Fabrication of Carbon Electrodes from Sago Midrib Biomass with Chemical Variation for Supercapacitor Cell Application

Rakhmawati Farma, Syarifah F Emera Maulani, Irma Apriyani, Awitdrus, Yanuar, Ari Sulisty Rini
Department of Physics, University of Riau, 28293 Simpang Baru, Riau, Indonesia
rakhmawati.farma@lecturer.unri.ac.id

Abstract. Activated carbon with high porosity and controlled pores structure are widely applied as supercapacitor electrodes biomass derived from sago midrib (PS). Activated carbon based on sago midrib without chemical agent and using chemical agent ZnCl₂ and NaOH by a concentration 0.5 M has been fabricated with a purpose to produce distribution of mesopores and micropores. Samples were carbonized at temperature 600℃ using N₂ gas followed by a physical activation process using CO₂ gas at temperature of 700℃. The highest mass loss percentage of carbon electrode PS-ZnCl₂ was 51.6% Microstructure analysis shows that amorphous structure for the activated carbon electrodes is shown by the presence of the peaks of 2θ around 24° and 44° with the highest Lc presented by ZnCl₂. SEM characterization showed the domination of mesopores and a few of micropores presented by ZnCl₂. EDX characterization showed the highest atomic carbon percentage is 90.27%. Specific capacitance was determined by cyclic voltammetry method and found the highest in PS-ZnCl₂ was 138 F/g. The result from the physical and chemical properties, ZnCl₂ is the best chemical agent from biomass-derived sago midrib for the best performance of supercapacitor cells.

1. Introduction
Sago plant is one of palmae types that grows and develops in Indonesia especially in Riau Island. This plant, which is also widely found in Malaysia and Singapore, is a plant that can grow well in freshwater marshes, lowlands and tropical rain forests [1]. Sago midrib is part of sago plant that contain cellulose by 68.42% , hemicellulose by 2.81% and lignin 3.84% [2] where the compiling element of this lignocellulose is a carbon that can be turned into activated carbon as a material of super capacitor cell electrodes that function as an energy storage devices.

Supercapacitor is special capacitors that have greater capacitance value that unites the character of the battery and capacitor into one device. The existence of supercapacitors has shown the potential for improvement in energy storage systems. The relatively faster charging time of supercapacitors makes it surpassing than batteries and conventional capacitors also eco-friendly [3]. One of the things that affect to value of the supercapacitor’s capacitance is the electrode material, this is because characteristics of the electrode’s surface would affect the capacitance supercapacitor cell. In EDLC there is also an electrolyte which is an important component where the cell voltage that can be achieved from the supercapacitor depends on the breakdown voltage of the electrolyte. EDLC also
consists of a current collector and a separator. The current collector is useful for capturing ions while the separator will prevent electrical contact between the two electrodes [4].

The electrode is the most influential part of the supercapacitor. The type and characteristic of the material of an electrode will affect the performance and storage capacity of a supercapacitor. The types of electrodes based on the material of manufacture are divided into four types, there are activated carbon, metal oxides, polymers and graphene. Activated carbon is a suitable material in the manufacture of electrodes due to its high porosity, good conductivity, thermal stability and the ease and availability of materials [4]. Activated carbon with biomass-based that has been used as material for electrodes such as oil palm empty fruit bunch [5], Wisteria Sinensis seeds [6], Palash trees [7], argan shells [8] and tea waste [9].

The manufacture of supercapacitor electrodes with variations of chemical activators has been carried out by researchers Chiu et al (2019) with variations of NaOH and ZnCl2 activators obtaining specific capacitance values of 69.5 F/g and 72.9 F/g, respectively. This study focuses on the fabrication of activated carbon made from sago midrib with variations without chemical activating agents and variations with chemical activating agents ZnCl2 and NaOH for applications as supercapacitor cell carbon electrodes. Variations with chemical activating agents show characteristic dehydrogenation which will make tar slowly formed and evaporate volatile compounds so that it will produce a carbon structure with better pores than carbon electrode pores without a chemical activation process [11].

2. Method and Characterization

Sago Midrib as the basic material for making carbon electrodes is synthesized through a pre-carbonization process, chemical activation with a variety of chemical activating agents ZnCl2, NaOH and without chemical activating agents which is to remove lignocellulose compounds and open the pores of activated carbon. Pre-carbonization was carried out at 200°C for 1 hour to produce a self-adhesive carbon powder. The next process is chemical activation using a hot plate and magnetic stirrer for 2 hours at 80°C. Carbon powder is changed into monolith or pellet using a hydraulic press with a pressure of 7 tons. The pyrolysis process is carried out in an manner in the furnace. The carbonization process uses a temperature of 600°C with nitrogen gas flowing at heating rate of 3°C/min for 1 hour and the physical activation process was carried out using a temperature of 700°C with carbon dioxide gas flowing at heating rate of 10°C/min for 2.5 hour. Furthermore, the carbon electrodes were neutralized using aquades until the pH of the residual water became neutral (pH=7) and dried using an oven at 110°C for 24 hours.

Characterization of physical in carbon electrodes consists of X-Ray Diffraction which was carried out to determine the crystallinity of carbon electrodes using the XRD Shimadzu 700 instrument with a scattering angle of 2θ using a Cu k-α light source and wavelength is 1.5418 Å. SEM-EDX characterization was was performed to determine the shape and surface morphology and also composition of the sample using the JEOL JSM-6510 LA. The characterization of electrochemical properties of supercapacitor cells was carried out with cyclic voltammetry method. This was carried out with CV UR Rad-Far 5841, where the supercapacitor cell component consisted of PS carbon electrodes, current collector, separator and H2SO4 electrolyte. Specific capacitance is measured from potential 0 to 1000 mV with scan rates of 1 mV/s, 2 mV/s, and 5 mV/s, which will produce current density relation curve and the voltage.

3. Results and Discussions

3.1 The Result of Measurement Density

The density measurement of carbon electrode carried out before and after the carbonization-physical activation process which aims to estimate the value of the specific capacitance of the carbon electrode. Figure 1 shows the decrease of density that occurs during the carbonization-physical activation process, impurity elements besides carbon and water content will disappear so that shrinkage occurs...
and the carbon electrode forming pores. The physical activation process can also trigger the decrease of the density. This result is caused by the formation of new pores and the evaporation of CO₂ gas causing the existing pores to open [12].

**Figure 1.** The Chart of The Density Comparison of PS with Chemical Activator Variations

Figure 2 shows the decrease of density percentage on PS-TA, PS-ZnCl₂, and PS-NaOH carbon electrodes after the pyrolysis process is 17.3 %, 51.6 % and 23.3 % respectively. PS-ZnCl₂ has the highest density percentage shrinkage of carbon electrodes, this result happens during the chemical activation process, ZnCl₂ afford to inhibit tar formation and encourage aromatization to produce a porous activated carbon product [13]. NaOH can increase the surface area, this is due to the ability of sodium metal to intercalate into the porous material structure so the number of pores increase on the carbon electrode and result in a fairly high density decrease [14]. Without a chemical activation process, pores will only be formed during the physical activation process, so the formation of pores becomes less than optimal. Carbon electrodes with many pores result in a greater decrease in density and will increase the specific capacitance value.

**Figure 2.** The Chart of Carbon Electrode Density Loss Percentage PS
3.2 X-Ray Diffraction Analysis

X-ray diffraction (XRD) is an analytical method that utilizes the interaction between x-rays and atoms arranged in a crystal system which aims to determine the microstructure of activated carbon electrodes. Figure 3 shows that each sample of sago midrib has two wide peaks at an angle of 2θ about 24° and 44° where the peak width indicating the carbon material that corresponds to the orientation of the (002) and (100) plane respectively. The X-ray diffraction pattern of the activated carbon electrode indicates the sago midrib carbon electrode is amorphous consisting of carbon atoms [5].

![Figure 3. X-Ray Diffraction Pattern of Carbon Electrodes PS](image)

Based on JCPDS (Joint Committee on Powder Diffraction Standard) data, there are sharp peaks at 2θ around 29°, 36°, 39°, 43°, 47° and 48°, indicating the presence of calcium carbonate (CaCO₃) compounds, whereas at 2θ around 12°, 22°, 25°, 31°, 34°, 47°, 49°, 56° and 57° indicated the presence of zinc oxide (ZnO) compounds. The sharp peaks at 2θ around 36° and 39° indicated the presence of silica or silicon dioxide (SiO₂) compounds. ZnO crystals consisting of O₂ can improve the performance of supercapacitors because several types of heteroatoms such as N, O, S and P can contribute to the pseudo-capacitance properties [15].

| Sample Code | 2θ (002) | 2θ (100) | d₀₀₂ (Å) | d₁₀₀ (Å) | Lᵣ (Å) | Lₓ (Å) | Lₓ / Lᵣ | Nₚ |
|-------------|----------|----------|----------|----------|--------|--------|---------|-----|
| PS-TA       | 24,254   | 44,539   | 3,666    | 2,032    | 14,321 | 8,453  | 0,590   | 2,305|
| PS-ZnCl₂    | 22,946   | 44,884   | 3,872    | 2,017    | 10,607 | 20,066 | 1,891   | 5,181|
| PS-NaOH     | 25,030   | 45,638   | 3,554    | 1,986    | 12,812 | 9,506  | 0,741   | 2,674|

The utilization of ZnCl₂ activating agent would increase the surface area due to the much numbers of good pore structures (micropores and mesopores) spread on the carbon electrodes. The chemical ZnCl₂ acts as a dehydrating agent and produces carbon electrodes with a porous structure. ZnCl₂
would catalyze the polymerization reaction between aromatic hydrocarbons and tar-forming compounds so during the carbonization process, large molecules in the polycyclic compound would evaporate and produce porous carbon electrodes [16]. The utilization of ZnCl\(_2\) activating agent causes the changes in the L\(_c\)/L\(_a\) ratio and related to the surface area. According to[17] L\(_c\)/L\(_a\) ratio are comparable to the surface area of the carbon electrode, so the higher of L\(_c\)/L\(_a\) ratio obtained, the higher the surface area of the carbon electrode. PS-ZnCl\(_2\) has the highest L\(_c\)/L\(_a\) ratio of 1.891 which indicates that the PS-ZnCl\(_2\) sample has the largest surface area compared to the other samples.

3.3 Surface Morphology Analysis

Figure 4. The SEM Images of Electrode with Magnification of 5000x (A) PS-TA, (B) PS- ZnCl\(_2\) (C) PS-Naoh, The SEM Images of Electrodes with Magnification of 40,000x (D) PS-TA, (E) PS- ZnCl\(_2\), And (F) PS-Naoh.

Figure 4 shows the scanning electron microscopy results of the surface morphology of PS carbon electrodes on different chemical activators. The magnification of the activated carbon sample of sago midrib biomass is shown in Figure 4 (a, b, c) with a low resolution magnification of 5, while Figure 4 (d, e, f) with a high resolution magnification of 0.5. PS-TA shows the shape of aggregates or wad of different sizes. This happens because chemical activators shows dehydrogenation properties which will inhibit the formation of tar and evaporate volatile compounds and samples produce a carbon structure with pores that are better than the pores of samples without a chemical activation process [10]. PS-ZnCl\(_2\) shows a mesoporous and a fiber rod-like and it can increase the number of micropores. These results occur due to the impregnation reaction of ZnCl\(_2\) which can form ZnOCl and it can reduce the pore width so the carbon electrodes produce microporous which causes the large surface area of the carbon electrode [18]. PS-NaOH is dominated by macropores and mesopores caused by a chemical activation process using NaOH activator so the carbon will react with NaOH and produce CO\(_2\). CO\(_2\) production would diffuse also corrodes the carbon wall and forms new pores so the pores will be wide open [19]. Macropores can facilitate the electrolyte access but it don't contribute the increase of the specific capacitance. Mesopores can increase the speed and facilitate the ion diffusion and movement from the electrolyte. Micropores can store ions in the electrode so it will increase the specific capacitance [20].
3.4 The Chemical Composition Analysis

EDX characterization is used to determine the content of chemical elements contained in PS carbon electrodes. The carbon electrodes PS have a percentage of chemical elements such as Carbon (C), Oxygen (O2), Silica (Si), Calcium (Ca), Magnesium (Mg), Chlorine (Cl), Zinc (Zn) and Sodium (Na). Table 2 presents the elemental analysis of the synthesized of PS-TA, PS-ZnCl2, PS-NaOH samples. The amount of oxygen is caused by imperfections in the carbonization process and the binding occur during physical activation [21].

The Other elements such as Silica (Si), Calcium (Ca) and Magnesium (Mg) are also identified in a relatively low percentage, this is due to the contribution of the basic ingredients of biomass [22]. The content of chlorine and zinc in the sample shows that the activated carbon sample still contains Zn and Cl and the chemical activation process carried out was successfully, characterized by the presence of Zn and Cl [23]. The sodium element contained in the sample is also the result of chemical activation using the activating agent NaOH where the component is still left behind and does not dissolve in the washing process [24]. Figure 5 shows that the element carbon has the sharpest peak, so the element carbon is the dominant element compared to the other elements. The carbon electrode which has the highest carbon element is owned by PS-TA with a percentage value of 90.27%. PS-ZnCl2 has a carbon element that is not much different from PS-TA, which is 84.33% this result is due to the many other chemical constituents contained in PS-ZnCl2.
3.5 The Electrochemical Analysis

Cyclic Voltammetry (CV) analysis aims to determine the specific capacitance value of supercapacitor cells made from sago midrib with a scanrate of 1 mV/s, 2 mV/s and 5 mV/s with voltage of 0-1 V. The results of cyclic voltammetry measurements for PS-TA, PS-ZnCl₂, PS-NaOH samples are shown in Figure 6.

The charge-discharge curve with the largest area is shown by the PS-ZnCl₂ sample with a specific capacitance value of 138.36 F/g and the charge-discharge curve with the smallest area is shown by the PS-TA sample with a specific capacitance value of 60.81 F/g. The area formed on the voltammetric cyclic curve in Figure 6 shows the amount of specific capacitance, the larger curve formed, the greater.
value of specific capacitance given [25]. The specific capacitance values of each sample for a scan rate of 1 mV/s are shown in Table 3

| Sample Code | Ic (A)   | Id (A)   | Csp (F/g) |
|------------|---------|---------|-----------|
| PS-TA      | 0.000404| -0.000246| 60.813    |
| PS-ZnCl₂   | 0.000763| -0.000696| 138.36    |
| PS-NaOH    | 0.000429| -0.000428| 111.37    |

The optimum specific capacitance value for supercapacitor cells with carbon electrodes derived from the sago midrib is owned by PS-ZnCl₂. The chemical activation process serves to reduce the water content and volatile compounds which is still left during the pre-carbonization process, so the generated pores become more open [26]. ZnCl₂ activator can form ZnOCl which can reduce the pore width so the generated pore size is microporous. ZnOCl also forms rod-like pores (nanofibers) which can increase the formation of micropores and mesopores. Activated carbon will be maximum if using ZnCl₂ as the activating agent at the appropriate carbonization temperature. The best results obtained were the formation of micropores and mesopores on the carbon electrodes. The chemical activator ZnCl₂ with an increase in carbonization temperature from 400°C to 600°C produce carbon electrodes with the domination of micropores and some mesopores [27].

These results can affect the domination of micropores and mesopores on the carbon electrodes formed. Micropores in PS-ZnCl₂ act as storage devices for ions in the carbon and mesoporous electrodes can increase the rate of diffusion and movement of ions. The combination of mesopores and micropores in PS-ZnCl₂ is the best result in increasing the specific capacitance value [20].

Figure 6.b shows that the specific capacitance value decreases as the scan rate increases. When the scan rate is given to the carbon electrode, the ions in the electrolyte solvent will diffuse into the pores on the carbon electrode. The high scan rate causes the ions to diffuse rapidly into the pores so the ions not completely saved in the electrodes carbon pores and this causes a low specific capacitance value. Otherwise, the lower the scan rate given, the longer the ions will diffuse so the ions can enter the pores completely to fill the micropores and produced the higher specific capacitance value [28].

4. Conclusion
Sago midrib have the potential to be used as supercapacitor cell electrodes by variating the chemical activators. The fabrication of sago midrib electrodes was successfully made without the use of chemical activating agents and the use of ZnCl₂ and NaOH as chemical activating agents, ZnCl₂ is the best chemical activating agent for carbon electrodes from PS. The highest mass loss percentage was obtained by PS-ZnCl₂ with a value of 51.7% which could increase the porosity of the carbon electrode. The highest Lc/La ratio was obtained by PS-ZnCl₂ with a value of 1.891. PS-ZnCl₂ is dominated by mesoporous and rod-like fibers which increase the number of micropores at the carbon electrode. The optimum specific capacitance value of the supercapacitor cells using the Cyclic Voltametry method was obtained by PS-ZnCl₂ with a value of 138.36 F/g.

Acknowledgements
The authors are grateful to the DRPM Kemenristek/BRIN, Republic of Indonesia for financial support through first year project of World Class Research (WCR), with contract number: 477/UN.19.5.1.3/PT.01.03/2021

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