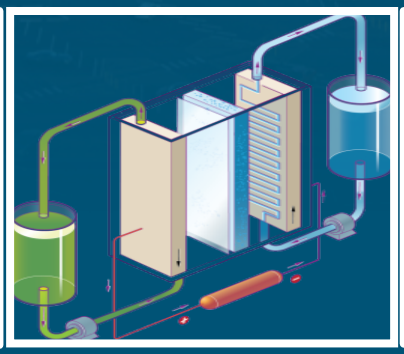
SAND2022-12910C

Sandia National Laboratories

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



PRESENTED BY

Travis M. Anderson, Sandia National Laboratories, Presentation ID#605

CO-AUTHORED BY

Claudina X. Kolesnichenko and Cassandria E. Poirier

U.S. DEPARTMENT OF ENERGY NNSA

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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

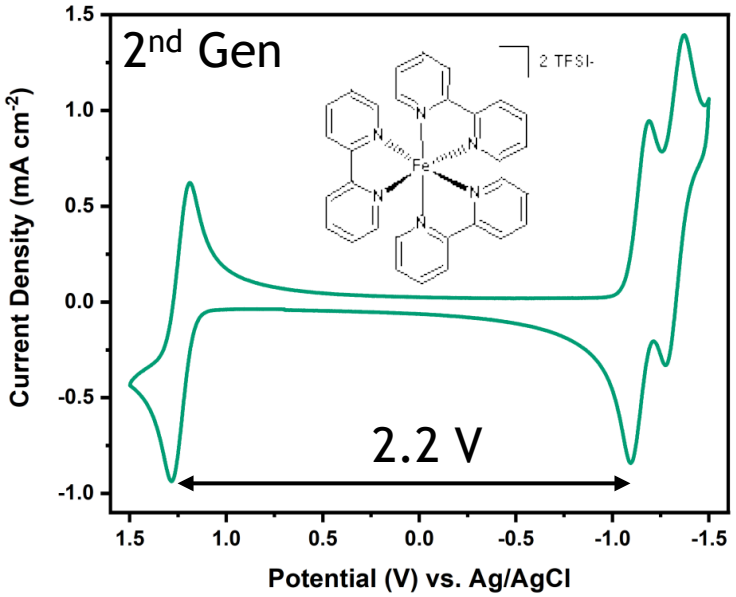
$ED_{MCC} = ½2F2.2_{cell}0.2_{active} = \mathbf{0.4F}$ **Low-Cost Materials** **Crossover** ☠

First Generation redox reactions (2.26 V)

Posolyte: $Fe(bpy)_3(BF_4)_2 \rightarrow Fe(bpy)_3(BF_4)_3 + e^-$

Negolyte: $Ni(bpy)_3(BF_4)_2 + 2\ e^- \rightarrow Ni(bpy)_3(BF_4)_2$

Second Generation (symmetric) all-iron battery minimizes issues with crossover and utilizes *non-innocent* ligands.



Next Generation

$ED_{MCC} = ½2F2.6_{cell}1_{active} = \mathbf{2.6F}$

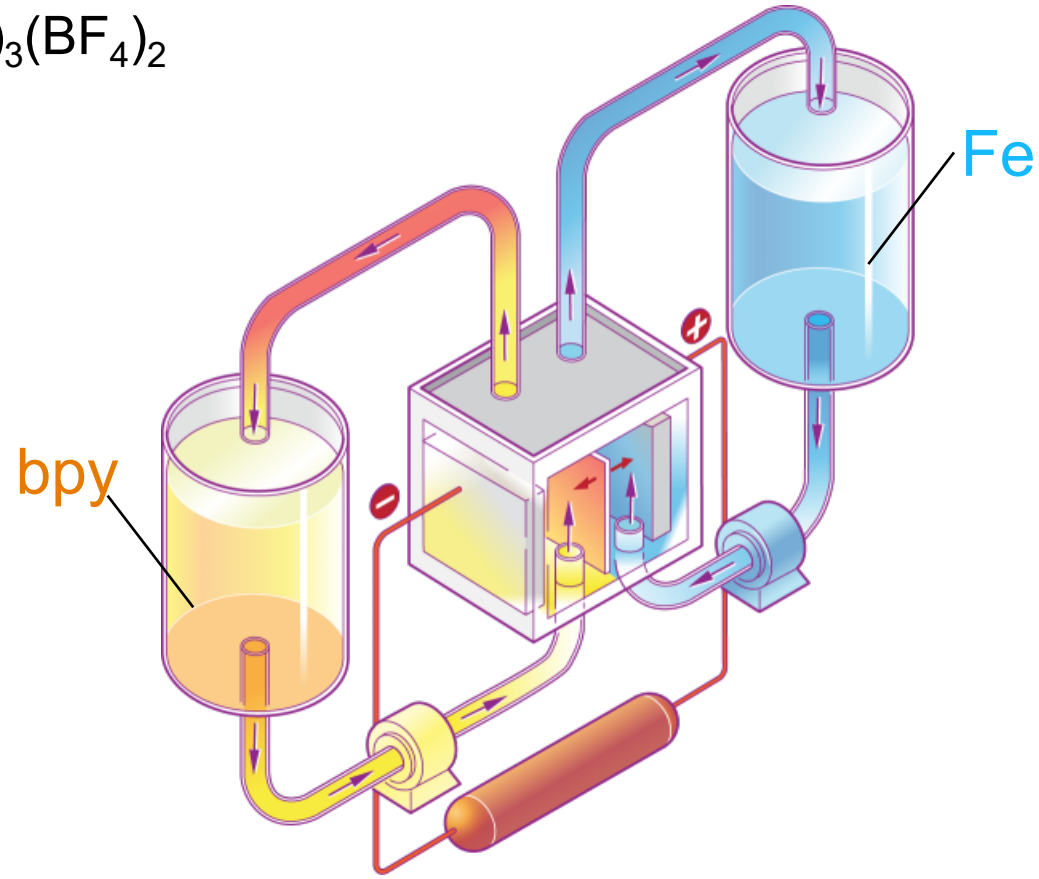
Lower Symmetry, Higher Solubility

Tunable Ligands, Wider Voltage

(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 & Toghill, *Curr. Op. Electrochem.*, **2019**, *18*, 37-45.

$Fe(bpy)_3(BF_4)_2$ Symmetric Flow Cell Studies

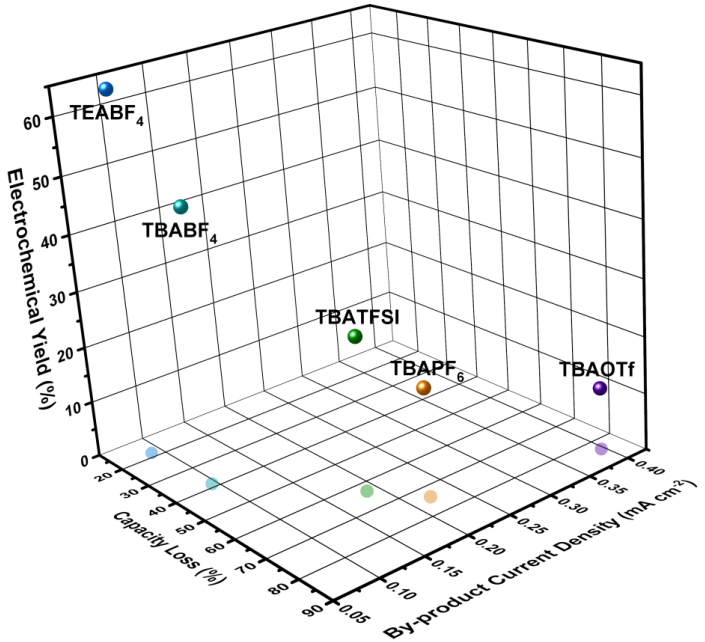
- Test materials and parameters
  - Membranes: Fumasep FAP-450 anion exchange membrane
  - Solvents: propylene carbonate
  - Electrolyte Salts: TEA-BF_4 , TBA-OTf, TBA-TFSI, TBA-BF_4 , and TBA-PF_6
  - 0.5 M electrolyte salt + 0.2 M $Fe(Bipy)_3(BF_4)_2$
  - Argon glovebox
  - 20 cycles at ±10 mA cm^{-2}



Symmetric $Fe(bpy)_3(BF_4)_2$ Salt Study

Varied supporting electrolyte to observe performance (like mixed acid vanadium battery)

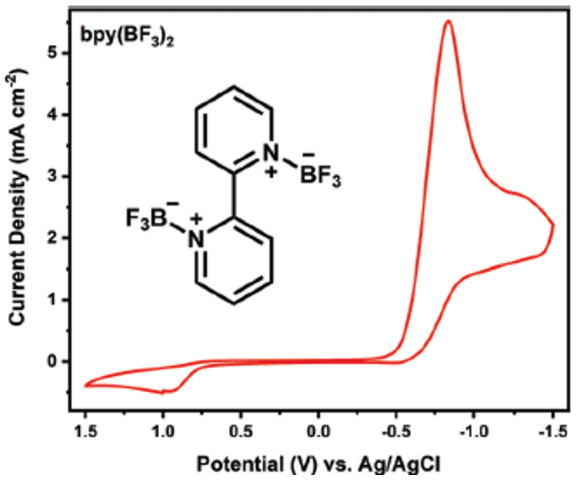
- TEA^+ is superior to TBA^+
- BF_4^- is a superior anion
- $TEABF_4$: 96.5 % CE
- Degradation is exacerbated by the flowing cell
- Solubility and conductivity are increased in acetonitrile
- Little crossover observed, but a **common by-product** forms upon cycling
- Found a relationship between capacity fade and by-product formation

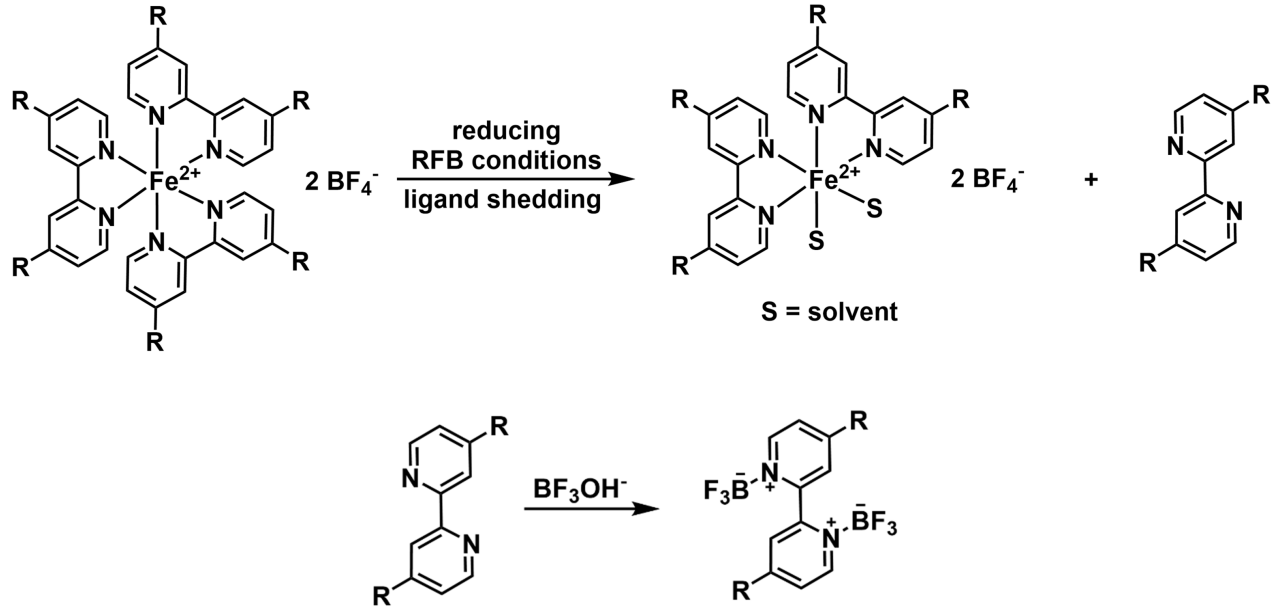


By-product formation correlates with RFB EY, CE, capacity loss

C. X. Cammack *et al*. *Dalton Trans.*, **2021**, *50*, 858-868.

Mechanism of Symmetric $Fe(bpy)_3(BF_4)_2$ Capacity Fade



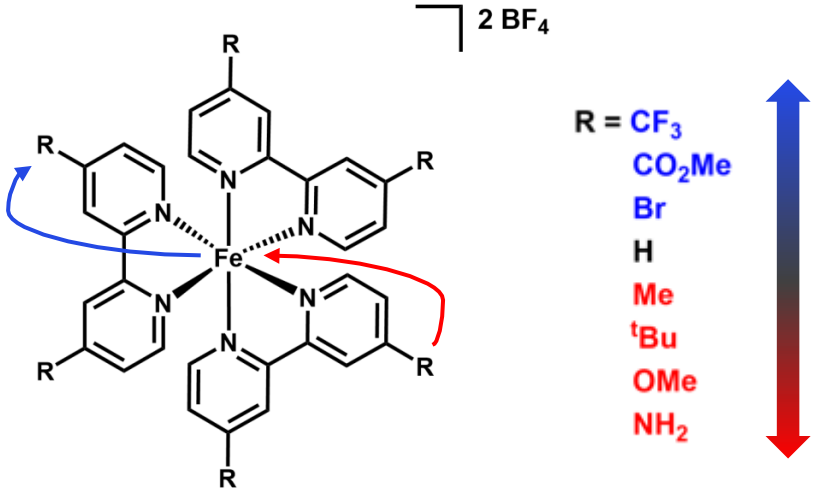


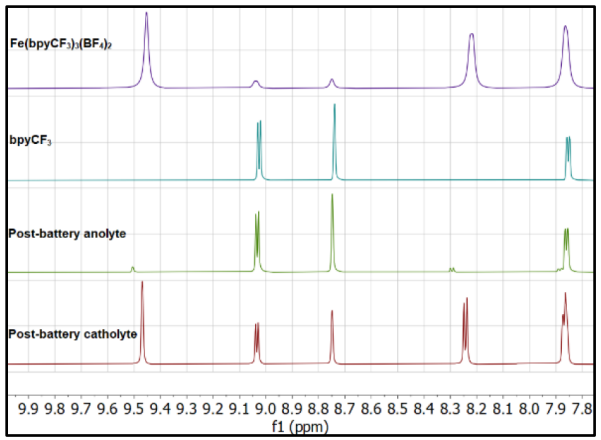
- Ligand shedding, posilyte BF_4^- crossover and hydrolysis, followed by nucleophilic attack.
- Final product was confirmed by MS
- "Mechanistic studies (e.g., molecular dynamics, decompositions, and electrode-solution interface) are essential as they can gain insights into this complex battery system and may inspire crucial factors that revolutionize control of key physicochemical properties."

C. X. Cammack *et al*. *Dalton Trans.*, **2021**, *50*, 858-868.

Synthesis of the Substituted Bipyridine Ligands

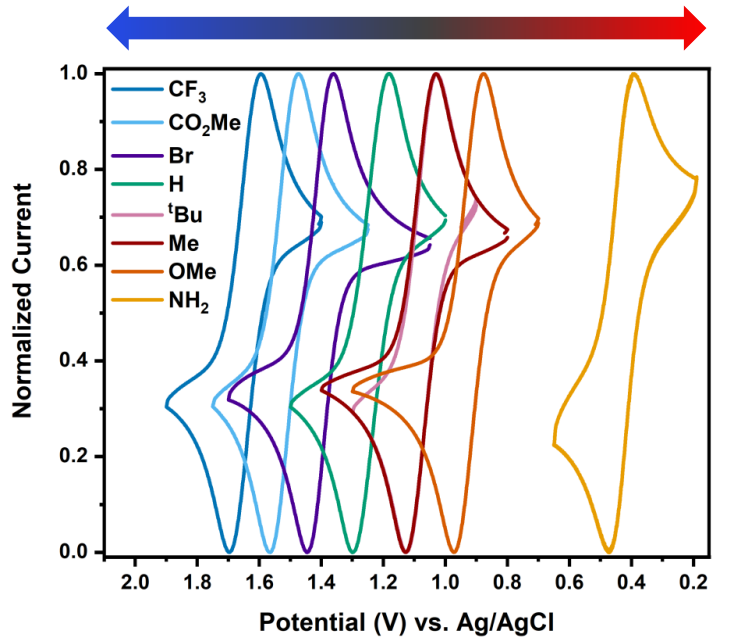
$$Fe(BF_4)_2 \cdot 6H_2O + 3\ R\text{-bpy} \xrightarrow{\text{methanol}} Fe(bpyR)_3(BF_4)_2$$

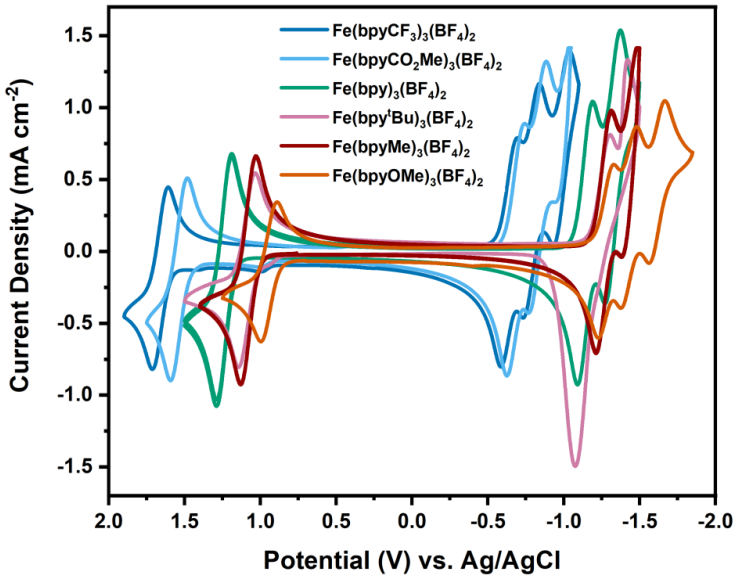




- High yields using earth abundant precursors
- Purity was confirmed by proton NMR (also provides information about structural integrity during battery cycling)
- EWGs shift resonances downfield as expected (and vice-versa EDGs shift resonances upfield)
- UV-Vis data suggest the bpy ligands maintain 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)	$\Delta E_{1/2}$ (V)
$Fe(bpyCF_3)_3(BF_4)_2$	1.65	-0.63	2.28
$Fe(bpyCO_2Me)_3(BF_4)_2$	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
$Fe(bpy^tBu)_3(BF_4)_2$	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	-	-

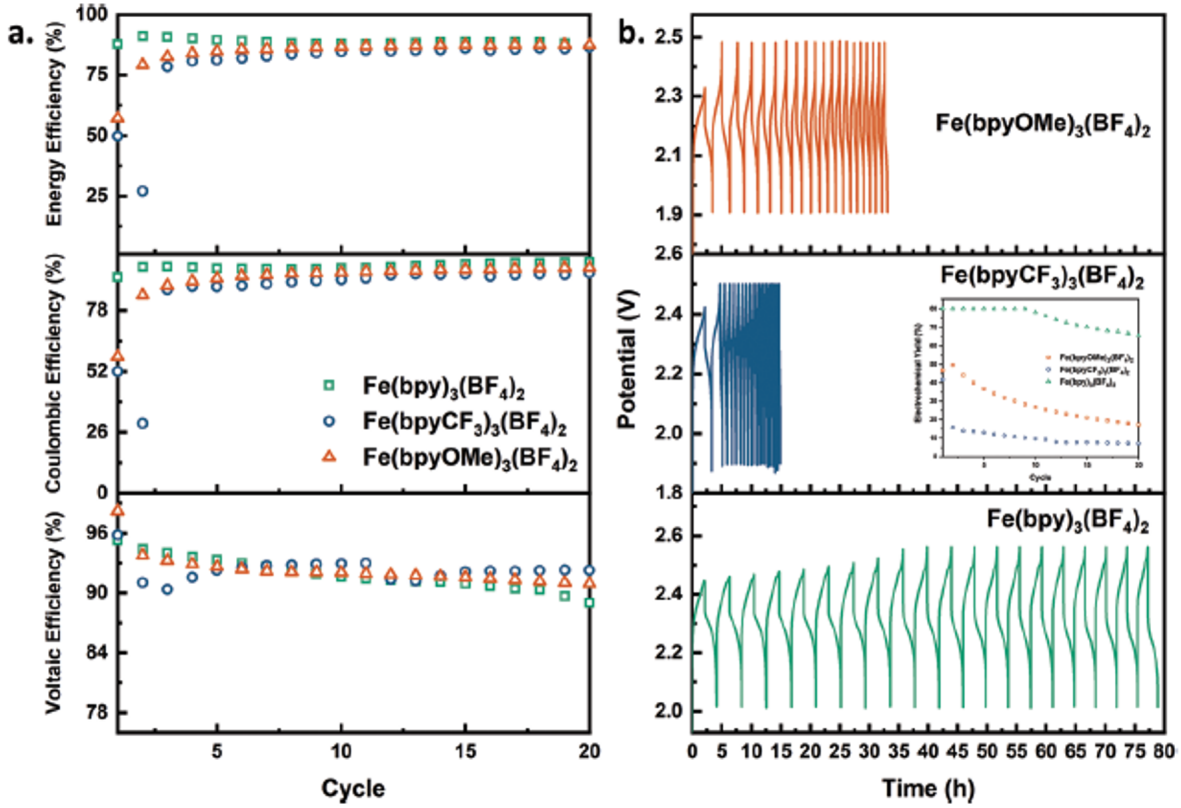
Fe(II)/(III) ligand voltage gap

Inductive effects change ease oxidation of Fe(II)
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 $Fe(bpyR)_3(BF_4)_2$ in Symmetric RFBs

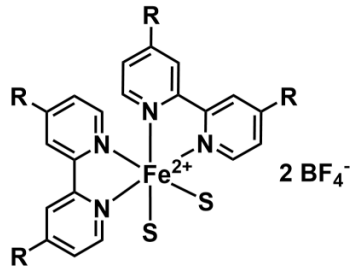
- Analyzed the effect substituents on bpy have on cycling in a RFB
- The most EWG and EDG were compared to the unsubstituted $Fe(bpy)_3$
- The unsubstituted showed greatest cycling stability, followed by the EDG (-OMe), then the EWG ($-CF_3$)
  - Capacity fade (& electrochemical yield inset)
  - Negolyte degradation due to ligand shedding

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



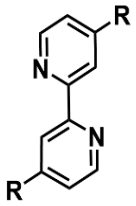
Why Pseudo-Symmetric?

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

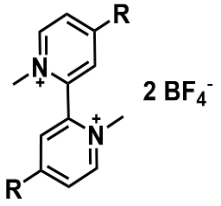


S = solvent

This entire portion of the molecule is not being used in the anode.



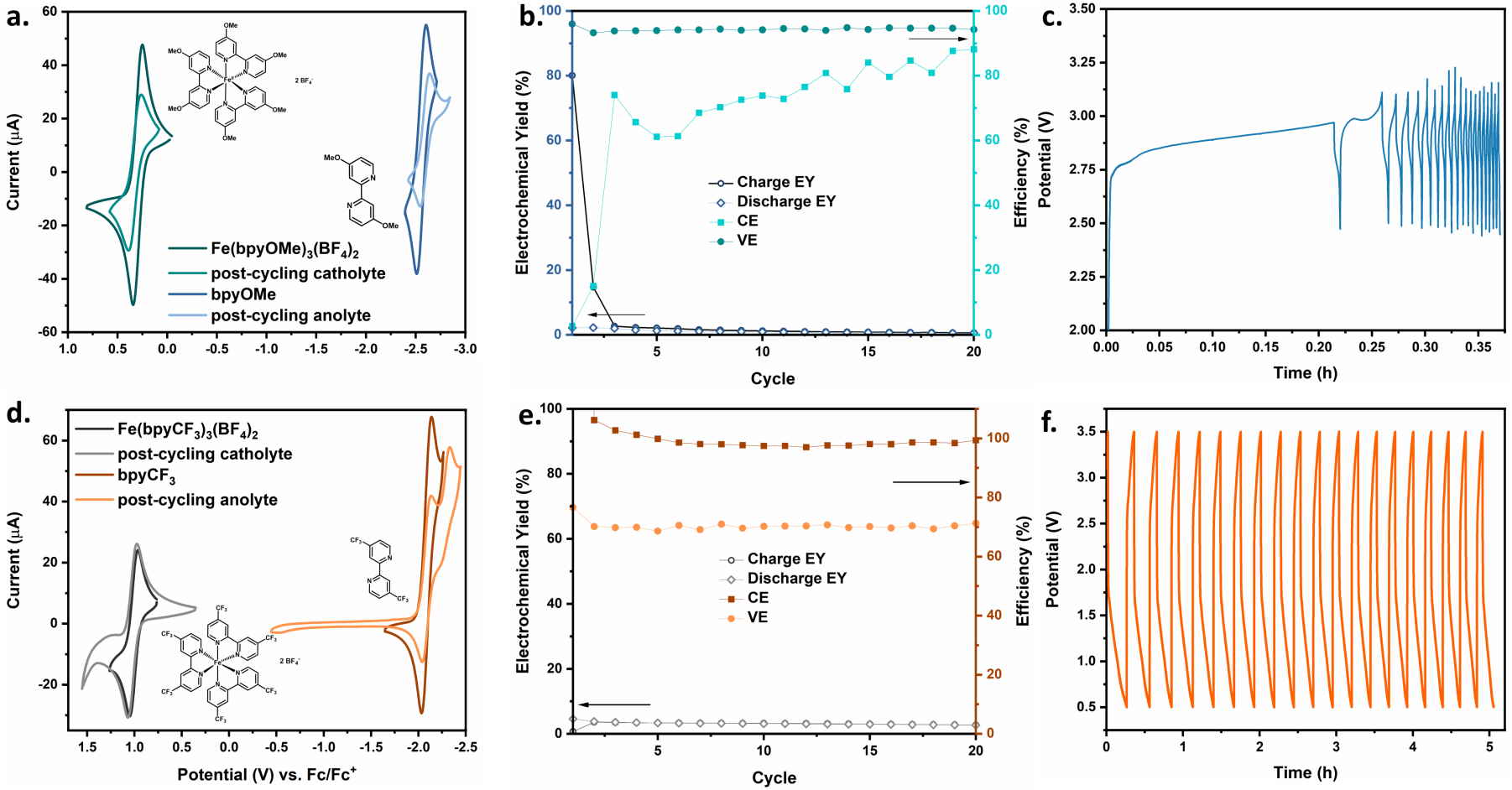
R = CF_3, OMe

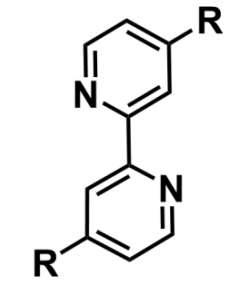


R = H, Me, OMe, CO_2Me

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

First Generation Pseudo-Symmetric Flow Cell Studies



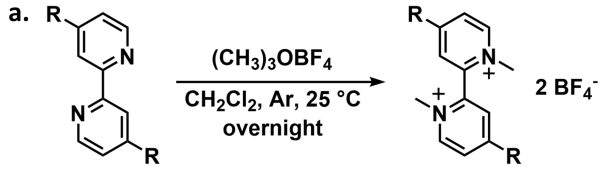


R = CF_3, OMe

C. X. Kolesnichenko *et al*. *ChemElectroChem*, **2022**, e202101490.

Second Generation Pseudo-Symmetric Flow Cell Studies

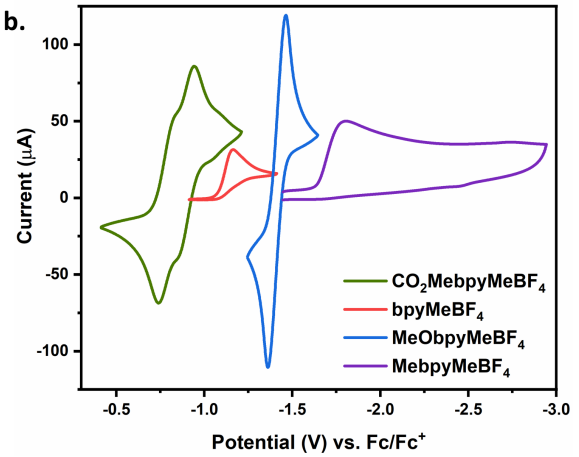
a.



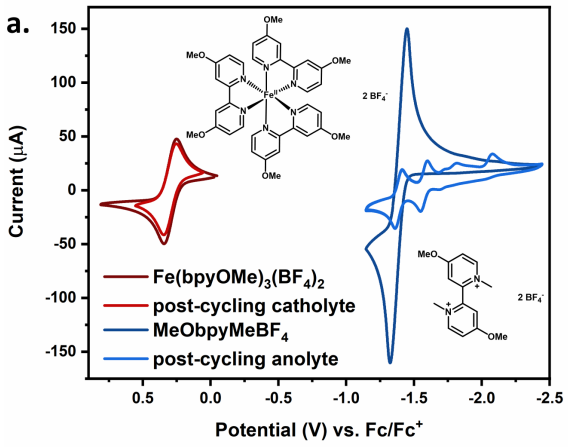
bpyR anolytes showed no discharge so we methylated them to:

- Stabilize bipyridinium radicals upon reduction
- Form the salt to increase solubility in polar electrolyte
- Prevent by-product formation with hydrolyzed electrolyte

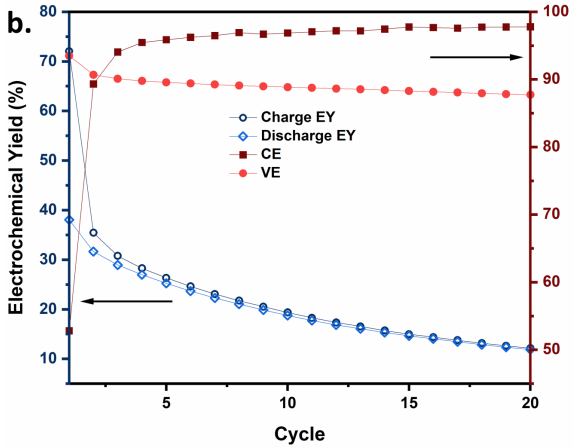
b.



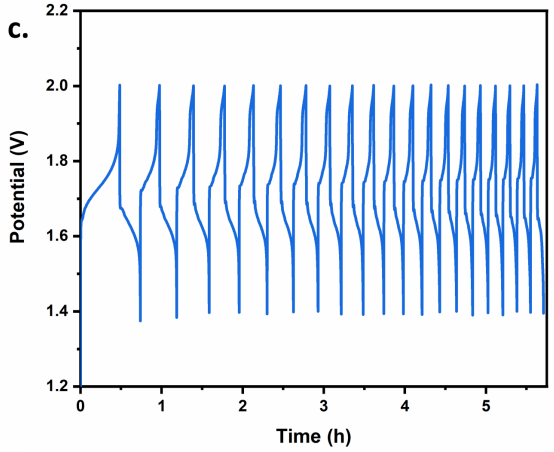
a.



b.



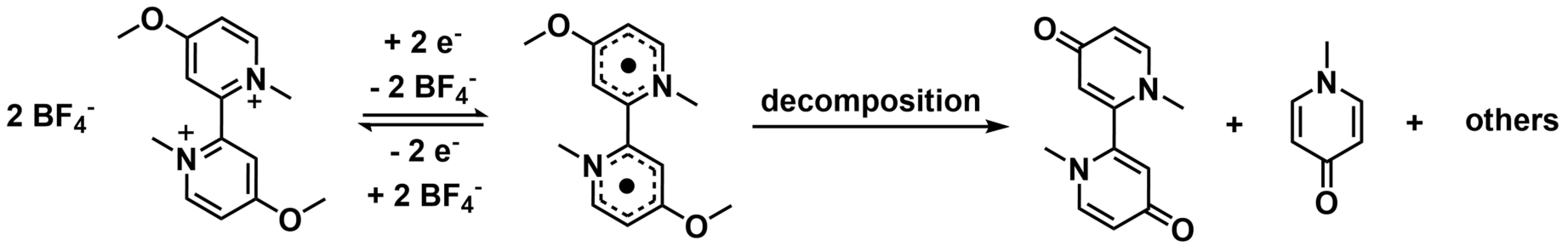
c.

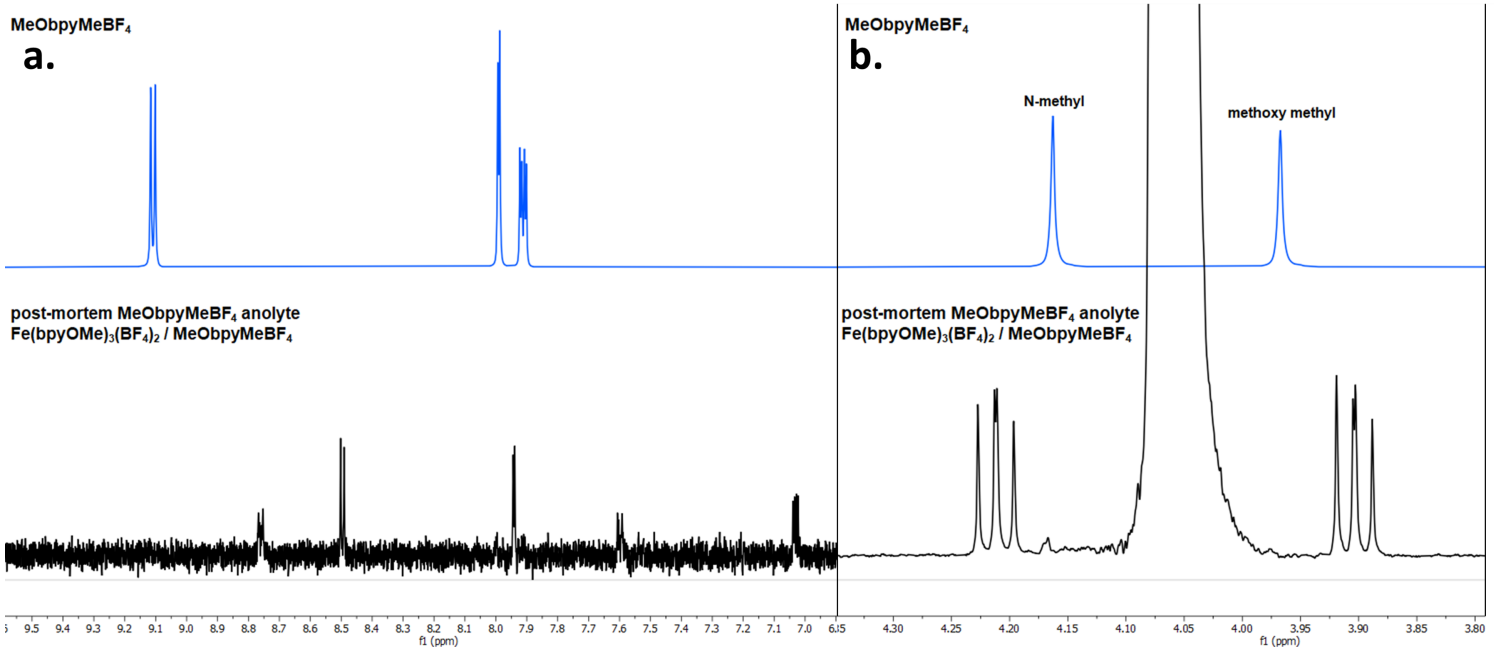


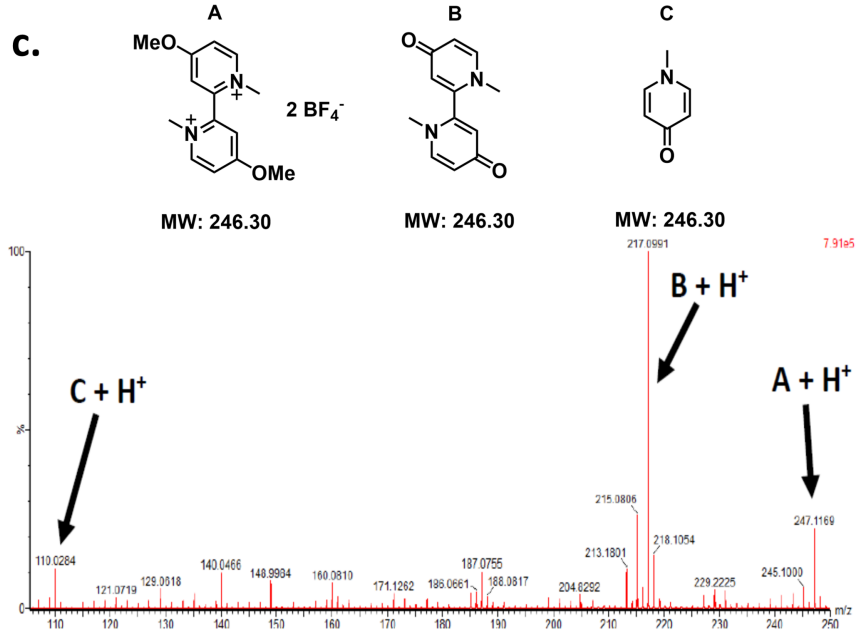
The methylated, OMe derivative showed **improved cycling** over first generation but poor material utilization.

Mechanism of Second Generation, Pseudo-Symmetric Capacity Fade

Significant degradation was observed in the first cycle, forming various by-products.

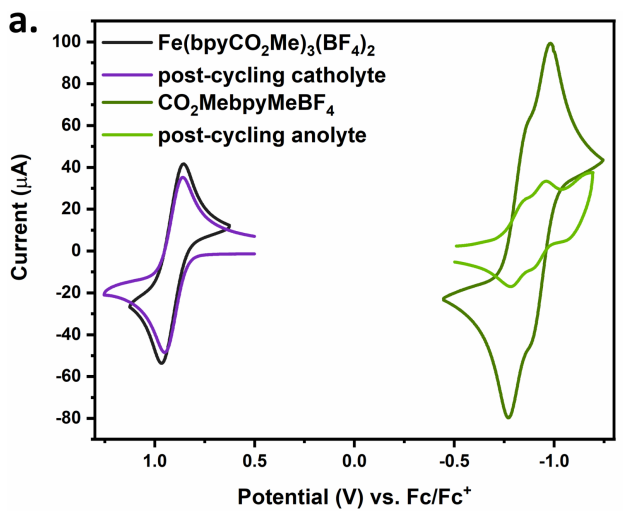


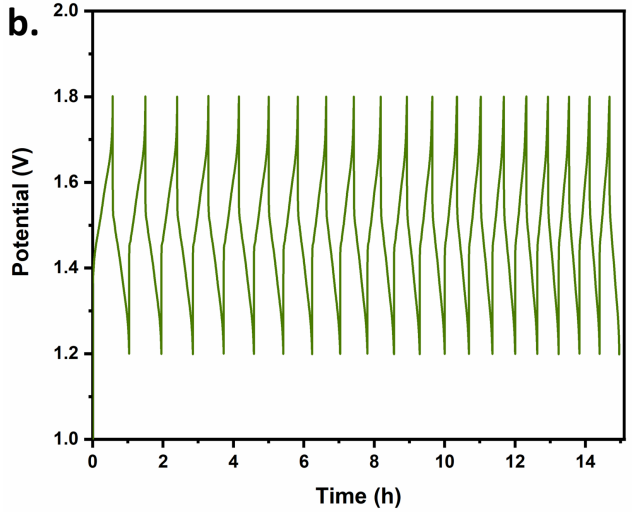


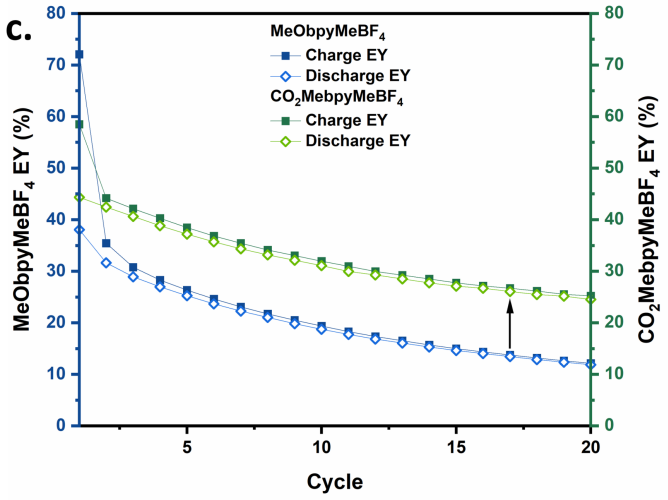


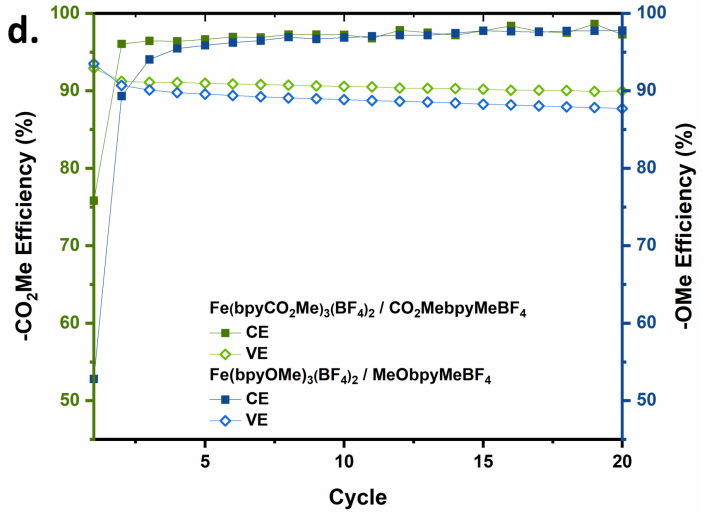
Third Generation Pseudo-Symmetric Flow Cell Studies

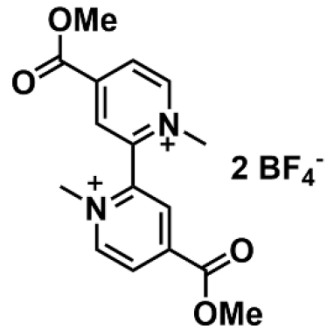
The methylated, CO_2 derivative showed an **18% improvement** of material utilization over second generation.











Conclusions

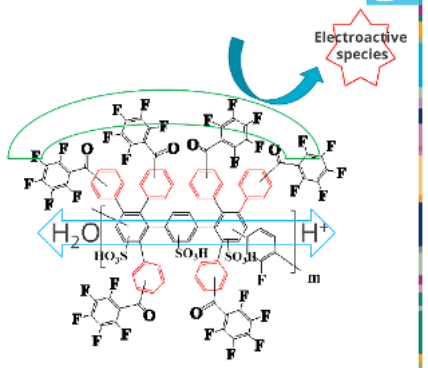
- We have identified the mechanism for capacity decay in the symmetric iron-bipyridine flow battery.
- We have determined that chemical substitutions can be made to increase voltage, but this can decrease the overall stability of the system.
- We have determined that this stability is primarily centered around the negalyte and identified (and executed) a path forward involving a pseudo-symmetric system (see below).
- The negalytes of pseudo-symmetric flow batteries can be stabilized with methylation and the addition of bulky CO_2 groups.

Related Sandia and External Projects

Advanced Membranes for Flow Batteries

Membrane Key Properties

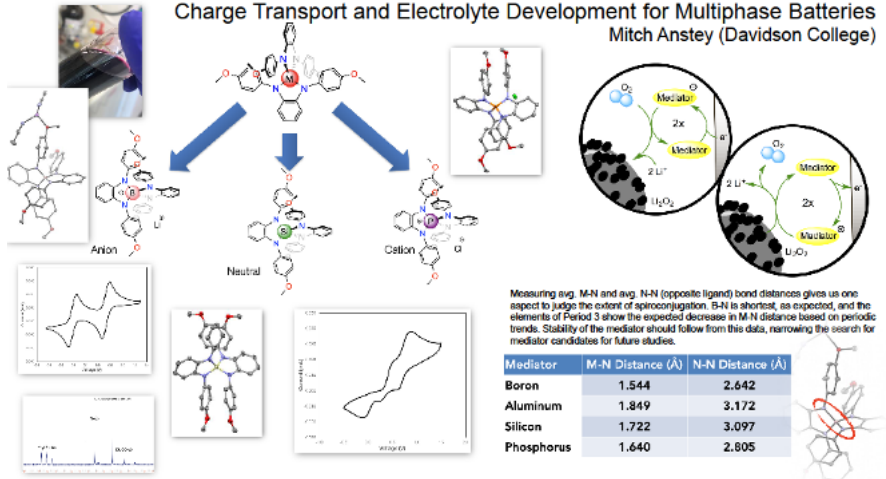
- **Cost:** Developing hydrocarbon based membranes. Targeting cost of < $20/m2
- **Performance:** Flow batteries are influenced by membrane properties. Developing membranes with low cell resistance (< 0.8 ohmcm2) and high coulombic efficiency (> 98%)
- **Durability:** Membranes need to have lifetimes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



Cy Fujimoto

Charge Transport and Electrolyte Development for Multiphase Batteries

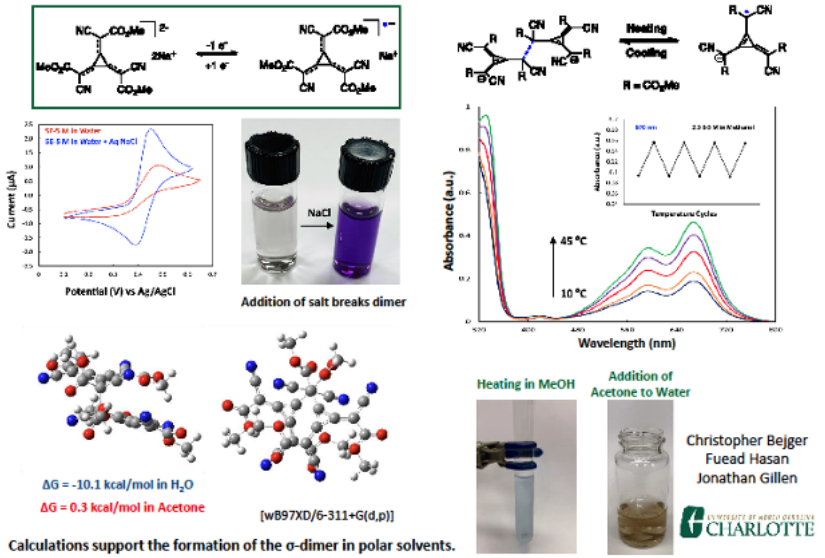
Mitch Anstey (Davidson College)



Measuring avg. M-N and avg. N-N (opposite ligand) bond distances gives us one aspect to judge the extent of spiroconjugation. B-N is shortest, as expected, and the elements of Period 3 show the expected decrease in M-N distance based on periodic trends. Stability of the mediator should follow from this data, narrowing the search for mediator candidates for future studies.

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

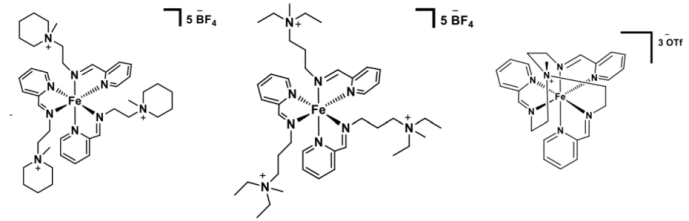
Capacity Fade in [3]radialene Aqueous Organic Catholytes – Dimerization Studies



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

Christopher Bejger
Fuead Hasan
Jonathan Gillen

UNIVERSITY OF NORTH CAROLINA CHARLOTTE

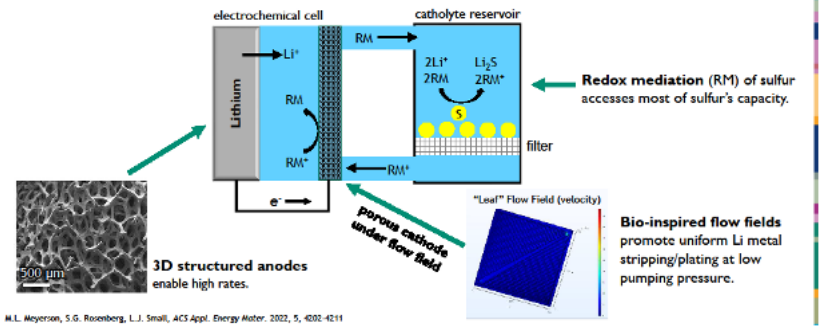


LANL

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.



Redox mediation (RM) of sulfur accesses most of sulfur's capacity.

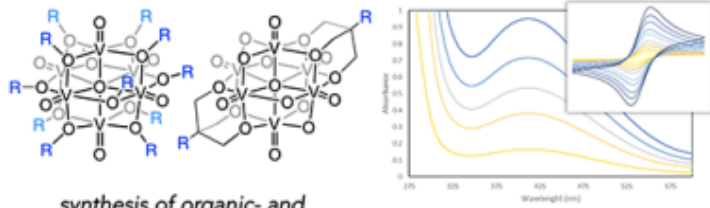
3D structured anodes enable high rates.

Bio-inspired flow fields promote uniform Li metal stripping/plating at low pumping pressure.

M.L. Meyerson, S.G. Rosenberg, L.J. Small, *ACS Appl. Energy Mater.* 2022, 5, 4202-4211

Leo Small

Metal Oxide Clusters for Energy Conversion and Storage



synthesis of organic- and heteroatom-functionalized POVs → physicochemical analysis

Structure-activity Relationships

Ellen Matson

Project Contacts

THIS WORK WAS SUPPORTED THROUGH THE ENERGY STORAGE PROGRAM, MANAGED BY DR. IMRE GYUK, IN THE U.S. DEPARTMENT OF ENERGY'S OFFICE OF ELECTRICITY.

Travis Anderson, PI

Sandia National Laboratories

tmander@sandia.gov

505-844-4766