Operando Investigations of Bismuth Additives on the Rechargeability of MnO_2 in Alkaline Batteries

Northeastern University

Andrea M. Bruck, Matthew Kim, Joshua Gallaway

Northeastern University

Department of Chemical Engineering, Northeastern University

Background

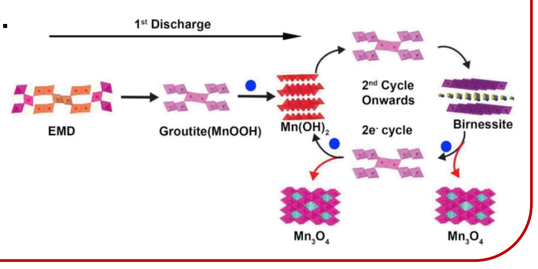
Zn/MnO_2 alkaline batteries have been identified as a viable option for the modernization of grid scale energy storage due to their projected cost (~$50/kWh), scalability, and safer components when compared to non-aqueous alternatives. For this system to reach its maximum capacity, the full $Mn^{4+/2+}$ redox couple must be reversible over thousands of cycles with high mass loading. The following reaction has been proposed to occur in alkaline systems:

$$MnO_2 + xH_2O + xe^- \leftrightarrow MnO_{2-x}(OH)_x + xOH^- \quad \text{where } x = 2$$

Recently, success in rechargeability > 3000 cycles has been demonstrated with the incorporation of various electrode constituents which alter the fundamental discharge and charge process and form the δ-MnO2 (birnessite) on the first cycle which is identified as the reversible reaction.

Gallaway et al.; *Journal of The Electrochemical Society*, (2018) 165, 13, A2935-A2947

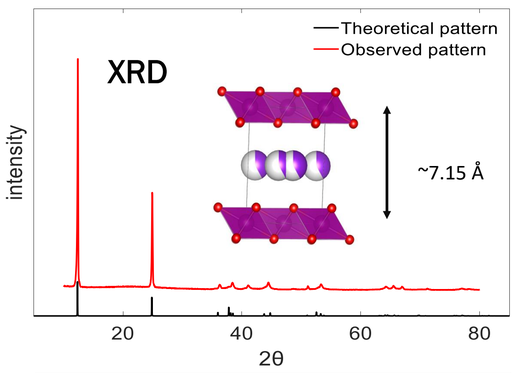
Yadav et al.; *Materials Today Energy*, (2017) 6, 198-210

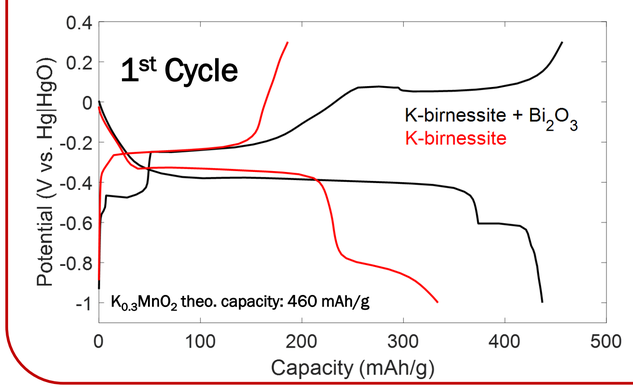


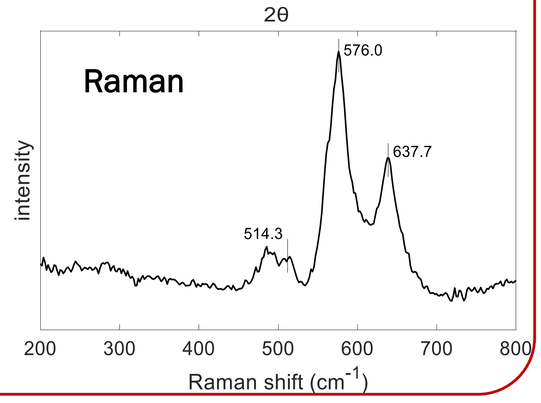
K_xMnO_2 as model material

Potassium birnessite was synthesized in our lab. Considering birnessite as the reversible phase we want to understand:

(1) What is the role of Bi_2O_3 in the electrode
(2) What is the mechanism for MnO_2 reversibility
(3) What is the optimal way to incorporate Bi into the electrode*



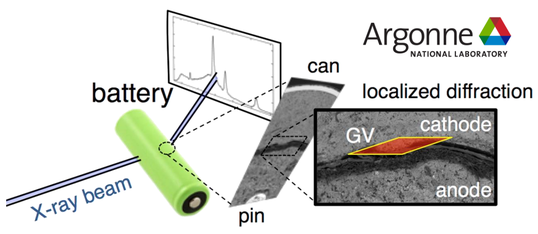


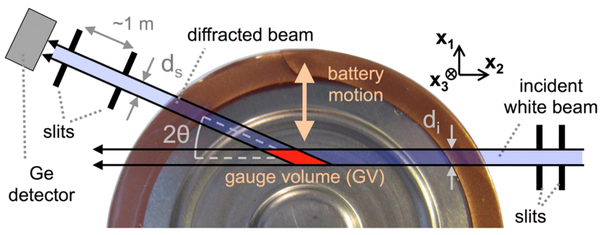


Operando studies of K_xMnO_2

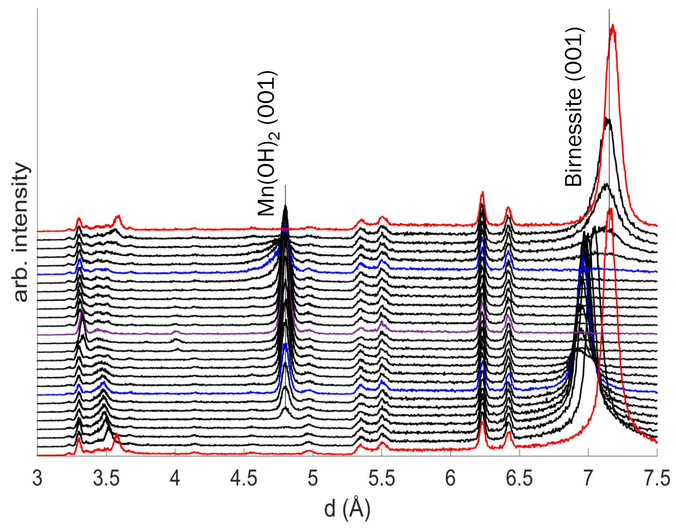
Synchrotron Energy Dispersive X-ray Diffraction

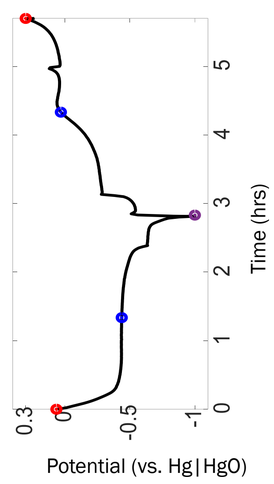
- Fully intact batteries are cycled at Argonne National Lab's Advanced Photon Source
- The white beam (~50-200 keV) penetrates the cell casing and subsequent diffraction on the internal material changes are detected
- Non-destructive technique identifies intermediates and kinetically driven reactions that may be unstable for ex situ characterization

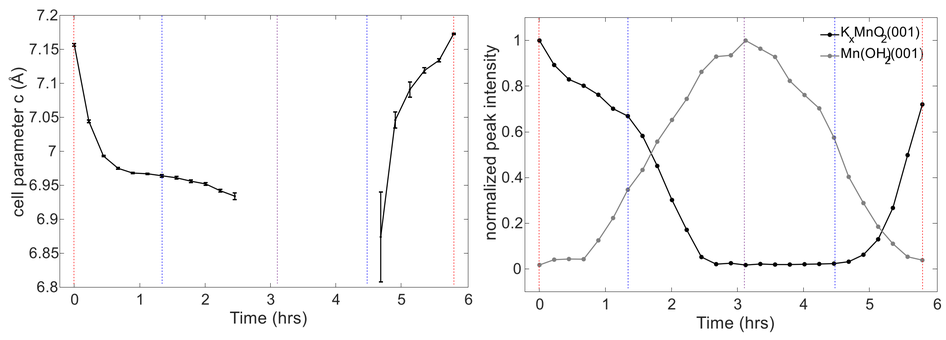


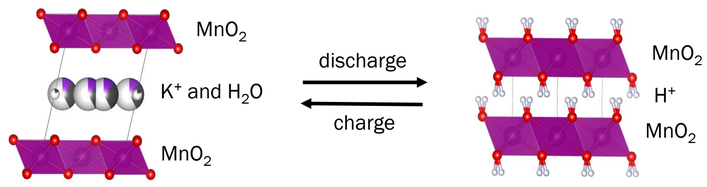


Gallaway et al.; *Journal of Power Sources*, (2016) 321, 135-142









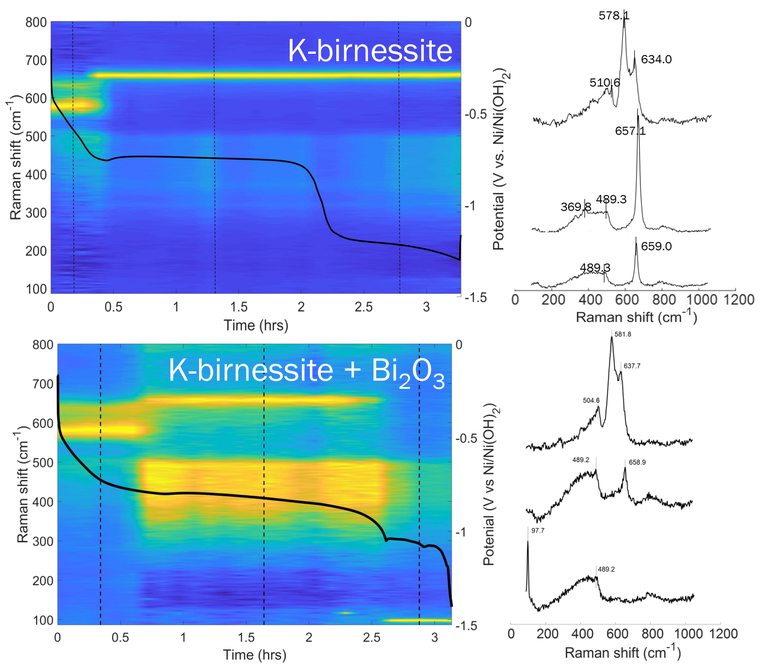
- Most notably, no intermediate phases such as MnOOH or Mn_3O_4 were detected by diffraction experiments indicating a two-phase reaction

EDXRD Collaboration:

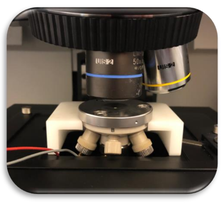
Matthew Kim (Northeastern) and David Arnot (Sandia) testing batteries at beamline 6BM-A of APS. Our institutions are working together for the operando characterization of battery reactions.

Sandia National Laboratories

Laboratory-based Raman Spectroscopy for non-crystalline intermediates

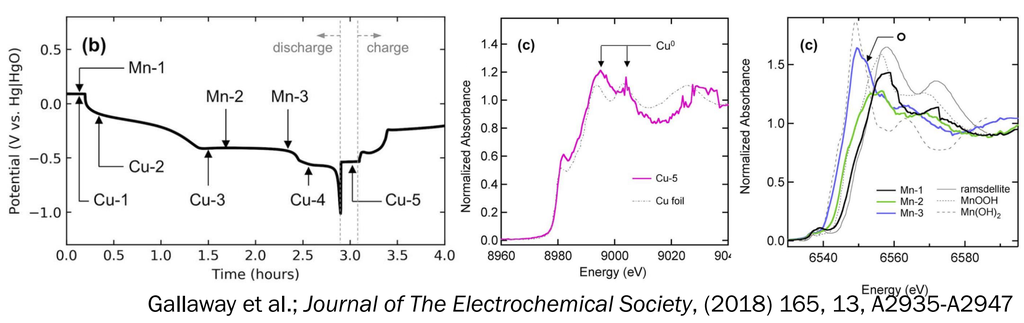


- Birnessite, Mn_3O_4, and $Mn(OH)_2$, and Bi metal could be identified
- In the presence of Bi_2O_3 small quantities of Mn_3O_4 form but disappear during the second plateau
- Bi_2O_3 suppresses the formation of the irreversible phase and allows for the full conversion to $Mn(OH)_2$



Gosztola et al.; *Journal of Electroanalytical Chemistry*, (1989), 271, 141-154

Summary and Next Steps



Gallaway et al.; *Journal of The Electrochemical Society*, (2018) 165, 13, A2935-A2947

1. Diffraction methods detect two crystalline phases in the reversible reaction, birnessite (MnO_2) and $Mn(OH)_2$
2. However, Raman spectroscopy revealed the formation of Mn_3O_4 during discharge which is suppressed in the presence of Bi_2O_3
3. We are specifically interested in the final plateau of the discharge where Bi_2O_3 redox activity is possible with the disappearance of Mn_3O_4

Our next beamline run is scheduled at NSLS-II for XAS to better probe the redox activity of Bi and Mn with improved temporal resolution.

Acknowledgements

This work was supported by the U.S. Department of Energy (DOE) Office of Electricity, 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.

U.S. DEPARTMENT OF ENERGY