High Voltage Electrolyte for Lithium Batteries

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Argonne National Laboratory
Vehicle Technologies Program
Annual Merit Review and Peer Evaluation Meeting

Washington, D.C.
May 14-18, 2012

Project ID #: ES113

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Project Overview

Timeline
- Project start date: FY10
- Project end date: FY14
- Percent complete: 25%

Barriers
- Battery life: conventional organic carbonate electrolytes oxidatively decompose at high potential (> 4.5V vs Li+/Li )
- Battery performance: poor oxidation stability of the electrolyte limits the battery energy density
- Battery Abuse: safety concern associated with high vapor pressure, flammability and reactivity

Budget
- Total project funding - 100% DOE funding
- Funding received in FY11: $300K
- Funding for FY12: $400K

Partners
- US Army Research Lab – Interaction
- Dr. Larry Curtiss – Theoretical modeling
- Daikin Chemical Company - Materials
- Saft and ConocoPhilips - Electrode
- Project Lead: Zhengcheng Zhang
Project Objective

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

- To develop electrolyte materials that can tolerate high charging voltage (>5.0V vs Li+/Li) with high compatibility with anode material providing stable cycling performance for high voltage cathode including 5V LNMO cathode and high energy LMR-NMC cathode recently developed for high energy high power lithium-ion battery for PHEV and EV applications.

- FY11’s objective is to identify and screen several high voltage electrolyte candidates including sulfone, silicon-based and fluorinated compounds with the aid of quantum chemistry modeling and electrochemical methods and to investigate the cell performance of the selected electrolytes in LNMO/LTO and LNMO/graphite chemistries.
Approach

- R&D groups all over the world work on improving electrodes materials in order to maximize both energy and power density of Li batteries. High voltage cathode (Li[MMn]2O4, M=Ni, Cr, Cu) and high capacity layered cathode (Li[NiMnCo]O2) red-ox potentials approach 5.0V and 4.6V vs Li+/Li. Conventional alkyl carbonates/LiPF6 tend to be oxidized around 4.5V. Development of high voltage electrolyte is urgent and challenging.

- Our overall approach for high voltage electrolyte research is to first design, synthesize and characterize high oxidation stable solvent candidates with the aid of theoretical calculation method; then screen the electrochemical properties of the synthesized using cyclic voltammetry and validate their oxidation stability using high voltage and high capacity cathode Li metal or LTO cells. Tailored electrolyte additive will be developed coupled with main electrolyte to enable the graphite cells is the ultimate target.

- High voltage electrolyte research will be integrated with high voltage/capacity cathode project in DOE ABR program. Various new solvent systems including sulfones, silane, fluorinated esters, fluorinated ethers and ionic liquids. Synergy effect of electrolyte containing hybrid solvents will also explored to enable the high energy high power lithium-ion battery for PHEV and EV applications.
Technical Accomplishments and Progress
Argonne’s Fluorinated Compounds as High Voltage Electrolytes (HVEs)
**DFT Calculation to Predict the Oxidation Stability of Fluorinated Carbonate Compounds**

<table>
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<tr>
<th>Code Name</th>
<th>Chemical Structure</th>
<th>$P_{\text{ox}}$ / V</th>
<th>$P_{\text{red}}$ / V</th>
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<tr>
<td>FE-1</td>
<td><img src="image" alt="FE-1 Structure" /></td>
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</table>
Li⁺ Conductivity of High Voltage Electrolyte Candidates

- Compared to Gen 2, all fluorinated electrolytes are less conductive. EC/EMC/FE-1 showed the highest ambient conductivity of $6.5 \times 10^{-3}$ S/cm among all the fluorinated electrolyte candidates.
- Addition of FCC-1, FLC-1 and/or FE-1 reduces the conductivity.
- FCC-1/FLC-1/FE-1 formulation shows the lowest conductivity due to the overall low dielectric constant and high viscosity (see Technical Backup Slides).
Electrochemical Oxidation Stability of Fluorinated Carbonate Electrolyte: Floating Test*

* Three-electrode electrochemical cell with Pt as working electrode and Li as reference and counter electrode.
Electrochemical Oxidation Stability of Fluorinated Carbonate Electrolyte: Floating Test

- **Gen 2 E1-E6**: 5.3 V
- **Gen 2 E3**: 5.7 V
- **Gen 2**: 6.0 V
- **E6** (EC/FLC-1/FE-1 = 2:6:2): 6.8 V, 6.7 V, 6.6 V, 6.5 V, 5.3-6.4 V
- **E5** (FCC-1/FLC-1/FE-1 = 2:6:2): 6.8 V, 6.7 V, 6.5 V, 5.3-6.6 V
Electrochemical Oxidation Stability of Fluorinated Carbonate Electrolyte: Floating Test*

(1) Working electrode: LiNi_{0.5}Mn_{1.5}O_{4} /Carbon Black/Binder: 84%/8%/8% in weight
(2) Electrode disc area: 1.6cm^2
(3) Reference electrode: Li metal
(4) CC-CV charge the LNMO/Li cell with C/10 rate to 5.0V, 5.1V, 5.2V and 5.3V, respectively. Maintain at each voltage for 10h to observe the leakage current.

* E5: All Fluorinated Electrolyte
Electrochemical Oxidation Stability of Fluorinated Carbonate Electrolyte: Floating Test*
# Floating Test Leakage Current Summary

<table>
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<tr>
<th>Electrolyte</th>
<th>Formulation</th>
<th>Leakage Current (A)</th>
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<tr>
<td></td>
<td></td>
<td>5.0V</td>
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<tr>
<td>Gen2</td>
<td>EC/EMC (3/7)</td>
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<td>EC/EMC/FE-1 (2/6/2)</td>
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<tr>
<td>E2</td>
<td>EC/EMC/FE-1 (2/5/3)</td>
<td>0.8x10^-5</td>
</tr>
<tr>
<td>E3</td>
<td>FCC-1/EMC/FE-1 (2/6/2)</td>
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<tr>
<td>E4</td>
<td>FCC-1/EC/EMC/FE-1 (1/1/6/2)</td>
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<td>E5</td>
<td>FCC-1/FLC-1/FE-1 (2/6/2)</td>
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</tr>
<tr>
<td>E6</td>
<td>EC/FLC-1/FE-1 (2/6/2)</td>
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</table>
The capacity of LNMO/Li cell degrades dramatically (>20% loss of its initial capacity) even in 150 cycles. Although cathode (active material, binder) and other factors (separator, Li anode), electrolyte is the main contributor to the poor electrochemical performance.

Cell Testing Condition:

- Electrolyte: 1.2M LiPF$_6$ in EC/EMC (3/7)
- LNMO/Li
- Cut-off voltage: 3.2~4.95 V
- Chg-dchg current rate: C/10
- Separator: Celgard 2325
- Testing vehicle: CR 2032

High Reactivity of Conventional Electrolyte in LNMO Cell at High Temperature 55°C
F-EC Electrolyte Performance in LiNi$_{0.5}$Mn$_{1.5}$O$_4$ / Li$_4$Ti$_5$O$_{12}$ Cell at Elevated Temperature

- FEC/ether electrolyte showed excellent cycling performance at RT;
- However at elevated temperature, both cell started to degrade at 100$^{\text{th}}$ cycle due to the instability of the electrolyte (FEC-electrolyte showed quick degradation);
- With accelerated C-rate, the FEC electrolyte performs well but degrade fast at 55$^\circ$C (right figure).

Cut-off voltage: 2.0-3.45V
New Fluorinated Electrolytes To increase the Thermal/Chemical Stability

FEC Thermal decomposition:

\[ \text{FEC} \rightarrow \text{HF} \]

FCC-1

FLC-1

FE-1
LNMO/LTO Cycling Performance Improvement

Gen 2 electrolyte (1.2 M LiPF$_6$ EC/EMC (3/7))
1.0M LiPF$_6$ FEC/DMC/FE-1(3/4/3)
1.2M LiPF$_6$ EC/DMC/FE-1(2/6/2)
1.2M LiPF$_6$ EC/EMC/FE-1(2/6/2)

25°C

Capacitance Retention (%)

Cycle Number

55°C
**Cycling Performance of LNMO/LTO Cell with Fluorinated Electrolytes at 55 °C**

LiNi$_{0.5}$Mn$_{1.5}$O$_4$(LNMO)/Li$_4$Ti$_5$O$_{12}$ (LTO)

High temperature: **55 °C**

Current density: C/10 for formation, and C/2 for cycling

Cut-off voltage: 2.0-3.45 V

- The Gen2 electrolyte cell lost 13% of initial capacity in 100 cycles;
- FCC-1/EMC/FE-1 electrolyte showed improved cycling performance than Gen2;
- All-fluorinated electrolyte FCC-1/FLC-1/FE-1 showed the best capacity retention among all the fluorinated electrolytes.
First Cycle Potentiostatic Profile of LNMO/Graphite Cell
LNMO/Graphite Cell Performance

Cycling performance, Room temperature (25°C), C/10, cutoff voltage : 3.5-4.9 V

Room Temp. (25°C)

High Temp. (55°C)
Collaboration and Coordination with Other Institutions

**Partners:**
- Center of Nano-Materials at Argonne (DOE Lab)
  Dr. Larry Curtiss for theoretical calculation of red-ox potentials by quantum chemical methods.
- Daikin Industries, Ltd. (Chemical Industry)
  Dr. Meiten Koh for the electrolyte material synthesis discussions.

**Collaborators:**
- US Army Research Laboratory (DOD Lab)
  Dr. Richard Jow and Kang Xu for information and technical exchanges.
- ConocoPhillips, Saft, and EnerDel (Battery Industry)
  High voltage spinel cathode, LTO and A12 graphite anode supply.
During the rest of the FY12, our research will continue the exploration of the fluorinated carbonate-based electrolytes as high voltage electrolytes:

- Scientific write-up for publication in peer-reviewed journals;
- Optimal formulation including hybrid electrolyte approach will be sought for best performance (Power, Cycling);
- New fluorinated carbonate solvent design, synthesis, characterization and electrochemical performance evaluation;
- Tailored SEI additives to enable the graphite high voltage cell especially at elevated temperatures.

In the year of FY13, we propose the following work in order to achieve the milestones and the final goal of this project:

- Design and synthesis of fluorinated non-carbonate solvents as backup high voltage electrolytes;
- Electrochemical properties investigation of new electrolyte systems.
Summary

PHEV and EV batteries face many challenges including energy density, calendar life, cost, and abuse tolerance. The approach of this project to overcome the above barriers is to develop highly stable electrolyte materials that can significantly improve the high voltage cell performance without sacrificing the safety to enable large-scale, cost competitive production of the next generation of electric-drive vehicles.

- Argonne has initiated the fluorinated carbonate-based electrolytes as high voltage electrolyte to improve the battery energy density by enabling the high voltage cells;
- Determination of electrolyte oxidation stability was established by floating test using both inert working electrode and high voltage cathode;
- Fluorinated carbonate electrolytes showed promising performance both in theory and in real cell: superior capacity retention at elevated temperature compared to the conventional one using 5V spinel LNMO/LTO cell.
- Argonne’s fluorinated carbonate electrolytes improved the cell capacity fading for graphite cells. FY12 plan was prosed to address the low first cycle capacity loss through additive approach.