

# Advanced Materials for Flow Batteries

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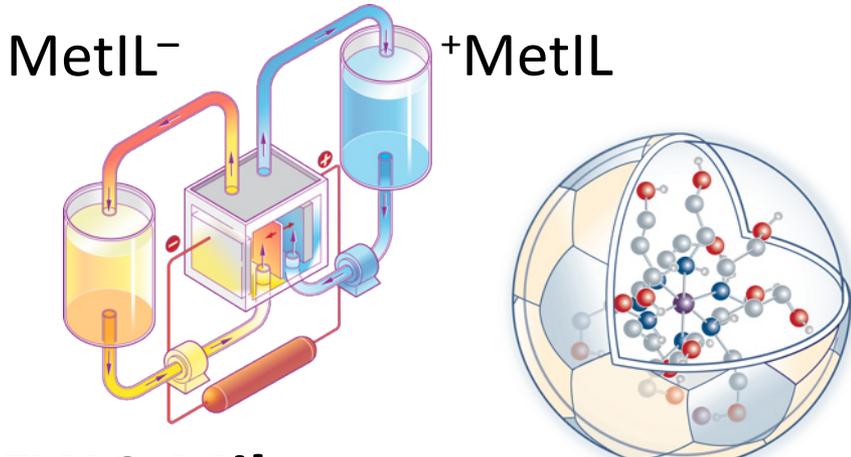


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# Ionic Liquid Flow Batteries

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

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



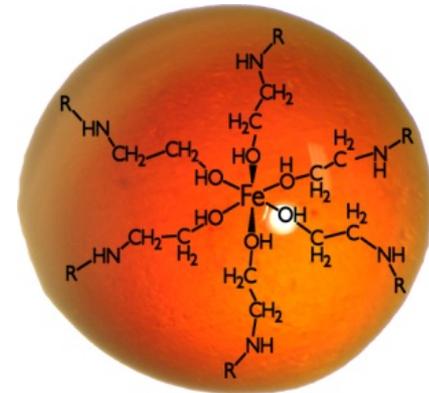
MetIL<sup>-</sup>      +MetIL

**FY12 Milestones**

- 59 mV/n separation (ideally  $n > 1$ )
- Viscosity < 500 cP
- Conductivity > 0.5 mS cm<sup>-1</sup>
- Open Circuit Potential > 1.5 V

## MetILs

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



# Energy Density/Costs

**SNL APPROACH:** Consider a compound  $\text{CuL}_2\text{BF}_4$  (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?**

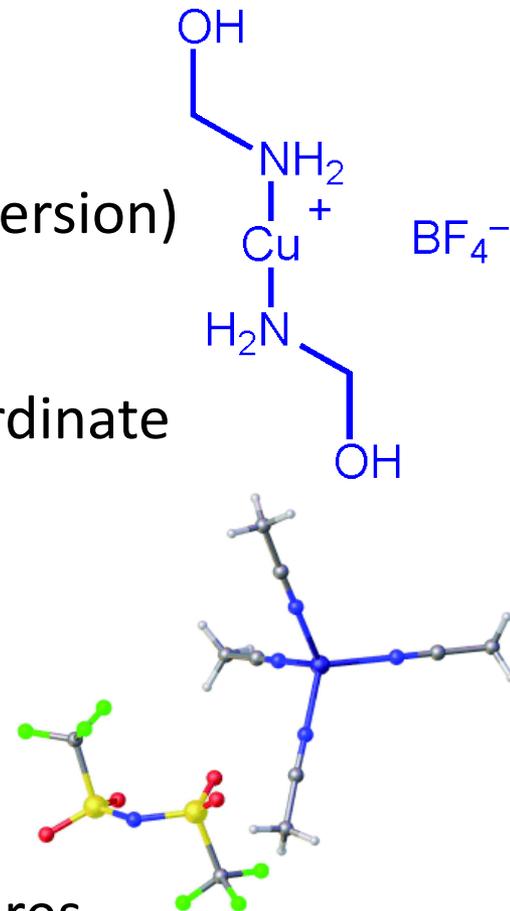
Divide density by formula weight (x1000 unit conversion)

**6.6 M redox active copper**

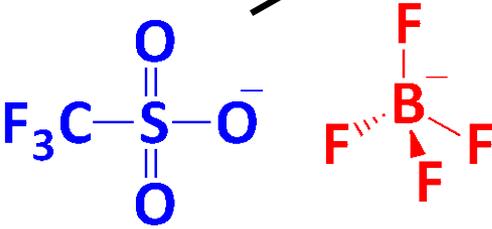
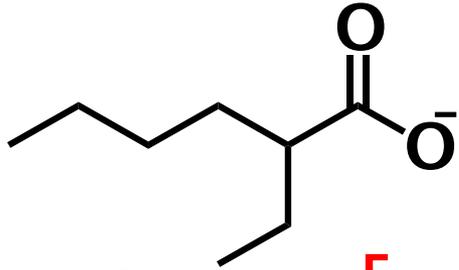
**Leuven APPROACH:** Prepared two- and four- coordinate MetILs with **4.5** and **3.1 M redox active copper**.

**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



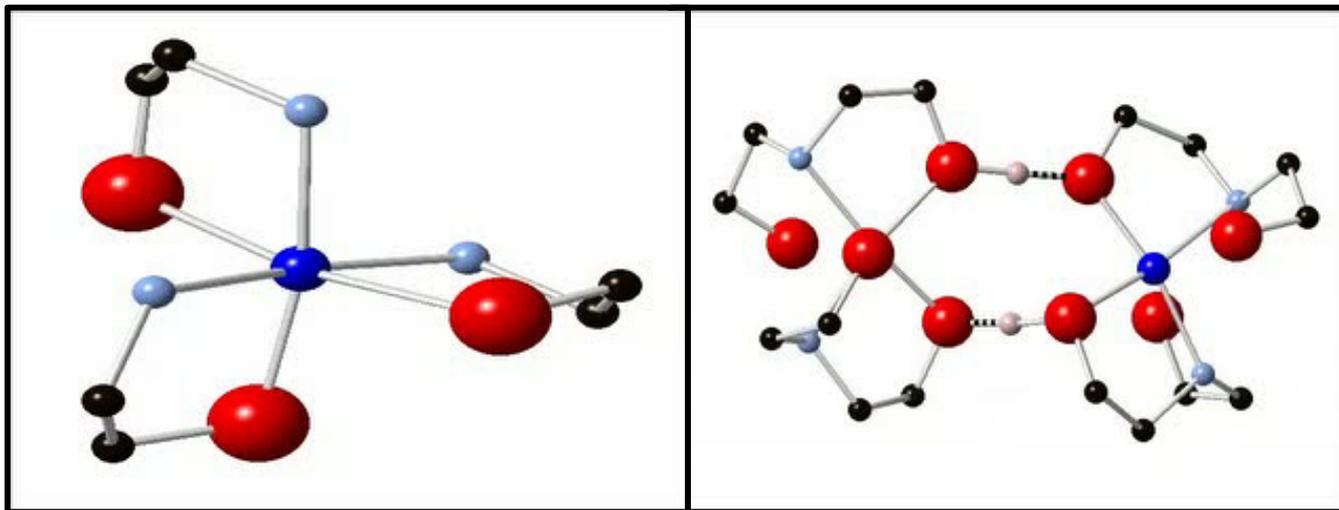
EA ethanolamine

DEA diethanolamine

Ligand	Anion 1	Anion 2	State at 25 °C	$\sigma$ [mS/cm]	$\Delta E$ [mV]
EA			Liquid	0.207	244
EA			Solid	---	158
EA			Solid	---	158
EA			Liquid	6.80	102
EA			Solid	---	256
EA			Liquid	0.586	187
DEA			Liquid	0.014	522
DEA			Liquid	0.067	566
DEA			Solid	---	507
DEA			Liquid	1.05	150
DEA			Liquid	0.210	159
DEA			Liquid	0.142	201



# Crystal Structures

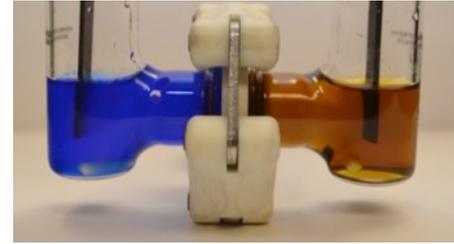
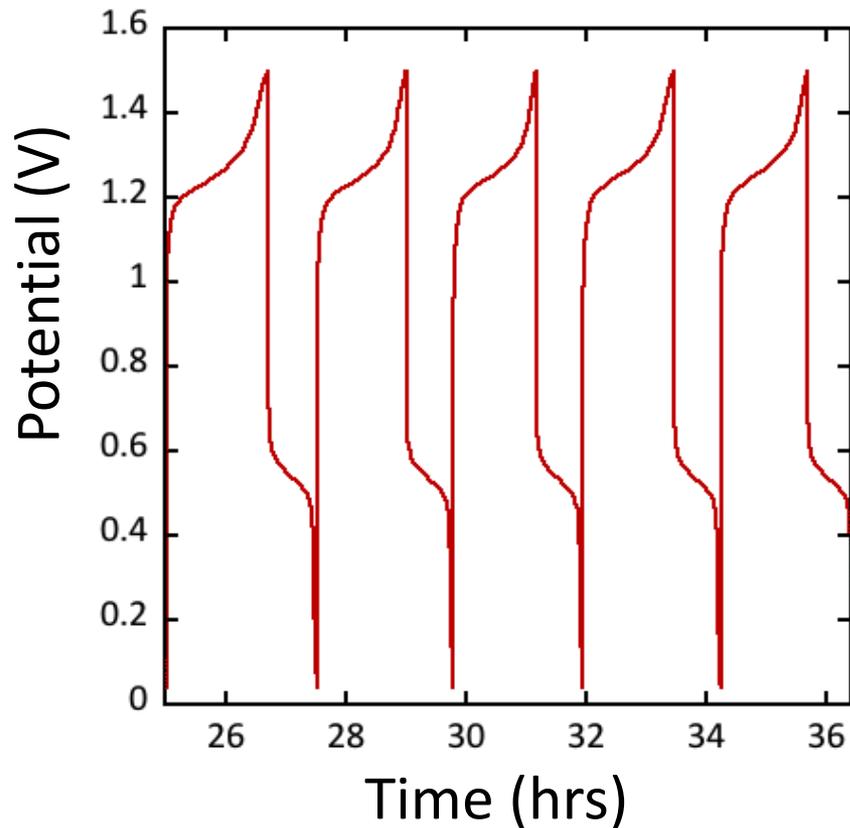


## Key Accomplishments:

- Copper is *divalent*, complex is *monovalent*
- Alkanolamines display *non-innocence*
- Compounds still display *low melting temperatures*
- *Triflate* facilitates crystallization

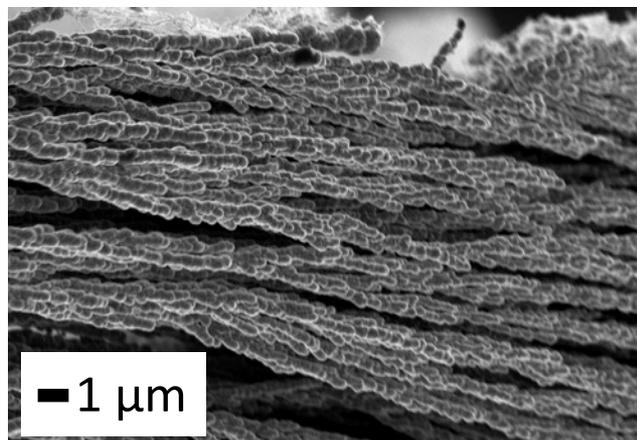
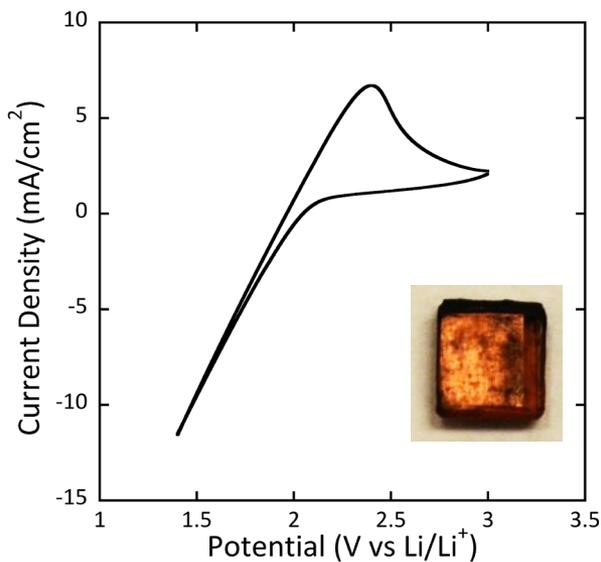
# Ionic Liquid H-Cell Testing

Fe MetIL cathode  
 Cu MetIL anode  
 0.1 mA charge/discharge

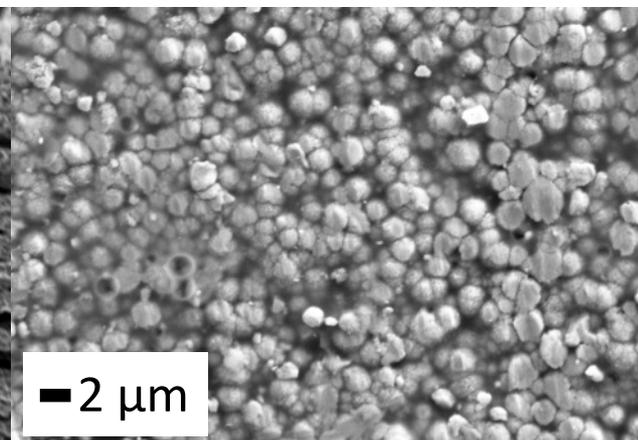


- System was validated using a literature standard.
- First tested system (Mn/Cu MetIL) resulting in reduced capacity due to copper plating.
- Improved results of a Cu MetIL/Fe MetIL system with a porous separator.

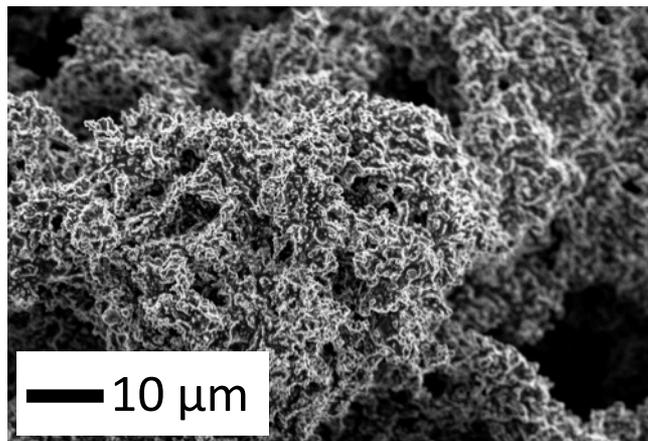
# Electrodeposition



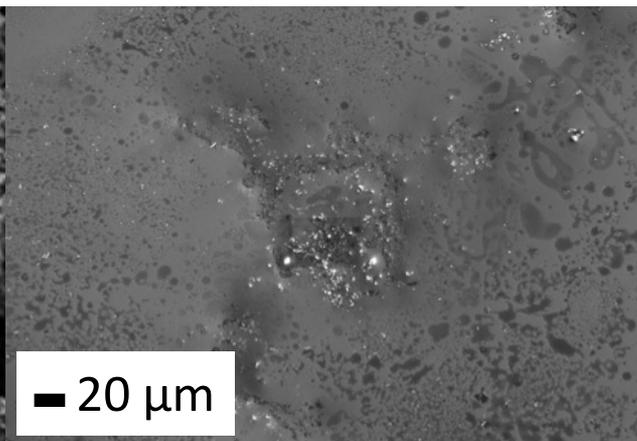
Cu—EA



Cu—DEA



Zn—EA

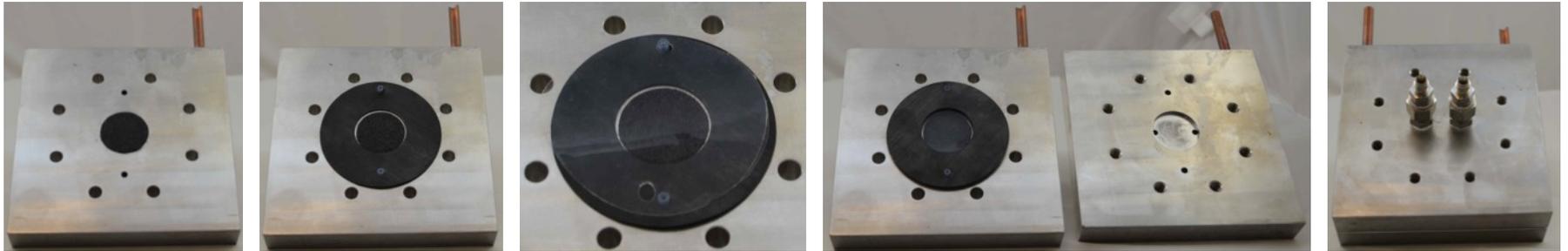


Zn—DEA

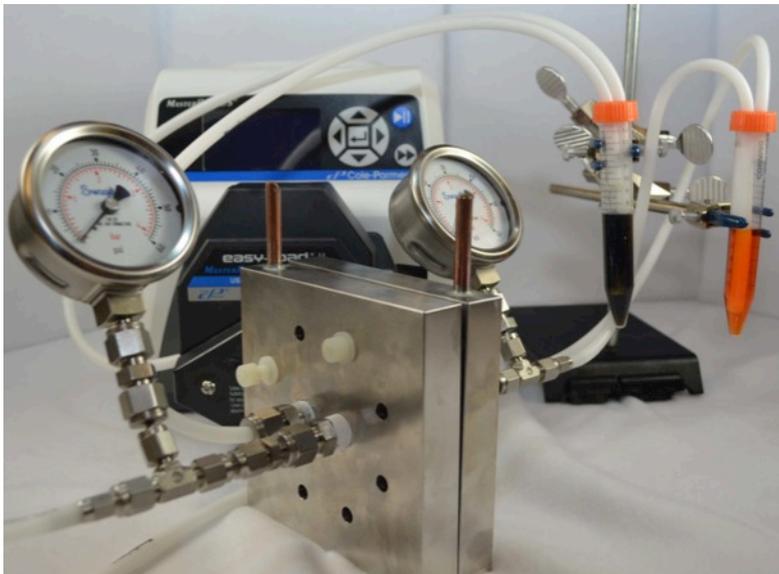


Zinc dendrite suppression with tridentate ligand

# Flow Cell Tester



assembly



## Key Issues:

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

# Summary/Future Work

## 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  $0.5 \text{ mS cm}^{-1}$ , 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.

# Acknowledgements

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