Iron-Based Soluble Electrolytes For Redox Flow Systems

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Project Profile

Topic: Next Generation, Large Scale Energy Storage, Vertical: Materials and Systems Innovation, Strategic Pathway: Grow: Long-term expansion by enabling innovation, advancing new technologies, and building capacity for a future-ready electricity system. Project start and finish: FY2021-Present

Introduction

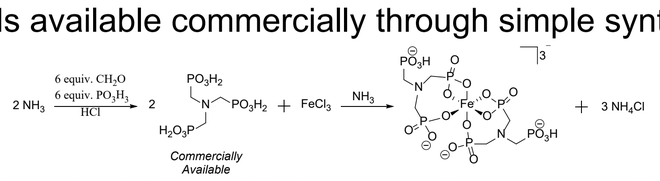
Iron-based electrolytes offer a low-cost option for redox flow batteries (RFBs) and can serve as an alternative to vanadium. By employing ligands to adjust iron ion characteristics, redox flow batteries can be constructed using soluble $Fe^{2+/3+}$ compounds as both catholyte and anolyte, which eliminates the complications associated with hybrid all-iron (Fe^0 anode) systems.

Objective and Approach

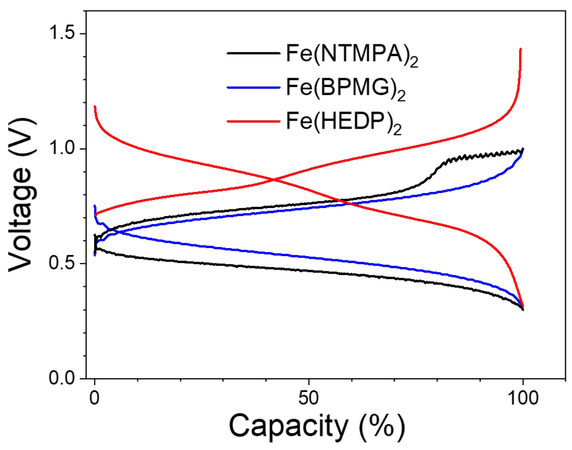
The objective is to design and develop cost-effective coordinating ligands for all-soluble iron chemistries in RFBs, focusing on novel anolyte candidates to complement established ferrocyanide catholyte. Diverse ligand groups producing soluble iron complexes across distinct pH conditions (near-neutral pH 8 and alkaline pH 13-14) were evaluated to determine performance and stability considerations.

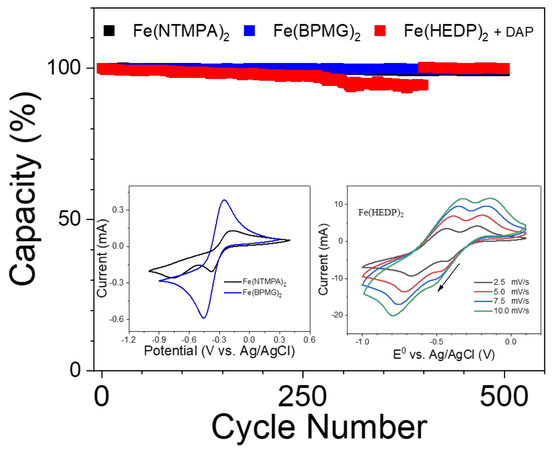
Mild pH (Phosphonate-based Ligands)

- Numerous ligands available commercially through simple syntheses

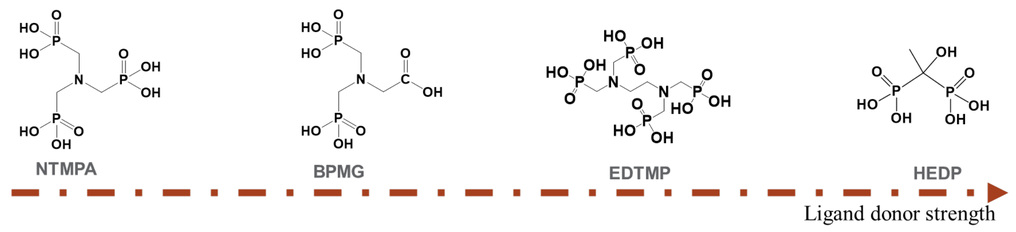


- Phosphonic acid ligands yield soluble iron complexes at nearly neutral pH 8
  - Moderate working pH attributed to phosphonic acid acidity (readily deprotonated)
    - Weaker donor to the iron center → lower cell voltages (0.6-0.85 V)

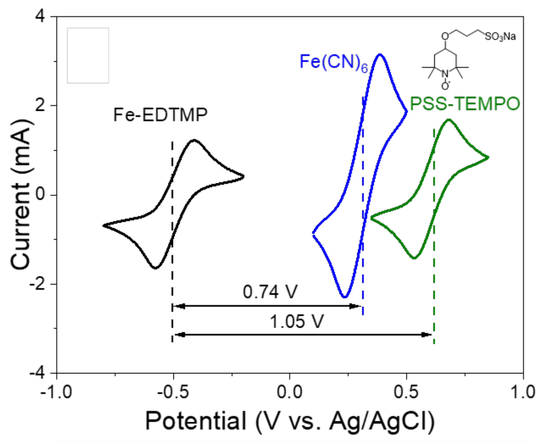


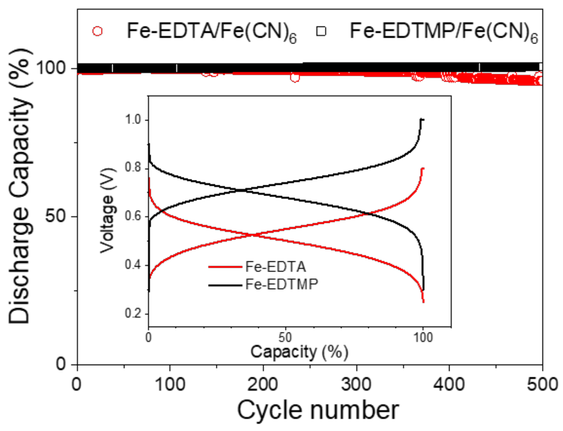


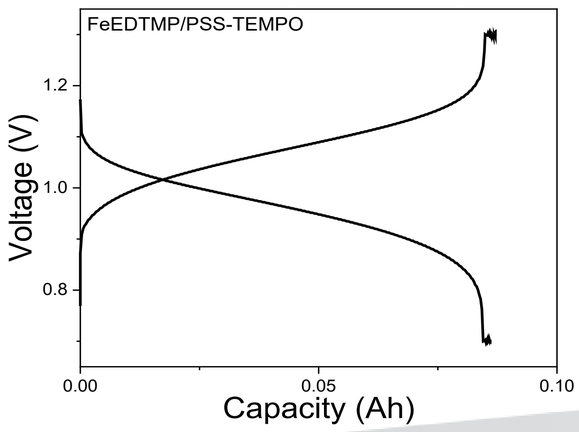
- Distinct phosphonic acid groups (NTMPA, BPMG, EDTMP HEDP) and differences in acidity (donor strength) cause variation in cell voltages. Highly functionalized ligands can lead to multiple, distinct structures that lead to multiple voltage plateaus (NTMPA & HEDP) – ligand alteration can lead to a single predominant structure with a single voltage plateau (BPMG & EDTMP).



- FeEDTMP: More negative redox potential than other nitrogenous carboxylate/phosphonates-based iron complexes.
  - FeEDTMP electrolyte exhibit greater stability at mild pH.
  - FeEDTMP paired with organic catholyte (PSS-TEMPO) achieve high cell voltage.

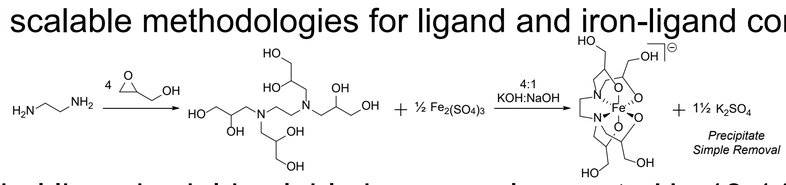




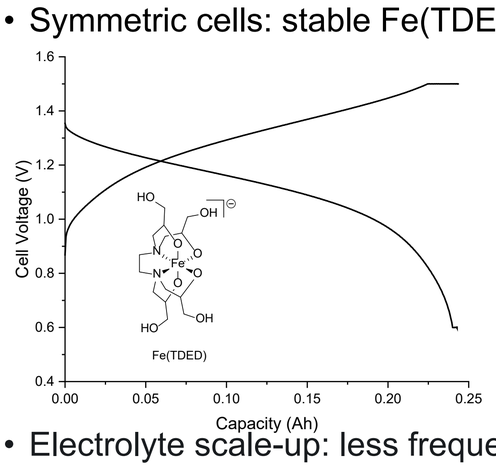


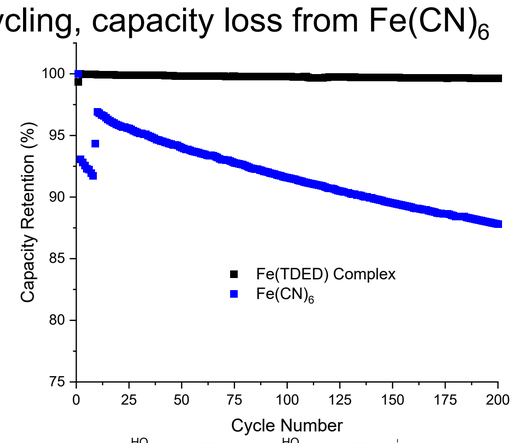
High pH (Aminoalcohol-based Ligands)

- Simple and scalable methodologies for ligand and iron-ligand complex synthesis

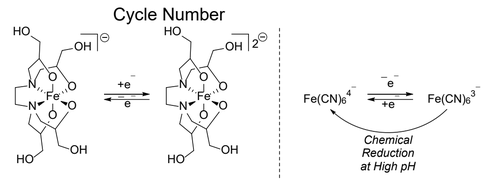


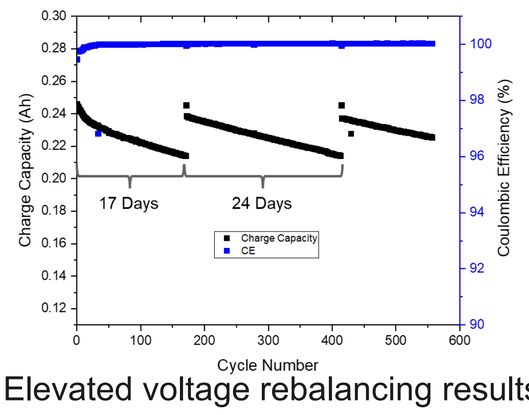
- Amino-alcohol ligands yield soluble iron complexes at pH ~13-14
  - High operative pH resulting from alcohol's acidity (not readily deprotonated)
  - Stronger donor to the iron center → higher cell voltages (1.2 V)
  - Symmetric cells: stable Fe(TDED) cycling, capacity loss from $Fe(CN)_6$

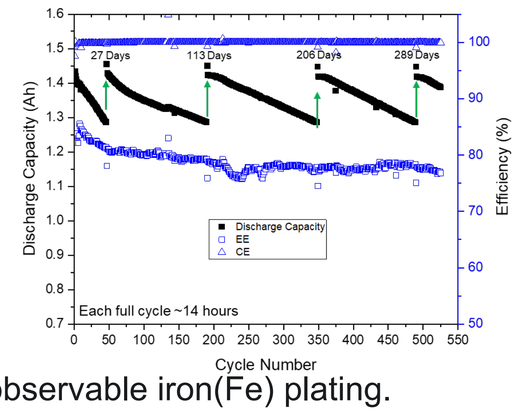




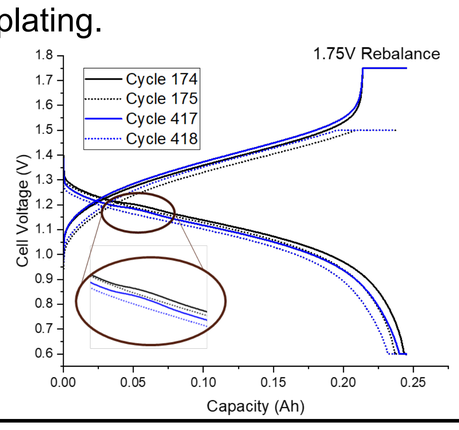
- Electrolyte scale-up: less frequent rebalance as electrode surface is significant in SOC imbalance in ↑pH $Fe(CN)_6$

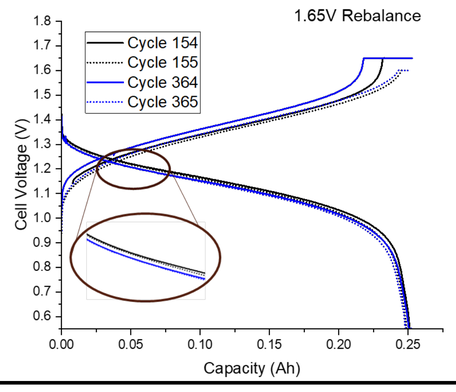






- Elevated voltage rebalancing results in observable iron(Fe) plating.
  - A moderate voltage rebalancing process does not exhibit any observable Fe plating.





Impact, Summary and Future Work

- Soluble iron-based RFBs present a promising solution for cost-effective, long-duration energy storage applications.
- Anolytes utilizing iron coordination complexes with phosphonic acids (neutral pH) and aminoalcohols (alkaline pH) exhibited notable stability.
  - Complexes based on phosphonic acid yielded low cell voltage but enhanced compatibility with the $Fe(CN)_6$ catholyte.
  - Complexes based on aminoalcohol produced elevated cell voltage, but $Fe(CN)_6$ -derived SOC imbalance necessitates periodic SOC rebalancing.
- Alternative catholytes with higher redox potentials will be evaluated with phosphonic acid complexes to achieve higher cell voltages.
- The influence of multiple variables on the required rebalancing interval for Fe(TDED) / $Fe(CN)_6$ systems will be assessed.

PNNL Publications/References
1. *Nature Communication* 2024, 15, 2566.
2. *Advanced Energy Materials* 2025, 15, 2403149.
3. *Cell Reports Physical Science* 2025, 6, 102615.

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