Potentiodynamically Deposited Cobalt Hydroxide [$Co(OH)_2$] Thin Film Electrode For Redox Supercapacitor

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Abstract. Nanoflakes of cobalt hydroxide [$Co(OH)_2$] were potentiodynamically deposited onto stainless steel substrate. Electrolyte medium used for the deposition was 0.1M $Co(NO_3)_2$ and the scan rate of the deposition was 50 mVs^{-1}. X-ray diffraction (XRD) and scanning electron microscope (SEM) was used for structural and morphological study respectively. The X-ray diffraction pattern revealed the formation of $Co(OH)_2$ with hexagonal crystal structure. SEM images showed the development of nanoflakes like morphology over the substrate. Supercapacitive properties of $Co(OH)_2$ thin film electrode were studied using cyclic voltammetry and charge-discharge techniques. The $Co(OH)_2$ thin film electrode showed maximum specific capacitance of 980 Fg^{-1} at 5 mVs^{-1} in 1M KOH electrolyte.

Keywords: Thin film, cobalt hydroxide, supercapacitor.

1. INTRODUCTION

Electrodeposition process is basically used to prepare nanostructured materials in thin film form. This has been employed for the deposition of different metal oxides, conducting polymers and alloys [1-3]. Among these materials metal oxide thin films have been widely prepared from electrodeposition technique via direct growth [4] or after thermal oxidation [5] of metal hydroxides. Metal oxide films can be deposited through three different modes of electrodeposition such as potentiodynamic, potentiostatic and galvanostatic. These different modes of electrodeposition affect the film microstructure and performance in the corresponding application. Currently, we have reported the potentiodynamic electrodeposition method for the preparation of CoO(OH) thin films from an aqueous alkaline bath [6]. In another study, Lee et al have prepared manganese oxide thin films by potentiodynamic electrodeposition for supercapacitor application [7]. With potentiodynamic deposition, one can prepare porous and nanostructured thin films.

In present work we have successfully deposited $Co(OH)_2$ thin films via potentiodynamic mode of electrodeposition. These films are characterized using X-ray diffraction (XRD) and Scanning electron microscopy (SEM). Supercapacitive properties are tested using cyclic voltammetry and charge-discharge techniques.

2. EXPERIMENTAL

The $Co(OH)_2$ film was deposited on to the stainless steel SS (grade 304, 0.1 mm thick) substrate by potentiodynamic mode of electrodeposition in an acidic 0.1 M cobalt nitrate ($Co(NO_3)_2$) solution at room temperature (300 K). The pH of cobalt nitrate solution was 4. The substrates (4×1.2 cm^2) were first polished with zero-grade polish paper and finally washed with double distilled water in an ultrasonic bath for about 20 min. A graphite plate (4×4 cm^2) was used as the counter electrode and saturated calomel electrode (SCE) as the reference electrode in conventional three-electrode system.

3. RESULTS AND DISCUSSION

3.1 Structural Study

Fig. 1 shows the XRD pattern of $Co(OH)_2$ deposited at the scan rate of 50 mVs^{-1}. The planes (102), (003) and (104) are attributed to the $Co(OH)_2$ with hexagonal crystal structure. The peaks marked with an asterisk (*) are assigned to the characteristic peaks of the SS substrate.

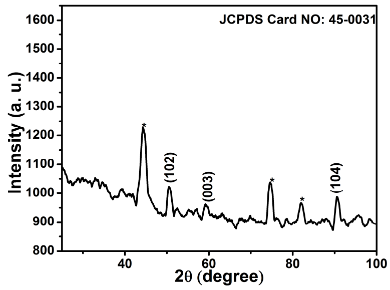

FIGURE 1. XRD pattern of $Co(OH)_2$ thin film on stainless steel substrate

3.2 Morphological Study

Surface morphology of $Co(OH)_2$ film was studied with scanning electron microscopy. Fig. 2 (a and b) shows SEM micrographs of $Co(OH)_2$ deposit at two different magnifications (×20,000 and ×100,000).

The SEM images revealed the formation of well adherent and porous nanoflake like structure with apparent breadth in the range of 100 nm. Such type of morphology can provide greater surface area and porous morphology for electrode, which is the prime requirement in supercapacitor [8].

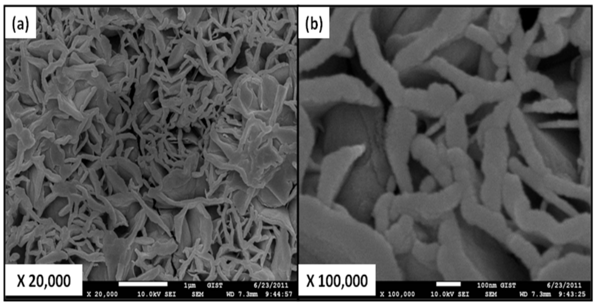

FIGURE 2. Scanning electron micrograph (SEM) images of $Co(OH)_2$ thin film at (a) ×20,000 and (b) ×100,000 magnifications.

3.3 SUPERCAPACITIVE STUDY

Cyclic voltammetry (CV) is considered to be an ideal tool to indicate the capacitive behavior of any material. A large magnitude of current and a rectangular type of voltammogram, symmetric in anodic and cathodic directions, are the indications of ideal capacitive nature of any material. $Co(OH)_2$ thin film electrode is a supercapacitive material with redox transition peaks at prescribed potentials. Fig. 2 (A) shows the typical CV curve (at 5 mVs^{-1} scan rate) of $Co(OH)_2$ thin film electrode prepared at 50 mVs^{-1} scan rate. This indicates that the capacitance characteristics are mainly governed by Faradaic reactions. These redox peaks are the main contributor to the capacitance of $Co(OH)_2$ and corresponding reduction and oxidation peaks are observed in the figure. The electrochemical reaction corresponding to the redox peaks can be expressed as follows:

$$Co(OH)_2 + OH^- \xleftrightarrow{\text{Oxidation/Reduction}} CoOOH + H_2O + e^- \quad (1)$$

The $Co(OH)_2$ thin film electrode showed maximum specific capacitance of 980 Fg^{-1} at 5 mVs^{-1} in 1M KOH electrolyte.

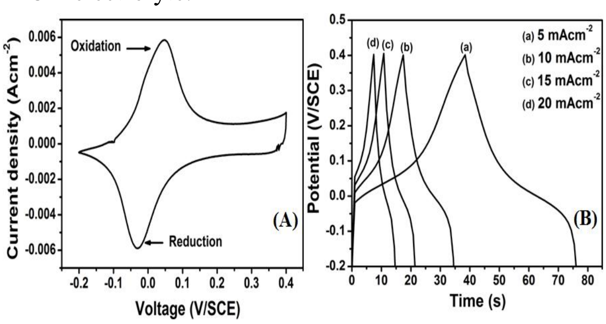

FIGURE 3. (A) the cyclic voltammogram of $CO(OH)_2$ film electrode at the scan rate of 5 mVs^{-1} in 1m KOH electrolyte. (B) Charge–discharge curves of $Co(OH)_2$ film electrode at various current densities.

Fig. 3(B) shows the galvanostatic charge–discharge curves of the $Co(OH)_2$ for constant current densities of 5, 10, 15 and 20 $mAcm^{-2}$. The charge–discharge curves appear like mirror images and the shape of the charge–discharge curves does not show the characteristic of a pure double-layer capacitor, but mainly pseudocapacitance, which corresponds with the result of the CV test. The $Co(OH)_2$ shows maximum values of specific capacitance, specific energy, and specific power of 874 F g^{-1} 350 $Whkg^{-1}$ and 0.93 $kWkg^{-1}$ at 5 $mAcm^{-2}$ respectively. This increment in the values of supercapacitive parameter is very high as compared to the values reported in the literature [9, 10] and it may be due to the nanoflakes-like and porous structure of $Co(OH)_2$ which provides maximum surface area at electrode-electrolyte interface.

4. CONCLUSIONS

Cobalt hydroxide [$Co(OH)_2$] thin films have been successively deposited using potentiodynamic mode of electrodeposition. Cobalt hydroxide with nanoflakes like morphology showed excellent supercapacitive performance.

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