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Highly porous nickel cobaltite film composed of nanosheets with attached nanowires as an electrode material for electrochemical capacitors

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ABSTRACT

Nickel cobaltite hetero-nanostructure with superior capacitive behavior is grown on stainless steel mesh by one-pot hydrothermal synthesis at slow cooling rate. Porous nickel cobaltite film composed of nanosheets with attached nanowires (NS-NW) provides numerous pore channels for fast transport of electrolyte, large surface area for reversible Faradaic reaction, and short diffusion pathways in solid phase. The specific capacitance of NS-NW reaches 775 F g^{-1} at 5 A g^{-1}, which is higher than that of nanosheet (435 F g^{-1}). Porous film with nanosheet and nanowire configuration exhibits low charge-transfer resistance, diffusive impedance, and volumetric strain, leading to high specific capacitance, rate performance, and cycle-life stability.

1. Introduction

Metal oxides/hydroxides are promising electrode materials for electrochemical capacitors. Among them, nickel cobaltites show good electroactivity and electrical conductivity compared with cobalt and nickel oxides/hydroxides, rendering them promising for the use in alkaline capacitors [1–3]. Nanostructured nickel cobaltites generally offer better capacitive performance than bulk ones because of their large surface area and appropriate pore size for easy access and transport of electrolyte ions [4]. Nickel cobaltites featuring nanosheet, nanoflower, nanorod, and nanowire structures have been made to improve the capacitive performance of electrodes [5–15]. Therefore, shape control of nickel cobaltite nanostructures has become an important factor for the success of electrochemical capacitors [16]. To achieve high power density of capacitors, conductive materials which act as additives or electrode scaffolds are employed in preparing the electrodes. Adding conductive carbon material to the electrode has shown superior capacitive performance due to the reduced internal resistance of electrode [17]. In addition, the nickel cobaltites grown on porous nickel and graphene scaffolds also show an improved capacitive behavior due to the enhanced transport of electrolyte and electron through the porous electrodes [18–20].

In this work, we propose a one-pot hydrothermal synthesis of highly porous nickel cobaltite film composed of nanosheets with attached nanowires as an electrode material for high-performance electrochemical capacitors. Nickel cobaltite nanowires can be attached to the nanosheets by tuning the cooling rate during the hydrothermal synthesis. Porous film with nanosheets provides conductive networks for fast transport of electron and accommodates large amounts of electrolyte for easy transport of electrolyte. A large space between nanowires offers large surface area for charge storage through the redox Faradaic reactions and alleviates mechanical damage of electrode caused by volume expansion/contraction during cycling test.

2. Experimental

Nickel cobaltite was grown on the SS (stainless steel, type 304) mesh (with a spacing size of 0.15 mm) by hydrothermal method. A solution (30 mL) containing $NiSO_4 \cdot 6H_2O$ (2.5 mM), $CoSO_4 \cdot 6H_2O$ (5.0 mM), and urea (25.0 mM) was added into a Teflon-lined SS autoclave. SS mesh (2×2 cm^2) was put into the autoclave, and then heated to 95 °C at a rate of 10 °C min^{-1} and held at that temperature for 6 h in a programmable electric oven. After cooling to room temperature, the autoclave was removed from the oven and allowed standing for 13 h before it was opened. The electrode with attached nickel-cobalt hydroxide was rinsed with deionized water, and then heat-treated at 300 °C for 1 h in air to obtain nickel cobaltite (about 0.4 mg).

Transmission electron microscopy (TEM) and scanning electron

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microscopy (SEM) were used to analyze the internal microstructure and surface morphology of nickel cobaltite samples, respectively. Surface area and crystal structure of samples were measured by BET (Brunauer-Emmett-Teller) analyzer (Micromeritics, ASAP 2020) and X-ray diffractometer (Bruker, D8), respectively. The supercapacitive behavior of electrodes was determined in 1 M KOH solution by cyclic voltammetry in a three-electrode cell equipped with a working electrode, counter electrode (Pt), and reference electrode (saturated Ag/AgCl electrode) at room temperature. Galvanostatic charge and discharge tests were measured by a source meter (Keithley, 2400) under different current densities. Electrochemical impedance was carried out under an open-circuit condition (about 0.2 V). A sinusoidal perturbation with amplitude of 0.01 V versus open-circuit potential was applied over a frequency range of 0.1 Hz to 50 kHz.

3. Results and discussion

Fig. 1 shows the SEM and TEM images of nickel cobaltites prepared at various cooling rates. The cooling rate of the autoclave chamber plays a key role in determining the shape of nickel cobaltite. Porous nickel cobaltite film composed of self-folded nanosheets (denoted as NS electrode) can be uniformly formed on SS mesh at faster cooling rate (1 °C min^{-1}). The formation of the nanosheet film relies on the heterogeneous nucleation and growth due to the lower interfacial nucleation energy on the SS mesh [21]. Porous film composed nanosheets with attached nanowires (denoted as NS-NW electrode) can be grown on SS mesh at slower cooling rate (0.5 °C min^{-1}). Specific surface areas of the NS and NS-NW samples are measured to be 49 and 62 $m^2 g^{-1}$, respectively. X-ray diffraction (XRD) pattern (inset of Fig. 1) reveals that the prepared nickel cobaltite can be assigned to $NiCo_2O_4$ spinel.

Fig. 2a displays the cyclic voltammograms (CVs) of nickel cobaltite electrodes at a scan rate of 10 mV s^{-1}. Both electrodes show one pair of redox peaks beside the oxygen evolution reaction at potentials more positive than 0.45 V. The redox reaction of nickel cobaltite in alkaline electrolyte can be expressed as follows [22]:

$$NiCo_2O_4 + OH^- + H_2O \leftrightarrow NiOOH + 2CoOOH + e^- \quad (1)$$

In addition to the size of area surrounded by the CV curve, both electrodes show a similar CV shape. The specific capacitance of electrodes is proportional to the area integrated within the CVs. The higher the redox current density, the larger is the specific capacitance of the nickel cobaltite electrode. Thus, NS-NW electrode offers more active sites to store plenty of charge through Faradaic reaction than NS electrode, leading to an increase in specific capacitance.

Fig. 2b shows the galvanostatic charge/discharge curves of nickel cobaltite electrodes at a current density of 10 A g^{-1} for two cycles. The specific capacitance (C_{sp}) of electrodes in units of F g^{-1} can be calculated using $C_{sp}=(i\times\Delta t)/\Delta V$, where i is the discharge current density (A g^{-1}), Δt is the elapsed time for discharge (s), and ΔV is the potential window (V). The discharging (charging) time of NS-NW electrode in each cycle is considerably extended compared to that of NS electrode. NS-NW electrode delivers a specific capacitance of 728 F g^{-1} at 10 A g^{-1}, which is superior to NS electrode (389 F g^{-1}). Both electrodes exhibit high coulombic efficiency since the charge and discharge times for each electrode are almost the same. Fig. 2c shows the variation in C_{sp} associated with the current density. C_{sp} of NS-NW electrode is about 775 F g^{-1} at 5 A g^{-1}, which is considerably higher than that of NS electrode (435 F g^{-1}). As discharged at 50 A g^{-1}, NS-NW electrode still retains a high capacitance of 595 F g^{-1}, while the capacitance of NS electrode decreases to 283 F g^{-1}. In addition, NS-NW electrode also shows a stable cycle-life performance (Fig. 2d), its C_{sp}

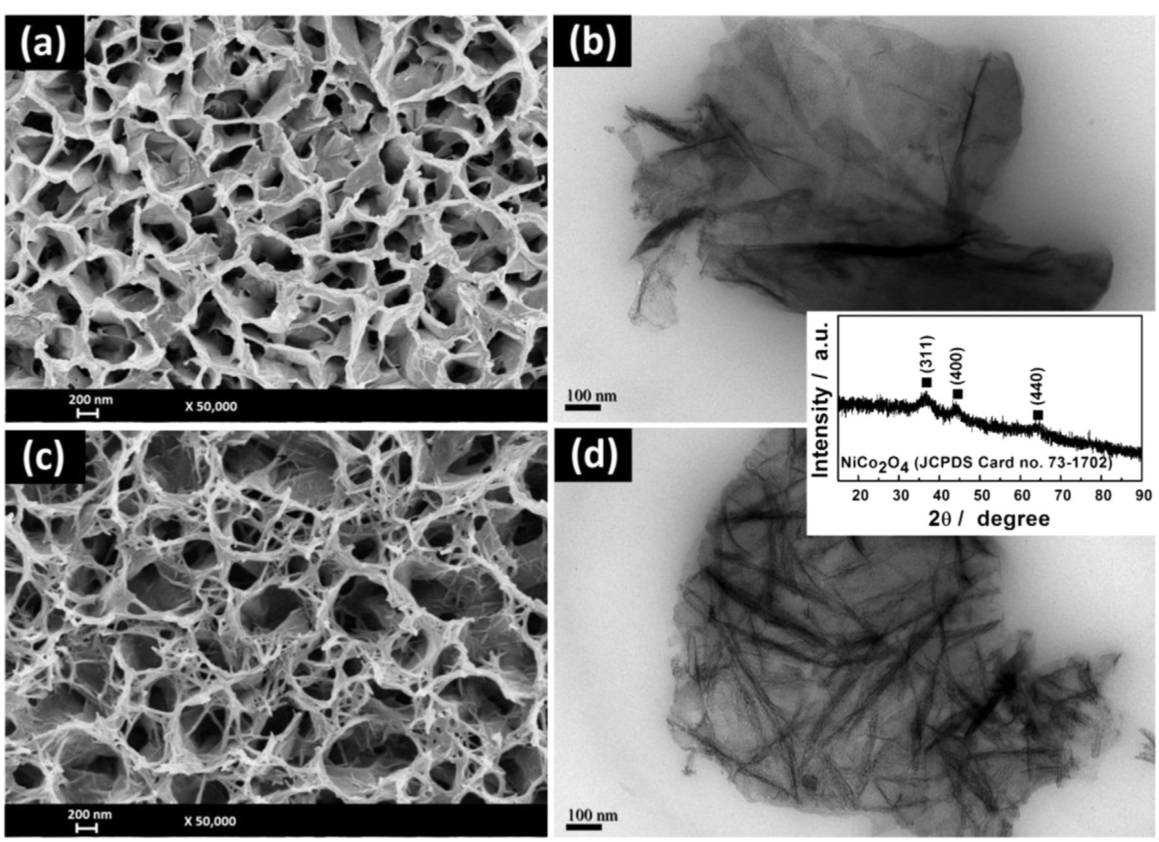

Fig. 1. SEM and TEM images of (a, b) NS and (c, d) NS-NW samples. Inset shows the XRD pattern of the prepared nickel cobaltite.