Effect of Adding Activated Carbon of Palm Kernel Shell on Carbon Papers as Electrochemical Double Layer Capacitors

O N Tetra[1], Syukri[2], and H Aziz[1]

1 Laboratory of Photo/Electrochemistry, Department of Chemistry, Faculty of Mathematics and Natural Sciences, Andalas University, Indonesia
2 Laboratory of Material, Department of Chemistry, Faculty of Mathematics and Natural Sciences, Andalas University, Indonesia

Email : haziz13@yahoo.com

Abstract. The activated carbon from palm kernel shell has been activated using NaOH at 400 °C. The activated carbon sample has been characterized using FT-IR spectroscopy, X-ray diffraction and scanning electron microscopy techniques to be used as carbon electrodes in Electrochemical Double Layer Capacitors (EDLC). Addition of activated carbon of palm kernel shell with 45 μm particle size on carbon paper as electrode at EDLC with mass ratio between carbon paper and activated carbon of palm kernell shell 1: 4, plate surface area 3 x 11 cm^2, concentration of electrolyte solution of H_3PO_4 is 0,6 N and charge time of 30 minutes can improve EDLC ability to store charge up to 387.14 μF and conductivity values of 52.2811x10^{-5} Ω^{-1}cm^{-1}. The desired capacitive performance of waste from palm kernel shells can be a source of carbon material biomass for high performance EDLC and low-cost energy storage devices.

Keyword: activated carbon, palm kernel shell, capacitance, and activator

1. Introduction

EDLC is one of the most environmentally friendly energy storage devices with high storage capability. [1] EDLC is widely used in electronic appliance, electric vehicle, pulsing technique and also as source of power and energy in industry. [2,3] EDLC with the commercial name of supercapasitor uses porous carbon as its active material. Where the charge storage occurs on the electrolyte interface and carbon through the adsorption of reversible ions from the electrolyte to the carbon surface. [4].

Porous carbon has been widely used as an electrode on EDLC. The porous carbon material provides a high internal surface area, which is an important condition for storing the charge in a double layer through physical adsorption and electrostatic interaction. In addition to the capacitance of the double layer, the resistance faced by the ion in rea ching the end of the pore, during charging or discharging, determines the effectiveness of storage.[5] Various biomass activated carbon materials have been widely used as electrode materials in EDLC, including rubber seeds [6], corn stalks [7], tea leaf waste [8], rice husks [9] and palm kernel shells. [10, 11] The effect of activation on carbon from tea waste as a super capacitor electrode greatly affects the resulting capacitance value because it is related to surface area, pore volume and pore size of carbon. [12] The utilization of carbon from palm kernel shells as supercapacitor electrodes has been used both without activators and with activators, [13] it was found that the effects of chemical activators such as NaOH and KOH will provide different charge storage capabilities depending on the purity, particle size and pore size distribution. [14]

Good performance is found in the activated carbon of coffee bean waste by comparing the mesoporous and micropore regions, the large surface area and the abundance of the nitrogen functional groups, the contribution of micropores to the specific capacitance rapidly decreases with quick charging and

dischaging and the specific capacitance depends on the number of mesopores that exists during the process, due to ion transport through the pore network. In addition, several investigations have investigated carbon materials rich in nitrogen, oxygen and phosphorus for use in electrochemical capacitors. [15] More activated mesoporous carbon will retain higher specific capacitances at rapid discharge rates because mesopores act as ducts or reservoirs for electrolyte transport. A better model for the test contribution to the capacitance of the micropore surface and mesoporous surfaces is proposed. The contribution of micropores to capacitance decreases at rapid discharge rate and is found to depend on the number of mesopores, which affects the transport of ions through the pore network of carbon.

The use of carbon papers added with activated carbon of palm kernel shell as an EDLC electrode material has not been reported. The carbon paper in this study has two functions where the paper is as template while the carbon attached to the paper is to add of micropore and mesoporous structures on the activated carbon of the palm kernel shell. Utilization of the double function of carbon paper is a new breakthrough in the assembly and manufacture of electrode materials, because in addition to facilitate the creation of templates also provide a variety of pore structure that can improve the ability of electrodes in storing the charge.

The non-activated carbon use of palm kernel shell waste added to carbon paper as a super-capacitor electrode with a particle size of 90 μm has been performed and provided a capacitance value of 1338.1 μF with a rolling method.[13] In this study we studied the effect of activated carbon addition from palm kernel shells on carbon paper as EDLC electrodes using a smaller particle size of 45 μm with a NaOH activator and sandwich method.

2. Materials and Methods

2.1. Equipments and materials

Equipments which were used are LCR-Meter (Tonghui Electronic TH2820-LCR), Multimeter (Heles UX-838TR), petridish, and other laboratory glasses equipment's.

Waste palm kernel shells materials were obtained from Agam regency, West Sumatra, NaOH (Merck), H_3PO_4 (Merck), Polyvinil alcohol (PVA), carbon paper (Munix Kangaro) and distilled water.

2.2. Activation of carbon palm kernel shell with NaOH

Palm kernel shells were dried and carbonized at 400°C for 4 hours. After the carbonization process has been completed, the palm kernel shells is smoothed to 45 μm. The activation process was carried out by adding 10 M NaOH to the mass ratio between carbon and NaOH 1: 4. and soaked for ± 4 hours. Carbon burned with furnace temperature at 400 ° C for 4 hours. Activated carbon was washed by adding HCl 0.1 M to pH 7, and continued washing with distilled water. The activated carbon is produced, heated at a temperature of ± 105°C [11].

2.3. Preparation of palm kernel shell carbon on the carbon paper

Carbon paper cut with size 3 x 11 cm^2 as much as 2 pieces. Each carbon paper was coated with activated carbon of palm kernel shell which is used as an electrode with weight ratio. Both electrodes are arranged like sandwiches separated by a PVA separator (Polyvinyl Alcohol) in the center. Then both electrode plates are flanked by copper plates as current collectors.[14] (Figure 1)
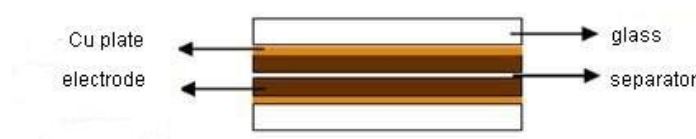

Figure 1. Schematic illustration of the Sandwich Method

2.4. Characterization techniques

X-ray diffractograms of the samples were recorded using a GE XRD 3003TT X-ray diffractometer with monochromatic nickel filtered CuKα (λ = 1.5416 Å) radiation in the 2θ range of 20° to 80°. The morphology and elemental composition of the carbon were determined by scanning electron microscope (SEM) that has the attachment of an energy dispersive X-ray analyzer (EDX).

3. Results and Discussions

The result of surface morphologies of activated carbon palm kernel shells consisted of an amorphous surface structure. Figure 2(A) shows the XRD pattern and two peaks were observed over the examined range (10 - 90°), corresponding to graphite and (100) peaks respectively observed over the examined. The results of X-ray diffraction patterns show that the structure of the activated carbon is amorphous, which is marked by a wide peak, since the crystal structure usually has many periodic peaks and peaks of sharp and narrow energy. The sharp and narrow peaks in Figure 2(A) are the peaks generated from the activation process with the NaOH still remaining on the carbon because the washing process is not completely clean. The same pattern for palm kernel carbon on diffraction peak lies at 2θ which ranges from 25º and 47º has also been reported [11].

SEM-EDX studies of activated carbon after pyrolysis consists of 83.75% carbon, 15.42% oxygen, 0,37 silicon and 0,44% calcium and particles sizes of NaOH-activated carbon palm kernel shell were under 10μm. Carbon of palm kernel shell with activators NaOH at 400ºC burning temperature show the pore volume size becomes larger and widened on its surface (Figure 2(B)) From these results, it is evident that a high percentage of carbon from palm kernel shells proves that palm kernel shell waste can be used as the basic ingredient of activated carbon.
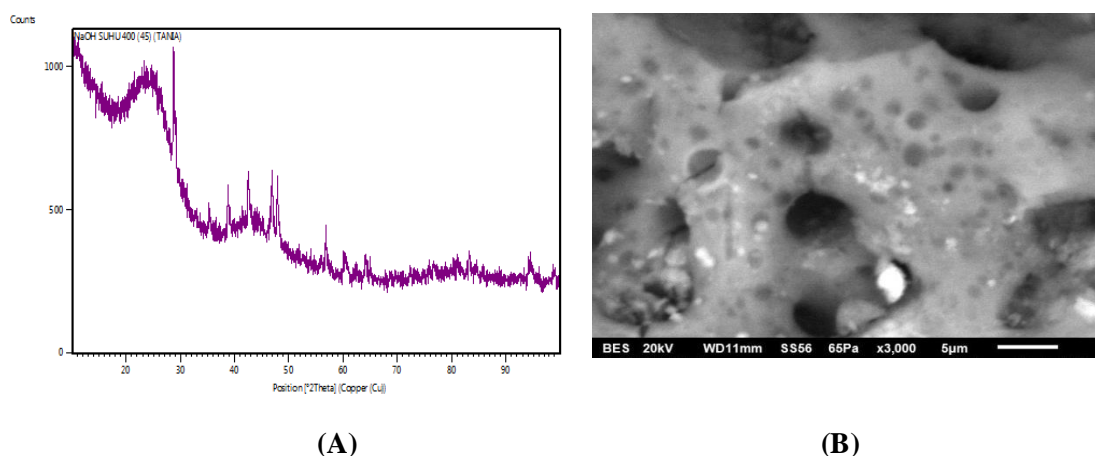

(A)   **(B)**

Figure 2. (A) XRD pattern of activated carbon palm kernel shells **(B).** SEM images of activated carbon palm kernel shells

3.1 *Effect of addition of activated carbon palm kernel shell on carbon paper*

The addition of activated carbon from the palm kernel shell on the carbon electrode enhances the ability of the electrode capacitors to store the charge [3]. In this study, activated carbon from palm kernel shells is added to the mass ratio of carbon paper and activated carbon from palm kernel shell. The addition of carbon is carried out at the optimum state that is on the size of a 3 x 11 cm^2 carbon paper with a concentration of 0.3 N H_3PO_4 electrolyte solution and a charging time of 15 minutes. The addition of carbon from palm kernel shell has be done by mass ratio variation as much as 1 : 0, 1: 1, 1: 2, 1: 3, 1: 4, and 1: 5. The greater the mass ratio between the carbon paper and the activated carbon of the palm kernel

shell, the electrode will become thicker so that the transfer of charge to the separator will further decrease the capacitance value.

The EDLC electrode with carbon-base material without the addition of carbon to the palm kernel shell gives a capacitance value of 0.353 μF. The addition of carbon palm kernel shells with a mass ratio of 1: 1 turned out to increase the capacitance of 31.60 times greater with NaOH as an activator.

In this study carbon attached to carbon paper was useful to increase the amount of carbon in electrodes other than carbon from palm kernel shells. Variations of different carbon sources and different pore structures will improve the performance of the electrodes. Different pore contributions provide channels for fast mass-transport at high charge and discharge densities [15].
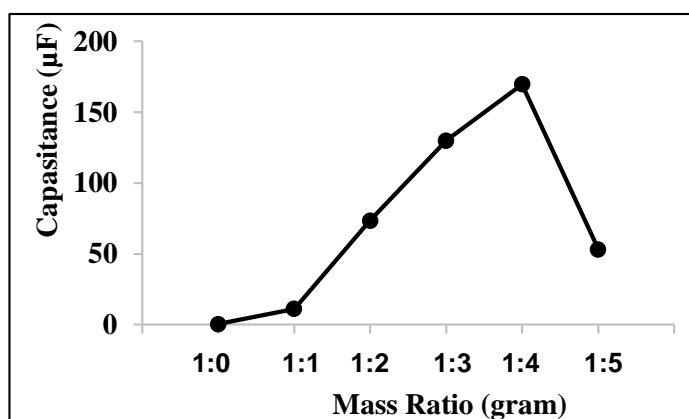

Figure 3. Effect of addition activated carbon activation of palm kernel shell on carbon paper

3.2. Effect of variation concentration of H_3PO_4 as electrolyte

Figure 4. shows that the higher the concentration of H_3PO_4 the greater the capacitance value, after the concentration of 0.6 N there is a decrease in the capacitance value of the capasitor electrode. This is because the more acid the electrolyte solution will damage the carbon pores on the carbon paper so that its ability to store the load will decrease. The higher the concentration of the electrolyte solution the moving charge to each electrode will be more so that at the time of charging, the ions will move slowly to the surface of the electrode and eventually accumulate on the electrolyte interface and separator. The large number of ions around the electrode surface will disrupt the discharge process because of the large amount of ions accumulating on the electrode interface and result in the difficulty of the ions to return to the separator and then disrupt the transport of charge to each electrode. The acidic state of the electrolyte solution can also damage the carbon pore so that the ability to store the charge becomes reduced.[17]
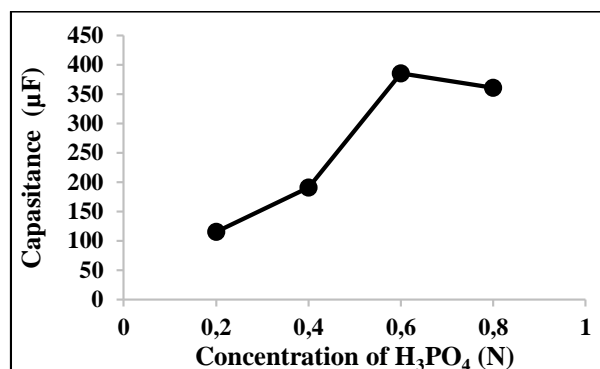
Figure 4. Effect of H_3PO_4 concentration on capacitance value

3.3. Effect of H_3PO_4 concentration on conductivity of electrode capacitors

Conductivity is the opposite of electrical resistance that depends on the amount of ions present [19]. The higher the concentration of H_3PO_4 the greater the conductivity value of the capacitor electrode, but after the concentration of 0.6 N there is a decrease in conductivity value. This is because higher concentrations will result in more electrolyte ions, so that when charged they will accumulate and accumulate on the surface of the electrode. The number of ions that are too much will disrupt the discharge process because of the large number of ions that make the ions or the load is difficult to return to its original position so that it will interfere with polarity of H_3PO_4 electrolyte ions.The higher the concentration of H_3PO_4 the greater the conductivity value of the capacitor electrode, but after the concentration of 0.6 N there is a decrease in conductivity value. This is because higher concentrations will result in more electrolyte ions, so that when charged they will accumulate and accumulate on the surface of the electrode. The number of ions that are too much will disrupt the discharge process because of the large number of ions that make the ions or the load is difficult to return to its original position so that it will interfere with polarity of H_3PO_4.
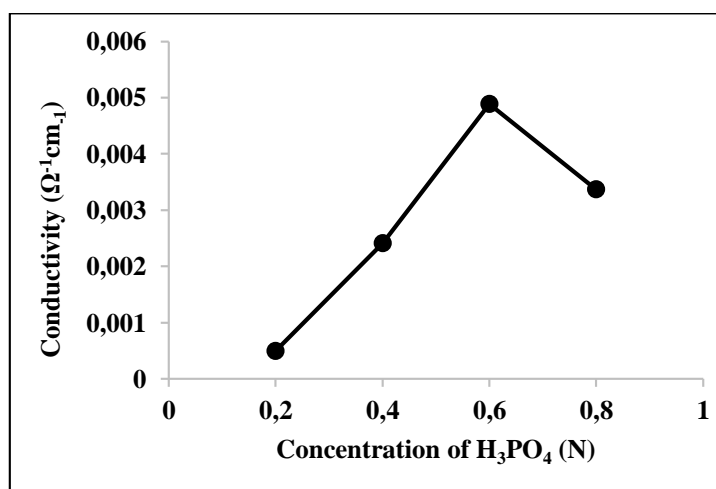

Figure 5. Effect of H_3PO_4 concentration on conductivity value

KOH activated carbon has a conductivity value of 5.6188×10^{-5} $\Omega^{-1}cm^{-1}$ (Figure 5). This shows that the activated carbon conductivity is 8.69 times greater at concentration H_3PO_4 0.3 N. This is related to the capacitance value where the smaller the resistance value, the greater the capacitance value. If the capacitance value gets bigger, more electrons are flowing and increasing the conductivity [17]. Reported

that the directly deposited PANI nanofibers on carbon paper substrate can effectively avoid the use polymer binders and conducting additivies [18].

3.4 Effect of variation of charging time
The longer the charging time the more the charge is stored so that the capacitance value will increase. The greater the surface area of the electrode, the more carbon present in the electrode and the greater the ability to store the charge to form a double layer of electricity on the surface of the electrode.
After 30 minutes the capacitance value decreases, since all the ions in the separator have moved to the electrode surface to form a double layer of electricity. The longer the charging time then the current flow will cause the increase in temperature so that the PVA polymer will undergo a mechanical change (swelling). The mechanical changes in the PVA will cause the PVA function as a separator to decrease resulting in accumulation of charge and lower the capacitance value.
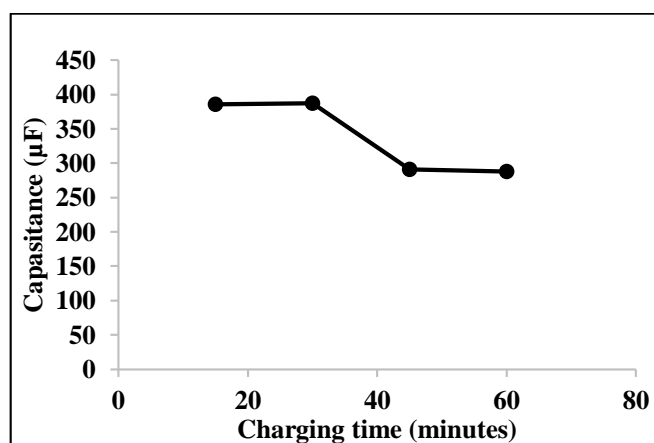

Figure 6. Effect of variation of charging time on capacitance value

4. Conclusion
The carbon paper can be used as an EDLC electrode material with a sandwich plate method with a capacitance value of 0.353 μF. The effect of activated carbon from palm kernel shell on carbon paper as EDLC electrode with NaOH activator can increase optimum capacitance that is to 387,14 μF with ratio of carbon paper mass and activated carbon 1: 4, surface area 3 x 11 cm^2, concentration of electrolyte H_3PO_4 0.6 N, charging time is 30 minutes.

Acknowledgements

References

[1]   Peter K 2015. *Electrochemical Energy Storage for Renewable Sources and Grid Balancing*, (Amsterdam, Netherlands Elsevier) p 345
[2]   Simon P and Gogotsi Y 2008 *Nat. Mater.* **7** 845
[3]   Pech D, Brunet M, Durou H, Huang P, Mochalin V, Gogotsi Y,2010 *Nat. Nano* **5** 651.
[4]   Zifeng L, Pierre-Louis T and Patrice S 2017 *Current Opinion in Electrochemistry,* **6** 115-119
[5]   Singh, S, Supriya, S. Rakib K, Chavhan M and Ganguly S 2016 *J. Chem. Eng.* **11** 296–304

[6]   Gesti U, Olly N.T, Emriadi 2015 *Jurnal Kimia Unand* **4 no 4** 23-27

[7]   Yuhe C,Keliang W, Xiaomin W, Zhengrong G, Qihua F, William G, James D. Hoefelmeyer, Parashu R. K, Maheshwar S 2016 *Electrochimica Acta*, **212** 839 – 847

[8]   Isil G, Stuart M. Holmes, Anthony B, Zeki A, 2015 *Applied Surface Science* **357** Part A, 696-703

[9]   Khu L, Van T, Thuy L. T 2014 *Progress in Natural Science: Materials International* **24** 191-198

[10]   Izan I, Misnon N. K, Mohd Zain R, Abdul A, Baiju V, Rajan J 2015 *Electrochimica Acta* **174** 78-86

[11]   Hermansyah A, Olly N.T, Admin A, Syukri and Wahyu, R 2016 *Der Pharma Chemica* **8(15)** 227-232

[12]   Chao P, Xing-bin Y, Ru-tao W, Jun-wei L, Yu-jing Q, Qun-ji X, 2013, *Electrochimica Acta*, **87** 401 -408

[13]   Olly N. T, Syukri, Admin A, Rahma F and Hermansyah A 2017 *IOP Conf. Series: Earth and Environmental Science* **65** 012053

[14]   Olly N. T, Hermansyah A, Emriadi, Hanif W and Admin A 2016 *Der Pharma Chemica* 6, **8(17)** 26-30

[15]   Chen-Hao W, Wei-Chen W, Hsin-Cheng H, Bing-Yuan Y *Advanced Powder Technology* **27, Issue 4** 1387-1395

[16]   Thomas E. Rufford, Denisa Hulicova-Jurcakova, Zhonghua Z and Gao Q. L 2009 *J. Phys. Chem.* C **113** 19335–1934

[17]   Daud T 2011 *Jurnal Ilmiah Sains* **11(1)** 97 – 101.

[18]   Guangjing, W. Yue, Z. Fen, Z. Zixu, S. Fei, H. Yi=Yu, Lei, C. Mu,P. 2016 *Journal of Energy Storage* **7**, 99 – 103

[19]   P.W.Atkins 1993. Physical Chemistry. Fifth Edition Oxford University Press 836-839