AC-MnO2-CNT composites for electrodes of electrochemical

by Agus Subagio

AC-MnO$_2$-CNT composites for electrodes of electrochemical supercapacitors

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Abstract. Electrodes for electrochemical supercapacitors were fabricated by doctor blade method of composite of activated carbon (AC), MnO$_2$ and carbon nanotubes (CNTs). The AC-MnO$_2$-CNTs composites were synthesized by solution processing method in pH variation of 3, 7 and 11. The composites were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy and impedance spectroscopy. The XRD pattern shown the crystalline structure and the SEM image observed that the distribution of CNTs was homogeneous between carbon particles. The electrodes were fabricated for supercapacitor cells with 316L stainless steel as current collector and 1 M Na$_2$SO$_4$ as electrolyte. An electrochemical characterization was performed by using an electrochemical impedance spectroscopy (EIS) method using a LCR Hi-Tester HIOKI 3522 instrument and the results showed an increase in the value of specific capacitance at the AC-MnO$_2$-CNT on the acidic condition.

Introduction

Supercapacitors as energy storage devices fill the gap between conventional batteries and capacitors, i.e. they have high specific energy and power density [1]. Supercapacitors are considered to have high-power electrical capacitance, excellent reversibility, long life and potentially in the development of technologies that support applications including electric vehicles, portable computers, and other devices [2]. There are two kinds of supercapacitors depending on charge storage mechanism and active materials: (i) electrochemical double layer capacitors (EDLC) and (ii) redox supercapacitors or pseudo-capacitors [3]. In EDLCs, carbon-based materials with high specific surface area are most widely used and energy storage mechanism is based on simple physical movement of ions to and from the carbon electrode surface. In redox supercapacitors, metal oxides or conducting polymers are commonly employed and energy is stored through fast and reversible electrochemical charge transfer process. The specific and area capacitance is dependent primarily on the characteristics of the electrode material that is, surface area, pore size distribution, i.e. active area in the pores on which the double-layer is formed. Thus, providing highly porous carbon as an electrode material can offer high stability and cyclability in supercapacitors.

Material carbon nanotubes (CNT) is one nanomaterial that has excellent mechanical properties. CNT structure, length and diameter as well as the direction of crystal growth properties of CNTs provide elastic moduli which has 5 times greater than the strong steel and tensile strength up to 100 times greater. Carbon nanotubes are considered as composite electrode materials for supercapacitors because of potential excellent mechanical properties and good electrical conductivity [4].

The addition of a metal oxide on the carbonaceous increases the electrochemical performance of electrode material. Metal oxide is a material that has properties suited to optimizing the performance of a supercapacitor. RuO$_2$ as an example, the specific capacitance is reported 720 F/g

in a state of acid electrolyte. However, Ru is a type of precious metal and at the same time RuO_2 is a poison, which blocked commercialization [5]. Currently, manganese dioxide (MnO_2) has attracted due to its superior capacitive performance, abundance and environmental friendliness. The theoretical specific capacitance of MnO_2 is high (1232 F/g), however, it cannot be achieved even for the ultra thin MnO_2 film because the poor electrical and ionic conductivities greatly limit the practical performance of MnO_2 based materials for supercapacitors [6]. Furthermore, to increase the capacitance supercapacitors and improve the transport of electrons and ions in the electrode efficiently, MnO_2 was made as a composite structure [7].

Many approaches have been applied to prepared MnO_2-CNT composites for supercapacitors application. A microwave assisted reaction was developed to synthesize the compocite based on the mass of MnO_2 along [8]. CNT has been modified by MnO_2 using acetic acid to achieve a pH of 2.3 of the mixing process. The results showed CNT-MnO_2 nanocomposite shows the specific capacitance of 162.2 F/g [9]. Reddy et al. have prepared Au-MnO_2/CNT hybrid coaxial arrays, resulting in a specific capacitance of 68 F/g based on total massa of materials and current collectors [10]. The MnO_2 and SWNT composites have been successfully synthesized via a novel room temperature route starting with $KMnO_4$, ethanol and commercial SWNT. The MnO_2:20 wt% SWNT composite showing the best combination of coloumbic efficiency of 75% and specific capacitance of 110 F/g [11].

For the MnO_2 synthesis based on the direct reaction between the CNT and permanganate, synthesis condition such as reaction time, CNT amounts, solution acidity, preparation method and CNT oxidation degree will affect the properties of prepared supercapacitor materials. Therefore, the goal of the present work is to optimize the parameter of synthesis condition, i.e. the pH variation of the mixing process of activated carbon, MnO_2 and CNT. Characterization of AC-MnO_2-CNT composite is done by using XRD, SEM, TEM and EIS method.

Experimental

The AC-MnO_2-CNT composite materials were synthesized using sol-gel method. Briefly, 2 grams of $KMnO_4$ were dissolved in 20 ml of demineralized water and stirred until for 15 minutes. Next, 2 grams of purified CNT and activated carbon (AC) were dissolved in 10 ml of demineralized water. To increasing dispersion of CNT, the surfactant sodium dodecyl sulfate (SDS) of 5% of the weight of CNT was added. The resulting suspension was stirred for 15 minutes. $KMnO_4$ solution was slowly inserted into the sol of CNTs that have been made in a container in pH of 3, 7, and 11. The AC-MnO_2-CNT mixture was added by acetic acid for pH of 3, without addition of a solution for pH of 7 and added by ammonium hydroxide for pH of 11. After conditioning in pH variation, the AC-MnO_2-CNT composite were stirred for 24 hours. Finally, the resulting AC-MnO_2-CNT composit were filtered and washed with ethanol to remove the residual of $KMnO_4$. The solid products were dried in a vacuum at 100 ºC for 5 h to obtain the powder of AC-CNT-MnO_2.

Microstructures of AC-MnO_2-CNT products that have been formed were characterized using X-ray diffraction (XRD) with a CuK_α target. Morphology of samples was examinained using a scanning electron microscope (JEOL-6510LA) and transmission electron microscope. The specific capacitance of products were investigated by LCR Hi-Tester HIOKI 3522 instrument.

Result and Discussion

In order to show actual size and formation of deposited MnO_2 particle, Fig. 1 present TEM image of the pristine CNTs and AC-MnO_2-CNT composite material. From this result, our attempt to prepare the AC-MnO_2-CNT composite materials was successful and the deposited MnO_2 grains clumped together. It can be seen that agglomerated MnO_2 particles with an average size of about 50 ~ 150 nm were attached to the CNT.
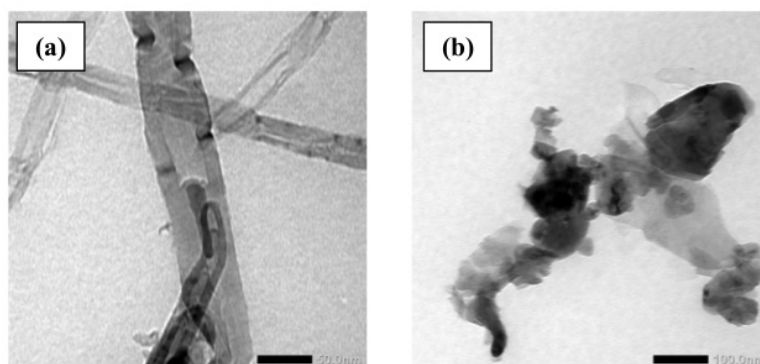
Fig 1. TEM images of (a) the pristine CNT and (b) AC-MnO$_2$-CNT composite.

Fig. 2 shows the morphologies of the AC-MnO$_2$-CNT composites. It can be seen obviously that MnO$_2$ are distributed on the surface of CNT, meanwhile the AC formed mounds as background of the morphologies and will play a role as a storage of charge in supercapacitors.
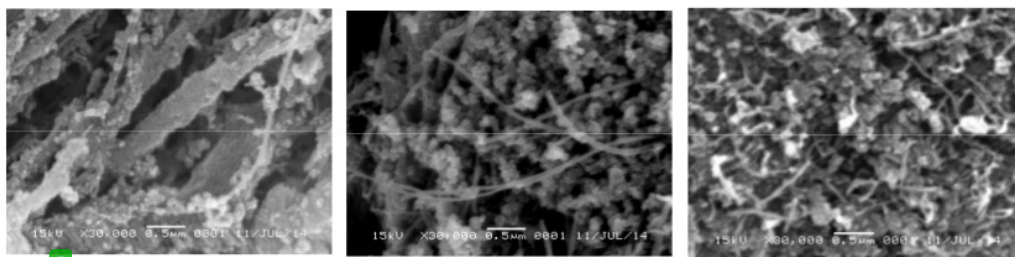

Fig. 2. SEM images of the AC-MnO$_2$-CNT composites in pH of (a) 3, (b) 7 and (c) 11.

To determine the crystal structure, X-ray diffraction (XRD) was employed and the XRD patterns of the products obtained under different in pH of AC-MnO$_2$-CNT composites are shown in Fig. 3. The diffraction peaks at 2 theta of 25.66° and 42.50° can be attributed to the (002) and (100) planes of AC-CNT with hexagonal graphite structure [12]. The diffraction peaks at 2 theta of 28.65°, 37.63° and 41.91° are corresponding to (310), (211) and (411) planes of α-MnO$_2$ orientation (JCPDS 44-0141), respectively [13]. The intensity of the MnO$_2$ peaks is lower, indicating amorphous structure. The amorphous structure will support electrolyte into the electrode matrix and increases the contact between electrolyte and electrodes [9].
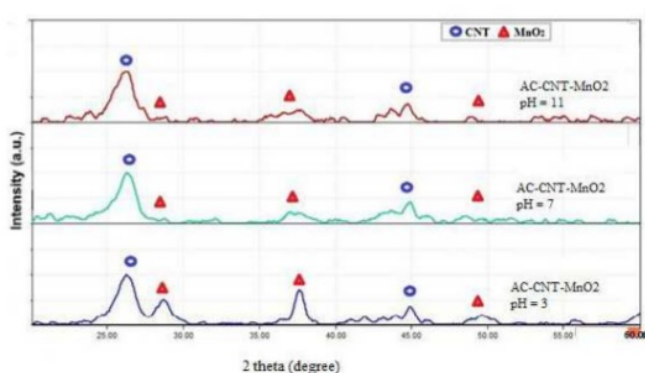

Fig. 3. X-ray diffraction patterns of AC-CNT-MnO$_2$ composites in pH value.

Electrochemical impedance spectroscopy testing need preparation of an requires a procedure to form a supercapacitor modeling. Preparation of composites made by mixing AC-MnO$_2$-CNT with hydrogel electrolyte made by poly vinyl alcohol and Na$_2$SO$_4$ with ratio of 1:9. Once formed pellets were wet by the electrolyte, then later assembled into a simple double layer supercapacitors modeling with SS foil as current collector and celgard as separator.

The main objective in this EIS characterization was to determine the ability of the specific capacitance of the sample AC-MnO$_2$-CNT modified by variation in pH value. After the samples were model as a double layer supercapacitors, the samples were connected and energized AC of 0.1 V at a frequency range of 0.1 Hz -100 kHz. From the data processing results obtained the difference value of specific capacitance (C$_S$) each particular frequency variations in the supercapacitor, which was presented by the graph in Fig. 4.
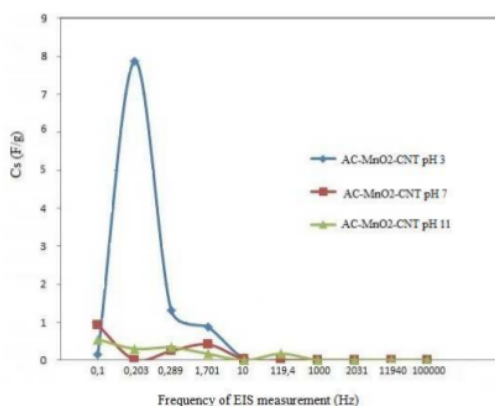

Fig. 4. Curves of specific capacitance as function of frequency.

Based on the data obtained specific capacitance (C$_S$), the greatest value of the C$_S$ of the AC-MnO$_2$-CNT composite in pH condition of acid, neutral and alkaline were 7.86, 0.93 and 0.55 F/g, recpectively. Measurement of specific capacitance that occurs in acidic reaction condition increased significantly compared to neutral and alkaline state was related to the formation of MnO$_2$ cathodic reduction reaction. In reaction to the atmosphere slightly acidic and neutral atmosphere, ion MnO$_4^-$ with +7 oxidation number would be reduced to MnO$_2$ precipitate with oxidation number +4, while in a state of MnO$_4^-$ alkaline ions would be reduced to manganate (MnO$_4^{2-}$) which was described by the following reaction:

1) The reduction reaction MnO$_4^-$ acidic condition:
$$MnO_4^- + 4H^+ + 3e \longrightarrow MnO_2 + 2H_2O$$

2) The reduction reaction MnO$_4^-$ neutral condition:
$$MnO_4^- + 2H_2O \longrightarrow MnO_2 + 4OH^-$$

3) The reduction reaction MnO$_4^-$ alkaline condition:
$$MnO_4^- + 4OH^- \longrightarrow 4MnO_4^{2-} + 2H_2O + O_2$$

This reaction has been evidenced from the XRD pattern of AC-MnO$_2$-CNT composite that the presence of MnO$_2$ has the greatest intensity was at the AC-MnO$_2$-CNT composite in acidic conditions. The MnO$_2$ produced was in the form of α-MnO$_2$ as the crystallographic groups of MnO$_2$. In general α-MnO$_2$ is a type of crystal that comes into the group of the tetragonal crystal. The stability of α-MnO$_2$ structure is dependent on the protonation effect of the crystal. The presence of high H$^+$ ion at low pH is a condition in which crystals of this type exist in the most stable state.

The presence of H^+ ions will support and stabilize cavities in the crystal structure of α-MnO_2. The ability of the double layer capacitance supercapacitors conductivity associated with strength and mobilization of ions in accessing all parts of the electrode active material contained in the supercapacitor cells. Strength conductivity is expressed through the movement of ions in an electric field. If the number of ions increases, the current flow in the cell also increases. The presence of H^+ ions on the structure of α-MnO_2 will give a donations more ions inside the cell so that the conductivity of supercapacitor cell will be increases [14]. Unfortunately, in this work the specific capacitance of model was still lower. The decrease in the CNT amount will decrease the total mass of the MnO_2 coated due to a reduced surface area or a lower conductivity. As a result, the specific capacitance decreases [15].

Summary

In this work, we designed and prepared the AC-MnO_2-CNT composite materials for supercapacitors. The process of modification of AC-MnO_2-CNT in acidic pH atmosphere can increase the ability of electrically with a maximum value of the specific capacitance of 7.86 F/g, where in neutral and alkaline atmosphere obtained a maximum specific capacitance were 0.93 and 0.55 F/g, respectively.

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