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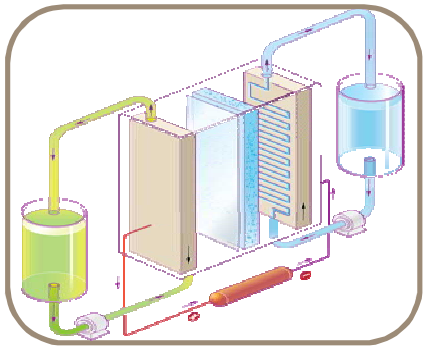

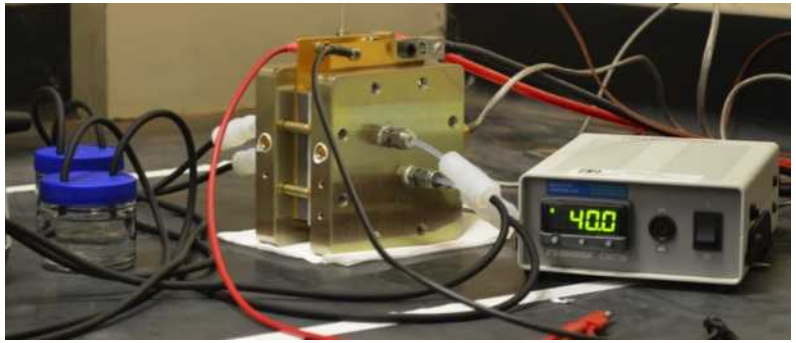


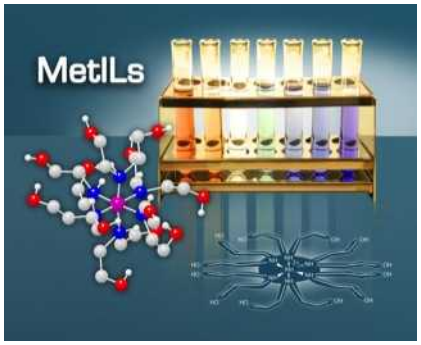


# MetILs: Ionic Liquids for Redox Flow Batteries

*Travis M. Anderson* and Harry D. Pratt III*

*Renewable Energy Storage Summit, August 14th, 2013*

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OFFICE OF ELECTRICITY DELIVERY & ENERGY RELIABILITY

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# Project Goals and Approach

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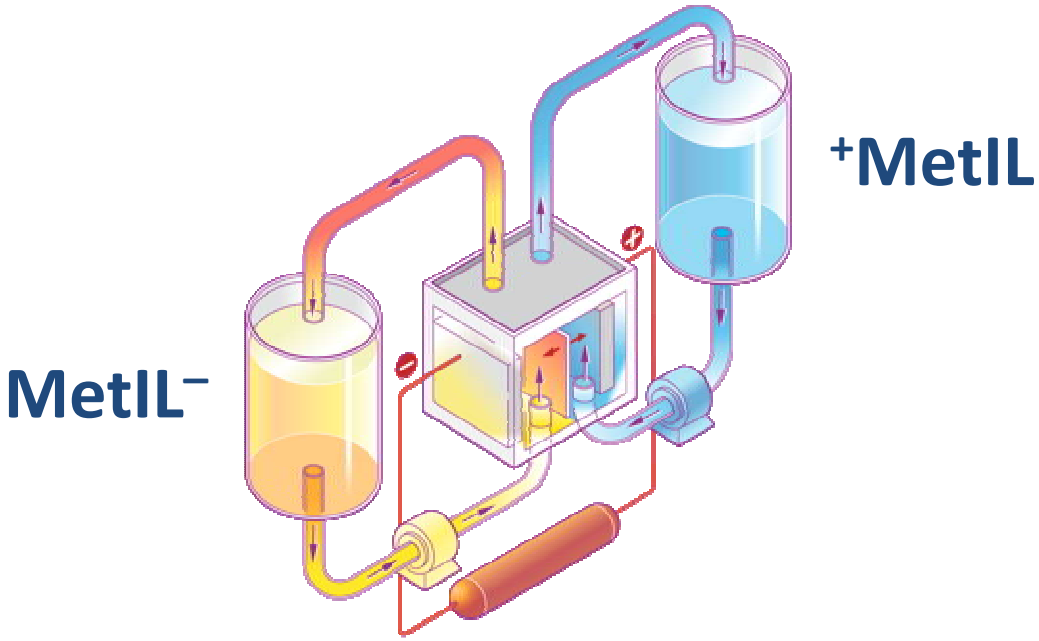
**Goal:** **Design and implement metal-based ionic liquids for higher energy density, lower cost redox flow batteries for stationary energy storage**

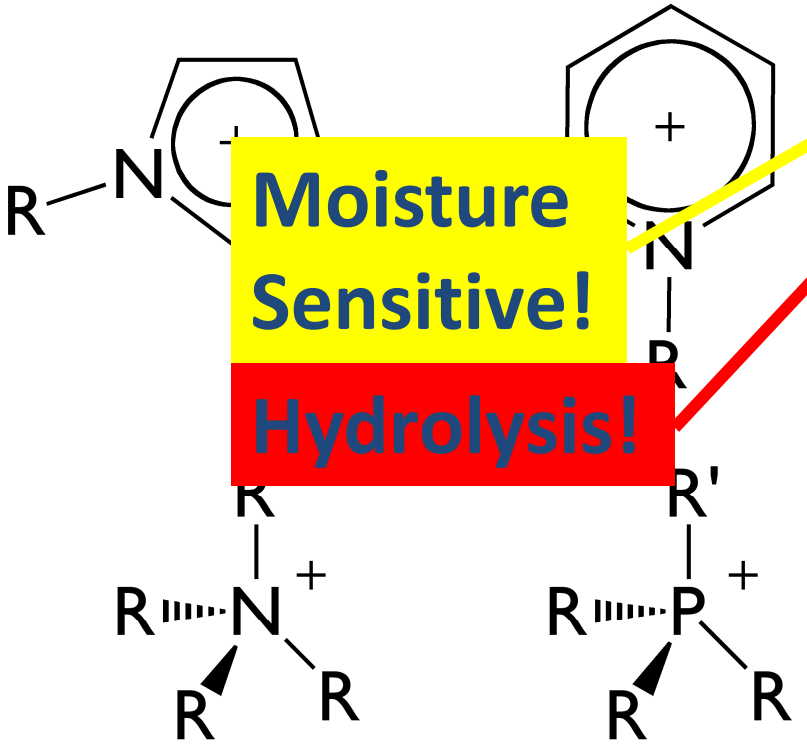
**Approach:** **Synthesize ionic liquids with redox-active species in the molecular formula and tunable properties *via* judicious ligand and anion selection**




Staiger, Pratt, Leonard, Ingersoll, and Anderson, *EESAT* **2011**.

# Ionic Liquids

Ionic liquids are solvents that consist entirely of ions; they conduct electricity by ion migration.




**Three Groups**

(1)Based on $AlCl_3$/cations

(2)Based on fluorinated anions ($BF_4^-$, $PF_6^-$)/cations

(3)Based on $CF_3SO_3^-$, $(CF_3SO_2)_2N^-$, etc./cations

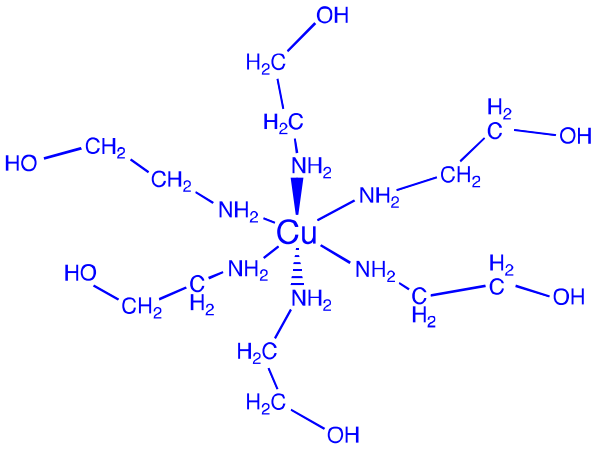
**Advantages Over Water**

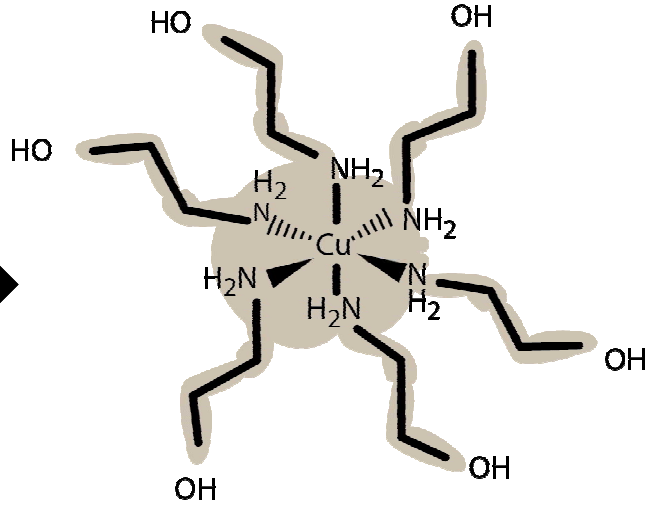
(1) Wider window helps prevent side reactions

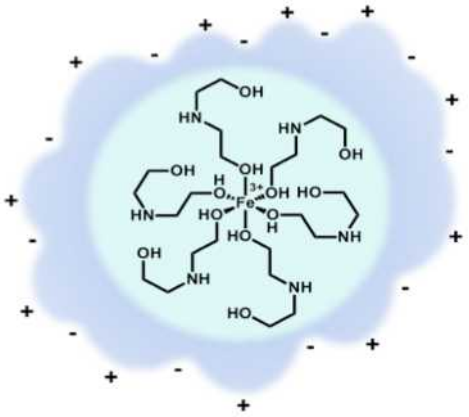
(2) Can vary temperature over wider ranges

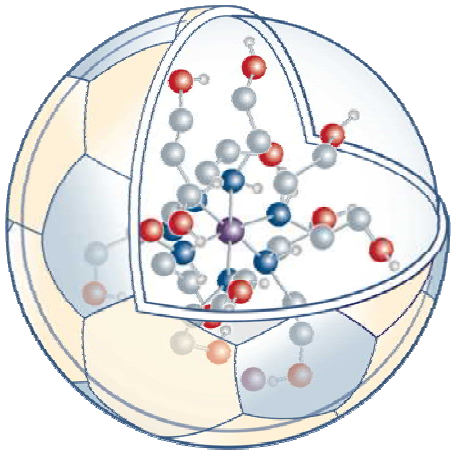
F. Endres, *ChemPhysChem*, **2002**, p. 144.

# MetILs Concept Evolution



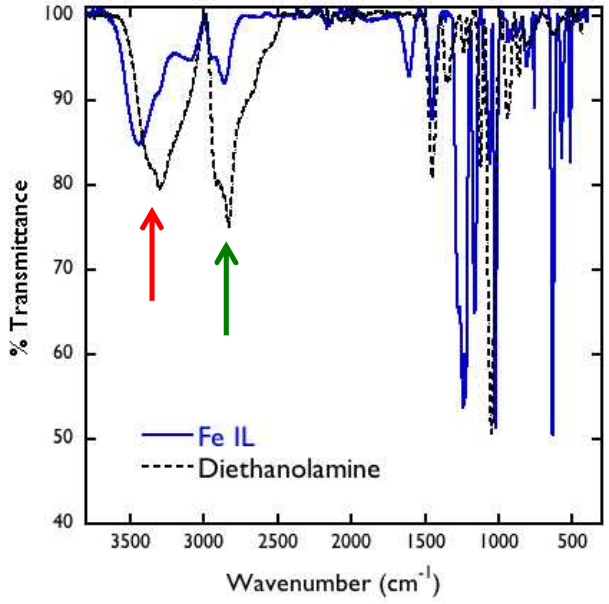



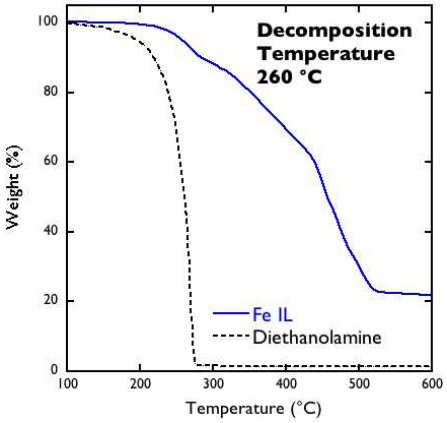



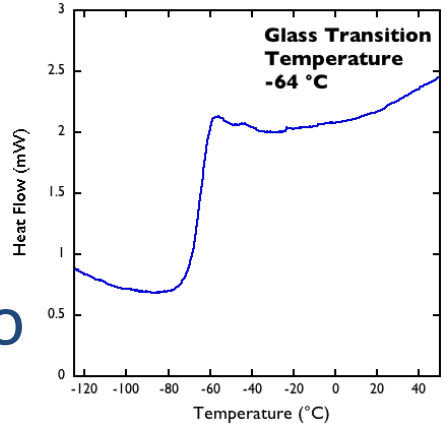
# Synthesis of an Iron Ionic Liquid

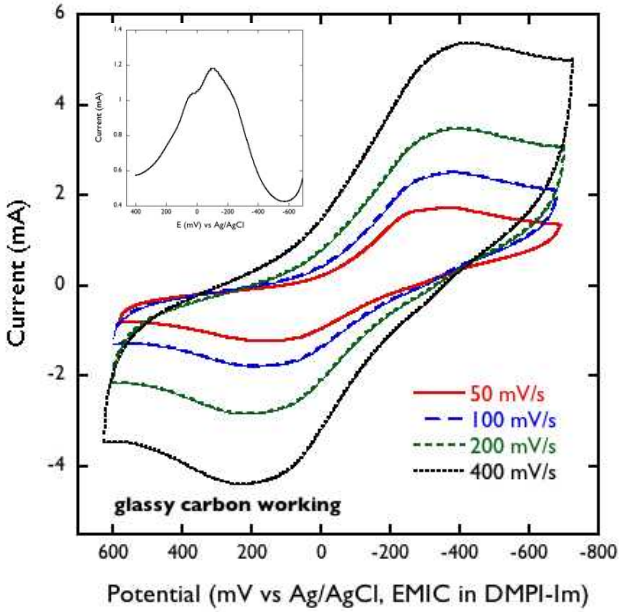
$(CF_3SO_3)_3Fe + 6\ NH(CH_2CH_2OH)_2 \xrightarrow{\Delta}$  $+3\ (CF_3SO_3)^-$




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



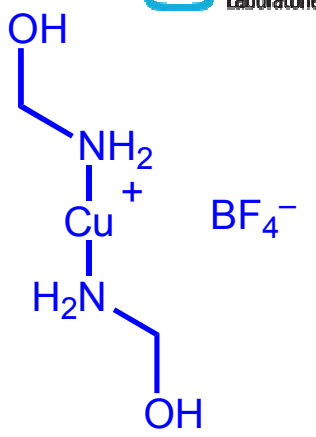




$\sigma = 0.207$ mS $cm^{-1}$

$\mu = 4482$ cP

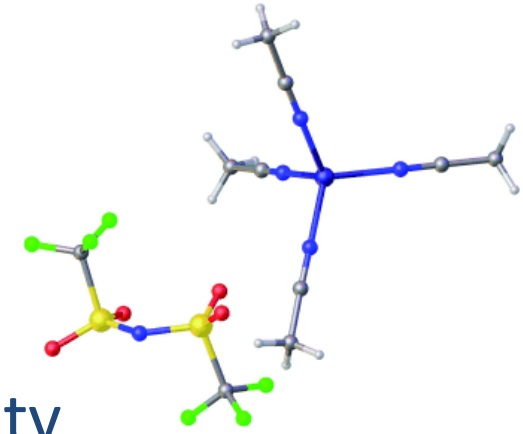
Anderson, Ingersoll, Rose, Staiger, and Leonard, *Dalton Trans.* **2010**, 8609.

# Energy Density and Molarity




**SNL Approach**: Consider a compound $CuL_2BF_4$ (L = methanolamine, MW = 47 g/mol), measured density 1.6 g/mL, formula weight, 244 g/mol; concentration is **6.6 M in redox-active copper**

**Leuven Approach:** Prepared two- and four-coordinate MetILs with **4.5 M** 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.

# $Cu(NH(CH_2CH_2OH)_2)_6^{2+}$ Complexes

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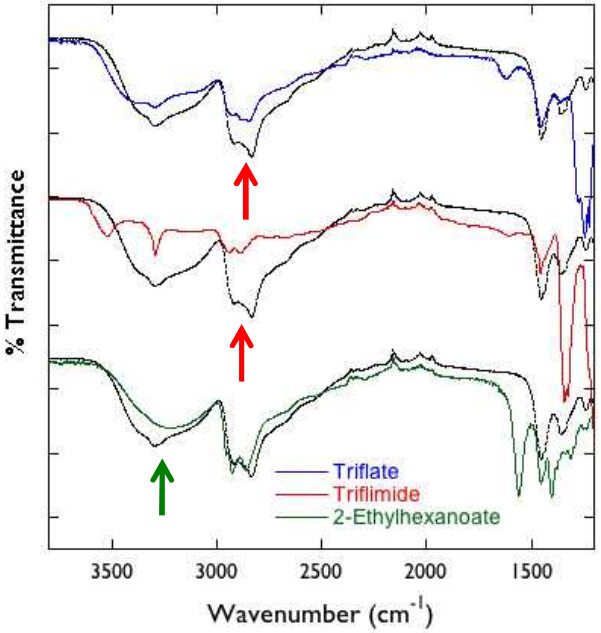
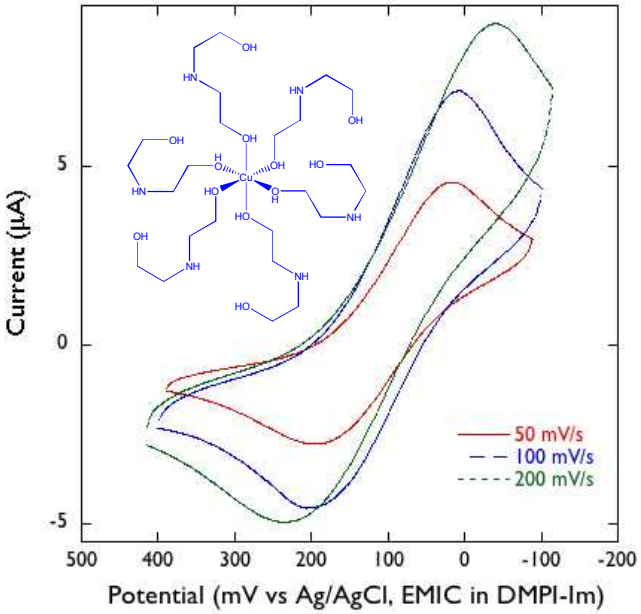
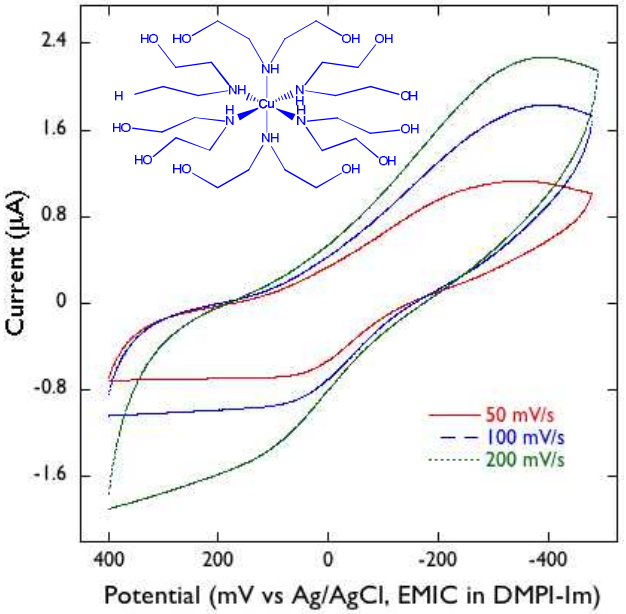
**Anion:** Influences ligand coordination and electrochemistry.

**Ligand Coordination:** Hydroxyl-coordinated complexes display *quasi*-reversible Cu(II) reduction at lower potentials and have much higher reversibility.



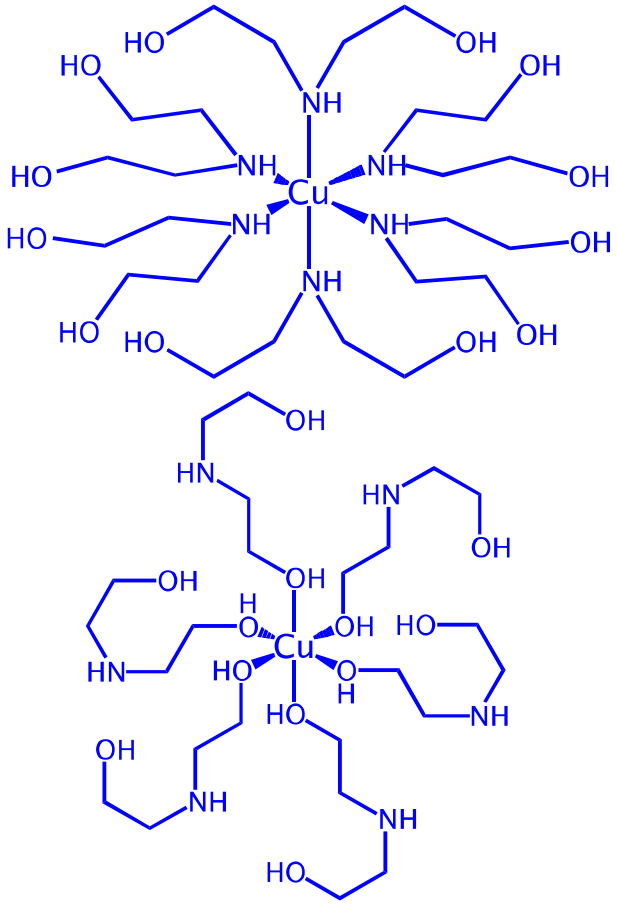



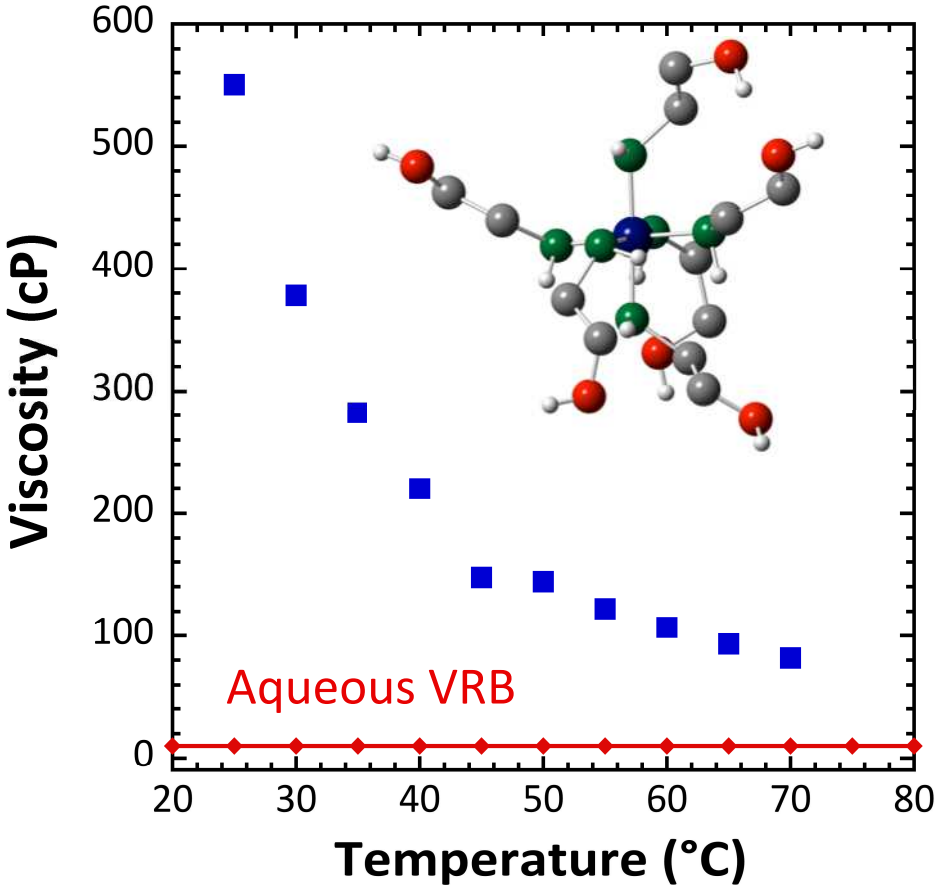
# Copper IL Viscosity

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

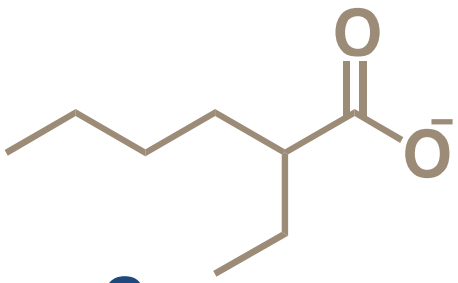
## Approach 1: Coordination




## Approach 2: Temperature



# Role of the Anion

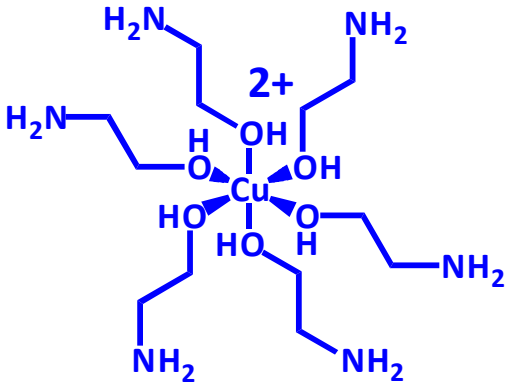


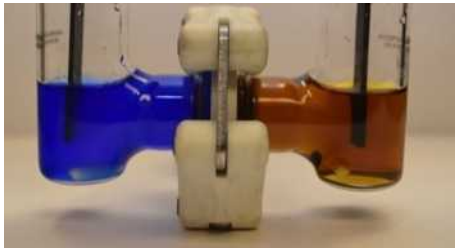
**EA** ethanolamine
**DEA** diethanolamine

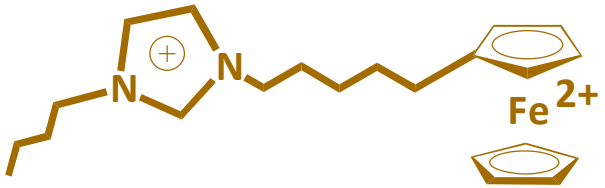
| Ligand | Anion 1 | Anion 2 | State at 25 °C | σ [mS/cm] | ΔE [mV] |
|---|---|---|---|---|---|
| EA | | | Liquid | 0.207 | 244 |
| EA | | | Solid | --- | 158 |
| EA | | | Solid | --- | 158 |
| EA | | | Liquid | 6.80 | 102 |
| EA | | | Solid | --- | 256 |
| EA | | | Liquid | 0.586 | 187 |
| DEA | | | 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 |

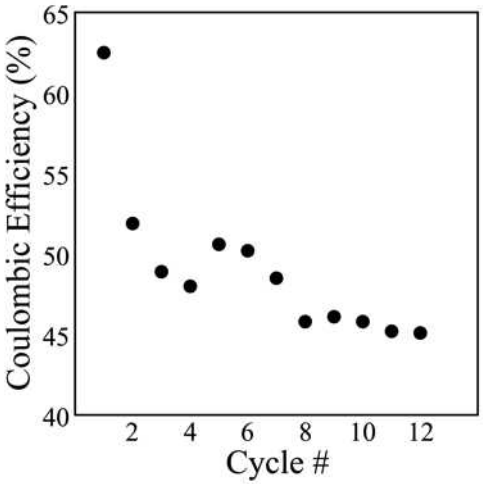
Pratt, Leonard, Steele, Staiger, and Anderson, *Inorg. Chim. Acta.* **2013**, 78.

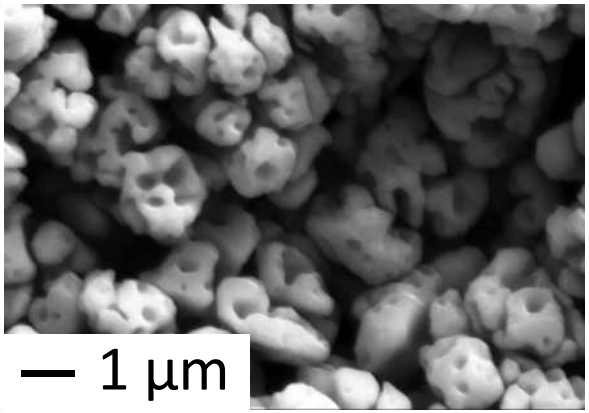
# Static Cell Testing





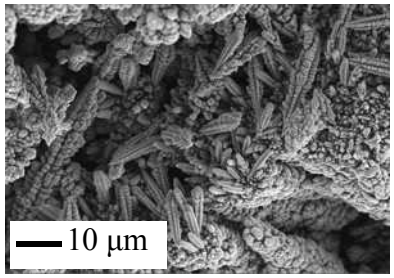




Partially irreversible copper plating on the electrode results in a lower coulombic efficiency. However this reversibility can be controlled by utilizing different anions.

# Copper Plating

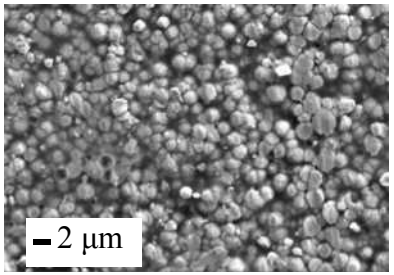
EA




$BF_4^-$

Ligand Change

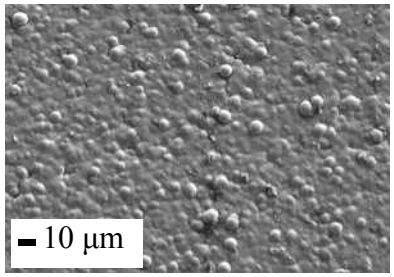
DEA



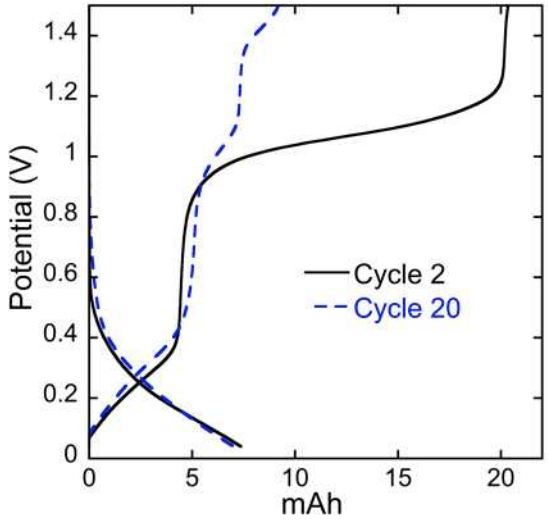

$BF_4^-$

Anion Change

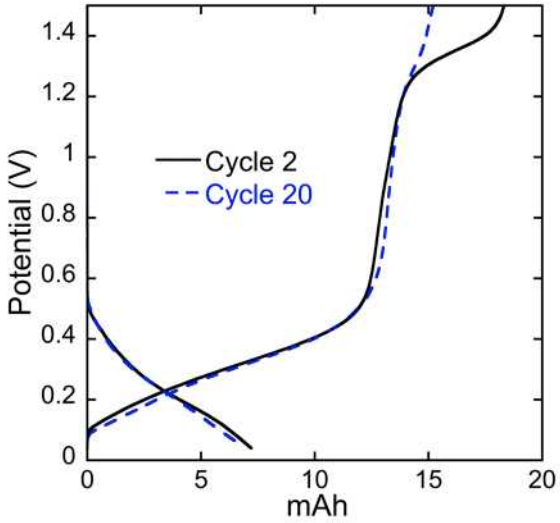
DEA




$CF_3SO_3^-$




Ligand Change




Significant improvements in the battery performance were achieved and three oxidation states of copper have now been utilized.

Lloyd, Vainikka, and Kontturi, *Electrochim. Acta.* **2013**, 18.

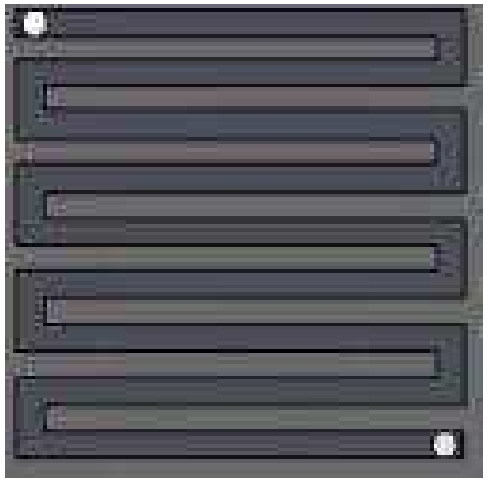
# Flow Cell Tester

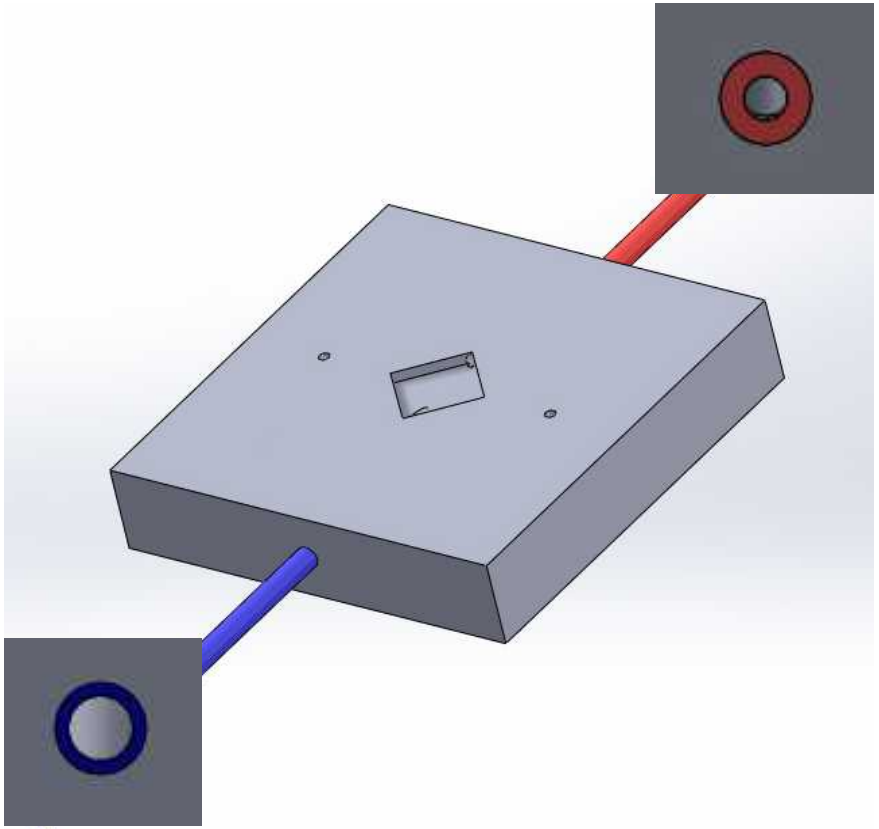
assembly

## Key Issues:

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

# Design Considerations

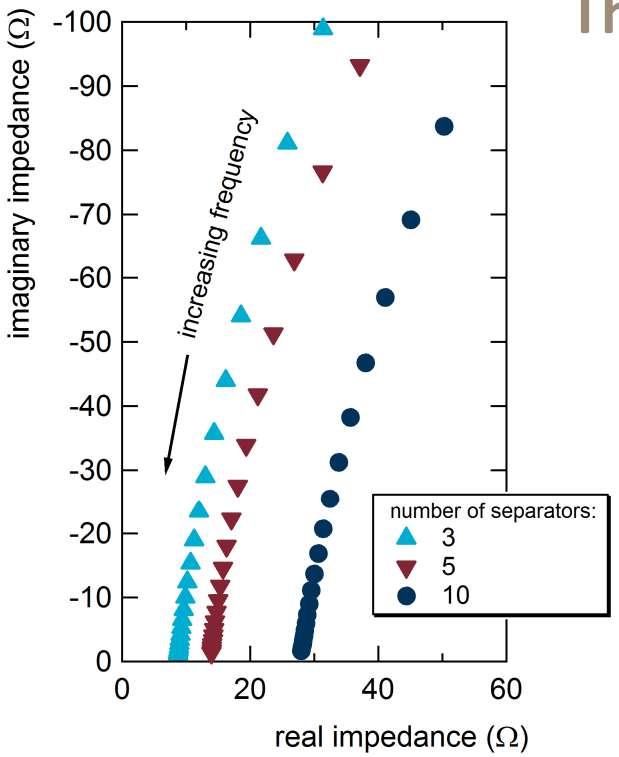




The back pressures from the viscous materials are minimized by increasing the outlet to inlet ratio and by smoothing the turns in the flow field.

# Membrane/Separator Characterization

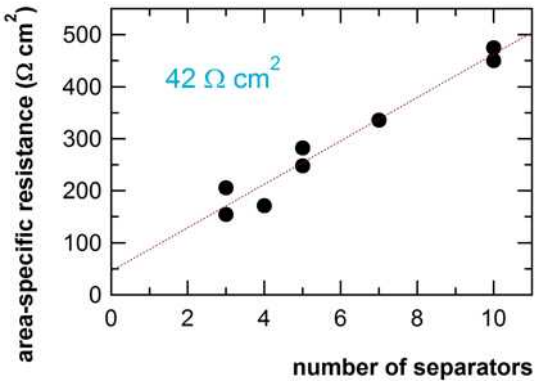
## Electrochemical Impedance Spectroscopy Used to Measure Through-Plane Resistance



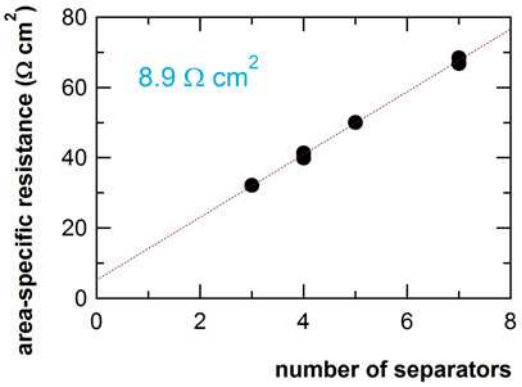

- Impedance spectra gives through-plane resistance of cell, which includes contact resistance with electrodes
- Several membranes are stacked, and a plot of resistance vs. number of membranes is linear.
- Technique verified by comparing to published results.

Ionic liquid with nanoporous polycarbonate membrane: effect of pore size is observed.

Nuclepore (15-nm)




Nuclepore (50-nm)



# Conclusions

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- Ionic liquids containing transition metal elements offer the unique opportunity to have high concentrations of active metal in non-aqueous environments.
- Static cell testing shows that improvements in performance can be achieved through the judicious choice of ligands and anions.
- Current efforts are focusing on cell engineering to accommodate viscous materials.
- There is still a need for improved membranes and separators.

# Acknowledgments

Sandia National Laboratories


OFFICE OF
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ENERGY RELIABILITY


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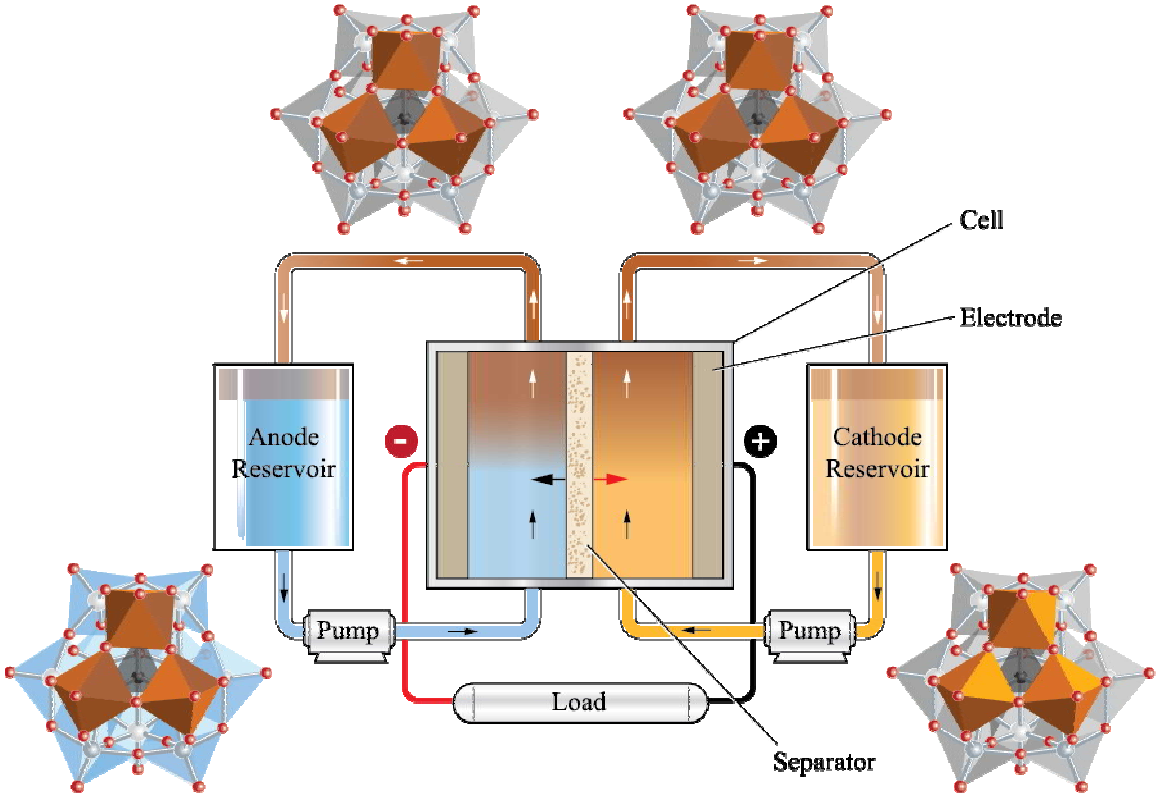
- Sean Hearne, Sandia Program Manager
- Tom Wunsch, PSTG Manager
- MetILs team:  Nick Hudak and Jonathan Leonard

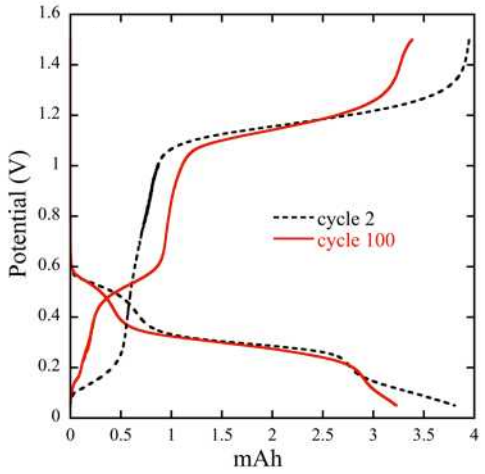
# Additional Slides

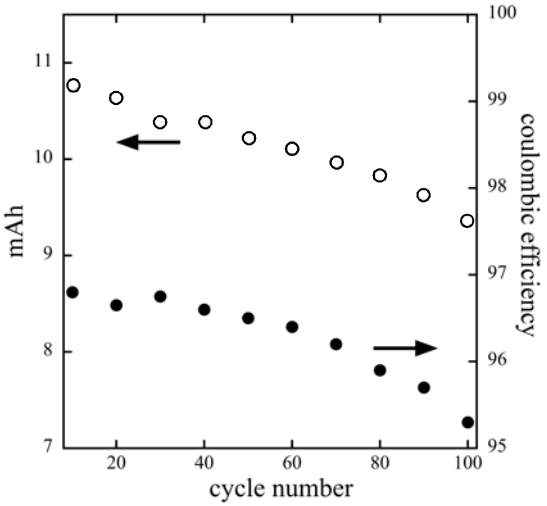
Sandia National Laboratories

- A Polyoxometalate Flow Battery
- Redox Active Ligands

# A Polyoxometalate Flow Battery



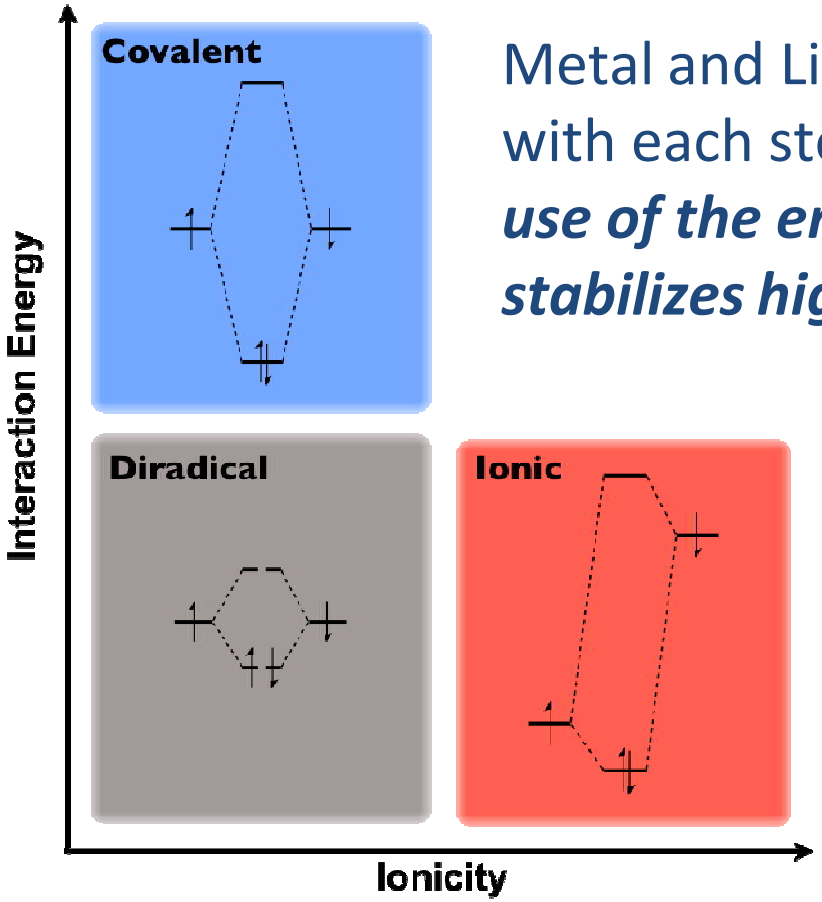

Pratt, Hudak, Fang, and Anderson, *J. Power Sources* **2013**, 259.

# Redox Active Ligands

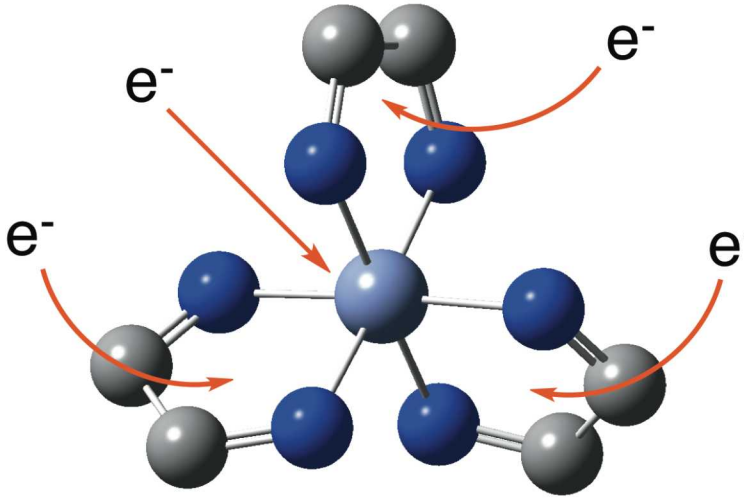
Sandia National Laboratories

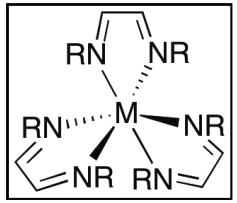
Paradigm of metal-based electrolytes uses metal as "redox center"

– Leads to *instability in geometry and chemical bonding*




Metal and Ligands can be isolated, *electronically*, with each storing electrons separately, ***makes better use of the entire mass of the electrolyte*** and ***stabilizes highly reduced and oxidized species***




$\ddot{M}^{(n)+}—L^{0}$ or $\dot{M}^{(n+1)+}—\dot{L}^{1-}$ or $M^{(n+2)+}—\ddot{L}^{2-}$