Research Article

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Biomass-derived Nanoporous Carbon-based Electrodes for High-performance Symmetric Supercapacitor

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ABSTRACT

The high-performance symmetric supercapacitor electrodes were fabricated using peanut shell-activated porous carbon, synthesized by chemical activation method. The textural and surface morphologies were analyzed. The electrochemical studies of fabricated electrodes were carried out by 6 M KOH as an aqueous electrolyte using two electrodes system. From charge-discharge process, gravimetric capacitance and volumetric capacitance values were calculated such as 160 Fg^{-1} and 116.8 Fcm^{-3} at a current density of 1 Ag^{-1} in 6 M KOH solution. Energy density and power density values were calculated as 5.5 $Whkg^{-1}$ for 1 Ag^{-1} and 4 $kWkg^{-1}$ for 10 $Ag^{-1,}$ respectively. This electrode has excellent cyclic stability and has revealed 80% capacitance retention even after 8,000 charge/discharge cycles at 1 Ag^{-1}. The result clearly demonstrated that the natural resource of specific biomass could be an economic and eco-friendly alternative raw material for supercapacitor electrodes with efficient volumetric energy and power densities.

Keywords: Activated Porous Carbon; Energy Storage Device; KOH activation; Peanut Shell; Symmetric Supercapacitor Electrode.

1. INTRODUCTION

High energy cost, continuous depletion of fossil fuel reserves and climate change due to excessive greenhouse gases lead to the society turning towards renewable and sustainable energy sources (Farma *et al.* 2013). Hence, sustainable and renewable energy resources are strongly needed in order to reduce the environmental pollution. Sunlight and wind generation are good candidates, but they cannot be used at night or without wind. In order to store and use the harvested energy, efficient energy storage devices such as battery and supercapacitor are necessary (Kalyani and Anitha, 2013).

Generally, the rechargeable batteries are widely used for electrical energy storage (Jinglong *et al.* 2011); but supercapacitors has high power density, rapid charge/discharge, long cycle life (>100 000 cycles) and low maintenance cost. Despite the advantages of high power density and high cycle life of supercapacitors, their intrinsically low energy density (the amount of energy stored per unit weight) has limited them from widespread commercial applications as compared with batteries (Burke *et al.* 2000) .

These drawbacks can be mitigated by developing a new class of high-performance carbon electrodes which consists of a combination of materials produced from abundant, cheap and environmentally friendly resources with low processing costs (Wei *et al.* 2012). Activated Carbon materials are good alternative electrode materials for EDLC in comparison to other forms of carbon because of their good electrical conductivity, large-scale production and low cost (Frackowiak and Béguin *et al.* 2001) (Jambulingam *et al.* 2007). In the present study, activated porous carbon was prepared using peanut shell as carbon precursor by KOH activation process (Yang *et al.* 2017). The obtained activated porous carbon was used as a supercapacitor electrode and the electrochemical performance was investigated.

2. EXPERIMENTAL SECTION

2.1. Synthesis of Activated Porous Carbon

The unique biomass (i.e) peanut shell, collected from agricultural farmers in Erode, India, was used to prepare Activated carbon, which has high surface area derived by chemical activation. Briefly, the collected and dried biomass was washed clearly and dried in an

oven at 90 °C for 24 h. The dried shell was then squeezed into a fine powder, using mortar and pestle. Briefly, the fine powder was pre-carbonized by using a tubular furnace under N_2 flow at 600 °C for 1h with a heating rate of 5 °C min^{-1} and the carbon yield from the pre-carbonization of is around 30 wt.%. After pre-carbonization, the resulting carbon powder was mixed with potassium hydroxide (KOH) in the mass ratio of 1:4, respectively. Then, the above mixture was placed in the alumina crucible and kept in a stainless steel tube within a tubular furnace at 800 ºC for 1h for activation with a heating rate of 5 °C min^{-1} under N_2 flow. The revealed activated porous carbon sample was stirred with 1M HCl for 1hr and washed thoroughly with double distilled water until a neutral pH was reached. Then, the resulting nano porous carbon was dried at 80 °C for 12 h.

2.2 Characterization of the Materials

The surface morphologies of the AC materials were analyzed by using Scanning electron microscopy (SEM, Hitachi SU-70 analytical ultra-high resolution SEM (Japan)). The specific surface area (SSA) of the AC samples were measured by N_2 adsorption–desorption isotherms at 77 K using a Micromeritics, ASAP 2020 surface area analyzer. Prior to the measurements, the APC samples were degassed at 350 ºC under vacuum (10^{-3}mbar) for 8 h.

2.3 Preparation of the Electrodes

Preparation of Symmetric Carbon-Carbon electrodes was prepared by using the mixer of 80 wt.% of nano porous active carbon 10 wt.% of carbon black and 10 wt.% of Polyvinylidene Difluoride (PVDF) binder. The uniform slurry was made by adding a few drops of N-Methyl-2-pyrolidone (NMP) and then worked out until smoothness was attained. In this work carbon coated aluminium foil was used as a current collector of 12 mm diameter and a thickness of ~200 µm and then the slurry was coated on it; and in vacuum, the coated electrode was dried under at 170 ºC for overnight. The two identical disk-shaped electrodes were prepared from the dried electrode and weighted. The thickness of electrode and the corresponding mass loading of the electrode per cm^2 were managed and then the final thickness ca.120 ± 10 µm and the mass loading of the electrode ca. 9 ± 10 mg/cm^2 were taken.

2.4 Fabrication of Symmetric Supercapacitor

Using two symmetric carbon electrodes, symmetric supercapacitor was fabricated with the help of Teflon Swagelok® cell and the efficient glassy fibre which is soaked in 6M KOH electrolyte acts as a porous membrane separator.

2.5 Electrochemical Measurements

The fabricated symmetric Supercapacitor were analyzed by the techniques of Cyclic Voltammetry (CV), and Galvanostatic Charge Discharge (GCD) studies, CV measurements were performed at scan rate of 5mVs^{-1} using potential static electrochemical work station Solartron SI-1287 for potential window of 0V-1V. GCD study was expertised at the current density of 0.5 Ag^{-1}. The specific capacitance of the supercapacitor electrodes was estimated from the discharge curves by using the equation (1) and (2) respectively (Voloshin *et al.* 2016).

$$C_{sp}(F/g)=4*C/m \quad (1)$$

Galvanostatic or constant current (CC) discharge curves are used to measure cell capacitance using equation (2) (Frackowiak *et al.* 2012).

$$C(F) = I / (dV/dt) \quad (2)$$

where, $C_{sp}(Fg^{-1})$- specific capacitance of the electrode; C(F) - measured capacitance for the two-electrode cell; m (g) - average active mass of the both electrodes; I (A) - the discharge current; dV (V) - the total potential window and dt (s) - the discharge time, respectively.

The energy and power densities of the two symmetrical supercapacitor electrodes were calculated by using equation (3) and (4) (Ming-boWu, *et al.* 2015)

$$E\ (Wh/kg) = 1/2\ C\ V^2 \quad (3)$$

where, C(Fg^{-1}) - the specific capacitance of the symmetrical supercapacitor, calculated from equation 1, V (V) refers to the potential difference.

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

where, E consigns the calculated energy density (Wh/kg) value from equation 3, t (s) is the discharge time.

3. RESULTS AND DISCUSSION

3.1 Structural and Textural morphology of Nanoporous Activated Carbon (NAC)

For the as-prepared Nanoporous Activated Carbon, specific surface area are calculated as 1400 m^2g^{-1} from BET analysis which provides the competetive value than the reported article (Arjunan and Balasubramanian *et al.* 2018) and it can offer sufficient electrode-electrolyte interaction to form electric double

layers. Fig. 1 shows the surface morphology of the Nanoporous Activated Carbon which reveals the fibrous and random particle morphologies.

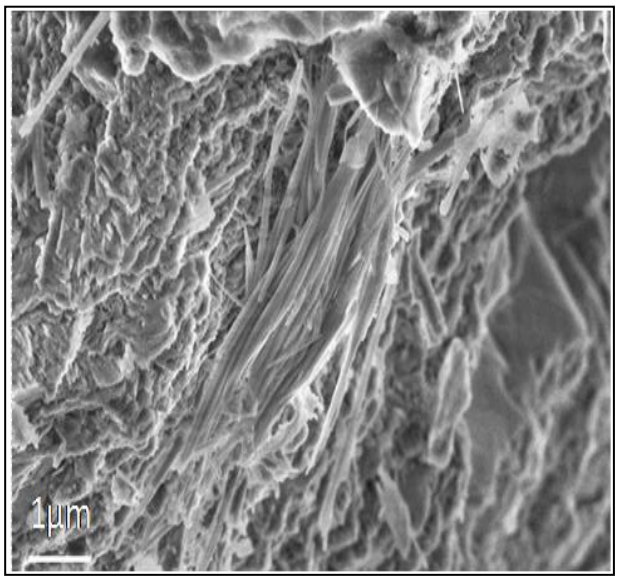

Fig. 1: Surface morphology of Nanoporous activated carbon after KOH activation.

3.2 Electrochemical Performance

Under voltage window of 6M KOH electrolyte, the CV curves of the electrode were examined at the scan rate of 5 mVs^{-1} and the results are shown in Fig. 2. It can be noticed that the CV curve of the fabricated Symmetric Supercapacitor exhibits rectangular shape which specify the ideal EDLC behavior of the electrode. The rectangular shape is maintained up to 1.0 V. The GCD study was carried out at current density of 1 Ag^{-1} as illustrated in Fig 3. The perfect triangular shape with small IR drops explained the excellent reversibility and good Coulombic efficiency of electrodes.

The specific capacitance of Symmetric Supercapacitor electrode is calculated by GCD curve using equation 1 and 2 and gravimetric capacitance and volumetric capacitance of the electrodes are around 160 Fg^{-1} and 116.8 Fcm^{-3} at a current density of 1 Ag^{-1} respectively (XU Tao *et al.* 2008).

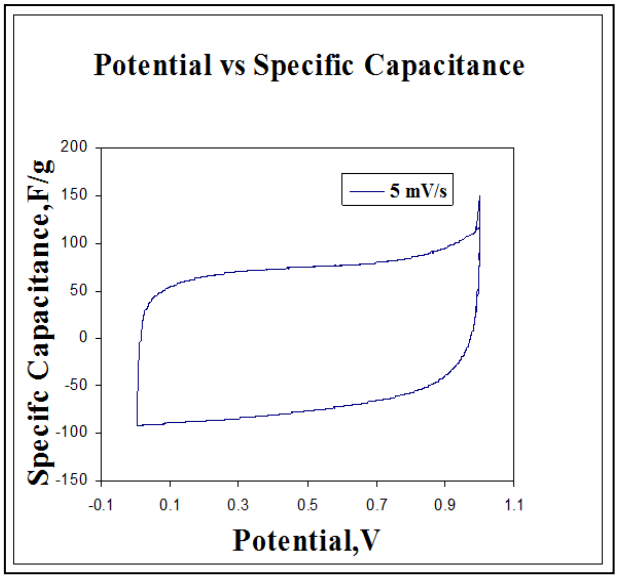

Fig. 2: CV curve of symmetric supercapacitor at a scan rate of 5 mVs^{-1}

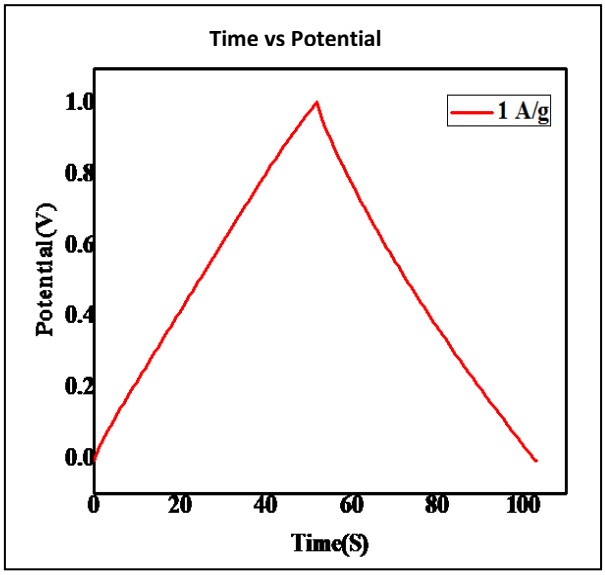

Fig. 3: GCD curve of symmetric supercapacitor at a current density 1 Ag^{-1}

Table 1. Calculation of Gravimetric and Volumetric capacitance, Energy Density and Power Density of BAC electrode using 6M KOH as Electrolyte

Current Density (Ag^{-1})	C_g (Fg^{-1})	C_v (Fcm^{-3})	Discharge Time (s)	E_g ($WhKg^{1}$)	E_v (WhL^{-1})	P_g (WKg^{-1})	P_v (WL^{-1})	*P_g ($KwKg^{-1}$)
1	160	116.8	51	5.5	4.05	388	283	0.388

C_g-Gravimetric Capacitance, C_v-Volumetric Capacitance, E_g-Gravimetric Energy density, E_v-Volumetric Energy Density, P_g-Gravimetric power density, P_v-Volumetric Power density. *P_g- Gravimetric power density in $kWkg^{-1}$

In Fig. 4, the Nyquist plot of the BAC electrodes were illustrated which indicated the impedance in the frequency range between 0.01 Hz and 100 kHz. The measured value of resistance for symmetric BAC supercapacitor electrode is 0.53 Ω (Gomadam *et al.* 2005).

For practical applications, the energy density and power density of the supercapacitor device are the major parameters. These values were calculated using equation 3 and 4 as 5.5 $Whkg^{-1}$ for 1 Ag^{-1} and 4 $kWkg^{-1}$ for 10 Ag^{-1} respectively (Figure not mentioned). All the calculated values are reported in Table 1. This electrode has excellent cyclic stability and capacitance retention is 80% even after 8,000 charge/discharge cycles at 1 Ag^{-1}.

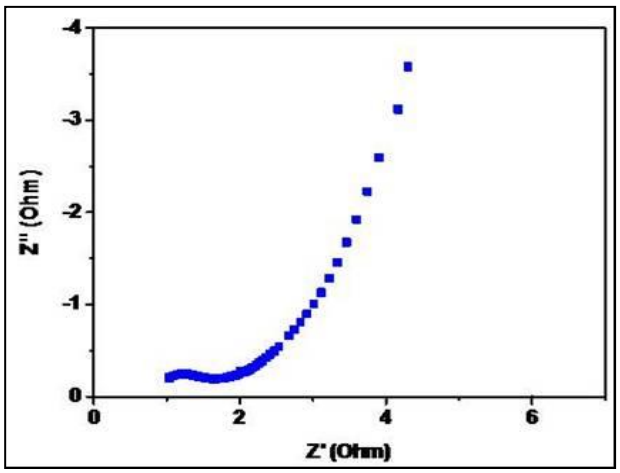

Fig. 4: Nyquist plots for symmetric supercapacitor

4. CONCLUSION

The high-performance symmetric supercapacitor electrodes were fabricated using biomass activated porous carbon synthesized by chemical activation method. The Electrochemical studies of fabricated electrodes were investigated by 6M KOH as an aqueous electrolyte using two electrodes system. From charge-discharge process, gravimetric capacitance and volumetric capacitance values were calculated such as 160 Fg^{-1} and 116.8 Fcm^{-3} at current density of 0.5 Ag^{-1} in 6M KOH solution. Energy density and Power density values were calculated as 5.5 $WhKg^{-1}$ for 1 Ag^{-1} and 4 WKg^{-1} for 10 Ag^{-1} respectively. This electrode has attained 80% capacitance retention even after 8,000 charge/discharge cycles at 1 Ag^{-1}. Thus fabricated symmetric supercapacitor may be used as an alternative raw material for supercapacitor electrodes.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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