IJNRD.ORG ISSN : 2456-4184
INTERNATIONAL JOURNAL OF NOVEL RESEARCH AND DEVELOPMENT (IJNRD) | IJNRD.ORG
An International Open Access, Peer-reviewed, Refereed Journal

Green synthesis of cobalt oxide thin films as an electrode material for electrochemical capacitor application on stainless steel substrate

Vijay A.Tarate

Department Of Chemistry, G.M.Vedak College Of Science Tala Raigad, 402111, Maharashtra, India.

Abstract

In this research, we report on the fabrication and characterization of cobalt oxide (Co_3O_4) thin film that is potentially important for electrochemical capacitor applications. For that purpose, the precursor powder of Co_3O_4 was prepared using the cost-effective sol-gel synthesis route and heat treatment at a relatively low temperature. A thin film of Co_3O_4 was prepared on a stainless steel (SS) substrate using a simple doctor-blade method. X-ray diffraction confirmed the formation of pure Co_3O_4 thin film on SS, SEM & TEM confirmed the nano scale nature of the particles in the film. The electrochemical studies Showed a specific capacitance of 225 F g^{-1} for the Co_3O_4 electrode, with a remarkable cycling stability in 1 M NaOH electrolyte, and 80% capacity retention after 1000 cycles at 5 mA cm^{-2} current density (830mA g^{-1}); this demonstrates that Co_3O_4 is a promising material for electrochemical devices.

1. Introduction

The tremendous increase in energy demand for sustainable social and economic development, there is the inefficiency of fossil fuel to meet these demands and the global environmental objectives, are strong driving forces toward a new energy transformation era. To address these problems, human being in the search for green energy sources and development of efficient designs for energy harvesting and storage had become very important. The super capacitor, used as a potentially important energy storage device that offers several advantages including high power density, fast charge/discharge rates, long cycle lifetime, wide range of operating temperatures, environmental friendliness and safety

These features are expected to place ECs(Electrochemical Capacitors) in the list of important solutions for future energy management and the provision of high-pulse power needed for a variety of applications[1-4]. ECs are used as power sources for emergency energy applications, low-voltage portable devices such as cameras, computers, mobile phones and energy generating systems[4-6a]. To meet the requirements of a power source, appropriate electrode materials are needed to ensure satisfactory performance of a super capacitor. To that end, several materials such as carbon materials, conducting polymers, metal[6b-f], metal sulfides, metal hydrides, metal carbides, metal nitrides, metal hydroxides, metal oxides[2-6g] and metal oxyhydroxides[6h-i]were used. In the

middle of these electrode materials, hydrous ruthenium dioxide (RuO_2) finds a unique potential due to its high conductivity and substantial environmental, chemical and thermal stabilities. Nevertheless, several factors such as its high cost, scarcity, and toxic nature are prohibits us for commercial use[7]. Therefore, cheaper metal oxides with various oxidation states and excellent electrochemical behaviors, including cobalt oxide[8] nickel oxide[9], manganese oxide[10], , iron oxide[11], etc., can be appropriate alternatives to RuO_2. On the other hand, cobalt oxide (Co_3O_4) demonstrated suitable functionality as an electrode material in pseudo capacitors[13-14]. This spinel oxide material is one of the most important metal oxides due to its abundance.

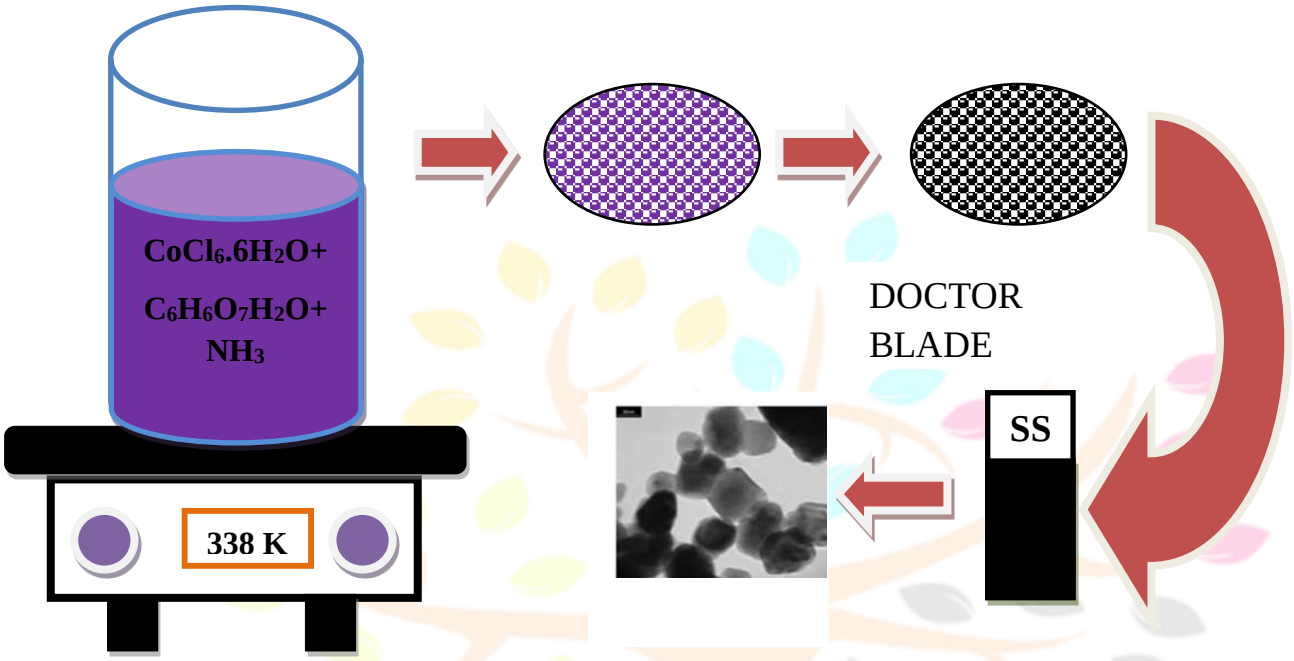


Fig 1.formation of a Co_3O_4 thin film on the SS substrate

The promising advantages of Co_3O_4 for practical applications, we investigated the performance of a thin film of this oxide material as an electrode component for electrochemical capacitor applications[15[a-d]-17]. The film was prepared on a Stainless Steel (SS) substrate which is a conducting material that is widely for different applications including electrode substrates for electrochemical applications[18-20]. The sol-gel technique was adopted to prepare the Co_3O_4 precursor powder owing to its effectiveness in preparing high quality nanoscale oxide particles with homogeneous distribution and controllable chemical Stoichiometry. Citric acid was used in a sol-gel process as a chelating agent[21-23]. X-ray Diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM)[24-25]. measurements were used to examine the structural and morphological properties of the produced Co_3O_4 film. Finally, a thorough electrochemical investigation of the Co_3O_4 electrode was carried out.

2. Experiential Details

2.1. chemicals

Analytical grade starting powders of cobalt Chloride [$Co(Cl)_2.6H_2O$], citric acid [$C_6H_8O_7.H_2O$], and ammonia [NH_3] were provided by SRL Chemicals Ltd, and used in this study without additional purification. Throughout the experiment, double-distilled water was used.

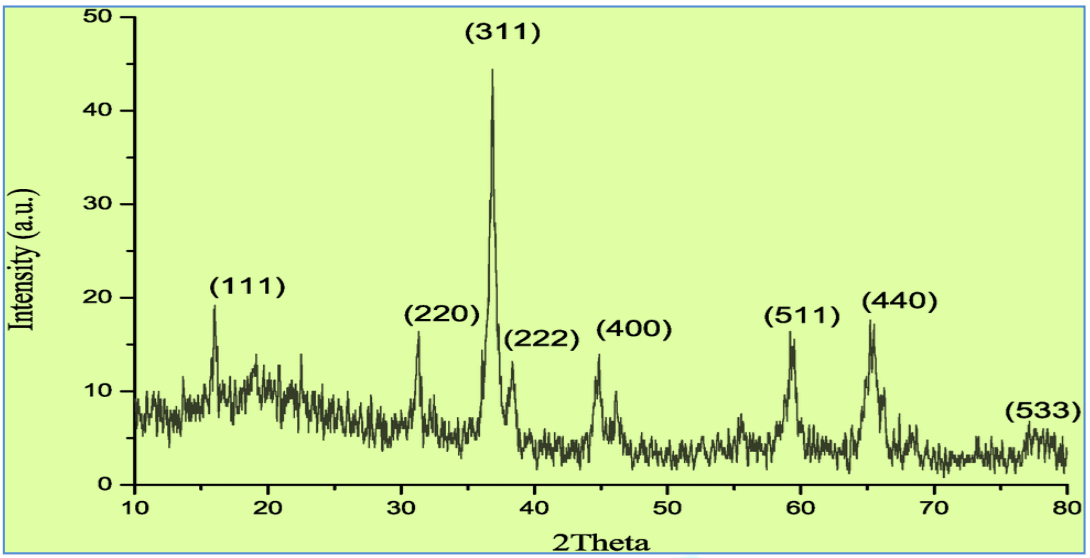


Fig.2 XRD Pattern of Co_3O_4

2.2. Preparation Of Co_3O_4 Thin Film

The sol-gel procedure used for the preparation of the Co_3O_4 precursor powder. In the process, a solution of 0.3 M $Co(Cl)_2.6H_2O$ was prepared by dissolving the powder in double-distilled water, and subsequently introduced drop-by-drop into an aqueous solution of 0.3 M citric acid under magnetic stirring. The pH value was adjusted to ~7 by adding liquid ammonia solution to the mixture, which was heated at 338 K under continuous stirring until the gel was formed after 4 h. The gel was then calcined for 60 min at 623 K to obtain the desired Co_3O_4 powder. A viscous paste of the powder was then prepared with the aid of polyvinyl alcohol (PVA) as a binder. Since Stainless Steel(SS) is a suitable electrode material for solar cells owing to its durable and conducting nature, a thin film of the Co_3O_4 paste was spread on a 1cm * 1 cm SS substrate using the doctor-blade method. The film was subsequently annealed to remove the binder and improve adherence and compactness. The mass of the total active material of Co_3O_4 on the SS substrate was 6 mg. A schematic representation of the formation of a $Co3O_4$ thin film on the SS substrate is shown in Fig. 1.

2.3. Characterizations

The structural analysis of the Co_3O_4 thin film was carried out by XRD technique using RIGAKU, R1NT 2100 with Cu-K_α radiation (λ=1.5406 Å) operating at 40 kV. The patterns were collected in the angular range of $10^0 < 2\theta < 80^0$. Scanning electron microscope (SEM, Model: JEOLJSM6360) and transmission electron microscope (TEM, model: Philips CM30) were used to examine the film's surface morphology, and obtain information relevant to the size distribution of the particles in the film.

2.4. Electrochemical Measurements

The electrochemical study was carried out using a single channel potentiostat (Model: WPG 100 Won A-Tech). In the three-electrode electrochemical cell configuration, a platinum plate serves as the counter electrode, silver-silver chloride (Ag/AgCl) as the reference electrode, and the Co_3O_4@SS film was used as the working electrode. The experimental conditions were initially optimized for the electrochemical measurements, and based on the results, 1 M NaOH was chosen as the most appropriate electrolyte. Subsequently, the cyclic voltammetry (CV) measurements were carried out at a scan rate of 1–10 mV s^{-1} with a potential window of -0.3 to +0.6 V. In addition, the galvanostatic charge discharge (GCD) measurements were performed at current densities of 1–5 mA cm^{-2} (167–833 mA g^{-1}) in the potential range of -0.3 to +0.6 V.Further, the electrochemical impedance spectroscopy (EIS) was carried out using an IVIUM electrochemical workstation system (Ivium, n State),(CV) measurements were

carried out at a scan rate of 1–10 mV s^{-1} with a potential window of -0.3 to +0.6 V. In addition, the galvanostatic charge discharge (GCD) measurements were performed at current densities of 1–5 mA cm^{-2} (167–833 mA g^{-1}) in the potential range of -0.3 to +0.6 V.

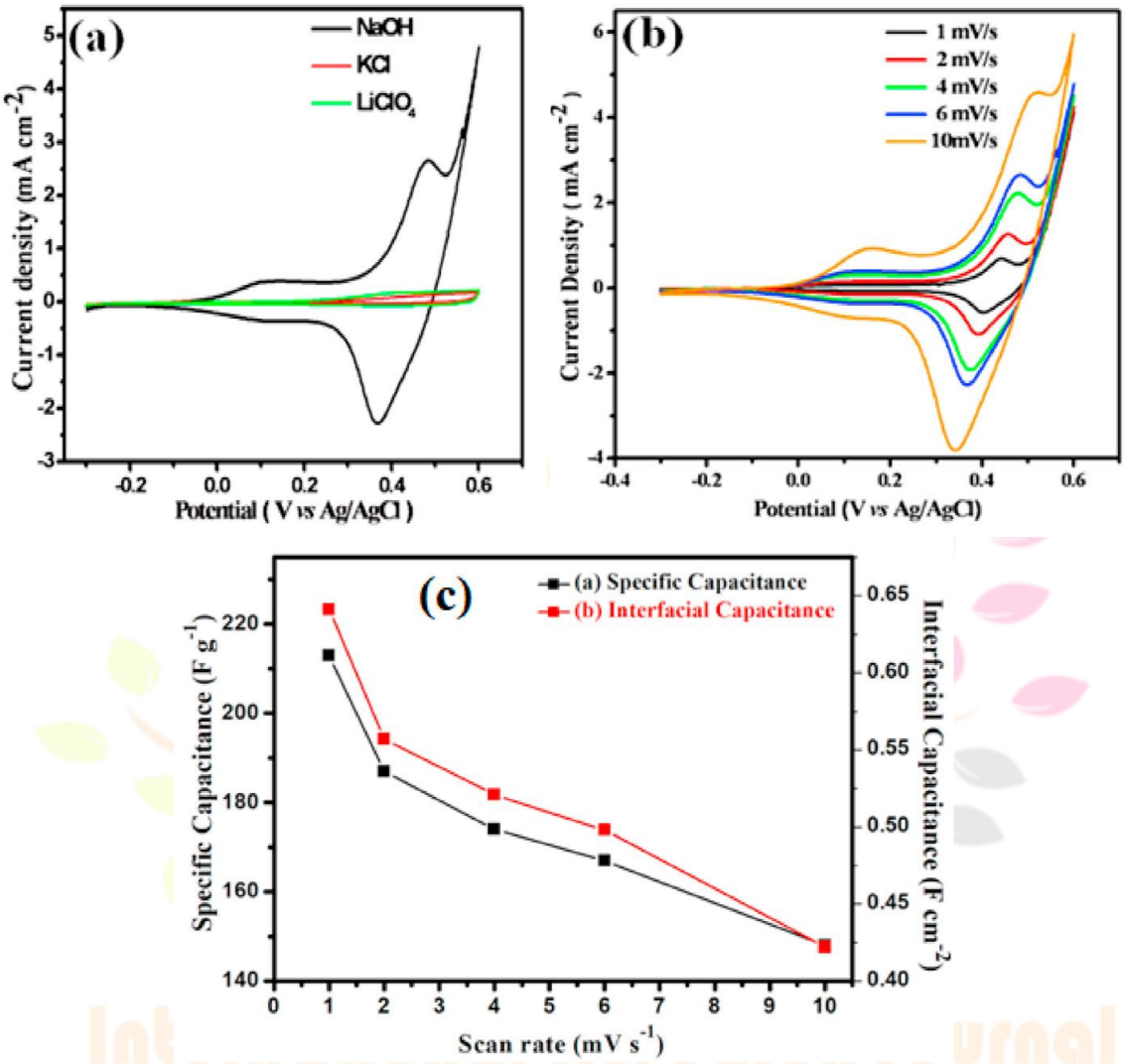


Fig. 3. a)CV scans in NaOH, KCl, and $LiClO_4$ electrolyte at a scan rate of 6 mV s^{-1}, b) CV curves in NaOH at 1, 2, 4, 6, and 10 mV s^{-1} scan rates, c) effect of scan rate on the specific and interfacial capacitance value of the Co_3O_4 electrode.

3. Results And Discussion

3.1. Structure Confirmation

Fig. 2 shows the XRD pattern of the as-prepared Co_3O_4 film on the SS substrate. The figure shows the characteristic diffraction peaks of cubic Co_3O_4 consistent with the standard pattern JCPDS Card No.: 43–1003). Specifically, the peaks at $2\theta = 19.30^0$, 31.50^0, 37.01^0, 38.12^0, 44.80^0, 59.66^0, 65.56^0,76.92^0 correspond to the (111), (220), (311), (222), (400), (511), (440), and (533) reflections of Co_3O_4. The peaks labeled by correspond to the SS substrate and no additional peaks were observed, demonstrating the formation of pure Co_3O_4 spinel phase.

3.2. Electron Microscopy

Fig. 4 (a & b) shows the SEM images, recorded at various magnifications, of the Co_3O_4 thin film surface. Presence of agglomerated, almost spherical-shape Co_3O_4 nanoparticles of different sizes, mostly in the range of 35–50 nm. This is consistent with the crystallite size determined from the broadening of the diffraction peaks, and demonstrates that these particles are single-crystals. Irregular air voids are also detected. TEM of the Co_3O_4 is shown in Fig. 4 (c) with an average diameter of particles was found in the range of 15–20 nm. Since this

diameter is significantly smaller than the average crystallite size, we conclude that the TEM image represents the lower end of the particle size distribution, probably due to the poor suspension of larger particles in the volatile solution carrying the particles SEM images confirmed the 3.3.

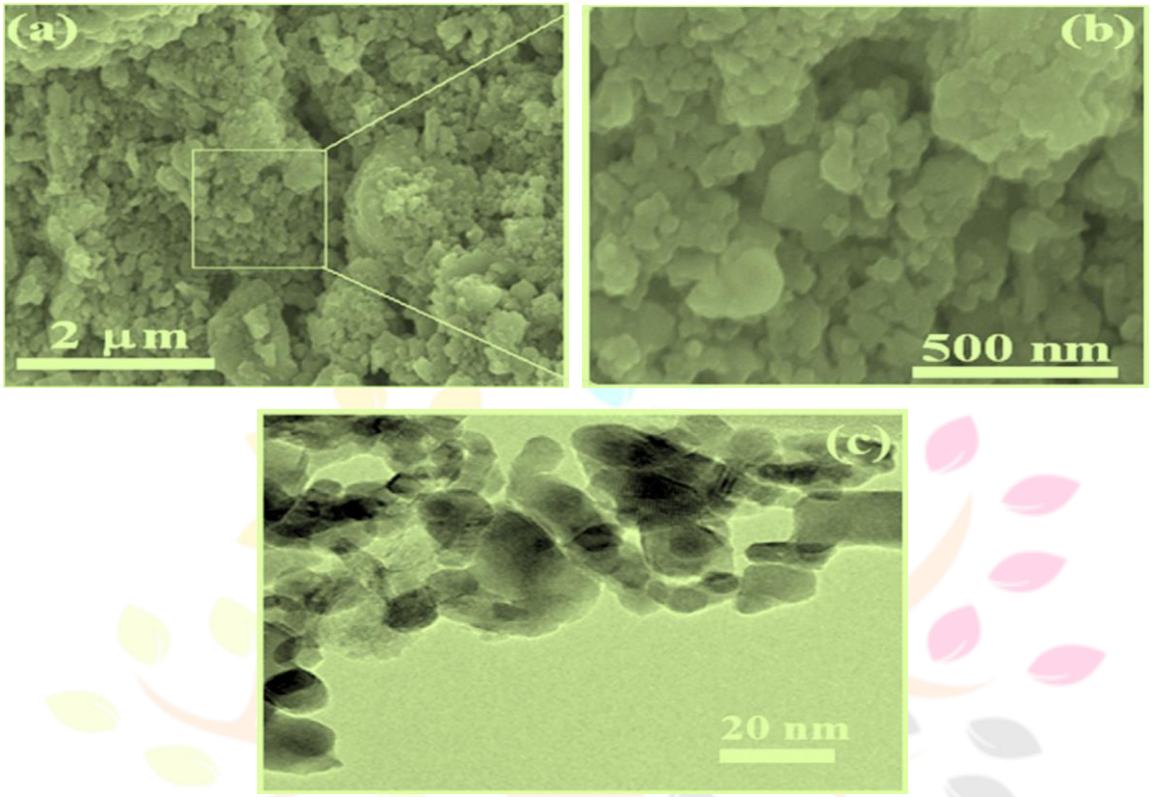


Fig. 4. (a & b) SEM images of Co_3O_4 thin film recorded at different magnifications and (c) TEM image of the Co_3O_4 thin film.

3.3. Electrochemical Measurements

3.3.1. Cyclic-Voltammetry

The cyclic voltammetry (CV) and the galvanostatic charge-discharge (GCD) measurements were used to investigate the super capacitive performance of Co_3O_4 as an electrode material. To identify the most appropriate electrolyte for the present study, the CV measurements of the Co_3O_4 electrode were first performed at a scan rate of 6 mV s^{-1} using three different electrolytes, namely, NaOH, KCl, and $LiClO_4$, and the results are shown in **Fig. 3 (a)**. The superiority of NaOH electrolyte compared to the other electrolytes is evidenced by the well resolved oxidation and reduction peaks of the Co_3O_4 electrode. Also, the area under the curve that was obtained by using NaOH is significantly higher than that obtained by using KCl and $LiClO_4$ electrolytes. Consequently, NaOH was employed as an optimal electrolyte for the subsequent studies. Next, the CV measurements of the Co_3O_4 electrode in 1 M
NaOH electrolyte were performed at scan rates in the range 1–10 mV s^{-1} and potential window of -0.3 to +0.6 V; the results are shown in **Fig. 3 (b).** Evidently, the anodic peaks shift positively with the increase of the scan rate, where as the cathodic peaks shift negatively. This is attribute to the degree of diffusion behavior of OH into the Co_3O_4 matrix at different sweep rates. Further, the observation of a couple of redox reaction peaks in the CV curves indicates that the electrochemical capacitance of the Co_3O_4 electrode originates predominantly from pseudocapacitance[26-28]. The oxidation of CoII→CoIII→CoIV
(charging) and the reduction of CoIV→CoIII→CoII (discharging) produce the anodic and cathodic peaks, respectively[29-30]. According to previous reports concerning the CV

measurements of Co_3O_4 electrode in alkaline electrolytes, the oxidation-reduction reactions may lead to the evolution of a number of cobalt oxide phases signified by the reactions[29-31].

$$Co_3O_4 + H_2O + OH^- \rightarrow 3CoOOH + e^- \quad (1)$$

$$3CoOOH + OH^- \rightarrow 3CoO + H_2O + e^- \quad (2)$$

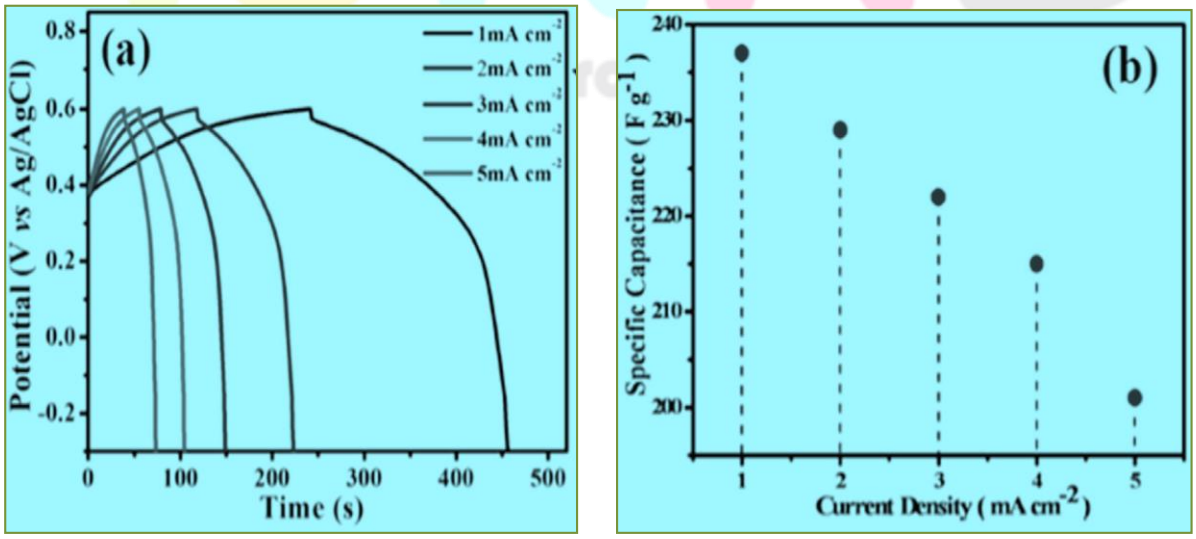
The specific capacitance (SC) is one of the most important indices for evaluating the electrochemical performance of the electrode material. **Fig. 3 (c)** demonstrated that the specific and interfacial capacitance

3.3.2. Galvanostatic Charge-Discharge

The galvanostatic charge-discharge (GCD) curves were used to assess the rate performance of the Co_3O_4 electrode. Fig. 5 (a) shows the GCD curves recorded at various current densities of 1–5 mA cm^{-2} (167–833 mA g^{-1}) in an aqueous 1 M NaOH electrolyte at potentials ranging from -0.3 to+ 0.6 V. It is evident that the cycle period decreases with the increase of the current density, and the shape of the discharge curve is different from that for a pure doble layer capacitor. The curves demonstrated rapid charging and discharging with obvious non-linear behavior of the potential with time, confirming the pseudo-capacitance behavior observed in the CV curves. The small initial sharp drop in the discharge regime is associated with the internal resistance, whereas the subsequent slow potential decay is associated with the Faradaic redox reaction (Eq. (2)). The last rapid potential decay in the GCD curves is due to the electric double layer capacitance. The SC value was calculated from the GCD data in accordance with the relation:

$$SC = I * t \div m * \Delta V \quad (3)$$

Here I is the discharge current, t is the discharge time, m is the mass of the electro-active material, and ΔV is the potential window for the cycling test. The calculated SC values are 237, 229, 222, 215, and 201 F g^{-1} at the different current densities as indicated by Fig. 5 (b). Similar trends of decreasing the SC with the increase of current density were reported by others for different electrode materials . The inaccessibility of some active surface areas for charge storage could be responsible for the decrease in the SC value. For practical usage, good cycling performance is an important feature of high-performance supercapacitors. The cycle performance of Co_3O_4 electrode measured at 5mA cm^{-2} current density for 2000 cycles is shown in Fig. 5 (c). Negligible decrease of the capacitance was observed in the first 200 cycles, and ~ 80% retention of SC was observed after 1000 cycles. This indicates good stability of the Co_3O_4 electrode performance The decrease in performance after 2000 cycles could be associated withthe loss of active material (due to shrinkage) in the current accumulator which results in blockage of the ordered structure[32-35].



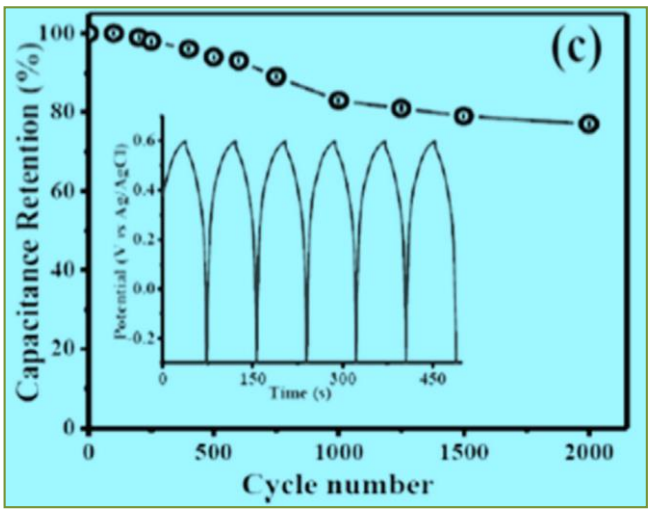


Fig. 5. (a) Galvanometric charge-discharge measurement recorded at a current density of 1, 2, 3, 4, and 5 mA cm^{-2}, **(b)** plot of the effect of current density on SC value of Co_3O_4 electrode, and **(c)** variation of capacitive retention as a function of the number of cycles.

4. Conclusions

In conclusion, using a simple sol-gel approach, we were able to successfully synthesize Co_3O_4 nanoparticles for electrode material and investigated its characteristics and potential for electrochemical applications. The super capacitive performance of Co_3O_4 electrode demonstrated high sensitivity to experimental conditions. Of the three electrolytes investigated in this study, NaOH was found to be the most appropriate. However, the specific capacitance decreased by ~ 30% with the increase of the scan rate from 1 mV s^{-1} to 10 mVs^{-1}. The GCD study of the Co_3O_4 electrode revealed a specific capacitance as high as 237 F g-1 at a current density of 1 mA cm^{-2} in aqueous NaOH electrolyte. However, the specific capacitance decreased monotonically down to 201 F g^{-1} with the increase of the current density up to 5 mA cm^{-2}. Further, after 1000 charge-discharge cycles at a current density of 5 mA cm^{-2}, the specific capacitance of the Co_3O_4 electrode retained 80% of its original value, indicating that the produced Co_3O_4 electrode could be a possible candidate in electrochemical storage devices. charge-discharge cycles at a current density of 5 mA cm^{-2}, the specific capacitance of the Co_3O_4 electrode retained 80% of its original value, indicating that the produced Co_3O_4 electrode could be a possible candidate in electrochemical storage devices.

References

1. Paresh S. Gaikar [a], Ankita P. Angre [b], Gurumeet Wadhawa [c], Pankaj V. Ledade [d], Sami H. Mahmood [e], Trimurti L. Lambat [f], "Green synthesis of cobalt oxide thin films as an electrode material for electrochemical capacitor application" Current Research in Green and Sustainable Chemistry 5 (2022) 100265 https://doi.org/10.1016/j.crgsc.2022.100265.
2. G. Wang, L. Zhang, J. Zhang, "A review of electrode materials for electrochemical supercapacitors" Chem. Soc. Rev. 41 (2012) 797–828.
3. P.S. Gaikar, S.L. Gaikwad, R.K. Mahadule, G.C. Wakde, A.P. Angre, A.S. Bandekar, P.R. Arjunwadkar, "Cobalt hydroxide as an efficient electrode for electrochemical supercapacitor application" J.Nanoeng.Nanomanufacturing 6 (2016) 157–160.
4. K. Xiang, Z. Xu, T. Qu, Z. Tian, Y. Zhang, Y. Wang, M. Xie, X. Guo, W. Dinga, X. Guo, "Two dimensional oxygen-vacancy-rich Co_3O_4 nanosheets with excellent supercapacitor performances,"Chem. Commun. 53 (2017) 12410–12413.

5. **a)** P.S. Gaikar, S.T. Navale, S.L. Gaikwad, A. Al-Osta, V.V. Jadhav, P.R. Arjunwadkar, Naushad Mu, R.S. Mane, "Pseudocapacitive performance of a solution processed β-Co(OH)2 electrode monitored through its surface morphology and area" Dalton Trans. 46 (2017) 3393–3399;
b) A. Mahmood, J.L. Wang, "A review of grazing incidence small-and wide-angle Xray scattering techniques for exploring the film morphology of organic solar cells" Solar RRL 4 (10) (2020) 2000337.

6. **a)** X. Xia, Y. Zhang, D. Chao, C. Guan, Y. Zhang, L. Li, X. Ge, I. Bacho, J. Tu, H. Fan,"Solution synthesis of metal oxides for electrochemical energy storage applications" Nanoscale 6 (2014) 5008–5048;
b) A.V. Thakur, B.J. Lokhande, "C 10 H 8 N 2-PPy hybrid flexible electrodes: SILAR synthesis and electrochemical study" J. Mater. Sci. Mater. Electron. 29 (2) (2018) 1630–1635;
c) A.V. Thakur, B.J. Lokhande, "Effect of the molar concentration of pyrrole monomer on the rate of polymerization, growth and hence the electrochemical behavior of highly pristine PPy flexible electrodes,"Heliyon 5 (11) (2019) e02909;
d) A.V. Thakur, B.J. Lokhande, "Morphological modification for optimum electrochemical performance of highly pristine polypyrrole flexible electrodes, via SILAR immersion time and fabrication of solid state symmetric device, Port" Electrochim. Acta 36 (6) (2018) 377–392;
e) A.V. Thakur, B.J. Lokhande, "Dip time-dependent SILAR synthesis and electrochemical study of highly flexible PPy-Cu (OH) 2 hybrid electrodes for supercapacitors" J. Solid State Electrochem. 21 (9) (2017) 2577–2584;
f) A.V. Thakur, B.J. Lokhande, "Effect of dip time on the electrochemical behavior of PPy-Cu (OH) 2 hybrid electrodes synthesized using pyrrole and $CuSO_4$" E-Polymers 17 (2) (2017) 167–173;
g) A. Mahmood, "Recent research progress on quasi-solid-state electrolytes for dyesensitized solar cells" J. Energy Chem. 24 (6) (2015) 686–692;
h) A.V. Thakur, B.J. Lokhande, "Effect of Number of Silar Cycles on Cyclic Voltammetric Performance of ppy:CoO(OH) Flexible Hybrid Electrodes Prepared Using Pyrrole and Co(NO3)2" vol. 5, 2017, pp. ,146–149, 12;
i) A.V. Thakur, B.J. Lokhande, "Effect of precursor bath temperature on the morphology and electrochemical performance of SILAR-synthesized PPy: FeOOH hybrid flexible electrodes" Chem. Pap. 73 (4) (2019) 833–841.

7. C.M. Chuang, C.W. Huang, H.S. Teng, J.M. Ting, "Hydrothermally synthesized RuO_2/Carbon nanofibers composites for use in high-rate supercapacitor" Compos. Sci. Technol. 72 (2012) 1524–1529.

8. A.D.Jagadale,V.S.Kumbhar,C.D.Lokhande* "Supercapacitive activities of potentiodynamically deposited nanoflakes of cobalt oxide (Co_3O_4)thin film electrode" https://dx.doi.org/10.1016/j.jcis.2013.05.037

9. Y.B. Xie, C.J. Huang, L.M. Zhou, Y. Liu, H.T. Huang, "Supercapacitor application of nickel oxide–titania nanocomposites" Compos. Sci. Technol. 69 (2009), 2108–2014.

10. Q. Li, Z.L. Wang, G.R. Li, R. Guo, L.X. Ding, Y.X. Tang, "Design and synthesis of MnO_2/Mn/MnO_2 sandwich-structured nanotube arrays with high supercapacitive performance for electrochemical energy storage" Nano Lett. 12 (2012) 3803–3807.

11. C.Z. Yuan, L. Yang, L.R. Hou, L.F. Shen, X.G. Zhang, D. Lou, "Growth of ultrathin mesoporous Co_3O_4 nanosheet arrays on Ni foam for high-performance electrochemical capacitors" Energy Environ. Sci. 5 (7) (2012) 7883–7887.

12. W.H. Shi, J.X. Zhu, D.H. Sim, Y.Y. Tay, Z.Y. Lu, X.J. Zhang, "Achieving high specific charge capacitances in Fe_3O_4/reduced graphene oxide nanocomposites" J. Mater. Chem. 21 (10) (2011) 3422–3427.

13. P.S. Gaikar, S.T. Navale, V.V. Jadhav, Mu Naushad, F.J. Stadler, R.S. Mane, P.R. Arjunwadkar, "A simple wet-chemical synthesis, reaction mechanism, and charge storage application of cobalt oxide electrodes of different morphologies" Electrochim. Acta 253 (2017) 151–162.

14. S. Chen, J. Zhu, X.J. Wang, "One-step synthesis of graphene-cobalt hydroxide nanocomposites and their electrochemical properties" J. Phys. Chem. C 114 (27) (2010) 11829–11834.

15. S.T. Navale, C. Liu, P.S. Gaikar, V.B. Patil, R.U.R. Sagar, B. Dua, R.S. Mane, F.J. Stadler, "Solution-processed rapid synthesis strategy of Co_3O_4 for the sensitive and selective detection of H2S," Sensor. Actuator. B 245 (2017) 524–532.

16. X. Xie, Y. Li, Z.Q. Liu, M. Haruta, W. Shen, "Low-temperature oxidation of CO catalyzed by Co_3O_4 Nanorods" Nature 458 (7239) (2009) 746–749.

17. a) X. Lou, D. Deng, J. Lee, J. Feng, L. Archer, "Self-supported formation of needlelike Co_3O_4 nanotubes and their application as lithium-ion battery electrodes" Adv. Mater. 20 (2) (2008) 258–262;
b) A. Mahmood, J.L. Wang, "Machine learning for high performance organic solar cells: current scenario and future prospects" Energy Environ. Sci. 14 (1) (2021) 90–105;

c) A. Mahmood, J.L. Wang, "A time and resource efficient machine learning assisted design of non-fullerene small molecule acceptors for P3HT-based organic solar cells and green solvent selection" J. Mater. Chem. 9 (28) (2021) 15684–15695;
d) A. Mahmood, A. Irfan, J.L. Wang, "Developing efficient small molecule acceptors with sp2-hybridized nitrogen at different positions by density functional theory calculations, molecular dynamics simulations and machine learning" Chem–A Eur J (2021). https://doi.org/10.1002/chem.202103712.

18. B.J. Hwang, R. Santhanam, D.G. Liu, "Characterization of nanoparticles of $LiMn_2O_4$ synthesized by citric acid sol–gel method" J. Power Sources 97 (2001) 443–446.

19. A. Al-Hunaiti, Q. Mohaidat, I. Bsoul, S. Mahmood, D. Taher, T. Hussein, "Synthesis and characterization of novel phyto-mediated catalyst, and its application for a selective oxidation of (VAL) into vanillin under visible light" Catalysts 10 (2020) 839.

20. V.G. Hadjiev, M.N. Iliev, I.V. Vergilov, "The Raman spectra of Co_3O_4,, J. Phys. C Solid State Phys". 21 (1988) L199–L201.

21. K.S.W. Sing, "Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity", Pure Appl. Chem. 54 (11) (1982) 2201–2218.

22. W. Liu, X. Li, D. Jiangm, J. Qian, Q. Liu, X. Yang, K. Wang, "Reactable ionic liquid assisted preparation of porous Co_3O_4 nanostructures with enhanced supercapacitive performance" Cryst Eng Comm 16 (12) (2014) 2395–2403.

23. M.X. Liao, Y.F. Liu, Z.H. Hu, Q. Yu, J., "Novel morphologic Co_3O_4 of flower-like hierarchical microspheres as electrode material for electrochemical capacitors" J. Alloys Compd. 562 (2013) 106–110.

24. C. Xu, B. Li, H. Du, F. Kang, Y. Zeng, "Electrochemical properties of nanosized hydrous manganese dioxide synthesized by a self-reacting microemulsion Method" J. Power Sources 180 (2008) 664–670.

25. K.H. Chang, C.C. Hu, "Oxidative synthesis of RuOx .n H_2O with ideal capacitive characteristics for supercapacitors" J. Electrochem. Soc. 151 (2004) 958–964.

26. S.K. Meher, G.R. Rao, "Effect of microwave on the nanowire morphology, optical, magnetic, and pseudocapacitance behavior of Co_3O_4" J. Phys. Chem. C 115 (51) (2011) 25543–25556.

27. S.K. Meher, G.R. Rao, "Ultralayered Co_3O_4 for high-performance supercapacitor applications" J. Phys. Chem. C 115 (31) (2011) 15646–15654.

28. a) V. Subramanian, S.C. Hall, P.H. Smith, B. Rambabu, "Mesoporous anhydrous RuO_2 as a supercapacitor electrode material" Solid State Ionics 175 (2004) 511–515;
b) A.V. Thakur, B.J. Lokhande, "Electrolytic anion affected charge storage mechanisms of Fe_3O_4 flexible thin film electrode in KCl and KOH: a comparative study by cyclic voltammetry and galvanostatic charge–discharge" J. Mater. Sci. Mater. Electron. 28 (16) (2017) 11755–11761;
c) A.V. Thakur, B.J. Lokhande, "Synthesis and electrolytic cation-dependent cyclic voltammetric study of SILAR deposited PPy-Cr_2O_3 in equimolar aqueous solutions of H_2SO_4, Na_2SO_4, and K_2SO_4" Mater.Renew. Sustain. Energy 7 (3) (2018) 1–8.

29. S.G. Kandalkar, J.L. Gunjakar, C.D. Lokhande, "Preparation of cobalt oxide thin films and its use in supercapacitor application" Appl. Surf. Sci. 254 (17) (2008) 5540–5544.

30. V.R. Shinde, S.B. Mahadik, T.P. Gujar, C.D. Lokhande, "Supercapacitive cobalt Oxide (Co_3O_4) thin films by spray pyrolysis" Appl. Surf. Sci. 252 (20) (2006) 7487–7492.

31. R. Tummala, R.K. Guduru, P.S. Mohanty, "Nanostructured Co_3O_4 electrodes for supercapacitor applications from plasma spray technique" J. Power Sources 209 (2012) 44–51.

32. H. Li, M. Yu, F. Wang, P. Liu, Y. Liang, J. Xiao, C.X. Wang, Y. Tong, G. Yang, "Amorphous nickel hydroxide nanospheres with ultrahigh capacitance and energy density as electrochemical pseudocapacitor materials" Nat. Commun. 4 (2013) 1894–1902.

33. L. Mei, T. Yang, C. Xu, M. Zhang, L. Chen, Q. Li, T. Wang, "Hierarchical mushroomlike $CoNi_2S_4$ arrays as a novel electrode material for supercapacitors" Nano Energy 3 (2014) 36–45.

34. S. Mondal, U. Rana, S. Malik, "Graphene quantum dot-doped polyaniline nanofiber as high performance supercapacitor electrode materials" Chem. Commun. 51 (62) (2015) 12365–12368.

35. Z. Fan, J. Yan, T. Wei, L. Zhi, G. Ning, T. Li, F. Wei, "Asymmetric supercapacitors based on graphene/MnO2 and activated carbon nanofiber electrodes with high power and energy density" Adv. Funct. Mater. 21 (12) (2011) 2366–2375.