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Effective cost and high-performance supercapacitor electrodes from *Syzygium oleana* leave biomass wastes

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Abstract. Effective cost and high-performance supercapacitor electrodes were prepared using *Syzygium oleana* leave biomass wastes. Simple one-stage integrated pyrolysis is adopted to get the porous activated carbon monolith without the addition of synthetic materials. The carbon samples were chemically activated by using sodium hydroxide. Four different carbonization temperature of 550 ºC, 600 ºC, 650 ºC, and 700 ºC have been evaluated and compared for their electrochemical behavior in supercapacitor cells. The physical characteristics were obtained using dimensions reduction and an X-ray diffraction method. The electrochemical properties of the porous activated carbon monolith were studied using cyclic voltammetry technique. Furthermore, two different aqueous electrolytes were selected to improve the electrochemical behavior of the electrode such as 1 M H_2SO_4 and 6 M KOH with low scanning rate of 1 mV s^{-1}. The capacitive of symmetric supercapacitor showed high specific capacitance of 153 F g^{-1}. Moreover, the maximum specific energy and specific power were found as high as 21.25 Wh kg^{-1} and 76.57 kW kg^{-1} at the voltage window of 0-1.0V. The simple and economically friendly method demonstrated to obtained porous activated carbon monolith derived from *Syzygium oleana* leaves waste makes them excellent candidates for future electrode materials of energy storage technologies.

1. Introduction

Supercapacitor as known as electrochemical capacitor is a new type of energy storage device with wide application prospects and high economic value compared to other energy storage devices such as conventional capacitors and batteries. Supercapacitors, in particular the electrical double layer (EDLC) type have a much higher energy density than conventional capacitors and a much higher power density than batteries [1,2]. However, the supercapacitor energy density is still relatively small and is not balanced with the high power density. Electrode material and electrolyte are the main factors for increasing and maintaining the supercapacitor energy density [2–4]. Of the various electrode materials, porous carbon is the most effective and most successful electrode material in creating high surface area, simple preparation process, low cost, good conductivity and high chemical stability thus imparting supercapacitor performance [5,6]. Recently, relevant studies have shown that the performance of electrode materials depends mainly on the specific surface area and pore size distribution [5,7]. Therefore, increasing the surface area and controlling the pore structure of carbon has been the center of attention of researchers [8].

Many studies have reported that porous carbon with high surface area and controlled pore structure can be synthesized from waste biomass by pyrolysis including carbonization and activation which has a high potential as electrode material for EDLC [4,9]. Biomass precursors for porous carbon can save costs, reduce fossil fuel use and environmental pollution. To date, potential biomass wastes include *mangosteen* [10-11], sakura flower [12], bamboo [13], rotten carrots [14], durian shell [15,16], banana stems [17], and acacia leaves [18]. In contrast, there are few reports of porous carbon derived from ornamental plant waste biomass. *Syzygium oleana* are one of the ornamental plants that are most often found in Indonesia, especially in the province of Riau. This plant is found in pots, on roadsides, both in cities and in villages. Apart from being an ornamental plant, it can control air pollution in the city. However, this plant waste is still underutilized but is rich in lignocellulose which has the potential as a raw material for activated carbon. In this paper, we synthesize porous activated carbon derived from *Syzygium oleana* leaves through carbonization pyrolysis and physical activation and activation of NaOH for its application in supercapacitors as electrode materials. The results show that the prepared porous carbon has high amorphous properties, high specific capacitance, and excellent performance.

2. Materials and Methods

2.1. Synthesis of activated carbon

In this study, an effective, environmentally friendly, and low-cost method was used to obtain a monolithic activated carbon electrode derived from biomass waste for supercapacitor applications. *Syzygium oleana* leaves are used as a precursor for preparation activated carbon powders and monoliths through chemical activation, carbonization, and physical activation. 250 g of the precursor was pre-carbonized in a vacuum oven for 2.5 hours, followed by a conversion process to obtain powder precursor using milling tools and sieving 270 mesh. Subsequently, the powder precursor was chemically activated using NaOH solution with a concentration of 0.5 M. The chemical activation process was carried out using a hotplate and magnetic stirrer at a temperature of 80 ºC in 300 rpm. Furthermore, chemically activated samples were converted into pellets/monoliths using a hydraulic press without the addition of other synthetic materials such as PVDF or PTFE. For the carbonization and physical activation processes, 20 pellets are placed in a carbonized furnace at target temperatures including 550, 600, 650, and 700 ºC in a nitrogen gas environment, which it is continued with physical activation up to a high temperature of 850 ºC with a gas flow rate of 10 C / min in carbon dioxide gas atmosphere for 2.5 hours. After cooling naturally to room temperature, the product obtained was immersed and washed with distilled water to neutral/pH=7, then dried in an oven at a temperature of 110 ºC for 8 hours. The samples obtained are denoted SO550, SO600, SO650, and SO700, respectively. A schematic illustration for the synthesis of activated carbon monoliths derived from *Syzygium oleana* leave is shown in Schematic 1.
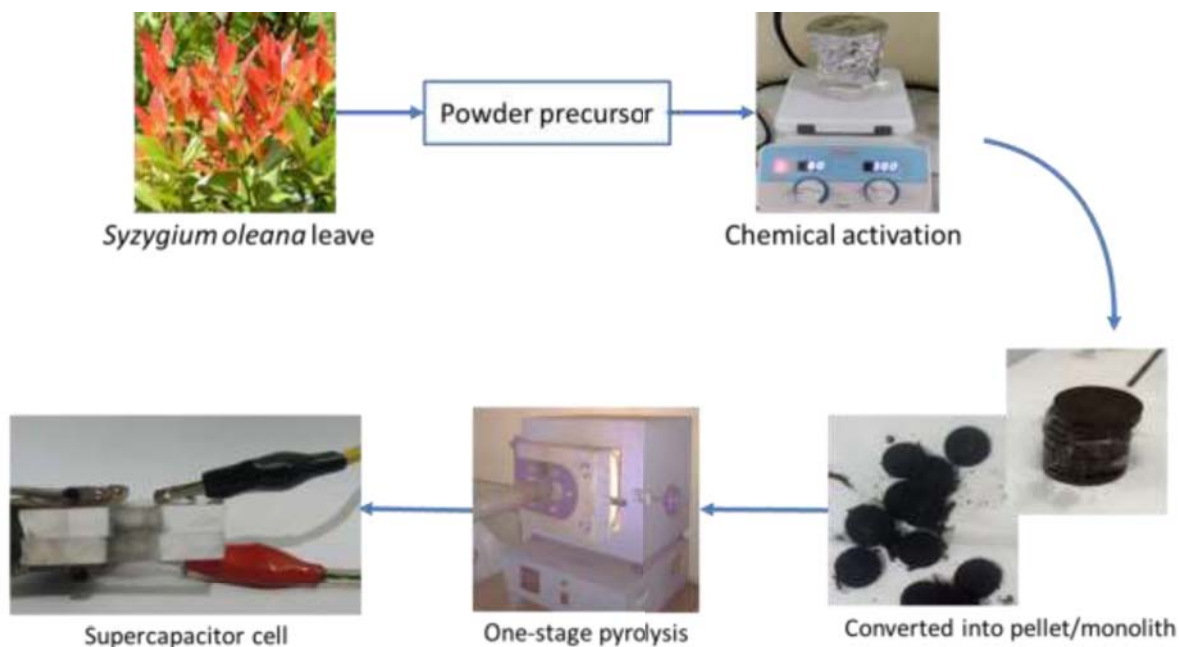
Scheme 1. Synthesis of activate carbon derived from *Syzygium oleana* leave

2.2. Characterizations

The activated carbon monoliths that have been obtained are characterized including shrinkage in mass, thickness, diameter and density of the monolith. Dimensions of 20 pellets were evaluated to determine the effect of pyrolysis on activated carbon monolith. Furthermore, the microstructural properties of activated carbon were evaluated using the X-ray diffraction method. XRD characterization was performed using a Shimadzu 7000 instrument in the range 10-60 with Cu-Kα radiation (Kα = 1.5418 Å) as the source. In addition, crystalline dimensions such as L_c and L_a are evaluated using the Scherer equation.

2.3. Electrochemical measurement

The electrochemical behavior was evaluated by using cyclic voltammetry with UR Rad-Er 5841 instrument, calibrated by VersaStat II Princeton Applied Research, an error of ±6%. The symmetric supercapacitor were arrange with coins-type consist of activated carbon electrode, separator, and electrolyte. The organic duck eggshell membrane was chosen as separator. Two aqueous electrolyte of 1 M H2SO4 and 6 M KOH was selected to improve the capacitive performance of the supercapacitor with low scanning rate of 1 mV s^{-1}. The specific capacitance, energy density, and power density were calculated by using standard equations.

3. Result and Discussion

The conversion of biomass to activated carbon through pyrolysis, including carbonization and physical activation, certainly caused a reduction in the dimensions of activated carbon monoliths including mass, diameter, and thickness. This monolith reduction is caused by the compounds and constituent elements of biomass that are decomposed and evaporated at high temperatures, especially in *Syzygium oleana* leave as shown in Figure 1. Pyrolysis process which begins with carbonization from a temperature of 30 ºC to temperatures round of 550-700 ºC using N_2 gas environment reduces the concentration oxygen to prevent agglomeration during heating. Over a temperature range of 30-200 ºC, water content is evaporated, while

chemically bound organic acids, volatile compounds, and tar are removed at 200-400 ºC [19]. Decomposition of the biomass caloric content begins in the final stage at temperatures above 350 ºC, where all adhered gases develop, and the carbon conversion process is stable [20]. This process leads to a reduction in dimensions including mass, diameter and thickness of the carbon monolith.
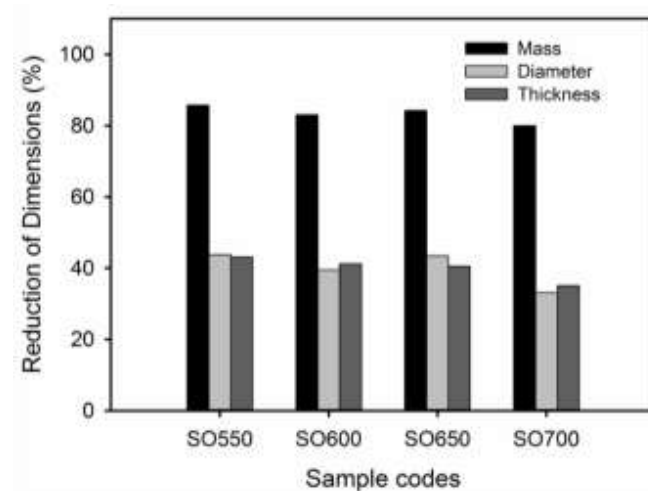

Fig. 1. Reduction of mass, diameter, and thickness

Mass showed the highest percentage reduction occurred at 83.00%, followed by thickness and diameter, respectively 39.75% and 39.50%. The addition of carbonization temperature in the range of 550 ºC to 700 ºC significantly reduced the monolithic carbon density for SO550, SO600, SO650, and SO700, respectively 21.73%, 25.40%, 19.72% and 30.56%. The importance of the carbonization process is to convert the raw material to charcoal and develop the initial pores and surface area [21]. The physicochemical properties of raw charcoal and the resulting pores are too small for practical applications. Therefore, an increase in the quality of the specific surface area and pore properties was achieved by physical activation at a high temperature of 850 ºC with a CO_2 gas environment for 2.5 hours [22]. The density of carbon monolith before pyrolysis for SO550, SO600, SO650, and SO700 was 0.8244, 0.9015, 0.9031, 0.8951 g cm^{-3} and after pyrolysis, this density was reduced to 0.6452, 0.6725, 0.7257, and 0.6215 g cm^{-3}, respectively with a mean deviation of 0.02, as shown in Figure 2.
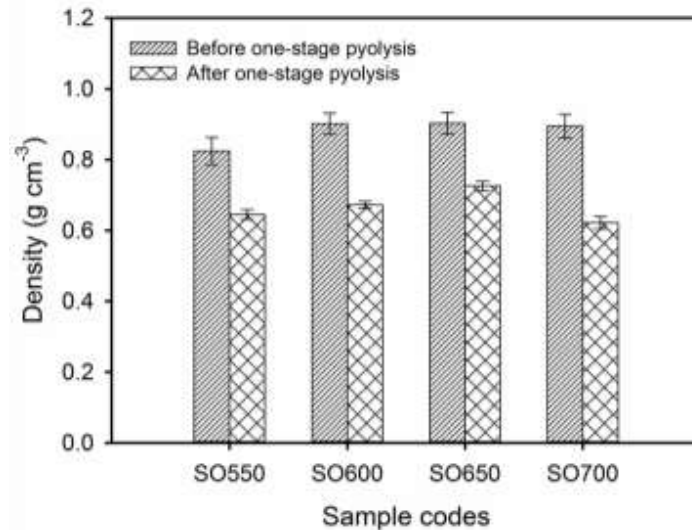
Fig. 2. Reduction in density of carbon monolith

The microstructure of activated carbon was evaluated using the X-ray diffraction method at an angle range of $2\theta=10-60^{\circ}$. The XRD patterns of SO550, SO600, SO650, and SO700 are shown in Figure 3, highlighting two strong broadening peaks at the angles of $2\theta=22-24^{\circ}$ and $2\theta=43-45^{\circ}$ corresponding to the reflection plane of (002) and (100). This indicates the good amorphous behavior of activated carbon monolith [23,24]. Furthermore, the observed sharp peaks at 26.3-27.3° for SO600, SO650, and SO700 are assigned to the graphical plane (002) according to JCPDS 00-75-2078. These results are very interesting, and clearly indicate that for thermal treatment the average formation of graphite carbon and its proportion will probably increase with increasing treatment temperature increase [25].
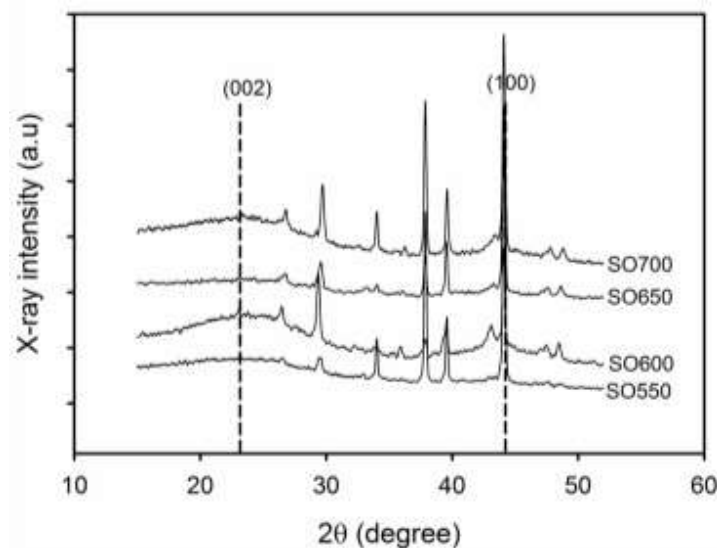

Fig 3. XRD pattern of activated electrode

Table 1. The interlayer spacing and microcrystalline dimensions of activated carbon electrodes

Monolithic Carbon	$2\theta_{002}$ (°)	$2\theta_{100}$ (°)	d_{002} (Å)	d_{100} (Å)	L_c (Å)	L_a (Å)
SO550	22.684	44.159	3.916	2.049	9.109	37.638
SO600	24.122	43.899	3.686	2.060	10.019	41.928
SO650	24.377	43.324	3.648	2.086	11.217	43.536
SO700	25.255	43.499	3.523	2.078	11.315	48.264

XRD data could be used to determine the interlayer spacing (d_{002} and d_{100}) and the microcrystalline dimensions (L_c and L_a) of activated carbon made from *Syzygium oleana* leave, as shown in Table 1. Interlayer spacing (d_{002} and d_{100}) are still in the normal range of values for activated carbon made from biomass. Microcrystalline dimensions are may related to the empirical formula for the surface area of carbon, specifically the L_c value [26,27]. Based on several reported it could be found that the SO550 sample has the largest surface area, contributing to improving the capacitive properties of the supercapacitor electrode.

Cyclic voltammetry is a technique that is always used to evaluate the electrochemical properties of symmetric supercapacitors. The electrochemical properties of activated carbon monolith made from *Syzygium oleana* leave were evaluated using two-electrode systems on the 1 M H_2SO_4 aqueous electrolyte. At the relatively low scan rate of 1 mV s^{-1}, all CV curves show a distorted rectangular shape, confirming the normal double electric layer nature of the supercapacitor [28,29]. Furthermore, it is well known that the specific capacitance is proportional to the area of the CV curve in the low scanning rate. We can see from Figure 4a that the capacitance for this sample decreases in the order SO550, SO600, SO650, and SO700. The highest specific capacitance was found in the sample SO550 of 153 F g^{-1} followed by SO600, SO650, and SO700 are 119 F g^{-1}, 108 F g^{-1}, and 99 F g^{-1}, respectively. The carbonization temperature significantly affects the specific capacitance of the supercapacitor. Increasing the temperature carbonization from 550 ºC to 700 ºC reduces the specific capacitance as high as 35.29%. This may be due to the combined action of surface area, pore size distribution, and surface functional groups of the sample [30]. Furthermore, the CV SO550 curve shows the ideal capacitor rectangular shape, which is attributed to the good ion diffusion rate in the pores of the carbon electrode and confirms the ideal electric double layer properties. This was due to a good combination of pore structures for the EDLC-type supercapacitor [5,31]. The results of this study proved that the porous carbon obtained better capacitance characteristics. Moreover, Figure 4b shows the specific capacitance at different scanning rates in the range of 1 to 10 mV s^{-1}. As the scanning rate increases, the specific capacitance is reduced dramatically, due to enough time for electrolyte ions to move into the available pores and an increase in redox reaction in the outer surface of the electrode carbon monolith [32]. Based on the standard equation [31,33], the highest specific energy and specific power are 21.25 Wh kg^{-1} and 76.57 W kg^{-1}, respectively. This result is almost the same as several previous studies from different raw materials such as sakura flower [12], bamboo [34], and mangosteen [10].
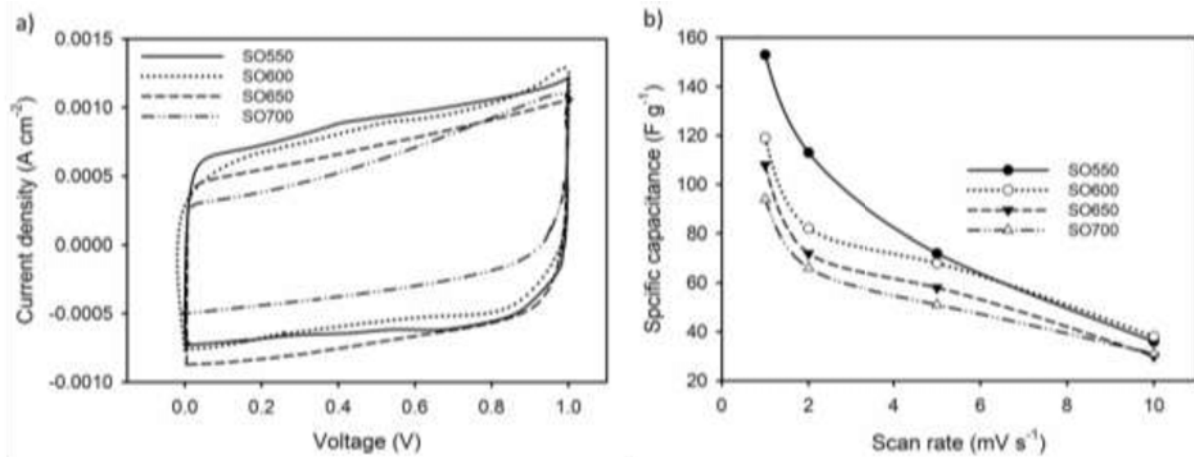
Fig 4. (a) The CV curve of the supercapacitor cell, and (b) The specific capacitance of carbon electrode at different scan rates

To improve the supercapacitor performance, two different electrolytes were applied to the SO550 activated carbon electrode including 1 M H_2SO_4 and 6 M KOH, as shown in Figure 5a. The CV curve still retains a rectangular shape for both electrolytes, confirming the strong double layer electric properties of the supercapacitor. The 1 M H_2SO_4 electrolyte still showed a large CV curve area compared to 6 M KOH, indicating that the highest specific capacitance was found in the H_2SO_4 electrolyte of 153 F g^{-1} while the 6 M KOH electrolyte had a specific capacitance of 103 F g^{-1}. This is due to the H_2SO_4 acid electrolyte which is considered to have an ion diameter that is more suitable for diffusion to the pores of biomass-based activated carbon compared to KOH which is a base electrolyte. As has been widely reported, the differences observed in the CV curves of the carbon monolith electrode in different electrolytes stem from the different ionic physical properties of these different electrolytes. Some of these properties include ionic radius, a spherical radius of ionic hydration, molar conductivity, and ionic mobility. Furthermore, scanning rates varying from 1 to 10 mV s^{-1} were also carried out to determine the capacitive resistance of the supercapacitor carbon electrode. Figure 4b shows the capacitance curve specific to the scan rate. The specific capacitance was reduced from 153 F g^{-1} to 38 F g^{-1} for the H_2SO_4 electrolyte and from 103 to 28 F g^{-1} for the 6 M KOH electrolyte at 10 mV s^{-1}. This may be due to sufficient time for the electrolyte ions to move to the available pores and an increase in redox reactions on the outer surface of the carbon monolith electrode [21]. Interestingly, the specific capacitance generated from the 6 M KOH electrolyte is more stable than the H_2SO_4 at high scanning rates which is shown in Figure 5b. The 6 M KOH electrolyte could maintain a specific capacitance of around 72.81% compared to 1 M H_2SO_4 of around 75.16%.
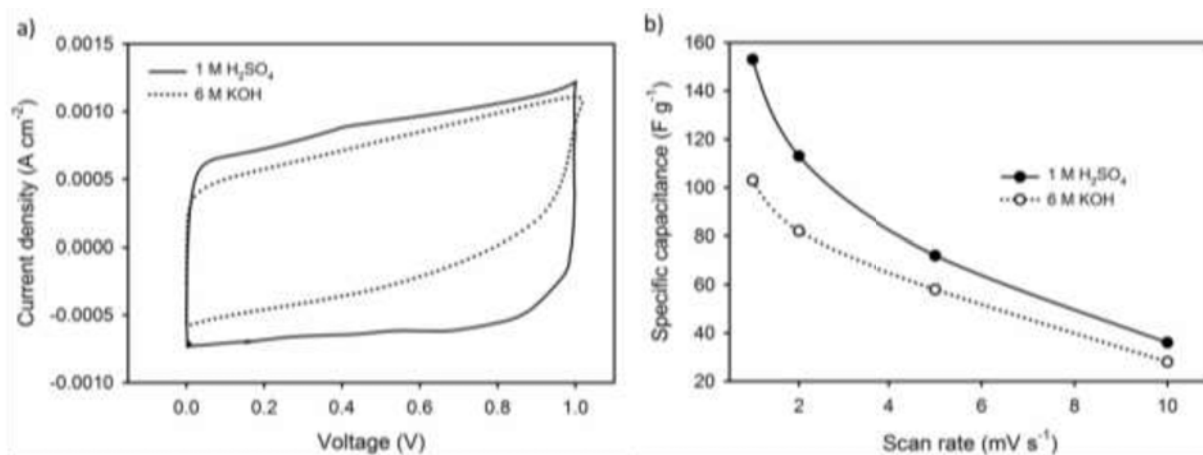
Fig. 5. (a) CV curve, and (b) The specific capacitance of carbon electrode at different scan rates of monolith carbon electrode with H_2SO_4 and KOH electrolyte

4. Conclusion

In this study, the activated carbon monolith was synthesized from *Syzygium oleana* leaves trough carbonization and activation for supercapacitor application. The different carbonization temperature has been effected the carbon electrode. In general, monolithic activated carbon shows good amorphous behavior, confirmed by X-ray diffraction method. Furthermore, Monolith activated carbon SO550 has a maximum specific capacitance of 153 F g^{-1} in a 1 M H_2SO_4 based electrolyte and 103 F g^{-1} in a 6 M KOH electrolyte, both determined at a low scan rate of 1 mV s^{-1}. On the other hand, 6 M KOH electrolytes can maintain a greater specific capacitance as high as 72.16% compared to 1 M H_2SO_4 electrolyte. In summary, this study suggests that monolithic activated carbon derived from *Syzygium oleana* leaves could be a promising low-cost and environmentally friendly material for supercapacitor electrode applications.

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