

Nano Carbon-based as Supercapacitor Electrode from Cocoa Skin

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Abstract. Most cocoa shells contain carbon which can be used as an electrode. Through nano carbon, cocoa skin has the potential to be an electrode material in supercapacitors. Nano carbon is a form of carbon that has a large surface area and pore volume. Material characteristics through FT-IR test showed that the intensity of wave absorption in the graphite group (C-C) decreased which indicates an increase in carbon. The XRD results show that carbon nano has a peak of purity close to graphite at 2θ : 24.75° on the lattice values (002). So that the nano carbon based supercapacitor electrode has an electrode resistance value of 0.0307 S/m with a specific capacitance value of 5.19 F/g.

Keywords: Cocoa skin, nano carbon, supercapacitor

Abbreviations: HEM (High Energy Milling), FT-IR (Fourier Transform Infrared Spectroscopy), XRD (X Ray Diffraction), Brunauer Emmett-Teller (BET), Carbon from pre carbonization (S1), Nano carbon after activation (S2)

INTRODUCTION

Nowadays electricity has become a part of human life and also influences technological development. All of these technologies can't be separated from electricity as a source of energy. Electronic devices currently require large electrical power, in other words, they require large energy storage devices as well. Batteries as one of the energy storage devices that are currently mass used, still have some disadvantages, one of which is the small load capacity and the charging rate is still low. So that the use of this technology requires more efficient storage of electrical energy.

Supercapacitors are a form of energy storage that has advantages over conventional capacitors and batteries. The supercapacitors sophistication is shown in its high energy density (103-104 W/kg) (Goubard, 2016), long cycle life stability (>100,000 cycles) (Feroldi, 2016), fast charging time (Hsu, 2014), and safe for the environment (Yin, 2016). Supercapacitors are usually used to manage electric and hybrid vehicle loads, as conventional vehicle starters, telecommunications, electronics that require high power impulses (electrical devices, digital cameras, cellular devices), and electricity storage in solar and wind power plants or as backup power.

On the other hand, Cocoa (*Theobroma cacao L.*) is one of Indonesia's mainstay commodities, thus placing Indonesia as the third largest cocoa producing country in the world. The total area of cocoa plantations in Indonesia reaches 959,000 ha. Over the past fifteen years, cocoa production increased to 70,919 tons in 2010. If the proportion of waste reaches 75% of production, then cocoa pods reach 53, 190 tons per year

(Kamelia, 2017). Nowadays the use of cocoa waste is limited to animal feed and fertilizer.

Based on research that has been done (Misran, 2009) that the skin of cocoa contains about 23-54% cellulose, lignin of 60.67%, holocellulose 36.47% and hemicellulose 18.90% (Wijaya, 2014). The content indicates that the skin of cocoa can be processed into charcoal which contains a lot of carbon. Cocoa skin charcoal is produced from the pyrolysis process at a temperature of 350°C with a total carbon of 42.57-45.53% (Loppies, 2016).

In some studies, cocoa skin carbon is only used as a waste adsorbent. Though carbon is one of the important components in making electrodes for supercapacitors. Judging from the carbon potential of cocoa skin as the adsorbent, it does not demand the possibility for cocoa skin carbon to be processed into supercapacitor electrodes. Activated carbon has characteristics of a large surface area, by modifying the surface also has an influence on the characteristics of a carbon material, especially as a supercapacitor electrode material. Modification of activated carbon into nano size can increase its performance by increasing surface area so that it can increase ion capture and charge storage.

MATERIALS AND METHODS

Tools and materials

The tools that used in this research are furnace, HEM, BET, XRD, FTIR, potentiostat and multimeter. Materials that used in this research are cocoa skin, KOH, KCl solution, aquades, PVA, 96% ethanol, carbon glue and stainless steel.

Procedures

Carbonization of cocoa skin

Dry cocoa skin are inserted into the pyrolysis column for combustion and take place continuously at 350°C for 2-3 hours under little or no oxygen.

Reducing carbon size

The process of reducing carbon size using the HEM PW 700i Mixer Mill for 60 minutes, so it become nanometer-sized particles.

Nano carbon activation

Activation by mixing carbon with 3.5 M KOH at a ratio of 1:4 at 50 + 1°C for 18 hours and then dried using an oven at 120°C. The carbon which has undergone drying is pyrolysis at 700°C for 2 hours before it is cooled using a desiccator. After being cooled then washed using hot water to neutral pH and HCl 0.1 M (Fitrah, 2017).

Hydrogel manufacturing

Hydrogel production is synthesized by dissolving the PVA polymer into distilled water and KCl as an electrolyte source.

Supercapacitor manufacturing

Supercapacitor electrodes are made by mixing nano carbon with conductive carbon glue then weighed in 1:1 weight ratio. The results of the mixture are glued to stainless steel measuring 3x5 cm with a surface area of 1x1 cm. The procedure for making supercapacitors, two activated carbon electrodes are weighed. After weighing each of these electrodes along with a separator in the form of a hydrogel soaked with a 1 M KCl electrolyte solution, two active carbon electrodes and a KCl moistened separator are arranged, where the separator is between the two electrodes.

Data analysis

In this study, data obtained from the results of experiments and were characterized to obtain final conclusions. The form of analysis of the test results are:

1. Analysis of cocoa skin carbon (S1) functional groups and cocoa skin nano carbon (S2) using FT-IR. Furthermore, the transmittance value in the measurement spectra is matched with the data in the reference table from Ochem Online.
2. Testing the volume and distribution of nano carbon pores using V-Sorb 2800TP and calculated using the BET method.
3. Analysis of the structure of S1 crystals and S2 perform testing using XRD. The results of the analysis are processed and presented in a specific graphical form.
4. Conductivity analysis of supercapacitor electrodes using LCR meters. Then calculate the conductivity using the following equation:

$$\text{Conductivity} = \frac{\text{Thick Material}}{(\text{Material Area} \times \text{Resistance})} \quad (1)$$

Supercapacitor electrode capacitance analysis uses the Cyclic Voltametry method to determine the electrode capacitance value. The charge capacitance capability of the electrodes is then calculated using the equation:

$$\text{Capacitance} = \frac{(Id+Ic)}{(\text{Scan Rate} \times \text{Mass})} \quad (2)$$

FTIR function group spectrum

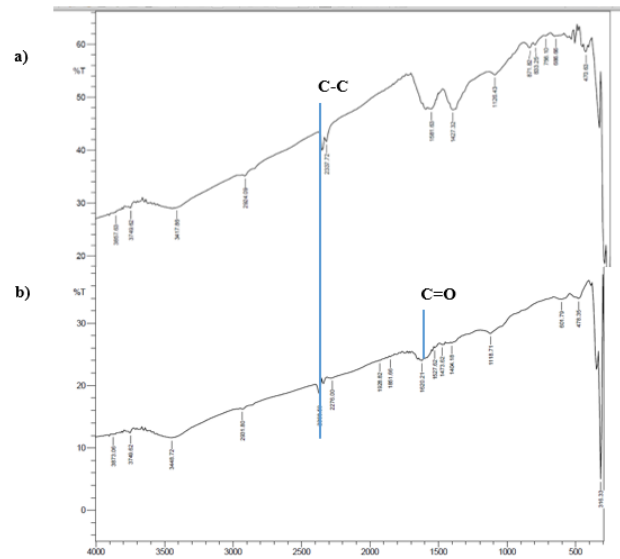


Figure 1. FTIR Spectrum, a) Carbon before activated; b) Nano Carbon after activated and in nanosize

Cristall structure

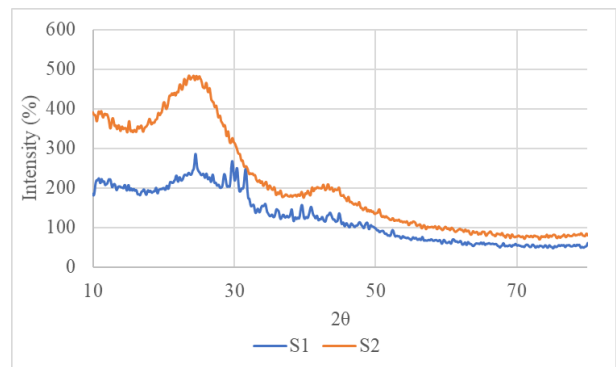


Figure 2. XRD Graph S1 and S2.

Pore volume and distribution (BET)

Table 1. Porous character of charcoal without activation and nano carbon.

Porous Character	Charcoal without activation (Sianipar, 2016)	Nano carbon (S2)
Surface Area	5,594 m ² /g	179.15 m ² /g
Total pore volume	0,028 cc/g	0.136 cc/g
Pore size	20,543 nm	1.518 nm

Specific capacitance

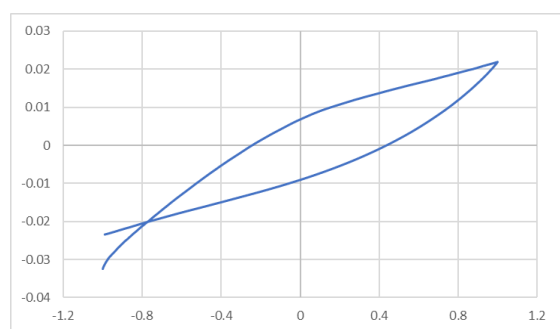


Figure 3. Cyclic Voltametric graph of of cocoa skin supercapacitor electrode.



Figure 4. Cocoa skin supercapacitor electrode.

DISCUSSION

Graphite group (C-C bending) is a constituent of the compound from weathering or combustion of organic compounds with the main constituent elements in the form of carbon (Malarvizhi, 2013) and is present at wavenumbers 2450-2300 cm^{-1} (Aslam, 2011). S1 was formed at 2337.72 cm^{-1} with transmittance values of 41.56% and 18.68% for S2. The transmittance value of the graphite group (C-C bending) has decreased which indicates the percentage of graphite group presence increases. The formation of graphite groups is due to the high temperature pyrolysis process that has been carried out so that it evaporates almost all organic elements and leaves carbon elements (Oschatz, 2015). The increasing presence of graphite groups shows that the carbon graphite material formed is purer and more conductive to electricity (Konikkara, 2016).

The C=O group is a typical group on activated carbon with a peak absorption of numbers 1820-1600 cm^{-1} (Mentari, 2018). In this case, S2 having a peak of 1620 cm^{-1} have formed carbon active substances.

As for S1 crystallinity, it has a peak value that is not in accordance with the crystal structure pattern in the JCPDS-ICDD graphite data which is 26.23°. Whereas S2 has a crystal structure pattern which is not much

different from JCPDS graphite data. This shows that the process of pyrolysis S1 to S2 makes its crystal structure close to pure graphite with S2 crystal size of 9.35 nm.

After reducing the size and activation, the surface area of the S2 increases. The surface area of S2 is 32 times greater than the cocoa shell charcoal before activation. This happens because in the pyrolysis of high temperature conversion from waste material to carbon material also occurs in the release of volatile components (Abioye, 2015). The increase in surface area is also influenced by the decay of organic components from the carbon matrix which forms a pore resulting from chemical activation using KOH (Tang, 2015).

S2 pore volume also increased 4 times greater than cocoa shell charcoal. This is caused by the pyrolysis process that forms pore structures at the internal level of molecules and forms carbonic structures in the sample (Channu, 2013). Increased temperature and chemical activation using KOH will also spur the formation of pore volume in S2 material (Ferrari, 2013; Konikkara, 2016).

The measurement result of S2 electrode resistance is 0.0307 S/m with a resistance value of 265 Ω . The resistance of the electrode is inversely proportional to its conductivity. High conductivity causes electron transfer to be more effective during the filling / discharging process and causes specific capacitance values to be large

CV testing was performed using a potentiostat with a scan speed of 10 mV/s on a 6 M KCL electrolyte. The CV test results obtained the specific capacitance value of S2 of 5.19 F/g. The specific capacitance value tends to be small because the purity of the crystal S2 is far from graphite. Mismatch of peak crystal purity (2θ) due to pyrolysis temperature has not been able to destroy and vaporize components other than the element carbon. Therefore, causing large S2 resistance and the current flowing during CV testing tends to be small so that the specific capacitance value of S2 is small.

CONCLUSIONS

Material characteristics through FT-IR test showed that the intensity of wave absorption in the graphite group (C-C) decreased which indicates an increase in carbon. The XRD results show that carbon nano has a peak of purity close to graphite at 2θ : 24.75° on the lattice values (002). So that the nano carbon based supercapacitor electrode has an electrode resistance value of 0.0307 S/m with a specific capacitance value of 5.19 F/g.

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