Biocarbon Derived from Seeds of Palmyra Palm Tree for a Supercapacitor Application

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ABSTRACT

Carbon-based materials are among the most promising materials for future electrochemical energy storage and conversion. Eco-friendly Palmyra palm seed derived microporous biocarbon was fabricated on the graphitic sheet. Palm seed derived carbon was carbonized by using 0.5 M H\textsubscript{2}SO\textsubscript{4} without any activating agent. Morphological characterization of PSDC investigated through SEM (Scanning Electron Microscopy). It shows PSDC is microporous with carbon network like structure. Physiochemical characterization performed through XRD, FT-IR and Raman studies. Raman studies confirm the PSDC having carbon based material. Electrochemical performance by using Cyclic voltammetry (CV), Galvanostatic charge discharge (GCD) and Electrochemical Impedance spectroscopy (EIS). PSDC exhibits the specific capacitance of 220 F/g at 5 A and 276.5 F/g at 1 A current as well as remarkable capacitance retention after 500 cycles is 63.1%. It shows PSDC having remarkable electrochemical storage application.

Keywords: Palmyra palm tree seeds, Supercapacitor, Biocarbon

1 Introduction

The depletion of non-renewable fuel resources and eco system contamination are worldwide. Over the last few decades, sustainable and environmentally friendly energy storage and conversion system solutions have been developed to address these issues [1]–[3]. Energy storage devices, stores energy in the forms of electrochemical, chemical, and thermal using batteries, capacitors, etc. Among these, supercapacitors play an important role in hybrid, power grid, electric vehicles, and low-energy industrial equipment, etc. As a promising energy storage system, supercapacitors have attracted numerous [4]–[6]. Supercapacitors or ultracapacitors are electrical energy repository devices. When compared to conventional storage devices like capacitors, batteries, and supercapacitors with high power density. The longer life-cycle of a supercapacitor is highly reversible, which is due to the charge-storage process when compared to other power storage devices [7], [8]. In the meantime, numerous efforts are ongoing to improve the energy capacity of the supercapacitors using carbon electrode materials.

Using the energy store mechanism, Super capacitors may be divided into two types such as electrical double-layer capacitors (EDLCs) and pseudocapacitors. Electrochemical dual-layer (EDLC) capacitors, which employ electrostatic charge storage or non-faradic processes without charge transfer between
electrode/electrolyte interface, constitute one of the most promising electrochemical energy storage devices among various forms of electrical capacitors [9], [10]. EDLC performance depends on the electrical materials, such as conductivity, porosity, wettability, and stability. Carbon-based materials are generally utilized as EDLCs as electrical materials such as graphene, activated carbon, carbon nanofiber, and carbon nanotube are widely used as electrode materials EDLCs [11]–[13]. Whereas, the redox processes employed in its charge storage mechanism are based on pseudocapacitors such as MnO₂ and RuO₂ [14], [15] and conducting polymers such as polypyrrole, polyaniline, and polydiphenylamine are extensively used. During the cycling process, the redox reactions are typically unstable and provide a low power density that is less to that in the EDLC [16]–[18].

Recently, sustainable biomass carbon sources were highlighted by comparatively cheap, easy processing methods and eco-friendly. Almost all commercial EDLCs use varied sizes of pores and excellent cyclical stability. The rising scarcity of fossil fuels has particularly garnered considerable attention from biomass and organic waste generated by activated carbon as a viable electrode material, which includes the various form of organic materials such as orange peel, rice straw, corncob, tea seed shell, and Thespesia populnea Seeds, etc. [10], [11], [19]–[22]. These biomass carbons are readily available, clean, and renewable for a sustainable and cheap-cost carbon source compared to the pseudocapacitors, but it suffers from very low capacitance and energy capacitance [23]. This can be overcome by enhancing high super capacitive performance by due considering the electrode material for EDLCs. Biomass is present excess in nature, environment-friendly renewable resource and its low cost has attracted the researchers. Biomass derived carbon electrode material is successful for supercapacitor and also for re-cycling, reduces the use of non-renewable resources and also creates a green environment [24]–[27]. Numerous research efforts have been focused on biomass as precursors for an electrode in energy storage applications. The production of biocarbon at a cheap cost is important for commercial use. Palmyra palm trees belong to the Areaceae family, found in many different countries, particularly in Asia and the African continents. In this biomass of palmyra palm seed was utilized as a carbon electrode material for supercapacitor performance. Herein, we demonstrate a simple synthesis of natural biocarbon derived from palmyra palm seeds for supercapacitor application. The morphology, elemental composition and structure of the carbon materials were examined using field emission scanning electron microscopy (FE-SEM), Fourier-transform infrared spectroscopy (FT-IR) and X-ray diffraction studies (XRD), and Raman analysis. Furthermore, the electrochemical studies of the biocarbon samples as anode materials by using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) as well as galvanostatic charge/discharge (GCD) studies.

2 Experimental

2.1 Synthesis of biocarbon from palm seeds

The biomass of carbon is derived from palmyra palm seed was prepared by carbonization. In typical carbonization, the palm seeds were collected from various fields nearby Karaikal, Puducherry, India. Further, the dried palm seeds were broken and well cleaned with acidic and deionized water allowed to dry in sunlight for 12 h. The dried broken seeds were carbonized in a muffle furnace at 600 °C for 4 h with a heating rate of 5 °C/min under an inert atmosphere to obtain the biocarbon. The resulted carbon has been denoted as palm seed derived carbon (PSDC) in the subsequent discussions.

2.2 Material characterization

Field-Emission Scanning Electron Microscopy (FE-SEM) utilizing Oxford equipment and energy-dispersive X-ray Spectroscopy investigated the morphological structure and elemental composition of palm-seeded carbon (EDX). The PSDC was structurally characterized by X-ray (XRD), Cu Kx μ = 1.54 Å radiation (Bruker). The Bruker OPUS spectrometer was used with wavelength ranges from 500 to 4000 cm⁻¹ to record Fourier transform infrared (FTIR) spectrums. For samples of carbon with a laser wavelength of 532 nm as the excitation source, Raman spectrum analysis was seen.
2.3 Electrochemical measurements

An electrochemical workstation was used to study the CV, EIS, and GCD (OrigaLys-OFG500, France) techniques. The working electrode was fabricated by mixing PSDC, conductive carbon black and polyvinylidene difluoride (PVDF, as a binder) in the presence of dimethylformamide (DMF) with a weight ratio of 80:10:10, respectively. After grinding, the paste is overcoated on the graphite sheet. The three-electrode setup consists of PSDC coated on the graphite substrate as a working electrode, calomel as a reference electrode, and Platinum wire as a counter electrode, respectively. The electrochemical supercapacitor performances of PSDC electrode materials were studied in three-electrode configurations using 0.5 M H₂SO₄ as the electrolyte. Overall schematic diagram of the PSDC towards supercapacitor performance is shown in Fig.1.

![Overall scheme of PSDC towards supercapacitor application](image)

**Figure 1:** Overall scheme of PSDC towards supercapacitor application

3 Result and discussion

3.1 Morphological and elemental analysis of PSDC

SEM was utilized for morphological analysis of palm seed derived biocarbon, as shown in Fig.2 (a) and (b) as lower and higher magnification, respectively. The morphology of palm seed derived biocarbon is macroporous with a carbon network like structure. Such a morphology of porous microstructure of biocarbon is known to help in electrode and electrolyte interface reaction and also to enhance the electrochemically active sites. The EDX analysis confirms only the elements of carbon and oxygen present in the palm seed derived biocarbon, which reveals from Fig.2 (c).
Biocarbon Derived from Seeds of Palmyra Palm Tree for a Supercapacitor Application

3.2 XRD, FT-IR and Raman studies of PSDC

Furthermore, chemical characterizations such as XRD, FT-IR, and Raman spectroscopy were used to confirm the precise macrostructure of the carbon network and the graphitic carbon-like network. Biocarbon samples were subjected to X-ray diffraction (XRD) studies to determine their crystallinity behavior. As shown in Fig. 3 (i), the XRD pattern of PSDC has a pair of diffractive peaks having the planes (002) and (100). The presence of peaks at $2\theta = 24^\circ$ and $43^\circ$ shows the formation of a graphitic carbon-like structure. The XRD study indicates that the palm seed biowaste material has been effectively transformed into carbon by the process of carbonization [11].

FTIR spectroscopy examination is used to further assess the surface nature of the produced carbon samples (Fig. 3 (ii)). The characteristic peak observed around 3440 cm$^{-1}$ was attributed due to O–H stretching of
the surface hydroxyl groups and the C-H Stretching was found at 2890 cm$^{-1}$. The detected bands at 1710 and 1600 cm$^{-1}$ are ascribed to C=O and C=C stretching vibrations, indicating the presence of furanic and aromatic groups, respectively. The C-O and C-C stretching vibration can be ascribed for the bands at 1200 and 594 cm$^{-1}$, respectively [10], [19], [20], [27]. The obtained spectra for biocarbon (PSDC) indicate the existence of oxygen-containing functional groups on their surface. Raman spectroscopy is an effective analytical technique for determining the degree of functionalization in carbon-based materials. The Raman spectra of the PSDC sample are depicted in Fig.3 (iii). In general, the intensity ratio of the D band and the G band show the degree of graphitization as well as the defective site on the carbon network. The PSDC sample shows characteristic D and G bands at 1380 and 1575 cm$^{-1}$, respectively [27]. Based on these findings, biocarbon produced from palm seed was thought to be a potential candidate for electrochemical supercapacitor applications.

![Figure 3: XRD, FT-IR Raman spectra of PSDC](image)

### 3.3 Electrochemical performance of PSDC

#### 3.3.1 Cyclic Voltammetry analysis

A three-electrode setup for CV analysis was carried out in 0.5 M H$_2$SO$_4$ electrolyte to evaluate their electrochemical performance. The CV plot of bare GS and GS-PSDC at a potential range from−0.2 to 1 V versus Ag/AgCl, with a scan rate of 100 mVs$^{-1}$, is shown in Fig.4 (i). The area under the CV cycle of the GS-PSDC electrode is significantly greater than that of the bare GS electrode, which indicates an improvement in electrochemical energy storage, and the typical rectangular box-like profile shows EDLC with a little pseudocapacitance contribution from the GS-PSDC electrode contribution due to the influence
of surface heteroatom functionalities. The CV profile of the GS-PSDC at different scan rates (100–5 mV/s) shows a consistent rectangular box like shape profile, indicates that the electrode has significant rate performance. Fig. 4 (ii) shows different scan rates of GS-PSDC, demonstrating that the peak current density enhanced as the scan rate increases. However, at higher current densities, the specific capacitance was considerably reduced due to insufficient electrolyte diffusion at the electrode surface.

The GS-PSDC electrode-specific capacitance can be determined using the CV curves by using the following Eq (1).

$$C_{sp} = \frac{\int I \, dv}{2mu \Delta V}$$

Where $C_{sp}$ is the specific capacitance in F/g, $\int I \, dv$ signifies the integral area of the CV loop, $\Delta V$ denotes the potential window (V), $\nu$ is the scan rate (V/s) and $m$ remains the mass of the active material (g), respectively [17]. At 5 mV/s, the specific capacitance obtained using the preceding equation (1) is 220 F/g. The estimated specific capacitance steadily decreases from 220 F/g to 77.8 F/g as the scan rate increases from 5 to 100 mV/s. The plots of specific capacitance vs potential scan rate of CV analysis are shown in Fig. 4 (iii).

![Graphs showing CV curves and specific capacitance vs scan rate](image)

**Figure 4:** (i) CV Curves of (a) Bare GS and (b) GS-PSDC in 0.5 M $\text{H}_2\text{SO}_4$ at scan rate 100 mV/s (ii) CV of GS-PSDC at different scan rate (5–100 mV/s) in 0.5 M $\text{H}_2\text{SO}_4$ and (iii) CV Curves of Specific capacitance vs scan rate of GS-PSDC

### 3.3.2 Galvanostatic Charge-Discharge studies

The galvanostatic charge/discharge (GCD) approach is a general way to achieve electrochemical super capacitance. The GCD of GS-PSDC electrode at various current densities from 1 to 5 A/g within a
potential window between 0.2 V to 1 V as depicted in Fig.5 (i). The GS-PSDC electrode specific capacitance is calculated from GCD curves using equation (2).

\[ C_{sp} = \frac{It}{m\Delta V} \quad (2) \]

Where, \( C_{sp} \) is the specific capacitance in F/g, \( I \) represent the current (A), \( t \) is the discharge time (s), \( m \) is the mass of the active material (g) and \( \Delta V \) is the potential window (V), respectively [17]. Fig.5 (ii) shows the specific capacitance dropped progressively from 276.5 to 140 F/g as the current density rose from 1 to 5 A/g, respectively. The cycling stability of the supercapacitance is an important characteristic. The electrochemical cyclic stability of GS-PSDC electrode is demonstrated in Fig.5 (iii) by performing a charge-discharge procedure between 0.2 and 1 V for 500 cycles at a current density of 10 A/g. The capacitance retention measurements of the GS-PSDC electrode after 500 cycles were 63.1%, as shown in Fig.5 (iv). Table 1 Shows the comparison of ‘\( C_{sp} \)’ with the other reported biocarbon electrodes [28]–[30].

![Figure 5](image_url)

**Figure 5:** (i) GCD curves of PSDC in 0.5 M \( \text{H}_2\text{SO}_4 \) at different current densities (1–5 A/g). (ii) GCD curves of Specific capacitance as a function of current density. (iii) GCD curves of 1\textsuperscript{st} and 500\textsuperscript{th} cycle at 10 A/g and (iv) Cycling stability of GCD curves at 10 A/g.
Table 1: Shows the comparison of $C_{sp}$ with the other reported biocarbon electrodes.

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<th>Measurement condition</th>
<th>Specific capacitance (F/g)</th>
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<td>1 A/g</td>
<td>213</td>
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<td>1 A/g</td>
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<tr>
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<td>This work</td>
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</table>

3.3.3 Electrochemical Impedance studies

In order to understand the electrochemically active behavior of biocarbon produced electrodes and augment the data from the CV and GCD studies, electrochemical impedance spectroscopies (EIS) were further conducted. Fig. 6 shows the EIS for bare GS and GS-PSDC electrodes in 0.5 M H$_2$SO$_4$ aqueous electrolyte. The Nyquist plot (Imag Z vs Real Z) indicated in EIS studies a depressed little arc on a high frequency and sloppy region in the mid-to-low frequency area. The bare GS and GS-PSDC electrodes $R_{ct}$ value are 51 Ohm and 21 Ohm respectively [17], [31]. This clearly shows that palm seed derived biocarbon is a significant electrode material for supercapacitor applications.

![Nyquist plot](image)

Figure 6: Nyquist plot of (a) Bare GS and (b) GS/PSDC in 0.5 M H$_2$SO$_4$ and inset shows the Nyquist plot of PSDC

4 Conclusion

In concluding, biocarbon was derived from palmyra palm seed via carbonization process. The morphology and elemental analysis of PSDC are macroporous with carbon network like structures examined by SEM images. The existence of various functional groups and the nature of biocarbon was confirmed using FTIR, Raman studies and XRD techniques. The electrochemical performance of GS-PSDC electrode is studied by CV, GCD, EIS techniques. According to CV and GCD measurements, the specific capacitance of
GS-PSDC electrode in 0.5 M H2SO4 is 220 F/g at 5 mV/s and 276.5 F/g at 1 A current density. Up to 500 cycles, the capacitance retention of the GS-PSDC electrode was found to be 63.1 %, which shows that GS-PSDC electrode significant cycle stability. In, GS-PSDC electrode less impedance values are also observed, which demonstrates the presence of electroactive sites required for charge transfer reaction. As a result, it has been established that the GS-PSDC electrode can be regarded as a significant electrochemical performance for supercapacitor application.

5 Declarations

5.1 Acknowledgments

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5.2 Competing Interests

The author declares no conflict of interests.

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