

ON THE (PSEUDO) CAPACITIVE PERFORMANCE OF JACK FRUIT SEED CARBON

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Abstract

Today, the idea of utilizing biomass from agricultural wastes as a raw material for producing (activated) carbons has attracted the interest of researchers worldwide for the obvious multifarious applications of carbon. As a novel attempt, carbon has been derived from a domestic biomass waste viz., the jack fruit seeds (*Artocarpus heterophyllus*) and tested its prospects as electrodes in energy storage devices namely electrochemical capacitors. Jack Fruit Seed Carbon (JFSC) is produced by simply pyrolyzing JFS under N_2 atmosphere without making use of any activating agents. Capacitive behavior in 1M H_2SO_4 & 1M Na_2SO_4 electrolytes are evaluated by impedance spectroscopy, cyclic voltammetry and galvanostatic charge-discharge studies. N_2 sorption studies evince the presence of microporous nature of the JFSC. Cyclic voltammetry estimates specific capacitance as high as 316 and 203 Fg^{-1} respectively in H_2SO_4 and Na_2SO_4 at a scan rate of $10mVs^{-1}$. JFSC show excellent electrochemical cycle stability in 1M H_2SO_4 with 93% of the initial capacitance being retained at the end of 500th cycles. The studies infer that JFSC has immense potential as an electrode material in electrochemical capacitors while its performance largely depends upon physical features, surface functional groups or the hetero atoms contributing pseudocapacitive nature to the JFSC. Thus the work not only describes a waste utilization scheme but also presents a new and valuable dimension to the usefulness of jack fruit seeds in electrochemical capacitors

Keywords: Electrochemical capacitors; Pseudocapacitors, Biomass Carbon electrode and Jack Fruit seeds

1. INTRODUCTION

Electrochemical capacitors are attractive energy storage devices owing to its long cycle life, high efficiency, high power density and eco-friendliness. Specifically, pseudocapacitors store energy in two ways: (a) by capacitive charging of the double layers of the electrodes i.e. energy is stored electrostatically in proportion to the area of the double layers and (b) through the products of Faradaic (eg. redox) reactions at the electrode surfaces i.e. energy is stored electrochemically. The capacitance due to the former is called electric double layer capacitance and the latter is called pseudo-capacitance. Whatever the instance may be, selection of appropriate electrode and electrolyte are the fundamental factors in determining the overall capacitor performance. Thus exploding research is being conducted to engineer novel materials for lowering the costs of the capacitors for various projected applications and for realizing in the commercial energy front.

The prospective electrode materials for electrochemical capacitors are carbon [1-7], the reasons being its abundance, lower cost, easy processing, non-toxicity, higher specific surface area, good electronic conductivity, high chemical stability, and wide operating temperature range [8]. High surface area carbon materials mainly include activated carbon [9-14], carbon aerogels [15], CNTs [16, 17], templated porous carbons [18-21], and carbon nanofibres [22]. Normally carbon materials with larger specific surface

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areas have a higher capability for charge accumulation at the electrified interface, rather than in bulk of the capacitive material. Therefore, the capacitance predominantly depends on the surface area of the electrode accessible to the electrolyte ions so that activated carbons with a large surface area are generally preferred. On the other hand, due to the contact resistance between carbon particles resistivity of the carbon particles will increase resulting in a high internal series resistance with an ultimate reduction in electrochemical performance [8]. In addition to the above fact, the electrode surface area inaccessible to electrolyte ions [23] also impedes the capacitance performance of carbon materials, resulting in limited capacitance. Further, all micropores in the electrode may not necessarily be accessible to electrolyte ions. Hence sometimes specific capacitance may not be directly proportional to the surface area. So in order to off-set these effects researchers employ pseudocapacitive electrode materials to realize improved specific capacitance.

Pseudo-capacitive materials reported in the literature mostly are conducting polymers and electroactive metal oxides [24]. These reports stress that carbonaceous materials with surficial organic functional groups or heteroatoms would be a choice for electrode materials and that the hetero-groups help the adsorption of the electrolytes ions thereby improving the hydrophilicity or lipophilicity, wettability and rapid electrolyte ions transport within the micropores of the carbon materials [25]. Carbons with heteroatoms like oxygen and nitrogen would induce Faradaic redox reactions leading to a 5-10% increase in the total capacitance when

compared with carbon containing no heteroatoms [26]. Recently Leitner et al. reported a nitrogen-containing carbon material with high pseudo-capacitance even in the absence of substantial surface area [27]. Faradaic redox reactions exhibited by carbon materials containing nitrogen are extensively studied for the capacitors applications by many researchers over the globe [28-31].

The presence and the amount of functional groups containing oxygen, such as $-\text{COOH}$ and $\text{C}=\text{O}$, depends mainly on the precursors used and preparation conditions for deriving the carbon powders. It is well known that these functional groups are acidic and electrochemically active too that contributes to the pseudo-capacitance by large [32]. The article by Jurewicz et al. [28] with six activated carbon samples with $S_{\text{BET}} = 1156\text{--}2571 \text{ m}^2\text{g}^{-1}$ stresses the importance of the surface groups towards achieving pseudo-capacitance. It is interesting to observe that oxygen atoms on the surface has ill-effects like self-discharge, leakage current, only in non-aqueous electrolytes, whereas in aqueous electrolytes especially in H_2SO_4 solution, the total capacitance increases due to pseudo-capacitance.

Pseudocapacitance credited with Faradaic reactions of oxygen-containing functional groups with electrolyte ions is identical with the capacitance developed by Faradaic materials like transition metal oxides, such as RuO_2 and MnO_2 [24]. Thus, carbons with surface functional groups or heteroatoms appear to be cost-effective alternative electrode materials. Consequently, materials of vegetable origin has thus been given importance as they contain appreciable amount of carbon and would offer high valued scientific, industrial and engineering product namely carbon (with heteroatoms) through the carbonization of these zero-cost biomass. Sometimes the utilization of biomass wastes also provides a solution for waste disposal.

Survey of recent research reports shows that carbon materials derived from biomass has the potential of being utilized as electrode materials in electrochemical capacitors [33-40]. Hence, the purpose of this study is to examine the feasibility of obtaining carbon from a common domestic vegetable waste viz., the Jack Fruit Seeds (JFS) and to completely evaluate the applicability of the obtained carbon as an electrode material for electrochemical capacitor (pseudocapacitors) in acid as well as neutral medium. Jack fruit is consumed as such or can form an important ingredient in jellies, jams, salads and other delicious sweets. The seeds of jack fruit also have food value which contains glucose and proteins and are used in many varieties of food stuffs. Even so the seeds are discarded from most of the houses and food processing units. On the other side our attention focussed on utilizing the excess or unused seeds to show their potential in industrial and scientific applications as electrode materials. It is an interesting fact that jack fruit seeds can serve as a cheap raw material source for carbon for electrodes in capacitors and further upgradation of vegetable wastes to valuable energy can be realized.

To best of our knowledge the use of jack fruit seeds for obtaining carbon has never been attempted. Nevertheless, it is interesting and valuable to note that Prahas et al. [41] had made use of jack fruit peel to derive activated carbon for adsorbing methylene blue dye and have explored the pore structures and surface chemistry in detail [42]. Kannan et al. [43] used carbon derived from JFS as an alternative adsorbent to commercial activated carbon for effluent treatment, especially for the removal of cadmium (II) ions. Further, Tamez et al. [44] applied jack leaf powder as an adsorbent for methylene blue removal. All the above investigations reveal that biomass offers multifarious applications in one or the other advanced technologies. Thus in the present work we have explored the physical features of the jack fruit seed derived carbon and have evaluated the capacitive nature in acid and neutral electrolyte medium to establish the usefulness of the discarded jack fruit seeds in the area of capacitors.

2. EXPERIMENTAL

2.1 Preparation of JFSC

Seeds from a ripe jack fruit were collected from the farm house of one of the authors, located at Madurai and washed several times with hot de-ionized water after which the white outer cover (arils) as well as the brown colored inner seed coat (spermoderm) were peeled off with a little hand pressure. The seeds were finally washed with de-ionized water and diced (5mm thick). The pieces were pat dried with wet tissue paper and ~10g sample was immediately pyrolyzed under flowing nitrogen at 500 °C at a heating ramp of 5 °C/min for a hold period of 1 hour, furnace cooled to give a mass of char. Peled et al. [45] have observed that larger sample size may lead to abundant pyrolysis products which may attack the newly formed carbon surface, causing an increase in the surface area and destruction of the carbon bulk. This may have bad effects on the electrochemistry of the carbon powders. The authors of the present investigation also agree with this fact and hence took an optimum size of 10g of the raw material. The char was finally washed with hot de-ionized water until the pH of the decant solution was approximately 7. The powder so obtained after drying and grinding is hereafter called JFSC. Finally JFSC powder was sieved to 250 mesh size and used for further studies.

2.2 Physico-Chemical Characterization

X-ray diffraction patterns were recorded between 10 to 80° on X'Pert Pro X-ray diffractometer with CuK_α radiation source. The specific surface functional groups on the surface of the biomass carbon were ascertained using FT-IR spectrometer (Model # Nexus 670) in the range from 4000 cm^{-1} to 400 cm^{-1} . Elemental analysis of the JFSC was done by Vario ELIII CHNS/O elemental analyzer. The morphology of the carbon was examined with Hitachi S-4700, field emission scanning electron microscope. The pore structure of the JFSC was characterized by N_2 adsorption at 77K using Micromeritics ASAP 2020 instrument

(Micromeritics, USA). Surface area of the JFSC powder was determined by BET (Brunauer, Emmet and Teller) method.

2.3 Electrode Preparation and Electrochemical Measurements

JFSC, poly vinylidene fluoride binder and carbon black respectively in the weight ratio 85:10:5 were mixed to get a paste using N-methyl 2 pyrrolidone. The paste was applied on to the circular end of an SS rod of 1 cm² area & length 8cm. The electrode was dried at 80 °C for 1hour. Heat shrinkable sleeve was used to mask rest of the electrode portion. Electrochemical studies (Impedance, Cyclic Voltammetric (CV) and galvanostatic charge-discharge) were performed with CH Instruments (Model # CHI660a) in a three-electrode configuration using the SS rod coated with JFSC as the working electrode, Pt wire as the counter, and saturated calomel electrode as the reference. 1M H₂SO₄ & 1M Na₂SO₄ were employed as the electrolytes. The specific capacitance was evaluated from the area of the CV curves. Galvanostatic charge discharge experiments were performed in a similar setup as described above with a specific current density of 10 mA g⁻¹ and between 0.0 and 1.0 V. AC impedance measurements were taken with a superimposing AC voltage of 5 mV within a frequency range of 1 mHz – 100 kHz.

3. RESULTS AND DISCUSSION

3.1 Burn-off

Conversion of JFS biomass in to carbon was carried out around 500 °C under flowing N₂ and weighed the residue to calculate the yield otherwise termed as burn-off. Burn-off was calculated by applying the following formula [46] and was found to be 76% on dry basis. $X(\%) = (m/m_0) \times 100$, where X is carbon yield (%), m is the carbon mass (g) and m₀ is the raw sample mass (g).

It can thus be concluded that JFS can give high % yield of carbon. The reason for high % yield may be due to the thermal processing of the samples under controlled atmosphere where oxygen is inaccessible to prevent the transformation of hetero elements in to their corresponding oxide gases or even ash. Nonetheless, it will be proved from the FT-IR spectroscopic studies (or ultimate elemental analysis) that organic groups are still present in the carbon structures to play a part in the electrochemical features of the carbon samples derived from JFS.

3.2 Ultimate Analysis

The biomass derived carbon samples consists principally of carbon atoms (which form aromatic sheets cross-linked in a random manner) and heteroatoms like oxygen, nitrogen, sulphur, hydrogen depending on the nature and source of the raw material considered and obviously on the thermal, physical or chemicals treatments [47]. Consequently the type and % of the constituents is expected to influence the electrochemical parameters and hence ultimate elemental analysis has been conducted on the JFSC. Added to the

above, it is well known that the heating rate controls the rate of volatile evolution from the biomass during pyrolysis and so slow heating and longer volatile times would promote high char yield [48]. This fact is obvious in the present work that the pyrolysis of JFS yielded a mass that was analyzed to contain 71.4 wt% carbon with certain amount of H (1.476%), S (0.836%) and N (3.821%) also existing in the JFSC, but the total amount of these elements in weight is less than 100%. On the basis of previous reports about thermally-treated carbon material, the remaining component of the carbon material should be oxygen [49, 50]. Significant % of N, S & H in the sample shows the presence of various organic functional groups. FTIR data also bears support for these organic functional groups, the presence of which is expected to influence the electrochemical behavior of the carbon samples prepared as discussed in the latter sections.

3.3 Phase analysis by X-ray Diffractometry (XRD)

The XRD pattern of the biomass carbon is shown in Fig. 1. The presence of a strong peak between 23° and 30° is definitely attributed to (002) diffraction peak, indicating the amorphous and low graphitization features of the carbon produced from JFS. The nature of the peak may also indicate the evolution of microporous carbon and the microporous structure is amorphous with enormous degree of non-crystalline signatures [51]. Concisely, a large number of disordered single graphene layers and stacked structures of graphene sheets may be present simultaneously in the texture of the carbon powder [52] and the slightly broad shape also indicates the highly disordered structure in the carbon [53]. It is to be noted that the interplanar space (d_{002}) calculated for the JFSC is 3.78 Å, higher than that reported for graphite (3.354 Å) again indicating considerable disorderliness in the carbon produced [54-56].

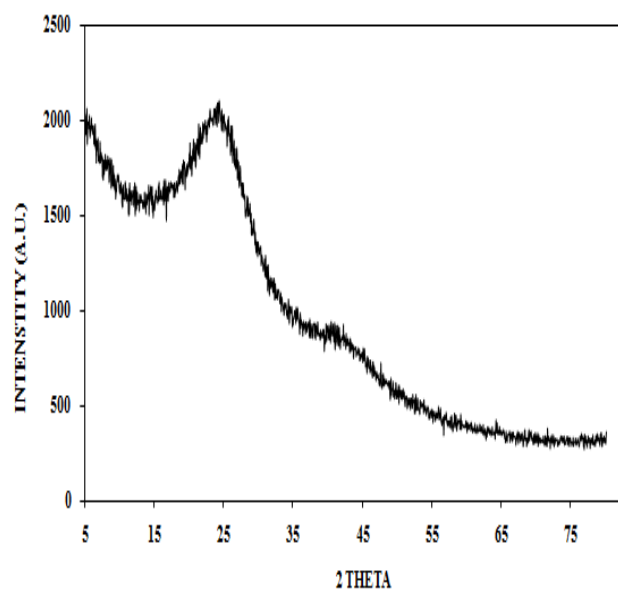


Fig 1 X-ray diffractogram of JFSC

Generally the value of d_{002} is taken as a measure of estimating the degree of graphitization in the carbon and the

growing disorder is now reflected in the observed larger values of d_{002} in JFSC. The XRD of the JFSC at the same time exhibits a broad peak around 43° and has been attributed to the (1 0) bidimensional planes [57]. The existence of $h k (l 0)$ lines may be an evidence for the turbostratic or convoluted stacking of hexagonal layers of carbon resulting in disordered structure and lower crystallinity [58, 59] thus demonstrating amorphous nature of the JFSC and hence better capacitance may be expected.

3.4 Scanning Electron Microscopic (SEM) Imaging, Pore Structure and Surface Area Measurements

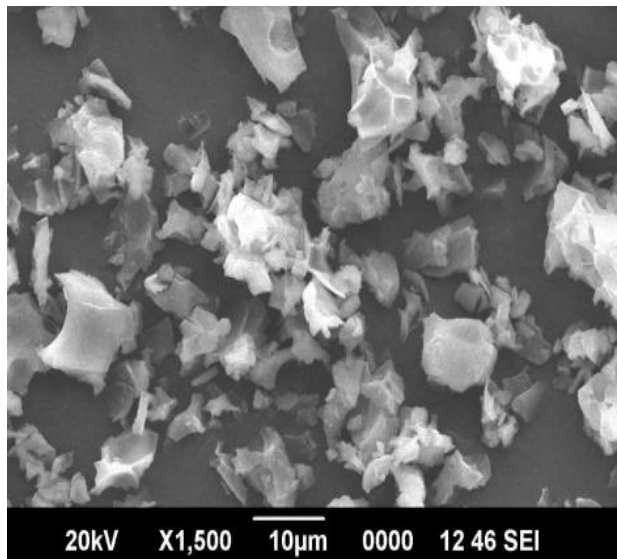


Fig 2 SEM image of JFSC

Fig. 2. depicts the SEM of JFSC. The micrograph shows a loose, disjointed structure with carbon particles of irregular size and ununiform distribution featuring crumbled/crushed morphology, entirely lacking porosity. This peculiar morphology may be due to the force of the gases escaping from the biomass during the pyrolysis process [60]. It is now rather difficult to offer any correlation between the particle morphology and the electrochemical activity. Regardless of this fact, the pore structure of the JFSC was characterized by N_2 adsorption and the isotherm has been presented in Fig. 3. It is to be mentioned that the carbonization process enriches the carbon content with concomitant removal of volatile matters which may create the initial porosity in the biomass carbon. The isotherm was found to be the type-1 characteristic, with a broad knee within low relative pressure range [61], reflecting the high microporosity in the sample. In general, microporous solids generally show Type-I adsorption isotherms [62]. N_2 adsorption isotherm curve features a plateau indicating that the adsorption might have been stopped. The quick saturation of N_2 adsorption in fact is due to proximity of the pore walls such that the multilayers of N_2 would not be formed. This result means that the sample would not be containing large numbers of mesoporous or macroporous structures and only micropores.

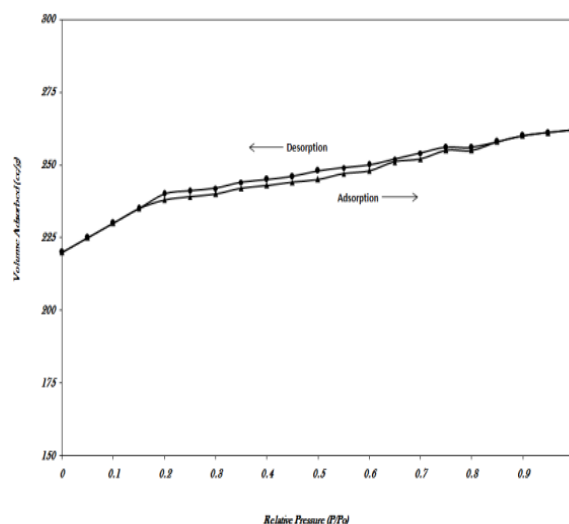


Fig 3 N_2 sorption isotherm of JFSC powder

BET surface area of JFSC calculated using BET equation is $932 \text{ m}^2\text{g}^{-1}$ having micropore and mesopore surface area of $898 \text{ m}^2\text{g}^{-1}$ and $34 \text{ m}^2\text{g}^{-1}$ respectively. The total pore volume of carbon measured at relative pressure of 0.995 is $0.51 \text{ cm}^3\text{g}^{-1}$ whereas micropore and mesopore volumes are of 0.46 and $0.05 \text{ cm}^3\text{g}^{-1}$ respectively. Micropore volume accounts for 90% of total pore volume, which has its proof in the adsorption isotherm curve. Surface area of the JFSC seem to lie within the range of many biomass derived activated carbons reported and this high value of the surface area may probably indicate the presence of enormous electrochemically accessible sites or area thereby resulting in increased electrochemical performance ultimately, which will be made obvious from the discussions made under electrochemical studies section.

3.5 Functional Group Analysis or Surface Chemistry Characterization Studies

The carbon matrix of JFSC contains heteroatoms like, oxygen, nitrogen, sulfur etc., besides carbon and hydrogen atoms. These heteroatoms bonded to the edges of the carbon layers govern the surface chemistry of the carbon [63]. The surface chemistry of carbon materials is basically determined by the acidity and basicity of their surface. The existence of surface functional groups such as carboxyl, lactone, phenol, carboxylic anhydride, etc., may constitute the source of surface acidity, while the basic properties of the carbon may likely be associated with two types of structures: (i) the presence of oxygen containing groups, i.e. pyrone, chromene and carbonyl structures, at the edge of carbon crystallite; and (ii) oxygen free Lewis basic site on the graphene layers. The Lewis basicity of delocalized π electrons is influenced by the aromatic system on the carbon surface as stipulated by Wibowo et al. [63].

Electrochemical features of carbon electrode material seem to depend upon the physical properties as well as the nature and chemical reactivity of the functional groups that may be present on the carbon surface. Accordingly, gaining knowledge on surface functional groups would give us a

chance of correlating with the electrochemical properties of the carbon. FTIR spectroscopy is a technique for qualitative characterization of the surface functional groups on the carbon samples. Fig. 4 depicts the FTIR spectrum of JFSC. The spectrum shows highly complex signatures, which is due to the presence of many polar functional groups on their surface. These organic, especially oxygen containing functionalities may help in imparting hydrophilicity to the carbon electrode that favors strong interaction of the aqueous electrolyte ions with the polar groups in the carbon material and thus plays an important role for the performance of a capacitor [64].

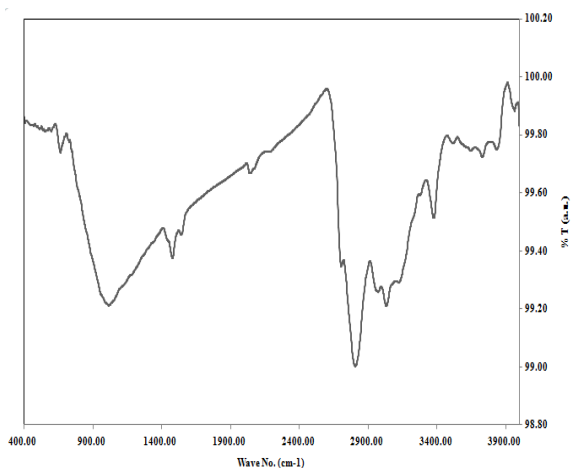


Fig. 4 FT-IR of JFSC powder

The spectrum obtained for JFSC sample shows the characteristic peak at 3388 cm^{-1} corresponding to the O–H stretching vibration of the surface hydroxyl groups. The peak around 2923 cm^{-1} and 671 cm^{-1} in the sample indicates the presence of aliphatic C–H bond and C–C bond respectively corresponding to the methylene group. A characteristic peak observed at 1595 cm^{-1} corresponding to C=O (carbonyl) stretching vibration in quinone structure. In addition, the isolated –OH functional group is observed at 3737 cm^{-1} for the sample. On the other hand, characteristic peak at 1367 cm^{-1} corresponding to the stretching mode of C=N group and the peak around 1024 cm^{-1} corresponds to C–O bond in alcohol. From this study it could be inferred that the surface of the JFSC might contain carbonyl and/or quinone type groups. A medium intense band around $3400 - 3500\text{ cm}^{-1}$ may be attributed to the stretching mode of N–H group.

Organic groups with oxygen, typically, phenols, carbonyls, lactones, quinone and quinone-like structures are expected to form on the surface during the thermal treatment of the biomass precursors and may appear at the edge carbon atoms as indicated by Subramanian et al. [36]. This fact may also be applied to JFSC samples and the effect or mechanism of action of these organics on the electroactivity of the carbon samples may be complex and forms an exclusive research object. Centeno and Stoeckli [64] have reported that oxygen containing functionalities impart good features to the performance of the carbons and hence comparatively acceptable electrochemical behavior may be

expected from JFSC. The influence of organic groups H, N, O on the electrochemical performance may be important but it is difficult to explain the electrochemical behavior because we do not know the exact location of these elements in the carbon structures where these groups undergo electrochemical transformation under the influence of electrical signal during electrochemical studies or chemical reactions with the electrolyte species.

3.6 Effects of Electrolytes on the Capacitive Behavior of JFSC as Evaluated from Impedance

Data

The frequency dependence of the impedance of the JFSC has been studied through Electrochemical Impedance Spectroscopy at a bias voltage of 5mV between 1 mHz and 100 kHz using the three electrode assembly in two different electrolyte medium. The electrochemical impedance studies conducted on the JFSC electrodes in the two electrolytes are compared in Fig. 5 as Nyquist plots. The data was fit based on Randles equivalent circuit and various parameters include C_{dl} derived are given in Table 1.

It is well known that the impedance of an ideal capacitor has no real component and its imaginary component is a function of both capacitance and frequency. The current through a capacitor is always 90° out of phase with the voltage across it and current leading the voltage. Because the impedance of a capacitor varies inversely with frequency, at high frequencies a capacitor acts as a short circuit - its impedance tends towards zero. At low frequencies (approaching DC) a capacitor acts as an open circuit, and the impedance tends towards infinite. So for an ideal EDLC the imaginary part of the impedance spectra at lower frequencies would be a vertical line and the impedance of a capacitor diminishes as the frequency increases. The observed impedance of electrodes fabricated using JFSC in the high frequency region is mainly contributed by the total resistance that includes contribution from the solution resistance (R_s), intrinsic carbon resistance and constant phase element (CPE). R_s is known as the ohmic or uncompensated resistance of the solution between the working and reference electrodes. Diffusion of electrolyte ions in to the electrode matrix can create impedance known as the Warburg impedance (W). This impedance depends on the frequency of the perturbing potential.

At high frequencies, the Warburg impedance is small since diffusing ions or reactants do not have to move very far. At low frequencies the reactants have to diffuse farther, thereby increasing the Warburg impedance. On a Nyquist plot the infinite Warburg impedance appears as a diagonal line with a slope of 0.5 (or 45° in the Bode plot). Thus a vertical line in the low frequency region in the Nyquist plot indicates ionic diffusion process and the observed semicircle in the middle frequency range reveals the charge transfer resistance (R_{ct}) or polarization resistance (R_p). The amplitude and width (diameter) of the semicircle indicates

the accessibility of active electrode surfaces due to factors such as pore shape, size, and the variations in pore distribution within the electrodes [65].

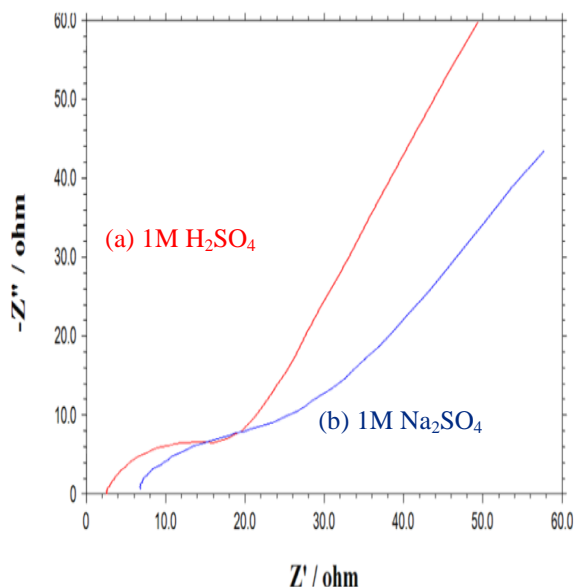


Fig 5 Nyquist AC impedance plots for JFSC electrode in (a) 1M H₂SO₄ and (b) 1M Na₂SO₄.

Obviously Fig. 5 features a 45° Warburg region at low frequencies in the two electrolytes studied. This phenomenon hence is attributed to the diffusion of ions and hence an increase of electrolyte ions diffusion resistance is observed. The line in Fig. 5 depicts the capacitive nature of JFSC in the two electrolytes. The impedance plot also shows apparent semicircle corresponding to double layer charging at mid-high frequencies in the two electrolytes and this observation can be related to the charge transfer resistance. A larger single semi-circle in neutral medium indicates that charge transfer in carbon electrode is higher than that in the acid electrolyte. Furthermore, the knee frequency occurs much earlier in terms of both real and imaginary impedance components in acid compared with the neutral electrolyte, indicating the potential of JFSC as an electrode material in electrochemical capacitors, where its total impedance is the least in the former.

From the Nyquist plot, the specific capacitance of the JFSC electrode in the two electrolytes tabulated in Table 1 has been calculated using the formula [39]: $C = 1/(2\pi fZ''m)$, where f , Z'' and m are the frequency (1 mHz), the imaginary impedance and the mass of the JSFC in the electrode respectively. It is to be appreciated that the capacitance values from the impedance studies are comparable with those calculated from CV studies and this result thus supports the observation made by Garcia-Gomez et al. [66] to corroborate the fact that the specific capacitance value evaluated from AC impedance studies would be comparable to that obtained from CV or charge-discharge studies provided the low frequency set in impedance studies, the sweep rate in CV studies and the current in charge-discharge studies are comparable enough.

Table 1 Analysis results of impedance spectroscopic data on JFSC

Electrolyte medium	R_s (ohm)	R_{ct} (ohm)	C_{dl} (F/g)
1M H ₂ SO ₄	2.6	21.4	321
1M Na ₂ SO ₄	6.8	24.2	212

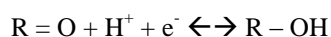
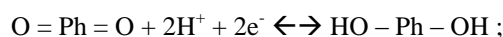
3.7 Electrochemical Investigation by Cyclic Voltammetric (CV) and Galvanostatic Charge-Discharge Cycling Studies

Capacitive behavior of the JFSC electrode has been explored through CV studies in the two electrolyte systems chosen. Further, the effects of scan rates have also been investigated. Accordingly, CVs have been recorded at scan rates from 10 to 40 mVs⁻¹ with increments of 10 mVs⁻¹ and the voltage window in each case is as marked in the CV illustrated in Fig. 6a and b respectively in 1M H₂SO₄ and 1M Na₂SO₄. The specific capacitance values have been calculated using the equation, $C = i/s m$ (Fg⁻¹), where i , s and m are the average current, the scan rate and the mass of the active material [67]. The authors of the present communication had reviewed more than 100 research articles describing the utility of biomass (wastes) for deriving carbons or activated carbons for the title subject to signify the waste to energy concept through utilization of wastes [68]. Reference to this review article had been made here to compare the capacitance values of the various biomass derived carbons in different electrolyte medium with our present studies using JFSC. Reports establishing the results of biomass derived carbon electrode materials for capacitors in neutral medium is rather less and to cite a few; banana fiber [36], fir wood [69] and pistachio shells [70] respectively in NaNO₃, seaweed [71] in sodium sulphate solution, coconut shells [72] in KCl solution exhibited good capacitive nature. Analysis illustrates that extensive research with various other classes of neutral electrolyte medium is still open for obtaining capacitors with good performance.

The observed capacitive currents in 1M H₂SO₄ is higher than in 1M Na₂SO₄ and increase with the increase in scan rate but is not proportional to the square root of the scan rate. This implies that there would be redox transitions of various organic functionalities and the ultimate capacitance is of pseudocapacitive type. Hu et al. [70] and Wu et al. [72] in their studies with KOH-activated pistachio shells and coconut shells respectively in acid and neutral electrolytes observed the current variation with respect to the type of electrolytes and they presumed to be due to the better conductivity of the acid by proton hopping mechanism [73] and also redox reactions (see later sections) at the carbon electrode. In the neutral medium the bigger electrolyte ions offer restricted ionic movements in the solution and hence lesser voltammetric currents are obtained. This fact is also supported by AC impedance studies, where $\log Z_{re}$ and R_s is higher in neutral medium than the acid electrolyte.

The presence of heteroatoms and organic functional groups in JFSC would present pseudocapacitance nature to JFSC based electrode and this is apparent from the distorted rectangular shape of CVs, as seen in Fig. 6a and b. Further, non-linear current with increasing voltage is the characteristic feature observed in both the electrolytes, indicating the large Faradic nature of our JFSC electrodes. In general, CVs in the two electrolytes exhibit symmetric responses in their positive as well as negative scans and the integrated voltammetric charges in the positive and negative scans evolves to be closer. It can thus be concluded that the charges stored in the positive scans could be delivered during the negative scans and consequently good electrochemical behavior of the JFSC is indicated. It can also be noted that the current rapidly reach their respective plateau values when the scan is reversed. This demonstrates lower ESR of the JFSC electrode in the chosen electrolytes.

The CV in acid the electrolyte as depicted in Fig.6a exhibits discernible redox transitions irrespective of the scan rates. It can be stressed from the FTIR studies and from the results of other authors [74, 75] that the JFSC like any other biomass derived carbons contains various organic moieties that would interact with the electrolyte ions leading to interesting electrochemical picture. In a typical acid, the following interactions with the phenyl (-Ph) and alkyl (-R) groups were reported by Hu et al. [70] as,



Reversible quinone/hydroquinone transformation has been reported in acid electrolyte by several other authors also [76, 77]. These reactions are known to offer pseudo-Faradaic capacitance. Further, proton has the tendency to get adsorbed over the carbonyl groups on the JFSC due to the induced ion-dipole attraction. Consequently, the electric charge density gets changed adding to the double layer capacitance in the acid electrolyte [73].

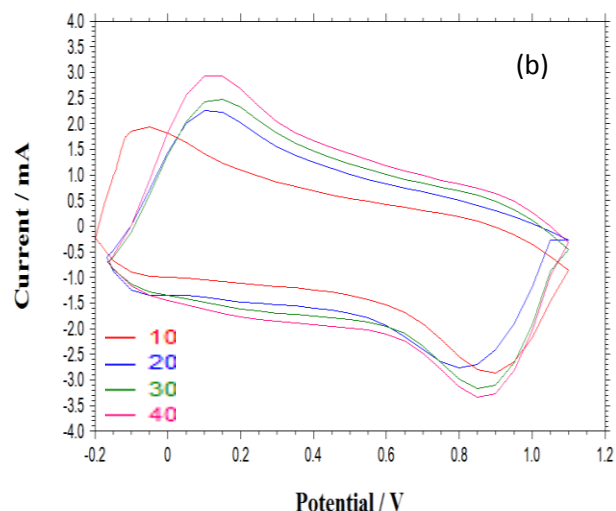
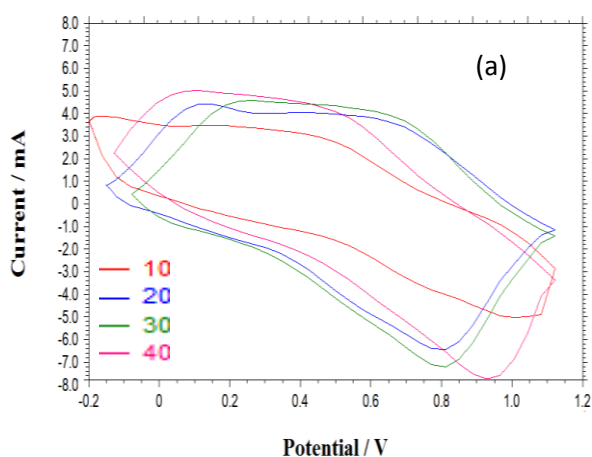
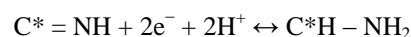


Fig 6 CV of JFSC electrode in 1M H₂SO₄ (a) and 1M Na₂SO₄ (b) at various scan rates (mVs⁻¹ Vs SCE)

Frackowiak et al. [78] concluded that the electrochemical behaviour of the carbon materials used as electrodes is related to their pore size and redox properties. Further, the above authors' electrochemical measurements showed a proportional increase of the specific capacitance with the nitrogen content in acid electrolyte medium and that the nitrogen content in the final product reflects its amount in the starting materials. Higher the amount of nitrogen higher is the basicity of the carbon surface (as evaluated by the values of pH_{PZC}). The above authors attributed to the enhancement in the capacitance values in the acidic medium by the following pseudo-Faradaic reactions [79].



Where C* stands for the carbon network. The same of kind of reactions are expected in the JFSC to conclude that capacitive currents and the total capacitance values has a contribution not only from the electric double layer charging but also from the pseudocapacitance of electroactive functional moieties significantly. This result is also corroborated again through impedance studies that the specific capacitance value in the acid is the highest.

It is reported that when the pH of the electrolyte is increased, the redox reactions involving surface quinone groups may become less important, but some other surface functionalities as pyrone-like groups can be active [80]. Though these reactions are not visible in our studies with JFSC at the scan rate investigated the above reasons may still be valid to explain the capacitance obtained. Few studies on the electrode cell performance of activated carbons in Na₂SO₄ show that the pseudo-Faradaic redox transitions of O and N-containing electroactive surface groups are depressed in this electrolyte in comparison with H₂SO₄ [36, 70, 81-83]. Nevertheless, Andreas and Conway [77] have indicated that the pseudo-capacitive contribution of surface oxygenated groups is negligible at neutral pH but Bichat et al. [71] have affirmed that pseudo-Faradaic

reactions with seaweed derived carbon are possible in 0.5M Na_2SO_4 with adequate surface functionalities on the carbon surface. In the present study with JFSC also reversible redox peaks are observed and it is presumed that contribution from pseudo-capacitance may be expected in the neutral electrolyte medium also.

The results discussed above establish the complex interactions or influence of the electrolytes with pH and species involving cations and anions. Thus it is very difficult to provide insight on how the pH and the nature of the electrolytes influence the capacitive behavior of the carbon electrodes and research is invited in this direction. Hu et al's [70] work on KOH-activated pistachio shells in 1M NaNO_3 and 0.05M Na_2SO_4 distinguishes fantastically the CV features and that the electrochemical reversibility in 1M NaNO_3 was better than Na_2SO_4 , though the mechanism of operation of these radicals has been explained by the adsorption ability.

Dependence of specific capacitance of JFSC electrode with scan rates and electrolyte medium is understood from Fig. 7. At 10 mVs^{-1} scan rate, specific capacitance value as high as 316 Fg^{-1} has been obtained in 1M H_2SO_4 whereas it is 202 Fg^{-1} in 1M Na_2SO_4 . Despite the decrease in the capacitance JFSC has yielded appreciable capacity at lower scan rates. At 40 mVs^{-1} rate, the delivered capacity in 1M H_2SO_4 and 1M Na_2SO_4 is 252 and 137 Fg^{-1} respectively, which means that JFSC has retained 80% and 68 % of the respective capacitance at 10 mVs^{-1} rate in the electrolyte order mentioned. This value is comparable with the other biomass derived carbon electrodes reported [36, 69, 84]. Thus, jack fruit seeds being a zero-cost source and cost-effective nature might put JFSC as a prospective candidate for electrode material in electrochemical capacitors or pseudocapacitors.

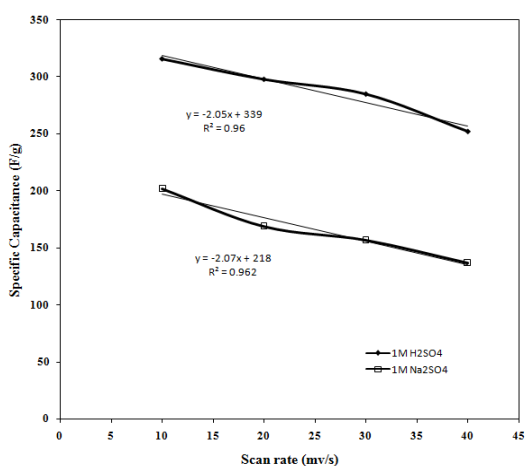


Fig 7 Dependence of specific capacitance of JFSC on scan rate

The corresponding maximum storage energy has been calculated as 87.8 Wh kg^{-1} in H_2SO_4 and 56.1 Wh kg^{-1} in Na_2SO_4 using the formula with CV_i^2 where C is the specific capacitance (316 and 202 Fg^{-1} respectively in the two medium) and V_i is the initial voltage (1.0 V). As stated previously, the specific capacitance decreases with the scan

rate. It is well known that for carbons, higher the capacitance, longer is the time required to acquire/release charges. The high specific capacitance that is observed at the lowest scan rate of 10 mVs^{-1} may be attributed to the fact that the ions can diffuse into pores more easily (faster kinetic process) when the first cycle is completed [85]. The electrochemical storage in activated carbon electrodes has been explained by the electrical double layer theory and it is suggested that ions occupy the pores within the carbon to participate in the formation of the electrochemical double layer. So at higher scan rates when each cycle finishes quickly the ions cannot diffuse in to the pores as faster as the cycles are completed. Thus the poor performance at higher scan rates has been ascribed to [34].

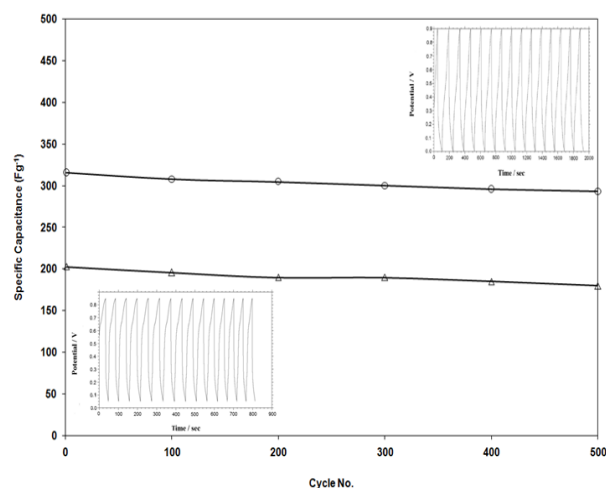


Fig. 8 Cycling performance of JSFC at 10 mV s^{-1} between -0.6 and 1.0 V in $1 \text{ M H}_2\text{SO}_4$ (a) and $1 \text{ M Na}_2\text{SO}_4$ (b). Inset shows the corresponding galvanostatic charge/discharge cycling behavior at 10 mA g^{-1}

Cycling performance of JSFC at 10 mVs^{-1} between -0.6 and 1.0 V in $1 \text{ M H}_2\text{SO}_4$ and $1 \text{ M Na}_2\text{SO}_4$ is understood from Fig. 8a and b. The inset in Fig. 8 shows the corresponding galvanostatic charge/discharge cycling behavior at 10 mA g^{-1} . For CV a wider potential range of -0.6 to $+1.0 \text{ V}$ was selected to find the useful practical range for the charge-discharge of JFS based carbon electrodes at constant current and subsequently evaluated to be between 0.0 and 1.0 V . Accordingly, inset in Fig. 8a and b shows the galvanostatic charge-discharge cycle profile (for the first 15 cycles) of JFSC electrodes in $1 \text{ M H}_2\text{SO}_4$ and $1 \text{ M Na}_2\text{SO}_4$ respectively recorded in the range $0 - 1 \text{ V}$ at a 10 mA g^{-1} .

The results of each galvanostatic charge-discharge measurement was similar and all curves exhibited isosceles triangular shape with the discharge time close to that of charge, reflecting high charge-discharge efficiency of the JFSC electrodes in two electrolyte medium. The difference of charge and discharge time influences the symmetric nature of the isosceles triangle. If the difference of charge and discharge time was less, then the isosceles triangle shape is more symmetric. The more symmetric the triangle, the higher will be the charge-discharge efficiency [86]. Although the triangles are similar, the information derived

are different. We have seen that the area of the CV of JFSC in acid medium is broader when compared with the electrochemical features in neutral medium indicating that the capacitance of JFSC in acid medium would be higher. The reversible redox reactions of functional groups on the carbon surface occur to build up pseudocapacitance during charge-discharge processes and so the total capacitance is enhanced [86].

In general, capacitive behavior shows a strong dependence on the concentration of the electrolyte supported by the high surface area arising from the porous structure of the carbon. As explained from the results of CV studies because of the presence of H^+ ions as the mobile species in H_2SO_4 electrolyte better ionic diffusion in to the pores of the carbon is observed, resulting in an enhanced capacitive performance. Ultimately, the capacitive currents and hence the total capacitance values of JFSC has contributions mainly from pseudocapacitance of electroactive functional moieties in addition to double layer charging. From the galvanostatic charge-discharge studies, the gravimetric specific capacitance was calculated using the formula [36], $C (Fg^{-1}) = i\Delta t/m\Delta V$, where i is the current used for charge-discharge; Δt is the time elapsed for the charge or discharge; m is the mass of the active electrode and ΔV is the voltage interval of the charge or discharge. Specific capacitance calculated from the charge-discharge cycling studies at the end of the 5th cycle has been evaluated to be $318 Fg^{-1}$ and $211 Fg^{-1}$ respectively in 1M H_2SO_4 and 1M Na_2SO_4 , further presenting a stable performance at least up to 500 cycles in the acid as well as neutral medium as shown the Fig. 8 insets. The specific capacitance of JFSC electrode in H_2SO_4 medium is $316 Fg^{-1}$ in the first cycle and $293 Fg^{-1}$ after 500 cycles with 93% coulombic efficiency while in Na_2SO_4 medium it is 203 and $180 Fg^{-1}$ for the 1st and 500th cycle respectively exhibiting an efficiency of 87%. The high charge-discharge efficiency of JFSC based electrodes indicates that electroactive carbon particles contacted well with electrolyte solution, or in other words the electrodes had a high hydrophilicity of their surface. Despite these advantages, the main disadvantage of the acid electrolyte is the high corrosion rate of the current collectors in actual capacitors. Here, both ion dissolution into the electrolyte combined with corrosion of the current collector will deteriorate the cycling performance of the capacitor [36]. Nevertheless, proper choice of hardware in the capacitor fabrication would tend to alleviate this drawback, leading to widespread application of acid based capacitors.

On investigating the JFSC performance in a neutral electrolyte such as 1 M Na_2SO_4 , the specific capacitance is lower than the acid medium. The charge-discharge time is also reduced. The specific capacitance is mainly governed by the non-Faradic electrostatic sorption of ions at the double layer in the case of neutral electrolytes [87]. As the H^+ concentrations in neutral electrolyte are too low to induce gas evolution reactions [88], ions diffusing in to the pores of the carbon matrix are reduced and there would be only minimal chance of the bigger SO_4^{2-} and Na^+ ions diffusion, resulting in lowered specific capacitance [89].

These results coincide with the observation of Swiatkowski et al. [90].

Centeno and Stoeckli [91] have published an excellent work on the specific double-layer capacitance of activated carbons in relation to their structural and chemical properties of various carbon varieties. Their studies provide an empirical correlation between the current density and the oxygen content of the carbon and with the capacitance. They have also suggested that C_o , the limiting capacitance at a low current density of 1 mAcm^{-2} of electrode surface, does not depend significantly on the oxygen content but the decrease of capacitance with increasing current density (of electrode surface) as a function of the oxygen content in the carbon seems to be valid and an empirical equation has also been proposed. It is apparent from the functional group analysis (FTIR spectroscopic) studies that the surface oxygen present in our JFSC may be distributed as acidic, phenolic and basic groups (carbonyl) and in order to prove the influence of the different oxygen-containing surface groups and electrochemical properties obviously requires additional study. Centeno and Stoeckli [91] suggest that the above correlation can be used as a tool to evaluate the performance of an unknown carbon for a capacitor. Studies involving enthalpies of immersion [92] and TPD [93] (temperature programmed desorption) would help with regards above.

It is interesting to note from the work of Centeno and Stoeckli [91] with 41 kinds of carbon and by Barranco et al. [94] on KOH activated carbon nanofibre (CNF) that the specific capacitance in H_2SO_4 depend not only on the total surface area S_{tot} (the sum of the micropore and external areas) and also on oxygen containing surface groups that desorb as CO from surface basic groups in TPD studies. A correlation between the specific capacitance and the CO contents at lower current densities has been proposed by Centeno and Stoeckli [91] and at higher current densities CO_2 generating groups (acidic groups) also contribute to the total specific capacitance of the electrode materials. Barranco et al. [94] also state that the pseudocapacitance contribution is more for H_2SO_4 electrolyte. This observation matches with ours. Further activation with KOH had introduced additional micropores, high surface area and higher CO contents improving the specific capacitance but the amount of CO_2 is not affected by KOH activation in their samples. It is to be recollected that JFSC, the subject material of ours has presented good pseudocapacitive behaviour, has been obtained without any chemical or physical activation and that does not prevent the application of the as-prepared JFSC as electrodes for capacitors.

Finally, it is to be mentioned that biomass precursors for preparing carbon electrodes for electrochemical capacitors is plenty and hence a comparison of the capacitance values reported for those samples with our JFS derived carbon sample would weigh our sample for the intended application. A partial list of specific capacitance values (with their BET specific surface areas) reported for various biomass derived carbons including our samples has been provided in Table 2. Nevertheless, a complete review on the

similar subject has been carried out by the present authors and has been published elsewhere [68].

Table 2 Comparison of specific capacitance and surface area of various biomass in different electrolytes

Biomass Precursor	Electrolyte	Specific Capacitance (Fg ⁻¹)	BET Surface Area (m ² g ⁻¹)	Reference #
Cassava peel	H ₂ SO ₄	153	1352	25
Bamboo	Et ₄ NBF ₄	65	1413	33
Banana fiber	Na ₂ SO ₄	74	686	36
Sugar cane bagasse	H ₂ SO ₄	300	1788	38
Egg shell	Acidic	284	221	40
	Basic	297		
Fir wood	NaNO ₃	89	1016	69
	HNO ₃	120		
	H ₂ SO ₄	96		
Pistachio shell	H ₂ SO ₄	122	1013 - 2145	70
	NaNO ₃	81		
Seaweed	KOH	201	750 - 1080	71
	H ₂ SO ₄	255		
	Na ₂ SO ₄	125		
Apple pulp	H ₂ SO ₄	232	1200	95
	Et ₄ NBF ₄	120		
Jack fruit seed carbon (JFSC)	H ₂ SO ₄	316	932	Present work
	Na ₂ SO ₄	203		

A comparison would show that our results are within the typical range reported by other researchers, indicating that JFSC proposed in the present study is applicable for electrochemical capacitors. Thus JFSC appears to be an attractive cost-effective substitute for commercial activated carbon as a pseudocapacitor electrode in acid as well as neutral medium.

4. CONCLUSIONS

The sphere of usefulness of biomass wastes for producing carbon materials has increased manifold in the recent times. Vegetable sources are gaining significance as hi-end products like carbon and activated carbon could be effectively produced from these zero-cost raw materials. The fact has been established through our results reported here by way of utilizing a household waste biomass. Carbon powder has successfully been produced by pyrolyzing the biomass of jack fruit seeds and has been electrochemically characterized for the possible application as electrode material for electrochemical capacitors (or pseudocapacitors). Performance of the biomass derived carbon has been completely evaluated in, 1M H₂SO₄ and 1M Na₂SO₄ aqueous electrolytes. Studies show that the pH of the electrolytes influences both the capacitance values and electrochemical reversibility. Thus in 1M H₂SO₄, 316 Fg⁻¹ was the delivered capacitance while it is 203 Fg⁻¹ in 1M Na₂SO₄ at 10 mVs⁻¹ scan rate. The observed capacitance values has been attributed to the combination of pseudocapacitance and double layer charging coupled with physical properties and the surface organic functionalities on the biomass carbon with more of micropores in JFSC. The authors express through their studies that the carbons need not always be activated to give better (pseudo)capacitive performance. Nevertheless, control of mesopores and micropores in the carbon matrix through

KOH [95] or ZnCl₂ activation [96, 97] may be one of the ways to realize enhancement in electrode performance.

The studies have also revealed the flexibility of jackfruit seeds as a good rated precursor for the preparation of electroactive carbon for making green technology viable. Its simple preparation process and the availability of the biomass in large scale might put JFSC as a prospective material for capacitor electrode applications. In addition to the excellent electrochemical features of JFSC, it is worthwhile to observe that the source for the carbon is renewable and natural, obviously cost effective. Thus the study opens up new doors in the search for new carbon materials for EDLC or pseudocapacitor applications. Finally it is relevant to consider the correlation that can exist between the jack varieties and its cultivation management for future developments in the technologically important area like energy. Although many uncertainties in understanding the mechanisms involved in electrochemical capacitors still remain, genuine progress continues to be made in the development of newer electrode materials. Consequently it is suggested that an intensified collaborative research is necessary to fully develop and tap the potential of electrochemical capacitors.

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