P-ISSN: 2303-1832
e-ISSN: 2503-023X
April 2019

Jurnal Ilmiah Pendidikan Fisika Al-BiRuNi 08 (1) (2019) 109-116
DOI: 10.24042/jipfalbiruni.v8i1.3780

THE POTENTIAL OF PEPPER SHELL (*Piper Nigrum*) FOR SUPERCAPACITOR ELECTRODES

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Received: January 21st, 2019. Accepted: April 23rd, 2019. Published: April 29th, 2019

Abstract: *A study has been carried out on supercapacitor electrodes as an electrical energy storage media based on pepper shell activated carbon. The Synthesis is done by mixing the waste carbon pepper shell with an activator HCl with a ratio of 1 : 4. Furthermore, the activated carbon is activated physically by using a pyrolysis temperature of 600 ^{0}C. The SEM results indicate that carbon has a porous morphology with a pore size of 24.6 nm which is a mesoporous category. Electrochemical properties are analyzed using cyclic voltammetry (CV). The CV results at the scan rate of 1 mV/s indicate the specific capacitance value generated is 0.45 Fg^{-1}. The results showed that pepper shell waste has the potential to be used as a supercapacitor electrode material.*

Keywords: *activated carbon, BET, cyclic voltammetry, pepper shell waste, SEM.*

INTRODUCTION

In the last few decades, the demand for electricity has increased (Mubarak, Maulani, & Hidayat, 2018). Therefore, we need a new breakthrough in terms of saving and increasing the effectiveness of the use of electrical energy, namely using energy storage media. One of the electrical energy storage media is a supercapacitor (Rosalina, Suprihatin, & Karo, 2017).

Supercapacitor attracts considerable attention because they have high power densities and long life cycles compared to batteries, and also high energy densities when compared to existing conventional capacitors (Li, Shi, & Qin, 2010). Basically, the supercapacitor also has the same principle as a battery consisting of electrodes, electrolytes, a separator, and current collector. Therefore, a supercapacitor is stated to be good when it has electrodes with high absorption capacity so that it produces a large specific capacitance. The absorption ability is highly dependent on the micro and messo pores structure on the electrodes (Arif, Taer, & Farma, 2015)

Materials that can be used as supercapacitor electrodes include metal oxides and polymers, graphene, carbon nanotubes, carbon aerogels, porous carbon or carbon active, and carbon-mineral composites (Xiao, Chen, Liu, Cui, & Zhan, 2018). However, more than 80% of commercial supercapacitor currently utilizes carbon. This is due to its abundance in nature, has a high surface area, good power density and reversibility, and the price is relatively cheap (Hao, Li, & Zhi, 2013).

Porous carbon-based supercapacitor electrodes can be produced through carbonization of natural materials, such as coal, biomass (for example: corn humps, rubber seeds, hazelnut shells, coconut shells, banana peels) or can also be synthetic materials such as polyaniline, melamine formaldehyde, and so on (Ariyanto, Prasetyo, & Rochmadi, 2012).

Carbon electrodes from biomass are the main attraction for researchers because of their availability and the relatively cheap price compared to metal oxide. The conducted of the research on supercapacitor electrodes from durian, lily, and oil palm seed waste which obtained specific capacitance values with the energy storage capabilities of 89.05 F/g, 0.201 Fg^{-1} and 1.7554 F/g respectively (Hendriansyah, Prakoso, Widiatmoko, Nurdin, & Devianto, 2018; Kurniawan, Taer, Malik, & Taslim, 2018; Syarif & Pardede, 1985).

The study by (Xiao et al., 2018) also examines the nutshell pore biomass and (Arie, Kristianto, Halim, & Lee, 2016) who examine the synthesis and modification of Indonesian local orange peel carbon using ZnCl activator, which obtained the high capacitance of 340 F/g and 56.3 F/g and the current density of 0.3 mA/g.

The porous carbon based material and synthesis method greatly influence the results of specific capacitance values. In addition, the temperature variation of physics activation on the physical and electrochemical properties of supercapacitor electrodes is also very influential. The higher the physics activation temperature, the lower the density and capacitance values linearly (Arif et al., 2015).

Based on the description of the problems, the synthesis of pepper shell waste-based supercapacitor electrode material will be carried out in this study. This is because until now, there have been no studies that examine the supercapacitor electrode material synthesized from pepper shell waste. In addition, based on data from the Central Statistics Agency (CSA) of the Province of Bangka Belitung, the amount of pepper production that is a main agricultural sector tends to increase. However, the problems regarding the processing waste in the form of shells and stalks have not yet been utilized and their economic value also has not been increased so that they tend to be a river pollution problem which is due to the waste being thrown away when washing and separating the shell and seeds.

The purpose of this study is to be able to provide knowledge about the characteristics, capacitance, and conductivity of the electrodes supercapacitor of pepper shell waste.

METHOD

Tools and Materials

The tools used in this study are Agate mortar, Mesh, magnetic stirrer, tool pressing, inert furnace with N_2 gas, HITACHI SU-3500 SEM, Quantachrome Nova 4200e BET and CV. While the materials are: pepper shell waste, HCl, aquades.

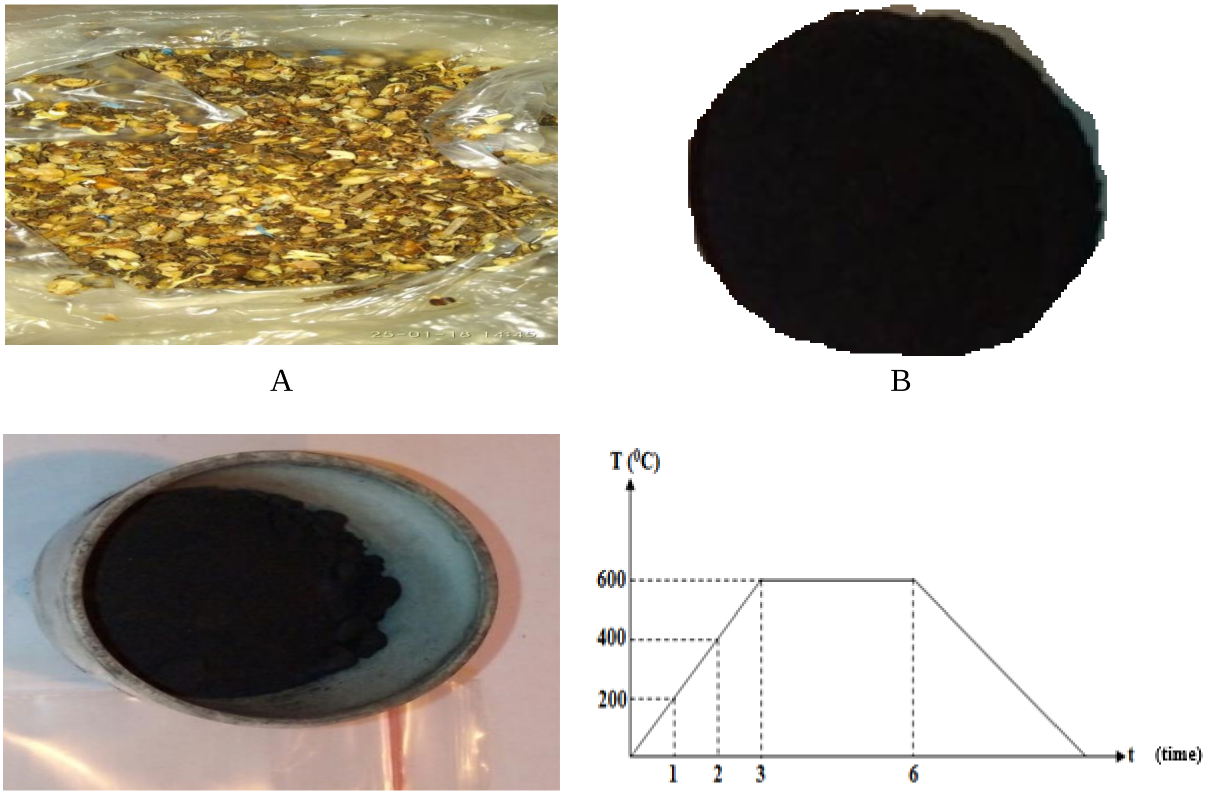
Research Procedure

1. Producing activated Carbon

The production of activated carbon from pepper shells waste (ACPSW) was carried out by preparing pepper shell waste obtained from pepper processing residues around Bangka Belitung region. The pepper shells were then dried in the sun. After that, the shells were roasted in order to be carbon (charcoal). The resulting carbon was then grinded using agate mortar and then filtered with a size of 200 mesh.

The pepper shell carbon from the filtering results was then put into a container and then mixed with 32% HCL activator solution with a volume ratio of HCL of carbon mass to 1:4. The mixture was then stirred for 30 minutes using a magnetic stirrer to make it homogeneous. Then the mixture was left for 48 hours. Furthermore, the carbon that has been left idle for 48 hours was washed with distilled water with neutral pH and filtered using a Buchner funnel. The filtered carbon was then physics activated using a furnace of N2 gas with a temperature increase of 200^0C/hour to reach 600^0C and then continued with steady temperature for 3 hours. After that, the temperature was naturally reduced. The activated carbon produced was then printed using PVA adhesive to be tested for electrochemical properties using Cyclic Voltammetry (CV).

The ACPSW results and treatment graph of the hydrolysis temperature are shown in Figure 1.



A B

C D

Figure 1. A). Pepper Shell Waste, B). Activated Carbon from Pepper Shell Waste (ACPSW), C). Post Physics Activated Carbon, D). Physics Activation Process of Pepper Waste Carbon

2. The Characteristics of Activated Carbon

To determine the morphological characteristics of the ACPSW samples, the tests using SEM and BET were conducted

3. The Production of Supercapacitor Electrode

The production of supercapacitor electrodes in the form of pellets was done by mixing activated carbon with an adhesive in the form of PVA of 2% of the mass of the activated carbon. Furthermore, the activated carbon mixed with PVA was printed with a diameter of 1 cm and pressed weighted by 4 tons for 2 minutes. The mold was then immersed in electrolyte H_2SO_4 solution for at least 1 day. After that, the electrode was ready to be tested for stability and capacitance value.

4. Electrochemical Analysis

The electrochemical analysis was carried out to determine the amount of specific capacitance and electrical conductivity of the supercapacitor electrodes using a cyclic voltammetry (CV) test.

RESULTS AND DISCUSSIONS

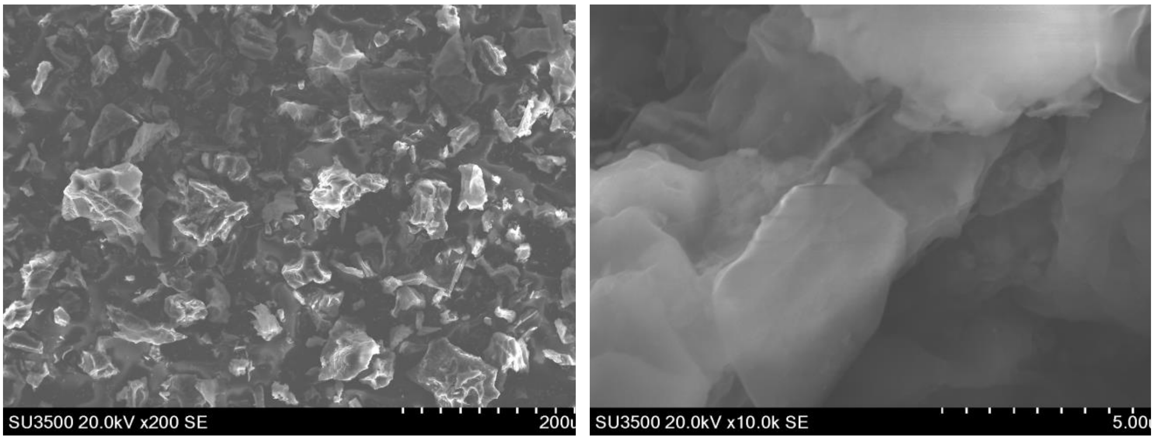
The Morphological Analysis of the Samples

Based on EDX test data, it was found that the samples had a fairly high carbon content of 70.76% by weight and 79.13% atoms. In addition, the samples also contain other elements such as oxygen, silica, and chlorine as shown in Table 1.

Table 1. Elemental Content in Pepper Shell Carbon Sample

Elemental	% Weight	% Atom
CK	70.76	79.13
OK	22.53	18.91
Si K	1.12	0.54
Cl K	0.98	0.37
Ni K	4.61	1.05
Total	**100.00**	

SEM testing result with 200 times magnification showed that carbon samples are porous. The sample pores are increasingly apparent under the 10,000 magnifications as shown in Figures 2A and 2B. However, based on SEM results, it turned out that the samples still had white spots. These white spots can be caused by the remaining volatile activator (in this case HCl) so that the pore breaking process in the physics activation was not optimum. Therefore, it is necessary to increase the activation temperature so that the heat energy produced is higher and the collisions between particles are faster which results in fragments of particles becoming smaller (Efendi & Astuti, 2016).



A B

Figure 2. SEM Results of 200 Mesh Activated Carbon Samples; A). Magnification 200 times; B).10, 000 times

Magnification of The SEM image shows that ACPSW material has porous morphology which has the potential to be used as an electrode material for supercapacitor. This is because one of the criteria for supercapacitor electrode material has been fulfilled in which it must have absorption ability. This absorption ability is strongly influenced by micro and messo pores structures (Arif et al., 2015). According to (Simon & Gogotsi, 2010) to produce high energy and energy density on supercapacitor electrodes, the electrode material must have a pore with an average size of 2-5 nm so that the ion transfer process on the electrode surface runs well.

The SEM result that shows porous ACPSW material is also supported by the data of isotherm absorption-deabsorption N_2 (Figure 2). According to (Sing et al., 1985) the absorption isotherm N_2 curve shows the type IV absorption with H2 hysteresis loop at a relative pressure $(P/P_0)<1$ which belongs to the mesoporous material category as shown in Figure 3.

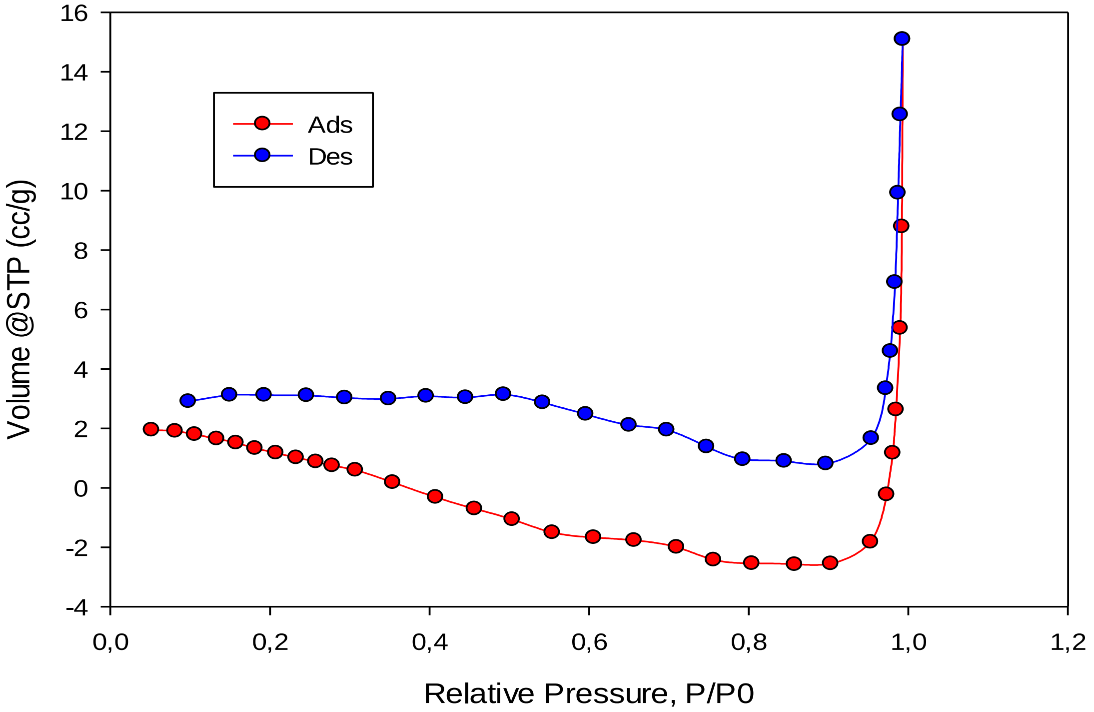


Figure 3. Isotherm Absorption-Deabsorption N_2

The results of the sample morphology in the form of pore size, surface area, and pore average volume are also showed that ACPSW samples had mesoporous sizes (Table 2).

Table 2. BET Result for Pepper Shell Activated Carbon Samples at $P / P_0 = 0.99$ and Temperature 77 K

Material Name	Pore Radius average (nm)	Surface Area (m^2/ g)	Average Volume (cc / g)
Pepper Shell Activated Carbon 200 mesh	24.6	2,258	$23.5e^{-2}$

The activated carbon samples produced in the form of slabs with a diameter of approximately 1 cm then analyzed their electrochemical properties by using cyclic voltammetry (CV). The measurement results of CV will produce a curve called voltammogram in the form of a relationship between changes in current measured to a certain potential value so that the value of specific capacitance from the electrode supercapacitor can be determined using equation [1] (Zulkifli, Awitdrus, & Taer, 2018) namely:

$$C_{sp} = \frac{I_c - I_d}{Sxm} \quad \text{.................................} \quad [1]$$

with:

C_{sp} = Specific Capacitance (F/g)
I_c =Current Charge (A)
I_d =Flow Discharge (A)
S = Balance Rate or Scan Rate (V/s)
m = Electrode Mass (g)

The analysis of the electrochemical properties Characteristics of electrodes supercapacitor was carried out using CV at a potential range of 0.0 - 0.5 V with a scan rate of 1 and 2 mV/s, as shown in Figure 4.

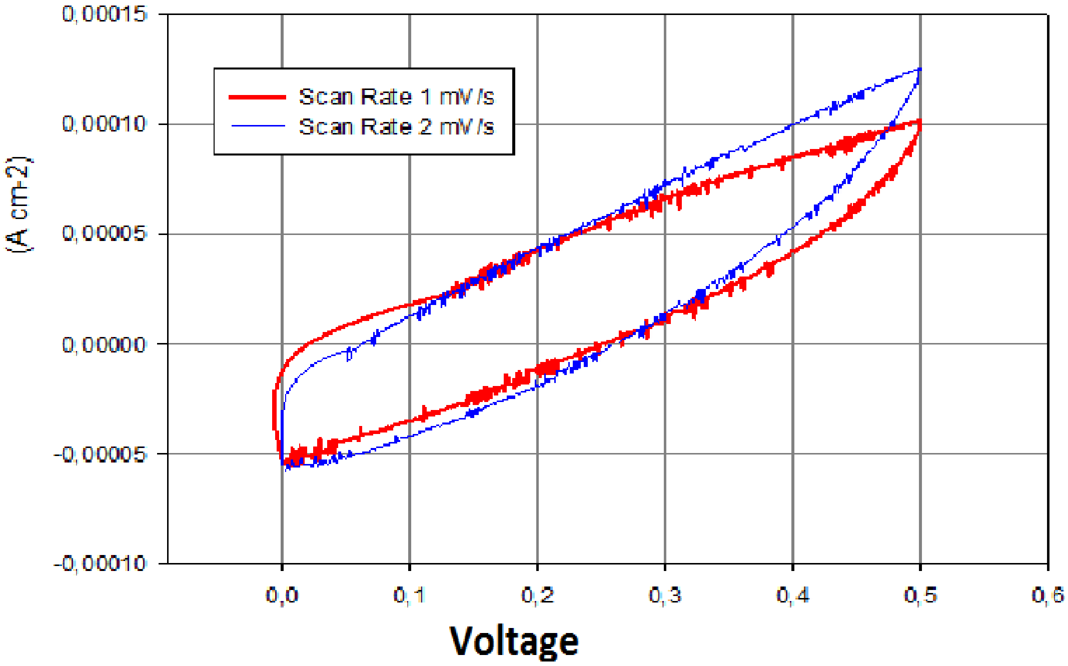


Figure 4. Cyclic Voltammetry Electrode Based on Pepper Shell Waste at the Scan Rate *of* 1 mV/s

The difference in the cycle charge-discharge current both at scan rate 1 and 2 mV/s from the voltammogram (Figure 4) are not significantly different so that the specific capacitance values produced are also not much different, namely 0.48 F/g and 0.5 F/g respectively. The value of the specific capacitance produced can be seen in the form of the voltammogram curve, i.e the wider the shape of the voltammogram curve indicates the greater the difference between the charge current (I_c) and the discharge current (Id) occurs at 2.5 volts so that the specifics capacitance value produced are also getting higher (Farma, Melinda, Taer, & Hamzah, 2017). The amount of charge and discharge currents from the ACPSW-based supercapacitor electrodes in CV testing are shown in Table 3.

Table 3. Results of CV Supercapacitor Electrode cm^{-2}

Scan Values (V/s)	Elektrode Mass (g)	Ic (A)	Id (A)	C_{SP} (F/g)
0,001	0,12	0,00005	0,00000	0,458
0,002	0,12	0,000057	-0,000003	0,50

The specific capacitance value generated in this research is still relatively small. It is possible because of several things: 1) There is an activator on activated carbon which allows the opening of the pore to be less than optimal. This is indicated by the results of SEM as shown in Figure 2; 2) In this study, the physics activation temperature used was 600^0C. The activation temperature is very influential on specific capacitance values because the higher the activation temperature, the bigger the pore diameter to be able to evaporate volatile compounds (Farma et al., 2017); 3) The soaking process of the sample electrode in an electrolyte solution H_2SO_4 is less than 24 hours, so the ion transfer exchange process, when subjected to current, does not function optimally; 4) The thickness of the electrode plate is still around 1 cm; 5) The size of the average pore diameter is still large even though it is already in the mesoporous category. According to

(Simon & Gogotsi, 2010) the size of the pore average is 2-5 nm to produce high energy and energy density on the supercapacitor electrodes.

CONCLUSION AND SUGGESTION

Based on the results of the study, it is found that the ACPSW material has a porous structure with a pore average size of 24.5 nm. The specific capacitance value of the energy storage capability produced is 0.45 Fg^{-1}.

Further research is needed regarding the structure and how to modify the pore size of the activated carbon and the adhesive material used in making the supercapacitor electrode pellet to increase its specific capacitance value.

ACKNOWLEDGMENT

The researcher’s gratitude is directed to the Ministry of Research, Technology and Higher Education that has provided support through the Beginner Lecturer Research Grant (BLRG) fund in 2018 with the contract number**: 120.V/ UN50.3.1 / PP / 2018**. Last but not least, the researcher’s gratitude for the University of Bangka Belitung for providing support in this research and also other parties that the researchers cannot mention one by one.

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