SAND2016-8877C

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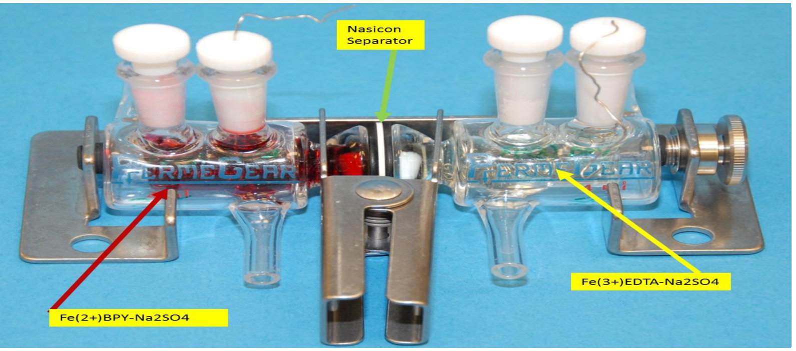
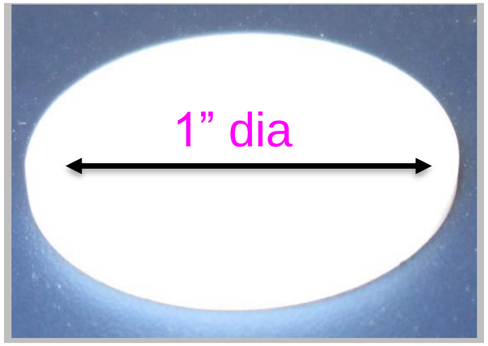
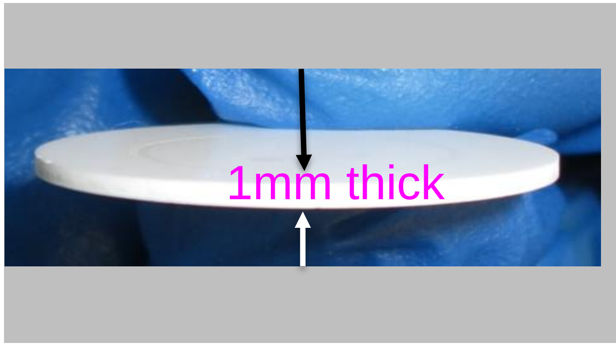
Studies of Earth Abundant Metal complexes for Near Neutral Aqueous Redox Flow Battery (RFB) for Grid Storage







PRiME 2016/230th ECS Meeting (October 2-7, 2016)

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Takeaways

- This is an exploratory research project
- Explored the feasibility of using *Sodium (**Na**) **S**uper-**I**onic **Con**ductor (NaSICON) with a typical composition of* $Na_3Zr_2Si_2PO_{12}$, {produced by our industry partner (Ceramatec)}, as a separator in RFBs
  - Measured ionic conductivity of NaSICON (Solid state) is ~3 mS/cm
  - Calculated ionic conductivity in aqueous solution containing 0.4M Na_2SO_4 as supporting electrolyte is ~6 mS/cm which is virtually similar to that of solid state measurement
- Demonstrated full-cell performance of two earth abundant iron complexes in a sodium sulfate electrolyte NaSICON Na-ion RFBs.

Holy Grail of Electricity Storage is Large-Scale Grid Energy Storage

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- Burning fossil fuel to generate electricity needs to be replaced with renewable energy sources
- Wind, Solar and Tidal sources of renewable energy are stochastic in nature
- Large-Scale Grid energy storage is a must to harvest and store the intermittent energy to wean our dependence off of the conventional energy sources such as fossil, hydro etc.
- Among the many potential options Redox-Flow-battery (RFB) looks very attractive since
  - The storage of catholyte and the anolyte is decoupled from the cell reaction location
- Normally ion permeable membrane is used as a separator
- Additionally, non-aqueous electrolytes are being investigated for enhancing cell voltage
- Others have used metallic anodes (Li or Na) to improve cell voltage

Potential Problems with the current Approaches

- Use of Non-aqueous solvents, although yields higher cell voltages, exhibits propensity for combustion as amply shown by the problems with Li-ion batteries
- Use of molten sodium and lithium enhance thermal problems as well
- Li and Na when used as anodes at room temperature the integrity of the interface decreases with cycling which leads to cell performance degradation
- Use of redox couples containing expensive metals like Co and Ru could drive up the cost
- Finally, environmental consequences need to be addressed

Our Approach to mitigating these problems

- Use of aqueous solutions----Freedom from fire
- At or near PH 7--------minimize hardware corrosion
- We use cheaper and earth abundant elements such as Fe, Mn and their complexes
- Replace polymer based separators with a ceramic disc of high ionic conductivity and voltage stability
  - Although the overall goal of this exploratory research effort is to produce a large scale cell pack the current work focuses on:
    - Evaluating ceramic disc for electrochemical properties
    - Developing low cost redox couples for use in aqueous solutions

Materials studied in our work

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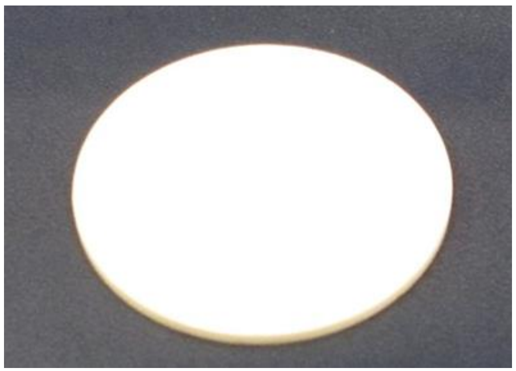
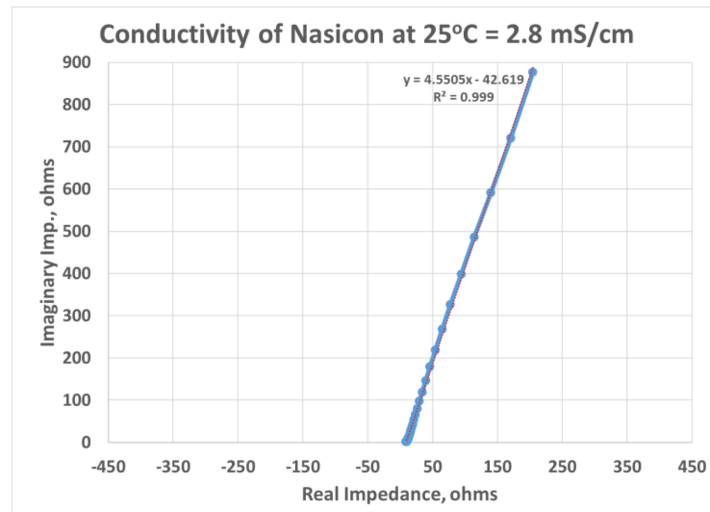
Sodium Superionic Conductor Solid Separator



1” Dia and 1mm thick

Impedance Plot

- NaSICON ($Na_3Zr_2Si_2PO_{12}$)



Solid State Conductivity ~ 3mS/cm

Similar value has been reported by others in:

Chem. Mater., Publication Date (Web): 20 Jun 2016 and in Ionics (2015) 21:3031–3038

Impedance comparison at 25°C of 0.4 M Na_2SO_4 solution w and w/o NaSICON

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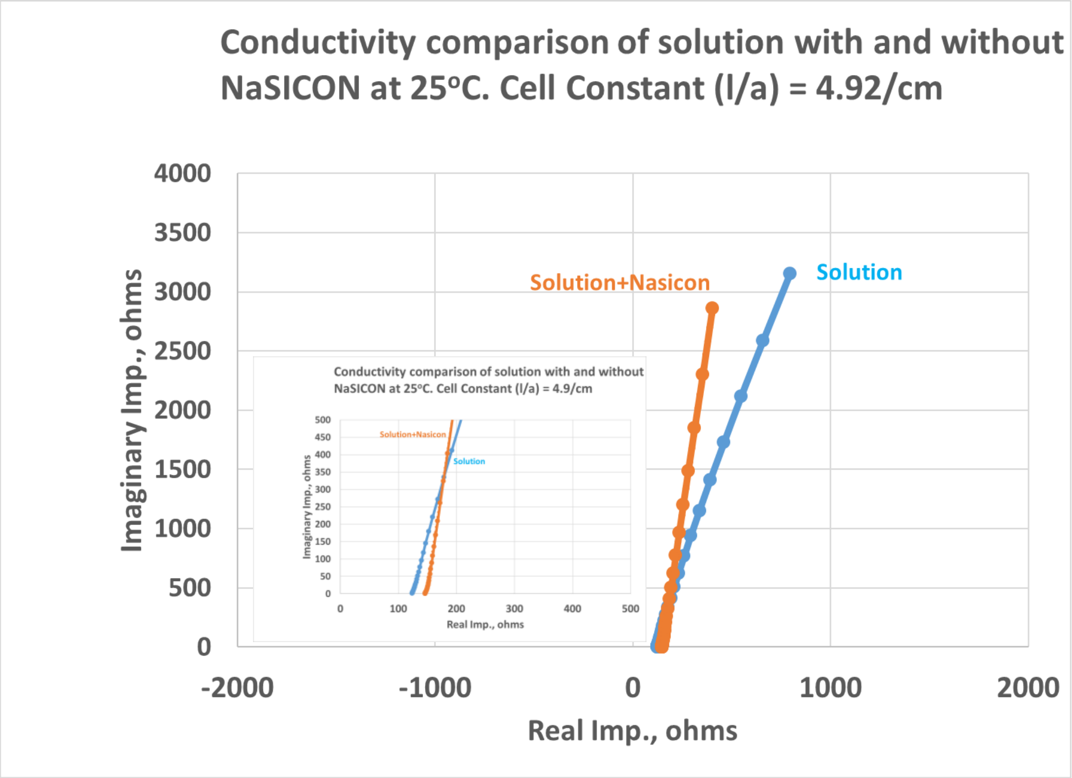
NaSICON Disc



	Resistance (ohms)	Conductivity mS/cm
Solution (W/O NaSICON)	118	41.6
Solution (With NaSICON)	147	33.5
NaSICON	29	5.6

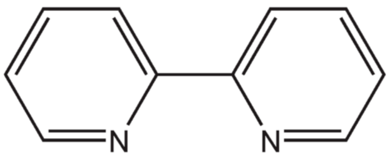
For NaSICON:
Solution conductivity is comparable to solid state conductivity

Materials Continued

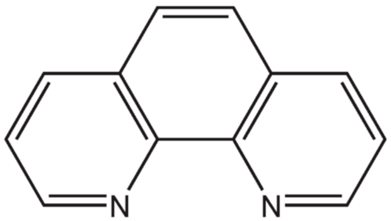
Innocent Ligand Metal Complexes

- Fe complexes: Chelating agents: Phenanthroline, EDTA BPY, $(CN)_6$ etc.
- Mn complexes: Chelating agents: EDTA etc.

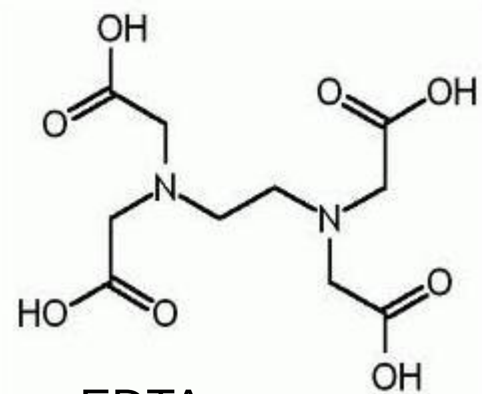
Structure of Ligands



Bipyridine



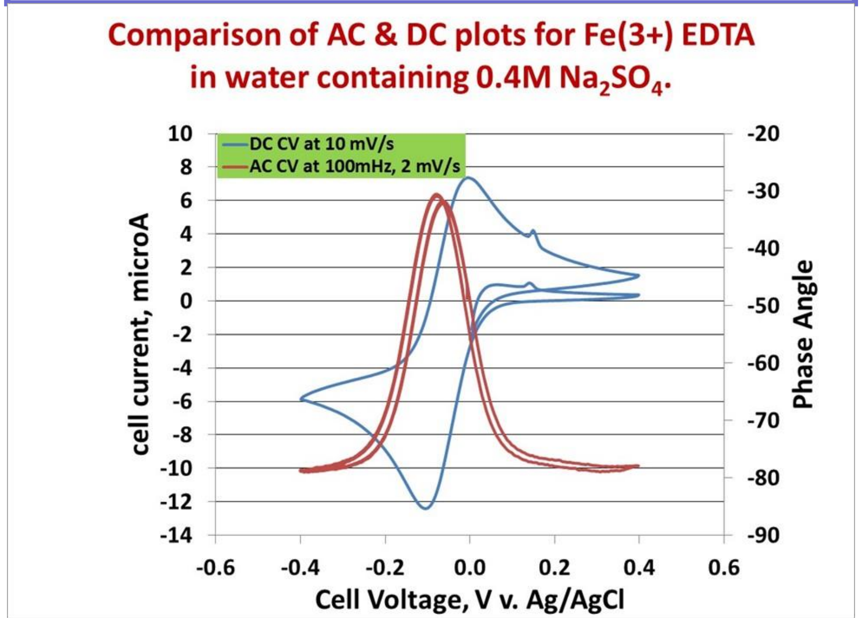
Phenanthroline



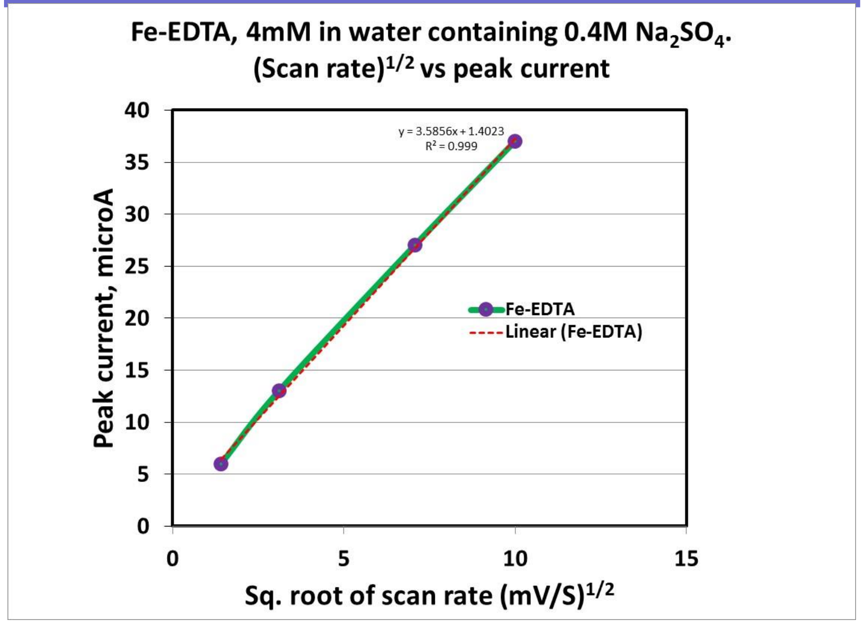
EDTA

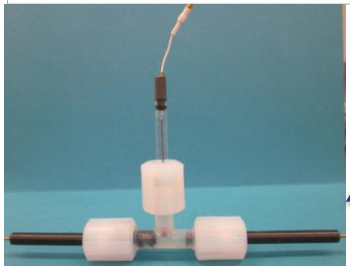
Anolyte Solution. Redox Properties

4 mM Fe(3+) EDTA, 0.4M Na_2SO_4



I_p Varies linearly with √SCAN RATE



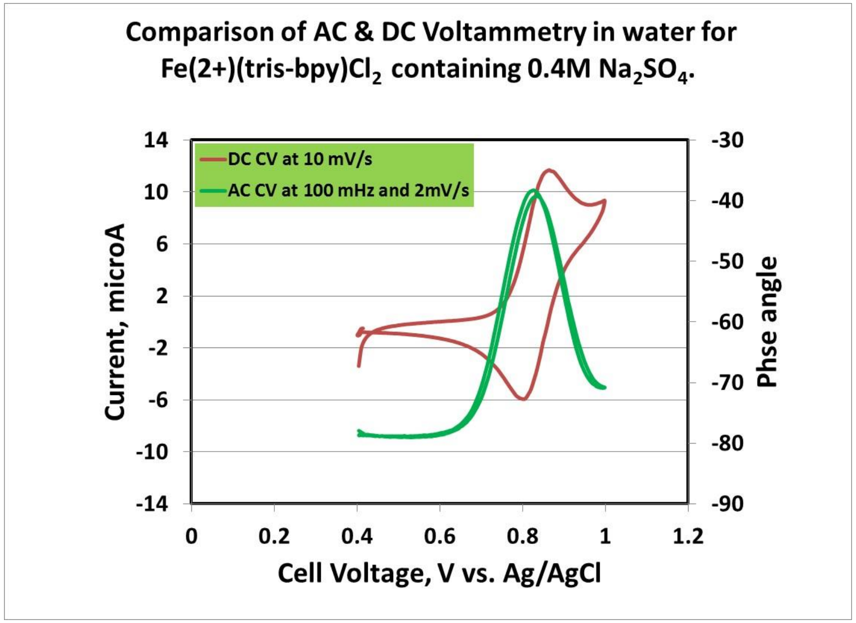


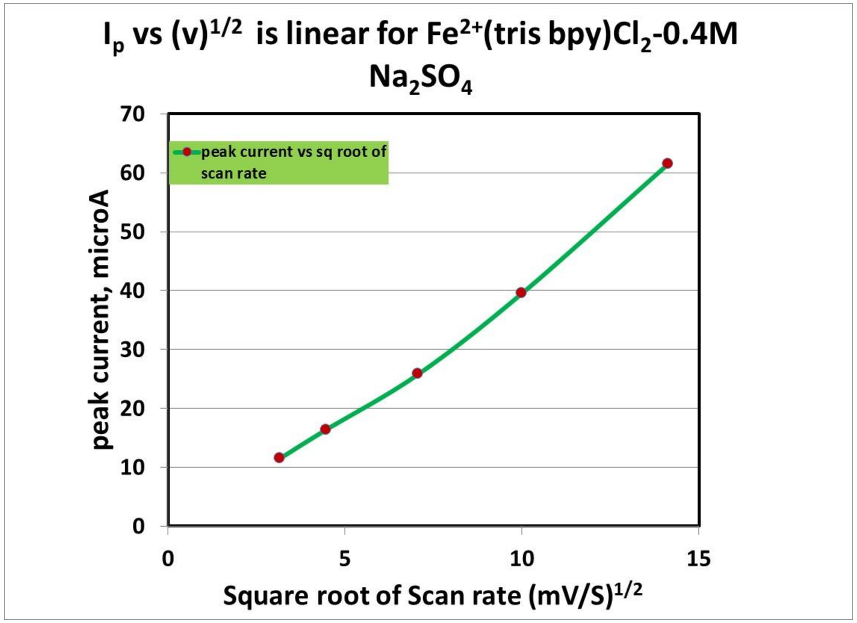
Tee cell with an Ag/AgCl reference electrode

Catholyte Solution. Redox Properties

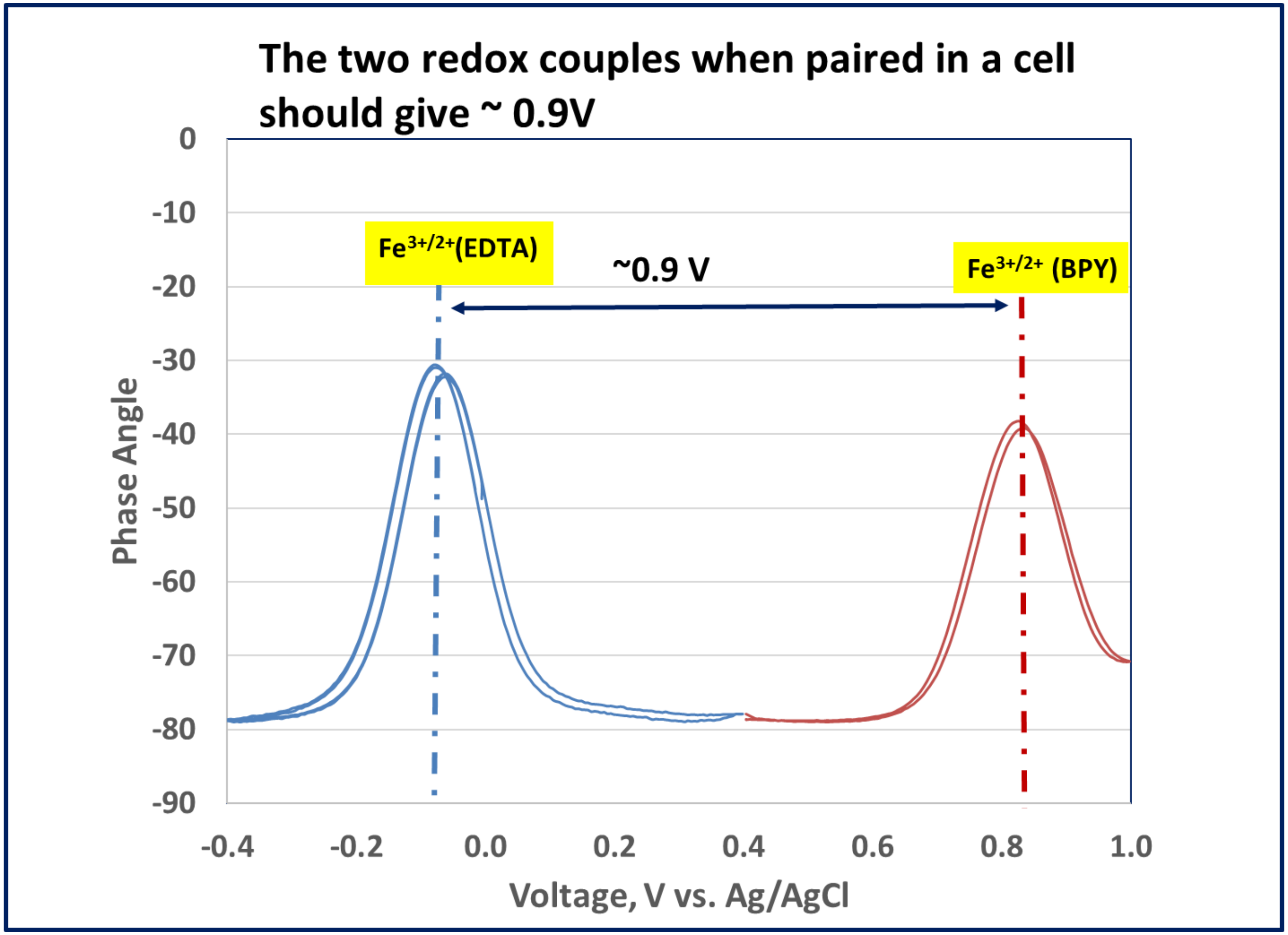
Fe(2+) tris BPY, 0.4 M Na_2SO_4

Ip linear with √scan rate





AC Voltammetry peak voltages against Ag/AgCl



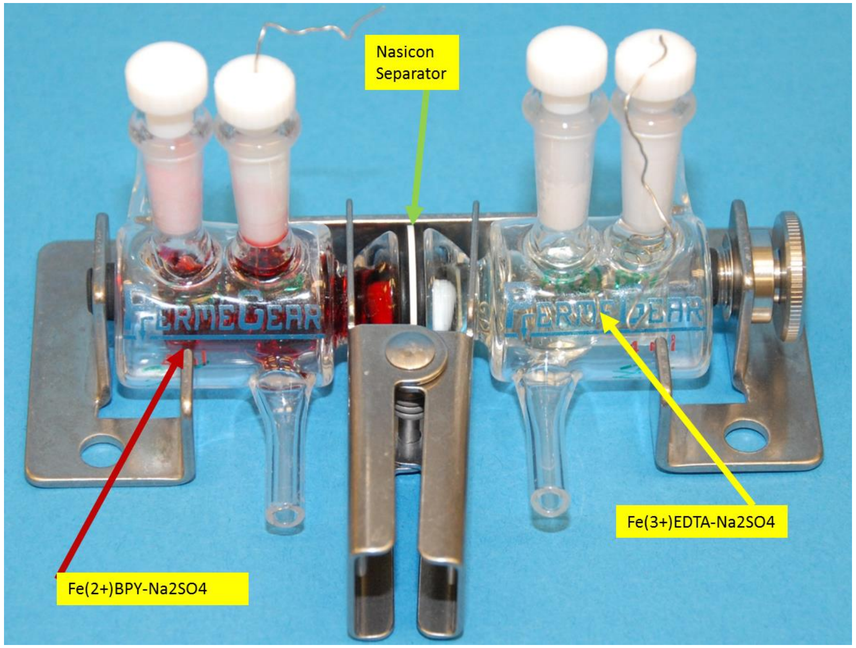
Partial List of Redox Couples Evaluated

Anolyte →

Metal Complex	Ox/Red peak potential vs Ag/AgCl	Peak Reversibility	Tested Salts
$Fe(edta)^{2-/3-}$	0.0/-0.1	Reversible	Na_2SO_4
$Fe(phen)^{2+/3+}$	+ 0.9 V /+ 0.84 V	Reversible Unstable	Na_2SO_4, Na_3PO_4, Na_2HPO_4, NaH_2PO_4, NaCl
$Fe(tiron)^{3-/4-}$	+ 0.9 V / + 0.4 V	Irreversible	Na_2SO_4
$Fe(CN)_6$ $^{2-/3-}$	+ 0.18 V / + 0.29 V	Reversible Stable	Na_2SO_4
$Mn(phen)^{3+/4+}$	N/A	N/A	Na_2SO_4
$Mn(edta)^{2-/3-}$	none	N/A	Na_2SO_4
$Fe(bpy)^{2+/3+}$	+ 0.86 V / + 0.80 V	Reversible Unstable	Na_2SO_4, Na_2HPO_4, NaH_2PO_4,

Electrochemical Cell

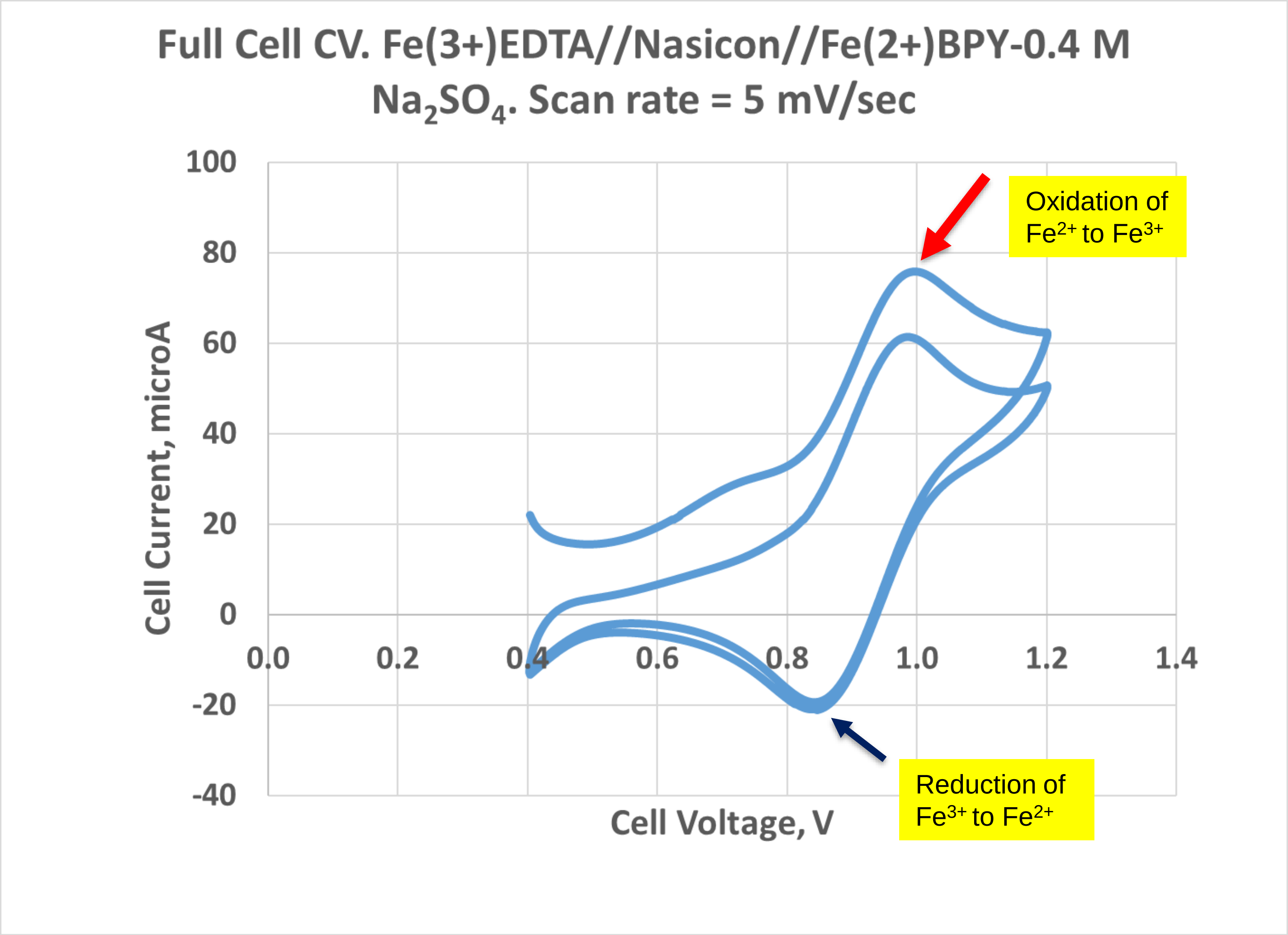
Electrochemical cell



Typical solution composition

- Supporting Salt: Na_2SO_4 at 0.4m in de-ionized water
- Redox couple: 4 mM metal (Fe or Mn) chloride or sulfate
- Chelating agent: at 8-12 mM

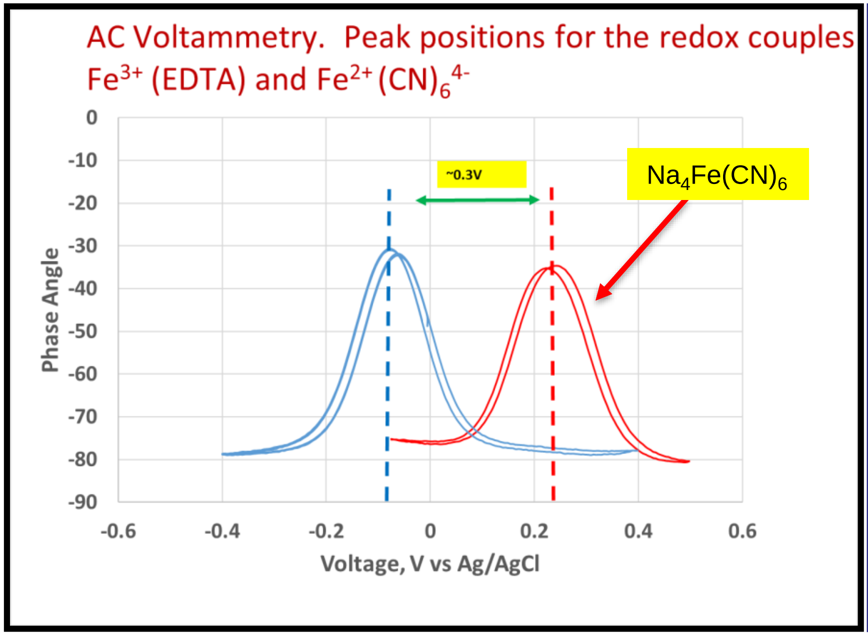
Cyclic voltammetry of the full cell

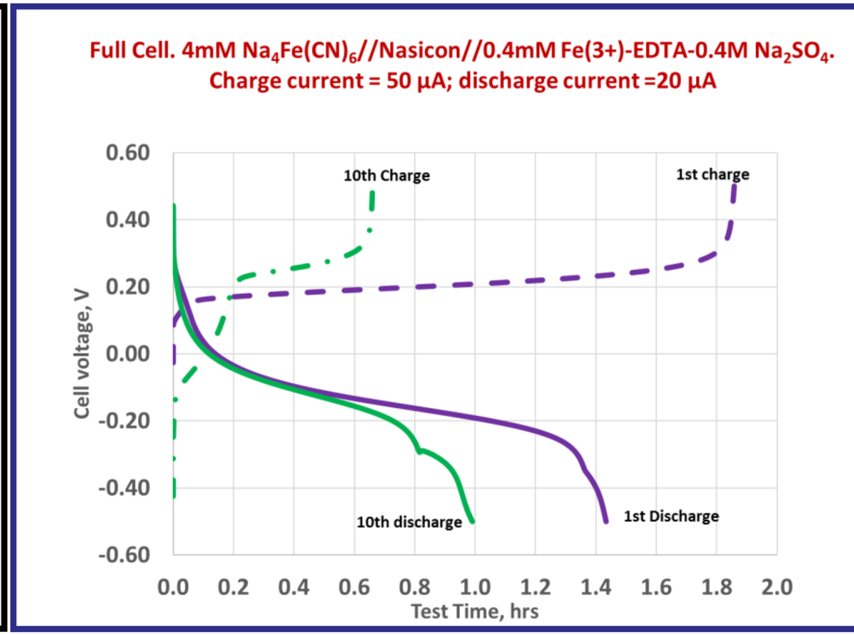


Full cell cycling

These couples when paired should give ~ 0.3V

Charge Discharge Traces





Catholyte: $Na_4Fe(CN)_6$

Full cell Measurement--Results

- Fe^{3+}(EDTA) was used as anolyte
- Fe^{2+} chelated with phenanthroline or Bipyridine were used as catholyte
- Overall cell reaction:
  - Charging
    - The anolyte gets reduced to Fe^{2+} (EDTA) and
    - The catholyte gets oxidized to Fe^{3+} (Phe or BPY)
- Unfortunately at high voltages the Fe^{3+} complexes are not stable and form bi-nuclear Fe complexes aided by the presence of OH^- in water. Consequently, the performance degradation was severe.

Summary

- Demonstrated that NaSICON can be used as separator in Na-RFB
  - High voltage Fe^{3+} complexes {e.g. Fe(3+) BPY} as cathode are unstable. However, low voltage cathodes ($Na_4Fe(CN)_6$)appear to be stable
  - Low voltage Fe^{3+} complexes {e.g. Fe(3+)EDTA} as anode are stable
- Future Work
  – Synthesize new redox couples based on Cr or Ti
    - These show redox activity at negative voltages (-0.6V Vs Ag/AgCl) and hence can be used as anode and will be paired with a cathode like $Na_4Fe(CN)_6$

Acknowledgment

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