Research Article

Journal of Environmental Nanotechnology

Nanoporous Activated Carbon and Multi-walled Carbon Nanotubes from Renewable Botanical Hydrocarbons and their Impact on Efficiency of Supercapacitor Performance

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Received: 23.01.2020 Accepted: 28.02.2020 Published: 30-03-2020
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ABSTRACT

Highly activated carbon and Multi-walled carbon nanotubes (MWCNTs) are preferable materials for supercapacitor electrode. Activated Carbon was prepared from *Pongamia pinnata* shell by Chemical Activation process and MWNTs were prepared from *Pongamia pinnata* oil by Spray pyrolysis method, respectively. The electrochemical capacitor has been assembled with Multi-walled carbon nanotubes/Graphene composites as negative electrode and activated carbon as positive electrode with 6 M KOH as an aqueous electrolyte. The charge-discharge performance of fabricated electrodes was satisfactory for energy storage applications. It has to be improved by the addition of MWCNTs in anodes. It can be executed with a specific capacitance of 148 Fg^{-1} at a current density of 0.5 Ag^{-1}. The maximum energy density and power density were up to 5.1 $Whkg^{-1}$ at 0.5 Ag^{-1} and 5.0 $kWkg^{-1}$ at 10 Ag^{-1}, respectively. The galvano-static charge-discharge cycling studies have revealed the excellent capacity retention of 81% even after 4000 cycles. The unique fabrication strategy for the two-electrode SC assembly with highly conducting and stable-natured carbon nanomaterials expand the arms of energy storage devices.

Keywords: Activated Carbon and Multi-wall Carbon Nanotubes; Bio-waste *Pongamia pinnata* Shell and Oil; Electrochemical Analysis; Spray Pyrolysis; Supercapacitor Electrode.

1. INTRODUCTION

Electrochemical capacitors are rechargeable electrochemical energy storage devices, which can store a much larger amount of electrical energy with the capacitance of thousands of Farads in the interfaces between electrodes and electrolytes. Compared with other energy storage devices, nowadays, Lithium-ion batteries (LIBs) and electrochemical capacitors (ECs) are the important chemical energy storage devices (Miller and Simon, 2008; Kang *et al.* 2010). EC can offer great advantages of high-power capability, high rates of charge and discharge, flexible packaging and low weight. The invention of EC aims to bridge the critical performance gap between the higher energy density of battery and high-power density of conventional electrolytic capacitor (Zhang and Zhao, 2009; Zhai *et al.* 2011; Kotz and Carlen, 2000; David *et al.* 2011; Pasquier *et al.* 2004; Lee *et al.* 2010).

LIBs have a high energy density, but lower power density and lesser cycle life. ECs have high power density and long cycle life, but their energy density is far lower than the lithium-ion battery (Simon and Gogotsi, 2008; Winter and Brodd, 2004).

Compared to Activated carbon, graphene and MWCNTs also have good chemical stability and high electrical conductivity. It was considered as a promising material for high-performance super capacitors. The high-performance ECs with activated carbon as positive electrode and MWCNT/graphene composite as the negative electrode have been reported in this work. Their energy density, power density and cyclic performance were investigated.

2. MATERIALS AND METHODS

2.1 Synthesis of Activated Carbon

The *Pongamia pinnata* shell, collected from Erode region, India, was used to prepare Activated carbon, which has a high surface area derived by the chemical activation process. The collected and dried biomass was washed clearly and dried in an oven at 90 ºC for 24 h. The dried shell was then squeezed into a fine powder. Briefly, the fine powder was carbonized by using a muffle furnace at 450 ºC for 1 h with a heating rate of 5 ºC min^{-1}, and the carbon yield from the carbonization was around 80 wt. %. After carbonization, the resulting carbon powder was mixed with potassium hydroxide (KOH) in the mass ratio of 1:3. Then, the above mixture was placed in the quartz boat and kept in the quartz tube in the tubular furnace at 850 ºC for 1 h for activation with a heating rate of 5 ºC min^{-1}, under N_2 atmosphere. The resulting nanoporous activated carbon was stirred with 1 M HCl for 1 h and washed thoroughly with double distilled water until a neutral pH was reached. Then, the carbon sample was dried at 80 ºC for 12 h.

2.2 Synthesis of Multiwalled Carbon Nanotubes (MWCNTs)

Pongamia pinnata oil has to be an efficient precursor for preparing MWCNTs by Spray pyrolysis technique (Jambulingam *et al.* 2007). Silica-supported Fe-Co catalyst (Fe: Co: SiO_2 =1:0.6:4) was prepared by wet impregnation method. Exact quantities of metal salts (Merck), $Fe(NO_3)_3 \cdot 6H_2O$ and $Co(NO_3)_3 \cdot 3H_2O$ were dissolved in methanol and mixed thoroughly with methanol suspension of silica (Merck). The solvent was then made to evaporate and the resultant cake heated to 90-100 ºC for 3 hrs. Then it was removed from the furnace and ground into an agate mortar. The grounded fine powders were then calcined for 1 h at 450 ºC and then re-ground before loading into the reactor. The prepared catalyst was directly sited in a quartz boat and kept at the center of a quartz tube placed inside a tubular furnace. The carrier gas (N_2)nitrogen was introduced at the rate of 100 mL/min into the quartz tube to remove the presence of any oxygen inside the quartz tube. The temperature was raised from room temperature to the desired growing temperature of 650 ºC. Subsequently, methyl ester of *Pongamia pinnata* oil was introduced into the quartz tube through a spray nozzle, and the flow was maintained at the rate of 0.5 mL/min. Spray pyrolysis was carried out for 45 minutes and thereafter the furnace was cooled to room temperature. A nitrogen atmosphere was maintained throughout the experiment.

2.3 Preparation of Negative Electrode

The negative electrode was composed of grown MWNTS prepared from *Pongamia pinnata* oil (Mahalingam *et al.* 2014) and Graphene nano-platelets. Graphene nano-platelets (GS-030P) have been purchased from iENT TECH Inc. with 2 mm thickness and 3-6 layers; the addition of graphene can enhance the durability and conductivity. It acts as a barrier to electromagnetic interference. MWCNTs/graphene composite was dispersed by sonication in N-methyl-2-pyrrolidone (NMP) for 2 h. The polyvinylidene difluoride (PVDF) was used as a binder. The mass ratio of MWNTs/graphene composite, super carbon black (SP), polyvinylidene difluoride (PVDF) with a weight ratio of 8:1:1, were mixed by ultrasonic and high-shear processes in NMP. The slurry was coated on the aluminum foil, which acts as a current collector. Then the negative electrode was dried at 60 ºC under vacuum for 12 h and then cut into a disc of diameter 12 mm. The active material coating was accomplished through direct physical contact of as-prepared MWCNTs/graphene electrode and carbon-coated aluminum foil with electrolyte under constant pressure.

2.4 Preparation of Positive Electrode

The positive electrode was prepared by coating a mixture of activated carbon, superconductive carbon black (SP) and polyvinylidene difluoride (PVDF) with a mass ratio of 8:1:1 on aluminum foil which can act as a current collector. Then the positive electrode was dried at 60 ºC under vacuum for 12 h and then was cut into a disc of diameter 12 mm.

2.5 Fabrication of High-performance Supercapacitor using MWNTs / Graphene composite as Negative Electrode

The fabrication of electrodes can be done with the help of Teflon Swagelok® cell, and it can be assembled with AC positive electrode and MWCNTs/graphene negative electrode; the corresponding ECs were recorded. The electrode was drenched in 6 mol L^{-1}. KOH was used as an electrolyte and Celgard 2400 polypropylene microporous membrane was used as the separator.

2.6 Characterizations

The fabricated ECs were characterized by potential stat/galvanostat (PARSTAT 4000) to

evaluate electrochemical properties like cyclic voltammetry and galvanostatic charge-discharge and electrochemical stability measurements. The specific capacitance was calculated based on the total mass of the activated carbon, MWCNTs, graphene and super carbon black.

3. RESULTS AND DISCUSSION

3.1 Electrochemical Measurements

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

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

Galvanostatic or constant current (CC) discharge curves were used to measure cell capacitance using the equation,

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

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

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

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

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

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

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

Under the voltage window of 6 M KOH electrolyte, the CV curves of the electrode were examined at the scan rate of 5 mVs^{-1} and the results were shown in Fig. 1. It can be noticed that the CV curve of the cell has exhibited a rectangular shape, specifying the ideal EDLC behavior of the electrode. The rectangular shape was maintained up to 1.0 V.

The GCD study was carried out at a current density of 0.5 Ag^{-1}, as illustrated in Fig 2. The perfect triangular shape with tiny IR drops has revealed the excellent reversibility and good columbic efficiency of the electrodes.

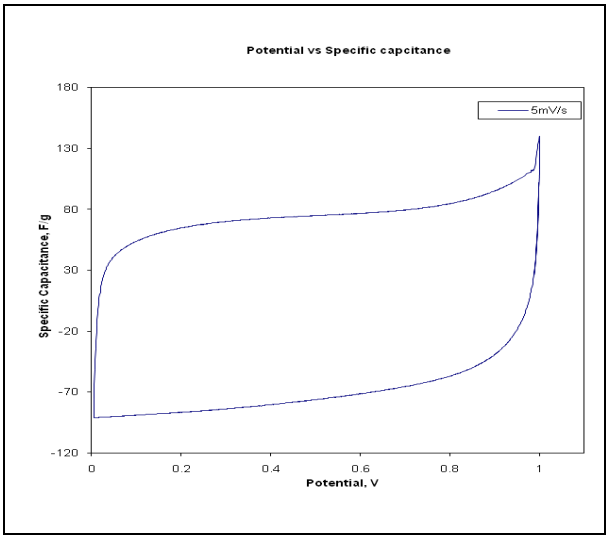

Fig. 1: CV curve at a scan rate of 5.0 mVs^{-1}

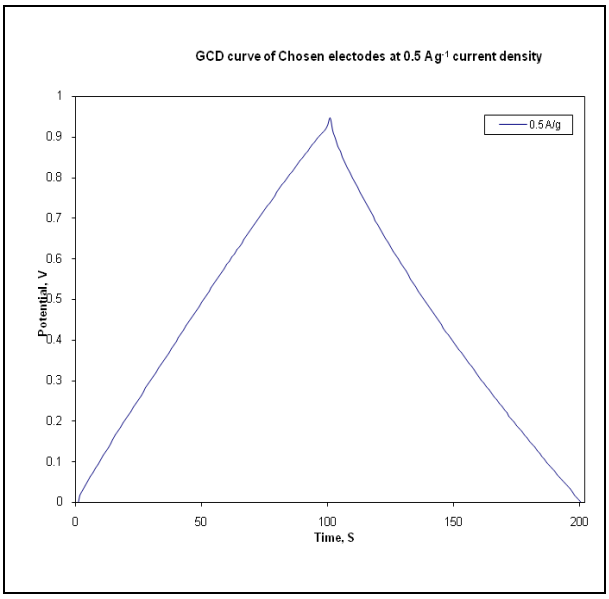

Fig. 2: GCD curve at 0.5 Ag^{-1} current density

The specific capacitances of chosen electrode materials were calculated by these GCD curves using equation (1); the gravimetric capacitance of the electrodes were around 148 Fg^{-1} at a current density of 0.5 Ag^{-1}.

For practical applications, the energy density and power density of the supercapacitor device are the major parameters. Essential energy density and power density were calculated using equations (3) and (4) as 5.1 $Whkg^{-1}$ for 0.5 Ag^{-1} and 5.0 $kWkg^{-1}$ for 10 Ag^{-1}, respectively. This electrode has excellent cyclic stability and capacitance retention was 80% even after 4000 charge/discharge cycles at 1 Ag^{-1}.

4. CONCLUSION

A simple, cost-effective and high performance as-prepared supercapacitor using MWNTs / Graphene composite as negative electrode has successfully enriched the electrochemical performances. A specific capacitance of 148 Fg^{-1} has been achieved at the current density of 0.5 Ag^{-1}. The maximum energy density and power density were up to 5.1 $Whkg^{-1}$ at 0.5 Ag^{-1} and 5.0 $kWkg^{-1}$ at 10 Ag^{-1}. The continuous galvano-static charge–discharge cycling studies revealed excellent capacity retention of 81% even after 4000 cycles. MWCNTs/Graphene electrodes have exhibited a great potential application for high-performance supercapacitors in the future. The extraordinary perspective of MWCNTs and graphene-based electrochemical capacitors will unveil new doors for competent future energy storage systems at the global scale.

ACKNOWLEDGEMENTS

We acknowledge Director, Institute for Environmental Nanotechnology, Erode, Tamilnadu, India, for providing all facilities for our material characterization and electrochemical studies.

FUNDING

This research received no specific grant from any funding agency in the public, commercial, or not-for-profit sectors.

CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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