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Rika Taslim, Maya Novita Sari, Agustino, Apriwandi, and Erman Taer

Electrode of Supercapacitor Synthesized from Leaf Bunch of Oil Palm for Enhancing Capacitive Properties

Rika Taslim[1, a)], Maya Novita Sari[1], Agustino[2], Apriwandi[2] and Erman Taer[2]

[1]*Departement of Industrial Engineering, State Islamic University of Sultan Syarif Kasim, Jl. Subrantas Km. 15, Pekanbaru, Riau 28293, Indonesia.*
[2]*Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Riau, Kampus Bina Widya, Km 12,5 Simpang Baru, Panam, Pekanbaru, Riau 28293 Indonesia.*

[a)]Corresponding author: rikataslim@gmail.com

Abstract. Supercapacitor electrodes made from leaf bunch of oil palm were prepared by carbonization and activation process which consist of several steps such as pre-carbonization, milling, sieving, chemical activation, pelletization, and carbonization-physical activation. Chemical activation was performed by 0.4 M KOH, meanwhile carbonization and physical activation were used N_2 and CO_2 gas. The physical properties of electrodes analyzed are density, degree of crystallinity, surface morphology, and surface area while the electrochemical properties are focused on the analysis of specific capacitance of the supercapacitor cell using cyclic voltammetry method. XRD pattern indicates the crystallinity of the electrodes is amorphous structures. The SEM micrographs clearly exhibit electrode surface morphology that is quite smooth and regular with fine particles that are spread evenly on the surface of the electrode. The physical properties of the activated carbon electrodes are correlated in generating the optimum conditions of the specific capacitance of supercapacitor cells. The optimum specific capacitance was obtained as high as 52 F g^{-1} with a specific surface area of 639. 836 m^2 g^{-1}.

INTRODUCTION

Indonesia is one of the countries with the largest oil palm plantations in the world. Based on statistical data, Indonesia's oil palm plantations reached 10.9 million hectares with production of 29.3 million tons in 2014 [1]. The area of this plantation is expected to continue increase due to the opening of plantation land every year. The oil palm plantation and production certainly have several negative impacts such as the waste generated are quite large. Leaf bunches of oil palm is one of the largest solid wastes produced by oil palm plantations. Each fresh fruit bunches results 2-3 leaf bunches waste. The leaf bunch of oil palm is lignocelluloses wastes that have not been utilized optimally. The components of lignocellulose in leaf bunch as high as 65% which includes cellulose, hemicellulose and lignin. The high lignocellulose component in leaf bunches of oil palm has potential to be used as a raw material of active carbon electrodes as a supercapacitor application [2]. To ensure this, many previous studies have suggested the use of high lignocelluloses materials as carbon electrodes with high performance such as durian shell [3], coconut [4] and tobacco [5]. Based on the description above, a study was conducted on the manufacture of carbon electrodes made from leaf bunches of oil palm as supercapacitor cell applications. Activated carbon is prepared by the single-step carbonization and activation process. 0.4 M KOH was chosen as a chemical activator agent. The focus of this study is the variation of leaf bunches of oil palm powder particles. It is hoped that this study can be used as an alternative utilization of the potential of leaf bunches waste so as to reduce the problem of oil palm waste and environmental pollution in Indonesia.

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MATERIAL AND METHODS

The leaf bunches of oil palm are collected from oil palm farmers in Riau Province. Samples are dried in the oven to reduce the moisture content. Furthermore, the pre-carbonization process is carried out at room temperature to 250 ˚C. The powder preparing process is carried out using a milling instrument. The powder was sieved using two types of sieve sizes such as 100 µm and 38 µm sieves. From the results of this sieve, we found a variety of powder sizes. Based on the sieve variations, the samples were labeled AC-100 and AC-38. The chemical activation process was carried out using a hot plate at a temperature of 80 C in 0.4 M Potassium Hydroxide. The sample powder was changed into monolith form using a hydraulic press. The process of pyrolysis is carried out in single step including the carbonization process by flowing N_2 gas and followed by a physical activation process in CO_2 gas atmosphere at a temperature of 900 ˚C [6, 7]. Finally, the sample is arranged into supercapacitor cells in form of sandwich [8].

The physical properties of the activated carbon electrode were evaluated using several analyzes. Density as the initial analysis is determined based on mass and volume of activated carbon electrodes. The structure of activated carbon was reviewed by X-ray diffraction using Cu kα radiation (λ = 1.5406 Å). The surface morphology is evaluated by scanning electron microscopy at a magnification of 20000 times. Pore properties and surface area were analyzed using the N_2 gas absorption method. Electrochemical properties were evaluated using the cyclic voltammetry method with two electrode system and 1M H_2SO_4 as an electrolyte. The potential window chosen is 0-0.5V at a relatively low scan rate (1 mV s^{-1}). Specific capacitance is calculated using a standard formula based on CV measurement data [9].

RESULT AND DISCUSSION

One analysis of the initial electrode physical properties which is usually evaluated is the density analysis. Density is calculated based on the mass and volume of the electrode during the pyrolysis process. Figure 1(a) shows the results of density before and after the pyrolysis process. The highest density was found in the AC-100 while the smallest density was found in the AC-38. This density result is consistent with the other study reported [10] with a sample of empty fruit bunches of oil palm stated that the largest sieve size produced the highest density. Decreasing density after the pyrolysis process is due to the evaporation of water content and decomposition of complex compounds in the sample which last for 10.6 hours. Evaporation and decomposition of these complex compounds result in the formation of pores on the electrodes so that the density decreases.The X-ray diffraction pattern of AC-100 leaf bunch of oil palm activated carbon is shown in Fig. 1(b). The curve presents two wide peaks and several sharp peaks. Two wide peaks located at 23° and 44° indicate the characteristic peak of the diffraction plane (002) and (100), indicating amorphous carbon structures [11]. Furthermore, sharp peaks in the XRD pattern indicate the presence of crystal structures from other elements such as $CaCO_3$ which are located at an angle of 29° and 48°.

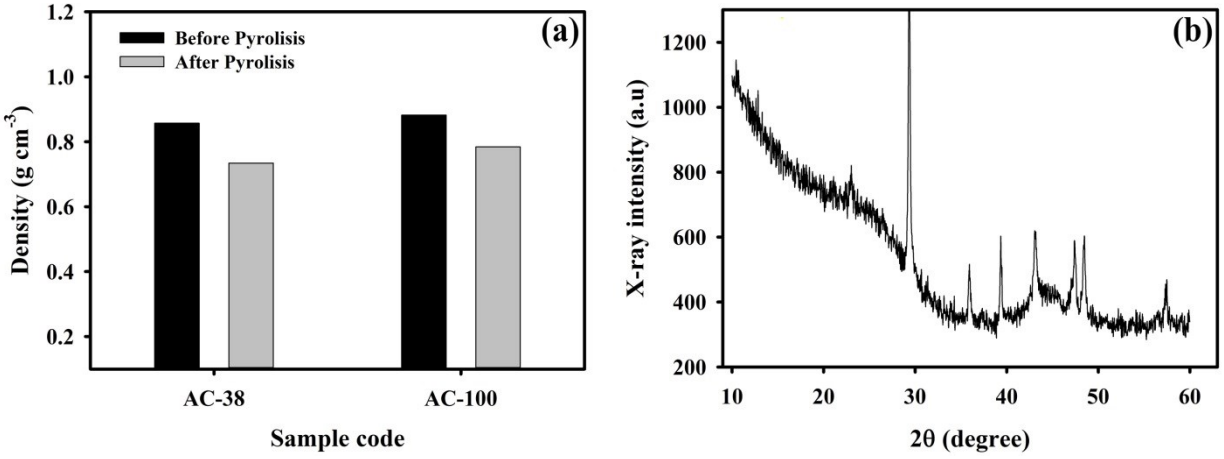

FIGURE 1. (a) Density for before and after pyrolysis process, (b) XRD pattern for AC-100 sample

The surface morphology of AC-38 and AC-100 is characterized by SEM with a magnification of 20000 times which shown in Fig 2. SEM micrographs clearly exhibit electrode surface morphology that is quite smooth and regular. Figure 2(a) presents fine particles that are spread evenly on the surface of the electrode. However, the presence of

larger particles is abundant in AC-100 from Fig. 2(b). Larger particle sizes adorn the surface of the carbon electrode. This is influenced by the size of the sieve. A larger sieve automatically results in larger particle size, as seen in the SEM micrograph in this study.

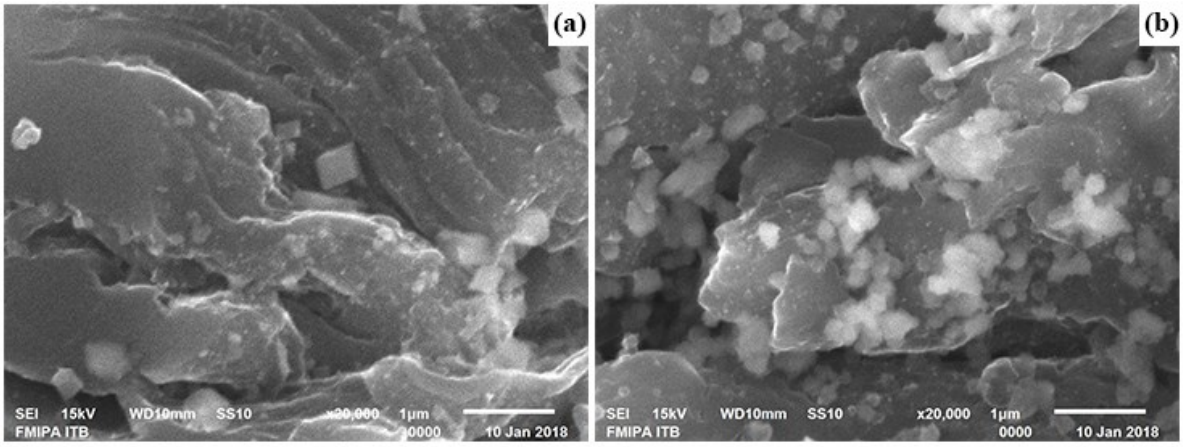

FIGURE 2. SEM micrographs for (a) AC-38, (b) AC-100

Nitrogen adsorption isotherms for AC-38 and AC-100 are shown in Fig. 3(a). According to isotherm tendencies, Figure 3(a) presents type-IV isotherms. Hysteresis loops are characteristic of type-IV isotherms which indicate the presence of wide expanding mesopores [12,13]. The hysteresis loop starts from a relative pressure of 0.4 to a relative pressure of 0.9, indicating that in the relative pressure range, N_2 gas is absorbed more by the mesopores. At relatively lower pressures than 0.4 seem faster saturation curves which indicate the presence of relatively fewer micropores. Surface area was examined using the BET method for AC-38 and AC-100 as high as 479. 975 $m^2\ g^{-1}$ and 639. 836 $m^2\ g^{-1}$, respectively. The pore size distribution of AC-38 and AC-100 is shown in Figure 3(b). Many pore distributions concentrate at a pore diameter of 3.8 nm, which facilitates electrolyte ion transfer and increases the capacity of the electrode material. The average pore diameter produced was 3.8 nm which was evaluated using the BJH method. The surface area shown in this study corresponds to other studies that also discuss carbon electrodes from biomass waste as shown in Table 1.

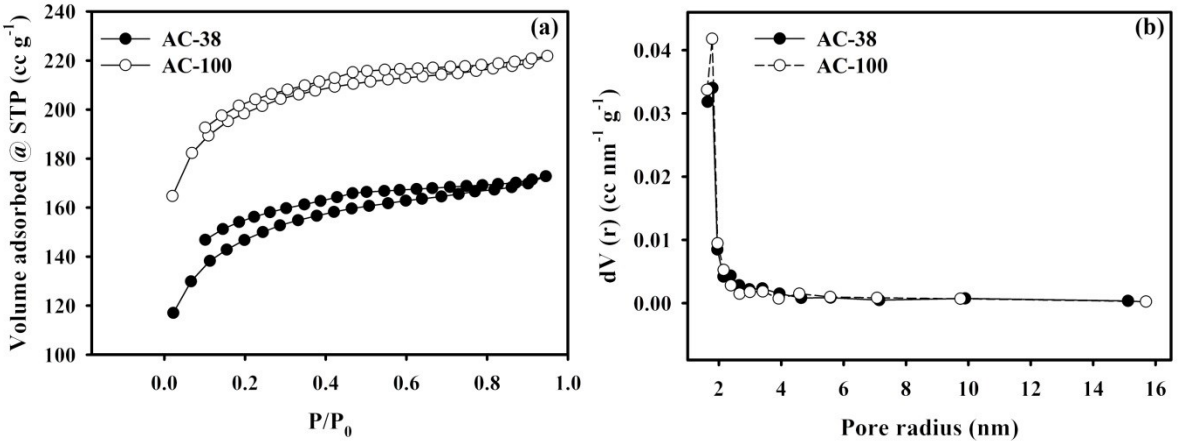

FIGURE 3. (a) N_2 gas adsorption/desorption for AC-38 and AC-100, (b) The distribution pore radius for AC-38 and AC-100

TABLE 1. Comparison of S_{BET} for different lignocellulose biomass resources of supercapacitor electrodes

Biomass resources	S_{BET}	References
Leaf bunches of oil palm	639.836	This work
Gelatin	416	[14]
Kombucha	917	[15]
Crude auricularia	80.08	[16]
Leaves (Fallen)	1078	[17]
Corncob residue	1210	[18]
Coconut kernel pulp (Milk free)	1200	[19]

The cyclic voltammetry is a method used to determine the relationship between charging-discharging current density with a certain potential window. The results from the CV measurements are used to evaluate the capacitive properties of a supercapacitor cell that is presented in a curve. The resulting curve area represents the specific capacitance of the measured supercapacitor cell. Measurement is carried out at a scanning rate of 1 mV s^{-1} at a potential window of 0-0.5V. The selection of the relatively low scanning rate because the ions will diffuse evenly and optimum into the pores of the carbon electrode surface so as to produce maximum specific capacitance . Figure 4 shows the CV curves for AC-38 and AC-100. The rectangular shape shown in Fig. 4 is a normal curve for supercapacitor electrodes from biomass material [20]. The specific capacitance produced for AC-38 and AC-100 is 33 F g^{-1} and 52 F g^{-1}, respectively. AC-100 samples show that the capacitive is better than AC-38. Based on these results, it can be seen that AC-100 has a faster ion transfer with more electrolyte ion accumulation. This analysis is supported by a greater surface area at AC-100 of 639.8 m^2 g^{-1} thus allowing more pore accumulation of ions. Surely it will produce better capacitive properties.

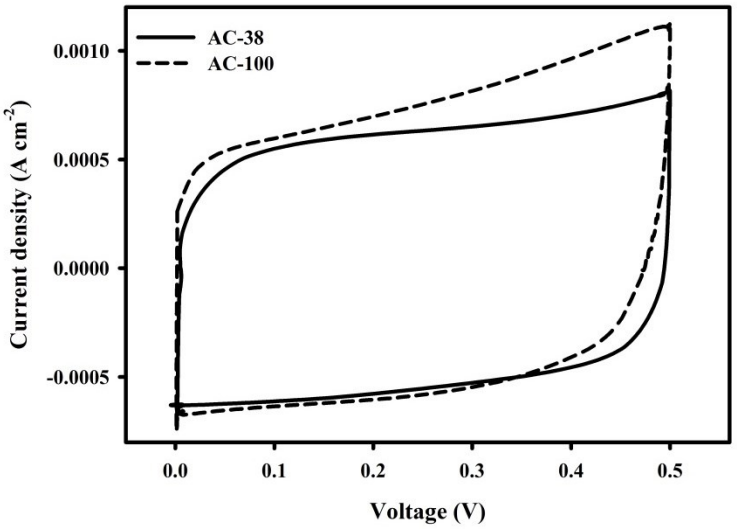

FIGURE 4. The CV curve for AC-38 and AC-100

CONCLUSIONS

Supercapacitor electrode made from leaf bunches of oil palm successfully prepared by using single step carbonization and activation process with powder size particle variation as the main focus. The carbon electrode prepared by multi-activation such as chemical activation by 0.4 M KOH and physical activation in CO_2 gas atmosphere at a temperature of 900 ˚C. Smaller powder particles exhibit smaller density as high as 0.67 g cm^{-3}. Electrode microstructure presenting amorphous carbon with smooth and regular surface morphology. Particle size also affects pore properties and surface area of carbon electrodes. Smaller pore size indicates smaller surface area and the highest surface area is found in larger particle size of AC-100 as high as 639.836 m^2 g^{-1}. This physical property supports the capacitive properties of supercapacitor cells. The highest specific capacitance was found in AC-100 of 52 F g^{-1}. Based on the excellent properties of this carbon electrode, the leaf bunches of oil palm has potential to be further developed as a raw material from activated carbon electrodes as supercapacitor applications.

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