Prototype Profile of Supercapactors with Activated Carbon/Fe₃O₄ Electrodes Natural Materials and Celgard Li-Ion Battery Separators

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Abstract. The electrode composition material in the supercapacitor affects the storage performance of the supercapacitor. In this study, the electrodes were made from coconut shell activated carbon and Fe₃O₄ from iron sand. To be used as electrodes, the two materials are mixed with PVDF and a solution of Dimethylacetamide at a temperature of 70°C; then, a coating process is carried out by layering the electrode material onto aluminium foil to obtain an electrode sheet. The coin cell assembling process was then carried out by arranging the electrode sheets and the Celgard Li-ion battery separator in the glove box and then tested for charge/discharge with a current density of 5-81 mA/g and cycle stability at a current of 20 mA/g. The study results show that the activated carbon/5 wt% Fe₃O₄ supercapacitor has the best capacitance value for charging at 8.03 F/g and discharging at 8.55 F/g at a current density of 5 mA/g. The activated carbon/5 wt% Fe₃O₄ supercapacitor has cycle stability of up to 200 cycles and can withstand up to 95% with a capacitance of 6.6 F/g.

Keywords: Activated carbon/Fe₃O₄, Electrode, Supercapacitor

1 Introduction

At this time, many electronic devices require electrical energy storage devices such as electric cars, electric bicycles, cell phones, and laptops. Usually, the battery on the market is not environmentally friendly (toxic), which causes environmental pollution. Therefore, energy storage devices that are efficient and environmentally friendly are desirable. Supercapacitors are efficient energy storage devices because of their enormous power density and charge storage capacitance, fast and long-lasting charging processes with excellent cycle life compared to conventional batteries and capacitors [1]. The supercapacitor component consists of two electrodes and a separator [2].

The supercapacitor electrode can be activated carbon [3]. However, due to its low energy density, it limits its widespread use in energy storage applications. Therefore, alloys with metal oxides such as Fe₃O₄ are needed in addition to their high electrical conductivity, affordable prices, and environmentally friendly [4]. Chen et al. [5] succeeded in making Fe₃O₄/biocarbon electrodes from bagasse (*Saccharum officinarum* L) with various mass ratios (0.5:1; 0.75:1; 1:1; 1.5:1) Fe₃O₄

with the best results at a ratio of 1:1 Fe₃O₄ at a scan rate of 0.01 V/s resulting in a high specific capacitance value of 342 F/g. Rohmawati et al. [2] succeeded in making Fe₃O₄ supercapacitor electrodes from the extraction of iron sand and activated carbon from coconut shell (*Cocos Nucifera*) with a mass of 5 wt% Fe₃O₄ in 1M Na₂SO₄ solution with a scan rate of 1 mV/s with a high specific capacitance value of 357.3 F/g.

The separator function is a barrier between the two electrodes to prevent direct contact due to a short circuit. The separator must be thin and porous enough for the movement of electrolyte ions to work appropriately to increase the electrical conductivity [6]. PVA/H₃PO₄ electrolyte polymer has the potential to be used as a separator with a mesoporous pore size category so that charge transfer from electrolyte ions to diffuse into the electrode pores works optimally during the charging-discharging process. This electrolytic polymer is chemically stable, non-toxic and relatively inexpensive [2]. However, during the manufacture of the separator, the results obtained were too thick and bubbly, so that it did not match the specifications for the charging-discharging test characterization. Therefore, in this study, a commercial Celgard Li-ion battery separator was used in the form of a thin sheet with the primary material of polypropylene (PP), which has microporous

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characteristics, low electrical resistance, high leakage resistance, and has strong resistance to oxidation [7].

In order to further study, the potential of activated carbon/ Fe_3O_4 as a supercapacitor material, the researchers carried out a charging-discharging characterization to know the best specific capacitance value for current variations. Du et al. [8] tested supercapacitor materials with two electrodes, namely Fe_3O_4 electrodes (80 wt% Fe_3O_4 , 15 wt% acetylene black, 5 wt% PTFE) and active carbon electrodes (85 wt% AC, 10 wt% acetylene black, 5 wt% PTFE) and then charging-discharging characterization was carried out with variations in the current (0.5; 1; 2) mA/cm², and the best results were obtained at 0.5 mA/cm² current with a specific capacitance value of 37.9 F/g. Sinan and Unur, [4] reported that the composition of 43 wt% Fe_3O_4 -carbon with various currents (0.25; 0.5; 0.75; 1; 1.52) A/g obtained the best results at a current of 0.25 A/g with a specific capacitance value of 280.8 F/g. Meng et al. [9] reported that 80 wt% Fe_3O_4 -carbon with charging-discharging characterization with various currents (0.5; 1; 2; 5) A/g and obtained the best results at a current of 0.5 A/g with a specific capacitance value of 139 F/g.

Based on the results above, this study's optimization of the supercapacitor characteristics of activated carbon/5 wt% Fe_3O_4 was carried out through a charging-discharging test. This test was carried out with a current variation of 5–81 mA/g. This current range was chosen because of the several studies above [4], [9] shows that the smaller the current, the greater the capacitance value. The supercapacitor made in this study was expected to be used as an alternative battery that is environmentally friendly.

2 Materials and Method

2.1 Materials

In this study, the materials used include: coconut shell, iron sand, NH_4OH 6 M (SAP 37%), HCl 12 M (SAP 37%), H_3PO_4 5 M (SAP 50%), LiPF_6 1 M (Sigma-Aldrich), Dimethyl-acetamide (DMAC) Sigma-Aldrich, Polyvinylidene fluoride (PVDF) Sigma-Aldrich, Super P, and celgard Li-ion battery

2.2 Preparation of activated carbon

Activated carbon was made from coconut shells in several stages; the first stage is dehydration; namely, the coconut shells were dried in the sun for 12 hours. The second stage is carbonation; namely, the coconut shell is calcined at a temperature of 400°C for 6 hours, the last is the activation stage, namely, the carbon is calcined at a temperature of 800°C for 5 hours and cooled at room temperature.

2.3 Preparation of Fe_3O_4

Fe_3O_4 was extracted from Lumajang iron sand by coprecipitation method, namely iron sand stirred in HCl solution at 70°C in 35 ml 12 M HCl solution for 35

minutes. After that, it was filtered to produce a thick yellow solution. The solution is then stirred and dripped with 6 M NH_4OH 24 mL at a temperature of 70°C for 30 minutes, serves as a precipitant of the Fe_3O_4 material indicated in dark black. After that, it was washed using distilled water to remove impurities, then filtered to obtain a solid black precipitate. Then in the oven at 70°C for 12 hours, and cooled to room temperature.

2.4 Fabrication of activated carbon/ Fe_3O_4 electrode

Activated carbon/5 wt% Fe_3O_4 with a total of 1 gram was sieved using a 400 mesh sieve to obtain a fine and uniform particle size; the next step was 0.125 g of PVDF (functions as an adhesive) dissolved with 3 ml of Dimethyl-acetamide (DMAC) at a temperature of 70°C for 15 minutes, then mix 0.125 grams of Super P to increase the electrical conductivity value and then add 1.5 ml of DMAC. After that, mix the sifted main ingredients (Composite activated carbon/ 5 wt% Fe_3O_4) and stir for 30 minutes until the mixture is homogeneous. In the last step, the coating process is carried out, namely coating the material onto aluminium foil using an Automatic Thick Film Coater, which results in a sheet of electrodes. After that, it was dried at 80°C for 30 minutes.

2.5 Fabrication of supercapacitor prototype

At this stage, the electrode sheet was cut to a diameter of 1.6 cm, and the celgard Li-ion battery separator was cut to a diameter of 1.9 cm. It provided that the size of the separator is larger than the electrode so that there is no direct contact which can cause a short circuit between the cathode and anode while in the coin cell. Previously, the coin cell was washed with ethanol to make it clean and sterile. Next, the coin cell assembly process is carried out in the glove box with use 50 μl LiPF_6 as an electrolyte in the supercapacitor battery. In the next stage, the supercapacitor with an arrangement like Fig 1 was pressed using a Hydraulic Crimping Machine at a pressure of 1000 Psi to become a prototype as Fig 2, and the charging/discharging test process is carried out.

Fig. 1. Arrangement prototype of supercapacitor.

Fig. 2. Prototype of supercapacitor.

2.6 Instrumentations

To determine the phase of a material, in this study, activated carbon and Fe₃O₄ preparation results were characterized by X-ray diffraction (XRD), with the following specifications: Bragg-Brentano Philips X'pert Diffractometer, Cu-K α radiation with an angle range of 15-70° step data 0.02°/min. The data from the characterization was then analyzed quantitatively using Match! Software. This identification was made by matching the diffraction peaks of the research results with the powder diffraction file (PDF) database.

The functional groups of activated carbon and Fe₃O₄ samples and their composites can be identified by the Fourier Transform Infrared Spectroscopy (FTIR) characterization of the Shimadzu brand IRPrestige 21 with a wavenumber range of 4000-400 cm⁻¹. The Brunauer Emmet Teller (BET) characterization of Quantachrome NovaWin version 11.0 was carried out to determine the surface area and pore size of activated carbon/5 wt% Fe₃O₄ through an adsorption-desorption isotherm graph.

This study's capacitance value of the activated carbon/5 wt%Fe₃O₄ supercapacitor can be analyzed using the charging/discharging characterization with the WonATech WBCS3000 automatic battery cycler. The test was carried out at a current of 5-81 mA/g with a potential range of 0-1.2 V. The capacitance value can be calculated from the integration voltage time, according to the following equation [8]:

$$C_m = \frac{i \times t}{\Delta E \times m} \quad \dots\dots\dots (1)$$

where C_m is the specific capacitance (F/g), i is the current charging-discharging(A), t is the discharging time(s), ΔE is window potential (V), m is the mass of the supercapacitor (g).

3 Results and Discussion

3.1 X-ray Diffraction (XRD)

The results of XRD characterization for activated carbon, Fe₃O₄ and composite samples can be seen in Fig 3. Phase analysis can be done by matching the X-Ray Diffraction (XRD) data with the database in the Match software, namely PDF no 96-900-7645. The results of the Match analysis show that the diffraction pattern of the Fe₃O₄ sample is single phase with diffraction peaks

at diffraction angles $2\theta = 30.29^\circ, 35.61^\circ, 43.39^\circ, 53.52^\circ, 57.35^\circ, 62.72^\circ$ and Miller's index (hkl) (220), (311), (400), (422), (333), (404). Meanwhile, the XRD pattern on the activated carbon/5 wt% Fe₃O₄ sample shows a specific peak position identical to Fe₃O₄, but at an angle of $2\theta = 20^\circ$ - 30° , an amorphous pattern is formed with broad and sloping peaks, as well as at $2\theta = 40^\circ$ - 50° a diffraction pattern is formed activated carbon [10]. This study is the same as what was done by Intifadhah et al. [11] where at an angle of 43° and 45° , it is an activated carbon phase whose atoms are irregular in a particular orientation (amorphous).

Fig. 3. XRD patterns in the sample (a) Fe₃O₄ and (b) activated carbon/5 wt% Fe₃O₄.

3.2 Fourier Transform Infrared (FTIR)

FTIR spectra of activated carbon/Fe₃O₄ in Fig 4, appear to have decreased absorption peak at wavenumbers between 3000 cm⁻¹ and 3500 cm⁻¹ and the disappearance of the C-H functional group between 2850 cm⁻¹ to 3000 cm⁻¹ which is an indication of activated carbon. It might be magnetically bound to the functional group due to the milling process when making activated carbon/Fe₃O₄ composites. Increased absorption peak occurs at wave number 1091 cm⁻¹, a C-O stretching function group in carboxylic acids, alcohols, phenols, and esters [12]. The absorption of Fe-O function groups is located at wave number 690 cm⁻¹, 798 cm⁻¹, 877 cm⁻¹ [13-14] and 474 cm⁻¹; 428 cm⁻¹ [15].

Fig. 4. FTIR spectra of activated carbon/5 wt% Fe₃O₄.

3.3 Brunauer Emmet Teller (BET)

BET characterization was carried out to determine the surface area and pore size of a material. BET characterization results from activated carbon/5 wt% Fe_3O_4 shown in Fig 5. The isotherm curve forms a hysteresis loop in the relative pressure range about 0.85–0.97 P/P_0 . The isotherm curve (Fig 5) shows a type IV adsorption-desorption process which is characteristic of mesoporous with type H_1 of hysteresis loop with cylindrical pores [16]. The results of the BET test show that the surface area of the sample is $320.626 \text{ m}^2/\text{g}$; this value is relatively good if applied as a supercapacitor electrode material. The curve also shows an open-end, indicating that the adsorbed nitrogen gas was retained in the pores during the adsorption process. As a result, the volume of the gas is greater than the volume of gas released during the adsorption-desorption process. So that when applied as a supercapacitor electrode, it will provide a high specific capacitance value during the process of discharging or discharging because the electric charge will be retained in the electrode pores.

Fig.5. Isotherm curve of Activated Carbon /5 wt% Fe_3O_4 .

3.4 Charging/Discharging

The galvanostatic charging-discharging process on the activated carbon/5 wt% Fe_3O_4 supercapacitor was carried out in a potential range of 0-1.2 V with a current variation of 5-81 mA/g. The results were shown in Fig 6. The charging-discharging curve of the relationship between the applied potential (V) on the y-axis and time (s) on the x-axis. The curve shows the behaviour of the charge storage process that takes place reversibly at the electrodes, as evidenced by the shape of the curve resembling a symmetrical triangle [17], for a current variation of 5 mA/g to 81 mA/g. Based on this curve, it can be seen the specific capacitance value of the supercapacitor using equation (1), the specific capacitance value for the charging and discharging process shown in Table 1.

Fig. 6. Charging-discharging curve of activated carbon/5 wt% Fe_3O_4

The data in Table 1 shows that the specific capacitance value decreases as the current value increases. At a higher current level, the ion diffusion time is short; only the outer surface of the electrode experiences an energy storage mechanism so that the energy storage process does not occur ideally [4].

Table 1. Specific capacitance values for charging-discharging with current variations in supercapacitor (activated carbon /5 wt% Fe_3O_4)

Current variations (mA/g)	Charging capacitance (F/g)	Discharging capacitance (F/g)
5	8.03	8.55
9	7.89	7.64
17	7.06	6.79
28	6.33	6.13
47	5.52	5.26
81	4.64	4.43

Fig. 7. Stability of cycle capacitance in supercapacitors activated carbon/5 wt% Fe_3O_4

The stable performance of the activated carbon/5 wt% Fe_3O_4 supercapacitor at 200 cycles with a current of 20 mA/g can be observed in Fig 7. The activated carbon/5 wt% Fe_3O_4 supercapacitor has good capacitance stability. At the zero cycles, the capacitance

as 6.9 F/g decreased by about 8% to 6.3 F/g and stabilized in the 50th cycle. However, it decreased back 10% to 6.2 F/g on the 150th cycle and persisted to 95% after 200 cycles with a capacitance value of 6.6 F/g. It can be caused by the addition of Fe_3O_4 to activated carbon which can increase electrical conductivity and cycle stability (reversibility) by increasing the accessibility of ions [18] (Zeng et al. 2014).

4 Conclusion

Based on the results of this study, it can be concluded that the results of the charging-discharging characterization obtained the best value at the current density of 5 mA/g with a value of Specific capacitance for charging 8.03 F/g and discharging 8.55 F/g. The capacitance value decreases at a higher current level the greater it is. Cycle stability at a current of 20 mA/g shows the capacitance value of the activated carbon supercapacitor/5 wt% Fe_3O_4 is relatively good; it can last 95% to 200 cycles with a capacitance value of 6.6 F/g.

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