Molecular dynamics simulation and ab intio studies of electrolytes and electrolyte/electrode interfaces

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Project ID es058

Overview

Timeline

- Start 1/01/11
- Complete 12/31/12
- 20% complete

Budget

- Total project funding
  - DOE $544 K
  - Contractor $ 0 K
- Funding received
  - $272 K FY10
  - $272 K FY11

Barriers

- Barriers addressed
  - operating temperature range
  - power density
  - energy density

Partners

- Collaborations
  - Arizona State University (Angell)
  - Penn State University (van Duin)
  - Université de Picardie (Armand)
  - Army Research Lab (Jow)
  - Argonne National Laboratory (Curtiss)
  - University of Rhode Island (Lucht)
  - North Carolina State University (Henderson)

Objectives

- Use molecular simulations to gain understanding into the chemical composition of the electrode/electrolyte interface as a function of electrode potential

- Understand double layer structure, capacitance and transport at the anode and cathode interface as a function of potential and temperature

- Use ab initio calculations to gain insight into electrolyte oxidation (cathode) and reduction (anode) mechanisms

- Use molecular simulations to predict the chemical composition and structure of SEI layers at the anode and cathode

- Use molecular simulations to understand the role of additives in the formation of SEI layers

- Gain molecular level understanding of Li^+ cation transport mechanisms in SEI layers

- Gain molecular level understanding of Li^+ cation transport mechanisms in electrolytes comprised of new salts and solvents in collaboration with experimental BATT projects

- Provide guidance for design of electrolytes with improved lithium transport, reduced interfacial resistance and/or improved electrochemical stability

Impact

<u>Provide guidance for design of electrolytes with</u>

- improved lithium transport
- reduced interfacial resistance
- improved electrochemical stability
- ability to form stable SEI with good transport properties at high density anodes
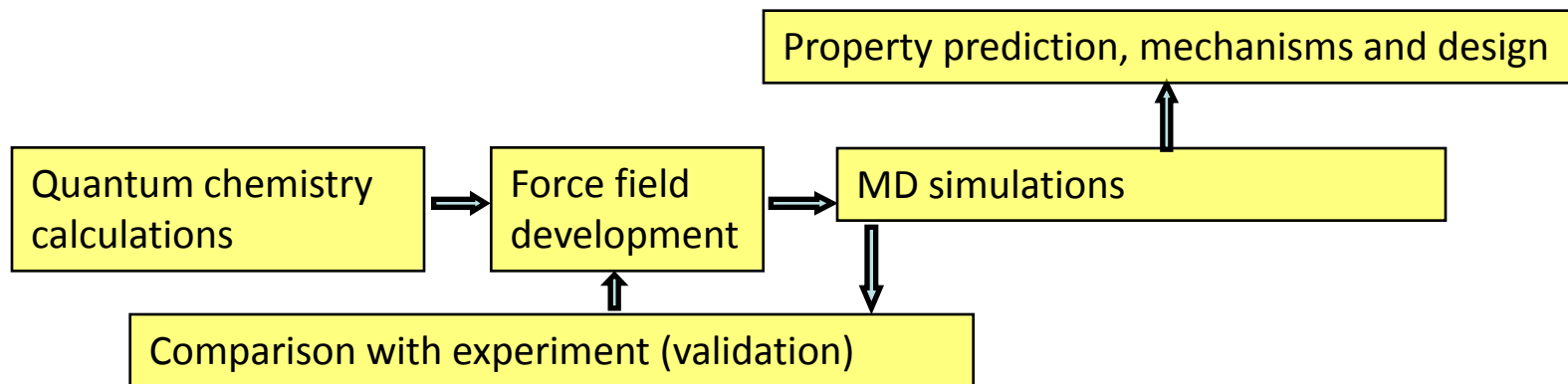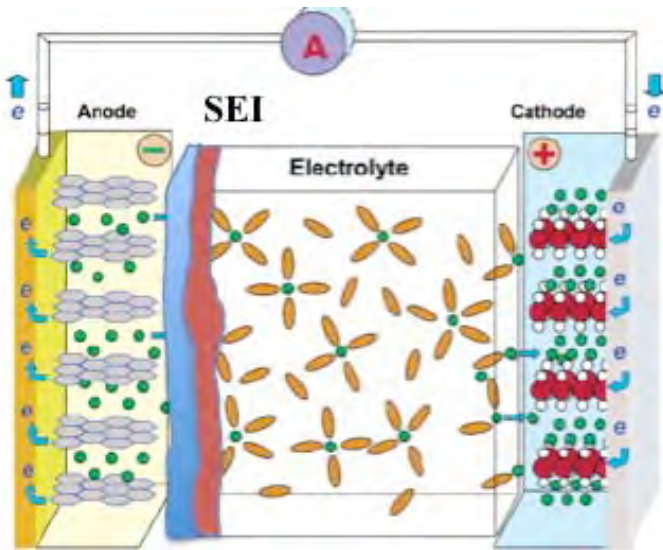- ability to form stable SEI with good transport properties at high voltage cathodes

Milestones

- Complete investigation of electric double layer structure and charge transfer resistance as a function of electrode potential for model electrodes. (Feb. 2011, delayed)

- Complete investigation of conductivity of novel high voltage electrolytes. (Apr. 2011, on target)

- Complete study of SEI formation and role of additives for model anodes. (Sep. 2011, on target)

Approach

Molecular level modeling and prediction of:

•structure and transport properties of bulk electrolytes

•oxidation and reduction reactions

•structure, composition and transport properties of electrode/electrolyte interfaces

•SEI formation, structure and properties

Property prediction, mechanisms and design

Quantum chemistry calculations → Force field development → MD simulations

Comparison with experiment (validation)

Approach

- **<u>Ab initio (Quantum Chemistry)</u>** studies of molecules, clusters, surfaces and reactions

- **<u>ReaxFF</u>** (reactive molecular dynamics (MD) simulations)
    - parameterized to reproduce quantum chemistry calculations
    - allow for chemical reactions in a classical MD framework
    - no predefined reactive sites or reaction pathways
    - allows simulation of systems containing thousands of atoms on nanosecond timescales
    - investigate condensed-phase oxidation and reduction mechanisms and SEI formation

- **<u>Molecular Dynamics Simulations</u>**
    - parameterized to reproduce quantum chemistry calculations
    - allows for chemically accurate prediction of structure, thermodynamics and transport properties
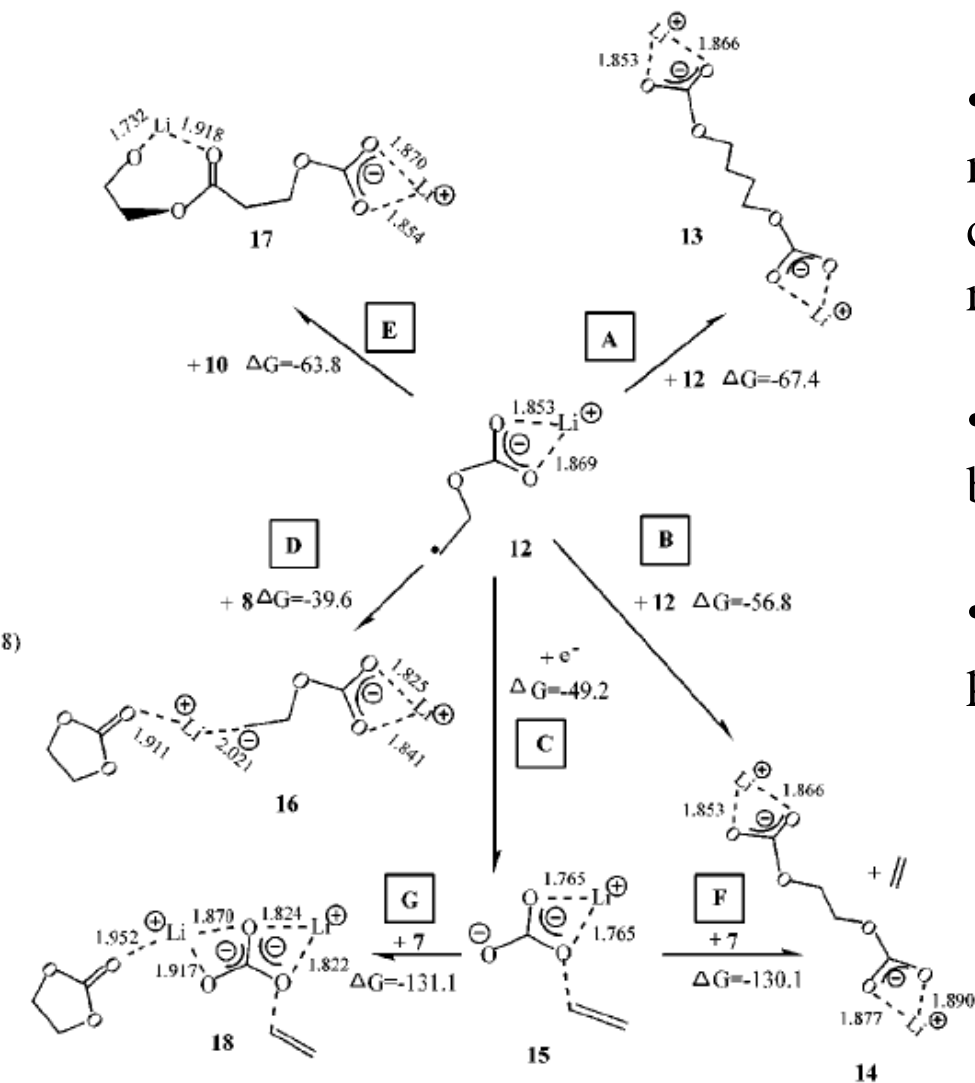   - investigate bulk electrolyte and interfacial properties

Technical Accomplishments

ReaxFF Simulations of Reduction Pathways

Dilithium ethylene dicarbonate is believed to be the most dominant component with the following mechanism of formation:

$$2EC + 2e^- + 2Li+ = (CH_2OCO_2Li)_2 + C_2H_4$$
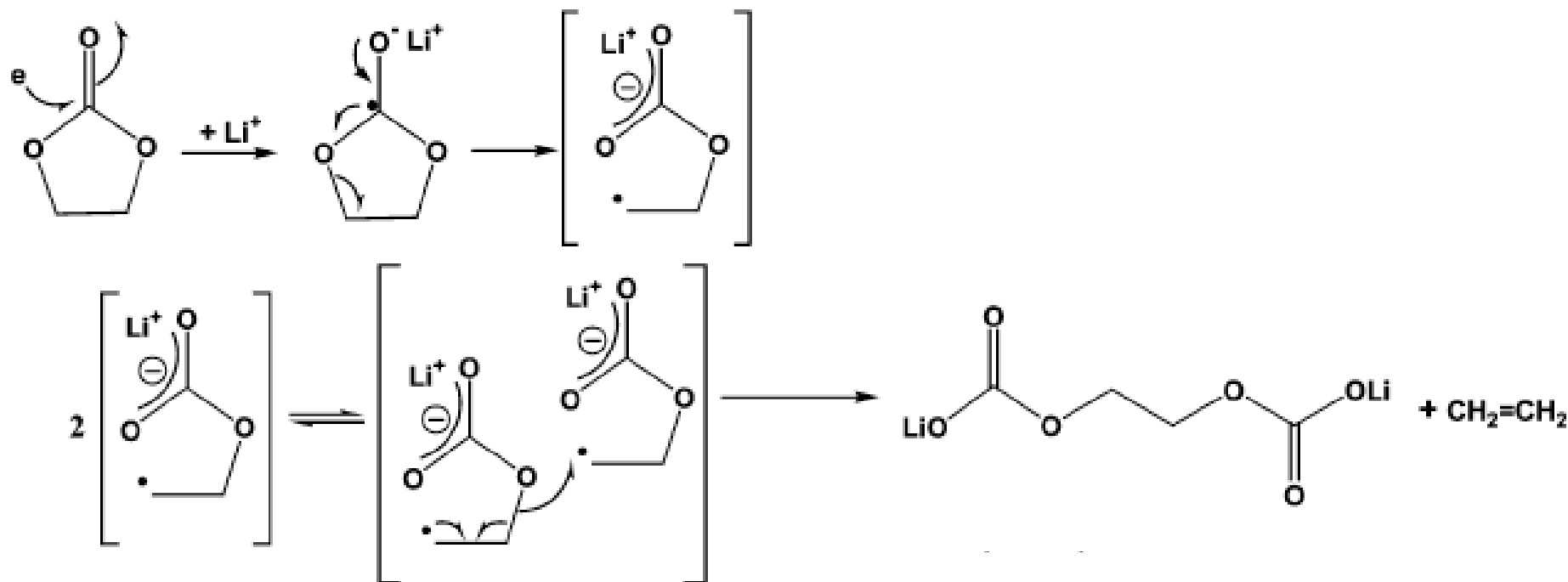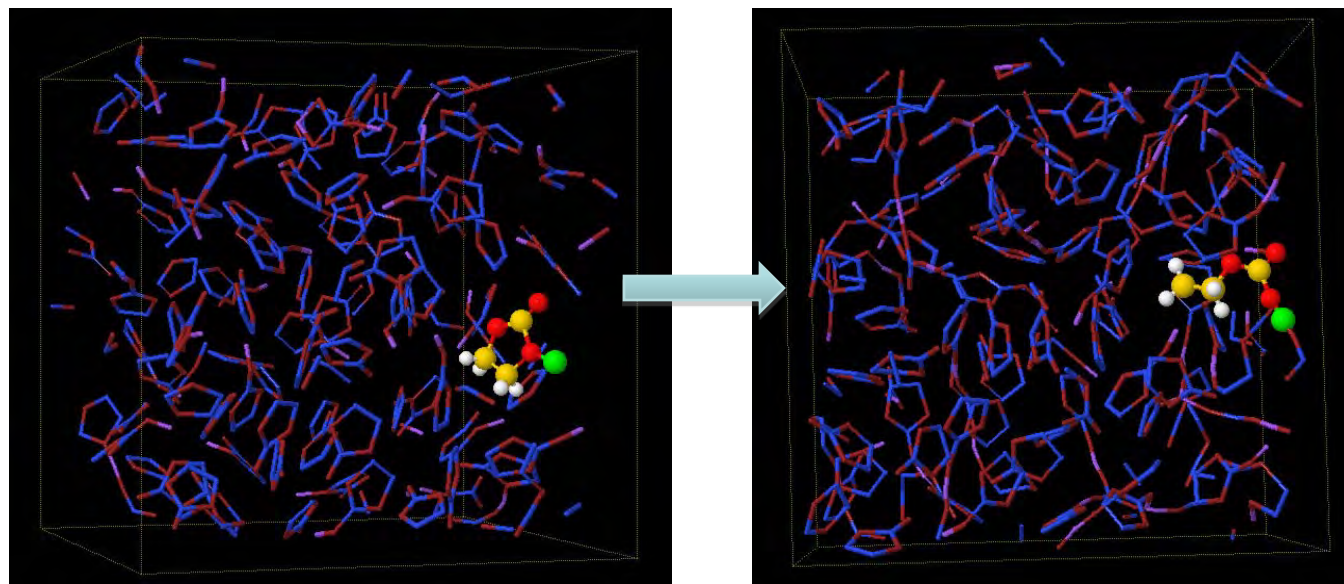
ReaxFF Simulations of Reduction Pathways

• Wang, Balbuena et al. have conducted numerous studies using gas phase quantum chemistry calculations of recombination reactions of singly-reduced EC

• The lowest energy compound is dilithium butylene dicarbonate

• Other radical recombination products are possible

ReaxFF Simulations of Reduction Pathways

•In bulk EC: barrier for ring opening is 11-13 kcal/mol (similar to gas phase)

•In a mixture of EC and EC radical/Li+ complexes: 20-25 (kcal/mol)

For the elementary reaction A⟷ A*, where A* represents an activated complex, the Eyring rate equation is given:

$$k = \frac{k_b T}{h} \exp\left[-\frac{\Delta G *}{k_b T} \right]$$

• For 12 kcal/mol barrier at 298K the EC cyclic radical will have a lifetime on the order of 100 μs.

•Hence, reactions involving the high-energy but long-lived cyclic-EC radical should be considered as a possible contributor to the outer SEI in EC-based electrolytes
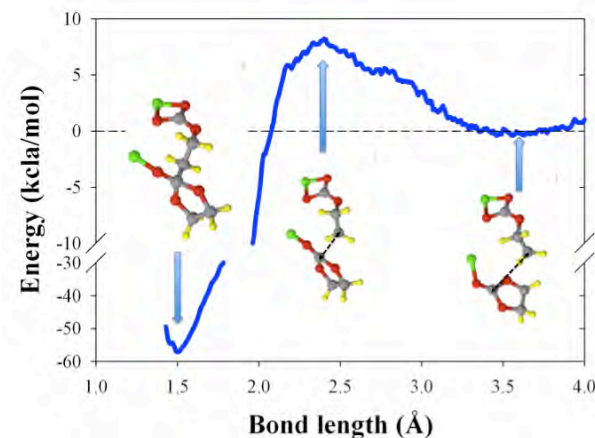
ReaxFF Simulations of Reduction Pathways
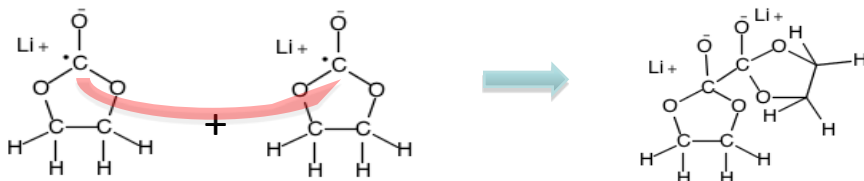
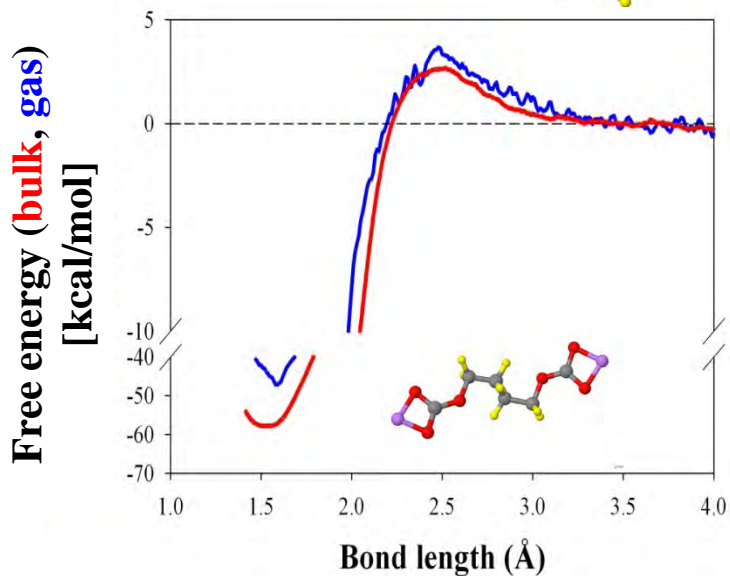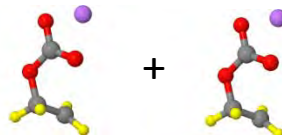•The barrier for this reaction is large hence recombination of two cyclic EC radicals is unlikely
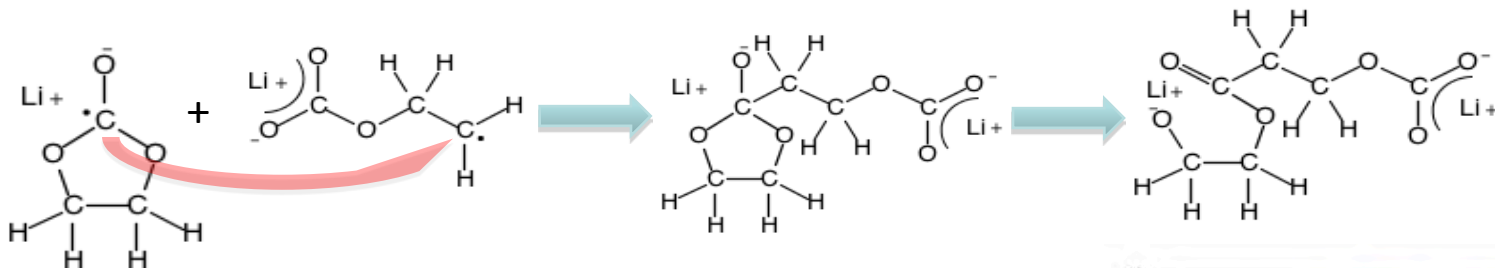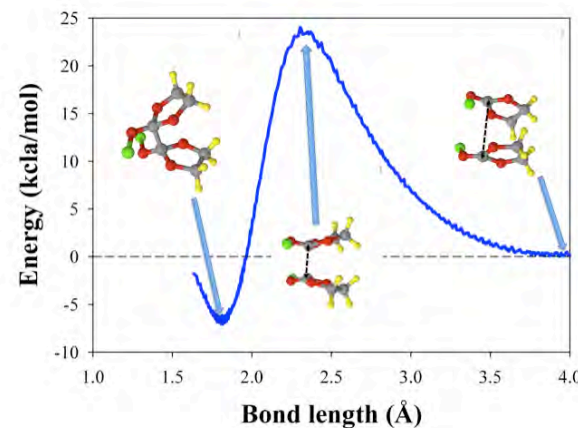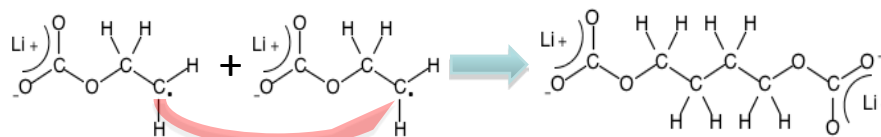

•The barrier for this reaction is on the order of 8 kcal/mol, which is smaller than the barrier for linearization of cyclic EC radical (12-13 kcal/mol)
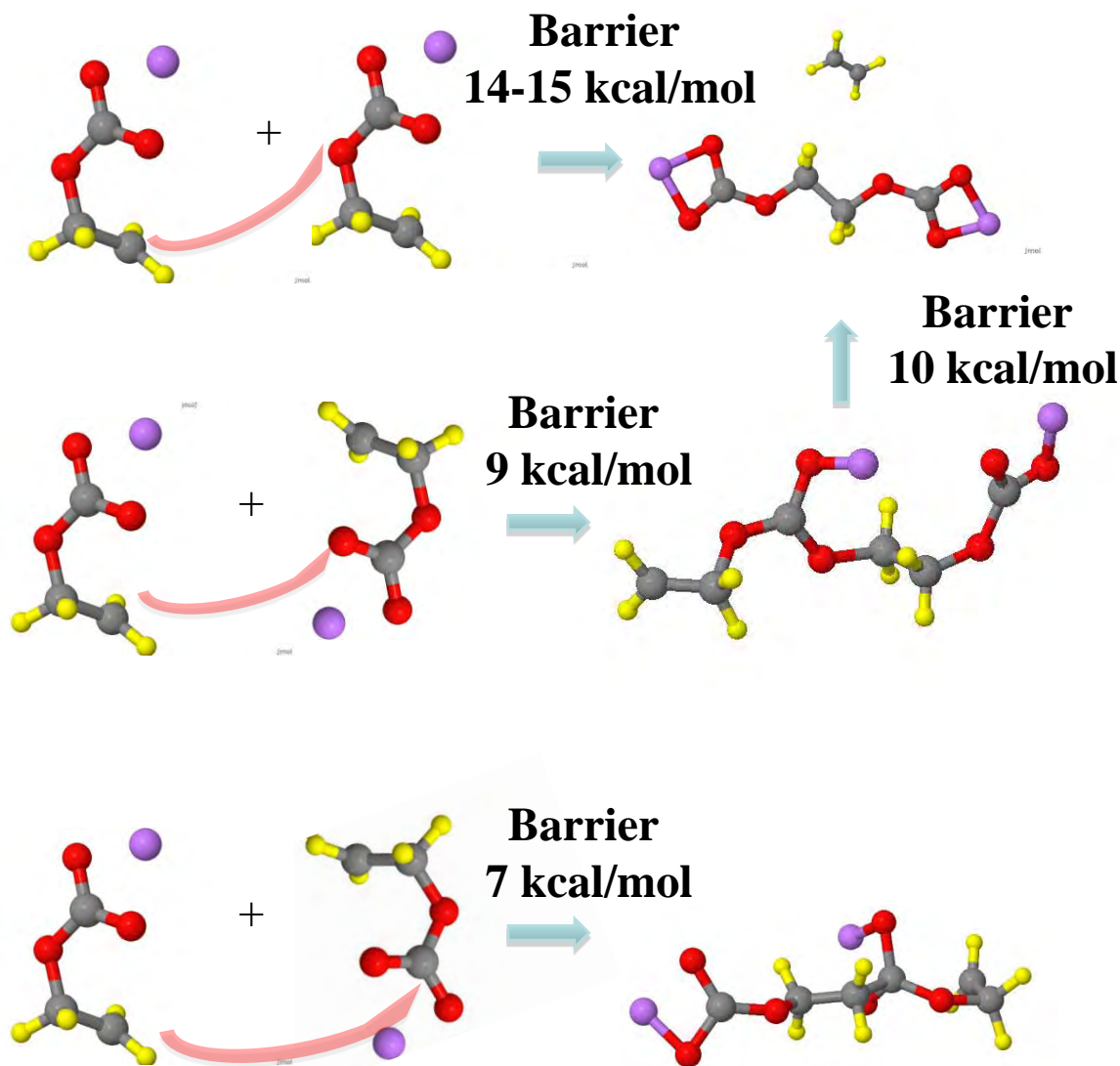
ReaxFF Simulations of Reduction Pathways

Gas phase simulations and EC solvent

• Formation of butylene dicarbonate shows 3.5 kcal/mol (QC: 4 kcal/mol L.Curtiss ANL)

• Condensed phase effect in bulk EC (polar solvent) is not significant

ReaxFF Simulations of Reduction Pathways

Barrier 14-15 kcal/mol

Barrier 10 kcal/mol

Barrier 9 kcal/mol

Barrier 7 kcal/mol

• The barrier for this radical elimination reaction is larger than the barrier for closed EC radical opening (QC: barrier 27 kcal/mol, <u>L. Curtiss, ANL</u>).

• These two reactions have relatively small barrier but do not lead to radical elimination, instead di-radicals are formed. The first one can split the ethylene therefore leading to formation of the dilithium ethylene dicarbonate.
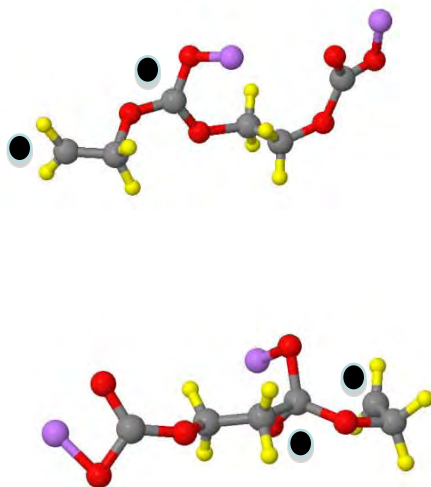
ReaxFF Simulations of Reduction Pathways
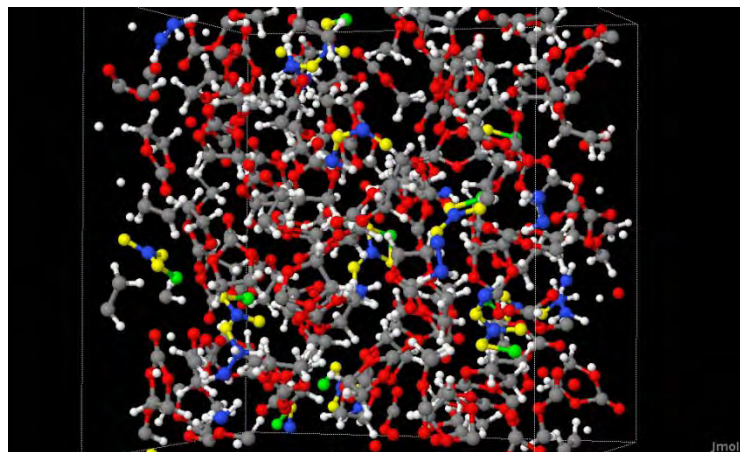
- No predefined reaction coordinates

- Various mixtures of linear, cyclic EC radicals and electrolyte

- Systems are heated to allow reactions to occur on ps-ns time scales

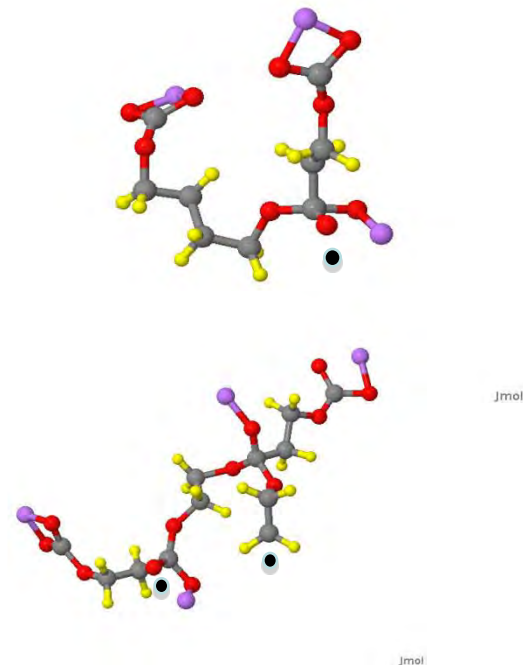- Compound observed in condensed phase simulations:

radical termination
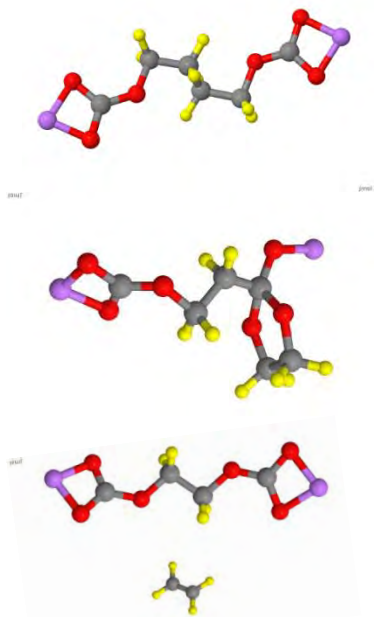
radical propagation

longer alkylcarbonates

ReaxFF Simulations of Reduction Pathways

In the gas phase and bulk EC:

• the lowest barrier reaction is for the formation of dilithium *butylene* dicarbonate (~4 kcal/mol)

• Other reactions have noticeably larger barriers (8-16 kcal/mol)

• Formation of di-lithium *ethylene* dicarbonate requires either one-step reaction with 16 kcal/mol barrier, or two-step reaction with 9 and 10 kcal/mol barriers.

• Hence, one might expect butylene compounds to dominate the SEI.

**In condensed phase with reasonable and large ion concentration:**

• formation of various compounds via radical termination and propagation reaction is observed

• dilithium *butylene* dicarbonate is not the most dominant compound despite the lower barrier for the reaction in the gas, *ethylen*e dicarbonate is rare

These result shows that reaction barriers/mechanisms strongly depend on local environment of the radicals

MD Simulations of Electrode/Electrolyte Interfaces

- MD simulations of the graphite | electrolyte interface were performed for the EC:DMC(3:7)/LiPF$_6$ 1 M electrolyte to study electrical double layer (EDL) vs. potential.
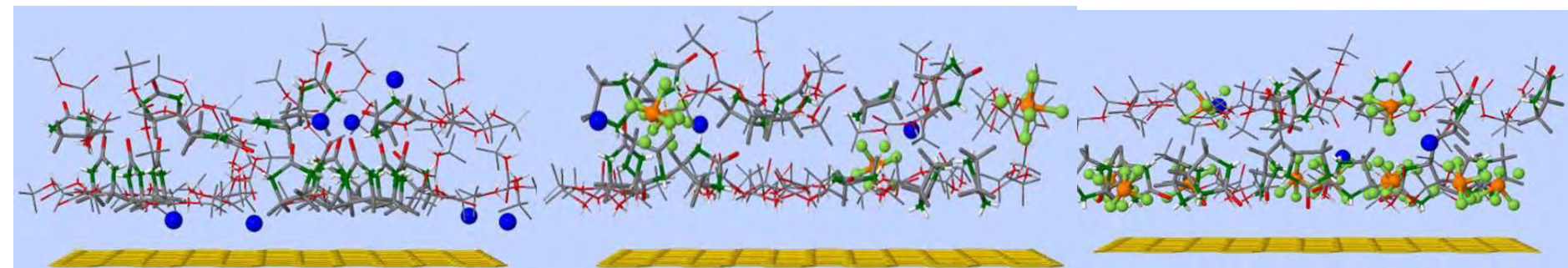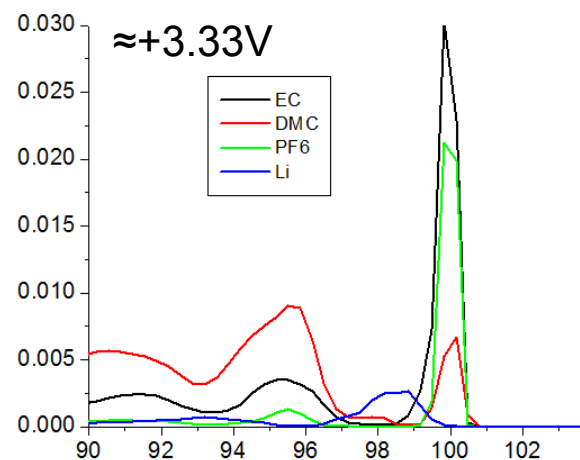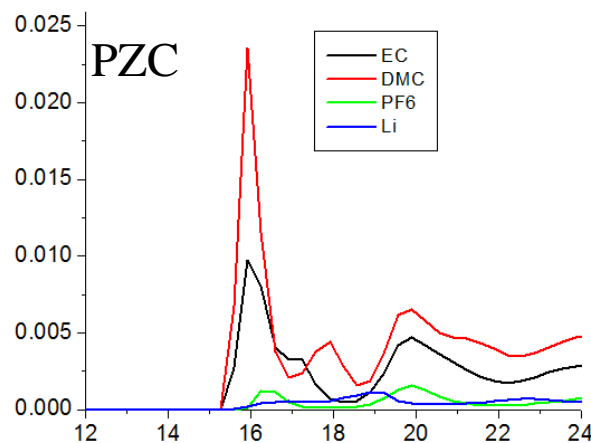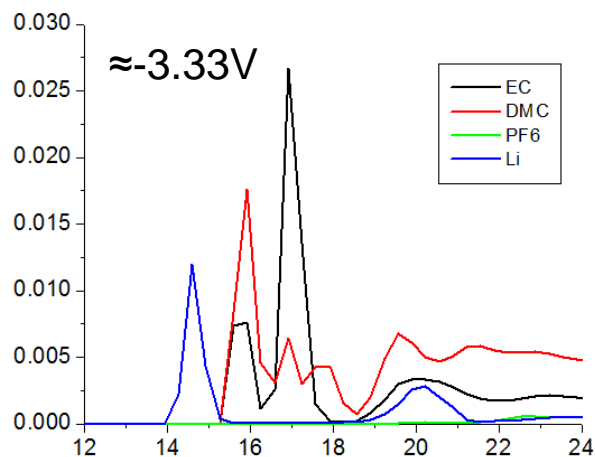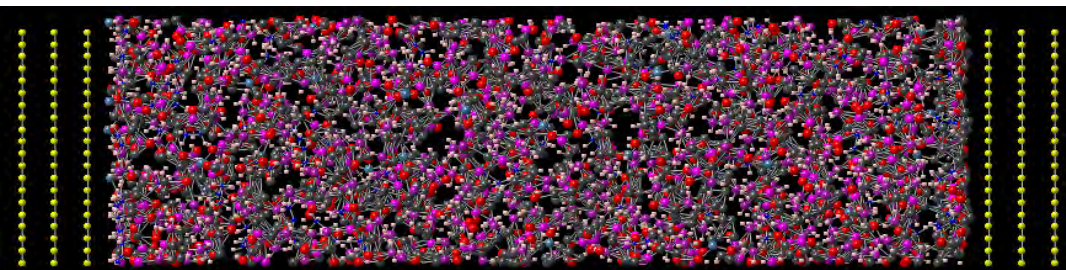
MD Simulations of Electrode/Electrolyte Interfaces
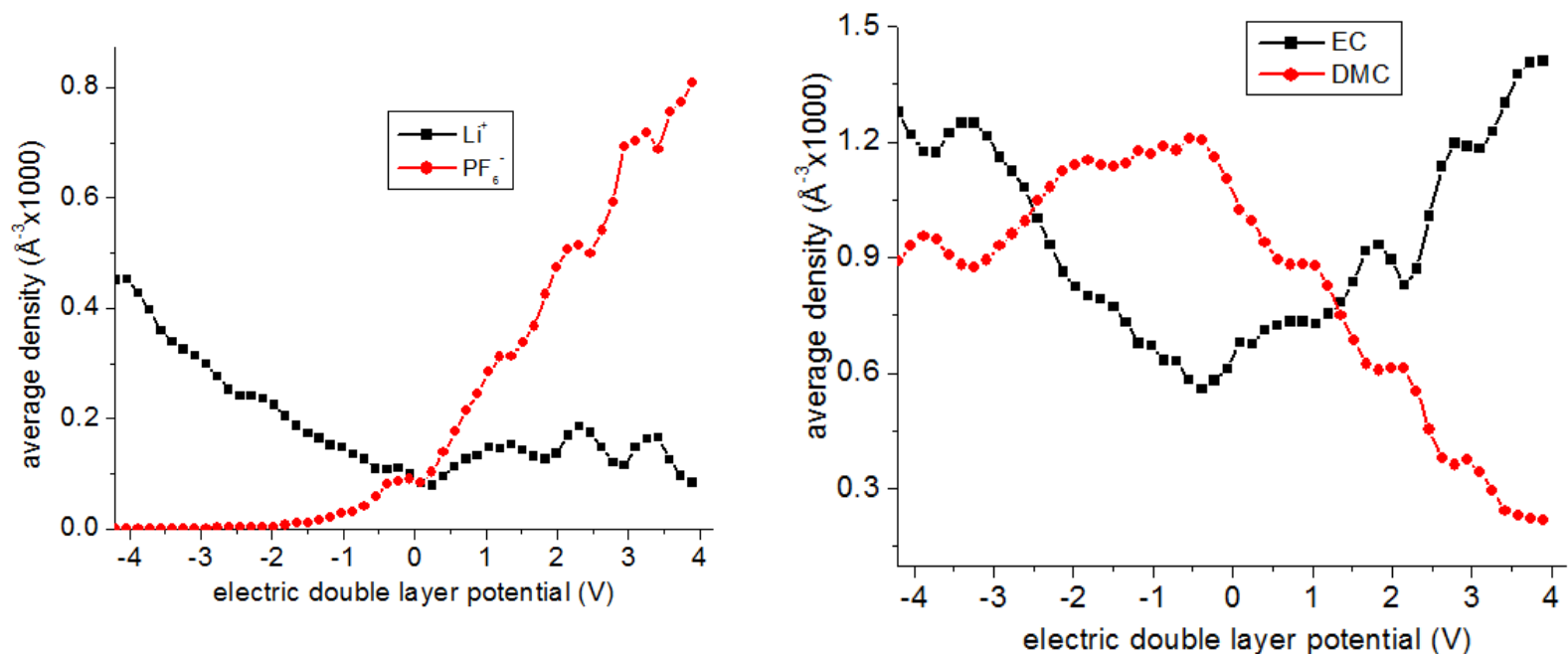
- At high and low electrode potential the electrode surface is coordinated primarily by EC, therefore, at the EC:DMC/LiPF$_6$ | graphite interface EC is more likely to be subjected to oxidation and reduction

- The higher the potential the more EC and less DMC is found next to graphite

- At 3 V EDL a significant population of PF$_6^-$ anion is observed next to graphite indicating that anion is readily available to play role in the oxidation process. Its role is studied by QC at UofU and ARL (Jow Group)

Ab initio Studies of the Influence of Anion on Solvent Oxidation
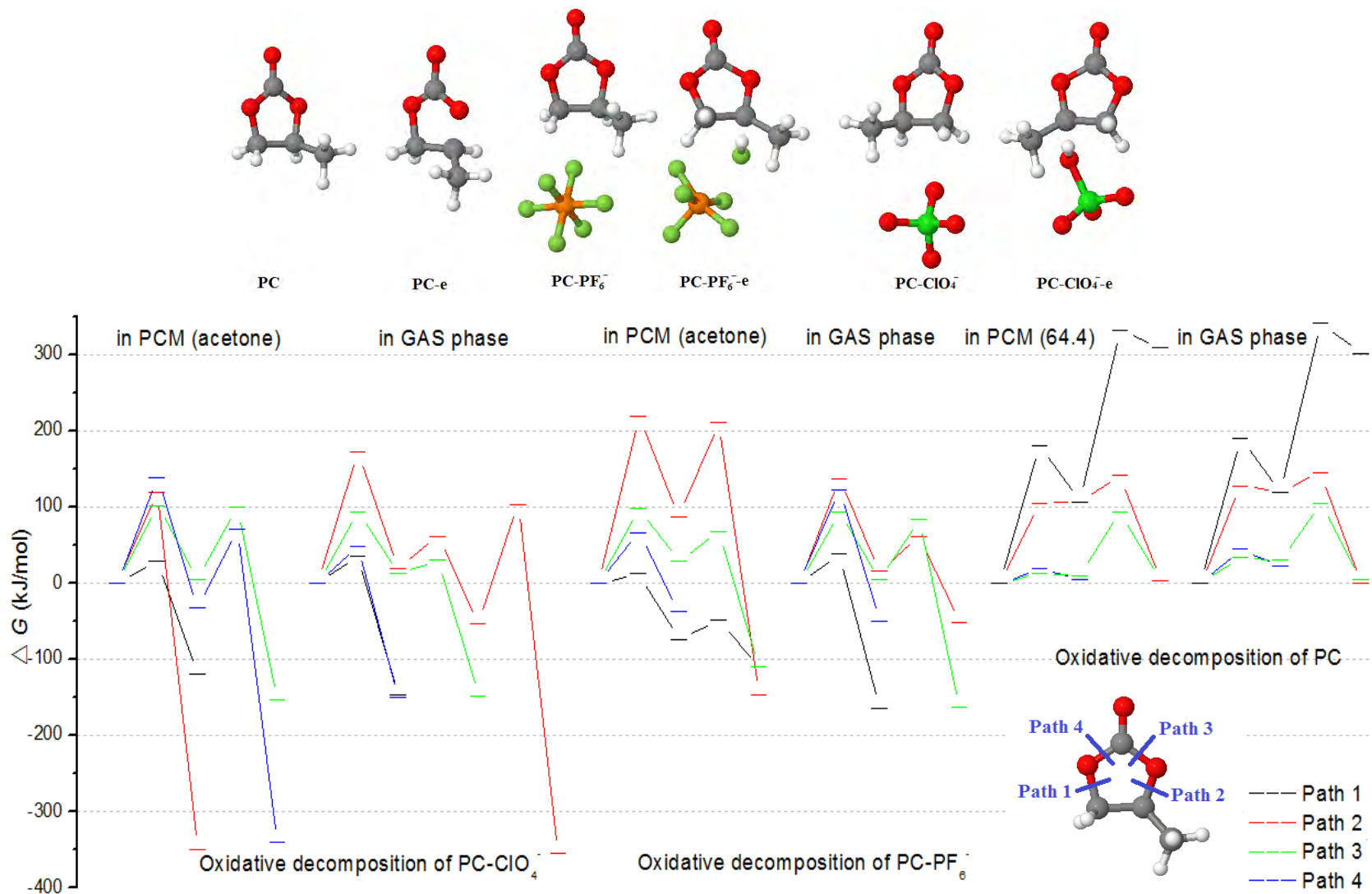
- Oxidative decomposition of the propylene carbonate/PF_6^- and PC/ClO_4^- oxidative complexes is more energetically favorable compared to the oxidative decomposition of PC (no anion).
- Anion influences the order of the oxidative PC decomposition pathways.

Ab initio Studies of the Influence of Anion on Solvent Oxidation

Path 1: the lowest barriers and energy of the intermediate in calculations with PCM (implicit solvent)

in PCM (acetone)   in GAS phase

Path 1
Path 2
Path 3
Path 4
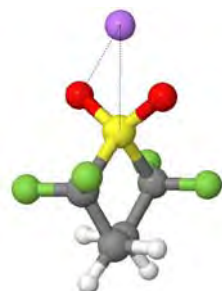
Oxidative decomposition of PC-PF$_6$
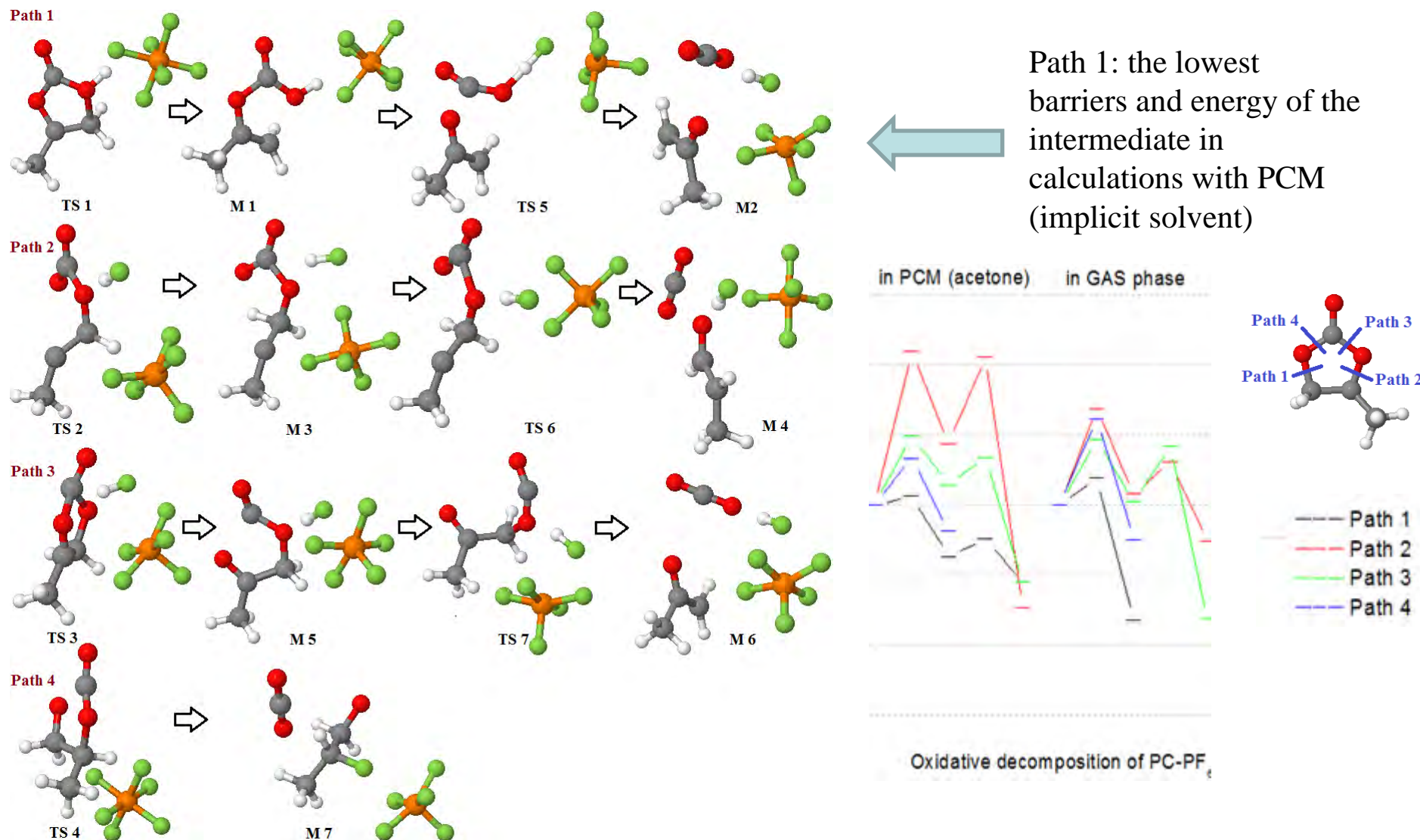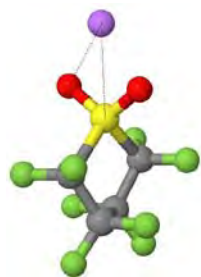
•Probability of reactions: Path 1 > Path 4> Path 3 > Path2

Semifluorinated Sulfone-Based Electrolytes
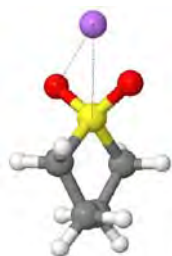
TMS

TMS$_{F4}$

TMS$_{F8}$

The Li$^+$/solvent binding energy (in kcal/mol) from QC					
	Li$^+$/SL	Li$^+$/TMS$_{F4}$	Li$^+$/TMS$_{F8}$	Li$^+$/EC	Li$^+$/DMC
MP2/cc-pvTz or *MP2/aug-cc-pvTz*	-52.7	-40.8	-29.5	*-47.5*	*-40.9*
Pure solvent self-diffusion coefficient					
T (K)	303	303	303	313	298
D (10^{-10} m^2/s)	1.1	1.4	4.5	8	25.4

	λ (mS/cm)	D(Li) 10^{-10} m^2/s	ionicity
TMS/LiTFSI (10:1)	2.1	0.35	0.84
TMS$_{F4}$/LiTFSI (10:1)	0.16	0.13	0.12
TMS$_{F8}$/LiTFSI (10:1)	did not dissolve salt		

- Fluorination improved TMS oxidative stability
- Completely fluorinated TMS$_{F8}$ does not dissociate LiTFSI salt at 1 M and phase separates when mixed with TMS (1:1) in TMS$_{F8}$:TMS(1:1)/LiTFSI 1 M
- TMS$_{F4}$ has ability to dissociate LiTFSI and LiPF$_6$ similar to that of DMC.
- TMS$_{F4}$/LiTFSI conductivity is lower than conductivity of TMS/LiTFSI.

in collaboration with ASU and ARL

Collaboration and Coordination with Other Institutions

- Argonne National Laboratory
  - Collaboration, Federal laboratory, within VT
  - Ab initio/MD simulations of electrolyte reduction/oxidation reactions

- Arizona State University
  - Collaboration, University, within VT
  - Properties of high voltage electrolytes

- North Caroline State University and Universite' de Picardie
  - Collaboration, University, within and outside VT
  - Transport properties of electrolytes

- Army Research Laboratory
  - Collaboration, Federal laboratory, outside VT
  - Analysis of SEI compounds

- University of Rhode Island
  - Collaboration, University, inside VT
  - Analysis of oxidation reactions at cathode surface

- Pennsylvania State University
  - Subcontract, University, outside VT
  - Parameterization of ReaxFF for cathode reactions, code development

Proposed Future Work

- Investigate reduction and oxidation reactions on inert and high voltage cathode materials (Curtiss, ANL; van Duin, Penn State; Lucht, URI)

- Investigate the role of sacrificial additives on cathode SEI formation (Lucht, URI)

- Investigate electrode/electrolyte interfacial composition of mixed high-voltage electrolytes as a function of electrode potential (Angell, ASU)

- Investigate SEI formation at anode and cathode as a function of electrolyte composition (Lucht, URI; Jow, ARL)

Summary

- Ab initio studies and molecular dynamics simulation reveal that electrolyte oxidative and reductive decomposition (related to cathode and anode SEI formation) depend strongly on the local chemical composition

- Molecular dynamics simulations reveal that the local chemical environment depends on electrode potential and the presence of the interface and can differ significantly from the bulk electrolyte composition

- Improvement of oxiditative stability of solvents through fluorination can lead to reduced ability to dissolve lithium salts and reduced conductivity