

Short communication

Effect of ZnO nanomaterials associated with $\text{Ca}(\text{OH})_2$ as anode material for Ni–Zn batteries

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Abstract

Prism ZnO nanomaterials coated with $\text{Ca}(\text{OH})_2$ were prepared by direct precipitation. TEM micrographs showed that dendritic $\text{Ca}(\text{OH})_2$ seemed to attach on the surface of nanosized ZnO. The XRD patterns indicated that the coating was $\text{Ca}(\text{OH})_2 \cdot 2\text{Zn}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$. The nanosized ZnO coated with $\text{Ca}(\text{OH})_2$ as the anode materials were investigated by the charge–discharge cycle measurement and EIS. The combination of ZnO nanomaterials and $\text{Ca}(\text{OH})_2$ prevented the discharge product ZnO from dissolving in the electrolyte. Therefore, the $\text{Ca}(\text{OH})_2$ -coated ZnO nanomaterials exhibited higher electrochemical activity than the pure nanosized ZnO, including high the discharge capacity and discharge middle voltage, low the charge middle charge voltage. Although $\text{Ca}(\text{OH})_2$ resulted in more difficult activation, EIS showed that the charge-transfer resistance was lower than that of the pure ZnO nanomaterials.

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1. Introduction

The secondary zinc batteries have advantages of high specific energy, high specific power and low cost. Nevertheless, the secondary zinc batteries are usually limited in widespread commercialization by poor cycling characteristics, which mainly resulted from the high solubility of discharge products of zinc electrode in alkaline electrolyte. Approaches reducing the problems include the use of additives in either the anode [1–3] or the electrolyte [4,5], so that there are very few discharge products available in the electrolyte. These additives include alkaline earth metal hydroxides, halides, sulfates and titanates. The addition of calcium hydroxide to the zinc electrode decreases zincate concentration and increases the life of secondary zinc batteries [6,7]. The reason is that calcium hydroxide reacts with the discharge product ZnO to give a compound calcium zincate with the molecular structure of $\text{Ca}(\text{OH})_2 \cdot 2\text{Zn}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ [7,8].

The formation and decomposition kinetic of calcium zincate have been investigated [9,10], and the physico-chemical properties of calcium zincate have been reported [11]. The utilization way of $\text{Ca}(\text{OH})_2$ is mainly mechanical mixture, but the

utilization ratio of mechanical mixture is relatively low. Calcium zincate as the anodic active material has been also investigated [12]. However, the specific capacity of calcium zincate is just 346 mA h g^{-1} , only about 52.5% of specific capacity of ZnO. The utilization of $\text{Ca}(\text{OH})_2$ should preserve the advantages of $\text{Ca}(\text{OH})_2$, not decreasing specific capacity of zinc electrode at the same time. Therefore, ZnO coated with $\text{Ca}(\text{OH})_2$ was prepared and investigated in the present work.

2. Experimental

2.1. Preparation and characterization of $\text{Ca}(\text{OH})_2$ -coated ZnO

For coating $\text{Ca}(\text{OH})_2$ on ZnO surface, nanosized ZnO powders were added into 150 ml of 0.11 M KOH solution and then stirred at room temperature. One hundred millilitres of 0.3 M CaCl_2 was added dropwise to the resulting solution. High purity argon was used as shielded atmosphere to prevent $\text{Ca}(\text{OH})_2$ from changing to CaCO_3 by CO_2 of air. After coating, ZnO powders were dried under vacuum at 90°C for 5 h. The morphology and composition of as-prepared $\text{Ca}(\text{OH})_2$ -coated ZnO powders were characterized with a transmission electron microscope (TEM, JEM-200CX) and powder X-ray diffraction (XRD, Model D/MAX-RA).

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2.2. Electrochemical tests

The electrochemical behavior of Ca(OH)_2 -coated ZnO was examined by two electrode test cells consisted of a Ni(OH)_2 cathode, ZnO anode and separator. A certain amount of as-prepared Ca(OH)_2 -coated ZnO and the binder (PTFE) were mixed thoroughly. The mixture obtained was incorporated into a foam nickel substrate ($2\text{ cm} \times 2\text{ cm}$). Afterwards, the pasted zinc electrodes were pressed to a thickness of 0.4 mm. The ratio of the capacity of the cathode and anode was about 3:1. A solution of 4 M KOH and 17 g l^{-1} ZnO, was used as the electrolyte. For comparison, the electrodes with pure nanosized ZnO and the physical mixture of nanosized ZnO and 10 wt.% Ca(OH)_2 were also fabricated.

The charge–discharge cycle tests of the cells were performed using a DC-5 battery-testing apparatus at room temperature ($25 \pm 2^\circ\text{C}$). The cells were circularly charged at 0.2 C (15 mA) for 5.5 h, and then discharged at 0.2 C down to 1.2 V cut-off.

Electrochemical impedance spectroscopy (EIS) measurements were performed on a CHI 640B type electrochemical system (Shanghai). The frequency range applied was between 0.01 Hz and 100 KHz and the amplitude of AC single was 5 mV. A three electrode cell assembly was used with a Hg/HgO electrode as reference, a Ni(OH)_2 electrode as counter-electrode and a pasted zinc electrode as working electrode. The electrolyte was ZnO-saturated 6 M KOH solution.

3. Results and discussion

Fig. 1 shows TEM micrographs of (a) nanosized ZnO and (b) Ca(OH)_2 -coated ZnO particles, respectively. The nanosized ZnO powders were well-crystallized hexagonal prism, and the particle sizes were about 100–300 nm, as shown in Fig. 1(a). From Fig. 1(b), it could be clearly observed that the nanosized ZnO particles were successfully coated with Ca(OH)_2 layer. The coating was dendrites attached on the ZnO particles. Fig. 2 shows the XRD pattern of Ca(OH)_2 -coated ZnO powders. The presence of $\text{Ca(OH)}_2 \cdot 2\text{Zn(OH)}_2 \cdot 2\text{H}_2\text{O}$ is detected in the pattern. Since ZnO was amphoteric oxide, ZnO reacted with Ca(OH)_2 and changed to $\text{Ca(OH)}_2 \cdot 2\text{Zn(OH)}_2 \cdot 2\text{H}_2\text{O}$, which conducted to decreasing the loss of active material ZnO during the wetting process of the electrodes. On discharging, $\text{Ca(OH)}_2 \cdot 2\text{Zn(OH)}_2 \cdot 2\text{H}_2\text{O}$ lost Zn(OH)_2 and transformed to Ca(OH)_2 [12]. That was to say, the coating repeatedly transformed between Ca(OH)_2 and $\text{Ca(OH)}_2 \cdot 2\text{Zn(OH)}_2 \cdot 2\text{H}_2\text{O}$ during the charge–discharge cycling process.

The electrochemical cycle behaviors of the pasted zinc electrode for nanosized ZnO, the physical mixture of nanosized ZnO and Ca(OH)_2 (10 wt.% ZnO), and the Ca(OH)_2 -coated ZnO in 6 M KOH + 17 g l^{-1} ZnO are illustrated in Fig. 3. At the beginning of cycling, the nanosized ZnO showed the highest rate capacity. However, the electrochemical performance of nanosized ZnO decayed rapidly. The rate capacity at 20th cycle decreased to about 46% of that at the 1st cycle. Due to the high solubility of ZnO in KOH electrolyte, the discharge product of Zn electrode would dissolve into the electrolyte and formed a high content of zincate in the electrolyte, which led to

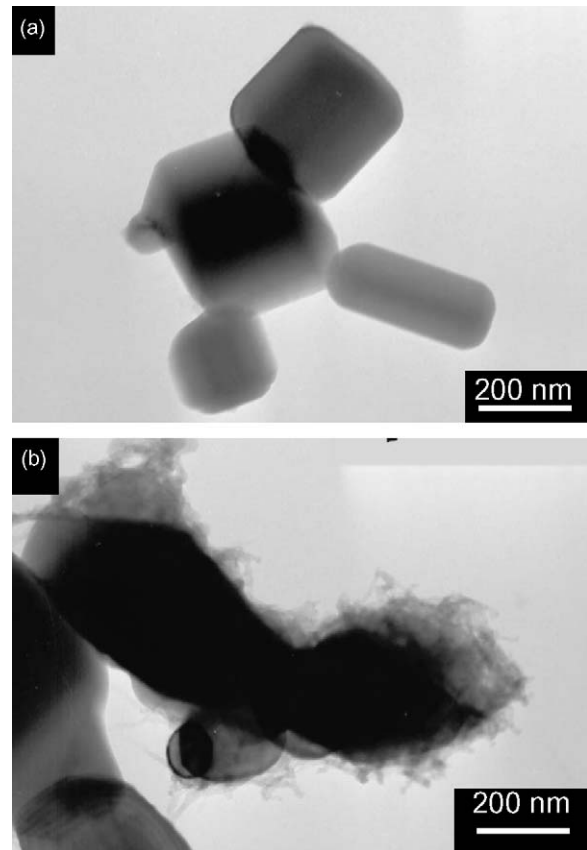


Fig. 1. The morphology of (a) nanosized ZnO and (b) Ca(OH)_2 -coated nanosized ZnO.

serious shape change, densification and dendrite growth during cycling. Thereby, the nanosized ZnO showed relatively poor electrochemical performance. As compared with that of the nanosized ZnO, the electrochemical performance of the mixture of nanosized ZnO and Ca(OH)_2 , Ca(OH)_2 -coated ZnO gradually increased and surpassed that of pure nanosized ZnO at 12th cycle, which should result from difficult activation caused by Ca(OH)_2 . The Ca(OH)_2 coating on the surface of ZnO resulted

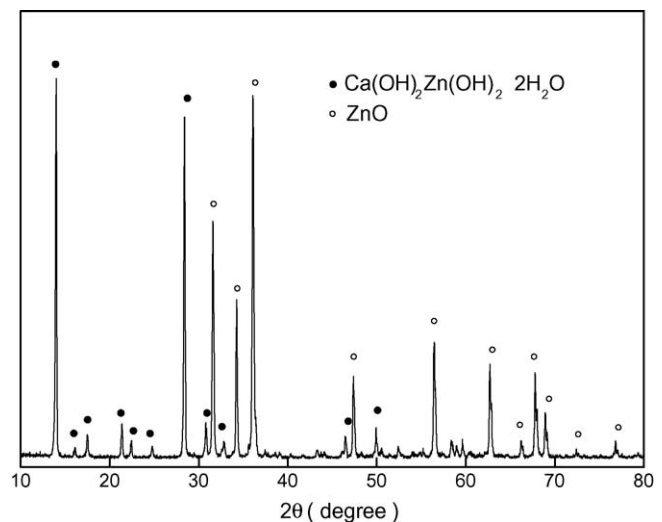


Fig. 2. The XRD diffractogram of Ca(OH)_2 -coated ZnO.

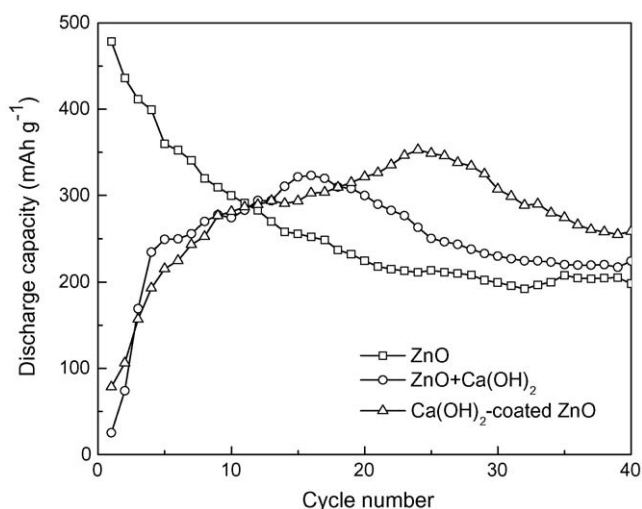


Fig. 3. The electrochemical cycle behavior of various electrodes.

in more difficult activation than the physical mixture of ZnO and Ca(OH)_2 . Therefore, the electrochemical performance of Ca(OH)_2 -coated ZnO delayed in comparison with that of mixture of ZnO and Ca(OH)_2 . However, the electrode of Ca(OH)_2 -coated ZnO had the largest discharge capacity among all the cells tested after the 18th cycle, which could result from that more active materials were retained by the coating and the coating excelled the physical mixture. The charge and discharge curves of Zn electrodes tested at 15th cycle are shown in Fig. 4. The nanosized ZnO after coating and addition of Ca(OH)_2 compared favorably with pure nanosized ZnO in terms of charge plateau voltage, discharge plateau voltage and discharge capacity.

Fig. 5 presents the impedance diagrams for Zn electrodes with the nanosized ZnO, the physical mixture of nanosized ZnO and Ca(OH)_2 (10 wt.% ZnO), and the Ca(OH)_2 -coated ZnO after 40 cycles. All experimental plots included a high-frequency capacitive semicircular loop and a low-frequency straight line. The

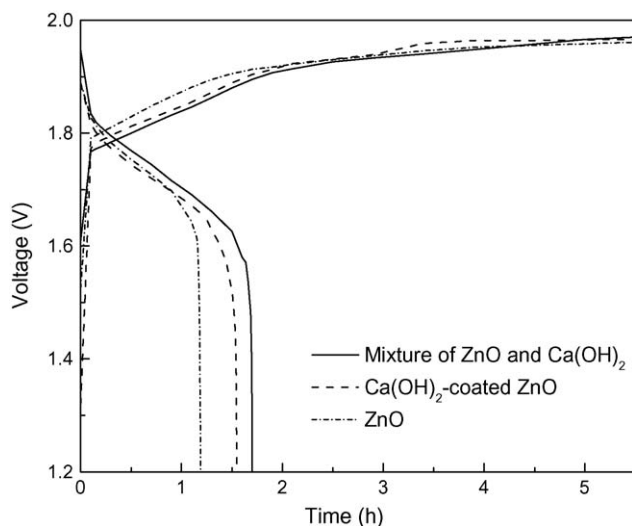


Fig. 4. Constant-current charge and discharge curves of various electrodes.

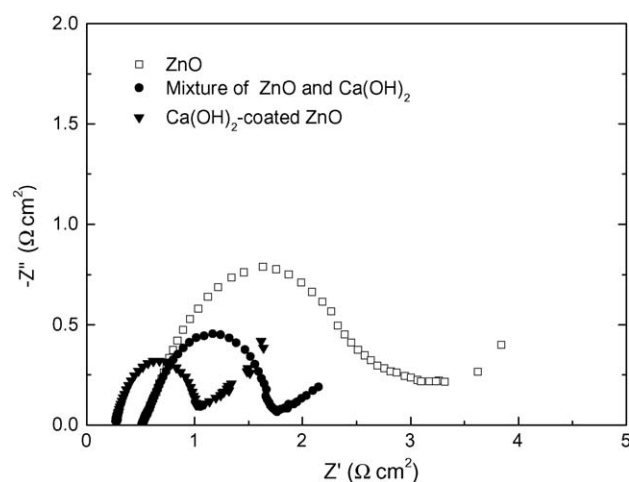


Fig. 5. EIS Nyquist plots for various anodes after 40 cycles.

high-frequency capacitive semicircular loop can be considered as due to the charge-transfer resistance in parallel with the double layer capacitance. The equivalent circuit (EC) is presented in Fig. 6. R_s represents the solution resistance, R_t represents the charge-transfer resistance and C_{dl} represents the electrochemical double layer capacitance. R_a and C_a are the equivalent components corresponding with the covering degree of ZnO. W represents the Warburg impedance. A large charge-transfer resistance indicated that the electrochemical reaction was more difficult and led to an increase in electrochemical polarization of Zn electrodes and a decrease in the utilization of active material. The radius of high-frequency capacitive loop decreased by addition of Ca(OH)_2 , as compared with that of pure nanosized ZnO. The nanosized ZnO after coated show the smallest loop radius. This indicated that addition of Ca(OH)_2 and coating of Ca(OH)_2 conducted to decreasing the charge-transfer resistance and increasing the utilization of active material. Ca(OH)_2 trapped discharge product ZnO and prevented ZnO from entering into the electrolyte. Therefore, the shape change and densification of Zn electrode were alleviated. The activity of ZnO was retained and the electrochemical performance was also enhanced. The low-frequency straight line generally resulted from transport properties within porous electrodes. The slope of low-frequency straight line is less than $\pi/4$. According to Cao's theory [13], the reason is that the plain electrode has a rough surface so that its diffusion characteristic is more similar to that of spherical electrode.

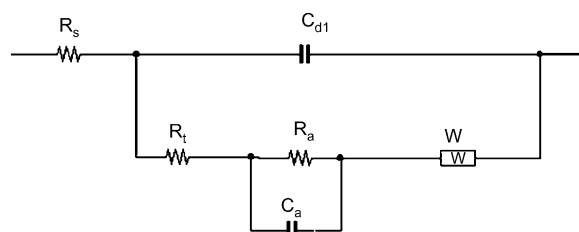


Fig. 6. Equivalent circuit model for electrochemical impedance measurements.

4. Conclusion

The addition of $\text{Ca}(\text{OH})_2$ decreased the loss of active materials and increased the discharge capacity. The discharge capacity of nanosized ZnO was improved after the coating of $\text{Ca}(\text{OH})_2$, as compared with the pure ZnO, and the physical mixture of ZnO and $\text{Ca}(\text{OH})_2$. The EIS of Zn electrodes with $\text{Ca}(\text{OH})_2$ -coated ZnO show the smallest high-frequency capacitive semicircular loop radius, which indicated that the coating did not remarkably decrease the charge-transfer resistance. Therefore, the coating of $\text{Ca}(\text{OH})_2$ did not decrease the activity of active material.

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