



Electrochemical behavior of potentiodynamically deposited cobalt oxyhydroxide (CoOOH) thin films for supercapacitor application

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ABSTRACT

In the present study, we report, for the first time, the synthesis of cobalt oxyhydroxide thin films on inexpensive stainless steel substrate using potentiodynamic electrodeposition method. These films were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM) techniques. The orthorhombic crystal structure was revealed by the X-ray diffraction study. The FT-IR spectrum confirmed the formation of cobalt oxyhydroxide. The SEM studies showed the nanoflakes-like morphology with an average thickness of 100 nm. The cyclic voltammetry study of the cobalt oxyhydroxide films in 1 M KOH showed maximum specific capacitance of 449 F g^{-1} at scan rate of 5 mV s^{-1} .

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1. Introduction

Great attention has been attracted by electrochemical capacitors (ECs) because of their higher power density and longer cycle life than conventional secondary batteries. According to their different mechanisms of energy storage, the ECs can be divided into electric double-layer capacitors and redox pseudocapacitors. The ECs are significantly applicable in several fields, such as hybrid electric vehicles, laser, fuel cells, cellular phones, digital camera, etc. It provides ultimate way to store a significantly higher energy than conventional capacitors and can deliver that charge in either a rapid rate of time or in a slower controlled rate of time. The electrode material for supercapacitors should possess high cyclability, long-term stability, high surface area and high rate of electrochemical oxidation/reduction [1].

Generally, conducting polymers, activated carbon and transition-metal oxides are widely used for supercapacitor electrode material [2–7]. Transition metal oxides like RuO_2 and IrO_2 are the promising electrode materials for supercapacitors, but the high cost, toxic and scarce source of ruthenium and iridium retarded its commercial acceptance. Therefore, other low cost materials such as NiO , Co(OH)_2 , Ni(OH)_2 , MnO_2 and CoO_x have attracted considerable attention [8–15]. Among these metal oxides and hydroxides, the cobalt hydroxide is a promising electrode material due to its layered structure with large interlayer spacing, well

defined electrochemical redox activity and the possibility of the enhanced performance through different preparative methods [16–18]. Further, the cobalt oxyhydroxide is a better charge storage material due to its innovative properties of high conductivity, morphology control nature of micrometer/nanometer scale. Cobalt oxyhydroxide fine nanoflake film revealed a maximum capacitance of 200 F g^{-1} [19]. Carbon nanotube/cobalt oxyhydroxide nanoflake multilayer film showed capacitive behavior with large specific capacitance of 389 F g^{-1} [20].

In present work, we have electrodeposited cobalt oxyhydroxide thin films on cost effective stainless steel substrate from an aqueous alkaline bath using potentiodynamic mode. The films are characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) techniques. The electrochemical characteristics of the cobalt oxyhydroxide films are evaluated using cyclic voltammogram (CV) and charge discharge techniques.

2. Experimental

2.1. Preparation of cobalt oxyhydroxide thin films

The cobalt oxyhydroxide film was electrodeposited on to the stainless steel substrate using potentiodynamic mode of electrodeposition from an alkaline solution of 0.1 M cobalt chloride (CoCl_2) at room temperature (300 K). The cobalt chloride solution was complexed with ammonium hydroxide and pH of the solution was maintained at ~ 12 . The substrates ($4 \text{ cm} \times 1.5 \text{ cm}$) were first polished with zero-grade polish paper and finally washed with double distilled water in an ultrasonic bath for about 20 min. A

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graphite plate (4 cm × 4 cm) was used as the counter electrode and saturated calomel electrode (SCE) as the reference electrode in conventional three-electrode system. An automatic battery cycler (WBCS3000) was employed for the potentiodynamic deposition. The deposition of cobalt oxyhydroxide film was performed in the potential window 0 to +1.2 V/SCE. After the deposition, the electrode was dried in air.

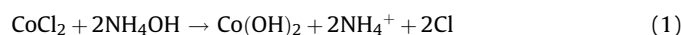
The amount of cobalt oxyhydroxide loaded onto the stainless steel substrate was then weighed using a microbalance. For the structural elucidation of the film, X-ray diffraction analysis was performed with chromium (Cr K α radiation $\lambda = 2.2897 \text{ \AA}$) target with in a diffraction angle 2θ from 20 to 100°. The surface morphology of cobalt oxyhydroxide was studied by scanning electron microscopy (SEM) (JEOL JSM model 6360). The Fourier transform infrared (FTIR) spectrum of the sample was collected using a 'Perkin Elmer, FTIR Spectrum one' unit. The electrodeposited cobalt oxyhydroxide thin films were tested for the application in supercapacitor by studying the cyclic voltammogram curves. The cyclic voltammograms were obtained at 5 mV s $^{-1}$ scan rate in 1 M KOH electrolyte within the window -0.2 to $+0.45$ V/SCE. Galvanostatic charge–discharge curves at constant current density of 5 mA cm $^{-2}$ were evaluated from automatic battery cycler (WBCS3000).

3. Results and discussion

3.1. Film formation

Cobalt oxyhydroxide films were deposited on to stainless steel substrates with voltage cycling (scan rate 20 mV s $^{-1}$) between 0 and +1.2 V/SCE. The cyclic voltammogram obtained during continuous potential cycling for cobalt oxyhydroxide growth on a stainless steel substrate is shown in Fig. 1.

Initially, 0.1 M CoCl $_2$ was used as a source of cobalt and aqueous ammonia (NH $_4$ OH) solution (25% extrapure) was added with constant stirring to make it alkaline. When aqueous ammonia solution was added in cobalt chloride, the ionic product of Co(OH) $_2$ exceeds the solubility product and the solution becomes turbid due to formation of Co(OH) $_2$ precipitation.



With, further addition of surplus ammonia solution reduces Co $^{2+}$ ion by producing the complex ion of type Co(NH $_3$) $_4^{2+}$. This avoids precipitation and makes solution clear and transparent. This can be explained by the following reaction

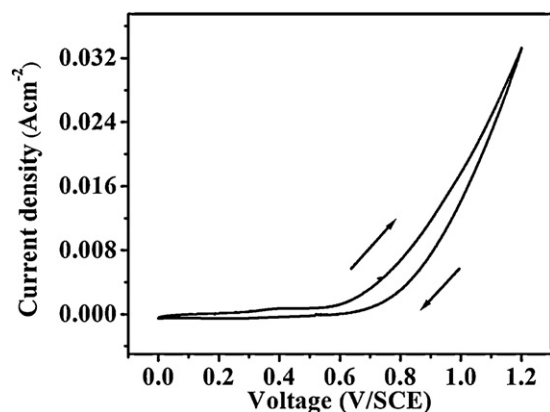
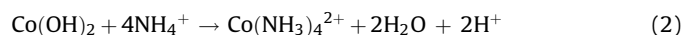
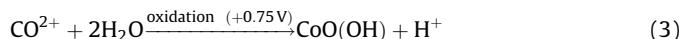


Fig. 1. Cyclic voltammogram for 0.1 M CoCl $_2$ in ammonium solution (30%) at a stainless steel electrode.

During the positive potential scan, a mild oxidation curl appeared at about +0.75 V/SCE which probably corresponds to the Co $^{II} \rightarrow$ Co III redox couple. The electrochemical reaction mechanism for deposition of cobalt oxyhydroxide may be presented as follows,



In film formation, the cobalt deposit continues electroactive during prolonged electrodeposition so that the redox transition wave grows with number of cycles. A total of 30 potential cycles provides optimum film thickness. Cobalt oxyhydroxide film appears to be uniform, smooth and good degree of adhesion on the stainless steel surface [21].

3.2. Thickness measurement

The thickness of the cobalt oxyhydroxide film was measured by means of weight difference method. The variation of thickness (mg cm $^{-2}$) with cycle number is shown in Fig. 2. The inset shows the photograph of cobalt oxyhydroxide thin film deposited on stainless steel substrate. As the number of deposition cycles increased, the film thickness also increased and maximum thickness of 3.01 mg cm $^{-2}$ was attained after 30 deposition cycles. Above 30 cycles, the film peeled off from the substrate and no further deposition was observed which is attributed to the development of tensile stress that tends to cause delamination when film becomes thick [22,23]. Therefore these films were used for the further characterization.

3.3. Structural study

In order to study crystalline nature of thin film, the XRD patterns were recorded in the 2θ range 20–100°. Fig. 3 shows typical XRD pattern from which it is evident from figure the film is nanocrystalline. The characteristic peaks observed corresponding to the planes of (1 1 0), (1 4 0) and (1 3 1) are in good agreement with the standard JCPDS card No. 26-0480 with orthorhombic crystal structure [24]. Kandalkar et al. [25] have reported the orthorhombic crystal structure for CoOOH deposited using chemical bath deposition method. Yang et al. [26] have reported as prepared phase of cobalt oxyhydroxide by employing simple soft chemistry. From the XRD study the average crystallite size of CoOOH was calculated on the basis of full width at half maxima

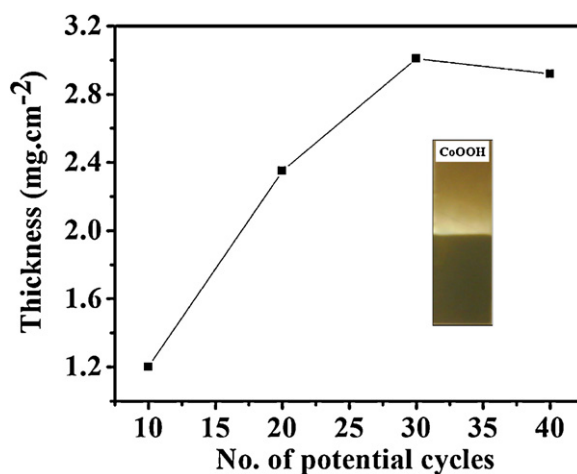


Fig. 2. Thickness variation of cobalt oxyhydroxide thin film as a function of no. of potential cycles [inset shows the photograph of cobalt oxyhydroxide thin film at maximum thickness].

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