Effect of Depth of Discharge on the Performance of Zn-Mn and Zn-Ni Battery

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In this communication, the zinc anode electrode was prepared by electroplating. MnO2 cathodes and Ni(OH)2 cathode electrodes were prepared by the pressing process. KOH 6 M with 40%ZnO were used as the electrolyte solution of a battery. X-ray diffraction (XRD) was used to study the complexation of cathode electrodes. The Fourier transform infrared spectroscopy (FTIR) analysis showed some peaks which ascertain chemical interlinking of Zn-MnO2 and Zn-Ni(OH)2 on cathode electrodes. After performance testing, morphology characterization of zinc anode electrode was performed by scanning electron microscopy (SEM). The electrodes were tested for performance by a battery analyzer for 100 cycles with a depth of discharge (DOD) at 10%, 20%, 40%, and 80%. It was found that zinc electrodes had branching of a dendrite, which quickly grew at a high depth of discharge. The depth of discharge influenced dendrite growth and the battery performance during cell discharging at high DOD. The Zn anode was damaged due to the excessive dissolution of Zn⁺ in the electrolyte, causing the decay of the Zn anode. On the other hand, during cell charging, Zn⁺ was not uniformly deposited on the anode, resulting in dendrite branching.

Zinc electrode in Zn-MnO2 cell had more dendrite than zinc electrode in Zn-Ni(OH)2 cell at 10% DOD. The results also showed higher efficiency of 99.08% and better stability for Zn-Ni(OH)2 than Zn-MnO2 cells in similar conditions. This was due to the fact that during cell discharge, Mn⁺ in the electrolyte continuously reacts with Zn⁺ to form other complex compounds. On the contrary, Ni(OH)2 cathode exhibited better recyclability than MnO2 cathode. Therefore, Ni(OH)2 cathode offers excellent potential for use as a cathode electrode because it can be used at high DOD. Another advantage of Ni(OH)2 cathode is that it can be prepared from a simple process by making use of readily available non-toxic materials.

Key Words
Depth of discharge, Zinc anode, Zn-MnO2 battery, Zn-Ni(OH)2 battery, Dendrite

1. Introduction
Electrical energy storage has been the subject of many investigations. Zinc-based batteries have attracted considerable attention due to their safety, low cost, non-toxicity, and abundance1–3. These features make it an interesting candidate for electrode materials in rechargeable electrical energy storage. One of the most important energy storage applications is their use as cathode materials for rechargeable batteries. Zinc anode is commonly used with metal-oxide cathodes such as graphene oxide (GO), MnO2, Al2O3, SiO2, and Ni(OH)2.4–6

MnO2 and Ni(OH)2 have similar properties, and they are good candidates for energy storage applications because of their high practical, specific energy, excellent...
specific power \(6\). Zn-MnO\(_2\) battery could achieve a long cycle life, but it cannot be used at high DOD because of MnO\(_2\) electrode that does not accumulate irreversible redox reaction products \(7^\text{—}^9\). From the past research using fiber-shaped Zn/Ni(OH)\(_2\) battery, which had good rate capability and good cycling stability, the method to fabricate Ni@Ni(OH)\(_2\) fiber was difficult, and the material used expensive. The method also required a specific suitable support material \(10\). In addition, there is a study in Zinc-Nickel Hybrid Battery using a Ni(OH)\(_2\)-O\(_2\) Composite by complex method, which achieved high efficiency. This battery used high-concentration KOH-K\(_2\)[Zn(OH)\(_4\)] solution, which was relatively unsafe \(11\).

Zn-MnO\(_2\) and Zn-Ni(OH)\(_2\) batteries have the advantages of Zn Mn and Ni, including rechargeability, high conductivity, good redox reversibility, and environmental preservation. A few methods can achieve the preparation of cathodes and anodes: rolling, forming, and impregnating. In this research, pressing with pressure and temperature was chosen due to the durability of the obtained electrodes. If it is desirable to fabricate the electrodes by forming, PVDF is required as a binder. In the present study, PTFE was used as the binder because of its less toxicity and greater safety. Use of PVDF requires N-Methyl-2-Pyrrolidone (NMP) as the solvent. The solvent gives off vapor with high concentration, causing irritation to the skin, eyes, and nasal tissues \(12\). As previously mentioned, the impregnation method requires a specific and usually expensive material for support resulting in high production cost. Obviously, pressing and rolling are simpler, and safer. Generally, binders and additives such as graphite are used to enhance electrical conductivity \(12^\text{—}^15\). Zinc anode was prepared by electroplating following the method of our previous study because this method proved to give good morphology of evenly packed zinc surface, thus a better performance of zinc electrode \(16\).

Our literature review found that the production cost of the battery was high because it required specific and expensive materials. Furthermore, the battery has low efficiency at high DOD. Therefore, our approach focused on inexpensive material, environmental friendliness, cycle life, and discharge rates, which could be achieved at relatively high depths of discharge (DOD). This research aimed to improve the performance of Zn-MnO\(_2\) and Zn-Ni(OH)\(_2\) by developing a suitable cathode preparation method and investigating the cycling behavior of Zn-MnO\(_2\) and Zn-Ni(OH)\(_2\) battery at various DODs.

### 2. Methodology

#### 2.1 Zn anode electrode

A copper plate was the substrate for zinc anode prepared by electroplating. First, the copper substrate (Sincharoen Metal, Bangkok, Thailand) was prepared in a size of 2.5 cm \(\times\) 5 cm, then polished with 380-grit sandpaper and rinsed with acetone. Pure Zinc (99.9998%) was obtained for electroplating (Samliam Chromium, Thailand) and using 20 cm\(^3\) ZnSO\(_4\) (RCI Labscan) 1M as an electrolyte solution. The electroplating process was started by using a power supply machine (GPC-3030D) by connecting the anode to a power supply at 0.1 A/cm\(^2\) current densities for 1 hour of plating duration.

#### 2.2 MnO\(_2\) and Ni(OH)\(_2\) cathode electrode

Nickel foam (MTI Corporation) was used as the substrate for preparing cathode by pressing pressure and temperature. 60%wt MnO\(_2\), 20%graphite, 20% Teflon powder (PTFE, Polytetrafluoroethylene) were obtained from SCI Labscan. A cathode sheet was made in the same size as an anode. MnO\(_2\), graphite, and PTFE were wet-mixed in a mixer with isopropanol (2-propanal, RCI Labscan). The wet-mixed was embedded into the above nickel foam, and the cathode was dried at 373 K for 6 h. Then it was pressed with a temperature of 513 K at 8200 kPa. for 15min. Ni(OH)\(_2\) was similarly prepared.

#### 2.3 Characterization and cycling test

The cathode was investigated for its crystal structure and recovered MnO\(_2\) and Ni(OH)\(_2\) by means of X-ray diffraction (XRD, PANalytical, EMPYREAN). Fourier transform infrared spectrometer (FTIR, Tensor 27, Bruker, Germany) was used to investigate interlinking of Zn-MnO\(_2\) and Zn-Ni(OH)\(_2\) on the cathode. After performance testing, morphology characterization of zinc anode was analyzed for its crystal structure with scanning electron microscopy technique (SEM, S-3000N, Hitachi, Japan). The battery cell was assembled as illustrated in Fig. 1. Cycle voltammetry

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**Fig. 1** Schematic of battery cell
was performed by a battery analyzer (NEWARE Technology Co., LTD China) with the potential range of 0.6 to 1.8 V. for 100 cycles per cell at the current charge-discharge rate of 20 mA in 6 M KOH with 40%ZnO which was the electrolyte of the battery cell 10 cm³ at 10%, 20% 40% and 80% depth of discharge.

3. Results and discussion

3.1 Recharge ability of cathode electrode

Zn-MnO₂ cells were cycled at 10%, 20%, 40%, and 80% DOD for 100 cycles at a discharge rate of 20 mA. It was found that, at 20%, 40%, and 80% DOD, battery efficiency decreased quickly in the first ten cycles to be 89%, 59%, and 52%, respectively. After 100 cycles, the efficiency decreased to 61%, 45%, and 51%, respectively. At high DOD, the loss of efficiency might be due to the formation of Mn₃O₄ (hausmannite) and ZnMn₂O₄ (hetaerolite). Other products were also possibly apparent, as in the work of Grey and co-workers 17).

Cycling at 10% DOD for 53 cycles resulted in an efficiency of 98.87%. Beyond 53 cycles to 100 cycles, the efficiency decreased to about 83.97%. Cycling results are shown in Fig. 2. This figure indicated that, when DOD was more than 10%, the efficiency loss was rapid in the first ten cycles so that the MnO₂ cathode would be suitable for 10% DOD. The efficiency might decrease due to the dissolution of Mn³⁺, which caused the decrease of electrolyte concentration while charging and discharging 18).

Zn-Ni(OH)₂ cells were cycled in a similar condition. For 40% DOD, the efficiency could be maintained above 98% for ten cycles; after that, the efficiency gradually decreased to 91% after 100 cycles. For 80% DOD, 72% efficiency could be maintained after 100 cycles. Cycling at 10% DOD and 20% DOD gave higher efficiency and more stability, with the efficiency being above 99.08% for 100 cycles, as shown in Fig. 3. Ni(OH)₂ cathode gave better efficiency and more stability at higher DOD than MnO₂ cathode.

Fig. 4 shows the surface XRD of a new cathode, and after 100 cycles at 10% DOD, a cathode cycled 100 times at 80% DOD. After 100 cycles at high DOD, it was found that one or a combination of electrochemically inactive products such as Mn(OH)₃, Mn₃O₄, Mn₂O₃, or ZnMn₂O₄ were formed 18–23. At 10% DOD, the battery efficiency was relatively high because the battery discharged at 10% of the battery capacity. In such a case, MnO₂ did not have sufficient time to continue the reaction to form more complex products during the discharge. On charging, the MnO₂ cathode, which transformed to MnOOH during the discharge, reverses back to become MnO₂ according to equation (1).

\[
\text{MnO}_2 + \text{H}_2\text{O} + e^- \leftrightarrow \text{MnOOH} + \text{OH}^- \quad (1)
\]

At 20-80% DOD, the efficiency of the battery was quite low and unstable because there was sufficient time for the reaction to continue to form more complex products. The reduction of MnOOH proceeds by dissolution and precipitation, as shown in equation (2) - (3). And formation of Mn₃O₄ leads to hausmannite, Mn₃O₄, via equation (4).

\[
\text{MnOOH} + \text{H}_2\text{O} + 3\text{OH}^- \leftrightarrow \text{Mn(OH)}_6^{3-} \quad (2)
\]

\[
\text{Mn(OH)}_6^{3-} + e^- \leftrightarrow \text{Mn(OH)}_2 + 4\text{OH}^- \quad (3)
\]

\[
2\text{MnOOH} + \text{Mn(OH)}_2 \leftrightarrow \text{Mn}_3\text{O}_4 + 2\text{H}_2\text{O} \quad (4)
\]

For the Zn-MnO₂ battery, the anode discharge reaction of Zn to zincate was shown in equation (5) - (6).

\[
\text{Zn} + 4\text{OH}^- \leftrightarrow \text{Zn(OH)}_4^{2-} + 2e^- \quad (5)
\]

\[
\text{Zn(OH)}_4^{2-} \leftrightarrow \text{ZnO} + \text{H}_2\text{O} + 2\text{OH}^- \quad (6)
\]

formation of Mn₃O₄ leads to hausmannite, Mn₃O₄, via equation (4).

\[
2\text{MnOOH} + \text{Zn(OH)}_2^-\text{H}^- \leftrightarrow \text{ZnMn}_2\text{O}_4 + 2\text{H}_2\text{O} + 2\text{OH}^- \quad (7)
\]
For the MnO₂ electrode, it is known that it gave Mn⁴⁺ and Mn³⁺ ions in the active material. This explains the key of efficiency fade cycling, mainly due to the formation of irreversible redox reaction products in the MnO₂ cathode. In contrast, Ni(OH)₂ cathode can reverse from NiOₓ and NiOOH back to Ni(OH)₂, as evident in Fig. 5.

The FTIR results in Fig. 6 revealed that the new MnO₂ cathode gave absorption bands at 652 cm⁻¹ assigned to Mn-O stretching of the MnO₂. The bands around 1206 and 1147 cm⁻¹ were assigned to the existence of C-O epoxy and C-O alkoxy group. And after MnO₂ were tested for 100 cycles at 10% and 80%DOD, it was found that the bands near 1369 and 1607 cm⁻¹ were attributed to vibrations of C-C aromatics and C-O carboxy groups, and there appeared a peak at 3256 cm⁻¹ which was assigned to the symmetric stretching vibrational mode of hydroxyl groups. Fig. 7 shows the FTIR spectra for the new Ni(OH)₂ cathode and Ni(OH)₂ cathode after 100 cycles at 10% and 80%DOD. It was found that the bands were attributed to vibrations of C-C aromatics, C-O carboxy groups, and OH groups.

After efficiency testing, D-band peaks were detected at 1360, 1369 cm⁻¹ which was the structure of graphite with various crystalline patterns. D band should be observed after the electrochemical reduction of oxidized graphite. This appearance comes from the amorphous character of graphite, for a large distortion of the aromatic rings in amorphous carbon. And the G band is located at 1629, 1633 cm⁻¹, which is close to the value of graphite and confirms
Fig. 5 Surface XRD of (A) fresh Ni(OH)₂ cathode, (B) Ni(OH)₂ cathode after 100 cycles at 10% DOD and (C) Ni(OH)₂ cathode after 100 cycles at 80% DOD.

Fig. 6 FTIR spectrum of (A) new MnO₂ cathode, (B) MnO₂ cathode after 100 cycles at 10% DOD and (C) MnO₂ cathode after 100 cycles at 80% DOD.

Fig. 7 FTIR spectrum of (A) new Ni(OH)₂ cathode, (B) Ni(OH)₂ cathode after 100 cycles at 10% DOD and (C) Ni(OH)₂ cathode after 100 cycles at 80% DOD.
Fig. 8 SEM image of dendrite sprouting of zinc anode after tested cycling for 100 times. (A) fresh Zn anode, (B) Zn-MnO₂ cathode with 10% DOD, (C) Zn- MnO₂ cathode with 20% DOD, (D) Zn-MnO₂ cathode with 40% DOD, (E) Zn-MnO₂ cathode with 80% DOD, (F) Zn- Ni(OH)₂ cathode with 10% DOD, (G) Zn-Ni(OH)₂ cathode with 20% DOD, (H) Zn- Ni(OH)₂ cathode with 40% DOD and (I) Zn-Ni(OH)₂ cathode with 80% DOD
the reduction of MnO₂ and Ni(OH)₂ during the discharge. Failure of the battery cell with two phenomena: the Zn dendrite leading to short-circuit and Zn shape change, causing gradual capacity loss. For the Zn anode after 100 cycles at varied %DOD with MnO₂ cathode and Ni(OH)₂ cathode, when the Zn anode decayed into the electrolyte, Zn ions in the electrolyte would be deposited on the Zn anode when the cell was charged. DOD deteriorated Zn anode and cause of Zn shape change. The formation of anode might be growing up and may contact the cathode, Zn dendrite leading to short-circuit and Zn shape change, causing gradual capacity loss. For the Zn anode after 100 cycles with MnO₂ cathode and Ni(OH)₂ cathode, when the cell was charged. DOD deteriorated Zn anode and unstable cycling behavior, whereas Ni(OH)₂ can be discharged at higher discharge depths. Therefore, Ni(OH)₂ cathode is a good candidate for cathode electrode and suitable for use with the Zn anode because Ni(OH)₂ cathode are mechanically stable. Even though the battery tested in this study gave high efficiency at high DOD, it was not without a drawback. Branching of Zn during cell charging can pose a problem of a short circuit. This problem warrants some further investigation.

4. Conclusion

The important key to battery efficiency is the electrodes of the cell. The efficiency of the battery cell, which uses Zn-Ni(OH)₂ at the same %DOD, gave higher efficiency around 99.08% and more stability than Zn-MnO₂ because of the reversibility between Ni(OH)₂ and NiOOH. On the other hand, MnO₂, after the decay, is not reversible and then the circuit would be shortened. The formation of Zn dendrites at anodes had seriously caused the decrease of cycling life and charging capacity. The Zn battery was the limited lifetime of a cell by zinc anode problem, so it is necessary to inhibit dendrite growth.

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