Zn-Air Flow Batteries: One Step at a Time

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Motivation

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

In the past, we were after GENERAL approaches that cut across battery types, chemistry, operating modes etc

Low Energy Density is a Big Problem for Aqueous Systems

Low Current Density is a Big Problem for Non-Aqueous Systems

Proposed General Solution (Aqueous Systems):

Multiphase Systems

From Last Year: Looking Forward

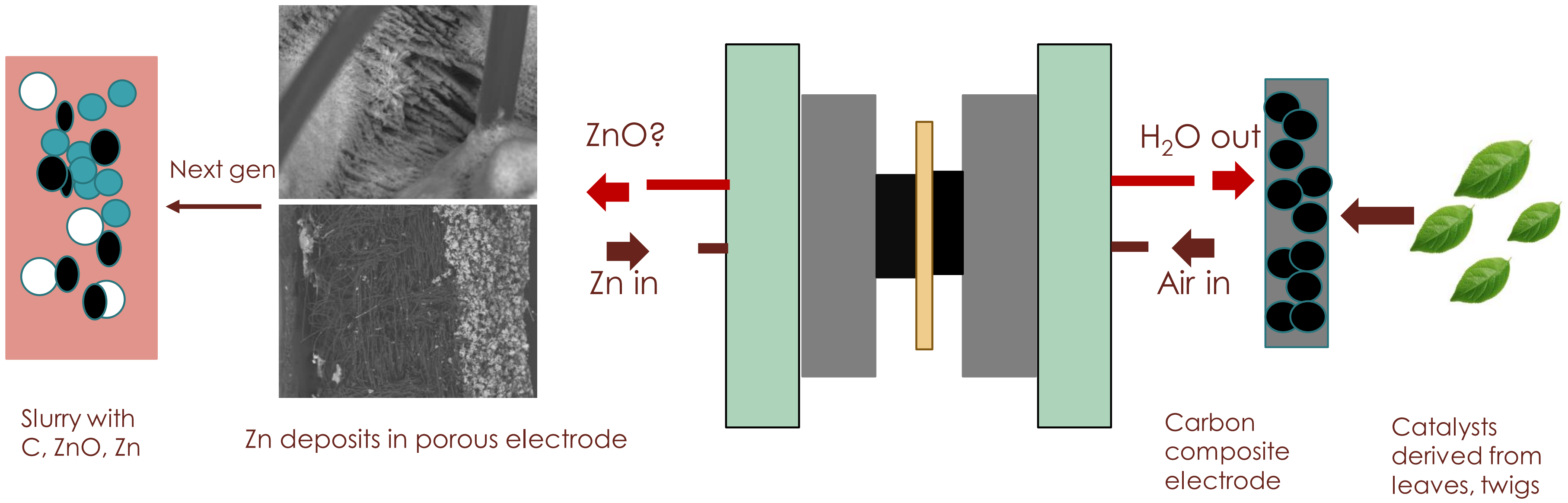
- Next FY **Test Beds**
  - Membrane chemistry designed based on Donnan derived specs;
  - New testing Focal Point: **Capacity fade** mechanisms
  - Non-cross-over mechanisms
    - Electrode evolution during test
    - Side-reactions
    - Coupled solution chemistry
    - Combine models, experiments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

High energy Density Zn-air Batteries—Toward Slurries



Project Description: Development of advanced Zn –air flow batteries with high energy and power density.

Motivation: Zn-air has high intrinsic theoretical energy density. Flow battery designs for Zn-air battery can allow higher performance, capacity.

Technical Barriers Addressed: Need higher capacity Zn-electrode, high performance & low cost air electrode to allow longer duration storage.

Project Approach: (i) Continue development of Zn-in-porous-carbon matrix negative electrode, determine maximum capacity, current density trade-off; (ii) develop high performance air electrode with non-precious catalysts; (iii) explore high capacity system based on Zn slurry electrode; (iv) technoeconomic analysis of several system approaches.

Expected Outcomes (FY22): (i) Biomass-derived air electrode operating at 0.8V discharge at > 50 mA/cm^2 at RT. (ii) TEA comparing several Zn-air system configurations, incorporating 'max capacity' information; (iii) demonstration of Zn slurry electrode; (vi) Zn-air cell that cycles at > 50 mA/cm^2 at RT.

High energy Density Zn-air Batteries: Overview of This FY

1. Began development of Zn slurry electrodes
    a. Some initial challenges with slurry formulation.
    b. Needed to modify test hardware to allow flow of slurry.
    c. Focus has been on achieving functionality first, primarily in discharge direction, then proceeding to optimize hardware and operation mode

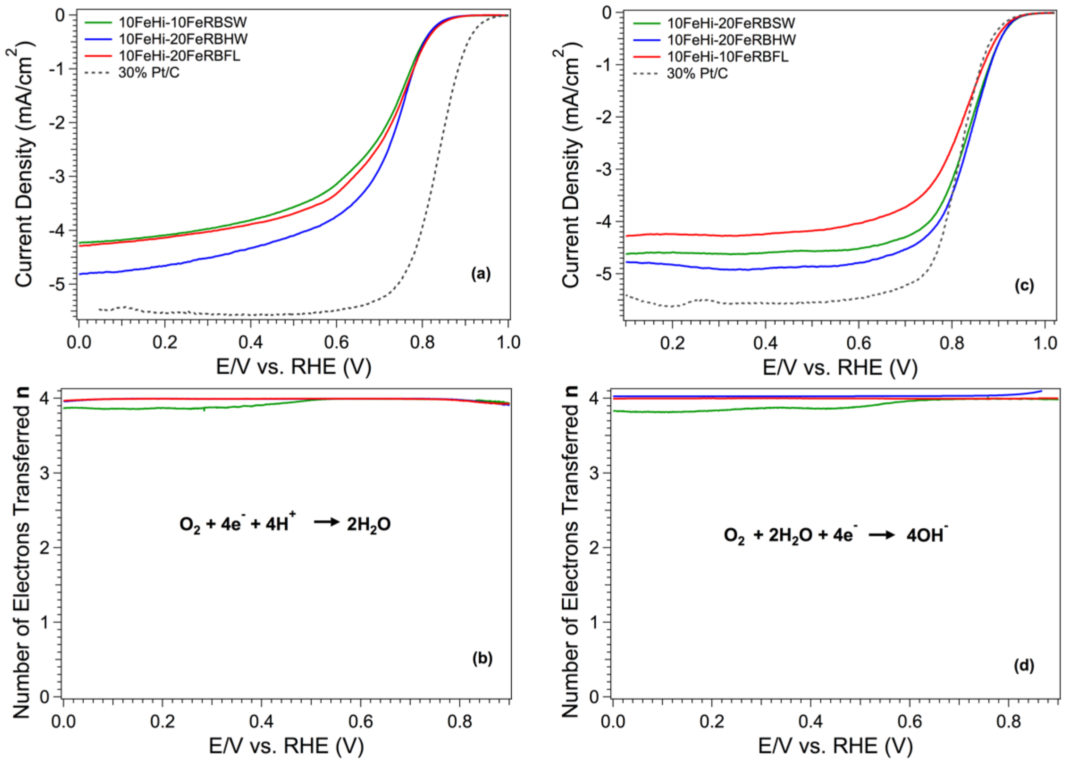
2. Implemented Air Electrode using Pyrolyzed Biomass
    a. Again, focus on discharge mode (more driven by the Zn electrode right now)

3. Cost Analysis
    a. Developed to allow comparison of technologies, operating scenarios
    b. Used ARPA-E DAYS LCOS analysis for bottom-line; develop inputs and scenarios for Zn-air
    c. Should allow us too assess whether LCOS, CAPEX targets can be met with relatively low RTE

Properties of zinc slurries

- 35 w/o slurry in aq. KOH solution
- Equivalent concentration of Zn ~ 8.3M (16.6 N)
- Slurry is somewhat viscous but readily pumpable

Air Electrodes Prepared from Pyrolyzed Backyard Sweepings (BY-air catalyst)



(a) RRDE plots and (b) number of electrons transferred in acid electrolyte (0.1M H_2SO_4, RE:Hg/$HgSO_4$, WE: GC, CE:Au coil) (c) RRDE plots and (d) numbers of electrons transferred in alkaline electrolyte (0.1M KOH, RE:Hg/HgO, WE: GC, CE:Au coil)

- RDE performance comparable to Pt.
- We have made high surface area electrodes with these catalysts that produce 100's of mA/cm^2 in current density

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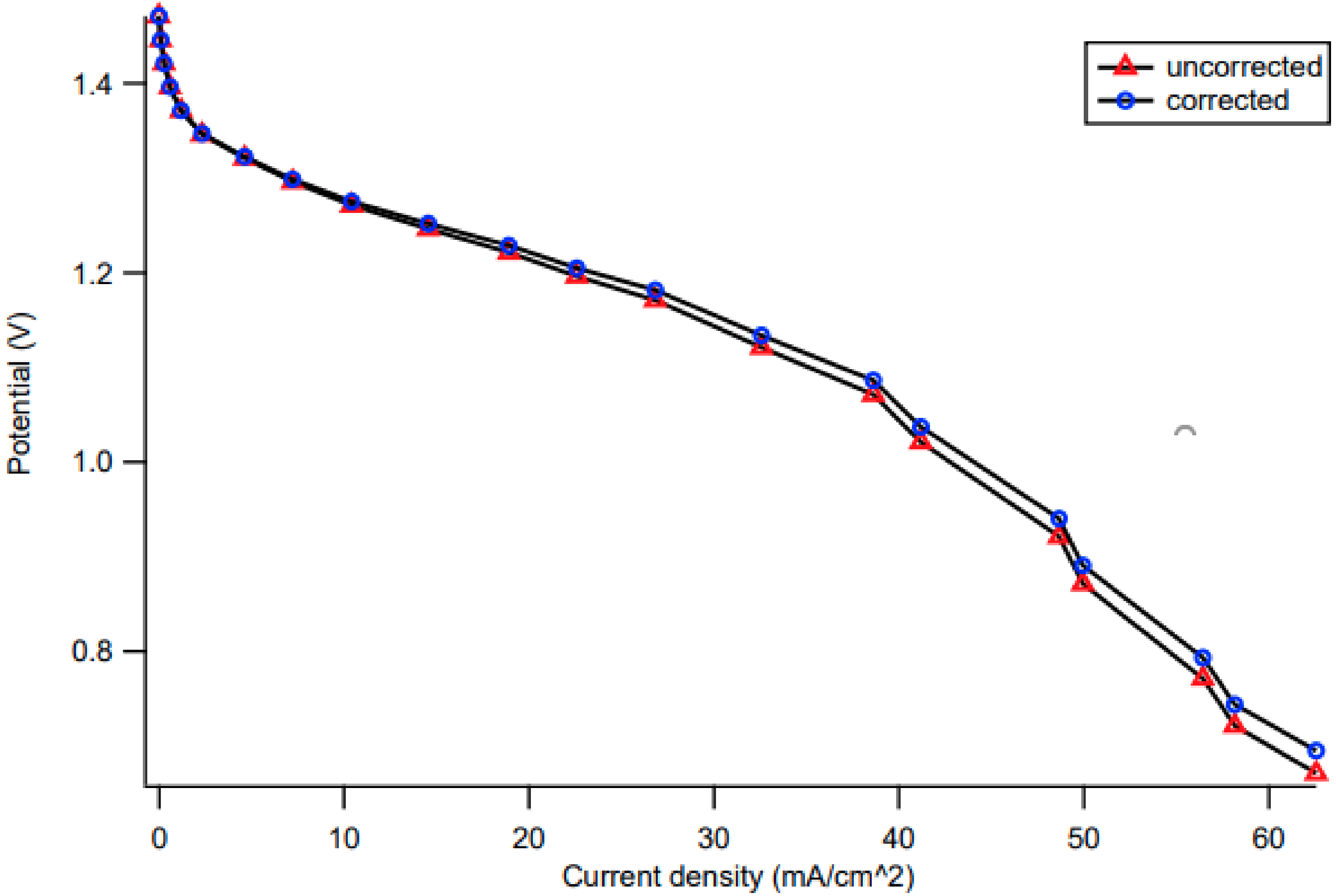
Real polarization curve for zinc slurry/BY-air electrode



O2 electrode: Pt/C, carbon felt ; Zn electrode: Zn powder + PAA + KOH. Membrane: CLAM, thickness ~ 50 um. Flow rate: 40 rpm. Electrolyte: 4M KOH
Temperature: ambient. HFR = 0.077 ohms, ASR = 0.385 ohm*cm^2

- Most of the loss is due to the air electrode up to ~30 mA/cm^2
- Detailed evaluation under investigation—separating contributions
- Now working to optimize details of components:
  - We are sensitive to wetproofing of electrodes.
  - Also working on slurry composition.
- Even the operating mode of the cell is open for further optimization—need to consider how to add the slurry

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Cost Analysis: Uses ARPA-E DAYS LCOS

$$LCOS = \left[\left(\frac{1}{\eta_{RTE}} - 1\right) P_c \sum_{t=1}^{T} \frac{n_c(t)}{(1+r)^t} + \sum_{t=1}^{T} \frac{O\&M(t)}{(1+r)^t} + \left(\frac{C_E}{\eta_D} + \frac{C_P}{d}\right)\right] * \left[\sum_{t=1}^{T} \frac{n_c(t)}{(1+r)^t}\right]^{-1} \quad [1]$$

Some assumptions in DAYS LCOS

- $0.025/kWh cost of electricity for charging
- 100 kW system for calcs (we relax this—aim for 10 MW)
- Cost of money fixed
- Open possibilities for duty cycle—oriented toward LDES
- O&M, DC-DC etc included but similar for all technologies

Steps in Our Analysis

- System design
- Input performance
- Design space defined
- Cost modeling: 'Bill of Materials'
- CAPEX, OPEX
- Baseline Calculations
- Sensitivities and Use Cases

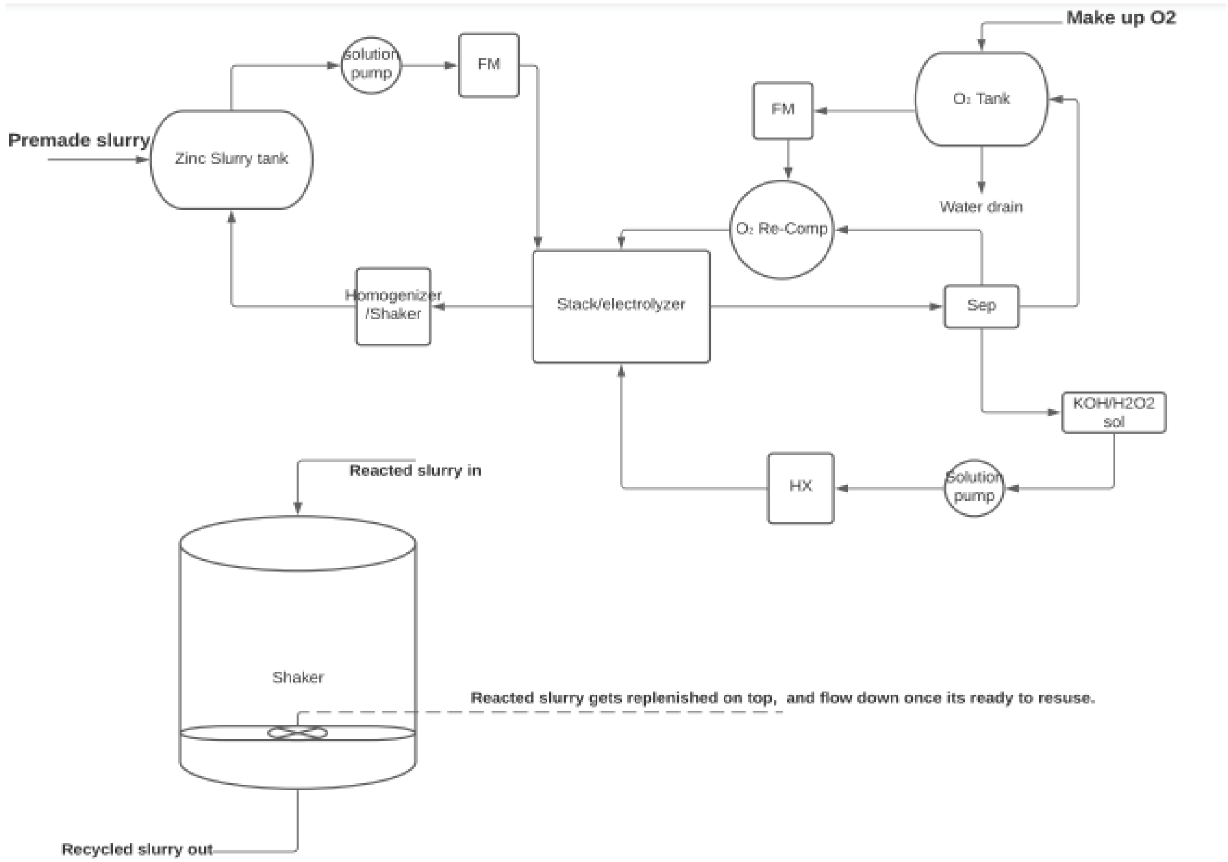
This analysis helps us to compare system designs

Cost Analysis for Zn-air Batteries

Steps in Our Analysis

- System design: Multiple possible systems…
- Input performance: Evolves, so we start with where we are and extrapolate for use cases
- Cost modeling: ‘Bill of Materials’: Build from Generic Stack Model (from PELoDEES system—stack part costs don’t vary too much)
- CAPEX, OPEX: Calculated As Input for LCOS
- Baseline LCOS Calculations: Using our current SOTA components, performance
- Sensitivities and Use Cases: Varying performance, system, design.

Simple System Mechanization Used in Modeling



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Cost Modeling – Stack Components Input Examples

Current Cost

Output at 1,000 stacks/yr		Assumptions	$/kW	$/m2
Seals	$ 12,240	$5/cell	$ 122	$ 50
Nickel Foil	$ 5,946	$25/kg, die cut	$ 59	$ 24
PVC Frame	$ 14,564	Injection molded frames, $2/kg material	$ 146	$ 59
Membrane	$ 55,623	$200/m2 for Nafion membrane	$ 556	$ 227
~~Nickel Felt~~ Carbon Felt	$ 3,483	$550/m2 for nickel felt, die cut	$ 35	$ 14
Carbon Felt	$ 3,483	~$15/m2 for carbon felt, die cut	$ 35	$ 14
Anode Electrode	$ 8,485	$5/m2 material, slot die coating costs from DOE	$ 85	$ 35
Cathode Electrode	$ 8,485	$5/m2 material, slot die coating costs from DOE	$ 85	$ 35
Stack Assembly	$ 5,655	$250K/line, 2 seconds per process step	$ 57	$ 23
Total Stack Cost	**$ 117,964**		**$ 1,180**	**$ 482**

Baseline - Projected Cost (developed supply chain)

Output at 1,000 stacks/yr		Assumptions	$/kW	$/m2
Seals	$ 10,240	$5/cell	$ 102	$ 42
Nickel Foil	$ 5,946	$25/kg, die cut	$ 59	$ 24
PVC Frame	$ 11,458	Injection molded frames, $2/kg material	$ 115	$ 47
Membrane	$ 9,240	$20/m2 for ~~Nafion~~ UTK membrane	$ 92	$ 38
Carbon Felt	$ 3,483	~$15/m2 for carbon felt, die cut	$ 35	$ 14
Carbon Felt	$ 3,483	~$15/m2 for carbon felt, die cut	$ 35	$ 14
Anode Electrode	$ 8,485	$5/m2 material, slot die coating costs from DOE	$ 85	$ 35
Cathode Electrode	$ 8,485	$5/m2 material, slot die coating costs from DOE	$ 85	$ 35
Stack Assembly	$ 5,655	$250K/line, 2 seconds per process step	$ 57	$ 23
Total Stack Cost	**$ 66,475**		**$ 665**	**$ 272**

Other Inputs

System Performance Specs
- Charge/Discharge Voltage
- Current Density
- Discharge Power
- Charge Discharge Time

Operational Parameters
- Reagent stoich in each direction
- Solution and Air dP

Operational Parameters
- Tanks, Compressors
- Recycle Pumps
- O&M
- Power Electronics

Cost Analysis for Zn-air Batteries

Key Questions

How does a ZAB stack up overall?

Levelized cost based on stack and chemicals ~$0.05/kWh or less is achieved already with modest performance;

Trade-offs in performance, capacity.

Improving the PD makes a large difference in cost.

Does ROUND TRIP EFFICIENCY matter? This is a key question for air electrodes especially. Results to date not conclusive.

From Last Year: Side Work from Test beds (Test beds, methods developed over 8 Years)

Need to Know

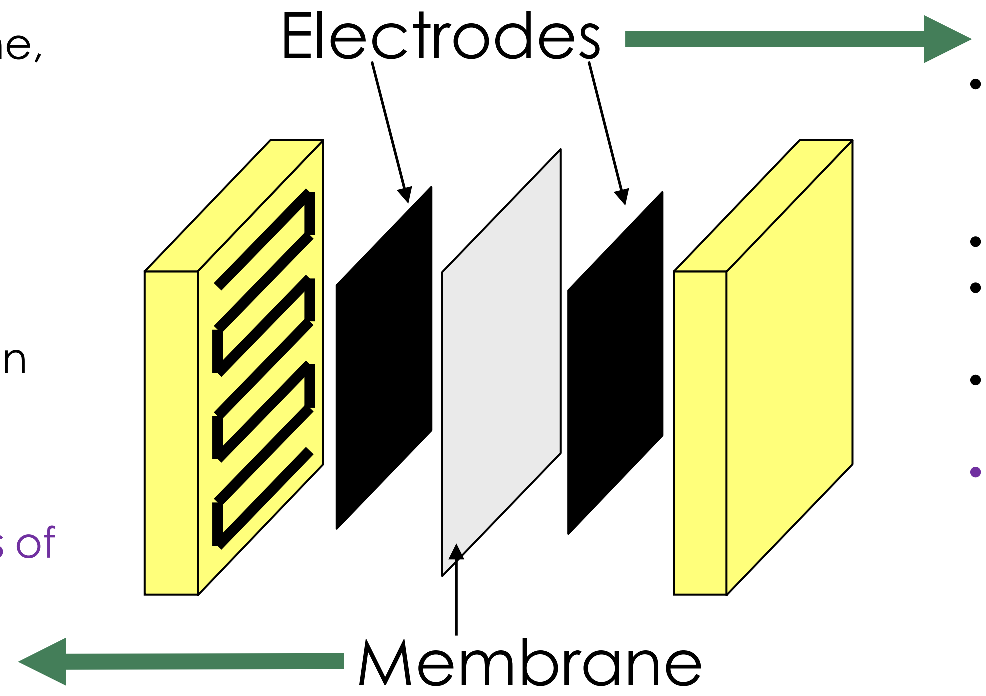
- Conductivity, cross-over, other transport for different membrane, electrolyte chemistry

Test beds

- <u>Rigorous</u> 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, NREL, 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)

High energy Density Zn-air Batteries: Summary

1. Began development of Zn slurry electrodes
   a. Demonstrated a useable slurry-hardware combination

2. Implemented Air Electrode using Pyrolyzed Biomass in Zn-Air cells
   a. Air electrode has no precious metal catalyst
   b. Discharge mode shown; presently analyzing contributing losses

3. Cost Analysis
   a. Developed an ARPA-E DAYS LCOS analysis for bottom-line
   b. Develop inputs and scenarios for Zn-air
   c. Should allow us too assess whether LCOS, CAPEX targets can be met with relatively low RTE

All is Work in Progress

Looking Forward

Expected by Next Year

1. Detailed diagnostics of Zn, air electrodes leading to first steps toward optimization

2. Zn slurry-air battery cycling tests

3. Detailed cost comparisons for many scenarios

4. Multiple publications on this and other program-related work (10 manuscripts in pipeline)

Acknowledgements

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