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A HISTORY OF BI-REDOX MOLECULES (BRMS) FOR NEXT-GENERATION FLOW BATTERIES AT SANDIA

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**Presenting*

Sandia National Laboratories

DOE OE Energy Storage Peer Review & Annual Meeting, 2026

U.S. DEPARTMENT of ENERGY

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PROJECT OVERVIEW

- Goal: To develop a low-cost, robust, and scalable flow battery active material to advance grid energy storage
- Current Practice: Deployed systems primarily use Vanadium active material (expensive, temperature sensitive)
- Why SNL: Unique personnel skills (electrochemistry, synthesis), rich history in flow batteries, state-of-the-art prototyping laboratory
- Innovation: New synthetic protocol to develop active materials – scaffold generated with high solubility & stability
- Duration: FY21-Present
- Impact: Flow battery development companies, lower cost for grid energy consumers
- Vertical/Investment Area: Materials and Systems Innovation
- Alignment/Supports strategic pathway: Optimize & Grow

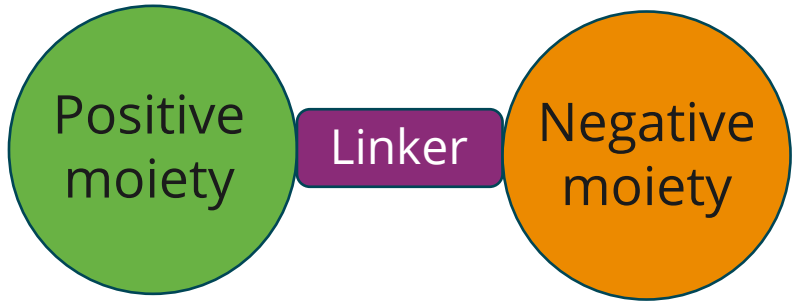
WHY BI-REDOX MOLECULES (BRMS) FOR FLOW BATTERIES (FBS)?

All Vanadium (standard)

- Standard Vanadium FBs acts as a symmetric system - V on both sides
  - Losses from crossover can be easily mitigated by rebalancing
- Vanadium redox is extremely stable
- Vanadium is temperature sensitive (precipitation of active material) and sourcing is expensive

BRMs

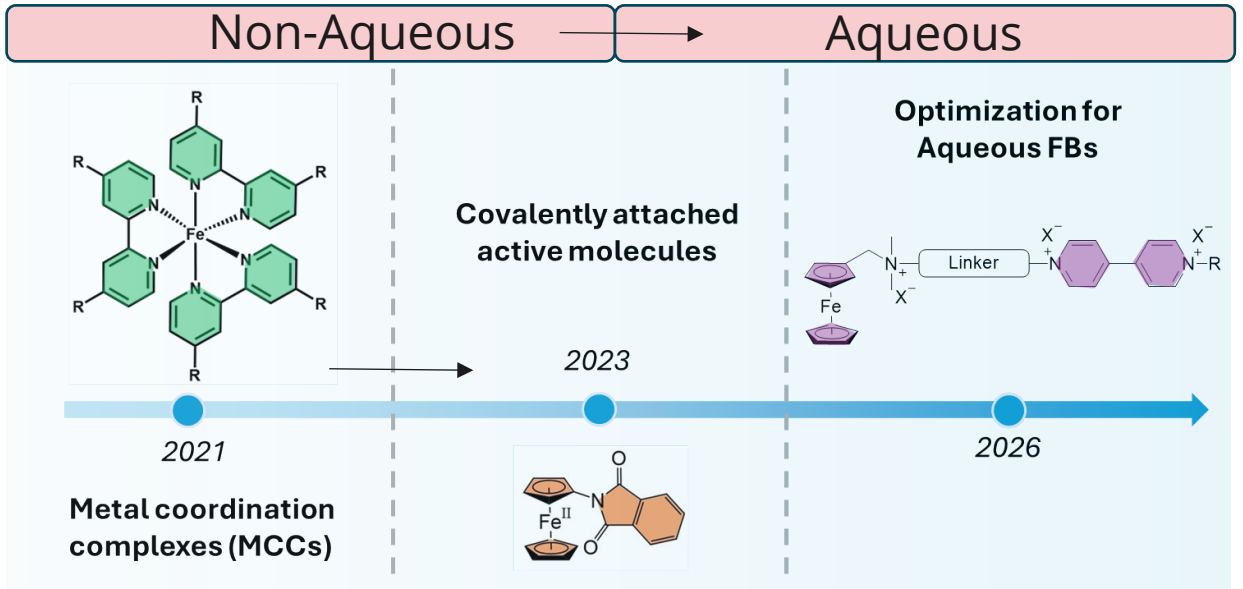
- Retain the positive characteristics of the all-Vanadium design
- Developed from **low-cost, Earth-abundant** elements



HOW TO ACHIEVE A BETTER FLOW BATTERY

- **Project Goal:** Build a better flow battery by targeting:

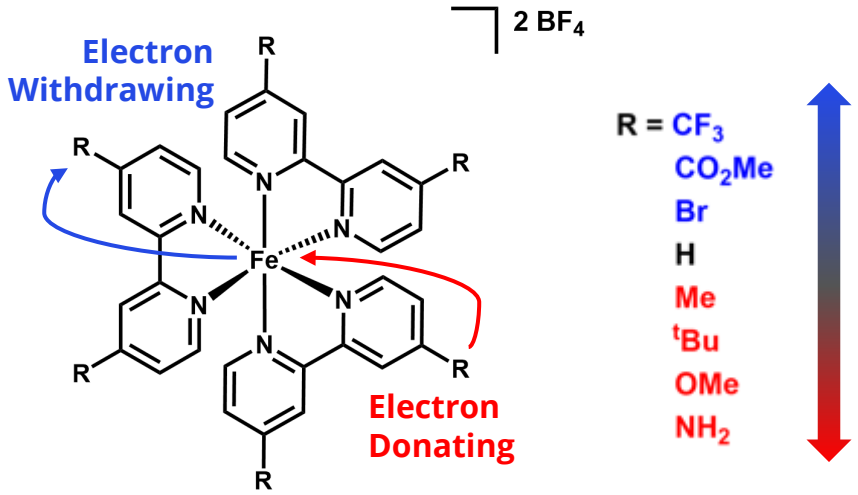
1) Energy Density (ED)	2) Active Material Cost	3) Capacity Fade
$ED = \frac{1}{2} n F V_{cell} C_{active}$ Increase **electron transfer #** Increase **concentration** Widen **cell voltage** F=Faraday's constant (charge/mol e^-)	Utilize low-cost elements Organic (C, N, O) Inorganic (Fe, Zn)	Identify failure modes & mitigate Molecular degradation Crossover Component failure



METAL COORDINATION COMPLEXES AS BRMS (1ST GENERATION)

- Iron-based MCCs are simplistic to synthesize in high yield, iron is low-cost/abundant
  - Ligand exchange rate is slow in non-aqueous electrolyte
- Iron bipyridines, $Fe(bpy)_3$ derivatives, have a wide potential difference (>2.2 V)

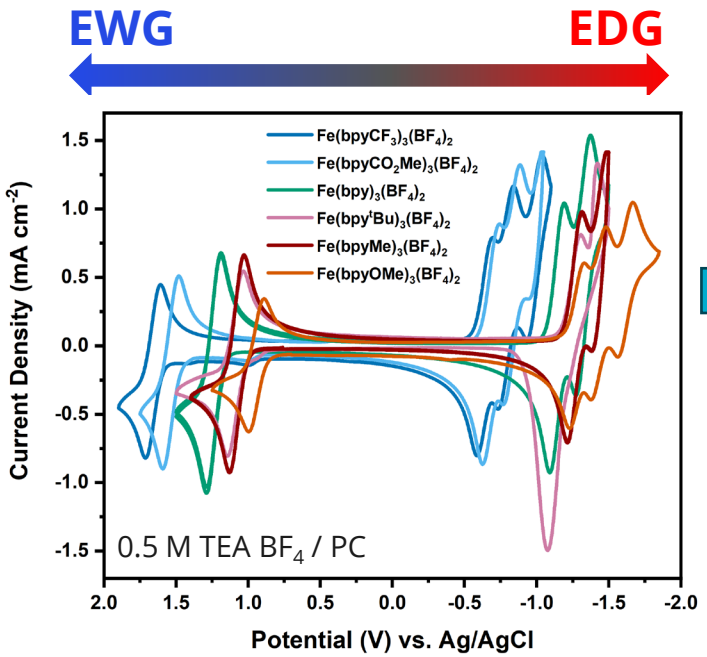
$$ED = \tfrac{1}{2} n F V_{cell} C_{active}$$



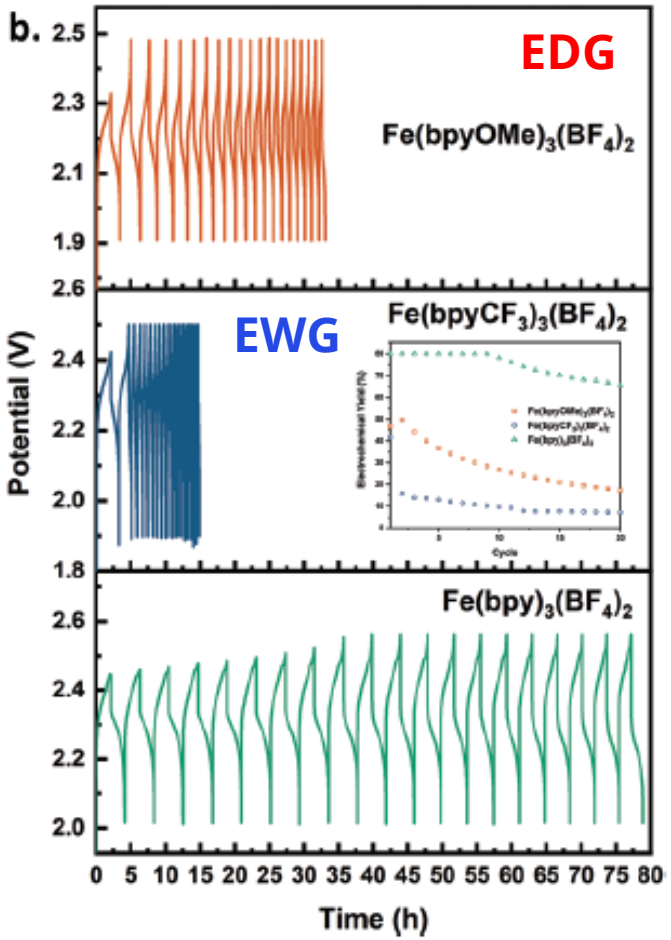
$Fe(bpyR)_3(BF_4)_2$

- Simplistic, single-step reaction to yield a library of $Fe(bpy)_3$ derivatives
- Looking specifically at how adding Electron Withdrawing Groups (EWGs) and Electron Donating Groups (EDGs) influences electrochemical properties & stability of bpy

SUBSTITUTION TUNES VOLTAGE – AND STABILITY!



Battery Testing

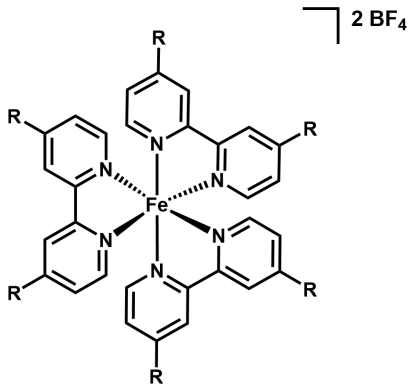


- Tuning voltage is simplistic
- Tuning **molecular stability is harder**

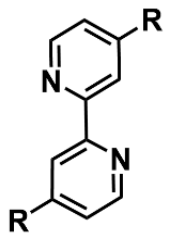
Negolyte instability – performance loss

PSEUDO-SYMMETRIC DESIGN – 2ND GEN

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

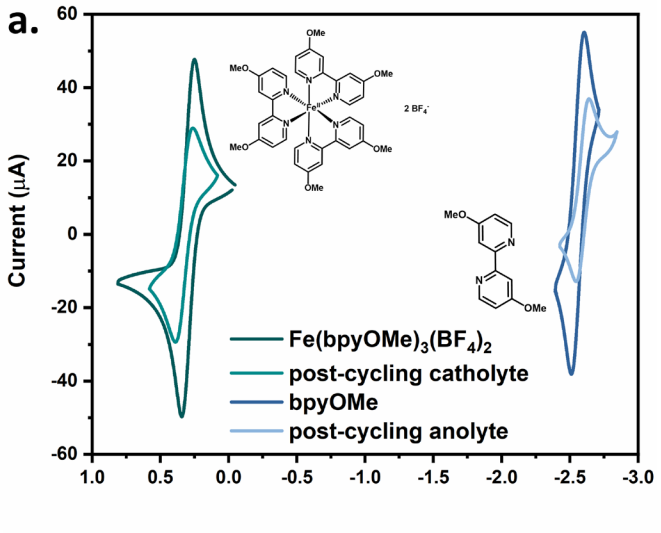


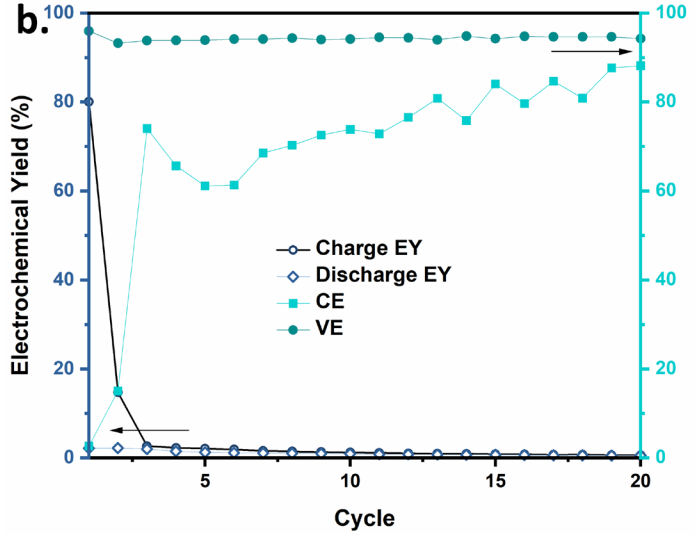
Posolyte

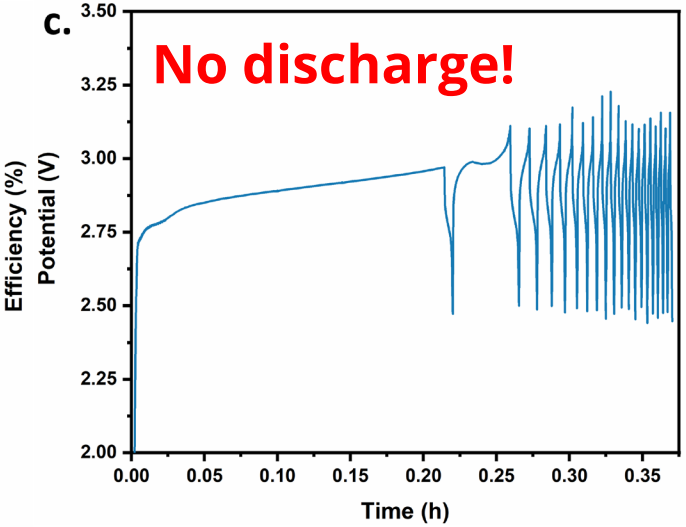


R = CF_3, OMe

Negolyte

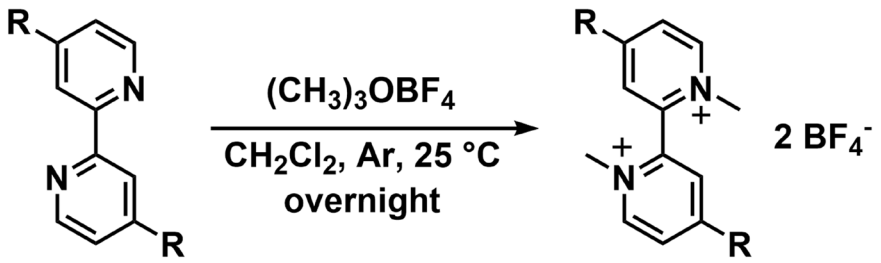


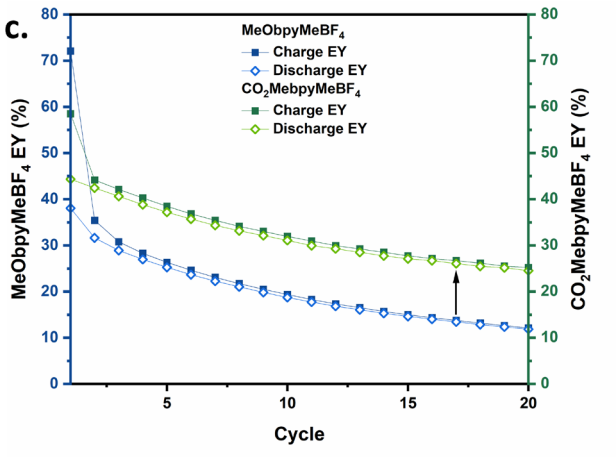


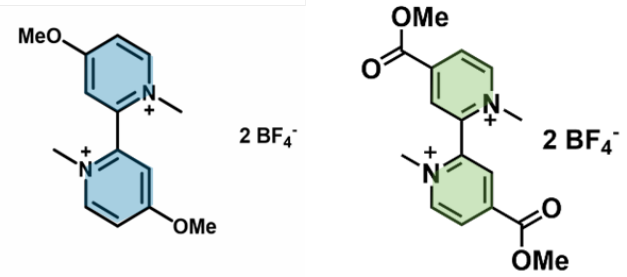


C. X. Kolesnichenko *et al*. *ChemElectroChem*, **2022**, e202101490.

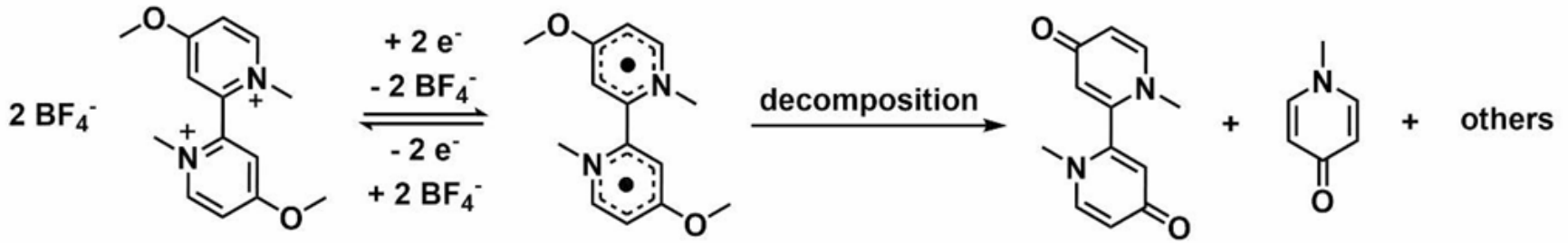
TUNING ONLY THE LIGAND SHOWED FURTHER IMPROVEMENT





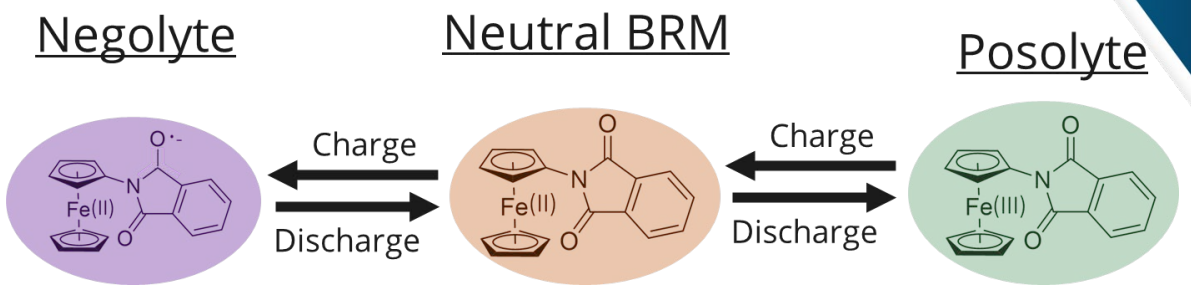


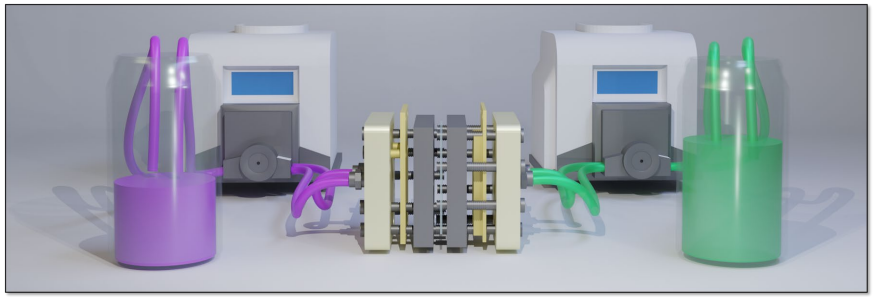
- Tuning the ligand (on anolyte side only) is facile and greatly improves cycling performance
- However, still unstable – **radical reactivity difficult to stabilize**

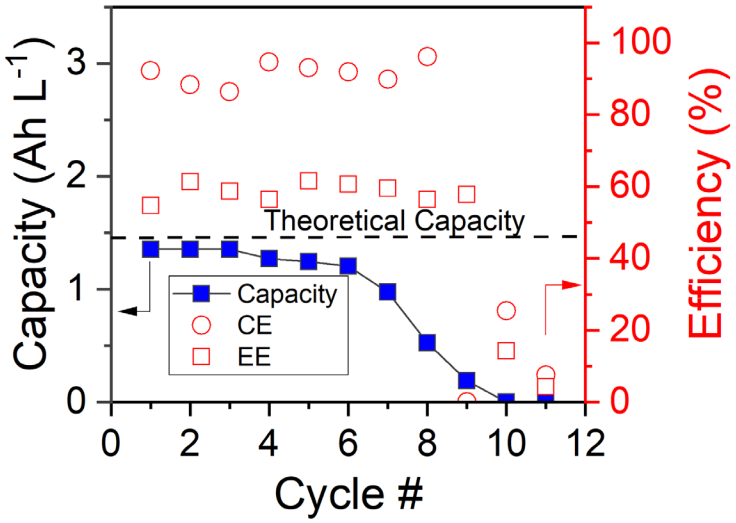


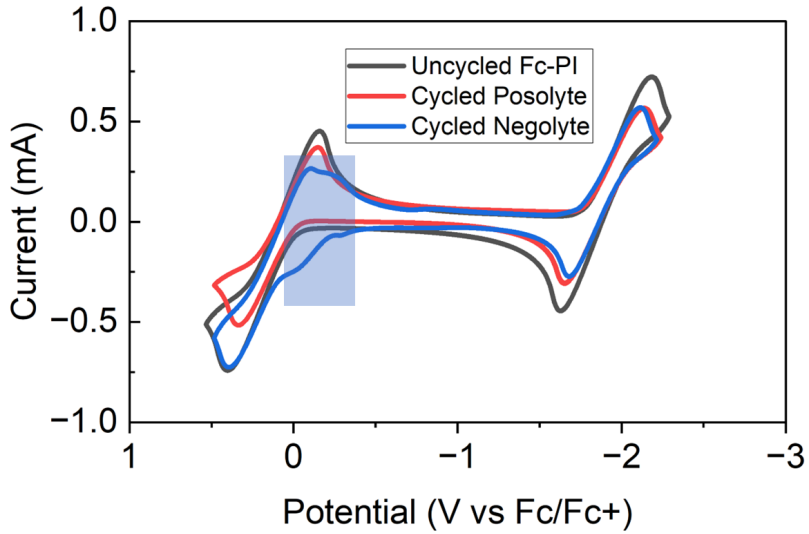
3RD GENERATION – COVALENTLY LINKED BRMS

- Mitigation of ligand shedding degradation
- Literature showed these BRMs were stable when cycled in coin cells (not flowing systems!)
- Full loss of capacity in only **10 cycles** in flow cell!

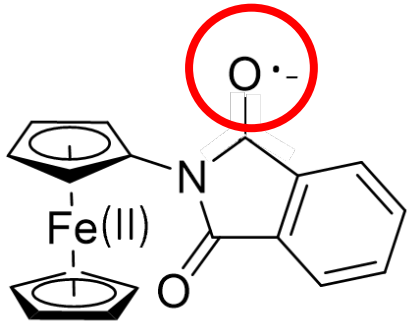






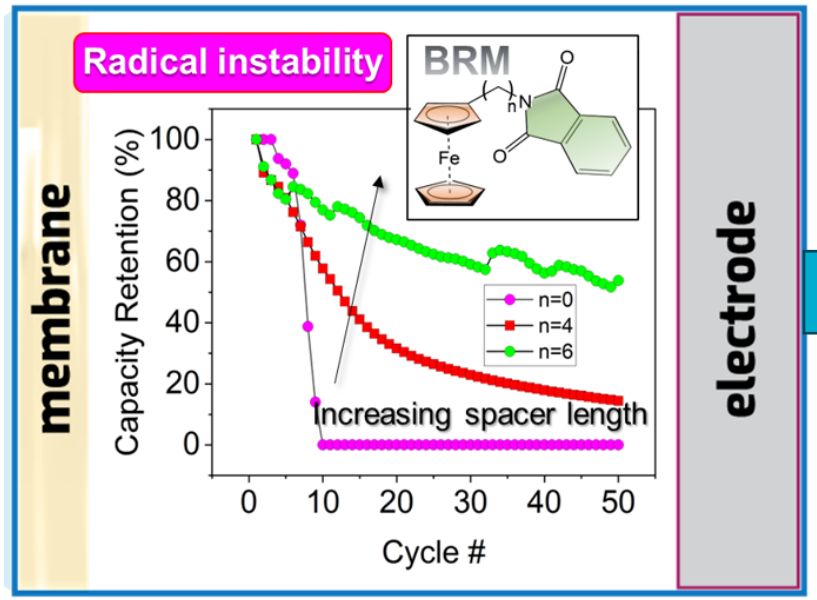


Radical induced degradation

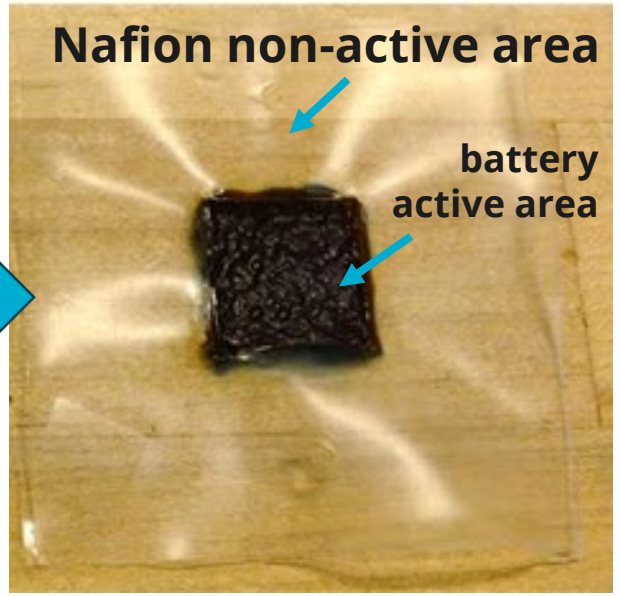


PERFORMANCE OPTIMIZATION – COVALENT LINKERS

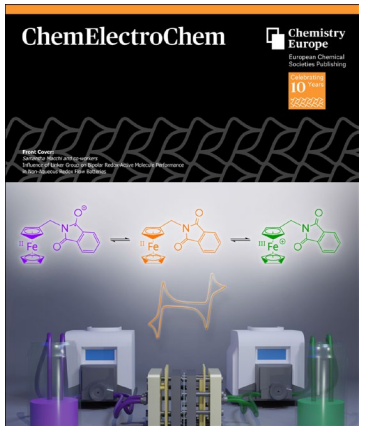
- Intramolecular stability could be reasonably achieved by extending the length of the linker between active groups
- However, plagued by additional degradative modes - **membrane fouling**



membrane fouling



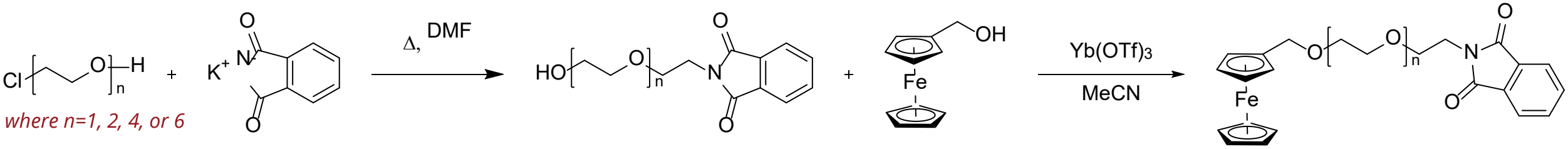
[1] Macchi et al., *ChemElectroChem* **2024**, 11, e202400450



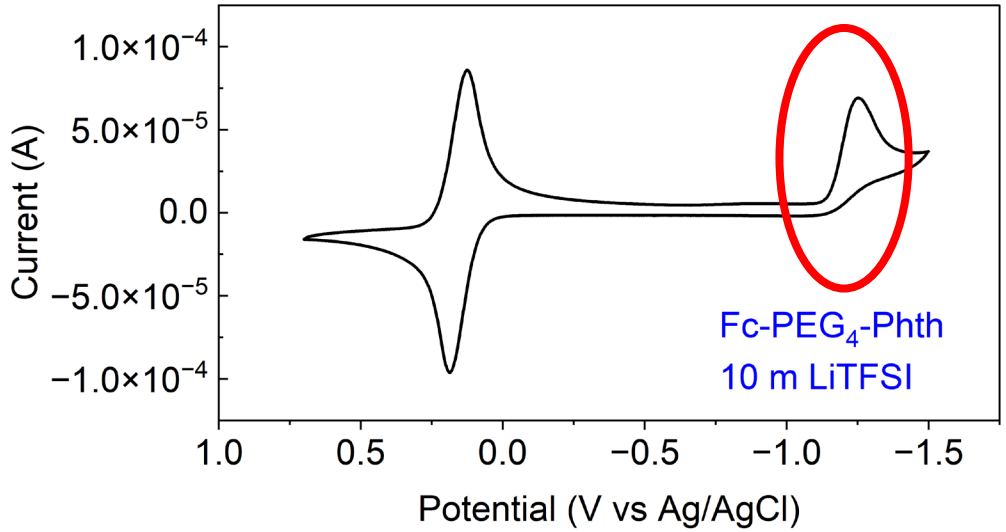
- Moving towards aqueous batteries – **even more cost competitive**

MOVING TOWARDS AQUEOUS

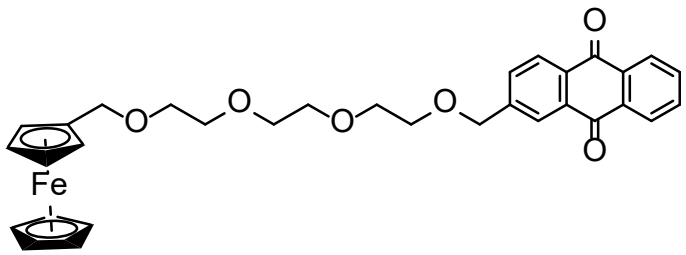
- Much lower cost compared to NA as water is much less expensive than organic solvents
- Aqueous batteries have narrower electrochemical stability window (~1.23 V) – can be overcome with “water-in-salt” systems
- From previous Non-Aqueous work, a PEGylated derivative has the most promise for water solubility:



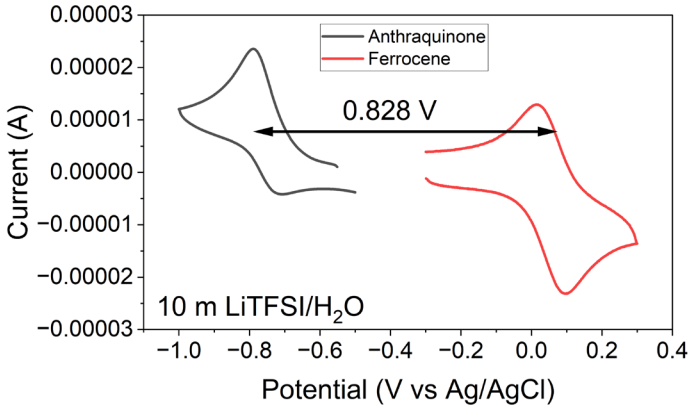
Ferrocene-PEG$_n$-Phthalimide-based BRMs showed **little to no water solubility** even up to 6 PEG units. Sparing solubility was obtained in 10 m LiTFSI. But **phthalimide reduction is irreversible.**



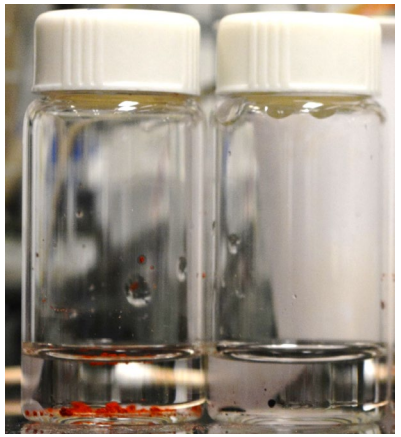
SWAPPED OUT PHTHALIMIDE FOR ANTHRAQUINONE



Fc-PEG$_4$-AQ was found to also be **mostly insoluble** in common aqueous electrolyte, but **showed a reversible reduction in 10 m LiTFSI**

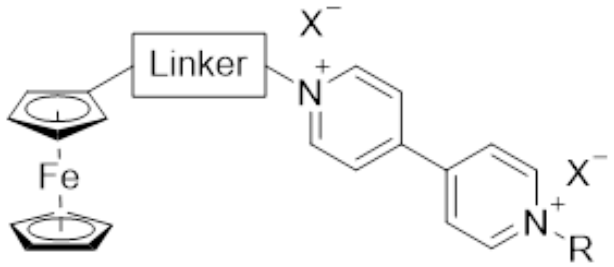


Added an amine group to help with solubility



Not water soluble

PRESENT FISCAL YEAR – HIGHLY SOLUBLE & ELECTROCHEMICALLY STABLE BRM



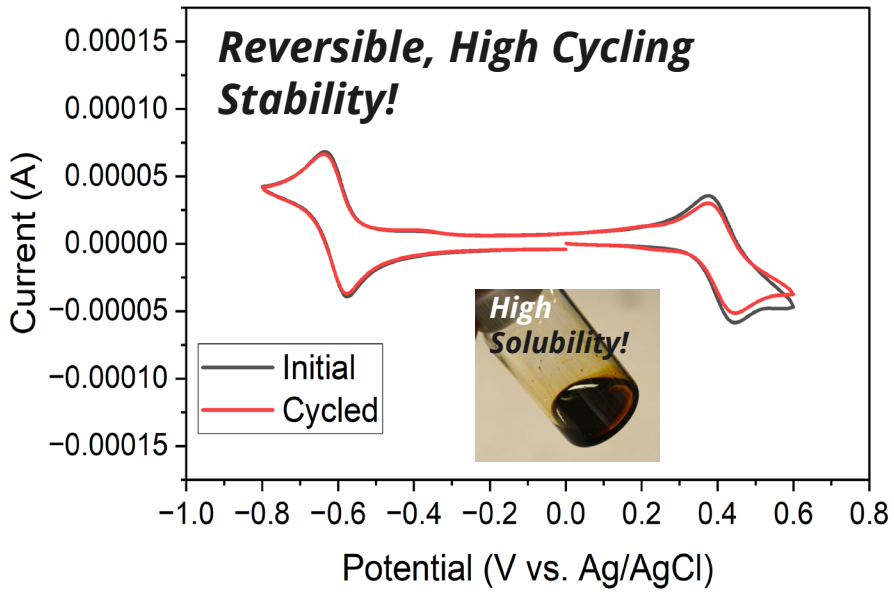
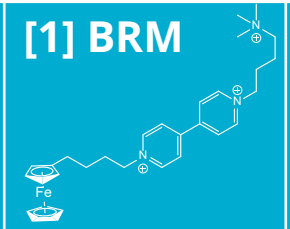


Fig. 2. Cyclic voltammograms of BRM before and after cycling, inset shows highly concentrated (>2M) BRM solution

- Comparison to literature confirms that the **driver of performance** is in the linker identity and **how the molecules are connected**

Parameter	[1] BRM 	SNL BRM
Water Solubility (M)	1.2 ✗	**>2** ✓
Cell Voltage (V)	0.7 ✗	**1.04** ✓
Capacity fade (%/cycle) @10 mA/cm²	0.00625 ✗	**0.00024** ✓

***See Poster: "Development of a Stable, Highly Water-Soluble Bi-Redox Molecule for Aqueous Flow Batteries"**

ACKNOWLEDGEMENTS

- *We acknowledge past members of the flow battery R&D group at Sandia including:*
  - *Claudina X. Cammack*
  - *Randi Porier*
  - *Harry D. Pratt*

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