Performance of Candlenut Shell (*Alleuretus moluccana*) Based Supercapacitor Electrode with Acid Electrolytes and Their Salts

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Abstract. Candlenut shell was used as the precursor for activated carbon-based electrodes which prepared through two stages, namely carbonization and activation. The surface of the activated carbon was modified with HNO₃. Characterization of carbons and activated carbon was performed by SEM, BET, FT-IR test and capacitance analysis using Cyclic Voltammetry. The result of SEM analysis shows that carbon pore formation has occurred after activation with H₃PO₄. The surface area of carbon and activated carbon determined by the BET method is 125,828 m²/g and 142,435 m²/g, respectively. The results of FTIR and Boehm titration analysis showed an increase in oxygen-containing functional groups after modification with HNO₃. Based on the results of the analysis using Cyclic Voltammetry obtained the highest specific capacitance of unmodified activated carbon is 145.49 mF/g in H₂SO₄ 0.5M electrolyte. In addition, the highest specific capacitance of activated carbon modified with HNO₃ is 155.92 mF/g obtained in HCl 0.1 M electrolyte. In the same condition, the contribution of salt electrolyte (Na₂SO₄ 0.5 M and 0.1 M) in the specific capacitance of candlenut shell based supercapacitor electrodes is a little bit lower compared to the acid electrolytes.

1. Introduction

Technological advancements and an increasingly modern age demands enormous and growing energy consumption. Various technologies also require energy storage devices. Therefore, it takes a device that has a large energy and power and a shorter charging time to meet future technology needs. One of them is a supercapacitor [1,2].

Supercapacitors utilize electrode surfaces and electrolyte solutions to achieve greater capacitance. Supercapacitors are also more attractive because the main material used as an electrode is activated carbon. One of the raw materials for the manufacture of activated carbon is agricultural waste such as candlenut shell [3,4]. To maximize the function of activated carbon, a surface modification with HNO₃ to add active groups was reported to have an effect in increasing the specific capacitance of activated carbon as a super capacitor electrode material [5, 6].

Another way to improve the energy storage efficiency of a supercapacitor is the proper electrolyte selection. Commonly used electrolytes on supercapacitors include acid, base and salt electrolytes that have high conductivity, low resistance, easy wetting the electrode surface and lower cost [7]. Acid and alkaline electrolytes have compatibility with supercapacitors as they indicate the formation of rapid
electric double coatings and salt electrolytes have high electrochemical potential stability that can increase the energy tension and density [7,8,9].

The use of acid and salt electrolytes with the same electrode material shows different values of different capacitances. Different concentrations also show different specific capacitances. This indicates that the type and concentration of the electrolyte affect the specific capacitance of the supercapacitor electrode [10,11].

Based on this, the research was conducted surface modification candlenut shell activated carbon with HNO$_3$ and determine the specific capacitance values using the electrolyte acids, bases and salts which, H$_2$SO$_4$, HCl, and Na$_2$SO$_4$.

2. Materials and Methods
2.1. Materials
Candlenut shell, aquades, H$_3$PO$_4$ 85%, HNO$_3$ 65%, H$_2$SO$_4$ 0.1: 0.5: 1 M, HCl 0.1: 0.5: 1 M, Na$_2$SO$_4$ 0.1: 0.5: 1 M, Na$_2$CO$_3$ 0.05 N, NaHCO$_3$ 0.05 N, 0.05 N HCl, 0.05 N NaOH, copper wire, platinum wire, Whatman filter paper 42, paraffin, aluminum foil, universal pH paper, MO indicator, PP indicator, paraffilm and tissue roll.

2.2. Methods
The samples of the candlenut shell were washed thoroughly and split into small pieces. Furthermore, dried under the sun.

Candlenut shell samples were clean and dry put in a porcelain dish and heated in a furnace at 400 °C for 2 hours. This process will produce a carbon of candlenut shell. After carbonization, the resulting carbon is then cooled, smoothed, then sieved with a size of 100 mesh [12].

Candlenut shell carbon soaked with activator solution of H$_3$PO$_4$ 85% by volume ratio H$_3$PO$_4$/carbon mass of 6:1 with a 24 hour soak time. Then the pecan shell carbon is filtered using a Buchner funnel and washed with distilled water until a neutral pH. Samples were obtained dried in an oven at 110 °C for 1 hour. Activated carbon of hazelnut is cooled in desiccators [12].

Activated carbons are mixed with a chemical agent HNO$_3$ 65%, with a mass ratio of 2:1 (volume: active carbon mass). Then, shaked at a constant rate (120 oscillations per minute) for 24 hours. Afterwards washed with aquades repeatedly until the pH is neutral. Then dried in the oven for 24 hours at 110 °C [13].

A total of 0.25 g of activated carbon put into four 25-mL volumetric flask, each containing Na$_2$CO$_3$ 0.05 N, 0.05 N NaHCO$_3$, NaOH 0.05 N and 0.05 N HCl and then the mixture allowed to stand for 24 hours. After that the solution is separated from the carbon by decantation. The separated solution, each taken 5 mL of Na$_2$CO$_3$, NaHCO$_3$ and NaOH solution, then added PP indicator, added excess HCl, then reversed using 0.05 N NaOH solution and for HCl solution was taken as much as 5 mL, added MM indicator and added excess NaOH, then titrated back using 0.05 N HCl [14].

The electrode body is made by connecting copper and platinum wires using steam solder. Once it is inserted into the pipette and glued using paraffilm. The activated carbon shell of hazelnut is mixed with paraffin wax with carbon mass ratio / paraffin wax mass is 1:1 and stirred until homogeneity. Subsequently, the carbon paste is fed into the electrode body by being pressed using a spatula to solidify and flatten [15,16].

This measurement uses three electrodes, Pt electrode, an electrode Ag/AgCl and carbon paste electrodes. Electrode test was performed with 50 mV/s scan rate using electrolyte solution of H$_2$SO$_4$, HCl, Na$_2$SO$_4$ with concentration 0.1 M, 0.5 M, and 1 M so as to obtain voltage and current voltammogram, then calculated value of specific capacitance of energy storage. The electrode body was prepared by connecting copper and platinum wires using a steam solder. The electrode body was then inserted into a tulip pipette and glued together using paraffilm. CSAC sample was mixed with paraffilm wax with a mass ratio of 1:1 and stirred until homogeneous by using a spatula in a petri dish. The carbon paste was inserted into the electrode body by being pressed using a spatula for solidifying and flattening.
carbon paste electrode. Electrode testing was performed with scan rate of 50mV/s using electrolyte solution of H₂SO₄ 0.1M to obtain voltage-current voltammogram. Based on that data, specific capacitance (Cs) was calculated.

3. Results and Discussions

3.1. Surface Analysis Activated Carbon of Candlenut Shell

The surface morphology and pore formation of activated carbon is shown from the results of the Scanning Electron Microscope (SEM) analysis with magnification of 3000, 7500 and 10000 times as shown in Figure 1.

![Figure 1](image)

**Figure 1.** (a) SEM of carbon, (b) SEM of activated carbon

SEM analysis results show that the formation of carbon pores before irregular activation and many impurities that cover the carbon surface compared with after activation. The surface of the carbon pores after activation is cleaner and more open and the pore structure is formed more neatly and regularly.

The surface area, size and volume of activated carbon pores are confirmed from the measurements using the Brunauer-Emmett-Teller isotherm (BET) method shown in Table 1.

| Sample     | S (m²/g) | Vₚori (cc/g) | rₚori (Å) |
|------------|----------|--------------|-----------|
| Carbon     | 125,828  | 0.116        | 16,072    |
| Activated Carbon | 142,435  | 0.121        | 17,134    |

Based on the results of SEM and BET analysis showed that the activation process with H₃PO₄ increased pore formation, surface area, volume and pore size of activated carbon candlenut shells. This is expected to facilitate the access of electrolyte ions to the supercapacitor.

**Modification of the Activated Carbon Surface of Candlenut Shell**
Modification of the surface of activated carbon with HNO₃ is done to increase the group containing oxygen. The presence of this group on the carbon surface can increase the hydrophilicity of the carbon which supports the absorption of electrolyte ions into the pores of the carbon and can give the effect of pseudocapacitance [8].

The presence of oxygen-containing functional groups is determined by FTIR analysis as shown in Figure 2 and chemical characterization by the titration Boehm method shown in Table 2.
Figure 2. FTIR spectra of (a) activated carbon, (b) activated carbon modification

The FTIR results have a functional group absorption which is each functional group for \(-\text{C}-\text{O}, \ -\text{C}=\text{O}\) and \(-\text{OH}\). This absorption shows the presence of carbonyl, hydroxyl, quinone and lactone groups. The results of the FTIR analysis of activated carbons before modification showed absorption bands in the 3387 cm\(^{-1}\) that indicated OH. The absorption band of 1597 cm\(^{-1}\) region indicates the presence of C=O group of quinone.

FTIR results after modification indicate an uptake in an area of 3392 cm\(^{-1}\) indicating the presence of OH from a carboxylic group reinforced by a C-O group in an area of 1246 cm\(^{-1}\). The 1606 cm\(^{-1}\) absorption band indicates the presence of a C=O group of quinones. The absorption band of 1722 cm\(^{-1}\) indicates the presence of C=O of the lactone reinforced by the absorption area of 1340 cm\(^{-1}\) which is the C-O group.

Table 2. Active Carbon Functional Groups based on Boehm Titration

| Sample          | Acid groups (meq/g) | Base groups |
|-----------------|---------------------|-------------|
|                 | Carboxyl Lakton Phenol Total       |
| Activated carbon| 0,34 0,5 0 1,18       | 0,7218      |
| Activated carbon modification | 1,87 1,52 1,83 5,22   | 0,4392      |

Increased uptake from FTIR analysis and increased acid concentration from Boehm titration showed increased oxygen-containing groups after HNO\(_3\) modification.

3.2. Determination of Specific Capacitance Using Electrolyte H\(_2\)SO\(_4\)

H\(_2\)SO\(_4\) electrolyte is one of the commonly used acid electrolytes in the measurement of specific capacitance of supercapacitor. Figure 3 shows the voltamogram of the activated carbon candle nut shell electrode using H\(_2\)SO\(_4\) electrolyte.
Figure 3. Voltammogram of the KATK electrode (a) before modification (b) after modification in H$_2$SO$_4$ electrolyte 0.1 M, (c) 0.5 M, (d) 1 M.

Table 3. Specific capacitance values of activated carbon using electrolyte H$_2$SO$_4$

| Sample | Electrolyte concentration (M) | Cs (mF/g) |
|--------|------------------------------|-----------|
| Before modification | 0.5 | 145.49 |
| | 0.1 | 2.26 |
| After modification | 0.5 | 23.68 |
| | 1 | 2.37 |

The electrolyte concentration of H$_2$SO$_4$ 0.5 M shows a high specific capacitance because the use of electrolytes equal to different concentrations is influenced by the velocity and amount of ions for the formation of electric double layers. If the concentration is low then the amount of ions is inadequate and if high concentrations can reduce ion mobility [7,11].

The decrease of specific capacitance after modification is predicted due to the decrease of the concentration of base group so that the use of acid electrolyte is not maximal in the formation of electric double layer.

3.3. Determination of Specific Capacitance Using HCl Electrolyte

HCl electrolyte is one of the acid electrolyte used in measuring the specific capacitance supercapacitor. Figure 4 shows a voltammogram of candlenut shell activated carbon paste electrode using a HCl electrolyte.
The voltammogram of the carbon paste electrode using the HCl electrolyte exhibits a different cyclic pattern with the H₂SO₄ electrolyte. The curve with the HCl electrolyte exhibits a deviation or peak current caused by the high acid concentration of the carbon.

![Voltammograms](image)

**Figure 4.** Voltammogram of the KATK electrode (a) before modification (b) after modification in HCl electrolyte 0.1 M, (c) 0.5 M, (d) 0.7 M and (e) 1 M.

| Sample                | Electrolyte concentration (M) | Cs (mF/g) |
|-----------------------|-------------------------------|-----------|
| Before modification   | 1                             | 0.08      |
|                       | 0.1                           | 155.92    |
| After modification    | 0.5                           | 35.88     |
|                       | 1                             | 0.83      |

The concentration of HCl 0.1 M shows the highest specific capacitance probably because of the pseudocapacitance effect. Increased specific capacitances after modification indicate that surface modification with HNO₃ affects the specific capacitance of the supercapacitor electrode material with a particular electrolyte. This is because the modification of HNO₃ increases the acid group on carbon so that the electric double layer formation is faster by using HCl electrolyte. In addition, the peak current of the electrolyte voltammogram HCl indicates the effect of pseudocapacitance.

**3.4. Specific Capacitance Determination Using Na₂SO₄ Electrolyte**

The Na₂SO₄ electrolyte is one of the salt electrolytes which is widely studied as a supercapacitor electrolyte.
Figure 5. Voltammogram of the KATK electrode (a) before modification (b) after modification in Na$_2$SO$_4$ electrolyte 0.1 M, (c) 0.5 M, (d) 1 M.

Table 5. Specific capacitance values of activated carbon using electrolyte Na$_2$SO$_4$

| Sample            | Electrolyte concentration (M) | Cs (mF/g) |
|-------------------|------------------------------|-----------|
| Before modification| 0.1                          | 78.20     |
|                   | 0.1                          | 67.21     |
| After modification| 0.5                          | 34.47     |
|                   | 1                            | 12.92     |

The concentration of Na$_2$SO$_4$ 0.1 M shows a high specific capacitance because the SO$_4^{2-}$ anion in Na$_2$SO$_4$ is one of the largest molecules in the dissolved structure so that if the concentration is high then the electrolyte/electrolyte interface is saturated with ions which can disrupt the formation of the electric double layer.

The specific capacitance differences obtained from the use of electrolytes H$_2$SO$_4$, HCl and Na$_2$SO$_4$ indicate that not only the electrode material influences the specific capacitance of the supercapacitor. This is because the ion mobility and ion solubility of each electrolyte vary and the presence of an oxygen-containing group which can increase the specific capacitance for a particular electrolyte.

Based on the specific capacitance data, activated carbon of candlenut shell before and after modification has potential to be made of supercapacitor electrode material because its value is more than 1 mF/g [17].

4. Conclusions
Oxygen-containing group can affect the value of specific capacitance candlenut shell activated carbon based electrolyte. The number of concentration for acid and salt electrolytes influenced the ion mobility, existence of active group of electrode material and solubility of ion electrolyte. The highest specific capacitance of candlenut shell based supercapacitor electrode is obtained in HCl 0.1M electrolyte.

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