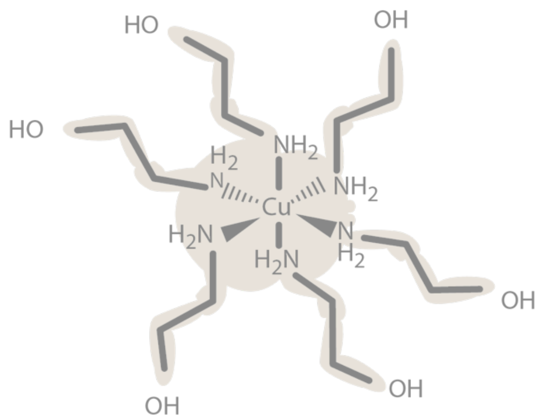
SAND2011-7712C

MetILs: A Family of Metal Ionic Liquids for Redox Flow Batteries

October 18, 2011



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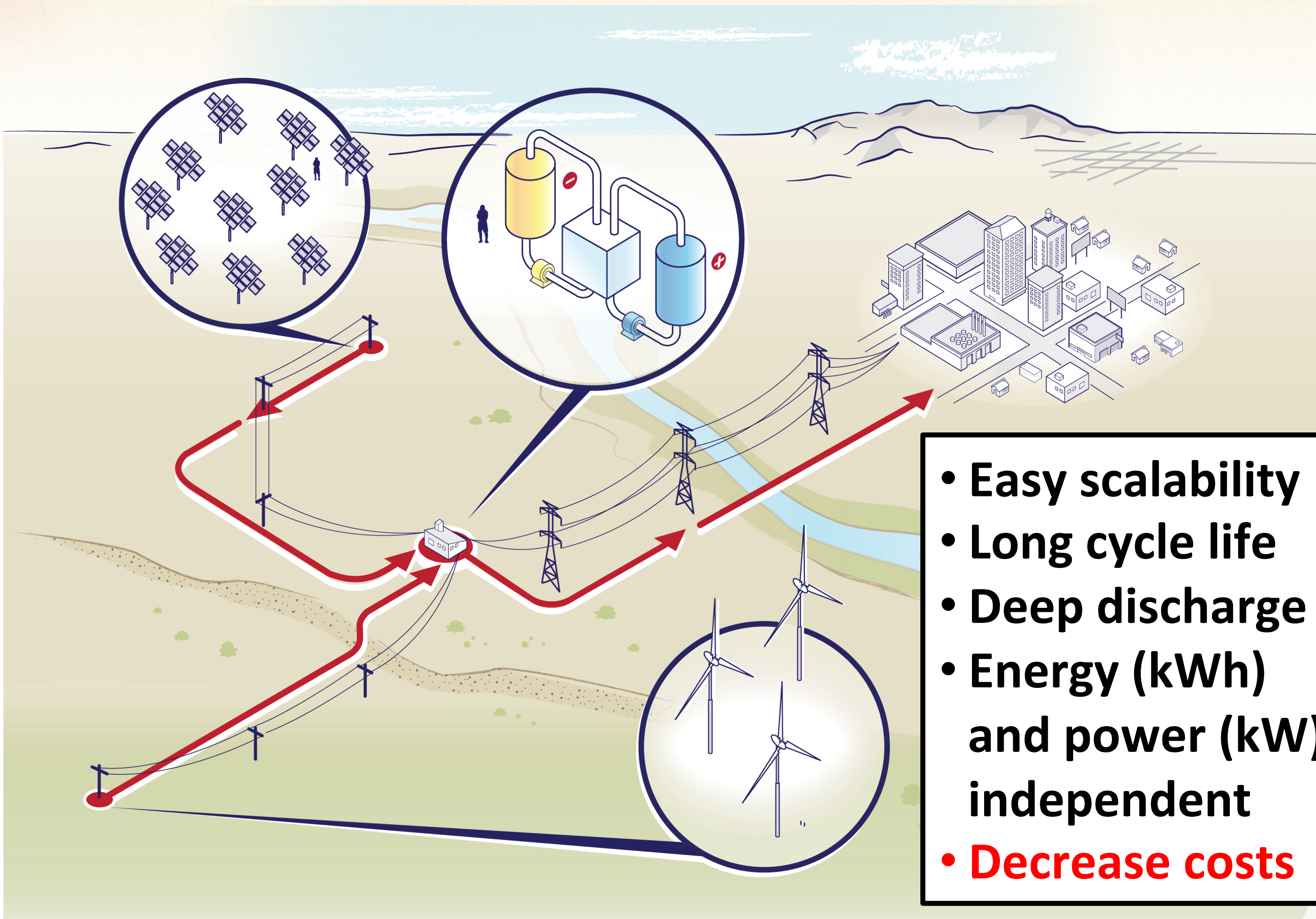
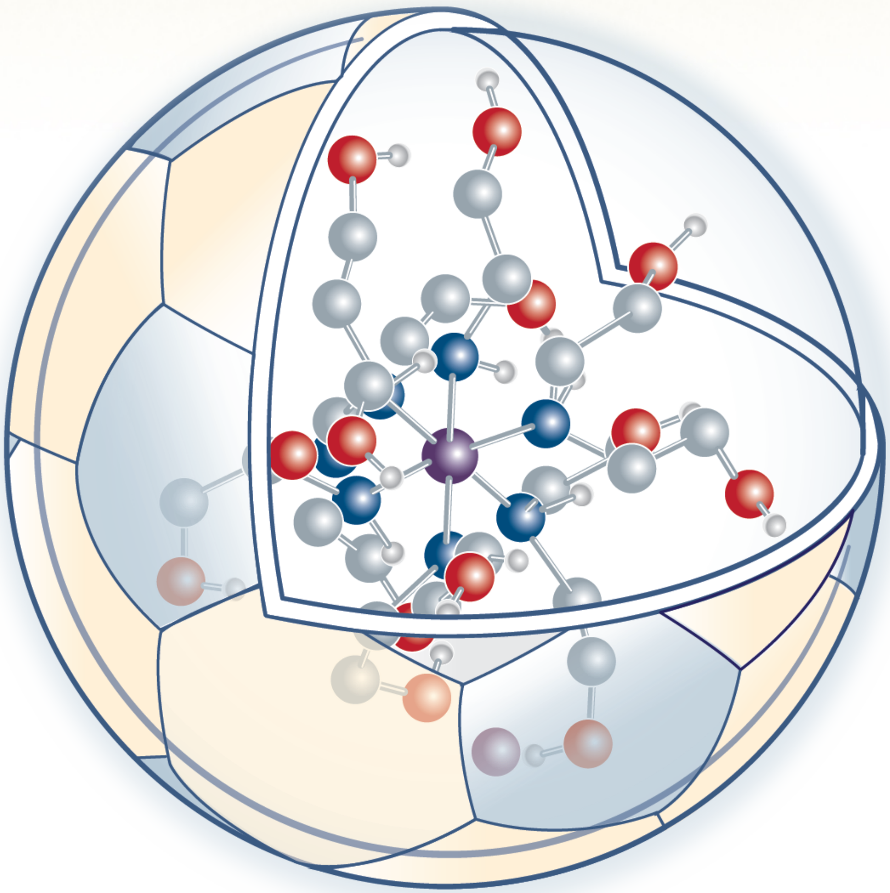
Why Flow Batteries?



- Easy scalability
- Long cycle life
- Deep discharge
- Energy (kWh) and power (kW) independent
- Decrease costs

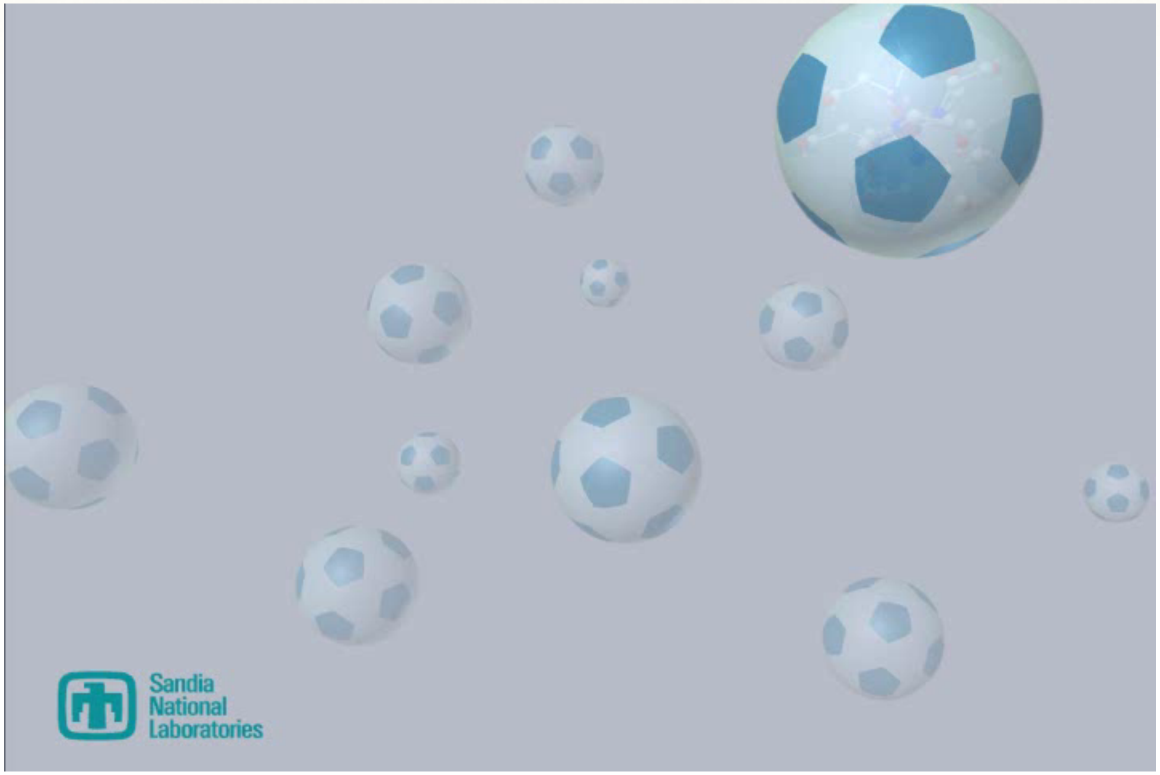
Metal Ionic Liquids (MetILs)



Why MetILs?

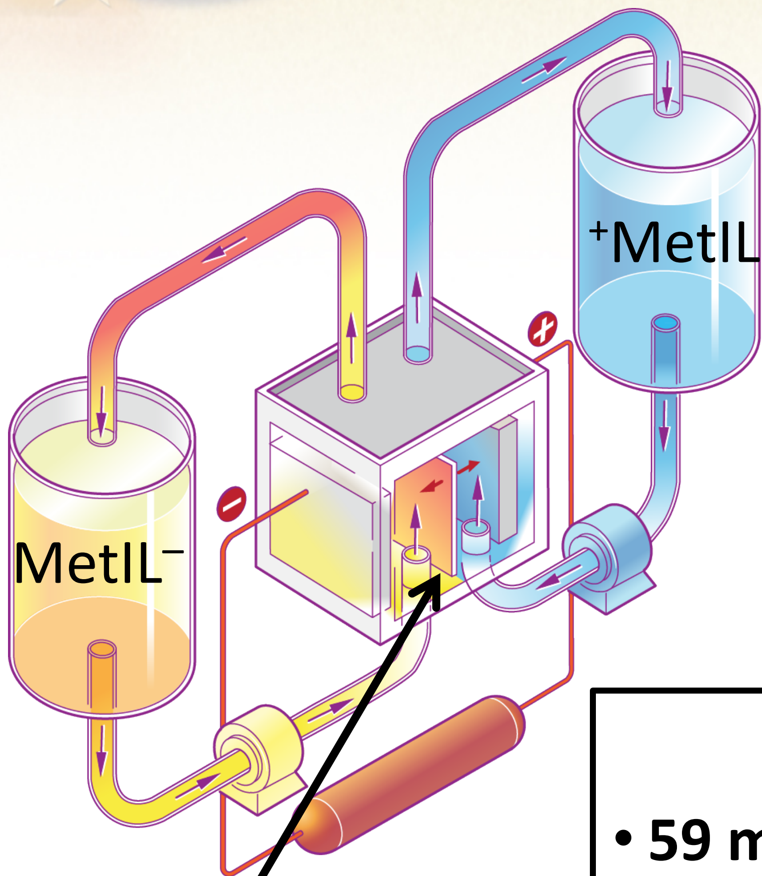
- Higher energy density
- Negligible vapor pressure
- Non-corrosive
- Polarizable functional groups

Ion Pairing



Bottom Line: Strong Ion Pairing Does NOT occur

MetIL Flow Battery Cell



Anion exchange membrane

$Mn^{2+} \rightarrow Mn^{4+} + 2e^{-}$

$\uparrow$ 2 OTf^{-} (membrane)

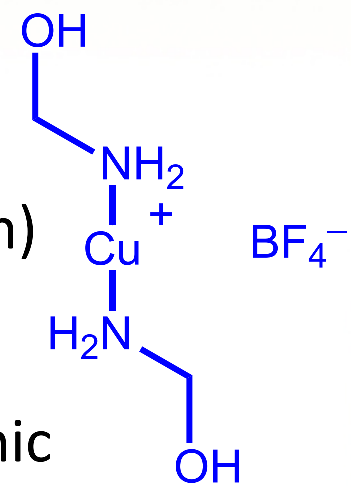
$Zn^{2+} + 2e^{-} \rightarrow Zn^{0}$ (s)

Targets

- **59 mV/n separation (ideally n > 1)**
- **Viscosity < 500 cP (pressurization issues!)**
- **Conductivity > 500 mS cm^{-1}**
- **Open Circuit Potential > 1.5 V**

Higher Energy Density

<u>EXAMPLE ONE</u>: Consider a compound CuL_2BF_4 (L = methanolamine, MW = 47 g/mol), measured density 1.6 g/mL, formula weight, 244 g/mol

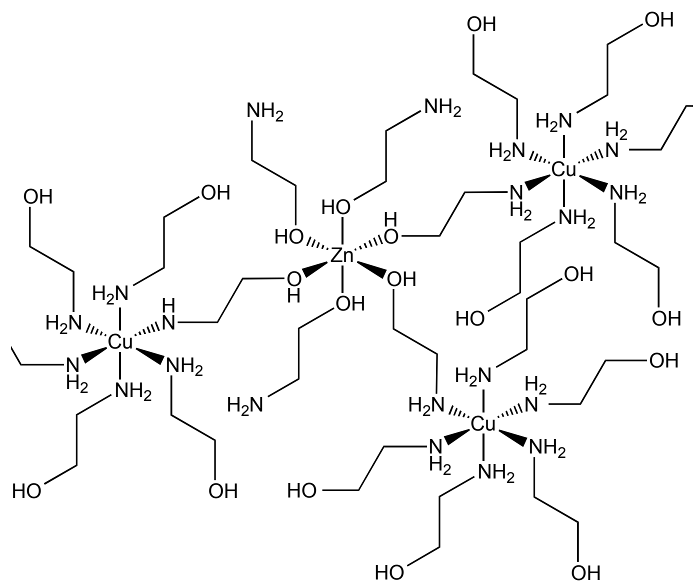


What is the molarity of redox active metal?

Divide density by formula weight (x1000 unit conversion)

6.6 M redox active copper

<u>EXAMPLE TWO</u>: What about a liquid MOF (metal-organic framework)?



Costs

How do we get costs below $100/kWh?

Compound	$/g
$Cu(BF_4)_2$	0.88
HBF_4	1.52
HCF_3SO_3	2.39
V_2O_5	5.04
$VOSO_4$	8.67
$Cu(CF_3SO_3)_2$	11.94

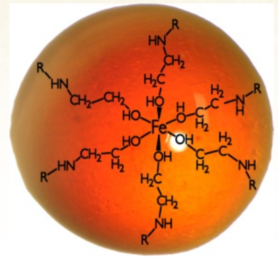
Cost Reduction

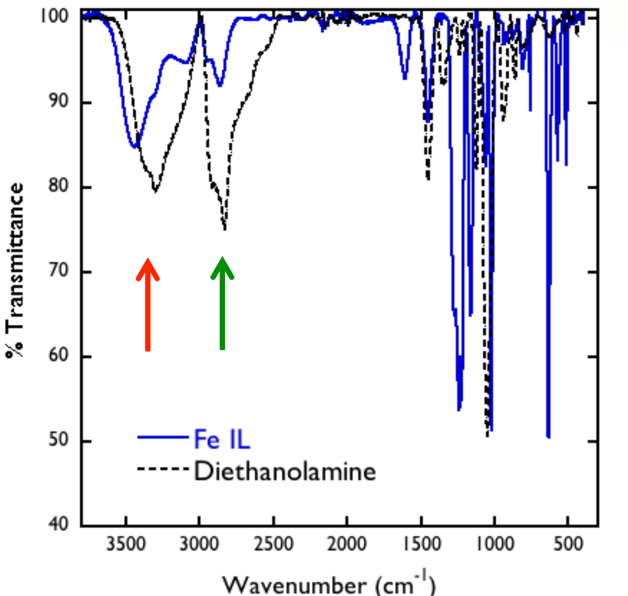
- Drop material costs
- Increase concentration of the redox active species
- Increase voltages higher than 1.5 V
- Multi-electron reactions

Cost Increase

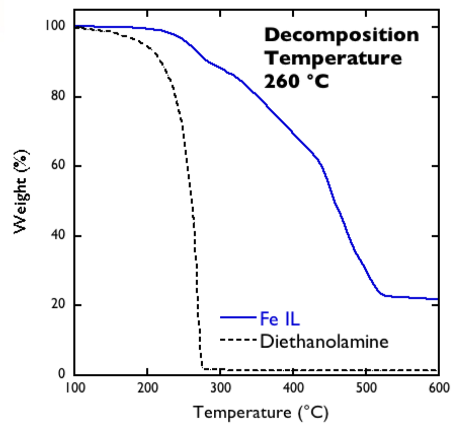
- Pumping higher viscosity fluids

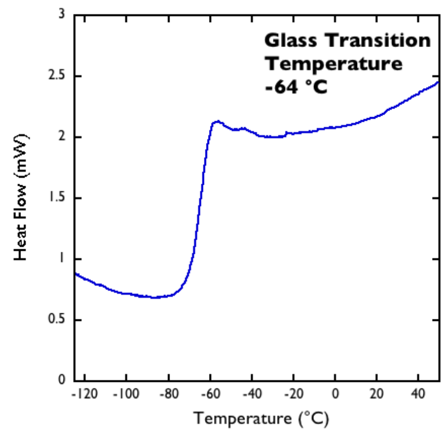
Iron Ionic Liquid (FY10)

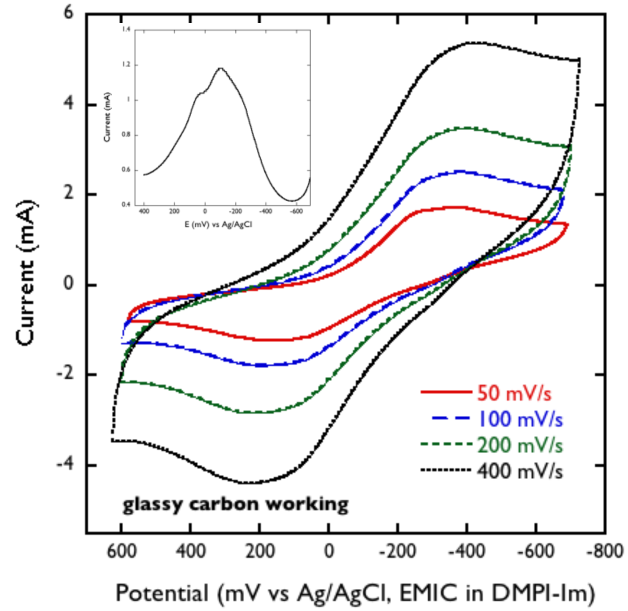
$(CF_3SO_3)_3Fe + 6\ NH(CH_2CH_2OH)_2 \xrightarrow{\Delta}$  $+3\ CF_3SO_3^-$



Hydroxyl (↑) and amine bands (↑) of Fe IL are blue shifted 200 and 30 cm^{-1} relative to diethanolamine.







$\sigma = 0.207$ mS cm^{-1}

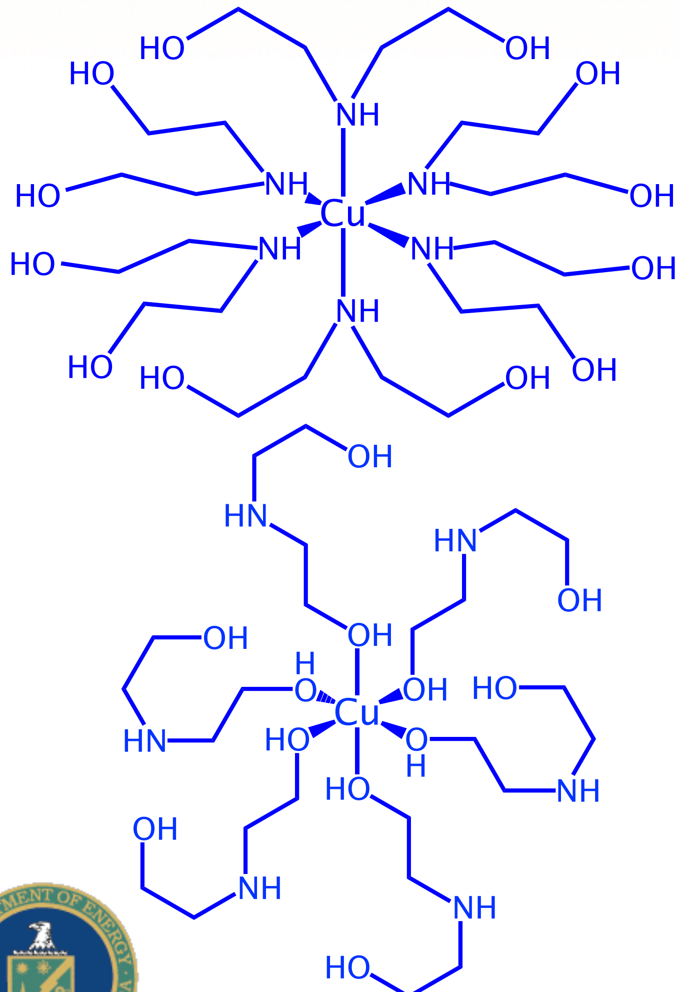
$\mu = 4482$ cP

Anderson *et al*, *Dalton Trans.* **2010**, 8609–8612.

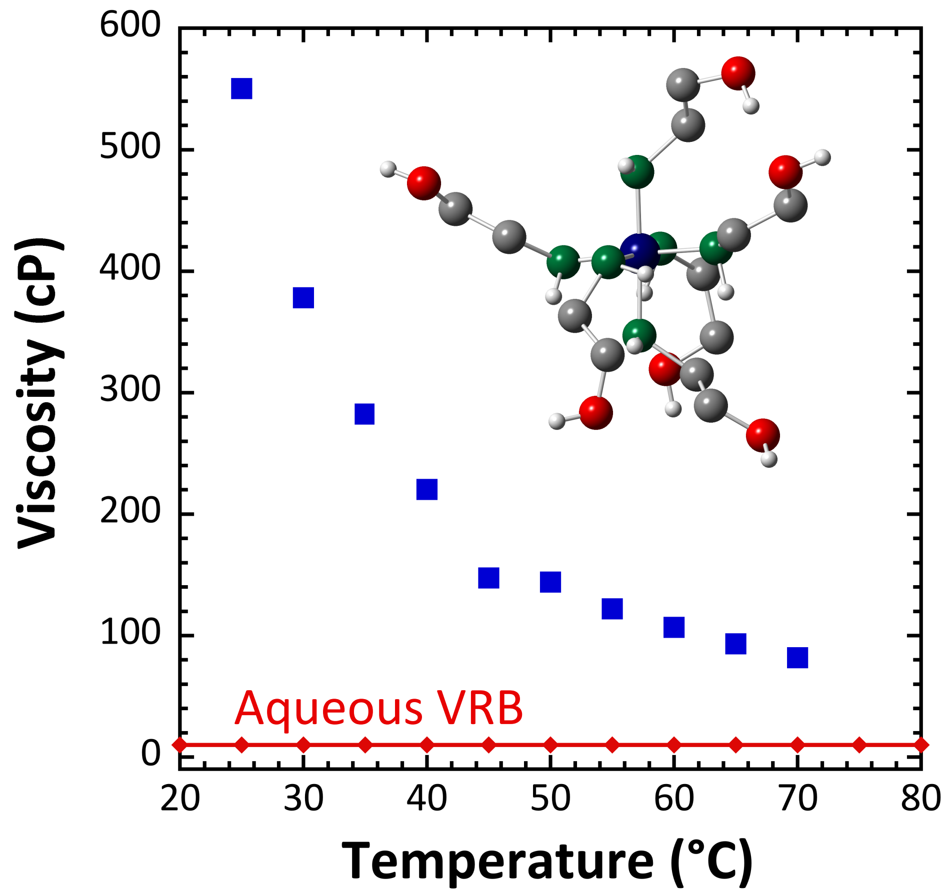
Viscosity (FY11)

Issue: Ionic liquids are orders of magnitude more viscous than water.

Approach One: Coordination



Approach Two: Temperature



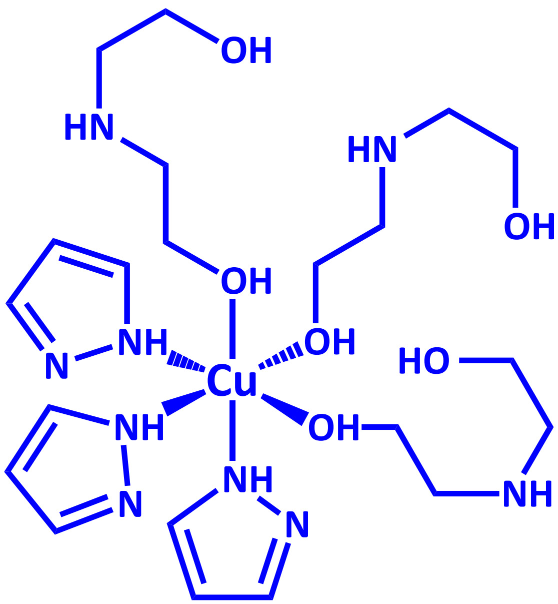
Pratt *et al*, *Dalton Trans.* **2011**, DOI: 10.1039/C1DT10973A.

Conductivity (FY11)

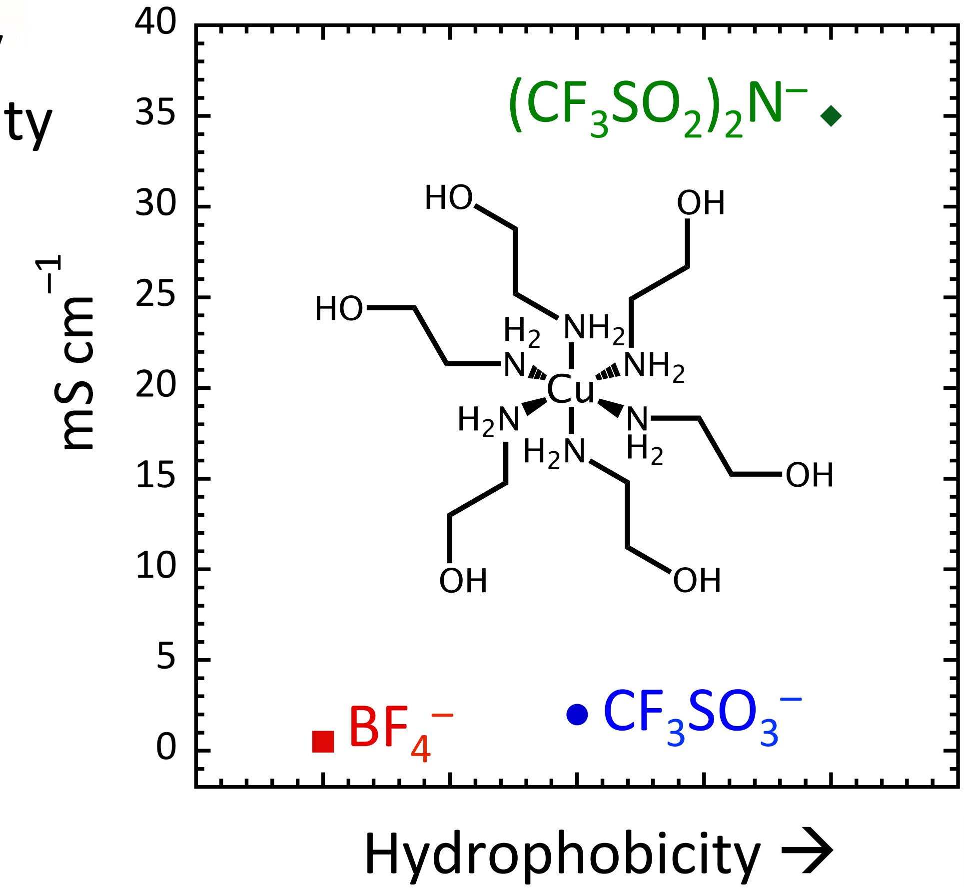
Issue: Ionic liquids typically display conductivity <5 mS cm^{-1}.

Approach One: Cyclic ligands

- Significantly higher conductivity
- Does **NOT** correlate with viscosity
- No pronounced temperature dependence



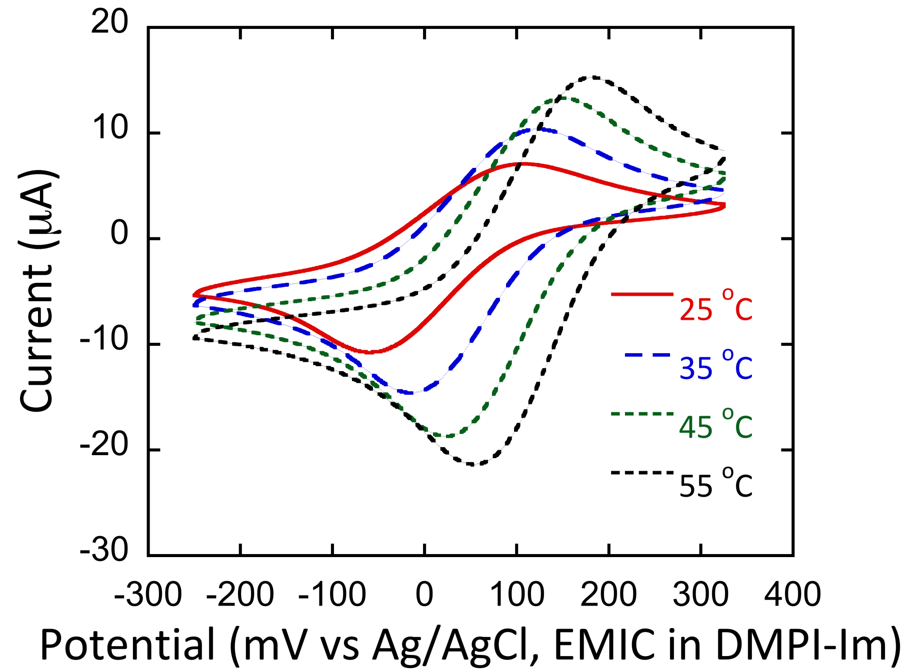
Approach Two: Anions



Electrochemical Reversibility (FY11)

Several MetILs have electrochemical reversibility better than ferrocene ($\Delta E < 300$ mV)

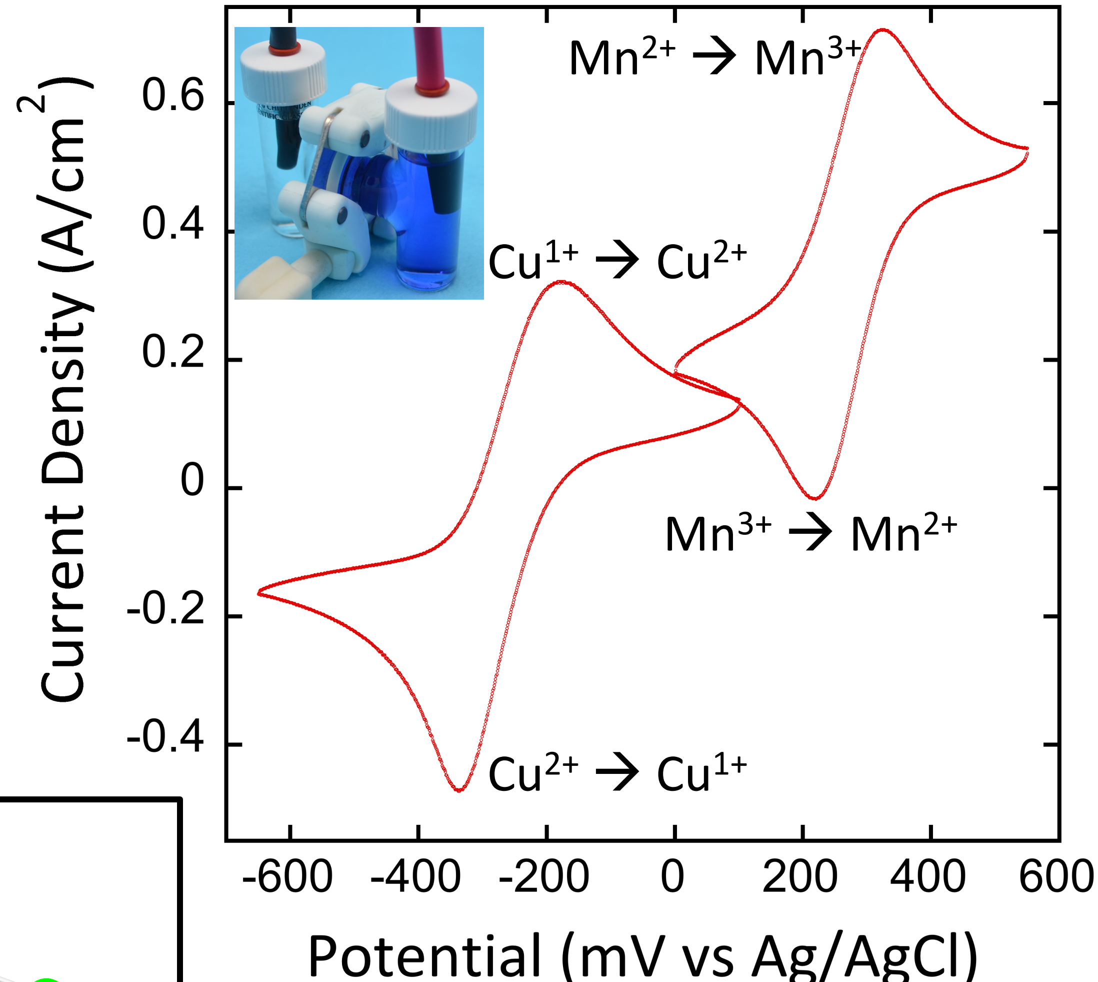
Compound	ΔE
$[Cu(DEA)_6](OAc)_2$	170 mV
$[Cu(DEA)_6](BF_4)_2$	190 mV
$[Cu(MEA)_6](BF_4)_2$	120 mV
$[Cu(DEA)_6](NTf_2)_2$	250 mV
$[Fe(MEA)_6](BF_4)_2$	160 mV
$[Mn(DEA)_6](OTf)_2$	60 mV

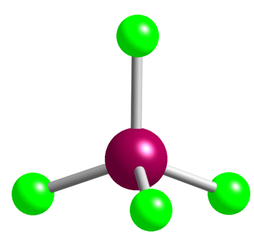


Increased temperature improves reversibility.

Cell Testing (FY11/12)

- Testing activity has just commenced
- Commercial anion exchange membranes have been identified
- H-cell and flow tests will be performed
- Narrow voltage window (0.6 V) suggests new anolytes need development

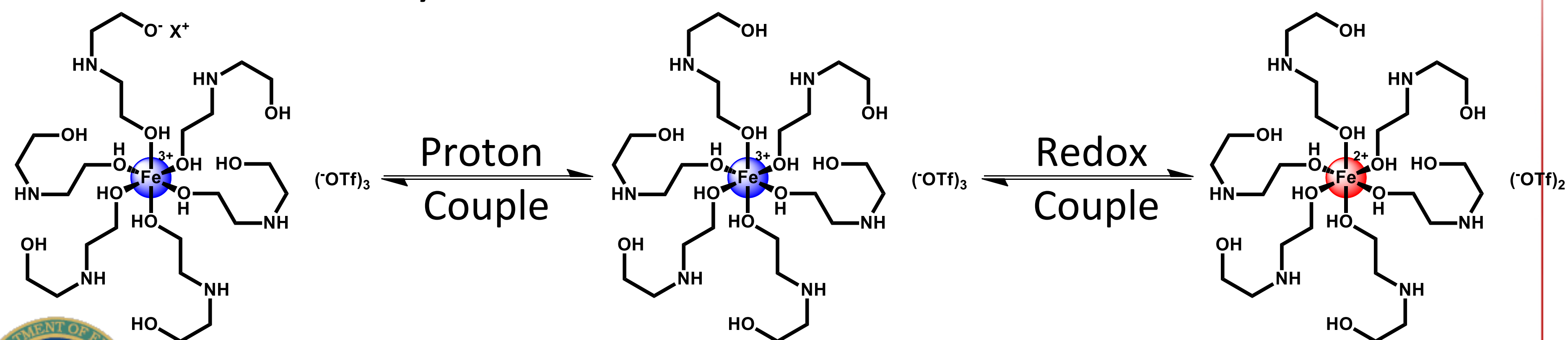




$[CoCl_4]^{2-}$ MetIL

Summary/Path Forward (FY12)

- Low cost ionic liquid energy storage materials based on new methodology
- Approximately 200 combinations of metal cations, ligands, and anions reacted to date
- Tunable chemical and physical properties
- Cell testing in progress
- BF_4^- salts are current focus based on cost of $1/g, low viscosity, reasonable conductivity, and Cu(II)/Cu(I) reversibility



Potential Reaction Mechanisms

Acknowledgements

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