Materials Science Forum
ISSN: 1662-9752, Vol. 966, pp 444-450
doi:10.4028/www.scientific.net/MSF.966.444
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Submitted: 2018-11-28
Revised: 2019-05-24
Accepted: 2019-05-24
Online: 2019-08-06

Synthesis and Characterization of Supercapacitor Electrode from Fiber of *Borassus flabelifer* L by Activation Method

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Keywords: *Borassus flabelifer* L, Reduced Graphene Oxide, Supercapacitor

Abstract. Supercapacitor require electrode which has high surface area so that it able to store large amounts of charge. In this study, electrode was synthesized from carbon of *Borassus Flabellifer L* fiber which was carried out through activation and carbonization processes. Raw material was calcined at 400^0C for 4 hours followed by activation with NaOH 1 M. The carbonization was then conducted in Nitrogen gas flowing by temperature variations; 650^0C, 750^0C, and 850^0C with a constant heating rate of 20 ^{0}C/min. Based on XRD data, it was shown that the material has formed Reduced graphene Oxide (RGO) which has main peaks at (2θ) 24^0 and 44^0 with higher purity in higher temperature. SEM results clarified more pores formation at higher temperature which is mesoporous. Cyclic Voltammetry (CV) test was done to determine the capacitance value. By RGO forming with high porosity, it is suitable for supercapacitor electrode application and CV test has examined that heating of *Borassus Flabelifer L* fiber at 850^0C with 5 mV/s scan rate has the highest specific capacitance by 8.25 F/gram with Energy density is 4.125 watt/gram.

Introduction

Cellulose, hemicellulose, and lignin are carbon polymers that are commonly found in natural materials such as coconut shell, rice husk [1] and bagasse. Fandi et al [2] have successfully synthesized Reduced Grapheme Oxide (RGO) by utilizing coconut shell through heat treatment up to 1000^0C. The process of purifying cellulose, hemicellulose, and lignin from complex compounds consisting of Carbon, Oxygen, Hydrogen, and other impurities such as Potassium, Magnesium, and Chlorine can be carried out through several methods, such as excofiliation [4], heating at high temperatures [6], and hydrothermal [7]. Through the process of breaking non-carbon chains and impurities, several phases derived from carbon will be obtained, including Graphite Oxide [8], Graphene Oxide [9], until Reduced Graphene Oxide [10]. These phases has superior electrical and thermal properties, good mechanical properties and high surface area so that it is suitable to be applied as supercapacitor electrodes [11] and catalysts [12]. In this study, heat and chemical treatments will be carried out to the materials which contain cellulose, hemicellulose, and lignin, namely fiber of *Borassus Flabelifer L* which are easily found especially in the Indonesian coastal regions [13].

Some great properties of Graphene; has high electrical conductivity and good electrical properties, and has good mechanical strength. Usually graphene is made through a reduction and oxidation process from GO and rGO [14]. One on its application is used as charge storage or called a supercapacitor. Supercapacitor is a device that has high energy density, fast charging ability, and has a very large life cycle. Based on the energy storage mechanism, supercapacitors can be classified into two types, namely Electrochemical double layer capacitor (EDLC) and pseudocapacitor [15]. EDLC and batteries can be distinguished from the type of electrode used. The battery uses alkaline metal oxide as an anode and carbon as a cathode with the Alkali- ion intercalation - deintercalation in active materials scheme. While EDLC uses carbon with a high surface area in both electrodes with the ion adsorption-desoprtion scheme on the surface. In this study, the physical and chemical treatment was carried out to fiber of borassus flabellifer L to obtain carbon with a high surface area with the RGO phase so that it can be used as an electrode for EDLC supercapacitors. Calcination at low temperatures, activation with alkaline NaOH and carbonization with a temperature variation of 650^0C - 850^0C is the main process that will be carried out with the aim to break the van der walls bond so that the material is not only purer by decreasing impurity levels, but also having dipole moments due to asymmetrical bond and high surface area.

Methods

Fiber of *Borassus Flabelifer L* was obtained around Gresik City, Indonesia. The main process to synthesize it into supercapacitor electrode was started by the initial preparation to separate it from macro impurities and remove water content. Initial characterization by *Different Scanning Calorimetry - Thermal Gravimetry Analysis* (DSC-TGA) METTLER was carried out to determine decomposition temperature. Furthermore, calcination was carried out at 400^0C for one hour to decompose certain impurities. Some of the remaining impurities from the results of calcination are tied through activation process with NaOH 1 M which continued by heating process in Nitrogen gas flow. Temperature variations were 650^0C, 750^0C and 850^0C for one hour with a temperature increase of 20^0C / minute.

Furthermore, result of heating material was rinsed with distilled water four times to dissolve the impurities which was followed by re-heating at 110^0C to reduce water during rinsing process. To prove the carbon phase formed from the results of calcination and activation, it was tested using the X-Ray Diffractometer (XRD) MPD Philips Xpert. Scanning Electron Microscopy (SEM) was done to determine the semi-quantitative surface morphology and pore size formed on the surface. The calcination and activation materials were then characterized by CV test to measure capacitance. Previously, the material was mixed with Polyvinyl Alcohol (PVA) and N-Methyl-2-Pyrroliodine (NMP) solvent which was then coated on nickel foam. The CV test was carried out in Na_2SO_3 electrolyte with scan rate variation of 5 mV/s, 10 mV/s, 50 mV/s, and 100 mV/s with 0 V - 1 V input voltage.

Result and Discussion

DSC-TGA Data

DSC-TGA test was conducted with the aim to determine the effect of temperature on changes in mass and decomposition processes. DSC-TGA test was carried out at 0^0C - 1000^0C with heating rate of 20^0C / minutes. Fig. 1 shows the DSC-TGA data of *Borassus Flabelifer L* which is divided into two curves; Mass change (TGA) and heat change (DSC). On the TGA curve, there are two-stages of mass reduction that occurs around 1,235 mg at 50^0C - 100^0C and 6,892 mg at 200^0C - 600^0C. The initial stage at a temperature of 50^0C - 100^0C is a process of dehydration which indicates water evaporation. This is also proven by the DSC curve in the form of an exothermic graph indicating the release of water accompanied by the release of heat into the environment. In the second stage at a temperature of 200^0C - 600^0C, high mass reduction indicates a high process of compounds decomposition. Among the compounds that allow decomposition based on EDS data are Mg, Zr, S, K, S, Cl, and Na. But decomposition does not indicate that all the compounds are lost, only the amount is reduced. Therefore in this study based on DSC-TGA data, an activation process with NaOH 1 M was carried out to bind the remaining impurities to form a carbon material with good porosity structure for supercapacitor electrodes. Based on DSC-TGA data, the heating temperature variables after activation; 650 ^{0}C, 750^0C, and 850 ^{0}C were used in this research.

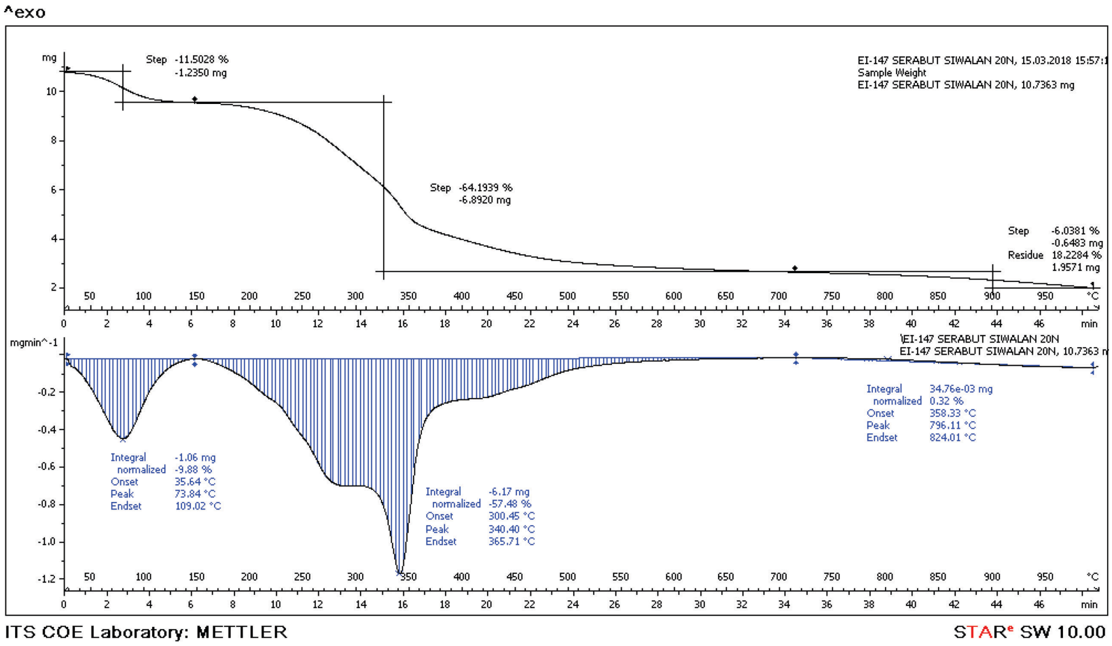

Fig. 1. DSC-TGA Curve of Borassus Flabelifer with Nitrogen flow and 20^0C/min of Heating rate.

XRD Data

To determine the structure and phase of the carbon formed, XRD characterization is carried out at short angles in the range (2θ) 10^0 - 60^0. The results of the XRD pattern from *Borassus Flabelifer L* are shown in Fig. 2a with temperature variations during heating after activation process. The XRD pattern has a low degree of crystallinity showed by a fairly high peak width which indicates that the carbon formed has an amorphous structure. This is also marked by the number of peaks with low intensity. However, there are two peaks which have high intensity at (2θ) 24^0 and 44^0. Based on a study conducted by *Sungjin Park et. al.* which synthesized Reduced Graphene Oxide (RGO) from natural graphite using the Hummer method, RGO was obtained through the XRD with peak at (2θ) 24^0 and 44^0 as shown in Fig. 2b [16]. The XRD patterns are similar to peaks produced on the heating of *Borassus Flabelifer L* with the main peaks at (2θ) 24^0 and 44^0 so that this process can be concluded to produce carbon with the RGO phase. The RGO phase was obtained due to the heating and activation process that had been carried out which resulted in the loss of many impurity compounds and the breaking of several van der walls bonding. This makes the material thickness decrease and carbon only binds to oxygen. However, with the high temperature heating done in this study, some oxygen is lost, leaving some of the carbon bonds that are empty of oxygen. The temperature difference on heating after activation does not provide a much different XRD pattern. However, the higher temperature results the two main peaks with the higher the intensity. RGO is formed through a scheme of cutting impurity bonds in carbon polymers both chemically through activation and physics through heating. This process leaves a large portion of carbon and a small portion of oxygen. Through the XRD test by matching with the reference it can be concluded that the phase formed is RGO. The RGO phase will be better if added to the sonication treatment to remove the weakest impurities that may still remain.

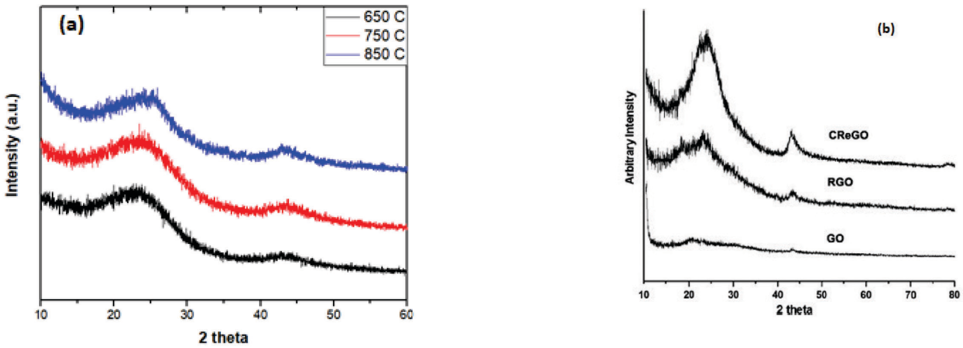

Fig. 2. XRD Data of (a) *Borassus Flabelifer L at Various Temperature of Heating* (b) RGO phase determined from natural Graphite (Sungjin Park, et al, 2011).

SEM Image

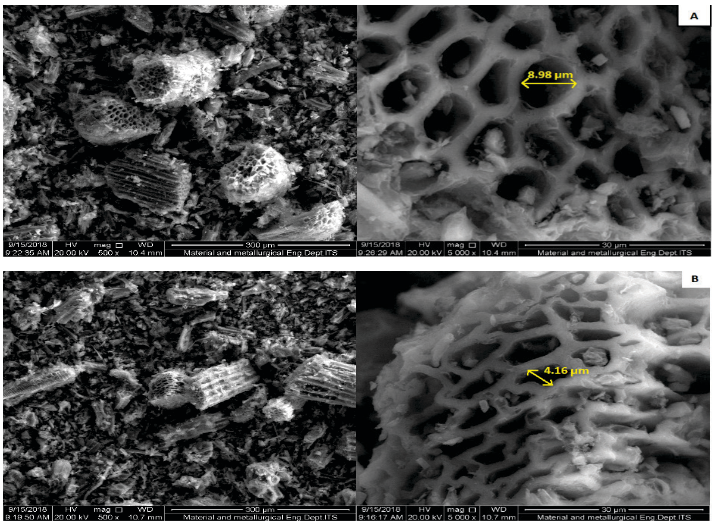

Fig. 3. SEM Image of *Borassus Flabelifer L* by heating at (a) 650^{0}C and (b) 750^{0}C.

One of the important things in EDLC is making electrodes from carbon with high porosity. This is intended so that higher charge can be stored in the capacitor. In this study a semi quantiative test was conducted to determine the pore morphology on the material surface and its diameter by SEM test. Fig. 3 shows the SEM image of *Borassus flabelifer L* which has been heated at 650 ^{0}C and 750 ^{0}C. Porous has been formed on the fiber base and its size is smaller with increasing temperature. At 650 ^{0}C it is known that one pore has diameter of 8.98 µm and at 750 ^{0}C has a diameter of 4.16 µm. Because the material used in this study is fiber of *Borassus Flabelifer L* which has a tube-like dimension, it only has a pore on the base. Whereas in the blanket section of the fiber, it has a compact structure with pores that is almost nonexistent. This will certainly affect the amount of load that can be stored in an EDLC. The porosity formation scheme occurs when many impurities have left material both through chemical activation and heating processes. This process results in the formation of vacancies in the material in the form of porosity. The more impurities that are lost, the higher the amount of porosity so that the surface area also gets higher.

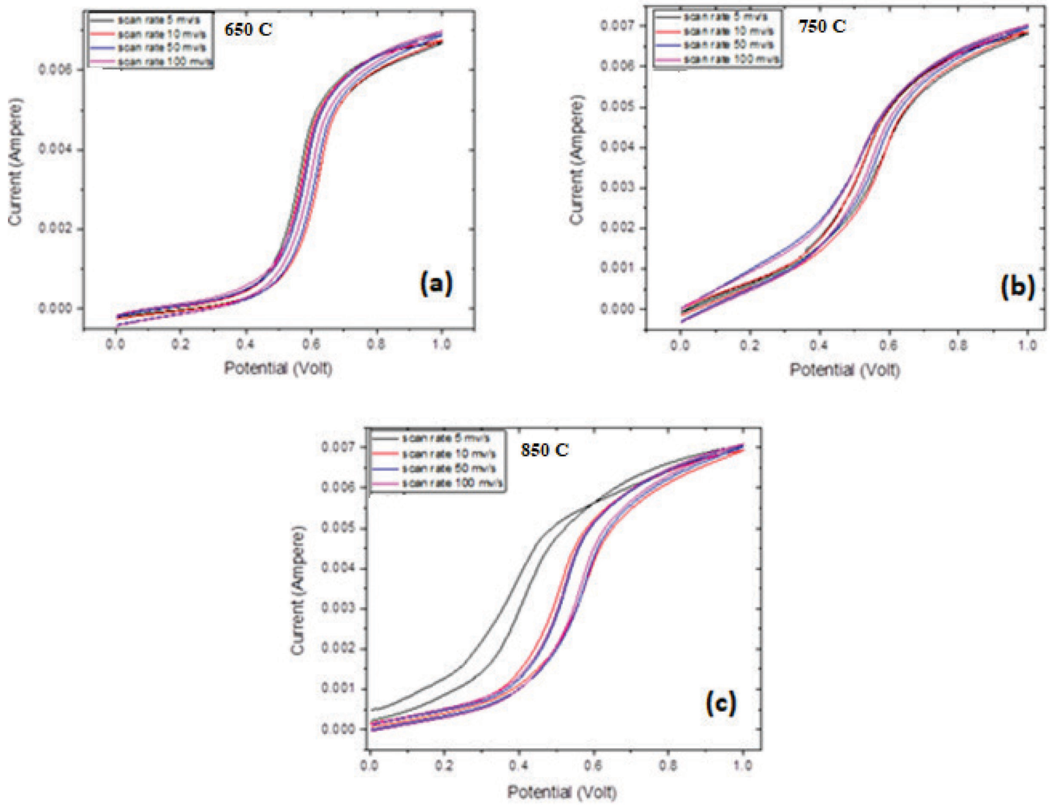

Fig. 4. CV curve of *Borassus Flabelifer L* at (a) 650^{0}C, (b) 750^{0}C, and (c) 850^{0}C.

Cyclic Voltammetry

Cyclic Voltammetry (CV) test was carried out with the aim to determine the capacitance of Borassus Flabelifer L which was treated by heating and activation. The principle of this CV test is to record the current response to the voltage variation applied to the electrode in the range 0 V - 1 V with a variation of the scan rate. The response is described in the Flow vs. Voltage curve which can be determined broadly between curves as data in determining capacitance. The capacitance value is obtained through Eq. 1 with m is the mass of the electrode, v is the scan rate, V_1 and V_2 are the range of voltage given and I is the current produced. While energy density is obtained from Eq. 2. Based on the CV test that has been done, it is obtained a plot of the current response to the voltage given in the curve presented in Fig. 4. The cyclic or hysteresis curve produced by the RGO carbon electrons as a result of activation and heating at a temperature of 650^{0}C, 750^{0}C and 850^{0}C are shown in Fig. 4a, 4b and 4c respectively. Based on the calculations that have been done, the capacitance value of each variable presented in table 1. The higher the heating temperature produces the highest value capacitance. The smaller the scan rate, the higher the capacitance value. The highest capacitance was obtained through a heating process after activation at a temperature of 850 C with a scan rate of 5 mV / s with a value of 8.25 F / gram and a meeting energy of 4.125 Watts / gram. Hidayat and darminto, 2016 have reported that RGO from coconut shell produces a capacitance of 13 F/g which means it has a higher capacitance value. This is due to the fact that the study uses higher temperatures so that it allows a wider surface area to be formed for the adsorption and desorption of charges [17].

Table 1. Capacitance data of *Borassus Flabelifer L* at (a) 650^{0}C, (b) 750^{0}C, and (c) 850^{0}C.

Sample	T (^{0}C)	Scan Rate (mV/s)	Capacitance (F/gram)	Energy Density (Watt/gram)
1	650	5	5.96	2.98
		10	2.632	1.316
		50	0.59	0.29
		100	0.27	0.135
2	750	5	6.4	3.2
		10	3.25	1.625
		50	0.692	0.346
		100	0.335	0.1675
3	850	5	8.25	4.125
		10	3.221	1.6105
		50	0.6319	0.31595
		100	0.316	0.158

$$\boldsymbol{C} = \frac{1}{mv(V2-V1)}\int_{V1}^{V2} I\, dV \quad (1)$$

$$\text{Energy density} = \frac{1}{2}.C.|V2-V1| \quad (2)$$

Conclusion

RGO phase was determined from treatment of activation followed by heating to fiber of *Borassus Flabelifer L* which is showed by XRD data with (2θ) 24^0 and 44^0. SEM image clarify that porous on RGO surface has been formed especially on the base. By RGO forming with high porosity, it is suitable for EDLC application and CV test has examined that heating of *Borassus Flabelifer L* fiber at 850^{0}C with 5 mv/s scan rate has the highest specific capacitance by 8.25 F/gram with Energy density is 4.125 watt/gram.

Aknowledgement

This research funding is supported by Directore of Research and Community Service (DPRM), Directore General Research and Development of the Ministry of Research and Development of the Ministry of Research, Technology and Higher Education of Indonesia (RISTEK DIKTI) under PDP Grant. This supported is gratefully aknowledge.

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