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Electrochemical Properties of CNF/$CoFe_2O_4$ Composite for Supercapacitor Application

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ABSTRACT

This paper presents the facile technique of decoration of $CoFe_2O_4$ nanoparticles on electrospun carbon nanofibers (CNF) by two step approach via electrospinning and hydrothermal for supercapacitor. Fabrication of CNF by electrospinning process is followed by decoration of $CoFe_2O_4$ on CNF using one pot hydrothermal method. CNF/$CoFe_2O_4$ nanocomposite hybrid was characterized by x-ray diffraction, scanning electron microscopy and energy dispersive x-ray spectroscopy for their structural, surface morphological and elemental properties. The charge transfer mechanism and mass diffusion process was studied using electrochemical impedance technique using frequency range 0.01Hz to 1MHz. Electrochemical behavior was studied using cyclic voltammetry and galvanostatic charge-discharge that showed the maximum specific capacitance 188.36 Fg^{-1} at current density 0.5 Ag^{-1} with potential window -0.2 to 1.0 V. Results showed that CNF/$CoFe_2O_4$ nanocomposite is potential candidate as electrode for supercapacitor.

Keywords : Electrospun Carbon Nanofibers, Scanning Electron Microscopy, Polyacrylonitrile, Dimethylformamide, EIS, EDLC

I. INTRODUCTION

Over the past decade, the rapid development of industrialization has resulted in increased demand for energy [1]. Supercapacitors can be considered as a great alternative to conventional energy sources in the application where we need to store or release the huge amount of energy in very short time [2]. Supercapacitor can be divided into two basic types according to their charge storage mechanism. First one is electric double layer capacitor which stores the charge non-faradically and the second one is pseudocapacitor which stores the charge faradically [3]. The porous carbon materials such as carbon aerogel, graphene, carbon nanotubes, activated carbon and carbon nanofibers with high surface areas have been mostly used electrode materials in EDLCs. Typical active pseudocapacitive materials includes metal oxides/ hydroxides such as RuO_2, MnO_2, $NiO/NI(OH)_2$, $Co_3O_4/Co(OH)_2$, etc and conducting polymers [4,5]. Among them RuO_2 was once the most studied metal oxide for supercapacitors because of its ultrahigh theoretical capacitance [4]. EDLC suffers from low specific capacitance and energy density whereas pseudocapacitive material suffers from limited stability during long term cycling. So, the use of single material as an electrode is definitely limits some practical applications. So, in order to go beyond the limitations of using single component electrode materials, multi-component electrode materials have

been explored to enhance the energy storage performances by taking advantage of each component's unique functionality and their synergistic effects [4].

Spinel ferrites (MFe_2O_4, M = Mn, Co or Ni) are of great interest for their remarkable magnetic, catalytic, optical and electrical properties, especially they exhibit attributes such as different redox states, electrochemical stability [6]. Among these materials, $CoFe_2O_4$ exhibits a good theoretical capacity (916 mAh g^{-1}) [7], excellent chemical stability, naturally abundance and environmental benignity [8]. Electrospun carbon nanofibers (CNF) have been considered as the promising conductive support for metal oxides due to their high surface area, excellent mechanical property, high electrical conductivity, chemical stability and low cost of synthesis [9]. Therefore, the combination of CNF and $CoFe_2O_4$ are expected to enhance the conductivity, specific capacitance and cycling stability of composite electrode. Herein, we focus on the decoration of $CoFe_2O_4$ on CNF by simple one-pot hydrothermal method whereas the CNF are fabricated using electrospinning.

II. EXPERIMENTAL

2.1 Fabrication of CNF by electrospinning

The electrospinning solution was prepared by adding 10 wt % of polyacrylonitrile (PAN) in 10 ml of N-N dimethylformamide (DMF) with continuous magnetic stirring at 70 °C for 2 hrs. The prepared solution was then transferred to syringe for electrospinning. Processing parameters like flow rate 1 ml/hr, voltage 20 kV and distance between the needle tip and collector 15 cm were fixed during electrospinning. The electrospun PAN fibers were collected and dried overnight at 70 °C. These PAN nanofibers were first stabilized in muffle furnace at 200 °C for 1 hr, carbonized at 600 °C for 1 hr in nitrogen atmosphere and finally activated at 400 °C for 1 hr in presence of air. The nitrogen supply was maintained till the temperature reduced to 400 °C.

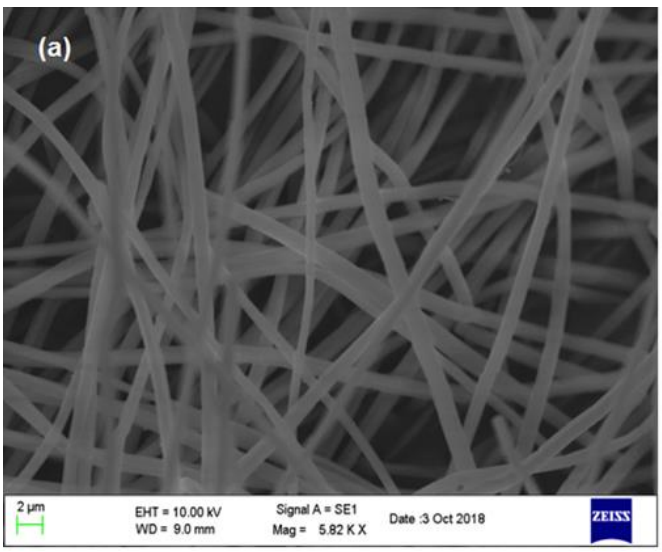
2.2 Decoration of $CoFe_2O_4$ on CNF by hydrothermal

The uniform dispersion of CNF was done by sonicating it in distilled water for 3 hr. Fe and Co precursors were taken in 1:2 stoichiometry ratio with 24 mmol urea dissolved in distilled water and magnetically stirred for 1 hr. The two solutions were then mixed well together by 1 hr magnetic stirring. The prepared solution was transferred to the 100 ml stainless steel Teflon autoclave for hydrothermal process at 120 °C for 10 hr. The as-synthesized material was centrifuge and washed several times with distilled water and finally dried.

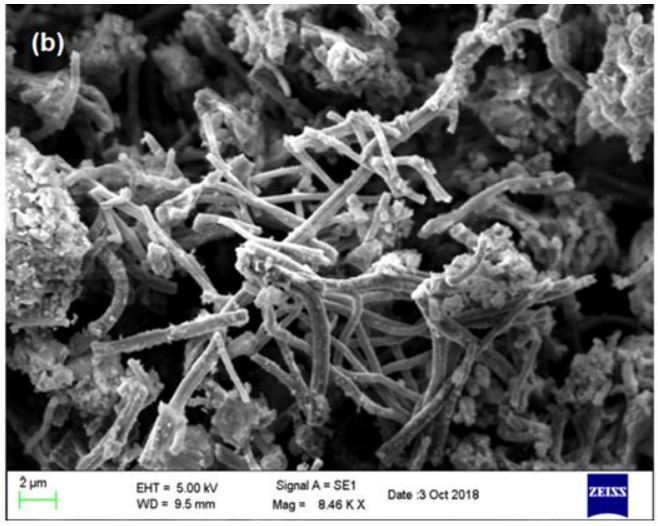
III. RESULTS AND DISCUSSION

3.1 Scanning electron microscopy (SEM)

SEM images of CNF and CNF/$CoFe_2O_4$ are shown in Fig. 1(a) and (b) respectively. SEM images display the fabrication of CNF by electrospinning and hydrothermally decorated $CoFe_2O_4$ nanoparticles on carbon nanofibers. The heavy decoration of $CoFe_2O_4$ nanoparticles on CNF is helpful for electrolyte transport, thereby creating surface area for redox reaction and high specific capacitance.



(a)



(b)

Fig. 1: SEM images of (a) CNF and (b) CNF/$CoFe_2O_4$ composite

3.2 Electrochemical properties

CV curves of CNF/$CoFe_2O_4$ before and after cycling at different scan rate are shown in Fig. 2(a) and (b) respectively. In the CV curve of CNF/$CoFe_2O_4$, a pair of redox peaks indicates the pseudocapacitive behavior of CNF/$CoFe_2O_4$. Reduction peaks are correspond to the conversion reaction of Fe^{3+} and Co^{2+} to their metallic states and oxidation peak are observed which attributed to the oxidation of the Fe and Co to Fe^{3+} and Co^{2+} respectively. As the scan rate is increased from 5 mV/s to 75 mV/s, the total peak current increases demonstrating the good rate property and excellent capacitance behavior [6]. It was clearly found that the shape of CV curves maintained similar with the increment of scan rate from 5 to 75 mV/s, indicating electrode possesses an excellent rate capability. Additionally, the oxidation and reduction peaks were slightly shifted to a higher and a lower potential with increase of scan rate respectively. This should be due to polarization effect of electrode material at high scanning speeds [8]. The frequency response of an electrode material is studied using an electrochemical impedance spectroscopy. EIS measurement was performed in the frequency range from 0.01Hz – 1MHz under open-circuit potential conditions. Nyquist plot of CNF/$CoFe_2O_4$ composite electrode is represented in Fig 2(c). The semicircle in the high frequency region represents the charge- transfer resistance found to be 10.1 Ω arises due to charge transfer process at the electrode-electrolyte interface, whereas the straight line in the low frequency region represents the ion-diffusion, associated with the mass transfer [7]. An intercept at high frequency region with real part (Z') is attributable to solution resistance found to be 0.337 Ω which includes ionic resistance of electrolyte, intrinsic resistance of active material and contact resistance of active material and current collector [10].

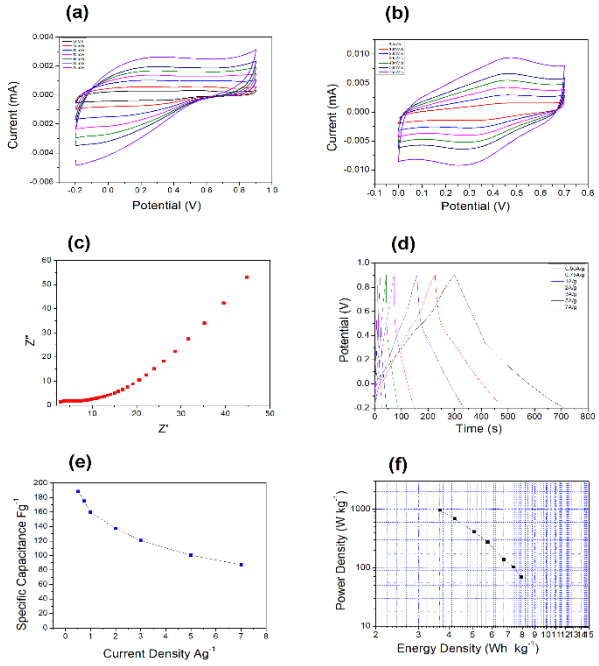


Fig. 2: (a) CV curve before cycling (b) CV curve after cycling at different scan rate (c) Nyquist plot (d) GCD curve at different current density (e) Specific capacitance at different current density (f) Ragone plot.

To further calculate the specific capacitance of CNF/$CoFe_2O_4$ composite hybrid electrode, the GCD measurements were performed with potential range -0.2 to 1.0V at different current density of 0.5-7 Ag^{-1}. GCD curve of CNF/$CoFe_2O_4$ is shown in Fig 2(d).

Based on the discharge time of electrode, the specific capacitance of electrode was calculated by using equation (1);

$$C = \frac{I \times \Delta t}{\Delta V} \quad (1)$$

Where, C is specific discharge capacitance in Fg^{-1}, I is current density in Ag^{-1}, Δt is the discharge time and ΔV is potential drop during discharge. The nonlinear variation of potential versus time indicates that the capacitive performance due to both electric double layer and pseudocapacitance. This might be due to electrochemical adsorption-desorption reaction at the interface between electrode and electrolyte [10]. Fig. 2(e) shows the specific capacitance at different current density. The specific capacitance could reach to 188.36 Fg^{-1} at lowest current density of $0.5Ag^{-1}$. Ragone plot of CNF/$CoFe_2O_4$ is shown in Fig. 2(f) which shows the maximum energy density 7.91 $Whkg^{-1}$ at power density 963.67 Wkg^{-1} could be achieved.

IV. CONCLUSION

CNF/$CoFe_2O_4$ composite was successfully fabricated by simple electrospinning and hydrothermal method. $CoFe_2O_4$ nanoparticles were heavily decorated on the surface of CNF. The specific capacitance of CNF/$CoFe_2O_4$ was found to be 188.36 Fg^{-1} at lowest current density of 0.5 Ag^{-1}. The maximum energy density 7.91 $Whkg^{-1}$ at power density 963.67 Wkg^{-1} was achieved. The results showed that CNF/$CoFe_2O_4$ composite material is a potential candidate for supercapacitor application.

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