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Electrochemical Supercapacitive Performance of Sprayed Co_3O_4 Electrodes

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ABSTRACT
Nanocrystalline cobalt oxide (Co_3O_4) thin film electrodes were fabricated by spray pyrolysis method on conducting fluorine doped tin oxide (FTO) substrates using ammonia complexed with cobalt chloride ($CoCl_2.6H_2O$) solution. The structural and morphological properties of Co_3O_4electrodes were studied using X-ray diffraction (XRD) and scanning electron microscopy (SEM).The surface morphology study showed the film formation of porous surface with clusters. The electrochemical supercapacitive properties ofCo_3O_4 electrodes were evaluated using cyclic voltammetry and galvanostatic charge-discharge method. The Co_3O_4electrodes showed maximum specific capacitance of 168 F/g in 1 M aqueous KOH electrolyte at the scan rate of 20 mV/s. The maximum specific energy and specific power of the cell are 2.2Wh/kg and 0.23 kW/kg, respectively.
Keywords: Co_3O_4; thin films; spray pyrolysis; supercapacitor.

I. INTRODUCTION

In the world of global warming and due to limited source of fossil fuels, gradually researchers driving toward clean energy storage alternatives. Due to continuous growth of population and rising living standards increase the world demand for energy which leads to research and development in energy sectors and have attracted much attention for seeking alternative energy sources. Electric energy storage devices with high energy storage capacity and fast charge-discharge ability are very important and desirable today as they can find potential applications in plug-in electric vehicles, back-up power sources, energy storage for wind and solar energy and so forth [1, 2]. Supercapacitorsor electrochemical capacitors have put considerable attention over the past decades because of their higher power density and longer cycle life than secondary batteries and their higher energy density compared to conventional electrical double layer capacitors. The charge storage mechanism in supercapacitor is based on either non-Faradaic electrochemical double layer capacitor (EDLCs) or fast, reversible Faradaic redox reactions (pseudocapacitor) [3]. EDLCs includes carbonaceous materials, such as activated carbon, carbide derived carbon, grapheme and carbon nanotubes [4-7] with a large surface area on which charge can reside but unfortunately due to low supercapacitor performance restricts its use as compared with pseudocapacitor. In pseudocapacitors the charge storage occurs through faradic reactions in which transition metal oxides and conducting polymers are used as electrode materials [8-10].Due to the fast redox reactions in transition metal oxide exhibits high-rate capacity, high rate capability, and cycling stability. RuO_2 is one of the prominent electro-active materials for pseudocapacitor but limits due its expensive nature, rare resources, and environmental toxicity. Therefore, recently great efforts have been devoted to searching for inexpensive and environmentally friendly transition metal oxides with good capacitive characteristics, such as CuO [11] ,NiO [12, 13], RuO_2 [14], MnO_2 [15-17], Co_3O_4 [18, 19], have been widely investigated as promising electrode materials for supercapacitors.

In the present investigation, nanocrystalline Co_3O_4 thin films have been obtained using chemical spray deposition technique from an aqueous medium. Their structural, surface morphological, optical characterizations and electrochemical supercapacitive properties like specific capacitance, specific energy, and specific power have been studied.

II. EXPERIMENTAL

Co_3O_4 films were deposited by spray pyrolysis method using an aqueous 0.05 M cobalt chloride ($CoCl_2$: $6H_2O$) solution. The thickness of the films was varied by varying the quantity of spray solution from 20 to 60 cc. The solution was sprayed through a glass nozzle onto the ultrasonically cleaned glass substrates kept at temperature of 623 K. The spray rate was maintained using air as a carrier gas and the spray rate of 4 cc/min was optimized. The nozzle to substrate distance was 28 cm. The temperature was

controlled using electronic temperature controller. Hazardous fumes that evolved during the thermal decomposition of initial ingredient were expelled out. In the spray deposition method, a precursor solution is pulverized by means of a natural gas so that it arrives at the substrate in the form of very fine droplets. The electrochemical measurements for supercapacitor were carried out in a three electrode electrochemical cell, in which the Co_3O_4thin film electrode was used as the working electrode, platinum as the counter, and saturated calomel electrode (SCE) as the reference electrode. The cyclic voltammetry (CV) experiments were performed using potentiostat/galvanostat (EG & G PAR 263-A) to determine the specific capacitance of the Co_3O_4film electrode in 0.025 - 2 MKOH electrolyte solution. The capacitance 'C' of film was calculated from the relations

$$C = I /(dV / dt) \qquad (1)$$

Where, '*I*' is the average current in amperes and (*dV/dt*) is the scan rate in $mV.s^{-1}$. Similarly the interfacial capacitance (C_i) is obtained by dividing the capacitance by respective electrode area in the electrolyte.

$$C_i = C / A \qquad (2)$$

Where '*A*' is the area (1 cm^2 in this study) of electrode dipped in the electrolyte. The specific capacitance (C_s) of the electrode is obtained by dividing the capacitance by the weight of Co_3O_4electrode dipped in the electrolyte.

$$C_s = C / W \qquad (3)$$

Where '*W*' is the weight of the Co_3O_4electrode dipped in the electrolyte.

III. RESULTS AND DISCUSSION

3.1 Film Formation

Cobalt chloride solution was sprayed onto preheated FTO substrate which undergoes pyrolytic decomposition thereby resulting in the formation of Co_3O_4 thin films according to the following reaction;

$$3CoCl_2;6H_2O \xrightarrow{623\ K} Co_3O_4 \downarrow +3Cl_2 \uparrow +4H_2 \uparrow +2H_2O \uparrow$$

The role of water is probably to control the rate of supply of Co^{2+} ions to the substrate [20]. Similar film formation mechanism was reported by Patil et al [21]. The films deposited using spray pyrolysis at 573-623 K having Co_3O_4 phase [20, 22]. The as-deposited films were blackish in color and found to be uniform, pin hole free and strongly adherent to the substrates. The formed Co_3O_4thin films were used for the further characterization.

3.2 Thickness Measurement

The increase in film thickness with quantity of spraying solution is obvious. However, it is not increasing in proportion to the volume of sprayed solution. This may be due to change in the deposition efficiency with the solution volume. Thickness of Co_3O_4film was measured by the weight difference method. The graph of thickness of Co_3O_4film with quantity of the cobalt chloride solution for 0.05 M concentrations of the solution is shown in Fig.1 and observed that the film thickness is increased with the quantity of the spray solution upto 40 cc of solution and then decreased afterwards. This behavior can be attributed to the formation of powdery film at higher solution quantity, due to the decomposition of the droplets before reaching to the substrate. The terminal thickness obtained was 0.450 mg/cm^2 on the FTO substrate and used as electrode in the supercapacitor.

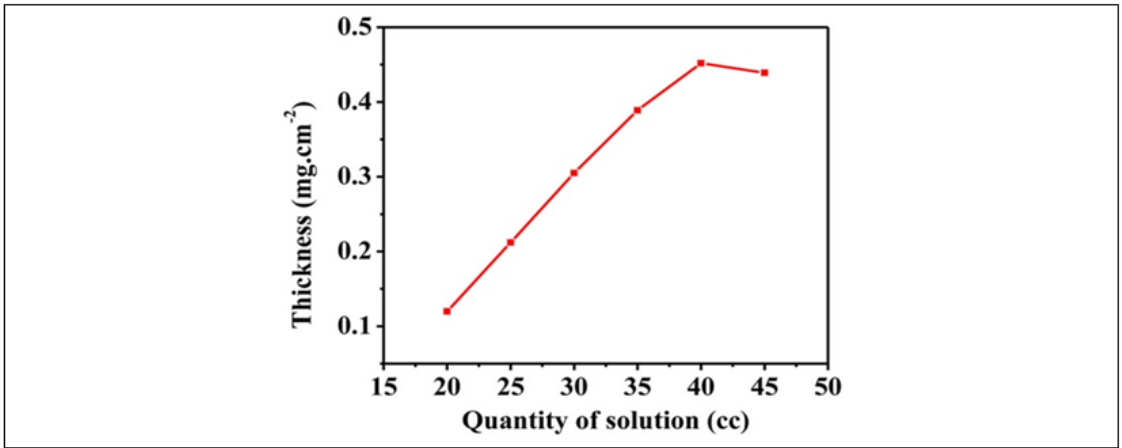

Fig.1 Variation ofCo_3O_4film thickness with quantity of the solution.

3.3 X-ray Diffraction Study

Structural analysis of Co_3O_4 films was carried out on a Philips PW-1710 diffractometer by varying diffraction angle from 10º to 80°. Fig. 2shows a typical XRD pattern of as-deposited Co_3O_4thin films onto FTO substrate. The XRD pattern shows the formation of nanocrystalline$Co_3O_4$with cubic structure with peak reflection along (111) plane (JCPDS card no: 41-1445). No other additional peak corresponding to other phases of cobalt oxide is seen to be emerged.

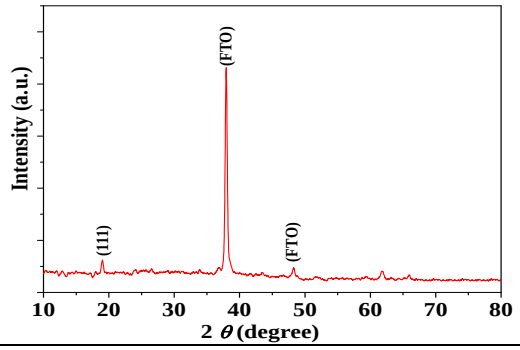

Fig. 2 X-ray diffraction pattern of cobalt oxide thin film onto FTO substrate.

3.4 SEM and TEM Study

Fig. 3 (a) shows the low magnified SEM image of Co_3O_4thin film onto FTO substrate. From the micrographs, one can see that Co_3O_4 is well covered to substrate with relatively porous surface with clusters. Inset of Fig. 3 (a) shows that water contact angle measurement images of Co_3O_4 thin film and is observed 70 °. It reveals the hydrophilic behavior of Co_3O_4 films due to porous nature of Co_3O_4 which suggest that the Co_3O_4 has potential application as an electrode material for supercapacitors.Fig.3 (b) and (c) shows TEM image and corresponding selected area electron diffraction (SAED) pattern of sprayed Co_3O_4 film. It shows that the film is composed of nanocrystals of average size ~ 20 nm which confirms the nanocrystalline nature of spray deposited Co_3O_4films. The SAED pattern is shown in Fig. 3 (c) consists of blurred bright electron diffraction rings for Co_3O_4 film showed film is nanocrystalline. This fact is also supported by the XRD results, where the peak intensities of Co_3O_4film were small.

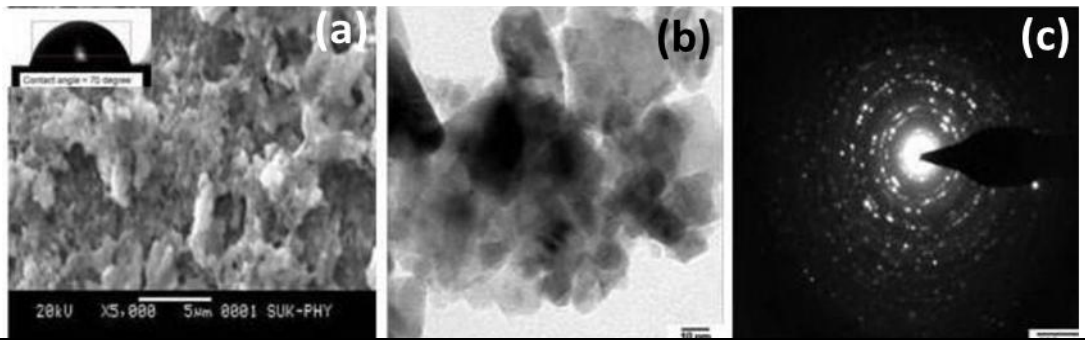

Fig. 3(a) SEM, (b) TEM and (c) SEAD pattern of Co_3O_4 film. Inset of (a) shows water contact measurement over Co_3O_4 thin film surface.

3.5 Optical Absorption

The optical absorption of Co_3O_4 film in the wavelength range 300-900 nm has been investigated. Fig. 4(a) shows the variation of absorbance (αt) of Co_3O_4 with wavelength (λ) and it is seen that the absorbance decreases upto wavelength 630 nm and then increases upto 750 nm and further it decreases, depicting two regions of optical transitions. The theory of optical absorption gives the relationship between the absorption coefficient (α) and the photon energy (hν) for direct allowed transition. The recorded data was further used to estimate the band gap energy of the cobalt oxide film. Fig. 4 (b) shows the plot of $(\alpha h\nu)^2$ vs. (hν) for Co_3O_4 film. The plot consists of two straight-line regions, designated as region A (higher energy side) and region B (lower energy side). The estimated band gap energy for as-deposited Co_3O_4 film was found to be 1.50 and 1.95 eV for region A and B, respectively similar to

reported literature of existence of two band gap values for Co_3O_4[23].

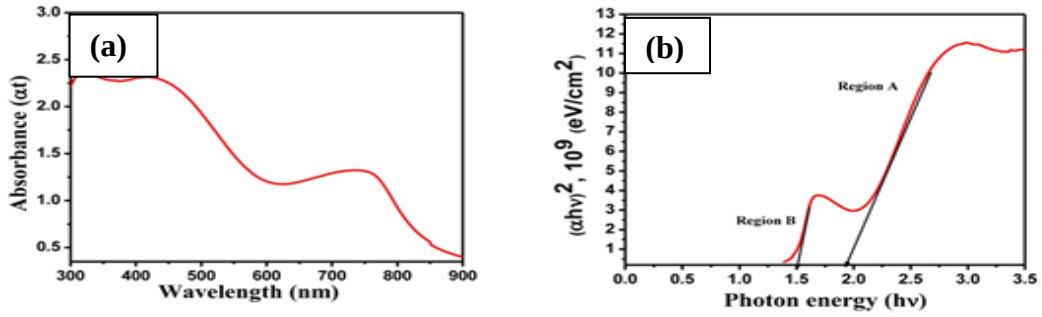

Fig. 4 (a) Variation of absorbance (αt) with wavelength (λ) and (b) variation of $(\alpha h\nu)^2$ against (hν) for Co_3O_4 film.

3.7 Supercapacitor Performance of Spray Deposited Co_3O_4 Electrodes

Effect of KOH Electrolyte Concentration

The effect of concentration of KOH (0.25–2 M) electrolyte was studied by keeping scan rate constant. Fig.5 shows the CV curves of Co_3O_4electrode at the scan rate 20 mV/s within the potential range of 350 to 550 mV v s. SCE in KOH electrolyte of different concentrations. It is seen from the figure that the current under curve increased as the concentration of KOH electrolyte increased from 0.25 to 1.0 M. The voltammograms were more distorted at low electrolyte concentration. At the 1.0 M concentration of KOH the CV curve showed maximum current under curve. After that current density decreases with increasing concentration of electrolyte this is due to free electrolyte starvation since, for the amount of electrolyte present in that solution; almost all its ions become adsorbed at the high area interface enhancing the internal resistance effect towards full state of charge and due to a combination of the usual distributed resistance effect.

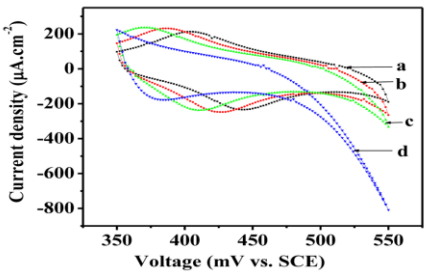

Fig.5 CV curves of Co_3O_4electrode at different concentrations of KOH electrolyte a) 0.25, b) 0.50, c) 1.0 and d) 2.0 M at scanning rate of 20 mV/s

Effect of Film Thickness

The effect of thickness of the Co_3O_4electrode on the capacitive behavior was studied in 1.0 M KOH electrolyte at the scan rate of 20 mV/s. Fig. 6shows CV curves of Co_3O_4 electrode of different thicknesses from 0.21 to 0.45 mg/cm^2 which indicate that the current increased with thickness. The interfacial and specific capacitance is increased from 0.0042 to 0.0216 F/cm^2 and 60 to 168 F/g, respectively.

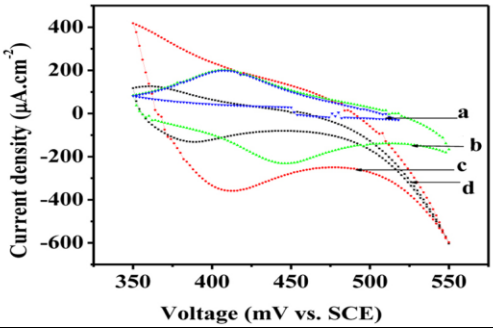

Fig.6 CV curves of Co_3O_4electrodes for different thicknesses (a) 0.21, (b) 0.305, (c) 0.39and (d) 0.45 mg/cm^2 at scanning rate 20 mV/s.

Effect of Scan Rate

The effect of the scan rate on electrochemical capacitor formed by spray deposited $Co_3O_4$was studied at a film thickness 0.45mg/cm^2 and concentration 1.0 M of KOH electrolyte in voltage range of 350 to 550 mV v s. SCE. Fig. 7shows the CV curves with different scan rates. It was found that the current under curve is slowly increased with scan rate. The specific and interfacial capacitance values are decreased from 208 to 40 F/g and 0.0343 to 0.0031 F/cm^2, respectively, as the scan rate was increased from 10 to 100 mV/s.

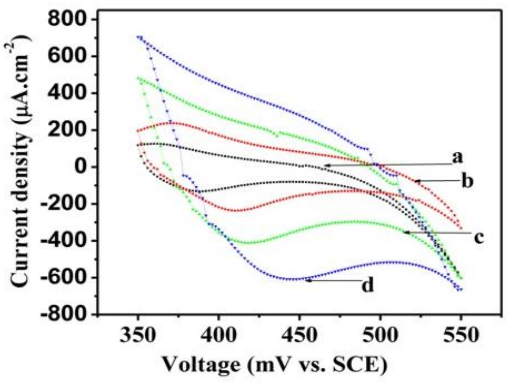

Fig.7CV curves of Co_3O_4electrode at different scanning rates a) 10, b) 20, c) 50 and d) 100 mV/s

Stability of Electrode

The cycle life (stability) of cobalt oxide electrode in 1.0 M KOH was tested by CV. Fig. 8shows the CV curves for 5th and 500th number cycle. The current under curve is decreased by 3% up to 500 cycles. The specific and interfacial capacitance values are decreased with the number of cycles due to the loss of active material.

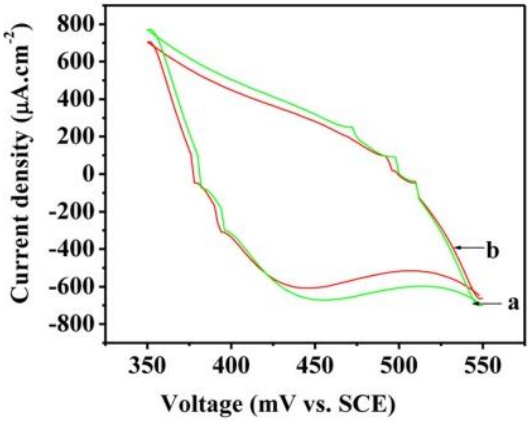

Fig.8(a) CV curves of 5 thand (b) 500th cycles. The scanning rate was 20 mV/s.

Charge-discharge

The galvanometric charge–discharge behavior of Co_3O_4 electrode was studied by at a constant current of 1 mA/cm^2 between 0 and 0.24 V and presented in Fig. 9. From figure, the symmetric behavior of voltage-time curve was seen. From charge-discharge curve specific energy and specific power was obtained 2.2 Wh/kg and 0.23 kW/kg, respectively.

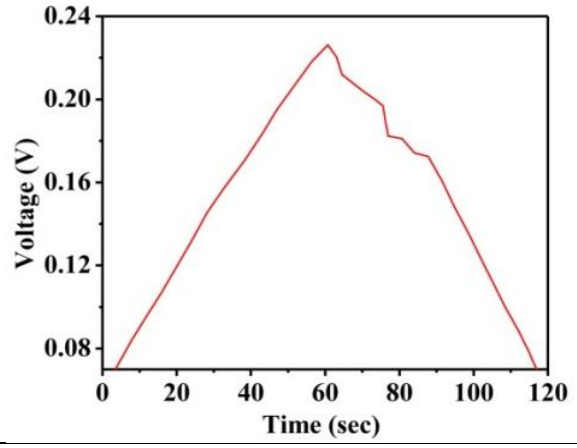

Fig. 9 The charge and discharge curves of cobalt oxide electrode in 1.0 M KOH electrolyte. The charging current was 1 mA/cm^2.

IV. CONCLUSIONS

The nanocrystallineCo_3O_4thin films were deposited onto FTO substrate at 623 K, using spray pyrolysis method from an aqueous bath of $CoCl_2$. The XRD studies showed the formation of nanocrystalline Co_3O_4 with cubic phase. The surface morphological study from SEM revealed the total coverage of substrates with nano-sized grains with particle size was approximately ~20 nm analyzed by TEM. The optical studies showed two band gap of 1.50 and 1.95 eV. The Co_3O_4 deposited films showed hydrophilic nature. The electrochemical study revealed that the Co_3O_4 electrode showed specific capacitance of 168 F/g. The specific energy (E) and specific power (P) was 2.2Wh/kg and 0.23 kW/kg, respectively.

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