



## NON AQUEOUS MEDIA DEPENDENT SCIENTIFIC SUPERCAPACITIVE MEASUREMENTS OF $\text{Co}_3\text{O}_4$ THIN FILM ELECTRODES PREPARED BY SPRAY PYROLYSIS

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### ABSTRACT

Present work reports scientific approach of spray pyrolytic decomposition of  $\text{Co}_3\text{O}_4$  thin film electrodes at 573 K on stainless steel substrates using different non aqueous medias. Prepared electrodes were characterized structurally, morphologically and electrochemically by means of XRD, SEM and cyclic voltammetry. Structural elucidation confirms the face centered cubic crystal structure with nano crystalline nature. Surface morphological study shows the continuous film growth, porous nature with little cracks observed due to stress effect in the film at higher concentration and temperature. Electrochemical study reveals the pseudocapacitive as well as double layer behaviour for methanol used sample, with optimum 193.10 F/g specific capacitance at the scan rate 1 mV/s in 1 M KOH electrolyte. Specific energy, specific power and columbic efficiency were calculated using chronopotentiometry. Electrochemical impedance spectroscopy measurements were carried out in the frequency range 1 mHz to 1 MHz. Randles equivalent circuit with cell parameters is reported.

**KEYWORDS:**  $\text{Co}_3\text{O}_4$ , Spray pyrolysis, Cyclic Voltammetry, Supercapacitor, Impedance.

### INTRODUCTION

Novel renewable natural energy sources and energy/power storage materials are the two major challenges in electrochemical technology. In this situation, supercapacitor shows a potential applicability in energy and power storage devices like laptop, simple consumer electronics to airbus, planes, military, missile *etc.* Supercapacitor has two types based on the Helmholtz's layer i.e. electric double layer and pseudocapacitor. In the preparations of supercapacitor electrodes different materials are used such as, conducting polymers, activated carbon and transition metal oxides, nano composites *etc.* and these were prepared by using different methods [1-8]. Among the array of electrode materials for supercapacitor application transition metal oxide (TMOs) are widely studied due to variable oxidation states of metal ions which facilitate redox transition and higher charge storage within the potential range of water decomposition [9]. Cobalt oxide is one of the promising candidates because of its low cost, environmentally friendly nature, easy availability, different oxidation states, redox reversibility, mixed capacitive behaviour, large potentials window, good electrical conductivity and different morphologies *etc.* [10]. Cobalt oxide thin films are used in different applications such as supercapacitors, solar cells, gas sensors *etc.* Cobalt oxides have been prepared via aqueous route by different methods [11-15]. Cobalt oxide thin films prepared using cobalt nitrate as a ingredient by centrifugal method in methanolic solution shows good uniformity and adherency. Materials shows nanocrystalline with highly ordered mesoporous frameworks, hollow spheres shaped and the dramatic tetragonal dipyrmaid structure [16]. As

compare to propanol and ethanol, methanol is more volatile and having low boiling point [16]. As the literature is concerned, very little work is observed related to cobalt oxide electrode preparation via different non aqueous media by spray pyrolysis and study of their supercapacitive properties. Therefore in the present investigation, cobalt oxide ( $\text{Co}_3\text{O}_4$ ) thin films have been prepared by spray pyrolysis using different non aqueous medias like methanol, propanol and ethanol *etc.* There supercapacitive properties were examined in depth. The prepared electrode itself shows good morphology and low electrochemical series resistance (ESR) that facilitates the use of it in supercapacitor.

### EXPERIMENTAL SECTION

#### Preparations of $\text{Co}_3\text{O}_4$

In the preparation of  $\text{Co}_3\text{O}_4$  thin films, first of all stainless steel (SS) substrates (no-304) on which deposition has to carry were well cleaned using the procedure explained in earlier report [17]. Initially 40 ml, of 0.1 M cobalt nitrate (s. d. fine chem. Mumbai) solution was prepared in methanol, ethanol and propanol. These prepared solutions were sprayed using air as a carrier gas on to the well cleaned stainless steel substrates kept on the hot plate of the spray pyrolysis unit at the constant temperature 573 K. Throughout the process spray rate was maintained constant as ~ 8 ml/min. Prepared samples were nomenclatured as M, E, P respectively, were characterized using cyclic voltammetry. Cyclic voltammetry (CV) measurement shows good capacitive results for the films prepared using methanolic solution. Then by using different concentrations (like 0.05 M, 0.1 M, 0.6 M, and

1M etc) of the methanolic solution of Co<sub>3</sub>O<sub>4</sub>, numbers of electrodes were prepared and are designated as M<sub>1</sub>, M<sub>2</sub>, M<sub>3</sub> and M<sub>4</sub> respectively. To study the effect of thickness on the supercapacitive behaviour of Co<sub>3</sub>O<sub>4</sub>, numbers of electrodes were prepared by varying the volume of spraying solution from 20, 40 and 60 ml. These samples were designated as V<sub>1</sub>, V<sub>2</sub> and V<sub>3</sub>. All prepared electrodes were characterized by CV analysis. Optimized electrodes were used for further characterizations.

#### Characterization techniques

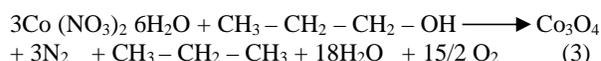
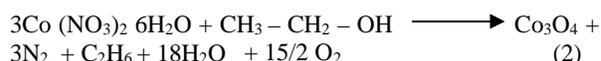
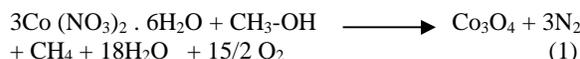
Structural analysis of the prepared samples was made using X-ray diffractometer (Rigaku D/max 2550 Vb<sup>+</sup> 18 kW with Cu k<sub>α</sub>) in the range of diffraction angle (2θ) from 20° to 85°. A scanning electron microscope (SEM) JEOL JSM-6360 was used to perform the surface morphological analysis. Weight of the deposited material was measured by weight difference method using 1x10<sup>-5</sup> high accuracy microbalance (Contact C-84). Computer controlled potentiostat (H CH 600D spl. electrochemical analyzer/workstation) with standard three electrode cell was used for electrochemical characterization. In the supercapacitive study, the cyclic voltammetry of the samples (size 1 cm x 1 cm) was carried out within the potential window - 0.30 to 0.40 V in 1 M KOH electrolyte using platinum wire as a counter electrode and saturated Ag/AgCl as a reference electrode. CV curves were used to calculate the SC using the relations (1) and (2). The charge-discharge behavior of the prepared samples was studied using galvanostatic charge-discharge method for different current densities. Multi frequency impedance

measurements were carried out in the frequency range 1 mHz to 1 MHz using AC signal of - 0.102 V. Electrochemical Impedance spectroscopy (EIS) data was fitted with standard data to search an Randle's equivalent circuit using ZsimpWin software.

## RESULTS & DISCUSSION

### Film formation Kinetics

During spray deposition, thermal decomposition of the fine droplets of 0.1 M non aqueous cobalt nitrate solution occur on to the surface of SS substrate, resulting into the formation of well adherent and uniform Co<sub>3</sub>O<sub>4</sub> thin films.



Obtained thin film electrodes were found highly stable against environmental conditions.

### Structural analysis and morphological elucidations

The XRD spectrums of the deposited samples were carried out to know the crystal structure, orientation of the planes and crystallite size of the prepared electrodes. Fig.1a) shows XRD spectras of the samples M, E and P.

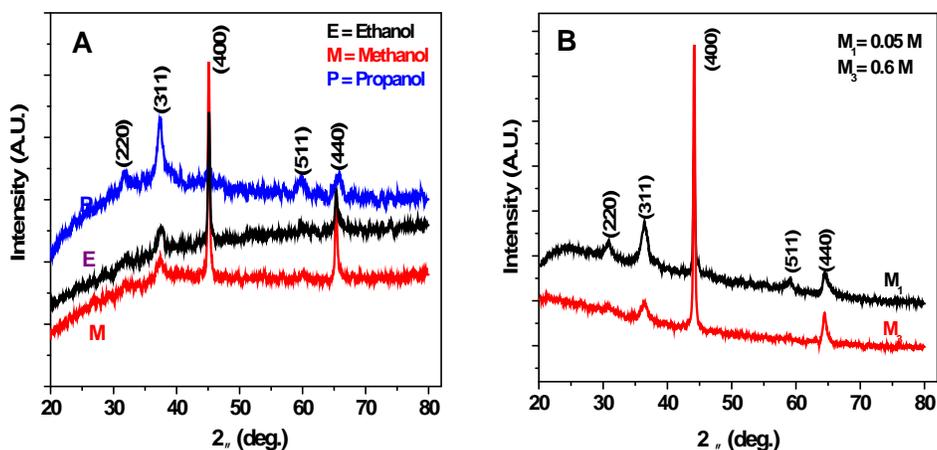


FIGURE 1: A) XRD of 0.1 M cobalt nitrate prepared using different Medias  
B) XRD's of typical samples M<sub>1</sub> and M<sub>3</sub>.

In the XRD spectra it is observed that electrode deposited using methanol (M) shows very good reflections along (2 2 0), (3 1 1), (4 0 0), (5 1 1) and (4 4 0) directions as compare to electrode deposited using ethanol (E) and propanol (P). Fig.1 b) shows XRD patterns of the samples M<sub>1</sub>, M<sub>2</sub>, M<sub>3</sub> and M<sub>4</sub>. The observed 'd' values matches properly with the standard 'd' values taken from JCPDS data card no. (78-1970) of Co<sub>3</sub>O<sub>4</sub>. All deposited samples are of nanocrystalline nature having face centered cubic crystal structure (FCC). Mostly all deposited samples shows dominant orientation along (4 0 0) plane. Electrode M<sub>3</sub> shows more crystalline nature as compared to M<sub>1</sub> and

M<sub>2</sub>. Using Scherer's formula (4) crystallite size 'D' of the deposit was calculated [18].

$$D = \frac{0.9\lambda}{S \cos \theta} \quad (4)$$

Where, 0.9 is the Scherrer's constant, λ is the wavelength of X-ray, S is the full-width at half-maximum and θ is the diffraction angle. The observed average crystallite size for (4 0 0) plane is around 35 nm.

Morphological analysis of the prepared electrodes was made using SEM. Fig.2 shows SEM image of M<sub>3</sub> electrode. It clearly shows continuous soft growth of the

particles with small hair like cracks. The observed cracks may be due to effect of stress occurring during sample

formation<sup>[19]</sup>.

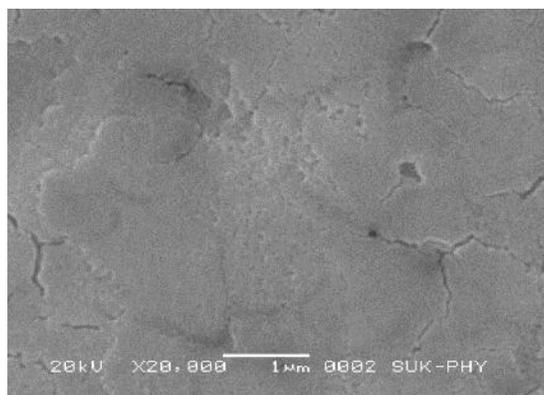


FIGURE 2. SEM image of M<sub>3</sub>.

### Supercapacitive measurements

Supercapacitive behaviour of as prepared electrodes was carried out using cyclic voltammetry. Generally it is used

to measure the electrode kinetics of the anodic and cathodic reactions. Fig. 3A) shows the CVs of E, P and M electrodes.

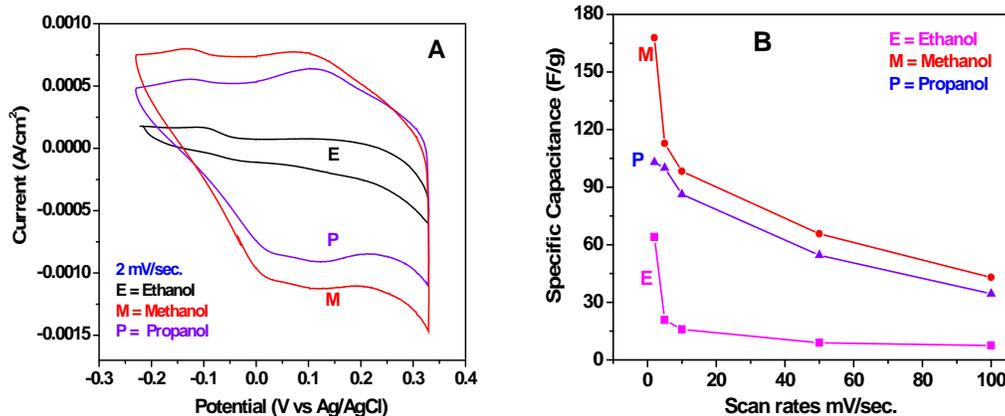


FIGURE 3 A) CVs of Co<sub>3</sub>O<sub>4</sub> prepared using different medias at the scan rate 2 mV/s.

B) Variation of specific capacitance (F/g) with scan rate (mV/s) for different samples

All prepared electrodes were scanned at 2 mV/s in 1 M KOH electrolyte within the potential window – 0.30 to 0.40 V Vs Ag/AgCl. All CVs shows nearly rectangular double layer and pseudocapacitive behaviour. The shape of CV curves nearly remains same but area under curve shows much change. Electrode prepared using ethanolic media shows small area under curve and current. Electrode prepared using propanolic media shows moderate area under curve and current. Whereas electrode prepared using propanolic media shows gigantic area under curve and gives good value of SC. The highest value of SC for M electrode is 167.07 F/g at 2 mV/s in 1 M KOH electrolyte. This highest value of SC may be attributed to volatile nature of methanol assisting proper thermal decomposition of the ingredient and uniformity of the film<sup>[16]</sup>. The specific capacitance (SC) associated with the working electrode was calculated using the following relations<sup>[20]</sup>.

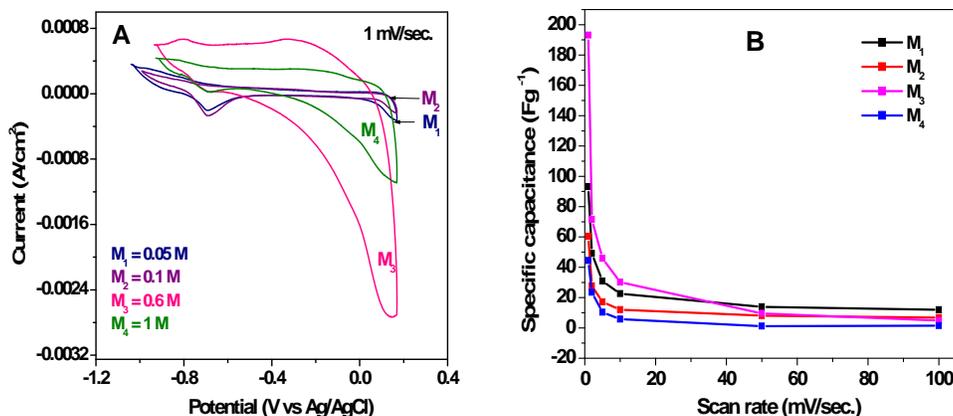
$$C = \frac{\int Idt}{dV/dt} \quad (1)$$

$$SC = \frac{C}{W} \quad (2)$$

Where  $\int Idt$  is the area under curve,  $dV/dt$  is voltage scan rate

C is capacitance, W is weight of the active material dipped in the electrolyte.

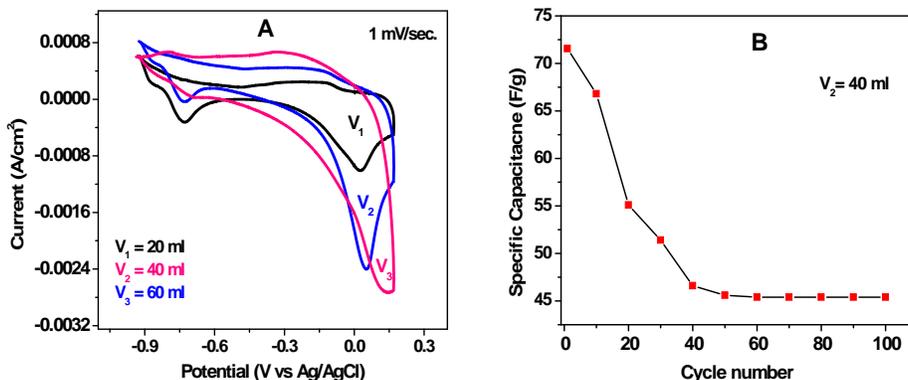
Fig. 3B) depicts the variation in calculated values of SC in F/g of E, M and P electrodes with variable scan rates in mV/s. It is observed that with increase in scan rate, SC decreases fastly in initial cycles. The decrease in SC itself indicates some irreversibility in the system<sup>[21]</sup>. In the supercapacitive systems, linking faradaic process undergo polarization effects and ideal reversibility cannot be practically realized in the kinetics sense for the redox process<sup>[22]</sup>.



**FIGURE 4** A) CVs of Co<sub>3</sub>O<sub>4</sub> prepared by different concentration using methanolic route  
B) Variation of specific capacitance (F/g) with scan rate (mV/s) for different molar samples

Fig. 4A) shows the CV curves of M<sub>1</sub>, M<sub>2</sub>, M<sub>3</sub> and M<sub>4</sub> electrodes. It is observed that with increase in concentration of the solution redox peak decreases. Sample M<sub>3</sub> shows large area under the curve. The maximum value of SC, 193.10 F/g at the scan rate 1 mV/s. in 1 M KOH electrolyte, is observed for M<sub>3</sub> electrode. Fig. 4B) shows the variation in observed SC values for M<sub>1</sub>, M<sub>2</sub>, M<sub>3</sub> and M<sub>4</sub> electrodes in F/g vs scan rate in mV/s. From

the plot it is observed that all samples shows stabilization within 10 to 20 cycles. The fast stabilization of the electrode is may be due to fast degradation of the active material from the electrode surface. During fast scanning inner active sites of the electrode material do not take part in fast redox reaction, therefore SC goes on decreasing [23].



**FIGURE 5** A) CVs of Co<sub>3</sub>O<sub>4</sub> prepared by different volumes  
B) Stability curve of V<sub>2</sub>.

Fig. 5A) shows the CVs of V<sub>1</sub>, V<sub>2</sub> and V<sub>3</sub> electrodes carried by varying the volumes of 0.6 M solution of cobalt nitrate at the scan rate 1 mV/s. All CVs curves show redox peaks indicating mixed capacitive behavior. The observed values of SC are for V<sub>1</sub> = 90.25, V<sub>2</sub> = 193.10 F/g and V<sub>3</sub> = 117.92 F/g in 1 M KOH electrolyte. The electrode V<sub>2</sub> itself shows huge redox peaks and high value of SC. The V<sub>1</sub>, V<sub>2</sub> electrodes shows reduction peaks at -0.73 V and 0.026 V. Whereas V<sub>3</sub> shows reduction peak at 0.13 V and shoulder peak at -0.73 V. The reduction peaks are formed due to irreversibility of the redox reaction and pseudocapacitive effect. In the electrode preparation, the electrode prepared by 40 ml spraying solution shows proper film thickness, uniformity, adherency and porous continuous morphology which is necessary to improve the performance of supercapacitor electrode [16].

Fig. 5 B) shows the variation of specific capacitance with cycle number for the V<sub>2</sub> electrode examined at the scan rate 2 mV/s in 1 M KOH electrolyte. Variation shows, in

the early stage SC decreases somewhat linearly, after completion of 40 cycles, SC becomes stable at 45.6 F/g. Fig.6 shows chronopotentiometric test of V<sub>2</sub> electrode for different current densities like 2, 4, 6 and 8 mA/cm<sup>2</sup> at the potential 0.4 V. Curve shifts from asymmetrical to symmetric type of behaviour with increase in current. Charge-discharge curve of V<sub>2</sub> electrode was used to calculate the specific energy (SE), specific power (SP) and columbic efficiency ( ) using following relations [21].

$$SE = \frac{V \times I_d \times T_d}{W} \quad (5)$$

$$SP = \frac{V \times I_d}{W} \quad (6)$$

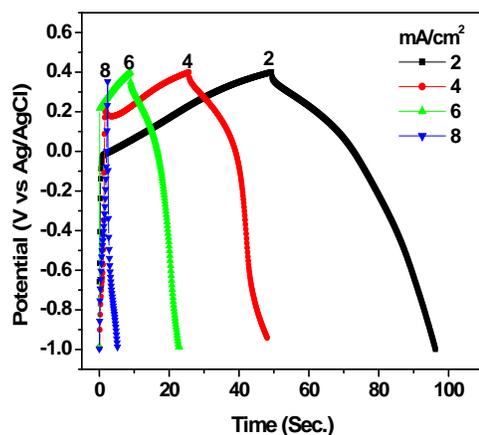
$$y = \frac{t_d}{t_c} \times 100 \quad (7)$$

It is observed that with increase in current density, SP increases and SE decreases. The inner active sites of the deposited electrode material do not take part in redox reaction occurring at higher current densities [19]. Electrode operated at 8 mA/cm<sup>2</sup> current density shows nearly

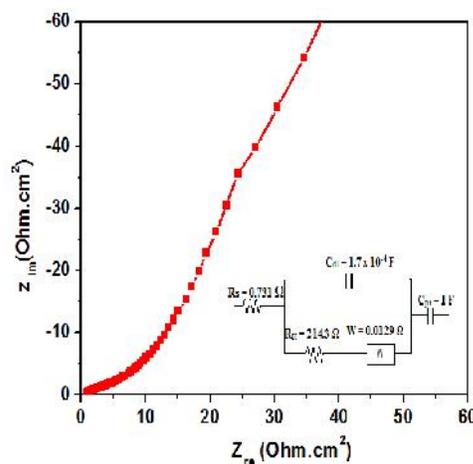
symmetric nature and shows maximum efficiency. Electrode operated at other current densities shows small potential drop along y- axis representing the presence of internal resistance [23].

**TABLE.1** Variation of Specific energy (SE), Specific power (SP) and Coulombic efficiency ( ) at different current densities of M<sub>3</sub>

Current density (mA/cm <sup>2</sup> )	Specific energy (Wh/kg)	Specific power (kW/kg)	Coulomb efficiency ( %)
2	1.60	0.88	89.9
4	0.89	1.11	88.8
6	0.82	1.35	94.9
8	0.62	1.85	96.2



**FIGURE 6:** Charge-discharge curves of V<sub>2</sub> at different current densities.



**FIGURE 7:** Nyquist plot of V<sub>2</sub>.

### Super capacitive impedance

To know the obscured electric parameters like equivalent serious resistance (ESR) of the cell which is the combination of ionic resistance of electrolyte, intrinsic resistance of active material and contact resistance at the active material-current collector interface are the important parameters of supercapacitor studied using EIS of Nyquist plot. The Nyquist impedance plot implies that V<sub>2</sub> thin film electrode show a blocking (resistive) behavior at high frequency and capacitive behavior at low frequency region [19]. EIS measurements were carried out at open circuit potential – 0.102 V in the frequency range of 1mHz to 1MHz (Fig.7). The observed internal resistance is around 0.87 . Lower frequency region demonstrates capacitive behaviour called Warburg (W) impedance due to interfacial diffusive resistance of the OH<sup>-</sup> ions in to the layered Co<sub>3</sub>O<sub>4</sub> electrode. For V<sub>2</sub> electrode, impedance line is not remarkably parallel to Y axis but inclined nearly by 45° suggesting increasing state of charge called double-layer capacitance [9]. The values of R<sub>ct</sub>, R<sub>1</sub> C<sub>dl</sub>, C<sub>ps</sub> and W of Randles equivalent circuit was obtained by simulations fitting of experimental and standard data curves.

### CONCLUSIONS

Co<sub>3</sub>O<sub>4</sub> thin film electrode preparation via different non aqueous medias is possible by spray pyrolysis. Structural and morphological analysis shows face centered cubic poly crystalline nature of the deposit with nanosized

grains. Electrodes prepared via methanolic route shows good electrochemical properties exhibiting highest value of SC 193.10 F/g. for V<sub>2</sub> electrode in 1 M KOH electrolyte

### ACKNOWLEDGEMENTS

Authors are grateful to thanks Bhabha Atomic Research Center (BARC), Mumbai for providing financial support through the project scheme 2010/34/46/BRNS/2228.

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