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Ultrasound assisted polymerization for synthesis of ZnO/Polypyrrole composites for zinc/nickel rechargeable battery

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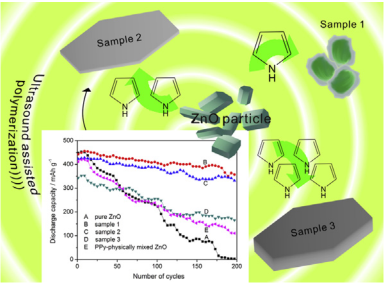
HIGHLIGHTS

- ZnO/Polypyrrole (PPy) composites with different morphology are synthesized.
- ZnO/PPy composites are utilized as anode material in Zn/Ni rechargeable battery.
- ZnO/PPy composites possess higher capacity retention than that of pure ZnO.

GRAPHICAL ABSTRACT



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ABSTRACT

ZnO/Polypyrrole (PPy) composites are synthesized by ultrasound assisted chemical polymerization of PPy in the presence of ZnO particles. With different initial content of pyrrole, granular and layered ZnO/PPy composite are formed. The fourier transform infrared spectra (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are adopted to characterize the as-prepared samples. ZnO/PPy composites are used as anode material for Zn/Ni batteries. Galvanostatic charge/discharge experiments, cyclic voltammograms (CV) and electrochemical impedance spectroscopy (EIS) are conducted to evaluate the cycle performance of electrodes. ZnO/PPy composites show superior capacity stability, more stable charge plateau and higher discharge plateau compared to conventional ZnO electrode. Furthermore, rate performance is also improved by ZnO/PPy composites.

1. Introduction

With the development of electrification era, more and more electric productions are emerging, which require of a reliable, stable and cost effective energy storage device. The zinc/nickel electrochemical system is a promising candidate for alkaline storage batteries owing to its good performance such as high energy density, high power density, high open-circuit-voltage, and a small self-discharge rate [1–3]. What matters more is that the electrode active materials used in the Zn/Ni system are low-toxic and inexpensive materials, and exist in abundance in nature. So the Zn/Ni system is a suitable substitute for the lead-acid and nickel–hydrogen system, and remains a serious candidate for electromobiles. However, the biggest challenge with zinc electrodes is their shape changes and dendrite growth during cycling caused by high solubility of discharge product in alkaline solution, which results in relatively low cycle life of this system [4,5]. In past decades, numerous works have been undertaken to improve the anodic properties of zinc electrode in alkaline solution.

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Improvements initiatives in zinc electrode include the use of additives, morphology control of zinc particle and seeking novel active material. Electrode additives include conductive ceramic [6,7], Bi_2O_3 [8], Ag [9], TiO_2 [10], $In(OH)_3$ [11] and so on. The additives, added through the physical entrapment or by localized precipitation of zinc-containing species, can restrain the migration of zincate away from zinc electrode and improve electronic conductivity and current distribution of the zinc electrode [12]. Different morphology of zinc particle, such as nanoplate [13], nanowire [14], nanorod [15], hollow fusiform and hexagonal taper-like ZnO [16], are prepared to investigate their influences on electrochemical character. And some zinc-containing material as active anode material for Zn/Ni rechargeable battery, such as calcium zincate [17] and zinc-containing hydrotalcite [18], were investigated.

Functional organic-inorganic composite with desired properties is an important research field. They provide a new functional hybrid, with synergetic or complementary behavior between organic and inorganic materials, which have attracted considerable attention for their potential applications. As we know, Polypyrrole (PPy), a conducting conjugated polymer, has tremendous potential application due to its low cost, facile synthesis, air and thermal stability, significant electrical conductivity, electrochemical properties and environmentally benign performance. It can be used in following fields: polymeric rechargeable batteries for energy-storage purposes, electrode materials for electrochemical supercapacitors, metal corrosion protection coating materials, matrix for structural composite materials, sensors, gas/humidity testing, electrochromic devices and photovoltaic (solar cell) materials [19,20]. In previous work, Suga et al. [21] proposed that anodes, comprising zinc active material and a polymer layer, could suppress dendrite growth and shape change. Furthermore, dip coating, brush coating and electrodeposition coating of polyaniline or polypyrrole on zinc electrode have been found to be useful in stabilizing the capacity of electrode on repeated cycling [22,23]. In addition, Zhou et al. [24] and Abe et al. [25] investigated the effect of ionomer on zinc electrode. The polymer or ionomer layer on the surface of zinc foil limited the diffusion of the discharge products due to its fine porous structure and re-complexation with zincate ions. In this paper, we prepared ZnO/Polypyrrole (ZnO/PPy) composite using an ultrasound assisted chemical polymerization with the aim to improve cycle life of zinc electrode. The electrochemical behavior of as-prepared ZnO/PPy composite was investigated.

2. Experimental

2.1. Materials preparation

ZnO/PPy composites were synthesized by using a polymerization of the monomer in the present of ZnO particles accompanied by continuous ultrasound and mechanical stir. Compared with conventional magnetic stirring in the polymerization process, ultrasound can provide intense turbulence associated with shear and liquid circulation, it not only results in improved particle distribution of ZnO particles, but also provides a faster dissociation of pyrrole, which generates an enhanced quantum of radicals during the polymerization process and thus gives an improved polymerization efficiency. The pyrrole monomer obtained from Sinopharm Chemical Reagent Co., Ltd. was distilled under reduced pressure. ZnO particles were obtained from Xilong chemical Co., Ltd. Ammonium persulfate (APS), p-toluenesulfonic acid (p-TSA) were both purchased from Sinopharm Chemical Reagent Co., Ltd. NaOH was obtained from Tianjing Chemicala Reagent Research Institute, and they were used as received without further treatment. In a typical synthesis, 0.6 g ZnO was dispersed in 20 mL distilled water under ultrasound. 1.5 mmol sodium p-toluene sulfonate (prepared from NaOH and p-toluenesulfonic acid) and 1.85 (sample 1), 3.7 (sample 2) and 7.4 (sample 3) mmol pyrrole monomer were added to above ZnO suspended solution under constant sonication and continuously stirred for 5 min. Afterward, 0.9 mmol Ammonium persulfate was promptly mixed into the above solution at room temperature. The resulting solution was kept under ultrasound and stir for 40 min. During the polymerization, the color of the system changed from white to grey slowly, and the more the initial pyrrole content, the blacker the color of sample: sample 3 is blacker than sample 2 which is blacker than sample 1. The products were filtered and washed thoroughly with distilled water (to remove the unreacted ammonium persulfate and sodium p-toluene sulfonate) and then with methanol (to remove the oligomers). The filtered sample was dried in a vacuum oven at 333 K for further analysis. The amount of polymer in the total composition is determined by the mass difference before and after calcinations treatment of samples in the oxygen atmosphere at 873 K for 90 min. The content of polymer for sample 1, sample 2 and sample 3 is 5.1%, 11.4% and 16.8% respectively. Pure PPy was also synthesized following the same procedure as described before but without ZnO, and PPy-physically mixed ZnO with 11.4% PPy was synthesized in order to compare its electrochemical property with ZnO/PPy composites.

2.2. Characterization of ZnO/PPy composites

Fourier transform infrared (FT-IR) spectroscopy of as-prepared samples was conducted on a Nicolet Nexus-670 FT-IR spectrometer (as KBr discs, with wave number 400–4000 cm^{-1}). The morphology and structure were observed on scanning electron microscope (SEM) (JSM-6360LV) and transmission electron microscope (TEM) (JEOL-2010). The X-ray diffraction (XRD) pattern was conducted using X-ray diffractometer (Philips X' Pert Pro).

2.3. Preparation of ZnO/PPy electrodes

For fabrication of ZnO/PPy electrodes, 85 wt. % of ZnO/PPy powder was mixed with 10 wt. % acetylene black and 5 wt. % Polytetrafluoroethylene (PTFE) (served as conductive agent and binder respectively). And the mixture was grinded with agate mortar until it became muddy mixture with proper viscosity. Then above muddy mixture was incorporated to a copper mesh which served as current collector. For comparison, similar zinc electrode with pure ZnO was fabricated. The obtained electrodes were dried at 333 K in a vacuum oven for further testing. And the weight of active material in negative zinc electrode is about 30 mg per electrode.

2.4. Electrodes testing

For galvanostatic charge/discharge cycle test, a two-electrode cell was adopted, which includes working electrode and counter electrode, but without reference electrode compared with a three-electrode system. The capacity of chosen counter electrode (sintered $Ni(OH)_2$ electrode) was three times higher than working electrode in the aim of making sure that the capacities of cells was controlled by working electrode. In addition, 6.0 M KOH solution with saturated ZnO was used as the electrolyte, multilayer polypropylene micro-porous membranes as the separator. The two-electrode system were charged at 1 C (or 3 C) for 60 min (or 20 min) and discharged at 1 C (or 3 C) down to 1.2 V cut-off, the current for 1 C is about 14 mA. Cycle test was performed with a battery test apparatus NEWWARE BTS-610 (Newware Technology Co., Ltd., China).

For cyclic voltammetry test (CV) and electrochemical impedance spectroscope (EIS), a three-electrode cell was used with an Hg/HgO