Preparation and Characterization of Electrospun Nickel Oxide/Polymer Fibrous Electrodes for Electrochemical Capacitor

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ABSTRACT

Electrospinning is a versatile method for the preparation of submicron fibers under ambient temperature. We demonstrate a new approach based on this method for preparing an electrode which consists of fibers coated with metal oxide particles on their surface. The electrochemical characterization of the electrode was performed and compared with those of the conventional metal oxide film electrode. We prepared nickel oxide (NiO)/polymer fibrous electrodes by electrospinning technique. The capacitance of the as-prepared NiO/polymer fibrous electrode in 1 mol l^{-1} KOH aqueous solution was 5.8 F g^{-1} (per gram of NiO). Heat treatment (at 150°C for 1 h in the air) of the NiO/polymer fibrous electrode enhanced the capacitance of the NiO/polymer fibrous electrode. The capacitance of the heat treated NiO/polymer fibrous electrode was 187 F g^{-1} (per gram of NiO).

Keywords: electrospinning, electrochemical capacitor, nickel oxide, heat treatment

1 INTRODUCTION

Electrospinning provides a simple and unique technique for preparation of fibers with the diameters ranging from the nano- to micro-scale [1]. The spun fibers have been applied in the filtration of particles smaller than 100 nm in diameter with products. Other application of the fibers is very wide range from scaffold for tissue engineering, nanoparticle carriers in controlled drug release, wound dressings, and sensors in electronic applications. The fibers with high specific surface area are advantageous as electrodes for the energy storage devises, such as batteries and capacitors [2]. The high specific surface area electrodes bring high utilization of the electrochemical active materials and high charge-discharge rate to battery and capacitor devices.

Metal oxide, such as ruthenium oxide, nickel oxide (NiO), has been identified as ideal electrode materials for electrochemical capacitors. NiO is a dominant candidate because NiO is a cheap material for electrochemical capacitors. However, the instability of NiOOH in alkaline electrolyte and the high resistance of NiO limit their applications [3]. To resolve such problems, we applied the electrospinning technique to construction of NiO fibrous electrodes. We prepared the electrospun fibers which contain nickel oxide (NiO) as the electrochemical active material and acetylene black (AB) as the conducting agent on a Pt plates as a current collector. The electrochemical performance of the NiO/polymer fibrous electrodes was investigated with cyclic voltammetry technique and charge-discharge cycle test of the test cells with the fibrous electrodes.

2 EXPERIMENTAL

2.1 Materials

Poly(vinylidene fluoride-*co*-hexafluoropropylene), PVDF-HFP and nickel oxide (NiO) were purchased from Aldrich and used as received. Acetylene black (AB, Denki Kagaku Kogyo Co.) was purchased and used without further any treatment.

2.2 Preparation of NiO/polymer fibrous electrodes

The NiO/polymer fibrous electrode was prepared by the following procedure. A well dispersed solution (DMF and acetone mixture) containing PVDF-HFP, NiO and AB was used for electrospinning process. Applied voltage was 15 kV, distance between the injector charged the solution and the Pt electrode (0.35 cm^2) for the current corrector was 15 cm, and the flow rate was 1 ml h^{-1}. The resulted fibrous electrodes were heated at 80°C for 24 h to remove the solvent in the fibers. The NiO/polymer fibrous electrode was presented as PVDF-HFP/NiO/AB(10:5:1)-n, the number in the parentheses is the weight ratio of each component and n means the turn number of the electrode production. Heat treatment of the NiO/polymer fibrous electrode was performed in a muffle furnace (FO 100, Yamato). Typical heat treatment condition was at 150°C for 1 h in the air.

2.3 Measurements

Electrochemical behavior of the composite electrode was investigated in 1 mol l^{-1} KOH aqueous solution. Before electrochemical measurements, the electrodes were immersed into 1 mol l^{-1} KOH aqueous solution at room

temperature for 24 h. Electrochemical measurements were performed with electrochemical measurement equipment, HZ-3000 (Hokuto Denko). An Ag/AgCl electrode was used as a reference electrode and a Pt plate (9 cm^2) was used as a counter electrode. The test cells with the composite electrode were charged and discharged under constant current condition with a HJ-101SM6 charge-discharge controller (Hokuto Denko). The specific capacitance of the electrode was calculated from equation 1,

$$C = I \times \Delta t / (m \times \Delta V) \qquad (1)$$

where C(F g^{-1}) is the specific capacitance of the electrode, I(A) is the discharge current, Δt (s) is the discharge time, m is the weight of active material (NiO) in the electrode, and ΔV(V) is the voltage between the operative voltage width of the capacitor.

The SEM images were recorded with a VE-9800 scanning electron microscope (KEYENCE) and EDX measurements were performed with a Genesis 4000 (EDAX Japan).

3 RESULTS AND DISCUSSION

3.1 Electrochemical performance of NiO/polymer fibrous electrodes

Appearance of nickel oxide/polymer fibrous electrodes was black sheet because of the color of acetylene black in the fibers. Figure 1 shows the SEM images of two types of the electrospun (PVdF-HFP/NiO/AB/(a:b:c)-n electrodes. The image in Figure 1 (a) is that of PVDF-HFP/NiO/AB(10:5:1)-2 (a), and -1 electrode (b), respectively. The average diameter of the fiber was 260 nm (a) and 270 nm (b). As shown in Figure 1 (b) many beads (5 μm - 10 μm in diameter) were observed on the fiber. The EDX analysis for the beads suggested that the beads contain many NiO particles.

The electrochemical responses of the PVDF-HFP/NiO/AB composite electrodes in 1 mol l^{-1} KOH aqueous solution were recorded by cyclic voltammetric measurements. Figure 2 shows the electrochemical responses of the electrospun fiber electrodes. The electrochemical responses of the PVDF-HFP/NiO/AB (10:5:1)-1 electrode were more distinct than those of the PVDF-HFP/NiO/AB (10:5:1)-2, 3, or 4 electrode. The obvious responses for the PVDF-HFP/NiO/AB (10:5:1)-1 electrode based on oxidation and reduction of NiO in the alkaline aqueous solution [4].

$$Ni(OH)_2 \leftrightarrow NiOOH + H^+ + e^- \qquad (2)$$

The number of the beads on the fibrous electrodes was estimated from their SEM observations. The threshold size between fiber and bead was 12 μm. The number of the beads in the PVDF-HFP/NiO/AB (10:5:1)-1 electrode was

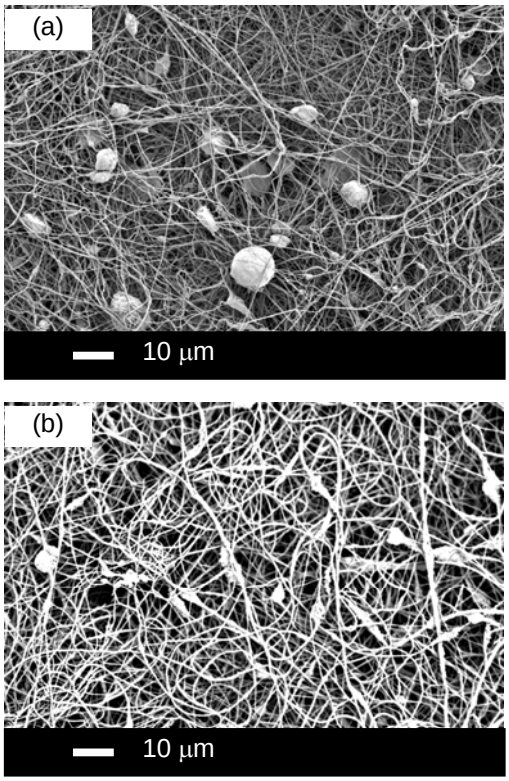

Figure 1: SEM images of the electrospun fibrous electrode, (a) PVDF-HFP/NiO/AB(10:5:1)-1 electrode and (b) PVDF-HFP/NiO/AB(10:5:1)-2 electrode.

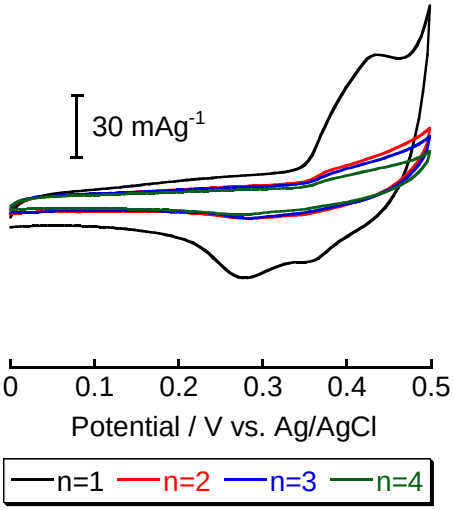

Figure 2: Cyclic voltammograms for PVDF-HFP/NiO/AB(10:5:1)-n electrode in 1 mol l^{-1} KOH aqueous solution. Scan rate 5 mV s^{-1}.

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2.2×10^6 cm^{-2} and that in the PVDF-HFP/NiO/AB (10:5:1)-2 electrode was 5.7×10^5 cm^{-2}. The amount of the beads in the PVDF-HFP/NiO/AB (10:5:1)-1 electrode is about 4 times higher than that in the PVDF-HFP/NiO/AB (10:5:1)-2 electrode. The specific capacitance estimated by the cyclic voltammograms of the PVDF-HFP/NiO/AB (10:5:1)-1 electrode was 9.5 F g^{-1} and that of PVDF-HFP/NiO/AB (10:5:1)-2 electrode was 3.1 F g^{-1}. The beads structure should be significant for achievement of high capacitance.

Figure 3 shows the charge-discharge curves of the test capacitor (half cell type) with the electrospun composite electrode (b) and the columbic efficiency of the cell. Average specific capacitance of the electrospun fiber electrode (b) was 5.8 F g^{-1} (per gram of NiO) under the charge-discharge current of 130 mA g^{-1}. Capacitance degradation after 1000 cycle charge-discharge test was about 9 %.

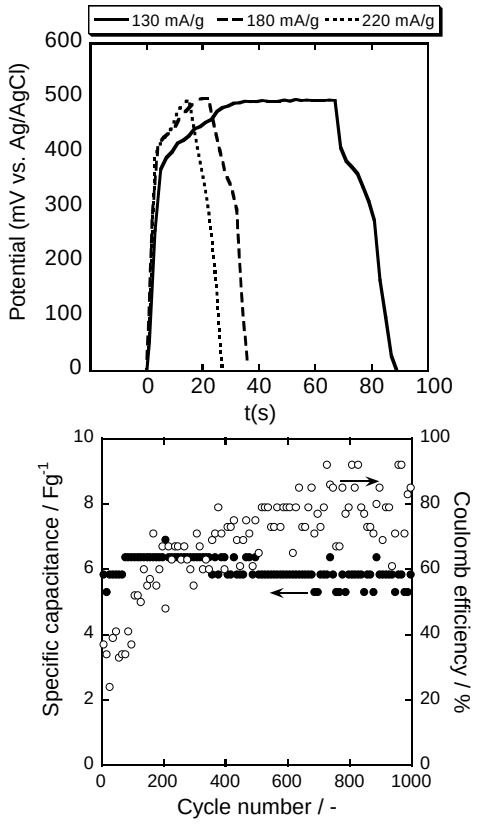

Figure 3: Charge-discharge curves of the test capacitor (half cell) with the PVDF-HFP/NiO/AB(10:5:1)-1 and the variation of the specific capacitance and coulomb efficiency with the charge-discharge cycle number.

3.2 Electrochemical performance heat treated NiO/polymer fibrous electrode

The capacitance of the as-prepared NiO/polymer electrodes and the utilization of the NiO in the electrode were very low. To improve the capacitance and utilization of the NiO/polymer electrode, we heated the NiO/polymer electrode at 150°C for 1h in the air. Figure 4 shows the SEM image of the heat treated NiO/polymer fibrous electrode (HT-PVDF-HFP/NiO/AB (10:5:1) electrode). The electrode was heated at 150°C for 1 h in the air. The fibers on the current collectors were crosslinked each other and form mesh structures. Melting point of PVDF-HFP is about 140-145°C [5]. The fibers partially melted and fused each other.

Figure 5 shows the cyclic voltammograms for the as-prepared and heat treated PVDF-HFP/NiO/AB(10:5:1)-n electrode in 1 mol/l KOH solution. The current peaks corresponding to the redox reaction of NiO for heat treated fibrous electrode are larger than those of the fibrous electrode without heat treatment. The capacitance of the heat treated electrode is about 60 times larger than that of the as-prepared electrode.

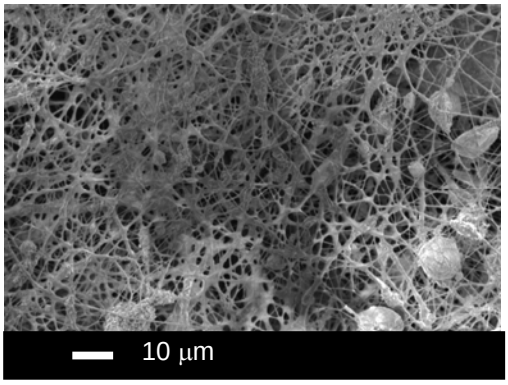

Figure 4: SEM image of the heat treated (HT-) PVDF-HFP/NiO/AB (10:5:1)-1 electrode. Heat treatment condition; 150°C, 1 h in the air.

The SEM image of the heat treated fibrous electrode suggests that the heat treatment of the electrode increased the number of the conduction path from each NiO particles on the fiber to the collector plate. Improvement of the conduction between NiO and the current collector provides the rise of the capacitance of the fibrous electrode.

The stability of the capacitance of the heat treated NiO/polymer fibrous electrode can be examined by repeated charge-discharge cycling test. The capacitors were charged and discharged between 0 and 0.5V at 880 mA g^{-1} (per gram of NiO) in 1 mol l^{-1} KOH aqueous solution to confirm the stability. The variations of the discharge capacitance and the coulomb efficiency with cycle number are illustrated in Figure 6. The results exhibit that the capacitance of the heat treated NiO/polymer fibrous electrode has a higher specific capacitance than as-prepared NiO/polymer electrode. Hence, the heat treated NiO/polymer fibrous electrode is a suitable electrode for application to electrochemical capacitors.

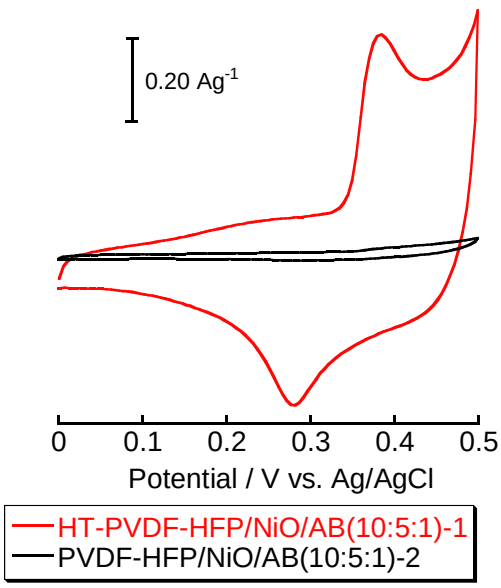

Figure 5: Cyclic voltammograms of as-prepared and heat treated (HT-) PVDF-HFP/NiO/AB(10:5:1)-n fibrous electrode in 1 mol l^{-1} KOH aqueous solution.

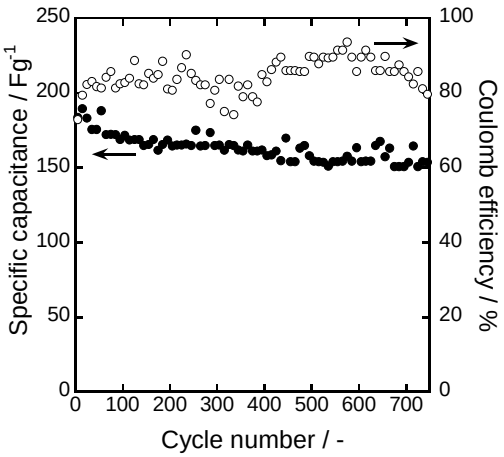

Figure 6: Variation of specific capacity and coulombic efficiency with number of cycles of heat treated (HT-) PVDF-HFP/NiO/AB(10:5:1)-1 electrode.

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