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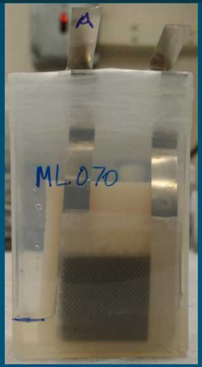
SAND2020-10557C

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



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ENERGY NNSA

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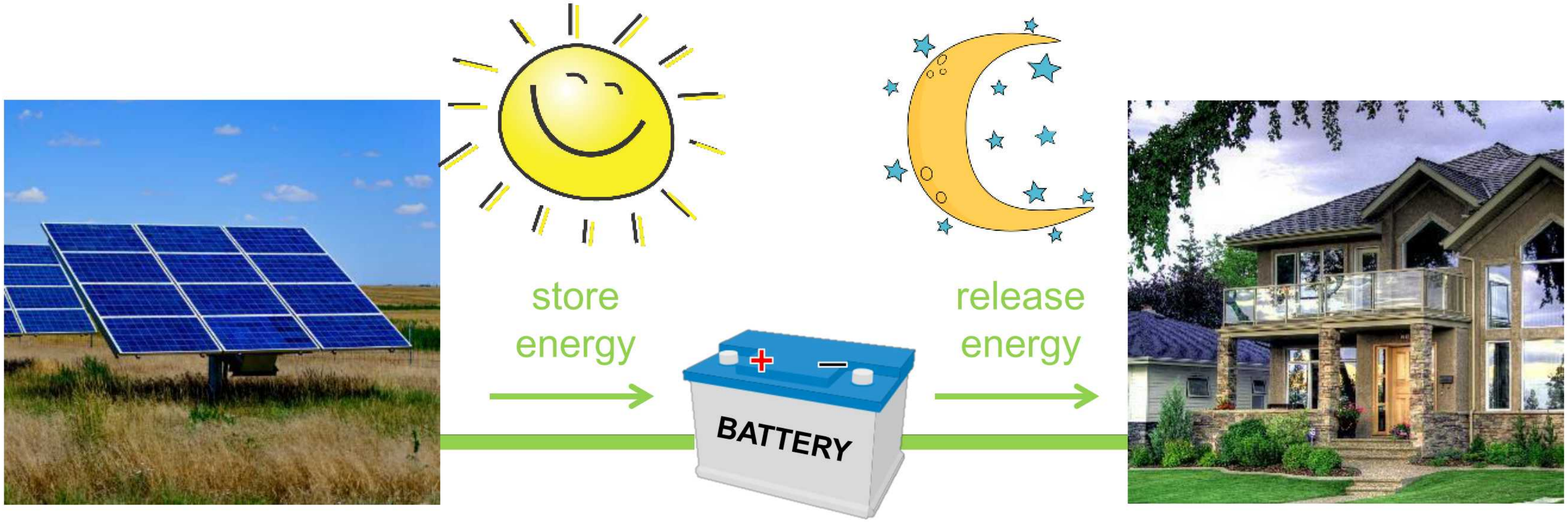
Grid Energy Storage

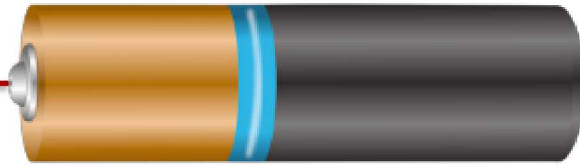


- Grid-level energy storage systems needed to enable intermittent renewables
- Li-ion, Pb-acid battery systems have been implemented but pose safety and environmental risks
- Successful grid storage must be safe, reliable, and low-cost

Center for Sustainable Systems, University of Michigan. 2016. "U.S. Energy Storage Factsheet." Pub. No. CSS15-17.
Energy Sage. n.d. “Ground Mount Solar Panels: Top 3 Things You Need to Know.”

Alkaline Zn-MnO_2 Batteries

Zn-MnO_2



Up to 400 Wh/L or 150 Wh/kg, $18/kWh as primary cell

MnO_2

- 617 mAh/g
- ~ $1.11 /lb (2012)
- 466,000 tons (2013)
- Safe, recyclable

KOH

- Potash ~ $357/ton (2018)
- 2.2 million tons (2018)
- Aqueous, non-flammable

Zn

- 820 mAh/g
- ~ $1.37 /lb (2018)
- 13.2 million tons (2018)
- Safe, recyclable

$$2MnO_2 + H_2O + 2e^- \rightarrow Mn_2O_3 + 2OH^- \qquad [E^0 = +0.15\ V]$$

$$Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^- \qquad [E^0 = +1.28\ V]$$

$$\boldsymbol{Zn + 2MnO_2 \rightarrow ZnO + Mn_2O_3} \qquad [\boldsymbol{E^0 = +1.43\ V}]$$

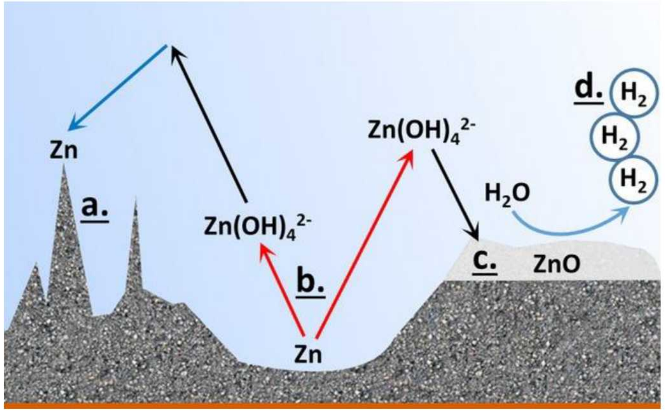
Co	$13-15/lb	**Li**	$2.5/lb
V	$11-12/lb	**Al**	$0.8-0.9/lb
Ni	$6-9/lb	**Cu**	$2.5-3.5/lb

The ultimate challenge in rechargeable Zn/MnO_2 batteries is increasing energy density while maintaining reversibility

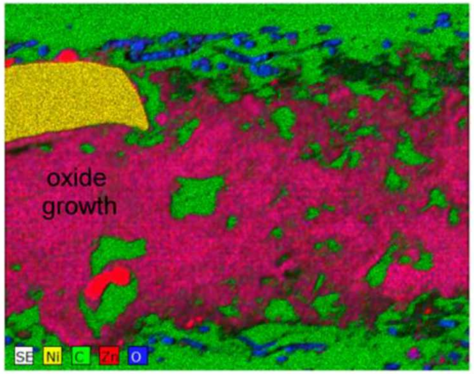
Images adapted from Gautam Yadav

Zn Anode Problems at High DOD

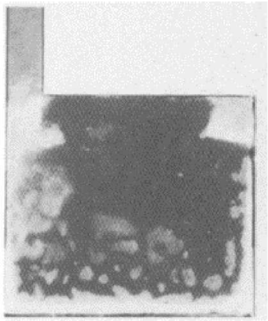
- Shape change
- Dendrite formation
- Passivation
- H_2 evolution



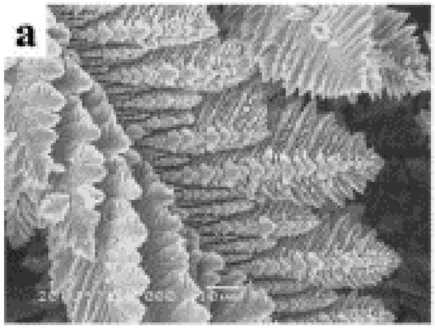
J. Fu et al., *Adv. Mater.* 29, 1604685 (2017)



D. Turney et al, Chem. Mater., 29 (11), 4819 (2017)



J. Electrochem. Soc., 138 (2), 645 (1991)

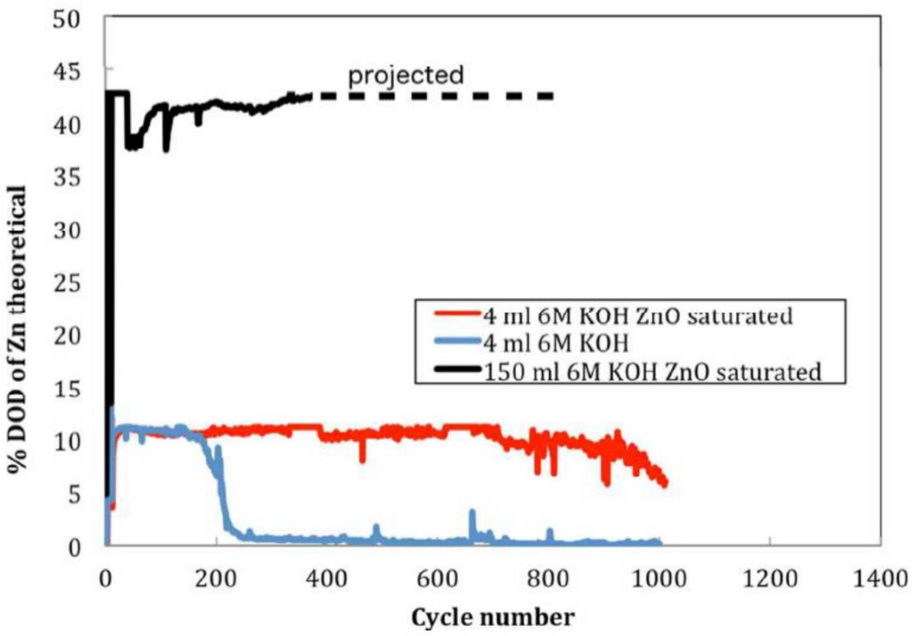


J. Electrochem. Soc., 163 (9), A1836 (2016)

ZnO-Saturated Electrolyte

- Pre-saturating electrolyte with ZnO can minimize dissolution and long-range migration of zinc from anode
- Can also reduce the rate of H_2 evolution
- Saturated-ZnO electrolytes have been previously reported for Zn-Ni cells but most do not mention the amount of electrolyte relative to anode
  - Leads to artificially inflated metrics if cell is flooded
- No systematic study to date on effect of ZnO saturation alone at different levels of Zn DOD

J. Fu et al., *Adv. Mater.* **29**, 1604685 (2017).
A. Mainar et al., *Energy Science & Engineering* **6**, 174 (2018).



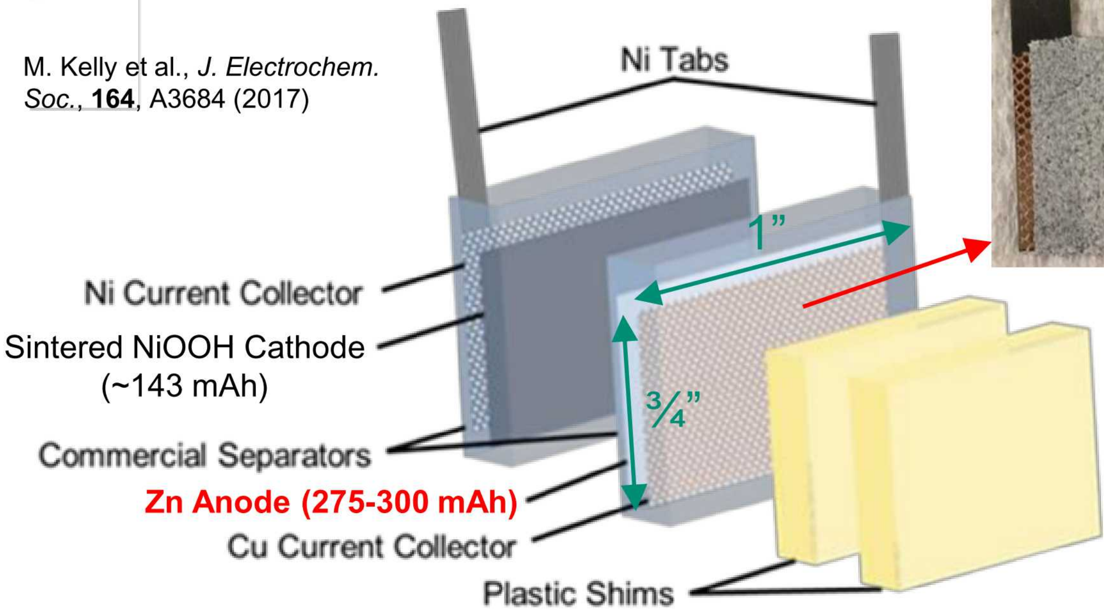
D. Turney et al, *Chem. Mater.*, **29** (11), 4819 (2017)

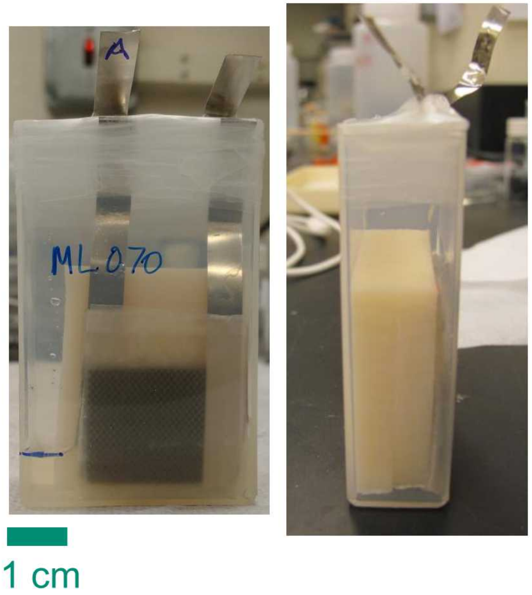
Z. Zhang et al, *Electrochim. Acta*, **155**, 61 (2015)

Battery Assembly and Testing

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.

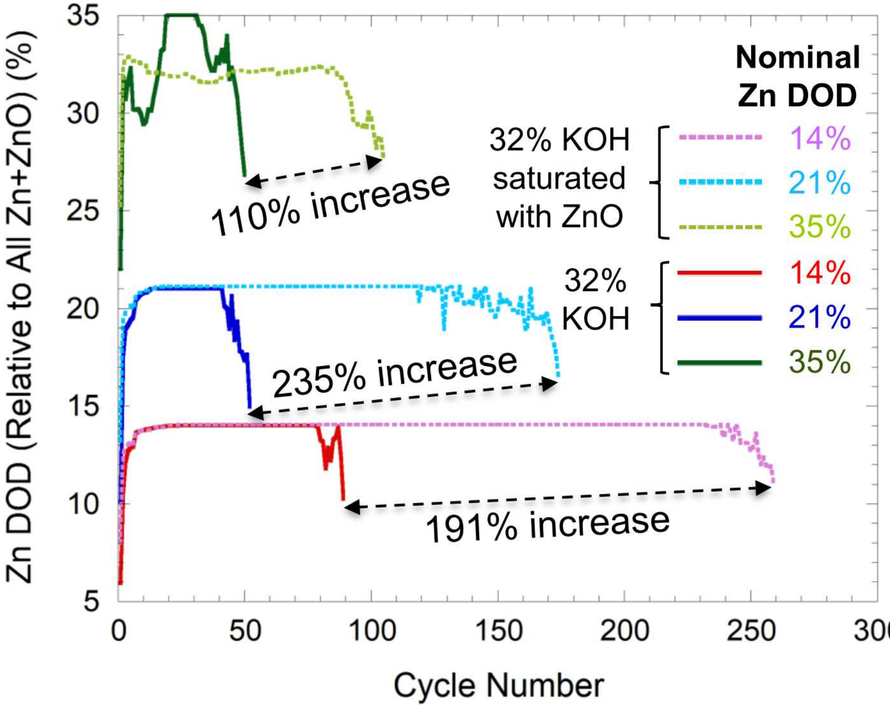
M. Kelly et al., *J. Electrochem. Soc.*, **164**, A3684 (2017)

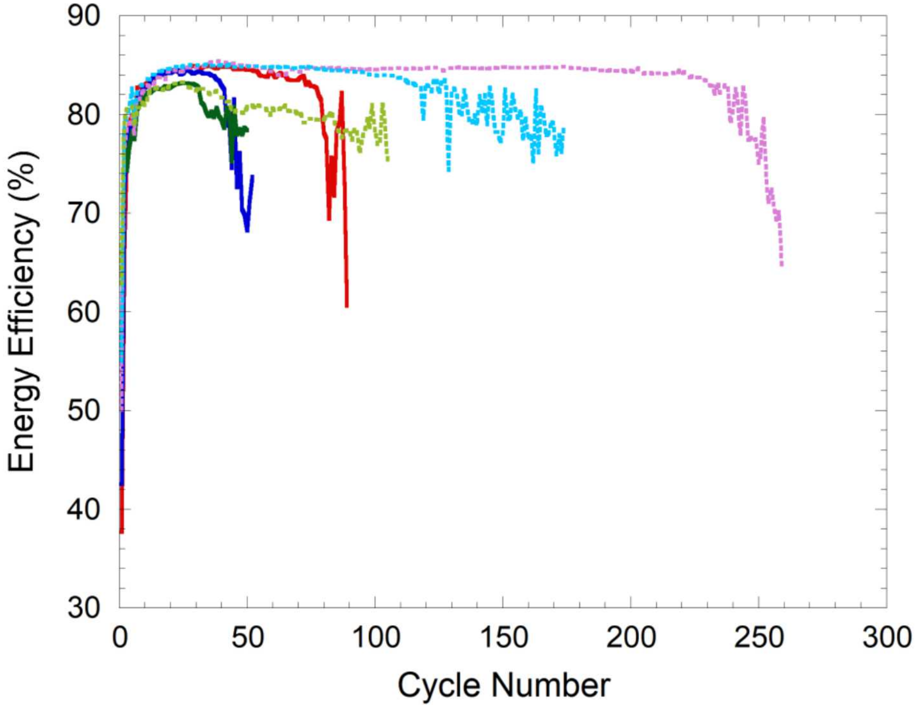




- 3 mL 32% KOH electrolyte with/without saturated ZnO
  - Zn(II) saturation concentration ≈ 0.74 mol/L → **119 mAh** in dissolved ZnO
- Cycled between 1 and 1.93 V vs. Zn at C/10 relative to full anode capacity = **75 mA/g$_{anode}$**
- Zn DOD limits of 14%, 21%, 35% **relative to all Zn+ZnO in system**

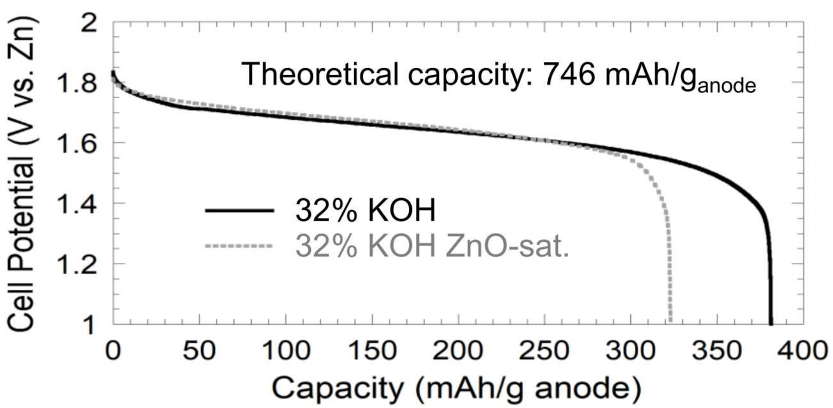
Improved Cycle Life at High DOD





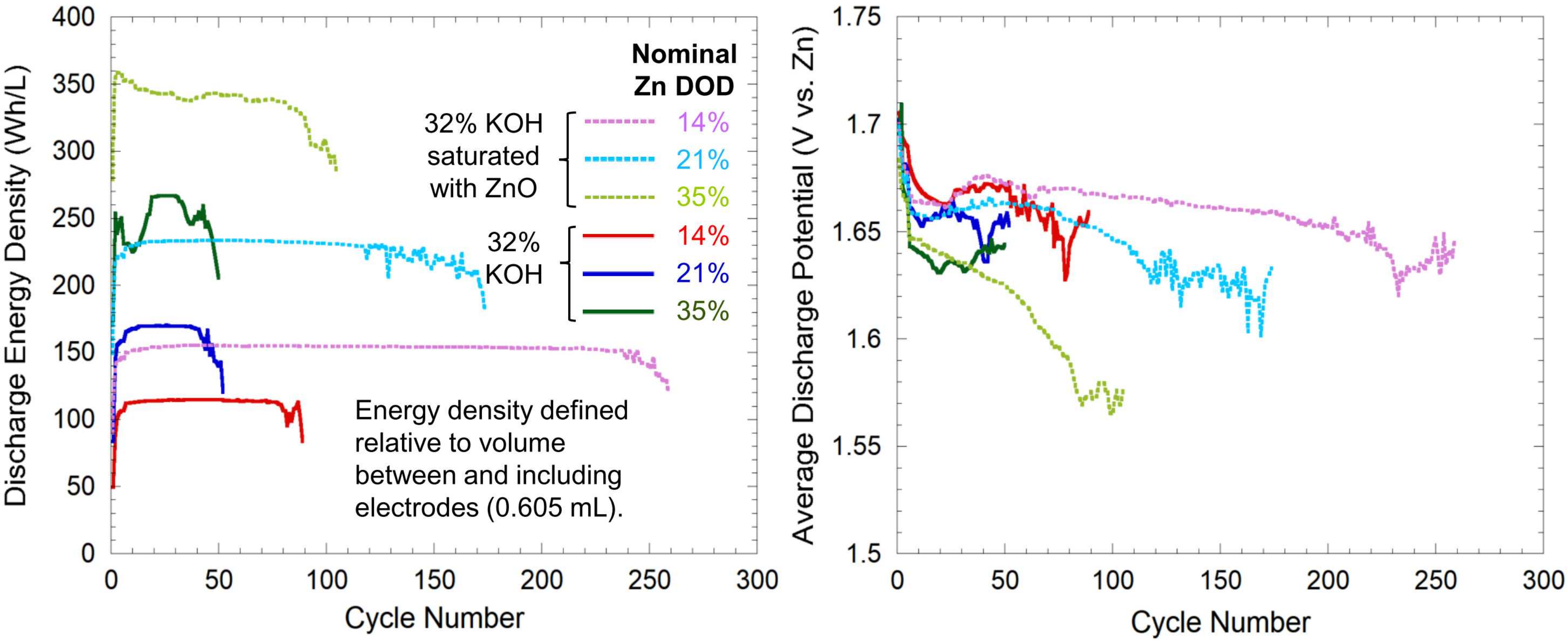
Cells with ZnO-saturated electrolyte last significantly longer with similar energy efficiency to cells with regular electrolyte cycled at same DOD, *even when including dissolved ZnO in capacity*

Full discharge of Zn anode vs. NiOOH at C/10 to 1 V actually delivers slightly lower capacity in ZnO-saturated electrolyte, suggesting that effective DOD is much higher for the above cells cycled in ZnO-saturated electrolyte



M. Lim, T. Lambert, E. Ruiz, *in preparation.*

Cell Energy



- Energy density is a misleading metric due to possible contribution of pre-dissolved ZnO from the electrolyte reservoir and higher cycled capacity of cells with saturated electrolyte
- Average discharge potential is more informative (= discharge energy / discharge capacity)
  - No energy losses due to voltage between cells cycled in saturated vs. regular electrolyte at same DOD

M. Lim, T. Lambert, E. Ruiz, *in preparation.*

Post-Mortem Anode Characterization

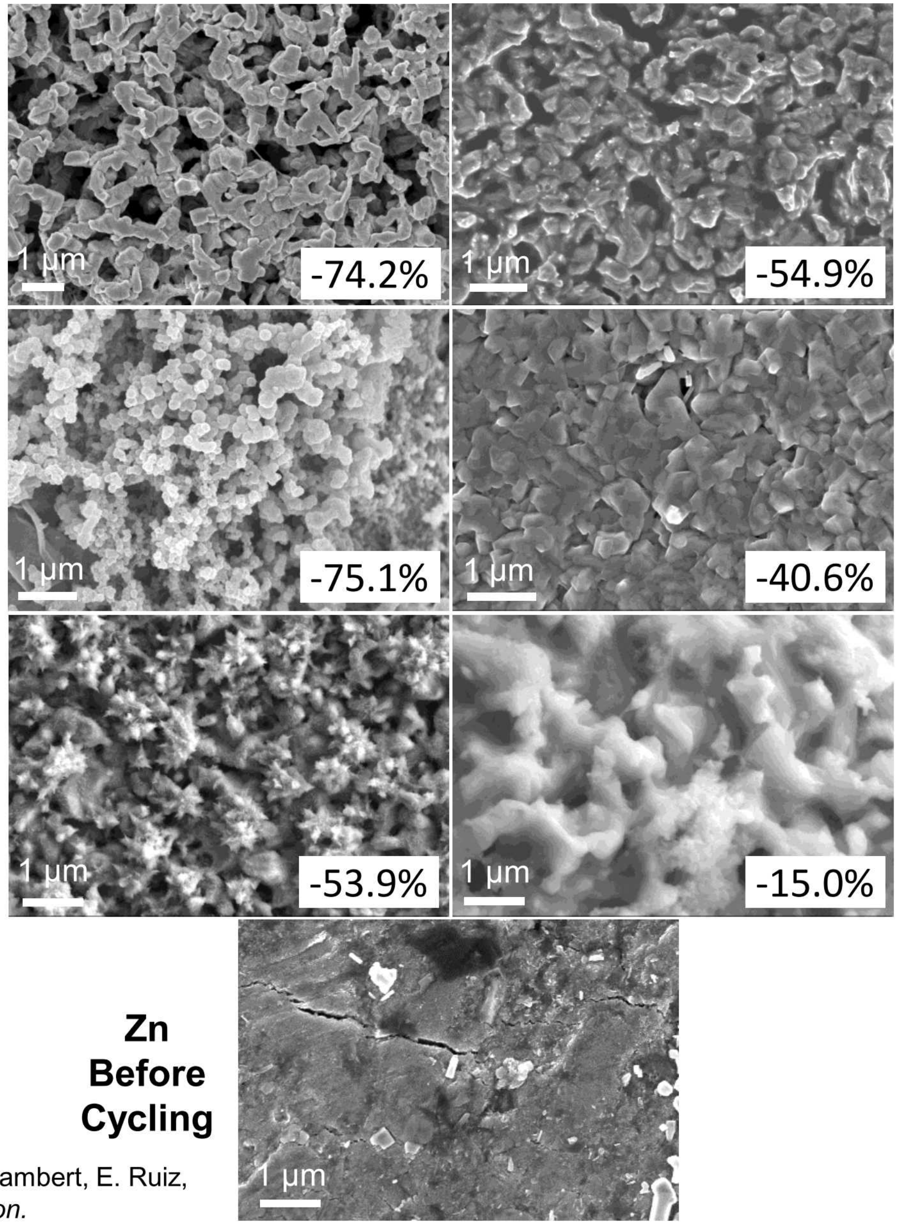
32% KOH | **32% KOH ZnO-saturated**

14% Zn DOD

21% Zn DOD

35% Zn DOD

Zn Before Cycling



M. Lim, T. Lambert, E. Ruiz, *in preparation.*

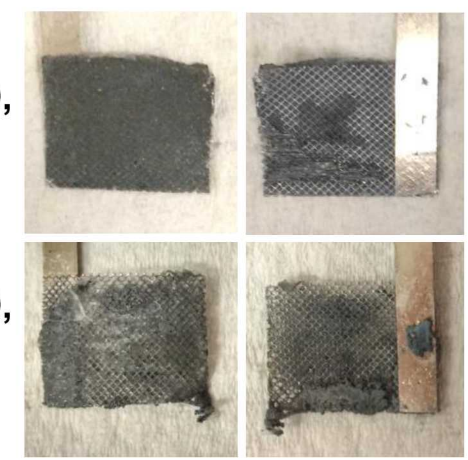
Cells disassembled in charged state following failure (80% of nominal cycled capacity).

Inset = % mass loss of anode after cycling

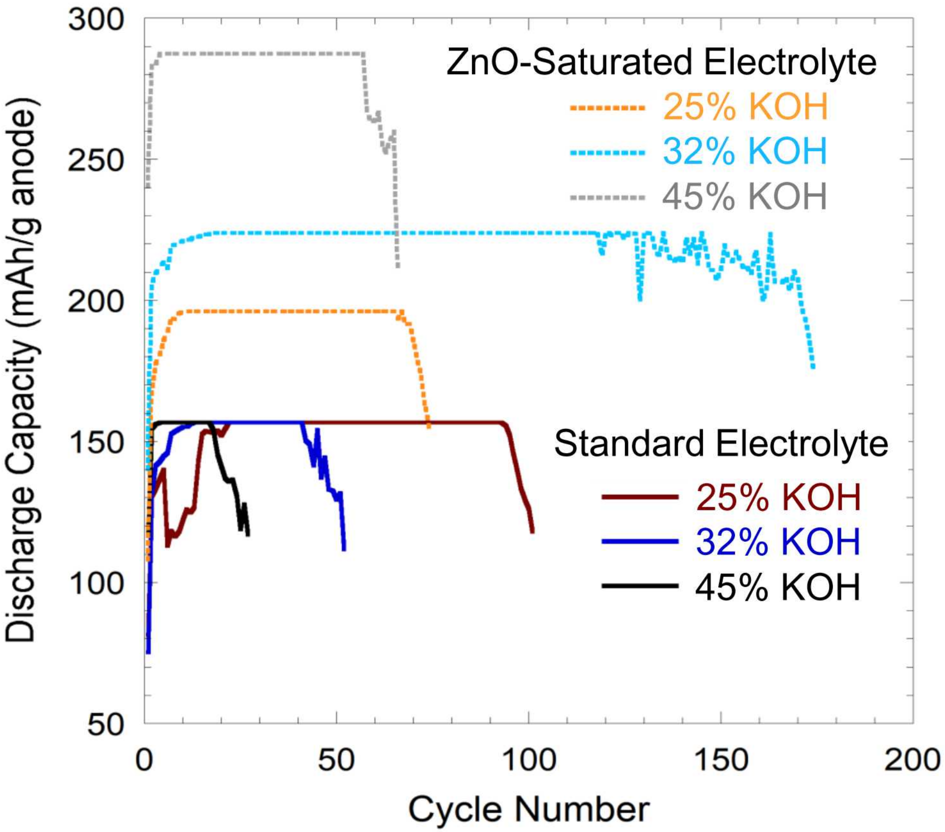
- Anodes cycled in ZnO-saturated electrolyte yield more compact Zn deposits indicative of more homogeneous current density
- They also lose less mass despite showing significant Zn deposition on the bottom of the electrode and through the separator
- Re-pairing experiments confirm that failure was due to anode

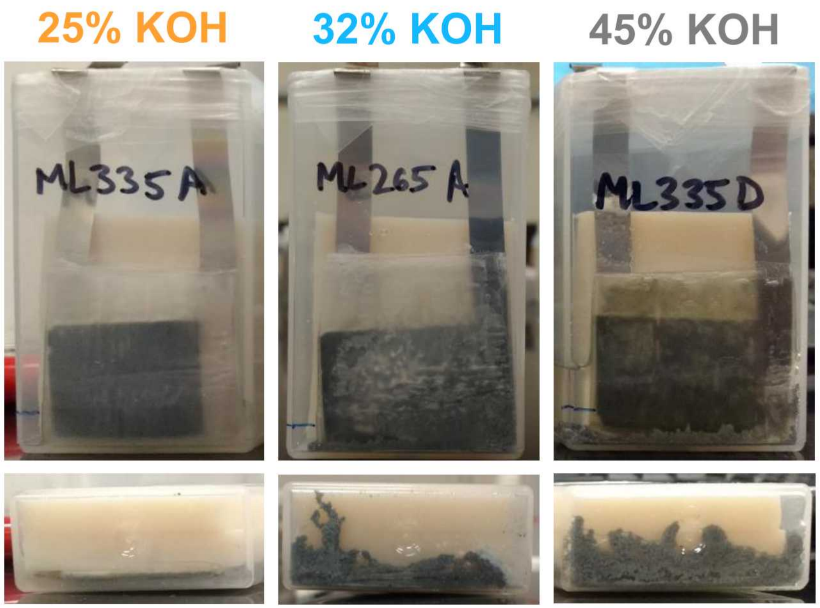
21% Zn DOD, 32% KOH

21% Zn DOD, 32% KOH ZnO-sat.



Effect of KOH Concentration 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.

- Cells with 45% KOH fail more quickly with more zinc growth outside the electrode than cells with less concentrated electrolyte
- ZnO saturation *reduces* cycle life in 25% KOH
  - May be due to lower saturation concentration of ZnO → increased passivation

M. Lim, T. Lambert, E. Ruiz, *in preparation.*

Summary

- Pre-saturating electrolyte with ZnO increases lifetime of limited-electrolyte Zn-Ni batteries at high Zn utilization without energy losses, but only at higher KOH concentrations
- Anodes cycled in ZnO-saturated electrolyte develop more compact Zn morphologies with less overall mass loss

Future Work

- Develop flexible polymeric zincate-blocking, hydroxide-conductive separators for cells with lower-cost, more energy-dense 2e- MnO_2 cathodes that are sensitive to zincate
  - Recently showed zincate-blocking ability and increased cycle life of Zn-MnO_2 cells with commercial NaSICON separators at limited DOD
  - Potential for >250 Wh/L and <$100/kWh
  - Ongoing collaboration with CUNY

J. Duay, M. Kelly, T. Lambert, *J. Power Sources* **395**, 430 (2018)

G. Yadav *et al.*, *Nat. Commun.* 8:14424 (2017).
G. Yadav *et al.*, *J. Mater. Chem. A* **5**, 15845 (2017).

Acknowledgments

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