

Conference Paper

Preparations and Characterizations of Hierarchical Macropore Activated Carbon Monolith Electrode from Rubber Wood for Supercapacitor Application

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Abstract Preparation of hierarchical macropore activated carbon monolith (HMACM) from rubber wood was investigated. The samples were prepared with small cutting of rubber wood in cross sectional method. The electrode preparation was started by pre-carbonization process followed by carbonization at 600°C and physical activation process at 900°C in N₂ and CO₂ gas atmosphere, respectively. The samples then were followed by chemical activation process with combination of chemical activation agent of KOH and HNO₃ solutions. The HMACMs were neutralized by immersing the samples in copious amount of water and dried the samples for 24 hours. Porosity properties were performed by N₂ adsorption-desorption data and morphology characterization was analyzed by scanning electron microscope (SEM) instrument. The electrochemical properties was studied by electrochemical impedance spectroscopy, cyclic voltammetry and charge-discharge at constant current method. The SEM micrograph and adsorption-desorption data were also proved that the HMACM sample have a hierarchical macropore at the surface and cross-sectional section. The porosity data shown the HMACM sample have BET surface area of 331 m²/g with average pore diameter of 1.7 nm. Equivalent series resistance and optimum capacitance specific of the HMACM electrode of 0.77 Ohm and 154 F/g, respectively. In conclusion, this study showed that the preparation method would propose as a simple method of HMACM electrode preparation technique for supercapacitor applications.

Keywords: Hierarchical Macropore, Rubber wood, Supercapacitor.

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1. Introduction

Supercapacitor was one of the energy storage devices beside the capacitor, batteries and fuel cell [1]. Supercapacitor has a higher energy than capacitors but showed lower power. If was compared to batteries, supercapacitors has a higher power but a lower energy. Supercapacitor comprises two current collectors, two electrodes that were restricted by separator and dipped into the electrolyte [2]. An electrode was an important component in determining the capacity of energy and power that can be

storage in supercapacitor cells. In the past decade has been done a lot of research to get the best supercapacitor with modifications to the electrode. The supercapacitor electrode can be made from a porous carbon material [3]. One source of carbon that is cheap and easily obtained materials derived from biomass. Several reports have been revealed the energy and power generated by a carbon electrode from biomass materials [4]. Biomass materials that has been used as a precursor for carbon electrode for supercapacitor application such as rubber wood sawdust [5], peanut shells [6], and emptyfruit bunches [7], poplar wood [8] and paulownia flower [9].

The ability to store the energy and power at an electrode were determined by the nature of the porosity of the material. The main properties of pore which includes an average pores size and pores distribution. An electrode materials with an average pore were micro-porous will tend to produce supercapacitor cells with higher energy density but lower power density [10]. On the other side, carbon material with an average pore was meso-pore will tend to produce supercapacitor cells with higher power density [10]. Materials with pores which were dominated by micro pores will produce a high surface area. The surface area is often believed to be a key factor for determining the energy value of a cell supercapacitor. Some reports also stating some materials with low surface area was capable to produce a supercapacitor cell with relatively high energy.

This study was shown the carbon electrode with relatively low surface area can produce a supercapacitor cell with good electrodes properties. Carbon electrodes have been made from rubber wood branch. Rubber wood branch was cut by cross section side to preserve the nature of the existing of natural macro-pores. Fabricating of carbon electrodes such as this way has an advantage that without need for adhesive materials and pore composed with uniformly. The absence of adhesive on the electrode may decrease the electrode intrinsic resistance and the existing a hierarchical macro-pores would increase the charge transfer in the electrode. Both of these factors are believed a carbon electrodes from rubber wood as a potential candidate as a supercapacitor electrode material.

2. Experimental

HMCM were made from rubber wood that was cutted by transversely to maintain the hierarchical macro-pore structure on the electrode. The sample was then carbonized in N_2 gas atmosphere at a temperature of $600\text{ }^\circ\text{C}$ and then the followed by physical activation by using CO_2 gas at a temperature of $900\text{ }^\circ\text{C}$. Chemical activations were performed by using the activating agent of 3 M KOH and $25\% HNO_3$. Supercapacitor cells were assembled in the form of coins cell type using two electrodes, two current collector, and a separator. Physical properties and electrochemical characterization were performed on the HMCM samples. The physical properties such as surface morphology and surface area of carbon electrodes were characterized. The electrochemical properties were measured includes the specific capacitance, cells resistance, energy density and power density. The electrode surface morphology was performed with a scanning electron microscopy (SEM) measurement and the surface area studied by N_2

gas isothermal absorption-desorption method. The electrochemical properties testing carried out using the electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and charge and discharge (CDC) method by solatron 1286 measurement.

3. Results and Discussions

Figure 1 was shown the EIS data for supercapacitor cell with HMAC electrode from rubber wood. Figure 1A displays a Nyquist plot where the shape of the curve obtained were a semicircle, a line with 45 degree and a line with 90 degree to the Z' axis. Semicircular shape can be used to determine the equivalent series resistance (ESR), contact resistance an electrode with current collector and combined with an electrolyte resistance (R_p) which is the intersection of the curve to the Z' axis with a lower resistance value [2]. Carbon electrode intrinsic resistance (R_s) which was the intersection of the curve on the Z' axis at a larger value. The magnitude of ESR, R_p , R_s were 0.77Ω , 0.73Ω and 1.5Ω , respectively. The resistive properties of the supercapacitor cell was comparable to the supercapacitor cell electrode from poplar wood [8]. Figure 1B and 1C showed the relationship between frequency with the real and imaginary capacitance. The data in Figure 1C can be used to determine the relaxation time (τ) which to be related to the frequency peaks, where $\tau = 1/f$, where relaxation time was 25,12 seconds. The relaxation time is related to the time required for the ions can diffuse in completely into the pores of electrodes. Figure 1D showed the relationship specific capacitance (C_{sp}) against frequency. The highest C_{sp} value was shown at the lowest frequency of 0.01 Hz was 154.03 F/g. The specific capacitance value of the supercapacitor cell in current study was comparable to the specific capacitance value for supercapacitor was fabricated from the electrodes from other biomass materials as listed in Table 1.

Figure 2A showed the measurement data of the electrochemical properties of supercapacitor cells using cyclic voltammetry method. Cyclic voltammograms showing a rectangle shape, this shape was a good capacitive characteristic of electrodes for carbon supercapacitor [3]. Figure 2B displays measurement data for galvanostatic charge-discharge of supercapacitor cell. The CDC measurement data showed the standard form for supercapacitors using carbon materials electrodes. Based on the data in Figure 2B by using the formula $P = vi/m$ dan $E = vit/m$ [4] can be determined the relationship between power density (P) versus energy density (E) and was shown in Figure 2C. Figure 2C showed that maximum power density and maximum energy density, respectively 420 Watt / kg and 2.8 Watt h/kg. The magnitude of power density and energy density, which is related to a supercapacitor with HMCM electrode was a commonly reported by other researcher, the comparison of power density and energy density of supercapacitor cells with HMACM electrodes was shown in Table 1. Figure 2D was showed the N_2 gas isotherm adsorption-desorption data for HMACM sample. The isotherm data was showed the type 1 based on UPAC classification [11]. The type 1 absorption-desorption data indicated the HMACM eletroda have a pores in the range of microporous [11]. Based on DR equation can be obtained the SBET, S_{micro} , SEXTERNAL, pore diameter and pore volume were 331.54 m^2 / g , of 224.704 m^2/g , 106.830 m^2/g , 15.491 Å, 0.051 cm^3/g . respectively.

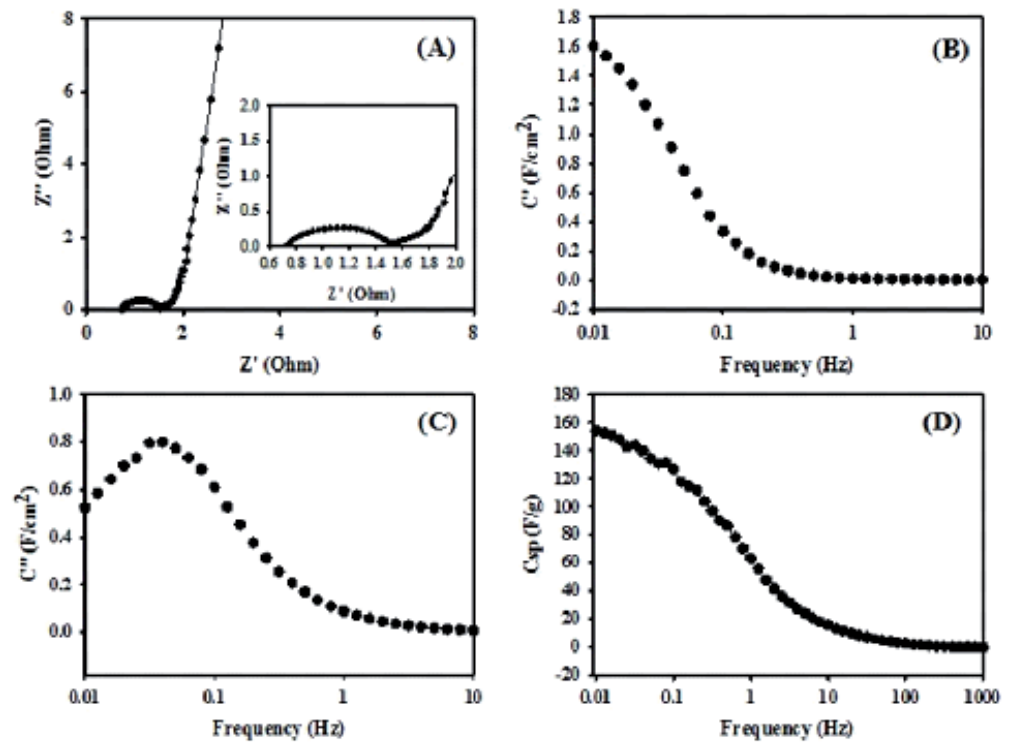


Figure 1: The electrochemical properties of supercapacitor cells were elucidated by using EIS method.

Type of biomass	Energy (Wh.Kg ⁻¹)	Power (W Kg ⁻¹)	Capacitance (F g ⁻¹)	Reference
Peanut Shell	19.30	1007	99	[6]
Rubber wood sawdust	2.63	291	138	[4]
Oil palm fruit bunches	4.297	173	150	[7]
Paulownia flower	44.5~22.2	247~3781	297	[9]
Poplar wood			234	[8]
Rubber wood	2.90	420	154	Present study

TABLE 1: Comparison of energy, power, and capacitance various types of biomass material.

Figure 3 were shown the SEM micrograph of the surface (A) and cross sectional (B) part of HMCM electrode. Figure 3A shows that HMCM electrode has pores with uniform in size macro of pores. Figure 3B was showed that the macro pores has a shape like an elongated pipe, this shape will provide convenience for the ion can penetrate further into the meso and micro pore of carbon electrode.

4. Conclusions

Preparation of HMCM electrode for supercapacitor application has successfully carried out. HMCM electrode showed good resistive properties and capacitive characteristic, from the all of analysis the HMCM route was an interesting strategy for the used at rubber wood as a potential candidate for supercapacitor electrodes.

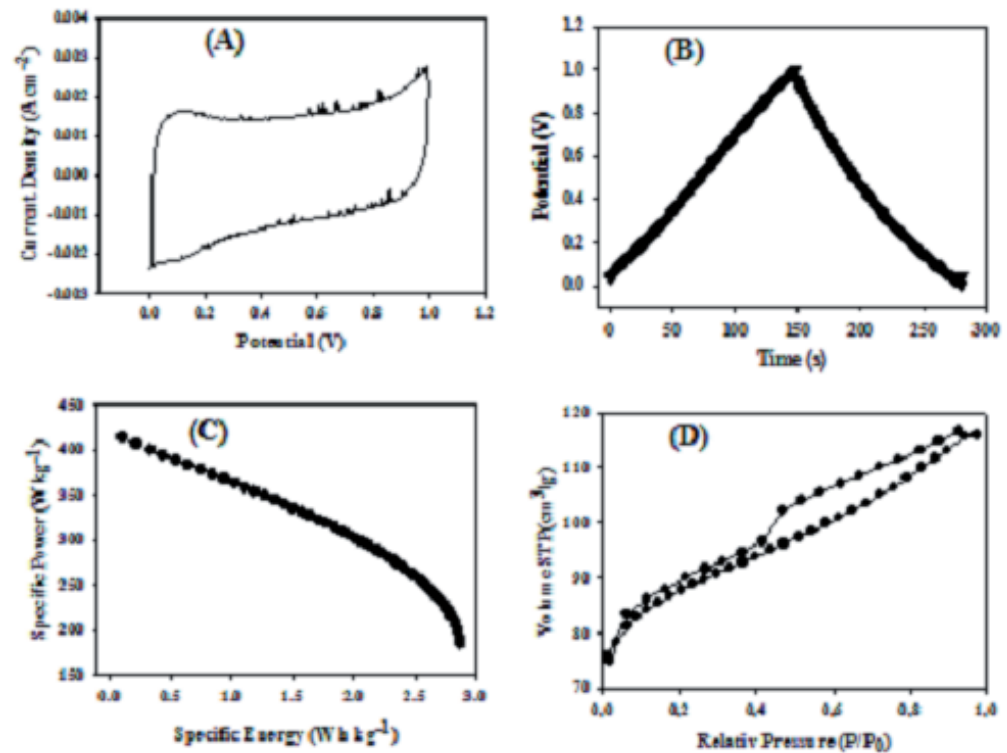


Figure 2: CV data (A), CA data (B), energy density versus power density (C) and the N_2 gas adsorption-desorption data for the HMCM electrodes.

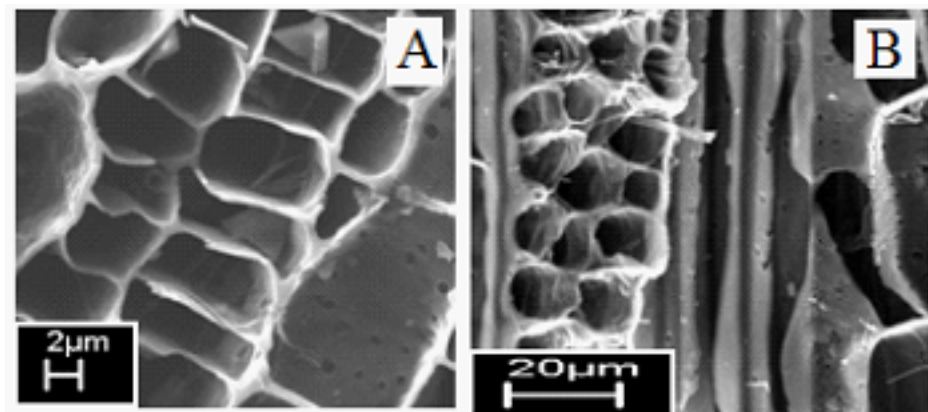


Figure 3: SEM micrograph of HMCM electrode from rubber wood, (A) surface and (B) cross-sectional section.

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