1005

Development of Copper Oxide Cathodes for Rechargeable Alkaline Zinc Batteries

Joshua W. Gallaway

Northeastern – Sandia Collaboration

DOE OE Energy Storage Peer Review

Zinc & Lead Batteries, Thursday Aug 7, 2025 2:00-2:15 PM

Timothy Lambert
SNL

Yogesh Agilan
Northeastern U

Northeastern University
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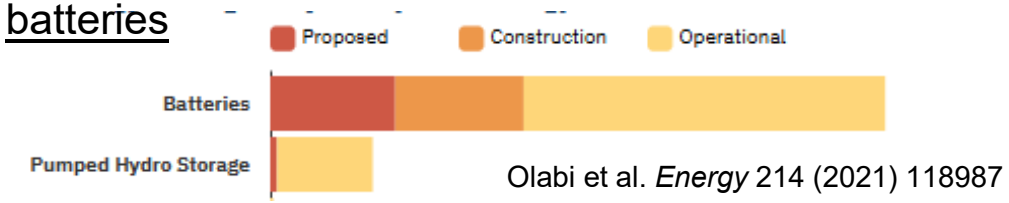
Project Overview

- **Project Goal:** This project will develop alkaline CuO cathodes for large-scale energy storage in rechargeable Zn-CuO batteries.
- **Current Practice:** Most electrochemical storage in the grid is from Li-ion batteries, which are well-suited to high power applications but too expensive and flammable for extensive use at the grid scale.
- **Why Northeastern:** Our expertise in electrochemical testing and advanced materials characterization enable us to link physical phenomena to battery performance.
- **Innovation:** Mechanical and physical effects like compression are demonstrated to have a large impact on performance. Controlling these effects will lead to successful rechargeable alkaline battery development.
- **Impact:** Grid scale batteries will enhance the reliability and resilience of the power grid by providing rapid response capabilities to provide stored energy.
- **Alignment:** Inexpensive rechargeable alkaline batteries will lead to safe, reliable, and cost-effective grid storage. This will enable grid modernization and microgrids.

Lost-cost and safe batteries for the grid

Grid storage new additions are almost exclusively batteries



Olabi et al. *Energy* 214 (2021) 118987

Moss Landing battery fire
January 16, 2025
Credit: Anadolu via Getty Images

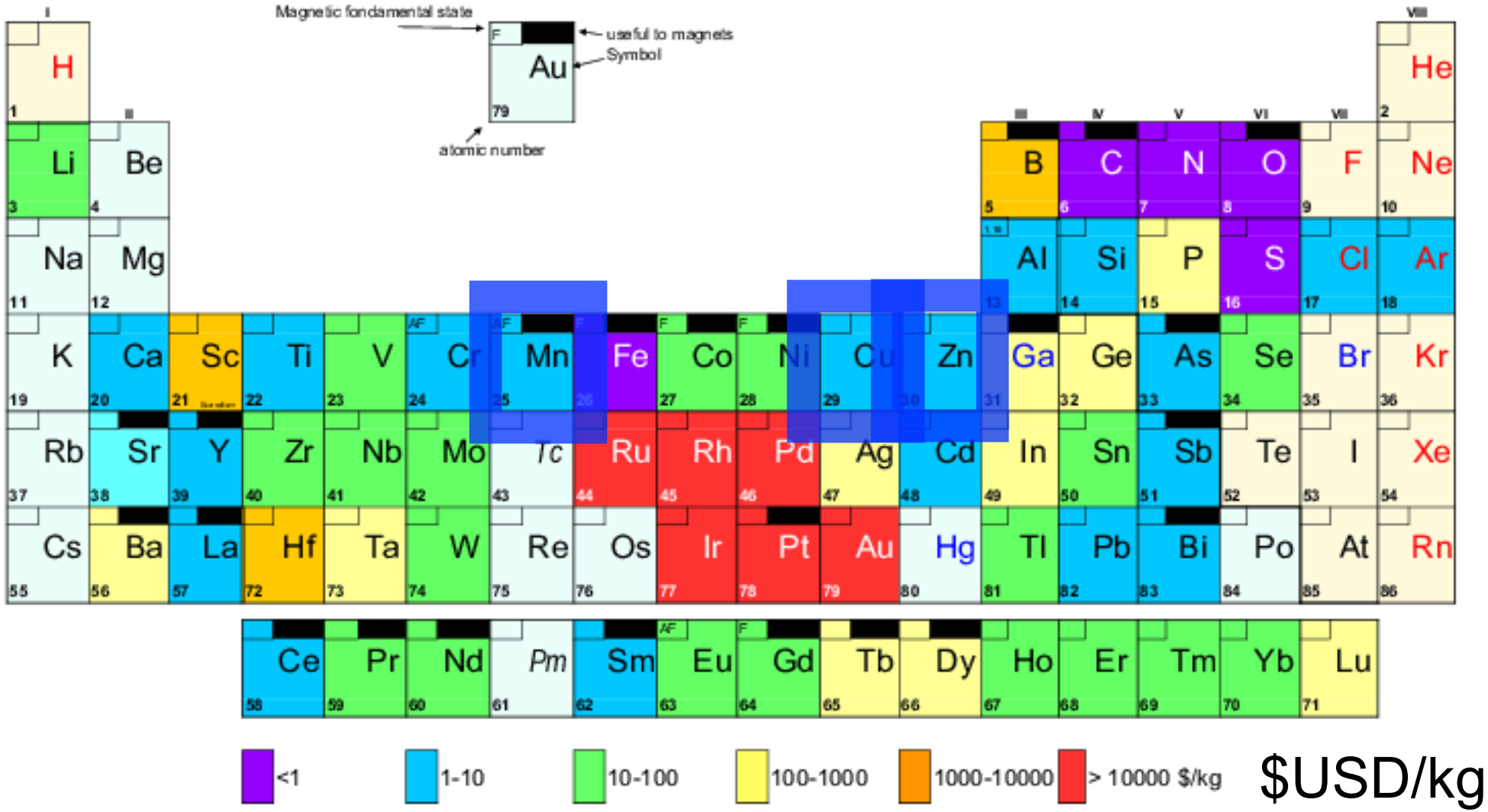
- Li-ion safety and cost are not well-suited to the grid
- Portfolio of electrochemical energy storage options is desired
- Using more abundant and domestic materials
- Cost ($USD/kWh) and energy density (Wh/L) are functions of voltage V and specific capacity Q

Table: cathode materials

Material	Voltage V (V)	Specific capacity Q (mAh/g)
Non-aqueous		
NMC532	3.7 (vs. Li)	180
LFP	3.2 (vs. Li)	170
NVP	3.4 (vs. Na)	117
Aqueous		
PbO_2	2.1 (vs. Pb)	224
NiOOH	1.73 (vs. Zn) 1.35 (vs. MH) 1.35 (vs. Cd)	292
MnO_2	1.0 (vs. Zn)	617
CuO	1.05 (vs. Zn)	674

$$E_{cell} = Q_{cell}V$$

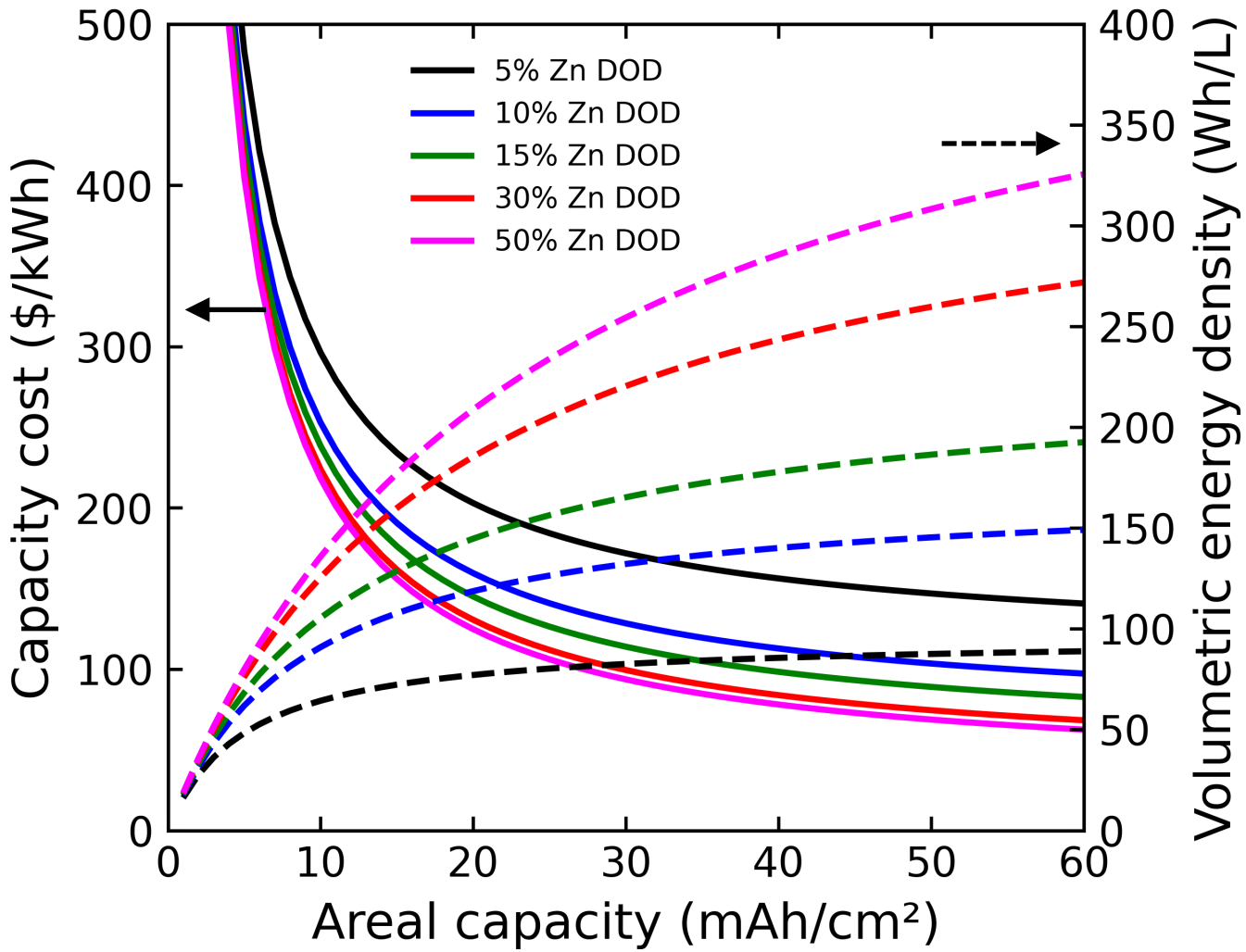
Low-cost battery materials

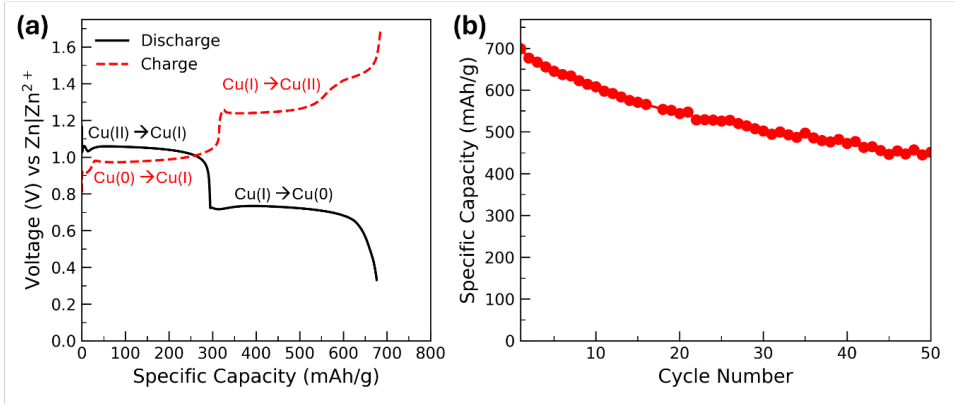


$USD/kg
log scale

F. Mazaleyrat, Getting Rid of Critical Raw Materials in Hard Magnets: Is it Feasible?, *IEEE Transactions on Magnetics,* 58:2, 2022.

Rechargeable Zn-CuO batteries for the grid

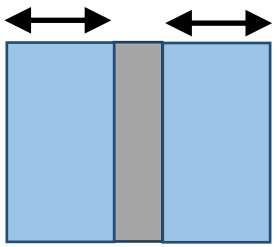




Cu^{II} to Cu^{I} reaction (1st electron):
$2Cu^{II}O + H_2O + 2e^- \leftrightarrow Cu^{I}_2O + 2OH^-$

Cu^{I} to Cu^{0} reaction (2nd electron):
$Cu^{I}_2O + H_2O + 2e^- \leftrightarrow 2Cu^0 + 2OH^-$

Bi is physically added as Bi_2O_3 to promote rechargeability.



Areal capacity is a measure of thickness and loading

Rechargeability of CuO: Compression effect

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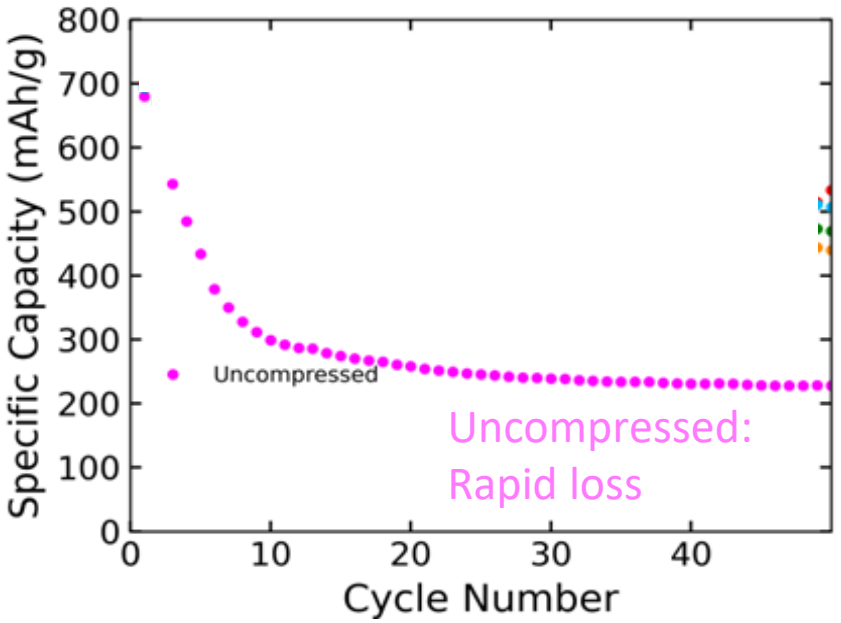
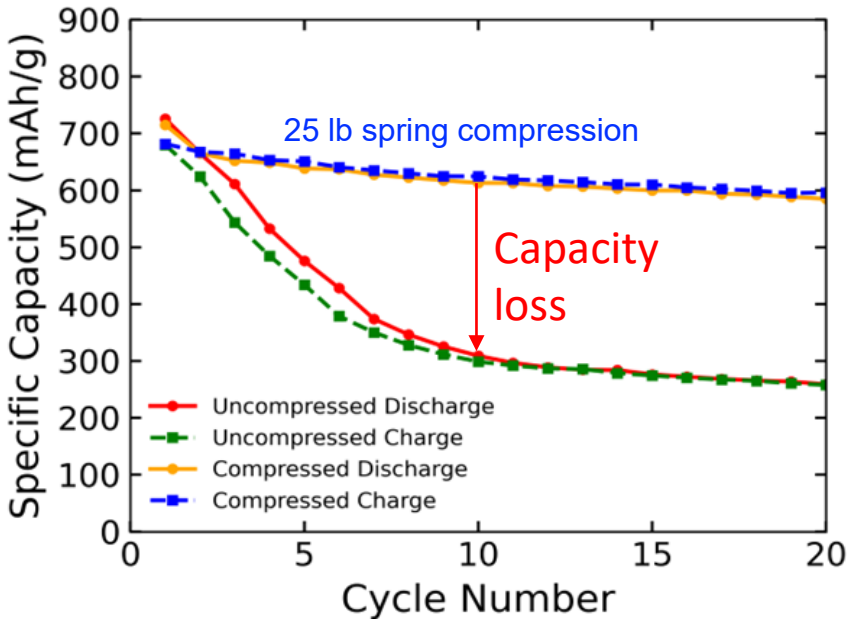
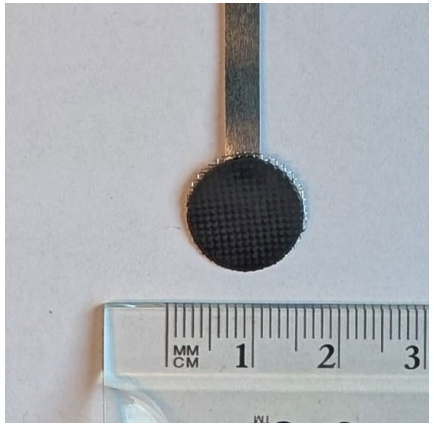
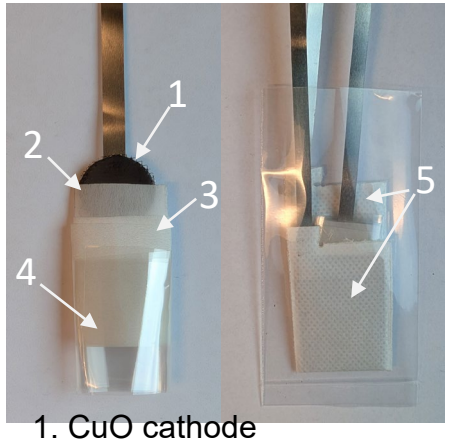




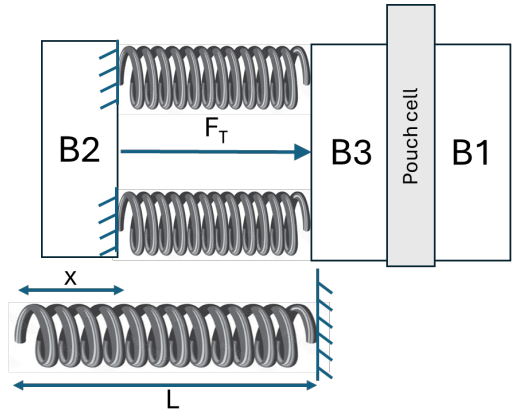
- Mechanical compression greatly improves rechargeability
- Comparable to pressures in commercial cells (100 psi in Ni-Cd)

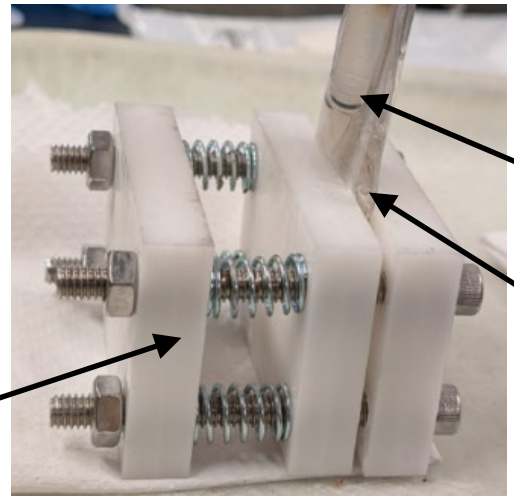


Cathode
$CuO + Bi_2O_3 + C$
25 mAh/cm^2

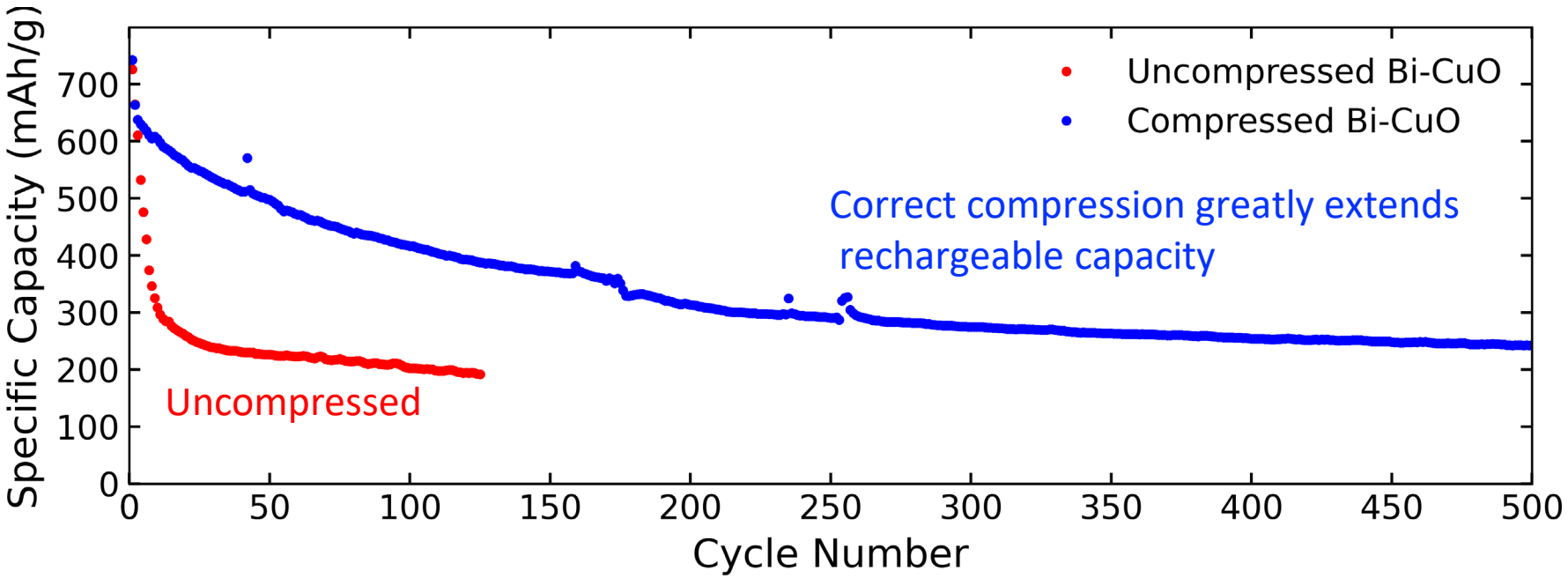


1. CuO cathode
2. Freudenberg separator
3. Kimwipe
4. Cellophane
5. NiOOH counterelectrodes

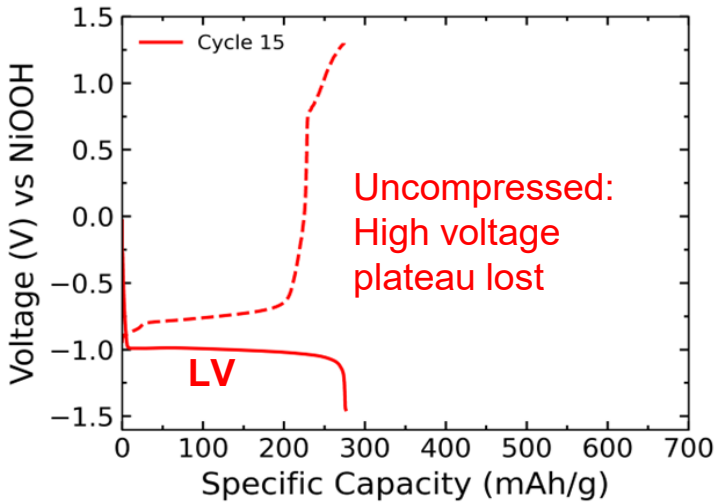


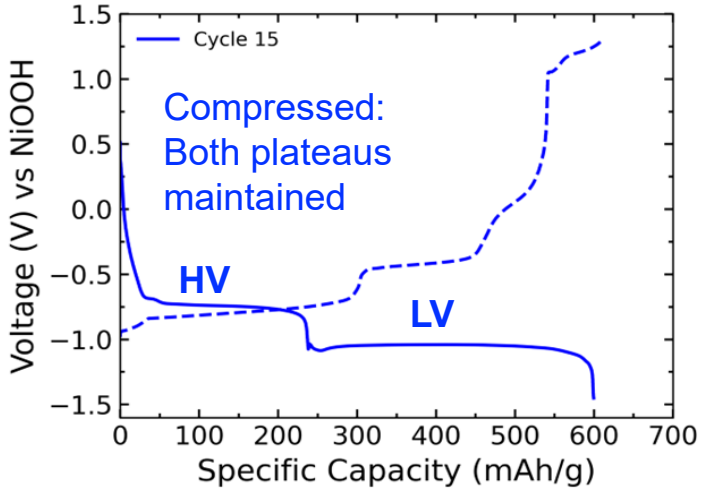


Rechargeability of CuO: Compression effect



- Uncompressed quickly loses the high voltage (HV) plateau
- Loss of $Cu^{II}O \leftrightarrow Cu^{I}_2O$
- For rechargeability, must maintain oxidation to Cu(II)





Uncompressed cathode failure mechanism

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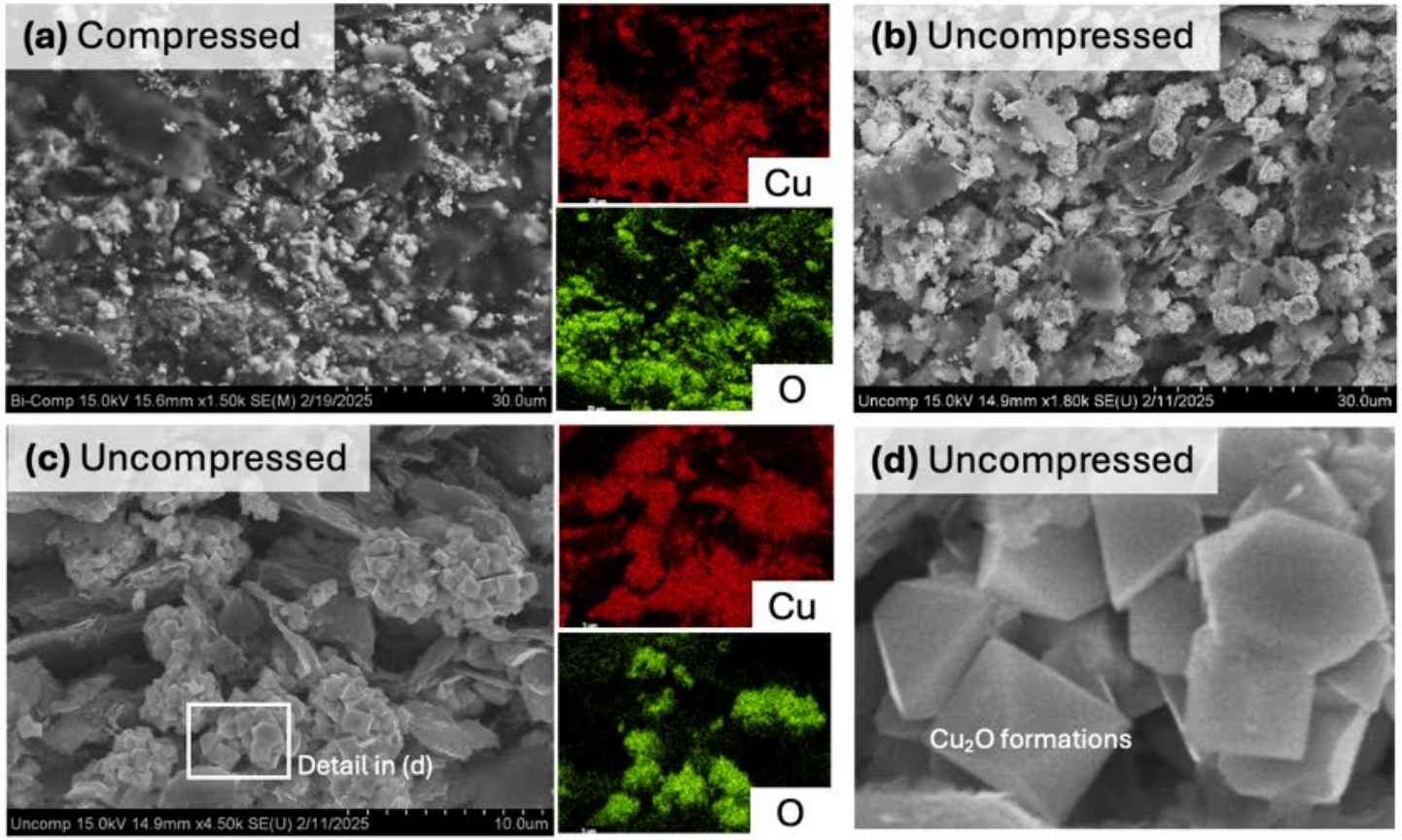
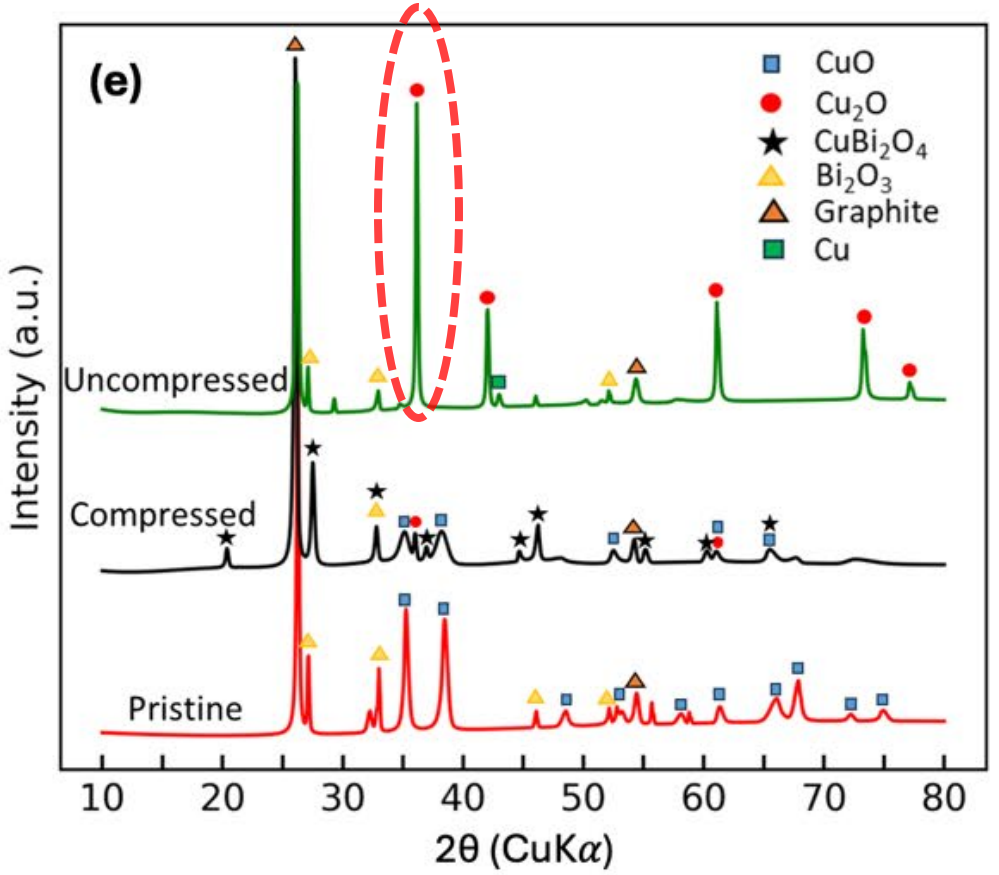
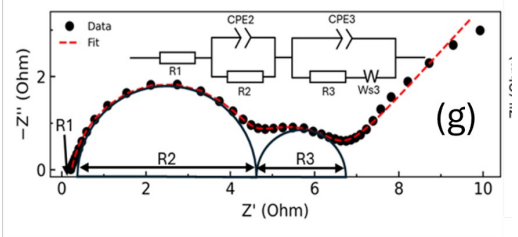
Analysis at cycle 100, charged





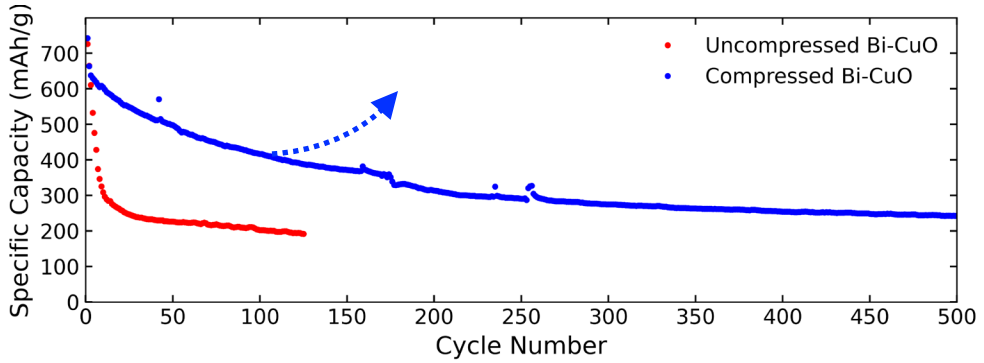
- **<u>Compression</u>** keeps particle size small and contact good **(a)**
- **<u>Without compression</u>**, large granules form **(b)**

- These large granules are highly crystalline, resistive **Cu_2O (c-e)**

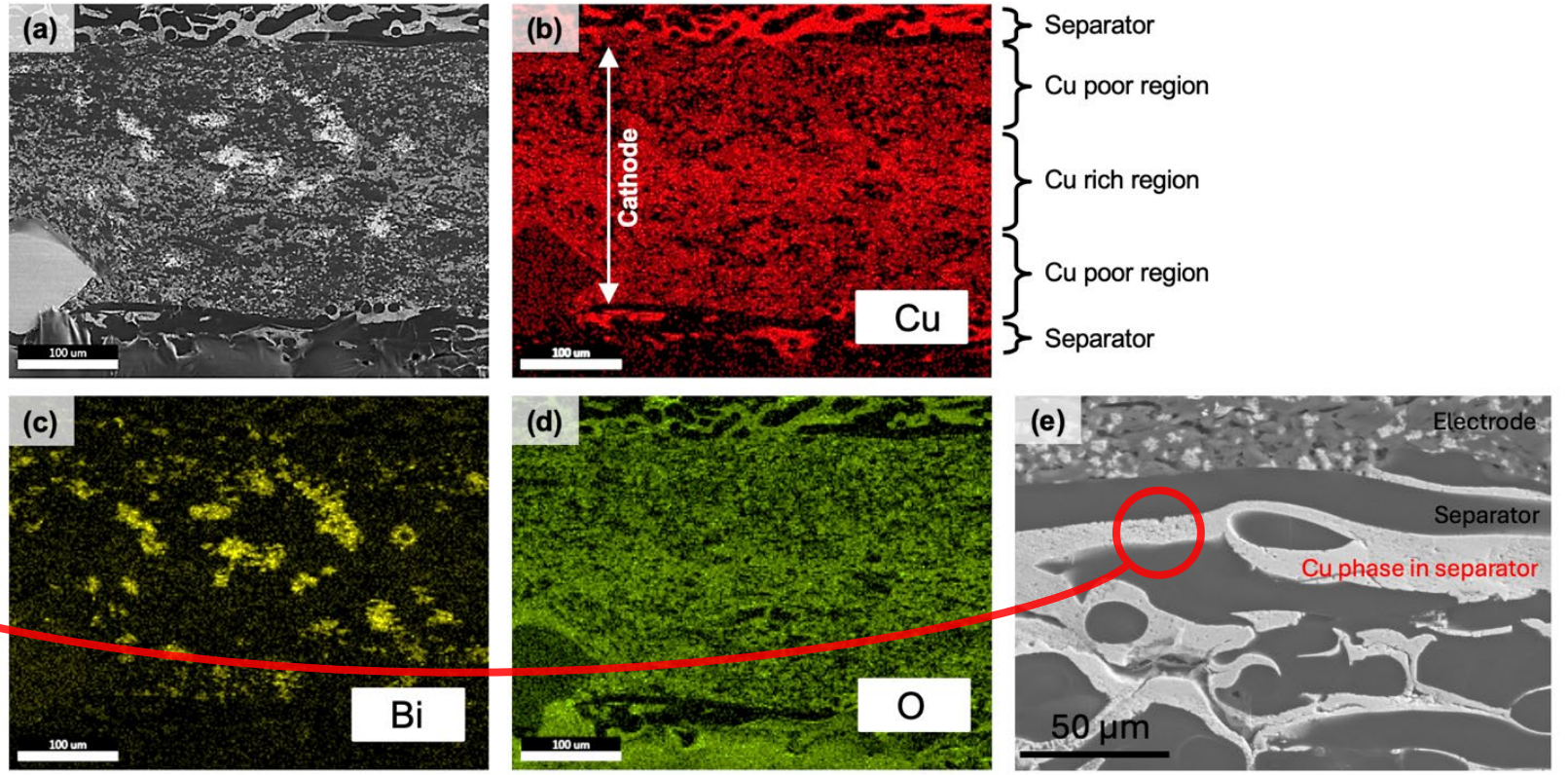


Capacity decay mechanism in compressed case

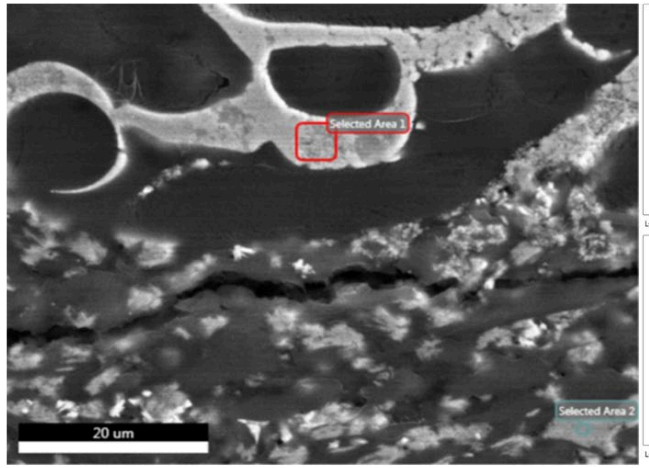
- The **slow capacity decay** with compression must be slowed
- Analysis of the coulombic efficiency showed 0.414% decay per cycle
- Loss occurs during discharge
- Hypothesis: Cu^{+} migrating away from the cathode
- Cross-section reveals separator pores infiltrated by Cu+O species

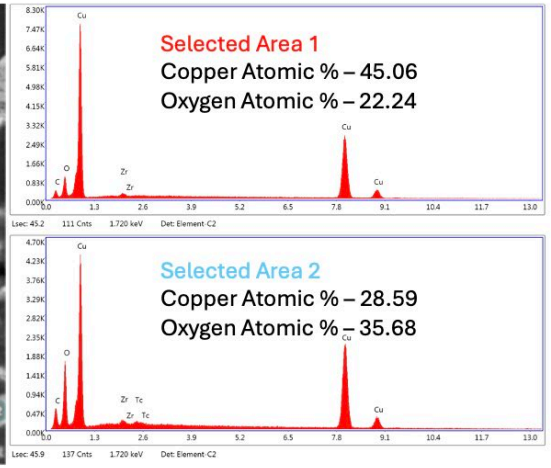


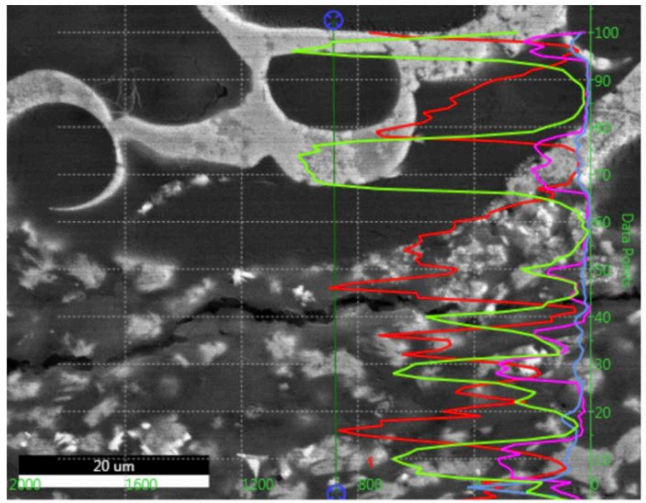
Embedded cross-sections:
SEM + **EDS** analysis

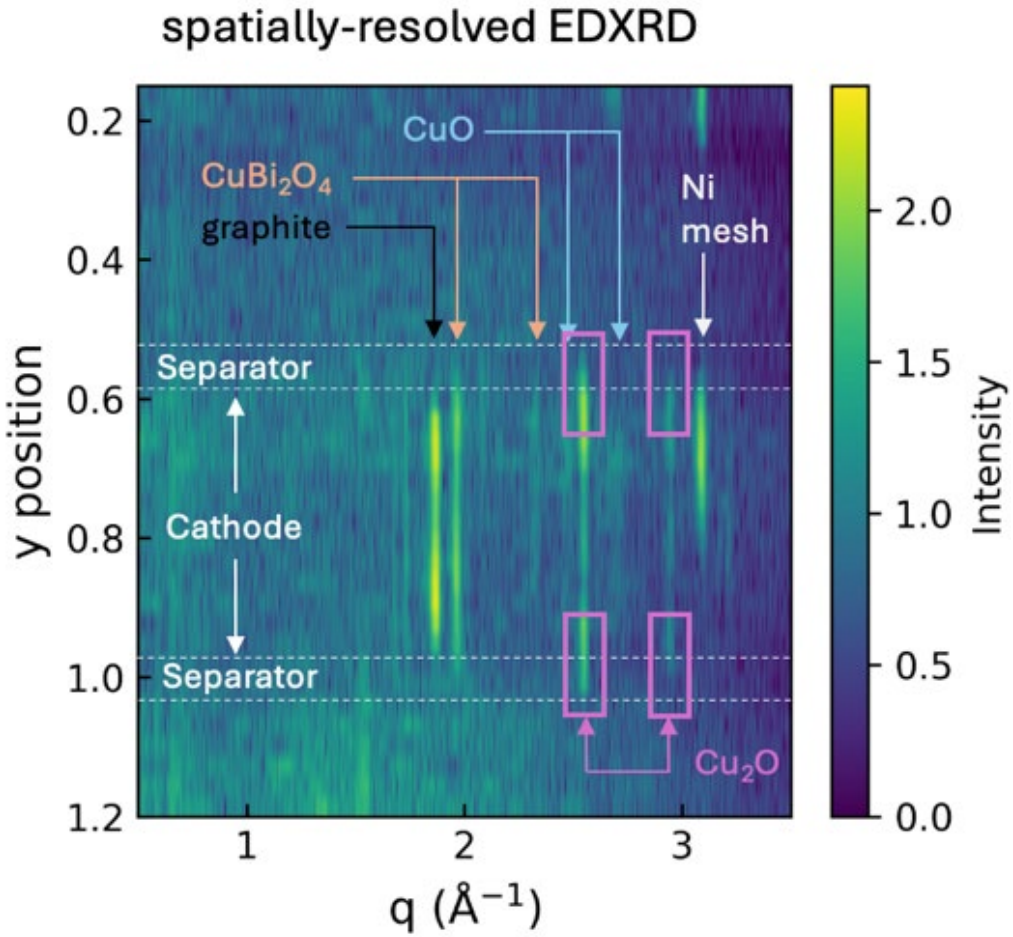


Migration of Cu^+ and precipitation as Cu_2O







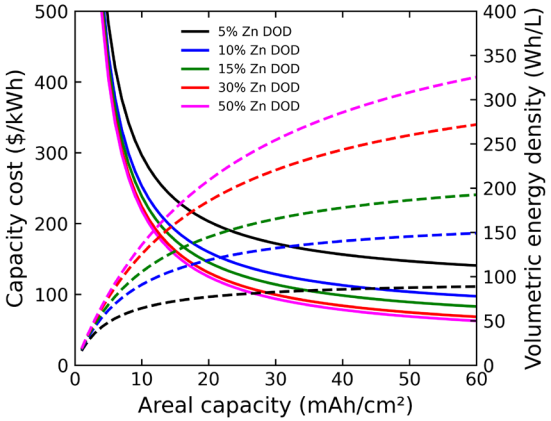


- EDS shows Cu:O of 2:1 in the cross-sectioned separator
- EDXRD shows crystalline Cu_2O overlapping into the separator region in situ

Rechargeable Zn-CuO batteries for the grid

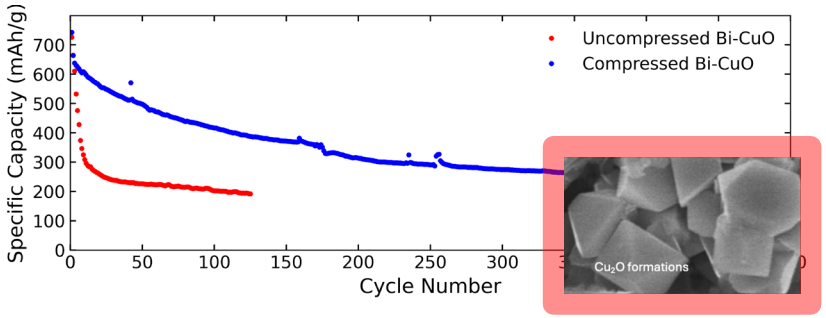
Alkaline Zn-CuO batteries can offer low-cost and safe storage

- CuO is inexpensive and abundant
- Cu can reversibly cycle two electrons of capacity per transition metal atom
- Specific capacities are favorable:
  - 674 mAh/g of CuO
  - 820 mAh/g of Zn



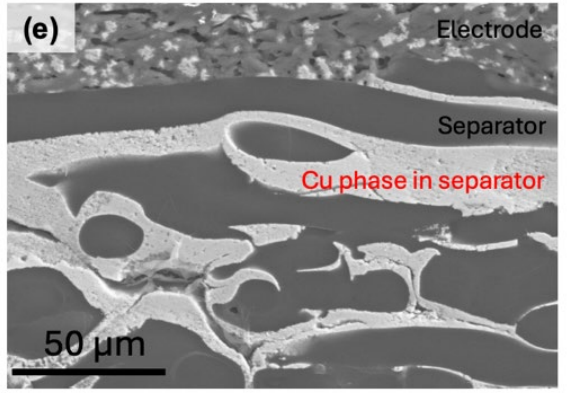
Applying mechanical compression greatly increases CuO rechargeability

- There is an optimal compression (25 lbs spring-loaded)
- Cu_2O granules build up in the uncompressed case



Migration of Cu^+ species away from the cathode causes capacity decay

- Cu material was imaged in the separator pores, which precipitates as Cu_2O.
- Engineering the electrolyte and separators to block migration holds the key for development.



Acknowledgment

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Northeastern University

Sandia National Laboratories

Gallaway Lab, Northeastern University

Dr. Andrea Bruck
Dr. Qing Zhang
Dr. Bebi Patil
Dr. Saiful Islam
Dr. Jillian Rix Mulligan
(Dr.) Matthew Kim
(Dr.) Alyssa Stavola
(Dr.) Benjamin Howell
(Dr.) Dominick Guida
Eric Zimmerer
Benjamin Leifer
Yogesh Agilan
Chi Nguyen
Surafel Mustefa Beyan
Zhicheng Lu, M.S.
Pushkar Gokhale, M.S.
Maximilian Ulbert, M.S.
Tristi Owen, M.S.
James Goulart, M.S.
Austin Breed

Undergrads
Rachana Somaskandan
Miko Stewart
Elizabeth Detoma

Collaborators

Dr. John Okasinski (APS)
Dr. Andrew Chuang (APS)
Dr. Steve Erlich (NSLS-II)
Dr. Lu Ma (NSLS-II)
Dr. Andrew Kiss (NSLS-II)
Dr. Wentao Liang (KRI)
Dr. Timothy Lambert (SNL)
Michael Rickley (MIT LL)
Matthew Wendling (Energizer)
Dr. Xiaotong Chadderdon (Energizer)
Prof. Hongli Zhu (Northeastern)
Prof. Robert Messinger (CCNY)
Prof. Manuel Smeu (SUNY Binghamton)
Prof. Ertan Agar (UMass Lowell)

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