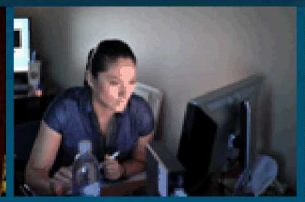
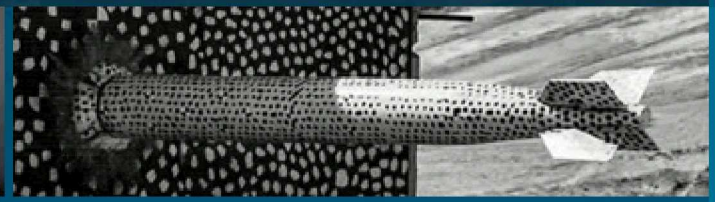
SAND2020-9519PE

Higher Voltage Iron Bipyridines for Non-Aqueous Redox Flow Batteries





PRESENTED BY

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Non-aqueous Flow Batteries

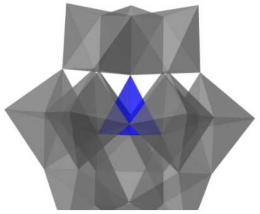
Project Goal: Build a better flow battery* by targeting (1) Energy Density (2) Materials Cost (3) Mechanisms of Capacity Fade

$\text{Energy Density}_{RFB} = \frac{1}{2}nFV_{cell}c_{active}$

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

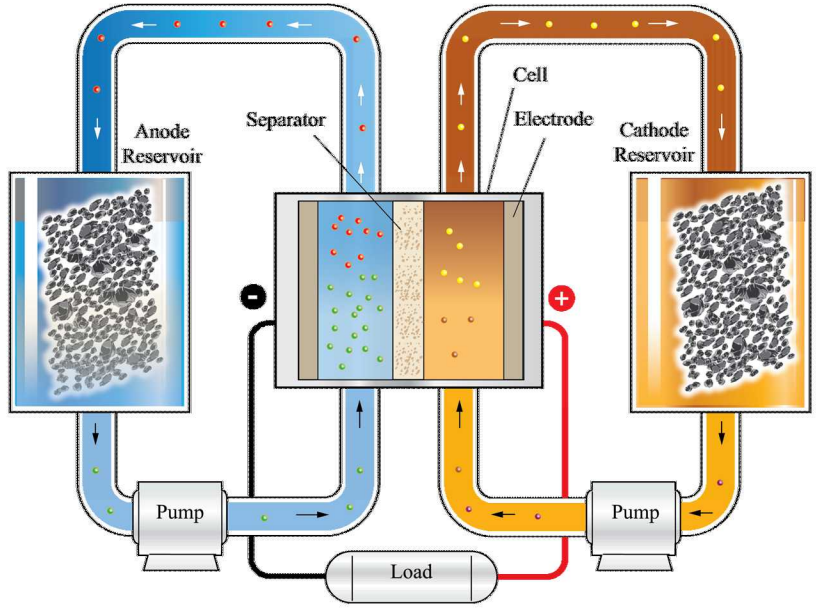
$ED_{MetIL} = \frac{1}{2}2F2_{cell}3_{active} =$ **6.0F** **Low Cost Materials** **Viscosity** ☠☠

$ED_{MacM} = \frac{1}{2}2F2_{cell}0.1_{active} =$ **0.2F**



$ED_{RedTarg} = \frac{1}{2}1F3_{cell}5_{active} =$ **7.5F** **High Energy Density**

Surface Area Kinetics ☠



*>4.4 mol e^-/L according to Darling *et al.*, *Energy Environ. Sci.*, **2014**, *7*, 3459-3477.

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

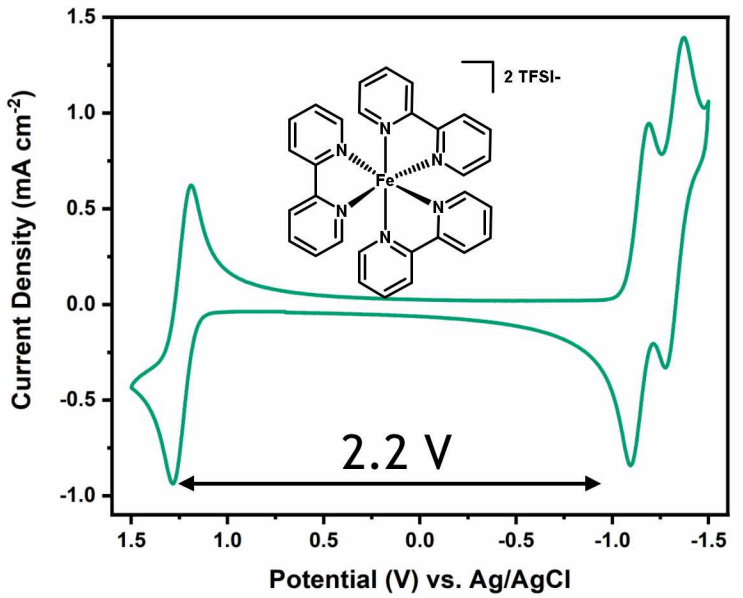
$ED_{MCC} = ½2F2.2_{cell}0.2_{active}$ = **0.4F** **Low Cost Materials** **Crossover** ☠

First Generation redox reactions (2.2 V)

Catholyte: $Fe(Bipy)_3(BF_4)_2 \rightarrow Fe(Bipy)_3(BF_4)_3 + e^-$

Anolyte: $Ni(Bipy)_3(BF_4)_2 + 2\ e^- \rightarrow Ni(Bipy)_3$

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



Next Generation

$ED_{MCC} = ½2F2.6_{cell}\,I_{active}$ = **2.6F**

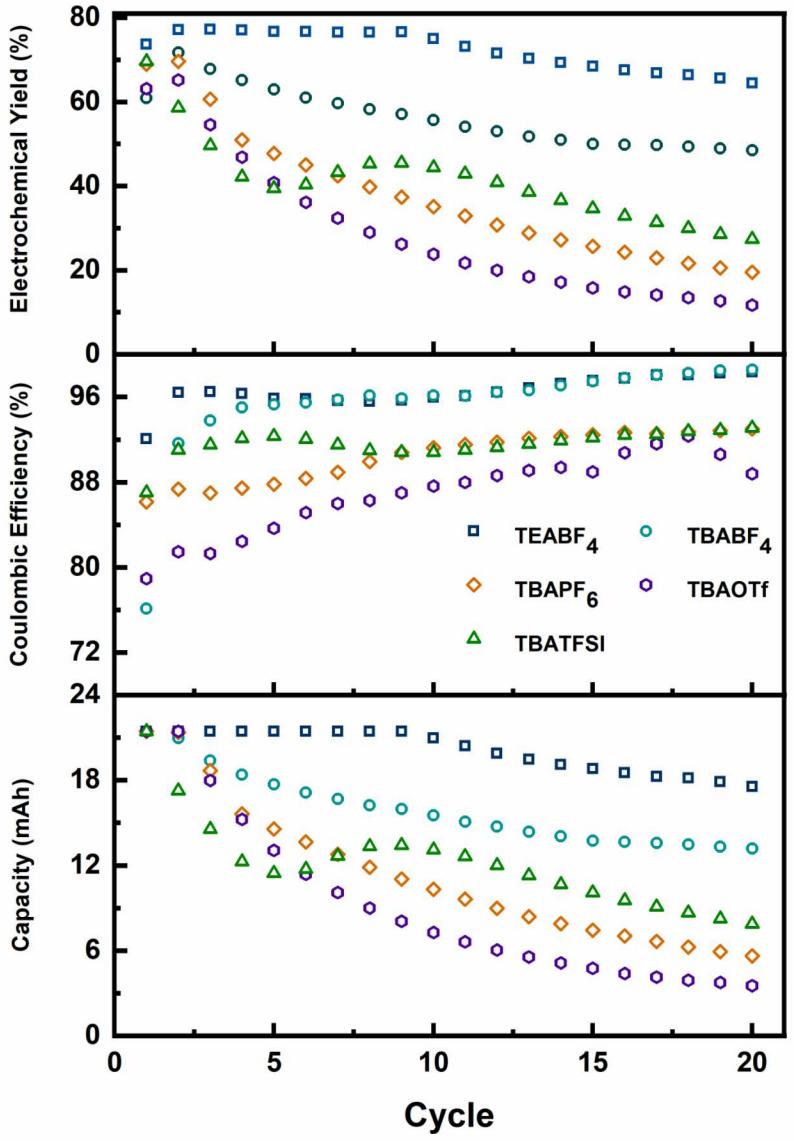
Lower Symmetry, Higher Solubility

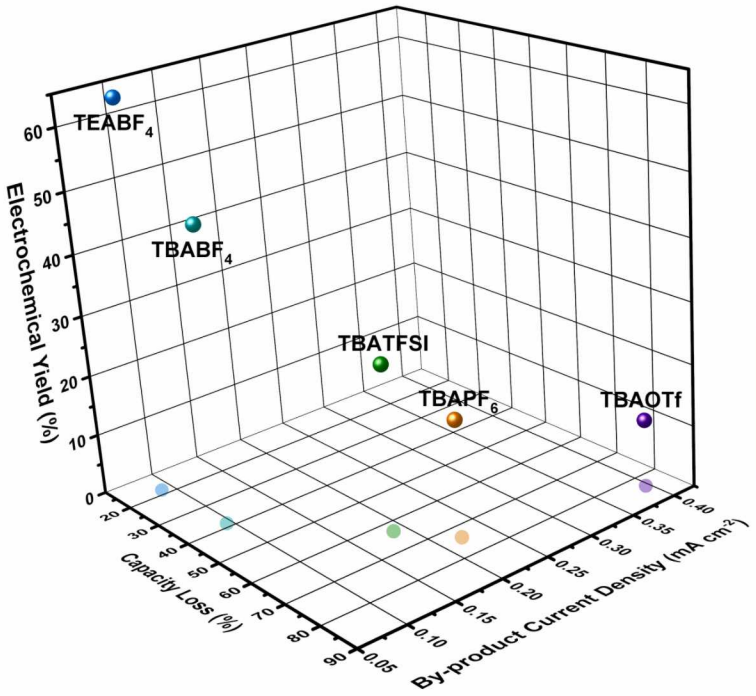
Tunable Ligands, Wider Voltage

(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.

Second Generation Salt Study

- Argon Glovebox, 0.5 M electrolyte, 0.2 M MCC, PC, unsupported AEM, 10 mA cm^{-2}
- TEA^+ is superior to TBA^+
- BF_4^- is a superior anion
- $TEABF_4$: 96.5 % CE
- A by-product forms upon cycling
- Common decomposition mechanisms: ligand shedding and oxidative degradation
- Built RFBs with impure $Fe(bpy)_3(BF_4)_2$
- 30 % impurity = 30% decrease in EY, CE, capacity
- Currently in the process of characterizing impurity



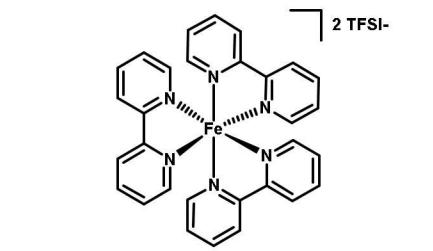


By-product formation correlates with RFB EY, CE, capacity loss

Tuning Bipyridine Ligands

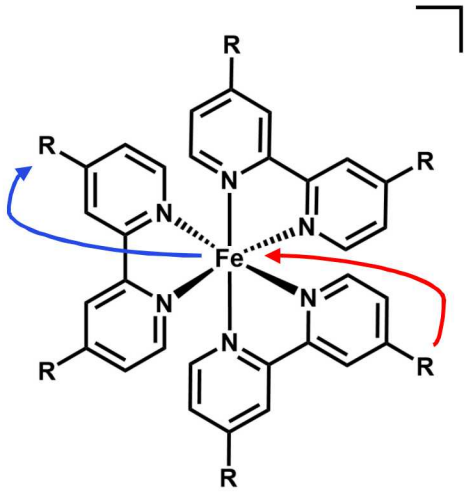
Goal: produce a higher voltage symmetric RFB

Samsung RFB



Fe(II)/(III)

Our complexes



R = CF_3, CO_2Me, Br, H, Me, ^tBu, OMe, NH_2

Movement of e- density with substituents

Substituent inductive effects

Electron-withdrawing

More positive $E_{1/2}$

More difficult to oxidize Fe(II)

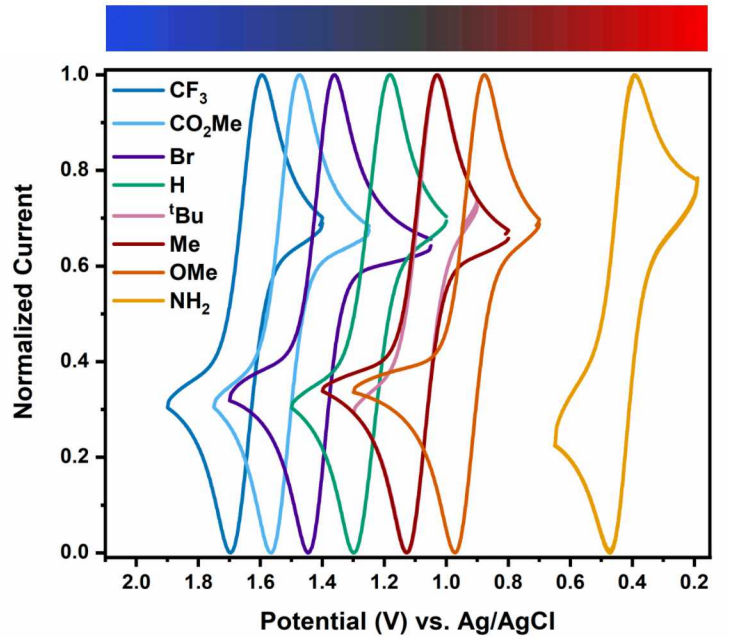
Electron-donating

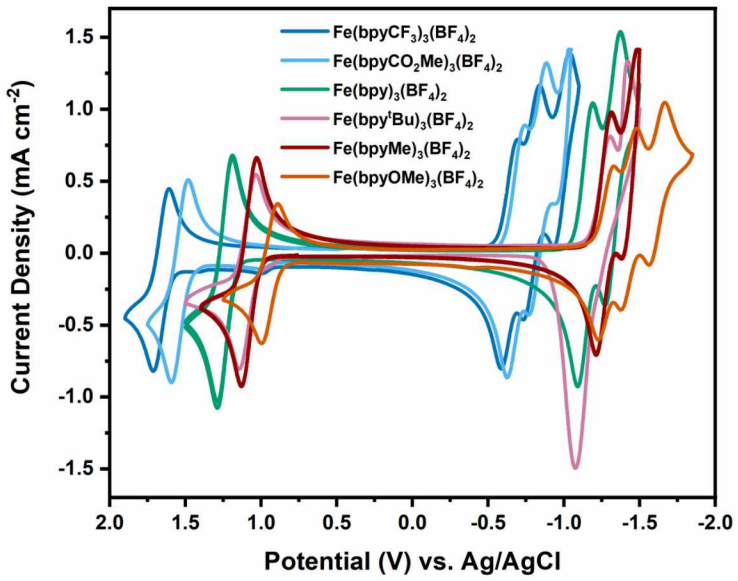
More negative $E_{1/2}$

Easier to oxidize Fe(II)

bipyridine: traditional π-acceptor ligand

Ligand Effects on Redox Potentials





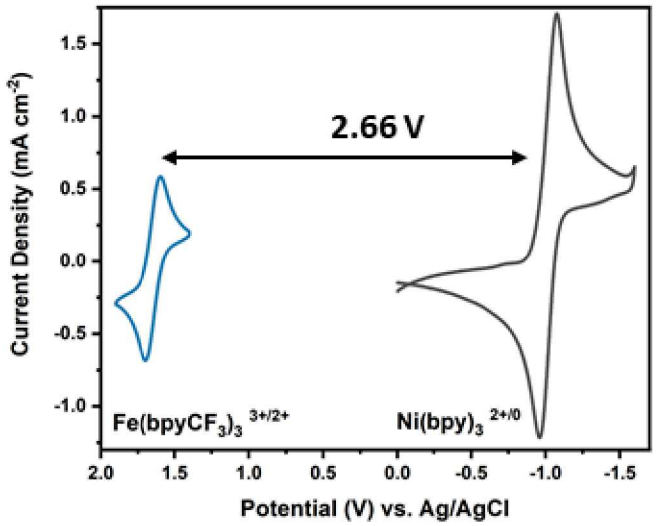
	$Fe^{3+/2+}$ $E_{1/2}$ (V)	$Fe^{2+/+}$ $E_{1/2}$ (V)	$\Delta E_{1/2}$ (V)
$Fe(bpyCF_3)_3(BF_4)_2$	1.65	-0.63	2.28
$Fe(bpyCO_2Me)_3(BF_4)_2$	1.53	-0.68	2.21
$Fe(bpyBr)_3(BF_4)_2$	1.43	-	-
$Fe(bpy)_3(BF_4)_2$	1.25	-1.12	2.37
$Fe(bpy^tBu)_3(BF_4)_2$	1.09	-1.19	2.28
$Fe(bpyMe)_3(BF_4)_2$	1.07	-1.25	2.32
$Fe(bpyOMe)_3(BF_4)_2$	0.94	1.27	2.21
$Fe(bpyNH_2)_3(BF_4)_2$	0.43	-	-

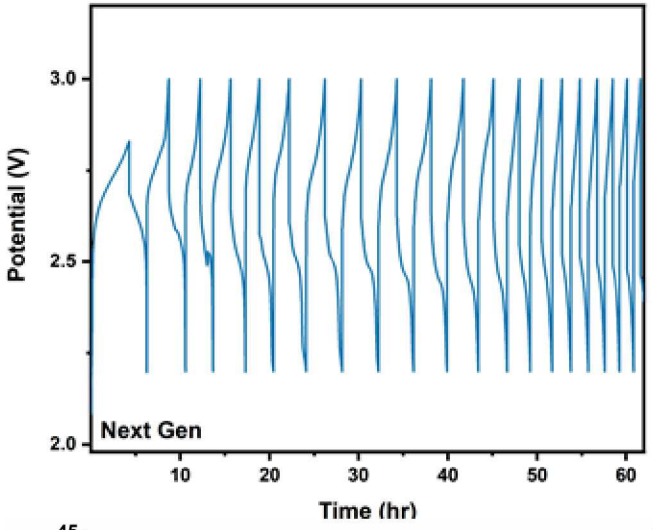
Fe(II)/(III) ligand voltage gap

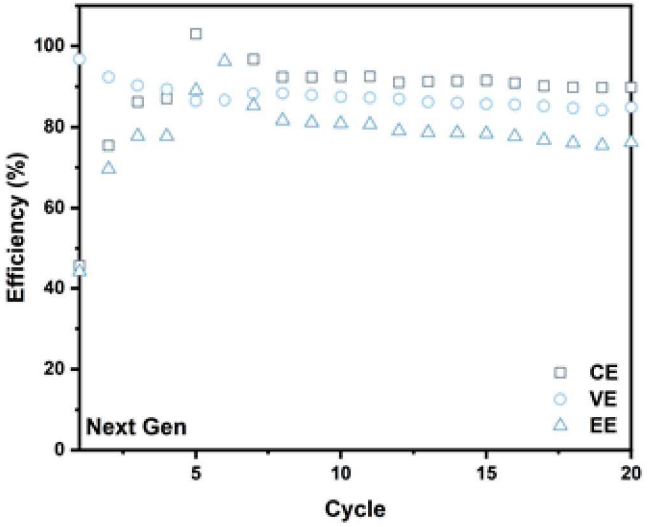
Inductive effects change ease oxidation of Fe(II)
EWGs shifted positively by up to 0.4 V
EDGs shifted negatively by up to 0.8 V
Fe(II) and ligand-centered redox shifted together

Asymmetric 2.6 V Fe-Ni RFB

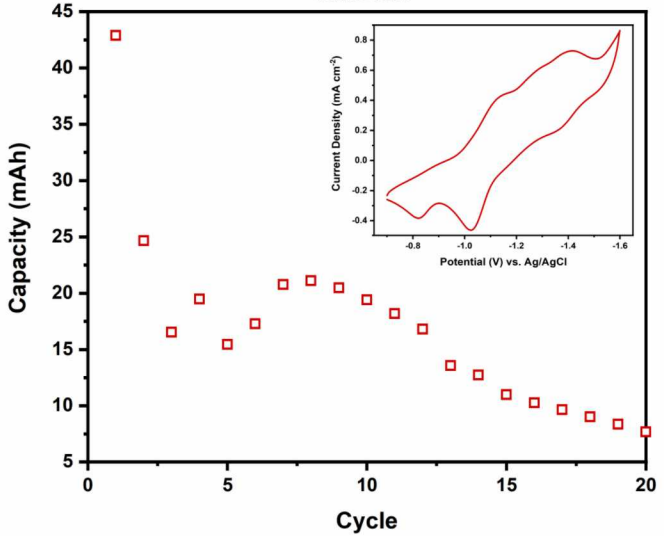
$Fe(bpyCF_3)_3(BF_4)_2$ had highest catholyte $E_{1/2}$ of 1.65 V (0.4 V increase)
Built $Fe(bpyCF_3)_3(BF_4)_2$/$Ni(bpy)_3(BF_4)_2$ to understand stability limits of cathode







Average CE and EE:
90.6 and 78.0 % over 20 cycles



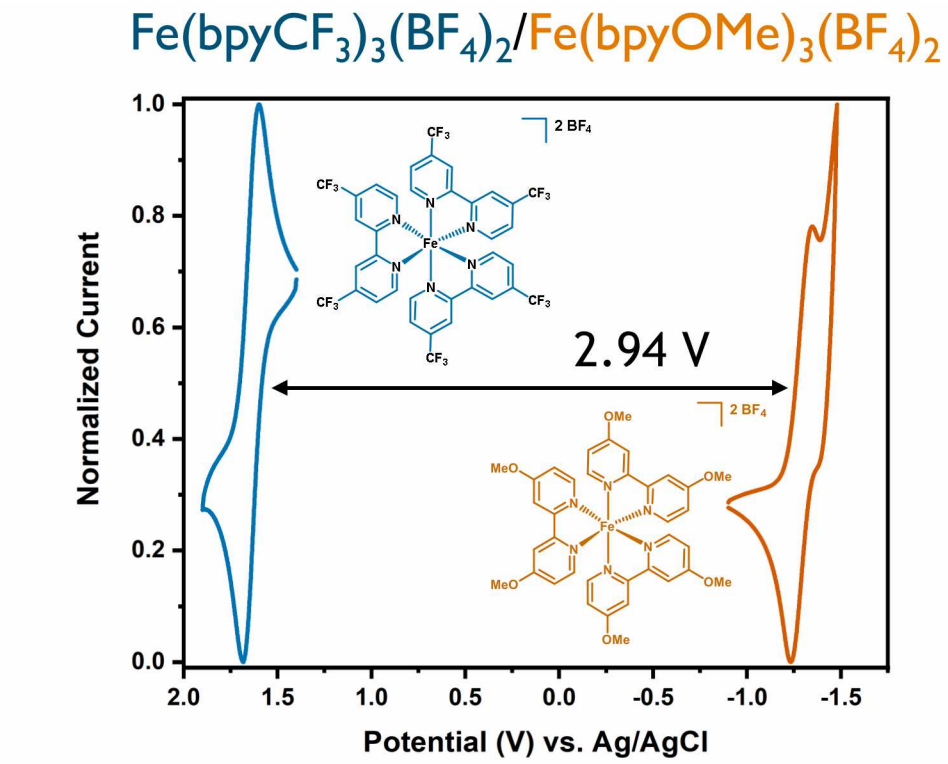
Catholyte showed cycling stability at high voltage but anolyte degraded, resulting in capacity fade

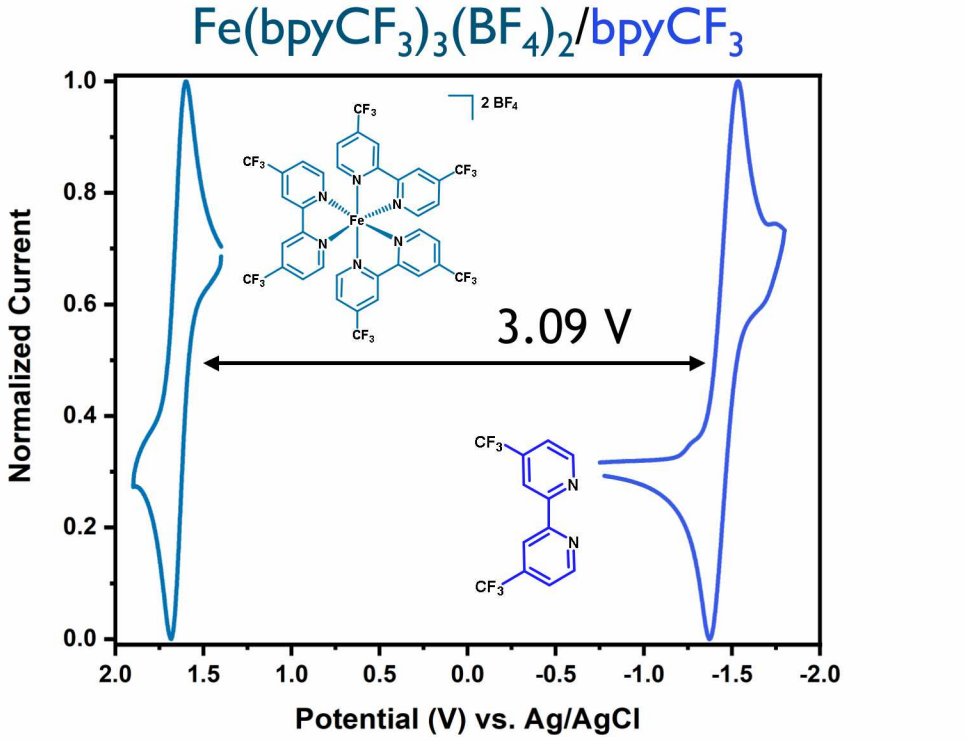
Future Directions

We learned that:

- Crossover is less observed in symmetric RFBs
- $Ni(bpy)_3(BF_4)_2$ has poor stability as an anolyte
- Symmetric $Fe(bpyR)_3(BF_4)_2$ redox couples shift together

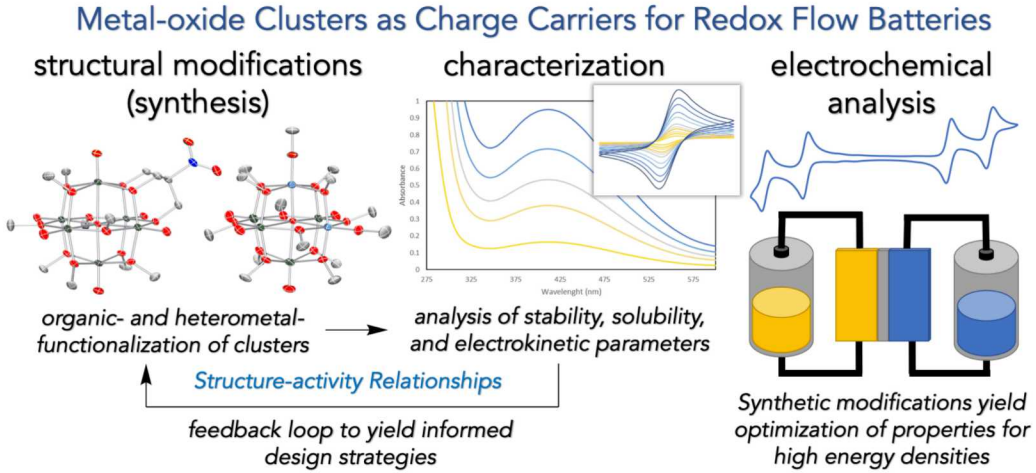
Pseudo-symmetric RFBs may extend voltage window, show low crossover, and solve anolyte stability issue

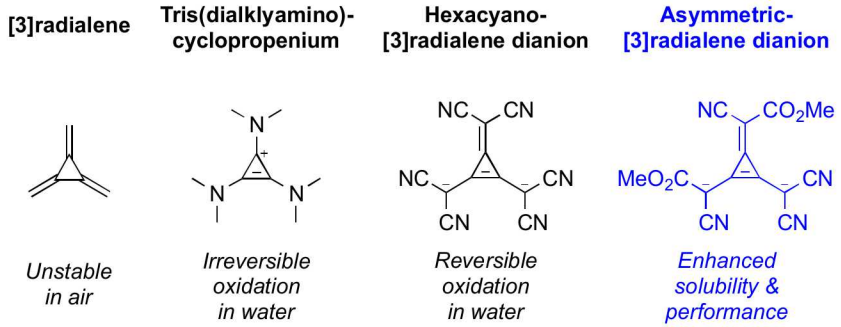




External Collaborations

UNIVERSITY COLLABORATORS		PROJECT
Mitch Anstey	Davidson College	Redox molecules
Ellen Matson	University of Rochester	Redox molecules
Christopher Bejger	UNC Charlotte	Redox molecules





Accomplishments

Technical Presentations

H. Pratt, L. Small, T. Anderson "Diagnostics for failure modes in non-aqueous flow batteries" 236th ECS Meeting, Atlanta, GA, October 13-17, 2019.

Invited Talks

H. Pratt, L. Small, T. Anderson "Elucidating failure modes in non-aqueous flow batteries" 2020 Spring MRS Meeting and Exhibit, Boston, MA, November 28-December 4, 2020.

Patents Issued

D. Sava Gallis, H. Pratt, T. Anderson, N. Hudak "Metal-Organic Framework Electrodes for Sodium Ion Batteries" U. S. Patent 10,497,971, December 3, 2019.

Journal Publications

L. VanGelder, H. Pratt, T. Anderson, E. Matson "Surface functionalization of polyoxovanadium clusters: generation of highly soluble charge carriers for nonaqueous energy storage" Chemical Communications, October 18, 2019, vol. 55, 12247-12250, https://doi.org/10.1039/C9CC05380H

N. Turner, M. Freeman, H. Pratt, A. Crockett, D. Jones, M. Anstey, T. Anderson, C. Bejger "Desymmetrized hexasubstituted [3]radialene anions as aqueous organic catholytes for redox flow batteries" Chemical Communications, March 4, 2020, vol. 56, 2739-2742, https://doi.org/10.1039/C9CC08547E

Project Contacts

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