Inexpensive, Nonfluorinated (or Partially Florinated) Anions for Lithium Salts and Ionic Liquids for Lithium Battery Electrolytes

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Overview

Timeline
Project Start: April 24, 2009
Project End: Mar 31, 2013
Percent Completed: 100%

Budget
Total Project Funding: $763,057
Funding Received FY10: $245,450
Funding Received FY11: $245,882
Funding Received FY12: $271,725

Barriers
Low cost cell materials
Abuse tolerance
Low temperature performance

Partners
Project Lead: Wesley Henderson
Co-PI: Michel Armand
Collaborators:
- Oleg Borodin (Army Research Laboratory)
- Vincent Battaglia (Lawrence Berkeley National Laboratory)
- Bryant Polzin (Argonne National Laboratory)
- Marshall Smart (NASA Jet Propulsion Laboratory)
Objectives

- Develop techniques to synthesize electrolytes that allow for lower cost of production
- Develop low-cost, thermally stable electrolytes to replace ones now commonly used
- Develop electrolyte/additive combinations that will facilitate a more stable solid-electrolyte interphase (SEI) on the anode
- Develop additives that allow for the formation of protective coatings on the cathode (i.e., a cathode SEI) and enhances electrochemical stability above 4.3 V
## Milestones

<table>
<thead>
<tr>
<th>Milestone</th>
<th>Completion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Determination of the solution structure and transport properties of solvent-LiBF&lt;sub&gt;4&lt;/sub&gt;, LiDFOB and LiBOB mixtures</td>
<td>Completed</td>
</tr>
<tr>
<td>Determination of the phase behavior/properties of solvent-LiTDI mixtures</td>
<td>Completed</td>
</tr>
<tr>
<td>Preparation/characterization of LiTDI-based and concentrated electrolytes. Conduct half/full-cell electrochemical testing (graphite and NMC electrodes) to demonstrate improved cycling behavior performance over 200+ cycles</td>
<td>Completed</td>
</tr>
</tbody>
</table>
**Approach**

Synthesize and fully characterize two classes of nonfluorinated (or less fluorinated) anions:

1. chelated and non-chelated organoborate anions (related to bis(oxalate)borate or BOB⁻), and
2. Hückle-type anions in which the charge is stabilized on a 5-member azole ring and noncyclic cyanocarbanions. Characterize the physical properties of these new anions, incorporated in both lithium salts and ionic liquids, by examining the thermal phase behavior (phase diagrams); thermal, chemical and electrochemical stability; transport properties; interfacial properties; molecular interactions and cell performance. These salts will be compared with widely used salts such as LiPF₆ and LiBOB and ionic liquids based upon the bis(trifluoromethanesulfonyl)imide anion (TFSI⁻).

To enable electrolytes for high-voltage, sulfur and other cathodes, an approach based upon "concentrated electrolytes" is being adopted. It is the bulk (uncoordinated) solvent that typically degrades at high potential. Thus, the goal is to minimize the amount of uncoordinated solvent in the electrolytes. Solvent-lithium salt and ionic liquid (IL)-lithium salt-solvent mixtures are being formulated which have desirable properties (high Li⁺ cation concentration, high conductivity, limited volatility, high oxidative stability, cathode SEI forming capability, stability with Al, etc.).
**Technical Accomplishments - Overview**

- The solution structure of electrolytes with LiBF$_4$, LiDFOB and LiBOB with cyclic carbonate (EC, PC) and ester (GBL, GVL) solvents has been determined and linked with the transport properties (viscosity, conductivity) of the electrolytes.

- LiTDI appears to be a promising new salt, but limited information is currently available. An improved synthesis method has been developed and a more extensive characterization of its interactions and properties is underway.

- LiTFSI-EC mixtures with high concentrations of lithium salt (little to no uncoordinated EC) have been prepared with favorable electrolyte properties - high oxidative stability, inhibited Al corrosion, low volatility, etc.
Solution Structure-Transport Properties

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Structure</th>
<th>$T_m$ (°C)</th>
<th>$T_b$ (°C)</th>
<th>DN</th>
<th>$\varepsilon$</th>
<th>$\eta$ (mPa s)*</th>
<th>$\rho$ (g cm$^{-3}$)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC</td>
<td><img src="image1" alt="EC Structure" /></td>
<td>32</td>
<td>248</td>
<td>16.4</td>
<td>89</td>
<td>1.44</td>
<td>1.29</td>
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<tr>
<td>PC</td>
<td><img src="image2" alt="PC Structure" /></td>
<td>-49</td>
<td>242</td>
<td>15.1</td>
<td>69</td>
<td>1.23</td>
<td>1.16</td>
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<tr>
<td>GBL</td>
<td><img src="image3" alt="GBL Structure" /></td>
<td>-44</td>
<td>204</td>
<td>18.0</td>
<td>42</td>
<td>1.09</td>
<td>1.08</td>
</tr>
<tr>
<td>GVL</td>
<td><img src="image4" alt="GVL Structure" /></td>
<td>-31</td>
<td>208</td>
<td>-</td>
<td>34</td>
<td>1.10</td>
<td>1.02</td>
</tr>
</tbody>
</table>

*60°C
(EC)$_n$-LiBF$_4$ Electrolytes
Crystalline Solvate Phases

\((\text{EC})_2:\text{LiBF}_4\)

\((\text{GBL})_4:\text{LiBF}_4\)
Ion Solvation

EC

![Graph showing Raman shift vs. EC/Li and LiBF4 concentration](image-url)
Ion Solvation

EC

EC...Li+

NC STATE UNIVERSITY
(Solvent)$_n$-LiBF$_4$: Ion Solvation

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Uncoordinated (cm$^{-1}$)</th>
<th>Coordinated (cm$^{-1}$)</th>
<th>Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC</td>
<td>717</td>
<td>728</td>
<td>symmetric ring deformation</td>
</tr>
<tr>
<td></td>
<td>895</td>
<td>905</td>
<td>C-O stretching</td>
</tr>
<tr>
<td>PC</td>
<td>712</td>
<td>722</td>
<td>symmetric ring deformation</td>
</tr>
<tr>
<td>GBL</td>
<td>675</td>
<td>690</td>
<td>C-C stretching</td>
</tr>
<tr>
<td>GVL</td>
<td>651</td>
<td>660</td>
<td>ring deformation</td>
</tr>
<tr>
<td></td>
<td>942</td>
<td>950</td>
<td>C-C Stretcing</td>
</tr>
</tbody>
</table>
(Solvent)$_n$-LiDFOB and LiBOB: Ion Solvation
Ion Solvation

### Solvent DN and ε

<table>
<thead>
<tr>
<th>Solvent</th>
<th>DN</th>
<th>ε</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC</td>
<td>16.4</td>
<td>89</td>
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<td>42</td>
</tr>
<tr>
<td>GVL</td>
<td>-</td>
<td>34</td>
</tr>
</tbody>
</table>
(Solvent)$_n$-LiX: Viscosity

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\eta$ (mPa s) @ 60°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC</td>
<td>1.44</td>
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<td>1.09</td>
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</tbody>
</table>
(Solvent)$_n$-LiX: Viscosity

(solvent)$_n$-LiBOB mixtures are much more viscous than analogous -LiBF$_4$ or -LiDFOB mixtures
(Solvent)$_n$-LiX: Conductivity

**EC**
- Increasing association: LiBOB
- Increasing viscosity: LiDFOB
- Increasing conductivity: LiBF$_4$

**PC**
- Increasing association: LiBOB
- Increasing viscosity: LiDFOB
- Increasing conductivity: LiBF$_4$

**GBL**
- Increasing association: LiBOB
- Increasing viscosity: LiDFOB
- Increasing conductivity: LiBF$_4$

**GVL**
- Increasing association: LiBOB
- Increasing viscosity: LiDFOB
- Increasing conductivity: LiBF$_4$

$60^\circ C$
(Solvent)$_n$-LiX: MD Simulations

(EC)$_n$-LiPF$_6$ ($n = 20$)
(Solvent)$_n$-LiX: MD Simulations

(EC)$_n$-LiPF$_6$ (n = 20)

(EC)$_n$-LiBF$_4$ (n = 20)
LiDCTA vs. LiTDI

PROBLEM: LiDCTA is high associated in electrolytes solutions

SOLUTION: modify anion → LiTDI


(diglyme)$_2$:LiTDI
LiTDI Cell Cycling

EC/DEC 3/7 (v/v) + 1 wt% LiDFOB

1M LiTDI and LiPF$_6$ on LiNMC (5:3:2)
Concentrated Electrolytes

\[ \text{fraction of uncoordinated EC} \]

Raman analysis of solvent bands (20°C)

\[ \text{fraction of coordinated EC} \]
LiTFSI-EC Mixtures

examples of solvates from MD simulations
LiTFSI-EC Mixtures

ILEET

Current Density

0.01 mA cm\(^{-2}\)

10-1

6-1

2-1

Pt

Current Density

0.1 mA cm\(^{-2}\)

10-1

6-1

3-1

Cycle 3

2-1

E (V vs. Li/Li\(^+\))

2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0

EC-Li

Conductivity (mS cm\(^{-1}\))

10^{-3} 10^{-2} 10^{-1} 10^{0} 10^{1} 10^{2}

0 0.10 0.20 0.30 0.40

x_{LiTFSI}

EC/DEC-Li

100°C

-20°C
Collaborations/Coordination with Other Institutions

- **Oleg Borodin** (Army Research Laboratory):
  We have formed an extensive collaboration with Oleg to marry experimental characterization work with quantum chemical (QC) calculations and molecular dynamics (MD) simulations to greatly aid in determining the molecular-level interactions of electrolytes (carbonate, ester solvents...LiBF$_4$, LiDFOB, LiBOB, etc.)

- **Vincent Battaglia** (Lawrence Berkeley National Laboratory):
  Vincent supplied us with cathodes for testing of the LiTDI and concentrated electrolytes

- **Bryant Polzin** (Argonne National Laboratory):
  Bryant supplied us with graphite anodes and cathodes for testing of the LiTDI and concentrated electrolytes

- **Marshall Smart** (NASA Jet Propulsion Laboratory):
  Marshall provided cell testing guidance for the LiTDI and concentrated electrolytes

- **Steve Greenbaum** (Hunter College):
  Steve is conducting NMR measurements to determine diffusion coefficients

- **Daniel Abraham** (Argonne National Laboratory):
  Daniel is working with electrolytes containing the PY$_{14}$FSI IL supplied by us
Anions containing oxylate groups (i.e., LiDFOB and LiBOB) have, surprisingly, been found to be highly dissociated (much more so than for LiBF₄) for dilute salt concentrations. For more concentrated mixtures, however, the DFOB⁻ and BOB⁻ anions are found to aggregate with Li⁺ cations to a greater extent than for other anions.

Several salts for which only limited information is available (i.e., LiDFOB, LiFSI, LiTDI, etc.) are in the process of being extensively characterized.

The thermal phase behavior of a large number of solvent-LiX and IL-LiX-solvent mixtures have been examined. Promising concentrated electrolytes formulations with very high Li⁺ cation content have been identified with solvent-LiX and IL-LiX-solvent mixtures. Cell testing of these is underway.
Dr. Venkat Srinivasan, the staff at LBNL, the BATT Program and the U.S. DOE’s Vehicle Technologies Program are gratefully acknowledged for support for this research.