

Electrocatalytic Properties of Sol-Gel Derived Spinel $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ ($0 \leq x \leq 1.5$) Electrodes for Oxygen Evolution in Alkaline Solution

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The spinel-type oxide electrodes of $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ ($0 \leq x \leq 1.5$) have been studied for their electrocatalytic properties with regards to oxygen evolution reaction in 1M KOH solution at 25 °C. These oxides were prepared by ammonium hydroxide sol-gel auto-combustion method and reproduced in the form of film on nickel support by an oxide-slurry painting technique. Oxides, so synthesized, were characterized physicochemically by using scanning electron microscopy (SEM), infrared (IR) spectroscopy. Cyclic voltammetry and Tafel polarization techniques were used for electrochemical characterization. The study showed that substitution of cobalt in the base oxide greatly influences the electrocatalytic properties. Among synthesized oxides, the $\text{Co}_{1.5}\text{Fe}_{1.5}\text{O}_4$ electrode was found to be the most active electrode for oxygen evolution reaction. The Tafel slope values of the oxide electrodes were ranged between 44 – 56 mVdecade⁻¹. The order for the OER with respect to OH^- concentration was found to be ~ 2 with each oxide electrocatalyst. The catalytic activities of the electrodes are correlated with their surface roughness. The thermodynamic parameters for oxygen evolution reaction (OER) such as, standard electrochemical enthalpy of activation ($\Delta H_{\text{el}}^{0\#}$), standard enthalpy of activation ($\Delta H^{0\#}$) and standard entropy of activation ($\Delta S^{0\#}$) have also been calculated.

Keywords: Spinel oxides, Sol-gel method, Infrared spectroscopy, Electrocatalysis, Oxygen evolution

1. INTRODUCTION

In water electrolysis, oxygen evolution reaction is the basic anodic reaction process. A number of electrocatalysts, such as, transition metal oxides with spinel-structure (AB_2O_4 ; where, A & B are a bivalent & trivalent transition metal ions, respectively) and perovskite-structure (ABO_3 ; where, A is mainly La and B = Co, Ni or Mn), have been developed and considered most promising materials for anodic evolution of oxygen [1–3]. Among them, ferrosinels, $\text{M}_x\text{Fe}_{3-x}\text{O}_4$ (M is the bivalent metal ion)

are technologically important materials with regards to their structural, electronic, magnetic and catalytic properties [4]. These materials have been extensively used in several important heterogeneously catalyzed reactions, such as, an anode catalysts for chlorine and chlorate production [2], synthesis of ammonia [5], decomposition of H_2O_2 [6], application in the electron transfer of hemoglobin [7], selective oxidation of butane to butadiene [8] and in a biosensors [9]. Earlier, these oxides were prepared by conventional ceramic methods [10, 11], which usually produced materials of high resistivity and low specific surface area and thereby lead to relatively low electrocatalytic activities. The specific surface area vis-à-vis the electrocatalytic properties could be improved to a considerable extent by using relatively low temperature preparation methods, namely, precipitation [12, 13], sol-gel [14, 15] etc and substitution of suitable metal ions [16-21].

Recently, Singh et. al. prepared a series of metal-substituted binary and ternary ferros spinels [12, 19-23] using a low temperature precipitation method with a controlled pH (=11) and found considerable enhancement in the electrocatalytic properties towards the OER. Singhal et. al. [24] obtained Cr-substituted Co-Zn nanoferrites by sol-gel auto-combustion method and studied their structural, electrical, optical and magnetic properties. By adopting the same method, we synthesized pure and Co-substituted ferrites and studied their physicochemical and electrocatalytic properties for OER in alkaline solution. Results of the study are presented in this paper.

2. EXPERIMENTAL

Pure and Co-substituted spinel ferrites were synthesized by the method, recently reported in literature [24]. For the purpose, purified $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Merck 98%), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Merck 97%) and citric acid (Merck) were weighed in stoichiometric ratio and dissolved in minimum amount of double distilled water. The individual solutions were then mixed together and the pH of the solution was adjusted to 6 by adding NH_4OH solution. The solution was then slowly evaporated in a water bath till gel like mass was formed. The gel formed was then burnt to self ignition to obtain a loose powder. The powders were then sintered at 400°C for 3 hrs in muffle furnace to get the desired oxides.

Materials, so obtained, were characterized by recording IR spectra (JASCO FT/IR-5300) in the frequency range of $4000\text{--}400\text{ cm}^{-1}$. In case of IR, oxide powder and purified KBr were mechanically mixed and pressed to transfer in the pellet form. The morphology of the oxide powders was examined using a high performance scanning electron microscope (SEM; LEO 430). The identity of the oxide was confirmed by obtaining X-ray diffractograms using Cu-K_α radiation ($\lambda = 0.15418\text{ nm}$).

For electrochemical characterizations, materials, synthesized, were transformed in the form of oxide film electrode. For the purpose, slurry of the oxide-powder with few drops Triton X-100 was prepared and painted on one side of the pretreated Ni (Aldrich, 99.9%) support by using a fine brush and subsequently heat treated at 380°C for 1.5 h to obtain an adherent oxide film and desired loading as described elsewhere [25]. Before painting, the Ni substrates (1.5 cm^2) were mechanically polished on a fine Emery paper, treated with concentrated HCl for 20 min, washed with distilled water, degreased in acetone and finally washed with double distilled water and dried in air. The electrical contact with the oxide film was made on the back side of Ni substrate using plastic coated copper wire

and silver paste as described in the literature [25]. Only 0.5 cm^2 area of the film was used in electrochemical study and the remaining film including uncovered surface of Ni plate was covered with Araldite.

All the electrochemical studies, such as, cyclic voltammograms (CV) and Tafel polarization were performed in a conventional three-electrode single compartment Pyrex glass cell using a computerized potentiostat/galvanostat (Gamry, Reference 600). The potential of the working electrode was measured with respect to Hg/HgO/1M KOH electrode. All potentials mentioned in the text are based on the Hg/HgO ($E^0 = 0.098\text{ V}$ vs. NHE at 25°C) electrode only. A pure Pt-foil ($\sim 2\text{ cm}^2$) was used as an auxiliary electrode.

3. RESULTS AND DISCUSSION

3.1. Physicochemical Properties

3.1.1. Morphology of oxide powder

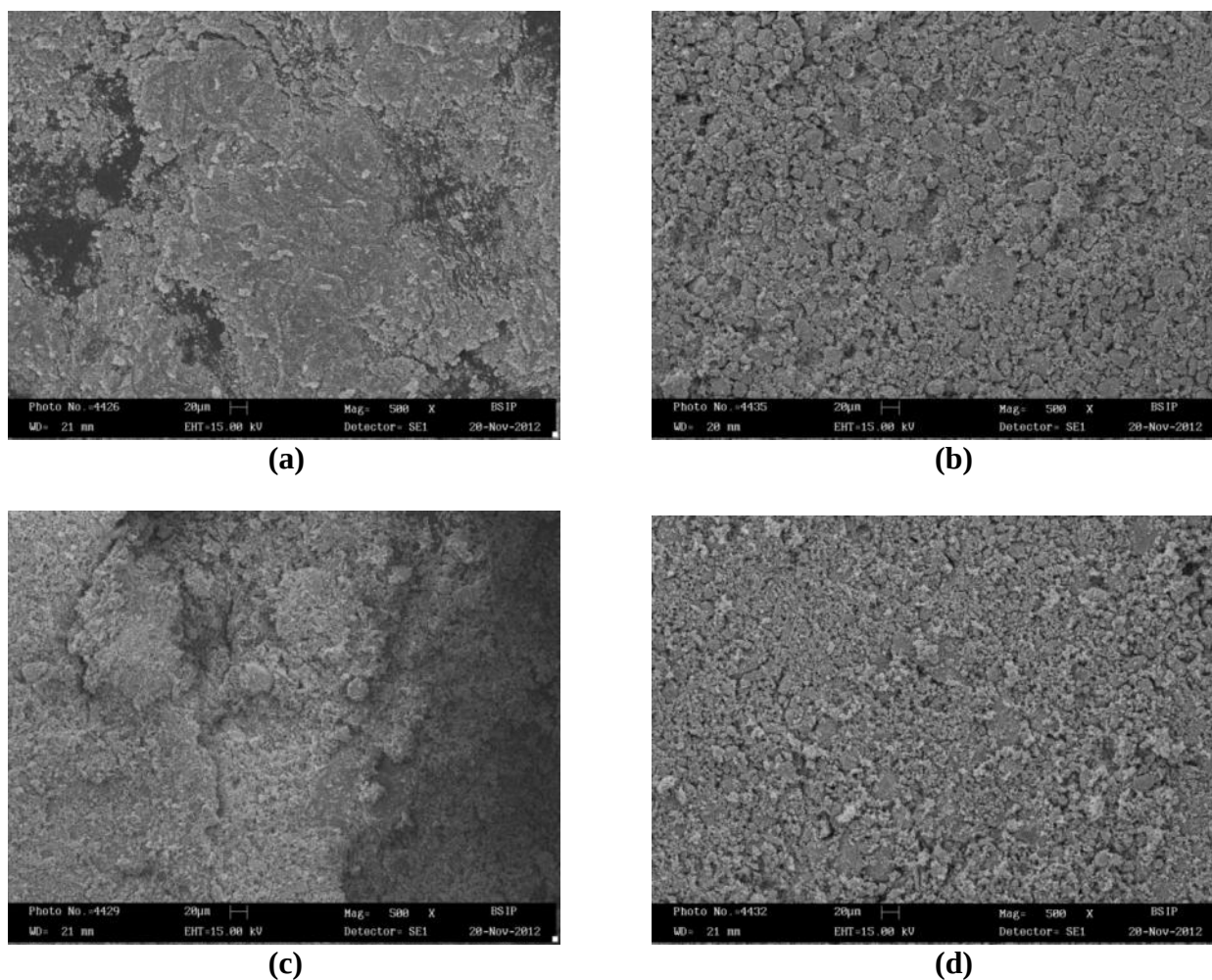


Figure 1. SEM micrographs of oxide powders heated at 400°C for 4 hrs at magnification ($\times 500$):
 (a) Fe_3O_4 (b) $\text{Co}_{0.5}\text{Fe}_{2.5}\text{O}_4$ (c) CoFe_2O_4 (d) $\text{Co}_{1.5}\text{Fe}_{1.5}\text{O}_4$

SE micrographs of pure and Co-substituted oxide powders, sintered at 400⁰C for 3 hrs, are represented in the Fig. 1 (a - d) at one magnification. From figure, it is revealed that the appearance of the oxide powder is almost similar. However, some aggregates have been observed in the case of Fe₃O₄ and CoFe₂O₄ [Fig.1 (a & c)]. These oxides also show compactness. Crystals of Co_{0.5}Fe_{2.5}O₄ and Co_{1.5}Fe_{1.5}O₄ [Fig.1 (b & d)] are distributed more uniformly and more homogeneous with smaller grain size. The grain size was found to be smallest with Co_{1.5}Fe_{1.5}O₄ [Fig. 1(d)].

3.1.2. Infrared

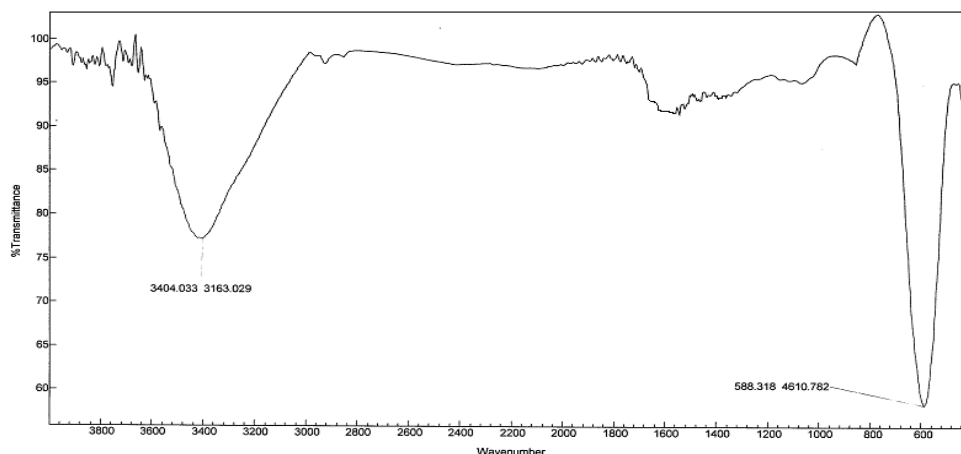


Figure 2. IR spectra of CoFe₂O₄ oxide sintered at 400⁰C for 3 hrs.

IR spectra of each oxide powder, sintered at 400⁰C for 3hrs, were recorded in the region of 4000-400 cm⁻¹. A strong peak at ~ 588 cm⁻¹ indicates the formation of pure spinel ferrite [26, 27]. A representative IR spectrum for the CoFe₂O₄ is shown in the Fig. 2. The peak value ~ 3404 represents the hydroxyl group of CoFe₂O₄. The presence of hydroxyl group on the ferrite may help in the conjugation and dispersion of nonmaterial [28].

3.2. Electrochemical properties

3.2.1. Cyclic Voltammetry (CV)

In order to know the electroactive species on the surface of oxide electrode with regard to the oxidation-reduction reaction, cyclic voltammograms of each oxide electrode were recorded at the scan rate of 20 mV s⁻¹ in the potential region of 0.0 – 0.7 V in 1 M KOH at 25⁰C. Typical CV curves for the base and Co-substituted species are shown in the Fig. 3. Cyclic voltammograms for the each oxide electrodes were quite similar, regardless of the nature of the oxide films. The observed peak currents (*j*_{pa} & *j*_{pc}) in the case of base oxide are very low. So, it is not clearly seen in the figure in combination with the other Co-substituted oxide electrode.

Each voltammogram shown in figure 3 exhibited a pair of redox peaks (an anodic and a corresponding cathodic peak) prior to the onset of the OER. Values of the anodic (*E*_{pa}) and cathodic

(E_{pc}) peak potentials, the separation potential ($\Delta E = E_{pa} - E_{pc}$), and the formal redox potential [$E^0 = (E_{pa} + E_{pc})/2$] were estimated and their values, at the scan rate of 20 mV s^{-1} , are listed in Table 1. The result shows that the ΔE value increases appreciably with the Co-substitution in the base oxide. The ΔE value was found to be greatest with 1.0 mol Co-substitution. The E^0 values were almost similar with each oxide electrode.

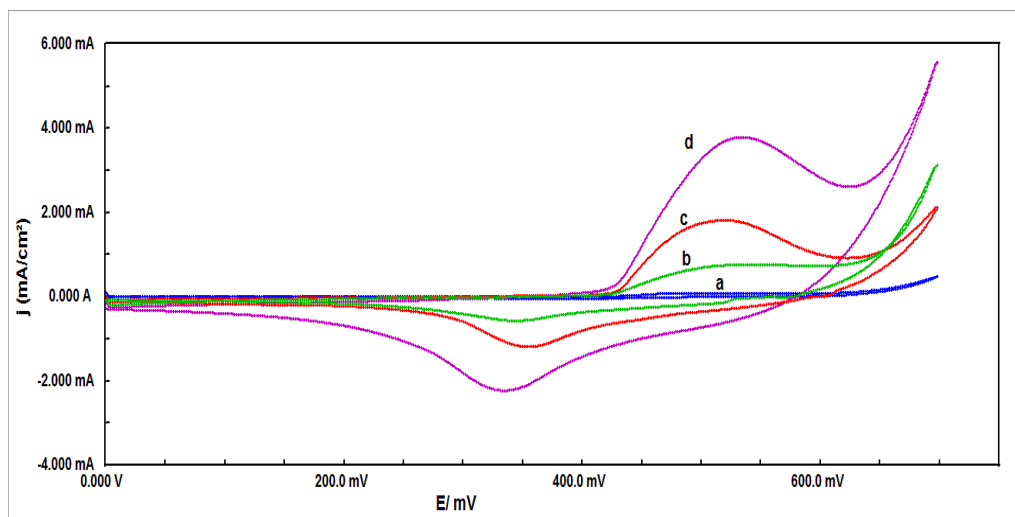


Figure 3. Cyclic Voltammograms of Co-substituted ferrite electrodes on a Ni-substrate at 20 mV s^{-1} in 1M KOH at 25°C ; (a) Fe_3O_4 , (b) $\text{Co}_{0.5}\text{Fe}_{2.5}\text{O}_4$, (c) CoFe_2O_4 and (d) $\text{Co}_{1.5}\text{Fe}_{1.5}\text{O}_4$

Table 1. Results of the cyclic voltammetry of $\text{Ni}/\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ ($0 \leq x \leq 1.5$) at the scan rate 20 mV s^{-1} in 1M KOH at 25°C .

Electrode	E_{pa}/mV	E_{pc}/mV	$\Delta E = (E_{pa} - E_{pc})/\text{mV}$	$E^0 = (E_{pa} + E_{pc})/2/\text{mV}$
Fe_3O_4	502	349	153	426
$\text{Co}_{0.5}\text{Fe}_{2.5}\text{O}_4$	527	347	180	437
CoFe_2O_4	540	337	203	438
$\text{Co}_{1.5}\text{Fe}_{1.5}\text{O}_4$	529	342	187	436

However, cyclic voltammetry of similar films on Pt under similar experimental conditions did not show any redox peak between the potential regions $0.0 - 0.7 \text{ V}$. This study showed that the observed redox peak is not originated from the oxide catalyst. Similar results of cyclic voltammograms have also been observed by some authors [12, 29, 30]. It is known that the oxides obtained at low temperature become hydrophilic in nature and that they undergo rapid hydration in aqueous solution and resulting the wetting of catalytic film. Also, it is considered that during the experiment, the electrolyte may penetrate [31] the catalytic layer through pores, cracks, crevices, inter-crystalline gap, etc., and came in contact with the substrate. However, it does not affect the stability of the oxide film.

Also, from figure 3, it is observed that anodic (j_{pa}) and cathodic (j_{pc}) peak current density increased, significantly, with the increase of Co-content in the base oxide. The effect is found to be greatest with $\text{Co}_{1.5}\text{Fe}_{1.5}\text{O}_4$ electrode. This increase in the peak current density might be due to the fact that the catalysts stimulate not only the oxygen evolution reaction but also the redox couple.

3.2.2. Electrocatalytic activity

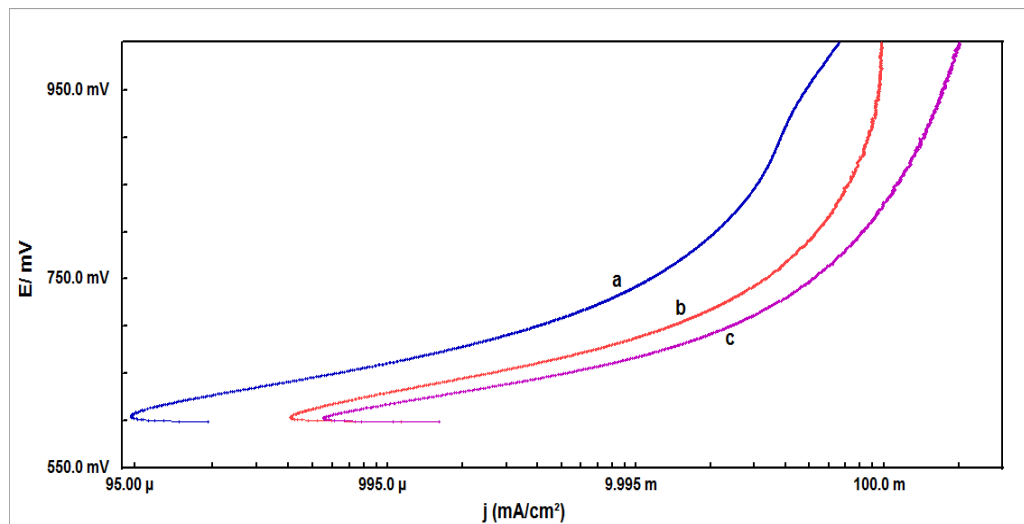


Figure 4. Tafel plots for oxygen evolution on the $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ ($0 \leq x \leq 1.5$) electrode in 1M KOH at 25^oC (scan rate = 0.2 mV s⁻¹). (a) Fe_3O_4 , (b) CoFe_2O_4 , and (c): $\text{Co}_{1.5}\text{Fe}_{1.5}\text{O}_4$

The electrocatalytic activity of each oxide electrode was determined by recording the anodic polarization curves (E vs $\log j$) for the OER at a slow scan rate of 0.2 mV s⁻¹ in 1 M KOH at 25^oC. The polarization curves for each oxide electrode, as shown in Fig. 4, were nearly similar regardless of the Co content. Due to complexity/overlapping in presentation, the Tafel plot for $\text{Co}_{0.5}\text{Fe}_{2.5}\text{O}_4$ is not shown the figure 4. The values of Tafel slopes (b) and apparent current density (j_a) at three different potentials were estimated from the polarization curve and shown in the Table 2. The Tafel slope values were ranged between 44 – 56 mV decade⁻¹. The b -values at low potential were ca. RT/F in the case of CoFe_2O_4 and $\text{Co}_{0.5}\text{Fe}_{2.5}\text{O}_4$ ($b = 56$ mVdecade⁻¹) and cs. $2RT/3F$ in the case of Fe_3O_4 ($b = 49$ mVdecade⁻¹) and $\text{Co}_{0.5}\text{Fe}_{2.5}\text{O}_4$ ($b = 44$ mVdecade⁻¹). These results indicate that the rate determining step is not the same for different catalytic films. From figure 4 and Table 2, it is observed that among all the oxide electrodes prepared, the $\text{Co}_{1.5}\text{Fe}_{1.5}\text{O}_4$ is electrocatalytically the most active whereas Fe_3O_4 is the least active. In terms of apparent current density (j_a) at three different potentials ($E = 650\text{mV}$, 750 mV & 850 mV) the $\text{Ni}/\text{Co}_{1.5}\text{Fe}_{1.5}\text{O}_4$ electrode showed about 3 - 9 times higher activity as compared to the base oxide. Based on the apparent current density at $E = 850$ mV, the electrocatalytic activity of different followed the order:

$\text{Co}_{1.5}\text{Fe}_{1.5}\text{O}_4$ ($j = 108.0 \text{ mA cm}^{-2}$) > $\text{Co}_{0.5}\text{Fe}_{2.5}\text{O}_4$ ($j = 71.8 \text{ mA cm}^{-2}$) $\approx$ CoFe_2O_4 ($j = 69.6 \text{ mA cm}^{-2}$) > Fe_3O_4 ($j = 31.0 \text{ mA cm}^{-2}$)

In order to determine the reaction order (p) with respect to OH^- concentration, the anodic Tafel polarization curve was recorded in different KOH concentrations by keeping the ionic strength of the medium constant ($\mu = 1.5$) (Fig. 5). An inert supporting electrolyte KNO_3 (Merck, purified) was used to maintain the ionic strength. The value of order (p) was estimated from the slope of the plot $\log j$ vs $\log [\text{OH}^-]$ (Fig. 6) at constant potential ($E = 650$ mV). The estimated values of p were found to be ~ 2 for each oxide catalyst and shown in Table 2.

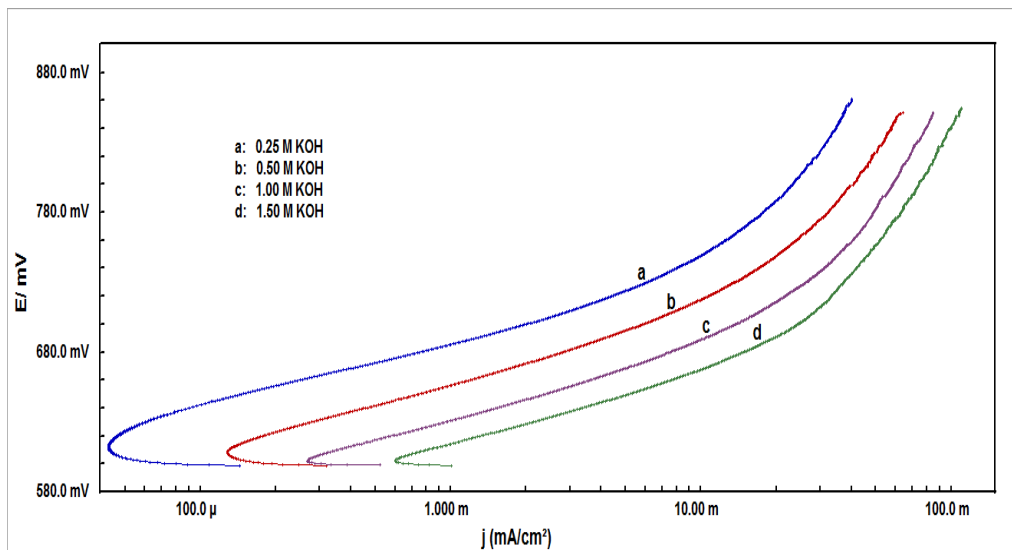


Figure 5. Tafel plots on $\text{Ni/Co}_{1.5}\text{Fe}_{1.5}\text{O}_4$ at potential scan rate of 0.2 mV s^{-1} in different KOH concentrations ($\mu = 1.5$).

As observed by us, Orehtsky et. al. [10] also found similar low Tafel slopes ($37\text{--}49 \text{ mV decade}^{-1}$) for oxygen evolution on $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ ($0.49 \leq x \leq 1.68$) prepared by a freeze-drying technique. The observed Tafel slope (b) values were in fair agreement with those recently reported for the $\text{CoFe}_{2-x}\text{Cr}_x\text{O}_4$ ($b = 40\text{--}51 \text{ mV decade}^{-1}$) [19], $\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$ ($b = 36\text{--}65 \text{ mV decade}^{-1}$) [12], $\text{MnFe}_{2-x}\text{Cr}_x\text{O}_4$ ($b = 34\text{--}41 \text{ mV decade}^{-1}$) [34], and $\text{NiFe}_{2-x}\text{Cr}_x\text{O}_4$ ($b = 38\text{--}41 \text{ mV decade}^{-1}$) [35]. Lyons et. al. also found same Tafel slopes ($b = 37\text{--}47 \text{ mV decade}^{-1}$) on oxidized nickel, cobalt and iron electrodes in basic medium for oxygen evolution reaction [36].

Table 2. Electrode kinetic parameters for O_2 evolution on $\text{Ni/Co}_x\text{Fe}_{3-x}\text{O}_4$ ($0 \leq x \leq 1.5$) 1M KOH at 25°C .

Electrodes	Tafel slope (b) /mV decade $^{-1}$	Order (P)	Current (j/mAcm^{-2}) at E/mV		
			650	750	850
Fe_3O_4	49	2.0	0.6	11.6	31.0
$\text{Co}_{0.5}\text{Fe}_{2.5}\text{O}_4$	56	2.1	2.7	33.5	71.8
CoFe_2O_4	56	1.8	5.5	36.8	69.6
$\text{Co}_{1.5}\text{Fe}_{1.5}\text{O}_4$	44	2.0	5.6	48.9	108.0

A similar value of electrode kinetic parameter (b) was also found in the case of sprayed NiCo_2O_4 film ($b = 42 \text{ mV decade}^{-1}$) [37], CuCo_2O_4 films ($b = 42 \text{ mV decade}^{-1}$), Ni , LaPO_4 bonded on Ni ; prepared by thermal decomposition of the metal nitrates [38, 39], electrodeposited Ni-Fe alloys on mild steel ($b = 37\text{--}45 \text{ mV decade}^{-1}$) [40]. As for as the order is concerned, both first and second order kinetics have been reported for oxygen evolution on the oxide electrodes with respect to $[\text{OH}^-]$.

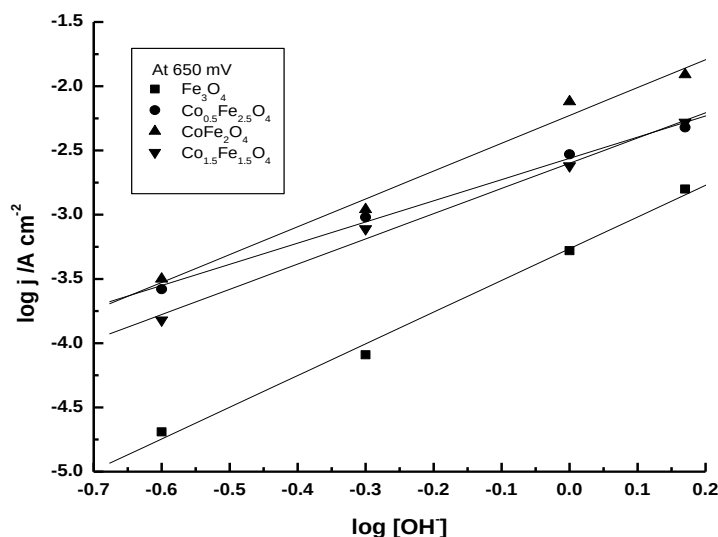


Figure 6. Plot of $\log j$ vs $\log C_{\text{OH}^-}$ of the oxide electrodes at a constant potential ($E = 650 \text{ mV}$) across the oxide/1M KOH interface at 25°C .

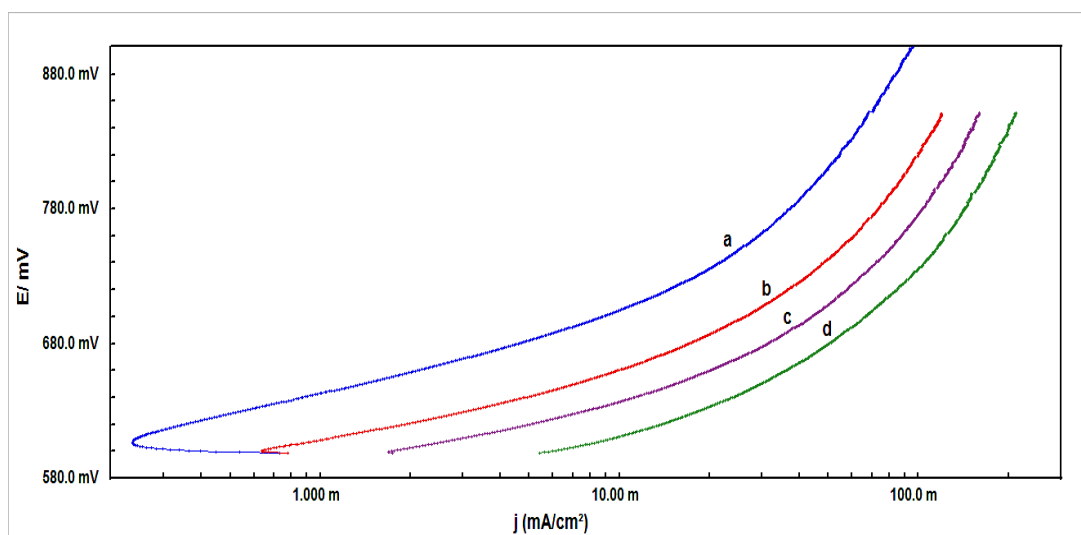


Figure 7. Tafel plots on $\text{Ni/Co}_{1.5}\text{Fe}_{1.5}\text{O}_4$ at potential scan rate of 0.2 mV s^{-1} in 1M KOH at different temperatures. (a) 20°C , (b) 30°C , (c) 40°C and (d) 50°C

It is noteworthy that the electrocatalytic activity of $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ ($0 \leq x \leq 1.5$) electrodes prepared in this study was much more active than those of the other spinel ferrite electrodes reported in the literature. For instance, Orehotsky et. al. [10] observed current density 10 mA cm^{-2} at $\eta_{\text{O}_2} = 0.34 \text{ V}$ for

NiFe_2O_4 in 30 wt% KOH. However, Co-substituted ferrite electrodes prepared by us gave the same current density at $\eta_{\text{O}_2} \approx 0.36$ V in 1M KOH at 25 °C. The η_{O_2} is the formal overpotential; $\eta_{\text{O}_2} = E - E_{\text{O}_2/\text{OH}^-}$, where E and $E_{\text{O}_2/\text{OH}^-}$ ($= 0.303$ V vs Hg/HgO) are the applied potential across the catalysts/1M KOH interface and the theoretical equilibrium potential in 1M KOH at 25 °C. Singh et. al. [20] observed 1.2 mA cm^{-2} (at $E = 0.7$ V) in 1M KOH at 25 °C, particularly, for the CuFe_2O_4 electrode prepared by the hydroxide precipitation method at controlled pH ($= 11$). Very recently, at the same potential, Al-Mayouf et. al. [41] observed $\sim 6 \text{ mA cm}^{-2}$ with nickel ferrite electrode prepared by hydrothermal method. However, cobalt ferrites in this study produced more than 10 mA cm^{-2} at the same potential.

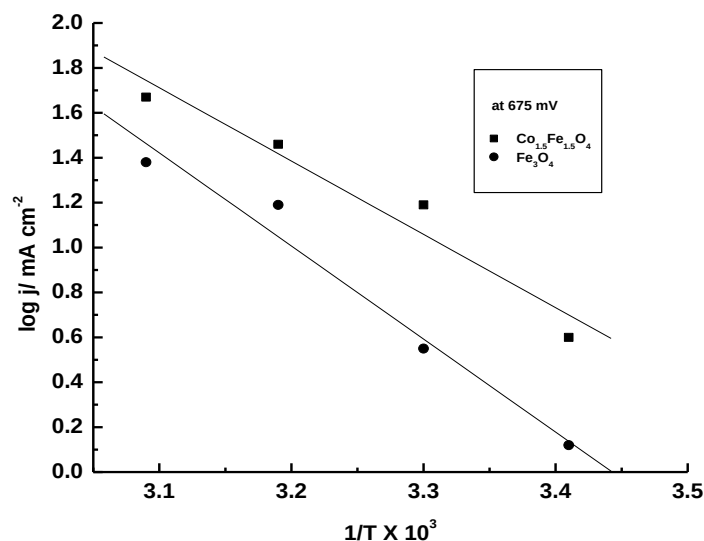


Figure 8. Arrhenius plot for oxygen evolution reaction on $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ at a constant potential ($E = 675$ mV)

The effect of temperature on the OER has also been studied at the two oxide electrodes i.e. Fe_3O_4 and $\text{Co}_{1.5}\text{Fe}_{1.5}\text{O}_4$. For the purpose, Tafel polarization curve was recorded in 1M KOH at four different temperatures (20, 30, 40 and 50 °C). A set of four anodic polarization curves is shown in the Fig. 7 for the case of $\text{Co}_{1.5}\text{Fe}_{1.5}\text{O}_4$. The standard enthalpy of activation ($\Delta H_{\text{el}}^{0\#}$) was estimated from the slope of the plot $\log j$ vs $1/T$ (Fig. 8) at constant potential ($E = 675$ mV). Values of activation energy were found to be 81.3 and 67.9 kJ mol^{-1} for Fe_3O_4 and $\text{Co}_{1.5}\text{Fe}_{1.5}\text{O}_4$, respectively, at $E = 675$ mV. These values of $\Delta H_{\text{el}}^{0\#}$ were very similar to that observed by Singh et. al. [19] at $E = 560$ mV. However, values were much higher than those reported on Adams- RuO_2 (49 kJ mol^{-1}) [42], oxide coated $\text{Co}_{50}\text{Ni}_{25}\text{Si}_{15}\text{B}_{10}$ amorphous alloy (40 kJ mol^{-1}) [43] and $\text{Cu}_{0.9}\text{Co}_{2.1}\text{O}_4$ (45.2 kJ mol^{-1}) [44].

The transfer coefficient (α) for the OER was estimated by using the equation $\alpha = 2.303RT/bF$, where, terms used in this equation have their usual meanings. The b value is calculated from the polarization curves obtained at different temperatures. The standard enthalpy of activation ($\Delta H^{0\#}$) or standard electrochemical enthalpy of activation at $\eta_{\text{O}_2} = 0$ was calculated from the relation, $\Delta H^{0\#}_{\text{el}} =$

$\Delta H^{0\#} - \alpha F\eta$ by using the average value of transfer coefficient. The data shown in Table 3 indicates that Co-substitution in the base oxide decreases the $\Delta H^{0\#}$ value. Values of standard entropy of activation ($\Delta S^{0\#}$) (Table 3) for oxygen evolution was found to be highly negative. This suggests the role of adsorption phenomenon in the electrochemical formation of oxygen. The $\Delta S^{0\#}$ values were calculated by using the relation [45].

$$\Delta S^{0\#} = 2.3R [\log j + \Delta H_{el}^{0\#}/2.3RT - \log (nF\omega C_{OH^-})]$$

Where, $\omega (= k_B T/h)$ is the frequency term and $n = 2$. All the terms in the above equation have their usual meanings. The estimated values of transfer coefficient (α), standard enthalpy of activation ($\Delta H^{0\#}$) and entropy of activation ($\Delta S^{0\#}$) as shown in Table 3, were found to be very close to that reported in literature [19].

Table 3. Thermodynamic parameters for O₂ evolution on Ni/Co_xFe_{3-x}O₄ (0 ≤ x ≤ 1.5) 1M KOH

Electrode	$\Delta H_{el}^{0\#}$ (kJ mol ⁻¹) at (E = 675 mV)	$-\Delta S^{0\#}$ (J deg ⁻¹ mol ⁻¹)	α	$\Delta H^{0\#}$ (kJ mol ⁻¹)
Fe ₃ O ₄	81.3	68.2 ± 23.4	1.3 ± 0.4	125.5 ± 6.6
Co _{1.5} Fe _{1.5} O ₄	67.9	96.5 ± 23.3	1.4 ± 0.3	116.6 ± 5.1

4. CONCLUSION

The study shows that the substitution of Co for Fe in the base oxide greatly enhances the electrocatalytic activity of the oxide toward the OER. The Co_{1.5}Fe_{1.5}O₄ electrode showed about 3 - 9 times higher activity as compared to the base oxide in 1M KOH at 25⁰C. Co-substitution also reduces the value of standard enthalpy of activation.

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