Effect of ZnO-Saturated Electrolyte on Rechargeable Alkaline Zinc Batteries at High Depth-of-Discharge

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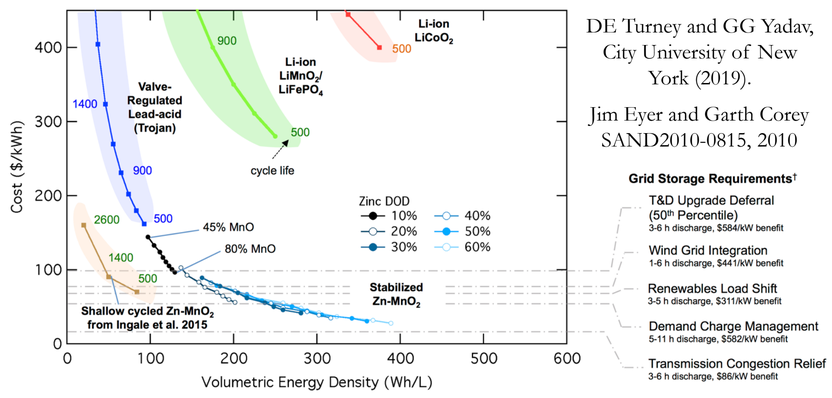
Background and Objectives

Zn/MnO_2 batteries for the grid: Energy-dense, safe, abundant, low-cost materials



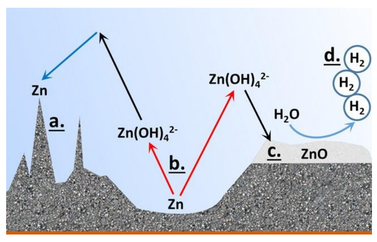
DE Turney and GG Yadav, City University of New York (2019).

Jim Eyer and Garth Corey SAND2010-0815, 2010

- Up to 400 Wh/L, 150 Wh/kg and ~$18/kWh as primary cell
- Commercialized by Urban Electric Power, ***but only under limited depth-of-discharge (DOD) conditions***
  - ~100 Wh/L, $200/kWh

Anode Issues to Address

- Shape change
- Dendrite formation
- Passivation
- H_2 evolution



J. Fu et al., *Adv. Mater.* 29, 1604685 (2017)

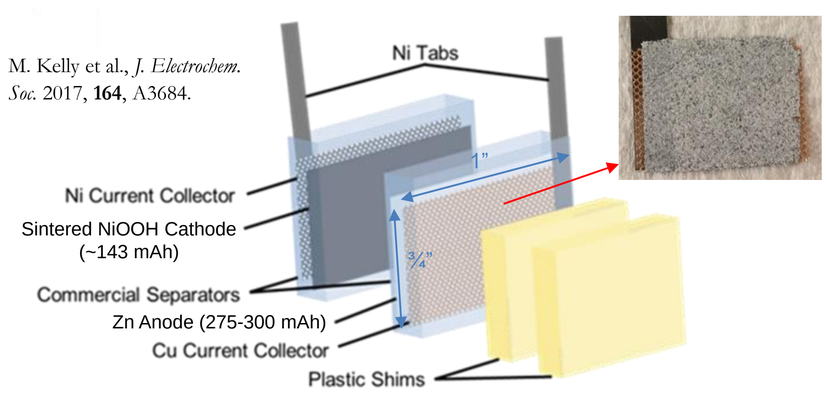
Objectives

- **Increase achievable cycle life and energy density by pre-saturating electrolyte with ZnO to inhibit dissolution and migration of zinc from the anode.**
- **Study effect of ZnO saturation at different depths of discharge, *relative to total zinc species in the system*, and at different KOH concentrations in a more commercially relevant limited-electrolyte system.**

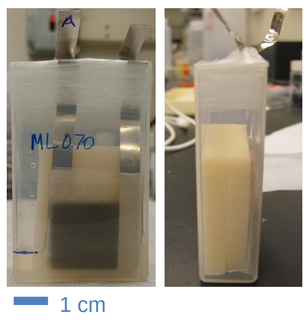
Experimental Plan

Due to the sensitivity of MnO_2 to $Zn(OH)_4^{2-}$, use NiOOH as the cathode material instead to examine the effect of ZnO saturation at different Zn DOD.

M. Kelly et al., *J. Electrochem. Soc.* 2017, **164**, A3684.



- 3 mL 25%, 32%, or 45% KOH electrolyte with/without saturated ZnO
- Cycled between 1 and 1.93 V vs. Zn at C/10 relative to full anode capacity ≈ **75 mA/g_{anode}**
- Zn DOD limits of 14%, 21%, 35% **relative to all Zn+ZnO in system**
- Cells considered failed when discharge capacity fell below 80% of DOD limit



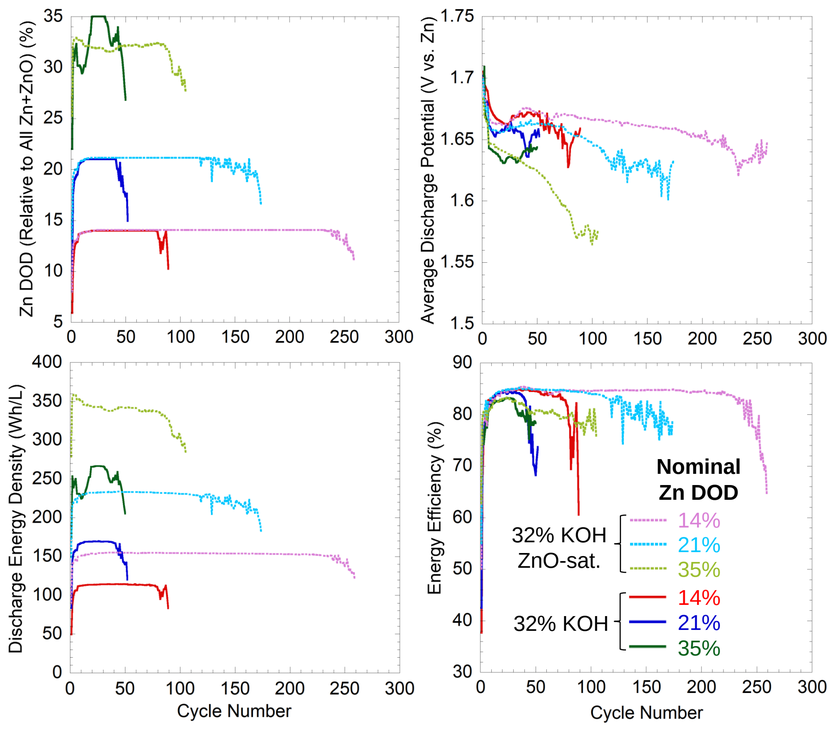
Acknowledgments

This work was supported by the U.S. Department of Energy, Office of Electricity, and the Laboratory Directed Research and Development program at Sandia National Laboratories. Sandia National Laboratories is a multi-program laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. The views expressed herein do not necessarily represent the views of the U.S. Department of Energy or the United States Government. Dr. Imre Gyuk, Director of Energy Storage Research, Office of Electricity is thanked for his financial support. The authors also thank Bonnie Mckenzie at Sandia National Laboratories for SEM characterization, and Michael Nyce at the CUNY Energy Institute for providing sintered NiOOH electrodes.

SAND No. SAND2019-11032 C

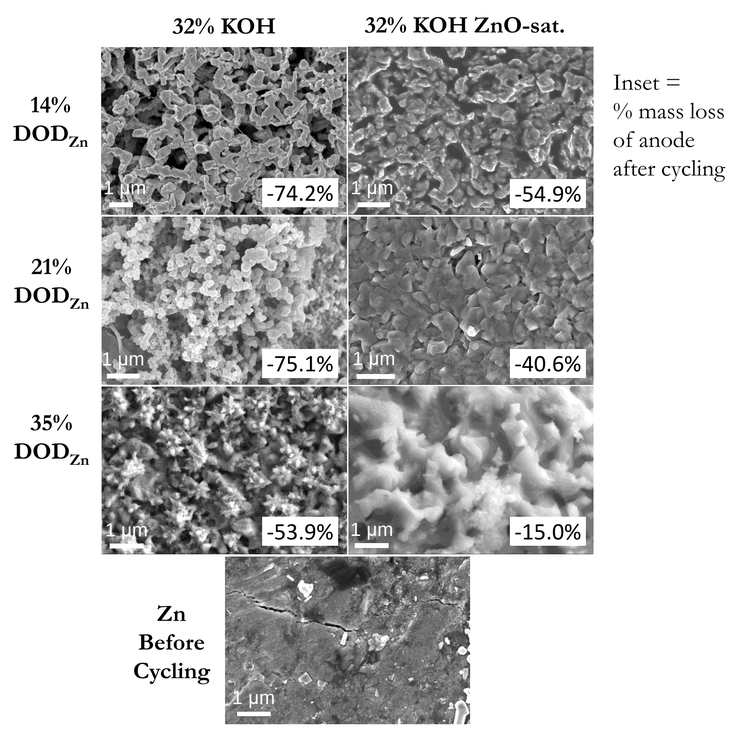
LDRD Laboratory Directed Research & Development · U.S. Department of Energy · NNSA National Nuclear Security Administration

Cycling Results



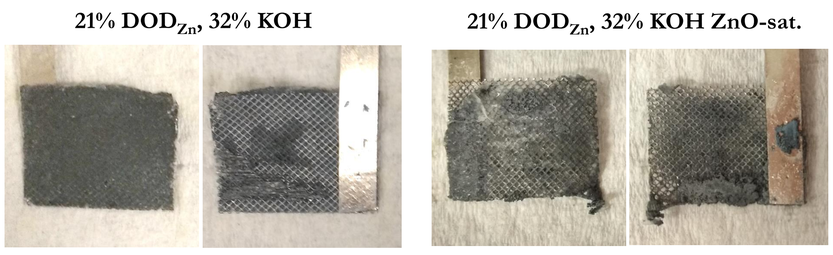
Cells with saturated electrolyte last significantly longer with no energy losses due to voltage and similar energy efficiency compared to cells with regular electrolyte cycled at same DOD, ***even when including dissolved ZnO in capacity***

Post-Cycling Characterization

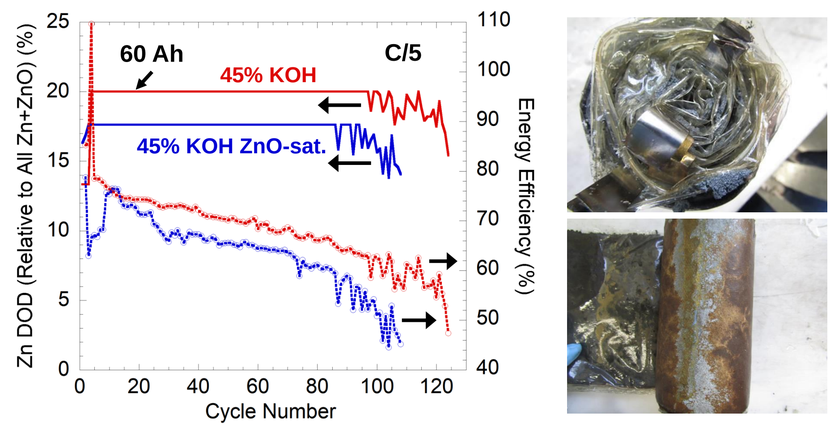


Inset = % mass loss of anode after cycling

- Anodes in ZnO-saturated electrolyte yield more compact Zn deposits indicating more homogeneous current density
- They also lose less mass during cycling despite significant Zn deposition on the bottom and through separator.



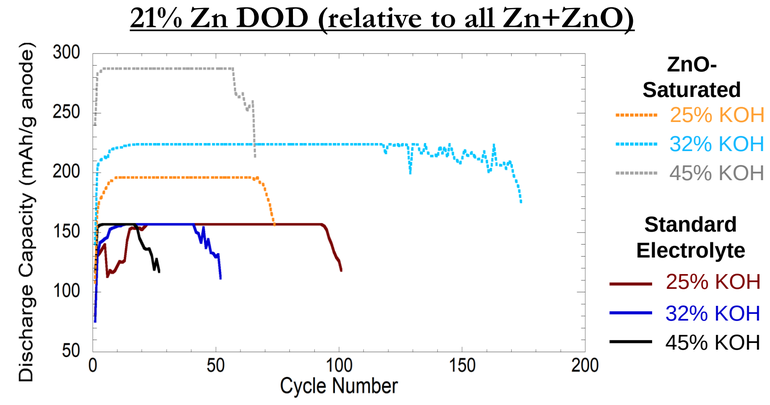
Large-Format Zn/MnO_2 Cell



- Cells with saturated electrolyte last >100 cycles, though slightly less than cells with 45% KOH only, and lower energy efficiency
  - Zinc clogs separator, creating soft short-circuit

Effect of KOH Concentration

21% Zn DOD (relative to all Zn+ZnO)

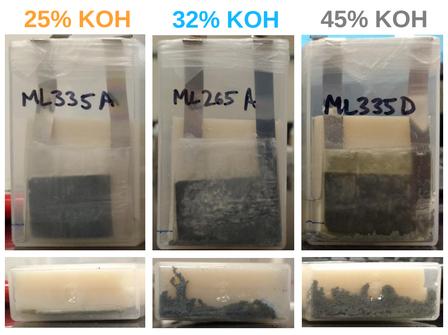


- Cells with 45% KOH fail more quickly with more zinc growth outside electrode than cells with less concentrated electrolyte
- ZnO saturation *reduces* cycle life in 25% KOH at 21% Zn DOD

Initial wt% KOH	mol/L Zn(II) at Saturation	mAh in Dissolved ZnO
25	0.45	72.4
32	0.74	119
45	1.50	241

J. Electrochem. Soc. 1967, **114**, 1045.
J. Chem. Soc, Faraday Trans. 2, 1974, **70**, 1978.

Cycled Cells with ZnO-Saturated Electrolyte



Bottom view (front of cell facing down)

Conclusions and Future Work

- Pre-saturating electrolyte with ZnO increases lifetime of Zn/Ni cells at high Zn utilization (≥14% DOD) without energy losses, but only at higher KOH concentrations
  - 32% KOH appears to be optimal concentration
- ZnO saturation has no benefit on Zn/MnO_2 cells with commercial separators → **Need to develop zincate-blocking separators** to isolate zincate in anode and suppress deposition away from anode
  - Should be **flexible and conductive**
  - Potential for >250 Wh/L and <$100/kWh
  - Ongoing collaboration with City College of New York
- Further reduce electrolyte usage to reduce material cost
  - Want **~2 mL/mL anode** (ours ~ 40 mL/mL anode)
  - Electrolyte is effectively saturated with zincate in operando

Research Output

Publications

- MB Lim, TN Lambert, EI Ruiz. "Effect of ZnO-Saturated Electrolyte on Rechargeable Alkaline Zinc Batteries at High Depth-of-Discharge", *to be submitted Sep-Oct 2019*.

Talks

- MB Lim, M Kelly, J Duay, IV Kolesnichenko, TN Lambert. "Improving Cycle Life and Active Materials Utilization for Rechargeable Alkaline Zn–MnO_2 Batteries". 235th Electrochemical Society Meeting, Dallas, TX (May 28, 2019).
- MB Lim, TN Lambert. "Effect of ZnO-Saturated Electrolyte on Rechargeable Alkaline Zinc Batteries at High Depth-of-Discharge". 31st Rio Grande Symposium on Advanced Materials, Albuquerque, NM (Sep 16, 2019).
- MB Lim, IV Kolesnichenko, DJ Arnot, TN Lambert. "Effect of ZnO-Saturated Electrolyte on Rechargeable Alkaline Zn–Ni and Zn–MnO_2 Batteries at High Zinc Depth-of-Discharge". 236th Electrochemical Society Meeting, Atlanta, GA. (Oct 15, 2019).

Poster

- MB Lim, IV Kolesnichenko, DJ Arnot, TN Lambert. "Effect of ZnO-Saturated Electrolyte on Rechargeable Alkaline Zinc Batteries at High Depth-of-Discharge". Los Alamos National Laboratory Postdoc Research Symposium, Los Alamos, NM (Aug 27, 2019).