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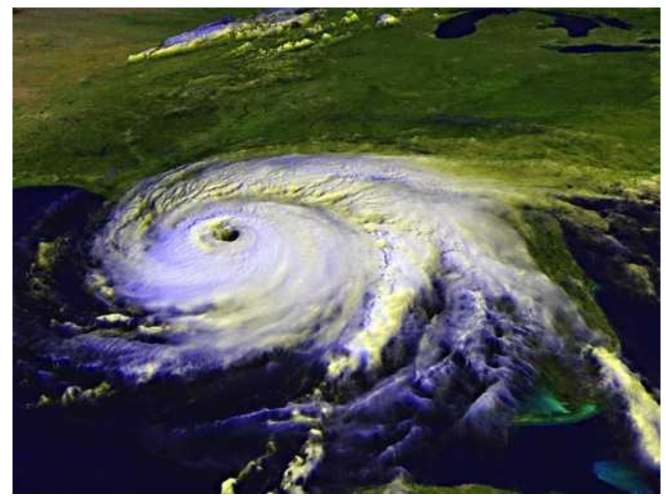

Advances in Materials for Ionic Liquid Flow Batteries

Wednesday, March 30, 2016

Travis Anderson, Leo Small, Harry Pratt, Cy Fujimoto

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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Project Overview

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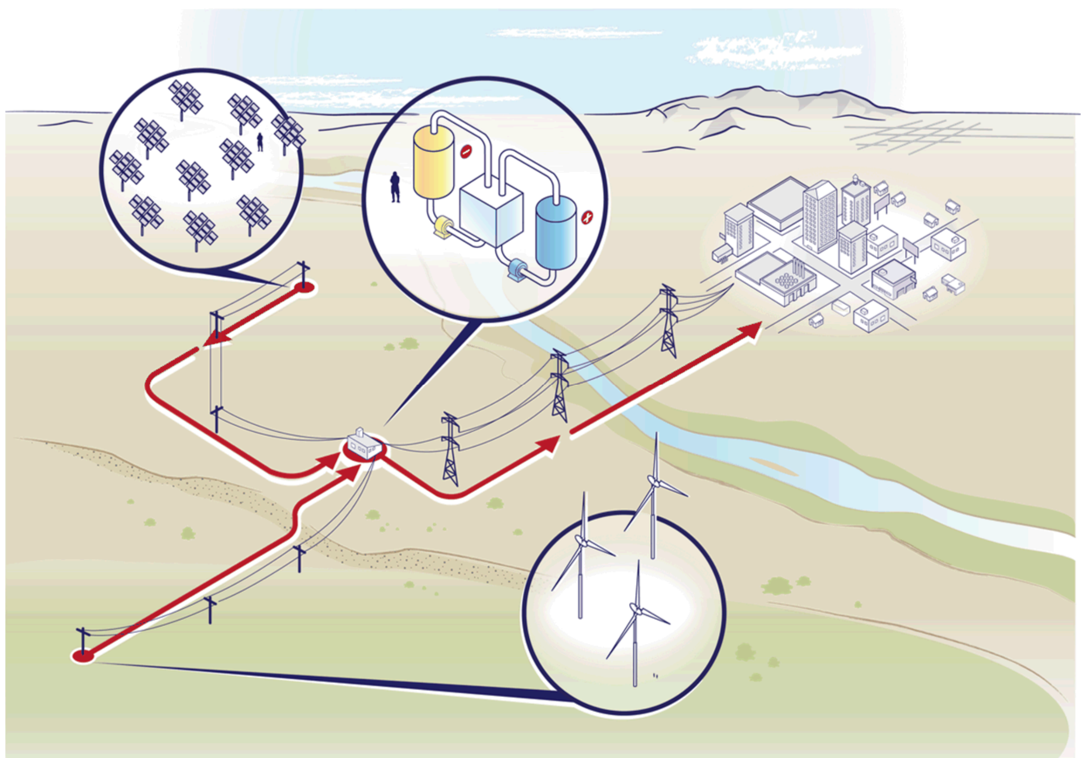
Problem: Cost competitive ionic liquids have high viscosities but are promising for higher energy density redox flow batteries due to higher metal concentrations and wider voltage windows.

Approach: Couple earth-abundant, tunable electrolytes with custom-synthesis non-aqueous membranes and rapidly test them using laboratory-scale cell designs.



Increased renewables penetration on the grid

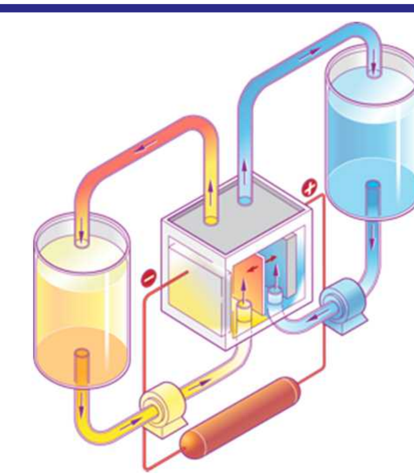
Energy Density$_{RFB}$ ≈ ½nFV$_{cell}$c$_{active}$

$$ED_{AQ} = \tfrac{1}{2}1F1.5_{cell}2_{active} = \mathbf{1.5F}$$

$$ED_{IL} = \tfrac{1}{2}2F2_{cell}3_{active} = \mathbf{6.0F}$$

Potential for **four-fold** improvement

MetIL^{-}

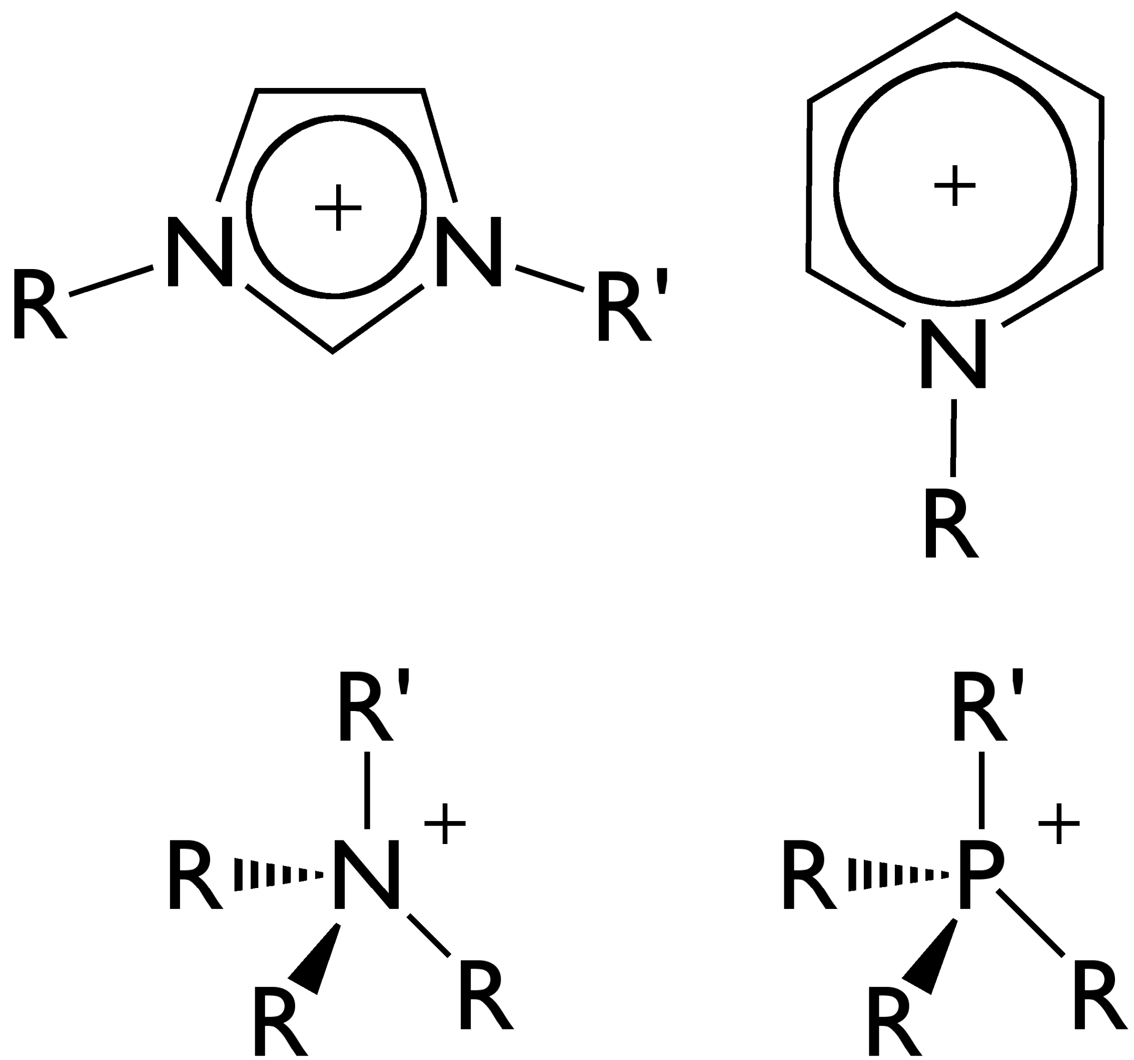


$^{+}$MetIL

Pratt, Leonard, and Anderson, *EESAT* **2013**.

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

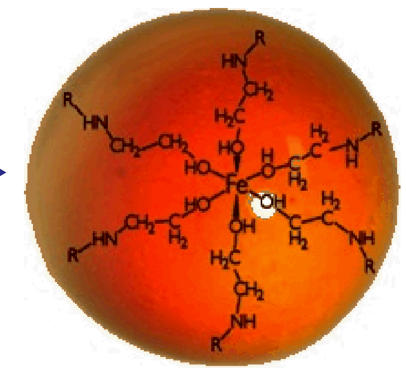
Advantages Over Water

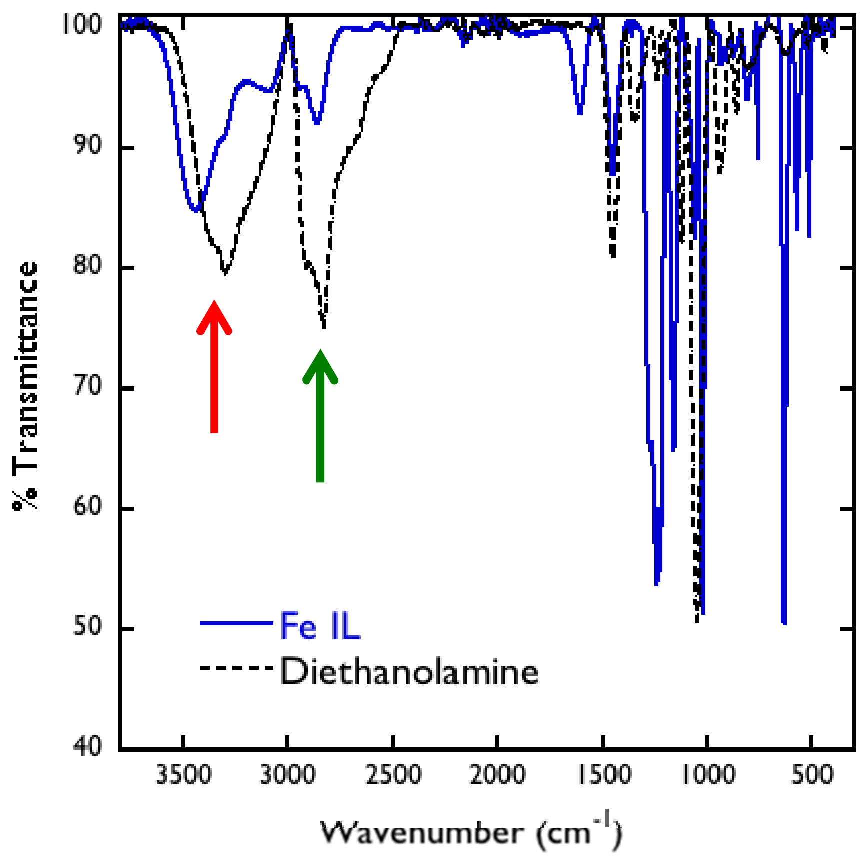
(1) Wider window helps prevent side reactions

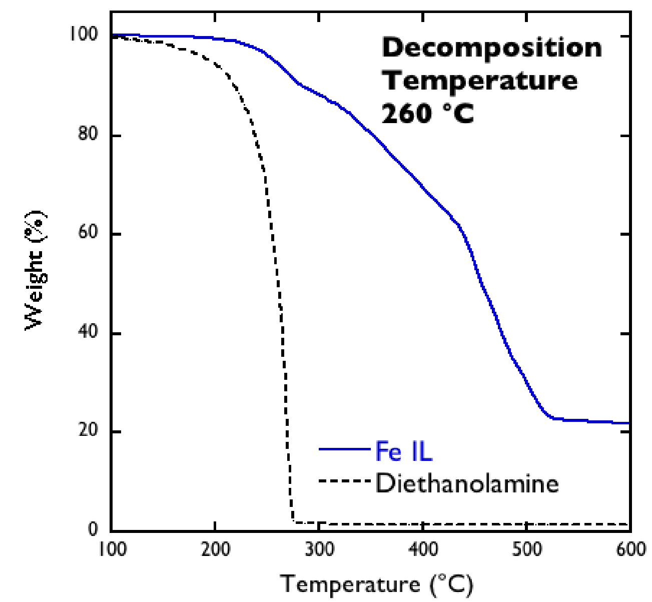
(2) Can vary temperature over wider ranges

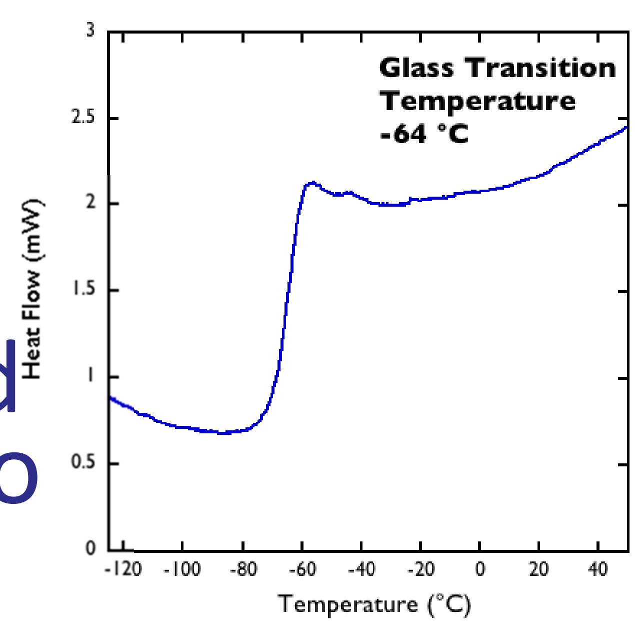
F. Endres, *ChemPhysChem*, **2002**, 144.

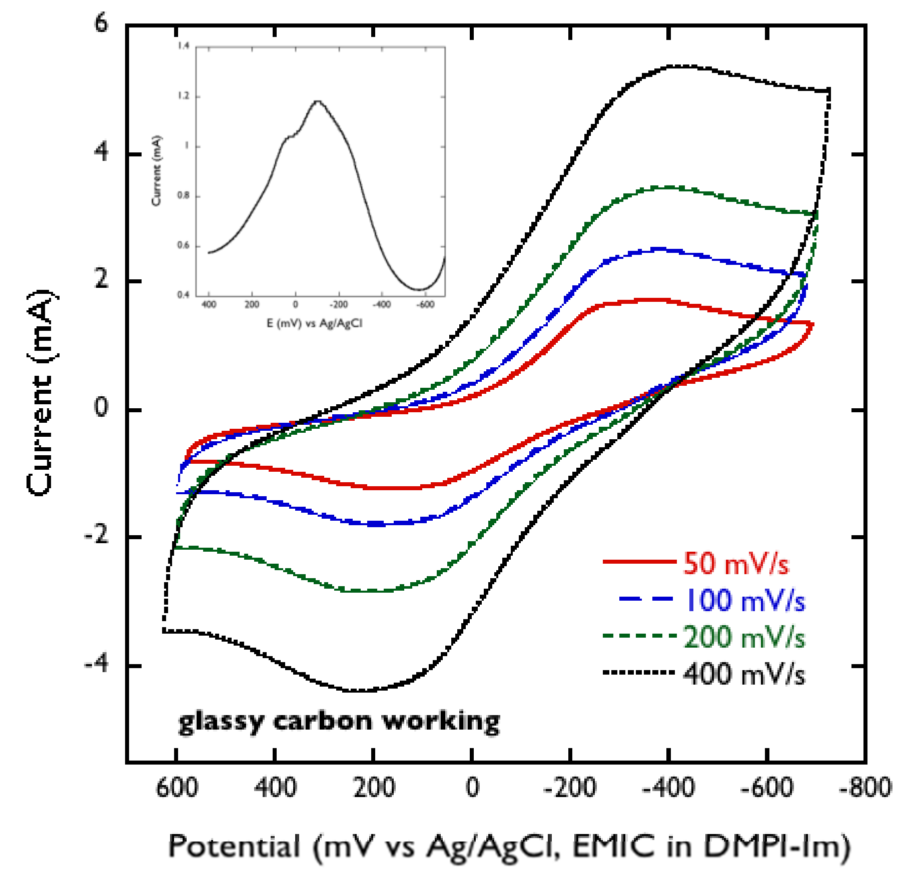
Synthesis of an Iron Ionic Liquid

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









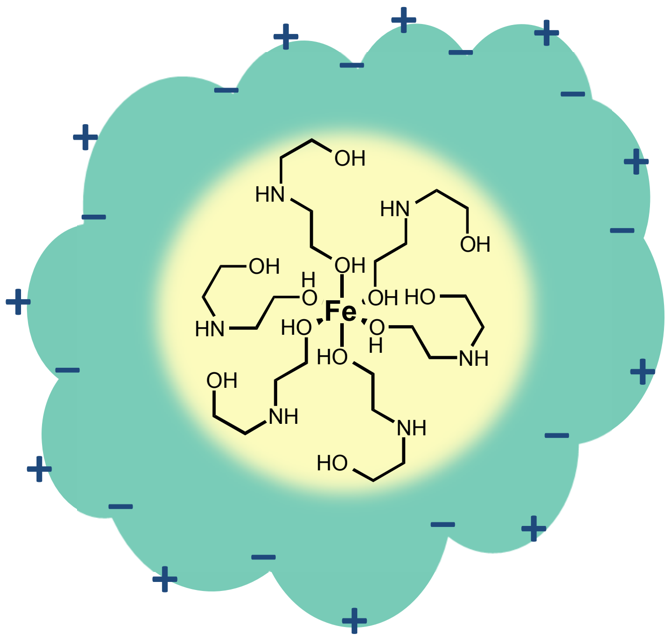
Hydroxyl (↑) and amine bands (↑) are blue shifted 200 and 30 cm^{-1} relative to diethanolamine.

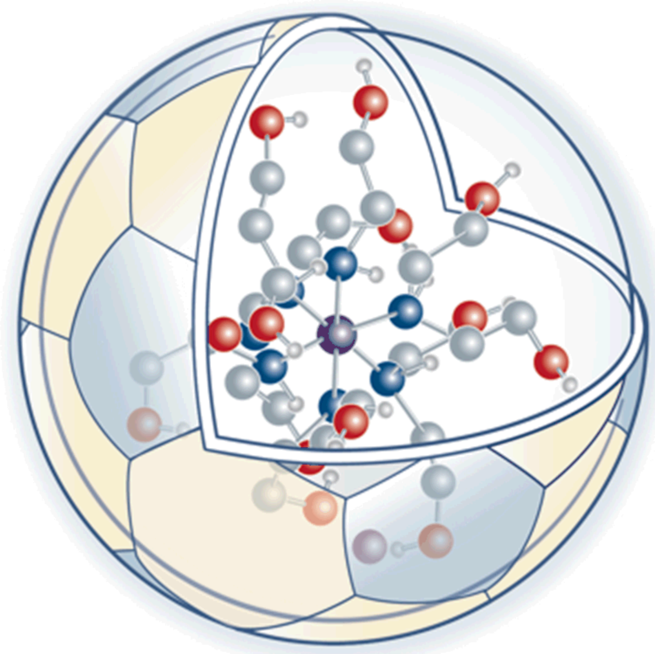
$\sigma = 0.207\ mS\ cm^{-1}$

$\mu = 4482\ cP$

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

Metal Ionic Liquid (MetIL) Concept

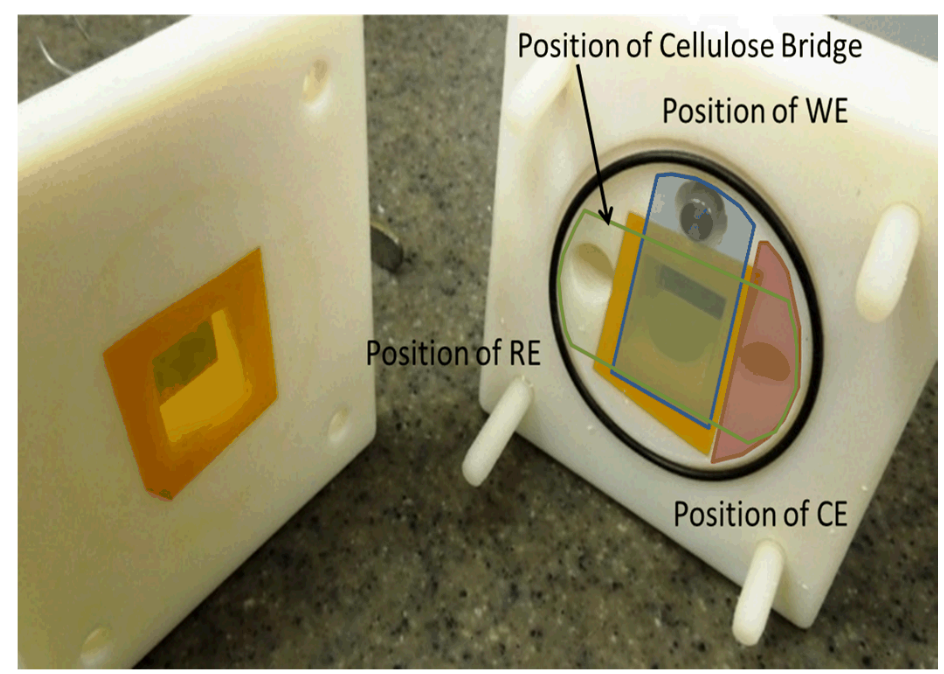




The "MetILs" Family

Approach: MetILs are synthesized in a single, high yield procedure using low cost, commercial precursors.

XANES/EXAFS*: *In situ* measurements show reduction of iron does not result in a decrease in iron-oxygen bond lengths, suggesting a significant shielding of the metal by the ligands from the external environment.



*Apblett et al., *Electrochimica Acta*, **2015**, 156.

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

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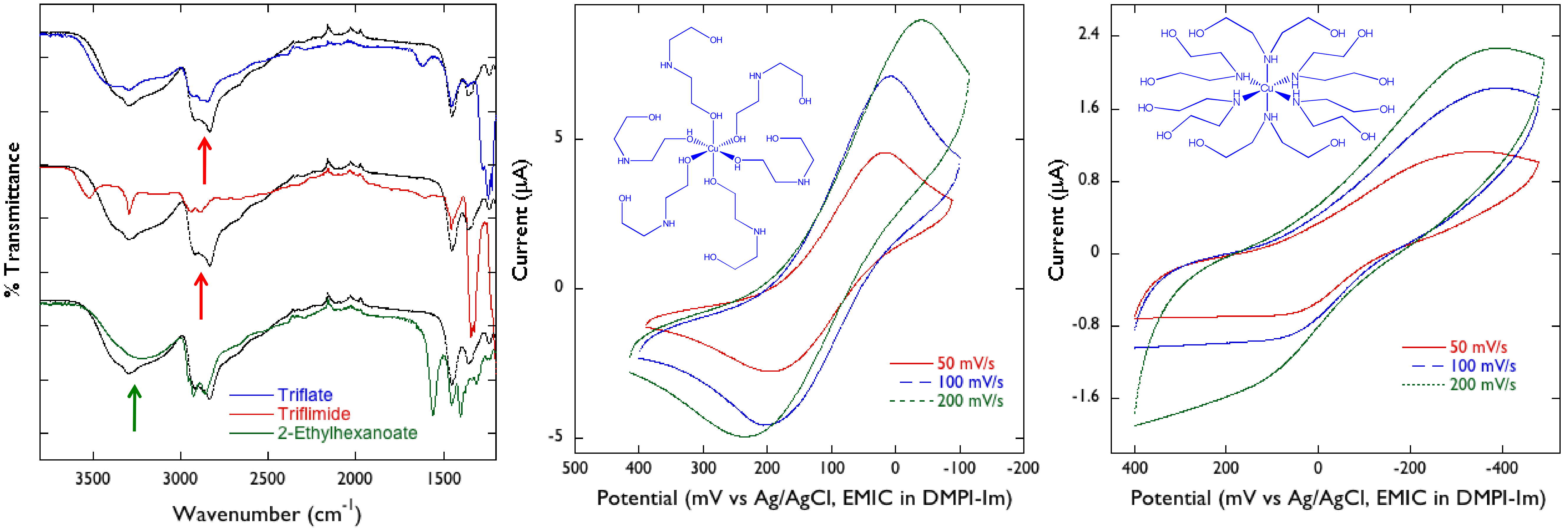
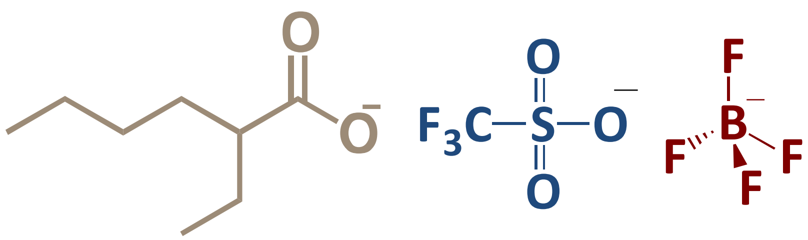
Anion: Influences ligand coordination and electrochemistry.

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

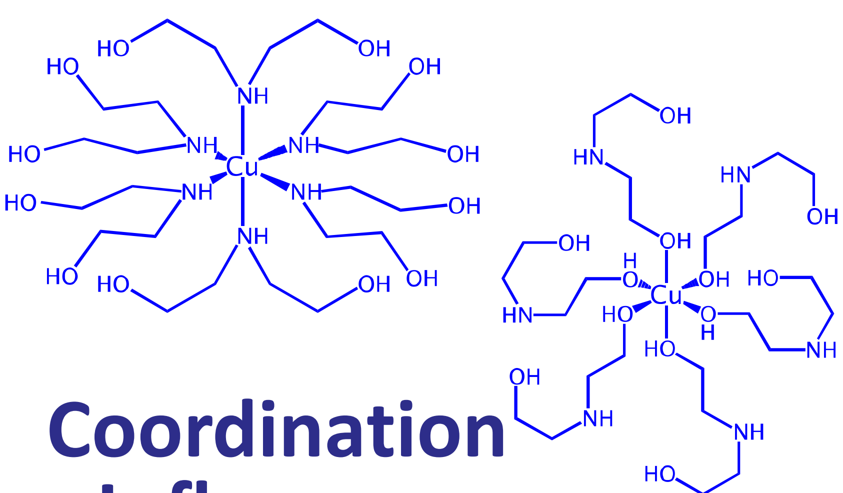


Pratt, Rose, Staiger, Ingersoll, and Anderson, *Dalton Trans.* **2011**, 11396.

Role of the Anion



EA ethanolamine
DEA diethanolamine



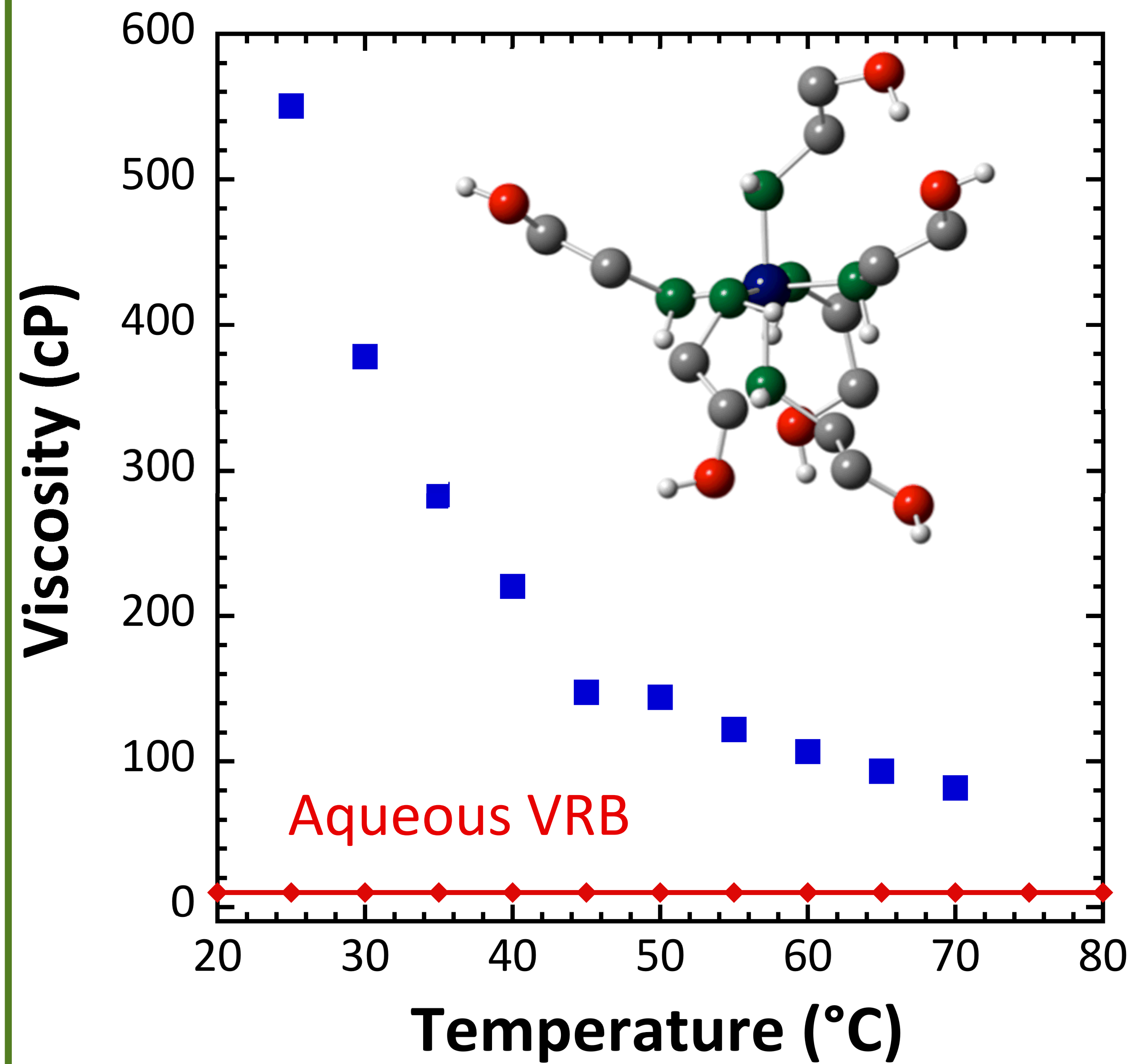
Coordination Influences Viscosity

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

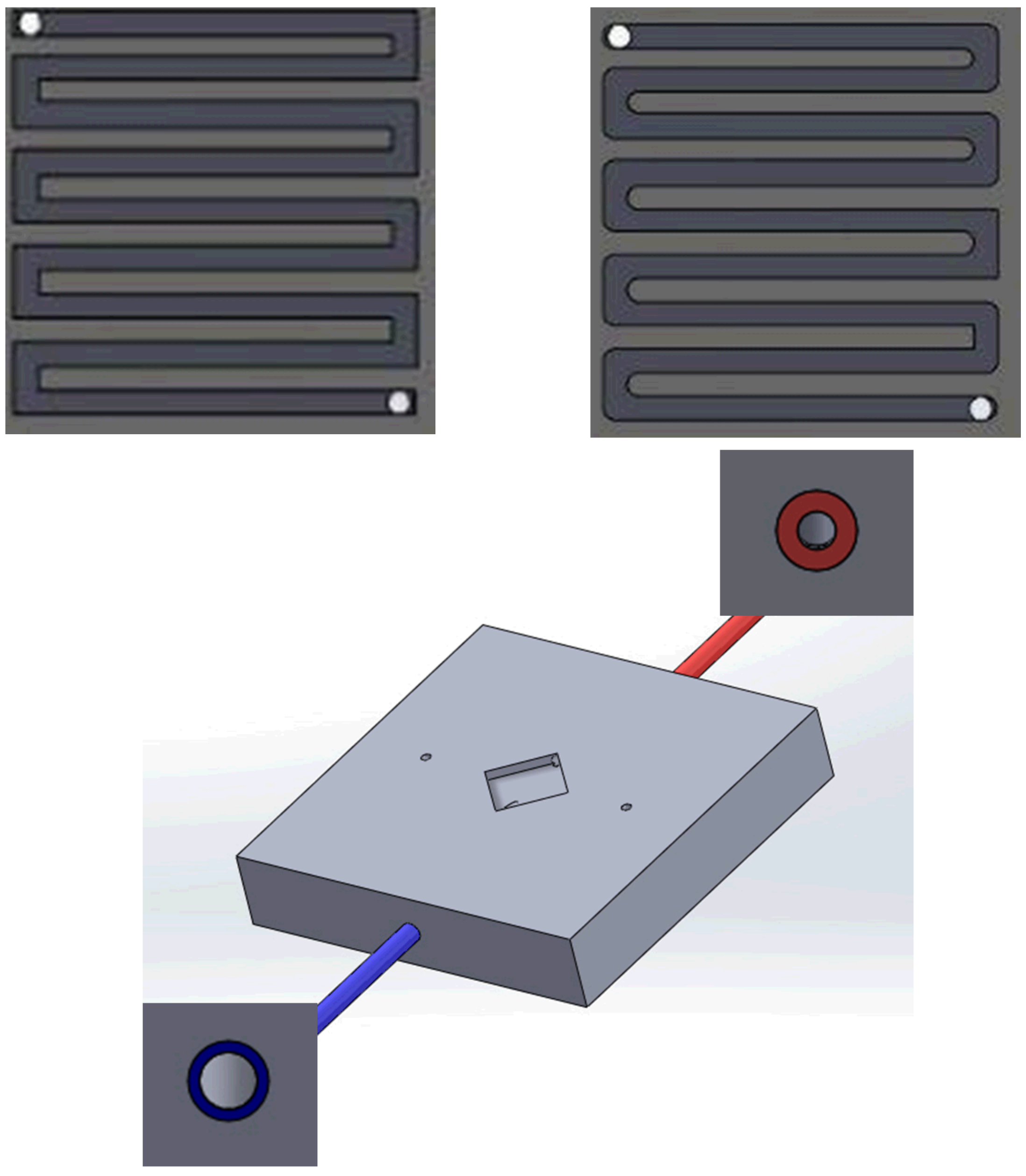
Pratt, Leonard, Steele, Staiger, and Anderson, *Inorg. Chim. Acta.* **2013**, 78.

Ionic Liquid Viscosity

Approach: Temperature

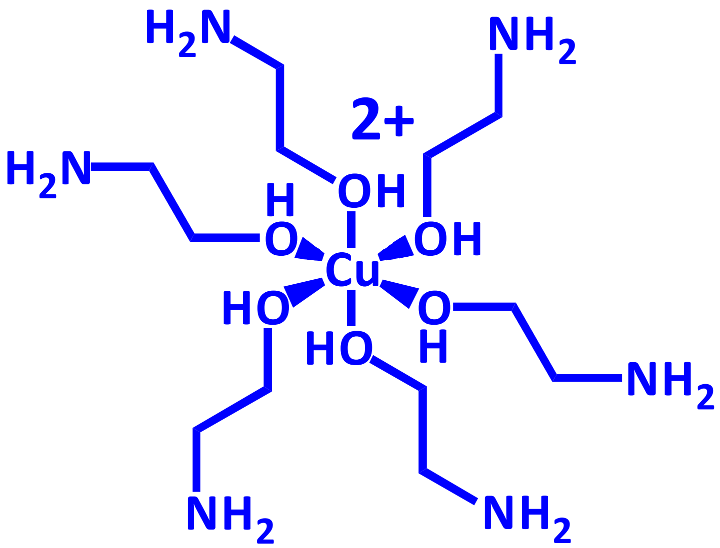


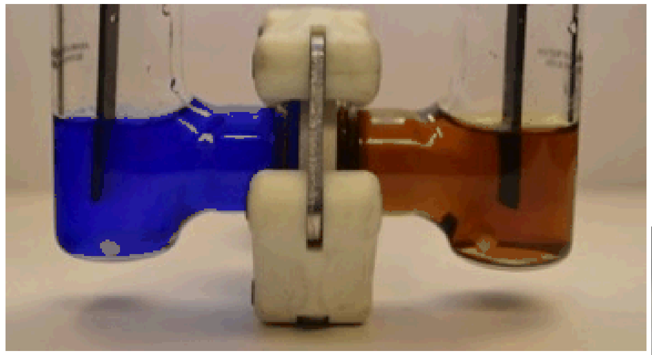
Approach: New cell designs

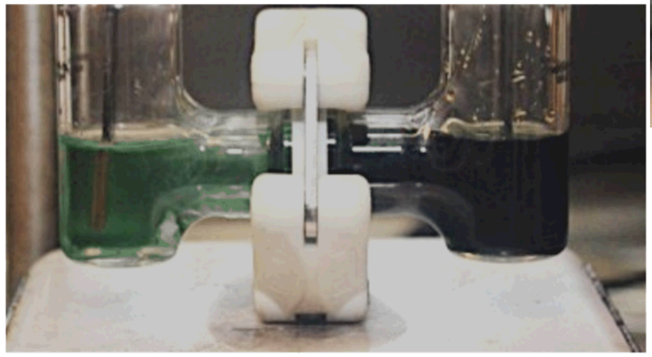


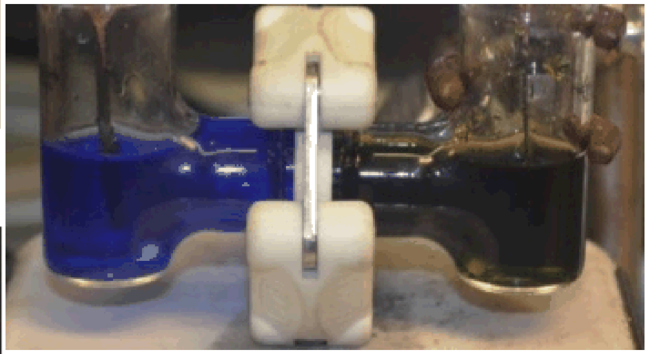
The back pressures from the viscous materials are minimized by increasing the outlet to inlet ratio and by smoothing the turns in the flow field.

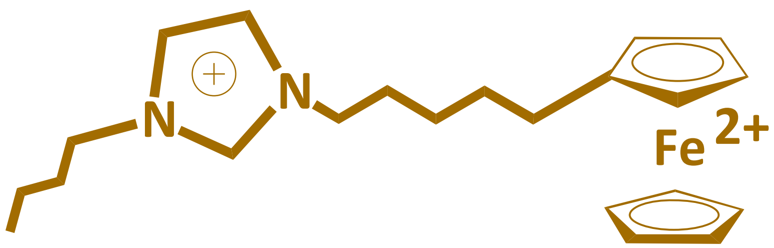
Static Cell Testing

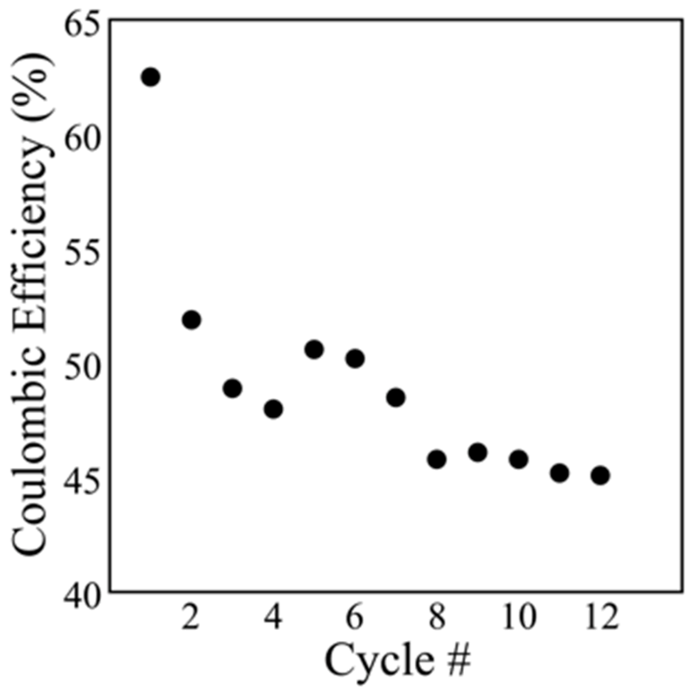


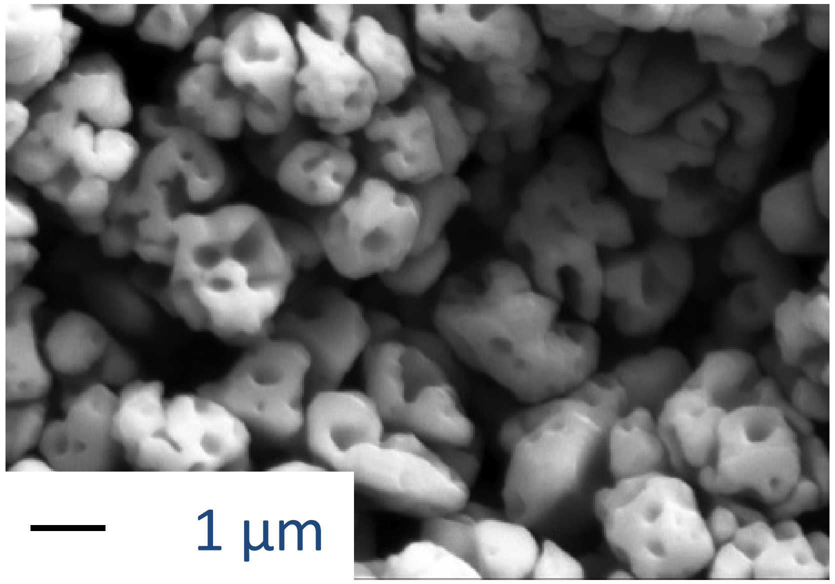










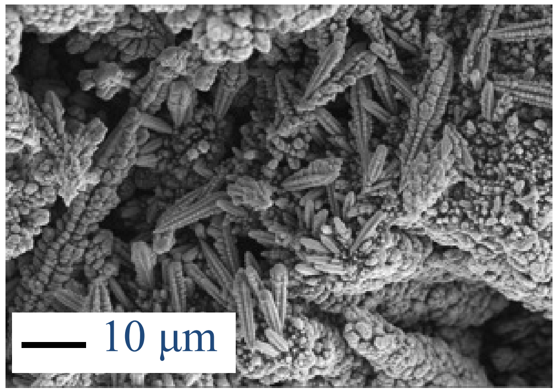


Partially irreversible copper plating on the electrode results in a lower coulombic efficiency. However this reversibility can be controlled by utilizing different anions.

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

Copper Plating

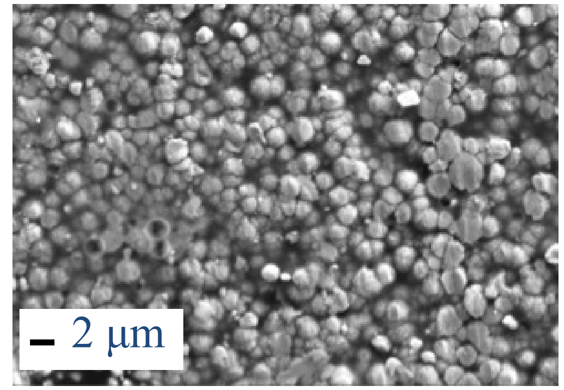
EA



BF_4^-

Ligand Change →

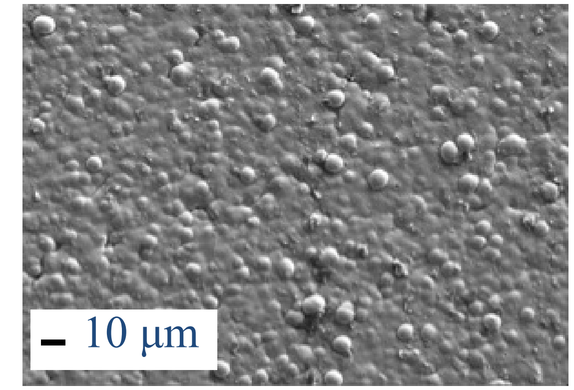
DEA



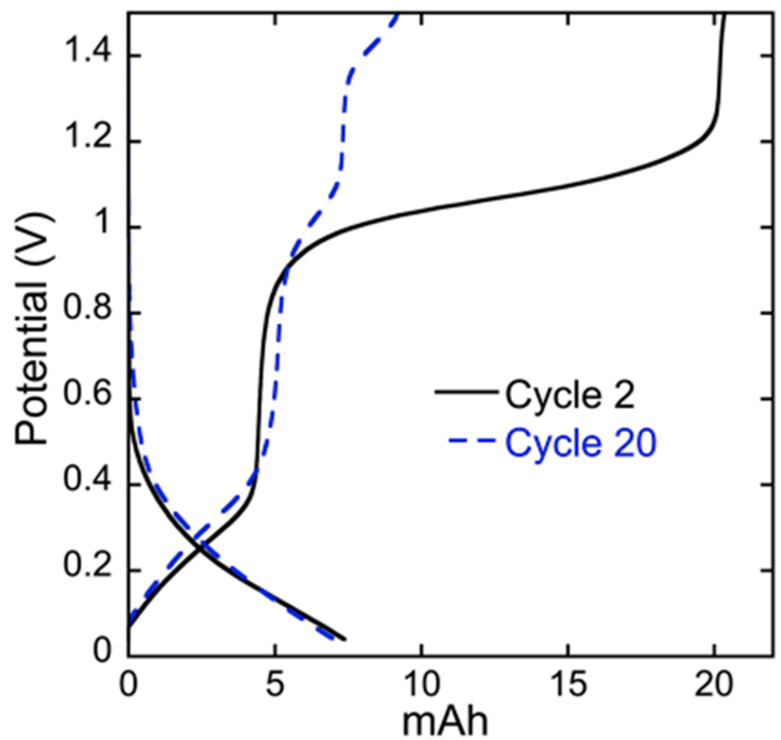
BF_4^-

Anion Change →

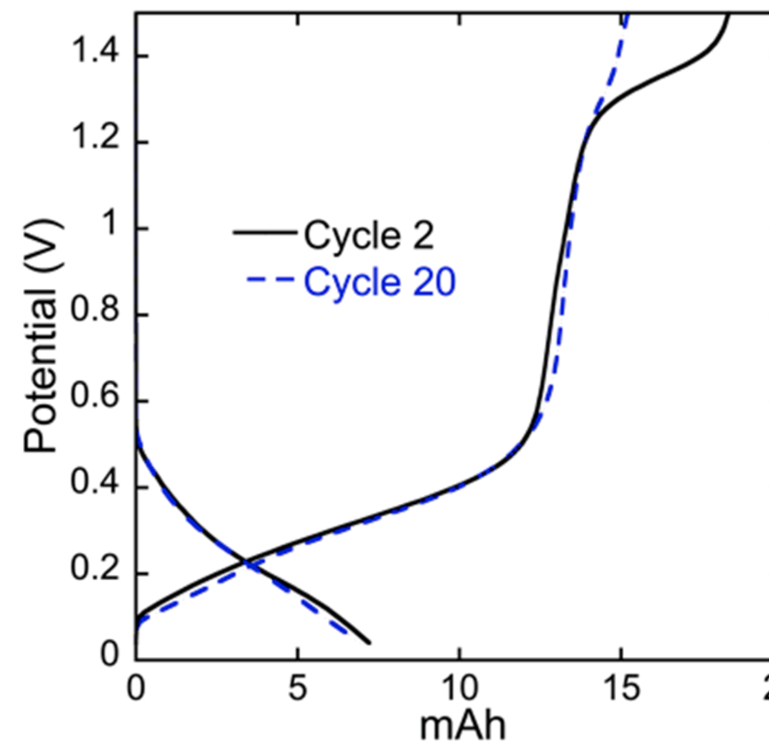
DEA



$CF_3SO_3^-$

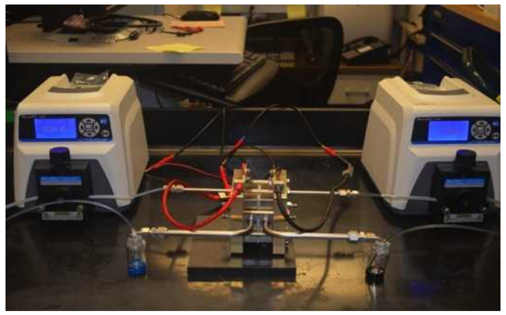


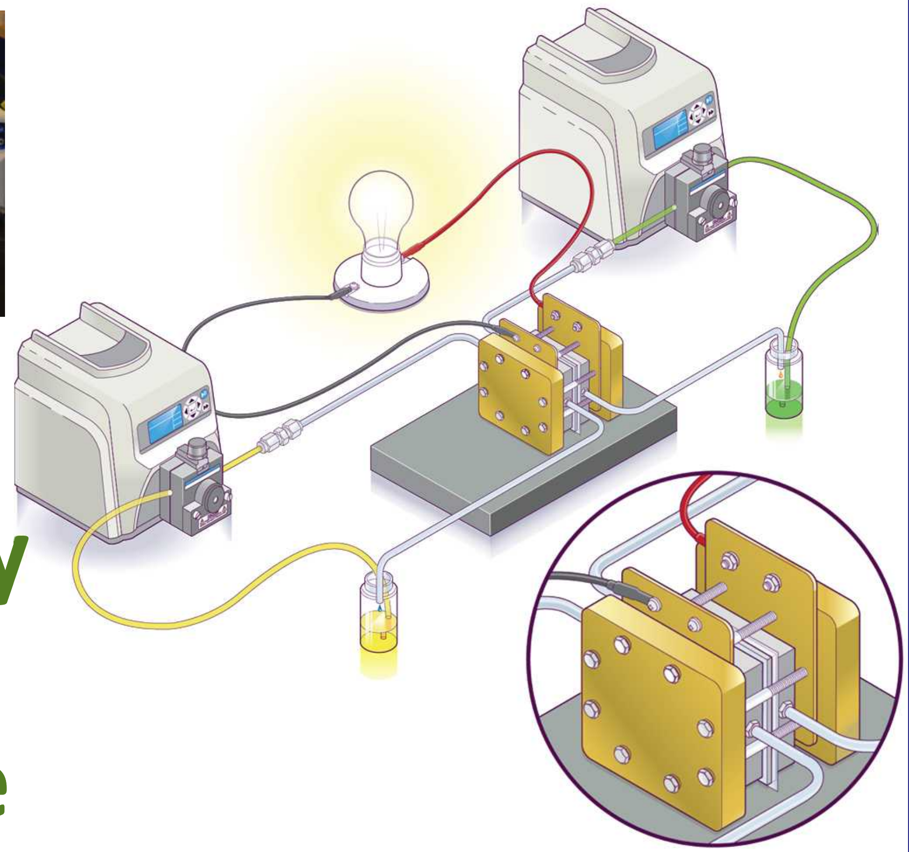
Ligand Change →



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

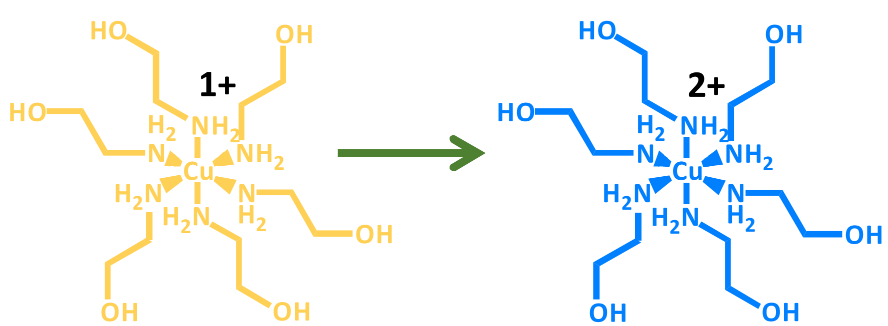
Ionic Liquid Battery Prototype





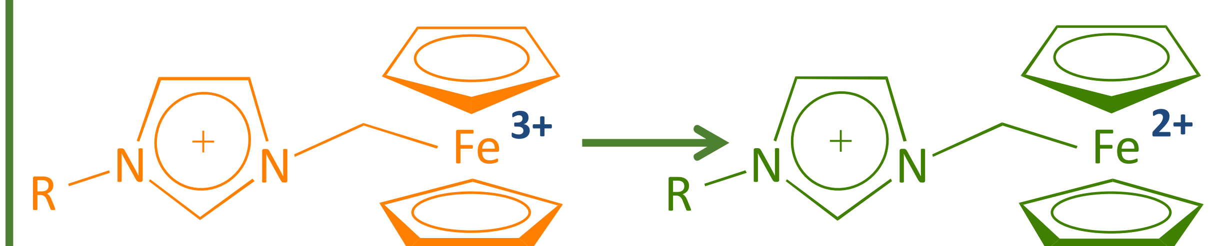
Laboratory Scale Prototype

- Initial tests on Cu-MetIL/Fe-MetIL system used commercial membranes.
- Neosepta AHA gave the best initial results for commercial membranes.
- Batteries were run at 50 ºC to improve the viscosity of the MetILs.



Negative Half-Cell Reaction

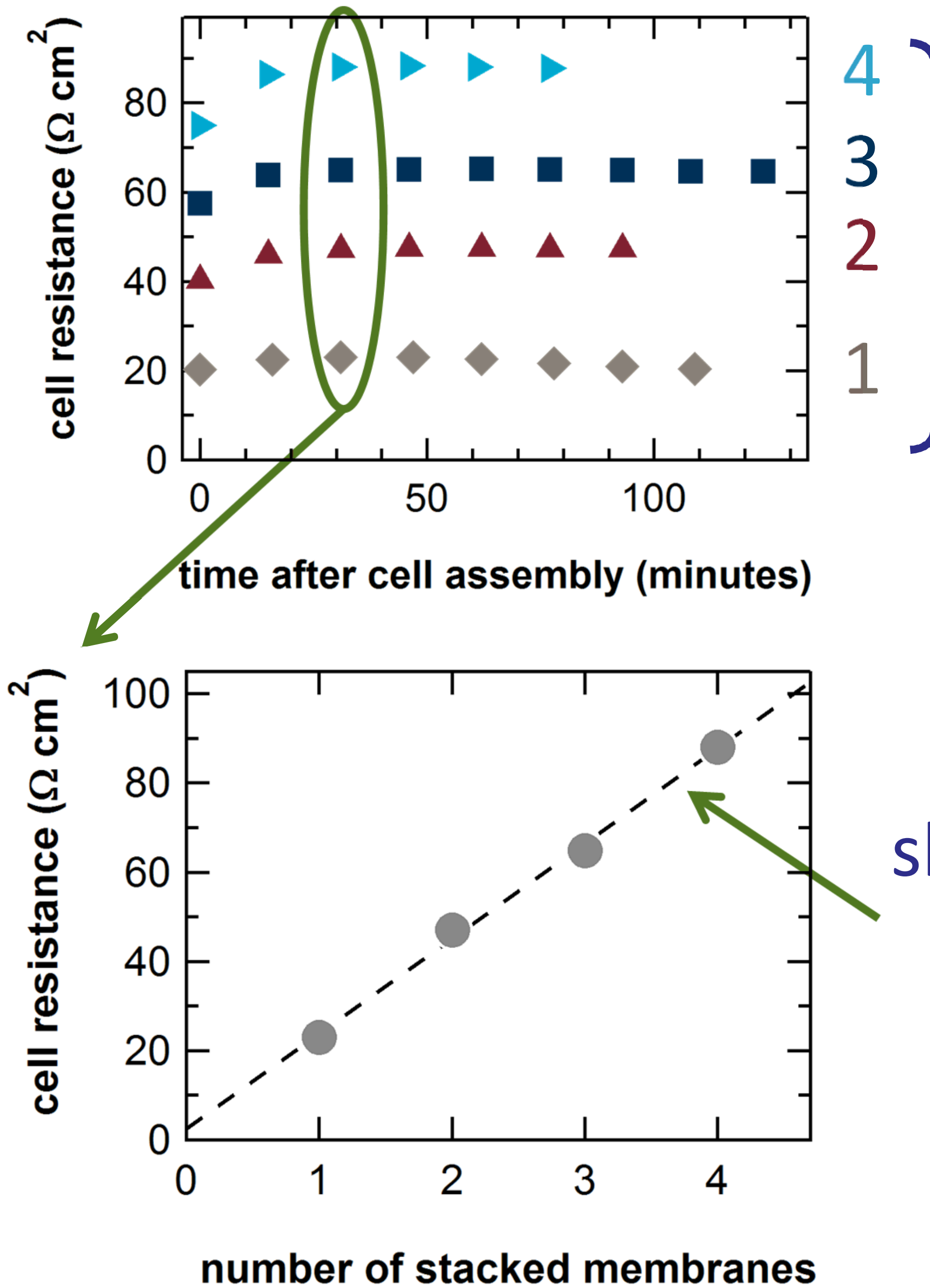
1.5 V



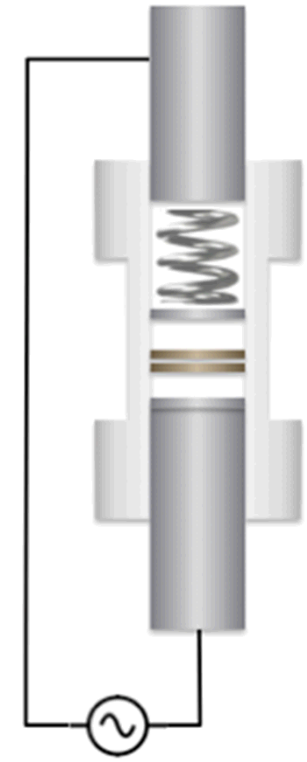
Positive Half-Cell Reaction

Highlight: First ionic liquid flow battery patent awarded in 2015

Membrane Through-Plane Resistance

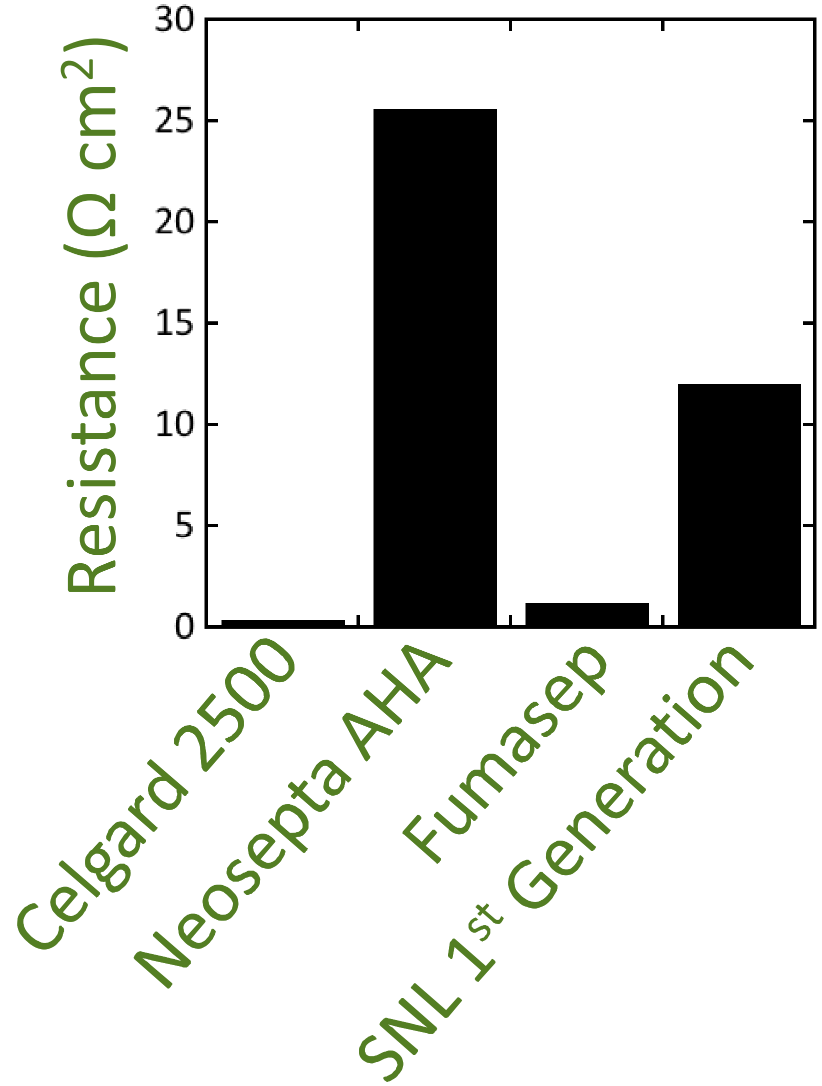


# of stacked membranes



slope of fitted line = 21.3 Ω cm² ≡ area-specific resistance

Membranes in 0.5 M TEA-BF_4/ACN



Different membranes in TEA-BF_4 illustrate a wide variability in resistances that in turn are solvent dependent.

Hudak, Small, Pratt, and Anderson, *J. Electrochem. Soc.* **2015**, p. A2188.

Flow Cell Studies

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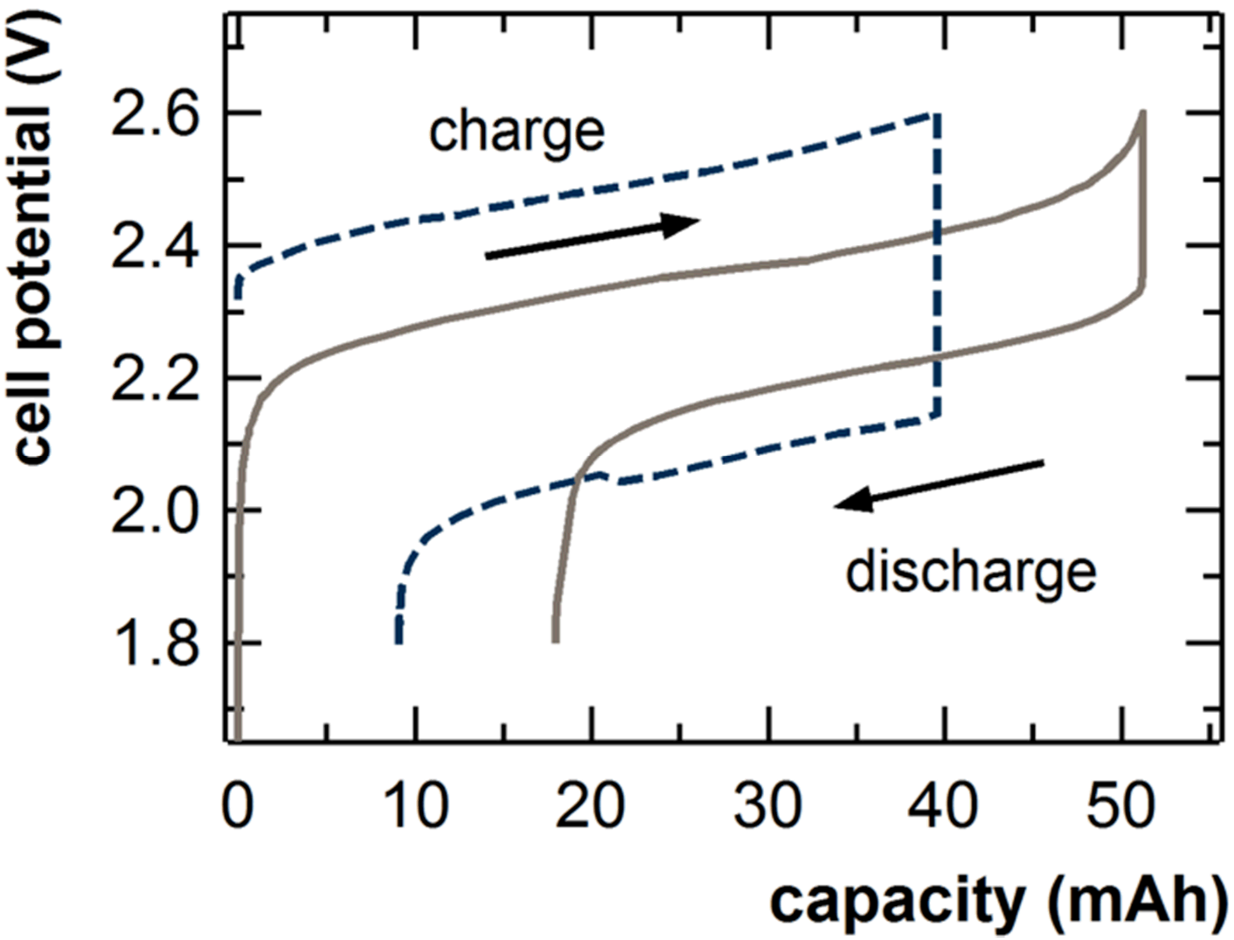
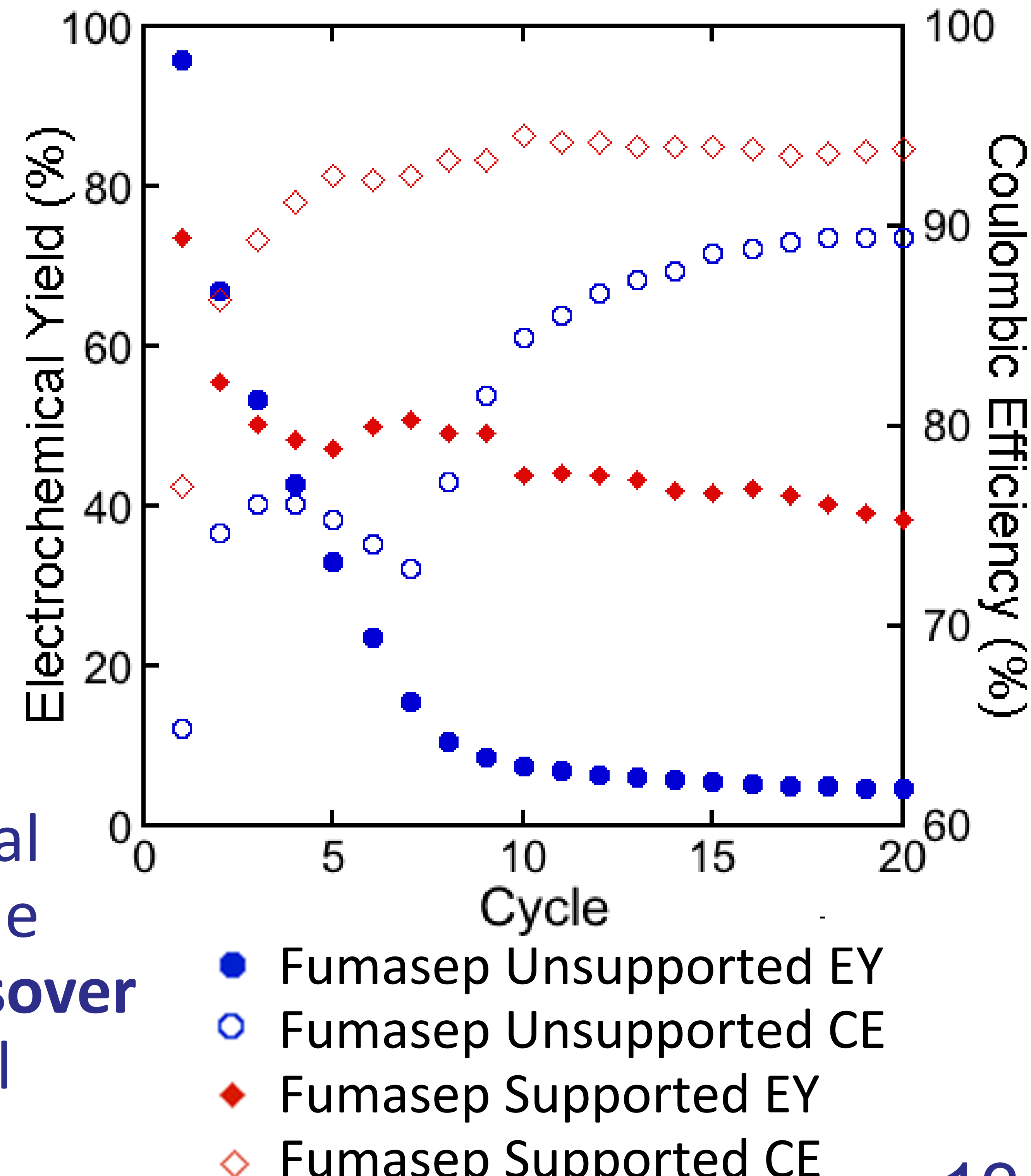


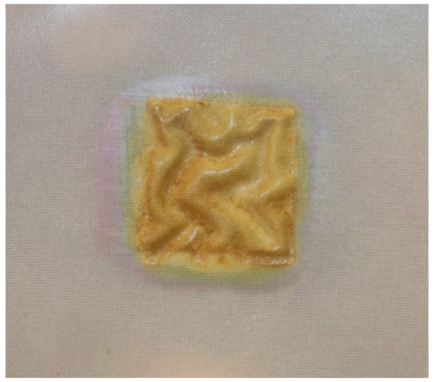
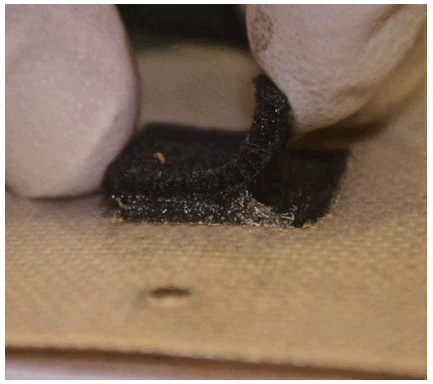
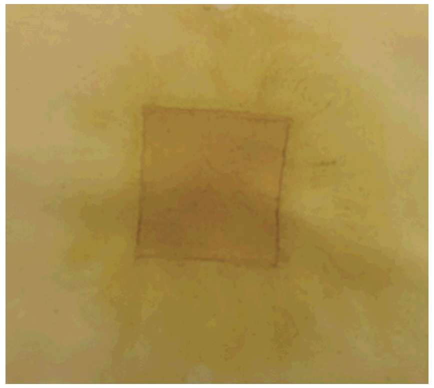


Highlight: The increased mechanical stability of the supported membrane suppressed **solvent-mediated crossover** and enabled higher electrochemical yields and Coulombic efficiencies.

Hudak, Small, Pratt, and Anderson, *J. Electrochem. Soc.* **2015**, p. A2188.

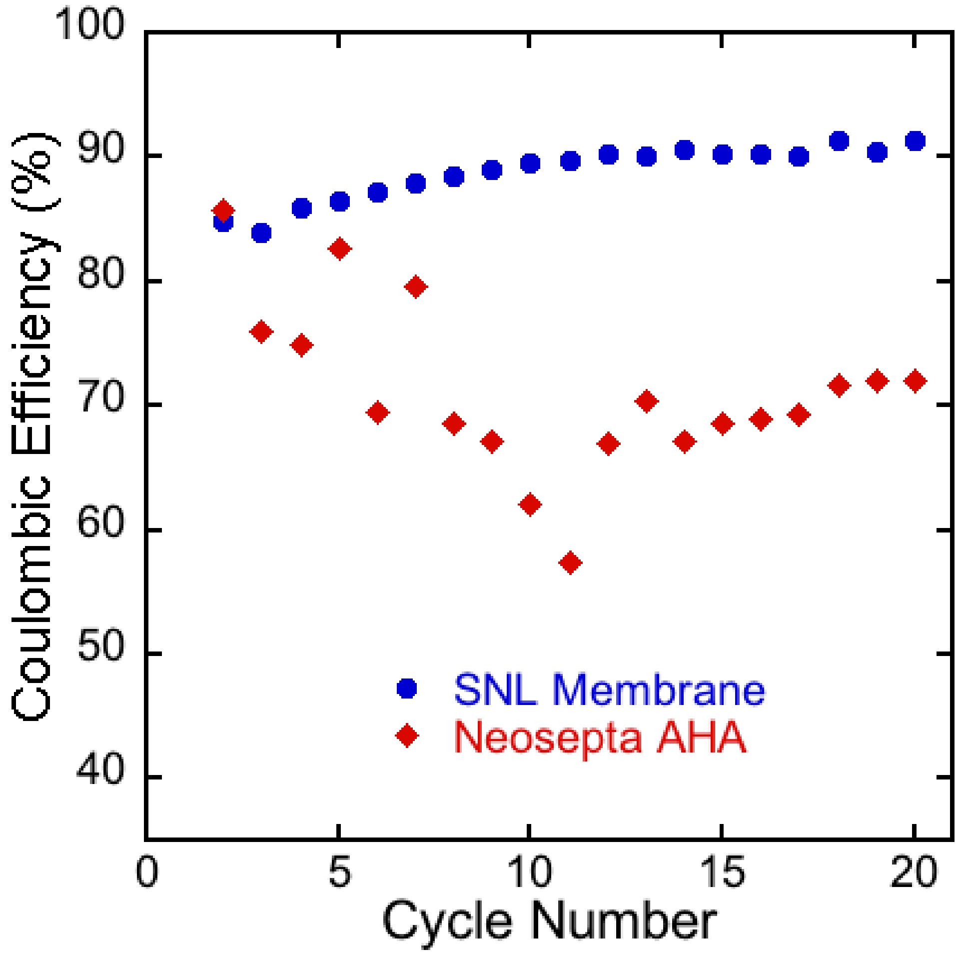
Membranes

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

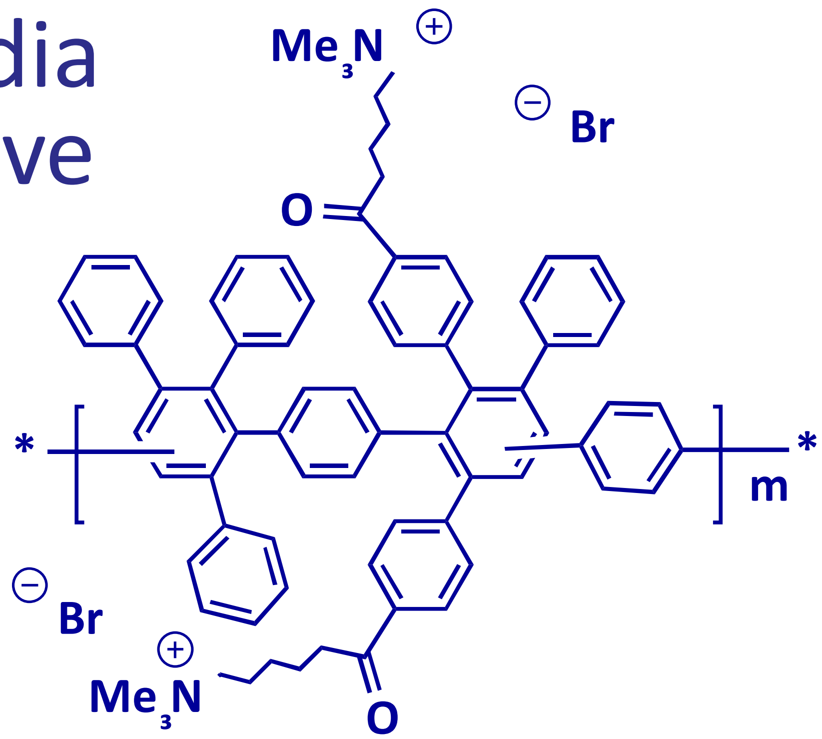
Commercial	1st Generation SNL*	2nd Generation SNL*
		

1st Generation Results:

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

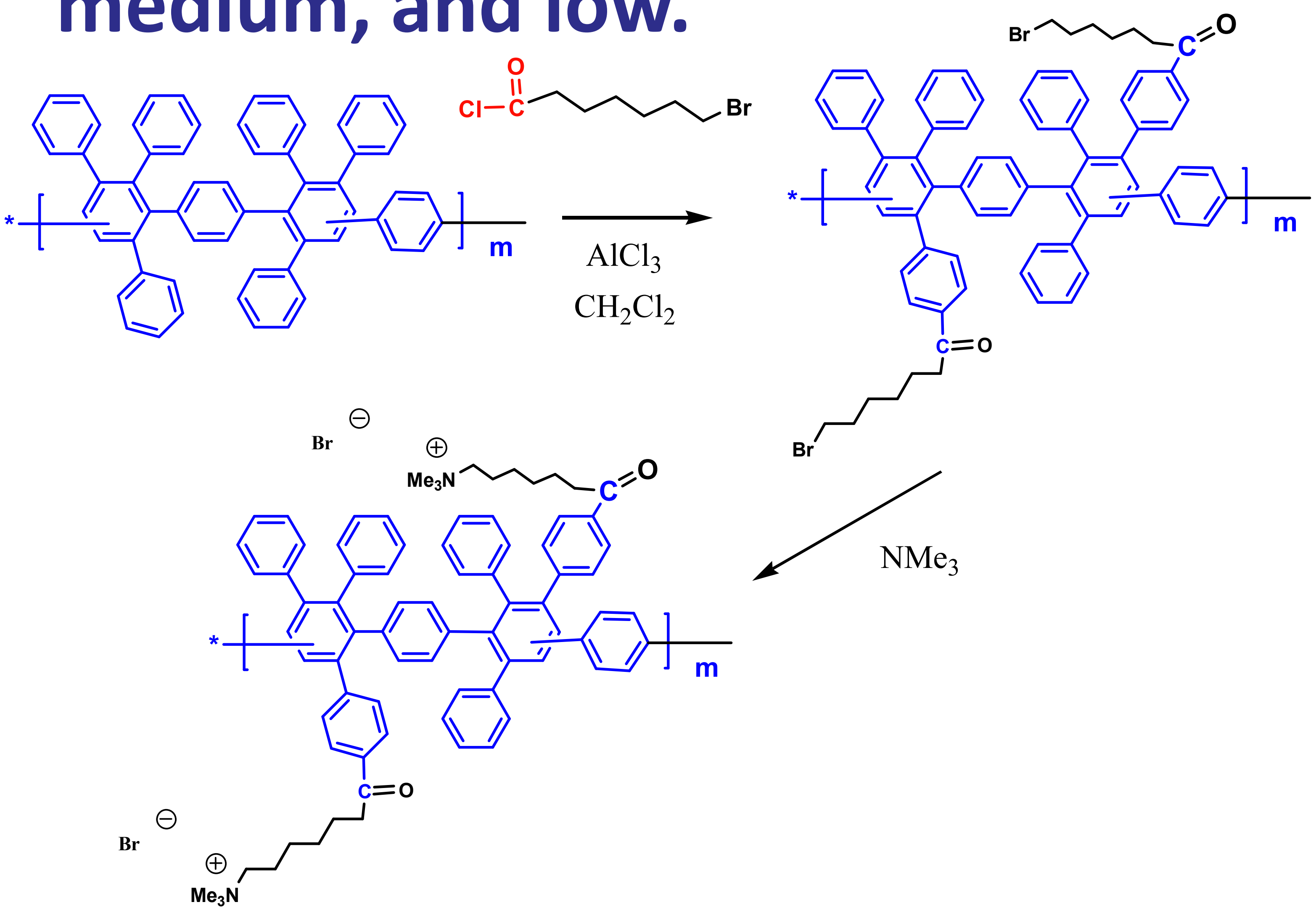


Highlight: Sandia membranes have increased chemical and temperature stability over commercial materials.



Membrane Ion Content

Membranes contain a polyphenylene backbone with pendant ionic groups; ionic content was varied qualitatively high, medium, and low.



<u>Low Ion Content</u>
Very brittle sample–no data

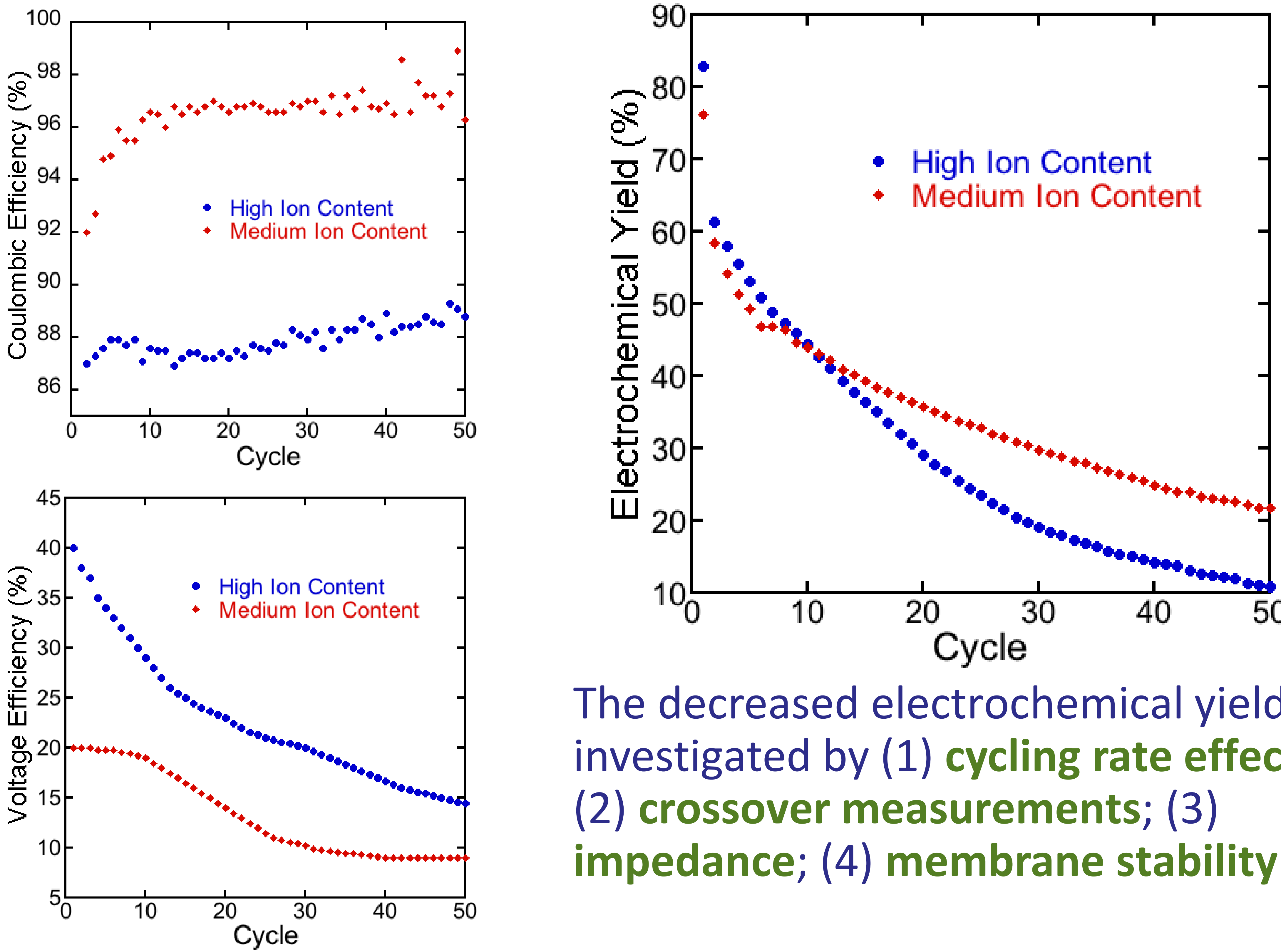
<u>Medium Ion Content</u>
Best Coulombic efficiency
Best electrochemical yield
Least crossover

<u>High Ion Content</u>
Good Coulombic efficiency
High crossover

The membranes are prepared by a propriety process using Friedel Crafts acylation with a ketone to add pendant ammonium groups and simultaneously lightly crosslink the polymer backbone.

Small, Pratt, Fujimoto, and Anderson, *J. Electrochem. Soc.*, **2016**, A5106.

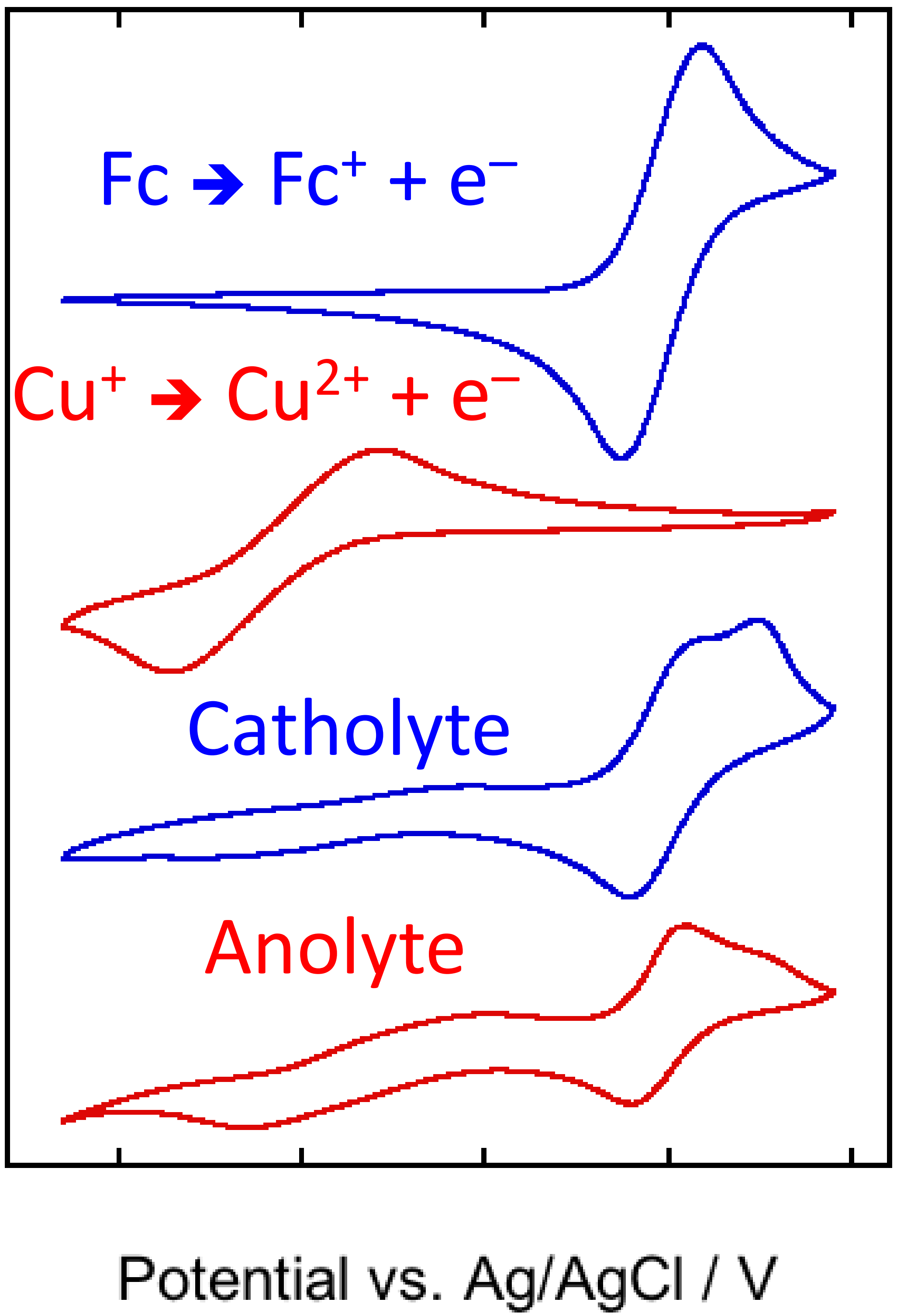
Cell Cycling High/Medium Ion Content

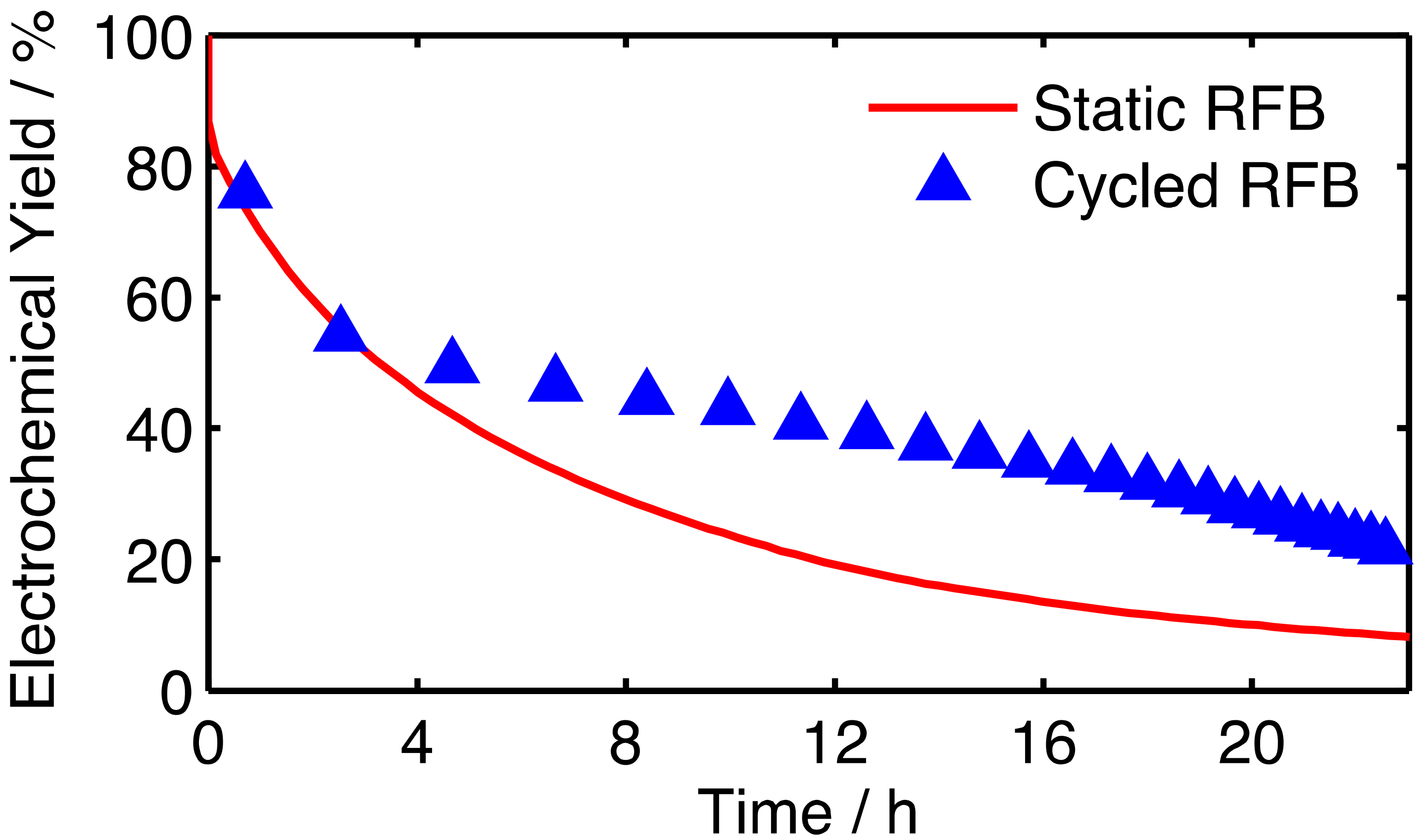


The decreased electrochemical yield was investigated by (1) **cycling rate effects**; (2) **crossover measurements**; (3) **impedance**; (4) **membrane stability**.

Small, Pratt, Fujimoto, and Anderson, *J. Electrochem. Soc.*, **2016**, A5106.

Post Cycling Studies

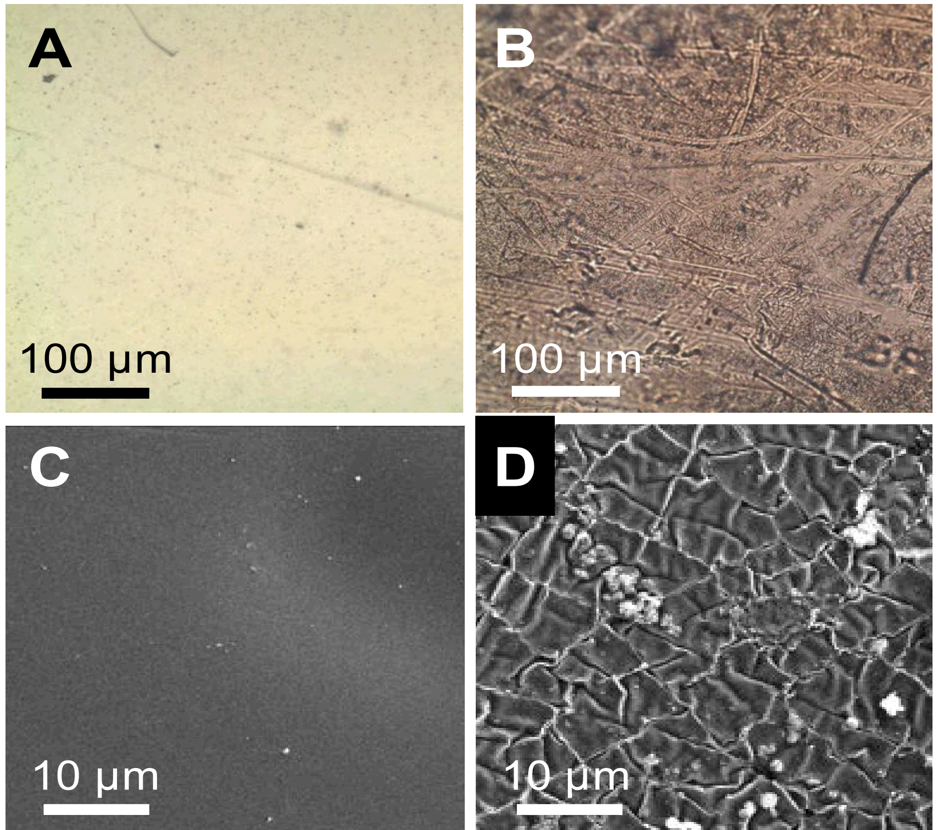




- Theoretical electrochemical yield for a static cell was determined from the OCP and the Nernst equation.
- The overlay of the static and cycled data show that crossover was responsible for the lowered electrochemical yield.

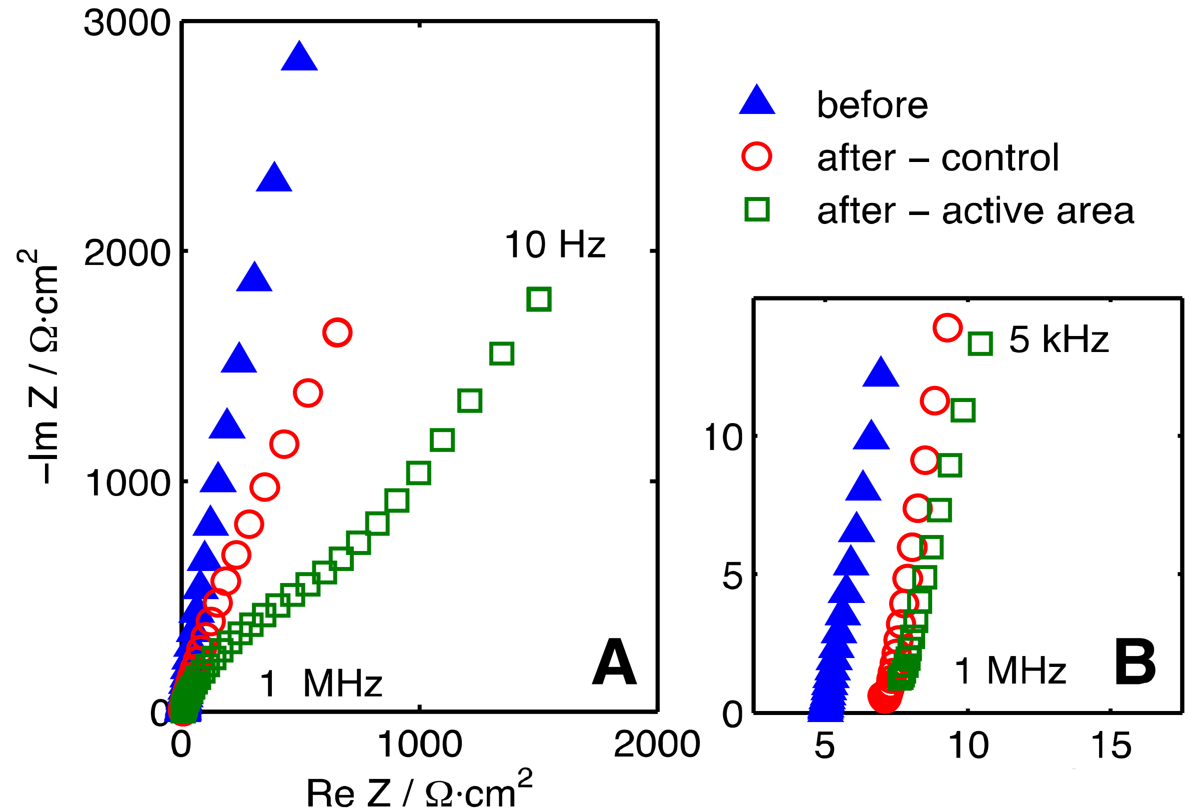
Small, Pratt, Fujimoto, and Anderson, *J. Electrochem. Soc.*, **2016**, A5106.

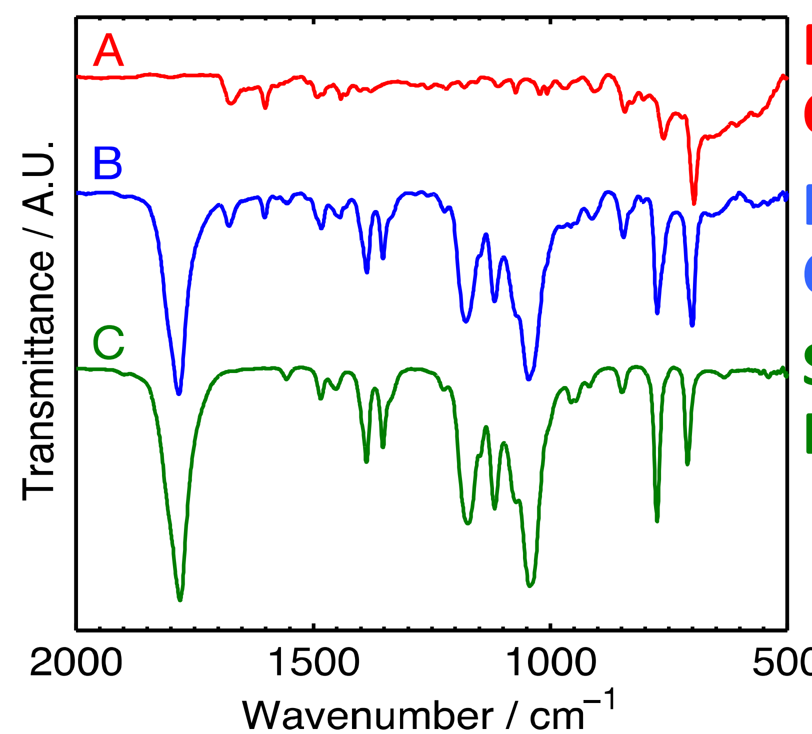
Chemical Stability



Before Cycling | **After Cycling**

- SEM and EDS data suggest that there was some decomposition of the ionic liquid.
- The increased resistance after cycling is attributed to the formation of a film on the surface of the membrane.





Membrane Before Cycling

Membrane After Cycling

Supporting Electrolyte

Infrared data shows membrane is stable.

Small, Pratt, Fujimoto, and Anderson, *J. Electrochem. Soc.*, **2016**, A5106.

Conclusions

Metallic ionic liquids address:

- **Energy density** through higher metal concentrations and wider voltage windows
- **Life cycle costs** through earth abundant materials
- **Round trip efficiency** through high electrochemical reversibility and conductive membranes
- **Cycle life** through chemically stable materials

Future Work:

- Move toward a more viable system through–
  - Addressing **capacity fade** through tunable membranes chemistries
  - Further increasing cell voltages through new chemistries-Leo Small's talk is next.

Thank you to the DOE OE and especially Dr. Imre Gyuk for his dedication and support to the ES industry and Sandia's ES Program.

Questions?

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