

Efficacy appraisal of Cobalt oxide electrode module as a patron of sustainable energy harvesting supercapacitor

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ABSTRACT

The objective of the investigation was to study the potential and efficacy of Cobalt oxide as a cost-effective ecofriendly substitute against the currently used high-cost supercapacitors. During the study, Cobalt oxide was successfully studied for its ecofriendly approach and cost-effective potential as a supercapacitor. Electrodeposited Cobalt oxide electrode, deposited on stainless steel substrates at room temperature using Cobalt acetate as the precursor solution by galvanostatic route was studied for its efficacy as a supercapacitor. The as-deposited electrodes were annealed at 400 °C, 500 °C and 600 °C and were analytically compared. The structural analysis was done by X-ray diffraction technique, morphological analysis by SEM and wettability studies were carried by contact angle measurement at different annealed temperatures. The electrochemical analysis to investigate supercapacitive behavior of the as-deposited Cobalt oxide thin film electrode was performed in aqueous 1M Na₂SO₄ at three different annealed temperatures. The electrochemical properties of the deposited thin film electrode were done through cyclic voltammetry and galvanostatic charge-discharge analysis. The thin film electrode showed maximum specific capacitance of 295 Fg⁻¹ at 5mVs⁻¹ scan rate in 1M aqueous Na₂SO₄ with Specific energy 3.642Wh/kg, Specific Power 3 kW/kg and 56.70 % Coulomb efficiency when annealed at 500 °C temperature.

Key words : Cobalt oxide, Electrodeposition, Thin films, Cyclic voltammetry, Supercapacitor, Charge–discharge.

Introduction

Batteries are a serious threat to the environment since batteries contain environmentally harmful chemicals like lead, cadmium, zinc, lithium and mercury that cannot be recycled. To overcome this problem these must be replaced with sustainable and renewable energy sources like alternative energy storage or conversion devices like supercapacitors and solar cells. For the reason that,

supercapacitors are more in demand among smart electronics for their ability to possess high energy or power density in comparison to batteries or fuel cells. The supercapacitor is recognized for its high power and a relative longer life cycle, approximately over 100 times as compared to the battery life.

Further the prime concern for the production of solar panel is the cost of manufacturing supercapacitors. Existing photovoltaic ranges depend on supercapacitors for the storage of energy

which is harvested from the sun. Since the growth rate of supercapacitors is increasing yet their cost is high because of the use of activated carbon. Cobalt oxide thin film was tried for its efficacy as a cheap and effective and ecofriendly alternative. It was successfully studied that use of Cobalt oxide is not only ecofriendly approach but it assures reduction in the cost of manufacturing supercapacitors by lowering the cost of the electrodes. Once such supercapacitors are available at a cheaper rate, they will become common and shall be integrated into more and more devices. This new approach overlays the way for development of durable, high-voltage supercapacitors with its promising use in applications (Pierre *et al.*, 2013).

Today the world is in urgent need of eco-friendly energy storage device with long life, high reliability and energy efficiency with high charge-recharge capacity. One of such energy sources with good storage mechanism, fulfilling the major requirement conditions is the Electrochemical capacitors. They are also termed as supercapacitors which have high power density, high charge–discharge cycle life and high energy efficiency. In recent years, they have attracted increased interest in power source applications such as hybrid electric vehicles, telecommunications, particularly associated with cellular phones for a reduction of the size of the batteries and pacemakers (Kotz *et al.*, 2000). Depending on the type of electrochemical reactions involved in the charge storage mechanism as well as the active materials used, ECs are of three types: electric double-layer capacitors (EDLCs), pseudo-capacitors, and hybrid electrochemical capacitors (Yuan *et al.*, 2011). In EDLCs, the charge storage takes place through the process of reversible ion absorption at the electrode/electrolyte interfaces, (Conway, 1999; Jayalakshmi *et al.*, 2008). In pseudocapacitors, the fast and reversible faradic redox reactions occur at the surface of the electroactive materials that are responsible for charge storage. Basically, the term pseudo is related to false and/or almost as pseudocapacitor electrodes behave like a capacitor in its electrochemical signature, i.e., demonstrating a linear dependence of the charge stored by the width of the potential window, however, where charge storage originates from different reaction mechanisms. In hybrid electrochemical capacitors usually combination of two materials, one battery-type faradic electrode (as energy source) and another capacitive electrode (as power source), in the same cell is considered

(Conway, 1999).

The most extensively used active material for supercapacitor electrode are various carbon, transition metal oxides/hydroxides and conducting polymer (Morita, 2008). TMO's are most preferred among the various electrode materials worked upon since recent years only because of their good chemical stability, capricious valence etc. (Zheng, 1995). Co_3O_4 has been widely investigated and can be considered as a replacement for RuO_2 , due to its low cost, low environmental hazardous impact, its number of stable oxidation states and subsequent high theoretical specific capacitance (Yuan *et al.*, 2012). Cobalt oxide has been is a most tempting electrode material for supercapacitor electrode due to its high theoretical SC (3560 Fig. 1) with good reversibility (Farhadi *et al.*, 2013). Cobalt oxide has excellent electrochemical performance (Lokhande *et al.*, 2011). The specific capacitance of as-deposited Cobalt oxide thin film electrode is found to be greater than the reported values (Kandalkar *et al.*, 2010; Jagadale *et al.*, 2013), and the specific energy so obtained was found to be greater than that reported (Jagadale *et al.*, 2014).

In the present research work Cobalt oxide thin films were deposited from aqueous solution of Cobalt acetate as the precursor solution using galvanostatic electrodeposition method. These as-deposited thin films were characterized by X-ray diffraction technique for their structural analysis and by SEM, AFM and EDAX technique for their morphological analysis respectively. The electrochemical properties of the Cobalt oxide thin film were studied in aqueous 1M Na_2SO_4 electrolyte using cyclic voltammetry and galvanostatic charge-discharge techniques.

Materials and Methods

Preparation of Cobalt oxide thin film electrode

Cobalt oxide thin films were deposited on stainless steel substrates using aqueous 0.1 M Cobalt acetate precursor solution by galvanostatic route of electrodeposition method (Bockris, 1963; Pandey, 1996; Chopra, 1969). The galvanostatic deposition of the thin film electrode was carried out at optimized current of 5mAcm^{-2} for 20 mins at room temperature in a three-electrode system with cobalt oxide as a working electrode, a platinum electrode as a counter electrode and saturated calomel electrode (SCE) as

the reference electrode. The galvanostatic deposition resulted in accumulation of cobalt material on the stainless substrates in the form of very sticky, uniform, well-adherent and homogeneous thin films, (Cho *et al.*, 2006). These deposited good quality films were then annealed at three different temperatures 400 °C, 500 °C and 600 °C respectively to produce the necessary Cobalt oxide material deposition. The structural investigation was done following the protocol for BENCHTOP POWDER X-RAY DIFFRACTION (XRD) INSTRUMENT, for Qualitative and quantitative phase analysis of poly-crystalline materials by RIGAKU MINIFLEX), with CuK α radiation between 20° and 80°. The chemical structure of Co₃O₄ was confirmed by the Raman spectrum (Hololab series-5000 Raman spectroscopy). The mass of the as-deposited electrode material was measured using high precision analytic balance (CONTECH, with 0.01 mg sensitivity). The electrochemical supercapacitor investigation of Cobalt oxide thin film electrode was done in CH Instruments Electrochemical Workstation (CH608E). All electrochemical studies were carried out in a conventional three-electrode system with 1M Na₂SO₄ electrolyte. The CV, CP, EIS and cycle stability characteristics of the deposited electrode were used to analyze the supercapacitive properties of Co₃O₄ electrode, (protocol for BENCHTOP POWDER X-RAY DIFFRACTION (XRD) INSTRUMENT, for Qualitative and quantitative phase analysis of poly-crystalline materials by RIGAKU MINIFLEX).

Results and Discussion

Structural elucidation studies and compositional analysis

The structural investigation of Cobalt oxide thin film was done using X-ray Diffraction technique. Fig. 1 (a) illustrates the XRD pattern of galvanostatically deposited Co₃O₄ thin film at 5mAcm⁻² current density and annealed at 400 °C, 500 °C, and 600 °C respectively. The diffraction pattern comprises of characteristic peaks of Cobalt oxide at 2 θ values 20.05°, 31.03°, 36.6°, 38.27°, 44.12°, 50.81°, 59.21°, 65.01°, 77.18° with (111), (220), (311), (212), (400), (422), (511), (440), (533) planes of Cobalt oxide which are equivalent to simple cubic crystal structure (JCPDS No. 42-146). The diffraction pattern consists of sharp peaks with the most prominent peak at 2 θ = 44.12° with (311) plane of Cobalt oxide crystal lat-

tice. The lattice constant at this prominent peak is a = 6.802Å and interplanar spacing is d = 2.050Å. Comparatively, with respect to the annealed temperatures the observed peaks are in accordance with each other but change in diffraction intensities are observed, indicating no much change in the crystal structure of the deposited material though annealed at different temperatures. Except Co₃O₄ phases, no diffraction peaks corresponding to CoO or Co phases are seen which thus approves the formation of pure cubic Co₃O₄ structure (Gwang-Su *et al.*, 2017). The effect of annealed temperatures is seen on the diffraction peaks which are sharper and fine with greater diffraction intensities with nearly same diffraction angles and are most remarkable at 500 °C, the optimized annealing temperature of electrode than at 400 °C and 600 °C annealing temperatures.

The average crystallite size of Co₃O₄ film was calculated along the prominent peak of 2 θ = 44.12° with (311) plane using Scherrer relation;

$$D = K\lambda/\beta\cos\theta \quad \dots (1)$$

Where, D = crystallite size

K = Scherrer constant (usually 0.89)

λ = Wavelength of the X-ray radiation (for Cu K α = 0.1540 nm)

β = Full width half maximum (FWHM) of diffraction peak measured at 2 ϵ .

The crystallite size of the most intense prominent peak (2 θ = 45.58°) was found to be 5.553 nm (at 400°C and 600 °C annealing temperature). The crystallite size at the most intense prominent peak (2 θ = 38.27°) was found to be 1.614 nm at 500 °C annealing temperatures.

The Raman spectra of Cobalt oxide thin film electrode prepared at 500 °C is displayed in Fig.1 (b). The vibrational frequencies of molecules are specific to their vibration, chemical bonding and symmetry. Raman spectra provides the finger print of molecules to identify them as specific molecules of the

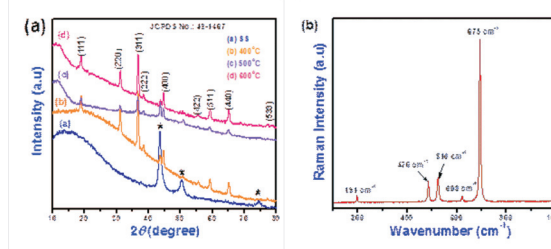


Fig. 1. XRD pattern of galvanostatically deposited CO₂O₄ thin film (at 5mA cm⁻² current density and annealed at 400 °C, 500 °C, and 600°C respectively)

material which are present in specific wave number region of the spectra. The Fig. 1 (b) above displays three peaks at 470 cm^{-2} , 510 cm^{-2} and 675 cm^{-2} accounted for oscillation of Co-O confirming the formation of Cobalt oxide (Sun *et al.*, 2001). These peaks confirm the presence of Cobalt oxide in the deposited material.

Surface Wettability study

The galvanostatically electrodeposited Co_3O_4 thin film was used to undergo surface wettability investigation by measurement of contact angle. The contact angle of material with water droplets on its surface determines the wettability property of material. In the surrounding of air, the wetting of solid with water is dependent on the relation among the interfacial tensions (i.e. water/air, water/solid and solid/air). The ratio between these tensions determines the contact angle θ between water droplets on a given surface. A surface with water contact angle 0° means complete wetting and greater than 180° means complete non-wetting (Singh *et al.*, 2006). The hydrophilic nature ($\theta < 90^\circ$) denotes the supercapacitive property of the electrode material surface to make close contact with the aqueous electrolyte necessary for charge transfer between the two. Fig. 2 represents the measured contact angles of Co_3O_4 electrode which were 87° , 85° and 86° at 400°C , 500°C and 600°C annealing temperatures respectively, which affirms the hydrophilic nature of the as-deposited Cobalt oxide material. The deposited material shows comparatively smaller contact angle of 85° at 500°C than at 400°C (87°) and 600°C (86°) annealing temperature, indicating more hydrophilic nature of the deposited material at 500°C , the optimized annealing temperature. This shows that

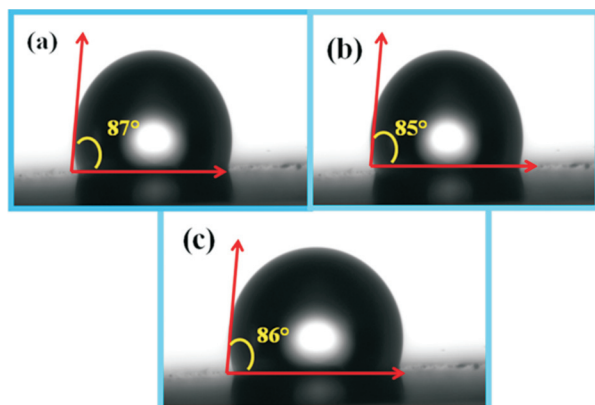


Fig. 2. Contact angle of CO_3O_4 thin film annealed at (a) 400°C (b) 500°C (c) 600°C .

the hydrophilic Co_3O_4 electrode material possesses high surface energy. It may due to cohesive force between water droplet and hydroxide of Co_3O_4 electrode material (Dhole *et al.*, 2017). This hydrophilic property of Co_3O_4 electrode material makes it feasible for supercapacitive energy storage devices.

Surface morphological studies

The display in Fig.3.(a), (b) and (c) is the SEM images of Co_3O_4 electrode annealed at 400°C , 500°C and 600°C respectively. The SEM images comprise of microspheres with highly porous network. The microspheres are aggregated nanoparticles uniformly arranged in the form of columns with empty spaces between giving them a spongy appearance with canal or ridges like structures throughout the sample surface resulting in an abundant porous structure. The images clearly represent increase in annealed temperatures increases the dense layers of spongy clusters caused due to agglomeration of nanoparticles. These clusters of spongy nanoparticles are inter-linked with each other forming a highly rough and porous surface. Such type of porous structure resulted due to the film formation is based on the nucleation and coalescence. Such surface morphology has attracted increasing interest due to its large surface area which is the key factor for efficient electrode in alkaline batteries and supercapacitor devices (Dubal *et al.*, 2010).

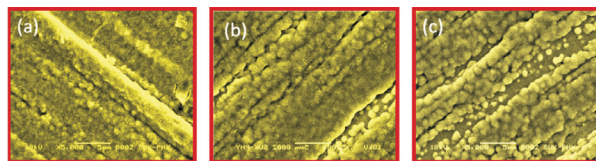


Fig. 3. SEM images of Co_3O_4 electrode annealed at 400°C , 500°C , and 600°C respectively.

The formation of porous Co_3O_4 was affirmed through elemental compositional mapping with profile spectrum obtained by EDAX analysis at 400°C , 500°C and 600°C annealing temperatures of the as-deposited Co_3O_4 electrode. The display in Fig.4 (a), (b) and (c) illustrate the element and weight percentage contribution of Co and O in the formation of cobalt oxide respectively. The presence of peaks of Co and O elements in the profile spectrum confirms the formation of cobalt oxide namely Co_3O_4 . The profile chart shows the weight percentage of Co (53.28 Wt. \%) and O (19.34 Wt. \%) at 400°C , Co (62.65 Wt. \%) and O (22.03 Wt. \%) at 500°C and Co

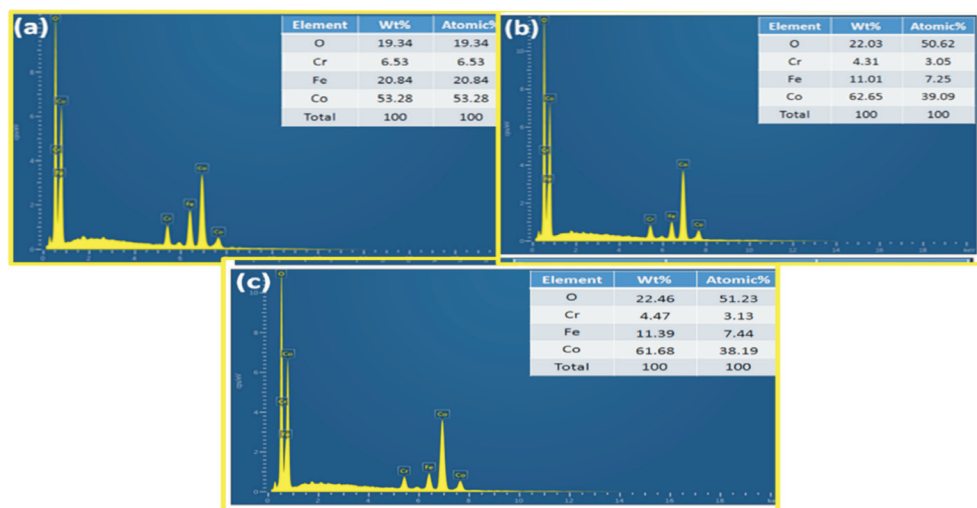


Fig. 4. EDAX spectrum of Co_3O_4 electrode with inset table showing wt% of Co and O elements at different annealed temperatures.

(61.68 Wt. %) and O (22.46 Wt. %) at 600 °C annealing temperature of the deposited electrode respectively. The weight percentage contribution of Co (62.65 Wt. %) and O (22.03 Wt. %) is found to be higher at the optimized annealing temperature 500°C.

The AFM images of Co_3O_4 electrode annealed at 400 °C, 500 °C and 600 °C respectively, are dis-

played in Fig. 5. Atomic Force Microscopy analysis was carried on using a Cypher ES (Asylum Research) model mounting probes OTESPA-R3 (Bruker) for high-resolution tapping mode analysis. At 400°C annealing temperature the Co_3O_4 film thickness appears to be smooth, uniform and much adherent as shown in Fig. 5(a). Clusters of agglomerated small grains with small empty spaces in between them are found to be present at regions of good nucleation process occurrence on the film surface. The surface of the deposited Co_3O_4 thin film is found to change with annealing temperature. As annealing temperature is increased the grains coagulate reducing the voids and arrange to form a compact structure. Remarkable enhancement in the surface roughness is observed with increase in annealing temperature. The surface of the deposited Co_3O_4 thin film annealed at 500 °C is observed to be most rough and uneven. The raised roughness enhances the supercapacitive property of the film annealed at 500° temperature.

Supercapacitive properties of Cobalt oxide electrode

Cyclic voltammetry

Electrochemical analyzer was used to conduct Cyclic voltammetry (CV) with saturated calomel electrode as the reference electrode, a platinum wire as counter electrode and stainless steel as working electrode. The specific capacitance was calculated from Cyclic voltammetry.

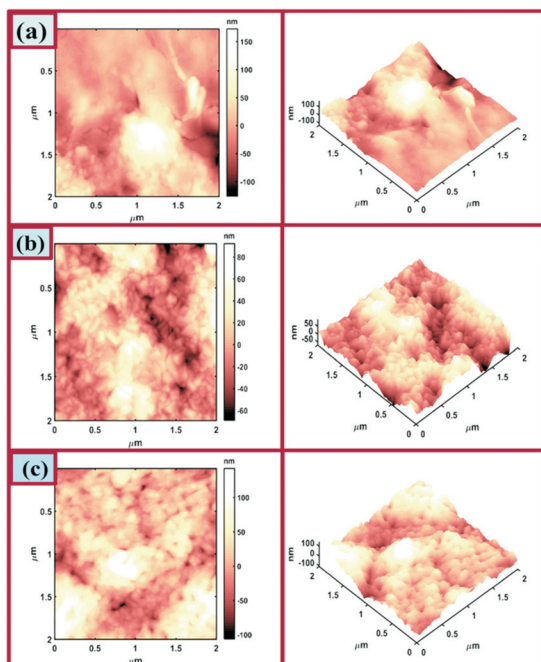


Fig. 5. 2D AFM and 3D AFM images of Cobalt oxide thin film annealed at (a) 400 °C (c) 600 °C

Annealing temperature influenced supercapacitive behavior of Co_3O_4 electrode

The galvanostatically electrodeposited Cobalt oxide thin film electrode was annealed at three different temperatures namely 400 °C, 500 °C and 600 °C, respectively. The specific capacitance increased upto a particular temperature and then decreased. The temperature at which the specific capacitance was maximum, i.e. 500 °C was taken as the optimized temperature for the electrode. The cyclic voltammetric curves for Co_3O_4 electrode at different annealed temperature in 1M aqueous Na_2SO_4 electrolyte are displayed in Fig. 6 (a). It is seen from the figure that both cathodic and anodic current peaks decrease with increase in the annealing temperature. This infers that more Cobalt hydroxide constituent is converted into Cobalt oxide leading to larger capacitance of the deposited film. As the annealing temperature increases, the cathodic and anodic peak currents continue to decrease until a temperature is reached at which only non-faradaic (capacitive) current exists (Kalu *et al.*, 2001).

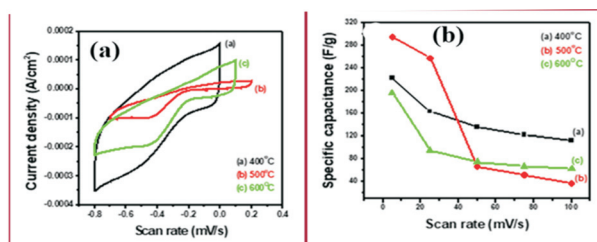


Fig. 6(a). CV for Co_3O_4 electrode at different annealed temperature in 1M aqueous Na_2SO_4 electrolyte. (b) Variation of Specific capacitance with Scan rate in 1M Na_2SO_4 electrolyte at different annealing temperatures

It is also observed that the annealing temperature brings about change in the capacitance of the electrode which is estimated from the area under the I-V curve. The surface density (q/cm^2) obtained from the integration of the area the I-V curve is proportional to the capacitance of the film since,

$$C(V_f - V_i) = q = \frac{1}{\nu} \int_{V_i}^{V_f} I(V) dV \quad \dots (2)$$

where C is the total capacitance, I the current density (A/cm^2), ν the sweep rate (V/s), V_i the initial and V_f the final voltages (V). The integral on the right-hand side of above equation is the area under the CV curve. Thus, the total surface charge, (or total capacitance) of the deposited material can be es-

timated by evaluating the area under the capacitive current-voltage curve portion of a CV (without faradaic reaction peaks) (Kalu *et al.*, 2001). The specific capacitance was observed to be maximum at 500°C optimized annealing temperature as 294.67 F/g in 1M aqueous Na_2SO_4 . Fig.6. (b) displays variation of Specific capacitance with Scan rate in 1M Na_2SO_4 electrolyte at different annealing temperatures. It is seen that there is decrease in specific capacitance of the Co_3O_4 electrode with increase in scan rate in 1M aqueous Na_2SO_4 electrolyte.

Effect of electrolytes and sweep rates.

The CV plot of Co_3O_4 electrode at scan rates from 5mV to 100 mV in potential window from 0.2 V to -0.7V in aqueous 1M Na_2SO_4 electrolyte are displayed in Fig.7(a). The rectangular CV plots indicate the potential capacitive behavior of electrodes. The current under curve is slowly increased with scan rate, which reveals that the voltammetric currents are directly proportional to the scan rates, suggesting a signature of an ideal capacitive behavior (More *et al.*, 2017). Increase in scan rates reduces specific capacitance due to decrease in diffusion time of the electrolyte ions from completely accessing the electrode surface. The decreasing tendency of the capacitance suggests that some part of the surface of the electrode material can be available at high charging-discharging rates. Hence, the SC value obtained at slow scan rates is supposed to be closest to that of full utilization of the electrode material (Yan *et al.*, 2009). Fig. 7(b) shows Variation of Specific capacitance with cycle number in 1M Na_2SO_4 at 500 °C annealing temperature. The specific capacitance of Co_3O_4 electrode is found to decrease with increase in the number of charge-discharge cycles indicating the utilization of the electrode material in the supercapacitive

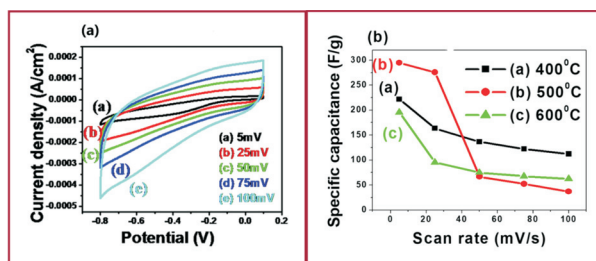


Fig. 7(a). CV curve of Co_3O_4 electrode in 1M Na_2SO_4 electrolyte at 500 °C annealing temperature. (b) Variation of Specific capacitance with scan rate in 1M Na_2SO_4 electrolyte at 500 °C annealing temperature.

operation. This behavior is clearly explained by the linear curves displayed in the graph of Fig. 7(b).

The detail findings are summarized in Table 1:

Charge-discharge study

The Charge-discharge study was carried out to evaluate the supercapacitive parameters of Co_3O_4 electrode like Specific Energy (SE) and Specific Power (SP). Fig. 8 displays the galvanostatic charge-discharge curves for the as-deposited Co_3O_4 electrode in 1 M Na_2SO_4 electrolyte. The curves are the result of two operations, the drop of potential due to the internal resistance and then the successive slow and steady decay of potential denoting the capacitive property of the deposited electrode. The Supercapacitive parameters such as SE, SP and coulombic efficiency % were calculated and the findings are tabulated in Table 1. The table shows maximum values of supercapacitive parameters of Co_3O_4 electrode in 1 M Na_2SO_4 electrolyte at 500 °C annealing temperature. It is observed from Fig. 8 that the discharging time is greater than charging time indicating good operation efficiency of the as-deposited electrode. The linear curves in Fig. 7(b) display the variation of specific capacitance with cycle number in 1 M Na_2SO_4 electrolyte at 500 °C annealing temperature. The practical application of supercapacitor requires good retention of specific capacitance over long cycles under high scan rate. The electrode showed cyclic stability 81% in 1M Na_2SO_4 electrolyte over its initial specific capacitance after 1000 cycles. This reveals that Co_3O_4 film has superior electrochemical stability and operates as good supercapacitor material for large number of charge-discharge cycles. Cyclic stability of 90% over 500 potential cycles for Co_3O_4 nanowires (Wang *et al.*, 2011).

Electrochemical Impedance Spectroscopy

The Nyquist plots for the as-deposited Co_3O_4 electrode in 1M Na_2SO_4 electrolyte is shown in Fig. 9 (a), (b) and (c) respectively. In the high frequency re-

gion, the plot is in the form of a small semicircle which specifies the charge transfer resistance in parallel with the double layer capacitance. Further towards the lower frequency region the plot becomes a straight line which indicates semi-finite diffusion (Warburg impedance). In all the three plots of the three electrolytes, the straight lines in the low frequency region indicates that ionic diffusion appears

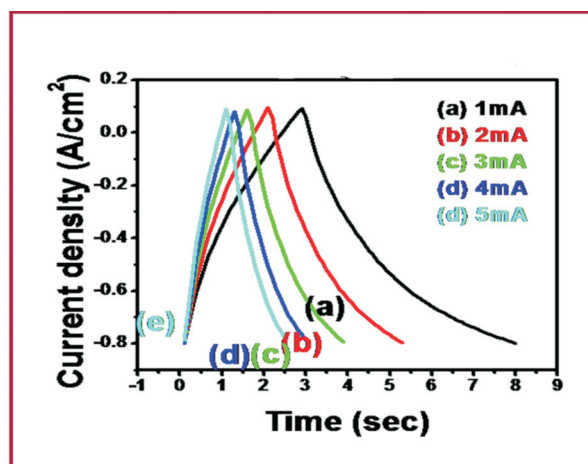


Fig. 8. Charge discharge curves of Co_3O_4 electrode at 500 °C annealing temperature in 1M Na_2SO_4 electrolyte

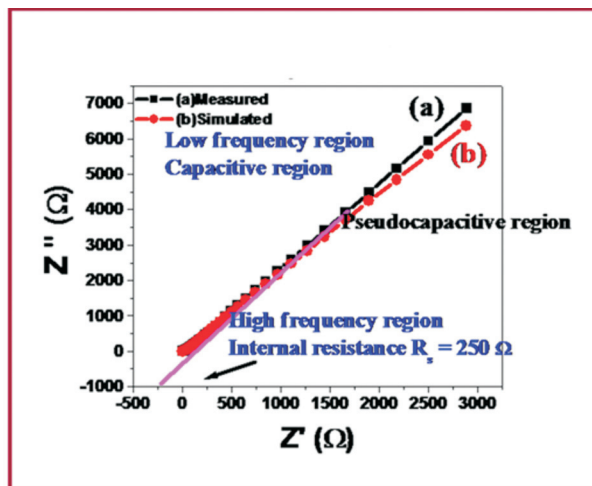


Fig. 9. Co_3O_4 electrode in 1M Na_2SO_4 electrolyte

Table 1.

Sr. No	Annealing Temperature °C	Electrolyte	Specific energy (W/h/kg ¹)	Specific power (kW kg ⁻¹)	Specific capacitance (F g ⁻¹)	Coulomb efficiency (%)
1	400°C	Na_2SO_4	4.900	4.000	222.05	54.30
2	500°C	Na_2SO_4	3.642	3.000	294.67	56.70
3	600°C	Na_2SO_4	4.189	4.000	166.69	50.28

during charging discharging process. From the plot, it can be seen that there is no semicircle, which indicate that the corresponding charge transition resistance decreased; lower the charge-transfer resistance higher specific capacitance of the electrode. The Co_3O_4 electrode has a minor charge-transfer resistance reflecting a higher specific capacitance because of the well-dispersed cobalt oxide electrode (Gujar *et al.*, 2007).

Conclusion

Cobalt oxide (Co_3O_4) electrode was deposited by a simple cost-effective electrodeposition method by galvanostatic mode. The X-ray diffraction analysis revealed the as-deposited Co_3O_4 electrode material to be nanocrystalline in nature with cubic crystal structure. The SEM investigation revealed the spongy surface with highly porous morphology which satisfies the requirement to enhance the supercapacitive performance of the Co_3O_4 electrode. The Contact angle of the material deposited was measured 87° , 85° and 86° at 400°C , 500°C and 600°C attributed Cobalt oxide electrode surface to be hydrophilic in nature. The electrochemical analysis manifested maximum supercapacitance of 294.67 Fg^{-1} , specific energy 3.642 Wh/kg , specific power 3 kW/kg in $1\text{M Na}_2\text{SO}_4$ electrolyte at 500°C optimized annealing temperature. The retentivity of Co_3O_4 electrode after 1000 cycles was 81% in Na_2SO_4 electrolyte. All these electrochemical parameters of Co_3O_4 electrode deposited by electrodeposition method via galvanostatic route depicts that, Cobalt oxide has excellent supercapacitive properties and is potential material for supercapacitor application.

Thus, Cobalt oxide thin film confirms to be a cheap and effective and ecofriendly substitute. Further it is not only ecofriendly but also assures manufacturing cost- reduction. Making it available at a cheaper rate, it assures to be a common integral of varied devices. Thus, it directs development of robust, high-voltage supercapacitors with varied applications. The studies conclude with the proclamation that, Cobalt oxide proved to be an efficient, ecofriendly, cost effective, assured technological advantage with its promising usage in the renewable energy innovation contest.

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References

- Cho, J. U., Liu, Q. X., Min, J. H., Ko, S. P. and Kim, Y.K. 2006. *J. Magn. Magn. Mater.* 304: e213.
- Chopra, K. L. 1969. *Thin Film Phenomena*. McGraw Hill, New York.
- Conway, B.E. 1999. *Electrochemical supercapacitors. Scientific fundamentals and technological applications*. Kluwer Academic, Plenum Publishers.
- Dhole, A., Navale, S.T., Navale, Y.H., Jadhav, Y. M., Pawar, C. S., Suryavanshi, S. S. and Patil, V. B. 2017. Performance evaluation of galvanostatically deposited nickel oxide electrode for electrochemical supercapacitors. *J. Mater. Sci. Mater. Electron.* 28: 10819-10829.
- Dubal, D. P., Dhawale, D. S., Salunkhe, R. R. and Lokhande, C. D. 2010. *J. Electrochem. Soc.* 157 : A812.
- Emma Metson, 2007. Green Environment News, Batteries and Their Effects on the Environment, retrieved from: <https://www.EcoFriendlyLink.com/blog/batteries-and-the-environment/>
- Farhadi, S., Safabakhsh, J. and Zaringhadam, P. 2013. Synthesis, Characterization, and Investigation of Optical and Magnetic Properties of Cobalt Oxide (Co_3O_4) Nanoparticles. *J. Nanostructure Chem.* 3(1): 69.
- Gujar, T.P., Kim, W., Puspitasari, I., Jung, K. D. and Joo, O. S. 2007. Electrochemically deposited Nanograin ruthenium oxide as a pseudocapacitive electrode. *Electrochem. Sci.* 22 : 666–673.
- Gwang-Su Jang, S. Ameen, M. S. Akhtar, E. Kim and H. Shin, J. 2017. *Mater Sci: inc. Nanomaterials & Polymers. Chemistry Select.* 2 : 8941-8949.
- J Bockris, O.M., Devanathan, M. A. and Muller, K. 1963. *Proc. Roy. Soc. (Lond.)*. A 55: 274.
- Jagadale, D., Kumbhar, V. S., Bulakhe, R. N. and Lokhande, C. D. 2014. Influence of electrodeposition modes on the supercapacitive performance of Co_3O_4 electrodes. *Energy.* 64: 234-241.
- Jagadale, D., Kumbhar, V. S., Dhawale, D. S. and Lokhande, C. D. 2013. Performance evaluation of symmetric supercapacitor based on cobalt hydroxide $[\text{Co}(\text{OH})_2]$ thin film electrodes. *Electrochimica Acta.* 98 : 32-38.

- Jayalakshmi, M. and Balasubramanian, K. 2008. Simple capacitors to supercapacitors—an overview. *Electrochem Sci.* 3 : 1196-1217.
- Kalu, E. E. and Nwoga, T. T. and V. Srinivasan, J.W. 2001. Weidner, *Journal of Power Sources.* 92 : 163-16.
- Kandalkar, S. G., Dhawale, D. S., Chang-Koo Kim and Lokhande, C. D. 2010. Chemical synthesis of cobalt oxide thin film electrode for supercapacitor application. *Synthetic Metals.* 160: 1299-1302.
- Kotz, R. and Carlen, M. 2000. *Electrochim. Acta.* 45: 2483.
- Lokhande, C. D. Dubal, and Joo, D. P. 2011. O-S. Metal Oxide Thin Film Based Supercapacitors. *Curr. Appl. Phys.* 11 (3) : 255-270.
- More, P.D., Jadhav, P.R., Ingole, S. M., Navale, Y. H. and Patil, V.B. 2017. Preparation, structural and electrochemical supercapacitive properties of sprayed manganese oxide film electrode. *J Mater Sci. Mat. in Electron.* 28(1) : 707-714.
- Morita, M. 2008. Advanced Polymers as Active Materials and Electrolytes for Electrochemical Capacitors and Hybrid Capacitor Systems. *J. Electrochem. Soc.* 17 (1): 44-48.
- Pandey, R. K., Sahu, S. N. and Chandra, S. 1996. *Handbook of Semiconductor Electrodeposition.* Marcel Dekker, Inc. (1996) pp.71
- Pierre-Olivier Logerais, Olivier Riou, Mohamed Ansoumane Camara and Jean-Félix Durastanti, 2013. "Study of Photovoltaic Energy Storage by Supercapacitors through Both Experimental and Modelling Approaches. *Journal of Solar Energy.* Article ID 659014, 9 pages, 2013. <https://doi.org/10.1155/2013/659014>
- Simon, P. and Gogotsi, Y. 2008. Materials for Electrochemical Capacitors. *Nat. Mater.* 7 (11) : 845-854.
- Singh, N., Charan, S., Patil, K. R., Viswanath, A. K. and Khanna, P. K. 2006. Unusual formation of nanoparticles of CdO and Cd (OH)₂ from the reaction of dimethyl cadmium with DMF. *Mater. Lett.* 60 : 3492-3498.
- Sun, R. D., Nakajima, A., Fujushima, A., Watanabe, T. and Hashimoto, K. 2001. *J Phys. Chem. B.*, 105: 1984-1989.
- Wang, L., Liu, X. H., Wang, L., Yang, X. J. and Lu, L. D. 2011. *J. Mater. Sci. Mater Electron.* 22: 601.
- Wu, M.S., Huang, C. Y. and Lin, K. H. 2009. *J. Power Sources*, 186, 557.
- X-ray diffraction (XRD) | Rigaku Website
- Yu, G., Hu, L., Vosgueritchian, M., Wang, H., Xie, X., Cui, J., Cui, Y. and Bao, Z. 2011. Solution- Process graphene/MnO₂ nanostructured textiles for high performance electrochemical capacitors. *Nano Lett.* 11 : 2905-2911.
- Yuan, C., Yang, L., Hou, L., Shen, L., Zhang, X. and Lou, X. 2012. Growth of Ultrathin Mesoporous Co₃O₄ Nanosheet Arrays on Ni Foam for High-performance Electrochemical Capacitors. *Energy Environ. Sci.* 5 : 7883-7887.
- Zheng, J. P. 1995. Hydrous Ruthenium Oxide as an Electrode Material for Electrochemical Capacitors. *J. Electrochem. Soc.* 142 (8) : 2699.