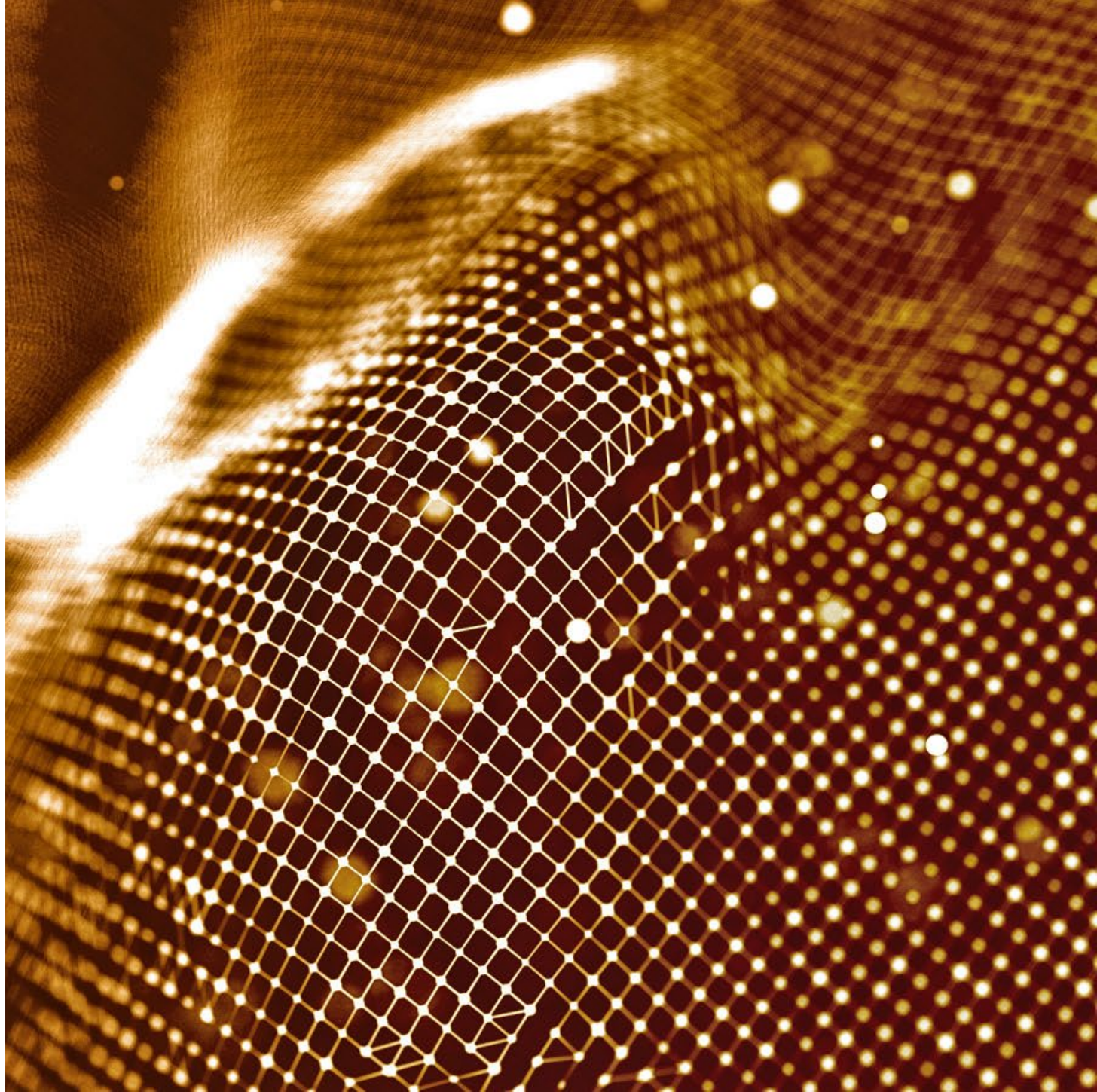
Pacific Northwest
NATIONAL LABORATORY

Zinc Battery Research at PNNL

October 14th, 2022

Matthew Fayette

Presentation #706



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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- **External collaborators**
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  - Dr. Kang Xu (Army Research Laboratory)
  - Prof. Nian Liu (Georgia Institute of Technology)
  - Dr. Cy Fujimoto (Sandia National Laboratory)
  - Prof. Sanjoy Banerjee (the City College of New York)

Project Objectives

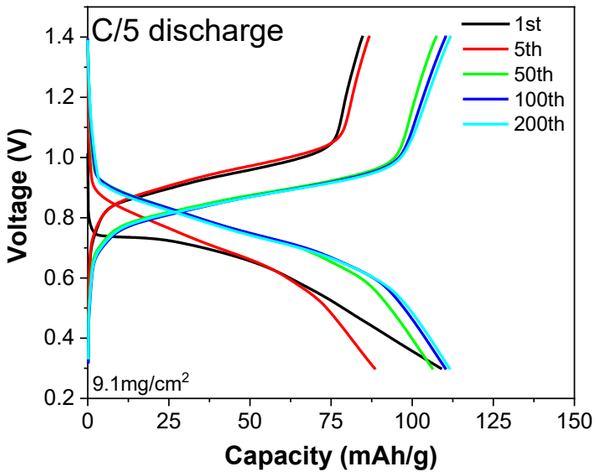
- Aqueous Zn batteries using earth abundant materials (H_2O, Zn, MnO_2 etc) have high degree of safety, low cost, and high specific energy. If rechargeable, they can provide a highly attractive solution to meet the cost and performance targets for electrochemical energy storage systems in electrical 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.
- FY2022 objectives/milestones
  - (1) Demonstrate >80% retention over 100 cycles for the PNNL's intercalation-based organic cathode while maintaining > 100 mAh/g specific capacity at ~ 1mAh/cm^2 electrode loading. (Achieved)
  - (2) Demonstrate stable cycling of 10 mAh/cm^2 Zn anodes over 100 cycles at greater than or equal to 1 mA/cm^2 current density and 50% DOD. (Achieved)
  - (3) Achieve >80% capacity retention over 50 cycles for the MnO_2 cathodes of ~2 mAh/cm^2 loading (33% increase in loading vs. previous year (Achieved)
  - (4) Publish 2 journal articles on Zn-MnO_2 technology. (Achieved)

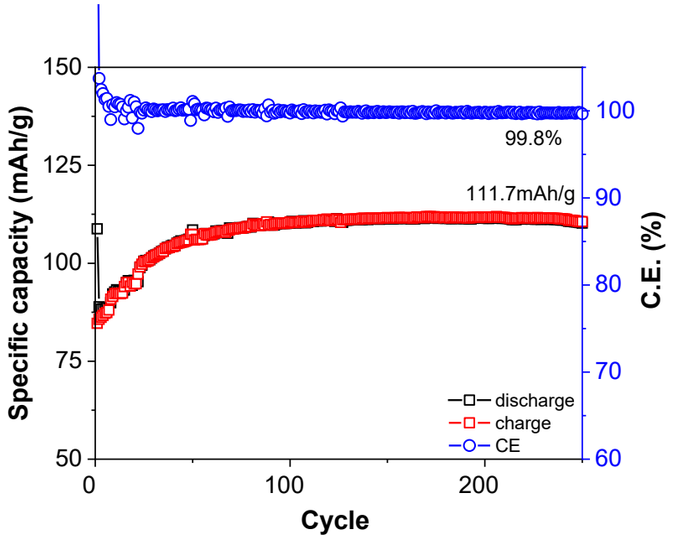
Project Achievements

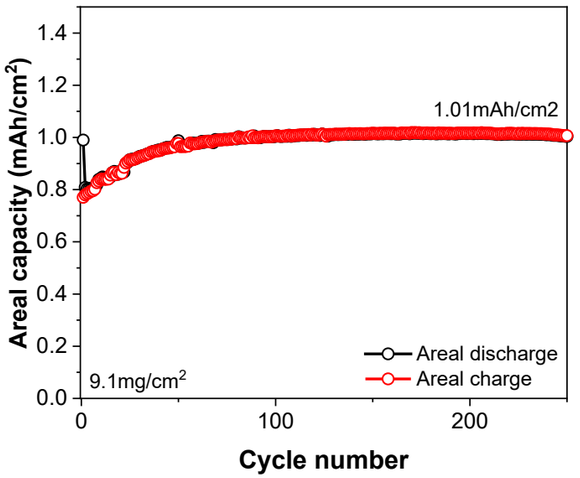
- **Research highlights**
  - (1) An DTT cathode has demonstrated a specific capacity of ~110 mAh/g and > 90% retention over 200 cycles at a loading of >1 mAh/cm^2.
  - (2) A Zn alloy anode can cycle 300 hr (~150 cycles) at ~7.5 mAh/cm^2 loading and ~10 mA/cm^2 current density without shorting. It can 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 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 100 cycles under 10 hr charge/discharge regime and 1000 cycles under a 0.5hr charge/discharge regime.

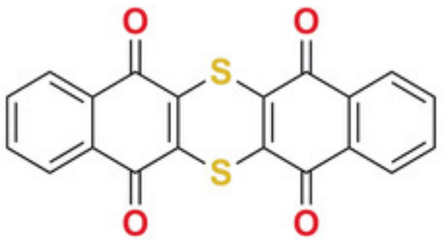
- **Publications: 2 papers published, and 1 provisional patent filed.**
  - (1) M. Fayette, et al., ***ACS Energy Letters*** 2022, 7, 1888-1895
  - (2) X Chen, et al., ***Nano Energy*** 2022, 98,107269.
- **Society impact and STEM outreach**
  - (1) One presentation at NAATBatt Zinc Workshop IV on “Zinc alloy anodes and a new cathode design for advanced aqueous Zinc batteries”

Results: Organic Cathode









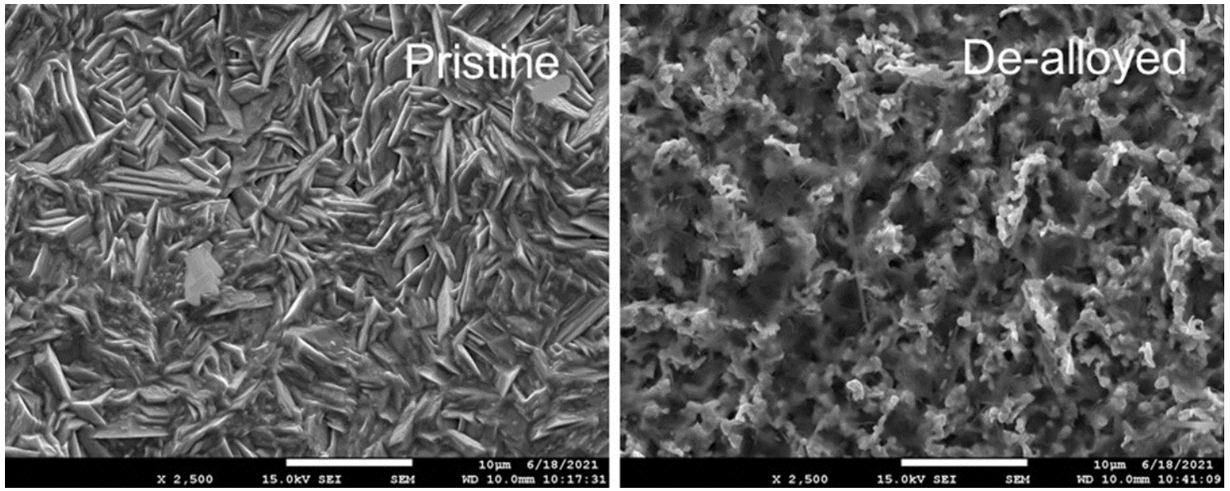
Sulfur heterocyclic quinone (DTT)

- An DTT cathode has demonstrated a specific capacity of ~110 mAh/g and > 90% retention over 200 cycles at a loading of >1 mAh/cm^2.

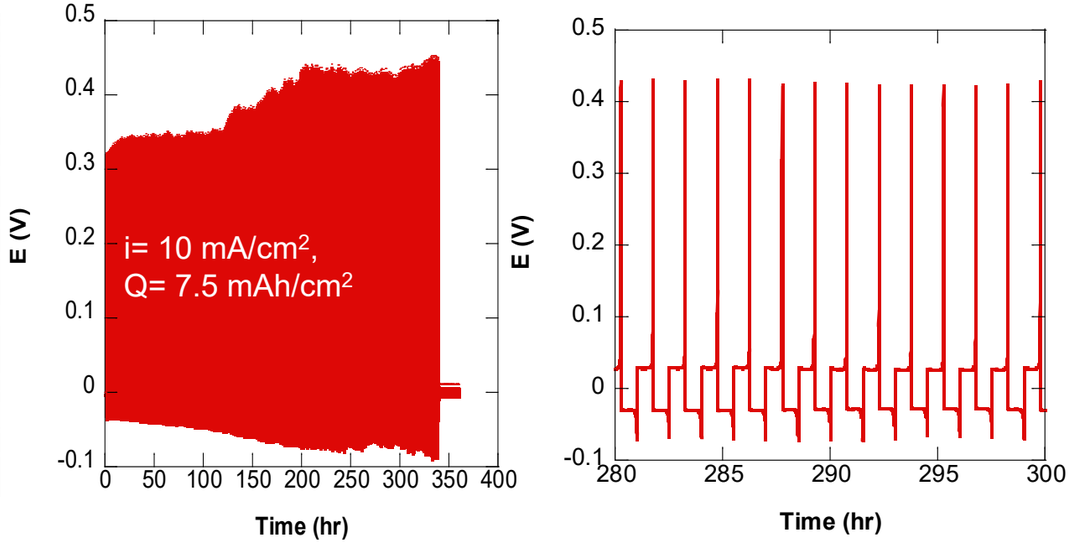
Zinc Anode

Zn alloy anodes

Anode morphology



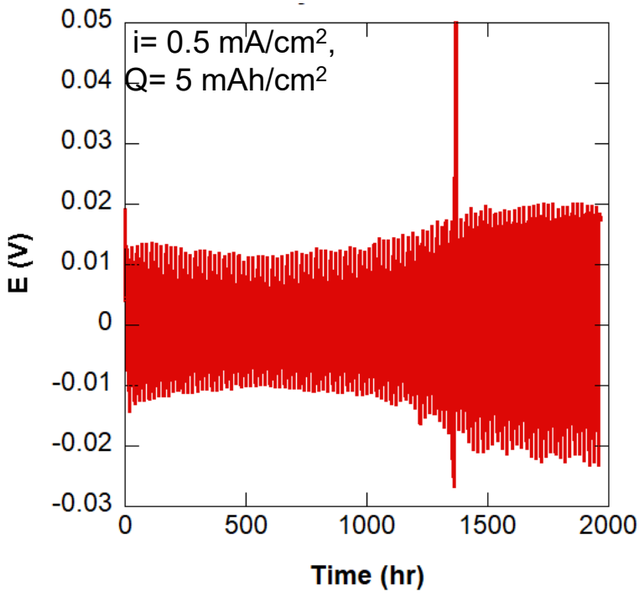
Performance in symmetric cells

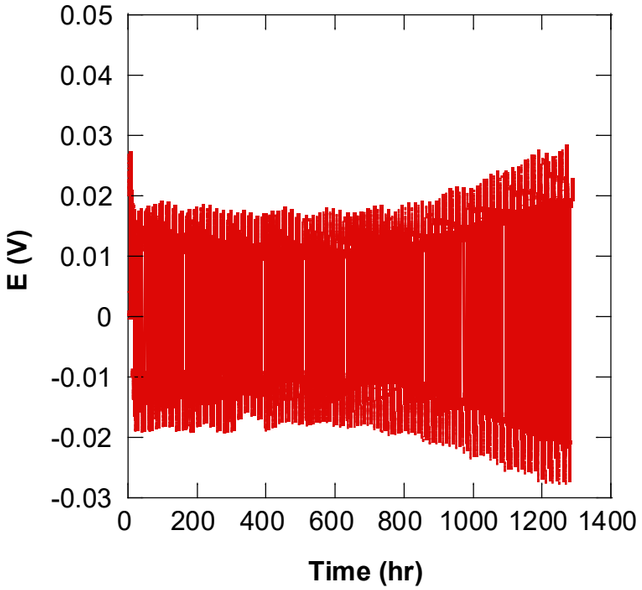


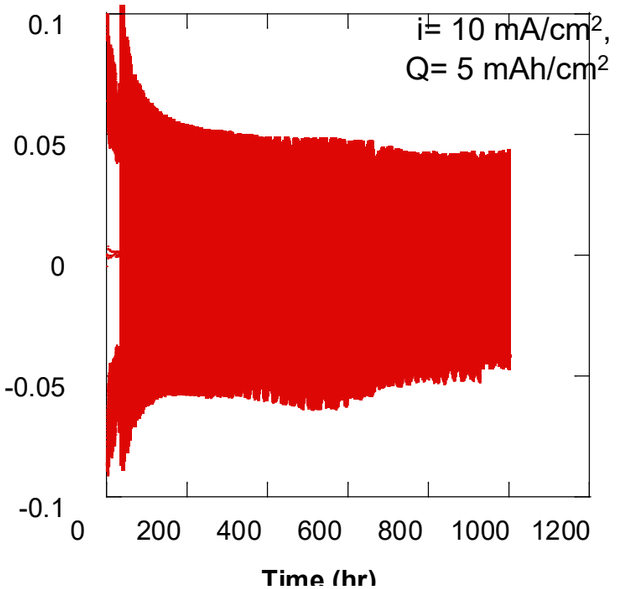
- The Zn alloy anode significantly improves the tolerance to dendrites by forming porosity after dissolution of Zn.
- It can cycle over 100 cycles at a capacity of ~7.5 mAh/cm^2 and a current density of ~10 mA/cm^2 (60% DOD), much better than the Zn foil tested at similar conditions (~100 hr).
- The 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

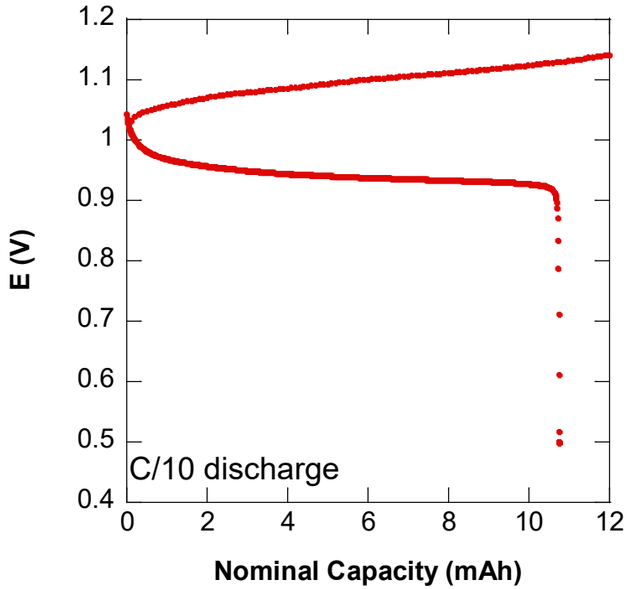


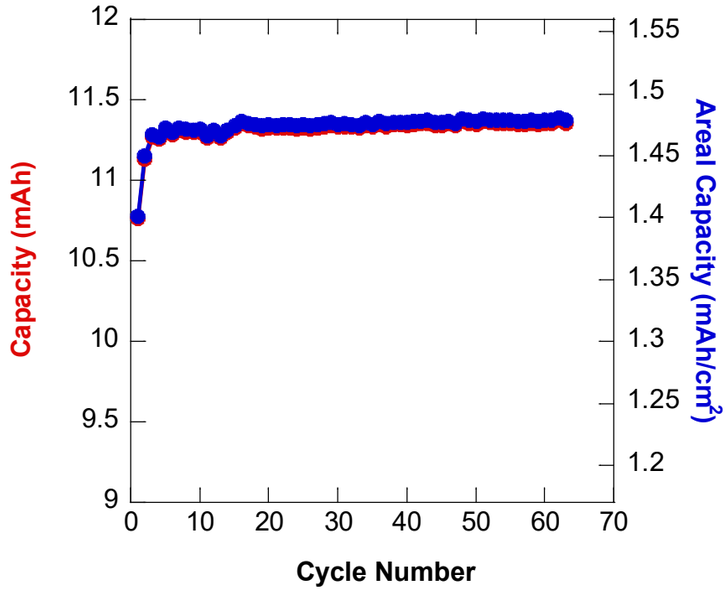


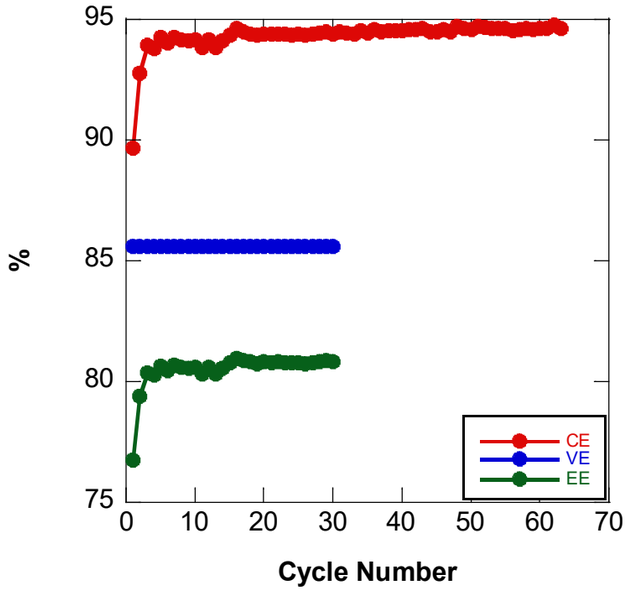


- The Cu anode is promising both for quick charge and long duration applications.
- It can last > 200 cycles (>2000 hr) with 10hr discharge and 1000 cycles (1000 hr) with 0.5 hr discharge.

Mn-Cu Proof of Concept

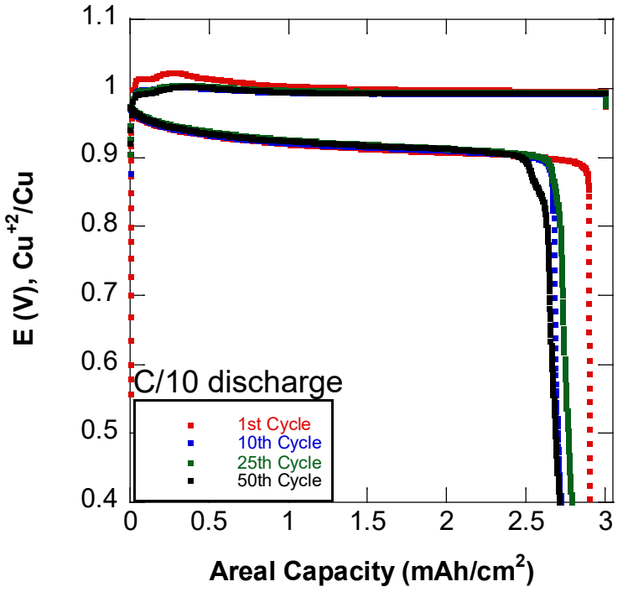


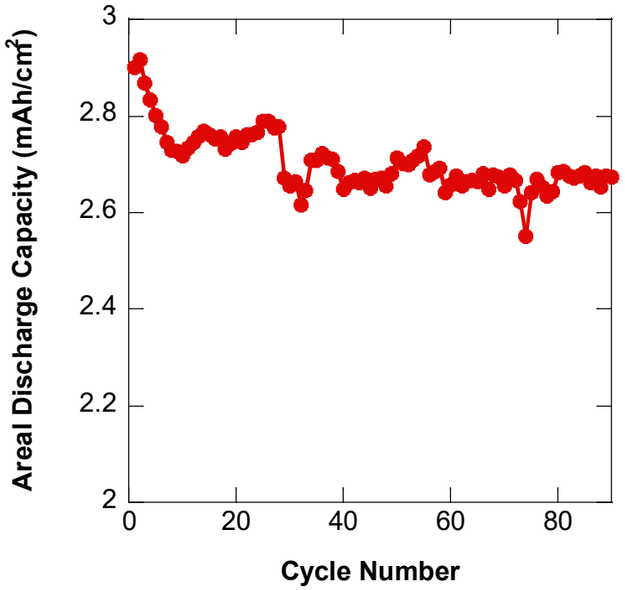


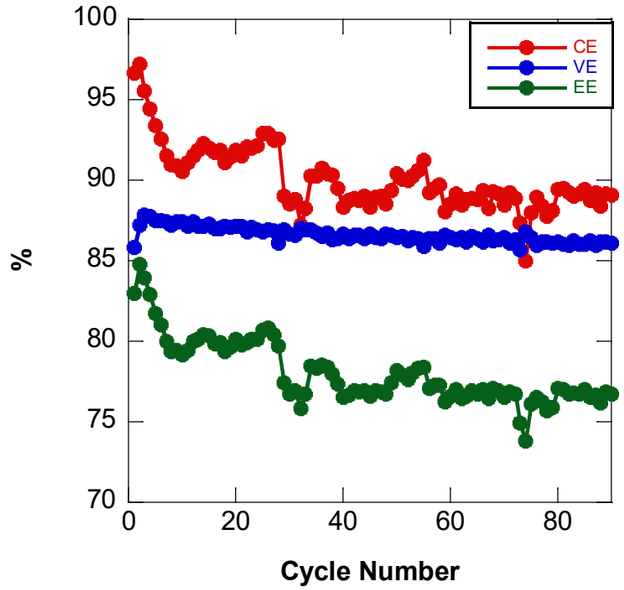


- By pairing Cu with Mn, a proof-of-concept cell has been demonstrated with a high discharge voltage of 0.9V vs Cu^{+2}/Cu.
- It can cycle at areal capacities over 1.4 mAh/cm^2 for over 60 cycles with an average CE of 94%(~60 hr).

Mn-Cu Scale-up

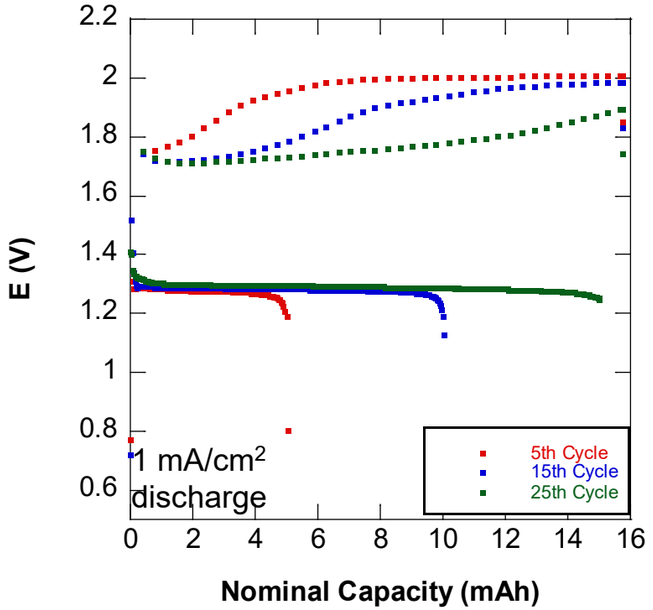


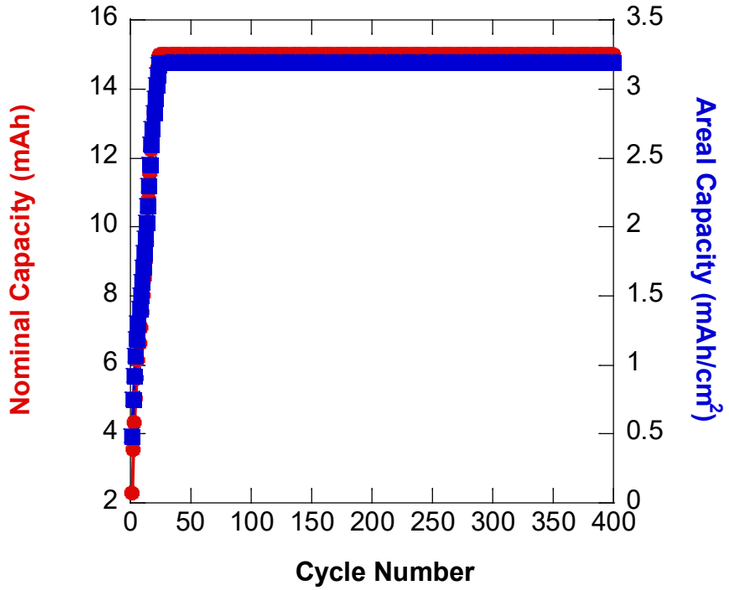


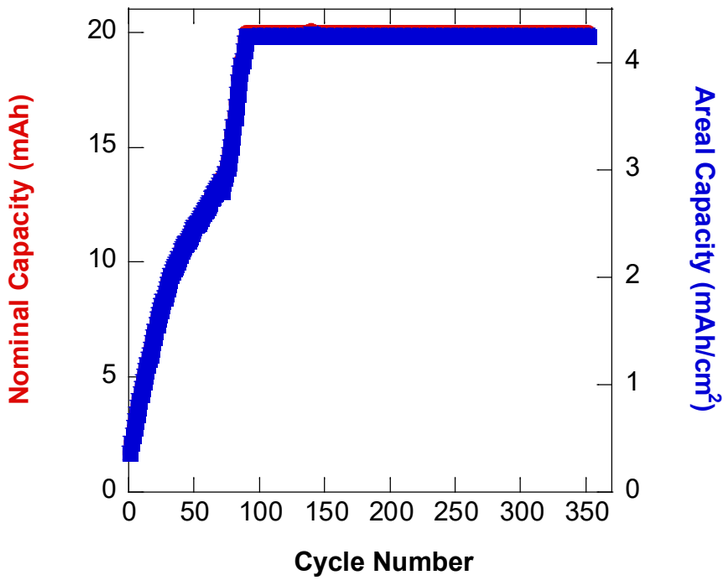


- The Mn-Cu cell significantly improves the performance of the cathode reaction compared to traditional EMD chemistry.
- It can cycle at areal capacities over 2 mAh/cm^2 for over 50 cycles with an average CE of 90%(~100 hr).

PbO_2/Cu







- The PbO_2/Cu cell significantly improves the anode durability of the Lead Acid battery compared to the Lead Anode.
- It can cycle at areal capacities over 3 mAh/cm^2 for over 300 cycles with an average voltage of 1.3V.

Summary

- An DTT cathode has demonstrated a specific capacity of ~110 mAh/g and > 90% retention over 200 cycles at a loading of >1 mAh/cm^2.
- A Zn alloy anode can cycle 300 hr (~150 cycles) at ~7.5 mAh/cm^2 loading and ~10 mA/cm^2 current density without shorting. 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 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 100 cycles under 10 hr charge/discharge regime and 1000 cycles under a 0.5 hr charge/discharge regime.
- A PbO_2/Cu Cell can cycle over 200 cycles at areal capacities greater than 3 mAh/cm^2 with a high voltage of 1.3V vs Cu^{+2}/Cu.

Proposed Work for FY2023

- Continue to improve the cycling stability of Zn-based anodes
- Further improvement of the Mn-Cu Cells and PbO_2/Cu
- Further development of low-cost cathode materials

Acknowledgements

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Thank you