Search for New Cathode Compositions for Mildly Acidic $Zn-MnO_2$ Batteries

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Manganese oxide has been used extensively since the invention of batteries. Structurally modified MnO2 is an appealing material for making primary Zn-MnO2 batteries not only rechargeable but also capable of improving the voltage profile. Moreover, Mn and Zn are attractive materials due to their abundance and low cost. Zn/MnO2 batteries could be well-suited for grid energy storage systems, making them more widely used. To achieve this goal, modifying the MnO2 cathode is crucial.

$Zn-MnO_2$ batteries are still being mass-produced as primary batteries. The primary battery cathode active material used is electrolytic manganese dioxide (EMD), which is a form of $\gamma-MnO_2$, and the electrolyte used is aqueous KOH. There is a lot of effort to make these batteries rechargeable by modifying the cathode and the electrolyte. Yadav et al. [1] were able to improve rechargeability and achieve a two-electron exchange by making $Mn(OH)_2$ reversible through the addition of Cu^{2+} and Bi_2O_3. Hertzberg et al. [2] studied the effect of mixing alkaline electrolytes KOH and LiOH, and found that a 1M KOH + 3M LiOH aqueous solution was the best electrolyte for a Bi_2O_3-added MnO_2/Zn foil cell. The addition of LiOH prevented the zincate poisoning. Shoji et al. [3] were the first to suggest in 1987 that $Zn-MnO_2$ batteries could be made rechargeable by using a slightly acidic electrolyte due to problems encountered with alkaline batteries. Sun et al. [4] reported that when a mildly acidic electrolyte is used, the mechanism of co-insertion of H^+ and Zn^{2+} is observed. XRD analysis showed that the main reaction during discharge to 1.3V is H^+ insertion, which forms the MnOOH phase, while discharging to 1.0V results in $ZnMn_2O_4$ formation, indicating Zn insertion.

The main objective of this thesis is to discover new compositions of MnO_2-based cathodes for Zn-ion batteries. To achieve this goal, a combinatorial approach was used by utilizing thick film cathodes that were deposited via magnetron sputtering. The system being studied is based on MnO_2 combined with $NaMnO_2$, Bi_2O_3, and NiO. To facilitate the process, four sputter targets were created, with the MnO2 target placed at the center and the other oxides placed in a triangle around it. The substrates placed in a substrate magazine with a triangular geometry, allowing for the deposition of 36 cathodes with distinct compositions in a single sputtering experiment.

In total, 216 cathodes were produced from six experiments. These cathodes were deposited on Ni foil current collectors and were tested using cyclic voltammetry and galvanostatic techniques. Results showed that Mn-rich cathodes performed the best, leading to the selection of three out of the six sets of cathodes for further analysis. The Mn-rich corner of the Bi-Mn-Ni ternary diagram, with varying levels of Na from 0 to 78%, was analyzed based on their capacities, cyclic stability, and discharge plateau potential. Three compositions with discharge capacities exceeding 400 mAh/g were chosen as candidates based on the analysis.

To verify if the selected cathodes can produce the same or similar capacities, they were also prepared using the slurry route. However, the highest capacity achieved using this method was only about 100 mAh/g. Therefore, more work is required to fully explore the potential of the chosen cathodes.

References

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