

Hydrothermal synthesis of $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot 5\text{H}_2\text{O}$ and its application as anode material for nickel/ zinc batteries^①

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Abstract: The anode material $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot 5\text{H}_2\text{O}$ for nickel/ zinc batteries was synthesized by hydrothermal method and was identified by XRD techniques. TG/ DAT measurements reveal that the products lose lattice water at 145 °C and decompose to $3\text{ZnO} \cdot \text{ZnSO}_4$ at 274 °C. Cyclic voltammetry and recharging/ discharging results show that CV curves have good symmetry, the ratio of oxidation area to reduction area for each curve is about 1, and the peak potential E_{pa} and E_{pc} have little change with the scanning rate. At 50th circle, more than 65% of theoretical capacity is obtained while at the same condition, zinc oxide electrode only remains 35% of theoretical capacity.

Key words: $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot 5\text{H}_2\text{O}$; nickel/ zinc battery anode material; hydrothermal synthesis

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1 INTRODUCTION

Nickel/ zinc battery has superior performance to both lead/ acid and nickel/ iron batteries. The reported specific energies are usually $55 - 75 \text{ W} \cdot \text{h} \cdot \text{kg}^{-1}$, the overall charge/ discharge energy efficiency is good ($> 70\%$) and the battery has excellent low-temperature performance (a $150 \text{ A} \cdot \text{h}$ cell discharged at -18°C delivers 80% of the energy available at 25°C)^[1]. This compares with only 50% for lead/ acid batteries, therefore, the nickel/ zinc battery is very attractive for electric vehicle applications^[2, 3].

The main problem is its limited cycle life. Development is slow because of the large solubility of the zinc electrode discharge products. The development efforts on nickel/ zinc batteries have been focused on solving the problems due to the large solubility of ZnO in the electrolyte and the disparity in charging efficiencies between the nickel and the zinc electrodes. Research on development of solid polymer electrolyte have also processed^[4-9], although no practical solid polymer is available.

The equilibrium solubility of ZnO in KOH depends on the KOH concentration and increases from 6 g/ L in 10% KOH to 53 g/ L in 30% KOH . One approach minimizing the problems of the zinc electrode is to reformulate the electrode or electrolyte composition so as to reduce the ZnO solubility either by incorporating $\text{Ca}(\text{OH})_2$ in the zinc electrodes or by use of electrolytes with minimal hydroxyl content containing highly soluble salts such as phosphate, borate, car-

bonate or fluoride^[1, 10-13]. These previous work show that anion groups such as PO_4^{3-} , CO_3^{2-} , BO_3^{3-} play an active role to the zinc oxide electrode stability.

In this study, however instead of studying the role of electrolyte composition such as PO_4^{3-} , CO_3^{2-} and BO_3^{3-} , a new candidate for anode material $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot 5\text{H}_2\text{O}$ for zinc-nickel battery will be synthesized and investigated, which has not been reported yet. This material is synthesized by hydrothermal method, and its characterization are detected by TG/ DTA and XRD techniques, cyclic voltammetry and recharging/ discharging techniques are also employed to study its electrochemical properties.

2 EXPERIMENTAL

$\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot x\text{H}_2\text{O}$ was prepared as follows: 100 mL 0.4 mol/ L $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ aqueous solution was mixed with 100 mL 0.6 mol/ L NaOH , then the mixed solution was transferred to a stainless steel air proofed hydrothermal reactor (150 mL), treated at 120°C for 2 d, naturally cooled to room temperature. The product was washed with distilled water and 95% alcohol, and dried subsequently at 90°C for 2 - 3 h.

The characterization was carried out by X-ray diffractometry (D/ Max-rB, $\text{CuK}\alpha$, 40 kV, 110 mA), and thermogravimetry/ differential thermal analysis (TG/ DTA, DUPOND 9900, heating rate $10^\circ\text{C}/\text{min}$, in air) were used for analyzing the characterization of the product.

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Copper foam substrate with dimension of 20.0 mm × 20.0 mm × 1.6 mm and porosity of 95% was prepared. Then 5% (mass fraction) PTFE dispersion were added and 10% wetting material were mixed. The pasty mixture was incorporated into the above-mentioned substrate using a spatula, then dried at 80 °C and rolled to a thickness of 0.5 mm. The thin layer of negative material weighted about 0.1 g. The as-prepared zinc electrodes were activated for three cycles prior to the electrochemical measurements. The activation, charge/discharge at different rates and cycle life tests were conducted in a tri-electrode system by an automatic cycler (IX DC-5) controlled by a microcomputer. Cyclic voltammeter (CHR600B) was used to measure the CV curves. The electrochemical measurements were conducted by an imitating cell. The zinc electrode under test was used as working electrode. The counter electrode was $\alpha\text{-NiOOH}$ electrode with excess capacity. The electrolyte was 4 mol/L KOH + 1.0 mol/L K_2SO_4 aqueous solution. An Hg/HgO electrode with the same alkaline solution was employed as the reference electrode.

3 RESULTS AND DISCUSSION

3.1 X-ray diffraction pattern and TG and DTA analysis

Fig. 1 shows that the XRD pattern of the product is identical with that of $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot 5\text{H}_2\text{O}$ (JCPDS No. 39-688). Those peaks marked with asterisk are those of ZnO. This demonstrates that in the hydrothermal synthesis process, some $\text{Zn}(\text{OH})_2$ decompose before $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot 5\text{H}_2\text{O}$ was synthesized. It can be deduced from the diffraction intensity that the amount of ZnO in the product is very small.

The TG and DTA curves of the product are shown in Fig. 2. The slow loss of mass and endothermal process from 80 °C to 145 °C are caused by the volatilization of adsorbed water. From 145 °C to 186 °C, the slow loss of mass and endotherm may be attributed to the dehydration of lattice water, and the mass loss value of about 15.9% obtained from experiment is close to the theoretical value of 16.4%. However, above 274 °C, where there is a sharp decrease on the TG curve and DTA curve, the sharp mass loss of about 11.0% which is close to the theoretical value of 11.8% is caused by inner molecule dehydration, i.e., the decomposition of $\text{Zn}_4\text{SO}_4(\text{OH})_6$ to $3\text{ZnO} \cdot \text{ZnSO}_4$.

3.2 Cyclic voltammetry and capacity decay at different charging and discharging rate

Fig. 3 gives the typical cyclic voltammograms at different scanning rates. The electrode reaction current peaks occurred at -1.465 V and -1.225 V can

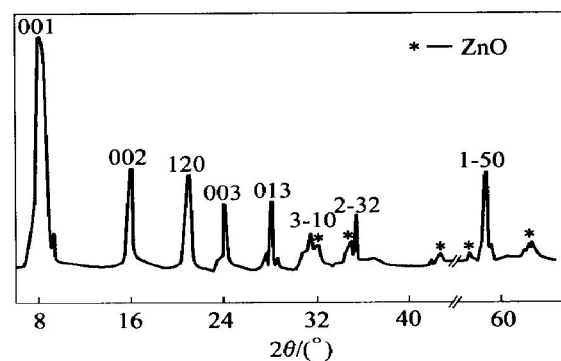


Fig. 1 X-ray diffraction pattern of product

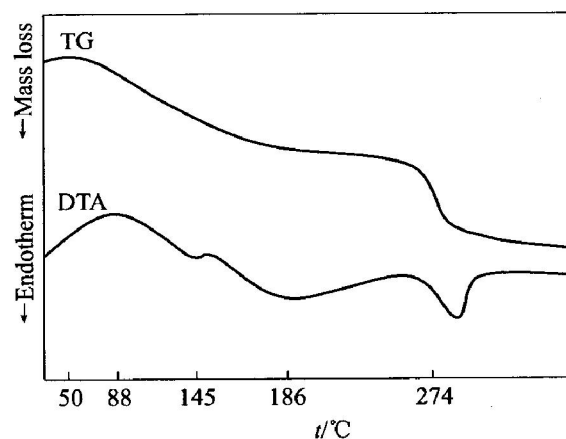


Fig. 2 TG and DTA curves of product $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot 5\text{H}_2\text{O}$

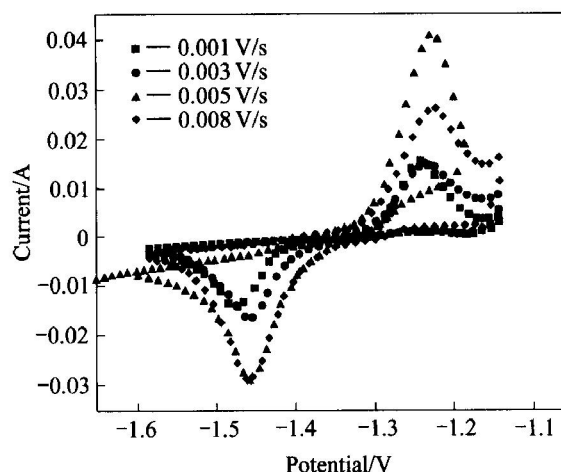
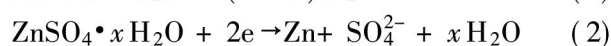
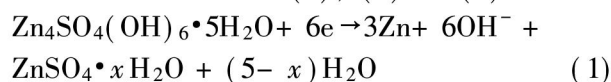


Fig. 3 Typical cyclic voltammograms at different scanning rates

be contributed to reactions (1), (2) and (3):



Notice that the current peaks I_p increase with the change of scanning rates from 0.001 to 0.008 $\text{V} \cdot \text{s}^{-1}$, and this tendency enhances with the increase of scanning rate, and the peak potential values have no

remarkable change. It is also found that CV curves have good symmetry, the ratio of oxidation area to reduction area for each CV curve is close to 1, and $I_{Pa}/I_{Pc} \approx 1$, $\Delta E_p \approx 220$ mV are calculated from Fig. 3. Here ΔE_p is obviously higher just for the supposed voltage hysteresis effect. These results show that the studied electrode has good reversibility and good electrochemical activity.

Fig. 4 gives the cycling behavior of the product at different charging and discharging rates. The theoretical capacity of the product is about $340 \text{ mA} \cdot \text{h/g}$ calculated by the amount of $\text{Zn}(\text{OH})_2$ contained in the product. Compared with curve 3 (the charging and discharging curve of the zinc oxide at the same condition), at 50th circle, the capacity of 75% of theoretical value at 0.2C and 65% at 1C are available, while the ZnO electrode only gives 35% of the theoretical capacity at 1C, which shows that the studied material has good stability in the charging and discharging process. Considering that PO_4^{3-} , CO_3^{2-} , BO_3^{3-} and F^- in electrolyte, as reported in Refs. [1, 11–13], play an active role to the zinc oxide electrode stability, it is reasonable to think that SO_4^{2-} in $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot 5\text{H}_2\text{O}$ has positive role in the charging and discharging process for its stability. It is suggested that the product may has lower solubility compared with zinc oxide or zinc hydroxide in alkaline solution, however, our experiment results show that the fresh product can also be easily dissolved, but after heat treatment under 300°C for several hours, the dehydrated $3\text{ZnO} \cdot \text{ZnSO}$ has good stability in potassium hydroxide solution but poor electrochemical properties. Therefore, a new composite compound either with a composition of $3\text{ZnO} \cdot \text{ZnSO} \cdot x\text{H}_2\text{O}$ or $3\text{Zn}(\text{OH})_2 \cdot \text{ZnSO} \cdot x\text{H}_2\text{O}$ may occur during the charging and discharging process. Further investigation on the electrochemical process of the electrode will be reported in future.

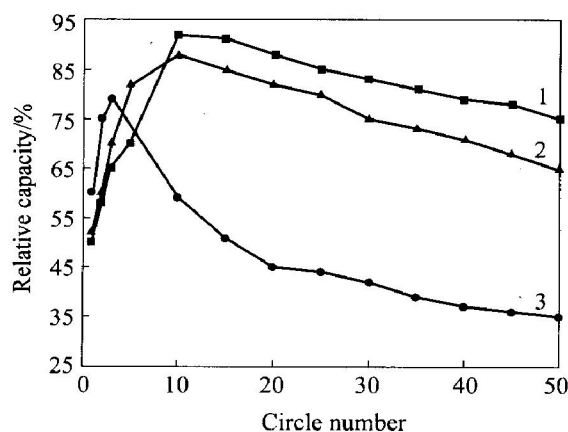


Fig. 4 Capacity decay at different charging and discharging rates
1— $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot 5\text{H}_2\text{O}$, 0.2C rate;
2— $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot 5\text{H}_2\text{O}$, 1C rate; 3— ZnO , 1C rate

4 CONCLUSIONS

The anode material of $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot 5\text{H}_2\text{O}$ for nickel-zinc batteries can be synthesized by hydrothermal method at 120°C for 48 h. The products lose lattice water at 145°C and dehydrate at 274°C and decompose to $3\text{ZnO} \cdot \text{ZnSO}_4$. This material has good electrochemical activity, reversibility and stability. The capacity of 65% of theoretical value is available at 50th circle, while the ZnO electrode only gives 35% of the theoretical capacity at 1C rate.

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