Sandia National Laboratories

Limited DOD Cycling Enabling Extremely Stable Cycling in Mildly Acidic Zn/MnO_2

Calvin D. Quilty[1], **Casey M. Davis[1]**, Lauren W. To[1], Timothy N. Lambert[1,2]

(1) Sandia National Laboratories (2) Center for Integrated Nanotechnologies

PROJECT PROFILE

Topic: Zinc & Lead Batteries | Vertical: Materials and Systems Innovation | Strategic Pathway: Grow

Project start and finish: FY25-FY27

PROBLEM

Zinc batteries are a promising technology for grid-based energy storage.

- Inexpensive, nontoxic, nonflammable, US-based supply chains
- Incorporation into the grid will improve reliability and is important for emerging technologies (*e.g.* AI data centers)

Currently, zinc batteries use alkaline electrolytes, but mildly acidic electrolytes may enable better reversibility at higher capacity (increased energy density and cycle life).

Cycling stability for commonly utilized MnO_2 cathodes is lacking.

Relatively heavy and expensive foils are often used as the cathode current collector (*e.g.* stainless steel, titanium).

APPROACH

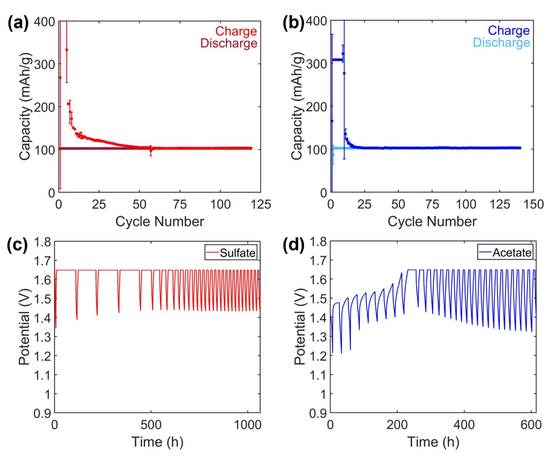
Zn/MnO_2 coin cells are cycled in mildly acidic electrolytes using a limited depth-of-discharge (DOD) protocol inspired by the alkaline system.[1]

The MnO_2 cathodes are aqueous-cast with non-fluorinated binder eliminating the need for organic solvents and per-fluoroalkyl substances.

Standard current collectors (Ti, stainless steel 316) are compared to lighter, less expensive Al current collectors as used in Li-ion batteries.[2]

Use of simple protocols and improved foils is promising for scale-up and manufacturing.

RESULTS—Titanium



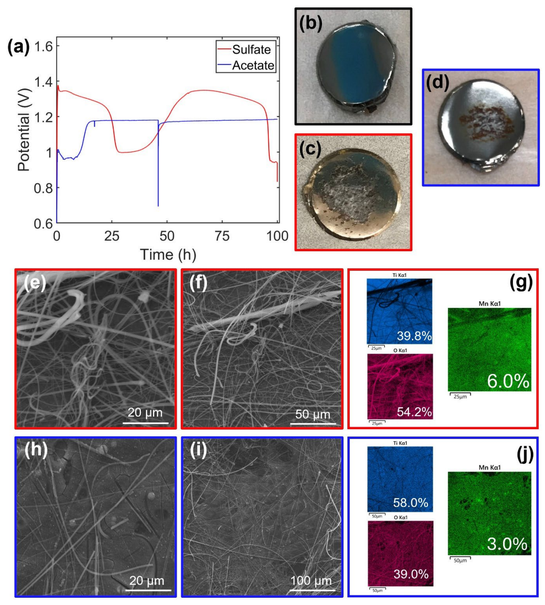
Zn/MnO_2 cells cycled under at 33% DOD (~103 mAh/g) with sulfate or acetate electrolyte.

Extremely stable cycling is observed for >100 cycles for titanium (shown) and stainless steel.

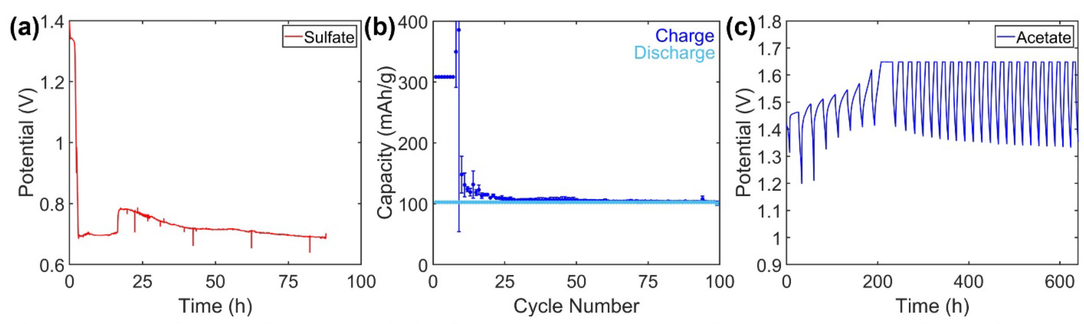
Break-in behavior is observed.

When a Ti foil "cathode" was charged, capacity was delivered and manganese oxide was deposited.

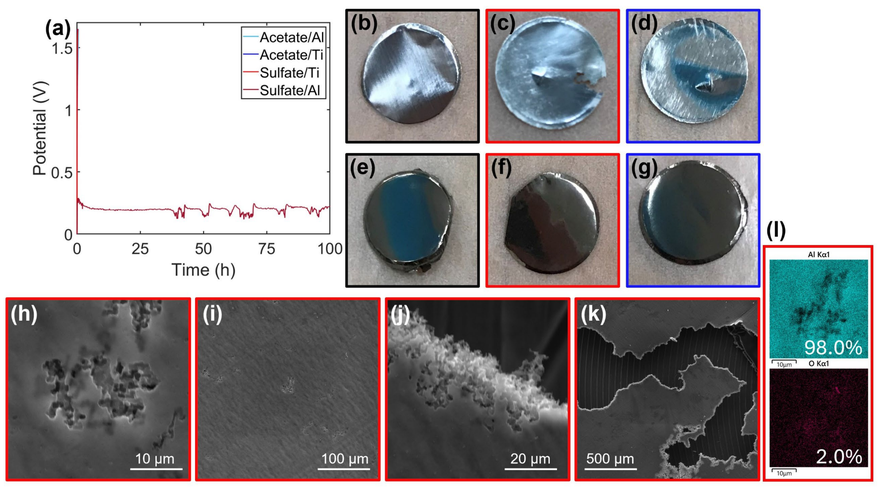
The oxidation of electrolyte Mn^{2+} species to manganese oxide on the cathode is a significant contributor to the early cycle charging break-in behavior observed.



RESULTS—Aluminum



Acetate electrolyte Zn/MnO_2 cells can cycle comparably with aluminum current collectors, while sulfate electrolyte leads to voltage instability.



Charging aluminum foil in acetate electrolyte (no added Mn^{2+}) or titanium foil in either electrolyte delivers minimal capacity.

Charging aluminum foil in sulfate electrolyte leads to significant corrosion (likely $2\ Al_{(s)} + 3\ SO_4^{2-}{}_{(aq)} \rightarrow Al_2(SO_4)_{3(aq)} + 6\ e^-$)

CONCLUSIONS & IMPACT

The long term cyclability of mildly acidic zinc-manganese oxide batteries can be greatly enhanced by using a limited DOD cycling protocol.

- No capacity losses for >100 cycles.

The protocol is likely to be highly scalable by virtue of its simplicity.

A near-neutral acetate electrolyte enables cycling with a lightweight, inexpensive aluminum current collector.

This work highlights a number of practical findings for improving the Zn-MnO_2 battery technology and it is anticipated that this will lead to further optimization in electrolyte engineering and cycling protocols towards facilitating the transition of mildly acidic Zn/MnO_2 from lab-scale to practical systems.

FUTURE DIRECTIONS

Scale-up of system: increase active material loading and increase thickness through use of larger form factors (prismatic, pouch *etc.*).

Determine how high DOD can be increased before cycling stability is compromised.

Technoeconomic analyses are ongoing to determine impact of current collector choice.

References

1. Kelly, M. and Lambert, T. N. *et al. J. Electrochem. Soc.*, **2017**, *164*, A3684-A3691.
2. Zhu, P. and Kendrick, E. *et al. J. Power Sources*, **2021**, *485*, 229321.

This material is based upon work supported by the U.S. Department of Energy, Office of Electricity (OE), Energy Storage Division. This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science. The views expressed in this article do not necessarily represent the views of the U.S. Department of Energy or the United States Government. This article has been co-authored by an employee of National Technology & Engineering Solutions of Sandia, LLC under Contract No. DE-NA0003525 with the U.S. Department of Energy (DOE). The employee owns all right, title and interest in their contribution to the article and is solely responsible for its contents. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this article or allow others to do so, for United States Government purposes. The DOE will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan https://www.energy.gov/downloads/doe-public-access-plan.

This material is based upon work supported by the U.S. Department of Energy, Office of Electricity (OE), Energy Storage Division.