

# Soluble Iron-Based Redox Flow Electrolytes

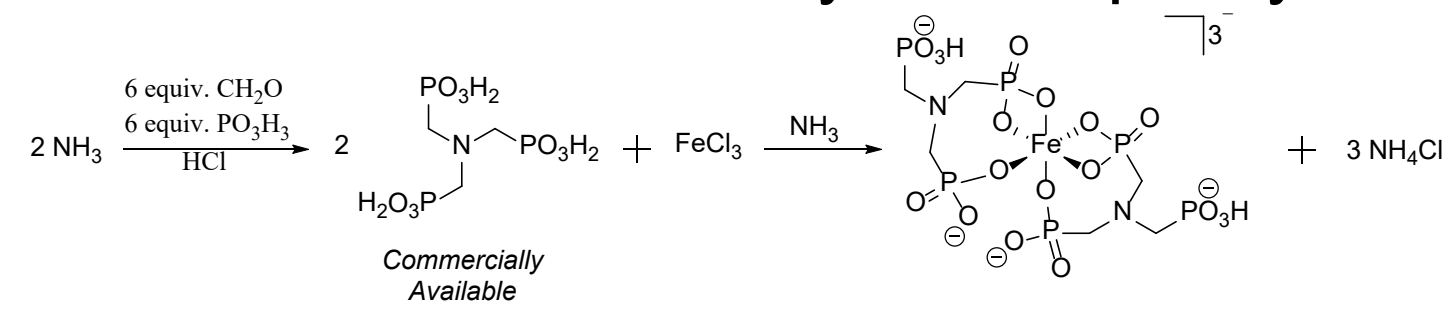
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## Introduction

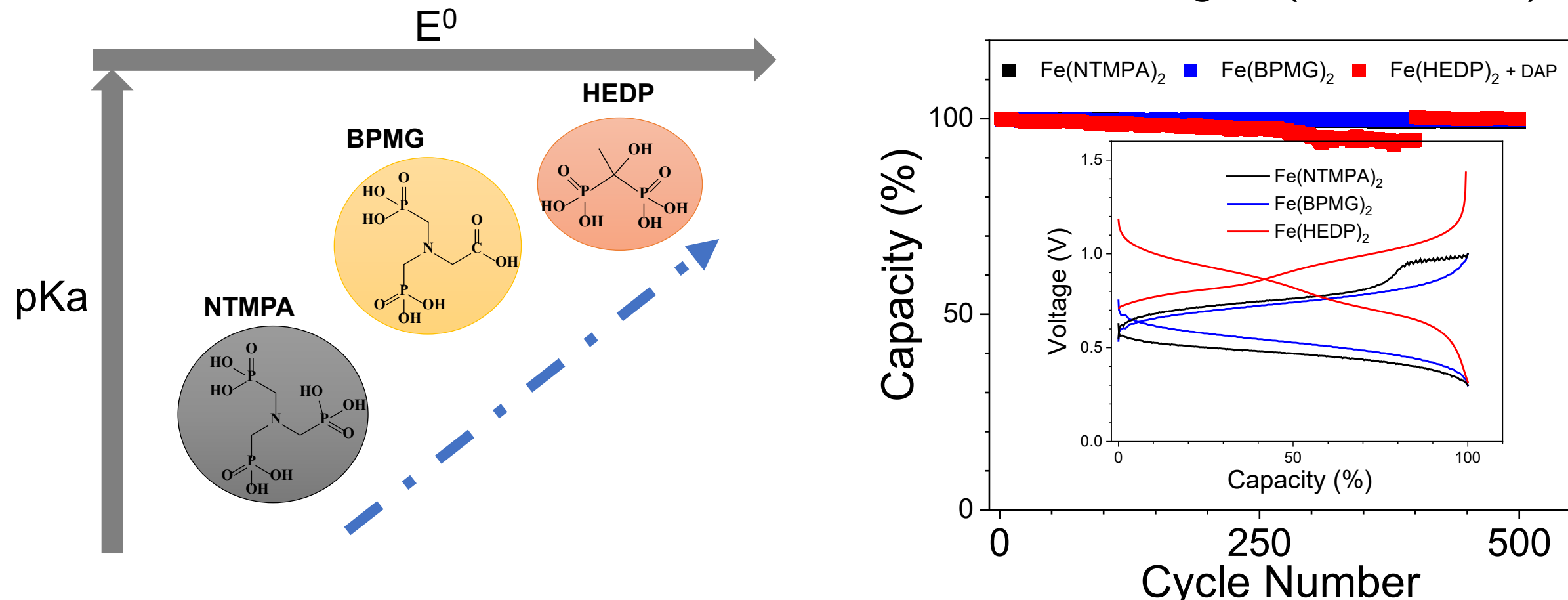
Iron-based electrolytes can be an abundant, low-cost option for redox flow batteries, potentially replacing more costly and supply-chain restricted vanadium. By utilizing ligands to control the properties of iron ions, a redox flow battery can be devised using soluble  $\text{Fe}^{2+/3+}$  species as both catholyte and anolyte, avoiding the technical challenges of hybrid all-iron ( $\text{Fe}^0$  anode) cells.

## Phosphonate-based Ligands

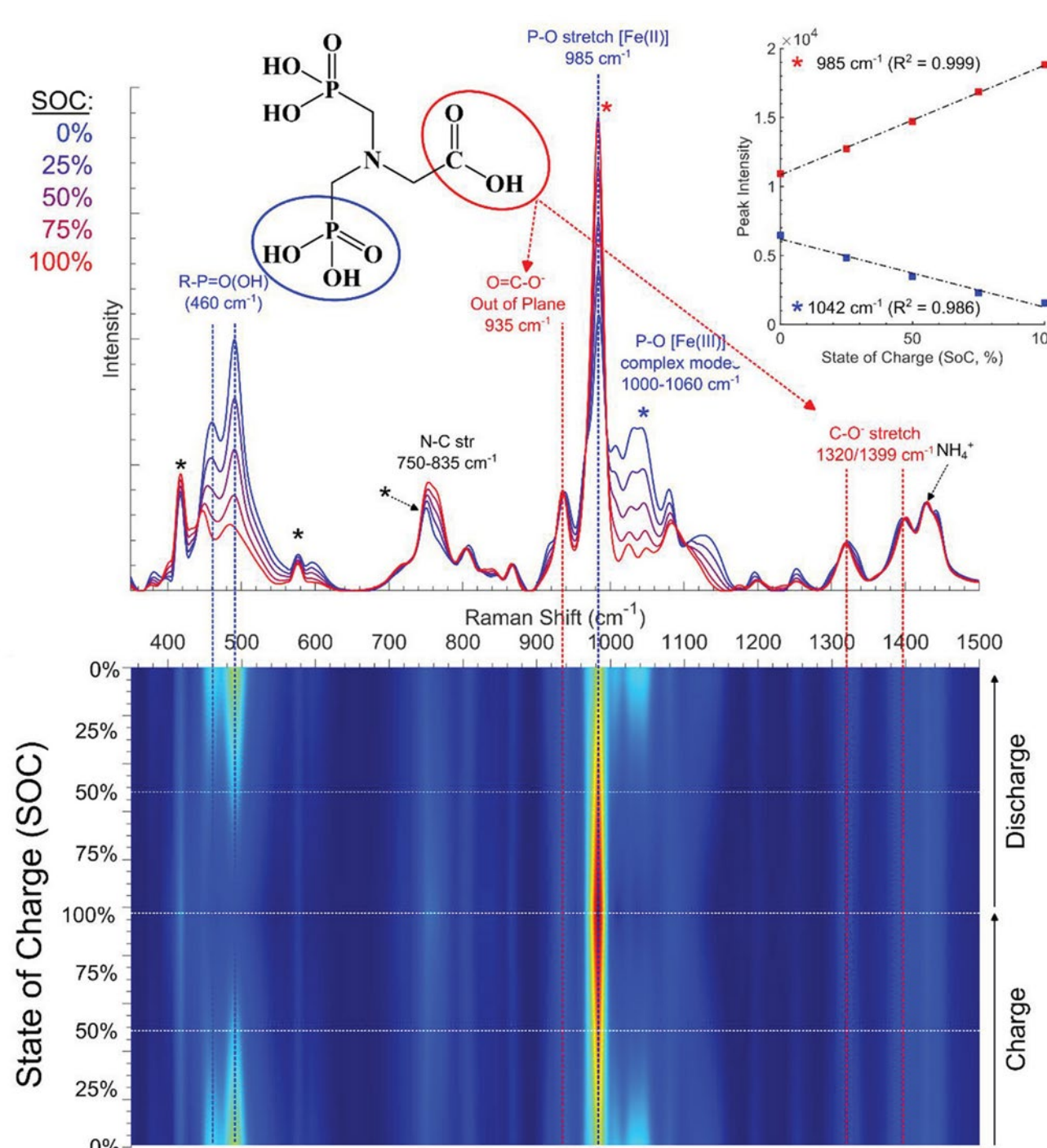
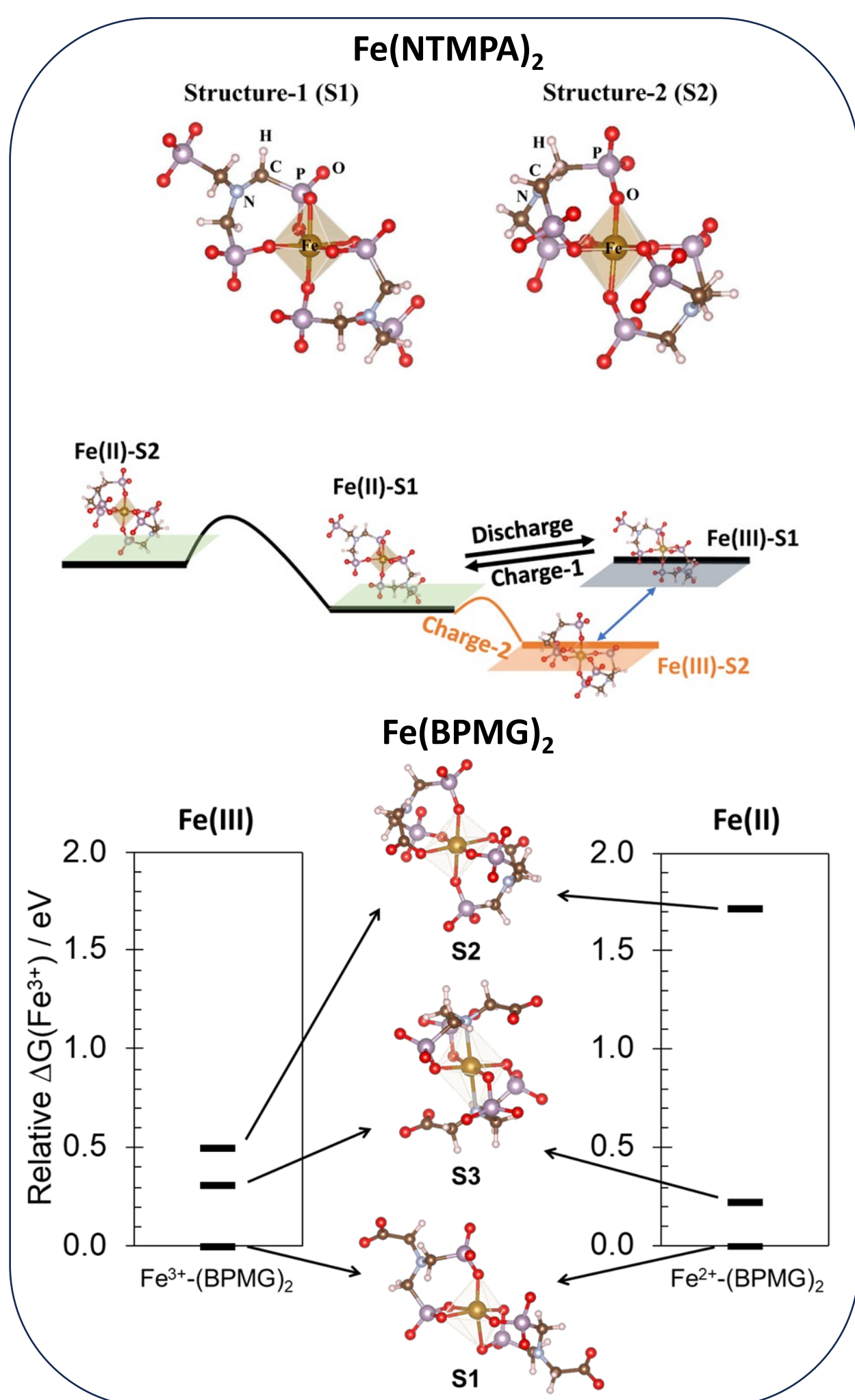
- Multiple derivatives available commercially via simple syntheses



- Phosphonic acid ligands produce soluble iron complexes at near neutral pH 8
  - Mild operative pH due to acidity of phosphonic acids (easily deprotonated)
  - Weaker donor to the iron center  $\rightarrow$  lower cell voltages (0.6-0.85 V)



- Varied phosphonic acid moieties (NTMPA, BPMG, HEDP) and acidity differences (donor strength) result in variable cell voltages
- Presence of multiple phosphonic acid groups yields more potential donor atoms than iron can accommodate  $\rightarrow$  Multiple possible coordination modes
  - $\text{Fe}(\text{NTMPA})_2$  – Two binding structures of similar free energy in Fe(III) state, but dissimilar free energy in Fe(II) state
    - Two charging plateaus due to ligand reorientation
  - $\text{Fe}(\text{BPMG})_2$  – Single binding structure is lowest energy in Fe(III) and Fe(II)
    - Single charging plateau capable of higher rate performance
  - $\text{Fe}(\text{HEDP})_2$  – Two voltage plateaus ( $\sim 50\%$  SOC) associated with a potential dimeric structure resulting from multi-dentate, multi-donor features of HEDP



- Operando Raman Spectroscopy corroborates DFT
  - Carboxylate groups exist as non-bonding moieties in the  $\text{Fe}(\text{BPMG})_2$  complex

## 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.

## Acknowledgement

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## PNNL Publications

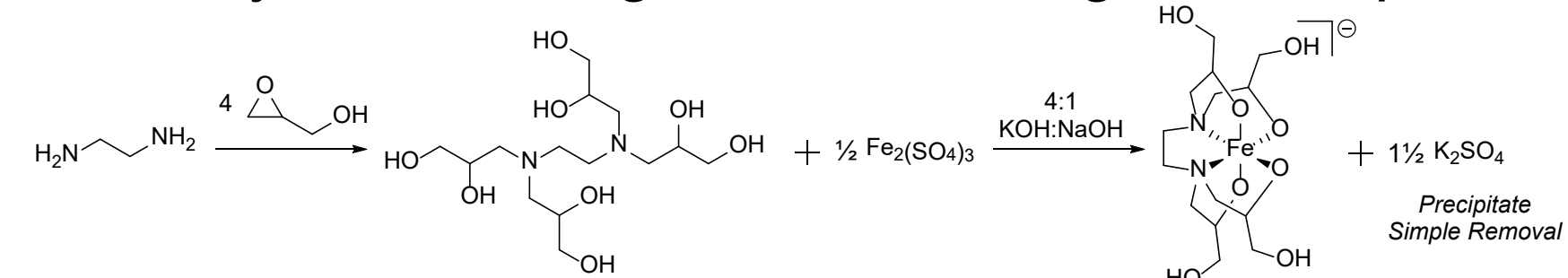
- Nature Communication 2024, 15, 2566.
- Advanced Energy Materials 2025, 15, 2403149.
- Cell Reports Physical Science 2025, 6, 102615.

## Objective and Approach

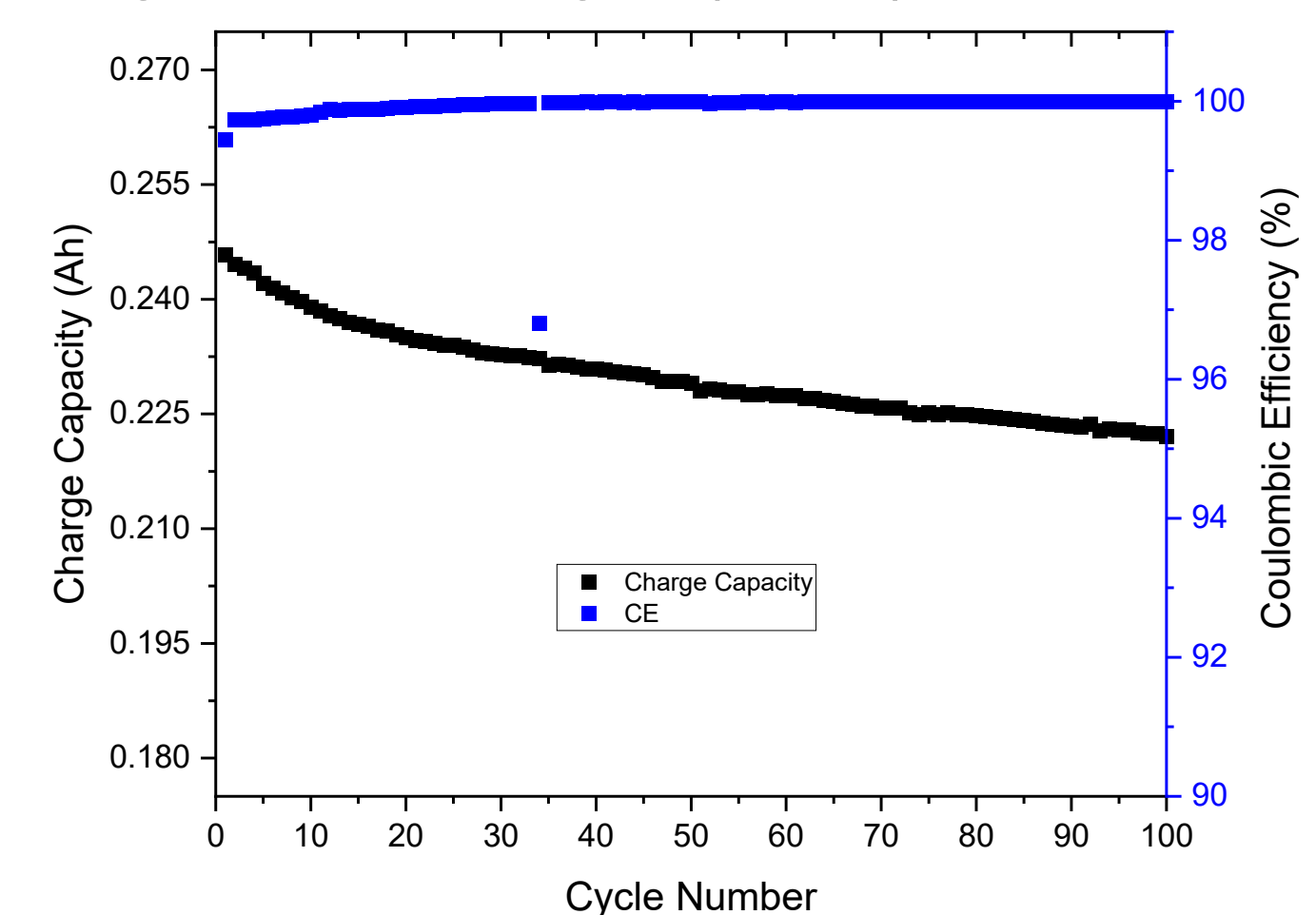
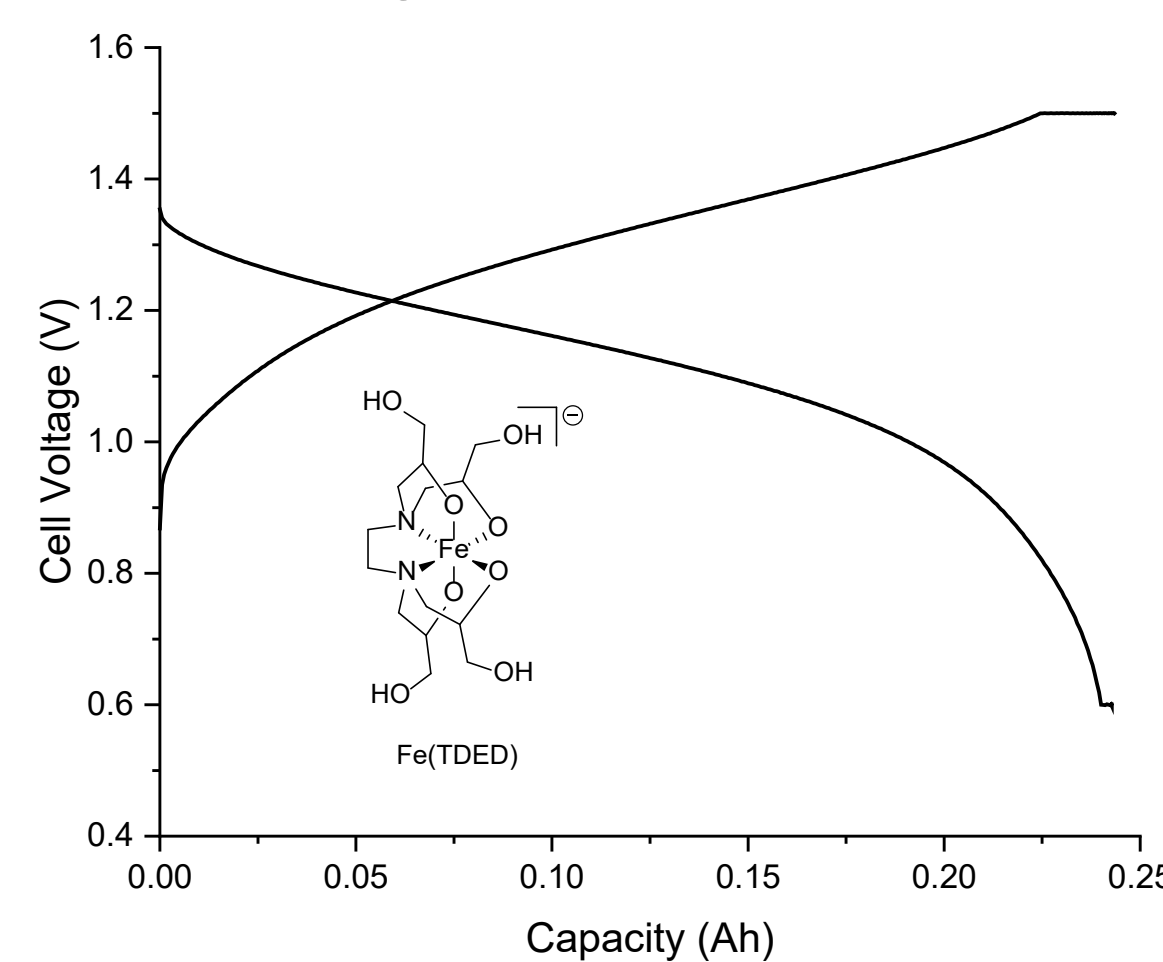
To identify and design low-cost coordinating ligands for the development of all-soluble iron chemistries for RFB application, targeting new anolyte materials to pair with the well-known ferrocyanide catholyte. Varied ligand sets which yield soluble iron complexes under different pH regimes (near-neutral pH 8 and alkaline pH 13-14) were tested to identify performance and stability tradeoffs.

## Aminoalcohol-based Ligands

- Simple and scalable synthesis of ligand and iron-ligand complex

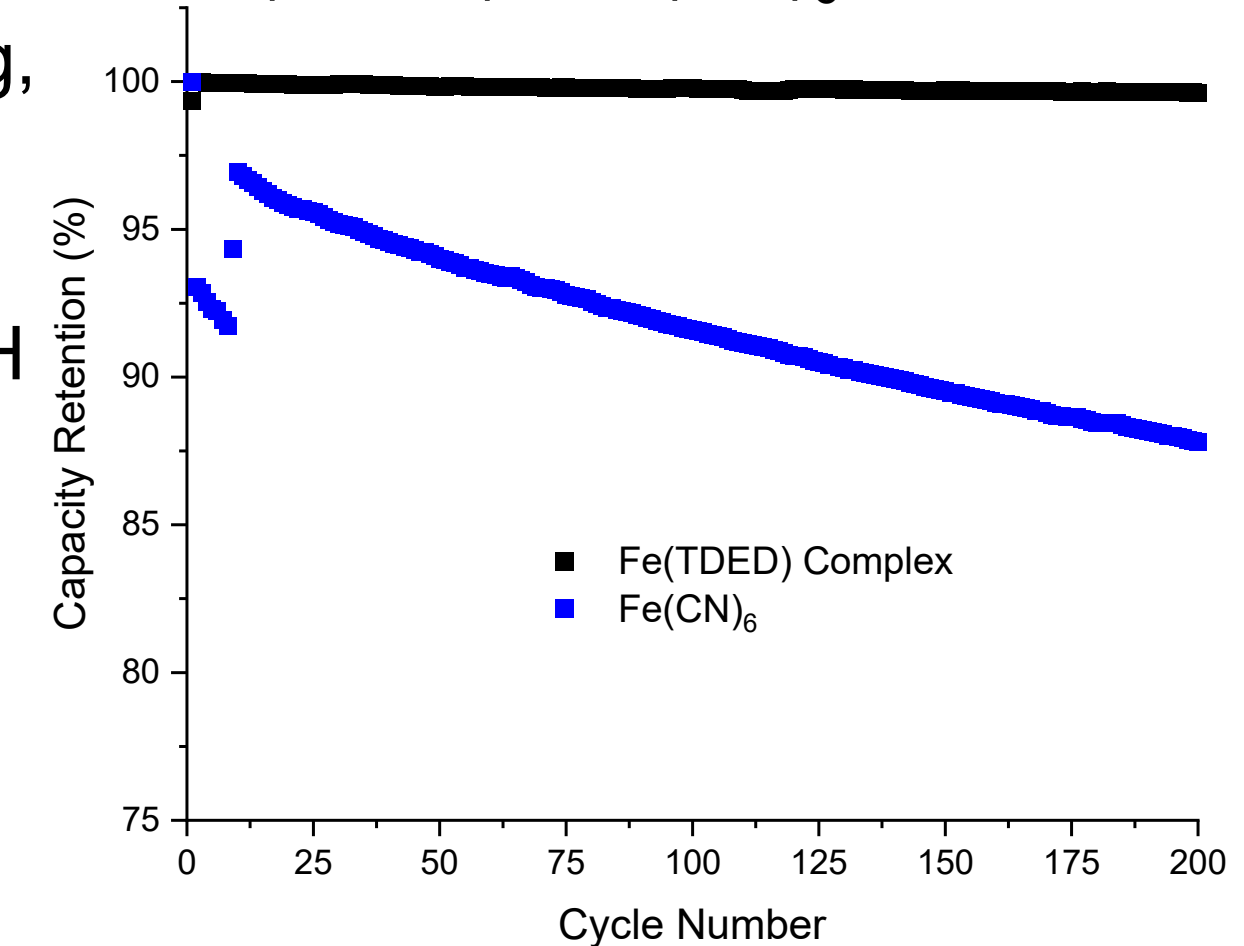
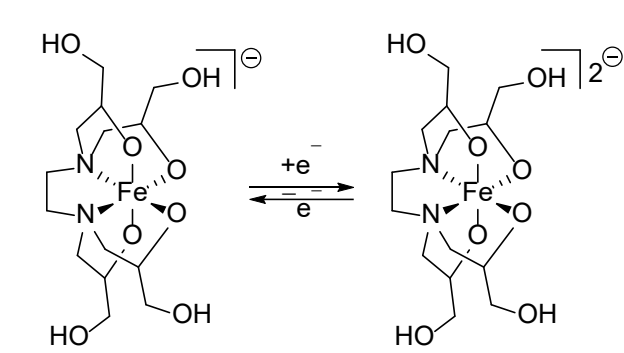


- Amino-alcohol ligands produce soluble iron complexes at pH  $\sim 13-14$ 
  - High operative pH due to lack of acidity of alcohol (not easily deprotonated)
  - Stronger donor to the iron center  $\rightarrow$  higher cell voltages (1.2 V)

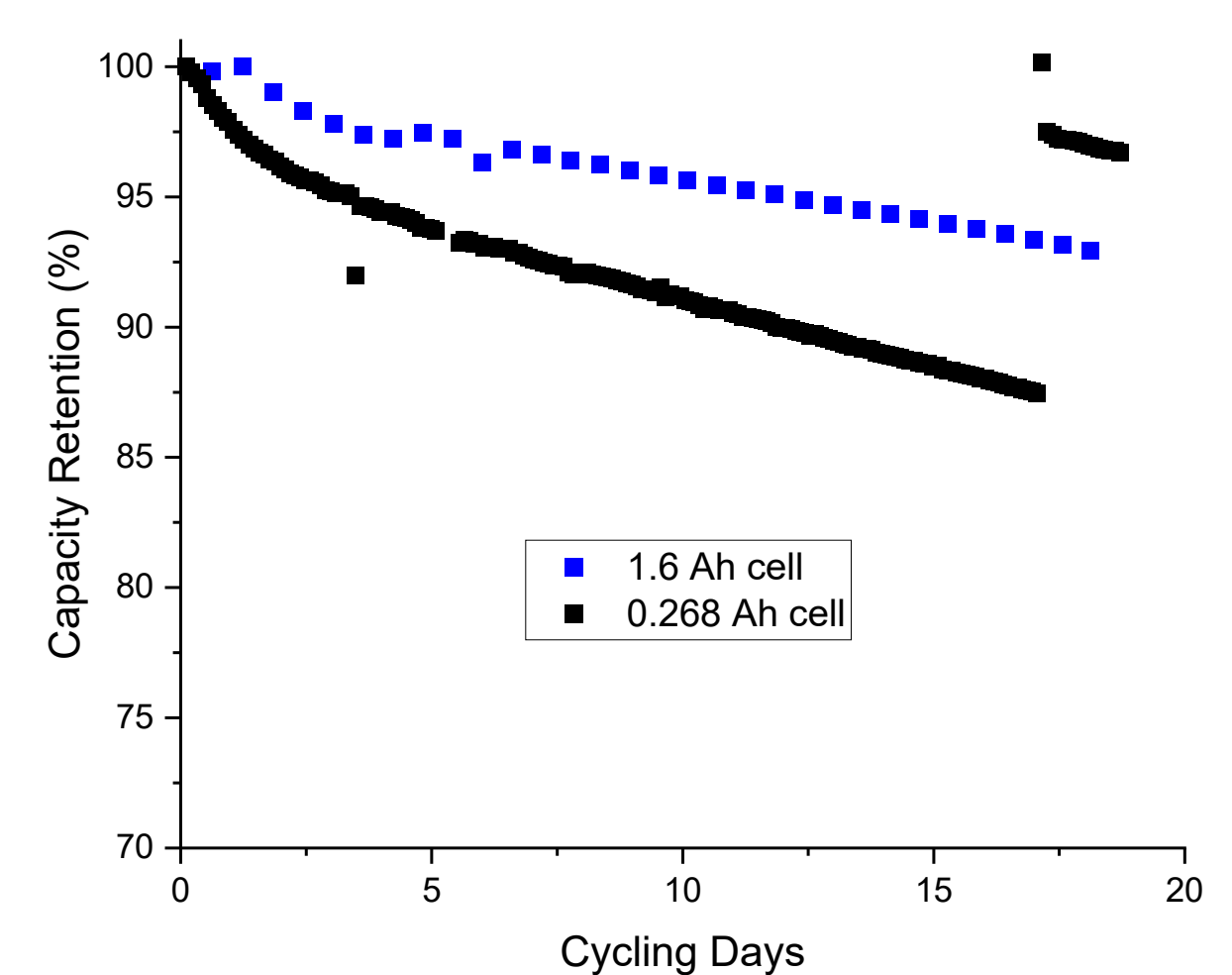
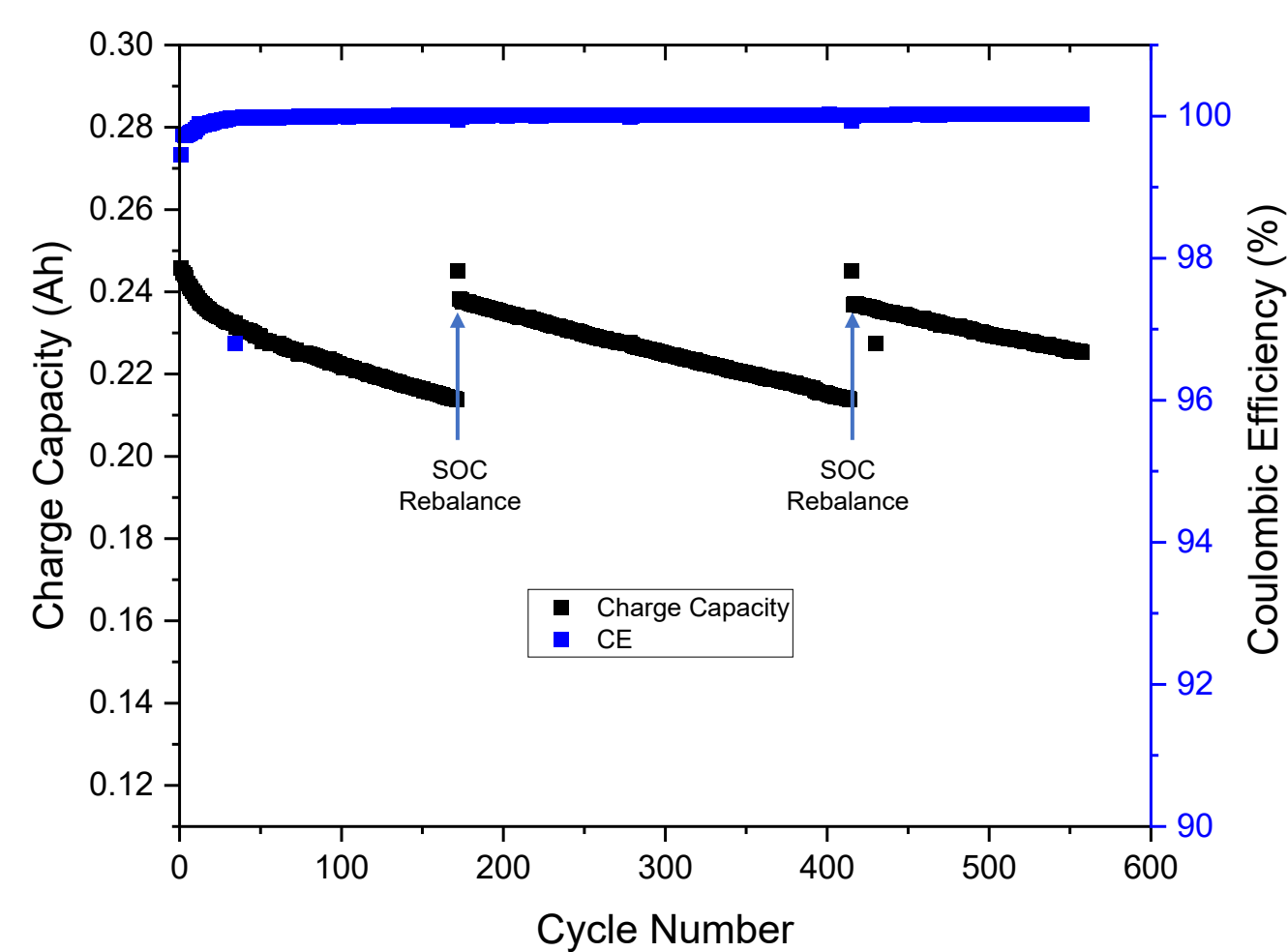


- Steady capacity decay is observed in full cells of  $\text{Fe}(\text{TDED}) / \text{Fe}(\text{CN})_6$

- Symmetric cells: stable  $\text{Fe}(\text{TDED})$  cycling, capacity loss from  $\text{Fe}(\text{CN})_6$
- Consistent with reported issues on chemical  $\text{Fe}(\text{CN})_6^{3-}$  reduction at high pH



- Capacity can be reset with intermittent electrochemical SOC rebalancing (HER)
  - Preliminary results show rebalancing may be needed less frequently in higher capacity (longer duration) cells



## Summary and Future Work

- Anolytes based on coordination complexes of iron with phosphonic acids (mild pH) and aminoalcohols (high pH) both showed good stability
  - Phosphonic acid complexes demonstrated lower cell voltage but better pH compatibility with the  $\text{Fe}(\text{CN})_6$  catholyte
  - Aminoalcohol complexes demonstrated higher cell voltage but at high pH  $\text{Fe}(\text{CN})_6$ -derived SOC imbalance requires intermittent SOC rebalancing
- Alternative catholytes with higher redox potentials will be tested with the phosphonic acid complexes to pursue higher cell voltages
- The impact of higher electrolyte volumes on the required rebalancing frequency of  $\text{Fe}(\text{TDED}) / \text{Fe}(\text{CN})_6$  cells will be determined