Carbon electrode based on durian shell: effects concentration of chemical activator agent (Potassium hydroxide)

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Abstract. This study aims to determine the optimum concentration of KOH activators in the preparation process of carbon electrodes made of durian shell. The electrode preparation process begins with pre-carbonization at 250 °C for 2.5 hours, followed by ball milling for 20 hours to find carbon powder with particle size ranging from 39 to 52 μm. Then the chemical activation using KOH activator agent with concentration variation of 0.5 M, 0.6 M, 0.7 M, 0.8 M, 0.9 M and 1.0 M. The conversion of activated carbon powder into pellet is done with a hydraulic press at 8-ton pressure. Different KOH concentrations affect the physical properties of carbon electrodes such as dimensions, crystallinity properties, carbon content and also effects on capacitor properties such as capacitance, energy, and strength. The optimum concentration KOH was found as high as 0.7 M, indicated by the optimal capacitor properties such as capacitance, energy, and power. Capacitance, energy and optimum strength are found as high as 1.87 F, 3.09 Wh kg⁻¹, and 22.29 W kg⁻¹.

1. Introduction

Supercapacitor or Electrochemical Double Layer Capacitor (EDLC) is an energy storage device that stores and releases energy by separating nanoscopic charges on the electrochemical surface between electrodes and electrolytes[1]. Electrodes used in supercapacitors usually carbon that has gone through the activation process. This is due to the lower cost, good electrical conductivity, and high specific surface area[2,3]. The utilization of biomass-based materials as supercapacitor electrodes has been studied previously. Such as corn stalks[4], empty fruit bunches of palm oil[5], rubberwood powder[6], tobacco leaf[7], poplar wood [8], cassava shell [9], sugarcane bagasse [10], and durian shell[11]. Durian shell contains cellulose in the range of 50% - 60%, lignin of 5% and starch of 5%. The higher content of cellulose and lignin indicate that the durian shell has a higher carbon content so that it can be used as a precursor material in the production of activated carbon for supercapacitor applications. Research on the use of durian shell as a carbon electrode was carried out using a variation time of physical activation and found the highest specific capacitance as high as 88.38 F g⁻¹[11]. This research focused on the synthesis of carbon electrodes from durian shell using a variety of KOH (Potassium Hydroxide) activator concentration.
2. Experimental method

2.1 The synthesis process of the activated carbon electrode

In the beginning, Durian shell as a raw material through the process of washing, cutting, and drying. After drying, the sample proceeds with the process of pre-carbonization, milling, sieving, chemical activation and pellet-shaped printing. Chemical activation using KOH activator with a concentration of 0.5 M, 0.6 M, 0.7 M, 0.8 M, 0.9 M and 1.0 M. Variations in KOH concentration were carried out because the differences in concentration were able to show the different effect in the remove impurities that still cover the carbon pores and finally the optimum porosity condition was found [12]. Samples were printed into a pellet shape using a Hydraulic Press instrument at an 8 tons compression pressure [13,14]. A sample that has been in the form of a pellet, then carried out a carbonization process using N\textsubscript{2} gas at a temperature of 600°C [15] and continued with physical activation using CO\textsubscript{2} gas at 900°C for 2 hours [16].

2.2 The characterization of physical properties

Physical characteristics such as density were carried out by calculating the mass, volume, and thickness of the durian shell carbon electrode. The crystallinity properties were investigate using X-ray Diffraction (XRD) instrument with X-pert powder panalytical diffractometer that uses Cu anode light source and K\textalpha\ wavelength of 0.154 nm. Morphological properties by analyzing by Scanning Electron Microscopy and the element content were studied using the Energy Dispersive X-ray (EDX) method.

2.3 The characterization of electrochemical properties

Characterization of the electrochemical properties of carbon electrodes was carried out by measuring the specific capacitance of supercapacitor cells using the Cyclic Voltammetry method at a scan rate of 1 mVs\textsuperscript{-1} [17,18,19]. The cyclic voltammetry measurement was performed in the 1 M sulfuric acid electrolyte solution. Specific capacitance values can be calculated using formula 1. The specific capacitance can be used to calculate the capacitance, specific energy, and specific power of the supercapacitor cell consist of carbon electrode made from durian shell.

\[
C_{sp} = \frac{I_c - I_d}{S \times m} \quad (1)
\]

Where \(I_c\) is the charging current (A), \(I_d\) is the discharge current (A), \(S\) is the scan rate and \(m\) is the mass of the electrode [20].

3. Result and Discussion

3.1 Analyze the dimensions of the electrode

![Figure 1. The bar chart of carbon electrode shrinkage dimensions](image)
Figure 1 shows a bar chart of the reduction in physical parameters such as mass, volume and thickness of carbon electrodes after carbonization and physical activation processes. The dimensions of the electrode in the form of volume and mass experience a very large decrease compared to the decrease in thickness. The highest percentage of decreasing in mass, volume and thickness is owned by the KD/0.9 sample. The amount shrinkage of mass, volume and thickness are 77.98%, 76.01% and 42.59%, respectively. The addition of KOH concentration did not show a significant difference in the reduction in sample dimensions. This is because activation using KOH concentration is also influenced by the touch surface between activator materials and the surface of the carbon powder and the varying particle size[11]. After the carbonization process is carried out, the smallest average mass and volume are 0.171 g and 213.93 cm$^3$ was found at KD/0.9 sample. This mass and volume will influence the density of the carbon electrode sample.

3.2 Analyze the degree of crystallinity

Figure 2 shows X-ray diffraction patterns for carbon electrodes with sample codes KD/0.7 and KD/0.9. The shape of the X-ray diffractogram which has a large and broadening peak shows the amorphous structure of the carbon sample made from biomass material[13]. The 2θ diffraction angle in carbon sample was correlated with the reflection planes of 002,100, and 112. For KD/0.7 sample has an 2θ angle of 24.967°, 44.315°, and 81.232° and the KD/0.9 sample has an 2θ angle of 43.996°, 81.648°. From these data shows the sample is at a good peak for carbon material[21]. The X-ray diffraction pattern in figure 2 was further analyzed by using microsoft origin to obtain the interlayers spacing (d), state high (Lc) and state width (La) in correlated with reflection planes of 002, 100, and 112. All this parameter listed in Table 1. Table 1 show the interlayers spacing data for $d_{002}$, $d_{100}$, and $d_{112}$ were 3.564 Å; 2.042 Å; 1.183 Å and 3.568 Å; 2.054 Å; 1.178 Å for KD/0.7 and KD/0.9 samples, respectively. In addition of the $d_{hkl}$ data can also to found the parameter of state high (Lc) and state width (La). The KD/0.7 sample has Lc and La of 11.575 Å and 47.839 Å, while the KD/0.9 sample has Lc and La of 12.301 Å and 43.272 Å. Based on the formula $S=2/\rho L_c$, the KD/0.7 sample has a larger surface area than the other samples because have a smaller the Lc data[22].

Figure 2. X-ray diffraction characterization results
Table 1. The diffraction angle (2θ), interlayers spacing (d), state high (Lc), and state width (La) 

| Sample Code | 2θ(002) (°) | 2θ(100) (°) | 2θ(112) (°) | d(002) (Å) | d(100) (Å) | d(112) (Å) | Lc (Å) | La (Å) |
|-------------|-------------|-------------|-------------|-------------|-------------|-------------|--------|--------|
| KD/0.7      | 24.967      | 44.315      | 81.232      | 3.564       | 2.042       | 1.183       | 11.575 | 47.839 |
| KD/0.9      | 24.932      | 44.048      | 81.648      | 3.568       | 2.054       | 1.178       | 12.301 | 43.272 |

3.3 Scanning Electron Microscopy

Figure 3. SEM micrographs a) KD/0.7 sample ; b) KD/0.9 sample with a magnification of 3000 times

The effect of KOH chemical activation on the surface morphology of activated carbon electrodes based on durian shell is reviewed in Figure 3. Figure 3.a is shown the agglomeration particles and the pores between particles are evident in KD/0.7 sample. KOH as a chemical activation agent can separated the existing particles in the durian shell material so that increasing the KOH concentration in the sample decreases the particle size and presenting pores between the particles. On the surface there are also found the small particles that are spread evenly. The addition of KOH concentration to 0.9 M in 3.b results in a denser of the surface morphology sample. Small particles are increasingly and pores between particles are cover up by this smaller particles. This is indicated by the addition of higher KOH causing small particles to fill the pores between the particles so that they look denser in surface sample.

3.4 Energy dispersive X-ray

Figure 4. EDX characterization results on carbon electrodes, (a) KD/0.9, (b) KD/0.7
Energy Dispersive X-ray Analysis (EDX) aims to determine the elements contained in the activated carbon sample. Figure 4 shows a graph of the dispersive energy of the element content values. The higher peak obtained, the greater the element content of the electrode sample. The dispersive energy such as 1.3 keV and 4 keV is the unique characteristic only for magnesium and potassium elements. Table 3 shows the constituent elements contained in the KD/0.7 and KD/0.9 samples. The higher concentration of activator material causes the higher carbon percentage. This is due to the use of different activator agent concentrations will produce the different surface morphology on carbon sample. Judging from, the greater percentage of the element contents weight, the greater percentage of the element contents atomic. The amount of carbon elements in atomic percentage in the KD/0.7 sample is 89.35% while the KD/0.9 sample is 94.67%. These results indicate the sample tested contains carbon that dominates as desired. In addition, the levels of oxygen elements have the most content after carbon, this is because there are raw materials left behind due to incomplete carbonization or can also occur in the activation process [23]. The use of biomass materials using banana stems obtained the largest carbon content of 87.86% [15], rubber wood sawdust of 91.28% [16] and durian shell of 97.22% [11].

| Element Contents | Sample KD/0.7 | Sample KD/0.9 |
|------------------|---------------|---------------|
|                  | Weight %      | Atomic%       | Weight %      | Atomic%       |
| Carbon           | 85.55         | 89.35         | 92.12         | 94.67         |
| Oxygen           | 12.74         | 9.99          | 5.92          | 4.57          |
| Magnesium        | 0.61          | 0.32          | 0.66          | 0.33          |
| Calcium          | 1.10          | 0.34          | 0.62          | 0.19          |
| Silica           | -             | -             | 0.22          | 0.10          |
| Potassium        | -             | -             | 0.46          | 0.14          |
| Totals           | 100%          |               |               |               |

3.5 Analysis of electrochemical properties

Figure 5. The cyclic voltammogram for each supercapacitor with different electrodes
The measurement of electrochemical properties of supercapacitor cells was carried out using the Cyclic Voltammetry (CV) method. Cyclic Voltammetry is a measurement used to determine the specific capacitance (CSP) of the supercapacitor electrode. Specific capacitance was measured at a scan rate of 1 mV/s with a voltage range of 0 to 0.5 volts. The figure shows that the KD/0.7 sample has the largest I-V curve compared to the other samples. While the KD/1.0 sample has the smallest curve. This shows that the KD/0.7 sample has the highest specific capacitance and the KD/1.0 sample has the smallest specific capacitance. The specific capacitance can be used to find the cell capacitance, specific energy, and specific power. Table 4 shows the electrochemical data for all electrode samples. From these data, we can see that along with the addition of specific capacitance, specific energy, and specific power also increase. The largest specific energy was obtained by a sample of KD/0.7 as high as 3.09 J kg$^{-1}$ and the lowest specific energy was found at KD/1.0 sample of 1.26 J kg$^{-1}$. In addition, the largest specific power is owned by the KD/0.7 sample as high as 22.29 Wh kg$^{-1}$ and the lowest specific power shown by KD/1.0 samples of 9.09 Wh kg$^{-1}$. Based on Table 3 can be seen that along with the addition of KOH concentration, the electrochemical properties of the sample will increase until it reaches an optimum condition at a concentration of 0.7 M. Addition of the KOH concentration above 0.7 M, causing the electrochemical properties of the sample to begin decrease.

### Table 3. The electrochemical properties of carbon electrodes

| Sample codes | $I_c$ (Acm$^{-2}$) | $I_d$ (Acm$^{-2}$) | $C_{sp}$ (Fg$^{-1}$) | Capacitance (F) | Specific Energy (J kg$^{-1}$) | Specific Power (Whkg$^{-1}$) |
|--------------|-------------------|-------------------|---------------------|----------------|-----------------------------|------------------------------|
| KD/0.5       | 0.000442          | -0.000378         | 41                  | 0.82           | 1.42                        | 10.24                        |
| KD/0.6       | 0.000528          | -0.000328         | 38.91               | 0.86           | 1.35                        | 9.74                         |
| KD/0.7       | 0.000973          | -0.000897         | 89.05               | 1.87           | 3.09                        | 22.29                        |
| KD/0.8       | 0.000577          | -0.000450         | 73.34               | 1.03           | 2.54                        | 18.32                        |
| KD/0.9       | 0.000390          | -0.000298         | 39.31               | 0.69           | 1.36                        | 9.81                         |
| KD/1.0       | 0.000415          | -0.000422         | 36.39               | 0.84           | 1.26                        | 9.09                         |

### Conclusion
The production of supercapacitor cell electrodes from durian shell has been successfully carried out with a variety of KOH concentrations. Based on physical properties analysis that has been carried out was found the KD/0.7 electrode shown the good characteristic of porosity and degree crystallinity. These physical properties support good electrochemical properties. The highest of specific capacitance, cell capacitance, specific energy and specific power was found at KD/0.7 sample as high as, 89.05 Fg$^{-1}$, 1.87 F, 3.09 J kg$^{-1}$ and 22.29 Wh kg$^{-1}$, respectively.

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