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Activated Carbon Monolith Derived from Coconut Husk Fiber as Electrode Material for Supercapacitor Energy Storage

Erman Taer[1,*], Verdy Manoto Naipospos[1], Rika Taslim[2], Agustino[1], Apriwandi[1]

[1]Department of Physics, University of Riau, 28293 SimpangBaru, Riau, Indonesia
[2]Departement of Industrial Engineering, State Islamic University of Sultan Syarif Kasim, 28293 Simpang Baru, Riau, Indonesia

[*]erman.taer@lecturer.unri.ac.id

Abstract. Biomass-derived porous activated carbon materials have been receiving considerable attention in energy-storage devices especially for supercapacitor due to abundant, renewable, sustainable, and cost-effective production. In this study, porous activated carbon material with monolithic form has been successfully prepared from coconut husk fiber through one-stage integrated pyrolysis and $ZnCl_2$ impregnation. Different physical activation temperature is the main focus in this study including 750, 800, 850, and 900 ºC. The reduction of monolith dimensions such as mass, diameter, thickness and density have been reviewed as physical properties. Furthermore, the supercapacitor cells were performed with cyclic voltammetry t 1 M H_2SO_4 aqueous electrolyte at low scan rate of 1 mV s^{-1}. The supercapacitor device based on the CFM-800 samples exhibited highest specific capacitance of 216 F g^{-1}. This sample also performed a promising performance with an energy density of 30.00 Whkg^{-1} and a high power density of 108.57 Wkg^{-1}. These results demonstrate that the coconut husk fiberhas been a high potential to as raw material for porous activated carbon monolith through low cost, vehicle and short-time processing with high-performance supercapacitors energy storage.

1. Introduction

Today, coconut is a valuable commodity due to its various uses including coconut oil, shredded coconut, coconut milk, butter, and super-hydrating coconut water. In 2016 and 2017, Indonesia was the largest coconut producer in the world with a total production of 18,983,378 tons in 2017[1]. However, coconut production produces a lot of waste, especially coconut husk which has about 85% from coconut plant. The fiber from coconut coir known as coconut coir is actually very versatile and can be used in a variety of different products such as growing media, materials for making mats and brushes, components for mattresses, and floor tiles [2]. As a waste management perspective, the coconut husk has high lignocellulose which considered as a key to valuable higher development.

Biomass waste containing lignocellulose could act as the main source of activated carbon material due to it is a low cost, easy to produce, renewable and sustainable, and has excellent physico-chemical properties[3,4]. Lignocellulosic waste could be converted into activated carbon through various processes such as pyrolysis, hydrothermal, chemical activation, carbonization, and physical activation[5,6]. Currently, many researchers focus more on the use of biomass waste as activated carbon for electrode materials as an energy storage device, especially supercapacitors, such as bamboo [7,8], mangosteen [9,10], sakura flower[11], and tobacco wastes[12,13]. They reported that the resulting activated carbon electrode material with high capacitive in the range of 200-300 Fg^{-1}. Furthermore, similar studies carried out to convert the from coconut husk fiber to activated carbon

which has the potential as a absorber that could solve the many wastewater problem[14,15]. Recently, our research group has successfully prepared the porous carbon monolith based on coconut husk as raw material through KOH impregnation in high-temperature physical activation [16]. This is performed that coconut husk can be converted into activated carbon for the supercapacitor electrode material. Moreover, the specific capacitance generated is still low at around of 184 Fg^{-1}. This may be due to the waste from coconut husk fiber that has not been separated from the coir.

In this study, we focused to investigate the electrochemical behavior of activated carbon derived from coconut husk fiber as an electrode material for supercapacitors. Coconut husk was pre-treated to separate coir from their husk fiber. The $ZnCl_2$ in 0.5 M concentration was selected as a chemical activating agent. The pyrolysis process is carried out in one-stage integrated pyrolysis both carbonization and physical activation. The temperature of physical activation was varied of 750, 800, 850, and 900 ºC, respectively. Activated carbon is prepared in a monolith/pellet form without the addition of adhesives materials such as PVDF and PTFE. The cyclic voltammetry analysis was employed to evaluate the capacitive properties of the symmetric supercapacitor cell. Furthermore, reduction of mass, thickness, diameter, and density were also reviewed to evaluate the initial physical properties of activated carbon monolith derived from coconut husk fiber.

2. Methods

The activated carbon monolith derived from coconut husk fiber through $ZnCl_2$ activation and one-stage-integrated pyrolysis. Coconut husk waste collected from traditional market in Pekanbaru, Riau province were sundried for two days and continued in vacuum oven at a temperature of 110 °C. Furthermore, the coconut husk waste is pre-treated to separate the fibersfrom the coir with boiledin electrical stove for 20 minutes. Subsequently, coconut husk fibers were pre-carbonized in a vacuum oven at a temperature of 250 °C. Furthermore, pre-carbonized samples converted into powder by using mortar and milling tools and it followed by $ZnCl_2$ impregnation in a hot plate at a temperature of 80 °C. Next, the carbon powders converted into monolith/pellet by using hydraulic press. The samples were prepared in 20 monoliths and subsequently pyrolyzed in one-stage integrated pyrolysis which begins with carbonized in an N_2 gas environment from a temperature of 30 °Cto 600 °C and followed by physical activation at a high temperature[17]. The temperatures of physical activation were varied of 750, 800, 850, and 900 °C, respectively. Based on the differences in chemical activation treatments, the samples were labelled CFM-750, CFM-800, CFM-850 and CFM-900, respectively. For more details of bamboo activated carbon preparation are shown in Figure 1.Finally, the activate carbon monoliths were neutralized with distilled water and polished in 0.2 mm thickness for electrode tested.

The initial physical properties of carbon monolith were evaluated in reduction of mass, diameter, thickness and density of the samples. The density was calculated with standard equation. Moreover, the electrochemical behavior were performed by using the cyclic voltammetry method (CV, CV UR Rad-Er 5841 instrument, calibrated with VersaStat II Princeton Applied Research, an error of ±6.05%) at Materials Laboratory, Department of Physics, University of Riau, Indonesia. The symmetric supercapacitor cells were assembled in the coins-type including activated carbon monolith as material electrodes, 1 M H_2SO_4 aqueous electrolyte, and egg duck shell membrane as separator. The electrochemical behaviors were calculated by using the standard equations based on CV curve data's [18,19].

$$C_{sp}\frac{2.I}{s.m} \tag{1}$$

$$E = \frac{1}{2}.C_{sp}.V^2.\frac{1000}{3600} \tag{2}$$

$$P = \frac{E}{\Delta t}.3600 \tag{3}$$

Were, I is the average current (A), s is the scan rate (mV s^{-1}), m is the average mass of the electrodes (g), V is voltage window (V), and Δt is time for discharge process (s).

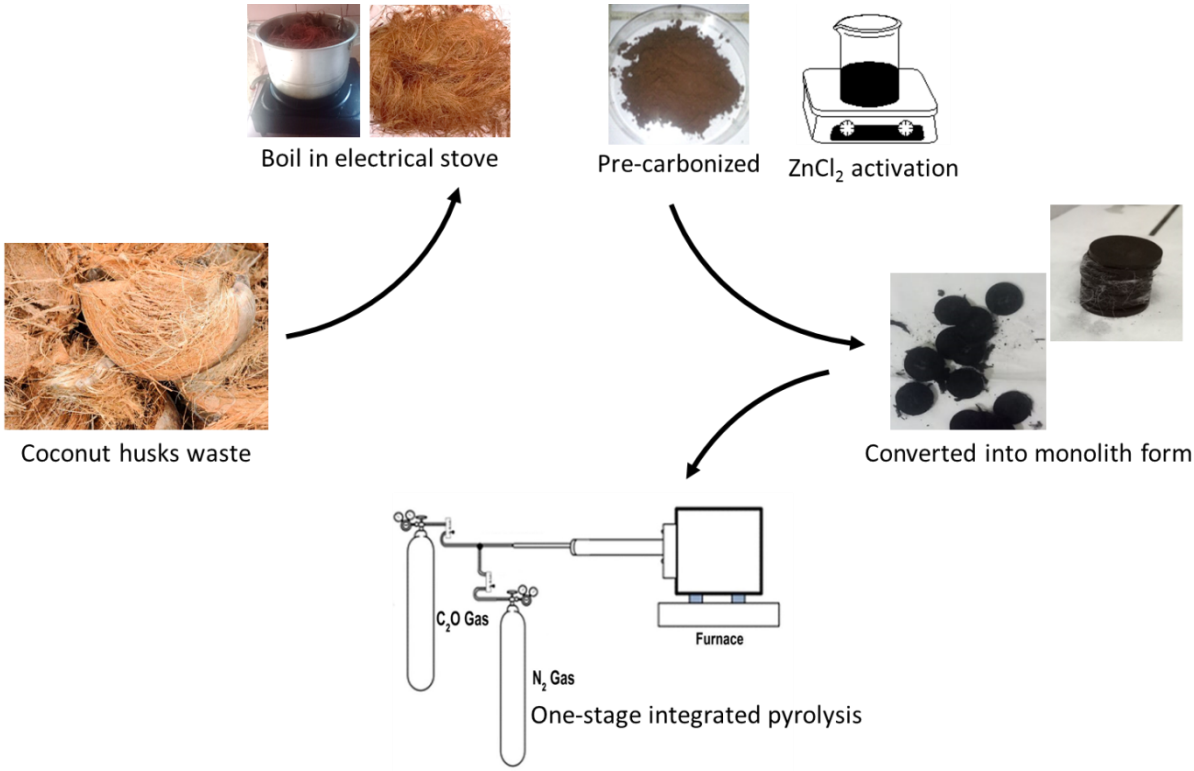

Figure 1. Schematic of production of activated carbon monolith derived from coconut husk fiber.

3. Results and Discussion

Reduction of mass, diameter, thickness, and density were a frequent initial review to evaluate the physical properties of activated carbon monoliths, as have been reported in previous studies. One-stage integrated pyrolysis both carbonization and physical activation and $ZnCl_2$ activation contributed to converting the raw material to porous activated carbon and it caused a reduction in the dimensions of the monolithic samples. In the one-stage integrated pyrolysis process, the carbon precursors are first carbonized in an inert atmosphere from 30 °C to 600 °C to remove most of the volatile matter and followed by partial gasification using CO_2 gas at a different level temperature of 750-900 °C[6]. Initially, the active oxygen in the activating agent burns out the impurity byproducts of the pyrolysis products trapped in the pores, leading to the opening of some of the closed pores[20]. Then the micropores structure was developed in a larger direction such as mesopores and macropores depending upon the level of physical activation temperature[21].

As shown in Figure 2a, mass, diameter, and thickness exhibit a greater reduction as well as an increase in physical activation temperature from 750-900 °C. This is caused by increasing the physical activation temperature erodes the wall of micropores and developed larger pores and it causes a reduction in mass. Monolith average mass were showed the greatest reduction of 73% and followed by diameter and thickness of 23% and 14%, respectively. The mass reduction for the CFM-750, CFM-800, CFM-850, and CFM-900 samples were 61.25%, 64.96%, 74.54%, and 75.31%, respectively. An increasing activation temperature could increase the reduction in mass. Based on the mass, diameter, and thickness data, the density could be calculated using a standard formula. The increase in physical activation temperature also affects the density of the monolith sample, as shown in Figure 2b. After the pyrolysis process, the reduced monolith density is 0.7499 g cm^{-3}, 0.8488 g cm^{-3}, 0.5710 g cm^{-3}, and 0.7158 g cm^{-3} for CFM-750, CFM-800, CFM-850, and CFM-900, respectively with a mean standard deviation of 0.081. This result was similar with other study in different biomass such as activated

carbon monolith derived from durian shell [22], pineapple crown [23], and pandanus tectorius leaves [24].

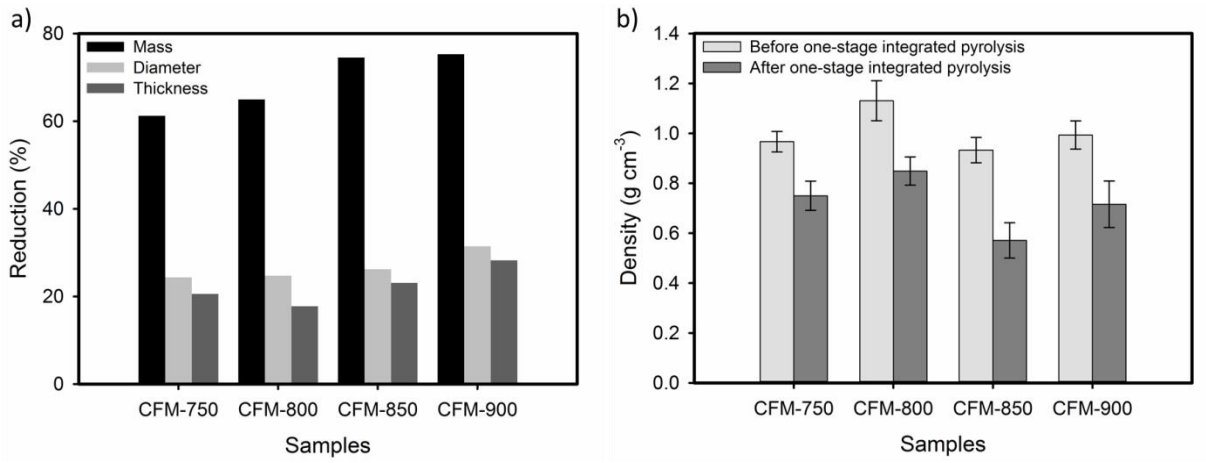

Figure 2. (a) Reduction of mass, thickness, and mass, and (b) Density of carbon monolith before and after physical activation.

The cyclic voltammetry (CV) method was evaluated in apotential window to evaluate the capacitive behaviours of the porous carbon monoliths as an electrode material. The samples ofCFM-750, CFM-800, CFM-850, and CFM-900 carbon monoliths were performed as the electrode monolith to evaluate the coconut husk fiber as raw material of porous carbon electrodes in supercapacitor application. The symmetric supercapacitor cells were tested in coin layers at a potential window of 0-1.0 V in 1 MH_2SO_4 aqueous electrolyte. In Figure 3a, all samples performed the CV curves of the different samples at a low scan rate of 1 mV s^{-1}. All the curves exhibit quasi-rectangular CV shapes, which correlated with a large part of electrical double-layer capacitor based on ideal ionic adsorption and desorption behaviours [22,25].Moreover, the CV integral area indicates the specific capacitance of the carbon monolith electrode. Clearly, the CFM-800 sample possesses the largest CV integral area than other which illustrated that CFM-800 showed the highest specific capacitance of 216 Fg^{-1}, followed by CFM-750, CFM-850, and CFM-900 of 202 F g^{-1}, 192 F g^{-1}, and 147 F g^{-1}, respectively. However, the current density of CFM-750, CFM-800, and CHF-850 were significant increase in low potential window of <0.1 V than CFM-900. This is confirmed that CFM-750, CFM-800, and CFM-850 have a good combination pores between micropores and mesopores that is suitable for ion diffusion on morphology surface which contribute to more electric double-layer[10,26]. In contrast withCFM-750, CFM-800, CFM-850, and CFM-900 showed a significant increase of specific capacitance in higher potential window of 0.4-1.0 V which due to the fact that the initial micropores developed tend to be larger and lead to the formation of combination mesopores and macropores[27]. Based on this result, the physical activation temperatures are affected to electrochemical behaviour of supercapacitor cell. Increasing the temperature from 750 ºC to 800 ºC could enhance the specific capacitance from 202 F g^{-1} to 216 F g^{-1}. Furthermore, in higher temperature, the specific capacitance is reduced from 216 F g^{-1} to 147 F g^{-1} for 800 ºC to 900 ºC. This is caused by higher temperature could develop the initial pores tend to be larger and lead to the new large formation of pores.

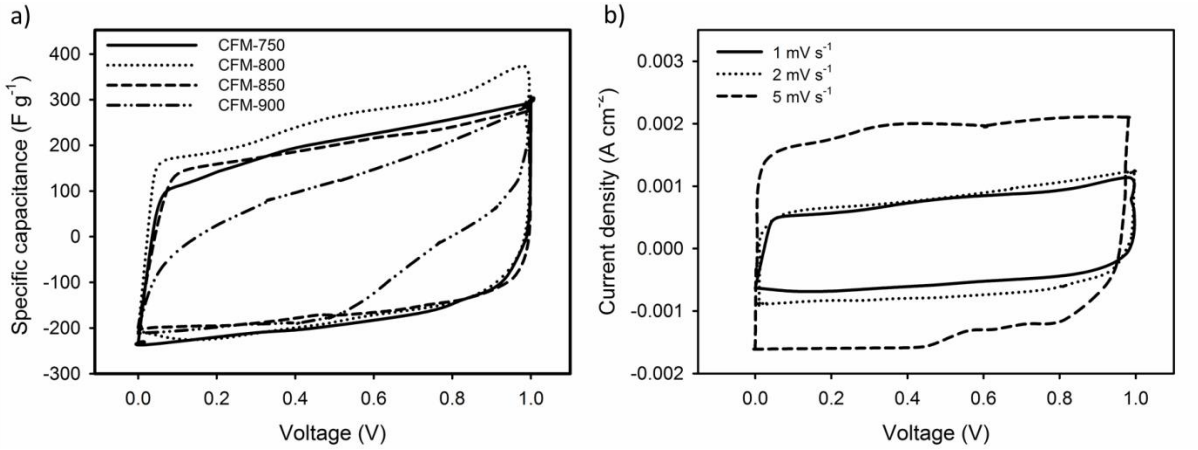

Figure 3. (a) CV curve of all samples (b) CV curve of CHF-800 at different scan rates.

Moreover, The CV curves of CHF-800 at different scan rates from 1 mV $s^{-1}$to 5 mV s^{-1} were shown in the Figure 3b. The rectangular shapes of CV curves were more stable gradually with the increasing scan rates, which had indicated the excellent capacitor behaviour of the carbon electrode materials[28]. Figure 4 was shown the specific capacitance versus the scan rate variations at 1 mVs^{-1}, 2 mVs^{-1}, 5 mV s^{-1} and 10 mV s^{-1} for all the samples. The increasing scan rates were caused the gradually decreasing specific capacitance. The decreasing specific capacitance was due to a different of factors controlling, including the pore size distribution, a combination of micro-,meso-, and macropores[29,30].Based on the standard formula which stated the previously, the energy density of CFM-750, CFM-800, CFM-850, and CFM-900 were 28.05, 30.00, 26.67, and 20.42Wh kg^{-1} with power density of 101.08, 108.57, 96.09 and 73.57 W kg^{-1}, respectively. These results are similar with other study with different biomass sources such as coffee wastes activated carbon were 34 $Whkg^{-1}$ and 215 Wkg^{-1}[31] and pistachio shell [32,33] porous carbon was 39 $Whkg^{-1}$ and 286 Wkg^{-1}.

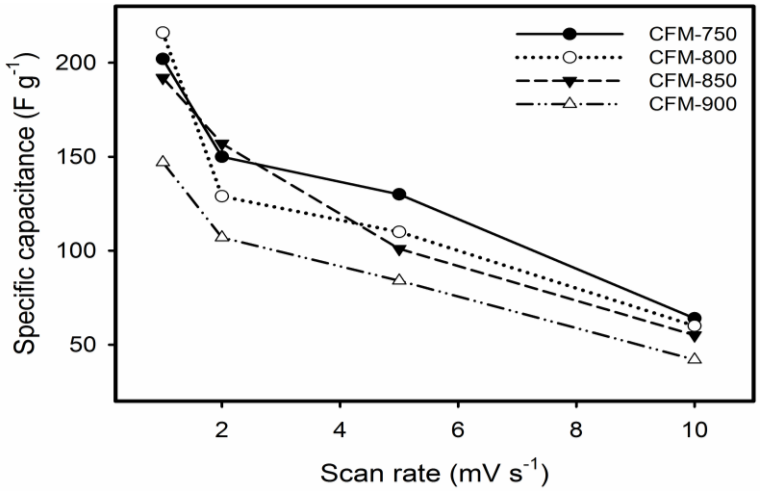

Figure 4. The specific capacitance versus the scan rate variation of all samples.

4. Conclusion

In this work, porous activated carbon monolith derived from coconut husk fiber through one-stage integrated pyrolysis and $ZnCl_2$ impregnation was successfully demonstrated for electrode supercapacitor. The physical activation temperature was varied including 750, 800, 850 and 900 ºC. Generally, different temperatures of physical activation were affected the electrochemical behaviour of symmetric supercapacitor cells. In 750 ºC to 800 ºC, the specific capacitance is increase from 202 to 216 F g^{-1}. However, in higher temperature of 800 ºC to 900 ºC, the specific capacitance is reduced

from 216 to 147 F g^{-1}. As a result, CFM-800 can act as a promising material as activated carbon monolith for supercapacitor electrode with the specific capacitances of 216 F g^{-1} with energy density and power density of 30.00 Wh $kg^{-1}$and 108.57 W kg^{-1}, respectively. Based on these results, the activated carbon monoliths derived from coconut husk fiberare promising as an electrode material through one-stage integrated pyrolysis and $ZnCl_2$ impregnation for supercapacitor energy storage.

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