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Hydrothermal Assisted Microwave Pyrolysis of Water Hyacinth for Electrochemical Capacitors Electrodes

Nirwan Syarif [a*] and Marini Cinthya Pardede [a]

[a] *Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Sriwijaya, INDONESIA*

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ABSTRACT

We develop 'green' approach to prepare conductive carbon material from water hyacinth (*Eichhornia crassipes*) powder for use in electrochemical capacitor device. The features on morphology, crystallography and surface functionality were analyzed based on SEM, XRD and FTIR instrumentation, respectively. The electrical conductivities were measured using four-point probe. Electrochemical properties were studied using cyclic voltammetry. SEM analyses indicated the existence of nanoparticles in the carbon samples. XRD analysis showed that carbon sample had sharp peaks indicating crystallite carbon and sylvite. FTIR analysis showed that the carbon have common surface functionalities which also can be found in other conductive carbon samples. The electrical conductivities test showed that the carbon had 0.001–1.5 S cm^{-1} of conductivity. The shape of the cyclic voltammograms were typical for carbon electrode that use in electrochemical capacitor

1. Introduction

Water hyacinth (WH) of the title as the most obnoxious aquatic plants in the world. It can be easily grown in various water sources, and becomes the issue for most of countries. It is estimated that the population in one acre area containing 2 million individuals with a total weight of 500 tonnes. With such rapid growth, WH become more worst as for urban

*Corresponding author (N. Syarif). Tel/Fax: +62-711-580269. E-mail address: nnsyarif@gmail.com. ©2014. International Transaction Journal of Engineering, Management, & Applied Sciences & Technologies. Volume 5 No.2 ISSN 2228-9860 eISSN 1906-9642. Online available at http://tuengr.com/V05/0095.pdf.

communities, because it is main factor on silting of rivers, breeding places of mosquitoes and snakes, and give the slum impression to the region.

There are many ways to overcome its growth problems, one of them is by using re-use approaching, i.e. by way of the process into a product that has economic value. It contains organic fiber that physically can be processed into raw material of fertilizers manufacture (Patil *et al.* 2012), fibre board (Markland 2003), and carbon absorbent (Somboon *et al.* 2012). The composition of WH plant consist of 3.50% lignin, 48.70%, hemicellulose, 18.20% cellulose and 13.30% crude protein (Magdum *et al.* 2012). Considering that organic matter content is quite large, therefore the WH has potential to be developed as carbon electrode material in electrochemical devices.

In this work, water hyacinth (*Eichhornia crassipes*) was used to prepare carbons using hydrothermal assisted microwave pyrolysis technique. The method was chosen based on the ability to transform cellulosic materials into conductive carbons without much change in pores structures. High electrical conductivity and pores volume are basic requirement for the best electrochemical performance of carbon electrodes.

The electrode was applied as working electrode in the three electrodes system using base, acid and salt aqueous medium. The materials were characterized in terms of crystallographic, surface chemistry and electrical conductivity. Carbon electrode would be applied in energy storage or conversion devices, such as, electrochemical capacitor (supercapacitor), fuel cell and battery.

2. Materials and Methods

WH powder was used as raw material to prepare carbon. The powder was rinsed in tap water and dried in the sun light after 24 hours. As much as 40 g dry WH powder, 20mL demin water and 200 mg catalyst KOH put into 250 mL hydrothermal reactor. The reactor was heated in electrical oven at 180 ˚C for 16 hour for generated 30 bar hydrothermic pressure inside reactor chamber. The process obtained brownish black constituent that called torrefaction material. The material was transferred from the hydrothermal reactor to microwave furnace and pyrolyzed in domestic microwave oven at 1000 watts full power for 25 minutes. In this condition, the temperature inside furnace can reached 800 ˚C. Carbon was

tapped from the furnace after being cold in room temperature.

The EC electrodes were fabricated by mixing the WH carbon powder and graphite (50:50) bind together with 10% w/w of bronze filled epoxy resin (Dexton, USA). Circular electrodes were obtained from 0.5 g of mixture paste in a 10 mm diameter mold, and pressed under 3 tons load and were heated on a hot plate at 50°C for an hour.

SEM micrographs were obtained on JEOL JED-2300. X-ray difraction (XRD) patterns of the carbons were obtained on a Shimadzu X-ray difractometer XRD 7000 operating at 40 kV and 30 mA, using Cu-K_α radiation. FTIR spectra were obtained on Shimadzu IR Prestige 21. The pore structures were determined using mathematical model derived from iodine number and methylene blue number suggested by Nunes (2011). The electrical conductivities were measured using four point probe. Electrochemical properties were studied using cyclic voltammetry (CV). Electrochemical test for the electrodes were conducted in potentiostat (Cheapstat, University of California Santa Barbara, CA, USA) in aqueous electrolytes, i.e. H_2SO_4, KOH, $NaHCO_3$ and $K_2C_2O_4$. The potentiostat is capable for doing three electrodes configuration CV measurement with Ag/AgCl electrode as reference electrode and platinum rod as the counter electrode (Rowe *et al.* 2011).

3. Results and Discussion

Hydrothermal assisted microwave pyrolysis of water hyacinth produced high crystallite material containing graphitic carbon (47%) and KCl (20%) as revealed by the EDX measurement (Figure 1 C). Figure 1 A-B show micrographic images from carbon with 300, and 2000 times magnification. It is clearly visible that the carbon consists two distinguish features, i.e. waffle structures with a lot of cavities or pores and shining bead chain. The structures with cavity are well known as carbon with pores and the bead chain are KCl (sylvite). The carbon pores have diameters in the range of 10-50 nm. KCl crystal built some clusters (particles) as shown in Figure 1B. The size of the KCl particles were vary in the range of 10-17 nm.

*Corresponding author (N. Syarif). Tel/Fax: +62-711-580269. E-mail address: nnsyarif@gmail.com. International Transaction Journal of Engineering, Management, & Applied Sciences & Technologies. Volume 5 No.2 ISSN 2228-9860 eISSN 1906-9642. Online available at http://tuengr.com/V05/0095.pdf.

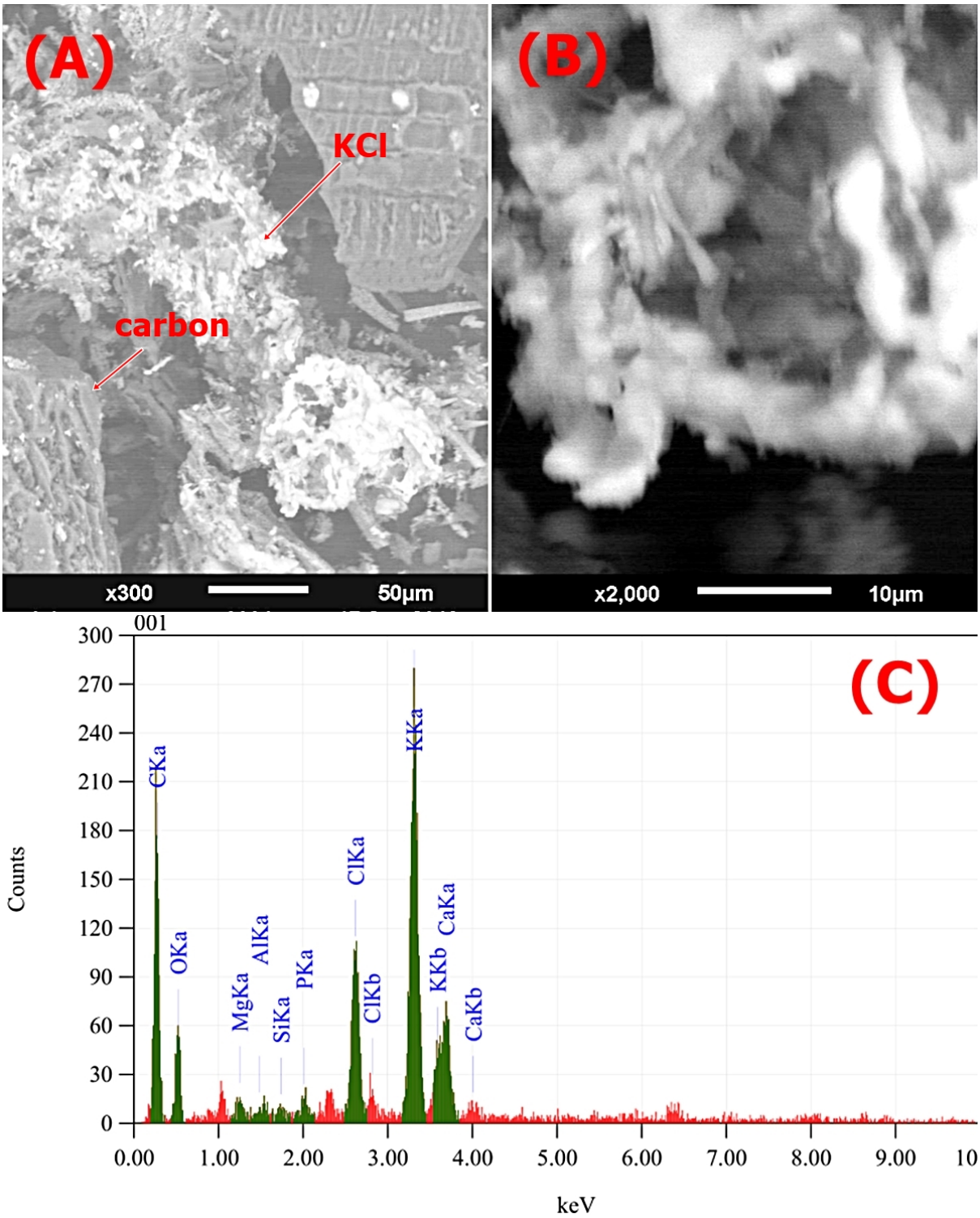

Figure 1: Micrographic image (A) 500 times (B) 20,000 times magnification and (C) EDX analysis of water hyacinth carbon

XRD difractogram (Figure 2) confirm that the material contained relatively large crystallite of KCl and turbostratic feature of carbon, i.e. mixing of amorphous and graphitic carbon or 2D carbon crystal. Figure 2 also reveals the excitation of other crystallite, that

match XRD pattern for KCl (sylvite) crystal. The crystal would become more attractive because present as larger crystallite detect as sharp peaks both 29˚ and 42˚.

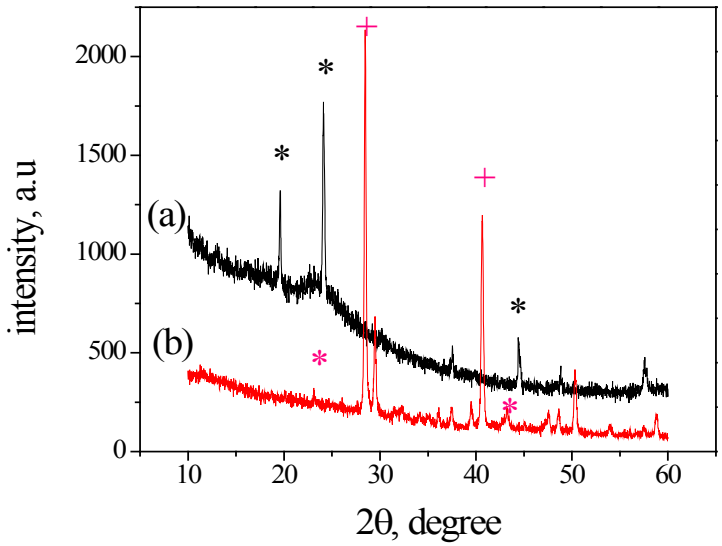

Figure 2: XRD spectrogram of (a) commercial activated carbon (Ciba) was added for clarify reading and (b) WH carbon,
(* = Carbon, ICDD no. 41-1487; + = KCl (Sylvite), ICDD no. 64-0312; others would be considerable as SiO_2, Al_2O_3, and CaO especially for WH carbon)

Other oxides might be co-exist in the carbon matrices, such as SiO_2, Al_2O_3 dan CaO because they inherently are important components or factors in plant histology. The XRD patterns of the carbon (Figure 2) show intense peaks at 2θ = 24° and 44° which respectively correspond to the [011] and [002] difractions of the graphitic framework confirm that the carbon materials have amount of graphitic carbon.

In 800 ˚C of temperature, the conductivity of the carbon started to be formed along with termination of the acid functional groups from the surface of the carbon. The decomposition of the functional groups produced H_2O and CO_2. In other words, carbon lost its functional group together with the increasing temperature followed by the reform of its hexagonal structures. It would be different after carbon was cooled. The hexagonal structure of the carbon would re-obtained with volatile molecule and reformed the functional groups of the carbon and thus the carbon increasing the resistivity as the functional groups formed on the carbon surface is quite excessive. It is clearly shown in Figure 3 that the carbon spectra has double small peaks in around 2300 – 2400 cm^{-1} which is the sum of some double bond stretching vibration of C=N, C=O and N=O. Single bond vibration band of C and O appears

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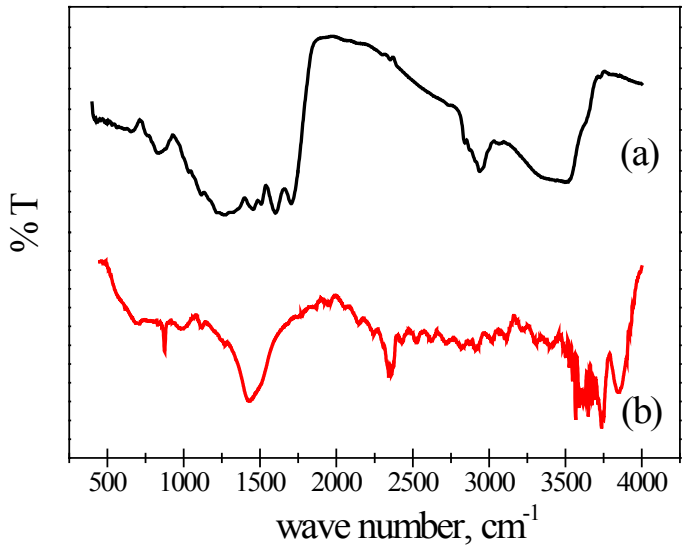

Figure 3: FTIR spectra of (a) commercial activated carbon (Ciba) was added for clarify reading and (b) WH carbon.

in 1400 cm^{-1} as broad peak. The height of the peaks indicated the presence of bending vibrations for same bonding configurations, such as C-O-C, C-O-O, and C-C-O (Matson *et al.* 1970). Spectrogram shows functional groups related to vibration presence of free O-H in 3800 – 4000 cm^{-1}.

The change in crystallography and surface functional groups will affect the electrical resistivity of carbon. Electrical resistivity is proportional to the magnitude of electrical conductivity (Mochidzuki *et al.* 2003). Therefore, conductivity can be explained by the results of resistivity measurement. Electrical conductivity values of carbon are influenced by the presence of sp^2 carbon in the activated carbon. The conductivity were measured between 0.001 – 1.500 S cm^{-1}.

Non-faradaic process in carbon electrode was detected in voltammogram with slope features indicating resistance of electrolyte solution that causes a voltage drop (Myland *et al.* 2002). The specific capacitance of carbon electrodes were calculated by using mathematical formula (equation [1]) and the integration of voltammogram curve $\left(\int IdV\right)$ were measured by using mathematical software (Kuo et al. 2007). Where ΔQ is the total amount of the charge accumulated over a potential window, ΔV, w is the mass of the electrode active material, I is the current, and s is the potential scan rate.

$$C_{avg} = \frac{\Delta Q}{(w \times \Delta V)} = \frac{\left(\int IdV\right)}{(s \times \Delta V \times w)} \quad (1)$$

The area in voltammogram curves for water hyacinth carbon electrode become wider as the increasing of scan rate and reach the maximum value of 0.26 Fg^{-1} in 2 mV/s (Figure 4). Specific capacitances were calculated and derived from acid (H_2SO_4), base (KOH) and salt electrolyte ($K_2C_2O_4$) were 0.0218, 1.4920 and 0.0168 Fg^{-1}, respectively (Figure 5). The surface area of WH carbon has 300 – 850 cm^2g^{-1} which dominated by micropores (60 – 80%) considerably support improving performance of the electrode. Effect of KCl (sylvite) crystal in carbon matrices should take into account because XRD difractogram suggested that the crystal is quite large. It is well known that KCl is generally used as the electrolyte. Therefore, it is make sense that KCl provides synergistic effect on the electrosorption process.

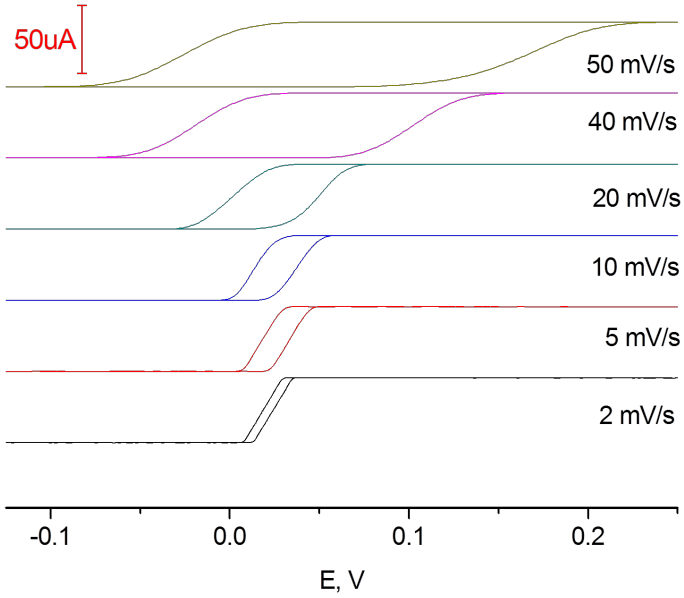

Figure 4: Voltammogram of water hyacinth carbon electrode in $K_2C_2O_4$ 4M and various scan rate.

Figure 5 shows the differences of voltammogram before and after the addition of surface active agent, triethanolamine (TEA). Voltammogram area of water hyacinth carbon electrode in $NaHCO_3$ and KOH are relatively the same before and after the addition of TEA but slightly shift to cathodic current. The situation is relatvely different if electrode was in H_2SO_4, whereas voltammogram area become narrower with addition of TEA, meaning that the capacitance of the electrode increased.

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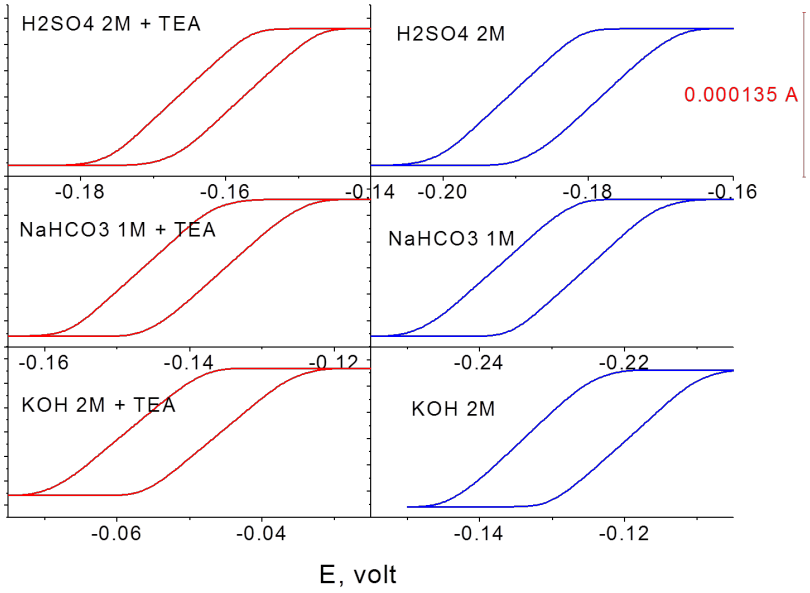

Figure 5: Voltammogram of water hyacinth carbon electrode in acid, base, salt electrolyte with and without TEA.

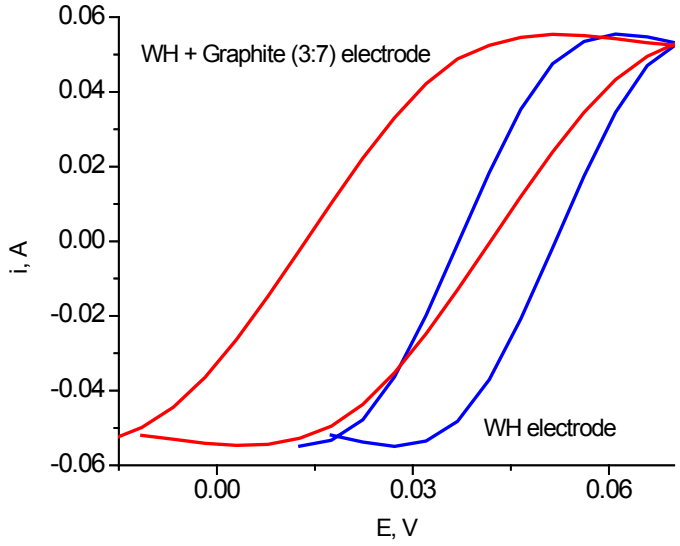

Figure 6: Voltammogram of water hyacinth (WH) carbon and WH + graphite electrodes in $K_2C_2O_4$ 1M. WH and WH + graphite electrodes were made from the mixtures of the materials and epoxy resin, respectively.

The capacitance of WH electrode was lower than WH + graphite electrode. The calculation of the voltammograms values in Figure 6 were performed using equation (1) revealed that the WH + graphite (3:7) and WH electrodes have 0.201 and 0.026 Fg^{-1} of capacitance, respectively. Therefore, the magnitude of capacitance reduced 10 times after whole graphite was changed to WH's carbon materials due to the reducing in graphitic carbon in electrode.

4. Conclusion

Hydrothermal assisted microwave pyrolysis of water hyacinth produced high crystallite material graphitic containing carbon (47%) and KCl, sylvite (20%) as revealed on EDX analysis. SEM image and XRD difractogram confirmed a few quantity of carbon nanoparticles and relatively large crystallite of KCl. The electrical conductivity value (0.001 – 1.5 Scm^{-1}) of carbon was complied with the category of carbon conductivity produced from biomass pyrolysis. Non-faradaic process of carbon composite was detected over voltammogram on all samples, which indicated the capability to carry capacitive process. The technique and the raw material used in this research should become green approach for making electrode material.

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*Corresponding author (N. Syarif). Tel/Fax: +62-711-580269. E-mail address: nnsyarif@gmail.com.

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Dr. Nirwan Syarif is an Assistant Professor in Department of Chemistry at Universitas Sriwijaya, Palembang, Indonesia. He received bachelor degree in Chemistry from Universitas Sriwijaya, the M.S. in Physical Chemistry from Bandung Institute of Technology, Bandung, Indonesia and the PhD in Physical Chemistry from University of Indonesia, Depok, Indonesia. His research interests involve studying materials for energy storage devices, such as fuel cell, battery and super capacitor.

Marini Cinthya Pardede is an undergraduate student in the Department of Chemistry at Universitas Sriwijaya, Sumsel, Indonesia. She is interested in doing research in the area of electrochemistry, especially carbon electrodes.

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