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Electrochemical Analysis of Cobalt Oxide Thin Film for Supercapacitor

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Abstract: *The cobalt oxide thin films were grown on steel substrate via sol-gel spin coating method followed by high temperature heat treatment at 890^0 C. The details of synthesis are reported in this paper. The structural and morphological properties of the films were studied by X-ray diffractometer (XRD) and Scanning Electron Microscopy (SEM). The XRD reveals crystalline nature of cobalt oxide and SEM images showed fully developed tetragonal grains of Co_3O_4. Electrochemical properties were examined using Cyclic Voltammetry (CV), Chronopotentiometry and Electrochemical Impedance Spectroscopy (EIS) technique. The Co_3O_4 thin film electrode showed excellent supercapacitive behaviour with increase in current along with scan rate and increase in specific capacitance with decrease in scan rate. The maximum specific capacitance $530Fg^{-1}$ was obtained at scan rate of $10mVs^{-1}$ with minimum ESR.*

Key words*: Cobalt Oxide; Spin Coating; XRD; SEM; CV*

1. INTRODUCTION

A novel technology, the supercapacitor has emerged with the potential to enable major advances in energy storage. Supercapacitors are power storage devices that are used in a diverse range of consumer and industrial applications. Supercapacitors can store large amount of charge in their porous electrodes that after discharge is converted both into energy and power. Supercapacitors are reviewed for number of electrode materials, including carbon, transition metal oxides and conducting polymers. However, among all three electrode materials, transition metal oxides are most promising materials for supercapacitor. Recently, cobalt oxides are the most studied materials due to their low cost and excellent performance in supercapacitor. To this regard, actual challenging issues concern the devising and optimization of synthetic strategies towards high purity nanomaterials with specific features, opening new frontiers not only for understanding their fundamental properties, but also for developing new generation nano devices with improved performances [1–5]. Co_3O_4, the most stable cobalt oxide with a spinel-type structure comprising both Co(II) and Co(III), is an important p-type semiconductor [4,6–11]

Cobalt oxide thin films are promising candidates for various applications such as, chemical sensors [12], solar thermal energy collectors [13] and electrochromic (EC) devices [14, 15]. In general, crystalline cobalt oxides exist in three different phases with stoichiometry of CoO, Co_2O_3 and Co_3O_4, but the crystalline Co_3O_4 phase has been largely reported for the above-mentioned applications because of its thermodynamic stability and desired electrochemical properties. The crystalline Co_3O_4 electrodes have been also investigated for the electrochromic devices, in which the material synthesis is done with different methods such as MOCVD [16], electrochemical deposition [17], Spray deposition [18] and sol–gel spin-coating [19]. In the present work simple sol-gel spin coating technique is adopted for the preparation of Co_3O_4thin film.

2. EXPERIMENTAL

2.1.Preparation of Gel

The samples of Co_3O_4 were prepared from 0.02M solution. The choice of selection of 0.02M is a compromise between quantity and quality. If we go for lower molarities, the quantity obtained will be very small, on the other hand high molarities will increase the size of the nanoparticles. For this precursor used was Cobalt acetate [(CH3COO) 2Co.4H2O]. To prepare 0.02M solution, 0.249gm of

cobalt acetate in appropriate proportions were dissolved in double distilled water and isopropyl alcohol and stirred at 50ºC on magnetic stirrer for four hours and then aged for two days. Then the sol is spin coated on cleaned steel substrate.

2.2.Deposition by spin coat method

In this method, excess amount of the solvent is placed on the substrate, which is then rotated at high speed in order to spread the fluid by centrifugal force. The film thickness can be adjusted by varying the rotation speed, the rotation time, and the concentration of the used solution. The spin coating process can be broken down into the four stages they are deposition, rotating, drying and repeating the same process for multilayers. Then films were placed into furnace. Before deposition, the steel substrates were polished with zero grade polish paper and washed with double distilled water in an ultrasonic bath for about 15 min. The different deposition conditions and parameters are as shown in table-1.

Table1. *Deposition parameters and conditions*

Sr. No	Parameters	Conditions
1	Precursor	Cobalt acetate
2	Substrate	Steel
3	Spin Time	60 sec
4	Spin Speed	3,000 RPM
5	Furnace Temperature	890^0c
6	Annealing Time	180 sec

3. RESULT AND DISCUSSION

3.1. Structural Analysis

Phase identification was carried out by XRD. A D2 PHASER diffractometer with source CuKα1 with λ =1.54184, the 2θ angle is varied from 10^0 to 90^0. Fig-1 shows the X-ray diffraction (XRD) patterns of Co_3O_4 thin film. The XRD pattern imply that as-deposited film is Co_3O_4 [JCPDS card number 78-1969, 76-1802] with cubic crystal structure. It is clear from the XRD pattern that the diffraction peaks at angle (2θ) of 44.806^0, 74.664^0 and 82.306^0 are assigned to [400], [620] and [444] planes of the Co_3O_4 crystal lattice respectively along with two diffraction peaks are observed for stainless steel (SS) substrate. The crystallite size 'G' of Cobalt oxide thin film for highest peak (400) is calculated using Scherrer's formula,

$$G = \frac{K\lambda}{\beta \cos\theta}$$

Where, 'G' is the crystallite size, constant 'K' is the shape factor = 0.94, 'λ' is the Wavelength of X-rays (1.5406 for Cukα), 'θ' is the Bragg's angle and 'β' is the full width at half maximum. The Crystallite size and lattice parameter 'a' are 226 nm and 8.111 A^o respectively.

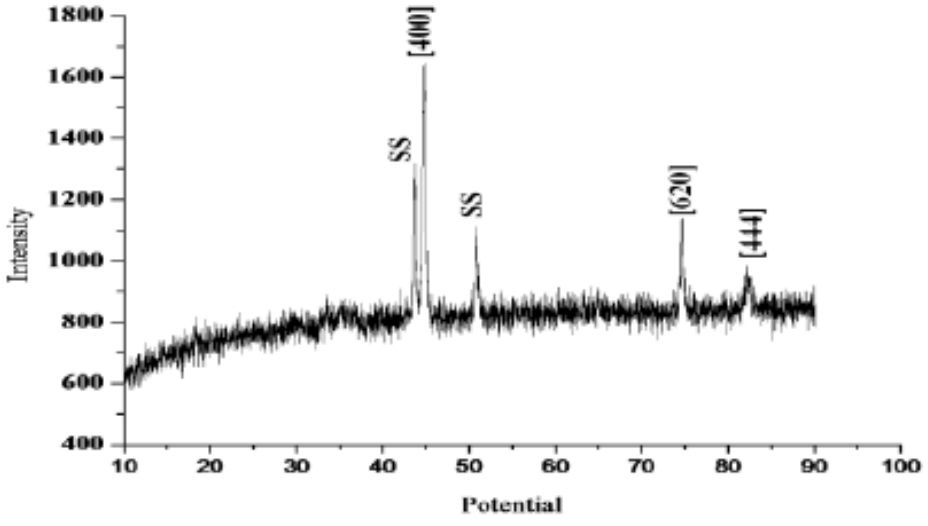

Fig1. *XRD pattern for Co_3O_4 thin film*

3.2. Surface Morphology

Surface morphological studies have been carried out by Scanning Electron Microscopy (SEM) using a JEOL JSM-6360 instrument. The SEM images revealed the formation of well adherent and porous tetragonal structure with apparent breadth in the range of 550nm. Such type of morphology provides greater surface area and porous morphology for electrode which is the prime requirement in supercapacitor [20]. Fig-2 shows SEM micrographs of Co_3O_4 at three different magnifications (x5,000, x10,000 and x20,000). At higher magnification (x20,000), it can be clearly observed certain extent of porous surface. The cobalt oxide film surface is well covered with fully developed grains.

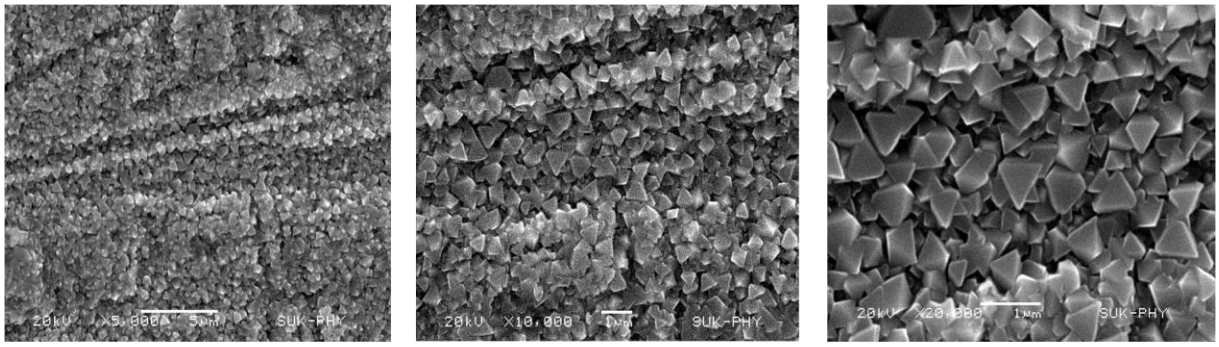

Fig2. *SEM images of Co_3O_4 thin film at different magnifications. (a) x5,000 (b) x10,000 and (c) x20,000*

3.3. Electrochemical property

Cyclic voltammetry is considered to be an ideal tool for indicating the capacitive behavior of any material. The cyclic voltammetry study is carried out with Co_3O_4 thin film as a working electrode and platinum wire as counter electrode and SCE as a reference electrode in 0.1 M KOH electrolyte. Fig - 3(a) shows the cyclic voltammograms for Co_3O_4 thin film electrode with potential window of 1V to -1.5V/SCE at various scan rates 10, 20, 40, 60, 80 and 100mV/sec.

From the CV curves, it is observed that the reduction and oxidation peaks are visible. This indicates that the electrochemical capacitance of the Co_3O_4 thin film electrode mainly results from pseudocapacitance. It is observed from the figure, the measured current densities increased and oxidation and reduction peaks are shifted in opposite direction with increase in scan rate. As current under curve slowly increased with scan rate, we conclude that the voltammetric current is directly proportional to scan rate and this is good indication of supercapacitive behavior [21]. Fig -3. (b) shows the graph of specific capacitance versus scan rate.

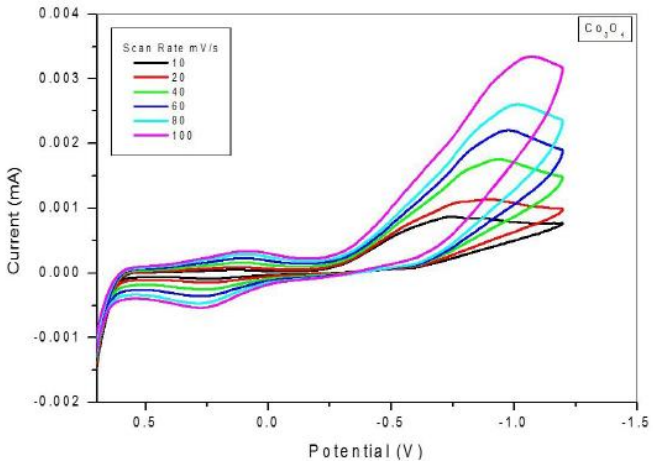

Fig3. *(a) Cyclic voltammetry of Co_3O_4 thin film at different scan rates*

Co_3O_4 thin film electrode exhibited a common trend of decreasing specific capacitance values against an increasing scan rate. It is well known that for very low scan rates, the specific capacitance values are higher because the ions have a much longer time to penetrate and reside in the electrode pores and form electric double layers, which are needed to generate higher capacitance. The specific capacitance of $530Fg^{-1}$ obtained at minimum scan rate of $10mVs^{-1}$.

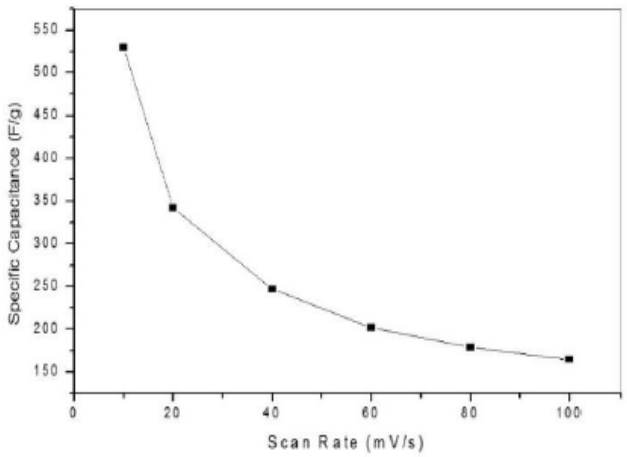

Fig3. *(b) Scan rate dependence Specific capacitance.*

3.4. Chronopotentiometry

Chronopotentiometry is the most reliable and accurate method for evaluating the super capacitance of electrodes because it gives closer estimation of close to the practical work of a capacitor. Typical charging and discharging curves of the deposited thin film measured between the voltage ranges of -0.2V to 0.5V at a current density of 2mA in 0.1M KOH electrolyte as shown in fig-4. The charging curves are mirror-symmetrical to their discharging counterparts.

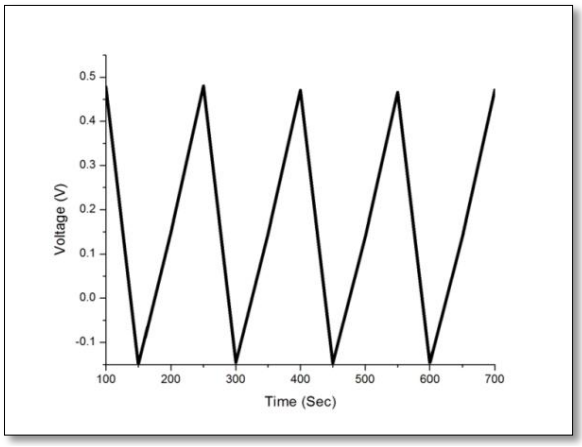

Fig4. *Charge /discharge curves of Co_3O_4 thin film.*

From this, the supercapacitive parameters such as specific energy, specific power and coulombic efficiency have been calculated using,

$$\text{Specific energy S.E} = \frac{V \times I_d \times T_d}{W} \quad (1)$$

$$\text{Specific energy S.P} = \frac{V \times I_d}{W}, \text{ and} \quad (2)$$

$$\text{Coulombic efficiency } \eta \ (\%) = \frac{T_d}{T_c} \text{ X } 100 \quad (3)$$

Where I_d and T_d are the discharge current and discharge time, respectively. The W is the mass of the film. Calculated values of the specific energy, specific power and coulombic efficiency for the Co_3O_4 film are 82.25 Wh kg^{-1}, 47 KW Kg^{-1} and 85% respectively.

3.5. Electrochemical Impedance Spectroscopy (EIS)

The EIS data expressed as Nyquist plots over the frequency range of 1Hz to 10^5Hz for Co_3O_4 thin film electrode is given in fig-5. The figure, clearly shows the small semicircle, Waburg diffusion line (straight line with a slope of approximately 45°) and capacitive line (straight lines sharply increasing at the low-frequency region). A relatively small semicircle in the high frequency region represents the dominant resistive nature of the supercapacitor system consisting of electrode/electrolyte/current-collector.

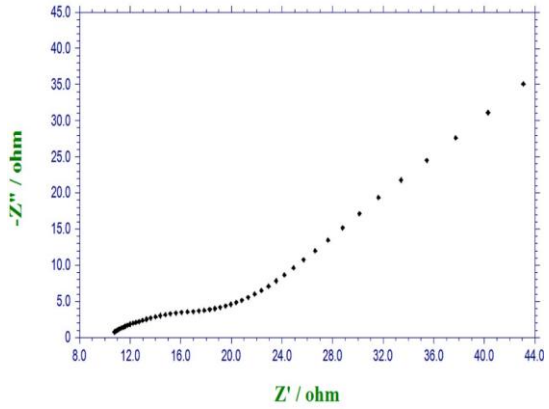

Fig5. *Nyquist plot for Co_3O_4 thin film.*

Table2. *EIS data analysis*

Parameter	Value
R_s (Ω)	10.6
R_p (Ω)	13.6
ESR (Ω)	3
f_k (Hz)	3.74
R_k (Ω)	49

The beginning of the semicircle line (left-intercept of Z'' at the Z' axis) represents the resistance (Rs) of the electrolyte in contact with the current collector and electrode. The termination of the semicircle line (right-intercept of Z'' at the Z' axis) represents the internal resistance (Rp) of the electrode. The diameter of the semicircle (Rp-Rs) is equal to the ESR value. The initiation point of capacitive line corresponds to the knee frequency (f_k), and its corresponding resistance (R_k) is given by Z'_k. The values of Rs, Rp, ESR, f_k and R_k determined from the data in figure.5 are listed in table-2.

4. CONCLUSION

We had successfully prepared Co_3O_4 thin films by sol gel spin coating deposition technique on stainless steel substrate. XRD revealed crystalline Co_3O_4 phase with cubic structure. SEM images exhibited the formation of well adherent and tetragonal structure of grains with average grain size is around 550nm. It also showed the highly porous nature of the film, which is needed for the supercapacitor application. The Co_3O_4 thin film electrode showed excellent supercapacitive behavior with minimum ESR and specific capacitance 530 Fg^{-1} at scan rate of 10mVs^{-1}.

5. ACKNOWLEDGMENT

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