High Voltage Electrolytes for Li-ion Batteries

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Overview

Timeline

- Start: June 2008
- End: May 2011
- 90% complete

Budget

- Total project funding
  - DOE $600K
- Funding received in FY08/09
  - $400K
- Funding for FY10
  - $200K

Barriers

- SOA electrolytes based on Carbonate Solvents decompose below 4.5 V;
- Sulfone-based solvents showed anodic stability up to 5.8 V but:
  - SEI chemistry from reduction of sulfones does not provide protection of graphitic anodes
  - Most sulfones are viscous liquids with m.p. near RT.
- Lack of a reliable 5 V cathode as characterization platform.
- Lack of additives for protecting high voltage cathodes.

Partners

- Argonne National Laboratory
- Saft Batteries
- U of Texas, Austin
- U of Maryland
- U of Utah

Milestones

- Sep 2009:
  - Synthesized sulfone based solvents with and without unsaturated bonds and evaluated their electrochemical properties
  - Synthesized various additives including fluorinated phosphate esters for both sulfone- and carbonate-based electrolytes
- Sep 2010:
  - Explored additives that passivates cathode surfaces at high voltages
  - Diagnostic studies: surface characterization and SEI chemistry
- May 2011:
  - Evaluate electrolytes with additives in both half cells and full cells
  - Understand reactive pathways of electrolyte components through computational effort, surface characterization and SEI chemistry studies

Objectives

- **Develop high voltage electrolytes that enable the operation of 5 V Li Ion Chemistry**
  - **Energy density**
    - **Increased energy density for HEV/PHEV**
  - **Power density**
    - **Faster kinetics for Li^+ charge transfer at the electrode/electrolyte interface**
    - **High charge/discharge efficiency**
  - **Life**
    - **Improved capacity retention**

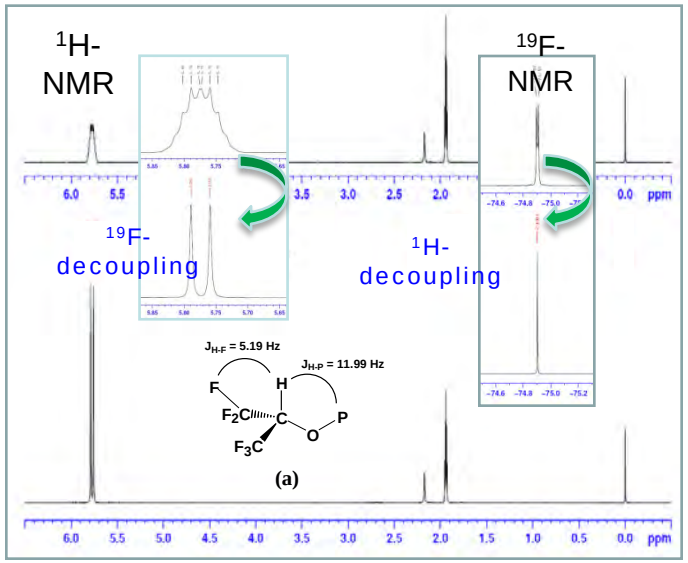
Approach

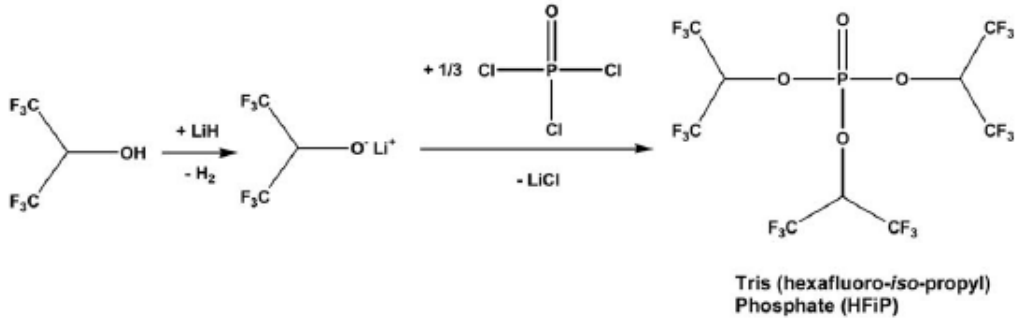
- **Sulfone based solvents approach**
  - **Synthesize and characterization of unsymmetric sulfones for lower viscosity**
  - **Synthesize and characterization of unsaturated sulfones for higher reactivity with potential for forming protective layer on cathodes**
- **Carbonate based solvents approach**
  - **Search additives that would decompose and form protective interface on cathode**
  - **Formulate electrolytes using fluorinated phosphate ester as additives for the state-of-the-art electrolytes**
- **Computational effort**
  - **Understand oxidative stability of solvents/electrolytes**
  - **Understand reactive pathways of additives and electrolytes**
  - **Develop ability to predict and design electrolyte components**

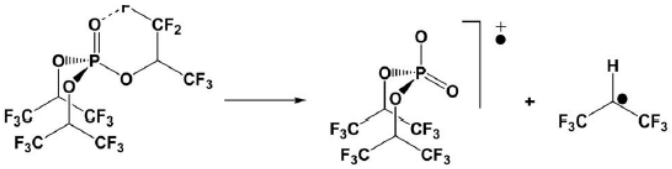
Technical Accomplishments

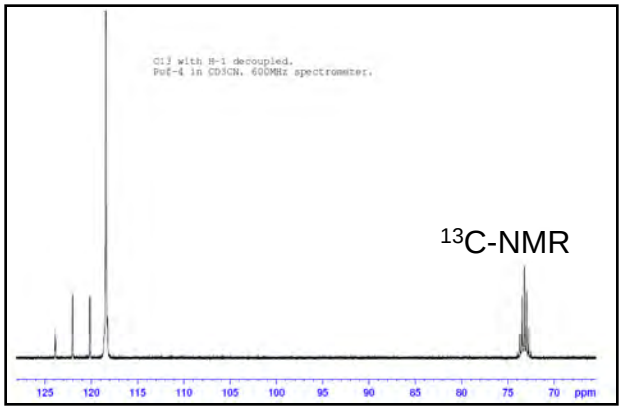
- **Discovered, synthesized and structurally characterized an additive, tris (hexafluoro-iso-propyl) phosphate (HFiP), for carbonate based electrolytes.**
- **Demonstrated that electrolytes with 1% of HFiP would enable improved performance for $LiNi_{0.5}Mn_{1.5}O_4$ and $LiCoPO_4$ high voltage cathodes vs. Li.**
- **Demonstrated that the SOA electrolyte with 1% of HFiP would enable the cycling of graphite anode vs. Li with no capacity loss.**
- **Investigated oxidative stability of the sulfone (and sulfonate)-based solvents, solvent/anion complexes and additives using quantum chemistry (QC) calculations**
- **Investigated structure and transport of $LiPF_6$ in sulfone and linear carbonate mixtures using molecular dynamics (MD).**

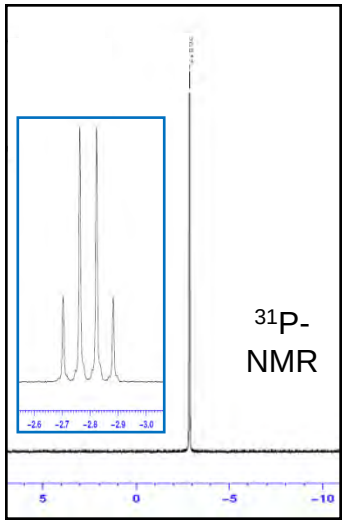
HFiP Synthesis and Structural Characterization

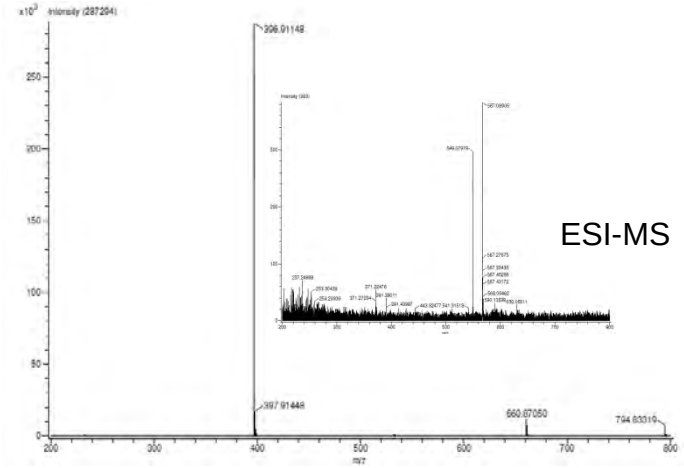












Vehicle Technologies Program

TECHNOLOGY DRIVEN. WARFIGHTER FOCUSED.

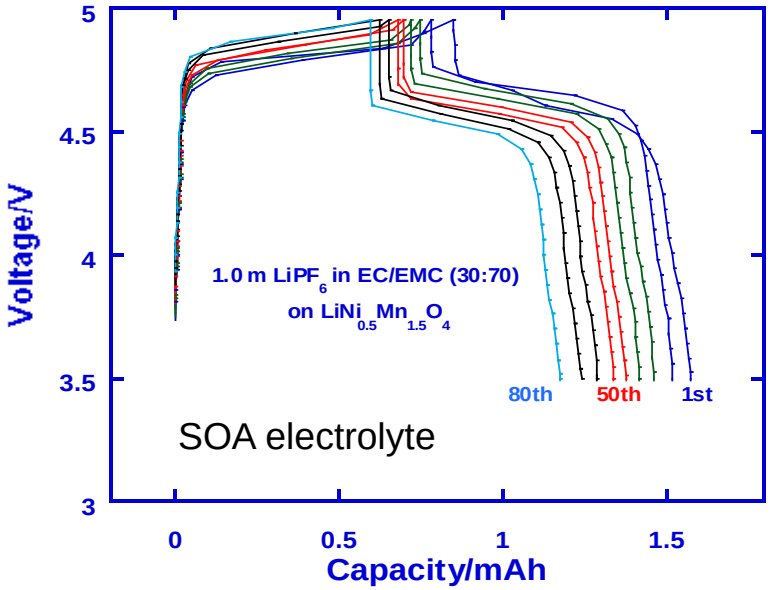
Cathode/Electrolyte Interphase

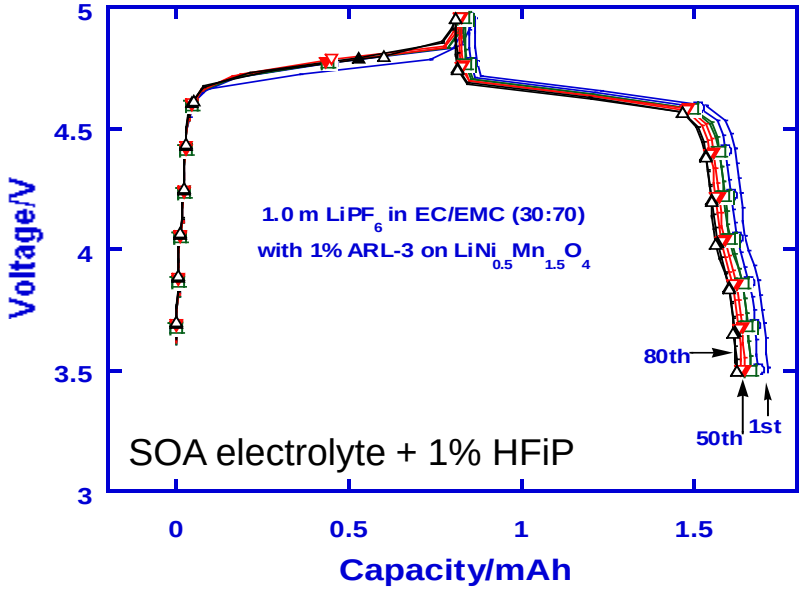
Interphase from SOA electrolyte fail beyond 4.5 V

- **SOA: 1.0 m $LiPF_6$ in EC:EMC(30:70)**
- **Cell impedance increasing with cycling**
- **Rapidly fading capacity**

1% HFiP presence dictates a new interphase

- **Flexible with different cathode chemistry**
  - **$LiCoPO_4$ (4.8 V) (shown later)**
  - **$LiNi_{0.5}Mn_{1.5}O_4$ (4.6 V) (shown below)**
- **Cell impedance stabilized over long cycling**

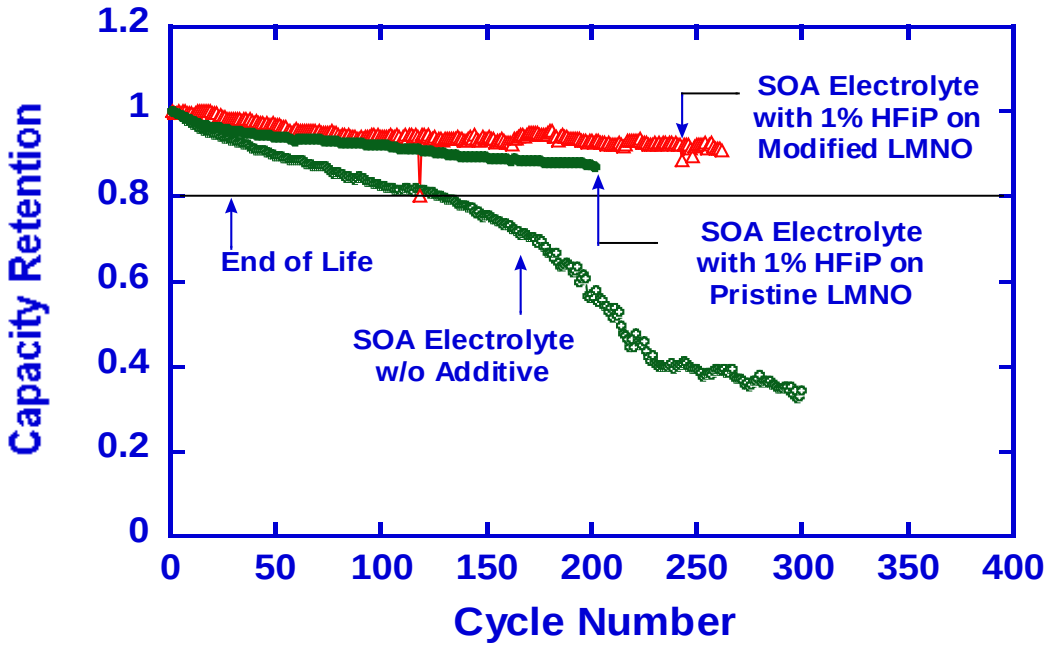




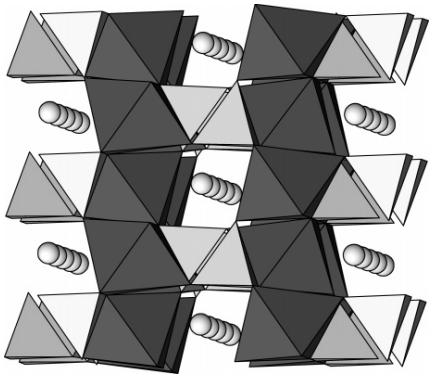
Cycling of LMNO Cathode Half Cells

Capacity retention > 90% at 300th cycle in $LiPF_6$ SOA electrolyte with 1% HFiP additive

Comparison of modified $LiNi_{0.5}Mn_{1.5}O_4$ to pristine $LiNi_{0.5}Mn_{1.5}O_4$ and SOA electrolyte.

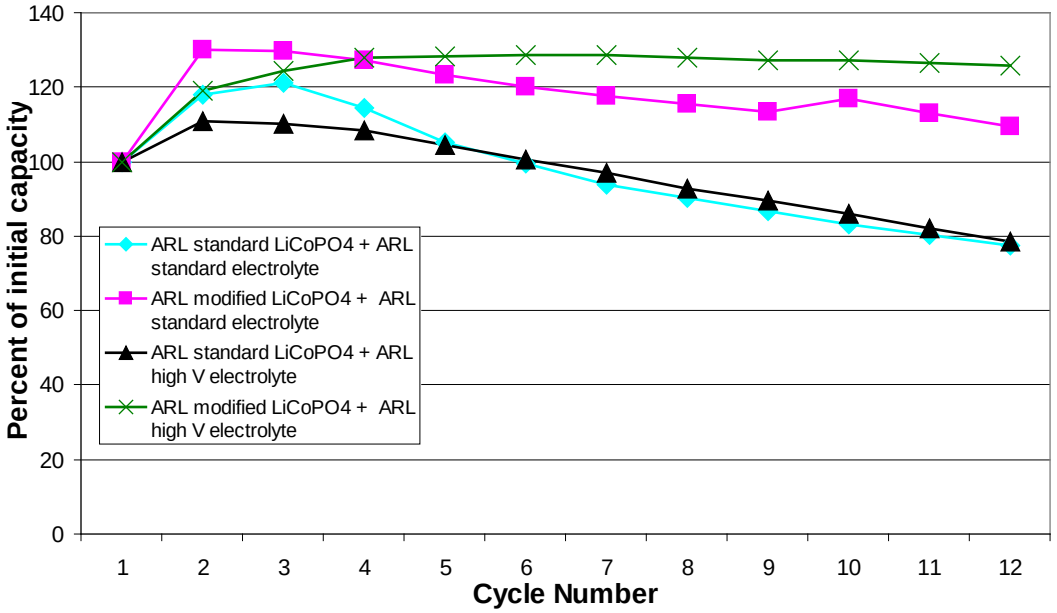


Stabilized $LiCoPO_4$ Cathode Half Cells



Structure of $LiCoPO_4$

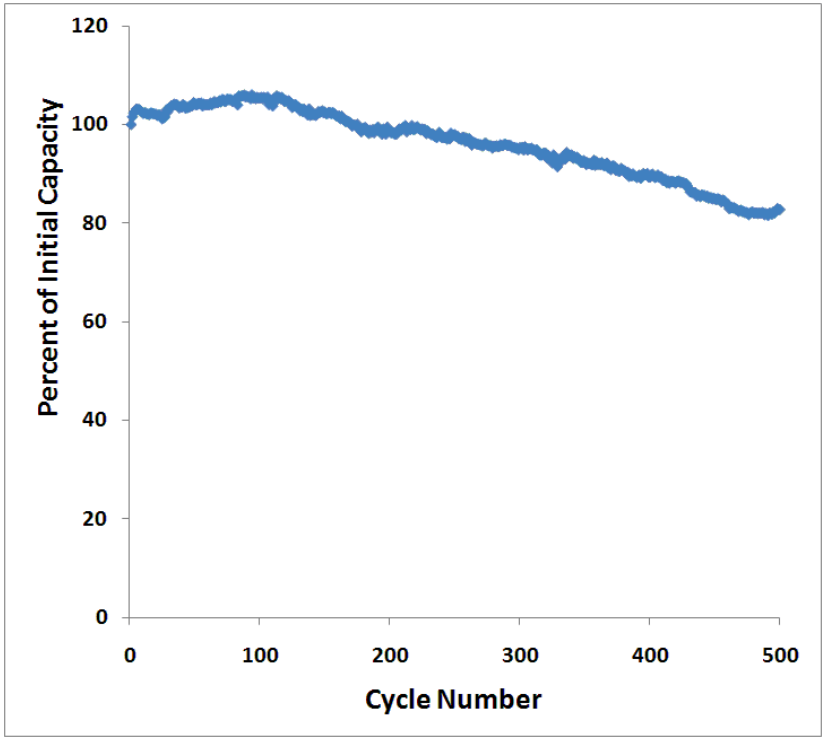
Electrochemical capacities of $LiCoPO_4$ stabilized by substitution are shown in the figure on the right.



Comparison to standard $LiCoPO_4$ and SOA electrolyte with and without additive.

Cycling of Stabilized $LiCoPO_4$ Cathode Half Cells

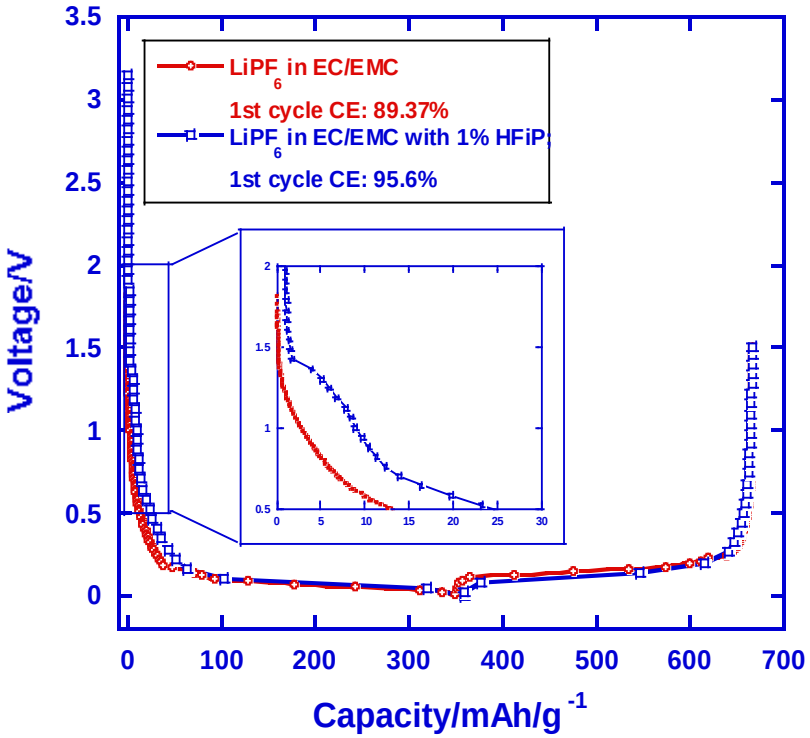
- **Cycling of stabilized LiCoPO4 with substitution in 1 m $LiPF_6$ in EC:EMC (30:70) with 1% HFiP**
- **Demonstrates high cycle life (capacity retention of >80% at 500 cycles shown here) with about 97% coulombic efficiency.**



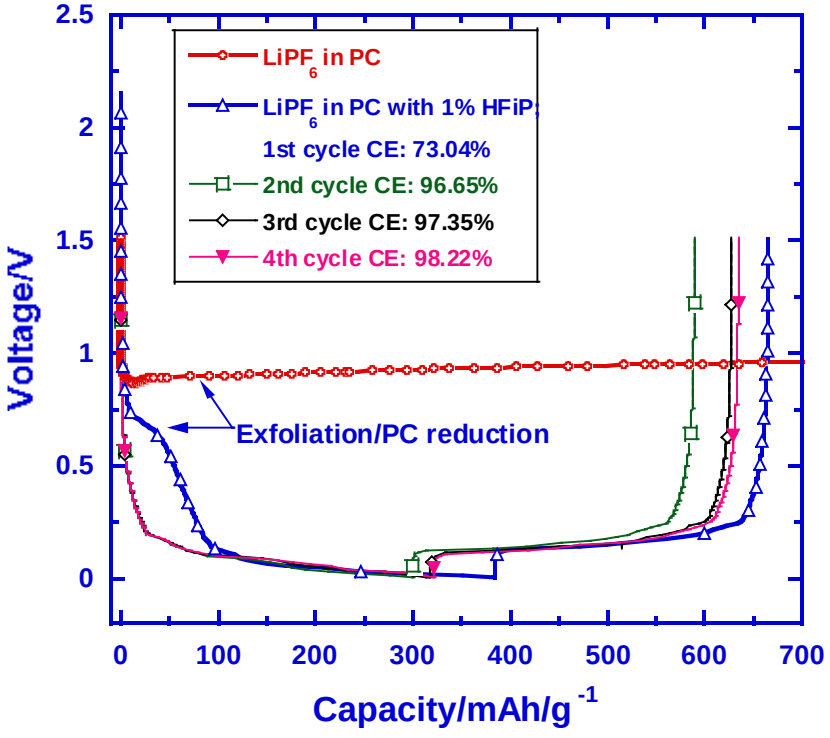
Anode/Electrolyte Interphase

Favorable interphase formed on graphitic anode

Graphite in $LiPF_6$ in EC:EMC with and without HFiP



Graphite in $LiPF_6$ in PC with and without HFiP



Computational Part: Outline

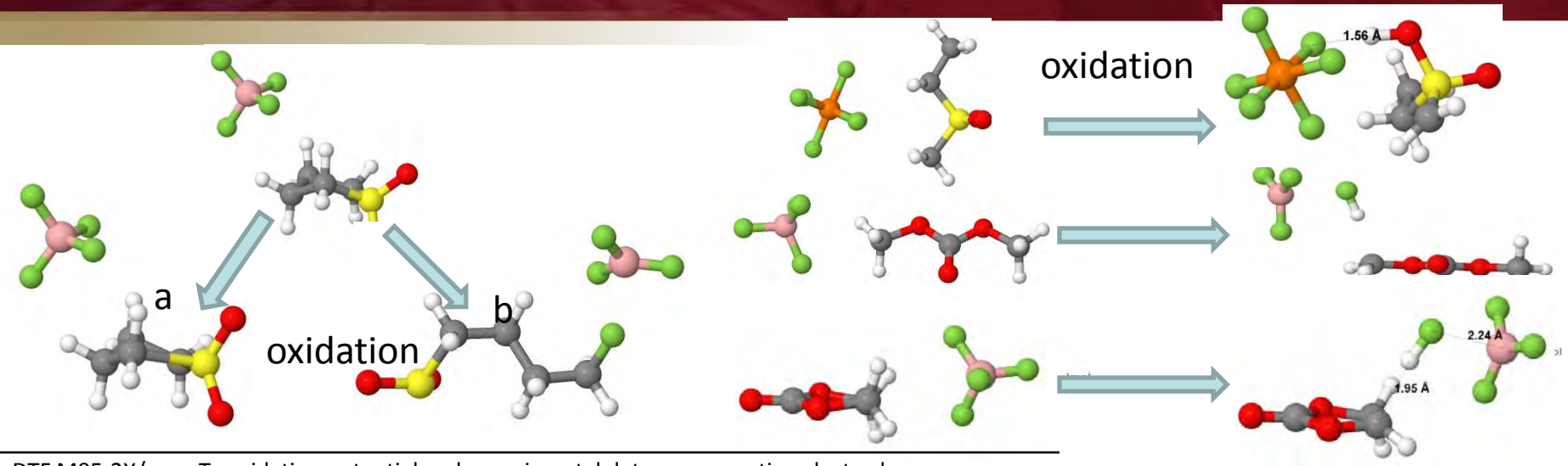
Quantum Chemistry: Explore oxidative stability of the sulfone (and sulfonate)-based solvents, solvent/anion complexes and additives using quantum chemistry (QC) calculations

- Compare with oxidative stability (E_{ox}) obtained from QC with experiments;
- Understand the influence of anion chemistry on the electrolyte oxidative stability;
- Understand the influence solvent dielectric constant on the electrolyte oxidative stability.
- Investigate oxidative decomposition of the additives with and without presence of anions.

Molecular Dynamics: Investigate structure and transport of the mixed sulfone : (linear carbonate)/$LiPF_6$ electrolytes. Compare with the previous results obtained for the EC:DMC /$LiPF_6$ electrolytes focusing on the following properties:

- Li^+ cation coordination;
- Fraction of free ions;
- Mechanism of the lithium transport (moving together with the solvent vs. solvent exchange)
- Set a stage for investigation of electrolyte interfacial properties

Influence of Anion on Solvent Oxidation



DTF M05-2X/cc-pvTz oxidation potential and experimental data on non-active electrodes

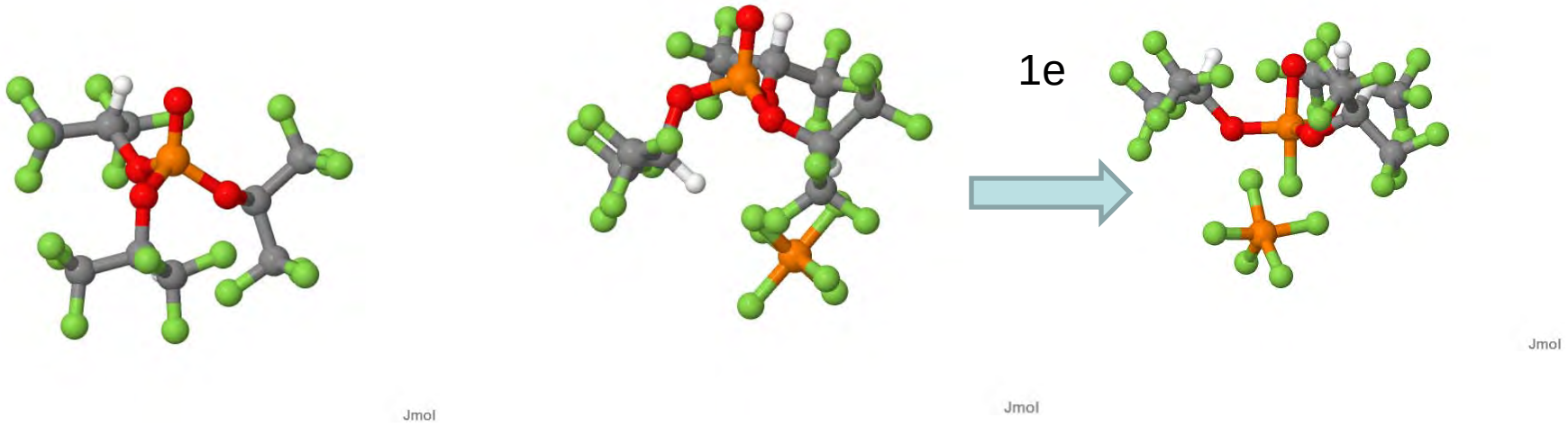
	ε=1	ε=4.2	ε=20.5	ε=78.4	**no anion ε=20.5**	published exp.
DMC/BF_4-	4.14	5.79	6.21	6.29	7.6	6.7 GC 0.65 M Bu_4NBF_4
EC/BF_4^-	4.55	5.95	6.28	6.34	7.6	6.2 GC 0.65 M Et_4NBF_4
PC/BF_4^-	4.57		6.25		7.3	6.6 GC 0.65 M Et_4NBF_4
(a)TMS/BF_4^-	5.23	6.33	6.49	6.52	6.7	5.8 Pt, 1 M $LiBF_4$
(b)TMS/BF_4^-	3.82		5.68			
DMC/PF_6^-	4.56	6.12	6.51	6.58	7.6	6.3 GC 1 M $LiPF_6$
EC/PF_6^-	4.94	6.27	6.57	6.63	7.6	
(a)TMS/PF_6-	5.44	6.36	6.54	6.57	6.7	5.8 Pt, 1 M $LiPF_6$
(b)TMS/PF_6-	4.25		5.59			
(a)EMS/PF_6-	5.46	6.47	6.66	6.69	6.9	
(b)EMS/PF_6-			5.93			
PMS/PF_6^-	4.29	5.55	5.84	5.89	7.0	6.2 PMS in EC:DMC/$LiPF_6$

- *Presence of BF_4^- and PF_6^- anions significantly reduces oxidation potential of electrolytes and improves agreement with experiment.*
- *Fluorine transfer (from BF_4^- or PF_6^-) to solvent molecules or proton transfer and HF formation is responsible for the reduction of the oxidation potential.*

(in collaboration with U. of Utah)

Electrochem. Soc., **144**, 2684 (1997), *Russ J Electrochem.*, **44**, 575 (2008), *J. Electrochem. Soc.*, **154**, A810 (2007).

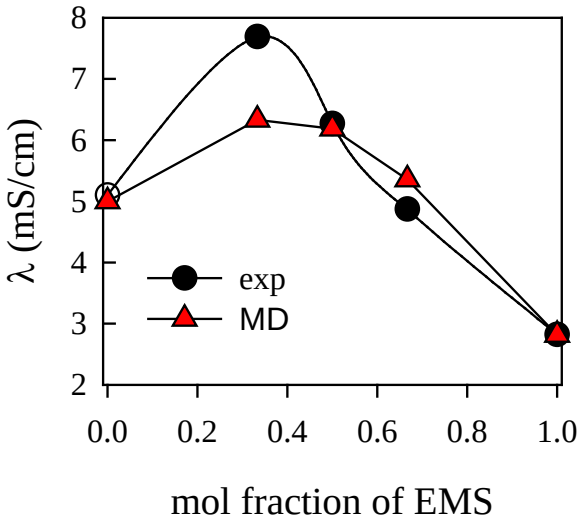
Tris(hexafluoro-*iso*-propyl)phosphate (HFiP) Additive



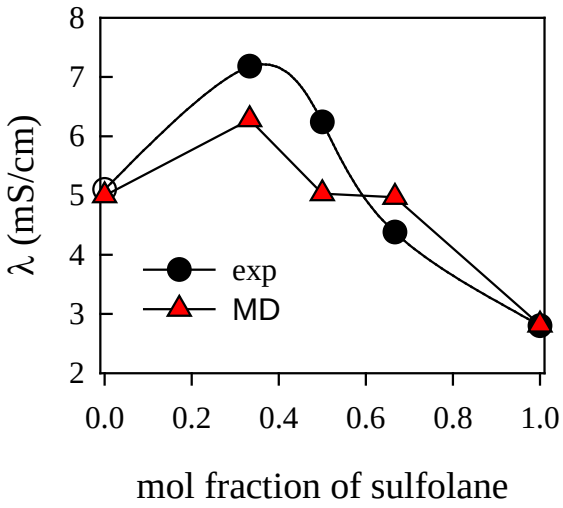
- In gas phase C-O bond of tris(hexafluoro-iso-propyl)phosphate (HFiP) has the lowest barrier to break.
- During oxidation a fluorine from PF_6^- in transferred to HFiP resulting in a PF_5 formation.
- In the oxidized HFiP/PF_6 complex the P-O bond was found to be the easiest to break, unlike results for the HFiP in gas-phase where C-O bond has the lowest barrier for breaking.

EMS-DMC/$LiPF_6$ and Sulfolane-DMC/$LiPF_6$ MD Simulations

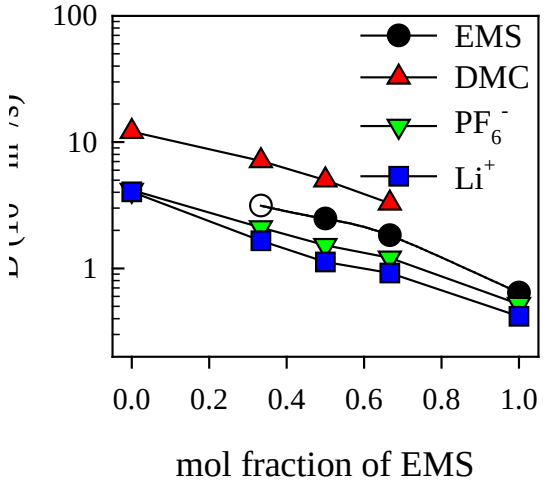
Ethylmethylsulfone (EMS):DMC/$LiPF_6$ solvent:Li=10



Sulfolane:DMC/$LiPF_6$, solvent:Li=10



Ethylmethylsulfone (EMS):DMC/LiPF6 solvent:Li=10



- *MD simulations employing developed force field predicted EMS-DMC/$LiPF_6$ and Sulfolane-DMC/$LiPF_6$ conductivity in good agreement with experiments.*
- *In agreement with QC studies Li^+ cation showed a higher affinity to EMS and Sulfolane than DMC. For example, at EMS:DMC=1:1 a Li^+ cation was coordinated by 0.54 DMC, 3.1 EMS and 0.57 PF_6^- on average.*
- *Solvent diffusion coefficient and ion aggregation monotonically increased with increasing DMC fraction.*
- *The Li^+-DMC residence time was 3 times shorter than the Li^+-EMS and Li^+-PF_6^- residence times indicating a much faster exchange of DMC than EMS or PF_6^-.*

Future Work

- **Demonstrate performance of the developed high voltage electrolyte in full cells**
  - **$LiNi_{0.5}Mn_{1.5}O_4/Li_4Ti_5O_{12}$**
  - **$LiNi_{0.5}Mn_{1.5}O_4$/graphite**
- **Optimization of carbonate-based electrolytes**
  - **Focus on performances at elevated temperatures**
  - **Study impedance in combination of interphasial chemistries**
- **Characterization and diagnostic studies**
  - **XPS, XRD, EIS, SEM/TEM**
- **Design and synthesis of new additives**
  - **Further improvements are expected with new additive structures**
- **Develop better understanding of electrolyte reactivity for the materials design ability through computational and SEI analytical efforts**

Summary

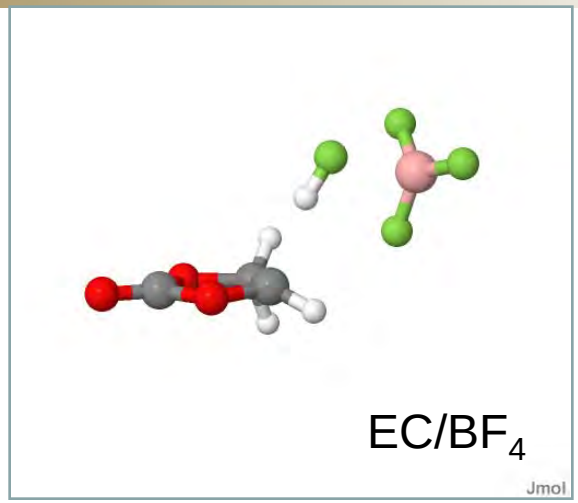
- Significant improvement has been made in the additive approach, where carbonate-based electrolytes containing 1% HFiP have been enabled to support the 5 V Li ion chemistry with spinel and $LiCoPO_4$ cathodes.
  - Further improvements are being made to optimize the performance;
  - Surface analysis on-going will reveal fundamental understanding on mechanism and interphasial chemistry.
- Modification of high voltage cathodes through substitution chemistry has resulted in more stable structures for improved cycling performance as shown in $LiNi_{0.5}Mn_{1.5}O_4$ and $LiCoPO_4$.
- Based on QC calculations, presence of BF_4^- and PF_6^- anions significantly lowers oxidation potential of electrolytes and improves agreement with experiment.
  - Fluorine transfer (from BF_4^- or PF_6^-) to solvent molecules or proton transfer and HF formation is responsible for the reduction of the oxidation potential.
  - In the oxidized HFiP/PF_6 complex, the P-O bond was found to be the easiest to break, unlike HFiP in gas-phase where C-O bond has the lowest barrier for breaking.

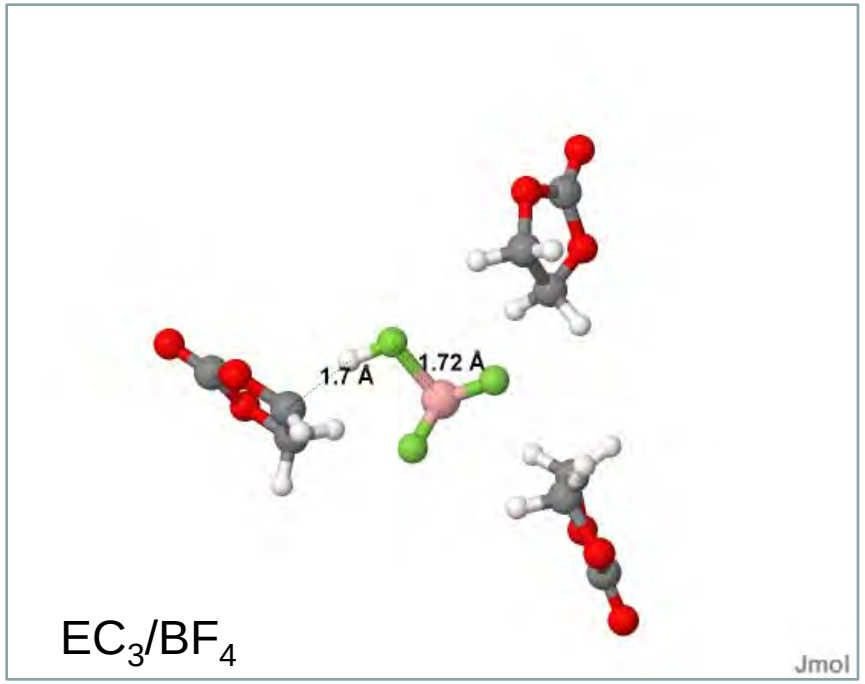
Publications

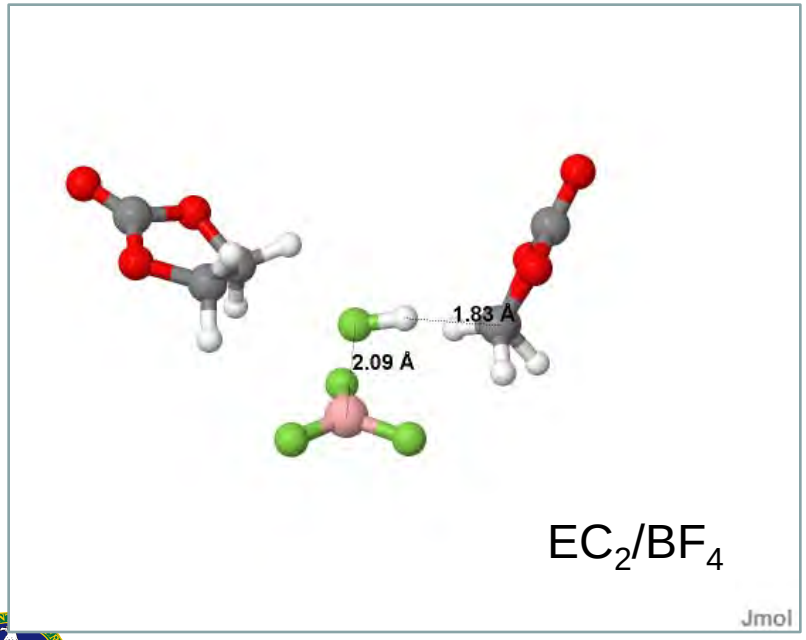
- A. v. Cresce, K. Xu, *J. Electrochem. Soc*. 2011, 158(3) A337-A342.
- A. v. Cresce and K. Xu, “Electrolytes in Support of 5 V Li Ion Chemistry”, *J. Electrochem. Soc*. , 2011, 158, A337~342
- K. Xu, A. v. Cresce, and U. Lee, “Differentiating contributions to “ion transfer” barrier at electrolyte/graphite interphase from Li^+- desolvation and interphasial resistance”, *Langmuir*, 2010, 26, 11538~11543
- A. v. Cresce, K. Xu, “High Voltage Electrolytes for Li Ion Batteries”, *Proceedings 44th Power Sources Conference*, Las Vegas, NV (June 14~17, 2010)
- J. L. Allen, J. Wolfenstine, T. R. Jow, "New Cathode Materials for Lithium Ion Batteries", *Proceedings 44th Power Sources Conference,* Las Vegas, NV (June 14-17, 2010)
- T. R. Jow, J. L. Allen, M. Marx, K. Nechev, B. Deveney, S. Rickman, “Electrolytes, SEI and Charge Discharge Kinetics of Li-ion Batteries”, *ECS Transactions*, 2010, 25 (36), 3.
- T. R. Jow, M. Marx, J. L. Allen, “Li^+ Charge Transfer Kinetics at 1. NCA/Electrolyte and Graphite/Electrolyte Interfaces, and 2. NCA/Electrolyte and LFP/Electrolyte Interfaces in Li-ion Cells,” *ECS Transactions*, accepted, 2011.
- O. Borodin, T. R. Jow, “Quantum Chemistry Studies of the Oxidative Stability of Carbonate, Sulfone and Sulfonate-Based Electrolytes Doped with BF_4^-, PF_6^- Anions,” *ECS Transactions*, accepted, 2011.

Technical Back-up Slides

Explicit Anion Solvation Shell: from 1 to 3 EC around BF_4^-

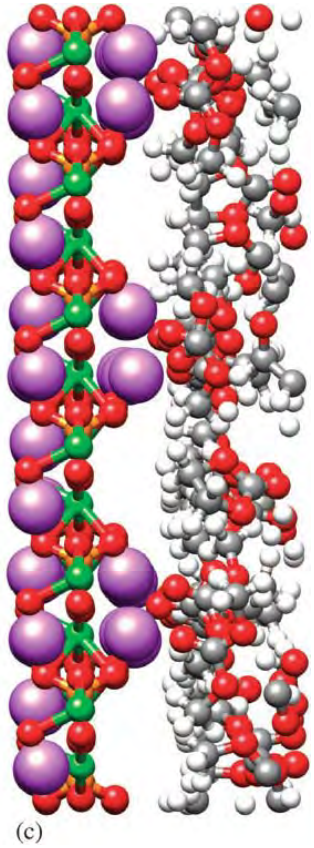






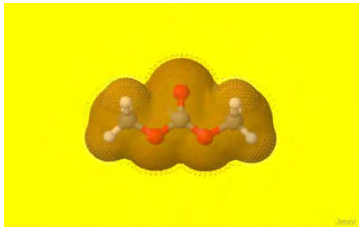
PCM (ε=20), M052-x/6-31G* opt for oxidized EC_2/BF_4 and EC_3/BF_4 ; M052x/cc-pvTz opt for EC/BF_4

Influence of the medium dielectric constant on DMC and DMC/BF_4^- E_{ox}



EC:DMC(3:7)/$LiPF_6$ EDL on metal oxide

Strong cathode-electrolyte interaction suggests a low dielectric constant at the surface



Low local dielectric constant and presence of anion leads to lower oxidation potential

Lower electrolyte stability on oxides compared to glassy carbon

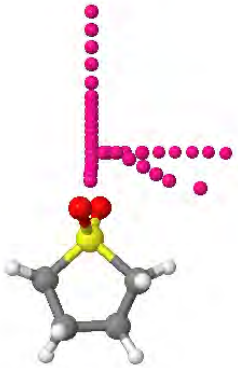
dielectric constant	E_{ox} vs. Li^+/Li (V)	
	DMC	DMC/BF_4^-
ε=1	9.9	4.1
ε=4.2	8.3	5.8
ε=20.5	7.9	6.2
ε=78.4	7.8	6.3

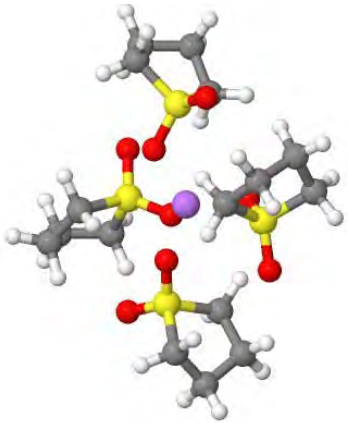
Calculated at M05-2X/cc-pvTz level

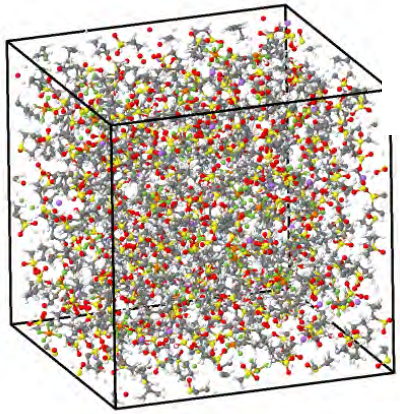
- *For pure DMC (no anion) E_{ox} decreases as the medium dielectric constant increases .*
- *Presence of anion changes the trend of the oxidation potential vs. solvent dielectric constant that might explain lower electrolyte oxidative stability on strongly interacting oxides compared to GC.*

Smith, G. D.; Borodin, O.; Russo, S. P.; Rees, R. J.; Hollenkamp, A. F. *Phys. Chem. Chem. Phys.* ***2009****, 11, 9884-9897.*

Modeling of the Sulfone:Carbonate/$LiPF_6$ Electrolytes







Step 1: Develop many-body polarizable force field for sulfolane/Li^+ , EMS/Li^+ interactions starting from APPLE&P force field.

$$U^{NB}(r) = \sum_{i>j}\left(A_{\alpha\beta}\exp(-B_{\alpha\beta}r_{ij}) - C_{\alpha\beta}r_{ij}^{-6}\right) + \sum_{i>j}\left(\frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}\right) - 0.5\sum_i \vec{\mu}_i \vec{E}_i^{\,0}$$

Step 2: Validate ability of the developed force field to predict binding energy of Li^+/Sulfolane and Li^+/EMS, and Li^+/(Sulfolane,DMC) clusters obtained from QC calculations.

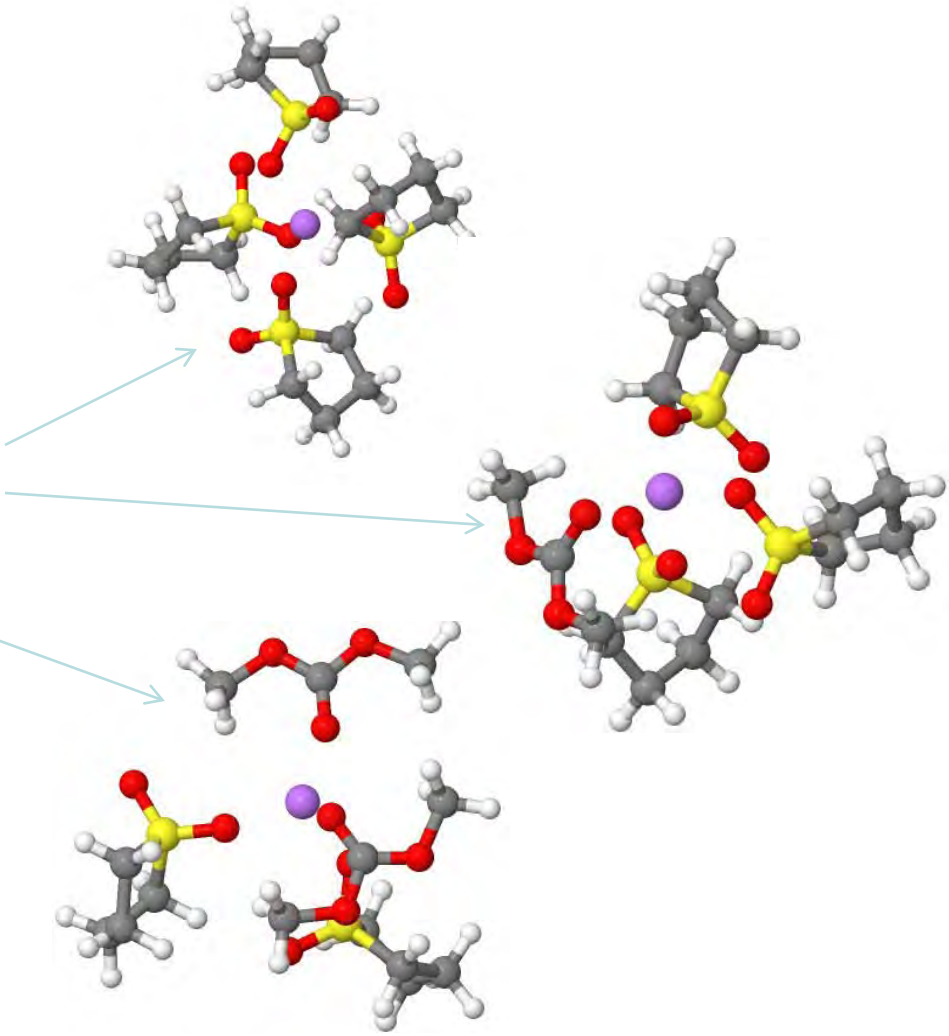
Step 3: Perform Molecular Dynamics (MD) simulations of Sulfolane-DMC/$LiPF_6$, EMS-DMC/$LiPF_6$; validate the force field; learn about Li^+ coordination and transport.

Step 4: (in progress) examine interfacial properties in collaboration with U. of Utah

APPLE&P: Borodin, O. *J. Phys. Chem. B* ***2009****, 113, 11463;*
Borodin, O.; Smith, G. D. *J. Phys. Chem. B* ***2009****, 113, 1763.*

TMS_n-DMC_m-Li Binding Energy from QC and Molecular Mechanics

Binding energy (kcal/mol)	MP2/cc-pvTz BSSE corrected	MM using Force Field
TMS_4-Li	-133.5	-133.9
TMS_3-DMC_{cc}-Li	-127.2	-129.2
TMS_3-DMC_{ct}-Li	-126.8	-128.3
(TMS_2,DMC_{cc},DMC_{ct})-Li	-122.0	-121.2
TMS_2-$DMC(cc)_2$-Li	-119.8	-123.0
TMS-$DMC(cc)_3$-Li	-116.3	-121.9



- *A strong preference for Li^+ complexation with sulfolane (TMS) vs. DMC is observed.*
- *Developed force field accurately predictions binding energy for TMS vs. DMC.*