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The effect of temperature deposited on the performance of ZnO-CNT-graphite for supercapacitors

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Abstract. Carbon nanotubes (CNTs), graphite are now widely studied as the electrodes of supercapacitor, owing to their high conductivity, large surface area, chemical stability, etc. A lot of research has been focused on Carbon/metal oxide nanocomposite electrode for Electrode supercapacitor because it will increase the total capacitance. In this research, ZnO nanoparticles were deposited onto substrate CNT:Graphite in different temperatures such as 300^o, 350^o, and 400^oC. The characterization of the crystal size using *X-Ray Diffraction (XRD)* patterns showed ZnO material peak was detected a ZnO crystallite. The size of ZnO crystallite in 300^o, 350^o, and 400^oC consecutively is 101.1; 103.4; and 116.7 nm. The test results are *Electrochemical impedance spectrometry* (EIS) high electrical conductivity values obtained on the composition of ZnO-CNT-graphite with a temperature of 350^oC 4.6 (S/m); and (2) the highest value of capacitance in 300^oC is 1.23 F /g.

1. Introduction

The energy crisis towards the end of the 20^{th} century cannot offset the high demand. Since electric energy becomes one of the best alternatives for future energy supply, research on renewable energy devices continues to grow. However, the constraints now are related to the energy storage. Supercapacitors are considered as an ideal energy storage device due to their long cycle-life, high power and energy density characteristics [1-2]. Currently, supercapacitors are developed for various functions such as military technology, aerospace, and electric cars [3]. There are two types of supercapacitors based charger principle namely electrochemical double layer supercapacitors (EDCL) and pseudocapacitors. Carbon nanotubes (CNTs) are now widely studied, the most notably for EDCL. Kim et al. [4] report supercapacitors based CNTs and graphite have electron storage principle which can increase conductivity, because it has large surface area. Metal oxides, such as RuO_2 , TiO_2 and MnO_2 have a redox reaction principle which were studied for supercapacitor, namely pseudocapacitor. It can increase a capacitance, but it has a weakness. It takes time for chargering compared to EDCLs type [5]. In recent years, there is a method that combines both these supercapacitors which can improve the performance of the charge transfer. In addition, the ability of

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material that is filled over and over again becomes more stable. Moreover, it has a high capacity and the characteristics of fast charger [6].

Zinc oxide (ZnO) is a semiconductor material that has a high power density, which is 650 Ah/g for supercapasitor. It happens because of the significant advantages of low cost, abundant availability and eco-friendly. Recently, ZnO has been used as supercapacitor electrodes with carbon nanocomposite material types [7]. In this research, the focus is on the exploration of supercapacitor electrode-based ZnO-CNT-graphite nanocomposites. The CNT-graphite were screen-printed on the stainless steel foil (SS foil) substrate and ZnO source precursors (zinc acetate) were deposited on CNT films by spraying pyrolysis of different temperatures. The purpose of this research is to look for good temperature deposited and to inverstigate the relation between ZnO crystal size with capacitance and conductivity supercapacitors.

2. Experimental

The materials used in this study is foil substrates (MTI, Malaysia). They were only 2 cm^2 used in this research. Zinc Acetat Tetrahydrate (Merck, Australia) was used as electrodes material. Electrolyte which consist of KCl (Merck, Germany) was used as the transport mechanism for the redox mediator of the electrode. The CNT powder which prepared using *spray pyrolysis method* as previous reported by Subagio, et al., 2009 [8-9] was used as electrode material. Ethanol (Merck, Germany), terpineol (Sigma Aldrich, USA), ethylcellulose (Sigma Aldrich, USA), monoethanolamine (Merck, Germany), and ISO-Propanol (Merck, Germany) were used without purification.

0.2 g of ethylcellulose was dissolved in 4 mL ethanol which is stirred for 10 minutes, followed by mixing 1.6 g terpineol into the binder. The CNT-graphite (composition of mass 1:1) was dispersed in the binder with stirrer for 10 minutes. Then, CNT paste was deposited onto the SS Foil substrate by using *doctor blade method* and drying in the temperature of 150 °C for 2 hours. Then, ZnO nanoparticles was synthesized by sol-gel method 0.5 M using $Zn(CH_3COO)_2.2H_2O$ as sources of Zn. In addition, isopropanol (IPA: $(CH_3)\ _2CHOH$), monoethanolamine (MEA: $HOCH_2CH_2NH_2$) were stirred for 30 minutes. ZnO liquid was sprayed onto CNT-graphite substrate in different temperatures, such as in 300, 350, 400 and, 450 °C. The surface structure of electrodes were characterized by X-ray diffraction spectroscopy (XRD, Philip Analytical X-Ray B.V) with Cu Kα radiation (λ=1.5418 Å) at 40 kV and 20 mA of Electrochemical impedance spectrometry (EIS, Hioki 3522-50) was performed to study the electrodes by using a standard double cell containing 1 M KCl aqueous solution.

3. Result and discussion

Supercapacitor electrode of the samples summarized in Table 1 shows the name of samples in this study.

Table 1. Samples of supercapacitors electrode

Sampel	Composition
S1	CNT-graphite
S2	CNT-graphite ZnO 300 °C
S3	CNT-graphite ZnO 350 °C
S4	CNT-graphite ZnO 400 °C
S5	CNT-graphite ZnO 450 °C

There were 4 samples (S1, S2, S3 and S4) can be tested, while sample S5 cannot be tested because the S5 sample was broken. This is due to high temperatures in coating so that the coating of CNT-graphite-ZnO cannot be included. The 4 samples test by XRD of ZnO layer coated on the CNT-graphite nanocomposite is shown in Figure 1.

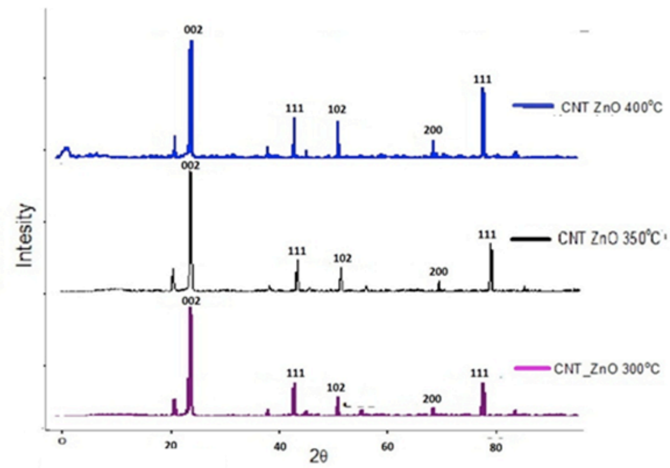

Figure 1. The XRD results of ZnO-CNT-graphite electrode at various temperatures of 300, 350 and 400 °C

Figure 1 shows that a diffraction pattern is dominated by diffraction peak of carbon. Those are adjusted with reference to the program *Powder Diffraction Standarts*. The carbon type detected in reference (JCPDS number 020 456) looks to dominate the summit between 26.29 - 26.39°. It shows the type of carbon with (002) orientation of the hexagonal structure of graphite [10]. Diamond structure was dominated by the peak between 43.44 - 43.91° with reference of JCPDS number 060 675 to the orientation (1 1 1). ZnO material and the peak were detected at peak 66.20 – 66.77° in JCPDS number 011 136 with the (200) orientation. Peak areas of the crystal orientation is used in the calculation to find crystallite size because the dominant peak is sharp and strong with a high intensity. Crystallite size was calculated using the scherer equation shown in figure 2.

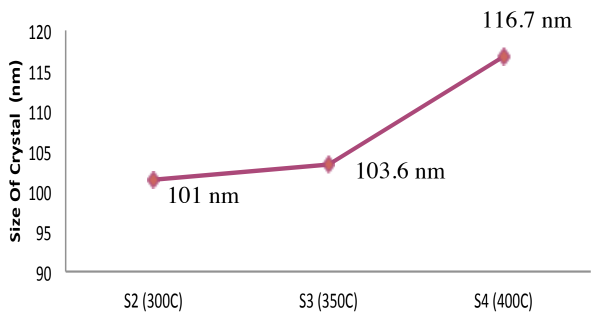

Figure 2. Crystalite size relationship chart with temperature variation of ZnO coating

ZnO resulted from the source of Zn acetate solution carried spray with high temperature will vaporize CH3COO and ZnO oxidizes with the air binds atoms into ZnO [11].

$$Zn(CH_3COO)_2.2H_2O_{(solid\ near\ substrate)} \xrightarrow{heat} Zn(CH_3COO)_2.2H_2O_{(gass)} \rightarrow ZnO + CH_3COO_{(gass)} \quad (1)$$

The size of ZnO crystallite in 300, 350 and 400 °C consecutively is 101.1; 103.4 and 116.7 nm. This indicates that the increasing of temperature coatings can increase the particle size of ZnO material. Crystallite size becomes larger when temperature increases during the ZnO deposition. The size of the crystal lattice parameter values increases due to the temperature increases. It is to produce a modified configuration for new crystal grain boundaries, so it looks as if the grain size becomes larger [12].

The purpose of testing Electrochemical Impedance Spectroscopy (EIS) is to find the value of the conductivity and capacitance of CNT-graphite-ZnO electrodes mode at frequency range that is given between 0.1 KHz to 100 KHz. It aims to further evaluate the electrochemical behavior of the fabricated electrodes. The S1, S2, S3, and S4 Nyquist curves exhibited a semicircular arc in the high-frequency region and a straight line in the low frequency region. Electrical conductivity value can be calculated using the equation (2). The results of the electrical conductivity of each sample sheet are shown in Figure 3 :

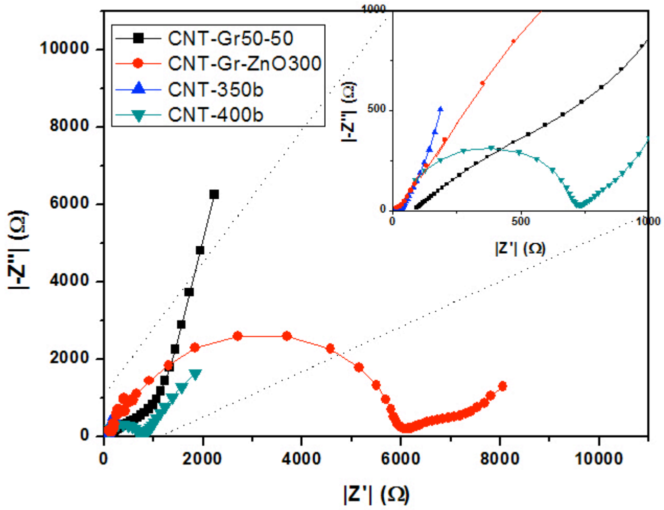

Figure 3. Nyquist impedance plots for electrode of different deposition temperature.

Figure 3 shows a graph of the nyquist impedance for samples S1, S2, S3 and S4. The graph explains the value of the charge transfer resistance (R_{ct}). The 45° slope portion in the low-frequency regions demonstrated the Warburg impedance of the electrolyte into the interior of the electrode surface and ion diffusion/transport into the electrode surface [13]. When ZnO material is add, the visible arc size enlarges. This can be saw in the sample S2, S3, and S4. Magnification corner semicircle described in the graph shows the capacitance properties of materials [14]. The height of conductivity is show in Table 2. When there is no addition of ZnO, it will increase conductivity.

Table 2. Conductivity (σ)and interfacial electron transfer resistance (R_{ct}) of the electrodes

	S1	S2	S3	S4
$R_{ct}(\Omega)$	974.04	6113.34	34.32	751.74
σ(S/m)	0.16	0.22	4.6	1.8

Results consecutive R_{ct} value sample respectively is 751.74; 34.32; 6113.33 and 974.04 Ω. The conductivity can be calculated from:

$$\sigma = \frac{t}{R.A} \quad (2)$$

t, R and A mean the thickness, resistance and surface area of electrode. For the cell with CNT-graphite (S1), the value of conductivity (Table 2) is 0.16 S/m. The increasing of conductivity with addition ZnO happened for the samples of S2, S3 and S4. However, there is a decrease in the conductivity of sample S4 to be 1.8 S/m, but it is still higher without the addition of ZnO. The addition of ZnO has a significant influence on the electrical conductivity. The smallest crystal sizes lead to facilitate the mobility of electrons. ZnO Crystals will produce a set of items denser. Moreover, it facilitates the electron transfer distance so that the conductivity of the electricity generated will be greater [15]. However, the deposition in temperature of 400 °C degrades the conductivity to be 1.8 S/m. This is because a large amount of ZnO covering the carbon destroys the surface structure of carbon morphology. The overall addition of ZnO increases a significant multiple value of conductivity without addition ZnO which is higher than multiple value addition MnO_2/CNT [6, 16] and TiO_2/CNT [17].

To investigate a specific capacitance calculation, it can be calculated with the equation (3). Specific capacitance can be defined as the ability of a capacitor to store charge at a certain frequency per unit

From the data processing results, EIS is formulated as follows:

$$C = \frac{1}{2\pi f Z m} \quad (3)$$

f, Z and m are the frequency, impedance and mass electrode. The result of calculation represented in diagram (Figure 4). Specific capacitance (Cs) on several frequencies obtained on the sample S2 has the largest capacitance is 1.23 F/g at a frequency of 0.1 Hz. Then sample S1 has a capacitance of 1.7 x 10^{-2} F/g at a frequency 0.5 Hz. Sample S3 has a frequency of 4.09 x 10^{-1} F/g at a frequency of 0.2 Hz. Then, sample S4 has a capacitance of 1.95 x 10^{-1} F/g at a frequency of 0.5 Hz.

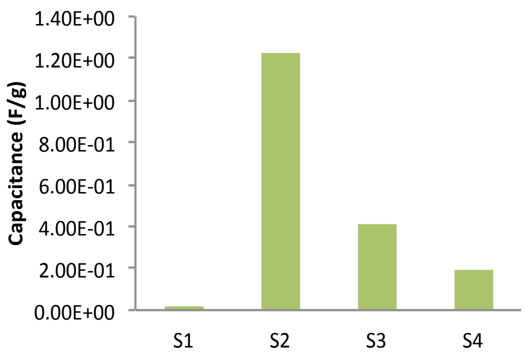

Figure 4. Diagram capacitance value analysis results on testing Electrochemical Impedance Spectroscopy

In addition, ZnO coating in the manufacture of ZnO-CNT-graphite nanocomposite electrode can improve conductivity and capacitance values. The high capacitance in S2 sample was caused by effect of the small crystallite size of ZnO. This effect will increase redox reaction and support electrons into electrolyte in the ZnO-CNT-graphite electrode and connect the contact between electrodes and electrolyte [14]. They can improve the utilization ratio of the electrode active material in storing an electric charge [18]. The increasing of the ZnO crystallite size will cover structure of carbon material, so it will intrude carbon to storage of the redox reaction from Zn. Value of conductivity increases until deposition temperature of 350 °C, the same result has been obtained by Aravinda [6] and Zhang [7]. The high deposition temperature will increases a crystallite size of ZnO and carbon materials, however above a temperature of 350 °C, ethylcellulose as a material binder of carbon is damage. It results carbon material inovolved broken and affect decrease of conductivity values.

4. Conclusion

Based on the results of the study, it can be concluded that manufacturing of ZnO-CNT-graphite nanocomposite with a different temperature of ZnO deposition has been successfully. The addition of ZnO with given temperature can affect the value of conductivity and capacitance at the electrodes. The studies reveal that the supercapacitors have good capacitance and conductivity. Hence, values obtained the best results with the highest capacitance in temperature 300^{o}C and high conductivity in 350^{o}C deposition.

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