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

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Overview

Timeline
- Project Start: April 24, 2009
- Project End: March 31, 2012
- Percent Completed: 66%

Barriers
- Low cost cell materials
- Abuse tolerance
- Low temperature performance

Budget
- Total Project Funding: $763,057
- Funding Received FY10: $245,450
- Funding Received FY11: $245,882

Partners
- Project Lead: Wesley Henderson
- Co-PIs: Michel Armand, Peter Fedkiw
- Collaborators:
  - Kang Xu, Richard Jow (ARL)
  - Patrick Judeinstein (Université Paris-Sud)
  - Steve Greenbaum (Hunter College of CUNY)
  - Patrik Johansson (Chalmers University)
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>
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</thead>
<tbody>
<tr>
<td>Characterization (properties/phase diagrams) of solvent-LiBF_4 mixtures as model electrolytes</td>
<td>ongoing</td>
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<tr>
<td>Characterization (properties/phase diagrams) of solvent-LiBOB and -LiDFOB mixtures to examine structural effects on solubility/properties</td>
<td>ongoing</td>
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<tr>
<td>Synthesis/characterization of ionic liquids containing cyanocarbanions and DFOB^-</td>
<td>ongoing</td>
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<tr>
<td>Synthesis of new partially fluorinated anions (with new ligands) and cyanocarbanions</td>
<td>ongoing</td>
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Approach

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

(1) chelated and non-chelated organoborate anions (related to bis(oxalato) 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⁻).
**Technical Accomplishments - Overview**

- Prepared phase diagrams of solvent-LiBF$_4$ mixtures (acetonitrile, adiponitrile) to serve as a model system (for comparison with new salts)

- Synthesized high purity lithium difluoro(oxalato)borate (LiDFOB) – determined the crystal structure of the LiDFOB·2H$_2$O dihydrate – prepared phase diagrams with a variety of solvents including carbonates, esters, sulfones and nitriles/dinitriles – numerous LiDFOB solvate crystal structures were determined providing insight into how the anion and solvent molecules interaction with Li$^+$ cations

- Characterized ionic liquid (IL) properties (conductivity, density, viscosity, diffusion coefficients) for ILs with cyanocarbanions: DCTA$^-$ (dicyanotriazolate) and DCA$^-$ (dicyanamide)
Lithium Difluoro(oxalato)borate (LiDFOB)
Crystal structure of LiDFOB dihydrate CIP $(\text{H}_2\text{O})_2$:LiDFOB
(Solvent)$_n$-LiX Mixtures: Ionic Association Interactions

- **Solvent-Separated Ion Pairs (SSIPs)**
  (uncoordinated anions)
- **Contact Ion Pairs (CIPs)**
  (anion coordinated to 1 Li$^+$)
- **Aggregates (AGGs)**
  (anion coordinated to 2 or more Li$^+$)

- LiTFSI, LiPF$_6$
- LiClO$_4$, LiI
- LiBF$_4$
- LiCF$_3$SO$_3$
- LiCF$_3$CO$_2$

Increasing association
AN-Li\(^+\) Solvation

C-C stretching mode (920 cm\(^{-1}\))
C≡N stretching mode (2250 cm\(^{-1}\))

LiBF\(_4\)

LiDFOB

LiCF\(_3\)CO\(_2\)
Carbonate & Ester Solvents

- Ethylene carbonate ($T_m \ 35^\circ C, T_b \ 244 \ C$)
- Propylene carbonate ($T_m \ -55^\circ C, T_b \ 242 \ C$)
- $\gamma$-Butyrolactone ($T_m \ -44^\circ C, T_b \ 204 \ C$)
- Dimethyl carbonate ($T_m \ 5^\circ C, T_b \ 91 \ C$)
- Diethyl carbonate ($T_m \ -74^\circ C, T_b \ 126 \ C$)
Ethylene Carbonate (EC)$_n$-LiX Phase Behavior

![Graph showing phase behavior](image)

- EC/Li ratios ranging from 1.2/1 to 39/1
- Temperature range from -150°C to 150°C
- Mole fraction of LiBF$_4$ and LiDFOB shown for each ratio

**Legend**

- EC
- LiBF$_4$
- LiDFOB
Propylene Carbonate (PC)$_n$-LiX Phase Behavior

![Graphs showing phase behavior](image)
$\gamma$-Butyrolactone (GBL)$_n$-LiX Phase Behavior

- GBL/Li
- mole fraction of LiBF$_4$

- GBL
- 0.00
- 19/1
- 0.05
- 9.0/1
- 0.10
- 5.6/1
- 0.15
- 3.9/1
- 0.20
- 3.0/1
- 0.25
- 2.3/1
- 0.30
- 2.1/1
- 0.32
- 2.0/1
- 0.33
- 1.9/1
- 0.35
- 1.7/1
- 0.37
- 1.5/1
- 0.40
- 1.4/1
- 0.42
- 1.2/1
- 0.45
- 1.1/1
- 0.47
- 1.0/1
- 0.50

- mole fraction of LiDFOB

- GBL
- 0.00
- 19/1
- 0.05
- 9.0/1
- 0.10
- 5.7/1
- 0.15
- 4.0/1
- 0.20
- 3.0/1
- 0.25
- 2.3/1
- 0.30
- 2.0/1
- 0.33
Dimethyl Carbonate (DMC)$_n$-LiX Phase Behavior

![Graph showing phase behavior of DMC$_n$-LiX mixtures](image)
Dimethyl Carbonate (DMC)$_n$-LiX Phase Behavior

AGG (DMC)$_{3/2}$:LiDFOB
Diethyl Carbonate (DEC)$_n$-LiX Phase Behavior

Images showing phase behavior with mole fraction of LiBF$_4$ and LiDFOB.
Sulfone Solvents for High-Voltage Electrolytes

- Ethyl methyl sulfone ($T_m$ 32-37°C, $T_b$ ??°C)
- Tetramethylene sulfone ($T_m$ 27°C, $T_b$ 285°C)

Sulfone-LiDFOB Phase Behavior

TMS/Li ratio vs. Temperature (°C)

mole fraction of LiDFOB

(1-x) TMS-(x) LiDFOB

TMS/LiDFOB

Temperature (°C)

x_{LiX}
(TMS)$_n$-LiDFOB Phase Behavior

CIP (TMS)$_2$:LiDFOB

\[\text{(1-x) TMS-(x) LiDFOB}\]

\[0 \leq x_{\text{LiDFOB}} \leq 1\]

Temperature (°C)

-150
-100
-50
0
50
100
150

6/1 4/1 2/1 1/1

TMS/LiDFOB

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Nitrile/Dinitrile Solvents for High-Voltage Electrolytes

- acetonitrile ($T_m -45°C$, $T_b 82 \ C$)
- glutaronitrile ($T_m -29°C$, $T_b 286 \ C$)
- adiponitrile ($T_m 4°C$, $T_b 295 \ C$)

Acetonitrile (AN)-LiBF$_4$ Phase Behavior
Acetonitrile (AN)$_n$-LiBF$_4$ Phase Behavior

SSIP (AN)$_1$:LiBF$_4$

AGG-II (AN)$_1$:LiBF$_4$

\[ (1-x) \text{AN} - x \text{LiBF}_4 \]

\[ \text{Temperature (°C)} \]

\[ \text{AN/LiBF}_4 \]

\[ x_{\text{LiX}} \]

6/1 4/1 2/1 1/1
Acetonitrile (AN)$_n$-LiDFOB Phase Behavior
Acetonitrile ($\text{AN}_n$)-LiDFOB Phase Behavior

$\text{AGG} \,(\text{AN})_3\cdot\text{LiDFOB}$
Acetonitrile (AN)$_n$-LiDFOB Phase Behavior

AGG (AN)$_1$:LiDFOB

\begin{figure} 
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{(1-x) AN-(x) LiDFOB}
\end{figure}
Adiponitrile (ADN)$_n$-LiDFOB Phase Behavior
Adiponitrile (ADN)$_n$-LiDFOB Phase Behavior

AGG (ADN)$_1$:LiDFOB

\[ (1-x) \text{ADN}-(x) \text{LiDFOB} \]
Ionic Liquids (ILs)

A number of ILs have been synthesized and their properties are currently being characterized.

**IM\textsubscript{10R}X** ILs prepared for comparison with **PY\textsubscript{1R}X** ILs rather than as electrolyte materials.
Ionic Liquids (ILs)

Temperature (°C)
84.0 60.2 39.4 21.0 4.6 -10.0 -23.1

Conductivity (S/cm)

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

1000/T (K^{-1})
2.6 2.8 3.0 3.2 3.4 3.6 3.8 4.0 4.2

DCA^{-} TCM^{-} DCTA^{-}

PY_{13}^{+} PY_{14}^{+}

IM_{102}^{+} IM_{104}^{+}

Density (g/cm³)
1.12
1.10
1.08
1.06
1.04
1.02
1.00

Viscosity (cP)
80
60
40
20
0

20 30 40 50 60 70 80 90 100

Temperature (°C)

Temperature (°C)
ILEET

Collaborations/Coordination with Other Institutions

**Army Research Laboratory (ARL)** – Joshua Allen (a graduate student) spent several weeks last year with Kang Xu and Richard Jow and will spend several months this year at ARL testing the properties of the salts.

**Université Paris-Sud & Hunter College of CUNY** – Patrick Judeinstein and Steve Greebaum have performed NMR diffusion measurement on the ILs.

**Chalmers University, Sweden** – Patrik Johansson is utilizing the known LiDFOB solvate structures to computationally analyze the Raman and IR vibrational bands for the different DFOB-solvate structures.
Future Work

- Continue with the phase diagram characterization of LiBF\(_4\) and LiDFOB with a wide variety of solvents – extend this to include LiPF\(_6\) and additional organoborate anions.

- Utilize Raman spectroscopy to further characterize the solvent and anion interactions in both the solid and liquid state...correlate this work with the phase diagrams and solvate crystal structures.

- Measure the transport properties (viscosity, conductivity, diffusion coefficients) of the solvent-LiX mixtures to determine the link between properties and structure (solvent and anion).

- Prepare/characterize ILs based upon the DFOB\(^-\) anion with varying cations – prepare phase diagrams of IL-LiX mixtures.

- Test solvent-LiX (nitrile/dinitrile) and IL-LiX mixtures in half- and full-cells.
Summary

- Phase diagrams have been prepared for (solvent)$_n$-LiBF$_4$ and -LiDFOB mixtures to characterize the solid-liquid thermal phase behavior – these diagrams, in concert with solvate crystal structures, provide tremendous insight into the solvent...Li$^+$ and anion...Li$^+$ interactions.

- The phase diagrams and solvate structures also greatly aid in interpreting Raman vibrational spectroscopic data used to characterize the solvent and anion interactions in both the solid and liquid phase – this enables the direct exploration of detailed solution structural information – a daunting challenge to date.

- Characterization of the thermal and transport properties ($T_m$, density, viscosity, conductivity, diffusion coefficients) of ILs is underway.
Acknowledgements

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- Joshua Allen (graduate student)
- Sang-Don Han (graduate student)

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