Journal of Energy Chemistry xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Journal of Energy Chemistry

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

ELSEVIER

JEC JOURNAL OF ENERGY CHEMISTRY
http://www.journals.elsevier.com/journal-of-energy-chemistry/

Porous $NiCo_2O_4$ nanowires supported on carbon cloth for flexible asymmetric supercapacitor with high energy density

Huifang Zhang[a,b], Dengji Xiao[a,b], Qian Li[a,b], Yuanyuan Ma[a,b], Shuxia Yuan[a], Lijing Xie[a,*], Chengmeng Chen[a,*], Chunxiang Lu[c,*]

[a] CAS Key Laboratory of Carbon Materials, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, Shanxi, China
[b] University of Chinese Academy of Sciences, Beijing 100049, China
[c] National Engineering Laboratory for Carbon Fiber Technology, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, Shanxi, China

ARTICLE INFO

Article history:
Received 28 September 2017
Revised 30 October 2017
Accepted 31 October 2017
Available online xxx

Keywords:
All solid-state
$NiCo_2O_4$ nanowires
Carbon cloth
Activated carbon cloth
Asymmetric supercapacitor

ABSTRACT

Recently, binary metal oxides have been considerably researched for energy storage since it can provide higher electrical conductivity and electrochemical activity than single components. Besides, rational arrays structure design can effectively enhance the utilization of active material. In this article, we synthesis a porous $NiCo_2O_4$ nanowires arrays, which were intimate contact with flexible carbon cloth (CC) by a facile hydrothermal reaction and calcination treatment. The rational array structures of $NiCo_2O_4$ facilitate the diffusion of electrolyte and effectively increase the utilization of active material. The as-obtained $NiCo_2O_4$@CC electrode exhibits a high capacitance of 1183 mF cm^{-2} and an outstanding capacitance retention of 90.4% after 3000 cycles. Furthermore, a flexible asymmetric supercapacitor (ASC) using $NiCo_2O_4$@CC as positive electrode and activated carbon cloth (ACC) as negative electrode was fabricated, which delivers a large capacitance of 750 mF cm^{-2} (12.5 F cm^{-3}), a high energy density of 0.24 mWh cm^{-2} (3.91 mWh cm^{-3}), as well as excellent cycle stability under different bending states. These remarkable results suggest that as-assembled $NiCo_2O_4$@CC//ACC ASC is a promising candidate in flexible energy storage applications.

1. Introduction

The increasing depletion of fossil fuel resources and growing environment crisis requires the development of clean and sustainable electrochemical rechargeable systems [1–4]. Compared with lithium-ion batteries, supercapacitor can charge and discharge at a much faster rate, therefore they have advantageous in high power density energy storage requirements [5–7]. Recently, in order to satisfy the demands for portable electronic devices, the development of flexible and wearable supercapacitors [8] becoming more and more urgent. A critical component of flexible supercapacitor is the flexible electrode material, which can maintain the electrochemical performance while endure large levels of bend, stretch or even compress.

Various flexible nanostructured electrode materials and supercapacitor configuration have been researched. Such as 3D paper-like graphene by the hard template-directed ordered assembly [9], highly compressible PANI-SWCNT-sponge electrode by "dipping and drying" strategy and subsequent chemical oxidation polymerization [10], high-strength graphene composite film by molecular level coupling [11], highly flexible free-standing epidermal supercapacitor with 1 micron thickness [12] etc. However, most of these reports are nanocarbon-based flexible electrodes and symmetric configurations. To get an enhanced energy density of supercapacitor, pseudocapacitor or design an asymmetric configuration is considered to be efficient strategies. Pseudocapacitor exhibits a higher capacitance and energy density compared with EDLCs supercapacitors owing to the fast redox reactions. If utilization of two different materials as positive and negative electrode to construct an ASC device, a higher energy density will be easily obtained [13] according to the equation $E = 1/2CV^2$ [14]. Up to now, a series of pseudocapacitor and ASCs have been reported, for example, Wu et al. fabricated a high performance pseudocapacitor with 2D heterostructure film of ultrathin thiophene (TP) and electrochemically exfoliated graphene (EG) nanosheets, which exhibit impressive volumetric capacitance, high energy density and power density [15]. Chodankar et al. synthesis a 2D ultrathin nanoflakes of MnO_2 film on the flexible stainless foil, the pseudocapacitor shows excellent energy density of 23 Wh kg^{-1} and power density of 1.9 kW kg^{-1} [16]. Zheng et al. constructed a

* Corresponding authors.
E-mail addresses: xielijing@sxicc.ac.cn (L. Xie), ccm@sxicc.ac.cn (C. Chen), lucx@sxicc.ac.cn (C. Lu).

https://doi.org/10.1016/j.jechem.2017.10.034
2095-4956/© 2017 Published by Elsevier B.V. and Science Press.

planar ASC with MnO_2/poly (3,4-ethylenedioxythiophene)-poly (styrenesulfonate) (MP) as positive electrode and electrochemically exfoliated graphene as negative electrode, which exhibit volumetric energy density of 8.6 mWh cm^{-3} [17]. Xie et al. reported a ASC with CoNi-LDH as positive electrode and activated carbon as negative electrode, which delivers a high energy density of 46.59 Wh kg^{-1} at a power density of 107 W kg^{-1} [18] etc.

Pseudocapacitive characteristics electrode materials, such as Co_3O_4 [6], $NiMoO_4$ [19], $CoMoO_4$ [20], $ZnCo_2O_4$ [21] and $ZnWO_4$ [22] have been widely researched. Among them, $NiCo_2O_4$ is regarded as one of the most attractive electrode materials owing to its higher electrical conductivity and superior electrochemical properties [23,24]. However, owing to the severe aggregation of oxide nanoparticles and the short diffusion distance of electrolyte into electrodes (~20 nm), only the materials surface of $NiCo_2O_4$ can participation in the electrochemical reactions, thus leading to unsatisfactory specific capacitance [25]. In order to boost the utilization of active materials, a rational arrays structure design [26,27] by directly grown the electroactive materials on current collector will facilitate electron and ion transport and benefit for the full utilization of electrode materials. In addition, the use of polymer binder and conductive additives can be avoided, thus reduce the contact resistance between current collector and electrode materials. At present, some $NiCo_2O_4$ nanostructures grown on CC have been prepared [28,29], to the best of our knowledge, the study on a $NiCo_2O_4$@CC electrode used in an flexible ASC has seldom been reported to date.

Here, a flexible solid-state ASC with $NiCo_2O_4$@CC as the positive electrode and ACC as the negative electrode in PVA/KOH gel electrolyte was successfully fabricated. The positive electrode material $NiCo_2O_4$ with hierarchical porous nanowires structure were grown on CC with the aid of hydrothermal treatment combined with subsequent calcination process. We studied the structural evolution process of NiCo-precursor@CC to $NiCo_2O_4$@CC with the increase of calcinations temperature, the results suggest that the spinel $NiCo_2O_4$ phase began to form at the calcination temperature of 250 °C and completely formed at 300 °C. In this paper, ACC was used as negative electrode in an flexible ASC for the first time due to their inherent porous structure and excellent mechanical flexibility. Our optimal ASC device could be operated at a high voltage of 1.5 V and exhibited a high areal capacitance of 750 mF cm^{-2} (12.5 F cm^{-3}), high energy density of 0.24 mWh cm^{-2} (3.91 mWh cm^{-3}) and power density of 0.75 mW cm^{-2} (12.51 mW cm^{-3}), as well as excellent cycle stability of 72.5% capacitance retention under different bending states after 3000 cycles. The stored energy density of our ASC device increased at least 6996 % when the voltage window increase from 0.6 V to 1.5 V. Such ASC device may open up opportunities for applications in flexible, lightweight and wearable electronics.

2. Experimental

2.1. Preparation of $NiCo_2O_4$@CC

CC (thickness: 0.36 mm, unit weight: 120 g m^{-2}) was cut into small pieces (2 cm × 3 cm), set aside. $Co(NO_3)_2$ $6H_2O$ (1.16 g), $Ni(NO_3)_2$ $6H_2O$ (0.58 g), and urea (0.6 g) were added into DI water (40 mL) under stirring for 15 min, then transferred to a 50 mL Teflon-lined stainless autoclave. A piece of CC was putting into the above soultion, after hydrothermal reaction heated at 120 °C for 4 h, CC was taken out and rinsed with DI water and ethanol to remove the other impurities. Finally, the dried product was annealed in a quartz tube at different temperatures ranging from 200 to 500 °C for 2 h.

2.2. Fabrication of $NiCo_2O_4$@CC//ACC solid-state ASC

The solid-state ASC was fabricated by using $NiCo_2O_4$@CC as positive electrode and ACC as negative electrode with PVA/KOH gel as electrolyte. In a typical process, 1.8 g KOH was added into 30 mL PVA solution (3 g PVA, 30 mL water) and heated at 80 °C until the solution became clear. $NiCo_2O_4$@CC and ACC electrodes were coated with a thin layer PVA/KOH gel electrolyte and assembled together.

2.3. Characterization

XRD spectroscopy (Bruker D8 Advance X-ray powder diffractiometer) and X-ray photoelectron spectroscopy (AXIS Ultra DLD spectrometer instrument) were carried out to examine the phase structures of the products. Thermogravimetric analysis (TGA) was performed on a NETZSCH STA409PC instrument. The morphology and mapping of the products were characterized by scanning electron microscopy (SEM, JSM-7001F), X-ray energy-dispersive spectra (EDAX) connected with SEM equipment and transmission electron microscope (TEM, JEM-2010) . The BET surface area and the pore size distribution were measured at 77 K on a nitrogen physisorption apparatus (JW-BK 122 W). Barrett–Joyner–Halenda (BJH) model was used to determine the pore size distribution of $NiCo_2O_4$@CC product. Density functional theory (DFT) was used to calculate the pore size distribution of activated carbon cloth.

2.4. Electrochemical measurements

The electrochemical performances of single electrodes were characterized by a three-electrode configuration in 6 M KOH aqueous electrolyte, with Pt foil as the counter electrode and Hg/HgO as the reference electrode. $NiCo_2O_4$ @CC and ACC (both 1.4 cm × 1 cm) were used directly as the working electrode. By TGA tests (Fig. S1), the mass loading of $NiCo_2O_4$ on CC was around 1.2 mg cm^{-2}. The areal capacitances (C_A, mF cm^{-2}) and gravimetric capacitances (C_M, F g^{-1}) were calculated from the galvanostatic discharge curves by the following equations::

$$C_A = 1000 I\Delta t / S\Delta V \quad (1)$$

$$C_M = I\Delta t / m\Delta V \quad (2)$$

where I (A) is the discharge current, Δt (s) is the discharge time, S (cm^2) is the area of single electrode, m (g) is the mass of active materials in single electrode, for positive electrode, m (g) is the mass of $NiCo_2O_4$, for negative electrode, m (g) is the mass of ACC, and ΔV (V) is the voltage window during the discharge process.

As for an ASC, the positive and negative electrode should follow the relationship $q_+ = q_-$. For each electrode, the charge (q) stored depends on the gravimetric capacitances (C_M), the voltage window during the discharge process (ΔV) and the mass of each electrode (m) according to the following equation [14]:

$$q = C_M \times \Delta V \times m \quad (3)$$

Therefore, in order to get the charge balance, the mass loading between the positive and negative electrode will follow the equation below [14]:

$$m_+/m_- = C_{M-} \times \Delta V_- / C_{M+} \times \Delta V_+ \quad (4)$$

Based on the gravimetric capacitances values and voltage window for two electrodes, the suitable mass ratio of $NiCo_2O_4$@CC/ACC was expected to be 1:2.18.

The electrochemical characterizations of the solid-state ASC were performed in a two-electrode system. The areal capacitance, areal energy density and power density, volumetric capacitance,

Please cite this article as: H. Zhang et al., Porous $NiCo_2O_4$ nanowires supported on carbon cloth for flexible asymmetric supercapacitor with high energy density, Journal of Energy Chemistry (2017), https://doi.org/10.1016/j.jechem.2017.10.034