Pacific Northwest
NATIONAL LABORATORY

Presentation #505: Soluble Iron-Based Redox Flow

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Pacific Northwest National Laboratory

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U.S. DEPARTMENT OF ENERGY BATTELLE

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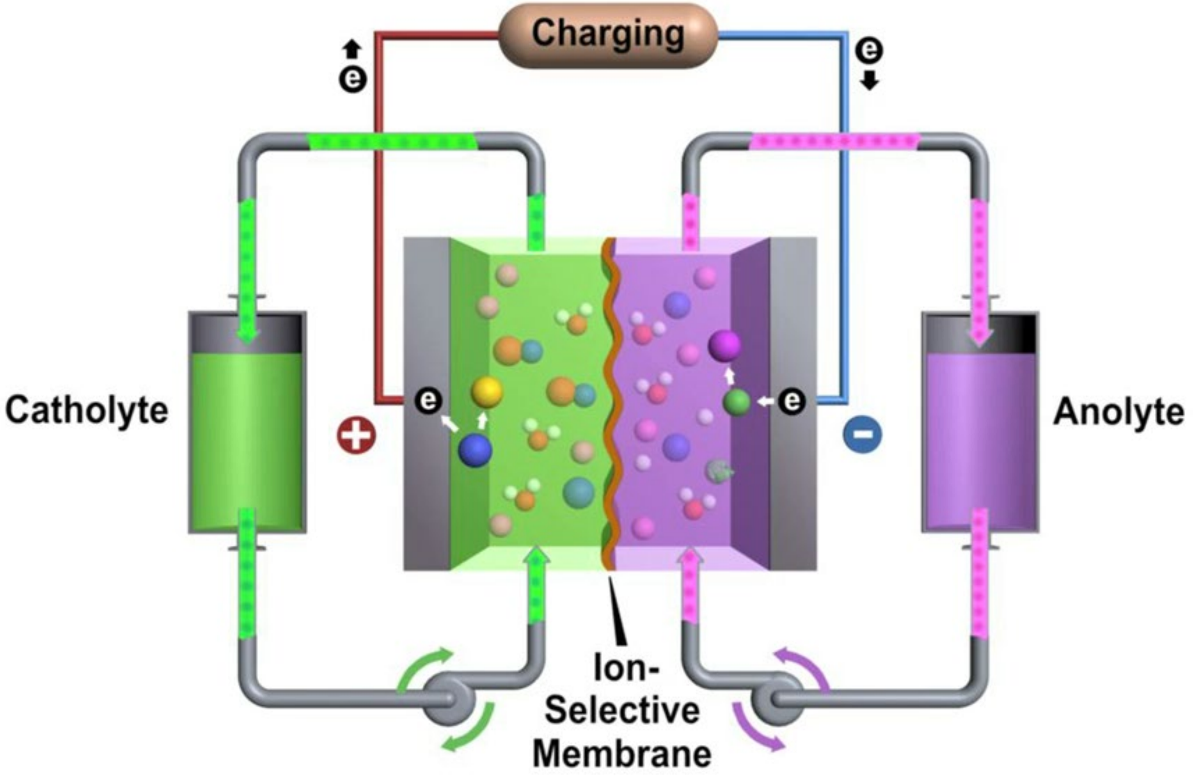
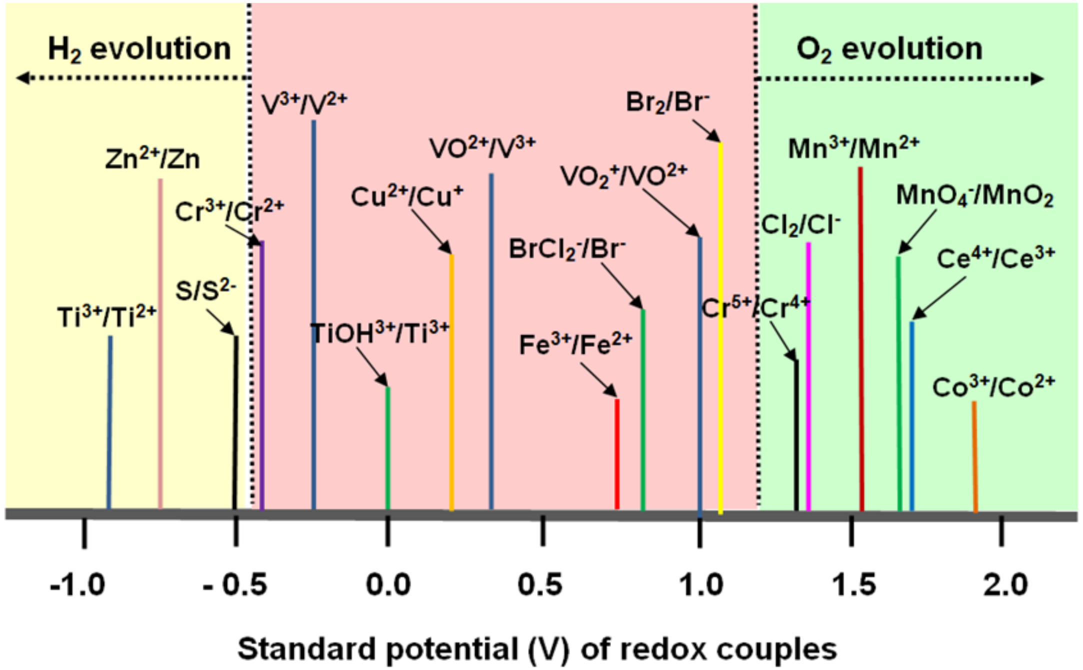
Redox Flow Batteries (RFB)



- **Decoupling of Power and Capacity**
  - Tailor system to application
  - Extend duration with storage tank size
- **High safety**
  - Spatial separation of reactive materials
  - Major constituent is water
  - Easy thermal management.
  - Battery health monitoring
- **Easy recycling after service life**
  - Consumption vs. Investment

Flow Battery Chemistries

- **Vanadium Redox Flow Battery (VRB)**
  - Symmetric: V^{2+}/V^{3+} vs. VO^{2+}/VO_2^+
  - Current state-of-the-art, highly studied
  - High/sporadic material cost
  - Precipitation (temperature window)

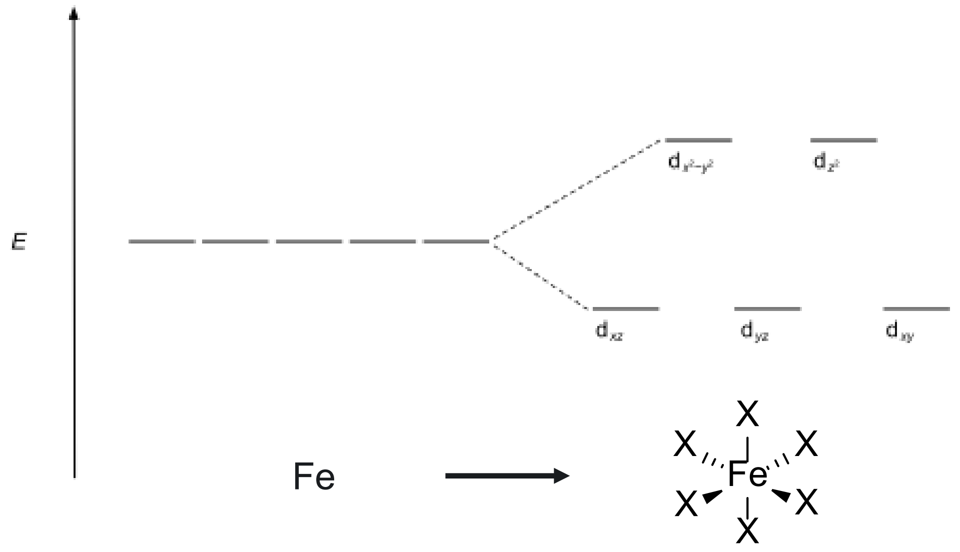


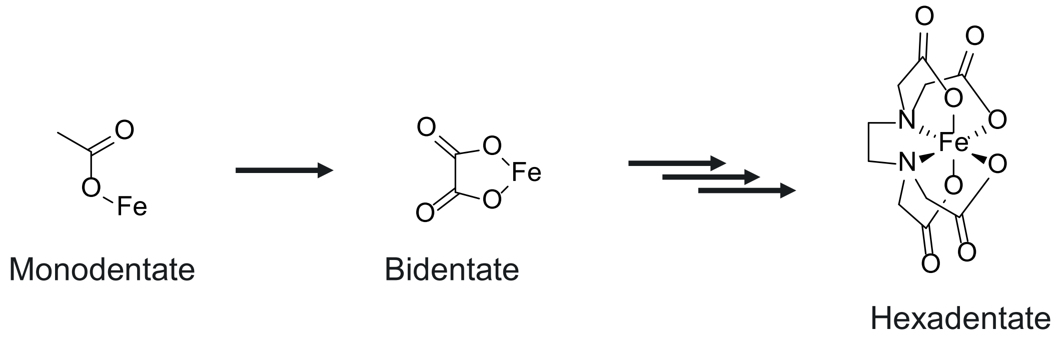
- **Hybrid Flow & Other RFB Chemistries**
  - Numerous options (metals, halides, etc.)
  - Aqueous soluble organics
    - Highly tunable
  - Hybrid Flow
    - Zn/Br
    - All Iron

- **Project Goal**
  - Identify all-soluble iron chemistries
    - Low-cost metal
    - Low-cost coordinating ligands

Iron Coordination Complexes

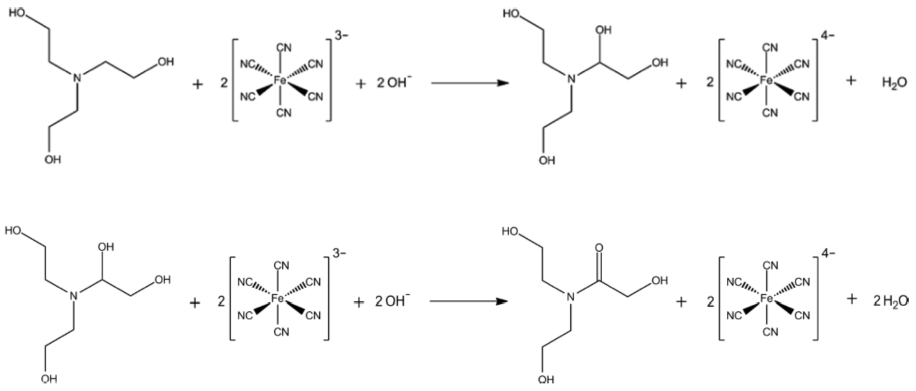
- Multitude of ligand options already produced at large scale (amines, carboxylates, alcohols, etc.)
- Tunable ionic charge, pH range, redox potential based on type and number of ligands
- Ligand denticity to control binding affinity

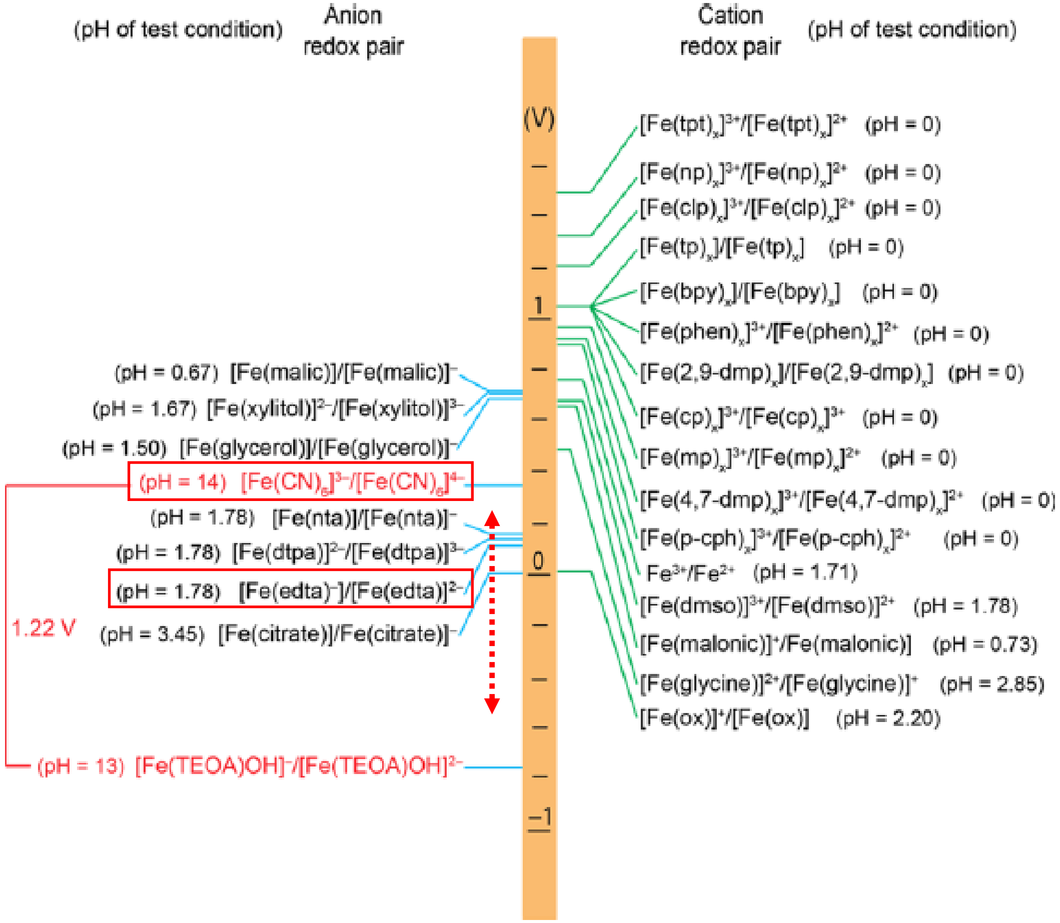




Iron Coordination Complexes

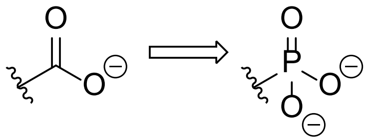
- Tunable ionic charge, pH range, redox potential
- Most reports based on small molecule alcohols, carboxylic acids, polypyridines
- Poor reduction potentials for carboxylic acid-based ligands (edta, nta, etc.) vs $Fe(CN)_6$
- Crossover of dissociated ligands





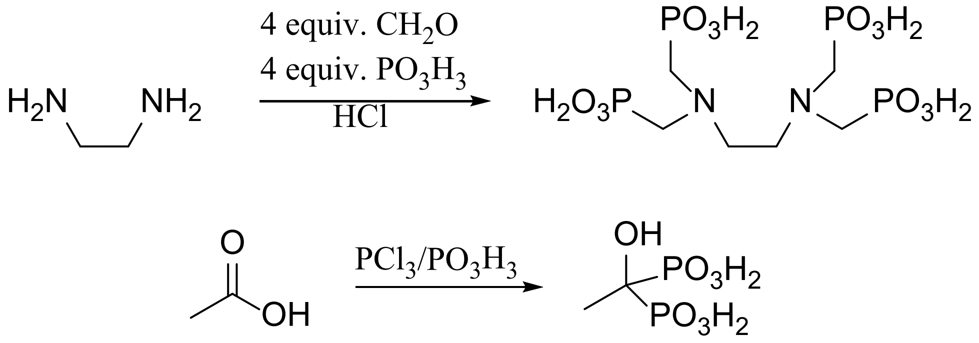
Gong, et.al. *ACS Energy Lett.*, **2016**, 1, 89-93.

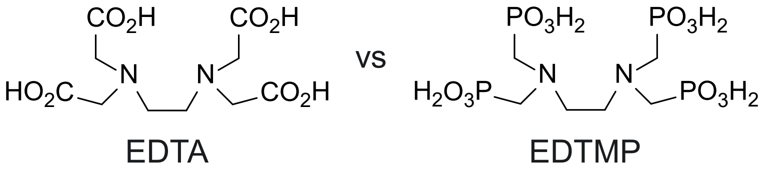
Ligand Modification Effects

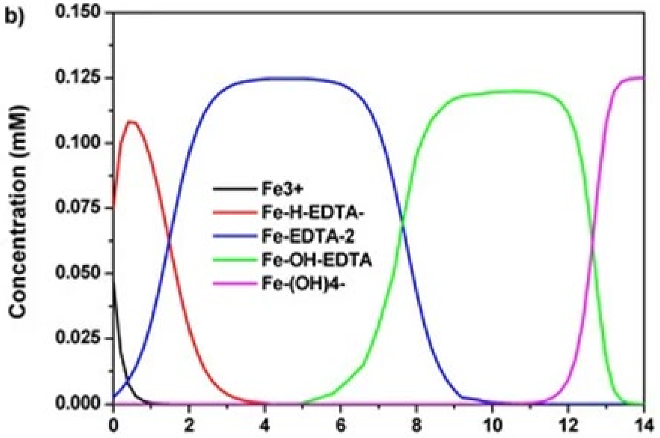


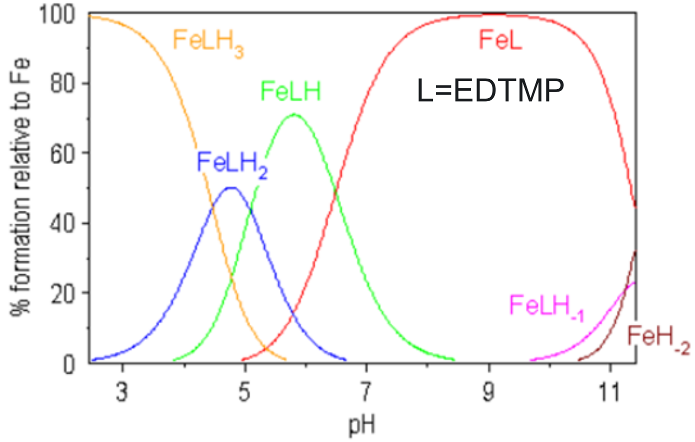
- Phosphonic acid analogues of carboxylic acid-based ligands
  - Stronger donor → More negative redox potentials
  - Improved resistance to hydrolysis (Fe-L -> Fe_xO_y)
  - Reduce ligand crossover

- Low-cost synthesis, tunable based on precursor – commercially available variants



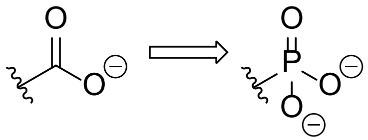


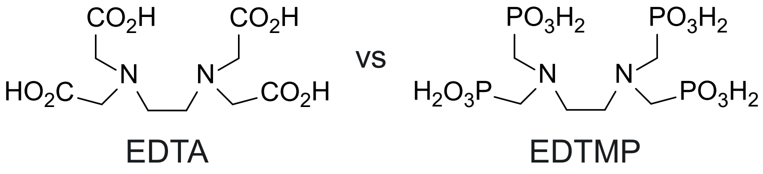




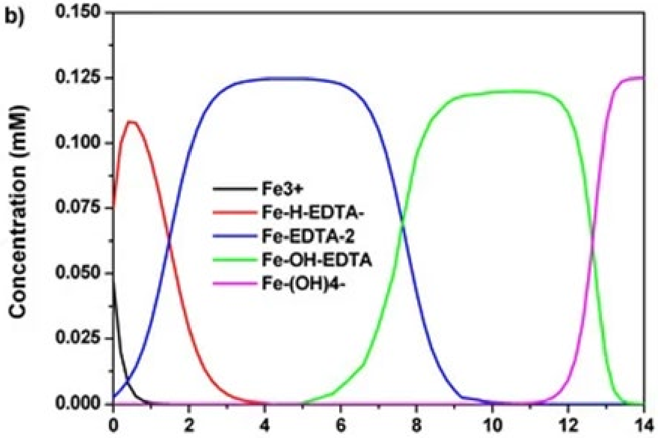
Mateescu, et al. DOI:10.1080/00207450500272230
Messele, et. al. Catalysts, **2019**, 5, 474.

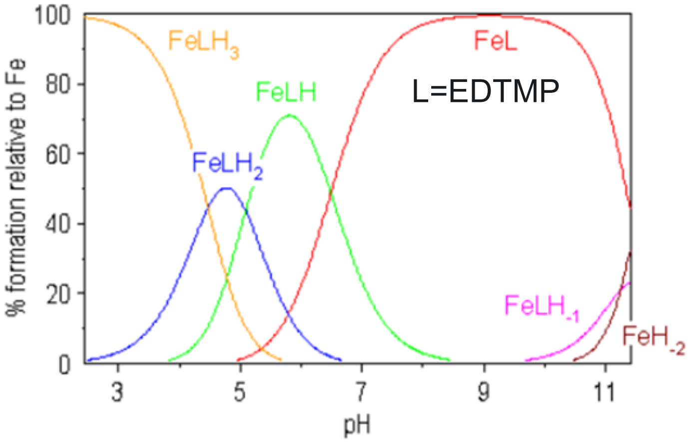
Ligand Modification Effects

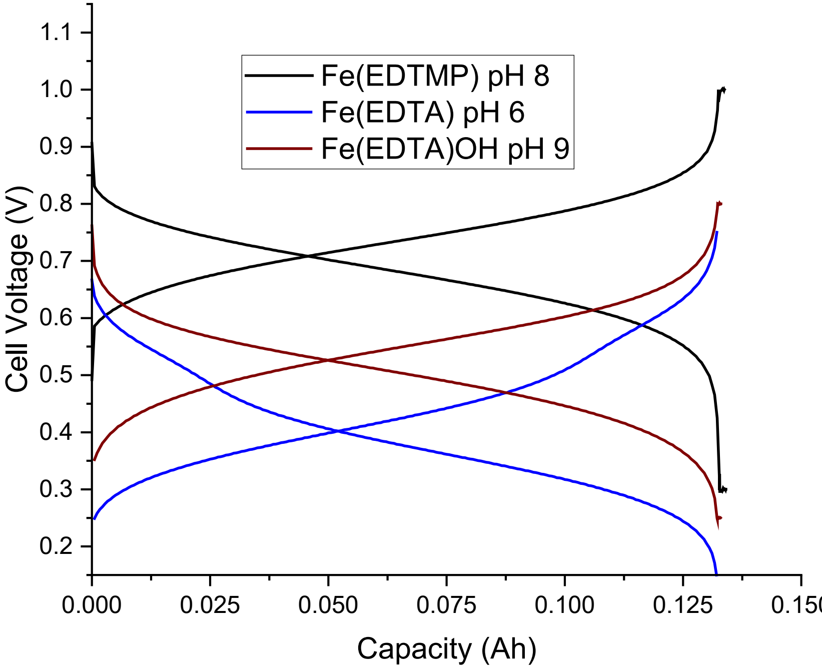


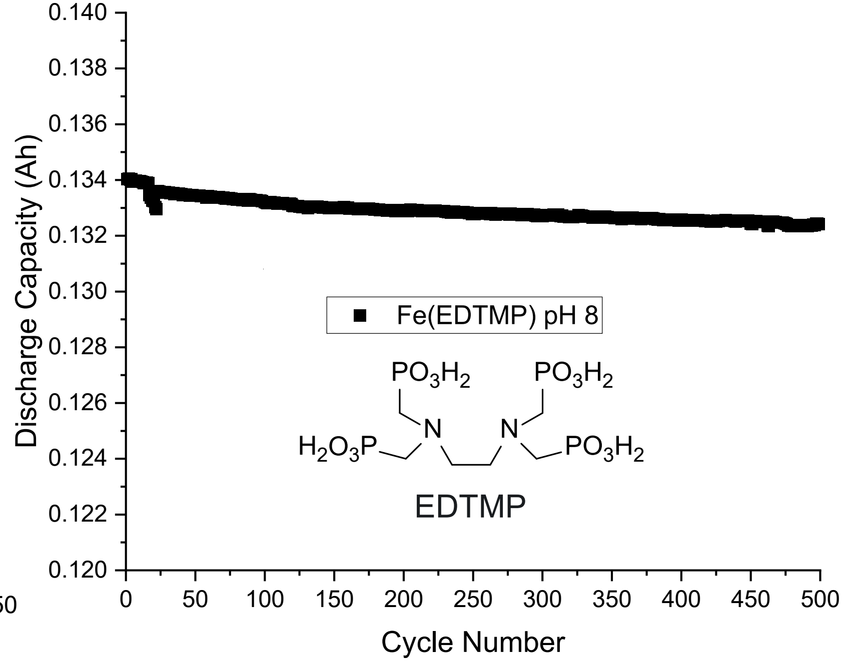


- ✧ Phosphonic acid analogues of carboxylic acid-based ligands
  - ✧ Stronger donor → More negative redox potentials
  - ✧ Improved resistance to hydrolysis (Fe-L -> Fe_xO_y)
  - ✧ Reduce ligand crossover







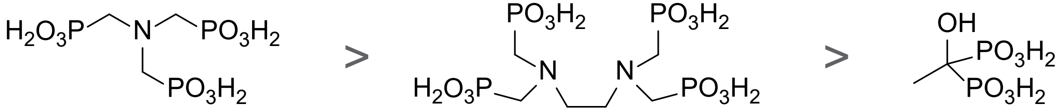


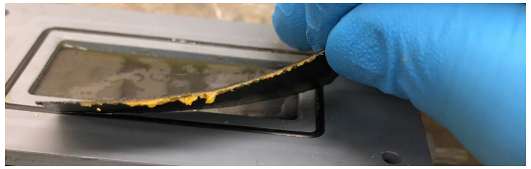
0.5M in [Fe], pH 8, cycled against $Fe(CN)_6$, 20 mA/cm^2 current density

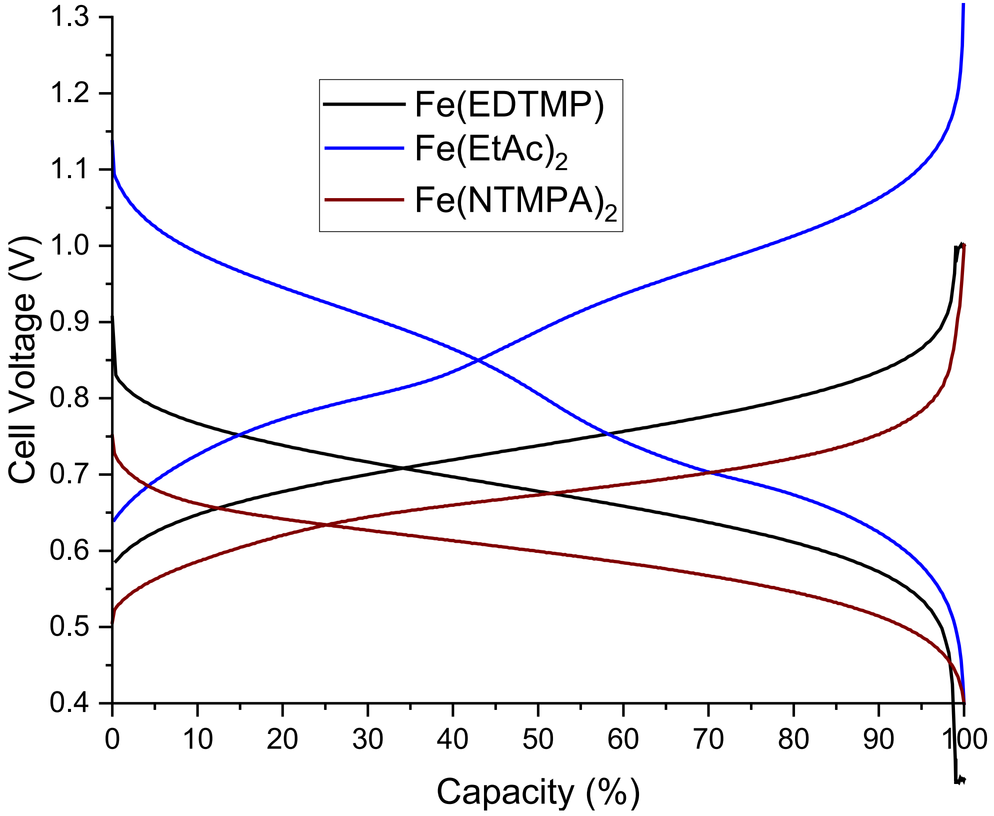
Mateescu, et al. DOI:10.1080/00207450500272230
Messele, et. al. Catalysts, **2019**, 5, 474.

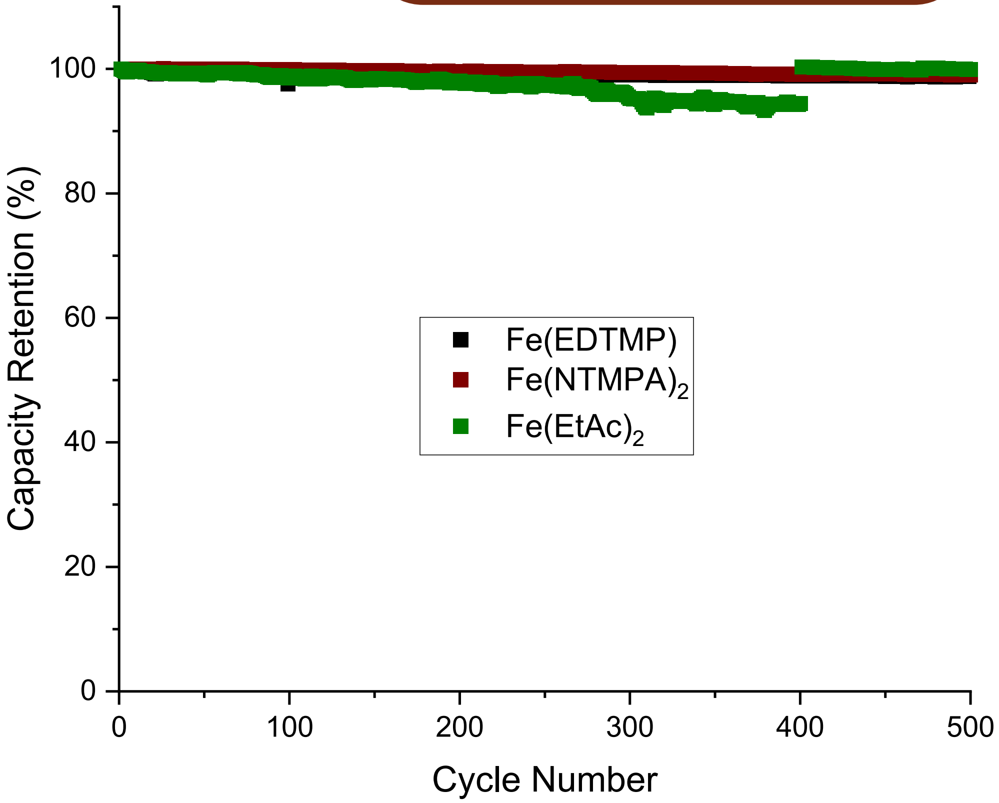
Impact of Specific Phosphonic Acid Variant

- Highly varied cell voltages from commercially available ligands
- Highly stable long-term cyclability




Pump tube spallation affecting cell cycling



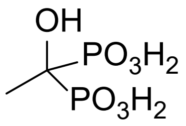


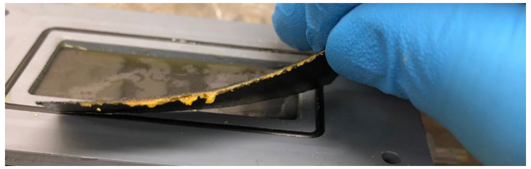
0.67M in [Fe], pH 8, cycled against $Fe(CN)_6$

Coordination Environments and Additives: $Fe(EtAc)_2$ Case Study

- Two distinct voltage plateaus → two unique species

$Fe(EtAc)_2$





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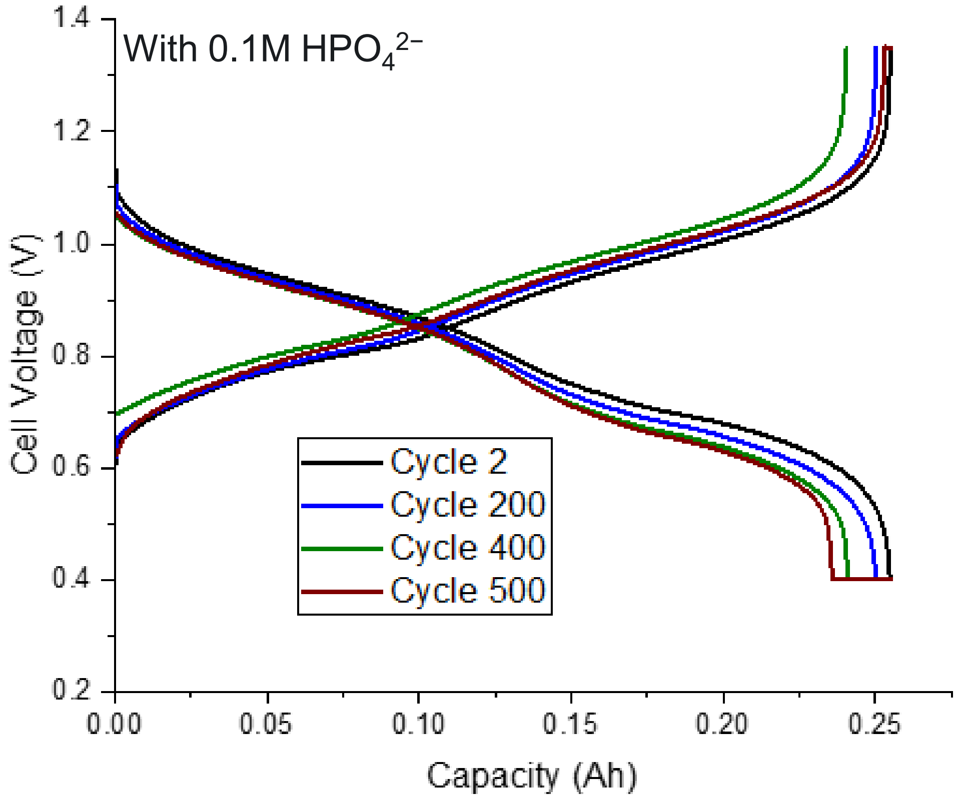
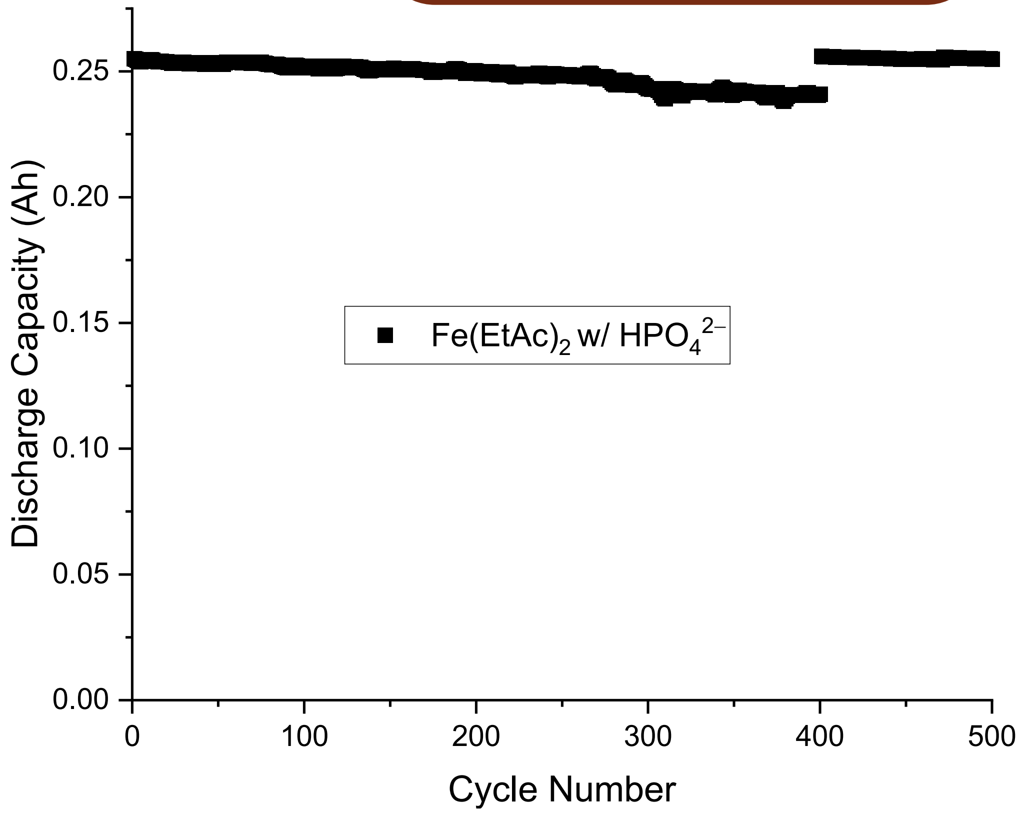


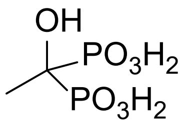


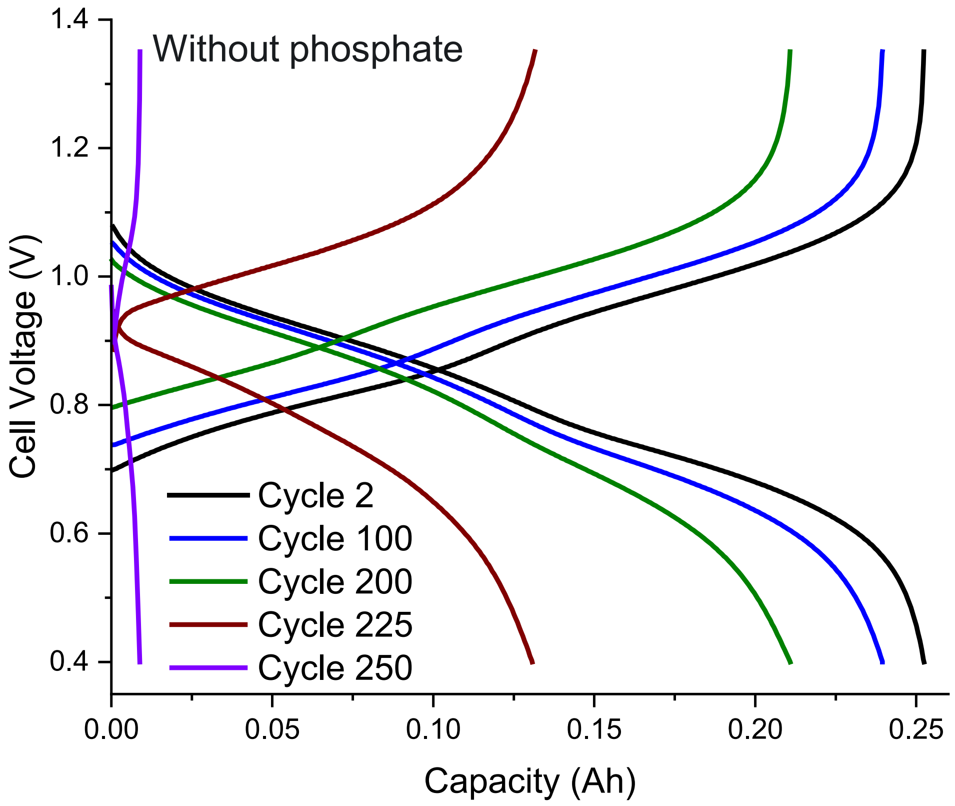
0.67M in [Fe], pH 8, cycled against $Fe(CN)_6$

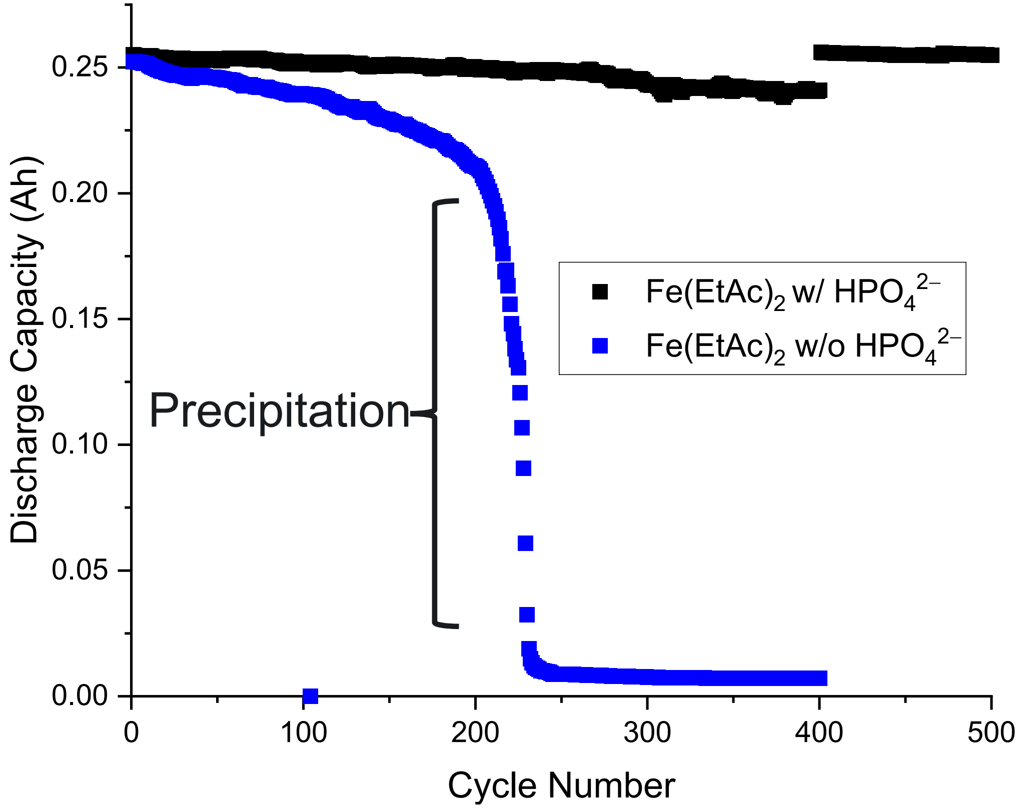
Coordination Environments and Additives: $Fe(EtAc)_2$ Case Study

- Accelerated capacity loss without added phosphate, loss of lower voltage capacity and subsequent precipitation

$Fe(EtAc)_2$



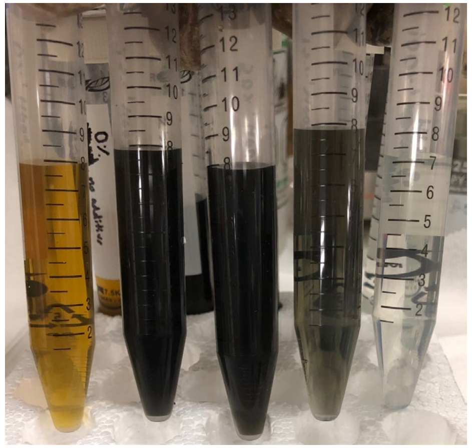


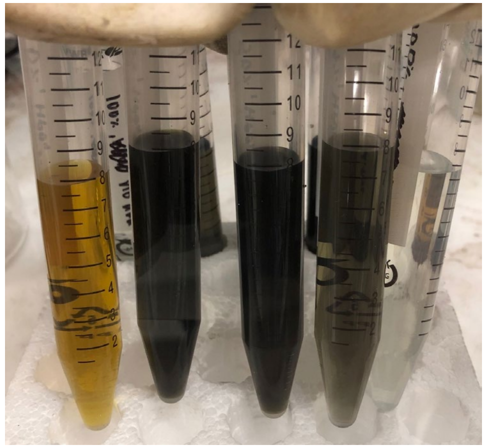


0.67M in [Fe], pH 8, cycled against $Fe(CN)_6$

Coordination Environments and Additives: $Fe(EtAc)_2$ Case Study

With phosphate. Fresh (left), 1 day (right)





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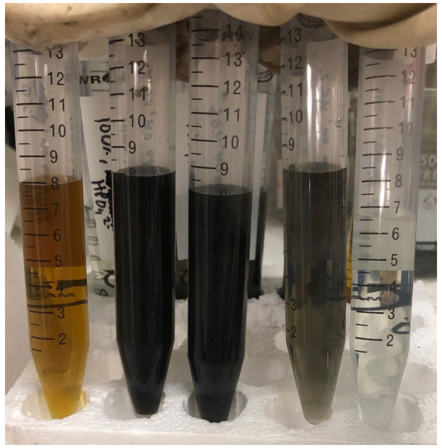
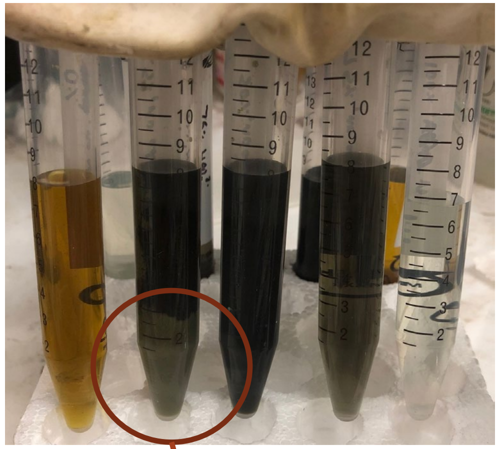
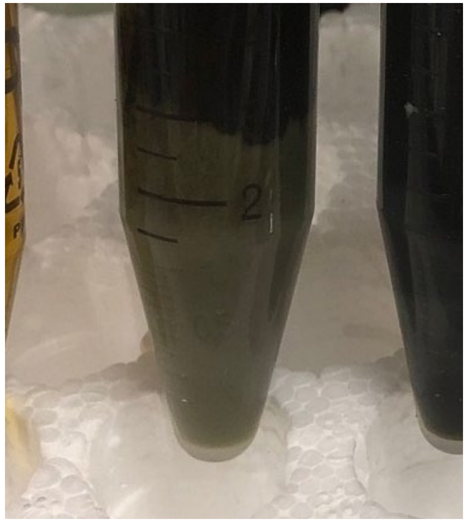
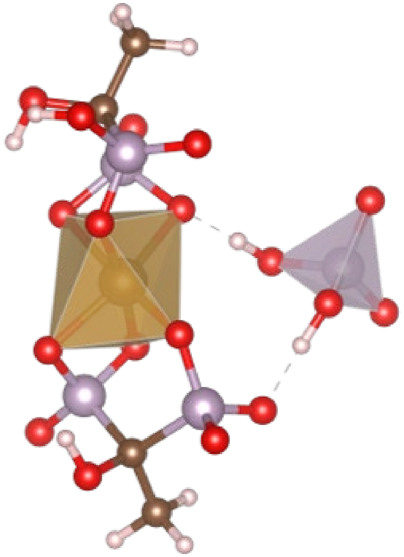






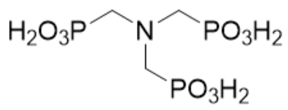
<u>pH at 0, 25, 50, 75, 100% SOC</u>
w/phosphate : 8.20, 8.67, 8.96, 9.01, 9.03
w/o phosphate: 8.14, 8.69, 8.92, 9.01, 9.05

- No notable phosphate effect on pH
- DFT supports a hydrogen-bonding effect between phosphate and $Fe(EtAc)_2$ species
  - Agglomeration mitigation

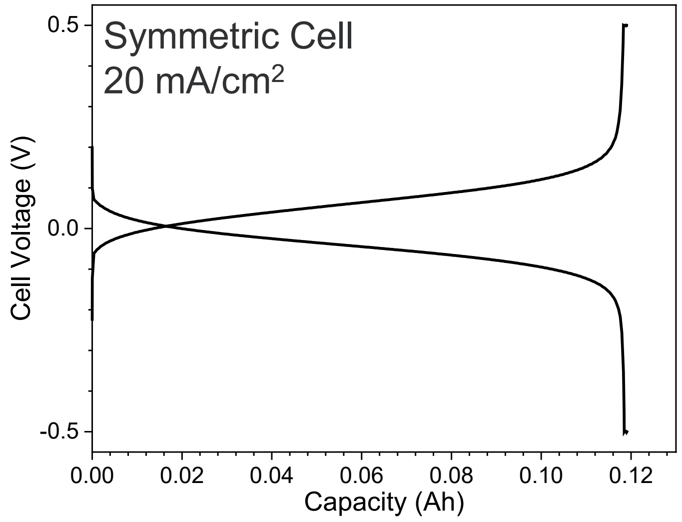


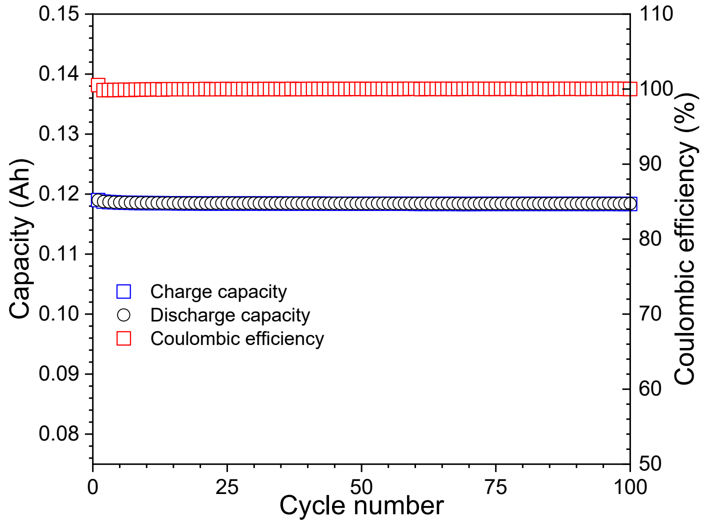
Dynamic Coordination Environments: $Fe(NTMPA)_2$ Case Study

$Fe(NTMPA)_2$

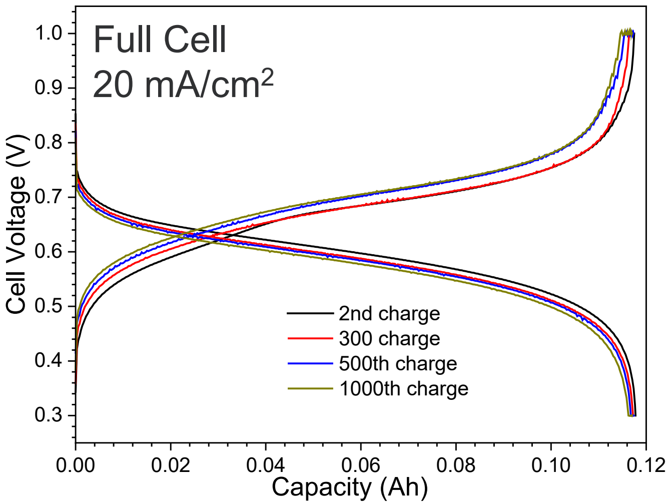


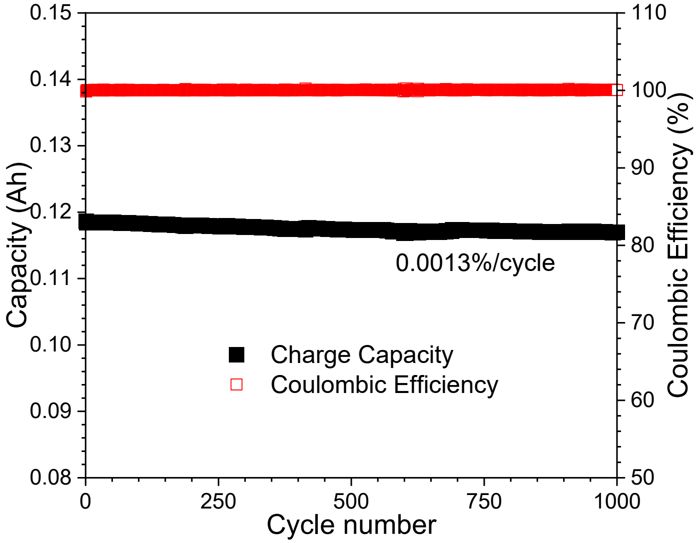
- Stable cycling in both symmetric & full cells
- New charging plateau observed at higher current density

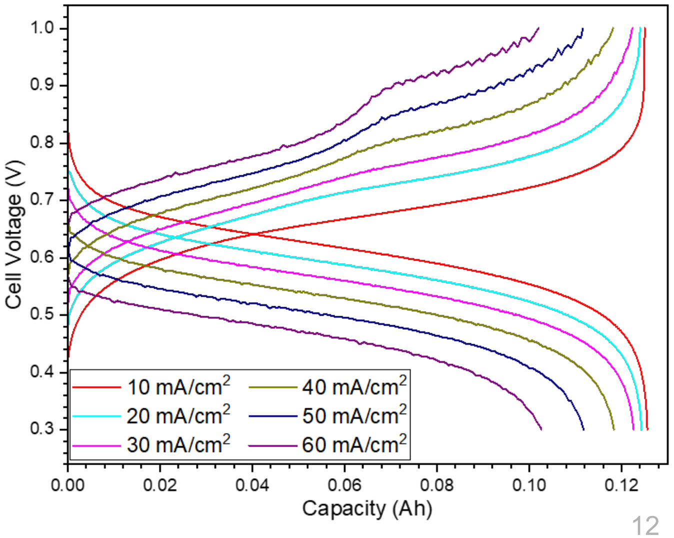




0.67M in [Fe], pH 8, ferrous vs ferric forms

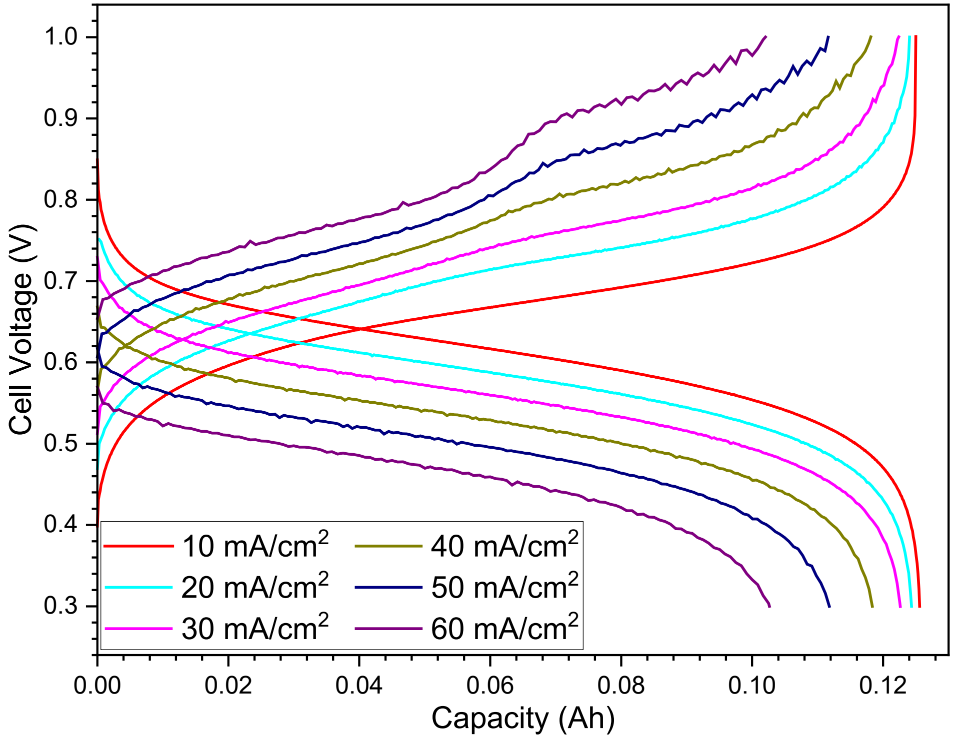


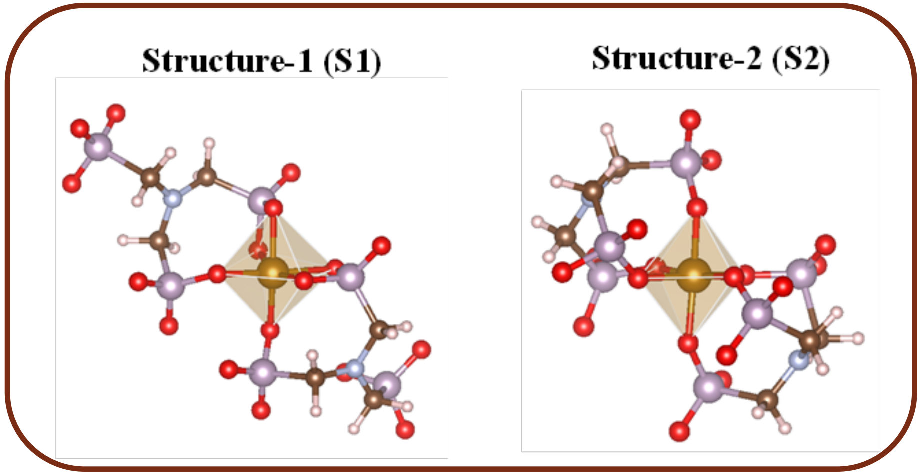


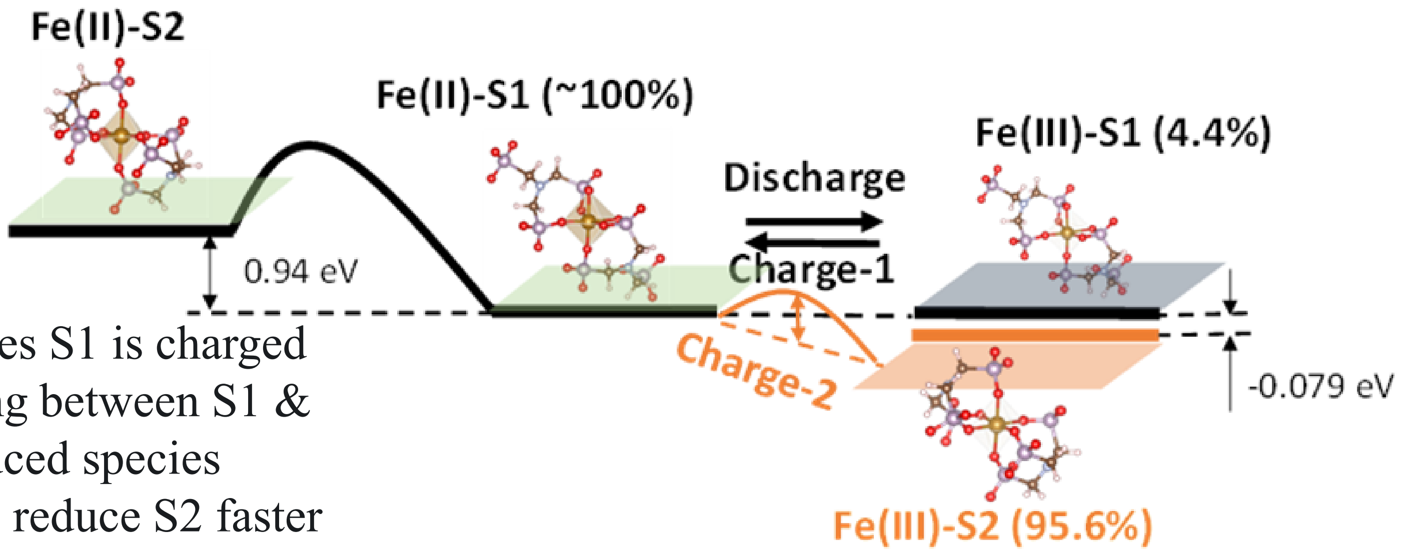


0.67M in [Fe], pH 8, cycled against $Fe(CN)_6$

Dynamic Coordination Environments: $Fe(NTMPA)_2$ Case Study







- At low charge current (longer times), only species S1 is charged
  - Slow charge times allow S1 (interconverting between S1 & S2 states) to be sole electrochemically reduced species
  - Fast charge times consume S1 and begin to reduce S2 faster than interconversion
  - Ligand re-organization leads to higher barrier → higher charge plateau

Manuscript submitted. See Poster by Gabriel Nambafu

Summary and Acknowledgements

Summary

- Identified phosphonic acid-based molecules as readily available ligands for iron-based anolytes with exceptional cyclability
- Determined battery relevant properties, behavior, and cell performance
- The most readily available derivatives tested require improved cell voltage

Future Direction

- Higher voltage systems/approaches in progress
- Pursue modified ligands which enable more negative reduction potentials

Support

- We acknowledge the support of Dr. Imre Gyuk and the OE Energy Storage Program for this work
- 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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