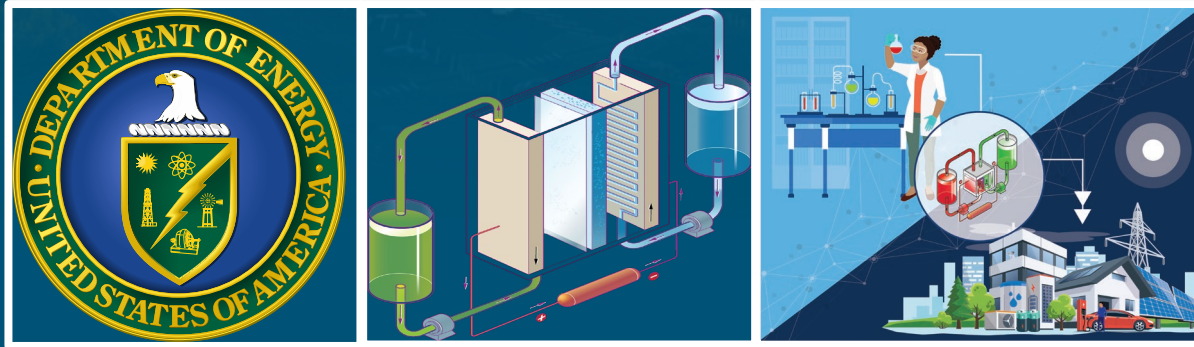


Iron-and Bipyridine-based Charge Carriers for Non- Aqueous Flow Batteries



PRESENTED BY

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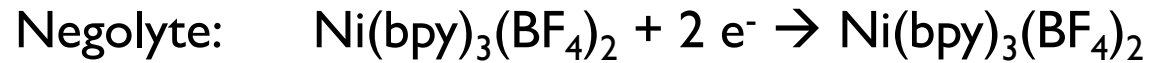
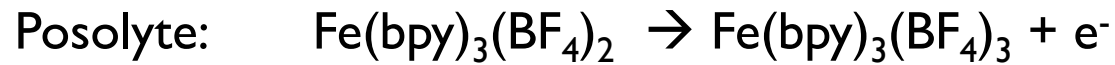
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2 Non-aqueous Flow Batteries-Metal Coordination Complexes (MCCs)



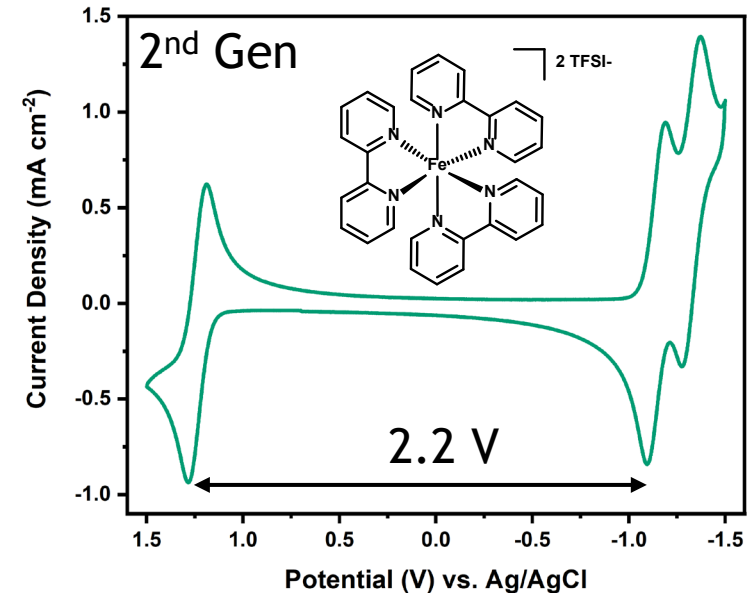
Project Goal: Build a better flow battery* by targeting (1) Energy Density (2) Materials Cost (3) Mechanisms of Capacity Fade

Asymmetric (2.26 V) Low-Cost Materials Crossover ☠️



$$\text{ED}_{\text{MCC}} = \frac{1}{2} \cdot 2F \cdot 2.2_{\text{cell}} \cdot 0.2_{\text{active}} = 0.4F$$

Symmetric all-iron battery minimizes issues with crossover and utilizes *non-innocent* ligands.



(1) Can we optimize $\text{Fe}(\text{bpy})_3(\text{BF}_4)_2$? (2) Can we chemically modify it to achieve a wider voltage window (ligand) or higher solubility (symmetry)?

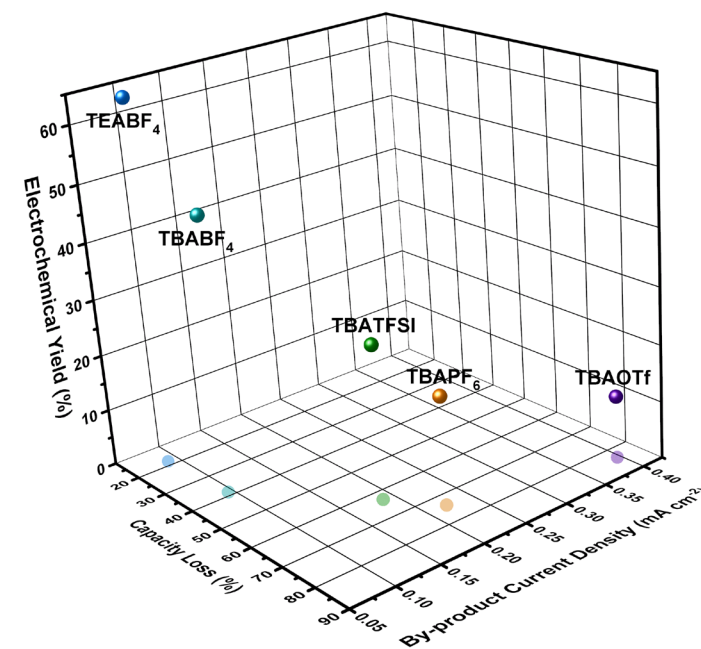
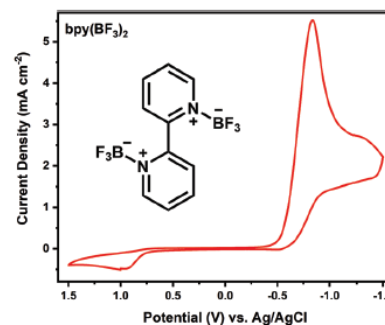
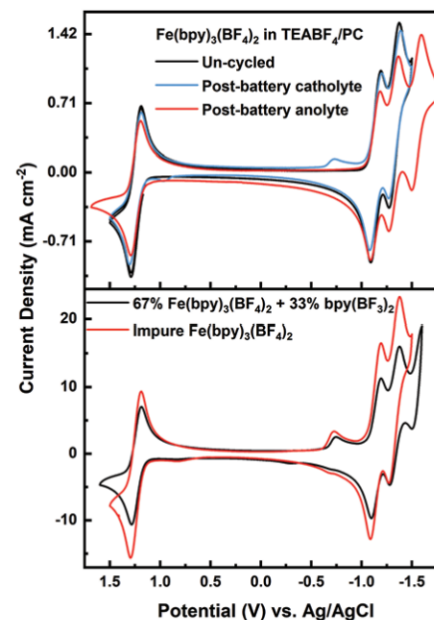
Next Generation

$$\text{ED}_{\text{MCC}} = \frac{1}{2} \cdot 2F \cdot 2.6_{\text{cell}} \cdot 1_{\text{active}} = 2.6F$$

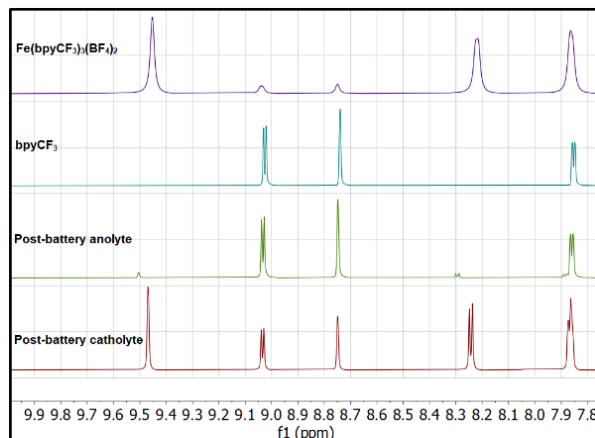
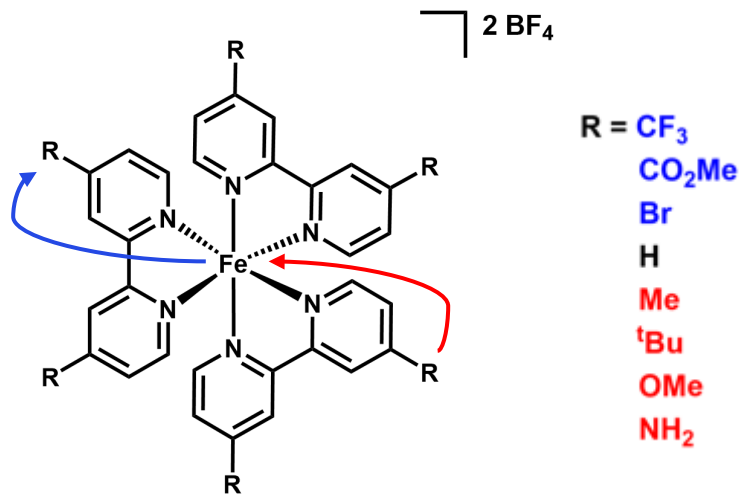
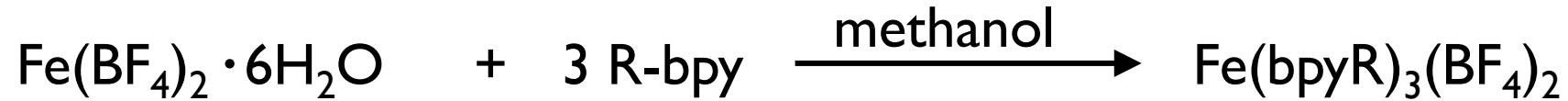
(1) Mun, Lee, Park, Oh, Lee, & Doo, *Electrochem. Solid-State Lett.*, 2012, 6, A80-A82 (2) Mn, Oh, Park, Kwon, Kim, Jeong, Kim, & Lee, *J. Electrochem. Soc.*, 2018, 165, A215-A219 (3) Hogue & Toghiani, *Curr. Op. Electrochem.*, 2019, 18, 37-45.

Varied supporting electrolyte to observe performance

- TEA^+ is superior to TBA^+
- BF_4^- is a superior anion
- Little crossover observed, but a common by-product forms upon cycling
- Found a relationship between capacity fade and by-product formation
- Negolyte ligand shedding, crossover, BF_4^- hydrolysis, followed by nucleophilic attack
- 15-20% improvement in performance when extra drying measures and higher purity precursors were used

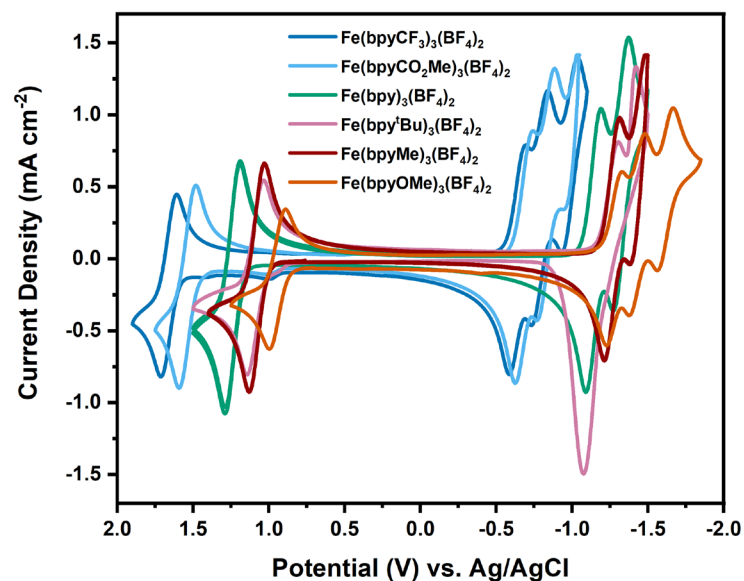
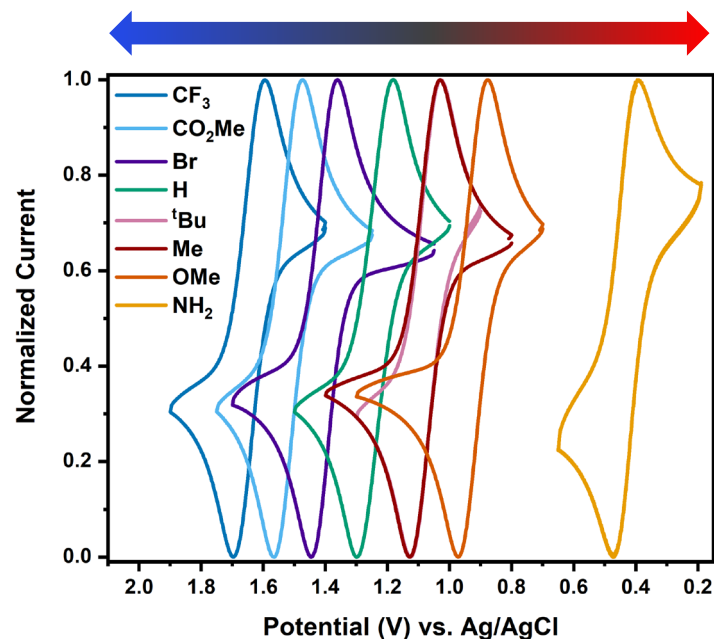


Synthesis of the Substituted Bipyridine Ligands



- High yields using earth abundant precursors
- Purity was confirmed by proton NMR (also provides information about structural integrity during battery cycling)
- **Electron Withdrawing Groups (EWGs)** shift resonances downfield as expected (and vice-versa **Electron Donating Groups (EDGs)** shift resonances upfield)
- UV-Vis data suggest the bpy ligands maintain their highly conjugated electronic structure (required for the voltage separation needed for the symmetric RFB)

Ligand Effects on Redox Potentials



	Fe ^{3+/2+} E _{1/2} (V)	Fe ^{2+/+} E _{1/2} (V)	ΔE _{1/2} (V)
Fe(bpyCF ₃) ₃ (BF ₄) ₂	1.65	-0.63	2.28
Fe(bpyCO ₂ Me) ₃ (BF ₄) ₂	1.53	-0.68	2.21
Fe(bpyBr) ₃ (BF ₄) ₂	1.43	-	-
Fe(bpy) ₃ (BF ₄) ₂	1.25	-1.12	2.37
Fe(bpy ^t Bu) ₃ (BF ₄) ₂	1.09	-1.19	2.28
Fe(bpyMe) ₃ (BF ₄) ₂	1.07	-1.25	2.32
Fe(bpyOMe) ₃ (BF ₄) ₂	0.94	1.27	2.21
Fe(bpyNH ₂) ₃ (BF ₄) ₂	0.43	-	-

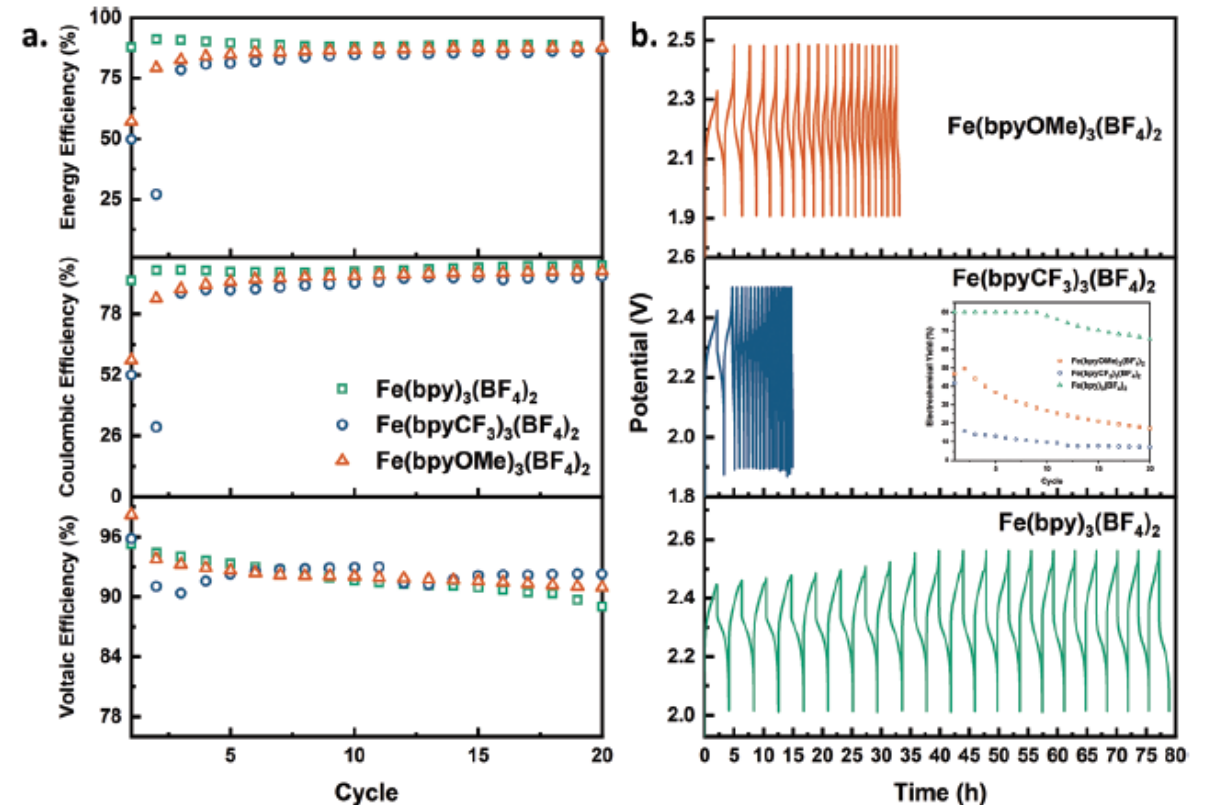
Fe(II)/(III) ligand voltage gap

- EWGs shifted **positively** by up to **0.4 V**
- EDGs shifted **negatively** by up to **0.8 V**
- Fe(II) and ligand-centered redox shifted together

Substituted $\text{Fe}(\text{bpyR})_3(\text{BF}_4)_2$ in Symmetric RFBs



- Analyzed the effect substituents on bpy have on cycling in a RFB
- The most **EWG** and **EDG** were compared to the unsubstituted $\text{Fe}(\text{bpy})_3$
- The unsubstituted showed greatest cycling stability, followed by the **EDG** (-OMe), then the **EWG** (-CF₃)
 - Capacity fade (& electrochemical yield inset)
 - Negolyte degradation due to ligand shedding

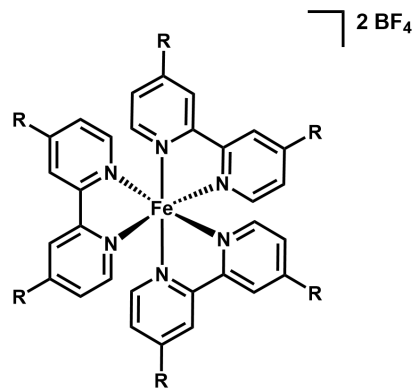
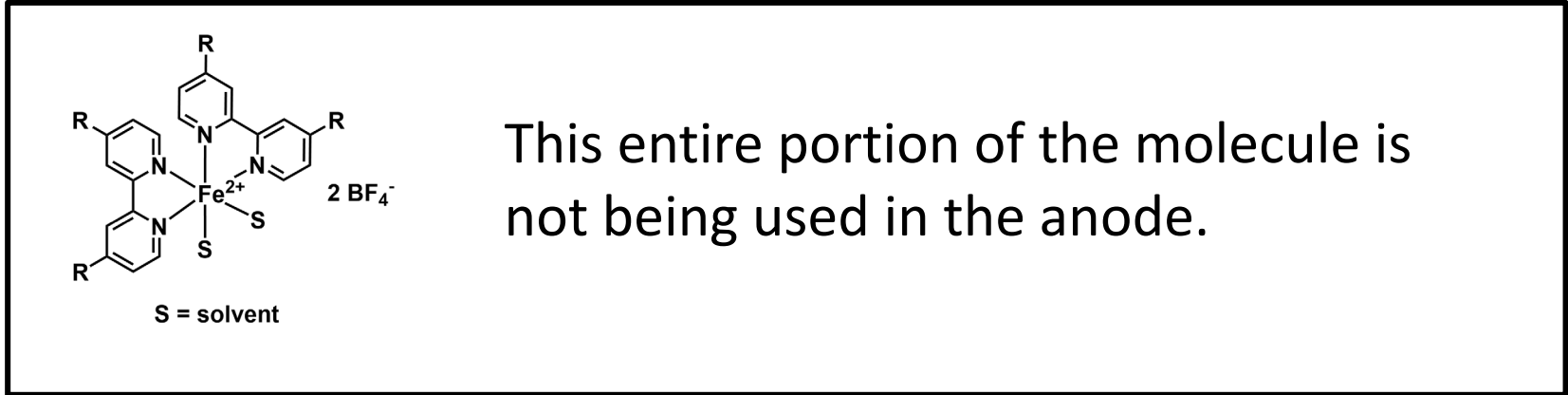


The **negolyte is unstable**. How can we fix it? Pseudo-symmetric flow batteries!

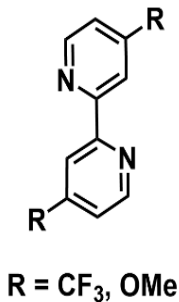
8 Why Pseudo-Symmetric?



- 1. More stable under highly reducing conditions
- 2. Coordinatively unsaturated complex can catalyze unwanted reactions
- 3. Free ligand is more tunable (synthetically)
- 4. Improve atom economy



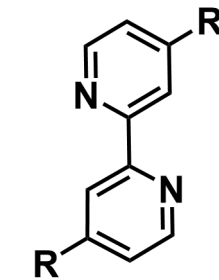
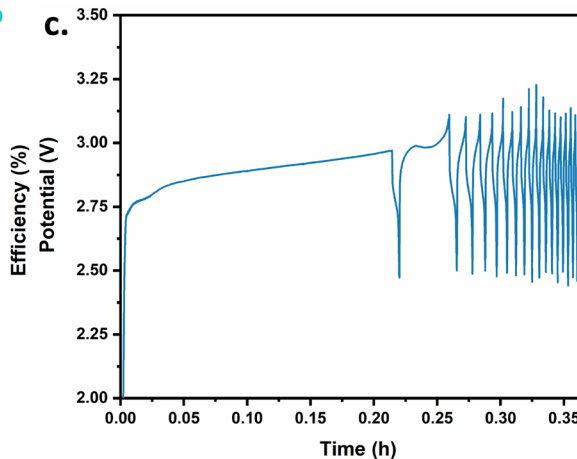
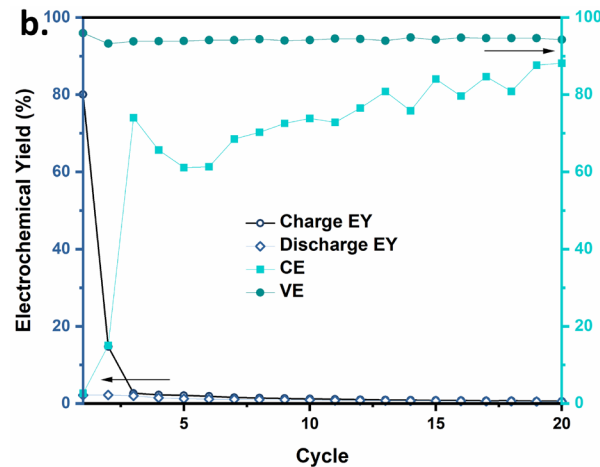
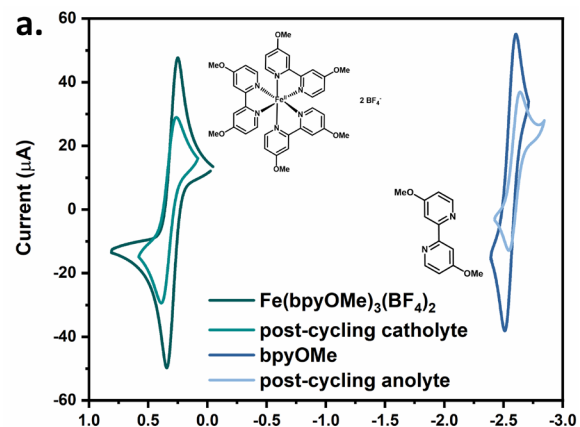
Posolyte



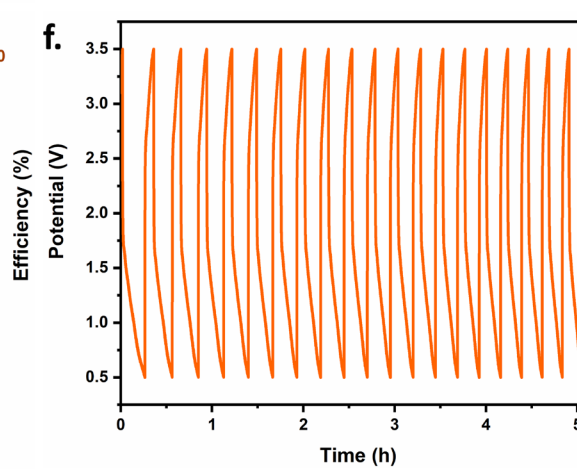
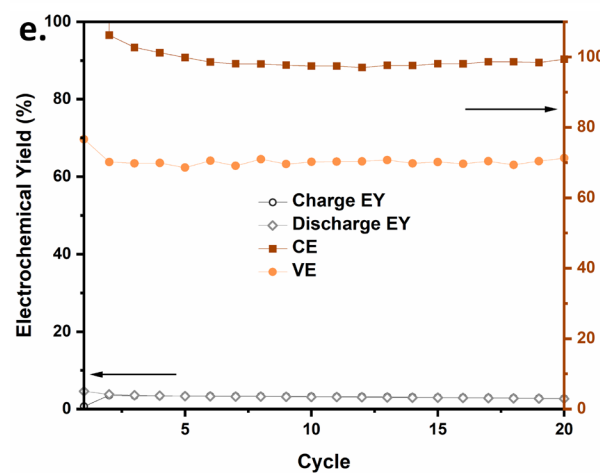
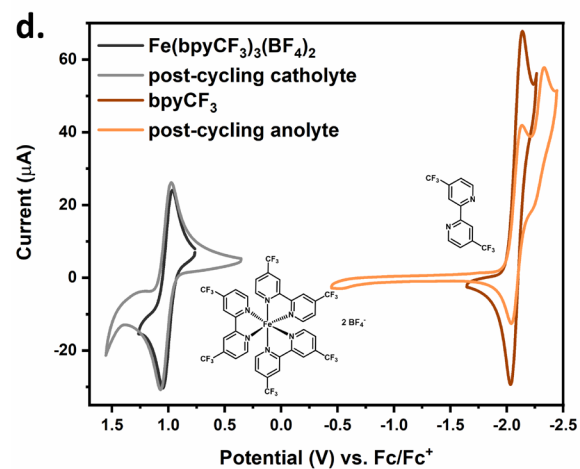
Negolyte

Pseudo-symmetric flow batteries will have **metal-free negolytes**.

First Generation Pseudo-Symmetric Flow Cell Studies



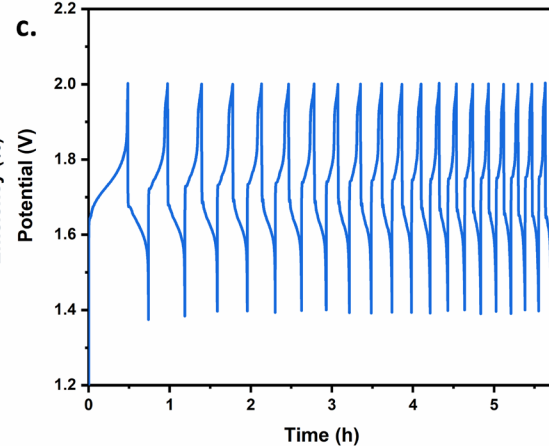
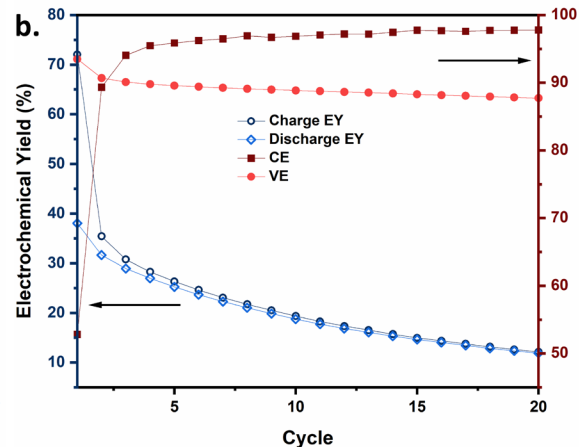
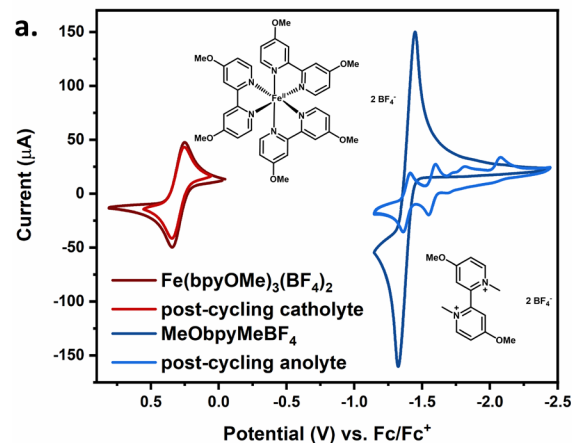
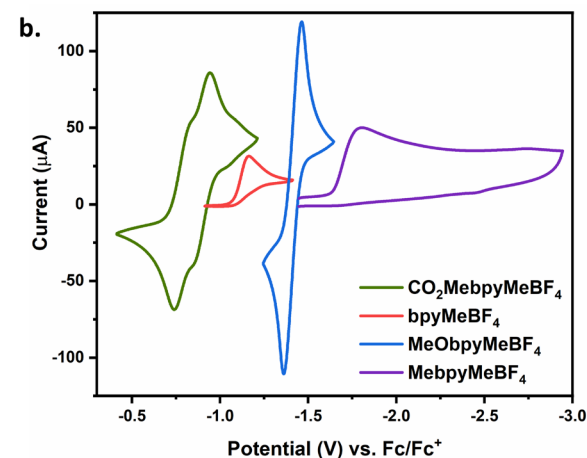
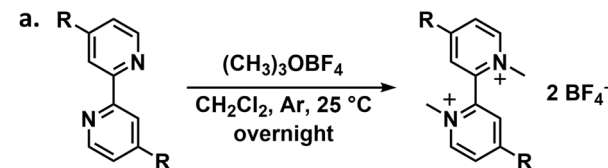
$\text{R} = \text{CF}_3, \text{OMe}$



No discharge!

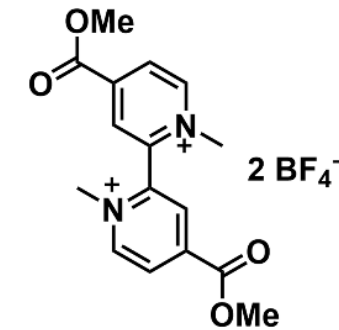
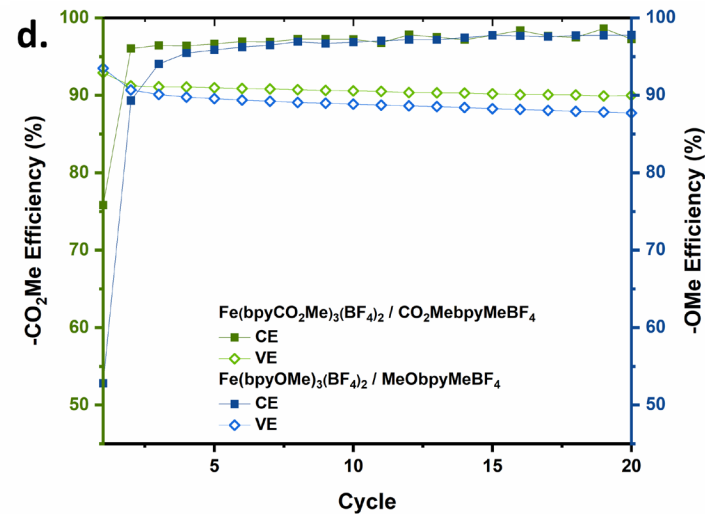
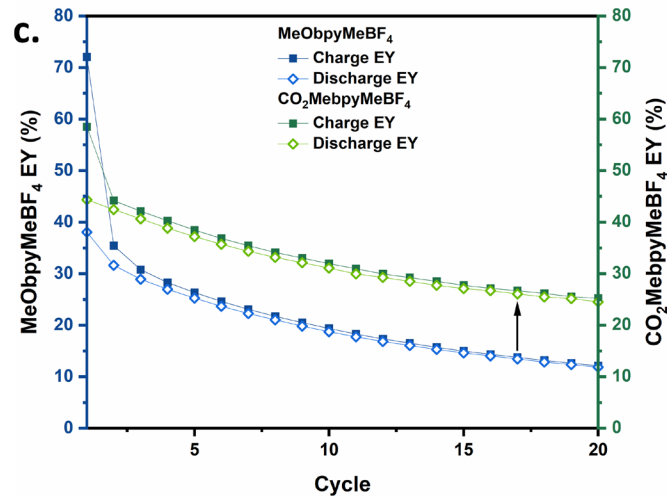
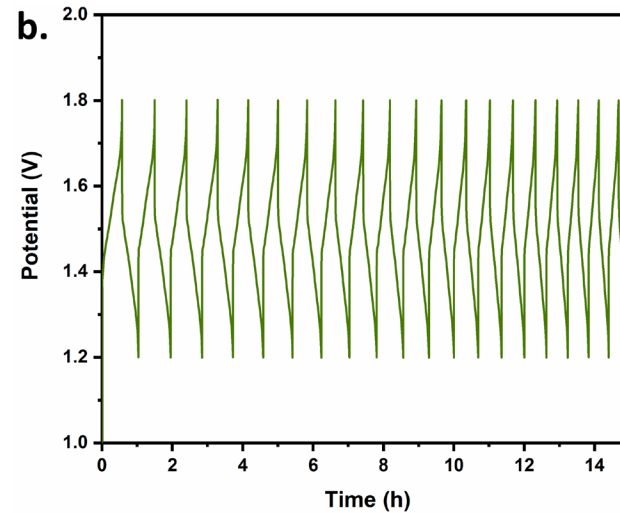
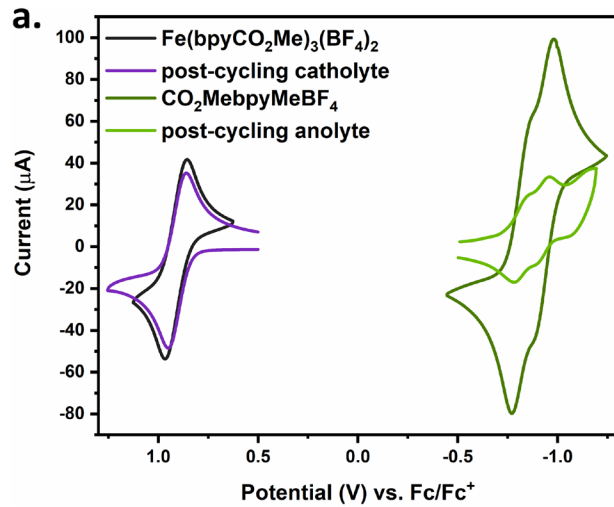


The second generation negolyte has a **methylated** nitrogen. The literature shows this significantly improves the electrochemistry.

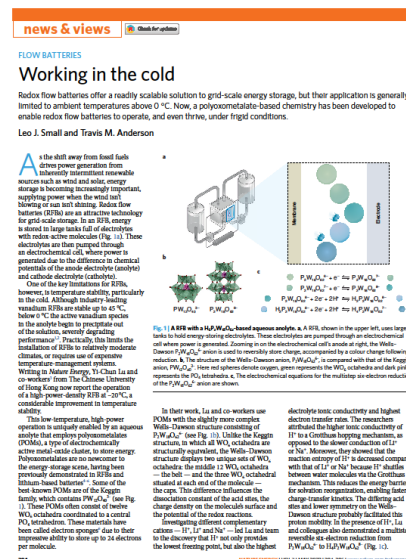


The methylated, OMe derivative showed **improved cycling** over first generation but poor material utilization.

The methylated, CO₂ derivative showed an **18% improvement** of material utilization over second generation.



- We have identified (and mitigated) the mechanism for capacity fade in the symmetric iron-bipyridine flow battery.
- We have determined that chemical substitutions can be made in MCCs to increase voltage, but this can decrease the overall stability of the system.
- We have determined that this stability is primarily centered around the negolyte and identified (and executed) a path forward involving a pseudo-symmetric system.
- The negolytes of pseudo-symmetric flow batteries can be stabilized with chemical modifications.

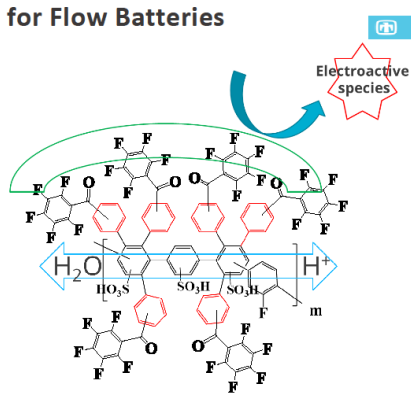


Related Sandia and External Projects

Advanced Membranes for Flow Batteries

Membrane Key Properties

- **Cost:** Developing hydrocarbon based membranes. Targeting cost of < \$20/m²
- **Performance:** Flow batteries are influenced by membrane properties. Developing membranes with low cell resistance (< 0.8 ohmcm²) and high coulombic efficiency (> 98%)
- **Durability:** Membranes need to have lifetimes of at least 20 years in flow battery deployment.



Charge Transport and Electrolyte Development for Multiphase Batteries

Mitch Anstey (Davidson College)

Mediator	M-N Distance (Å)	N-N Distance (Å)
Boron	1.544	2.642
Aluminum	1.849	3.172
Silicon	1.722	3.097
Phosphorus	1.640	2.805

Non-Aqueous Redox Flow Battery : Materials Development

All Iron based non-aqueous redox flow battery

- 3X solubility enhancement compared to Fe(PyIm) complex (First Gen LANL's Fe₂ complex).
- No noticeable degradation in CV of [FePy(TRENMe)](OTf)₂ after 50 cycles. Future work will evaluate cycling two negative waves to generate 1.67 V cell voltage, increasing the energy density > 25%.

Electron Transfer Processes in V(acac)₃ based Non-Aqueous Redox Flow Batteries: Effects of Solvent Properties

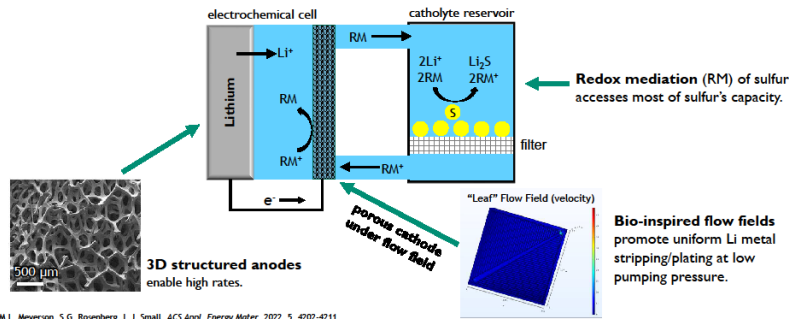
- Systematic approach to select suitable solvents for non-aqueous redox flow batteries.
- The reaction kinetics can be increased using solvents with low permittivity coefficients.
- Separation of the redox couples was determined to be dependent on the polarity of the solvent.
- High donor solvents undergo unique degradation pathway at positive potentials associated with V(III)/V(IV) species.

Cy Fujimoto

Mediated Li-S Flow Batteries

Melissa Meyerson, Adam Maraschky, Asahel Marinelarena, Leo Small (Sandia National Laboratories)

We are developing technologies to enable Li-S to be scaled to grid storage applications in a flow battery format.



Leo Small

Capacity Fade in [3]radialene Aqueous Organic Catholytes – Dimerization Studies

ME in MeOH

Addition of Acetone to Water

Calculations support the formation of the σ -dimer in polar solvents.

$\Delta G = -10.1$ kcal/mol in H₂O
 $\Delta G = 0.3$ kcal/mol in Acetone

[wB97XD/6-311+G(d,p)]

Christopher Bejger
 Fuead Hasan
 Jonathan Gillen

UNIVERSITY OF NORTH CAROLINA
 CHARLOTTE

LANL

Metal Oxide Clusters for Energy Conversion and Storage

synthesis of organic- and heteroatom-functionalized POVs \rightarrow physicochemical analysis

Structure-activity Relationships

Ellen Matson



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