Pacific Northwest
NATIONAL LABORATORY

Latest Developments in Mild Acidic Zinc Battery at PNNL

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Presentation #1002

U.S. DEPARTMENT OF ENERGY BATTELLE

PNNL is operated by Battelle for the U.S. Department of Energy

Project Team

- **PNNL Contributors**
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  - Ha Tran
  - Marcos Lucero
  - Zane Grady
  - Wonkwang Lim
  - Jung Hui Kim
  - Xiaolin Li
  - David Reed
  - Vincent L. Sprenkle

- **External collaborators**
  - Prof. Xingbo Liu (West Virginia University)

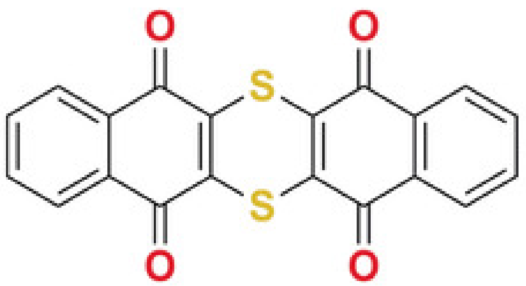
Project Objectives

- Aqueous Zn batteries using earth abundant materials (H_2O, Zn, MnO_2 etc) have **high degree of safety, low cost, and high specific energy**. If rechargeable, they can provide a highly attractive solution to meet the cost and performance targets for electrochemical energy storage systems in electrical grid applications.
- PNNL's overall goal is to **understand the fundamental mechanism** of rechargeable aqueous Zn batteries at mild acid or neutral conditions, to develop innovative low-cost chemistries to improve the cycle life and to drive it to commercialization.
- FY2024 objectives/milestones
  (1) Demonstrate >80% retention over 100 cycles for the PNNL's intercalation-based organic cathode while maintaining > 150 mAh/g specific capacity at ~ 3 mAh/cm^2 electrode loading. (Achieved)
  (2) Assess new electrolytes that allow for enhanced cyclability compared to baseline electrolyte. (Achieved)
  (3) Achieve >80% capacity retention over 100 cycles for the manganese cathodes of >3 mAh/cm^2 loading with Zn or advanced anodes. (Achieved)
  (4) Publish 1 journal articles on Zn-MnO_2 technology. (Ongoing)

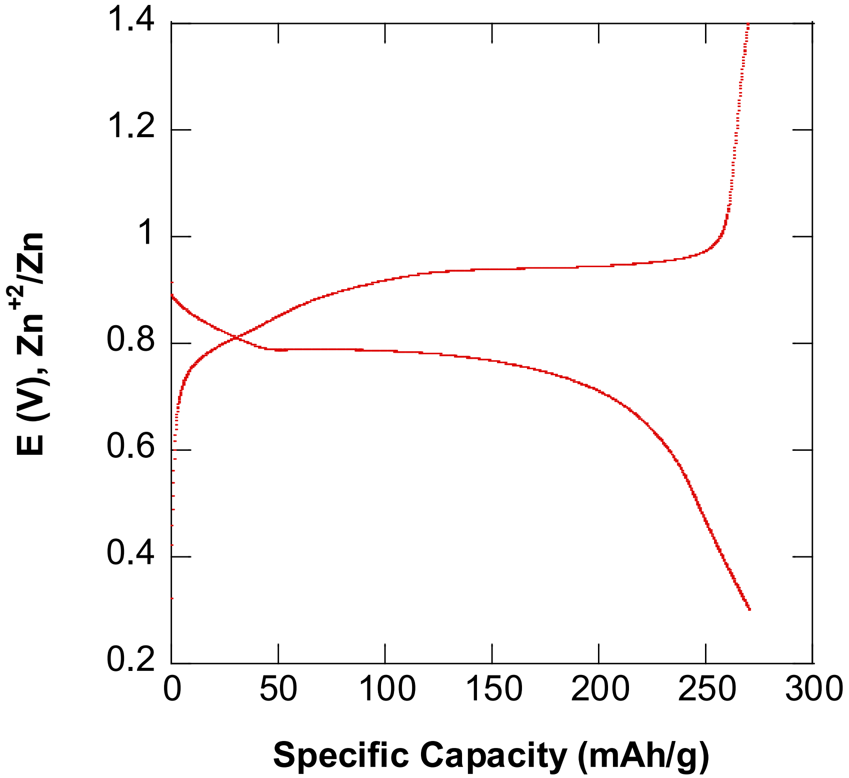
Project Achievements

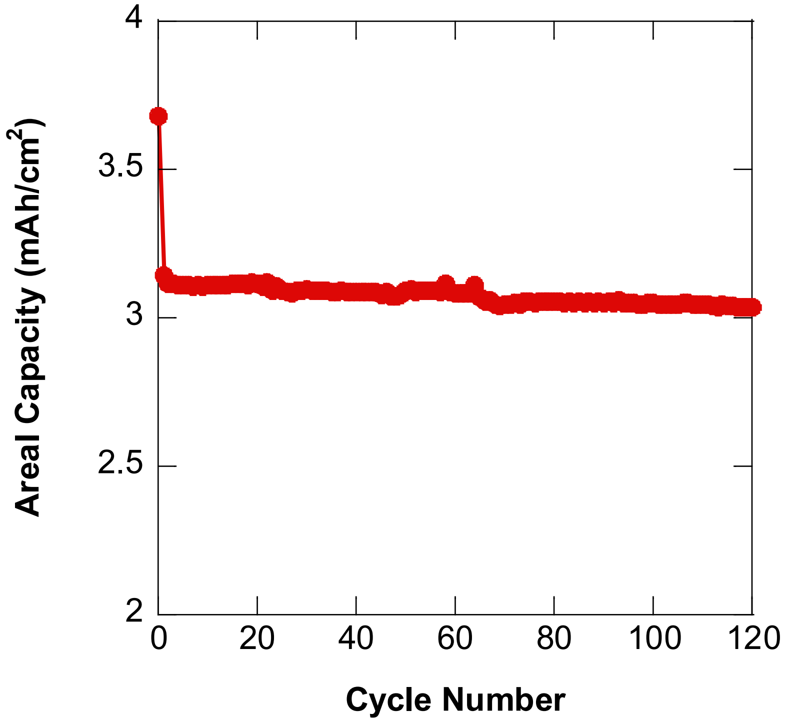
- **Research highlights**
  1. (1) An DTT cathode has demonstrated a specific capacity of >180 mAh/g and >97% retention over 120 cycles at a loading of 3 mAh/cm^2.
  2. (2) Improvements to the electrolyte through pH additives and/or sugar additives significantly improve the performance of the Zn metal anode. The effect of the pH additive allows for 5 times the cycle life of a Zn symmetric cell versus our standard electrolyte. The sugar electrolyte doubles the 10 hr cycle life of the PNNL developed alloy anode to over 100 cycles at a DOD of 40%
  3. (3) The PNNL developed Zn alloy anode has been improved upon by reducing the In concentration with less expensive elements (Cd, P). The new anode can cycle over 200 hr (~200 cycles) at ~5 mAh/cm^2 loading and ~10 mA/cm^2 current density without cell shorting.
  4. (4) Mn-Cu Flow Cells can cycle at a high voltage of 0.9V vs Cu^{+2}/Cu with areal capacities greater than 5 mAh/cm^2. The Mn-Cu chemistry has a long cycle life of over 300 cycles in part due to the development of a PNNL system refresher that restores lost performance to the cell .
- **Publications: 2 in preparation.**
  1. (1) Li, W-G., Li, X, Reed, D. In preparation 2024.
  2. (2) Grady Z. Fayette, M., Li, X, Reed, D. In preparation 2024.
- **Society impact and STEM outreach**
  1. (1) Contributor to the WVU Zinc Battery Workshop
  2. (2) Invited Speaker and Session Organizer at 245th Annual ECS Meeting
  3. (3) Invited Speaker at ECS Prime 2024

Organic Cathode

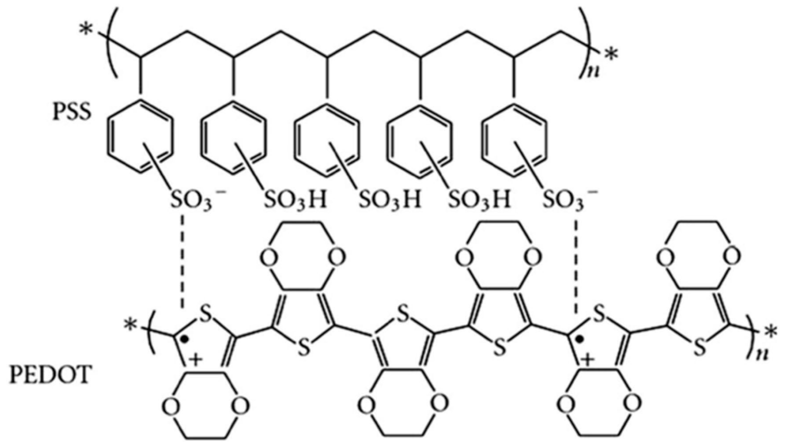


Sulfur heterocyclic quinone (DTT)



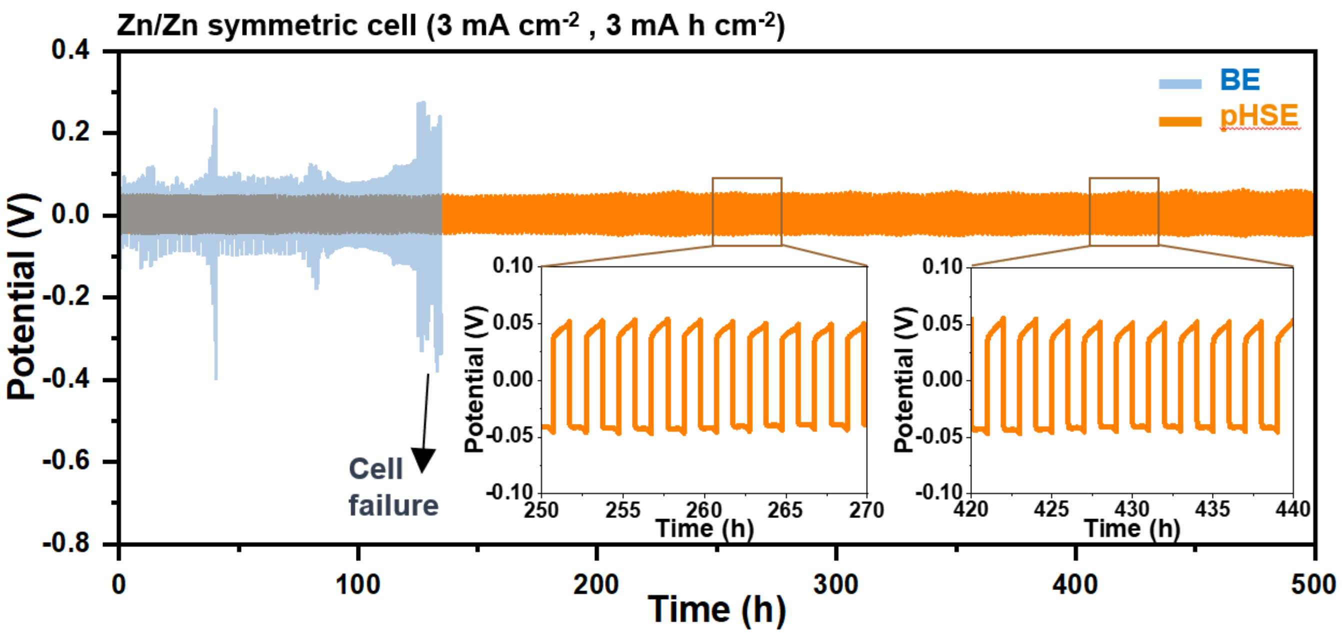


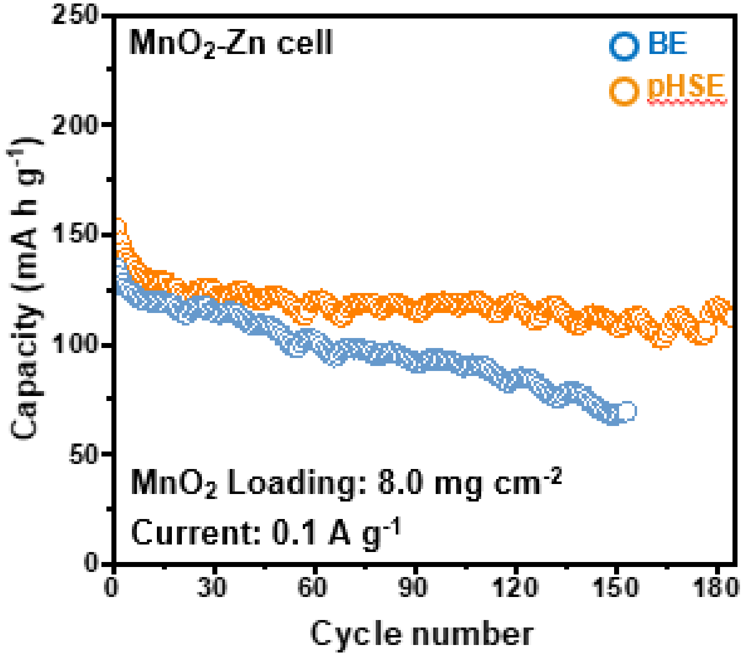
PDOT-PSS binder



- **The DTT cathode has demonstrated a specific capacity of >180 mAh/g and ~97% retention over 120 cycles at a loading of ~3 mAh/cm^2.**

Electrolyte Exploration (pH additive)

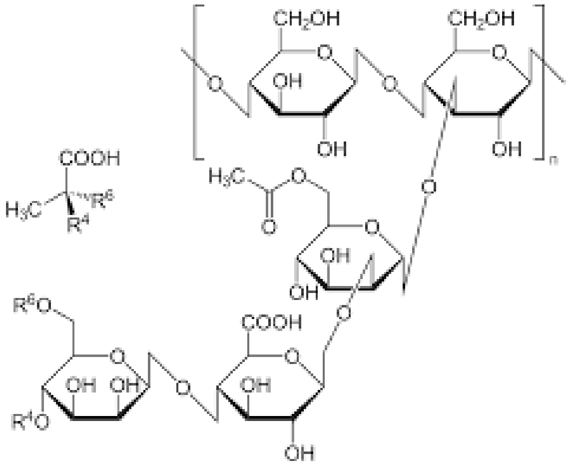




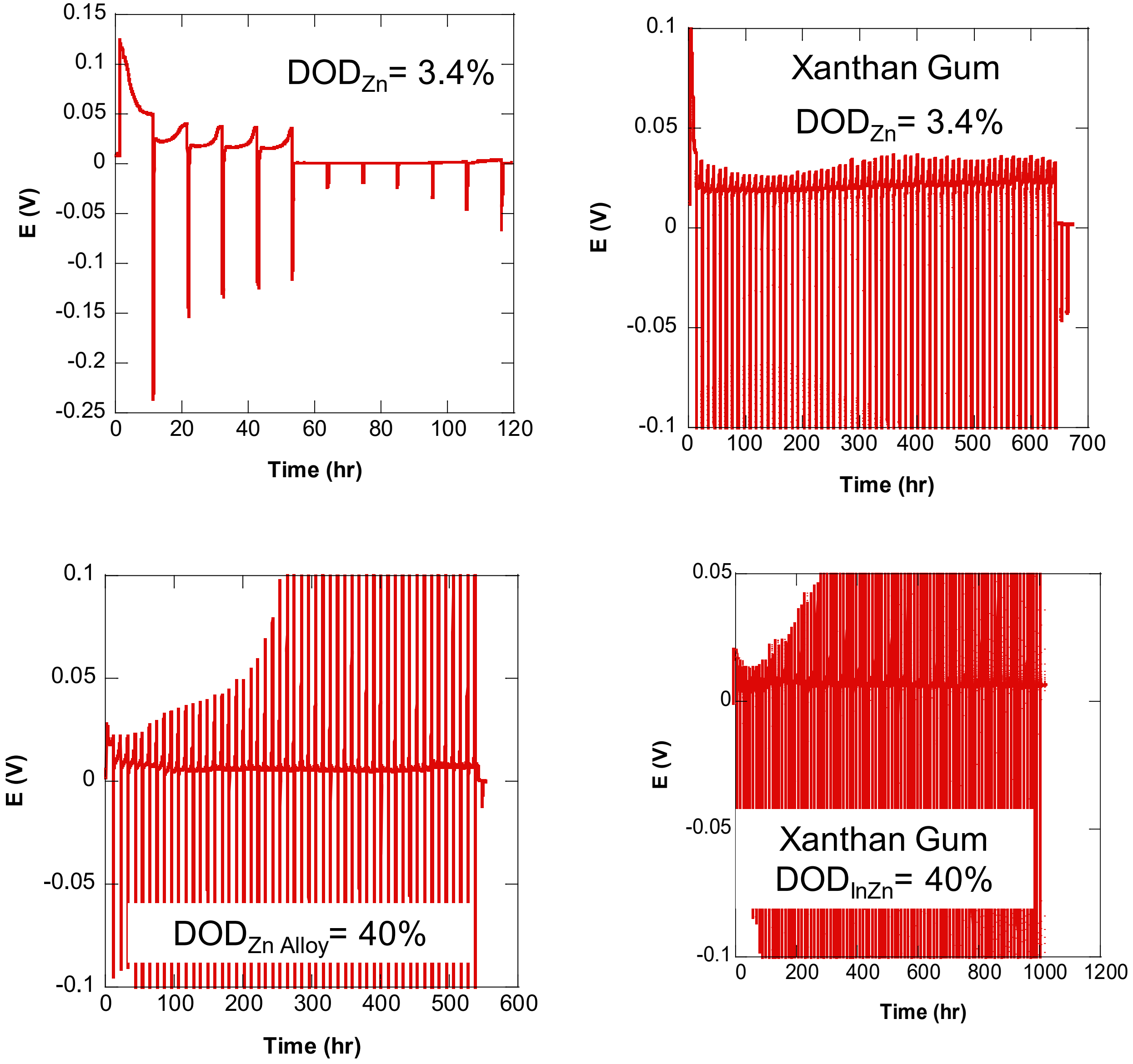
- The pH additive improves Zn metal (Q= 3 mAh/cm^2) cycling stability by ~5 times.
- In a full MnO_2-Zn full cell, the capacity retention is improved to ~80% retention over 180 cycles.

Electrolyte Exploration

Xanthan Gum



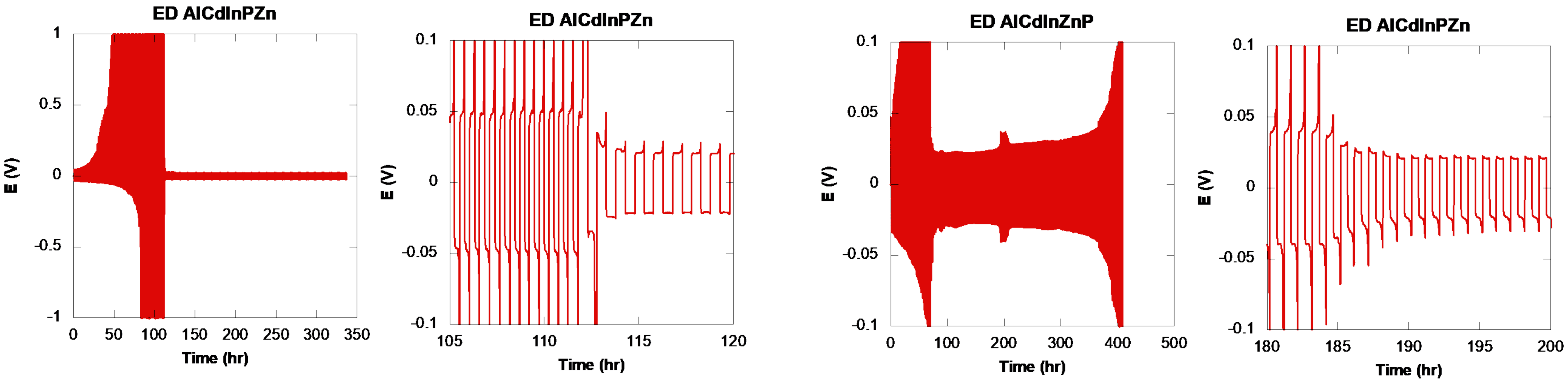
Zn Anode

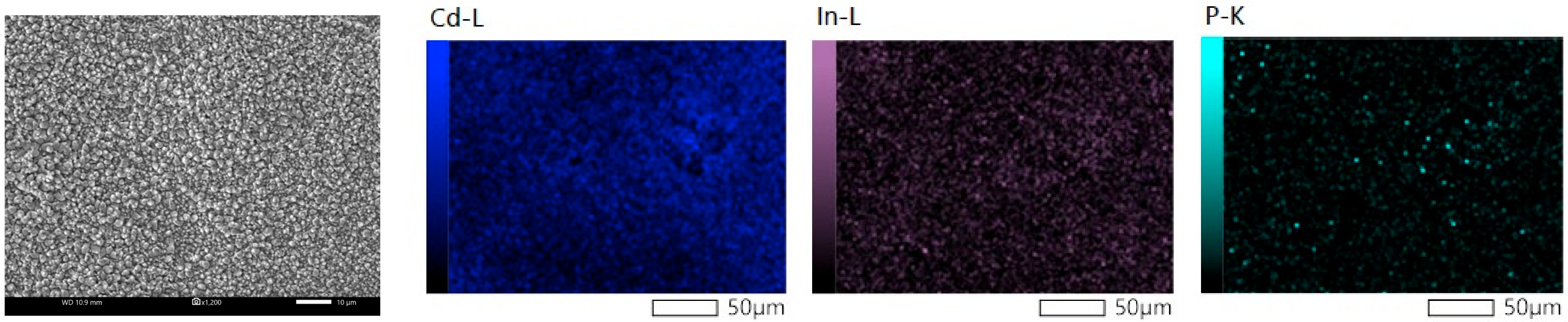


- **The addition of Xanthan Gum improves the cycling stability of Zn metal anode at 10hr discharge cycling conditions (10 mA/cm^2, Q= 5 mAh/cm^2)**

Anode Improvements

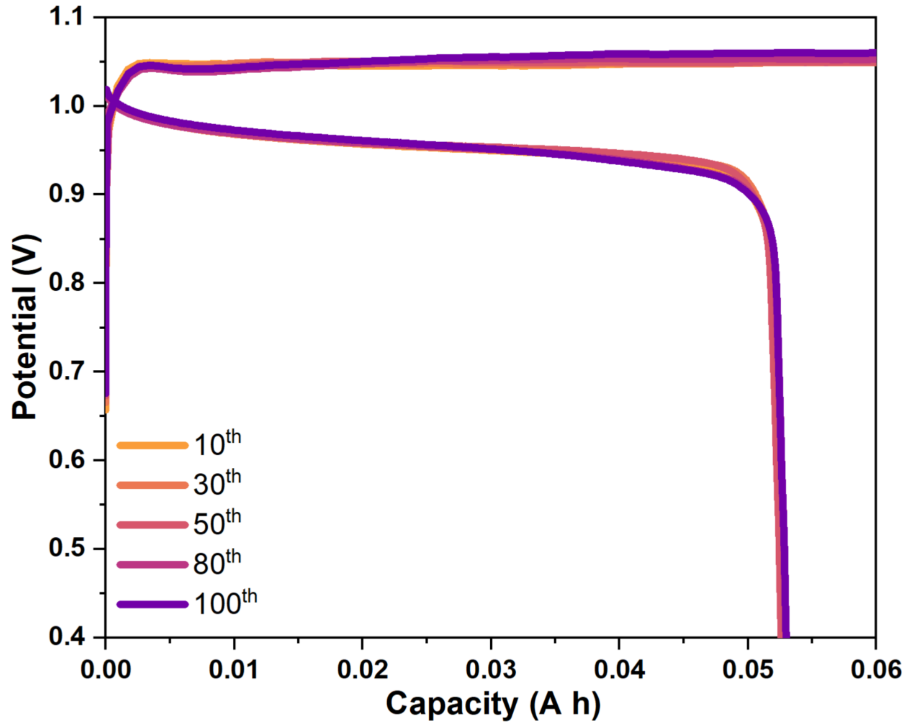
Zn alloy anodes with low-cost dopants

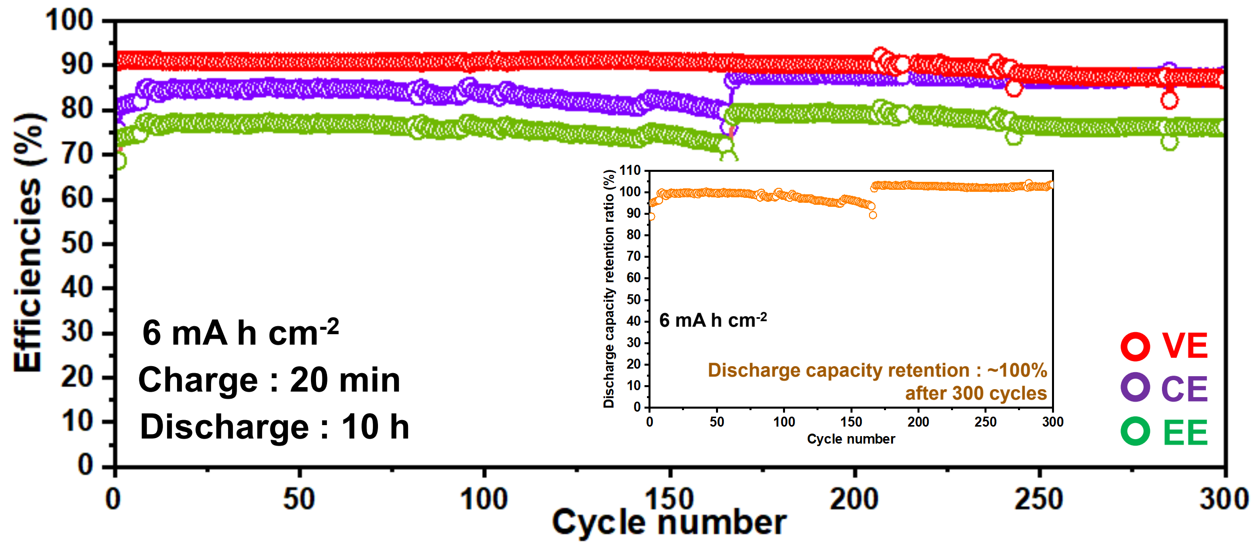




- The addition of low-cost dopants (Al, Cd, and P) has been introduced into the Zn-based alloys. Preliminary results show the In content was reduced by ~4 times over our previous alloy anode.
- The anode demonstrated >200 cycles in a symmetric cell without shorting (5 mAh/cm^2, 10 mA/cm^2, ~40% DOD).

Mn-Cu Flow Assisted





$$MnO_2 + 4H^+ + 2e^- \rightleftharpoons Mn^{+2} + 2H_2O \quad (E^o=1.23V)$$
$$Cu^{+2} + 2e^- \rightleftharpoons Cu \quad (E^o=0.34V)$$

- The Mn-Cu Flow cell significantly improves the performance of the cathode reaction compared to traditional EMD chemistry.
- It can cycle at areal capacities over 5 mAh/cm^2 for over 300 cycles with an average CE of ~88% at 1hr charge/10hr discharge conditions

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Summary

- An DTT cathode has demonstrated a specific capacity of >180 mAh/g and ~ 97% retention over 120 cycles at a loading of ~3 mAh/cm^2.
- Improvements to the electrolyte through pH additives and/or sugar additives significantly improve the performance of the Zn metal anode. The effect of the pH additive allows for 5 times the cycle life of a Zn symmetric cell versus our standard electrolyte. The sugar electrolyte doubles the 10 hr cycle life of the PNNL developed alloy anode to over 100 cycles at a DOD of 40%
- Further development of the Zn alloy anode lowered the In concentration while replacing some In with less expensive elements (Cd, P). The new anode can cycle over 200 hr (~200 cycles) at ~5 mAh/cm^2 loading and ~10 mA/cm^2 current density without cell shorting.
- Mn-Cu Flow Assisted Cells can cycle at at a relatively high voltage of 0.9V with areal capacities exceeding 5 mAh/cm^2. The Mn-Cu cell shows high stability under a 20 min charge/10 discharge regime as evidenced by 150 cycles before PNNL's refreshing of the system restores the cell performance and extends the cycle life.

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Proposed Work for FY2025

- Continue to improve the cycling stability/mitigation of side reactions of Zn-based anodes
- Further development of low-cost cathode materials
- Explore cathode systems beyond MnO_2.

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Acknowledgements

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Thank you