

# Development of MnO<sub>2</sub> Based Cathodes for Alkaline Batteries via Combinatorial Approach

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MnO<sub>2</sub> is a commonly used material in various types of batteries, as it is suitable for electrochemical applications due to its high defect density and structural disorder, including low crystallinity, small crystallite size, unoccupied lattice sites, and foreign cations and molecules within its structure [1]. In addition to its electrochemical properties, it is also abundant in nature and relatively inexpensive compared to other battery materials.

Although MnO<sub>2</sub> is commonly used in primary batteries, there is ongoing research into its use in secondary batteries. The main challenges with MnO<sub>2</sub>-based secondary batteries are their reversibility and cycle life due to irreversible reactions [2]. Many elements and compounds have been tested to address this problem, but only Bi has shown significant effects [2,3]. Yadav et al. achieved impressive results with Cu-intercalated Bi-birnessite (layered) MnO<sub>2</sub>, reaching 80-95% of the full 2 electron capacity (617 mAh/g) at high loadings and areal capacities for thousands of cycles (>6000 cycles) [4,5]. However, the battery's operating voltage was too low, particularly for the second electron process, resulting in a low energy density.

The objective of this research is to create layered  $\delta$ -MnO<sub>2</sub> with different compositions using a combinatorial approach in order to identify new compositions that can provide the full two electron capacity at an appropriate voltage value with high cyclic stability. The samples are fabricated using magnetron sputtering with NaMnO<sub>2</sub>, NiO, Bi<sub>2</sub>O<sub>3</sub>, and MnO<sub>2</sub> as targets. The thick film cathodes (2-3  $\mu$ m) are analyzed using cyclic voltammetry and galvanostatic cycling, as well as SEM and XRD.

The samples exhibited varying behaviors, with regions containing high nickel content demonstrating excellent cyclic stability but low capacity and voltage values. Conversely, regions with high bismuth content showed high capacity but acted more like primary batteries. The cathodes with improved electrochemical performance were found to have moderately rich Na content.

Structural investigations showed that preliminary amorphous cathodes as deposited state have been successfully converted to layered  $\delta$ -MnO<sub>2</sub> phase during testing.

All the samples showed drastic capacity decay at some point during testing. SEM studies revealed that the thick film coatings lose their integrity and peels off from the surface of the current collector. This is attributed to the volume change of the active material during operation. Preparation of the cathodes via traditional methods may eliminate this problem.

The cathodes tested with a narrow voltage window to speed up the testing of samples. Therefore, their capacities were lower than expected. When a sample from the best performing region is tested for full capacity, a value of nearly 550 mAh/g is reached. However, the capacity wasn't reversible. When the sample is removed from the battery it is seen that the coating was completely removed from the substrate. This may be due to the cathode completely dissolving and the dissolved species moving away, preventing re-precipitation on the substrate. This problem could be addressed by using a gel electrolyte or avoiding complete discharge of the battery.

The improved performance of the cathodes was achieved within a compositional range that is not too distant from NaMnO<sub>2</sub> and could be regarded as a doped version of this compound with Bi and Ni cations. NaMnO<sub>2</sub> and similar compositions were deemed promising, provided that fragmentation occurring in the cathode, which impairs their full performance, can be resolved through the slurry method with a carefully designed electrode architecture.

## References

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