High Voltage Electrolytes for Li-ion Batteries

PI: T. Richard Jow

U. S. Army Research Laboratory
2800 Powder Mill Road
Adelphi, MD 20783
17 May 2012

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Overview

Timeline
- Start: June 2011
- End: Dec. 2014
- 50% complete

Barriers
- SOA electrolytes based on carbonate solvents decompose near or above 4.5 V
- Lack of reliable 5 V cathodes as characterization platform.
- Lack of understanding of oxidation stability and reactive pathway of the electrolyte at the cathode/electrolyte interface

Budget
- Total project funding
  - DOE $1,250K
- Funding received in F2011
  - $250K
- Funding for FY12
  - $250K

Partners
- Argonne National Laboratory
- Saft Batteries
- U of Texas, Austin
- U of Utah
- U of Maryland
Objectives

• Develop high voltage electrolytes for high voltage Li-ion batteries for increased energy density
  – Explore and identify solvents or additives for electrolytes that allow the operation of high voltage cathodes
  – Understand the reactive pathways and reaction products at the electrode/electrolyte interface through computation and surface characterization for guiding the development of improved electrolyte components
  – Identify and/or develop structurally stable high voltage cathode materials
**Milestones**

- **Sep 2010 – Go/No-Go:**
  - Identify solvents and/or additives allowing the operation of high voltage cathodes
  - Develop or identify structurally stable cathodes as a testing vehicle for electrolytes
  - Understand oxidation stability and reactive pathway of electrolytes through computation and experiments

- **May 2011:**
  - Demonstrate the effectiveness of solvents or additives in allowing the improved operations of cells with 4.7 V LiNi$_{0.5}$Mn$_{1.5}$O$_4$ and/or 4.8 V LiCoPO$_4$ cathodes
  - Develop stabilized LiCoPO$_4$ with metal substitution
  - Calculate oxidation potential of solvents and validate with experiments

- **Sep 2012:**
  - Evaluate effectiveness of additives in both half cells and full cells with graphite anode
  - Understand reactive pathways of electrolyte components through computational effort, surface characterization and SEI chemistry studies
Approach

- **Identify and/or develop high voltage cathodes as a testing vehicle**
  - Collaborate with ANL on LiNi\(_{0.5}\)Mn\(_{1.5}\)O\(_4\) and \(x\)Li\(_2\)Mn\(_3\)·(1-x)LiMO\(_2\)
  - Investigate validity of LiCoPO\(_4\)

- **Computational effort**
  - Understand oxidative stability of solvents in electrolytes
  - Understand reactive pathways of additives and electrolytes on cathodes
  - Develop ability to predict and design electrolyte components

- **Develop additives for carbonate based electrolytes**
  - Search additives that would interact and form protective interfacial layers on cathodes
  - Understand interfacial chemistry at the cathode/electrolyte interface through surface characterization techniques
Technical Accomplishments

High voltage cathodes (J. Allen, R. Jow)
• Stabilized 4.8 V LiCoPO$_4$ by Fe doping demonstrated much improved rate capability and capacity retention.
• LiCoPO$_4$ can sustain polaron with slightly higher migration energy barrier than that in LiFePO$_4$ (DFT calculations).

Computational: Electrolytes and Electrode/Electrolyte Interface (O. Borodin, R. Jow)
• Oxidation potentials of solvents calculated using DFT would be lowered by the presence of anions and were more in agreement with experiments.
• Conductivity of Li$_2$EDC calculated using MD simulations agrees well with experiments.
• Energy barrier for conduction is 78 kJ/mol.

Additives for high voltage electrolytes (A. Cresce, J. Ho, J. Read, K. Xu)
• Demonstrated that the full cell, graphite/LiNi$_{0.5}$Mn$_{1.5}$O$_4$, cycled in electrolyte with HFiP additive achieved 80% capacity retention and 99.87% coulombic efficiency in 200 cycles.
• XPS surface analysis revealed the presence of fluorinated alkyl substructure on cathode.
• Higher degrees of fluorination of additives resulted in better cycling performance.
LiCoPO₄ and Stabilized LiCoPO₄

DFT calculations using validated HSE06 at steps along a linearly interpolated path between two calculated polarons.

<table>
<thead>
<tr>
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<th>Migration barrier, eV</th>
<th>σ, S/cm</th>
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<tbody>
<tr>
<td>LiFePO₄</td>
<td>0.20</td>
<td>1.8x10⁻⁸</td>
</tr>
<tr>
<td>LiMnPO₄</td>
<td>0.33</td>
<td>&lt;10⁻¹⁰</td>
</tr>
<tr>
<td>LiCoPO₄</td>
<td>0.23</td>
<td>~10⁻⁹</td>
</tr>
</tbody>
</table>

Li₀.⁹₂Co₀.⁸Fe₀.₂PO₄ demonstrated good rate capability.

Overview of Computational Studies

**Predict:** electrolyte reduction, SEI properties, SEI – electrolyte interface (quantum chemistry, MD)

**Oxidation potentials and decomposition reactions for solvent, solvent (or additive)-anion, solvent-lithium salt and additives (quantum chemistry)**

- SEI: Li$_2$EDC
- EC: DMC(3:7)/LiPF$_6$

**Structure and transport in bulk electrolytes (carbonate-alkylphosphate/LiPF$_6$) and SEI components with a focus of Li$^+$ competitive solvation in mixed solvents:** (MD simulations)

**MD and DTF studies revealed:**
- The presence of BF$_4^-$, PF$_6^-$, ClO$_4^-$, or B(CN)$_4^-$ anion lowered the carbonate solvent oxidation potential by H$^-$ and F$^-$ abstraction and promoted decomposition kinetics;
- Fluorine transfer was observed for HFiP/PF$_6^-$-complexes.

**λ** of Li$_2$EDC, (LiO$_2$COCH$_2$)$_2$, predicted using MD simulations with revised and validated FF.
- **λ** is in good agreement with experimental data.
- Activation energy: 78 kJ/mol

Experiment Phil Ross LBNL (ARL material)

Battery pic from Kang Xu
Influence of anions, salt, explicit solvent and CoPO$_4$ surface on EC oxidation was investigated.

- Oxidation potential of (EC)$_2$, at $\varepsilon=20$, is the lowest indicating that it might be the preferred pathway for oxidation at non-active electrodes compared to the EC-anion decomposition.
- Co-O bond is formed between CoPO$_4$ and EC.

**Vehicle Technologies Program** M052/cc-pvTz level calculations
Lindan Xing Uof Utah calculations. Relative energy (kcal/mol) from B3LYP/6-311++G(d) PCM(Solvent=water)

Vehicle Technologies Program

In collaboration with BATT program

Relative energy of initial product

Relative energy of TS
A revised polarizable force field has been developed for Li$_2$EDC that is compatible with APPLE&P electrolyte force field.

$E_a$ for Li$_2$EDC conductivity was 78 kJ/mol, which is similar to the 68 kcal/mol measured for the Li$^+$ charge transfer at the graphite/electrolyte interface.

The averaged conductivity of crystalline Li$_2$EDC is similar to conductivity of the amorphous phase.

At temperatures below 450 K anion motion contributes less than 15% to charge transport.
## Correlation of Experiment and Computation

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Experiment</th>
<th>Computation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Eₐ for Li⁺</strong> charge transfer at interface ¹</td>
<td><strong>Eₐ for Li</strong> diffusion</td>
<td>68 kJ/mol</td>
</tr>
<tr>
<td><strong>Graphite/Electrolyte interface</strong></td>
<td>78 kJ/mol for Li conduction barrier in Li₂EDC ³, a key SEI component</td>
<td></td>
</tr>
<tr>
<td><strong>NCA/Electrolyte interface</strong></td>
<td>52 kJ/mol</td>
<td></td>
</tr>
<tr>
<td><strong>LFP/Electrolyte interface</strong></td>
<td>32 kJ/mol</td>
<td></td>
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<tr>
<td><strong>Li diffusion in LFP</strong></td>
<td>29 kJ/mol ²</td>
<td>20 kJ/mol for polaron migration barrier in LFP ⁴</td>
</tr>
</tbody>
</table>

**NCA**: Lithium nickel cobalt aluminum mixed oxide, **LFP**: lithium iron phosphate

High Voltage Electrolyte Additives

A. v. Cresce, J. Ho, J. Read, and K. Xu

Electrochemistry Branch
U. S. Army Research Laboratory
Adelphi, MD 20783-1197, USA
Different Focuses on Anode- and Cathode-Interphases

Anode:
- Faster Li$^+$-transport
- Less consumption of Li$^+$ (irreversible capacity)

Cathode:
- Stabilization at high potential (> 4.5 V)

Li$^+$-solvation no longer plays directing role in cathode SEI formation mechanism
**Interphases on Anode and Cathode**

**Anode** (Graphitic)
- Reductive decomposition
- Lithiation process
  - Solvent co-intercalation
  - Lattice held together by van de Waals force
- 3D: partially penetrated graphene
- Coverage of Li\(^+\)-exit/entrance sites
  - kinetic control over Li\(^+\)-transport

**Cathode** (Metal Oxide)
- Doubt still exists about the existence
  - potential < 4.5 V vs. Li (\(~1.5\) V vs. SHE)
- Oxidative decomposition
- Delithiation
  - Solvent co-intercalation impossible
  - Lattice held together by Coulombic/covalent
  - “Patchy” instead of “continuous”
- No coverage of Li\(^+\)-exit/entrance sites
  - deactivation of metal cores

In the last two decades >90% effort are on anode SEI.
Preliminary Results (A. v. Cresce)

- New electrolyte forms stable interphase on both spinel LiNi0.5Mn1.5O4 and olivine LiCoPO4 surfaces
- Baseline electrolyte: LiPF6/EC/EMC (30:70)
- 1% additive causes significant impact on cell stability
- Further refinements are on-going

Cresce & Xu, JES, 2011, 158, A337
Confirmation from industry partner
• CE% ~ 99.87%
Surface Chemistries of HFiP

Where did HFiP end up with?
- Chemically phosphate can be reduced at anode
- It was found to even form good SEI on graphite in neat PC

What mechanism did it stabilize electrolyte against cathode surface?
HR-XPS conducted on both cathode and anode cycled in baseline and HFIP-containing electrolytes
- P 2p absent in control samples
- P2p on test samples
  - 5~10 X more on cathode than anode
- C1s for CF3 only found on cathode

The fate of phosphate in electrolyte
- Phosphate ends up on cathode and anode
- Fluorinated alkyls substructure on cathode
Even HR-XPS cannot pin-point the structure of cathode interphase
  • Perhaps inference from MS?

- Possible participation of TM cores (TM reduction)
- New bond-formation between M and O/P/F/C
- Deactivation on cathode surface at TM centers
  • similar to catalyst poisoning
  • spectroscopic evidence

1.2 Kg HFiP made at ANL
GC-MS by Dzwinel (ANL)
Interphase on Electrolyte/Cathode
Unlike Electrolyte/Anode Junction, interphase on cathode is little studied
- Oxidation Chemistry unknown
- Formation mechanism?
- Perfluorination helps
- Phosphazene might help (?)
Synthesis of Perfluorinated Additive PFBP
(Drs. XQ Yang and HS Lee, BNL)

- Presence of remaining H in HFiP undesired
- Perfluorinated additives synthesized

![Perfluorinated additive PFBP structure]

**Graph showing cycle number versus capacity/mAh for different electrolytes:**
- **Baseline: 1.2 M LiPF$_6$ in EC/EMC (30:70)**
- **Baseline + 5 mM PFBP**
- **Baseline + 10 mM AFAC**

**ANL LMNO/GR Full Cells**

- ARL-made PBFP additive
- New ARL Al-based additive
- Standard electrolyte
A New 5 V Battery Chemistry: Double Intercalation (J. Read, ARL)

- Double-intercalation chemistry
- Symmetric graphite cell
- High voltage (> 5.0 V)
- Concept was proposed in early 1990s (J. Dahn)
  - never realized due to lack of electrolytes:
    - good SEI on anode, high V stability on cathode
  - our high V electrolytes could revive this concept
Future Work

- Collaborate with ANL on $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ for the testing of ARL electrolytes.
- Continue the development of stabilized $\text{LiCoPO}_4$.
- Perform computational screening of redox stability and decomposition reactions of the fluorinated alkylphosphate-based additives using DFT calculations. Predict bulk and interfacial properties of electrolytes with fluorinated alkylphosphate-based additives.
- Study decomposition reactions of solvent and additives at cathode surfaces.
- In-situ/Direct characterization of SEI under Li ion chemistry environments
- Synthesis of new solvents/additive based on more understanding about the chemical processes at interphases
Summary

- Stabilized high voltage $\text{Li}_x\text{Co}_{0.8}\text{Fe}_{0.2}\text{PO}_4$ in couple with the high voltage electrolyte has greatly improved the capacity retention and rate capability
  - Stability of the cathode materials including $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{xLi}_2\text{MnO}_3\cdot(1-\text{x})\text{LiMO}_2$ are critical for the success of high voltage Li-ion batteries

- Oxidation potentials and reactive pathway of EC and alkyl phosphate has been successful calculated with respect to the influence of anion, salt, explicit solvent and $\text{CoPO}_4$ computationally.
  - The conductivity of $\text{Li}_2\text{EDC}$ was calculated using MD simulation and agrees with experiment.
  - The presence of $\text{BF}_4^-$, $\text{PF}_6^-$, $\text{ClO}_4^-$, or $\text{B(CN)}_4^-$ anion lowered the carbonate solvent oxidation potential by $\text{H}^-$ and $\text{F}^-$ abstraction and promoted decomposition kinetics;
  - Fluorine transfer was observed for $\text{HFiP/PF}_6^-$ complexes.

- Effectiveness of HFiP additive has been successfully demonstrated in a full cell, graphite/$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, cycled in electrolyte with HFiP additive achieved 80% capacity retention and 99.87% coulombic efficiency in 200 cycles.
  - XPS surface analysis revealed the presence of fluorinated alkyl substructure on cathode.
  - Higher degrees of fluorination of additives resulted in better cycling performance.
  - Elevated temperature tests are on-going