Controlled Synthesis of Cobalt Oxide Electrode by Electrodeposition for Supercapacitor Application

S.L. Jadhav[1,2], A.L. Jadhav[1*], V.S. Jamdade[2], K.R. Kharat[3], A.A. Deshmane[4], A.V. Kadam[1*]

[1]Department of Physics, The Institute of Science, Mumbai (Dr. Homi Bhabha state University), 15, Madam Cama Road, Mumbai-400 032. India.
[2]Department of Physics, D.P. Bhosale College, Koregaon (Satara), India.
[3]Department of Physics, Dr. N. D. Patil College, Malkapur, India.
[4]School of Chemical Science, P.A.H Solapur University, Solapur, India

*Corresponding author
doi: https://doi.org/10.21467/proceedings.118.56

ABSTRACT

Cobalt oxide (Co_3O_4) electrodes were prepared on conductive stainless still (SS) substrate using cobalt nitrate as a cobalt source by implementing simple and cost-effective chemical electrodeposition method and here, characterized for structural and electrochemical analysis for supercapacitor applications. The effect of different deposition potential on capacitance and charging-discharging stability of cobalt oxide electrode were studied. X-ray diffractions confirms the face centered cubic crystal structure of Co_3O_4 electrodes. Electrochemical capacitive analysis of cobalt oxide electrode was studied in 1MKOH aqueous electrolyte solution. The observed maximum specific capacitance attained with cobalt oxide was 273.3 F/g at scan rate 5mV/s. The observed specific power, specific energy and coulomb efficiency were 12.12W/kg, 74.75 Wh/kg, and 99.63%, respectively. The cycling stability of the cobalt oxides shows 62% up to 500 cycles.

Keywords: Cobalt Oxide, Supercapacitor, Electrodeposition, Cubic structure.

1 Introduction

A supercapacitor is a device that stores energy as well as converts it, so the researchers are attracted to it. Supercapacitors exhibits intermediate systems between traditional dielectric capacitors and batteries that bridge the power and energy gap. The need for energy in human life is increasing, this is the supercapacitor that contributes so much to fill the lack of energy. The supercapacitor classified as two categories, one is electric double layer supercapacitor (EDLCs) and another is pseudocapacitor [1]. Generally, carbon materials are used to EDLCs such as graphene, activated charcoal, multiwalled carbon nanotubes (MWCN) [2] and metal oxides/hydroxides and conducting polymers are used to make a pseudocapacitor behavior materials like $Cu(OH)_2$, Co_3O_4, TiO_2, CuO, Al doped NiO, Ru Doped CuO, [3-8],and PPy [9,10]. It is a biggest challenge to make the more suitable nanomaterials electrode for a supercapacitor application.

In the whole world researchers and scientists use different approaches to make different type nanomaterials because the larger the surface area of the electrode materials, the higher performance of the electrochemical supercapacitor. Highly porous nanomaterials exhibit higher specific capacitance with energy density due to more interactions between the electrolyte ions and electrode materials [11]. Recently, researcher have been used various techniques are used to for formation of the porous cobalt oxide like hydrothermal [12], chemical bath method [13], successive ionic layer adsorption and reaction (SILLAR) [14], and electrodeposition [15] to formations of the different type's morphologies such as rugby–shaped and spherical structure [16], nano particle [17], porous microsphere [18], nanowire [19], and so on. They also study of the result of the different morphologies structures on the performance of the electrochemical supercapacitor.

Proceedings DOI: 10.21467/proceedings.118; Series: AIJR Proceedings; ISSN: 2582-3922; ISBN: 978-81-947843-6-4

Recently, several researchers have been developed highly effective cobalt oxide nanomaterials on electrochemical capacitive performance. Liu et.al reported that cobalt oxide and their derivates exhibits interactive pseudocapacitive nature, so these properties of the cobalt oxide more suitable for supercapacitor applications [20]. Srinivasan et.al reported that the cobalt oxide is a positive electrode material and it is shows that the approximately capacitor like nature [21]. Kong et.al show that the cobalt hydroxide is a pseudocapacitor behavior and obtained maximum specific capacitance 1473 F/g in 1M KOH electrolyte at a current density 2A/g [22]. Jang et.al reported that highly porous Co3O4 electrode materials with maximum obtained specific capacitance is 430.6 F/g in 6M KOH electrolytes [23]. Klyani et.al reported that cobalt oxide (CoOOH) and Co_3O_4 nanomaterials specific capacitance value is 602F/g and 630F/g respectively in 1M KOH electrolytes at scan rate10 mV/s [24]. In the literature survey we observed that very little work found on cobalt oxide vai electrodeposited method for supercapacitor application.

In this research article, we demonstrated the controlled electrodeposition technique by using various parameters (like reaction time, deposition potential) in the reaction and to formation of Co_3O_4 thin films. During the formation of the cobalt oxide, all other parameters such as, pH of the solutions, concentrations of the percussor and quantities of the prepared solution are kept constant. Thus, controlled growth of Co_3O_4 thin films to use for the electrochemical supercapacitor applications.

2 Experimental Details:

2.1 Chemicals

The cobaltous nitrate hexa-hydrate ($Co(NO_3)_2.6H_2O$) and ammonium hydroxide (NH_4OH) were used as precursors. Stainless Steel (SS) used as a conducting substrate (grade no.304, 1× 5 cm^2) for the pristine deposition of Co_3O_4 thin film electrodes, Here SS substrate was cleaned by using emery polish paper and followed by ultrasonic treatment in double distilled water (DDW). The Double Distell Water were used as a solvent during the experiment work.

2.2 Preparation of Co_3O_4 Thin Films

All the chemicals used during the synthesis are of analytical grade, purchased from AMI and SD. Fine chemicals Mumbai and are used without any further purification. Template free and binder less cobalt hydroxide layers were deposited using conventional three electrode electrodeposition technique on ultrasonicated super cleaned SS substrate. Here the platinum plate was used as a counter electrode and Ag /AgCl was used as a reference electrode. Computer based potentiostat (CHI 600D) Electrochemical workstation was used to carry the potentiodynamic electrodeposition. For sample deposition, 1M solutions were prepared in double distilled water using ingredient source cobaltous nitrate hexa-hydrate ($Co(NO_3)_2.6H_2O$). The Stainless-Steel substrates were etched prior to using a diluted HCl for 1 min and finally washed and ultrasonically cleaned with double distilled water. The deposition potential window, deposition scan rate and deposition time maintained during the deposition of each electrode was kept at + 1.0 to − 0.1V, 50 mV/s and for 30 min., respectively. The deposited sample were annealed at 673 K for 2 hr.

2.3 Film formation mechanism

During the electrodeposition of the cobalt oxide thin films, the cobalt ions or complexes were hydrolyzed by the aqueous solution to form the hydroxide deposits on the SS substrate electrode. This prepared electrode annealed at 400^0C for 2 hr, the $Co(OH)_2$ was gets converted into Co_3O_4 nano materials. The possible kinetic reactions occurred during the deposition of cobalt hydroxide process are shown in following.

Proceedings DOI: 10.21467/proceedings.118
ISBN: 978-81-947843-6-4

Series: AIJR Proceedings
ISSN: 2582-3922

$$Co_2+ + 2\ OH- \ Co\ (OH)_2$$

after annealing at 400^{0}C or 673K, $Co(OH)_2$ converted into Co_3O_4

$$3\ Co(OH)_2 + O_2\ Co_3O_4 + 3H_2 \uparrow + 2\ O_2 \uparrow$$

3 Results And Discussion

3.1 Structural properties

The XRD patterns were carried out to get crystallographic in formations, orientation of the planes for all the prepared samples. Fig.1 show XRD patterns of the sample prepared using cobaltous nitrate hexa-hydrate, XRD data compared with the standard data (JCPDS, Card No. 80-1545), the peaks appearing at 2θ is 32.9^0, 37.8^0, 44.5^0,46.5^0, 54.5^0, 60.3^0, 66.1^0, corresponding to the crystal faces (220), (311), (400), (331), (422) (511), and (440) respectively. The XRD analysis confirms that the face centered cubic crystal structure of Co_3O_4 thin film electrode formed. The (∗) marked indicates to substrate stainless steel peak.

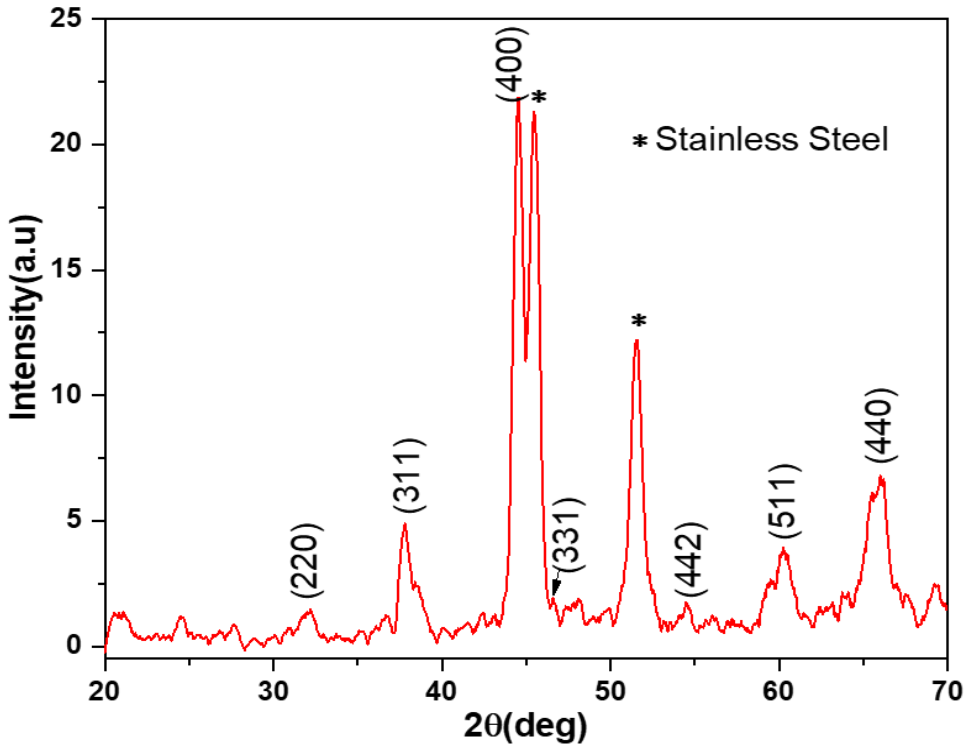

Fig.1 XRD patterns of the cobalt oxide.

3.2 Electrochemical characterization:

3.2.1 Cyclic voltammetry (CV)

Cyclic voltammetry was carried out using the electrochemical workstation to observe the electrochemical performance of the cobalt oxide thin film electrode. Fig.2 shows the typical CVs of the cobalt oxide electrode carried at the scan rate 5 to 80 mV/s in 1 M KOH between the suitable potential window − 0.3 to 0.6 V vs Ag/AgCl. During the cyclic voltammetry electrochemical two pairs of redox reaction occur. The initial reaction the conversion between Co(II) to Co(III) for the first reduction-oxidation reaction. The second reaction the conversion between Co(III) to Co(IV) for the reduction-oxidation reaction [25].These redox reactions confirm that the pseudocapacitive behaviors of cobalt oxide electrode. The increasing scan rates during the CV the specific capacitance decreases because the electrolyte ions improper interaction with electrode materials [8]. The maximum estimated specific capacitance of the cobalt oxide electrode is 273.3 F/g at scan rate 5mV/s.

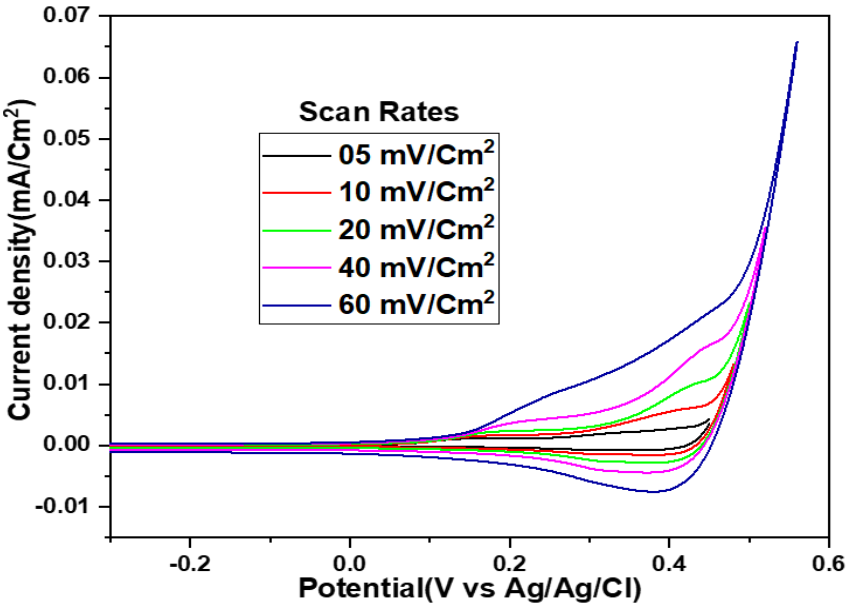

Fig.2 Cyclic Voltamograms of the cobalt oxide sample by varying scan rates.

3.2.2 Galvanostatic charging-discharge

In fig.3 clearly indicates the galvanostatic charge-discharge cycles of Co_3O_4 electrode with different current densities like 2, 4, 6, 8,10 and 12 mA/cm² within potential range 0.4V to -1.2V in 1 M KOH electrolytes. All curves showed nearly asymmetric charge - discharge nature. During the discharge time the potentials suddenly decrease (ohmic drop) was observed at lower current density may itself indicate the pseudocapacitive behavior of the prepared cobalt oxide electrode. Here, the energy and power density (SP) with columbic efficiency (η) of the cobalt oxide also calculated by using the galvanostatic charge-discharge data [1].

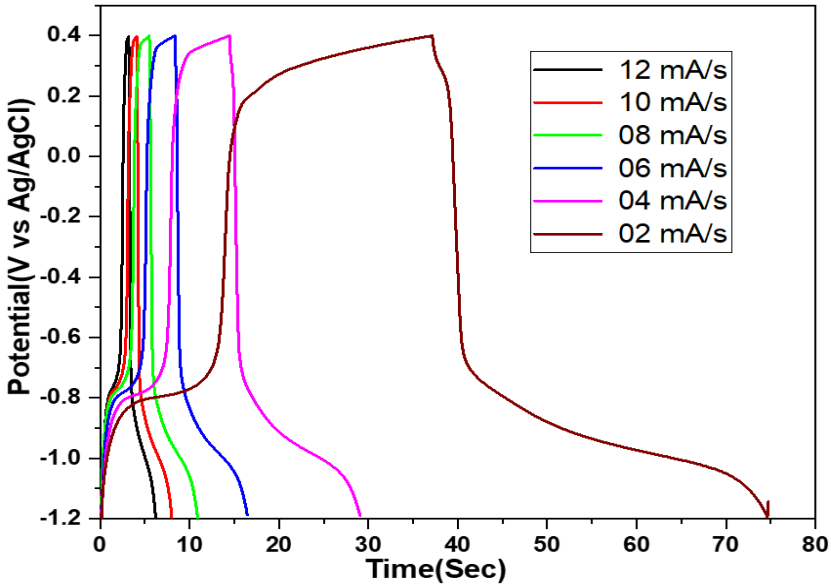

Fig.3 Galvanostatic charge discharge curve of cobalt oxide.

The calculated value of SE, SP and η are tabulated in Table 1. Electrode shows highest SE values at lower current densities and highest SP values at higher current densities. The highest calculated values of SE, SP and η are 74.75 Wh/kg, 12.12 W/kg and 99.63 % at 8 mA current density respectively.

Proceedings DOI: 10.21467/proceedings.118
ISBN: 978-81-947843-6-4

Series: AIJR Proceedings
ISSN: 2582-3922

Table 1. Specific energy, specific power, specific capacity and columbic efficiency variation of cobalt oxide with different current densities.

Sr. No.	Dischage Current (mA)	Charge Time (tc) (s)	Discharge Time (td) (s)	Specific power (Watt/g)	Specific Energy (watt hr/kg)	Efficiency (η %)
1.	2	37.71	37.00	2.02	74.75	98.12
2.	4	14.68	14.37	4.04	58.06	97.89
3.	6	8.28	8.09	6.06	49.03	97.71
4.	8	5.47	5.45	8.08	44.04	99.63
5.	10	4.08	3.89	10.10	39.29	95.34
6.	12	3.13	3.05	12.12	36.97	97.44

3.2.3. Cycling Stability Analysis

The electrochemical stability of the cobalt oxide was carried out by using scan rate 60 mV/s in 1 M KOH up to 500 cyclic voltammetry cycles. Fig.4. shows that specific capacitance vs number of cycles of the cobalt oxide electrode, which shows that a stable value of specific capacitance gets after 300 cycles. Here observed capacitance decreases in 62 % retention up to 500 cycles.

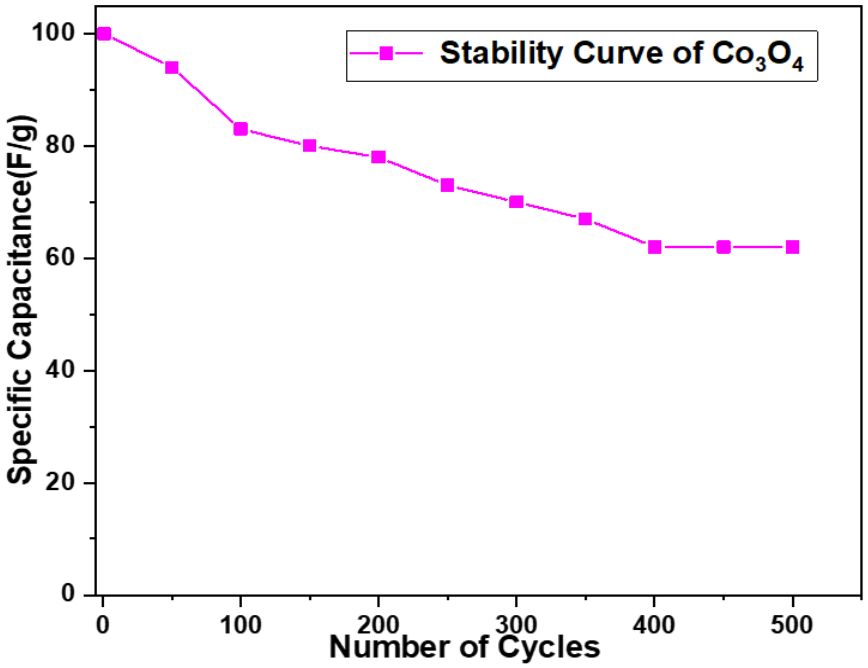

Fig.4. Electrochemical stability of cobalt oxide.

3.2.4 Electrochemical Impedance Spectroscopy

The electrochemical impedance spectroscopy is one of the tools for analysis of the circuitry parameter of the electrodes. The various impedance and capacitive behavior of the cobalt oxide electrode was studied at the operating open circuit potential – 0.789 V in 1 M KOH electrolyte between the frequency 1 mHz to 1 MHz. Fig.5(A). shows that the Nyquist plot of cobalt oxide. This Nyquist Plot consist of two regions one of the higher frequency region and other lower frequency region. In the higher frequency region act as an

interfacial resistance (Rs = 0.20 ohm) and charge-transfer resistance (Rct = 1.95ohm) caused by the faradaic reactions at the lower frequency region. The portion of the curve having an inclination of ~ 45^0 with imaginary axis gives the value of warburg resistance (W= 0.12 milli ohm) and it is related to the frequency dependent diffusion resistance of electrolyte ions resulted at the time of intercalation in pores of electrode. Fig.5(B) shows that the experimental electrochemical impedance data and standard impedance data by simulation using Zsimp Win 3.10 software of Co_3O_4 electrode and inset of it shows matched equivalent circuit.

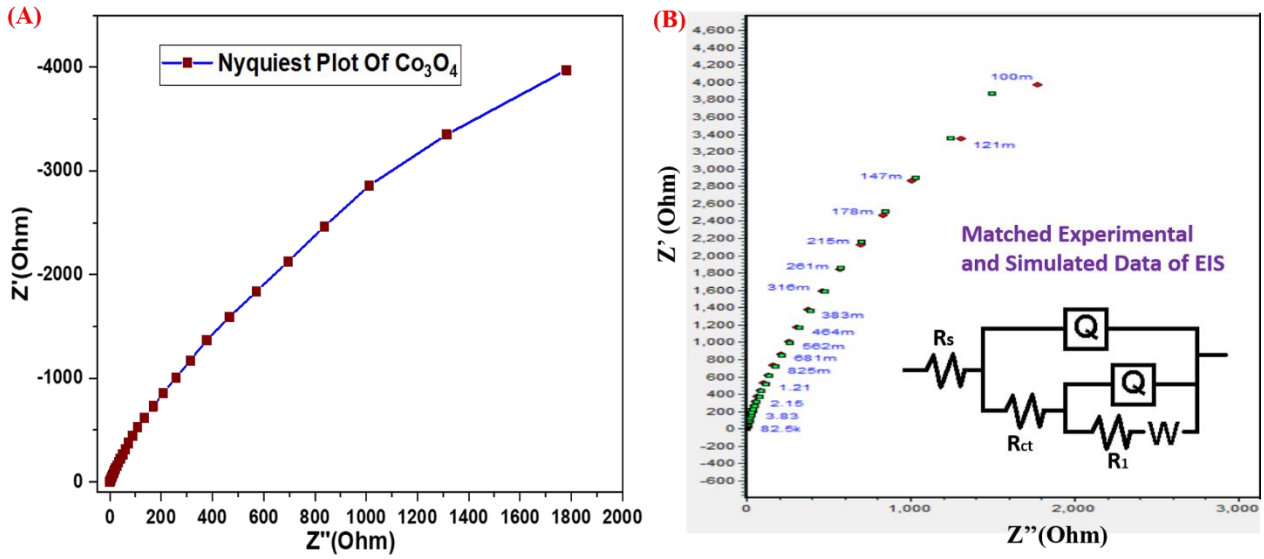

Fig.5(A) Nyquist plot of cobalt oxide. (B) Nyquist plot of Cobalt oxide Simulated and experimental matched.

4 Conclusions

The cobalt oxide (Co_3O_4) thin film electrode was successfully deposited on ss substrate by electrodeposition technique. The prepared cobalt oxide thin films were analyzed by XRD technique. It is shows that the polycrystalline nature with cubic face centered crystal structure of the Co_3O_4. Electrochemical capacitive CV analysis clearly indicates pseudocapacitive behavior of the cobalt oxide nanomaterials. The observed maximum value of specific capacitance (SC) in 1 M KOH electrolytes is 273.2 F/g. The obtained specific power, specific energy and columbic efficiency of the cobalt oxide thin film electrode is 74.75 W/kg, 12.12 Wh/kg, and 99.63%, respectively. The cycling stability clearly shows 62% retentions up to 500 cycles. The electrochemical impedance spectroscopy (EIS) observed that the cobalt oxide has a pseudocapacitive nature of the Co_3O_4 material with this cobalt oxide shows various circuitry parameters.

5 References

[1] TS Ghadge, AL Jadhav, YM Uplane, AV Thakur, SV Kamble, BJ Lokhande, Controlled synthesis, structural, morphological and electrochemical study of Cu (OH) 2@ Cu flexible thin film electrodes prepared via aqueous–non-aqueous routes, *Journal of Materials Science: Materials in Electronics* , 32 (7), 9018, (2021).

[2] Rujia Zou, Kaibing Xu, Teng Wang, Guanjie He, Qian Liu, Xijian Liu,Zhenyu Zhang, Junqing Hu, Chain-like NiCo2O4 nanowires with different exposed reactive planes for high-performance supercapacitors, *J. Mater. Chem. A*, 1 ,8560, (2013).

[3] Jizhang Chen, Junling Xu, Shuang Zhou,Ni Zhao, Ching-Ping Wong,Facile and scalable fabrication of three-dimensional Cu(OH)2 nanoporous nanorods for solid-state supercapacitors, *J. Mater. Chem. A*, 3, 17385, (2015).

[4] Sumanta Kumar Meher,G. Ranga Rao, Ultralayered Co3O4 for High-Performance Supercapacitor Applications, *J. Phys. Chem. C*, 115, 31, 15646,(2011).

[5] BY Fugare, BJ Lokhande,Temperature dependent morphological evaluation of spray pyrolysed TiO 2 thin films prepared via aqueous route: electrochemical characterizations, *Journal of Materials Science: Materials in Electronics* ,28 (22), 16847,(2017).

[6] D.P.Dubala G. S.Gundb, C. D.Lokhandeb, R.Holze, CuO cauliflowers for supercapacitor application: Novel potentiodynamic deposition, *Materials Research Bulletin*, 48,2,923, (2013).

[7] Jinping Chen, Xianyun Peng, Lida Song, Lihan Zhang, Xijun Liu, and Jun Luo, Facile synthesis of Al-doped NiO nanosheet arrays for high performance supercapacitors, *R Soc Open Sci*, 5(11): 180842, (2018).

[8] TS Ghadge, AL Jadhav, BJ Lokhande, Synthesis and electrochemical study of ruthenium influenced copper oxide electrodes prepared by self anodization, Journal of Alloys and Compounds, 824, 153860, (2020).

[9] AV Thakur, BJ Lokhande, Effect of precursor bath temperature on the morphology and electrochemical performance of SILAR-synthesized PPy: FeOOH hybrid flexible electrodes, *Chemical Papers* ,73 (4), 833,(2019).

[10] AV Thakur, BJ Lokhande, Morphological modification for optimum electrochemical performance of highly pristine polypyrrole flexible electrodes, via SILAR immersion time and fabrication of solid state, *Portugaliae Electrochimica Acta* ,36 (6), 377,(2018).

[11] Hoang Luan Jong, Hun Han Hyun, Wook Kang, Wonoh Lee, Highly porous and capacitive copper oxide nanowire/graphene hybrid carbon nanostructure for high-performance supercapacitor electrodes, *Composites Part B: Engineering*, 178, 107464, (2019).

[12] E.d.Lester,G.A.ksomaityte, J.Li,S.Gomez,J.G.Gonzalez, M.Poliakoff, Controlled continuous hydrothermal synthesis of cobalt oxide (Co3O4) nanoparticles, *Progress in Crystal Growth and Characterization of Materials*,58, 1, 3-13,(2012).

[13] Chung-Wei Kung, Chia-Yu Lin, Ta-Jen Li ,R.Vittal, Kuo-ChuanHo, Synthesis of Co3O4 thin films by chemical bath deposition in the presence of different anions and application to H2O2 sensing, *Procedia Engineering* ,25, 847,(2011).

[14] B. R. Sankapal, H.B. Gajare,S.S. Karade,D.P. Dubal,Anchoring cobalt oxide nanoparticles on to the surface multiwalled carbon nanotubes for improved supercapacitive performances, *RSC Adv.*, 5, 48426,(2015).

[15] S.V.Khavale, B.J.Lokhande, Electrochemical performance of potentio-dynamically deposited Co3O4 electrodes: influence of annealing temperature, *Journal of Materials Science: Materials in Electronics* ,28,5106, (2017).

[16] JianChen,NaZhao,Yinggang Zhao, Ji HuY anan, Wang Yujie Wu, Zhongyuan Zhang, Morphology–controlled synthesis of the porous Co3O4 with rugby–shaped and spherical structures and theirs electrochemical properties as negative materials for Li–ion batteries, *Journal of Alloys and Compounds*, 844,156058,(2020).

[17] V. Raman, S. Suresh, P. A. Savarimuthu, T. Raman, A. M. Tsatsakis, K. S. Golokhvast, V. K. Vadivel, Synthesis of Co3O4 nanoparticles with block and sphere morphology, and investigation into the influence of morphology on biological toxicity, *Experimental and TherapeuticMedicine*,553,(2015), https://doi.org/10.3892/etm.2015.2946.

[18] JingCao,Shuangming Wang, Haiming Zhang, TongZ hang, Facile construction of Co3O4 porous microspheres with enhanced acetone gas sensing performances, *Materials Science in Semiconductor Processing*, 101, 10, (2019).

[19] Jingfu Hea, Yanhua Penga, Zhihu Suna, Weiren Chenga, Qinghua Liua, Yajuan Fenga, Yong Jianga, Fengchun Hua, Zhiyun Pana, Qing Bianb, Shiqiang Wei Realizing High Water Splitting Activity on Co3O4 Nanowire Arrays under Neutral Environment, *Electrochimica Acta*,119, (5), 64, (2014).

[20] T.C. Liu, W.G. Pell, B.E. Conway, Stages in the development of thick cobalt oxide films exhibiting reversible redox behavior and pseudocapacitance, *Electrochim. Acta*, 44, 2829, (1999).

[21] V. Srinivasan, J.W. Weidner, Capacitance studies of cobalt oxide films formed via electrochemical precipitation, *J. Power Sources*, 108, 15, (2002).

[22] Ling-Bin Kong, Mao-Cheng Liu, Jun-Wei Lang, Min Liu, Yong-Chun Luo, Long Kang, Porous cobalt hydroxide film electrodeposited on nickel foam with excellent electrochemical capacitive behavior, *Journal of Solid-State Electrochemistry* ,15, 571, (2011).

[23] Gwang-Su Janga , Sadia Ameen, M. Shaheer Akhtarb , Hyung-Shik Shin, Cobalt oxide nanocubes as electrode material for the performance evaluation of electrochemical supercapacitor, *Ceramics International*, https://doi.org/10.1016/j.ceramint.2017.09.217 [24] M. Kalyani, R. N. Emerson, Electrodeposition of nano crystalline cobalt oxide on porous copper electrode for supercapacitor, *Journal of Materials Science: Materials in Electronics*, 30, 1214, (2019).

[25] S V Khavale, B J Lokhande, Optimizations of preparative parameters in potentiodynamic synthesis of cobalt oxide thin films: Capacitive approach, *Indian Journal of Pure & Applied Physics*, 57, 166, (2019).