Pacific Northwest
NATIONAL LABORATORY

Aqueous Zn batteries with mild acid/neutral electrolyte

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DOE OE Peer Review

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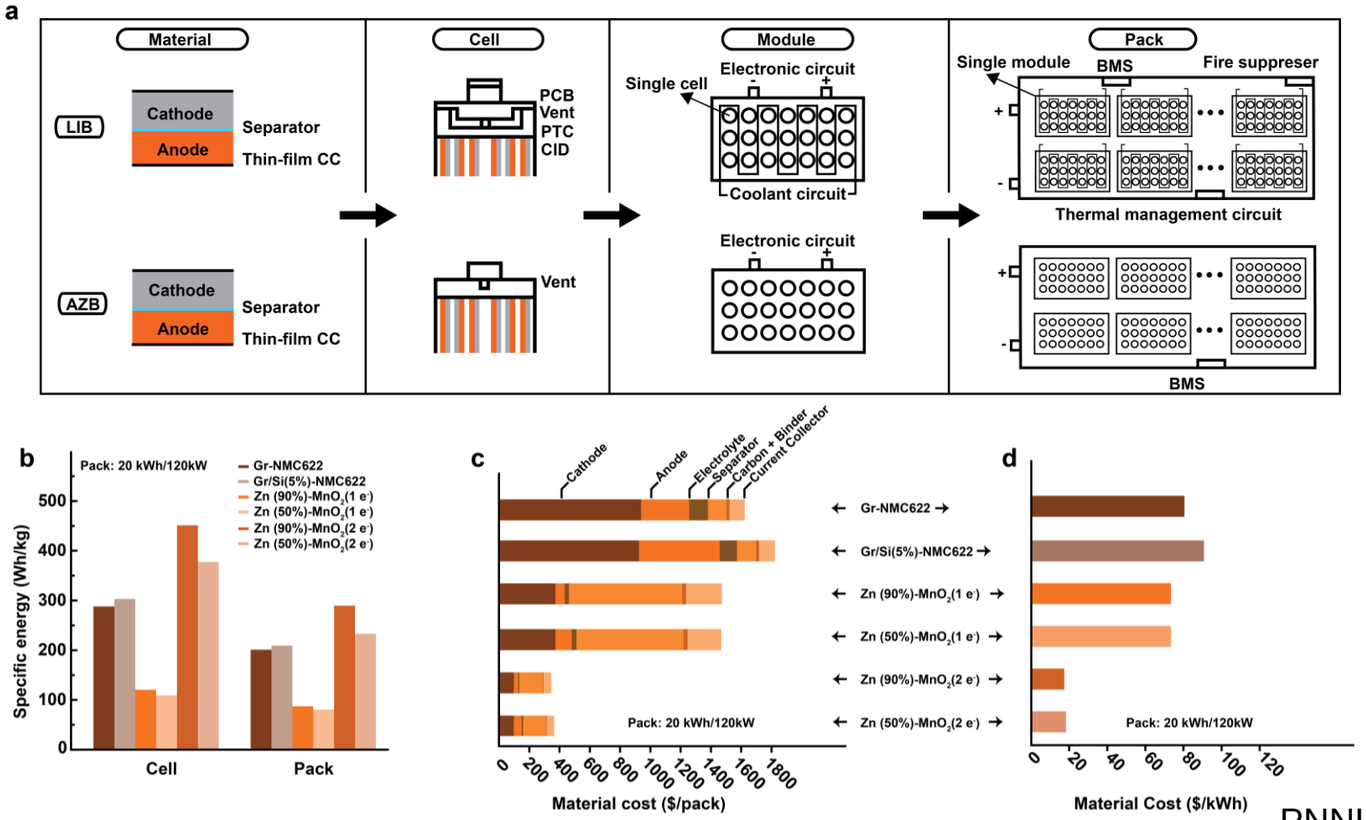
U.S. DEPARTMENT OF ENERGY BATTELLE

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

PROJECT OVERVIEW

- Aqueous Zn batteries using earth abundant materials (H_2O, Zn, MnO_2 etc) have high degree of safety, low cost, and high specific energy comparable to some Li-ion batteries. 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.
- The overall goal of the project is to develop rechargeable aqueous Zn battery chemistry and drive it to commercialization.

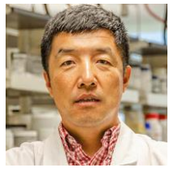


PNNL unpublished result

PROJECT TEAM

- **PNNL Contributors**
  - Matthew Fayette
  - Hee-Jung Chang
  - Hyungkyu Han
  - Ismael A Rodriguez Perez
  - Bhuvaneswari Sivakumar
  - Fredrick Omenya
  - Biwei Xiao
  - David Reed
  - Vincent L. Sprenkle

- **External Collaborators**
  - Prof. Xingbo Liu (West Virginia University)
  - Prof. Rohan Akolkar (Case Western Reserve University)
  - Prof. Sanjoy Banerjee (the City College of New Y
  - Dr. Kang Xu (Army Research Laboratory)
  - Prof. Nian Liu (Georgia Institute of Technology)



PROJECT OBJECTIVES

- 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.
- FY20 objectives/milestones
  (1) Demonstrate rechargeable Zn metal anode with stable cycling over 50 cycles at >0.5 mA/cm^2 current density (Achieved)
  (2) Benchmark MnO_2 cathode structure of medium loading (1.5 mAh/cm^2) for Zn-MnO_2 battery with >80% retention over 50 cycles (Achieved)
  (3) Quantification of the Mn^{2+} electrolyte additive contribution to the capacity in mild acid Zn-MnO_2 (On-going)
  (4) Publish 2 journal articles on Zn-MnO_2 technology (Achieved)

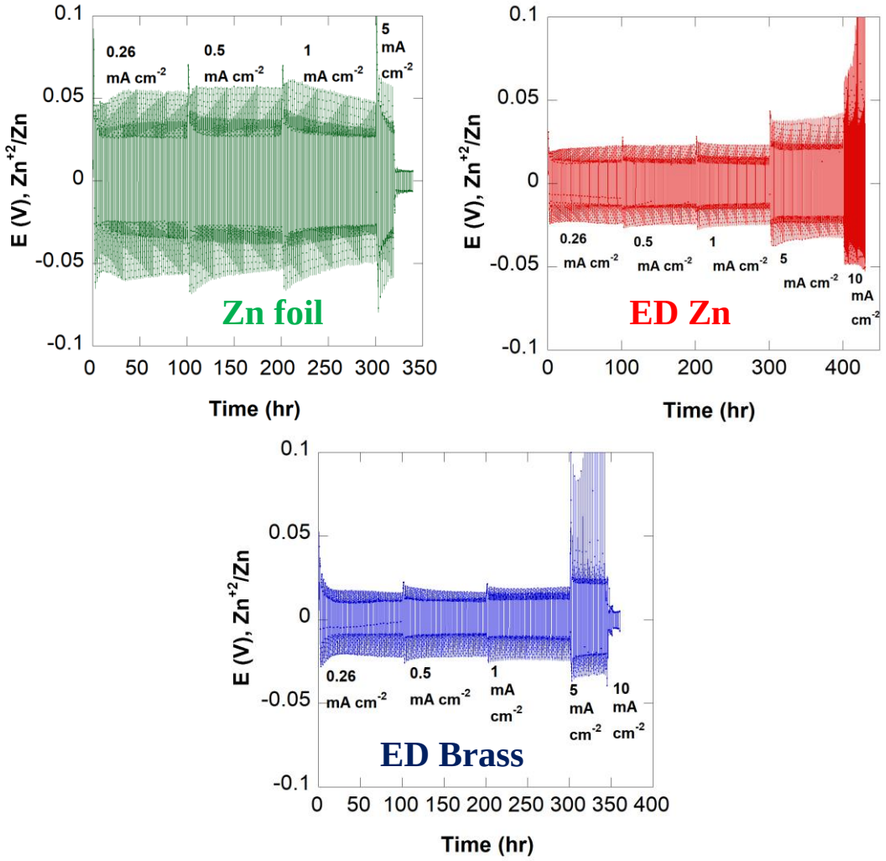
PROJECT ACHIEVEMENTS

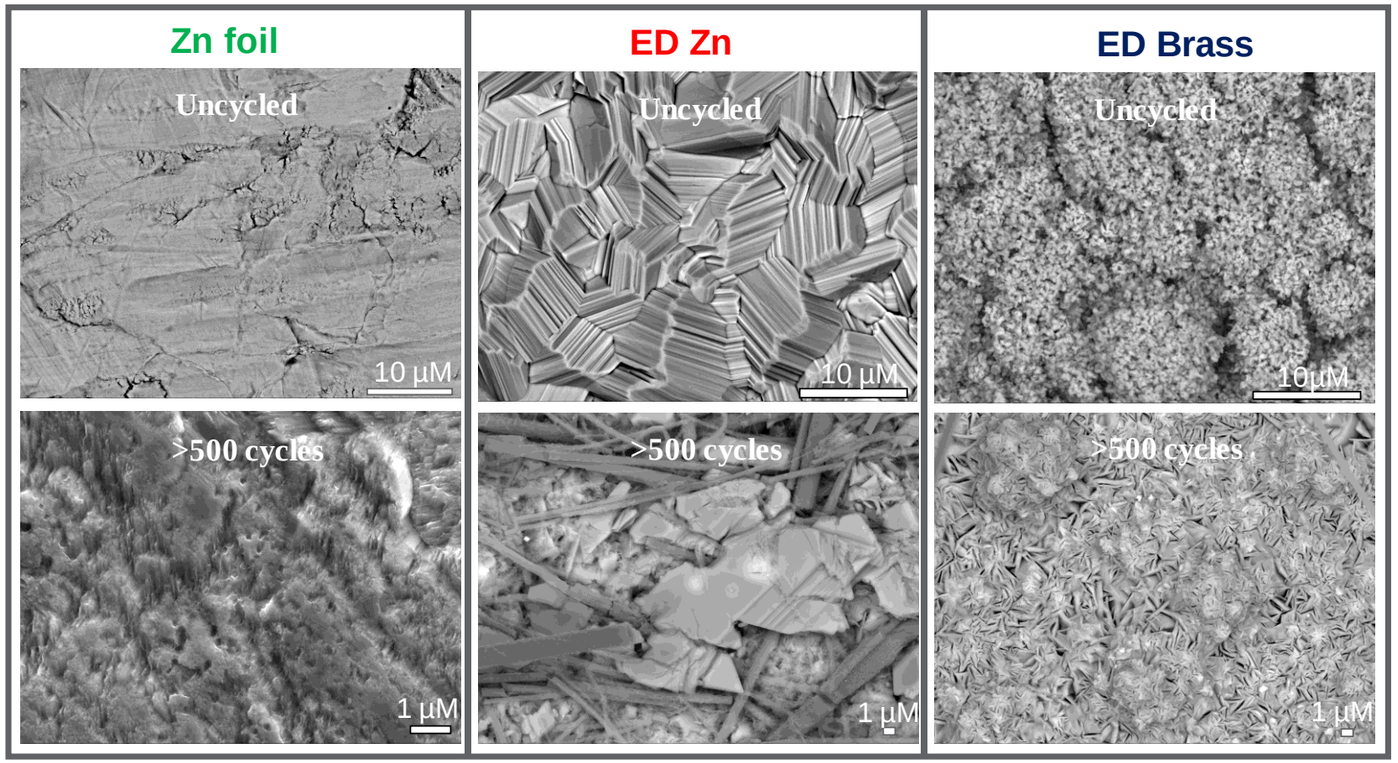
- **Research highlights**
  - (1) Zinc and brass anodes by electrodeposition show good stable cycling over 50 cycles in symmetric cells. (Milestone 1)
  - (2) Zn-MnO_2 battery with MnO_2 cathode of 1.5 mAh/cm^2 loading delivers >80% retention over 50 cycles. (Milestone 2)
  - (3) Mn^{2+} electrolyte additive deposits onto the cathode during charge and contributes to the capacity in mild acid Zn-MnO_2 batteries. (Milestone 3)
- **Publications: 3 papers published and 1 paper under preparation.**
  - (1) Matthew Fayette, et al. ACS. Appl. Mater. Interfaces 2020, accepted.
  - (2) Hee Jung Chang et al, Carbon Energy, 2020, accepted.
  - (3) Xiujuan Chen, et al. Nano Energy, 2020, 75, 104869. (with Prof. Xingbo Liu at WVU)
- **Collaborations established**
  - (1) Prof. Xingbo Liu at West Virginia University
  - (2) Prof. Rohan Akolkar at Case Western Reserve University
  - (3) Prof. Sanjoy Banerjee at the City College of New York
  - (4) Dr. Kang Xu at Army Research Laboratory
  - (5) Prof. Nian Liu at Georgia Institute of Technology
- **Professional activities to put OE in leading position of aqueous Zn battery development**
  - (1) Organized a symposium (Challenges in Battery Technologies for Next-Generation Electric Vehicles and Grid Storage Applications) at the 2019 Materials Research Society Fall meeting (December 2019)
  - (2) Contribute 3 presentations to the NAATBatt workshop on Zinc Battery Technology (November 2020).

PROJECT RESULTS

More detail in the poster by Matthew Fayette et al.

Electrodeposited (ED) Zn and brass anodes have improved tolerance to vertical dendrites compared to Zn foil.





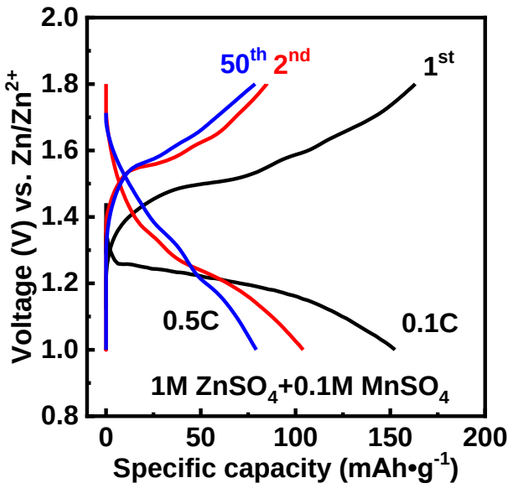
SEM images of Zn anodes before and after cycling in MnO_2-Zn full-cells

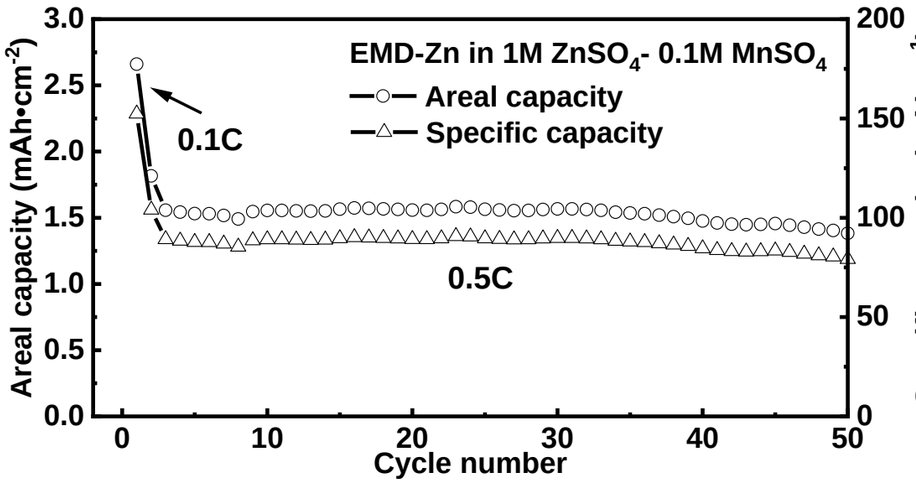
- At <5 mA/cm^2, ED anodes have lower polarization (symmetric cells) compared to Zn foil (0.025V vs. 0.050V)
- At >5 mA/cm^2, ED Zn and brass anodes (symmetric cells) have enhanced stability to shorting compared to Zn foil.

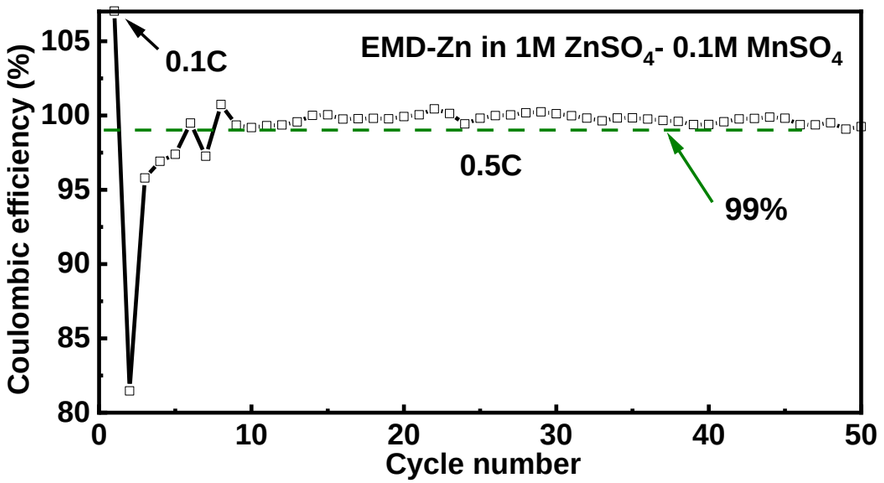
Matthew Fayette, et al. ACS. Appl. Mater. Interfaces 2020, accepted

PROJECT RESULTS

EMD-Zn cell shows good cycling stability at medium loading of ~1.5 mAh/cm^2





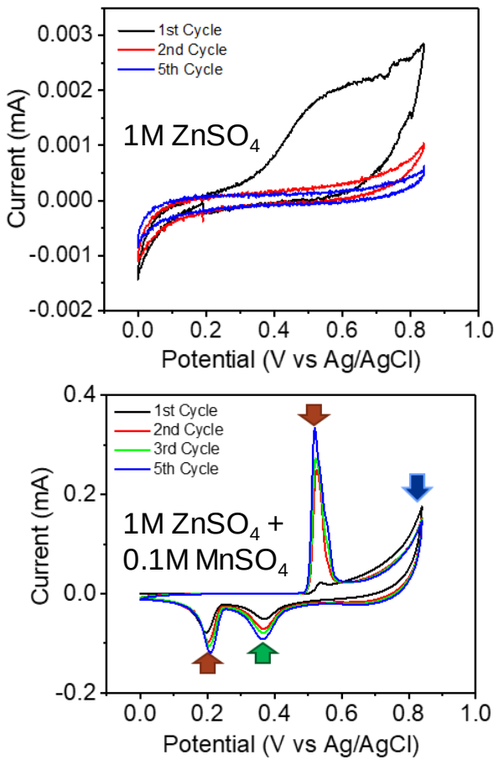


- A specific capacity of >150 mAh/g at 0.1C (1C= 308 mA/g) was achieved with >65 wt% EMD in the electrode
- Capacity retention >80% (compared to the 3rd cycle) has been achieved
- Cycling coulombic efficiency of >99% at 0.5C
- Cycling stability decreases if the specific capacity is >200 mAh/g
- Further improvement is undergoing.

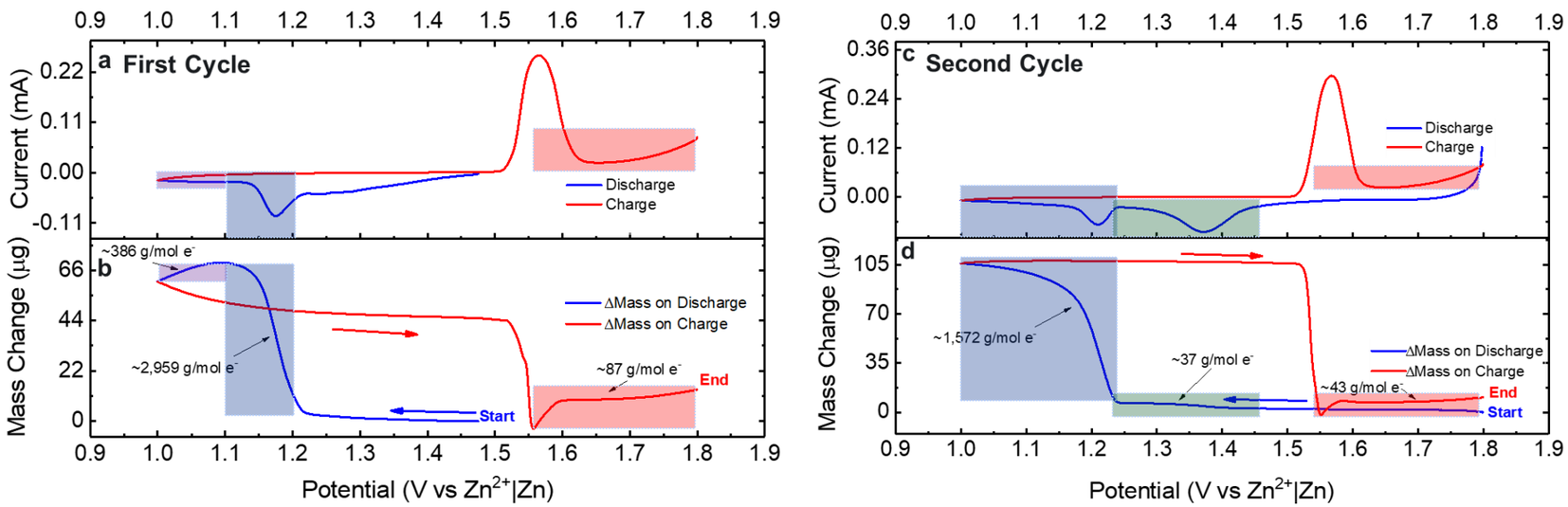
PROJECT RESULTS

Mn^{2+} electrolyte additive deposits onto the cathode during charge and contributes to the capacity

CV of acetylene black



Electrochemical Quartz Crystal Microbalance (EQCM) studies of EMD cathode



Cathode structure change and complex salt of $Zn_4(OH)_6(SO_4)*nH_2O$ deposition during discharge and dissolution during charge.

- Mn^{2+} additive deposits on the cathode in the charging process
- Further investigation is needed to fully understand the reaction mechanism of EMD in mild acid system

PNNL unpublished result

SUMMARY

- Zn and Zn_xCu_{1-x} (brass) alloys by electrodeposition show reduced polarization and improved tolerance to vertical dendrite compared to Zn foil. They have demonstrated good stability over 50 cycles at various current densities.
- EMD with medium loading (~1.5 mAh/cm^2) shows good cycling stability in mild acid electrolyte.
- Mn^{2+} additive deposits onto the cathode during charging process and involves in the following redox reactions.

PROPOSED WORK FOR FY21

- Further improvement of the cycling stability of Zn anodes
- Evaluate the performance of MnO_2 cathodes with ~3mAh/cm^2 loading
- Further investigation of the reaction mechanism using in-situ/post-mortem analyses
- Development of novel low-cost Zn battery cathode materials

ACKNOWLEDGEMENTS

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PROJECT CONTACTS

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Thank You!

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