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DEPARTMENT OF PHYSICS & RESEARCH CENTRE
NATIONAL SEMINAR ON
FUNCTIONAL MATERIALS AND ITS APPLICATIONS

CERTIFICATE

This is to certify that Mr./Ms./Dr./Prof. ....Dr. R. P. Jebin.......... Asst. Prof.......... affiliated to ......Muslim Arts College.......... has ~~participated/~~ presented paper in National Seminar On Functional Materials And Its Applications (NSFMA –2022), organized by the Department of Physics & Research Centre on 14th October 2022 at Muslim Arts College, Thiruvithancode, Kanyakumari District.

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Synthesis and Characterization of Nickel Doped Cobalt Oxide Thin Films for Electrochemical Applications

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Abstract

Present work has been focused on the synthesis and growth mechanisms of Nickel doped Co_3O_4 thin films were deposited on glass and fluorine-doped tin oxide (FTO) substrates by simple spray pyrolysis technique by varying the concentrations of Nickel at 300°C. The synthesized samples were characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM) and Cyclic Voltammetry techniques. XRD patterns shows cubic structured Nickel doped Co_3O_4 thin films and the crystallinity varies with concentrations and film thickness. Lattice constant was extracted from the constructed Nelson Riley plots and matched well with standard values. SEM images revealed the presence of spherical shaped particles with porous structure on the film surface. Cyclic voltammetry studies suggested that large integral CV area and the prepared thin films can be used for electrochemical applications.

Keywords: Nickel doped Cobalt oxide thin films, Spray pyrolysis, XRD, SEM, Electrochemical Application.

1 Introduction

Cobalt oxide is a one of the transition metal oxides which made a promising one for different fields such as optical smart windows, display devices, pigments for glass and ceramics, gas sensors, solid state sensors, magnetic material catalyst, anode materials for rechargeable Li-ion batteries, electrochemical systems, and high-temperature solar selective absorbers [1]. There are three stoichiometry forms of the Cobalt oxide are available. They are Cobalt(I)oxide (CoO), Cobalt(II)oxide (Co_2O_3) and Cobalt(III)oxide (Co_3O_4). Among these various oxidation state Co_3O_4 is most stable compound. Co_3O_4 is a largely reported, metal oxide compound in scientific filed and energy storage due to its electrochemical stability [2], good thermodynamic stability and preferred electrochemical properties. Co_3O_4 belongs to a spinel crystal structure [3] based on a cubic closed packed structure of oxide ions. The performance of Co_3O_4 depends upon the microstructure such as grain size, porosity, and crystallinity. Various routes of synthesis of Co_3O_4 thin films have been consider as Sol-gel, suppering, electrode deposition, electron-beam evaporation, spray pyrolysis, etc. Co_3O_4 is belongs to a p-type semiconductor. Hence the selection of dopant is a vital part in semiconductor doping. In this present research work Nickel is choose as the dopant. Nickel provide high specific capacity while maintain excellent cycling stability[4]. Herein, the $Ni_xCo_{3-x}O_4$ was prepared via an easy and effective spray pyrolysis method on fluorine-doped tin oxide (FTO) substrate for the electrochemical measurement. The results suggest that the electrochemical performance, increases the charge transfer abilities at the interface of the electrode and the electrolyte.

2. Experimental

2.1. Preparation of the FTO glass and Ni doped Co_3O_4

The FTO and glass substrates were gently cleaned with acetone and dried in air. Then the glass substrates were immersed in chromic acid and cleaned thoroughly using soap solution and finally sonicated in ultrasonic bath with acetone and distilled water to remove the contaminants over the surface of the substrates. Cobalt nitrate hexa hydrate ($Co(NO_3)_2.6H_2O$) was used as a starting precursor, dissolved in 1:1 water-ethanol mixture. Nickel (II) nitrate hexahydrate $Ni(NO_3)_2.6H_2O$ was added to the precursor solution and stirred continuously at room temperature for 30 min using a magnetic stirrer to get homogeneous solution. Obtained solution was then sprayed on to preheated substrate. For comparison various concentrations of Nickel (x=0.025, 0.05, 0.075, 0.1) which was deposited to substrate and sintered at 300°C.

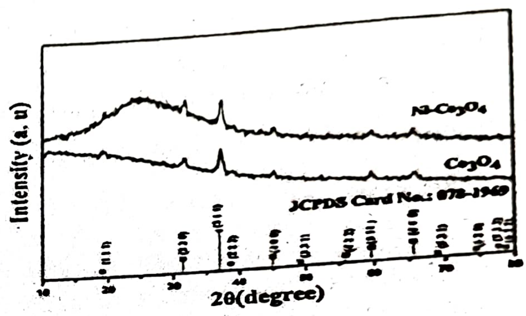
2.2. Characterization

The crystalline nature of the prepared of Co_3O_4 and Ni doped Co_3O_4 thin films are characterized by using PANanalyticalXpertPro X-ray diffractometer. Surface morphology of the prepared thin films were recorded by using SEM for x10,00 magnification. The electrochemical performance of the FTO coated Ni doped Co_3O_4 film electrodes was investigated in an electrochemical cell containing 0.5 M of NaOH electrolyte solution using a programmable electrochemical workstation (CH Instrument, model CHI604D)

3. Result and discussion

3.1. Structural studies

Fig.1(a &b) XRD spectrum and NR plot of Co_3O_4thin film and Ni doped Co_3O_4thin films



The crystalline structures of as synthesized Co_3O_4 and Nickel doped Co_3O_4 thin films at various concentration (X=0.025, 0.05, 0.075, 0.1) were studied using X-ray diffraction and the obtained XRD pattern are depicted in fig.1. All the thin film depositions are carried out at the temperature of 300°C. In all films multiple diffraction peaks are identified. The strong identified peaks such as (111), (220), (311), (222), (400), (422), (511), (440), (531), (620), (533) and (622).Among these peak (311) is the preferential one. It was found that the undoped and nickel doped Co_3O_4 conforms the formation of spinel cubic structure (fd^{3}m space group) which is in good agreement to the JCPDS card no: 078-1969. There was a slight shifting of diffraction peak observed by the addition of Nickel for different concentration. The lattice parameters are calculated by from the peak positions using the formula of cubic system [5]

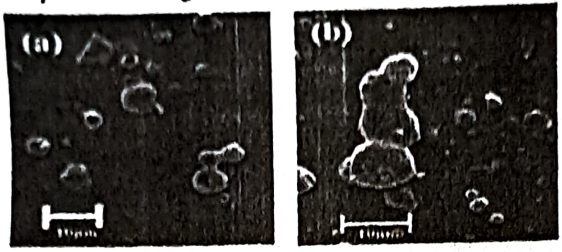
$$d = \frac{a}{\sqrt{h^2+k^2+l^2}} \quad (1)$$

where 'd' is the interplanar spacing, 'h', 'k' and 'l' refers to the Miller indices. By analysis the values, it is clearly shows that at the 0.050 concentration of Nickel doped Co_3O_4 successfully made a good agreement with the standard structural parameters such as lattice parameter, unit cell volume, and density. This implies that Nickel atoms are completely accompanied in Co_3O_4 lattice space. The average crystalline sizes of the synthesised films are calculated using the full width at half maximum (FWHM) of (311) peak from the Debye-Scherrer formula [6] knowing as the width increases crystalline size decreases. **3.2. SEM analysis**

Fig.2 (a and b) presents the SEM images of the optimized sample at the concentration of 0.050 of nickel in Co_3O_4 at the temperature of 300°C. There are microspheres are assembled in all the SEM images of synthesized pure Co_3O_4 and nickel doped Co_3O_4. Among these at the concentration of 0.050 of nickel made the surface as more porous one. This is a necessary structural aspect of electrochemical application. Hence the optimized sample has the most uniform structure and size, which helpful to enhance the surface area of Co_3O_4.

Cyclic voltametric studies

Cyclic voltammograms (CV) recorded for a Co_3O_4 and Ni doped Co_3O_4 thin films with linear potential sweep between -0.1 V and +1.0V at 100 mV/s scan rates are represented in fig. . Two distinct redox peaks could be observed at first anodic potential (0.02V) and first cathodic potential (-0.59V) are corresponds to the change between $Co(OH)_2$ (pale yellow) and Co_3O_4 (dark grey)[7]. Another set of peaks such as second anodic potential (0.38V) and second cathodic potential (0.45V) corresponds to the conversion between Co_3O_4 and CoOOH (dark brown) [8], represented by the reactions for the three electrodes, which are assigned to Co^{3+}/Co^{2+} and Co^{4+}/Co^{3+} redox processes[8], respectively. The doped films showed significantly larger current density than pure Co_3O_4 film thin films, which indicates that the presence of a greater number of active sites present on its surface.



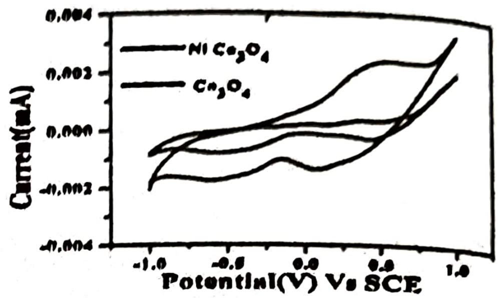


Fig.2 (a&b) SEM images of Pure and Ni doped Co_3O_4thin films(Magnificationx1000)

Fig.3.CV curve of Co3O4 and Ni- doped Co_3O_4

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