EFFECT OF OXIDATION TREATMENT ON AGRO-WASTE DERIVED CARBON FOR SUPERCAPACITOR APPLICATION

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Abstract: In this work, we present the effect of oxidation and optimum microwave irradiation time interval for the surface modification of agro-waste derived carbon and explore its application as high performing electrode material for supercapacitor application. The electrochemical performance of as-synthesized carbon was tested by using cyclic voltammetry (CV), galvanostatic charge- discharge (GCD), and the electrochemical impedance spectroscopy (EIS) with 1M H_2SO_4 as aqueous electrolyte in three electrode system. Highest specific capacitance obtained to be 215.7 Fg^{-1} at current density 0.5 Ag^{-1} for oxidized carbon material treated under microwave irradiation for 10s (FC-10) which is 61% higher as compare to untreated carbon derived from drump sticks (BC), with the capacitance retention of 94% at current density 5 Ag^{-1} over 2000 continuous charge discharge cycles. The highest energy and power density obtained to be 7.49 $Whkg^{-1}$ and 62.5 Wkg^{-1} at current density 0.5 Ag^{-1} retained to be 5.78 $Whkg^{-1}$ and 1250 Wkg^{-1} respectively, at current density 10 Ag^{-1} for FC-10. The modification of agro-waste derived carbon via oxidation followed by optimum irradiation approach demonstrates effective way to improve electrochemical properties for high performance supercapacitor application.

Keywords-Agro-waste, Electrode material, Microwave, Oxidation, Supercapacitor

I. INTRODUCTION

Agro-waste derived carbon with high surface area and energy density, low cost, ease of availability making them an ideal choice for viable application in supercapacitor. Electrochemical Supercapacitor also known as ultracapacitor receive more attention during past few year as a kind of fascinating energy storage device due to their high power density and long cyclic stability revealing the potential applications in power sources, electrical vehicles, and portable electronic device [1, 2]. In general supercapacitor fills the energy gap between conventional capacitors and batteries [3, 4]. On the basis of charge storage point of view the Supercapacitor are classified into two groups, Electric double layer capacitor (EDLC) where capacitance is due to pure accumulation of electrolyte ions on the electrode surface and pseudocapacitors where capacitance is due to contribution of fast surface redox reactions at the electrode-electrolyte interface [5, 6]. Major drawback regarding practical application of supercapacitor are low energy density and high production cost thus developing new electrode material with low cost and high capacitance with remarkable performance is great challenges to overcome above disadvantages [7]. Generally most commercially available supercapacitor are EDLC based which used carbon materials such as carbon nanotubes [8], activated carbon [9] carbon aerogel and carbon nanofibres [5] because of their high surface area, good electrical conductivity, and remarkable electrochemical stability. In order to enhance the specific capacitance of carbon electrode more attention had been taken to integrate well define micropores, mesopores, and macropores onto a three dimensional aperiodic graphitic carbon [10]. On the other hand specific capacitance of carbon electrode can be improved by introducing nitrogen based or oxygen based functional group on the surface of carbon. The oxygen based functional group are normally electron acceptor and while nitrogen based functional group are electron donors which can enhance surface wettability of carbon materials and support rapid adsorption of the electrolyte ions on the electrode surface [11]. The various oxidizing agents can be used to introduce functionalities upon oxidizing surface of carbon material and their performance is tested for supercapacitor applications [12-16]

In this work, agro-waste derived carbon synthesized by single step pyrolysis method. The as-synthesized mesoporous carbon material was further modified by oxidation treatment with concentrated sulfuric acid and nitric acid in ratio 3:1 with microwave irradiation under different interval of time and evaluates its electrochemical performance for supercapacitor application.

2. EXPERIMENTAL

2.1 Materials and reagents

All reagents in the experiment except Drump-stick are of analytical grade. Sulfuric acid (H_2SO_4 98%; Sigma-Aldrich, USA), hydrochloric acid (HCl 35-38%; Sigma-Aldrich, USA), polyvinylidene fluoride (PVDF; Sigma-Aldrich, USA), N-Methyl-2-pyrrolidone (NMP; SRL pvt.Ltd), acetylene carbon black (99.9%; Alfa Aesar).These reagents were used without further purification.

2.2 Preparation of Drump stick derived porous carbon

The waste Drump-sticks are collected from local market and subsequently washed, cleaned, and dried in oven at 80ºC for 12h which then crush to get fine powder, pre-carbonized at 300ºC for 2 hour in muffle furnace. Typically the grounded precarbonized carbon material pyrolyzed at 800ºC for 1 hour by double crucible method without any active agent. The resultant material was extensively washed with 1M HCl to remove all the impurities followed by distilled water until it attains neutral pH. The resultant sample was then dried at 80ºC over night obtained sample was name as bare drump stick derived carbon (BC). Further fictionalization of BC powder was carried out via liquid phase route. Approximately 0.2gm of BC was treated with concentrated H_2SO_4 and HNO_3 acid mixture in ratio 3:1 under sonication for 30 min and then kept at 48 h at room temperature. Acid treated BC was diluted with distilled water, filtered and again washed thoroughly with distilled water until a neutral pH is reached, then microwave treatment given for 10 and 15 second finally dried at 50ºC over night. The obtained functionalized BC denoted as FC-10 and FC-15 respectively.

2.3 Electrochemical Measurements

The cyclic voltammetry (CV) profile, electrochemical impedance spectroscopy (EIS) was studied using Metrohm Autolab-128N (Netherlands, USA). The galvanostatic charge discharge (GCD) curve was carried out using Multichannel Landet 2001A supercapacitor tester (Netherlands, USA). Electrochemical measurement was carried out using a conventional three-electrode system at room temperature, with a platinum foil and Ag/AgCl electrode as counter and reference electrode respectively. The working electrode was prepared by physically mixing as-synthesized carbon materials, acetylene carbon black and PVDF dissolved in NMP with ratio 80:10:10 by weight. The viscous slurry was coated on to stainless steel mesh and was then dried in vacuum oven at 80ºC for 12h to remove the organic solvent. All electrochemical measurement was carried at different scan rate in 1M H_2SO_4 aqueous electrolyte within the potential window -0.2 to 0.8V. The gravimetric capacitance (Fg^{-1}) was evaluated from charge/discharge curve according to equation

$$C_{g=\frac{I\times\Delta t}{m\times\Delta V}}$$

m(g) is mass of active materials of electrode, I(A) is the applied current, Δt(s) is the discharge time, ΔV(V) is the potential window. The energy density ($Whkg^{-1}$) and power density (Wkg^{-1}) were calculated according to equation

$$E = \frac{C_{g\times\Delta V^2}}{28.8}$$

$$P = \frac{E\times 3600}{\Delta t}$$

The electrochemical impedance spectroscopy (EIS) measurements were carried out in the frequency range of 100 kHz to 10 mHz at open circuit voltage with an AC perturbation of 10mV.

3. RESULTS AND DISCUSSION

The electrochemical performance of oxidised agro-waste derived carbon was studied by employing three electrode cell system with 1M H_2SO_4 aqueous electrolyte to investigate charge storage capability and mechanism. Figure 1a shows CV profile of BC, FC-10 and FC-15 sample within a potential range of -0.2 to 0.8 V vs. Ag/AgCl at a scan rate 10 mVs^{-1}. All the curve shows quasi-rectangular shape demonstrating typical EDLCs like behaviour with slight redox peak representing pseudocapacitive behaviour. The area under the curve of FC-10 electrode is larger than BC and FC-15 electrode revealing superior capacitive behaviour which might be due to large surface area over the other electrode which escalate the facile contact between electrode|electrolyte interface elucidate enhancing capacitance. The CV performance of FC-10 electrode at different scan rate varying from 10mVs^{-1} to 100 mVs^{-1} is shown in figure 2b exhibits similar rectangular shape even at high scan rate revealing excellent capacitive behaviours [17]. The GCD curve of BC, FC-10 and FC-15 electrode tested at current density 0.5 Ag^{-1} shown in figure 1c. FC-10 electrode reveals excellent capacitive behaviour as compare to BC and FC-15 electrode which is Supporting with results of CV profile shown in figure 1a. The GCD profile of FC-10 electrode at different current densities varying from 0.5 Ag^{-1} to 10Ag^{-1} is shown in figure 1d. Additionally, all the curve shows symmetric rectangular shape without IR drop symbolized small internal resistance and excellent capacitive behaviour [18]. The maximum specific capacitance of 215.7 Fg^{-1} was calculated at current density 0.5 Ag^{-1} for the FC-10 electrode. It was observed that with increasing in current density from 0.5 Ag^{-1} to 10Ag^{-1} there is progressively decreased in specific capacitance shown in figure 1e. The FC-10 electrode exhibits 77.2 % of capacitance retention of its initial values which is remarkable as compare to BC and FC-15 electrode showing capacitance retention of 48.9% and 69.4% respectively at current density 10 Ag^{-1} shown in figure 1e. The progressive decrease in specific capacitance with increase in current density is due to poor accessibility of electrolyte ions at electrode-electrolyte interface [19]. The long term stability of supercapacitor is the crucial parameter determines its practical applicability. The cyclic stability of FC-10 electrode was evaluate at current density 5 Ag^{-1}, exhibits capacitance retention of 94% of its initial values over continuous 2000 charge discharge cycle shown in figure 5f, inset figure shows few cycle before and after 2000 cycles which provide further evidence for the excellent long term stability of FC-10 electrode.

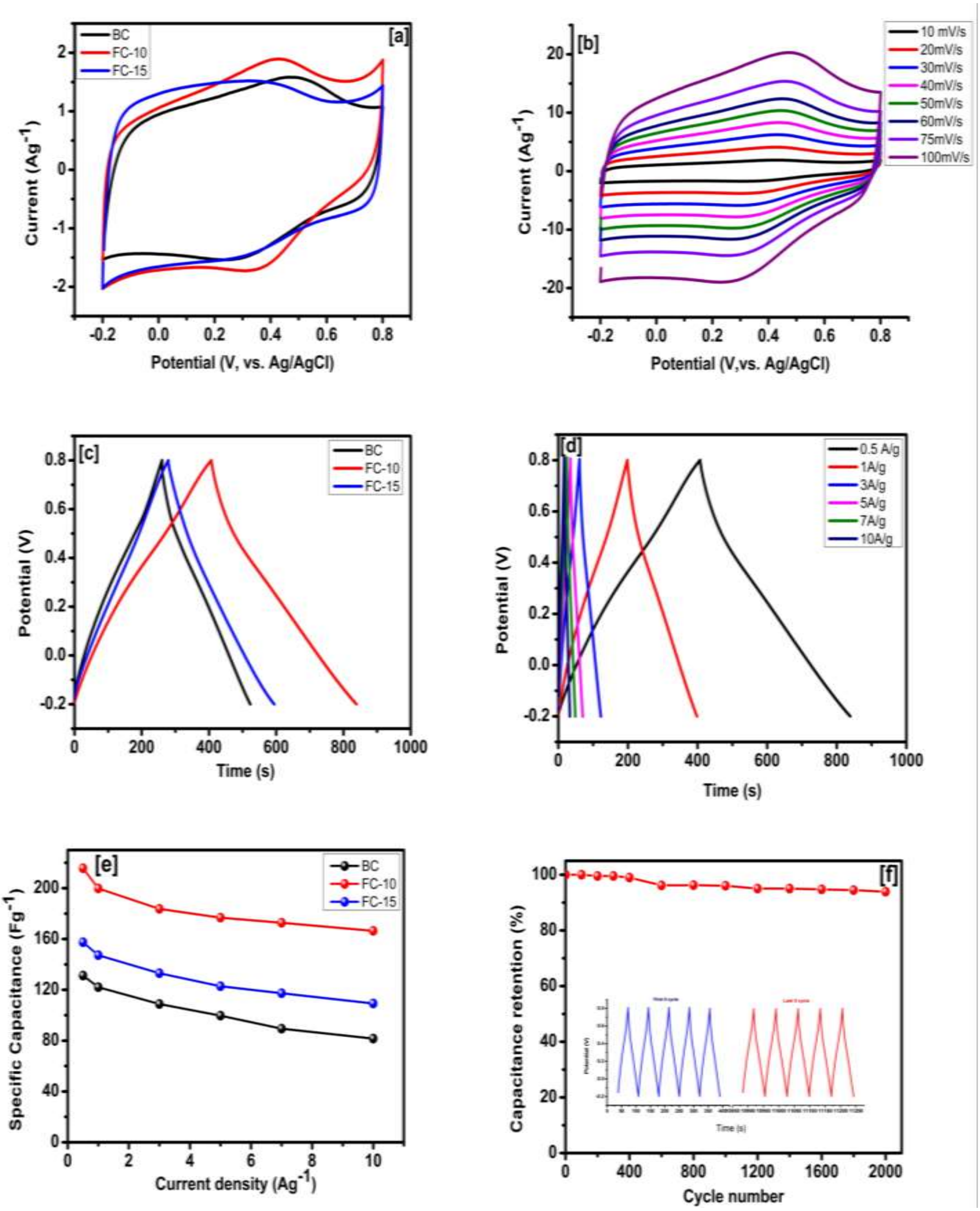

Figure1. (a) The CV profile of BC,FC-10, FC-15 at the scan rate 10mVs^{-1} (b) GCD profile of BC,FC-10,FC-15 electrode at current density 0.5 Ag^{-1} (C) CV profile of FC-10 electrode at different scan rates (d) CD profile of FC-10 electrode at different current density (e) specific capacitance as a function of current density for BC,FC-10,FC-15 electrode (f) capacitance retention as a function of cycle number for FDS-10 electrode at current density 5 Ag^{-1}.

The fundamental properties of supercapacitor electrode can also be explore by electrochemical impedance spectra (EIS) analysis [20]. The Nyquist plot of BC, FC-10, FC-15 electrode with 1M H_2SO_4 aqueous electrolyte in the frequency range from 10 kHz to 10 mHz is shown in figure 2a, inset figure shows equivalent electrical circuit of fitted data for FC-10 electrode. In general Nyquist plot consist of three significant region [20, 21]. The low frequency region shows vertical line parallel to imaginary axis (Z”) revealing capacitive behaviour [22]. The middle frequency region exhibits modest semicircle gives charge transfer resistance (Rct) which represent effect electrode thickness and porosity of electrode for diffusion of electrolyte ions at electrode-electrolyte interface [23]. In high frequency region intercept at Z real axis (Z') represent ohmic or series resistance (Rs) [24, 25]. The comparison of series resistance (Rs) charge transfer resistance (Rct) of BC, FC-10, FC-15 electrode shown in tabular form

Component	BDS	FDS-10	FDS-15
$R_s(\Omega)$	0.985	0.97	2.61
R_{ct} (Ω)	18.68	0.95	3.30

Which exhibits that FC-10 electrode possesses good electrical interconnectivity [26]. Figure 2b shows bode phase angle obtained to be 78.9°, 84° and 82° respectively for BC, FC-10, FC-15 electrode which revealing that as-synthesized FC-10 electrode is suitable for fabrication of low leakage capacitor. In general supercapacitor can be behaves as combination of resistor and capacitor in mid frequency region where capacitive values are depend upon adsorption of electrolyte ions on electrode surface, whereas shows pure capacitive behaviour in low frequency region and pure resistive behaviour in high frequency region [27].

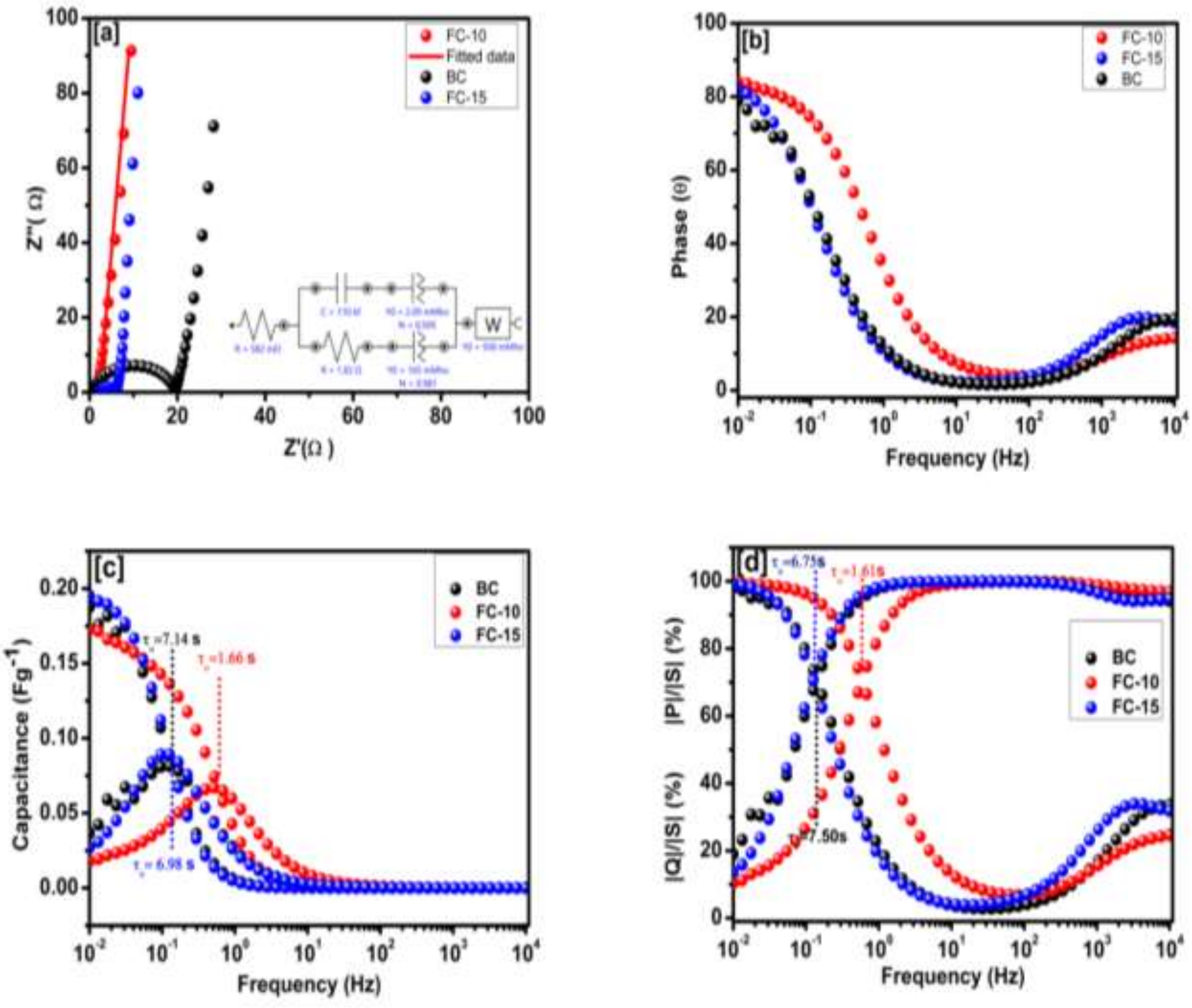

Figure2.(a)Nyquist plot of BC, FC-10, FC-15 electrode in 1M H_2SO_4 aqueous electrolyte (b) Bode phase angle as a function of frequency (c) Plot of real and imaginary part of capacitance as a function of frequency for BC, FC-10, FC-15 electrode (d) plot of normalized active power |P|/|S| and reactive power |Q|/|S| as a function of frequency for determination of relaxation time constant (τ_o) which is 1.61s for FC-10 electrode.

The plot of real (C') and imaginary (C") part of capacitance as a function of frequency is shown in figure 2c. The frequency corresponding to maximum values of imaginary capacitance gives the relaxation time constant. The more elucidate presentation of relaxation time constant can be obtained from figure 2d, which shows plot of normalize real |P|/|S| and imaginary |Q|/|S| part of complex power vs. frequency. The relaxation time constant (τ_o) calculated to be 1.61s for FC-10 electrode which is appreciable as compare BC and FC-15 electrode can be obtained from crossing point of two plot correspond to phase angle 45° and $\frac{|P|}{|S|} = \frac{|Q|}{|S|} = \frac{1}{\sqrt{2}}$ [20]. The relaxation time constant symbolize the minimum time needed to discharge all the energy from the device with an efficiency more than 50% [19].

4. CONCLUSIONS

Novel synthesis technique for the mesoporous carbon derived from readily available Drump Stick (M.oleifera) is adopted and obtained results direct that oxidation with optimum microwave assistance treatment is an efficient approach for high performance of bio-waste derived carbon as electrode for supercapacitor. Such carbon material reveals the maximum capacitance of 215.7Fg^{-1} at current density 0.5 Ag^{-1} with 94% capacitance retention over 2000 continuous charge discharge cycle at current density 5Ag^{-1}. The highest energy obtained 7.49 $Whkg^{-1}$ which retain to be 5.78 $Whkg^{-1}$ with increase in current density from 0.5 Ag^{-1} to 10Ag^{-1}. Simple synthesis method, ease of availability, cost effectively proposed that synthesized agro-waste derived carbon is suitable electrode for optimum performance of supercapacitor application.

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