

Electrocatalytic Reduction of Cobalt Oxide Spinel for Oxygen Reduction Reaction in Alkaline Media

Harsha P. Uskaikar

PES's RSN College of Arts & Science, Farmagudi, Goa, India 403001

Abstract

The cathode material were prepared by dispersing Co_3O_4 on vulcan carbon in situ and manually grinding in pestle and mortar. Co_3O_4 prepared by hydrazine based combustion method showed nanocrystalline nature. Surface area was found to increase on dispersing Co_3O_4 on vulcan carbon by manually grinding it in pestle and mortar. The kinetics of the oxygen reduction reaction (ORR) was studied on $\text{Co}_3\text{O}_4/\text{C}$ electrodes in KOH electrolyte by using cyclic voltammetry and steady state polarization measurements using Hg/HgO as the reference electrode. The morphological features of the electrocatalyst was studied by scanning electron microscopy (SEM), X-ray diffraction (XRD) & BET surface area. The polarization results showed higher electrocatalytic activity for the ORR on $\text{Co}_3\text{O}_4/\text{C}$ (G) cathode in comparison to $\text{Co}_3\text{O}_4/\text{C}$ (P) prepared by dispersing Co_3O_4 on a vulcan carbon. Electrocatalytic activity of N(G) & N(P) were compared with Pt/C electrodes.

Keywords: Spinel. Co_3O_4 . alkaline fuel cell. electrocatalyst. electrocatalytic activity.

Introduction

Usage of fossil fuels continuously for last decade has created severe environmental problems which calls for the urgent development of highly-efficient energy conversion and storage devices, such as fuel cells, supercapacitors and Lithium-ion batteries (LIBs) [1,2,3]. Fuel cells that use alkaline electrolyte solutions of potassium or sodium hydroxide have been studied, due to the possibility of using non-noble metal catalysts for both, the anode and cathode reactions[4–6]. Electrode materials are the most important components for the fuels cells, and their morphologies and structures plays important role in enhancement of electrochemical performance. Transition metal oxides can be applied as electrode materials for fuel cells so that a cost effective, non noble electrode material can be prepared. Furthermore, these electrode systems present advantages over all other low temperature fuel cell technologies, because the materials are more stable and the kinetics of the oxygen reduction is faster in alkaline environment. Thus, many of the recent studies aim to establish the best conditions for developing metal oxide as an effective low-cost electrocatalysts for alkaline oxygen/air electrodes, which can also find ‘applications in metal–air batteries [7,8]. Cathodic oxygen reduction is a widely studied, multistep reaction and both the products and the overpotential for the reaction depend strongly on the cathode material [9-14]. Oxygen reduction reaction proceeds via two pathways, direct $4e^-$ reduction is envisaged to result from mechanisms where there is cleavage of the O-O bond early in the reaction sequence. Whereas the alternative pathways involve $2e^-$ steps with hydrogen peroxide either as

the final product or as an intermediate further reduced or undergoing chemical disproportionation [15,16]. The rate of the further reduction and chemical decomposition of hydrogen peroxide depends strongly on the cathode and reaction conditions. Spinel's AB_2O_4 are promising electrocatalysts for the oxygen reduction reaction in alkaline fuel cells, since they have no noble metals & can be prepared by simple methods [17,18]. Among cobalt oxides, Co_3O_4 is an important oxide used for electrochemical, magnetic, and catalytic applications. It was usually prepared by thermal decomposition of cobalt salts under an oxidizing atmosphere at temperatures between 250–900°C [19]. In recent years, to easily obtain crystalline Co_3O_4 , many methods such as chemical vapour deposition method [20], sol-gel [21], spray pyrolysis [22], coprecipitation method [23], combustion method [24], solvothermal method [25]. However, a relatively high temperature is necessary in most of the above methods. The main thrust in the present work was to disperse Co_3O_4 produced by solution combustion method on support vulcan carbon, to get good electrocatalytic activity. So electrode material were prepared by insitu and manually grinding Co_3O_4/C in agate mortar pestle. Co_3O_4/C electrodes were than tested for electrocatalytic activity by cyclic voltametry and steady state polarisation study in presence of oxygen and air. The electrocatalytic activity of cobalt oxide spinel/ carbon electrode with Pt/C electrodes for ORR in alkaline medium was compared.

Experimental section

All the reagents used in the present study were AR grade.

Materials synthesis

Co_3O_4 spinel [N] was prepared by the solution combustion method reported in [26].



Fig. 1 Flow sheet for the preparation of Co_3O_4 (N), N(P) and N(G)

Electrochemical characterization

Firstly, Insitu electrode material was prepared by mixing vulcan carbon with aqueous solutions of cobalt nitrate, hydrazine hydrate and nitrilo triacetic acid (as per method). And then the mixture was strongly heated in a porcelain dish on a hot plate (at about 200–250 °C). The powder Co_3O_4/C obtained after decomposition was coded as N(P). Next, Co_3O_4 spinel (N) prepared by combustion method was grinded with vulcan carbon in agate mortar and pestle for almost 2 hrs. The powder Co_3O_4/C obtained was coded as N(G). 20% Pt/C was prepared by using $Na_6Pt(SO_3)_4$ salt and vulcan carbon was reduced with formic acid and dried in oven at 80°C for comparison purpose.

Activation energies for N(P) and N(G) were calculated by studying the decomposition of hydrogen peroxide reaction by using conventional gasometric technique proposed by [27,28]. 0.025 g catalyst was taken in a round bottom flask and 25 ml 6 M KOH was added to it, followed by addition of 2.5 ml of 1.3 M of H_2O_2 with the help of syringe in a glass set up.

Prior to measurement of electrochemical activity, electrode material **N(P)** and **N(G)** were mixed with 15% PTFE, few drops of water was added to form a dough, was ultrasonicated and dispersed in isopropyl alcohol. The mixture was homogenised properly and the paste obtained was pasted on carbon cloth with diffusion layer [29,30]. The electrodes were pressed at 240Kg/cm^2 and then sintered at 350°C for half an hour in muffle furnace. Electrodes **N(P)** and **N(G)** prepared were dried, sintered and mounted on the nickel mesh and were used for testing in a half cell, and use as working electrode in three electrode assembly. Front side the working electrodes was exposed to the 6M KOH electrolyte and back side there was nickel screen and tubing through which oxygen gas/air was passed to study the oxygen reduction reaction [31,32]. Steady state current potential curves for the teflon bonded **N(P)** and **N(G)** electrodes were obtained by galvanostatic polarization using Hg/HgO, (KOH, mol L⁻¹) reference electrode. The counter electrode was a nickel plaque. The catalyst loading was in the range of 7.45 mg/cm^2 . The same three electrode assembly was utilized for cyclic voltametry studies for **N(P)** and **N(G)** electrodes at the scan rate between ~ 20 to 300 mV/s .

Material structure characterization

Powder X-ray diffraction patterns were obtained by Phillips diffractometer PW 3710 & Cu K α radiation. The specific surface area of the powder was measured by Brunauer-Emmet-Teller (BET) method (N₂ adsorption) by using Nova 1200. All samples were activated around 300°C for 3hrs before adsorption was carried out. To investigate the characteristics surface morphology of the powders, as well as electrodes, scanning electron microscopy (SEM) were taken from JEOL JSM 5800.

Results and discussion

X-ray diffraction pattern as shown in figure 2, indicates cubic crystalline phase of Co₃O₄ with $a = 7.29\text{ \AA}$ & $V = 387$. The crystallite diameter was about 41 nm calculated by means of X-ray broadening method using Scherer's equation.

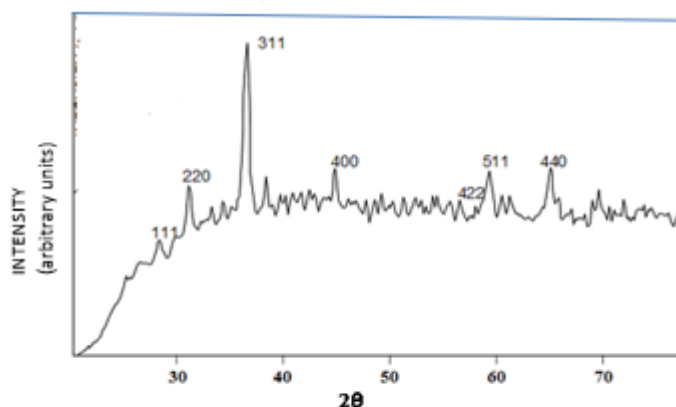


Figure 2. X-ray powder pattern of Co₃O₄ sample N

Figure 3 & 4 shows the current potential (i-E) curves of Co₃O₄/C for oxygen reduction reaction both in presence of oxygen and air. The corresponding tafel plots corrected for mass transfer[31] were presented in Figure 5 from which tafel slopes and exchange current densities were evaluated.

Relative current densities at an arbitrary potential of 400mV were measured by galvanostatic polarisation of **N(P)** and **N(G)**. These values along with other kinetic parameters obtained were

presented in Table 1. The electrocatalytic activity i_{400} was discussed in relation to the preparation of electrodes. A comparison of the electrocatalytic activity of the materials for the ORR was made from Tafel plots, obtained with current densities corrected for oxygen diffusion effects. Figure 3 & 4 shows results for the electrocatalysts and for the vulcan carbon with 20% Pt/C. As expected, much higher activity was observed for Pt/C the tafel plot shows two linear regions with slopes changing from ca. 60 mV/dec at lower overpotentials to 120 mV/dec at higher overpotentials. This was usually attributed to the different adsorbed oxygen coverage. As shown in Table 1 Tafel slopes were found to be close to 60 mV/dec, as reported by Sadiek M et al [33], for equivalent systems.

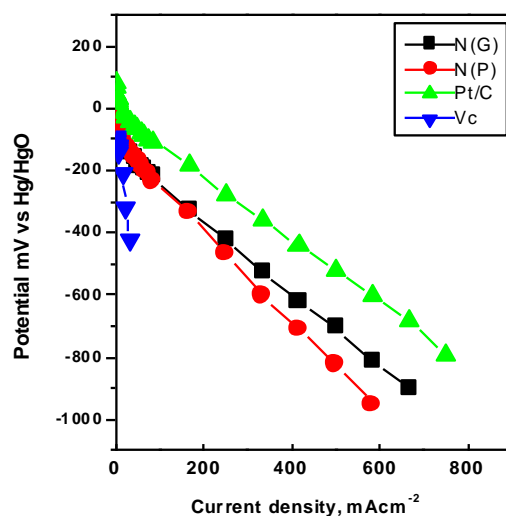


Fig.4 Current potential (*I-E*) curves for oxygen reduction reaction in presence of air.

Based on the *i-E* curve, when comparative studies were conducted N(G) & N(P) shows electrocatalytic activity between the vulcan carbon and Pt/C electrode. Between N(P) & N(G) cathodes obtained by mixing Co_3O_4 spinel (N) with vulcan carbon in agate mortar and pestle, N(G) cathode shows higher activity than N(P) prepared by in situ preparation. Therefore when vulcan carbon was mixed with Co_3O_4 by grinding in pestle & mortar shows higher electrocatalytic activity, higher current value as well as higher surface area of $190 \text{ m}^2/\text{g}$ confirming a proper interaction between vulcan carbon and Co_3O_4 was observed. Plain vulcan carbon commercially obtained, shows surface area of $250 \text{ m}^2/\text{g}$, which was found to decrease during electrode materials preparation of N(P) in situ preparation. The presence of bulky ligand i. e. nitritotriacetic acid, present as reactants may have some role in insitu preparation of the electrode material, which might be leading to the sintering of the catalyst particles, with consequent reduction of surface area. That the surface areas are indeed reduced was evident from the values of the surface area obtained by BET method as shown in Table 1. The insitu N(P) preparation of electrode material shows lower surface area of $91 \text{ m}^2/\text{g}$ and electrocatalytic activity compared to its counterpart. N(P) & N(G) shows exchange current density values almost very close to each other $\sim 1.2 \times 10^{-7}$ & $\sim 3.5 \times 10^{-7}$ but lower to the Pt/C electrodes value of 1.6×10^{-3} . but higher to the plain Vulcan carbon as shown in Fig, 3 & 4, showing facile oxygen reduction on the N(P) and N(G) electrodes. The i_{400} activity values were lower for O_2 reduction in presence of air then in presence of pure O_2 . It was also observed that the current potential data obtained by varying the concentration of the catalyst from 2%, 10% and 20% of $\text{Co}_3\text{O}_4/\text{C}$ gas diffusion electrode shows that there was increase in the electrocatalytic

activity from 2%, to 10%, but from 10% to 20% not much increase was observed. Fig. 7 shows the SEM/EDAX spectra of N(G) sample.

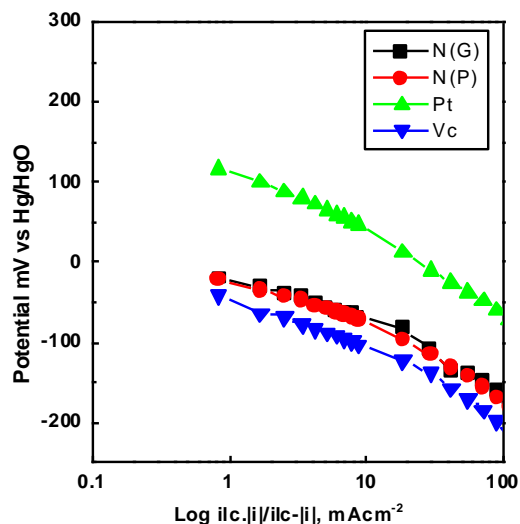


Fig 5: Tafel Plot for sample for mass transfer

Table 1: Showing Electrochemical data and BET Surface area

Sample code	BET Surface area m ² /g	i mA/cm ²		i _o	Tafel slopes mV/dec	R _u
		a (oxy)	b(air)			
Pt/c	92.99	420	376	1.6E ⁻³	75	0.807
Vc	250	200	--	2.2E ⁻⁹	78	0.535
N(P)	90.96	248	238	1.2E ⁻⁷	64	0.237
N(G)	190.91	293	284	3.5E ⁻⁷	64	0.107
N	9.8	-	-	-	-	-

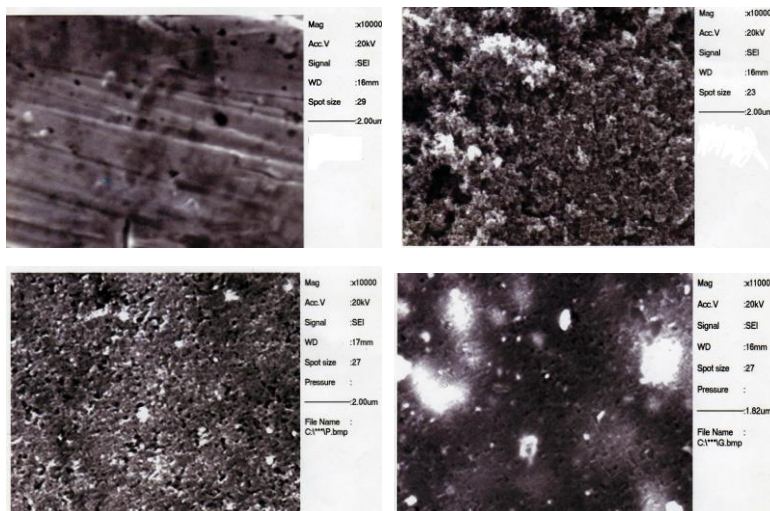


Fig. 6: Showing SEM of a) Pt/C, b) vc, c) N(P) & d) N(G)

CV profile of N(P) & N(G) were presented in Figure 7, which shows one oxygen reduction peak, which was obtained at -0.25mV at 20mV S⁻¹ scan rate. This peak was found to shift with increase in potential & decrease in current, as the scan rate was increased from 50, 100, 150, 200 mV S⁻¹ for N(P). CV profile of N(G), shows one reduction peak at high scan rate at 300 mV S⁻¹. At lower scan rates no reduction peak was obtained for N(G). From CV data it can be predicted that a direct 4e⁻ transfer takes place on Co₃O₄/C electrodes. N(G) shows better activity than N(P)[34]. May be manually grinding in pestle and mortar of electrode material leads to active Co³⁺ in the oxide lattice sites to be present on the surface thus, leading to higher activity, breaking the O-O bond preferentially leading to direct four electron transfer for oxygen reduction reaction. Activation energies obtained from decomposition of H₂O₂ also show lower activation energy for N(P). CV data with detailed peaks at different scan rates were presented in Table 2.

Mechanism can be depicted as shown in following reaction for N(G) & N(P).



Table 2. Shows the Electrochemical parameters with activation energies for N & N(G), N(P) samples.

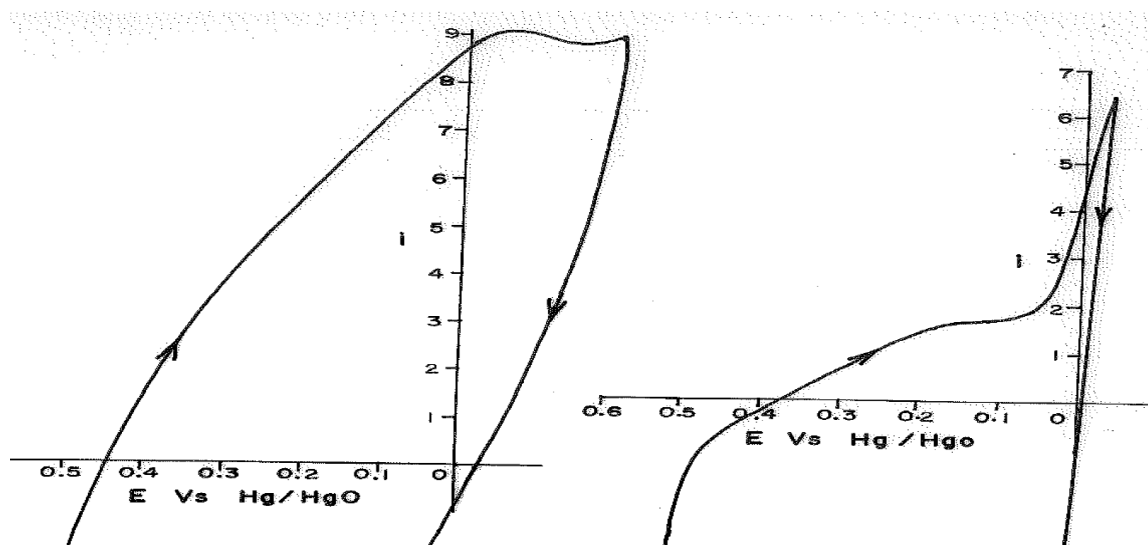


Figure 7: Oxygen reduction peaks observed in the cyclic voltammogram of N(P) & N(G).

Table 2: CV data and activation energies for N(P) and N(G).

Samples	Peak		i (oxy) mA cm ⁻²	Scan rate mV S ⁻¹	Ea KJ mol ⁻¹
	(Volts)	mA			
N(P)	-0.05	-9.0	248	200	2.75
	-0.1	-7.2		150	
	-0.15	-5.5		100	
	-0.20	-2.3		50	
	-0.25	-1.0		20	
N(G)	-0.26	-1.6	293	300	2.95

Conclusion

Cathode materials for the study of oxygen reduction reaction were prepared by hydrazine based combustion method. Nanocrystals of Co_3O_4 were dispersed on vulcan carbon in two ways, one by manually grinding and other by insitu preparation. 20% $\text{Co}_3\text{O}_4/\text{C}$ cathodes of N(P) & N(G) were used to measure electrochemical activity by steady state polarization technique and cyclic voltametry. N(G) cathodes showed higher electrocatalytic activity, higher activation energy, higher BET surface area. Thus showing that there was proper interaction between Co_3O_4 and vulcan carbon in N(G) where both components were manually grinded. From CV data it was predicted that oxygen reduction proceeds via four electron transfer, thus showing facile oxygen reduction reaction occurring on N(G). There was not very high difference between exchange current density values for N(G) and N(P). 20% $\text{Co}_3\text{O}_4/\text{C}$ cathodes showed lower electrocatalytic activity compared to Pt/C electrodes but higher to plain Vulcan carbon.

Supplementary Information

Not applicable

Author contribution

Writing original draft, material preparation, characterization Electrochemical study: Harsha P. Uskaikar

Funding

Not applicable

Data availability All data generated and analyzed during this study are included in this published article and its supplementary information files.

Declarations

Ethical approval Not applicable.

Competing interests

The authors declare no competing interests.

References

1. Sharma C, Awasthi R, Singh R, Sinha (2013) Graphene–cobaltite–Pd hybrid materials for use as efficient bifunctional electrocatalysts in alkaline direct methanol fuel cells. *Phys. Chem. Chem. Phys.* 15: 20333–20344
2. Dubal D, Dhawale D, Salunkhe S, Pawar S, Lokhande C (2010) A novel chemical synthesis and characterization of Mn_3O_4 thin films for supercapacitor application. *Applied Surface Science* 256 (14)1: 4411-4416
3. Yan, N, Hu L, Li Y, Wang Y, Zhong H, Hu X, Kong X, Chen Q (2012) Co_3O_4 nanocages for high-performance anode material in lithium-ion batteries. *J. Phys. Chem. C*, 116, 7227–7235.
4. Kiros, Y.; Schwartz, S(1991) Pyrolyzed macrocycles on high surface area carbons for the reduction of oxygen in alkaline fuel cells, *J. Power Sources.* 36:547.
5. Kiros Y, Lindstron O, Kaimakis T (1993) Cobalt and cobalt-based macrocycle blacks as oxygen-reduction catalysts in alkaline fuel cells. *J. Power Sources.* 45: 219-227.

6. Vogel W, Lundquist J (1970) Reduction of Oxygen on Teflon-Bonded Platinum Electrodes J. Electrochem. Soc, 117: 886.
7. Meadowcroft, D.B.; Low-cost Oxygen Electrode Material Nature (1970) 226: 847.
8. Maja M, Orechia C, Strano M, Tosco P, Vanni M (2000) Effect of structure of the electrical performance of gas diffusion electrodes for metal air batteries. *Electrochim Acta* 46: 423.
9. Kinoshita K (1992) *Electrochemical Oxygen Technology*, John Wiley & Sons Inc.
10. Hamdani M, Singh R and Chartier P (2010) Co_3O_4 and Co-based spinel oxides bifunctional oxygen electrodes *Int. J. Electrochem. Sci*, 5: 556
11. Jorissen L (2006) Bifunctional oxygen/air electrodes J. Power Sources 155: 23
12. Nikolova V, Iliev P, Petrov K, Vitanov T, Zhecheva E, Stoyanova R, Valov I and D. Stoychev (2008) Electrochemical catalysts for bifunctional oxygen/air electrodes,” J. Power Sources. 185: 727
13. Neburchilov V, H Wang, Martin J and Qu W (2010) A review on air cathodes for zinc-air fuel cells J. Power Sources. 195, 1271.
14. Vielstich W, Gasteiger H and Lamm, A (2003) *Handbook of Fuel Cells*, Volume 2. Eds.
15. Stephen T, Thompson J, Price Stephen W, Pletcher D and Andrea E (2016) Voltammetric Studies of the Mechanism of the Oxygen Reduction in Alkaline Media at the Spinel Co_3O_4 and NiCo_2O_4 . *Journal of The Electrochemical Society*. 163 : (10) H884-H890.
16. Kong F (2012) Synthesis of rod and beadlike Co_3O_4 and bifunctional properties as air/oxygen electrode materials *Electrochim. Acta* 68: 198.
17. Menezes P, Indra A, Gonz’alez-Flores D, Sahraie N, Zaharieva I, Schwarte M., Strasser P, Dau H and Driess M (2015) High-performance oxygen redox catalysis with multifunctional cobalt oxide nanochains: morphology-dependent activity *ACS Catalysis* 5: 2017-27
18. Suntivich J, Gasteiger H, Yabuuchi N and Shao-Horn Y (2010) Electrochemical measurement methodology of oxide catalysts using a thin-film RDE. *J. Electrochem. Soc.* 157: B1263.
19. Sakamoto S, Yoshinaka M, Hirota K, Yamaguchi O (1997) Fabrication, Mechanical Properties, and Electrical Conductivity of Co_3O_4 Ceramics. *J. Am. Ceram. Soc.* 80: 267-268.
20. Cheng C, Serizawa Sakata C, H Hirayama T (1998) Electrical conductivity of Co_3O_4 films prepared by chemical vapour deposition *Materials Chemistry and Physics* 53: 225-230
21. Pudukudy M, Yaakob Z (2014) Sol-gel synthesis, characterisation, and photocatalytic activity of porous spinel Co_3O_4 nanosheets, *Chemical Papers* 68: (8) 1087–1096
22. Nkeng P, Koenig J, Chartier, P, Poillerat G (1996) Enhancement of surface areas of Co_3O_4 and NiCo_2O_4 electrocatalysts prepared by spray pyrolysis. *J. Electroanal. Chem.* 402: 81-89.
23. Jang Y, Wang H, Chiang (1998) Y (Room-temperature synthesis of monodisperse mixed spinel $(\text{Co}_x\text{Mn}_{1-x})_3\text{O}_4$ powder by a coprecipitation method *J. Mater. Chem.* 8: 2761-2764.
24. Bedre M, Basavaraja S, Raghunandan D, Balaji D, Venkataraman (2009) A Preparation and characterization of cobalt oxide nanoparticles via solution combustion method. *NSNTAIJ* , 3:5-8
25. Cheng K, Cao D, Yang F, Xu Y, Sun G, Ye K, Yin J, Wang G (2014) Facile synthesis of morphology-controlled Co_3O_4 nanostructures through solvothermal method with enhanced catalytic activity for H_2O_2 electroreduction *J. Power Sources* 253 214–223
26. Uskaikar H and Ghazi S Synthesis of Co_3O_4 /Polyaniline nanocomposite: Structural, Morphology, electrical, and electrocatalytic properties, *J. Thermal Analysis calorimetry*. Communicated.

27. Sharifi S, Shakur H, Mirzaei A, Salmani A, Hosseini M (2013) Characterization of Cobalt Oxide Co_3O_4 Nanoparticles Prepared by Various Methods: Effect of Calcination Temperatures on Size, Dimension and Catalytic Decomposition of Hydrogen Peroxide, *Int. J. Nanosci. Nanotechnol* 51-58
28. Jiang S and Tseung A (1990) Homogeneous and heterogeneous catalytic reactions in cobalt oxide/graphite air electrodes III Deposition of cobalt oxide catalysts onto graphite electrodes for oxygen reduction *J. Electrochem. Soc* 137: 3442.
29. Kordesch K, Jehangir S, Schautz M (1984) Engineering concepts and technical performance of oxygen-reducing electrodes for batteries and electrochemical processes , *Electrochim. Acta.* 29:1589-1596
30. Bidault F, Brett D, Middleton P & Brandon N (2009) Review of gas diffusion cathodes for alkaline fuel cells. *J. Power Sources*, 187: 39-48.
31. Sugumaran N, Shukla A (1992) A novel approach for estimating the electrode kinetic parameters of gas-diffusion electrodes using the inflection point in steady-state current/potential data *J Power Sources.* 39: 249-254
32. Uskaikar H, Shetti N, Malode S (2018) Electrocatalytic reduction of oxygen on Co_3O_4 : Effects of processing method, *Materials Science for Energy Technologies* 1: 129–135
33. Sadiq M, Mohammad M, E-Shakre E, Awad M. Ismai D, Mohamed S.; and El-Anadouli, Bahgat E (2012) Electrocatalytic Evolution of Oxygen Gas at Cobalt Oxide Nanoparticles Modified Electrodes, CV mechanism CoO *Int. J. Electrochem. Sci.* 7: 3350 – 3361
34. Sönmez T, Thompson J, Price S, Pletcher D and Russell A, (2016) Voltammetric Studies of the Mechanism of the Oxygen Reduction in Alkaline Media at the Spinel Co_3O_4 and NiCo_2O_4 *Journal of The Electrochemical Society.* 163: (10) H884-H890