Characterization of Supercapacitor Fabricated from Beli Fruit (Aegle Marmelos) Shell Activated Carbon for the First Time

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Abstract: We developed activated carbon from the Aegle marmelos fruit shell also known as Beli. Firstly, its carbonaceous process is done by a typical process. H_3PO_4 treatment was used to activate the carbonaceous material. Activated material is characterized by using Scanning Electron Microscope and Brunauer-Emmett-Teller (BET) specific surface areas. Calculated BET surface area of the fabricated supercapacitor is 517 m^2/g. Electrochemical characterization was carried out through cyclic voltammetry, charge / discharge and electrochemical impedance spectroscopy. Highest specific capacitance of 59 F/g and energy density of 8.19 kW/h for highest specific capacitance was obtained from the charge discharge curve. Obtained equivalent serial resistance is 0.414 Ω from equivalent circuit.

Keywords: Activated carbon, Beli fruit shell, Specific capacitance, Supercapacitors.

I. Introduction

Supercapacitors are energy storage devices that combine the properties of capacitors and batteries. Batteries have a high-energy density, but their power density is low. Conversely, capacitors enjoy a high-power density while low energy density. A battery uses its whole bulk for charge storage, while a capacitor uses its surface. Supercapacitors use charge separation through fast ion adsorption, and very fast redox reactions with surface-bound molecules. They have a higher energy density than regular electrolytic capacitors, and also a much higher power density than batteries. Typically, supercapacitors are used in situations requiring many rapid charge / discharge cycles. Such as include protecting electronic circuits against power surges, regenerative breaking in cars and elevators, and burst-mode power delivery in camera flashes.

Electrode surface area is one of the most important parameter in the supercapacitors due to its ability to store more charges. So that the material which have highly porous concertation will improve the performance of supercapacitors. Activated carbon and graphene oxide based Nano composite are mainly used for the fabrication electrode. Activated carbon is a form of carbon that has been processed to create millions of tiny pores between the carbon atoms, resulting in a dramatically increased surface area. Activated carbon can be produced from various materials such as coconut shell [1], pistachio shell [2], walnut shell [3], tropical wood [4], saw dust [5] and palm shell [6]. Those are agricultural wastes. They were succeeded to produce activated carbon with high surface area and excellent adsorbent properties inexpensive ways. In this research, we have used activated carbon as electrode material. Its produces from the Aegle marmelos fruit shell. In Sri Lanka, it is known as Beli. It belongs to the family of Rutaceae (Genus - Aegle correa; Species - A marmelos), is a deciduous tree growing 12 m - 5 m in height. It is widely available in Sri Lanka as well as South Asia region. As reported in literature, Beli fruit shells use to produce activated carbon. It was used for removal to heavy metal in the waste water [7-9]. So, we also developed successfully Beli fruit activated carbon in the lab and they applied to supercapacitor. Activated carbon production process was more eco-friendly, non-toxic and easier as reported material activation process. Firstly, material of electrode was produced from Beli fruit shell. H_3PO_4 used as activating reagent to active carbonaceous shell. Surface morphology and BET surface area were investigated. Supercapacitor was assembled by using fabricated electrode in the test cell. It was assembled in the way of by sandwich two electrodes with paper separator. Separator was immersed in potassium hydroxide (KOH) 1 M solution. All electrochemical characterizations such as cyclic voltammetry, charge discharge and electrochemical impedance spectroscopy were performed using two-electrode configuration.

II. Experimental

A. Preparation of Material

i. Materials

Mature Beli was collected from western province in Sri Lanka. The shells were washed several times with distilled water with soap flex to remove adhered impurities from its surface. The sample were cut into small pieces and ultrasonically wash with distill water to remove excess chemical and finally dried at 80 °C in muffle furnace for carbonaceous on 5 hours.

ii. Methods

Activated carbon were prepared by one step pyrolysis by chemical treatment with 1.5 M Phosphoric acid of (H_3PO_4) of Beli fruit shell micro level particles at 360 °C heat rate of 10 °Cmin^{-1} in nitrogen atmosphere for 30 minutes. Then it was washed with distil-water at 1050 °C for 1 hour. In order to determine the activity level of the Beli activated carbon, iodine number was determined according to the standard test method ASTM D 4607. Before heat treatment, raw shell was ball milling at 450 rpm for 5 minutes. Then Belli shell micro level particles were leach with 1.5 M H_3PO_4 for 15 minutes. After, Beli pulp were filtered and separated.

B. Analysis of the Porous Structure of the Carbons

The activated carbon has been well characterized by N_2 adsorption. N_2 adsorption isotherms were measured at 196 ^oC on an ASAP 2010 volumetric analyzer (Micromeritics, Inc., Norcross, GA). Prior to adsorption measurements, all samples were out gassed under vacuum at 200 ^oC for 2 hours. The single-point pore volume (V_{sp}) was estimated from the amount adsorbed at a relative pressure (p/p_o) of ~ 0.98. The Brunauer-Emmett-Teller specific surface areas (S_{BET}) was calculated from the N_2 adsorption isotherms in the relative pressure range of 0.05-0.2 using a cross sectional area of 0.162 nm^2 per nitrogen molecule. Pore size distributions (PSD) were calculated from adsorption branches of nitrogen adsorption–desorption isotherms using the 2DNLDFT Heterogeneous Surface model for carbon materials implemented in SAIEUS program provided by Micrometrics [10-11]. The cumulative pore volume of microspores, (pores below 2 nm) was calculated on the basis of the PSD curves obtained by the DFT software. Adsorption parameters such as the single point pore volume (V_{sp}), specific surface area (S_{BET}), microspores volume (V_{mi}), total pore volume (V_t), and monolayer capacity (MLC) were calculated using nitrogen adsorption-desorption isotherms and listed in Table I. Also, scanning electron microscopy (SEM) were performed on ZEISS EVO LS 15 field emission scanning electron microscope with acceleration voltage of 20 kV.

Table I: Structural Parameters and Adsorption Values Obtained for Beli Activated Carbon Sample Studied

Content	V_{sp} *(cc/g)*	V_{mic} *(cc/g)*	S_{BET} *(m^2/g)*	*MLC (CC STP/g)*	V_t *(cc/g)*
Produced Carbon	0.20	0.16	517	119	0.25

C. Fabrication and Characterization of Supercapacitor

1 M potassium hydroxide solution was prepared as the electrolyte. Stainless steel was used as the current collector after subsequently washed with acetone, alcohol and distill water for 5 minutes in an ultrasonic bath. Produced activated carbon was used as active material for electrode. Firstly, carbon slurry was prepared by mixing a certain mass of Activated Carbon Powder and potassium hydroxide (Sigma-Aldrich) were mixed until the homogeneous slurry was obtained. Consequently, the paste was applied on two stainless steel current collector uniformly using spatula. Each electrode containing 12 mg of active material. Then the electrodes were placed in vacuum oven at 60 °C for 1 hour. Finally, both positive and negative electrodes are separated using paper separator containing the 1 M KOH as electrolyte. The electrode assembly holds tightly in prepared test cell.

The electrochemical properties and capacitance measurements of supercapacitor electrode were studied in a two-electrode system by Cyclic Voltammetry (CV) Galvano static charge / discharge and Electrochemical Impedance Spectroscopy (EIS) using AUTOLAB PGSTAT 128N (Metrohm, Netherlands). The CV responses of the supercapacitor were measured at different scan rates varying from 2 mV/s to 150 mV/s in the potential between -0.2 V and 0.8 V. As an electrolyte KOH, aqueous solution. Impedance spectroscopy measurements were carried out at 5 mV over frequency range from 500 kHz to 10 mHz. Charge / discharge measurements were performed at different current densities. Specific capacitance, equivalent series resistance, power density and energy density were calculated from the discharge curve for different current densities. All the calculations were done from the standard equation as reported for supercapacitors [8-10].

III. Results and Discussion

A. Porous Structure of the Activated Carbons

Adsorption-desorption isotherms measured for beli activated carbon sample is shown in Fig. 1. Nitrogen adsorption isotherm for the Beli carbon sample displays a type I isotherm with significant amount of N_2 adsorption at low relative pressure region (<0.01) with plateau at high relative pressure region characteristic for microporous materials. The result of the N_2 adsorption desorption isotherms for activated carbon is summarized in Table I which corresponds to a microspores volume V_{mi} = 0.16 cc/g, monolayer adoption capacity 119 and BET surface area 517 m^2/g. This result exhibit on adsorption capacity high. The surface area of activated carbon typically can range from 450-1400 m^2/g [14]. So, produced Beli fruit shell activated carbon shows good surface area.

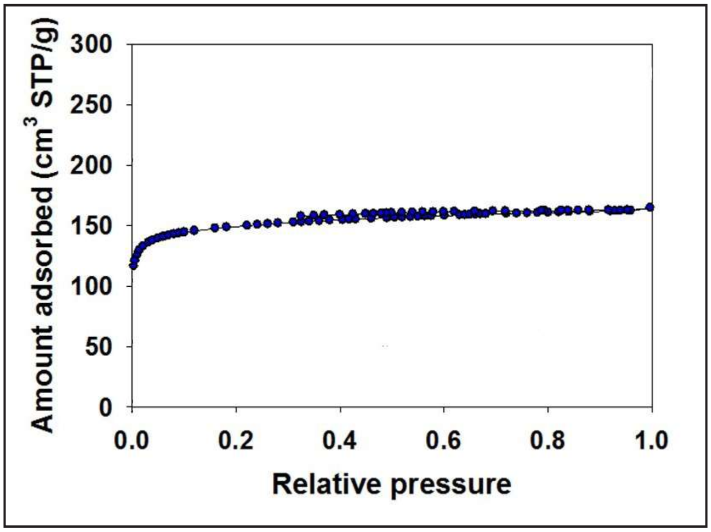

Fig. 1: Nitrogen Adsorption-Desorption Isotherms Curve

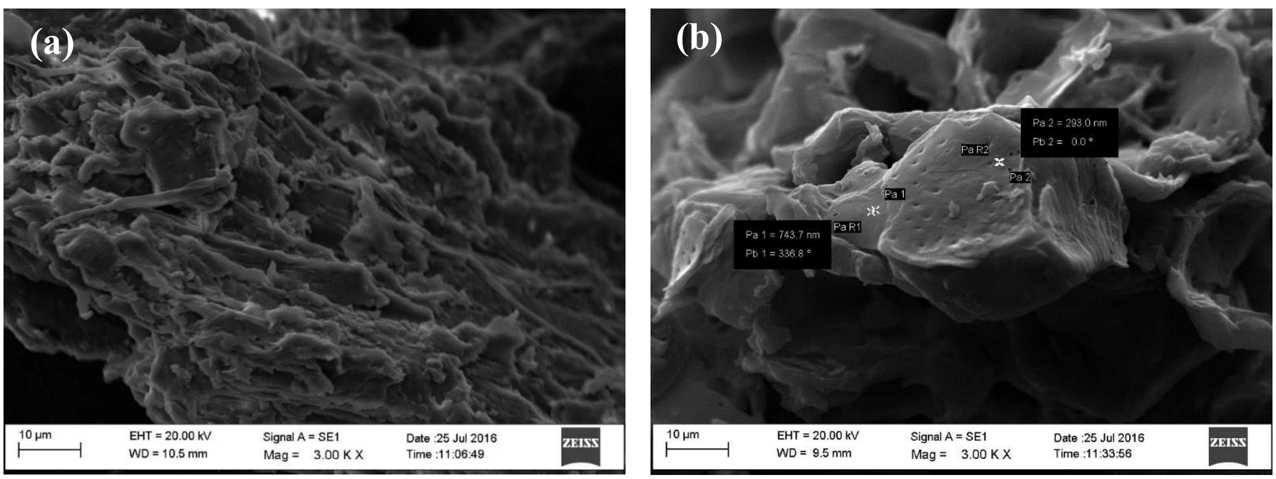

Fig. 2: (a) SEM Image Before the Activation, (b) SEM Image After the Activation

Fig. 2 micrograph shows the surface structure of the phosphoric treated Beli powder. It shows surface of sponge like structure. Clean and burn pore with no tunnel or honeycomb-like structures.

B. Electrochemical Characterization

Cyclic Voltammetry (CV), charge / discharge cycles and Electrochemical Impedance Spectroscopy (EIS) were carried out to evaluate electrochemical performance of fabricated Beli Electrode's supercapacitor using prepared two electrode test cell. Fig. 3 presents CV graphs of two electrode test cell for different scan rates and -0.2 V to 0.8 V operation voltage window. Highest specific capacitance was observed as 72 F/g at scan rate 25 mV/s. Specific capacitance is decreased when scan rate is increased.

The CVs of ideal capacitor perform with rectangular like shape. However, upon increasing the scan rate, this ideal behavior is distorted with a gradual loss in cell specific capacitance. This phenomenon is typical for all types of supercapacitors, reflecting the mass transfer kinetics within the porous electrode layer. Above CVs are obey with that phenomena. The CV curves of the Beli fruit shell activated carbon based electrode at low scan rates are in the typical rectangular shape, and no obvious redox peaks or hydrogen, oxygen peaks are observed. Thus, the as-prepared electrode exhibits good capacitance behavior [14]. The shape of the CV curves is not symmetrical, it can be due to none consistent of surface of both electrode. But most of the range in voltage window, it shows nearly constant current. Observed CV gives show similar shape, decrease specific capacitance as previously reported CV.

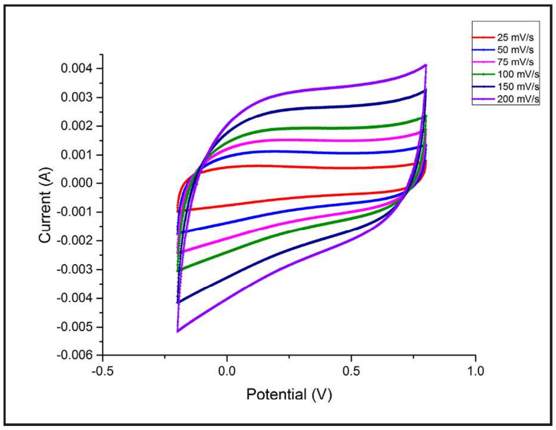

Fig. 3: Cyclic Voltammetry Curves at Different Scan Rates in the Same Voltage Window

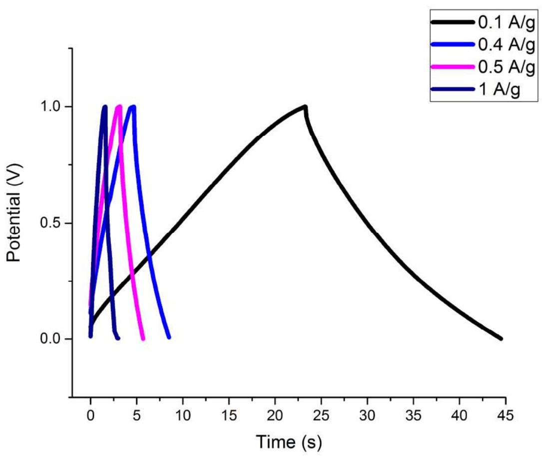

Fig. 4: Charge / Discharge of Fabricated Supercapacitor at Different Current Densities

The electrochemical performance was further studied using galvanotactic charge / discharge under different current densities 1 A/g, 0.5 A/g, 0.4 A/g and 0.1 A/g within the voltage limits +1 V and 0 V. Fig. 4 presents charge-discharge curves obtained from the fabricated supercapacitor. From this, we calculated specific capacitance, energy density and power density by using slope of discharge curve and total discharging time [12]. In this research, we obtained 59 F/g specific capacitance at lowest current density of 0.1 A/g. The energy density was calculated for highest specific capacitance. It was 8.19 kW/h. Specific capacitance value vary within the range of 50 F/g and 150 F/g for activated carbon based supercapacitor [13]. They use active reagents such as carbon black (acetylene black), Carbon Nano Tube. So, by considering those, we can imply, fabricated supercapacitor performs good charge-discharge performance without any binder or conductive reagent.

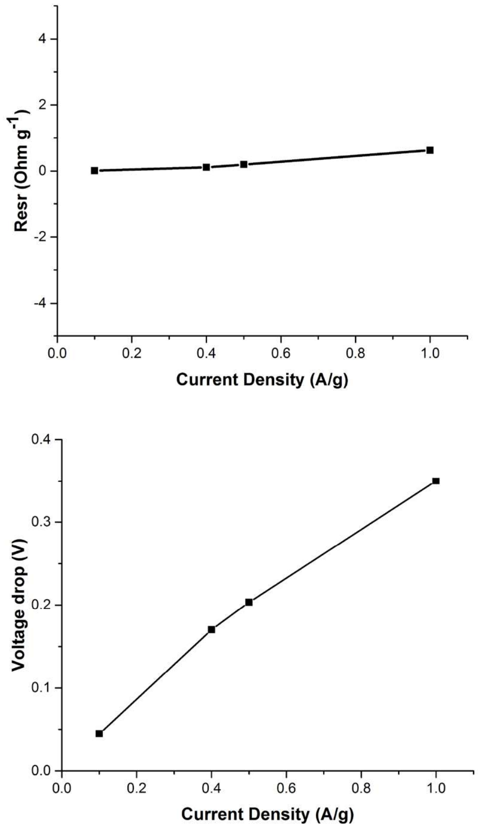

Fig. 5: Voltage Drop and Equivalent Serial Resistance Effect for Current Densities

The charge discharge curves obtained are nearly linear and symmetric, revealing a good capacitive behavior. Charging discharging cycle time is reduced when the current density is increased. At the initial discharge, a sudden drop in potential is observed that is referred as IR drop [13]. Simply it is different between maximum (last) charge voltage and starting discharge voltage. It shows different values due to changes of current. We can estimate the equivalent series resistant (R_{esr}), as $\Delta V = 2IR_{esr}$. Where; ΔV **-** voltage drop, I **-** discharge current. The principal resistance is the R_{esr} for supercapacitor, which includes ohmic resistance of the electrolyte, resistance of the cell design. According to previously mentioned equation, ΔV voltage drop should increase with increasing of current density. In the Fig. 5 clearly represents that. Also, it show R_{esr} value maintain nearly constant value during change of current density.

According to Fig. 6, it shows a decrease in specific capacitance, when increasing the current density. In the reported literature show specific capacitance value decrease with the current density. So, that fabricated supercapacitor show good qualitative behavior. The obtained specific capacitance value is less than reported values. Nonetheless, it gives considerable value because specific capacitance varying the 50 F/g**-**150 F/g range for activated carbon. Specific capacitance can be increased by adding some optimize mass of conductive material such as acetylene black.

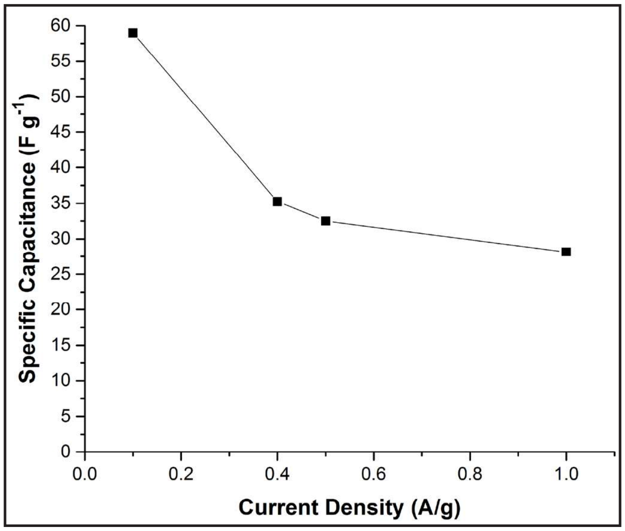

Fig. 6: Calculated Specific Capacitance from the Charge / Discharge Curve at Different Current Densities

Long life cycle of supercapacitor is most important parameter for its practical application. Life cycles test were performed for 1000 charge / discharge cycles. The voltage drop at 1^{st} cycle 0.16902 V and 0.26092 V at 1000^{th} cycle. That shows good stability for the supercapacitor.

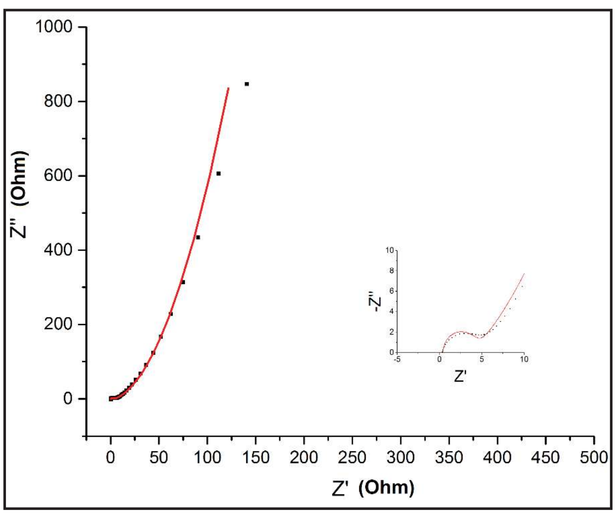

Fig. 7: Nyquist Plots for Beli Fruit Shell Activated Carbon Electrodes with the Stainless Cell at 10 mV Sinusoidal Signal of 10 mV over the Frequency Range from 500 kHz and 1 mHz. Z': Real Impedance. Z'': Imaginary Impedance. Inset Shows Enlarged Scale

In Fig. 7, the Nyquist plot of the supercapacitor electrodes shows straight line in low frequency region and inconspicuous arc in the high frequency region. This high frequency range is related to the electronic resistance between the active material [15]. The inconspicuous arc in the high frequency region shows that the electronic resistance between active material is low. The slope of the 45°-portion called Warburg resistance and is a result of the frequency dependence of ion in the electrolyte to the electrode interface. As seen from enlarge view, the Warburg curve is shorter than another reported supercapacitor electrodes, which is an indication that the supercapacitor has a short ion diffusion path. The vertical shape at lower frequencies indicates a pure capacitive behavior, representative of the ion diffusion in the structure of the electrode [16]. The more closely the supercapacitor behaves as an ideal capacitor [17]. According to the equivalent circuit, the equivalent series resistance is 414 mΩ. The maximum power density of the supercapacitor has been calculated from the low frequency data of the impedance spectra, according to the equation $P_{max} = V_i^2/4\,mR$, where V_i is the initial voltage, R is the ESR and m is the mass of electrodes. Thus, a maximum power density of 60 W/kg was obtained.

IV. Conclusion

In conclusion, we have produced Beli fruit shell activated carbon and supercapacitor fabricated from the activated carbon in this research work. SEM image of produced Activated carbon shows good porous shape sponge like structurewith surface area value 517 m^2/g. Clean and burn pore with no tunnel or honeycomb-like structures. Supercapacitor shows good electrochemical characteristics as well as considerable specific capacitance (59 F/g) and power density (60 W/kg). Further detailed studies and optimization are needed. We hope that Beli fruit shell activated carbon will lead to the development of high performance supercapacitor.

Acknowledgments

The Authors gratefully acknowledge the financial support from University Research Grant (SRHDC/RP/04/15-18) and Innovative Research Grant (UGC/VC/DRIC/IRG-2014/WUSL) from the Wayamba University of Sri Lanka. Also, Technical Officer Mr. SAD Wijesinghe to giving technical support throughout this research work.

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