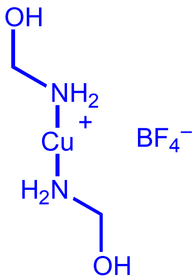

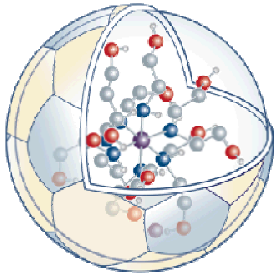

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SAND2013-8693C

Tailorable Ionic Materials for Higher Energy Density Redox Flow Batteries

EESAT, Tuesday, October 22, 2013

Travis Anderson, Harry Pratt, Jonathan Leonard, and Nick Hudak, Sandia National Laboratories

OFFICE OF ELECTRICITY DELIVERY & ENERGY RELIABILITY

Imre Gyuk, Energy Storage Program, Office of Electricity Delivery and Energy Reliability

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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Project Goals and Approach

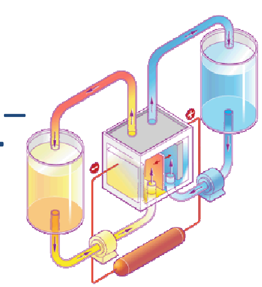
Sandia National Laboratories

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 selection of ligands and anions for lower viscosity AND new SNL rapid prototyping with 3-D printing to quickly evaluate membranes, solutions, and cell designs.**

Target Metrics

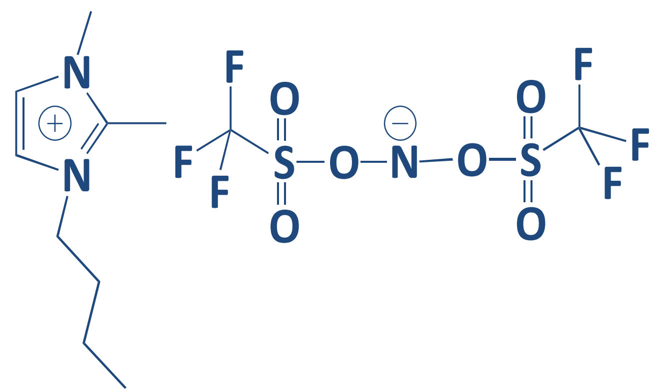
- 59 mV/n separation (n > 1)
- Viscosity < 500 cP
- Conductivity > 0.5 mS cm^{-1}
- Open Circuit Potential > 1.5 V

MetIL⁻  ⁺MetIL

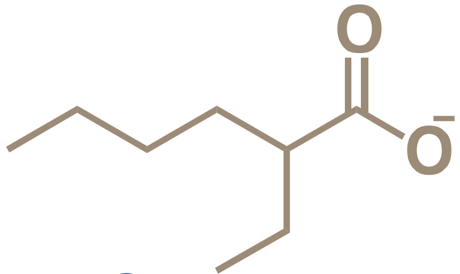
$$\text{Energy Density}_{RFB} \approx \tfrac{1}{2} nFV_{cell}c_{active}$$

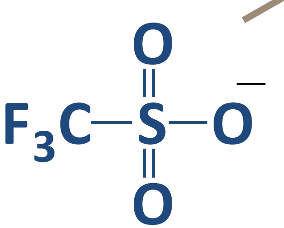
$$ED_{AQ} = \tfrac{1}{2}1F1.5_{cell}2_{active} = 1.5F$$

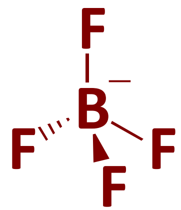
$$ED_{IL} = \tfrac{1}{2}2F2_{cell}3_{active} = 6.0F$$



Role of the Anion



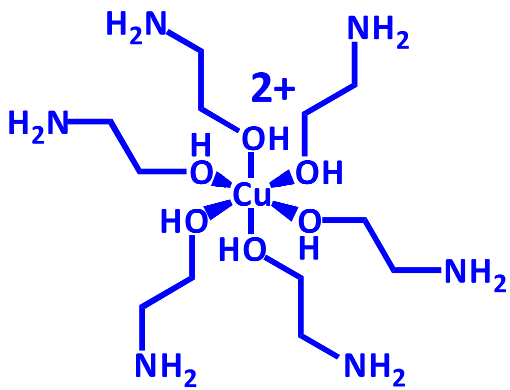


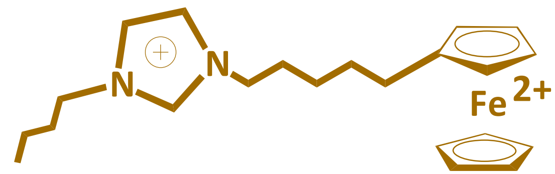


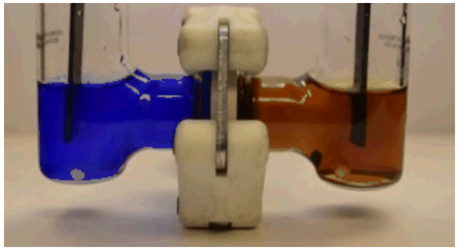
EA ethanolamine
DEA diethanolamine

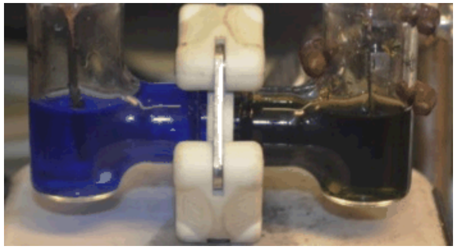
Ligand	Anion 1	Anion 2	State at 25 °C	σ [mS/cm]	ΔE [mV]
EA			Liquid	0.207	244
EA			Solid	---	158
EA			Solid	---	158
EA			Liquid	6.80	102
EA			Solid	---	256
EA			Liquid	0.586	187
DEA			Liquid	0.014	522
DEA			Liquid	0.067	566
DEA			Solid	---	507
DEA			Liquid	1.05	150
DEA			Liquid	0.210	159
DEA			Liquid	0.142	201

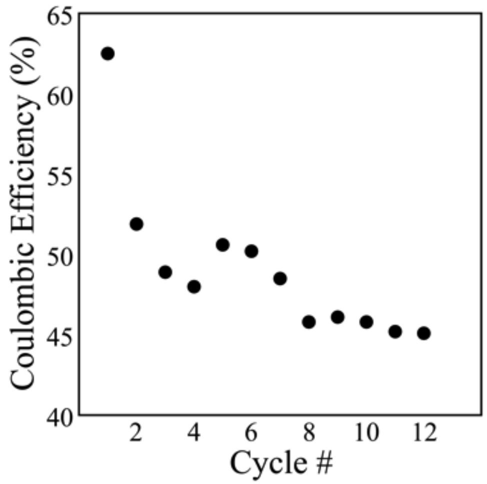
Static Cell Testing

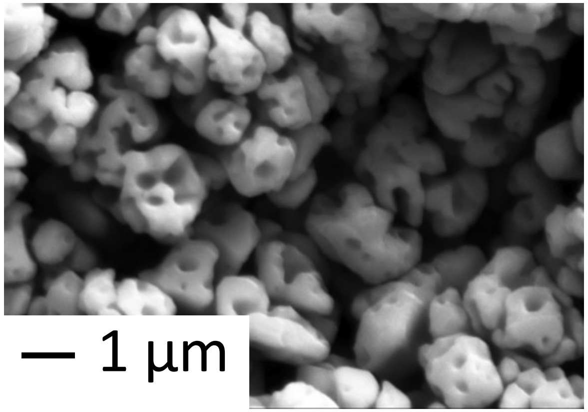












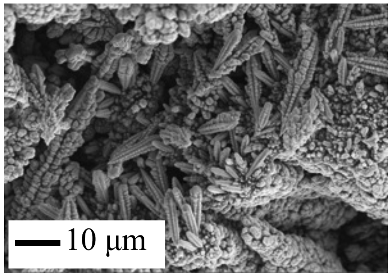
Partially irreversible copper plating on the electrode results in a lower coulombic efficiency. However this reversibility can be controlled by utilizing different anions.

Copper and Iron are relatively plentiful and inexpensive.

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

Copper Plating

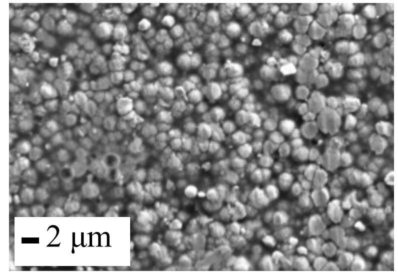
EA



BF_4^-

Ligand Change

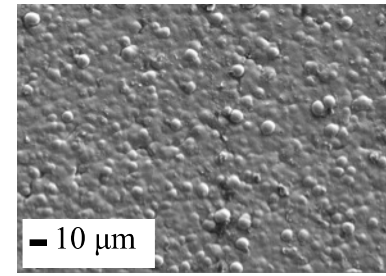
DEA



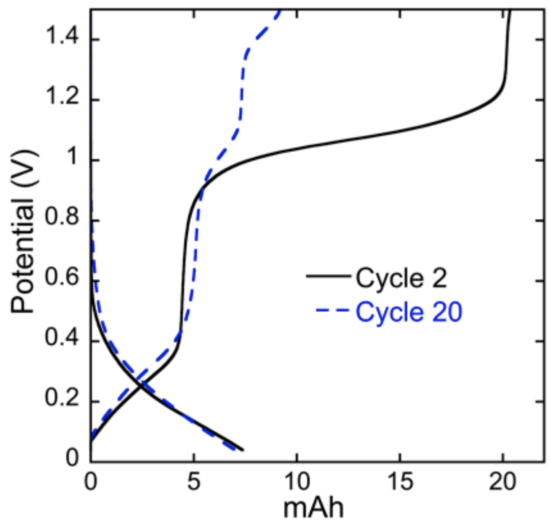
BF_4^-

Anion Change

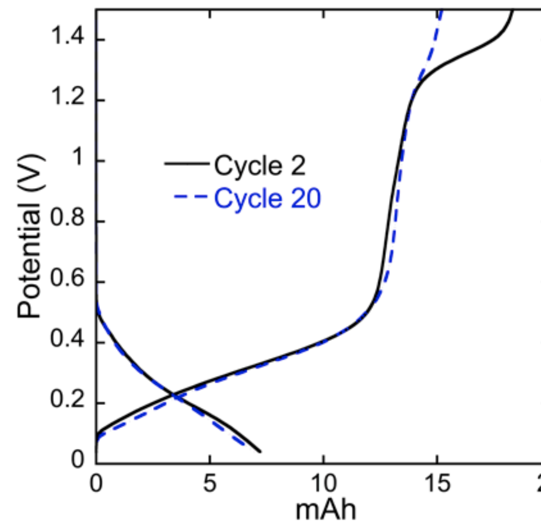
DEA



$CF_3SO_3^-$



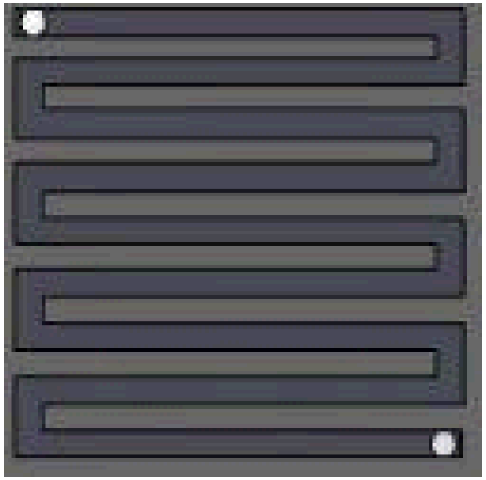
Ligand Change

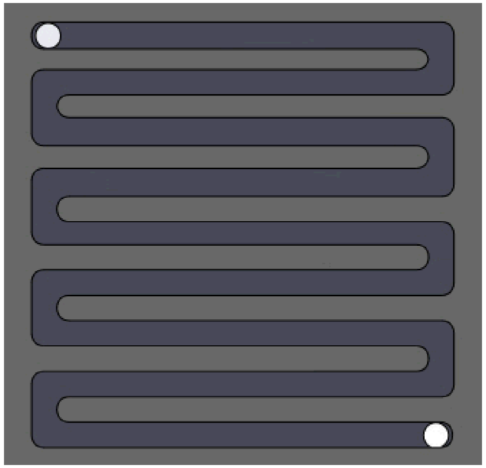


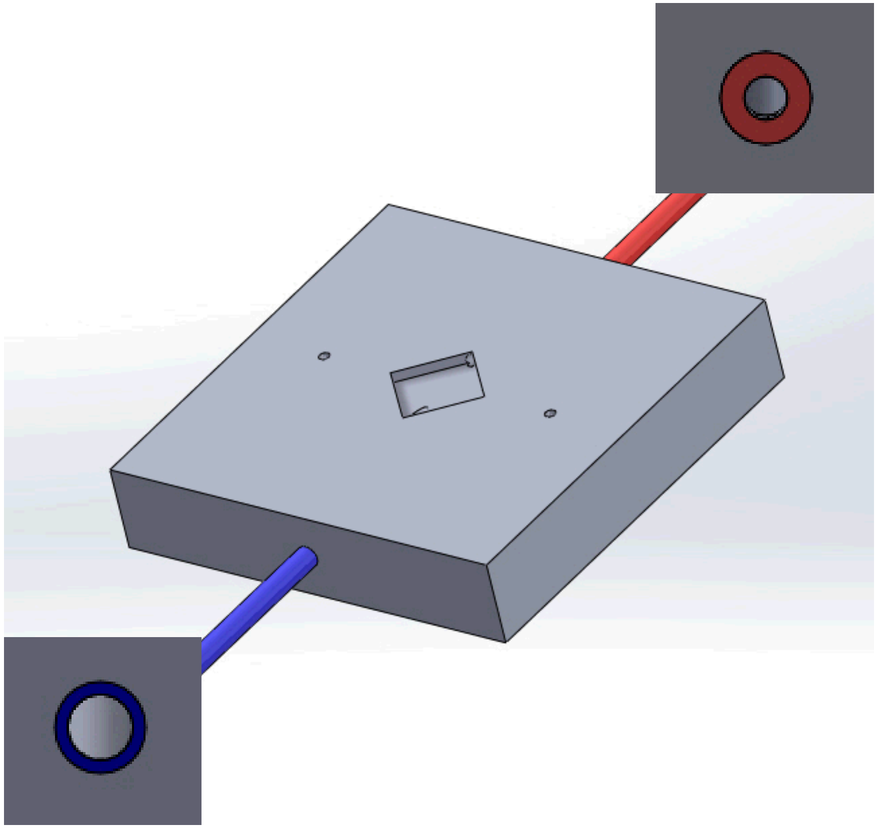
Significant improvements in the battery performance were achieved and three oxidation states of copper have now been utilized.

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

Design Considerations

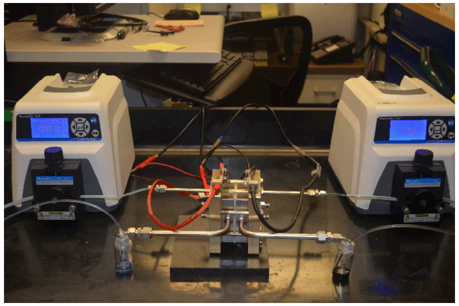




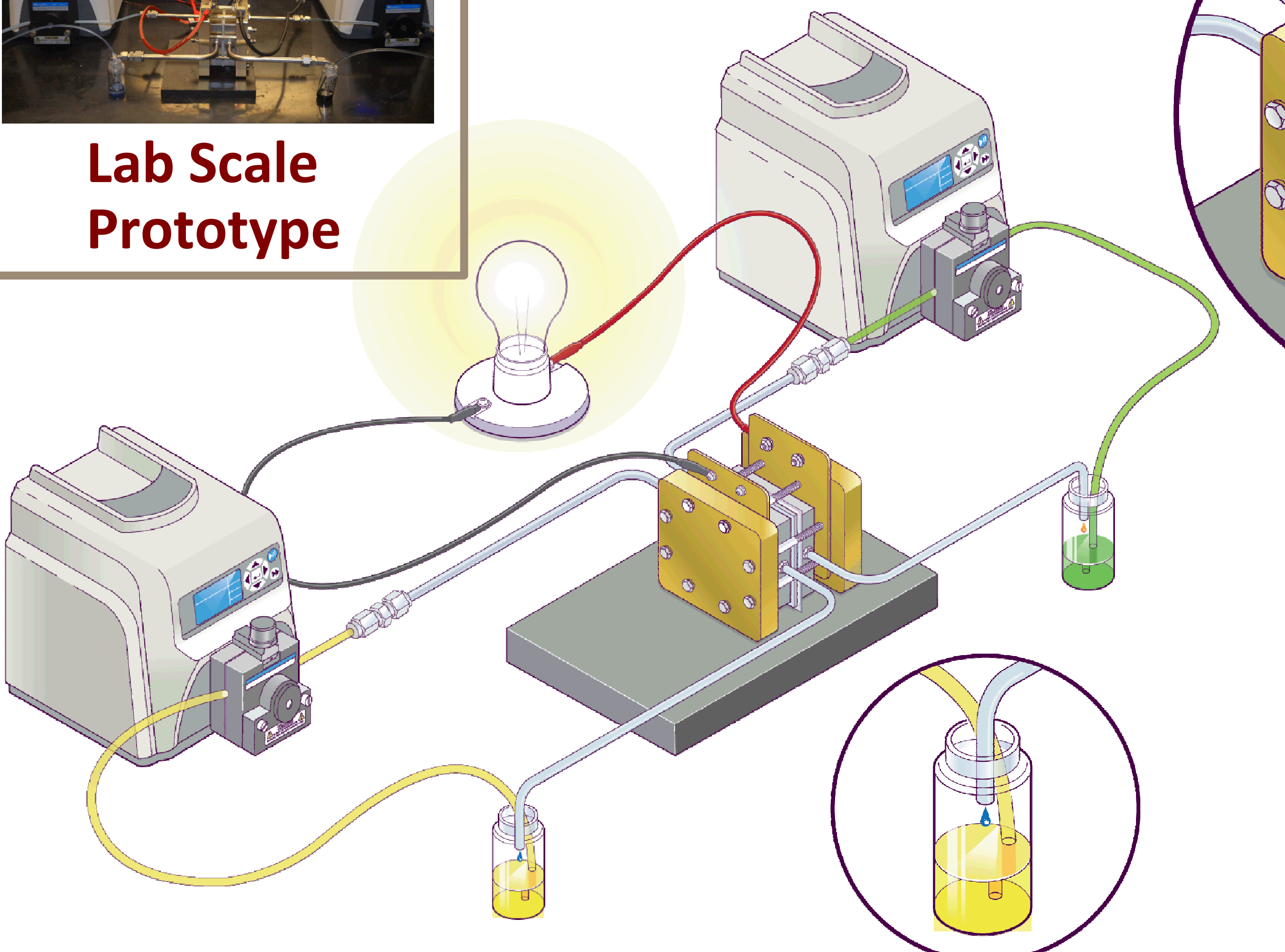


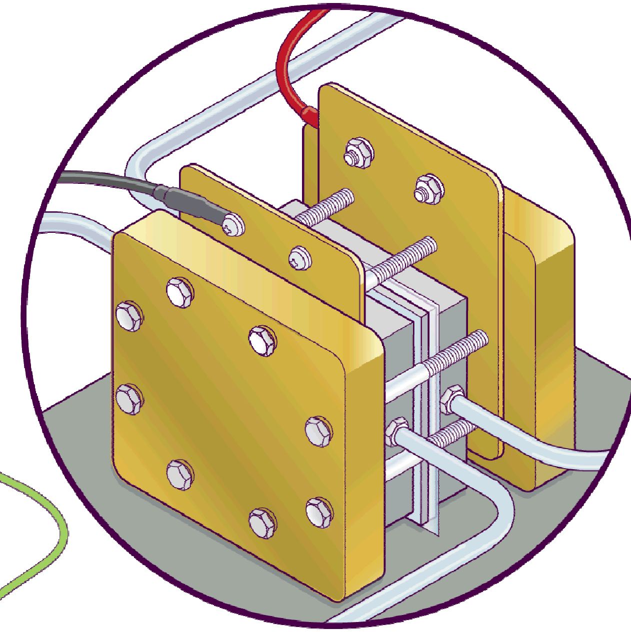
Back pressures were reduced from 100 psi to zero with a 500 cP fluid. Membranes typically rupture at 40-60 psi.

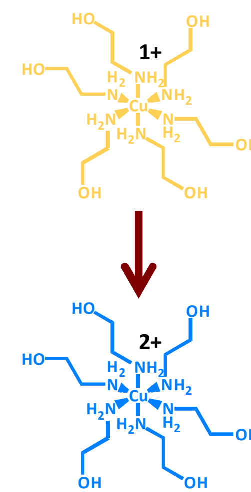
Ionic Liquid RFB Prototype



Lab Scale Prototype

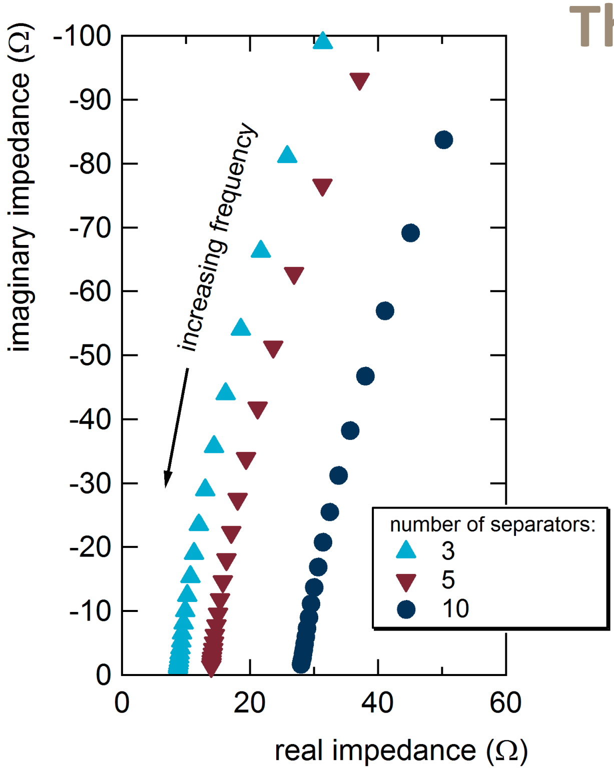






Membrane/Separator Characterization

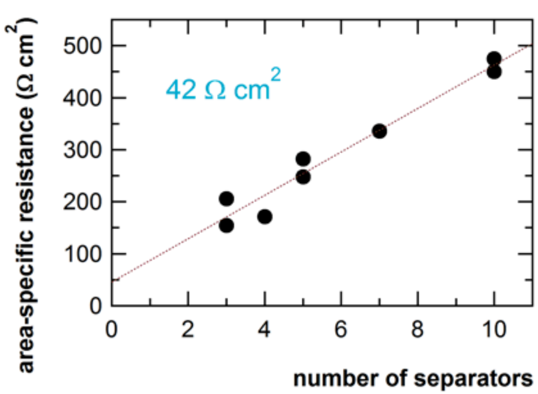
Electrochemical Impedance Spectroscopy Used to Measure Through-Plane Resistance



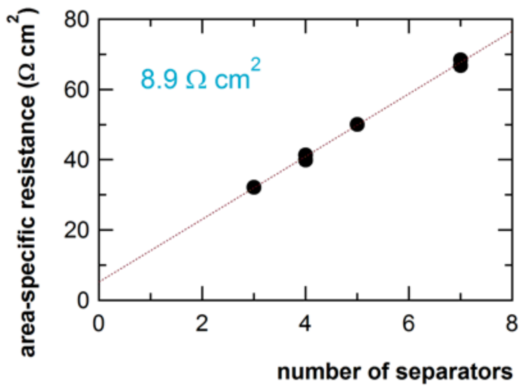
- Impedance spectra gives through-plane resistance of cell, which includes contact resistance with electrodes
- Several membranes are stacked, and a plot of resistance *vs.* number of membranes is linear.
- Technique verified by comparing to published results.

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

Nuclepore (15-nm)



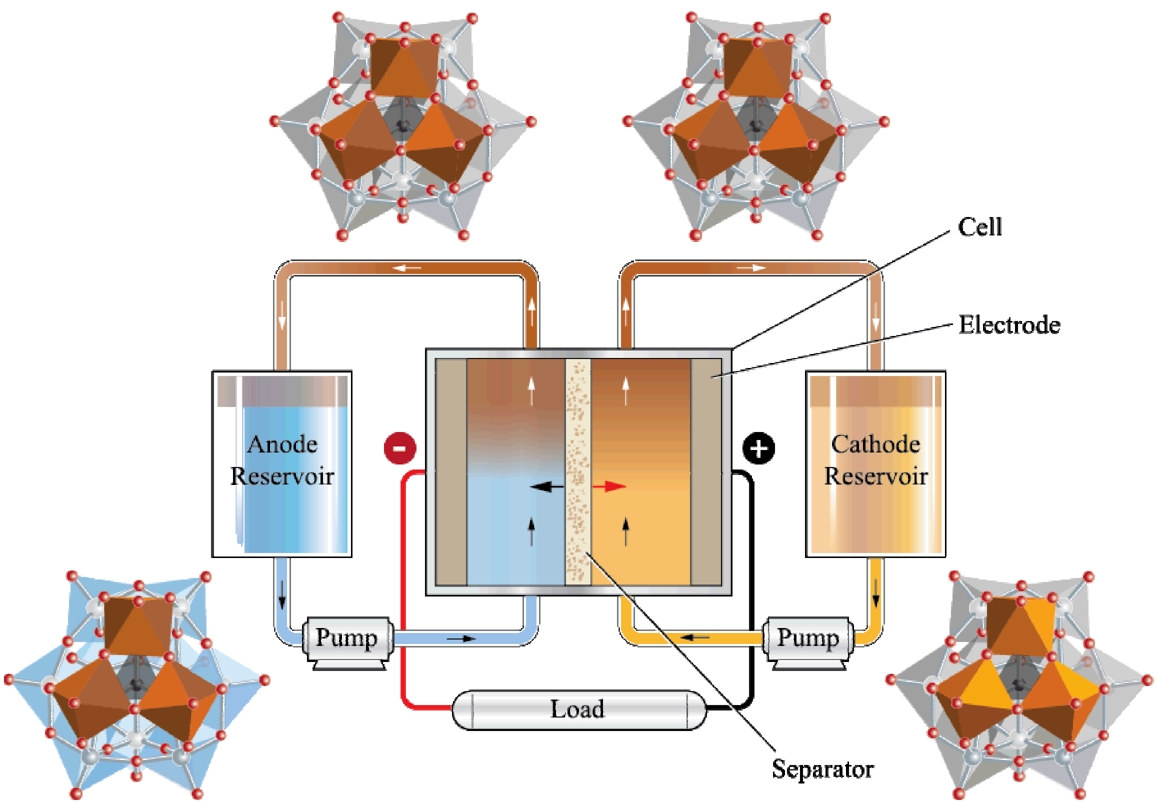
Nuclepore (50-nm)

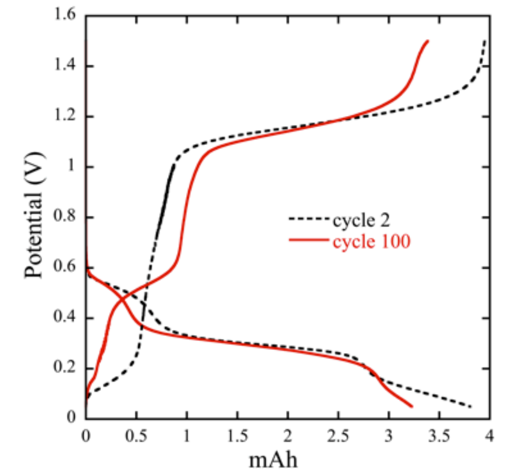


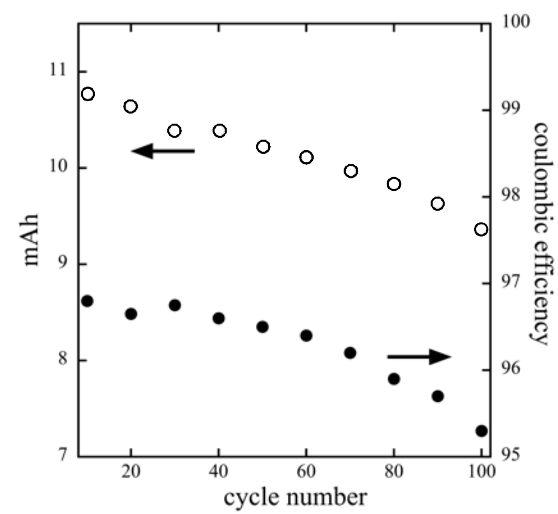
Anion Development Work

Highlights

- Coulombic efficiencies >95% with low capacity fading
- Three-electron process
- “Self-healing” compounds







Summary/Conclusions

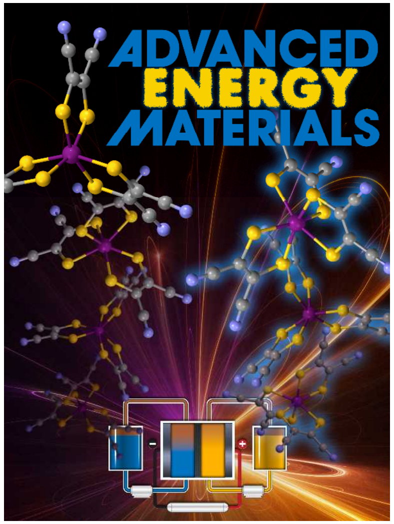
FY13 Accomplishments

- Published five papers in peer-reviewed journals and filed two patents
- Static cell testing shows that improvements in performance can be achieved through the judicious choice of ligands and anions.
- Developed new three-electron redox multi-valent solutions using SNL prototyping platform
- Demonstrated redox multi-valent solution in a battery with >50% improvement in utilization of the material to store charge.

FY14 Plans

Use newly developed platform:

- to demonstrate laboratory-scale prototypes targeted towards commercialization
- maximize electron transfer and
- minimize back pressures associated with viscous fluids



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