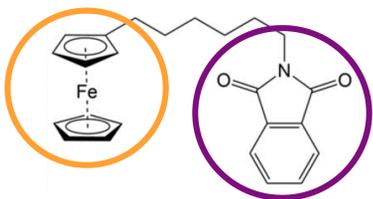


Mediated Biredox Flow Batteries

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Overview:
Aqueous redox flow batteries represent a scalable, cost-competitive solution to grid-scale energy storage. One of the more common failure modes for flow batteries involves “crossover” of the energy storing molecules from one side of the battery to the other. In the first year of this project, we are tackling this problem by synthesizing novel biredox molecules (BRMs). These energy-storing molecules can act as either cathode or anode materials, allowing the electrolytes in the anode and cathode to be the same and minimizing crossover. In parallel, we are working to increase the relatively low energy density of flow batteries via chemical mediation of solid energy-storing materials in the electrolyte tanks. The increased energy density will drive down costs for BRM-based flow batteries. Lastly, complementary membrane chemistries are being developed.

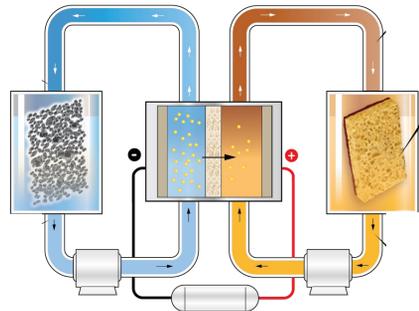
Operating Principles



A **Biredox molecule** is a single molecule that contains two redox-active moieties – **one optimized for the catholyte** and **one for the anolyte**.

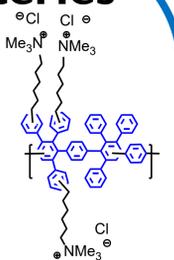
Macchi et al., *ChemElectroChem* 2024, 11, e202400450

Mediated flow batteries use solid particles to store energy, effectively boosting the energy storage capacity of the liquid phase. The redox-active molecules dissolved in the liquid phase react with the energy storing particles in tanks to access the additional energy storage capacity.

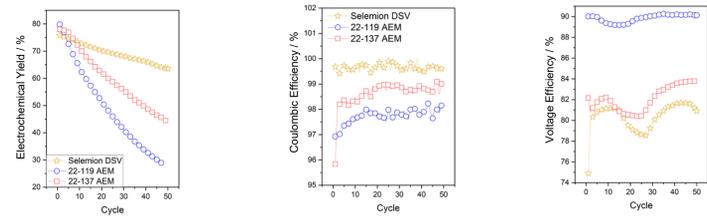


Membranes for Biredox Flow Batteries

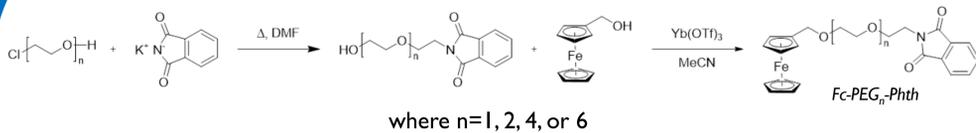
Membranes play a critical role in flow batteries to regulate charge balancing ion mobility and prevent electroactive species crossover. We began probing membrane selectivity by studying a model battery of methyl viologen/ $\text{Fe}(\text{CN})_6^{3-}$ with anion exchange membrane (AEM) Selenion DVS as a baseline against SNL AEM with the structure shown. The ability to tune the SNL AEM ion exchange capacity and thickness allows us to fine tune membrane properties to battery performance.



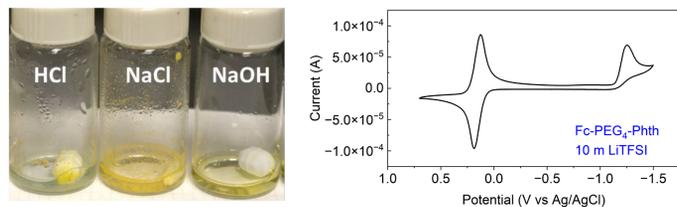
Selenion DVS (93 μm) displayed the highest ECV with nearly 100% CE, however VE maximized at 80%. To improve VE we first designed a membrane with a high IEC (2.2 meq/g) and thickness of 40 μm . The battery performance displayed high VE at 90%, but lower CE and ECV. To improve performance a thicker membrane was cast (100 micron) which did increase CE but also lowered VE. Our next step is synthesize a slightly lower IEC material with low thickness (20-30 micron).



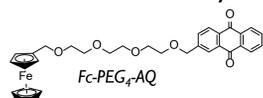
BRM Synthesis and Screening



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. However, we found that the phthalimide reduction is irreversible in water.

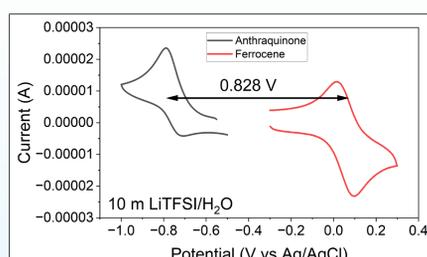


Thus, we sought out an alternative anolyte moiety based on anthraquinone (shown below) to improve electrochemical stability in aqueous solution.



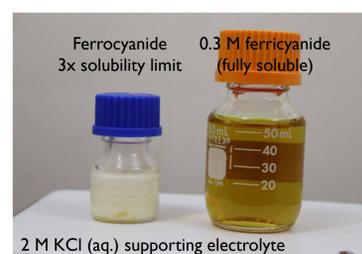
Fc-PEG_4 -Anthraquinone was found to also be mostly insoluble in common aqueous electrolytes, but anthracene shows a reversible reduction in 10 m LiTFSI

Solution	Soluble?
0.1 M NaOH	No
0.1 M HCl	No
5% MeOH	No
2% MeOH	No
2 M KCl	No
1 M NaCl	No
DI H ₂ O	No
10 m LiTFSI	Yes, 5 mM



Idealized Mediated Flow Battery

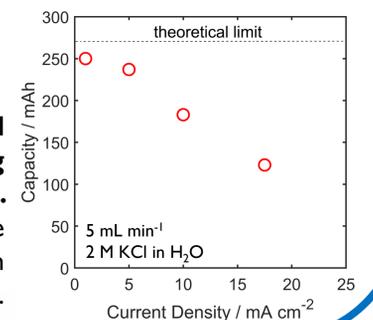
While BRMs were being synthesized, a mediated flow battery setup was developed using the commercially available ferricyanide system.



The anolyte tank contained ferrocyanide at 3x the solubility limit, while the catholyte tank contained ferricyanide below the solubility limit, using a larger volume to provide excess capacity.

At 1 mA cm⁻², >93% of the theoretical capacity is accessible, confirming successful mediation of the solid particles.

At 17.5 mA cm⁻², however, the accessible capacity decreases to 46%, slightly more than fraction of soluble ferrocyanide (35%).



Future Work

- Optimize BRM molecule structure to increase solubility while minimizing synthetic cost.
- Revise mediation flow cell to tolerate very high (>10 vol%) solids, while encouraging good mixing of solids with flowing electrolyte.
- Further fine tuning membrane IEC, thickness and polymer structure to optimize battery performance.