



## Presentation 102:

# Redox Flow Batteries Utilizing Soluble Iron Complexes

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DOE-OE Peer Review 2025  
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PNNL is operated by Battelle for the U.S. Department of Energy





# Project Overview

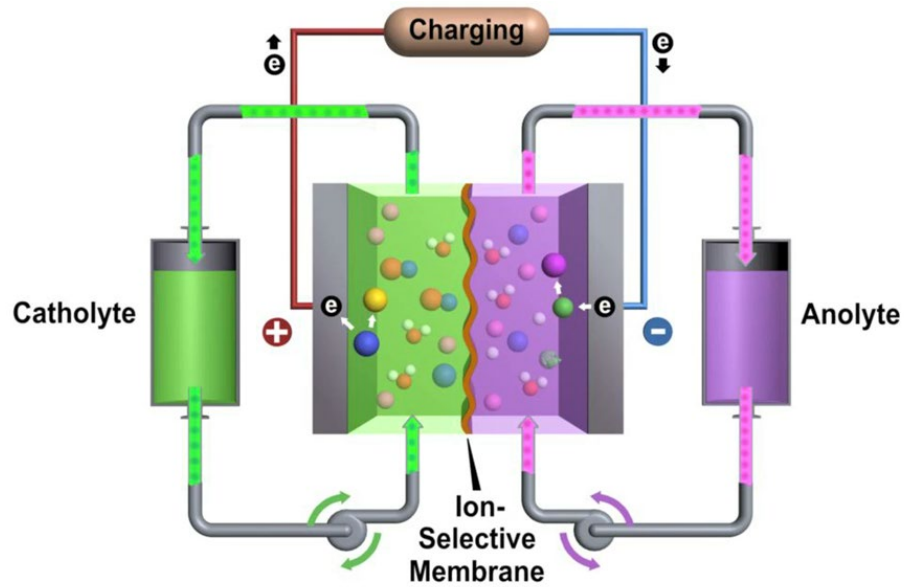
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- ✧ **Project Goal:** This project seeks to develop redox flow battery electrolytes based on low-cost and abundant iron, utilizing ligand coordination to enable stable, high performance iron electrolytes.
- ✧ **Current Practice:** The current state-of-the-art flow batteries utilize vanadium, which is more costly and faces more potential supply chain constraints than iron.
- ✧ **Why PNNL:** PNNL has extensive experience and capabilities for developing redox flow battery technologies, ranging from molecular-scale analysis of electrolytes to kW-scale prototyping.
- ✧ **Innovation:** The use of tailored ligands to bind iron can enable specific tuning of critical properties, such as solubility, stability, and redox potential.
- ✧ **Impact:** Successful development of these iron-based electrolytes could provide RFB developers with a scalable, abundant-material-based electrolyte suitable for large-scale deployments.
- ✧ **Alignment:** This project is accelerating the development and testing of a new energy storage technology that is cost-effective, safe, and durable, which is crucial to meeting the Administration's goal of providing reliable, affordable, secure, and resilient energy.



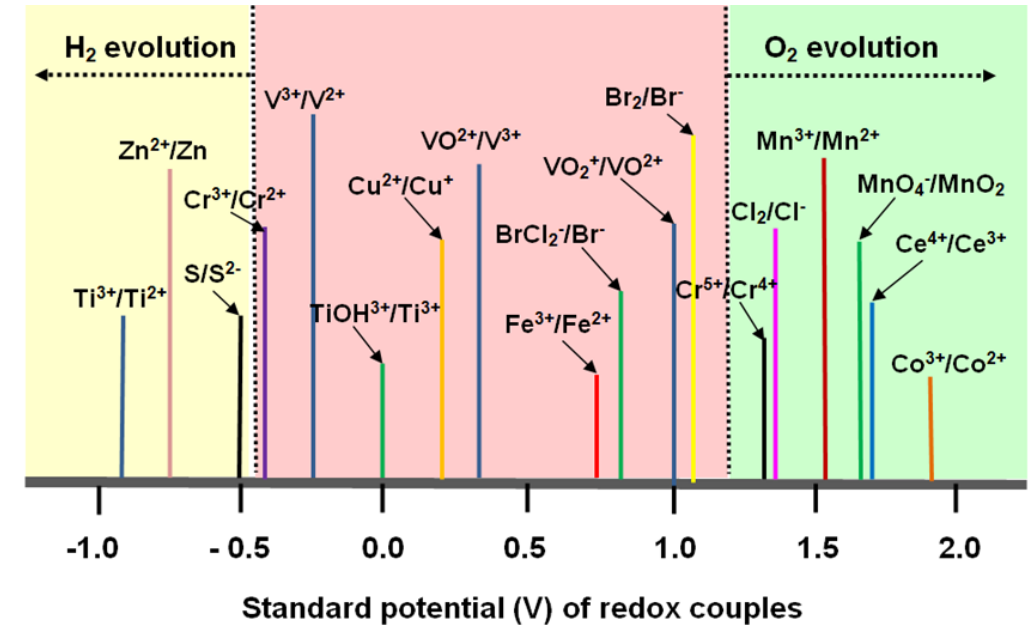
# Redox Flow Batteries (RFB)

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- **Decoupling of Power and Energy**
  - ✧ Extend duration with storage tank size
- **High safety**
  - ✧ Major constituent is water
  - ✧ Easy thermal management
  - ✧ Battery health monitoring
- **Easier recycling after service life**
  - ✧ Re-use/recycle active material

## ➤ Multitude of available chemistries



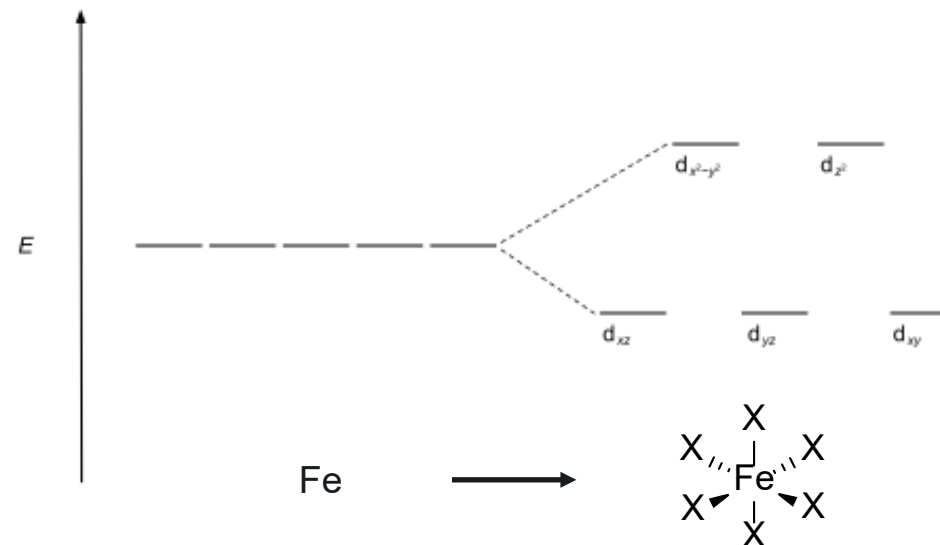
- **All iron systems**
  - ✧ Hybrid – Fe<sup>2+/3+</sup> / Fe<sup>2+/0</sup>
  - ✧ Coordination chemistry
    - ✧ Split redox potential of Fe<sup>2+/3+</sup>
    - ✧ Same metal/redox couple as catholyte/anolyte



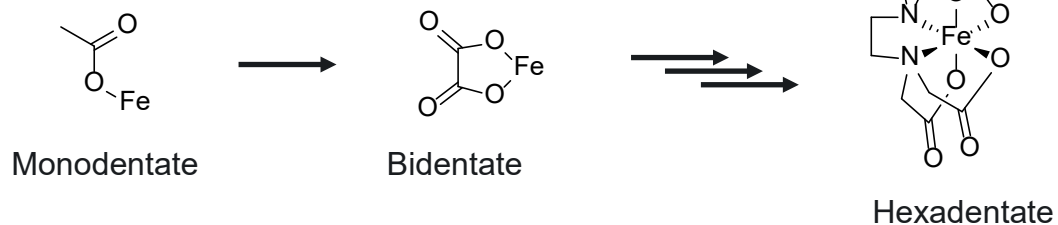
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# Iron Coordination Complexes

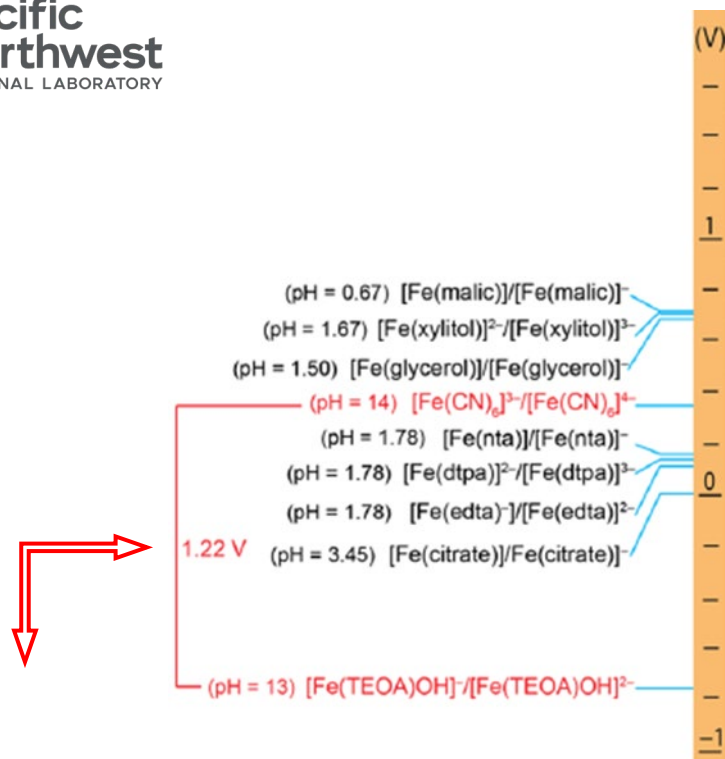
- ✧ Multitude of ligand options already produced at large scale (amines, carboxylates, alcohols, etc.)
- ✧ Tunable ionic charge, pH range, redox potential based on type and number of ligands
- ✧ Ligand denticity to control binding affinity



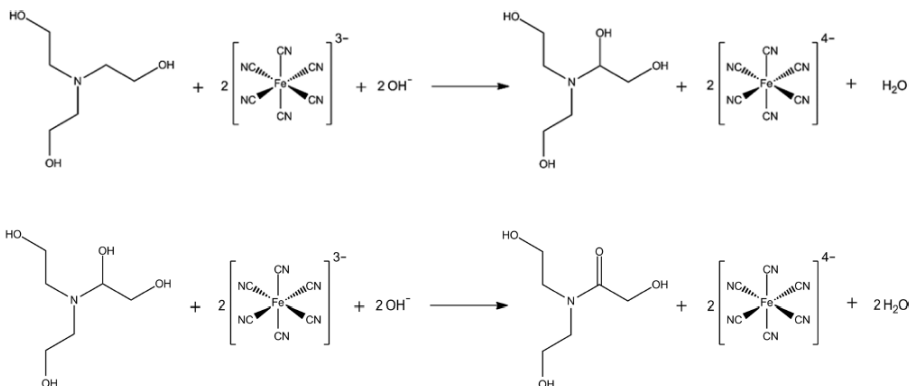
- ✧ Nature of ligand moves potential positive or negative



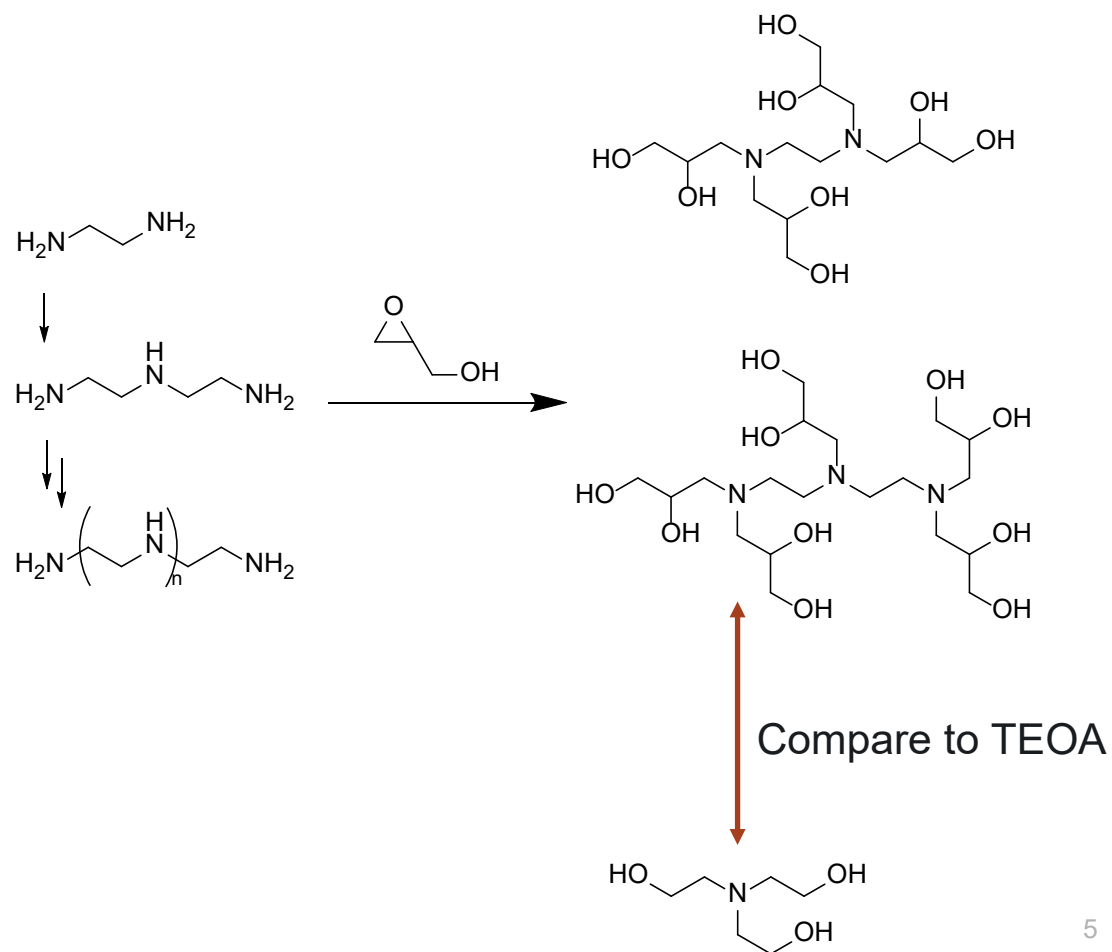
# From Peer Review 2024 – Ligand Size



## ✧ Crossover of dissociated ligands



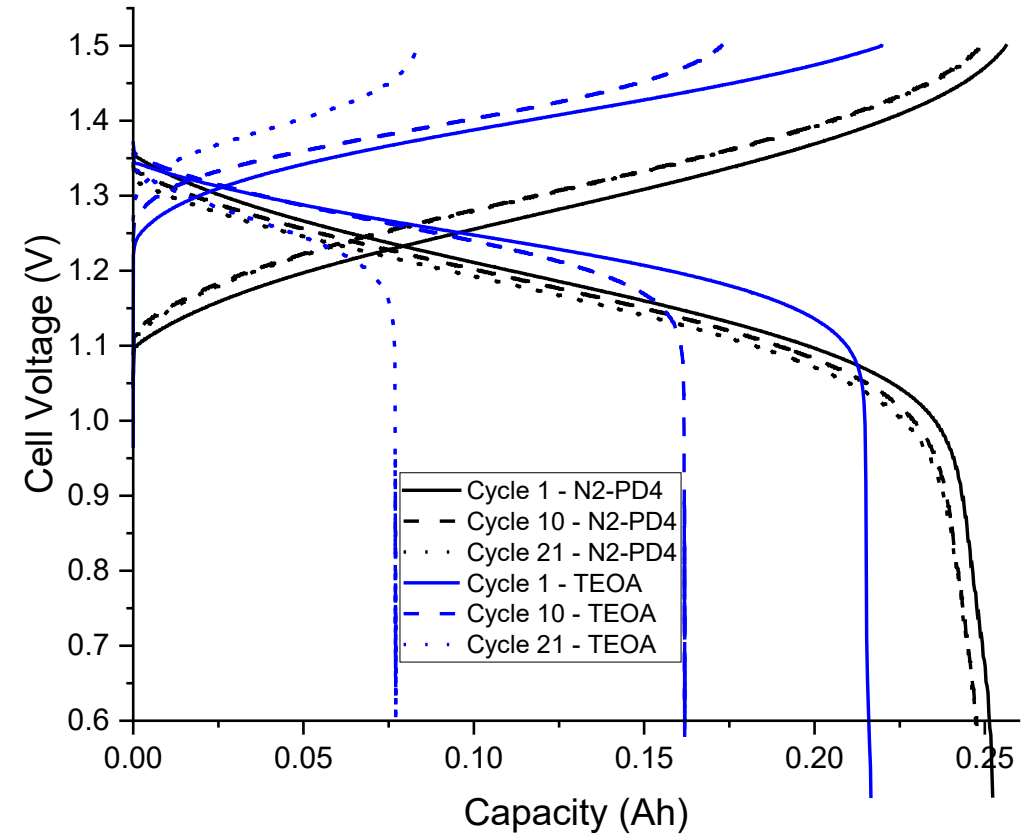
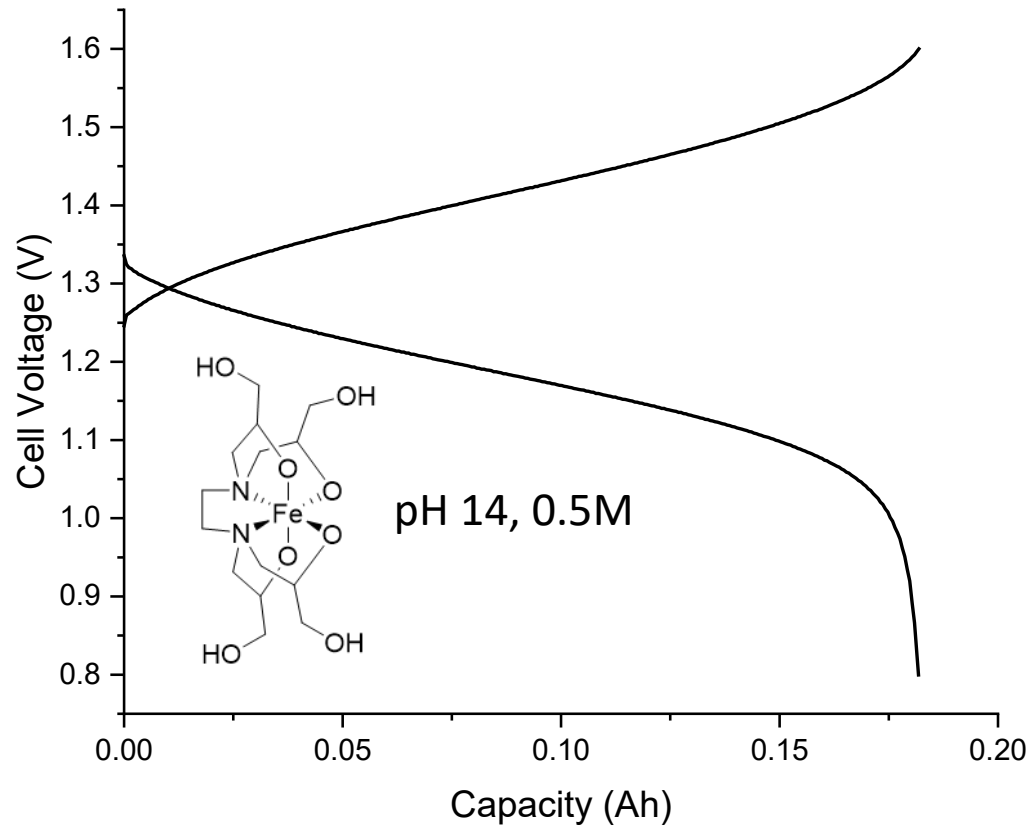
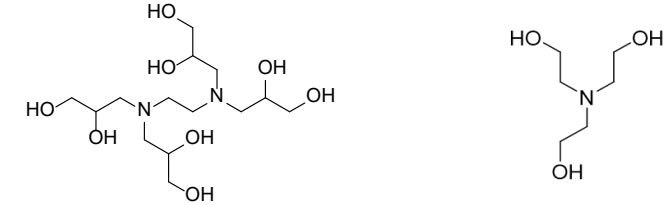
- ✧ Simple functionalization
- ✧ Size-based / increased functionality approach



# From Peer Review 2024

## Size-based Approach: Cell Performance

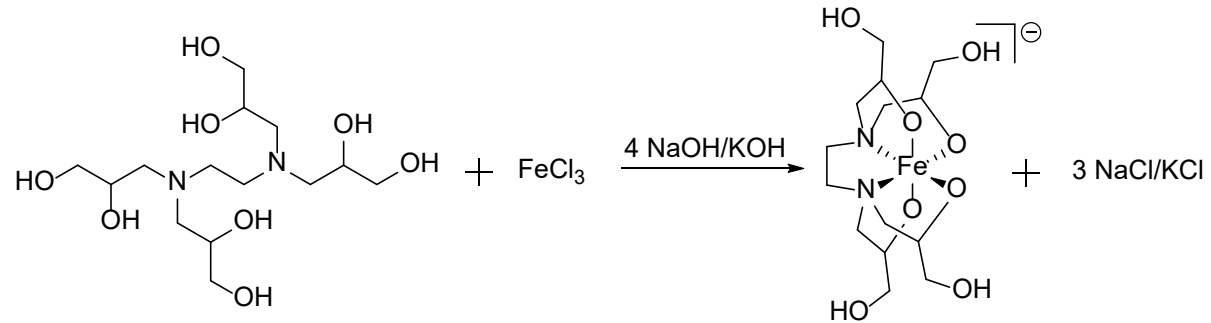
- ✧ Cell Voltage > 1V coupled w/  $\text{Fe}(\text{CN})_6$  catholyte
- ✧ Promising initial capacity retention



# Improving Properties from Previous FY

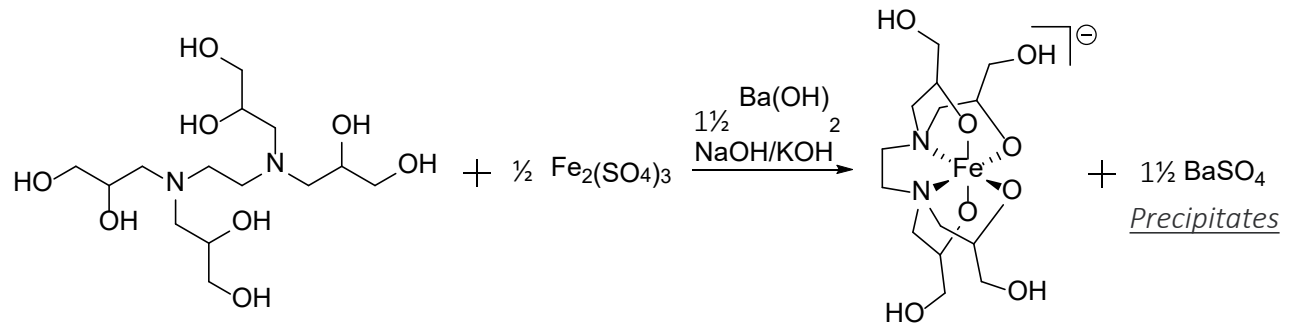
✧ Previous Results: ppt at elevated concentrations ( $> \sim 0.75\text{M}$ ); previous RFB tests up to  $0.67\text{M}$ .

✧ Impact of by-product salts:



*Extra salt  $\rightarrow$  precipitation*

✧ Fundamental study on by-product-salt-free electrolyte



*No extra salt in electrolyte*

✧ Inherent solubility of complex:  $\geq 2\text{M}$

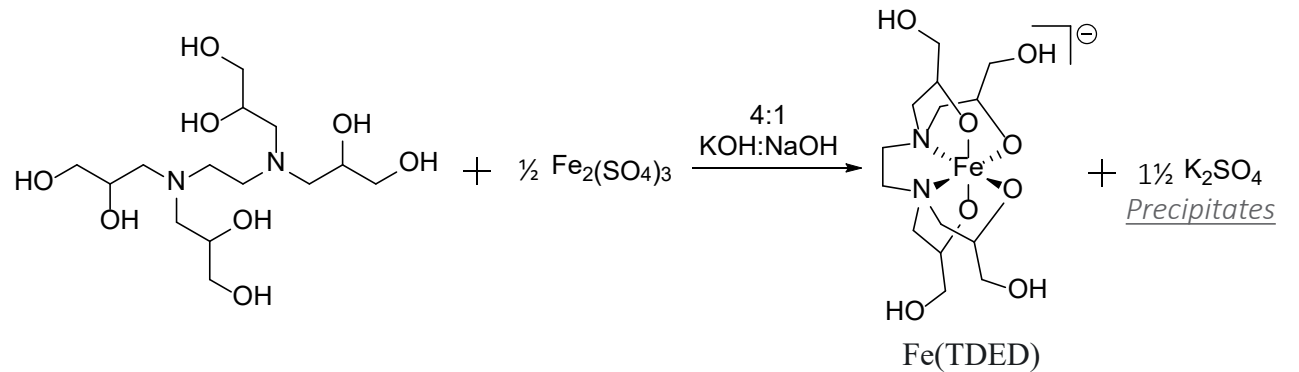


# Electrolyte Synthesis & Stability

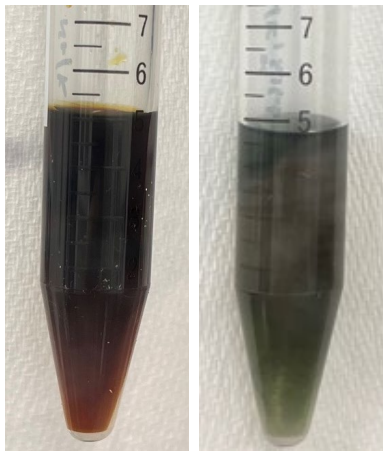
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✧ Straightforward approach to  $\text{SO}_4^{2-}$  removal  
*High concentration* → *Filter* → *Dilute to 1M*

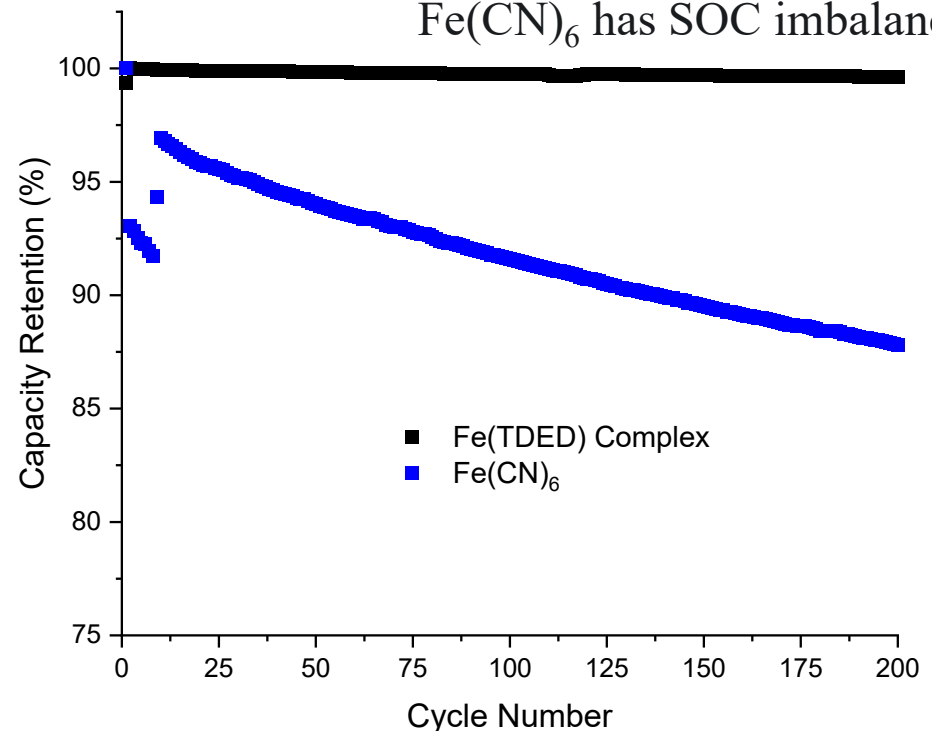
ICP Sample	Fe (g/L)	S (g/L)	Na (g/L)	K (g/L)
Electrolyte	56.66	0.58	10.57	17.63
Precipitate	0.0223	3.81	0.494	6.224



✧ 1M solutions at 0% and 100% SOC  
stable > 1 month

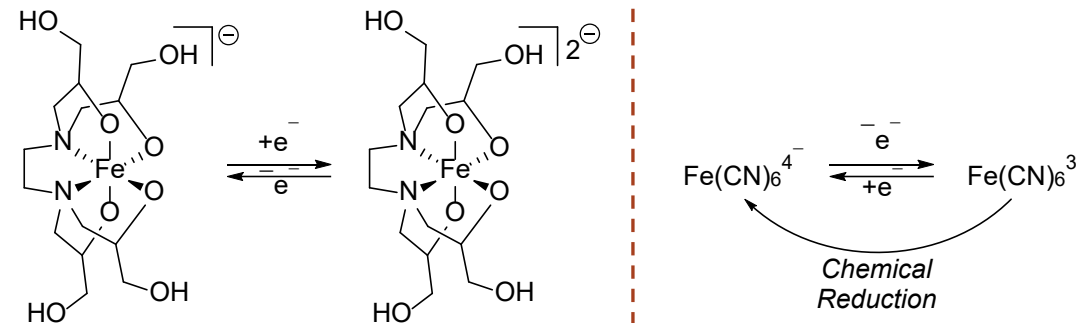


✧ Symmetric cells: Fe(TDED) stable,  
Fe(CN)<sub>6</sub> has SOC imbalance\*

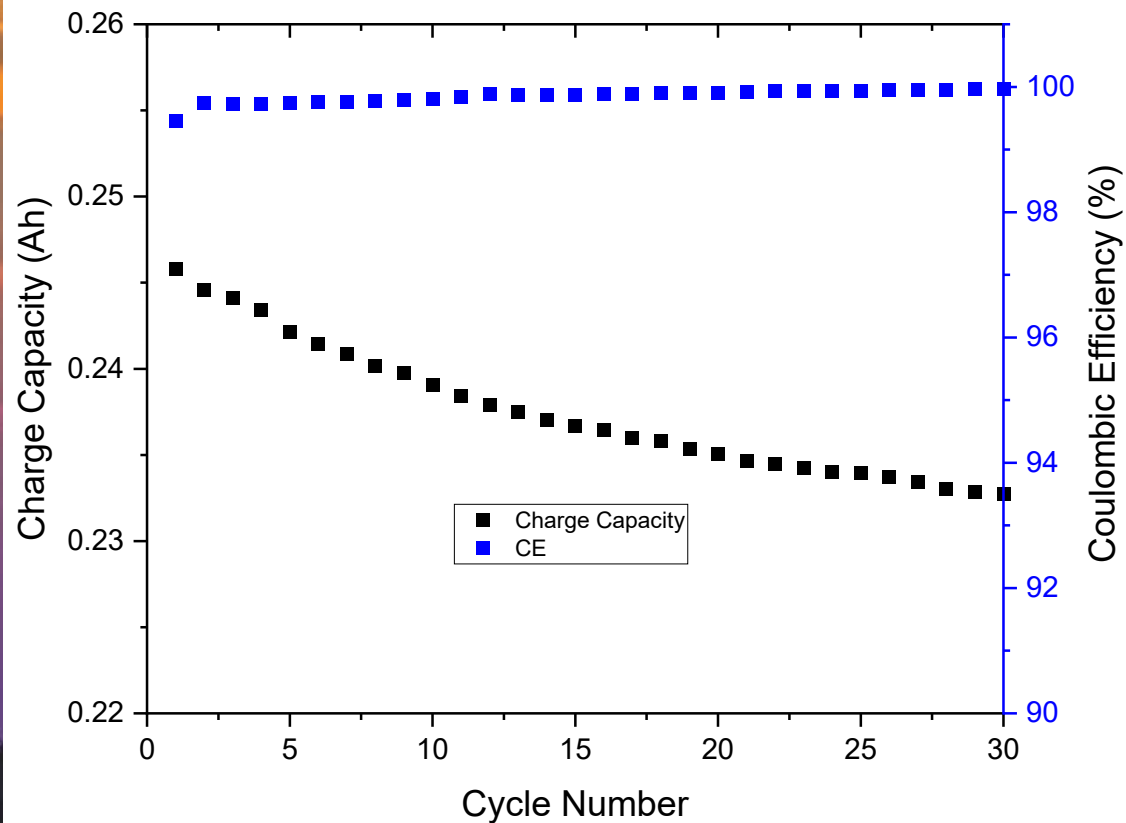


\* *J. Electrochem. Soc.*, 2023, 170, 070525. *Adv. Energy Mater.*, 2023, 13, 2203762.

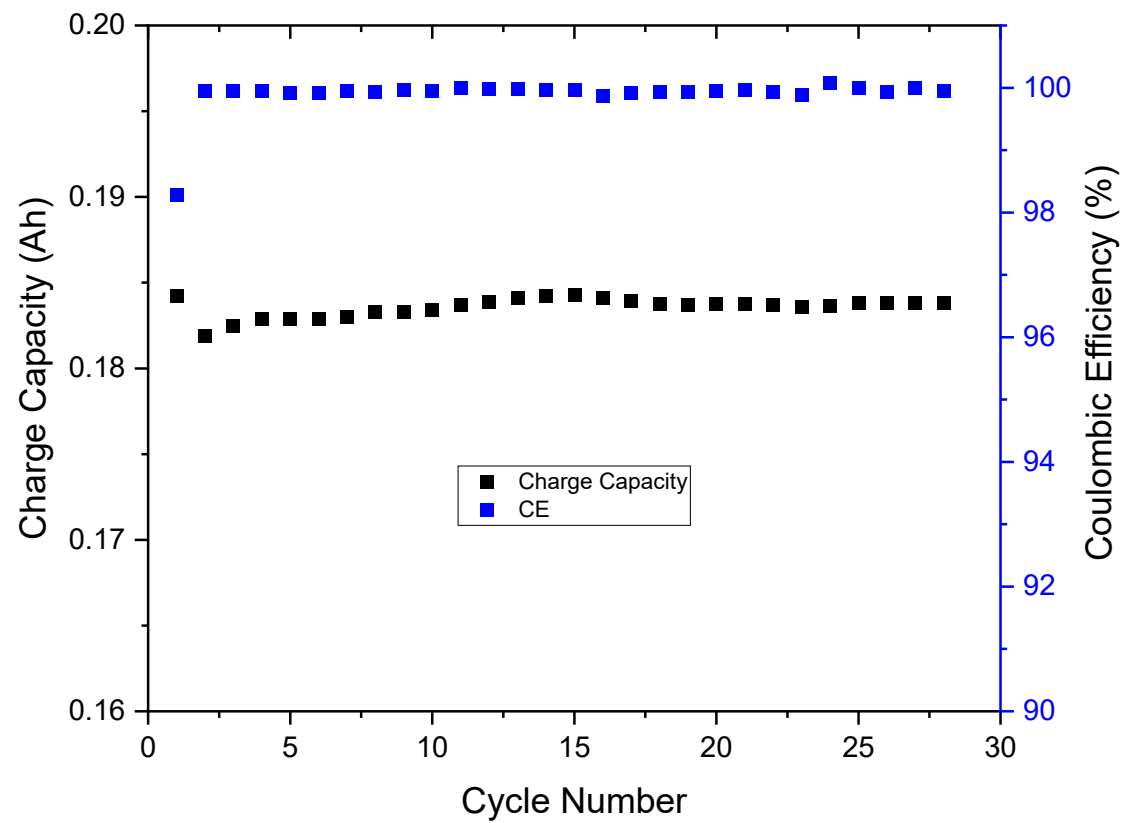
# Fe(TDED) Cycling



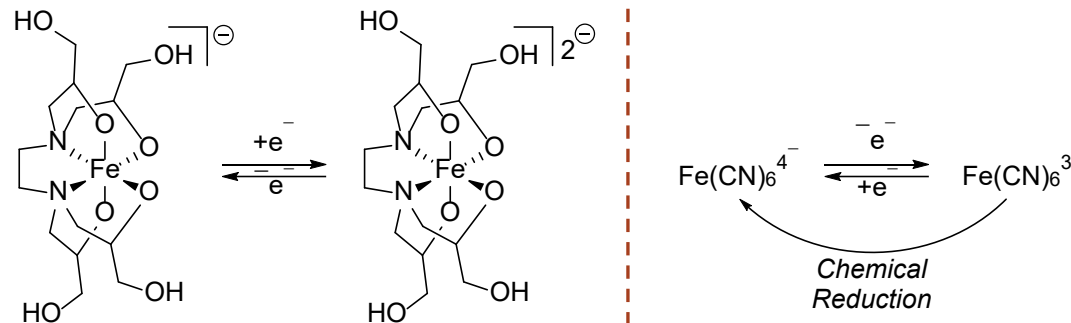
✧ Stoichiometric Fe(CN)<sub>6</sub>



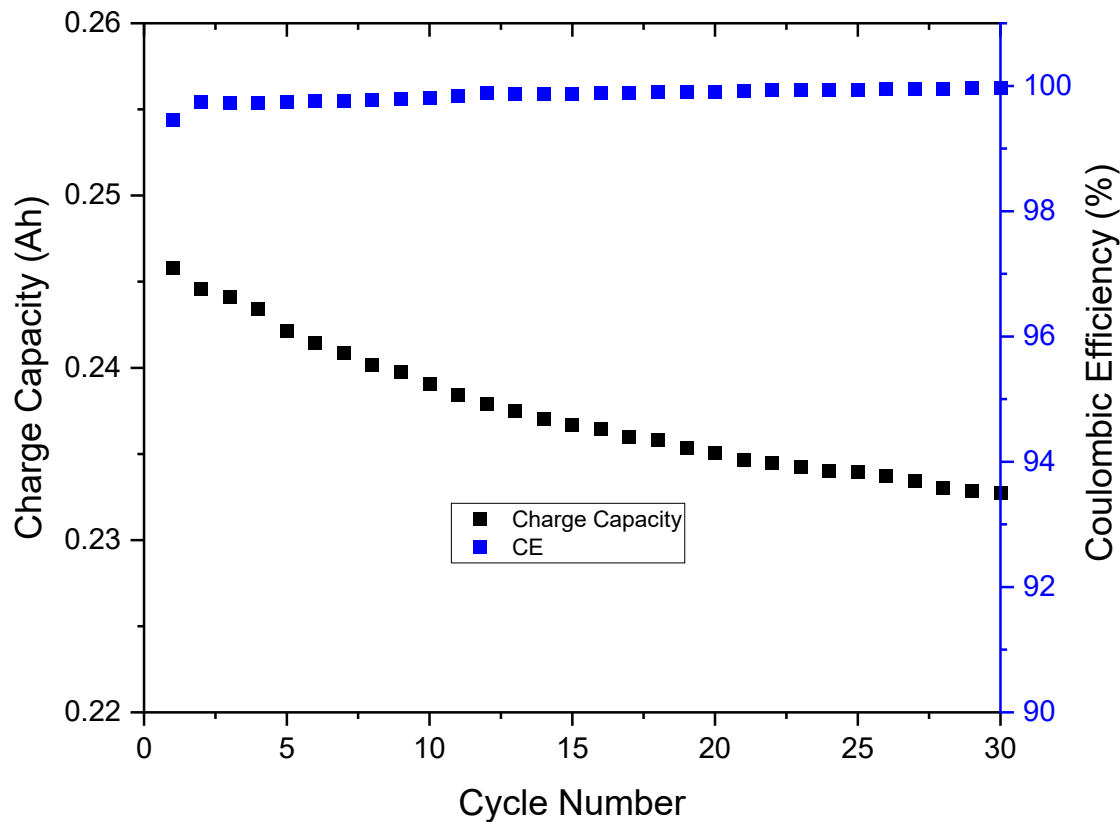
✧ Excess Fe(CN)<sub>6</sub>



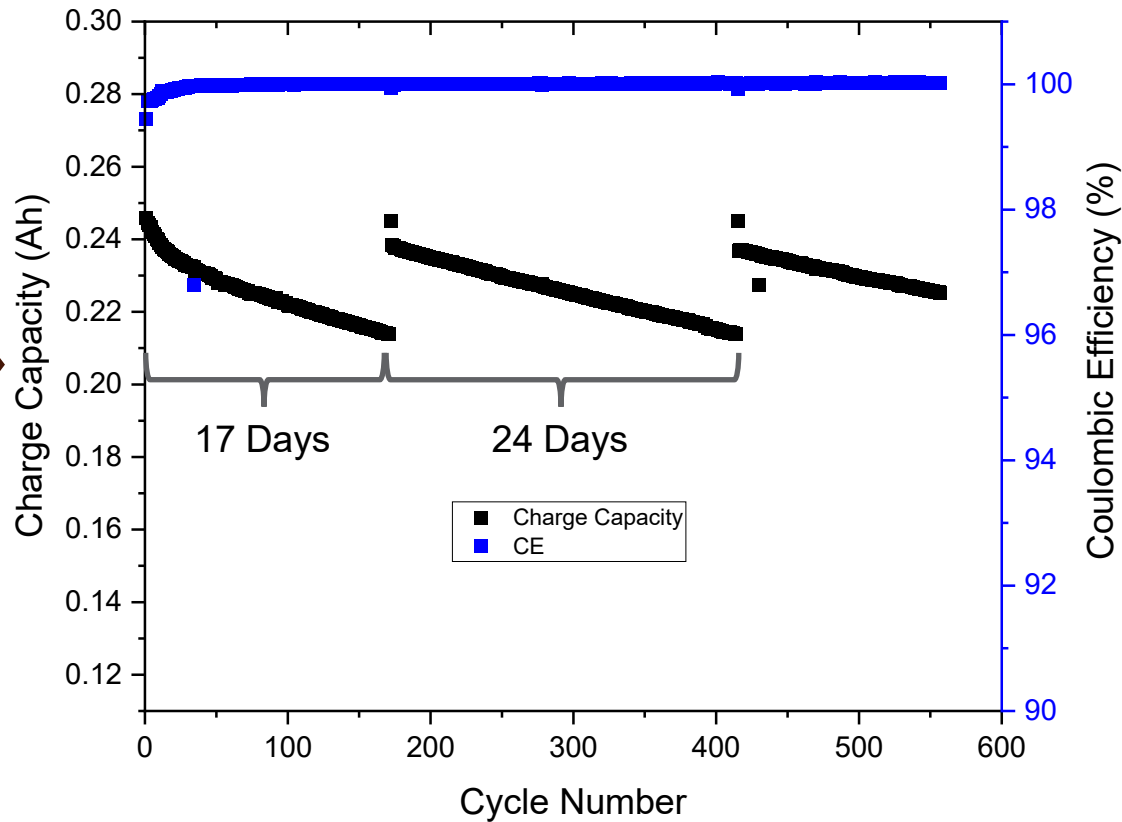
# Fe(TDED) Cycling - SOC Rebalancing



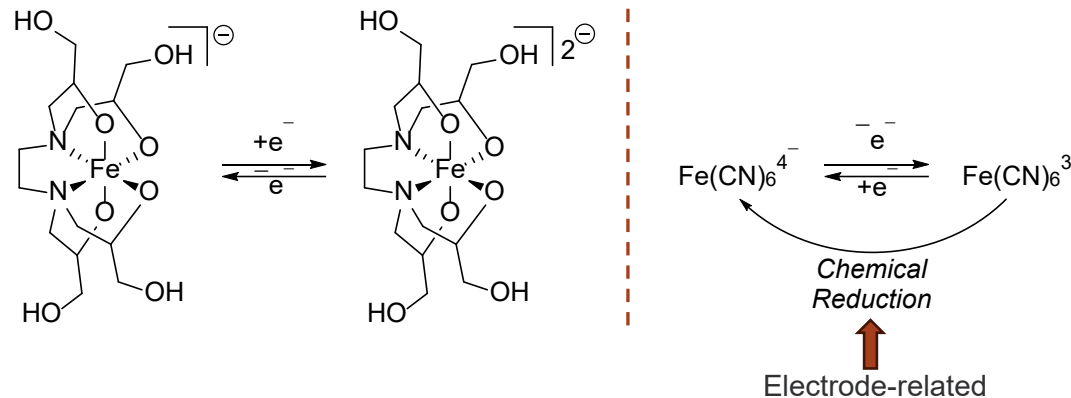
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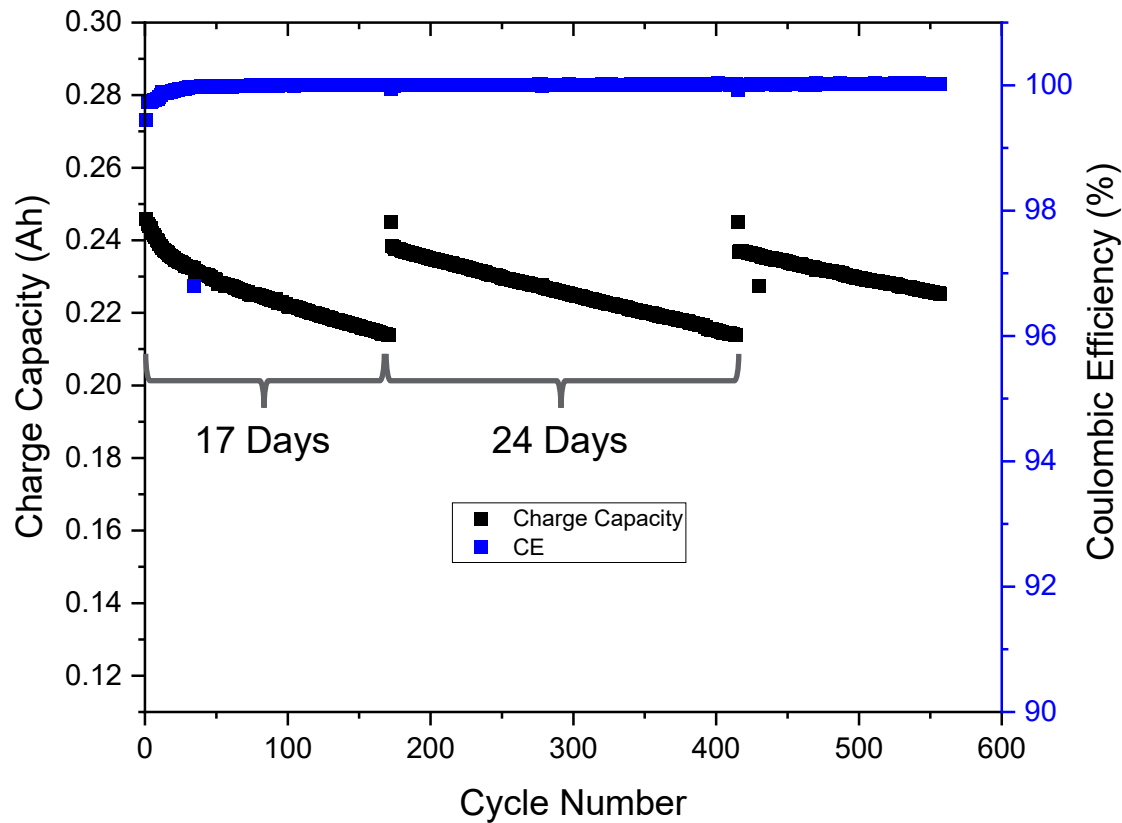
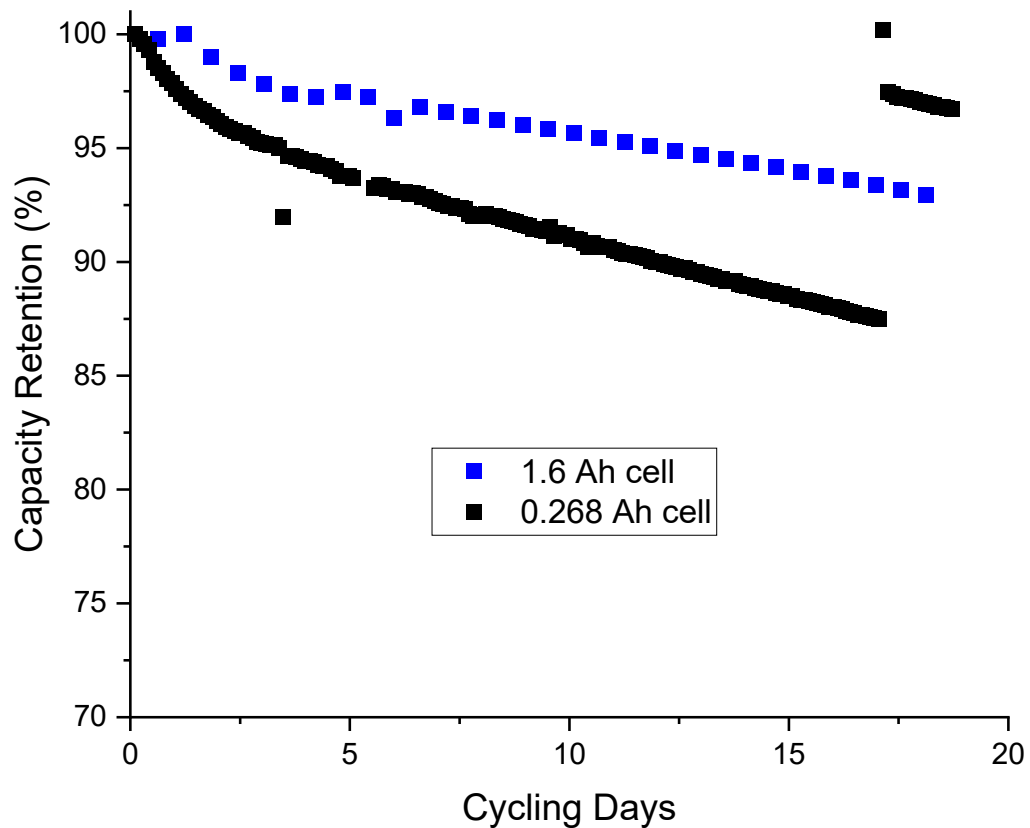
✧ Stoichiometric Fe(CN)<sub>6</sub> – SOC Rebalance



# SOC Rebalancing - Capacity Effect

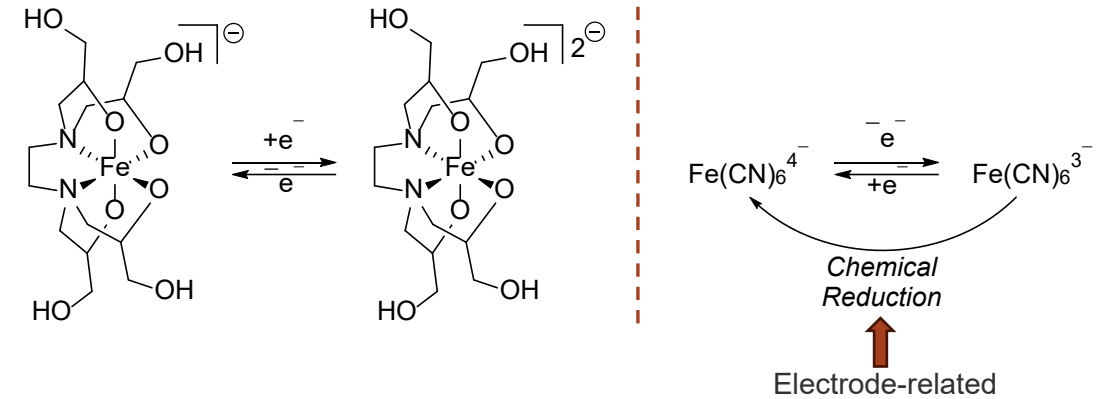
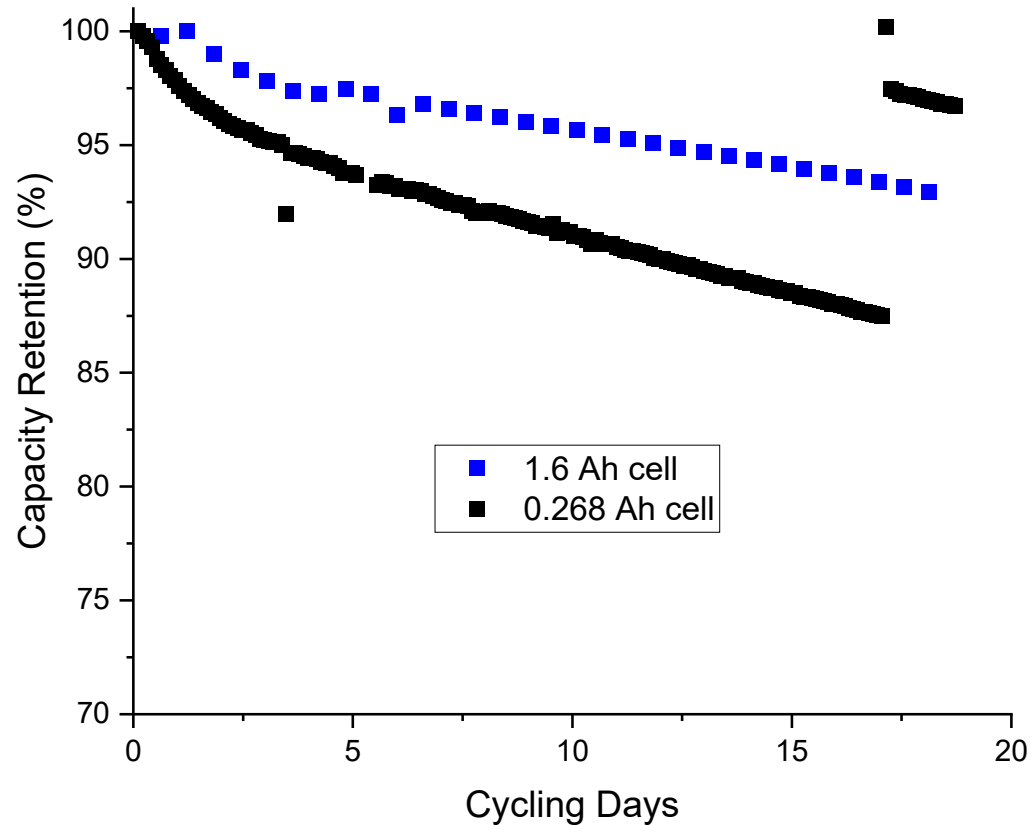


- ✧ 6x scale-up of electrolyte
- ✧ Same current, cell size



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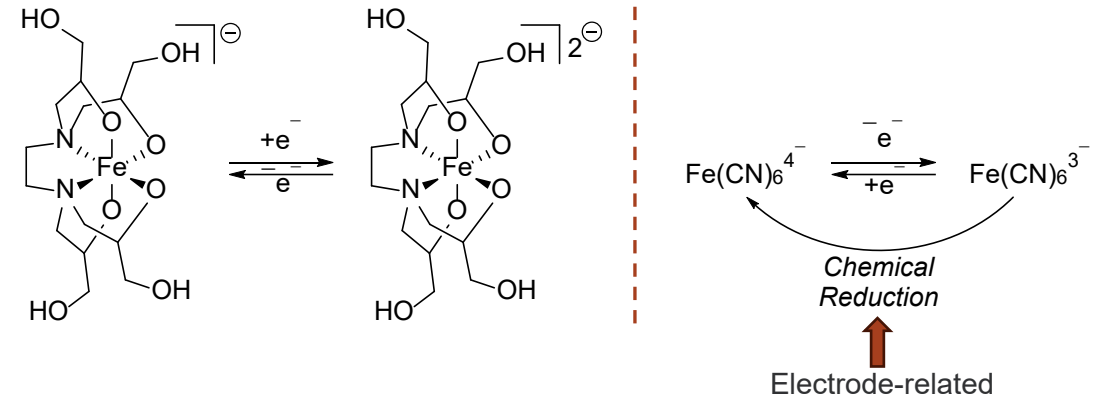
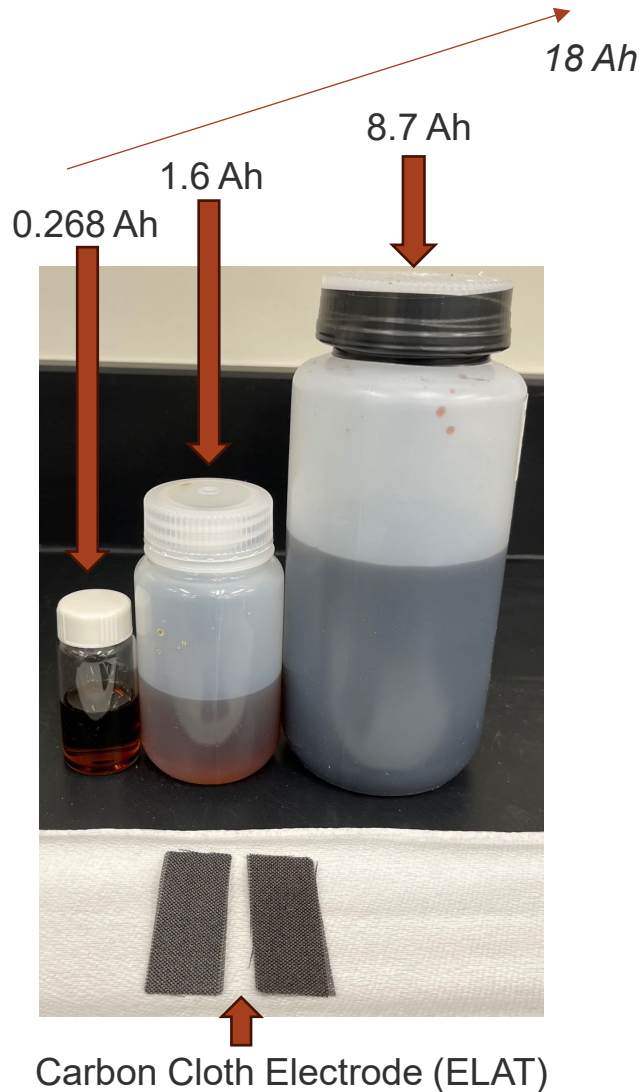
- ✧ 6x scale-up of electrolyte
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## Capacity Retention / Rebalancing Considerations

- 10 cm<sup>2</sup> cell
- Initial experiments: 0.2A / 0.268 Ah
  - ELAT to Fe(CN)<sub>6</sub> ratio is significantly higher than realistic cell
- More Realistic: 1.5A / 12-18 Ah – Same ELAT content  
45-80x more electrolyte
  - Since electrode surface is the most significant culprit in SOC imbalance in ↑pH Fe(CN)<sub>6</sub>, practical cells will need less frequent rebalance

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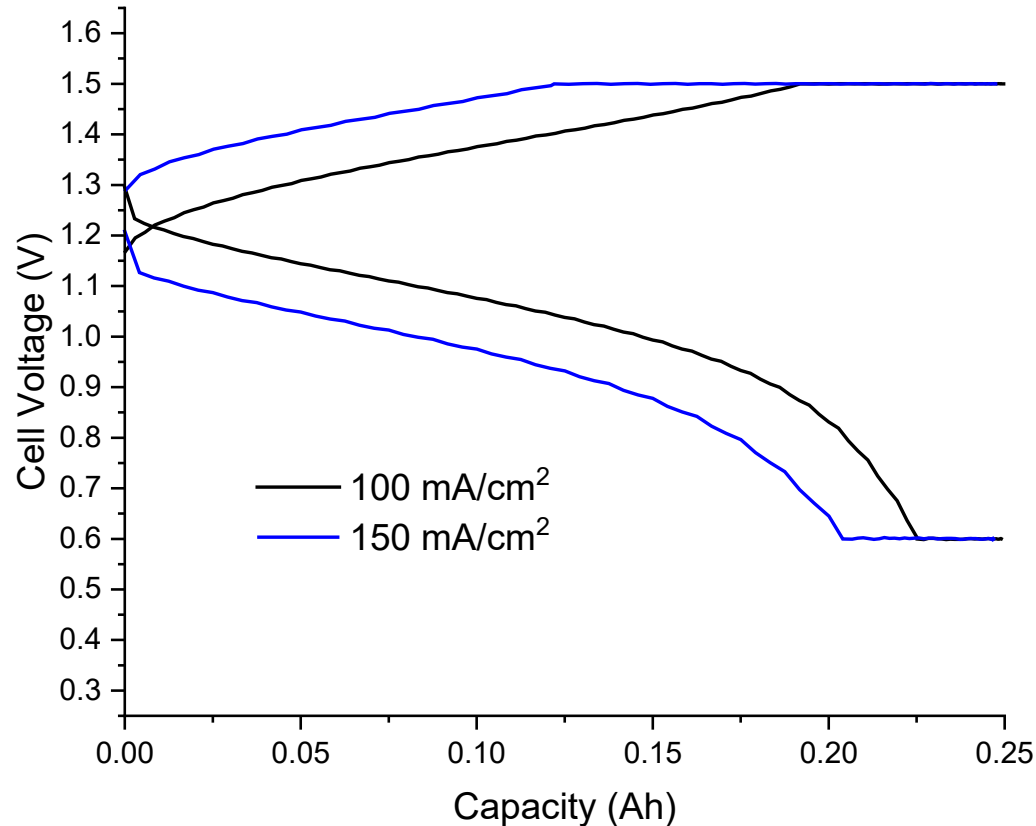


## Capacity Retention / Rebalancing Considerations

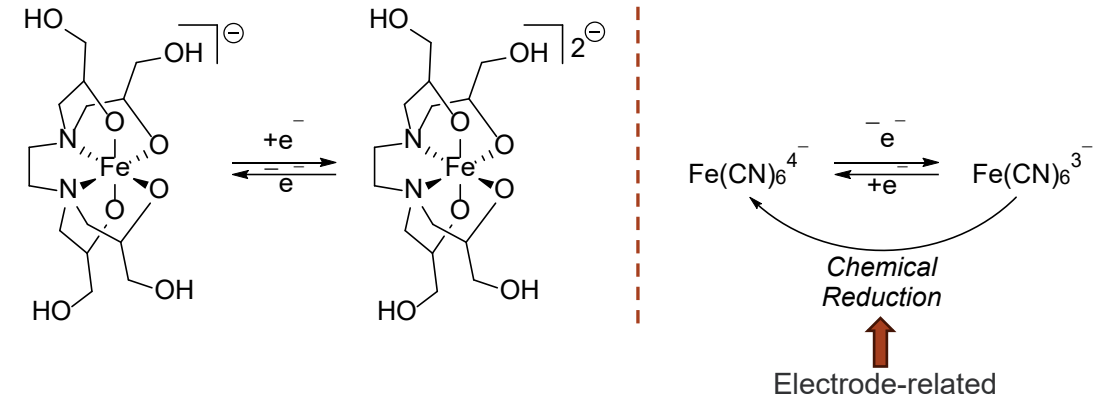
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# SOC Rebalancing - Capacity Effect

✧ Testing higher current conditions to enable high-capacity cell tests



1M Fe(TDED), E630K



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# Summary and Acknowledgements

## *Summary*

- Determined solubility limits, practical concentrations, and improved metrics relative to initial FY24 results
  - Demonstrated SOC rebalance and outlook for practical electrolyte volumes/RFB cycle durations
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## *Future Direction*

- Test long-term capacity retention and benchmark SOC rebalance needs/repeatability. Test alternative rebalance methods.
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## *Support*

- ▶ This material is based upon work supported by the U.S. Department of Energy, Office of Electricity (OE), Energy Storage Division.
- ▶ PNNL is operated by the Battelle Memorial Institute for the DOE under contract DE-AC05-76RL01830.



*Thank You For Your Attention*

Questions?

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