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Short communication

Electrospun nickel oxide/polymer fibrous electrodes for electrochemical capacitors and effect of heat treatment process on their performance

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ABSTRACT

Electrospinning is a versatile method for preparation of submicron-size fibers under ambient temperature. We demonstrate a new approach based on this method for preparing an electrode which consists of the fibers coated with nickel oxide (NiO) and acetylene black (AB) on their surfaces. The NiO/polymer fibrous electrodes show the electrochemical responses based on the electrochemical reaction of $Ni(OH)_2$ which is produced from NiO in alkaline aqueous solution. The capacitance of the test half cell with the as-prepared NiO/polymer fibrous electrode in 1 mol l^{-1} KOH aqueous solution is 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 increases the capacitance of the NiO/polymer fibrous electrode. The capacitance of the cell with the heat treated (HT) NiO/polymer fibrous electrode is 163 F g^{-1} (per gram of NiO). SEM observation of the heat treated electrode suggests that partial melt of the fibers on the current collector forms the conducting passes and networks between the NiO particles and the collector and increases the specific capacity of the fibrous electrode.

1. Introduction

Electrospinning provides a simple and unique technique for preparation of fibers with the diameters ranging from the nano- to micro-meter scale [1]. The spun fibers have been applied in the filtration of particles smaller than 100 nm in diameter with products [1]. Other applications of the fibers are of very wide range from scaffold for tissue engineering [2], nano-particle carriers in controlled drug release [3], wound dressings [4–6], and sensors [7–14] in electronic applications. The fibers with high specific surface area are advantageous as electrodes for the energy storage devises such as batteries and capacitors [15–20]. The high specific surface area electrodes bring high utilization of the electrochemical active materials and high charge–discharge rate to batteries and capacitors.

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. Charge–discharge performance of the cell with various NiO-based electrodes such as nanostructured NiO [21], mesoporous NiO [22,23], NiO nanoflakes [24], NiO nanoplatelets prepared by chemical precipitation [25], electrodeposited NiO [26], electrophoretic deposition of NiO particles [27], has been reported. To enhance the capacity of NiO-based electrodes, combination between NiO and carbon materials has been also investigated [28–30]. However, the instability of NiOOH in alkaline electrolyte and the high resistance of NiO limit their applications [31].

We applied the electrospinning technique for the construction of NiO fibrous electrodes. We prepared the electrospun fibers which contain nickel oxide (NiO) as an electrochemical active material and acetylene black (AB) as a 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. We point out that some problems (low utilization of active material, low reproducibility, and so on) exist in the fibrous electrodes and improve their performance by heat treatment process.

2. Experimental

2.1. Materials

Poly(vinylidene fluoride-*co*-hexafluoropropylene), PVDF-HFP (average molecular weight = 400,000) and nickel oxide (NiO, 99.8%, average particle size is smaller than 50 nm) were purchased from Aldrich and used as received. Acetylene black (AB, Denki Kagaku Kogyo) was purchased and used without further any treatment. Other reagents were also purchased and used as received.

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2.2. Preparation of NiO/polymer fibrous electrode

The NiO/polymer fibrous electrode was prepared by the following procedure. A well dispersed mixture (DMF and acetone mixture, 1:1 by vol.) containing PVDF-HFP (10 wt.%), NiO (5 wt.%) and AB (1 wt.%) were used for electrospinning process. Applied voltage was 15 kV, the distance between the injector charged the mixture and the Pt electrode (0.35 cm^2) for the current corrector was 15 cm, and the feeding rate of the mixture was 1 ml h^{-1}. The resulted fibrous electrodes were heated at 80 °C for 24 h under reduced pressure (about 400 Pa) to remove the organic solvents in the fibers. The NiO/polymer fibrous electrode was presented as NiO/PVDF-HFP (5:10)-*n*, the number in the parentheses is the weight ratio of each component in the mixture 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 Co.). Typical heat treatment condition was at 150 °C for 1 h in the air. The heat treated electrode is presented as HT-NiO/PVDF-HFP(5:10)-*n* electrode.

2.3. Measurements

Electrochemical behavior of the fibrous 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 for penetration of the electrolyte solution into them. Electrochemical measurements were performed with an electrochemical analyzer, 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 half test cells with a NiO/polymer electrode and a Pt plate electrode were charged and discharged under constant current condition with a charge–discharge controller (HJ-101SM6, Hokuto Denko). The specific capacitance of the electrode was calculated from Eq. (1),

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

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 scanning electron microscope (VE-9800, KEYENCE) and EDX measurements were performed with a Genesis 4000 (EDAX Japan). All samples were observed without carbon or metal sputtering process.

The weight ratio of the PVDF-HFP, NiO, and AB in the electrospun fibers was determined from the thermal gravimetric measurements with a TG/DTA 220 analysis system (SII). Heating rate was 10 °C min^{-1} under argon atmosphere.

3. Results and discussion

3.1. Structure of NiO/polymer fibrous electrodes

Appearance of nickel oxide (NiO)/polymer fibrous electrodes was black non-woven sheet because of the color of acetylene black in the fibers. TG/DTA analysis (*not seen here*) for NiO/PVDF-HFP (5:10) electrodes indicated that the weight ratio of NiO in the resulted fibers is lower than that in the dispersed solution for electrospinning process. Average weight ratio of NiO, PVDF-HFP and AB was 1.5:11:1. About a third amount of NiO in the dispersed solution for electrospinning process was loaded into the fibers. Hereafter, current density values and specific capacity of the electrodes are corrected by the loaded weight of NiO in the fiber. We also tried to prepare the NiO/polymer composite electrodes with other composition of NiO, PVDF-HFP, and AB. However, some cases provided no fibers, but many small particles on the current collector which are produced by electrospray deposition (*not seen here*).

Fig. 1 shows the SEM images of two types of the electrospun NiO/polymer electrodes (NiO/PVDF-HFP(5:10)-*n* electrodes). The image in Fig. 1(a) is that of Ni/PVDF-HFP(5:10)-1 electrode, and (b) is -2 electrode, respectively. As shown in Fig. 1, some bead-like structures are also observed. The average diameter of the fiber was 260 nm in Ni/PVDF-HFP(5:10)-1 electrode and 270 nm in Ni/PVDF-HFP(5:10)-2 electrode without accounting of the bead-like structures. The EDX analysis for the beads suggested that the beads contain many NiO particles. Fig. 2 shows the distribution of the diameter of the fibers. The fiber diameters lay in the distribution range of 100–400 nm, mainly. Variation of diameter of the fibers was in very small range.

3.2. Electrochemical performance of NiO/polymer fibrous electrodes

The electrochemical responses of NiO/polymer fibrous electrodes in 1 mol l^{-1} KOH aqueous solution were recorded by cyclic voltammetric measurements. Before the electrochemical measurements, all the electrodes were immersed into the electrolyte solution (1 mol l^{-1} KOH aqueous solution) at room temperature for 24 h. Fig. 3 shows the electrochemical responses of the NiO/polymer fibrous electrodes. The electrochemical responses of the NiO/PVDF(5:10)-1 electrode are more distinct than those of the NiO/PVDF-HFP (5:10)-2, 3, or 4 electrode. The obvious responses for the NiO/PVDF-HFP (5:10)-1 electrode based on redox reaction of nickel hydroxide ($Ni(OH)_2$) in the alkaline aqueous solution are presented as Eq. (2) [32].

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

The appearance of the electrochemical responses suggests that $Ni(OH)_2$ in the electrode is produced by immersing the

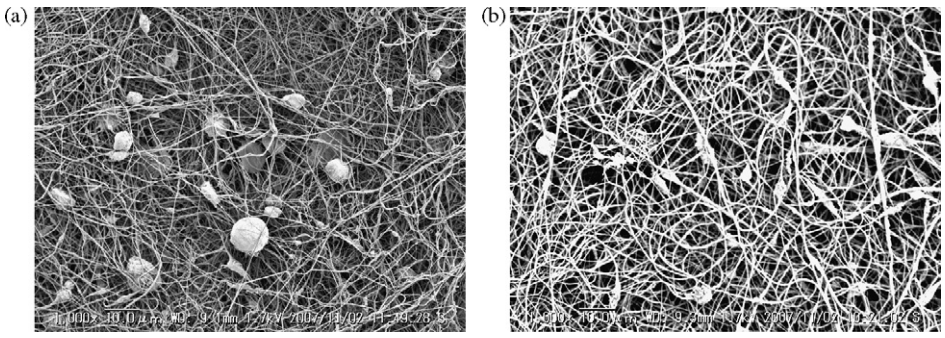

Fig. 1. SEM images of the electrospun fibrous electrode, (a) NiO/PVDF-HFP (5:10)-1 electrode and (b) NiO/PVDF-HFP (5:10)-2 electrode.

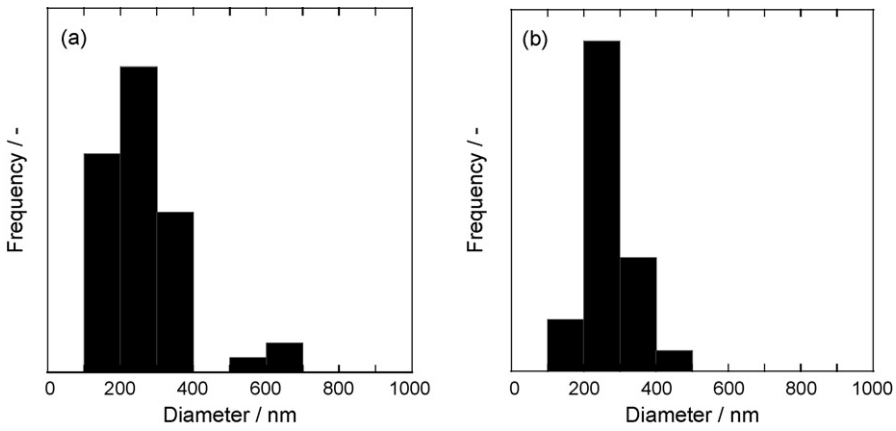

Fig. 2. Distribution of the diameter of the electrospun fibers in NiO/PVDF-HFP (5:10)-1 electrode and (b) NiO/PVDF-HFP (5:10)-2 electrode.

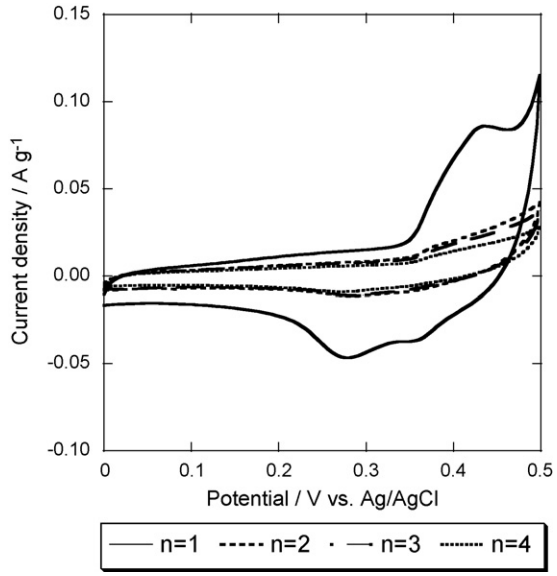

Fig. 3. Cyclic voltammograms for NiO/PVDF-HFP (5:10)-*n* electrode in 1 mol l^{-1} KOH aqueous solution. Scan rate at 5 mV s^{-1}.

NiO/polymer electrode into alkaline aqueous solution for 24 h at room temperature.

The number of the beads on the fibrous electrodes is estimated from their SEM observations. We defined that the threshold size between fiber and bead is 12 μm (1200 nm). The estimated number of the beads in the NiO/PVDF-HFP (5:10)-1 electrode was 2.2×10^6 cm^{-2} and that in the NiO/PVDF-HFP (5:10)-2 electrode was 5.7×10^5 cm^{-2}. The amount of the beads in the NiO/PVDF-HFP (5:10)-1 electrode is about four times higher than that in the NiO/PVDF-HFP (5:10)-2 electrode. The specific capacitance estimated by the cyclic voltammograms of the NiO/PVDF-HFP (5:10)-1 electrode was 9.5 F g^{-1} and that of NiO/PVDF-HFP (5:10)-2 electrode was 3.1 F g^{-1}. The results suggest that the bead-like structure should be significant for achievement of high capacitance in the as-prepared electrodes. However, their estimated capacity is very lower than that of theoretical capacity of $Ni(OH)_2$ (2584 F g^{-1} within 0.5 V) [33].

3.3. 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. SEM observation of the as-prepared NiO/polymer electrodes suggests that the lack of the contact between the fibers and the current collector causes low utilization of NiO in the electrodes. To improve the capacitance and utilization of the NiO/polymer electrode, we heated the NiO/polymer electrode at 150 °C for 1 h in the air. Fig. 4 shows the SEM images of the heat treated NiO/polymer fibrous electrode (HT-NiO/PVDF-HFP (5:10)-1 electrode). The electrode was heated at 150 °C for 1 h in the air. Melting point of PVDF-HFP is about 140–145 °C [34]. The fibers on the current collectors were cross-linked each other and form mesh structures. The fibers partially melted and fused each other and form the network structure.

Fig. 5 shows the cyclic voltammograms for the as-prepared and heat treated NiO/PVDF-HFP (5:10)-1 electrode in 1 mol l^{-1} KOH solution. The current peaks corresponding to the redox reaction of NiO for heat treated fibrous electrode are larger than those of the as-prepared fibrous electrode. The estimated capacitance of the heat treated electrode (64 F g^{-1}) is about 6–20 times larger than that of the as-prepared electrode (3.1–9.5 F g^{-1}). The SEM image of the heat treated fibrous electrode suggests that the heat treatment of

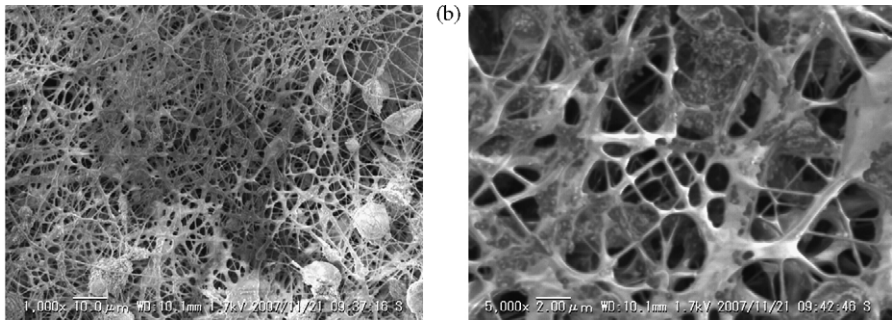

Fig. 4. SEM images of (a) the heat treated (HT)-NiO/PVDF-HFP (5:10)-1 electrode and (b) its expanded figure. Heat treatment of the electrode at 150 °C for 1 h in the air.

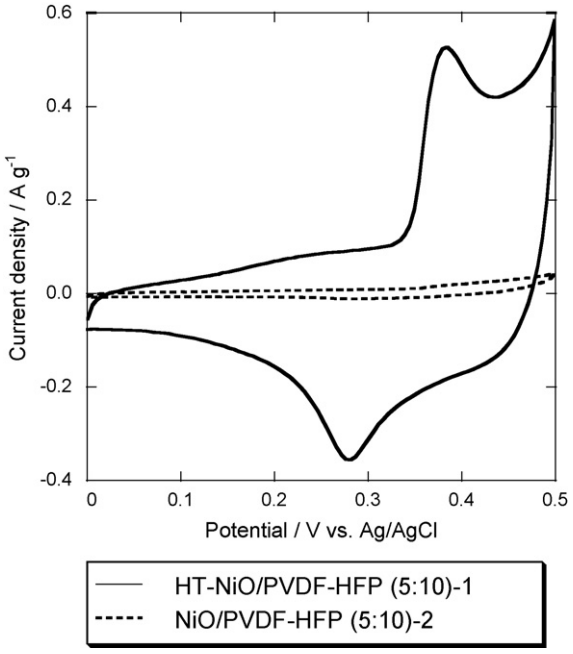

Fig. 5. Cyclic voltammograms of as-prepared and heat treated (HT)-NiO/PVDF-HFP (5:10)-*n* fibrous electrode in 1 mol l^{-1} KOH aqueous solution. Scan rate at 5 mV s^{-1}.

the electrode increases 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.

Fig. 6 shows charge–discharge curves of the test half cell with HT-NiO/polymer electrode under various current densities. The presence of some flat parts in the curves indicates that the electrochemical reaction of $Ni(OH)_2$ on the fibers as presented in the Eq. (2) occurs in this condition.

Variation of the capacitance of the heat treated NiO/polymer fibrous electrode can be examined by repeated charge–discharge

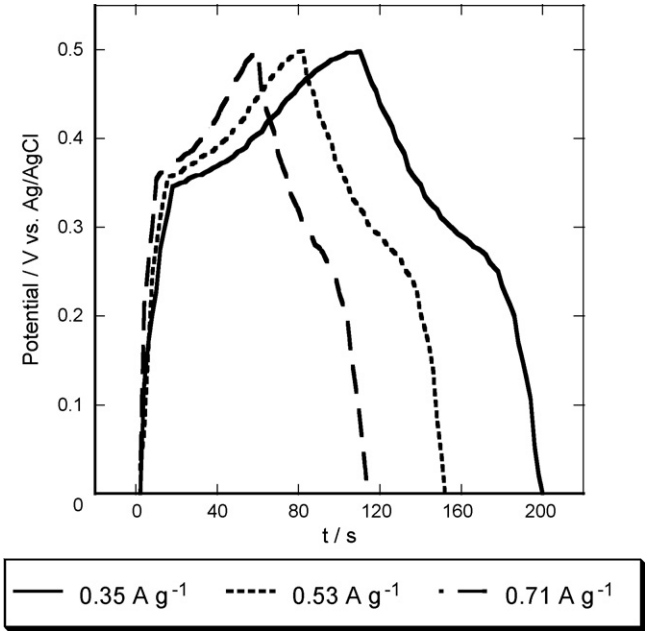

Fig. 6. Charge–discharge curves of test half cell with HT-NiO/PVDF-HFP (5:10)-1 electrode, charge and discharge condition is between 0 and 0.5 V in 1 mol l^{-1} KOH aqueous solution.

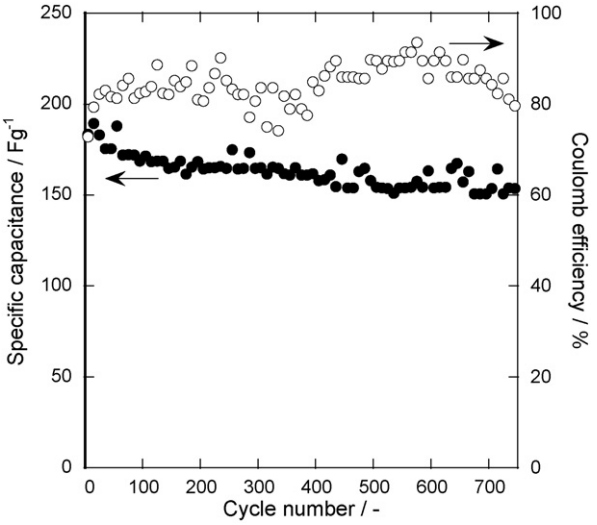

Fig. 7. Variation of specific capacity and coulombic efficiency with number of cycles of HT-NiO/PVDF-HFP (5:10)-1 electrode, charge and discharge condition is between 0 and 0.5 V at 0.88 A g^{-1} (per gram of NiO) in 1 mol l^{-1} KOH aqueous solution.

cycling test. The capacitors were charged and discharged between 0 and 0.5 V at 0.88 A 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 Fig. 7. The average specific capacity was 163 F g^{-1} and average coulomb efficiency was 85%. The reason of low average coulomb efficiency is not clear. After the charge–discharge cycle tests, some peeled part of the non-woven mat with NiO and AB from the current collector was observed. Poor mechanical strength of the fibrous electrodes should be related to the phenomena.

The coefficient of variation (Cv) is a normalized measure of dispersion of a probability distribution. It is defined as the ratio of the standard deviation (s) to the mean (m) as the Eq. (3),

$$\mathrm{Cv} = \frac{s}{m} \tag{3}$$

Larger Cv means that the values are dispersed wider range. The Cv of the NiO/PVDF-HFP (5:10)-*n* electrode is 0.79. The value of heat treated fibrous electrodes is 0.34. This indicates that heat treatment of the fibrous electrode also improves deviation of the capacity of the fibrous electrodes.

Our fibrous electrodes with NiO and AB for electrochemical capacitors do not have efficient capacity for practical application, because of their lower capacity and larger deviation of capacity based on the electrode preparation procedure. However, heat treatment of the electrodes provided higher capacity electrodes and lower deviation of the capacity.

Our further investigation for the electrospun fibrous electrodes for electrochemical capacitors and batteries is in progress now, to enhance capacity and improve reproducibility.

4. Conclusions

We prepared nickel oxide (NiO)/polymer fibrous electrodes by electrospinning technique. Suitable composition of NiO, PVDF-HFP, and AB exists to prepare fibrous structure on the current collector. The electrochemical responses of the fibrous electrode are based on the redox reaction of $Ni(OH)_2$ in alkaline aqueous solution. The peak current of the electrodes depended on the number of bead-like structure in the fibers. Heat treatment of the electrodes enhanced the capacity of the electrode. The capacitance of the heat treated electrode is about 6–20 times larger than that of the as-prepared electrode. SEM observation of the heat treated electrode suggests

that partial melt of the fibers on the current collector forms the conducting passes and networks between the NiO particles and the collector and enhances the specific capacity of the fibrous electrode. Heat treatment of the NiO/polymer fibrous electrode is effective in increasing the capacity of the electrode and decreasing the capacity deviation of the electrodes.

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