Fluorinated Electrolyte for 5-V Li-Ion Chemistry

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Argonne National Laboratory

Vehicle Technologies Program
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Project ID #: ES218

Project Overview

Timeline

- Project start date: Oct. 1, 2013
- Project end date: Sept. 30, 2015
- Percent complete: 25%

Barriers

- Battery life: conventional organic carbonate electrolytes oxidatively decompose at high potential (> 4.5 V *vs* Li^+/Li)
- Battery performance: poor oxidation stability of the electrolyte limits the battery energy density
- Battery Abuse: safety concern associated with high vapor pressure, flammability and reactivity

Budget

- Total project funding
  - 100% DOE funding
- Funding received in FY14: $362 K
- Funding for FY15: $338 K

Partners

- U.S. Army Research Lab (collaborator)
- Brookhaven National Laboratory (collaborator)
- University of Rhode Island (interaction)
- Jet Propulsion Laboratory (interaction)
- Dr. Larry Curtiss – Theoretical modeling
- Project Lead - Argonne National Laboratory

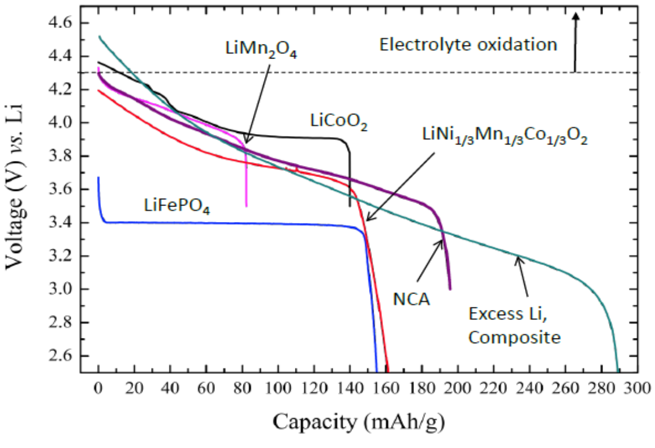
Project Objective

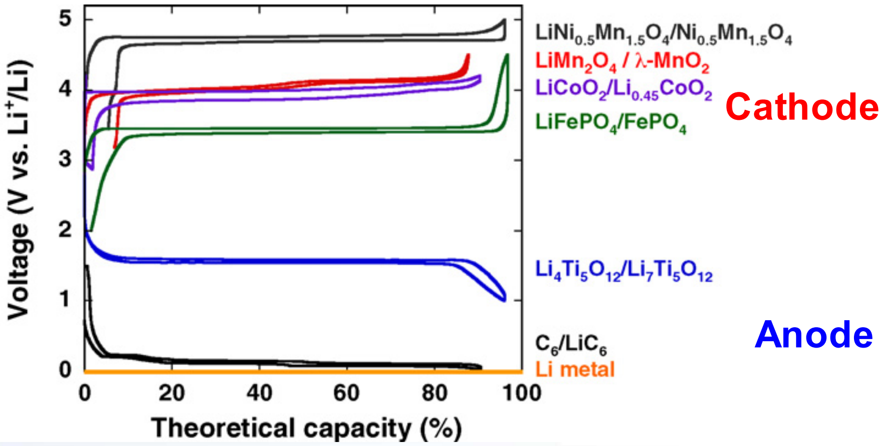
- ❑ To develop advanced electrolyte materials that can significantly improve the electrochemical performance without sacrificing the safety of lithium-ion battery of high voltage high energy cathode materials to enable large-scale, cost competitive production of the next generation of electric-drive vehicles.
- ❑ To develop electrolyte materials that can tolerate high charging voltage (>5.0 V vs Li^+/Li) with high compatibility with anode material providing stable cycling performance for high voltage cathode including 5-V $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) cathode and high energy LMR-NMC cathode recently developed for high energy high power lithium-ion battery for PHEV and EV applications.
- ❑ FY14's objective is to identify and screen several high voltage electrolyte candidates including fluorinated carbonates with the aid of quantum chemistry modeling and electrochemical methods and to investigate the cell performance of the formulated electrolytes in LNMO/LTO and LNMO/graphite chemistries.

<u>Advanced Electrolytes Enabling High Voltage and High Capacity Cathode Materials</u>

Capacity ⇨

Voltage ⇨





Approach

- ☐ R&D groups all over the world work on improving electrode materials in order to maximize both energy and power density of Li batteries. High voltage cathode ($Li[MMn]_2O_4$, M=Ni, Cr, Cu) and high capacity layered cathode ($Li[NiMnCo]O_2$) red-ox potentials approach 5.0 V and 4.6 V *vs* Li^+/Li. Conventional alkyl carbonates/$LiPF_6$ tend to be oxidized around 4.5 V. Development of high voltage electrolyte is urgent and challenging.

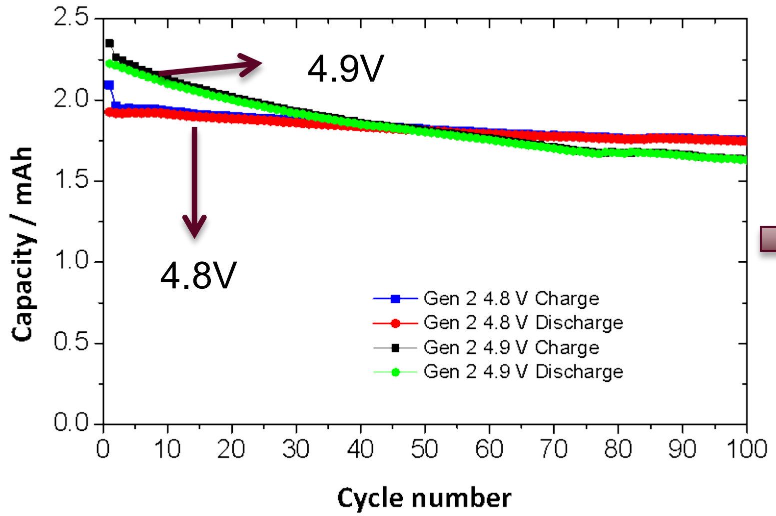
- ☐ Our overall approach for high voltage electrolyte research is to first design, synthesize and characterize fluorinated solvent candidates with the aid of quantum chemistry calculation; then screen the electrochemical properties of the synthesized solvents and validate their oxidation stability using 5-V $LiNi_{0.5}Mn_{1.5}O_4$ /Li or $LiNi_{0.5}Mn_{1.5}O_4$ /LTO cells. Tailored electrolyte additive will be developed in combination with the main fluorinated electrolyte to enable the high voltage cathodes coupled with graphite and silicon anode.

- ☐ Fluorinated High Voltage Electrolyte research will be integrated with high voltage/capacity cathode projects in DOE ABR and BATT program. Various new fluorinated solvent systems including fluorinated carbonates, fluorinated sulfones, and fluorinated esters. Synergy effect of electrolyte containing hybrid solvents will also be explored to enable the high energy high power lithium-ion battery for PHEV and EV applications.

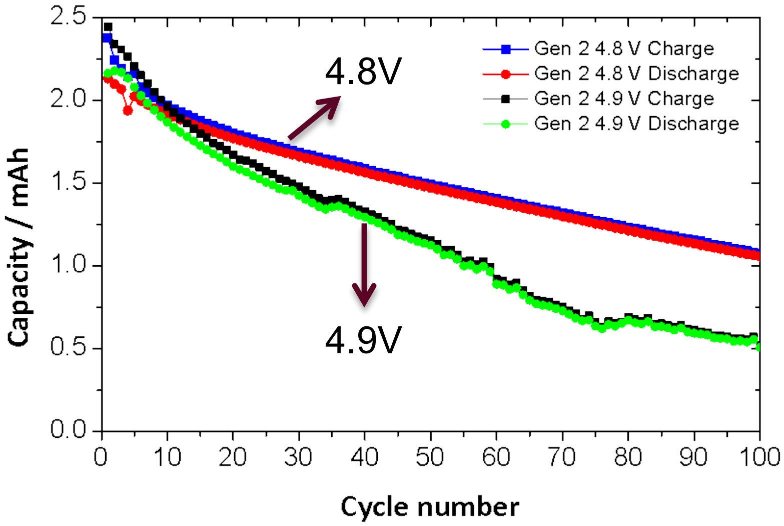
Technical Accomplishments and Progress

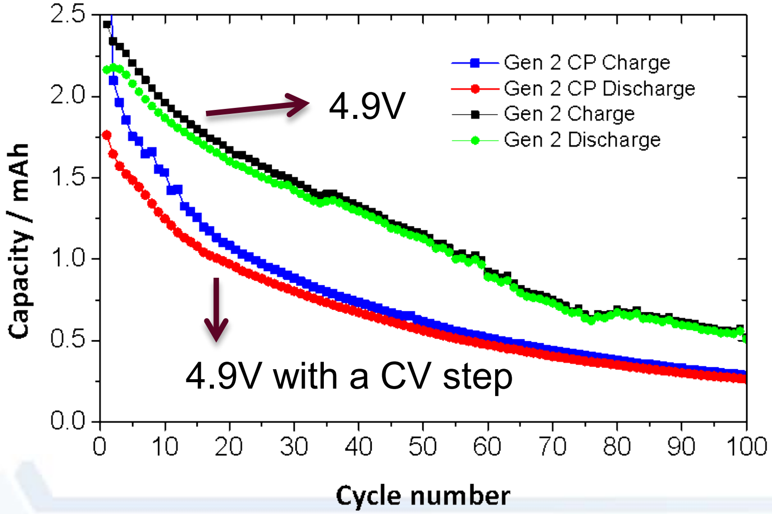
- 5-V Ni/Mn Spinel $LiNi_{0.5}Mn_{1.5}O_4$: the Challenge
  Instability of the cathode surface in contact with electrolyte at 4.8 V, especially at high T

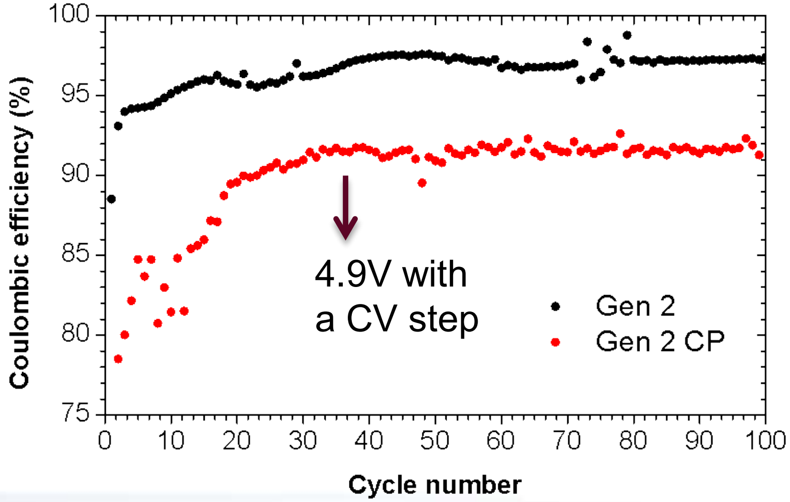
$LiNi_{0.5}Mn_{1.5}O_4$/1.2M $LiPF_6$ EC/EMC (3/7 wt%) / Graphite, cycled at RT and 55°C



55°C



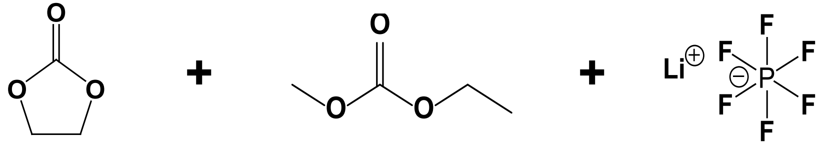


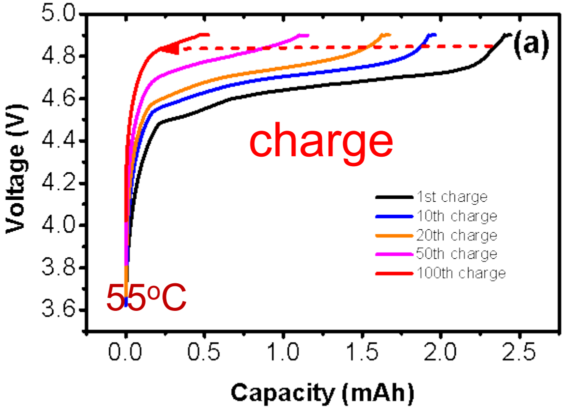


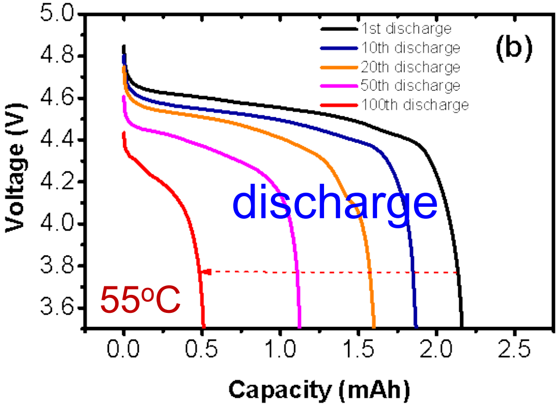
❑ 5-V Ni/Mn Spinel $LiNi_{0.5}Mn_{1.5}O_4$: the Challenge

LNMO and graphite electrode surface morphology change when cycled with electrolyte at high T

1.2M $LiPF_6$ EC/EMC 3/7 in weight



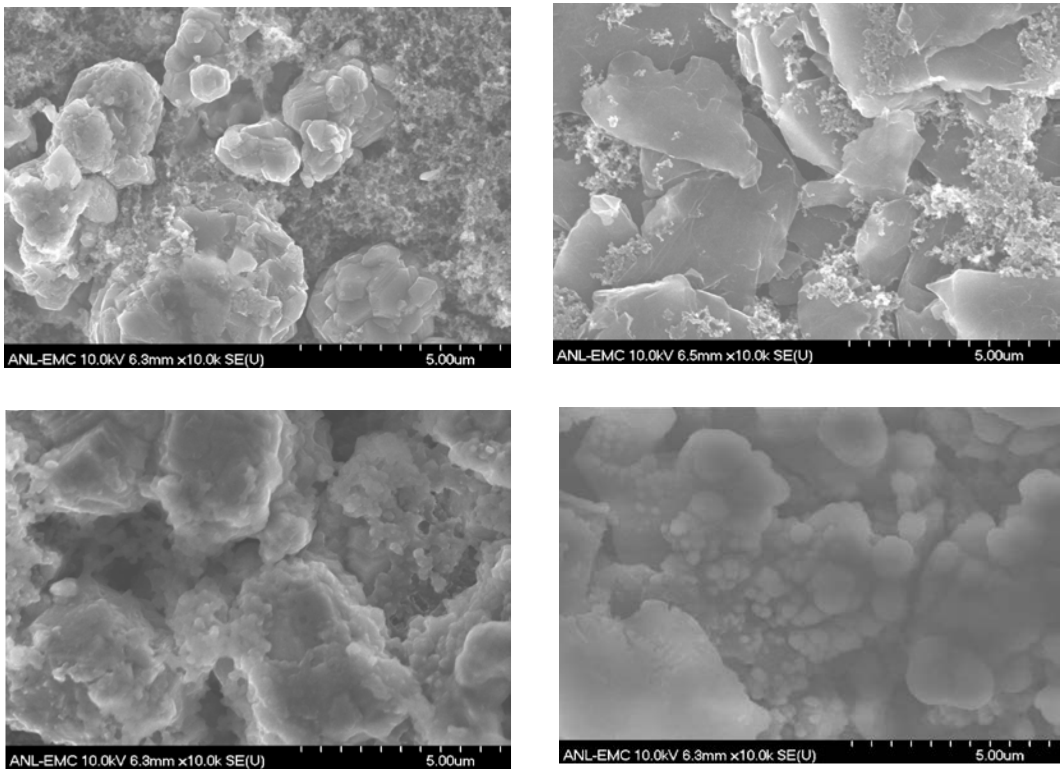




$LiNi_{0.5}Mn_{1.5}O_4$ **Graphite (A12)**

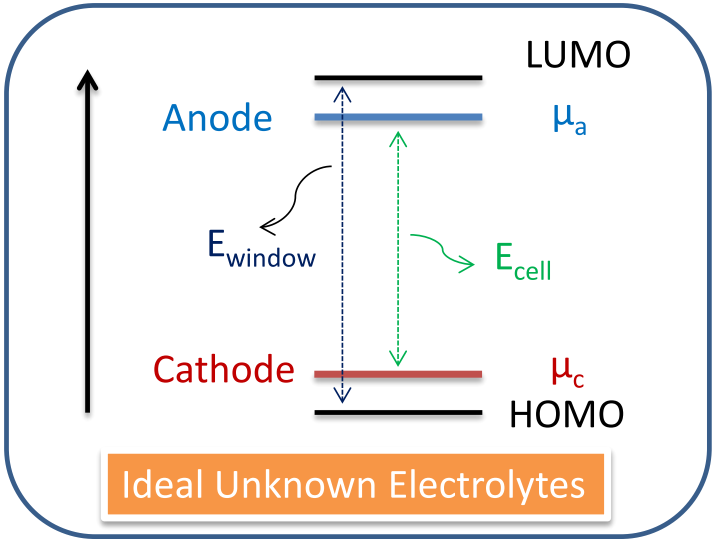
Pristine

Cycled at 55°C

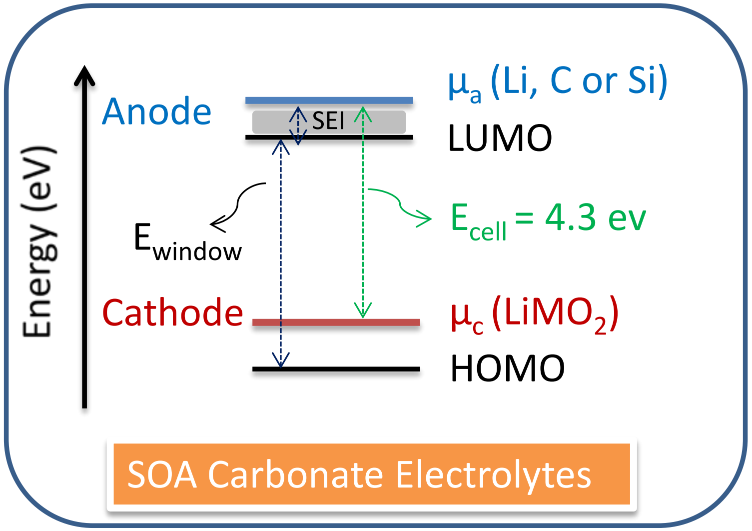


Thick layer of electrolyte deposition on both electrode surfaces

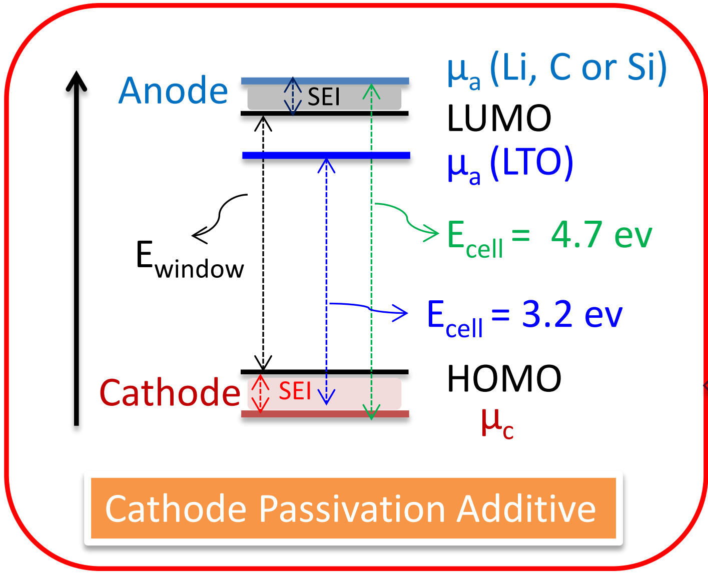
Electrolyte Design for High Voltage Cathode Materials



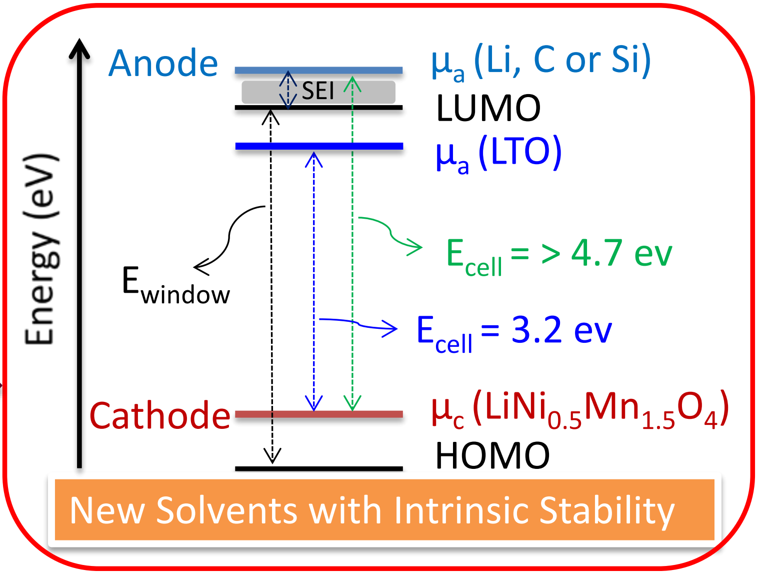
Ideal Unknown Electrolytes



SOA Carbonate Electrolytes



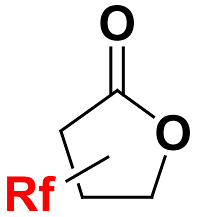
Cathode Passivation Additive



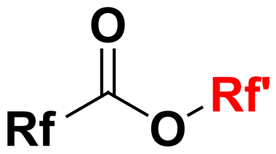
New Solvents with Intrinsic Stability

Combined Approach for this Electrolyte Project

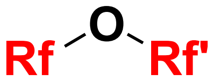
Molecular Engineering Towards Intrinsic Oxidation Stability



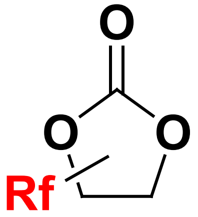
F-cyclic ester



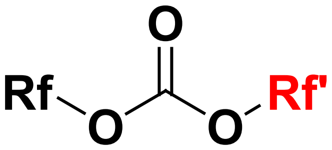
F-ester



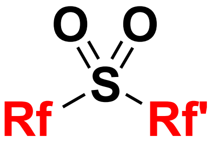
F-ether



F-cyclic carbonate



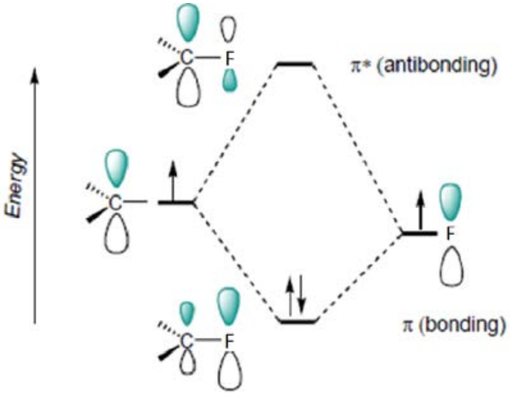
F-linear carbonate

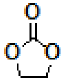
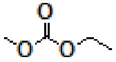
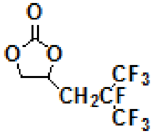
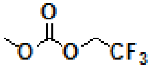
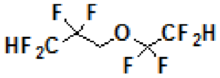


F-sulfone

- ❑ Introduction of fluorine (F) and/or fluorinated alkyl groups (Rf) to organic solvents including cyclic and linear carbonates, sulfones, cyclic and linear esters, and ethers to increase the voltage stability of electrolyte.
- ❑ Molecular engineering to obtain partially or per-fluorinated solvents to afford an improved oxidation stability.

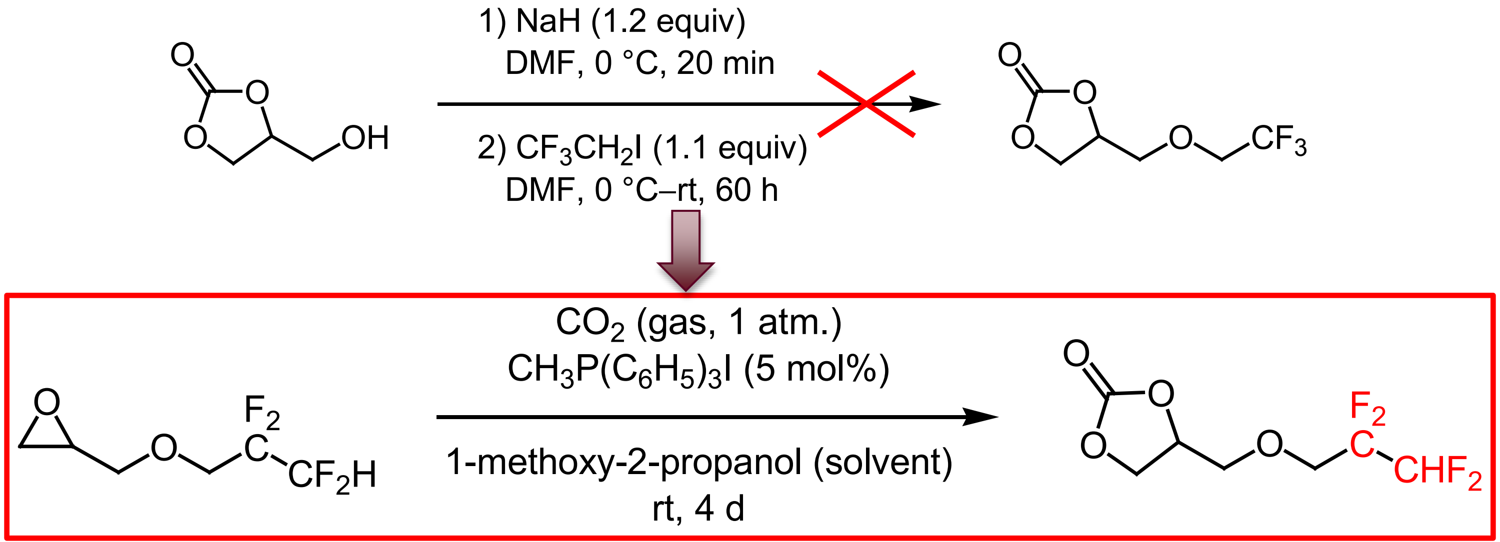
DFT Calculation to Predict the Oxidation Potentials of Fluorinated Molecules Prior Organic Synthesis

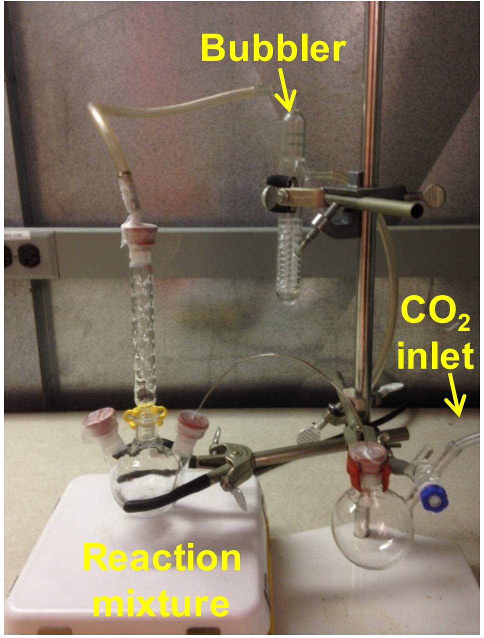


Molecule	Structure	Pox (V Theory)	HOMO (au)	LUMO (au)
EC		6.91 (6.83 open)	-0.31005	-0.01067
EMC		6.63	-0.29905	0.00251
EPE		5.511	-0.26153	0.00596
F-AEC		6.98	-0.31780	-0.01795
F-EMC		7.01	-0.31946	-0.00363
F-EPE		7.24	-0.35426	-0.00356

- Electron-withdrawing groups of -F and -Rf groups lower the energy level of the HOMO, thus increase the theoretical oxidation stability of the F-compounds.
- DFT calculation indicates fluorinated molecules generally have much higher theoretical oxidation potentials than their non-fluorinated counterparts.

Synthesis of Fluorinated Carbonates: Cyclic Carbonates





Reaction setup

Vacuum distillation-purification

TFP-PC-E

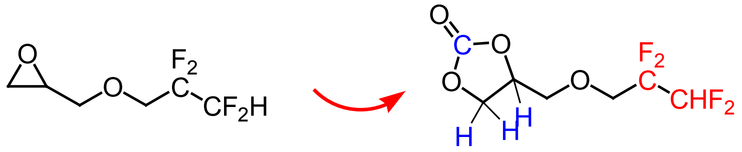
(**Tetrafluoropropyl-Propylene Carbonate-Ether**)

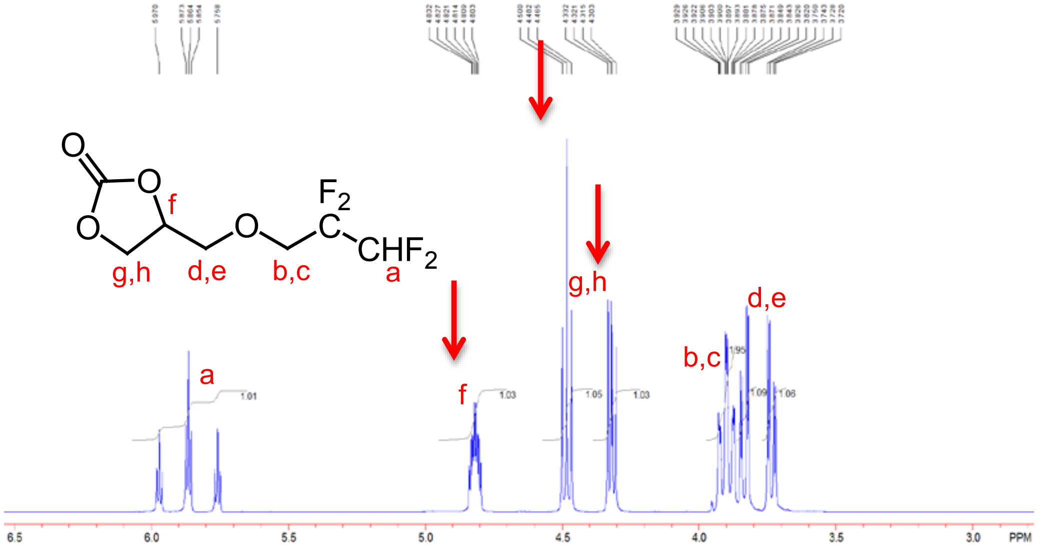
1) Reaction proceeded cleanly to 80% conversion after day 1, then gradually increased to >97% on day 4 (GC-MS without internal standard calibration);
2) Crude product was obtained after removal of the solvent and dried by 4Å molecular sieves;
3) Vacuum distillation (90 C/0.3 mmHg) twice gave pure product (>99.8% by GC-MS), ~45% yield;
4) Pure product was further characterized by ^{1}H NMR, ^{13}C NMR, FT-IR, and K-F titration (~80 ppm H_2O content).

Spectroscopic Identification of Tetrafluoropropyl-Propylene Carbonate-Ether

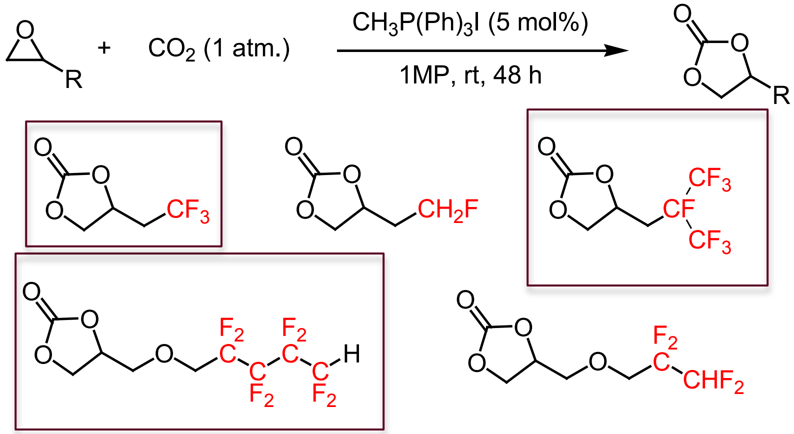
TFP-PC-E

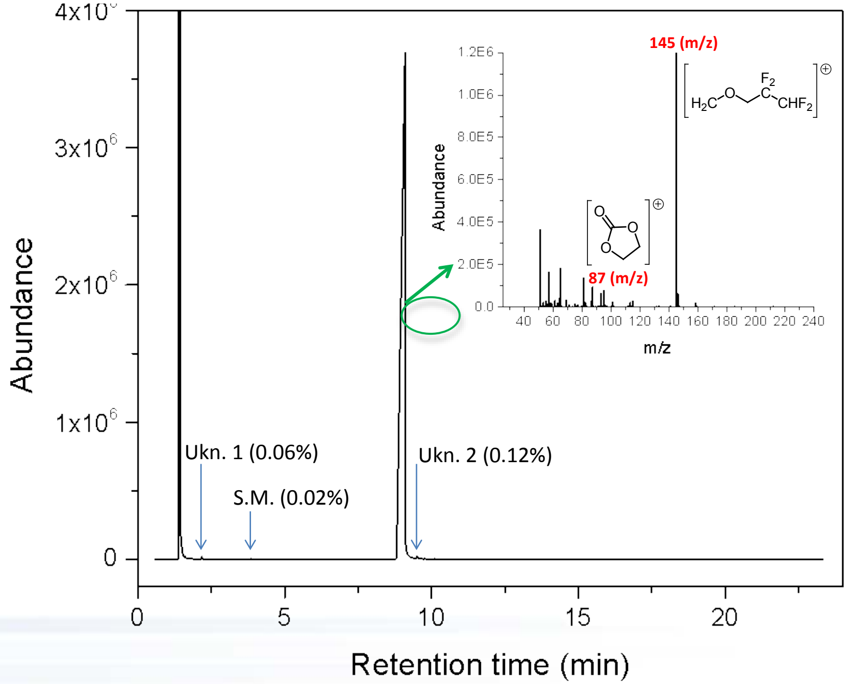
(Tetrafluoropropyl-Propylene Carbonate-Ether)



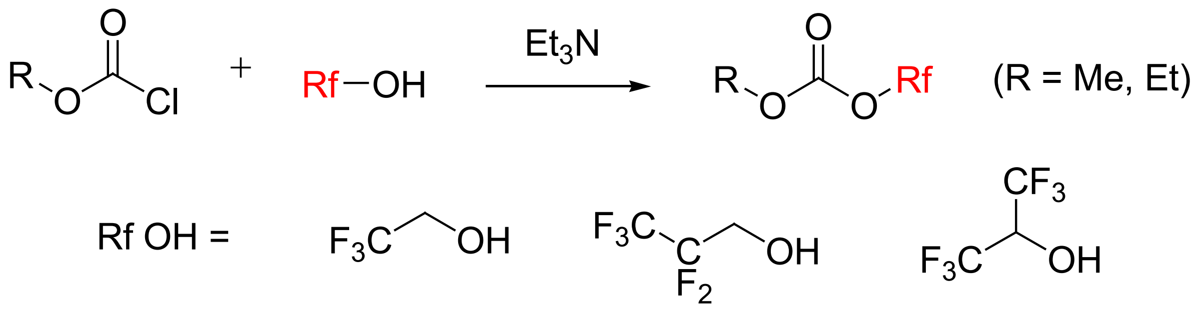


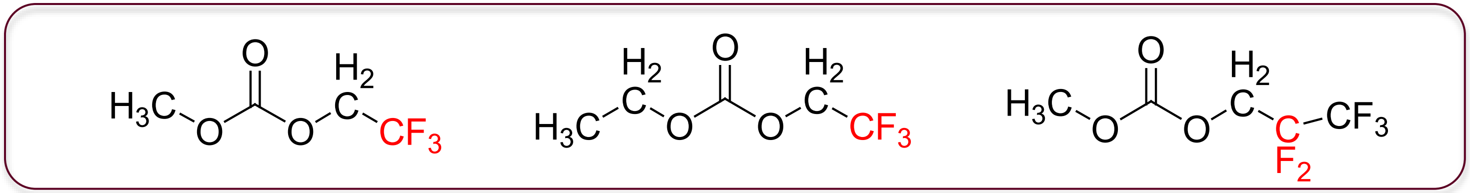
Other cyclic carbonate targets



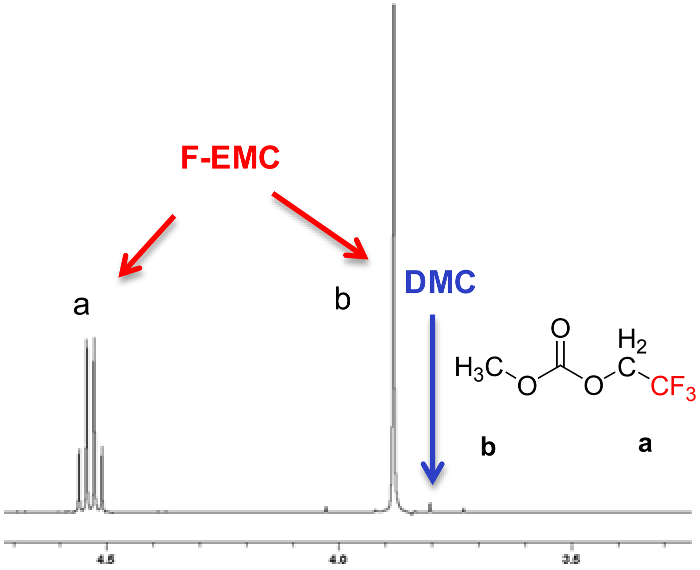


Synthesis of Fluorinated Carbonates: Linear Carbonates



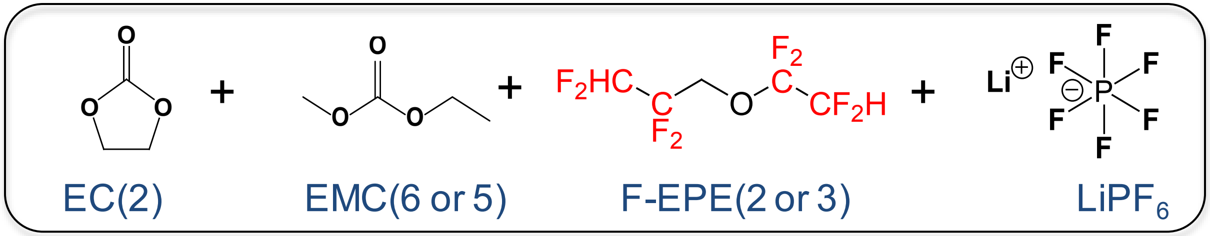


- GC-MS analysis: purity > 99.8%, (carbonate vs. DCM and TFE)
- NMR analysis: DCM and TFE is trace and cannot be accurately integrated. The amount of dimethyl carbonate is around 0.5 mol %, and the amount of F-DEC can be disregarded.
- Karl-Fischer titration: < 20 ppm moisture.



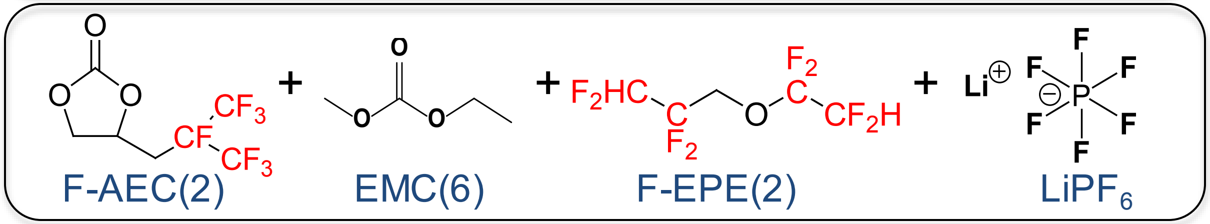
Formulation of Fluorinated Carbonates-Based Electrolytes

E1
E2



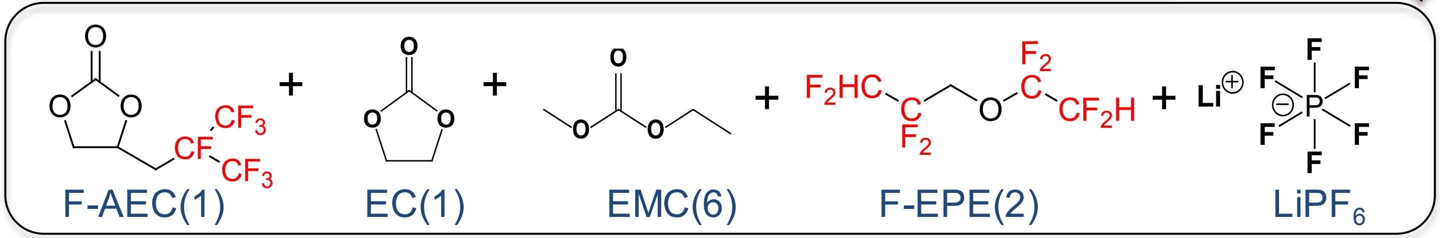
EC(2) + EMC(6 or 5) + F-EPE(2 or 3) + $LiPF_6$

E3



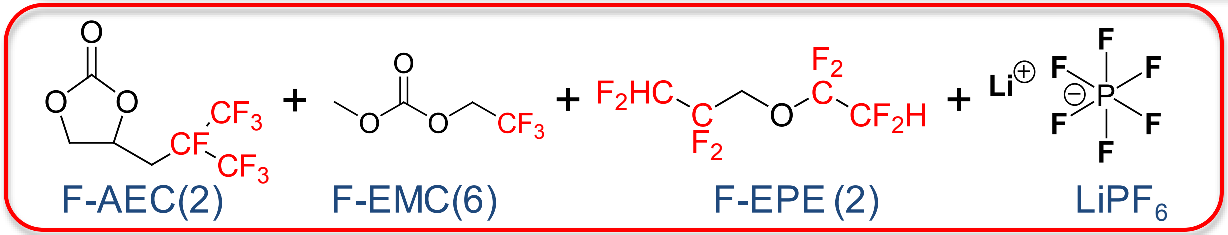
F-AEC(2) + EMC(6) + F-EPE(2) + $LiPF_6$

E4



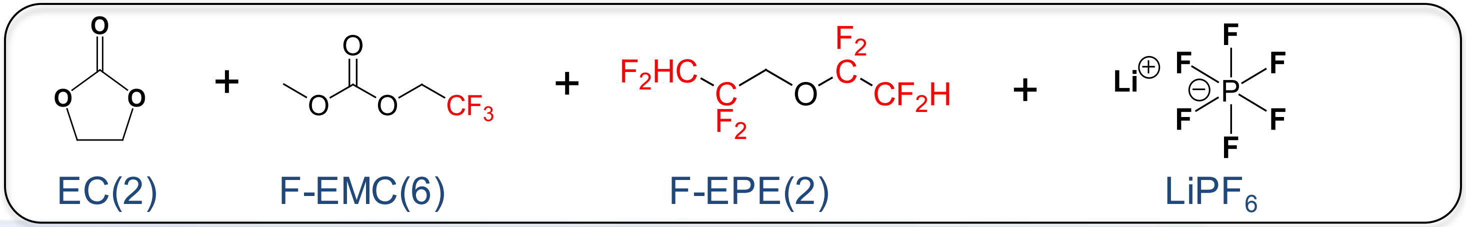
F-AEC(1) + EC(1) + EMC(6) + F-EPE(2) + $LiPF_6$

E5



F-AEC(2) + F-EMC(6) + F-EPE (2) + $LiPF_6$

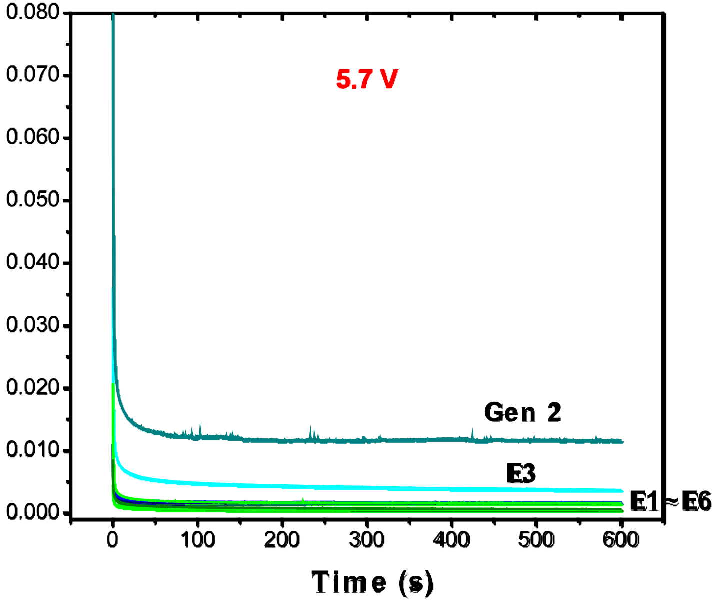
E6



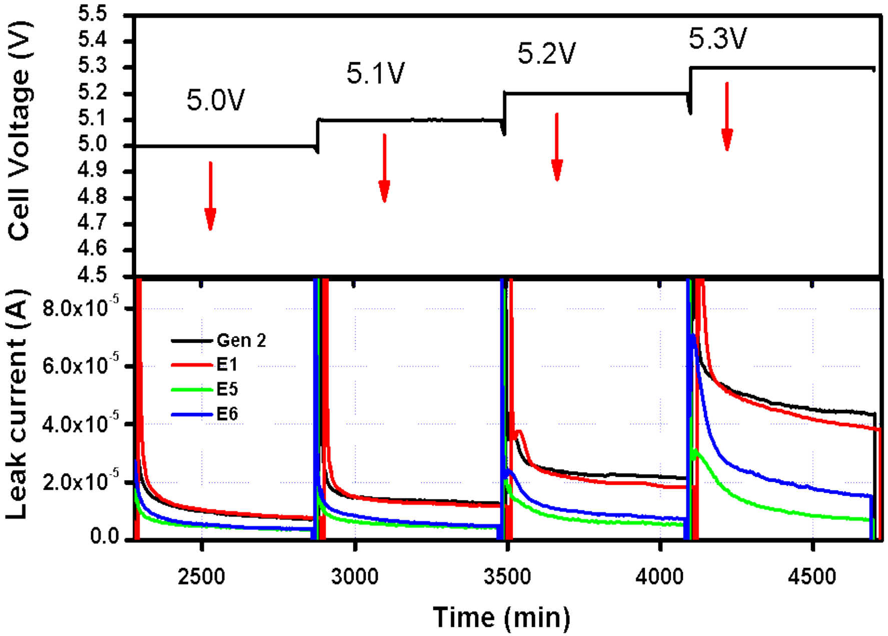
EC(2) + F-EMC(6) + F-EPE(2) + $LiPF_6$

Electrochemical Oxidation Stability of Fluorinated Carbonate Electrolytes - Floating Test

❑ Three-electrode electrochemical cell with Pt as working electrode and Li as reference and counter electrode.



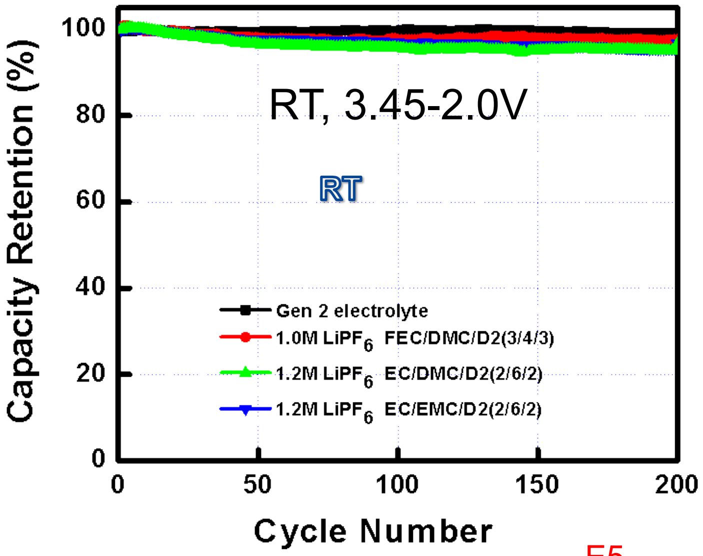
❑ *Constant voltage charge curve of $Li/LiNi_{0.5}Mn_{1.5}O_4$ half cells maintained at 5.0 V, 5.1 V, 5.2 V, and 5.3 V for 10 hours at RT.*

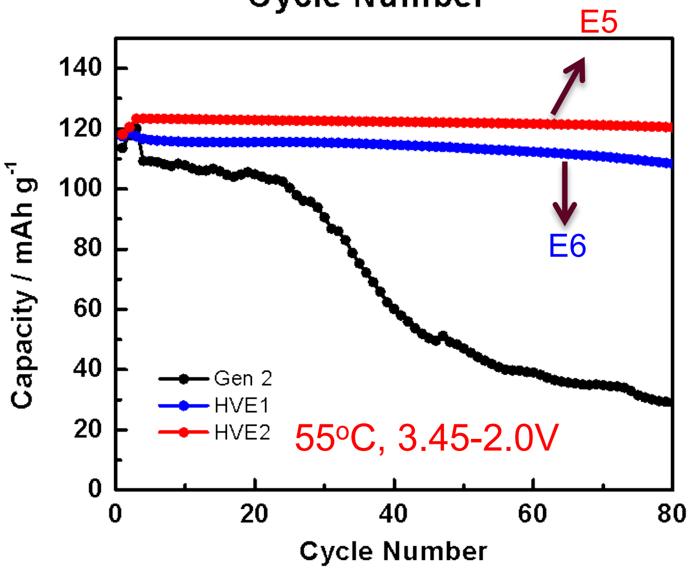


- ✓ Formulations with fluorinated solvent, especially the all-fluorinated formulation E5, shows much higher oxidation stability (lower leakage current) than the conventional electrolyte Gen 2.
- ✓ The leakage current tested with the active electrode material LNMO is similar to the results obtained from the cyclic voltammetry using three electrode electrochemical cells.

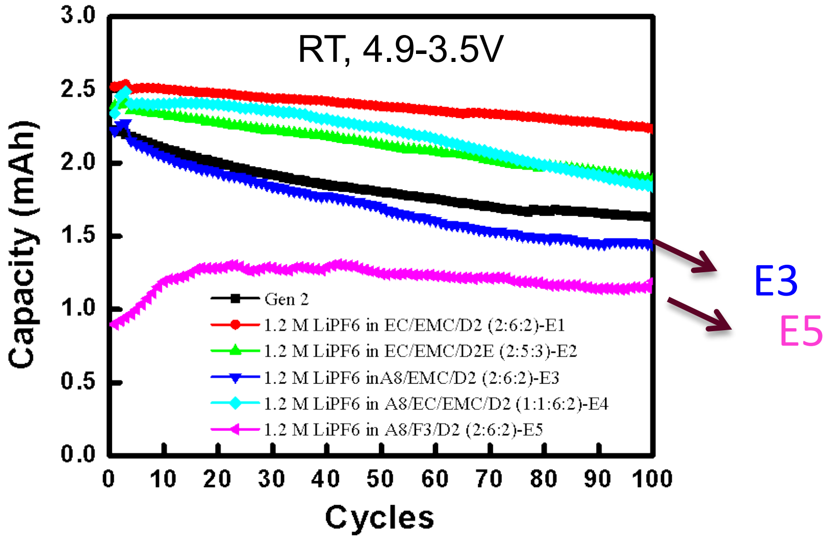
High Temperature Performance of Fluorinated Electrolyte

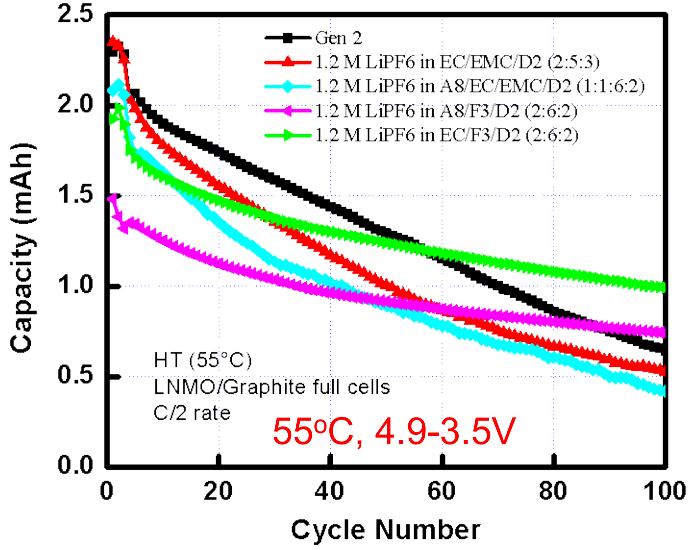
LNMO/LTO





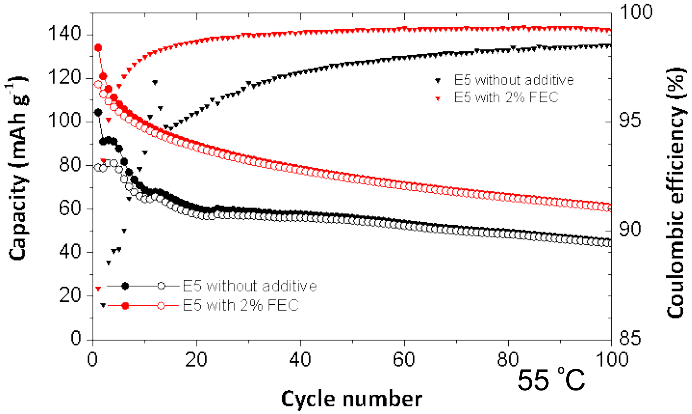
LNMO/Graphite

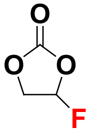




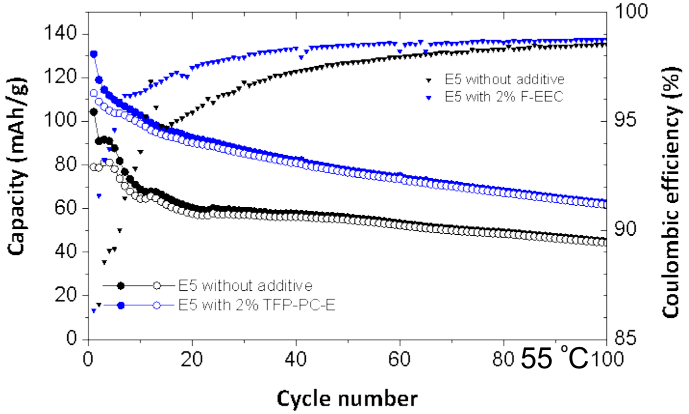
Electrolytes with F-AEC as the only cyclic carbonate (E3 and E5) have SEI formation issue on graphitic anode.

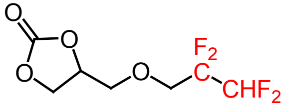
Fluorinated Carbonate Electrolyte with Graphite SEI Formation Additives





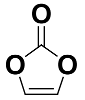
FEC



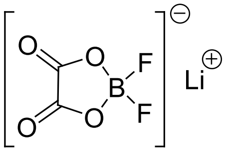


TFP-PC-E

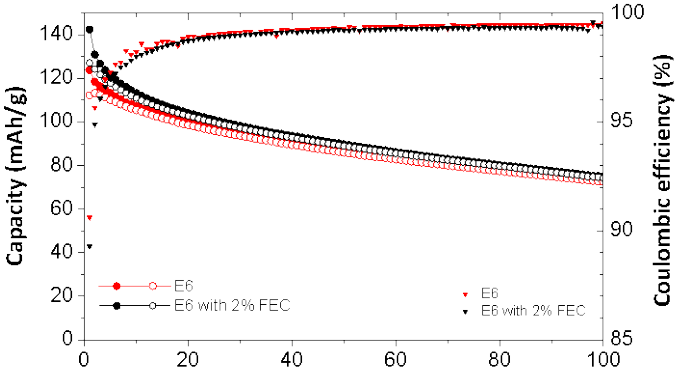
SEI formation additives works moderately well with E5 electrolyte , but has minimal effect on E6 electrolyte in which ethylene carbonate (EC) was used.

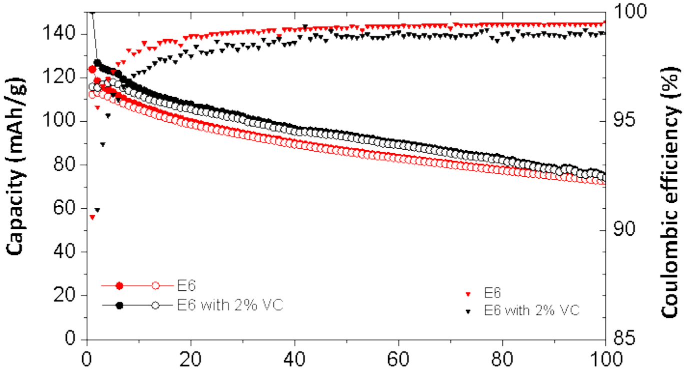


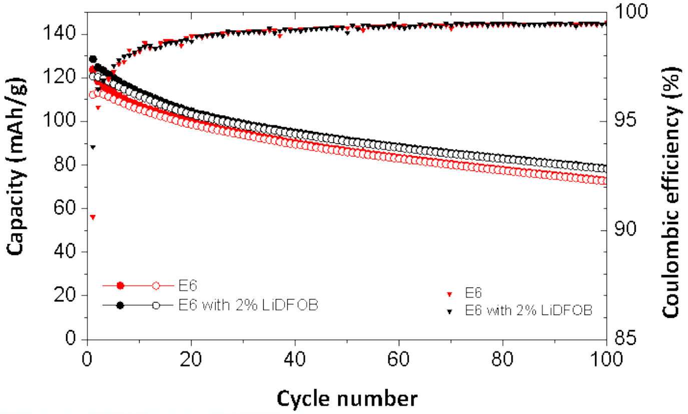
VC



LiDFOB

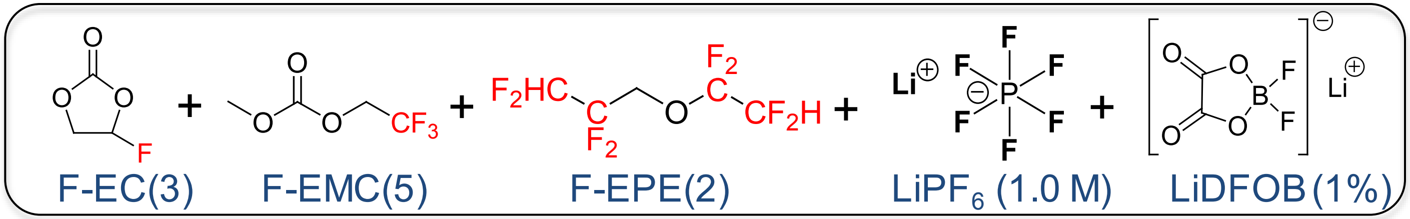


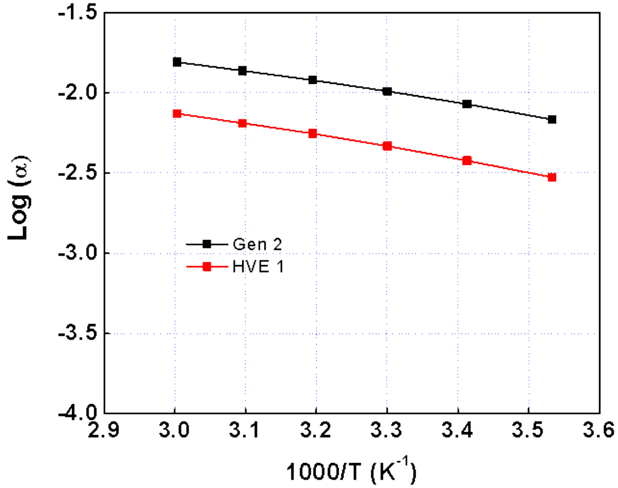




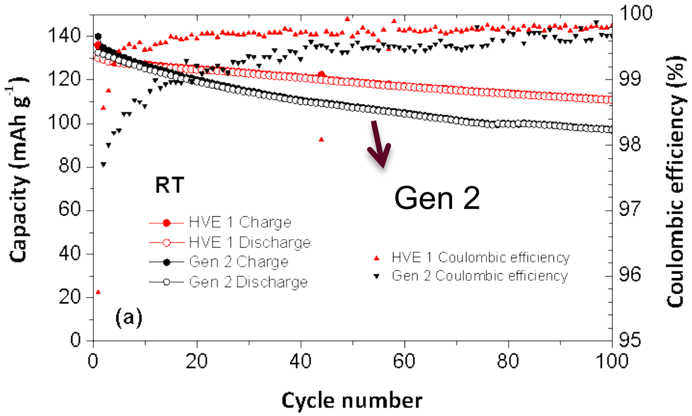
New Generation of Fluorinated Carbonate Electrolyte for LNMO/Graphite Cells

HVE 1



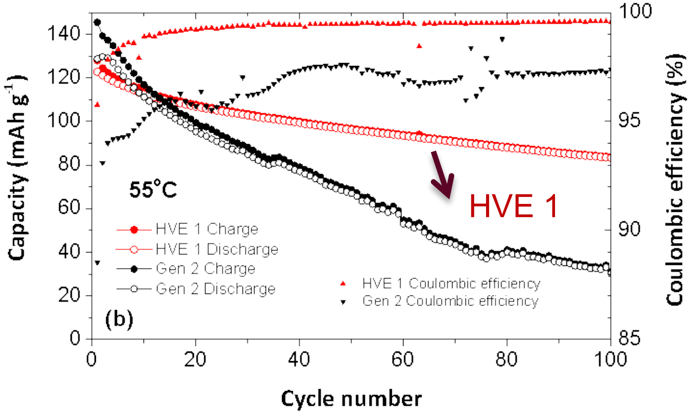


RT



LNMO/graphite cell
Cycled between 3.5-4.9 V,
C-rate: C/3,
Tested at RT
and 55 ºC, respectively.

55ºC



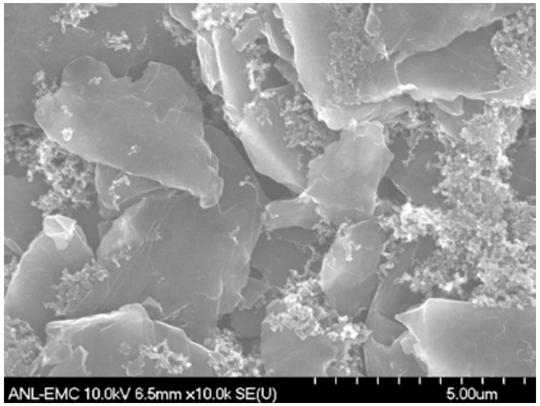
The new formulation HVE 1 shows tremendous compatibility with graphite surface as indicated by the improvement in LNMO/graphite cells compared with Gen 2 electrolyte, especially at 55 ºC.

Electrode Morphology after Cycling with HVE 1 at 55 °C

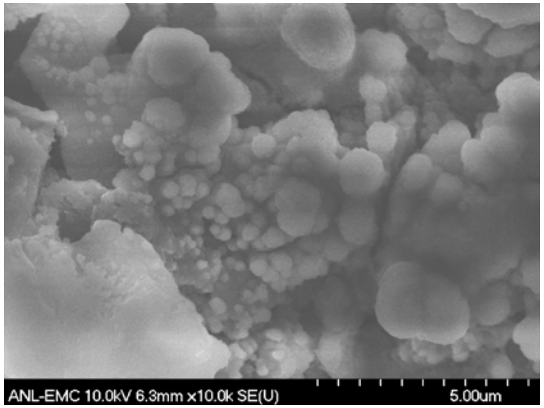
Pristine Electrode

Cycled Electrode @ 55°C, 100th cycle

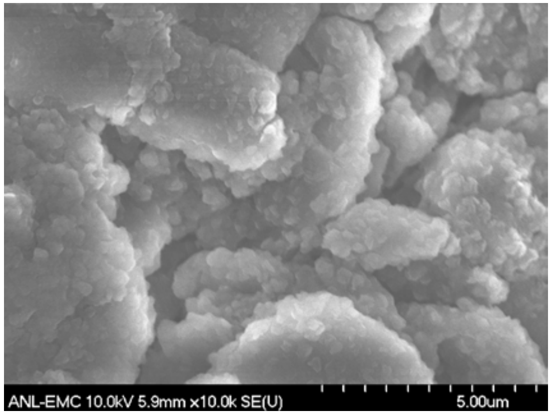
Cycled Electrode @ 55°C, 100th cycle



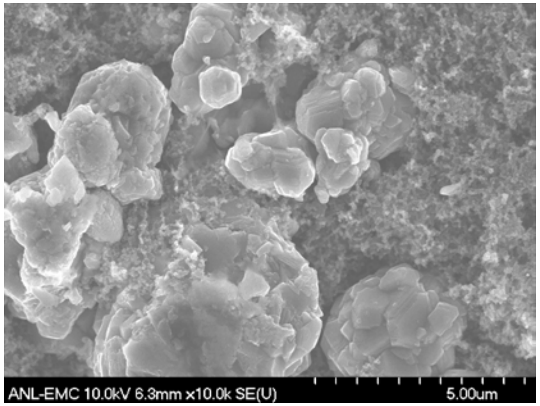
Pristine graphite



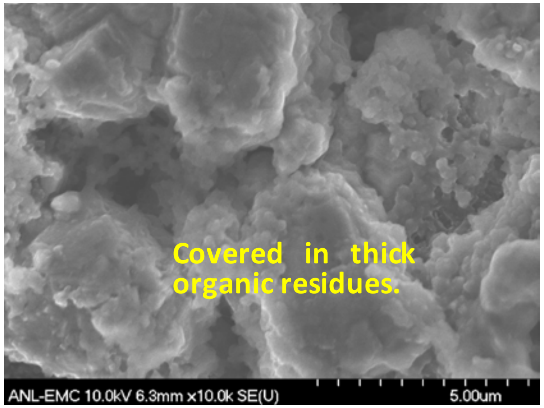
Gen 2 graphite



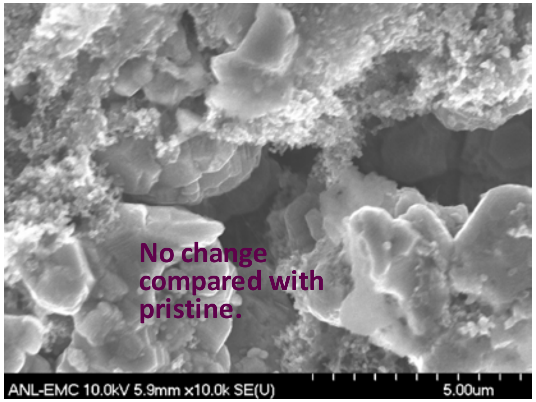
HVE 1 graphite



Pristine LNMO


Covered in thick organic residues.

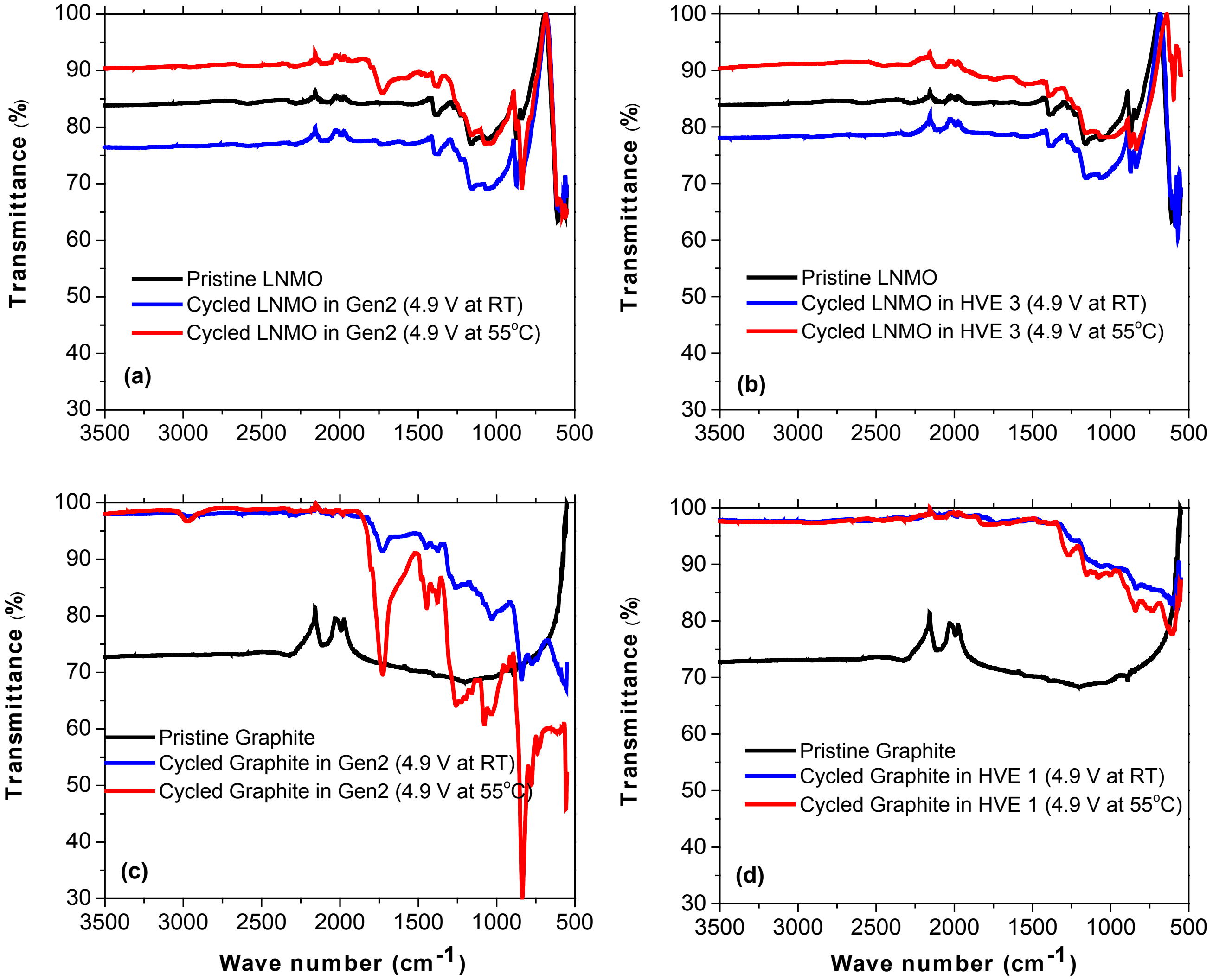
Gen 2 LNMO


No change compared with pristine.

HVE 1 LNMO

Cycled Electrodes Harvested from LNMO/Graphite Cells

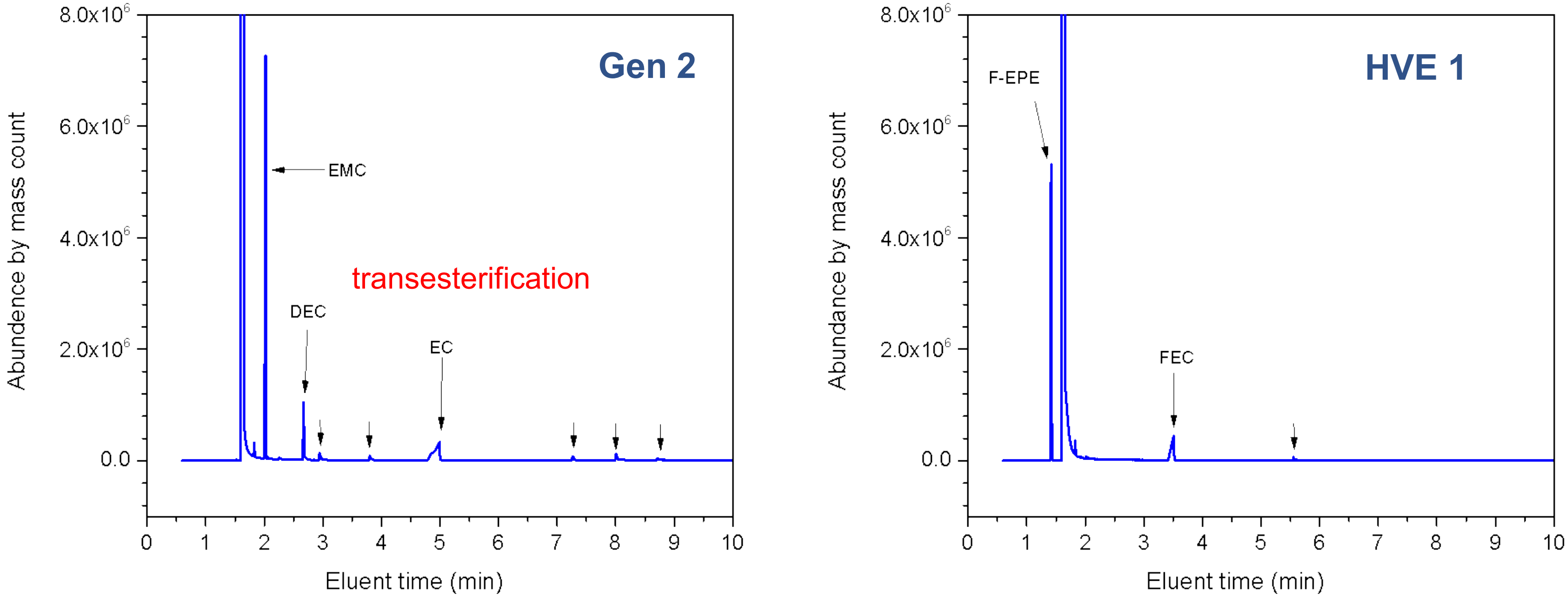
FT-IR of both cycled LNMO cathode and graphite anode showed less decomposition when HVE 1 electrolyte was used at RT and 55°C.



FT-IR spectra of pristine and harvested cathodes from cycled LNMO/graphite cells with (a) Gen 2 and (b) HVE electrolytes and harvested anodes from cycled LNMO/graphite cells with (c) Gen 2 and (d) HVE electrolytes. All cells cycled at RT and 55 ^{0}C.

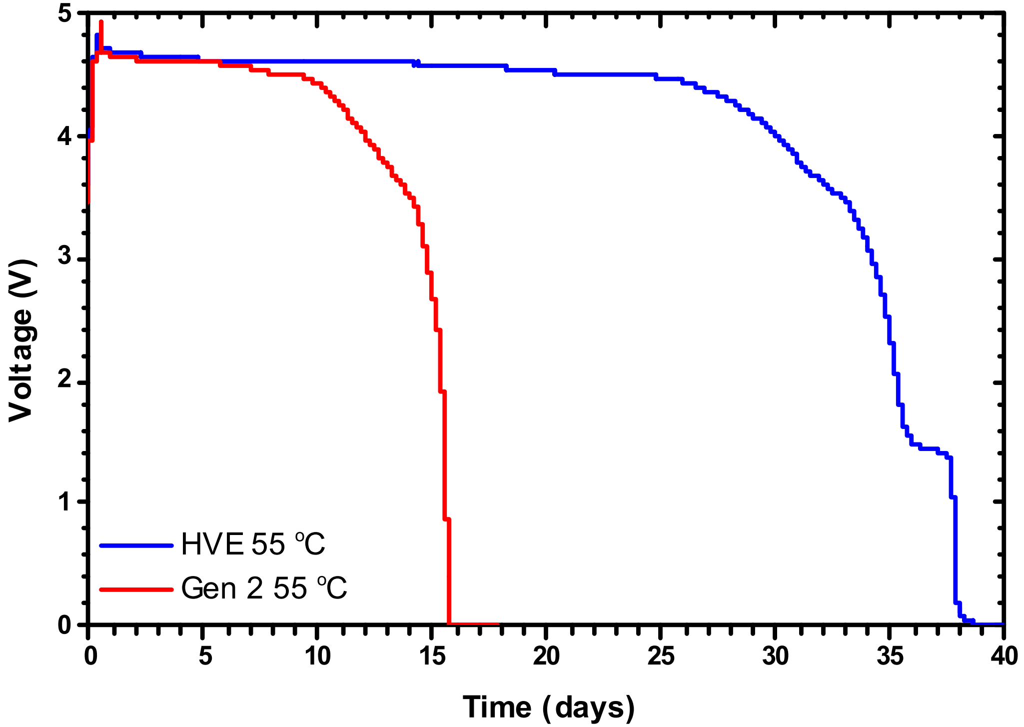
New Formulation of Fluorinated Carbonate Electrolyte in High Voltage LNMO/graphite System

GC-MS of harvested electrolyte from cells cycled at 55 ºC.



Gen 2 showed a large amount of varieties of decomposition products in the harvested electrolyte, while no side products were observed in the cycled HVE 1 electrolyte by GC-MS.

Self-Discharge Performance of HVE Electrolyte with LNMO/Graphite (A12) Cells

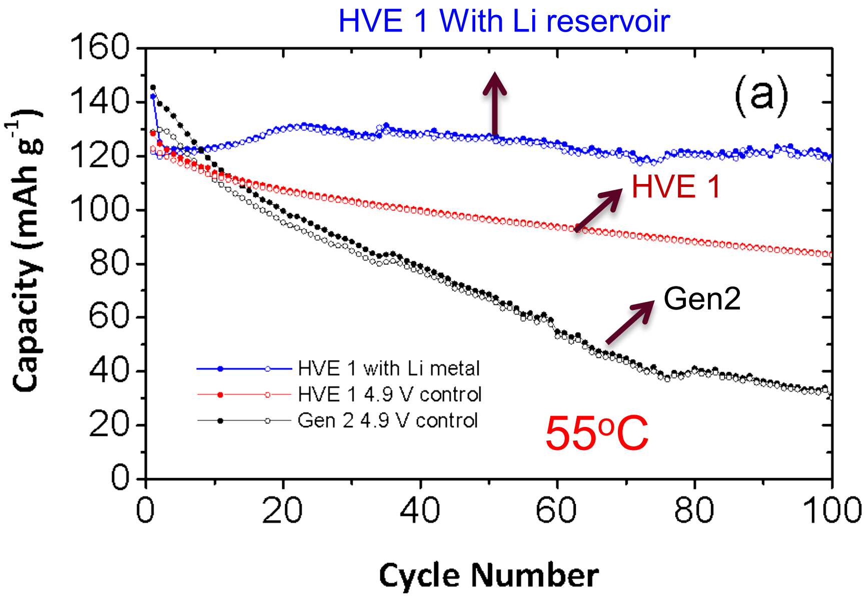


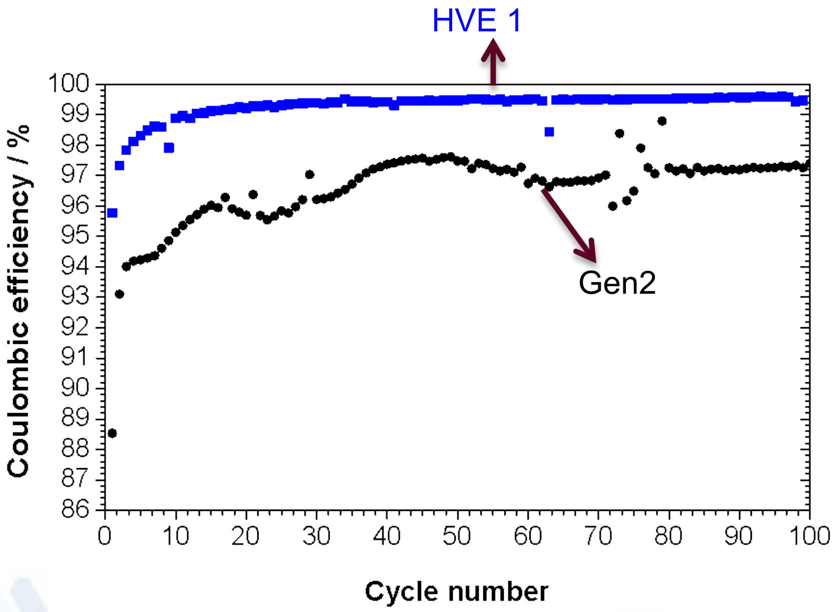
Condition: 3-cycle formation; cutoff voltage: 3.5-4.9 V; C/10; at room temperature.

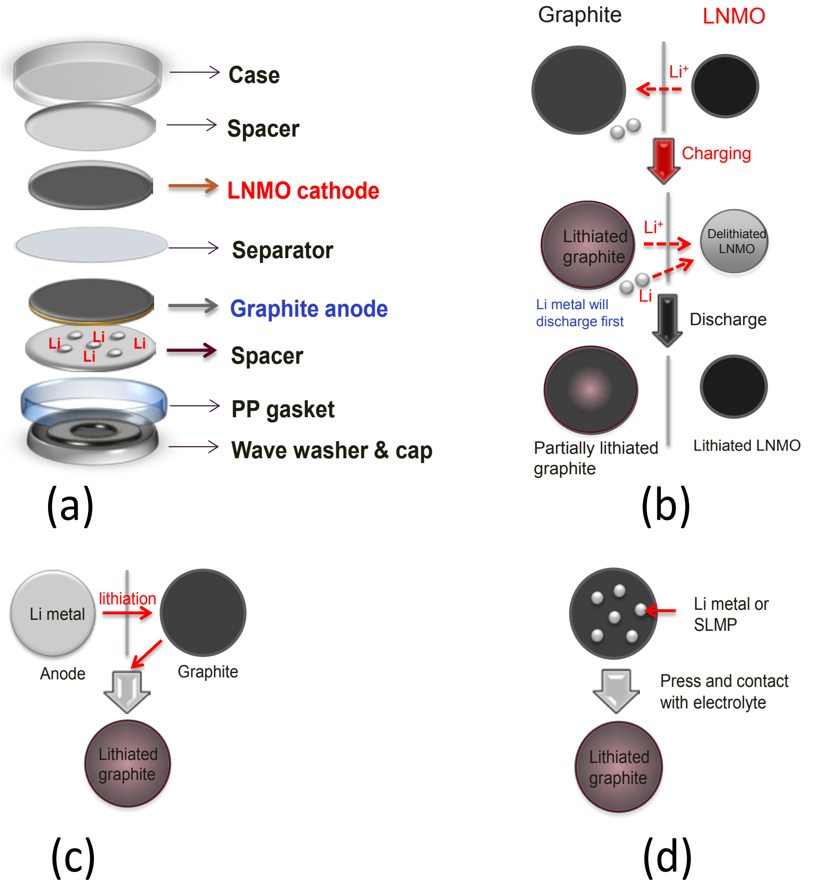
Self Discharge Test: charge to 4.9 V at C/10 at 55 °C, then rest at the same temperature (55°C) and monitor the voltage change. Data points are taken every 5 minutes.

In LNMO/graphite coin cells, HVE electrolyte has improved storage stability than Gen 2 at high temperature.

Lithium Reservoir to Compensate Active Lithium Loss

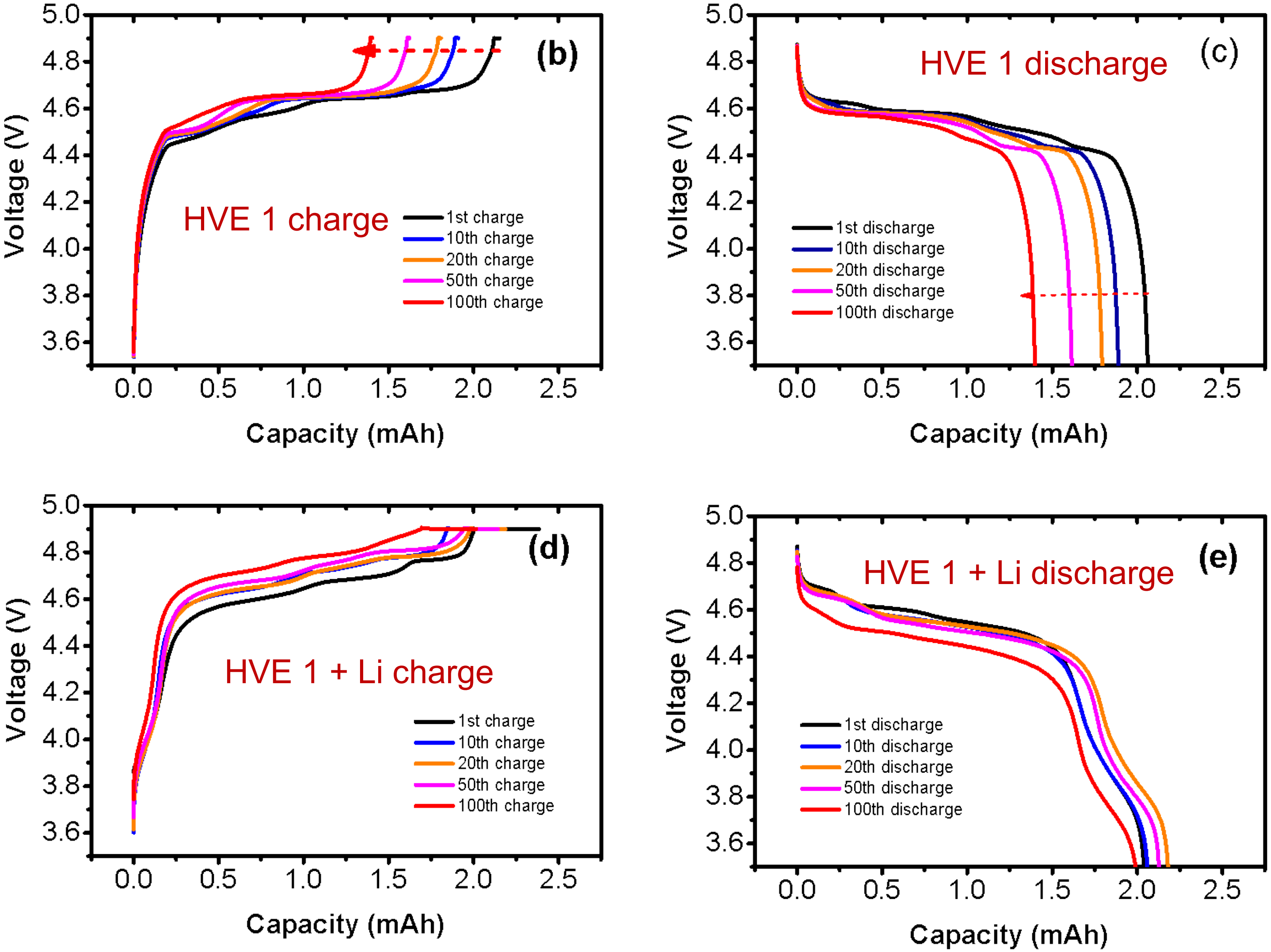






(a) LNMO/graphite cell assembly with incorporated lithium metal; (b) lithium metal working mechanism at the formation cycles; (c) prelithiation of graphite anode using electrochemical method; (d) direct shorting of graphite anode.

Voltage Profiles of LNMO/Graphite Full Cells with HEV1 and HVE1 + Li Reservoir Cycled at 55 ºC



Reversibility of the charge and discharge profiles of LNMO/graphite cells using HVE 1 electrolyte with lithium reservoir was greatly improved. (Cut-off voltage: 3.5-4.9 V at C/3 rate at 55 ºC)

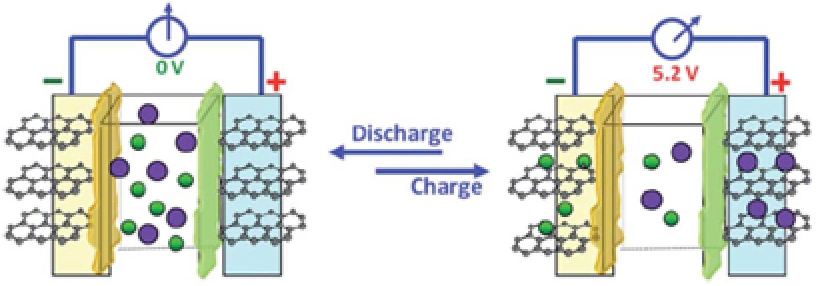
Electrolyte Additive Research

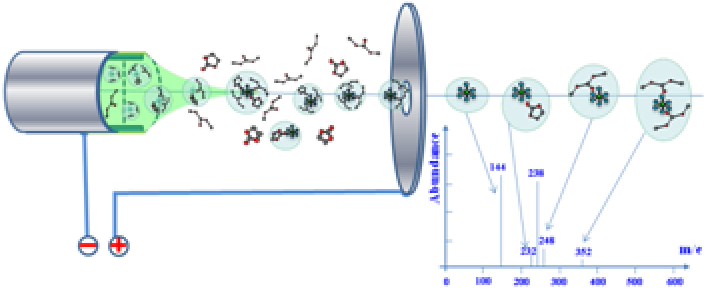
Team Objective:

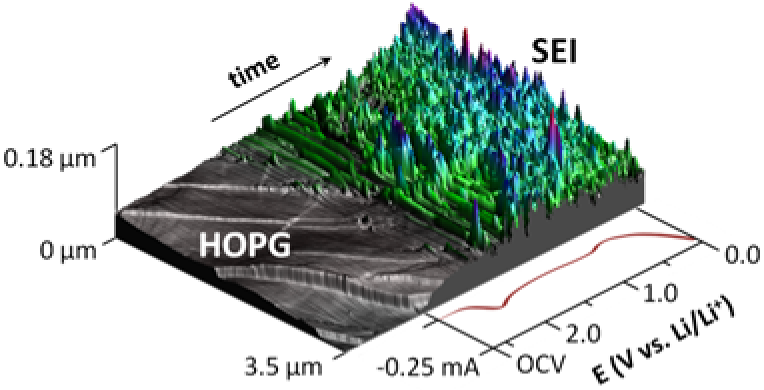
- Synthesize new electrolyte additives for 5 V cathode chemistry;
- Fundamental investigation of Li$^+$-solvation and interphasial chemistry;
- In-situ imaging of SEI formation with electrochemical AFM

Accomplishment:

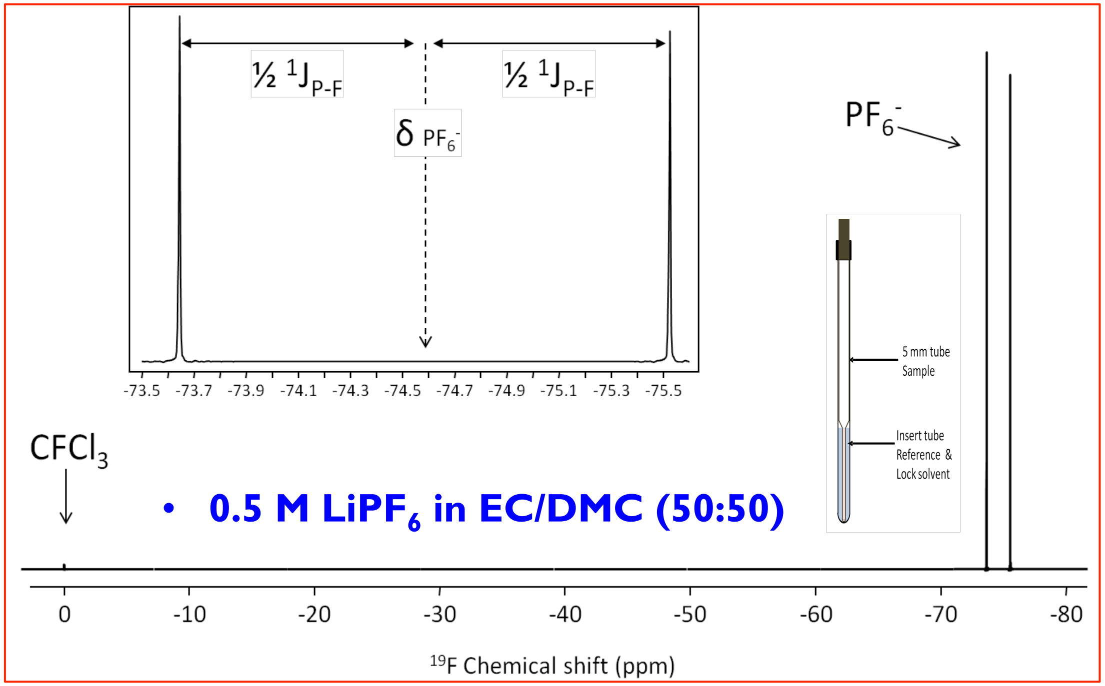
- Synthesized and structurally characterized 5 new additives;
- Formulated high V electrolyte to support dual-graphite intercalation chemistry;
- Understood anion-solvent interaction with ESI-MS and ^{19}F-/^{31}P-NMR;
- Observed live-formation of SEI with in-situ electrochemical AFM
- Additive-effect confirmed with AFM: F-solvent leads to thinner upper-layer

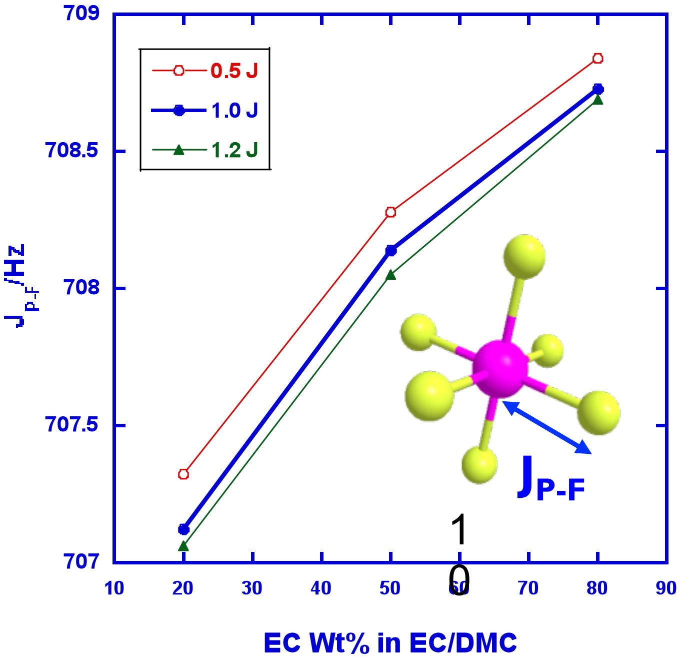






Anion-Solvation: ^{19}F-NMR





No apparent effect of solvent ratio on ^{19}F-chemical shift

- **~0.10 ppm variations (negligible compared with ^{17}O-chemical shift changes of carbonyl group ~20 ppm)**
- **Dependence within experimental error**

<u>Hence, there is little anion-solvent interaction</u>

With increase salt concentration, ^{19}F-chemical shift changes down-field, still with small variations (~0.19 ppm)

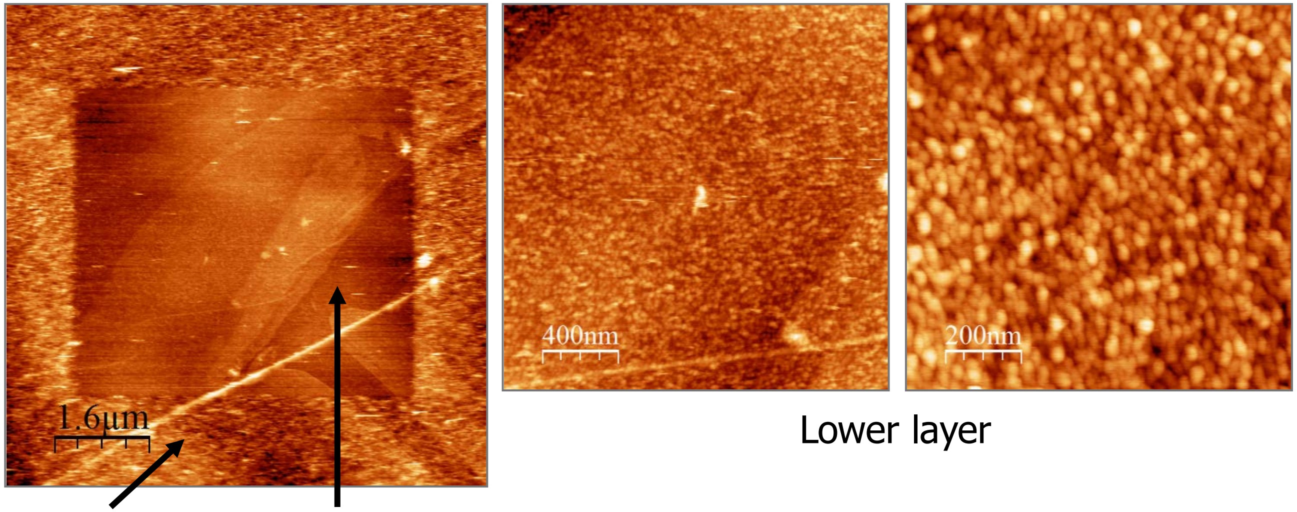
However, coupling constant between P-F ($J_{P\text{-}F}$) reveals interesting solvent preference information

- **With increasing EC concentration $J_{P\text{-}F}$ decreases**
- **DMC presence interferes the P-F bonding more than EC**

<u>Hence, PF_6 slightly prefer DMC than EC.</u>

In-situ AFM of SEI on Model Graphite Anode

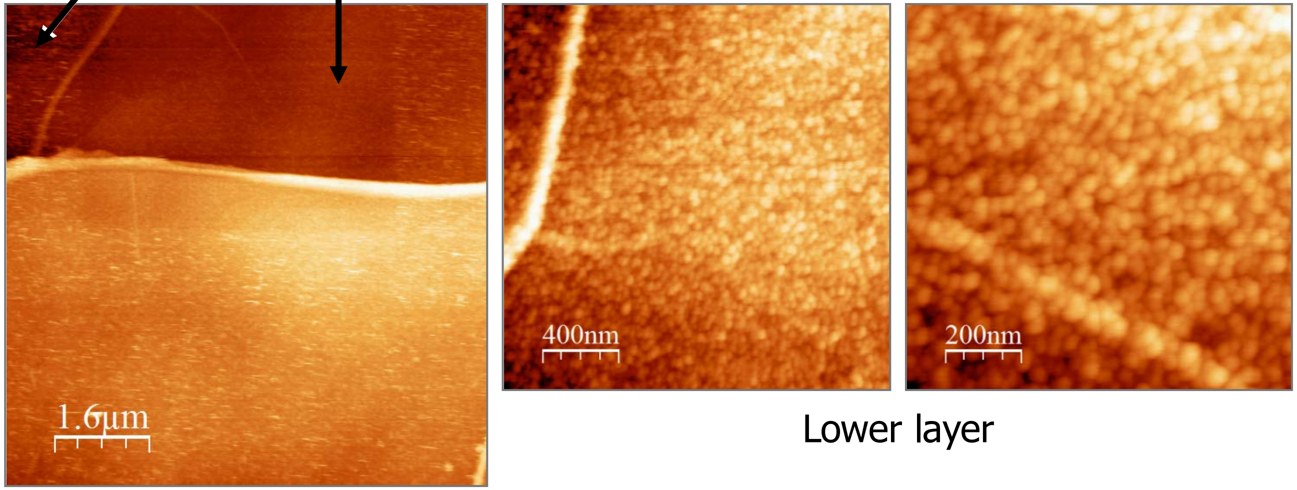
Control: 1.3 M LiTFSI in **EC**



Lower layer

Upper layer Lower layer

Control + 5 v% **FEC**

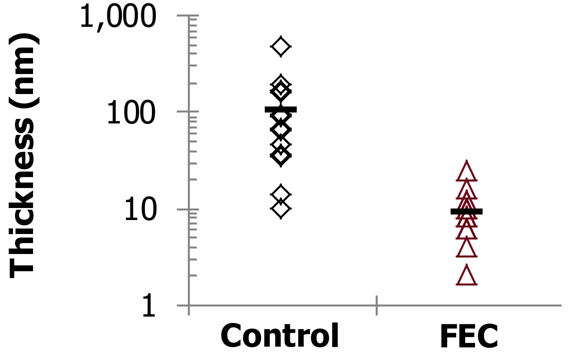


Lower layer

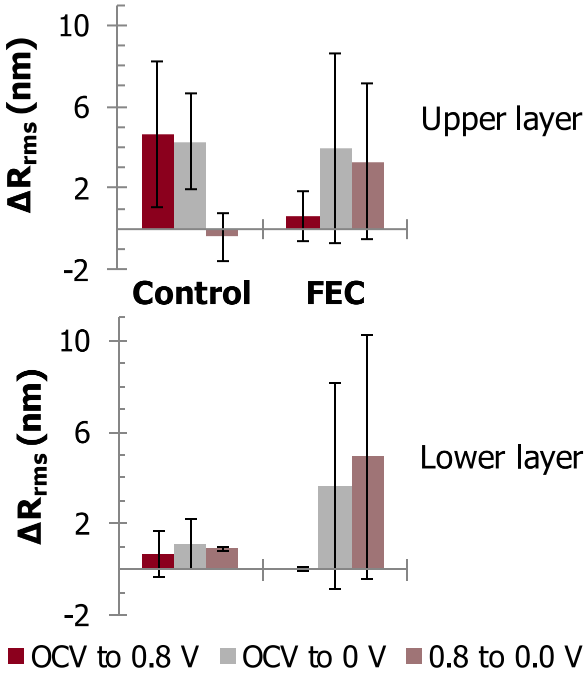
HOPG (WE, sample) at **0V vs. Li** (RE/CE), 1st cycle

SEI upper layer thickness

derived from F-d curves



Roughness change



Collaboration and Coordination with Other Institutions

Collaboration:

(1) U.S. Army Research Laboratory (Dr. Kang Xu, Project team member)
(2) Brookhaven National Laboratory (Dr. Xiao-Qing Yang, Project team member)
(3) Center of Nano-Materials at Argonne (Dr. Larry Curtiss)

Interactions:

(4) University of Rhode Island (Dr. Brett Lucht)
(5) Jet Propulsion Laboratory (Dr. Marshall Smart)
(6) Lawrence Berkeley National Laboratory (Dr. Vincent Battaglia)
(7) Cell Analysis, Modeling, and Prototyping Facility (CAMP) (Dr. Andrew Jansen)
(9) Material Engineering and Research Facility (MERF) (Dr. Gregory Krumdick)
(10) Arkema (Dr. Ryan Dirkx)

Proposed Future Work

✓ During the rest of the FY14, we will continue to explore the fluorinated carbonate-based electrolytes to enable the high voltage high energy cells.

- Explore the additive effect on the new developed high voltage fluorinated electrolyte HVE 1 on graphite electrode.
- Further design and synthesize new fluorinated carbonate solvents based on the recent research results.
- Tailored cathode electrolyte interphase (CEI) additives to further improve the instability on the LNMO/electrolyte interphase, especially at elevated temperatures.
- Expand the electrode surface diagnosis using X-ray and XPS in addition to AFM.
- Scientific write-up for publication in peer-reviewed journals of the recent results.

✓ In the year of FY15, we propose the following work in order to achieve the milestones and the final goal of this project:

- Design and synthesis of fluorinated non-carbonate solvents as backup high voltage electrolytes.
- Optimization of fluorinated electrolytes.
- Fabrication and evaluation of 10 mAh pouch cells in the lab.
- Delivery of twelve 10 mAh pouch cells to DOE for testing and verification.

Summary

PHEV and EV batteries face many challenges including energy density, calendar life, cost, and abuse tolerance. The approach of this project to overcome the above barriers is to develop highly stable electrolyte materials that can significantly improve the high voltage cell performance without sacrificing the safety to enable large-scale, cost competitive production of the next generation of electric-drive vehicles.

- ☐ Argonne took a combined approach to tackle the voltage instability of electrolyte by developing the fluorinated carbonate-based electrolytes with intrinsic stability and the passivating cathode additive to afford a stable electrode/electrolyte interphase.
- ☐ Fluorinated cyclic carbonates and fluorinated linear carbonates were synthesized, characterized and purified and their electrochemical performance in high voltage cell were evaluated in LNMO/Li, LNMO/LTO and LNMO/graphite cells.
- ☐ FEC-based electrolyte HVE 1 has achieved superior capacity retention at both ambient and elevated temperatures for 5 V LNMO/graphite cell. Post-test analysis showed that the fluorinated electrolyte HVE 1 is much more stable in both the liquid electrolyte phase and on the electrolyte/electrode interface.
- ☐ LNMO/graphite (A12) cells with fluorinated electrolyte showed less self-discharge even at elevated temperature with 100% SOC.
- ☐ Lithium compensation provides an efficient way to enhance the cycle life with LNMO/graphite cells even with conventional electrolyte; however a more stable electrolyte, like fluorinated electrolyte, in combination with an active lithium reservoir is still preferred for desired performance.
- ☐ New electrolyte additives were synthesized and characterized; Live-formation of SEI by F-solvent was observed by *in-situ* electrochemical AFM.