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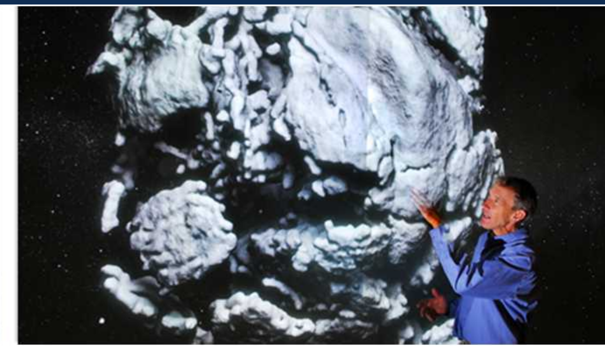

Ionic Liquid Flow Batteries

Travis M. Anderson and Harry D. Pratt III*

Beyond Lithium Ion VIII, June 3rd, 2015

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OFFICE OF ELECTRICITY DELIVERY & ENERGY RELIABILITY

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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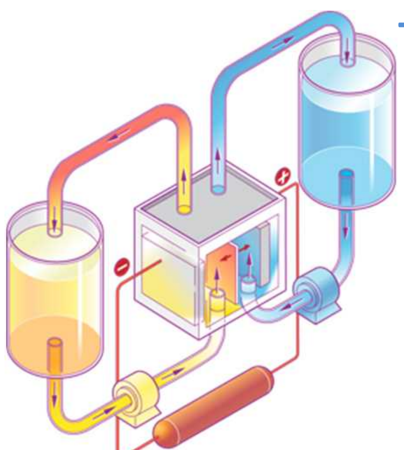
Project Overview

Problem: Ionic liquid flow batteries suffer from high viscosities but hold the promise of higher energy densities due to higher metal concentrations and wider voltage windows

Approach: New multi-valent anode/cathode materials by judicious ligand/anion selection for lower viscosity, tunable membranes for non-aqueous compatibility, AND rapid laboratory-scale prototyping to quickly evaluate materials and cell designs.



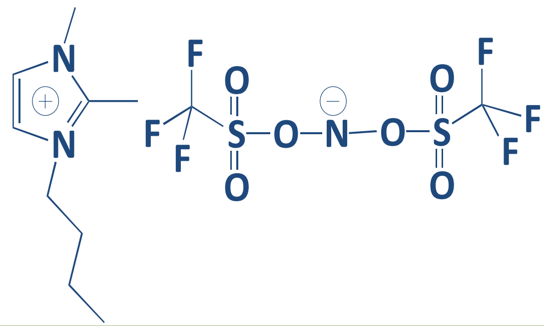
$^{+}$MetIL

MetIL^{-}

Energy Density$_{RFB}$ ≈ ½nFV$_{cell}$c$_{active}$

$ED_{AQ} = \frac{1}{2} 1F 1.5_{cell} 2_{active} = \mathbf{1.5F}$

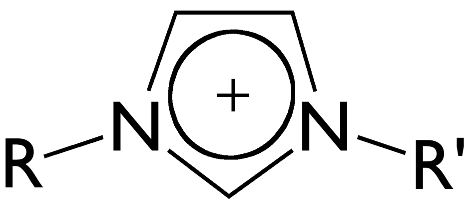
$ED_{IL} = \frac{1}{2} 2F 2_{cell} 3_{active} = \mathbf{6.0F}$

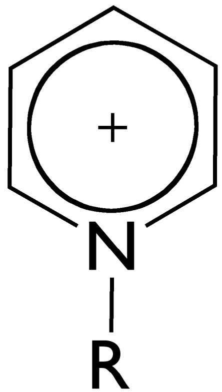


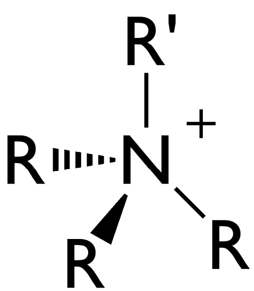
Four-Fold Improvement

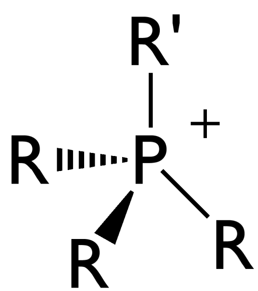
Ionic Liquids

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









<u>Three Groups</u>

(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

<u>Advantages Over Water</u>

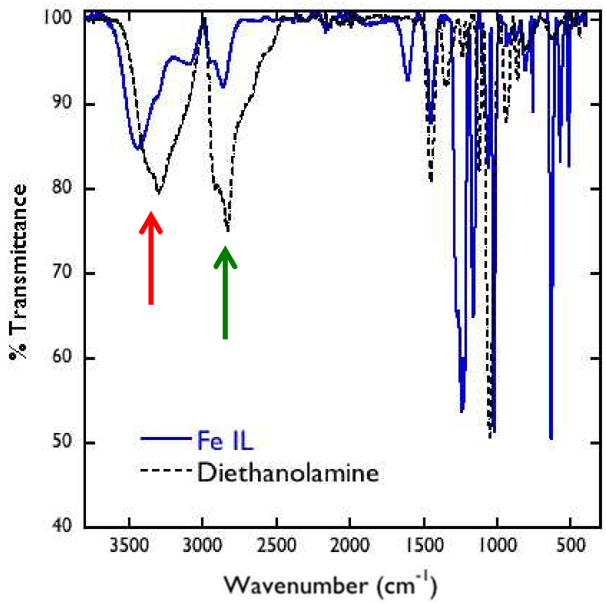
(1) Wider window helps prevent side reactions

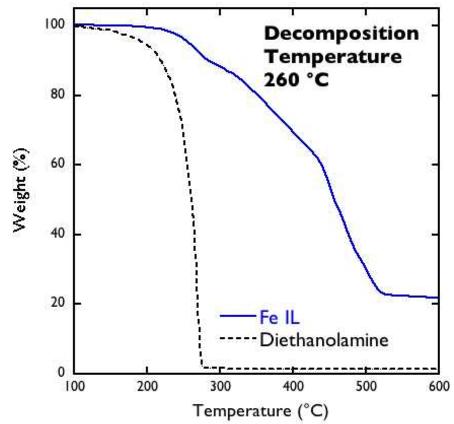
(2) Can vary temperature over wider ranges

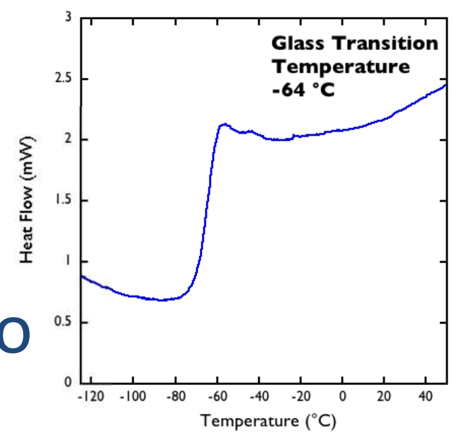
F. Endres, *ChemPhysChem*, **2002**, 144.

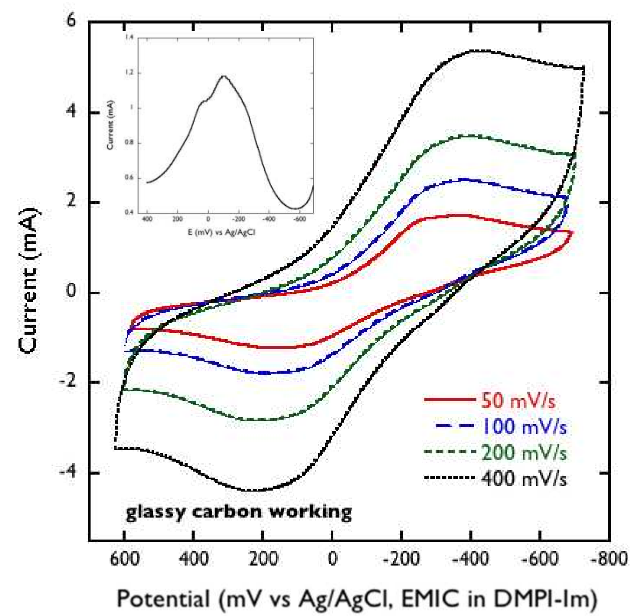
Synthesis of an Iron Ionic Liquid

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









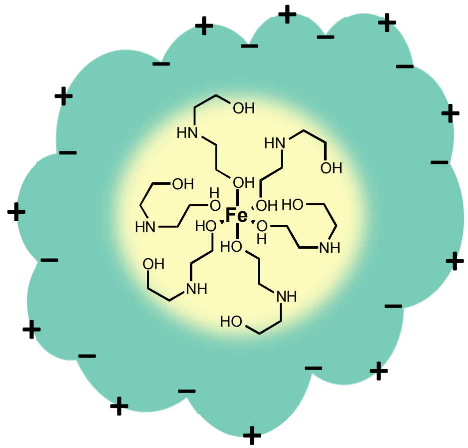
Hydroxyl (↑) and amine bands (↑) are blue shifted 200 and 30 cm^{-1} relative to diethanolamine.

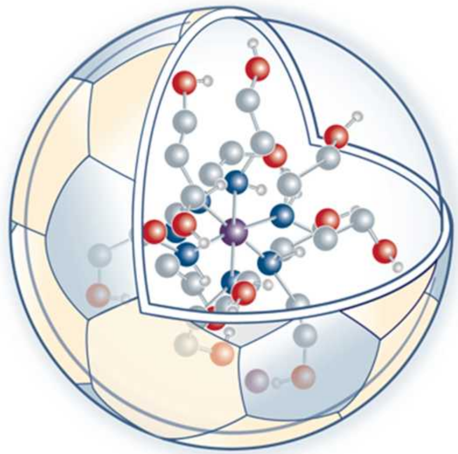
$\sigma = 0.207$ mS cm^{-1}

$\mu = 4482$ cP

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

MetILs Concept and Energy Density





The "MetILs" Family

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

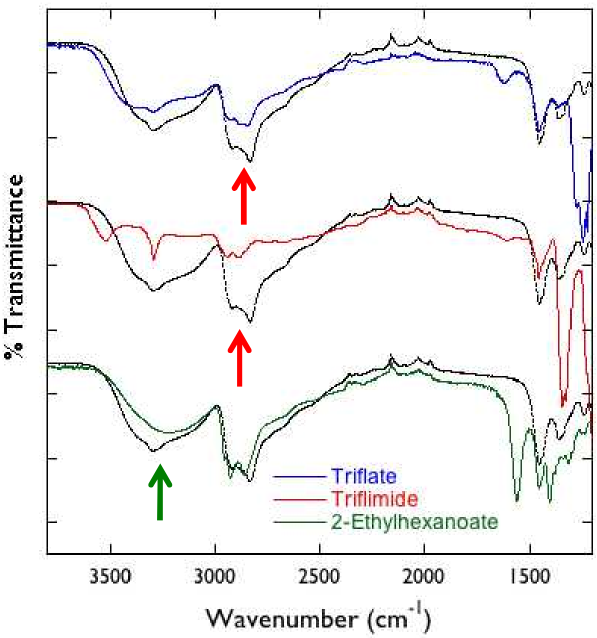
Organic Approach*: (MetILs) are an attractive approach to reach high energy density; however there is an environmental concern due to the heavy metals and lower energy density caused by the bulky cations

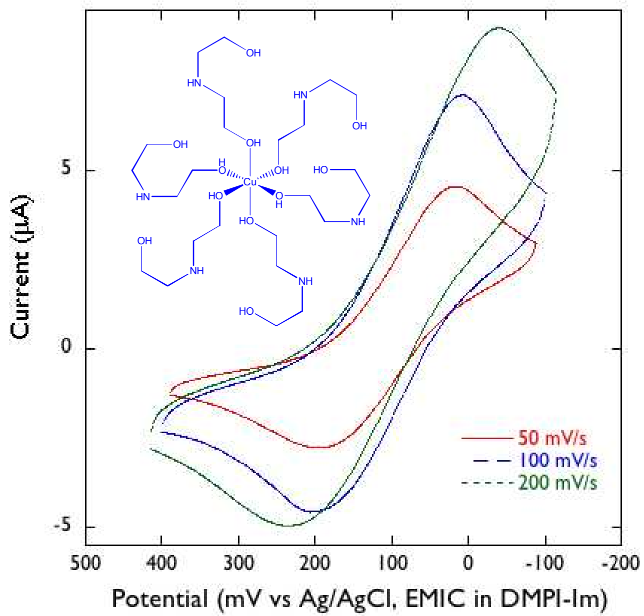
*Takechi, Kato, and Hase, *Adv. Mater.* **2015**, 2501.

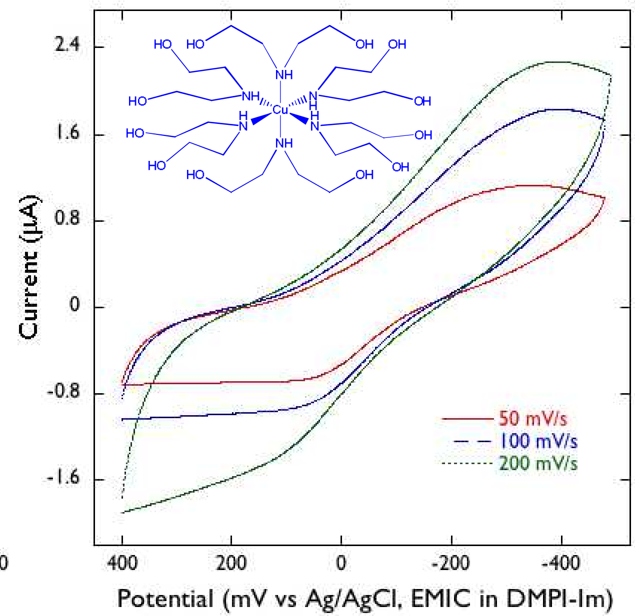
$Cu(NH(CH_2CH_2OH)_2)_6^{2+}$ Complexes

Anion: Influences ligand coordination and electrochemistry.

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

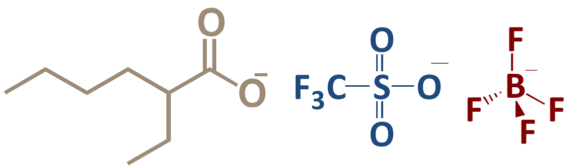




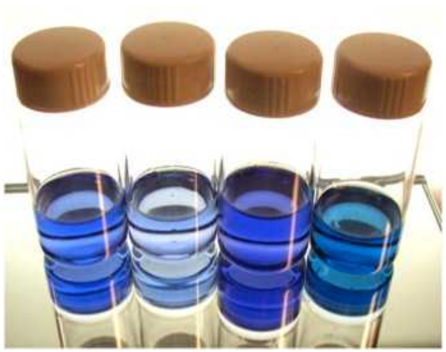


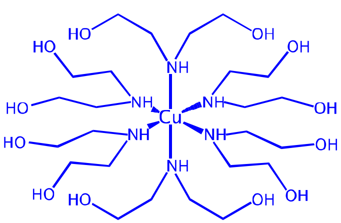
Pratt, Rose, Staiger, Ingersoll, and Anderson, *Dalton Trans.* **2011**, 11396.

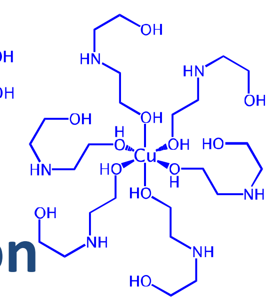
Role of the Anion



EA ethanolamine
DEA diethanolamine







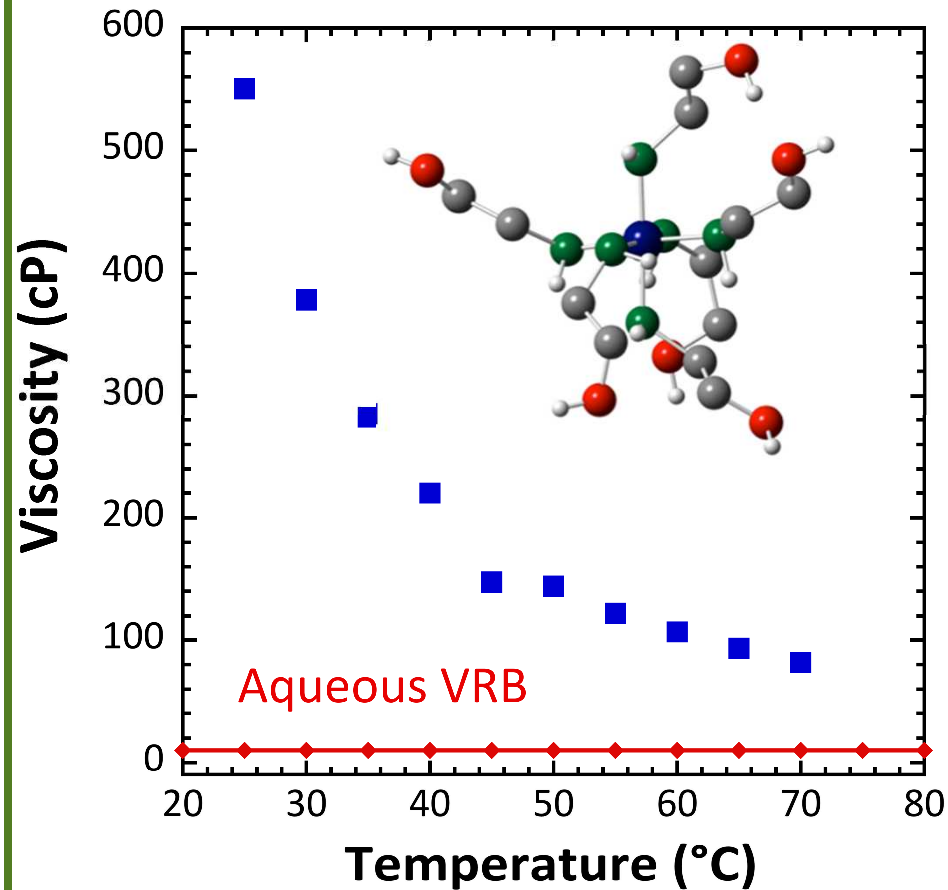
Coordination Influences Viscosity

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

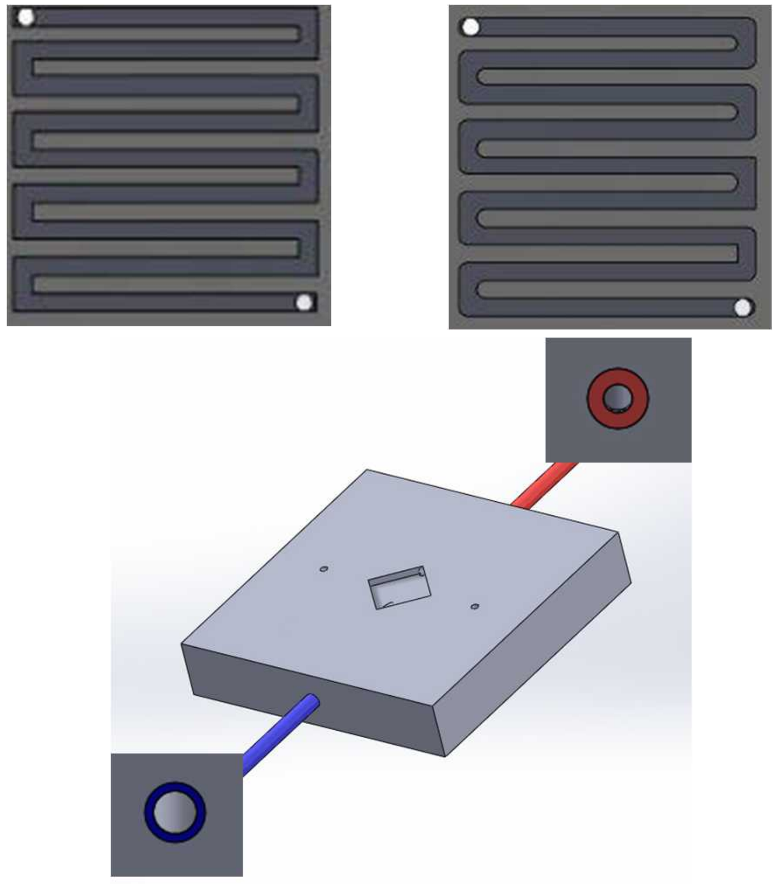
Pratt, Leonard, Steele, Staiger, and Anderson, *Inorg. Chim. Acta.* **2013**, 78.

Ionic Liquid Viscosity

Approach: Temperature

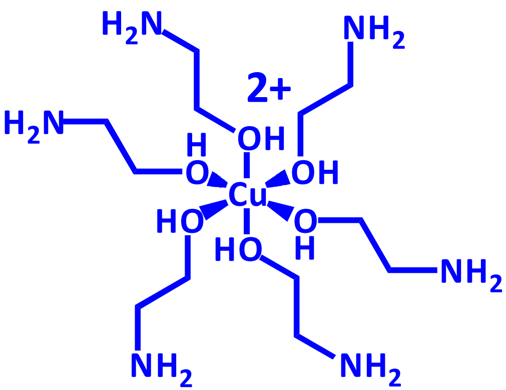


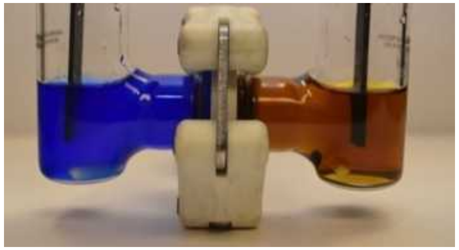
Approach: New cell designs

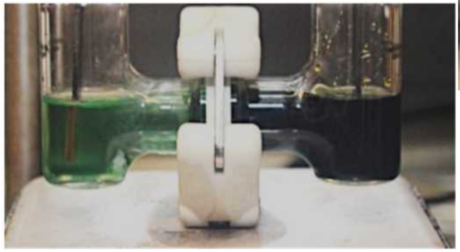


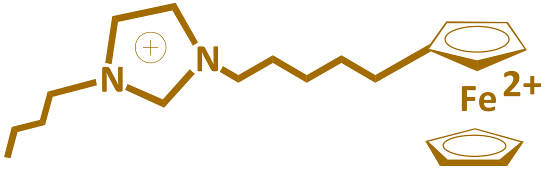
The back pressures from the viscous materials are minimized by increasing the outlet to inlet ratio and by smoothing the turns in the flow field.

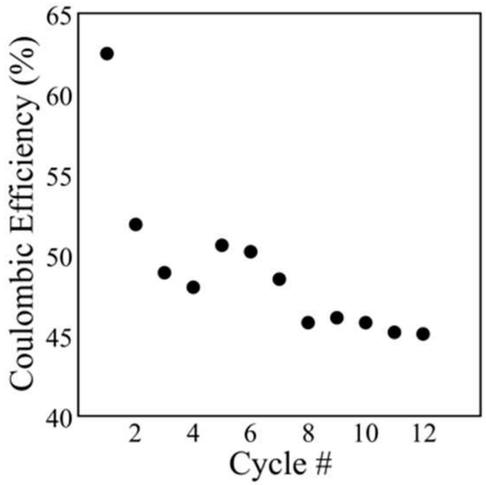
Static Cell Testing

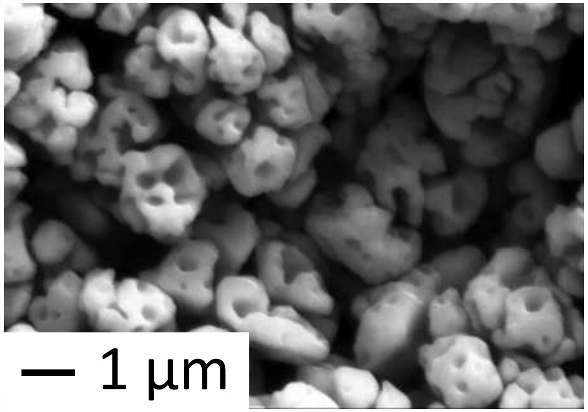










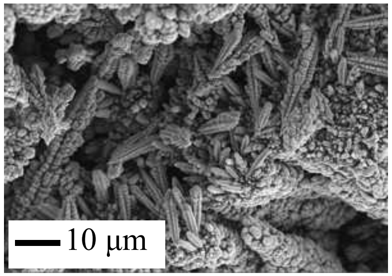


Partially irreversible copper plating on the electrode results in a lower coulombic efficiency. However this reversibility can be controlled by utilizing different anions.

Pratt, Ingersoll, Hudak, McKenzie, and Anderson, *J. Electroanal. Chem.* **2013**, 153.

Copper Plating

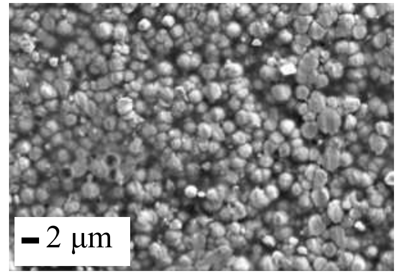
EA



BF_4^-

Ligand Change →

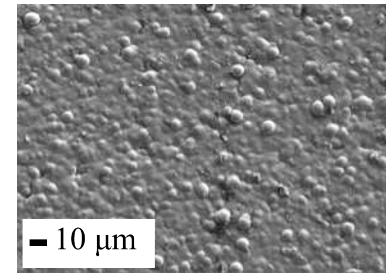
DEA



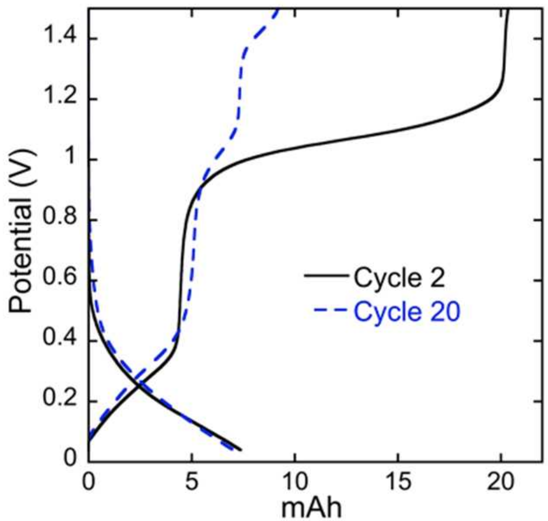
BF_4^-

Anion Change →

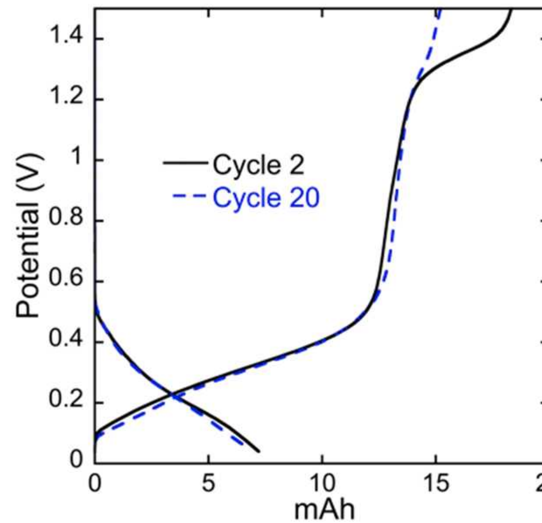
DEA



$CF_3SO_3^-$

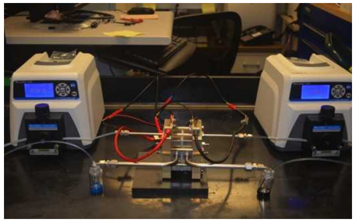


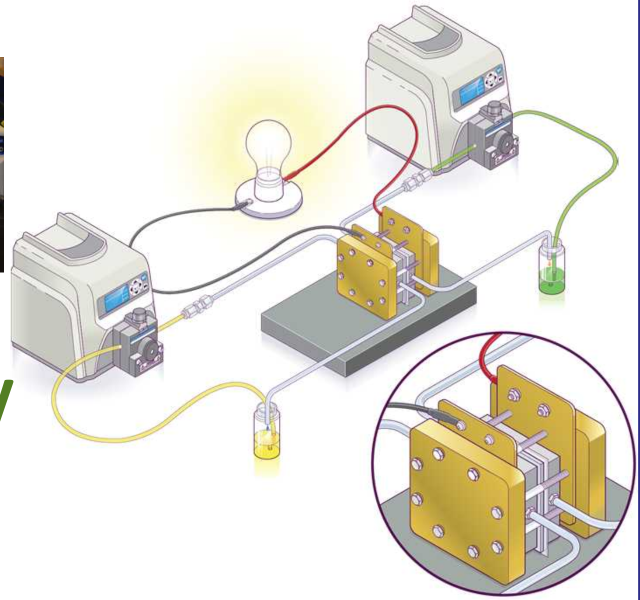
Ligand Change →



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

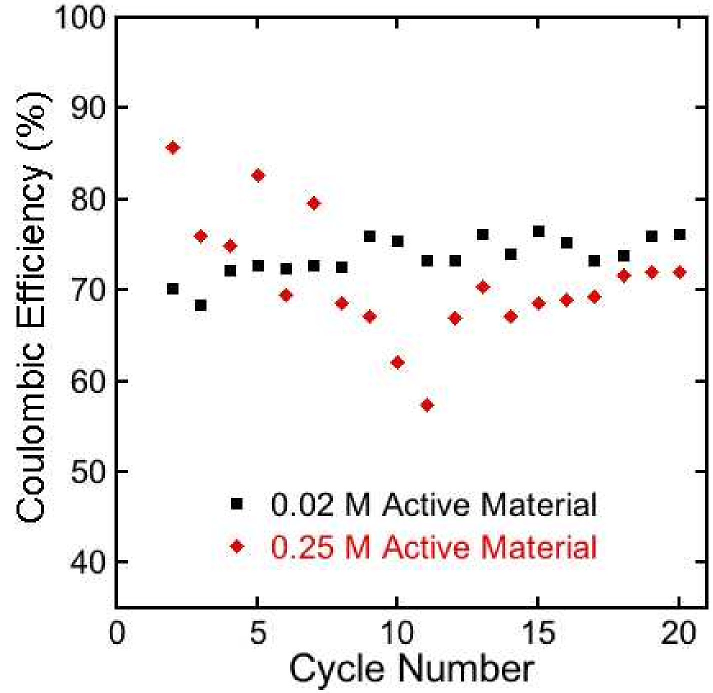
Ionic Liquid Battery Prototype





Laboratory Scale Prototype

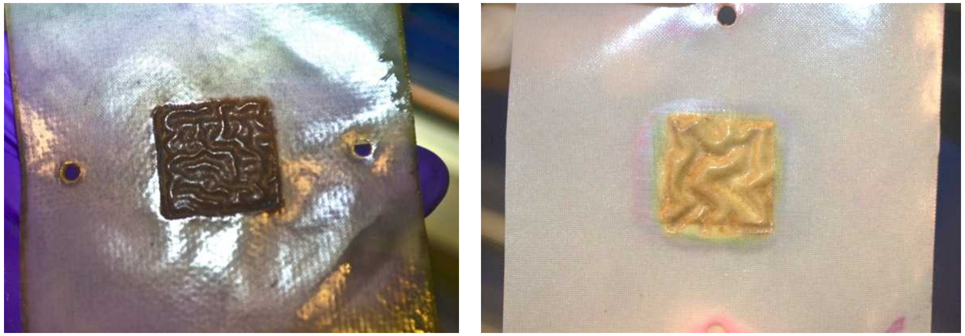
- Initial tests on Cu-MetIL/Fe-MetIL (1.5 V) system used commercial membranes.
- Neosepta AHA gave the best results.



- Batteries were run at 25 ° C and 50 ° C
- Increased concentration gave more scatter in the data but higher energy density.
- Highest current density achieved was 0.5 mA/cm^2

Membranes*

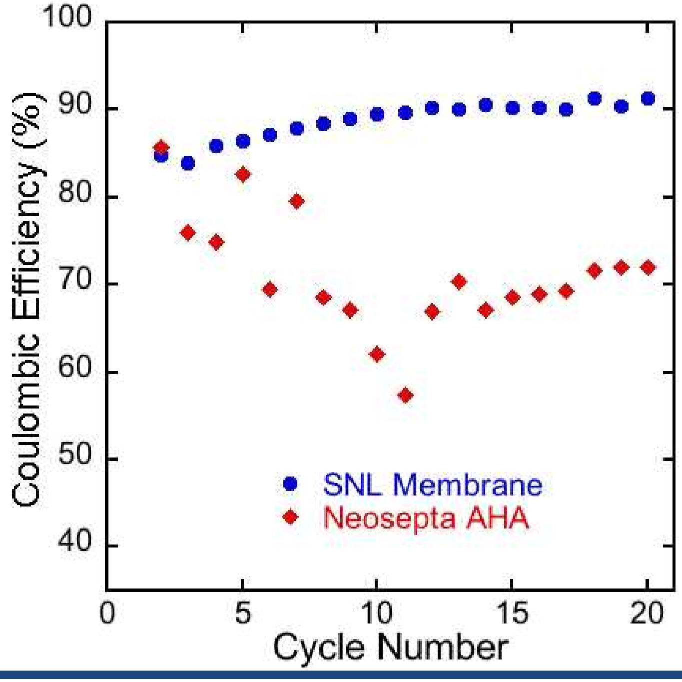
Commercially available, ion selective membranes are not designed for non-aqueous use.



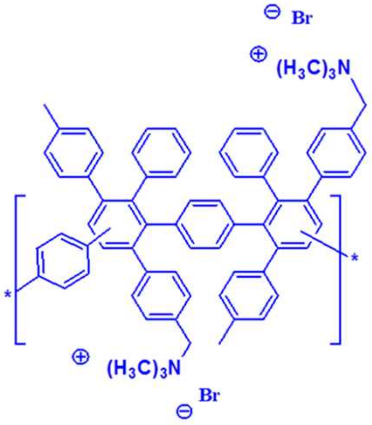
Ionic Liquid **Ionic Liquid/ACN**

Neosepta® AHA

- **Coulombic efficiency increased from 70% to 90%.**
- **Current density was increased from $0.5\ mA/cm^2$ to $10\ mA/cm^2$.**



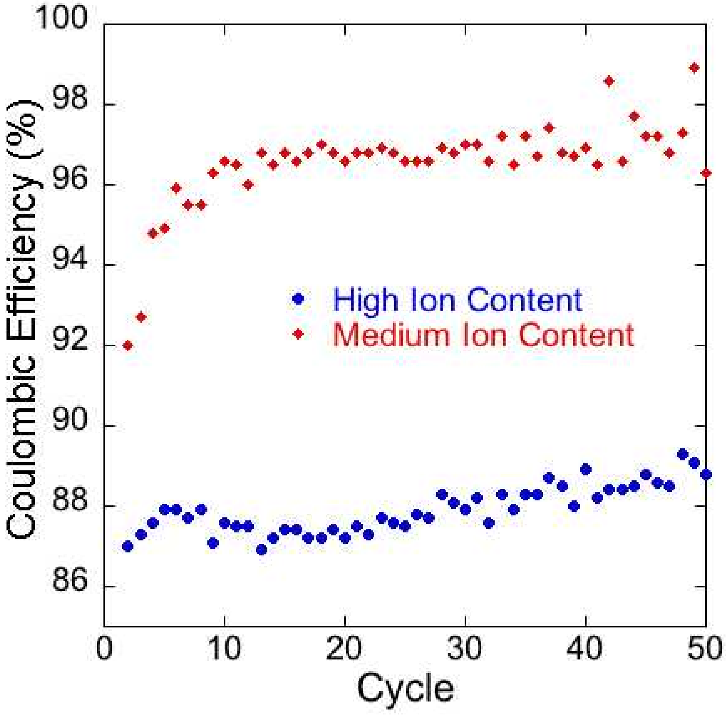
Sandia technology membranes are now being tested because their detailed chemical structures are known.



*Cy Fujimoto, Principal Investigator

Membrane Ion Content

Membranes contain a polyphenylene backbone with pendant ionic groups. The ionic content was varied qualitatively high, medium, and low. Membranes were cast and flow cells were constructed and tested.



Low Ion Content

Very brittle sample–no data

Medium Ion Content

Best Coulombic efficiency

Best electrochemical yield after 15 cycles

Least crossover

High Ion Content

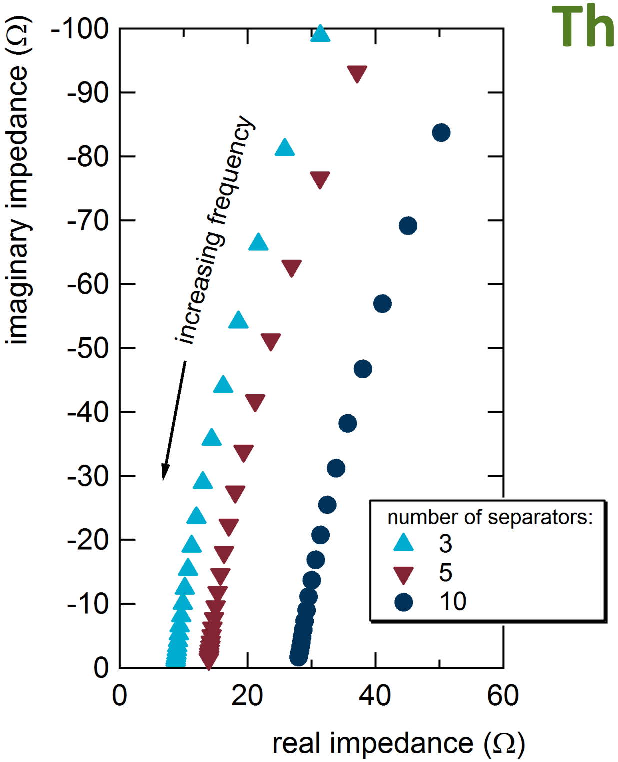
Good Coulombic efficiency

High crossover

The membranes can be "tuned" to improve performance.

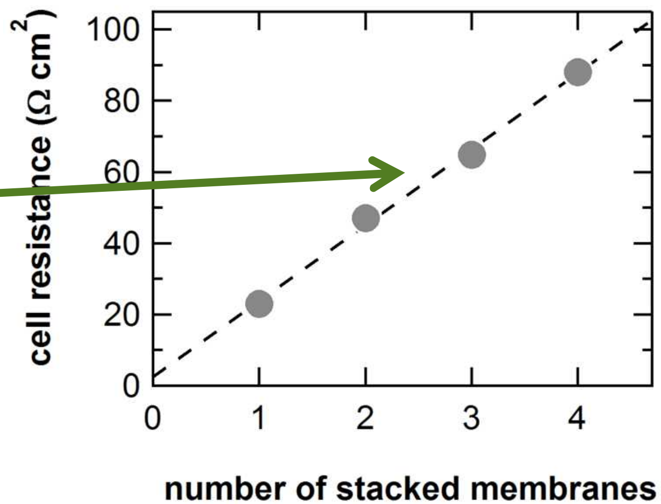
Membrane Characterization

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.

slope of fitted line = 21.3 Ω cm^2
≡ area-specific resistance of membrane without contact resistance

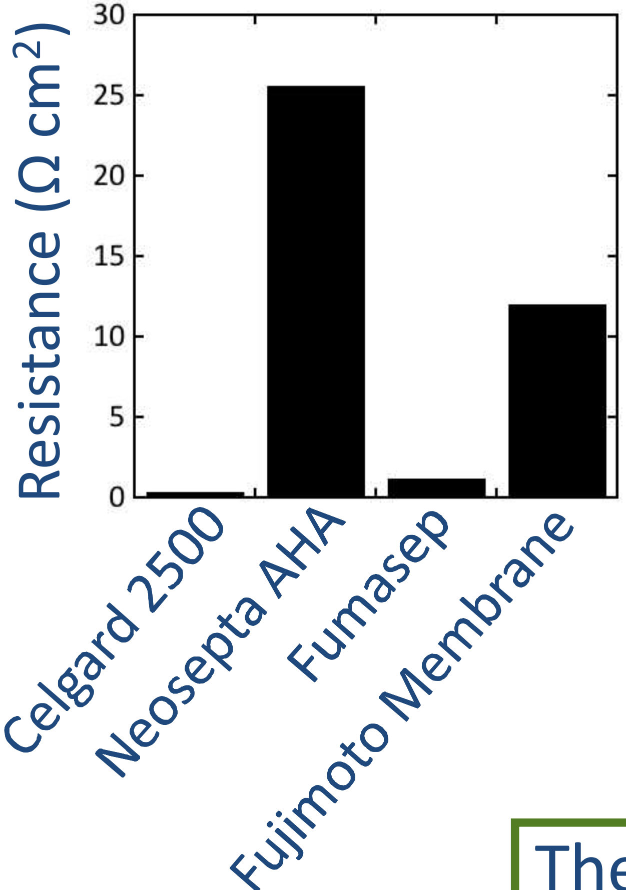


Hudak, Small, Pratt, and Anderson, manuscript submitted

Through-Plane Resistances (EIS)

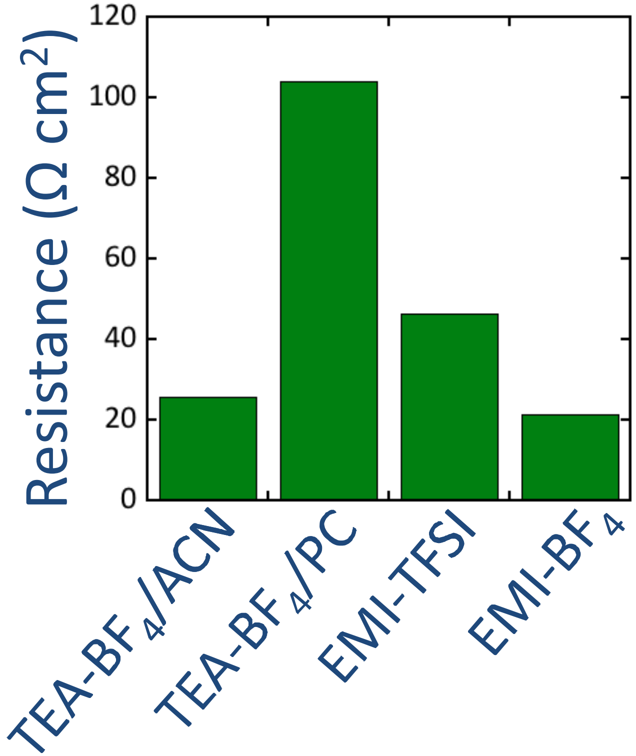
Sandia National Laboratories

Membranes in 0.5 M $TEA\text{-}BF_4/ACN$



The goal is to obtain low ionic resistance with higher selectivity/less crossover.*

Neosepta® AHA in Different Solvents



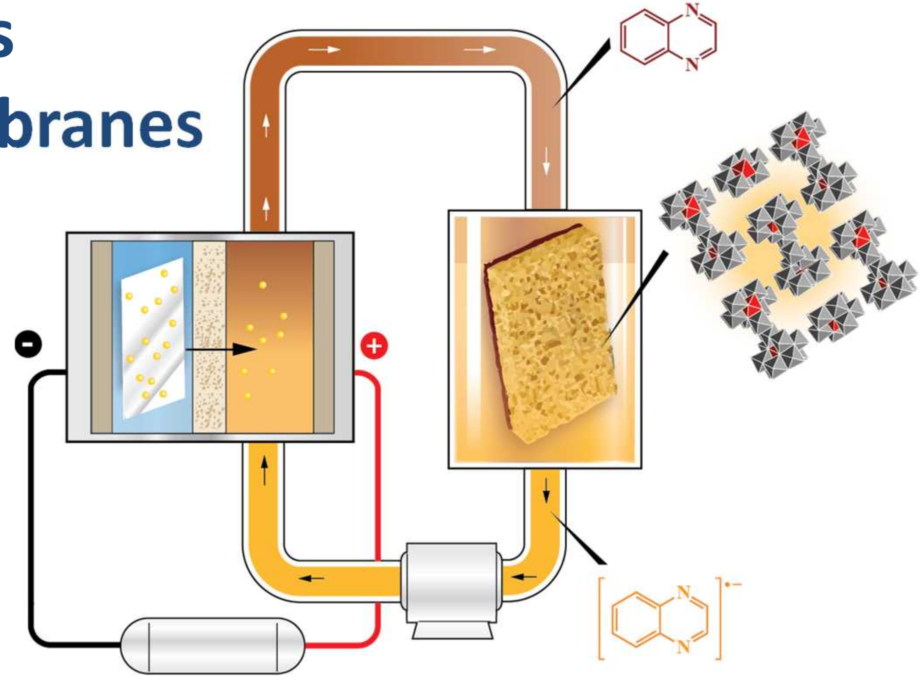
There is a wide variability in resistances that in turn are solvent dependent.

*Escalante-García, Wainright, Thompson, and Savinell, *J. Electrochem. Soc.*, **2015**, A363.

Concluding Statement

Redox-active ionic liquid flow batteries offer the potential of higher energy densities compared to aqueous chemistries due to larger voltage windows, but they are limited by their higher viscosities and potentially higher costs. We seek to overcome these hurdles by developing:

- **New electrolyte chemistries**
- **Tunable non-aqueous membranes**
- **Unique cell designs**
- **Mediators***



*Huang and Wang, *ChemPlusChem.*, **2015**, 312.

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- **Imre Gyuk**, Energy Storage Program, Office of Electricity Delivery and Energy Reliability
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- Tom Wunsch, PSTG Manager
- MetILs team: Leo Small and Cy Fujimoto