The Effects of Different Activation Agents on the Physical and Electrochemical Properties of Carbon Electrodes Produced from Banana Stem Fiber

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Abstract. This study focuses on the effects of chemical activation materials on the physical and electrochemical properties of carbon electrodes made from banana stem fiber. The carbon electrodes were activated with different activators such as KOH, NaOH and $ZnCl_2$ at a constant concentration of 0.5 M. Also, the electrodes were carbonized at a temperature of 550˚C followed by a physical activation process using CO_2 at 900˚C for 2.5 hour, after which the density, surface morphology, element contents, degree of crystallinity and surface area of carbon electrodes were analyzed. In general, the activator used determines both the physical and electrochemical properties of the electrodes. Also, activating materials have the capacity to improve the physical properties of the samples as well as increase its specific capacitance. According to this research, AC-$ZnCl_2$ shows better physical and electrochemical properties having a specific capacitance as high as 130 F g^{-1}.

1. Introduction

Banana is one of the most popular fruits in the community because it is relatively cheap, high in nutritional value and abundantly available in both traditional and modern markets. These make it an important fruit for consumption as well as raw materials in food companies. The increase in the production of banana, especially in Indonesia, has significantly increased the quantity of wastes from its stems to about 100 times. Also, banana production in 2019 is estimated to reach 7,907,545 tons, hence, the wastes from its stem could be around 790,754,500 tons/year [1]. Banana stem, which is the major waste, has a chemical constituents made up of 35.3% cellulose and 6% lignin [2]. The cellulose content impact on the carbon biomass, as the higher the cellulose content, the more carbon biomass it produces. This carbon biomass is the original material with the potential to be used as an electrode for supercapacitor cells as previously investigated, with similar original materials from cassava [3], banana peels [4], bagasse [5], remains of paper [6], and banana stems [7]. Previous researchers have worked on the utilization of carbon biomass from banana stems waste as a supercapacitor device. According to some of these studies, wastes from its stem were used by observing variations in the concentration of KOH activator [8] and variations in the temperature during physical activation [7]. The aim of this activation process was to improve the pore structure where impurities found in carbon electrodes will be removed thereby forming new pores. Then, these are expected to become ordinary pore structures which could increase the surface area of the electrodes thereby improving the cell

performance of the supercapacitors [9]. Specific capacitances obtained were 170 F g^{-1} [8] and 104 F g^{-1} [7] for optimal conditions of 0.5 M KOH and physical activation temperature of 900˚C, while the physical properties of carbon electrodes gave fibers to the electrode surface [7, 8]. The optimal conditions from previous studies will be used in this study, which are: (i) a concentration of 0.5 M KOH and (ii) physical activation of the carbon material at 900°C, without the addition of adhesives. The purpose of selecting these conditions is to obtain supercapacitor cells with good physical and electrochemical properties.

2. Research Methods

2.1. Carbon Electrode Preparation

The carbon electrodes were prepared from the fibers obtained from the banana stem. It was then sundried for 2 days, followed by oven drying for 48 hours. The dried samples were pre-carbonized for 150 minutes from room temperature to 250˚C in an oven, then grinded using the mortar and ball milled for 20 hours till the sample became powder. This was sieved to obtain a homogeneous particle size of 52 - 39 micrometers. The sample was then activated using different chemical activators such as KOH, NaOH, and $ZnCl_2$ at a constant concentration of 0.5 M. The activated sample was dried in the oven for 48 hours and then converted into pellet shapes using an hydraulic press at a pressure of 10 tons. The pyrolysis process, carbonization as well as the physical activation were carried out in an integrated stage. The carbonization process was initiated at room temperature using N_2 gas till it reached a temperature of 550˚C, followed by physical activation using CO_2 gas at 900˚C [10,11]. The activated carbon electrodes were washed in distilled water till it became neutral. Finally, the supercapacitor cell was prepared in the form of sandwich having components such as Teflon, which acts as a support, carbon electrodes, stainless steel as current collector, separator from the duck egg membrane [12], and 1 M H_2SO_4 as electrolytes.

2.2. Physical Characteristics

The physical properties of carbon electrodes which include its density and degree of crystallinity were subjected to X-ray Diffraction (XRD), the surface morphology and chemical composition were checked through Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS), and the specific surface area was measured using the BET method. The density was analyzed by determining the mass, thickness, and diameter of the pellets. XRD characterization was analyzed using the XRD 7000 SHIMADZU instrument with a wavelength of 1.5418 Å. SEM and EDS were analyzed using the JEOL-JSM 6510 LA instrument while BET was analyzed using the Quantachrome Nova Win version 11.0.

2.3. Electrochemical Characterization

The electrochemical properties of the carbon electrodes made from the banana stem fiber were reviewed using the Cyclic Voltammetry (CV) method. This was carried out to determine the electrode specific capacitance of supercapacitor cells. The instrument used was the Physics CV UR Rad-Er 5481 scan rate of 1 mV s^{-1} and a potential difference of 0.5 V.

3. Discussion

3.1. Density Analysis

The average density of activated carbon electrodes using various activating materials such as KOH, NaOH, and $ZnCl_2$ are shown in Figure 1. The results showed that the density decreased before and after the carbonization process, in which the greatest was seen in the AC-$ZnCl_2$ sample of 0.267 g cm^{-3} while the smallest reduction in density occurred in the AC-NaOH sample of 0.149 g cm^{-3}. There was

also decrease in density in other studies conducted with different biomass materials such as carbon electrodes made from sago waste [13]. The largest decrease in density was found in the samples activated with $ZnCl_2$. The decrease in density is caused through volume shrinking when the carbonization process, where the element contained in the electrode other than carbon and water are reduced. This results in the rearrangement of electrode component, especially after more carbon is formed, resulting in a decreasing in the electrode density [14].

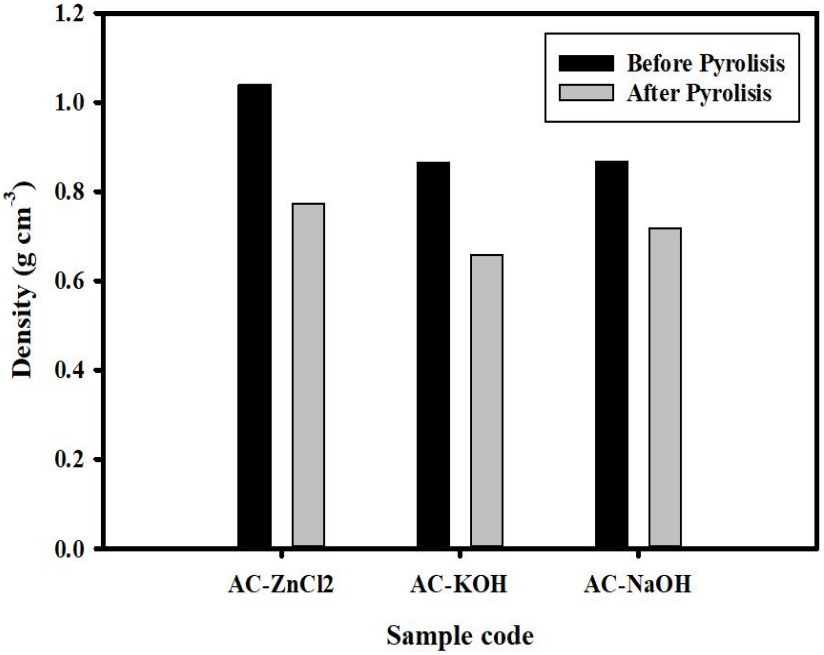

Figure 1. Diagram of the density of activated carbon electrodes

3.2. Surface Morphology Analysis

Figure 2 shows the surface morphology of the AC-$ZnCl_2$, AC-KOH, AC-NaOH samples where figures 2 (a), (c), and (e) are the SEM micrographs at 5000 X magnification, while 2 (b), (d), and (f) are SEM micrograph at 40000 X magnification. Also, figures 2 (a), (c), and (e) show the diversity of the surface appearance of each sample. Figure 2 (a) shows the surface of the AC-$ZnCl_2$ electrode, which is almost similar with (c), however, with relatively more fine fiber. The carbon fiber looks elongated with an average diameter of 1.0875 µm. Figure 2 (c) shows the presence of fine fibers between the chunks of carbon particles. A fine fiber looks very small with a diameter of 2.56 µm while the rest are part of the surface of shiny particles assumed to be the fracture part of carbon particles. Actually, there is fiber on the surface of the broken particle, but could not show because the preparation of samples for SEM was through cross-sectional fracture. Figure 2 (e) shows the surface of the AC-NaOH electrode with the surface of the micrograph electrode containing fine fibers and carbon particles with an average length of 4.49 µm and an average diameter of 4.73 µm. Then, NaOH as the activating material enters the fiber cracks binding to cellulose to produce hydrogen bond between the cellulose being broken so that it decreases. This is because the cellulose which binds to the fiber has a free hydroxide group as well as a very strong affinity for polar solvents. Figures 2 (b), (d), and (f) are the magnifications of 2 (a), (c), and (e) especially in the section marked with a blue rectangle. Figures (b), (d), and (f) are at much larger magnification and the selected part is shown clearly with the area photographed at 7.485 μm^2. This magnified micrograph image display presents the shape and amount of fiber which are much

clearer in the AC-$ZnCl_2$, AC-KOH, and AC-NaOH samples such that the calculation results and nano fibers are more accurate with an average diameter of 300 nm, 980 nm, 633 nm. There was a previous research work in which the biomass materials of banana stems had a diameter of 131 nm for KOH samples [7].

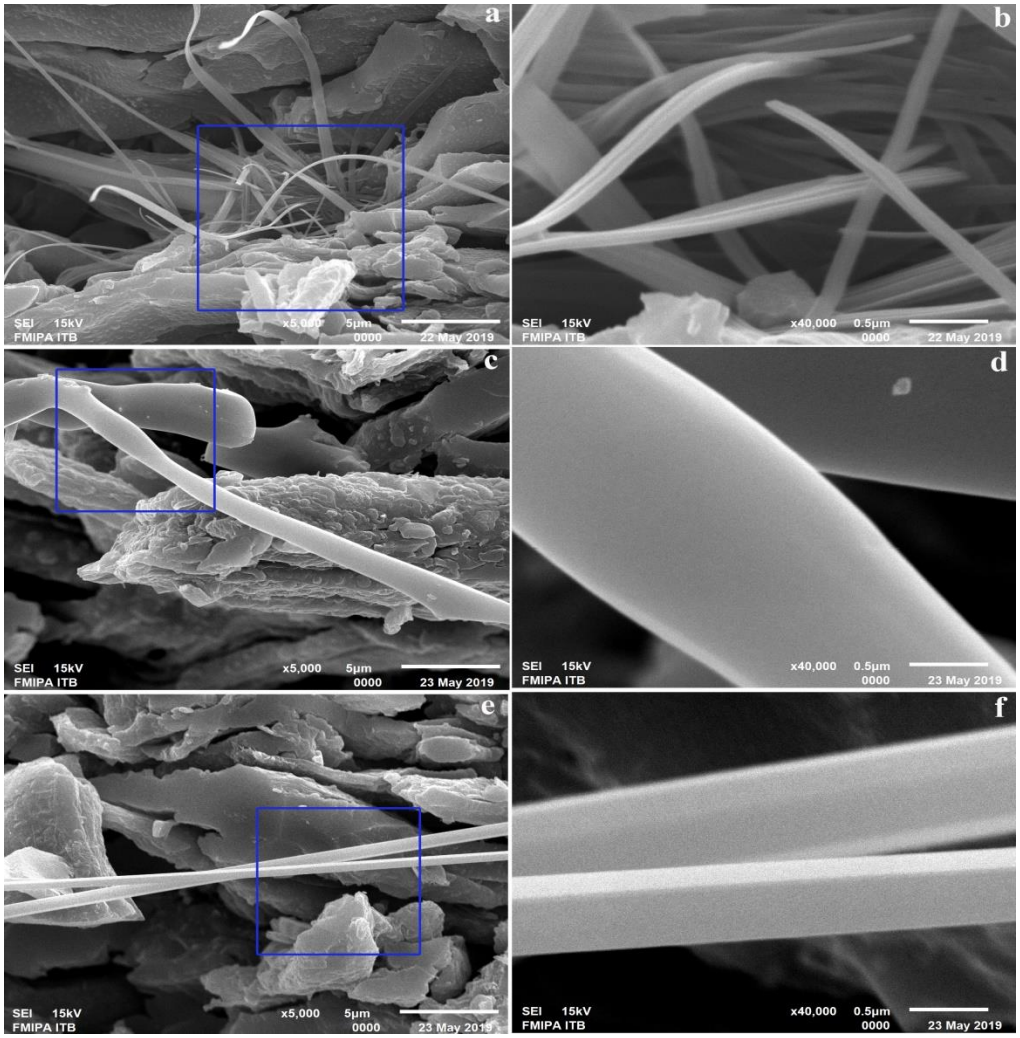

Figure 2. The results of SEM characterization of AC-$ZnCl_2$, AC-KOH, and AC-NaOH samples at 5000 X magnification shown by (a), (c), and (e), while a magnification of 40000 X was used in (b), (d), and (f).

3.3. Chemical Composition Analysis

The Energy Dispersive Spectroscopy (EDS) analysis was conducted to determine the elemental constituents of the activated carbon sample. Based on the results, carbon element was found more than other elements in the samples. The highest carbon content in the AC-$ZnCl_2$ sample was 96.16% and oxygen was present in AC-$ZnCl_2$, AC-KOH, and AC-NaOH samples at 2.90%, 6.15%, 7.36% respectively. These results were predicted to arise in a research due to the oxygen content present at the time of carbonization or the presence of chemical bonds during the physical activation process [15]. There are other basic components of the AC-$ZnCl_2$, AC-KOH, and AC-NaOH samples, namely, potassium (K) present at 0.93%, 2.84% and 1.68%, respectively. The percentage of the chemical composition of each activated carbon electrode samples are shown in Table 1.

Table 1. Percentage of the composition of surface constituents contained in banana stem fiber electrodes

Element content	Sample codes AC-$ZnCl_2$ Atom (%)	AC-KOH Atom (%)	AC-NaOH Atom (%)
Carbon	96.16	91	90.95
Oxigen	2.90	6.15	7.36
Silicon	-	-	-
Potassium	0.93	2.84	1.68
Calcium	-	-	-
Sodium	-	-	-
Totals		100%	

3.4. Analysis of the Degree of Crystallinity

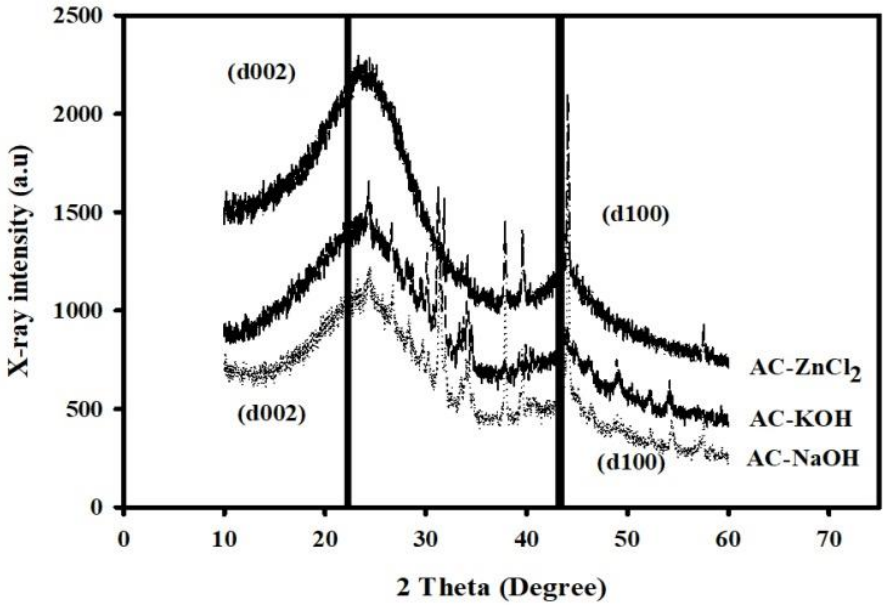

Figure 3. X-ray diffraction (XRD) pattern from banana stem fiber electrodes

Figure 3 shows an XRD pattern with a relationship between the intensity of X-rays and scattering angles (2Θ) of banana stem fiber electrodes. The characterization results show that there are 2 broad peaks in which each is located in a different hkl plane, correlated with 002 and 100 planes. The broad peaks in the scattering plane (002) and (100) with scattering angles of 22° - 24° and 42° - 45° indicate that the activated carbon electrodes from banana stem fibers are amorphous in structure. Also, the AC-$ZnCl_2$, AC-KOH, and AC-NaOH samples have peaks related to each scattering: plane (002) are 23.466°, 22.724°, and 22.540° while plane (100) are 45.297°, 44.629° and 44.079°, in which both planes generated peak values [16]. Figure 3 also shows a sharp peak at a 44.065° for AC-$ZnCl_2$ and 44.079° for AC-NaOH samples. This is an indication that silica (SiO_2) elements are present in the AC-$ZnCl_2$ and AC-NaOH samples.

Table 2. Data on the results of lattice parameters from banana stem fiber electrodes

Sample codes	$2\theta_{(002)}$ (^{0})	$2\theta_{(100)}$ (^{0})	$d_{(002)}$ (Å)	$d_{(100)}$ (Å)	Lc (Å)	La (Å)
AC-$ZnCl_2$	23.466	45.297	3.788	2.000	8.006	7.968
AC-KOH	22.724	44.629	3.910	2.028	8.509	3.695
AC-NaOH	22.540	44.079	3.941	2.053	13.918	22.973

3.5. Surface Area Analysis

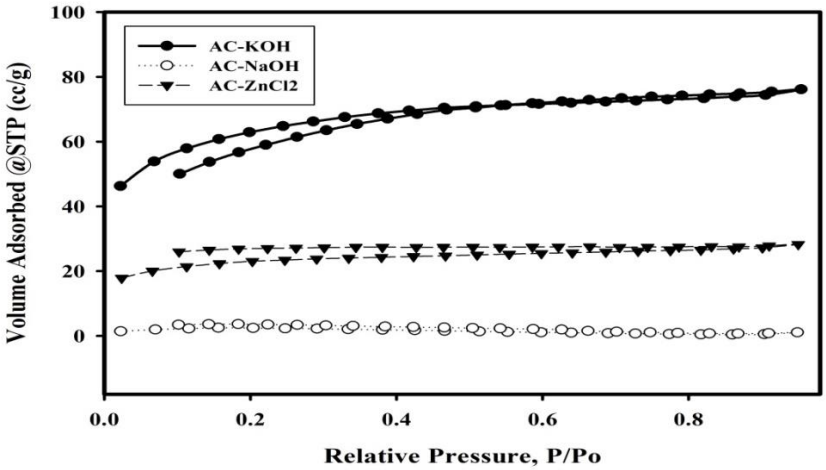

Figure 4. Isothermal curve adsorption and desorption of N_2 gas as a result of BET characterization of banana stem fiber electrodes

A temperature of 77.35 K was used to analyses N_2 gas absorption by displaying an isothermal curve between the relative pressure (P P_0^{-1}) and the volume at STP (cc g^{-1}) as shown in Figure 4. The N_2 gas increases with increasing relative pressure (P P_0^{-1}) given for each of the AC-$ZnCl_2$, AC-KOH, and AC-NaOH samples. Based on the IUPAC pore size type, Figure 4 is an isothermal curve with type IV for all samples considering the fact that the pore sizes are greater than 2 nm and it is a mesopore [16]. The isothermal curve of the N_2 gas adsorption process were found at relative pressure (P P_0^{-1}) of 0.1 to 0.9 and the desorption process with a relative pressure of 0.9 to 0.2. The highest N_2 gas absorption was in the AC-KOH sample at 45 cc g^{-1} and the lowest was in AC-NaOH sample at 3 cc g^{-1}. The isothermal curve in the AC-$ZnCl_2$ sample shows a hysteresis form at a relative pressure of 0.6. The surface area of each sample can be predicted from the figure, in which AC-$ZnCl_2$ sample has the highest surface area followed by AC-KOH and finally AC-NaOH sample.

3.6. Analysis of Cyclic Voltammetry Measurement

Table 3. Specific capacitance of activated carbon electrodes from banana stem fibers with a scan rate of 1 mV s^{-1}, voltage 0.5 V

Sample codes	Mass (g)	I_c (A)	I_d (A)	C_{sp} (F g^{-1})
AC-$ZnCl_2$	0.00525	0.000474	-0.00021	129.714
AC-KOH	0.0103	0.000745	0.000127	60
AC-NaOH	0.0095	0.000103	-0.000093	20.631

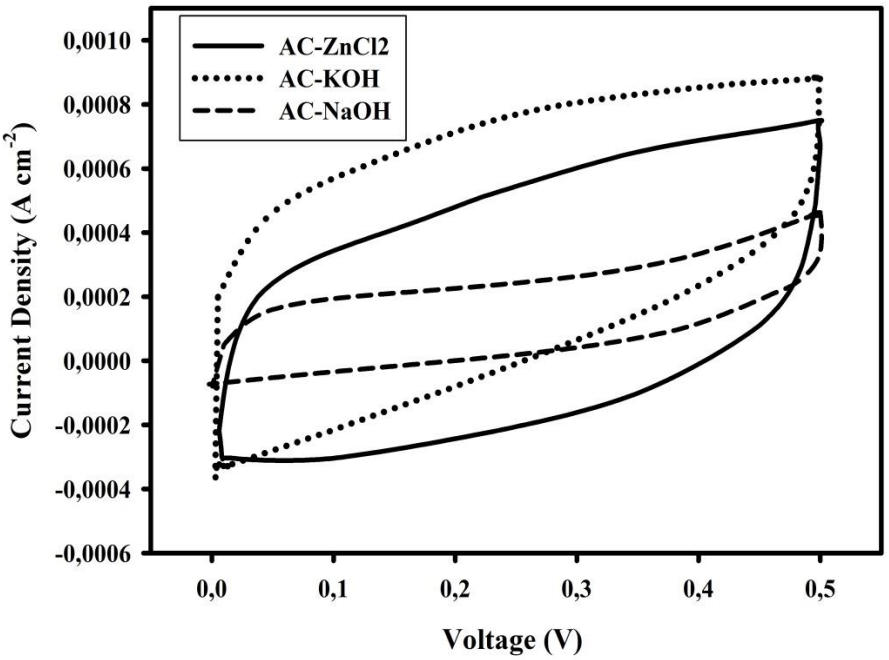

Figure 5. Cyclic voltammetry curve from banana stem fiber electrode with scan rate of 1 mV s^{-1}, voltage 0.5 V

The specific capacitance obtained in cyclic voltammetry measurements is displayed in the form of a curve shown in Figure 5. The specific capacitance produced can be seen from the width of the region (I_c-I_d) or the amount of current density. This shows that AC-$ZnCl_2$ sample has a larger area (I_c-I_d) compared with AC-KOH and AC-NaOH. The wider the current charge and discharge area, the greater the capacitance produced. This is because carbonization-activation process produces many pores, such that when more ions are stored in the electrode, its produces higher capacitance [17]. Based on the findings, the AC-$ZnCl_2$ electrode has a specific capacitance of 129,714 F g^{-1} which is the highest. This is in line with another study which found a capacitance of 103.4 F g^{-1}, 144 F g^{-1}, and 156 F g^{-1} for durian shell [18], hemp [19], and coffee shell [20]. The details of mass I_c-I_d and specific capacitance for all samples are shown in Table 3 and the active material used during the chemical activation process determines what is produced as the specific capacitance. The results from this study found $ZnCl_2$ as the most suitable activating material with carbon electrodes.

4. Conclusion

This study analysed the physical and electrochemical properties of activated carbon electrodes made from banana stem fibers. The activated carbon electrodes were made using various activating materials such as KOH, NaOH and $ZnCl_2$. However, the specific type of activator used is what determines the physical and electrochemical properties of the electrodes. Aside that, good activators have the capacity of improved the physical properties of the sample and also increase its specific capacitance. Hence, findings from this study showed that AC-$ZnCl_2$ have better physical and electrochemical properties considering the fact that it has a specific capacitance as high as 130 F g^{-1}.

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