Short communication

Formation of porous ZnO microspheres and its application as anode material with superior cycle stability in zinc-nickel secondary batteries

Limin Wang[a,b], Zhanhong Yang[a,*], Xi Chen[a,b], Haigang Qin[a,b], Peng Yan[a]

[a] Hunan Province Key Laboratory of Chemical Power Source, College of Chemistry and Chemical Engineering, Central South University, Changsha, 410083, China
[b] Innovation Base of Energy and Chemical Materials for Graduate Students Training, Central South University, Changsha, 410083, China

HIGHLIGHTS

- Mechanism analysis of the formation process of porous ZnO microspheres.
- Porous ZnO microspheres is evaluated as anode material for zinc-nickel battery.
- Porous ZnO microspheres possess outstanding electrochemical performance.
- Porous ZnO microspheres has good discharge properties at a large current density.

ARTICLE INFO

ABSTRACT

Porous ZnO microspheres and globular ZnO are synthesized by facile hydrothermal methods and the electrochemical performance as negative active ingredient of zinc-nickel secondary battery is compared with commercial ZnO. Throughout the process, we first characterize the material by X-ray diffraction (XRD) to confirm the samples and the morphology of the samples before and after charge-discharge process is determined by scanning electron microscope (SEM). Also, Brunauer-Emmett-Teller (BET) measures the specific surface area which plays a vital role in the galvanostatic charge-discharge measurements, cyclic voltammograms (CV) and electrochemical impedance spectroscopy (EIS). Porous ZnO whose maximum discharge specific capacity is up to $643.2 \, \text{mAh g}^{-1}$ (coulomb efficiency 97.60%) has outstanding cycling performance and large discharge capacity due to the porous structure and the large specific surface area, and the specific capacity remains essentially above $600 \, \text{mAh g}^{-1}$ in the first 600 cycles after the pre-activation process. In addition, the high rate performance of porous ZnO is also examined to demonstrate that porous ZnO as negative active ingredient of zinc-nickel secondary battery has good discharge properties under a large current density.

1. Introduction

Zinc is one of the most promising anode materials for future in aqueous solution for battery applications [1]. Zinc-nickel secondary battery that is composed of zinc anode and nickel cathode is a kind of high performance green secondary battery with the characteristics of high capacity of zinc anode electrode in zinc-silver oxide battery [2] and longevity of nickel cathode in cadmium-nickel battery [3]. It has received considerable attention, during the past few decades, due to the performance characteristics of zinc-nickel secondary battery including a high operating voltage, high energy density, high power density, wide temperature range, no memory effect, environmental friendliness and low price, achieving the honorable title "green battery" [4–8].

However, owing to the high solubility of ZnO as anode materials in alkaline electrolyte, the zinc electrode during charge-discharge cycles could be susceptible to deformation of zinc electrode [9–12], zinc dendrite formation [4,13–16], self-corrosion [17–19], passivation [17,20,21] and so forth, which are cut down the capacity of zinc electrode and shortened the longevity of secondary battery, restricting the extensive commercialization of zinc-nickel battery [14,16,22]. For one thing, some oxides or hydroxides, such as $Ca(OH)_2$、Bi_2O_3、PbO、CdO、In_2O_3 used as additives are deemed to be one of the effective measures to relieve dendrite growth [23–29]. The part of the additives, as mentioned above, could be reduced in the charging process, forming a conductive network, which could advance the conductivity of the electrode and alleviate the polarization of the electrode [30–32]. Besides, some additives could be combined with zinc active ingredients to form new materials with the aim of achieving the effect

of preeminent electrochemical properties [7].

For another, the attachment of additives has a negative impact on the actual specific capacity of zinc electrode more or less, therefore it is necessary to explore ZnO materials without additives. Yuan at al., for instance, demonstrated that nanosized ZnO with prismatic form exhibited higher midpoint discharge voltage, better cycle stability and passivation toleration than commercial ZnO [33]. Both ZnO nanosheets [16] and ZnO nanospheres [34,35] served as electrode materials were propitious to increase the capacity of the secondary battery. Accordingly, the discussion on the microstructure and electrochemical performance of ZnO is deemed essential, which could polish up the electrochemical performance by ameliorating the ZnO microstructure [36]. For materials with porous structure, the intimate contact between the electrode material with larger specific surface area and the electrolyte expands the electrochemical reaction area of the active ingredient, depressing the electrode resistance and enhancing the utilization ratio of the active ingredient. What's more, conductive paths throughout the entire internal structure in the porous material bring about a more uniform current distribution, reducing the formation of zinc dendrites caused by the concentration polarization. In present work, we have synthesized porous ZnO microspheres and globular ZnO using different facile hydrothermal synthesis approaches as anode material of zinc-nickel secondary battery. Then, the combination of structure characterizations and electrochemical performance tests was carried out to show that porous ZnO microspheres exhibited excellent electrochemical performance compared to commercial ZnO and globular ZnO.

2. Results and discussions

2.1. Formation mechanism of porous ZnO microspheres

$$CO(NH_2)_2 + 3H_2O \rightarrow 2NH_3{\cdot}H_2O + CO_2 \qquad ;(1)$$

$$NH_3{\cdot}H_2O \rightarrow NH_4^+ + OH^- \qquad ;(2)$$

$$2NH_3{\cdot}H_2O + CO_2 \rightarrow 2NH_4^+ + CO_3^{2-} + H_2O \qquad ;(3)$$

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \qquad ;(4)$$

$$4Zn^{2+} + 6OH^- + CO_3^{2-} + 3H_2O \rightarrow Zn_4(CO_3)(OH)_6{\cdot}H_2O \qquad .(5)$$
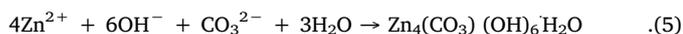
The formation mechanism of porous ZnO microspheres composed of nanosheets is shown as Fig.S5 (b) and analyzed as follows: Firstly, the hydrolysis of $CO(NH_2)_2$ generates OH^- until the solution reaches the super-saturated state, in which case the Zn^{2+} in the solution quickly reacts with OH^- and the precipitate of $Zn(OH)_2$ forms and grows by degrees. During the growth of these nuclei, they congregate with each other, which also serves as a "sacrificial template" for the formation of nanosheet structures. As the reaction proceeds, the OH^- in the solution gradually increases and the precipitate of $Zn(OH)_2$ generally dissolves, which occurs at the solid-liquid interface and is a dynamic equilibrium process where Zn^{2+} generated by the dissolution of $Zn(OH)_2$ could react with OH^-, CO_3^{2-}, and H_2O in solution to form the $Zn_4(CO_3)(OH)_6{\cdot}H_2O$ precursor. Since $Zn(OH)_2$ is a hydrophilic group, the obtained $Zn_4(CO_3)(OH)_6{\cdot}H_2O$ precursor slowly grows upright on the surface of $Zn(OH)_2$, and the sheet structure begin to take shape. With the extension of the reaction time, $Zn(OH)_2$ gradually dissolved and $Zn_4(CO_3)(OH)_6{\cdot}H_2O$ existing on the surface of $Zn(OH)_2$ progressively increases and grows until $Zn(OH)_2$ dissolves thoroughly, then forming monodisperse porous microspheres comprised of 2D nanosheets. Eventually, the $Zn_4(CO_3)(OH)_6{\cdot}H_2O$ precursor was calcined at high temperature to decompose into porous microspheres structure of wurtzite ZnO [37,38].

Table 1
Comparison of electrochemical performance of different ZnO as the negative active ingredient for zinc-nickel secondary batteries.

Sample	Discharge specific capacity (mAh g^{-1})	Cycle life	Reference
ZnO nanoplates	420	80	[16]
nanosized ZnO	600	300	[33]
ZnO nanowires	609	75	[22]
hollow fusiform ZnO	476	50	[39]
hexagonal taper-like ZnO	470	50	
carbon-coated ZnO	500	300	[40]
CeO$_2$/ZnO composite	550	50	[41]
porous ZnO microspheres	643	700	This work

2.2. Electrochemical performance

Cycle life is a pivotal indicator of battery performance for secondary batteries. The comparison of electrochemical performance of different ZnO as the negative active ingredient for secondary batteries is listed in Table 1, showing that porous ZnO microspheres has outstanding cycling performance and large discharge specific capacity. For the electrodes made from commercial ZnO, globular ZnO, porous ZnO respectively, as shown in Fig. 1 (a), porous ZnO exhibits outstanding cycling performance and the mass of the active ingredients in all three samples is 10.0 mg. The maximum specific capacity of the porous ZnO electrode is up to 643.2 mAh g^{-1} (coulomb efficiency 97.60%) and the specific capacity, by and large, remains above 600 mAh g^{-1} after undergoing 70 cycles. The specific capacity then started to have a relatively slow downward trend until after undergoing 601 cycles. Given that the porous structure is convenient for the full penetration of the electrolyte inside the material and makes contact with the nanosized primary ZnO, increasing the mass transfer during the charge-discharge process and advancing the utilization of the active ingredient, which guarantees the actual specific capacity of the porous ZnO electrode. The actual specific capacity of the globular ZnO electrode is slightly lower, with a maximum specific capacity of about 602.5 mAh g^{-1} (coulomb efficiency 94.15%), and the specific capacity tends to diminish after 437 cycles. As was mentioned previously, the cycle performance of those ZnO samples are pronouncedly superior to commercial ZnO with a maximum specific capacity of 590.2 mAh g^{-1} (coulomb efficiency 89.55%), and the discharge specific capacity of commercial ZnO dropped to 335 mAh g^{-1} after 205 cycles. For electrode whose active ingredient is commercial ZnO or globular ZnO, the high solubility of the discharge product in the alkaline electrolyte is the main factor that affect the capacity attenuation of the secondary battery, bringing about a substantial increase in the concentration of zincate ions, which can form an uneven deposition of the product during charging and cause the growth of zinc dendrites and the electrode shape in the electrolyte. As shown in Fig. 2, the generation of zinc dendrites resulted in non-uniform current distribution during the cycling process, which made the polarization of electrodes seriously and reduced the utilization rate of active ingredient of zinc electrodes, eventually leading to rapid and distinct capacity attenuation.

As can be seen from Fig. 1 (b), almost every charge-discharge process of porous ZnO as an active ingredient in the 251th to 270th cycles shows a good voltage-time response characteristic, illustrating the better cyclic stability of the composites.

Typical galvanostatic charge-discharge curves of zinc-nickel secondary batteries at the 200th cycle are presented in Fig. 1 (c) and (d), respectively. All samples have a stable charge-discharge platform, while porous ZnO has the lowest charge voltage and the highest discharge voltage compared to globular ZnO and commercial ZnO, suggesting that porous ZnO has outstanding electrochemical activity. Based on the