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High-performance Supercapacitor Cobalt Oxide thin films by the Influence of Copper Substrate

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Abstract

The Nanostructured Cobalt Oxide (Co_3O_4) thin films were electrodeposited onto a copper substrate. Cobalt oxide layer was strongly aligned with the film growth direction for the thick copper substrate exhibited the specific capacitance of 504 F/g at a scan rate of 10mV/s, and the current density was fairly stable over 600 cycles. The XRD pattern revealed that the electrodeposited Cobalt oxide film was comprised of Cobalt oxide nano crystalline. In the FESEM image, the cobalt oxide film was covered with cubical shaped particles. FT-IR study supports structural confirmation of Co_3O_4 materials. EDAX spectra of the film confirmed the presence of Co and O elements of the solid films. The charge-discharge test confirmed that capacitance of the electrodeposited Co_3O_4 electrode resulted from the electric double layer capacitance and pseudocapacitance.

Keywords: Cobalt oxide, Electrodeposition, super capacitor, Thin films

1. INTRODUCTION

Capacitors store electrical charge, because the charge is stored physically, with no chemical or phase changes taking place, the process is highly reversible and the discharge-charge cycle can be repeated over and over again, virtually without limit. Existing investigations and growth of electrochemical power sources are mainly paying attention on fuel cells, batteries and electrochemical capacitors (ECs) and are intended for achieving high specific energy, high specific power, long cycle life, etc., with relatively low cost [1]. ECs are also known as supercapacitors which store energy using either ion adsorption (electrochemical double-layer capacitors, EDLCs) or fast surface redox reactions (pseudocapacitors) [2]. Supercapacitors have higher energy density than conventional capacitors and higher power density than batteries. Due to these inimitable properties the field of supercapacitors has been attracted by the research community [3]. In most of the cases, carbonaceous materials are used in the fabrication

of supercapacitors due to its excellent cyclic stability and high specific capacitance. But, they are suffered from poor specific energy density and limited cell voltage. These difficulties could be minimized with the employment of metal oxides and conducting polymers [4, 5]. Survey through literature of supercapacitors shows that different types of metal oxide thin films have been studied. Namely, thin films of MnO_2 [6], NiO_2 [7], Co_3O_4 [8], RuO_2 [9], Fe_3O_4 [10], Bi_2O_3 [11], $NiFe_2O_4$ and conducting polymers [12] etc., have been reported as electrode material in supercapacitor applications. The Cobalt hydroxide based materials are widely used as precursors for the synthesis of various mixed oxide catalysts and absorbents, activity of which is highly depend on structure, morphology, composition and treatment method of the hydroxide precursor [13] Upon thermal treatment above 300ºC cobalt hydroxide usually transforms to black tricobalt tetroxide that is cobalt oxide Co_3O_4 [14,15]. The metal oxide Co_3O_4 are most prominent electrode materials for supercapacitor owing to their attractive properties like high conductivity and good cyclic stability. Generally, literature study revealed that the cobalt oxide thin films have been deposited using chemical bath deposition, [16] successive ionic layer adsorption and reaction (SILAR), [17], spray pyrolysis, [18] chemical vapour deposition, [19] Spin coating, [20] and pulsed laser deposition methods. [21]. Among these synthetic methods the electrodeposition technique has one advantage over the others; it is easy, economical, low temperature process, and the growth rate of the film can be controlled by depositing film in potentiostatic, galvanostatic, or potentiodynamic modes [22]. On the other hand, electrode composed of nano particles are more difficult to fabricate by traditional slurry coating methods, because nanoparticles have poor dispersibility in slurry. Thus it is more advantageous to have an electrode of nano sized cobalt oxide fabricated by electrodeposition directly on to the copper substrate at room temperature without any template or catalyst.

In this work, Cobalt oxide thin films with nanostructured morphology were synthesized as the electrode material for electrochemical capacitors on copper substrates using an electrodeposition method. The Structural and Morphological characteristics of these films were examined. Additionally the electrochemical capacitive behaviour of the electrodeposited Co_3O_4 electrode was investigated using Cyclic voltammetry (CV) and galvanostatic charge discharge test.

2. EXPERIMENTAL DETAILS

The cobalt oxide (Co_3O_4) films were prepared on a copper substrate through electrodeposition in an electrolyte containing 0.1M cobalt chloride ($CoCl_2$) and it was complexed with 30% aqueous ammonia by adjusting the pH around 12. The copper substrate has been cleaned by emery paper and washed with double distilled water in an ultrasonic bath for about 20 min. The electrodeposition process was carried out under galvanostatic conditions. The obtained results showed that the most stable films were obtained at current of density 5 mA/cm^2 with electrolysis duration of 30 min. After deposition, film was rinsed several times in de-ionised water and dried at 300ºC for 1 hour. The amount of the electrodeposited cobalt hydroxide was 0.5mg/cm^2 was weighted by using a microbalance.

The structural properties of the films were carried out using X-ray diffraction analysis comprising copper (Cu Ka target wavelength = 1.54060 Å) target at a diffraction angle 2θ from 20° to 100°. The surface morphology of the film was studied by scanning electron microscopy (SEM). The Fourier transform infrared (FTIR) spectrum of the sample was collected using a Perkin Elmer FTIR Spectrum one unit. The Co_3O_4 film was tested for the application in supercapacitor by studying the cyclic voltammograms. The voltammograms were evaluated at 10, 20, 30, 40, and 50 mV s^{-1} scan rate in 1 M KOH electrolyte within the potential window -0.6 to +0.6 V/SCE. Galvanostatic charge–discharge (GCD) was employed at constant current densities of 5, 10, and 15 mA cm^{-2}.

3. RESULT AND DISCUSSION

Figure 1. The XRD Patterns of Co_3O_4 thin film on copper substrate.

Figure 1 shows the XRD spectrum of the electrodeposited cobalt oxide thin film on copper substrate. The high intensity peaks at 2θ=43.14°, 50.30° and 73.91° were due to the (400), (331) and (620) planes of Co_3O_4 respectively (JCPDS card number 80-1545). The growth orientation of Co_3O_4 layer was in turn affected by copper substrate such that the c-axis of Co_3O_4 layer was strongly aligned with the film growth direction for the thick copper substrate. This copper substrate to better control the orientation and the crystalline structure of the films by epitaxial effects. Epitaxy is favoured by an almost perfect lattice matching between the Cu plane and the Co_3O_4 plane.

Further the crystallite size was estimated on the basis of full width at half maxima intensity of XRD peak by using scherrer's formula.

$$D=\frac{0.89\,\lambda}{\beta cos\theta}$$

Where, D is crystalline size, β is full width at half maxima, λ is wavelength of X-ray used and θ is diffraction angle. The average crystalline size of the film is 51.27 nm. It

revealed that the electrodeposited Co_3O_4 film was nano crystalline nature.

Figure 2. FTIR spectrum of Co_3O_4 thin films on copper substrate.

Also, FTIR study was the evident for the structural confirmation of Co_3O_4 materials. Figure 2 shows the FTIR spectra the Co_3O_4 film materials in the range of 4000 – 600 cm^{-1}. The broad peaks at the absorption bands at around 683 and 612 cm^{-1} are due to the IR absorption of Co_3O_4 with stretching vibration of the metal oxygen bond. The presence of this band indicates that cobalt is situated in an oxygen octahedral environment in the hexagonal structure so Co_3O_4 is formed. Similarly, A.D.Jagadale et al [23] have reported the FTIR analysis of nanocrystalline Co_3O_4 synthesized by various method using cobalt nitrate as a starting material.

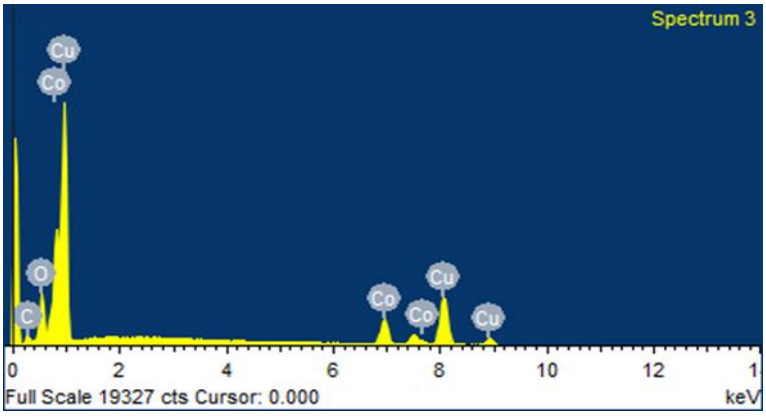

Figure 3. Energy dispersive analysis of Co_3O_4 thin film.

Furthermore, the elemental composition of prepared samples has been identified and confirmed by using EDAX pattern. Figure 3 shows the EDAX study of Co_3O_4 thin films. From this Co and O atoms has been confirmed to presence. Also some other

impurities such as Cu, C peak are observed. Cu peak has been presented due to the substrate and carbon has been presented may be due to some other impurities from dish wash powder used during the cleaning process of the substrate.

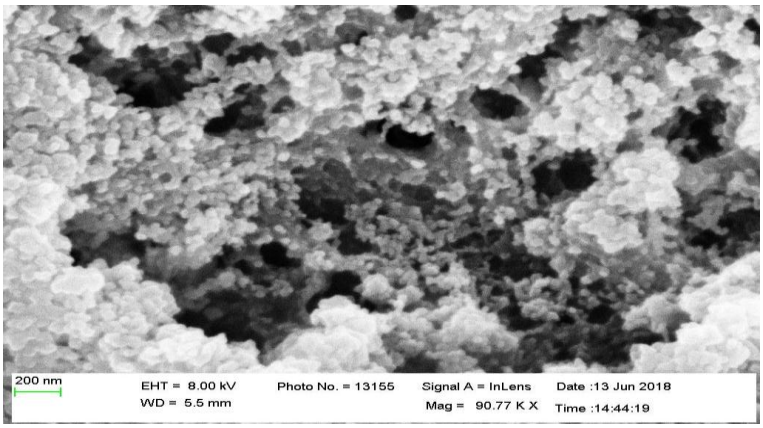

Figure 4. The FESEM image of Co_3O_4 thin film on copper substrate.

Figure 4 shows the FESEM image of the electrodeposited Co_3O_4 film. The substrate was well covered with fine cubical and hexagonal shaped particles having different sizes. Some nano porous spaces were also observed between the fine particles. The redox process was facilitated by high porosity and large pore size of the films because of high packing density of active material. This process may lead to a large surface area and porous volume, which are important requirements in electrochemical capacitor applications.

Figure 5. The curve of Co_3O_4 thin film electrode at different scan rate in 1M KOH electrolyte.

The electrodeposited Co_3O_4 thin films were used as the electrodes for the electrochemical capacitors. The supercapacitive behaviour of the electrodes was tested by Cyclic voltammetry (CV). Figure 5 shows the cyclic voltammograms of Co_3O_4 thin film electrode with potential window-0.6 to +0.6 V/SCE at scan rate 10, 20, 30, 40, and 50 mV s^{-1}. The charge storage mechanism of Co_3O_4 for a pseudocapacitors electrode in alkaline solution is represented as a simple OH^- entering reaction. The effect of scan rate on the Co_3O_4 film electrode was examined in 1 M KOH electrolyte. From the CV curves, it is clear that the reduction and oxidation peaks are visible.

From the CV curves, it is clear that the reduction and oxidation peaks are visible. The figure reflects positive and negative scans correspond to the Charging and discharging processes, which indicates that the electrochemical capacitance of the Co_3O_4 nanocrystalline electrode mainly results from the pseudocapacitance. The specific capacitance values are increasing the scan rate and decreasing the capacitance values. These values of capacitances are comparable with the values reported in the literature. For instance, kandalkar et al. Have reported the value of capacitance as 165 Fg^{-1} for chemically deposited Co_3O_4 electrode [24]. A.D.Jagadale et al have obtained specific capacitance of 248 Fg^{-1}, 193 Fg^{-1},224 Fg^{-1} [25].In present case Co_3O_4 films showed maximum specific capacitance as 504 Fg^{-1}. Hence, from the above electrochemical parameters the copper electrode prepared via electrodeposition method showed excellent supercapacitive performance.

Figure 6. Cycling stability of Co_3O_4 electrodes.

The stability of Co_3O_4 electrodes studied in 1M KOH was evaluated at various CV cycles. Figure 6 shows the CV curves of the 100^{th} ,200^{th} ,500^{th} and 1000^{th} cycles. The

current under the curve degreased around 3% after 200 cycles, illustrating the stability of the electrodeposited Co_3O_4 electrode in energy storage applications in the 600cycles of scan rate. The specific and interfacial capacitance values slightly decreased with respect to the number of cycles because of the loss of the active material.

Figure 7. The charge discharge curve of Co_3O_4 thin film electrode at different current densities in 1M KOH electrolyte.

Galvanostatic charge discharge is used to understand the supercapacitor properties of the electrode better and the curves are shown in figure 7. The galvanostatic charge discharge curves of the Co_3O_4 electrode films in 1M KOH electrolyte. The galvanostatic charge discharge of the electrode films were carried out at 5 mA/cm^2, 10 mA/cm^2 and 15 mA/cm^2 current density respectively for electrode Co_3O_4 in a potential window 0.6 to -0.2. Three variation range can be observed in the charge discharge curves of the electrodes. First, a sudden potential drop followed by a slow potential decay. The first potential drop results from the internal resistance (I.R) and the subsequent potential decay represents the capacitive feature of the electrode. The second is the linear variation of the time dependence of the potential, which is a characteristic of double layer capacitance. The third is the slope dependence of the potential, which is due to redox reactions resulting in pseudo capacitance at the electrode/electrolyte interface. As expected, the curves are not triangular in shape and present charge and discharge plateaus, resulting from the redox reactions that occur in this potential range. This confirms the pseudocapacitance behaviour of the Co_3O_4 in agreement with the cyclic voltammetry results. To further investigate the electrochemical performance of Co_3O_4, galvanostatic charge discharge tests of composite electrode were performed at different current densities.

4. CONCLUSION

The Co_3O_4 thin films were Electrodeposited onto the copper substrates. The XRD measurements revealed that the electrodeposited Co_3O_4 thin film was nanocrystalline Co_3O_4 on highly textured Copper substrate. The FESEM micrographs confirm the surface morphology of the prepared films and it is uniformly deposited all over the substrate. It showed that the cobalt oxide thin film was covered with cubical and hexagonal shaped particle. Micro porous spaces between the particles were also observed. The EDAX spectra of the prepared films confirmed the presence of Co and O elements of the starting solution in the solid films. FT-IR spectra of the film confirm all the functional groups corresponding to the cobalt oxide. The cyclic voltammetry study revealed that the electrodeposited Co_3O_4 electrode had a specific capacitance of 504 F/g at a san rate of 10 mV/s and current density was fairly stable over 600 cycles. So these electrodes are high potential and are significant candidate for the high performance energy storage devices.

List of symbols and Abberivation

θ	-	Diffraction angle
λ	-	Wavelength
Co_3O_4	-	cobalt oxide
ECs	-	electrochemical capacitors
EDLCs	-	electrochemical double-layer capacitors,
SILAR	-	successive ionic layer adsorption and reaction
CV	-	Cyclic voltammetry
$CoCl_2$	-	cobalt chloride
XRD	-	X-ray diffraction analysis
SEM	-	scanning electron microscopy
EDAX	-	Energy dispersive x-ray analysis
FTIR	-	Fourier transform infrared spectrum
KOH	-	Potassium hydroxide
JCPDS	-	Joint committee on Powder Diffraction Standards
GCD	-	Galvanostatic charge–discharge
Co	-	Cobalt
Cu	-	Copper
C	-	Carbon

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