Composite Electrodes of Activated Carbon Derived from Cassava Peel and Carbon Nanotubes for Supercapacitor Applications

E. Taer[1,*], Iwantono[1], M. Yulita[1], R. Taslim[1], A. Subagio[2], Salomo[1] and M. Deraman[3]

[1]Department of Physics, University of Riau, 28293 Simpang Baru, Riau, Indonesia
[2]Department of Physics, Dipenegoro University, 50275 Tembalang-Semarang, Central Java, Indonesia
[3]School of Applied Physics, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia
*erman_taer@yahoo.com

Abstract. In this paper, a composite electrode was prepared from a mixture of activated carbon derived from pre-carbonization of cassava peel (CP) and carbon nanotubes (CNTs). The activated carbon was produced by pyrolysis process using $ZnCl_2$ as an activation agent. A N_2 adsorption-desorption analysis for the sample indicated that the BET surface area of the activated carbon was $1336\ m^2\ g^{-1}$. Difference percentage of CNTs of 0, 5, 10, 15 and 20% with 5% of PVDF binder were added into CP based activated carbon in order to fabricate the composite electrodes. The morphology and structure of the composite electrodes were investigated by scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques. The SEM image observed that the distribution of CNTs was homogeneous between carbon particles and the XRD pattern shown the amorphous structure of the sample. The electrodes were fabricated for supercapacitor cells with 316L stainless steel as current collector and 1 M sulfuric acid as electrolyte. An electrochemical characterization was performed by using an electrochemical impedance spectroscopy (EIS) method using a Solatron 1286 instrument and the addition of CNTs revealed to improve the resistant and capacitive properties of supercapacitor cell.

Keywords: Activated carbon, Supercapacitor, Cell resistance, Carbon nanotubes.
PACS: 81.05.U-, 82.47.Uv, 87.15.Vc, 88.30.rh

INTRODUCTION

Supercapacitor or electrochemical double layer capacitor (EDLCs) is an energy storage device that uses to store and release energy [1]. Supercapacitor consists of electrodes, separator, current collector and electrolyte. The supercapacitor performances (energy and power density) mostly depend on the electrode and electrolyte properties. Many carbon based materials have been developed as electrodes for EDLCs, such as graphene, carbon nanotubes (CNTs), carbon aerogels and activated carbon [2]. The activated carbon is commonly used as electrode material for some advantages such as high surface area, wide availability and low cost production compared to other carbon based materials. Recently, many studies focus on EDLCs to produce activated carbon electrodes from biomass waste materials by chemical and physical activation process.

Biomass materials as carbon electrode precursor for supercapacitor application by using chemical and physical activation methods has been widely studied and reported [3]. Ismanto et al have used cassava peel (CP) to produce supercapacitor electrodes by using chemical activation process of KOH activation agent [4]. The activated carbon electrode with surface area and capacitance specific obtained of $1352\ m^2g^{-1}$ and $153\ Fg^{-1}$, respectively. A $ZnCl_2$ activation agent has also been used in chemical activation process for CP and had a surface area as high as $1500\ m^2g^{-1}$ [5]. In this paper a high surface area activated carbon from CP waste of Riau local area by using the $ZnCl_2$ activation agent will be demonstrated. The porosities properties of CP based activated carbon were investigated by using N_2 adsorption-desorption method. The influence of CNT addition in CP based activated carbon electrodes for improving supercapacitive properties such as equivalent series resistance and specific capacitance will be discussed in detail, the micro-crystallite and morphologies properties of the composite CP activated carbon and CNT electrode were also studied by X-ray diffraction and scanning electron microscopy measurement.

EXPERIMENTAL

CP was first pre-carbonized and followed by ball-milling and sieving to obtain carbon grains (CG) with particle size of less than 103 micron [6]. The CG was then mixed with an activation agent of ($ZnCl_2$) with a weight ratio of 1:1.5. Two hundred ml of distilled water was added into 100 g of the mixture materials and magnetically stirred in 2 hours before drying for 24 hours. Carbonization of the dried mixture materials was done at 600 °C under N_2 atmosphere (flow rate of 1.5 litter per minute) and activated carbon powder (ACP) produced were washed using 1% HCl and distilled water until the pH of distilled water turns to neutral, and finally dried it at a temperature of 100 °C for 24 hours before sieving to obtain an ACP with particle size of less than 103 micron.

Five different electrodes in coin shape were prepared from the ACP and CNTs (Nanostructured & Amorphous Materials.Inc), by using a PVDF (Acros Organics) adhesive as a binder material. Varies weight of these materials shows in Table 1 was carried out by ball-milling technique for 1 hour. Fabrication of an electrode in the form of sheet ~0.2 mm thickness from these materials was manually done using a mortar [7]. The produced sheet was then cut using coin shaped mold to get an electrodes with diameter of 15 mm. The coin shaped electrodes were followed by heating at 75 °C for 24 hours and the electrode was then used to fabricate a symmetrical supercapacitor cells based on our previous method [8,9].

TABLE 1. Electrode compositions.

Electrodes	Compositions by weight (%)		
	ACP	PVDF	CNT
A	95	5	0
B	90	5	5
C	85	5	10
D	80	5	15
E	75	5	20

The porosity characteristics such as BET surface area (S_{BET}), mesopore surface area (S_{meso}), micropore surface area (S_{mic}), external surface area (S_{ext}), average pores diameter (D_{av}) of ACP were determined by an adsorption-desorption isotherm experiment (N_2 gas at 77 K) using an accelerated surface area and a porosimeter system (ASAP 2010 micromeritic). The BET surface area was calculated from the isotherms using the BET equation [10]. In this experiment, the cross-sectional area of a nitrogen molecule was assumed to be 0.162 nm2. The Dubinin-Radushkevich equation was used to calculate the micropore volume from which the micropore surface area was then determined [10]. A surface microstructure of the electrodes was characterized by a FESEM (SUPRA

PV 55 model). The diffraction patterns were obtained using a diffractometer (Bruker AXS D8 advance) that employed CuKα radiation with a 2θ range from 0o to 70o.The performance of fabricated supercapacitor cells was investigated by an electrochemical impedance spectroscopy measurement using Solartron 1286 conducted at 10 mV over a frequency range of 100 kHz to 10 mHz.

RESULT AND DISCUSSION

Fig. 1 show an adsorption-desorption curve for the CP based ACP. This curve is typical behavior for a type IV material based on IUPAC classification [11], indicating the CP based activated carbon comprising both micro-pores and meso-pores. The pore size distribution can be observed in Fig. 1b.
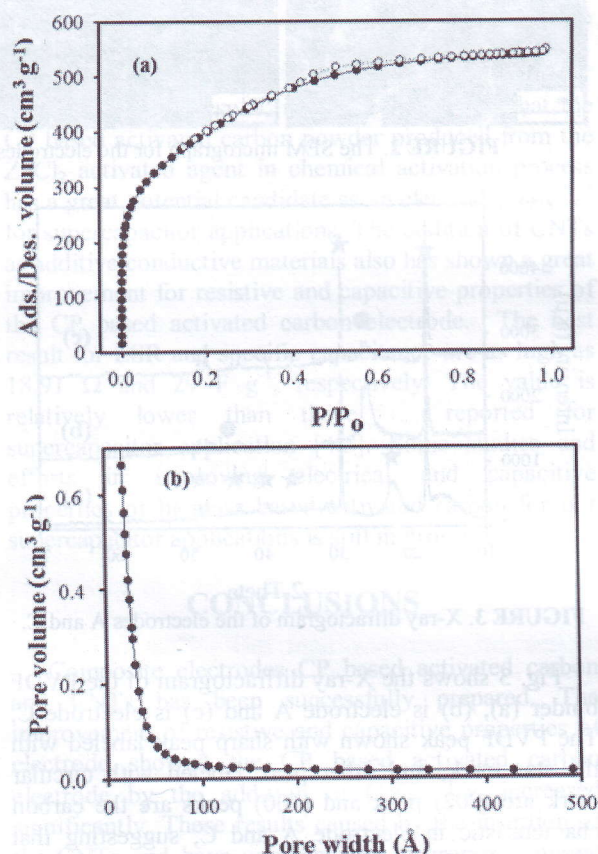

FIGURE 1. N_2 gas adsorption-desorption (a) and (b) pore size distribution of activated carbon from CP.

TABLE 2. Porosity data for CP based the ACP.

S_{BET} (m^2g^{-1})	S_{Mikro} (m^2g^{-1})	S_{Meso} (m^2g^{-1})	S_{Ext} (m^2g^{-1})	D $(Å)$
1374.27	185.17	1090.86	1189.10	24.41

The porosity properties are listed in Table 2. From the table shows the CP based activated carbon is very

porous material with mesopores as a main contributor to the S_{BET} value (almost 80%). A similar result was observed for activated carbon powder used the $ZnCl_2$ activated agent from biomass precursor with the optimum S_{BET} value as high as of 1489 m^2 g^{-1} (89% mesopores) for the bagasse based ACP [12]. The study of *camellia oleifera* shell based ACP found the maximum S_{BET} as high as of 2086 m^2 g^{-1} (87% mesopore) [13]. Our results show a messopores characteristic than those reported by Ismanto *et al.* [4].

Fig. 2 shows the SEM micrographs for electrodes A (2a and 2c) and C (2b and 2d) with different magnifications. The micrograph 2(a) shows the sizes of CP activated carbon particle are 1-2 μm in range with the presence of open macropores between the carbon particles. The addition of 10% CNTs (Fig. 2b), can be observed that the open macropore occupied by CNTs which distribute homogeneously. Meanwhile, Fig. (2b and 2c) are clearly seen that the surface morphology of the CP carbon electrode and the CNTs composite electrodes. The presence of CNTs should improve the resistive and capacitive properties of the CP based activated carbon electrode and will be discussed detail in section of cell properties discussion.
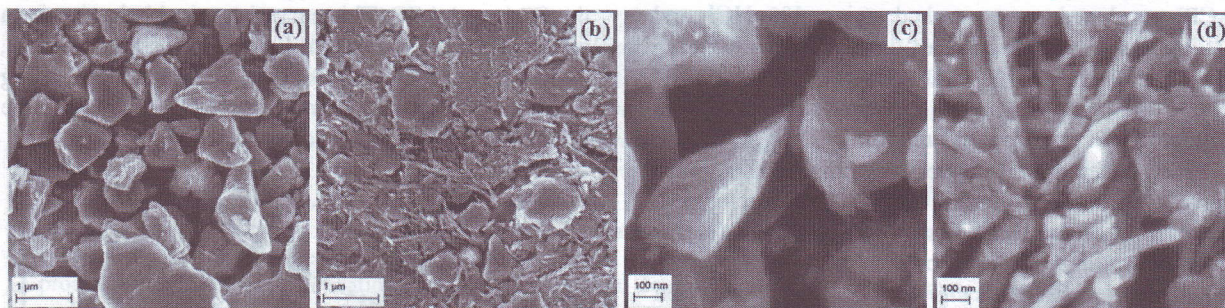

FIGURE 2. The SEM micrograph for the electrodes A (a and c) and C with different magnification (b and d).
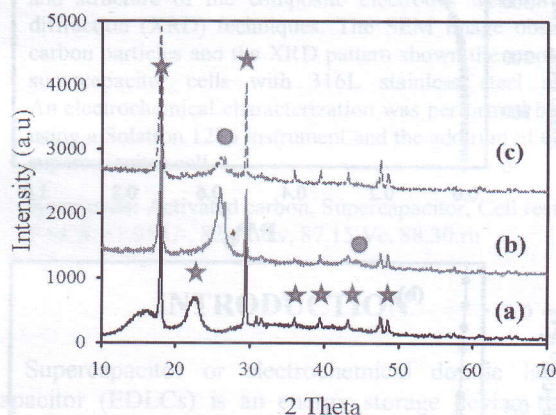

FIGURE 3. X-ray difractogram of the electrodes A and C.

Fig. 3 shows the X-ray diffractogram of the PVDF binder (a), (b) is electrode A and (c) is electrode C. The PVDF peak shown with sharp peak labeled with the star mark, and other peak labeled with circular mark are (002) peak and (100) peaks are the carbon characteristic in electrode A and C, suggesting that ACP and CNTs are amorphous structures [14]. However, for the electrode C, the peak (002) decreases sharply and the peak (100) is also very weak, this indicates that the addition of CNTs causes localized defects on ACP particles and suggest that composite electrode ACP and CNTs are more amorphous structures, which leads improve the porosity properties of the electrode. Finally the addition of CNTs may improve the electrical and capacitive properties of the electrode.

The electrochemical (resistive and capacitive) properties of the composite electrodes were obtained by an electrochemical impedance spectroscopy (EIS) measurement. Fig. 4 shows the Nyquist plot of different CNTs addition electrodes in the frequency region of 10 mHz to 1 MHz, the inset shows the Nyquist plot in frequency region of 10 mHz to 1 kHz. The figure clearly shows that the plot consists of three different regions, namely: a semi-circular section, a line with a slope of 45° and a line perpendicular to the axis of the real impedance (Z '). The first intersect of the curve with real impedance axis (Z ') contributes to the electrolyte resistance, contact resistance between the current collectors and electrodes (Rs), which is formed at a high frequency region (1MHz). A polarization resistance (Rp) was generated by fit of the Nyquist plot, the extended of the plot that intersects with the Z' axis is namely as Rp . The calculation of Rs, Rp and ESR values that are based on data in the Fig. 4 was carried out using standard Z-View software by the fitting technique [9]. The resistive properties of the cells (Rs, Rp and ESR (Rs-Rp)) are tabled in the Table 3.

TABLE 3. Resistive properties of CP activated carbon based with different CNTs percentages.

Sample Code	R_s (Ω)	R_p (Ω)	ESR(Ω)
A	19.33	4264.40	4283.70
B	3.70	645.53	641.83
C	2.93	84.62	81.70
D	1.39	20.30	18.91
E	0.68	13.61	12.92

FIGURE 4. Nyquist plot of the supercapacitor cell with difference percentage addition of CNTs electrodes.

directly proportional to the addition of CNTs, it is due to the reduction in cell resistance properties that have been described in the previous part.

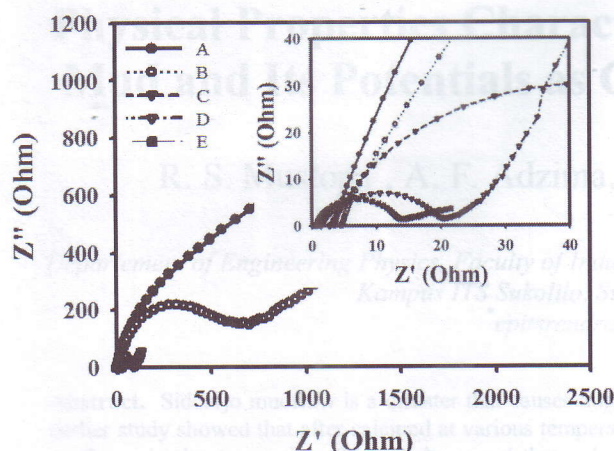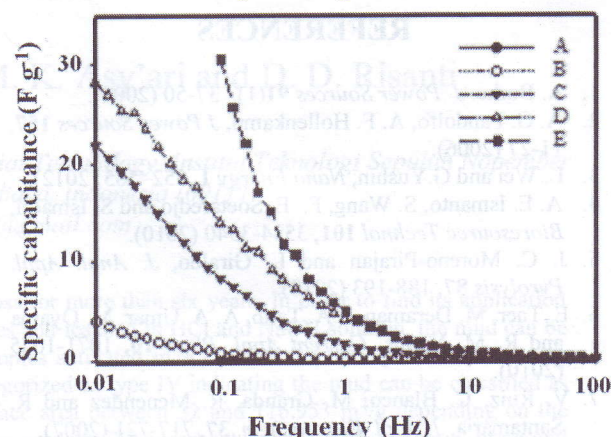**FIGURE 5.** The specific capacitance values versus frequency for the supercapacitor cell with difference percentage addition of CNTs electrodes.

From the Table 3, the influence of CNTs in CP based activated carbon electrode is clearly improved the electrical properties of the cells. The increasing of CNTs addition in the carbon electrode is proportional to the decrease of cell resistance properties. It is clearly shown that the values of R_s, R_p and ESR decreased significantly for the samples after CNTs additions. For example, the value of Rs, Rp and ESR are reduced significantly after 20% CNTs addition such as; from 19.33 Ω to 0.68 Ω, from 4264 Ω to 13.61 Ω and from 4283 Ω to 12.92 Ω, respectively. The improving Rs related to the closing of the open macro-pores among the carbon particles and improving the interfacial contact between the current collector and electrode and reducing the Rs value. The decrease of the electrode resistance value (Rp) is also observed by mean of the effect of the CNTs additions. This phenomenon has been expected previously since CNTs are good conductive materials. The insertion of CNTs between the carbon particles which fill in the open macropore has been giving a bridge for the electron transport that will lead reducing the electrode resistance. A reduction in ESR is due to the reducing of R_s and R_p. In conclusion, the addition of CNTs to the samples gave great affects on the resistance properties of supercapacitor cell.

By using a relation of $C_{sp} = -1/\omega Z''$ [8], the specific capacitance of the composite electrodes can be obtained from the Nyquist plot (Fig. 4). The specific capacitance versus frequency is shown in the Fig. 5. The CNTs addition has increased the specific capacitance values with significant increase were observed, especially at low frequency region (10 mHz). It is because the ions of electrolyte can be easily diffuse into the carbon pores in long cycle time and consequently more double layer of the ions-electrons pairs inform at the interface of the carbon surface and the electrolyte. Improving the specific capacitance is

Based on the results, it can be concluded that the CP based activated carbon powder produced from the ZnCl$_2$ activated agent in chemical activation process has a great potential candidate as an electrode material for supercapacitor applications. The addition of CNTs as additive conductive materials also has shown a great improvement for resistive and capacitive properties of the CP based activated carbon electrode. The best result for ESR and specific capacitance are as high as 18.91 Ω and 29 F g^{-1}, respectively. The value is relatively lower than those reported for supercapacitor application [4,5]. Some studies and efforts in improving electrical and capacitive properties of biomass based activated carbon for our supercapacitor applications is still in progress.

CONCLUSIONS

Composite electrodes CP based activated carbon and CNTs has been successfully prepared. The improvement of resistive and capacitive properties of electrode showed the CP based activated carbon electrode by the addition of CNTs has increased significantly. These results caused by the insertion of the CNTs and have occupied the macropores among the carbon particles. Finally, the composite electrode has been prepared by the simple and easy preparation method.

ACKNOWLEDGMENTS

(UKM-GUP-2011-216, UKM-DLP-2012-022 and UKM-DLP-2012-023) Malaysia.

REFERENCES

1. A. Burke. *J Power Sources* **91**(1), 37-50 (2000).
2. A. G. Pandolfo, A. F. Hollenkamp, *J Power Sources* **157**, 11-27 (2006).
3. L. Wei and G. Yushin, *Nano Energy* **1**, 552–565 (2012).
4. A. E. Ismanto, S. Wang, F. E. Soetaredjo and S. Ismadji, *Bioresource Technol* **101**, 3534-3540 (2010).
5. J. C. Moreno-Pirajan and L. Giraldo, *J. Anal. Appl. Pyrolysis* **87**, 188-193 (2010).
6. E. Taer, M. Deraman, I. A. Talib, A. A. Umar, M. Oyama and R. M. Yunus, *Current Appl. Phys.* **10**, 1071-1075 (2010).
7. V. Ruiz, C. Blanco, M. Granda, R. Menendez and R. Santamaria, *J. Appl. Electrochem.* **37**, 717-721 (2007).
8. E. Taer, I. M. Deraman, I. A. Thalib, A. Awidrus, S. A. Hashmi and A. A. Umar, *Int. J. Electrochem. Sci.* **6**, 3301-3315 (2011).
9. E. Taer, M. Deraman, I. A. Talib, S. A. Hashmi and A. A. Umar, *Electrochimica Acta* **56**, 10217-10222 (2011).
10. P. A. Webb and C. Orr, *Analytical Methods in Fine Particle Technology,* Georgia: Micromeritiecs Instrument Corp (1997).
11. K. S. W. Sing, D. H. Everret, R. A. W. Haul, L. Mouscou, R. A. Pierotti, J. Rouquerol and T. Siemieniewska, *Pure & Appl. Chem.* **57**, 603-619 (1985).
12. W. -J. Si, X. -Z. Wu, W. Xing, J. Zhou and S. -P. Zhuo, *J. Inorganic Mater.* **26** (1), 107-112 (2011).
13. J. Zhang, L. Gong, K. Sun, J. Jiang and X. Zhang, *J. Solid State Electrochem.* **16**, 2179–2186 (2012).
14. R. Farma, M. Deraman, A. Awitdrus, I. A. Talib, E. Taer, N. H. Basri, J. G. Manjunatha, M. M. Ishak, B. N. M. Dollah and S. A. Hashmi, *Bioresource Technol.* **132**, 254–261 (2013).

74