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Development of Copper Oxide Based Cathodes for Rechargeable Zinc Alkaline Batteries

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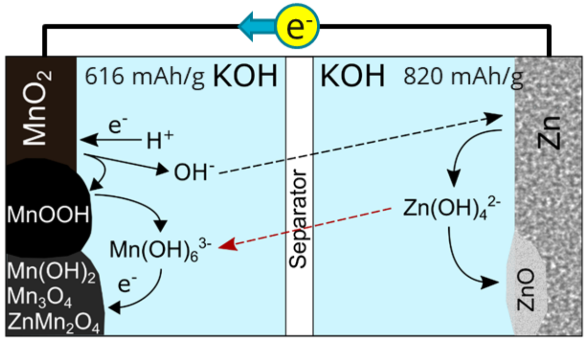
CuO Cathodes for Zn Alkaline Batteries

Batteries utilizing a zinc anode are well poised to be adapted for grid energy storage because of their high capacity and energy density, if rechargeability hurdles can be cleared

Primary commercial Zn-MnO_2 cells represent a system with advantageous attributes that would be ideal for a reversible battery

- Established supply chain
- 1º alkaline batteries ~ < \$20/kWh
- Aqueous, long shelf life,
- EPA certified for disposal
- High achievable energy density



Current MnO_2 cathodes have detrimental flaws making them unsuitable for reversible batteries

- Irreversibility of cathode
- Phase changes
- Susceptibility to zinc poisoning

Developments in our group have shown CuO represents a new class of material for cathodes in alkaline Zn batteries

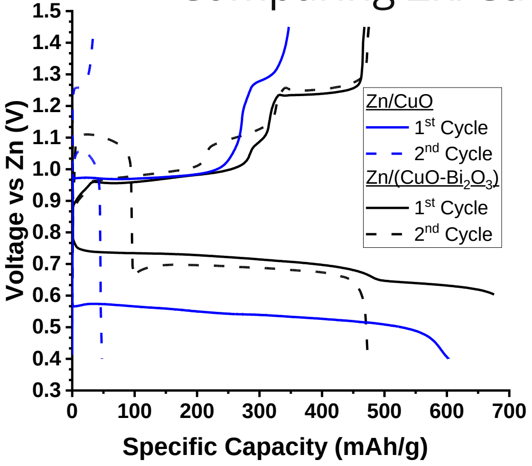
- High specific capacity (674 mAh/g)
- Tolerant to $Zn(OH)_4^{2-}$
- Demonstrated over 100+ cycles vs Zn
- Opens field to new additives/chemistries for future work

M. B. Lim; et al. Mater. Sci. Eng. R Rep. 2021, 143, 100593.

CuO as an Alternative Cathode for Zn Batteries

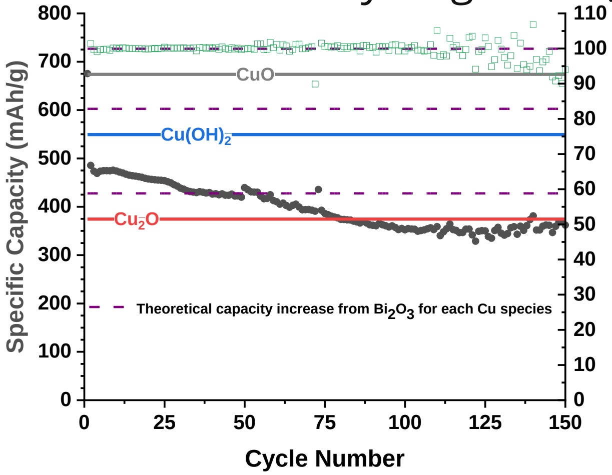
CuO is historically a primary high capacity (674 mAh/g) cathode, but a Bi additive enables reversibility in Zn alkaline cells

Comparing Zn/CuO vs Zn/($CuO-Bi_2O_3$) cells



Voltage curves show CuO without an additive fail to retain capacity past the 1st discharge, where inclusion of Bi_2O_3 in the cathode promotes rechargeability

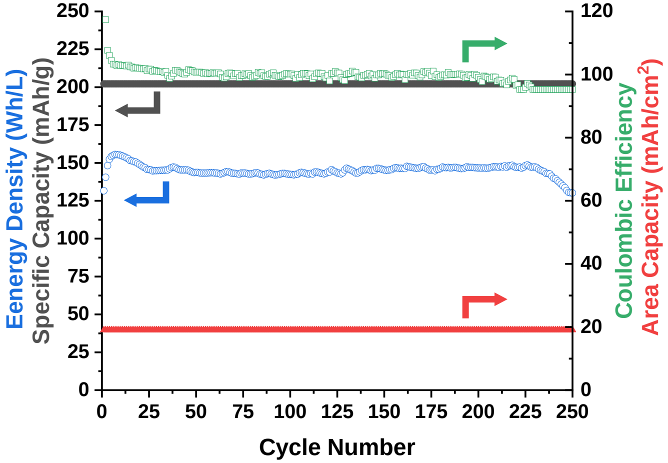
Cycling of Zn/($CuO-Bi_2O_3$)



Capacity of cycling Zn/CuO indicates the cathode is cycling Cu(II) → Cu(I)→Cu(0), eventually cycling Cu(I)→Cu(0) during cycle 100+

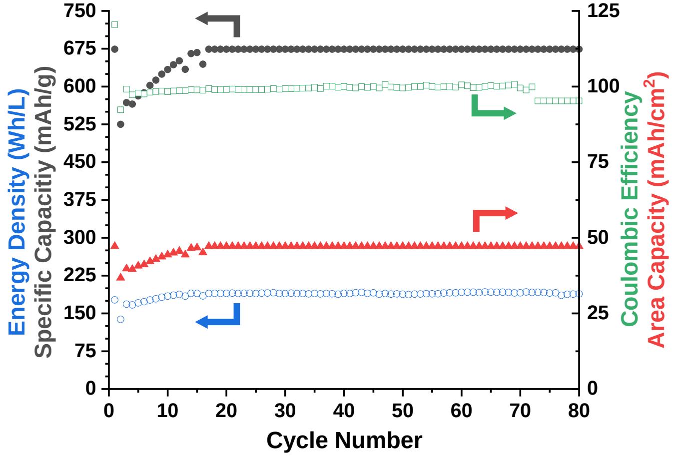
Two strategies for modifying performance show promising paths forward for long term cycling

Partial depth of discharge of $CuO-Bi_2O_3$



250 cycles:
30% DOD_{CuO}
Avg 19 mAh cm^{-2}
Coulombic Efficiency 99+%

Cu metal additive improves capacity retention



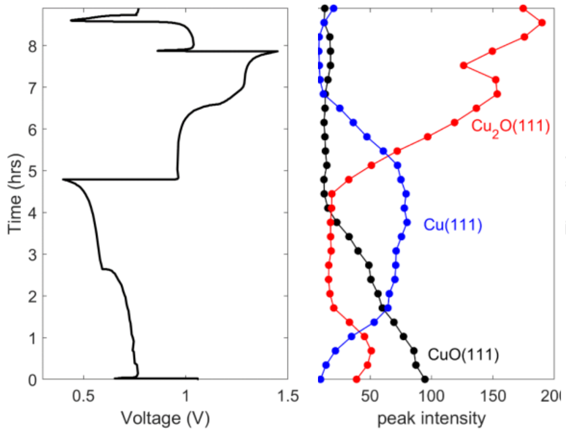
80 cycles:
100% DOD_{CuO}
Avg 46 mAh cm^{-2}
Avg 186 Wh L^{-1}

Schorr, N.B.; et al. ACS Appl. Energy Mater. 2021, 4, 7, 7073–7082

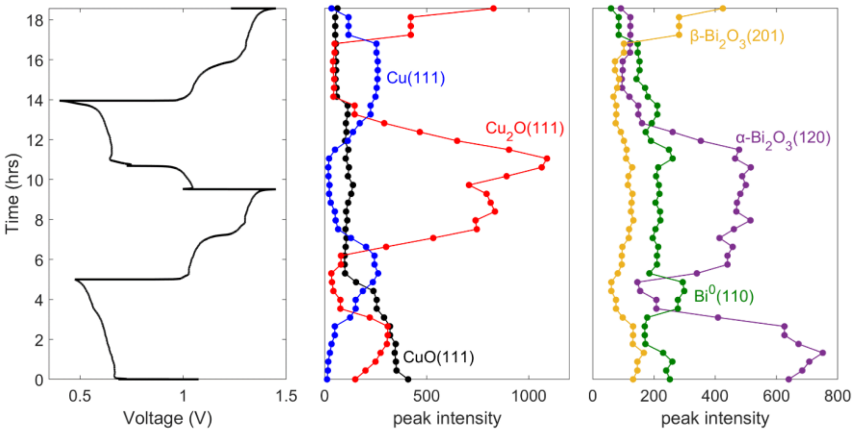
Role of Additive in Cathode

EDXRD identifies crystalline phases during discharge/charge

Zn/CuO



Zn/(CuO-Bi_2O_3)

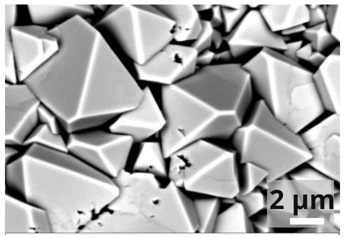


During 2nd discharge the high voltage causes the formation of more Cu_2O, indicating a non-crystalline Cu(II) phase not detectable by EDXRD

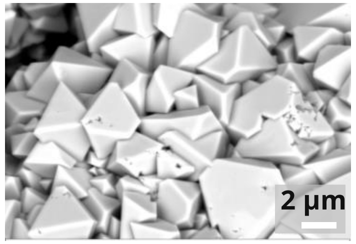
SEM images of cathode show Bi controls sample morphology

CuO

10 Charges

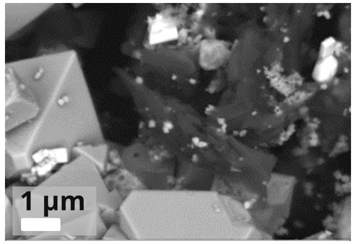


10 Discharges

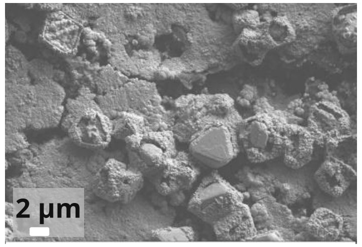


CuO-Bi_2O_3

10 Charges



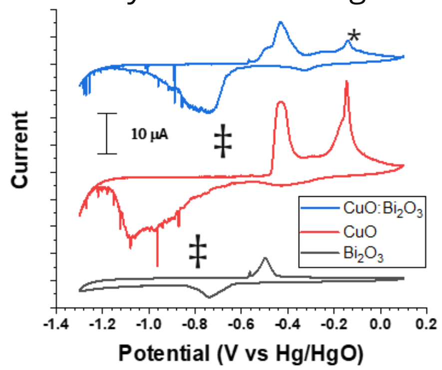
10 Discharges



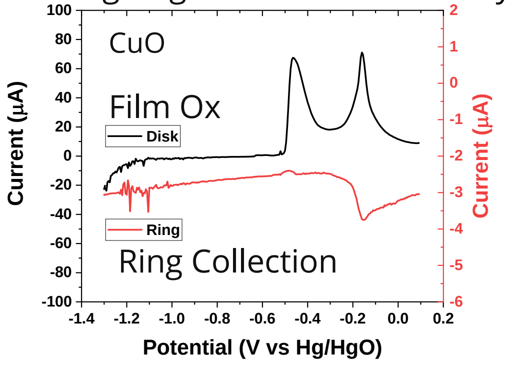
Octahedral Cu_2O seen in cathode without additive is the culprit behind electrode passivation, where this structure is scarce with inclusion of Bi_2O_3

CV and RRDE prove benefits of Bi additive

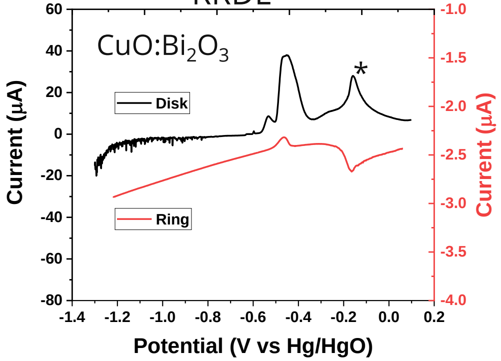
Film cyclic voltammograms



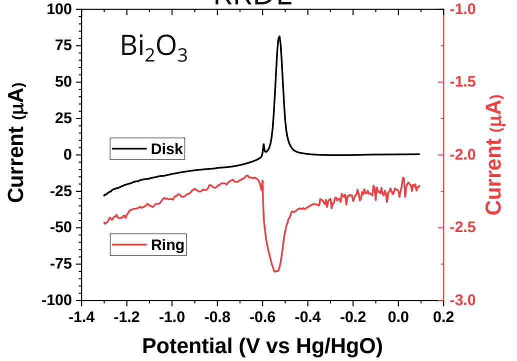
Rotating ring disk electrochemistry



RRDE



RRDE



Smaller 2nd oxidation peak * and lower ring RRDE collection confirms Bi reduces Cu(II) solubility

Onset of reduction peak ‡ is shifted positive with Bi indicating favorable Cu(I) reduction

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