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The Formation of Free Standing NiO Nanostructures on Nickel Foam for Supercapacitors

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In this study, free standing NiO nanostructures for supercapacitors were obtained by means of chemically depositing of nickel oxide on Ni foam and then they were annealed at various temperatures. The morphological properties of densely covered Ni foams were studied by scanning electron microscopy. Supercapacitor characteristics, such as charging/discharging and impedance characteristics, were also examined.

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1. Introduction

Capacitors have been studied intensively to store electrical energy in the last thirty years. There have been many studies on this topic such as: electrode type, shape, available electrode materials, especially with the electrochemical reduction and oxidation processes. Generally, the desired electrodes, which usually contain nanoparticles, have high surface area and high energy density. In addition, the other important features for supercapacitors and batteries are long life, low cost and stability.

In recent years, carbon aerogel, activated carbon, carbon nanotubes, conductive polymers, and various metal oxide structures have been investigated as a supercapacitor electrode material [1–6].

In the present study, chemically deposited NiO nanostructures on Ni foams were produced and then employed as the electro-active materials for the supercapacitor. The highest specific capacitance, 329 F/g, was observed at constant current-discharge with a current density 0.2 A/g in 6 M KOH.

2. Experimental

To obtain NiO nanostructures on Ni foam, first Ni foams were degreased with acetone, etched with 3 M HCl for 10 min and then washed thoroughly with deionized water, later acetone, again deionized water. 1.15 g $Ni(NO_3)_2$, 2.9 g urea, and 40 ml ethanol solution was mixed, then this solution was completed to 100 ml by adding water. Then the Ni foams were vertically dipped into the solution at 90 °C in a vacuum oven for the different times (4 h, 8 h, 12 h). Finally, foams were removed from the solvent and dried in the vacuum oven at 60 °C for 30 min. The formed nanostructures on Ni foam were heated from room temperature to various annealing temperatures (250 °C, 275 °C, 300 °C, 360 °C) in air at a rate of 2 °C/min and maintained for 2 h. This was followed by cooling to room temperature at a rate of 10 °C/min. The obtained material was used as a cathode, with an exposed area of approximately 1 cm^2 for the capacitance measurement. A three-electrode cell was used for the electrochemical experiments. The volume of the electrochemical bath was approximately 60 ml. An Ag/AgCl ceramic electrode (BAS, saturated KCl, and −42 mV versus SCE at 25 °C) was used as the reference electrode. A platinum electrode approximately 1 cm^2 was used as an auxiliary electrode. The electrolyte used was 6 M KOH. CV (cyclic voltammograms), charge–discharge and electrochemical impedance spectroscopy (EIS) measurements were performed using an electrochemical analyzer system, namely an Iviumstat potentiostat/galvanostat. The frequency limits were typically set between 10 mHz and 100 kHz. The AC oscillation amplitude was 5 mV. The morphology of the nanostructures was investigated by scanning electron microscopy (SEM; JEOL JSEM 7001F).

3. Results and discussion

The morphologies of the NiO nanostructures grown on Ni foam in the solution for 8 h are shown in Fig. 1. The annealing temperature effect can be obviously seen from Fig. 1. The nanothorny structure was observed for 250 °C annealed sample. There was also observed the nanowall structure for the sample annealed at 300 °C. It is worth noting that the specific surface area increases with the increasing annealing temperature. So the capacitance value also increases.

The electrochemical characteristics of the NiO nanostructures on nickel foam electrodes annealed at different temperatures were studied using cyclic voltammetry with 6.0 M KOH as the electrolyte, over the voltage range −0.5 V to +0.5 V (vs. Ag/AgCl) at 5–100 mV/s scan rates. Typical CVs of electrodes of samples annealed at different temperatures are shown in Fig. 2. The inset of Fig. 2 shows CV of only nickel foam electrode and NiO nanostructures on Ni foam electrode, both samples were annealed at 300 °C. There was a weak signal from Ni foam electrode compared to the NiO nanostructures on nickel foam. The ideal rectangular CV curve shape was not observed for all samples. This mainly results from that the pseudocapacitance occurred from redox mechanism. The estimated specific capacitances from the CVs by integrating the area under the current–potential

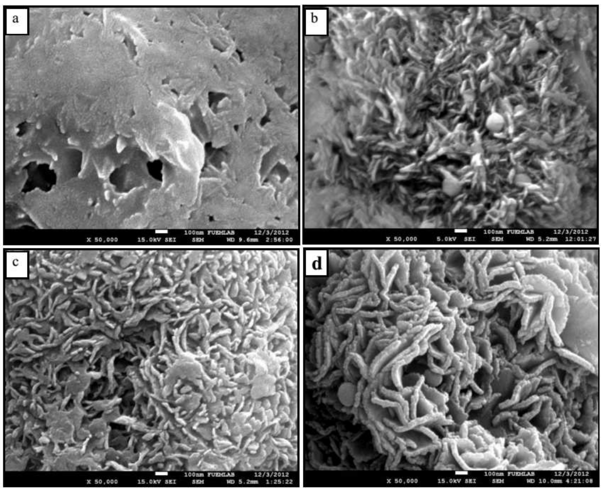

Fig. 1. SEM images of NiO nanostructures on Ni foam at various annealing temperatures: (a) as received, (b) 250 °C, (c) 275 °C, (d) 300 °C.

curve for the electrodes annealed at 300 °C and 360 °C were higher than the other electrodes. So, electrochemical properties of these electrodes are further discussed in the following part.

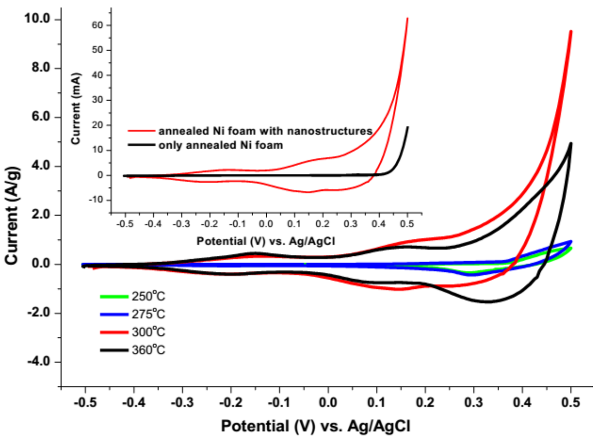

Fig. 2. Cyclic voltammograms of NiO nanostructure annealed at different temperatures in 6 M KOH solution. Inset shows the CV comparations of Ni foam and NiO nanostructures on Ni foam. Scan rate is 5 mV/s.

The inset of Fig. 3 shows the ten cyclic charge–discharge curves of heated to 300 °C sample at 0.2 A/g over the operating potential range 0–0.38 V (vs. Ag/AgCl). The discharge current curves are almost linear in the total range of potential, which shows a very good capacitive behavior [7–9]. The specific capacitance values can be calculated from the following formula [3]:

$$C_{\mathrm{s}} = \frac{I \times \Delta t}{m \times \Delta V}, \tag{1}$$

where C_{s} is the specific discharge capacitance, I is the discharge current, Δt is the discharge time, ΔV is the potential drop in the discharge progress and m is the active mass of the electrode (including only the mass of the NiO, not the Ni foam). The long term galvanostatic cycling stability of NiO nanostructures on Ni foam electrodes were investigated over 1000 cycles (Fig. 3). The capacitance of electrodes slowly reduces from 329 F/g and 286 F/g during the first 200 cycles and then reaches to the stable value of 285 F/g and 240 F/g for 300 °C and 360 °C, respectively. Voltammetric and galvanostatic results indicate that the nanoporous structure and large surface area on the Ni foam and also presence of NiO nanowalls play are mainly responsible for obtaining optimum capacitance values. The charge–discharge efficiency is 87% for nanowall-like NiO electrodes after 1000 charge/discharge cycles.

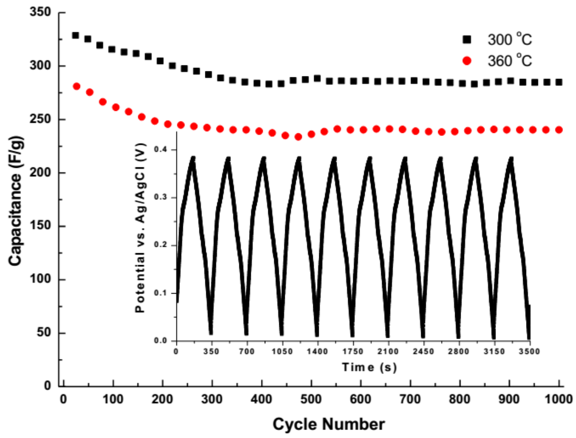

Fig. 3. The variation of specific capacitance as a function of cycle number of NiO electrodes. The inset shows the chronopotentiograms of NiO electrode annealed at 300 °C.

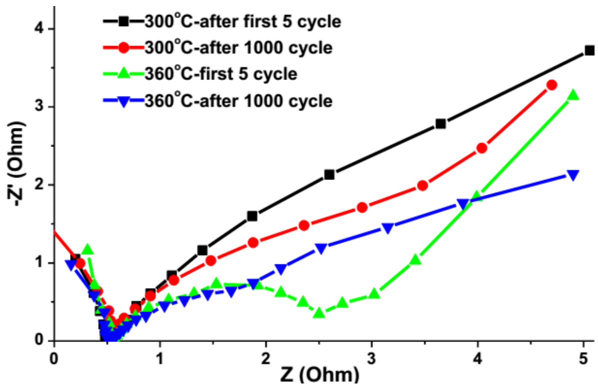

Fig. 4. Nyquist plots of NiO electrode heated to 300 °C and 360 °C at 0.2 A/g in 6 M KOH solution.

Figure 4 displays the Nyquist plots of the AC impedance of the NiO nanostructured electrodes for 300 °C and 360 °C (frequency range, 100 kHz–10 mHz) at open circuit potential. These impedance plots were measured after 5 or 1000 continuous charge and discharge cycles. After 1000 continuous cycles, 58° straight line of sample annealed at 300 °C at the low frequency range demonstrates a good capacitive feature, that is the typical characteristic of porous electrodes.

4. Conclusion

In this work, free standing NiO nanostructures on Ni foams were chemically deposited without need for mixing and pressing powders. These free standing nanostructures were employed as the electro-active materials for the supercapacitor. Voltammetric and galvanostatic results indicate that the nanoporous structure and large surface area of the Ni foam and also presence of NiO nanowalls play are mainly responsible for obtaining optimum capacitance values. The obtained discharge current curves for 300 °C annealed sample are almost linear in the total range of potential, which shows a very good capacitive behavior. The columbic efficiency remains above 87% within 1000 cycles.

Acknowledgments

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