

PREPARATION OF CARBON NANOTUBE FROM SESAME OIL AND ITS ELECTROCHEMICAL PROPERTIES

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ABSTRACT

The research of the development of carbon nanotube electrodes based on sesame oil soot and their application in electrochemical double layer capacitors has been conducted. Carbon nanotube was prepared by plasma pyrolysis of sesame oil with or without hydrothermally - catalytic treatment. XRD showed the existence of carbon crystal in $2\theta = 24^\circ$ and 45° . FTIR patterns showed that O – H, C = O and C = C groups existed on the surface of the carbon. Carbon pore structure measurement showed the pore surface area was $592,3 \text{ m}^2\text{g}^{-1}$ which was dominated by micropore. The conductivity was $0.1 - 1 \text{ S.cm}^{-1}$. The existence of carbon nanotube was confirmed by SEM image with percentage of C and O were respectively 88.82 % dan 11.18 %. The electrochemical properties were tested in 3-electrode system with H_2SO_4 , KOH dan NaNO_3 as electrolytes. Cyclic voltammetry showed that the highest capacitance was $0,0251 \text{ Fg}^{-1}$.

Keywords : EDX, potentiostat, voltammetry, hydrothermal, soot.

1. Introduction

Carbon nanotube (CNT) is very potential to be used as electrode material in electrochemical double layer capacitor (EDLC) due to its unique porosity. This is mesoporosity that induced by tube entanglement that makes CNTs highly accessible to the electrolyte, therefore [1], high electrolyte accessibility and thus high capacitance [2]–[4]. Low cost CNT can be made from natural precursor such as used palm oil [5], castor oil [6], mustard oil [7] and sesame oil [8]. Among those oils, sesame oil has shortest carbon chain, therefore it gives shortest tubes that their entanglements provide more electrolyte accessibility. Besides that, sesame oil can be obtained easily.

Plasma pyrolysis was performed to obtain carbon nanotube. The procedure was done by Prashant [7]. By using this technique, sesame oil mixed with fuel (ethanol) with a ratio (1:1) and fired to produce flame with soot. Soot comes out from flame accommodated with stainless plate. Pore structures, crystallography and morphology of CNT were characterized by using FTIR/Boehm titration, XRD and SEM techniques.

2. Methodology

CNT Preparation

Sesame oil was mixed with ethanol at a ratio of 1:1 and burned to produce sooty flame. Soot was collected on a steel plate and collected from the plate by using a razor blade. Soot generated was to be varied with or without hydrothermal treatment. Hydrothermal treatment was done by using isolative tube placed inside the electrical oven. A total of two reactors were provided to be placed together into an electric oven. The first reactor contained one gram of soot added with 0.08 grams of KOH. Second reactor contained one gram soot without catalyst. The reactor and its contents, respectively, stirred for one minute with a spatula. The reactors were put in the oven and heated to 200 ° C for 16 hours, so that the pressure inside the reactor reached 30 bar. Non-hydrothermal carbon was obtained directly from plasma pyrolysis.

The electrodes were made by mixing carbon and graphite with ratio 1: 2. 10% (w/w) of epoxy resin and 15 drops of triethanolamine (TEA). This mixture was homogenized, put into mold with 1 cm of diameter and then casted into pelet using stainless die. The pressure applied was 4 tons, heated at 60 °C for 30 minutes and then cooled.

Characterization

Pore structures, i.e. surface area, total volume ore and total micropore were determined by using mathematical relationship that used calculated values of iodine number (IN) and methylene blue number (MBN). The formulas are given below:

$$S_{(m^2g^{-1})} = 2,28 \times 10^2 - 1,01 \times 10^{-1} MBN + 3,00 \times 10^{-1} IN + 1,05 \times 10^{-4} MBN^2 + 2,00 \times 10^{-4} IN^2 + 9,38 \times 10^{-4} MBN IN \quad (1)$$

$$Vm_{(cm^3g^{-1})} = 5,60 \times 10^{-2} - 1,00 \times 10^{-3} MBN + 1,55 \times 10^{-4} IN + 7,00 \times 10^{-6} MBN^2 + 1,00 \times 10^{-7} IN^2 - 1,18 \times 10^{-7} MBN IN \quad (2)$$

$$Vt_{(cm^3g^{-1})} = 1,37 \times 10^{-1} + 1,90 \times 10^{-3} MBN + 1,00 \times 10^{-4} \quad (3)$$

Where S , Vm , Vt are respectively surface area, volume of micro pores and volume pores. The detail procedure can be found elsewhere [9].

CNTs were characterized using SEM, XRD and FTIR techniques to study morphologies, crystallographies and functionalities, respectively. SEM micrographs were obtained on JEOL JED-2300. X-ray diffraction (XRD) patterns of the carbons were obtained on a Shimadzu X-ray diffractometer XRD 7000 operating at 40 kV and 30 mA, using Cu-K α radiation. FTIR spectra were obtained on Shimadzu IR Prestige 21. The conductivity of electrode was calculated using mathematical relationship (4). CNT was put in the middle of PTFE test tube, covered with two stainless pistons in the both sides. Five tons load was applied to the test tube by using hydraulic jack.

$$K = \frac{d \times I}{V \times A} \quad (4)$$

Where K is electrical conductivity, I is electrical current, d is the thickness of electrode, A is cross-section area, and V is voltage. I and V were measured by using four-point method. A and d were measured by using digital caliper.

2.3. Electrochemical Measurements

The electrodes were fabricated by mixing the CNT and graphite (70:30), 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 20 mm x 30 mm mold, and pressed under 5 tons load and were heated on hot plate at 50°C for an hour.

$$C_{avg} = \frac{\Delta Q}{(w \times \Delta V)} = \frac{\left(\int IdV \right)}{(s \times \Delta V \times w)} \quad (5)$$

Electrochemical test for the electrodes were conducted in potentiostat (Cheapstat, University of California Santa Barbara, CA, USA) in aqueous electrolytes, i.e. H₂C₂O₄, KOH and NaNO₃. The potentiostat is capable for doing three electrodes configuration of CV measurement with Ag/AgCl electrode as reference electrode and platinum rod as the counter electrode. Capacitance were calculated using the mathematical relationship (5) and the integration of voltammogram curve, $\int IdV$ were measured by using mathematical software. Where ΔQ is the total amount of

the charge accumulated over a potential window, ΔV , w is the mass of electrode active material, I is the current, and s is the potential scan rate.

3. Results and Discussions

Table 1 shows the volume of micropores, total pore and surface area of carbons with treatment variations, with or without hydrothermal and with or without the addition of a catalyst (KOH), which are result of mathematical calculations using (1), (2) and (3).

Table 1. SA, V_m , and V_t for carbons and their treatments.

Carbon variations	SA, m^2g^{-1}	V_m , cm^3g^{-1}	V_t , cm^3g^{-1}
With KOH catalyst	381,90	0,46	0,72
Without catalyst	389,83	1,02	0,99
Without hydrothermal	592,35	1,76	1,13

The FTIR results show in Figure 2 (a, c and d) that the carbons have some peaks in $3600 - 4000\text{ cm}^{-1}$. This features indicate -OH group that resonates within the carboxyl group or -OH group in water. Peak in $2300 - 2500\text{ cm}^{-1}$ indicate the presence of C = O.

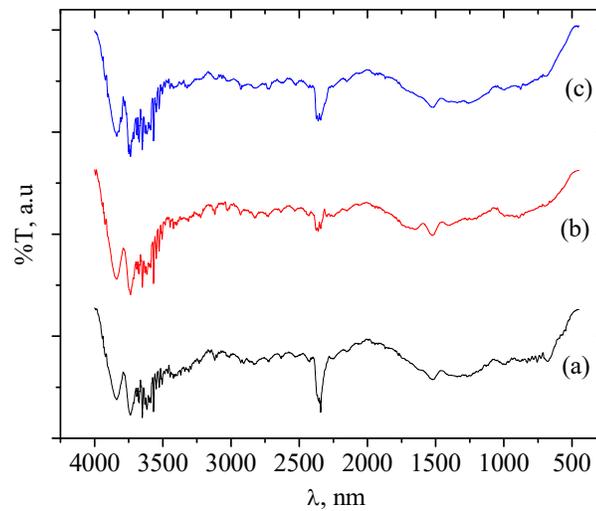


Figure 1. FTIR Spectra for (a) carbon without hydrothermal treatment, (b) carbon with hydrothermal and KOH catalyst (c) carbon with hydrothermal without catalyst.

Diffractograms give information about crystallinity of carbon (Figure 2). All diffractogram show two wide peaks, i.e. at $2\theta = 25^\circ$ and 42.5° . Very low intensity peak at $2\theta = 40^\circ - 45^\circ$ confirms diminishing of basal plane of carbon.

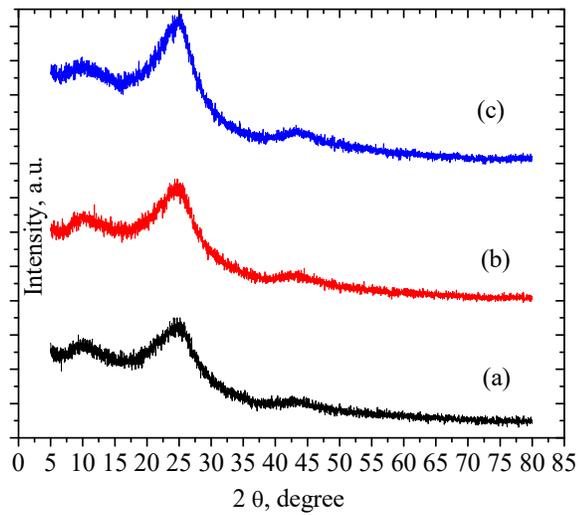


Figure 2. Diffractograms for (a) carbon without hydrothermal treatment, (b) carbon with hydrothermal and KOH catalyst (c) carbon with hydrothermal without catalyst.

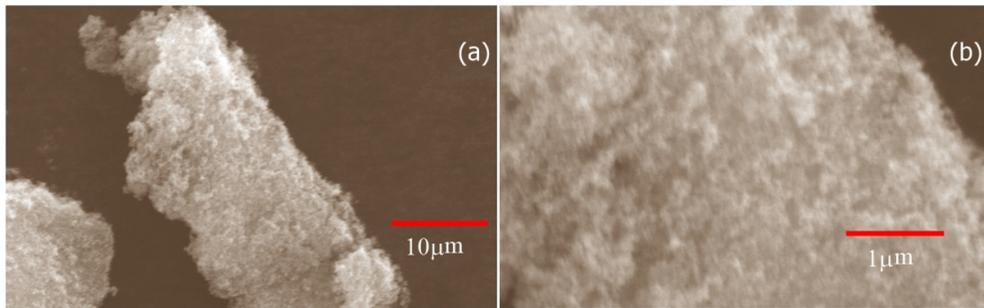


Figure 3. SEM image of carbon without hydrothermal treatment (a) magnification 750 times and (b) 3000 times.

The results of crystalline analysis of carbon was confirmed by SEM analysis (Figure 3) that show the presence of CNT. EDX analysis shows (Figure 4) information the content of CNT, i.e. carbon 88,82 % and oxygen 11,18 %.

Table 2 shows the carbon without hydrothermal treatment that has the highest conductivity i.e. 0.407 Scm^{-1} . Conductivity of carbons must have range from 0.0021 to 2 Sm^{-1} in order to develop carbons into electrode [10]. Electrochemical characters can be determined by measuring the current density and specific capacitance using cyclic voltammetry (CV) technique.

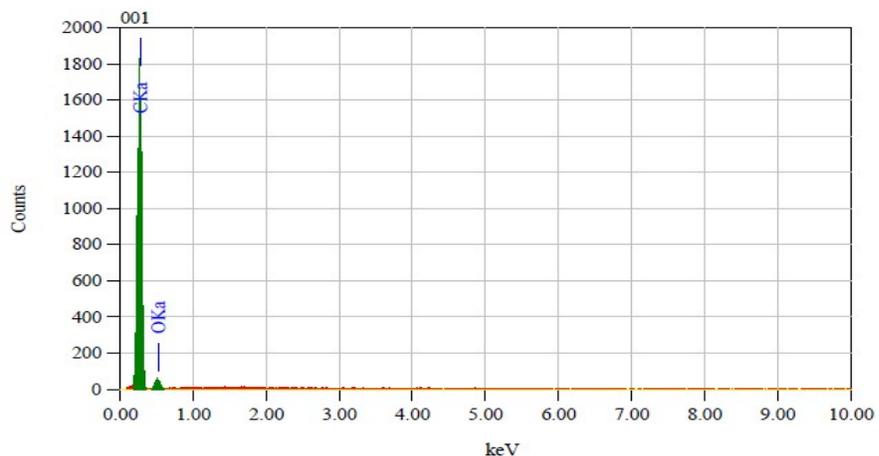


Figure 4. EDX Analysis of elemental content in the carbon without hydrothermal treatment

Table 2. Conductivity of carbon with and without hydrothermal treatment.

Carbon variations	I (Ampere)	V (Volt)	K ($S\ cm^{-1}$)
With catalyst KOH	4,33	4,42	0,193
Without catalyst	4,55	3,48	0,232
Without hydrothermal	3,29	8,36	0,407

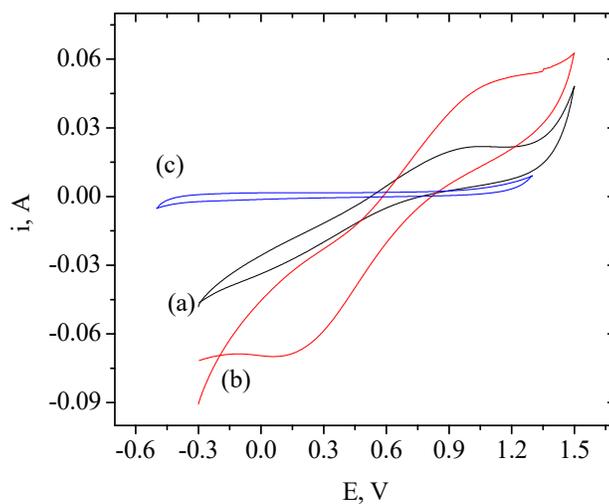


Figure 5. Voltammograms of electrodes in electrolytes, i.e. (a) H_2SO_4 , (b) KOH and, (c) $NaNO_3$.

Voltammograms in Figure 5 show the highest capacitance, i.e. $0.0251\ Fg^{-1}$ in 1M KOH electrolyte and scan rate of $5\ mVs^{-1}$. The lowest capacitance in 1M $NaNO_3$ electrolyte with the addition of TEA, i.e. $0.008\ Fg^{-1}$.

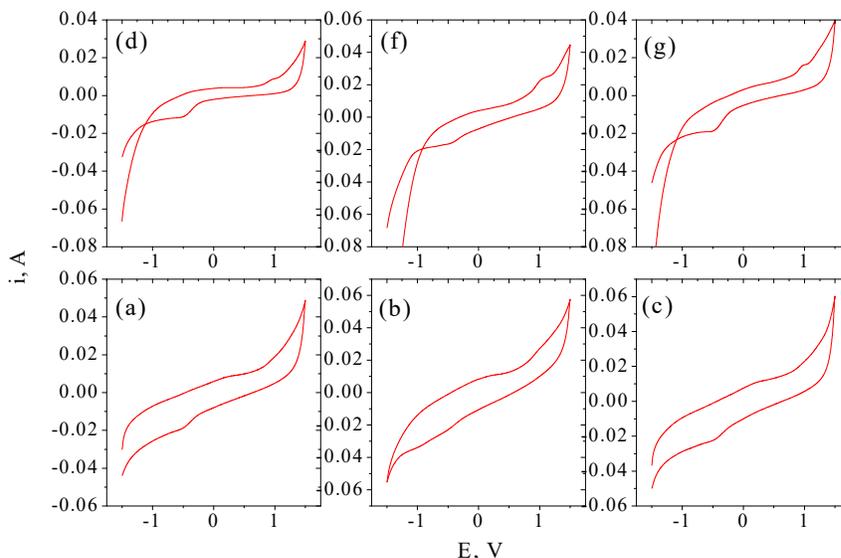


Figure 6. Voltammograms of electrodes in electrolyte KOH, concentration (a) 1M, (b) 2M (c) 4M (d) 1M + TEA (e) 2M + TEA (f) 4M + TEA

Figure 6 shows voltammogram the highest capacitance was 0.0246 Fg^{-1} in 1M KOH and the lowest capacitance was 0.0210 Fg^{-1} in 1M KOH electrolyte with the addition of TEA. One of the dominant factors in determining the electrochemical activity of electrolyte is ion mobility. Mobility of ions into the pore varies greatly and depends on the physical properties of the electrolyte used, the ionic strength, dielectric constant and interfacial tension. With the increasing in concentration of electrolyte ions, carbon mobility will decrease. Low concentrations of ions makes ion easy to move. Therefore an electric double layer relatively easily formed.

4. Conclusions

It can be concluded that the carbon has nanotube structures, generally consist 88.82% of carbon and 11.18% of oxygen. FTIR characterization indicated that O – H, C = O, and C = C bonds domination in the carbon. Diffractograms have narrow and low peaks at $2\theta = 24^\circ$ and 45° meaning that the presence of crystalline carbons were in the form of nanotubes. This results were confirmed by the SEM images. The electrodes were made of carbon without hydrothermal treatment as measured by cyclic voltammetry has the highest capacitance values of all measurement results with a variety of electrolytes is 0.0251 Fg^{-1} from 1M KOH electrolyte.

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