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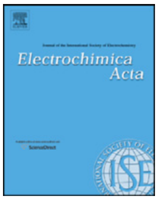

Preparation of Co_3O_4 nanowires grown on nickel foam with superior electrochemical capacitance

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ABSTRACT

Co_3O_4 nanowires have been successfully synthesized on nickel foam by a hydrothermal method. The morphology of Co_3O_4 is examined by scanning and transmission electron microscopy and the phase structure of Co_3O_4 nanowires is confirmed by X-ray diffraction. The electrochemical capacitance behavior of the Co_3O_4 nanowires electrode is investigated by cyclic voltammetry, galvanostatic charge/discharge test and electrochemical impedance spectroscopy in 6 mol dm^{-3} KOH solution. The results show that the Co_3O_4 nanowires have diameters of around 100 nm and the lengths up to 1–2 μm. The specific capacitance of Co_3O_4 nanowires is 1019.58 F g^{-1} at 3.38 A g^{-1} and 466.06 F g^{-1} at 33.80 A g^{-1}. The capacitance loss is less than 5% after 1000 charge/discharge cycles at 3.38 A g^{-1} and with columbic efficiency higher than 98%. The enhancement of pseudocapacitive properties at a higher charging/discharging rate is due to the porous nanostructure and the high utilization of active material.

1. Introduction

Electrochemical capacitors, also known as supercapacitors, are recognized as important electrical energy storage devices, which have a much larger capacity than conventional physical capacitors, and a much higher charging/discharging rate capability than primary/secondary batteries [1]. Electrochemical supercapacitors are classified into two types on the basis of their charge storage mechanisms, namely: (1) double-layer capacitors and (2) redox supercapacitors. Carbon (e.g., activated carbon, carbon nanotube and graphene) is recognized as a promising material for electrochemical double layer capacitors because of its low cost. The specific capacitance of some carbon materials already reaches 326.5 F g^{-1} in aqueous electrolytes [27]. RuO_2 and IrO_2 are well studied materials used as pseudocapacitive electrode materials with remarkable performance [2]. The RuO_2 electrode with its extraordinary specific capacitance (863 F g^{-1}) is the most suitable electrode material for supercapacitor [28–30]. The use of these materials, however, is limited due to their high cost. Therefore, the development of high performance and low cost electrode materials for supercapacitors has attracted increased interest in recent years. Alternative materials, such as NiO_x [3–6], CoO_x [7–17], CuO [18], FeO_x [19,20], V_2O_5 [21], and MnO_2 [22–24], have been fabricated by various groups in order to overcome the cost factor. Among these materials, Co_3O_4 has been demonstrated to be a promising electrode material for pseudo-capacitors due to its low environmental pollution, low cost and extremely high theoretical specific capacitance (3560 F g^{-1}) [13]. The morphology of electrode plays an important role in capacitance enhancement. In general, a porous structure with a large surface area significantly improves the charge transfer and capacitance of an electrode [7,8]. Previously, Gao et al. investigated the supercapacitor performance of nickel foam supported Co_3O_4 arrays prepared by an ammonia-evaporation induced method. Its high capacitance of 746 F g^{-1} is obtained at 5 mA cm^{-2} (0.312 A g^{-1}) [8]. Qing et al. prepared that Co_3O_4 with nanoflower structures exhibited a specific capacitance of 1936.7 F g^{-1} at 0.2 A g^{-1} and 1309.4 F g^{-1} at 3 A g^{-1} [10]. Importantly, a high-rate charge/discharge ability is highly desirable for the electrode materials used in supercapacitors. Recently, Xia et al. prepared Co_3O_4 nanostructured electrodes with nanostructures which displayed a high specific capacitances of (599 F g^{-1} at 2 A g^{-1} and 439 F g^{-1} at 40 A g^{-1}) [11,12]. Meher et al. used a facile hydrothermal technique to synthesize highly layered Co_3O_4 with excellent surface area and porosity. The as-prepared ultra-layered Co_3O_4 structures displayed a high specific capacitance of 548 F g^{-1} at a current density of 8 A g^{-1} and retained 66% of capacitance at 32 A g^{-1} [25]. The enhanced supercapacitor performances are due to their unique porous structure providing fast ion and electron transfer [11,14–16], large reaction surface area [7–10,12,13] and good electrochemical reversibility [7]. Recently, many groups use porous Ni frameworks as substrates (or current collectors) for loading the electro-active materials (e.g., NiO, CuO and Co_3O_4) to obtain nano-structured electrodes [4,6,8,10,11,13,18]. The electro-active materials were directly grown onto nickel foam via a

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hydrothermal method to obtain a conducting additive-free and binderless electrode with high utilization of the active material. Considerable improvement in the pseudocapacitive performance was confirmed (as compared to that obtained using a conventional flat substrate). The proposed protocol can be generally performed on any conductive surface, which can be inexpensive, lightweight, flexible, and wear able, allowing the prepared supercapacitors to be integrated into mobile micro-power systems.

In this study, Co_3O_4 nanowires have been successfully synthesized on nickel foam by a hydrothermal method. The superior capacitance properties and excellent cycling stability are due to the porous nanostructure and the high utilization of active material.

2. Experimental

2.1. Preparation and characterization of Co_3O_4 nanowires

Recently, the different electro-active materials were prepared by adding all kinds of complexing agent (e.g., ammonia and urea) into the corresponding metal salt aqueous solution. All kinds of shapes of nano-sized dimension, such as nanospheres, nanoflowers, nanowires, and nanotubes were obtained by thermal treatment. Li et al. also report an ammonia-evaporation-induced synthetic method for metal (Ni, Cu, Zn, and Cd) hydroxide/oxide nanostructures [31]. In this study, Co_3O_4 nanowires attached on nickel foam were prepared via a hydrothermal method. In detail, 2 mmol $Co(NO_3)_2$ and 10 mmol of $CO(NH_2)_2$ (urea) were dissolved respectively into 50 mL of water, the solution was magnetically stirred for 10 min at room temperature. The obtained homogeneous solution was transferred into autoclave and ready for the growth of nanowires. A piece of nickel foam (20 × 30 × 1.1 mm, 110 pores per inch (PPI), 320 g m^{-2}, Changsha Lyrun Material Co., Ltd., China) was degreased in acetone, etched with 6.0 mol dm^{-3} HCl for 10 min, rinsed with water, and immersed into the reaction solution. Then the autoclave was sealed and maintained at 90 ± 1 °C for 10 h to allow the growth of nanowires. After growth, the autoclave was cooled down to room temperature naturally. The purple precursors (major $Co_2(OH)_2CO_3$) were took out and rinsed with distilled water several times. Meher et al. also used urea as complexing agent to synthesize highly layered Co_3O_4 with excellent surface area and porosity. They confirmed proposed the reactions involved, as shown below mechanism [25]:

$$NH_2CONH_2 \xrightarrow{\Delta} NH_4{}^{+} + NCO^{-}$$

$$NCO^{-} + 3H_2O \rightarrow HCO_3{}^{-} + NH_4{}^{+} + OH^{-}$$

$$HCO_3{}^{-} \rightarrow CO_3{}^{2-} + H^{+}$$

$$2Co^{2+} + 2OH^{-} + CO_3{}^{2-} \rightarrow Co_2(OH)_2CO_3$$

$$3Co_2(OH)_2CO_3 + O_2 \xrightarrow{\text{calcine}} 2Co_3O_4 + 3H_2O + 3CO_2$$

The method is “hydrothermal”, consisting in the thermal decomposition of NH_2CONH_2 in presence of cobaltous ions Co^{2+}, water H_2O, hydroxyl ions OH^{-} and oxygen O_2. The global reaction is:

$$3NH_2CONH_2 + 3H_2O + 6Co^{2+} + 6OH^{-} + O_2 \rightarrow 2Co_3O_4 + 6NH_4{}^{+} + 3CO_2$$

The purple precursor (major $Co_2(OH)_2CO_3$) which appears in the course of the reactions was taken out and rinsed with distilled water several times. It was calcined as-synthesized at 300 °C for 4 h in air. Finally, the Co_3O_4 nanowires electrode was obtained (denoted as NWs-Co_3O_4/Ni-foam electrode). The morphology and supercapacitance performance of the NWs-Co_3O_4/Ni-foam electrode are different from layered Co_3O_4 films grown by Meher's group because of its different preparation conditions (e.g., raw material ratio, calcination time and calcinations heat). The loading of Co_3O_4 was measured using inductively coupled plasma mass spectroscopy (ICP-MS, Thermo XSeries II) by dissolving the electrode in aqua regia. The morphology was examined by scanning electron microscope (SEM, JEOL JSM-6480) and transmission electron microscope (TEM, FEI Teccai G2 S-Twin, Philips). The structure of nanowires was analyzed using X-ray diffractometer (XRD, Rigaku TTR III) with Cu K_{α} radiation (λ = 0.1506 nm). The 2θ ranges from 10° to 70° with a scan rate of 5° min^{-1} and a step width of 0.01°.

2.2. Electrochemical measurements

The cyclic voltammetries (CVs), galvanostatic charge–discharge and electrochemical impedance spectroscopy (EIS) measurements were performed in a conventional three-electrode electrochemical cell using a computerized potentiostat (VMP3/Z Bio-Logic) controlled by the EC-lab software. The prepared electrode (1 cm^2 nominal planar area) acted as the working electrode, a platinum foil (1 × 2 cm^2) served as the counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode. The cycle life tests were conducted on a LAND battery program-control test system. It should be pointed out that the NWs-Co_3O_4/Ni-foam electrode was first tested by many cycles of CVs, during which electrode were electrochemically activated [32–34]. All electrochemical measurements were performed in 6 mol dm^{-3} KOH. The solutions were made with analytical grade chemical reagents and Milli-Q water (18 MΩ cm, Millipore). EIS measurements were performed by applying an AC voltage with 5 mV amplitude in a frequency range from 0.01 Hz to 100 kHz.

3. Results and discussion

3.1. Characterization of the NWs-Co_3O_4/Ni-foam electrode

Fig. 1 shows the photograph and SEM images of the nickel foam after the hydrothermal process, the precursors and the Co_3O_4 nanowires attached on nickel foam. Fig. 1a(A) shows the nickel foam has no changes after the hydrothermal process and the surface is smooth. The SEM image at high magnification (Fig. 1b) confirmed this result. Fig. 1a(B) shows that the nickel foam substrate turned to purple after the precursor growth. The SEM image (Fig. 1c) shows that the nickel foam substrate was completely covered by the nanowires. Fig. 1a(C) shows that the electrode turned to black after the calcination treatment, which indicated the electroactive materials convert to be Co_3O_4 completely. The SEM image at high magnification (Fig. 1d) shows that the film is composed of clusters of crossed packed arrays of nanowires, of which the minority gather together. The Co_3O_4 nanowires form a thin film at a mass loading of 1.48 mg cm^{-2}. The Co_3O_4 nanowires cross each other and the lengths up to 1–2 μm. The TEM images (Fig. 1e and f) further confirms the nanowires shape and also shows that the nanowires are composed of interconnected nanoparticles with diameters of around 100 nm. The nanostructure can expand the electroactive area for pseudocapacitive reactions, provide effective electrolyte-accessible channels for ion transportation, and shorten the distance for ion diffusion, leading to considerably reduced internal resistance and substantially improved power performances.

Fig. 2 shows the XRD patterns of the Co_3O_4 powder scratched from nickel foam. The positions and relative intensities of diffraction peaks match well with standard Co_3O_4 patterns (JCPDS card No. 74-1656). The 2θ values are consistent with the standard crystallographic spectrum of the cubic phase Co_3O_4, with a space group of Fd-3m. The lattice constants were calculated to be