

Freestanding hierarchical NiO/MnO₂ core/shell nanocomposite arrays for high-performance electrochemical energy storage



Y.F. Yuan^{a,b,*}, J.X. Lin^a, D. Zhang^c, S.M. Yin^a, Y.L. Zhao^a, J.L. Yang^a, Y.B. Chen^a, S.Y. Guo^{a,b}

^a College of Machinery and Automation, Zhejiang Sci-Tech University, Hangzhou 310018, China

^b College of Materials and Textile, Zhejiang Sci-Tech University, Hangzhou 310018, China

^c Hang Zhou City of Quality and Technical Supervision and Testing Institute, Hangzhou 310019, China

ARTICLE INFO

Article history:

Received 19 October 2016

Received in revised form 26 December 2016

Accepted 1 January 2017

Available online 3 January 2017

Keywords:

NiO

MnO₂

Core/shell nanocomposite arrays

Electrochemical energy storage

ABSTRACT

Freestanding hierarchical NiO/MnO₂ core/shell nanocomposite arrays were synthesized by a two-step method including chemical bath deposition and hydrothermal reaction. Their morphology and structure were characterized by XRD and SEM. NiO net-like macroporous nanoflake arrays grow on Ni foam as freestanding core backbone material, and MnO₂ nanosized mesoporous foams grow on the two sides of NiO nanoflakes, forming secondary shell structure on NiO nanoflakes. Electrochemical performances were examined by cyclic voltammetry (CV), galvanostatic charge-discharge and electrochemical impedance spectroscopy (EIS). NiO/MnO₂ nanocomposite arrays show improved electrochemical performance: high specific capacity (190 mAh g⁻¹ at 1 A g⁻¹ and 167 mAh g⁻¹ at 20 A g⁻¹) and high cycling stability (92% retention at 2 A g⁻¹ after 4000 cycles) as well as good rate performance. CV testing indicates both NiO and MnO₂ participate in the Faradic reactions even though MnO₂ nanosized mesoporous foam covers the surface of NiO nanoflakes. EIS shows that charge-transfer resistance and Warburg resistance decrease, which reflects that the nanocomposite structure can improve electrochemical activity of NiO and MnO₂. SEM observation on the cycled electrode confirms the intense synergistic effect of NiO/MnO₂ nanocomposite. Electrochemical investigation reveals the freestanding hierarchical NiO/MnO₂ core/shell nanocomposite array designed here is a good electrode material for high-performance electrochemical energy storage.

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1. Introduction

Electrochemical energy storage device with higher power density, faster charge-discharge rate and longer cycle life have attracted research interests for various applications, which can substitute for the fossil fuel energy as a rechargeable and environmentally friendly power sources including secondary batteries and electrochemical capacitors [1,2]. The active materials for electrochemical energy storage device include transition metal oxides, conducting polymers, carbon-based materials, and so on [3–10]. Among them, NiO has been considered as one of the most attractive electrode materials because of its low cost, abundance, high theoretical specific capacity (SC) and good electrochemical reaction reactivity [11,12]. Nevertheless, low electrical conductivity of NiO leads to the fact that its real SC is far below the theoretical

value (718 mAh g⁻¹), and repeatedly structure shrinkage/expansion during the charge-discharge cycles results in poor cycling stability [13,14]. Therefore, it is a great challenge to improve the performance of NiO as electrode material for high-performance batteries and electrochemical capacitors.

The electrochemical reaction usually occurs at the surface and in the bulk near the surface of the electrode materials. It is reported that the effective depth of the bulk is around 20 nm. Therefore, material design is an important method to improve electrochemical performances. Various NiO materials have been studied, such as nanowires, nanoflakes, nanospheres, nanowalls, nanotubes and nanofibers [15–17]. Nevertheless, SC and cycling stability of NiO are still dissatisfactory. It is an effective solution that transition metal oxides are directly deposited onto current collector in binder-free model. The direct contact between active materials with current collector can facilitate electron transport and enhance the electron collection efficiency. In addition, the hierarchical composite structure is favorable for improving electrochemical activity and cycling stability of electrode materials. MnO₂ owns many attractive characteristics including high theoretical SC, low

* Corresponding author at: College of Machinery and Automation, Zhejiang Sci-Tech University, Hangzhou 310018, China. Tel.: +86 571 8684 3343.

E-mail addresses: yuanf@zstu.edu.cn, yyfzju@hotmail.com (Y.F. Yuan).

cost, environmentally friendly, non-toxicity and natural abundance [18,19], so it is an appropriate composite candidate for NiO. More recently, the hierarchical composites of NiO and MnO₂ have been investigated. Chen et al. synthesized MnO₂ nanosheets on NiO microtubes, exhibiting a SC of 37 mAh g⁻¹ at 0.5 A g⁻¹ [20]. Zhang et al. prepared NiO/MnO₂ core/shell composite through two-steps hydrothermal method, exhibiting a SC of 80 mAh g⁻¹ at 1 A g⁻¹ [21]. Liu et al. reported a core-shell NiO/MnO₂ heterostructured composite on Ni foam (*), showing a SC of 100 mAh g⁻¹ at 5 mA cm⁻² [22]. These works reveal that it is effective to design the hierarchical composite materials of NiO and MnO₂.

In this paper, we further report a simple and facile method to prepare freestanding hierarchical net-like array-structured NiO/MnO₂ nanocomposite. Through chemical bath deposition (CBD), the precursors grow on Ni foam without any binders and connect with each other to form freestanding net-like arrays. After calcination, the precursors decompose to NiO but the freestanding backbone maintains stable. Then, MnO₂ directly grows on the two sides of NiO nanoflakes as the structure of the nanosized mesoporous foam, forming a secondary shell structure. The prepared NiO/MnO₂ nanocomposite exhibits high SC of 190 mAh g⁻¹ at 1 A g⁻¹ and good capacity retention of 92% at 2 A g⁻¹ after 4000 cycles, showing good electrochemical energy storage performance.

2. Experimental

All of raw materials were of analytical grade and used without further purification. The precursors were prepared on Ni foam by CBD. 0.5 M NiSO₄ and 0.15 M K₂S₂O₈ were dissolved into 20 ml distilled water under constant magnetic stirring, respectively. Then, the solutions were mixed and transferred into the water bath at 50 °C. After 40 minutes, a piece of cleaned Ni foam (2 × 2 cm²) was immersed vertically into the solution. Meanwhile, 4 ml aqueous ammonia (25–28 wt% NH₃) was put into the reaction solution. After the CBD reaction for 40 min, Ni foam was taken out and washed in distilled water several times, then dried in an oven at 60 °C for a whole day. In order to get NiO, the Ni foams with the precursors were calcined at 350 °C in argon for 2 h.

MnO₂ grew on NiO by a hydrothermal reaction. 40 ml 0.02 M KMnO₄ was stirred for 1 h, then the solutions were transferred into 100 ml Teflon-lined stainless steel autoclave with above annealed Ni foams. After sealed, the autoclave was maintained at 120 °C for 12 h, and then cooled down to room temperature naturally. Finally, active materials-coated Ni foams were taken out and washed in distilled water several times, then dried in an oven at 60 °C for a whole day.

The electrochemical measurements were carried out in a three-electrode cell containing 2 M KOH aqueous solution as the electrolyte with a saturated calomel electrode as reference electrode and a Pt foil as counter-electrode. Cyclic voltammetry (CV) measurements and electrochemical impedance spectroscopy (EIS) were performed at an electrochemical workstation (Princeton Applied Research, 2273). CV measurements were conducted at various scan rates between 0 and 0.6 V at room temperature. EIS was tested with a superimposed 5 mV sinusoidal voltage over the frequency range of 0.01 Hz to 100 kHz. The galvanostatic charge-discharge tests were carried out by Neware battery program-control test system over the range of 0–0.45 V at various current densities.

3. Results and discussion

The phase structure and purity of the resulting product were analyzed by XRD (Fig. 1). The three intense peaks are typical

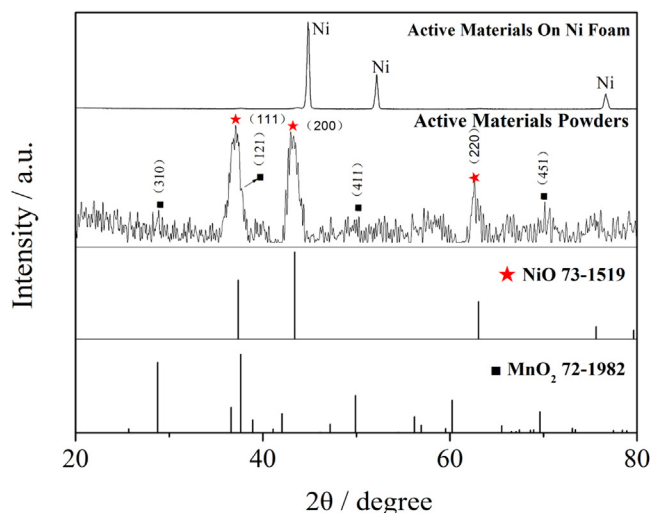


Fig. 1. XRD patterns of NiO/MnO₂ nanocomposite arrays on Ni foam and its corresponding pure powder scratched from the Ni foam.

diffraction peaks of Ni which comes from Ni foam substrates. Under the background of the three intense Ni diffraction peaks, the diffraction peaks of a small amount of active materials are too weak to be observed, and only two weak peaks appear at 2θ of around 37° and 43°. In order to eliminate this disturbance, the active materials were scratched from the Ni foam for XRD analysis. For pure active materials powder, the prominent peaks appear at 2θ of 37.1°, 43.0°, 62.6°, corresponding to the diffractions from (111), (200) and (220) of cubic NiO (JSPDS card no.73-1519). The average crystallite size of NiO is calculated to be 57.8 nm. Moreover, the other peaks marked as “■” at 2θ of 28.7°, 37.6°, 49.8° and 69.6° can be indexed to be (310), (121), (411) and (451) crystal planes of tetragonal MnO₂ (JSPDS card no.72-1982). XRD result confirms the successful preparation of NiO/MnO₂ composites on the Ni foam substrates. Furthermore, XRD does not detect any signals from other materials, which indicates the high purity of the synthesized product.

The morphologies of as-prepared NiO/MnO₂ composites were analyzed by SEM (Fig. 2). After the CBD reaction, NiO nanoflakes with 20 ~ 50 nm in thickness and 400 ~ 900 nm in length connect with each other and erectly grow on Ni foam, forming freestanding net-like macroporous nanoflake arrays whose pore diameter ranges from 100 to 400 nm (Fig. 2a). The net-like array structure provides good structure stability. The upright growth of the nanoflakes exposes NiO surface as large as possible. The two sides of NiO nanoflakes can be used as substrates for the growth of the shell materials. These factors make NiO net-like nanoflake array becoming an appropriate core backbone material. The mass of NiO is 1.5 mg. After the hydrothermal reaction, NiO still maintains the cross-linked net-like array architecture, but their surfaces are uniformly covered by burr-like MnO₂ (Fig. 2b) which forms a secondary shell structure on NiO nanoflakes. The thickness of the MnO₂ shell layer is about 40 to 60 nm and the mass is about 1.0 mg. In a higher magnification SEM image (Fig. 2c), it can be clearly seen that MnO₂ on NiO nanoflake presents nanosized mesoporous foam structure. The mesopore diameter ranges from 30 to 50 nm. The nanosized mesoporous foam architecture promotes the contact between the electrolytes with MnO₂, and improves electrochemical activity of MnO₂. The growth of MnO₂ on the two sides of NiO nanoflakes increases the loading mass of MnO₂ in unit area of foam Ni. For comparison, MnO₂ is directly synthesized on Ni foam by the same hydrothermal process and its SEM image is given in Fig. 2d.

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