

A study of calcium zincate as negative electrode materials for secondary batteries

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Abstract

The properties of calcium zincate as negative electrode materials for secondary batteries were examined by powder microelectrode, cyclic voltammetry, charge–discharge cycle measurements and X-ray diffraction (XRD) analysis. The results show that the cycleability of calcium zincate is obviously superior to that of ZnO and that of the mixture of ZnO and Ca(OH)₂ (the molar ratio of Zn:Ca = 2:1). Calcium zincate forms zinc metal during the charging and exhibits an initial discharge capacity 230 mAh g⁻¹. With the discharge cut-off voltage of 1.0 V, the discharge capacity of the experimental Zn/NiOOH cell does not decay much during 500 cycles, exhibiting good prospect for practical use. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Calcium zincate; Secondary battery; Negative electrode materials

1. Introduction

Due to its low equilibrium potential, good reversibility, low cost, high energy density and low toxicity, zinc has a wide variety of applications as a negative electrode material in batteries. However, during cycling of secondary zinc cell, dendrites formation, shape change, surface passivation and self-discharge of zinc electrode lead to gradual capacity loss, and these problems limit the practical application of zinc in secondary cell greatly. Cairns and co-workers [1–3] have found that the ternary KOH–KF–K₂CO₃ electrolyte can effectively reduce zinc electrode shape change and extend cycle life. Literature [4] listed many materials used as zinc electrode additives, including metal hydroxides, halides, sulfates and titanates. These materials can reduce the zincate concentration, enhance electronic conductivity, provide an improved substrate for zinc electrodeposition and improve electrode wetting. Especially, several researchers [5–8] reported that addition of calcium hydroxide to the secondary zinc electrode can lower the zincate concentration and increase the life of secondary zinc cell. The reason is that calcium hydroxide reacts with the discharge product ZnO to give a compound calcium zincate with the molecular structure of Ca(OH)₂·2Zn(OH)₂·2H₂O [7,8]. Wang [9,10] and Sharma [11] further investigated the formation and

decomposition kinetics of calcium zincate and obtained some related parameters. Meanwhile, Sharma [12] has reported the physico-chemical properties of calcium zincate. In this paper, the properties of calcium zincate as negative electrode materials for secondary batteries are studied by powder microelectrode, cyclic voltammetry, charge–discharge cycle measurements and X-ray diffraction (XRD) technique.

2. Experimental

2.1. Preparation of calcium zincate

Calcium zincate was made by adding calcium hydroxide slowly to the ZnO saturated KOH solution at continuous stirring. The solution was settled for 48 h, and then the liquid was decanted off. The solid product containing mainly the calcium zincate was rinsed with distilled water until the solution pH became about 7. More detailed preparation steps were described in [12].

2.2. Cyclic voltammetry for powder microelectrodes

The cyclic voltammetry of calcium zincate was carried out in a three-electrode system. The working electrode was a powder microelectrode filled with calcium zincate, whose fabrication has been reported in [13]. A large area nickel

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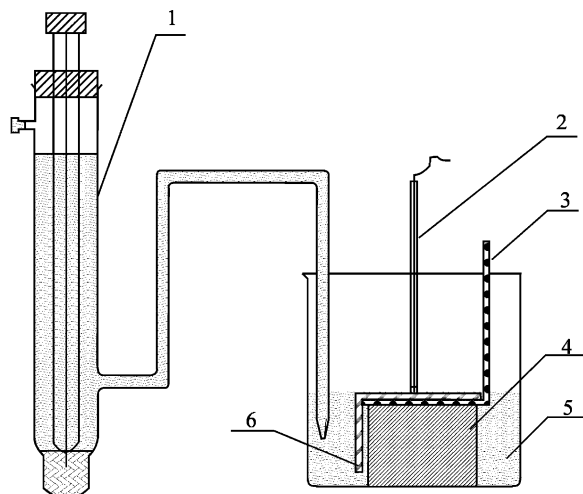


Fig. 1. Schematic of the three-electrode system: (1) HgO/Hg reference electrode; (2) powder microelectrode as working electrode; (3) nickel sheet as counter electrode; (4) Perspex padding; (5) electrolyte; (6) separator.

sheet was used as the counter electrode, and a HgO/Hg electrode was used as the reference electrode. Alkali-resistant nonwoven nylon membrane was used as the separator. Fig. 1 shows the schematic of the three-electrode system.

2.3. Charge–discharge behavior of experimental zinc/nickel oxide cell

The calcium zincate negative electrode was prepared by rolling the electrode paste into a 0.2 mm thick film and then pressing the film onto both sides of screened copper mesh. The negative electrode had a composition of 90% calcium zincate, 8% PTFE and 2% PbO. The experimental cell was made by placing a piece of calcium zincate electrode between two large area sintered NiOOH electrodes. The electrolyte was 4 mol l⁻¹ KOH solution saturated with ZnO. The separator consisted of three layers of polymer

membrane. The two outer layers were alkali-resistant nonwoven nylon membrane, and the inner layer was polythiophene membrane. The experimental zinc/nickel oxide cell was sealed by the use of plastic membrane. The charge–discharge cycle experiments were controlled by a computer.

2.4. X-ray diffraction analysis

Changes in the crystalline structure of the negative electrode during charge–discharge cycling were examined by ex situ XRD analysis. The XRD samples of the negative electrode was prepared by removing the electrodes from the experimental cell and rinsing them with distilled water and then transferring to a desiccator. A D/MAX III B type XRD was performed with a Cu K α source (30 kV, 30 mA).

3. Results and discussion

3.1. Cyclic voltammetry of powder microelectrodes

The cyclic voltammetry of powder microelectrodes for ZnO, the mixture of ZnO and Ca(OH)₂ (the molar ratio of Zn:Ca = 2:1), calcium zincate in the 2 mol l⁻¹ KOH solution is shown in Fig. 2. All of potential sweeps started from -1.2 V, going in the cathodic direction. Because the initial voltage–current curves for powder microelectrode are vibratile, the fifth cycle curve is recorded as the initial result. It can be seen from Fig. 2a that the cathodic and anodic current peaks for powder microelectrode of ZnO are separable. The characteristic current loop between the forward and the reverse direction indicates nucleation and growth of zinc. During the scanning, anodic peak current decays rapidly. The peak current for the 35th cycle has decreased to 30% of that for the fifth cycle. The possible explanation for this phenomenon is that ZnO exhibits a high solubility in KOH solution [9,12]. In Fig. 2b, two cathodic peaks at -1.38 and

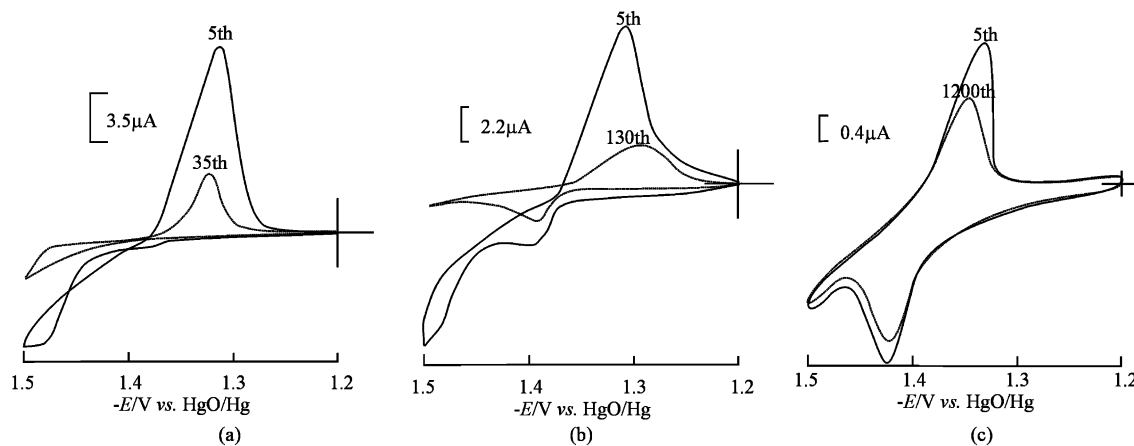


Fig. 2. Cyclic voltammograms of three powder electrodes in the 2 mol l⁻¹ KOH solution with scan rate 50 mV s⁻¹: (a) ZnO; (b) the mixture of ZnO and Ca(OH)₂ (the molar ratio of Zn:Ca = 2:1); and (c) calcium zincate.

–1.50 V were attributed to the reduction of calcium zincate and ZnO, respectively. At the beginning of cycling, the peak current at –1.38 V is less than that at –1.50 V. Owing to the loss of ZnO in KOH solution, the peak current at –1.50 V decreases rapidly and disappears eventually. In contrast, the anodic peak current at –1.38 V decays slowly, and the peak current for the 130th cycle still remains 26% of that for the fifth cycle. This indicates that the cycleability of the mixture is improved significantly compared with that of ZnO. The cyclic voltammetry for calcium zincate is also carried out. It can be seen from Fig. 2c that a single peak exists for both cathodic part and anodic part. Moreover, the peak current for the 1200th cycle changes little compared with that for the fifth cycle. This indicates that calcium zincate exhibits good cycleability. In addition, the cathodic peak potential for calcium zincate is –1.42 V, which is higher than that for ZnO. This suggests that the reduction of calcium zincate is easier than that of ZnO.

3.2. The effect of KOH concentration on the stability of calcium zincate

Fig. 3 shows the cyclic voltammograms for powder electrode of calcium zincate in three KOH concentration solutions. In the solution with 2 mol l⁻¹ KOH, the anodic peak current for the 1200th cycle still remains 93% of that for the 150th cycle. In the 4 mol l⁻¹ KOH solution, the anodic peak current for the 700th cycle decreases to 65% of that for the 150th cycle. When KOH solution increases to 6 mol l⁻¹, the anodic peak current for the 500th cycle rapidly decays to 26% of that for the 150th cycle. The fact indicates that an increase in the concentration of KOH solution leads to a higher capacity loss of calcium zincate. In other words, because calcium zincate is stable only in weak or moderate alkaline solutions [8,9], the decrease in KOH solution concentration helps improve the cyclic stability.

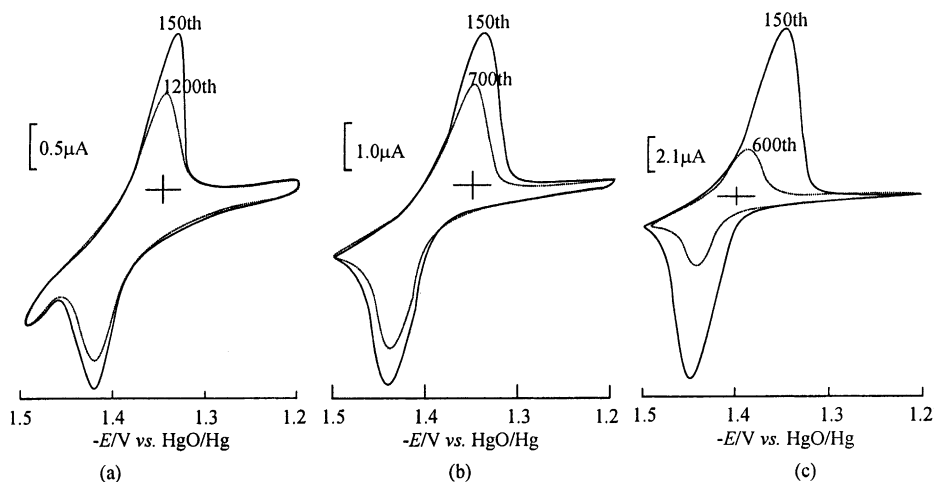


Fig. 3. The cyclic voltammograms for powder microelectrode of calcium zincate in different concentration KOH solutions with scan rate 50 mV s⁻¹: (a) 2 mol l⁻¹ KOH; (b) 4 mol l⁻¹ KOH; and (c) 6 mol l⁻¹ KOH.

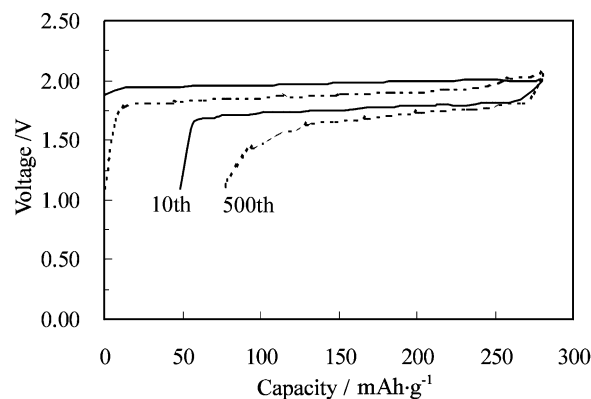


Fig. 4. The voltage–capacity curves for the 10th and 500th cycle of experimental Zn/NiOOH cell with the discharge current density of 70 mA g⁻¹ for negative electrode.

3.3. Charge–discharge behavior of experimental zinc/nickel oxide cell

The cell was charged at the current density of 70 mA g⁻¹ for 240 min, and discharged at the same current density to a cut-off voltage of 1.0 V. The voltage–capacity curves for the 10th and 500th cycle are illustrated in Fig. 4. It can be seen that the discharge capacity of calcium zincate at the 10th cycle is 230 mAh g⁻¹. With the charge–discharge cycling, discharge polarization of the cell increases, and its discharge platform voltage lowers gradually. Fig. 5 shows the plot of discharge percent capacity versus cycle number for the experimental cell, where the capacity percentage is defined as the ratio of the discharge capacity to the average discharge capacity. The waved behavior of cell capacity was mainly resulted in by the variations of room temperature caused by season change. It can be observed that the discharge capacity for the 500th cycle does not decay much compared with that for the 10th cycle. This suggests that calcium zincate as

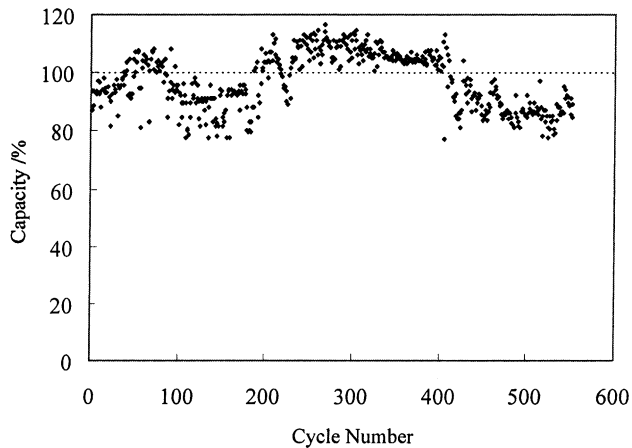


Fig. 5. The plot of capacity versus cycle number for experimental Zn/NiOOH cell with the discharge current density of 70 mA g^{-1} for negative electrode.

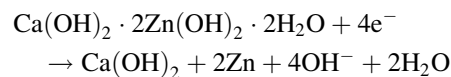
negative electrode materials for secondary battery exhibits good cycleability.

3.4. Chemical changes of calcium zincate during cycling

Two negative electrodes are removed from experimental zinc/nickel oxide cells at the end of charge and discharge state, respectively after 10 cycles. The distinction between

two negative electrodes can be observed by eyes. The former is greyish black which looks like the color of zinc, while the latter is greyish white which looks like the color of calcium zincate. The changes in the crystalline structure of two electrodes are examined by ex situ XRD analysis, and their XRD diffractograms are shown in Fig. 6. By comparing the XRD diffractograms of two electrodes, it can be seen that the characteristic (1 0 1) and (1 0 0) peak intensities of zinc metal in Fig. 7a are higher than those in Fig. 7b. While the characteristic (1 3 $\bar{1}$), (2 0 0) and (1 0 0) peak of calcium zincate in Fig. 7b are higher than those in Fig. 7a. In addition, the characteristic (1 0 1), (1 0 0) and (0 0 2) peak intensities of ZnO are much higher than those for the charge state. Therefore, it can be inferred that the negative electrode at the end of charge state contains zinc and calcium zincate, and the negative electrode at the end of discharge state contains calcium zincate and ZnO.

According to the chemical changes during cycling, the reduction of calcium zincate can be represented by the following equation



From the equation, we can see that neither of Ca(OH)_2 and H_2O is active material, only the Zn(OH)_2 participates the electrochemical reduction to form zinc [10]. As for the

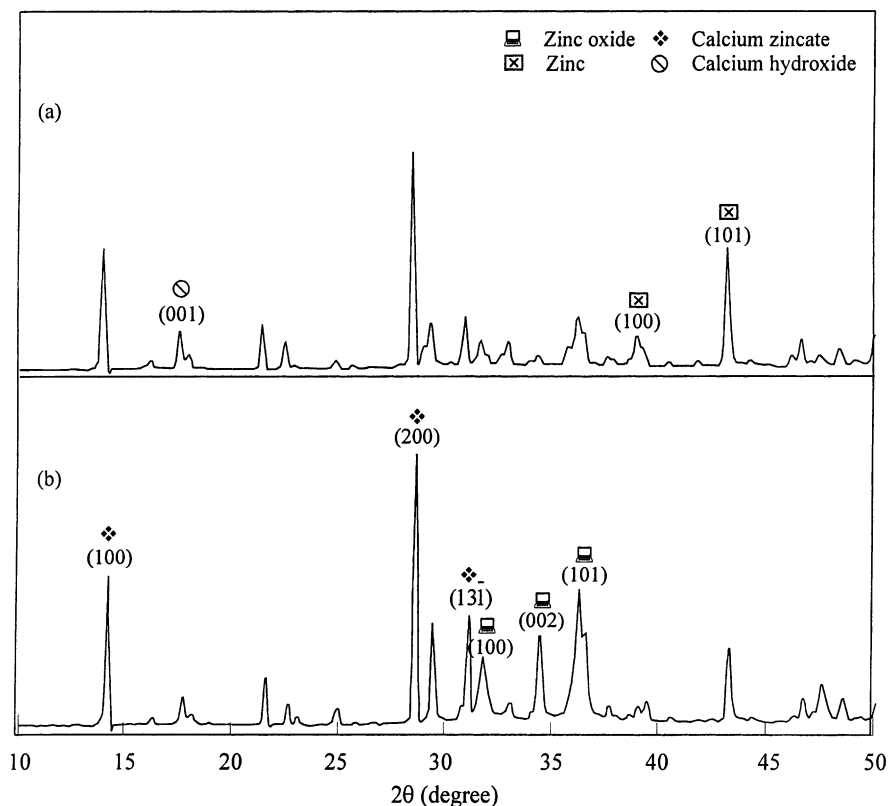


Fig. 6. The XRD diffractograms for calcium zincate anode at different charge–discharge states: (a) the end of charge state; (b) the end of discharge state.

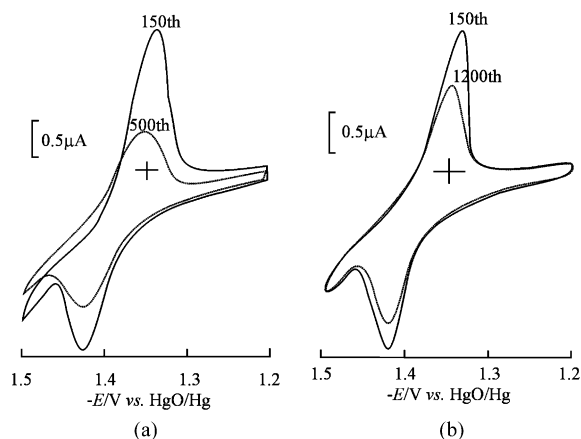


Fig. 7. The effect of settled time in the air on the cyclic voltammograms of calcium zincate with scan rate 50 mV s^{-1} in the solution of 2 mol l^{-1} KOH: (a) calcium zincate settled for 10 days in the air; (b) fresh calcium zincate.

existence of a little amount of ZnO in the negative electrodes at the end of discharge state, the possible explanation is that some ZnO can not promptly react with Ca(OH)_2 forming calcium zincate at the given discharge state. Theoretically, the specific capacity of calcium zincate is only 350 mAh g^{-1} which is less than that of ZnO, but as the cycle life of calcium zincate is extended significantly, calcium zincate still exhibits good prospect for practical use.

3.5. Chemical stability of calcium zincate in the air

In order to investigate the chemical stability of calcium zincate, the cyclic voltammetry of calcium zincate settled for 10 days in the air is carried out. It can be observed from Fig. 7 that the anodic peak current for the settled calcium zincate at the 500th cycle rapidly decreases to 37% of that at the 150th cycle. In contrast, the anodic peak current for fresh calcium zincate at the 1200th cycle still remains 93% of that at the 150th cycle. This suggests that exposure in the air will accelerate the capacity loss of calcium zincate. The reason

for this phenomenon is probably that the calcium zincate reacts with CO_2 in the air forming CaCO_3 .

4. Conclusion

In comparison with ZnO and the zinc/calcium mixture, calcium zincate exhibits the best cycleability in KOH solution. Even though it has a smaller specific capacity than ZnO, it still reveals good prospect for practical use.

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