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Cyclic Voltammometry of Binderless Activated Carbon Monoliths based supercapacitor from Mixtures of Pre-carbonized of Fibers of Empty Fruit Bunches and Green Petroleum Coke

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Abstract Binderless activated carbon monoliths (BACMs) prepared from mixtured of pre-carbonized of fibers of oil palm empty fruit bunches (EFB) and green petroleum coke were used for preparing the carbon based supercapacitor cells. The symmetrical supercapacitor cells were fabricated by using two BACMs electrode prepared for each selected holding time of activation and various compression pressure. The electrochemical behavior of supercapacitor cells were measured at room temperature by using cyclic voltammetry (CV) technique. The maximum specific capacitance (C_{sp}) of the cells values were 35.9 and 82.5 F/g for holding time of activation of 1.5 and 2 h, respectively, at the compression pressure of 7.5 metric tons.

Keywords: Fibers of oil palm empty fruit bunches, green petroleum coke, binderless activated carbon monolith, supercapacitor, cyclic voltammogram.

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1. Introduction

Supercapacitor is an energy storage device that stored energy at the interface of electrochemical double-layer formed by ionic charges electrolyte with electronic charges on the surface of pores in the electrode.Its energy and power density can complement the function of batteries and dielectric capacitors. Due to the outstanding properties of supercapacitors, the supercapacitor has been successfully used for a wide number of commercial and industrial equipment, such as digital telecommunication systems, hybrid electrical vehicles, uninterruptible power supply (UPS), and pulsed laser technique [1].

Common materials were used as supercapacitor electrodes including metal oxide [2], electronically conducting polymer [3] and porous materials such as activated carbon [4]. Activated carbon has advantageous because of its high surface area, good thermal and electrical conductivity, high stability, low cost and commercial-large scale availability [5]. Activated carbon can be prepared from biomass precursors and fossil-fuel based precursors by physical or chemical or combination of physical and chemical activation. For the activated carbon in the form of fine-grained, fabrication of

the electrodes for supercapacitorrequired an addition of binder in order to bind the carbon particles into pellets or monolith. However, the addition of binder can reduce the porosity and decreasing the electrical conductivity [5]. Therefore, the activated carbon monoliths (ACMs) without using binder is highly recommended in order to be potentially used as electrodes in supercapacitor.

In our previously studies, the ACMs were prepared without using binder from mixtures of various percentage of self-adhesive carbon grain (SACG) from fiber of oil palm empty fruit bunches (EFB) and green petroleum cokes (GPC) [6-7]. The mixture of 90% of SACG and 10% of GPC was found to yield the best result in term of a higher electrical conductivity, pores structure and electrochemical properties. Therefore, the present study, the BACMs from mixture with a such composition were used but with the adding of the treatment based on CO_2 activation with the different holding time of activation.

2. Materials and Methods

The raw materials used in this study were fibers of EFB supplied by Stable-Win Sdn. Bhd., Malaysia and GPC obtained from Pertamina UP II Dumai Refinery, Indonesia. Fibers of EFB were pre-carbonized at low temperature 280^oC in the vacuum furnace using our method previously reported to produce self-adhesive carbon grain (SACG) [8]. The GPC was milled for 36 h and sieved to produce fine powder that can pass through a 53 μm sieve. The SACG were then mixed with 10% by weight of GPC and then milled for 1 h to obtain homogeneous mixtures of SACG and GPC. The green monoliths (GM-A, GM-B, GM-C) were prepared by applying 4.5, 6 and 7.5 metric ton of compression pressure on ~0.75 g of powder in a mould with diameter of 20 mm respectively.

The carbonization of the GMs to obtain carbon monolith (CMs) was carried out in a carbonization furnace up to 800^oC under a 1.5 L/min flowing N_2 gas using our previous multi-step heating profile [7]. The CO_2 activation on the CMs to produce BACMs was carried out at 800^oC for 1.5 and 2 h in a flow of 1 L/min CO_2 gas with a heating rate of 10^oC/min, respectively. The BACMs were polished to a thickness of ~0.4-0.5 mm and then washed to remove the activating agent with distilled water until pH 7. The electrodes were labeled as BACM-A1.5, BACM-A2, BACM-B1.5, BACM-B2, BACM-C1.5 and BACM-C2. BACM-A1.5 corespond to the electrode prefared from 4.5 metric ton compression pressure and holding time of activation of 1.5 h, and etc.For studying of the electrochemical behavior of the BACMs electrodes, the symmetrical supercapcitor cells were fabricated using two BACMs electrode prepared for each selected holding time of the activation and compression pressure. The supercapacitor cells consist of stainless steel foil 316L as the current collector (thickness of 0.02 mm), 1 M of H_2SO_4 as the electrolyte and a teflon ring as separator (thickness 0.2 mm) were fabricated.

The electrochemical behavior of the supercapacitor cells was investigated by cyclic voltammetry (CV) technique. The CV measurement were carried out at the room temperature. From the voltammogram data, the C_{sp} of the electrode was determined using equation

$$C_{sp} = \frac{2i}{S\,m} \tag{1}$$

where i is the electric current, m is the mass of electrode and S is the scan rate.

3. Results and Discussion

Cyclic voltammogram (CV) of cells at voltage range of -1 – 1 V and a scan rate of 5 mV/s in 1 M H_2SO_4 electrolyte solution are shown in Fig. 1 and 2 for holding time of activation of 1.5 and 2 h respectively. In the middle of potential region of voltammogram there is a tiny peak (hump) for BACM-C2 cell as a result of redox reaction (based on Faradaic charge-discharge) (Fig. 2). The redox peaks occurred almost in the middle of voltage (∼0 V). This redox peaks indicate that the BACM-C2cell were formed by pseudocapacitance. While for BACM-A2 and ACM-B2 no redox peaks were observed indicating that these cells are based on the electrostatic supercapacitor. Fig. 1 shows a significant redox peaks for the cell of BACM-A1.5, while BACM-C1.5has no significant redox peaks. Compared to the holding time of activation of 1 hour [9], the holding time of activation of 1.5 and 2 hours were very effective to improve the performance of supercapacitor. Hu et al. reported that the effect of activation of CO_2 [10] and holding time of activation of carbon electrodes could eliminate the redox peaks as observed in our study.

Redox processes occurring at the electrode-electrolyte interface can improve pseudocapacitance electrodes. Since, the capacitance is the sum of the double-layer capacitance and pseudocapacitance (Faradaic) [11], these redox peaks arise as a result of the availability of surface functional groups [11,12]. Bichat et al. who researched on seaweed as starting material for electrode observed that the profile of CV in 1 Molar H_2SO_4electrolyte produced a similar curve inour study [13].

The anode and cathode peak arose due to the transformation reversible of quinones/hidroquinon (-OC = O). Wang et al. found that the redox peakwas expected to occur because of the concentration of anions on the pore surface of the electrode as a function of surface potential [14]. It is obvious that the surface anion concentration increased sharply with the potential increment. This regime corresponds to the increase of current density reaching maximum corresponds to crest of the hump. Then, the ion accumulation near the electrode surface became to be slower as the electric potential increased. In our study, these functional groups remain in all electrodes for activation timeof 1 h sufficiently removes all the functional groups from the electrodes.

The specific capacitance values for all the cells using BACMs measured at various compression pressures and activated at 800°C with holding time of activation for 1.5 and 2 hours are shown in Fig 3. As can be seen in this legend, each compression pressure, the specific capacitanceswere increased with increasing the holding time of activation.
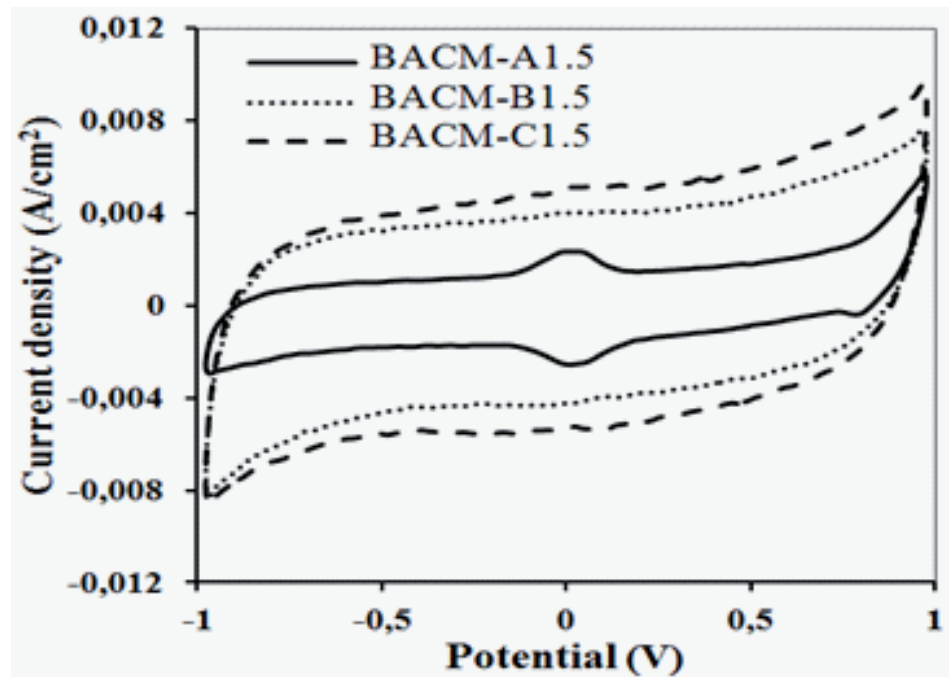
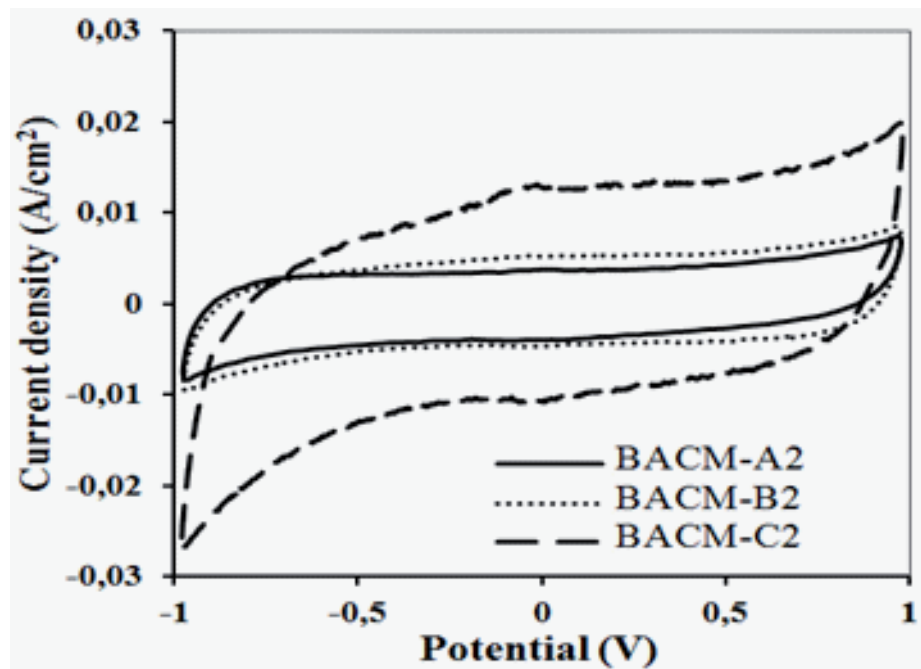**Figure** 1: Profiles of CV at a scan rate of 5 mV/s.

Figure 2: Profiles of CV at a scan rate of 5 mV/s.

The rofile of CV at various scan rates with the voltage range of -1 – 1 V for cells by using BACM-C1.5 and BACM-C2 electrodes are shown in Fig. 4 and5 respectively. As expected, as the scan rate increases, the potential window becomes to be larger since the current density increases. According to Xu et al., the current density increases with increasing scan rate because the cell has a faster reversibility response of charge-discharge [15]. For high voltage scan rate, the cyclic time becomes to be faster and
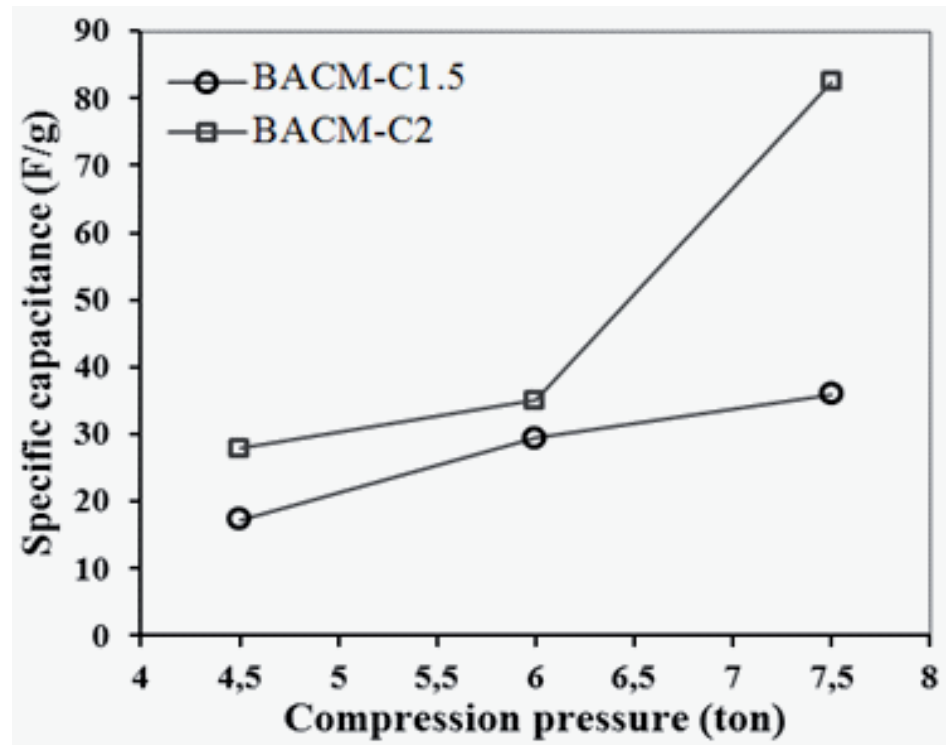
Figure 3: Specific capacitance with different holding time of activation.

No.	Sampel	Specific capacitance (F/g)				
		5 (mV/s)	15 (mV/s)	25 (mV/s)	50 (mV/s)	100 (mV/s)
1.	BACM-A1.5	17.3	14.0	11.5	8.9	6.5
2.	BACM-A2	27.1	24.9	23.0	19.8	15.8
3.	BACM-B1.5	29.5	26.9	23.9	20.7	13.4
4.	BACM-B2	35.1	32	29.0	24.3	18.5
5.	BACM-C1.5	35.9	30.9	28.3	23.0	17.3
6.	BACM-C2	82.5	76.0	68.6	53.3	38.1

TABLE 1: Specific capacitance of supercapaacitor with various scan rate.

therefore the electrolyte ions do not have time to diffuse into the pores. Consequently, the square characteristic of potential window decrease resulted from ain order pore structure, andhighly unordered pore network [16]. CV slowly becomes tilted from the horizontal line as the scan rate increase, which indicates the value of ESR significantly increase because of ionic conductivity of H_2SO_4 electrolyte becomes to be smaller [10].

The specific capacitance of the BACM-C1.5 and BACM-C2for various scan rates obtained from CV data is shown in Table 1. The increment of the scan rate caused specific capacitance decreased gradually. The specific capacitance decrease correspondent to scan rate increases due to the limited transfer of ions to the surface of the electrode pores causing some pores are not accessible at high scan rate. At low scan rate, the current is small, iR loss can be ignored, and supercapacitor cells can be considered as a pure capacitor. In contrast, at high scan rate, the current also increased and iR loss become significant and supercapacitor cells act as a pure resistive device
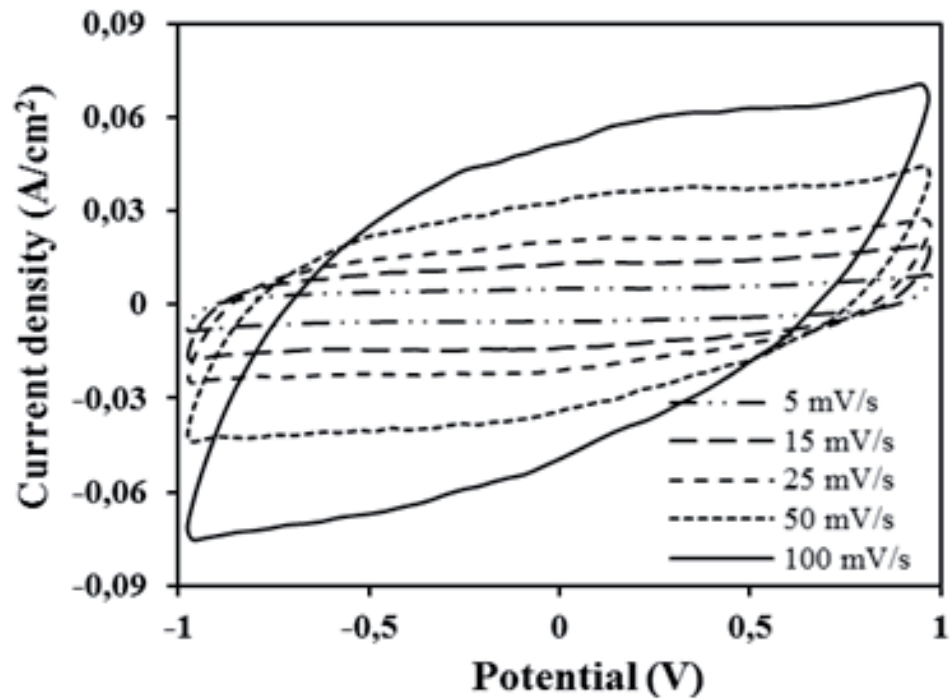
Figure 4: Profile of voltammograms with various scan rates for BACM-C1.5.
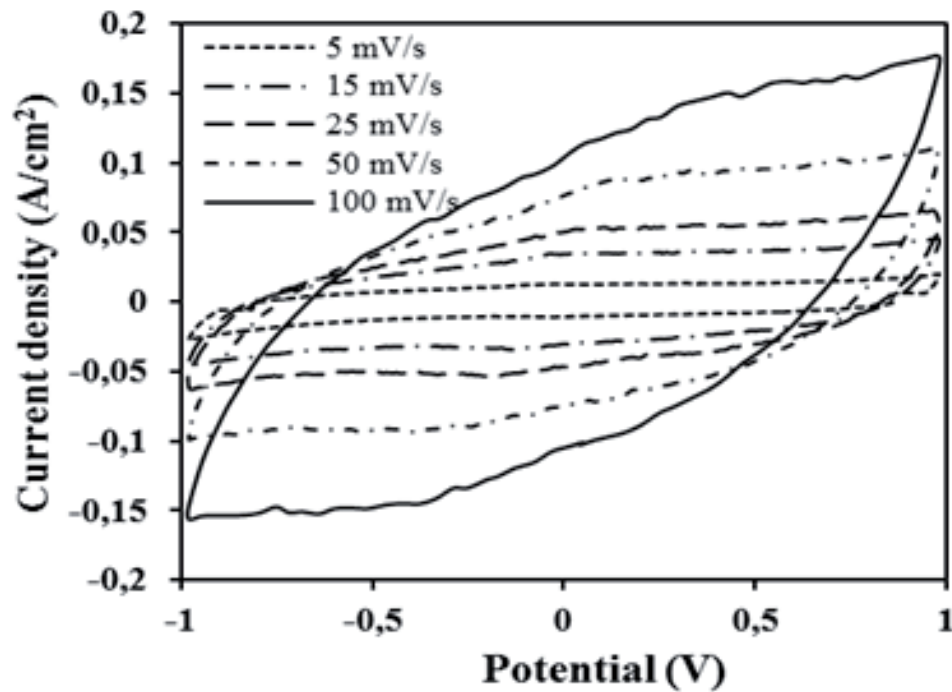

Figure 5: Profile of voltammograms with various scan rates forBACM-C2.

[17]. According to Ma et al., in a high scan rate (100 mV/s), electrons transfers and ion diffusion occurred quickly caused by the specific capacitance decreases [18].

4. Conclusion

BACM consisting of pre-carbonized of EFB (90% by weight) and GPC (10%) were pressed with various compression pressure of 4.5, 6 and 7.5 metric ton, respectively. These BACM were carbonized at 800^oC, and activated for 1.5 h and 2 h by CO_2 at 800^oC which were used as electrodes in symmetrical supercapacitor cells. We observe that the electrochemical behavior of supercapacitor cells were changed and strongly depending on the compression pressure and holding time of activation. The better specific capacitance were resulted from the compression pressure at 7.5 metric ton and holding time of activation of 2 h.

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