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Electrochemical performances of ZnO with different morphology as anodic materials for Ni/Zn secondary batteries

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ABSTRACT

The hollow fusiform ZnO and the hexagonal taper-like ZnO have been prepared by hydrothermal method. The synthetic materials have been characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). As anodic materials for Ni/Zn cells, electrochemical performances of the hollow fusiform ZnO and the hexagonal taper-like ZnO have been investigated by cyclic voltammetry (CV) and galvanostatic charge–discharge measurement. Compared to the conventional ZnO, the hollow fusiform ZnO and the hexagonal taper-like ZnO have shown better cycle stability than the conventional ZnO. Furthermore, the initial discharge capacity of hollow fusiform ZnO is 476 mAh g^{-1}, and the discharge capacity is almost unchangeable with the capacity retention ratio of 99.5% over 50 cycles. Comparatively, the hexagonal taper-like ZnO delivers an initial discharge capacity of 470 mAh g^{-1} and with the capacity retention ratio of 94.7% over 50 cycles. They are much higher than that of the conventional ZnO. The better electrochemical performance is attributed to higher electrochemical activity, which is ascribed to the novel initial morphology and size of as-prepared ZnO active material. And the formation of zinc dendrite is suppressed much essentially, the reason could be attributable to initial morphology of the active materials. And the zinc dendrite is suppressed effectively, which results in improvement of cycle stability of Ni/Zn secondary cells.

1. Introduction

Advanced rechargeable batteries have long been recognized for the capacity to convert efficiently and store electrical energy, which is now used in a myriad of devices, such as electric vehicles and power sources for cordless power tools, video equipment, communications equipment, and lap-top computers. The worldwide market for batteries is expected to grow along with our increasing use of electricity and electrical devices. Much of the recent research and development on advanced rechargeable batteries has been driven by such applications, and Ni–Zn alkaline secondary batteries is the leading candidates for the same reason, which has remarkable advantages of high specific energy and power, good low-temperature performance, low cost and environmental toxicity. ZnO is a versatile material, which is now wildly used in electrochemistry, catalysis, optoelectronics and photochemistry. ZnO morphology mainly shows hexagonal prism structure. As amphoteric oxide, ZnO is not only soluble in acidic solution but also alkaline solution. As a semiconductor, ZnO has a poor conductivity, but its theoretical capacity can reach 659 mAh g^{-1} as electrode materials. ZnO is an ideal material for electrode materials [1]. However, widespread commercialization of Ni–Zn alkaline secondary batteries has been prevented by the short and unpredictable lifetime of zinc electrode. This problem has been derived from the redistribution of Zn active material such as shape change and the formation of unwanted Zn electrode morphologies during recharge, which are mainly dendrites, filamentary growths and nodules. These phenomena are attributed to the high solubility of zinc discharge products in the electrolyte and the deposition of Zn during charging is non-uniform [2,3]. Increasing efforts have been devoted to overcome these difficulties, including: (1) additives to the anode and the electrolytes; (2) development and improvement of separators; (3) miscellaneous techniques such as pulse charging, electrode vibration and surface modification technique to improve the electrochemical performance of ZnO [4–9].

It is well known that these problems of Ni/Zn secondary batteries are tightly related to physical and electrochemical properties of ZnO. The initial morphology of ZnO was found to be able to influence the electrochemical performance of secondary Ni/Zn batteries [10,11]. However, little attention has been focused on the effects of different morphology of ZnO on electrochemical properties. Indeed, both the shape change and dendrite growth are related to the

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morphology of negative active material [12,13]. To further comprehend the point, it is very important to investigate electrochemical performances of ZnO with different morphology. In present work, hollow fusiform ZnO and hexagonal taper-like ZnO were prepared by hydrothermal method. As the anodic active materials for Zn/Ni cells, the electrochemical properties of them were investigated in detail. Then, the conventional ZnO was employed to compare the difference in the electrochemical properties.

2. Experimental

2.1. Preparation of different morphology ZnO samples

2.1.1. Preparation of hollow fusiform ZnO sample

The hollow fusiform ZnO samples were prepared via a simple hydrothermal method and the typical experimental operation was described as follows: 0.2 mol/L of zinc nitrate hexahydrate solution ($Zn(NO_3)_2{\cdot}6H_2O$, Tianjin City Fine Chemical Research Institute, China) and the 0.4 mol/L of sodium hydroxide solution (NaOH, Tianjin City Fine Chemical Research Institute, China) was prepared with deionized water respectively. Then, the sodium hydroxide solution was slowly added into zinc nitrate solution dropwise at a speed of 1 drop/s at room temperature under strong mechanical stirring for 10 min, which resulted in the formation of a white suspension. After stewing for 10 min, the resulted precipitate was filtrated and washed with deionized water and absolute ethanol (C_2H_5OH, Tianjin City Fine Chemical Research Institute, China), then dried at 60 °C for 10 h in an oven to obtain the precursor. Subsequently, 6 g precursor and 0.02 g CTAB (Tianjin City Fine Chemical Research Institute, China) and 1 g NaCl (Hunan Normal University Chemical Reagent Factory, Changsha, China) were completely dissolved into 30 mL of absolute ethanol. The CTAB is used as surfactant which can decrease the surface tension of dispersed phase and increase the power of dispersion in the solvent and make reaction system consistent. The mixture was then sealed into a Teflon-lined autoclave with a filling capacity of about 60% and maintained at 180 °C for 5 h. After reaction, the autoclave was allowed to cool to room temperature. Then the reaction product was separated from the solution by filtration and washed several times with deionized water and ethanol. Then, the precipitate was dried at 60 °C for 10 h.

2.1.2. Preparation of hexagonal taper-like ZnO sample

The hexagonal taper-like ZnO samples were prepared through the following process. 20 g $Zn(NO_3)_2{\cdot}6H_2O$ (Tianjin City Fine Chemical Research Institute, China) was dissolved into 85 mL deionized water to form nitrate solution, and 0.2 g CTAB was dissolved into 20 mL ethanol as alcoholic solution. Nitrate solution was splashed into alcoholic solution under a strong stirring, and then 15 mL 15 wt% $NH_3{\cdot}H_2O$ (Tianjin City Fine Chemical Research Institute, China) was added into the mixed solution. Subsequently, the as-prepared solution was sealed inside of Teflon-lined autoclave with a filling capacity under 70%. The autoclave was put into a water bath at 95 °C for 6 h and then the solution in the autoclave was delivered into a glass beaker with water bath controlled temperature at 50 °C and kept for 3 h under a mild stirring. After that the resulting white precipitate was washed with deionized water and ethanol for several times, and then was dried at 60 °C for 10 h in oven, subsequently calcined in the muffle oven at 500 °C for 2 h. The hexagonal taper-like ZnO particles were obtained.

2.2. Characterization techniques for prepared ZnO

X-ray diffraction (XRD) was performed on a Rigaku D500 (Siemens) diffractometer (36 kV, 30 mA) using Cu Kα radiation at a scanning rate of $2\theta = 4°$/min. The surface morphology of as-synthesized ZnO was observed using scanning electron microscope (SEM, JSM-6360LV).

2.3. Preparation of the Zn pasted electrodes

The secondary Zn-pasted electrodes were prepared by coat-and-press method; the preparation method was similar to Yang's procedure [14]. The zinc electrodes were prepared as follows: 80 wt% as-synthesized ZnO, 5 wt% Zn powder (95%, Tianjin City Fine Chemical Research Institute, China), 10 wt% graphite and 5 wt% additives which included 3 wt% polytetrafluoroethylene (PTFE, 60 wt%, in diluted emulsion, Tianjin City Fine Chemical Research Institute, China) 1 wt% In_2O_3 (Tianjin City Fine Chemical Research Institute, China), 1 wt% SnO (Hunan Normal University Chemical Reagent Factory, Changsha, China) were thoroughly mixed with a certain amount of deionized water to form mushy slurries. The mushy slurries obtained were incorporated in a copper mesh substrate (2.0 cm × 2.0 cm in size) with a spatula, which served as the current collector. The obtained zinc electrodes were dried at room temperature and then roll-pressed to a thickness of 0.3 mm. For comparison, a similar anode with conventional ZnO (Hunan Normal University Chemical Reagent Factory, Changsha, China) was also fabricated according to the same process. The positive electrode was the commercial sintered $Ni(OH)_2$ (Tianjin City Fine Chemical Research Institute, China) electrode which capacity was far higher than those of the zinc electrodes in the aim of making full use of the active material in zinc electrodes. A solution of 5.5 M KOH (Tianjin City Fine Chemical Research Institute, China), 0.5 M LiOH (Tianjin City Fine Chemical Research Institute, China), 1.0 M NaOH, saturated with ZnO, was used as the electrolyte. The alkaline Ni–Zn cells were pre-activated for eight times by the following operations: the cells were circularly charged at 0.1 C for 10 h, and then discharged at 0.2 C to 1.4 V cut-off. The charge/discharge cycle tests were performed at room temperature.

2.4. Electrochemical properties measurements

The galvanostatic charge–discharge tests were performed on BTS-5 V/100 mA battery-testing instrument (Neware, China) at room temperature (25 ± 2 °C). During the cycling procedure, the cells were charged at 0.1 C for 10 h and discharged at 0.2 C down to 1.4 V cut-off. Cyclic voltammetry (CV) was carried out using Electrochemical Workstation CS-350 (Wuhan Corrtest Instruments Co.) at room temperature (25 ± 1 °C) at a scanning rate of 1 mV s^{-1} shifting from −1.05 to −1.65 V. A three-electrode cell assembly was used in the test. An Hg/HgO electrode served as reference one. The working electrode was the preactivated pasted zinc electrode and the commercial sintered $Ni(OH)_2$ electrode was used as counter electrode and its capacity was far higher than that of zinc electrode. The electrolyte was 6 M KOH solution saturated with ZnO.

In all the above experiments, the reagents used were A.R. grade and the electrolyte was prepared with deionized water.

3. Results and discussions

3.1. XRD analysis of as-prepared ZnO

Fig. 1 shows the XRD patterns of the products prepared by the hydrothermal synthesis method. For comparison, conventional ZnO is also discussed. Comparing these XRD patterns with the XRD standard spectra of ZnO (PDF 36-1451) which belongs to the hexagonal crystal system [space group *P*63*mc*], all the diffraction peaks can be indexed to wurtzite ZnO, and no other impurity peaks are observed. On the whole, these diffraction peaks are sharp, narrow and symmetrical with a low and stable baseline, suggesting that the sample is well-crystallized. The diffraction peaks can be