

CARBON MATERIAL DERIVED FROM WASTE PAPER AS CARBON SOURCE AND ITS POTENTIAL AS ELECTRODE

Adibah Ninti Mohd Noor¹, Mohd Nazlan Bin Mohd Muhid²

¹*Faculty of Applied Sciences. Universiti Teknologi MARA, Tapah Campus,
Tapah Road, 35400, Perak, Malaysia*

²*Faculty of Science, Universiti Teknologi Malaysia, MALAYSIA*

Corresponding author: adibah_mnoor@perak.uitm.edu.my

ABSTRACT

Waste papers can be as alternative precursors of carbon material as these wastes are easily available, recyclable resources and the compositions are mainly cellulose, a natural polymer. The chemical bonding states of carbon material's surfaces were investigated by Fourier Transform Infrared Spectroscopy. The result revealed that C-O of the polymeric of cellulose, vibrations of C-O-C of glycosidic bonds, C = C and CH₂ group present. The synthesis route is accomplished by the sol gel technology that involved gel preparation, gel aging and gel drying as general steps where the polymer made up the frameworks of gel. The usage of supercritical drying and ambient pressure drying were implemented in the drying process. The morphology of newspaper-based carbon material is the mixture of cylindrical cube like form and irregular shaped. Carbon material from office paper has the texture of cubes and undefined shaped and samples from magazine paper shows the images of not uniform shape. The average particles size of all carbon materials is 10 - 50 μm when examined by Field-Emission Scanning Electron Microscopy. Besides, the density of the carbon material is 0.42- 0.83 g/cm^3 . The carbon material in made into a carbon electrode prepared from supercritical drying (SCD) has the specific capacitance (38.46 Fg^{-1}) with the scan rate 30 mV/s by Cyclic Voltammetry. The voltammograms showed some electrochemical properties in low potential window compared to graphite as working electrode due to high resistance of low surface area and conductivity of carbon material. Electrode prepared from supercritical drying method has high specific capacitance than electrode prepared from ambience pressure drying technique. The electrochemical properties of the electrode from SCD method is enhanced compared to electrode prepared from ambience pressure drying. The properties was measured by the detection by current in a low amount from the interaction of ions occurred between the bulks of electrolyte with the surface of electrode. This is due to high value of specific capacitant and the surface area of electrode produced from electrode prepared by supercritical drying method compared to electrode prepared from ambience pressure drying technique.

Keywords: Waste paper; carbon material; sol gel technique; electrode; supercapacitors

INTRODUCTION

Waste papers can be considered as carbon sources since their composition are mainly cellulose fibers, water and inorganic compound. There are one-fifth of the contents of household dustbins are waste papers and over 4 kg of waste papers produce per household each week [1]. Over 57,000 tons of paper per month is thrown into the landfills, which occupies 456,000 cubic meters of landfill space in our country, Malaysia [2]. This matter contributes the large percentage of waste stream. The major component of paper is mainly cellulose fibers with the addition of variety inorganic fillers and mostly of the fibers coming from wood. Carbon aerogel is one of the unique carbon materials especially about their pore characteristics. The material which composed of continuous rigid solid framework has high surface area, high electric conductivity, high meso-porosity and relatively small degree of micro-porosity [3]. The high porosity of carbon aerogel is about 80 - 98%, with controllable pore structure, opened and continuous network of pores. These attractive properties make this impressive material, a promising candidate for application in the fields of adsorption, advanced catalyst support, as porous electrodes in supercapacitors, rechargeable batteries, electrochemical devices, chromatographic packing and more. Carbon materials, for example activated carbon, aerogel particulates, carbon black and carbon cloth have extensively used as electrode materials for supercapacitors. Supercapacitor is an innovative sort of electrical energy storage devices that are able to store much energy than conventional capacitors. This great combination is desirable fabricating in electrodes from carbon material for supercapacitors with least expensive technology and environmental friendliness. In view of the fact that waste papers are found in large quantity and recyclable resources, these materials can be utilized as an alternative precursor of carbon source as their composition are mainly cellulose fibers. The recycled waste paper also used to obtain an activated carbon as supercapacitors [1]. Reuse of wastes will save the environment, cost effective and reduce the pollution. The utilization of waste papers as a carbon source will produce carbon material and forming an alternative electrode.

EXPERIMENTAL

Synthesis of potential Carbon Material from Waste Paper

The experimental work of this study basically contained three main stages comprising of synthesis, characterization and application. The first part is to synthesis of potential carbon material by using waste paper as a element of carbon sources. Then, the characterization of synthesized sample derived from wastes paper and the application as an electrode in electrochemical field. The type of waste paper used in this work is originally from newspaper only. The procedure starts with the preparation of sol mixture, gelation and curing the gel and drying process [1]. The methodology starts with the preparation of sol mixture, gelation and curing the gel. The steps were followed with the drying process [4,5]. Waste newspapers were dissolved and forming a thick paste solution. The solution was heated and undergo continuous stirred for 4 hours. Solution of potassium hydroxide was added to digest the waste papers. In a gel

preparation, the solution was left to cool before concentrated sulphuric acid (95 - 97 %) was added until pH of solution reached 6 – 7 and the waste paper solution turned to gel immediately. The waste paper based-gel washed with distilled water and undergoes aging process for few days. The hydrogel washed with absolute ethanol and the wet gel dried by using supercritical extraction (SCE) and ambient pressure drying. The supercritical drying solvent utilized is ethanol with the critical temperature is 239°C and critical pressure is 1200 psi. The other drying method was ambient pressure drying where calcinations process was employed at temperature between 100°C until 500°C. The samples prepared were labeled as CNP and CNP-1. The CNP sample referred as a carbon material prepared from newspaper based from drying method; supercritical drying while sample of CNP-1 labeled for carbon material prepared from newspaper based from ambience pressure drying method. The differences between two samples prepared is different mode of drying method applied.

Electrode preparation from synthesized Carbon Material

The powder formed used as material for electrodes in melted paraffin oil in the proportion 60%:40% (w/w). The ready prepared paste is packed into a hole in the electrode mould. The filling is made in small portions when the paste was being pressed intimately by stainless steel mesh with a 1 cm² geometrical area before adding the next one until forming a cylindrical paste. The electrode mould is then connected to copper wire in order to provide an electric contact to act as a working electrode.

RESULTS AND DISCUSSION

The infrared spectra of newspaper and newspaper based carbon materials after drying exhibit the framework vibration between of 3500 - 700 cm⁻¹ revealed as in Figure 1. The absorption bands of cellulose are still presence in both sample of carbon material after drying. The band represents for the stretching of C-O-C glycosidic and the stretching of C-O and O-H in glucose ring and CH₂ groups. The stretching of C-O and O-H, most likely from secondary and primary hydroxyl groups of cellulose [2]. C=C bond in lignin was appeared for all samples. They also preserved C-O-C linkage after drying. In Figure 1, band for 1018 cm⁻¹ (C-O bond) disappeared for samples of carbon material derived from APD method. This is due to C-O polymer linkage cannot be preserved when used this type of drying. By using Field Emission Scanning Electron Microscope (FESEM), Figure 2 show images of the surface of the carbon materials derived from newspaper from both types of drying method used. The average particles size is around 10 - 20 µm diameters and composed by the mixture of cylindrical cube like and irregular shaped. The temperature also had influenced towards the microstructure of the particles of the sample. The solution pH and ratio of precursors also influence the particle size [3]. The significant difference between both samples is the micrograph of the carbon material from APD in Figure 2b is look little fragile compare to micrograph in Figure 2a. Cyclic voltammetry measurements were carried out to examine the electrochemical properties of electrode from carbon material. Specific capacitance of the electrodes was estimated according to the Equation 1, where I_a + I_c are the current of anodic and cathodic of

voltammetric curves on positive and negative sweeps. W is mass of the electrode material and $[dV/dt]$ represents scan rate.

$$C = \frac{I_a + |I_c|}{2W [dV/dt]} \quad (1)$$

The common electrode used in electrochemical field is graphite electrode. The curves as in Figure 3 showed that the graphite electrode has high potential window from -150 to 150 mV. This revealed that the electrode has electrical double layer capacitance, highly reversible and has high conductive behaviour. The study was performed in a three electrode rearrangement over the potential range of -50 to 50 mV and of -100 to 100 mV by changing the scan rate from 20 - 50 mV/s in an aqueous solution of 6 M KOH electrolytes. An electrode carbon based material where acts as working electrode with Ag/AgCl and Pt plate as auxiliary and reference electrodes. Electrode material was prepared by using samples newspaper- based labeled as CA-NP and CA-NP1 together with graphite and paraffin oil as binders. Figure 4 shows the cyclic voltammograms of electrode from carbon material prepared by supercritical drying obtained at different scan rate. The curves of (a), (b) and (c) showed rectangular like, symmetry and reversible shape in the potential difference of 50 and 100 mV. The curves of (d) show slightly deviate from the rectangular like form. The data indicated that electrodes from newspaper-based prepared from SCD showed some electrochemical properties, indicated ideal double layer capacitance behaviour. When compared with the graphite electrode in Figure 3, the current detected in between – 500 to 2500 μA , larger and has high potential window than electrode from carbon materials derived from waste paper in Figure 4. This means that the electrode from newspaper has very low conductive compare to common electrode. The cyclic voltammograms of electrode from carbon material derived from waste paper showed some rectangular like, symmetry and reversible shape. Based on the result on Table 1, the specific capacitance of the electrodes was calculated according to the Equation 1. The electrode carbon material from newspaper from supercritical drying method has the value of specific capacitance is 38.26 Fg^{-1} by Cyclic Voltammetry while the specific capacitance for newspaper-based carbon material electrode prepared from ambient pressure drying is 17.09 Fg^{-1} .

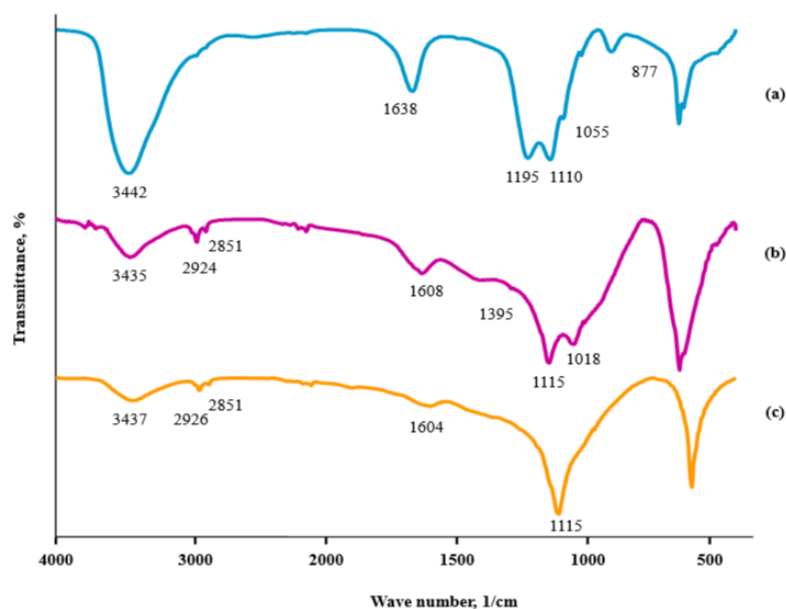


Figure 1: FTIR spectra of (a) newspaper; and samples derived from newspaper by (b) supercritical drying (SCD); and (c) ambient pressure drying (APD)

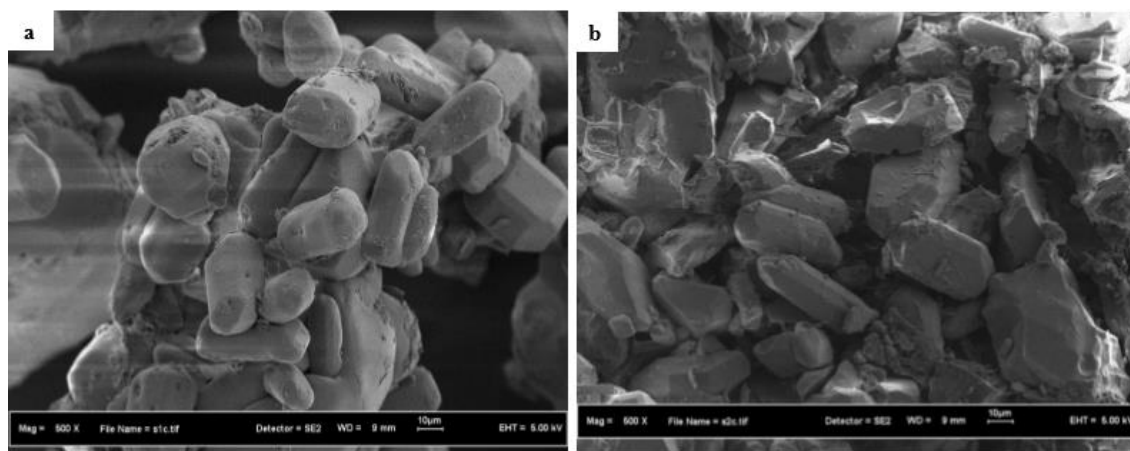


Figure 2: FESEM images of (a) carbon material derived from newspaper: prepared by supercritical drying and (b) prepared by ambient pressure drying

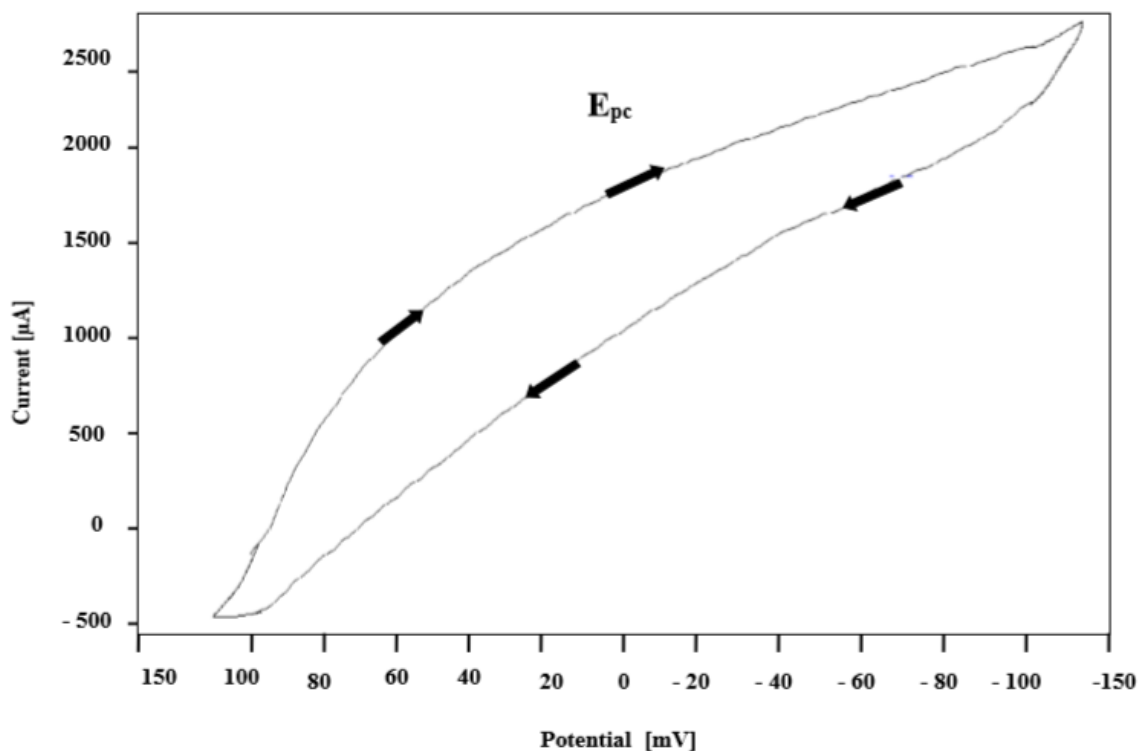


Figure 3: Cyclic voltammograms of graphite electrode at different scan rate 20 mV/s

From Table 1, when the scan rate increase from 20 to 30 mV/s, the maximum peak potential cathode of (a) in Figure 4 increase in potential from - 3.8 to - 4.4 mV corresponds that the applied potential becomes towards sufficiently negative to cause reduction reaction occur, where the curve is gradually increase continuously. The potential of anode in curve (a) increase from -1.8 to -2.0 mV when the scan rate increased from 20 to 30 mV/s. The applied potential becomes sufficiently towards positive to cause oxidation occur at electrode surface of anode when the curves gradually reversed. This revealed that the electrochemical properties from the curved are reversible where there occurred ions interaction between bulks of the solution with the surface of electrode and the redox reactions. Nevertheless, the peak potential of cathode and anode in (c) was decrease from - 3.8 to - 2.6 mV and - 1.8 to - 4.0 mV when scan rate increase. This can be observed by slightly deviation of rectangular like. However, the properties are detected by current in low amount between - 38 and - 41 μA even the conducting electrolyte was utilized. The increasing scan rate produced the narrowed curves, symmetry and specific capacitance are decreased. This is because of the low ion transfer rate in electrolyte at high scan rate. The diffusion layer above the electrode surface is decrease as the current, magnitude and flux to electrode surface increase. The network structure in the electrode material acts as obstacle that against ion diffusion in electrolyte when high scan rate is applied

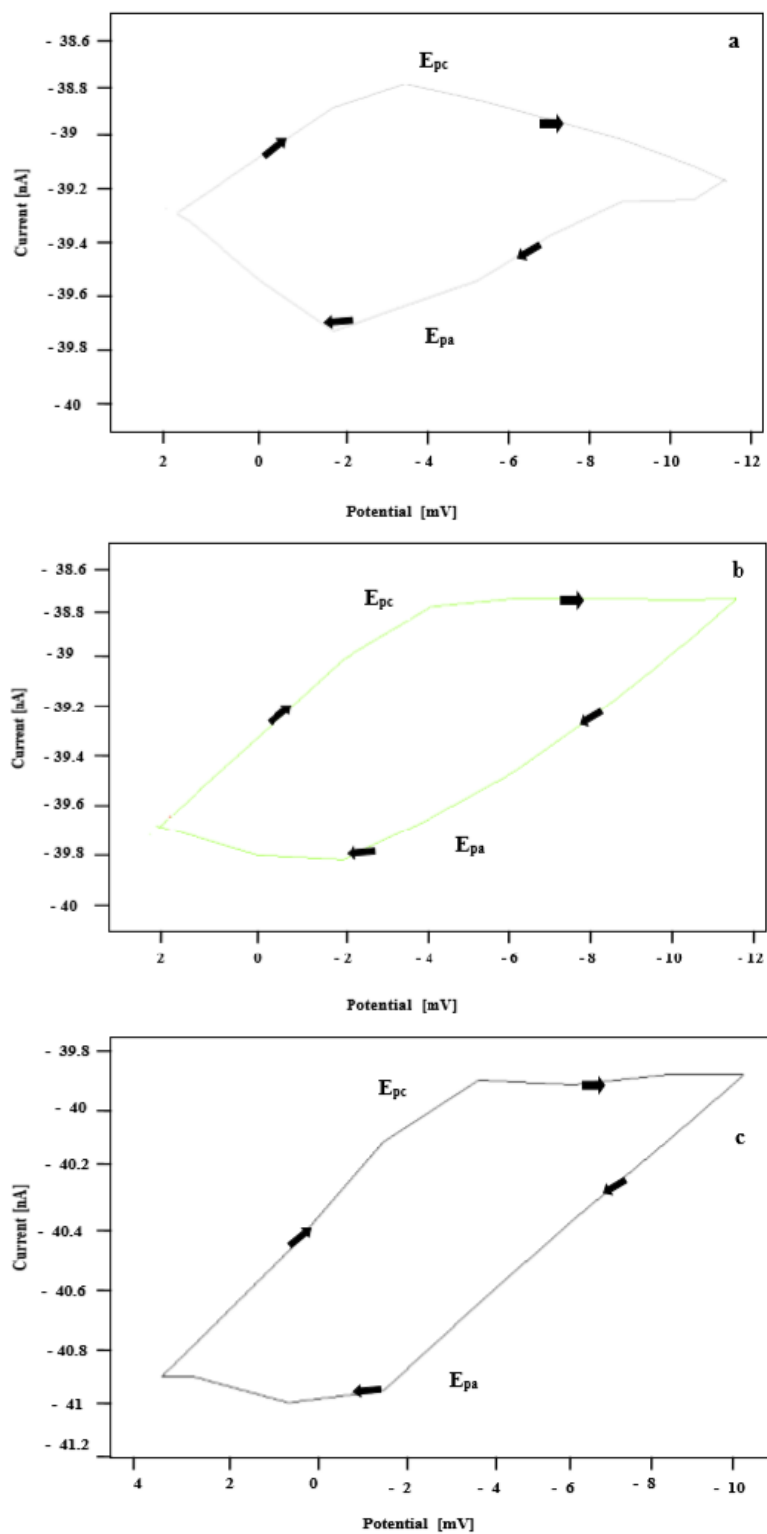


Figure 4: Cyclic voltammograms of electrode from carbon material derived from newspaper prepared by supercritical drying at different scan rate (20, 30 mV/s) with different potential; 50 and 100 mV

Table 1: Peak potential and specific capacitance of electrode prepared by supercritical drying

CV	Potential [mV]	Scan rate [mV/s]	Peak potential, Ep [mV]		Specific capacitance [F/g]
			Cathode, Epc	Anode, Epa	
(a)	50	20	- 3.8	- 1.8	19.23
(b)		30	- 4.4	- 2.0	12.82
(c)	100	20	- 3.8	- 1.8	38.46
(d)		30	- 2.6	- 4.0	25.64

The specific capacitance was closely related to the shrinkage behaviour and surface area [6]. Based the result on Table 1, the maximum specific capacitance of electrode from newspaper-based, C-NP (38.46 Fg⁻¹) was obtained at scan rate 20 mV/s with the density was 0.83 g/cm³. The values was slightly decreased compared to Cp of carbon aerogel electrodes is 180 F/g with surface area 553 m²/g and polybenzoxine carbon aerogel has 55.8 F/g with surface area 391 m²/g.. The value of specific capacitance is increase when the scan rate is decrease [7]. In this study, electrode from carbon materials was examined as electrochemical double layer capacitors (EDLCs). In EDLSs concept, they store energy at the electrolyte and electrode interface through reversible ion adsorption onto the carbon surface, thus charging the so called as double layer capacitance. There is no faradaic and redox reaction is involved in the charge storage mechanism. From FTIR spectroscopy, the bonding of the elements in the samples can be known where the samples produces containing polymeric linkage carbon which enhances the structure. The FESEM micrograph of the samples examined the surface characteristics of materials which then formed an electrode. The newspaper based electrode is used to enables the transfer of electrolyte ions by cyclic voltammetry technique and the electrochemical performance measured by the value of specific capacitance. The specific capacitance for C-NP sample is value 38.46 Fg⁻¹, while samples of CNP-1 is 17.09 Fg⁻¹ at potential 100 mV. Higher value for the sample C-NP show better electrochemical performance than sample C-NP1 due to effect of drying method which SCD preserve the polymer linkage and surface area.

CONCLUSION

A cost effective carbon material from waste resources, waste papers using two types of drying technique; supercritical drying (SCD) and ambient pressure drying method was

successfully synthesized by sol gel method. The electrochemical performance of electrode from waste paper has a slightly double layer capacitance behaviour and detected by current in a low amount due to high resistance and conductivity of material. The capacitance of carbon material is known to depend on surface area. Supercritical drying process can avoid capillary stress, less cracking and decrease the drying shrinkage compare to ambient pressure drying. These actions will get the better structure.

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