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Synthesis of Fe₃O₄/C Composite as Electrochemical Capacitor in Aqueous Electrolytes

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Abstract. The objective of this work is to investigate Fe₃O₄/C composite as an electrochemical capacitor. Fe₃O₄ nanoparticles were synthesized by oxidation of iron in water using either constant direct current (CDC) or pulse direct current (PDC). Fe₃O₄/C composite was prepared by two methods: (1) the nanoparticles were mixed with sucrose and carbonized at 500 °C under the mixture of 5% H₂ in N₂, and (2) the nanoparticles were mixed with carbon black. The electrochemical performance of the composite was evaluated by electrochemical impedance spectroscopy (EIS), and cyclic voltammetry (CV). The diameters of Fe₃O₄ particles obtained using CDC and PDC methods were approximately 18.7 nm and 20 nm, respectively. The specific surface area of composite with method (1) using PDC was 112.93 m²/g and using CDC was 111.58 m²/g, and method (2) using PDC was approximately 48.345 m²/g and using CDC was 40.77 m²/g. EIS analysis showed that the conductivity of the composite prepared by method (1) using CDC lower than that using PDC and method (2) gave the same result. The lower specific surface area gave better conductivity. Cyclic Voltammogram analysis for some cycles showed that the area under the anodic-cathodic curve for the both methods (1) and (2) using PDC or CDC did not give the good result and for method (2) gave the same area. This is affected by diameter particles of composite.

Keywords: Fe₃O₄/C composite, Capacitor, Electrochemical Impedance Spectroscopy, Cyclic Voltammetry

PACS:82.45.Aa

INTRODUCTION

Increasing environmental problems and the upcoming depletion of fossil fuels have stimulated great concern for more sustainable and efficient energy storage systems. Electrochemical capacitors (ECs) have drawn increasing attention due to their high energy density and power density, enhanced safety and long cycle life [1]. At present, carbon materials, conducting polymers and metal oxides have become the main types of electrode materials for this type of capacitor [2,3].

The advantages of using capacitors is eco-friendly, safe, efficient, and it can be operated at wide temperature range with a long life cycle. Therefore, supercapacitor has been widely used in a variety of applications in communications, consumer electronics, transportation, aviation, and related technologies.

ECs are divided into two groups: one group is electrical double-layer capacitance (EDLCs), of which the mechanism of charge (or energy) storage process is based on the non-Faradic or electrostatic phenomena. The mainly used electrodes for the EDLC are carbon materials and the common approach to improve the capacitance of EDLCs is to increase the specific surface area and electrical conductivity of the electrodes. Among the carbonaceous materials, carbon black, grapheme, carbon nanotube or carbon from organic sources such as biomass fibers [4,5] have been widely used in supercapacitors for their outstanding electrical and mechanical properties, extraordinarily high surface area, and charge-transfer features [6]. Another group of ECs is pseudocapacitor, whose capacitance arises from fast, reversible electrosorption or redox processes occurring at or near the solid electrode surface. The use of metal oxides as the main electrodes can generate larger pseudocapacitance and energy density than that of the EDLCs. Hydrous and

amorphous RuO₂ is considered to be an ideal electrode material for supercapacitors with high energy and power densities due to its high specific capacitance, highly reversible charge discharge features and excellent electrical conductivity. However, its high cost and toxic nature significantly limit its practical applications. Among the widely investigated transition metal oxides, magnetite (Fe₃O₄) is one of the promising electrode material due to its easy redox reaction, low cost and low environmental impact. However, its low electrical conductivity may hinder effective ion diffusion, thereby lowering its capacitances [7-9].

Recently, the fabrication of hybrid nanostructured electrodes comprise of metal oxide and conductive host material is considered to be effective to increase the conductivity, where carbon materials with high surface area/conductivity serve as the conductive network. In the present study Fe₃O₄ nanoparticles are easy to synthesized and directly incorporated within carbon host. Carbon black and carbonized sucrose were used as the host materials and the results demonstrated that they were suitable carbon source materials to function as a conductive system.

EXPERIMENTAL

The Fe₃O₄ nanoparticles were synthesized by electro-oxidation of iron in water, either using constant direct current (CDC) or pulse direct current (PDC) [9,10]. Fe₃O₄/C composite was prepared by two methods: (1) the nanoparticles was mixed with sucrose and carbonized at 500°C for 6 hours under the mixture of 5% H₂ in N₂ (Fig.1), and (2) the nanoparticles was mixed with carbon black. In the first method, Fe₃O₄ particles and sucrose were crushed thoroughly with a variation of mass ratio of Fe₃O₄ to sucrose. In the second method, Fe₃O₄ particles were mixed with carbon black at various mass ratio of Fe₃O₄ to carbon black.

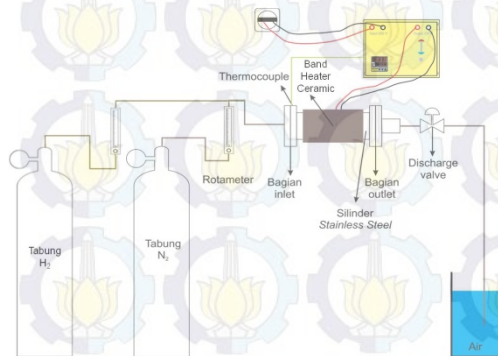


Fig. 1 Schematic diagram of carbonization device

The X-ray diffraction (XRD) pattern of composite electrodes was obtained using an X-ray diffractometer (X'pert PRO PANalytical). The specific surface area of composite electrodes was determined by Brunauer-Emmett-Taller (BET) (Nova 1200, Quantachrome). The morphologies of the composite electrodes were observed using scanning electron microscopy (SEM S-5000 Hitachi). Fourier transform infrared spectroscopy (FTIR) (Thermo Scientific Icolet iS10) was performed to evaluate the functional groups of specimens over the region of 500-4000 cm⁻¹. The thermal behavior of composite electrodes was investigated by thermogravimetry and differential Scanning Calorimetry (TGA/DSC 1 STARe System Mettler Toledo).

The electrochemical performance of composite electrodes were tested using Autolab PGSTAT 302N Metrohm using three electrode system with Fe₃O₄/C composite as working electrode, Pt foil as counter electrode and Ag/AgCl as reference electrode. Fe₃O₄ nanoparticles, carbon sources (carbon black or carbonized sucrose), and poly-vinylidenedifluoride (PVdF) were mixed in a mass ratio of 60:20:20 with N-methylpyrrolidone (NMP) as solvent. The slurry was cast onto a Cu foil as current collector, dried in an oven. The electrolyte used was 1 M Na₂SO₄ solution. Cyclic voltammetry (CV) was conducted with voltage scan rate of 1mVs⁻¹ and voltage range of -0.8 - 1.3V, and for AC impedance was recorded with frequency range from 100 kHz – 0.01 Hz.

RESULT AND DISCUSSION

Fe₃O₄ nanoparticles produced by the CDC and PDC method were found to have an average particle diameter of about 18.7 nm and 20 nm, respectively. The specific surface area of the composite prepared by PDC and CDC method (1) were 112.93 m²/g was 111.58 m²/g, and PDC and CDC method (2) were 48.34 m²/g and 40.77 m²/g, respectively. Fig. 2 shows the XRD patterns of Fe₃O₄/C composite produced by both CDC and PDC. It can be observed that the characteristics peaks of the XRD patterns match the standard pattern of Fe₃O₄ (JCPDS 19-0629).

The SEM images of Fe₃O₄/C composite produced by CDC and PDC shown in Fig.3, indicate that, the Fe₃O₄/C composite prepared by different methods have different morphological structure. For method (1), carbonization of crushed magnetite/sucrose at 500°C generated particles with a non-uniform shape, which fused to form a single entity between carbon and magnetite. Whereas in method (2) generated particles agglomerated between carbon and magnetite. The infra red spectrum of the Fe₃O₄/C

composite prepared using CDC based on the method (1) and (2), shown in Fig.4, exhibited different features. The bands appear at 680 and 508 cm^{-1} can be attributed to Fe_3O_4 and at 2100-960 cm^{-1} that represent C-C band.

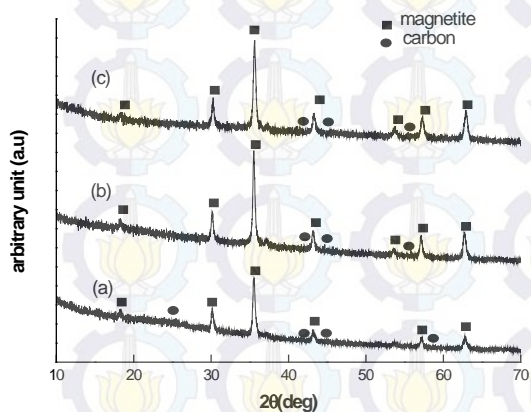


Fig. 2 The effect of different mix method at XRD pattern of composite (a) CDC method (2), (b) CDC method (1), (c) PDC method (2)

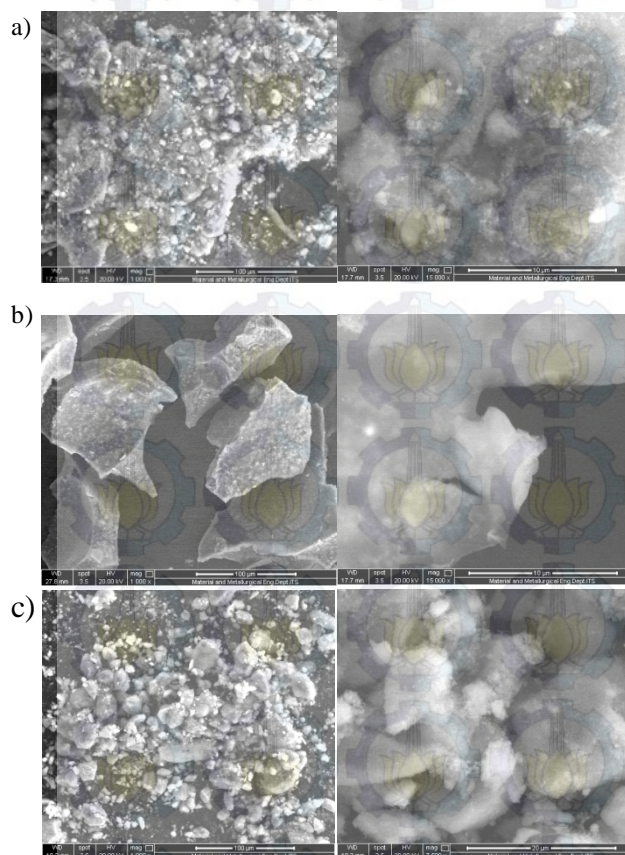


Fig. 3. SEM images of $\text{Fe}_3\text{O}_4/\text{C}$ composite, a) CDC method (2), b) CDC method (1), c) PDC method (2)

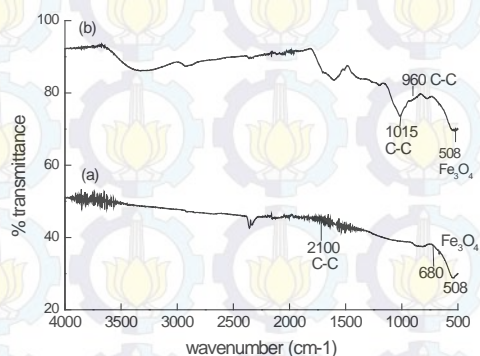


Fig. 4 FT-IR spectra of $\text{Fe}_3\text{O}_4/\text{C}$ composite a) CDC method (2), b) CDC method (1)

Fig.5 shows the TGA-DSC analysis of $\text{Fe}_3\text{O}_4/\text{C}$ composite using CDC by both method. It was predicted that there was a degradation of magnetite, carbon, and solvent inside the product. At around 110 $^{\circ}\text{C}$, water and volatile material were decomposed, while from 110-600 $^{\circ}\text{C}$ other organic molecules were decomposed. TGA result below 110 $^{\circ}\text{C}$ showed that the amount of solvent in the samples methods (1) and (2) were, 0.827 wt % and 0.417 wt %, respectively. From 110 $^{\circ}\text{C}$ -600 $^{\circ}\text{C}$, the carbon source underwent degradation and finally left carbon residue with the yields at 41.017 wt % and 5.242 wt % for the methods (1) and (2), respectively.

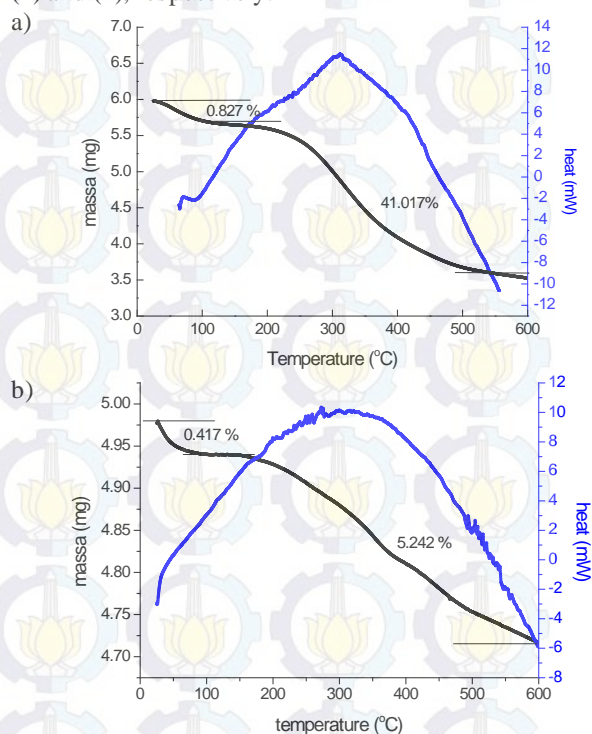


Fig. 5 DCS/TGA curves of $\text{Fe}_3\text{O}_4/\text{C}$ a) CDC method (2), b) CDC method (1)

Fig. 6a shows the Nyquist plot of $\text{Fe}_3\text{O}_4/\text{C}$ composites using CDC and PDC by method (2). The fitting curve using an equivalent electrical circuit, shown in figure 6b, provided a suitable electrical circuit. Nyquist that gave the value of resistance and conductivity. Diameter of semi circle achieved by $\text{Fe}_3\text{O}_4/\text{C}$ composite using PDC was wider than CDC, indicating that $\text{Fe}_3\text{O}_4/\text{C}$ composite using CDC had smaller resistance than that using PDC, which then allowed the ion of electrolyte to perform a faster charging. In fig. 6a, a semi circle the high frequency region represents the resistive behavior of the composite, whereas a straight line in the low frequency region represents the capacitive behavior of the composite resulted from the ions diffusion into pore network of composite. Fig. 7a shows that Nyquist curve of $\text{Fe}_3\text{O}_4/\text{C}$ composites from CDC and PDC with the method (1). This result was poorer than that in Fig. 6a because the composites from the method (2) had better accessibility to ion diffusion. The resistance of $\text{Fe}_3\text{O}_4/\text{C}$ composite using CDC was smaller than PDC, that is the same as for the method (2). The conductivity of composite from the method (2) was higher than that from the method (1), corresponding to the results that the method (2) produced composite with lower specific surface area.

CV analysis was carried out for voltage range of -0.8-1.3 V with a scan rate of 0.001 V/s. Fig. 8 and 9 show that the CV curves for the composites CDC and PDC method (2) were identical, indicating that the different approaches used to prepare, Fe_3O_4 particles did not effect the stability of $\text{Fe}_3\text{O}_4/\text{C}$ composite as electrochemical capacitor. This curve shows that there were peaks at the point 0 V and 0.55 V measured based on reference $\text{Ag}|\text{AgCl}$ or about 0.222 V and V 0.772 measured by reference $\text{H}^+|\text{H}^2$. The peak a 0.772 V corresponded to the reduction reaction of Fe^{3+} to Fe^{2+} . Other cathodic peak at 0.222 V corresponded to the reduction of Fe^{3+} to F, which was followed by the process of intercalation of the particle of Na ion. During the CV analysis, the color of electrolyte was found to change from transparent to light blue, resulted from the reaction between Cu foil (as current collector) and electrolyte.

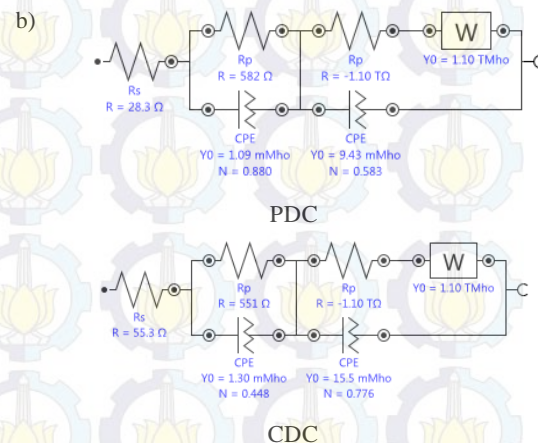
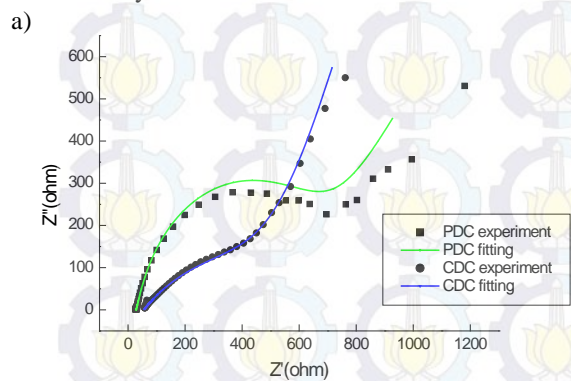


Fig. 6 Nyquist curve $\text{Fe}_3\text{O}_4/\text{C}$ using CDC and PDC method (2) and equivalent electrical circuit

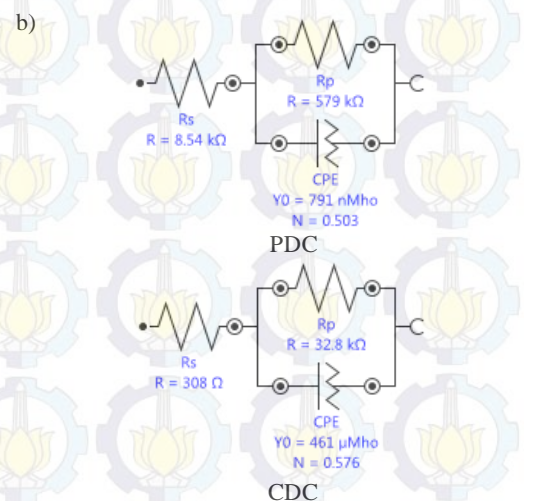
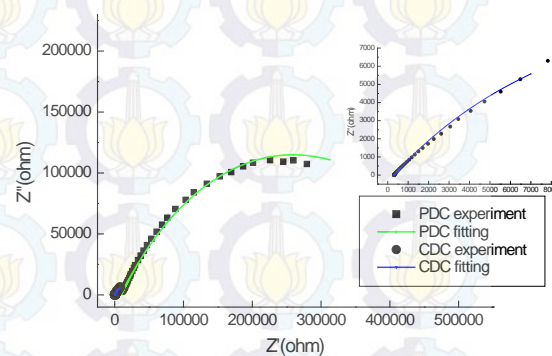


Fig. 7 Nyquist curve $\text{Fe}_3\text{O}_4/\text{C}$ using CDC and PDC method (1) and equivalent electrical circuit

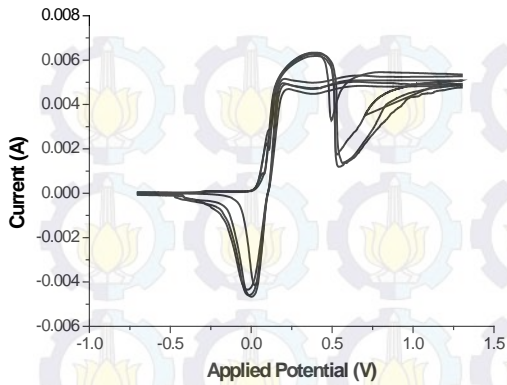


Fig. 8 CV curve Fe₃O₄/C using CDC method (2)

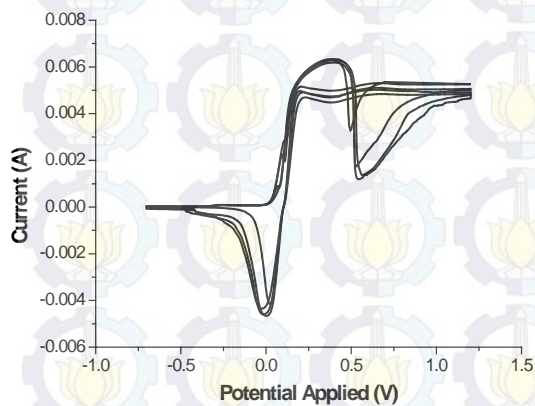


Fig. 9 CV curve Fe₃O₄/C using PDC method (2)

CONCLUSION

We have demonstrated that the Fe₃O₄ nanoparticles can be prepared by electrochemical pulsed direct current (PDC) or constant direct current (CDC) and then followed by a carbonization method or mixing method to produce Fe₃O₄/C composites from carbon sources. Both the PDC and CDC approaches can produce the composites with the stable cycles of electrochemical behavior. The specific surface area of Fe₃O₄/C composite was found to influence the charge transfer process, where the lower specific surface area contributed to a better conductivity.

ACKNOWLEDGMENTS

One of the authors (V.M. Pratiwi) would like to thank magister scholarship from the Ministry of Foreign Affairs at 2012.

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