

Transient Interface Evolution in Cycling Alkaline Batteries Resolved Using Synchrotron X-Rays

Joshua W. Gallaway^a, Can Erdonmez^b, Zhong Zhong^c, Mark Croft^{c,d}, Lev Sviridov^a, Sanjoy Banerjee^a, Daniel A. Steingart^c

^a The CUNY Energy Institute at the City College of New York, New York, NY 10031

^b Energy Storage Group, Brookhaven National Laboratory Upton, NY 11973

^c National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY 11973

^d Department of Physics and Astronomy, Rutgers University, Piscataway, NJ 08854

^e Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ 08544

Energy dispersive X-ray diffraction (EDXRD) using white beam synchrotron radiation allows electrochemical cells with centimeter-scale dimensions to be rapidly mapped crystallographically in both time and space.^{1,2} X-rays with a wide range of energies penetrate the cell, and X-ray diffraction intensity is measured at a single angle from a localized gauge volume within the cell.

We report in situ EDXRD diffraction contours collected on AA (LR6) alkaline Zn-MnO₂ batteries using the superconducting wiggler beamline X17B1 at the National Synchrotron Light Source (NSLS). Data was collected for cells undergoing both deep discharge and shallow cycling. As data collection time for an EDXRD diffraction contour was short compared to the duration of a battery cycle or discharge, material changes were resolved as a function of time as well as spatial location.

Data for a cell deep discharged at a high rate of 3A are shown in Figure 1. Characteristic MnO₂ reflections for a radial section of the annular cathode are shown in panel A. A full diffraction contour of the initial cell is seen in panel B, where pixel darkness is the logarithm of diffraction intensity at the indicated scan location. Scan direction was in the radial direction, from top to bottom of a horizontal cell, at its axial midpoint. Each scan location was separated by ~320 μm. Beam intensity was found not to affect the active material on the order of the experimental time.

During discharge, MnO₂ nearest the separator experienced significant lattice strain due to proton insertion (panel C).³ Zinc oxide deposited at the anode-separator interface.⁴ The penetration zone for ZnO formation increased as discharge continued (panel D). We found ZnO formation to be a function of current and cycling protocol. In some cycled cases ZnO was only transient. ZnO layer formation is believed to lead to failure of alkaline cells.⁵

It is generally recognized that electrochemical storage on a large scale is desirable for a number of societal reasons including electrical load leveling, power regulation, electrical demand peak shaving, the smart grid, and for firming intermittent renewables-based generation such as solar and wind power.⁶ The low cost and low environmental impact of the Zn-MnO₂ chemistry merits increased consideration of its use in large scale storage.

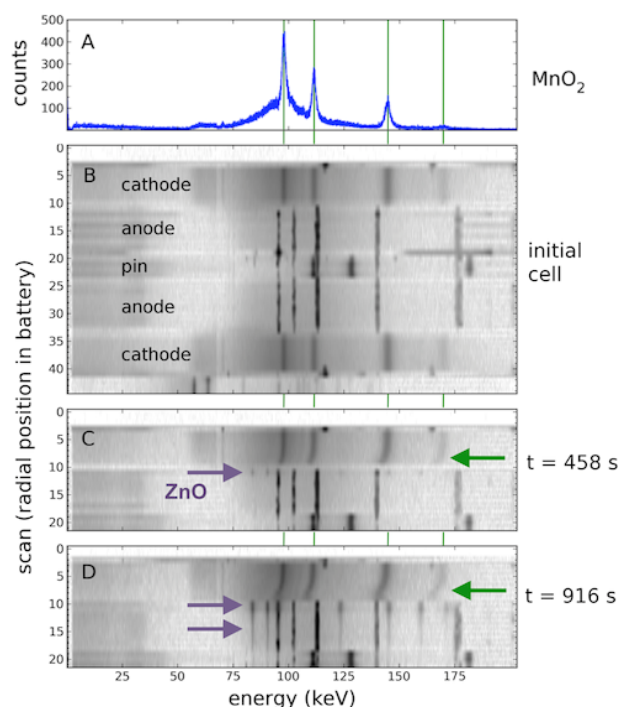


Figure 1. EDXRD results for a AA alkaline battery discharged at 3 A in situ. A: Cathode reflections showing characteristic MnO₂ peaks, from Scan 9 of Panel B. (Green lines mark peak energies for comparison to other panels.) B: Diffraction contour of initial cell, with annular cathode, anode, and central pin indicated. C: Scan completed at 458 s after beginning discharge, showing MnO₂ lattice strain (green arrow) and ZnO deposition at the separator (violet arrow). D: Scan completed at 916 s, in which strain and ZnO growth layers propagated away from the separator. At this time the separator was compressed to a size smaller than scan resolution and the cathode and can expanded by ~320 μm.

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