

Molecular dynamics simulation studies of electrolytes and electrolyte/electrode interfaces

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Project ID es058

Overview

Timeline

- Start 2/01/08
- Complete 12/31/10
- 66.7% complete

Budget

- Total project funding
 - DOE \$779 K
 - Contractor \$ 0 K
- Funding received
 - \$267 K FY09
 - \$272 K FY10

Barriers

- Barriers addressed
 - cycle life
 - operating temperature range
 - power density

Partners

- Collaborations
 - North Carolina State University (Henderson)
 - Arizona State University (Angell)
 - Lawrence Berkeley National Laboratory (Balsara, Kerr)
 - CSIRO (Best, Hollenkamp)
 - Penn State University (van Duin)
 - Clemson University (Creager)
 - Université de Picardie (Armand)
 - Army Research Lab (Jow)

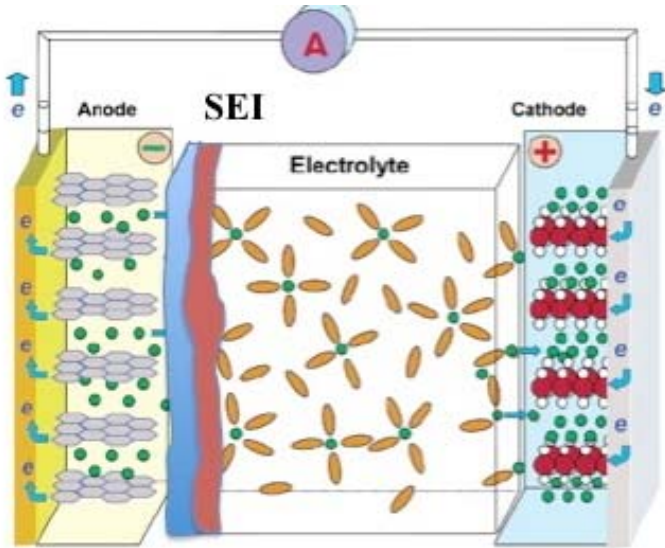
Objectives

- Use molecular simulations to predict the chemical composition and structure of SEI layers
- 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 liquid and ionic liquid electrolytes comprised of new salts and solvents in collaboration with experimental BATT projects
- Gain molecular level understanding of Li^+ intercalation/deintercalation into/from representative anode and cathode materials
- Understand double layer structure, capacitance and transport at the anode and cathode interface as a function of potential and temperature
- Provide guidance for design of electrolytes with improved lithium transport, reduced interfacial resistance and/or improved electrochemical stability

Milestones

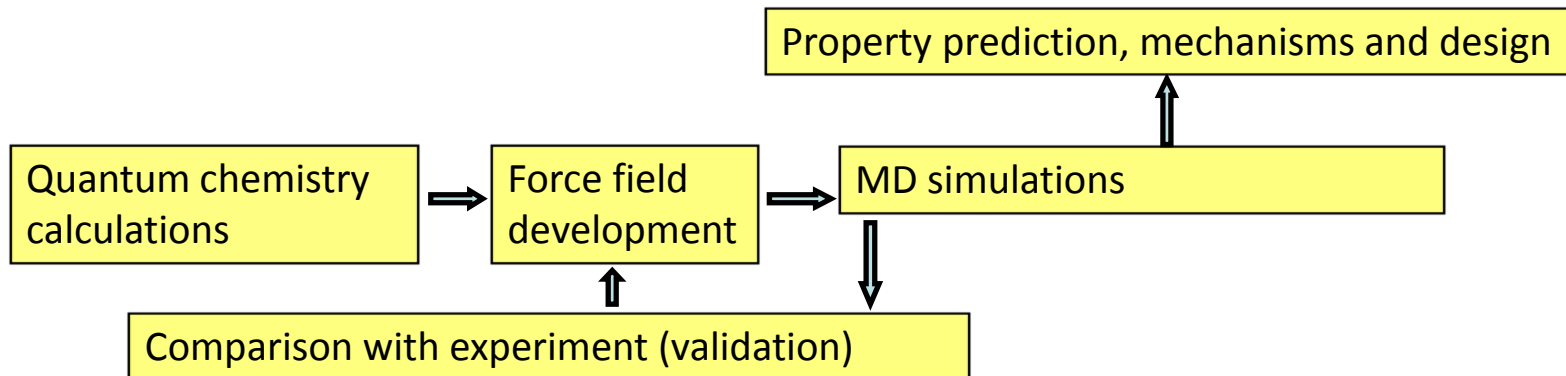
- Complete investigation of electric double layer structure for mixed carbonate electrolytes as a function of electrode potential (**March 2010**)
- Complete investigation of charge transfer resistance for graphite and LiFePO_4 electrodes (**Sept. 2010**).

Approach



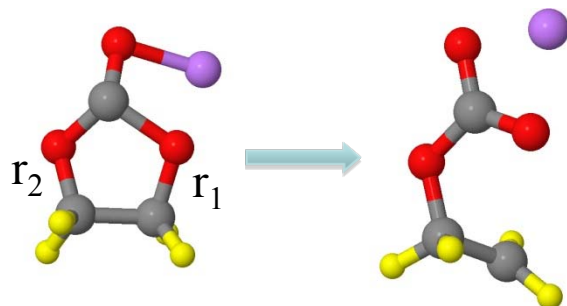
Molecular level modeling of structure, transport and mechanical properties:

- bulk electrolytes
- model SEI compounds
- electrode/electrolyte interfaces
- Li^+ intercalation



Technical Accomplishments

Mechanisms of outer SEI formation via single electron reduction of ethylene carbonate (EC)

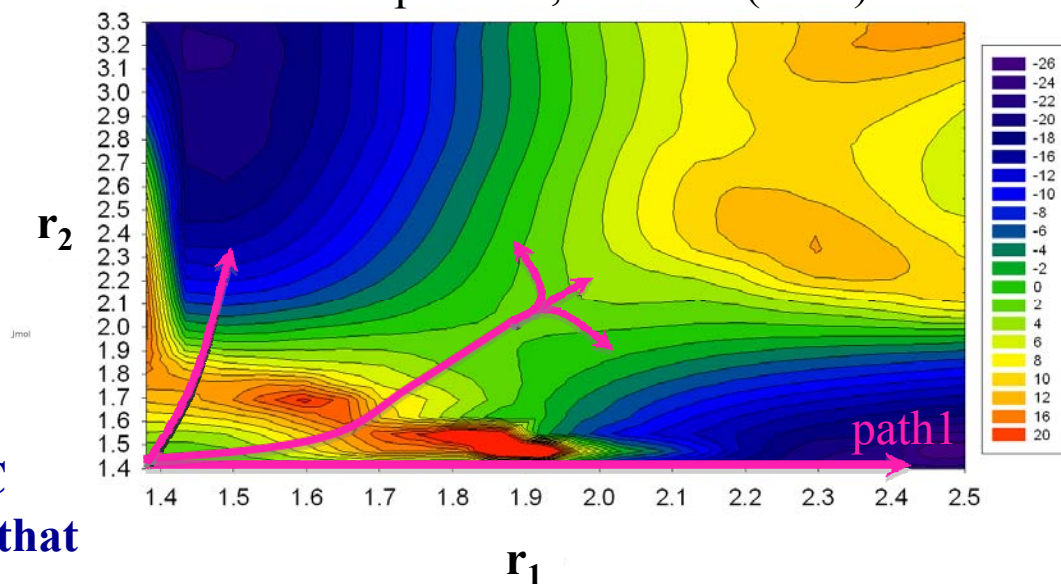


□ Detailed quantum chemistry (QC) studies reveal that opening of the EC cyclic radical anion is more complex than previously believed

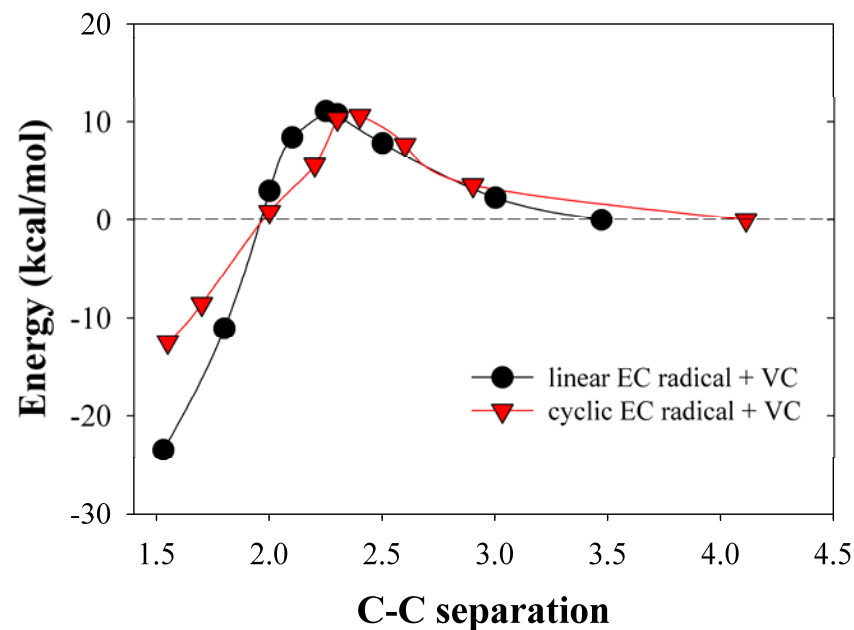
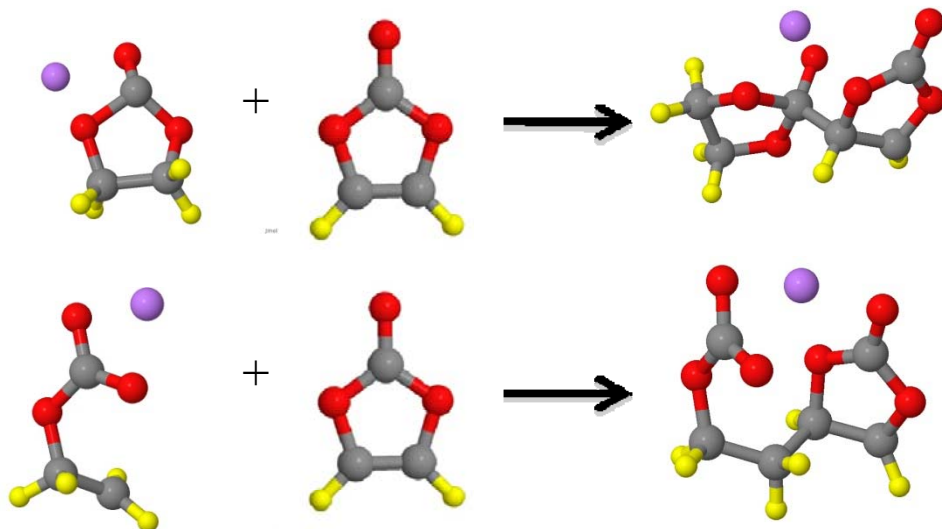
★ The energy barrier along path-1 investigated in previous QC studies strongly depends on the level of theory (DFT: 17 kcal/mol, MP2: 35 kcal/mol)

★ The lowest energy barrier for EC cyclic radical opening is about 12-13 kcal/mol and involves simultaneous deformation of bonds 1 and 2. This high barrier indicates that the EC cyclic radical will have a lifetime on the order of milliseconds

Energy surface (kcal/mol) for EC radical anion decomposition, ab initio (MP2)

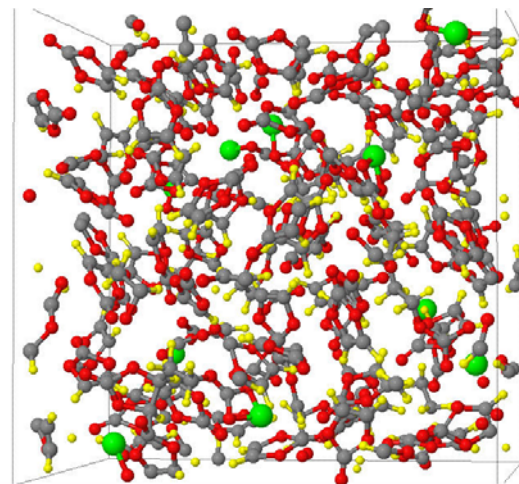


★Chemical reactions with the relatively long-lived closed EC radical likely play an important role in formation of outer SEI



★ For example, the energy barrier for reaction with VC is the same for cyclic and linear EC radicals, and is *lower* than the barrier for opening EC cyclic radical. ReaxFF molecular dynamics simulations show similar barriers in gas and condensed phases for these reactions.

★MD simulations using ReaxFF of EC radicals in bulk VC show formation of polyVC compounds initiated by open and closed EC radicals



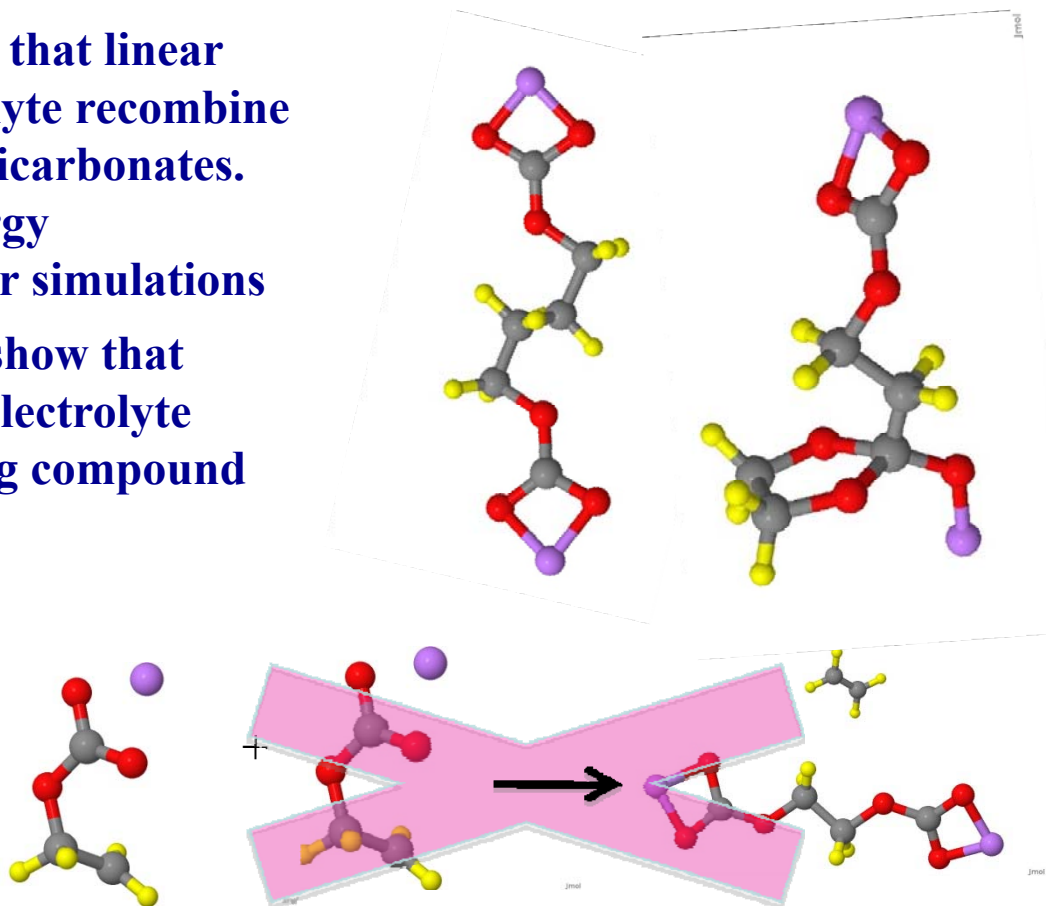
What happens to EC radical anions (linear and cyclic)?

★ Previous QC calculations (Balbuena et al.) suggest that EC radicals recombine to form lithium alkyl (ethylene and butylene) dicarbonates or ester-containing alkyl carbonate. However, recent experiments (Xu et al.) question the presence of lithium butylene dicarbonate and ester-containing alkyl carbonate compounds in the SEI

★ MD simulations using ReaxFF show that linear (open) EC radicals in the bulk electrolyte recombine to form exclusively lithium butylene dicarbonates. No ethylene dicarbonates (higher energy compounds) have been observed in our simulations

★ MD simulations using ReaxFF also show that linear and cyclic EC radicals in bulk electrolyte recombine to form the ester-containing compound shown on the far right

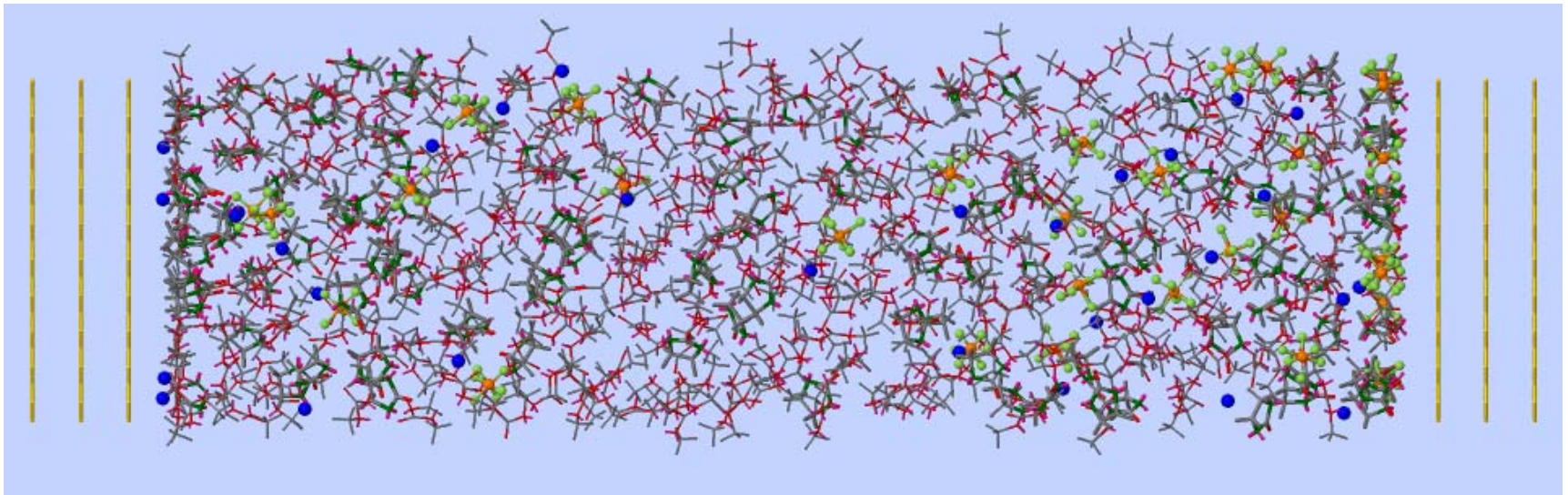
★ While we do not know yet how lithium ethylene dicarbonate forms, it is *not* through recombination of linear EC radicals. One possible path is through the elimination of ethylene from *cyclic* EC radical anions



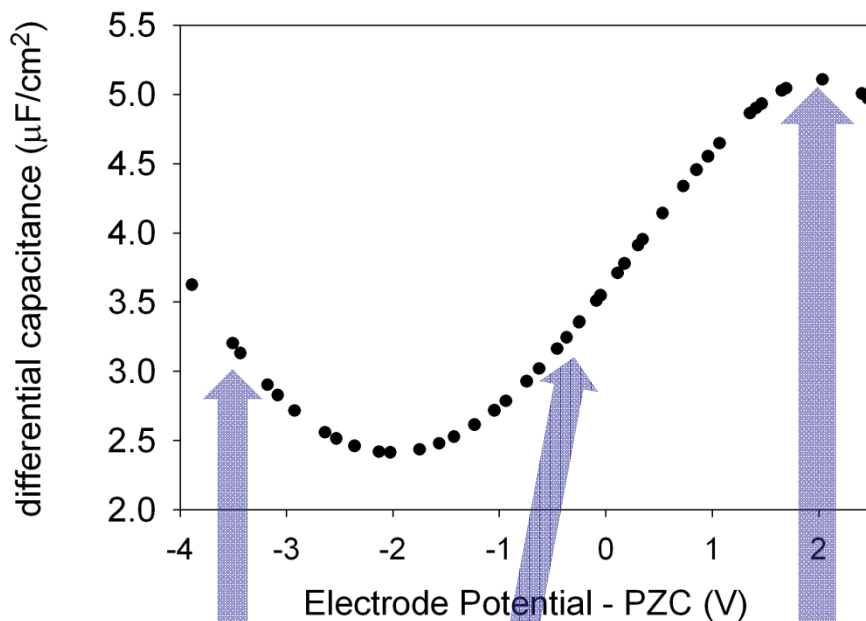
Simulations of Graphite || EC:DMC/LiPF₆ Interfaces as a Function of Electrode Potential

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★Molecular dynamics simulations with our electroactive interface model (controlled electrode potential) allow us to study the influence of electrode potential on the structure, capacitance, and transport properties of the electrolyte at the electrode/electrolyte interface

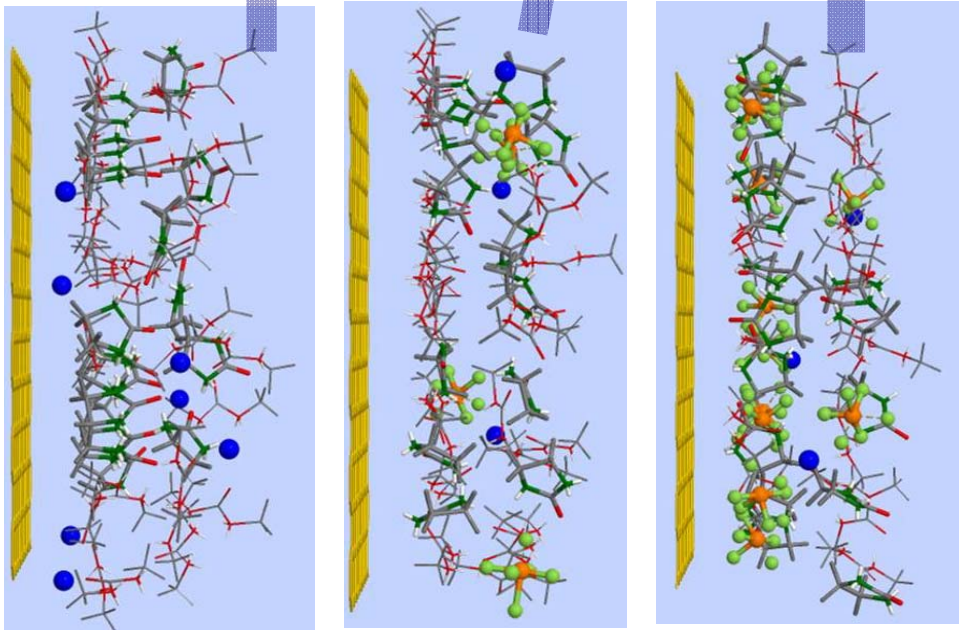


★The complex dependence of the electrode capacitance on electrode potential can be correlated with the structure of the electrolyte at the interface

--at low potential, the interface is dominated by the neutral solvent molecule

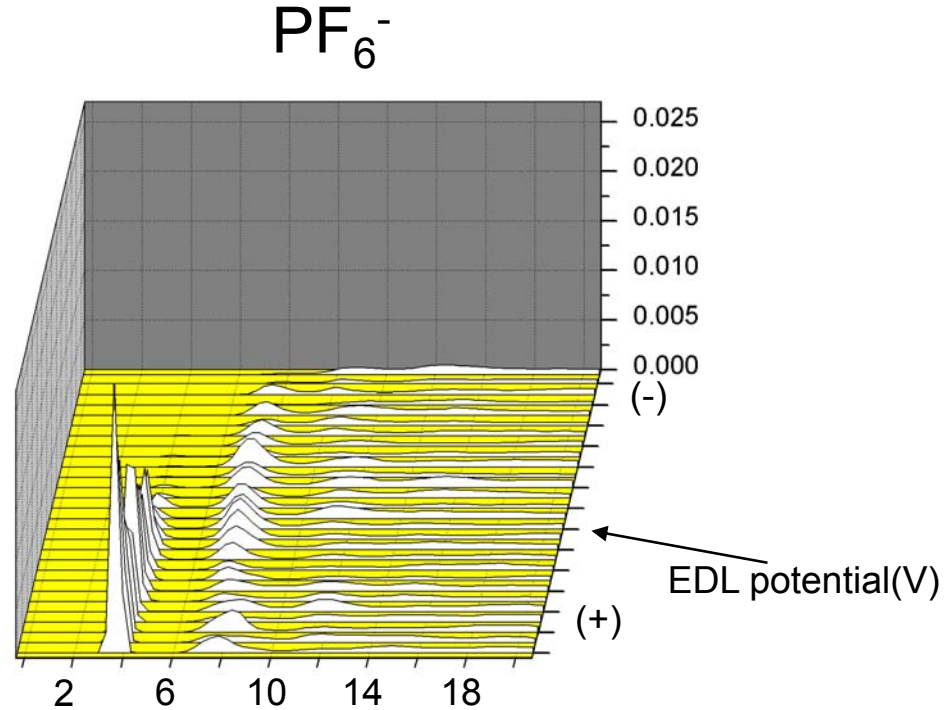
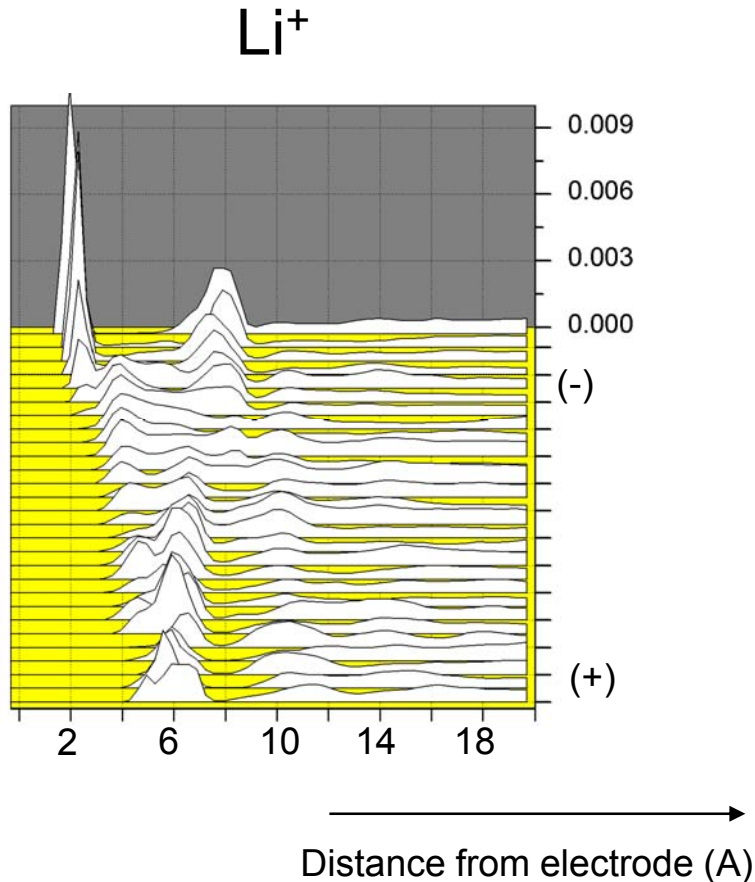
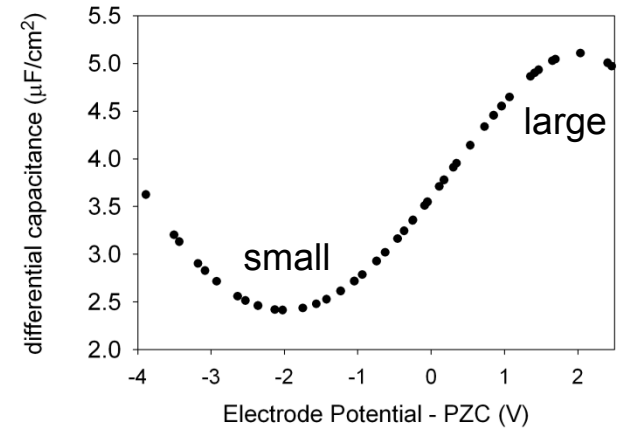
--at large positive potentials, a high concentration of anions can be found in the interfacial layer

--at large positive potentials, Li^+ begins to populate the interface but at relatively low densities

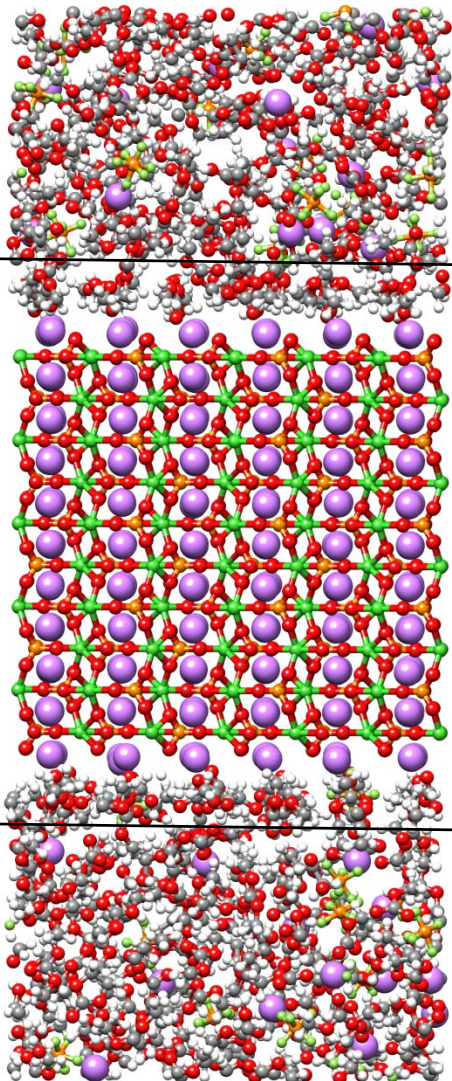


★ At larger potentials, the Stern layer is narrower on the negative electrode due to the small size of Li^+ compared with PF_6^-

★ However, the electrode capacitance is smaller for the negative electrode and exhibits an initial decrease with potential due to the free energy penalty for bringing Li^+ to the surface (desolvation)



Dynamics of Interfacial Electrolyte



★MD simulations of LiFePO_4 in contact with an EC:DMC/ LiPF_6 electrolyte were performed over the temperature range 363 K – 253 K

★Dynamics (diffusion and rotation) of the solvent in the interfacial layer are found to be about 200 times slower than in the bulk electrolyte due to strong coordination between EC:DMC and the LiFePO_4 surface

★This slowing of interfacial solvent dynamics is quite different to behavior observed for electrolyte in contact with graphite, where very little slowing down compared to the bulk was observed

★Over the temperature range for which surface dynamics can be quantified in simulations to date (> 300 K), the interfacial solvent exhibits weak temperature dependence similar to that for the bulk electrolyte

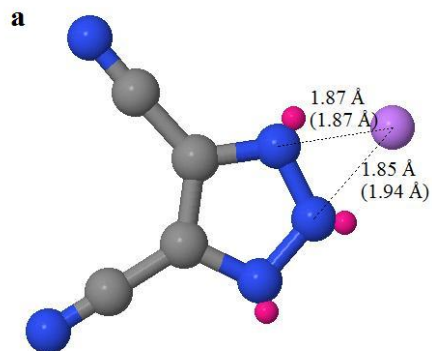
Novel Lithium Salts

★ Novel lithium salts based on the cyano-containing anions are investigated in collaboration with NCSU (W. Henderson) and Université de Picardie (M. Armand)

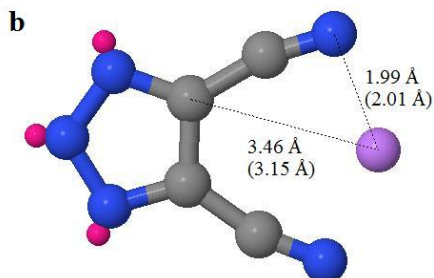
★ A quantum chemistry-based polarizable force field has been parameterized for the lithium dicyano-1,2,3-triazolate (LiDCTA) complex. Molecular mechanics (MM) calculations yielded the LiDCTA geometries (shown in parentheses in Figs. a-c) and binding energies in good agreement with QC calculations performed at M052x/cc-pvTz level

★ MD simulation were performed on γ -butyrolactone (GBL)/LiDCTA, GBL/LiPF₆ and GBL/LiTFSI at 298 K

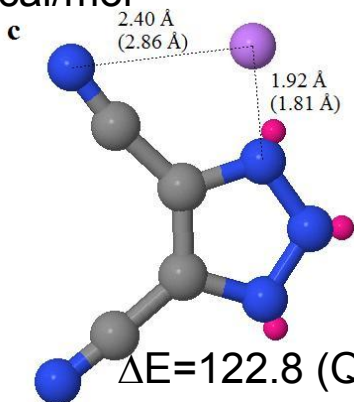
	GBL/LiDCTA	GBL/LiPF ₆	GBL/LiPF ₆	GBL/LiTFSI
Solvent:Li	10	10	20	10
λ (mS/cm)	4.1	12.2	13.0 (exp. 10.8)	10.4 (exp. 9.2)
degree of dissociation	0.42	0.55	0.72	0.58



$\Delta E=131.4$ (QC) 125.4 (FF)
kcal/mol



$\Delta E=123.9$ (QC) 120.7 (FF)
kcal/mol



$\Delta E=122.8$ (QC)
124.3 (FF) kcal/mol

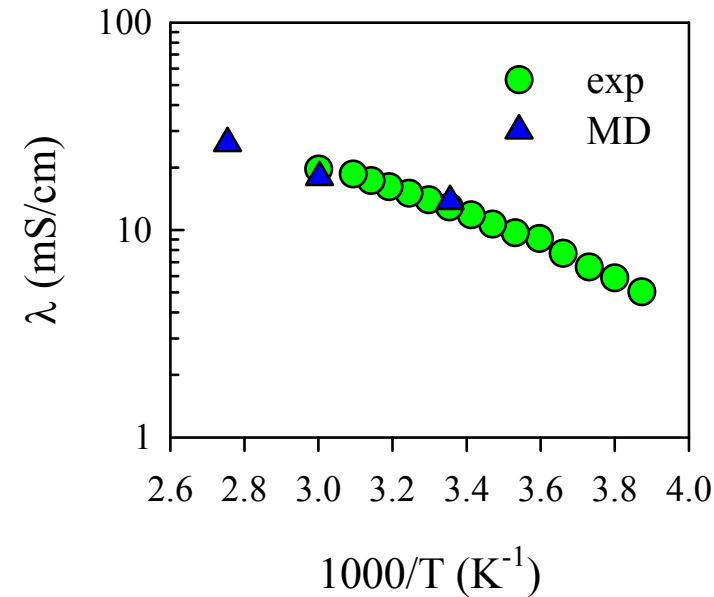
Fluorinated Solvents

- ★ Influence of sulfolane fluorination on the solvent oxidative stability, transport properties and its ability to coordinate Li^+ has been investigated complementing experimental studies that are currently performed by Austen Angell group (ASU)

The Li^+ /solvent binding energy (in kcal/mol) from QC					
	Li^+/SL	$\text{Li}^+/\text{SL}(\text{F}_4)$	$\text{Li}^+/\text{SL}(\text{F}_8)$	Li^+/EC	Li^+/DMC
MP2/cc-pvTz or <i>MP2/aug-cc-pvTz</i>	-52.7	-40.8	-29.5	-47.5	-40.9
Solvent self-diffusion coefficient					
T (K)	303	303	303	313	298
D ($10^{-10} \text{ m}^2/\text{s}$)	1.1	2.5	4.7	8	25.4

- ★ Completely fluorinated $\text{SL}(\text{F}_8)$ is not expected to be good solvent for typical Li salts such as LiPF_6 or LiTFSI .
- ★ Semifluorinated sulfolane $\text{SL}(\text{F}_4)$ is expected to have lithium salt dissociation similar to DMC, while $\text{SL}(\text{F}_4)$ dynamics is predicted to be a factor of 2.5 faster than SL but a factor of five slower than DMC.

Mixed Solvent Electrolytes



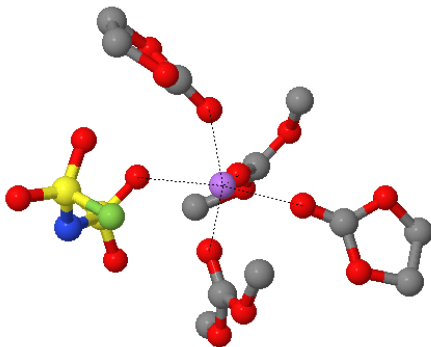
★ MD simulations accurately predicted conductivity of EC:DMC (1:1)/LiFSI 0.85 M electrolyte as a function of temperature.

★ Low activation energy for the conductivity was observed

★ High degree of the LiFSI salt dissociation in EC:DMC (1:1) was observed: 38% of the Li⁺ cations did not have oxygen atoms from FSI⁻ anions in its first coordination shell, while the dynamic degree of ion dissociation α_d was 47% - 52 %, which is slightly higher than α_d of 34%-44% observed for EC:DMC(1:1) 1 M LiPF₆ at 298 K - 363 K temperature range

★ At 298 K, the Li⁺ coordination shell (<2.8 Å) consisted of 2.0 carbonyl oxygens from DMC, 1.5 carbonyl oxygens from EC and 0.9 oxygen atoms from FSI⁻ anions

Exp. Abouimrane et al. *J. Power Sources* **2009**, 189, 693.



Future Work

- Utilize ReaxFF simulations to predict the structure and transport properties of SEI layers for relevant model chemistries with emphasis on the role of additives (particularly VC)
- Determine the free energy profile/interfacial impedance for Li^+ intercalation/deintercalation into LiFePO_4 and graphite electrodes as a function of temperature and electrode potential
- Explore the structure, transport, and stability of electrolytes comprised of new salts and solvents in collaboration with BATT investigators
- Perform whole-cell (anode/electrolyte/cathode) simulations with controlled electrode potential using relevant model chemistries
- Investigate oxidation mechanisms at the LiFePO_4 cathode

Summary

- Quantum chemistry (gas phase) and ReaxFF (condensed phase) simulations have revealed the importance of the cyclic EC radical in the formation of compounds believed to be important in the outer SEI
- Introduction of vinylene carbonate to the electrolyte leads to the formation of poly(vinylene carbonate) initiated by both cyclic and linear EC radicals
- The dynamics of the electrolyte near the LiFePO_4 interfacial are found to be dramatically slower than in the bulk or at the interface with graphite, but exhibit temperature dependence similar to the bulk
- Semifluorinated sulfolane-based solvents are promising candidates as electrolytes and/or co-solvents for operations with high voltage cathodes
- LiDCTA salt has an inferior conductivity to LiPF_6 and LiTFSI in GBL solvents at solvent:Li=10 salt concentration at room temperature
- EC:DMC/LiFSI 0.8 M electrolytes show higher conductivity than EC:DMC/ LiPF_6 1 M. A slightly higher fraction of DMC than EC was found in the first coordination shell of the Li^+ cations for the mixed EC:DMC (1:1)/Li salt electrolytes
- EC/DMC/ LiPF_6 electrolyte at the interface with graphite was found to exhibit a complex multilayer structure that depends strongly on electrode potential. The dependence of the interfacial (electrode) capacitance on potential correlates qualitatively but not quantitatively with the structure of the first interfacial electrolyte layer