Development of Electrolytes for Lithium-ion Batteries

Brett Lucht
University of Rhode Island

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ES067

Overview

Timeline

- 04/01/2009
- 12/31/2113
- 44 Percent complete

Budget

- Total project funding
  - DOE share $731 K
- Funding received in FY10 - $146 K
- Funding for FY11 - $146 K

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

Partners

- D. Abraham (ANL)
- M. Smart (NASA JPL)
- W. Li (S. China Univ. Tech.)
- V. Battaglia & J. Kerr (LBNL)
- M. Payne (Novolyte)
- F. Puglia & B. Ravdel (Yardney)
- G. Smith & O. Borodin (U. Utah)

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

FY10

- (a) Develop cathode film forming additives for high voltage (>4.5 V vs Li) cathode materials. (March 10) **Completed**
- (b) Investigate cell performance upon accelerated aging of graphite/$LiNi_xCo_{1-2x}Mn_xO_2$ cells with $LiPF_4(C_2O_4)$ electrolytes compared to $LiPF_6$ electrolytes. (March 10) **Completed**
- (c) Investigate cell performance of $LiPF_4(C_2O_4)$ compared to $LiPF_6$ in small cells with new chemistries graphite/$LiMn_2O_{4,}$ $LiNi_xCo_{1-2x}Mn_xO_2$ cells, or with PC electrolytes. (Sept 10) **completed**
- (d) Develop commercially viable synthesis for $LiPF_4(C_2O_4)$. (Sept 10) **completed**

FY11

- (a) Develop improved cathode film forming additives for high voltage Ni-Mn spinel cathode materials. (July 11) **on schedule**
- (b) Investigate cell performance upon accelerated aging of graphite/$LiNi_XCo_{1-2x}Mn_XO2$ with $LiPF_4(C_2O_4)$/PC electrolytes compared to LiPF6 electrolytes. (March 11) **delayed**
- (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) **On Schedule**.

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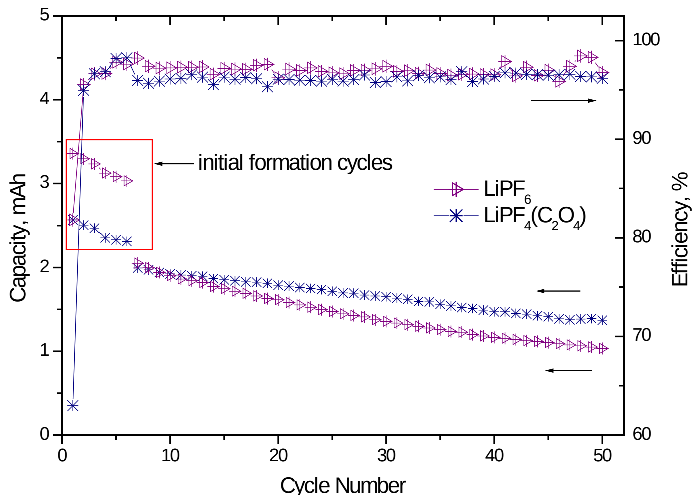
Approach

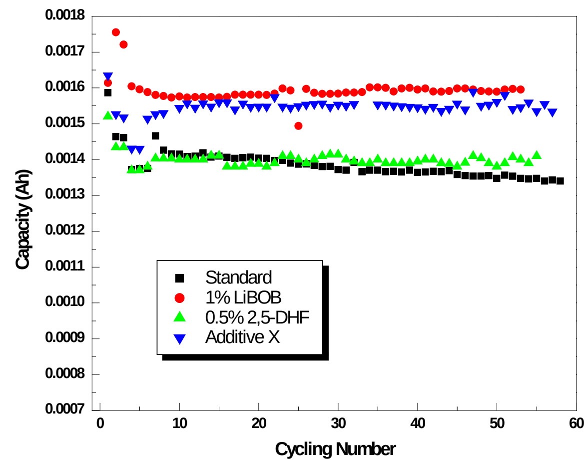
- Investigate properties of $LiPF_4C_2O_4$/carbonate electrolytes in small Li-ion cells.
- Investigate electrode surface films for cells cycled with $LiPF_4(C_2O_4)$ to determine source of performance differences.
- Investigate cathode film forming additives for high voltage (> 4.5 V) cathode materials.
- 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 combinations of additives for $LiPF_6$ electrolytes.
- Investigated cell performance upon accelerated aging of graphite/$LiNi_xCo_{1-2x}Mn_xO_2$ cells with $LiPF_4(C_2O_4)$ electrolytes compared to $LiPF_6$ electrolytes.
- Studied changes in anode SEI structure with $LiPF_4(C_2O_4)$.
- Investigated $LiPF_4(C_2O_4)$ in small cells and produce 100 g $LiPF_4(C_2O_4)$ for testing.
- Developed cathode film forming additives for high voltage (>4.5 V vs Li) cathode materials.



Cycling behavior of $LiPF_4(C_2O_4)$ and $LiPF_6$ in 1:1:1 (EC:DEC:DMC) in MCMB/$LiNi_{0.8}Co_{0.2}O_2$ cells before and after storage at 65 °C for two weeks.



The cycling performance of $Li_{1.17}Mn_{0.58}Ni_{0.25}O_2$ half cells charged to 4.9 V vs Li confirm superior cycling performance with additives.

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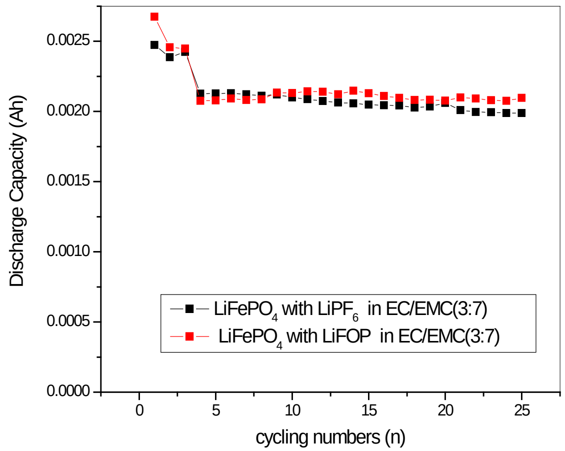
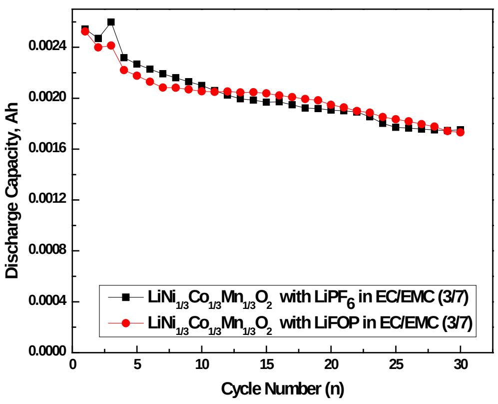
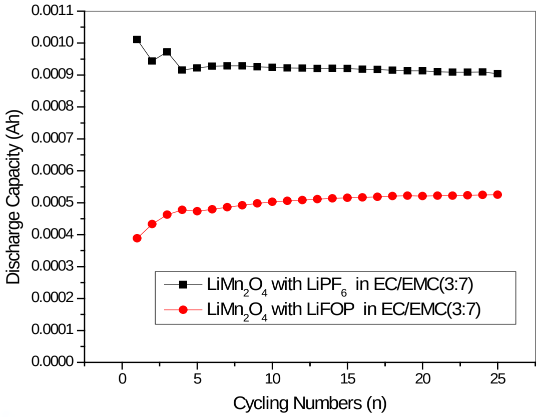
FY 10 Technical Accomplishments: Performance of $LiPF_4(C_2O_4)$



$LiPF_6$ and LiFOP electrolytes in natural graphite/$LiFePO_4$ cells.



$LiPF_6$ and LiFOP electrolytes in MCMB/ $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cells.



$LiPF_6$ and LiFOP electrolytes in MCMB/$LiMn_2O_4$ cells.

$LiPF_4(C_2O_4)$ Electrolytes cycles well for most Anode/Cathode pairs

Formation cycle irreversible capacity differences not observed for all cells

Cycles well with PC

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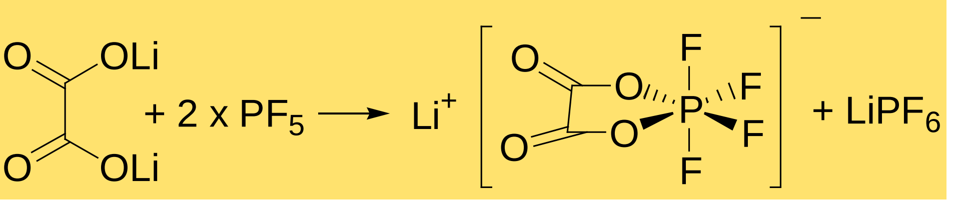
FY 10 Technical Accomplishments – Commercially Viable Synthesis of $LiPF_4(C_2O_4)$

- We have been investigating the novel lithium salt $LiPF_4(C_2O_4)$ for use in lithium ion battery electrolytes.
- The salt has been investigated in our laboratory by BATT investigators (V. Battaglia, LBNL), and companies under confidential non-disclosure agreements.
- The development of a commercially viable process has focused on PF_5 delivery methods and purification optimization



$LiPF_4(C_2O_4)$ is synthesized via the reaction of PF_5 with lithium oxalate. We have investigated several methods of synthesis and purification resulting in significantly higher yields of purified material (> 60 %).

We are currently working with industrial partners to analyze commercial viability of this salt and synthetic process under NDA.

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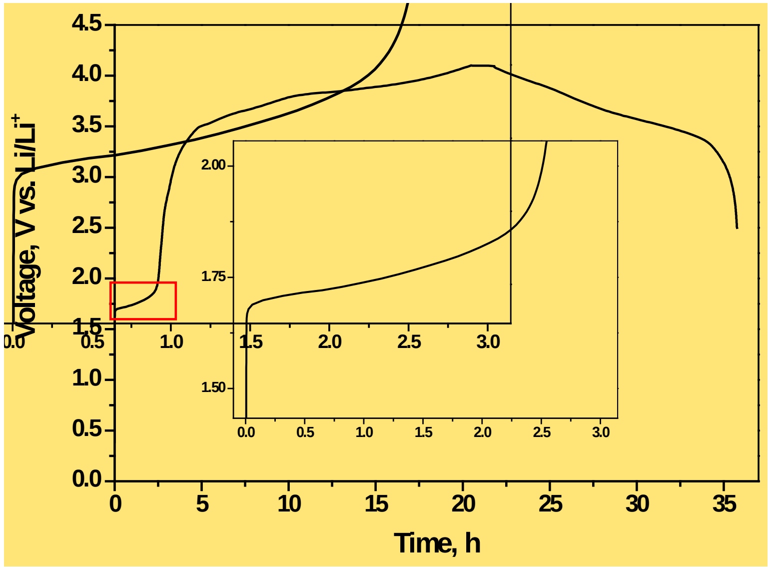
FY 11 Technical Accomplishments – Irreversible Capacity Loss with $LiPF_4(C_2O_4)$

Prepared several batches of $LiPF_4(C_2O_4)$ with different purity levels.

No correlation between salt purity and shoulder at 1.7 V vs Li irreversible capacity of first cycle for $LiNi_{0.8}Co_{0.2}O_2$/MCMB cells.

Source of irreversible capacity is not $Li_2C_2O_4$



1.0 M $LiPF_4C_2O_4$	Efficiency (%)
1st (C/20)	67.7
2nd(C/10)	97.3
3rd (C/10)	98.5
4th (C/5)	97.8
5th (C/5)	98.9

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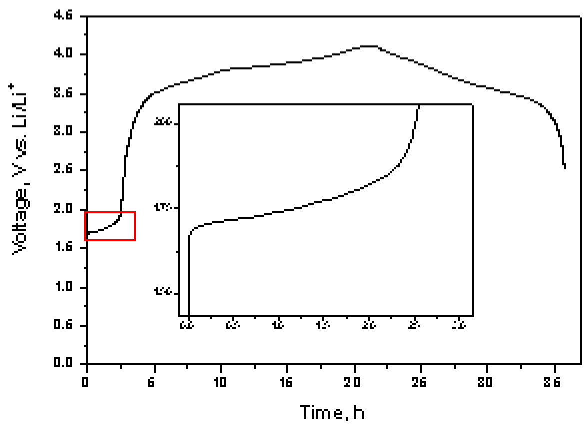
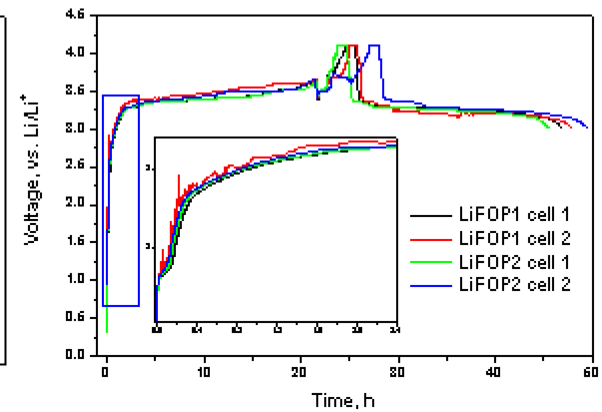
FY 11 Technical Accomplishments – Irreversible Capacity Loss with $LiPF_4(C_2O_4)$

First cycle irreversible capacity/shoulder at 1.7 V vs Li changes with different electrode materials.

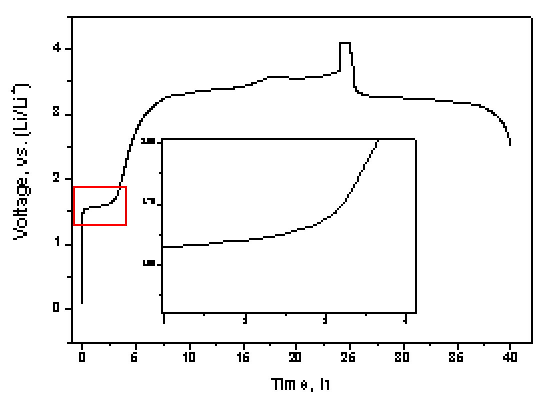
$LiPF_4(C_2O_4)$ cycled with Natural Graphite (NG) anodes has nearly identical first cycle efficiency.



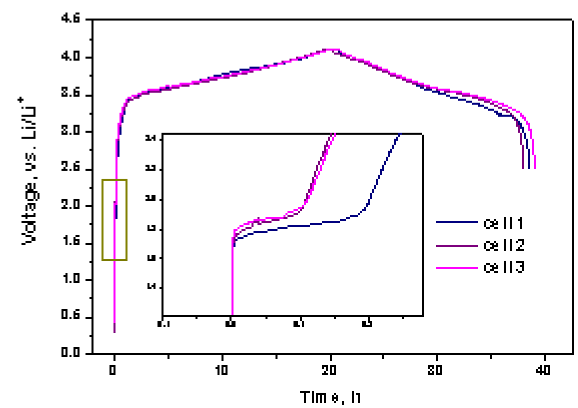
$MCMB/LiNi_{0.2}Co_{0.8}O_2$



$NG/LiFePO_4$

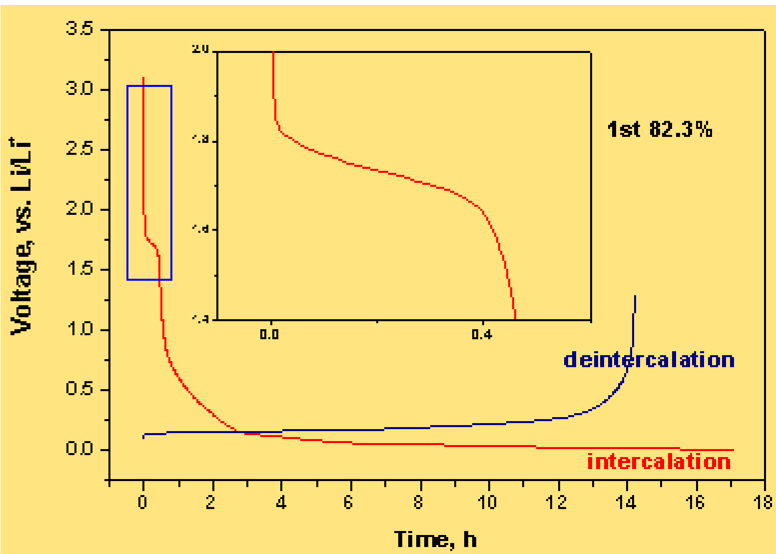


$MCMB/LiFePO_4$

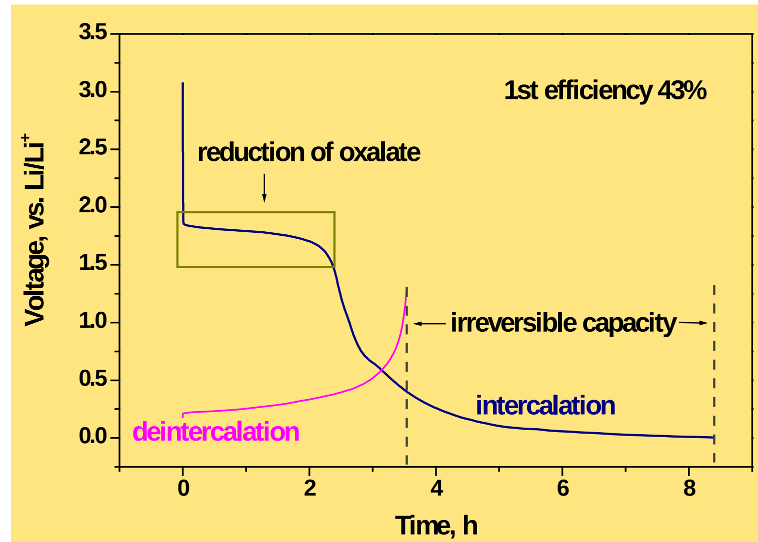


$NG/LiNi_{0.2}Co_{0.8}O_2$

FY 11 Technical Accomplishments – Irreversible Capacity Loss with $LiPF_4(C_2O_4)$



First charge-discharge curve of 1.2 M $LiPF_4C_2O_4$ NG/lithium metal half anode cell



First charge-discharge curve of 1.2 M $LiPF_4C_2O_4$ MCMB/lithium metal half cell

The first cycle irreversible capacity is dependent upon graphite structure.

Irreversible capacity loss can be reduced/eliminated by proper choice of graphite anode.

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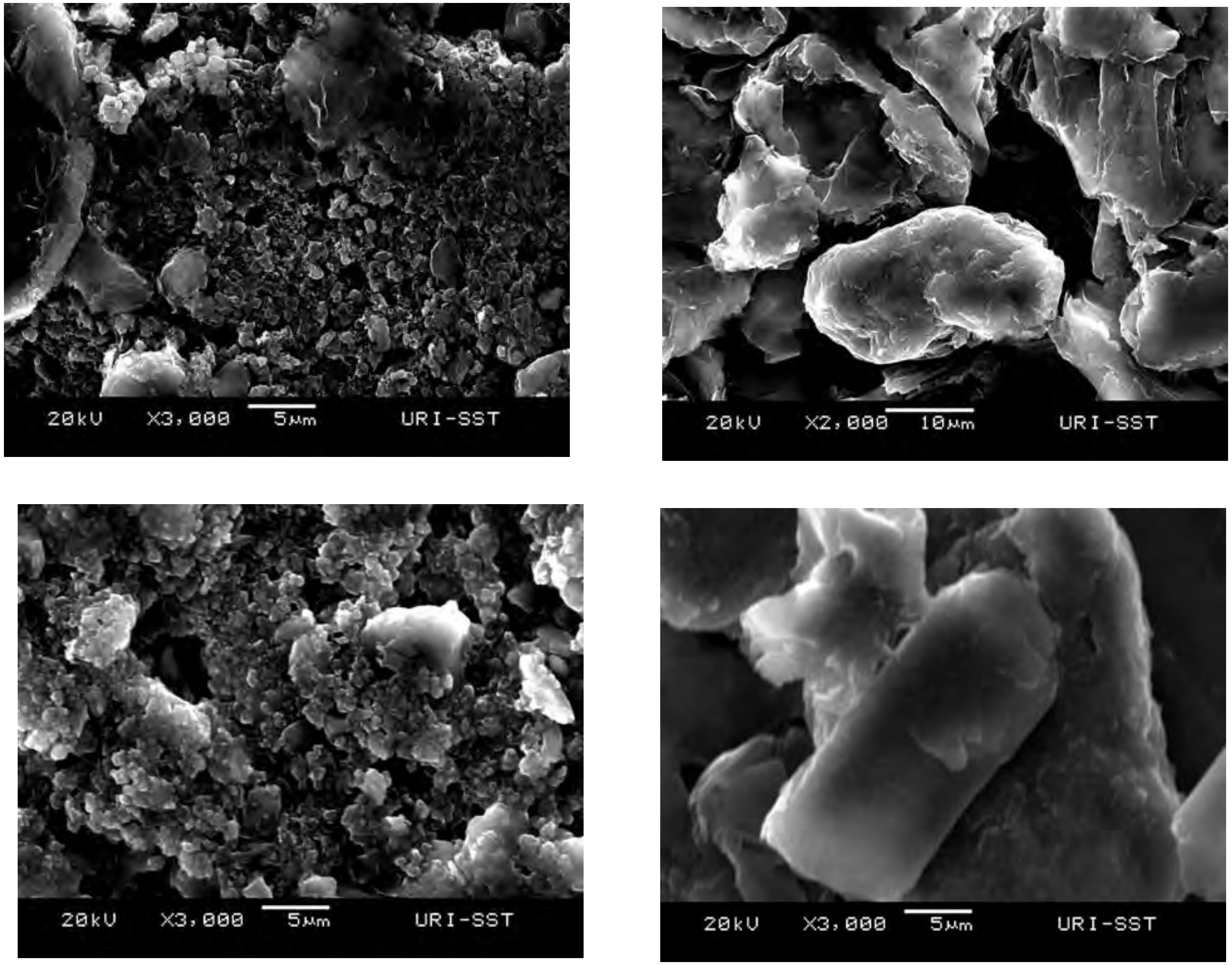
FY 11 Technical Accomplishments – Irreversible Capacity Loss with $LiPF_4(C_2O_4)$



SEMs of anodes before and after formation cycles, (top left) fresh MCMB, (top right) fresh CMS, (bottom left) MCMB after formation cycles, and (bottom right) NG after formation cycles, electrolyte composition 1.2 M $LiPF_4C_2O_4$ EC/EMC (3/7, v/v)

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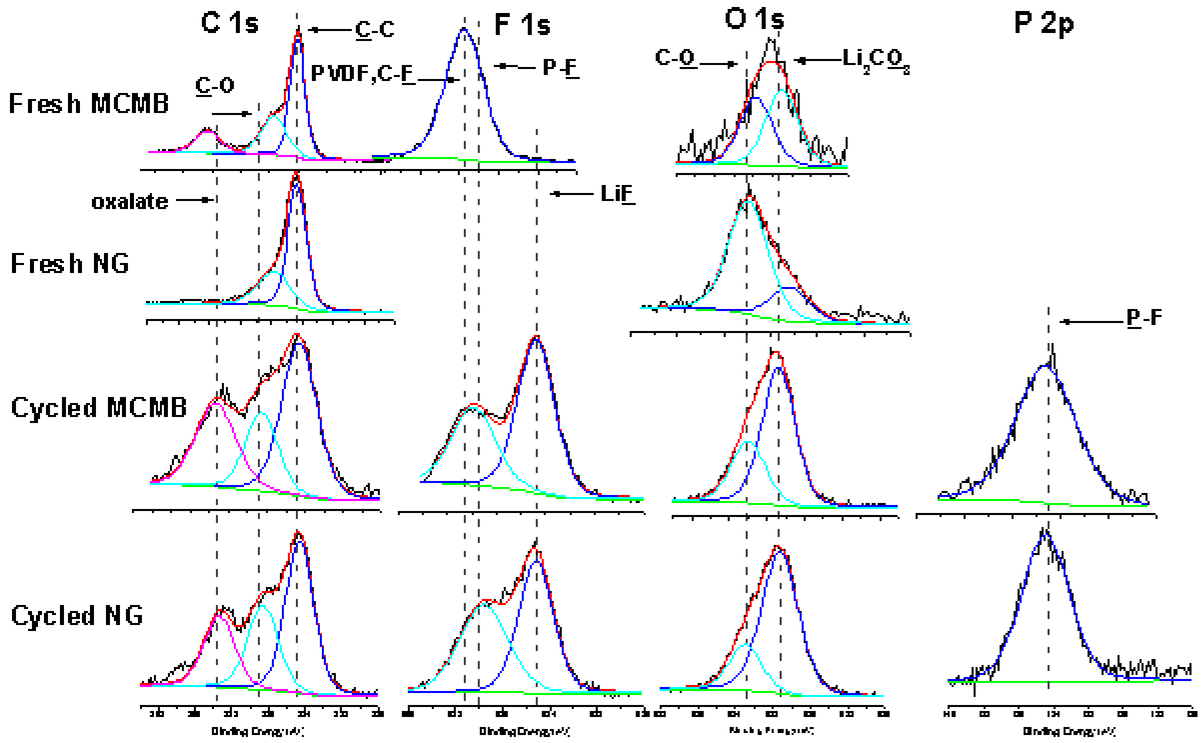
FY 11 Technical Accomplishments – Irreversible Capacity Loss with $LiPF_4(C_2O_4)$



C 1s, F 1s, O 1s and P 2p XPS spectra of fresh MCMB, fresh NG, cycled MCMB, and cycled NG graphite, electrolyte composition 1.2 M $LiPF_4C_2O_4$ EC/EMC (3/7, v/v)

The composition of the surface films is very similar on MCMB and NG.

The surface films on MCMB are thicker as suggested by sputtering experiments.

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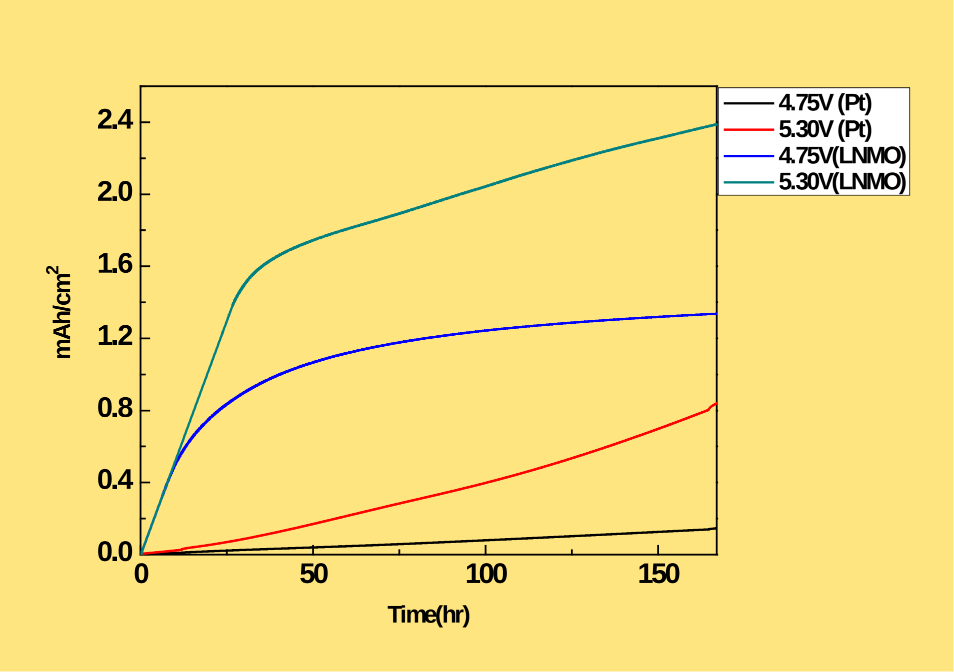
FY 11 Technical Accomplishments – Cathode film forming additives for HV Spinel

Investigation of electrochemical reactions

Does electrolyte react on metal oxide surfaces at lower potential?



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.

Upon subtracting the current associated with Li extraction the residual current is very similar.

The oxidation reaction of the electrolyte is similar for both surfaces.

Previous investigations uncovered the generation of polyethylene carbonate on cathode surfaces stored at high potential

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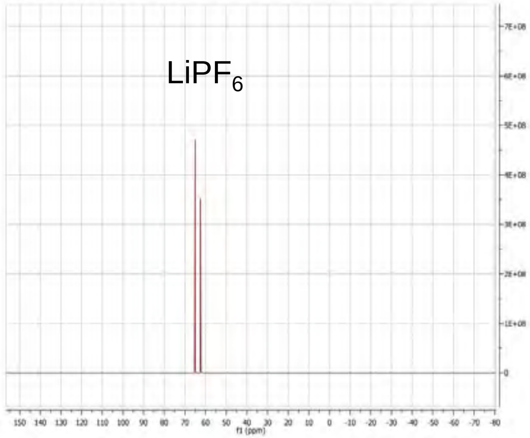
FY 11 Technical Accomplishments – Cathode film forming additives for HV Spinel

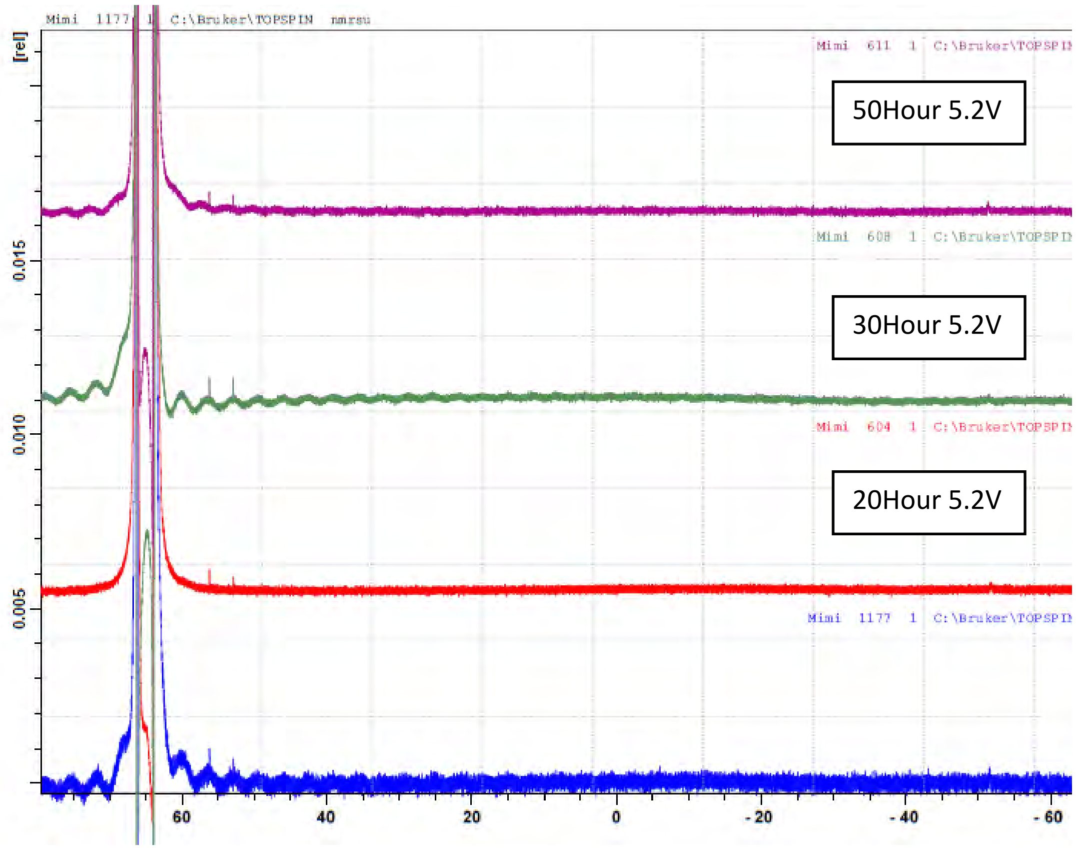


Investigation of the oxidation reaction of $LiPF_6$ in EC/EMC with glassy carbon electrode in solution.

Collaboration with Smith and Borodin – **Computational data suggests that oxidation of $LiPF_6$ with EC generates HF**

Oxidation experiments cannot detect HF (~ -17 ppm) or related species in solution by NMR.

Investigation of electrochemical reactions



^{19}F NMR spectra of electrolyte after storage.

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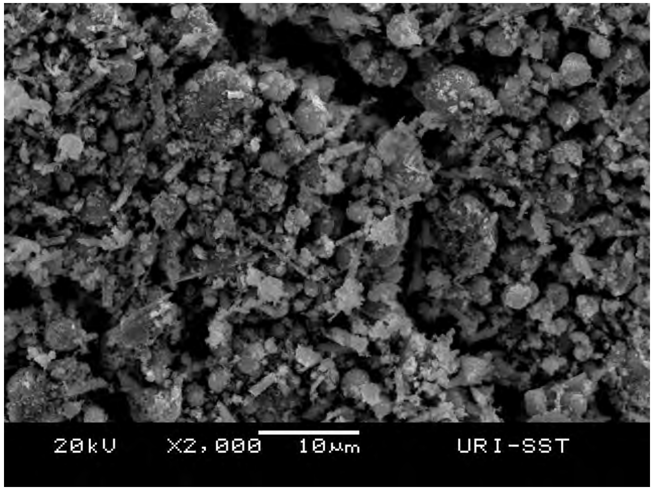
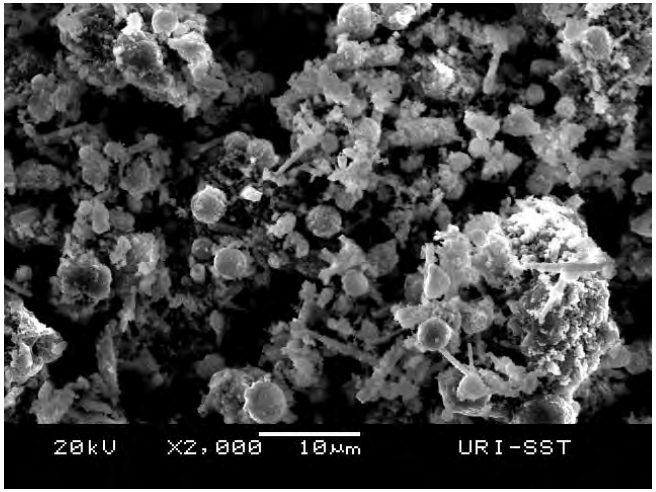
FY 11 Technical Accomplishments – Cathode film forming additives for HV Spinel



Before Storage



After Storage

Investigate thermal reaction of electrolyte with cathode surface and Mn dissolution.

Storage of $LiNi_{0.5}Mn_{1.5}O_4$ in 1.2 M $LiPF_6$ in 3/7 EC:EMC at 80 ^oC for 4 days.

XPS suggests presence of electrolyte decomposition products including polyethylene carbonate, $Li_xPF_yO_z$ LiF. (J. Electrochem. Soc. 153, A1617 (2006).

ICP Suggests concentration of Mn ~1 mM

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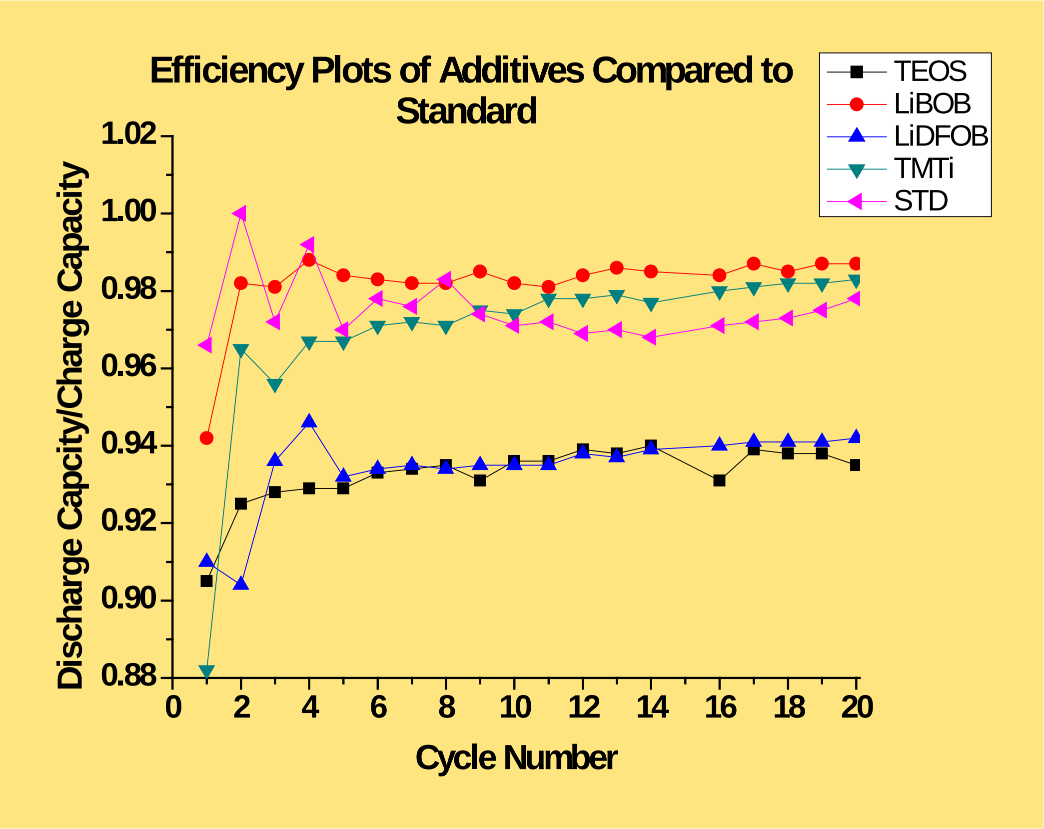
FY 11 Technical Accomplishments – Cathode film forming additives for HV Spinel



Incorporation of cathode film forming additives improve the cycling efficiency of Li/$LiNi_{0.5}Mn_{1.5}O_4$ cells cycled to 4.9 V vs Li.

(TEOS, Tetraethoxy silane; TMTi, Tetramethoxy Titanium; STD, $LiPF_6$ is 3:7 EC/EMC).

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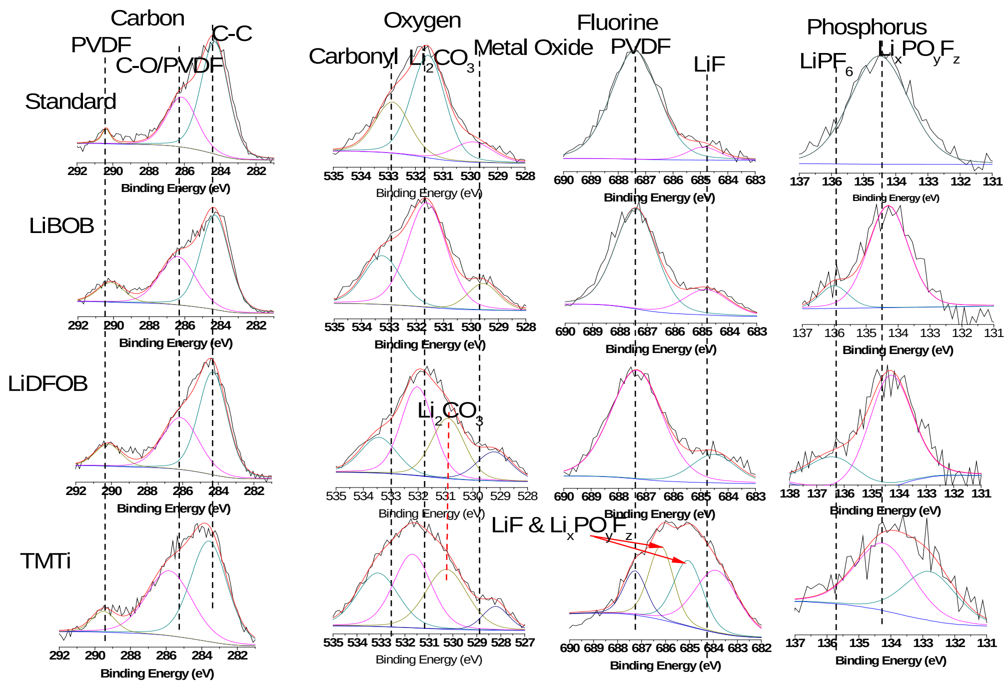
FY 11 Technical Accomplishments – Cathode film forming additives for HV Spinel



XPS surface analysis suggests similar cathode film structures with and without additives. Cells cycled with LiBOB have a significant concentration of B on the surface (7 %). Cells cycled with the standard electrolyte have thicker surface films.

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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.
- 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 $LiPF_4(C_2O_4)$ electrolytes in BATT program cells.
- J. Kerr (LBNL, National Lab, BATT Program): Collaboration on the investigation of novel electrolytes.
- M. Payne (Novolyte, Industrial): Collaboration on the investigation and commercialization of novel electrolytes.
- F. Puglia, J. Gnanaraj, and B. Ravdel (Yardney, Industrial): Collaboration on testing novel electrolytes in large format cells and investigation of high voltage LNMS (7 – 12 Ah).
- G. Smith & O. Borodin (U. Utah, BATT): Collaboration on investigation of electrolyte reactions with high voltage LNMS cathodes.
- High Voltage Spinel Focus Group (LBNL)

Proposed Future Work FY 10 – FY 11

- Investigate cell performance upon accelerated aging of graphite/$LiNi_XCo_{1-2x}Mn_XO2$ with $LiPF_4(C_2O_4)$/PC electrolytes compared to $LiPF_6$ electrolytes with a focus on low temperature behavior. (FY11)

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

- Develop a thorough understanding of the source of performance fade in high voltage Ni-Mn spinel cathode materials. (FY11-12)

- Develop improved cathode film forming additives for high voltage Ni-Mn spinel cathode materials. (FY 11-12)

- Investigate novel electrolytes to improve performance of Si-alloy anodes. (FY 11)

- Develop novel salts and additives for use in lithium ion batteries. (FY11 – 12)

Summary Slide

- Investigated cell performance of $LiPF_4(C_2O_4)$ compared to $LiPF_6$ in small cells with new chemistries graphite/$LiMn_2O_4$, $LiNi_xCo_{1-2x}Mn_xO_2$, $LiFePO_4$ cells, or with PC electrolytes.

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

- Developed an understanding of the source of irreversible capacity loss with $LiPF_4(C_2O_4)$ electrolytes during formation cycling.

- **$LiPF_4(C_2O_4)$ is a promising alternative to $LiPF_6$.**

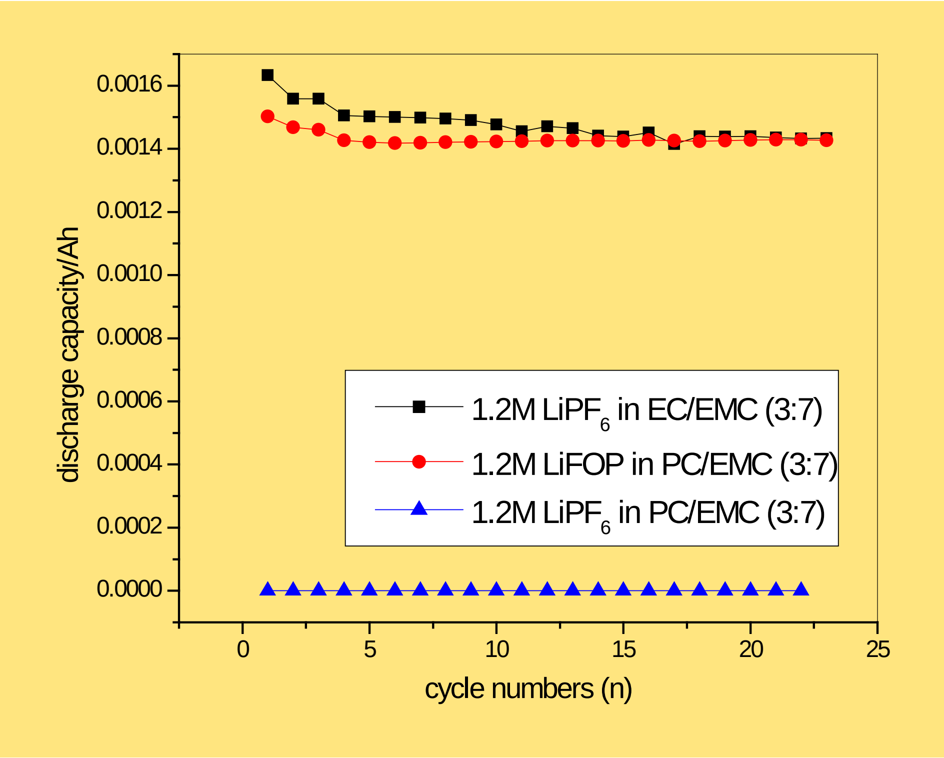
- Developed cathode film forming additives for high voltage (>4.5 V vs Li) cathode materials.

- Studied the reaction of High Voltage Ni-Mn spinel with electrolyte.

- **Cathode film forming additives can improve the performance of electrolyte at high voltage (> 4.5 V vs Li).**

Technical Back-Up Slides

FY10 Technical Accomplishments – Investigation of $LiPF_4(C_2O_4)$ with PC



Use of $LiPF_4(C_2O_4)$ salt allows the use of PC based electrolytes.
There is also less initial irreversible capacity loss.

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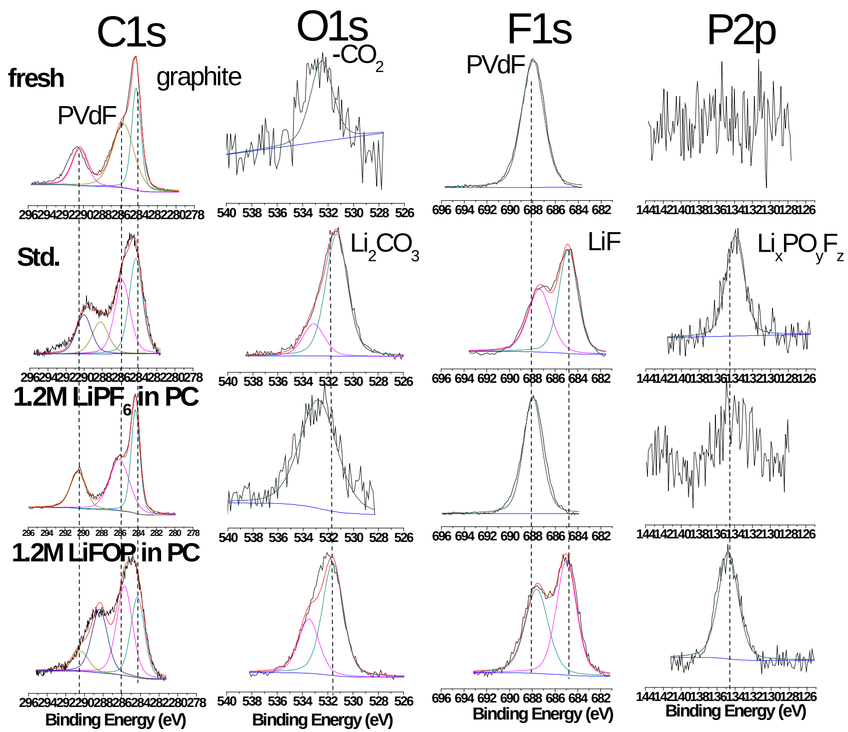
FY10 Technical Accomplishments – Investigation of $LiPF_4(C_2O_4)$ with PC



Stable anode SEI is formed with $LiPF_6$/PC

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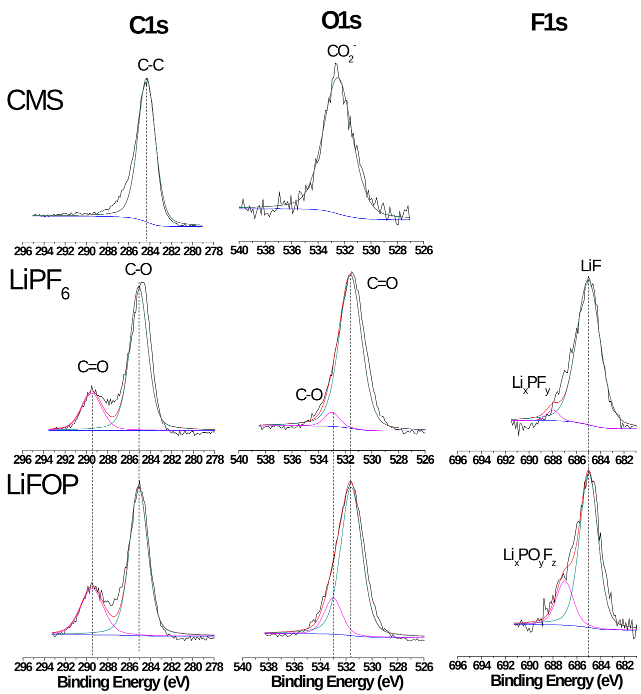
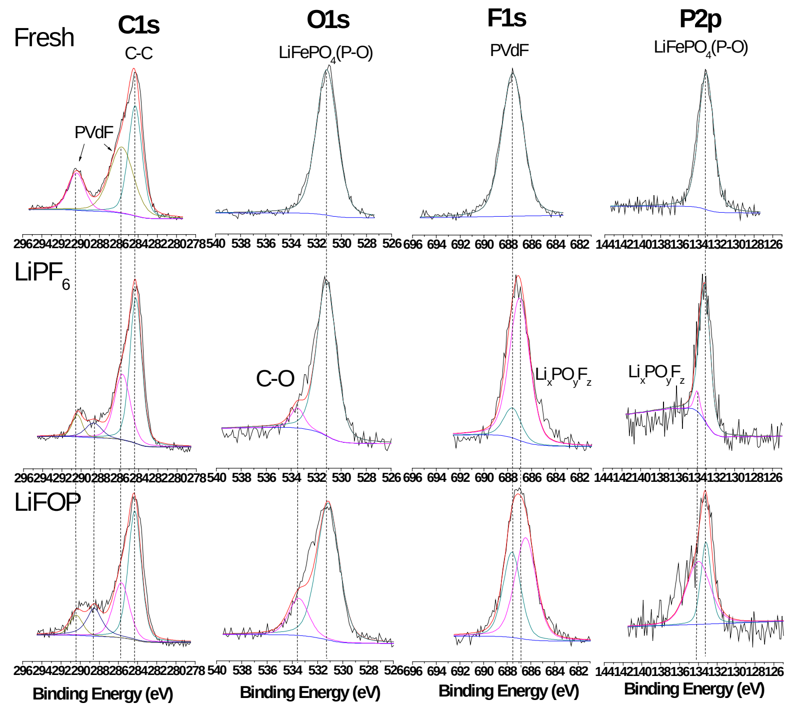
FY10-Technical Accomplishments – Investigation of $LiPF_4(C_2O_4)$ with Natural Graphite/$LiFePO_4$ cells - XPS



Similar anode SEI structure lithium alkylcarbonates, LiF and $Li_xPO_yF_z$



Cathode surface contains lithium oxalate with $LiPF_4(C_2O_4)$ and some LiF

XPS surface analysis suggests that both the anode and cathode surface films are very similar for $LiPF_6$ and $LiPF_4(C_2O_4)$

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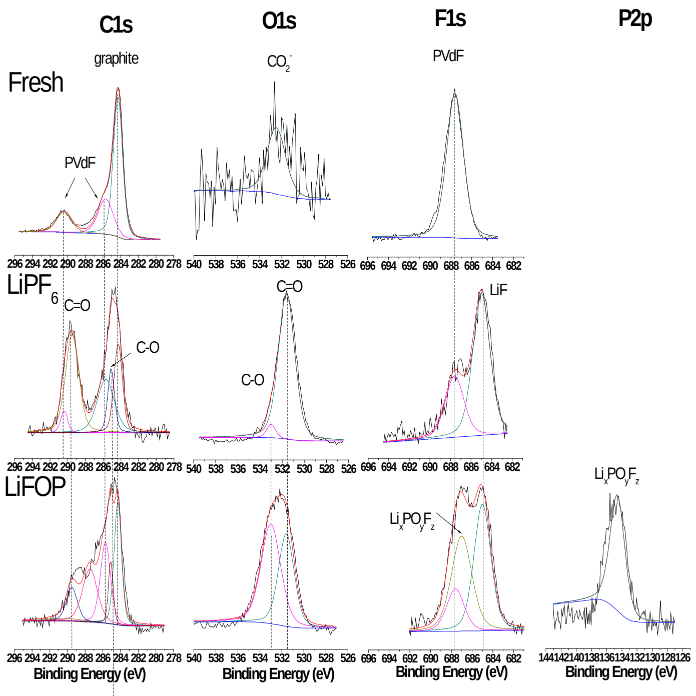
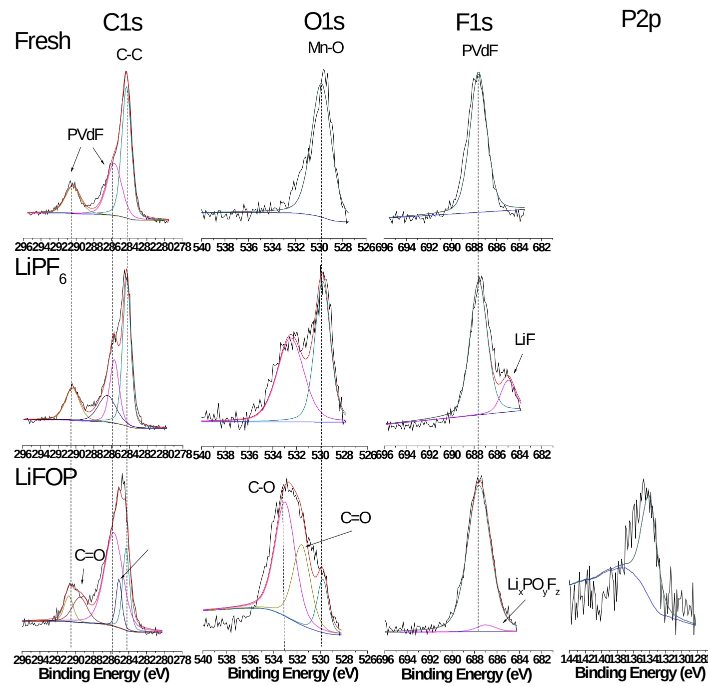
FY10-Technical Accomplishments – Investigation of $LiPF_4(C_2O_4)$ with Natural Graphite/$LiMnO_4$ cells - XPS





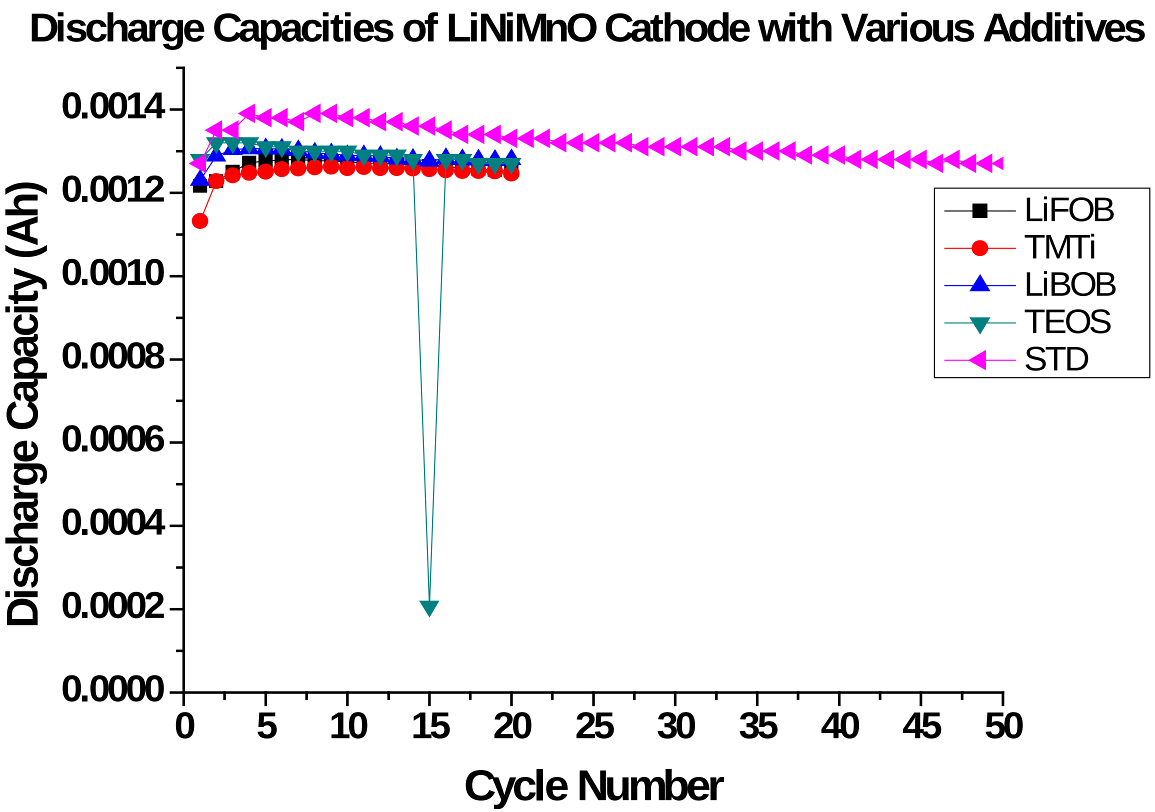
Anode surfaces are different and consistent with differences in initial irreversible capacity. Presence of oxalate and less LiF with $LiPF_4(C_2O_4)$

(top) fresh; (middle) cycled with electrolyte of $LiPF_6$ in EC/EMC (3:7, vol.); (bottom) cycled with electrolyte of LiFOP in EC/EMC (3:7, vol.)

Thicker cathode surface film with $LiPF_4(C_2O_4)$, presence of lithium oxalate and less metal oxide.

(top) fresh; (middle) cycled with electrolyte of $LiPF_6$ in EC/EMC (3:7, vol.); (bottom) cycled with electrolyte of LiFOP in EC/EMC (3:7, vol.)

FY 11 Technical Accomplishments – Cathode film forming additives for HV Spinel



Discharge Capacities of Half Cells (Li/$LiNi_{0.5}Mn_{1.5}O_4$) using 1.0M LiPF6 1:1:1 EC/DMC/EMC electrolyte with LiDFOB (2%), TMTi (0.5%), TEOS (0.5%), LiBOB (2%), & No Additive (STD). All percentages are based on weight.

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