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

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Texas A&M University

June 9th, 2016

Project ID #: ES214

Overview

Timeline

- Start date: April 1, 2013
- End date: March 31, 2017
- Percent complete: 75%

Barriers

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

Budget

- Total funding: $714,128
  - DOE share: $714,128
  - Contractor share: Personnel
- Funding received
  - FY13: $186,500
  - FY 14: $157,500
  - FY 15: $172,484
  - FY 16: $170,000

Partners

- Interactions/ collaborations
  - J. Seminario (TAMU Co-PI)
  - Sandia National Lab (Leung, Rempe)
  - NREL (Chunmei Ban)
- 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 2016 goals**: Identify SEI reactions in alucone-covered Si anodes; quantify chemical and electrochemical stability of SEI products; identify alternative electrolyte formulations.

- **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 (15-16)

- Q2/Y2: Clarify role of additives (VC, FEC) vs. electrolyte without additive on SEI properties. (Mar. 15) **Completed**
- Q3/Y2: Characterization of SEI mosaic formation from building blocks. (Jun 15). **Completed.**
- Q4/Y2: Prediction of irreversible capacity loss and electron transfer mechanisms through the SEI layer. (Sept. 15). **Completed.**
- Q1/Y3: Identify SEI nucleation and growth on Si surfaces modified by deposition of alucone coatings as a function of degree of lithiation of the films. (Dec-15) **Completed**
- Q2/Y3: Quantify chemical and electrochemical stability of various SEI components: competition among polymerization, aggregation, and dissolution reactions. Evaluate voltage effects on SEI products stability. (Mar-16)- **Completed**
- Q3/Y3: Identify alternative candidate electrolyte and coating formulations. (Jun-16)- **Ongoing**
- Q4/Y3: Test potential candidate electrolyte and coating formulations using coarse-grained model and experimentally via collaborations. (Sep-16)- **Ongoing**

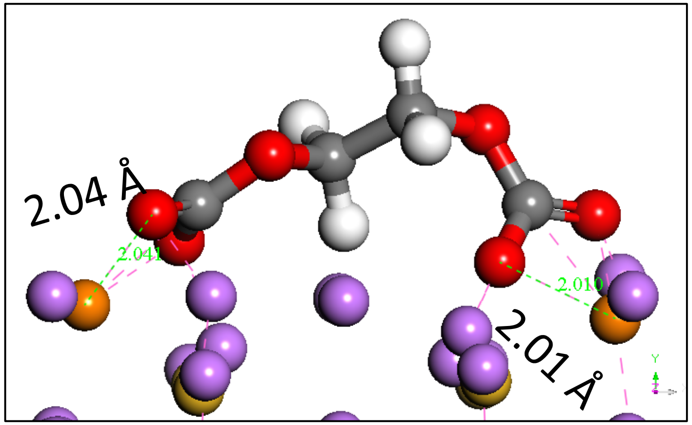
Approach/Strategy

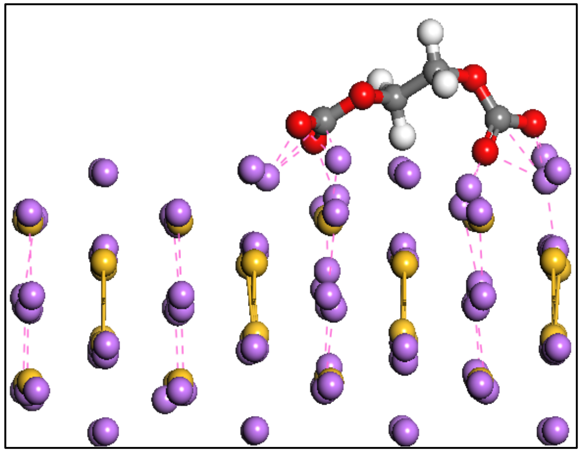
- **Overall technical Approach/Strategy:**
  - Reduction of solvents, additives, and salts evaluated on Li_xSi_y surfaces with increasing extent of lithiation. Effects of surface functionalization, surface structure, and surface oxide films investigated.
  - Once the main initial products are identified, 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. C. San Diego; analysis of coating effects complement NREL experimental studies.
- **Progress towards FY15 and FY16 milestones and Go/No Go decisions:** Chemical and electrochemical instability of SEI products demonstrated. Aggregation of SEI fragments and role of electrolyte elucidated. Ion transport through LiF characterized.

Technical Accomplishments: Barriers Addressed

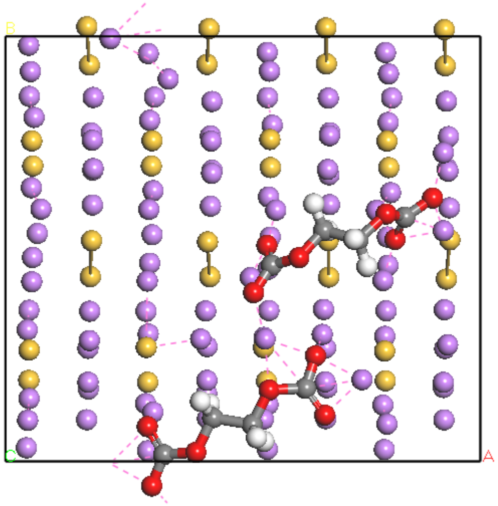
- Loss of available capacity
  - ***Identified instability of SEI products*** allows evaluation of the Li retention capacity of the film.
- Materials evolution during cycling
  - Study reveals ***nucleation and aggregation of SEI products*** as the surface lithiates due to cycling and/or due to the presence of additives.
- Lifetime of the cell
  - ***Characterized ion and electron conductivity*** through SEI shown to depend on nature, thickness, and packing properties of the film. SEI protective properties influence cell lifetime.

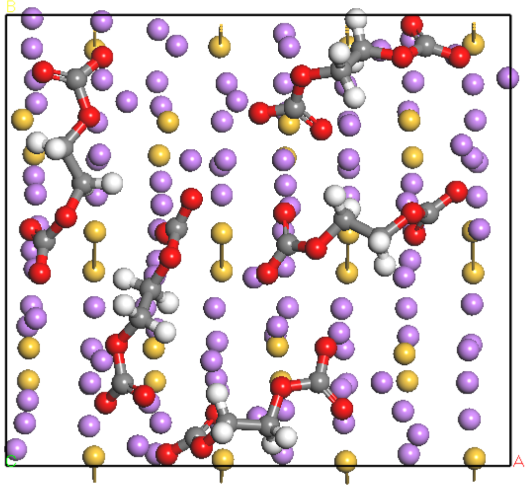
Technical Accomplishments: Oligomers Deposition on Lithiated Si Anode Surface





Soto and Balbuena to be published

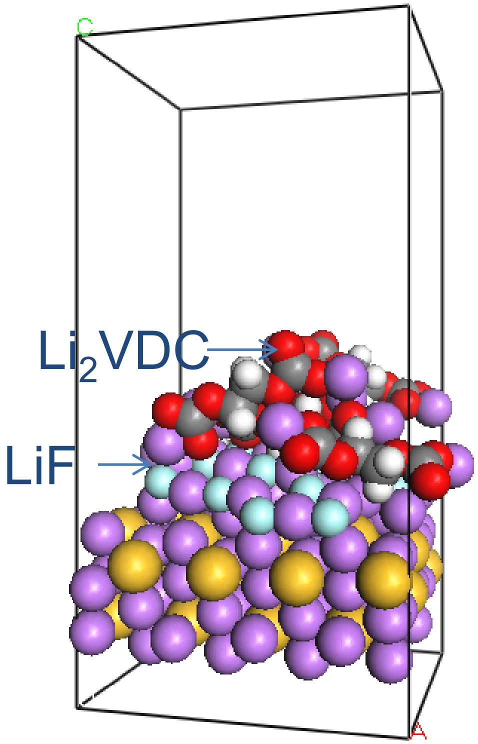


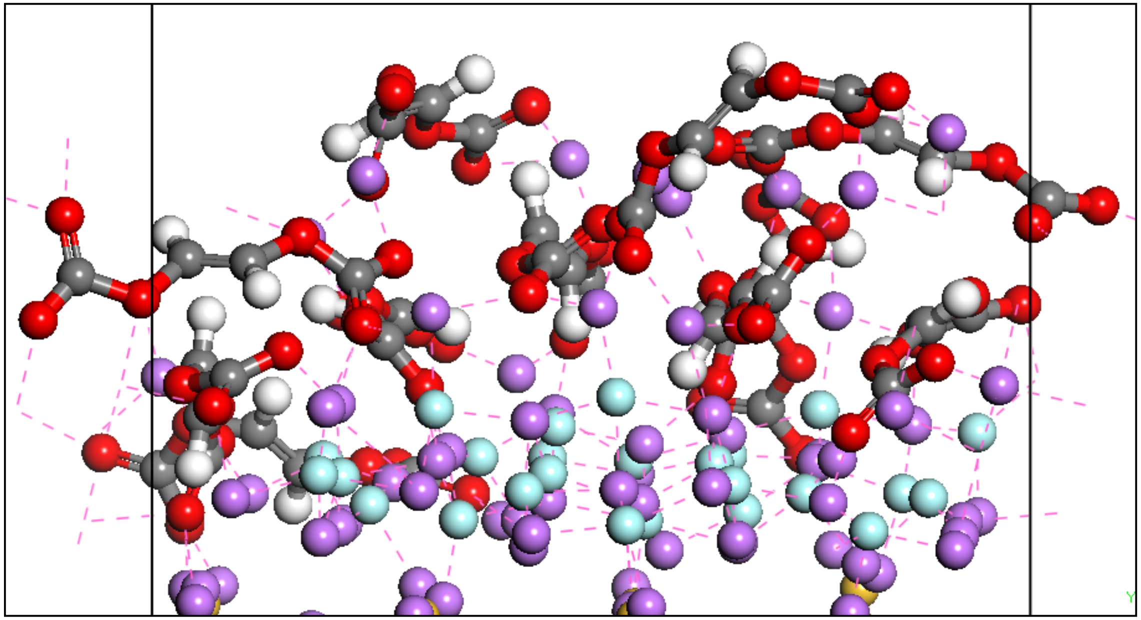


Strong adsorption of Li_2EDC over bare $Li_{13}Si_4$ (010) surface: -4.72 eV, caused by Si-Li and O-Li electrostatic interactions Oligomer adsorbs in bent configuration. Subsequent adsorption favored by O..Li..O interactions

Milestone Q3/Y2 : Characterization of SEI mosaic formation from building blocks. ✓

Technical Accomplishments:
Nucleation of SEI blocks



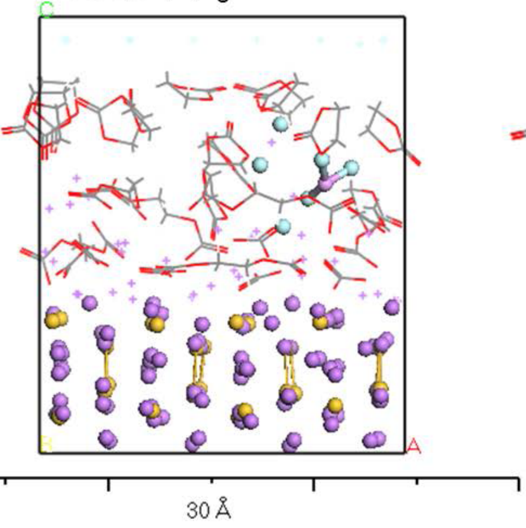


Soto and Balbuena, to be published

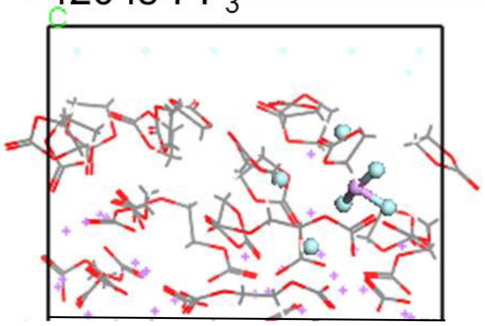
- **Li_2VDCs can be better packed in LiF and Li_2CO_3 pre-covered surfaces than Li_2EDC**
- **How organic compounds are packed, depends on whether the surface is bare or pre-covered**
- **Li_2VDC is more efficient at forming O-Li-O network and covering the LiF layer than Li_2EDC**

Milestone Q3/Y2 : Characterization of SEI mosaic formation from building blocks. ✓

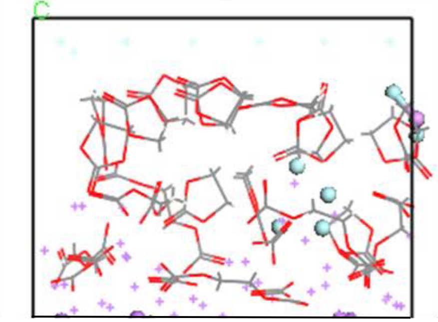
Technical Accomplishments: Nucleation of SEI blocks



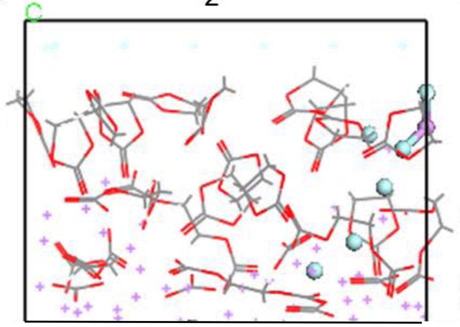
210 fs-PF_3



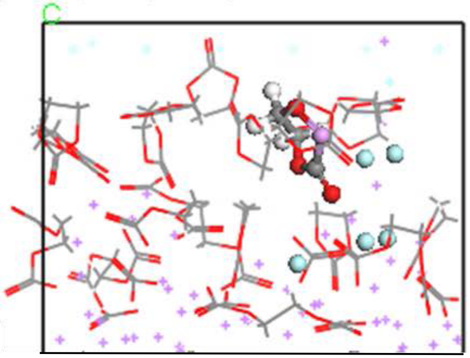
420 fs-PF_3



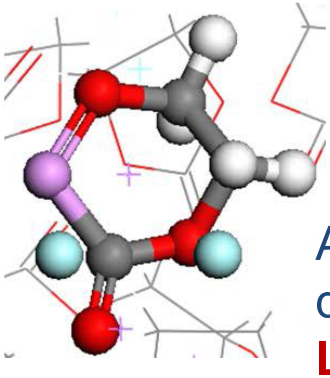
1448 fs-PF_2



2540 fs-PF_2



6882 fs-P-C



AIMD simulations of LiSi/**Li_2CO_3/Li_2EDC** + EC + $LiPF_6$ reveal PF_6^- decomposition over nucleating SEI layer. Similar results observed for **LiF/Li_2EDC** and **Li_2VDC** instead of Li_2EDC. Salt dissociates first and then anion decomposes. PF_x fragments associate with organic fragments.

Milestone Q3/Y2 : Characterization of SEI formation from building blocks. ✓

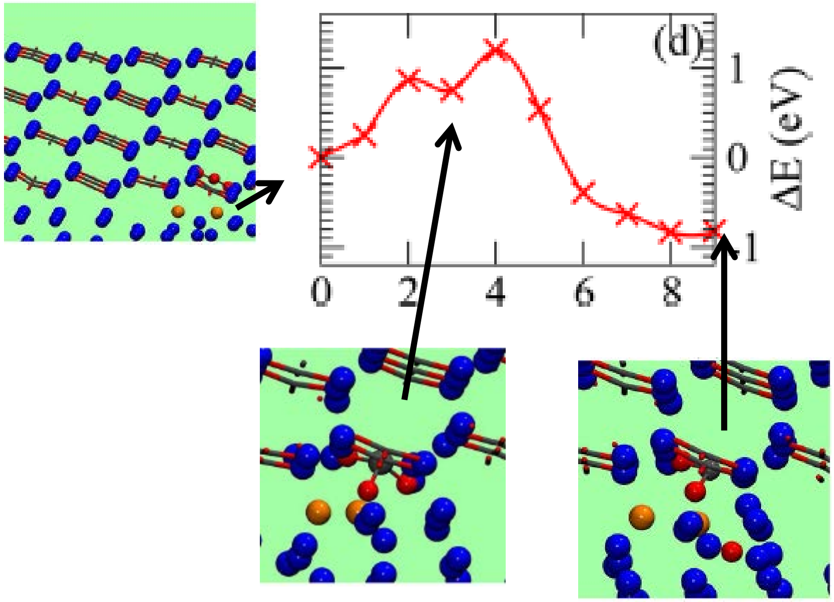
Technical Accomplishments: Instability of SEI Products

K. Leung et al, SNL

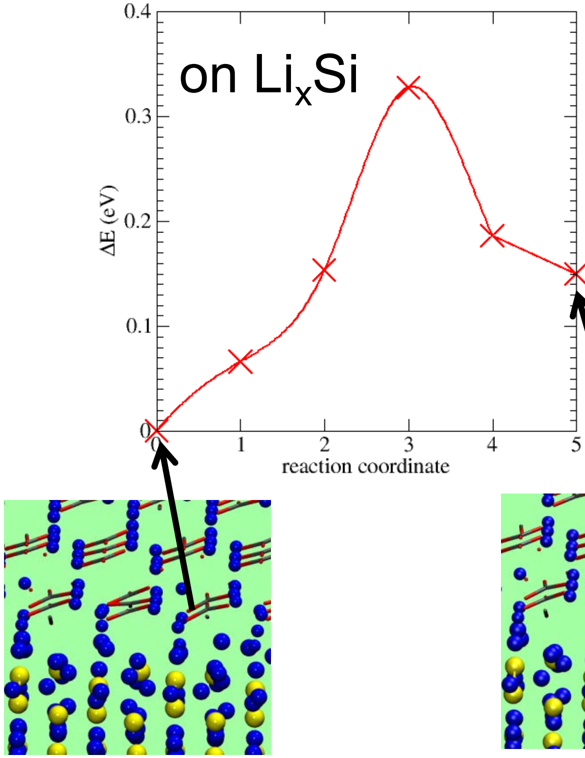
Li_2CO_3 thermodynamically unstable vs. Li(s), does the kinetics allow decomposition within 1 h?

on Li metal

after inserting **two extra Li, at 0.14 V vs. $Li^+/Li(s)$**, near target $CO_3{}^{2-}$ unit, *rate-determining step* (CO_3 bending) barrier is low, consistent with 1/s rate



after inserting **two extra Li (0.07 V)** near target $CO_3{}^{2-}$ unit, *rate-determining step* (CO_3 bending) barrier is very low, consistent with 1/millisecond rate



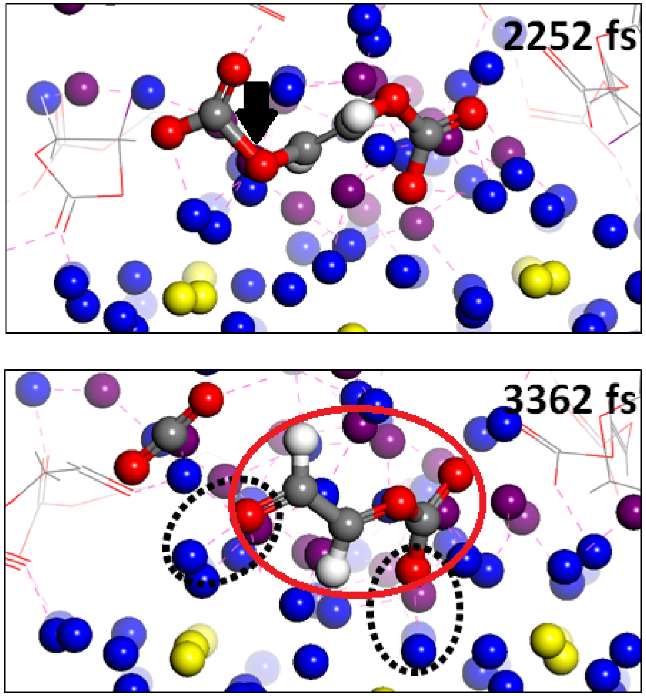
final C-O breaking step is exothermic

unpublished, preliminary results

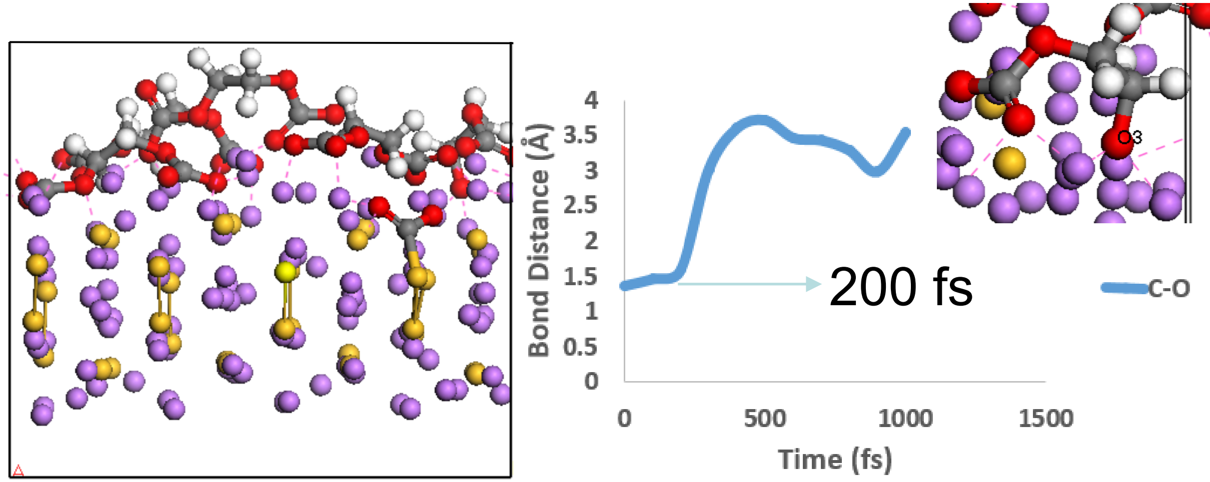
Kevin Leung,[*,†] Fernando Soto,[‡] Kie Hankins,[‡] Perla B. Balbuena,[‡] and Katharine L. Harrison[†]
J. Phys. Chem. C 2016, 120, 6302−6313

Milestone Q1/Y3 ✓ : Quantify chemical and electrochemical stability of SEI products

Technical Accomplishments:
Instability of SEI Organic Oligomers



Li_2VDC decomposes over LiF cluster-covered $Li_{13}Si_4(010)$ surface in 1M $LiPF_6$/FEC solution yielding CO_2 (neutral) and $OC_2H_2CO_3$ radical anion

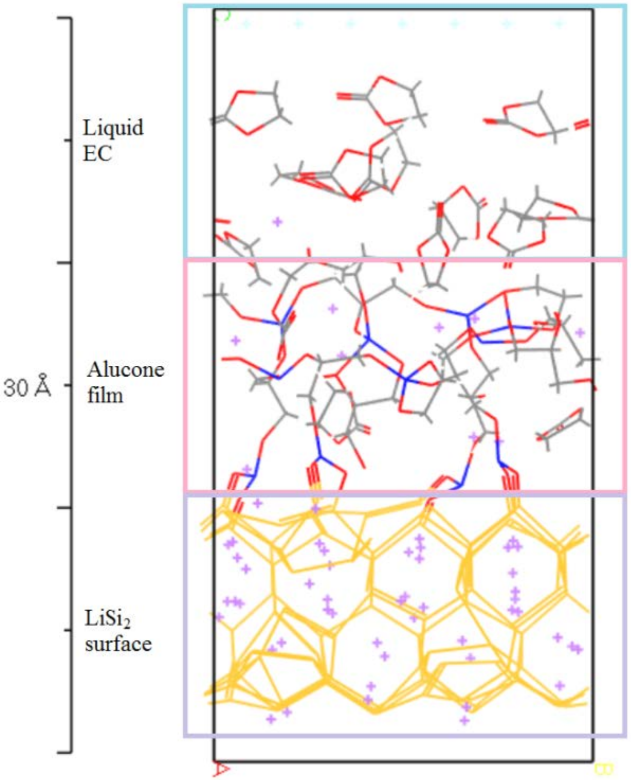


Li_2EDC nucleates over a bare $Li_{13}Si_4$ (010) surface through O-Si and O-Li interactions and O..Li..O interactions among Li_2EDC molecules. AIMD simulations detected decomposition of Li_2EDC molecules in the nucleating block in contact with the surface.

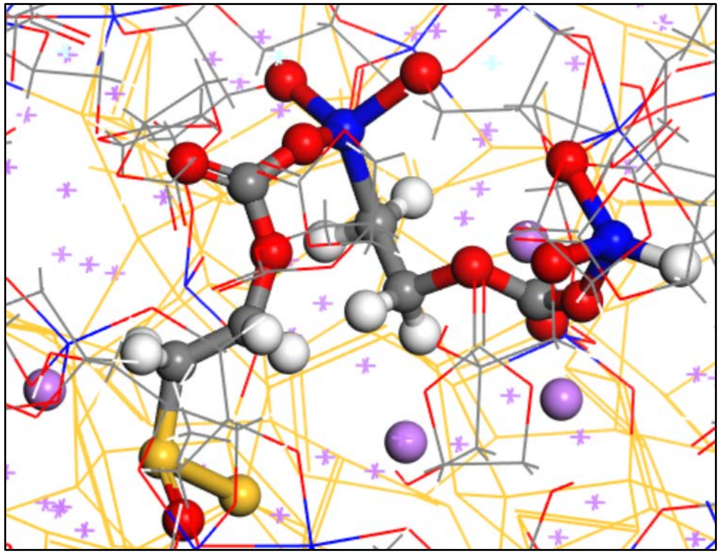
Leung et al, *JPCC* 2016; Soto et al, *Chem. Mater*. 2015

Milestone Q1/Y3: Quantify chemical and electrochemical stability of SEI products ✓

Technical Accomplishments: SEI on Alucone-Covered Lithiated Si Surfaces



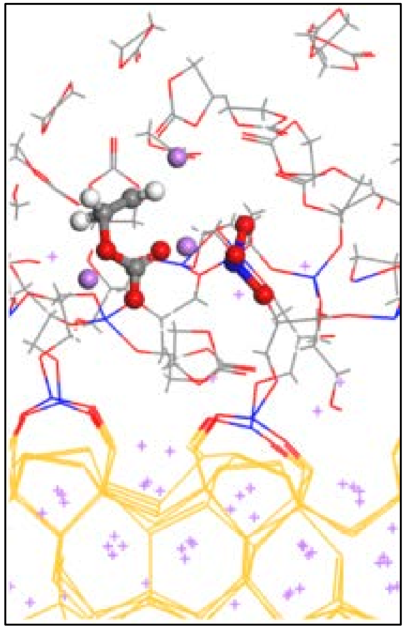
Gomez-Ballesteros and Balbuena, to be published



Al: blue; Li: purple; Si: yellow; C: grey; O:red

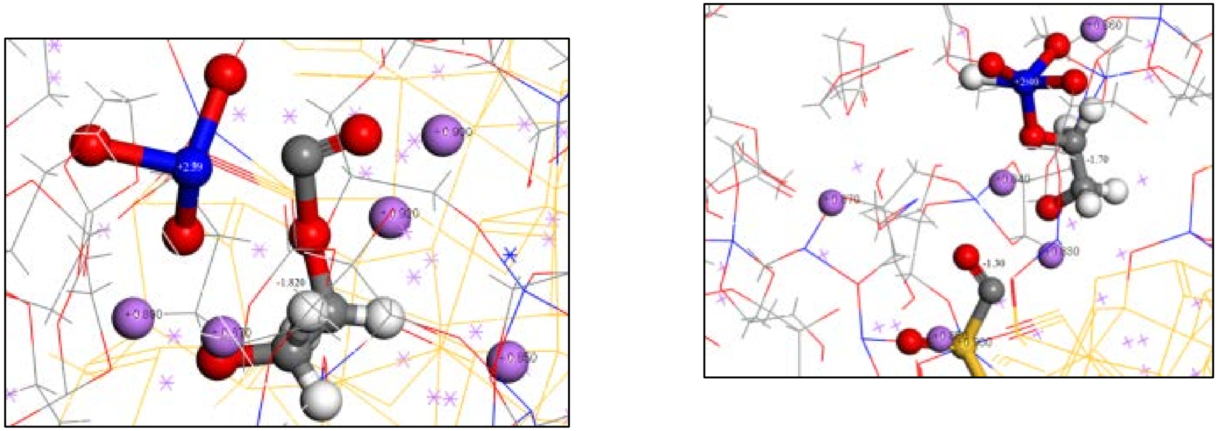
SEI fragments incorporated into alucone film

reactions inside the film or at the interfaces

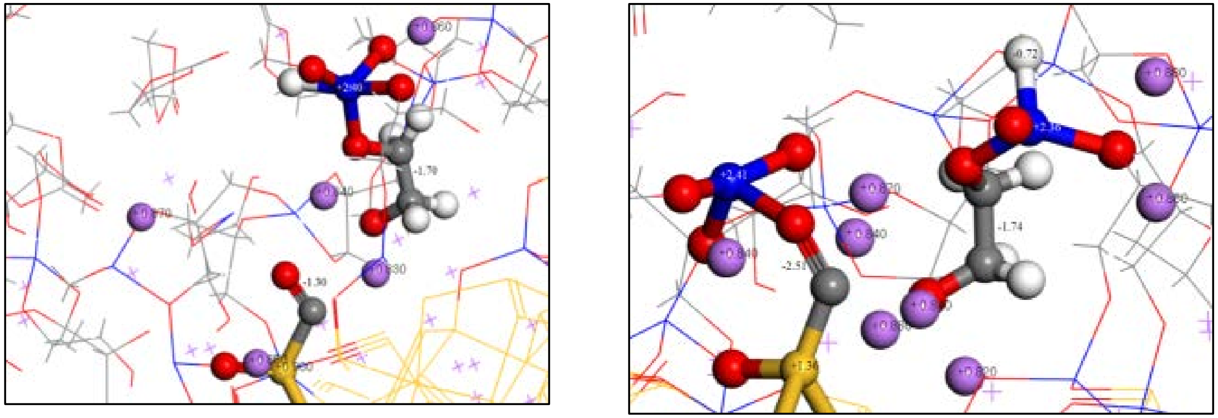


Milestone Q1/Y3 ✓ : Identify SEI nucleation and growth on Si surfaces modified by deposition of alucone coatings as a function of degree of lithiation of the films.

Technical Accomplishments: Artificial SEI Modified by Products of Natural SEI



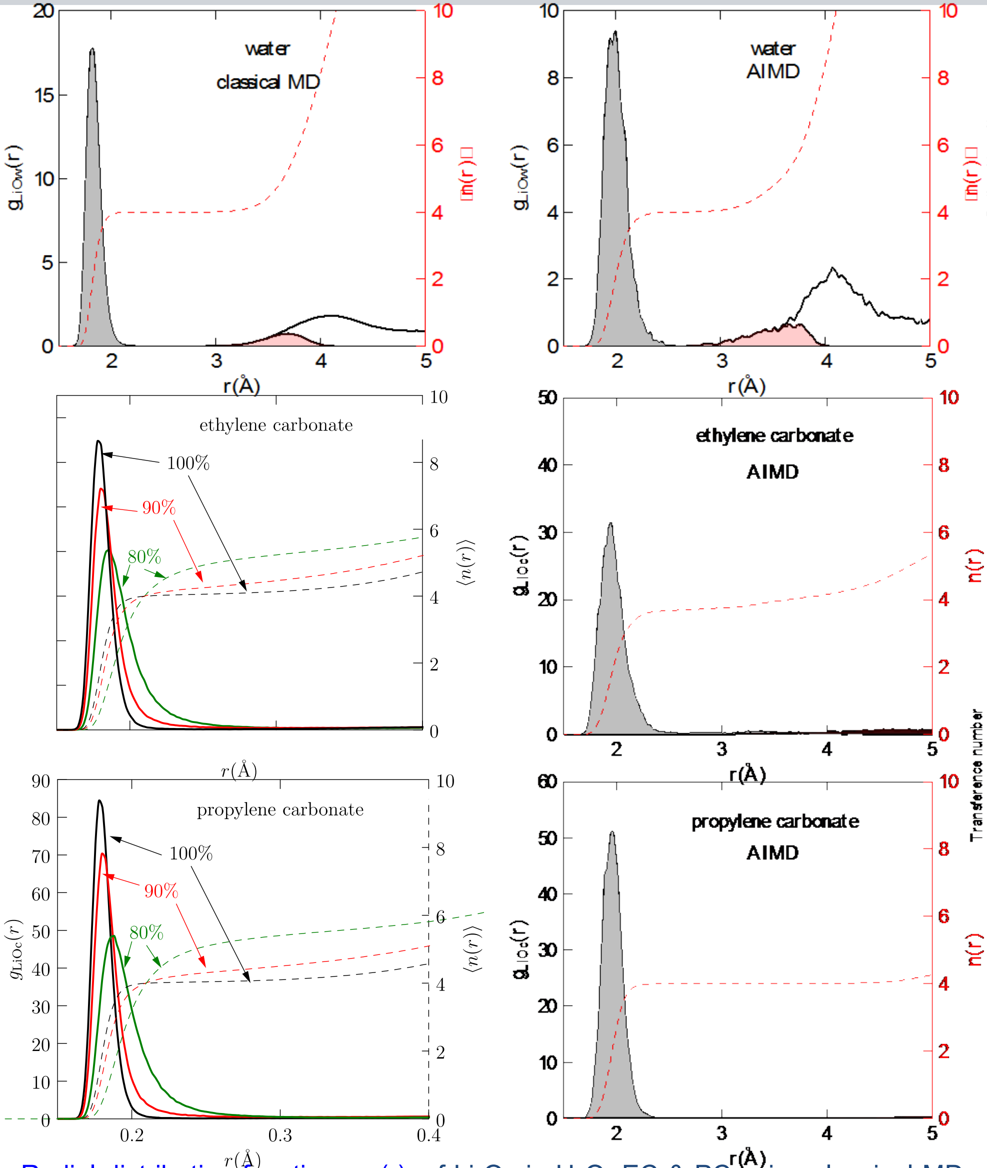
EC opening and binding to AlO_x group



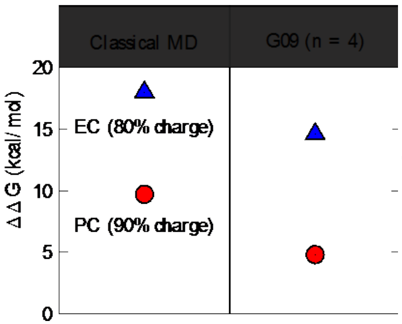
CO separates and fragments bond to film and Si

Milestone Q1/Y3 ✓: Identify SEI nucleation and growth on Si surfaces modified by deposition of alucone coatings as a function of degree of lithiation of the films.

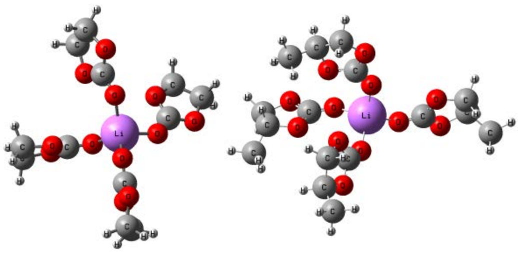
Technical Accomplishments: Solvation structures



Radial distribution functions, $g(r)$, of Li-O_C in H_2O, EC & PC using classical MD and AIMD. The Soeten *et al.* partial charges on EC & PC are reduced to 90% & 80% to probe effects on structure & solvation free energy. Gray shading: contribution from first 4 neighbors; red shading: contribution from 5th & 6th neighbors. At certain charge values, the MD & AIMD structures agree.

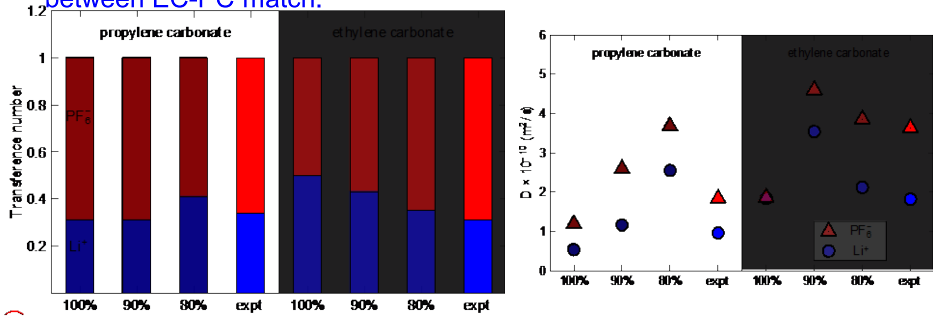


Free energy required to transfer Li^+ from water to the carbonate electrolytes for % partial charges used for EC & PC. We also used quasi-chemical theory & electronic structure methods (G09) with 4 ligands to calculate the free energies. Transfer between EC-PC match.



Energy-optimized structures of Li^+ and 4 electrolyte ligands using PBEPBE1 functional & 6-311++G(3df,2pd) basis set.

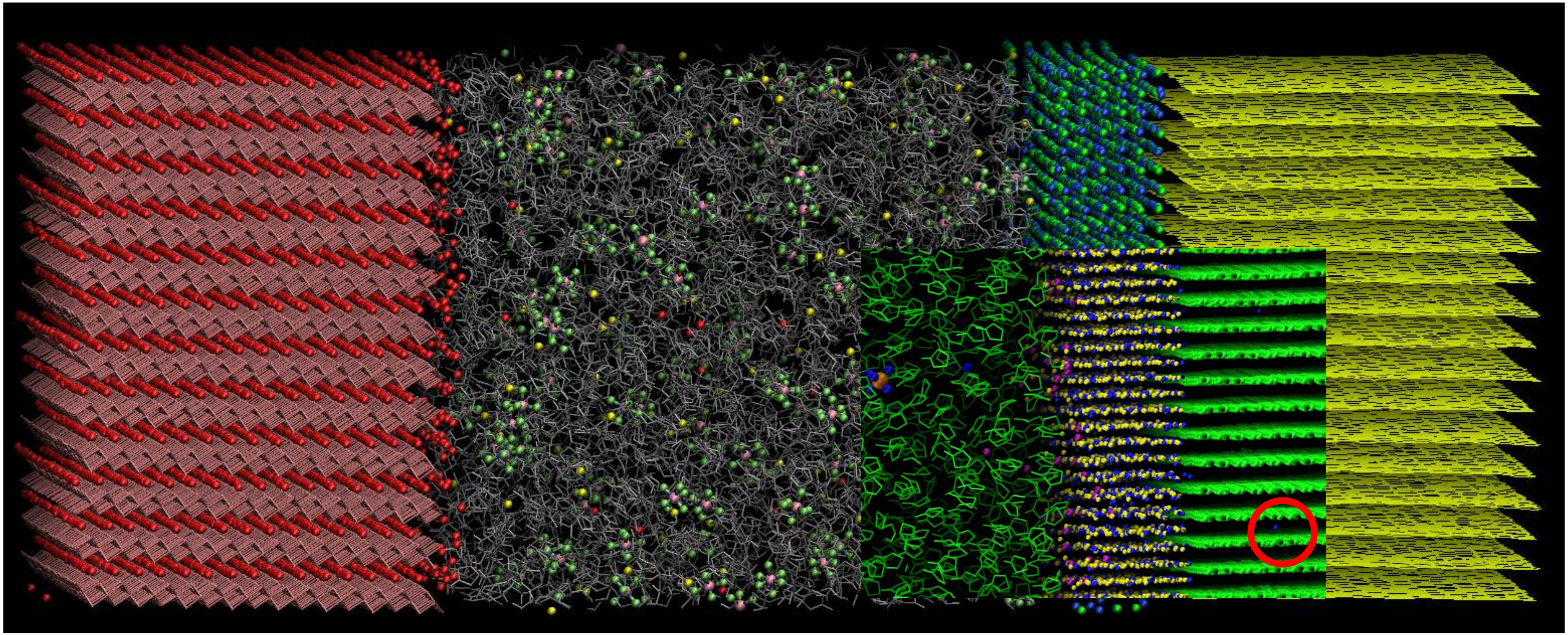
S. Rempe et al, SNL



Transference numbers and diffusion constants of Li^+ and PF_6^- in PC & EC plotted for different sets of partial charges. Experimental numbers are calculated using diffusion constants reported in Hayamizu, K. (2013), *J. Chem. & Eng. Data,* 57, 2012.

CONCLUSIONS: Non-polarizable force fields can predict solvation and transport properties of $LiPF_6$ salt with reasonable accuracy. Electrostatic interactions dominate structure & solvation free energy. Force field parameters can be tuned to achieve results comparable to experiments. Although diffusion constants change with changing partial charges, ionic transference numbers remain reasonably constant.

Technical Accomplishments: Molecular dynamics simulations of nanobattery charge



Defects needed for diffusion of Li^+ ions through LiF layer. An applied E Field yields the applied voltage during charge. Simulations reveal transport mechanism of ions

Current work on Si anodes

Seminario et al, TAMU, to be published

Milestone Q3/Y2: SEI blocks characterization ✓

Technical Accomplishments: Growth of Li_2EDC Film Over Anode Surface

(1) EC + * → EC* with adsorption rate k_1,

(2) EC* + e^- → c-EC^- with reduction rate k_2,

(3) c-EC^{--} → o-EC^- with conformational transition rate k_3,

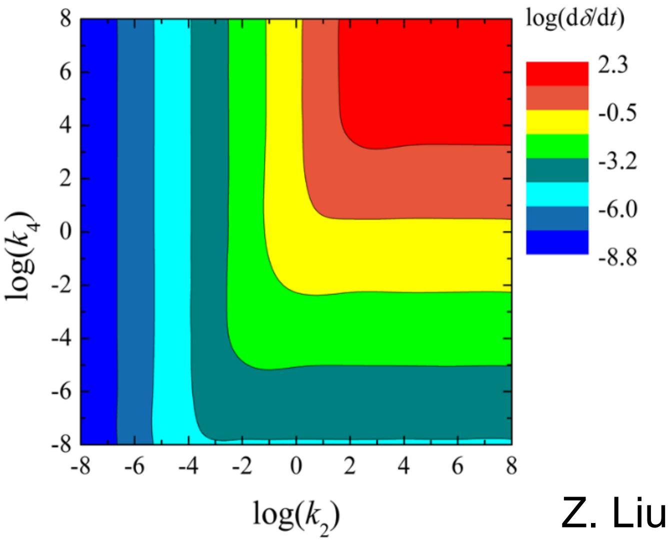
(4) 2 o-EC^- + 2 Li^+ → Li_2EDC + C_2H_4(↑) with formation rate k_4.

(a) Effect of electrochemical reduction rate k_2 and EDC formation rate k_4 on growth rate of EDC film.

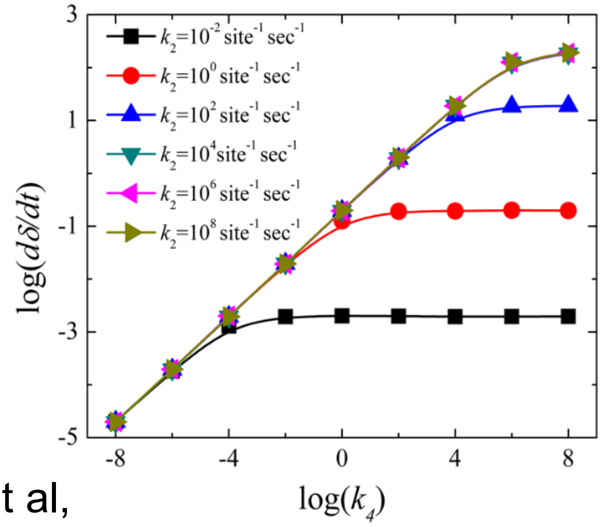
k_2 and k_4 vary from 10^{-8} to 10^8 /site/sec

(b) SEI growth rate vs. SEI formation rate k4 w/different electrochemical reduction rates.

Units of growth rate ($d\delta/dt$) are Å/sec.



(a)



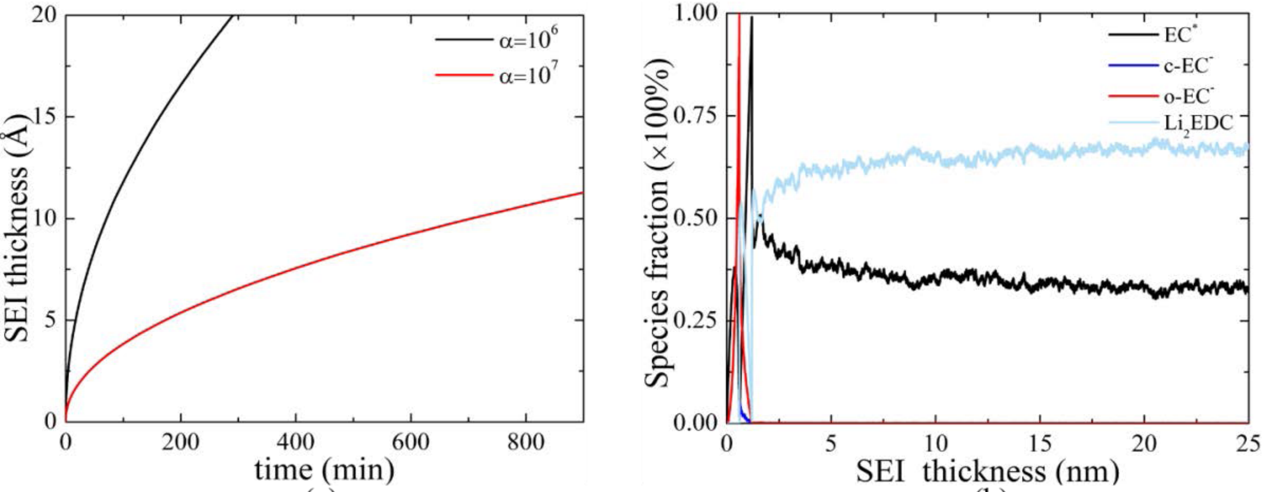
(b)

Z. Liu et al,
to be published

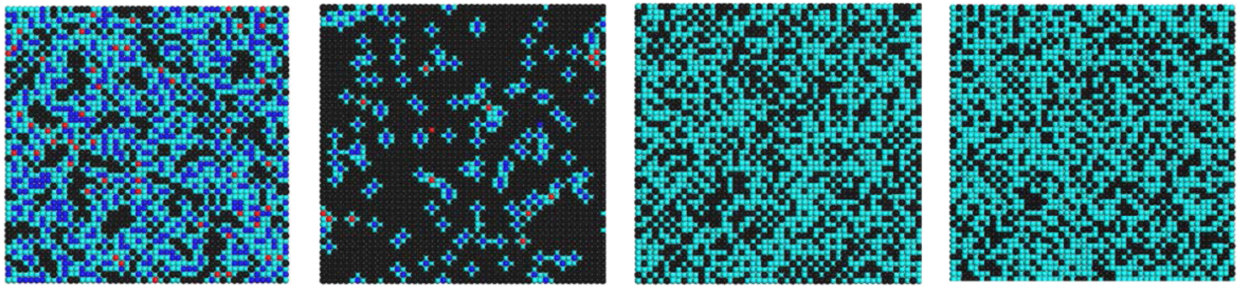
Collaboration with P. P. Mukherjee, TAMU

Milestone Q3/Y2: ✓ Characterization of SEI formation from building blocks

Technical Accomplishments: Growth of Li_2EDC Film Over Anode Surface



(a) (b)



(c) 0.75 nm (d) 1.05 nm (e) 3.15 nm (f) 6.15 nm

(a) SEI thickness-dependent reduction rates $k_2(\delta)$.
(b) Species fraction at the SEI/electrolyte interface; $\alpha = 10^7$;
$k_2(0) = 10^8$ site^{-1} sec^{-1}.
Snapshots: top view of SEI film in the KMC model
Black: EC^*, Red: $c\text{-}EC^-$,
Blue: $o\text{-}EC^-$ site,
Cyan: Li_2EDC.

A more accurate $k_2(\delta)$ equation will be used in the KMC model in future work where the α parameter will be obtained directly from the decay obtained for a given thickness from a first-principles approach

$$k_2(\delta) = k_2(0) \times \frac{l_0}{\alpha \times \delta + l_0}$$

Z. Liu et al,
to be published

Collaboration with P. Mukherjee, TAMU

Milestone Q3/Y2: ✓ Characterization of SEI formation from building blocks

Responses to Previous Years Reviewers' Comments

Q: The presentation of the PI at the AMR was largely qualitative. Unclear if statistical data analysis was performed to ascertain the conclusions.

A: First principles methods provide both qualitative and quantitative information. Elucidating reaction mechanisms and evaluating reaction barriers as shown in this report are quantitative measurements. As an example of the statistical analysis, we provide the standard deviations obtained in MD simulations (slide 33 for Reviewers only). Several initial configurations are tested to evaluate the dependence of the position, orientation, and environment of the molecule with respect to the surface, which are shown critical in reductions due to electron transfer from the electrode.

Q: It is hard to believe that the hydroxylated amorphous film LixSiO2.48H0.9 shown in Slide 7 exists only at this particular composition.

A: In the oral presentation due to time limitations we only show examples. Our paper *JPCC* 119, 16424-16431, (2015) has all the information for this case.

Q: What is "reasonable agreement' with experiments, slide 18.

A: Explicit experimental data is included in slide 33 for Reviewers only.

Q: It is difficult to assess the impact of the calculations and how to build on the conclusions.

A: Last year we obtained two significant conclusions. First, electron transfer through the SEI film for thicknesses beyond electron tunneling is catalyzed by radical species that are present not only by direct decomposition of the electrolyte components but also due to decomposition of the SEI products, *Chem. Mater.* 27 (23) 7990-8000 (2015). Thus the second conclusion relates to the SEI products instability and we elaborate in this aspect extensively in this presentation. The impact is clear if we think in the importance of developing a better understanding of the SEI layer.

Responses to Previous Years Reviewers' Comments

Q: Will HF be formed due to FEC dissociation as fluorine is generated..

A: HF was never observed in our DFT/AIMD analyses as a product of FEC decomposition. F radicals rapidly combine with Li ions forming LiF.

Q: It is not clear why it is claimed that EC leads to uncontrolled SEI growth.

A: The reason is that EC leads to products such as lithium ethylene dicarbonate and others that are unstable generating more radicals that keep the reduction reactions alive. Instead, VC tends to produce more stable polymers.

Q: More connections with the experiments can be made.

A: In our paper *Chem. Mater.* 27 (23) 7990-8000 (2015) we made extensive comparisons to experiments.

Q: Collaborations with experimentalists have not produced quantitative comparisons between theory and experiments. It is unclear whether the modeling effects have produced quantitative predictions to guide experiments.

A: Our collaboration with NREL published in *ACS Appl. Mater. Inter*., 7, 11948-11955, (2015) showed calculated electron transfer through alucone-covered Si anodes as a function of lithiation degree of the coating, which explains the increase of electronic conductivity of the alucone film as the film becomes lithiated. Furthermore, in this presentation we show new results of SEI reactions illustrating the different chemistry of these SEI films. It should be noted that we are not doing theory to see if we can reproduce the experiments. We are using theory as an additional tool which is able to provide new insights into these complex phenomena. In addition, other groups use our results to explain their experimental results, see for example Meng et al, *Chem. Mater.,* 27, 5531-5542, (2015) explaining the effect of FEC as an additive in lithiated Si anodes.

Responses to Previous Years Reviewers' Comments

Q: It is unclear how the microscopic models can be used effectively to develop mesoscopic models.
A: In this poster we give an example of this, where we use the rates of the reactions predicted by our microscopic models and built into mesoscopic models.
Q: Any suggestions on new additives and solvent molecules that should be tested in future work.
A: It is in our plans for this year, and we are currently working on it.

Collaboration and Coordination with Other Institutions

- Sandia National Lab (SNL): This proposal was written jointly with SNL. It was awarded separately to TAMU and SNL. This report includes both contributions from TAMU (Balbuena, Seminario) and SNL (K. Leung and S. Rempe). .
- National Renewable Energy Lab (NREL): Chunmei Ban (NREL, BATT program) developed and deposited a protective alucnone coating over a Si anode. This team (TAMU) modeled the nucleation, growth, and SEI reactions on the coated Si anode.
- University of California San Diego (UCSD): This team (TAMU) collaborated with Shirley Meng (UCSD, BMR) who studies the effects of additives on SEI formation reactions in Si anodes.

Remaining Challenges and Barriers

- We have made significant progress determining how the various products aggregate and nucleate forming the SEI building blocks. We still need to determine the ***effects of an applied voltage on aggregation and nucleation***.
- We reported initial studies towards ***ionic conductivity*** through the SEI blocks in model electrodes, additional challenges due to ***Si swelling*** will be addressed.
- A mesoscopic model to evaluate ***capacity fade as a function of SEI film properties*** needs to be refined to include other SEI products and reactions.
- A further challenge is to use the knowledge obtained from these studies to ***identifying alternative effective electrolytes***.

Proposed Future Work

- **Rest of FY16**:
  - aggregation and nucleation of SEI products
  - identify alternative electrolyte formulations
  - ionic conductivity through blocks
  - further developments of the SEI mesoscopic model

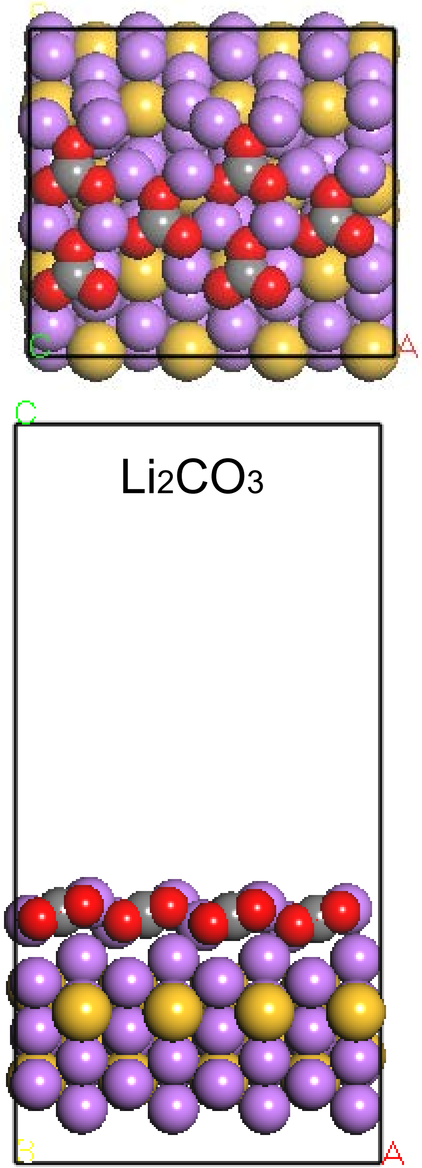
- **FY17 (this project ends in 3/31/2017):**
  - evaluating SEI mesoscopic model
  - testing alternative electrolyte formulations

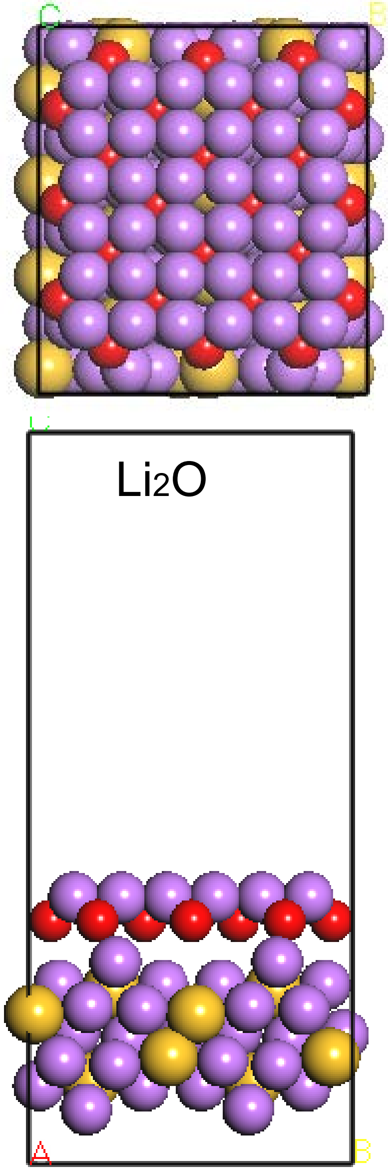
Summary Slide

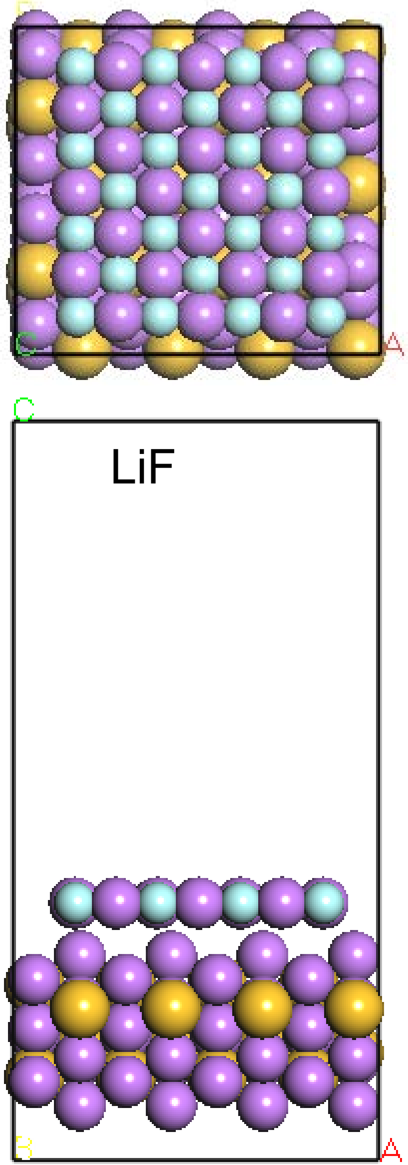
- **Relevance:** Elucidation of SEI layer nucleation and growth is crucial for evaluating irreversible capacity loss and designing improved electrolytes and electrodes.
- **Approach:** SEI product identification and assessment of electron and ion transfer through film at various stages of lithiation yield insights about *first cycle surface evolution* and *anode capacity loss*.
- **Technical Accomplishments:** characterization of SEI formed in artificial SEI layers; chemical and electrochemical instability of SEI products; nucleation and aggregation of SEI products; characterization of solvation and transference numbers in liquid electrolytes; ion transport mechanisms through SEI blocks; mesoscopic model of SEI growth.
- **Collaborations:** Instability of SEI products (with SNL); artificial coatings (with NREL); additives and salts (with UCSD and SNL).
- **Future Work:** Nucleation, aggregation, reaction of SEI products; ion transfer through blocks; alternative electrolytes.

Technical Back-Up Slides

Initial configurations for inorganic overlayers







Procedure for Adsorption of Fragments

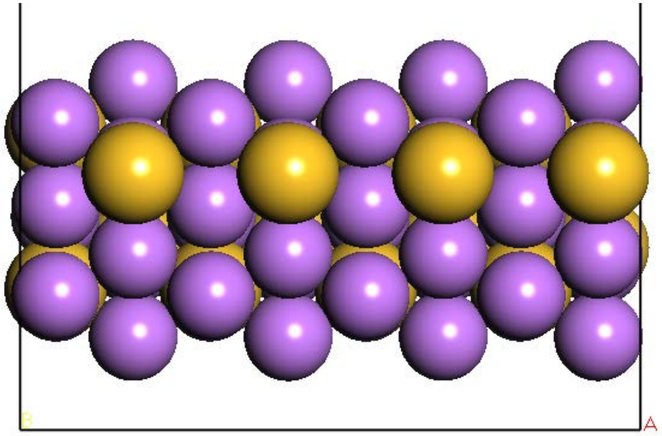
Step 1

Step 2

Step 3

Step 4

SEI



- The bare and pre-covered $Li_{13}Si_4$ anode is our surface model

Adsorption of Fragments

****For this example, Li_2EDC is placed on bare $Li_{13}Si_4$ surface**

Step 1

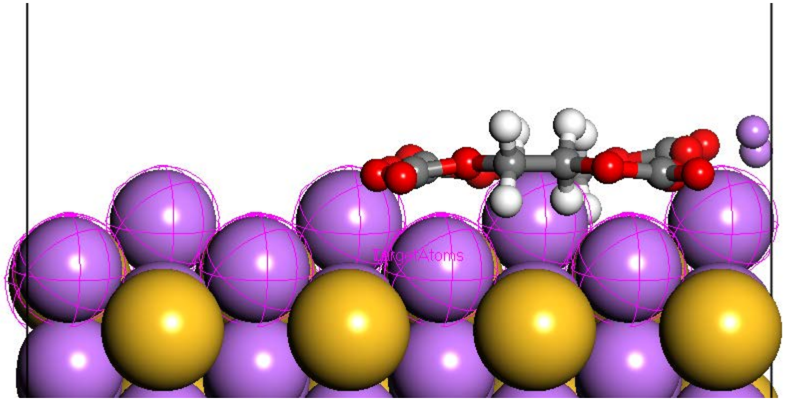
Step 2

Step 3

Step 4

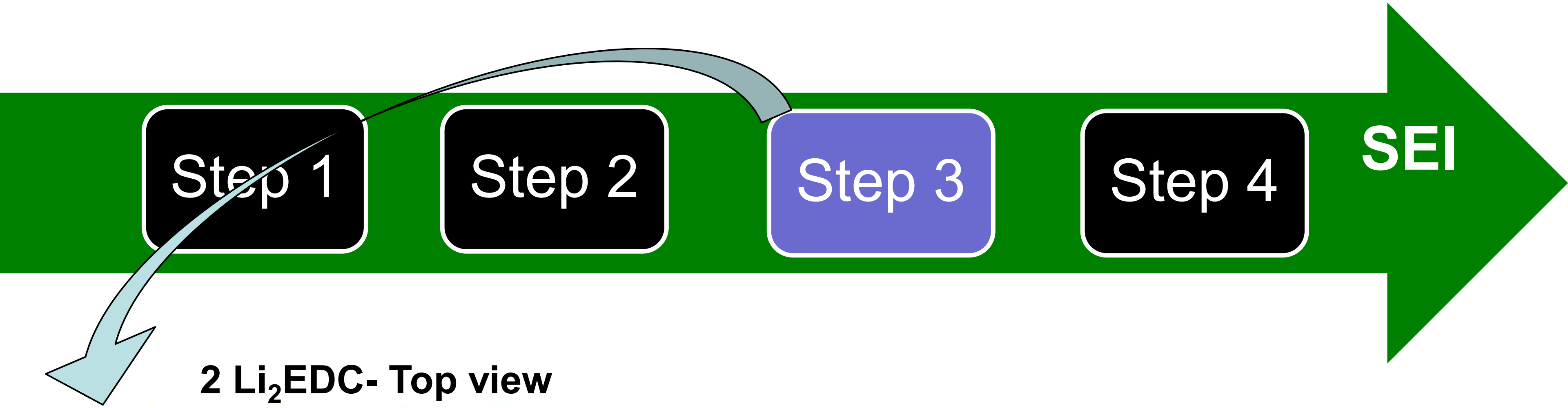
SEI

LiEDC- side view

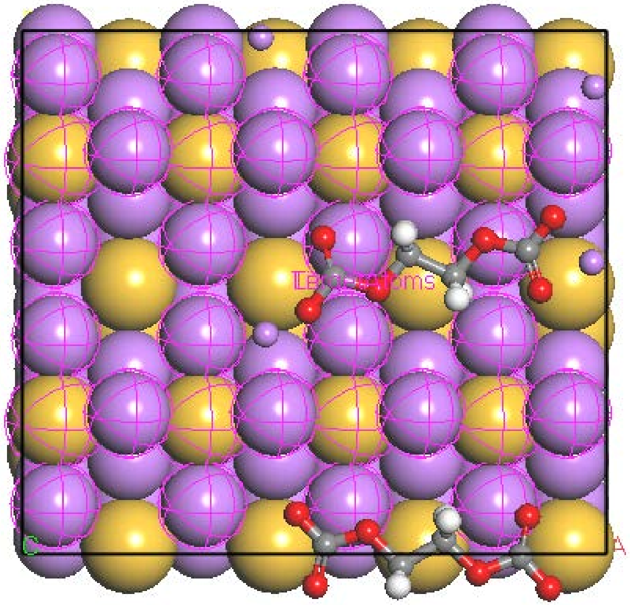


- Sequential addition of fragments
- Atom set is the surface region where fragments are adsorbed

Adsorption of Fragments



2 Li_2EDC- Top view



- 2^{nd} iteration : an additional fragment is added to the surface that already has 1 fragment

Adsorption of Fragments

Step 1

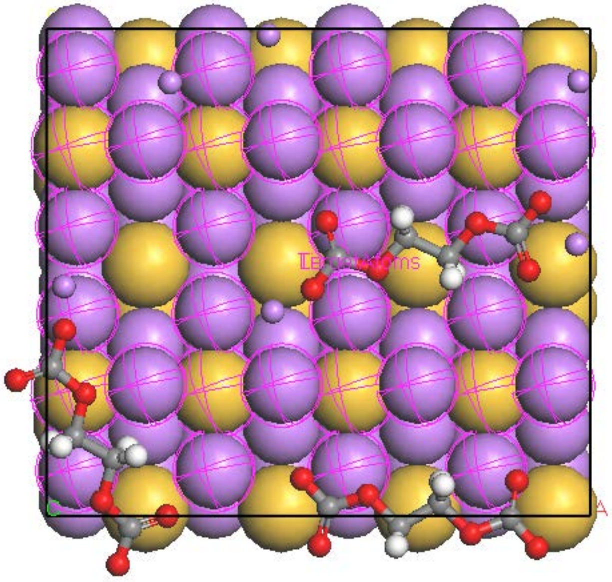
Step 2

Step 3

Step 4

SEI

3 Li_2EDC- Top view



- 3^{rd} iteration: an additional fragment is added to the surface that already has 2 fragments
- Process continues until no additional fragments can fit at one side of the anode
- The energy of fragments adsorption is calculated at each step

Reductive Decomposition of $LiFP_6$ in a covered $Li_{13}Si_4$ surface

- ***NOTE: Helium inserted in model to prevent surface interaction with solvent
- $LiPF_6$ reduction reaction depends on the composition of surface
- Salt dissociated in all cases (dissociation precedes decomposition)
- Inorganic Li salts and oligomers may decrease the frequency of reduction, prevent access to surface
- F radicals combine with Li to form LiF
- PF_x may be reduced and associated with the EC decomposition
- Li_2EDC and Li_2VDC break when in contact with bare surface