Journal of Energy Chemistry 25 (2016) 734–739

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/

Superior supercapacitive performance in porous nanocarbons

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ARTICLE INFO

Article history:
Received 12 January 2016
Revised 8 March 2016
Accepted 15 March 2016
Available online 25 April 2016

Keywords:
Porous carbon nanoparticles
Supercapacitor
Catalyst free
Biowaste

ABSTRACT

Porous nanocarbons with average particle size 20–40 nm were developed using biowaste oil palm leaves as a precursor. Simple pyrolysis was carried out at 700 °C under nitrogen atmosphere. Obtained porous nanocarbons showed excellent porous nature along with spherical shape. Symmetric supercapacitor fabricated from porous nanocarbons showed superior supercapacitance performance where high specific capacitance of 368 F/g at 0.06 A/g in 5 M KOH were reported. It also exhibited high stability (96% over 1700 cycles) and energy density of 13 Wh/kg. Low resistance values were obtained by fitting the impedance spectra, thus indicating the availability of these materials as supercapacitors electrode. The presented method is cost effective and also in line with waste to wealth approach.

1. Introduction

Carbon is conventionally preferred over metal oxide material in supercapacitor application for several good reasons such as its abundance, high surface area, excellent electrical conductivity and low production cost [1]. Owing to the enhanced pore volume distribution of carbon, it has high stability and conductivity.

Although there are various super capacitors made up of several materials available in the literature, biowaste approach is highly influential due its capacity to bulk produce. These materials are highly efficient for energy storage device [2]. In the recent past, carbon is focused upon as the precursor for the electrodes in supercapacitor application because of its extensive electrochemical storage property [3]. In addition to this, carbon electrodes can be easily polarized [4]. Electrodes synthesized from carbon are stable both in acidic and basic solutions [5]. Upon implication of several physical activation methods, electrodes with huge surface area can be obtained. These chemical and physical attributes of carbon contribute to the application of carbon in storage of energy [6].

Developing countries have rapid growth in the past few decades which is powered by coal and fossil fuels [7,8]. This growth which is accelerated by the consumption of fossil fuels is hazardous and also results in the greenhouse effect [9]. A healthy development needs source of abundant supply of clean energy. The statistics show that the biowaste materials make up major solid waste and a wise way to address this issue is to utilize biowaste materials for the commercial purpose [10,11]. The major advantage of the biowaste materials is that they possess cellulose, lignin and hemicellulose which are the potential material for energy storage devices [12,13]. In comparison with fossil fuels, biowaste materials have negligible negative impact to the environment [14].

Various carbon materials like single-walled carbon nanotubes, multi-walled carbon nanotubes, activated carbon, carbon nanospheres, carbon nano-onion, graphene have been tested as apt materials for the fabrication of EDL (Electrical Double Layer) electrodes [15–21]. The selection of the biowaste precursor and its activation process emphasizes the pore size distribution, surface area, specific capacitance and electrochemical performance of the supercapacitor.

In this paper we describe our continued investigation on Oil Palm Leaves (OPL) which are the lignocellulosic biowaste as the precursor for the electrode material. This study showed superior super capacitance performance in comparison with our earlier reports.

2. Experimental

2.1. Sample preparation

Oil palm leaves which are the biowaste material were used as a precursor for the production of porous carbon nanoparticles

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http://dx.doi.org/10.1016/j.jechem.2016.04.007
2095-4956/

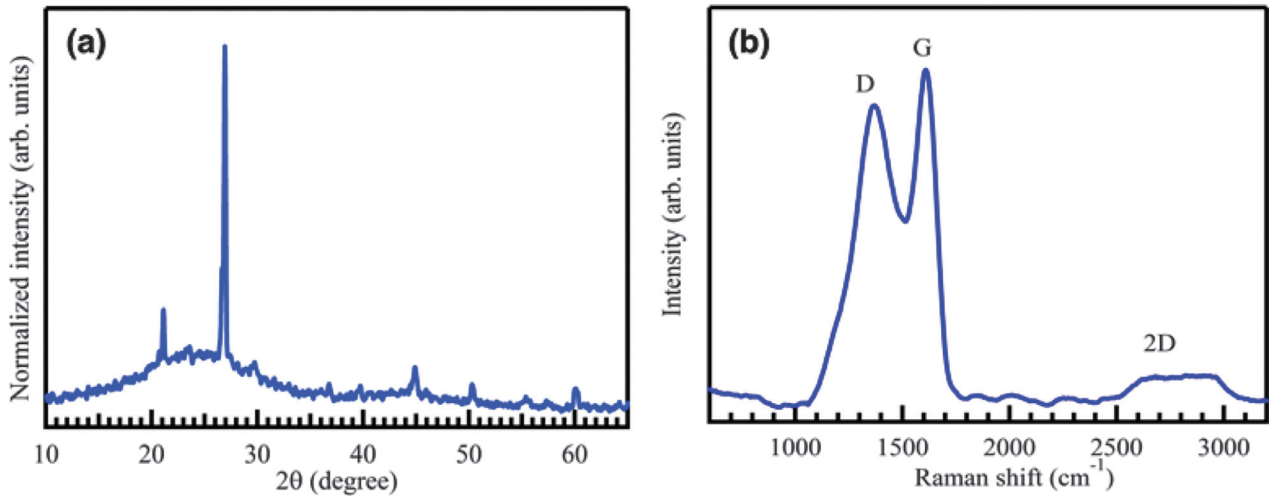

Fig. 1. (a) XRD pattern and (b) Raman spectrum for PCNs.

(PCNs). OPLs were dried in an oven at 110 °C for 48 h to eliminate all the moisture content in the sample. The dried sample was crushed and grinded at a speed of 12,000 rpm using a grinder. The ground sample was furthered sieved to the particle size of 63 μm. The sieved sample was synthesized by one step catalyst free pyrolysis technique in a tube furnace at 700 °C under nitrogen atmosphere (with continuous flow of 150 mL/cm^3) for two hours at a heating rate of 10 °C/min followed by cooling to room temperature. The aqueous NaOH, 2.5 M is employed to remove silica from the obtained product which converts the product in to carbon nanosphere (template approach). Detailed experimental method is discussed in our earlier papers [22–25].

2.2. Porous carbon nanoparticles characterization

PCNs were characterized using X-ray diffraction (XRD, Rigaku Mineflex II), field emission scanning electron microscope-energy dispersive X-rays (FESEM-EDX, JEOL, JSM-7800F), transmission electron microscopy (TEM, JEOL, JSM 1230) and N_2 adsorption–desorption (Micromeritics ASAP 2020) techniques. Full details about the PCNs were given in Ref. [22].

2.3. Electrochemical studies

The following procedure is adopted to prepare samples for electrochemical studies. PCNs with 5 wt% polytetrafluoroethylene (PTFE) and 15 wt% carbon black were mixed, followed by pressing the mixture onto a nickel foam to prepare the electrode. Coin cell design is adopted in this experiment to measure specific capacitance. The total mass of the both electrode is around 9.13 mg and the electrode dimension is around 1 cm × 0.8 cm. The electrochemical tests were performed using a two-electrode type system, in which the electrodes were electrically isolated from each other by porous membrane in 5 M KOH electrolyte. The data were collected using an electrochemical workstation (Autolab/PGSTAT M101) equipped with a frequency response analyzer. Cyclic voltammetry tests were performed between 0 and 1 V with scan rates range from 5 to 100 mV/s. Charge–discharge galvanostatic tests were performed at current densities up to 1 A/g. Impedance data were collected from 500 kHz to 0.01 Hz, with 10 mV in ac amplitude signal at open circuit potential (OCP).

3. Results and discussion

3.1. Structural and morphological characterizations

Fig. 1(a) shows XRD pattern for the PCNs synthesized at 700 °C from OPL. The peaks at $2\theta = 26.85^o$, 44.55^o, 50.45^o and 60.10^o are referring to graphite carbon according to ICDD card 96-901-2231. In addition, the peak at $2\theta = 21.10^o$ is close to the reflection for carbon (ICDD card 96-901-4005) [26]. The peak at 26.85^o is because of the high crystalline cellulose fibers which are formed due to the hemicelluloses and celluloses of OPL. The peaks at 44.55^o, 50.45^o and 60.10^o show graphitic nature of the PCNs. From these peaks, it is clear that the PCNs obtained from the synthesis of OPL show graphitic structure. In addition, we evidence another peak at 68^o, and this peak corresponds to the (2 2 0) plane. The reduction in the size of this peak in comparison to other peaks shows the reduction in the crystallinity facilitating the formation of the smaller particle size.

The lattice vibration of carbon materials was investigated by Raman spectroscopy. The D band at 1365 cm^{-1} is known as disorder-induced character of graphite (see Fig. 1(b)). The G band appears at 1610 cm^{-1} [26]. The Raman band between 2700 and 2900 cm^{-1} which corresponds to the overtone of D band is known as 2D. The I_D/I_G ratio is 0.903.

To investigate the morphology of the obtained PCNs, FESEM and TEM were performed. Fig. 2(a) shows the spherical shape without any irregularity in the PCNs. TEM analysis showed the average size of the PCNs to be 20–40 nm which is shown in Fig. 2(b). The particle size distribution was obtained from the TEM image and shown in Fig. 2(c). The histogram shows the average particle size of the PCNs in the sample. This fine particle size of the obtained PCNs would be ideal for electrochemical measurements as it facilitates the ion diffusion between the fine particles.

The surface area and pore width were measured using N_2 adsorption–desorption technique (BET method) (Micromeritics ASAP 2020) with degassing at 200 °C for 12 h. The results showed that, PCNs having a surface area of 37.3 m^2/g and 22 m^2/g of *t*-plot micropore values (see Fig. 3, left). In addition, PCNs showed a micropore percentage of 56.4% and pore diameter of 1.98 nm (Fig. 3, right).

Although the reason for decreasing surface area increasing specific capacitance with respect to high temperature is not completely sure, this phenomenon happened due to the aggregation of