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

- Funding received in FY2011
  - $250K
- Funding received in F2012
  - $250K
- Funding for FY13
  - $250K

Barriers

- SOA electrolytes based on carbonate solvents decompose near or above 4.5 V
- Lack of stable and 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
- U of Maryland
- U of Utah
- NRL

Objectives - Relevance

- **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

- **FY 2012:**
  - Identified LiPFB (lithium perfluorinated tert butoxide) was more effective than HFiP in improving cycle life in LNMO/graphite cells at RT.
  - Synthesized Al(HFiP) additives with electron deficient center Al
  - Calculated oxidation potential of solvents and validate with experiments
- **FY 2013:**
  - Synthesized a number of new additives including, Al(PFB), HFiP-grafted phosphazene, PFB-grafted phosphazene
  - Continue testing of LNMO/graphite and doped LCP/graphite full cells in electrolytes with additives at RT and 55 ^{o}C
  - Postmorten diagnostic for surface characterization and SEI chemistry studies
  - Computational studies of new additives and interactions with electrodes

Approach/Strategy

- **Develop new additives for carbonate based electrolytes**
  - Develop additives with electron deficient center such as Al
  - Perfluorinate additives to enhance their effectiveness
- **Understand and characterize capacity fading mechanism**
  - Electrochemical methods: Characterize capacity fading, kinetics, impedance changes w.r.t. rate and temperatures in half and full cells
  - Surface analysis: XPS, NMR, AFM
- **Identify and/or develop stable high voltage cathodes as a testing vehicle**
  - Focus on 4.7 V $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) spinel
  - Develop 4.8 V modified-$LiCoPO_4$ (LCP)
- **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

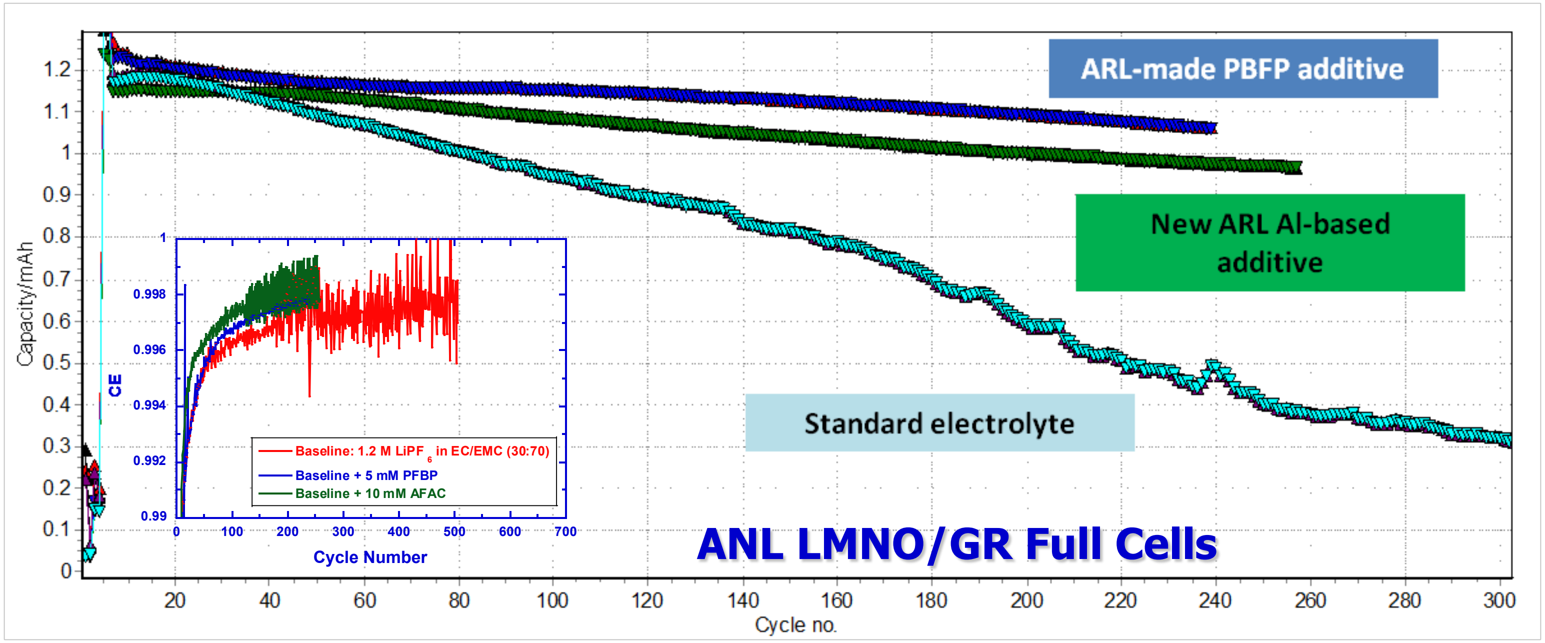
Technical Accomplishments

- **Designed and synthesized new additives**
  - Electron deficient additives: HFiP, Al(HFiP), HFiP-grafted phosphazene
  - Perfluorinated additives: PFBP, Al(PFB), PFB-grafted phosphezene
- **Evaluated perfluorinated additives**
  - Higher degrees of fluorination of additives such as PFBP resulted in better cycling performance.
- **Analyzed surface of graphite anode and LNMO cathode**
  - XPS surface analysis revealed the presence of fluorinated alkyl substructure on cathode.
- **Evaluated cycling performance of LNMO/graphite full cells**
  - Identified that a combination of HFiP and A-1 additives can reduce capacity fading at 55 °C.
- **Evaluated cycling performance of Fe doped LCP (LCFP)/Li half cells**
  - LCFP cycled well at RT but faded at 55 °C in baseline electrolyte.

Technical Accomplishments - continued

- **Computational: Calculated Oxidative stability of Electrolyte and Additives**
  - Oxidation potentials of solvents calculated using DFT would be lowered by the presence of anions and were in agreement with experiments.
  - Calculated oxidation potentials of major solvents including carbonates, sulfones, alkylphosphates with anions BF_4^-, PF_6^-, FSI, TFSI, DCTA, DFOB, ClO_4^-.
  - Calculated oxidation potentials of additives including HFiP and HFiP/BF_4^- cluster. As expected, BF_4^- lowers the oxidation potential of HFiP significantly.

Performance of Perfluorinated Additive LiPFB



- Test cells: LNMO/A12 (graphite) at RT
- Electrolytes: 1.2 M $LiPF_6$ in EC:EMC (3:7) with Al(HFiP) and LiPFB (shown as PBFP* in the above figure) and without.
- The electrolyte with LiPFB showed much improved cycle life for LNMO/A12 over the electrolyte without additives.

* PFBP identity was re-characterized and discussed in the next slide.

* All LNMO and A12 electrodes were provided by ANL.

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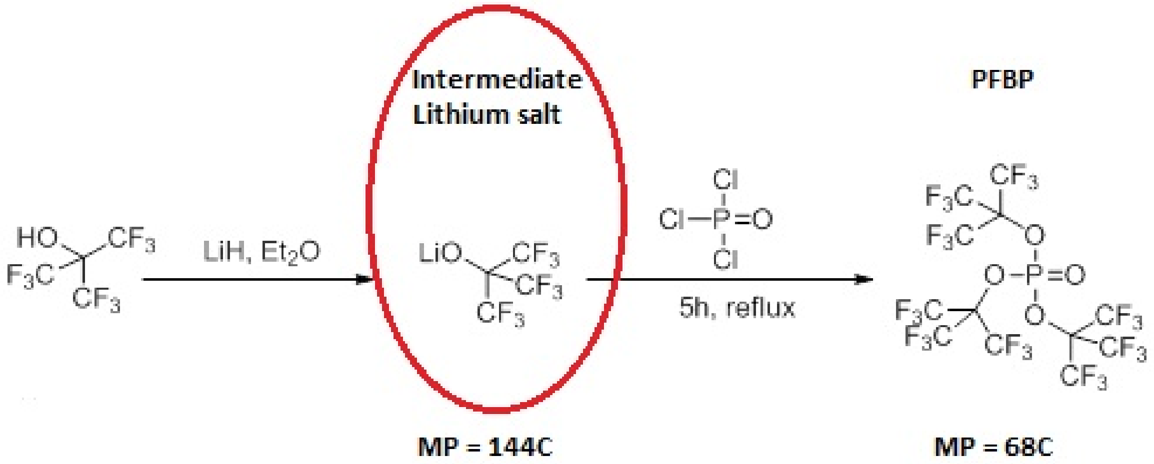
PFBP Identity



- Initially thought to be PFBP
- Actually an intermediate lithium alkoxide salt
- Bulky fluorinated *tert*-butyl groups prevented full esterification of phosphorus center
- Other additives being re-characterized
- Scale-up of Li perfluorotert-butoxide (LiPFB) by ANL ongoing

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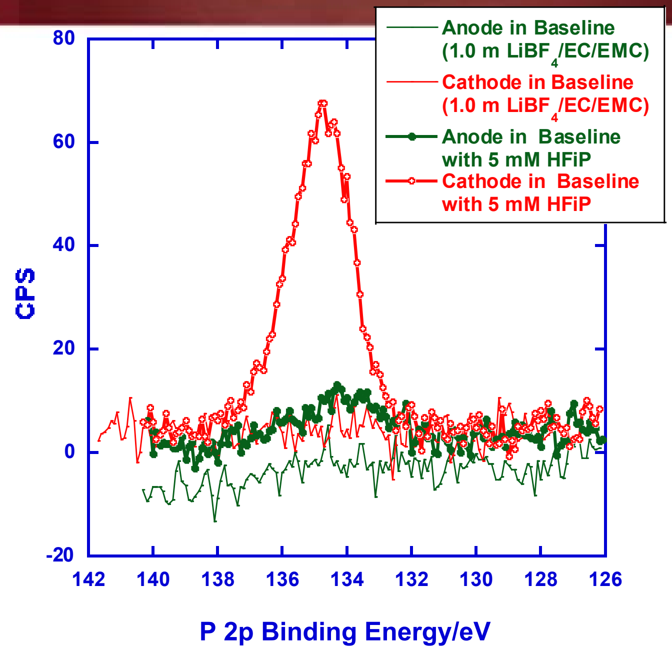
Surface Analysis with HR-XPS

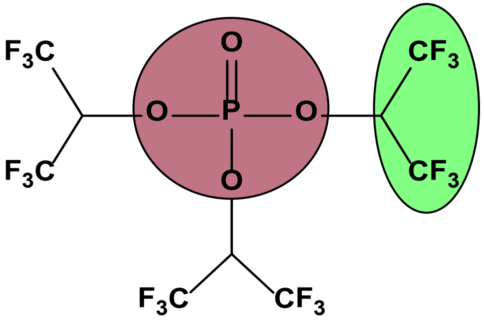
HR-XPS conducted on both cathode and anode cycled in baseline and HFiP-containing electrolytes

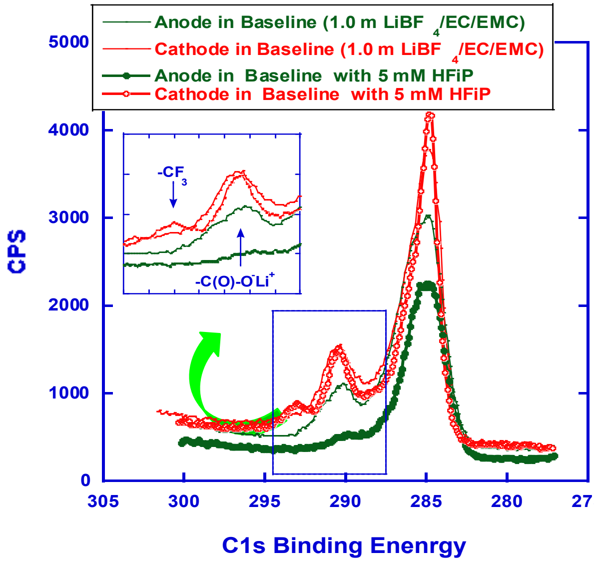
- P 2p absent in control samples
- P2p on test samples
    - 5~10 X more on cathode than anode
- C1s for CF_3 only found on cathode



The fate of phosphate in electrolyte

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





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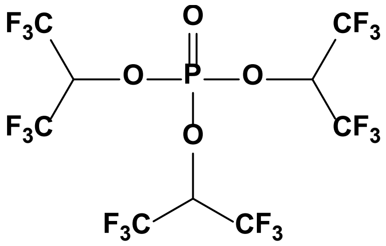
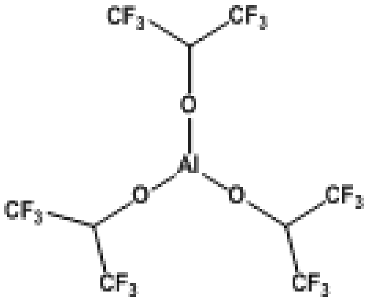
New Additives Synthesized

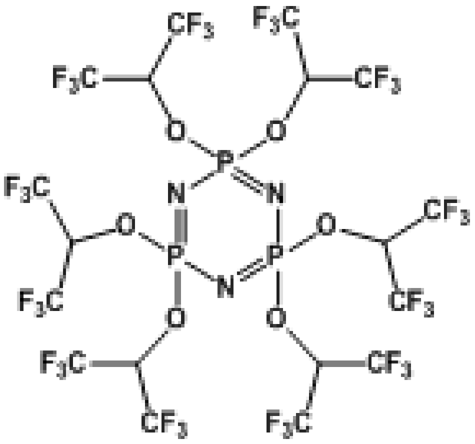
HFiP

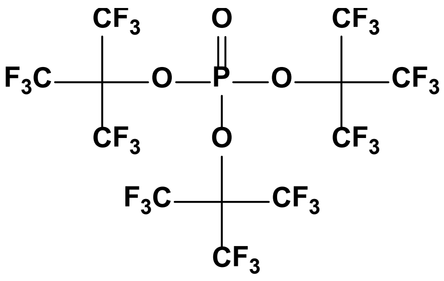


Al(HFiP)

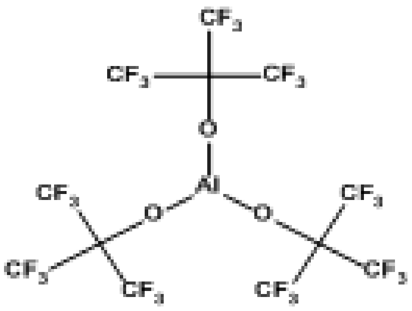


HFiP-grafted Phosphazene

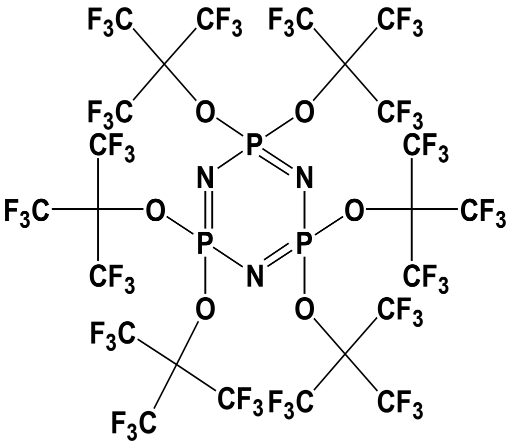




PFBP



Al(PFB)



PFB-grafted Phosphazene

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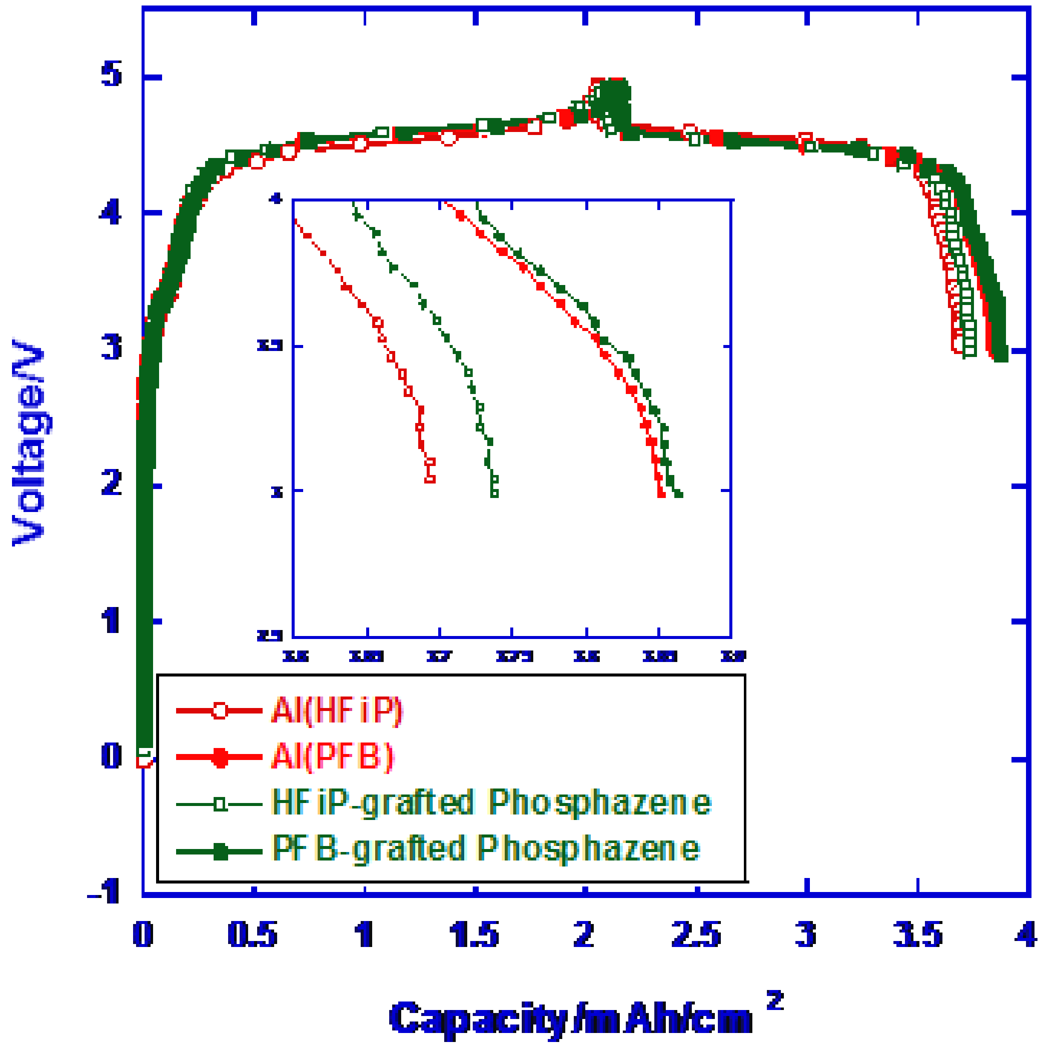
Capacity Improvement – Perfluorinated Additives



- Cells: LNMO/A12 (graphite) in baseline electrolyte with additives.
- Comparing to the partially fluorinated counterparts, Al(PFB) and PFB-grafted phosphezene were shown to improve the capacity utilization at RT.

* All LNMO and A12 electrodes were provided by ANL.

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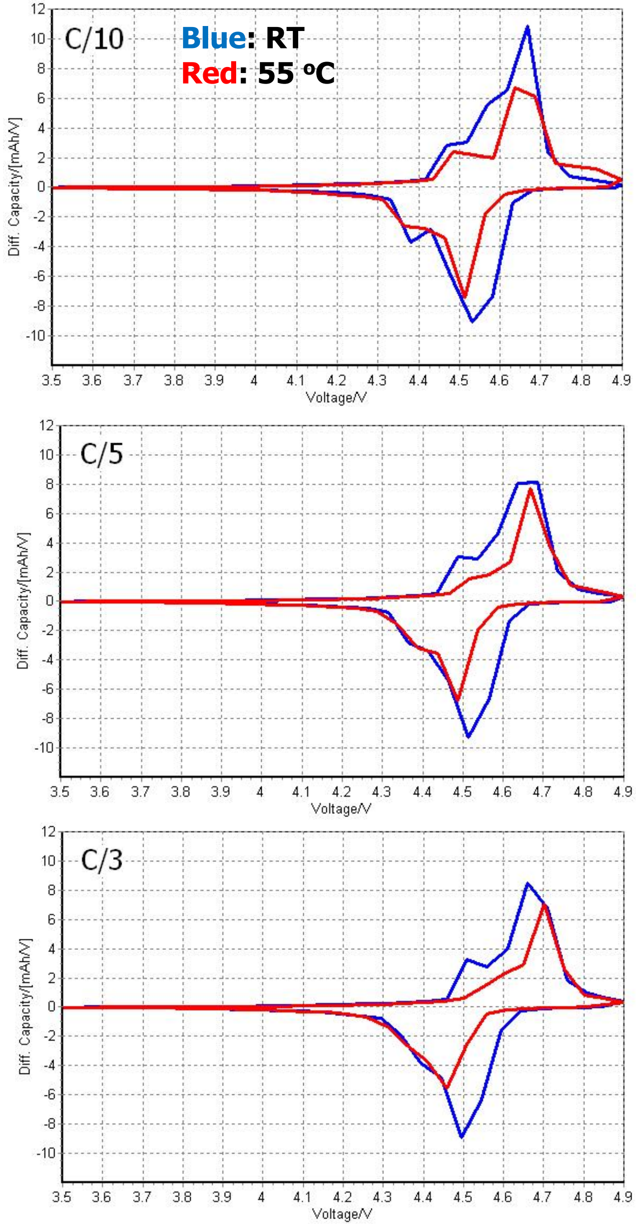
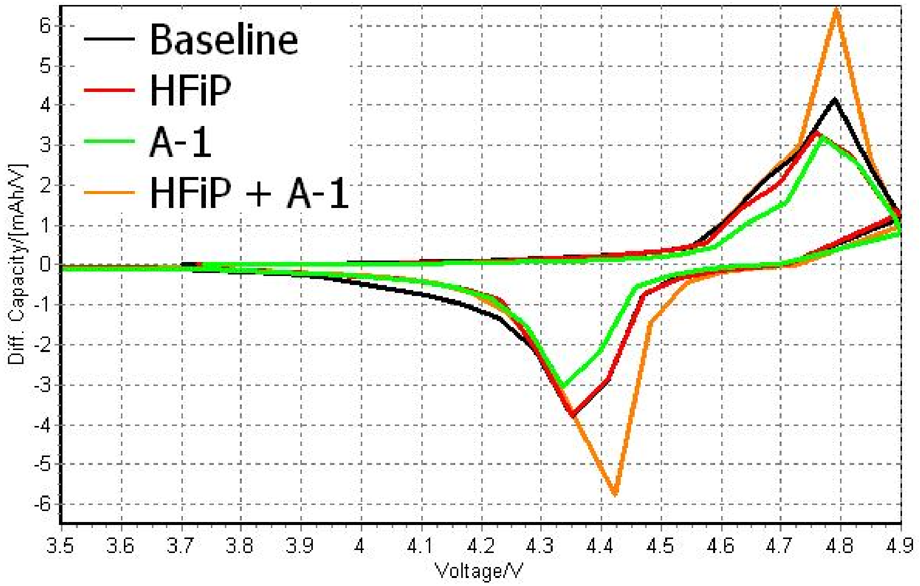
LNMO/Graphite at Room Temperature and 55 °C



- dQ/dV vs. V plots at C/10, C/5 and C/3 rates at RT and 55 °C.
- Test Cell: $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO)/Graphite (A12)
- Baseline electrolyte: 1.2 M $LiPF_6$ in EC:EMC (3:7)
- At 55 °C,
  - ✓ the cell capacity was reduced.
  - ✓ the cell impedance was increased.
- Cycling at elevated temperatures is a challenge.

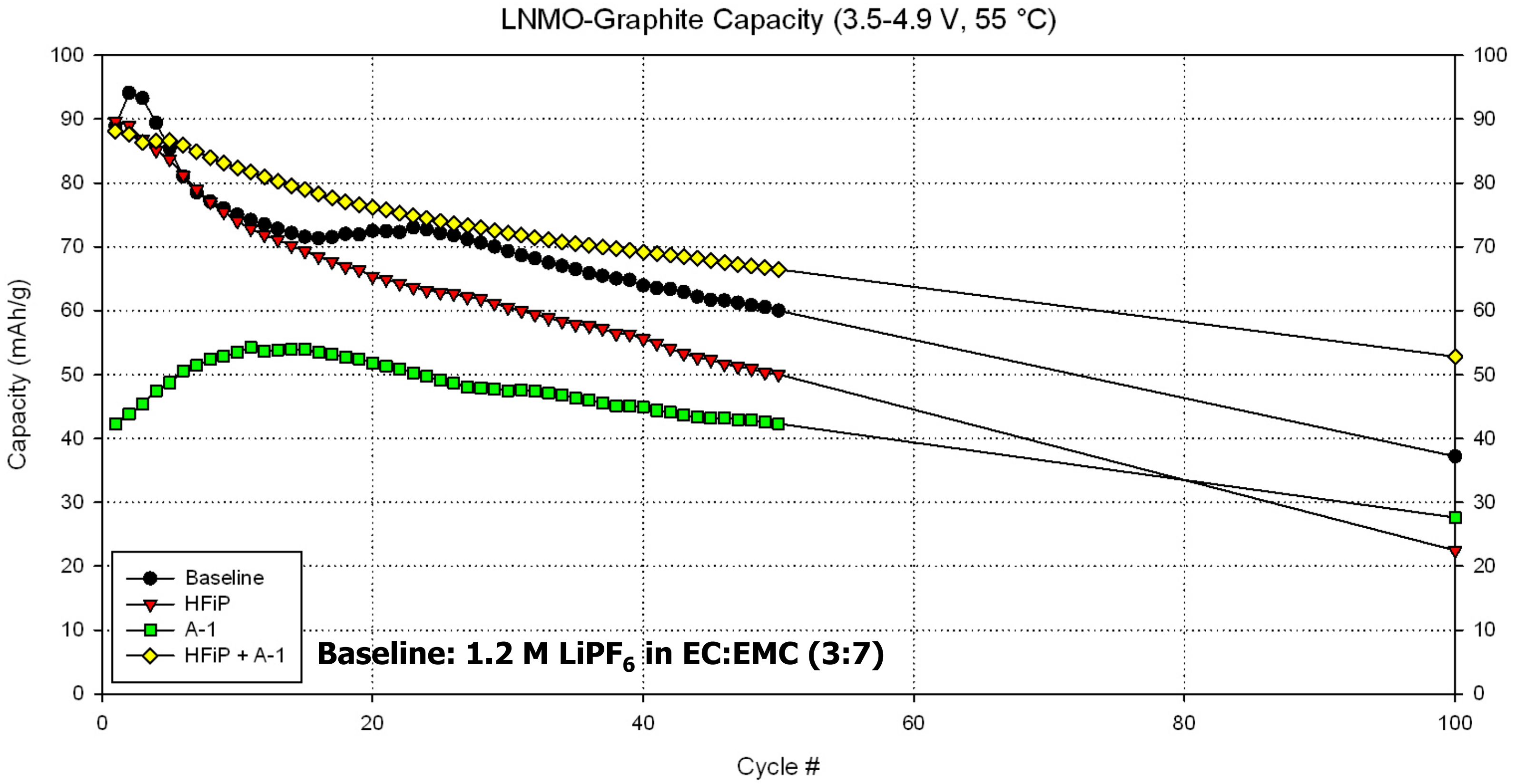
Additives in LNMO/Graphite at 55 ºC



55 ºC, 1 C Rate

- dQ/dV vs. V plots at 1 C rate at 55 ºC.
- Test Cell: $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO)/Graphite
- Electrolyte: 1.2 M $LiPF_6$ in EC:EMC (3:7) with and without additives.
- HFiP + A-1 led to faster kinetics and better performance for the cell.

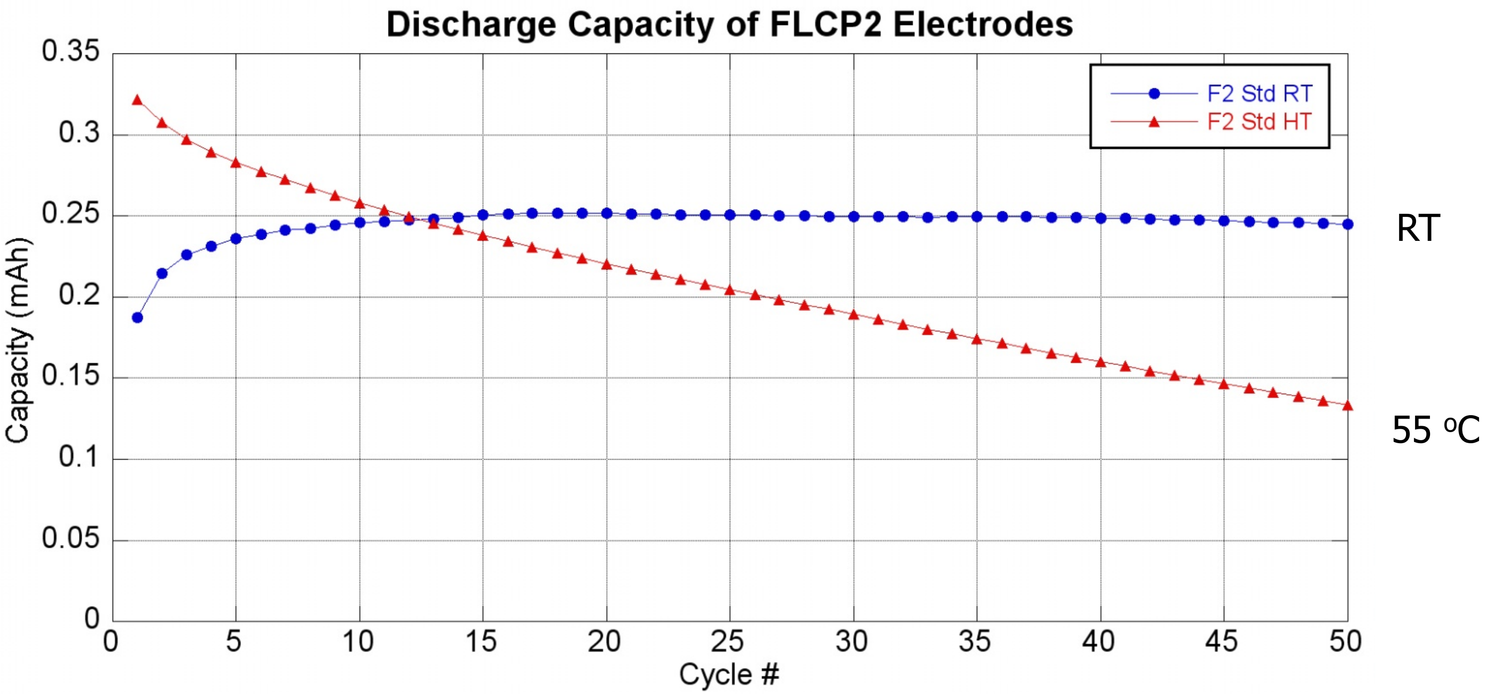
Impact of Additives in LNMO/Graphite at 55 ºC



Baseline: 1.2 M $LiPF_6$ in EC:EMC (3:7)

- At 55 ºC, either HFiP or A-1 additive alone couldn’t prevent the cell from losing capacity.
- A combination of HFiP and A-1 significantly improved the capacity retention at 55 ºC.

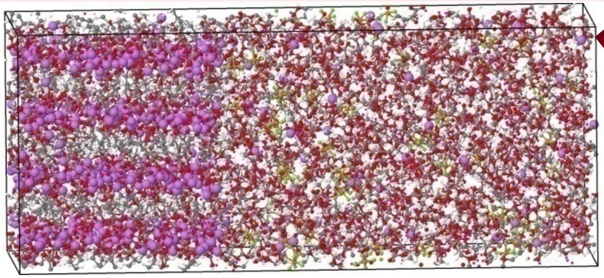
Stabilized LCP/Li at Room Temperature and 55 ^{o}C



- Test cells: Fe doped LiCoPO4 (LCFP)/Li
- Cycled between 3.5 and 4.95 V in 1.2 M $LiPF_6$ in EC:EMC(3:7)
- LCFP cycled well at RT in baseline electrolyte.
- The capacity of LCFP faded gradually at 55 ^{o}C in the baseline electrolyte suggesting thermally promoted reactions occurred between LCFP and the electrolyte.

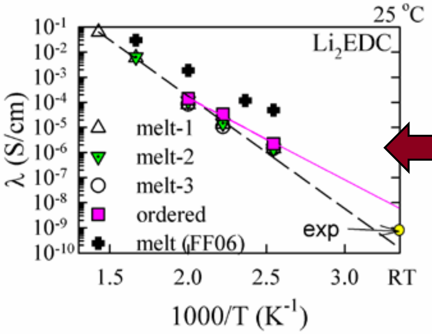
Overview of Computational Studies

Interfacial structure and the associated interfacial resistance at the SEI – electrolyte interface



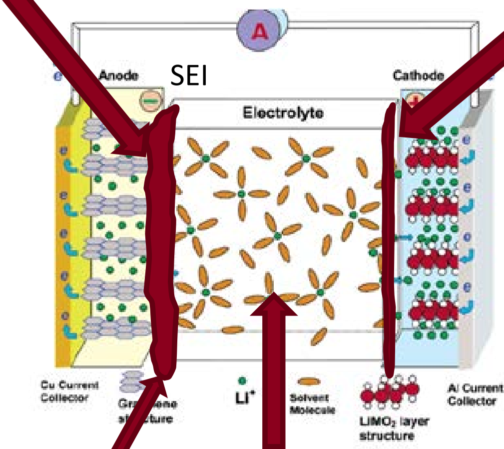
SEI : Li_2EDC EC:DMC(3:7)/$LiPF_6$

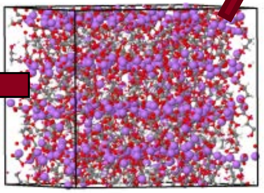
- ➢Investigating the structure and transport at SEI-electrolyte interface and SEI model compounds

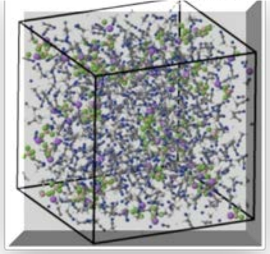


Conductivity of Li_2EDC (ΔE=64-84 kJ/mol) from Borodin, O.; Zhuang, G.V.; Ross, P.; Xu, K. J. Phys. Chem. C *2013 (in press)*

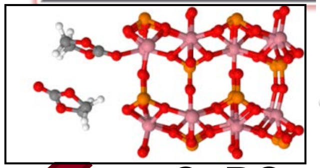
Battery picture from Kang Xu



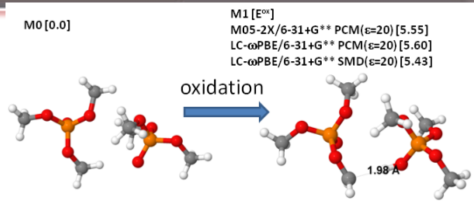




Oxidative stability and decomposition reactions of electrolytes



$CoPO_4$



Major Focus within ABR Program

Explore major classes of electrolytes:

- ➢ electrolyte additives ;
- ➢ carbonates;
- ➢ linear and cyclic sulfones (TMS, EMS);
- ➢ alkyl phosphates;
- ➢ solvents with anions : BF_4^-, PF_6^-, FSI, TFSI, DCTA, DFOB,ClO_4^-

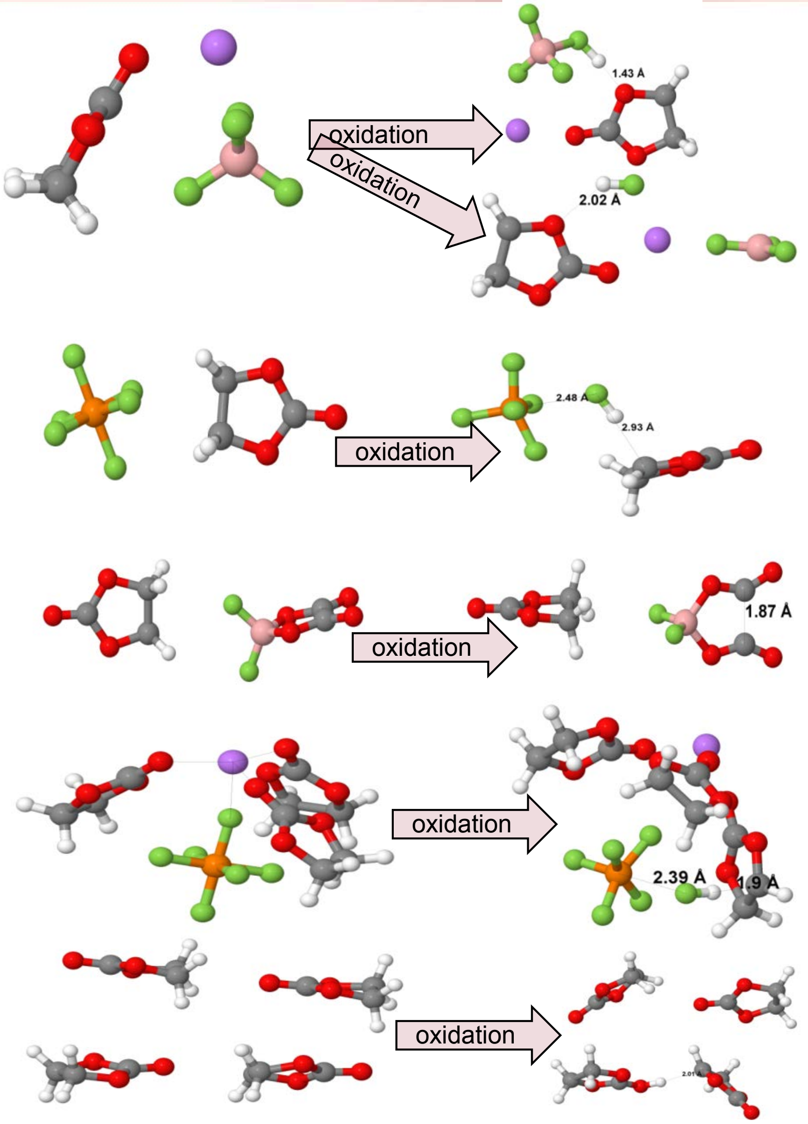
Focus on the influence of salt on the solvent and additive oxidative potential and condensed phase effects.

Xing, L.; Borodin, O. *PCCP,* **2012**, *14*, 12838
Borodin, O.; Jow. T. R. *ECS Trans. 2013* (in press)
Borodin, O.; Behl.; Jow, T. R. *J. Phys. Chem. C* 2013 *(in press)*

Structure and transport in bulk electrolytes and SEI components with a focus of Li^+ competitive solvation in mixed solvents.

Solvent-Anion Oxidation Stability

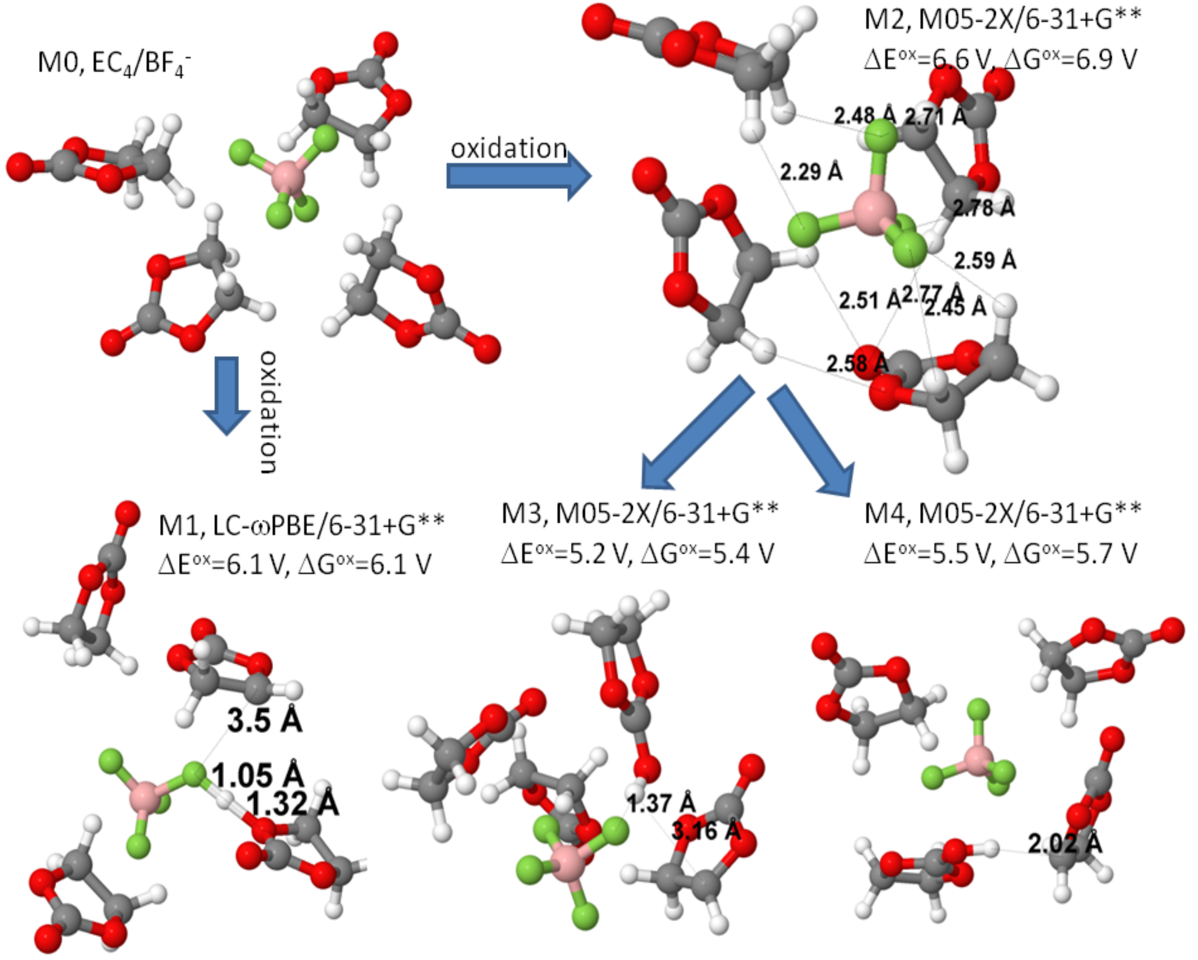
	H or F transfer	ε=1	ε=4.2	ε=20.5
DMC/BF_4^-	yes	4.14	5.79	6.21, 5.92[a]
EC/BF_4^-	yes	4.55	5.95	**6.07** (6.39, **6.21**)
EC_2/BF_4^-	yes	5.17		6.38 (6.46, **6.30**)
EC_3/BF_4^-	yes			6.55, **6.37**
EC/$LiBF_4$ (v1)	yes	8.74		6.64
EC/$LiBF_4$ (v2)	yes	8.46		6.82
$EC_2/LiBF_4$	no			(7.51, **7.31**)
$EC_2/LiBF_4$	yes			(6.72, **6.60**)
FEC/BF_4^-	yes	4.93	6.31	6.62
VC/BF_4^-	no	4.17	5.16	5.46, **5.47**
DMC/PF_6^-	yes	4.56	6.12	6.51, 6.29
EMC/PF_6^-	yes	(4.55, **4.44**)	(6.10,**5.91**)	(6.50,**6.31**)
EC/PF_6^-	yes	4.94, **4.71,**	6.27	6.57, **6.37**
EC_4/PF_6^-	yes			(6.47, **6.53**)
$EC_3/LiPF_6$	yes			6.94 (**6.78**)
PC/BF_4^-	yes	4.57		6.25
PC/PF_6-	yes	4.84, **4.63**		6.46,**6.29**
FEC/PF_6^-	yes	5.16		6.78, 6.48[a]
EMS/BF_4^-	no	5.31	6.41	6.62
TMS/PF_6^- (a)	no	5.44	6.36	6.54
TMS/PF_6^- (b)	no	5.48	6.35	6.49
EMS/PF_6^-	no	5.46	6.47	6.66
TMP/BF_4^- (a)	no			(6.47,**6.45**)
TMP/BF_4^- (b)	no			(6.68)
TMP/PF_6^-	no	5.07		6.62
EC/$DFOB^-$ (a)	No			6.03, **5.92**
EC/$DFOB^-$ (b)	No			6.08, **5.94**



Oxidation potential (adiabatic energy) of solvent/anion complexes from DFT calculations from the M05-2X/cc-pvTz and M05-2X/6-31+G** calculations denoted in parentheses.

Borodin, O.; Behl.; Jow, T. R. *J. Phys. Chem. C* 2013 *(in press)*

Oxidation of the EC_4/BF_4 Cluster



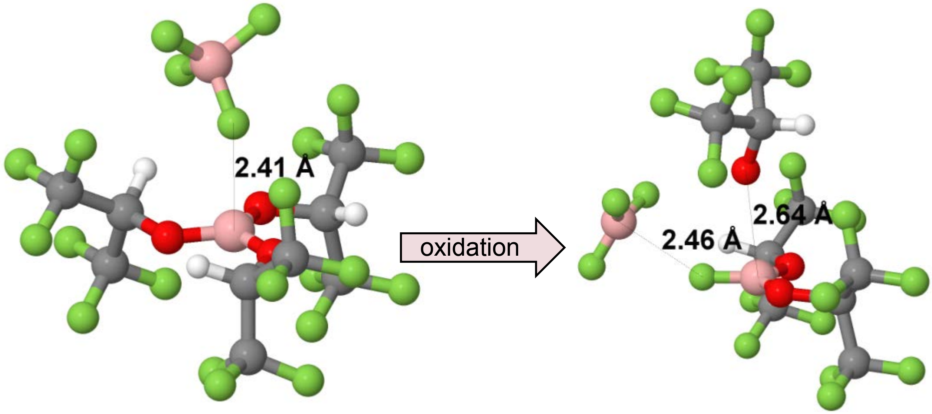
- The BF_4^- assisted H transfer from one EC to another was observed during oxidation.
- Oxidation potential for the cluster was significantly lower than the isolated EC oxidation potential of 7-7.2 eV calculated using PCM (ε=20)

Borodin, O.; Behl.; Jow, T. R. *J. Phys. Chem. C* 2013 *(in press)*

Oxidation Stability of Additives

Oxidation potential (adiabatic energy E and free energy G) vs. Li+/Li calculated using M05-2X/6-31+G** level with PCM(e=23)

	E (V)	G (V)
$PO(OCH_3)_3$ (TMP)	6.8	6.9
$PO(OCF_3)_3$ (f-TMP)	8.4	8.3
$PO(OCH(CF_3)_2)_3$ (HFiP)	8.1	
$B(OCH(CF_3)2)_3$ (HFiB)	8.6	8.5
$Al(OCH(CF_3)_2)_3$ (HFiAl)	8.0	8.0
$B(OCH(CF_3)_2)_3/BF_4^-$ ($HFiB/BF_4^-$)	7.0	6.9



Optimized geometry of HFiB/BF4- complex before and after oxidation. From M05-2X/6-31+G** calculations with PCM(ε=23)

- ➢Fluorination of trimethyl phosphate $PO(OCH_3)_3 \rightarrow PO(OCF_3)_3$ increases its intrinsic oxidation potential by 1.8 V.
- ➢HFiP and HFiAl additives have 0.3-0.4 V lower intrinsic oxidative stability compared to f-TMP, while HFiB has the highest oxidative stability of 8.6 V among additives.
- ➢Presence of fluorinated anions such as BF_4^- significantly decreases additive oxidative stability, for example, $HFiB/BF_4^-$ oxidative stability is 1.6 V lower than that of HFiB due to spontaneous fluorine transfer from BF_4^- to HFiB and B-O bond cleavage as shown in Figure above.

Collaboration/Coordination

- ANL – Gregory Krumdick: For scaling up ARL developed HFiP and PFBP additives.
- ANL – Bryant Polzin: Providing high voltage and high energy electrodes and A12 graphite electrodes.
- ANL – Javier Bareno Garcia-Ontiveros, Ira Bloom: Discussion on Post Test Facility.
- ANL – Zhengcheng John Zhang: Information exchange and discussion.
- ANL – Anthony Burrell, Dennis Dees, Khalil Amine: Coordination and discussion.
- LBNL – Michel Foure, Guoying Chen, Vincent Battaglia: Information exchange and discussion.
- U. of Rhode Island – Brett Lucht: Information exchange and discussion.

Future Work

- Continue testing of new additives or combination of additives in baseline electrolyte in LNMO/graphite full cells at elevated temperatures.
- Understand the capacity fading mechanism at elevated temperatures through more detail electrochemical methods and surface characterization analysis.
- Perform computational screening of redox stability and understand decomposition reactions of the electrolyte with electrode materials using DFT calculations.
- Continue to develop and collaborate with cathode materials developers for developing more stabilized high voltage cathode materials.

Summary

- Perfluorinated additives including PFBP and Al(PFB) showed much improved cycle life compared to the partially fluorinated counterparts in LNMO/graphite system at RT.
- Cycling of LNMO/graphite at 55 ^{o}C is a challenge. The capacity retention of LNMO/graphite system was greatly improved in the electrolyte containing a combination of HFiP and A-1 over that containing HFiP or A-1 alone.
- LCFP/Li half cell could be cycled well in baseline electrolyte at RT but showed gradual capacity fading at 55 ^{o}C.
- Oxidation potentials of solvents including additives calculated using DFT would be lowered by the presence of anions and were in agreement with experiments. EC/PF_6^- has higher oxidation stability than EC/BF_4^-.

Acknowledgements

- DOE ABR Program
  - Peter Faguy, Tien Duong, David Howell
- National Labs
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  - BNL: Dr. X. Yang
- NRL
  - Drs. Michelle Johannes, Khang Hoang
- U. of Maryland
  - Dr. Karen Gaskell