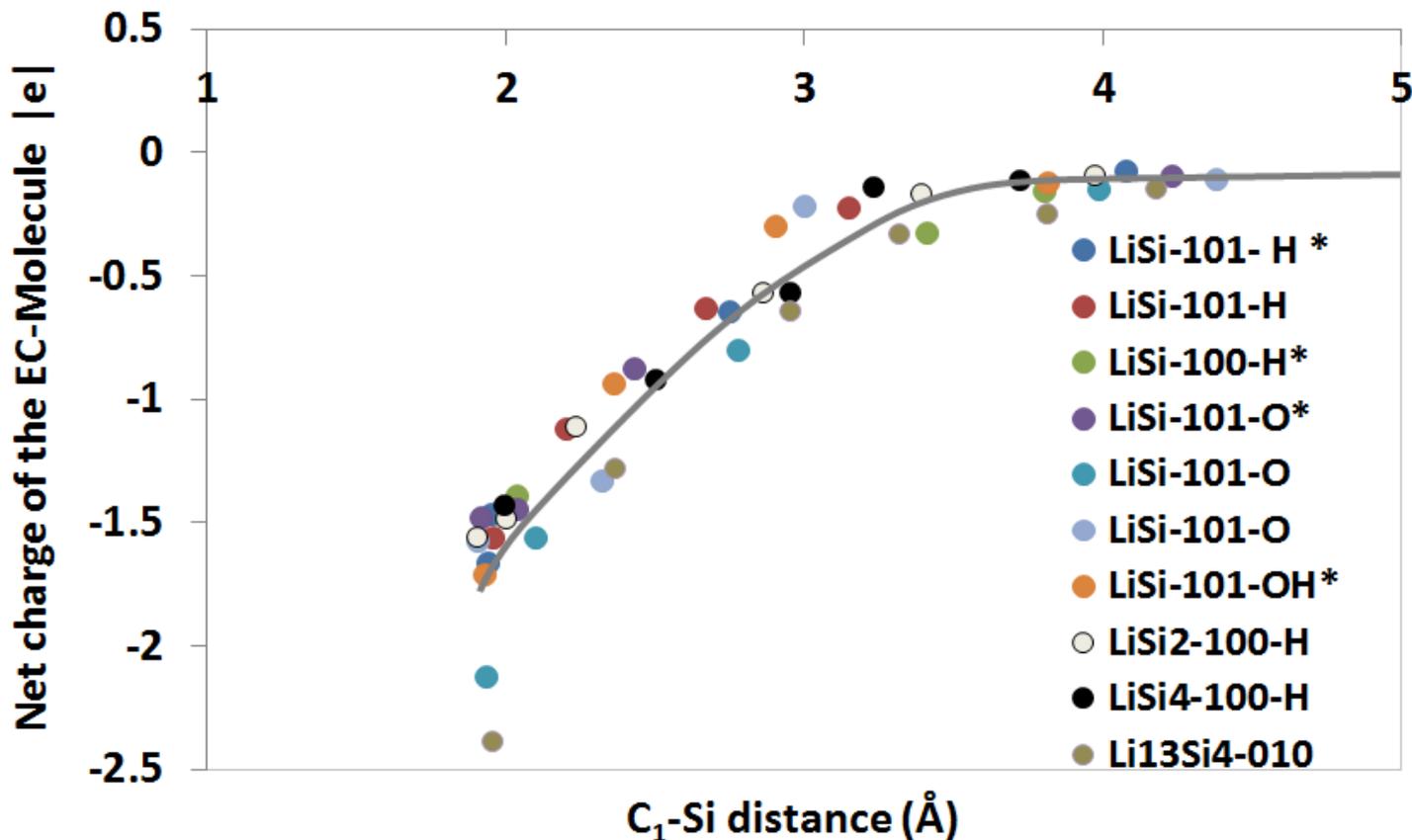
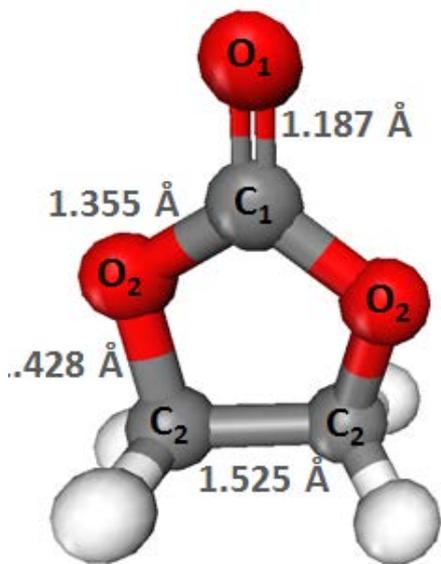


Early stages of lithiation

Highly lithiated

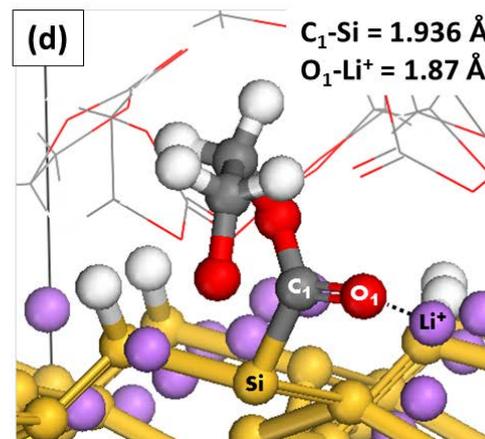
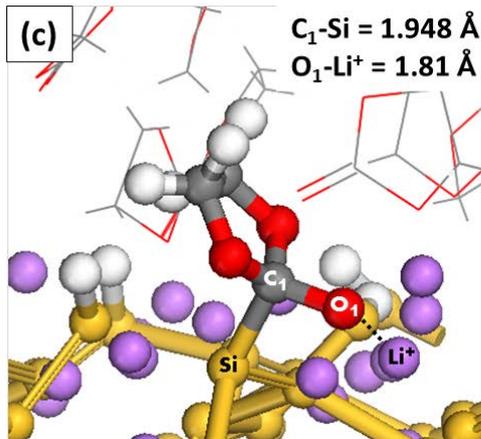
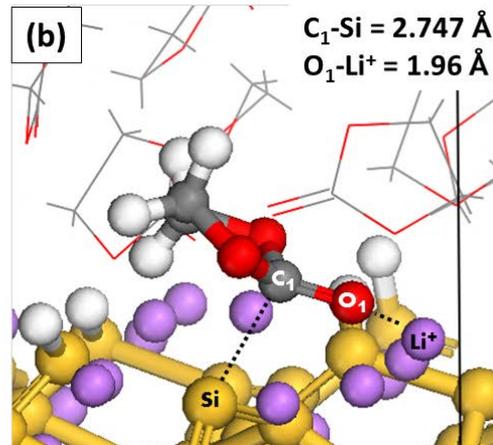
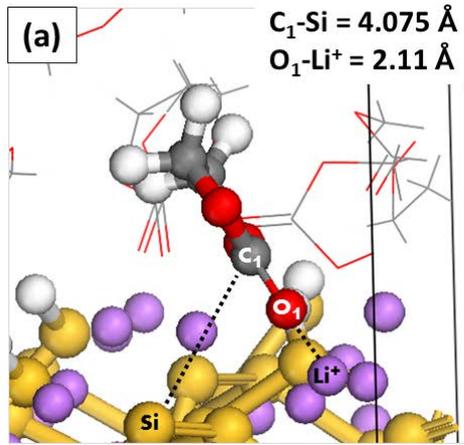
Milestone (a) ✓ : Thermodynamically most favorable surfaces identified for various degrees of lithiation, surface functionalization, and exposed facets

Technical Accomplishments: Identification of EC Reduction Pathways

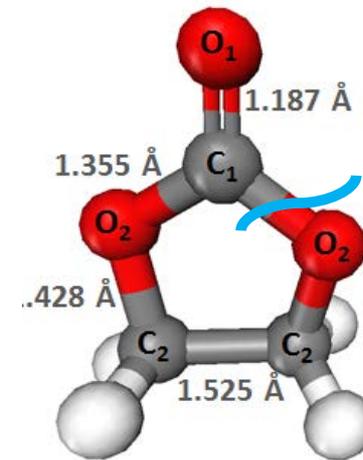


Milestone (d) ✓ For liquid EC interacting with many different surfaces (from LiSi₄ to Li₁₃Si₄), a C₁-Si bond is formed as the EC molecule becomes reduced receiving up to 2 electrons.

Technical Accomplishments: EC Reduction mechanism: Simultaneous 2 e⁻ Transfer



Liquid EC on LiSi(100) and LiSi(101) surfaces

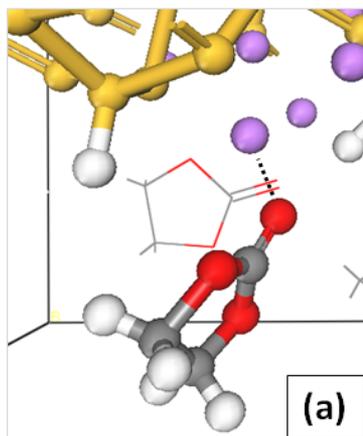


Mechanism 1 (2-electrons)

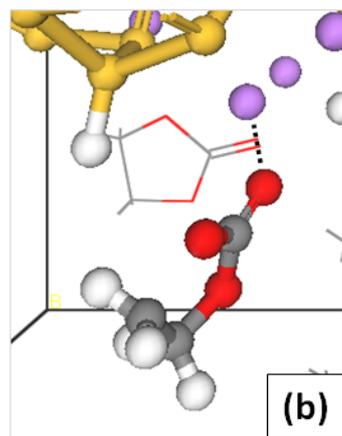


Milestone (d) ✓ : In this mechanism, while the C1-Si bond forms, a C1-O2 bond breaks and the EC ring opens, forming an adsorbed anion radical.

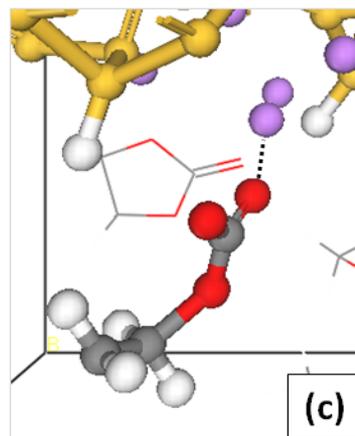
Technical Accomplishments: Alternative Sequential 2 e⁻ Transfer to EC



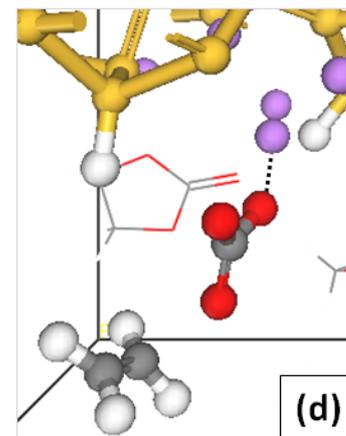
-0.20 |e|



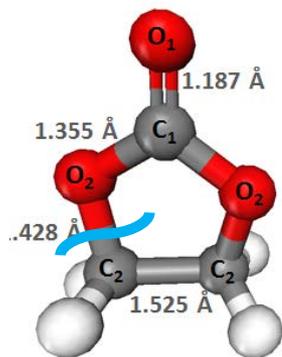
-0.61 |e|



-1.59 |e|



CO₃²⁻ = -1.54 |e|
C₂H₄ = -0.01 |e|



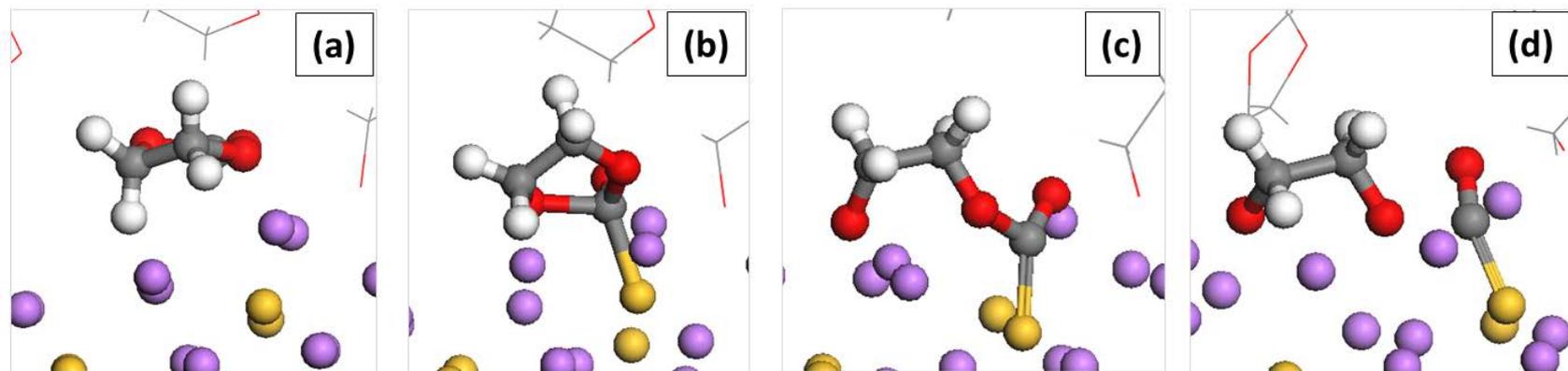
Mechanism 2 (2-electrons):

- (i) EC + 1e⁻ → EC⁻ (a and b)
 (ii) EC⁻ + 1e⁻ → CO₃²⁻ + C₂H₄ (c and d)

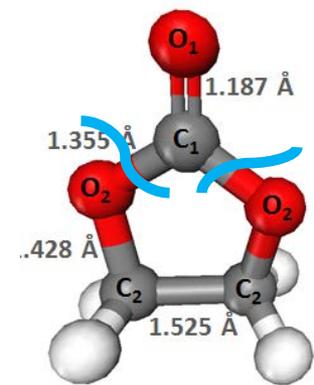
Milestone (d) ✓ In an alternative mechanism, EC is reduced in the liquid phase, the C2O2 bond breaks, and after a 2nd e⁻ transfer, ethylene gas and CO₃ anion are formed.

Technical Accomplishments:

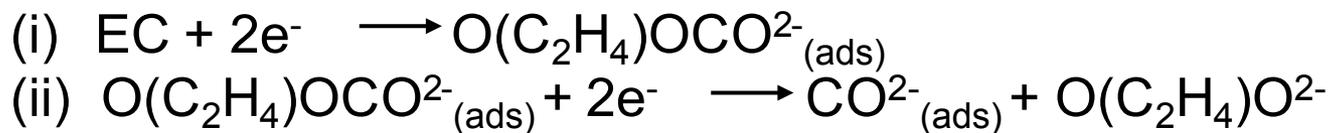
EC Reduction Mechanism in Highly Lithiated Surfaces



Two C1-O2 bonds break simultaneously at the interface with the highly lithiated surface



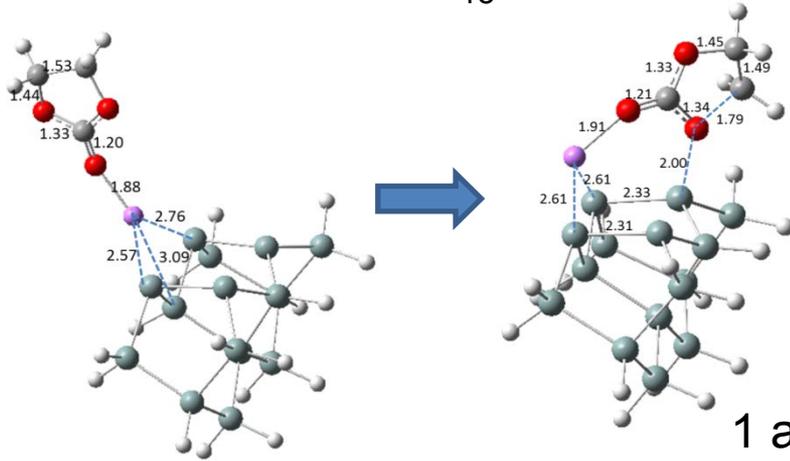
Mechanism 3 (4-electrons):



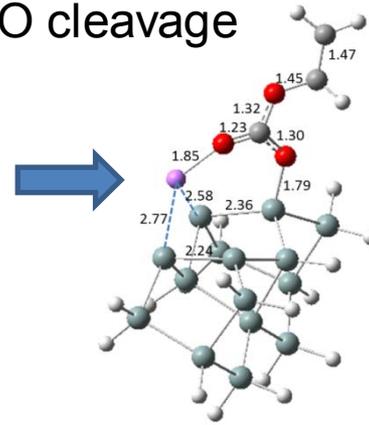
Milestone (d) ✓ Multiple electron transfer may occur at highly lithiated surfaces; adsorbed CO anion and a radical anion are detected

Technical Accomplishments: Summary of Surface Lithiation Effect on EC Reduction

1) Ultra- low lithiation: LiSi_{15}



$\text{C}_E\text{-O}$ cleavage

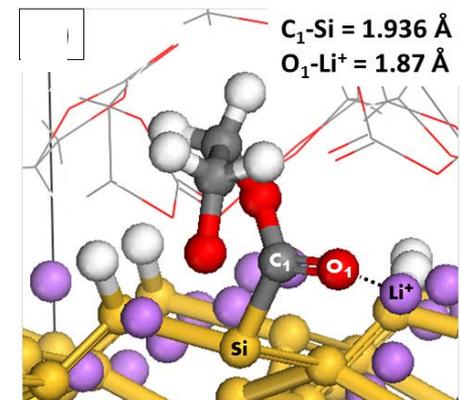
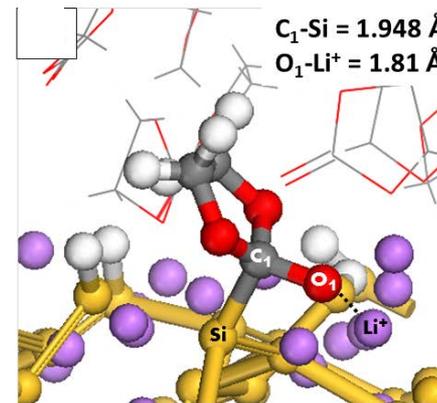
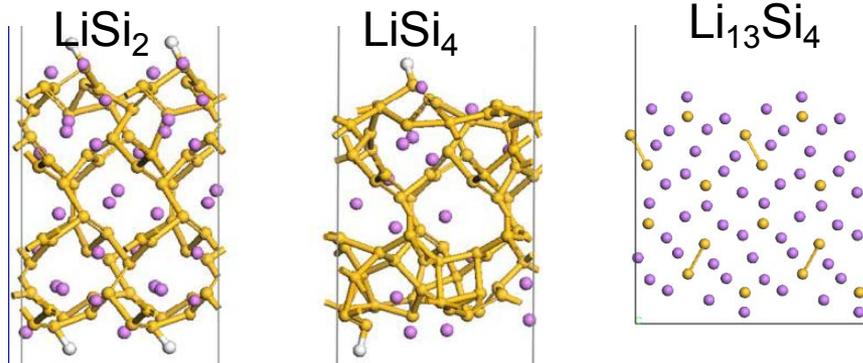


MILESTONES
(c) and (d) ✓

Li over the surface plane; Si-O_E bonds formed

1 and 2- e^- reduction mechanisms can coexist

2) Intermediate to high lithiation

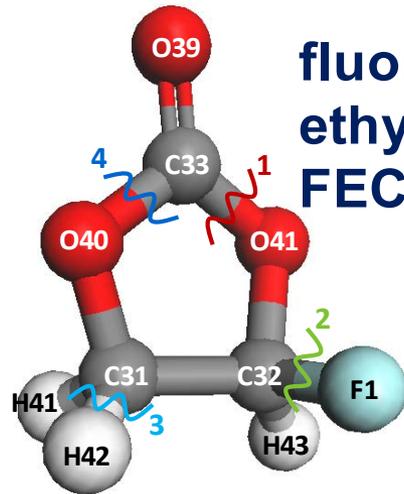


Li on the surface plane or in the subsurface: Si-C bonds are formed

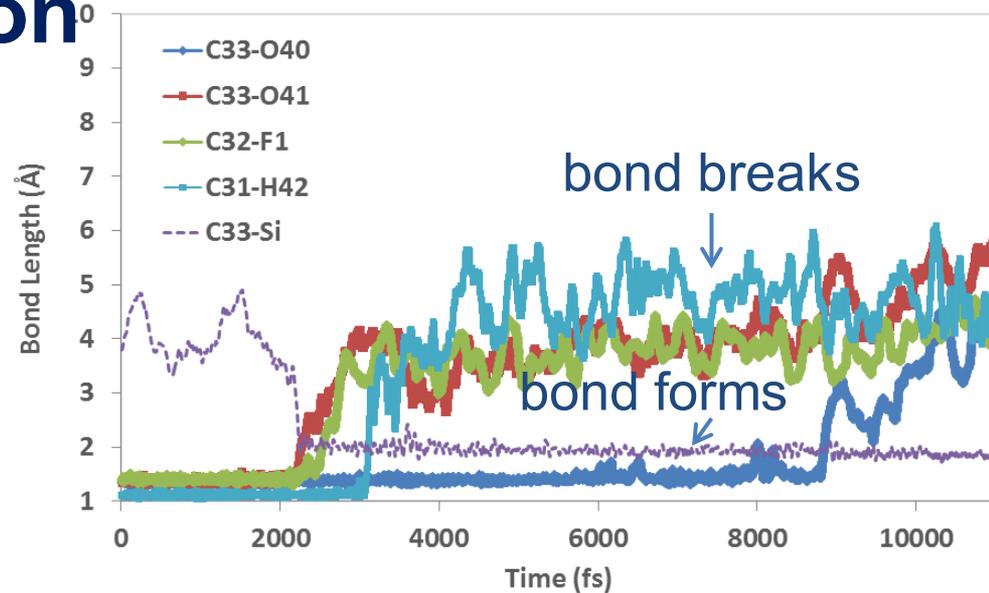
2- e^- mech. preferred; as degree of lithiation increases 4 e^- mech. observed

Technical Accomplishments:

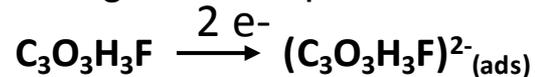
FEC Additive Reduction



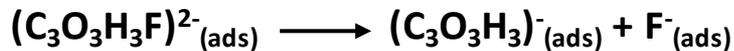
fluorinated
ethylene carbonate
FEC



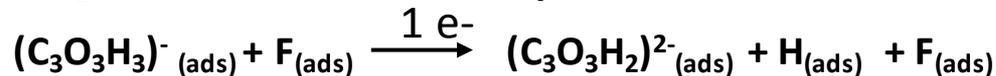
- (1) $C_{33}-O_{41}$ breaks during its adsorption on the surface



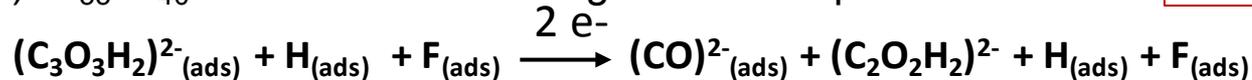
- (2) $C_{32}-F_1$ bond breaks and F adsorbs



- (3) $C_{31}-H_{42}$ bond breaks and H may adsorb



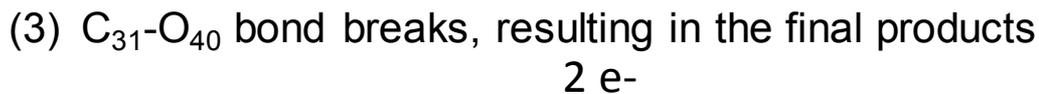
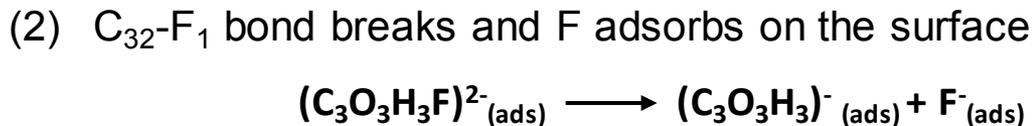
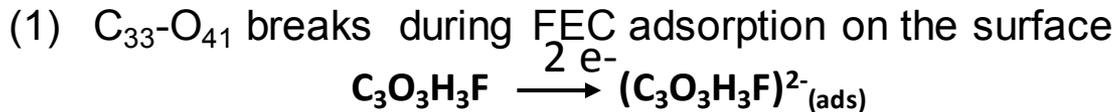
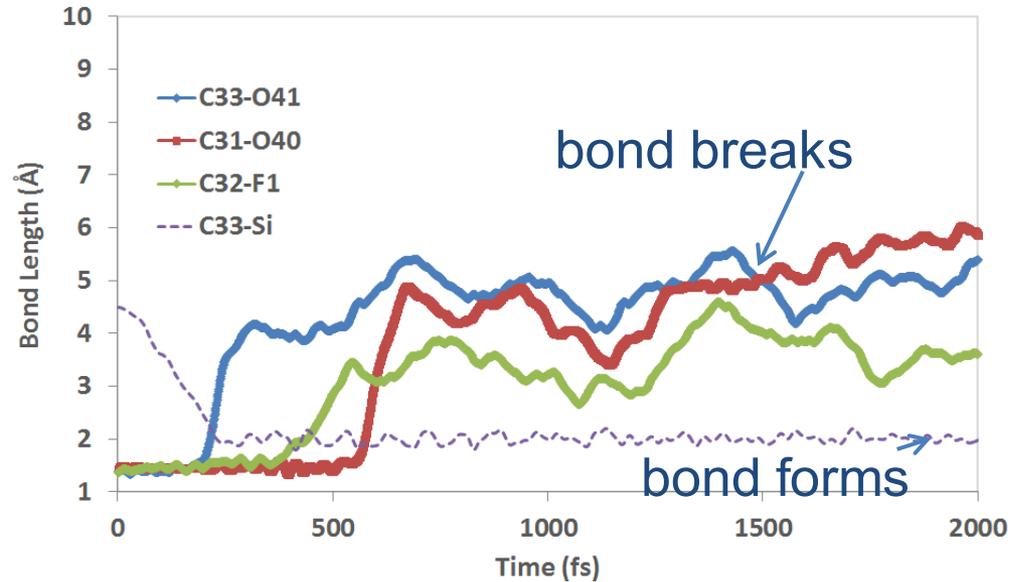
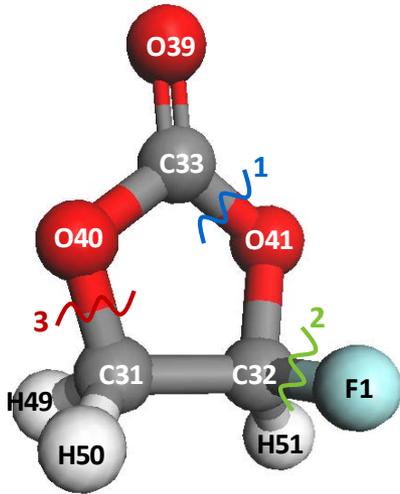
- (4) $C_{33}-O_{40}$ bond breaks resulting in the final products



MILESTONE (d) ✓

For $LiSi_4$ and higher lithiated surfaces, FEC reduction mechanism is independent of surface lithiation

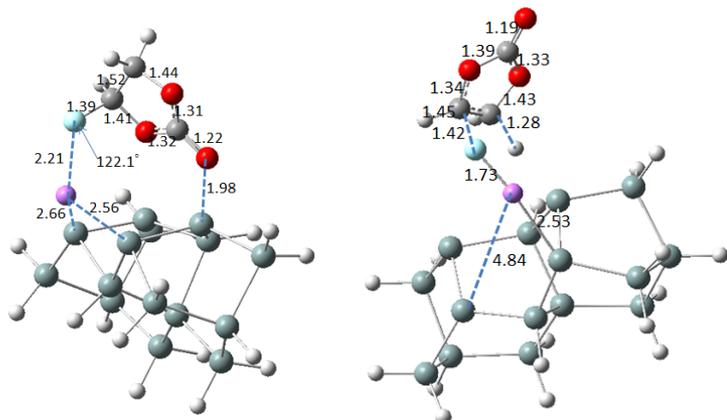
Technical Accomplishments: Alternative FEC Reduction



MILESTONE (d): ✓

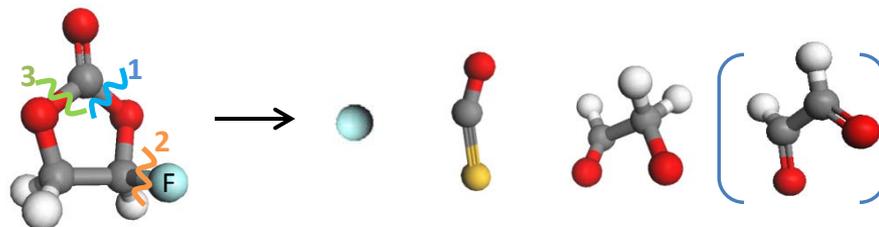
For $LiSi_4$ and higher lithiated surfaces, FEC additive reduction mechanism is independent of surface lithiation

Technical Accomplishments: Summary of Surface Lithiation Effect on FEC Reduction



MILESTONES (c) and (d) ✓

Ultra- low lithiation:
2 e⁻ mechanism preferred;
C_C-O_E and C_C-F bond cleavages:
low/moderate barriers

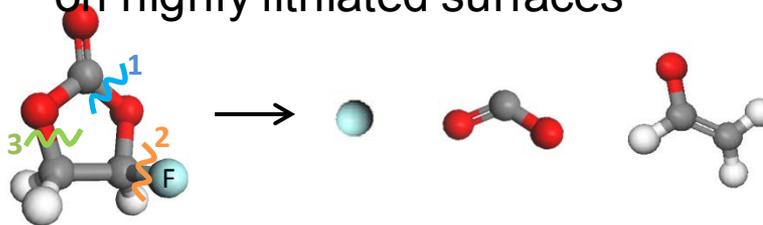


Mechanism 1 (4-electrons) :



**LiSi and
Li₁₃Si₄**

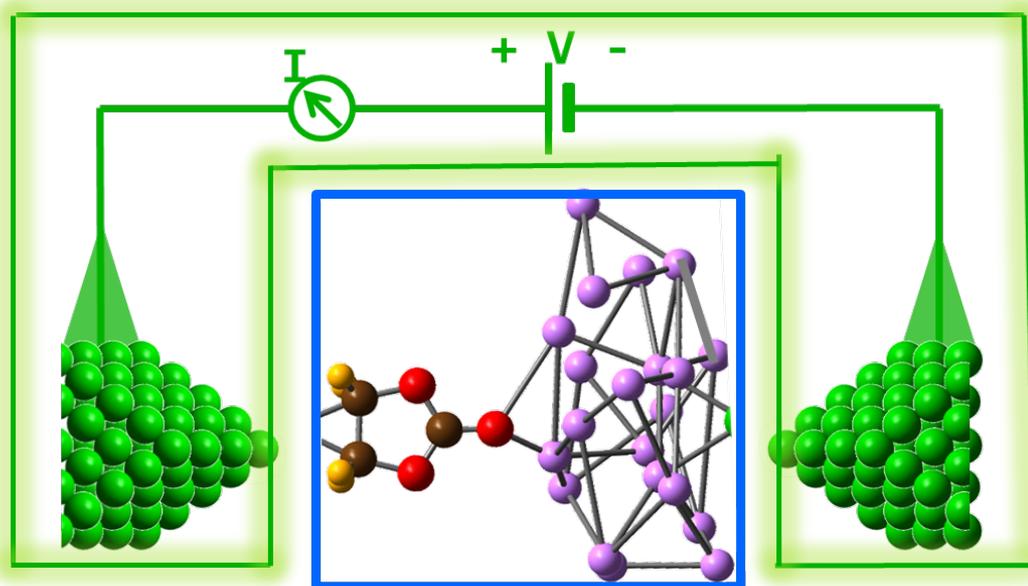
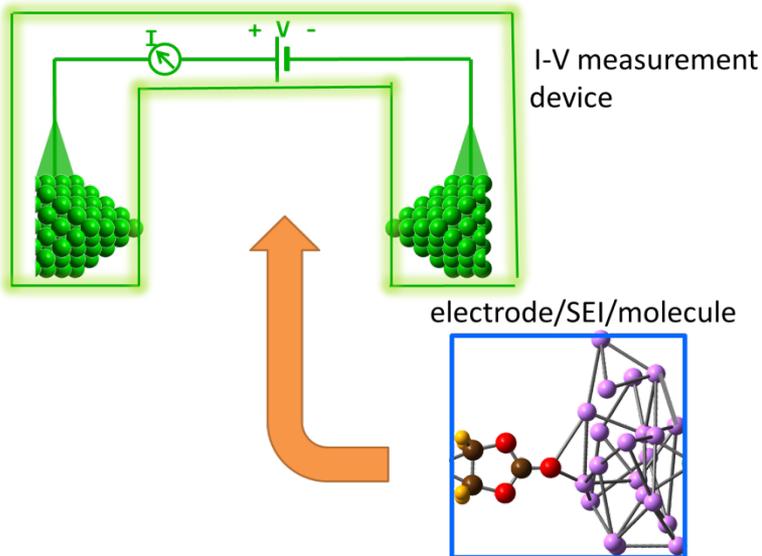
Multi-electron reactions
on highly lithiated surfaces



Mechanism 2 (4-electrons) :



Technical Accomplishments: Electron Transfer through a Model SEI Layer



Milestone (b) ✓

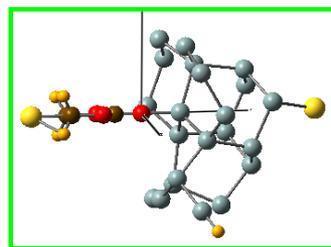
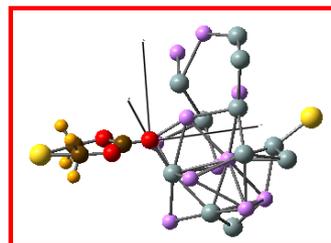
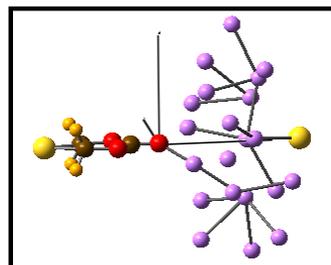
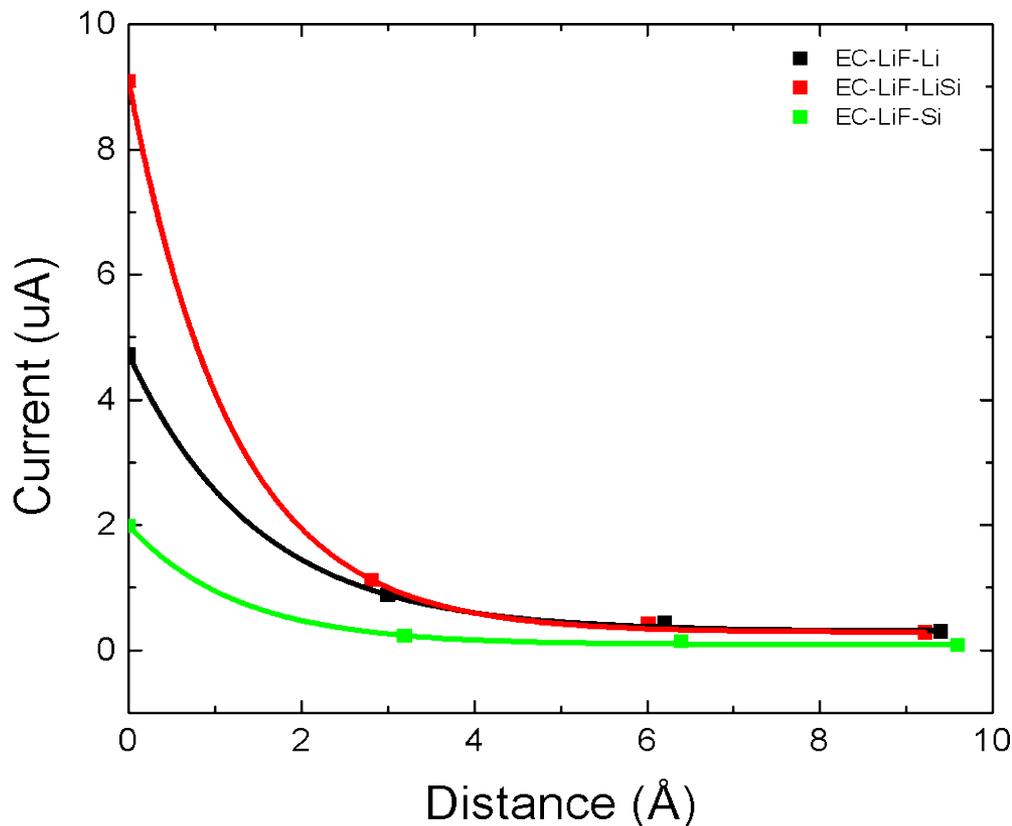
A DFT/Green's function model has been developed to evaluate electron transfer through composite electrode/SEI layer/electrolyte systems. The current-voltage characteristics are determined for any SEI block (LiF, LiO₂, LiCO₃), or aggregations of these blocks.

Technical Accomplishments: Electron transfer through a model SEI layer

Current vs SEI layer thickness

LiF Layer

Milestone (b) ✓



In this example, SEI is modeled as LiF; several other blocks have been tested

Electron transfer follows exponential decay through SEI thickness; a small non-zero constant current detected at large SEI thicknesses suggests sustained low-rate SEI formation in thicker films.

Responses to Previous Years Reviewers' Comments

**This project started FY13;
it was not evaluated last year**

Collaboration and Coordination with Other Institutions

- **Sandia National Lab (SNL):** This original BATT proposal was written in collaboration with SNL. However, the awarded SNL part of the contract is still under negotiation. Part of the reported FEC reduction calculations have been carried out in collaboration with K. Leung and S. Rempe (SNL) .
- **National Renewable Energy Lab (NREL):** Chunmei Ban (NREL, BATT program) has developed and deposited a protective coating over a Si anode. This team (TAMU) is modeling the nucleation, growth, and SEI reactions on the coated Si anode (ongoing).
- **University of Rhode Island (URI):** This team (TAMU) collaborates with Brett Lucht (URI, BATT program) who is experimentally studying SEI formation reactions on Si anodes (ongoing).

Remaining Challenges and Barriers

- After the initial SEI products are identified, the next challenge is to determine how the various **products aggregate and nucleate** forming the SEI building blocks.
- Once the building blocks are characterized, their **adhesion to the electrode surface** needs to be evaluated, and **ionic and electronic conductivity** through them assessed.
- The above information will be input to a mesoscopic model to evaluate **capacity fade as a function of SEI film properties**.
- A further challenge is to use the knowledge obtained from these studies to **identifying alternative effective electrolytes**.

Proposed Future Work

- **Rest of FY13:**
 - aggregation and nucleation of SEI products
 - adhesion of SEI blocks to anode surface
 - ionic and electronic conductivity through blocks
 - developing preliminary mesoscopic model of the SEI
- **FY14:**
 - evaluating SEI mesoscopic model
 - effect of packing and porosity on electron transfer
 - artificial coating effects on SEI reactions
 - voltage effect on reactions

Summary Slide

- **Relevance:** Elucidation of SEI layer nucleation and growth is crucial for evaluating irreversible capacity loss and designing improved electrolytes and electrodes.
- **Approach:** SEI product identification and assessment of electron transfer through film at various stages of lithiation yield insights about *first cycle surface evolution* and *anode capacity loss*.
- **Technical Accomplishments:** EC, VC, and FEC reaction mechanisms and products identified as functions of state of lithiation and electrolyte composition; electron transfer through SEI layer analyzed as a function of film thickness and structure.
- **Collaborations:** Evaluation of artificial coatings (with NREL); evaluation of additives and salts (with URI and SNL).
- **Future Work:** Focus on SEI growth; product nucleation into blocks; electron transfer through blocks; development of a mesoscopic model.

Technical Back-Up Slides

Methodology

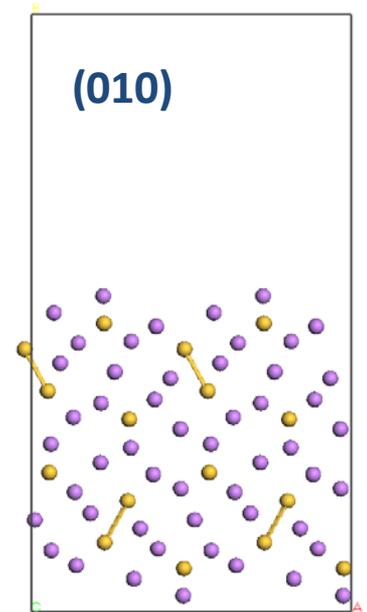
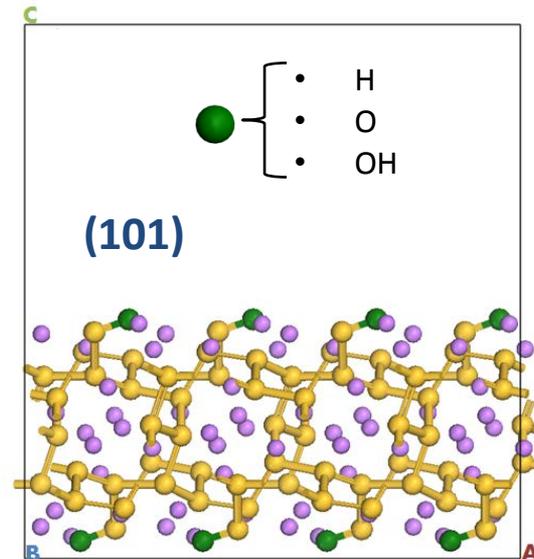
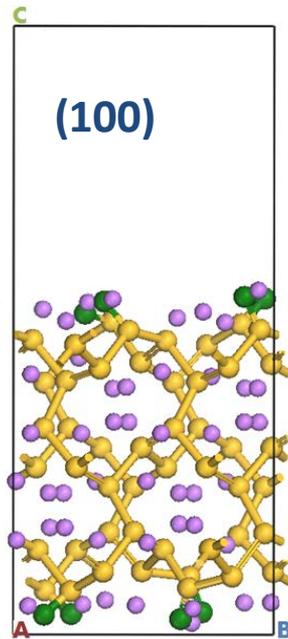
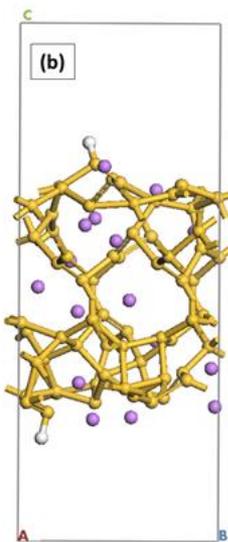
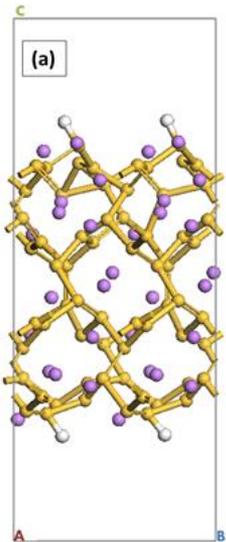
DFT optimization of Li_xSi_y surfaces with different Li content

LiSi_2

LiSi_4

LiSi

$\text{Li}_{13}\text{Si}_4$



Early stages of lithiation

Highly lithiated

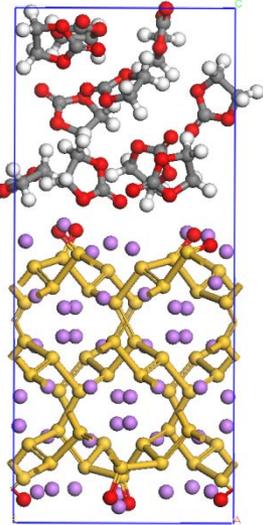
- Optimizations performed using the Vienna ab initio simulation package (VASP)
- Perdew-Burke-Ernzerhof functional (GGA-PBE) functional
- Cutoff energy of 400 eV
- 4x4x1 k-points Monkhorst-Pack mesh sampling

Methodology

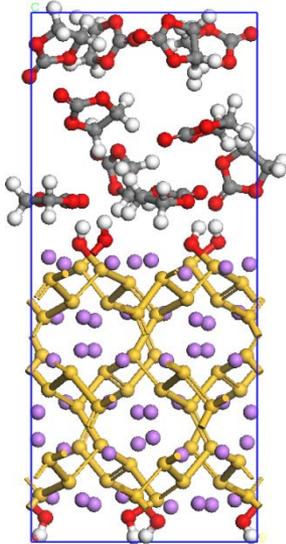
Ab-initio MD simulations at 400 K (≥ 8 ps)

LiSi

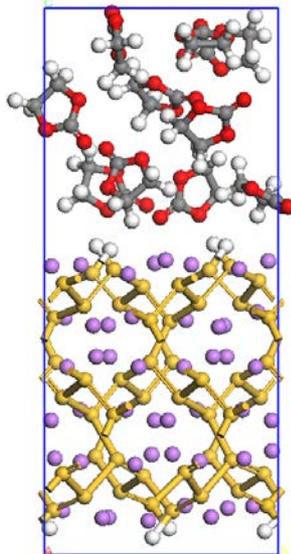
Si-O



Si-OH

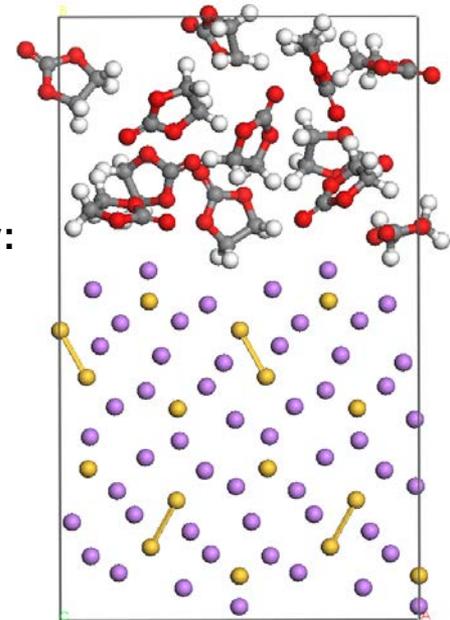


Si-H



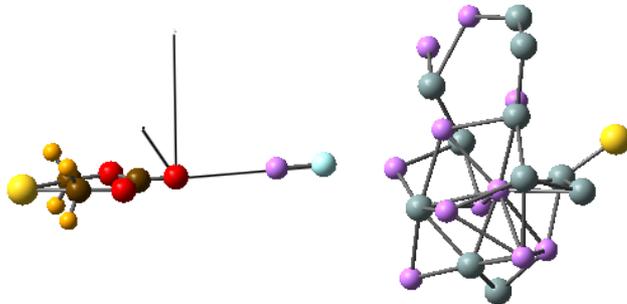
EC-liquid density:
1.32 g/cm³

Li₁₃Si₄

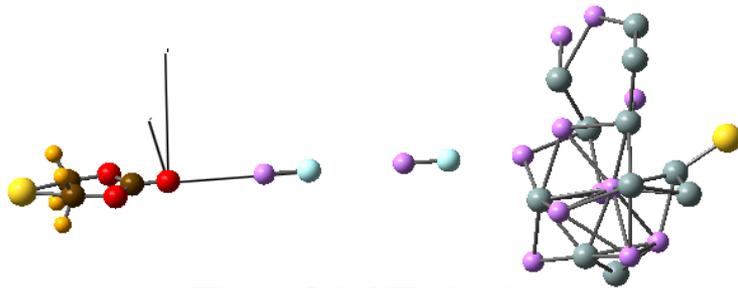


- Simulations performed using the Vienna ab initio simulation package (VASP)
- Perdew-Burke-Ernzerhof functional (GGA-PBE) functional
- Cutoff energy of 300 eV
- Γ k-points Monkhorst-Pack mesh sampling
- Timestep 1 fs

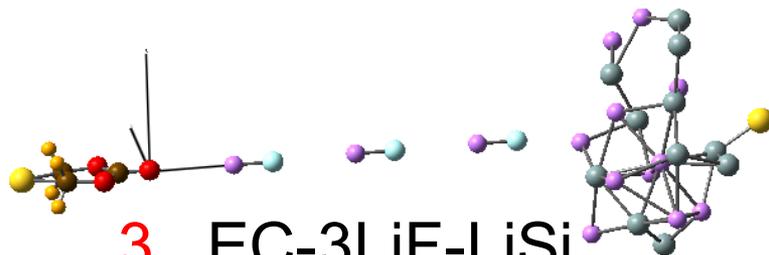
Methodology



1 EC-LiF-LiSi



2 EC-2LiF-LiSi



3 EC-3LiF-LiSi

- Li_xSi_y molecular structures optimized until local minima using B3PW91
- SEI product and oxide crystal structures from ICS Database
- Van der Waals radii for SEI/Oxide layer
- Gaussian 09
- I-V evaluated with Generalized Electron NanoInterface Program (GENIP)