Proceedings of the 2nd International Congress APMAS2012, April 26–29, 2012, Antalya, Turkey Electrochemical Capacitance of Cobalt Oxide Nanotubes on Nickel Foam

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In this study, densely packed Co_3O_4 nanotubes for supercapacitors have been obtained by means of chemically depositing cobalt hydroxide within a porous anodic aluminum oxide and then annealed at 360 °C. The morphological properties obtained Co_3O_4 nanotubes were studied by scanning electron microscopy, the chemical composition was determined by examination of the energy dispersive X-ray spectra. Supercapacitor characteristics such as charging/discharging and impedance (Z) characteristics were also examined.

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1. Introduction

Capacitors, which store the energy within the electrochemical double-layer at electrode–electrolyte interface have been called as supercapacitors, also known as electrochemical double layer capacitors (EDLC) [1, 2]. They have attracted much attention as they can serve as high energy and high power storage devices with a long cycle life [1–6]. Recently, there have been many reports about oxide supercapacitors, which possess excellent electrochemical capacitive behavior [1–6]. In the present study, chemically precipitated Co_3O_4 nanotubes on Ni foams were employed as the electro-active materials for the supercapacitor. The highest specific capacitance, 697 F/g, was observed at constant current discharge with a current density 0.1 A/g in 6 M KOH.

2. Experimental

 Co_3O_4 nanotubes were synthesized by mixing 1 M CoCl₂ solution and 1 M NH₄OH. A porous anodic aluminum oxide (AAO) membrane with 200 nm diameter was used as a template. In the growth of Co_3O_4 nanotubes arrays, four membranes were vertically dipped into the solution for 96 h at room temperature. The formed $C_0(OH)_2/AAO$ nanotubes arrays then were dried for 5 h in an oven at 60° C. Then they were heated from room temperature to $360\,^{\circ}$ C in air at a rate of $2\,^{\circ}$ C/min and maintained for 2 h. This was followed by cooling to room temperature at a rate of $10 \,^{\circ}C/min$. Later the samples were kept in 2 M NaOH until AAO template was entirely dissolved, then the liberated nanotubes were suspended in ethanol. Subsequently, the Co_3O_4 nanotubes (75%), acetylene black (20%) and PTFE (5%) were grinded and mixed in a Zr_2O_3 mortar for 30 min. 3.33 mg of this mixed material was placed on Ni foam sheet and compressed at a pressure of 10 MPa for 10 min. Ni foam was used to increase the surface area. The pressed 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 50 ml. An Ag/AgCl electrode with ceramic frit (Bioanalytical Systems BAS, 3 M NaCl, and -35 mV versus saturated calomel electrode (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. Cyclic voltammetry (CV) 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 nanoarrays was investigated by scanning electron microscopy (SEM; LEO-EVO-40) and transmission electron microscopy (TEM; FEI Tecnai G2 F30). X-ray diffraction measurement was performed on a Rigaku-Radb diffractometer equipped with Cu K_{α} radiation.

3. Results and discussion

The general morphology of the chemically precipitated, heated and then removed from AAO nanotubes was studied by SEM and TEM. SEM images of the nanotubes are shown in Fig. 1a. The TEM image of single nanotubes removed from AAO is shown in Fig. 1b. It can be seen from the figures that the diameters of the nanotubes are about 170–200 nm range and the length is up to 2 μ m. Also internal diameter of nanotubes was measured to be ≈ 100 nm.

Figure 1c shows the XRD profile for nanotubes arrays within AAO. The peaks observed at 2θ = $18.9^{\circ}, 31.16^{\circ}, 36.76^{\circ}, 44.68^{\circ}, 59.24^{\circ}$ and 65.1° can be indexed as the (111), (220), (311), (400), (422) and (440) reflections of the spinel Co₃O₄. The results are in good agreement with the standard spectrum (PDF CARD NO. 65-5745). The broad peak around at 30° arises from sample holder.

Typical CV for vitreous electrodes at 10 mV/s are shown in Fig. 2a. The redox signal did not occur at the PTFE and acetylene black electrode surface. In addition, there was a weak signal at Ni foam electrode surface



Fig. 1. (a) SEM images of Co_3O_4 nanotubes, (b) TEM image of single Co_3O_4 nanotubes, (c) XRD spectrum of Co_3O_4 nanotubes arrays within AAO.

compared with the Co_3O_4 nanotubes, PTFE and acetylene black electrode surface on nickel foam (COPANF). The electrochemical characteristics of the COPANF were studied using cyclic voltammetry with 6.0 M KOH as the electrolyte, over the voltage range 0-0.5 V (vs. Ag/AgCl) at various potential scan rates between 1 and 50 $\mathrm{mV/s}$ (Fig. 2b). The CV curves indicate that the electrochemical capacitance of the Co_3O_4 samples mainly results from the pseudo-capacitance, which is based on redox mechanism. Also, with increasing scan rate, it was observed that the peak current increases, which suggests good reversibility of fast charge-discharge response. The inset in Fig. 2b shows the effect of scan rate on the cathodic peak currents obtained from CV. The charge-storage mechanism of Co_3O_4 is not through a surface redox reaction at the interface but a diffusion controlled reaction.



Fig. 2. Cyclic voltammograms of (a) various electrodes at 10 mV/s, (b) COPANF electrodes in 6 M KOH solution at different scan rates. The inset shows cathodic peak current as a function of the square root of the scan rate.

The inset of Fig. 3a shows first two charge and discharge curves of COPANF electrode materials at 0.1 A/g over the operating potential range 0–0.36 V (vs. Ag/AgCl). The first potential drop arises from the in-



Fig. 3. (a) The specific capacitance as a function of cycle number. The inset shows the first two cyclic charge-discharge curves. (b) Nyquist plots of COPANF sample at 0.1 A/g in 6 M KOH solution.

ternal resistance and the subsequent potential decay indicates a typical pseudocapacitance behavior [3]. The specific capacitance values can be calculated from the following formula:

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

where $C_{\rm s}$ 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 Co_3O_4 , not the mass of acetylene black, PTFE or Ni foam). The long term galvanostatic cycling stability of COPANF electrode was investigated over 500 cycles (Fig. 3b). The inset shows the first two cyclic chargedischarge curves. The capacitance of COPANF electrode increased gradually during the first 40 cycles and then reached the maximum value of 697 F/g. Voltammetric and galvanostatic results indicate that the porous structure and large surface area of the Ni foam and also presence of nanoflakes on the Co_3O_4 nanotubes play are mainly responsible for obtaining optimum capacitance values. It exhibits good performance with a high specific capacitance of 598 F/g after 500 charge/discharge cycles, corresponding to retention of 86% of the maximum capacitance. Figure 3b displays the Nyquist plots of the AC impedance of the COPANF electrodes (100 kHz-10 mHz) at open circuit potential. These impedance plots were measured after 4 or 500 continuous charge and discharge cycles. After 500 continuous cycles, 67° straight lines in the low frequency range demonstrate a good capacitive feature that is the typical characteristic of porous electrodes.

4. Conclusion

Chemically precipitated Co_3O_4 nanotubes on Ni foams were employed as the electro-active materials for the supercapacitor. Voltammetric and galvanostatic results indicate that the porous structure and large surface area of the Ni foam and also presence of nanoflakes on the Co_3O_4 nanotubes play are mainly responsible for obtaining optimum capacitance values and long cycle life. The Coulombic efficiency remains above 86% within 500 cycles.

Acknowledgments

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