Development of Electrolytes for Lithium-ion Batteries

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ES067

Overview

Timeline

- 04/01/2009
- 03/31/2114
- 80 Percent complete

Barriers

- Barriers addressed
  - (Calendar Life (40 ^{o}C for 15 years)
  - Cycle life (5000 cycles)
  - Abuse Tolerance -Survival Temp Range (-46 to 66 ^{o}C)
  - Performance – Increased Energy Density

Budget

- Total project funding
  - DOE share $731 K
- Funding received in FY12 - $147 K
- Funding for FY13 - $147 K

Partners

- A. Garsuch (BASF)
- Spinel Focus group (LBNL-BATT)
- F. Puglia & B. Ravdel (Yardney)
- D. Abraham (ANL)
- M. Smart (NASA JPL)
- V. Battaglia & J. Kerr (LBNL)

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Objective

Develop novel electrolytes for lithium ion batteries that improve performance to meet or exceed DOE goals.

- Develop novel electrolytes with superior performance to SOA ($LiPF_6$ in Carbonates).
- Develop an understanding of the source of performance fade in graphite/$LiNi_{0.5}Mn_{1.5}O_4$ cells cycled to high voltage (4.8 V vs Li).
- Develop an electrolyte formulation that allows for superior performance of graphite/$LiNi_{0.5}Mn_{1.5}O_4$ cells.
- Develop additives that allow for formation of protective coatings on the cathode, i.e., a cathode SEI, and enhance electrochemical stability above 4.5 V.

- The development of improved electrolytes is of critical importance for meeting the DOE goals for cycle life, calendar life, temperature of performance, capacity loss, and Increased energy density.

Milestones

FY 12

- (a) Develop an understanding of the role of electrolytes in capacity fade and poor cycling efficiency of $LiNi_{0.5}Mn_{1.5}O_4$ cathodes. (March 12) **Completed**
- (b) Design electrolyte formulations to improve efficiency (>99 %) and decrease capacity fade (50 % of SOA) for high voltage Ni-Mn spinel cathode materials in Li/ $LiNi_{0.5}Mn_{1.5}O_4$ cells. (July 12) **Completed**
- (c) Optimize a $LiPF_4(C_2O_4)$ electrolyte for graphite/$LiNi_xCo_{1-2x}Mn_xO_2$ cells for high and low temperature performance (50 % of SOA capacity fade). (Sept. 12) **Completed**

FY 13

- (a) Develop an understanding of the role of electrolyte in capacity fade for graphite/ $LiNi_{0.5}Mn_{1.5}O_4$ full cells cycled at moderately elevated temperature (55 ^{o}). **Completed**
- (b) Design electrolyte formulations to decrease cell inefficiency (50 % of SOA) and decrease capacity fade (50 % of SOA) for graphite/$LiNi_{0.5}Mn_{1.5}O_4$ full cells. **July 13, on schedule**
- (c) Synthesize and characterize novel non-fluorinated lithium salts and test novel electrolytes in graphite/$LiNi_xCo_{1-2x}Mn_xO_2$ cells. **Sept 13, on schedule**

Approach

- Investigate electrochemical properties of $LiPF_4(C_2O_4)$/carbonate or ester electrolytes in small Li-ion cells.

- Investigate electrode surface films for cells cycled with $LiPF_4(C_2O_4)$ and $LiPF_6$ to determine source of performance differences.

- Use computational methods to screen potentially interesting additives.

- Investigate the mechanism of capacity fade for $LiNi_{0.5}Mn_{1.5}O_4$

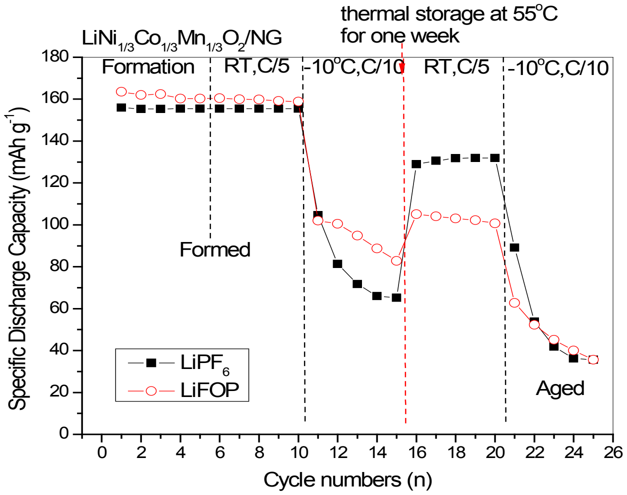
- Investigate cathode film forming additives for high voltage (> 4.5 V) cathode materials.

- Investigate the surface of cathodes and anodes cycled with novel electrolytes, with or without additives, to develop a mechanistic understanding of interface formation and degradation.

Previous Technical Accomplishments

- The use of the novel lithium salt lithium tetrafluorooxalatophosphate ($LiPF_4(C_2O_4)$, LiFOP) allows reversible cycling with PC based electrolytes with graphite anodes and both $LiFePO_4$ and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode.

  J. Power Sources **2012**, 205, 439-448.

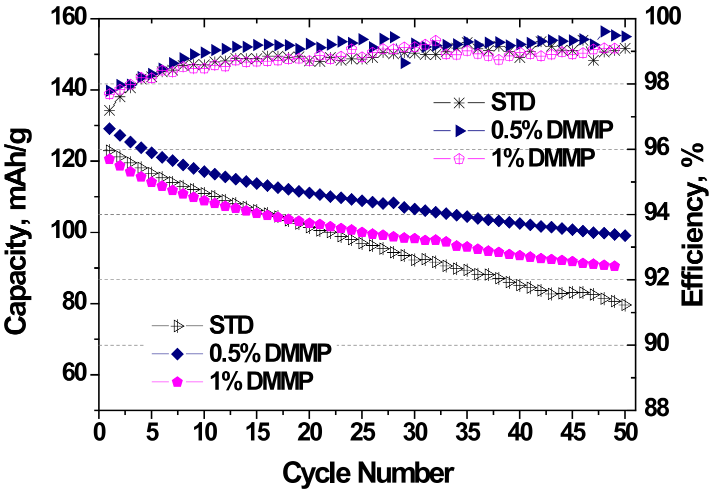


- Developed Cathode film forming additives which improve the performance of $Li/LiNi_{0.5}Mn_{1.5}O_4$ cells cycled to 4.9 V.

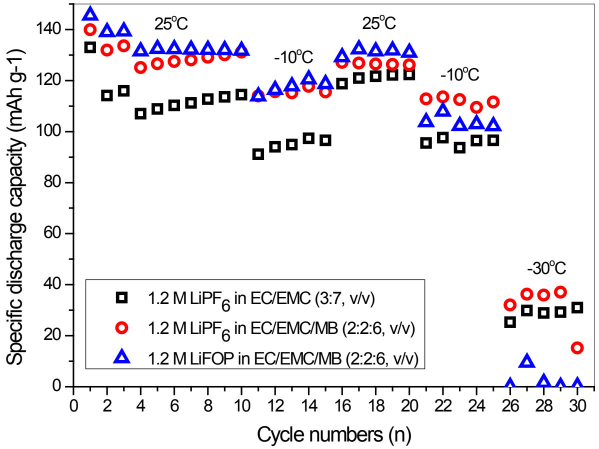
  Electrochem. Solid State Lett. **2012**, 15, A28-A31.

- Developed Lewis Basic/$LiPF_6$ stabilizing additives which improve the performance of $Li/LiNi_{0.5}Mn_{1.5}O_4$ cells cycled to 4.9 V

  J. Electrochem. Soc. **2012**, 159, A739-A751.

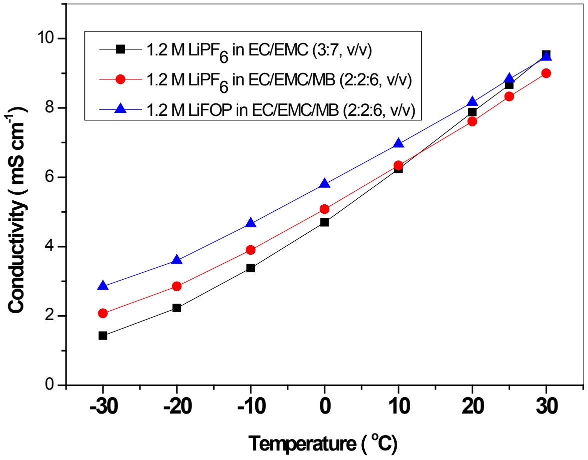


FY 12 Technical Accomplishments – Investigation of $LiPF_4(C_2O_4)$/MB Electrolytes



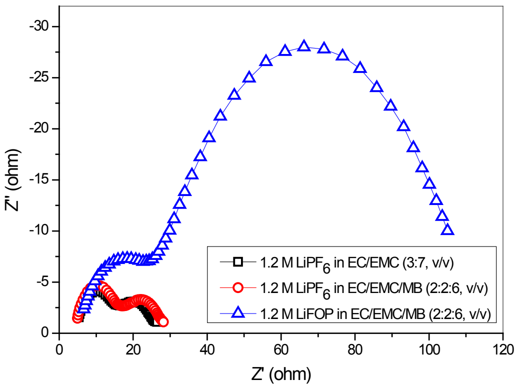
Cycling performance for natural graphite/ $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cells was investigated.

Comparable performance before storage at 55 °C, but worse after.



Ionic conductivity of electrolytes was investigated between +30 and -30°C.

LiFOP electrolyte has higher conductivity at low temperature.

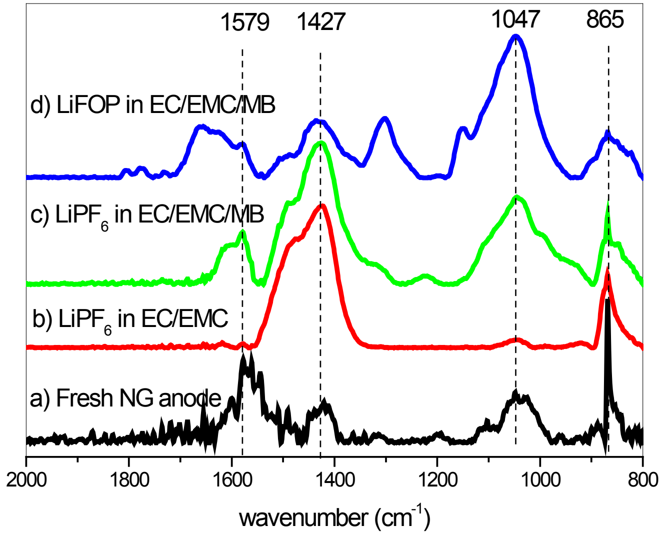


Electrochemical impedance spectra after accelerated aging.

LiFOP electrolyte has much higher impedance

While conductivity of LiFOP is comparable to $LiPF_6$, the interfacial films after accelerated aging have greater impedance

FY 12 Technical Accomplishments – Investigation of $LiPF_4(C_2O_4)$/MB Electrolytes



IR Spectra after accelerated Aging

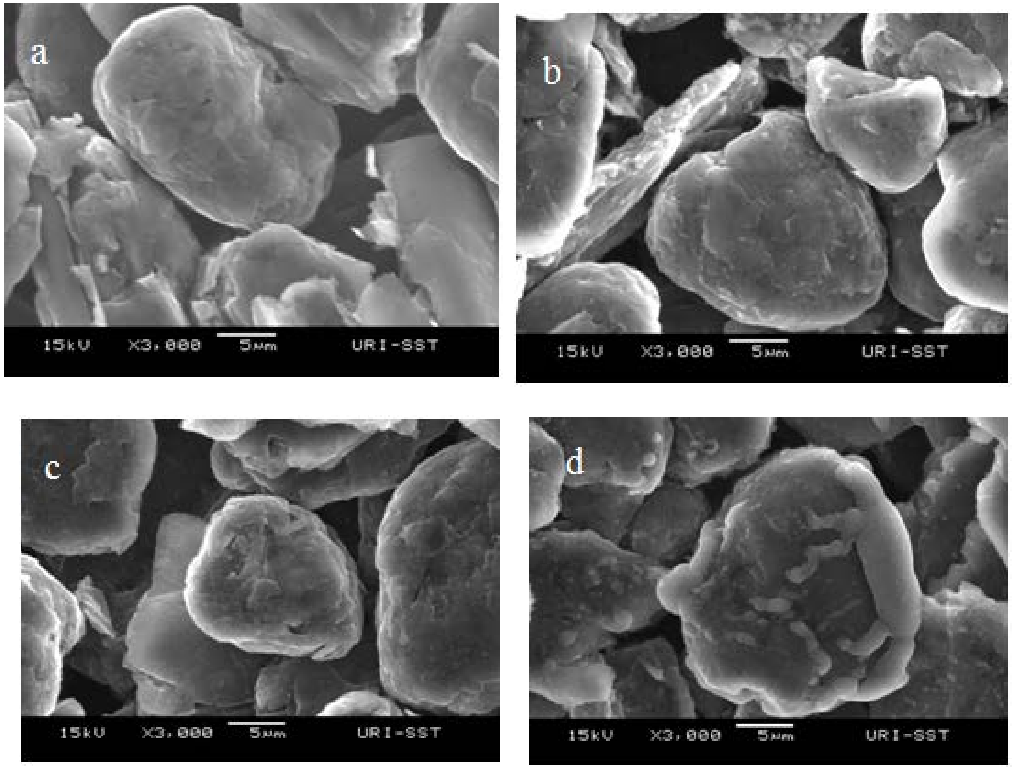
Baseline electrolyte has Li_2CO_3, 1427 cm^{-1} .

$LiPF_6$/MB electrolyte has Li_2CO_3 and an additional peak at ~ 1600 cm^{-1} for lithium alkyl carbonates.

LiFOP/MB electrolyte has Li_2CO_4 1640 cm^{-1} and 1323 cm^{-1}, poly(ethylenecarbonate) at 1760 cm^{-1}.

XPS provides corresponding results

Cathode Surface films similar



SEM Images After Accelerated aging

Baseline electrolyte or the $LiPF_6$/MB electrolyte have a thin SEI

LiFOP/MB electrolyte has a much thicker film consistent with a thicker anode SEI

J. App. Electrochem. In Press

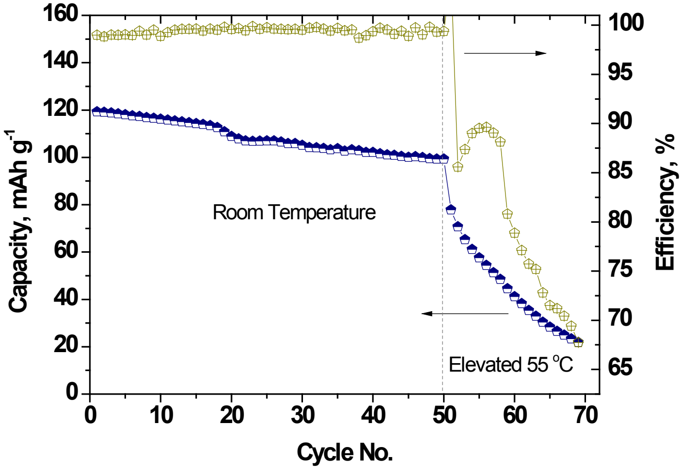
FY 13 Technical Accomplishments – Investigation of Electrolytes for HV Spinel

Preliminary investigations suggest two primary mechanisms of performance loss due to electrolyte ($LiPF_6$ in Carbonates)

- **Oxidation of the electrolyte on cathode surface**
- **Metal ion dissolution due to acidic electrolyte decomposition products**

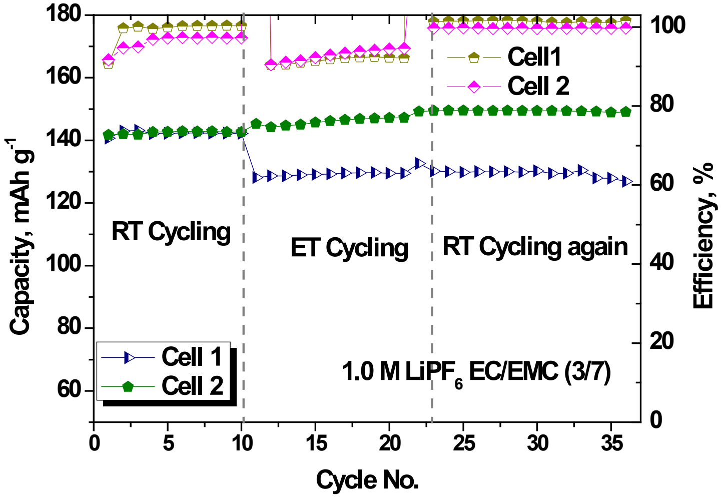
Investigation of novel electrolytes to Improve Performance of $LiNi_{0.5}Mn_{1.5}O_4$ cathodes cycled to high Voltage

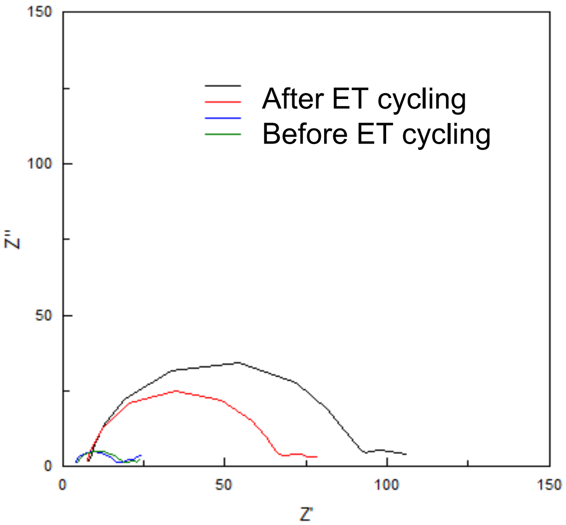
- **Cathode Film forming additives which generate a passivation layer inhibiting electrolyte oxidation**
- **Lewis Basic Additives which inhibit Mn dissolution**



Very little capacity fade at RT followed by dramatic capacity fade at 55 °C for graphite/$LiNi_{0.5}Mn_{1.5}O_4$ cells

FY 13 Technical Accomplishments – Investigation of Electrolytes for HV Spinel





Capacity loss upon cycling Li/$LiNi_{0.5}Mn_{1.5}O_4$ cells at 55 ^oC is minimal. Performance much better than in graphite/$LiNi_{0.5}Mn_{1.5}O_4$ cells.

Increased impedance is significant and efficiency is low during ET cycling. $LiNi_{0.5}Mn_{1.5}O_4$ surface changing upon cycling at 55 ^oC.

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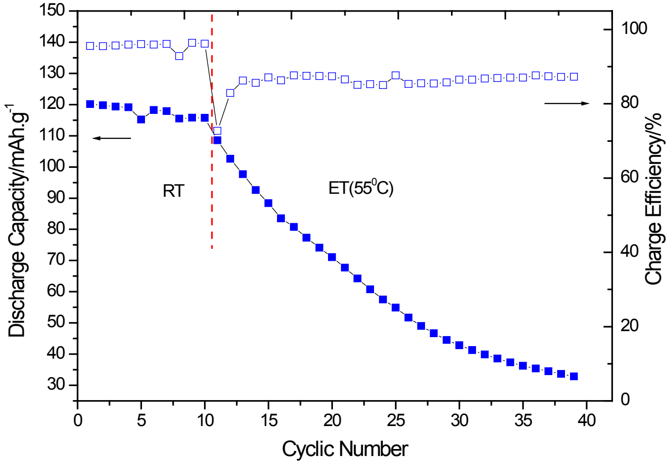

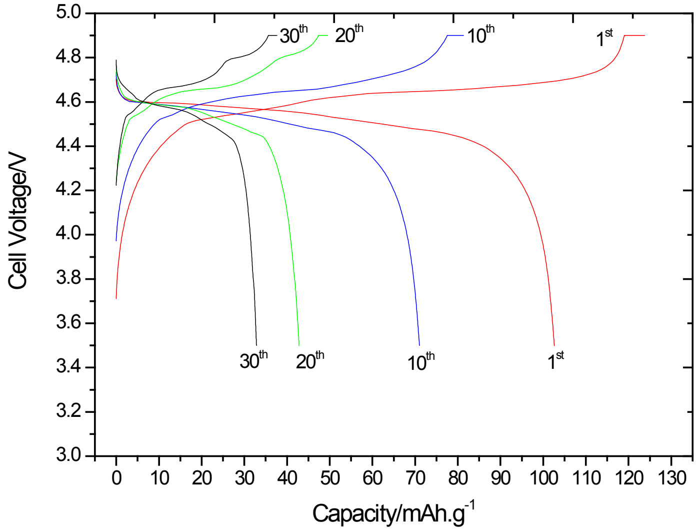

In graphite/$LiNi_{0.5}Mn_{1.5}O_4$ cells capacity loss accompanied by changing voltage profiles.

Charging shoulder at 4.6 V is lost upon cycling at 55 ^{o}C

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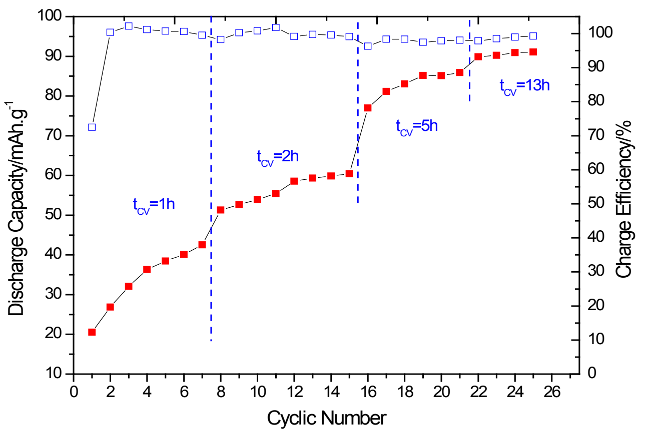
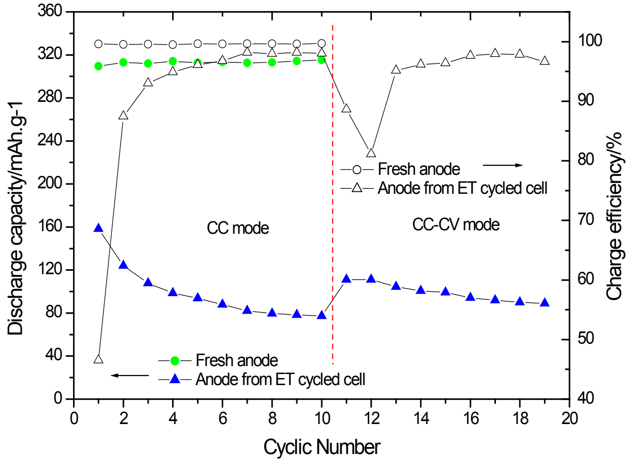
Cells were disassembled after aging. Li/ $LiNi_{0.5}Mn_{1.5}O_4$ and Li/ graphite cells were prepared from the cycled electrodes



Most of the capacity can be accessed for Li/ $LiNi_{0.5}Mn_{1.5}O_4$ cells , but the rates are much lower



Most of the capacity cannot be accessed for Li/ graphite cells, even with lower rates

Both electrodes contribute to performance fade

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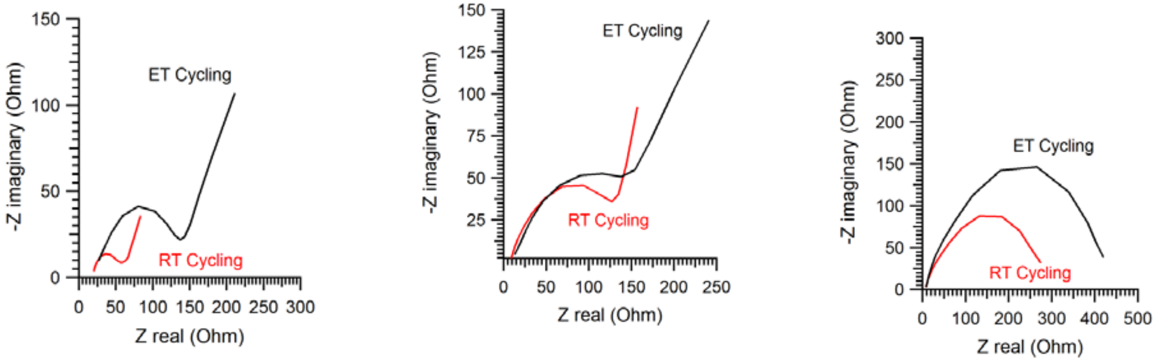


Electrochemical Impedance after cycling at 25 ^{o}C and after cycling at 55 ^{o}C (left) graphite/ $LiNi_{0.5}Mn_{1.5}O_4$ cells; (center) Li/ graphite cells; (right) Li/ $LiNi_{0.5}Mn_{1.5}O_4$ cells.

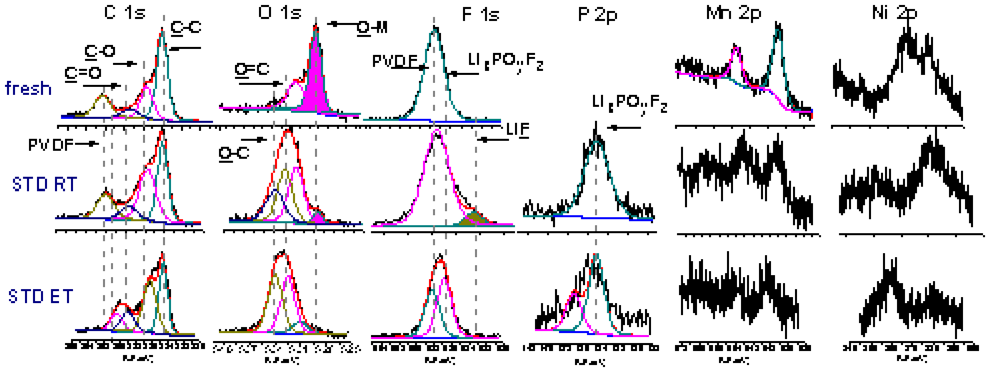
Half cells were prepared from electrodes extracted from cells cycled at ET

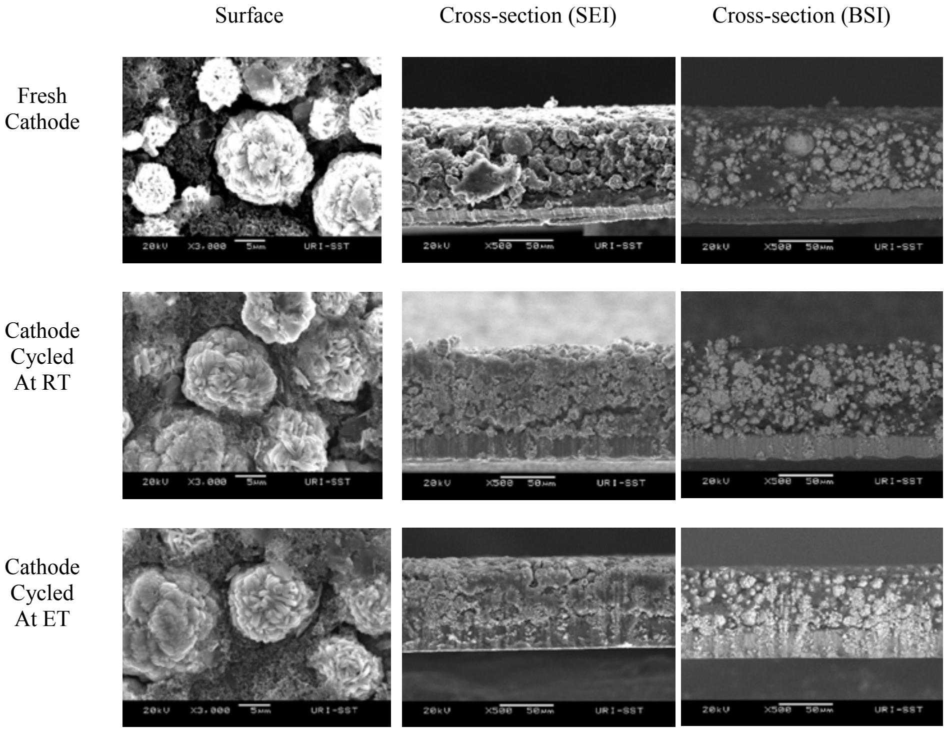
Most of the impedance growth occurs on the cathode

FY 13 Technical Accomplishments – Investigation of Electrolytes for HV Spinel

SEM images of a $LiNi_{0.5}Mn_{1.5}O_4$ cathode fresh, after cycling at 25 °C (RT) and after cycling at 55 °C (ET).

Cathode particles and laminate are retained after cycling at 55 °C.





XPS spectra a $LiNi_{0.5}Mn_{1.5}O_4$ cathode fresh, after cycling at 25 °C (RT) and after cycling at 55 °C (ET).

Cycling at 55 °C results in a slight thickening of the cathode surface film and possible decomposition of PVDF

Mn and Ni content at surface is decreased

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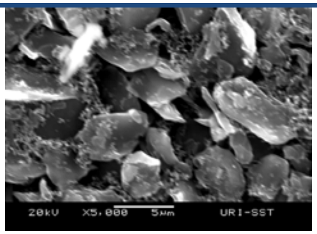
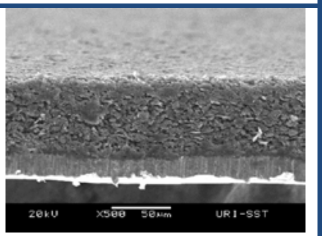
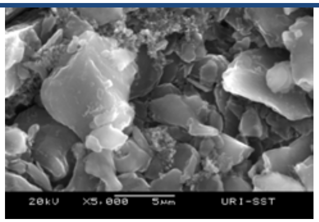
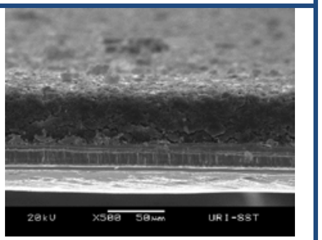
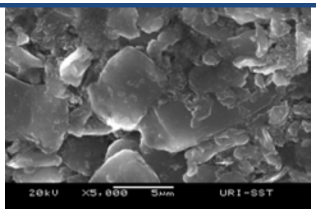
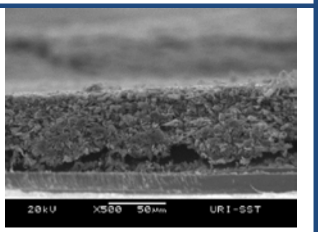
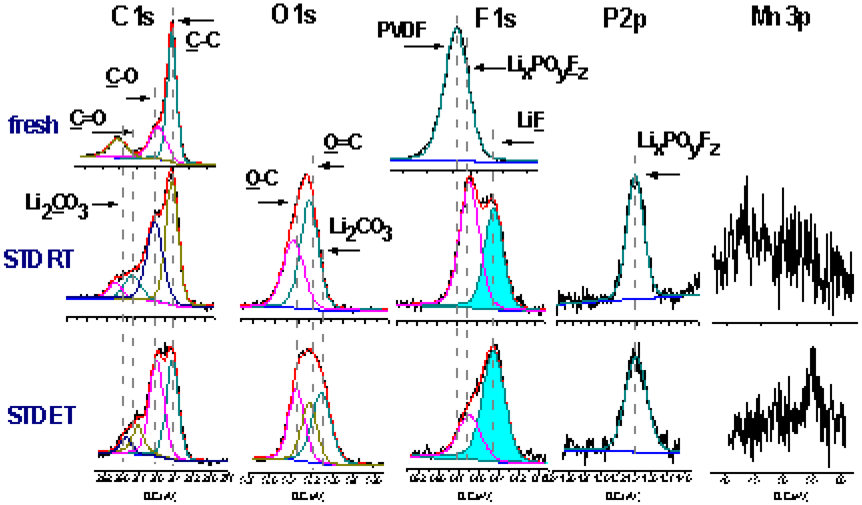
	Plane	Cross-section
Fresh anode		
Anode Cycled at 25 °C		
Anode Cycled at 55 °C		

SEM images of the graphite anode fresh, after cycling at 25 °C and after cycling at 55 °C.

Changes to bulk anode particles are consistent with SEI formation

Anode experiences delamination

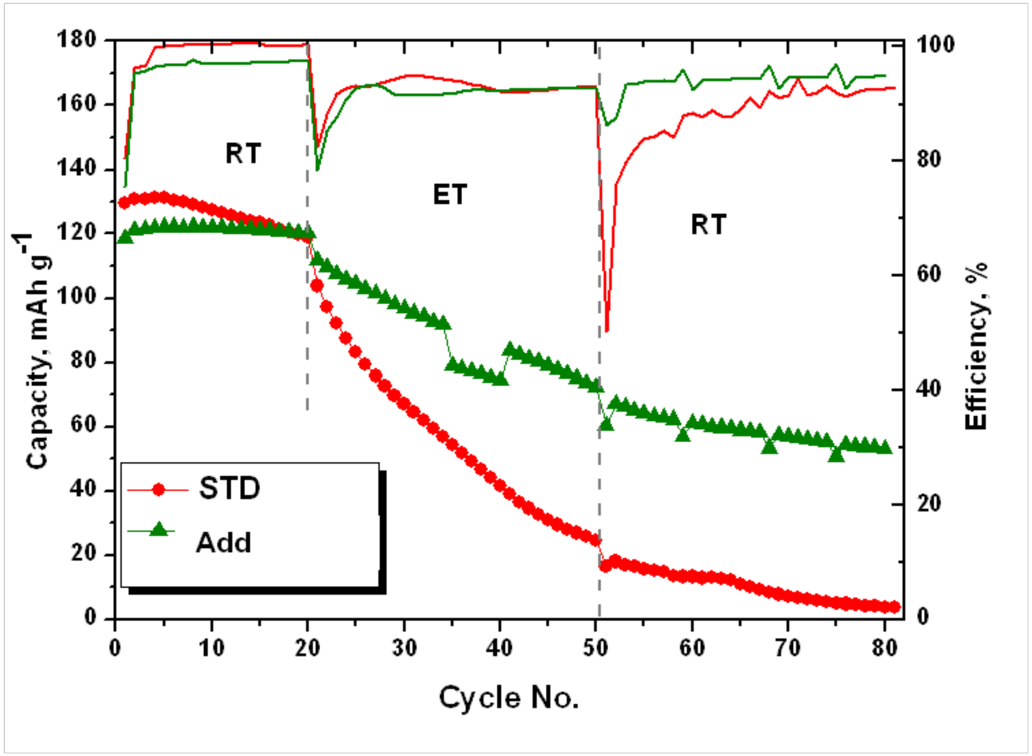


XPS spectra of the graphite anode fresh, after cycling at 25 °C and after cycling at 55 °C.

Significant electrolyte decomposition occurs upon cycling at 55 °C, products include lithium alkyl carbonates, Li_2CO_3 , LiF, and $Li_xPF_yO_z$

Mn is also present on the anode surface (ICP-MS)

FY 13 Technical Accomplishments – Investigation of Electrolytes for HV Spinel



Incorporation of electrolyte additive(s) results in dramatic decrease in capacity fade upon cycling at 55 °C for graphite/$LiNi_{0.5}Mn_{1.5}O_4$ cells

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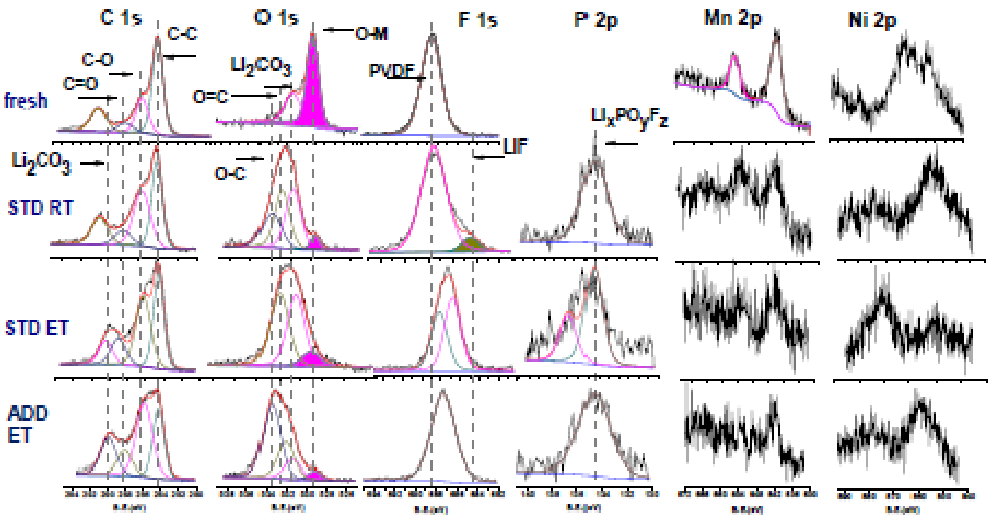
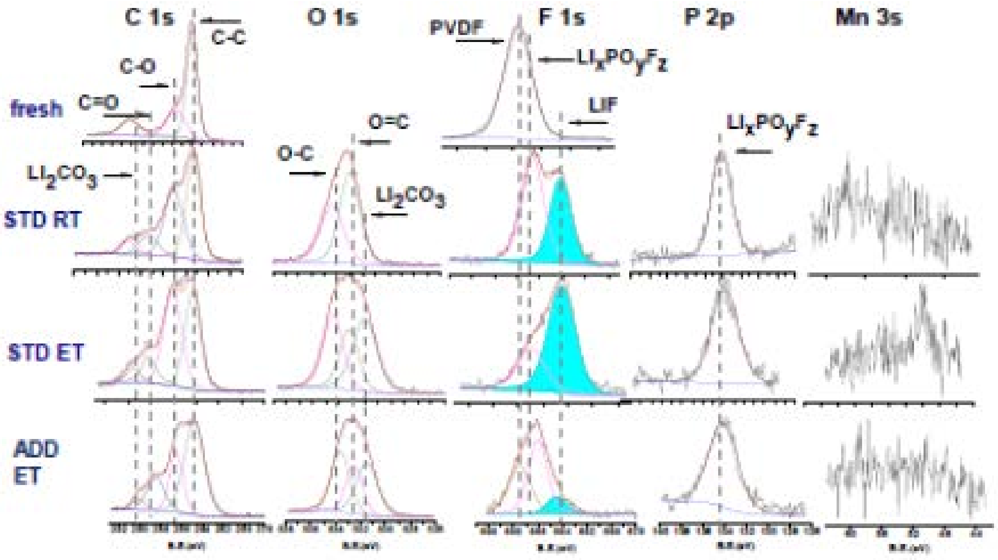


Changes to cathode surface are small upon incorporation of additive

XPS spectra of the anode

Additive inhibits LiF formation on Anode

Mn deposition is also inhibited, as supported by ICP-MS



Collaborations

- D. Abraham (ANL, National Lab, ABRT Program): Collaborations on the investigation of novel salts, solvents and additives in lithium ion battery electrolytes.
- M. Smart (NASA JPL, National Lab, ABRT Program): Collaborations on the investigation of novel salts, solvents and additives in lithium ion battery electrolytes.
- V. Battaglia (LBNL, National Lab, BATT Program): Collaboration on performance testing of novel salts and additives in BATT program cells.
- J. Kerr (LBNL, National Lab, BATT Program): Collaboration on the investigation of novel electrolytes.
- A. Garsuch (BASF, Industrial): Collaboration on the development of novel electrolytes for high voltage cathodes.
- F. Puglia and B. Ravdel (Yardney, Industrial): Collaboration on testing novel electrolytes in large format cells and investigation of high voltage LNMS (7 – 12 Ah).
- High Voltage Spinel Focus Group (LBNL, National Lab, BATT Program)

Proposed Future Work FY 13 – FY 14

- Develop an understanding of the role of electrolyte in capacity fade for graphite/ $LiNi_{0.5}Mn_{1.5}O_4$ full cells cycled at moderately elevated temperature (55 ^{o}) (FY 13).

- Develop improved cathode film forming additives for graphite/ $LiNi_{0.5}Mn_{1.5}O_4$ cells to improve cycling performance at 55 ^{o}C. (FY 13)

- Develop novel non-fluorinated salts for use in lithium ion batteries. (FY 13-14)

- Investigate novel electrolytes to improve performance of nanostructured Si anode materials (FY 14)

- Develop mechanistic understanding of performance limiting reactions of electrolytes in lithium ion batteries (FY 13-14)

Summary Slide

- **Investigated the performance of $LiPF_4(C_2O_4)$ electrolytes at low temperature before and after accelerated aging.**
- Developed an understanding of performance limiting reactions of $LiPF_4(C_2O_4)$/ EB electrolytes at low temperature: generates thick resistive anode SEI after aging.
- **Investigated the performance limiting reactions of $LiNi_{0.5}Mn_{1.5}O_4$ cathodes cycled to high voltage (4.9 V vs Li)**

❖ Discovered that the two leading sources of performance fade are electrolyte oxidation and Mn dissolution/reduction on anode

❖ Electrolyte oxidation below 4.9 V lesser contributor, thermal effects are larger contributor.

❖ Both the anode and cathode are damaged from cycling at 55 ^{o}C.

❖ Additives have been developed that inhibit Mn dissolution and improve performance of high voltage cathodes

❖ Novel electrolyte formulations can improve the cycling performance of $LiNi_{0.5}Mn_{1.5}O_4$ cathodes at high voltage (4.9 V vs Li)