Molecular dynamics simulation studies of electrolytes and electrolyte/electrode interfaces

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Project ID es_40_smith

Overview

Timeline

- Start 2/01/08
- Complete 1/31/10
- 66.7% complete

Budget

- Total project funding
  - DOE $441 K
  - Contractor $ 0 K
- Funding received
  - $181 K FY08
  - $260 K FY09

Barriers

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

Collaborations

- U.C. Berkeley (N. Balsara)
- CSIRO (T. Hollenkamp)
- Lawrence Berkeley National Laboratory (J. Kerr, R. Kostecki)
- Royal Melbourne Institute of Technology (S. Russo)
- Penn State University (A. van Duin)
- Army Research Lab (R. Jow)
- NCSU (W. Henderson)

Objectives

- Use molecular simulations to predict the chemical composition and structure of SEI layers and graphite and Sn-based intermetallic anodes
- Predict temperature dependence and gain molecular level understanding of the structure, mechanical properties and Li^+ cation transport in SEI layers
- Gain molecular level understanding of Li^+ cation transport mechanisms in liquid and ionic liquid electrolytes
- Gain molecular level understanding of Li^+ intercalation/deintercalation from/into graphite anode and model cathode materials
- Develop and apply simulation methods for electro-active interfaces that allow explicitly for charge transfer processes and controlled potential
- Develop an atomistic model for simulations of Sn-based intermetallic anodes
- Provide guidance for design of electrolytes with improved lithium transport, reduced interfacial resistance and/or improved electrochemical stability

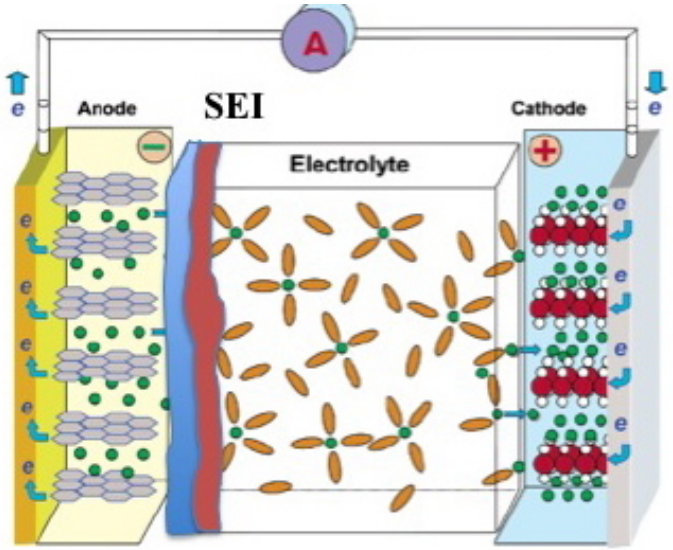
Milestones

- Complete simulations aimed at understanding the influence of composition and chemistry of carbonate electrolytes on the charge transfer resistance at graphite anode interface. **Completed June 2008**
- Parameterize potential and simulate $LiFePO_4$/organic liquid electrolyte and $LiFePO_4$/ionic liquid interface, predict interfacial structure and Li^+ transport. **Model development and initial study completed December 2008, extended study due August 2009 on schedule**
- Parameterize ReaxFF for molecular dynamics (MD) simulations with reaction and predict reduction products and SEI structures for EC and VC. **EC completed December 2008, VC delayed until June 2009**
- Complete classical MD of EC/DMC mixed electrolytes aimed at understanding the roles of EC and DMC in Li^+ solvation and transport. **Completed September 2008**
- Develop MD model of VC-based SEI (poly(vinylene carbonate) and predict Li^+ transport and mechanical properties. **Model development complete June 2008, property prediction due July 2009, on schedule**
- Complete MD simulations of bulk liquid electrolytes including ionic liquids with PEO and phosphate-based electrolytes. **September 2009 on schedule**
- Develop electro-active interface MD model and perform simulations aimed at understanding the role of electrode potential on electrolyte/electrode interface structure, interfacial impedance and interfacial capacitance. **Model development completed January 2009, simulations due September 2009 on schedue**

Milestones

- Develop a potential for MD simulations of Sn-based intermetallic anodes. **Due August 2009, delayed**
- Parameterize ReaxFF for molecular dynamics (MD) simulations with reaction and predict reduction products and SEI structures for EC and VC at the interface with Sn-based intermetallic anodes. **January 2010 on schedule**
- Develop MD model of siloxane-based SEI and predict Li^+ transport and mechanical properties. **Due September 2009, on schedule**

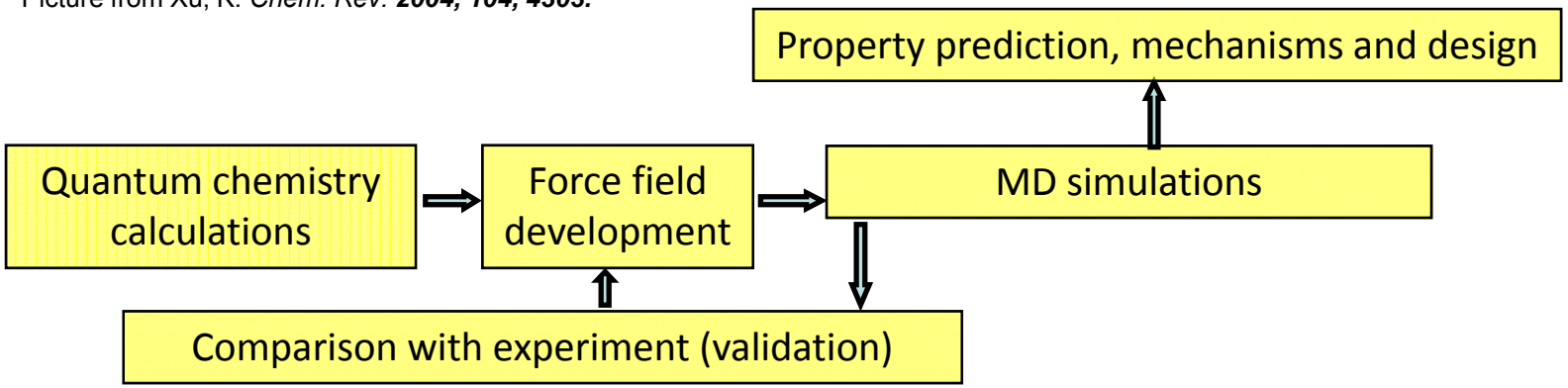
Approach



Picture from Xu, K. *Chem. Rev.* ***2004, 104, 4303.***

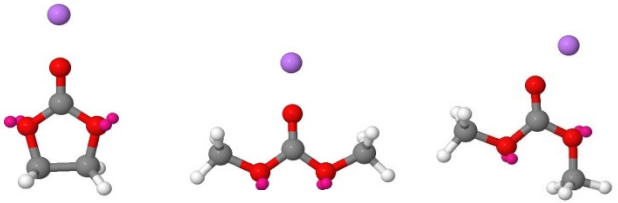
Molecular level modeling of structure, transport and mechanical properties:

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



Technical Accomplishments: Mixed Carbonate Electrolytes

Li^+/EC, Li^+/DMC gas-phase quantum chemistry



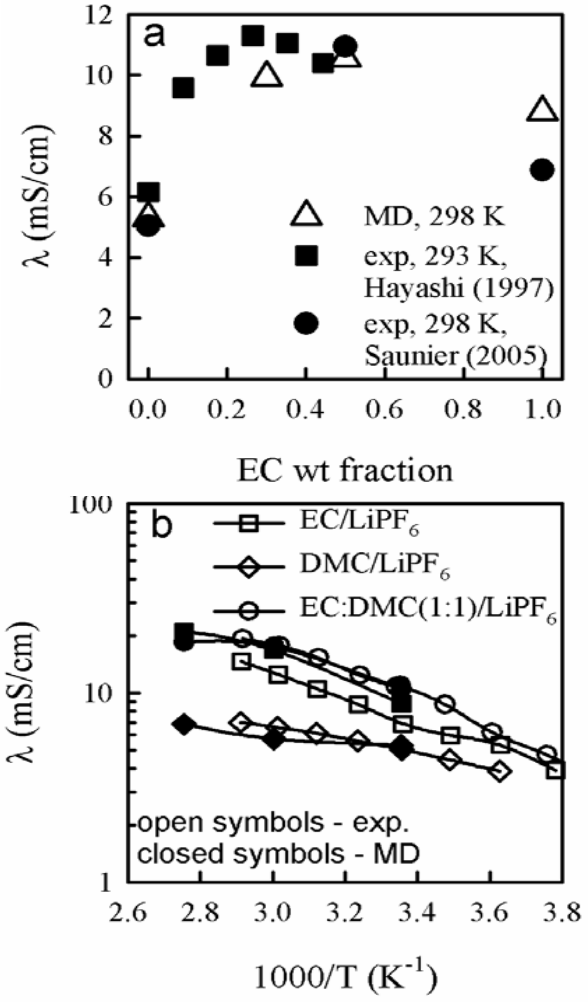
EC DMC(cc) DMC(ct)

Level of Theory	EC/Li^+	DMC(cc)/Li^+	DMC(ct)/Li^+
Binding energy (kcal/mol)			
MP2/Dz	-47.5	-40.9	-45.2
CCSD(T)/Dz//MP2/Dz	-48.0	-41.5	-45.6
Force Field (FF)	-45.4	-39.3	-42.9
ΔE (MP2/Dz)-(FF)	-2.1	-1.6	-2.3
Dipole Moment of (Debye)			
	EC	DMC(cc)	DMC(ct)
M05-2X/Dz	5.68	0.34	3.76

✓*While Li^+ binds stronger to EC than DMC(cc), binding to DMC(ct) is only about 2 kcal/mol weaker than binding to EC*

✓*DMC coordination is actually slightly preferred over EC for $LiPF_6$ ion pairs*

Technical Accomplishments: Mixed Carbonate Electrolytes



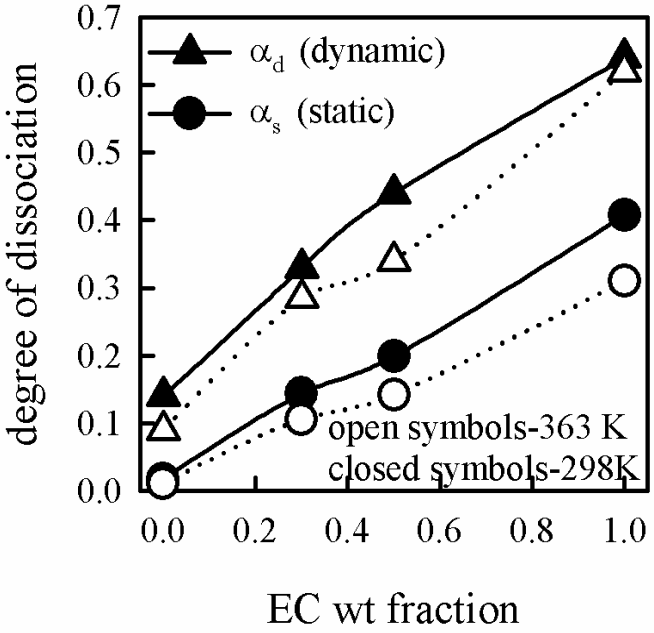
Lithium coordination in EC:DMC/$LiPF_6$ electrolytes 1M at 298 K

Electrolyte composition	Oc (EC) r_c=2.8Å	Oc (DMC) r_c=2.8Å	P(PF_6^-) r_c=4.4Å
EC/$LiPF_6$	3.6		0.7
DMC/$LiPF_6$		2.7	1.4
EC:DMC(1:1) /$LiPF_6$	**1.4**	**1.9**	1.0
EC:DMC(3:7) /$LiPF_6$	**0.9**	**2.3**	1.1

✓*MD simulations of EC/DMC $LiPF_6$ yield conductivity in good agreement with experiment*

✓*Lithium coordination from MD simulations indicating importance of DMC is consistent with the reanalyzed spectroscopy data*

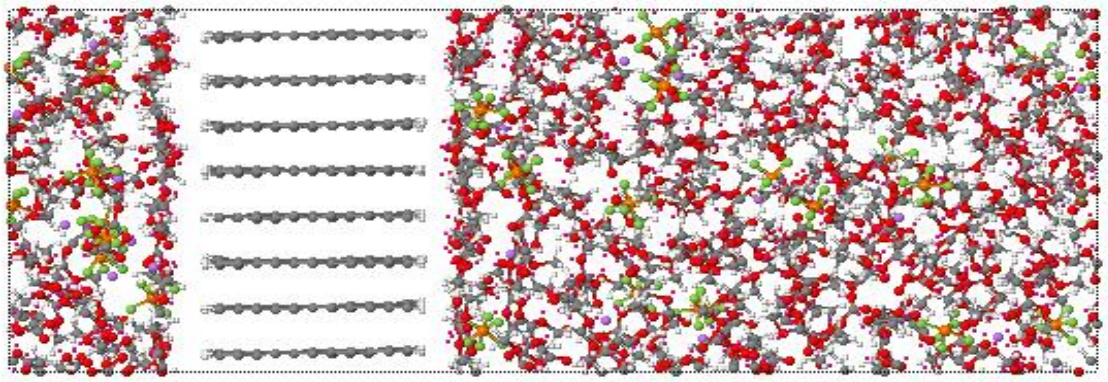
Technical Accomplishments: Mixed Carbonate Electrolytes

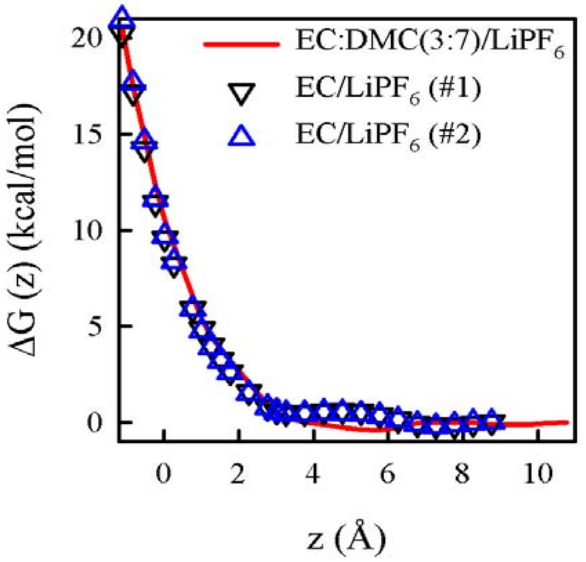


✓*The degree of dynamic ion dissociation (derived from pfg-NMR and conductivity measurements) is significantly higher than the fraction of free ions from static (structural) analysis*

✓*This is due to significant contribution to ion transport from charged aggregates*

Technical Accomplishments: Mixed Carbonate Electrolytes at a Graphite Interface



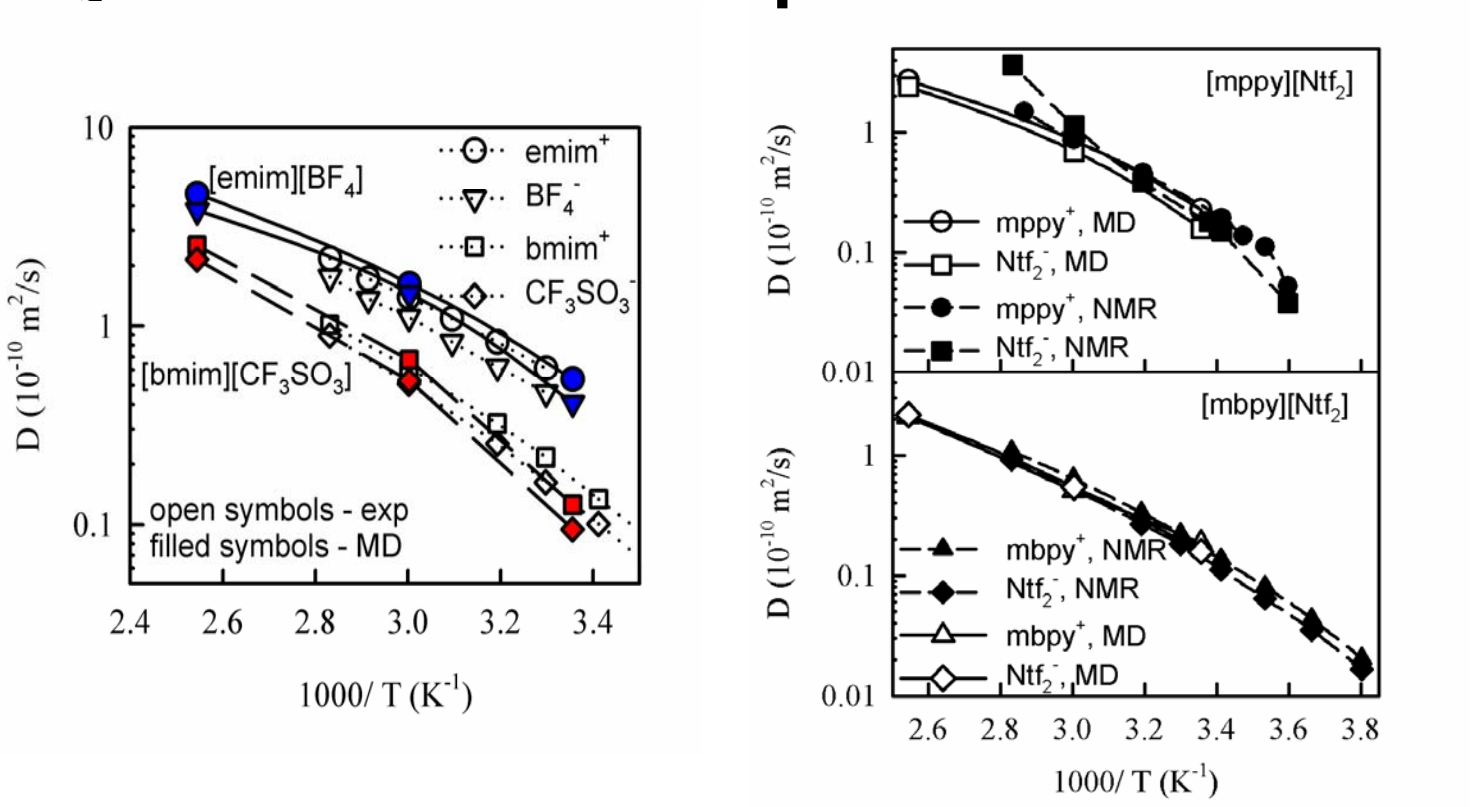


✓ ΔG(z) for EC/$LiPF_6$ and EC:DMC(3:7)/$LiPF_6$ are similar

✓A value of ΔG(z) around 12-19 kcal/mol is obtained for the barrier to bring Li^+ to the graphite/electrolyte interface (desolvation free energy), consistent with the experimental activation energies of 16.4-17 kcal/mol (Jow, ARL)

The Li^+ disolvation free energy profile for EC/$LiPF_6$ and EC:DMC(3:7)/$LiPF_6$ 1 M electrolytes next to graphite at 298 K

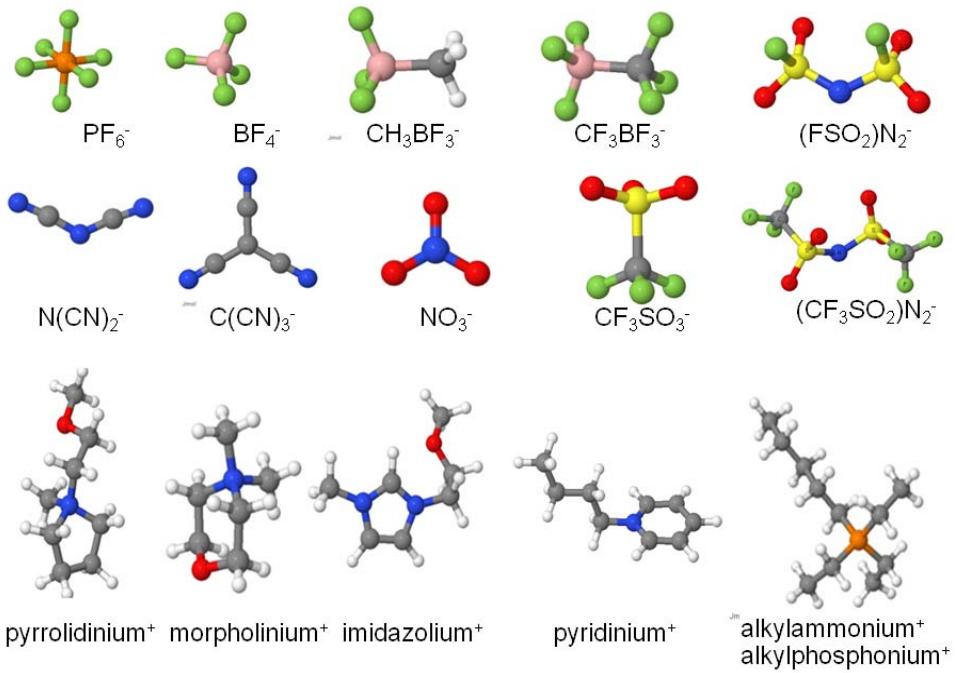
Technical Accomplishments: Dynamics in Ionic Liquids: Model Validation

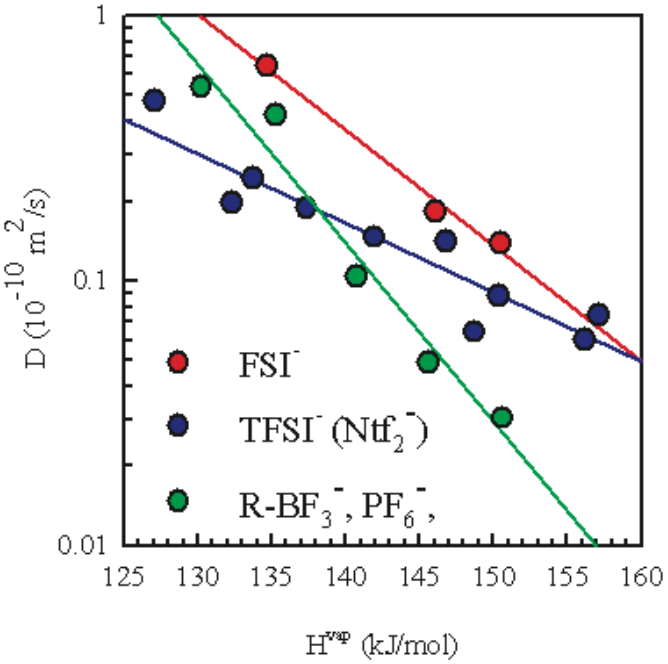


- ✓ Excellent agreement with experiment for a wide range of ILs over a wide range of temperature supports the accurately of our quantum-chemistry based atomistic potentials

[mppy][Ntf_2] NMR: Nicotera, I., C. Oliviero, W.A. Henderson, G.B. Appetecchi, et al., *J Phys Chem B,* ***2005, 109, 22814-22819.***
[bmpy][Ntf_2] NMR: Tokuda, H., K. Ishii, M.A.B.H. Susan, S. Tsuzuki, et al., *Journal of Physical Chemistry B,* ***2006, 110, 2833-2839.***

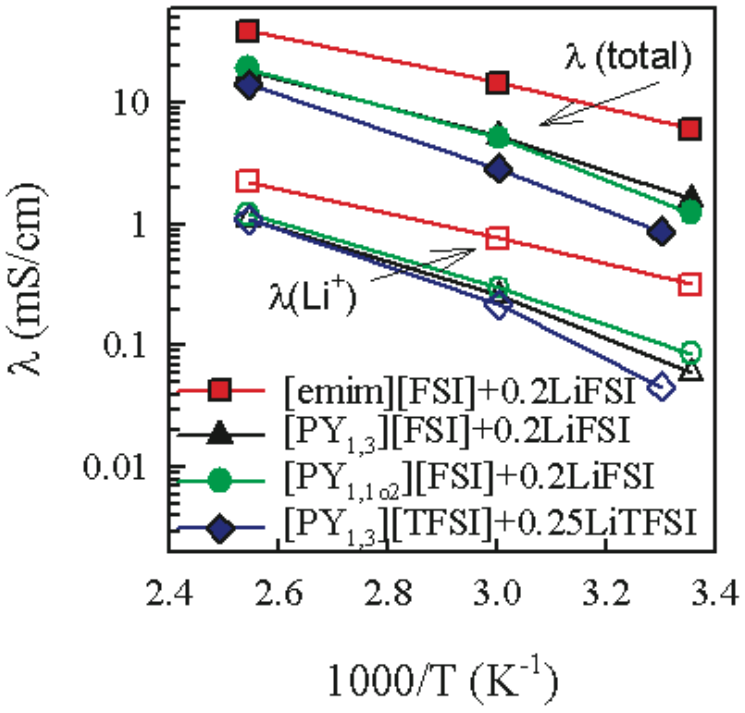
Technical Accomplishments: Heat of Vaporization and Dynamics in Ionic Liquids



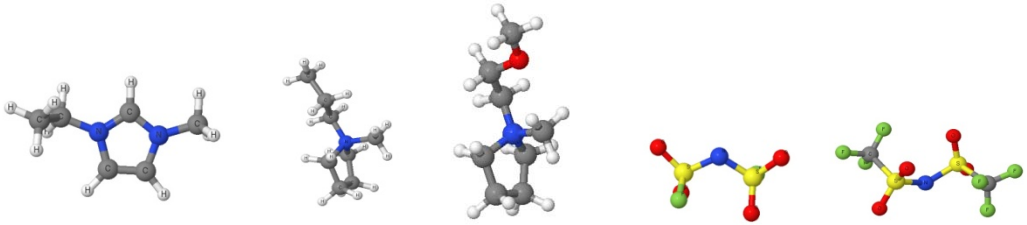


- ✓ An (unfortunate) correlation between heat of vaporization and ion diffusion was found for ILs
- ✓ The slope of D vs. H^{vap} was found dependent on the nature of anion

Technical Accomplishments: Li^+ Transport in Ionic Liquids



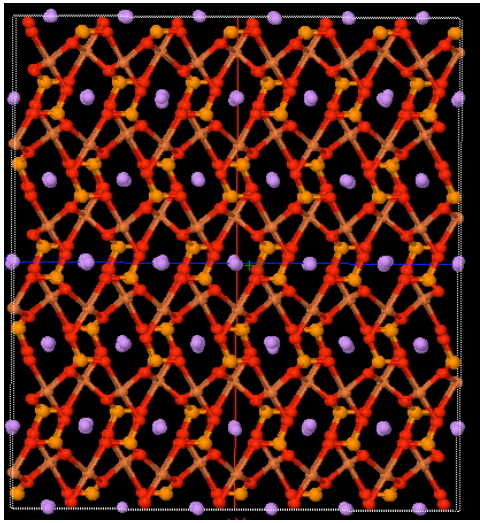
$$\lambda(Li^+) = \frac{n_{Li^+} D_{Li^+}}{n_{Li^+} D_{Li+} + n_+ D_+ + n_- D_-} \lambda$$



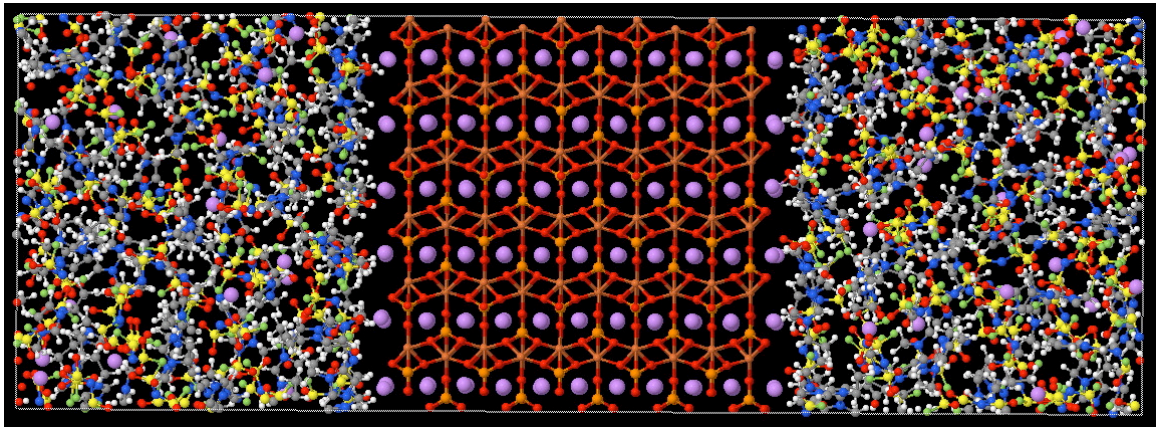
- ✓ FSI-based ILs doped with LiFSI have been investigated and compared with previous results for TFSI-based ILs.
- ✓ FSI-based ILs show improved overall and Li^+ conductivity, particularly at lower temperatures
- ✓ The best ILs exhibit Li^+ transport significantly better than polymer electrolytes but still lower than traditional organic liquid electrolytes

Technical Accomplishments: $LiFePO_4$/Electrolyte Interfaces

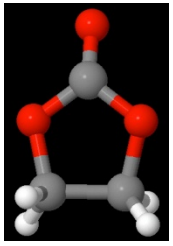
We have simulated $LiFePO_4$ in contact with
EMIM/FSI + LiFSI (ionic liquid electrolyte, ILE)
EC/DMC + $LiPF_6$ (organic liquid electrolyte, OLE)



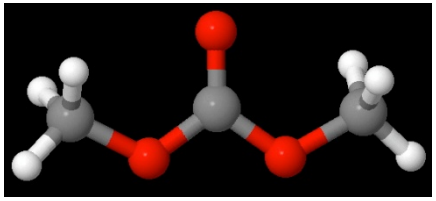
$LiFePO_4$ along the [010] direction



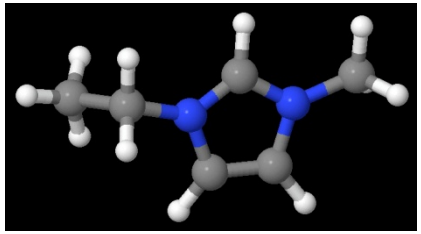
$LiFePO_4$/[EMIM][FSI] with 1 M LiFSI viewed along the [100] direction



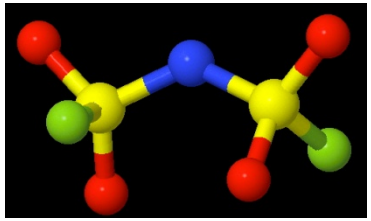
EC



DMC



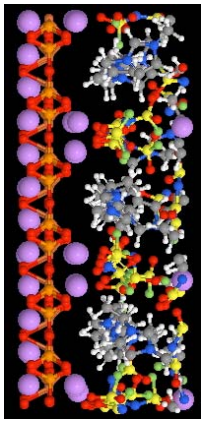
EMIM

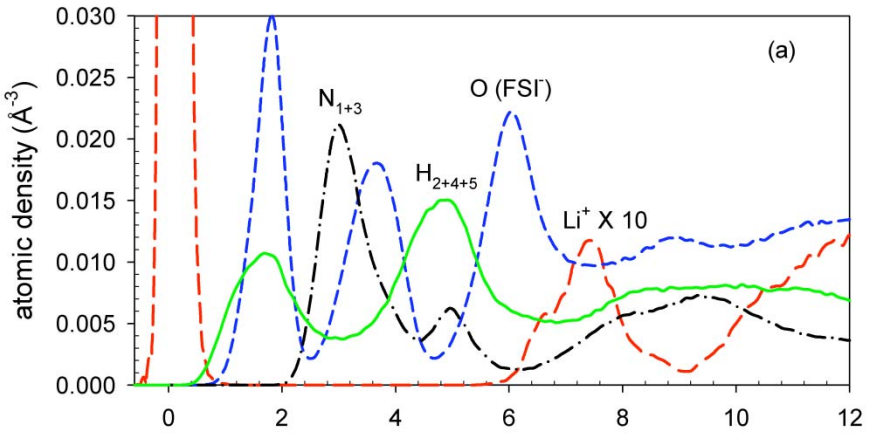


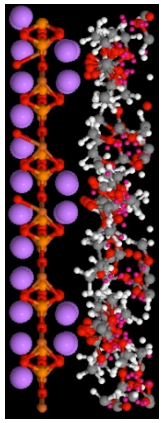
FSI

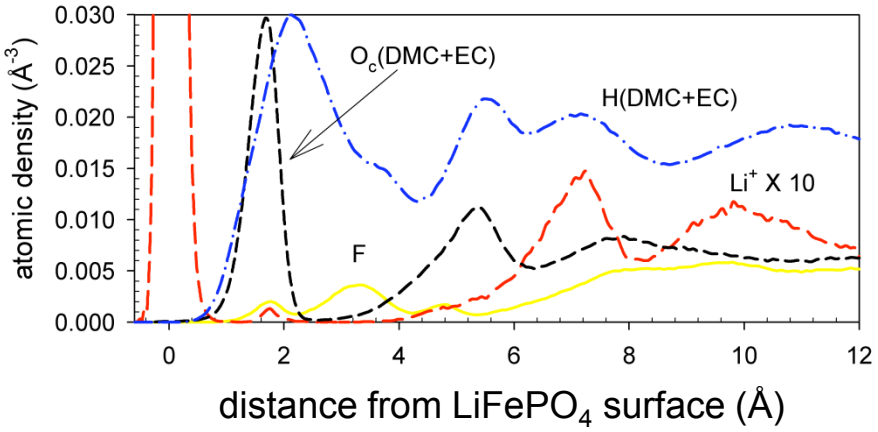
Technical Accomplishments: $LiFePO_4$/Electrolyte Interface

Atomic density profiles ILE (top) and OLE (bottom)









Simulations reveal:

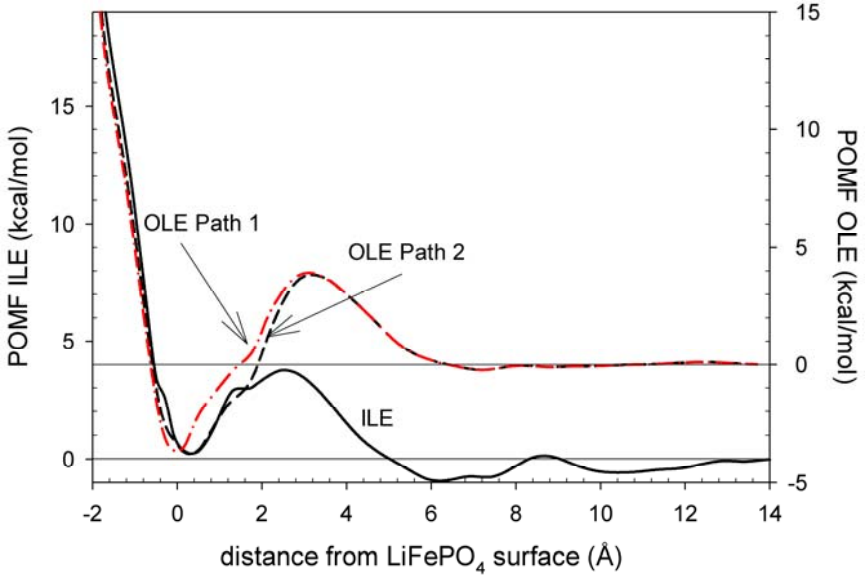
✓ substantial interface-induced structure in the electrolytes

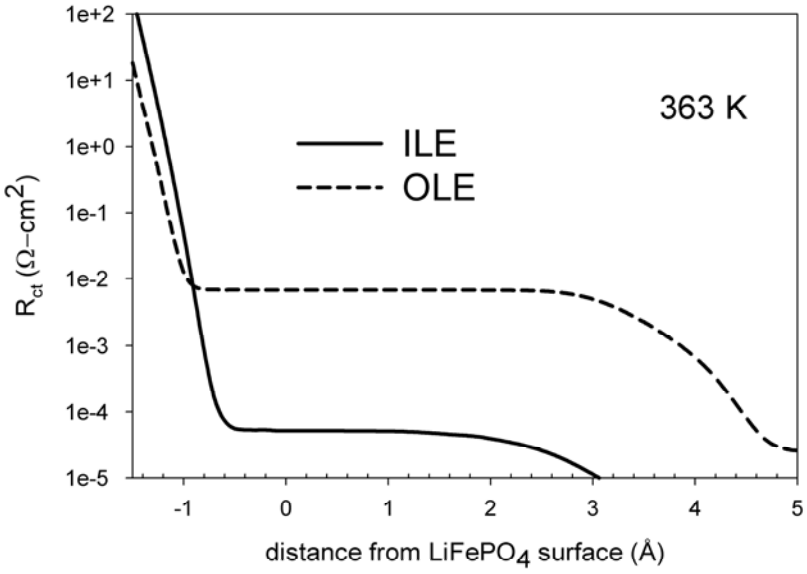
✓a large barrier to transport of Li^+ to the surface as evidenced by low Li^+ concentration near the interface

✓reduced Li^+ mobility near the interface unlike little reduction observed for liquid electrolytes near graphite

✓Dramatically different roles for EC and DMC in coordination of the $LiFePO_4$ surface

Technical Accomplishments: $LiFePO_4$/Electrolyte Interface





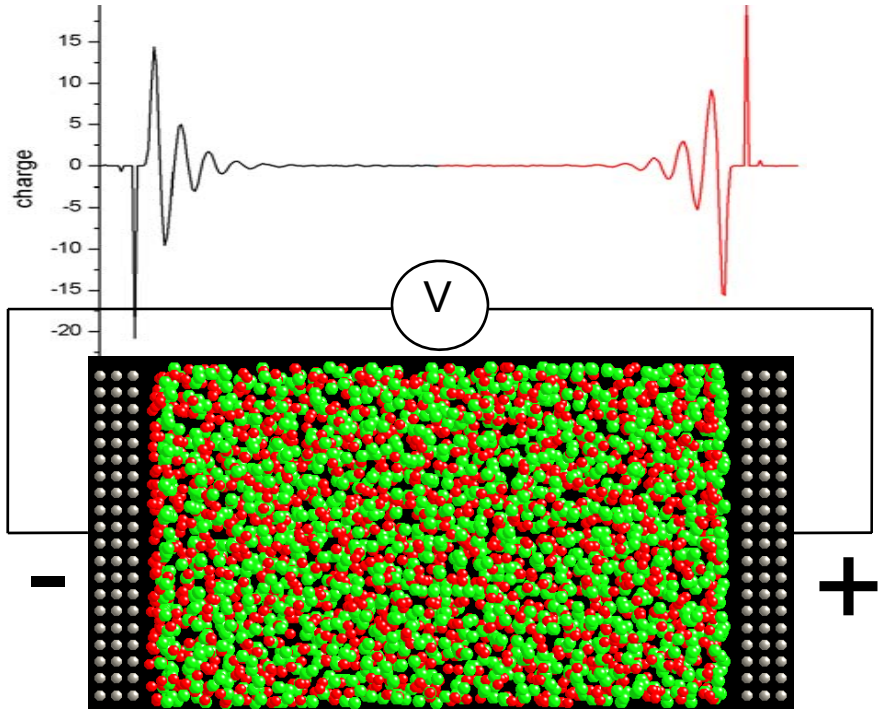
Knowledge of the local free energy and Li^+ allows for estimation of interfacial impedance and its activation energy

✓ Interfacial impedance is somewhat greater for the ILE than the OLE, in agreement with experiment

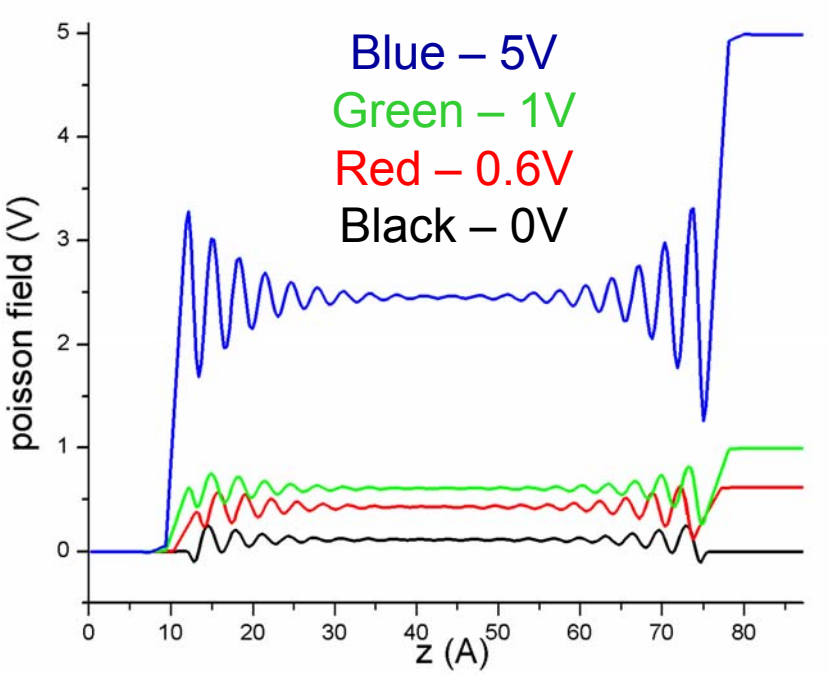
✓The activation energy for Li^+ desolvation in the ILE is slightly greater the for the OLE. Values of 13-17 kcal/mol are in good agreement with experiment

Technical Accomplishments: Electroactive Interface Model

- ✓New simulation methodology that allows for electron transfer
- ✓Maintains desired voltage on conducting electrodes by equilibrating charges



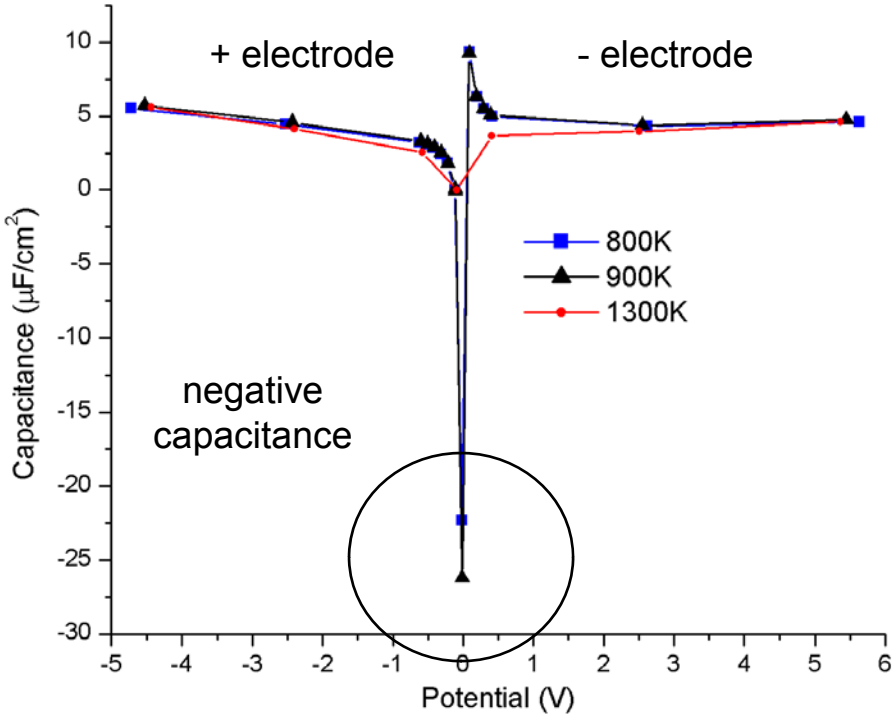
Red = Li^+
Green= Cl^-
Grey = electrode



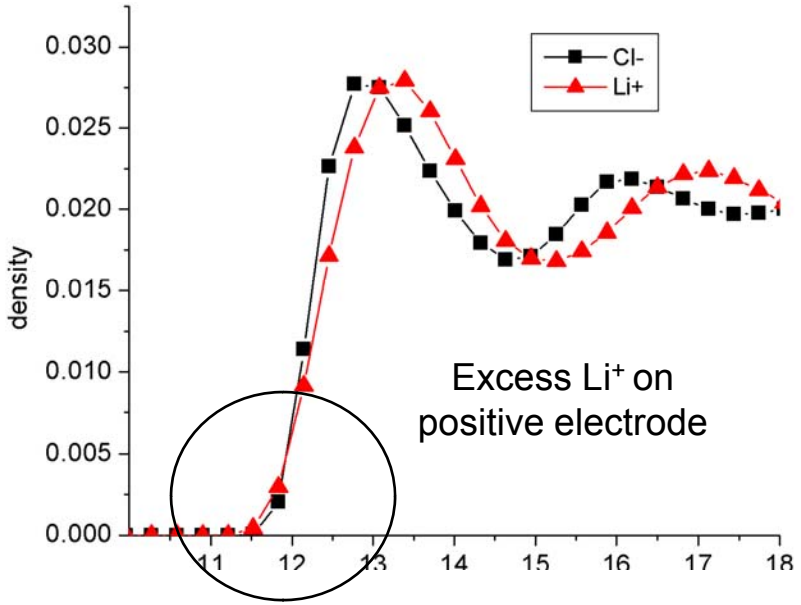
Technical Accomplishments: Electroactive Interface Model

✓electrode capacitances show a discontinuity at small potential
✓negative capacitances were found at small potentials
✓neither Helmholtz nor Stern's double layer models account for the observed structure and capacitance

Electrode capacitance vs. applied potential



Structure at positive electrode at a low voltage

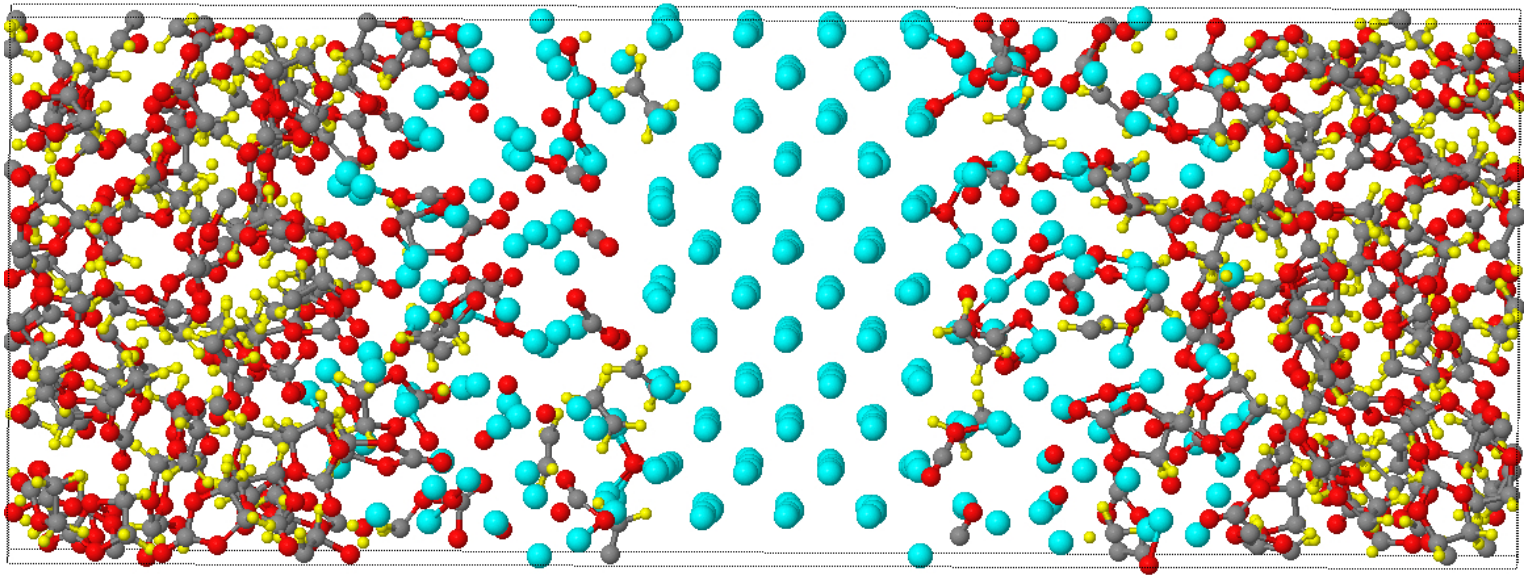


Technical Accomplishments: SEI formation Using Reactive Molecular Dynamics Simulations

✓Near Li rich surfaces our simulations show extensive and rapid two electron reduction of EC and formation of a layer consisting of Li_2CO_3 and Li_2O as well as generation of C_2H_4 and CO_2 gases.

✓As the interfacial layer widens reduction of EC electrolyte slows down considerably

✓Investigation of influence of the electrolyte composition on the structure and composition of the interfacial layer are currently underway



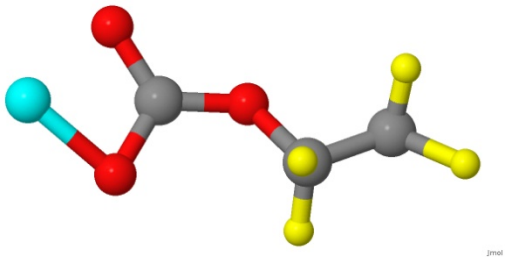
Technical Accomplishments: SEI formation Using Reactive Molecular Dynamics Simulations

Simulations at conditions corresponding to the outer SEI layer (excess of electrolyte) reveal mechanisms of:

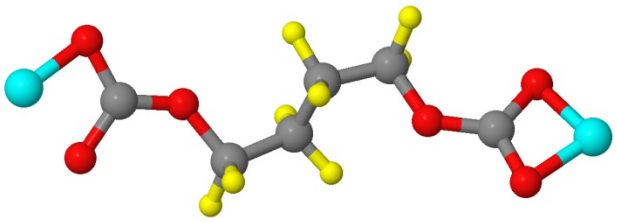
✓ring opening of EC to form $[EC^- Li^+]\bullet$ radical after single electron reduction

✓recombination of $[EC^- Li^+]\bullet$ radicals to form lithium butylene dicarbonate $(CH_2CH_2OCO_2Li)_2$

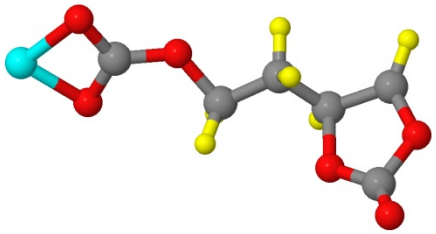
✓initiation of vinylene carbonate (VC) polymerization from radical



$[EC^- Li^+]\bullet$

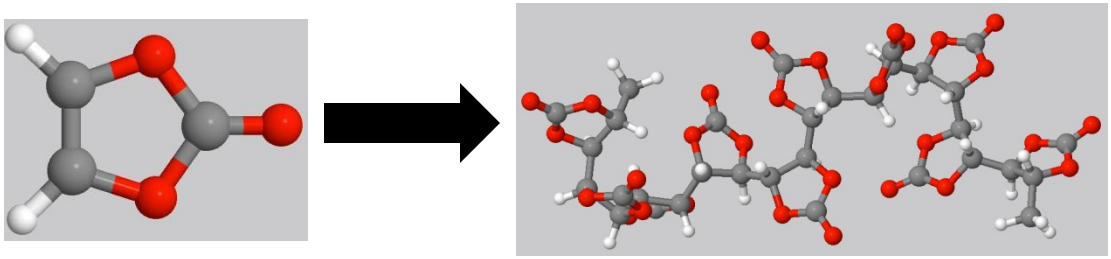


$(CH_2CH_2OCO_2Li)_2$

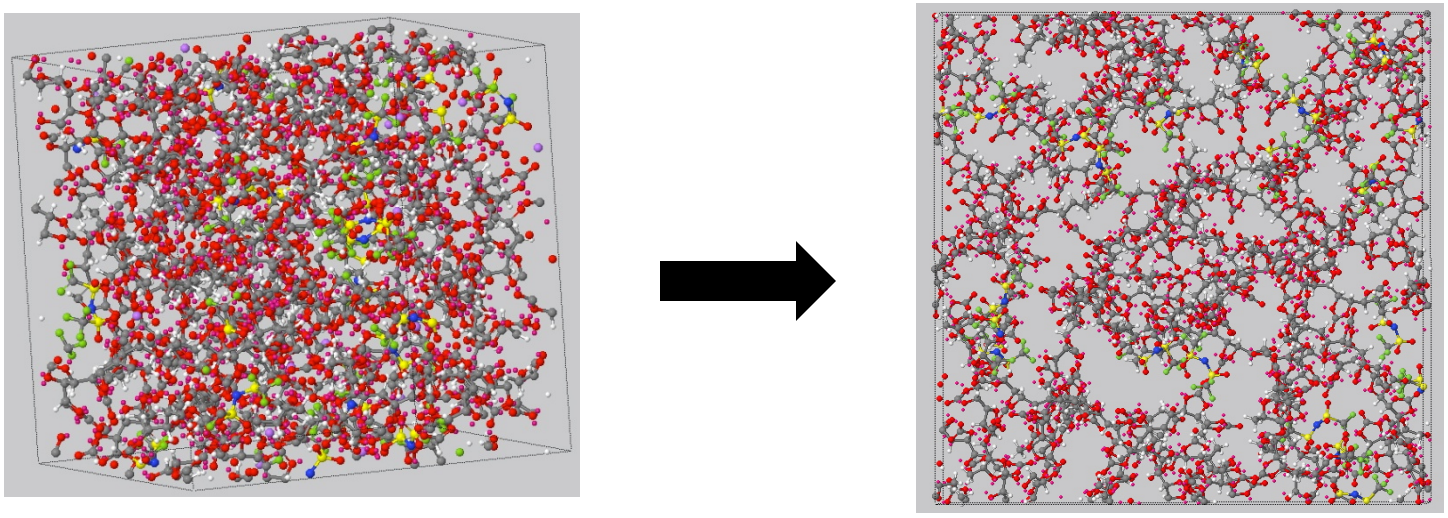


$[EC^- Li^+]VC\bullet$

Technical Accomplishments: Model SEI Materials



Simulations of poly(vinylene carbonate) doped with LiTFSI have been conducted:



✓Li^+ conductivity has been determined as a function of temperature

✓Mechanical properties of the SEI under high strains (e.g., Sn-based intermetallic anodes) have been studied and exhibits nanoscale fracture

Future Work

- Improve $LiFePO_4$ model to allow Li^+ intercalation
- Study $Li_4P_2O_7$ coated $LiFePO_4$ interface with electrolytes
- Investigate novel electrolytes in collaboration with NCSU team (Henderson).
- Study trialkyl phosphate-based electrolytes
- Study desolvation for Li^+ in IL/solvent mixtures at the $LiFePO_4$ interface (Kerr)
- Utilize electroactive interface model with realistic electrodes, electrolytes, and SEI layers to accurately model influence of potential on interface structure and dynamics as well as Li^+ desolvation and intercalation with electron transfer
- Study SEI layers (conductivity, mechanical properties) comprised of siloxanes
- Use ReaxFF to SEI layer formation at graphite-based and Sn-based intermetallic electrodes as a function of electrolyte composition (EC, VC, DMC, PC, salts).

Summary

- Mixed carbonate electrolytes and ionic liquid electrolytes have been studied in bulk and at interfaces using MD simulations providing details of lithium transport and solvation structure
- Lithium desolvation free energies (at interfaces) were found in accord with experimental observations. Ionic liquid electrolytes yielded higher desolvation free energies and interfacial resistance associated with it
- A methodology for simulations of interfaces with controlled potentials has been implemented
- Simulations using reactive force fields predicted EC decomposition products at the anode material
- Mechanical and transport properties of poly(vinylene carbonate) doped with LiTFSI (SEI model compound) were characterized from simulations