Effects of Activation Time on the Performance of Supercapacitor Binderless Activated Carbon Electrodes Derived from Fibers of Oil Palm Empty Fruit Bunches

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Abstract. Green monoliths (GMs) with different composition, labelled as GM1, GM2 and GM3, were prepared from self-adhesive carbon grains (SACG) produced from fibers of oil palm empty fruit bunches, SACG treated with 0.4 M H_2SO_4 and mixtures of SACG and carbon nanotubes (5 wt.%) treated with 0.4 M H_2SO_4, respectively. Each GMs was carbonized and then activated with holding time of 1 h and 2 h, respectively, to produce their respective activated carbon monoliths (ACMs). These ACMs were used as electrodes to fabricate supercapacitor cells using H_2SO_4 electrolytes, Teflon separator and stainless steel 316L current collector. The porosity of the ACMs, examined by nitrogen adsorption-desorption isotherm method were found affected after prolonging the activation time. From the electrochemical characterization of the ACMs electrodes using galvanic charge-discharge methods, it was found that supercapacitor cells fabricated using the ACMs produced by longer activation time (2 h) showed better performance, which had higher specific capacitance (113 F/g), specific power (159 W/kg) and specific energy (3.35 W h/kg), compared to the cells using ACMs produced by shorter activation time (1 h).

Introduction

Supercapacitors or also known as ultracapacitors or electric double layer capacitors (EDLCs) consist of a pair of electrodes, an electrolyte, a pair of current collectors, and a separator. Its electrical energy is stored in an electrochemical double layer formed at the interface between the electrically charged surface of the electrode and the ionic charges of the electrolyte solution [1]. Supercapacitors advantages are for energy storage applications that demand high energy density, high reliability, maximum power, long-cycle life or long-term operation stability, suitable dimensions and weight, low cost, fast discharge/charge time, low level of heating, safety, etc. Its energy capacities as energy storage devices allow supercapacitors to compliment the functions of batteries and conventional capacitors in term of energy and power requirements, merely making their application widely found in appliances such as electronic devices, electric vehicles, and military equipment. Typical materials used for supercapacitor electrodes are conducting polymers, metal oxides, and porous materials such as activated carbon, carbon aerogels, carbon nanotubes and graphene.

Activated carbon (AC) is widely used as electrodes because of its high surface area and porosity, good thermal and electrical conductivity, good anti-causticity, high stability, low cost and commercial-scale availability [2]. Its high specific surface area allows the electrostatic charges stored at the AC electrode/electrolyte double layer interface to produce a high capacitance of supercapacitor. However, AC with high surface area has a relatively low electronic conductivity, causing supercapacitor to have a high equivalent series resistance (ESR) and hence lower specific energy (E) and power (P) during charge and discharge. This drawback was resolved by mixing AC with carbon ___ ic conductivity [3]. Generally, the CNTs have a

lower specific capacitance (C_{sp}) than the AC, therefore the mixture was subjected to physical/chemical activation in an attempt to increase the surface area and specific capacitance (C_{sp}) of the electrode[3,4].

In the present study, the preparation and characterization of binderless AC monoliths (ACM) electrodes from the mixture of self-adhesive carbon grains (SACG) from oil palm empty fruit bunch (EFB) fibers, CNTs and potassium hydroxide (KOH) is reported. Here, the green monoliths (GMs) mixture were activated by CO_2 gas and two duration of activation time were selected in order to observe the effect of prolonging activation time on properties of the electrodes and performance of supercapacitor cells using these prepared electrodes.

Experimental

The activated carbon monoliths (ACMs) were prepared according to our previously reported method to produce SACG using fibers of oil palm empty fruit bunches as precursor [5–11]. The fibers has undergone a pre-carbonization process (Furnace CTMSB46) at temperature of ~280°C, ball milling (GEC BS2206H) for 36 h before being sieved (Matest 24030 Brembate Sopra (BG)) to produce SACGs with particles size $\leq$ 53 μm [12]. Three types of ACMs according to their composition were labeled as 1, 2 and 3 as shown in Table 1. The type 1, type 2 and type 3 were consisted of 100 wt.% SACG, SACG treated with 120 ml of 0.4 M H_2SO_4 and SACG mixed with 5 wt.% CNT and treated with 0.4 M H_2SO_4, respectively. These treatment process were conducted at the temperature of 100°C and were stirred for 1 h using magnetic stirrer (Cimarec (R) 2 04643-10). After 24 h, these treated mixtures were filtered for 3 days using distilled water to neutralize and to eliminate any chemical reagent residual that were remained in these mixtures. Drying process were done for 24 h at the temperature of 100°C in an oven before continuing with milling process for 20 min, with 10 g of powder at each operation time. Finally, these powders were converted into GMs without the presence of any binders using pelletizing machines (VISITEC 2009 – Malaysia), where 0.75 g of powder were inserted inside a 20 mm-diameter mold and pressed with applied pressure of 2.5×10^7 Pa.

The carbonization processes of all GMs were carried out in a carbonization furnace (Vulcan Box Furnace 3-1750) under N_2 atmosphere with flow rate of 1.5 l/min at 500°C [13]. These samples were then activated at 800°C under 1.0 l/min flow of CO_2 gas for 1 h and 2 h to produce two batches of ACMs with different duration of activation time [14]. The ACMs were polished to desired thickness in order to be employed as electrode in a supercapacitor cell consisted of Teflon ring with thickness of 0.1 mm as separator, 316L stainless steel current collector and 1.0 M H_2SO_4 electrolyte solution [15].

The density of the GMs and ACMs were determined by measuring their dimensions (Mitutoyo 193-253) and weight (Mettler Toledo AB204). The nitrogen adsorption-desorption isotherm experiments (Micromeretic ASAP 2010) were carried out at 77 K to investigate the porosity of the monoliths. The electrochemical performance of the cells produced from ACM electrodes was studied using galvanic charge-discharge (GCD) method, where an instrument (Solatron 1286) equipped with an electrochemical interface system was employed [16].

Result and Discussion

Comparison of nitrogen absorption-desorption isotherms plots (not shown here) for all samples found that all the isotherm curves exhibited a typical combination of type-IV and type-I curves, indicating that all ACMs were porous, contributed by both meso- and micro-pores with high internal surface area [17]. The nitrogen adsorption-desorption capacities are higher for 2 h activation time compared to 1 h. This enhancement depends on the type of GMs used to prepare ACMs. Table 2 show the values of the porosity parameters (S_{BET} = BET surface area, S_{meso} = meso- pore surface area, V_{micro} = micro-pore volume, V_{meso} = meso-pore volume, D = average pore diameter) using a standard procedure [17]. As can be seen in this table 0.3 %, 8.9 % and 2.9 % change in the S_{BET} values can be observed for the ACM1, ACM2 and ACM3, respectively. A similar or contrary behavior is also observed for other parameters shown in this table. The data in Table 2 show that the D values change due

to the change in activation time. It has been observed that increase of activation time can retard the growth of pores, leading to the destruction of adjacent pores and changing the pore shape, which can change the average pore diameter [18]. From these results, it can be concluded that activation time plays a very critical role in the formation of pores structure in carbon monoliths.

Table 1. Percentage of composition for ACM electrodes

Electrodes	SACG (wt.%)	H_2SO_4 (molarity)	CNT (wt.%)	Activation Time (h)
ACM11	100	-	-	1
ACM12	100	-	-	2
ACM21	100	0.4	-	1
ACM22	100	0.4	-	2
ACM31	95	0.4	5	1
ACM32	95	0.4	5	2

Table 2. Porosity data of electrodes activated for 1 h and 2 h, respectively

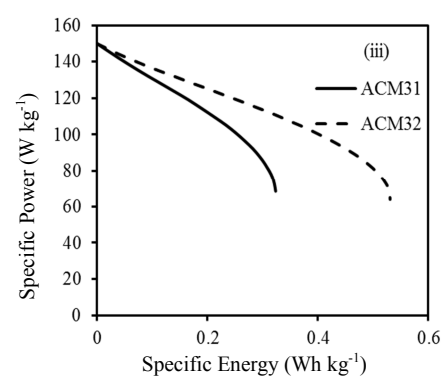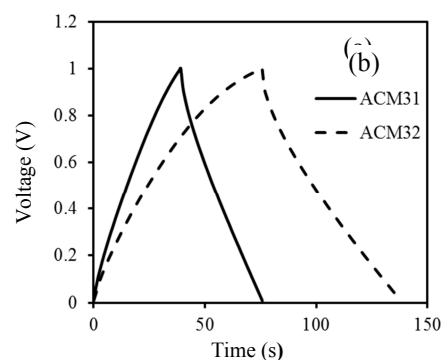| Electrodes	S_{BET} $(m^2 g^{-1})$	S_{meso} $(m^2 g^{-1})$	V_{micro} $(cm^3 g^{-1})$	V_{meso} $(cm^3 g^{-1})$	D (nm)
ACM11	465.58	41.74	0.11	0.03	1.95
ACM12	467.08	58.75	0.22	0.04	2.15
ACM21	348.46	38.82	0.15	0.03	2.00
ACM22	379.52	30.94	0.17	0.02	1.96
ACM31	305.80	30.49	0.13	0.05	2.30
ACM32	314.62	31.35	0.14	0.06	2.48

Fig. 1. Charge-discharge curves (a) and Ragone plots (b).

Table 3. Electrochemical parameter values from GCD data

Cells	ESR (Ohm)	C_{sp} $(F g^{-1})$	E $(Wh kg^{-1})$	P $(W kg^{-1})$
ACM11	3.13	110.25	2.58	153
ACM12	1.42	113.33	3.35	159
ACM21	5.08	5.75	0.12	130
ACM22	8.75	8.08	0.15	135
ACM31	4.28	12.31	0.32	145
ACM32	4.21	22.48	0.53	150

Table 3 shows the effect of changing activation time on the electrochemical parameter values of all the cells, which were obtained using a standard method from these GCD curves [19–21]. It was observed that the GCD curves (not all shown here) of all the cells recorded at a current density of 0.01 mA/cm^2 over a potential range of 0 to 1.0 V exhibit a symmetrical shape, with an almost equal duration of charge and discharge time, which is typical for a carbon based supercapacitors. This GCD curves behavior varies with activation time, as can be seen, for example for the ACM31 and ACM32 cells shown in Fig. 1 (a). This figure clearly shows that 1 h increase of activation time can prolong the charge-discharge times, depending on the types of electrode. As can be seen in Fig. 1 (b), changing activation time can also change the behavior of the P – E relationship; P and E values were determined from the GCD curves using a standard method.

Conclusion

Type 1, 2 and 3 ACM supercapacitor electrodes, prepared by activation at two different duration of CG, H_2SO_4 – treated SACG, and H_2SO_4 – treated

mixture of SACG (95 wt.%) and CNT (5 wt.%), respectively, were characterized by N_2 adsorption-desorption and electrochemical methods. It was found that extending activation time from 1 h to 2 h affected the porosity of the electrodes, which then affected the performance of the supercapacitor. It was observed that 3 %, 30 % and 4 % changes in the C_{sp}, E and P values, respectively, occurred for the cell with type 1 electrode, and 40 %, 25% and 4% changes for the type 2 electrode, and 80 %, 66 % and 3 % changes for type 3 electrodes. It can be concluded from these results that the level of effect arising from changing the duration of activation time is strongly dependent on the property of precursor used to produce the ACMs electrodes.

Acknowledgement

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