

Structural Variation in the γ/β -MnO₂ Series and its Influence on Cathodic Cyclability

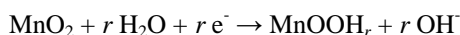
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Electrolytic manganese dioxide (EMD) remains a prominent cathode material in alkaline battery cells due to its low production costs, low toxicity, and excellent performance under low and moderate discharge rates. EMD is known to have the γ -MnO₂ structure, built up of edge- and corner-sharing [MnO₆] octahedra in a manner consistent with a random microscopic intergrowth of the pyrolusite (1×1) and ramsdellite (2×1) forms of manganese dioxide [1, 2]. Other key features associated with the γ -MnO₂ structure include microtwinning, cation vacancies, lower valent manganese cations (Mn³⁺), and structural water present as protons.

Reduction of γ -MnO₂ in alkaline electrolytes proceeds via concerted electron-proton insertion into the host γ -MnO₂ structure, and can be written formally as



Here the electrons come from an external circuit, reducing Mn⁴⁺ to Mn³⁺, and protons from the electrolyte are incorporated as OH⁻ in place of the original O²⁻ in the lattice [3]. Despite a significant history of study, the relationship between specific material properties, such as pyrolusite fraction, and the response of the γ -MnO₂ structure to cycling remains unclear.

Previously we have shown that the steady decline in rechargeable capacity observed for EMD could be primarily assigned to reduction in lower potential pyrolusite domains [4]. In this work we will expand on this by making use of the heat treatment of EMD to produce a series of γ -MnO₂ materials with an increasing fraction of pyrolusite (P_r). As shown in Figure 1, the heat treatment of EMD induces several distinct changes in the underlying structure, with the most prominent being the steady transition to a more pyrolusite-like structure.

By making use of non-aqueous chemical reduction, a series of partially reduced samples was prepared from selected heat treated materials. In this manner, detailed information was obtained on how the structure of each material is influenced by the reduction process. Electrochemical cycling and step potential electrochemical spectroscopy (SPECS) were subsequently carried out on each material to assess their performance.

The use of SPECS is particularly important here as it provides information on how the kinetics of the reduction process changes with applied potential. By relating the structural data gathered for each material to the extent of reduction at each potential step, the kinetics of proton diffusion can be determined. Thus, the change in proton diffusion for each material during the reduction process, and any variation resulting from increasing pyrolusite content, can be readily assessed. A comparison between the experimental values and the theoretical changes

reported by Balachandran et al. [5] will also be covered.

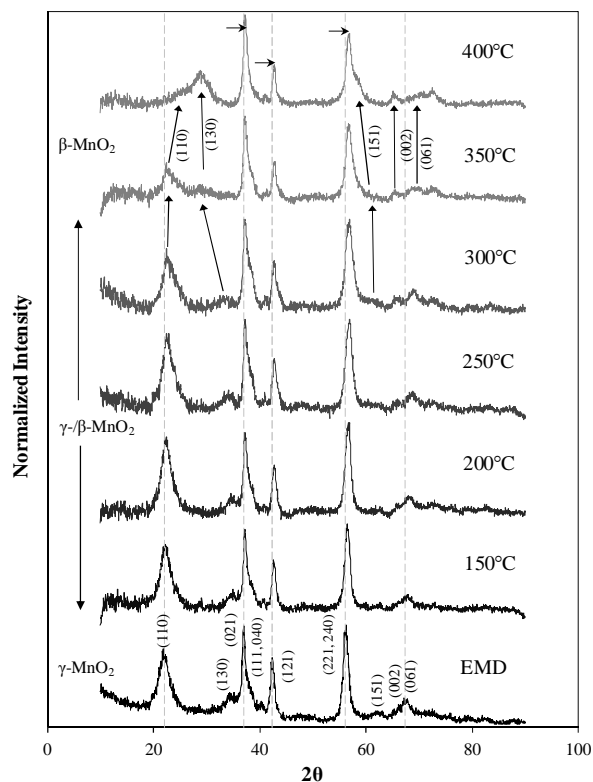


Figure 1. Effect of heat treatment on the orthorhombic γ -MnO₂ lattice, with the key peak shifts highlighted.

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