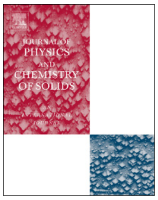
Journal of Physics and Chemistry of Solids 88 (2016) 60–67

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

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



Preparation and electrochemical investigation of the cobalt hydroxide carbonate/activated carbon nanocomposite for supercapacitor applications

Tshifhiwa M. Masikhwa, Julien K. Dangbegnon, Abdulhakeem Bello, Moshawe J. Madito, Damilola Momodu, Ncholu Manyala*

Department of Physics, Institute of Applied Materials, SARCHI Chair in Carbon Technology and Materials, University of Pretoria, Pretoria 0028, South Africa

ARTICLE INFO

Article history:
Received 23 July 2015
Received in revised form
16 September 2015
Accepted 29 September 2015
Available online 1 October 2015

Keywords:
Cobalt hydroxide carbonates
Activated carbon
Supercapacitor application
Electrode stability
Energy storage

ABSTRACT

Cobalt hydroxide carbonate/activated carbon (AC) composite was successfully synthesized by hydrothermal method. Morphological characterizations of cobalt hydroxide carbonate/AC composite were carried out by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), and the results show that the cobalt hydroxide carbonate nanorods are well dispersed on the AC. Due to the synergistic effects arising from cobalt hydroxide carbonate nanorods and AC, the electrochemical performances of pure cobalt hydroxide carbonate material is significantly improved by the addition of AC. The composite shows a specific capacitance of 301.44 F g^{-1} at a current density of 1 A g^{-1} in 6 M KOH electrolyte and exhibits good cycling stability. Based on the above results, the cobalt hydroxide carbonate/AC composite shows a considerable promise as electrode for electrochemical applications.

Crown Copyright © 2015 Published by Elsevier Ltd. All rights reserved.

1. Introduction

In recent years, electrochemical capacitors (ECs) have attracted much more interests due to their distinctive properties like high power density, good reversibility, and wide energy storage applications [1–4]. ECs are novel power devices, which lie between batteries and conventional dielectric capacitors in terms of energy and power densities with applications in computer power backup, electric vehicles and power electronics. The major aim of developing ECs materials is to improve on the energy density of the device without sacrificing the high power density and long cycle life. Electrical double layer capacitor (EDLC) is a very attractive energy storage device because, besides its high power density, it is maintenance-free, has long-life operation, quick charge–discharge rate, and is environmentally friendly energy technology. In general, the performance of ECs strongly depends on the electrode materials used in its fabrication [5]. Carbon-based materials are ideal electrode materials for ECs owing to their low price, high charge/discharge rate, and quite stable physicochemical properties. Typical electrode materials for EDLCs are activated carbon, graphene, carbon nanotubes, etc. [6]. In particular, carbon nanotubes have high electrical conductivity but a relatively low surface area, which causes a drastic drop in EDLC performance [7]. Graphene known for its high surface area and good surface exposure to electrolytes, has been recognized as an excellent component for supercapacitors. Nevertheless, other materials such as conductive polymers [8,9] and metal oxides [10,11] have been widely studied for ECs applications due to their unique properties such as high inherent capacitance [8,12].

Recently, three dimensional porous carbon materials have become attractive and are frequently used as electrode materials in the fabrication of EDLCs due to their good electrical conductivities and large surface area [13–17]. For examples Zhu et al. have produced carbon materials by microwave-assisted expansion of graphene oxide (a-MEGO) with exceptional properties. This material demonstrated excellent electrochemical properties in ionic electrolytes [2,18]. On the other hand faradaic materials utilize redox reaction to store charges at the surface or near surface region of the electrode materials [19]. Commonly used faradaic materials are transition metal oxides (TMOs) and conducting polymers (CPs) [20–25].

Cobalt hydroxide carbonate is considered as faradaic material and has attracted particular attention among researchers in recent years because of its unique properties such as easy synthesis route

---

* Corresponding author. Fax: +27 12 420 2516.
E-mail addresses: moureenmasikhwa@gmail.com (T.M. Masikhwa), dangbegnon01@googlemail.com (J.K. Dangbegnon), bellohakeem@gmail.com (A. Bello), jack.madito@gmail.com (M.J. Madito), dymomodu@yahoo.com (D. Momodu), ncholu.manyala@up.ac.za (N. Manyala).

http://dx.doi.org/10.1016/j.jpcs.2015.09.015
0022-3697/Crown Copyright © 2015 Published by Elsevier Ltd. All rights reserved.

and various morphologies [26–28]. Recently, different morphologies of cobalt hydroxide nanostructures intercalated with carbonate anions have been synthesized using block copolymers or surfactants. Such structures include: nanorods and nanowires, sisal-like, dandelion-like, pinecone-like, urchin-like and flower-like nanostructures [26–31]. Cobalt hydroxide carbonate is considered to be a suitable candidate for ECs applications due to its good electrochemical activity, low cost raw material and environmental friendly amongst other faradaic materials [32]. However, the specific capacitance of pure cobalt hydroxide carbonate is still low compared with other TMOs [33–36].

In this work, pure cobalt hydroxide carbonate and cobalt hydroxide carbonate/AC composite are synthesized by hydrothermal method. The AC material was added to improve on the electrochemical performance of the pure cobalt hydroxide carbonate. The composite exhibited a specific capacitance of 301.44 F g^{-1} at a current density of 1 A g^{-1} in 6 M KOH electrolyte and showed excellent long cycle life of ~95.6% capacitance retention after 1000 cycles.

2. Experimental

2.1. Materials

Cobalt chloride hexahydrate ($CoCl_2.6H_2O$, purity > 99.99%), Hydrochloric acid (HCl, ≥ 32%) and Polyvinyl alcohol (PVA, 99+% hydrolyzed) were purchased from Sigma-Aldrich. Nickel Foam was purchased from (Alantum, Munich, Germany). Potassium hydroxide (KOH, min 85%) and urea (purity ≥ 98%) were purchased from Merck (South Africa).

2.2. Synthesis of cobalt hydroxide carbonate

$CoCl_2 \cdot 6H_2O$ (1.0 mmol) and urea (1.0 mmol) were added to 20 mL of water and stirred for 10 min. The homogeneous mixture was then transferred to a Teflon-lined stainless steel autoclave and kept at 120 °C for 6 h. After cooling to room temperature the light-pink powder was washed with deionized water and dried at 60 °C. The growth mechanism of this material involves a hydrolysis-precipitation process in which urea can slowly provide both carbonate and hydroxyl anions to form cobalt hydroxide carbonate [28]. The main reactions in the system can be expressed as follows:

$$H_2NCONH_2 + H_2O \rightarrow 2\ NH_3 + CO_2 \qquad (1)$$

$$CO_2 + H_2O \rightarrow CO_3^{2-} + 2\ H^+ \qquad (2)$$

$$NH_3 + H_2O \rightarrow NH_4{}^+ + OH^- \qquad (3)$$

The formation of cobalt hydroxide carbonate can be formulated as:

$$2Co^{2+} + 2OH^- + CO_3^{2-} \leftrightarrow Co_2(OH)_2CO_3 \qquad (4)$$

2.3. Synthesis of cobalt hydroxide carbonate/activated carbon

Activated carbon used for the production of the composite material was prepared as follows [37,38]: graphene foam (GF) and polyvinyl alcohol (PVA) were used as starting materials for the production of the hydrogel, which was subsequently used to produce porous carbon material after the activation process. GF was prepared by chemical vapor deposition (CVD) onto a catalytic nickel foam as reported in our previous work [39]. The three dimensional hydrogel was synthesized via a hydrothermal process. Briefly, 100 mg of the GF was dispersed in 10 ml of polyvinyl alcohol (PVA) in a vial glass by ultrasonication followed by the addition of 1.5 ml of hydrochloric acid (HCl) as cross linker. The resultant mixture was transferred into a 150 ml Teflon-lined autoclave vessel and kept at 190 °C for 12 h [40]. After cooling to room temperature the hydrogel was washed several times with deionized water and dried for 6 h. The as-prepared hydrogel was then soaked in an aqueous KOH solution for 24 h. The KOH/hydrogel mass ratio was 7. The hydrogel was then placed in a horizontal tube furnace which was heated ramped from room temperature to 800 °C at a ramping rate of 10 °C/min under argon gas flow. The hydrogel was kept at this temperature for 1 h to complete simultaneously activation and carbonization processes. This procedure transforms the hydrogel into carbon material consisting of a continuous pore network distribution. The activated material was neutralized with 0.1 M HCl, washed with deionised water and dried at 120 °C for 12 h.

The cobalt hydroxide carbonate/activated carbon composites were prepared using a hydrothermal reduction technique. Typically, 15 mg of prepared AC was dispersed in 20 ml of water by ultrasonication for 12 h at room temperature. Then $CoCl_2 \cdot 6H_2O$ (1 mmol) and urea (1.0 mmol) was added to the AC dispersion and the mixture was stirred for 10 min. The obtained solution was then transferred to a Teflon-lined stainless steel autoclave and kept at 120 °C for 6 h. After naturally cooling to room temperature, the product was washed with deionized water and dried at 60 °C for 6 h.

2.4. Structure and morphology characterization

The morphology of the prepared cobalt hydroxide carbonate and cobalt hydroxide carbonate/AC was investigated using the high-resolution Zeiss Ultra plus 55 field emission scanning electron microscope (FESEM) operated at 2.0 kV. Transmission electron microscopy (TEM) was carried out with a JEOL JEM-2100F microscope operated at 200 kV (Akishima-shi, Japan). X-ray diffraction (XRD) patterns of prepared materials were collected using an XPERT-PRO diffractometer (PANalytical BV, Netherlands) with reflection geometry at 2θ values ranging from 30° to 90° with a step size of 0.01°. Co $K1\alpha$ radiation with a wavelength of 1.7890 Å was used as X-ray source and the X-ray tube was operated at 50 kV and 30 mA. The surface area of the synthesized materials was studied using Barrett–Joyner–Halenda (BJH) method from the desorption branch of the isotherm. Fourier transform infrared (FTIR) spectra of the cobalt hydroxide carbonate and cobalt hydroxide carbonate/AC were recorded using a Bruker Vertex 77v FTIR spectrometer.

2.5. Electrode preparation and electrochemical characterization

The electrochemical properties were investigated in a three-electrode configuration using a Bio-Logic VMP300 potentiostat (Knoxville TN 37930, USA) controlled by the EC-Lab® V10.37 software. The cobalt hydroxide carbonate and cobalt hydroxide carbonate/AC materials served as working electrodes in a 6 M KOH aqueous electrolyte, while glassy carbon plate was used as the counter electrode and Ag/AgCl (3 M KCl) as the reference electrode, respectively. The electrode materials were prepared according to the following steps: 85 wt% of the material was mixed with 10 wt% of carbon black and 5 wt% of polyvinylidene difluoride (PVdF) binder in an agate mortar. The mixture was then dissolved with 1-methyl-2-pyrrolidinone (NMP) to form a paste. The homogenous paste was coated onto a Ni foam current collector and dried at 60 °C in an electrical oven for 8 h to ensure complete evaporation of the NMP. The cyclic voltammetry tests were carried out in the potential range of 0 to 0.45 V (vs. Ag/AgCl)

Download English Version:

https://daneshyari.com/en/article/1515505

Download Persian Version:

https://daneshyari.com/article/1515505

Daneshyari.com