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Sandia National Laboratories

Developing New Chemistries for Alkaline Zn-based Batteries

PRESENTED BY

Timothy N. Lambert

NAATBatt Zn Battery Technology IV Workshop/Webinar, December 16, 2021

U.S. DEPARTMENT OF ENERGY NNSA

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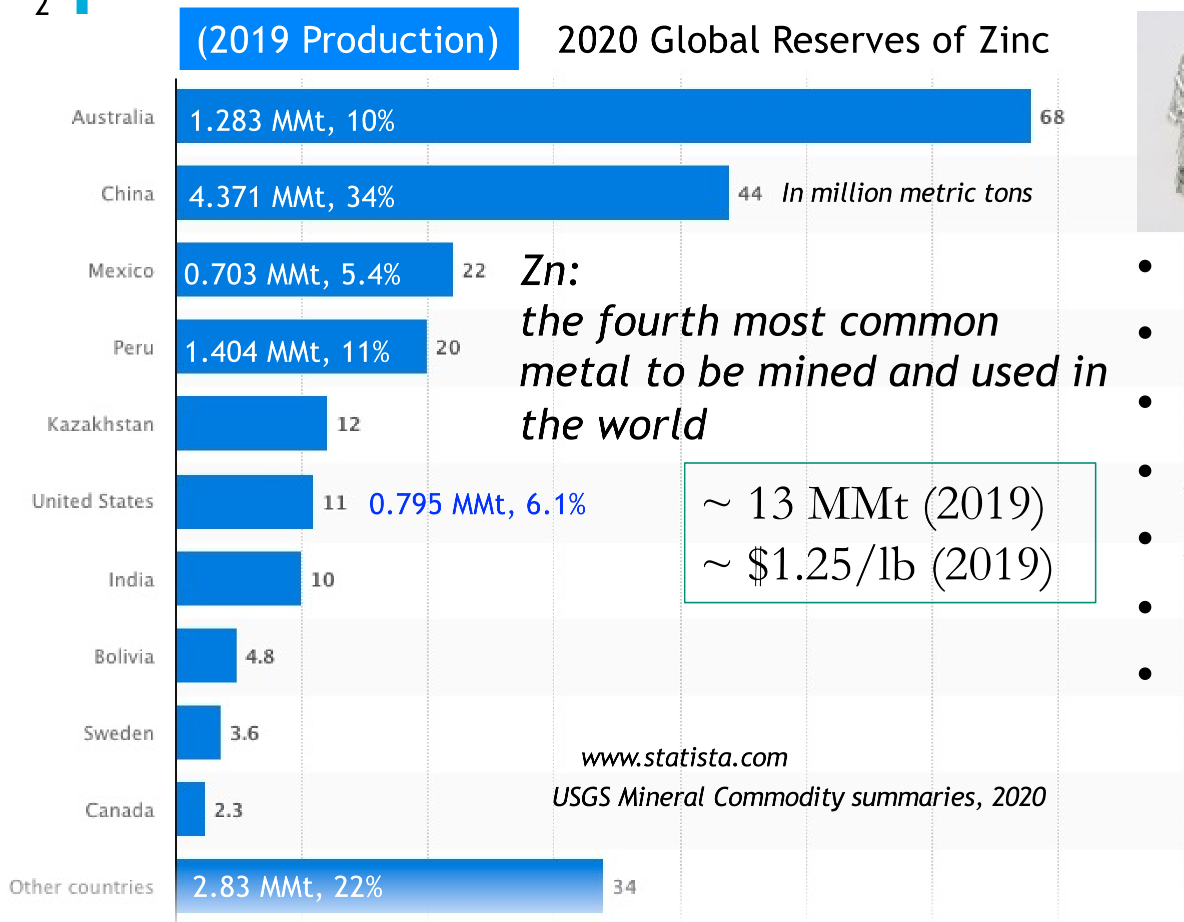
A case for Zn-based batteries



Zn: the fourth most common metal to be mined and used in the world

~ 13 MMt (2019)
~ \$1.25/lb (2019)

www.statista.com
USGS Mineral Commodity summaries, 2020

https://www.usgs.gov/centers/nmic/zinc-statistics-and-information

Zn

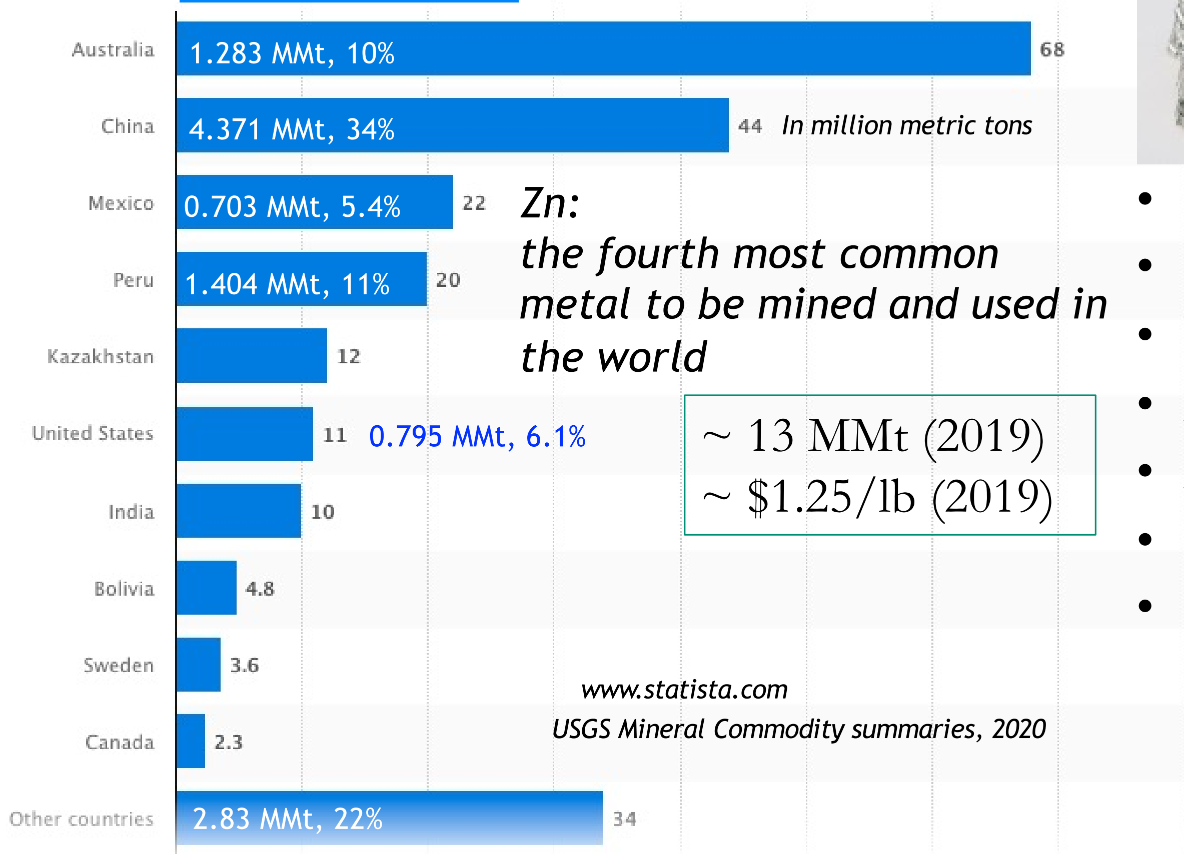
1° Alkaline Zn/MnO_2 as an exemplar

Wikipedia, user Aney, 2005

- Existing supply chain
- > 10B units Zn/MnO_2 produced (2019)
- \$7.5B global market (2019)
- Affordable ~ \$20/kWh
- Aqueous w/long shelf life
- EPA certified for disposal (safe)
- High achievable energy density
  - Zn/MnO_2 ~ 400 Wh/L

A case for Zn-based batteries

(2019 Production) 2020 Global Reserves of Zinc



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- High achievable energy density
  - Zn/MnO_2 ~ 400 Wh/L
  - Zn/Air ~ 1400 Wh/L
  - Zn/Ni ~ 300 Wh/L
  - Zn/CuO ~ 400 Wh/L

Low Cost, readily available ~ Energy Equity

High Energy Density ~ Long Duration Energy Storage

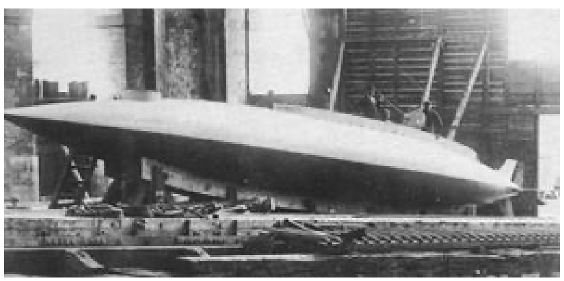
Zn-CuO Batteries

Primary Alkaline Zn/CuO Battery

Anode: $Zn^0 + 4OH^- \rightarrow [Zn(OH_4)]^{2-} + 2e^-$ $E^o = 1.285$ V

Cathode: $CuO + H_2O + 2e^- \rightarrow Cu^0 + 2OH^-$ $E^o = -0.29$ V

$Zn^0 + CuO + H_2O + 2OH^- \rightarrow [Zn(OH_4)]^{2-} + Cu^0$ Cell Voltage: 0.995 V



Gymnote in 1889

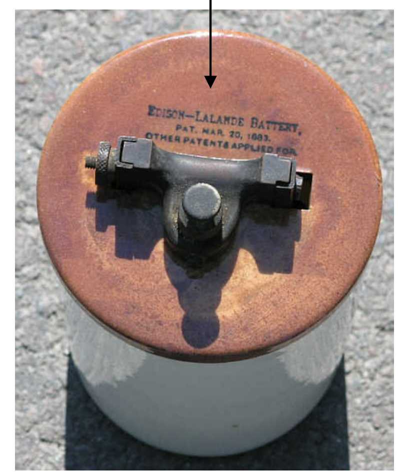
The name "Gymnote" refers to the Gymnotids, the "electric eels"
www.wikipedia.com

1st electric submarine with torpedoes - 2 x 355 mm (14 in)

55 horsepower (41 kW) at 200V and 200A

564 Primary Alkaline Zn/CuO Cells (Lalande-Chaperon Patent)

Edison-LaLande Battery.
PAT. Mar. 20, 1883.
OTHER PATENTS APPLIED FOR



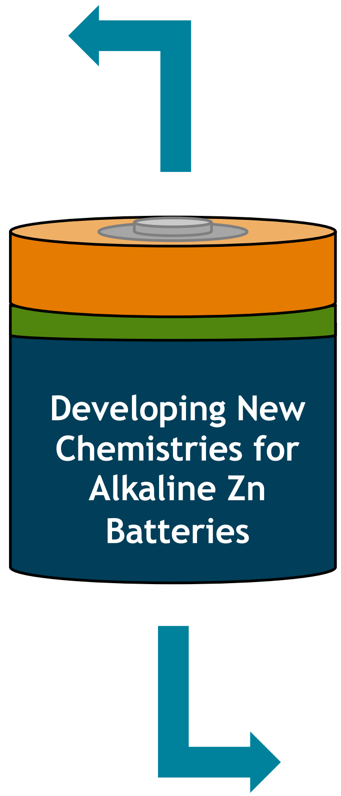
Edison-Lalande Battery (Primary Cell)

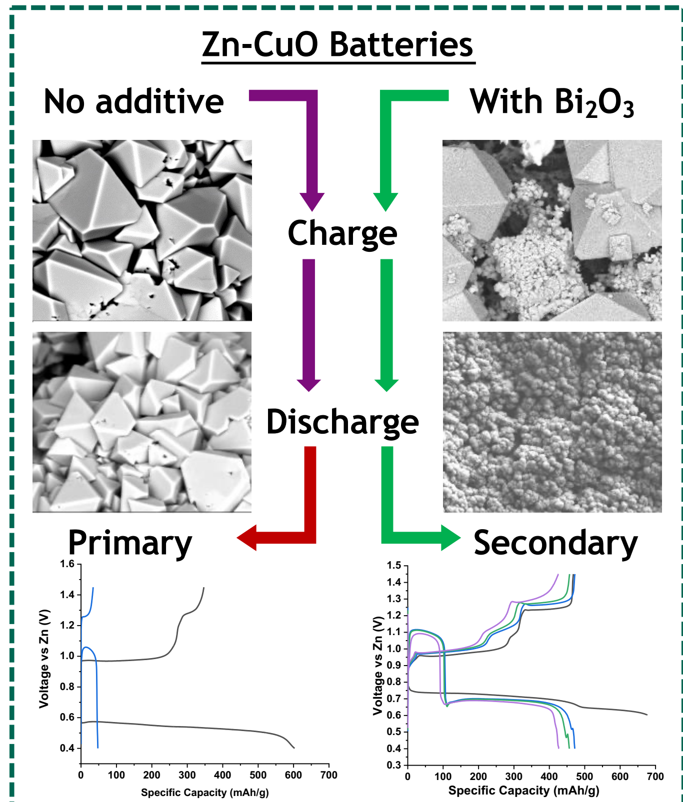
Low but stable voltage ~ 0.75 V
High current battery
Railway signaling,
Powering Edison's electric fans and phonographs
In use until the 1960's

Zn-CuO Batteries

- Zn/CuO (674 mAh/g) vs. Zn/MnO_2 (617 mAh/g)
  but lower voltage
- History books say higher power capabilities
- Zn and Cu both highly recyclable
- Expected to be low cost
- Expected to be safe

250 Wh/L already achieved in rechargeable R&D Batteries



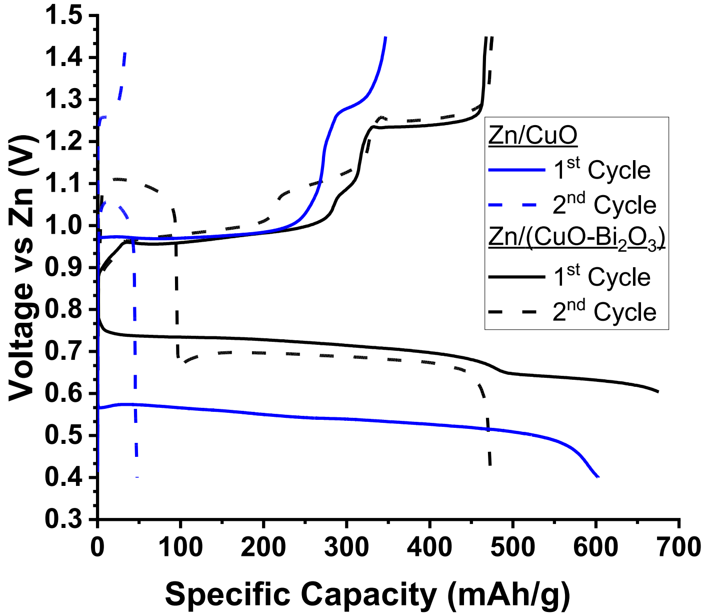


N. B. Schorr et al. ACS Appl. Energy Mater. 2021, *4*, *7*, 7073-7082

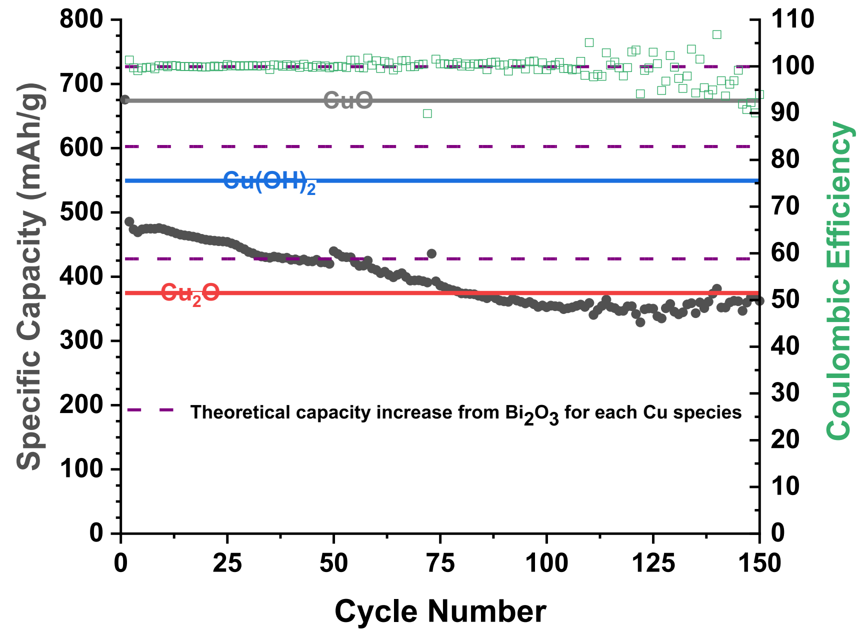
Cycling Zn-CuO

Independently CuO does not make a suitable cathode for a secondary cell, but by using additives reversibility is achieved.

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



Cycling of Zn/(CuO-Bi_2O_3)

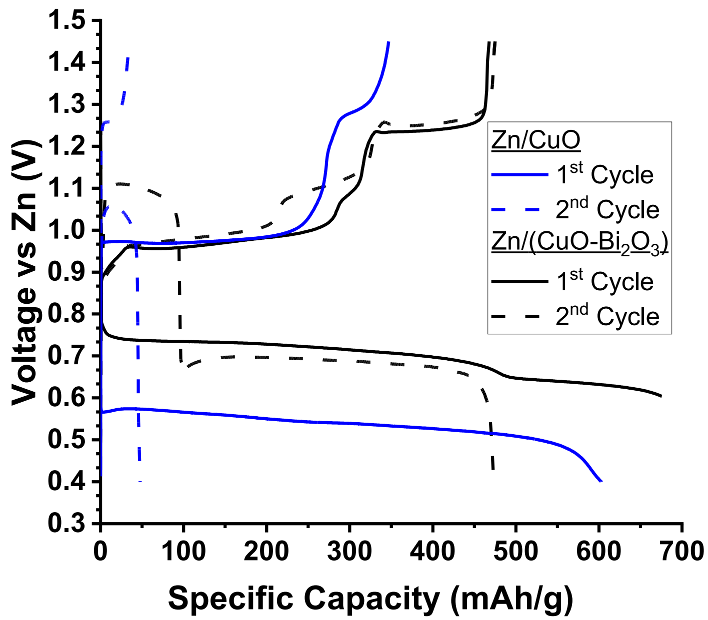


Why does Bi_2O_3 improve reversibility and what is happening during cell cycling?

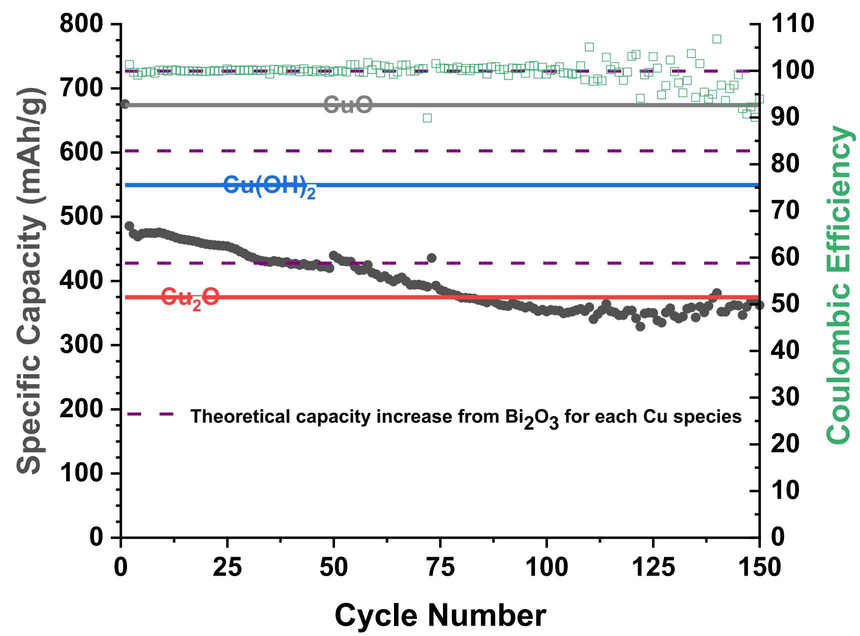
Cycling Zn-CuO

Independently CuO does not make a suitable cathode for a secondary cell, but by using additives reversibility is achieved.

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



Cycling of Zn/($CuO-Bi_2O_3$)

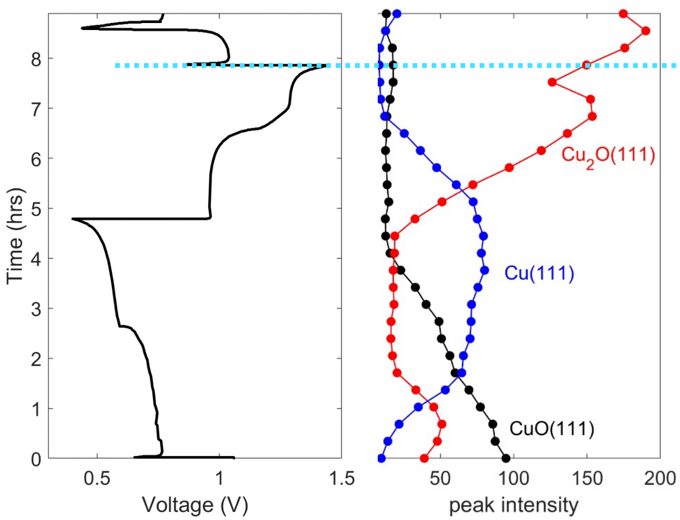


Why does Bi_2O_3 improve reversibility and what is happening during cell cycling?

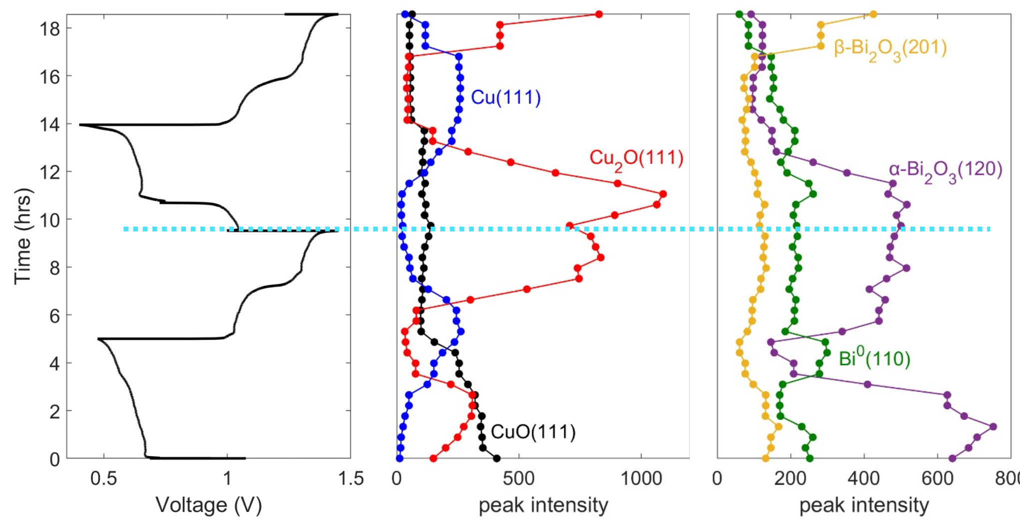
Operando Synchrotron Cycling Studies

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

Zn/CuO



Zn/(CuO-Bi_2O_3)



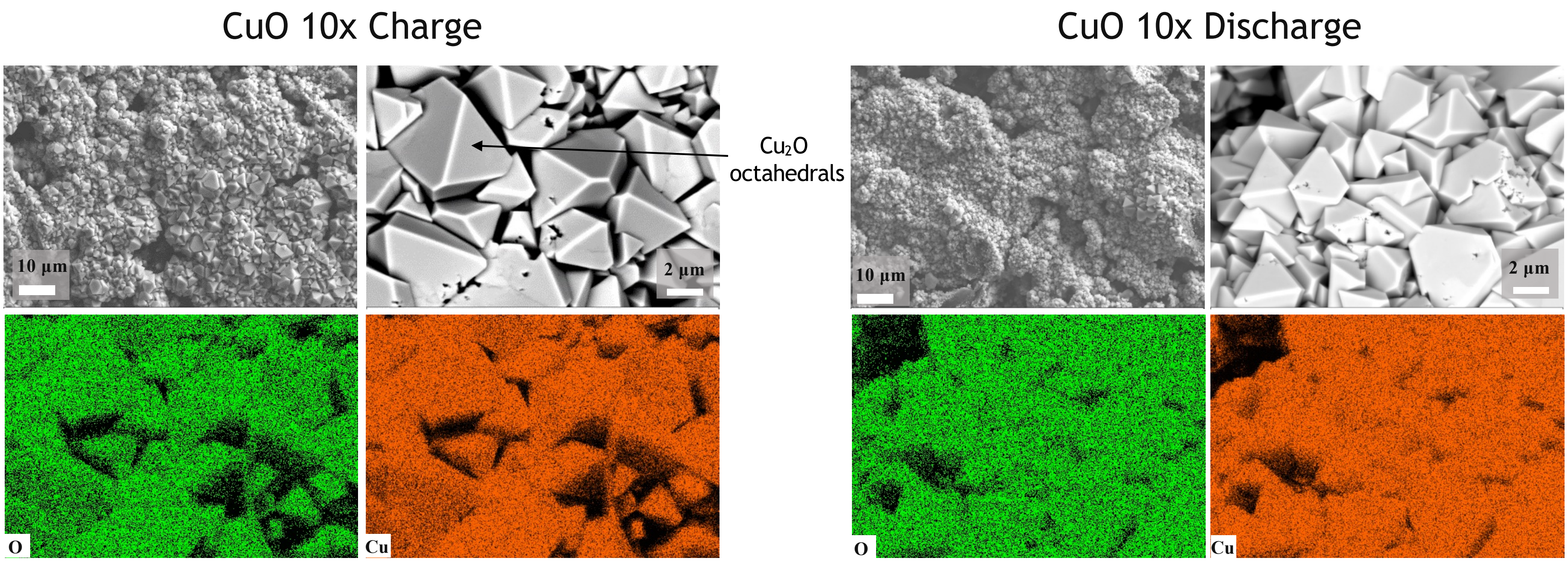
Crystalline CuO is not observed upon re-charging

During second discharge the high voltage causes the formation of more Cu_2O, indicating there is a non-crystalline Cu(II) species not detectable by EDXRD.

Prof. Joshua Gallaway
Andrea Bruck, Matthew Kim

Cathode Morphology

If seeing is believing, what does SEM and EDS tell us about CuO cathodes without any bismuth additive?

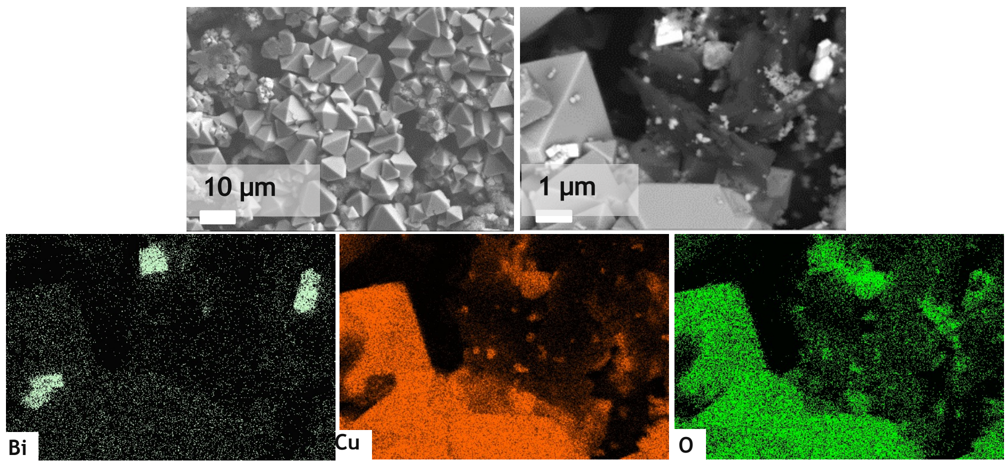


Identical morphology in a charged and discharged Zn/CuO indicates that the imaged phase is stable and electrochemically inactive (bad news for a battery).

Cathode Morphology with Additive

What does SEM and EDS tell us about CuO cathodes with bismuth additive?

CuO/Bi_2O_3 10x Charge

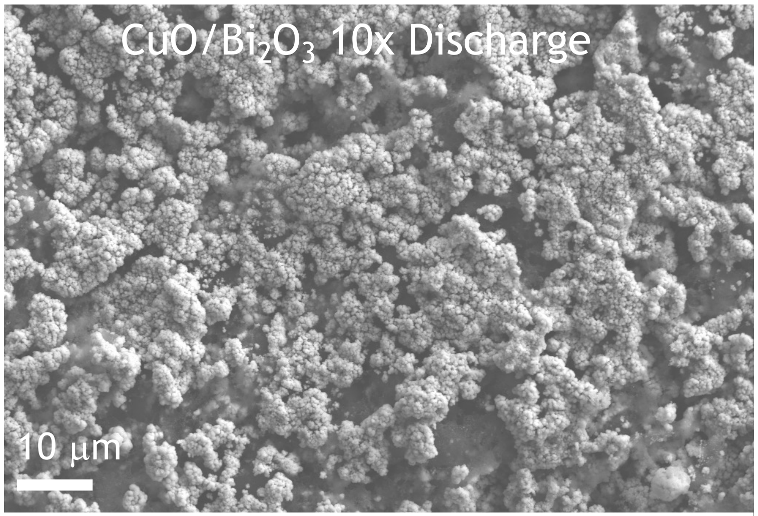


When cathodes are made with Bi_2O_3 similar octahedral seen on charge indicative of Cu_2O formation.

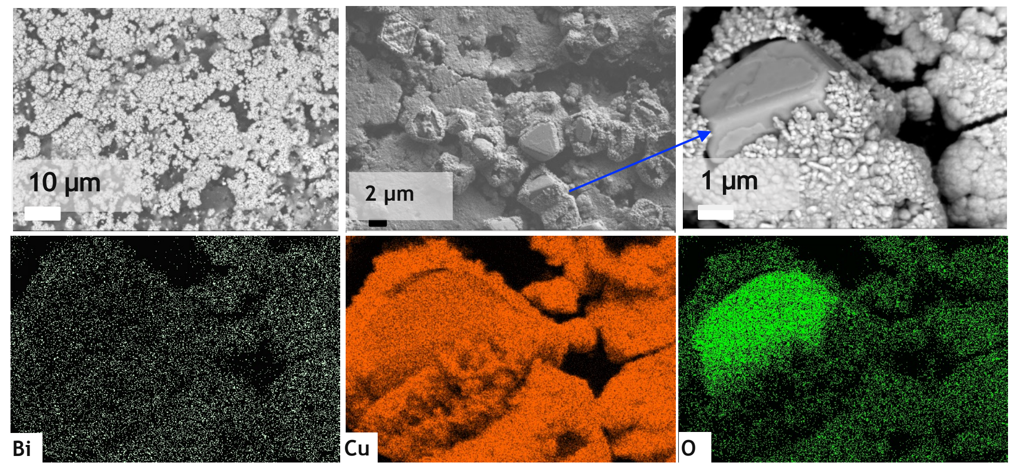
Bi distributed throughout as well a some concentrated areas

Cathode Morphology with Additive

If seeing is believing, what does SEM and EDS tell us about CuO cathodes <u>with</u> bismuth additive?



CuO/Bi_2O_3 10x Discharge

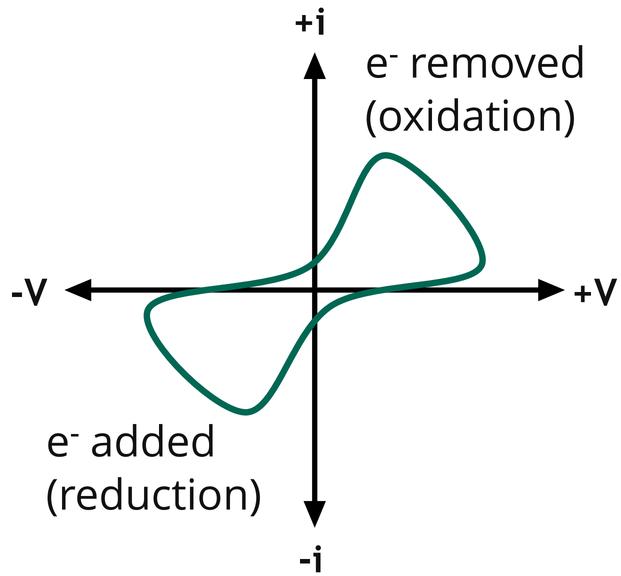


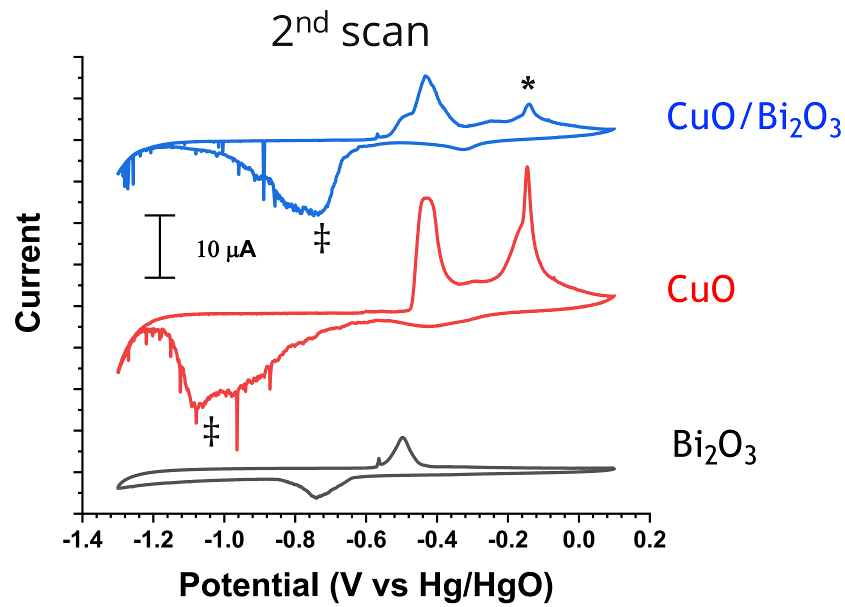
When cathodes are made with Bi_2O_3 we now see a different morphology on discharge

Some remnants of the octahedral that are seen on charge [and in CuO (no additive)] still appear.

Impact of Bi Additive

Cyclic voltammetry allows us to see at what potentials are electrons being supplied from or delivered to the system



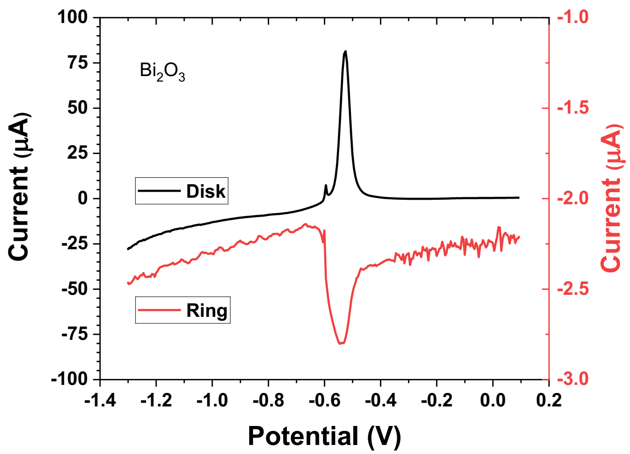


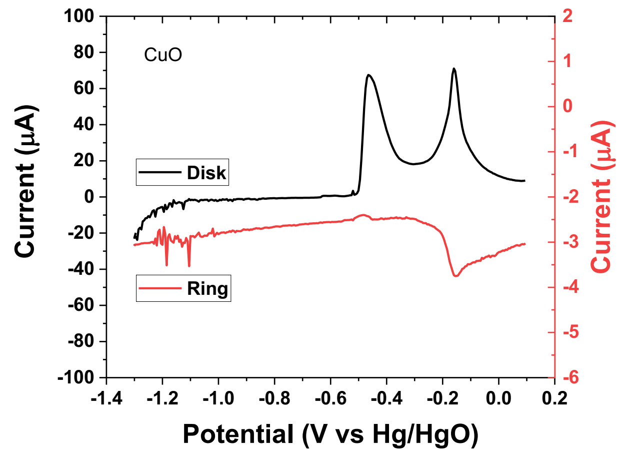
Two big differences between when Bi additive is included with CuO:

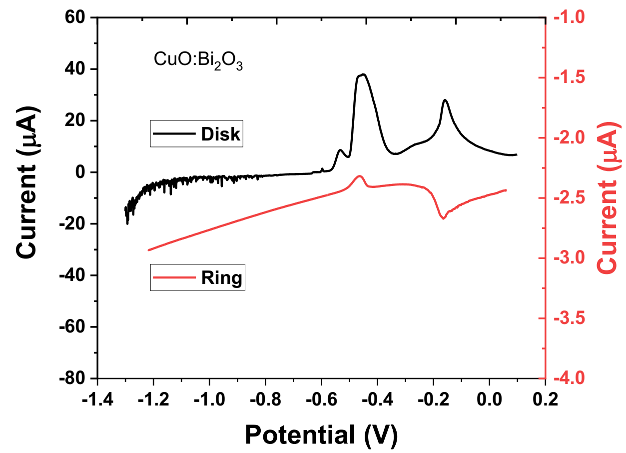
1. **Reduction peak is shifted positive (easier to put electrons into the material) ‡**
2. **Smaller 2nd oxidation peak *. RRDE confirms Bi reduces Cu(II) solubility**

Cu Oxidation Under Alkaline Conditions with Bi Additive

Rotating Ring Disk Electrode (RRDE) studies allows us to examine soluble species upon oxidation



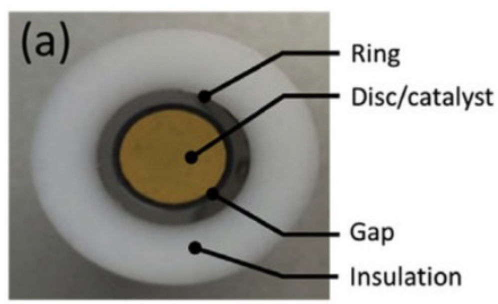




Disk potential raised to oxidize Cu/Bi while Ring held at reducing potential

1. Soluble Bi is observed upon oxidation
2. Cu to Cu_2O is a sold state transition
3. Cu_2O (or Cu) to Cu(II) results in soluble species
4. Bi additive lowers the observed Cu(II) species

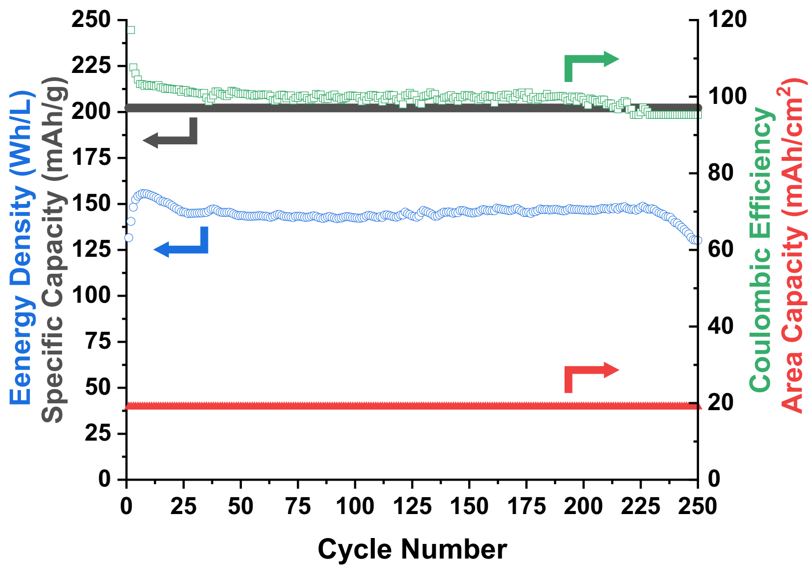
RRDE



Zn-CuO Batteries

Two strategies for modifying performance show promising paths forward.

1. Partial depth of discharge of $CuO\text{-}Bi_2O_3$ cathode causes increased lifetime



- ~140 Wh/L demonstrated

  30% CuO DOD and 1-3% Zn DOD

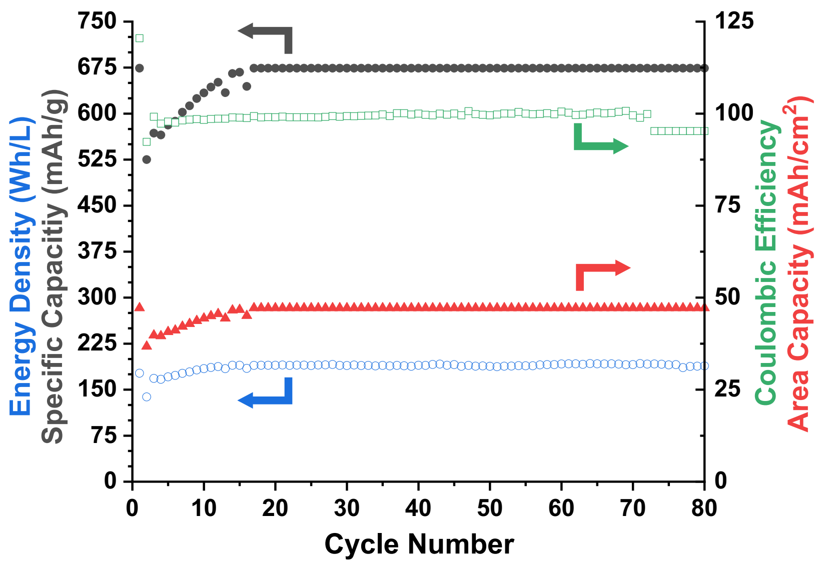
  Wh/L calculated using volume of electrode pack including current collectors

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

Zn-CuO Batteries

Two strategies for modifying performance show promising paths forward.

2. Using Cu as an additive improves capacity retention and energy density

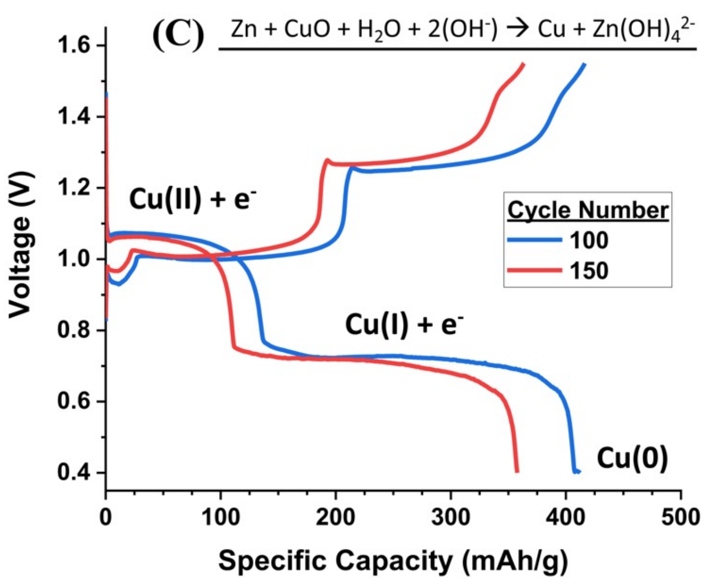


80 cycles: 100% DOD_{CuO} (674 mAh g^{-1} cathode)
Average areal capacity 46 mAh cm^{-2}
Average energy density 186 Wh L^{-1} (1% Zn)
Average energy density 263 Wh L^{-1} (10% Zn)

- ~ 100% CuO DOD can be achieved
- CuO is 'tolerant' of zincate but Zn/CuO is prone to shorting (soluble Zn and Cu)
- Tens to hundreds to thousands (?) of cycles depending on DOD, rate etc.
  Could cover from microsecond to day-long outages.
- Shorting can be mitigated with separators or polymer gel electrolyte
- Technical Challenges with Zn still apply

Gel Batteries for the Future

Zn/CuO gel batteries are the focus of a DOE Office of Technology Transitions - Technology Commercialization Fund Award



Acrylate-KOH based gel serves as a quasi-solid state electrolyte

Commercial Partner

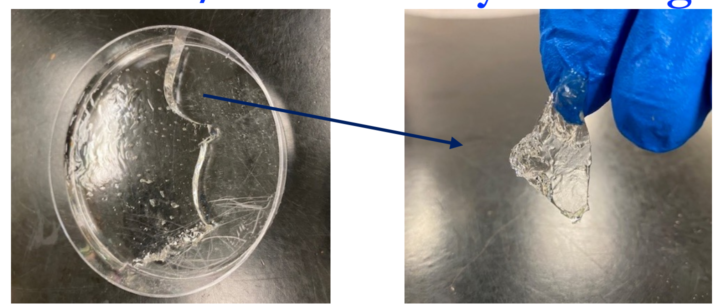
URBAN ELECTRIC POWER

Gabe Cowles

Gautam Yadav

Sanjoy Banerjee

Alkaline Zn/CuO Battery utilizing PGE



- Polymer gel electrolyte (PGE) minimizes shorting, extends cycle life, non-spillable
- ~Full 1e- equivalent at cycle 150 already demonstrated

Targets

- **10Ah, 100Ah @200 Wh/L for 100 cycles**
- **Use COTS power converters**
- **Demonstrate power, energy, lifetime and/or cost benefits over competing battery technologies**
- **Robust commercialization roadmap for large scale Zn/CuO manufacturing.**

PROJECT CONTACTS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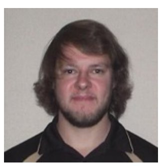
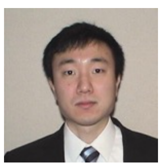
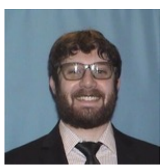
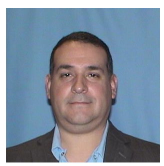
FY 20 Sandia Team


Igor Kolesnichenko

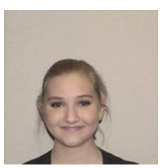

Matthew Lim

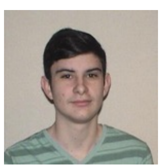

Noah Schorr

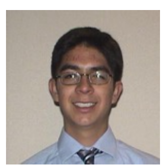

Stephen Budy


Bryan Wygant


David Arnot


Rachel Habing


Logan Ricketts


Elijah Ruiz

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Imre Gyuk

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& OUR MANY COLLABORATORS

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Thank you