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Presentation 102:

Exploring Soluble Iron Electrolytes in Redox Flow Systems

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Pacific Northwest National Laboratory

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U.S. DEPARTMENT of ENERGY BATTELLE

PNNL is operated by Battelle for the U.S. Department of Energy

- **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.
- **Duration:** FY21-Present
- **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.
- **Vertical/Investment Area**: Materials and Systems Innovation
- **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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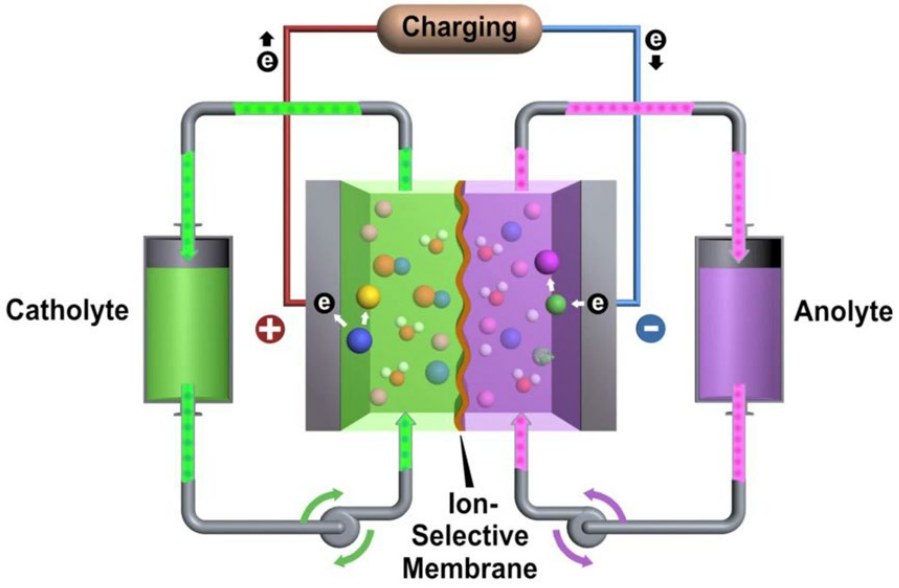
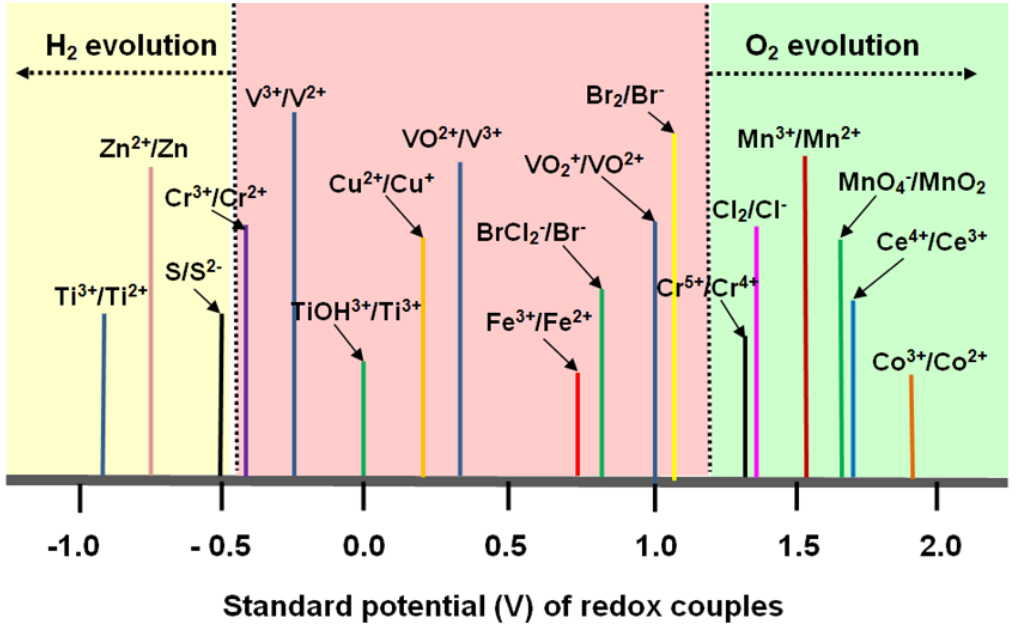


- **Decoupling of Power and Energy**
  - Extend duration with storage tank size
- **High safety**
  - Major constituent is water
  - Easy thermal management
  - Battery health monitoring
- **Easier recycling after service life**
  - Re-use/recycle active material

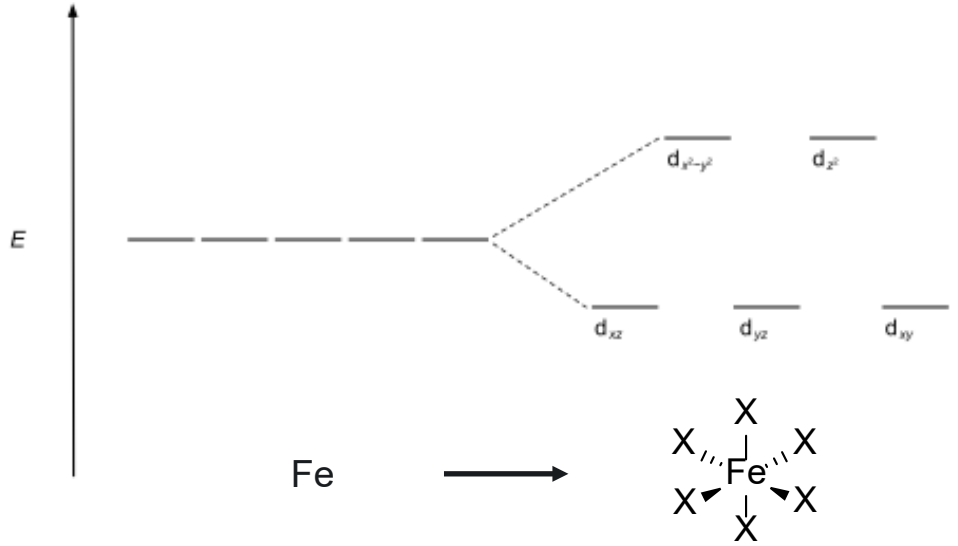
- **Multitude of available chemistries**



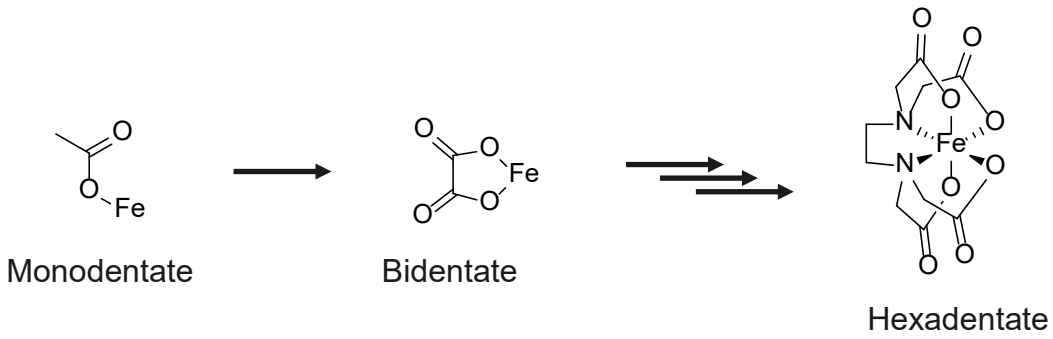
- **All iron systems**
  - Hybrid – $Fe^{2+/3+}$ / $Fe^{2+/0}$
  - Coordination chemistry
    - Split redox potential of $Fe^{2+/3+}$
    - Same metal/redox couple as catholyte/anolyte

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



Two Primary Approaches – Mild pH & High pH

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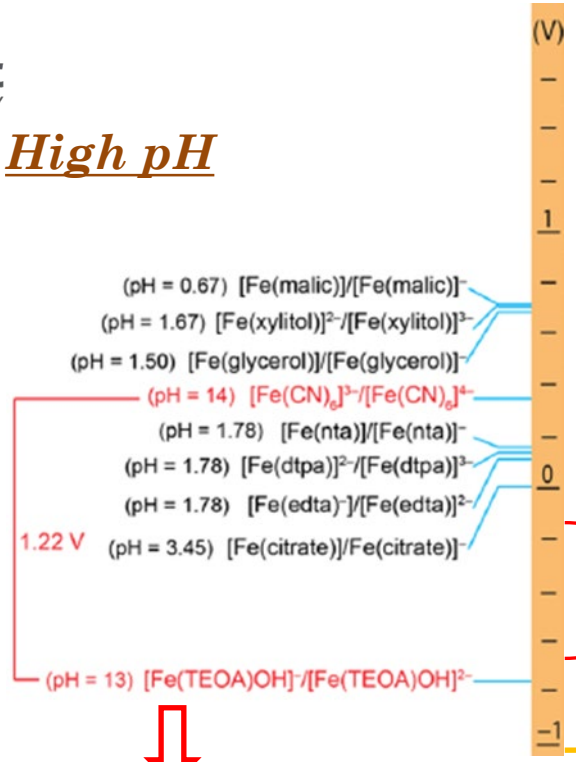
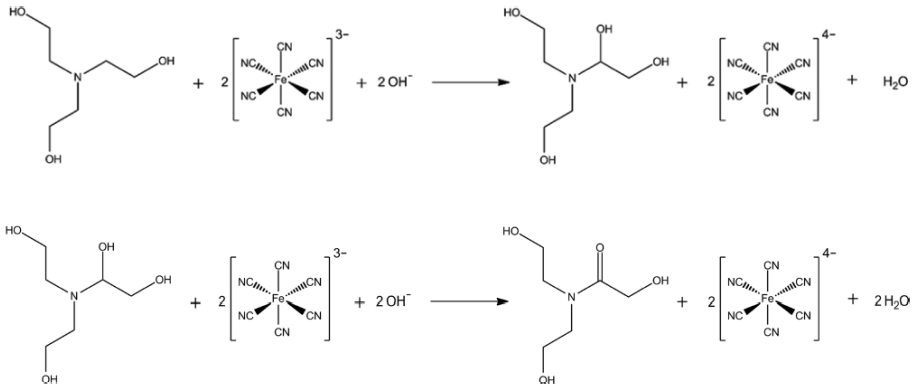
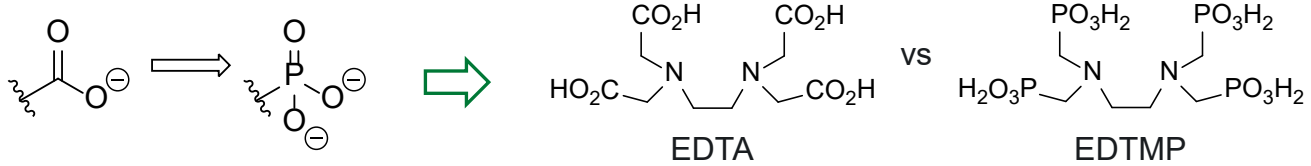
High pH



- Crossover of dissociated ligands



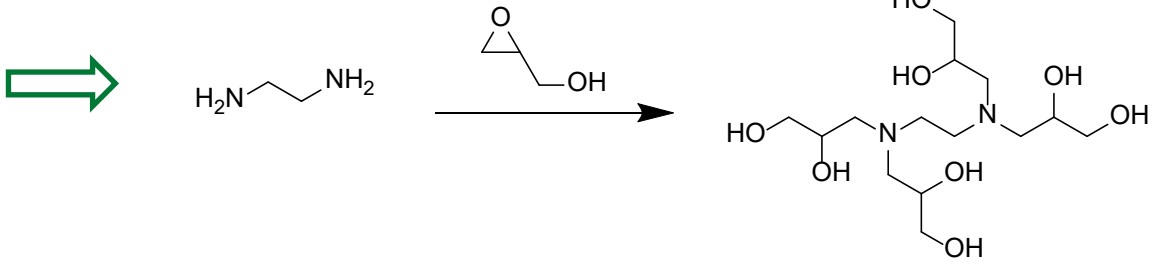
Mild pH



- Phosphonic acid analogues of carboxylic acid-based ligands
  - Stronger donor → More negative redox potentials
  - Improved resistance to hydrolysis (Fe-L -> Fe_xO_y)

Please visit the poster for further information.

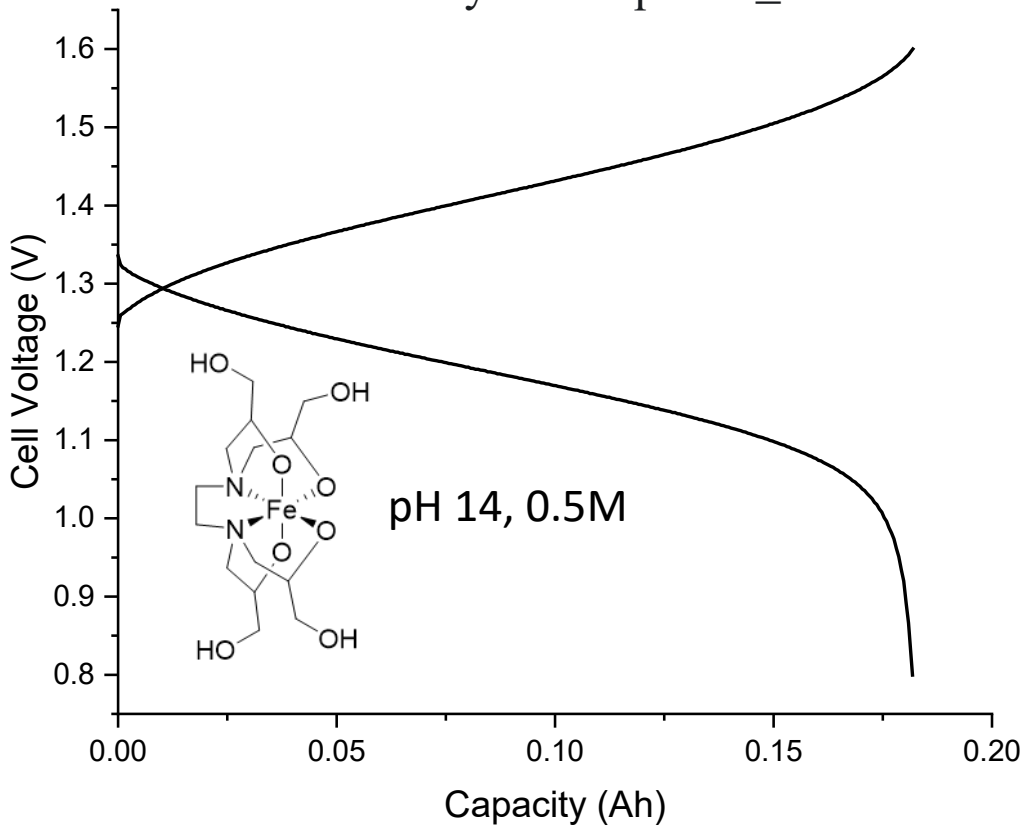
- Size-based / increased functionality approach
- Stronger binding, prevent crossover

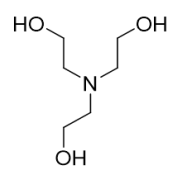


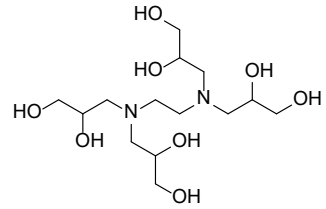
Gong, et.al. *ACS Energy Lett.*, **2016**, 1, 89-93.

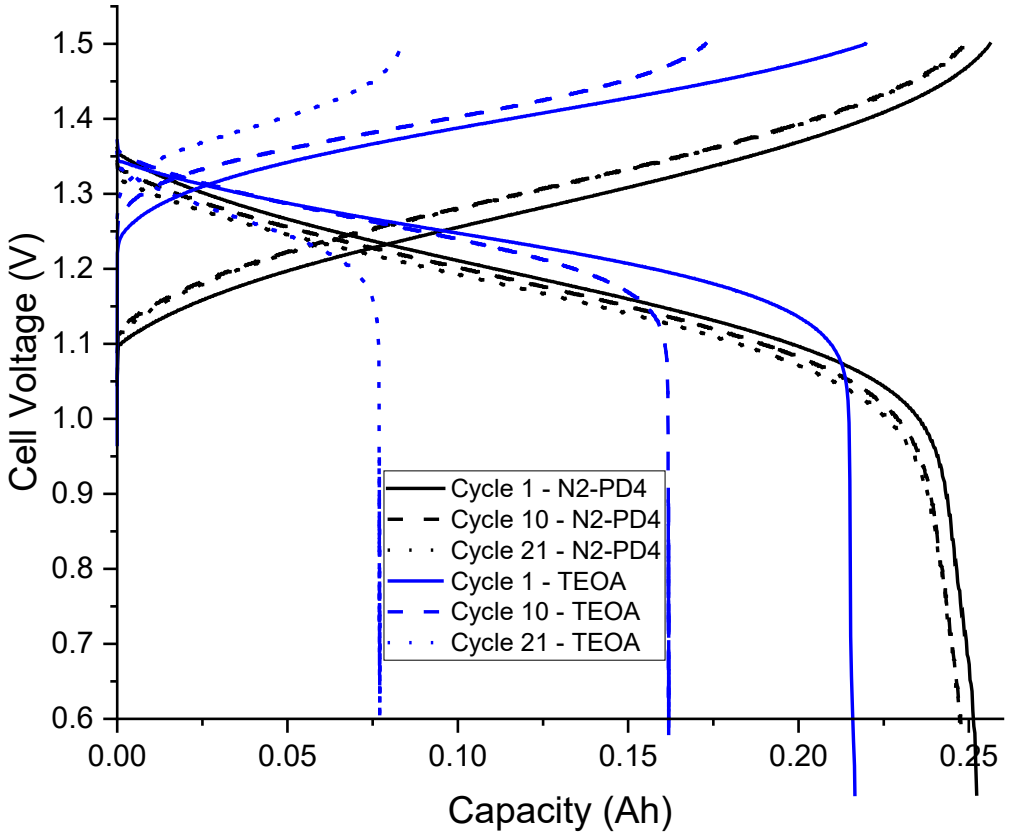
Size-based Approach: Cell Performance

- Cell Voltage >1V coupled w/ $Fe(CN)_6$ catholyte
- Promising initial capacity retention
- Inherent solubility of complex: ≥ 2M

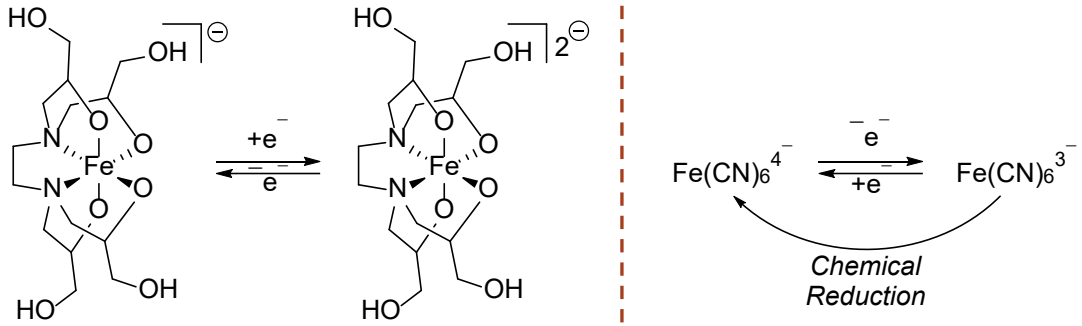




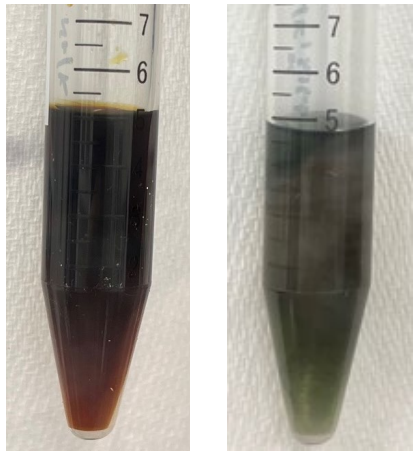




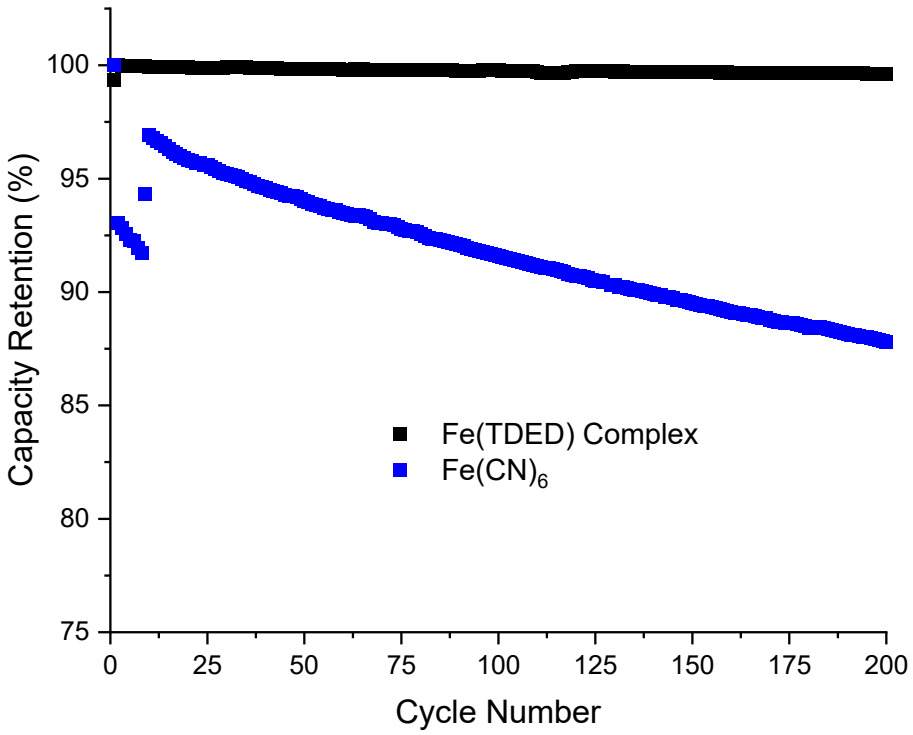
Fe(TDED) Stability



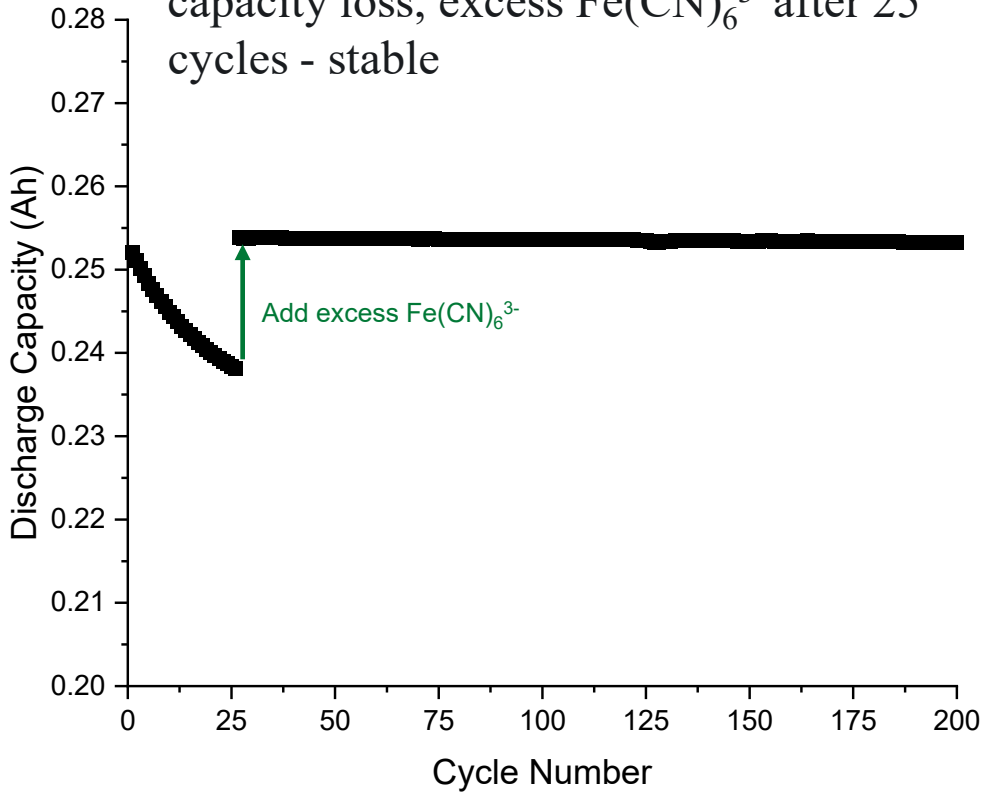
- 1M solutions at 0% and 100% SOC
  stable > 6 month



- Symmetric cells (high pH): Fe(TDED) stable, $Fe(CN)_6$ has SOC imbalance*

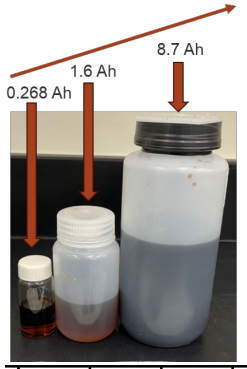


- Fe(TDED) vs $Fe(CN)_6$ cell: stoichiometric-capacity loss, excess $Fe(CN)_6^{3-}$ after 25 cycles - stable

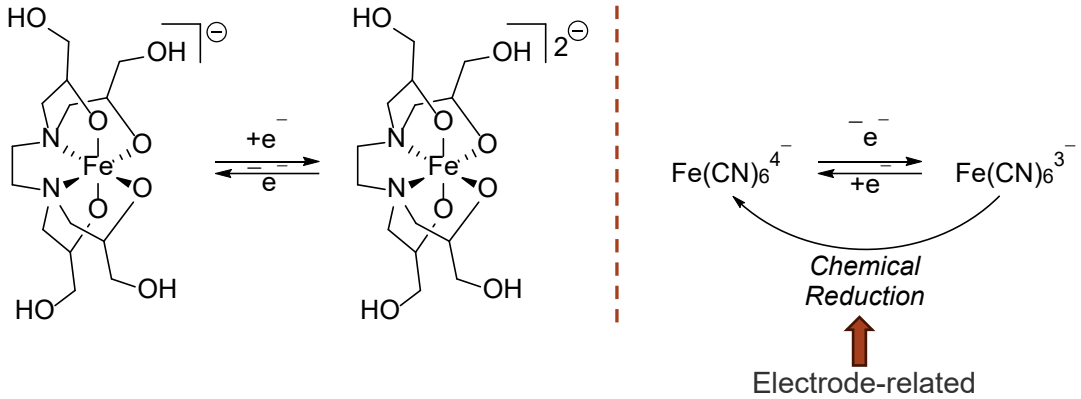


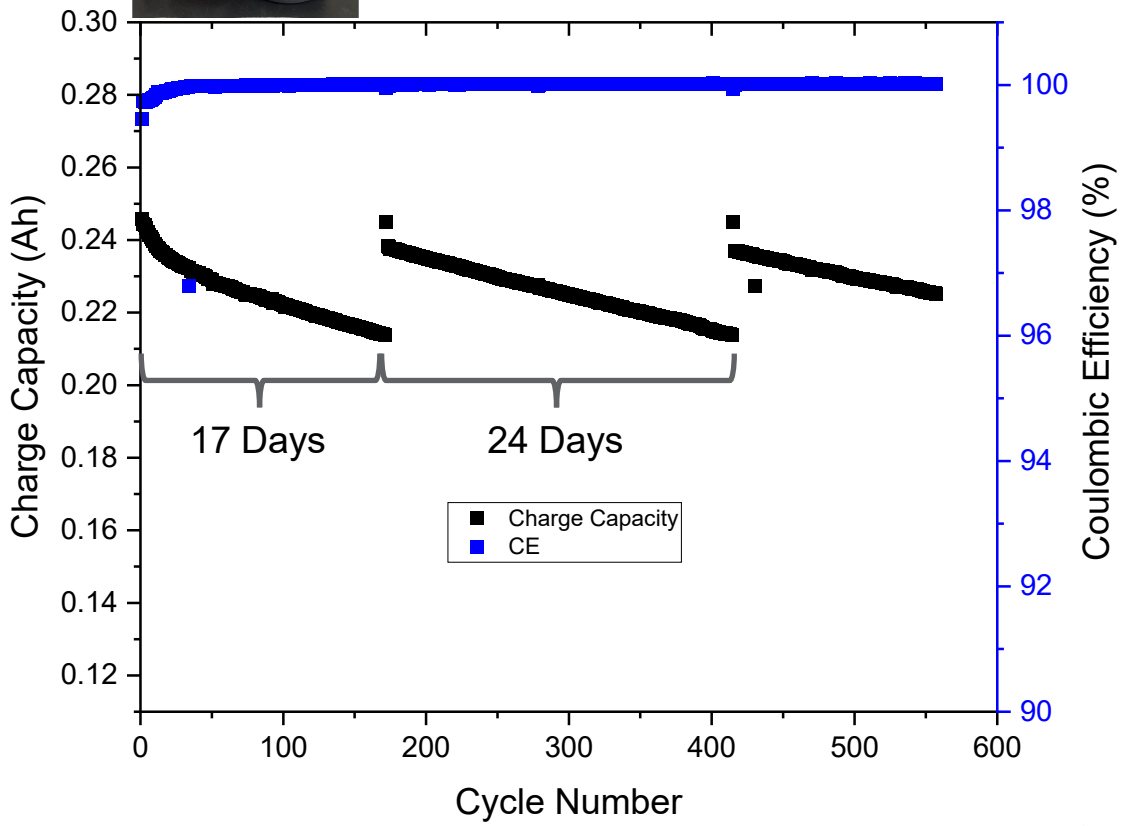
* *J. Electrochem. Soc.*, **2023**, *170*, 070525. *Adv. Energy Mater.*, **2023**, *13*, 2203762.

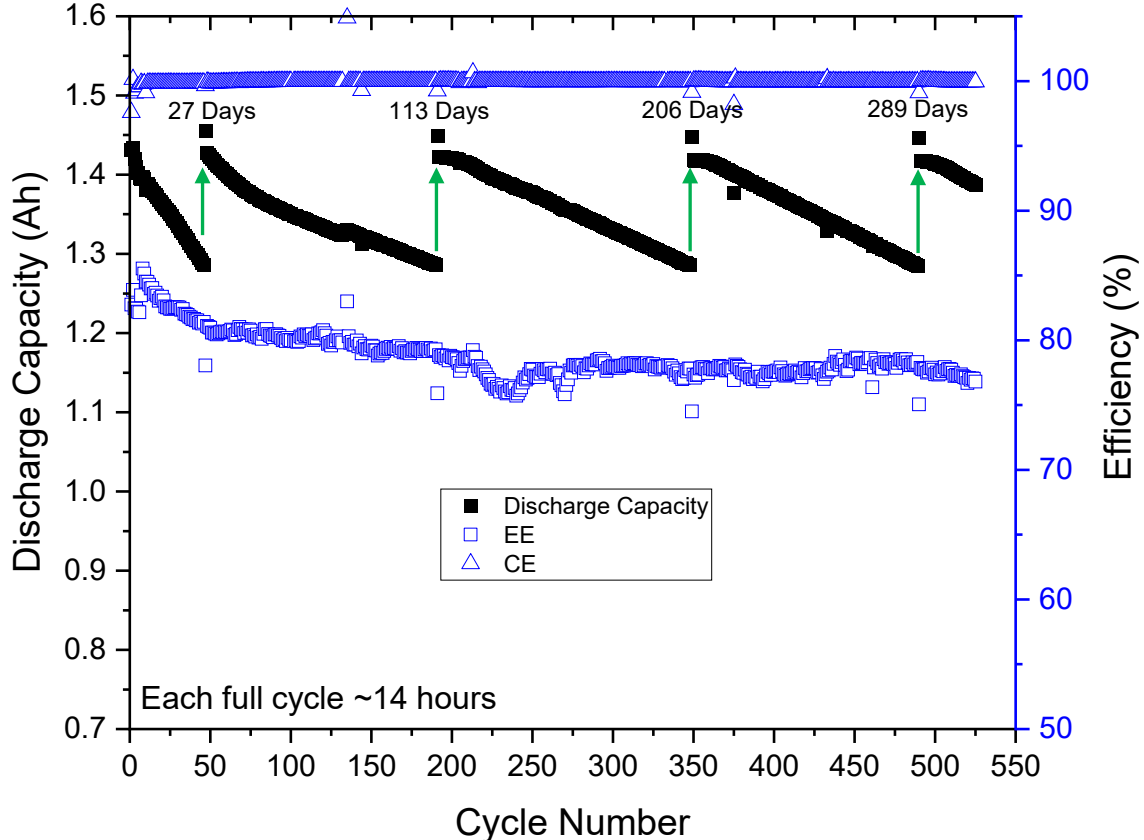
SOC Rebalancing - Capacity Effect



- 6x scale-up of electrolyte
- Same current, cell size
- Practical cells will need less frequent rebalance: electrode surface significant culprit in SOC imbalance in ↑pH $Fe(CN)_6$

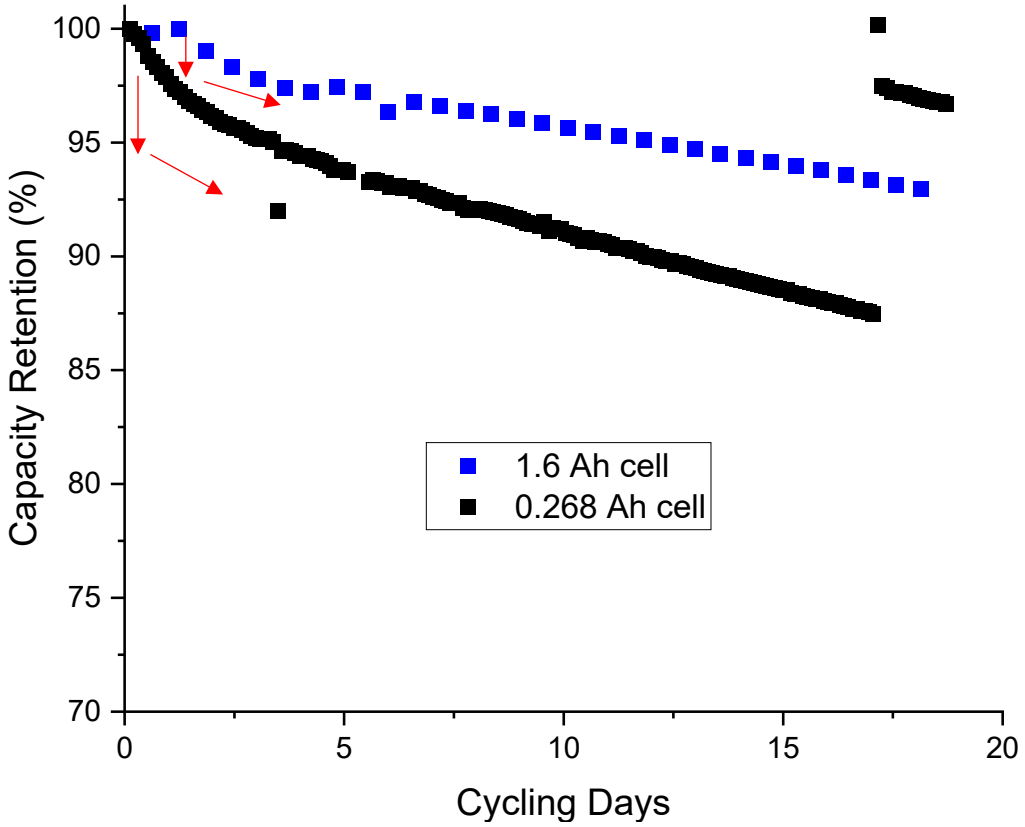




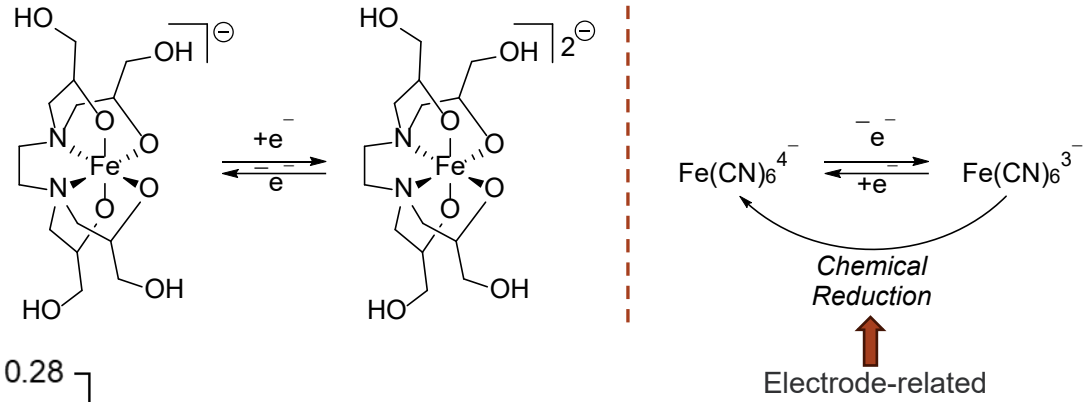


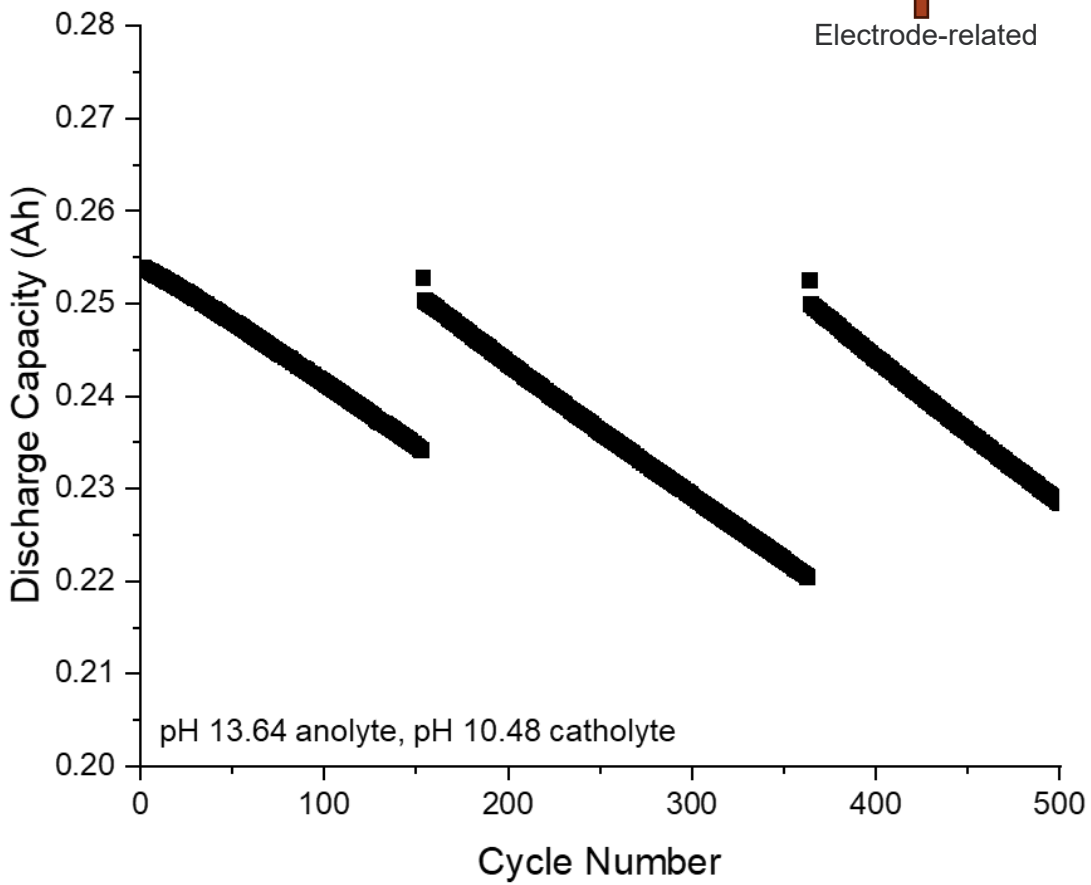
SOC Rebalancing - Capacity Effect

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



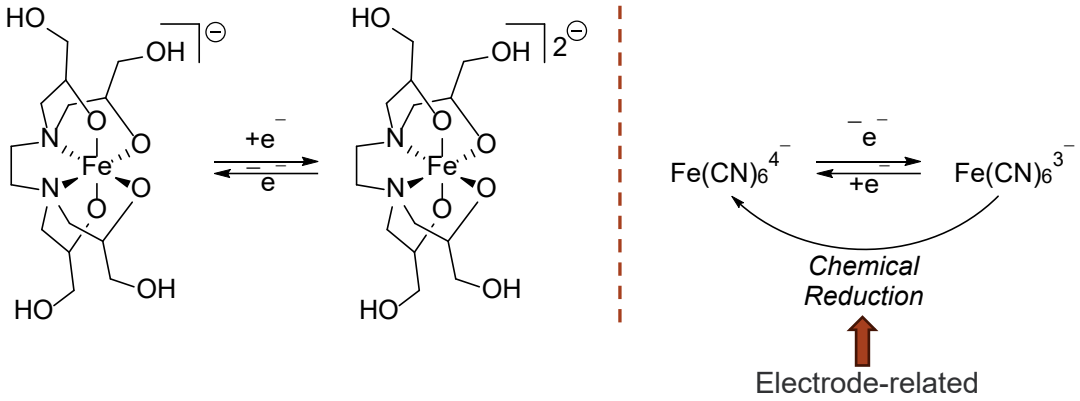
- Rapid initial capacity loss due to high catholyte pH



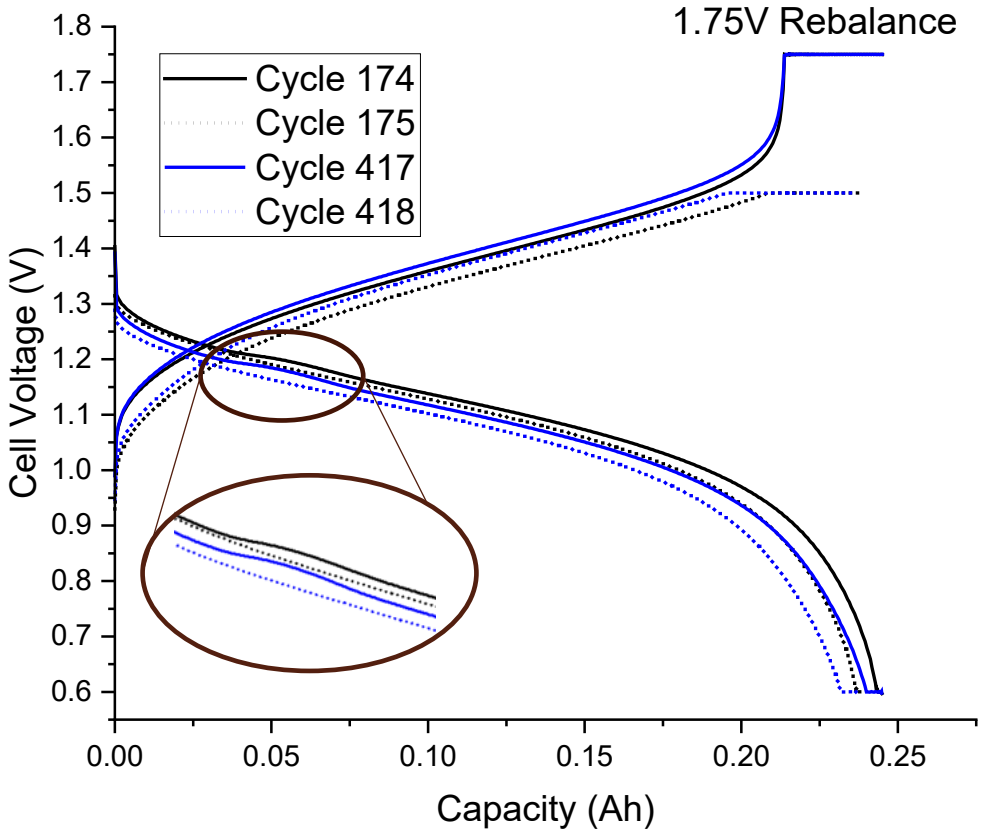


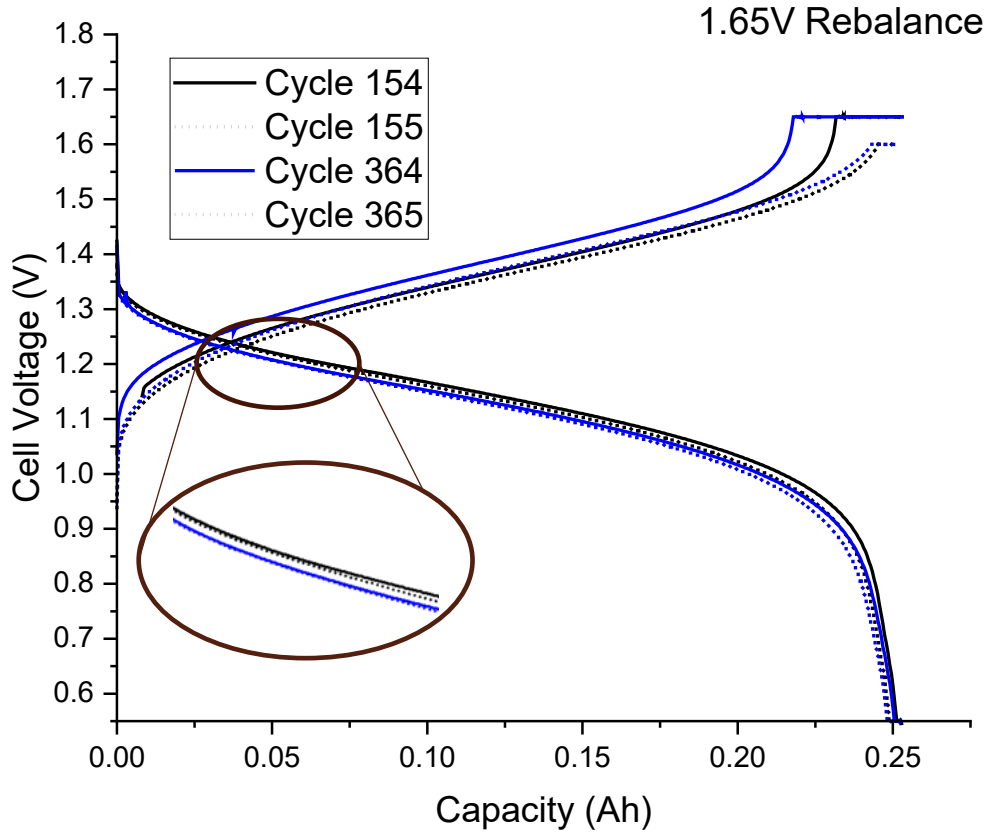
- Optimized by beginning with lower pH catholyte
  - Stabilized initial cycles

SOC Rebalancing - Capacity Effect



- High voltage rebalance leads to apparent Fe plating
- Moderate voltage rebalance shows no signs





Summary and Acknowledgements

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Summary

- Refined operating conditions for high pH iron complexes to establish long-term cycling/rebalancing
- Investigated the effects of rebalancing voltage on electrolyte stability, including observations related to iron plating.

Future Direction

- Continue testing long-term capacity retention and benchmark SOC rebalance needs/repeatability. Test alternative rebalance methods.
- Further determine the optimal membrane and electrode conditions at higher capacities and current densities.

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

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Questions ?

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