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

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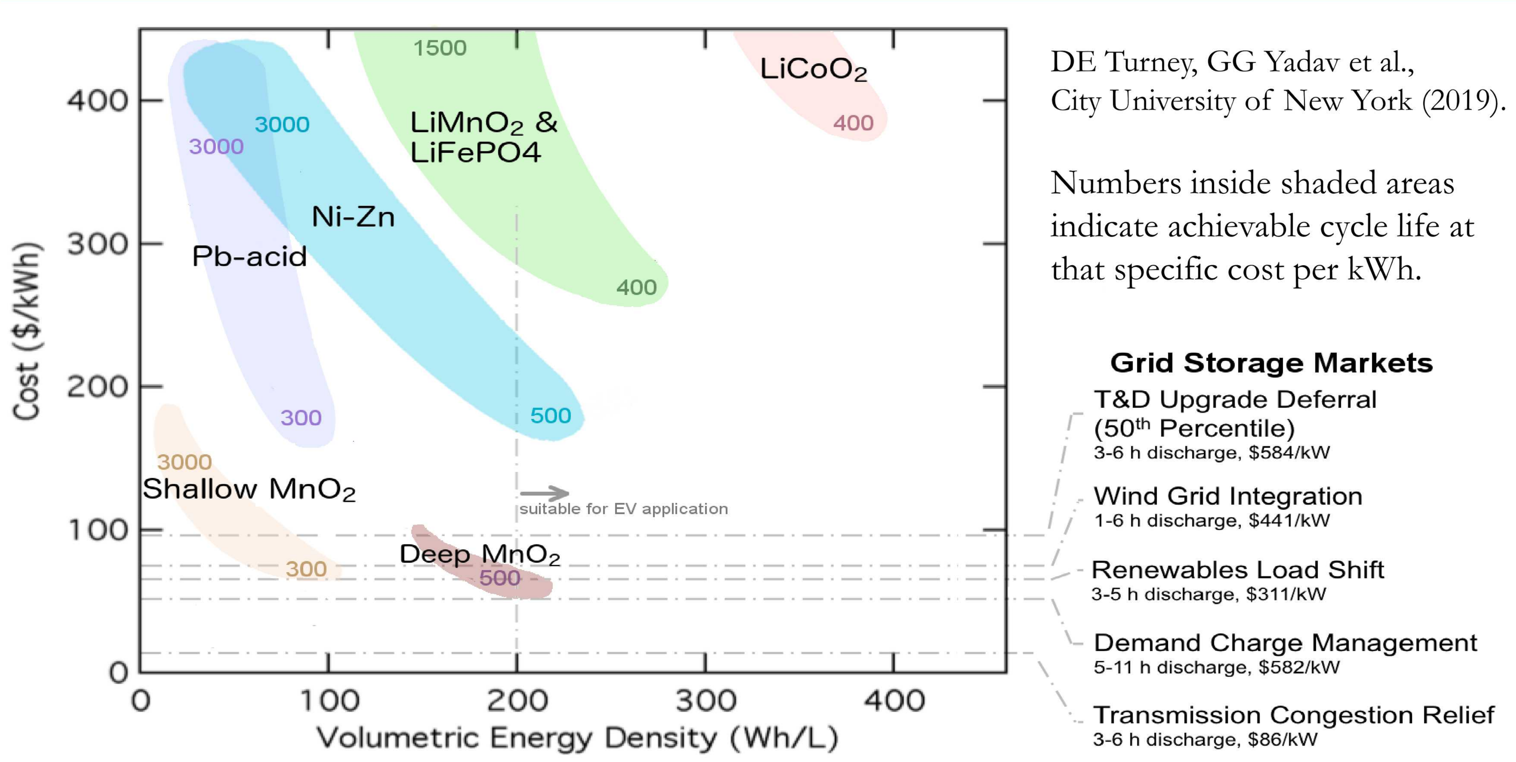
Introduction

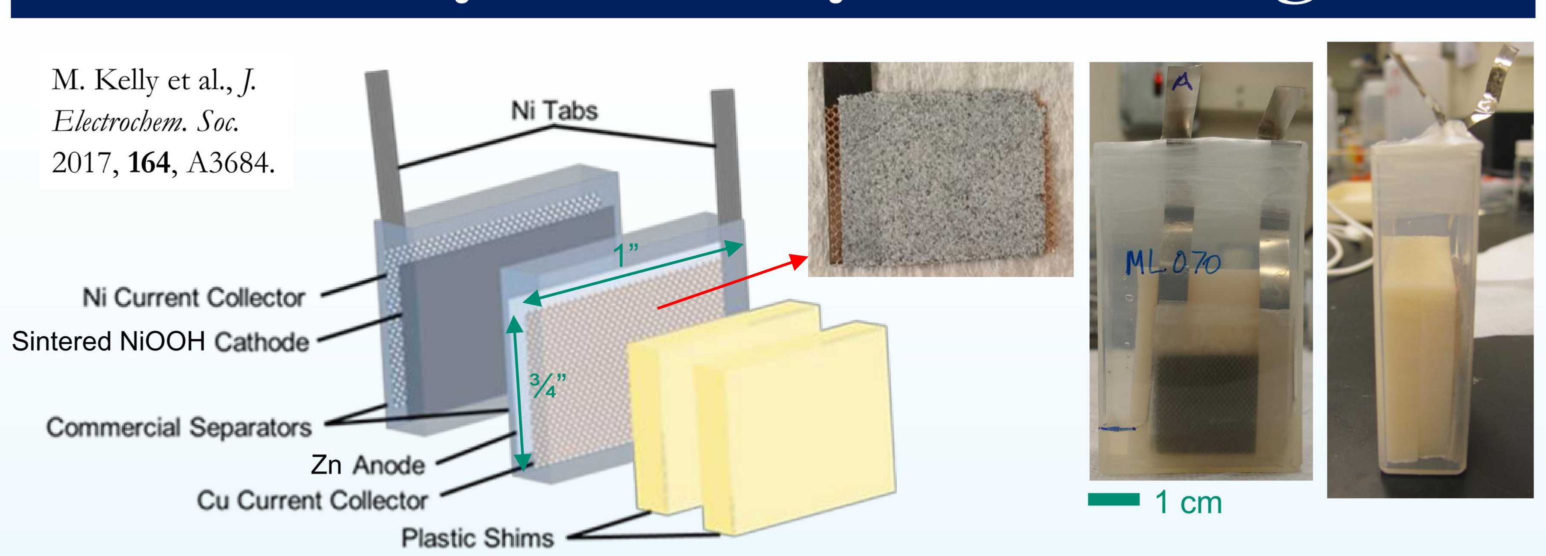
Rechargeable alkaline Zn/MnO_2 and Zn/Ni batteries are promising candidates for grid-level energy storage due to their low cost, theoretically high energy density, environmental compatibility, and non-flammable aqueous electrolyte. However, alkaline Zn anodes suffer from redistribution and passivation of active material over repeated cycling, leading to capacity loss. One strategy to overcome these issues is to pre-saturate the electrolyte with ZnO to inhibit dissolution and long-range migration of zinc from the anode. While not a new concept, most of the relevant literature uses flooded cells and disregards the large excess of Zn species in the electrolyte relative to the anode in evaluating performance. Here, we investigate the effect of ZnO-saturated electrolyte in more commercially relevant, limited-electrolyte Zn/Ni cells at high Zn depth-of-discharge (DOD_{Zn}).

Alkaline Batteries for Grid Storage



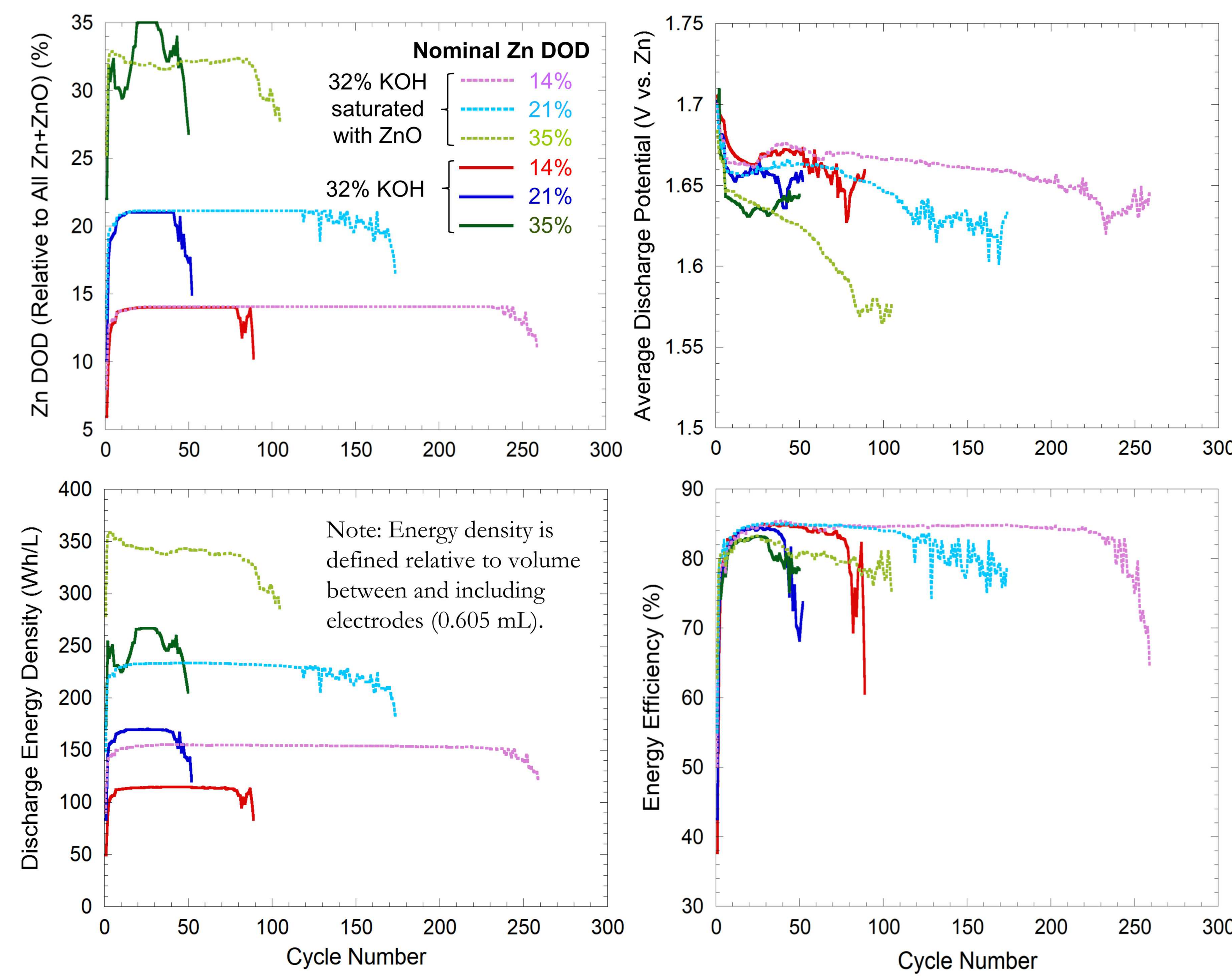
The ultimate challenge in rechargeable alkaline zinc batteries is increasing energy density while maintaining reversibility

Battery Assembly and Testing



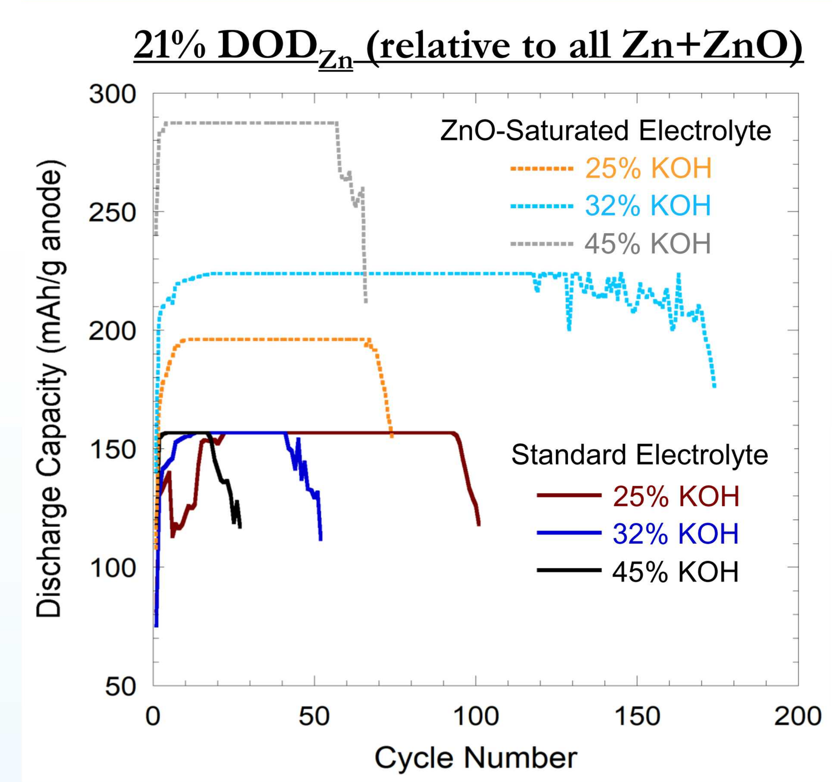
- 3 mL 32% KOH electrolyte with/without saturated ZnO
- Total anode capacity = 275–300 mAh; cathode capacity ≈ 143 mAh
- Cycled between 1 and 1.93 V vs. Zn at nominal DOD_{Zn} of 14%, 21%, 35% **relative to all Zn+ZnO in system**
- Rate = C/10 relative to full anode capacity ≈ **75 mA/g_{anode}**

Cycling Results

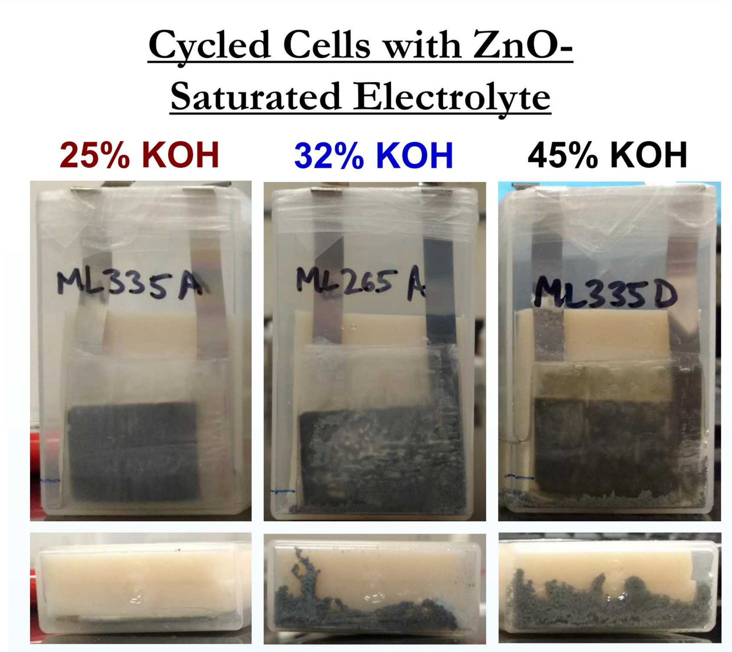


Cells with saturated electrolyte last significantly longer with no energy losses due to voltage and similar energy efficiency compared to cells with regular electrolyte cycled at same DOD, *even when including dissolved ZnO in capacity*

Effect of KOH Concentration



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

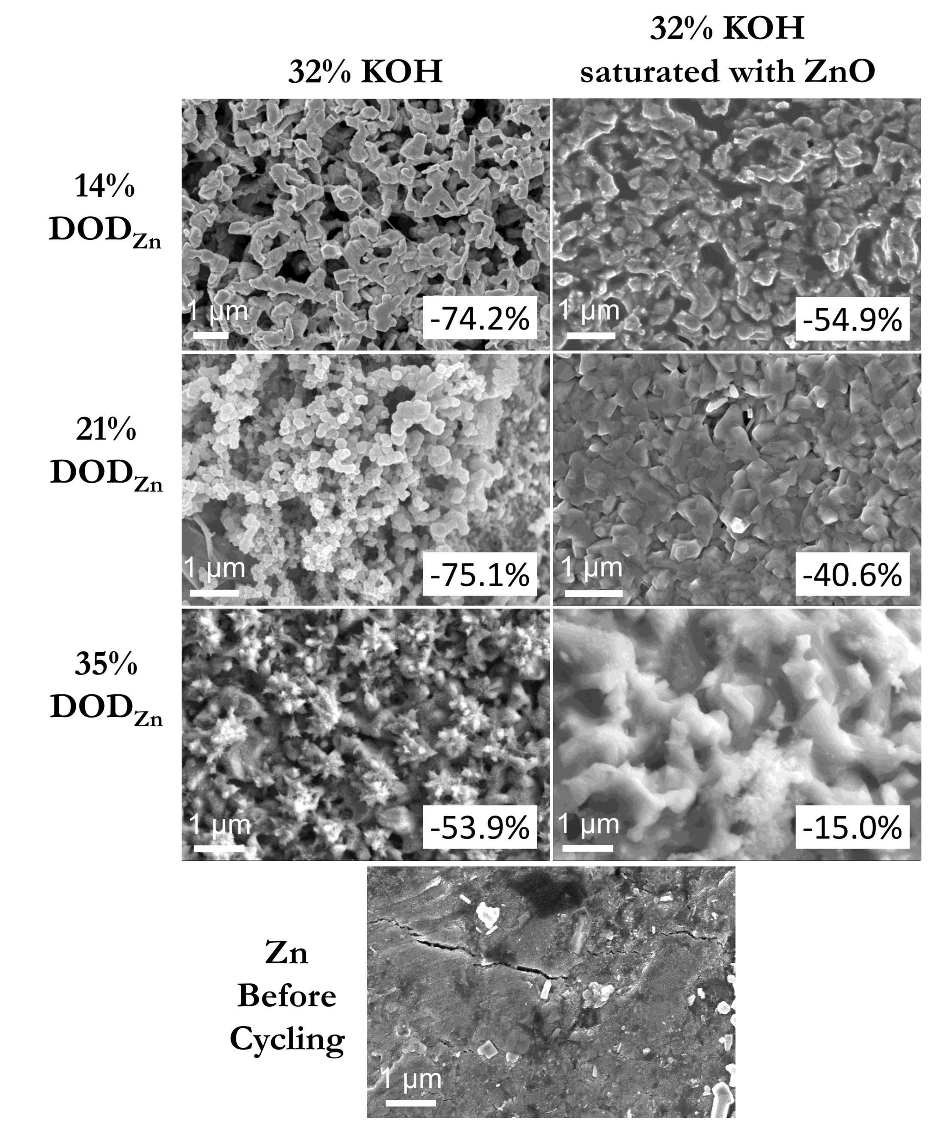


Bottom view (front of cell facing down)

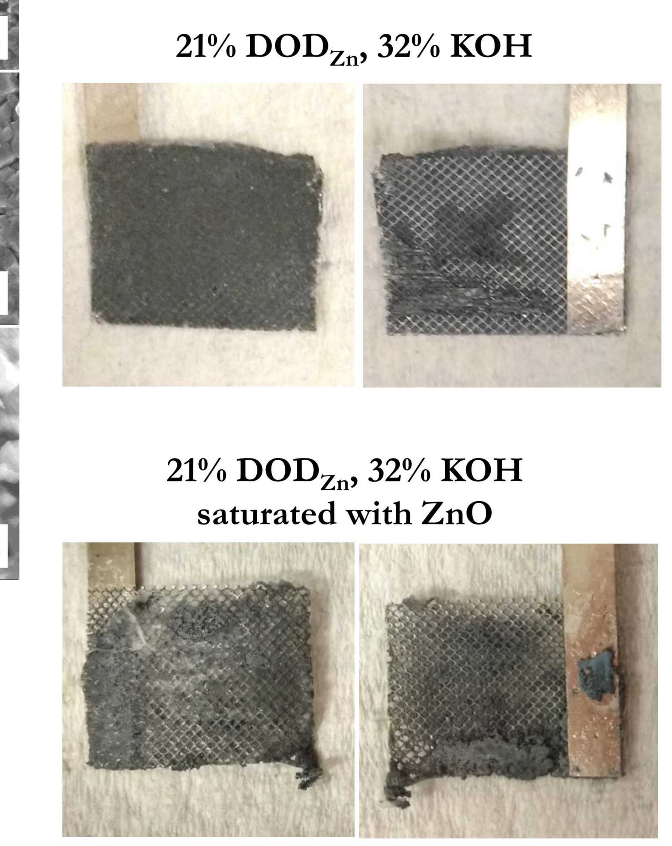
Initial wt% KOH	mol/L Zn(II) at Saturation	mAh in Dissolved ZnO
25	0.45	72.4
32	0.74	119
45	1.50	241

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

Post-Mortem Anode Characterization



Cells were disassembled in charged state following failure (discharge capacity falling below 80% of nominal cycled capacity). Percentage in inset indicates mass loss of anode after cycling.



- Anodes cycled in ZnO-saturated electrolyte yield more favorable compact, lower-surface-area Zn deposits indicative of more homogeneous current density[1]
- They also lose less mass during cycling despite showing significant Zn deposition on the bottom half of the electrode and through the separator.
- Re-pairing each cycled electrode with a fresh counter-electrode and running the same cycling protocol confirms that failure was due to anode (likely a soft short-circuit as previously observed in deep-DOD Zn/Ni cells[2])

[1] M. Shimizu, K. Hirahara, S. Arai, *Phys. Chem. Chem. Phys.* 2019, **21**, 7045.
[2] D. Turney, J. Gallaway, G. Yadav et al., *Chem. Mater.* 2017, **29**, 4819.

Conclusions

- Pre-saturating electrolyte with ZnO improves lifetime of limited-electrolyte Zn/Ni batteries at high Zn utilization, but only at higher KOH concentrations
- Cells with ZnO-saturated electrolyte develop lower-surface-area Zn morphologies with less overall anode mass loss
- Future work will focus on developing flexible polymeric zincate-blocking separators for cells with lower-cost, higher-capacity MnO_2 cathodes that are sensitive to zincate

Acknowledgments

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