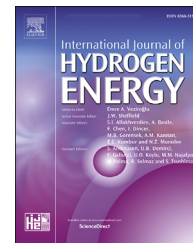




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Boosting the capacitance of NiCo₂O₄ hierarchical structures on nickel foam in supercapacitors

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ABSTRACT

A facile method of directly growing NiCo₂O₄ hybrid hierarchical nanostructures on nickel foam is developed by a hydrothermal and post heat-treatment method without using any surfactant, stabilizer or organic binder. Due to the rich porous nanostructures, relative large specific surface area (177.71 m² g⁻¹) of the NiCo₂O₄ hybrid structure and efficient electrical contact with the conductive nickel substrate, the NiCo₂O₄-NF hybrid electrode shows significantly enhanced specific capacitance (3105.1 F g⁻¹ at 1 A g⁻¹), outstanding rate properties (1621.3 F g⁻¹ at 20 A g⁻¹ and 1191.5 F g⁻¹ at 50 A g⁻¹) and high energy density (95.26 Wh kg⁻¹). This facile and effective design method opens up new possibilities for producing binder-free electrodes in high-performance electrochemical supercapacitors and miniaturized devices.

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Introduction

As an emerging energy storage device, supercapacitor holds an important and indispensable position due to its ultrahigh power density, quick charge-discharge ability, long cycle life and operational safety. Based on the energy storage mechanism, supercapacitors can be divided into electrochemical double layer capacitors (EDLCs), pseudocapacitors and hybrid supercapacitors [1]. The capacitances of EDLCs usually arise from the ions adsorption/desorption at the electrode/electrolyte interface. This type of supercapacitors has excellent cycling stability but usually unsatisfying energy density. As for pseudocapacitors, faradaic reactions occur at or near

surface of electrode, thereby higher capacitances and energy densities are usually obtained. Hybrid supercapacitors [2–5] are composed of two electrodes with different charge storage mechanisms, that is, one capacitive and one faradaic, aiming to combine the superiorities of high power density, long cycling life and high energy density together.

In recent years, pseudocapacitors use metal oxides/hydroxides [6–8] and conducting polymers [9,10] as electrode materials have been widely studied and have achieved notable improvements in energy density. Due to the multi-electron redox reactions in transition metal oxides, they usually deliver higher specific capacitances (C_{sp}) than those of conductive polymers. Compared to monometallic nickel and cobalt oxides, NiCo₂O₄ has a high C_{sp} value and higher

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electrical conductivity, which can be ascribed to the contribution of its $\text{Ni}^{2+}/\text{Ni}^{3+}$ and $\text{Co}^{2+}/\text{Co}^{3+}$ redox couples [11–13].

Since the first report of NiCo_2O_4 as a supercapacitor material in 2010 [14], many researchers have devoted themselves to improving the electrochemical performances of NiCo_2O_4 . One obstacle hindering the practical application of NiCo_2O_4 is its inadequate conductivity, which inevitably limits the fast electron transport at high rates. To solve this problem, one approach is to prepare electrode materials with rationally designed structures, for example, multishell [15], yolk shell [16] and core-shell [17] structures. These kinds of materials can combine the superiority of nano-sized subunits and hollow structures. The nanosized particles can shorten ion and electron transport pathways. The hollow space between the shells can ignore the aggregation of electroactive materials and release the volume expansion during the electrochemical cycling process, thus enabling excellent cycling stability. In addition, the porous structures usually endow the materials with high surface areas, which are helpful for the accessibility of electrolytes into the interior of the active materials, providing more opportunity for faradaic redox reactions. In this way, substantially improved electrochemical performance can be obtained [18,19].

Another efficient approach is growing NiCo_2O_4 with other metal oxides [20,21] and/or carbonaceous materials [17,22–24] to exert a synergetic effect between different components. Through this method, the rate capability of the material can be enhanced. However, the problem of unsatisfied energy storage capacity still exists, which is probably due to the addition of conductive additives and polymer binders in the preparation of electrodes. The addition would inevitably lower the C_{sp} value of the electrode due to the “dead” weight caused by electroinactive materials. In addition, a posttreatment with high pressures used in electrode preparation destroys the superiority of the original nanostructures and hinders the fast diffusion of electrolytes and ions through the entire electrode [25].

A feasible method to avoid this problem is to directly grow electroactive materials onto highly conductive metal substrates, such as Ni foam, stainless steel sheet and Ti foil. This type of “binder-free” electrode does not need the addition of conductive additives and polymeric binders in the preparation of the electrode, which can effectively avoid the “dead surface” and enhance the charge/mass exchanges. The many advantages of this type of electrode, including large electroactive area, good electrical/ionic conductivity, and easy electrolyte penetration, inevitably lead to an enhanced high rate performance and cycling stability. However, if the adhesion between the substrate and the electroactive material is poor, unsatisfactory cycling stability usually occurs. The nonuniform distribution or flaking off of aggregated active material from the substrate has proven to be the main reason for fading capacity in the cycling process [18].

In this work, we design a novel NiCo_2O_4 -NF electrode by directly growing 3D hierarchical NiCo_2O_4 nanostructures on nickel foam. The NiCo_2O_4 nanosheets have a relatively high specific surface area and an ample porous structure. When used in supercapacitors, the NiCo_2O_4 -NF electrode delivers a high C_{sp} value of 3105.1 F g^{-1} at a current density of 1 A g^{-1} .

Even at a high current rate of 50 A g^{-1} , the electrode maintains a C_{sp} value of 1191.5 F g^{-1} , showing superior rate capability. The maximum energy density reaches 95.26 Wh kg^{-1} . A preliminary investigation of a NiCo_2O_4 /NF//carbon asymmetric supercapacitor is also conducted.

Experimental section

Synthesis and characterization of NiCo_2O_4 microspheres

Prior to synthesis, the nickel foams (NF in short) were rinsed with acetone, etched in dilute HCl for 20 min, and then washed thoroughly with deionized water and absolute alcohol in order to remove possible surface oxide layers. Hierarchical NiCo_2O_4 /NF was prepared using a hydrothermal and annealing process. In a typical reaction, 1 mmol $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 2 mmol $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 70 ml water to form a transparent solution. Then, 15 mmol hexamethylenetetramine (HMT) was added while stirring. After it was dissolved completely, transfer the solution to a 100 ml Teflon-lined stainless autoclave and immerse a piece of pretreated NF in it. Place the sealed autoclave in an electric furnace and maintain at $120 \text{ }^\circ\text{C}$ for 12 h. Then the products were poured out, washed with water and ethanol for several times, and then dried under vacuum at $60 \text{ }^\circ\text{C}$ for 12 h. To further increase the crystallinity of NiCo_2O_4 , the NF with the precursor was annealed in air at $250 \text{ }^\circ\text{C}$ for 2 h. For comparison, the NiCo_2O_4 sample was prepared using the same method without adding nickel foam.

Active carbon used as negative materials were bought from Nanjing XFNANO Materials Tech Co., Ltd., and used without further purification.

Materials characterization

The crystallographic structure and composition of the as-prepared samples were detected using powder X-ray diffraction (XRD, Bruker D8 Advance). The morphologies were examined using a field emission scanning electron microscope (FESEM; JEOL JSM-6700F) and transmission electron microscope (TEM; Talos F200x G2) equipped with selected area electron diffraction (SAED). Elemental composition was characterized by an energy dispersive X-ray (EDX) equipment. The specific surface area was detected by nitrogen absorption-desorption using the Brunauer-Emmett-Teller (BET) method (autosorb-iQ-C). Surface elemental composition and valence state analysis was performed using XPS (Thermo Scientific K-Alpha).

Electrochemical measurements

All electrochemical performances of the electrodes were evaluated using a CHI 760C electrochemical workstation (CHI, Shanghai, China) and a CT2001A Land battery system using 2 mol L^{-1} KOH as an electrolyte. Saturated calomel electrode was used as the reference electrode and a bright Pt plate was used as the counter electrode. For the NiCo_2O_4 -NF sample, the fresh film on the NF ($1 \text{ cm} \times 1 \text{ cm}$) was used directly as the working electrode. For the NiCo_2O_4 sample, the working

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