Development of Electrolytes for Lithium-ion Batteries

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ES067

Overview

Timeline

- 04/01/2009
- 03/31/2114
- 60 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 FY11 - $146 K
- Funding for FY12 - $147 K

Partners

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

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 ($LiPF_6$).
- 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.
- Develop electrolytes for improved performance of Si-based alloy anodes.

- 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

FY11

- (a) Develop improved cathode film forming additives for high voltage Ni-Mn spinel cathode materials. (July 11) **Completed**
- (b) Investigate cell performance upon accelerated aging of graphite/$LiNi_XCo_{1-2x}Mn_XO_2$ with $LiPF_4(C_2O_4)$/PC electrolytes compared to $LiPF_6$ electrolytes. (March 11) **Completed**
- (c) Develop an understanding of the source of irreversible capacity loss with $LiPF_4(C_2O_4)$ electrolytes during formation cycling (July 11) **Completed**
- (d) Investigate novel electrolytes to improve performance of Si-alloy anodes (Sept 11) **Completed**.

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 coin cells. (July 12) **On schedule**
- (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) **On Schedule**

Approach

- Investigate properties of $LiPF_4(C_2O_4)$/carbonate or ester electrolytes in small Li-ion cells.
- Investigate electrode surface films for cells cycled with $LiPF_4(C_2O_4)$ to determine source of performance differences.
- Investigate cathode film forming additives for high voltage (> 4.5 V) cathode materials.
- Investigate incorporation of electrolyte SEI forming additives for Si-based Alloy anodes.
- 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.
- Use computational methods to screen potentially interesting additives.

Previous Technical Accomplishments

- Investigated performance of $LiPF_4(C_2O_4)$ electrolytes with different cathodes ($LiFePO_4$, $LiMn_2O_4$, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$).

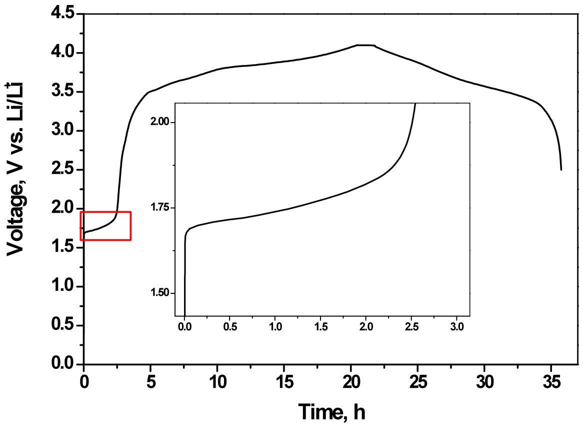
  J. Power Sources **2011**, 196, 8073-8084.

- Developed commercially viable synthesis of $LiPF_4(C_2O_4)$.

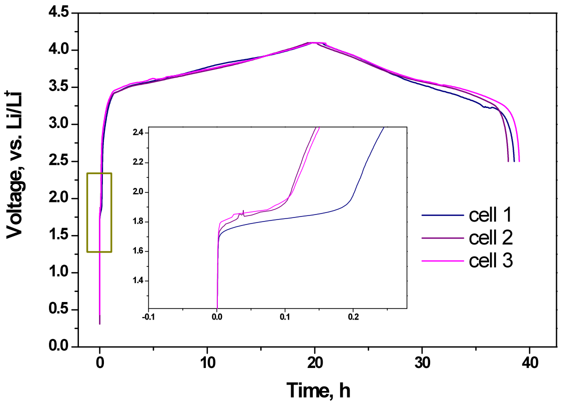
- Developed understanding of first cycle capacity loss for $LiPF_4(C_2O_4)$ electrolytes and method to decrease capacity loss.

- Investigate cathode film forming additive to improve performance of high voltage (>4.5 V) cathodes

  J. Power Sources **2011**, *196*, 2251-2254.



$MCMB/LiNi_{0.2}Co_{0.8}O_2$

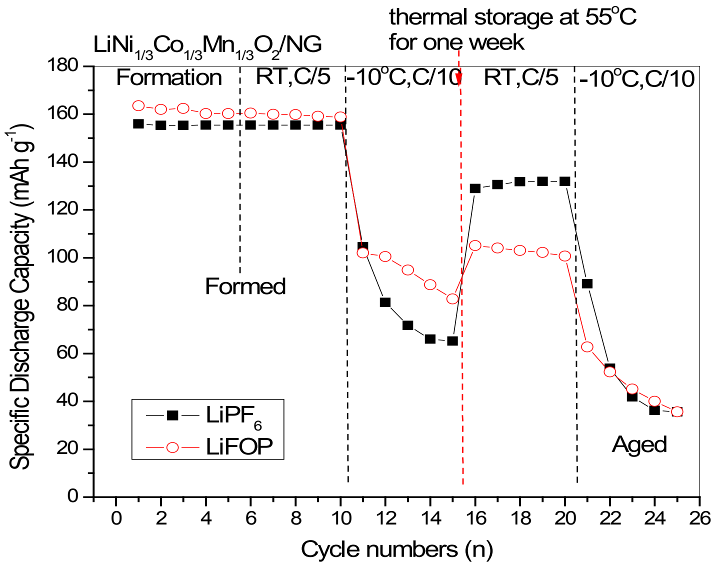


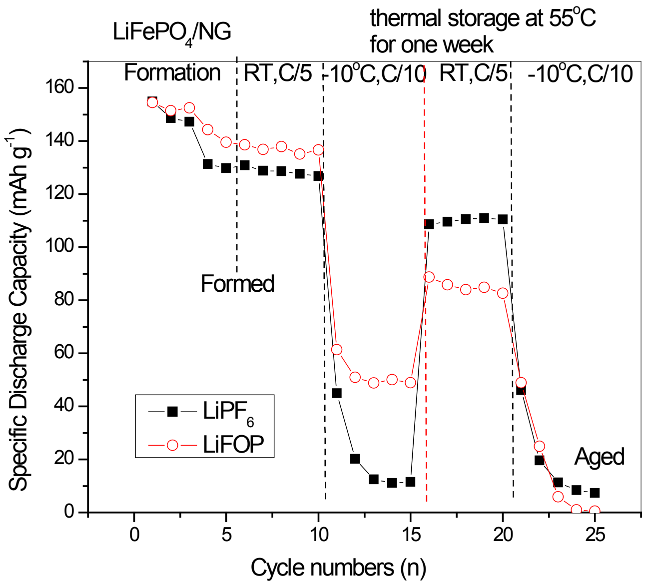
$NG/LiNi_{0.2}Co_{0.8}O_2$

First cycle irreversible capacity/shoulder at 1.7 V vs Li of cells cycled with $LiPF_4(C_2O_4)$ changes with different types of graphite materials.

J. Electrochem. Soc. **2011** 158, A1202.

FY 11 Technical Accomplishments – Investigation of $LiPF_4(C_2O_4)$/PC Electrolytes



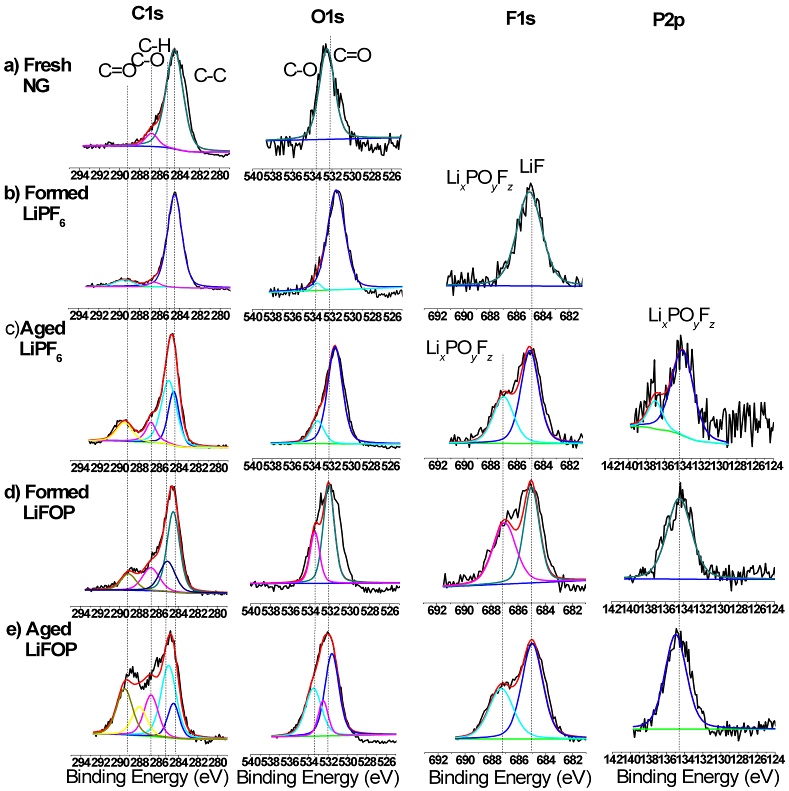


The use of the novel lithium salt lithium tetrafluorooxalatophosphate (LiFOP) allows reversible cycling with PC based electrolytes with graphite anodes and both $LiFePO_4$ and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode.

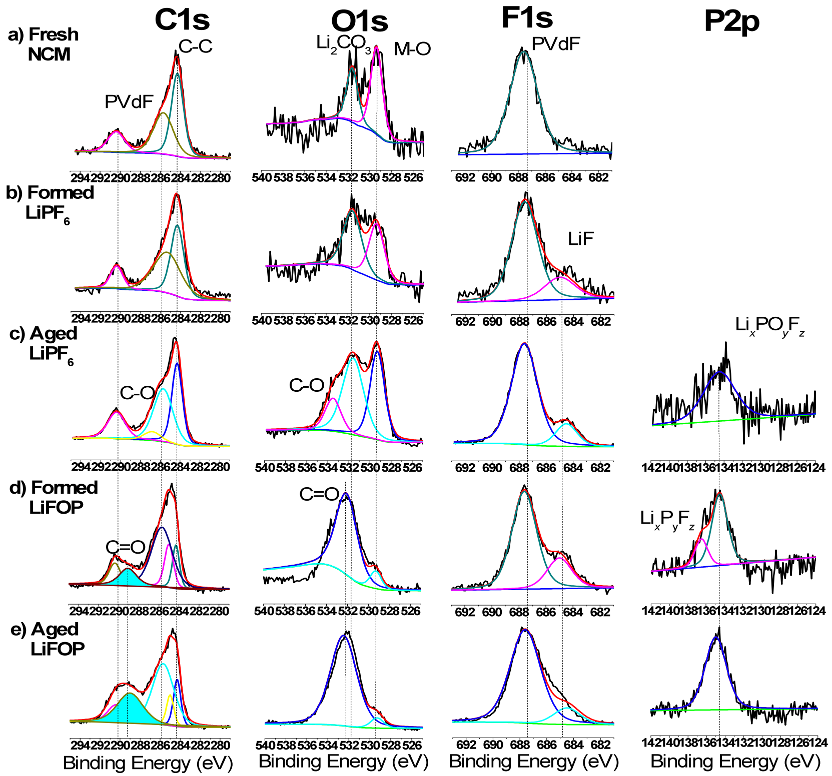
Initially the low temperature cycling performance of cells with LiFOP/PC electrolyte is superior to similar $LiPF_6$/EC electrolytes.

After accelerated aging the room temperature performance of cells with LiFOP/PC electrolyte is inferior to $LiPF_6$/EC electrolytes.

FY 11 Technical Accomplishments – Investigation of $LiPF_4(C_2O_4)$/PC Electrolytes



XPS spectra of graphite anodes

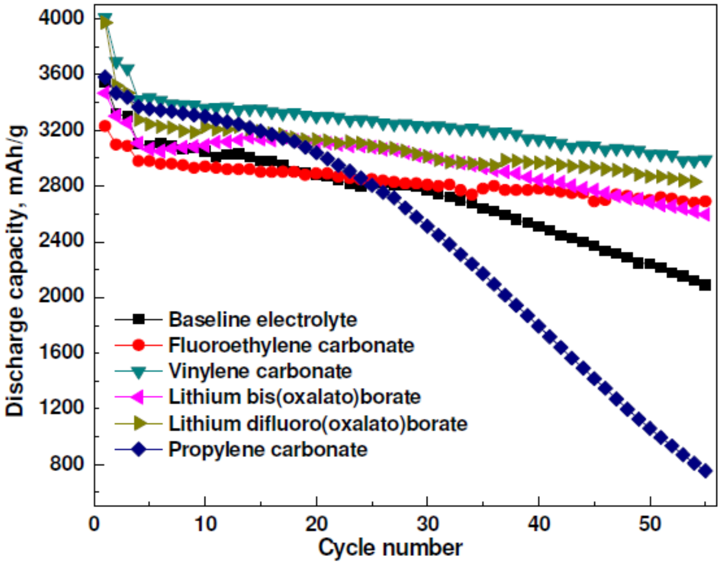


XPS spectra of NCM cathodes

LiFOP/PC electrolytes generate a unique and stable anode SEI which prevents graphite exfoliation by PC due to the presence of lithium oxalate.

The SEI film formed on the cells cycled with LiFOP/PC electrolyte is significantly damaged during accelerated aging leading to decreased capacity retention.

FY 11 Technical Accomplishments – Investigation of Electrolytes for Si Anodes



Si anodes were cycled with $LiPF_6$/carbonate electrolytes with various additives. Several of the additive electrolyte combinations provide superior cycling performance.

The best additives include VC and $LiBF_2(C_2O_4)$. Surprisingly, cells containing FEC did not perform as well as other electrolytes.

Ex-situ surface analysis suggests the cycling performance differences are due to differences in the structure of the Si anode SEI.

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Research suggests two primary mechanisms of performance loss of $LiNi_{0.5}Mn_{1.5}O_4$ cycled to high voltage (4.9 V vs Li) due to electrolyte

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

Investigation of novel additives 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

Different Sources of $LiNi_{0.5}Mn_{1.5}O_4$ and related materials have different performance

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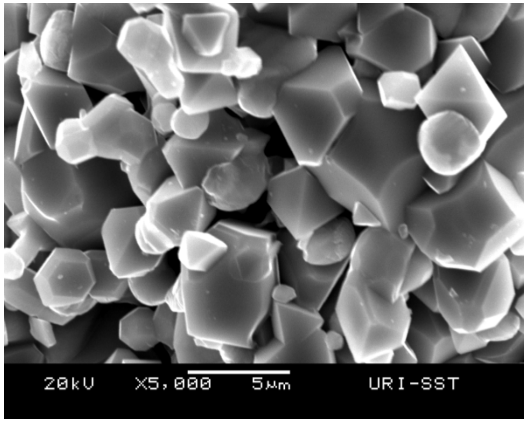
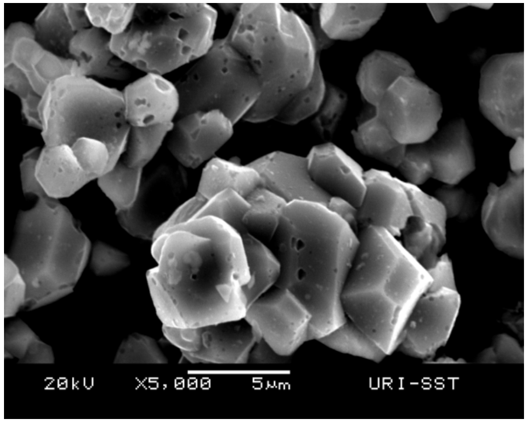
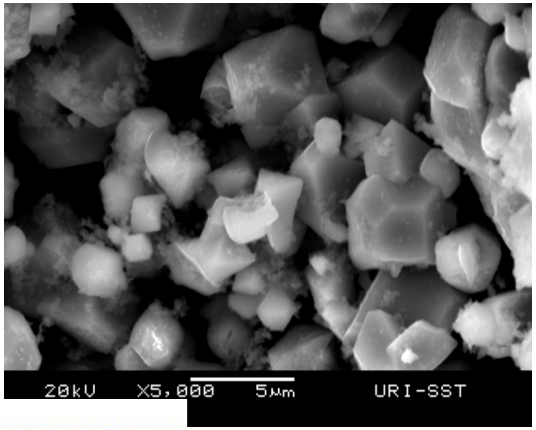


Fresh $LiNi_{0.42}Fe_{0.08}Mn_{1.5}O_4$



Aged 4 days at 85 °C with 1 M $LiPF_6$ in EC/EMC



Aged 4 days at 85 °C with 1 M $LiPF_6$ in EC/EMC and 1 % LB

	Mn dissolution (%)	Ni dissolution (%)	Fe dissolution (%)
STD electrolyte	1.7	0.51	0.25
STD + 1% LB1	0.72	0.14	0.046

Acidic Species in electrolyte etch Cathode particle surface

Lewis base inhibits cathode etching and TM dissolution

$LiNi_{0.42}Fe_{0.08}Mn_{1.5}O_4$, A. Manthiram

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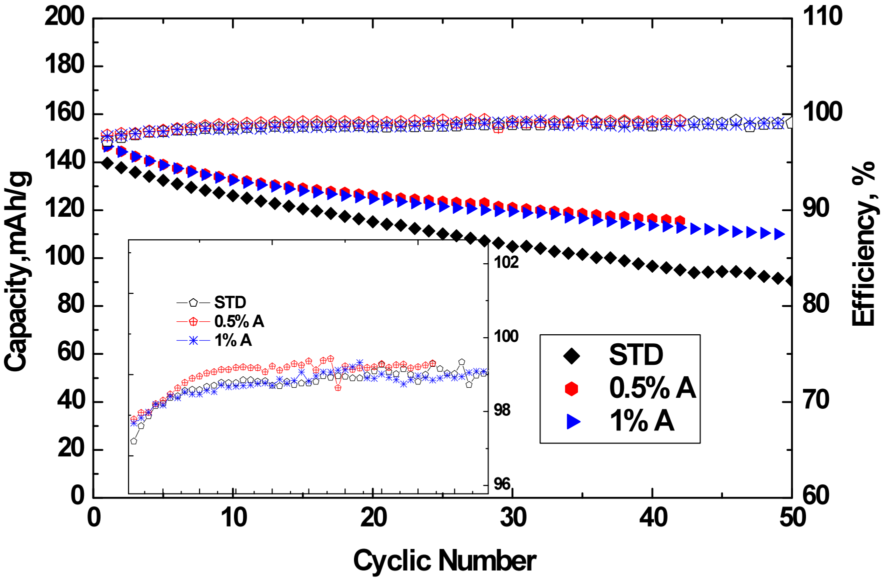
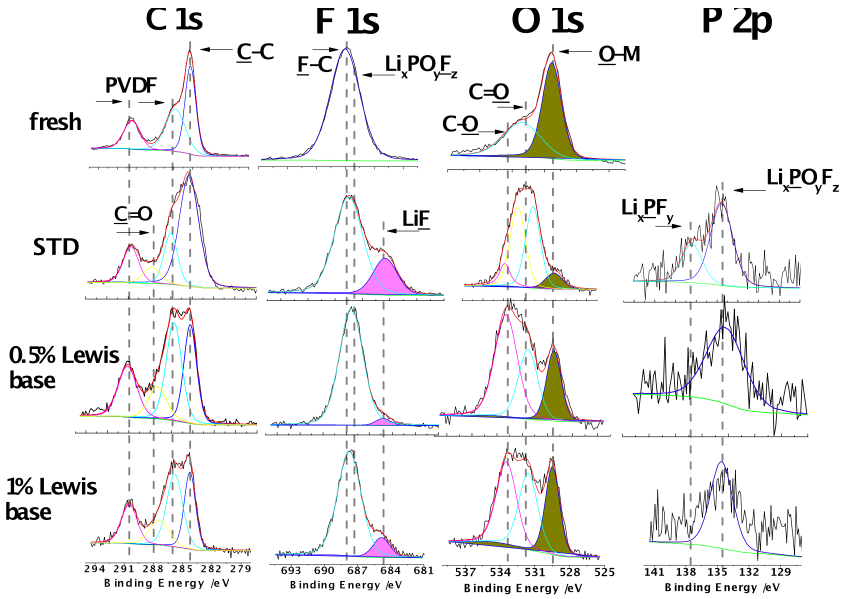


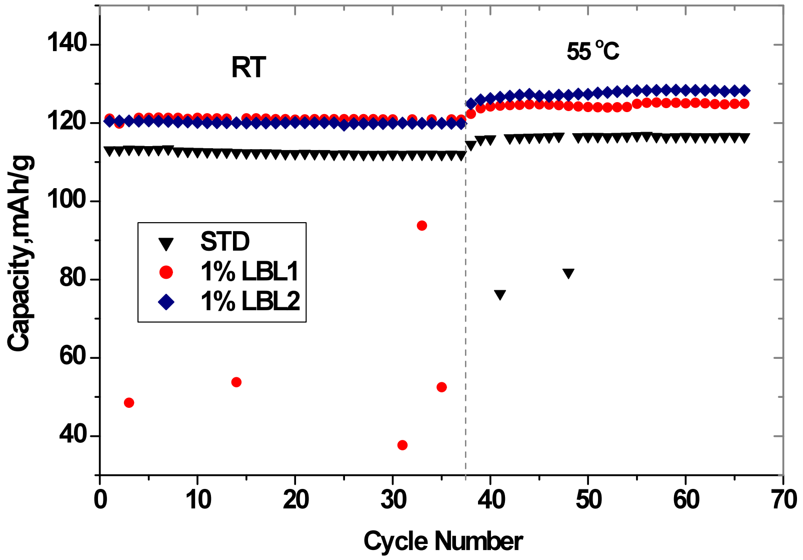
Incorporation of Lewis Base improves the efficiency and capacity retention of Li/ LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cells cycled to 4.9 V vs Li.
Improvement likely related to in decreased dissolution of Mn.

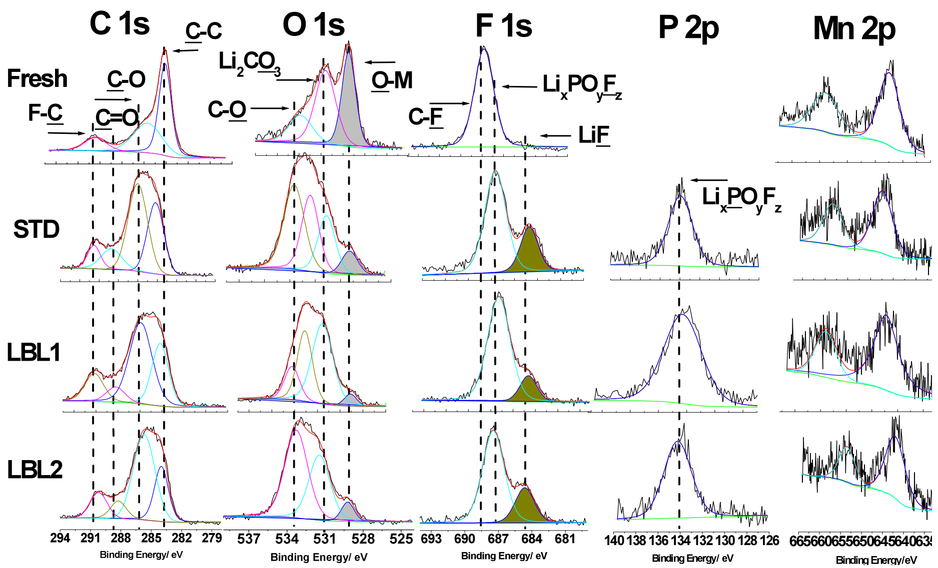


XPS spectra suggest that addition of Lewis Base decreases the film thickness on the cathode.
Less LiF and more metal oxide are observed on surface with Lewis base.

LiNi$_{0.5}$Mn$_{1.5}$O$_4$ from Hunan Shanshan

FY 12 Technical Accomplishments – Investigation of Electrolytes for HV Spinel





Addition of Lewis Base (LB) provides a slight increase in discharge capacity of $LiNi_{0.42}Fe_{0.08}Mn_{1.5}O_4$/Li cells.

XPS spectra suggest slight decrease in LiF on cathode surface and better retention of Mn.

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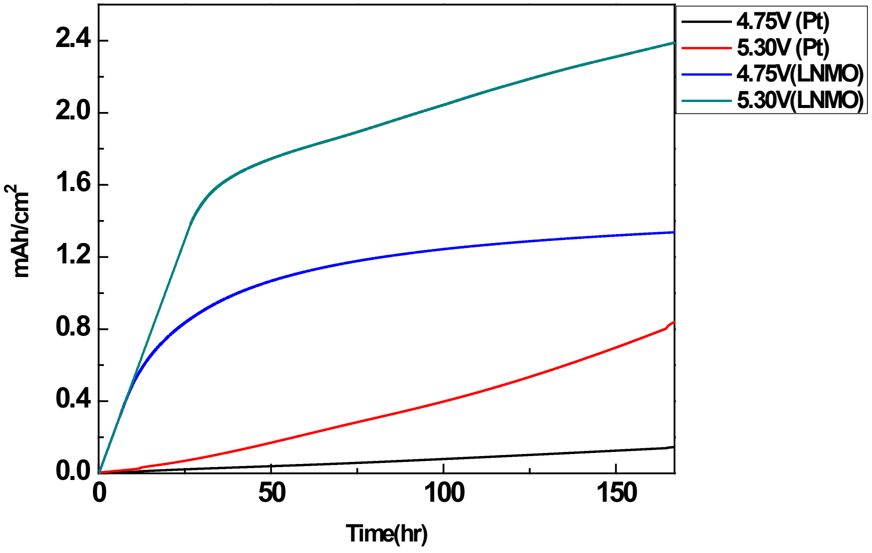
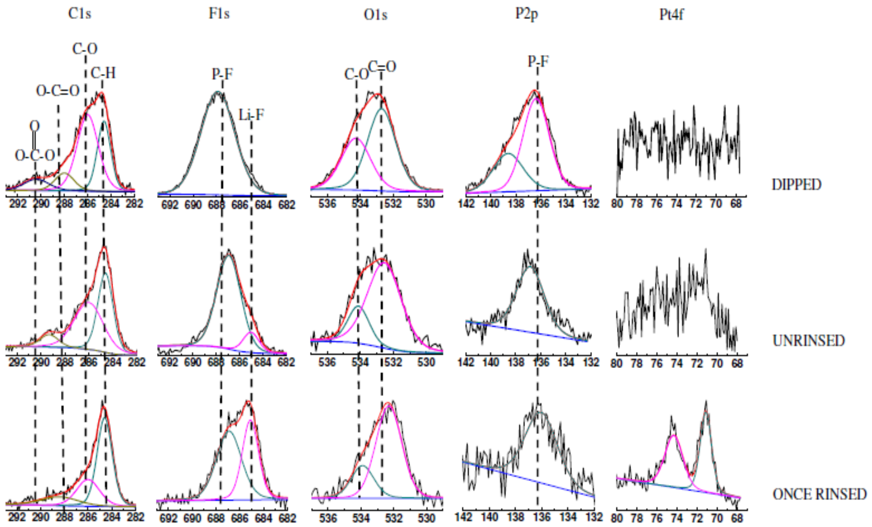
The oxidation reactions of the electrolyte with $LiNi_{0.5}Mn_{1.5}O_4$ and Pt surfaces was investigated.



C/20 charging to 4.75 & 5.30V and hold at same voltage on $LNi_{0.5}Mn_{1.5}O_4$ electrode and scan (5mV/S) and hold (4.75 & 5.30V) experiment on Pt electrode in $LiPF_6$ in 3:7 EC/EMC.



XPS Spectra of Pt surface dipped in electrolyte and after cycling

- Upon subtracting the current associated with Li extraction the residual current is very similar for $LiNi_{0.5}Mn_{1.5}O_4$ and Pt surfaces.

Similar surface species are observed on Pt to metal oxide, polyethylene carbonate and lithium fluorophosphates

The metal oxide does not appear to catalyze the oxidation of the electrolyte

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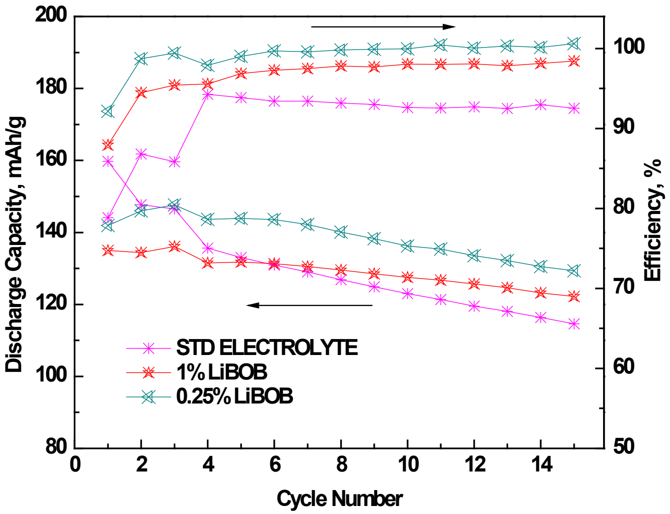

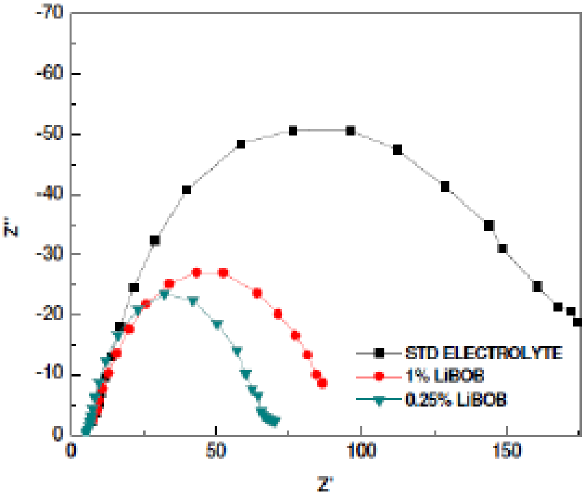

Cathode film forming additives including LiBOB were investigated to improve the performance of $LiNi_{0.5}Mn_{1.5}O_4$ cells.

$LiNi_{0.5}Mn_{1.5}O_4$ cells containing LiBOB had batter capacity retention and higher efficiency than cells with 1 M $LiPF_6$ in 1:1 EC/DEC.

Cells containing LiBOB retained almost 93% of the initial discharge capacity as compared to 71% capacity retention from baseline electrolyte cells.

Cells containing LiBOB have lower impedance after cycling consistent with thinner cathode surface films

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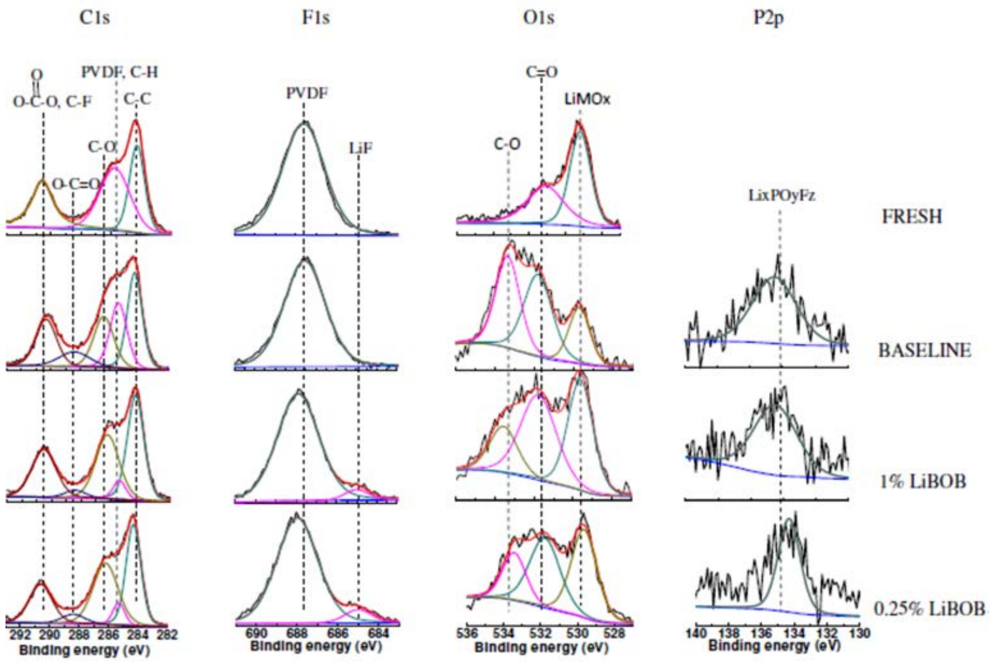
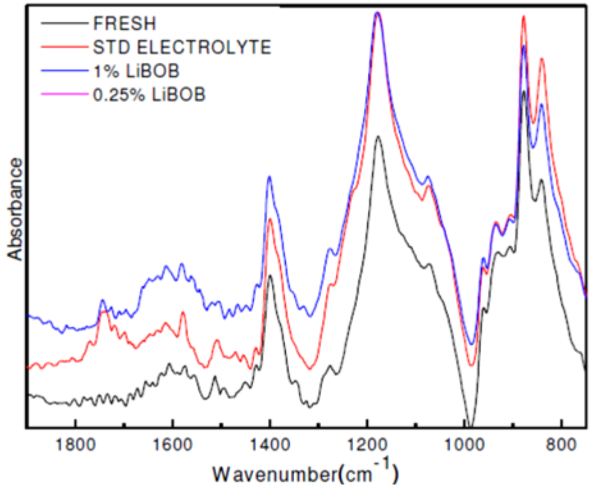
Surface analysis provides insight into performance enhancement with added LiBOB



XPS Spectra of $LiNi_{0.5}Mn_{1.5}O_4$



IR Spectra of $LiNi_{0.5}Mn_{1.5}O_4$

Ex-situ surface analysis of the cycled cathodes suggests the incorporation of LiBOB alters the surface chemistry of the electrode resulting in thinner cathode surface films (more metal oxide on surface) containing oxalate species (1640 cm^{-1}).

Addition of low concentrations of LiBOB appears generate novel cathode surface films which improve the performance of $LiNi_{0.5}Mn_{1.5}O_4$ cathodes cycled to high voltage.

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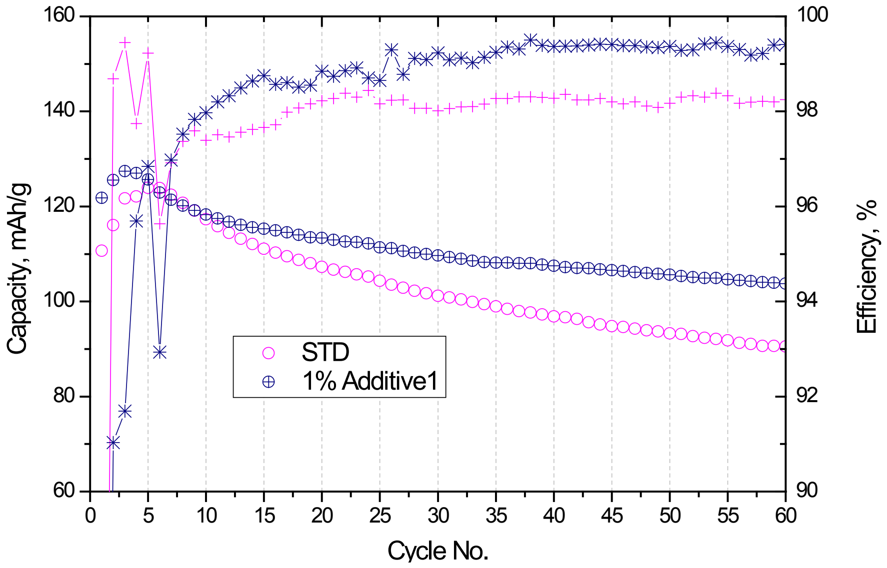

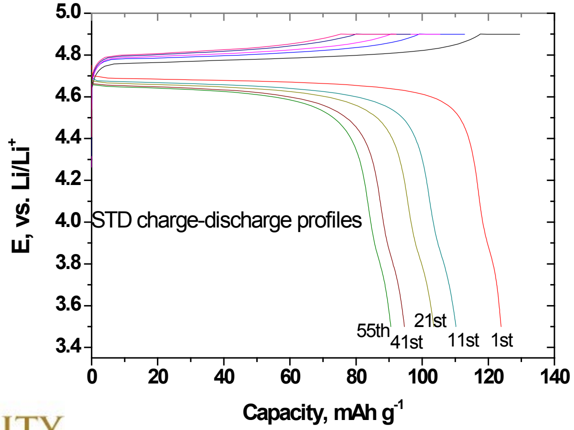

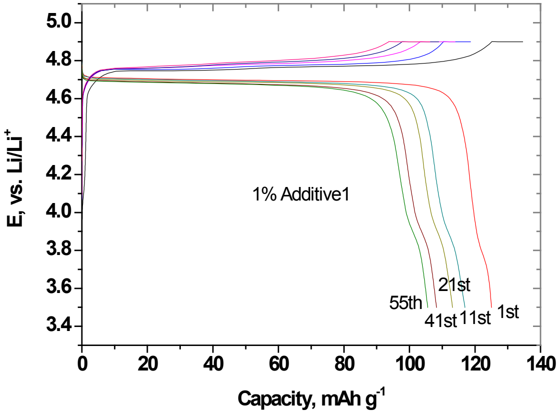

Other sacrificial cathode Film forming additives improve cycling performance of $LiNi_{0.5}Mn_{1.5}O_4$ at RT

Selection of Cathode film forming additives aided by calculation of HOMO and LUMO values (W. Li)

Voltage plateau at 4.7 V is retained in the presence of additive

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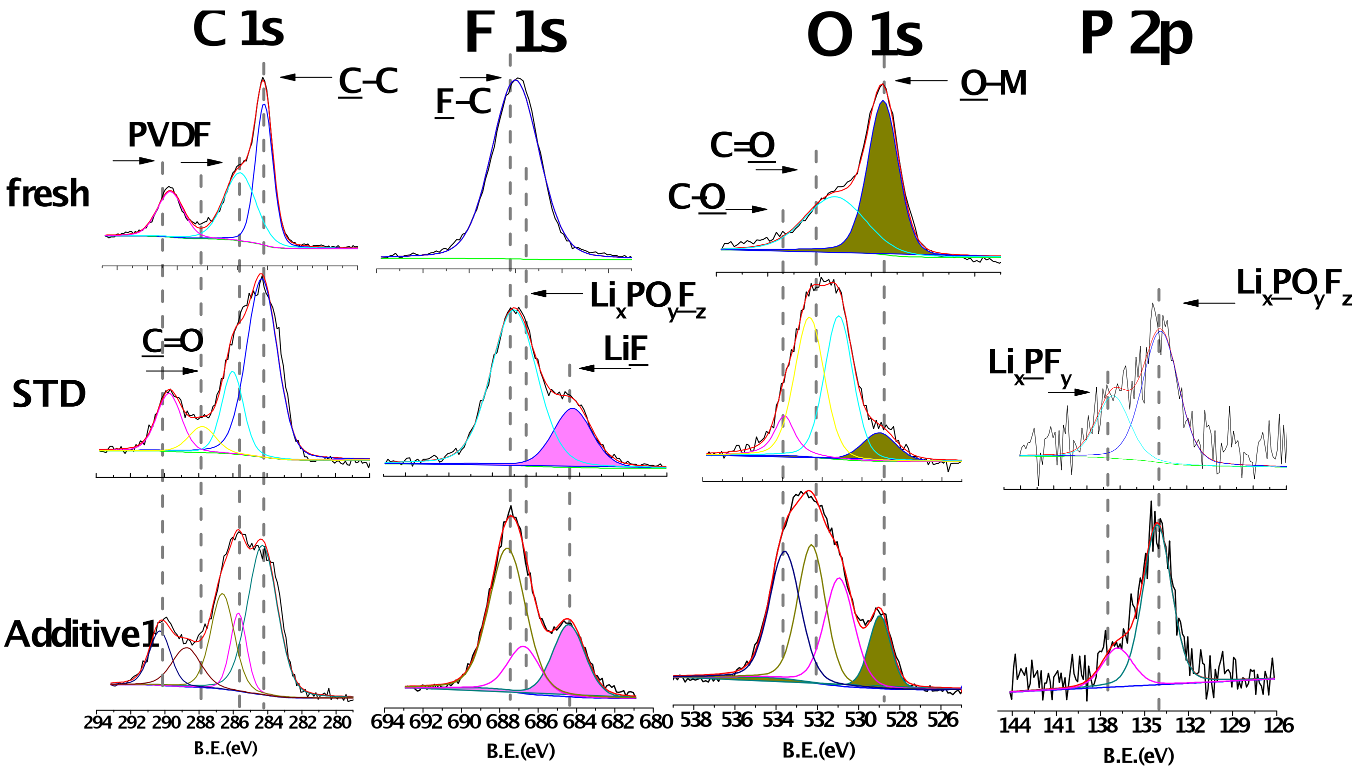

Sacrificial cathode Film forming additives change the surface chemistry of the interface resulting in thinner surface films

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.
- P. Guduru (Brown Univ., Academic): Collaborations on the investigations of electrolytes for Si andoes.
- W. Li (S. China Univ. Tech., Academic): Collaboration on the investigation of $LiPF_4(C_2O_4)$ and computational investigations of additives for cathode and anode film formation.
- 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 12 – FY 13

- Optimize $LiPF_4(C_2O_4)$ electrolytes for high temperature and low temperature performance. (FY 12)

- Develop improved cathode film forming additives for high voltage Ni-Mn spinel cathode materials. (FY 12)

- Develop novel salts and additives for use in lithium ion batteries. (FY 12 – 13)

- Develop mechanistic understanding of performance limiting reactions of electrolytes in lithium ion batteries (FY 12-13)

- Develop novel electrolytes for high capacity/high Volatge layered metal oxide cathode materials. (FY 13)

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 $LiPF_4(C_2O_4)$/PC electrolytes and initiated investigations of electrolytes with ester based co-solvents for improved low temperature performance
- **Investigation of novel electrolyte additives to improve performance of Si-based anodes.**
- **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
- Developed of cathode film forming additives that inhibit electrolyte oxidation and improve the performance of high voltage cathodes.
- Developed Additives that inhibit Mn dissolution and improve performance of high voltage cathodes