High Voltage Electrolytes for Li-ion Batteries

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Project ID: ES024

Overview

Timeline

- Start: June 2011
- End: Dec. 2014
- 50% complete

Budget

- Total project funding
  - DOE $1,250K
- Funding received in F2011
  - $250K
- Funding for FY12
  - $250K

Barriers

- SOA electrolytes based on carbonate solvents decompose near or above 4.5 V
- Lack of reliable 5 V cathodes as characterization platform.
- Lack of understanding of oxidation stability and reactive pathway of the electrolyte at the cathode/electrolyte interface

Partners

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

Objectives

- **Develop high voltage electrolytes for high voltage Li-ion batteries for increased energy density**
    - Explore and identify solvents or additives for electrolytes that allow the operation of high voltage cathodes
    - Understand the reactive pathways and reaction products at the electrode/electrolyte interface through computation and surface characterization for guiding the development of improved electrolyte components
    - Identify and/or develop structurally stable high voltage cathode materials

Milestones

- **Sep 2010 – Go/No-Go:**
  - Identify solvents and/or additives allowing the operation of high voltage cathodes
  - Develop or identify structurally stable cathodes as a testing vehicle for electrolytes
  - Understand oxidation stability and reactive pathway of electrolytes through computation and experiments
- **May 2011:**
  - Demonstrate the effectiveness of solvents or additives in allowing the improved operations of cells with 4.7 V $LiNi_{0.5}Mn_{1.5}O_4$ and/or 4.8 V $LiCoPO_4$ cathodes
  - Develop stabilized $LiCoPO_4$ with metal substitution
  - Calculate oxidation potential of solvents and validate with experiments
- **Sep 2012:**
  - Evaluate effectiveness of additives in both half cells and full cells with graphite anode
  - Understand reactive pathways of electrolyte components through computational effort, surface characterization and SEI chemistry studies

Approach

- **Identify and/or develop high voltage cathodes as a testing vehicle**
  - Collaborate with ANL on $LiNi_{0.5}Mn_{1.5}O_4$ and $xLi_2MnO_3 \cdot (1-x)LiMO_2$
  - Investigate validity of $LiCoPO_4$
- **Computational effort**
  - Understand oxidative stability of solvents in electrolytes
  - Understand reactive pathways of additives and electrolytes on cathodes
  - Develop ability to predict and design electrolyte components
- **Develop additives for carbonate based electrolytes**
  - Search additives that would interact and form protective interfacial layers on cathodes
  - Understand interfacial chemistry at the cathode/electrolyte interface through surface characterization techniques

Technical Accomplishments

High voltage cathodes (J. Allen, R. Jow)

- Stabilized 4.8 V $LiCoPO_4$ by Fe doping demonstrated much improved rate capability and capacity retention.
- $LiCoPO_4$ can sustain polaron with slightly higher migration energy barrier than that in $LiFePO_4$ (DFT calculations).

Computational: Electrolytes and Electrode/Electrolyte Interface

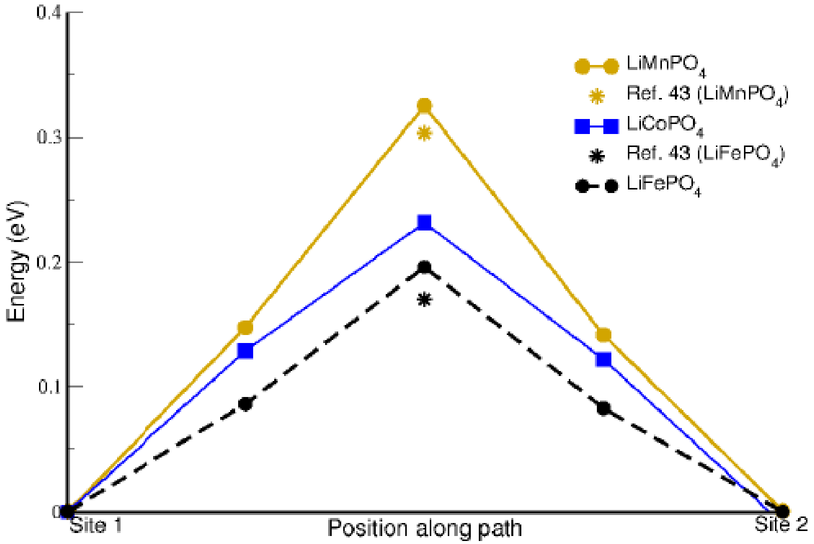
(O. Borodin, R. Jow)

- Oxidation potentials of solvents calculated using DFT would be lowered by the presence of anions and were more in agreement with experiments
- Conductivity of Li_2EDC calculated using MD simulations agrees well with experiments.
- Energy barrier for conduction is 78 kJ/mol.

Additives for high voltage electrolytes (A. Cresce, J. Ho, J. Read, K. Xu)

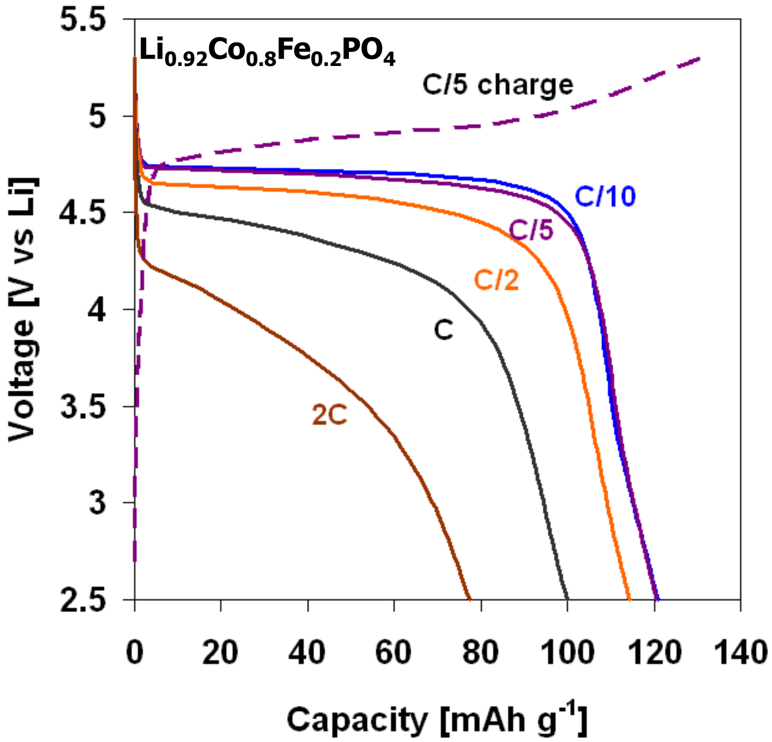
- Demonstrated that the full cell, graphite/$LiNi_{0.5}Mn_{1.5}O_4$, cycled in electrolyte with HFiP additive achieved 80% capacity retention and 99.87% coulombic efficiency in 200 cycles.
- XPS surface analysis revealed the presence of fluorinated alkyl substructure on cathode.
- Higher degrees of fluorination of additives resulted in better cycling performance.

$LiCoPO_4$ and Stabilized $LiCoPO_4$



DFT calculations using validated HSE06 at steps along a linearly interpolated path between two calculated polarons+.

	Migration barrier, eV	σ, S/cm
$LiFePO_4$	0.20	1.8×10^{-8}
$LiMnPO_4$	0.33	$<10^{-10}$
$LiCoPO_4$	0.23	$\sim 10^{-9}$



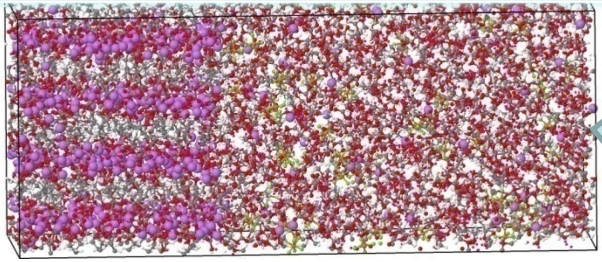
$Li_{0.92}Co_{0.8}Fe_{0.2}PO_4$ demonstrated good rate capability.

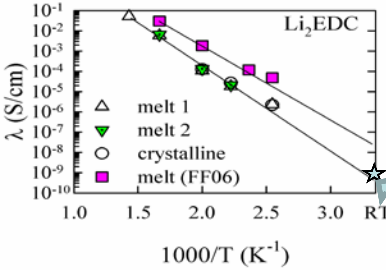
+ M.D. Johannes, K. Hoang, J.L. Allen, K. Gaskell, *Phys. Rev. B*, **2012**, 85, 115106..

* S. P. Ong, V. L. Chevrier, and G. Ceder, *Phys. Rev*. B, **2011**, 83, 075112.

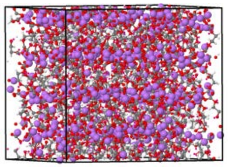
Overview of Computational Studies

Predict: electrolyte reduction, SEI properties, SEI – electrolyte interface (quantum chemistry, MD)



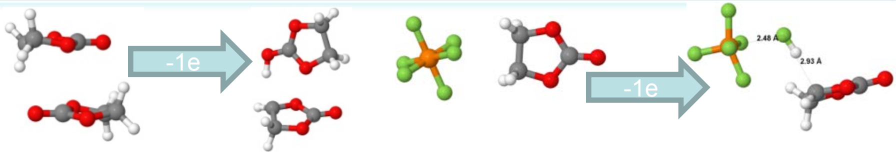


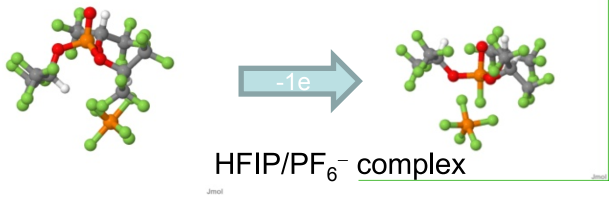
Experiment
Phil Ross LBNL
(ARL material)



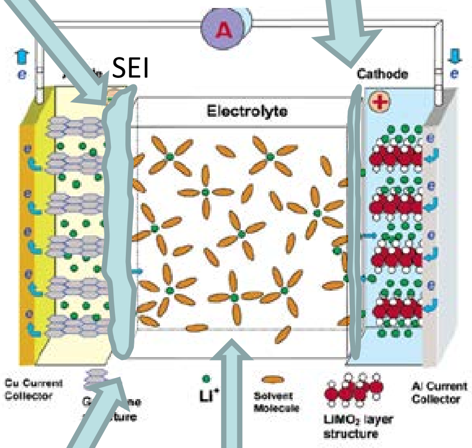
- λ of Li_2EDC, $(LiO_2COCH_2)_2$, predicted using MD simulations with revised and validated FF.
- λ is in good agreement with experimental data.
- Activation energy: 78 kJ/mol

Oxidation potentials and decomposition reactions for solvent, solvent (or additive)-anion, solvent-lithium salt and additives (quantum chemistry)



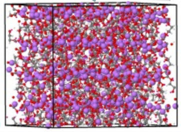


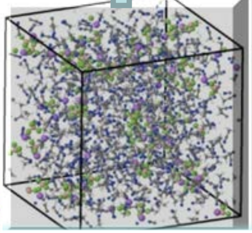
HFIP/PF_6^- complex

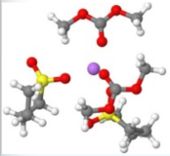


MD and DTF studies revealed:

- The presence of BF_4^-, PF_6^-, ClO_4^-, or $B(CN)_4^-$ anion lowered the carbonate solvent oxidation potential by H^- and F^- abstraction and promoted decomposition kinetics;
- Fluorine transfer was observed for HFiP/PF_6^-complexes.







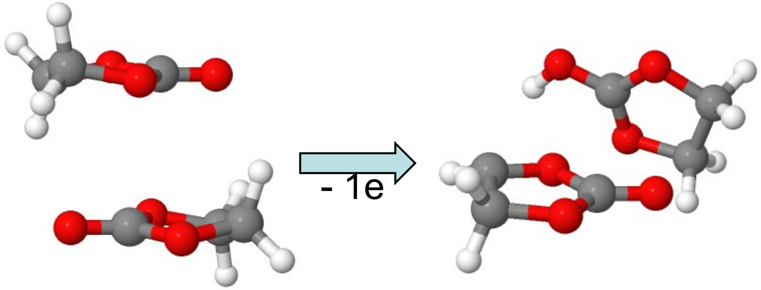
Structure and transport in bulk electrolytes (carbonate-alkylphosphate/$LiPF_6$) and SEI components with a focus of Li^+ competitive solvation in mixed solvents: (MD simulations)

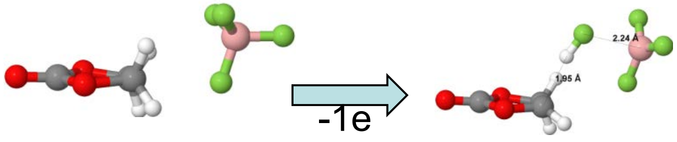
Battery pic from Kang Xu

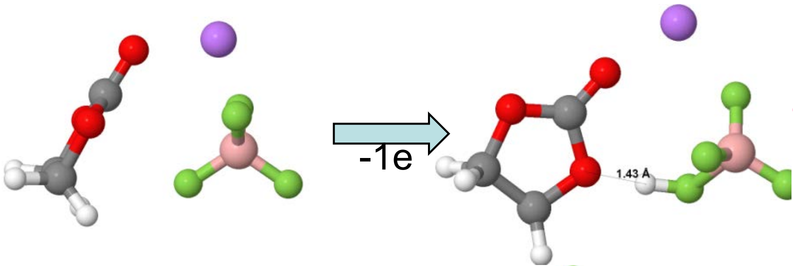
EC oxidation

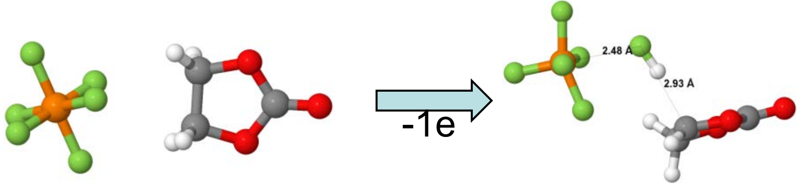
Oxidation Potential in eV

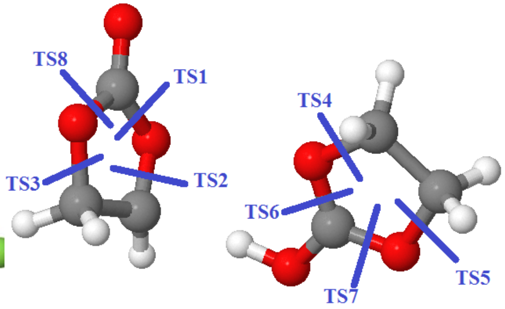
	ε=1	ε=4.2	ε=20.5	ε=78.4
$(EC)_2$		6.2	5.9	5.9
EC/BF_4^-	4.6	6.0	6.3	6.3
$EC/LiBF_4$	8.7		6.6	
EC/PF_6^-	4.9	6.3	6.6	6.6

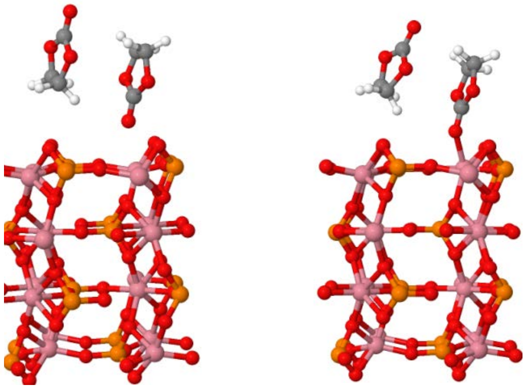










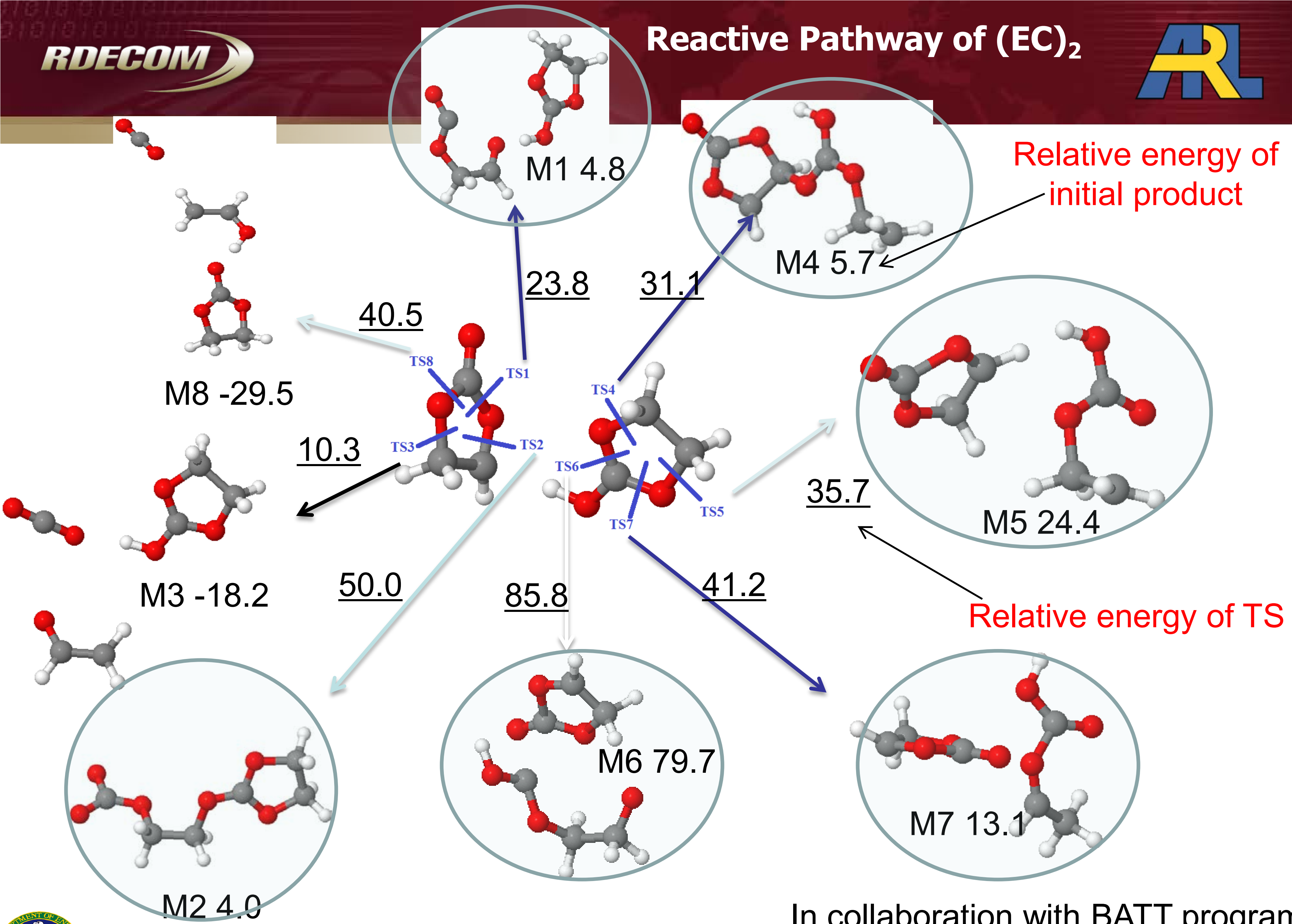


$CoPO_4/(EC)_2$ GGA+U (periodic DFT)

- Influence of anions, salt, explicit solvent and $CoPO_4$ surface on EC oxidation was investigated.
- Oxidation potential of $(EC)_2$, at e=20, is the lowest indicating that it might be the preferred pathway for oxidation at non-active electrodes compared to the EC-anion decomposition.
- Co-O bond is formed between $CoPO_4$ and EC.

M052/cc-pvTz level calculations

Reactive Pathway of $(EC)_2$



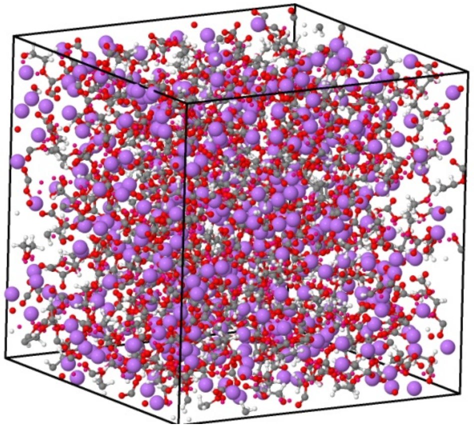
Relative energy of initial product

Relative energy of TS

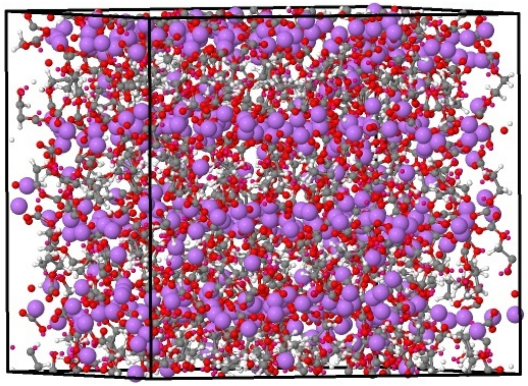
In collaboration with BATT program

Lindan Xing Uof Utah calculations. Relative energy (kcal/mol) from B3LYP/6-311++G(d) PCM(Solvent=water)

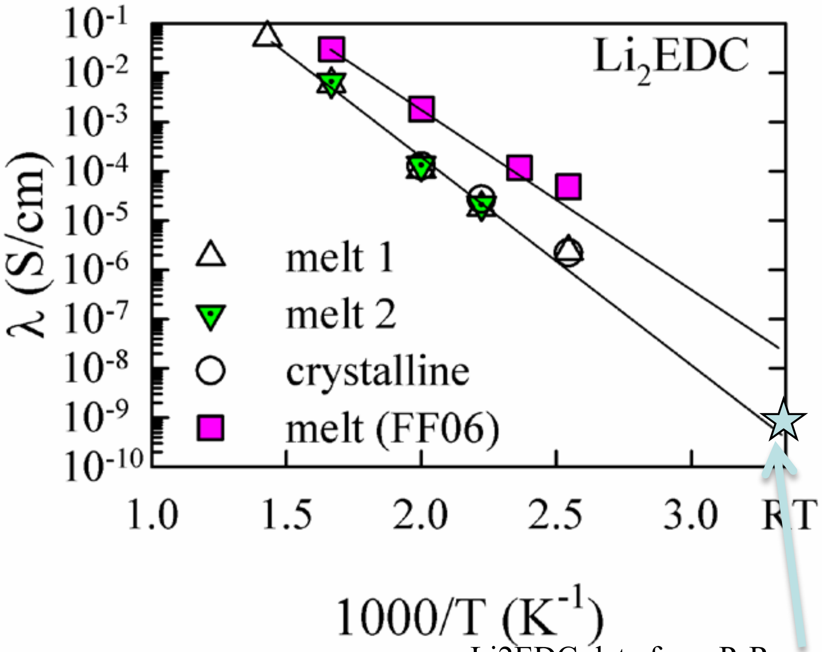
Li_2EDC Amorphous (melt) vs. Crystalline



Amorphous (melt)



Crystalline (layered)



Li2EDC data from P. Ross LBNL

- ✓ A revised polarizable force field has been developed for Li_2EDC that is compatible with APPLE&P electrolyte force field.
- ✓ E_a for Li_2EDC conductivity was 78 kJ/mol, which is similar to the 68 kcal/mol measured for the Li^+ charge transfer at the graphite/electrolyte interface.
- ✓ The averaged conductivity of crystalline Li_2EDC is similar to conductivity of the amorphous phase.
- ✓ At temperatures below 450 K anion motion contributes less than 15% to charge transport.

Correlation of Experiment and Computation

Conditions	Experiment		Computation
	E_a for Li^+ charge transfer at interface [1]	E_a for Li diffusion	
Graphite/Electrolyte interface	**68 kJ/mol**		**78 kJ/mol for Li conduction barrier in Li_2EDC [3], a key SEI component**
NCA/Electrolyte interface	**52 kJ/mol**		
LFP/Electrolyte interface	**32 kJ/mol**		
Li diffusion in LFP		**29 kJ/mol [2]**	**20 kJ/mol for polaron migration barrier in LFP [4]**

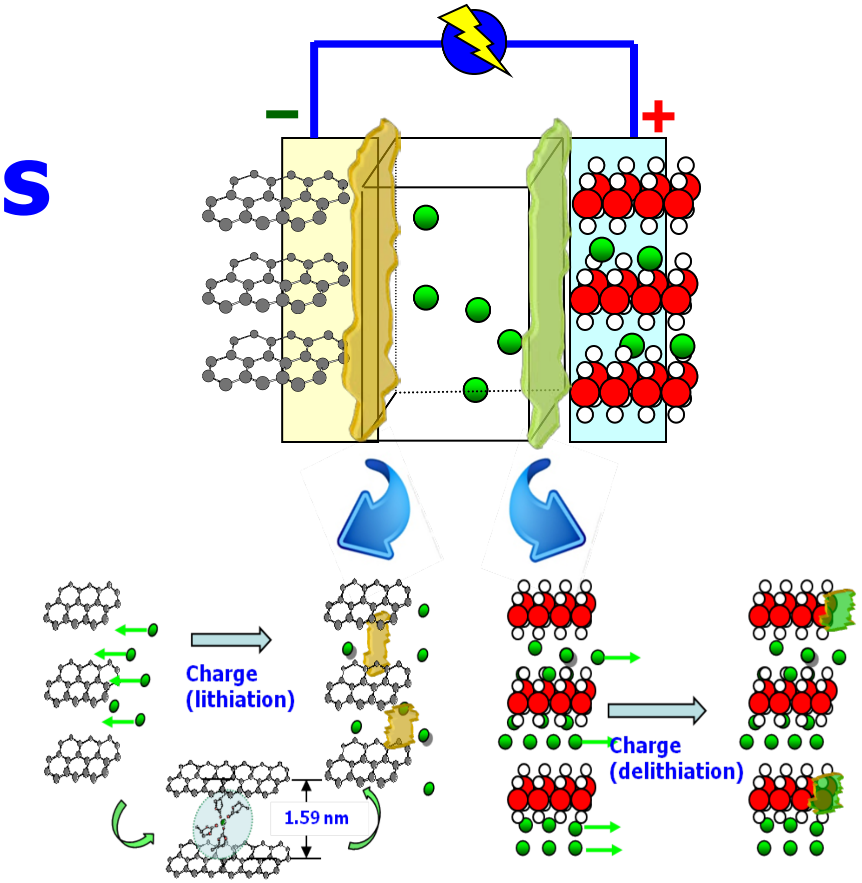
NCA: Lithium nickel cobalt aluminum mixed oxide, **LFP**: lithium iron phosphate

1. Jow, T. R.; Marx, M. B.; Allen, J. L., *J. Electrochem. Soc.,* **2012**, 159(5), A604.
2. Allen, J. L.; Jow, T. R.; Wolfenstine, J., *Chem. Mater.*, **2007**, 19, 2108-2111.
3. Borodin, O. et al., unpublished.
4. Johannes, M. D.; Hoang, K.; Allen, J. L.; Gaskell, K., *Phys. Rev. B*, **2012**, 85, 115106.

High Voltage Electrolyte Additives

A. v. Cresce, J. Ho, J. Read,
and K. Xu

Electrochemistry Branch
U. S. Army Research Laboratory
Adelphi, MD 20783-1197, USA



Cathode/Electrolyte Interphases

Different Focuses on Anode- and Cathode-Interphases

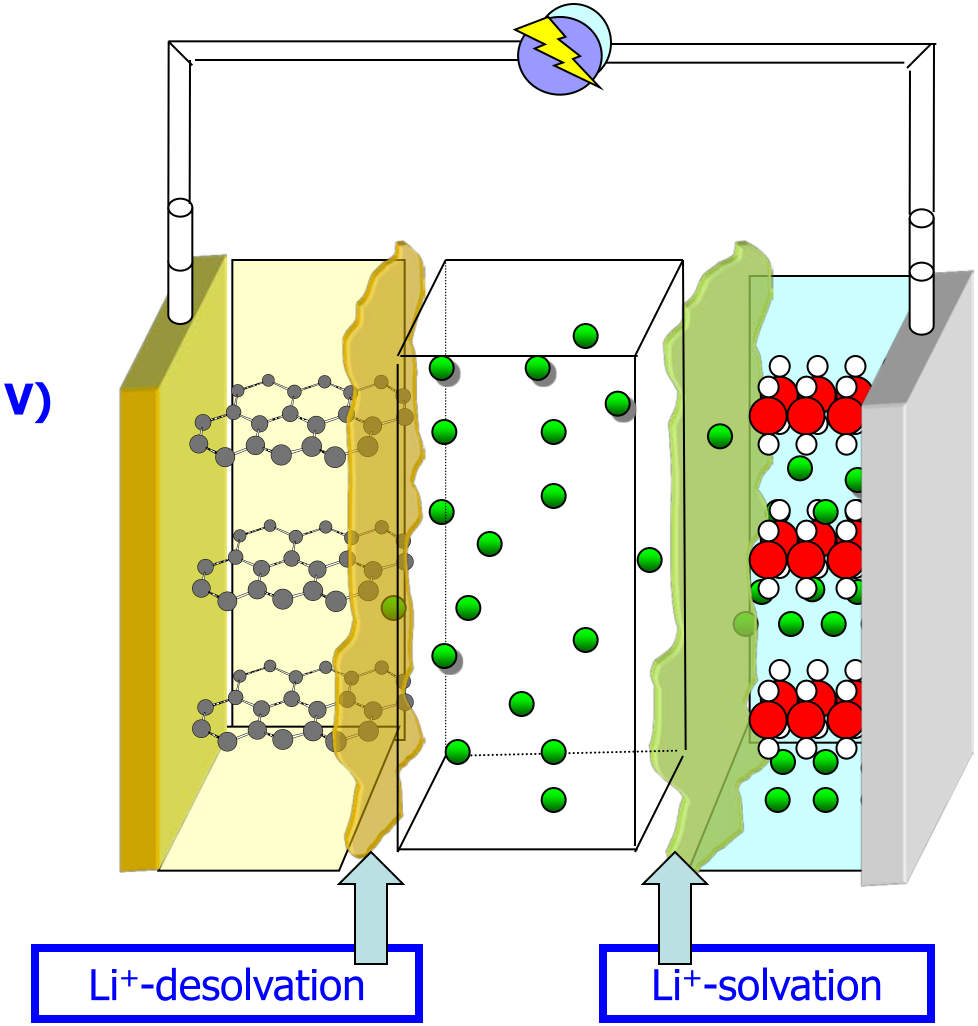
Anode:

- **Faster Li$^+$-transport**
- **Less consumption of Li$^+$ (irreversible capacity)**

Cathode:

- **Stabilization at high potential (> 4.5 V)**

Li$^+$-solvation no longer plays directing role in cathode SEI formation mechanism

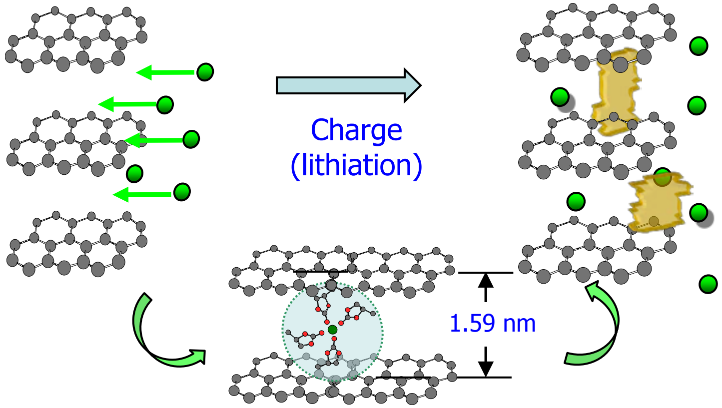


Interphases on Anode and Cathode

- Both are related to electrode structure
- Both are little understood

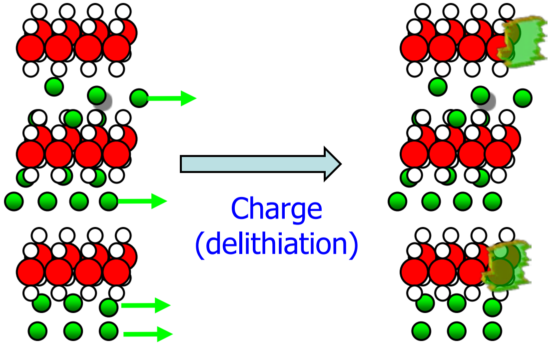
Anode
(Graphitic)

- Reductive decomposition
- Lithiation process
  - Solvent co-intercalation
  - Lattice held together by van de Waals force
- 3D: partially penetrated graphene
- Coverage of Li^+-exit/entrance sites
  - kinetic control over Li^+-transport



Cathode
(Metal Oxide)

- Doubt still exists about the existence
  - potential < 4.5 V vs. Li (~1.5 V vs. SHE)
- Oxidative decomposition
- Delithiation
  - Solvent co-intercalation impossible
  - Lattice held together by Coulombic/covalent
- “Patchy” instead of “continuous”
- No coverage of Li^+-exit/entrance sites
  - deactivation of metal cores



In the last two decades >90% effort are on anode SEI

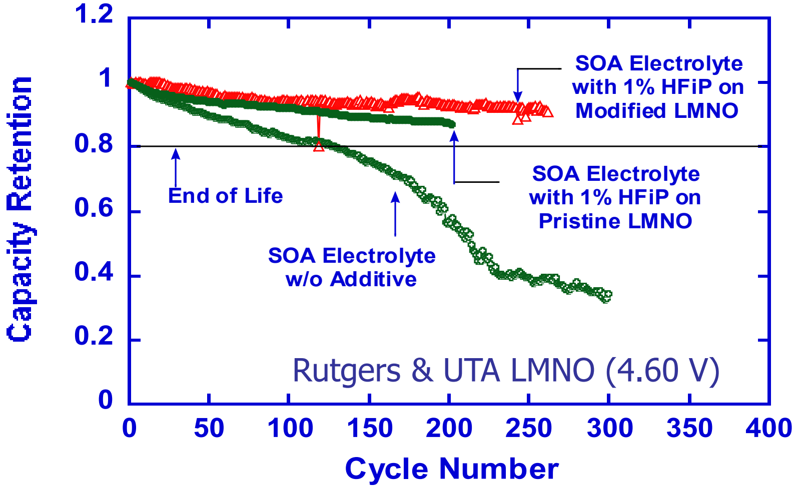
Cathode SEI: on 5.0 V Class Cathodes

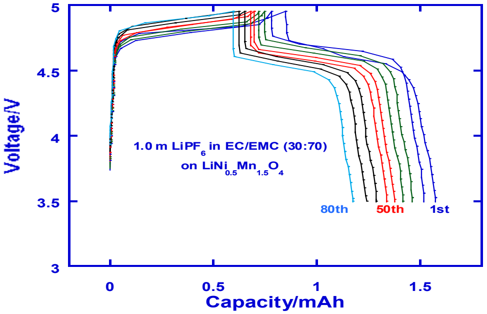
A. v. Cresce, K. Xu

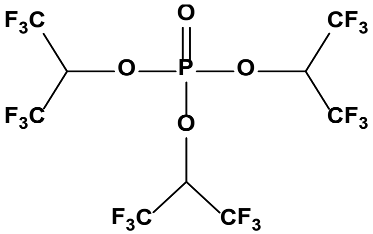
Preliminary Results (A. v. Cresce)

- New electrolyte forms stable interphase on both spinel LiNi0.5Mn1.5O4 and olivine LiCoPO4 surfaces

- Baseline electrolyte: LiPF6/EC/EMC (30:70)
- 1% additive causes significant impact on cell stability
- Further refinements are on-going

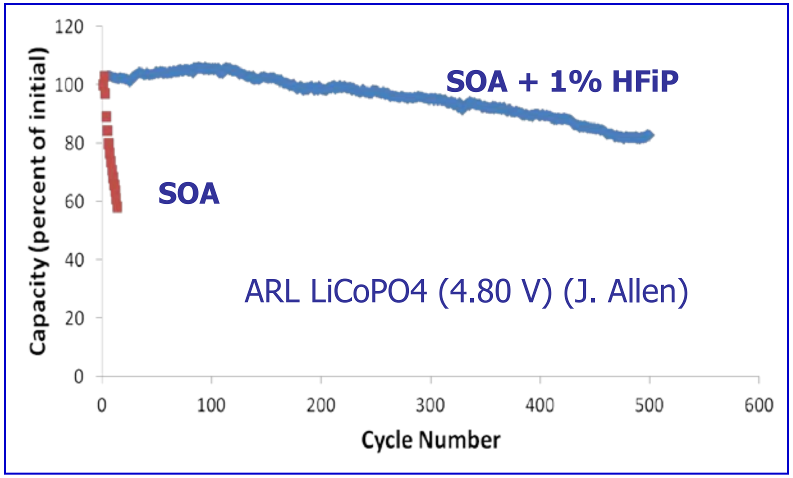


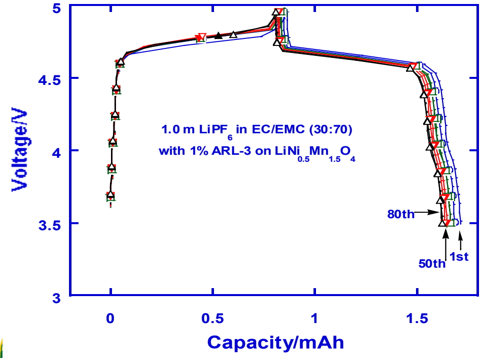




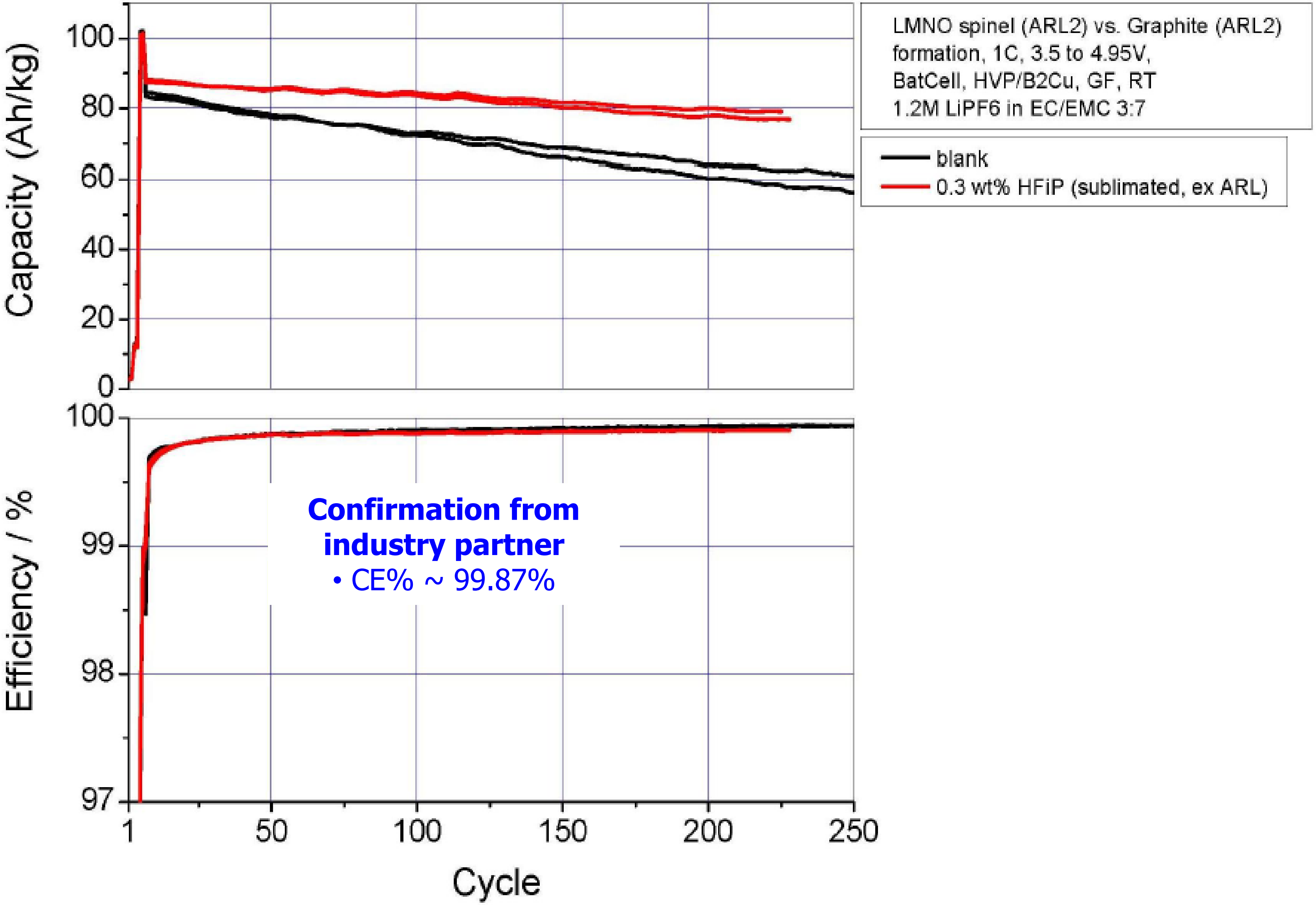
HFiP

Cresce & Xu, *JES*, 2011, 158, A337





ANL LMNO: Full Cells



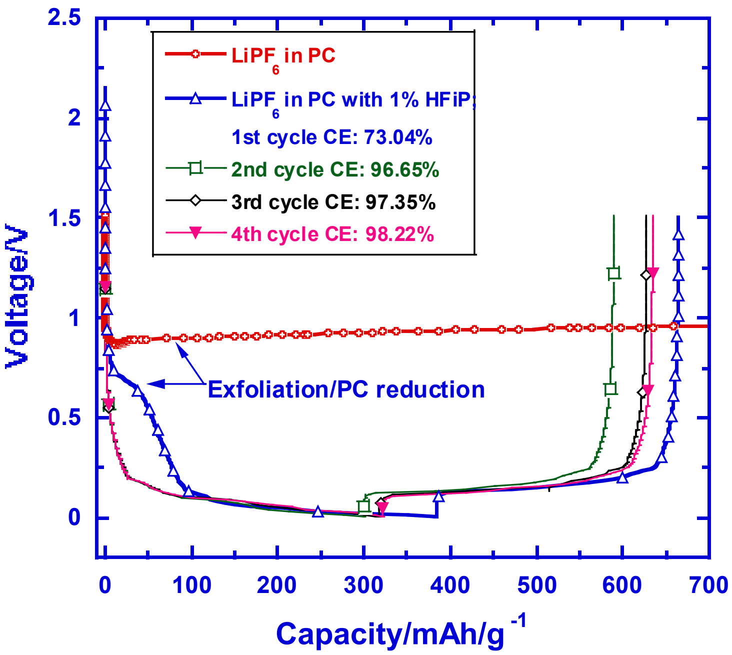
Confirmation from industry partner

- CE% ~ 99.87%

Surface Chemistries of HFiP

Where did HFiP end up with?

- Chemically phosphate can be reduced at anode
- It was found to even form good SEI on graphite in neat PC

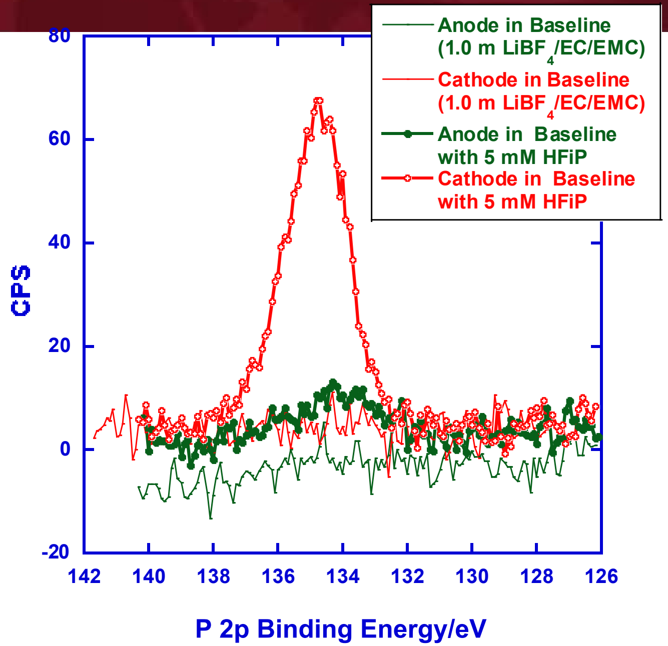


What mechanism did it stabilize electrolyte against cathode surface?

Surface Analysis with HR-XPS

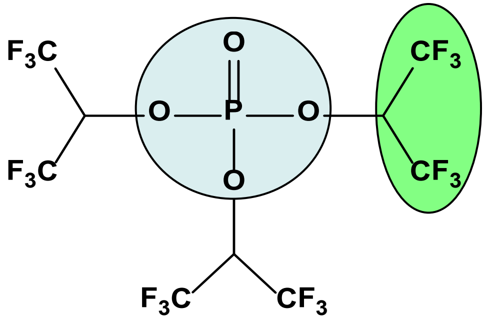
HR-XPS conducted on both cathode and anode cycled in baseline and HFiP-containing electrolytes

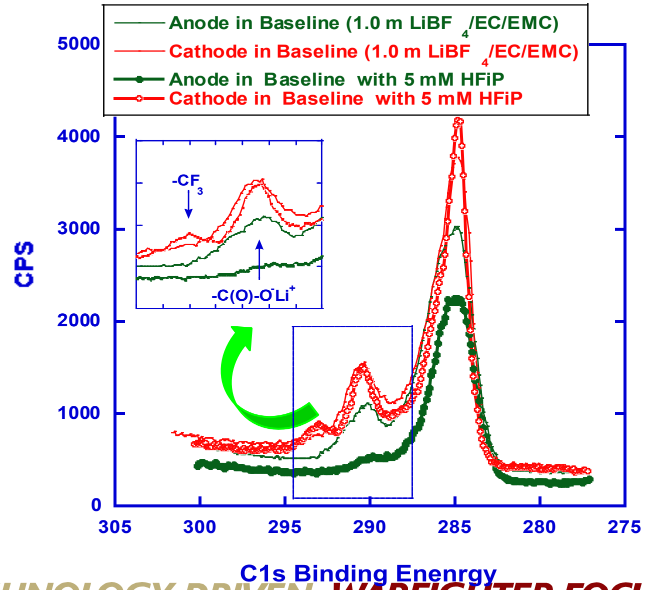
- P 2p absent in control samples
- P2p on test samples
  - 5~10 X more on cathode than anode
- C1s for CF3 only found on cathode



The fate of phosphate in electrolyte

- Phosphate ends up on cathode and anode
- Fluorinated alkyls substructure on cathode





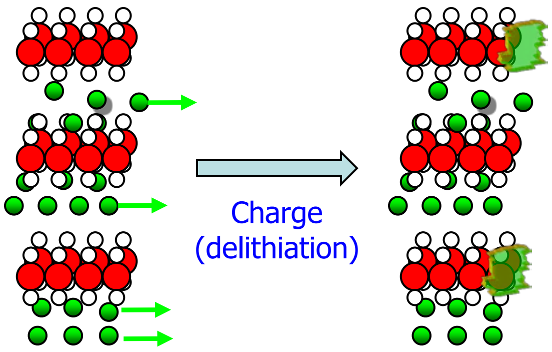
HFiP Scaled Up by ANL

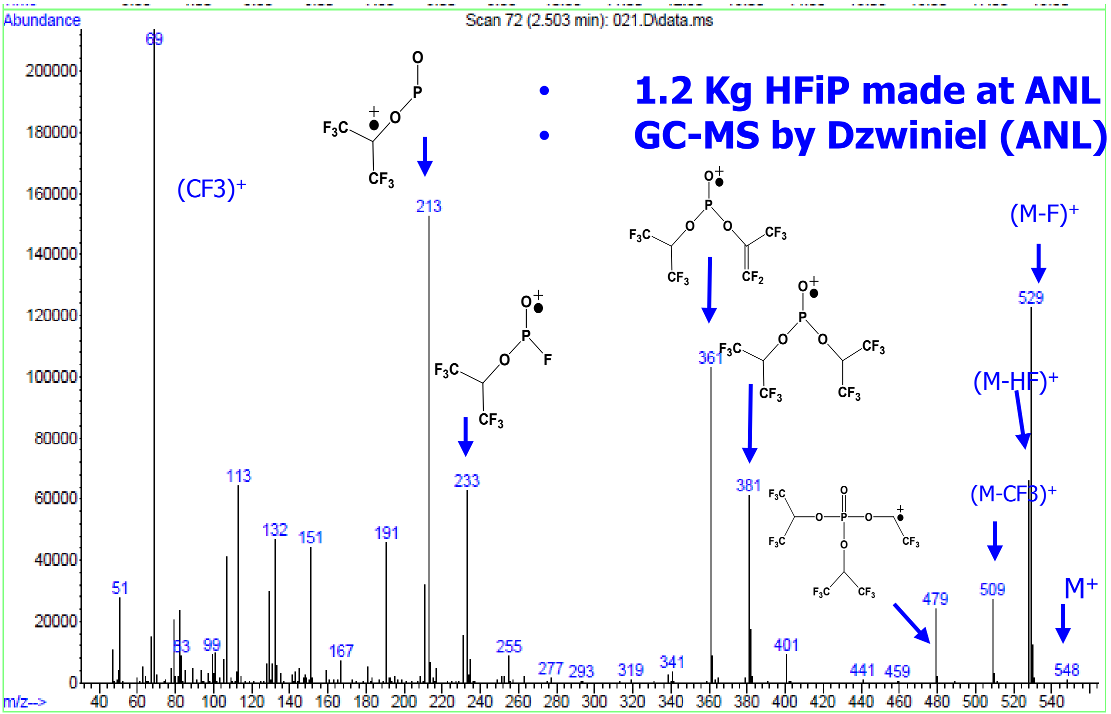
P. Faguy (DOE)

Even HR-XPS cannot pin-point the structure of cathode interphase

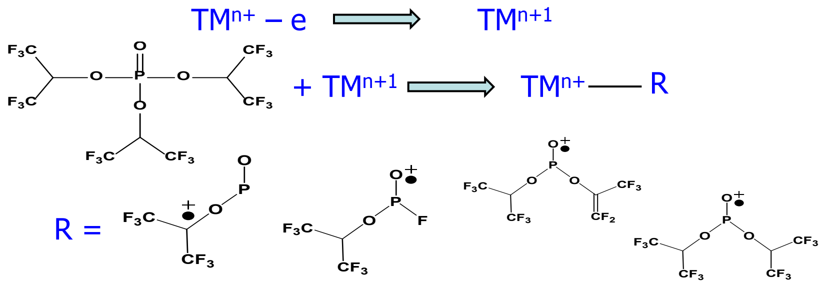
- Perhaps inference from MS?

- **Possible participation of TM cores (TM reduction)**
- **New bond-formation between M and O/P/F/C**
- **Deactivation on cathode surface at TM centers**
  - **similar to catalyst poisoning**
  - **spectroscopic evidence**





- **1.2 Kg HFiP made at ANL**
- **GC-MS by Dzwiniel (ANL)**



$TM^{n+} - e \longrightarrow TM^{n+1}$

$+ \; TM^{n+1} \longrightarrow TM^{n+}$ — R

R =

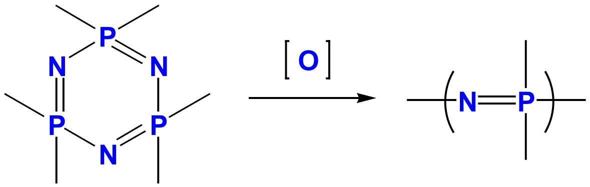
Tailoring an Interphase
----- on Cathode Surface

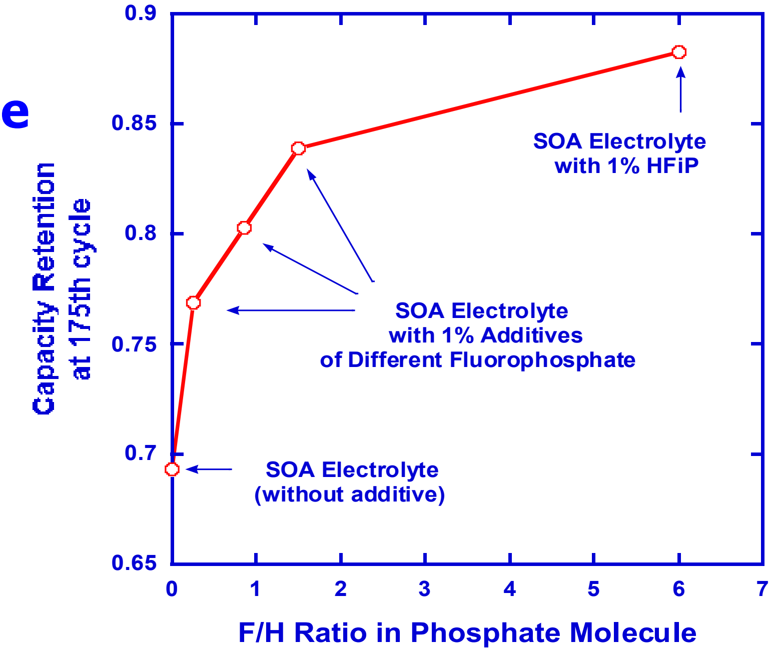
Interphase on Electrolyte/Cathode

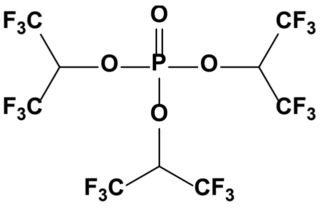
Unlike Electrolyte/Anode Junction, interphase on cathode is little studied

- Oxidation Chemistry unknown
- Formation mechanism?

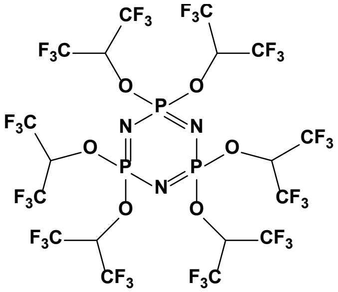
- Perfluorination helps
- Phosphazene might help (?)



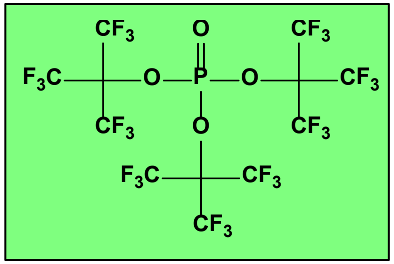




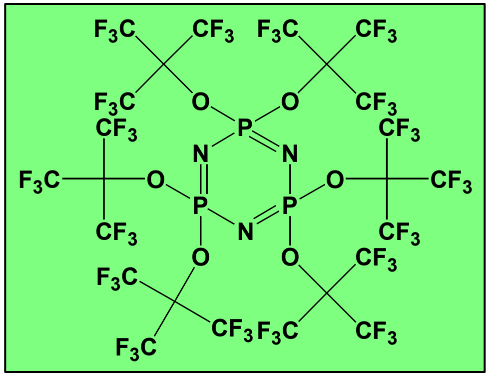
1. HFiP



2. PNF-2

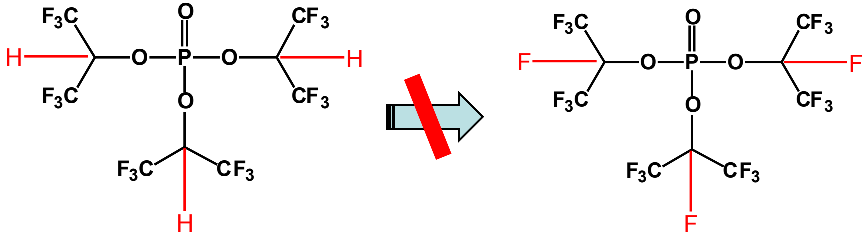


3. PFBP

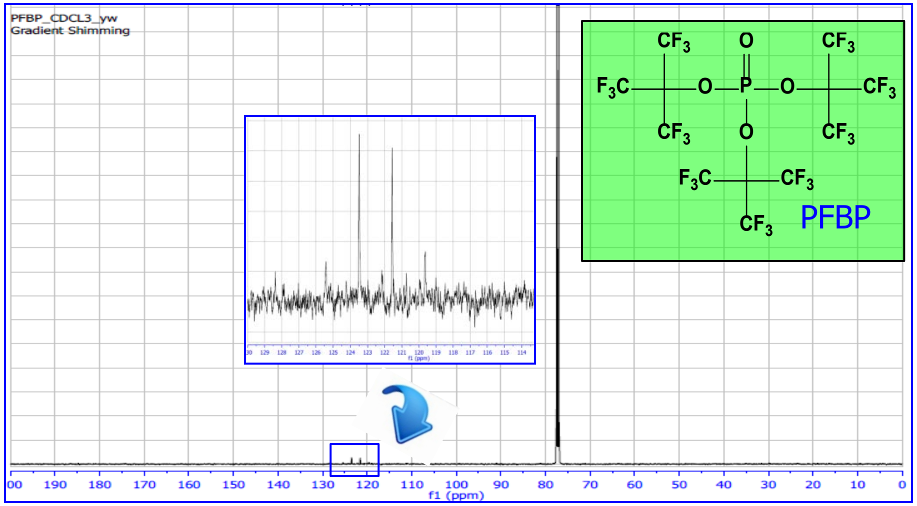


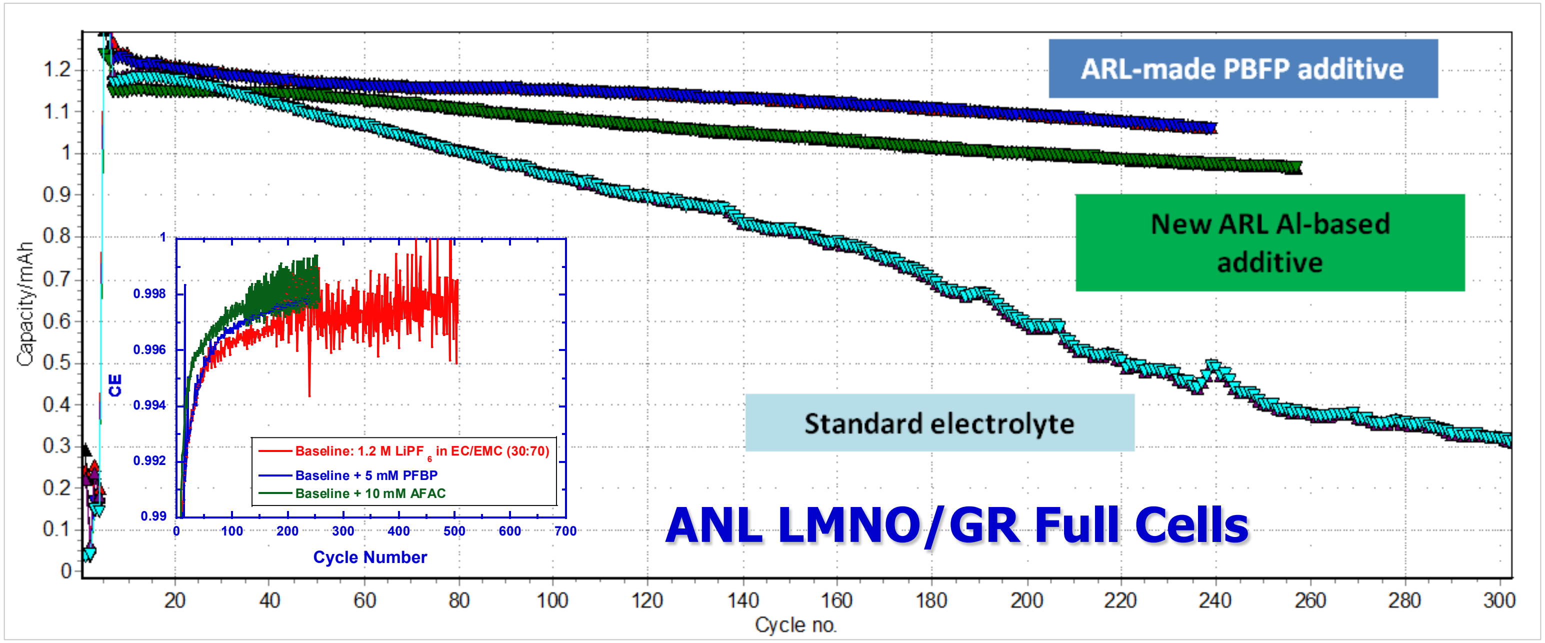
4. ??

Synthesis of Perfluorinated Additive PFBP (Drs. XQ Yang and HS Lee, BNL)



- Presence of remaining H in HFiP undesired
- Perfluorinated additives synthesized





ARL-made PBFP additive

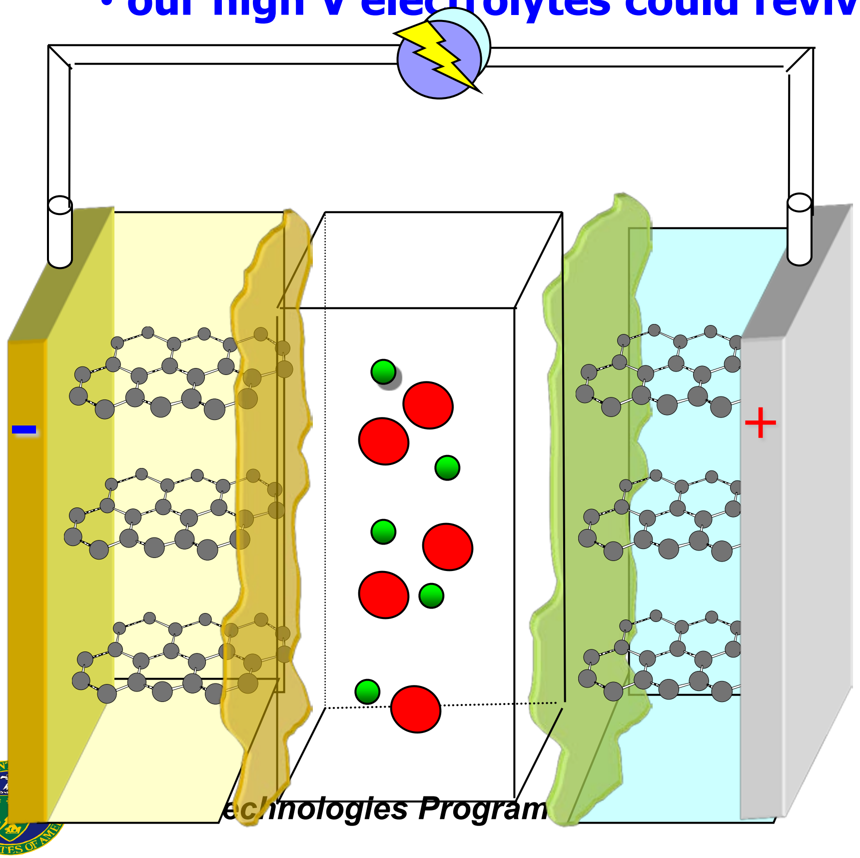
New ARL Al-based additive

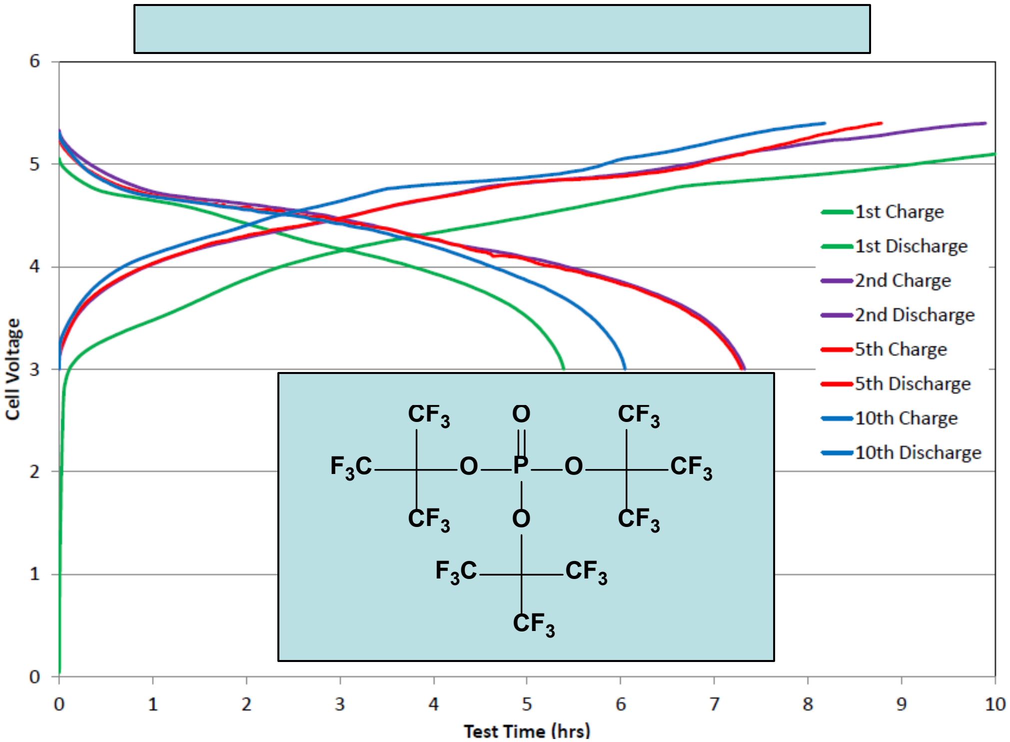
Standard electrolyte

ANL LMNO/GR Full Cells

A New 5 V Battery Chemistry: Double Intercalation (J. Read, ARL)

- **Double-intercalation chemistry**
- **Symmetric graphite cell**
- **High voltage (> 5.0 V)**
- **Concept was proposed in early 1990s (J. Dahn)**
    - **never realized due to lack of electrolytes:**
        - **good SEI on anode, high V stability on cathode**
    - **our high V electrolytes could revive this concept**





Future Work

- Collaborate with ANL on $LiNi_{0.5}Mn_{1.5}O_4$ and $xLi_2MnO_3\cdot(1\text{-}x)LiMO_2$ for the testing of ARL electrolytes.
- Continue the development of stabilized $LiCoPO_4$.
- Perform computational screening of redox stability and decomposition reactions of the fluorinated alkylphosphate-based additives using DFT calculations. Predict bulk and interfacial properties of electrolytes with fluorinated alkylphosphate-based additives.
- Study decomposition reactions of solvent and additives at cathode surfaces.
- In-situ/Direct characterization of SEI under Li ion chemistry environments
- Synthesis of new solvents/additive based on more understanding about the chemical processes at interphases

Summary

- Stabilized high voltage $Li_xCo_{0.8}Fe_{0.2}PO_4$ in couple with the high voltage electrolyte has greatly improved the capacity retention and rate capability
    - Stability of the cathode materials including $LiNi_{0.5}Mn_{1.5}O_4$ and $xLi_2MnO_3 \cdot (1-x)LiMO_2$ are critical for the success of high voltage Li-ion batteries
- Oxidation potentials and reactive pathway of EC and alkyl phosphate has been successful calculated with respect to the influence of anion, salt, explicit solvent and $CoPO_4$ computationally.
    - The conductivity of Li2 EDC was calculated using MD simulation and agrees with experiment.
    - The presence of BF_4^-, PF_6^-, ClO_4^- , or $B(CN)_4^-$ anion lowered the carbonate solvent oxidation potential by H^- and F^- abstraction and promoted decomposition kinetics;
    - Fluorine transfer was observed for HFiP/PF_6^-complexes.
- Effectiveness of HFiP additive has been successfully demonstrated in a full cell, graphite/$LiNi_{0.5}Mn_{1.5}O_4$, cycled in electrolyte with HFiP additive achieved 80% capacity retention and 99.87% coulombic efficiency in 200 cycles.
    - XPS surface analysis revealed the presence of fluorinated alkyl substructure on cathode.
    - Higher degrees of fluorination of additives resulted in better cycling performance.
    - Elevated temperature tests are on-going