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Application of Cobalt Oxide Thin Films for Electrochemical Supercapacitor

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ABSTRACT

Cobalt oxide thin film with nanotubes-like morphology was successfully synthesized by chemcical solution method such as sol-gel reflux method. The cyclic voltammetry studies reveal that Co3O4 electrode exhibited maximum specific capacitance of 125.7 Fg-1 at scan rate 20mVs-1. The GCD studies the Co3O4 electrode at shows that the charge-discharge curves indicating the large specific capacitance, promising for the development of high-performance supercapacitors. EIS analysis is a principal method to examine the fundamental behavior of electrode materials for supercapacitors.

KEYWORDS Thin films, chemical solution method, sol-gel method, cobalt oxide

1. Introduction

Energy storage devices with high performance are called for electrochemical capacitors, because of the higher power density than the batteries and higher energy density than the conventional capacitors. Supercapacitors (SCs), featuring fast-growing demand for high performance energy storage devices for consumer and have received great interest for many potential applications such as electric vehicles, medical electronics, telecommunication devices and stand-by power systems, due to their high power density, energy efficiency, excellent reversibility and longer cycle life [1]. In SCs, active materials are playing important role for electrochemical performance. Generally, in SCs three types of electrode materials namely carbon material, conducting polymers and transition metal oxides [2]. Carbon based and polymers materials have better electrical properties, long life-cycles and mechanical properties, but metal oxide materials have high specific capacitance and high energy density than carbon and polymer electrode. In SCs the energy storage mechanism is usually attributed due to faradic and non-faradic reactions [3]. Faradic reactions of SCs are fast and reversible faradic redox reactions within the electroactive material on the electrode, which exhibit higher capacitance and superior energy density than EDL capacitors. Different metal oxide such as RuOx, NiOx and IrOx have serve as excellent electrode materials for SCs with their charge-storage mechanism based on the pseudocapacitance. In particular, RuO_2 has been shown excellent electrode, which exhibit a high specific capacitance. It is less attractive for application due to high cost. [4]. The Co_3O_4 electrode has been found good efficiency and long-term stability performance, good corrosion stability and low cost, due to this attractive properties. It is used for commercial application [5].

Now a day's many researchers have been synthesized of Co_3O_4 nanostructures with different morphologies such as nanoparticles, hollow spheres, nanorods, nanoplates, nanowires and nanocubes. Among, Co_3O_4 nanoparticles have been prepared by various physical and chemical methods such as combustion method [6], microwave irradiation [7], sol–gel process [8], chemical spray pyrolysis [9] and sonochemical method [10].

In the paper the investigation one-step, simple and inexpensive sol-gel reflux method is used for the synthesis of Co_3O_4 electrode. After, previous characterization, the films were studied for electrochemical performance in supercapacitor properties using CV, GCD, and EIS techniques.

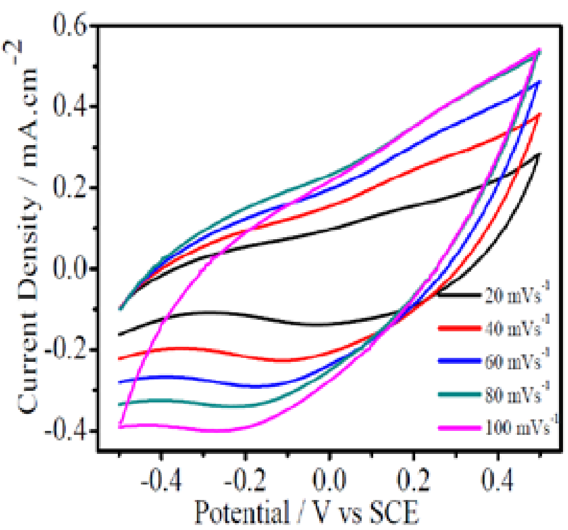
2. Experimental work

In a typical synthesis, nanotube-like Co_3O_4 thin film deposited on steel substrate. The method used was sol-gel reflux method. In the process of film formation, firstly, then 0.04M cobalt (II) nitrate hexahydrate (AR) was taken as precursor and dissolved in doubly distilled water. Thereafter, 28% ammonia was added as complexing agent. The pH of the solution was adjusted to 12. The deposited films were then annealed at 773 K temperature and characterized for structural details. The electrochemical performance of the cobalt oxide films as electrodes in supercapacitor applications was studied by CV, GCD, and EIS measurement. The electrolyte such as aqueous solution of 1.5M KOH was applied as an electrolyte. The XRD analysis confirmed the pure phase formation of the cobalt oxide. The SEM images revealed the development of well adherent and nanotube like formation with evident length of tube in the range of 250-300 nm, such type of morphology provide accessibility of OH^- ions of electrolyte and electrode, which is the most important requirement in supercapacitor application.

3 RESULTS AND DISCUSSION

3.1 Cyclic Voltammetry Study

The electrochemical properties of Co_3O_4 electrode were performed by CV in 1.5M KOH electrolyte with potential window of -0.5 to +0.5 V/SCE is shown in Fig.1.



"Figure 1 about here"

The CVs of Co_3O_4 electrode are recorded at different scan rates. During the scans, reduction and oxidation peaks are observed, in which CoO_2 is formed at the surface of Co_3O_4. Here the capacitance is mainly based on the redox reaction because the shape of CV is different from that of electric double layer capacitance. The general chemical redox reaction for Co_3O_4 electrode in alkaline electrolyte is given below [11].

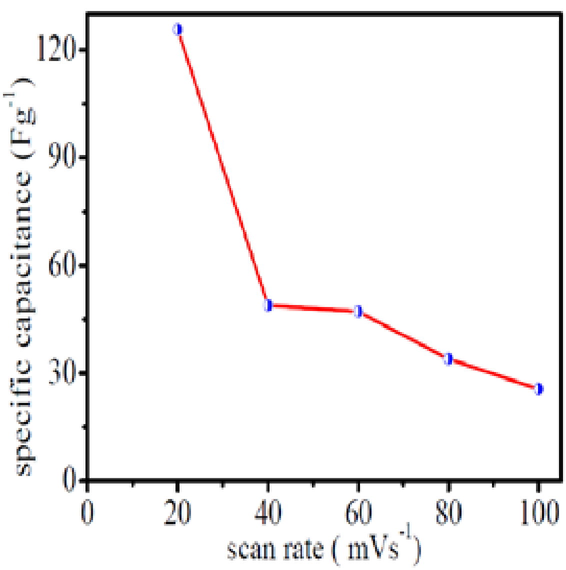
$$Co_3O_4 + OH^- + H_2O \rightarrow 3CoOOH + e^-$$

$$CoOOH + OH^- \rightarrow CoO_2 + H_2O + e^-$$

It is found that the current under curve slowly increased with scan rate. This concluded that the voltammetry current is directly proportional to the scan rates and this is indication of supercapacitive behavior [12]. The specific capacitance was calculated using the following relations,

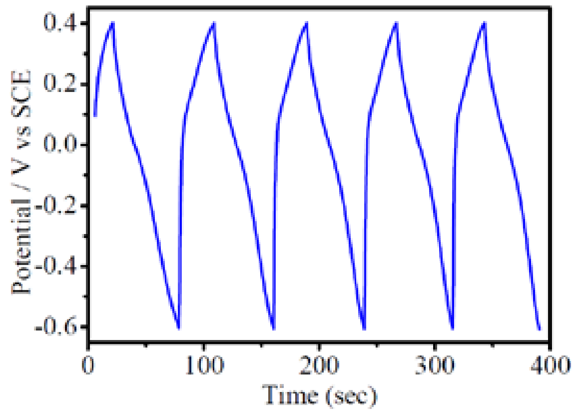
$$C = \frac{I}{dV/dt} \qquad Cs = \frac{C}{2W}$$

where, 'C' and 'Cs' stand for average, specific capacitances, dV/dt is the scan rate, and 'W' is the weight of deposited material respectively. The variation of specific capacitance versus scan rate is shown in Fig.2, which reveals that Co_3O_4 electrode exhibited maximum specific capacitance of 125.7 Fg^{-1} at scan rate $20mVs^{-1}$. The reported value of specific capacitance for Co_3O_4 is 74 Fg^{-1} at scan rate $5mVs^{-1}$[13].



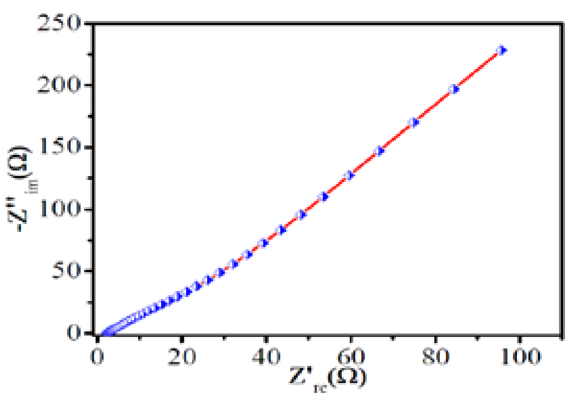
"Figure 2 about here"

3.2 Galvonostatic Charge – Discharge Study (GCD)
The GCD studies are the most direct approach to evaluate the applicability of supercapacitors. The GCD curves of the Co_3O_4 electrode at 2 $mAcm^{-2}$ galvanostatic current densities in 1.5M KOH electrolyte. Fig.3 shows that the charge-discharge curves which remain undistorted and symmetric. The Co_3O_4 gives a large specific capacitance, promising for the development of high-performance supercapacitors. From the discharge curve, a sudden potential drop is due to internal resistance (IR) and subsequent potential decay represents the capacitive behavior of the electrode. The supercapacitive behavior of chemically deposited Co_3O_4 electrode can be attributed to its morphology which provides large electrochemical active surface for electrolyte. It improves the surface adsorption/desorption processes.



"Figure 3 about here"

3.3 Electron Impedance Spectroscopy (EIS) Study
EIS analysis is a principal method to examine the fundamental behavior of electrode materials for supercapacitors. Fig.4 shows the Nyquist plot of the Co_3O_4 electrode. It shows the inclined line which indicates a lower diffusion resistance and charge-transfer resistance. The impedance spectra of Co_3O_4 was composed a linear component at low-frequency i. e. the point of intersection on real axis in the high frequency region indicates internal resistance of the electrode in an open circuit condition. The internal resistance is the combination of ionic resistance of electrolyte, intrinsic resistance of the active material, and contact resistance at the active material/current collector interface. The linear part of the impedance spectrum corresponds to the Warburg impedance (Zw), is a result of the frequency dependence of ionic diffusion/transport in the electrolyte and to the surface of the electrode, and also typical characteristic of the capacitive behavior.



"Figure 4 about here"

4. Conclusion
The Co_3O_4 thin film was successfully synthesized by sol-gel reflux method. The cyclic voltammetry studies reveal that Co_3O_4 electrode exhibited maximum specific capacitance of 125.7 Fg^{-1} at scan rate $20mVs^{-1}$. The GCD studies the Co_3O_4 electrode at shows that the charge-discharge curves indicating the large specific capacitance, promising for the development of high-performance supercapacitors. EIS analysis is a principal method to examine the fundamental behavior of electrode materials for supercapacitors.

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