Molecular Simulations of Electrolytes and Electrolyte/Electrode Interfaces

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"This presentation does not contain any proprietary or confidential information"

02/18/2008

Outline

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Summary

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Barriers and Objectives

Barriers

- **Poor ambient temperature Li^+ transport**

- **High interfacial resistance of cells at low temperature**

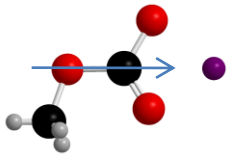
Objectives

- **Extend computational tools to include**
  - **electroactive interfaces (charge transfer)**
  - **chemical reactions (SEI formation)**

- **Understand mechanisms/barriers of ion transport**
  - **Ionic liquids**
  - **SEI components**
  - **Intercalation/deintercation at anode/cathode**
  - **Low temperature behavior**

- **Design novel electrolytes with improved lithium transport/interfacial resistance**

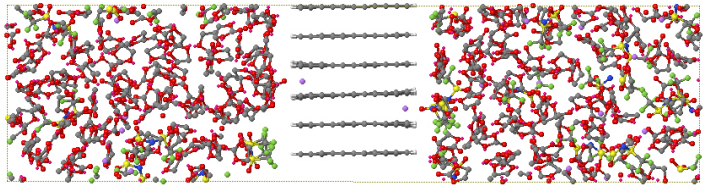
Approach

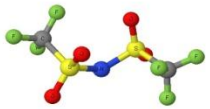


Property prediction, mechanisms and design

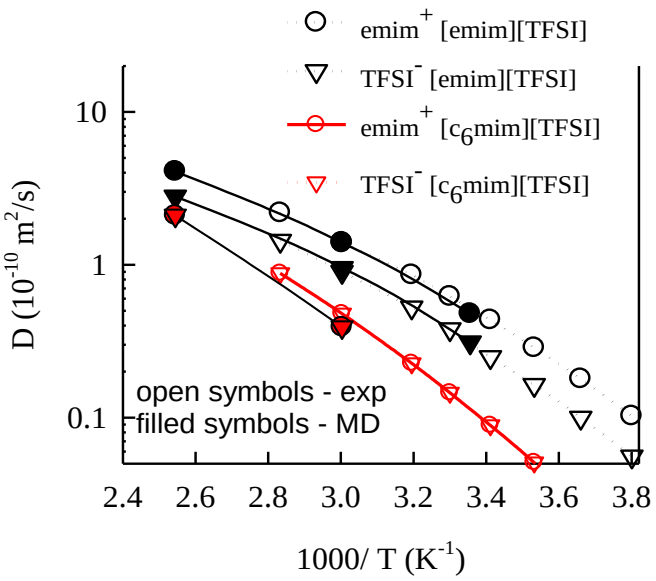
Quantum chemistry calculations → Force field development → MD simulations

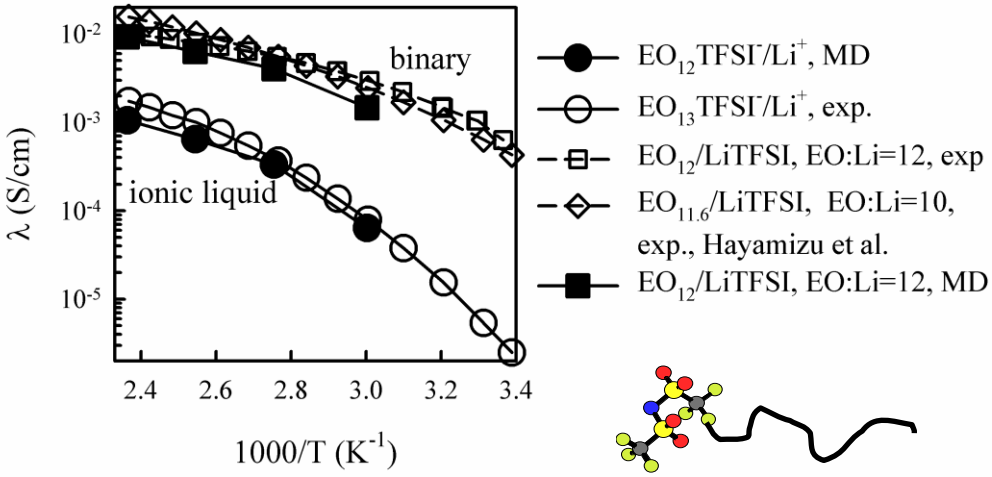
Comparison with experiment (validation)





Exp. Data from Hayamizu et al., J. Phys. Chem. B, 108, 19527 (2004)





Exp. data from D. DesMarteau / S. Creager Clemson U.

Responses to Previous Reviewers' Comments

- *"There should be far more collaboration between Utah and the other BATT PIs, particularly those at LBNL. The group should be collaborating with anyone synthesizing and characterizing new electrolytes."*
- *"PI would benefit from studying appropriate chemistry selections by talking to electrolyte chemists and then working with experimental validation of trends using model systems."*
- *"good collaboration with Kerr and Clemson"*

➢ Our simulation efforts are interfaced with experimental efforts at Clemson and LBNL resulting in joint experimental/simulation publications

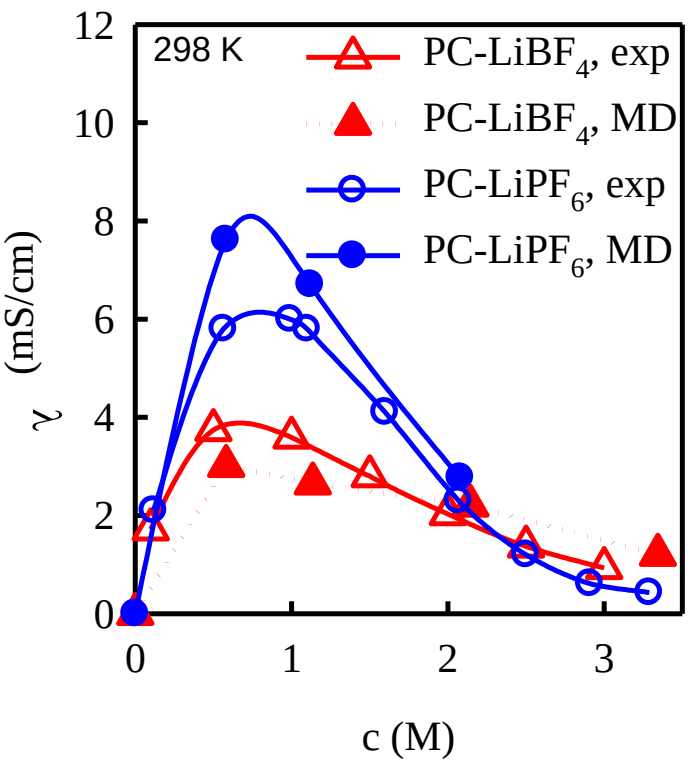
- *"With so many questions still to be answered about present and near-term electrolytes and interfacial phenomena, it is unnecessary to seek out unique electrolytes for study."*

➢ Our research is split in two directions: a) understanding the underlying phenomena in representative electrolytes; b) predicting properties of novel electrolytes.

- *"Continue the tool development. The IL and solid state electrolyte may not provide needed performance."*

➢ Developed tools and force fields are applicable to a broad range of electrolytes from liquids to ionic liquids, to SEI components, to polymers and their interaction with electrodes. We are extending tools to handle chemical reactions and electroactive interfaces

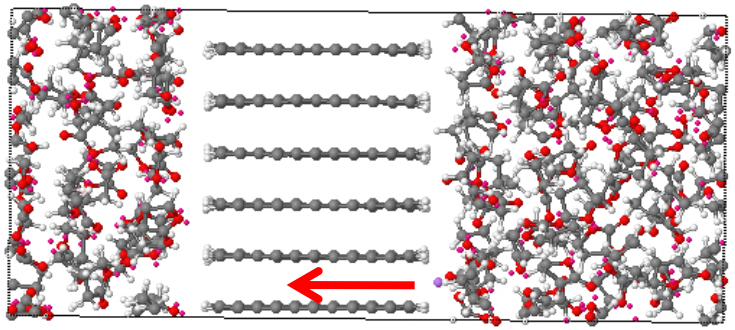
Accomplishments: Liquid Electrolytes

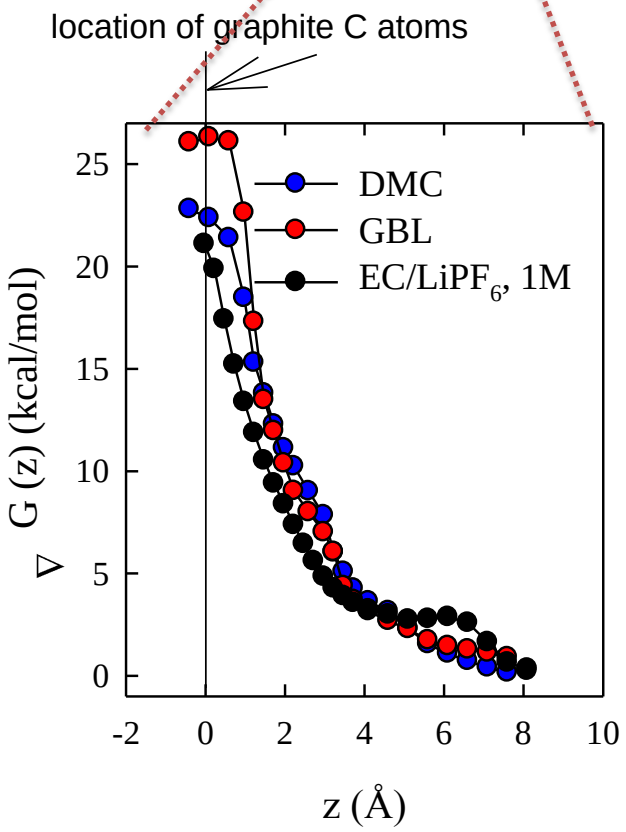


❖ A new generation of force fields has been developed for simulations of carbonate solvents (PC, EC, DMC, GBL, ethers) with $LiBF_4$, LiFSI, $LiPF_6$ salts

❖ MD simulations using developed force fields yield accurate predictions of electrolyte conductivity as a function of salt concentration and temperature, ion and solvent self-diffusion coefficients, degree of ion aggregation and electrolyte density

Accomplishments: Interfacial Properties





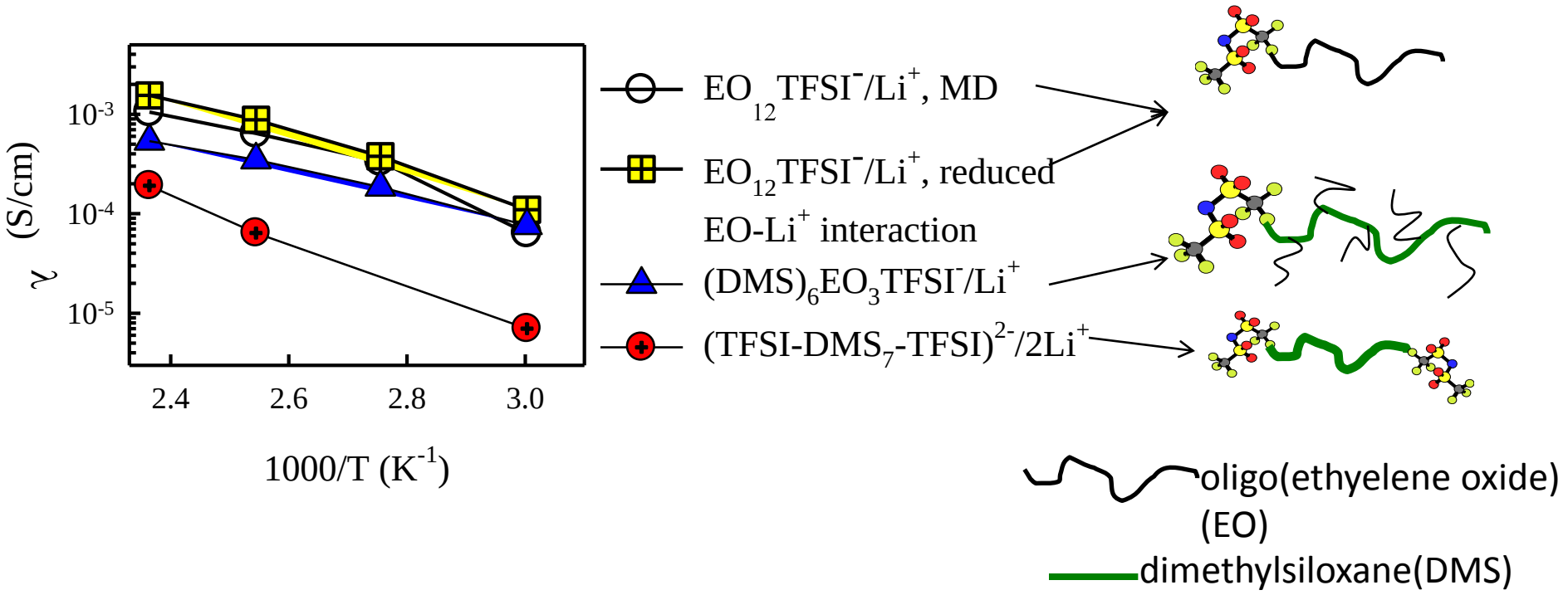
- The contribution to the charge transfer resistance (R_{ct}) from the Li^+ desolvation from electrolyte and intercalation into graphite has been determined

$$R_{ct} = \int_{outside}^{z} \frac{\exp\left(\Delta G(Z')/RT\right)}{D(Z')} dZ'$$

where $\Delta G(Z)$ is the potential of mean force of a Li^+, D(Z) is a local diffusion coefficient.

- D(Z) changes only one order of magnitude through the interface, with most contribution to R_{ct} coming from the free energy barrier.
- ΔG correlates well with the activation energy for R_{ct}=17.1 kcal/mol for EC/LiPF6, 1 M obtained by *Richard Jow Group (ARL)*
- R_{ct} for EC/$LiPF_6$ 1 M at 298 is ~ 10 Ω cm^2
- R_{ct} is dependent of the choice of electrolyte and on the presence of anion and dramatically increased with decreasing temperature

Accomplishments: Novel Ionic Liquid Structures



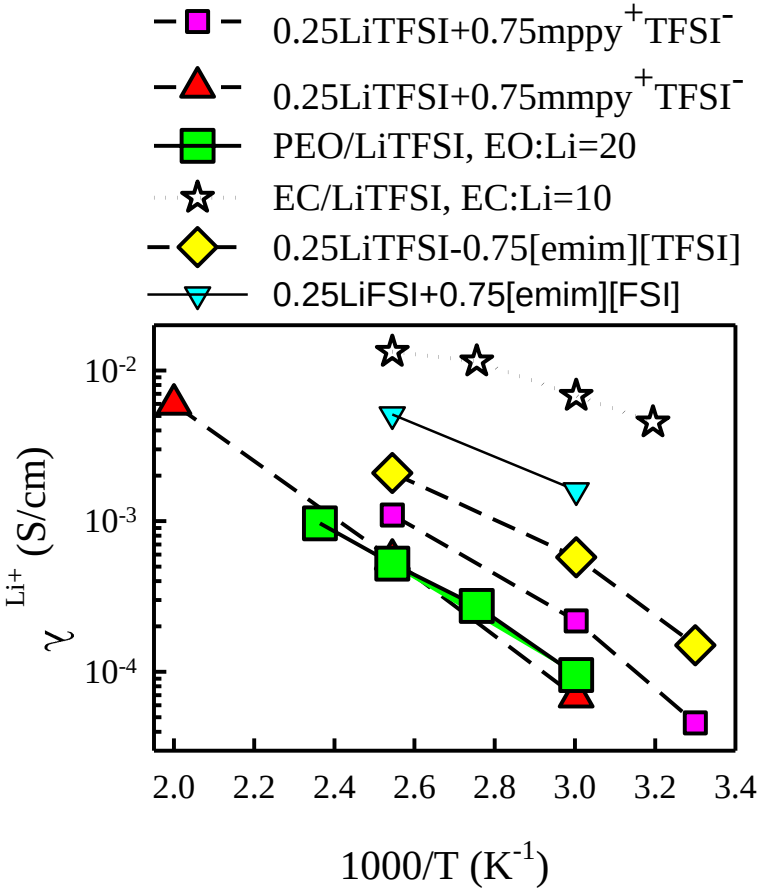
- Influence of the oligomer/Li^+ interactions on lithium transport has been investigated
- Reduction of the Li^+/oligomer interaction can slightly improve lithium transport
- Replacing oligoether with siloxane-oligoether comb-branched structure reduces activation energy but yields only marginally better performance at room temperature
- $(TFSI\text{-}DMS_7\text{-}TFSI)^{2-}/2Li^+$ molten salts do not show promising behavior

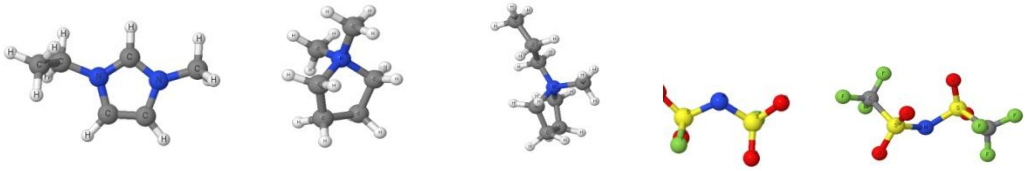
in collaboration with Clemson group (S. Creager) and LBNL (J. Kerr)

Accomplishments: Lithium Transport in Various Electrolytes

Lithium contribution to ion conductivity for polymeric (PEO-LiTFSI), IL, and liquid electrolytes (EC-LiTFSI) from our MD simulations was estimated from:

$$\lambda^{Li+} = \frac{n_{Li^+} D_{Li^+}}{n_{Li^+} D_{Li+} + n_{py^+} D_{py^+} + n_{TFSI^-} D_{TFSI^-}} \lambda$$



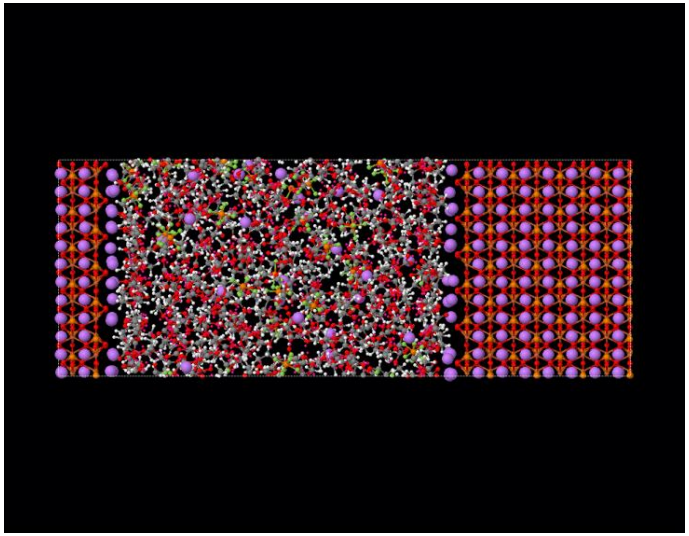


emim$^+$ mmpy$^+$ mppy$^+$ FSI$^-$ TFSI$^-$

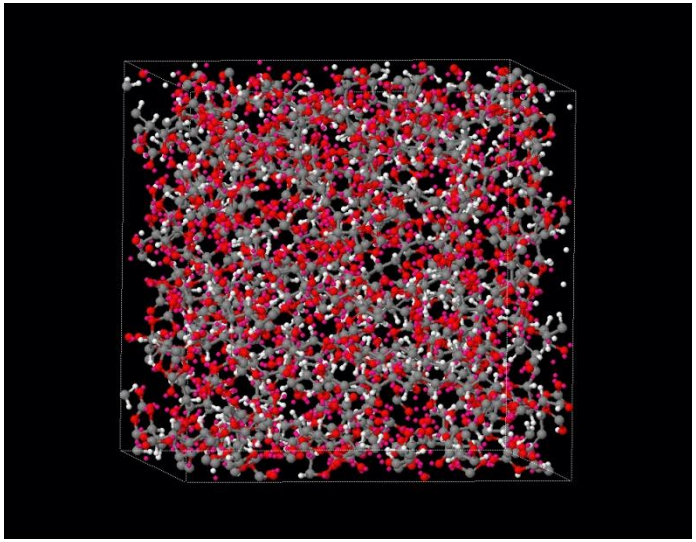
- MD simulations using developed force fields accurately predicted IL and IL + Lisalt transport properties (within 10-50% of exp.)
- Best ILs have lithium transport significantly better than polymer electrolytes but still lower than traditional liquid electrolytes
- Details of the lithium transport mechanism, ion correlations have been elucidated
- Ion transport as a function of anion size has been studied

in collaboration with J. Kerr

Accomplishments: Cathode and SEI Models

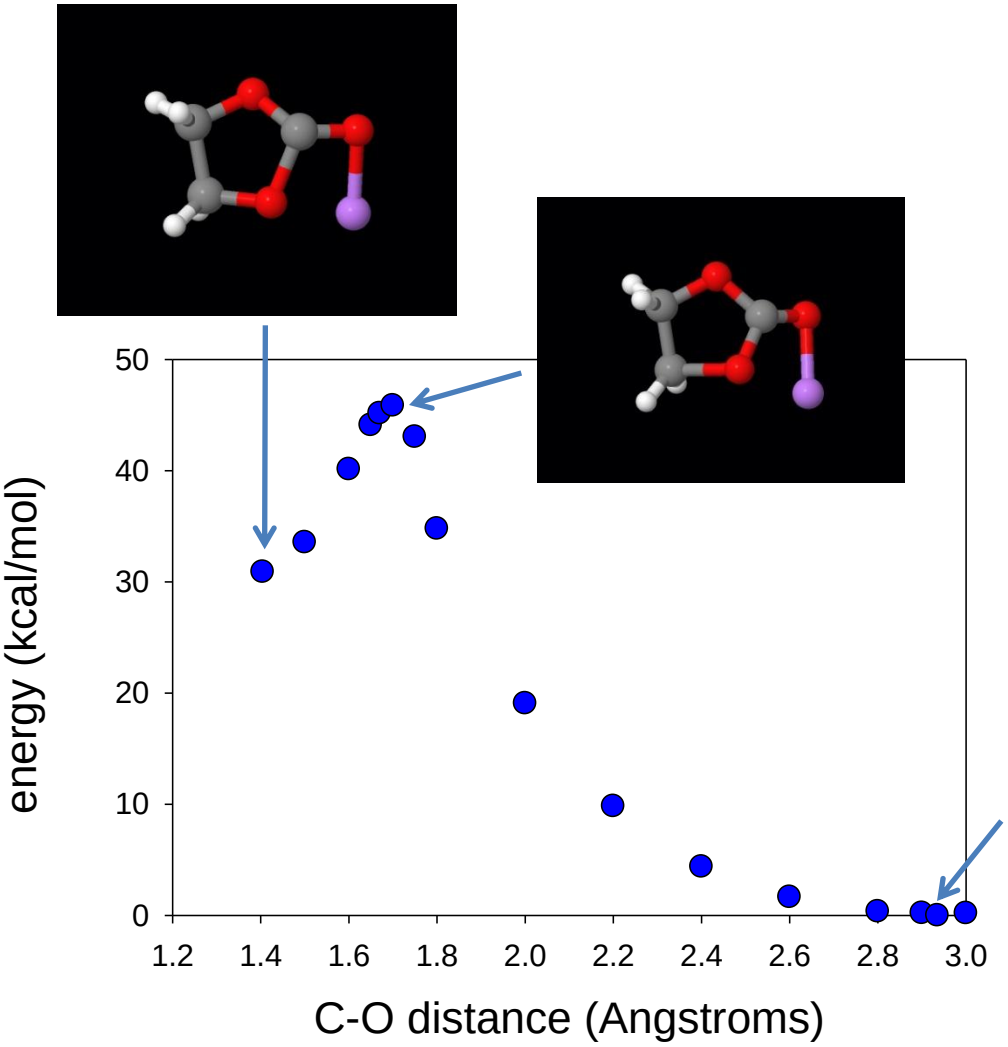


- We have established a first-generation atomistic model for $LiFePO_4$ based upon DFT calculations



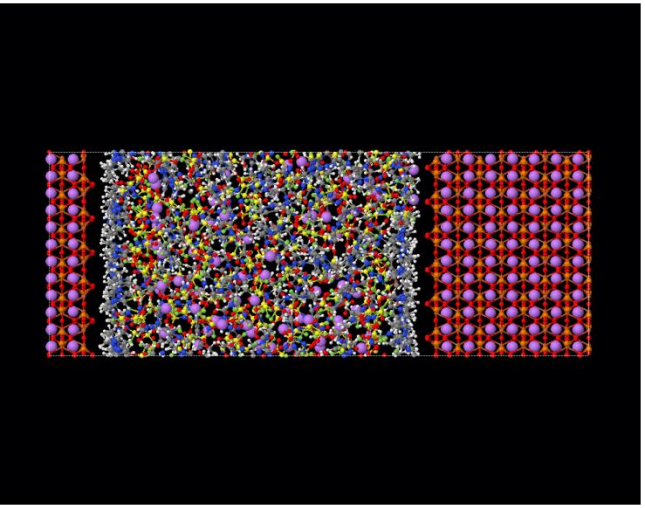
- We have established a quantum chemistry-based atomistic model for poly(vinylene carbonate)

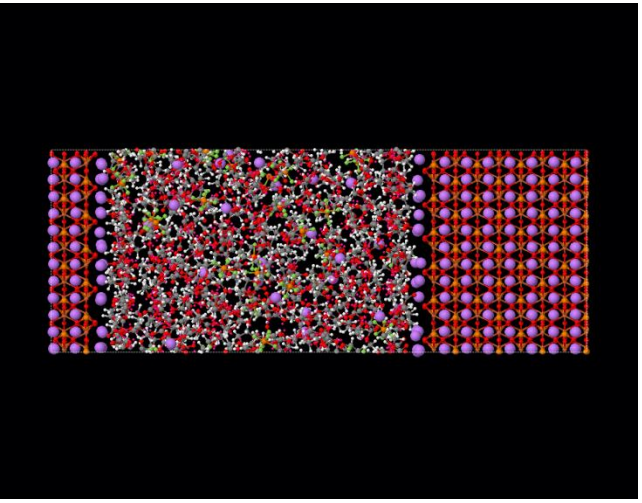
Accomplishments: Chemical Reactions



- Working with Goddard's group (CalTech), we have conducted extensive quantum chemistry calculations necessary for training of the ReaxFF for prediction of chemical reactions in MD simulations

Current/Future Work





- Interfacial structure and resistance for various electrolytes at the cathode
- Improved force fields for cathode/electrolyte interface (Ceder, MIT)
- Electroactive interfaces
- ReaxFF simulations of EC reduction
- Extension of ReaxFF to other compounds (VC)
- Modification of anode with polymers

Current/Future Work

- Investigate dependence of the R_{ct} for electrolyte/graphite interface on the composition of electrolyte and choice of anion. Compare BF_4^- and PF_6^- and FSI^- anions. Find electrolytes with low R_{ct} that are expected to show improved low temperature performance

- Predict structure and transport in selected SEI components such as pVC. Investigate interfacial resistance at the interface between a carbonate electrolyte and an SEI component (Li_2DEC) (Kerr, LBNL)

- Compare R_{ct} of the anode side with that on the cathode side for carbonate electrolytes

Publications

1. Borodin, O.; Smith, G. D.; Geiculescu, O.; Creager, S. E.; Hallac, B.; DesMarteau, D. "Li^+ Transport in Lithium Sulfonylimide-Oligo(ethylene Oxide) Ionic Liquids and Oligo(ethylene oxide) Doped with LiTFSI" *J. Phys. Chem. B* **2006**, *110,* 24266 - 24274.
2. Borodin, O.; Smith, G. D. "Molecular Dynamics Simulations of Lithium Alkyl Carbonates" *J. Phys. Chem. B* **2006**, *110,* 22773 – 22779.
3. Borodin, O.; Smith, G. D. "Structure and Dynamics of *N*-Methyl-*N*-Propylpyrrolidinium$^+$TFSI$^-$ Ionic Liquid From Molecular Dynamics Simulations" *J. Phys. Chem. B*, **2006**, *110,* 11481-11490.
4. Borodin, O.; Smith, G. D.; Henderson, W. "The Li^+ Cation Environment and Transport Mechanisms in Propylpyrrolidinium$^+$/TFSI$^-$ Ionic Liquid" *J. Phys. Chem. B* **2006**, *110,* 16879 -16886.
5. Borodin, O.; Smith, G. D. "LiTFSI Structure and Transport in Ethylene Carbonate from Molecular Dynamics Simulations" *J. Phys. Chem. B*, **2006**, *110,* 4971 – 4977.
6. Borodin, O.; Smith, G. D. "Development of The Many-Body Polarizable Force Fields For Li-Battery Applications: 1. Ether, Alkane And Carbonate-Based Solvents" *J. Phys. Chem. B.,* **2006**, *110*, 6279-6292.
7. Borodin, O.; Smith, G. D. "Development of The Many-Body Polarizable Force Fields For Li-Battery Applications: 2. LiTFSI-Doped Oligoether, Polyether, And Carbonate-Based Electrolytes" *J. Phys. Chem. B.,* **2006**, *110*, 6293-6299.

Publications (cont'd)

8. Borodin, O.; Smith, G. D. "Li^+ Transport Mechanism in Oligo(Ethylene Oxide)s Compared To Carbonates" *J. Solution Chem.* **2007**, 36, 803.
9. Borodin, O.; Smith, G. D. "Mechanism Of Ion Transport In Amorphous Poly(Ethylene Oxide)/LiTFSI From Molecular Dynamics Simulations" *Macromolecules,* **2006,** *39*, 1620-1629.
10. Borodin, O.; Smith, G. D. "Molecular Dynamics Simulations of Comb-Branched Poly(epoxide ether)-Based Polymer Electrolytes" *Macromolecules* **2007***, 40*, 1252-1258.
11. Hallac, B. B. ; Rajagopal, R. V.; Geiculescu, O, Creager, S. E; DesMarteau, D. D.; Borodin, O.; Smith, G. D. "The effect of low molecular weight polyethers as plasticizers on the transport properties and rheology of fluoro-sulfonimide ionic melts" *J. Phys. Chem. B (to be submitted)*

Presentations

- Borodin, O.; Smith, G. D. MD Simulations Study of Liquid Electrolytes and SEI Components ECS 2006 Joint International Meeting, Cancun, Mexico, Oct. 29 – Nov 3. 2006
- Borodin, O.; Smith, G. D. Ion Transport in Single Ion Conductors ECS 2006 Joint International Meeting, Cancun, Mexico, Oct. 29 – Nov 3. 2006
- Borodin, O.; Smith, G. D. Understanding Lithium Cation Environment and Transport in Imidazolium and Pyrrolidinum-Based Ionic Liquids ECS 2006 Joint International Meeting, Cancun, Mexico, Oct. 29 – Nov 3. 2006
- Borodin, O.; Smith, G. D.; Molecular Dynamics Simulations of Lithium Transport in Bulk Electrolytes and at Interfaces, 212th ECS October 7 - October 12, 2007, Washington, DC
- Borodin, O.; Smith, G. D. "Structure and Transport in Pyrrolidinium- and Imidazolium-TFSI Ionic Liquids Doped with LiTFSI" The 2006 Annual Meeting of AIChE, San Francisco, CA, November, 12-17, 2006.
- Borodin, O.; Smith, G. D. "Lithium Transport in Binary and Single Ion Conductor Liquid, Gel and Polymer Electrolytes" The 2006 Annual Meeting of AIChE, San Francisco, CA, November, 12-17, 2006.

Presentations (cont'd)

- Borodin, O.; Smith, G. D.; Rees, R. "Molecular Dynamics Simulations of Ionic Liquids and Lithium Transport in Them" The 2007 Annual AIChE Meeting Salt Lake City, UT (11/03-11/09)
- Borodin, O.; Smith G. D.; "Molecular Dynamics Simulations Of Lithium Transport In Bulk Electrolytes And At The Electrolyte/Electrode Interface" (11/03-11/09)
- Borodin, O. "Molecular Dynamics Simulations of Electrolytes and Electrolyte-Electrode Interfaces" ARL, Adelphi, MD, May 2007
- Borodin, O "Multiscale Modeling of Energetic Materials and Materials for Energy Applications" ARL, Aberdeen, MD, May 2007