



A nickel foam supported copper core/nickel oxide shell composite for supercapacitor applications



J.L. Yin, J.Y. Park*

Department of Electronic Engineering, Kwangwoon University, Republic of Korea

ARTICLE INFO

Article history:

Received 2 June 2014

Accepted 1 August 2014

Available online 15 August 2014

Keywords:

Supercapacitors

Branched microstructure

Mesoporous

Core-shell structure

Nickel oxide

ABSTRACT

Micro porous and branched copper/nickel oxide composite with novel core-shell structure was fabricated on the nickel foam by using two consecutive electroplating processes and normally used electrochemical oxidation process. Nickel foam was used as the current collector to deposit more electroactive material, and it also helped to rapidly disperse hydrogen bubbles generated during the copper electroplating process. Field emission-scanning electronic microscopy (FE-SEM) images showed that mesoporous NiO wrinkles with lateral sizes of tens of nm were well grown and dispersed on the surface of 3-dimensional copper core. The electrochemical measurements of the as prepared Ni foam/Cu/NiO composite were performed to determine its performances. A maximum specific capacitance of 416 F/g and energy density of 11.2 Wh/kg at the 3.6 kW/kg were obtained, indicating its excellent ions accessibility and charge storage ability. Moreover, the developed composite material exhibited low inner resistance (0.6 Ω) and good cycling performance along with 71.1% specific capacitance retained after 5000 cycles. These results reveal that the developed composite electrode could be a promising positive electrode candidate material for supercapacitor applications.

© 2014 Elsevier Inc. All rights reserved.

1. Introduction

The increasing demands for energy and growing concerns on air pollution have called for intense research on energy storage and conversion devices for alternative energy sources. Supercapacitors, also known as electrochemical capacitors or ultracapacitors, are considered as promising energy storage devices that are able to compete with secondary batteries. Supercapacitors are able to provide higher power density and longer life cycle than batteries as well as higher energy density than traditional electric capacitors [1–3]. According to the charge storage mechanisms, supercapacitors can be classified into electrical double layer (EDL) capacitors, pseudocapacitors and hybrid type. In general, carbon based materials such as active carbon [4–6], carbon nanotubes (CNTs) [7,8], graphene based materials [9,10] and carbon aerogel [11,12] have been developed for EDL capacitors due to their high specific surface area and excellent electrochemical stability in certain electrolytes. On the other hand, transition metal oxides [13–15] and conductive polymers [16] are widely researched for pseudocapacitors with the advantages of ultra-high energy capacity. Typically, supercapacitor electrodes are composed of a current collector and electrode

materials with high specific surface area. Both current collectors and electrode materials with high conductivity, active surface area and electrochemical stability are important to make supercapacitors with high performance [17–18]. Nowadays, transition metal oxides are widely researched because of their various properties, such as high theoretical specific capacitance, environmental friendly, low cost and so on. However, the poor electric conductivity, densely packed structure and poor adhesion with current collector of these materials will limit their power performance. To improve the electric conductivity, various kinds of composites consisting of carbon and transition metal oxides or conductive polymers [19] have been developed. However, contact resistance across the carbon-binder and carbon-metal interfaces could be another issue since it will dissipate power and decreases energy density. Since the maximum power density is inversely proportional to the equivalent series resistance (ESR), it is very important to decrease the electrode resistance for improving the performance of supercapacitors.

Owing to the high porosity, stability, thermal conductivity and mass transfer ability, the nickel foam was widely used as the current collector for the energy storage applications. For instance, Cai et al. developed porous Ni–Mn oxide nanosheets (3DH-NM/NF) as 3D hierarchical monolith de-NO_x catalyst using nickel foam as catalyst support [20]. Dong et al. reported the formation of 3D

* Corresponding author.

E-mail address: jaepark@kw.ac.kr (J.Y. Park).

graphene foam by chemical vapor depositing graphene on the nickel foam and then etching the nickel foam substrate [21]. Wang et al. developed Ni–Al layered double hydroxide on nickel foam for supercapacitor applications with improved energy density [22].

Recently, the topic of directly growing nanostructures on the metal surface has attracted researchers' interest. Those methods are expected to result in more facile electrical conductivity through decreasing contact resistance and simpler fabrication processes without using additive binders for versatile application [23–27]. For instance, Li et al. reported an in situ hydrothermal method to grow NiMnFe mixed metal oxides catalyst on iron wire meshes [23]. Du et al. directly in situ grew the monolithic catalysts derived from hydrocalcite-like films on the aluminum wire substrate [24]. In addition, nickel could achieve high electrochemical performance due to the conversion from Ni to Ni(II), which possesses multiple oxidation states and enables rich redox reactions for higher pseudocapacitance. Nickel and other metals based composites with various structures were developed for supercapacitor applications. Niu et al. developed Ni@C core–shell composite by using hydrothermal synthesis and annealing processes [25]. Lu and his partners fabricated monolithic Ni–NiO nano composite with low resistivity and high power density using a modified polyol process and a subsequent thermal annealing process [26]. And Kim et al. have synthesized 3D ordered Ni core–NiO shell inverse opal using the polystyrene bead template-assisted electrochemical approach [27]. However, their limited thickness of the electroactive material and complicated fabrication process involving binder or surfactants still are the points to be optimized for large-scale applications [28].

Based on the above considerations, we aimed to develop a novel metal based composite electrode with high surface area, high conductivity and low internal resistance for supercapacitor applications. In detail, a nickel foam supported three-dimensional copper core–nickel oxide shell electrode was newly developed by using a two-step electroplating process and electrochemical oxidation process. The macro-porous nickel foam served as the backbone and conductive pathway for mesoporous nickel oxide. In the composite, the micro-porous and branched copper can provide ultra-high surface area and improved adhesion effect for the location of electroactive NiO materials. Monolithic layer of mesoporous nickel oxide grew on the nickel surface during the electrochemical cycling process while the micro branched structure remained. This novel structure and composition of the composite material are expected to result in more facile electrical conductivity when compared with conventional transition metal oxide materials.

2. Experimental

2.1. Preparation of core–shell structured copper/nickel oxide composite

Nickel foam (size: 1 cm × 1 cm), was cleaned by rinsing in the acetone, methanol and deionized water for 10 min, respectively, and served as the current collector. The micro porous and branched copper layer was electroplated from a mixture solution consisting of 0.4 M CuSO₄ and 1.5 M H₂SO₄ and 0.1 M acetic acid. The acetic acid was added to stabilize hydrogen bubbles generated during the electroplating process [29]. With a platinum electrode (size: 1 cm × 1 cm) used as the anode electrode, the copper electroplating process was performed at a constant current as high as 1 A/cm² for 20 s. Under such a high current density, a great number of micro bubbles were generated and rapidly removed at the surface of cathode electrode. With numerous hydrogen bubbles serving as the micro templates while copper was electroplating, a novel

porous and branched copper layer was evenly deposited on the surface of nickel foam structure. Then, we directly electroplated nickel through a commercial nickel salt bath at a low current density of 7 mA/cm² for 30 min, using a nickel plate as the anode electrode. The used salt bath for nickel electroplating was composed of nickel sulfate (200 g/L), nickel chloride (5 g/L), boric acid (25 g/L) and saccharin (3 g/L) with steady stirring (80 rpm) at room temperature. As a result, nickel layer was deposited on the surface of previously formed copper fully while retaining its novel micro porous and branched structure. After finishing two electroplating processes, the sample was washed with deionized water, dried for 5 min at 95 °C on the hotplate. At last, the as-prepared sample was cycled in the 2 M KOH electrolyte for 200 cycles in the potential range of 0–0.6 V (vs. Hg/HgO) by using the chronopotentiometric technique, which resulted in oxidation of nickel forming a thin film of nickel oxide. All the reagents used in the experiments were of analytical grade and without further purification.

2.2. Characterization

The surface morphology and structure of as-prepared core–shell structured copper/nickel oxide composite was investigated by FE-SEM (Hitachi S-4300) and BET measurement (ASAP 2010, Micromeritics Inc. USA) and X-ray diffraction (Rigaku Model D/MAX-2500V/PC, 40 kV/100 mA) using Cu K α radiation ($\lambda = 1.5418\text{\AA}$) within the scanning range from 10° to 90°. In addition, cyclic voltammetric (CV), galvanostatic charging and discharging (CDC) and electrochemical impedance spectroscopic (EIS) techniques were performed using a potentiostat (CH Instrument 660D). All the electrochemical measurements were carried out in the 2 M KOH electrolyte solution using a three-electrode system. The electrochemical cell comprises platinum as counter electrode, Hg/HgO (1 M NaOH) as reference electrode and the previously prepared Ni foam/Cu/NiO composite as working electrode. Before the measurement, the working electrode was soaked in 2 M KOH for 2 h to fully wet the electrode materials. All the potentials were recorded with respect to Hg/HgO (1 M NaOH) reference electrode.

The specific capacitance was calculated according to the CV curves using the Eq. (1), and specific capacitance, energy density and power density were calculated from charging/discharging curves using the Eqs. (2–4):

$$C_s = \frac{\int_V I(V) \cdot dV}{m \cdot v \cdot \Delta V} \quad (1)$$

$$C_s = \frac{I \cdot t}{m \cdot \Delta V} \quad (2)$$

$$E = \frac{1}{2} C_s \cdot (\Delta V)^2 \quad (3)$$

$$P = \frac{E}{t} \quad (4)$$

where C_s represents the specific capacitance, the ratio between the integration and scan rate (v) indicates the total charge transferred during oxidation or reduction process, m indicates the mass of the active material, I is the applied constant current in the galvanostatic measurement, t is the discharge time, ΔV is the potential window, E is the energy density and P is the average power density [26,30].

3. Results and discussion

Fig. 1 shows the FE-SEM measurement results of the as-fabricated Ni foam/Cu/NiO composite to demonstrate its morphology characteristics. Fig. 1(a) shows a three-dimensional cross-linked structure of the nickel foam with considerable grids on its plane

Download English Version:

<https://daneshyari.com/en/article/72686>

Download Persian Version:

<https://daneshyari.com/article/72686>

[Daneshyari.com](https://daneshyari.com)