Fabrication of supercapacitor electrode based on pepper peel activated carbon

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Abstract. Pepper peel waste is one of the byproducts of pepper production, especially in the Province of Bangka Belitung Islands. One of the efforts to utilize pepper peel, which is used as an activated carbon material that can be used as supercapacitor electrodes, has been carried out. Activated carbon based on pepper peel is synthesized by drying it to dry and then pre-carbonization. The next step is chemical activation using ZnCl₂ and followed by physical activation at 700 °C in nitrogen flow conditions (N₂) for 3 hours. Characterization of activated carbon material was carried out using SEM-EDX and BET, while the electrode performance used CV (Cyclic Voltammetry). The SEM-EDX and BET test results show that the activated carbon material has a porous structure with an average pore diameter of 2.059 nm. The CV test results were used to determine the energy storage capability with a specific capacitance value of 7.77 F/g at a scan rate of 1 mV/s.

1. Introduction

Bangka Belitung Province is one of the largest pepper producing provinces in Indonesia. The byproduct of pepper production in the form of pepper peel residue has not been widely used and is eyeing for further study by researchers. Basically, pepper peel waste is one of the wastes that is classified as biomass waste [1], [2].

Utilization of biomass waste is currently an attraction for researchers to develop in terms of its application. One of the uses of biomass waste is used as an activated carbon material [3], [4]. Biomass activated carbon tends to be the choice for researchers because activated carbon has a fairly wide scope of use, for example as a water purifying material [1], absorbent material [5], [6], sensor materials and energy storage materials [7], [8], [9].

Activated carbon is used as an energy storage material, usually in the form of an electrode. One of the energy storage media that uses electrodes and has attracted researchers in the last ten years is the supercapacitor [10].

Supercapacitor electrodes can be synthesized from conductive polymer materials, metal oxide and activated carbon. However, electrode material based on biomass activated carbon is a separate choice because it has several advantages including unlimited quantity, low cost, high energy capacity and long cycle life [11], [12].

The use of waste pepper peel as an activated carbon material has not been widely reported. Based on research [13], [1] stated that the waste of pepper peel has a carbon content of 79.13% carbon atoms using HCl activator and 82.17% carbon atoms when synthesized using KOH activators. Type of
activator, synthesis method, activation temperature are several factors that can affect the capacitance value of the supercapacitor electrode based on biomass activated carbon [14]. Therefore, this study examines the synthesis of supercapacitor electrodes from pepper peel waste using ZnCl₂ activator with pre-carbonization treatment.

2. Materials and methods
2.1. Material and equipment
The tools used in this study were SEM-EDS, BET (JWGB Meso 112), Inert Furnace with nitrogen gas (N₂) and CV (Cyclic Voltammetry) test equipment, mesh, agate mortar and magnetic stirrer. The materials used are waste of pepper skin, distilled water, and zinc chloride (ZnCl₂).

2.2. Synthesis of Activated Carbon
Activated carbon synthesis refers to research that consists of three stages: The first stage was the preparation of the pepper peel waste sample by cleaning it from impurities and drying it to dry. After the sample was dry, pre-carbonization was carried out at a temperature of 120 °C for 2 hours using an oven.

The second stage is the chemical activation stage. Before being chemically activated, the pre-carbonized sample was ground to a size of 100 mesh. After that the sample is activated using an activating agent in the form of zinc chloride (ZnCl₂) with a ratio of 5:1 for the ratio of the volume of the activator to the mass of carbon. After mixing, the mixture is stirred until homogeneous and let stand for 48 hours. Samples that have been allowed to stand for 48 are then washed using distilled water until they are neutral (pH 7).

The third stage is the physical activation stage at 700 °C using an inert furnace with nitrogen gas flow (N₂) with an increase rate of 100 °C/hour and temperature holding for 3 hours. Then proceed with a natural decrease in temperature.

2.3. Sample characterization
The Activated carbon samples that have been prepared are then characterized using SEM-EDX to determine morphology and BET to analyze pore size data from activated carbon samples.

2.4. Electrode Manufacture
The electrodes were made by mixing the activated carbon sample with PVA as much as 2% of the mass of the sample. Then the sample was put into a 1 cm diameter mold and pressed under 4 tonnes for 2 minutes. The printed samples were then immersed in H₂SO₄ solution for 24 hours. Then the sample is ready to be tested using CV (Cyclic Voltammetry) to determine the ability to store the electric charge from the fabricated supercapacitor electrodes.

2.5. Data Analysis
Data from CV measurement results are then processed using an equation that refers to research [15] to determine the specific capacitance value associated with storage capability. The specific capacitance is expressed as:

\[ C_{sp} = \frac{I_c - I_d}{S/m} \]  \hspace{1cm} (1)

where: \( C_{sp} \) is the electrode-specific capacitance (F/g), \( I_c \) is the charge current (A), \( I_d \) is the discharge current (A), \( S \) is the scan rate (V/s) and \( m \) is the electrode mass (g)

3. Results and Discussion
To observe the morphological characteristics of activated carbon samples prepared from pepper peel waste, the SEM test was used as shown in Figure 1.
Based on the results of the SEM image shown in Figure 1, it shows that activated carbon which is activated using ZnCl$_2$ tends to have a non-uniform pore shape and there are still some pores that have not been fully formed. This is due to several things including the presence of residual activator in the form of white spots that are still attached to the surface of the pore wall and also the effect of activation temperature which needs to be increased. This is also supported by data from the test results of elemental composition contained in activated carbon samples. Based on the results of the EDS test data as shown in Table 1, it shows that the carbon element content tends to be low at 76.31 At%.

**Table 1. The Elemental Content Test Results Using EDS**

| Element | Weight (Wt) % | Atom (At) % |
|---------|---------------|-------------|
| CK      | 67.87         | 76.31       |
| OK      | 22.68         | 19.15       |
| MgK     | 00.78         | 00.43       |
| AlK     | 02.07         | 01.04       |
| SiK     | 05.96         | 02.86       |
| CaK     | 00.64         | 00.22       |
| Total   | 100           | 100.01      |

Based on the data in Table 1, the high content of silica elements can affect the pore size and surface area formed because the silica element can inhibit the formation of pores. Pore size, surface area and pore volume can be known through test results using BET as shown in Table 2.

**Table 2. BET Result of Activated Carbon**

| Pore Size (nm) | BET Surface Area (m$^2$/g) | Pore Volume (cm$^3$/g) |
|----------------|-----------------------------|------------------------|
| 2.059          | 3.416                       | $2 \times 10^{-3}$     |

Pore size is one of the factors that affect the specific capacitance value on activated carbon-based supercapacitor electrodes. The larger the pore size and surface area, the greater the capacitance value produced. The value of the specific capacitance is measured using cyclic voltammetry and eq (1) as shown in Figure 2 and Table 3.
Figure 2. Cyclic Voltammetry of Supercapacitor Electrode Samples

Based on Figure 2, it shows that the higher the scan rate value associated with the increase in time unit voltage, the larger the area of the curve formed and the smaller the capacitance value. This is because the greater the scan rate value, the faster the CV data sampling time, which results in less electrolyte ions that accumulate and adhere to the surface of the electrode, so that the stored charge is less so that it will affect the decrease in the value of capacitance specifics and vice versa [16]. The resulting curve pattern is in accordance with the results of research conducted by [17] with a pattern resembling a rectangle with an area that is getting bigger as the scan rate value increases. The slope pattern of the curve in Figure 1, describes the magnitude of the ohmic resistance value. At a scan rate of 10 mV/s the slope of the curve tends to be greater than the scan rate of 1 mV/s, which means that there is resistance to electrolyte ion movement which limits the formation of a double layer between the electrode and the electrolyte ion which is quite large, causing its specific capacitance value be smaller [12].

The magnitude of the capacitance value of the activated carbon of pepper peel waste synthesized using the ZnCl₂ activator are shown in Table 3.

Table 3. The CV Test Results of The Electrode Sample Based on Pepper peel Activated Carbon

| Scan rate | Electrode Mass (g) | Iₑ (A)      | Iₛ (Ampere) | CₛP (F/g) |
|-----------|-------------------|-------------|-------------|-----------|
| 1 mV/s    | 0.000167          | 0.000032    | 7.77        |
| 2 mV/s    | 0.000238          | -0.000016   | 6.58        |
| 5 mV/s    | 0.000349          | -0.000053   | 4.16        |
| 10 mV/s   | 0.000476          | -0.000068   | 2.81        |

The capacitance value produced in this study is higher than the previously reported [13]. According to [14] the low value of the resulting capacitance can be caused by the small surface area and pore size of the activated carbon being synthesized, the type of activator that is not in accordance with the sample of activated carbon, the activation temperature and also the type of adhesive material. Therefore, it is necessary to have further studies, especially related to the use of adhesives that are more conductive in nature and also the method of synthesizing activated carbon.
4. Conclusion
The synthesis of activated carbon-based supercapacitor electrodes from waste pepper shells using \( \text{ZnCl}_2 \) activator has been carried out. SEM-EDX and BET test results show that the sample has a porous structure with an average pore diameter of 2.059 nm. The CV test results to identify the storage and ion transfer capabilities of the synthesized electrodes produced the optimum value of 7.77 F/g at a scan rate of 1 mV/s.

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Acknowledgments
We gratefully acknowledge the funding from Universitas Bangka Belitung through UBB PDTU funding from LPPM UBB which has financed this research.