Non-aqueous Flow Battery : Materials Development

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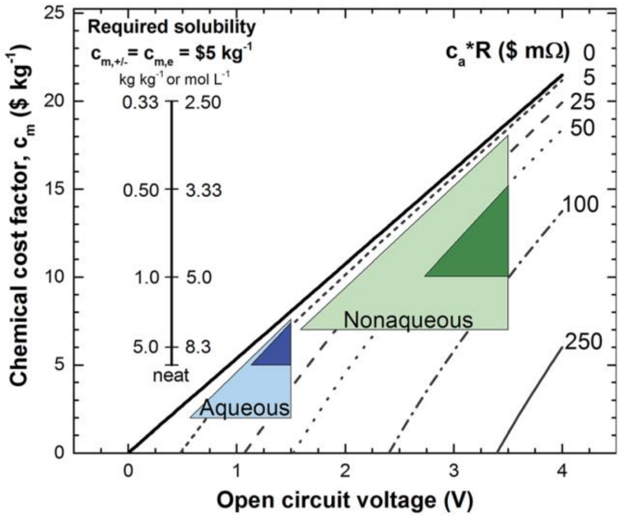
Motivation

- NARFBs opens up design space for redox-active materials; metal-ligand, or organic molecules (ROMs)
- More expensive solvents and electrolytes and lower power density
- Compensated by higher energy density
- NARFBs are ideally suited to take advantage of low-cost, multi-electron, metal/ligand and organic molecule based chemistries if they can address long term stability.



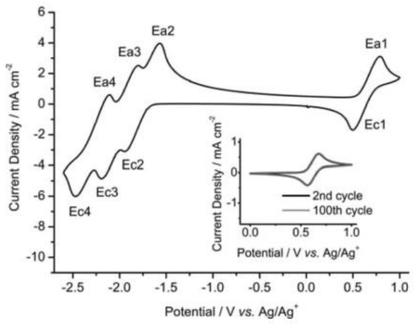
R. Darling et al, *Energy Environ. Sci*, 7 3459-3477 (2014)

Table 6 Performance and cost parameters required to meet cost effective energy storage

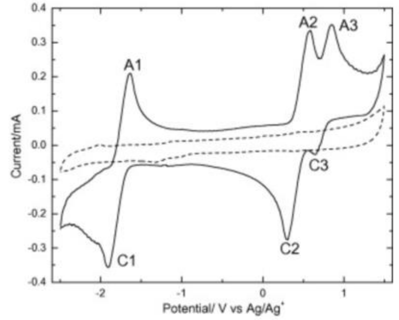
	U_{ave}, V	ASR, Ω cm^2	Equivalent weight, g (mol e−)$^{-1}$	Solubility mass basis, kg kg^{-1}	Solubility molar basis, mol L^{-1}	Material c_m, \$ kg^{-1}	Electrolyte c_e, \$ kg^{-1}
Nonaqueous	3	5	150	0.8	~4–5	5	5
Aqueous	1.5	0.5	150	0.05	~1–2	5	0.1

Approach

1. Synthesize/Evaluate Metal-ligand based redox active molecules
    a) Single molecule as both anolyte and catholyte
    b) Iron based chemistries to expand on the reported Iron bi-pyridine system
    c) Evaluate solubility and stability to discover promising systems
    d) Expand to ROMs (different materials as anolyte and catholyte)
2. Synthesize/evaluate membranes/electrolytes
    a) Use $V(acac)_3$ systems as model non-aqueous system to evaluate electrolytes and membranes
    b) Developed transference number measurement apparatus to evaluate membranes



J. Mun et al, *Electrochemical and Solid-State Letters*, 15 (6) A80-A82 (2012)



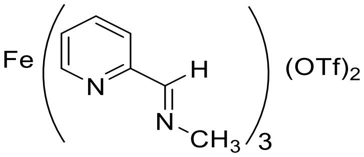
Q. Liu et al, *Electrochemistry comm.*, **11(12)** 2312-2315 (2009)

Timeline

- LANL LDRD-DR – October 2016 to September 2019
  - Established LANL capabilities in non-aqueous flow batteries
  - Theoretical modeling of non-aqueous flow battery materials : potentials and solubility
  - Membrane development for aqueous systems
  - Flow battery testing/characterization capability : Nickel and Iron based chemistries for non-aqueous flow battery systems
- Workshop – January 2019
  - Development of stable low-cost redox couples that exhibit a > 3V potential window
  - Development of high conductivity (area specific resistance ≤ 3 Ωcm^2) durable membranes/separators compatible with non-aqueous solvents
  - Development of non-hazardous (lower toxicity and flammability than acetonitrile) electrolytes
- This project – February 2020
  - Development of Fe and organic compound based active materials for NARFBs
  - Understand effect of membranes and solvents on NARFB stability

Iron Iminopyridine - Solubility

Low Solubility (~0.1 M in MeCN)



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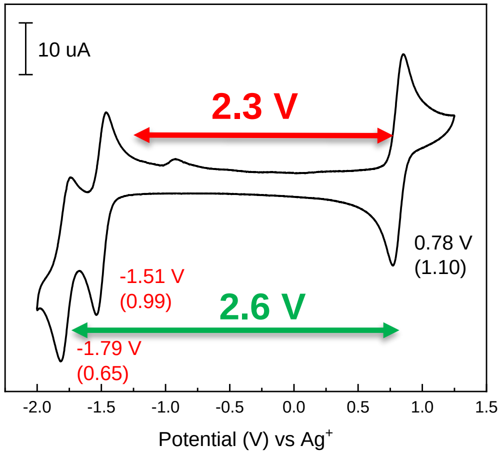
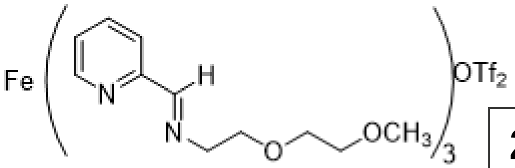


- Supports multi-electron Redox
- Supports high voltages
- Easily modifiable
- Inexpensive system

1 mM Fe(Me-PyIm) in 0.1 M $TBAPF_6$/ CH_3CN, 100 mV/s

High Solubility (~1.5 M in MeCN)



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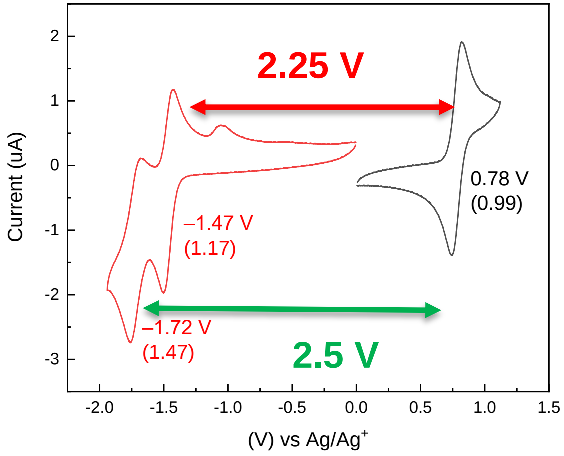


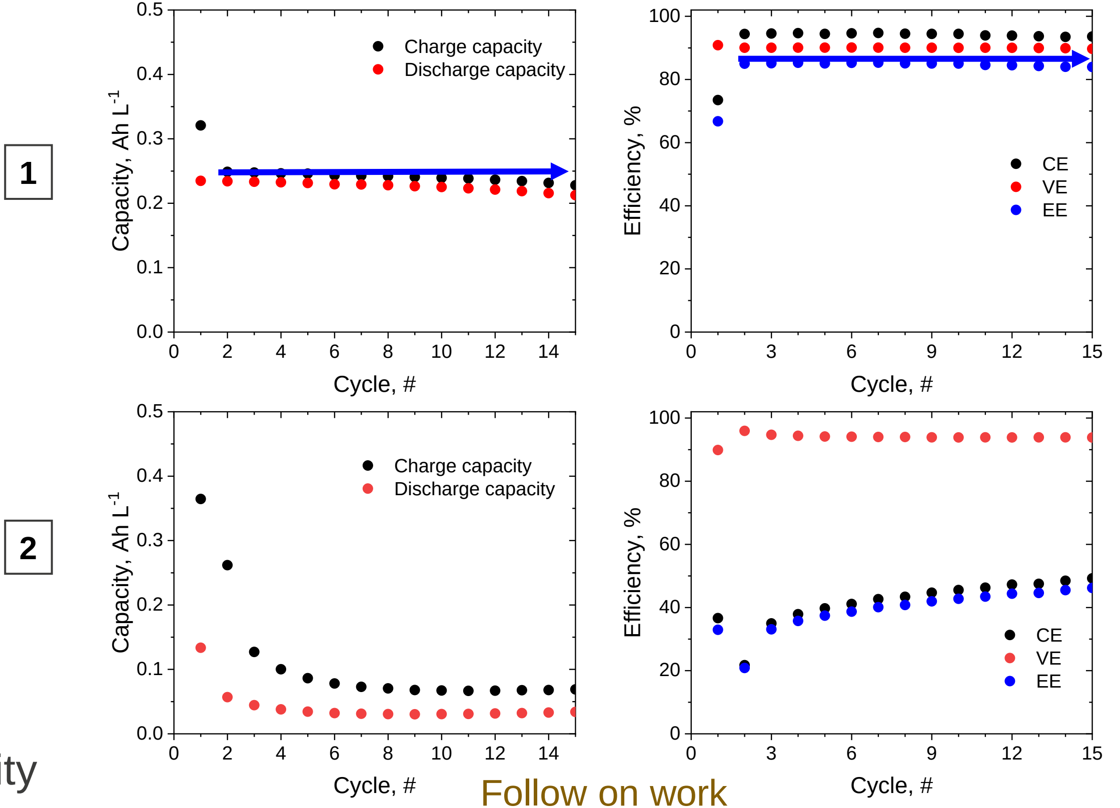
Energy Storage Materials 37, 576-586

Iron Iminopyridine - Stability

Energy Storage Materials 37, 576-586

~ 50% SOC

Conditions:
0.05 M Fe(Me-PyIm) + 0.5 M $TEABF_4$ / CH_3CN
40 ml each side
Flow rate: 20 ml/min
Cut-off voltage: 1.0 – 2.3 V (50% SOC)
Operating current density: 5 mA/cm^2
Separator: Celgard 2325 – 3 pieces



1 Unstable @ 100% SOC

2 Unstable @ 50% SOC
Unstable @ 100% SOC

Future work

Further enhance solubility and stability

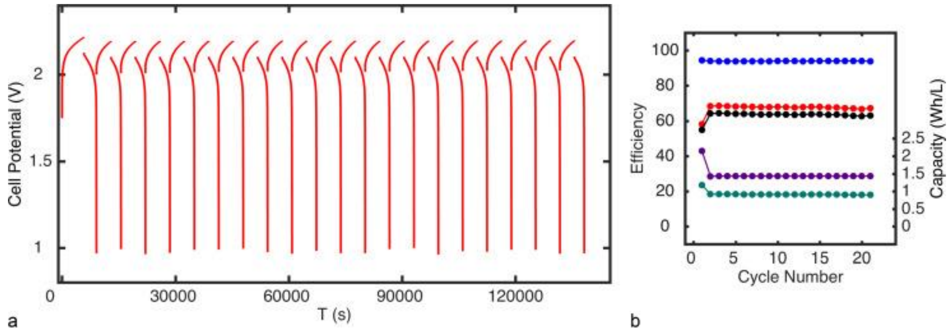
V(acac)$_3$ as model non-aqueous system

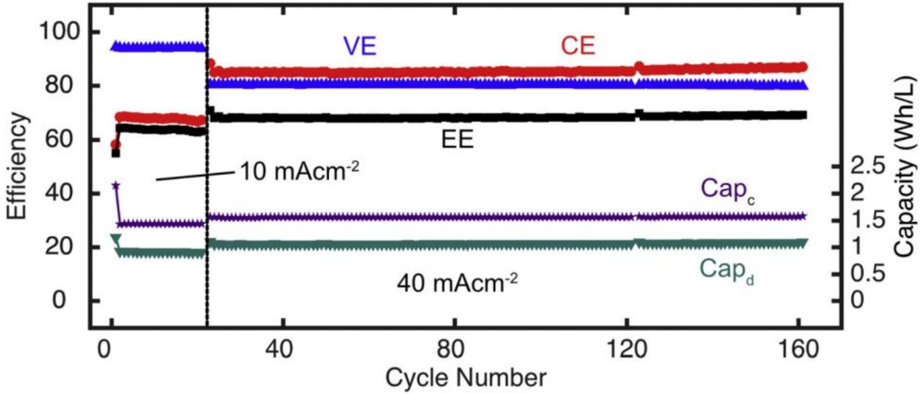
ELSEVIER
Journal of Power Sources
Volume 412, 1 February 2019, Pages 384-390

Nonaqueous vanadium disproportionation flow batteries with porous separators cycle stably and tolerate high current density

James D. Saraidaridis [b], Charles W. Monroe [a]

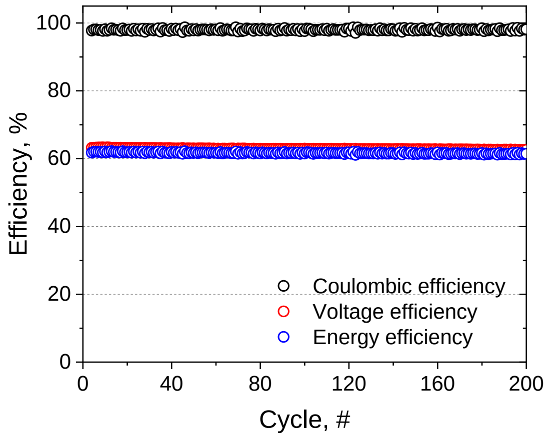
- Vanadium acetylacetonate cycles stably, supporting charge/discharge for >150 cycles.
- The nonaqueous support (Acetonitrile) does not strictly limit power; cells can tolerate high current densities.
- **Very stringent control over moisture and purity of RFB components are required.**



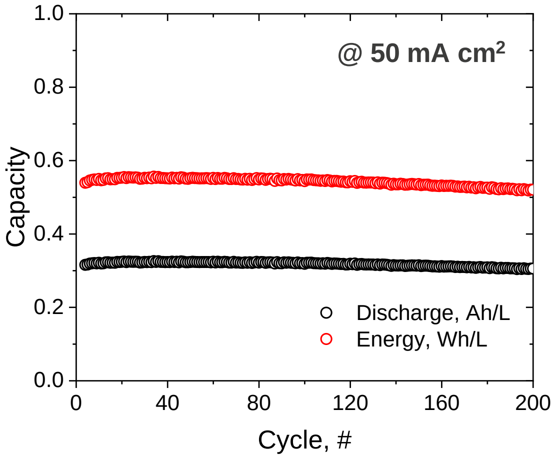


Solvent Effect

Acetonitrile (ACN)



No efficiency loss



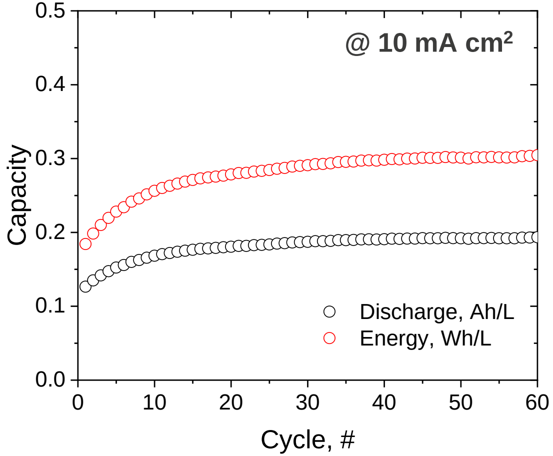
0.016% per cycle

0.16% per hour

Electrolyte: 0.05 M V(acac)$_3$/0.5 M TEABF$_4$
Flow rate: 40 ml/min
Voltage: 1.0 -3.0 V
Celgard Porous 4560 separator x 2
Impervious bipolar plate
Cell Area: 10 cm^2

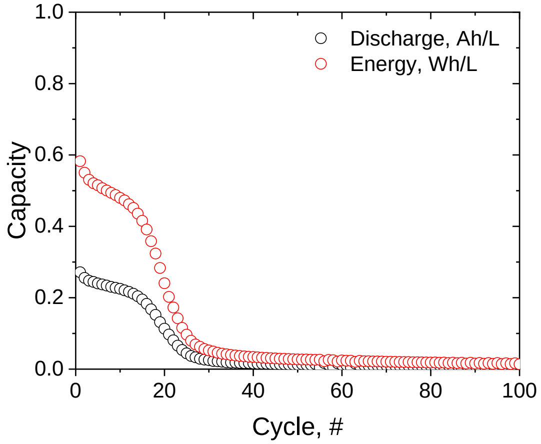
- Electrolyte is stable for 100+ cycles
- Solvent controls electrolyte conductivity
- Higher currents in ACN and lower currents in PC

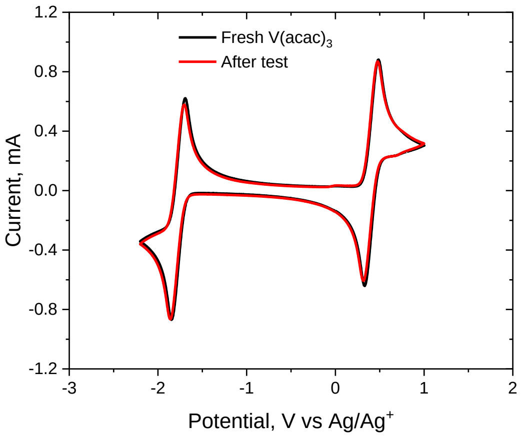
Propylene Carbonate (PC)

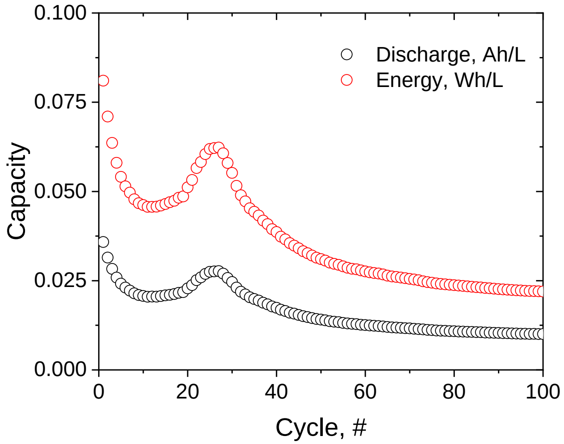


Electrolyte: 0.05 M V(acac)$_3$/0.5 M TEABF$_4$
Flow rate: 20 ml/min
Voltage: 1.0 -2.7 V
Celgard Porous 4560 separator x 1
Impervious bipolar plate
Cell Area: 10 cm^2

Membrane Effect







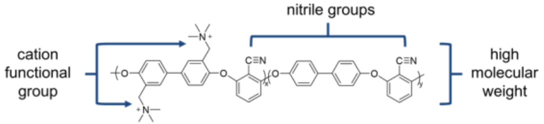
Electrolyte: 0.05 M $V(acac)_3$/0.5 M $TEABF_4$
Flow rate: 20 ml/min
Voltage: 1.0 -2.7 V
FAP-375-PP
Impervious bipolar plate
Cell Area: 10 cm^2
Solvent: **Acetonitrile**

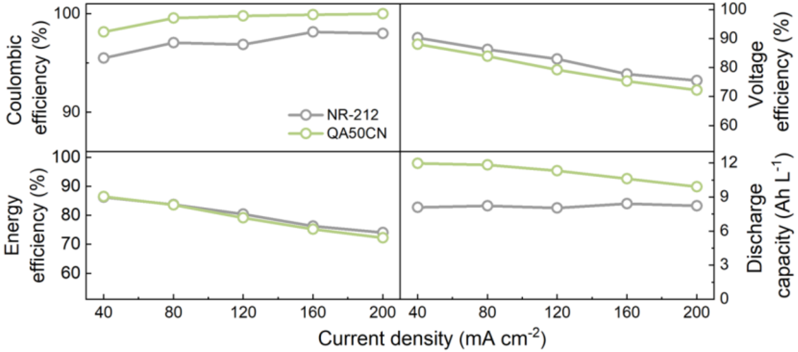
- Membrane failure after 25 cycles
- 3.45% energy loss per cycle
- 13.24% energy loss per hour
- Electrolyte is stable
- Nafion® electrolyte also unstable for NARFBs
- Fumasep FAB-PK-130 also unstable

Electrolyte: 0.05 M $V(acac)_3$/0.5 M $TEABF_4$
Flow rate: 20 ml/min
Voltage: 1.0 -2.7 V
FAP-375-PP
Impervious bipolar plate
Cell Area: 10 cm^2
Solvent: **Propylene Carbonate**

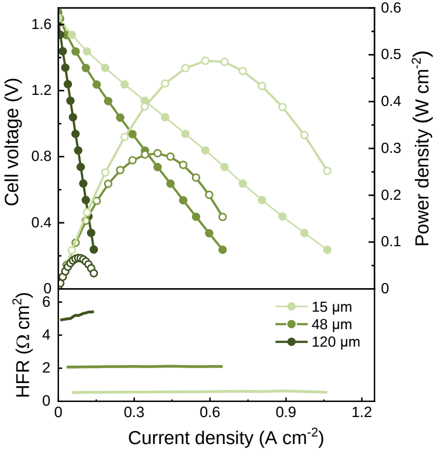
Membrane Development

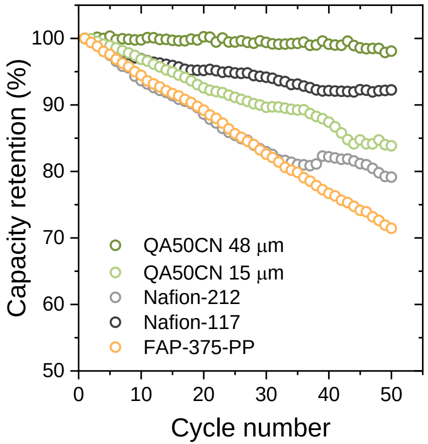
Synthesized by Dr. Park @ LANL





Quaternized poly(arylene ether benzonitrile) membranes





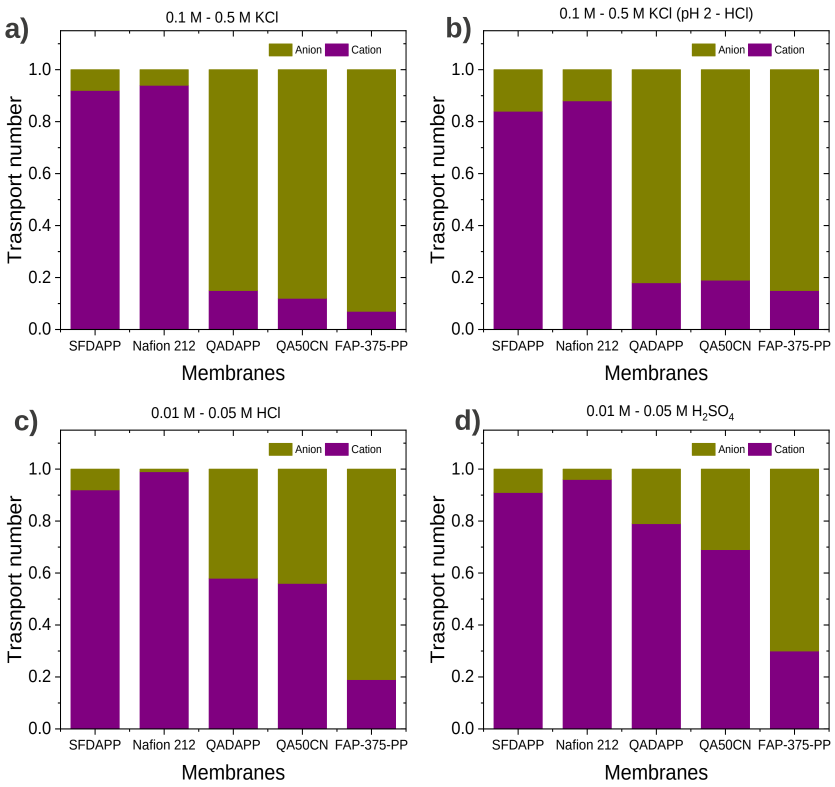
Polarization curves and capacity decay of QA50CN Membranes

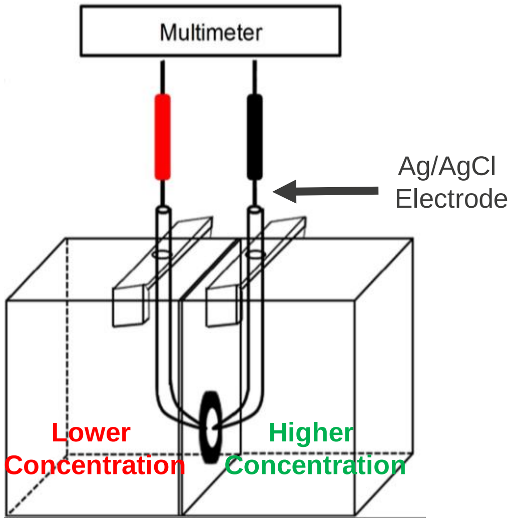
- High MW polymer, easy membrane fabrication
- Highly selective for Vanadium ions, no crossover in 500 h

Conditions:
1 M $VOSO_4$ / 2.5 M H_2SO_4
~100%SOC
60 ml/min flow rate
60 ml volume each side

Journal of Membrane Science 617, 118565 (2021)

Transport Number Determination





- Proton gradient affects the selectivity of membranes.
- Protons are major charge transport carrier in aqueous flow batteries where proton gradient exists.

Collaboration with ORNL (Jagjit Nanda) and SNL (Cy Fujimoto)

Acknowledgements

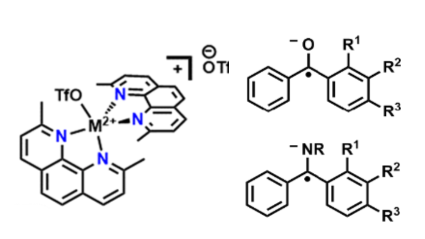
- Dr. Imre Gyuk. Director of Energy Storage Research, Office of Electricity
- Dr. Sandip Maurya : Flow battery testing and membrane development lead at LANL
- Dr. Benjamin Davis : Redox active Materials synthesis lead at LANL
- Dr. Travis Palmer and Dr Kate Ashley Jesse : LANL post docs
- Sergio Diaz Abad, Guest Researcher at LANL (Universidad de Castilla – La Mancha)
- Dr. Travis Anderson : Technical point of contact from SNL
- Dr. Erik Spoerke and Dr. Babu Chalamala : Program Management of Sub-contract from SNL

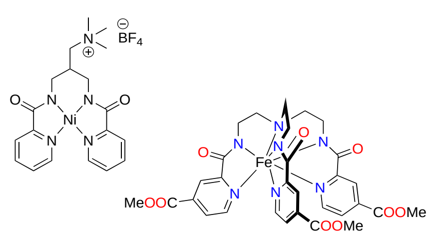
Conclusions/Future Work

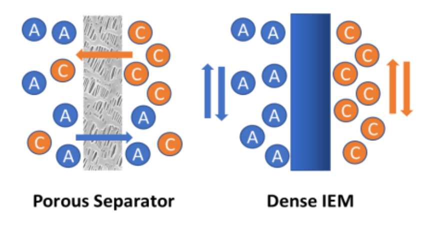
- **Redox active molecule development:**
- Our focus will continue to be on the development of redox chemistries based on abundant materials *e.g.,* Iron and/or redox active organic molecules.
- We have developed Iron pyridylimine complex for symmetric flow cell with 2.29 V cell voltage. Further, solubility of complexes will be improved by introducing zwitterionic or ester groups.
- Non-aqueous flow battery field is in its nascent state and as of now no chemistry possess enough calendar life for commercial use (< 10% capacity loss per year).
- We will study calendar shelf life of molecules in charged state to evaluate long term chemical stability.

- **Membranes:**
- Very few chemistries can be used as anolyte and catholyte. Therefore, lot of efforts are independently focused on development of either anolyte or catholyte.
- Our preliminary data suggest, commercial membranes are not suitable for non-aqueous redox flow battery.
- Apparatus developed for measuring transport number and $V(acac)_3$ system used to evaluate membrane stability.

- **Publications:**
- Three papers published in 2021 (One joint paper with SNL)
- One paper submitted in 2021 (Joint paper with SNL)







Publication List

- Sandip Maurya, Ehren Baca, Karteek K. Bejagam, Harry Pratt, Travis Anderson, Rangachary Mukundan and Cy Fujimoto, Durable and Highly Selective Ion Transport of a Sulfonated Diels Alder Poly(phenylene) for Vanadium Redox Flow Batteries, Submitted to *Journal of Power Sources*.
- Travis C. Palmer, Andrew Beamer, Tristan Pitt, Ivan A. Popov, Claudina X. Cammack, Harry D. Pratt, Travis M. Anderson, Enrique R. Batista, Ping Yang, Benjamin L. Davis, A Comparative Review of Metal-Based Charge Carriers in Nonaqueous Flow Batteries, *ChemsusChem* 14 (2021) 1214-1228.
- S. Sharma, G.A. Andrade, S. Maurya, I.A. Popov, E.R. Batista, B.L. Davis, R. Mukundan, N.C. Smythe, A.M. Tondreau, P. Yang, J.C. Gordon, Energy Storage Mater., 37 (2021) 576-586
- E. J. Park, S. Maurya, U. Martinez, Y. S. Kim, and R. Mukundan, “Quaternized poly (arylene ether benzonitrile) membranes for vanadium redox flow batteries”, Journal of Membrane Science, 617, 118565 (2021)