Sandia National Laboratories

UNDERSTANDING FAILURE MECHANISMS IN CUPRIC OXIDE CATHODES FOR RECHARGEABLE ALKALINE ZINC BATTERIES

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PROJECT PROFILE

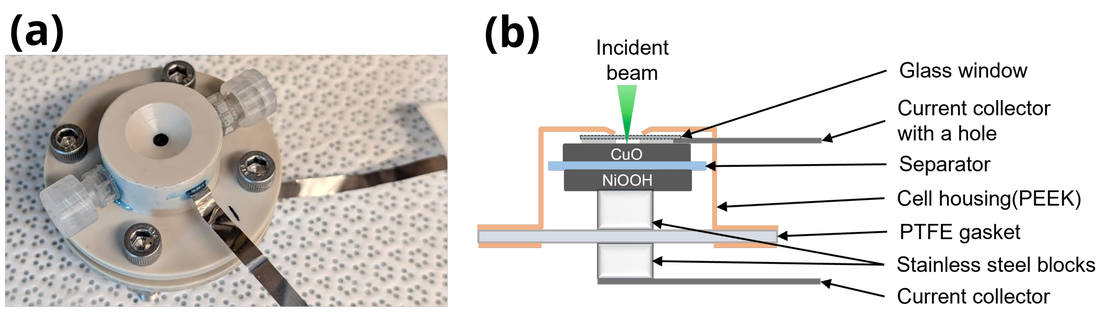
Topic: Zinc & Lead Batteries
Vertical: Materials and Systems Innovation
Strategic Pathway: Grow
Project start and finish: FY25-FY26

PROBLEM

- Cupric oxide (CuO) is an ideal cathode for alkaline zinc batteries due to its earth abundance, safety, high theoretical capacity of 674 mAh/g, and nominal voltage of 0.85 V vs. Zn.
- Bi_2O_3 has been shown to improve CuO reversibility, but it is limited to low depth of discharge (DOD) of 30%.[1,2]
- Ambiguity in the reaction pathways persists, as $Cu(OH)_2$ is difficult to characterize using X-ray techniques.
- Unclear failure mechanisms in CuO cathodes at high DOD.
- Capacity gradually decays from 674 mAh/g to ~300 mAh/g in 300 cycles when cycled at 100% DOD at 0.2 C rate.

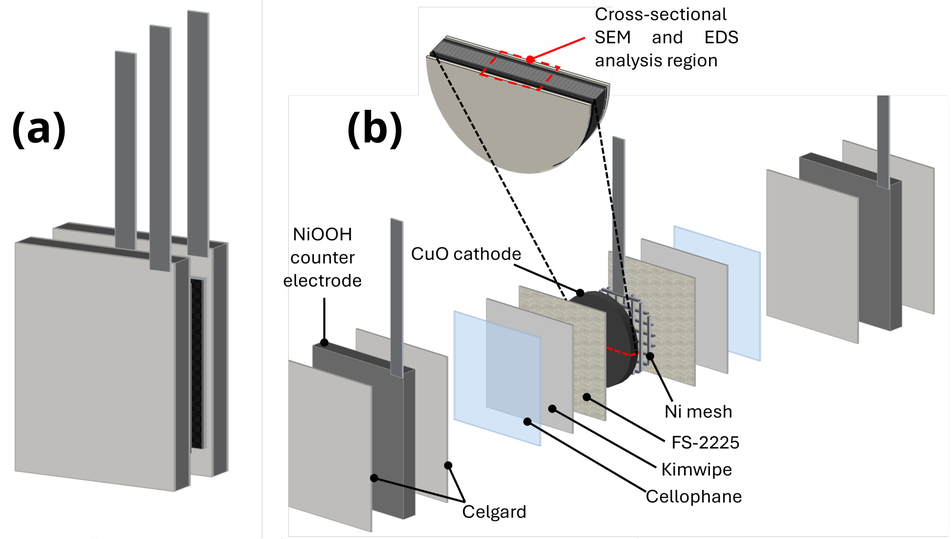
APPROACH

1. Reaction pathway characterization using in situ Raman spectroscopy at **Gallaway Lab**



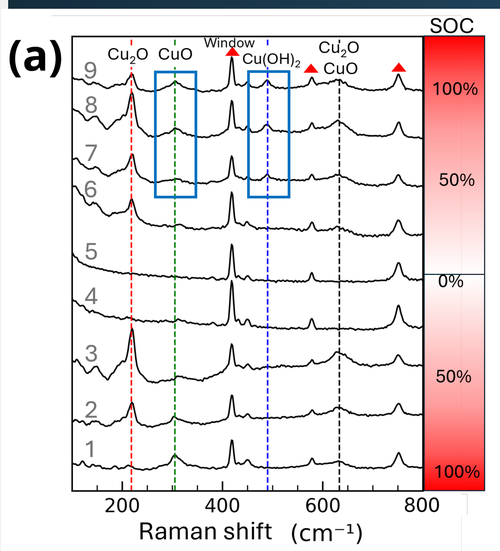
Windowed cell designed by Gallaway Lab

2. Failure analysis on a cycled CuO cathode using SEM, EDS and electrolyte characterization using UV-Vis.

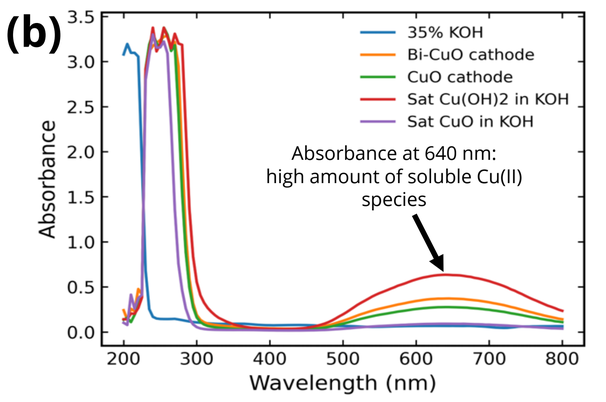


Schematic of electrode setup used for CuO cycling

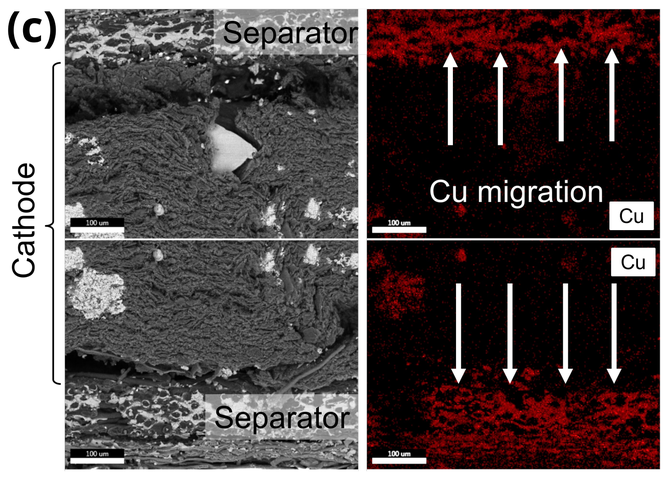
RESULTS



Operando Raman spectroscopy confirms the formation of $Cu(OH)_2$ along with CuO during charge.



UV-Vis analysis suggests that $Cu(OH)_2$ generates a high concentration of Cu(II) soluble species in 8.4 M KOH, and the same soluble species are present in the electrolyte extracted from the cycled cell.



- Cross-sectional EDS results after 475 cycles suggest that the active material migrated from the cathode and deposited inside the separator.
- The capacity is lost when Cu deposits inside the separator.

CONCLUSIONS & IMPACT

- Cu migration out of the cathode via a dissolution-precipitation process is identified as the primary capacity fade mechanism.
- $Cu(OH)_2$ and CuO are confirmed as the final charge products.
- $Cu(OH)_2$ is highly soluble in KOH electrolyte, forming soluble $[Cu(OH)_4]^{2-}$ and driving active material loss, whereas CuO exhibits lower solubility.

FUTURE DIRECTIONS

- Developing engineering strategies to confine the soluble species within the electrode structure.
- Investigating electrode additives to suppress or trap Cu(II) species.
- Exploring methods to improve the selectivity of CuO formation over $Cu(OH)_2$.

References
1. *Schorr, N. et al.* Rechargeable alkaline zinc/copper oxide batteries. ACS Applied Energy Materials 2021, 4 (7), 7073-7082.
2. *B. R. Wygant et al.* Optimization of Bi Additive Concentration and the Impact on the Performance of Secondary Zn/CuO Alkaline Batteries" J. Electrochem. Soc. 2025, 172, 080525

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