



## Study of the performance of secondary alkaline pasted zinc electrodes

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### Abstract

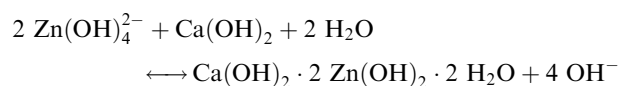
Calcium zincate was prepared by a chemical coprecipitation method and characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The electrochemical performance of pasted zinc electrodes with bismuth and calcium additives was investigated by the charge–discharge method. The addition of metallic bismuth powder improves the discharge performance of zinc electrodes due to the formation of an electronic conduction matrix. The calcium-containing zinc electrodes showed higher discharge capacity, less shape change and longer cycle lifetime. Moreover, zinc electrodes using calcium zincate as active material show better electrochemical performance than those with the physical mixture of zinc oxide and calcium hydroxide.

### 1. Introduction

Zinc is a commonly used battery electrode because of its low equilibrium potential, reversibility, compatibility with aqueous electrolytes, high specific energy and low cost. The use of primary zinc electrode batteries is widespread. However, zinc electrodes have found only limited use in secondary alkaline batteries. The fundamental problem is the short and unpredictable cycle life of the zinc electrode when subjected to charge–discharge cycling [1]. This problem has been traced to shape change and dendrite growth during recharge. Shape change and dendrite growth result from the high solubility of the discharge product (zinc oxide) in the alkaline solution [1].

Many attempts have been made to improve the performance of secondary alkaline zinc electrodes. One approach is to apply additives to the electrodes [2–17]. Bismuth oxide has been found to be beneficial in improving the performance [4–10], and its effect is attributed to a substrate effect. Since bismuth has a more positive electrode potential than zinc, bismuth oxide is reduced to metallic bismuth prior to zinc deposition. Metallic bismuth has high hydrogen evolution overpotential and excellent conductivity; therefore, its addition to the zinc electrode produces beneficial effects on performance. However, very few studies on the addition of metallic bismuth powder in secondary zinc electrodes have been undertaken. Calcium hydroxide has also been found to be an effective electrode additive [10–17]. Calcium hydroxide reacts with zincate

ion to form a crystalline calcium zincate complex  $[\text{Ca}(\text{OH})_2 \cdot 2 \text{Zn}(\text{OH})_2 \cdot 2 \text{H}_2\text{O}]$  upon electrochemical cycling in alkaline solutions [18–21]. The formation and decomposition reaction of calcium zincate can be represented as follows [21]:



During discharge of the zinc electrode, the discharge product, zincate  $[\text{Zn}(\text{OH})_4^{2-}]$ , will react with  $\text{Ca}(\text{OH})_2$  immediately to form calcium zincate. During charge, since calcium zincate is close to the reaction sites, it will provide an ample supply of zincate for the zinc reduction reaction, and the conditions for zinc dendrite formation will not be reached. Furthermore, the solubility of the calcium zincate complex is lower than that of zinc oxide when the KOH concentration is below 34 wt % [20], and this leads to less shape change, less dendrite growth, better capacity retention and longer cycle lifetime of the zinc electrodes.

In previous studies [11, 14, 15], calcium hydroxide was added to zinc oxide by the physical mixture method. However, this could lead to uneven distribution of calcium hydroxide and to a decrease in efficiency of the additive. In the present work, the influences of metallic bismuth powder as an additive and chemically coprecipitated calcium zincate as active material on the performance of secondary alkaline zinc electrodes have been investigated.

## 2. Experimental details

### 2.1. Preparation of chemically coprecipitated calcium zincate complex

Under vigorous stirring, 2.0 M NaOH, 4.5 M NH<sub>4</sub>OH and a mixed solution of Zn(NO<sub>3</sub>)<sub>2</sub> and Ca(NO<sub>3</sub>)<sub>2</sub> with different Zn/Ca ratios were simultaneously added slowly to a well-sealed reaction vessel containing a solution of 1.0 M NaOH and 1.5 M NH<sub>4</sub>OH. The reaction temperature was controlled at 60 ± 1 °C and the pH of the solution was held at 11.1 ± 0.1. After reaction for 8 h, the solution was aged for another 12 h. Then, the reaction precipitate was separated from the solution by filtration, washed several times with hot deionized water and dried at 120 °C. Calcium zincate obtained through the above procedure was in the form of a very fine crystalline powder.

### 2.2. Characterization of chemically coprecipitated calcium zincate crystal

Scanning electron microscopy (SEM) was performed using a S-570 microscope (Hitachi Ltd). The crystal structure of calcium zincate was determined by X-ray diffraction (XRD) analysis using a Philips PC-APD diffractometer with CuK<sub>α</sub> radiation at 40 kV and 30 mA.

### 2.3. Preparation of pasted zinc electrodes

Bismuth-containing pasted zinc electrodes were prepared as follows: 350 mg zinc oxide powder and different quantities of metallic bismuth powder sieved through 500 mesh were thoroughly mixed with a certain amount of 2% PVA solution. The paste obtained was incorporated in a tin-electroplated porous nickel substrate (2 cm × 2 cm) with a spatula. Pasted zinc electrodes were dried at room temperature and then roll-pressed to a thickness of 0.8 mm. The zinc electrode was spot-welded with a tin-electroplated nickel ribbon as current collector.

The preparation of calcium-containing pasted zinc electrodes was similar to that of bismuth-containing zinc electrodes. The compositions of the calcium-containing pasted zinc electrodes are listed in Table 1. The contents of zinc and calcium in the calcium zincate complex were determined by atomic absorption analyses. The content of zinc in the pasted zinc electrode was kept constant and 10 wt % metallic bismuth powder was used as additive.

### 2.4. Charge–discharge cycling test

The electrochemical cell is shown in Figure 1. The cell body was machined from Perspex. The main electrode compartment contained the zinc electrode, the nickel electrode, a separator, the electrolyte and Perspex shims. A sintered nickel hydroxide electrode served as counter

Table 1. Composition of calcium-containing pasted zinc electrodes

Electrode	A	C1	M1	C2	M2
Preparation	/	C	M	C	M
ZnO/mg	220	220*	220	220*	220
Ca(OH) <sub>2</sub> /mg	0	36*	98	98*	116
Ca/Zn/mol	0	0.18	0.49	0.49	0.58
Bi/wt %	10	10	10	10	10
PVA/wt %	≤2	≤2	≤2	≤2	≤2

M: Physical mixture of zinc oxide and calcium hydroxide.

C: Chemically coprecipitated calcium zincate.

\*Contents of zinc and calcium from atomic absorption analyses of calcium zincate powder.

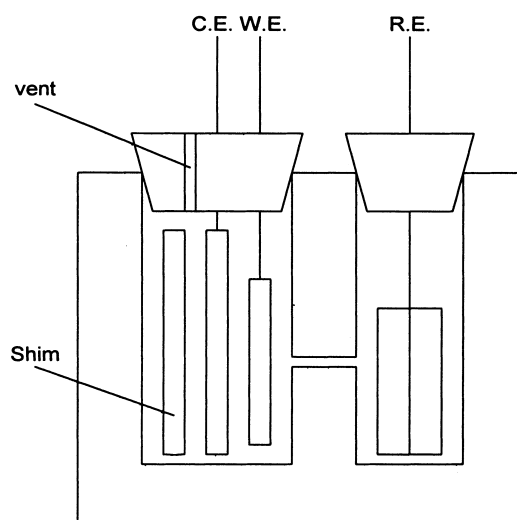


Fig. 1. Electrochemical cell for charge–discharge cycling test.

electrode, and its capacity was far higher than that of the zinc electrodes. The amount of electrolyte in the main electrode compartment was no more than 6 ml. A Hg/HgO electrode served as reference. The reference electrode compartment was connected to the main electrode compartment through a small hole plugged by a porous ceramic. A vent hole was drilled in the rubber cover to exhaust H<sub>2</sub> and O<sub>2</sub>.

The performance of pasted zinc electrodes was tested using a DC-5 cell performance-testing instrument (made in China). The temperature was 25 °C. Pasted zinc electrodes and sintered nickel hydroxide electrodes were wrapped with separator. Bismuth-containing pasted zinc electrodes with 5.3 M KOH solution containing 0.5 M ZnO as electrolyte were charged at a constant current of 34 mA for 6 h and discharged at 68 mA down to –1130 mV cut-off. Calcium-containing pasted zinc electrodes and calcium-free zinc electrodes with 3.52 M KOH solution as electrolyte were charged at 16 mA for 5 h and discharged at 32 mA down to –1130 mV cut-off. After 100 charge–discharge cycles, the cells were disassembled and X-ray photographs (40 kV, 2 mA s) of the electrodes were taken.

In all the above experiments, the reagents used were AR grade and the electrolytes were prepared with deionized water.

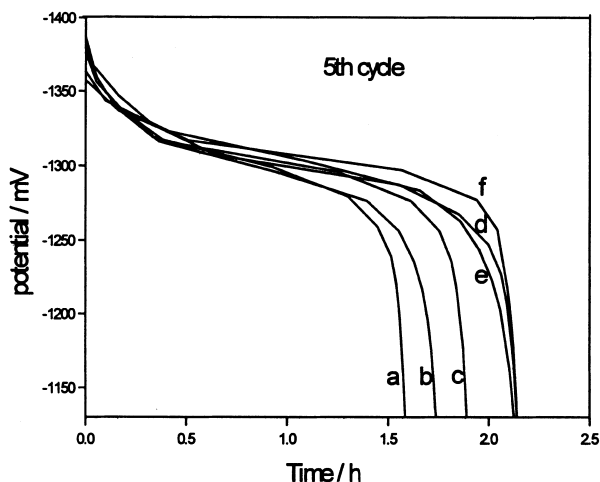


Fig. 2. Discharge curves with various quantities of bismuth powder additive (500 mesh). Electrolyte: 5.3 M KOH + 0.5 M ZnO. Key: (a) without bismuth, (b) 2.5 wt % bismuth, (c) 5 wt % bismuth, (d) 10 wt % bismuth, (e) 20 wt % bismuth, (f) 30 wt % bismuth.

### 3. Results and discussion

#### 3.1. Performance of pasted zinc electrodes with various quantities of metallic bismuth additive

The typical discharge curves of pasted zinc electrodes with various quantities of metallic bismuth additive are shown in Figure 2. The addition of metallic bismuth improves the discharge performance, and their discharge capacities increase with the increase in bismuth content. However, when the bismuth content is more than 10 wt %, the discharge capacity improves little with increase in bismuth content. Therefore, for increasing the specific energy of zinc-based cells, the optimum bismuth content is about 10 wt %.

Zinc oxide has poor electronic conductivity, and this leads to high polarization overpotential and low discharge capacity of the bismuth-free zinc electrode. Metallic bismuth is an excellent electronic conductor, moreover it is not oxidized during normal charge and discharge of zinc electrodes. The function of bismuth

additive is a substrate effect, which provides electronic conduction paths. The addition of metallic bismuth powder improves the electronic conductivity of zinc electrodes and lowers the polarization. Consequently, the discharge performance of pasted zinc electrodes is improved. In addition, since bismuth is a high hydrogen overpotential metal, its addition does not increase the corrosion rate of zinc in alkaline solutions, which is also the reason why metallic bismuth powder is used to replace graphite in zinc electrodes.

#### 3.2. Performance of pasted zinc electrodes with calcium hydroxide additive

Figure 3 shows the plot of discharge capacity against cycle number for pasted zinc electrodes in 3.52 M KOH solution. Electrode C2 with chemically coprecipitated calcium zincate as active material has the highest discharge capacity during all the cycles. Its discharge capacity at the 100th cycle retains above 80% of its original value. Electrode A, with calcium-free zinc oxide as active material, has the lowest discharge capacity throughout the cycles, and it tends towards zero after 20 cycles. Although electrodes M1 and C2 have the same chemical composition, electrode M1 with the physical mixture of zinc oxide and calcium hydroxide has lower discharge capacity than electrode C2. Electrode M2 was obtained by physically mixing zinc oxide with calcium hydroxide at the optimum Ca/Zn molar ratio recommended by [14]. However, it also has lower discharge capacity than electrode C2. Electrode C1, which uses chemically co-precipitated calcium zincate with small Ca/Zn molar ratio as active material, shows low discharge capacity, but it still has higher discharge capacity and longer cycling lifetime than the calcium-free zinc electrode.

The typical discharge curves of pasted zinc electrodes at the third cycle are displayed in Figure 4. The addition of calcium hydroxide leads to more negative discharge plateau potential and higher discharge capacity. The zinc electrode with coprecipitated calcium zincate as

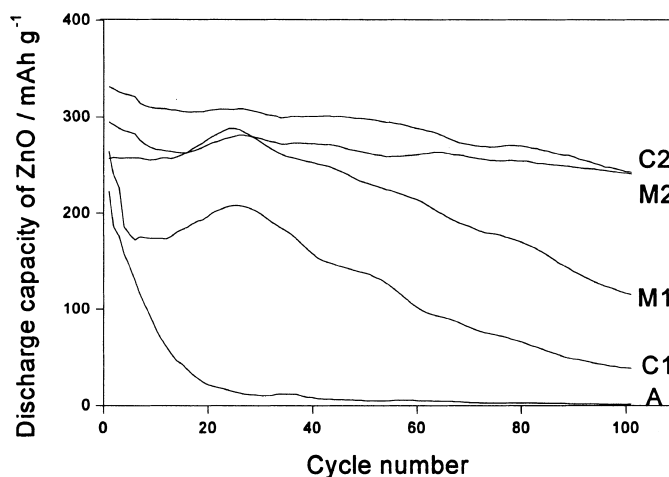


Fig. 3. Plot of discharge capacity against cycle number. Electrolyte 3.52 M KOH.

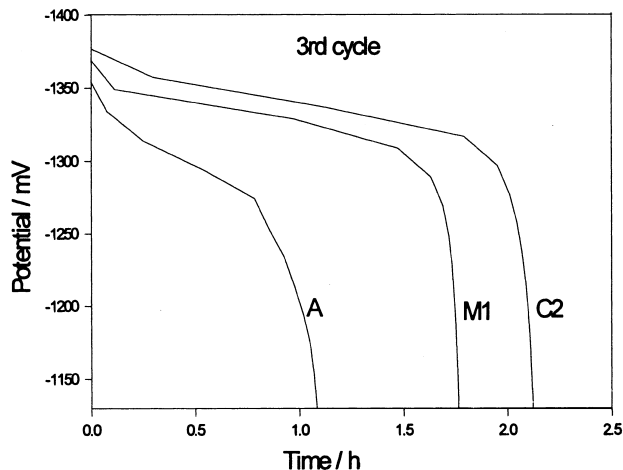


Fig. 4. Typical discharge curves of calcium-containing pasted zinc electrodes and blank pasted zinc electrode. Electrolyte 3.52 M KOH.

active material shows better discharge performance than that with a physical mixture of zinc oxide and calcium hydroxide.

The discharge product (zinc oxide) of calcium-free pasted zinc electrodes dissolves to form high content zincate in the electrolyte, which results in serious shape change and heavy dendrite growth during charge–discharge cycling. Shape change decreases electrode capacity, while dendrite growth leads to short circuits [13, 15, 22]. Therefore, the calcium-free zinc electrode has lower discharge capacity and shorter cycle lifetime. In the presence of calcium hydroxide, zincate ions react with calcium hydroxide to form calcium zincate. Insoluble and immobile calcium hydroxide traps soluble

zincate within its structure, and the discharge product is present as calcium zincate. Since calcium zincate has lower solubility than zinc oxide in alkaline solutions, the zincate concentration in the electrolyte decreases dramatically. Lower zincate concentration leads to less shape change and less dendrite growth [13]. Therefore, calcium-containing pasted zinc electrodes have higher discharge capacity and longer cycle life. Moreover, lower zincate content in the electrolyte also results in more negative discharge potential of zinc electrodes [21, 23]. Chemically coprecipitated calcium zincate has more homogeneous crystalline structure than the physical mixture of zinc oxide and calcium hydroxide. Zinc and calcium are evenly distributed, which enables calcium zincate to be formed more effectively during discharge. This leads to much lower concentration of zincate ion in the electrolyte, much higher discharge capacity and much more negative discharge plateau potential. Therefore, zinc electrodes with chemically coprecipitated calcium zincate as active material show better electrochemical performance than those with the physical mixture of zinc oxide and calcium hydroxide.

Figure 5 shows X-ray radiographs of pasted zinc electrodes after 100 charge–discharge cycles. Dark areas have more active material than the bright areas. The dark areas in the radiographs of electrodes M1, M2, C1 and C2 are larger than that of electrode A, and electrode C2 has the largest dark area. This indicates that the addition of calcium hydroxide decreases shape change and that zinc electrodes containing coprecipitated calcium zincate with high Ca/Zn ratio has the least shape change. The radiograph of electrode C2 shows that active material is uniformly distributed on the electrode substrate. This is

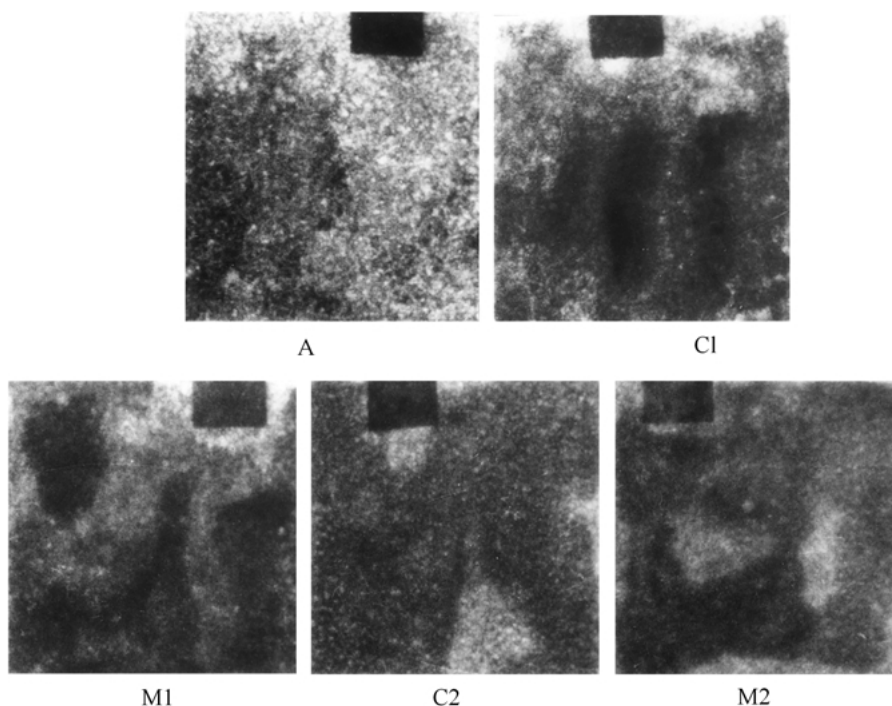


Fig. 5. X-ray radiographs of calcium-containing pasted zinc electrodes and blank pasted zinc electrode after 100 charge–discharge cycles.

beneficial to increased utilization of active material. Radiographs of electrodes M1 and M2 with the physical mixture of zinc oxide and calcium hydroxide show an uneven distribution of active material. These results are in good agreement with the experimental results of the preceding charge/discharge testing.

### 3.3. Characterization of chemically coprecipitated calcium zincate crystal

The above experimental results indicate that zinc electrodes with chemically coprecipitated calcium zincate have better discharge performance and longer cycle life. To obtain a thorough understanding of the properties of chemically coprecipitated calcium zincate crystals, XRD analysis and SEM observation were performed. Figures 6 and 7 show, respectively, XRD pattern and SEM photographs for chemically coprecipitated calcium zincate which served as active material in electrode C2. Table 2 shows the data for the XRD spectrum. Most of the characteristic peaks (e.g.,  $d = 4.1259$ ,  $3.9346$ ,  $3.1229$ ,  $2.8842$ ,  $2.4558$  etc.) belong to the calcium zincate crystal  $[\text{Ca}(\text{OH})_2 \cdot 2 \text{Zn}(\text{OH})_2 \cdot 2 \text{H}_2\text{O}]$  phase [24]. Some peaks of the zinc oxide phase (e.g.,  $d = 2.8169$ ,  $2.6049$ ,  $2.4767$  etc.) also appear [25]. In this sample, calcium zincate is

Table 2. X-ray powder diffraction data for chemically coprecipitated calcium zincate

2 Theta	$d$	Norm. Int.	Int.	Int. width
21.520	4.1259	20	2726	0.270
22.580	3.9346	13	1779	0.300
24.940	3.5673	7	981	0.300
28.560	3.1229	100	13529	0.300
29.380	3.0375	7	905	0.300
30.980	2.8842	27	3654	0.300
31.740	2.8169	23	3093	0.330
32.840	2.7250	8	1103	0.270
32.980	2.7137	8	1147	0.300
34.400	2.6049	10	1325	0.330
35.800	2.5062	8	1040	0.300
36.240	2.4767	20	2761	0.300
36.560	2.4558	10	1404	0.270
46.640	1.9458	8	1111	0.330
50.060	1.8206	11	1459	0.330
54.960	1.6693	6	774	0.420
56.580	1.6253	7	911	0.420
58.500	1.5764	7	916	0.360

the main crystal. SEM photographs in Figure 7 show that chemically coprecipitated calcium zincate crystal has well defined monoclinic form. The crystal is of hexagonal shape and its largest size is about  $125 \mu\text{m}$ .

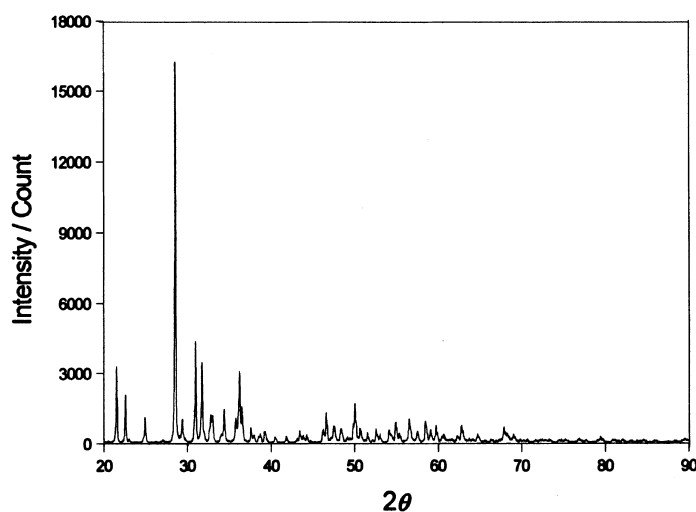


Fig. 6. X-ray powder diffraction pattern for chemically coprecipitated calcium zincate.

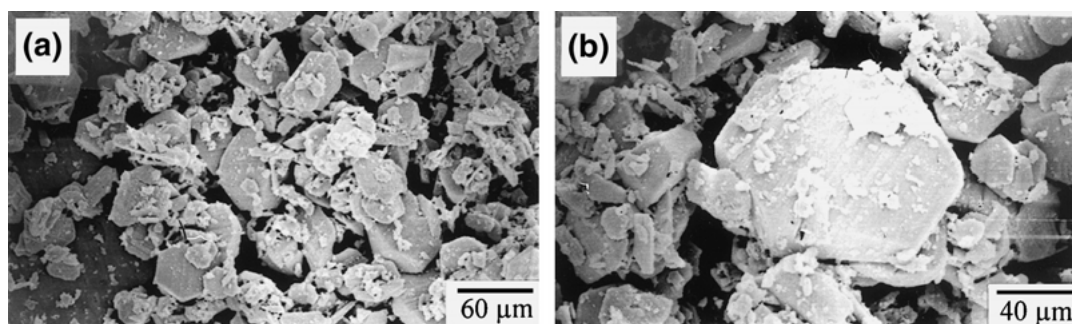


Fig. 7. SEM photographs for chemically coprecipitated calcium zincate crystal.

#### 4. Conclusions

- (i) The addition of metallic bismuth powder in pasted zinc electrodes enhances electronic conductivity, increases active material utilization and improves discharge performance. The optimum quantity of bismuth powder additive in zinc oxide is about 10 wt %.
- (ii) In the presence of calcium hydroxide, the discharge product of zinc electrodes is calcium zincate rather than zinc oxide. Calcium zincate has lower solubility than zinc oxide in 3.52 M KOH solution. The lower solubility of calcium zincate leads to less shape change, less dendrite growth and a more negative discharge potential plateau of zinc electrodes. Therefore, calcium-containing zinc electrodes have higher discharge capacity and longer cycle lifetime.
- (iii) Chemically coprecipitated calcium zincate has more homogeneous crystalline structure than the simple physical mixture of zinc oxide and calcium hydroxide. Pasted zinc electrodes with chemically coprecipitated calcium zincate as active material have better electrochemical performance. XRD pattern and SEM photographs show that chemically coprecipitated calcium zincate crystal phase belongs to  $\text{Ca}(\text{OH})_2 \cdot 2 \text{Zn}(\text{OH})_2 \cdot 2 \text{H}_2\text{O}$  and the crystal is of hexagonal shape.

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