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Adv. Materials for Ionic Liquid Flow Battery

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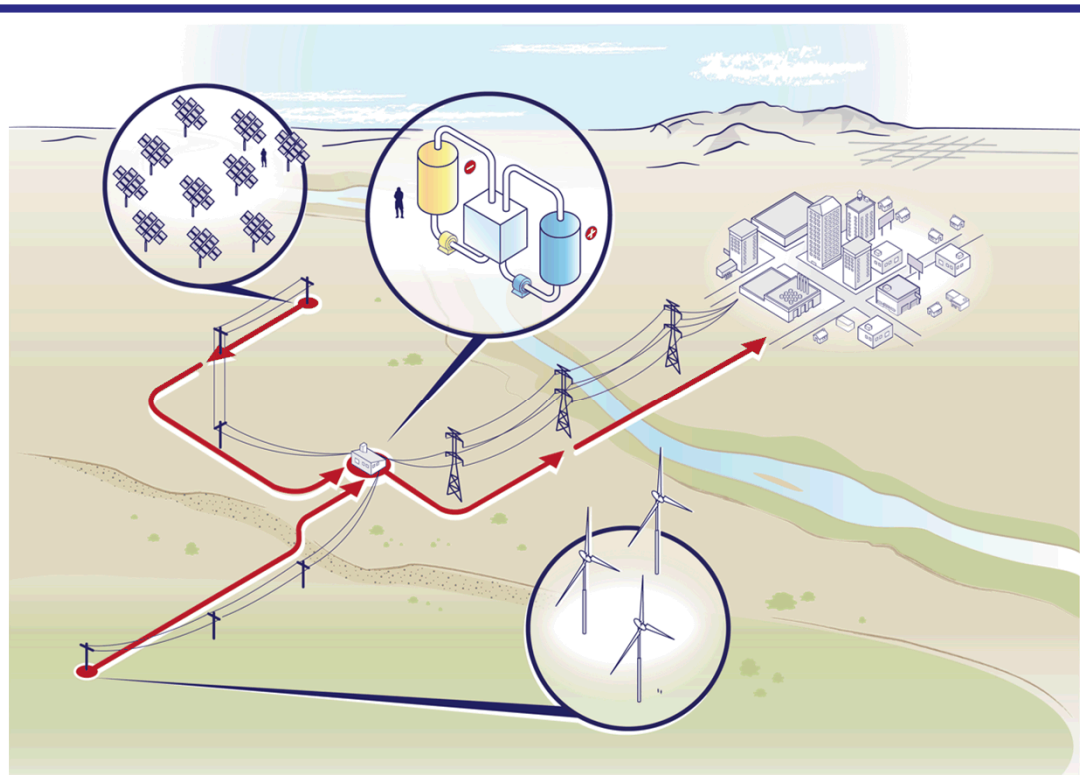


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Project Overview

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 $\text{RFB} \approx \frac{1}{2}nFV_{\text{cell}}C_{\text{active}}$

$$\text{ED}_{\text{AQ}} = \frac{1}{2}1F1.5_{\text{cell}}2_{\text{active}} = 1.5F$$

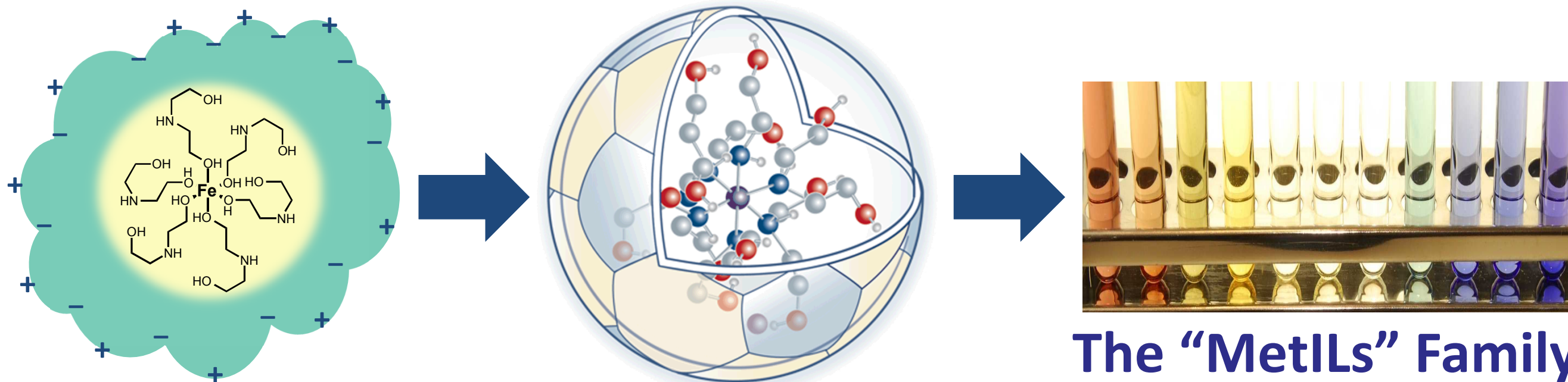
$$\text{ED}_{\text{IL}} = \frac{1}{2}2F2_{\text{cell}}3_{\text{active}} = 6.0F$$

Potential for **four-fold** improvement

2015 Highlights:

- First ionic liquid RFB patent
- Membrane conductivity paper
- Significantly increased current densities

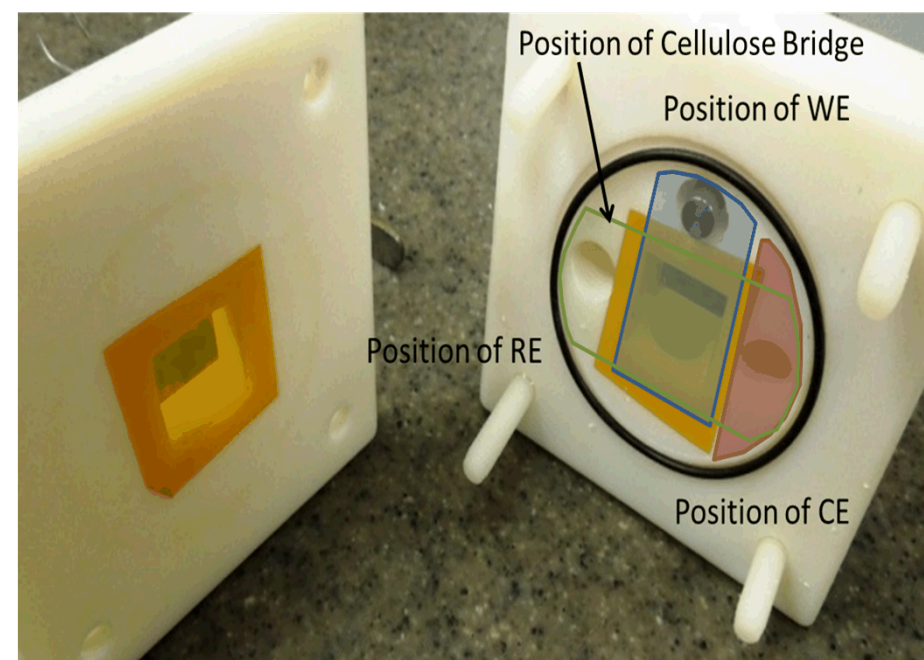
Metal Ionic Liquid (MetIL) Concept



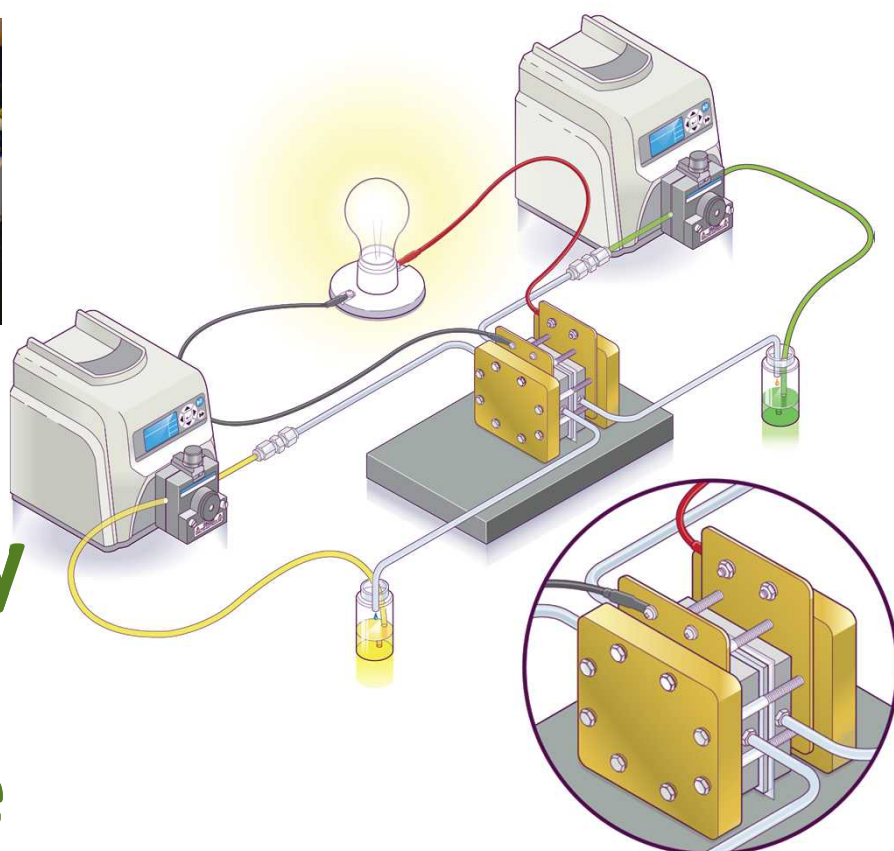
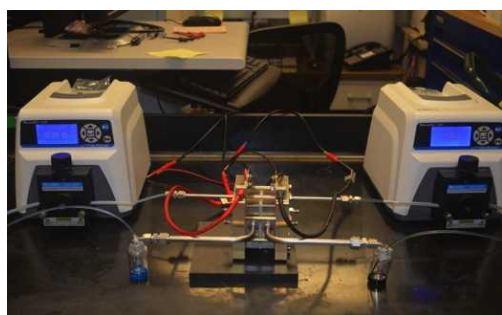
The “MetILs” Family

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.

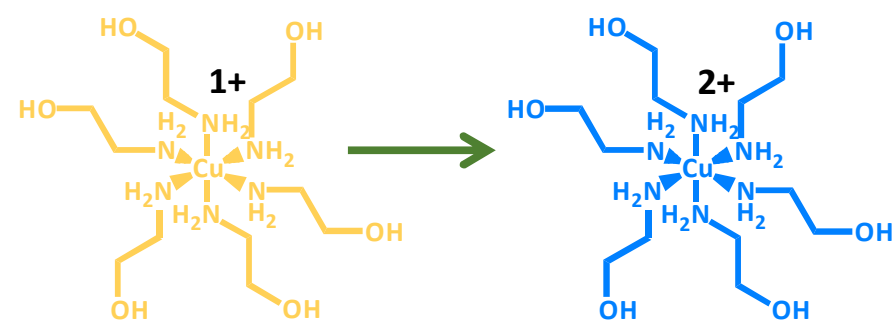


Ionic Liquid Battery Prototype



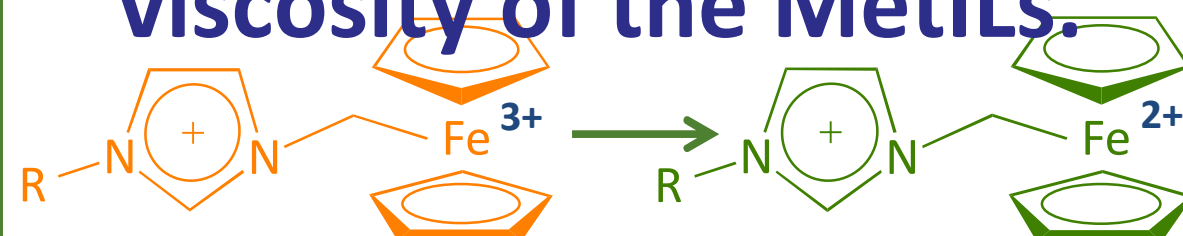
Laboratory
Scale
Prototype

- 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 °C to improve the viscosity of the MetILs.



Negative Half-Cell Reaction

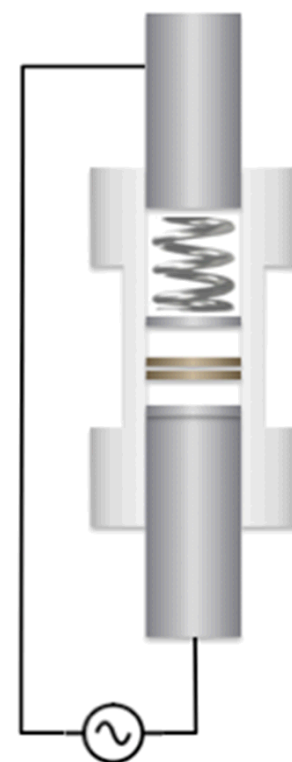
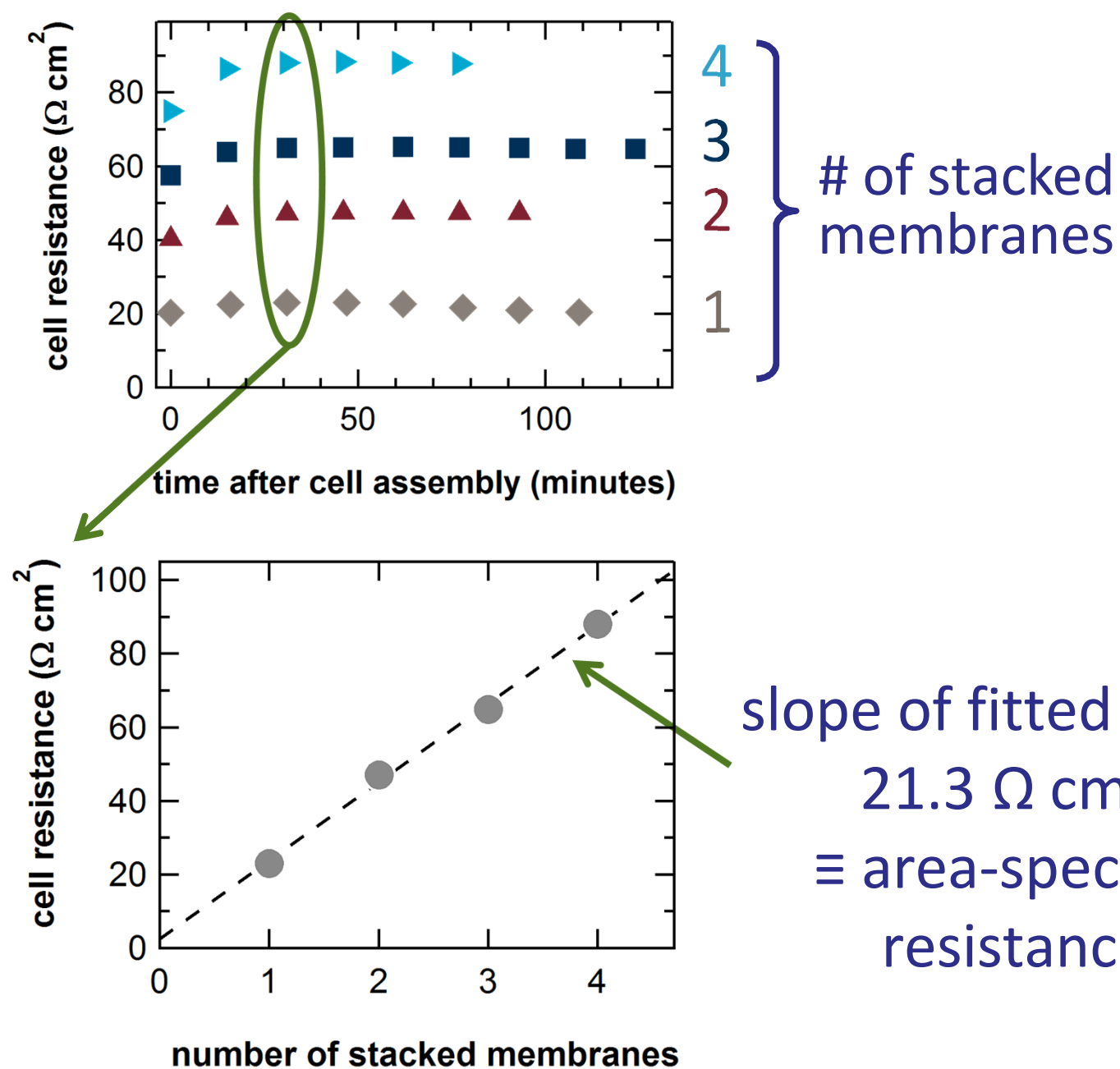
1.5 V



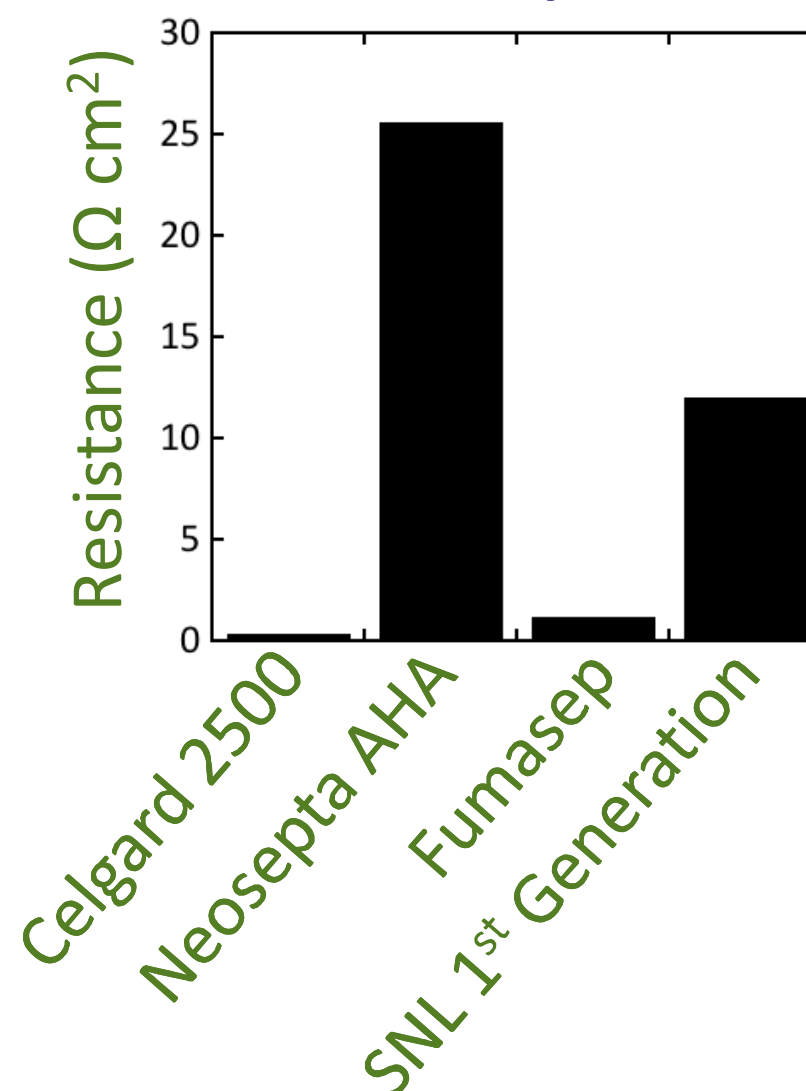
Positive Half-Cell Reaction

Highlight: First ionic liquid flow battery patent awarded in 2015

Membrane Through-Plane Resistance

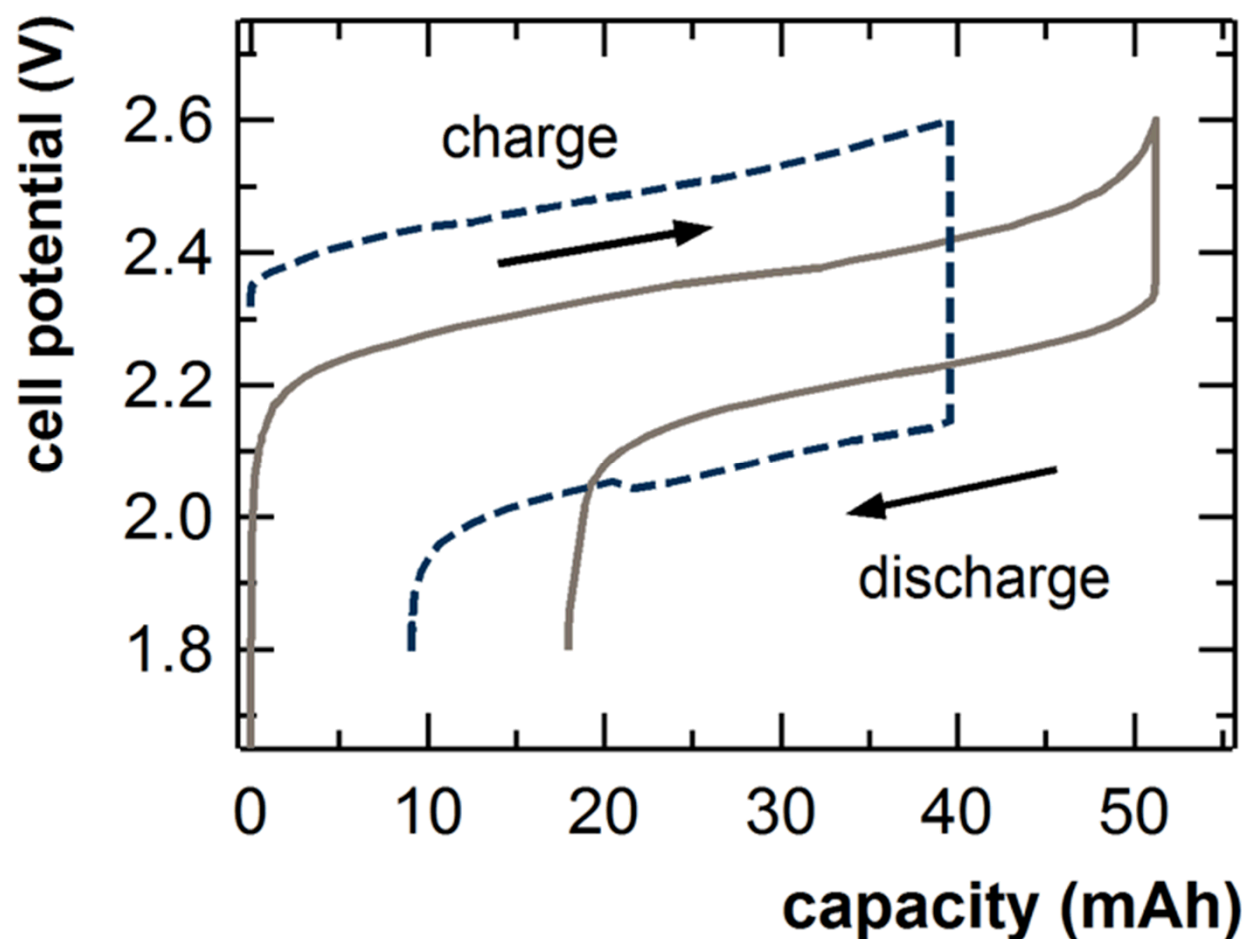


Membranes in 0.5 M TEA-BF₄/ACN

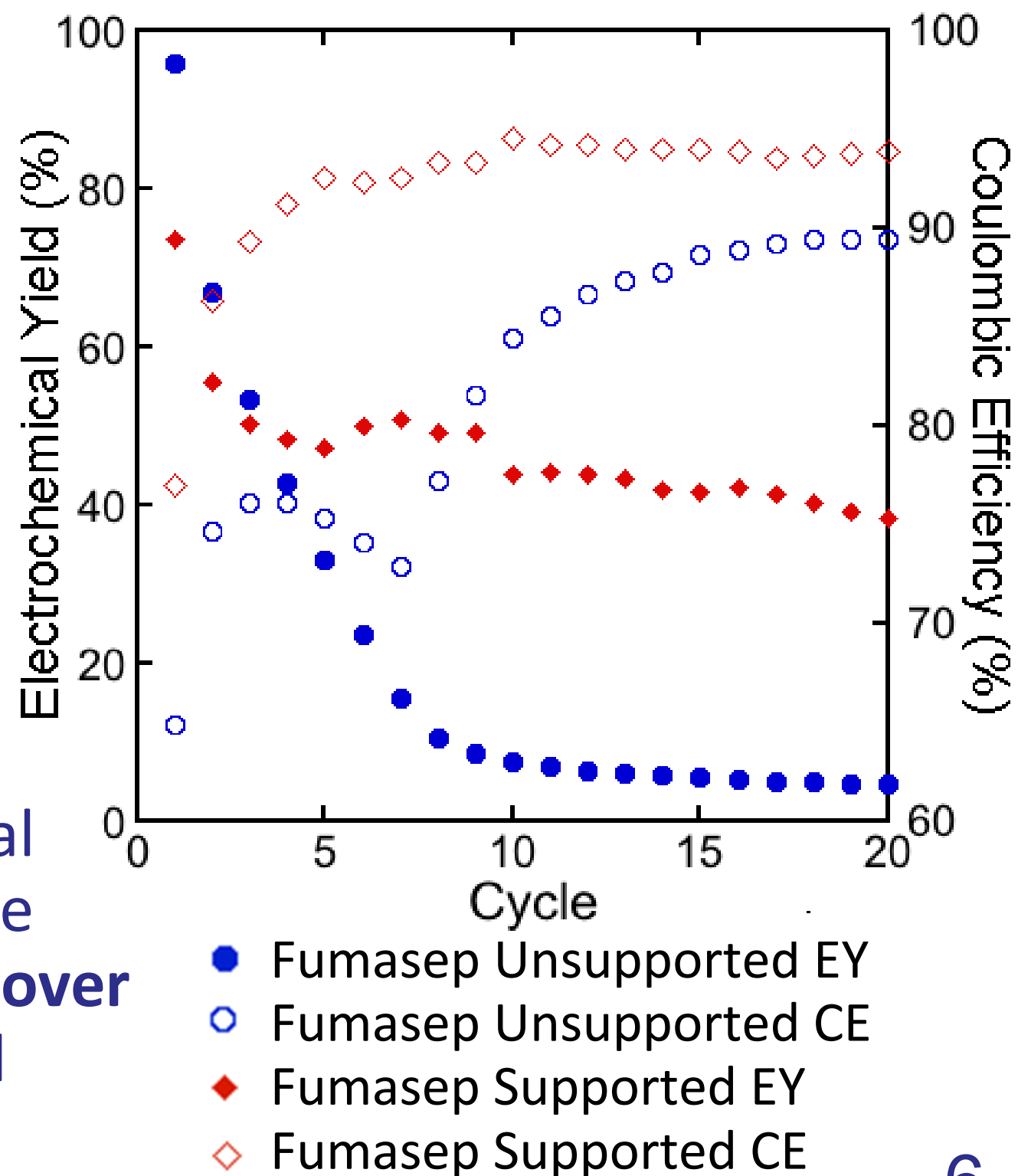


Different membranes in TEA-BF₄ illustrate a wide variability in resistances that in turn are solvent dependent.

Flow Cell Studies

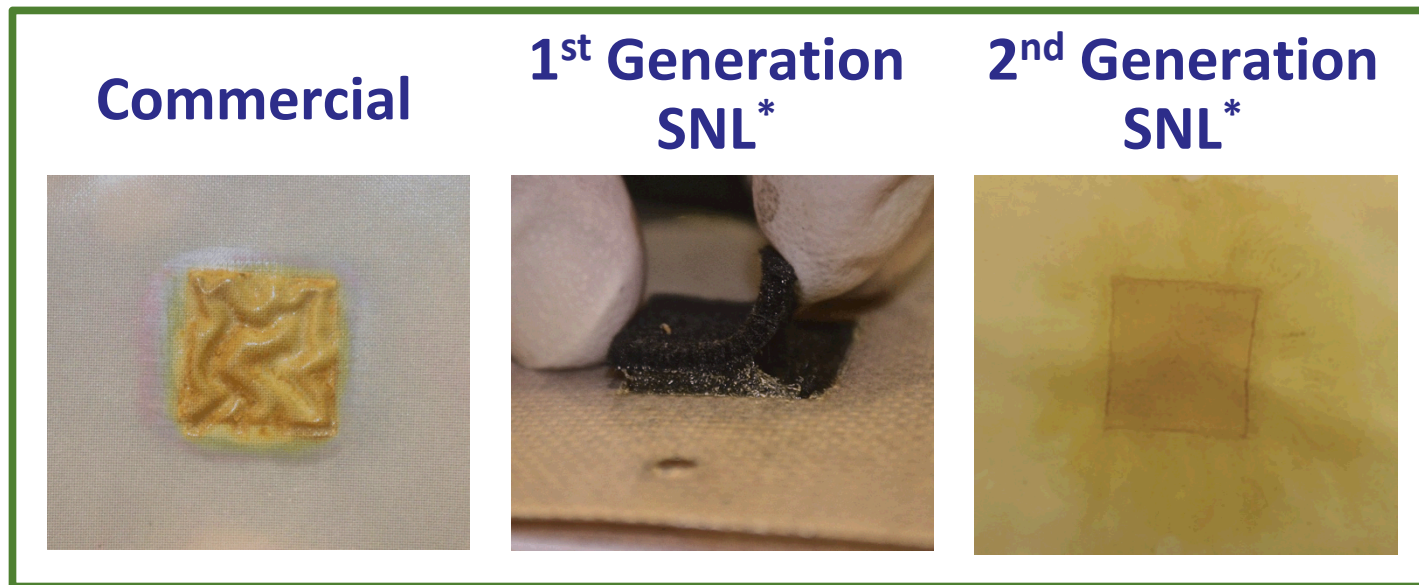


Highlight: The increased mechanical stability of the supported membrane suppressed **solvent-mediated crossover** and enabled higher electrochemical yields and Coulombic efficiencies.

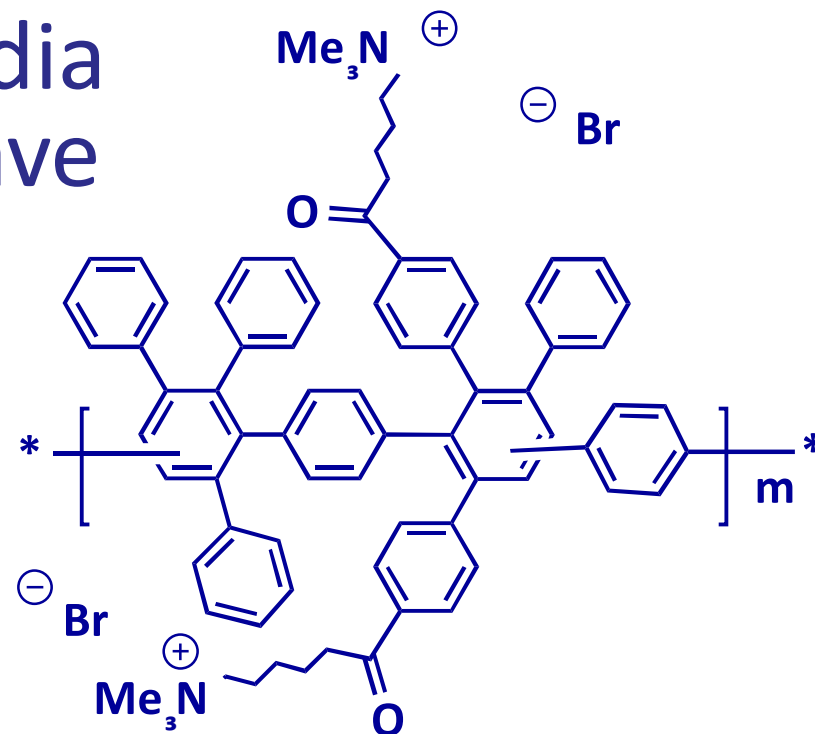


Membranes

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

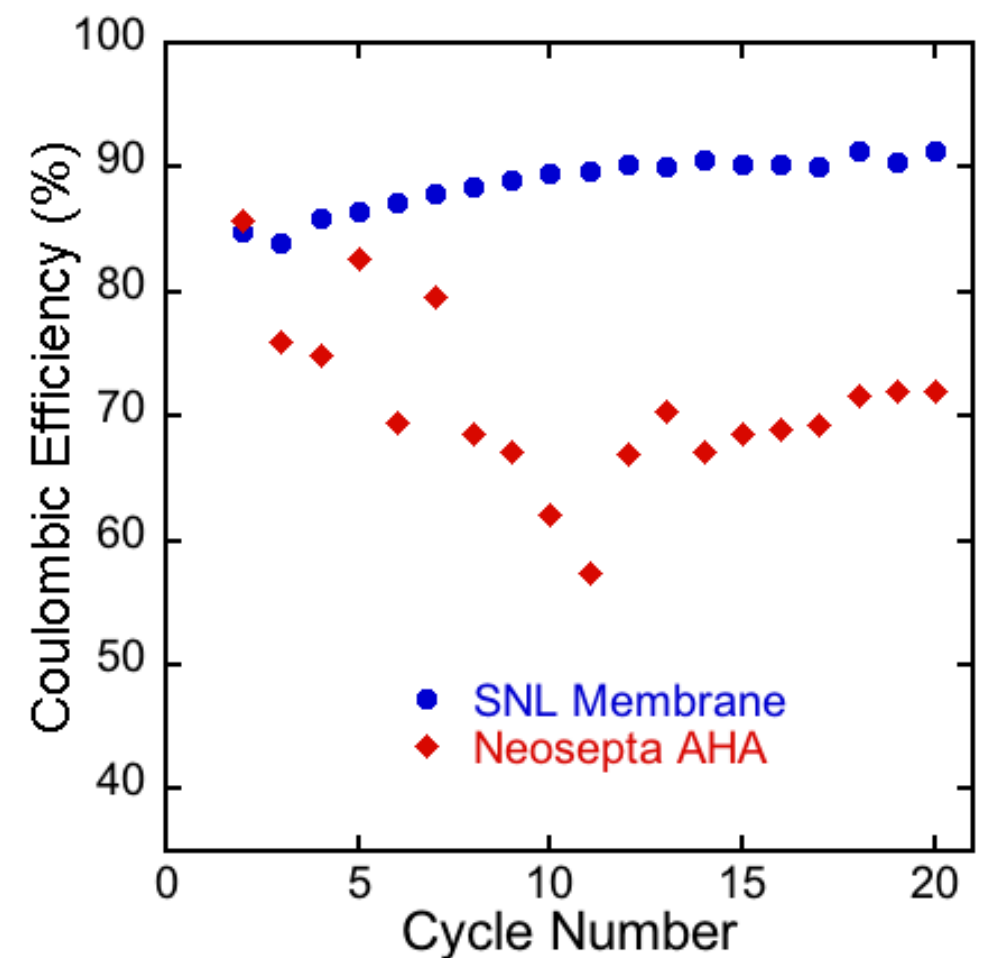


Highlight: Sandia membranes have increased chemical and temperature stability over commercial materials.



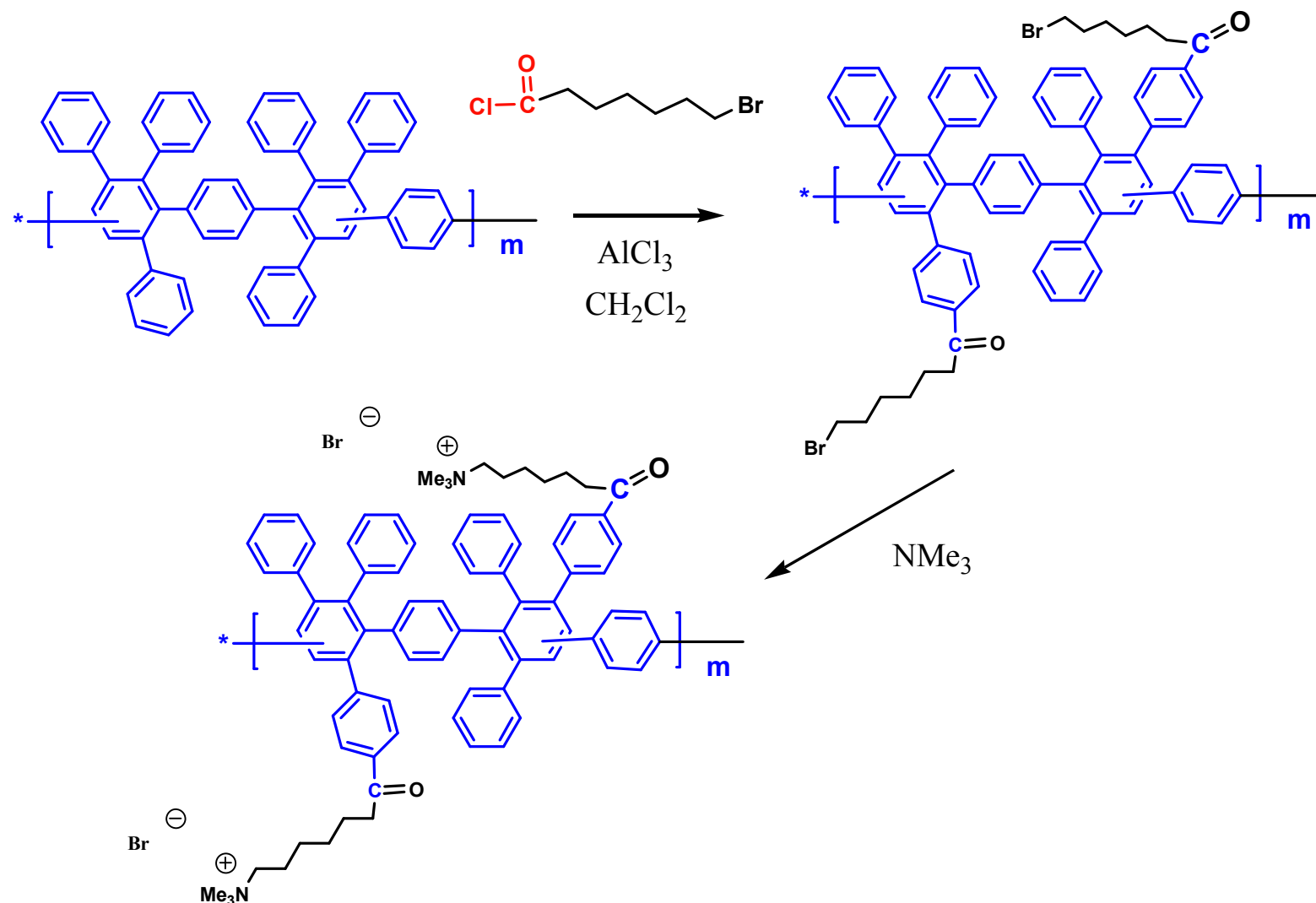
1st Generation Results:

- Coulombic efficiency increased from 70% to 90%.
- Current density increased from 0.5 to 10 mA/cm².



Membrane Ion Content

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



Low Ion Content

Very brittle sample—no data

Medium Ion Content

Best Coulombic efficiency

Best electrochemical yield

Least crossover

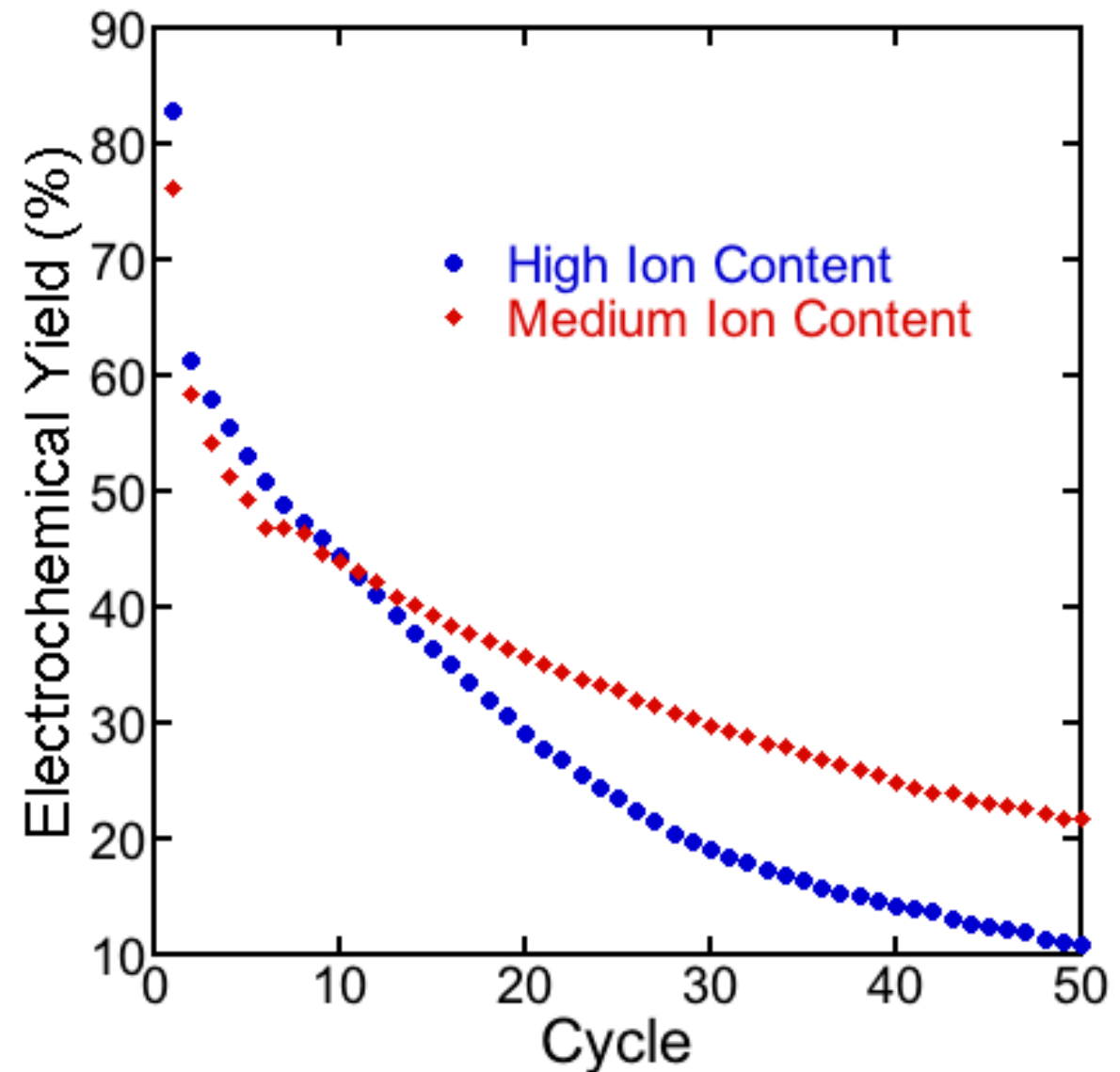
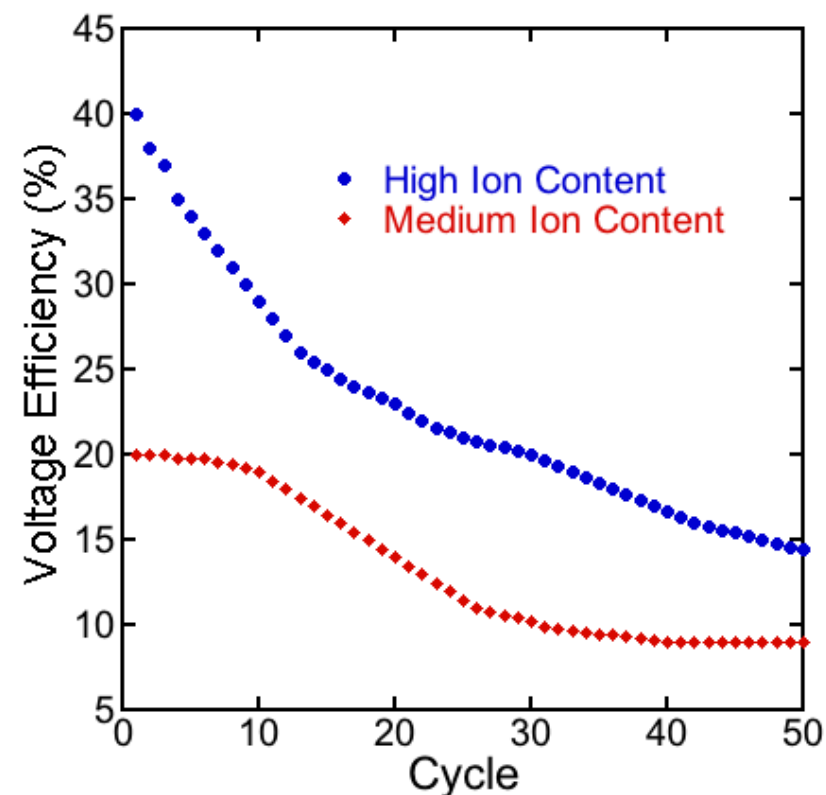
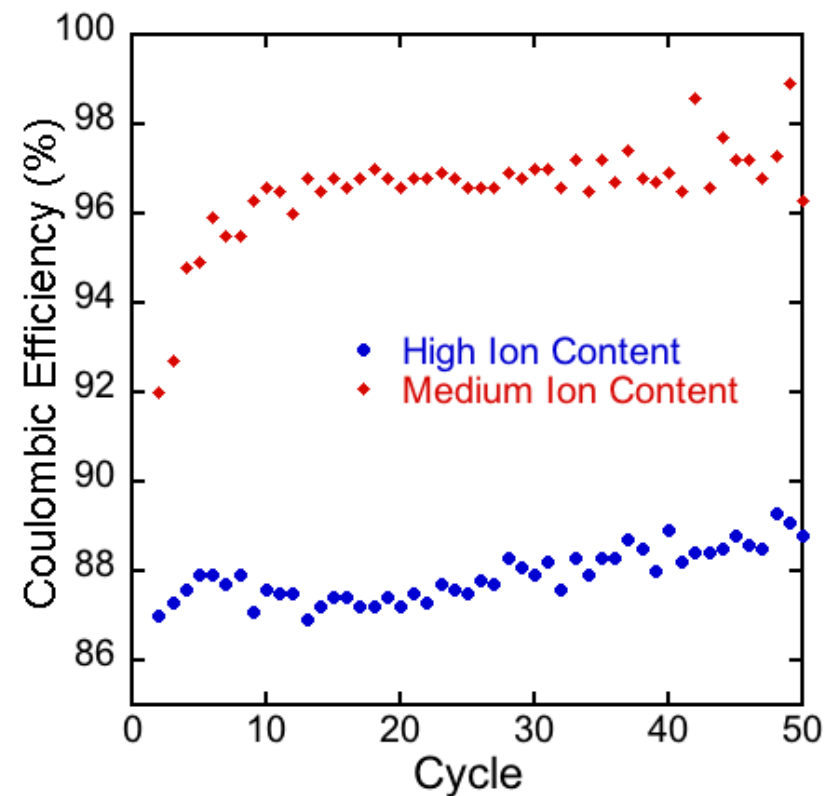
High Ion Content

Good Coulombic efficiency

High crossover

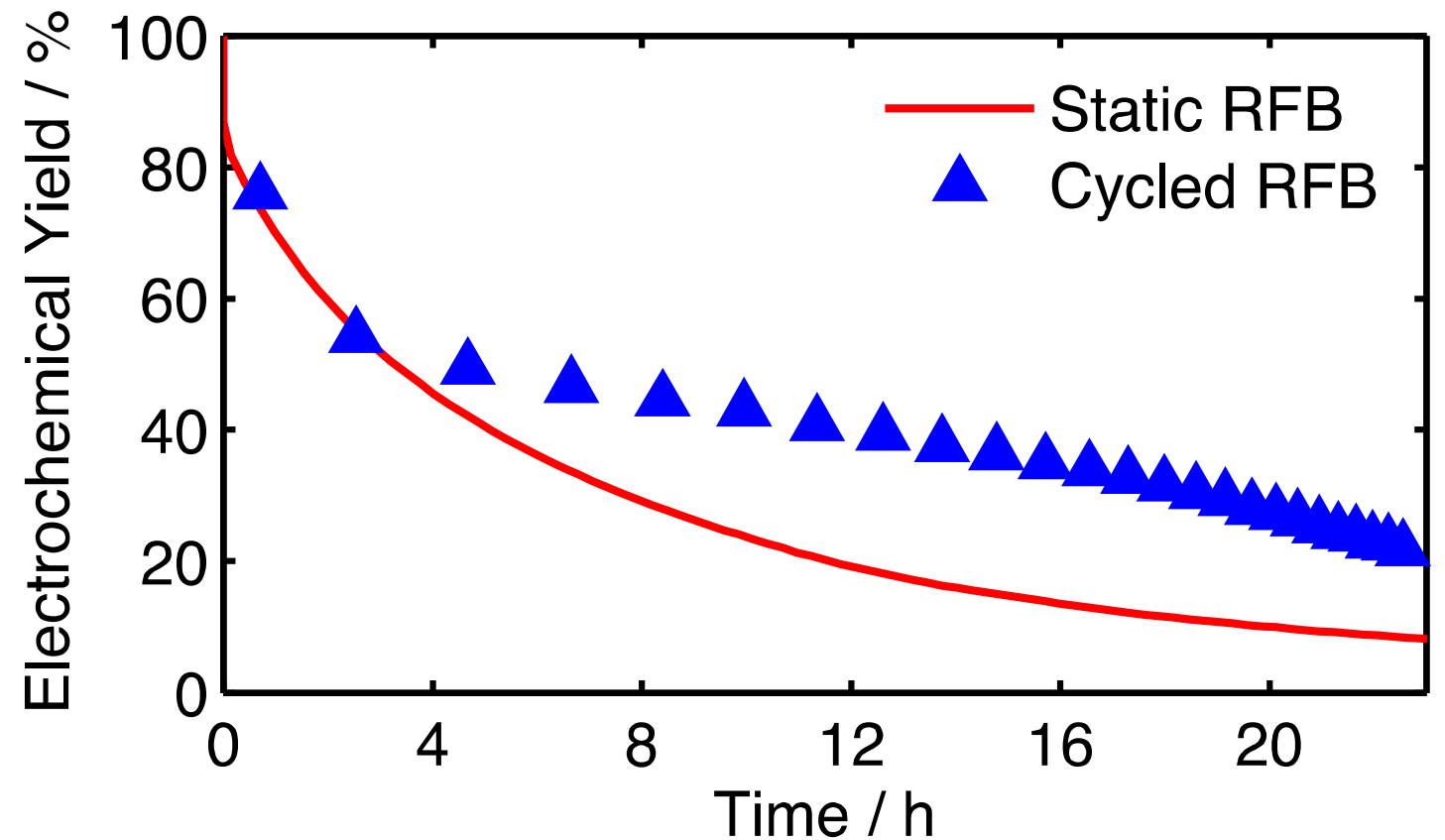
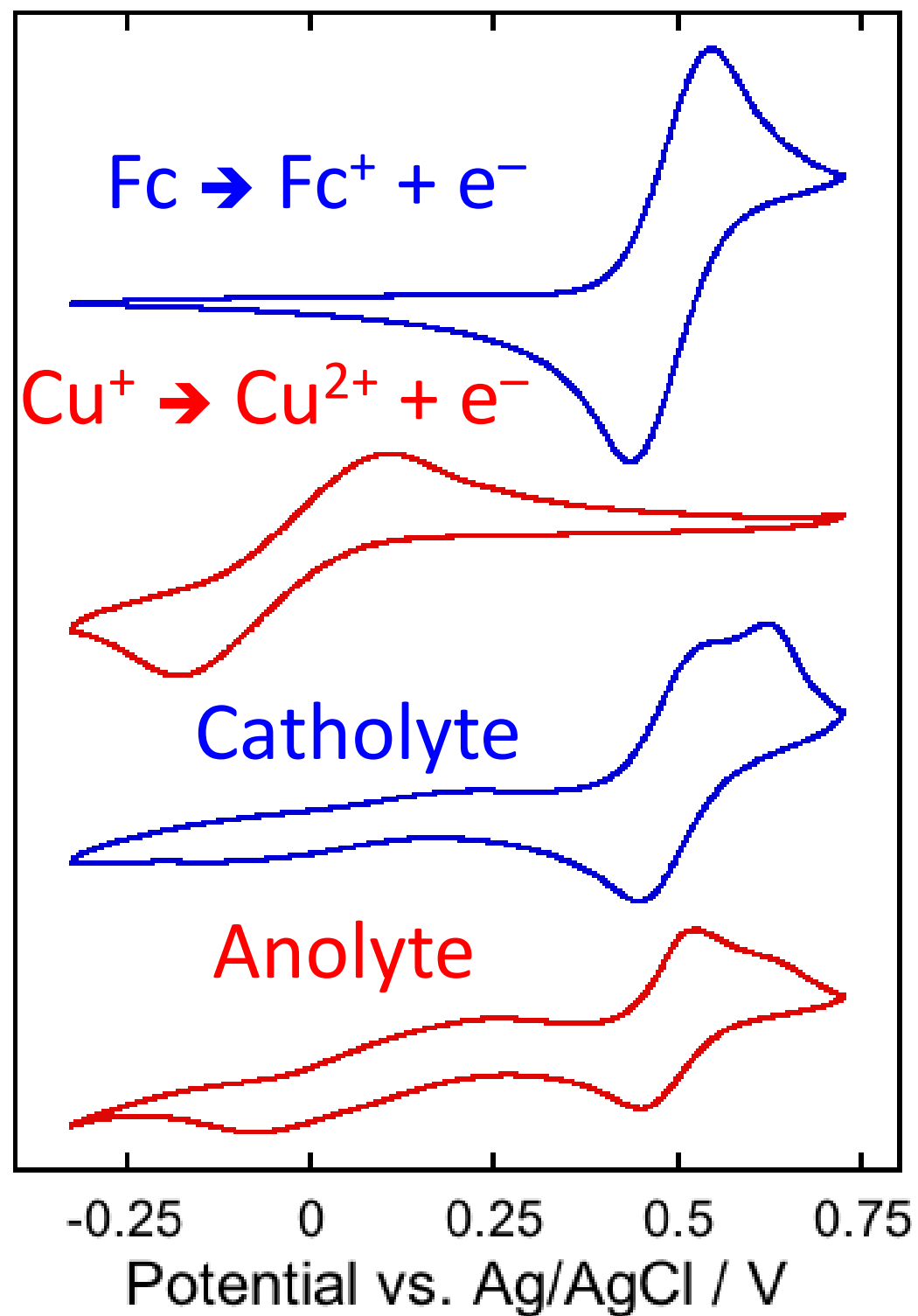
The membranes are prepared by a propriety process using Friedel Crafts acylation with a ketone to add pendant ammonium groups and simultaneously lightly crosslink the polymer backbone.

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**.

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.

Summary/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

FY15 Accomplishments:

- Developed new polyphenylene membranes with 20% increase in Coulombic efficiency and 30% increase in electrochemical yield
- As of FY15, published 12 articles, 15 conference papers, two journal covers, and submitted 4 patents (one awarded)

FY16 Plans:

- Move toward a more viable system through—
 - Addressing **capacity fade** through tunable membranes chemistries
 - Further increasing cell voltages through new lead and cobalt electrolytes

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Questions?

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