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Sandia National Laboratories

Copper Oxide Cathodes for Rechargeable Alkaline Zinc Batteries

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MRS Fall Meeting EN12.12: Beyond Li-Ion IV

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U.S. DEPARTMENT OF ENERGY
NNSA National Nuclear Security Administration

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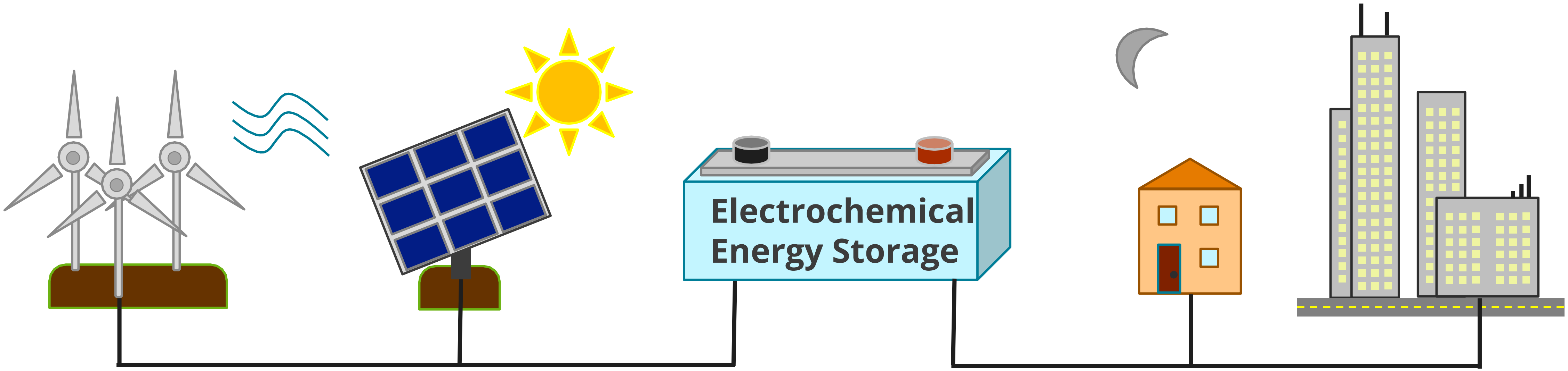
Importance of Storing Energy for the Grid



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

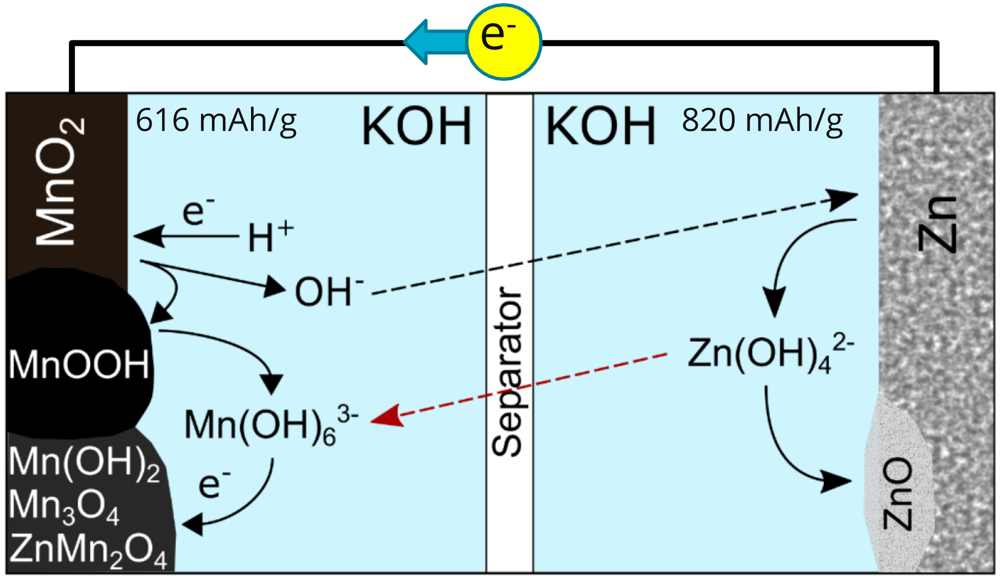
M. B. Lim, et al Mater. Sci. Eng. R Rep. 2021, 143, 100593. https://doi.org/10.1016/j.mser.2020.100593
Posada, J.O.G.; et al. Renewable Sustainable Energy Rev. 2017, 68, 1174-1182. doi.org/10.1016/j.rser.2016.02.024

Zn-Based Batteries for Grid Energy

Batteries utilizing a zinc anode are well poised to be adapted for grid energy storage

- **high capacity (817 mAh/g), energy density**
- **Established supply chain, earth abundant material**
- **1º alkaline batteries ~ < $20/kWh (Zn//$MnO_2$)**
- **Aqueous with long shelf life**
- **EPA certified for disposal**
- **High achievable energy density (~400 Wh/L)**

Zn//MnO_2 Cell



Issues with commercial primary MnO_2

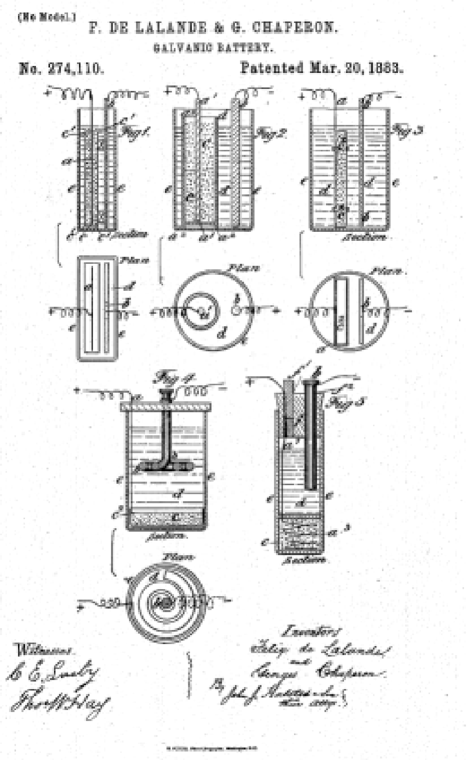
- **Irreversibility of Cathode (phase change)**
- **Susceptibility to Zinc poisoning**
- **Matching Zn DOD**

M. B. Lim; et al Mater. Sci. Eng. R Rep. 2021, 143, 100593. https://doi.org/10.1016/j.mser.2020.100593

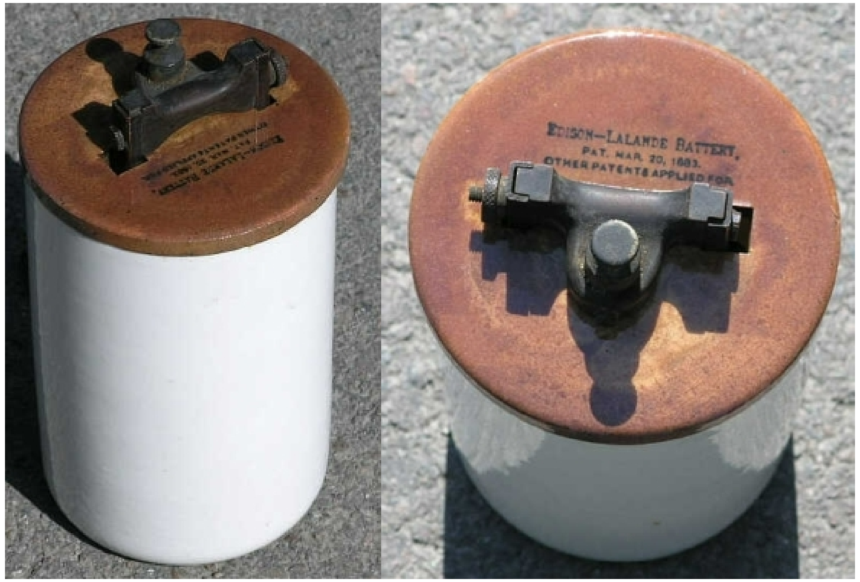
Choosing an Alkaline Cathode

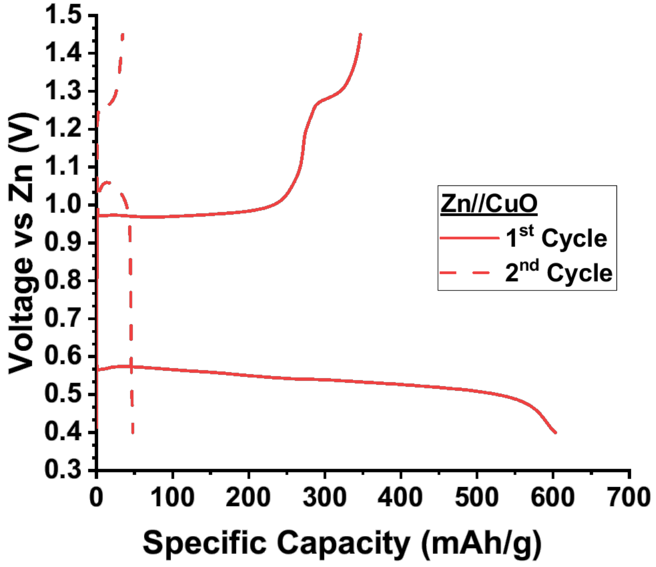
Historically CuO has been used as a cathode to pair with Zn for primary batteries

Unfortunately it does display reversibility, though has an attractive capacity (674 mAh/g)



Edison-Lalande Primary Battery



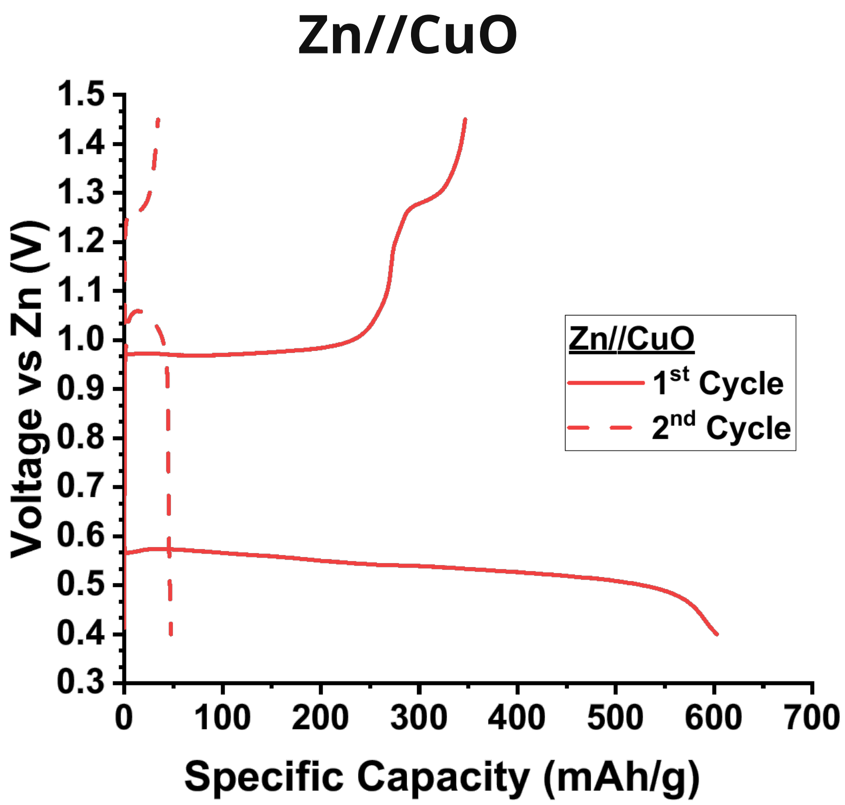


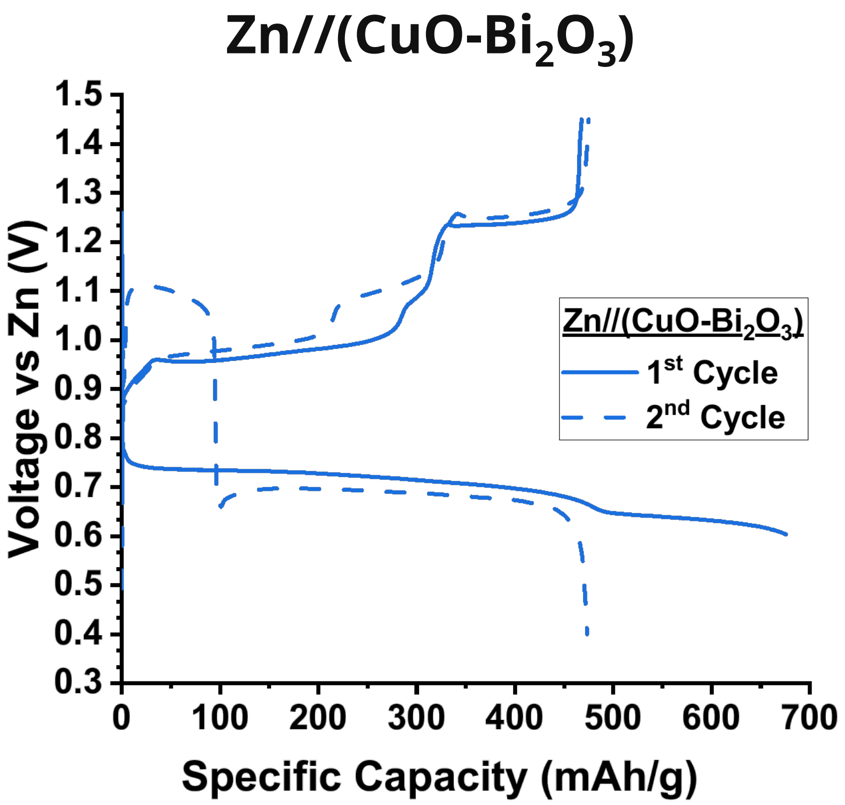
~140 years of no reported rechargeable CuO cathode

1881 → **2021**

Cycling Zn//CuO

Revisiting CuO cathodes with the addition of additives shows rechargeability is possible





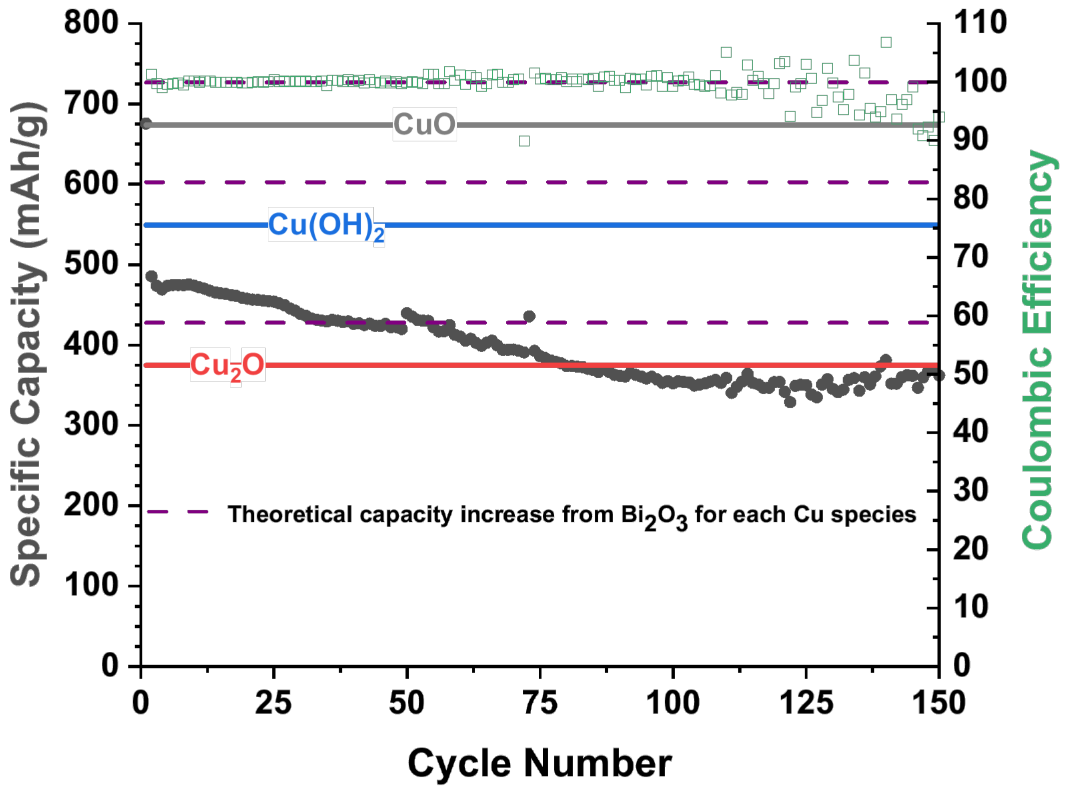
Mixing Bi_2O_3 into the cathode formulation promotes cyclability

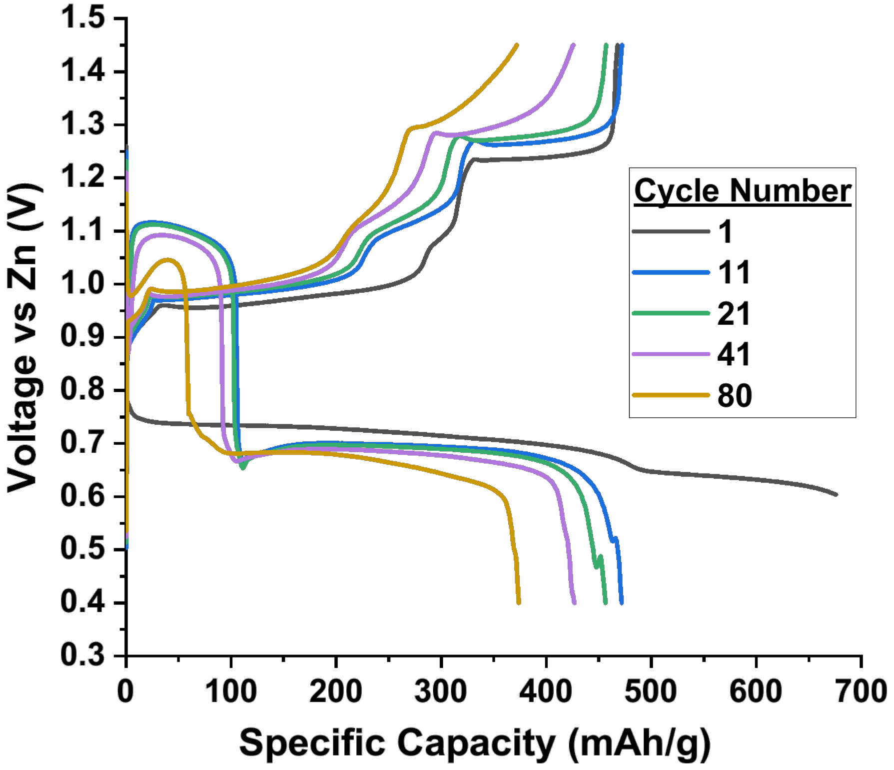
Schorr, N.B.; et al. ACS Appl. Energy Mater. 2021, 4, 7, 7073–7082

Cycling Zn//($CuO-Bi_2O_3$)

Bismuth additive promotes rechargeability for over a 100 cycles

There is not enough bismuth additive to supply the observed capacities



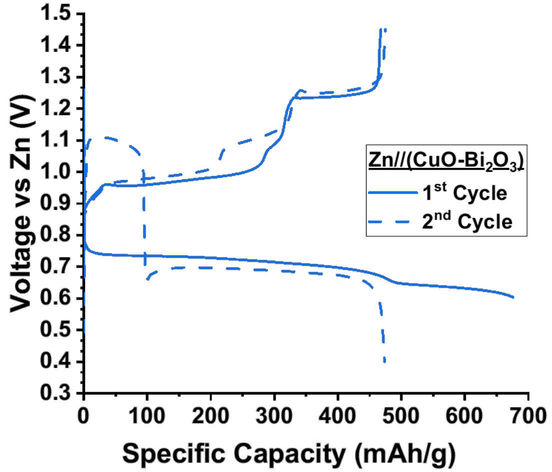


Average energy density of 157 Wh/L for cycles 2-75, 124 Wh/L for cycles 75-150

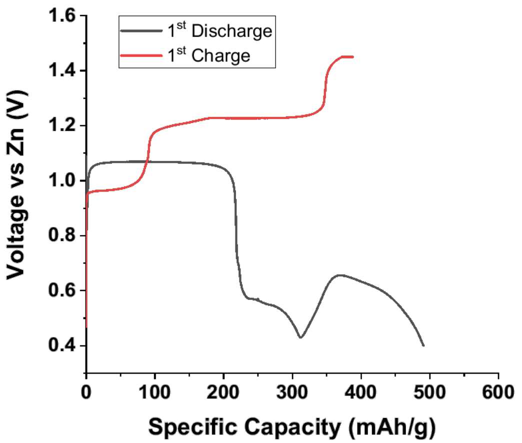
Delivered capacities and voltage curves indicate a mixed Cu species mechanism

Cycling Zn//(CuO-Bi_2O_3)

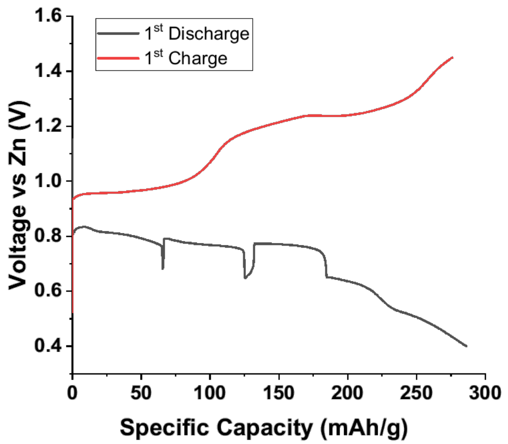
The profile of the second discharge gives us clues to the identity of Cu species playing a role in the cathode and the impact of Bi additive



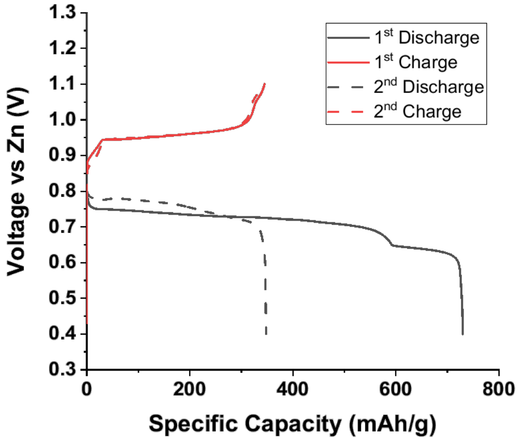
Zn//$Cu(OH)_2$



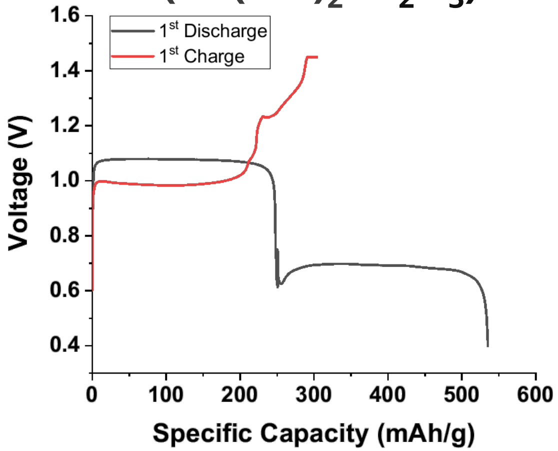
Zn//Cu_2O



Zn//(CuO-Bi_2O_3), limited voltage charge



Zn//($Cu(OH)_2$-Bi_2O_3)

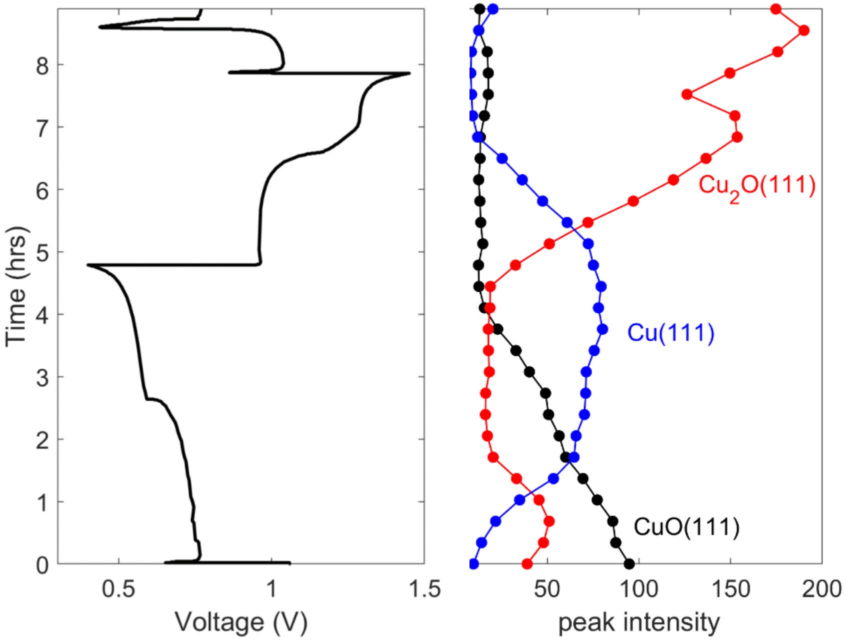


Transient resistive phases during discharge appear to be minimized with the inclusion of Bi_2O_3, which also does not display sporadic voltage changes during discharge

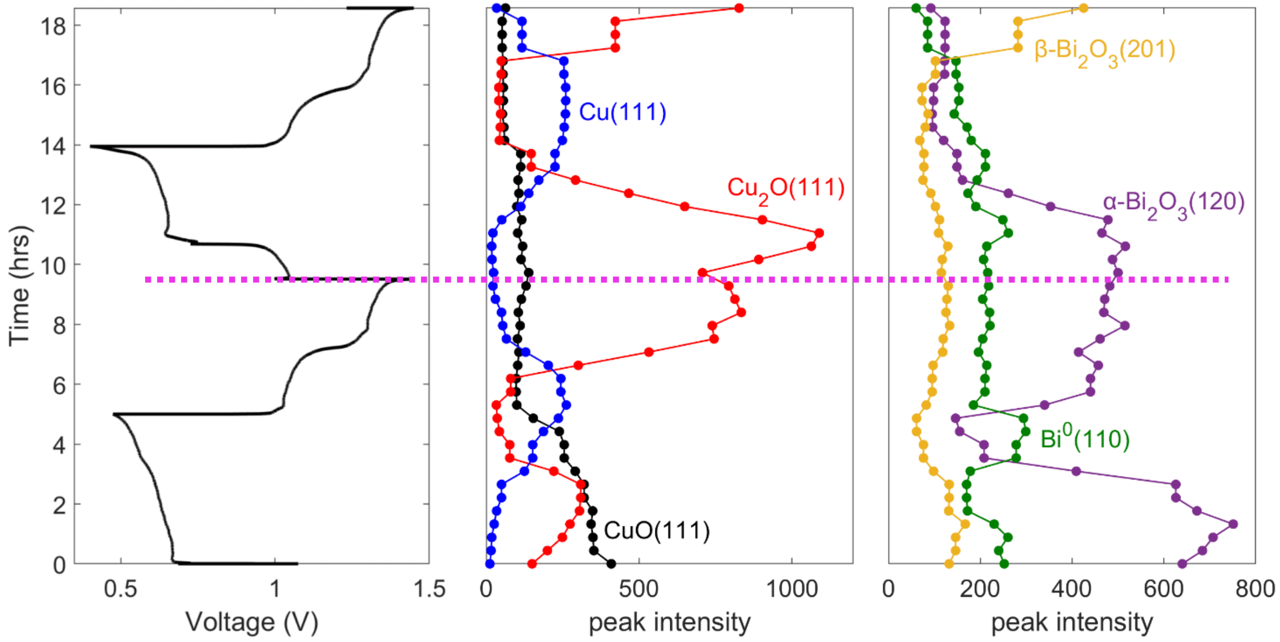
Operando Synchrotron Cycling

EDXRD data allows us to see what crystalline phases exist at certain potentials

Zn//CuO



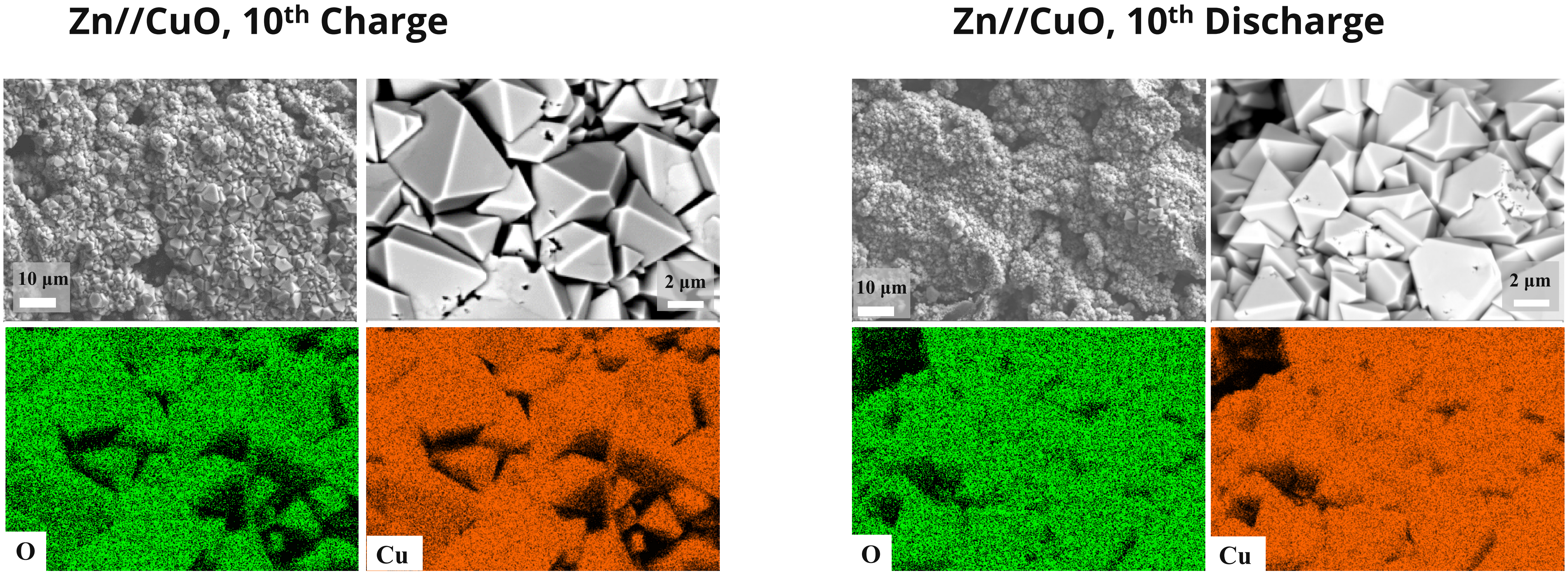
Zn//(CuO-Bi_2O_3)



Inclusion of Bi does not create any Cu-Bi crystalline phases

The synchronous intensities of the Cu_2O and Bi_2O_3 signals support that the additive is responsible for promoting Cu_2O and Cu(II) reduction.

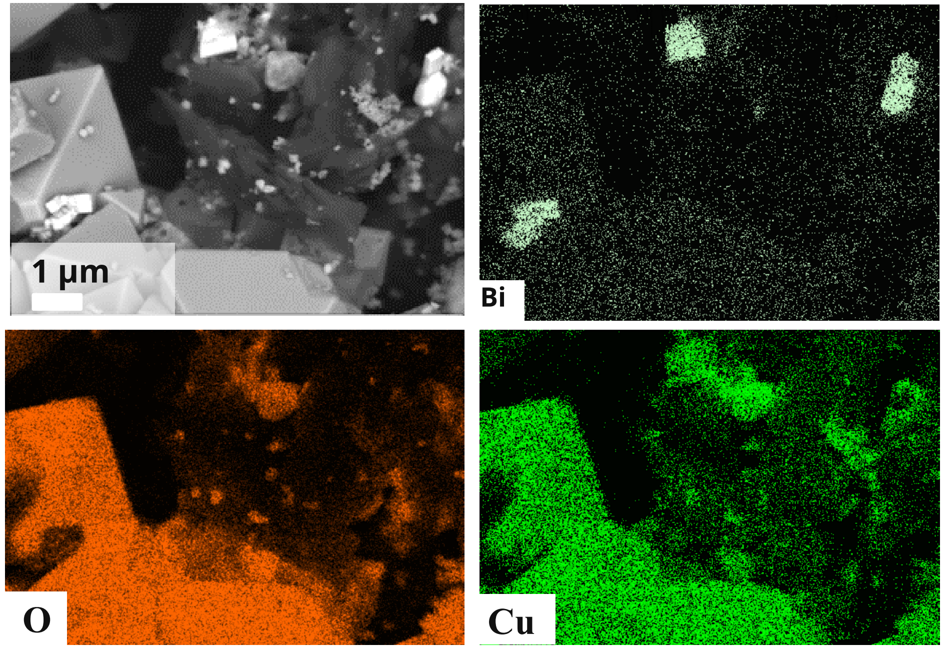
Cathode Morphology of CuO



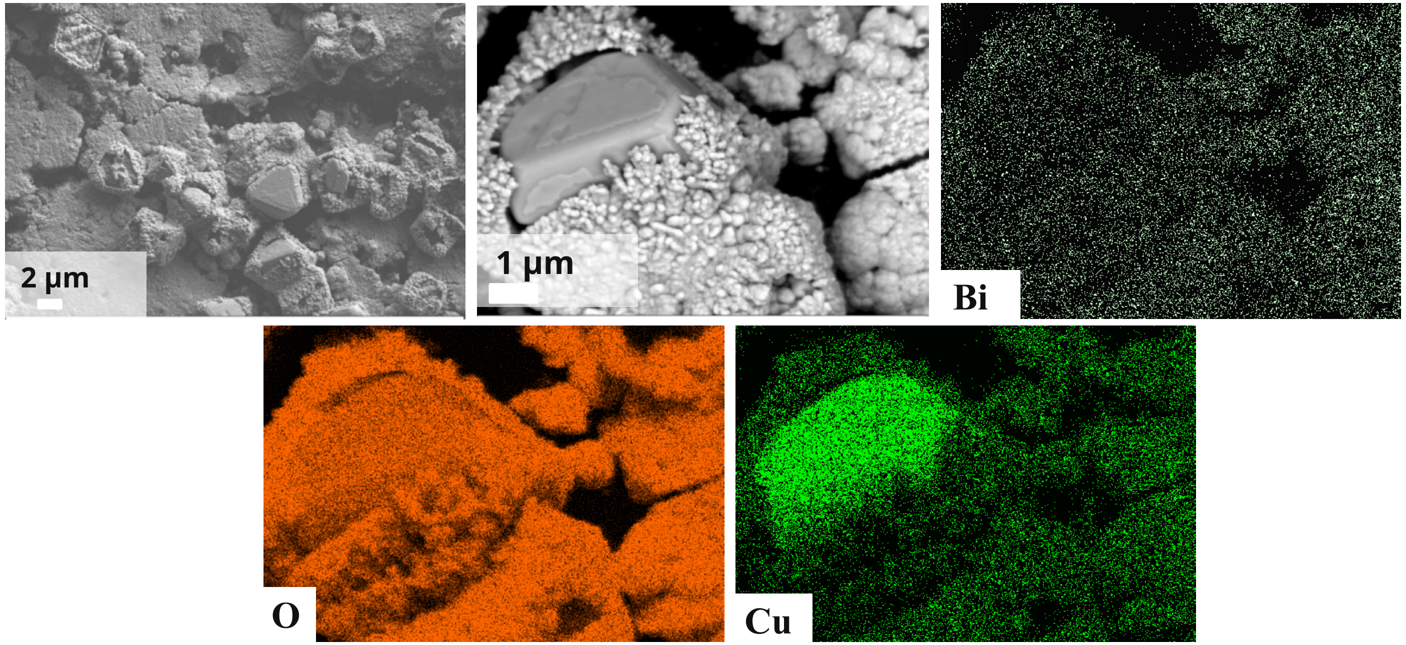
Identical morphology in a charged and discharged Zn//CuO indicates that the imaged phase is stable and electrochemically inactive in the conversion cathode

Cathode Morphology of $CuO\text{-}Bi_2O_3$

Zn//($CuO\text{-}Bi_2O_3$), 10^{th} Charge



Zn//($CuO\text{-}Bi_2O_3$), 10^{th} Discharge



When cathodes are made with Bi_2O_3 we now see a different morphology on discharge, but some remnants of the octahedral seen on charge and in CuO (no additive) still appear.

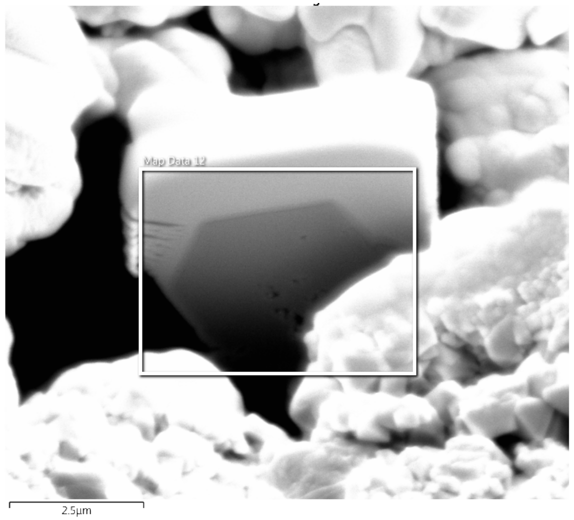
These are essentially the microscopic signatures of the imperfect cycling behavior and the reason for the decrease in the capacity with cell cycling

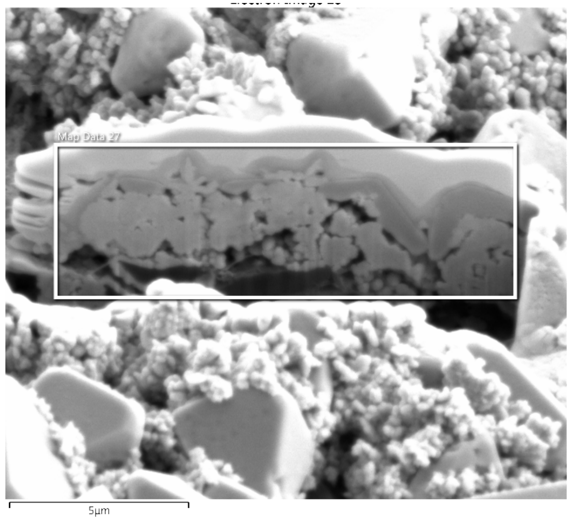
Internal Cathode Morphology

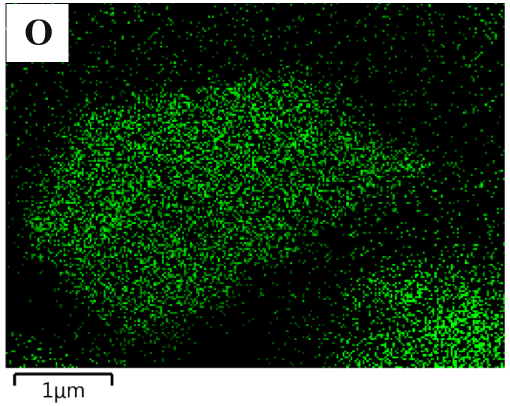
Zn//CuO

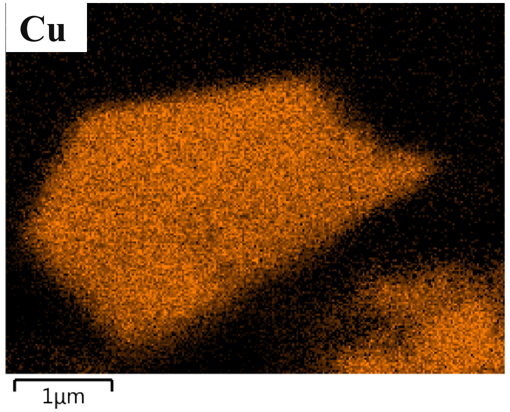
10^{th} Discharge

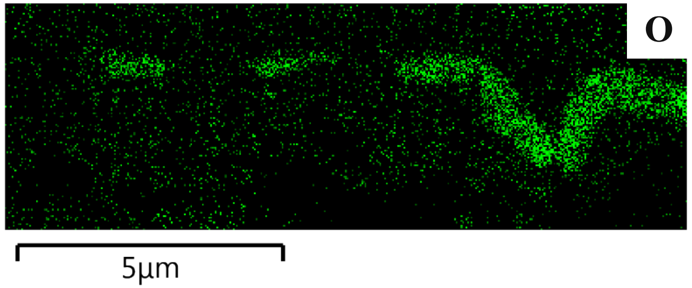
Zn//(CuO-Bi_2O_3)

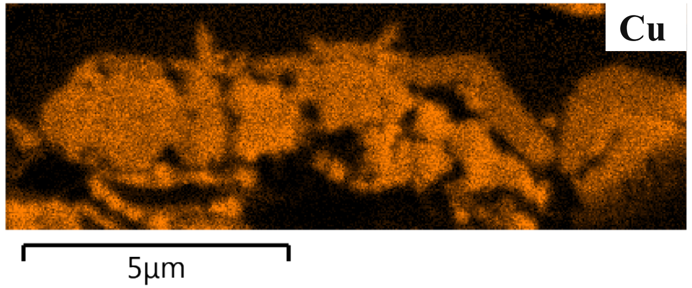


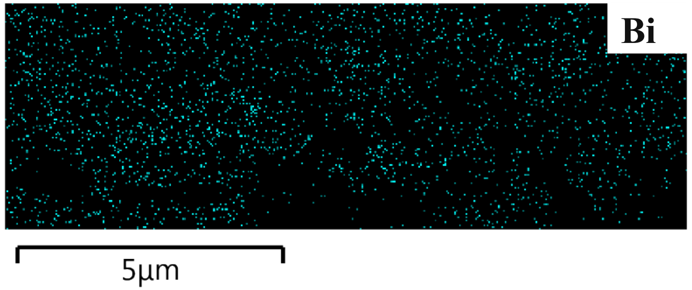








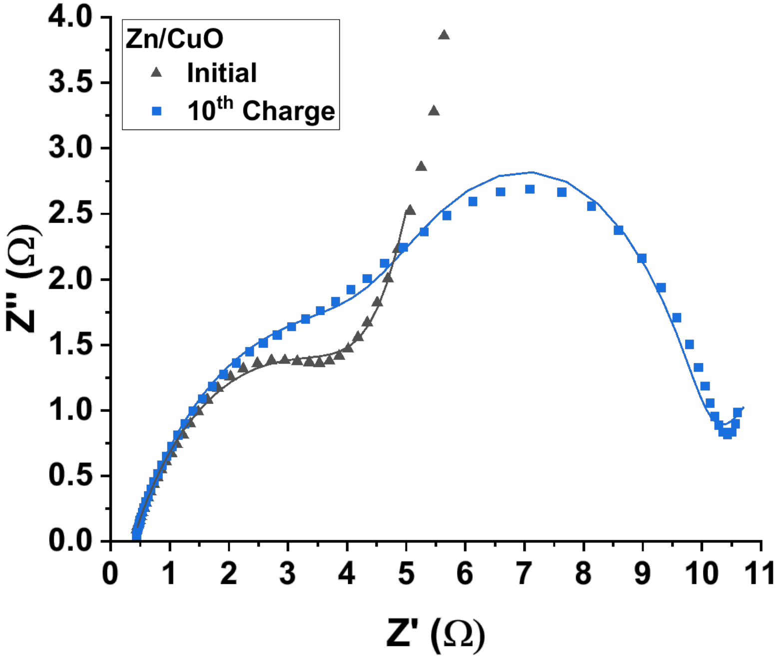




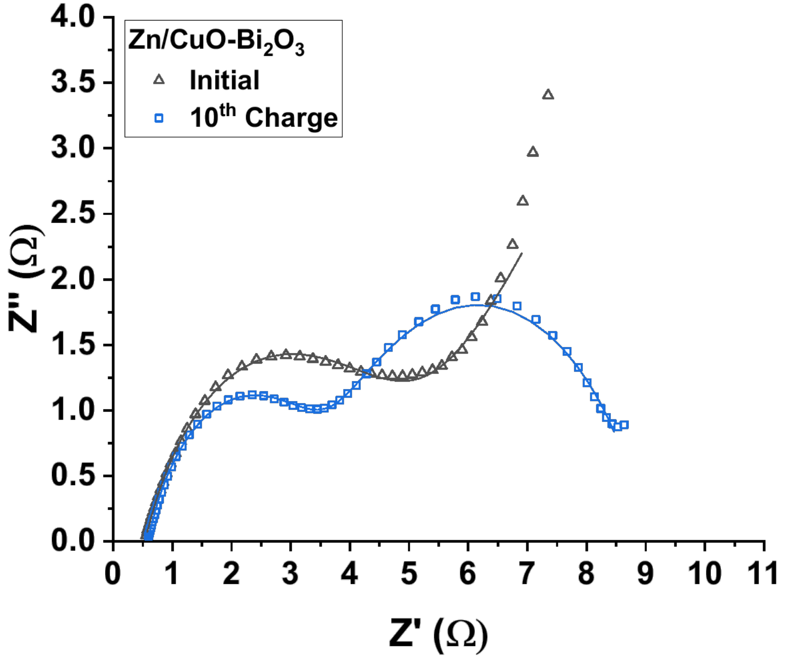
Impact of Bi in CuO Cathode

Bi contributes to minimizing cathode passivation through decreasing interfacial and charge transfer resistance upon cycling

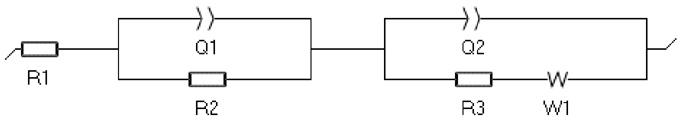
Zn//CuO



Zn//(CuO-Bi_2O_3)



EIS model



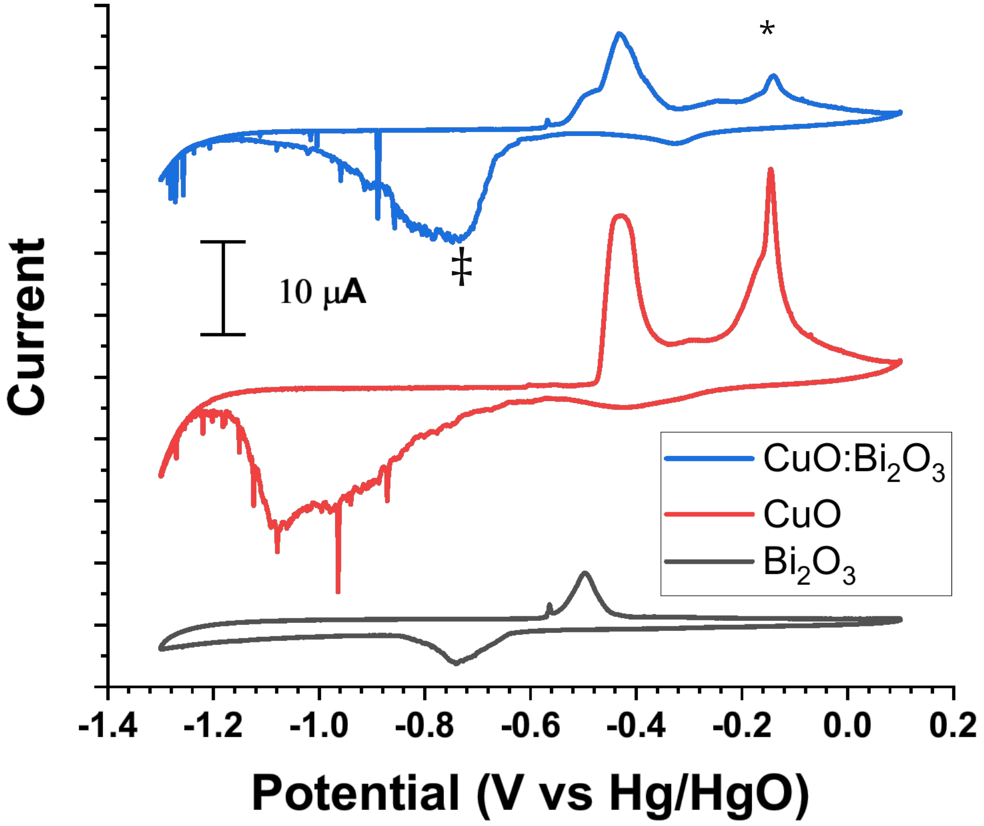
The equivalent circuit model, consisting of two Voigt type elements in series (Q/R) with ohmic resistance (R) and semi-infinite diffusion (W)

The two Voigt type elements account for distinct 2e- reactions and formation of surface layers, with a Warburg element accounting for semi-infinite diffusion from the electrode

Impact of Bi Additive on CuO film

Cyclic voltammetry of film with and without Bi_2O_3

- Less resistive slope of the second reduction
- Smaller 2nd oxidation peak
- Onset of reduction peak is shifted positive



Bismuth forming a beneficial conductive matrix when incorporated as an additive in battery systems has been reported before for Zn anodes

Gallaway, J. W; et al . J. Electrochem. Soc. 2014, 161, A275.
McBreen, J.; et al J. Power Sources 1985, 15, 169-177. doi.org/10.1016/0378-7753(85)80070-7

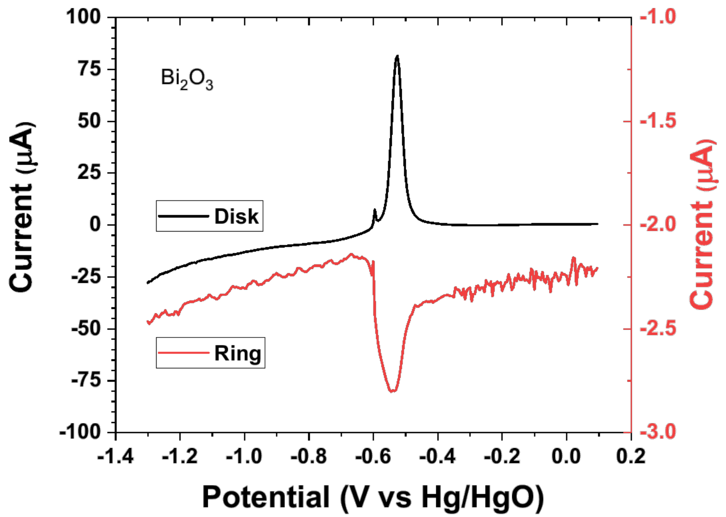
Bi electrodes are also a common for use in anodic stripping voltammetry of copper

Duay, J.; Electroanalysis 2017, 29, 2685-2688. doi.org/10.1002/elan.201700526

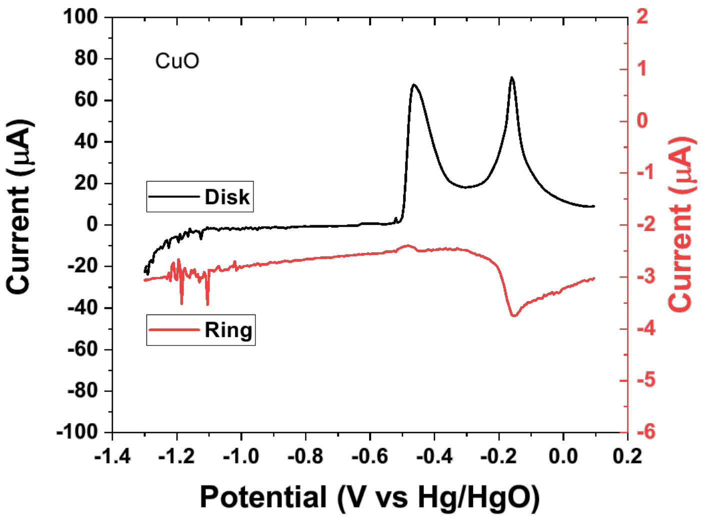
Impact of Bi Additive on CuO film

For RRDE three films: Bi_2O_3, CuO, and CuO:Bi_2O_3 were first reduced then potential was swept positive to oxidize the film while the ring was held at a constant negative potential to reduce redox active species formed at the disk

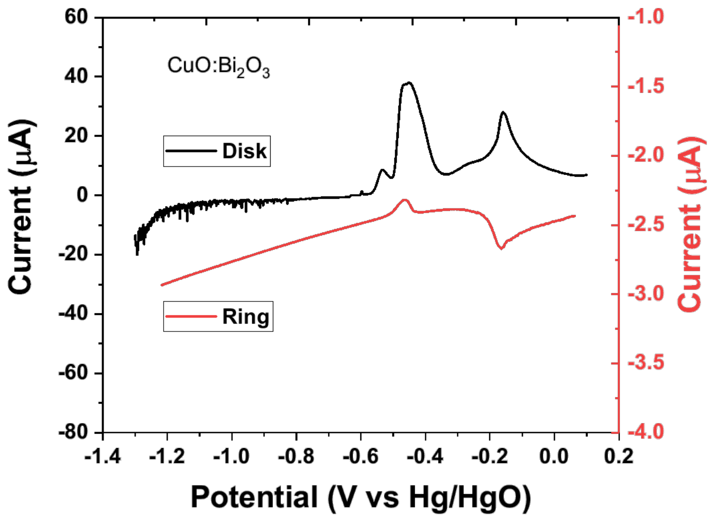
Bi is soluble upon oxidation

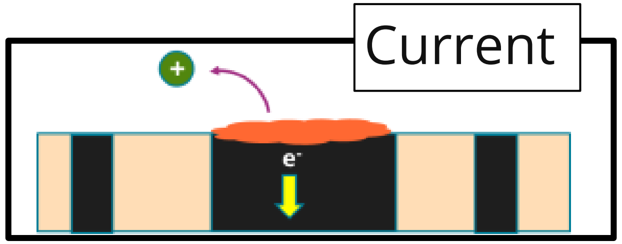


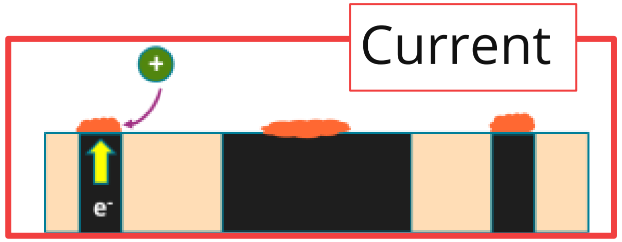
Cu is soluble upon 2nd oxidation



Cu solubility is reduced when Bi is present





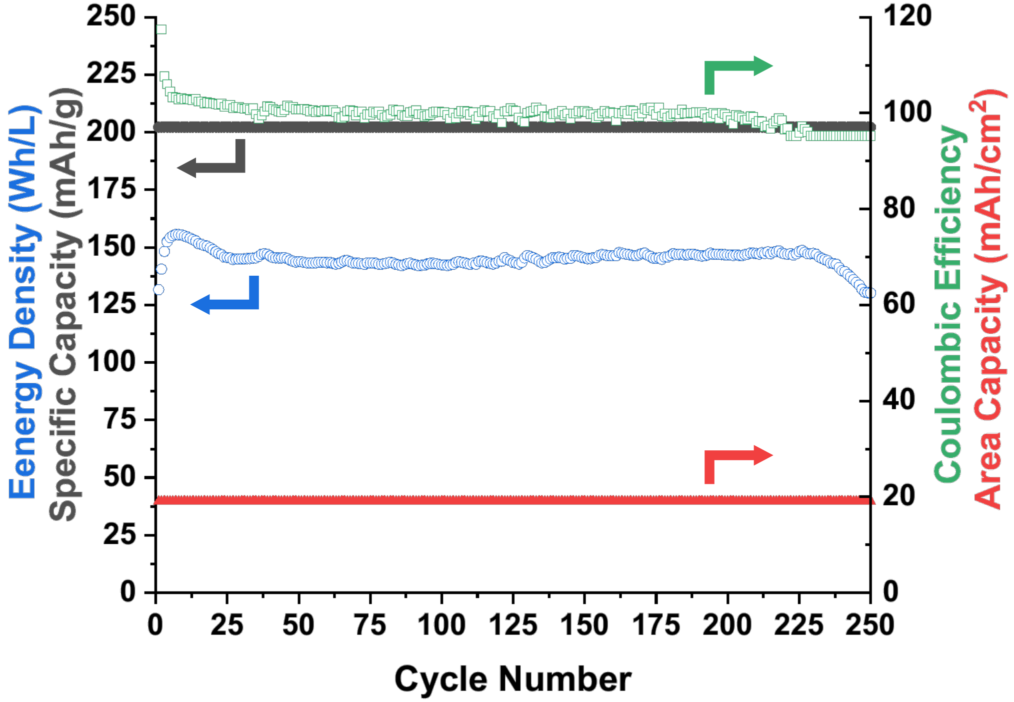


Collection efficiency drops over 65% from the collection during the oxidation of the CuO film to the CuO–Bi_2O_3 film

Improving Zn//CuO Cycling

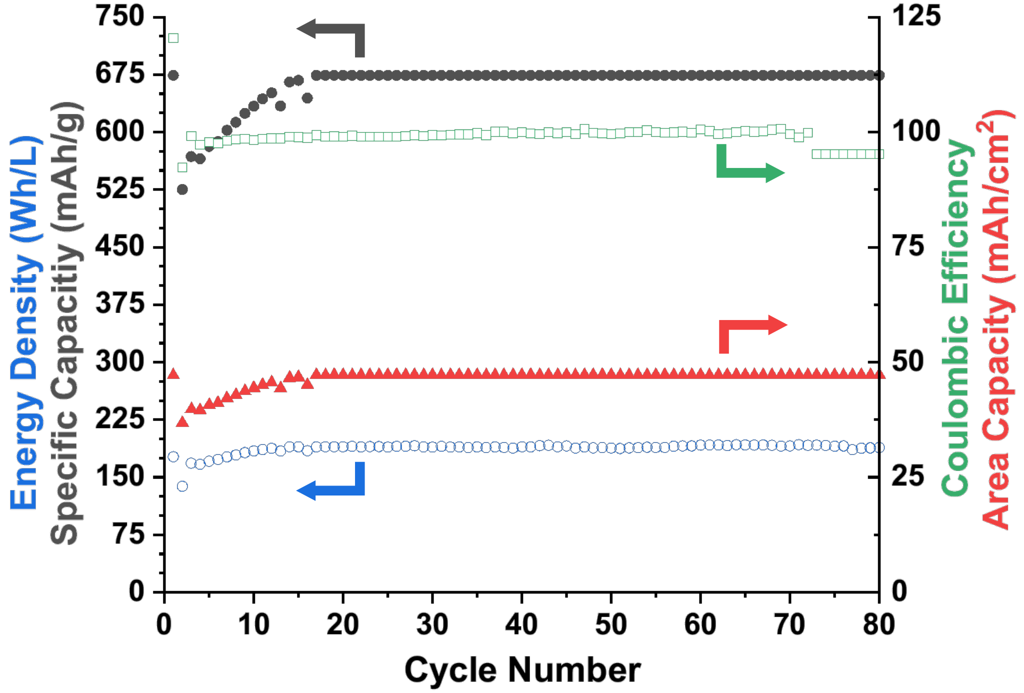
Two strategies for modifying performance show promising paths forward

Partial depth of discharge of CuO-Bi_2O_3 cathode causes increased lifetime



250 cycles: 30% DOD_{CuO} (200 mAh g^{-1} cathode)
Average areal capacity 19 mAh cm^{-2}
Coulombic Efficiency above 99%

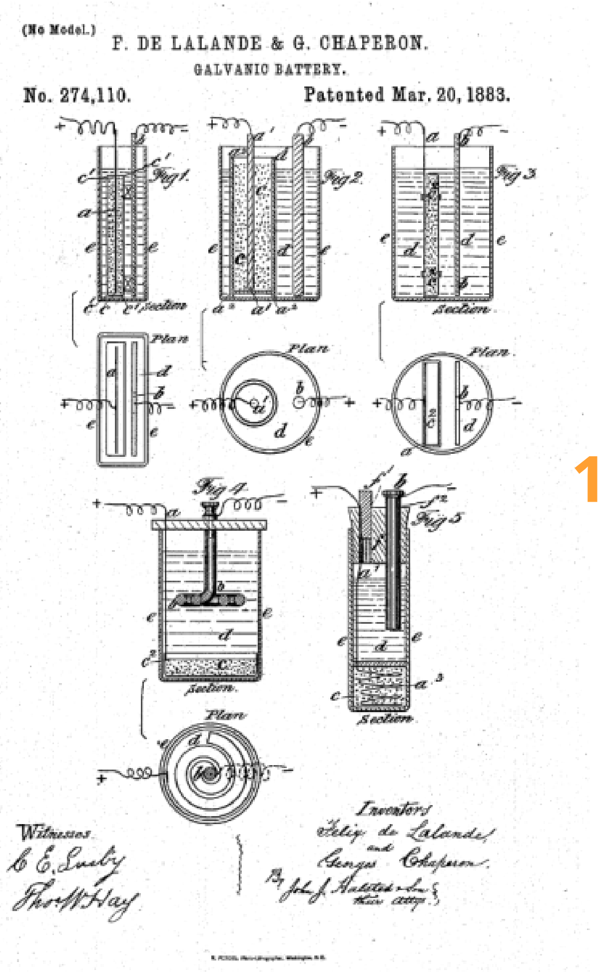
Using Cu as an additive improves capacity retention and energy density



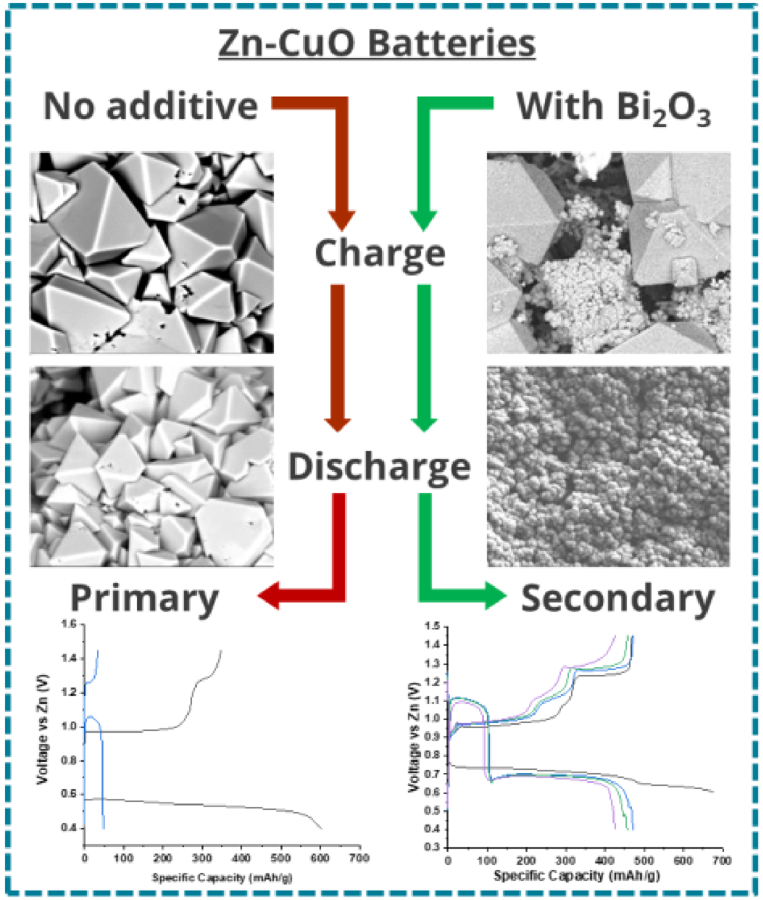
80 cycles: 100% DOD_{CuO} (674 mAh g^{-1} cathode)
Average areal capacity 46 mAh cm^{-2}
Average energy density 186 Wh L^{-1}

Takeaway

Almost 140 years later the alkaline Zn//CuO Cell is cyclable



1881 → 2021



Questions to still answer: Importance of initial particle size, ratio Bi:Cu, dependance on conductive carbon, solution phase interaction of Bi and Cu species

Acknowledgments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David Arnot


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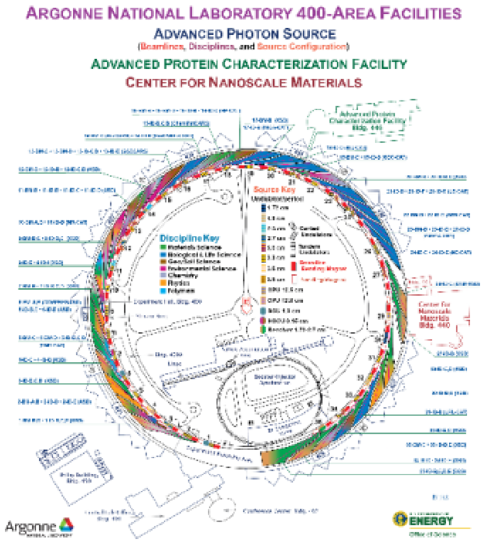

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Imre Gyuk

THIS WORK WAS SUPPORTED THROUGH THE ENERGY STORAGE PROGRAM,
MANAGED BY DR. IMRE GYUK,
WITHIN THE U.S. DEPARTMENT OF ENERGY'S OFFICE OF ELECTRICITY

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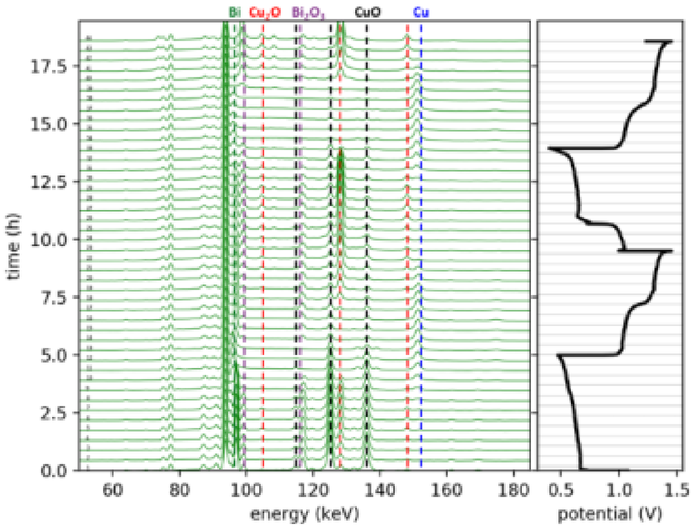
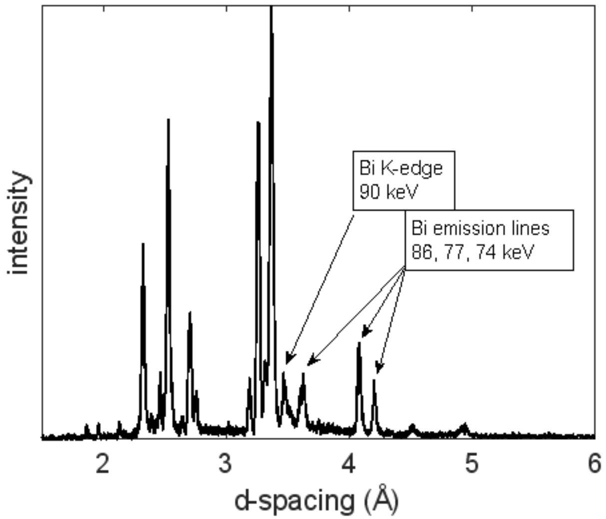
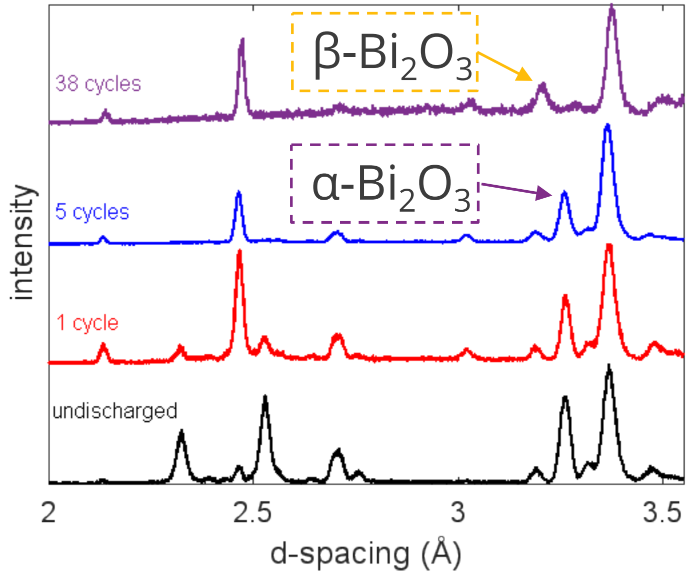
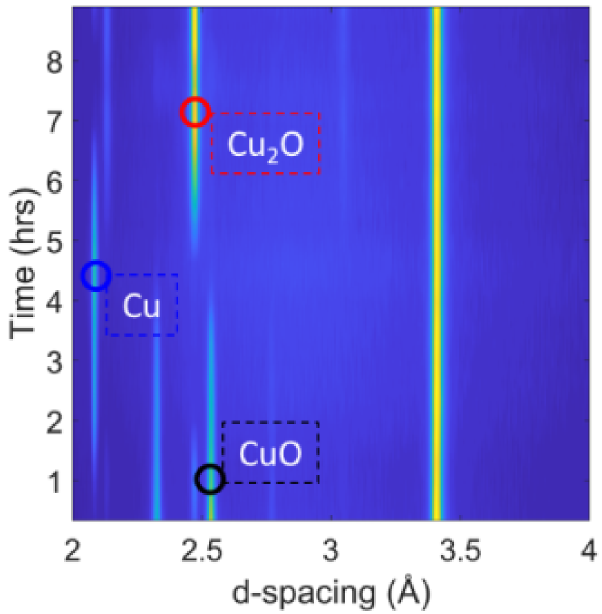
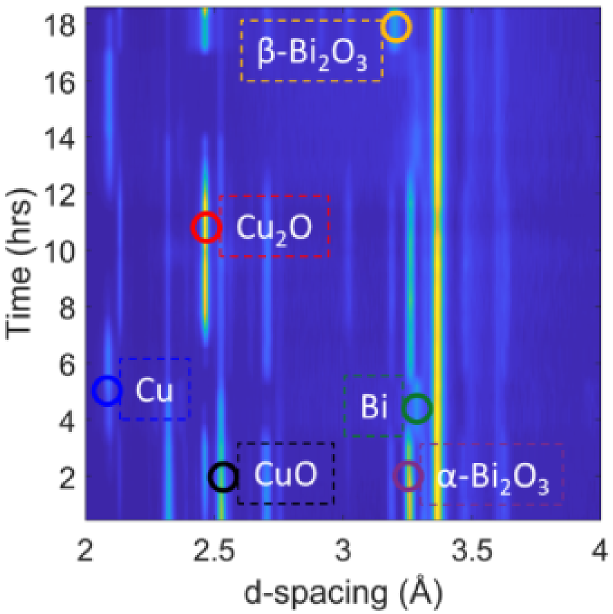
Supplemental







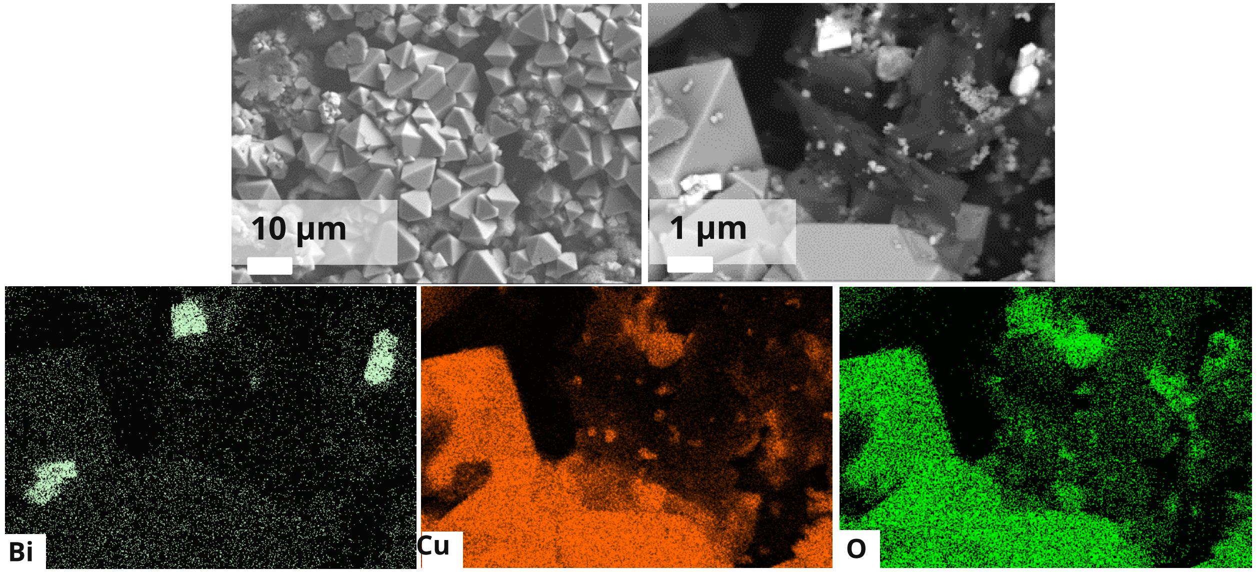




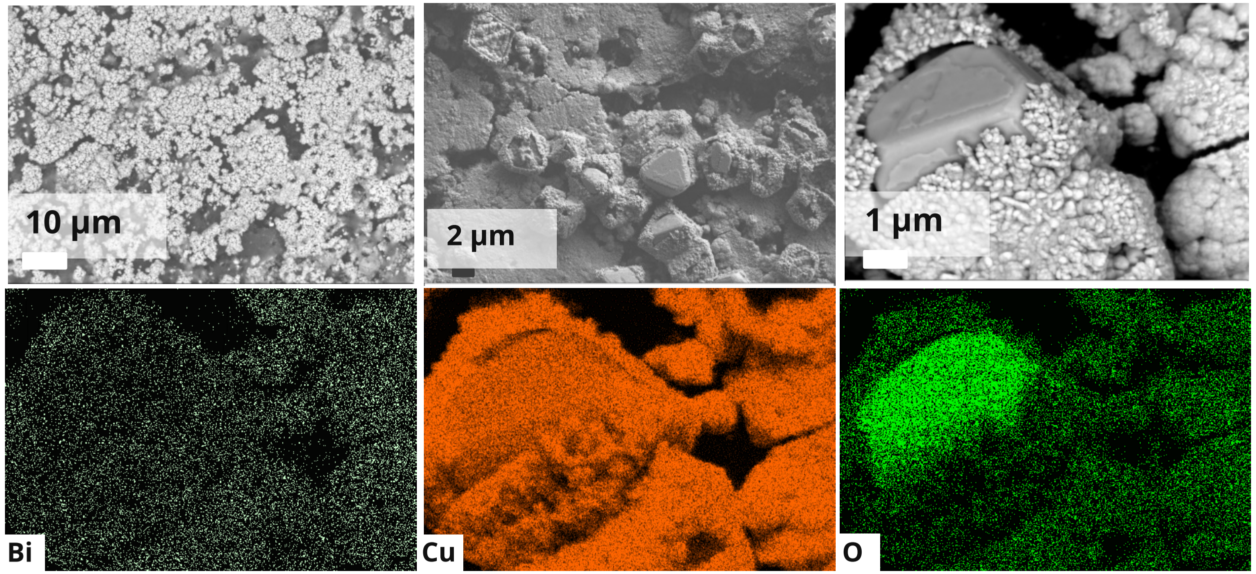
When the in situ spectra of charged cells cycled 0, 1, 3, 5, and 38 times are compared, β-Bi2O3 is only seen in the cell cycled 38 times, whereas α-Bi2O3 is present in cells cycled 1, 3, and 5 times

Cathode Morphology of CuO-Bi_2O_3

Zn//(CuO-Bi_2O_3), 10th Charge



Zn//(CuO-Bi_2O_3), 10th Discharge



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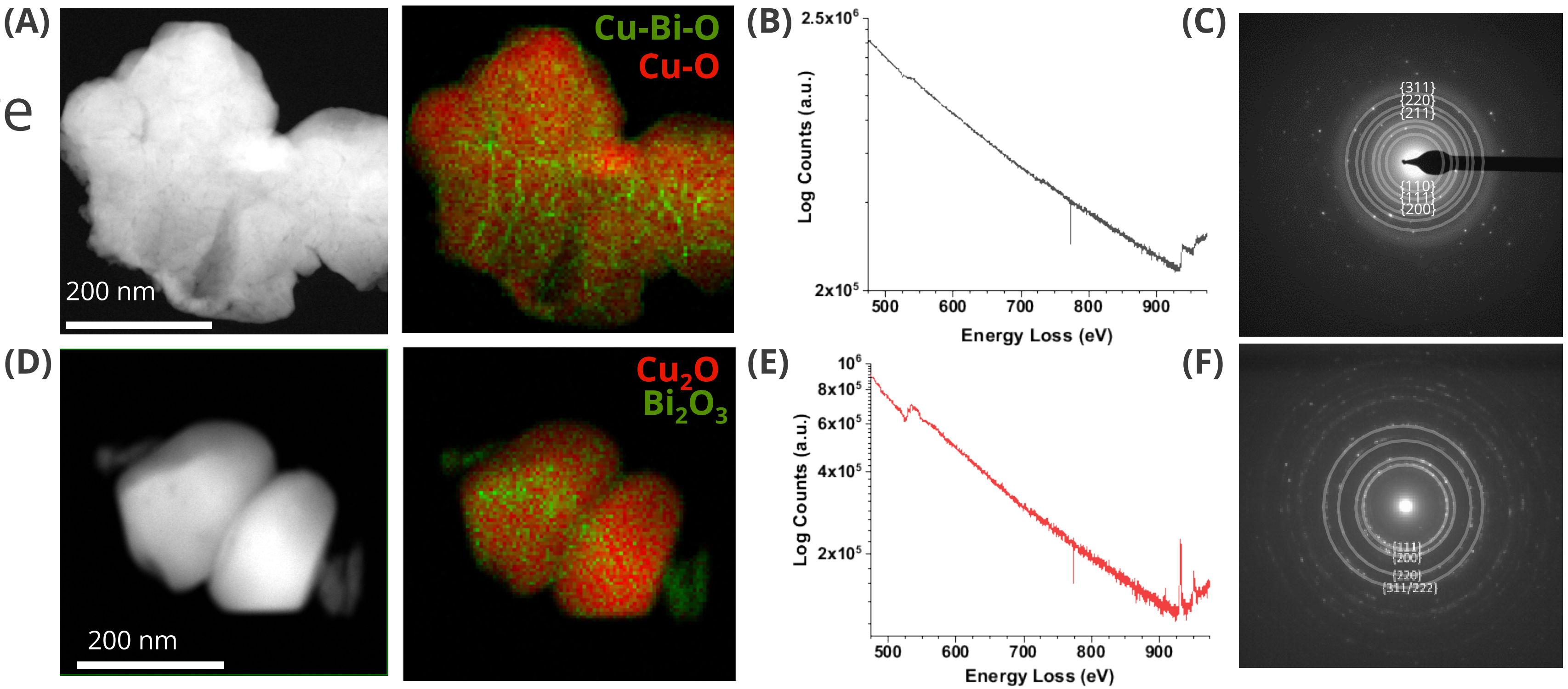
Supplemental

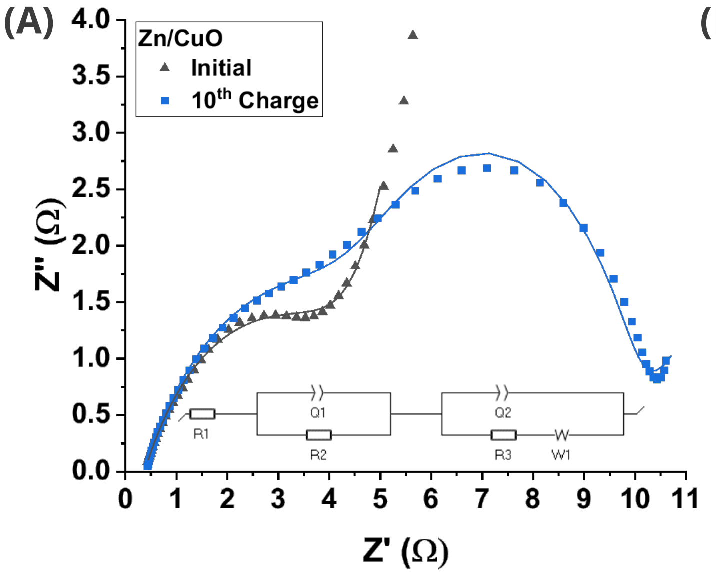
CuO/Bi_2O_3 10 Discharge

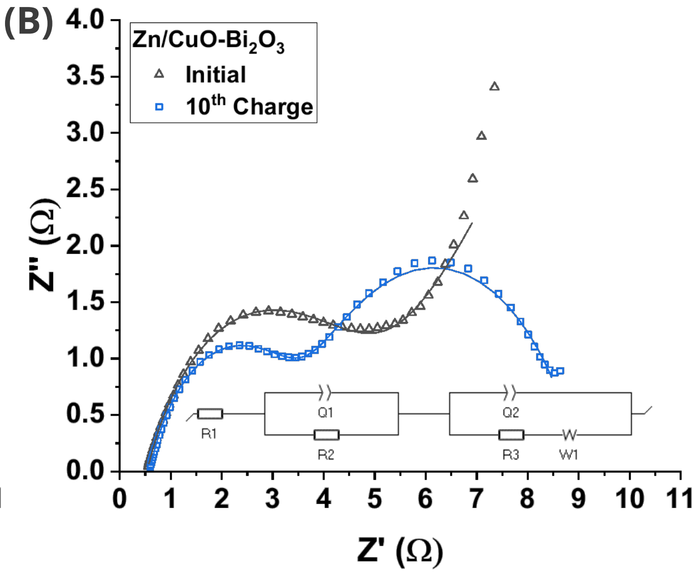
CuO/Bi_2O_3 10 Charge



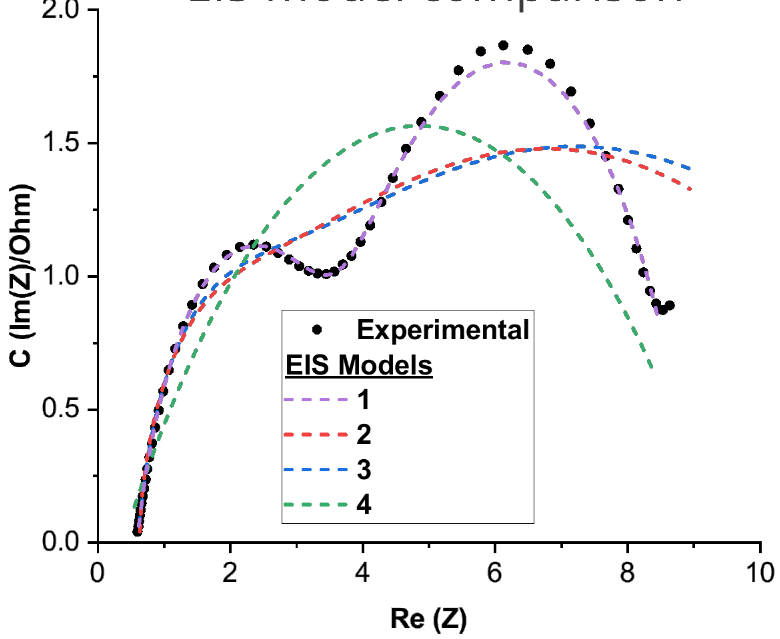
The O−K and Cu $L_{3,2}$ peaks from EELS and the SAED pattern of the charged cathode materials agree with EDXRD that copper is in the form of Cu_2O with a = 4.267 Å, $Pn\bar{3}m$

Supplemental



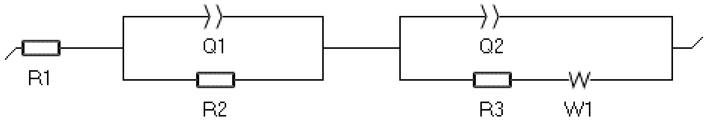


EIS model comparison



EIS models

1 Used in manuscript



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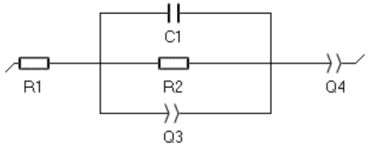

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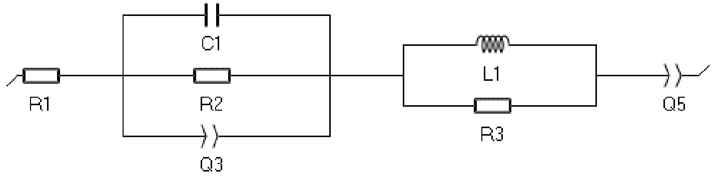

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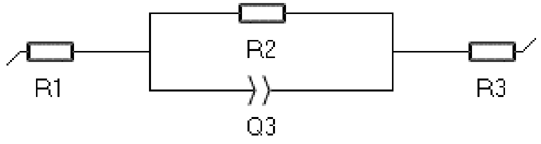

Journal of Membrane Science 548 (2018) 247–253

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Regenerable Cu-intercalated MnO2 layered cathode for highly cyclable energy dense batteries

DOI: 10.1038/ncomms14424

Energy storage performance of CuO as a cathode material for aqueous zinc ion battery

J. Meng et al. / Materials Today Energy 15 (2020) 100370

Supplemental

Reduction of films used for RRDE experiments