Electrochemical oxygen evolution on fabricated Ni/$Ni_{0.3}Co_{2.7}O_4$ in alkaline medium

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Abstract

The $Ni_{0.3}Co_{2.7}O_4$ was prepared by the low temperature sol-gel route using span-60 as precursor for electrochemical formation of oxygen in alkaline medium. The prepared oxide was characterized by the FTIR, P-XRD and SEM techniques to ensure their formation, structure and morphology. The oxide electrode was fabricated on nickel support and tested for their electrochemical activity by the cyclic voltammetry and the Tafel polarization techniques. The cv curve of oxide electrode exhibited a couple of redox peaks, one cathodic peak (E_{pa} = 168 mV) and another anodic peak (E_{pa} = 550 mV). The electrocatalytic activity for OER was tested by the Tafel polarization technique. Investigation showed that $Ni_{0.3}Co_{2.7}O_4$ was found to be highly electrode for OER with the Tafel slope value 128 mV dec^{-1} and current density (j) of 50 mA cm^{-2} at 379 mV oxygen over potential and the OER followed first order reaction kinetics with respect to the change in [OH^-] concentration.

The temperature-dependent parameters such as electrochemical activation energy (Ea) and standard entropy of reaction ($\Delta S_{el}^{0\neq}$) were also determined for the OER and their respective values are ~27 kJ $mol^{-1}$and -303 J $deg^{-1}mol^{-1}$. A highly negative value of entropy of reaction suggests the involvement of adsorption phenomenon in OER.

Keywords: Sol-gel synthesis, Oxide roughness factor, Cyclic voltammetry, Tafel polarization, OER.

Introduction

Environment and energy are the two most important concerns in the current scenario[33]. According to International Energy Outlook 2021 published by Energy Information Administration (EIA), 15% more energy is projected to be needed in 2050 compared to 2023, due to increase in population and modernisation in developing countries[9].

However, most of the energy comes from the fossil fuels that have limited and non-sustainable resources. The use of the fossil fuels is also responsible for the air pollution, global warming and other health issues[41]. The increasing energy demand and its impact on environment impelled to find energy resources that are renewable and can be efficiently used as substitute of fossil fuels[40]. There are many alternative renewable energy resources like solar energy, wind energy but hydrogen is one of the efficient substitutes for energy production.

Hydrogen's potential to become a clean fuel can be credited because of the electrolytic splitting of water as it accounts to be one of the most promising methods[13]. Also, the performance of electrocatalysts plays a major role to determine the efficiency of this water splitting which would hence play an important role in reducing the energy barrier for the hydrogen evolution reactions and the oxygen evolution reactions. So, considering these points, the transition metal-based compounds have drawn significant attention because of their abundance, low cost and excellent catalytic properties[30].

For hydrogen evolution reactions (HER) and oxygen evolution reactions (OER), nickel cobaltite which is a mixed metal oxide, has proven to be a very effective electrocatalyst for both of them more specifically in the alkaline media[11,32]. What makes this metal a perfect choice is its perfect amalgamation of electronic, structural and chemical properties that in turn enhances its electrolytic activity, stability and durability. Also, for the optimal charge transfer and its reaction kinetics, we have the spinel structure of nickel cobaltite that provides a stable framework for the active sites[5]. Another factor that makes this metal a suitable and an ideal option for the sustainable electrochemical applications is the mutual interaction occurring between nickel and cobalt ions, thereby enhancing the overall performance of nickel cobaltite[38].

It is very important to understand the fundamental mechanisms underlying its catalytic activity as well as the strategies undertaken to improve its performance in the alkaline media which is crucial for practical implementation. The objective of this research paper is to investigate the electrocatalytic properties of synthesised nickel cobalt oxide nanoparticles in oxygen evolution reaction in alkaline medium. There are various methods for the synthesis of nickel cobalt oxide depending on the desirable properties and application of the nano particles namely, sol-gel method[3,13,19,20] co-precipitation method[6,7,15,39] hydrothermal method[22,35] electrodeposition method[4,12,18,21,28,34,36], microwave assisted flame pyrolysis[23] and green methods[16,24].

In the current study, the nickel cobalt oxide nanoparticles are prepared by economical sol -gel method using Span-60 and cobalt (II)nitrate as precursors. The prepared nickel cobaltite nanoparticles were characterised by X-Ray diffraction,

Scanning electron microscopy and Fourier Transform Infrared spectroscopy. The electrochemical properties and activity are studied by the Tafel slope measurement and cyclic voltammetry.

Material and Methods

Synthesis: The nickel doped cobalt oxide were prepared by sol-gel method[2]. The method involved addition of cobalt (II)nitrate hexahydrate (ACS, AR, Sigma Aldrich ≥98%) and nickel (II)nitrate hexahydrate (ACS, AR, Sigma Aldrich ≥98%) to the molten Span-60(CDH, India). The mixture was then dried to give gel, which was then calcined in a Muffle furnace for five hours at 350°C to produce the desired spinel oxide.

Characterisation: The characterisation of the $Ni_{0.3}C0_{2.7}O_4$ prepared by the sol-gel method using Span-60 was done by Fourier Transform infrared (FTIR) spectroscopy and X-ray diffraction (XRD) method. The FTIR was done on IRSPIRIT-T Shimadzu spectrometer and powder XRD was done with Cu-Kα radiation in the range of phase angle 20 to 80^0 at wavelength (λ = 1.54059 Å). The morphology and the particle size were investigated by Scanning Electron Microscopy (SEM) using Zeiss Scanning electron microscope.

Electrochemical characterisation: To study the electrochemical properties, the electrode of the $Ni_{0.3}C0_{2.7}O_4$ was prepared by repeated coating of oxide slurry in triton X-100 to one side of nickel plate pre- treated by HCl and rinsed by acetone ultrasonically followed by washing with double distilled water and then sintered at 300°C in an electrical furnace for one hour to have oxide loading of ~ 5 mg/cm^2. A flattened end of the copper wire was joined at the back side of nickel plate using silver paste and mounted with Araldite (epoxy resin) leaving an exposed area of about 0.5 cm^2. It was done to maintain the electrical connect. The electrocatalytic properties of the prepared electrode were investigated in a single compartment Pyrex glass cell consisting three electrodes system having a working electrode (Ni/oxide electrode), a counter electrode (graphite rod) and a reference electrode (Hg/HgO/1MKOH (0.098V vs NHE)) using the CHI electrochemical work station.

Results and Discussion

FT-IR Analysis: The two peaks in FTIR at 560 and 605 cm^{-1} is due to the characteristic stretching vibrations of metal-oxygen (Ni-O and Co-O) spinel structure of cobaltite's having tetrahedral and octahedral sites. Moreover, an additional absorption at 477 cm^{-1} is a characteristic absorption of nickel oxide and the variation can be due to doping of nickel[37]. The broad peaks at 3525 and 1620 cm^{-1} are caused by the stretching and bending vibrations of hydroxyl group of water molecules and a small peak at 2462 cm^{-1} is due to adsorbed atmospheric carbon di-oxide.

XRD Analysis: The crystallite size of $Ni_{0.3}C0_{2.7}O_4$ was investigated by the powder XRD in the range of phase angle (2θ) from 20 to 80^0 at λ = 1.54059 Å. Figure 2 depicts the XRD powder pattern indicating the formation of nano-sized crystalline nickel cobaltite exhibiting the peaks at (111), (220), (311), (400), (111), (511) and (440) in agreement with previous works[1] and matched with JCPDS file no. 76-1802. The crystallite size was calculated with the help of Debye Scherrer equation:

$$S = \frac{K\,\lambda}{\beta\,\cos\theta}$$

where S is crystallite size, θ is Braggs angle in radians, β is full width at half maximum (FWHM) in radians of the most intense peak and K is the Scherrer constant. The calculated value of crystallite size of nickel cobaltite prepared by sol-gel method was found to be 10 nm that was comparatively lower than previous synthesis[10]

SEM Analysis: The surface morphology of $Ni_{0.3}Co_{2.7}O_4$ synthesised by sol-gel method was investigated by conducting Scanning electron microscopy at different modifications (10000X, 25000X and 50000X) as shown in figure 3.

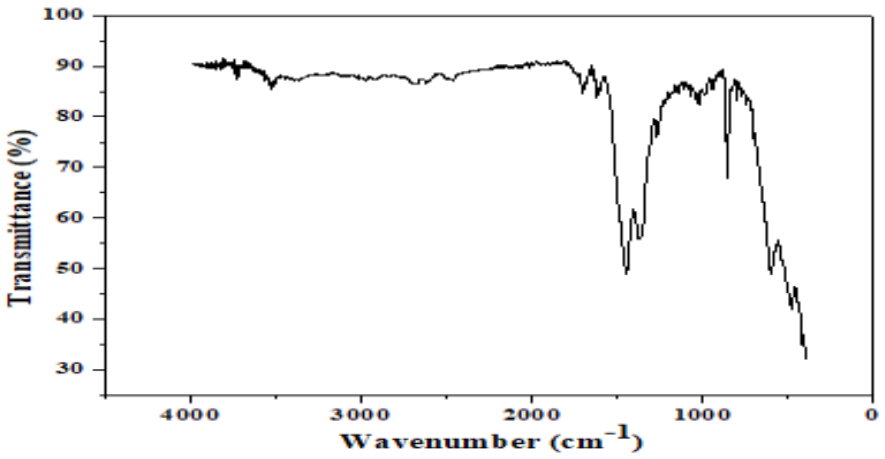

Fig. 1: FTIR spectra of nickel-doped cobalt oxide ($Ni_{0.3}Co_{2.7}O_4$) prepared at 350°C

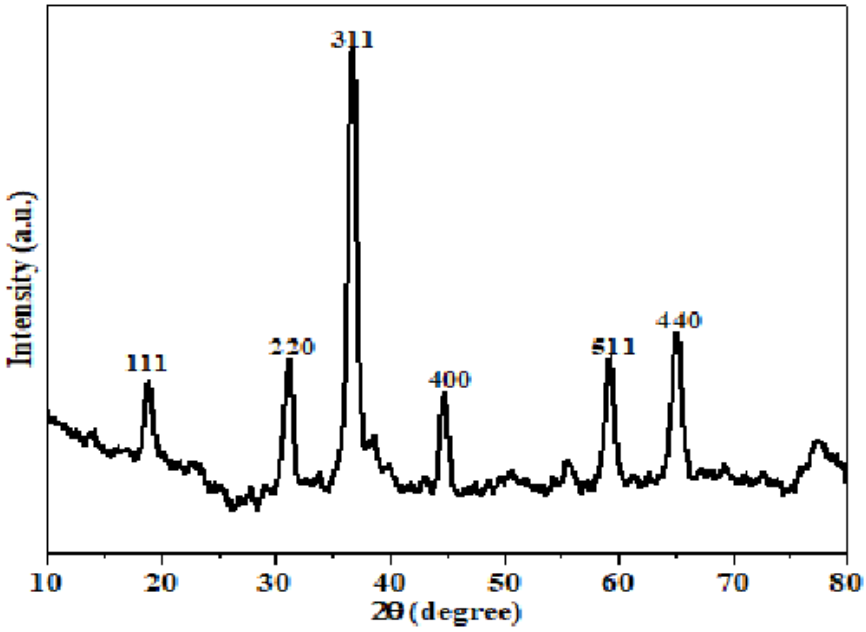

Fig. 2: XRD of nickel substituted cobalt oxide ($Ni_{0.3}Co_{2.7}O_4$) prepared at 350°C

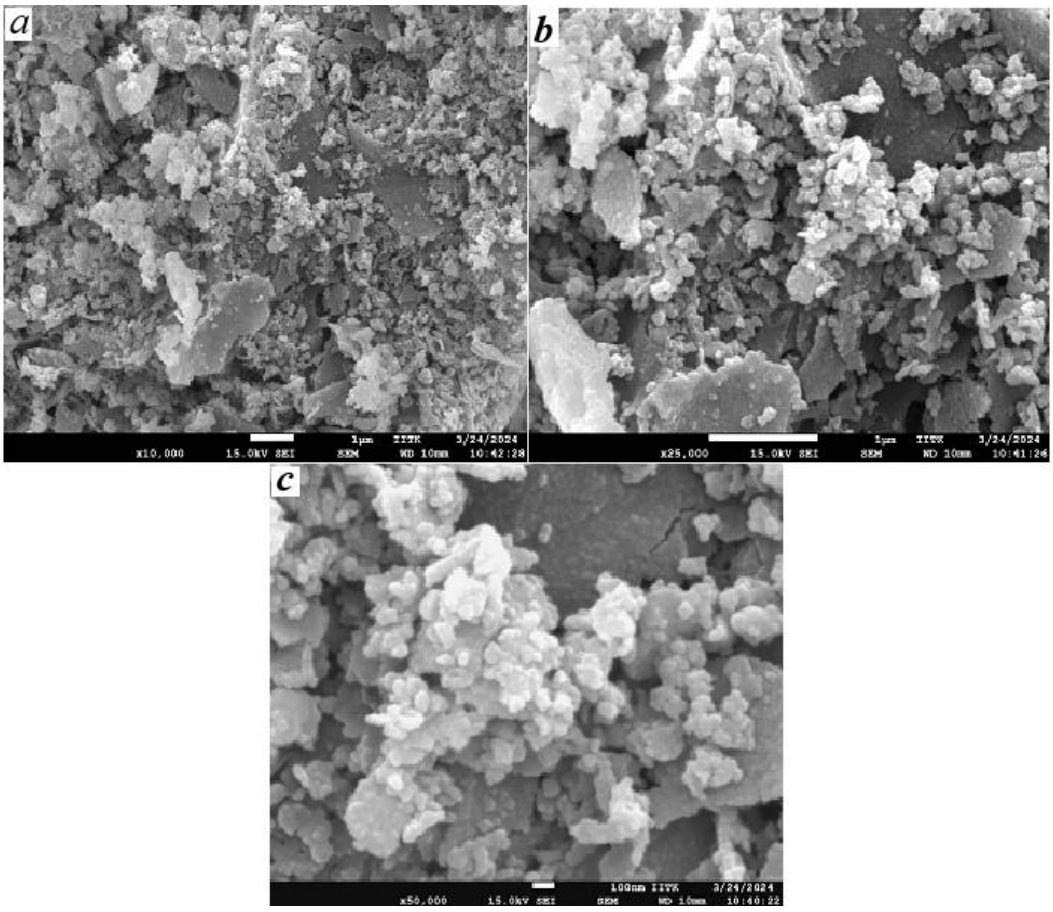

Fig. 3: FE SEM of $Ni_{0.3}Co_{2.7}O_4$ at different magnifications: (a) X 10000 (b) X 25000 and (C) X 50000

According to the SEM image, the oxide nanoparticles are agglomerated in granular shape with particle size ranging between ≈ 13-24 nm.

Cyclic Voltammetry: Figure 4 depicts the cyclic voltammogram of fabricated electrode of nickel substituted cobalt oxide ($Ni_{0.3}Co_{2.7}O_4$) vs Hg/HgO noted between potential range 0 to 0.7 V at the scan rate of 20 $mVsec^{-1}$ at 25°C in 1M KOH. The voltammograms showed redox reaction at the interface of electrode with an anodic peak potential range (E_{pa}= 550 mV) and corresponding cathodic peak potential range (E_{pc}= 169 mV), ΔE_p= 381 mV and

formal redox potential (E^o = 359 mV). The peak potential values correspond to the redox process[14,29] $Ni(OH)_2 + OH^- \leftrightarrow NiOOH + H_2O + e^-$. The voltammogram also revealed that the ratio of peak currents at the anodic and cathodic peaks is greater than unity, indicating that the redox process is irreversible.

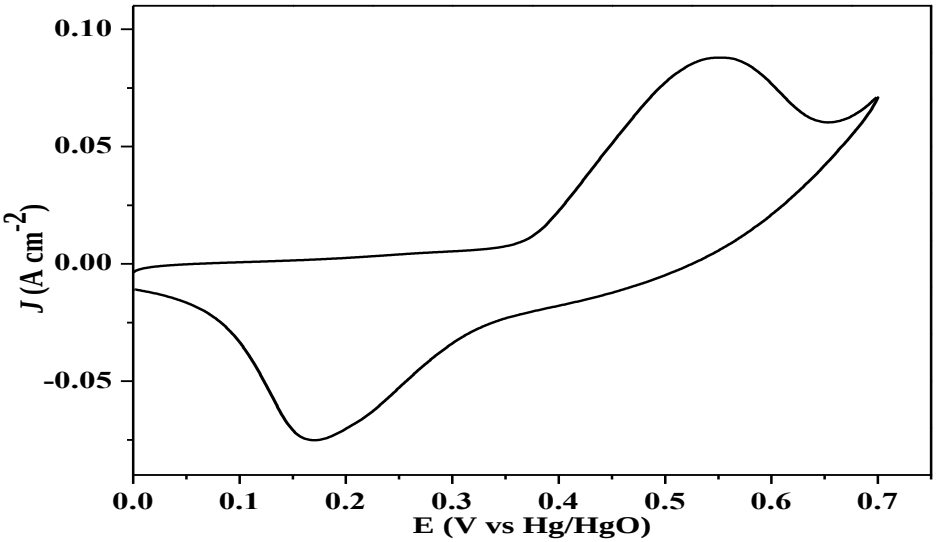

Fig. 4: Cyclic voltammogram of Ni/$Ni_{0.3}Co_{2.7}O_4$ for OER in 1M KOH at 25°C.

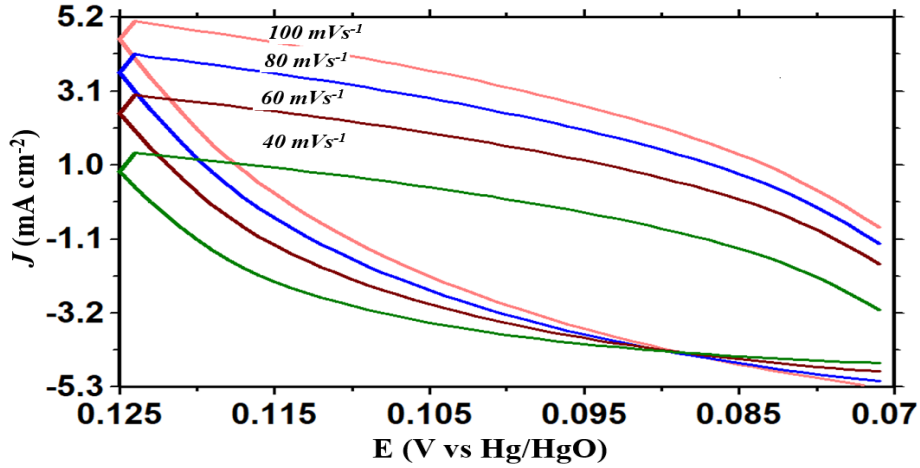

Fig. 5(a): Cyclic voltammograms of Ni/$Ni_{0.3}Co_{2.7}O_4$ electrode at various scan rates in 1M KOH at 25°C

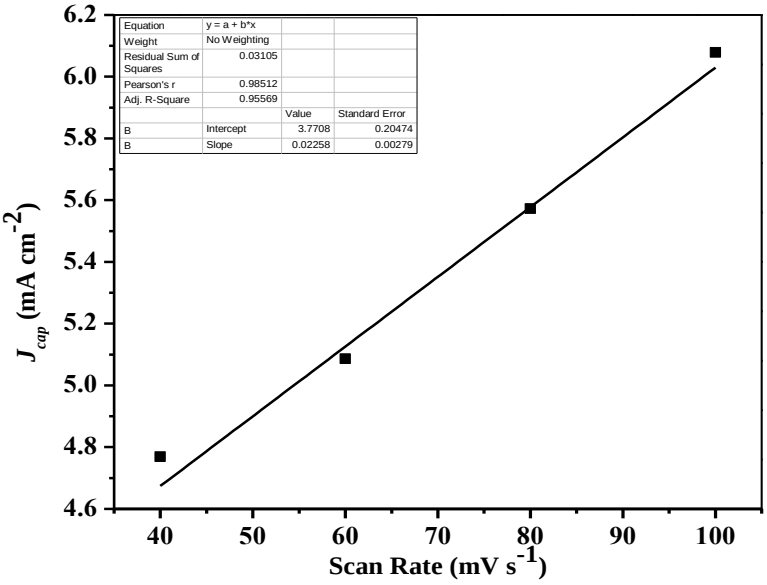

Fig. 5(b): Plot of Charging current density vs scan rate for the Ni/$Ni_{0.3}Co_{2.7}O_4$ electrode.

Roughness Factor: The roughness factor (R_F) of the prepared nickel cobaltite was studied by conducting the cyclic voltammetry at different scan rates like 12, 20, 40, 60, 80 and 100 $mVsec^{-1}$ at 25^0C in 1 M KOH solution in potential regions between 0.06 and 0.1 V to avoid interference from Faradic reaction as shown in figure 5(a).The double layer capacitance (C_{dl}) was calculated from the slope of the straight line curve between log *j* and the scan rate) shown in figure 5(b) and its value was 22580 μFcm^{-2}. The roughness factor (R_F) is important to study the electrochemical performance of the electrode and it was calculated from C_{dl} values, assuming the C_{dl} of smooth oxide surface[17] to be 60 μFcm^{-2}. The resultant value of R_F was found to be ~376 and electrochemical surface area (ECSA) of the oxide electrode was also estimated as ~226 cm^2.

Electrocatalytic Characterisation: The electrocatalytic performance of fabricated nickel cobaltite electrode for oxygen evolution reaction was analysed from the Tafel polarisation that was recorded at the scan rate of 0.5 mVs^{-1} in 1M KOH at 25^0C (Figure 6). The Tafel slope value from the polarisation curve of nickel cobaltite electrode was found to be 128 $mVdec^{-1}$ and current density at 650 mV is 35 mA cm^{-2}. The polarization curve of fabricated electrode indicated higher electrocatalytic activity for oxygen evolution reaction than the cobatite obtained by other different methods, such as spray pyrolysis Co_3O_4 film coated on CdO glass and Ti[26,27] and sol-gel method Co_3O_4 film on graphite polyisobutylene[8]. High catalytic activity is most probably due to the synergistic effect of nickel and cobalt ions and also higher oxygen voids in oxide matrix.

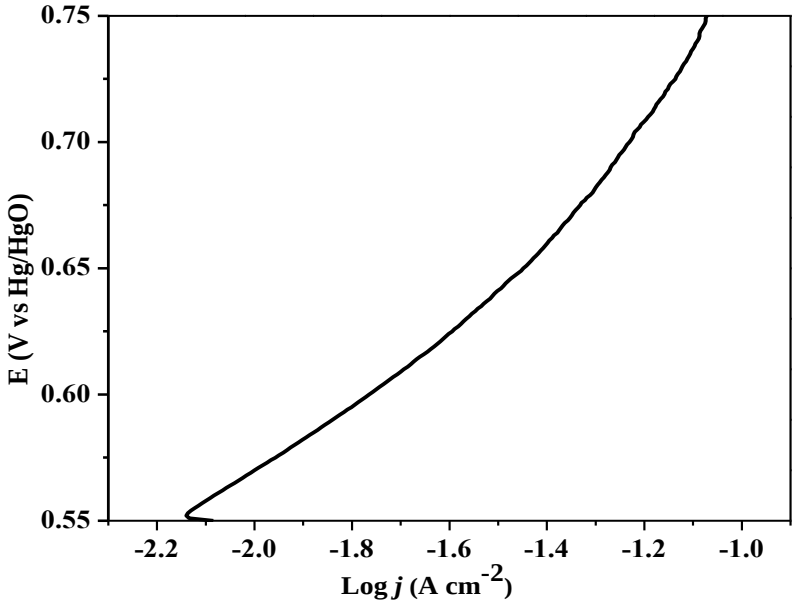

Fig. 6: Tafel polarization curve for oxygen evolution on $Ni/Co_{2.7}Ni_{0.3}O_4$ in 1M KOH at 25°C

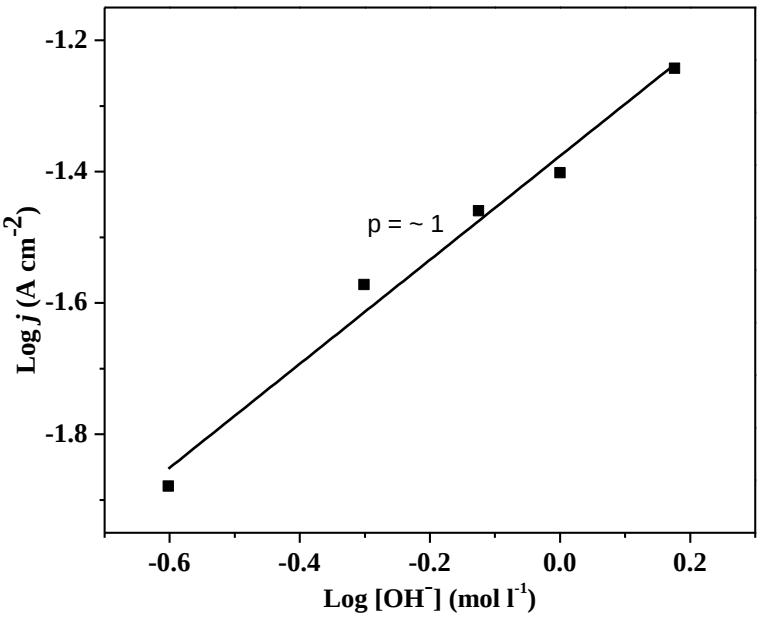

Fig. 7: Log *j* vs log $[OH^-]$ plot for oxygen evolution on $Ni/Co_{2.7}Ni_{0.3}O_4$ at E = 0.65 V

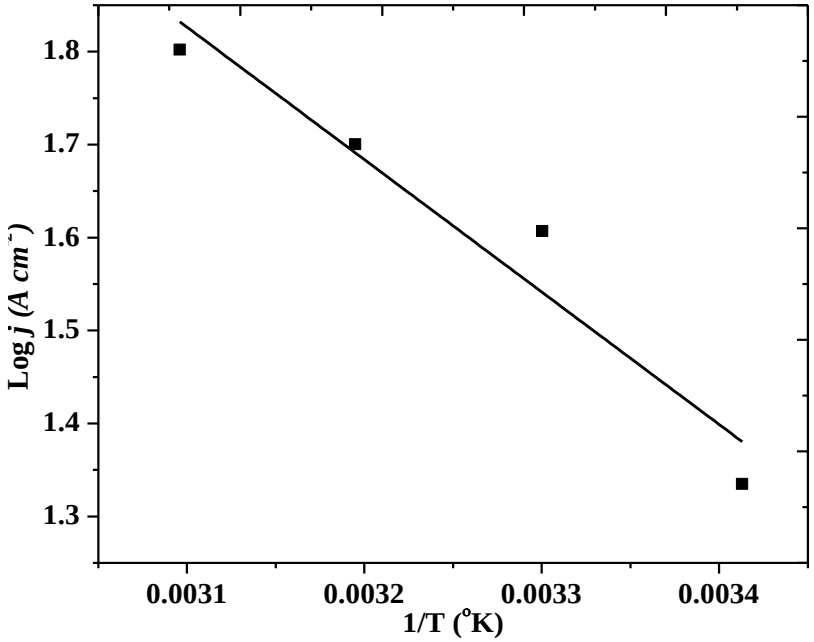

Fig. 8: Arrhenius plot for oxygen evolution on Ni/$Co_{2.7}Ni_{0.3}O_4$ at E = 0.65 V

Order of Reaction: The order of reaction was determined by the Tafel polarisation curve recorded at different concentrations of KOH (0.25,0.5,0.75.1.0 and 1.5 M) with constant ionic strength of the medium (μ= 1.5) at 25^0C. The order of reaction of the oxide electrode was calculated from the slope of log J vs log [OH^-] plot (figure 7) keeping the potential constant (0.65V). The order of reaction was approximately one that confirmed similar mechanism for the electrochemical evolution of oxygen on the electrode surface as indicated by Lal and other coworkers[16,17].

Activation Energy: The kinetic parameters like apparent electrochemical activation energy at reversible potential ($\Delta H_c^{o\neq}$), standard electrochemical activation energy at applied potential ($\Delta H_{el}^{o\neq}$) and standard entropy of reaction ($\Delta S_{el}^{o\neq}$) of the nickel doped cobalt oxide electrode were calculated from the Tafel plot recorded at various temperatures in 1M KOH solution (Figure 8). The standard electrochemical activation energy($\Delta H_{el}^{o\neq}$) was calculated from the slope of log j vs 1/T in the Arrhenius plot and was found to be 27.278 kJ mol^{-1}. The values of electrochemical activation energy at reversible potential ($\Delta H_c^{o\neq}$) and standard entropy of reaction ($\Delta S_{el}^{o\neq}$) were 38.7 kJ mol^{-1} and -303 J deg^{-1} mol^{-1} respectively. The negative value of entropy of the reaction indicates the presence of adsorption phenomenon in the oxygen evolution reaction at the surface of electrode.

Conclusion

The current investigation includes the preparation of nickel doped cobaltite by sol-gel route with the help of span-60 which has been used as a precursor. IR, XRD and SEM analyses have been used for the formation of the spinel phase of oxide. Also, this method of using Span-60 sol-gel is established to be the cheaper method of production of oxide electrocatalysts for the evolution of oxygen reaction in the alkaline medium.

Hence the cobaltite which is prepared by this method, has a higher electrocatalytic activity as compared to the oxides that are obtained by other conventional high-temperature methods and therefore, the present study suggests them as beneficial candidates for the electrocatalytic applications and energy storage devices.

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References

1. Ali G.A., Fouad O.A. and Makhlouf S.A., Structural, optical and electrical properties of sol–gel prepared mesoporous Co_3O_4/SiO_2 nanocomposites, *Journal of Alloys and Compounds*, **579**, 606 **(2013)**

2. Babu G.A., Ravi G. and Hayakawa Y., Microwave synthesis and effect of CTAB on ferromagnetic properties of NiO, Co_3O_4 and $NiCo_2O_4$ nanostructures, *Appl. Phys. A*, **119**, 219 **(2015)**

3. Burke M.S., Zou S.E., Lisa J.K., Jaclyn E.G., Christian A.P., Erica B. and Shannon W., Revised oxygen evolution reaction activity trends for first-row transition-metal (oxy)hydroxides in alkaline media, *Journal of Physical Chemistry Letters*, **6(18)**, 3737 **(2015)**

4. Chen X., Li H., Xu J., Jaber F., Musharavati F., Zalnezhad E., Bae S., Hui K.S., Hui K.N. and Liu J., Synthesis and

characterization of a $NiCo_2O_4$@$NiCo_2O_4$ hierarchical mesoporous nanoflake electrode for supercapacitor applications, *Nanomaterials*, **10(7)**, 1292 **(2020)**

5. Chen X., Xie R. and Li H., Supercapacitor performance of porous nickel cobaltite nanosheets, *Sci. Rep.*, **10**, 18956 **(2020)**

6. Chi B., Li J.B., Han Y.S. and Dai J.H., Effect of precipitant on preparation of Ni–Co spinel oxide by coprecipitation method, *Materials Letters*, **58(9)**, 1415 **(2004)**

7. Dongale T.D., Khot A.C. and Takaloo A.V., Facile synthesis of nickel cobaltite quasi-hexagonal nanosheets for multilevel resistive switching and synaptic learning applications, *NPG Asia Mater*, **13**, 16 **(2021)**

8. El Baydi M., Poillerat G., Rehspringer J.L., Gautier J.L., Koenig J.F. and Chartier P., A sol-gel route for the preparation of Co_3O_4 catalyst for oxygen electrocatalysis in alkaline medium, *Journal of Solid State Chemistry*, **109(2)**, 281 **(1994)**

9. Global outlook report, according to International Energy Outlook 2021 published by Energy Information Administration (EIA) **(2024)**

10. Gomathi Manoharan, Suresh Kumarasamy and Muthusamy Ranganathan, Synthesis of Silver Nanoparticles using Streptomyces variabilis MGR21: Characterization, Cytotoxicity and Photocatalytic Applications, *Res. J. Biotech.*, **19(12)**, 118 **(2024)**

11. Hu L., Wu L., Liao M. and Fang X., High-Performance $NiCo_2O_4$ Nano film photodetectors fabricated by an interfacial self-assembly strategy, *Advanced Materials*, **17(23)**, 1988 **(2011)**

12. Jianyu G., Xuan Z., Chao S., Xiaoming S. and Weikeduo W., The insight into enhanced oxygen evolution reaction on electronic modulation of phosphorus doped $NiCo_2O_4$, *Electronic Journal*, https://doi.org/10.2139/ssrn.4055973 **(2022)**

13. Kaur M., Chand P. and Binder H.A., Free electrodeposition fabrication of $NiCo_2O_4$ electrode with improved electrochemical behaviour for supercapacitor application, *Journal of Energy Storage*, **52**, 2352 **(2022)**

14. Khan M.A. et al, Recent Progresses in Electrocatalysts for Water Electrolysis, *Electrochemical. Energ. Rev.*, **1**, 483–530 **(2018)**

15. Klissurski D. and Uzunova E., Synthesis of nickel cobaltite spinel from coprecipitated nickel-cobalt hydroxide carbonate, *Chemistry of Materials*, **3(6)**, 1060 **(1991)**

16. Lal B., Chauhan P. and Gangwar B., Electrocatalytic activity of Ni/Co_3O_4 obtained by span-60 sol-gel route for oxygen evolution in 1M KOH at 25°C, *Ind. J. Chemistry*, **62(12)**, 1298 **(2023)**

17. Lal B., Singh N.K., Samuel S. and Singh R.N., Electrocatalytic properties of $Cu_xCo_{3-x}O_4$ (0<= x<= 1) obtained by a new precipitation method for oxygen evolution, *J. New. Mat. Electrochem. System.*, **2(1)**, 59 (**1999)**

18. Lee J.K., Kim G.P., Kim K.H., Song I. and Baeck S.H., fabrication of mesoporous cobalt oxide (Co_3O_4) film by electrochemical method for electrochemical capacitor, *Journal of Nanoscience and Nanotechnology.* **10**, 3676 **(2010)**

19. Liu M.C., Kong L.B., Chao Lu, Li X.M., Luo Y., Kang L., Xiaohong L. and Walsh F., A sol-gel process for the synthesis of $NiCo_2O_4$ having improved specific capacitance and cycle stability for electrochemical capacitors, *Journal of the Electrochemical Society*, **159**, A1262 **(2012)**

20. Marco J.F., Marco J.R., Gracia M., Gautier J.L., Rios E. and Berry F.J., Characterization of the nickel cobaltite, $NiCo_2O_4$, prepared by several methods: An XRD, XANES, EXAFS and XPS study, *Journal of Solid State Chemistry*, **153(1)**, 74 **(2000)**

21. Nguyen V.H. and Shim J.J., Microwave-assisted synthesis of porous nickel cobaltite with different morphologies in ionic liquid and their application in supercapacitors, *Materials Chemistry and Physics*, **176**, 6 **(2016)**

22. Pore O.C., Fulari A.V., Chavare C.D., Sawant D.S., Patil S.S., Shejwal R.V., Fulari V.J. and Lohar G.M., Synthesis of $NiCo_2O_4$ microflowers by facile hydrothermal method: Effect of precursor concentration, *Chemical Physics Letters*, **824**, 140551 **(2023)**.

23. Safdar A., Mohamed H.E.A., Muhaymin A., Hkiri K., Matinise N. and Maaza M., Biogenic synthesis of nickel cobaltite nanoparticles via a green route for enhancing the photocatalytic and electrochemical performances, *Sci Rep.*, **31(14)**, 17620 **(2024)**

24. Silva T.R., Rafael A.R., Vinícius D.S., Jakeline R.D., Santos L. Ferreira S., Allan J.M.A., Francisco J.A. Loureiro F., da Silva F., Duncan P. and Fagg D.A.M., Green synthesis of $MnCo_2O_4$ nanoparticles grown on 3D nickel foam as a self-supported electrode for oxygen evolution reaction, *Colloids and Surfaces A: Physicochemical and Engineering*, **672**, 131626 **(2023)**

25. Singh J., Dutta T. and Kim K.H., 'Green' synthesis of metals and their oxide nanoparticles: applications for environmental remediation, *J. Nanobiotechnol*, **16**, 84 **(2018)**

26. Singh R.N., Hamdani M., Koenig J.F., Poillerat G., Gautier J.L. and Chartier P., Thin films of Co_3O_4 and $NiCo_2O_4$ obtained by the method of chemical spray pyrolysis for electrocatalysis III, The electrocatalysis of oxygen evolution, *Journal of Applied Electrochemistry*, **20**, 442 **(1990)**

27. Singh R.N., Koenig J.F., Poillerat G. and Chartier P., Electrochemical Studies on Protective Thin Co_3O_4 and $NiCo_2O_4$ Films Prepared on Titanium by Spray Pyrolysis for Oxygen Evolution, *Journal of The Electrochemical Society*, **137(5)**, 1408 **(1990)**

28. Srinivasan V. and John W., Capacitance studies of cobalt oxide films formed via electrochemical precipitation, *Journal of Power Sources*, **108(1–2)**, 15 **(2002)**

29. Trasatti S., The Electrochemistry of Novel Materials, VCH Publishers, Weinheim **(1994)**

30. Vazhayil A., Vazhayal L., Thomas J., Shyamli A.C. and Thomas N., A comprehensive review on the recent developments in transition metal-based electrocatalysts for oxygen evolution reaction, *Applied Surface Science Advances*, **6**, https://doi.org/10.1016/j.apsadv.2021.100184 **(2021)**

31. Voronova A. and Ivanenko I., Synthesis methods and modern direction in modification of nickel cobaltite and composite nanoparticles with its participation, IEEE 8th International Conference Nanomaterials: Application & Properties (NAP), Zatoka, Ukraine, https://doi.org/10.1109/NAP.2018.8915243 **(2018)**

32. Wang J., Qiu T.Q., Chen X., Lu Y. and Yang W., Hierarchical hollow urchin-like NiCo2O4 nanomaterial as electrocatalyst for oxygen evolution reaction in alkaline medium, *Journal of Power Sources*, **268**, 341 **(2014)**

33. Wang S., Lu A. and Zhong C.J., Hydrogen production from water electrolysis: role of catalysts, *Nano Convergence*, **8**, 4 **(2021)**

34. Wei T.Y., Chen C.H., Chien H.C., Lu S.Y. and Hu C.C., A cost-effective supercapacitor material of ultrahigh specific capacitances: spinel nickel cobaltite aerogels from an epoxide-driven sol-gel process, *Advanced Materials*, **3(22)**, 347 (**2010)**

35. Wu J.B., Lin Y., Xia X.H., Xu J.Y. and Shi Q.Y., Pseudocapacitive properties of electrodeposited porous nano-wall Co_3O_4 film, *Electrochimica Acta*, **56(20)**, 7163 **(2011)**

36. Yang C.C., Sun W.C., Kumar A., Pattanayak B. and Tseng Y., Templating synthesis of nickel cobaltite nanoflakes and their nanocomposites for making high-performance symmetric supercapacitors, *Materials Today Energy*, **14**, 2468 **(2019)**

37. Yuan Y.F., Xia X.H, Wu J.B., Huang X.H., Pei Y.B., Yang J.L. and Guo S.Y., Hierarchically porous Co_3O_4 film with mesoporous walls prepared via liquid crystalline template for supercapacitor application, *Electrochemistry Communications*, **13(11)**, 1123 **(2011)**

38. Zhang C., Geng X., Tang S., Deng M. and Du Y.J., $NiCo_2O_4$@rGO hybrid nanostructures on Ni foam as high-performance supercapacitor electrodes, *Mater. Chem. A.*, **5**, 5912 **(2017)**

39. Zhang J., Sun Y., Xianchun L. and Xu J., Fabrication of $NiCo_2O_4$ nanobelt by a chemical co-precipitation method for non-enzymatic glucose electrochemical sensor application, *Journal of Alloys and Compounds*, **831**, 154796 **(2020)**

40. Zhang Y., Luo M., Yang Y., Li Y. and Guo S., Advanced multifunctional electrocatalysts for energy conversion, *ACS Energy Lett.*, **4** 1672 **(2019)**

41. Zhu J.H., Zhao L., Lee P., Lawrence Y.S. and Wong Kwok-Yin, Recent Advances in Electrocatalytic Hydrogen Evolution Using Nanoparticles, *Chemical Reviews*, https://doi.org/120. 10.1021/acs.chemrev.9b00248 **(2019)**.

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