Development of Electrolytes for Lithium-ion Batteries

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ES067

Overview

Timeline

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

Barriers

- Barriers addressed
  - Calendar Life (40 ^{o}C for 15 years)
  - Cycle life (5000 cycles)
  - Survival Temp Range (-46 to 66 ^{o}C)

Budget

- Total project funding
  - DOE share $731 K
- Funding received in FY09 - $145 K
- Funding for FY10 - $146 K

Partners

- D. Abraham (ANL)
- M. Smart (NASA JPL)
- W. Li (S. China Univ. Tech.)
- V. Battaglia (LBNL)
- M. Payne (Novolyte)
- F. Puglia (Yardney)
- W. Henderson (N.C. State)

Objective

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

- Develop electrolytes with improved thermal stability and superior calendar life performance.
- Develop novel electrolytes or electrolyte/additive combinations that will facilitate a more stable SEI on the anode.
- 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, and capacity loss.

Milestones

- ***FY09***
- (a) Investigate $LiPF_4(C_2O_4)$ in small cells. (Aug. 09) **Completed**
- (b) Produce 100 g $LiPF_4(C_2O_4)$ for testing. (Sep. 09) **Completed**
- (c) Investigate combinations of additives for $LiPF_6$ electrolytes. (Sep. 09) **Completed**

- ***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) **On Schedule**
- (d) Develop commercially viable synthesis for $LiPF_4(C_2O_4)$. (Sept 10) **On Schedule**

Approach

- Develop novel additives and additive combinations to improve the performance of $LiPF_6$ electrolytes.

- Investigate properties of $LiPF_4(C_2O_4)$ /carbonate electrolytes in small Li-ion cells with multiple cell chemistries.

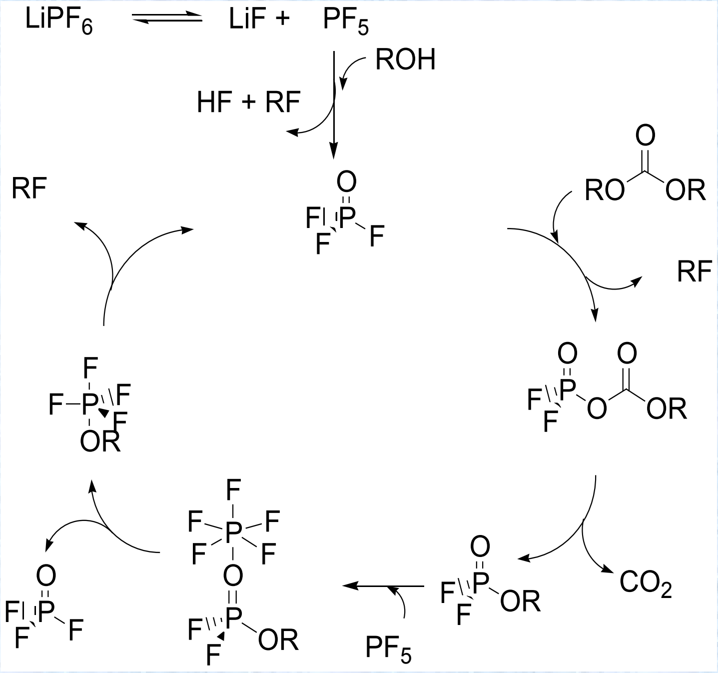
- Develop commercially viable low-cost synthetic method for production of $LiPF_4(C_2O_4)$ and produce high purity $LiPF_4(C_2O_4)$ for additional testing.

- Investigate novel cathode film forming additives, aided by computational methods, to improve performance of 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 for standard and novel electrolytes.

Previous Technical Accomplishments

- Developed a mechanistic understanding of the thermal decomposition of $LiPF_6$/carbonate electrolytes
- Developed Lewis Basic additives that inhibit the thermal decomposition of $LiPF_6$ /carbonate electrolytes
- Developed integrated method of electrode surface analysis to understand how changes to electrolyte formulations effect the surfaces of the electrodes and related electrochemical performance of the cells



The auto-catalytic decomposition of $LiPF_6$ is initiated by trace impurities of water and can be inhibited by Lewis basic additives.

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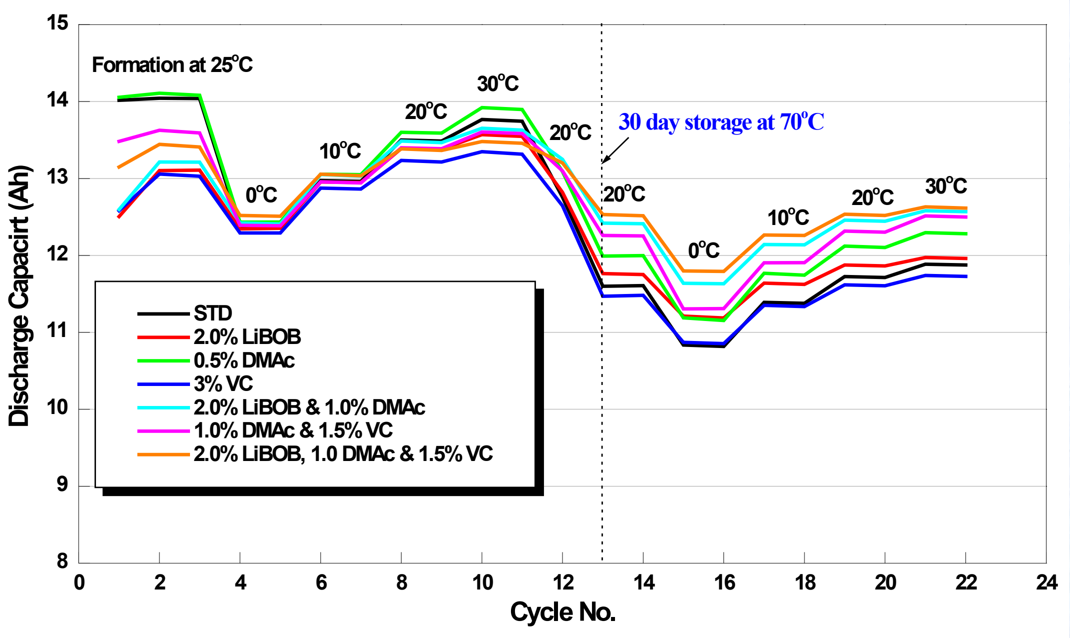
FY09 Technical Accomplishments – Electrolyte with Mixed Additives

- We have conducted an investigation of the effect of thermal stabilizing additives, including dimethyl acetamide (DMAc), vinylene carbonate (VC), and lithium bis(oxalato) borate (LiBOB), on the performance of lithium ion batteries after accelerated aging experiments.
- Cells containing mixtures of two or more electrolytes have superior performance after accelerated aging than cells containing a single additive or standard electrolyte.
- Additive with different mechanisms of improving thermal stability can work cooperatively.
- Surface analysis of the electrodes provides support for cooperative surface film structures along with a better understaniding of the source of performance differences



Discharge capacities vs. cycle number for 12 Ah cells ($MCMB/LiNi_{0.8}Co_{0.2}O_2$) with and without electrolyte additives. The cells were cycled at 25°C, 0°C, 10°C, 20°C & 30°C temperatures before and after high temperature storage at 70 °C for 30 days.

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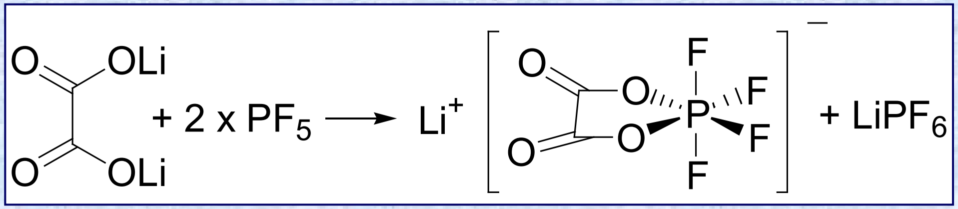
FY 09 Technical Accomplishments – Investigation of $LiPF_4(C_2O_4)$

- We have been investigating the novel lithium salt $LiPF_4(C_2O_4)$ for use in lithium ion battery electrolytes.

- We have synthesized ~100 g of salt for initial investigations.

- The salt has been investigated in our laboratory and samples have been investigated by F. Puglia (Yardney Technical Products), V. Battaglia (LBNL, BATT program), and two other companies under confidential non-disclosure agreements.



$LiPF_4(C_2O_4)$ is synthesized via the reaction of PF_5 with lithium oxalate. The reaction is conducted in organic solvents as opposed to HF (as conducted for $LiPF_6$). We are developing a commercially viable route (in collaboration with a commercial partner) that will likely be cost competitive to the production of $LiPF_6$.

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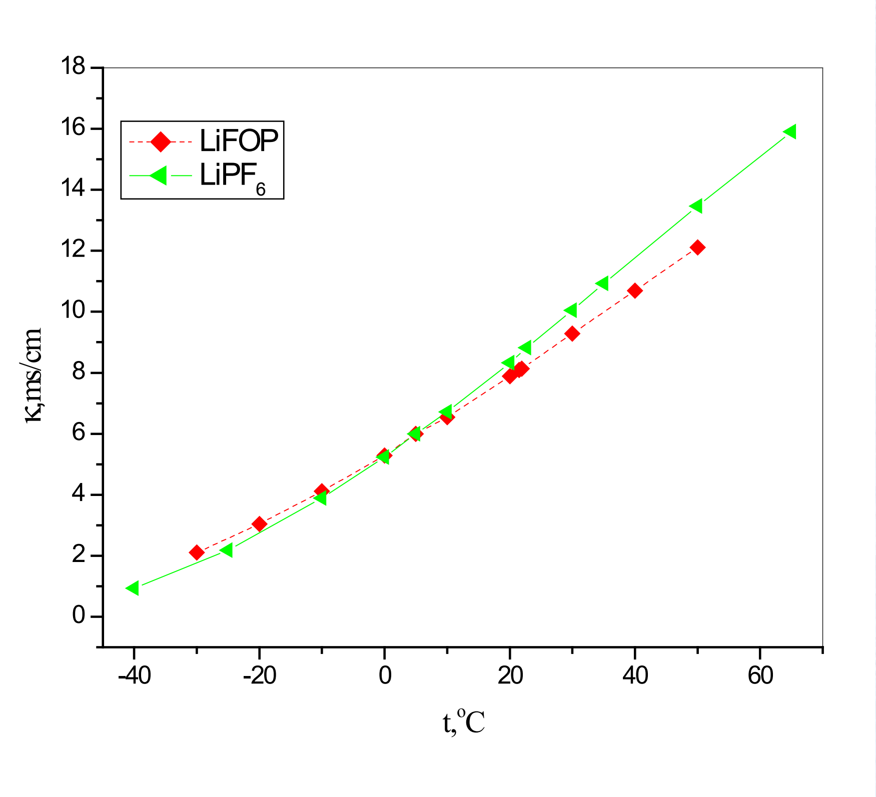
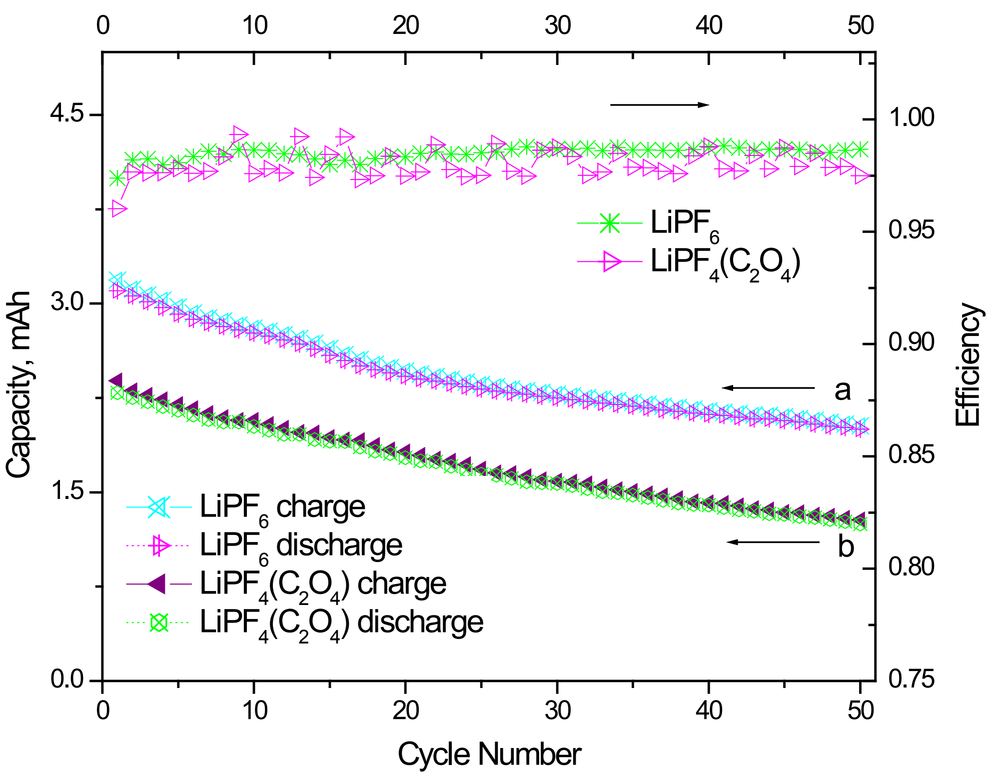
FY09 Technical Accomplishments – Investigation of $LiPF_4(C_2O_4)$

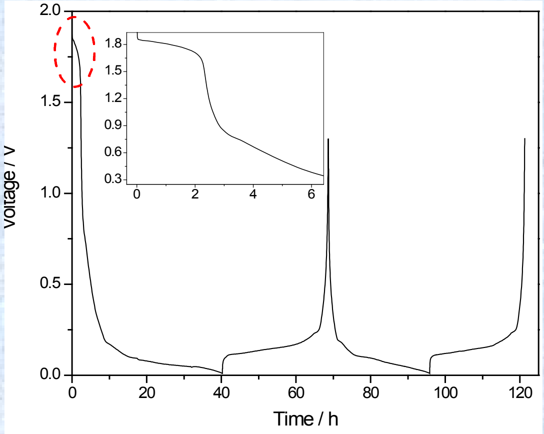
Investigation of the solution conductivity of $LiPF_4(C_2O_4)$ over a broad temperature range (-30 to + 50 ^oC) suggests very similar conductivity in carbonate solution (EC:DEC:DMC, 1:1:1) to $LiPF_6$.



FY09 Technical Accomplishments – Investigation of $LiPF_4(C_2O_4)$



Room temperature cycling behavior of $LiPF_4(C_2O_4)$/carbonate and $LiPF_6$/carbonate electrolytes (MCMB/$LiNi_{08}Co_{0.2}O_2$) cells



The lower initial reversible capacity for cells containing $LiPF_4(C_2O_4)$ is due to reduction of oxalate impurities (1.8 V), however cycling efficiency is comparable after formation cycles.

Similar results have been observed for graphite/ $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ cells.

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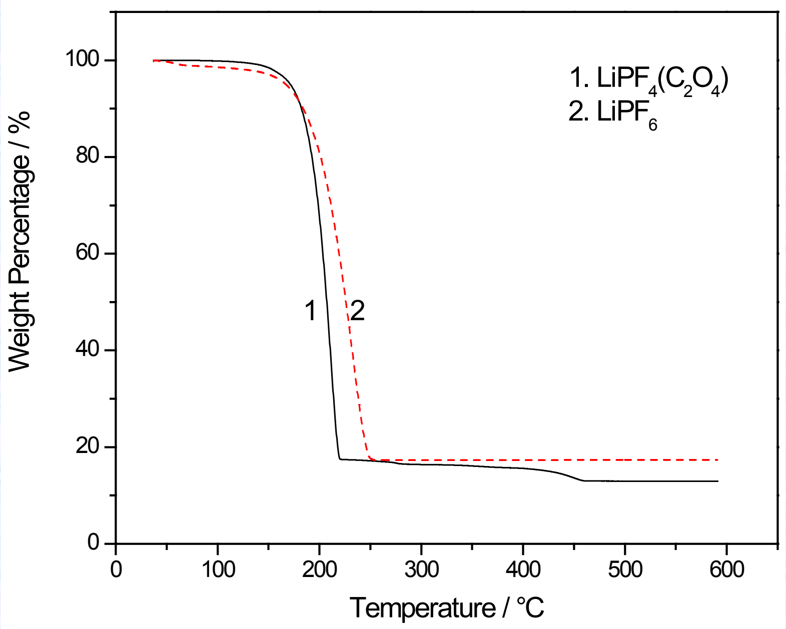
FY10 Technical Accomplishments – Investigation of $LiPF_4(C_2O_4)$ – High Temperature Stability



The thermal stability of $LiPF_4(C_2O_4)$ and $LiPF_6$ were analyzed in the solid state by TGA.

The thermal stabilities of the solids are very similar.

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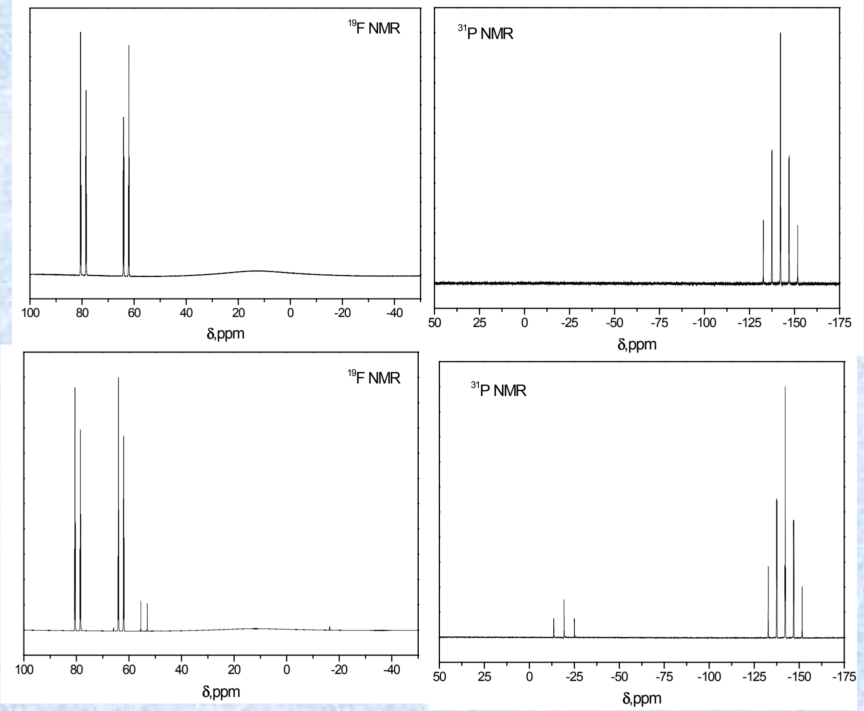
FY09 Technical Accomplishments – Investigation of $LiPF_4(C_2O_4)$ – High Temperature Stability

$LiPF_4(C_2O_4)$ liquid electrolyte before storage

$LiPF_4(C_2O_4)$ liquid electrolyte after storage at 85 °C for 1 month



Analysis of the thermal stability of $LiPF_4(C_2O_4)$ in solution {EC:DEC:DMC (1:1:1)} was conducted by multi-nuclear (^{19}Fand ^{31} P) NMR spectroscopy. The $LiPF_4(C_2O_4)$ liquid electrolyte stable for 1 month at 85 °C with only low concentrations of impurities.

Similar conditions quantitatively degrade $LiPF_6$

$LiPF_4(C_2O_4)$ is also more stable to low concentrations of H_20

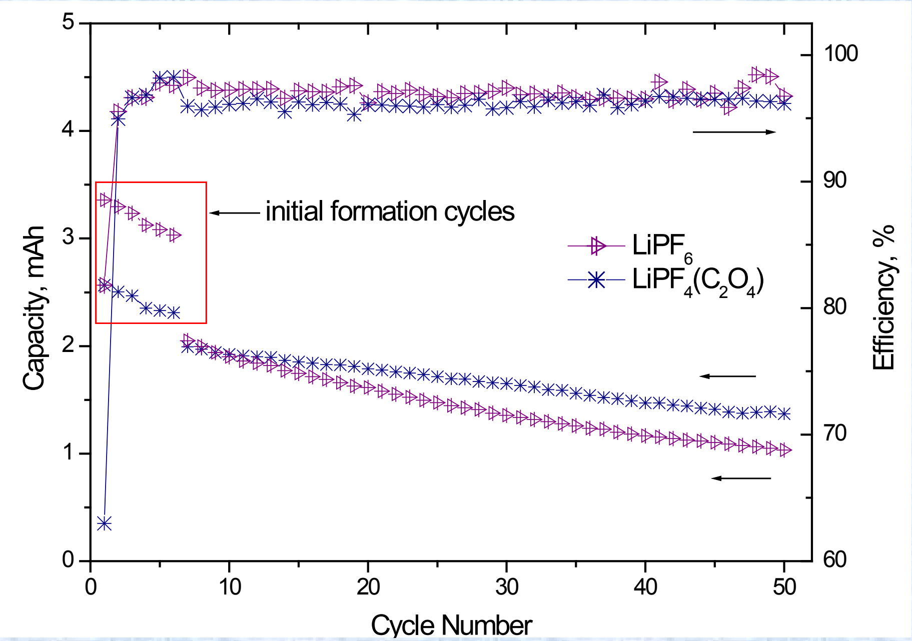
While the thermal stability of solid $LiPF_6$ and $LiPF_4(C_2O_4)$ are very similar the stability of the liquid electrolytes are very different, suggesting that the inherent stability of the solid may not be a good predictor of the stability of the electrolyte

FY10 Technical Accomplishments – Investigation of $LiPF_4(C_2O_4)$ – Accelerated Aging

The cycling performance of cells containing $LiPF_4(C_2O_4)$ electrolyte after accelerated aging (storage at 65 °C for two weeks) was conducted.

While cells containing $LiPF_4(C_2O_4)$ have lower initial capacity, after accelerated aging cells containing $LiPF_4(C_2O_4)$ have superior cycling performance.

Similar results have been observed for graphite/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ cells.



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.

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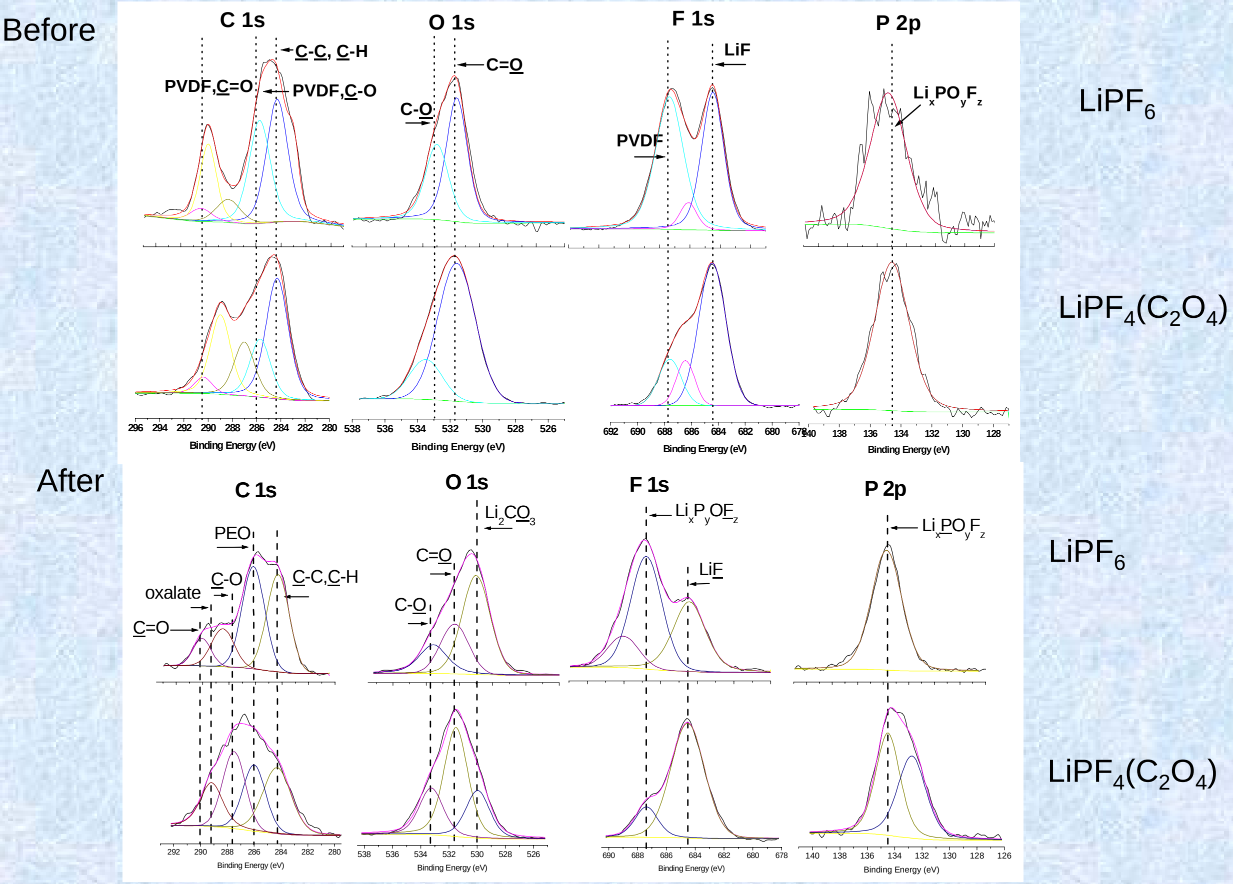
FY09 Technical Accomplishments – Investigation of $LiPF_4(C_2O_4)$ – Accelerated Aging

In order to develop and understanding of the superior cycling performance after accelerated aging experiments, post-mortem analysis of the electrodes was conducted and cells before and after accelerated aging.

Smaller changes to Anode SEI were observed for cells containing $LiPF_4(C_2O_4)$

Anodes form cells cycled with $LiPF_4(C_2O_4)$ have higher concentration of oxalate (286-288 eV) and a higher concentration of LiF (684.5 eV).



XPS analysis of the anodes before and after accelerated aging experiments containing $LiPF_4(C_2O_4)$ and $LIPF_6$ in EC:DMC:DEC (1:1:1).

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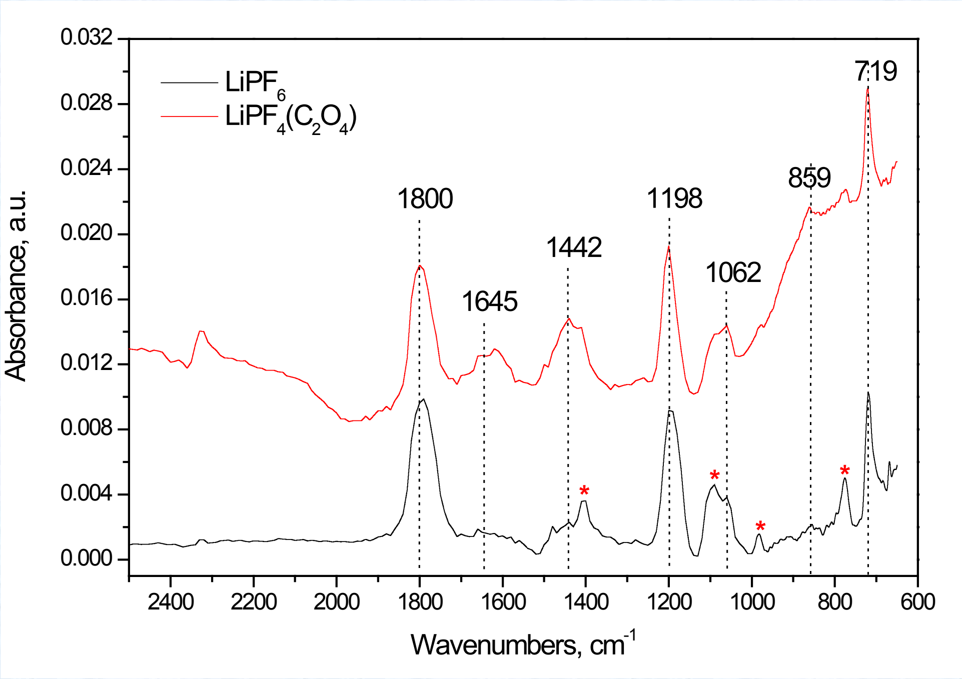
FY09 Technical Accomplishments – Investigation of $LiPF_4(C_2O_4)$ – Accelerated Aging

Most of the IR absorptions present on both anodes are similar and consistent with the presence of the EC/Li solvate.

Cells containing $LiPF_4(C_2O_4)$ have additional absorption at 1645 cm^{-1} consistent with the presence of oxalates.



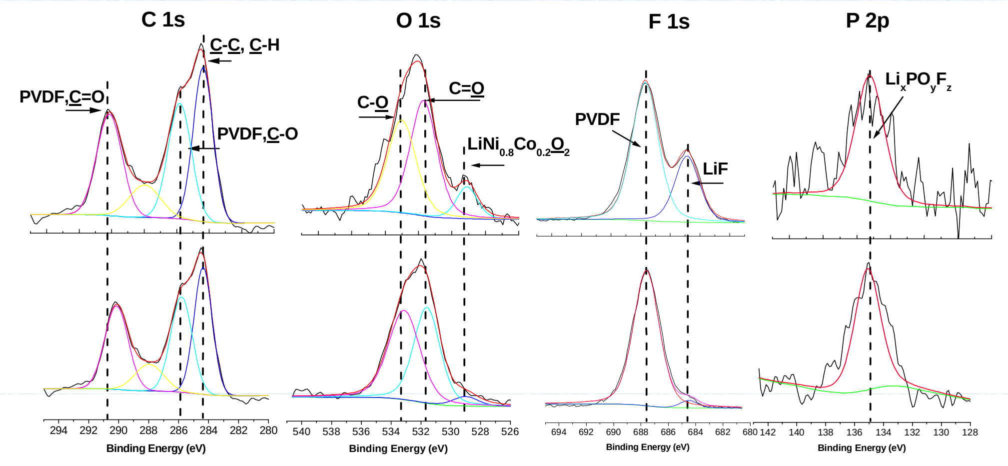
IR-ATR analysis of the anodes after accelerated aging experiments containing $LiPF_4(C_2O_4)$ and $LIPF_6$ in EC:DMC:DEC (1:1:1).

FY10 Technical Accomplishments - Investigation of $LiPF_4(C_2O_4)$ – Accelerated Aging

The XPS data suggests that the surface film on the cathode is thinner with $LiPF_4(C_2O_4)$.

The cell containing $LiPF_4(C_2O_4)$ has more surface metal oxide (529 eV) and less LiF (684.5 eV).

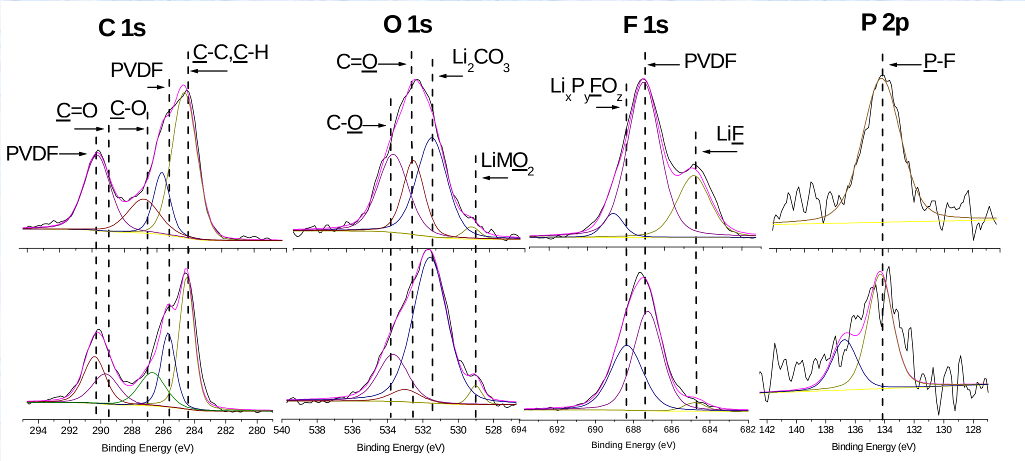
Before



$LiPF_6$

$LiPF_4(C_2O_4)$

After



$LiPF_6$

$LiPF_4(C_2O_4)$

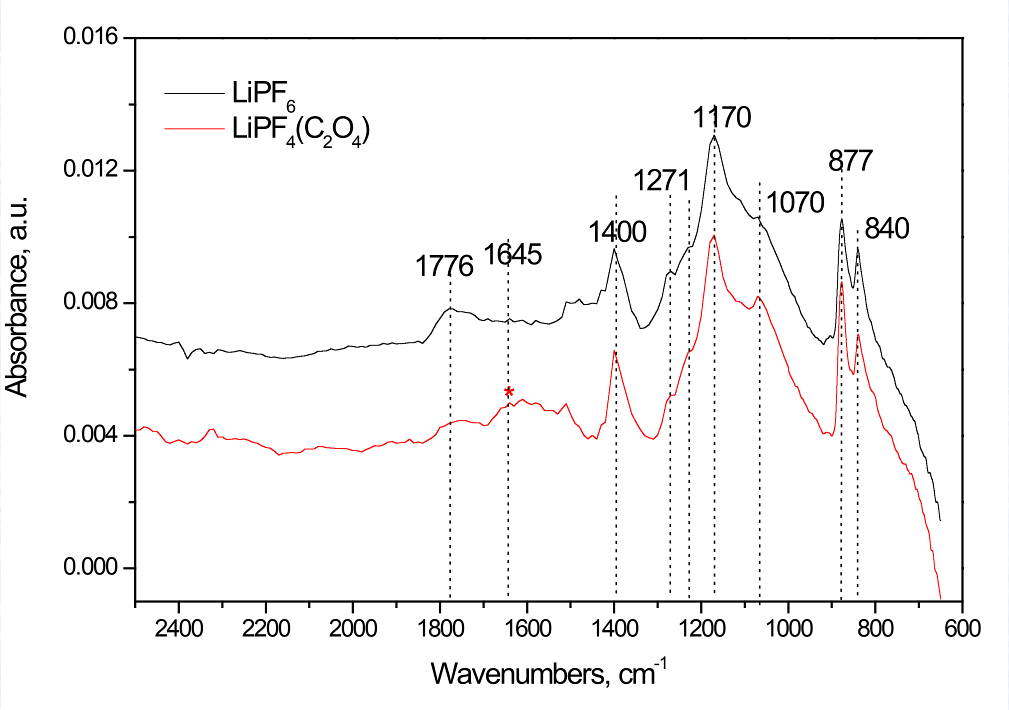
XPS analysis of the cathodes before and after accelerated aging experiments containing $LiPF_4(C_2O_4)$ and $LIPF_6$ in EC:DMC:DEC (1:1:1)

FY09 Technical Accomplishments – Investigation of $LiPF_4(C_2O_4)$ – Accelerated Aging

Most of the absorptions are associated with PVDF.

The cell with $LiPF_4(C_2O_4)$ has less polycarbonate (1776 cm $^{-1}$) some oxalate (1645 cm^{-1}).

The superior cycling behavior of cells containing $LiPF_4(C_2O_4)$ electrolyte can be attributed to differences in the electrode surface films.



IR-ATR analysis of the anodes after accelerated aging experiments containing $LiPF_4(C_2O_4)$ and $LIPF_6$ in EC:DMC:DEC (1:1:1)

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FY10 Technical Accomplishments – Cathode film forming additives

- It has been previously reported that the cathode SEI responsible for increased impedance of aged cells.
- While there is significant interest in the use of higher voltage cathodes (>4.5 V vs Li), cathode electrolyte reactions limit voltage.
- Several additives/salts have been reported to react on the cathode surface.
- We are interested in the development of novel additives that will generate cathode surface passivation films which improve cycling performance to higher voltages (> 4.5V).

Abraham et.al *J. Electrochem. Soc.* **149**, A1358 (2002)
Wu et. al. *Electrochem. Comm.* **11**, 526 (2009)
Xu *J. Electrochem. Soc.* **155,** A733 (2008)

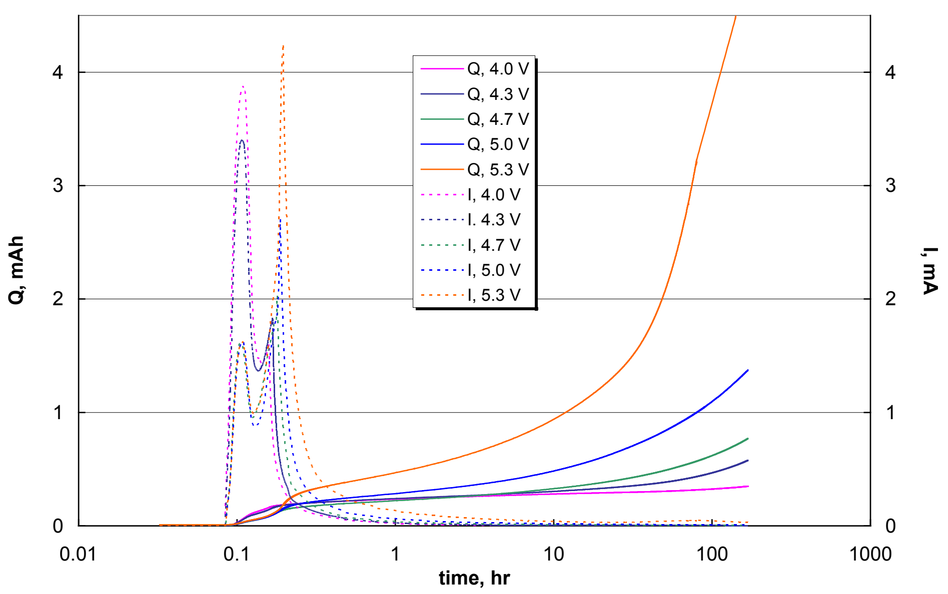
FY10 Technical Accomplishments – Cathode film forming additives

In order to develop cathode film forming additives to improve the performance of cathodes at high voltage (>4.5 V vs Li), we initially investigated the reactions of the electrolyte with the cathode surface.

LNMS/Li cells were stored at various voltages between 4.0 and 5.3 V vs Li for one week.

At low voltages, below 4.7 V, there is very little current flow through the cells. As the voltage surpasses 4.7 V vs Li there is a significant increase in charge flow through the cells.

The increased charge flow is consistent with electrolyte oxidation on the surface of the cathode at high potential.



Oxidation of the electrolyte solution (1 M $LiPF_6$ in 1:1:1 (EC:DEC:DMC) at various potentials with a $LiNi_{0.5}Mn_{1.5}O_4$ /Li half cell.

FY10 Technical Accomplishments – Cathode film forming additives

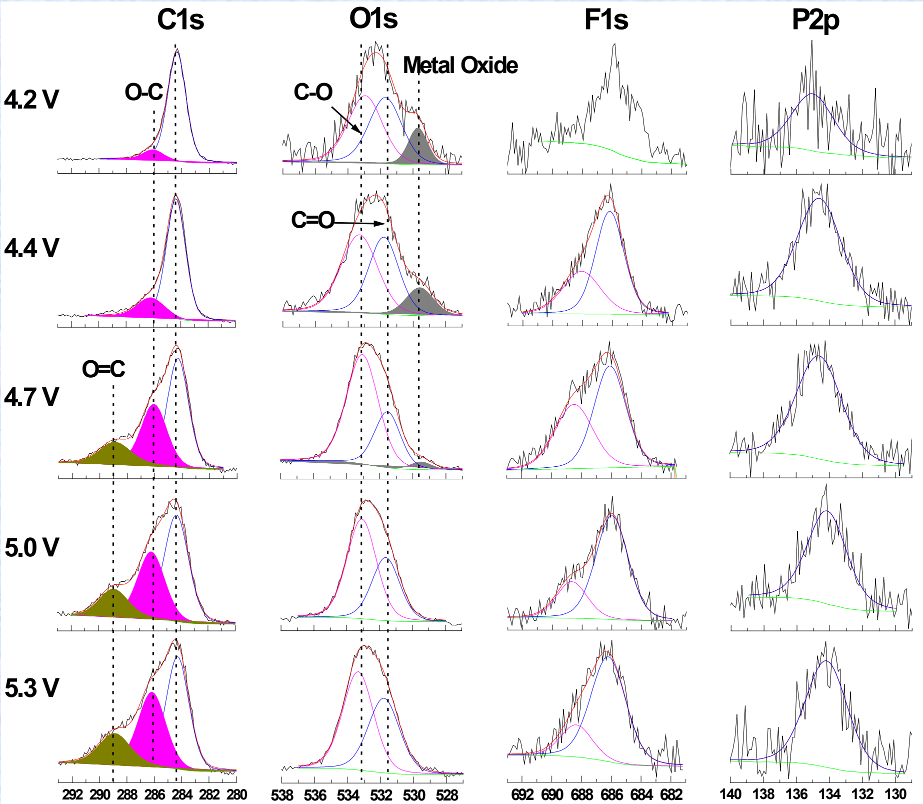
After retention at the desired voltages for one week the LNMS/Li cells were disassembled and the surface of the cathodes were analyzed by XPS and FTIR-ATR.

EPDM binder was used to avoid overlap of the peaks associated with PVDF binder. Similar results were observed for cells with PVDF binder.

At low voltages (< 4.7 V vs Li) the surface contains EPDM, metal oxide, and $Li_xPF_yO_z$.

As the potential is raised above 4.7 V vs Li the relative intensity of the C-O and C=O peaks increase while the metal oxide peaks decrease.

The changes in the surface are consistent with oxidation of the electrolyte to generate poly(ethylene carbonate) on the surface.



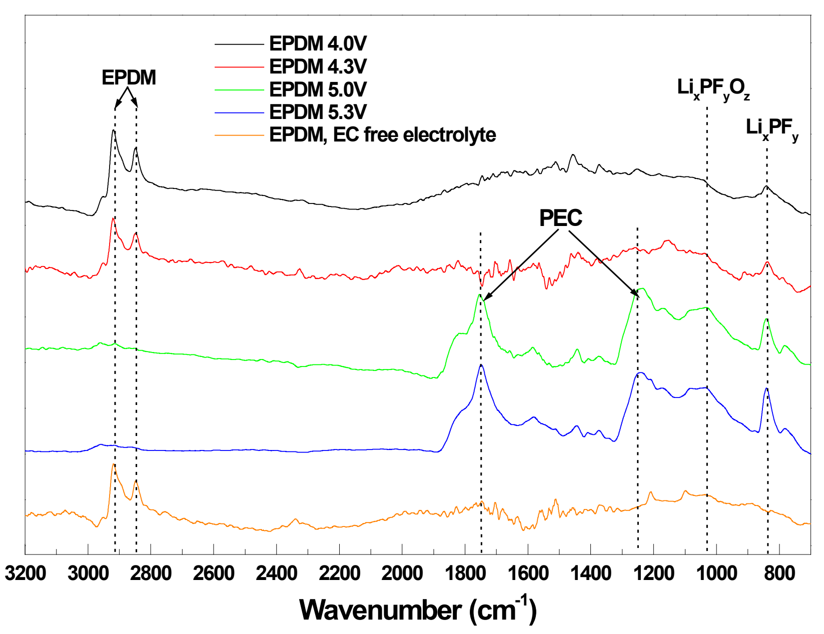
XPS spectra of cathodes with Ethylene Propylene Diene Monomer (EPDM) as the binder after storage for one week at various voltages.

FY10 Technical Accomplishments – Cathode film forming additives

Electrodes stored at lower potentials (4.0 and 4.3 V) contain absorptions characteristic of EPDM including absorptions at 2920 cm^{-1} and 2850 cm^{-1} corresponding C–H stretching and 1300 – 1500 cm^{-1} characteristic of C-H bending.

At higher cathode potentials (5.0 and 5.3 V), the relative intensity of the C-H absorptions are decreased while absorptions at 1750 cm^{-1} and 1250 cm^{-1}, characteristic of the C=O and C-O absorptions, respectively, of poly(ethylene carbonate) (PEC) are increased.

In an effort to confirm that EC is the source of the PEC on the surface cells containing EC free electrolyte (1 M $LiPF_6$ in DMC/DEC/EMC) were prepared and retained at 5.0 V. No PEC was observed



IR-ATR spectra of cathodes with Ethylene Propylene Diene Monomer (EPDM) as the binder after storage for one week at various voltages.

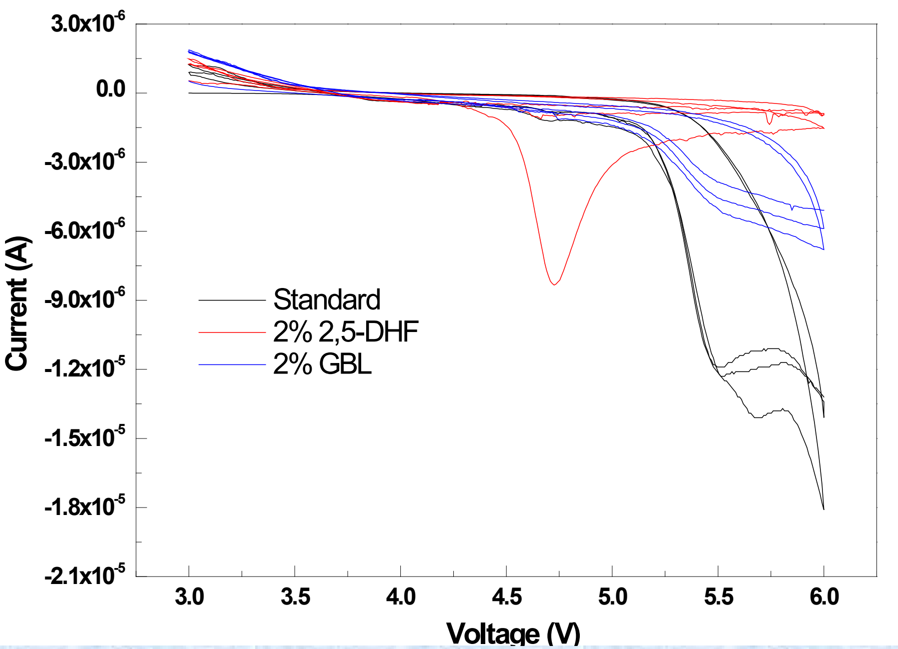
FY10 Technical Accomplishments – Cathode film forming additives

Initial experiments to determine if sacrificial additives can be incorporated into electrolytes to generate a cathode passivation layer.

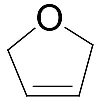
The addition of 2,5-DHF has lower voltage oxidation on first cycle, but higher stability on later cycles.

GBL reduces the decomposition current.

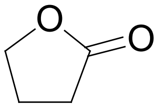
The additives generate a stable passivation layer which inhibits electrolyte oxidation.



Cyclic voltammetry of 1 M $LiPF_6$ in 1:1:1 EC/DEC/DMC with/without additives vs glassy carbon electrode.



2,5-DHF



GBL

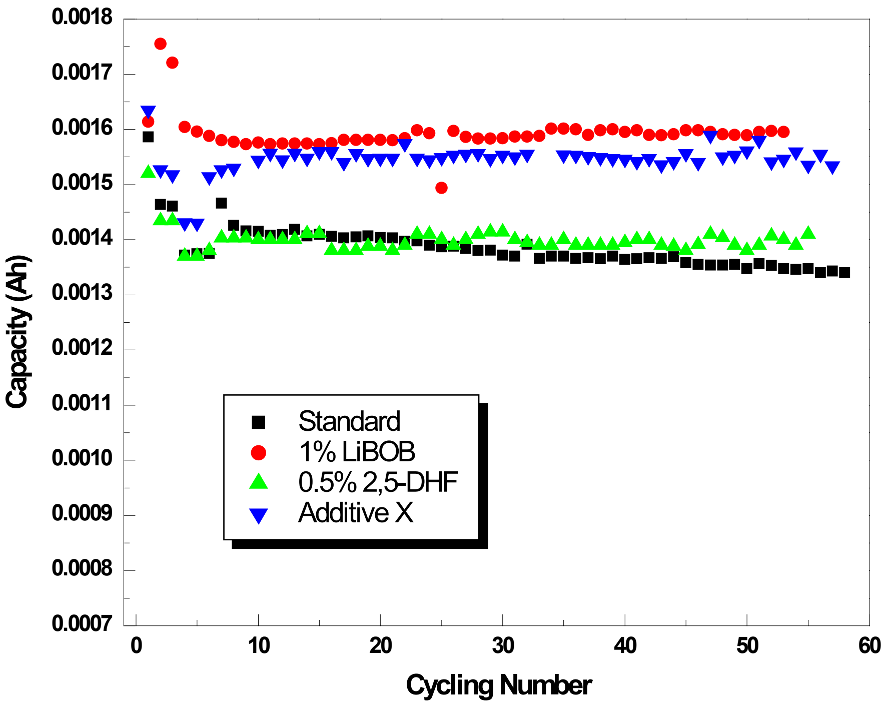
FY09 Technical Accomplishments – Cathode film forming additives

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.

Similar results have been observed with $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ charged to 4.8 V vs Li.

Incorporation of LiBOB and Additive X provide the best performance.

The decreased initial capacity loss for LiBOB and Additive X is likely due to inhibition of oxygen evolution at the cathode surface.



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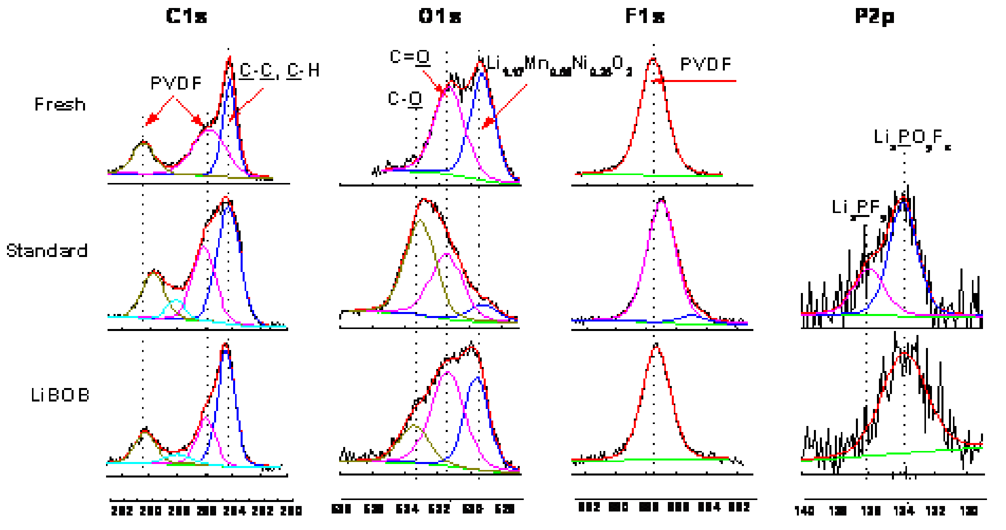
FY10 Technical Accomplishments – Cathode film forming additives

The incorporation of additives results in a greater retention of surface metal oxide (529.5 eV) and less PEC C-O (533.5 eV) and C=O (531.8 eV).

Cathode film forming additives result in thinner surface films on $Li_{1.17}Mn_{0.58}Ni_{0.25}O_2$ cathodes.

Cells cycled with LiBOB contain B on the surface of the cathode confirming reaction of LiBOB on the surface.

Similar results have been observed with $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ charged to 4.8 V vs Li.



XPS analysis of cathodes extracted from $Li_{1.17}Mn_{0.58}Ni_{0.25}O_2$ half cells cycled to 4.9 V vs Li.

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, BATT 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.
- M. Payne (Novolyte, Industrial): Collaboration on the scale-up and commercialization of novel electrolytes.
- F. Puglia, J. Gnanaraj, and B. Ravdel (Yardney, Industrial): Collaboration on testing novel electrolytes in large format cells (7 – 12 Ah).
- W. Henderson (N.C. State, Academic, BATT Program): Collaborations on the development of novel salts for lithium ion battery electrolytes.

Proposed Future Work FY 10 – FY 11

- Investigate the cycling behavior of $LiPF_4(C_2O_4)$ with Propylene Carbonate (PC) electrolytes to determine if novel SEI allows efficient cycling of PC with graphite anode.
- Investigate the cycling behavior of $LiPF_4(C_2O_4)$ other cathodes $LiMn_2O_4$ or LiFePO4 or novel cathode materials being developed as part of the BATT program.
- Develop commercially viable synthesis of $LiPF_4(C_2O_4)$.
- Optimize novel cathode film forming additives for different cell chemistries ($LiMn_2O_4$ or LiFePO4 or novel cathode materials being developed as part of the BATT program).
- Develop novel anode film forming additives for new anode materials being developed as part of BATT program.

Summary Slide

- The investigation of combinations of different types of thermal stabilizing additives provides a cooperative beneficial effect to lithium ion batteries.

- A novel lithium salt $LiPF_4(C_2O_4)$ has been developed and investigated in lithium ion cells.
- Cells containing $LiPF_4(C_2O_4)$ electrolytes have greater initial capacity loss, which is likely due to oxalate impurities, but otherwise comparable room temperature performance to $LiPF_6$.
- $LiPF_4(C_2O_4)$ has superior performance to $LiPF_6$ after accelerated aging.
- Larger quantities of $LiPF_4(C_2O_4)$ (100 g) have been prepared and provided to collaborators for independent confirmation. Similar results have been obtained.

- The oxidation reactions of electrolytes on the surface of cathodes retained at high voltage (>4.5 V vs Li) have been investigated.
- Cathode film forming additives have been developed, with the assistance of computational chemistry, which improve the cycling performance of lithium ion cells at high voltage (>4.5 V vs Li)