Background

Zn/MnO₂ 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 Mn⁴⁺/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:

\[
\text{MnO}_2 + x\text{H}_2\text{O} + xe^- \leftrightarrow \text{MnO}_2-(\text{OH})_x + x\text{OH} \quad \text{where } x = 2
\]

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.


δ-MnO₂ – Bi₂O₃ system

We use K-MnO₂ as a model material to answer the following questions:

1. What is the role of Bi₂O₃ in the electrode
2. What is the mechanism for MnO₂ reversibility

Mechanistic Insight into δ-MnO₂ – Bi₂O₃ cyclability

X-ray absorption spectroscopy (XAS) provides oxidation state change and local structure

- Fully intact batteries are cycled at Brookhaven National Lab’s NSLS-II QAS beamline
- Both the Mn K- and Bi L₃ edge were scanned with over 1 cm² electrode area in fluorescence mode
- Limited Mn redox without Bi₂O₃ present, full reduction to Mn²⁺ when present
- Second plateau shows initial Mn redox slow then quickly converts above Mn³⁺
- Bi is partially redox active but does not fully convert to Bi metal
- Bi-O from [BiO]₃⁻ cluster is present even at full discharge indicating Bi³⁺ is present, possibly an amorphous or a dissolved species

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