

Nanostructured cobalt oxide and cobalt sulfide for flexible, high performance and durable supercapacitors



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ABSTRACT

Transition metal oxides and sulfides have great potential for energy storage devices due to their large theoretical energy storage capacities. A facile technique was used for the synthesis of nanostructured and phase pure cobalt oxide (Co₃O₄) and subsequently converting it to cobalt sulfide (Co₉S₈). The effect of sulfurization on energy storage capacity of the cobalt oxide was explored. Microstructural characterizations using X-ray diffraction and scanning electron microscopic reveal formation of phase pure and nanostructured Co₃O₄ and Co₉S₈. It was observed that the areal capacitance of Co₃O₄ (983 mF/cm²) improved significantly after converting to Co₉S₈ (7358 mF/cm²). The CV curves of the Co₉S₈ electrode on bending showed outstanding stability with no change in energy storage properties. New insights into the better performance of Co₉S₈ over Co₃O₄ based on electrochemical investigations are presented. The performance of the Co₉S₈ as an electrode material for energy storage applications was further investigated by fabricating a supercapacitor device. The supercapacitor device showed outstanding stability up to 5000 cycles of charge-discharge study. The performance of the supercapacitor was observed to be improving with temperature. The supercapacitor displayed ~100% enhancement in energy storage property on increasing temperature from 10 to 70 °C. Our results suggest that hydrothermally grown Co₉S₈ on nickel foam can be utilized for high capacity, flexible and binder free electrode for energy storage applications.

1. Introduction

Electrochemical capacitors are attracting considerable attention as advanced energy storage applications because of their decent energy storage capacity, fast energy storage and release time, and long-cycle life [1–4]. Metal oxides, metal sulfides, conducting polymers and various forms of carbon are being used as active materials for electrochemical capacitors [5–22]. Metal oxides provide high energy storage capacity due to redox reactions involved in energy storage process compared with carbonaceous materials where electrochemical double layer is primarily responsible for energy storage [23–25]. Among various metal oxides, Co₃O₄ is particularly appealing due to its low price, high faradic activity, ease to synthesize in nanostructured forms and high calculated specific capacitance (~3560 F/g) [26–28].

Energy storage capacity of cobalt oxides depends on their morphol-

ogy and thus various forms of Co₃O₄ such as nanosheet arrays [29], nanorod assembled microsphere [30], nanoflower [31], nanowires [32], nanotubes [33], nanobelts [34], nanocubes [35] have been reported. Wang et al. have observed a specific capacitance of 394 F/g for multi-shelled Co₃O₄ hollow microspheres [30]. The reported superior electrochemical property was due to multi-shelled hollow structures which provide larger number of active sites for easy diffusion of electrolyte ions in such structure. Electrochemical testing of hollow Co₃O₄ boxes were compared with commercial Co₃O₄ [36]. The specific capacitance of 278 and 77 F/g (at 0.5 A/g) was observed for hollow Co₃O₄ boxes and commercial Co₃O₄ powders, respectively. As found above, the observed charge storage capacity of Co₃O₄ is significantly smaller than its calculated specific capacitance, which could be due to its low conductivity which affects its electron transport during energy storage process. Yang et al. have improved the electrochemical proper-

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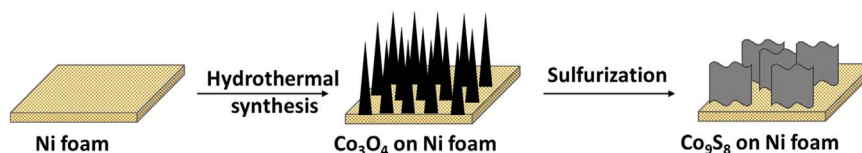


Fig. 1. Schematic illustration of formation of cobalt oxide (Co_3O_4) and cobalt sulfide (Co_9S_8) on Ni foam.

ties of Co_3O_4 by directly growing over nickel foam [29]. Co_3O_4 grown on nickel displayed a specific capacitance of 1782 F/g at 1.8 A/g. Sulfurization is another way to enhanced charge storage capacity of Co_3O_4 . Transition metal sulfides have better electronic conductivity compared with their oxides [37]. Higher electronic conductivity reduces the sheet and charge transfer resistance of the electrodes and thus improves electrochemical properties [38].

Recently, sulfides of transition metals for instant cobalt sulfide, nickel sulfide and nickel cobalt sulfide are being used for energy storage applications with decent performance [39–43]. In this paper, we utilize a facile technique to synthesize phase pure Co_3O_4 and then conversion of Co_3O_4 to Co_9S_8 using a hydrothermal process. Electrochemical testing of both the electrodes showed more than 7 times improvement in charge storage capacity by converting Co_3O_4 to Co_9S_8 . In addition, temperature depended electrochemical properties of a supercapacitor device fabricated using Co_9S_8 showed 100% enhancement in the specific capacitance with increase in temperature from 10 to 70 °C.

2. Experimental details

All the chemicals were of analytical grade and used without further purification. Chemicals such as cobalt nitrate hexahydrate was purchased from Strem Chemicals, USA and polyvinylpyrrolidone, urea and sodium sulfide from Sigma Aldrich. Cobalt oxide on nickel foam (from MTI corporation) was synthesized using 3 mM of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 18 ml of water/ethanol (1:1 v/v) solution, followed by addition of 300 mg of polyvinylpyrrolidone. Into this mixture, 18 ml of urea solution (12 mM of urea in 1:1 water/ethanol) was added. The resulting mixture was placed in to a 45 mL Teflon autoclave (Parr Instrument Company) and heated for 12 h at 140 °C at heating rate of 5 °C/min. A pre-cleaned nickel foam was placed in the reactor before start of the reaction. Nickel foam was cleaned using 3 M HCl followed by washing with DI water and ethanol. After reaction, nickel foam was cleaned by washing with DI water. The nickel foam was kept at 60 °C for 8 h and then at 350 °C (at heating rate of 5 °C/min) for additional 3 h to make Co_3O_4 deposited nickel foam.

The synthesized cobalt oxide was sulfurized using a hydrothermal method. For this cobalt oxide coated Ni foam was dipped in 30 ml of 0.2 M Na_2S solution in a hydrothermal reactor heated for 24 h at 140 °C at heating rate of 5 °C/min. After 24 h of reaction, the Ni foam was taken out and rinsed with DI water and ethanol. The resulting foam was kept in vacuum oven for 6 h to dry.

The structural characterizations of the prepared materials were performed using x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). The x-ray patterns were recorded with Shimadzu X-ray diffractometer in 2θ – θ mode. The $\text{CuK}\alpha_1$ ($\lambda=1.5406 \text{ \AA}$) radiation was used to record the XRD patterns. A Thermo Scientific K α XPS system was used to record XPS spectra. The x-ray power of 75 W at 12 kV was used for the experiment with a spot size of 400 mm^2 . The XPS data acquisition was performed using the “Avantage v5.932” software provided with the instrument. A JEOL JSM-840A scanning electron microscope was used to investigate the microstructure of the synthesized samples. The SEM was equipped with an Oxford INCA 250 silicon drift X-ray energy dispersive spectrometer (EDS).

Electrochemical measurements were performed using a Versastat4-500 electrochemical workstation (Princeton Applied Research, USA) in standard three electrode method. Cobalt oxide and cobalt sulfide

deposited on nickel foam were directly used as working electrode. A spiral platinum was used as counter electrode. A saturated calomel electrode (SCE) was used as a reference electrode for all the electrochemical measurements. Electrochemical properties were studied using cyclic voltammetry (CV), constant current charge-discharge and electrochemical impedance spectroscopy techniques. Supercapacitor device was fabricated using cobalt sulfide deposited nickel foams, ion transporting layer as separator and KOH as an electrolyte. The ion transporting layer was 25 μm thick (Celgard, 39% porosity). Ion transporting layer (soaked with KOH electrolyte) was sandwiched between two cobalt sulfide deposited nickel foams to fabricate the device.

3. Results and discussion

A facile hydrothermal method was used to deposit binder free cobalt oxide on nickel substrate and subsequently it was converted to cobalt sulfide (Fig. 1). Under the hydrothermal condition, urea gradually decomposed into NH_3 and CO_2 . During this process, NH_3 reacted with water to form ammonium and hydroxyl ions. Cobalt ion (from cobalt nitrate) precipitated as cobalt hydroxide due to raise in the pH of the solution. As deposited cobalt precursor on Ni foam was further treated with Na_2S in hydrothermal reactor where anion-exchange process occurred to form cobalt sulfide. During anion exchange process, nanowires of cobalt precursor combined and formed a sheet-like structures [44]. The hydrothermal growth of cobalt oxide, a binder free approach, has an advantage of providing direct contact of the cobalt oxide on conducting nickel and thus reducing the contact resistance and facilitating the charge transfer. In addition to reduced contact resistance, hydrothermal synthesis provides materials with nanostructure which will be very beneficial for energy storage applications.

The crystallinity and phase purity of the prepared cobalt oxide and cobalt sulfide were studied utilizing x-ray diffraction technique. X-ray patterns of the prepared cobalt oxide and cobalt sulfide are shown in Fig. 2. As seen in the Fig. 2, the synthesized compounds are crystalline in nature. The diffraction peaks and their corresponding angles correlate well with diffraction pattern of standard Co_3O_4 (JCPDS 00-042-1467) and Co_9S_8 (JCPDS 00-003-0631). No additional peaks other than peaks due to Co_3O_4 and Co_9S_8 were observed, indicating phase purity of the Co_3O_4 and Co_9S_8 . The observed diffraction peaks were indexed as (220), (311), (222), (400), (422), (511) and (440) planes of Co_3O_4 , whereas the patterns for the Co_9S_8 were indexed as (222), (400), (511), (440), (531), (622) and (711).

X-ray photoelectron spectroscopy was used to study the chemical nature of the prepared cobalt oxide and cobalt sulfide. Fig. 3a displays the deconvolution pattern of Co 2p. The presence Co^{2+} and Co^{3+} is quite evident. The peaks around 794.6 and 779.4 eV are matching well to the Co $2p_{1/2}$ and Co $2p_{3/2}$ spin-orbit peaks of Co_3O_4 . Fig. 3b displays the O 1s XPS pattern of Co_3O_4 . The peak at 529.7 eV is corresponding to the lattice oxygen in Co_3O_4 [45]. The other observed peaks are associated with the oxygen of OH ions and the H_2O adsorbed onto the surface of Co_3O_4 [46,47]. The high resolution XPS spectrum of Co 2p matches well with two spin-orbit doublets for Co_9S_8 is shown in Fig. 3c. The doubles are typically due to Co^{2+} and Co^{3+} . Fig. 3d displays the S 2p spectrum of Co_9S_8 . The peaks around 161.6 and 162.7 eV are due to $2p_{3/2}$ and $2p_{1/2}$ core levels of S²⁻ in Co_9S_8 [48].

Structural and morphological investigations on the synthesized

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