

Effects of pH value of reaction solution on structure and electrochemical performance of calcium-containing active material of secondary zinc electrodes^①

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Abstract: The calcium-containing active material of secondary alkaline zinc electrodes was prepared by a chemical coprecipitation method and characterized by scanning electron microscopy (SEM) and X-ray diffractometry (XRD). Their electrochemical performance was tested by the Galvanstatic charge-discharge method. The experimental results show that the sample synthesized at pH = 11.15 has a typical calcium zincate crystal. The zinc electrode using this sample as active material shows higher discharge capacity, more negative discharge plateau potential and longer cycle lifetime.

Key words: calcium zincate; zinc oxide; zinc electrode; electrochemical performance

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1 INTRODUCTION

Secondary alkaline zinc-based batteries have high energy/power densities, no environmental pollution, abundant resources and low cost compared with other traditional secondary batteries. In recent decades, how to improve the cycling performance of zinc electrodes has been always one of the focuses in the electrochemical field^[1, 2]. However, the use of secondary alkaline zinc-based batteries is still limited by the short and unpredictable cycle life of the zinc electrode when being subjected to charge-discharge cycling. This problem has been traced to shape change and dendrite growth which result from the high solubility of the active material (zinc oxide) of zinc electrodes in the alkaline solution^[3-5]. Shape change can be defined as the redistribution of the active material on the electrode surface during electrochemical cycling, which results in the smaller effective electrode area, the lower discharge capacity and the shorter cycle lifetime^[6-9]. In addition, during charging the deposition speed of zinc on the tip of the electrode is accelerated under bulk diffusion control. This trend results in the dendrite growth that can lead to eventual battery failure due to short circuiting^[10, 11].

Many attempts have been made to solve these problems^[12-15]. One of the effective approaches is to apply additives such as CaO or Ca(OH)₂ to zinc electrode, which improves the performance of zinc elec-

trodes by decreasing the solubility of the active material in the alkaline solution. Moreover, adding calcium to active material by different methods can lead to different effects on improving the performance of zinc electrodes. The chemically coprecipitated calcium zincate has been found to be the most beneficial way to improving the electrode performance therein^[16]. However, very few studies of calcium zincate prepared by chemical coprecipitation have been undertaken. The relation between the performance of calcium zincate and its preparation conditions keeps unclear. In the present work, the effects of the reaction solution pH values on the structure and electrochemical performance of the chemically coprecipitated calcium-containing zinc active material are investigated.

2 EXPERIMENTAL

2.1 Preparation of samples

Under vigorous stirring, 0.5 mol/L Ca(NO₃)₂, 2.0 mol/L NaOH and a mixed solution of Zn(NO₃)₂ and NH₄OH with a molar ratio of 1:4 were simultaneously added slowly to a well-sealed reaction vessel, containing a solution with suitable pH value. The reaction temperature was controlled at (50 ± 1) °C and the pH value of reaction solution was held at a given value. After the precipitation reaction had been undertaken for 7 h, the reaction solution was aged for another 24 h with continual stirring. Then, the prod-

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ucts were separated from the solution by filtration, washed for several times with hot deionized water, and dried at about 60 °C. The samples were obtained by the above procedure. A series of samples can be obtained by changing the pH values of the reaction solution (listed in Table 1).

Table 1 Samples prepared at various pH values

A	B	C	D	E	F ¹
11.70	11.45	11.15	10.85	10.55	–

1—sample F is commercial zinc oxide

2.2 Characterization of samples

The crystal structure of the product was determined by X-ray diffraction (XRD) analysis using Philips PC-APD diffractometer with Cu K α radiation operated at 40 kV and 300 mA. The morphology of the samples was examined using scanning electron microscope (SEM, Philips XL 30 ESEM).

2.3 Measurement of electrochemical performance

Calcium-containing pasted zinc electrodes were prepared as follows: 90% sample and 10% (mass fraction) metallic bismuth powder ($\leq 33 \mu\text{m}$) were thoroughly mixed with a certain amount of 2% PVA solution. The paste obtained was incorporated into a tin-electroplated porous nickel substrate (20 mm \times 20 mm) with a spatula. Pasted zinc electrodes were dried at room temperature and then rolled to thickness of 0.5 mm. The zinc electrode was spot welded with a tin-electroplated nickel ribbon as current collector.

A three-compartment electrochemical cell is shown in Fig. 1. The working electrode was the pasted zinc electrode. A sintered nickel hydroxide electrode served as counter electrode, and its capacity was far higher than that of the zinc elec-

trode. The working electrodes and the counter electrodes were wrapped with separator. A Hg/HgO electrode served as reference electrode. The electrolyte was 4 mol/L KOH. The performance of pasted zinc electrodes was tested using a DC-5 cell performance-testing instrument. Charging was carried out at 0.2C for 5 h, and discharging was carried out at 0.4C down to -1.10 V (vs Hg/HgO). After 50 charge-discharge cycles, the cell was disassembled and X-ray photographs of the electrodes were taken.

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

3 RESULTS AND DISCUSSION

3.1 Morphology and structure of samples

The XRD patterns of the samples synthesized at various pH values are displayed in Fig. 2. The main characteristic peaks of sample C appear at $d = 3.2463, 5.0130, 3.1274, 2.8859$ and 2.4571 \AA etc, which coincides with the standard pattern of typical calcium zincate crystal [$\text{Ca}(\text{Zn}(\text{OH})_3)_2 \cdot 2\text{H}_2\text{O}$] phase (JCPDS 24-0222). This implies that calcium zincate is the main crystal in this sample. With the decrease of the pH value, there is nearly no characteristic peak of calcium zincate crystal phase appearing in sample D. The main peaks of this sample appear at $d = 4.4095, 4.2552, 3.2804, 2.7251, 2.2807, 2.2138$ and 2.1455 \AA , which is well conformable with the standard pattern of zinc hydroxide crystal [$\text{Zn}(\text{OH})_2$] phase (JCPDS 38-0385). This shows that zinc hydroxide is the main crystal in sample D. When the pH value decreases to 10.55, the XRD pattern of sample E is very similar to that of sample D. With the increase of the pH var-

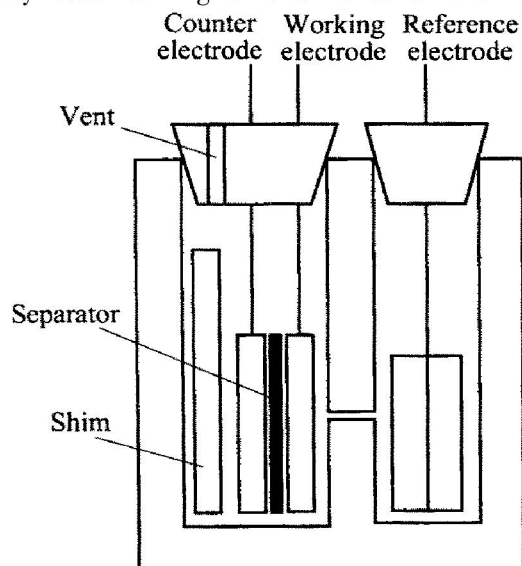


Fig. 1 Schematic apparatus of electrochemical cell for charge/discharge cycling test

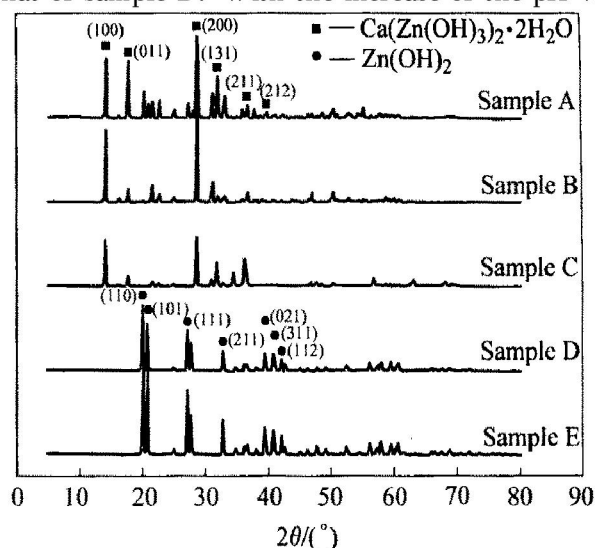
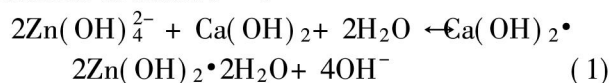


Fig. 2 XRD patterns of samples synthesized at various pH values

lue, it can be seen from the Fig. 2 that the XRD pattern of sample B is almost the same as that of sample C except for some weak peaks of zinc hydroxide phase. When the pH value increases to 11.70, calcium zincate is also the main crystal in the sample, but intensity of the peaks belonging to zinc hydroxide phase increases.

The formation reaction of calcium zincate can be represented as follows^[17]:



When the pH value of reaction solution is relatively low (e. g. 10.55 and 10.85), the main reaction product of OH^- and Zn^{2+} is $\text{Zn}(\text{OH})_2$. Therefore, it can be seen from reaction(1) that calcium zincate is difficult to form, and zinc hydroxide becomes the main crystal phase in sample D and E. When the pH value is relatively high (e. g. 11.15, 11.45 and 11.70), $\text{Zn}(\text{OH})_4^{2-}$ and $\text{Ca}(\text{OH})_2$ are easy to form, thus

calcium zincate becomes the main crystal phase in sample A, B and C. However, too high pH values are also disadvantageous to the formation of calcium zincate according to reaction(1), so some zinc hydroxide crystals are found in sample A and B.

Fig. 3 shows the SEM images of the samples. It can be seen from Figs. 3(c) and (d) that in sample C it appears monoclinics with tetragonal-shape particles. Sample A displays monoclinics with tetragonal-shape particles too, and some particles with polyhedral shape are also found in Figs. 3(a) and (b). The particles of sample E appear to be polyhedral but not tetragonal-shape (as shown in Figs. 3(e) and (f)). Since the particles of zinc hydroxide and calcium zincate appear in polyhedron and monoclinics respectively under certain preparation conditions^[18, 19], it can be recognized from the SEM images that sample C is mainly calcium zincate, the samples synthesized at lower pH value (e. g. pH= 10.55) are zinc hydroxide, and the samples

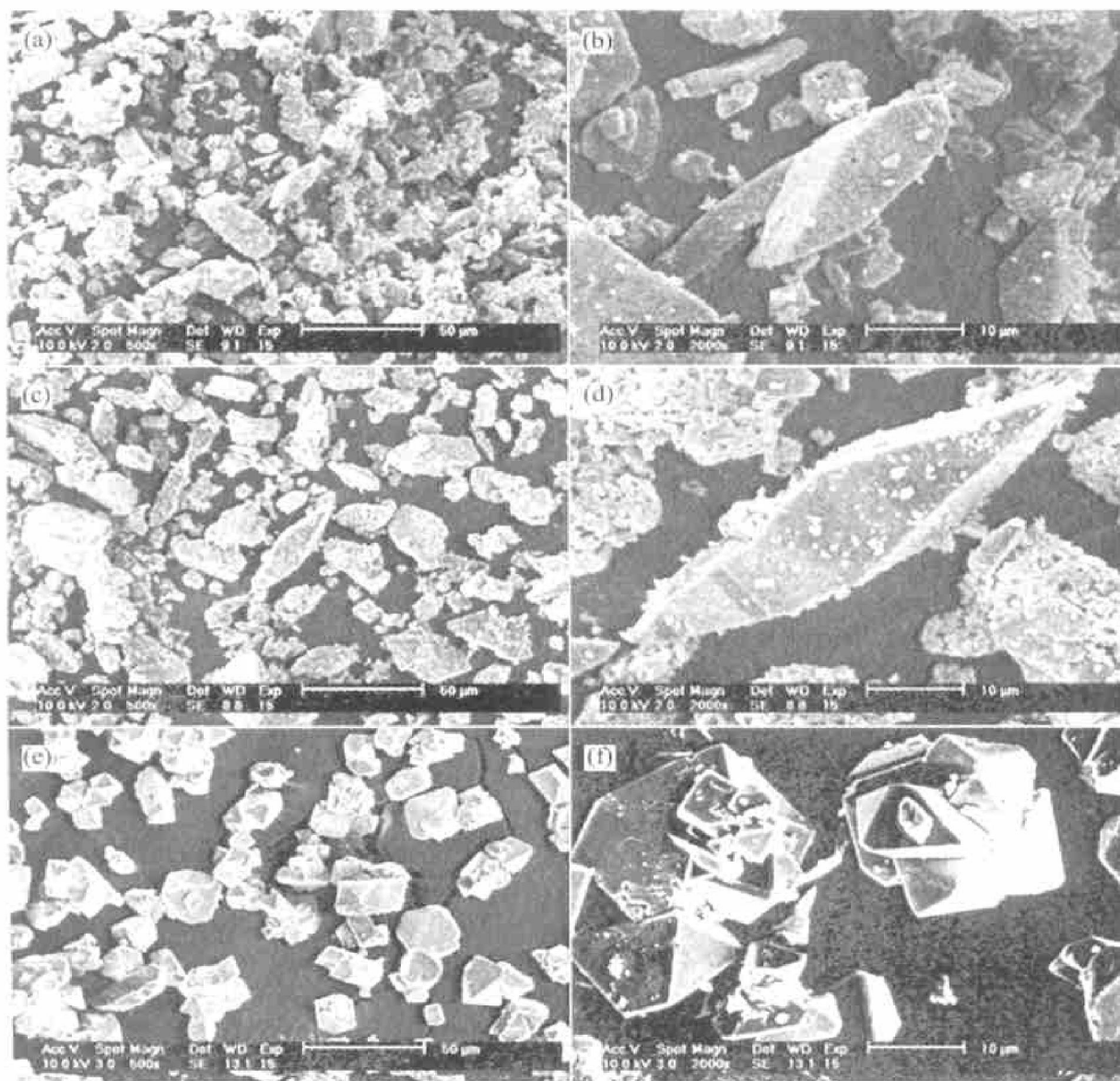


Fig. 3 SEM images of samples synthesized at various pH values

(a) —Sample A at lower magnification; (b) —Sample A at higher magnification; (c) Sample C at lower magnification; (d) Sample C at higher magnification; (e) Sample E at lower magnification; (f) Sample E at higher magnification

synthesized at higher pH value (eg pH = 11.70) are the mixture of calcium zincate and zinc hydroxide. These results are in agreement with those concluded by XRD. In addition, it can be seen from the Figs. 3 (a), (b), (c) and (d) that sample C shows higher crystal degree than that of sample A.

3.2 Electrochemical performance of samples

The discharge curves of the pasted zinc electrodes at the third cycle are displayed in Fig. 4(a). It can be seen that the electrochemical performance of the samples synthesized at higher pH values (eg 11.15, 11.45 and 11.70) is much better than other samples and commercial ZnO. They show higher discharge capacity, more smooth discharge plateau and more negative discharge plateau potential. Sample C has the best electrochemical performance in those samples because of larger content and higher crystal degree of calcium zincate^[16, 19-21]. However, when the pH values of reaction solution are relatively lower (eg 10.55 and 10.85), calcium zincate can not be synthesized effectively. Therefore, compared with commercial ZnO, the electrochemical performance of these samples shows a little improvement. Fig. 4(b) shows that the samples synthesized at higher pH value still have smooth discharge plateau and higher discharge capacity at the 27th cycle. However, the discharge capacity of the samples synthesized at lower

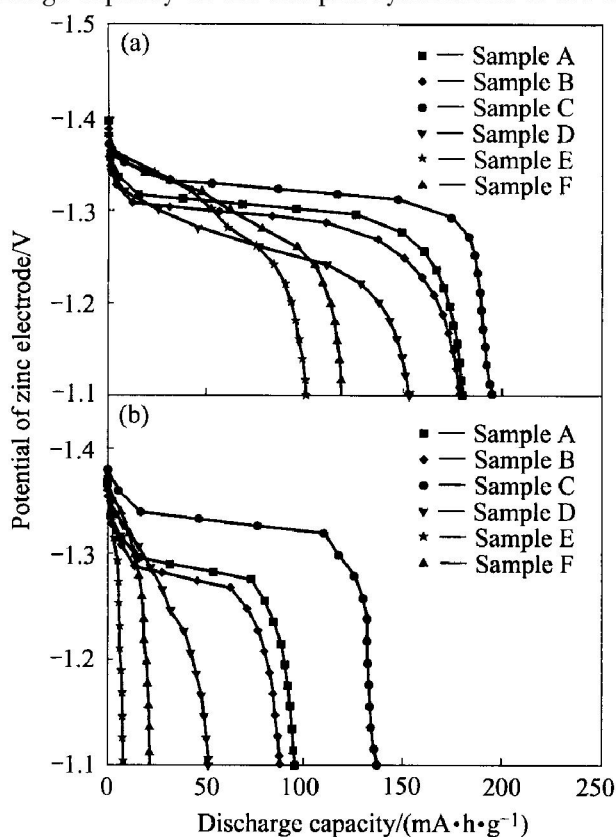


Fig. 4 Discharge curves of samples synthesized at various pH values
(a) -3rd cycle; (b) -27th cycle

pH values decreases greatly and almost no discharge plateau appears.

Fig. 5 shows the plot of the discharge capacity against cycle number for pasted zinc electrodes. Due to the higher solubility of ZnO in alkaline solution, the electrode with commercial ZnO as active material has serious shape change and heavy dendrite growth during charge-discharge cycling^[5-8, 10-11], which results in quick decline in discharge capacity. After 20 cycles, the discharge capacity decreases to 34% of its original value. Since calcium zincate has lower solubility in alkaline solution, higher calcium zincate content in the samples synthesized at higher pH value leads to less shape change and less dendrite growth of the zinc electrodes. Consequently, the stability of electrochemical cycle is obviously improved^[16]. There is a certain amount of zinc hydroxide in sample A and B, so their cycle stability and discharge capacity are lower than those of sample C. The discharge capacity of the samples synthesized at lower pH value declines very quickly because calcium zincate is not effectively synthesized. In addition, since zinc hydroxide has much higher solubility in alkaline solution, the sample synthesized at pH = 10.55 (sample E) shows worse cycle stability than commercial ZnO does.

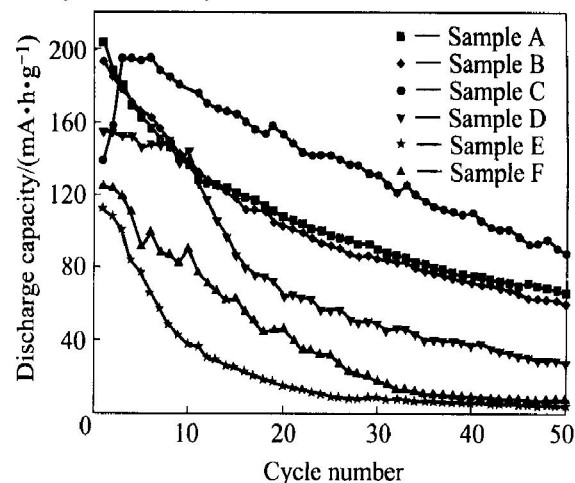


Fig. 5 Cycling performance of samples synthesized at various pH values

X-ray radiographs of pasted zinc electrodes after 50 charge-discharge cycles are shown in Fig. 6, which can reflect the amount and distribution of the active material on the electrodes. Dark areas have more active material than bright ones do. It can be seen that the electrode using commercial ZnO as active material (Fig. 6(f)) is very similar to blank electrode (Fig. 6(g)), which indicates that there is almost no active material on the electrode. The electrode using sample C as active material (Fig. 6(c)) has the largest dark area that distributes most evenly, which shows the electrode has

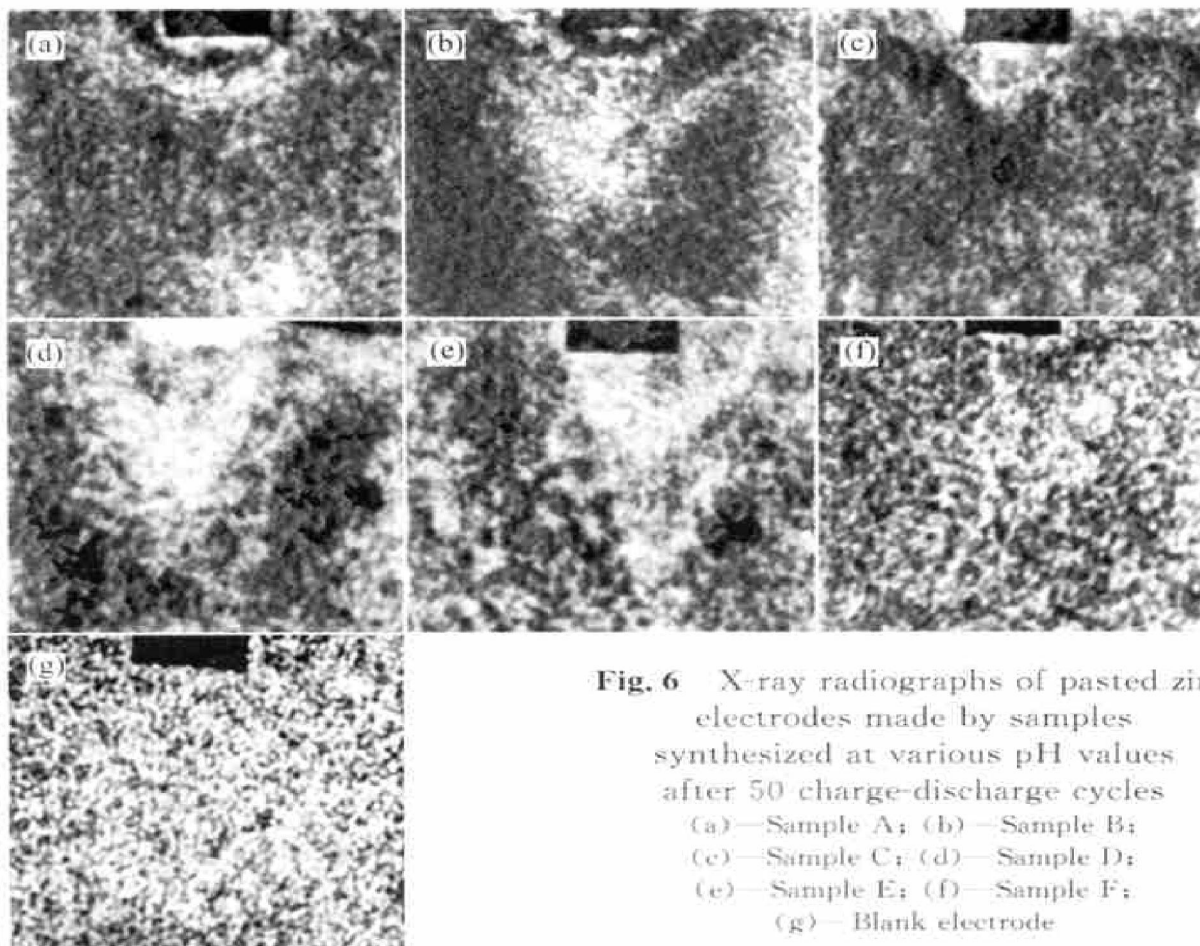


Fig. 6 X-ray radiographs of pasted zinc electrodes made by samples synthesized at various pH values after 50 charge-discharge cycles
(a)—Sample A; (b)—Sample B;
(c)—Sample C; (d)—Sample D;
(e)—Sample E; (f)—Sample F;
(g)—Blank electrode

the least shape change. Although the electrodes using sample A and B as active material (Figs. 6(a) and (b)) have relatively large dark areas, their distribution evenness is worse than that of sample C. The electrodes using sample D and E as active material (Figs. 6(d) and (e)) have smaller dark areas that do not distribute evenly. These results are in good agreement with the experimental results of the charge-discharge test.

4 CONCLUSIONS

Calcium zincate, the main crystal phase of the active material, can be synthesized at $\text{pH} = 11.15 - 11.70$ by chemical coprecipitation method. Calcium zincate samples with tetragonal-shape particles display relatively more negative discharge plateau potential, higher discharge capacity, more smooth discharge plateau and longer cycle life. The results of X-ray radiographs show that the pasted zinc electrodes with calcium zincate as the main composition of the active material have less shape change. Furthermore, the sample synthesized at $\text{pH} = 11.15$ has the best electrochemical performance among these samples due to larger content and higher crystal degree of calcium zincate in this sample.

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