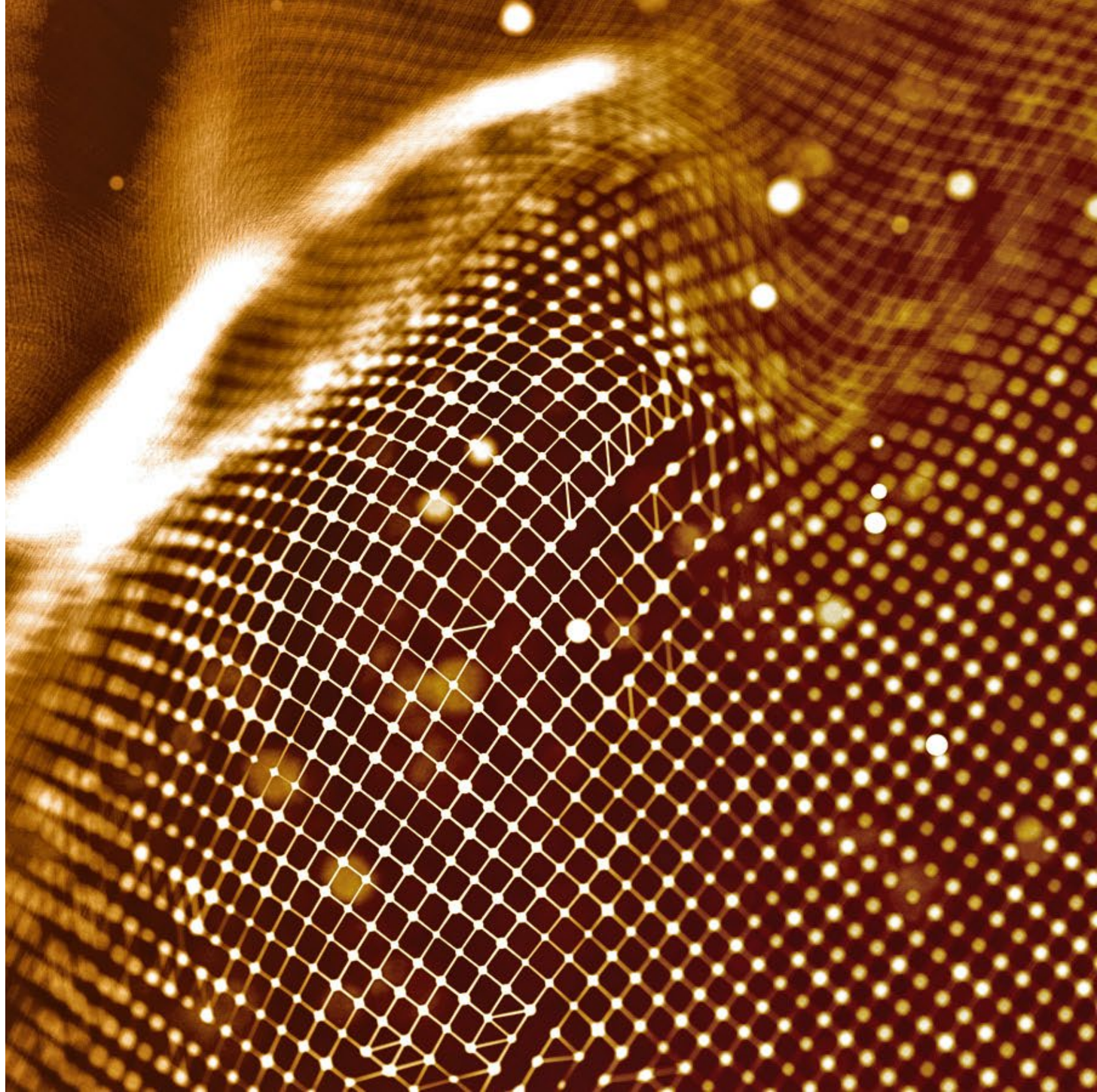
Pacific Northwest
NATIONAL LABORATORY

Zinc Battery Research at PNNL

October 25th, 2023

Matthew Fayette

Presentation #704



U.S. DEPARTMENT OF ENERGY BATTELLE

Project Team

- **PNNL Contributors**

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  - Xiaolin Li
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- **External collaborators**

  - Prof. Xingbo Liu (West Virginia University)
  - Prof. Nian Liu (Georgia Institute of Technology)
  - Prof. Sanjoy Banerjee (City University of New York)

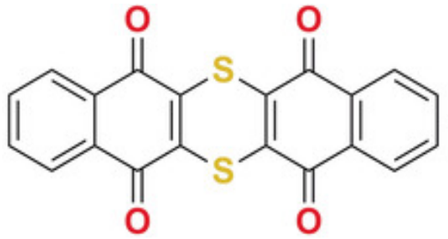
Project Objectives

- 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.
- FY2023 objectives/milestones
  - (1) Demonstrate >80% retention over 100 cycles for the PNNL's intercalation-based organic cathode while maintaining >120 mAh/g specific capacity at ~ 1.5 mAh/cm^2 electrode loading. (Achieved)
  - (2) Demonstrate stable cycling of 10 mAh/cm^2 Zn anodes over 200 hours at greater than or equal to 1 mA/cm^2 current density and 50% DOD in a large cell design . (Achieved)
  - (3) Achieve >80% capacity retention over 100 cycles for the MnO_2 cathodes of ~2 mAh/cm^2 loading with Zn or advanced anodes. (Achieved)
  - (4) Publish 1 journal articles on Zn-MnO_2 technology. (Achieved)

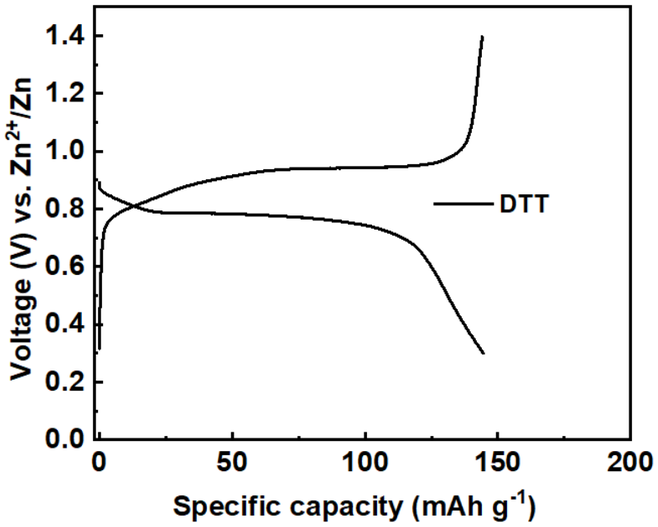
Project Achievements

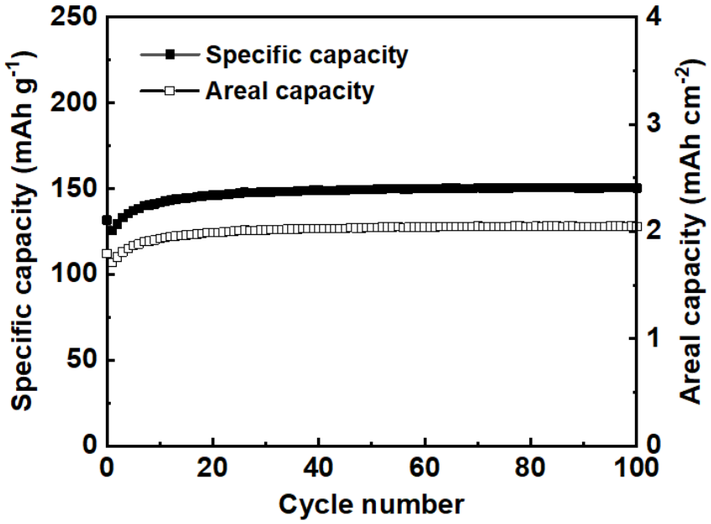
- **Research highlights**
  - (1) An DTT cathode has demonstrated a specific capacity of ~150 mAh/g and >90% retention over 100 cycles at a loading of >1.5 mAh/cm^2.
  - (2) A Zn alloy anode can cycle 250 hrs (~250 cycles) at ~5.4 mAh/cm^2 loading and ~10 mA/cm^2 current density without shorting in a large pouch cell configuration. It can last >30 cycles (>300 hr) in a symmetric cell with 10hr discharge and 100 cycles (>1000 hr) with 5hr discharge, promising towards long duration application.
  - (3) Mn-Cu Flow Cells can cycle at a high voltage of 0.9V vs Cu^{+2}/Cu with areal capacities greater than 2.5 mAh/cm^2. The Cu anode shows enhanced tolerance to dendrite formation as evidenced by 200 cycles under 10 hr charge/discharge regime and 1000 cycles under a 0.5hr charge/discharge regime.
  - (4) Exploratory work has begun to evaluate potential long duration battery chemistries that can discharge at $\gtrsim$10hrs while also having the ability to fast charge (1C or greater) with relatively low loss to coulombic efficiency. These chemistries include a Pb/Cu Flow Assisted Cell can cycle over 150 cycles at areal capacities >9 mAh/cm^2 with a high voltage of 1.1V vs Cu^{+2}/Cu.
- **Publications: 1 paper published, 1 in preparation and 1 patent filed.**
  - (1) Fayette, M. et al. Indium zinc-based alloy anodes forming porous structure for aqueous zinc batteries. US20230282816 A1.
  - (2) Li, W-G., Li, X, Reed, D. Small Methods 2023. doi/10.1002/smtd.2023009653
  - (3) Fayette, M., Li, X, Reed, D. In preparation 2023.
- **Society impact and STEM outreach**
  - (1) Poster presentation at 232nd Annual ECS Meeting on “Zinc alloy anodes”
  - (2) Zinc Battery Session Organizer and Lead at 232nd Annual ECS Meeting

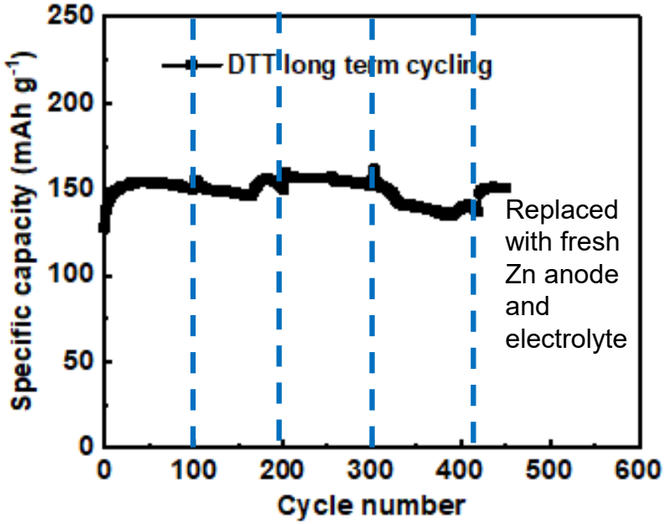
Organic Cathode



Sulfur heterocyclic quinone (DTT)



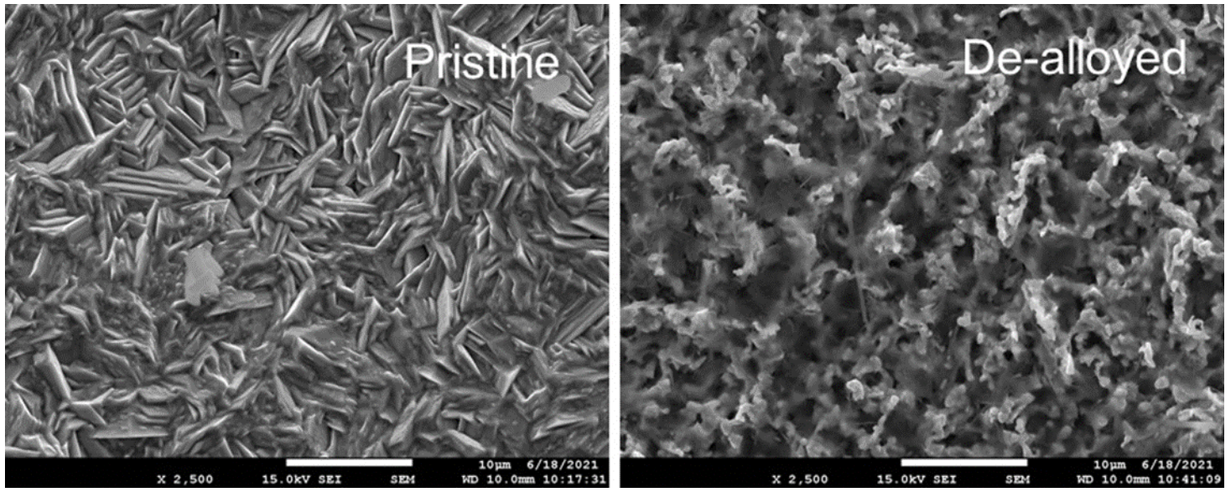




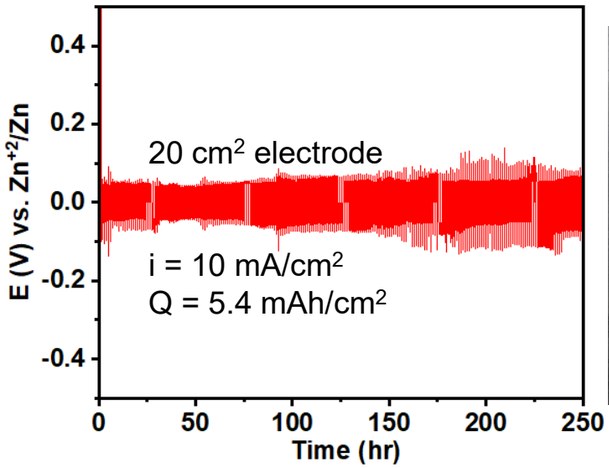
- **An DTT cathode has demonstrated a specific capacity of ~150 mAh/g and ~99% retention over 100 cycles at a loading of ~2 mAh/cm^2.**

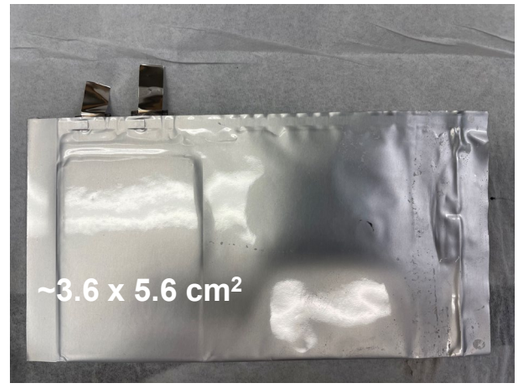
Zn Metal Anode

Anode morphology



Performance in Pouch Cells

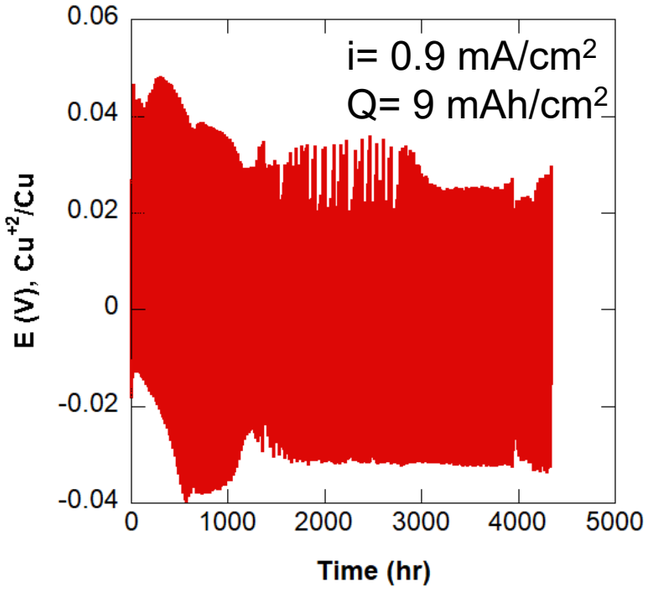


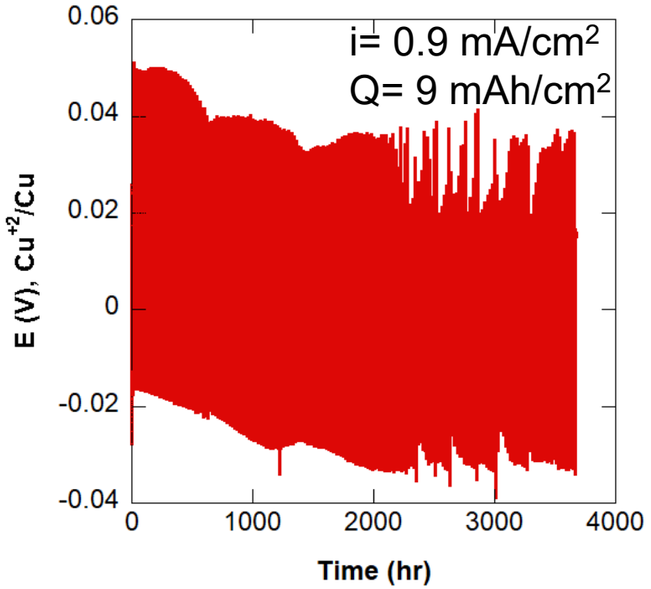


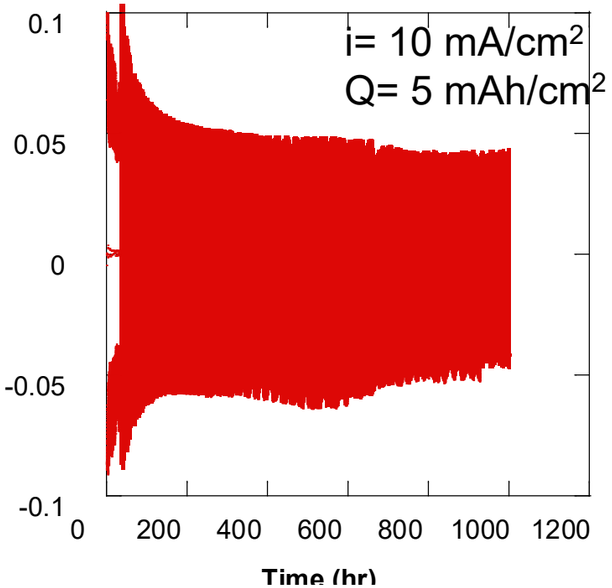
- **The Zn alloy anode significantly improves the tolerance to dendrites by forming porosity after dissolution of Zn.**
- **It can cycle over 250 cycles at a capacity of ~5.4 mAh/cm^2 and a current density of ~10 mA/cm^2 (52% DOD).**
- **The alloy anode is also promising towards long duration applications. It can last >30 cycles (>300 hr) with 10hr discharge and 100 cycles (>1000 hr) with 5hr discharge.**

M. Fayette, et al., ***ACS Energy Letters*** 2022, 7, 1888-1895

Cu Anode

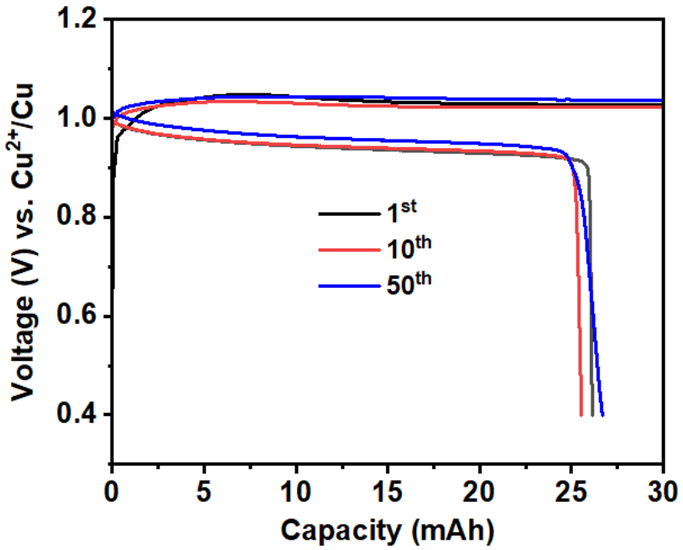


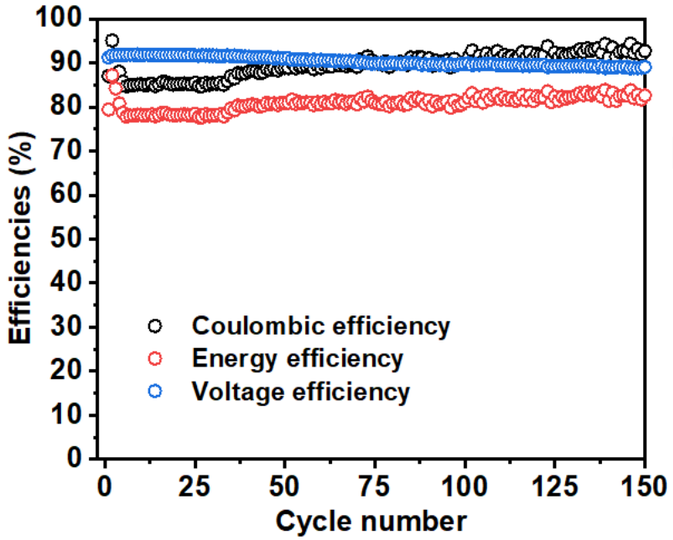




- **The Cu anode is promising both for quick charge and long duration applications.**
- **It can last >200 cycles (>4000 hr) with 10hr discharge and 1000 cycles (1000 hr) with 0.5hr discharge.**

Mn-Cu Flow Assisted

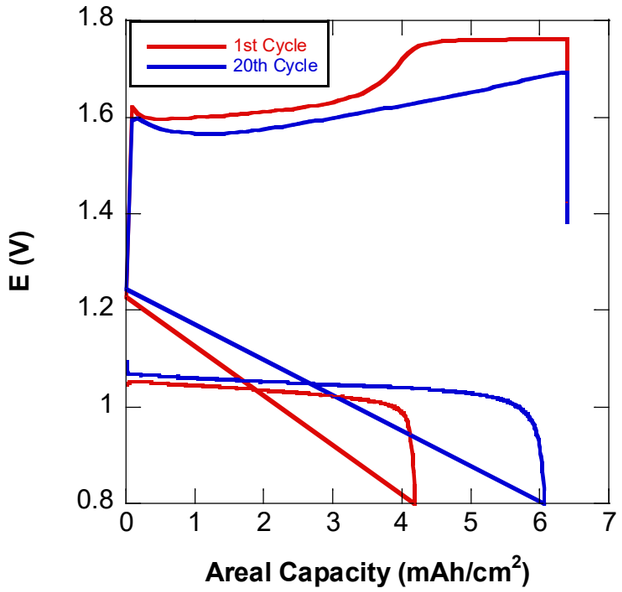


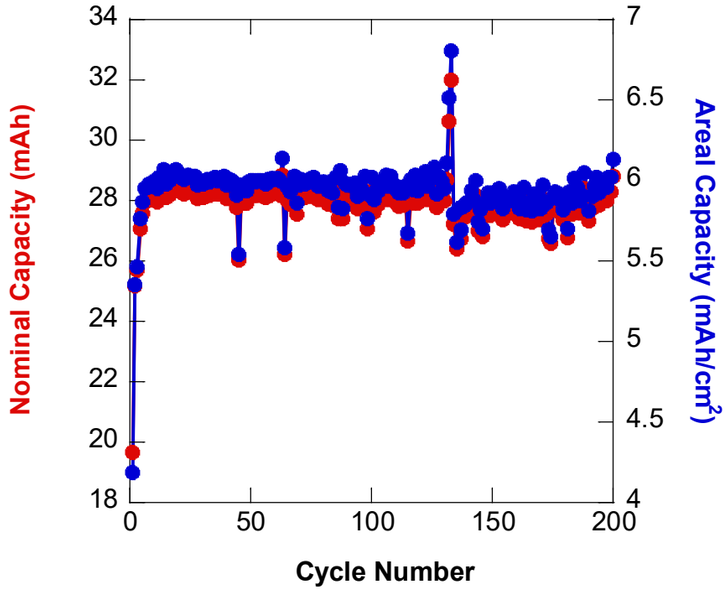


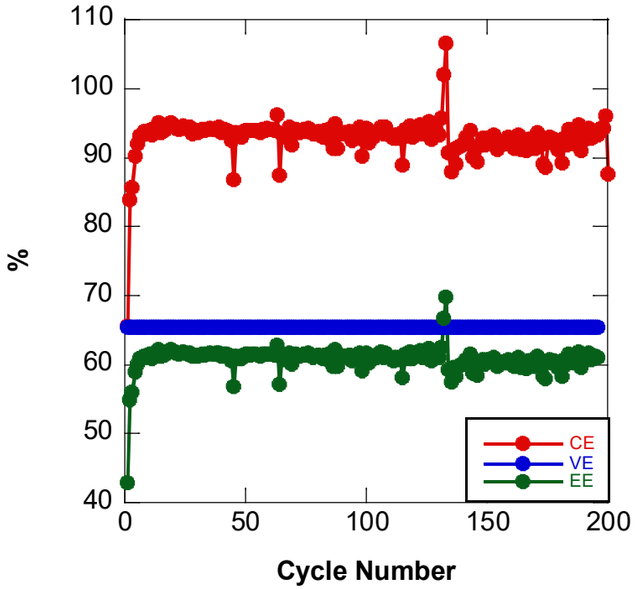
$$MnO_2 + 4H^+ + 2e^- \rightleftharpoons Mn^{+2} + 2H_2O \quad (E^o=1.23V)$$
$$Cu^{+2} + 2e^- \rightleftharpoons Cu \quad (E^o=0.34V)$$
$$E_{cell} = 0.89V$$

- 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 2.5 mAh/cm^2 for over 150 cycles with an average CE of ~90% at 1hr charge/10hr discharge conditions

Pb-Cu Concept



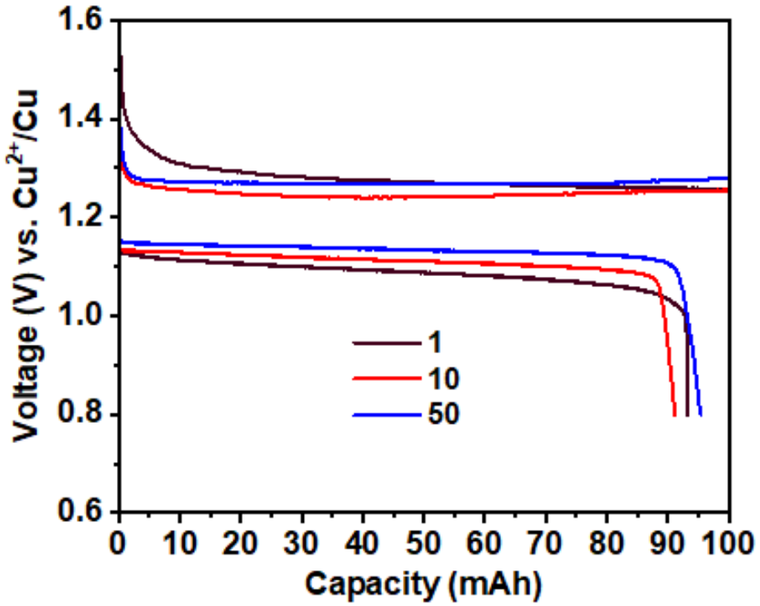


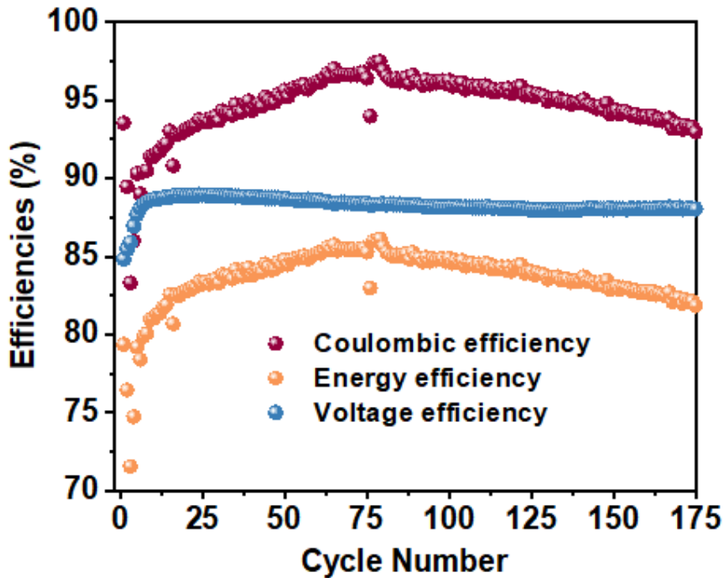


$$PbO_2 + 4H^+ + 2e^- \rightleftharpoons Pb^{+2} + 2H_2O \quad (E^o=1.46V)$$
$$Cu^{+2} + 2e^- \rightleftharpoons Cu \quad (E^o=0.34V)$$
$$E_{cell} = 1.12V$$

- The Pb-Cu chemistry shows improved discharge voltage (1.1V) compared to the Mn-Cu chemistry (0.9V)
- It can cycle at areal capacities of 6 mAh/cm² in a proof of concept cell.

Pb-Cu Flow Assisted





- The Pb-Cu Flow cell significantly improves the performance of the anode reaction compared to traditional All Pb flow chemistry.
- It can cycle at areal capacities >9 mAh/cm^2 for over 150 cycles with an average CE of >90% at 1hr charge/10hr discharge conditions

Summary

- An DTT cathode has demonstrated a specific capacity of ~150 mAh/g and ~ 99% retention over 100 cycles at a loading of ~2 mAh/cm^2.
- A Zn alloy anode can cycle over 200 hr (~200 cycles) at ~5.4 mAh/cm^2 loading and ~10 mA/cm^2 current density without dendrite in a large pouch cell configuration. It can last > 30 cycles (>300 hr) in a symmetric cell with 10hr discharge and 100 cycles (>1000 hr) with 5hr discharge, promising towards long duration application.
- Mn-Cu Flow Assisted Cells can cycle at a high voltage of 0.9V vs Cu^{+2}/Cu with areal capacities greater than 2.5 mAh/cm^2. The Cu anode shows enhanced tolerance to dendrite formation as evidenced by 200 cycles under 10 hr charge/discharge regime and 100 cycles under a 1hr charge/discharge regime.
- A Pb/Cu Flow Assisted Cell can cycle over 150 cycles at areal capacities >9 mAh/cm^2 with a high voltage of 1.1V vs Cu^{+2}/Cu.

Proposed Work for FY2024

- Continue to improve the cycling stability of Zn-based anodes
- Further improvement of the Mn-Cu and Pb-Cu Flow Assisted Cells
- Further development of low-cost cathode materials

Acknowledgements

We acknowledge the support of Dr. Imre Gyuk and the OE Energy Storage Program for this work.

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Thank you