Journal of Energy Chemistry xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Journal of Energy Chemistry

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

http://www.journals.elsevier.com/journal-of-energy-chemistry/

KOH activated carbon derived from biomass-banana fibers as an efficient negative electrode in high performance asymmetric supercapacitor☆

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ARTICLE INFO

Article history:
Received 25 April 2016
Revised 6 June 2016
Accepted 20 June 2016
Available online xxx

Keywords:
Asymmetric supercapacitor device
Activated porous carbon
High energy density
Cyclability
Power source

ABSTRACT

Here we demonstrate the fabrication, electrochemical performance and application of an asymmetric supercapacitor (AS) device constructed with β–$Ni(OH)_2$/MWCNTs as positive electrode and KOH activated honeycomb-like porous carbon (K-PC) derived from banana fibers as negative electrode. Initially, the electrochemical performance of hydrothermally synthesized β–$Ni(OH)_2$/MWCNTs nanocomposite and K-PC was studied in a three-electrode system using 1 M KOH. These materials exhibited a specific capacitance (*Cs*) of 1327 F/g and 324 F/g respectively at a scan rate of 10 mV/s. Further, the AS device i.e., β–$Ni(OH)_2$/MWCNTs// K-PC in 1 M KOH solution, demonstrated a *Cs* of 156 F/g at scan rate of 10 mV/s in a broad cell voltage of 0–2.2 V. The device demonstrated a good rate capability by maintaining a *Cs* of 59 F/g even at high current density (25 A/g). The device also offered high energy density of 63 Wh/kg with maximum power density of 5.2 kW/kg. The AS device exhibited excellent cycle life with 100% capacitance retention at 5000th cycle at a high current density of 25 A/g. Two AS devices connected in series were employed for powering a pair of LEDs of different colors and also a mini fan.

1. Introduction

The huge promulgation of consumer electronics especially smart devices necessitates high energy density and enduring power sources. These smart electronic devices such as mobile phones, phablets, tablets, watches, wrist bands, key chains, require light weight and eco-friendly energy storage devices with high energy density. Supercapacitors (SC) are the most suitable energy storage devices for such applications due to their higher energy density and power density than that of capacitors and batteries respectively [1,2]. SC are categorized mainly into electrical double layer capacitors (EDLC) and pseudo capacitors (PC) on the basis of their difference in energy storage mechanism [3]. Carbonaceous materials such as activated carbon, mesoporous carbon, graphene oxide and carbon nanotubes (CNTs) are the most suitable electrode materials for EDLC whereas transition metal oxides (TMO's) and conducting polymers are appropriate for PC [4,5]. A nanocomposite of carbon material and TMO's is found to exhibit superior electrochemical properties in SC [6]. There are many reports available in literature on the electrode materials developed by the combination of CNTs and TMO's due to their excellent synergistic properties. Studies are made using these materials not only to develop supercapacitor electrodes but also to fabricate a supercapacitor device with high specific capacitance (*Cs*), energy density and power density. The SC devices are of two types; symmetric supercapacitors (SS) and asymmetric supercapacitors (AS). It is well understood that, SS devices are fabricated using only one type of electrode material; on the other hand AS devices utilize a combination of different kinds of electrode materials. In the latter case one of the electrode materials used is of battery type while the other is a capacitor kind. Thus, these AS devices offer the advantages of both the electrode materials such as good cycle life, high energy density and broad operating voltage by utilizing their different potential windows [7,8]. TMO's and conducting polymers are the widely studied positive electrode materials, whereas carbon materials such as activated carbon (AC), activated graphene, CNTs and reduced graphene oxide are used as negative electrode materials

☆ This work was supported by the Naval Research Board (NRB); Project Number: NRB-290/MAT/12-13.

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http://dx.doi.org/10.1016/j.jechem.2016.07.003
2095-4956/

in AS devices [9–12]. In recent past, there is a substantial interest in deriving carbon from biomass or waste and their activation using different activating agents and investigating their use in SC as electrode materials [13–18]. This is because of easy and abundant availability of the raw materials, besides reducing the dependence on fossil fuels for energy. A few research groups have fabricated AS devices using carbon derived from biomass as negative electrode. For instance, Fan et al. have obtained carbon from willow catkins (CCNs) and fabricated MnO_2-CCNs//CCNs AS device which exhibited an energy density of 23.6 Wh/kg [19]. $NiCo_2O_4$-Co_3O_4//JF AS device was fabricated using activated carbon derived from waste jackfruit peel (JF) which gave a high energy density of 42.5 Wh/kg with good cyclability [20]. Jing et al. reported fabrication of an AS device using nitrogen activated porous carbon (PC) derived from loofah sponge and MnO_2-PC, which exhibited an energy density of 34.7 Wh/kg with 2000 cycles stability [21].

In the process of developing new electrode materials for SC, herewith we report a cost effective and eco-friendly porous carbon obtained from banana fibers as high performance supercapacitor material. To the best of our knowledge, the electrochemical performance of carbon derived from banana fibers has not been reported in the literature either in SS or in AS devices. In the present study we describe the fabrication of a novel AS device with a broad operating potential of 0–2.2 V in an aqueous electrolyte using K-PC derived from banana fibers as negative electrode and previously developed β-$Ni(OH)_2$/MWCNTs [22] as positive electrode. The fabricated AS device exhibited good electrochemical performance with respect to *Cs*, energy density (ED), power density (PD) and cycle stability. Further, the AS device was tested in powering LED's of different color, and a mini fan to prove its practical applications.

2. Experimental

2.1. Preparation of KOH activated porous carbon (K-PC)

Banana fibers were obtained from Tamil Nadu Agricultural University, India. The material was dried at 110 °C in a hot air oven for 24 h and carbonized at 450 °C for 1 h in nitrogen atmosphere, cooled mixed well with 10 M KOH solution (KOH:carbon = 4:1 weight ratio) left overnight at 110 °C [23] and further calcined at 750 °C for 1 h in N_2 atmosphere. The obtained solid was cooled to room temperature, powdered well and washed with 6 M HCl to remove KOH, followed by washing with distilled water until pH of the filtrate was neutral to litmus and finally dried overnight at 110 °C. The potassium hydroxide activated porous carbon thus obtained is abbreviated as K-PC.

Guo et al. [24] reported that when carbon derived from biomass is treated with KOH solution, several simultaneous chemical reactions occur, finally producing porous carbon.

Multiwalled carbon nanotubes (MWCNTs) and β-$Ni(OH)_2$/MWCNTs nanocomposite were prepared as reported in our previous works [22,25].

The prepared materials, K-PC & β-$Ni(OH)_2$/MWCNTs were characterized by different analytical techniques to evaluate their physico-chemical properties. Powder XRD patterns were recorded using Panalytical X'pert pro X-ray diffractometer with Cu K_α radiation ($\lambda = 0.154$ nm) in a 2θ range of 5° to 70° using 40 kV at a scanning rate of 2°/min. BET surface area was determined by N_2 adsorption data using Micromeritics TriStar 3000 instrument. SEM images and EDS profiles for elemental composition were obtained from Quanta 200 FEI instrument. High resolution transmission electron microscopy (HR-TEM) images were obtained on Tecnai 10 Philips microscope. Raman spectra were recorded on EN Wave optronics ez Raman pro at room temperature using 532 nm green laser beam.

2.2. Electrode fabrication

The electrochemical properties were initially studied in a three electrode system using standard calomel as reference electrode, Pt wire as an auxiliary electrode and the prepared materials coated on Toray carbon paper as working electrode. The working electrode was fabricated by mixing 85 wt% of β-$Ni(OH)_2$/MWCNTs (or) K-PC with 10 wt% of ketjen black (EC 600JD) in an agate mortar along with a binder, 5 wt% of PVDF (polyvinylidene difluoride) dissolved in NMP (1-methyl-2- pyrrolidinone). The obtained slurry was coated on a carbon paper of area 1 cm^2 and vacuum dried at 70 °C for 8 h.

2.3. Fabrication of asymmetric supercapacitor (AS) device

In the fabrication of AS device, to accomplish maximum capacitance it is important to keep in mind that the charges on positive and negative electrodes are balanced. This is achieved by loading an optimum mass of materials used as positive and negative electrodes as per the mass ratio equation [26]. Accordingly, a mixture of 3.2 mg of K-PC and 1.6 mg of β-$Ni(OH)_2$/MWCNTs along with ketjen black and binder in the weight ratio of 85:10:5 were coated on a 1 cm^2 carbon paper. Two such carbon papers were sandwiched with a capacitor grade separator paper. Thin stainless steel sheets were wrapped on either side of the electrodes as current collectors. The entire set up was sealed in a self-sealing pouch containing 1 mL of 1 M KOH solution.

Electrochemical performance of materials in three electrode system and two electrode systems were studied by Cyclic Voltammetry (CV), Chronopotentiometry (CP) and Electrochemical Impedance Spectroscopy (EIS) using CHI 660E electrochemical workstation. The Cs, ED, PD and Columbic efficiency (η) were evaluated using appropriate standard equations relevant to above mentioned electrochemical techniques [27].

3. Results and discussion

Positive electrode is made up of a composite of β-$Ni(OH)_2$ and MWCNTs. The X-ray diffraction studies of this material showed sharp diffraction peaks indicating its crystalline nature (Fig. S1a). The diffraction peaks obtained are indexed to β-$Ni(OH)_2$ [JCPDS No.14-0117] [28]. The SEM image of nanocomposite (Fig. 1a) showed the formation of uniform flake like β-$Ni(OH)_2$ nanoparticles in the matrix of MWCNTs. The elemental composition obtained from EDS profile indicated the atomic wt% of Ni as 42 and the rest being carbon and oxygen (Fig. 1a inset). TEM image of the nanocomposite clearly revealed the association of hexagonal structure of β-$Ni(OH)_2$ along with mesoporous, tubular MWCNTs. The size of hexagonal particles is in the range of 50–250 nm (Fig. 1b).

The BET surface area, pore volume and pore diameter of the nanocomposite were found to be 135 m^2/g, 0.24 cc/g and 10.9 nm respectively. The BJH isotherms of β-$Ni(OH)_2$/MWCNTs showed H4 hysteresis indicating the mesoporous nature of the material (Fig. S1b). Raman spectroscopy characterization of functionalized MWCNTs and β-$Ni(OH)_2$/MWCNTs has been described in the previous study. The nanocomposite exhibited a high I_D/I_G ratio indicating high degree of defects during the formation of nanocomposite [22].

The negative electrode is KOH activated porous carbon (K-PC). K-PC showed broad peaks at 2θ around 26° and 43° which correspond to (002) and (100) graphitic plane of turbostratic carbon [13] (Fig. S1c). SEM images of the K-PC (Fig. 1c & d) revealed clusters of porous, hollow carbon cavities with diameter ranging from 8–20 µm. SEM images clearly indicated that K-PC has microporous structure. The purity of sample is evident from EDS profile where carbon is 79 atomic% and the rest being oxygen. TEM and HR-TEM

Please cite this article as: Chaitra K et al., KOH activated carbon derived from biomass-banana fibers as an efficient negative electrode in high performance asymmetric supercapacitor, Journal of Energy Chemistry (2016), http://dx.doi.org/10.1016/j.jechem.2016.07.003