Spectroscopic Characterization of Rechargeable Alkaline Batteries for the Grid

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Background

As global energy production becomes increasingly dependent on renewable sources, the development of improved energy storage systems has become a mission of global importance. **Rechargeable alkaline batteries** have the potential to meet the demanding cost and safety requirements for grid storage, i.e. Zn-MnO_2 and Zn-CuO. The cathodes of these cells are metal oxides that can deliver 2 electrons per transition metal. The simplified cathode half-cell reactions are below:

Mn^{IV} to Mn^{III} reaction (1st electron):
$Mn^{IV}O_2 + H_2O + e^- \leftrightarrow Mn^{III}OOH + OH^-$

Mn^{III} to Mn^{II} reaction (2nd electron):
$Mn^{III}OOH + H_2O + 3OH^- \leftrightarrow Mn^{III}(OH)_6^{3-}$
$Mn^{III}(OH)_6^{3-} + e^- \leftrightarrow Mn^{II}(OH)_2 + 4OH^-$

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

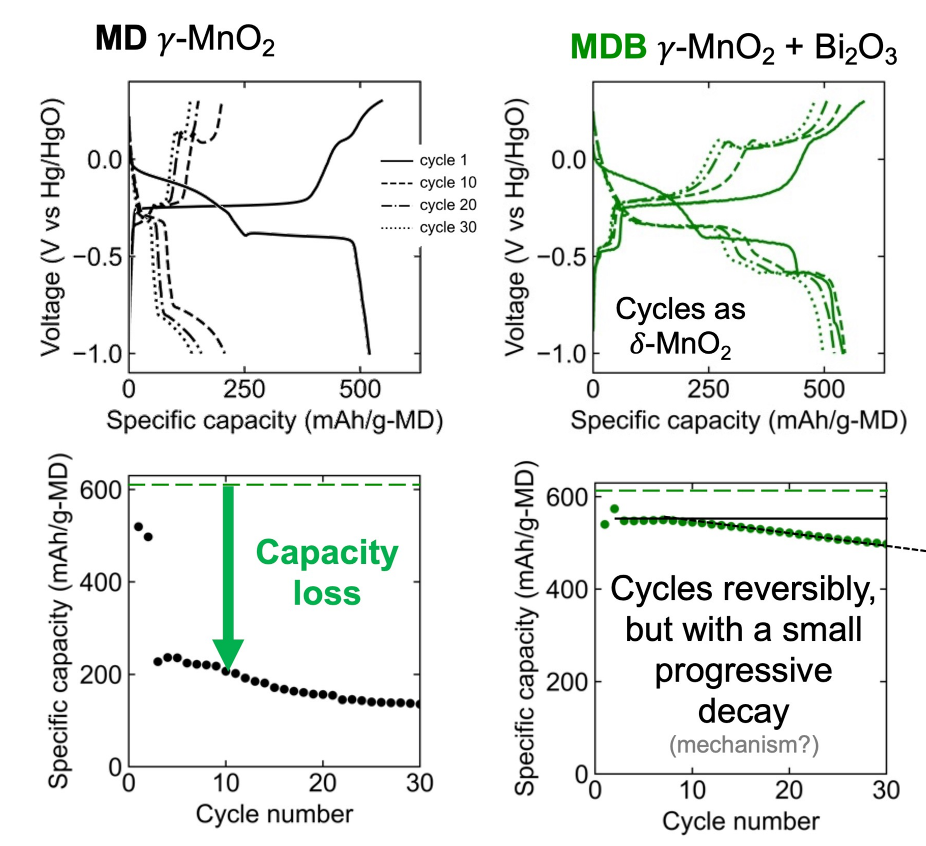
Cu^{I} to Cu^{I} reaction (2nd electron):
$Cu^{I}_2O + H_2O + 2e^- \leftrightarrow 2Cu^0 + 2OH^-$

However, in practice these reactions are more complex than portrayed. To enable rechargeability, both materials must be modified with Bi_2O_3, introducing another redox-active atom. This and the importance of short-lived intermediate species (Mn^{III}, Cu^{I}) make the reaction pathways challenging to accurately define. This work clarifies these mechanisms.

Achievements

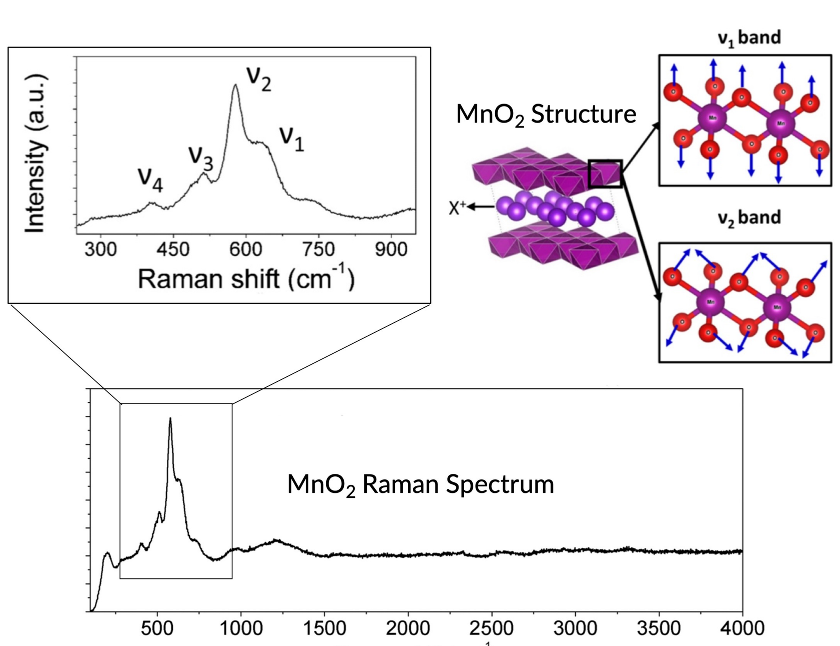
To rationally engineer the rechargeable MnO_2 and CuO cathodes, their electrochemical mechanisms must be well understood. We have ongoing projects that will (1) identify intermediates and causes of irreversibility in MnO_2 (shown at right)*; (2) increase the areal capacity of in MnO_2†; (3) identify intermediates in the CuO system developed at SNL†.

Plots to the right show the dramatic rechargeability that Bi species impart. However, a small degradation process can be seen.



Our work has identified the importance of Mn^{III} species, e.g. α-MnOOH during discharge and β-MnOOH during charge.

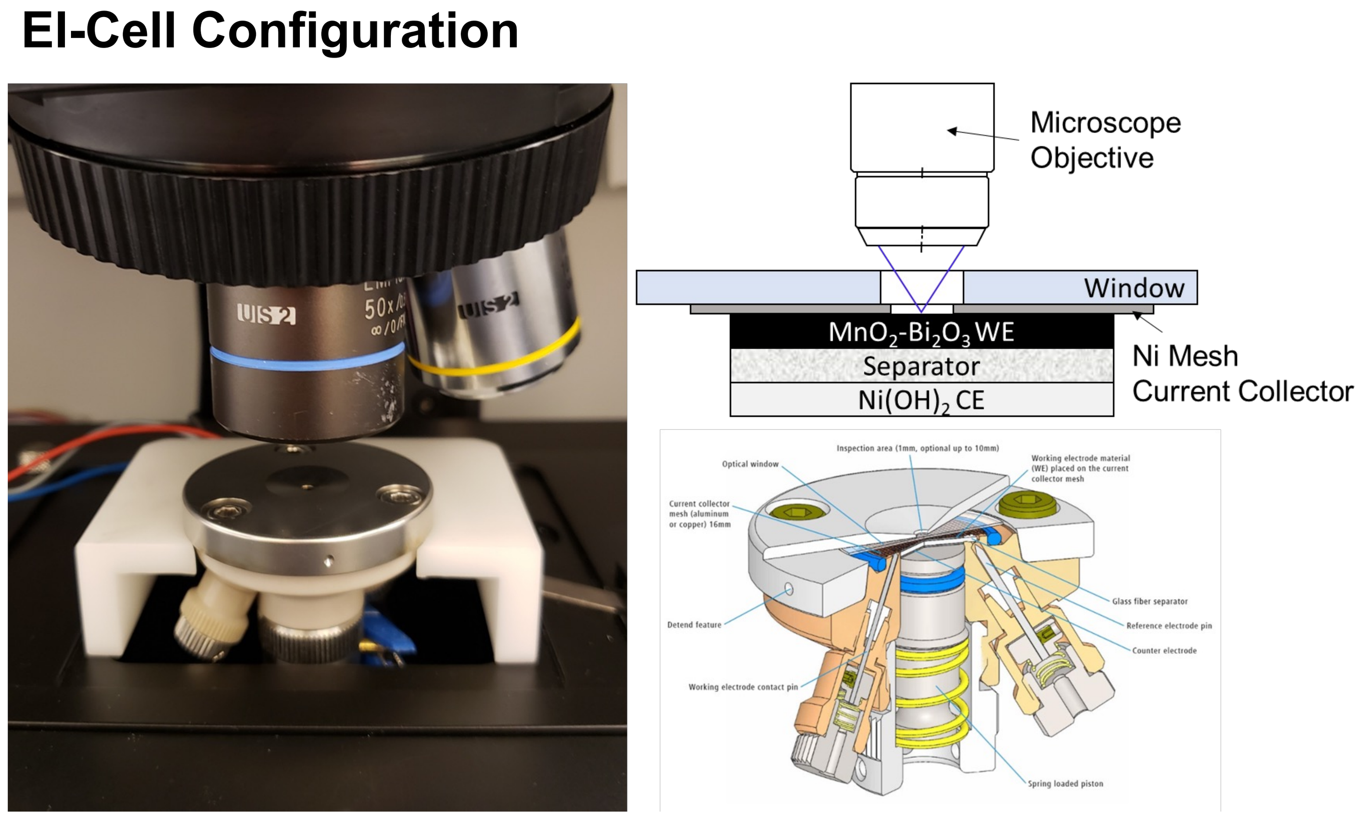
Confocal Raman Spectroscopy



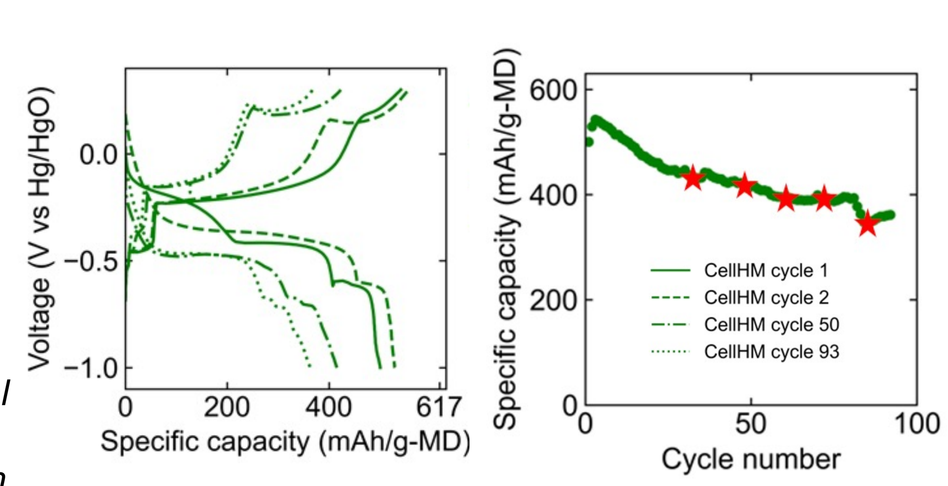
Operando Raman analysis of the MnO_2 cathode

- Slow decay in the MDB system may be due to progressive Mn_3O_4 formation
- Both MnO_2 and Mn_3O_4 are highly Raman active
- High cycle numbers are needed to adequately judge

EI-Cell Configuration

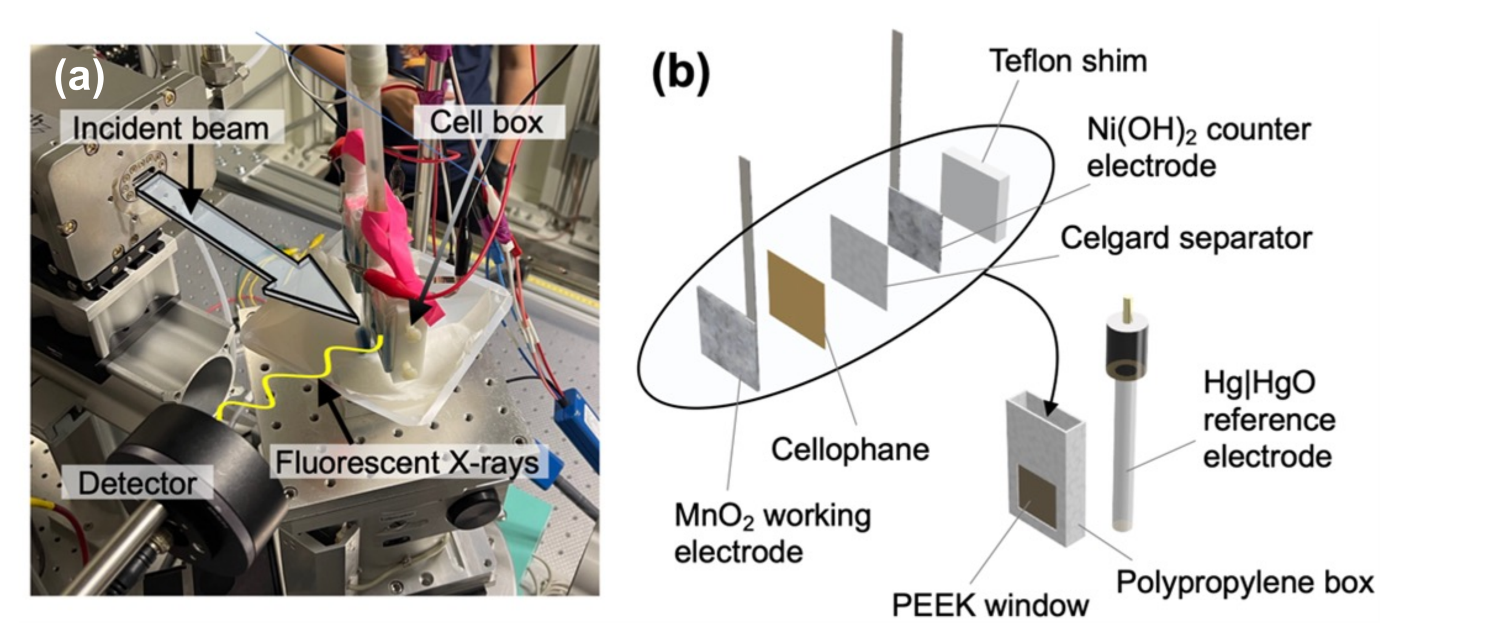


- Achieving high cycle life in an operando cell requires good compression and no leaks. Therefore a specialized cell was designed.
- Progressive decay was observed. However, No Mn_3O_4 was detected even at cycle 93.
- Thus the decay is not caused by the same mechanism by which standard MnO_2 fails.

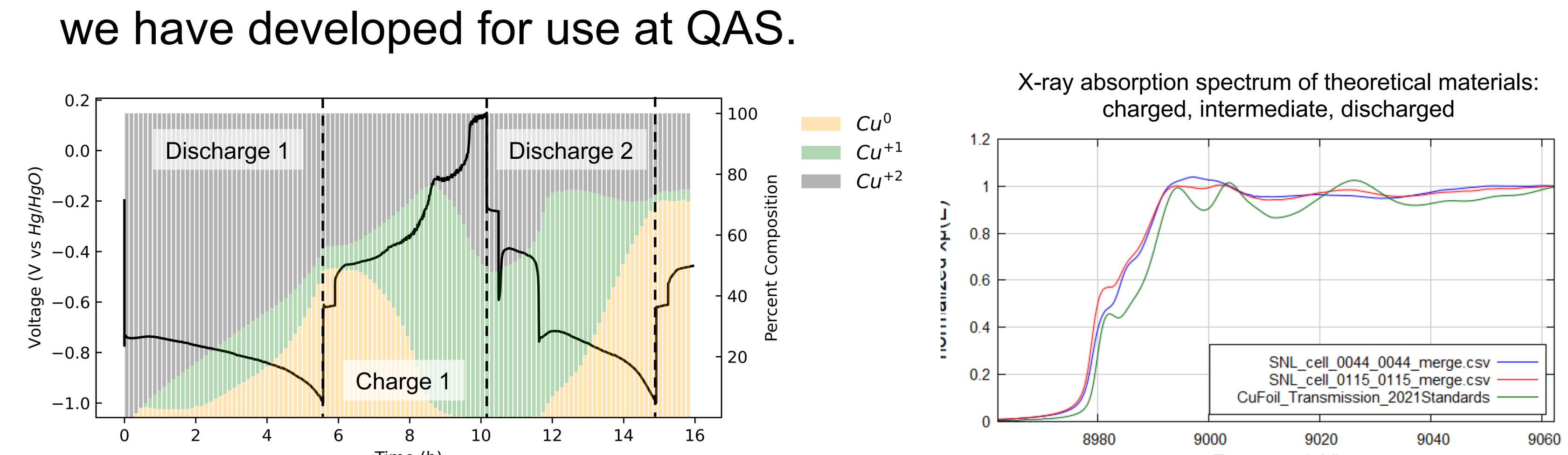


Bruck and Gallaway et al.; *J. Electrochemical Soc.* **2020,** *167* (11), 110514.
Zimmerer and Gallaway, et al.; *in preparation*.

Operando EXAFS Analysis



Many of the materials (intermediates and products) formed lack long-range crystallinity. This makes them impossible to detect/characterize by X-ray diffraction techniques. We use X-ray absorption spectroscopy, particularly Extended X-ray Absorption Fine Structure (EXAFS) to detect species via short-range (molecular) order. Beamline 7-BM (QAS) at NSLS-II features quick data collection, making it ideal for operando analysis during battery cycling. Panels (a-b) above show the alkaline cell we have developed for use at QAS.



Operando X-ray spectroscopy analysis of the CuO cathode

- The Cu^{II} charge product is non-crystalline/amorphous
- Operando X-ray spectroscopy results above show that the 1st discharge is a formation cycle, and following cycles proceed through a different mechanism
- Cu^{I} is present at limited amount during discharge 1, but is extensive during discharge 2
- Ongoing Multivariate Curve Resolution analysis (MCR-ALS) will determine material compositions (multiple Cu^{II} species are suspected)

Schorr, Bruck, Gallaway, Lambert et al.; *ACS Appl. Energy Mater.* **2021**, 4, 7073−7082.
Wygant, Zimmerer, Gallaway, and Lambert, et al.; *in preparation*.

Acknowledgements

†This work was supported by the U.S. Department of Energy (DOE) Office of Electricity Delivery and Energy Reliability, Dr. Imre Gyuk, Energy Storage Program Manager. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02- 06CH11357. This research used beamline 7-BM (QAS) of the National Synchrotron Light Source II, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Brookhaven National Laboratory under Contract No. DE-SC0012704. *Some fundamental MnO_2 work was support by the National Science Foundation under award number CBET-ES-2044602. We thank Dr. Andrea Bruck for our poster design.

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SAND No. SAND2023-10402C