Development of Fluorinated Electrolytes

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Argonne National Laboratory

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Project ID # BAT335

Overview

Timeline

- Project start June. 1, 2017
- Project end Sept. 30, 2010
- 33% complete

Barriers

- Low oxidation stability
- High, low temperature performance
- Instability of electrode/electrolyte interface
- Safety concern associated with high flammability and reactivity

Budget

- Total project funding
  - 100% DOE funding
- Funding received in FY17: $300 K

Partners

- Dr. Jason Croy (ANL)
- Dr. Larry Curtiss (ANL)
- Dr. Vojislav Stamenkovic (ANL)
- Dr. Gregory Krumdick (ANL)
- Prof. Reza S. Yassar (UIC)
- Prof. Ju Li (MIT)

Relevance/Project Objectives

- Next generation lithium-ion battery for vehicle application requires high charging voltage and high capacity. For the cathode materials, the high capacity could be achieved by raising the charging voltages.

- However, under high voltage conditions, the conventional electrolyte solvents suffer from oxidative cleavage casuing transition metal dissolution, self-discharge and lithium plating on the anode.

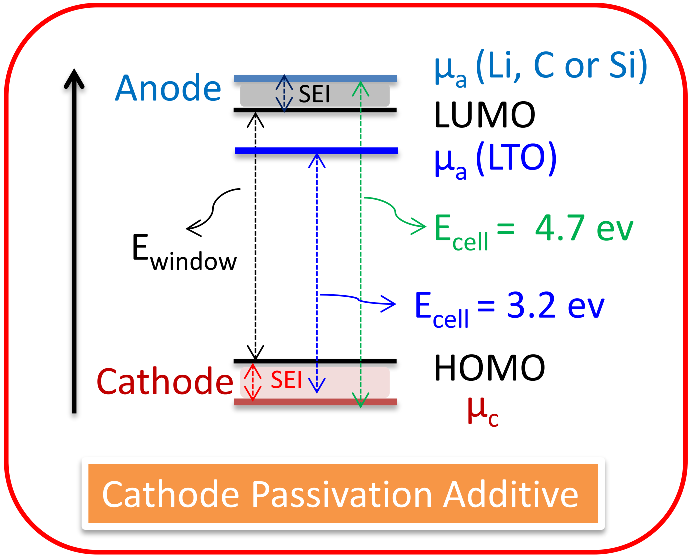
- The objective of this project is to develop advanced electrolyte materials that can significantly improve the high voltage performance without sacrificing the safety of lithium-ion battery to enable large-scale, cost competitive production of the next generation of electric-drive vehicles.

- The objective of this project is to develop fluorinated compounds as electrolyte solvents and electrolyte additives to afford thermodynamic/kinetic stability at high voltage cathode/electrolyte interface.

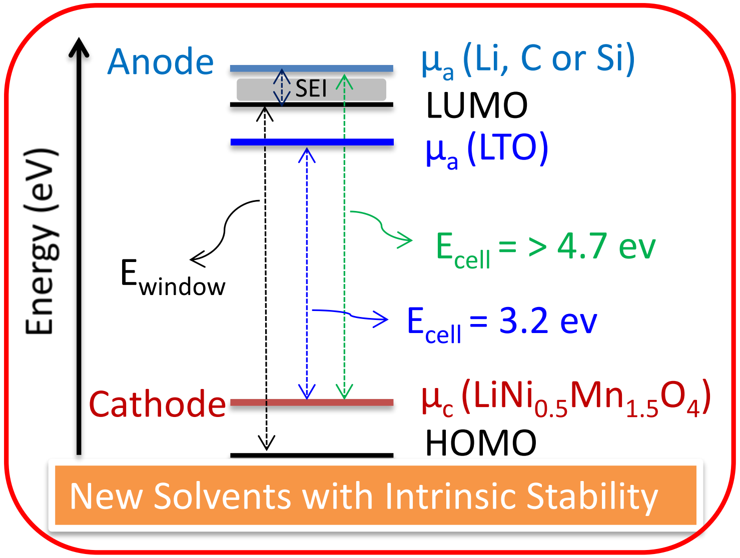
- The new electrolyte materials can tolerate high charging voltage (>5.0 V *vs* Li^+/Li) and are capable of passivating anode electrode providing stable cycling performance for high voltage cathodes including 5-V $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) cathode, high energy LMR-NMC and Ni-rich NMC cathodes.

Approach/Strategy

Electrolyte Additives



Electrolyte Solvents

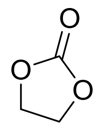


- ✓ Introduce fluorine and fluorinated alkyl groups onto the carbonate structure to lower the HOMO energy level of the electrolyte solvents for thermodynamic stability at high voltage cathode surface (up to 5.0 V vs Li^+/Li).
- ✓ Molecular design of oxidizable compounds which could passivate the high voltage cathode by forming a cathode-electrolyte-interphase (CEI) for kinetic stability.
- ✓ Expand the electrochemical window of electrolyte by new designed solvents which are capable of SEI formation on the anode surface through reductive decomposition without external SEI additives.

Design and Synthesis of Fluorinated Solvents

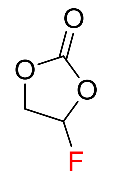
Fluorinated Carbonates

EC



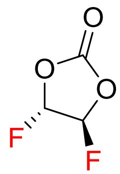
ethylene carbonate

FEC



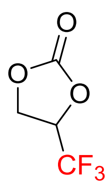
fluoroethylene carbonate

DFEC



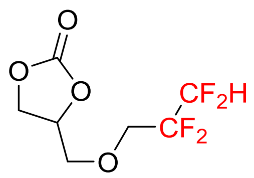
difluoroethylene carbonate

TFPC



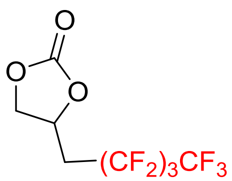
trifluoropropylene carbonate

HFEEC



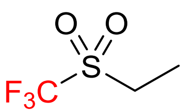
4-((2,2,3,3-tetrafluoropropoxy)methyl)-1,3-dioxolan-2-one

NFPEC

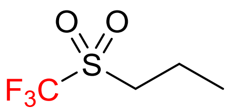


4-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-1,3-dioxolan-2-one

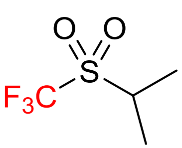
Fluorinated Sulfones



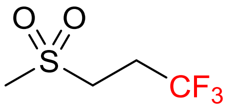
((trifluoromethyl)sulfonyl)ethane



1-((trifluoromethyl)sulfonyl)propane



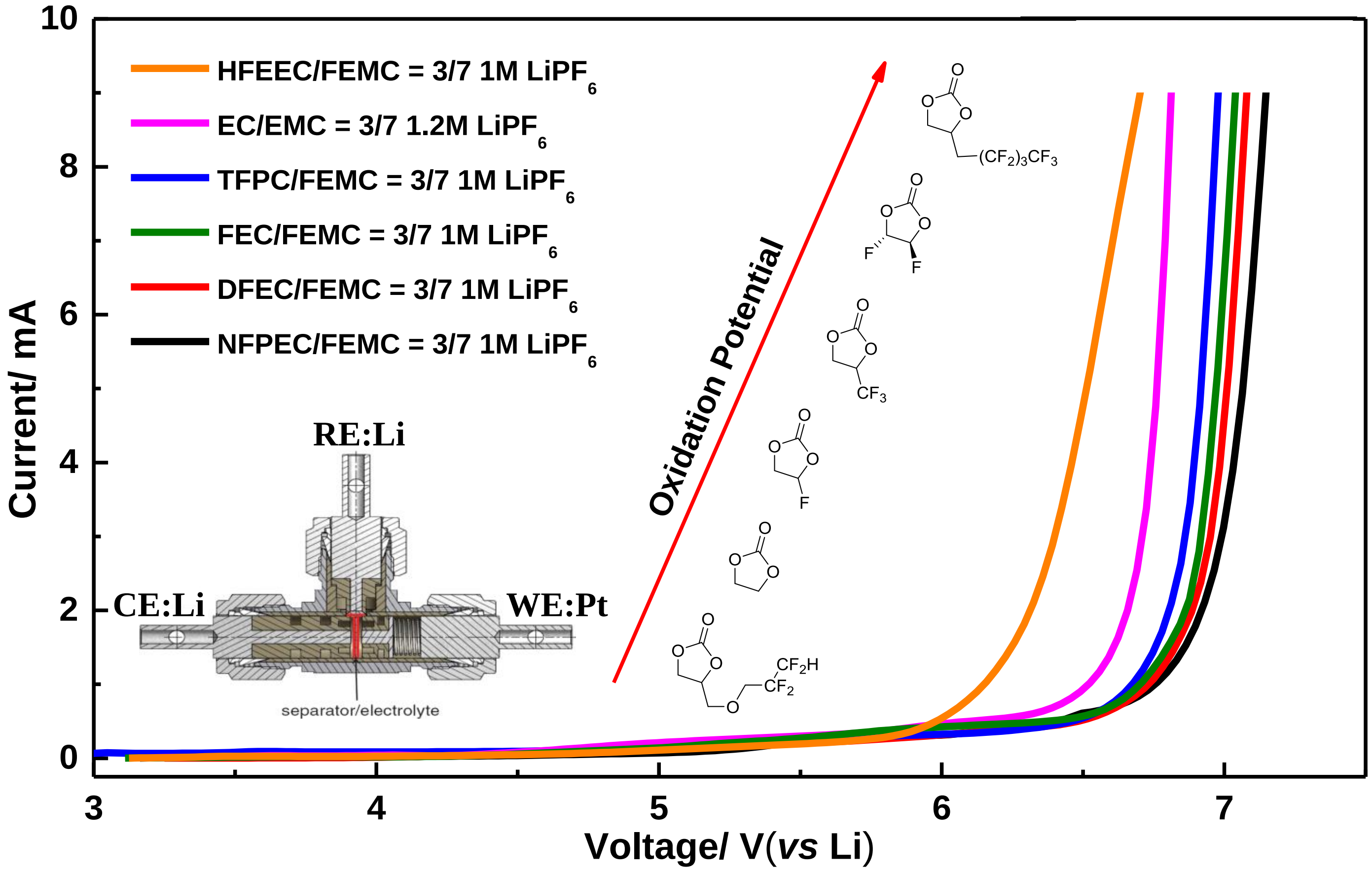
2-((trifluoromethyl)sulfonyl)propane



1,1,1-trifluoro-3-(methylsulfonyl)propane

Oxidation Stability of F-Carbonate Electrolytes

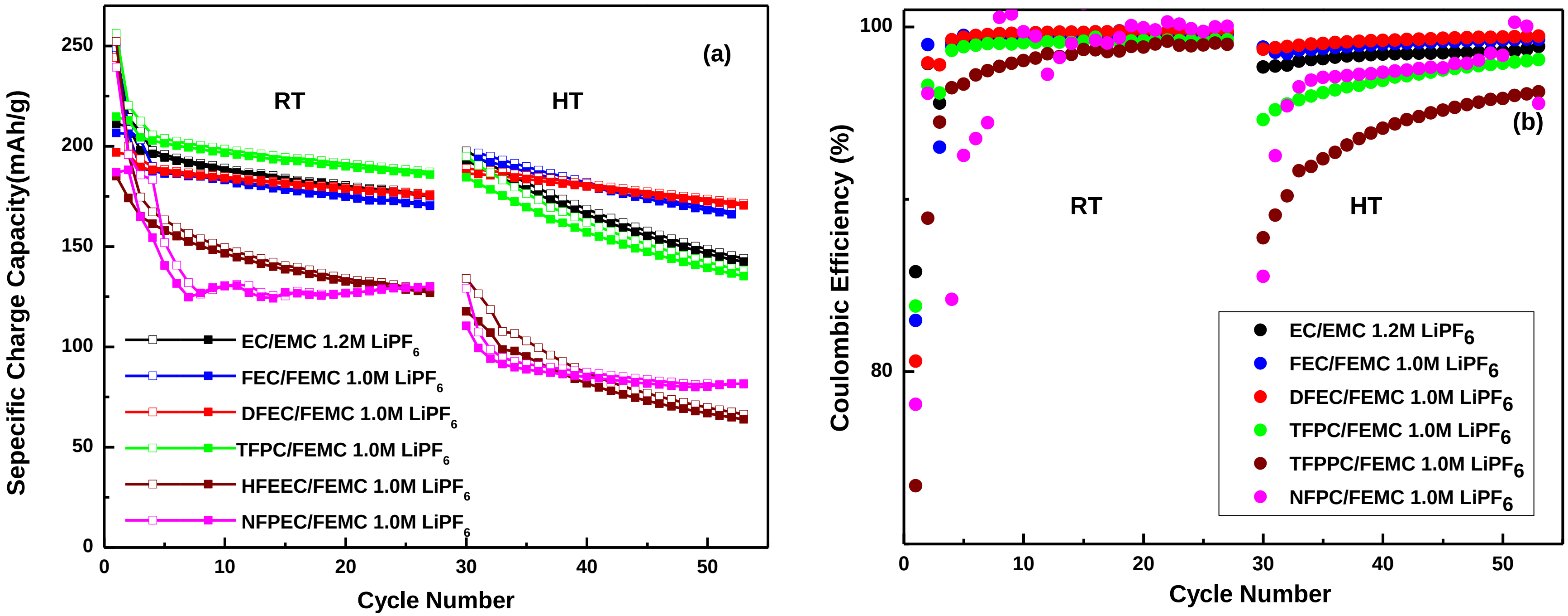
linear sweep voltammetry (LSV) profiles
(Pt/Li/Li three-electrode cell)



Fluorinated electrolytes showed exceptional oxidation stability except the HFEEC, which is less stable than the conventional Gen 2 electrolyte (EC/EMC=3/7 1.2 M $LiPF_6$).

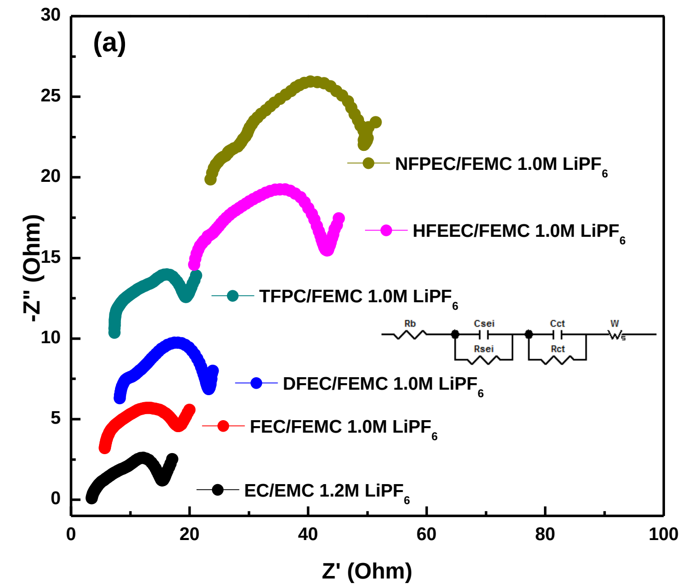
NMC532/Graphite Cell Performance at High Voltage

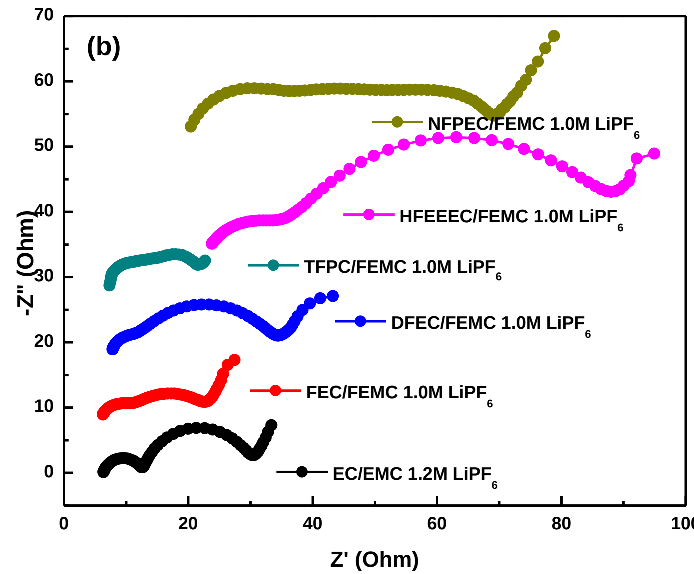
$LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$/graphite cells evaluated at room temperature (RT) and high temperature (HT=55^{o}C), cutoff voltage 3.0-4.6 V with a C/3 cycling rate.

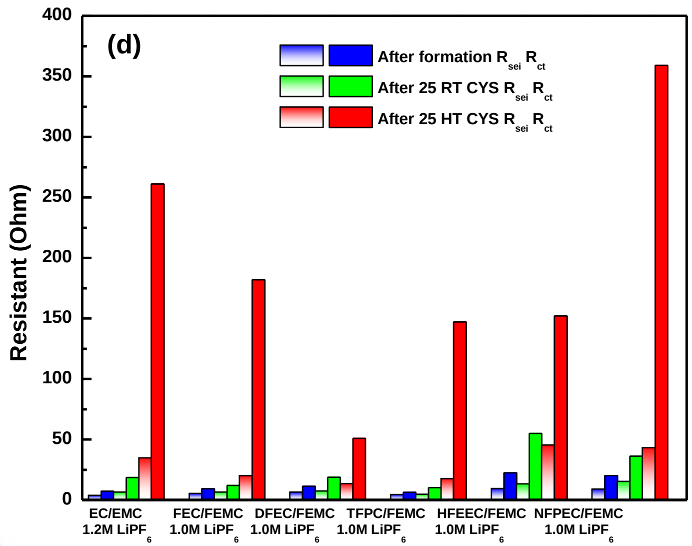


- HFEEC and NFPEC electrolytes are not capable of passivating the graphite during the initial formation cycle leading to poor cyclability and low coulombic efficiency
- At room temperature and elevated temperature (55^{o}C), the FEC- and DFEC- based electrolytes showed improved capacity retention and coulombic efficiency, which is more significant at HT.

Stabilized Electrode/Electrolyte Interface - Impedance Spectroscopy (EIS)





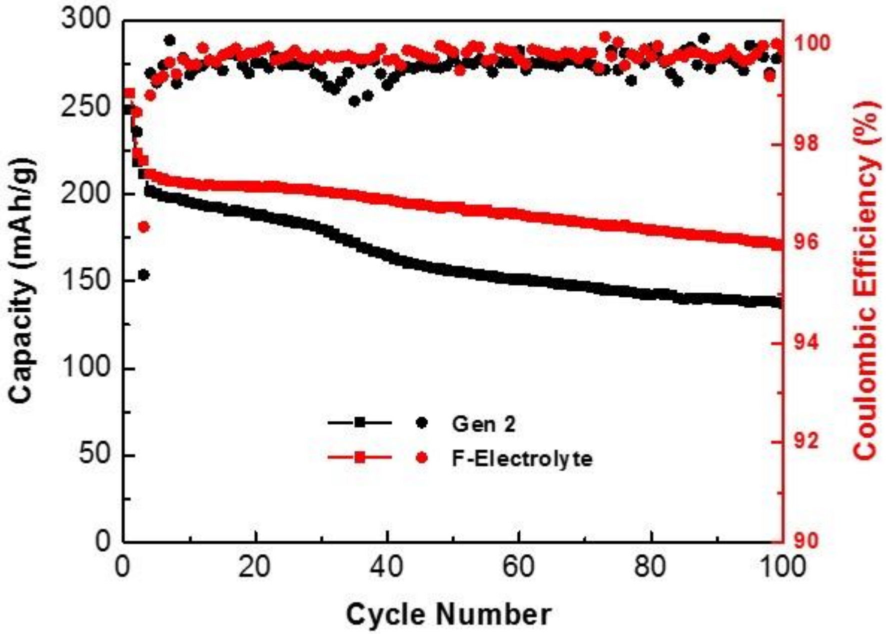


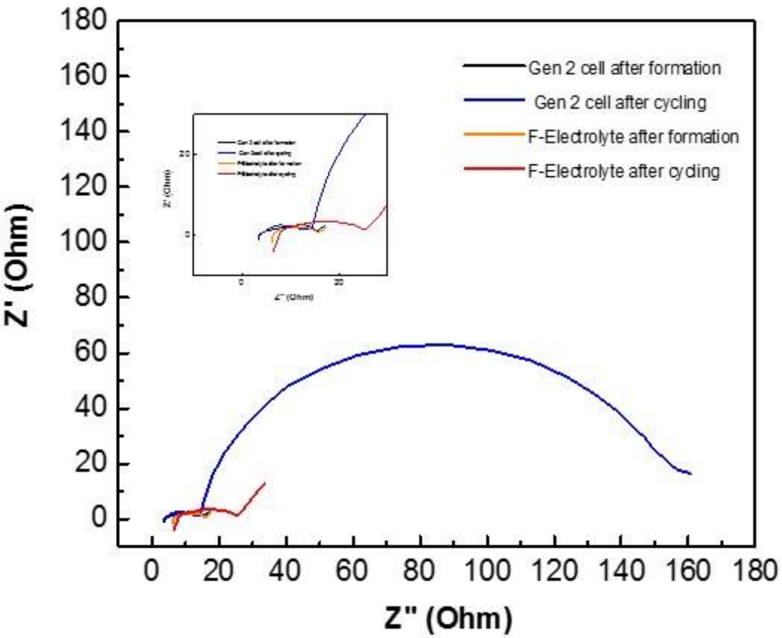
EIS for $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$/graphite cells:

(a) After formation cycles
(b) After 25 cycles at RT
(c) After 25 cycles at 55^{o}C.
(d) Summary of the fitted data

Cycling Performance

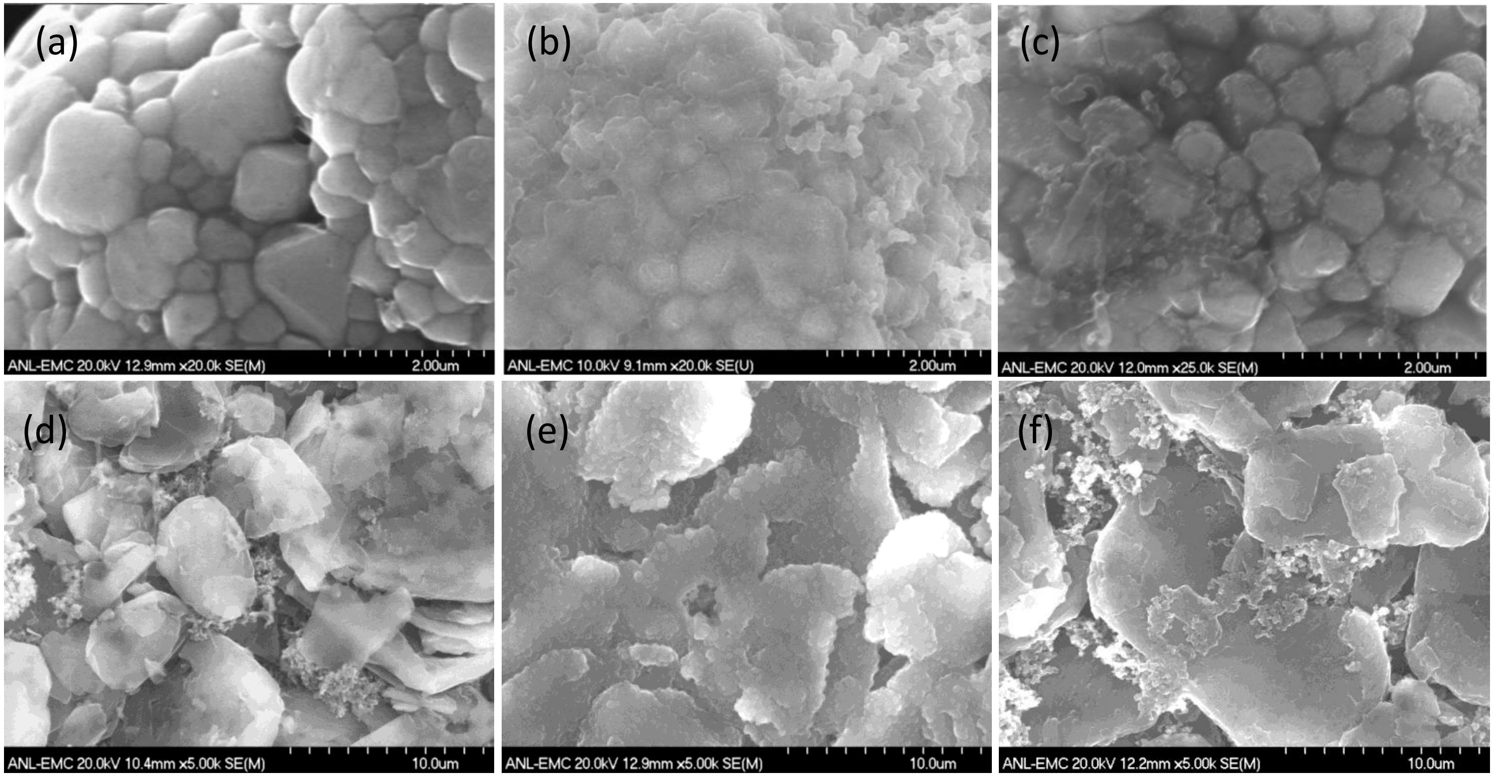
C/10 for 2 cycles formation, C/3 for cycling Cutoff voltage: 3.0-4.6





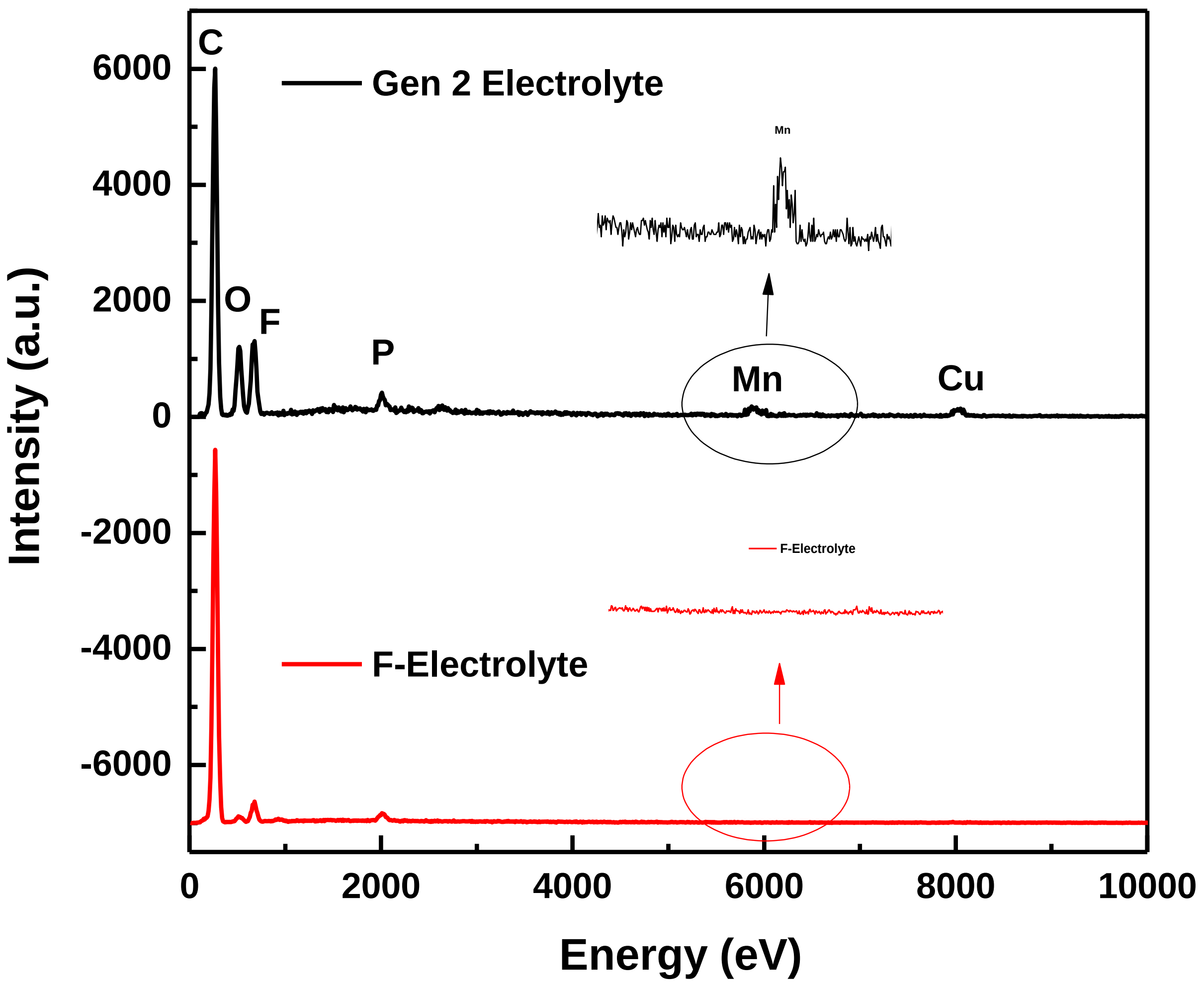
- Cycling performance of $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$/graphite full cells with Gen 2 electrolyte and fluorinated electrolyte (cycling condition: C/10 for 2 cycles formation and then C/3 for 100 for cycling with 3.0-4.6 V cutoff voltage).
- Oxidation stability of the fluorinated electrolyte leads to a stabilized electrode/electrolyte interface evidenced from the EIS data obtained after two C/10 formation cycles and 100 cycles at C/3. (All impedance experiments were conducted at fully discharged state).

SEM Images after Cycling



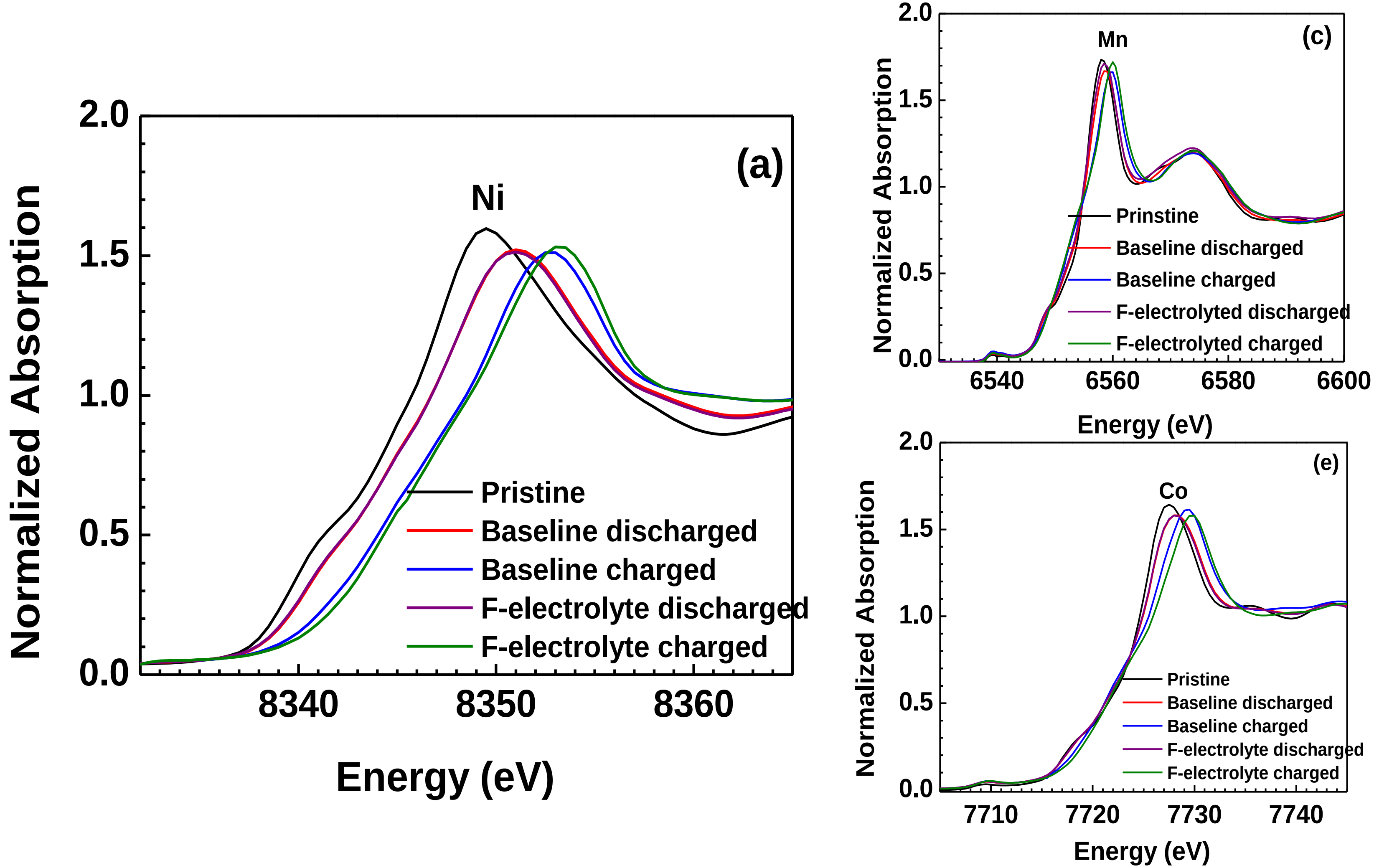
(a) Pristine NMC532 cathode, (b) cycled cathode with Gen 2 electrolyte, (c) cycled cathode with fluorinated electrolyte, (d) pristine anode, (e) cycled anode with Gen 2 electrolyte, and (f) cycled anode with fluorinated electrolyte. Magnification for cathode is higher than for anode in order to show the surface morphology change.

- Morphology of the cycled cathode is witbin expectation; however, the cycled graphite anode is beyond our expectation, which alomost resembles the morphology of the pristine graphite.



- ❑ EDS spectra of the harvest graphite anode cycled with Gen 2 electrolyte (black curve) and with fluorinated electrolyte (red curve).
- ❑ A variety of areas on cycled anode were analyzed and the results are representative of the overall cycled anode electrode.

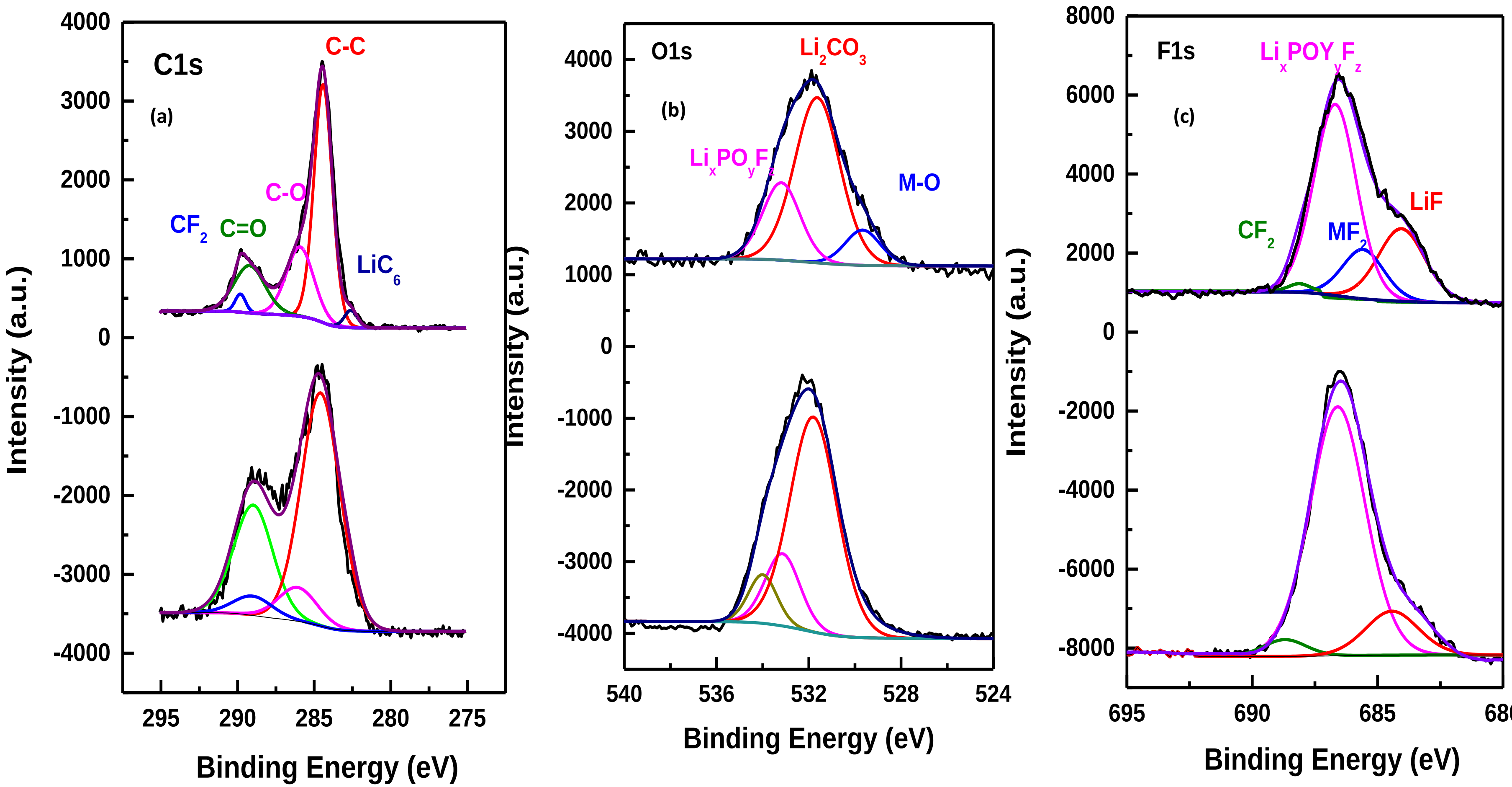
Post-Test Analysis by XAS at Advanced Photon Source



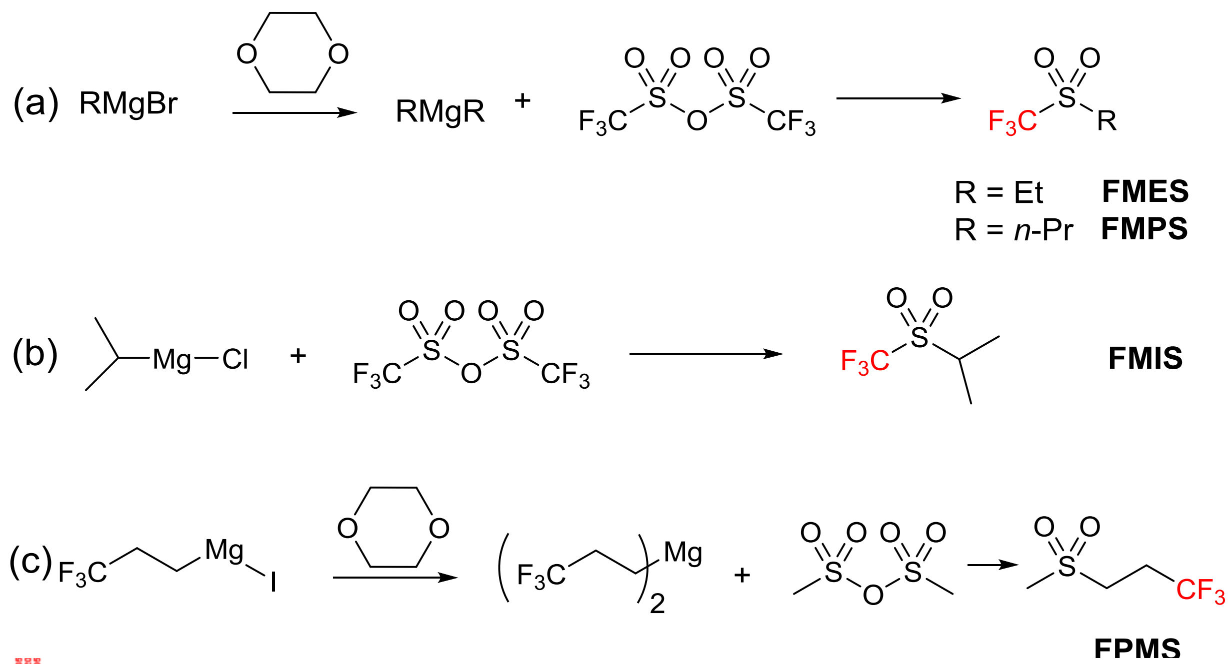
- ❑ Normalized K-edge X-ray near edge structure (XANES) spectra at (a) Ni K-edge, (c) Mn K-edge, (e) Co K-edge for NMC532 in pristine, charged (4.6 V) and discharged (3 V) states using Gen 2 (baseline) and fluorinated electrolytes after 100 cycles.
- ❑ For Ni XANES, large shifts was observed for fluorinated electrolyte cycled cathode indicating Ni could be charged to higher oxidation state contributing more capacity.

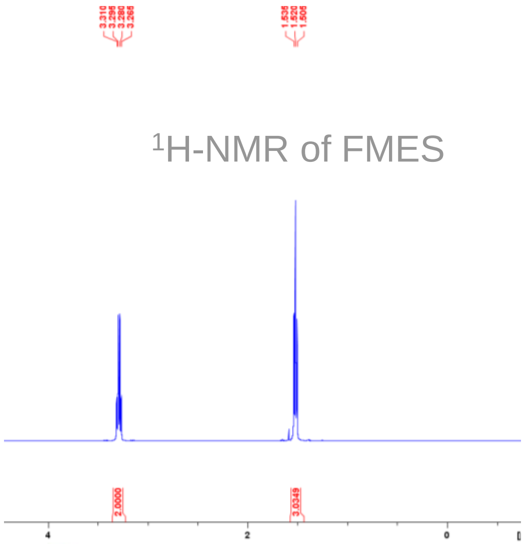
Surface Analysis of Cycled Graphite Anode with F-Carbonate Electrolytes

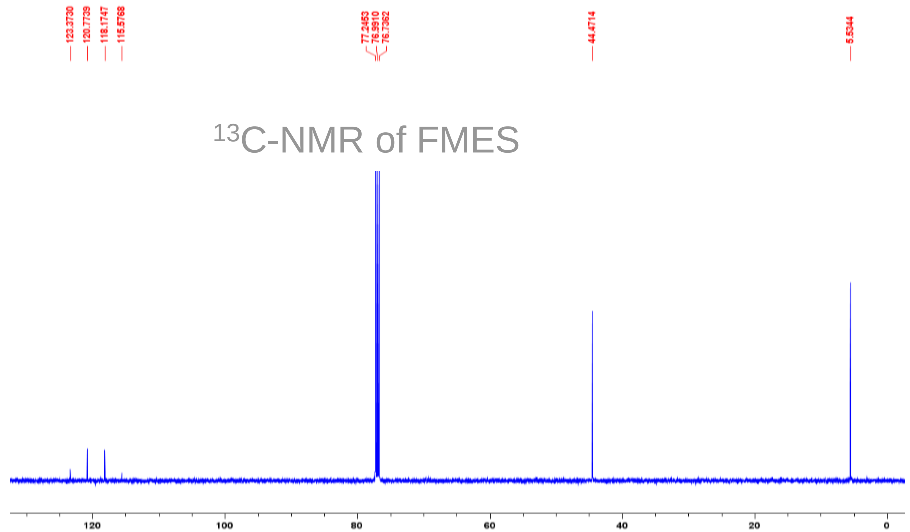
XPS spectra of cycled anode. (a) C_{1s}, (b) O_{1s}, (c) F_{1s}. Top: fluorinated electrolyte.

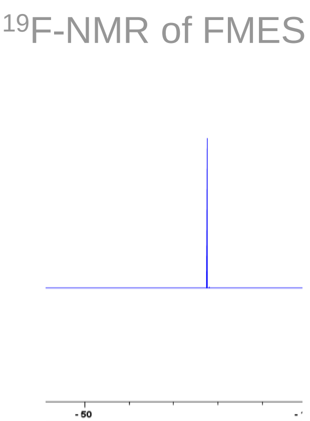


Design and Synthesis of Fluorinated Sulfones

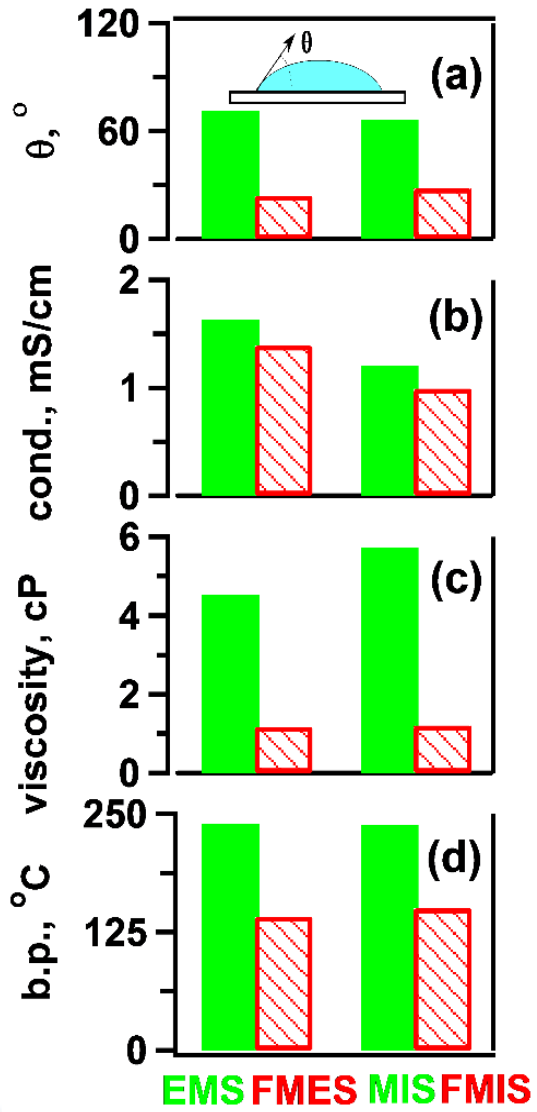








Physical Properties of the Fluorinated Sulfone Electrolytes



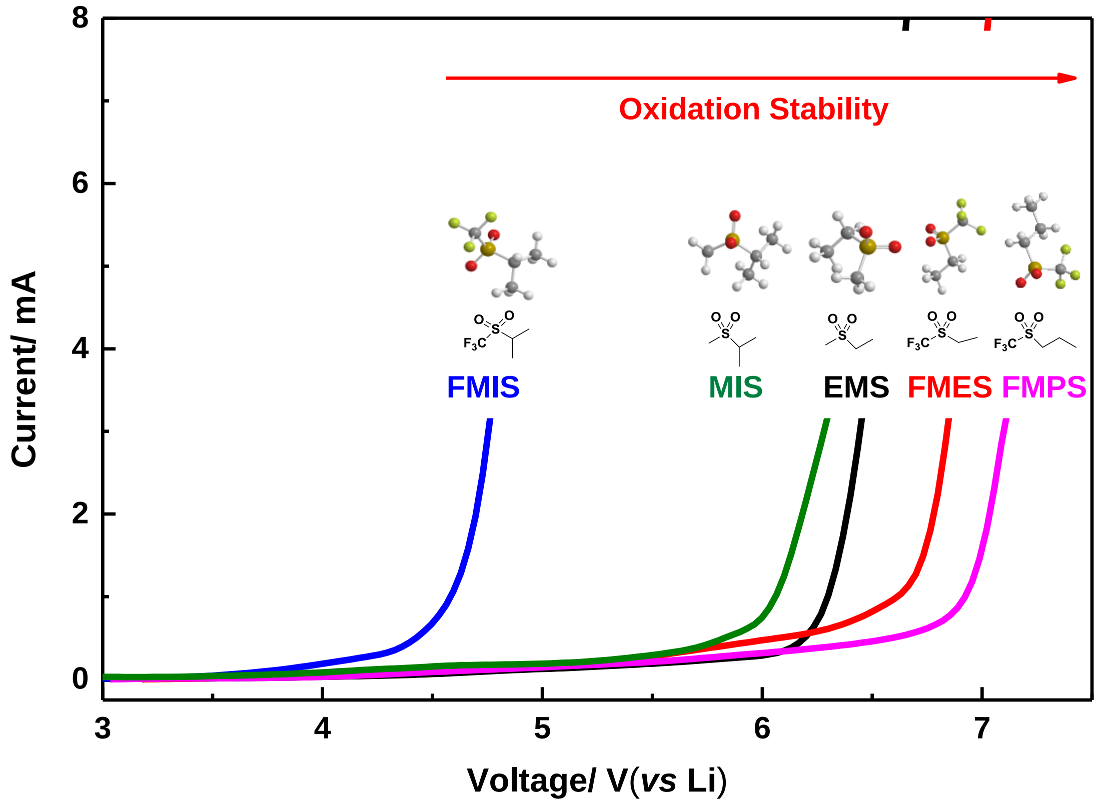
Wetting improvement

Graphical comparison of physical properties for homologous fluorinated (*red*) and non-fluorinated (*green*) sulfones: EMS vs. FMES and MIS vs. FMIS.

(a) Contact angle measured at 25°C using Celgard2325 separator as substrate and 0.5 M $LiPF_6$/sulfone as electrolyte,
(b) Conductivity measured at 25°C for 0.5 M $LiPF_6$ in sulfone,
(c) Viscosity measured at 25°C and
(d) Boiling point (b.p. data for EMS and TMS were obtained from reference 44 and 47, respectively).
(e) Separator wetting images with regular sulfone (up row) and fluorinated sulfone (bottom row).

Linear Sweep Voltammetry of Fluorinated Sulfone-Based Electrolytes

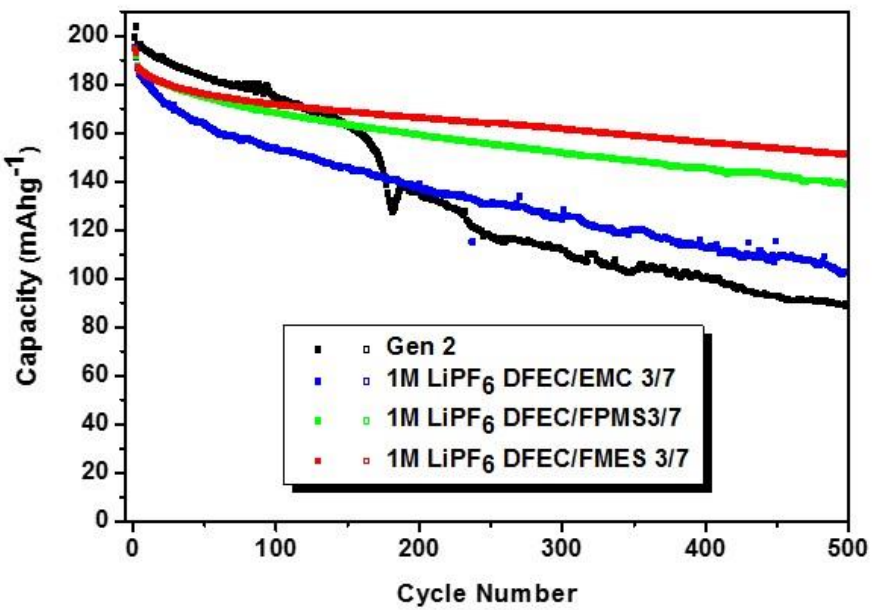
(0.5 M $LiPF_6$ in sulfones, scan rate 10 mV s^{-1}, Pt/Li/Li 3-electrode cell

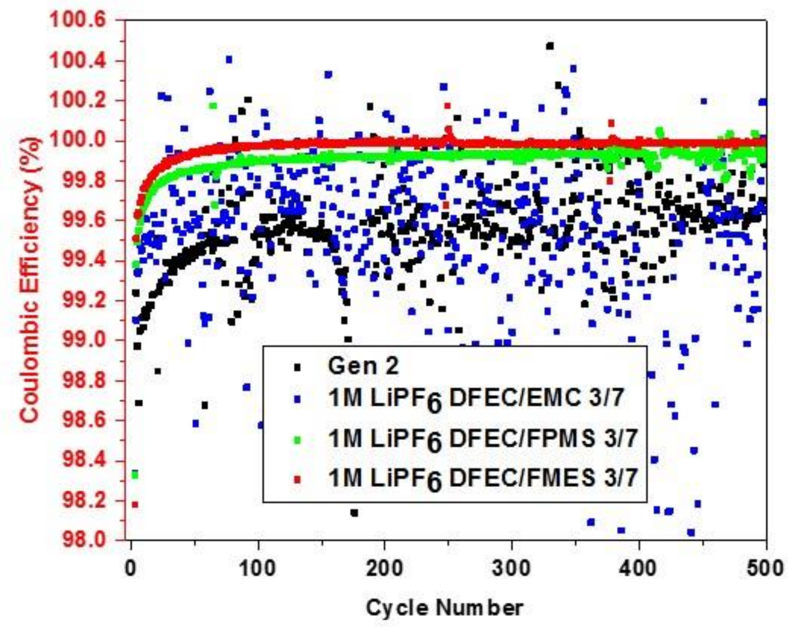


- Fluorination enhances the oxidation stability of the EMS and MPS sulfone solvents.
- After fluorination, the FMIS becomes less stable (4.4 V) compared with non-fluorinated EIS. The strong electron withdrawing $-CF_3$ group activates the α-proton of the sulfone ($-CH(CH_3)_2$) and renders its chemical reaction with lithium or lithiated graphite limiting its application in Li-ion battery.

Cycling Performance of NMC532/Graphite Cell

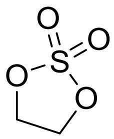
$LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$/graphite full cells
C/10 for 2-cycle formation, C/3 for 100 for cycling
Cut-off voltage: 3.0-4.6 V



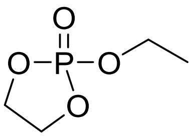


FMES/DFEC cell demonstrated superior cycling performance with > 80% capacity retention at 500th cycle and still maintained 70% capacity retention at 1000th cycle.

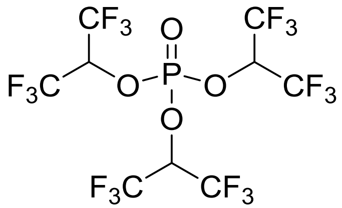
Synthesis and Characterization of Fluorinated Cyclic Phosphate as New Additives (On-going research)



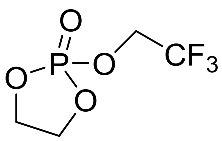
DTD



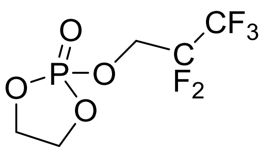
EDP



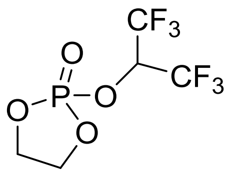
THFPP



TFEOP

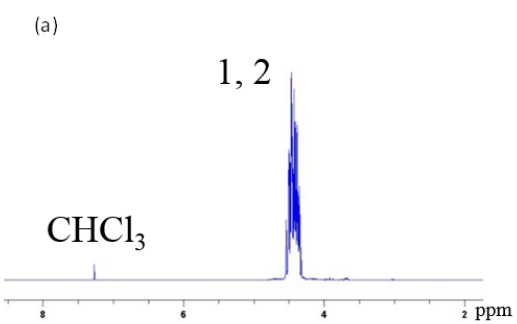


PFPOP

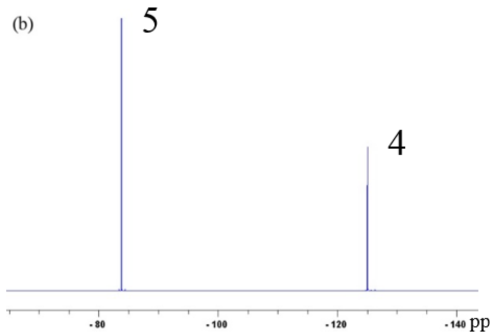


HFiPOP

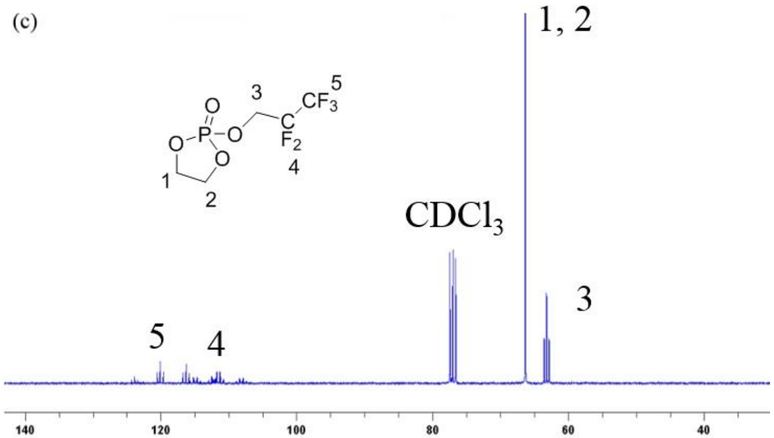
Chemical Structures of reported electrolyte additives DTD, EDP, THFPP and new additive TFEOP, PFPOP, and HFiPOP.



^{1}H-NMR of PFPOP



^{13}C-NMR of PFPOP



^{19}F-NMR of PFPOP

Response to Previous Year Reviewer's Comments

This project

was not reviewed last year

Collaborators/Partners

- Dr. Jason Croy (ANL) – Cathode/electrolyte interface
- Dr. Larry Curtiss (ANL) – Computation study
- Dr. Vojislav Stamenkovic (ANL) – Characterization and Diagnosis
- Dr. Gregory Krumdick (ANL) – Electrolyte scaling up
- Prof. Reza S. Yassar (UIC) – HR-TEM
- Prof. Ju Li (MIT) – *In-situ* TEM

Remaining Challenges and Barriers

- ✓ Synthetic challenges for low boiling point fluorinated solvents, especially F-sulfones.
- ✓ Further molecular design aiming for anode (graphite) passivating electrolytes.
- ✓ Further simulation of electrolyte/cathode and electrode/anode interface interaction.
- ✓ Chemical/electrochemical reactions at silicon anode could be very different compared with those on graphite anode.
- ✓ Material scaling up research for high purity, low cost electrolyte materials.

Proposed Future Research

- ✓ We have demonstrated that the formulated fluorinated solvents (carbonate and sulfone) with $LiPF_6$ salt could or partially could passivate the graphite anode.
- ✓ Future plan is to analyze the stabilization mechanism on the cathode side by *in-situ* and *ex-situ* analysis. The data will shed light on the new molecular design and synthesis for new electrolyte solvents and additives.
- ✓ Future plan also includes the investigation of the impact of SEI additives on high voltage cell performance of the new fluorinated electrolytes.
- ✓ Performance verification in a pouch cell format by collaboration with CAMP facility at Argonne.

Summary

- ✓ Argonne took a combined approach to tackle the voltage instability of electrolyte by developing the fluorinated electrolytes with intrinsic stability and the cathode additives with passivation capability.

- ✓ A high voltage electrolyte 1.0 M $LiPF_6$ FEC/HFDEC was demonstrated for $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$/Graphite Cell cycling at 4.6 V. The fluorinated electrolyte showed much improved Coulombic efficiency and capacity retention when a higher cutoff voltage (4.6 V) was applied. SEM/EDS and XPS data clearly demonstrated the superior oxidative stability of the new electrolyte on the charged cathode. The structural stability of the bulk cathode materials cycled with different electrolytes were extensively studied by XANES and XRD.

- ✓ A new class of fluorinated sulfones was synthesized by a novel methodology, and their physical and electrochemical properties as high voltage electrolytes were systematically studied. Fluorination enables a feasible electrolyte with low viscosity, excellent separator wetting and enhanced safety. More importantly, this study offers a breakthrough electrolyte technology for the high voltage cells. Trifluoromethyl substituted fluorinated sulfones proved to be a promising next generation electrolyte for high voltage high energy application as evidenced by the long term cycling performance in NMC532/graphite cell cycled at 4.6 V.