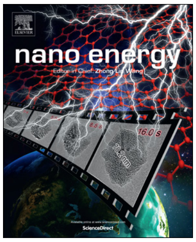
Nano Energy (2014) **10**, 229-234

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/nanoenergy



RAPID COMMUNICATION

High-performance aqueous battery with double hierarchical nanoarrays

Xiaochao Wu, Zhiyi Lu, Wei Zhu, Qiu Yang, Guoxin Zhang, Junfeng Liu, Xiaoming Sun*

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, PR China

KEYWORDS
Hierarchical nanoarrays;
Aqueous battery;
Energy density;
Power density

Abstract
Considerable efforts have been devoted to pursue both higher energy density and power density for a number of energy storage devices. Here we report a hierarchical $Co_xFe_{3-x}O_4$ nanoarray which is directly grown on three-dimensional conductive substrates by a facile two-step hydrothermal reaction and a following annealing treatment. This hierarchical structure provides several advantages including a large contact surface area, short ion diffusion path and good charge transport, which are all beneficial for improving the electrochemical performance. As an integrated anode electrode in aqueous electrolyte, it delivers a high discharge capacity of ~2.13 mAh cm^{-2} (or ~304.30 mAh g^{-1}) at a scan rate of 1 mV s^{-1}, retains at ~1.68 mAh cm^{-2} at 10 mV s^{-1}, and preserves ~88% of the initial capacity after 500 cycles. Combining our hierarchical Co_3O_4@Ni-Co-O nanoarray as the cathode electrode, we assemble a double hierarchical structured aqueous battery, which achieves an energy density and power density of ~2.1 mWh cm^{-2} and 42.8 mW cm^{-2}, respectively. It also exhibits good cycling stability with a capacity of ~1.8 mAh cm^{-2} after 500 charge/discharge cycles.

Introduction

Popularization of portable electronics and electric vehicles worldwide stimulates the development of energy storage devices, such as lithium ion batteries [1-4], metal-air batteries [5], aqueous batteries [6] and supercapacitors [7,8], toward higher power density and energy density, which significantly depends upon the advancement of new materials used in these devices. These characteristics are also important for storing energy from electrical grids supported by intermittent energy sources such as solar [9], wind [10] and hydropower [11]. Currently lithium ion batteries are dominantly powering most of today's portable electronics due to the high efficiency and energy density, but the high expense and possible unsafety originated from the flammability of organic electrolytes and high reactivity of Li containing materials are two major concerns for our daily life [1]. Instead, alkaline electrolyte rechargeable battery is thought of an advanced energy storage system [12,13], among which the century-old nickel-iron battery is one of the most promising members because of its

---

*Corresponding author.
E-mail address: sunxm@mail.buct.edu.cn (X. Sun).

http://dx.doi.org/10.1016/j.nanoen.2014.07.026

high theoretical energy density (267 Wh kg^{-1}), long cycling life and low cost [14,15]. Recently, Wang et al. and Long et al. have paired two hybrid materials ($Ni(OH)_2$/C and FeO_x/C) affording an ultrafast version of Ni-Fe aqueous battery with higher energy density and power density than traditional Ni-Fe battery [16,17]. Despite these great efforts [18], the performance needs to be further improved, which is highly dependent on the structure and morphology design of the active materials.

Constructing hierarchical nanoarray architecture has been demonstrated as one of the most efficient routes to significantly improve the electrochemical energy storage performance of the electrode materials. Specifically, hierarchical nanoarray architecture can offer a direct growth of the active materials on conductive substrates, which ensures a good electric contact and consequently enhances the rate capability. Moreover, the three dimensional structure possesses a much higher contact area with the electrolyte and thus offers a larger electrochemical surface area. In addition, the hierarchical nanoarray may even circumvent the conflict between the mass loading of electrochemically active material and its utilization efficiency [19-21]. These above advantages promote the hierarchical nanoarrays for energy storage devices, such as SnO_2/MnO_2 [20], Co_3O_4@Ni-Co-O [21], $MnMoO_4$/$CoMoO_4$ [22], Co_3O_4 [23,24], Co_3O_4@NiO [25] and Co_3O_4/Fe_2O_3 [26]. However, most of the above works are concentrated on the development of the electrode materials with positive potential window, while few efforts are devoted to the exploration of active materials within the negative potential window, which is equally important for increasing the operation voltage and thereby improving the energy density of the energy storage devices. Carbonaceous materials can act as negative materials, but their specific capacitances are usually less than 300 F g^{-1} in aqueous electrolyte [27].

Here in this work, we have successfully fabricated hierarchical $Co_xFe_{3-x}O_4$ nanoarray which composed of well aligned nanowire@nanorods arrays on Cu foam by a simple two-step hydrothermal reaction and a following annealing treatment. This hierarchical architecture showed a high areal capacity (~2.13 mAh cm^{-2}) and excellent rate capability, owing to the high mass-loading and high porosity of the active materials, and the direct contact to the current collector underlying. To the best of our knowledge, this is the first report on Fe-based hierarchical nanoarray as anode for aqueous batteries. In addition, by employing hierarchical Co_3O_4@Ni-Co-O nanoarray [21] as the positive electrode, a new battery system was established as shown in Figure 1, which delivered a high energy density of ~2.08 mWh cm^{-2}, and a power density of ~42.56 mW cm^{-2} with less than 3 min for one charge-discharge cycle. Combination of these features endows the double hierarchical nanoarrays-based aqueous battery as one of the most potential candidates for next generation energy storage devices.

Experimental section

Synthesis of $Co_3Fe_{3-x}O_4$ hierarchical nanoarray

The hierarchical $Co_xFe_{3-x}O_4$ nanoarray was synthesized by a simple route. In a typical procedure, $Co(NO_3)_2 \cdot 6H_2O$ (2 mmol), NH_4F (8 mmol) and urea (10 mmol) were dissolved in 36 mL of distilled water and stirred to form a clear solution. Cu foam (approximately 3 cm × 2 cm) was carefully cleaned with concentrated HCl solution (37 wt%) in an ultrasound bath for less than 3 min in order to remove the surface metallic oxide layer, and then cleaned with deionized water and absolute ethanol for 5 min each. The aqueous solution and the conductive metal foam were transferred to a 40 mL Teflon-lined stainless-steel autoclave, which was sealed, maintained at 120 °C for 12 h and then allowed to cool to room temperature within 15 min using cooling water. The thin film on the conductive substrate was rinsed several times with distilled water and ethanol with the assistance of ultrasonication, and dried at 80 °C for 6 h. In the second step, $Fe(NO_3)_3 \cdot 9H_2O$ (3 mmol) NH_4F (8 mmol) and urea (10 mmol) were dissolved in 36 mL of distilled water and stirred to form a clear solution. Then the as-prepared sample mentioned above and the aqueous solution were transferred to a 40 mL Teflon-lined stainless-steel autoclave, which was sealed, maintained at 100 °C for 6 h and then allowed to cool to room temperature within 15 min using cooling water. The thin film on the Cu foam was rinsed several times with distilled water and ethanol with the assistance of ultrasonication, and dried at 80 °C for 6 h. Finally the sample was put into a quartz tube and annealed in N_2 gas at 450 °C for 3 h.

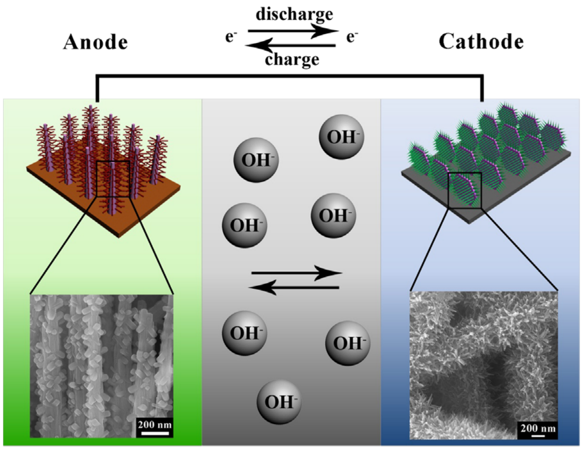


Figure 1 The schematic drawing of the double hierarchical nanoarrays-based aqueous battery.

Synthesis of FeO_x film

The FeO_x film was synthesized by a similar route above. In a typical procedure, $Fe(NO_3)_3 \cdot 9H_2O$ (3 mmol), NH_4F (8 mmol) and urea (10 mmol) were dissolved in 36 mL of ethylene glycol and stirred to form a clear solution. A piece of precleaned copper foam and the solution were transferred to a 40 mL Teflon-lined stainless-steel autoclave, which was sealed, maintained at 100 °C for 6 h and then allowed to cool to room temperature within 15 min using cooling water. The thin film on the Cu foam was rinsed several times with distilled water and ethanol with the assistance of ultrasonication, and dried at 80 °C for 6 h. Finally the sample was put into a quartz tube and annealed in N_2 gas at 450 °C for 3 h.

Characterizations

X-ray powder diffraction (XRD) patterns were recorded on an X-ray diffractometer (Rigaku D/max 2500) at a scan rate