Pacific Northwest
NATIONAL LABORATORY

Advanced Aqueous Zn Batteries

Xiaolin Li

DOE OE Peer Review

October 26-October 28, 2021

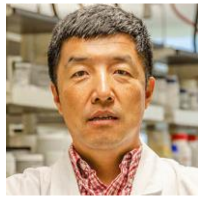
U.S. DEPARTMENT OF ENERGY BATTELLE

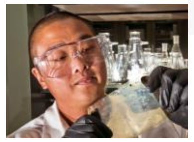
PNNL is operated by Battelle for the U.S. Department of Energy

PROJECT TEAM

- **PNNL Contributors**
  - Matthew Fayette
  - Hee-Jung Chang
  - Hyungkyu Han
  - Biwei Xiao
  - Bhuvaneswari Sivakumar
  - Fredrick Omenya
  - Qian Huang
  - David Reed
  - Vincent L. Sprenkle

- **External collaborators**
  - Prof. Xingbo Liu (West Virginia University)
  - Prof. Rohan Akolkar (Case Western Reserve University)
  - 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 OVERVIEW & 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.
- FY21 objectives/milestones
  (1) Benchmark EMD MnO_2 cathode structure to achieve >100 mAh/g specific capacity at a loading of ~3 mAh/cm^2. (Achieved)
  (2) Demonstrate rechargeable Zn metal anode with stable cycling over 200 cycles at >1 mA/cm^2 current density. (Achieved)
  (3) Develop a new low-cost Zn intercalation cathode with > 100 mAh/g specific capacity and 80% retention over 50 cycles. (Achieved)
  (4) Publish 2 journal articles on Zn-MnO_2 technology. (Achieved)

PROJECT ACHIEVEMENTS

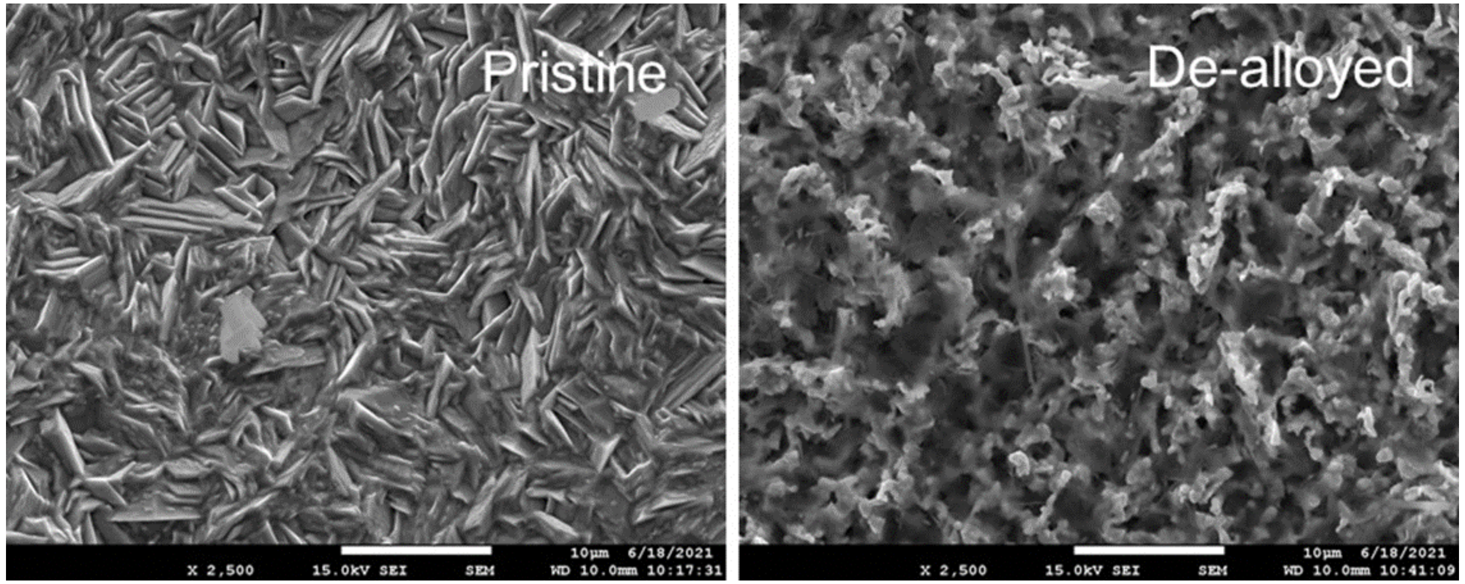
- **Research highlights**
  1. (1) MnO_2 cathodes with controlling the electrode porosity or tuning the electrolyte and cell design can deliver a specific capacity of > 200 mAh/g at a loading of ~3 mAh/cm^2.
  2. (2) A Zn alloy anode can cycle 700 hr (~700 cycles) at ~5 mAh/cm^2 loading and ~10 mA/cm^2 current density without dendrite. 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. (3) Surface coating and electrolyte additive selective adsorption also have been investigated to mitigate the dendrite formation on Zn foil. Polymer coating enabled preferential Zn deposition and smooth surface. The concept and feasibility of electrolyte additive selective adsorption enables localized dendrite suppression also has been demonstrated.
  4. (4) An organic intercalation cathode has demonstrated a specific capacity of ~140 mAh/g and > 90% retention over 500 cycles.
- **Publications: 3 papers published and 2 papers under preparation.**
  1. (1) J.H. Song, et al., ***Materials Today*** 2021, 45, 191-212
  2. (2) I.A. Rodriguez-Perez, et al. ***J. Mater. Chem. A*** 2021, 9, 20766.
  3. (3) X.J. Chen, et al. ***Chem. Eng. J.*** 2021, 405, 126969.
- **Society impact and STEM outreach**
  1. (1) One MRS symposium on “Advanced Materials and Chemistries for Low-Cost and Sustainable Batteries”
  2. (2) One PhD student supported by the subcontract with West Virginia University graduated this year and will stay on as a postdoc.
  3. (3) The postdoc supported by the subcontract with Case Western Reserve University joined Sandia National Laboratory

PROJECT RESULTS: Zn metal

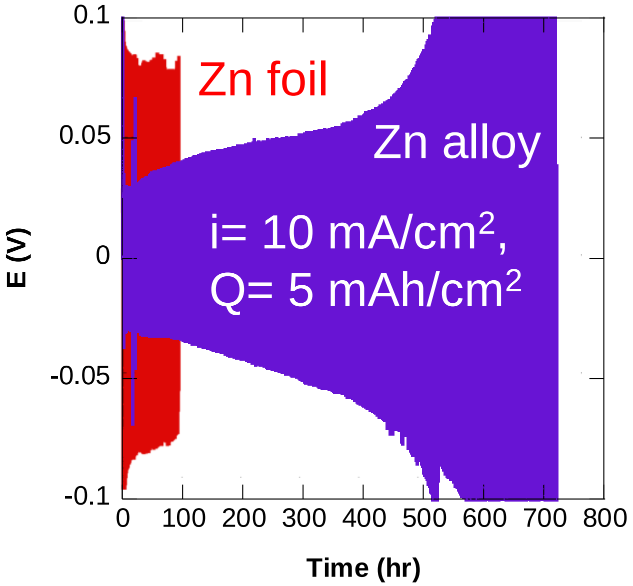
Matt Fayette

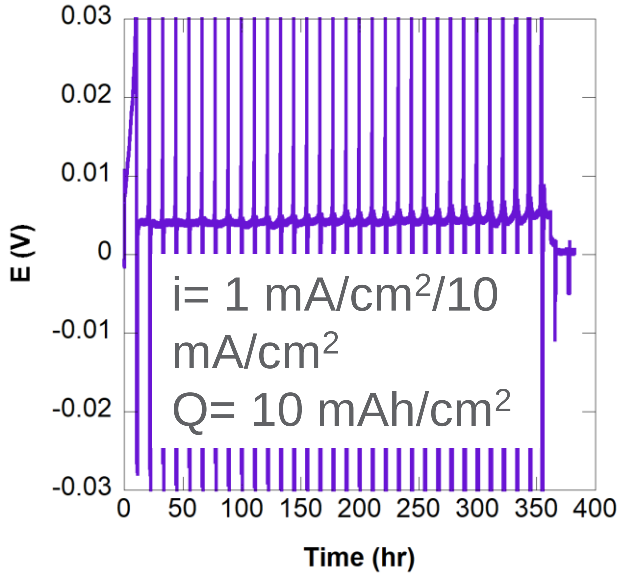
Zn alloy anodes

Anode morphology



Performance in symmetric cells



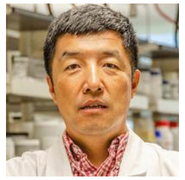


- The Zn alloy anode significantly improves the tolerance to dendrites by forming porous structure after stripping off the Zn content.
- It can cycle 700 hr at a capacity of ~5 mAh/cm^2 and a current density of ~10 mA/cm^2 (700 cycles), much better than the Zn foil tested at similar conditions (~100 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.
- See Matt's poster for more detail results.

Matthew Fayette, et al. manuscript in preparation

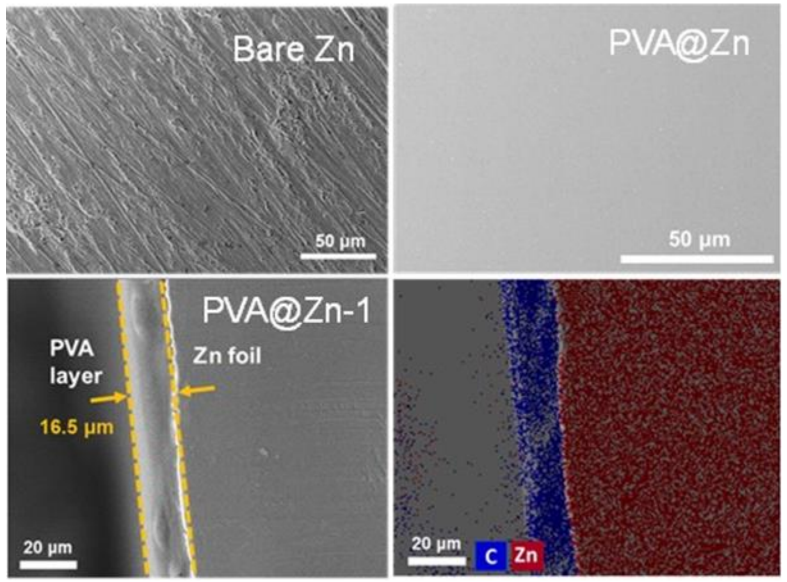
PROJECT RESULTS: Zn metal

Dendrite suppression with Polyvinyl alcohol (PVA) Coating



PI: Xingbo Liu

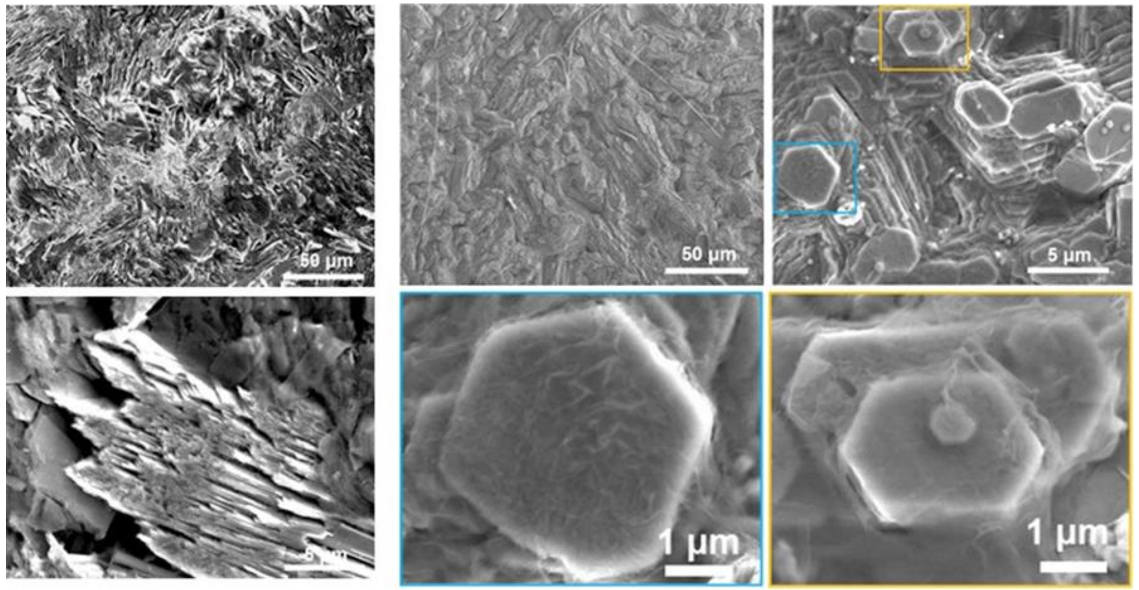
Zn foil morphology



PVA-coating (~17 micron) enables a smooth surface morphology

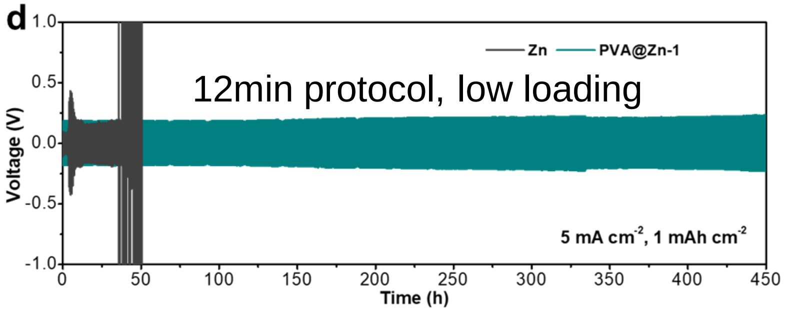
Cycled Zn electrode

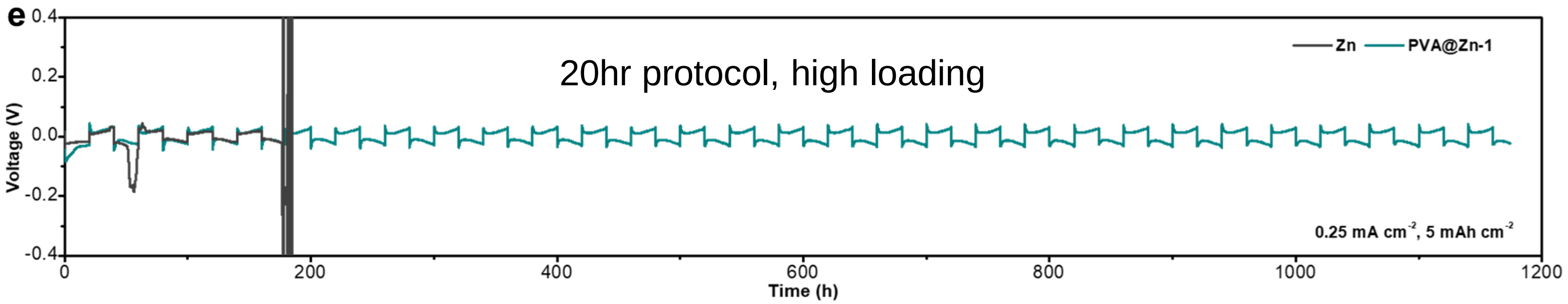
Cycled PVA@Zn electrode



PVA-coated Zn shows preferential deposition along $(002)_{Zn}$ while bare Zn shows dendrite.

PVA@Zn electrode shows good cycling stability in symmetric cells





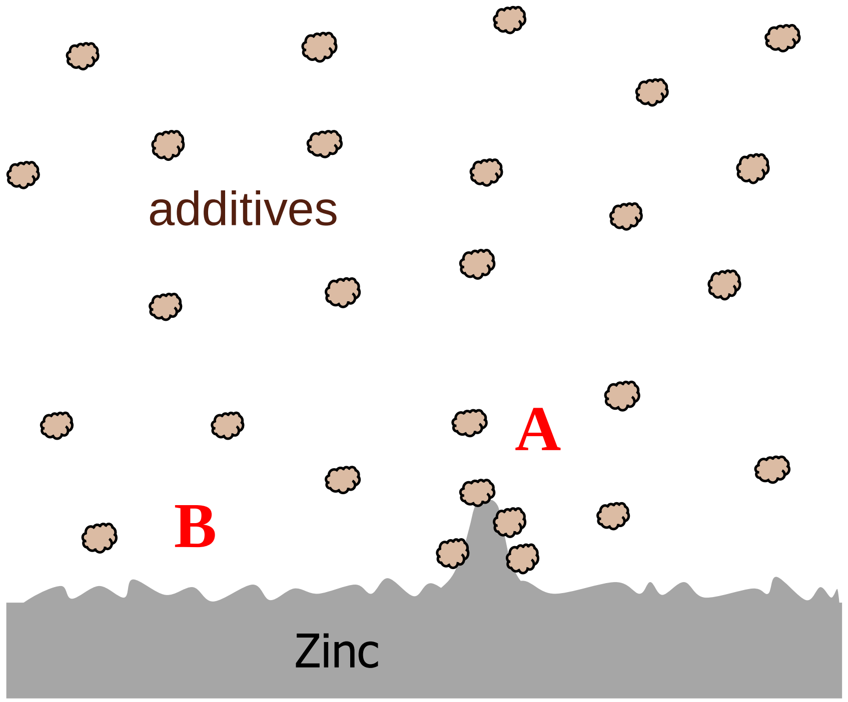
PVA-coated Zn foil can cycle 450 hr at low areal capacity and >50 cycles (> 1000 hr) at high loading and 20hr discharge.

X. Liu, et al. manuscript in preparation

PROJECT RESULTS: Zn metal

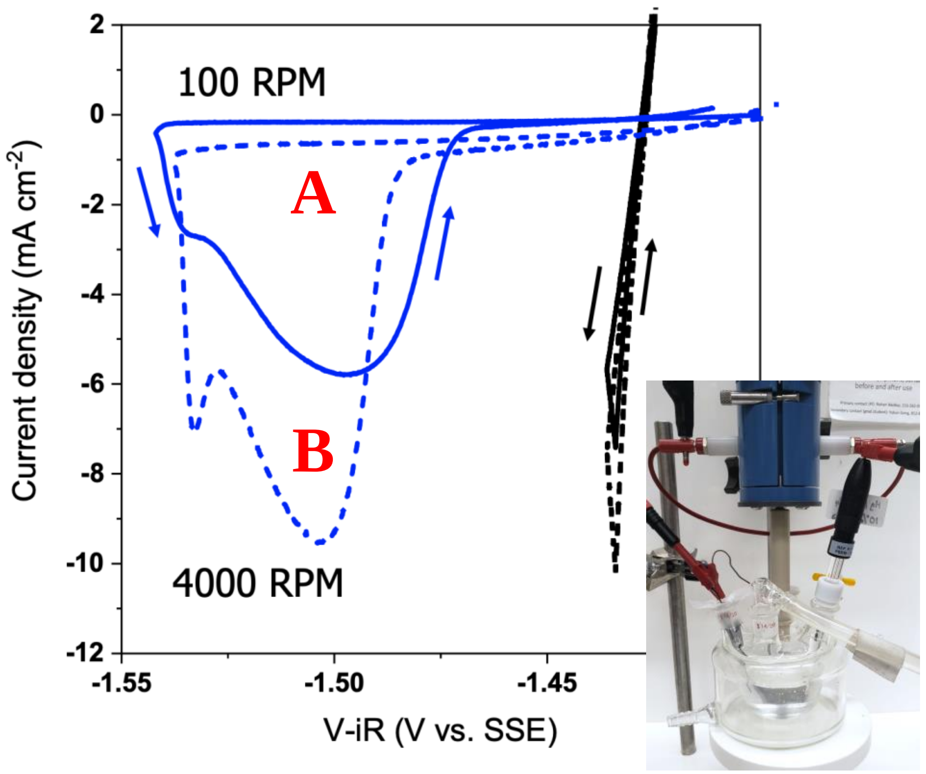
Selective electrolyte additive adsorption

PI: Rohan Akolkar



<u>Concept of selective additive adsorption:</u>
A = additive diffuses fast and adsorbs
B = additive-free because slow transport

Selective adsorption enables localized dendrite suppression while preserving high voltaic efficiency



On rotating disk electrode, voltammetry in the presence of 40 μM BDAC (additive) shows hysteresis. Polarized state refers to additive adsorption (A) and depolarized state refers to additive-free (B)

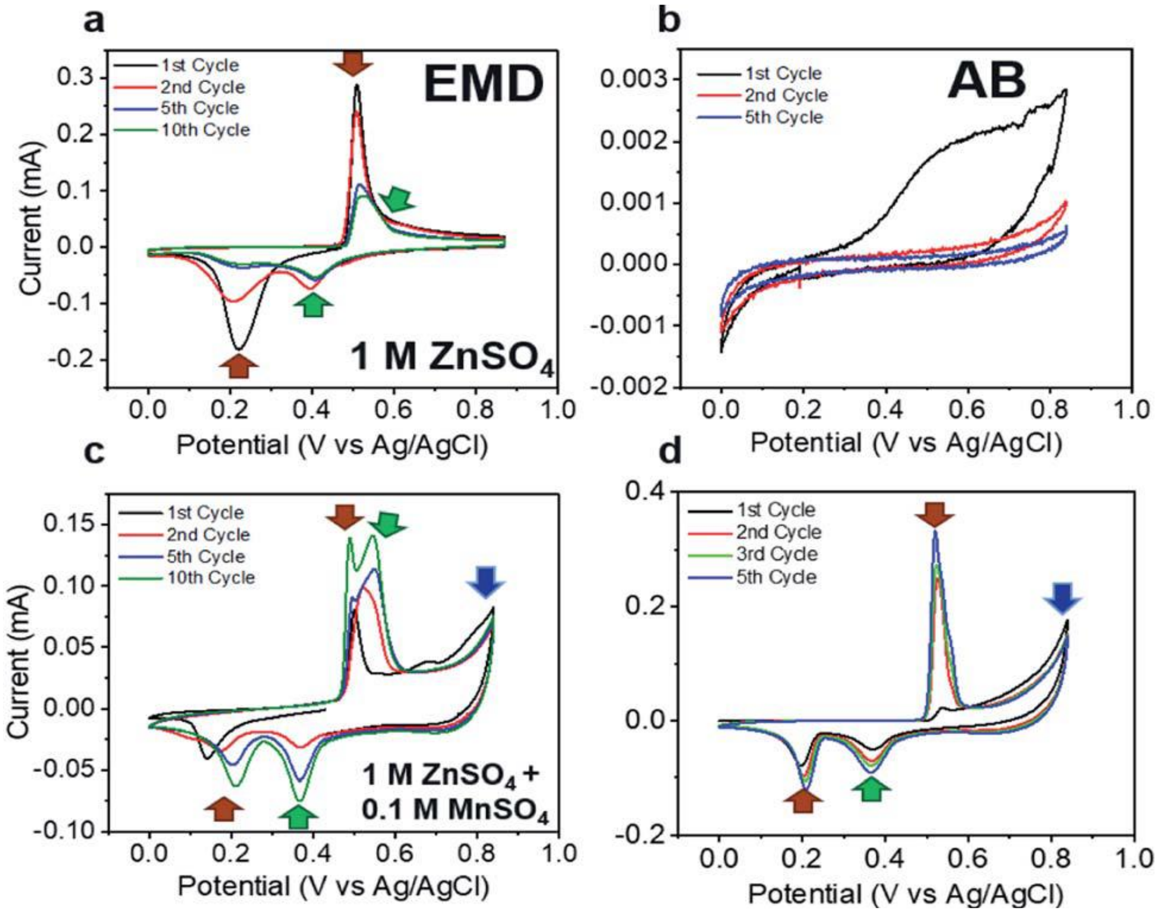
- Fundamental additive behavior needed for selective Zn dendrite suppression has been demonstrated.
- Several additives and their concentration ranges were identified based on polarization measurements on RDE.
- Performance on Zn anode half-cells during deposition/stripping to be investigated.

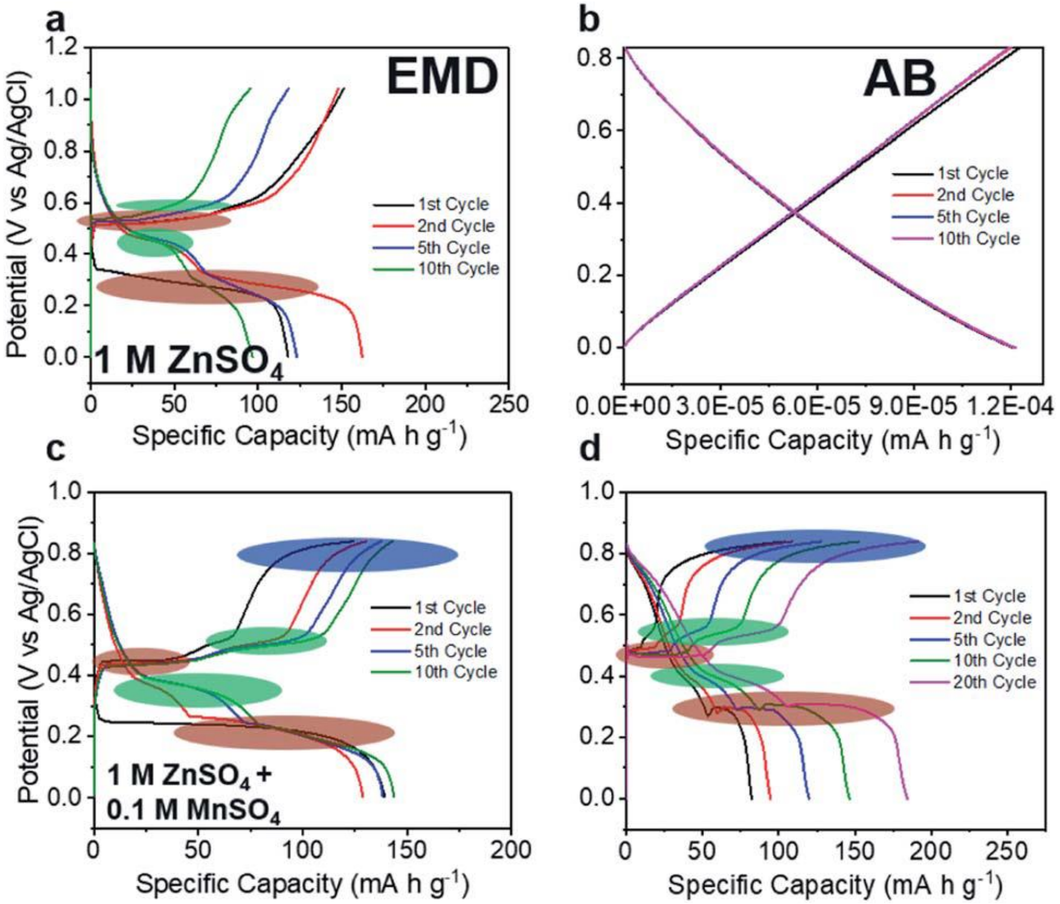
Adam Maraschky & Rohan Akolkar, unpublished result.

PROJECT RESULTS: MnO_2

Understanding the redox processes in Zn-MnO_2 battery


Hee-Jung Chang
Matt Fayette





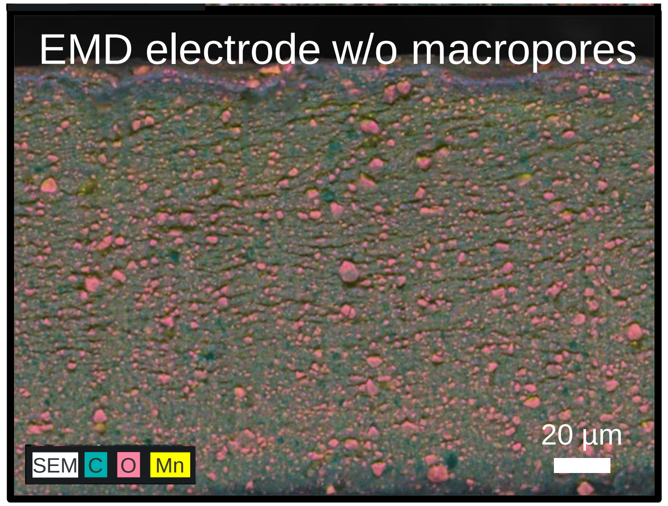
- Mn^{2+} additive in the electrolyte can deposit on the cathode during charging (0-0.8V vs. Ag/AgCl is ~1-1.8V vs. Zn)
- See Hee-Jung's poster for more results.

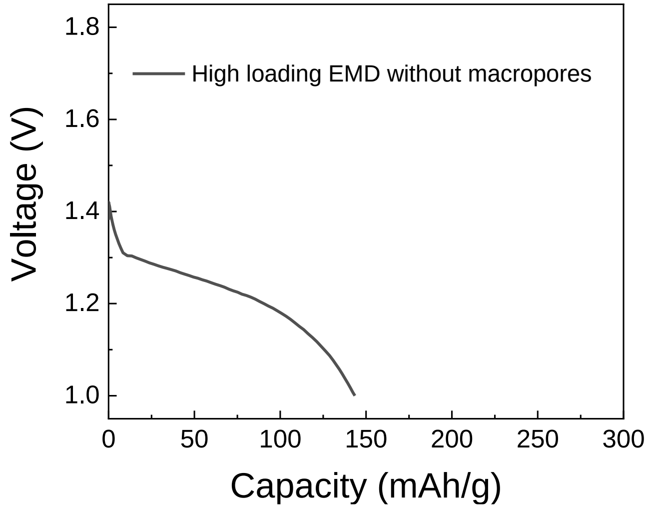
I.A. Rodriguez-Perez, et al. J. Mater. Chem. A 2021, 9, 20766

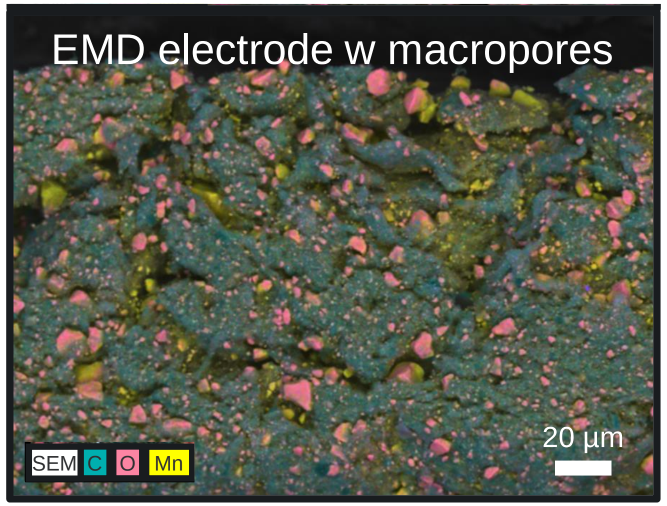
PROJECT RESULTS: MnO_2

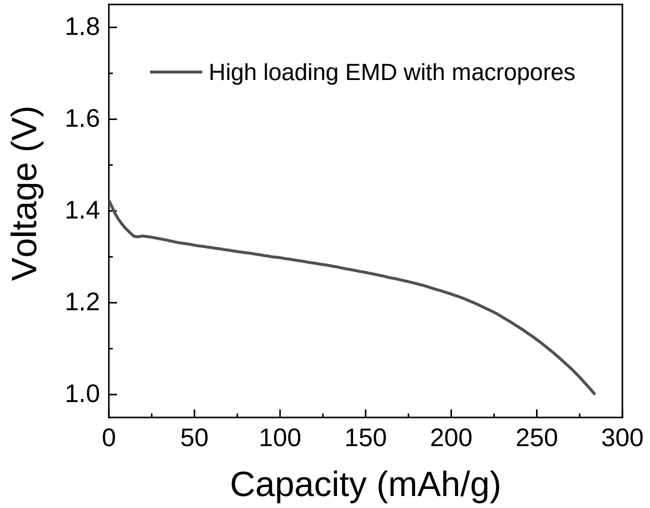
EMD cathode: porosity control

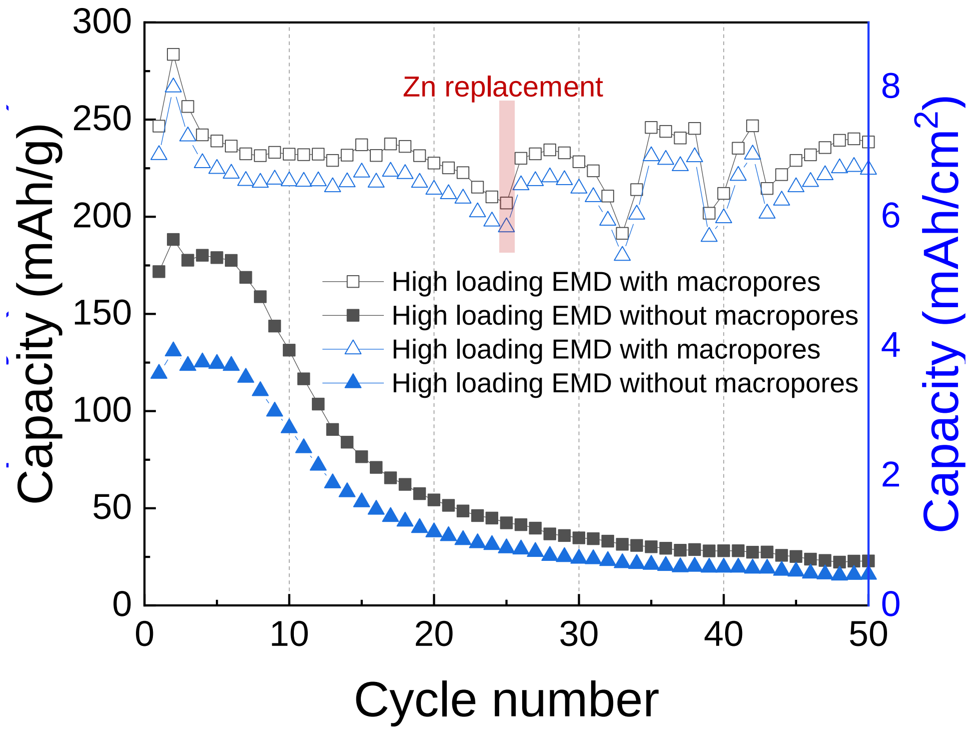
Hyungkyu Han









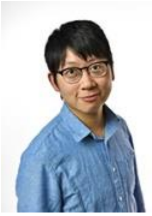


- EMD cathodes with improved porosity can deliver a specific capacity of >250 mAh/g, ~40% higher than that of the regular EMD cathodes. The electrode areal capacity is ~3 mAh/cm^2.
- The porous electrode also delivers improved cycling stability.

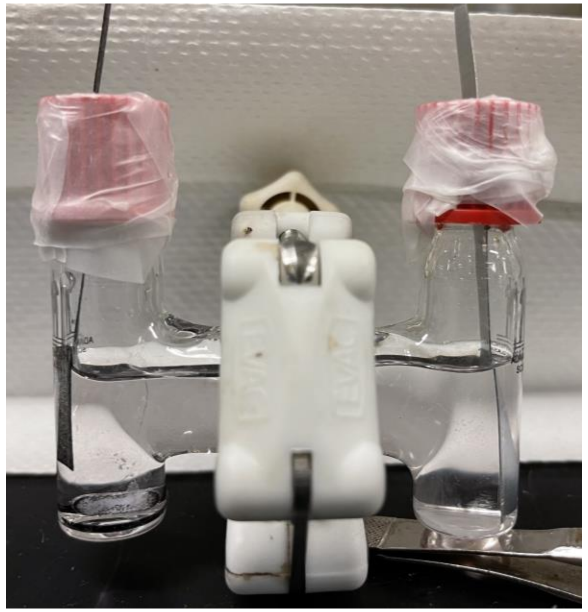
Hyungkyu Han, et al. manuscript in preparation

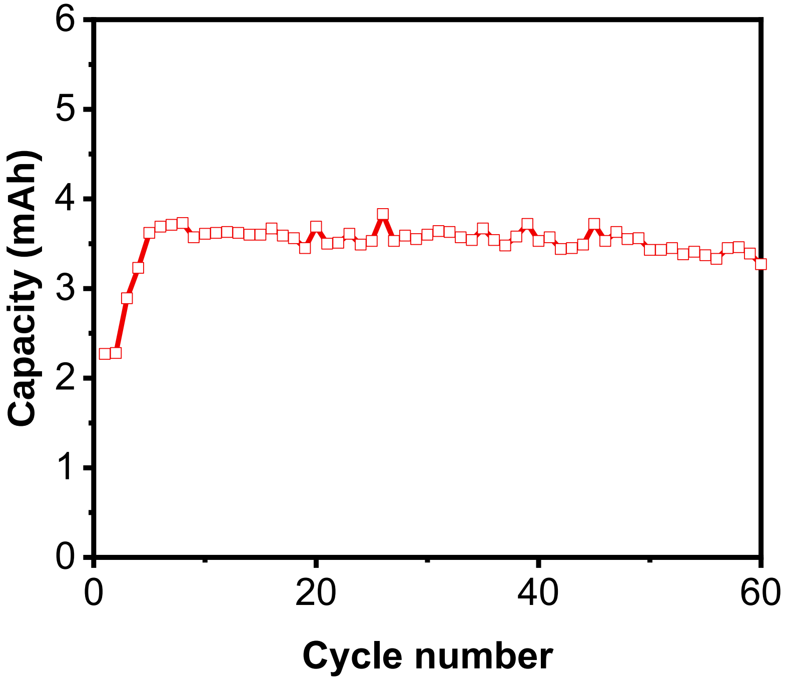
PROJECT RESULTS: MnO_2

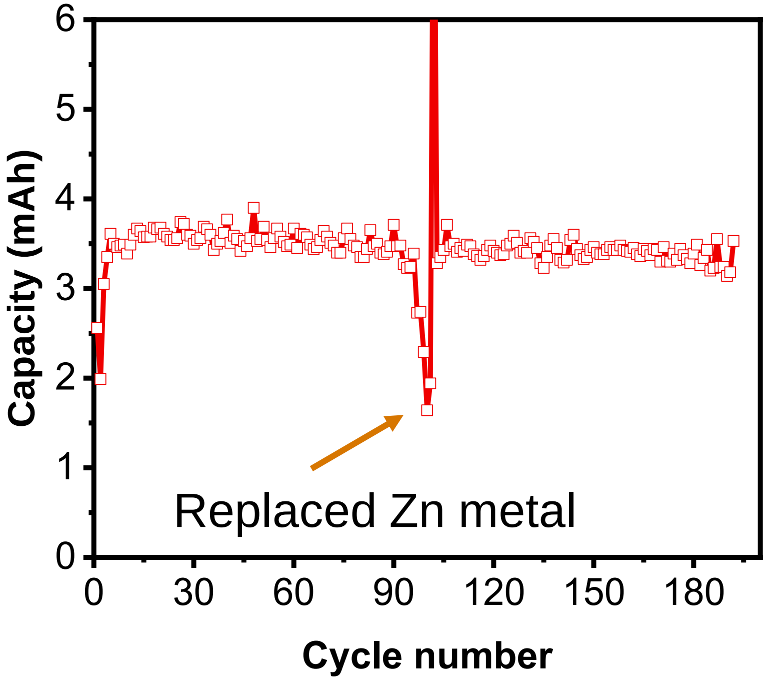
Tuning the electrolyte and cell design



Biwei Xiao







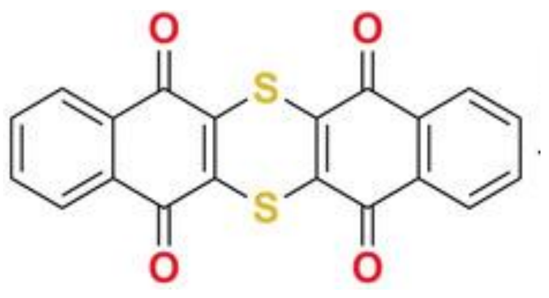
- Tuning the electrolyte and cell design enables good cycling stability of MnO_2 cathodes. The battery can have >90% capacity retention over tens of cycles at an areal capacity of ~3 mAh/cm^2.
- Zn metal anode has significant contribution to the battery fading after long term cycling. The cell capacity can be recovered after switching to a fresh Zn metal anode.
- Further improvement of the system including fine tuning of the electrolyte and metal anodes are undergoing.

PNNL unpublished results

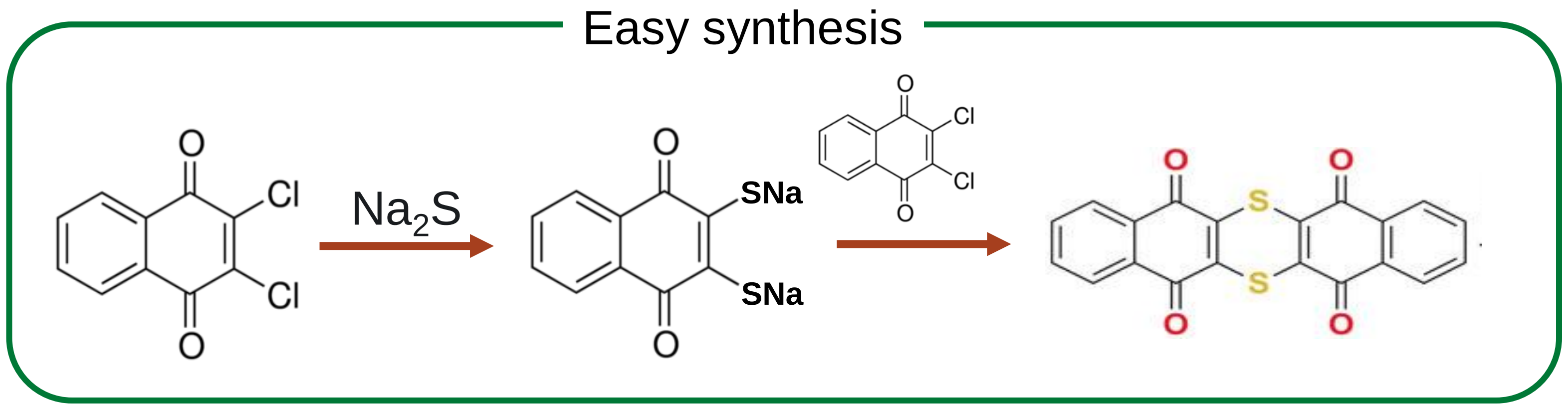
PROJECT RESULTS: NEW CATHODE

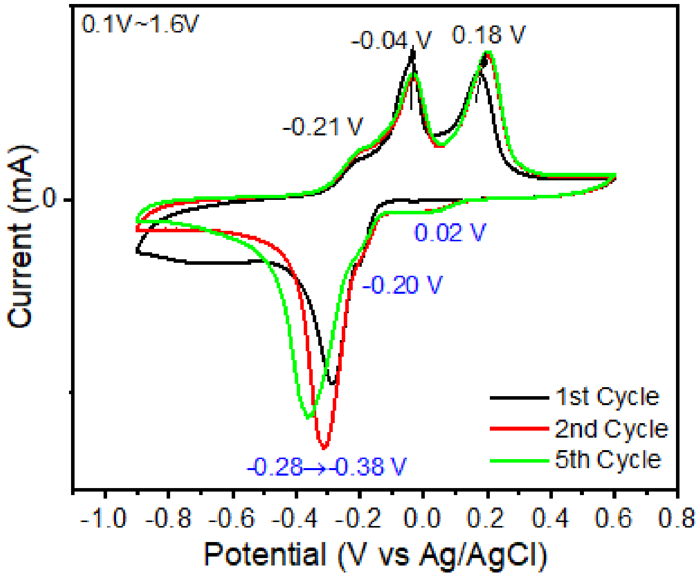
Hee-Jung Chang

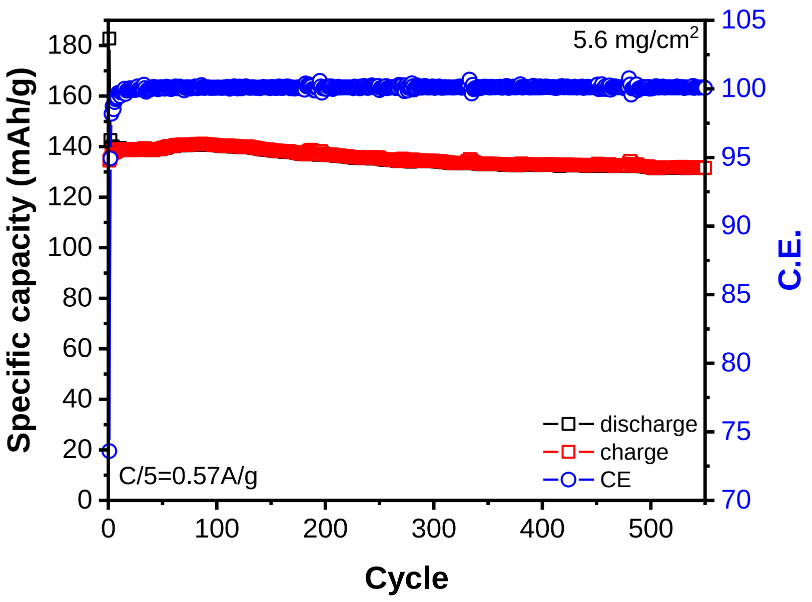
Organic intercalation cathodes

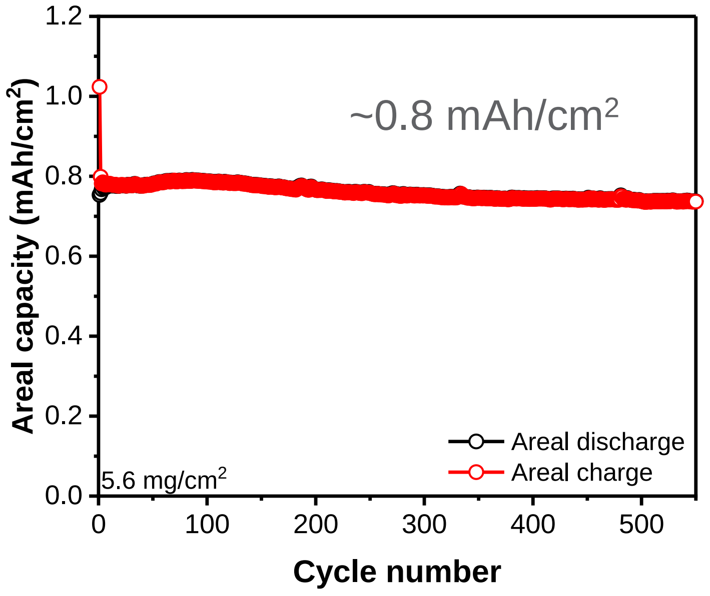


Sulfur heterocyclic quinone (DTT)









Inexpensive organics can be long-cycle life aqueous Zn battery cathodes. The DTT/Zn cell delivers a specific capacity of ~140 mAh/g (theoretical capacity of ~285 mAh/g) and > 90% capacity retention over 500 cycles.

Hee Jung Chang, et al. manuscript in preparation

SUMMARY

- Based on the understanding of the redox processes, MnO_2 cathodes with controlling the electrode porosity or tuning the electrolyte and cell design have demonstrated a specific capacity of > 200 mAh/g at an areal loading of ~3 mAh/cm^2.
- A Zn alloy anode can cycle 700 hr (~700 cycles) at ~5 mAh/cm^2 loading and ~10 mA/cm^2 current density without dendrite. 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.
- Surface coating and electrolyte additive selective adsorption also have been investigated to mitigate the dendrite formation on Zn foil. Polymer coating enables a smooth surface and preferential Zn deposition, thus suppresses dendrite. The concept and feasibility of electrolyte additive selective adsorption enables localized dendrite suppression also has been demonstrated.
- An organic intercalation cathode has demonstrated a specific capacity of ~140 mAh/g and > 90% retention over 500 cycles.

PROPOSED WORK FOR FY22

- Continue to improve the cycling stability of Zn-based anodes
- Further improvement of the performance of high loading MnO_2 cathodes
- Further development of low-cost cathode materials

ACKNOWLEDGEMENTS

We appreciate the support from **Dr. Imre Gyuk**, manager of the Energy Storage Program, DOE Office of Electricity.

Thank You!