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

Perla B. Balbuena

Texas A&M University

June 11th, 2015

Project ID #: ES214

Overview

Timeline

- Start date: April 1, 2013
- End date: March 31, 2017
- Percent complete: 50%

Budget

- Total funding: $714,128
  - DOE share: $714,128
  - Contractor share: Personnel
- Funding received
  - FY14: $157,500
  - FY 15: $61,250

Barriers

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

Partners

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

Relevance

- **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 2014 goals**: Characterize SEI *growth differences* due to the nature of the solvent/additive/salt/surface structure and chemistry; characterize *electron/ion transfer* through growing 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 capacity* Si anodes depends on controlling *structural evolution* during battery operation. Understanding SEI growth will allow **rational electrolyte and electrode design.**

Milestones

- a) 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)- **Completed**
- b) Characterize reactivity of additives; identify reaction pathways and interactions of reaction products with electrolyte components; assess aggregation effects. (Jun-14)- **Completed**
- c) Go/No-Go: Development of a coarse-grained Kinetic Monte-Carlo approaching approach for assessing long-time evolution (order of days) of SEI films. (Sep-14)- **Completed**
- d) Identification of lithiation and SEI formation mechanisms through alucon coatings on Si surfaces. (Dec-14) **Completed**
- e) Clarify role of additives VC vs. FEC vs. solvent without additive on SEI properties. (Mar- 15) **Completed**
- f) Characterization of SEI mosaic formation from building blocks. (Jun-15) **Ongoing**
- g) Go/No-Go: Prediction of irreversible capacity loss and electron transfer mechanisms through the SEI layer. Criteria: Stop KMC approach if no new physical insights are obtained (Sep-15) **Ongoing**

Approach

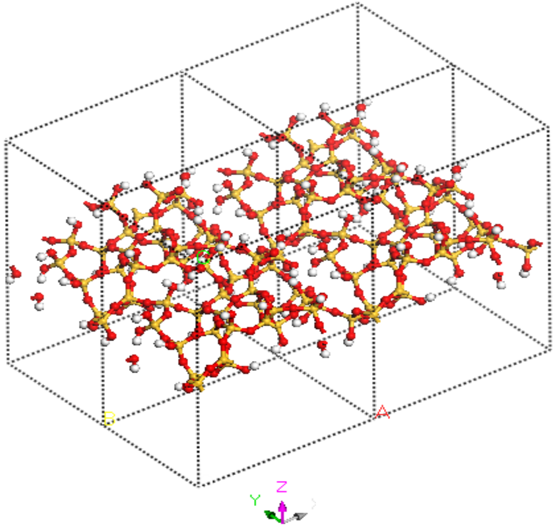
- **Overall technical Approach**:
  - Effects of native oxides and artificial surface coatings on lithiation and SEI nucleation.
  - Effects of electrolyte composition (solvents + additives + salts) on SEI nucleation.
  - Ion and electron transfer; voltage effects during SEI growth
  - Defining a big picture through a mesoscopic model
  - Addresses technical barriers/targets: Realistic surfaces and electrolyte compositions to understand *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; voltage and solvation analyses done at SNL.
- **Progress towards FY14 and FY15 milestones and Go/No Go decisions**: SEI growth and electron transfer studies build basis for planned mesoscopic scale model.

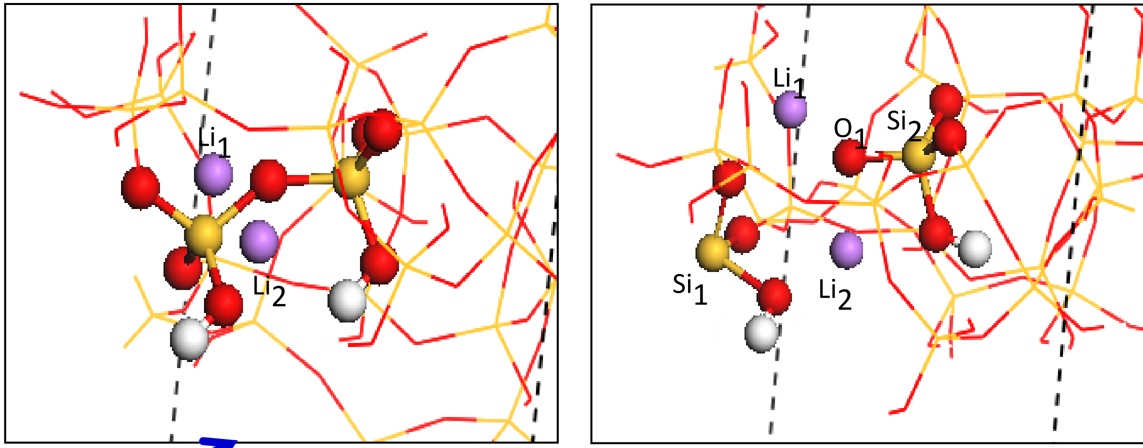
Technical Accomplishments: Barriers Addressed

- **Loss of available capacity**
  - Effects of *electrolyte composition and surface structure/chemistry* on SEI products and therefore Li retention capacity of the film.
- **Materials evolution during cycling**
  - SEI *differences between additives vs. solvents* allows characterization of possible electron transfer mechanisms → SEI growth.
- **Lifetime of the cell**
  - *Electron conductivity* through SEI –driving SEI growth- shown to depend on nature, thickness, and packing properties of the film. SEI properties influence cell lifetime.

Technical Accomplishments: Effects of surface structure & chemistry

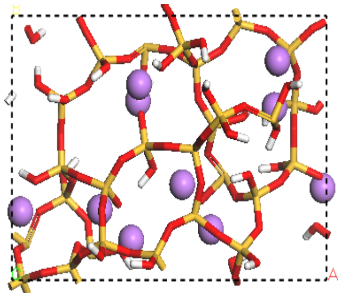
Milestone (d) ✓ lithiation mechanisms in native oxides



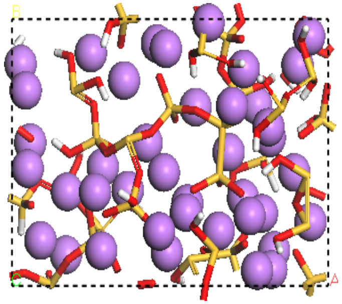


SiO broken, Si-Si formed, Li_6O complexes formed

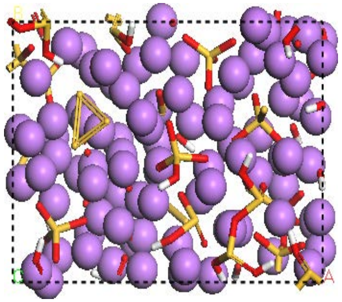
hydroxylated amorphous film $Li_xSiO_{2.48}H_{0.97}$



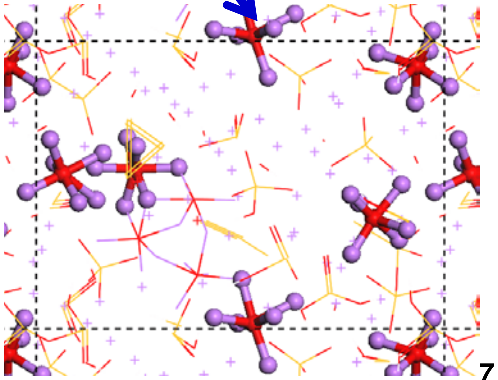
x = 0.37



x = 1.48



x = 3.33



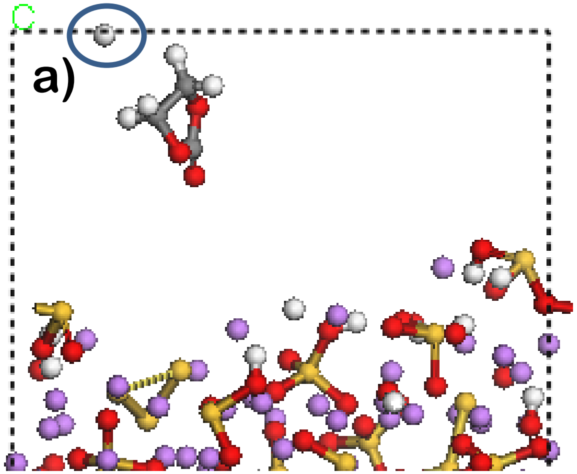
Perez-Beltran & Balbuena, submitted

Technical Accomplishments:

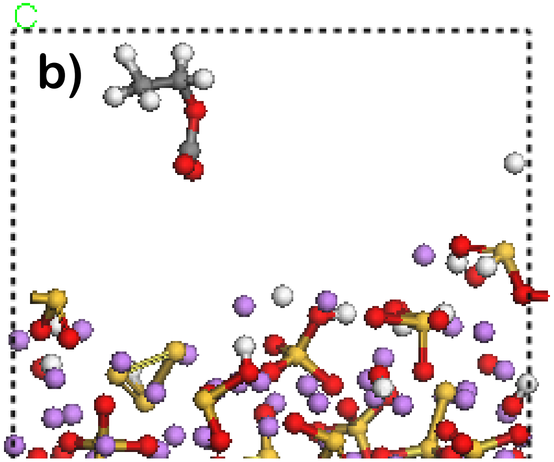
New reactivity pathways on hydroxylated SiO_2

Milestone (d) ✓

In liquid phase



EC = -0.009 |e|
H = -0.244 |e|



$C_3H_5O_3$ = -0.8612 |e|

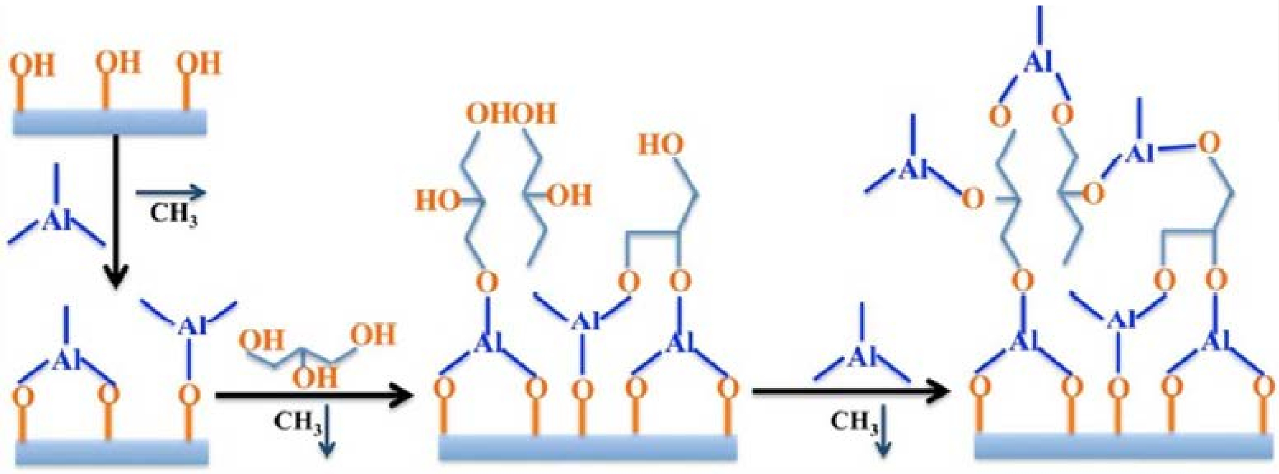
EC reduction by a H radical transferred from a decomposed surface hydroxyl group

Importance of silanol groups on reactivity

Technical Accomplishments

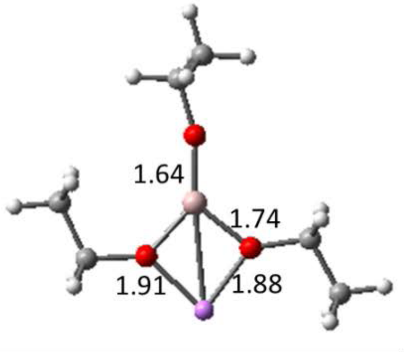
Effects of surface chemistry &structure

Milestone (d) ✓

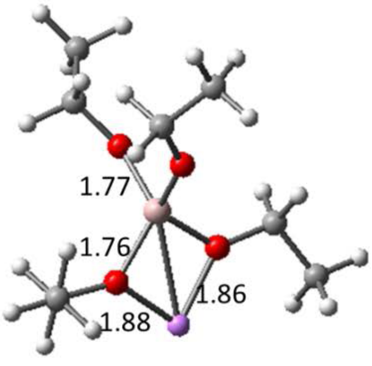


Al alcoxide (alucon) film on Si surface

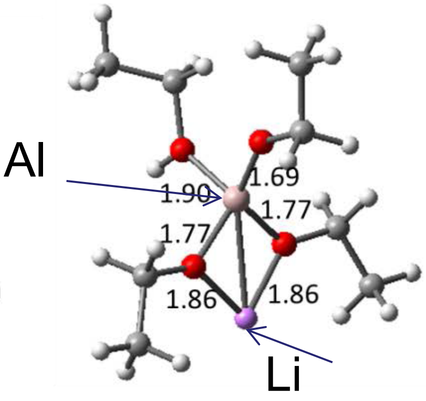
Conformal coating and fast film lithiation; strong Li-film interaction



-2.63 eV



-3.15 eV

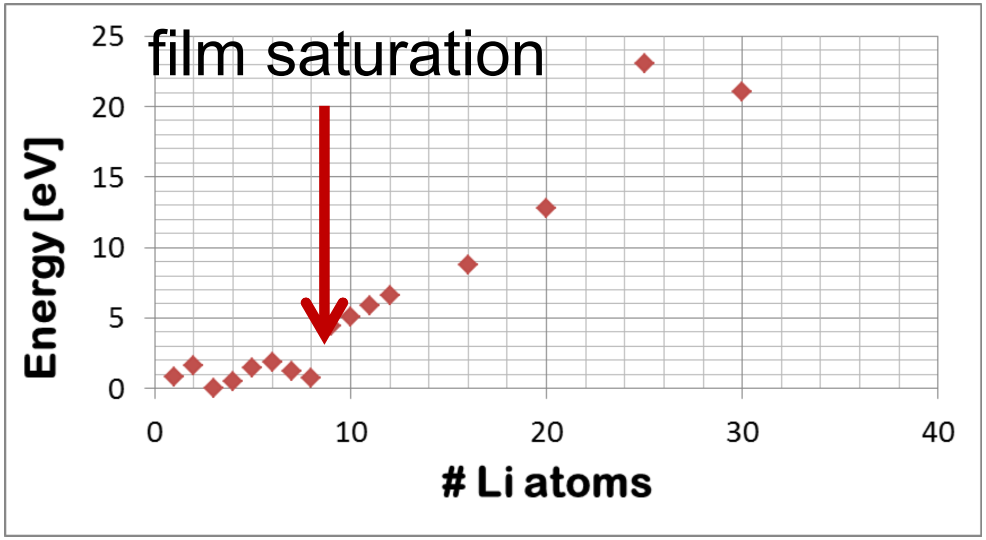


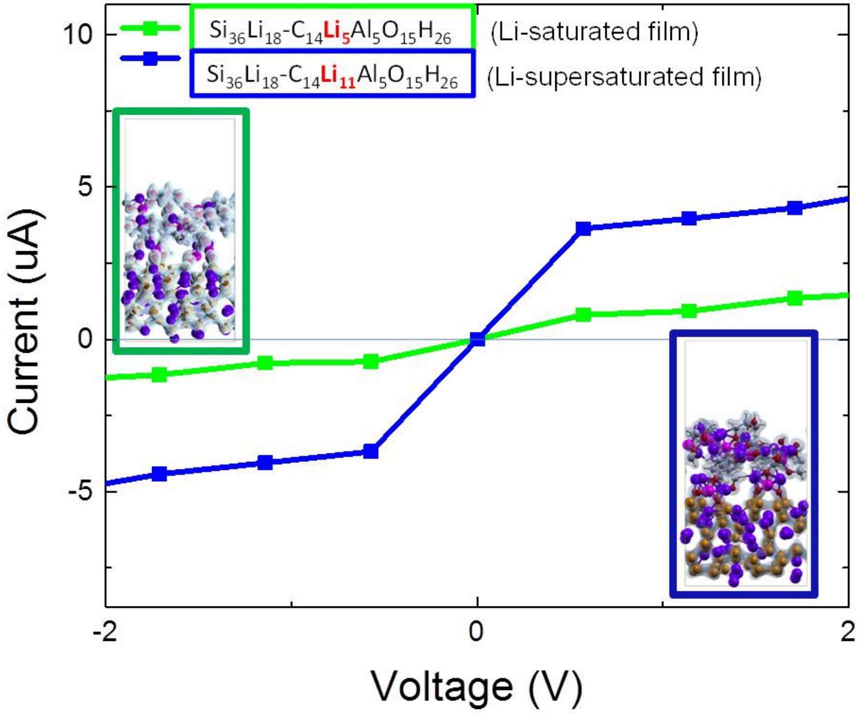
-3.3 eV

Collaboration with C. Ban (NREL)

Technical Accomplishments:
Electronic conductivity in alucone film

Milestone (d) ✓



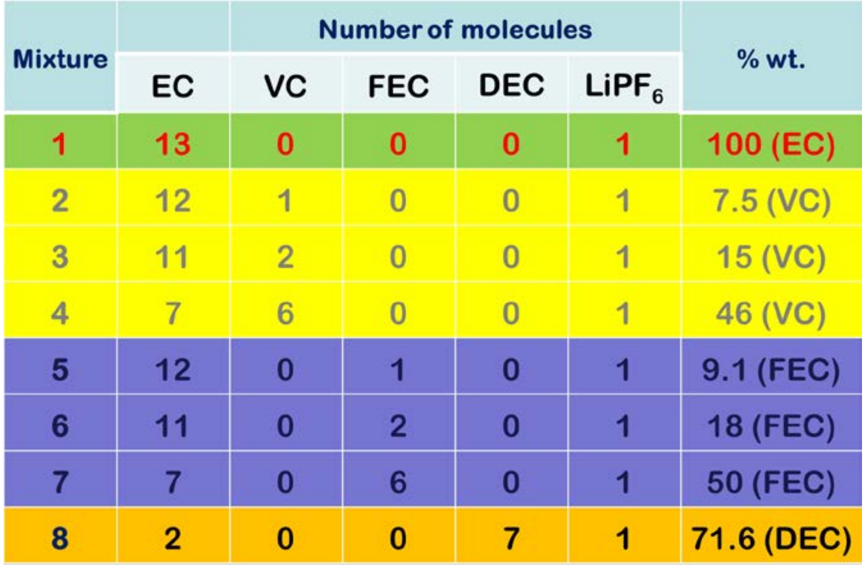


once the film is saturated with Li,
it becomes electronically conductive;
SEI reactions observed

Collaboration with C. Ban (NREL)

Seminario, Ban, Balbuena, et al. ACS Appl. Mater & Interfaces, in press

Technical Accomplishments:
Effects of electrolyte composition



Mixture	Number of molecules					% wt.
	EC	VC	FEC	DEC	$LiPF_6$	
1	13	0	0	0	1	100 (EC)
2	12	1	0	0	1	7.5 (VC)
3	11	2	0	0	1	15 (VC)
4	7	6	0	0	1	46 (VC)
5	12	0	1	0	1	9.1 (FEC)
6	11	0	2	0	1	18 (FEC)
7	7	0	6	0	1	50 (FEC)
8	2	0	0	7	1	71.6 (DEC)

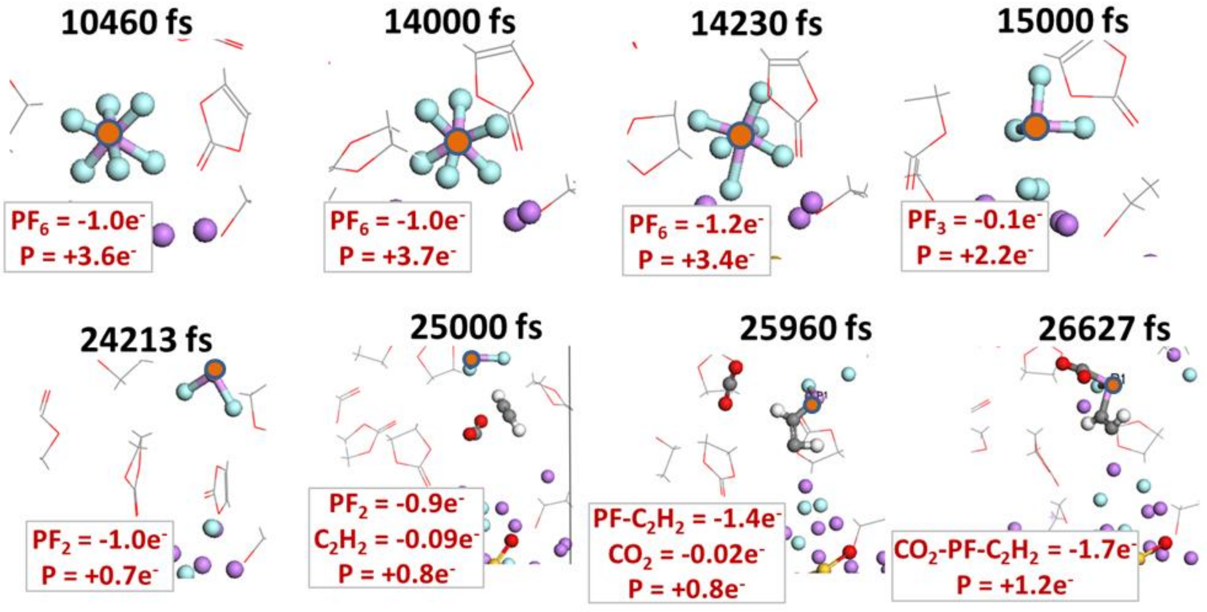
AIMD simulations of mixtures of various compositions

Milestones (b) and (e): ✓

Goals: clarify additive and salt effects in mixtures

Illustration:

mixture 3
15% wt VC



Technical Accomplishments:

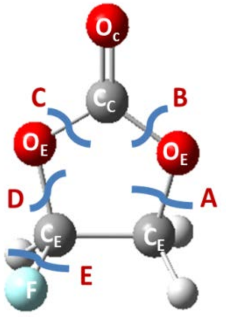
Effects of electrolyte composition

Milestones (b) and (e): ✓

- Strong competition: salt vs. solvent/additive for reduction sites
  - EC/FEC in many cases reduce before $LiPF_6$: high reactivity and relatively higher concentration
  - Radical anions from solvent/additive reduction reduce salt anion or salt fragments
  - Solvent polarity influences salt decomposition
- Rich chemistry:
  - LiF nucleation on surface, organic radical anions (adsorbed or in liq. phase), O radicals (→ Li_2O and silicates), P-species (P-Si or P-radical bonding), gas products, new pathway for CO_2 from VC

Martinez, Soto, & Balbuena, JPCC 2015

Technical accomplishments:
Role of Additives



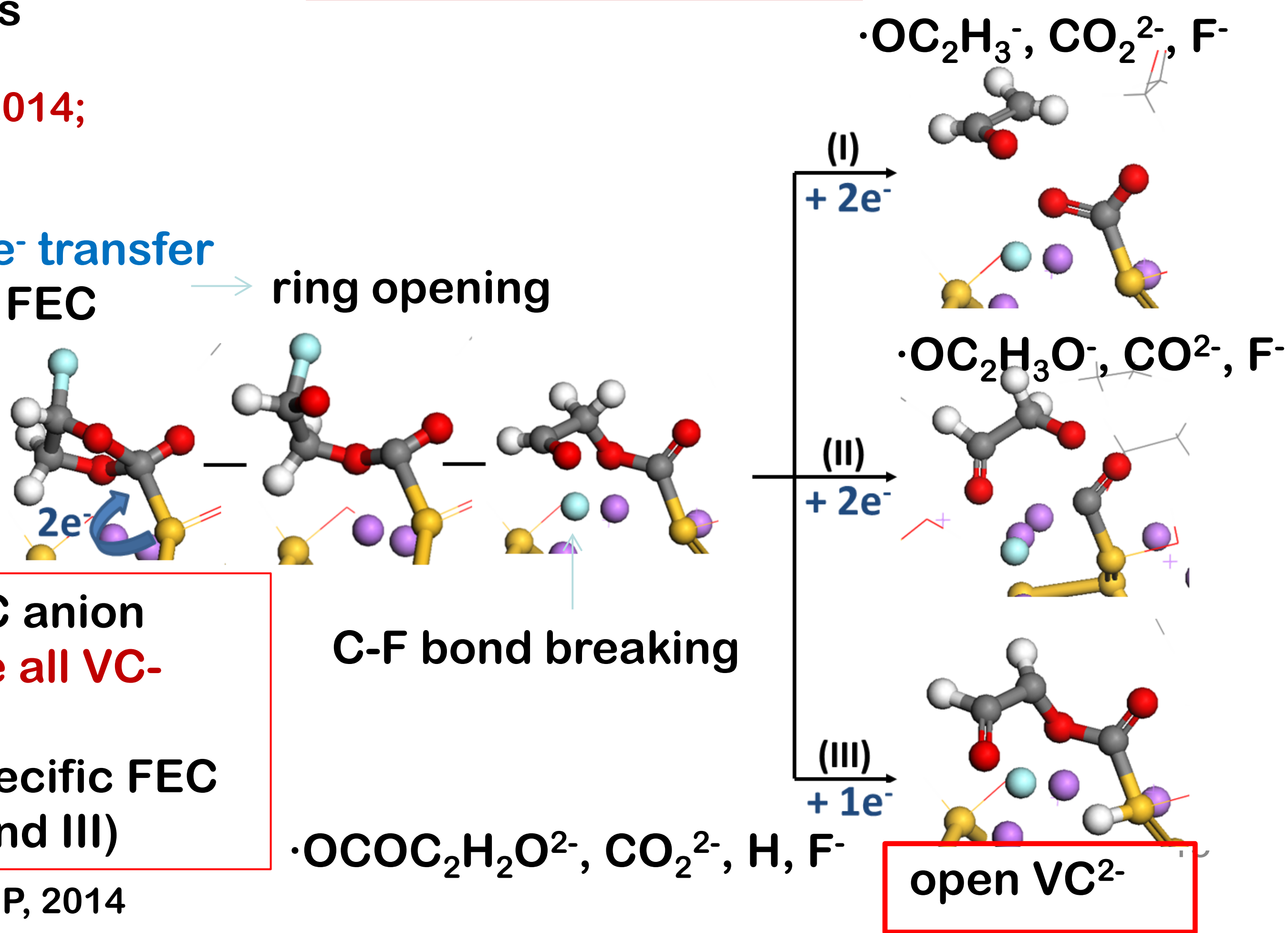
at very low lithiation

FEC: 2 e^- mechanism preferred;
C_C-O_E and C_c-F bond cleavages: low/moderate barriers

Milestone (b) ✓

Ma and Balbuena JES, 2014;
K. Leung et al JES 2014

multi-electron reactions on highly lithiated surfaces



2 e^- transfer to FEC

ring opening

C-F bond breaking

(I) + $2e^-$

$\cdot OC_2H_3^-$, CO_2^{2-}, F^-

(II) + $2e^-$

$\cdot OC_2H_3O^-$, CO^{2-}, F^-

(III) + $1e^-$

$\cdot OCOC_2H_2O^{2-}$, CO_2^{2-}, H, F^-

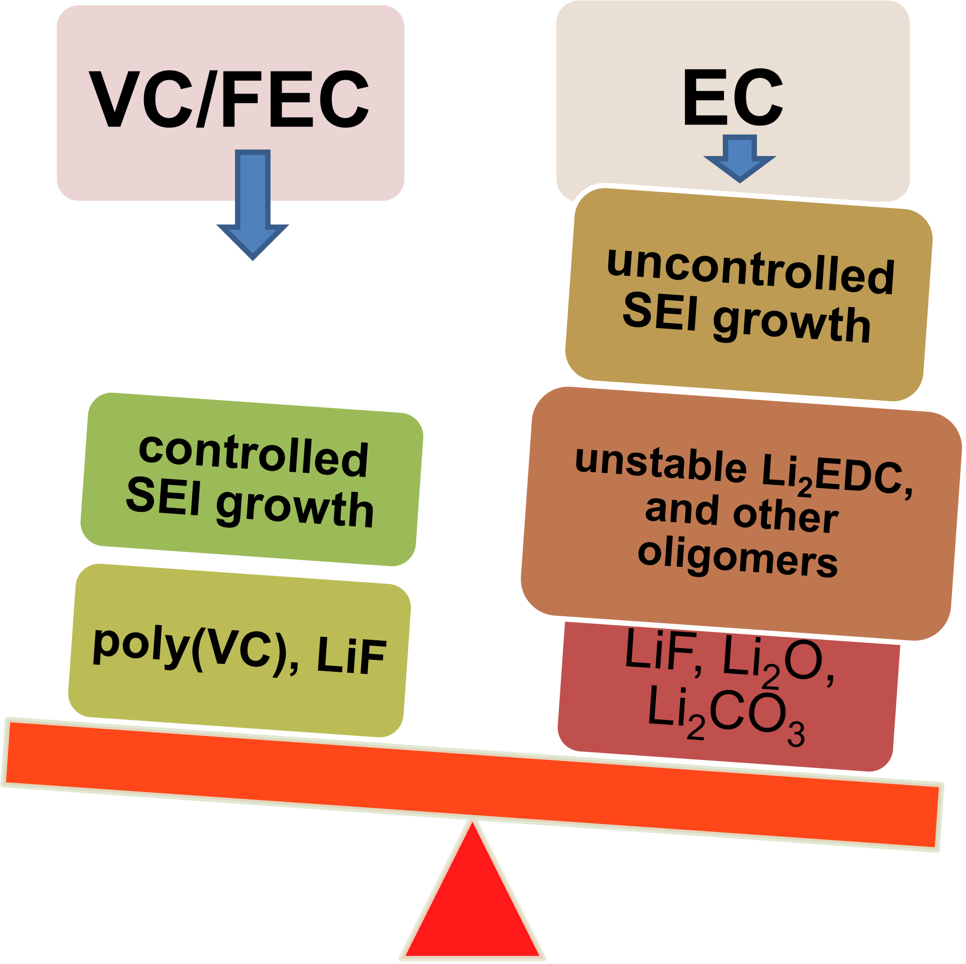
open VC^{2-}

FEC can yield open VC anion (path III) and therefore all VC-derived products ,
in addition to other specific FEC products (paths I, II, and III)

Martinez and Balbuena, PCCP, 2014

Technical Accomplishments:
SEI from VC/FEC vs. EC

Milestone (b) ✓



VC/FEC

controlled SEI growth

poly(VC), LiF

EC

uncontrolled SEI growth

unstable Li_2EDC, and other oligomers

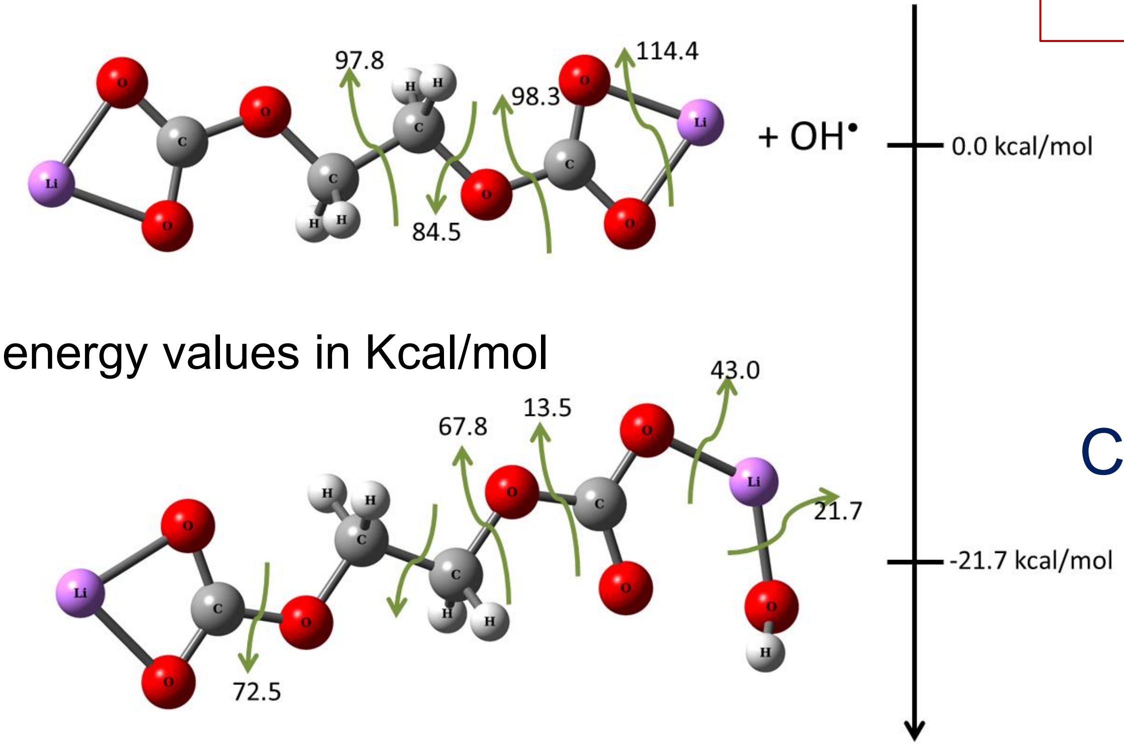
LiF, Li_2O, Li_2CO_3

oligomers (formed from Li_2EDC, Li_2VDC and others) decompose by radical attack; generate more radicals→ SEI uncontrolled growth

best additive controls excessive radical formation

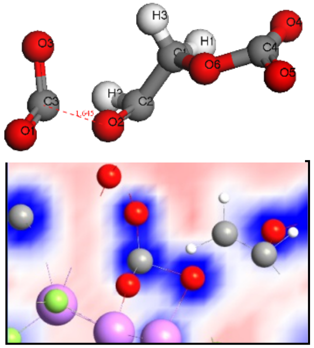
Technical Accomplishments:
Electron transfer through growing SEI

Unstable Li_2EDC, Li_2VDC

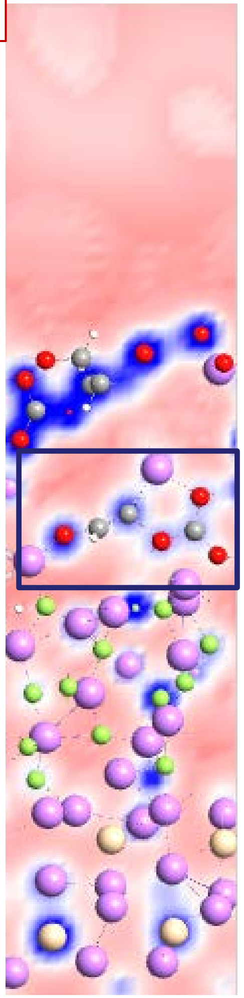


energy values in Kcal/mol

Milestone (b) ✓



CO bond breaking

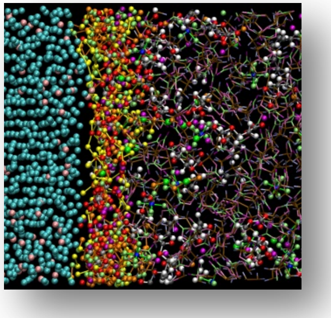


new radicals
are formed;
electron transfer
shown by
blue regions

Attack of Li_2EDC by a radical species debilitates its bonds causing fast decomposition. Same for Li_2VDC

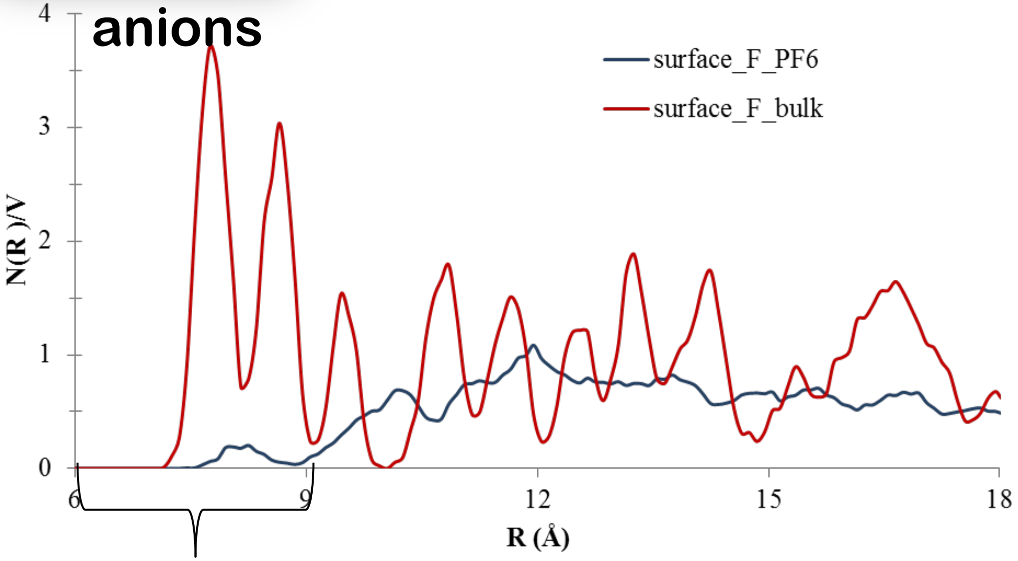
Technical Accomplishments:
Ion transfer through growing SEI layer

Milestone (b) ✓

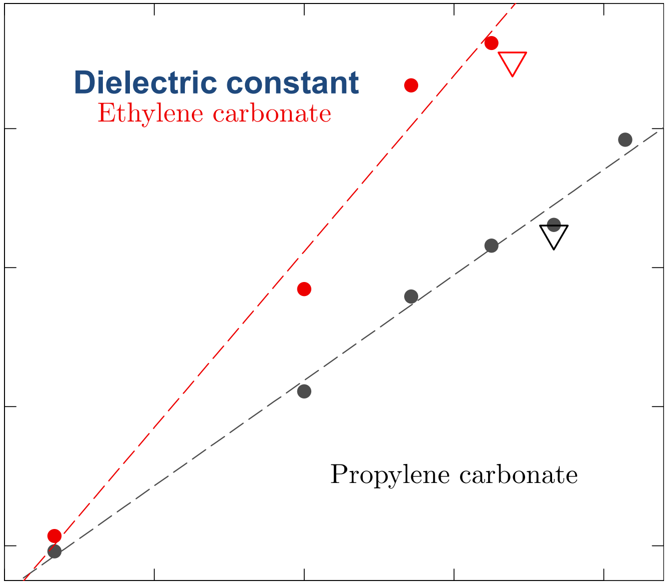


Li ions and small anions diffusion through SEI; classical MD simulations

J. Seminario et al, TAMU



SEI



- solvent dielectric properties vs T:

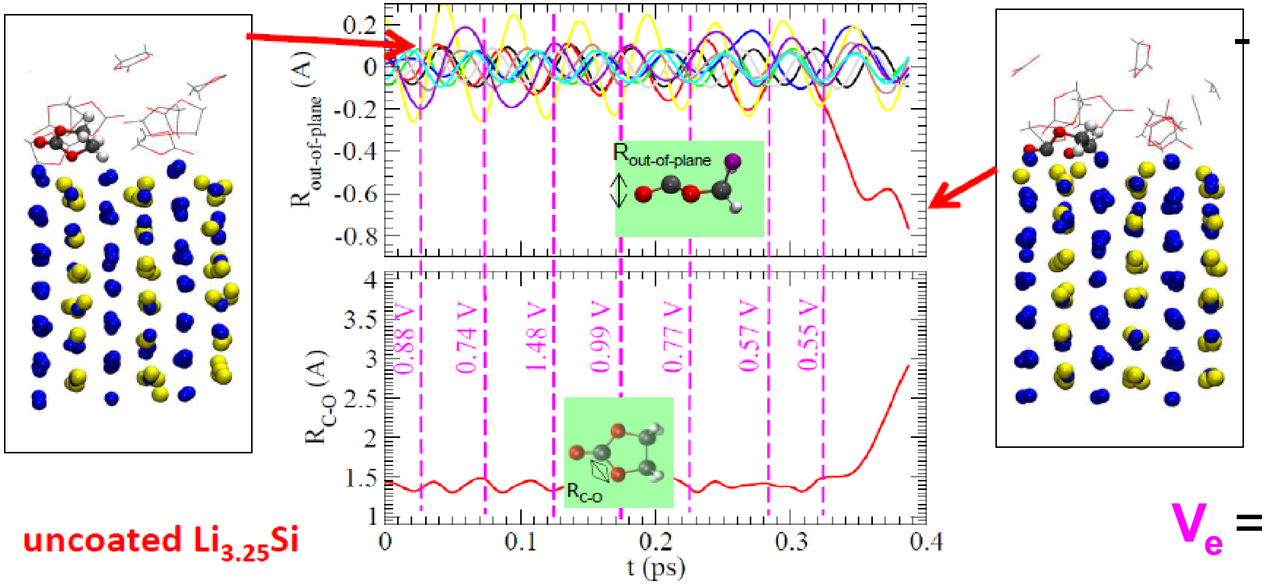
- important for solvation & dynamics
- reasonable agreement w/ experiments

S. Rempe et al, SNL

Technical Accomplishments:

Milestone (a) ✓

Voltage effects on electrolyte decomposition on Li_xSi crystal



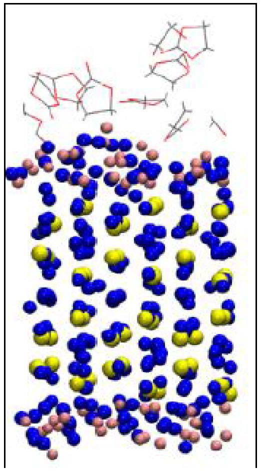
uncoated $Li_{3.25}Si$

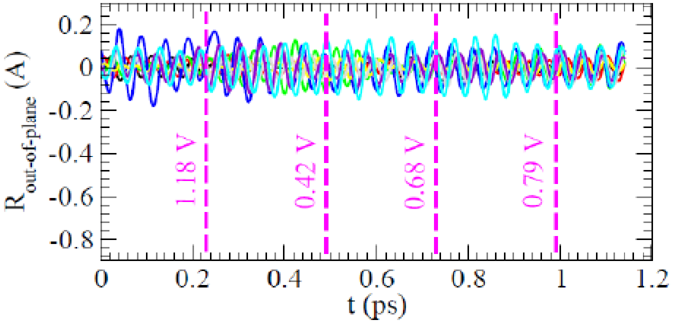
- electrolyte decomposition w/improved control of electronic voltage, V_e

- EC decomposes when V_e < 0.55 V

V_e = work function - 1.37 V

- At equilibrium, voltage governs Li and e^- content





$LiF_{0.93}$-coated $Li_{3.25}Si$

No EC decomposition (yet)

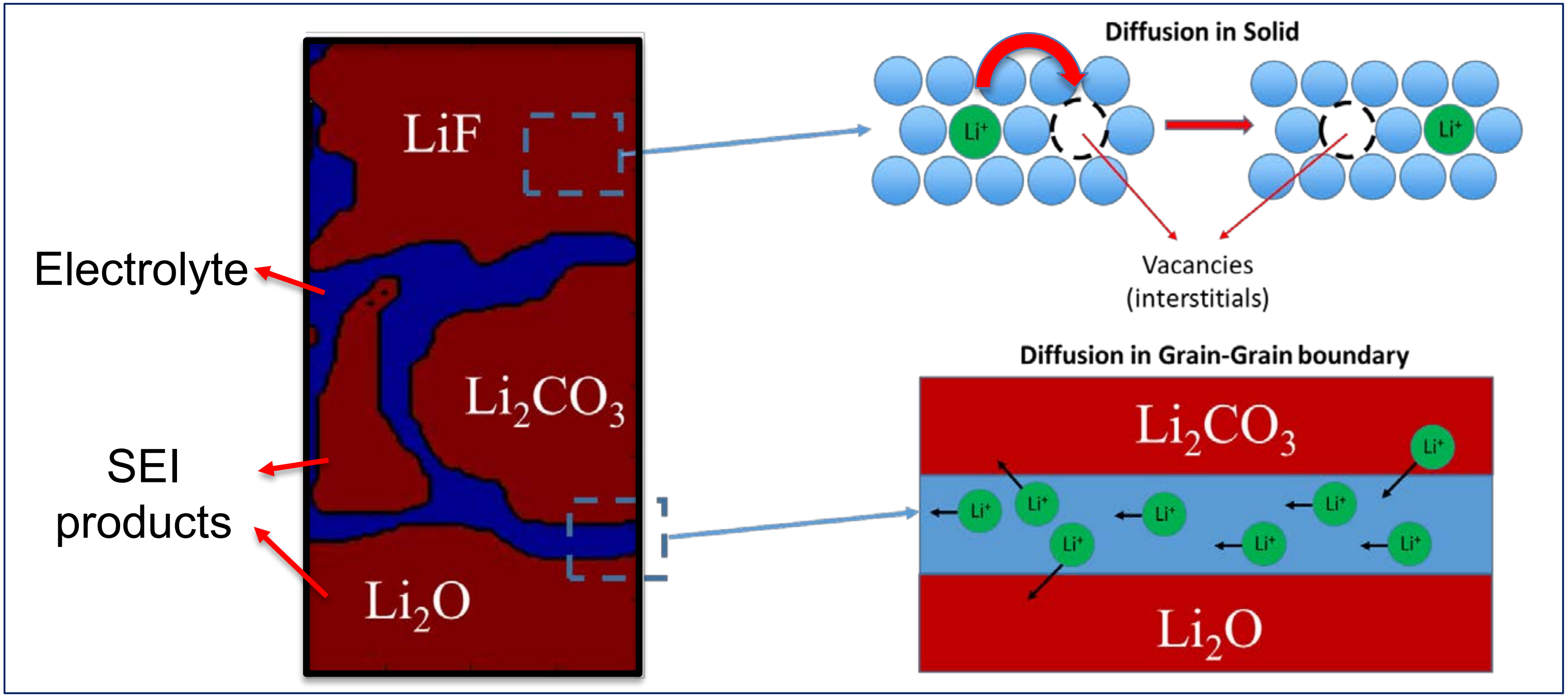
- V sensitive to surface coating

K. Leung, SNL

Technical Accomplishments:
The big picture: mesoscopic model

1st principles information→ mesoscopic model →macroscopic behavior of electrode, crack formation, SEI growth

Milestone (c) ✓



Collaboration with P. Mukherjee, TAMU

Responses to Previous Years Reviewers' Comments

- Q: "not clear how the surface was treated as the initial state and structure. Si surface is terminated by oxides…"
- **A: Lithiation and reactivity of hydroxylated SiO_2 surfaces addressed**.
- Q: "The reviewer asked about experimental confirmation for the given reaction mechanism or reaction products."
- **A: Both XPS and FTIR measurements (Langmuir, 965, 2011, and JES, 1042, 2012) reveal similar polymeric species derived from VC and FEC respectively. We show that FEC decomposition yields open VC, and therefore similar products are derived from both.**
- Q: "the project team can go back to their models and explain why certain reactions are preferred."
- **A: Analyses of our own work and experimental data gives the first clear explanation of the differences of SEI growth in VC/FEC vs. EC.**
- Q: The reviewer added that there did not seem to be any effort to improve the interface, such as predicting better additives.
- **A: This is our ultimate goal, here we have shown some initial guidelines.**
- Q: The team should model a mixed solvent electrolyte and salt.
- **A: The effect of mixed compositions was discussed in this report.**

Collaboration and Coordination with Other Institutions

- **Sandia National Lab (SNL):** K. Leung (SNL) is responsible for the analysis of the voltage effects on solvent decomposition reactions and S. Rempe (SNL) carried out studies of dielectric properties of the solvents that are relevant to ion transport.
- **National Renewable Energy Lab (NREL):** Chunmei Ban (NREL) has developed and deposited a protective coating over a Si anode. This team (Balbuena, Seminario, TAMU) modeled the nucleation, lithiation, and SEI reactions on the coated Si anode reported here.
- **University of Rhode Island (URI):** This team (TAMU) collaborates with Brett Lucht (URI) who is experimentally studying SEI formation reactions on Si anodes.

Remaining Challenges and Barriers

- Use all the new knowledge about SEI nucleation and growth for **identifying alternative effective electrolytes**.

- Interface all the concepts and discoveries from the microscopic model into an **effective mesoscopic model.**

- Determine **the effects of cracking and SEI reconstruction** at a microscopic level.

- Evaluate **capacity fade** as a function of SEI film properties and electrode microstructure.

Proposed Future Work

- **Rest of FY14**:
  - elaborate design principles for alternative electrolytes
  - electrode surface cracking from first principles
  - ionic and electronic conductivity through blocks
  - refining mesoscopic model of the SEI

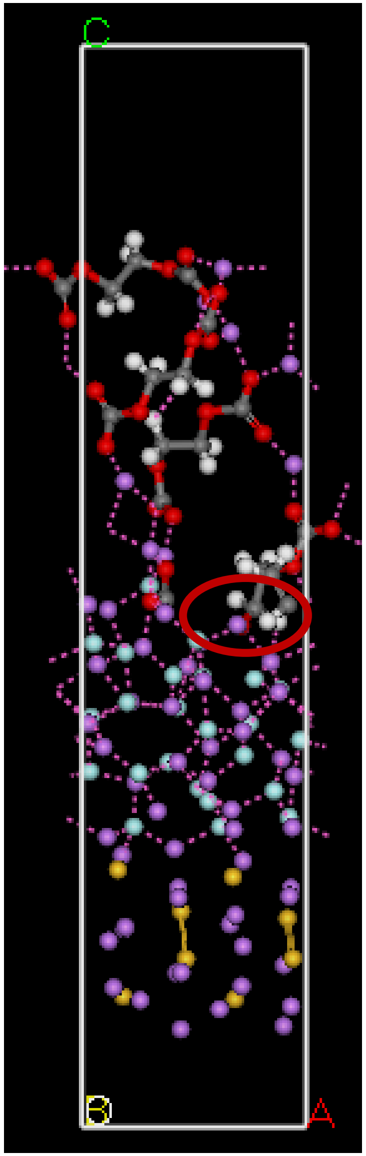
- **FY15:**
  - capacity fade from mesoscopic model
  - computational test of selected additives
  - elaborate design principles for effective coatings
  - SEI reactions in cracks

Summary Slide

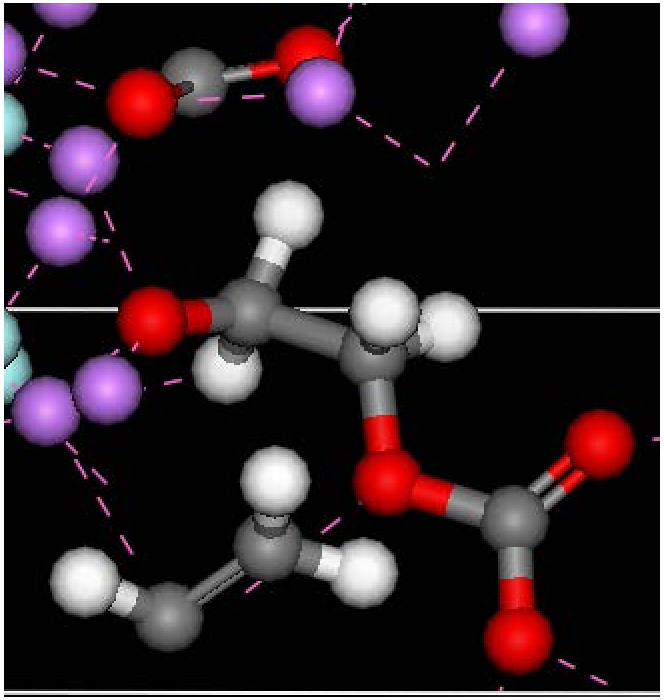
- **Relevance:** SEI layer nucleation and growth behavior crucial for irreversible capacity loss and improved electrolytes and electrodes.
- **Approach:** Characterization of SEI nucleation & growth as functions of surface chemistry & structure, voltage, and electrolyte composition yield insights about *first cycle surface evolution* and *anode capacity loss*.
- **Technical Accomplishments:** Surface native oxides and Al alcoxide films induce rich SEI chemistry. Competition among reduction of electrolyte components → nucleation of blocks from multiple fragments. FEC decomposition may lead to open VC. Differences between additives and solvent/salt products clarified. Electron transfer mechanism during growth identified. Voltage effects on decomposition reactions characterized. Mesoscopic model constructed.
- **Collaborations:** Evaluation of artificial coatings (with NREL); voltage and solvation effects (with SNL), identification of products (with URI), mesoscopic model (with TAMU).
- **Future Work:** Refinement and evaluation of mesoscopic model. Design principles for alternative electrolytes. Cracking of SEI films: microscopic and macroscopic effects. Ionic and electronic conductivity through blocks.

Technical Back-Up Slides

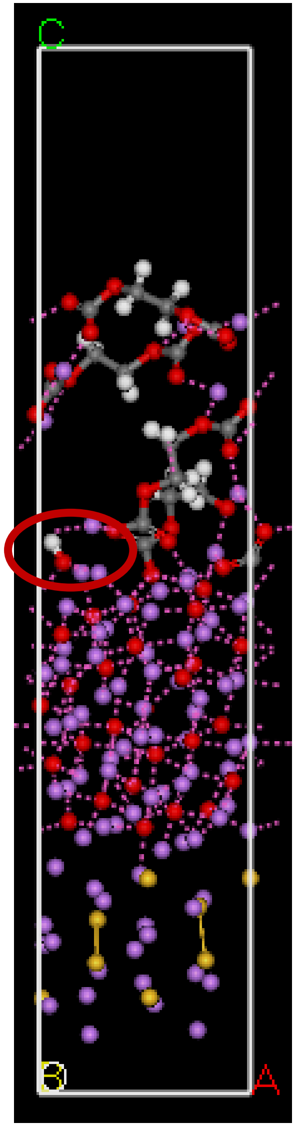
electron transport via radicals



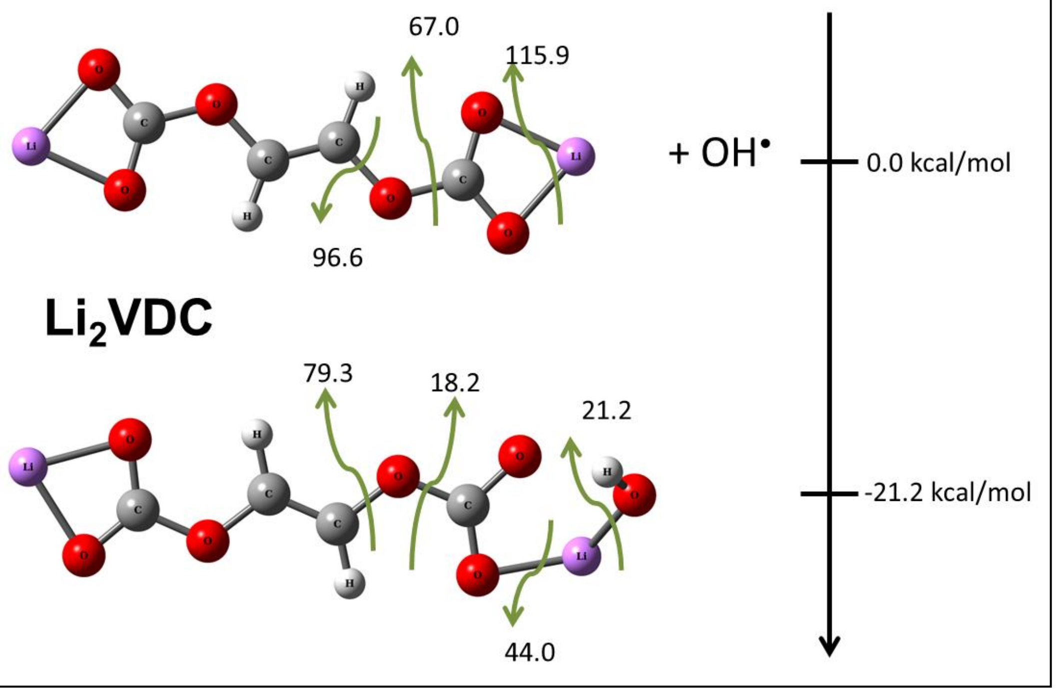
C_2H_{3}-LiF-Li_2EDC model

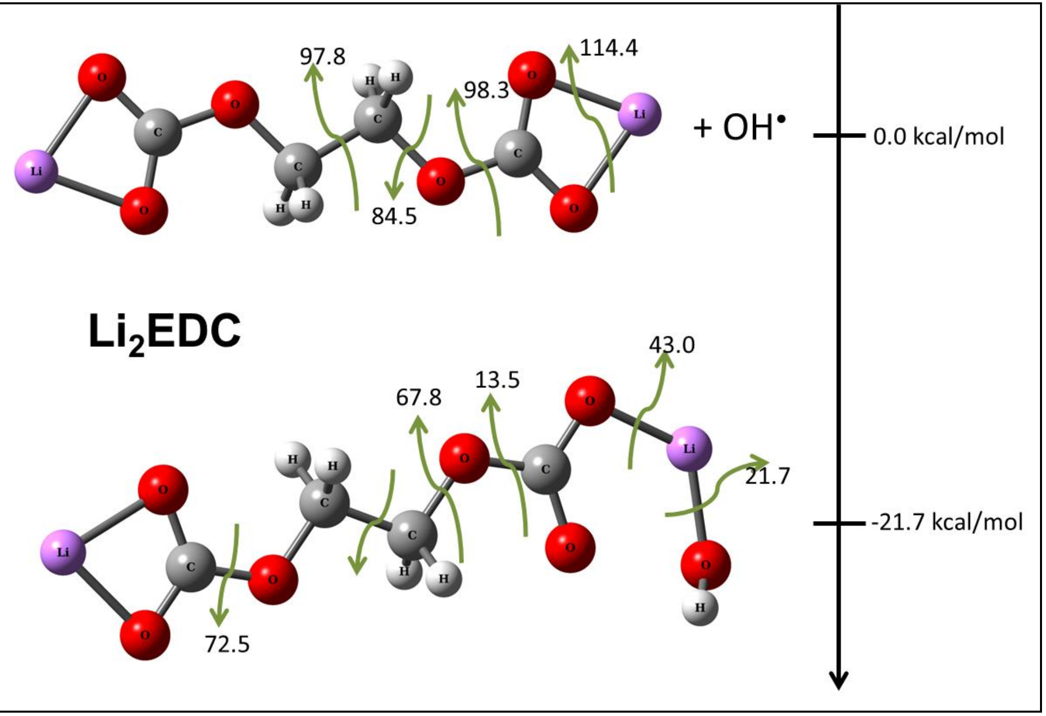


Li_2EDC closest to LiF block reacts w/ C_2H_3 → CO_2 and $CO_3C_2H_4O$



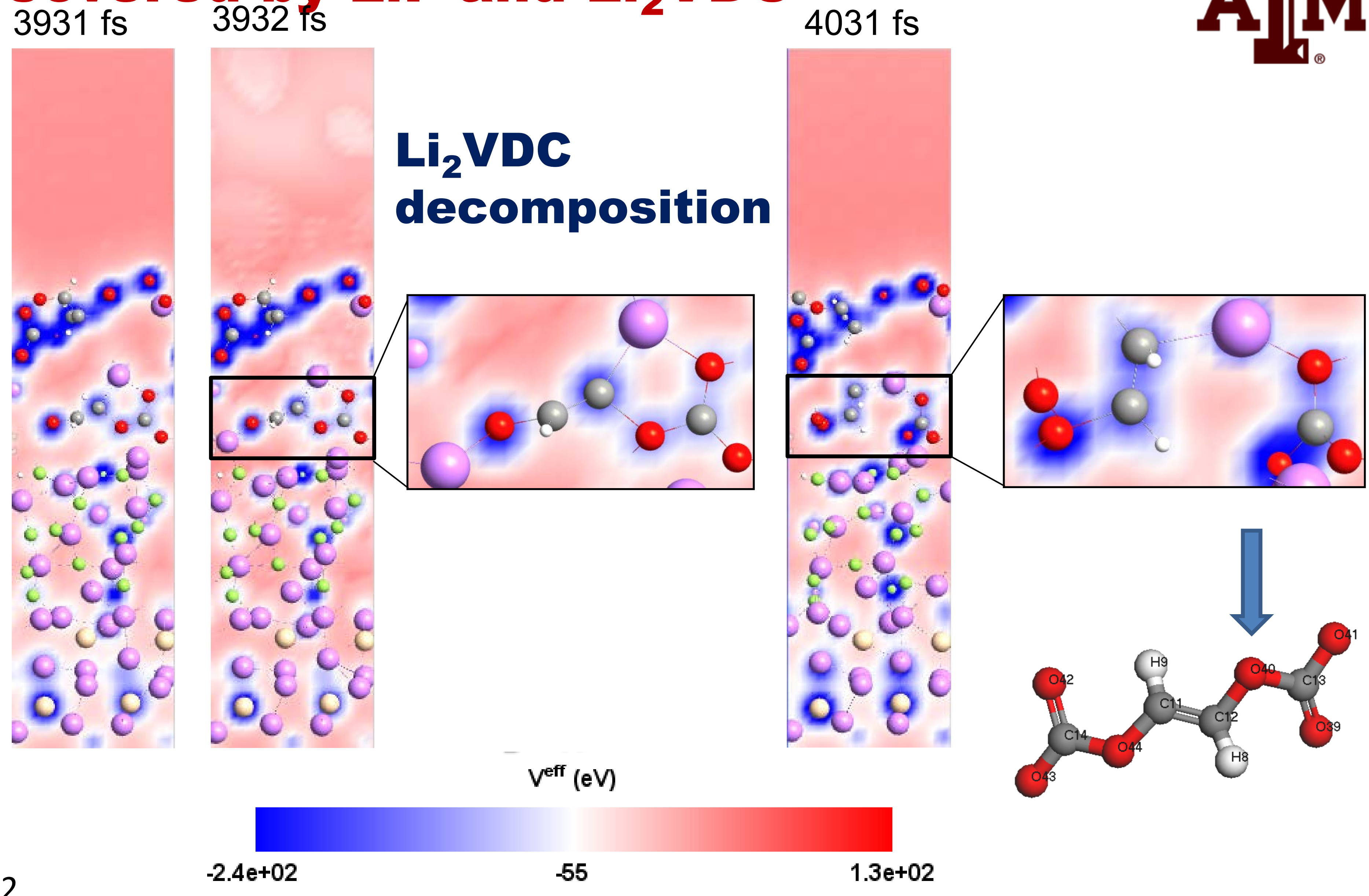
O—Li—O network disrupted





Li_2VDC and Li_2EDC are easily attacked by radical species. DFT calculations show the values of the energies needed to break each bond. Note that after interaction with the OH radical the system becomes stabilized; however the energy needed to break the various bonds decreases significantly. (Energy values in Kcal/mol)

Electrostatic Potential Map, anode covered by LiF and Li_2VDC



3931 fs

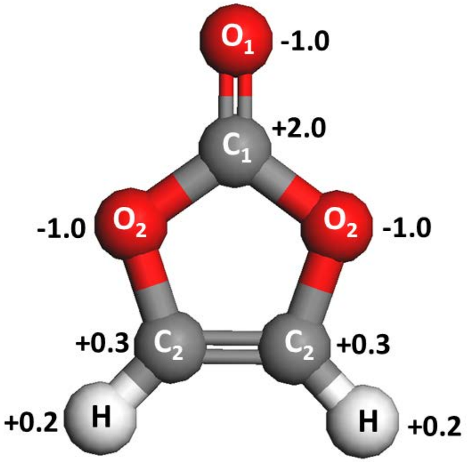
3932 fs

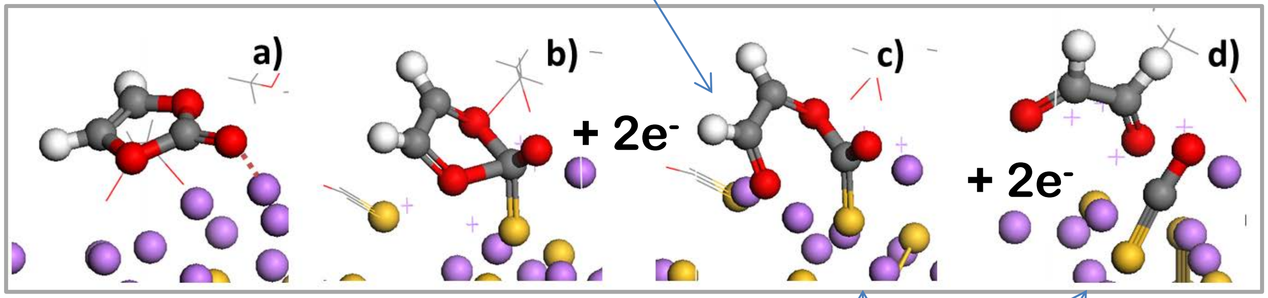
4031 fs

Li_2VDC decomposition

VC reduction on lithiated Si anodes

Cleavage of C1O2 bond: $VC_{(ads)} + 2e^- \rightarrow \cdot OC_2H_2OCO^{2-}_{(ads)}$





All surfaces
- **a) Li-O interaction**
- **b) Formation of C-Si bond**
- **c) Ring opening (open VC^{2-})**

Higher lithiated
- **d) Cleavage of a 2nd C1O2 bond**

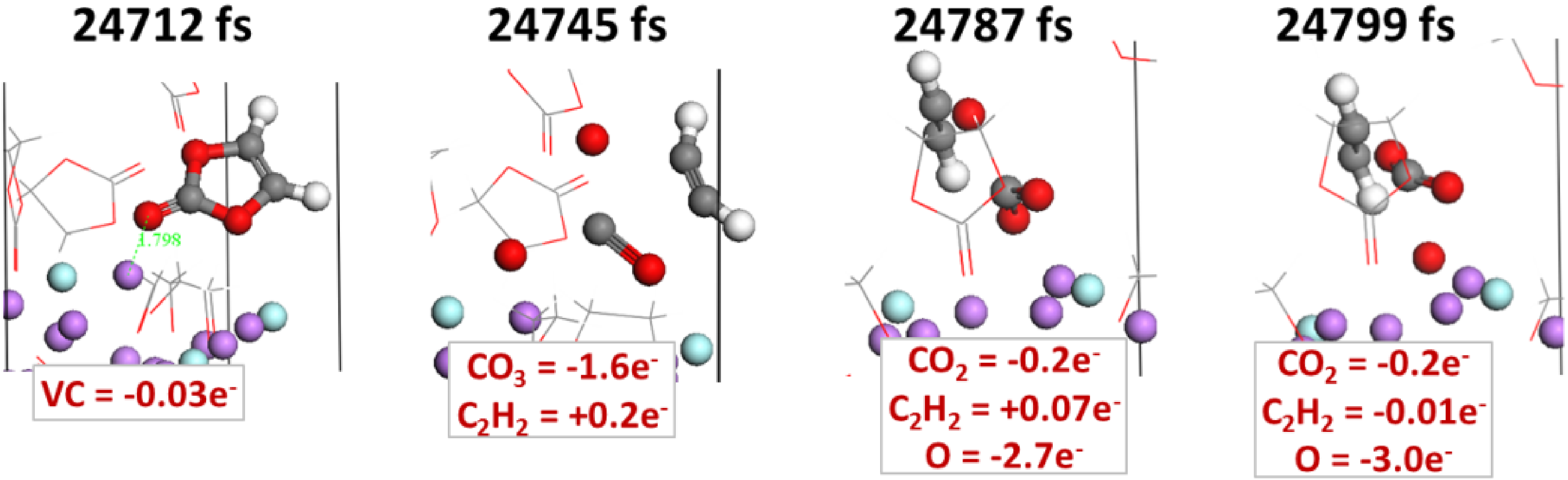
CO_2 formation results from: $VC + CO_3^{2-} \rightarrow \cdot OC_2H_2OCO_2^{2-} + CO_2$

CO_3^{2-} is a product of EC decomposition
(alternative mechanism to Ushirogata et al, JACS 2013)

VC products: $\underbrace{\text{open } VC^{2-}, OC_2H_2O^{2-}, OC_2H_2OCO_2^{2-}}_{\text{C=C containing species}}, CO, CO_2$

J. M. Martinez de la Hoz and P. B. Balbuena, PCCP, 16 (32), 17091-17098 (2014)

decomposition of VC on the surface: new pathway



formation of CO_2 and O radicals on surface

Martinez, Soto, Balbuena, JPCC 2015