



Development of Copper Oxide Cathodes for Rechargeable Alkaline Zinc Batteries

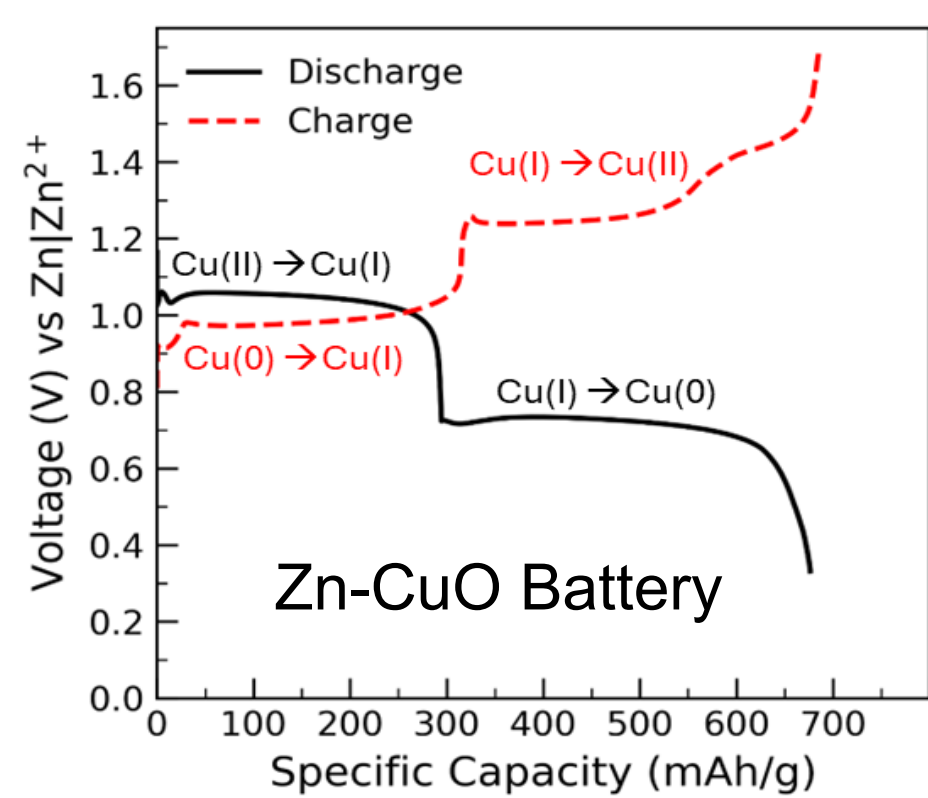
Yogeshwaran Agilan¹, Eric K. Zimmerer¹, Bryan Wygant², Huang Jason², Timothy N. Lambert^{2,3*}, and Joshua W. Gallaway^{1*}

1. Department of Chemical Engineering, Northeastern University 2. Department of Photovoltaics and Materials Technology and 3. Center for Integrated Nanotechnologies, Sandia National Laboratories



Background

- 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.



Zn-CuO batteries offer a high, stable discharge potential and has a high theoretical capacity (674 mAh/g of CuO and 820 mAh/g of Zn). CuO is ideal because Cu can reversibly cycle two electrons of capacity per transition metal atom. For reference Li-ion batteries cycle less than one electron.

In this study, we investigated

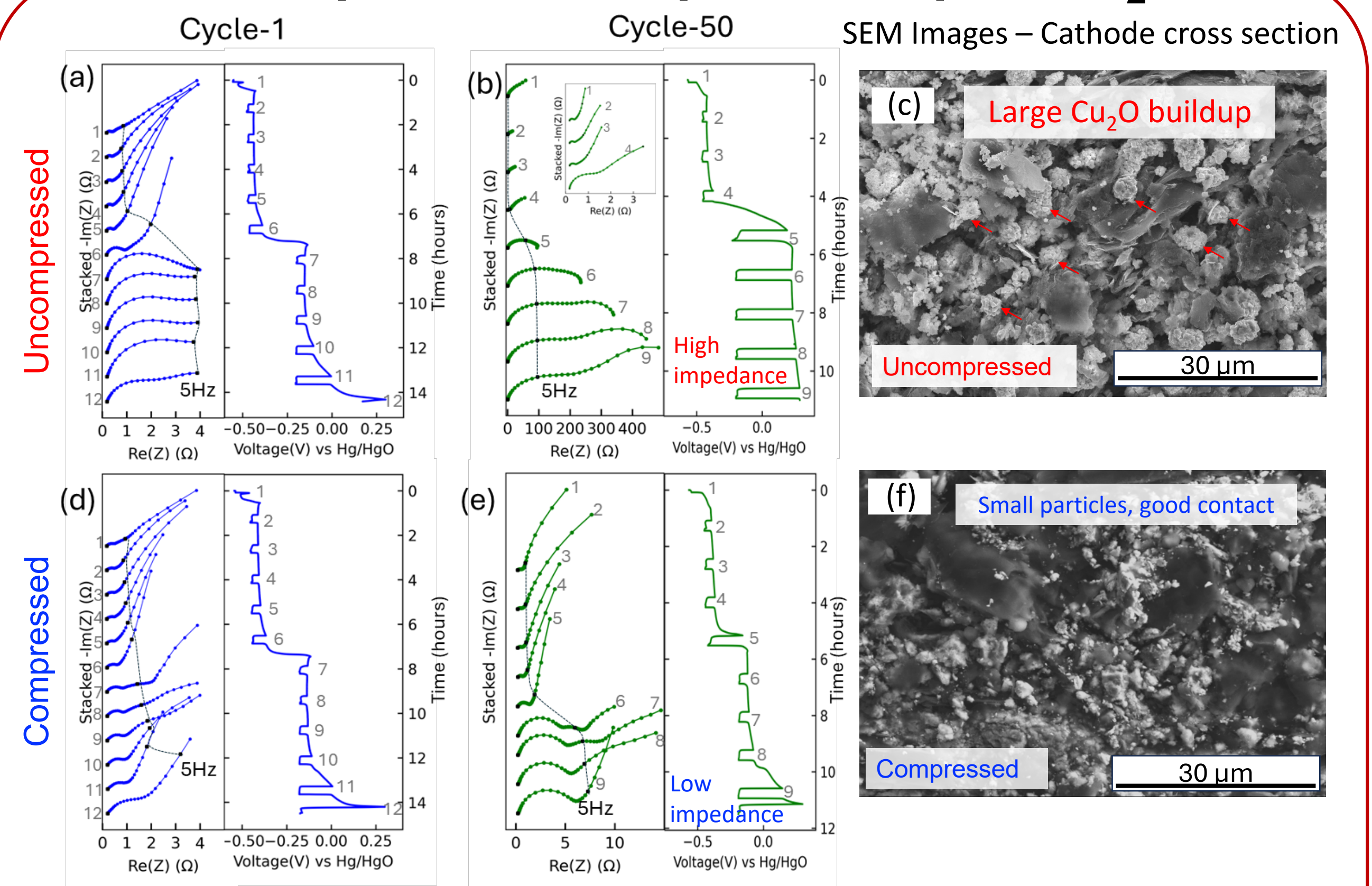
- 1) effect of compression on CuO cathodes,
- 2) mechanisms causing capacity decay in the compressed cathodes.

We demonstrated that [controlling compression greatly increases stability and rechargeability of CuO cathodes](#).

Cu^{II} to Cu^I reaction (1st electron):
2Cu^{II}O + H₂O + 2e⁻ ↔ Cu₂O + 2OH⁻

Cu^I to Cu⁰ reaction (2nd electron):
Cu₂O + H₂O + 2e⁻ ↔ 2Cu⁰ + 2OH⁻

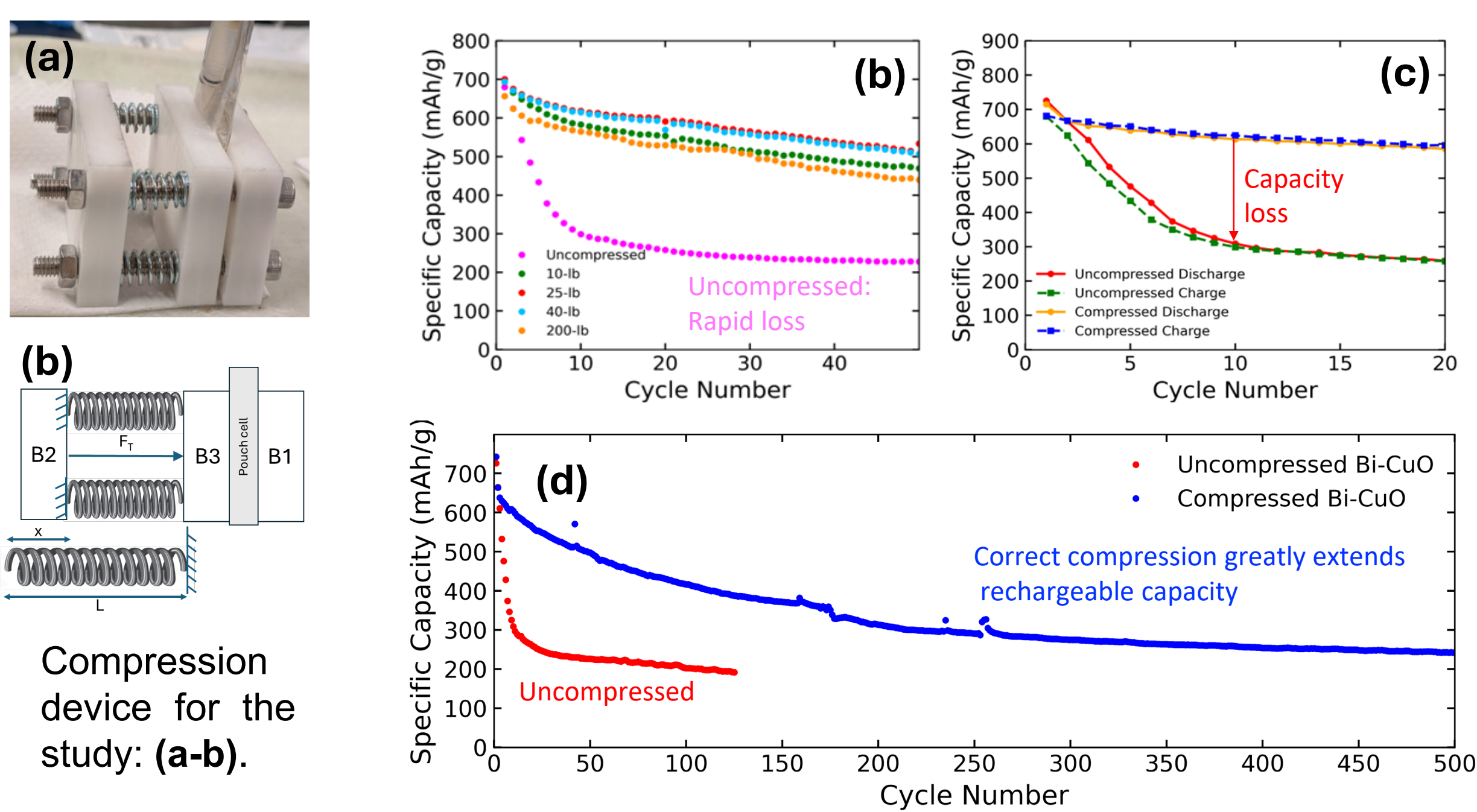
2. Compression Stops Buildup of Cu₂O



To determine why cells failed without compression, we correlated impedance to materials distributions in the cathodes.

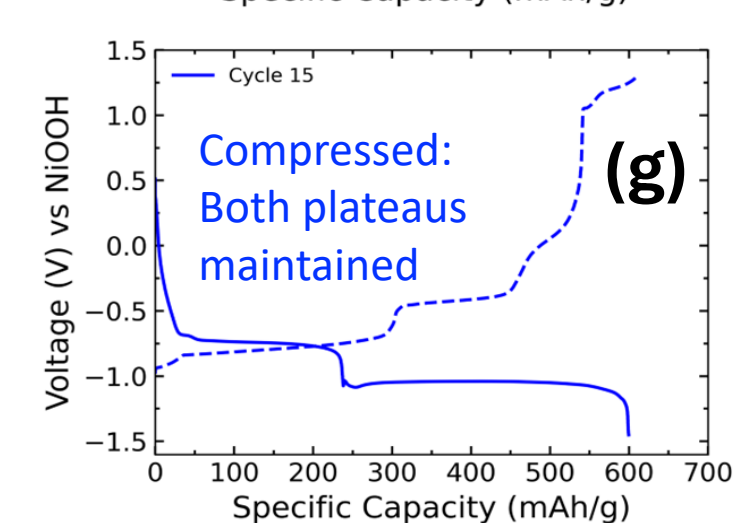
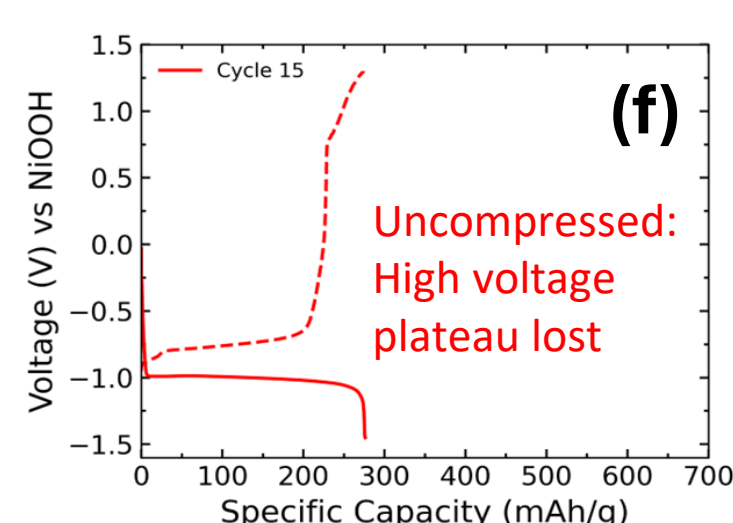
- Uncompressed cells (a-b): charge transfer resistance (R_{ct}) increased significantly during the high voltage plateau of charging. Compression stopped this (d-e).
- **Large, resistive Cu₂O crystals** buildup throughout uncompressed cathodes (c). With compression this buildup was prevented. This led to smooth cycling (f).

1. Compression Study of CuO Cathodes

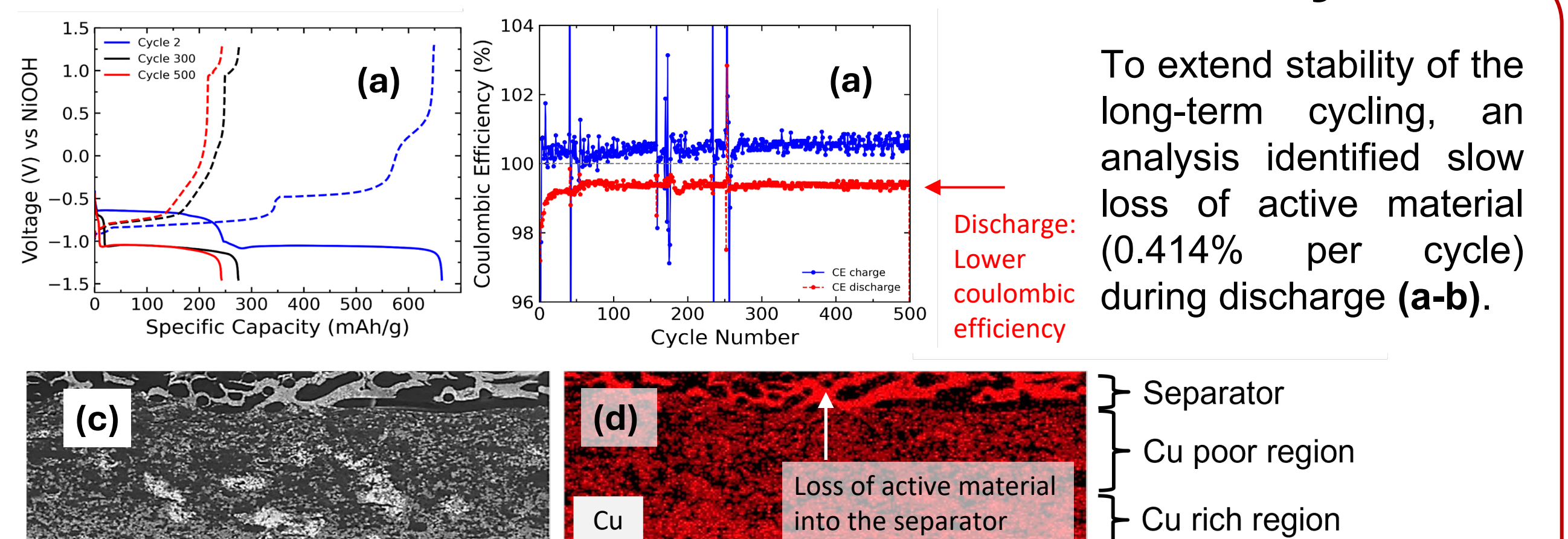


Uncompressed cathodes exhibited sudden capacity loss. [Compression stopped this sudden capacity loss](#) in the cathodes (b-d).

- In uncompressed cathodes, the high voltage capacity (Cu(I) ↔ Cu(II)) was lost due to inefficient oxidation of Cu₂O. These cycled only the low voltage capacity (Cu(0) ↔ Cu(I)) (f).
- Compression effectively mitigated this rapid capacity loss, enabling the cathode to cycle with two electron capacity (g).



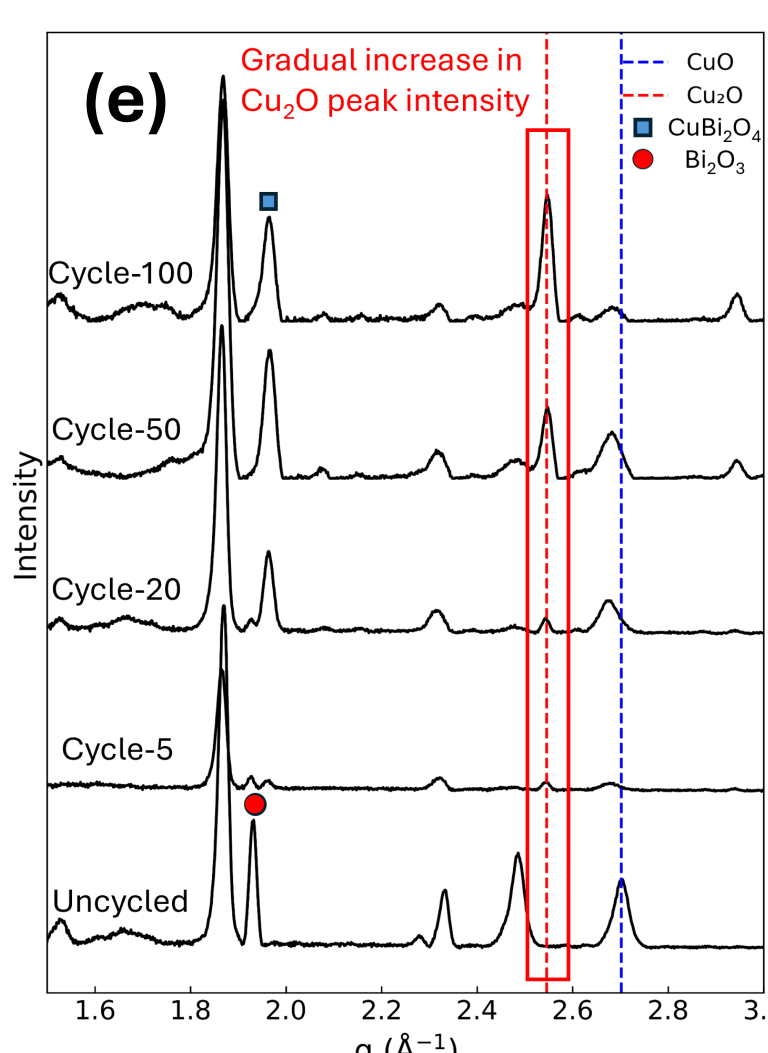
3. Path Forward to Increase Stability



To extend stability of the long-term cycling, an analysis identified slow loss of active material (0.414% per cycle) during discharge (a-b).

Cathode was found to lose capacity over 500 cycles (see panel (d) to the left), which was predominantly high voltage capacity.

- A compressed cathode was fractured and imaged at cycle 100 in the charged state (c). An EDS analysis showed locations of Cu, O, C, and Bi (not shown).
- The cathode cross-section in (c) includes the pore space of the separator, shown at the top. The Cu signal in (d) showed [active material migration into the separator pores](#), which was found to be mainly Cu₂O. This slow loss is driven by the dissolution-precipitation mechanism, predominantly during discharge. Ongoing work aims to reduce solubility of the Cu species to stop this migration.



In situ EDXRD results showed that the material diffusion into and near the separator is a gradual process, evidenced by a progressive increase in Cu₂O peak intensity (e). We also observed a mixed Cu-Bi oxide, CuBi₂O₄, which replaced Bi₂O₃.

- The loss of Cu₂O material into the separator corresponded to loss of the high voltage capacity and cycling of Cu(0) and Cu(I) only.
- The formation of CuBi₂O₄ was confirmed which correlates with a greatly lessened amount of Cu₂O buildup. Ongoing work aims to further understand the function of CuBi₂O₄.

Acknowledgements

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