Advanced Materials for Flow Batteries

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Travis M. Anderson and Harry D. Pratt III
Sandia National Laboratories
Ionic Liquid Flow Batteries

**Problem:** Getting high concentrations of redox active species.

**Approach:** Design electrolytes with charge storage species as part of their chemical composition.

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**MetILs**

- Transition Metal Cation
- Weakly Coordinating Anions
- Alkanolamine Ligands
- Negligible Vapor Pressure
- Non-toxic

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**FY12 Milestones**

- 59 mV/n separation (ideally n > 1)
- Viscosity < 500 cP
- Conductivity > 0.5 mS cm\(^{-1}\)
- Open Circuit Potential > 1.5 V
Energy Density/Costs

**SNL APPROACH:** Consider a compound CuL₂BF₄ (L = methanolamine, MW = 47 g/mol), measured density 1.6 g/mL, formula weight, 244 g/mol

What is the molarity of redox active metal?
Divide density by formula weight (x1000 unit conversion)

6.6 M redox active copper

**Leuven APPROACH:** Prepared two- and four- coordinate MetILs with 4.5 and 3.1 M redox active copper.

**Costs:**
- Higher metal concentrations/energy density
- Single-step synthesis with low cost precursors
- Higher viscosity and pump consumption can be partially offset by operating at higher temperatures.
## Role of the Anion

### Ligands and Anions

- **EA** (ethanolamine)
- **DEA** (diethanolamine)

### Table: Anion States and Conductivity

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Anion 1</th>
<th>Anion 2</th>
<th>State at 25°C</th>
<th>$\sigma$ [mS/cm]</th>
<th>$\Delta E$ [mV]</th>
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<tbody>
<tr>
<td>EA</td>
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<td>158</td>
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<td>158</td>
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</table>
Crystal Structures

Key Accomplishments:
• Copper is *divalent*, complex is *monovalent*
• Alkanolamines display *non-innocence*
• Compounds still display *low melting temperatures*
• *Triflate* facilitates crystallization
Ionic Liquid H-Cell Testing

- System was validated using a literature standard.
- First tested system (Mn/Cu MetIL) resulting in reduced capacity due to copper plating.
- Improved results of a Cu MetIL/Fe MetIL system with a porous separator.
Electrodeposition

Zn—EA

Zn—DEA

Cu—EA

Cu—DEA

Zinc dendrite suppression with tridentate ligand
Flow Cell Tester

Key Issues:
- Force fluid against gravity
- Avoid sharp turns
- Carbon felt/membrane contact
- Wettability
- Membrane

assembly
What have we accomplished in FY12?
• Construction of flow cell testers designed to accommodate ILs.
• Met milestone of establishing a cell with high electrochemical reversibility, viscosity under 500 cP, conductivity greater than 0.5 mS cm⁻¹, and open circuit potential of 1.6 V.
• Enhanced spectroscopic tools for improved structure determination and controlling chemical properties.
• Filed a patent.

What are our plans for FY13?
• Continued testing of our suite of MetILs to identify the best candidates.
• Development of new MetILs with non-innocent ligand technology.
• Electrode and separator research to improve compatibility with ionic liquids.
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Sandia National Laboratories
PO Box 5800, MS0614
Albuquerque, NM 87185
tmander@sandia.gov