Component Research for Redox Flow Batteries and ‘Open’ Batteries

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Project Overview

Overarching Objective: improving energy density without lower power density, driven by work on components

We are after GENERAL approaches that cut across battery types, chemistry, operating modes etc

Two main elements to our work

1. Test Beds for components
2. New materials for specific battery types based on understanding from test beds.

*Colors: Test bed; Batteries

Project Challenges: test bed to component solution

Challenge

1. Obtaining high performance in RFBs, strongly influenced by electrode properties
2. Capacity fade in RFBs
   a. Experimental methods to determine cross-over
   b. Other capacity fade mechanisms?
3. Cost, performance of non-aqueous system

Opportunity

1. Probe electrodes, using ex situ, simple testing method; new general high ED battery concept
2. Capacity fade in RFBs
   a. Developed and extended methodology
   b. Identified several other pathways, built methods to test, control
3. Developed low cost membrane additives, testing new couples

*Colors: Test bed; Batteries

Information from Test beds
(Test beds, methods developed over 8 Years)

Need to Know

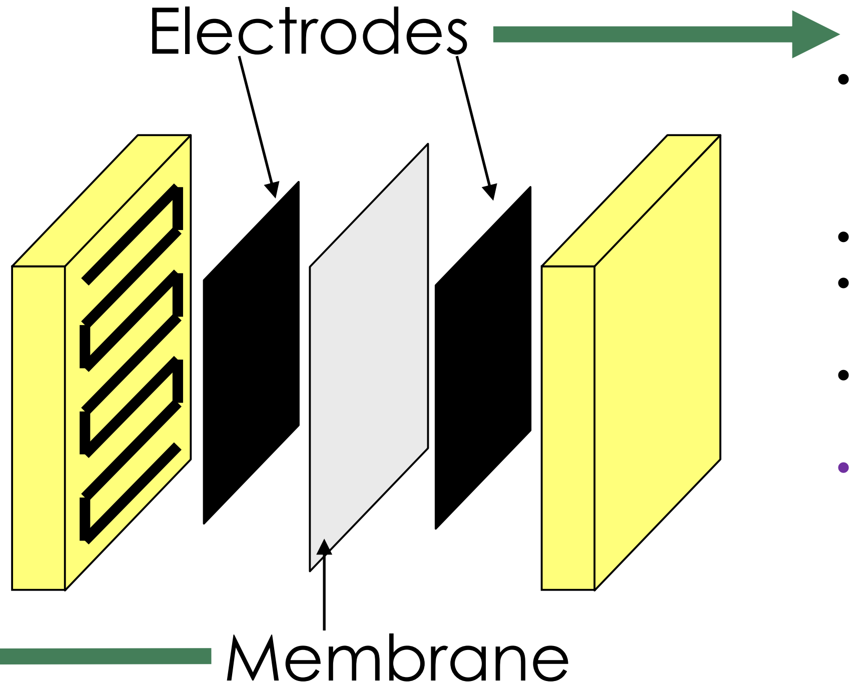
- Conductivity, cross-over, other transport for different membrane, electrolyte chemistry

Test beds

- Rigorous transport theory, experiments that match
- Conductivity
- Cross-over cells—multi-detection
- Material stability
- **New, simple method for accelerated probe of intrinsic stability, degradation pathways of redox active compounds**

Results

- Defined test methods reflect operating conditions
- Approaches to new materials
- Collaborations: SNL, vendors



Testbed Evolution: New test methods, approaches, details for different chemistry Results inform next material development, cell tests

Need to Know

- Electrode processes, kinetics, mass transport
- Wettability, accessible surface

Test beds

- Cells, electrochemical methods
- Critical performance parameters vs. structure, composition
- Design new tests: capacity fade, durability
- **New method for assessing intrinsic transport resistance of electrode materials such as carbon felts**

Results

- High performance
- Improved architecture
- No need to develop specific catalysts in some cases (VRBs)

*Colors: Test bed; **NEW this year**

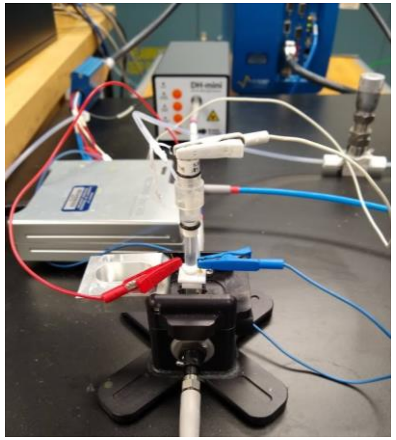
Project Metrics and Milestones:

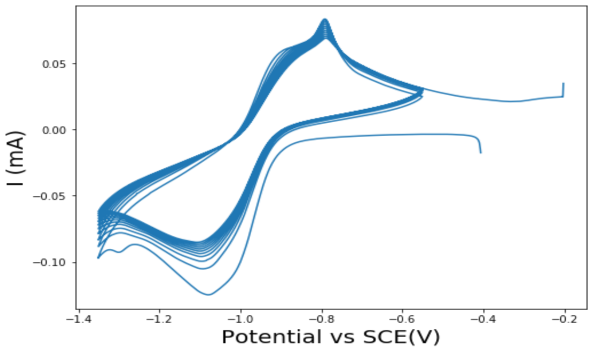
- *Task 1 Metal-air (Zn-air) Batteries* **Technoeconomic analysis** of studies of structured Zn electrodes for high performance by systematically understanding electrode losses during charge and discharge June 20
- *Task 2 Conventional Flow Batteries: Durability* **Design and build multicell durability** test bed capable of full electrochemical diagnostics during cycling or other aging approaches. April 20
- *Task 3 FY20 Conventional Flow Batteries: Components* Describe work on new membrane characterization, partly in collaboration with SNL (Fujimoto) in a **submitted publication.** Publish Donnan-potential based comparison of multiple membranes and pretreatments with structural data. Discuss key elements of capacity fade in a publication. June 20
- *Task 4 FY20 Non-aqueous Flow Batteries:* **Develop high solubility, medium voltage redox couple** for use with high performance electrolytes described in FY18/19. Implement techno-economic analysis for NARFBs. May 20

All delayed/deferred by COVID + funding limitations

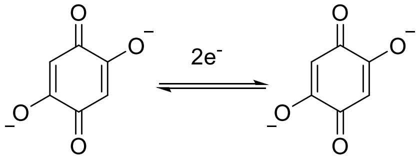
Accelerated degradation of AO redox active species

- **Thin layer spectroelectrochemistry—test case Aziz initial quinones**
- **Find ‘stress potential’**
- **Spend all time at stress potential**

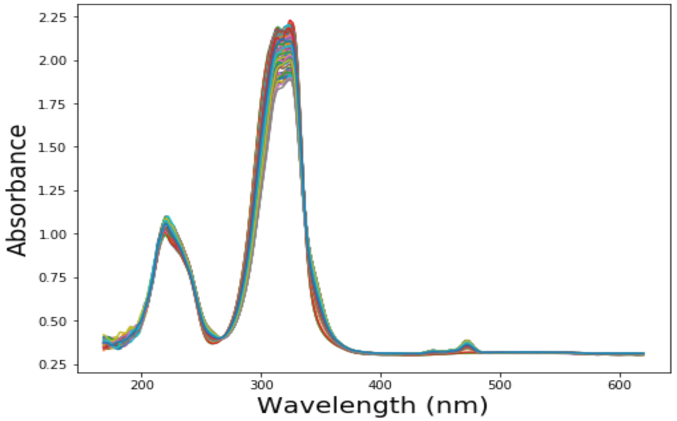




CV of 1 mM DHBQ in 1 M KOH**Scan rate**: 10 mV/s, **WE**: Au gauze, **CE**: Pt wire, **RF**: Calomel. N_2 atmosphere

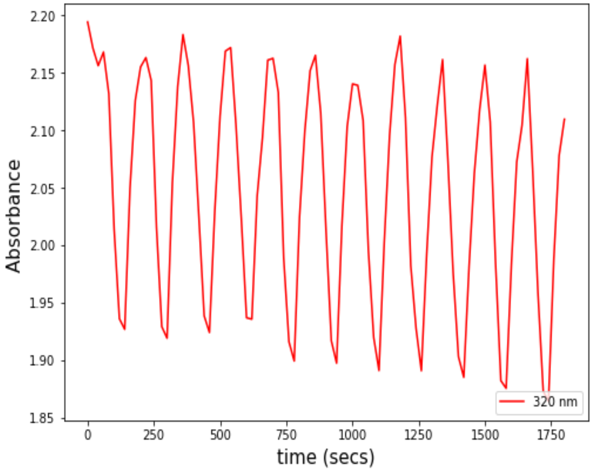


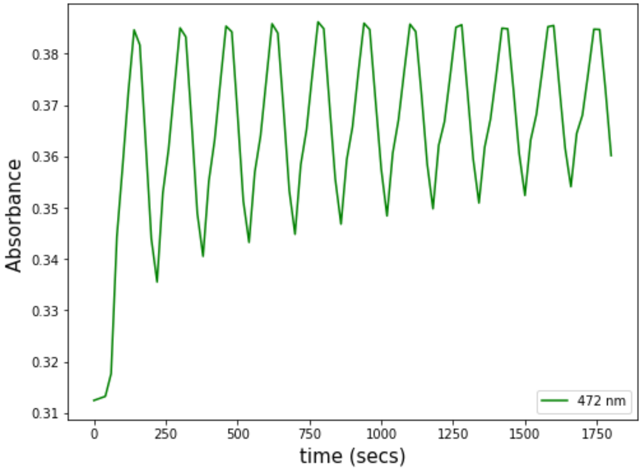
DHBQ

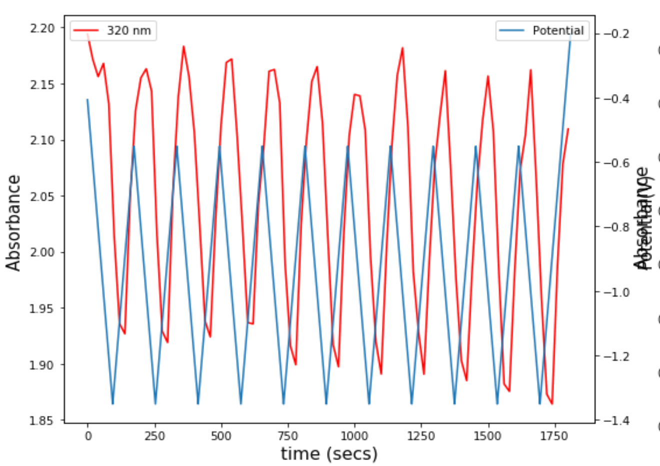


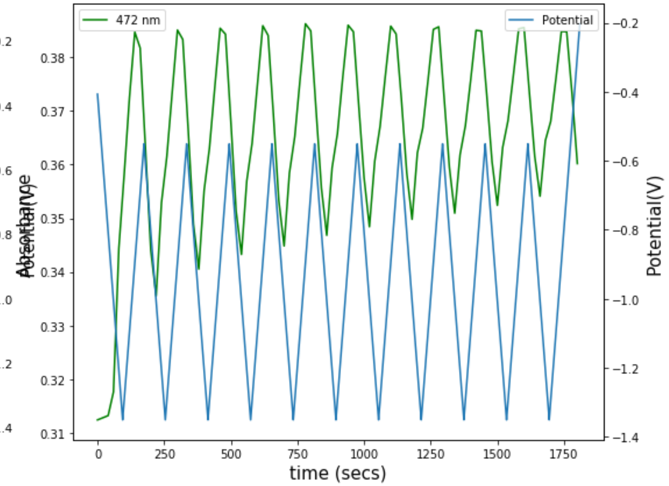
320 nm DHBQ

472 nm side product



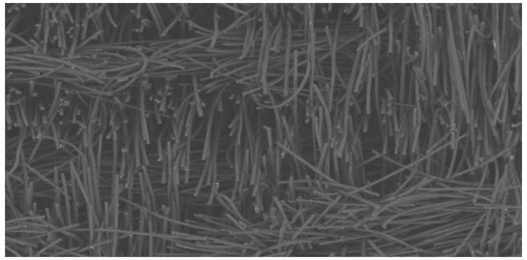






Understanding Transport in Electrodes

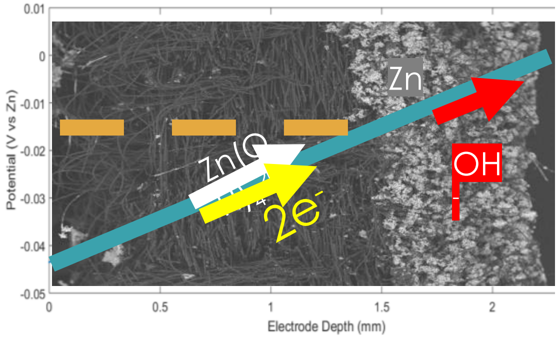
- **Characterizing Porous Flow Through Electrodes**



SEM image 2.5EA Carbon Felt at 150x Mag

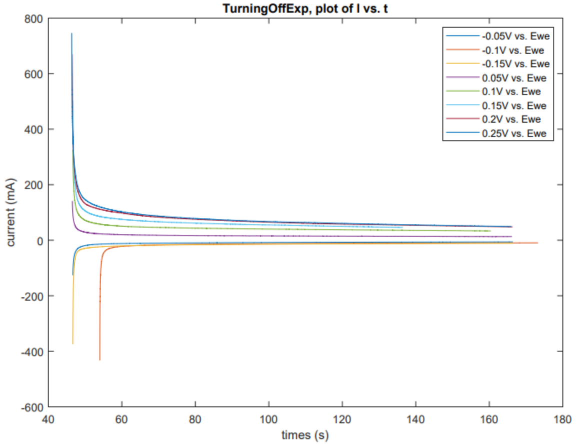
Some previous methods

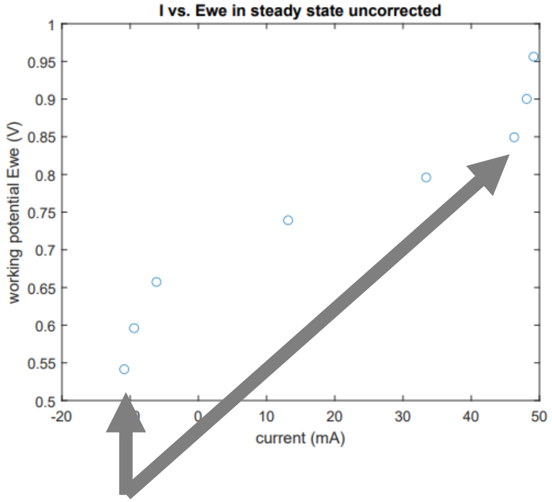
- **Wettability**
- **Impedance or Voltammetry to measure capacitance and utilization**
- **Metal Plating**



Can we create an standard method for comparing materials of different classes?

Response to a series of potential step in cell under certain conditions





Limiting current reflects permeability of electrode layer to active species

Status: Still working out some final analytical kinks

Project Results-Publications etc.

- Peng, J. and T. A. Zawodzinski (2019). "Describing ion exchange membrane-electrolyte interactions for high electrolyte concentrations used in electrochemical reactors J. Memb. Sci.
- Wittman, R. M., et al. (2019). "Elucidating mechanisms of oxide growth and surface passivation on zinc thin film electrodes in alkaline solutions using the electrochemical quartz crystal microbalance." J. Power Sources 438: 227034.

Publications in process, September 2020

1. *Use of Carbon Supports to Improve Performance of Negative Electrode of Zn air batteries*; Reed M. Wittman and Thomas A. Zawodzinski
2. *COMSOL Modeling of Electrochemical performance of microfludic in situ Liquid ec-S/TEM Cell in Quiescent Electrolyte,* Reed M. Wittman, Robert L. Sacci, Raymond R. Unocic, Thomas A. Zawodzinski
3. *Changes in Alkaline Zinc Passivation Mechanism from Variations in OH^- Concentration* Reed M. Wittman, Robert L Sacci, Thomas A Zawodzinski
4. *Evaluating Cation Transport in Membranes for Nonaqueous Flow Batteries*, Kun Lou, Jing Peng, Zhijiang Tang, Thomas A. Zawodzinski
5. *Dependence of Membrane Transport Properties on Acetonitrile Content in TXA-exchanged IEMs*, Kun Lou, Jing Peng, Zhijiang Tang, Thomas A. Zawodzinski
6. *Nanoscale Mobility of Organic Cations in ACN-swollen PFSA Membranes*, Kun Lou and TZ, Kun Lou and Thomas A. Zawodzinski
7. *IR Studies of Stepwise Solvation of Organic Cations in PFSA Membranes*, Kun Lou and Thomas A. Zawodzinski
8. *Hydrogen Bonding and the Origin of the Conductivity Peak in Acid-loaded PFSA Membranes*, Kun Lou, Vito DiNoto and Thomas A. Zawodzinski
9. *The Influence of Complexation Chemistry on Redox Flow Battery Behavior,* Laura Meda, Chiara Gambaro, Chuanyu Sun, Agnieszka Zlotorowicz, Keti Vezzù, Enrico Negro, Vito Di Noto, Giuseppe Pace, Thomas A. Zawodzinski

Looking Forward

- Next FY **Test Beds**
  - Membrane chemistry designed based on Donnan derived specs;
  - New testing Focal Point: **Capacity fade** mechanisms
  - Non-cross-over mechanisms
    - Electrode evolution during test
    - Side-reactions
    - Coupled solution chemistry
    - Combine models, experiments
  - More emphasis on aqueous organics: accelerated test implemented

Approaches
1. Share approaches with NL team (e.g. PNNL) and community
2. New experiments and other approaches to probe capacity fade
3. Scaled-up cell designs
4. Stack designed to be 'pull-apart' (materials replaceable)

- Next FY New **Components/Batteries**
  - **Zn-air battery**
  - New electrodes specifically for Zn batteries
  - Cell tests of NARFBs

Approaches
1. **New concept for high ED battery**
2. Zn-air battery tests
3. Improved air electrode for Zn-air
4. Different electrode concept for Zn
5. Add membrane additive to electrolyte solution
6. Zn-peroxide battery testing, analysis

Project Contacts

Thanks to Imre Gyuk and OE

Project Team

- ORNL: Tom Zawodzinski, Robert Sacci, Kun Lou (NA batteries, Zn systems)
- UTK: Yuanshun Li, Camilo Zuleta, Gabriel Goenaga (electrode, spectroelectrochemistry test development)
- University of Massachusetts: Pat Cappillino
- SNL: Cy Fujimoto and co.

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