Journal of Industrial and Engineering Chemistry 33 (2016) 374–380

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

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

Porous 3D-β-nickel hydroxide microflowers for electrochemical supercapacitors

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ARTICLE INFO

Article history:
Received 13 September 2015
Received in revised form 19 October 2015
Accepted 24 October 2015
Available online 30 October 2015

Keywords:
Microflowers
Nanorods
Single crystals
Three dimensional

ABSTRACT

In this work we have carried out synthesis of porous three dimensional nickel hydroxide (3D-β-$Ni(OH)_2$) microflowers by chemical bath deposition. The structure of the porous 3D-β-$Ni(OH)_2$ microflowers characterized by using FT-IR, TGA, XRD, FE-SEM, TEM and XPS. The specific capacitance of the porous 3D-β-$Ni(OH)_2$ microflowers were showing around 249 F/g from cyclic voltammetry. The discharge specific capacitance of the porous 3D-β-$Ni(OH)_2$ microflowers were found to be 170 and 245 F/g for the 1st and 8000th cycles, respectively. The energy and power density of the porous 3D-β-$Ni(OH)_2$ microflowers found to be 8.5 W h/kg and 2497.9 W/kg, respectively at the discharge current density of 0.05 A/g.

Introduction

Supercapacitors are bridge the gap between conventional capacitors and batteries in the energy storage devices have been the theme of revitalize interest. Supercapacitors have two types of energy storage mechanisms. One of the charge storage mechanisms in supercapacitors is the Faradaic pseudocapacitance arising from fast, reversible electron-sorption/desorption or redox processes [1–3]. The electrode active material used in the pseudocapacitors are conducting polymers and transition metal hydroxides and oxides. This charge storage mechanism introduces transitional metal hydroxides and oxides as promising candidates. Among these (Ru, Co, Ni, Mn, Sn oxides or hydroxides), nickel hydroxides are easily obtainable, economical and safe, thus different synthesis methods have sprung up to accomplish the optimal structure and ultrahigh specific capacitance [4–6].

Nickel hydroxide exists in a four different variety of forms are observed, namely: α-$Ni(OH)_2$, β-$Ni(OH)_2$, β-NiOOH and γ-NiOOH. Among the four different form, the most common forms are the α and β- $Ni(OH)_2$ polymorphs, α-$Ni(OH)_2$ consists of stacked β-$Ni(OH)_2$ layers intercalated with interlayer anions water molecules and is isostructural with hydrotalcite-like compounds ($Ni(OH)_2{\cdot}xH_2O$: $0.41 \leq x \leq 0.7$). The β-$Ni(OH)_2$ does not have intercalated species has a isostructural with brucite-like structure. Therefore various phases of nickel hydroxide (α and β- $Ni(OH)_2$ polymorphs) differ from each other by degree of hydration, chemical structure and morphology. α-$Ni(OH)_2$ is a hydroxyl-deficient form (with interlayer contains anions and water molecules) rather than a stoichiometric composition in β-$Ni(OH)_2$. However, α-$Ni(OH)_2$ under the strong alkaline media is unstable and easily converts into β-$Ni(OH)_2$ phase. Therefore, α-$Ni(OH)_2$ is restricted in practical applications, although it has a high potential as an electrode active material for applications in energy storage devices [7].

Dubal and Fulari et al., synthesized the nickel hydroxide nanostructures by chemical bath deposition (CBD) method using different nickel precursors [8]. The prepared nickel hydroxide present in the β-form. Scanning electron microscope shows the surface morphology of the nickel hydroxide is present in the form of multilayer nanosheets. From the surface area analysis nickel hydroxide nanosheets are showing the surface area of 75 and 65 m^2/g. Electrochemical analysis showing the specific capacitance of the prepared nickel hydroxide nanostructures is around 462 F/g in 2 M KOH. Gund et al. prepared the nickel hydroxide micro-belts by hydrothermal method. As prepared nickel hydroxide is present in the 'β' phase. From the electrochemical study nickel hydroxide micro-belts showing the specific capacitance of 324 F/g and 78% retention of capacitance after 500 cycles in 2 M KOH [9]. Gund et al. prepared the crystalline β-$Ni(OH)_2$ thin film with various morphologies such as nanoplates, stacked nanoplates, nanobelts and nanoribbons at different temperature by hydrothermal method. The maximum specific capacitance of 357 F/g by β-$Ni(OH)_2$ nanoplates [10].

Here in we report the synthesis of porous three dimensional nickel hydroxide (3D-β-$Ni(OH)_2$) microflowers thin films on SS

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http://dx.doi.org/10.1016/j.jiec.2015.10.036
1226-086X/

substrate by CBD using nickel chloride and sodium dodecyl sulfate micellar solution. Porous nickel hydroxide microflowers thin films properties are analyzed by diffraction, X-ray photo electron microscopy and morphology. The electrochemical properties of the porous 3D-β-$Ni(OH)_2$ microflowers thin films are analyzed by cyclic voltammetry and galvanostatic charge–discharge study.

Experimental

Materials

Nickel chloride (anhydrous, $NiCl_2$), sodium dodecyl sulfate (SDS), ammonium hydroxide (NH_4OH) and potassium hydroxide were purchased from Sigma-Aldrich and used as received without further purification. All the reactions were carried out with millipore water.

Preparation of $Ni(OH)_2$ thin film

The stainless steel (SS, MTI Korea) substrates were polished with emery paper to a rough finish and washed with millipore water and acetone to remove the emery particles and dried in oven. Porous nickel hydroxide microflowers were deposited on the SS substrates as follows: in a typical synthesis 0.15 g of SDS dissolved in 90 ml of millipore water in 100 ml beaker, stirred the solution until getting homogeneous solution, for that 1.5 g of $NiCl_2$ added and stirred the solution further for 2 h. The solution containing beaker was dipped inside the water bath and stirred the solution under constant stirring. The cleaned SS substrates were dipped inside the solution vertically with help of clamp. 10 ml of NH_4OH was added to the above prepared solution, after addition of NH_4OH blue precipitate was formed, when heating the reaction mixture the initial precipitate was disappeared. When the reaction mixture was attains the temperature of 60 °C, precipitation was started in the bath. During the precipitation, heterogeneous reaction occurred on the substrate and deposition of $Ni(OH)_2$ takes place on the SS substrate. The reaction further continued at 70 °C for 4 h under vigorous constant stirring. After completion of the 4 h reaction SS substrates were removed and washed with ample amount of millipore water and dried in oven for overnight. The deposited porous nickel hydroxide microflowers thin films on SS substrate used further characterization.

Physical characterization of $Ni(OH)_2$ thin film

Attenuated total reflectance fourier transform infrared (ATR-FTIR) spectra of porous 3D-β-$Ni(OH)_2$ microflowers thin film were recorded on a Nicolet Nexus FTIR spectrometer (model: iS10, Minnesota). The phase purity of synthesized materials was studied using X-ray diffraction (XRD). XRD profiles for the porous 3D-β-$Ni(OH)_2$ microflowers thin film were obtained on a smartlab (Rigaku). The particle morphology and structural properties of the prepared porous nickel hydroxide (3D-β-$Ni(OH)_2$) microflowers thin films were further elucidated by field emission scanning electron microscopy (FE-SEM) (Hitachi S-4300 SE/N, Hitachi, Tokyo, Japan), the porous 3D-β-$Ni(OH)_2$ microflowers thin film sample was sputtered on a carbon disc with the help of double-sided adhesive tape and sputter-coated with a thin layer of gold to prevent sample charging problems and transmission electron microscopy (TEM) measurement was performed by casting sample dispersion on carbon coated copper grids and allowing it to dry at room temperature. Measurements were done on FE-TEM, JEM-2100F (HR) (JEOL LTD, Japan). Thermogravimetric analysis (TGA) was performed SCINCO (TGA 1000) series thermal analyzer system at a heating rate of 10 °C/min from ambient to 700 °C under nitrogen atmosphere. The surface characterization of porous 3D-β-$Ni(OH)_2$ microflowers thin film was carried out at room temperature using a monochromatic Al-$K\alpha$ X-ray source (1486.6 eV) by AXIS-NOVA XPS instrument.

Electrochemical characterization of porous 3D-β-$Ni(OH)_2$ microflowers

The electrochemical properties (cyclic voltammetry) of porous 3D-β-$Ni(OH)_2$ microflowers thin films measurements were carried out using versaSTAT 3 electrochemical workstation (Princeton Applied Research, Oak Ridge, USA) with a standard three-electrode cell in 2 M KOH in the range of 0–0.38 V. The porous 3D-β-$Ni(OH)_2$ microflowers thin film, platinum wire and saturated calomel electrode used as working electrode, counter electrode and reference electrode, respectively. The cyclic voltammetry experiments were carried out at scanning rates varied from 5–50 mV/s. Galvanostatic charge–discharge experiments were carried out with a WonATech multichannel potentiostat/galvanostat (WBCS3000, Gyeonggi-do, Korea) at the current density of 0.05 A/g in the voltage range of 0–0.5 V. All the electrochemical studies carried out at room temperature.

The specific capacitance (C_{sp}: F/g) and energy density (ED) and power density (PD) of the porous 3D-β-$Ni(OH)_2$ microflowers thin films were calculated from cyclic voltammograms and charge–discharge curves using the following equation:

$$C_{sp} = \frac{q}{m \times \Delta V} \tag{1}$$

$$C_{sp}^{d} = \frac{I \times \Delta t}{m \times \Delta V} \tag{2}$$

$$ED = \frac{C_{sp}^{d} \times V^2}{2} \tag{3}$$

$$PD = \frac{ED}{\Delta t} \tag{4}$$

where q is the charge, ΔV is the voltage range of one scanning segment, I is the applied current in A/g, m is the weight of the porous 3D-β-$Ni(OH)_2$ microflowers thin film and Δt is the time of a discharge cycle. C_{sp} and C_{sp}^{d} (specific capacitance) were calculated from cyclic voltammetry and galvanostatic charge–discharge methods, respectively.

Results and discussion

The composition and form of the as-synthesized products were examined by X-ray diffraction analysis. X-ray diffractogram of the as prepared porous 3D-β-$Ni(OH)_2$ microflowers thin film was shown in Fig. 1(a). All of the diffraction peaks could be clearly indexed to the hexagonal phase of β-$Ni(OH)_2$ structure in accordance with the standard JCPDS card No: 14-0117. No peaks attributable to other form of $Ni(OH)_2$ as observed from the XRD patterns, indicating the high purity of the samples obtained. The crystallite size of β-$Ni(OH)_2$ was calculated on the basis of full width at half maxima intensity of most intense XRD peak by using Scherrer's formula [11].

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

where D is crystallite size, λ is the wave length X-ray used, β is the full width at half maxima and θ is the diffraction angle. The average crystallite size of porous nickel hydroxide (3D-β-$Ni(OH)_2$) microflowers thin films was found to be about 41 nm for (0 0 1) plane. Gund et al. have reported the crystallite size of 52 nm