Synthesis and Electrocatalytic Properties of Ni-substituted \( \text{Co}_3\text{O}_4 \) for Oxygen Evolution in Alkaline Medium

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Abstract: Cobalt based Ni-substituted spinel-type oxides were synthesized by carbonate co-precipitation method using \( \text{Na}_2\text{CO}_3 \) as precipitant and studied their electrocatalytic properties towards oxygen evolution reaction (OER) in alkaline medium. Materials were synthesized by using nitrates of nickel and cobalt. For electrochemical studies, oxide powder was transformed in the form of oxide film electrode on nickel substrate. Techniques used were cyclic voltammetry, electrochemical impedance spectroscopy (EIS) and anodic Tafel polarization. Results obtained show that the Ni-substitution in \( \text{Co}_3\text{O}_4 \) matrix increase the oxide roughness factor considerably but did not significantly contribute in electrocatalytic properties for oxygen evolution reaction (OER). Tafel slope and order of reaction with respect to [OH\(^-\)] concentration at low overpotential were found to be \( \sim 2.303RT/nF \) and \( \sim 1 \), respectively. The effect of temperature on the electrochemical behavior has also been investigated for oxide electrode. Thermodynamic parameters such as, standard electrochemical enthalpy of activation (\( \Delta H^{0*} \)), standard enthalpy of activation (\( \Delta H^{0\circ} \)) and standard entropy of activation (\( \Delta S^{0\circ} \)) were estimated by recording the Tafel polarization curves at different temperatures. X-ray diffraction (XRD), infrared (IR) spectroscopy and scanning electron microscope (SEM) techniques have been used to characterize the materials physicochemically.

Keywords: Oxygen evolution reaction, Spinel type oxide, Electrocatalysis, Tafel slope, Roughness factor

1. INTRODUCTION

Transition metal mixed oxides of spinel (e.g. \( \text{Co}_3\text{O}_4 \), \( \text{CuCo}_2\text{O}_4 \), \( \text{NiCo}_2\text{O}_4 \), etc.) and perovskite (\( \text{LaCoO}_3 \), \( \text{LaMnO}_3 \), etc.) families are considered as promising electrode material for the application in electrochemical devices such as water electrolysis cells, fuel cells and metal air batteries [1-8]. Ni-substituted oxide materials were found to be useful in many electrode reactions from \( \text{O}_2 \) and \( \text{Cl}_2 \) evolution to \( \text{O}_2 \) reduction [9,10]. \( \text{NiCo}_2\text{O}_4 \) is generally regarded as mixed valent oxide that adopts a spinel structure in which nickel occupies the octahedral site and cobalt is distributed over both octahedral and tetrahedral sites. But, cobalt electrode of these materials obtained by conventional methods usually have low electrochemically active (or real) surface area and hence the electrocatalytic activity. It is, therefore; desire to improve their specific surface area to the reasonable extent.

The efficiency of these oxide materials can be enhanced by developing suitable low temperature preparative methods based on the knowledge of solution chemistry. The textural characteristic and hence the electrochemical interfacial properties of the oxide electrode can also be changed by the partial replacement of constituent metal ion by suitable transition metal ions. Chi et al. [14] synthesized \( \text{Ni-Co} \) spinel oxide by using different methods and studied the effect on the physicochemical and electrochemical properties. The lattice parameters, crystalllite size (S) and surface composition of the material were investigated by De Faria et al. [15]. Recently, B. Cui et al. [16] synthesized core-ring structured \( \text{NiCo}_2\text{O}_4 \) nanoplatelets by hydroxide co-precipitation decomposition method and characterized their electrocatalytic properties for the OER. In general, it is observed that both electronic and geometrical factors influence the electrocatalytic properties of the material. The former are governed by the
electronic structure and the nature of the active sites such as Co$^{3+}$ in NiCo$_2$O$_4$\cite{9,17,18}, while the latter by the surface concentration of the active sites as well as the extent of actual surface area \cite{15}. In the present investigation, pure and Ni-substituted spinel oxides were synthesized by low temperature carbonate co-precipitation method and studied their physicochemical as well as electrochemical properties with regards to oxygen evolution in alkaline medium. Results, so obtained, are described here.

2. EXPERIMENTAL

Pure and Ni-substituted co-baities were prepared by carbonate co-precipitation method \cite{19}. In each prepreparation, chemicals and reagents used were of analytical grade and purified. In order to get the desired oxide, aqueous solution of metal nitrates, Ni(NO$_3$)$_2$ and Co(NO$_3$)$_2$2H$_2$O (Merck) were taken in stoichiometric ratio and saturated solution of Na$_2$CO$_3$ was added to this in a drop wise manner with constant stirring at 60$^\circ$C, so as to precipitate metal ions as metal carbonate, completely. The precipitate was filtered and washed thoroughly with double distilled water, dried at 120$^\circ$C for 12 h and decomposed at 350 $^\circ$C for 4 h in air to obtained desired oxide. The materials were characterized by recording infrared (IR) spectra (JASCO FT/IR-5300) and XRD powder patterns (Guiner-Wolf Chamber with the Co-K$_\alpha$-radiation, $\lambda = 0.178889$ nm). The morphological information of the oxide powder was obtained by a scanning electron microscope (SEM) using JEOL (JSM 6490). For electrochemical investigation, the oxide film was obtained by painting the slurry of oxide powder with glycerol (2 drops/100 mg of oxide) onto one side of pretreated nickel support (geometrical surface area: 1.5 cm$\times$1 cm, Aldrich 99.9% purity) and on subsequent sintering at 340 $^\circ$C for 2 h. At temperature below 340$^\circ$C, the catalytic film obtained was not reasonably adherent. The procedure adopted for the pretreatment of nickel support and electrical contact is similar to those reported in literature \cite{20, 21}. In each experiment, reference electrode is separated from test solution by using luggin capillary containing an aqueous agar-agar (KCl) salt bridge. All the potential values reported in the text correseponds to the reversible potential for the reference electrode Hg/HgO/1M KOH (98 mV vs NHE) only. The instrument used in the investigation was the electrochemical impedance system (EG & G, PARC, USA) comprising with lock-in-amplifier (model 5210), and potentio-galvanostat (model 273A).

3. RESULTS AND DISCUSSION

3.1. XRD, IR and SEM Studies

Formation of spinel phase of Co$_2$O$_4$ and its Ni-substituted derivatives was confirmed by XRD powder patterns and IR spectroscopy. Powder X-ray diffraction (XRD) of two representative oxides viz. Co$_2$O$_4$ and NiCo$_2$O$_4$ were recorded between 20 = 0 and 20 = 100 and the spectra, so obtained, are shown in Fig. 1. Figure shows that the carbonate method produces almost pure and crystalline nanosized spinel product and followed cubic crystal geometry (a = b = c and a = $\beta$ = $\gamma$ = 90°). The crystallographic density (d) was estimated using the relation, d = 8 M/V, where M and V are corresponding molecular mass and volume of the material assuming 8 molecules of oxide in a unit cell. The cubic cell parameters a were computed and found to be $\sim$8.07Å and $\sim$8.12Å for Co$_2$O$_4$ and NiCo$_2$O$_4$, respectively. These values are very close to their respective literature values, 8.08Å (JCPDS ASTM 9-418) and 8.128Å (JCPDS ASTM 20-78).

It is observed that Ni-substitution in Co$_2$O$_4$ matrix increased the a-value. similar increase in a-value has also been reported by other worker \cite{9, 22-25} wherein oxides were obtained by other methods. The crystalllite size (S) of the oxide was estimated by using Scherrer’s formula, S = $0.9 \lambda / \beta \cos \theta$, where, $\lambda$ is the wavelength of radiation used, $\beta$ is full width at half maximum of the most intense peak in radian and $\theta$ is corresponding angle in degree. The average crystal dimensions were 33.5 nm and 28.4 nm for Co$_2$O$_4$ and NiCo$_2$O$_4$, respectively. The results show that carbonate co-precipitation produces nano sized spinel oxides with comparatively
smaller size than those obtained by oxalic acid precipitation method [26]. However, the observed values are larger than those prepared by ethanol evaporation method [27].

Fig. 2 represents the IR-spectra of 1.0 mol Ni-substituted oxide recorded between 4000 – 400 cm⁻¹. The observed two strong peaks at 662 and 565 cm⁻¹ corresponds to the pure phase of spinel cobaltite and are ascribed to stretching and bending modes of vibrations of Co³⁺/ or Ni³⁺ in octahedral site [28].

SE-micrographs of each oxide powder obtained at the magnification × 2500 are shown in the Fig. 3 (a-f). Morphology of each ox-
3.2. Cyclic voltammetry (CV)

In order to investigate the behavior of the oxide surface with regard to oxidation reduction reaction, cyclic voltammogram of pure and Ni-substituted oxides was recorded in 1M KOH over the potential range of 0.0 to 650 mV at the scan rate of 20 mV sec\(^{-1}\) at 25°C. Cyclic voltammetric curves of Co\(_2\)O\(_4\) and NiCo\(_2\)O\(_4\) are given in Fig. 4.

Cyclic voltammogram of Co\(_2\)O\(_4\) showed a pair of redox peaks, an anodic and a cathodic, prior to the onset of oxygen evolution reaction. However, in the case of Ni-substituted oxide electrodes, two pairs of redox peaks have been observed. These two different kinds of surface redox processes have \(E^\circ\) values 490±30 and 321±30mV.

Table 1 shows that \(E^\circ\)-value for Co\(_2\)O\(_4\) and Ni-substituted co-precipitates are 509 mV and 490±30mV corresponding to the redox reaction Co(IV) + e\(^-\) ↔ Co(III) [1,29,30]. However, Ni-substituted co-precipitates also show another couple of peaks with \(E^\circ\)-value 321±30mV, which corresponds to redox reaction Ni(III) + e\(^-\) ↔ Ni(II) [30]. With exception of 0.5 mol Ni, substitution of nickel for cobalt in Co\(_2\)O\(_4\) matrix marginally reduces the \(E^\circ\)-value and this effect of reduction is being observed maximum in case of 1.0 mol Ni-substituted oxide. The values of peak potentials \(E_{pa}\) and \(E_{pc}\), the formal redox potential (\(E^\circ\) = \((E_{pa}+E_{pc})/2\)) were analyzed from the cyclic voltammetric curve and are listed in Table 1.

3.3. Impedance spectroscopy/Roughness factor (\(R_F\))

The electrochemically active area of the oxide electrode is determined in terms of roughness factor. For the purpose, impedance spectra were recorded at three different potentials 0, 50 and 100 mV in 1 M KOH at 25°C in the frequency range from 0.1 to 10\(^6\) Hz. The DC potentials chosen were in the region wherein the contribution of faradic processes was practically negligible as it is quite evident from cyclic voltammogram shown in Fig. 4. The capacitance double layer (\(C_a\)) of the catalyst/1M KOH interface was determined by analyzing impedance data using series LRQC equivalent circuit model [31], where \(L\), \(R\), \(Q\) and \(C\) are the inductance (henri), resistance (ohm), constant phase element (FS\(^{-n}\)) and capacitance (farad), respectively. The series model is fairly reproduced the feature of experimental curves. Some representative impedance spectra in both Nyquist and Bode model at 50 mV are shown in Fig. 5 (a & b). Relative values of oxide roughness factor was determined from the \(C_a\) value of the oxide/solution interface by assuming 60\(\mu\)F cm\(^{-2}\) as the \(C_a\) for smooth oxide surface [1,9,32]. The value of \(C_a\) and other circuit parameters determined at three DC potentials were approximately the same and their average values are given in Table 2. The introduction of Ni in Co\(_2\)O\(_4\) matrix increases the oxide roughness factor and it is found to be higher in the case of lower Ni-substitution (i.e. in 0.25 and 0.5 mol). It is noteworthy that the roughness factor of oxides produced by this method is, in general, higher than those reported for the similar oxide film electrodes prepared by other methods. For example, the Co\(_2\)O\(_4\) film electrode on Ni, Ti, and Cd/glass prepared by spraying [20], on Ni prepared by sequential solution coating [9] and hydroxide co-precipitation method [24] were ~530, ~9, and ~63, respectively. While, the present method produced the oxide roughness ~1030 for the same oxide on Ni. Similarly, NiCo\(_2\)O\(_4\) obtained by this method exhibited many times higher roughness than the same oxide obtained by spray pyrolysis method on Ni [20]. However, this value was similar to that the same oxide film obtained by the hydroxide co-precipitation method [24] (\(R_F\) = 1460). It is worth mentioning that the \(R_F\) values quoted in the literature were determined by cyclic voltammetry.

3.4. Electrocatalytic activity

The electrocatalytic activity of pure and Ni-substituted Co\(_2\)O\(_4\) have been examined with respect to the electrolytic oxygen evolution reaction (OER) in 1M KOH at 25°C. For the purpose, the anodic polarization curves were recorded for each oxide catalyst in 1M KOH at the scan rate of 0.2 mV sec\(^{-1}\). The polarization curve,
Figure 5. (a): Complex impedance (Nyquist) plots for Co$_3$O$_4$, Ni$_{0.5}$Co$_{2.5}$O$_4$ and NiCo$_2$O$_4$ electrodes in 1M KOH at E = 50 mV (25 °C). (b): Bode plots for Co$_3$O$_4$, Ni$_{0.5}$Co$_{2.5}$O$_4$ and NiCo$_2$O$_4$ electrodes in 1M KOH at E = 50 mV (25 °C).
so recorded, was almost similar with each catalyst and representative polarization curves for CoO₄ and NiCoO₄ are shown in Fig. 6. Values of Tafel slope corresponding to each polarization curve were estimated from the polarization curve and found to be ranged between 63-74 mV decade⁻¹ and 98-134 mV decade⁻¹ at lower and higher potential region, respectively. To compare the electrocatalytic activity of catalysts, the apparent current density (jₐ) and true current density (jₐ) determined at two potentials 650 and 700 mV from polarization curves are given in Table 3. It is observed that jₐ-value at both potentials did not follow a definite pattern with Ni-substitution in cobaltite matrix. However, jₐ-value at both potentials reduces considerably with Ni-substitution in cobaltite matrix and maximum reduction observed with NiCoO₄.

To determine the order of reaction (p) with respect to [OH⁻] for OER, the anodic Tafel polarization curves on CoO₄ and NiCoO₄ were recorded at varying KOH concentrations keeping the ionic strength (μ) of the medium and temperature constant. The ionic strength of the medium was maintained constant by using KNO₃ as an inert electrolyte. The order of OER was estimated from the slope of linear plot log j vs log [OH⁻] (Fig. 7) and found to be approximately unity (1.0 & 1.2). Values of Tafel slopes and order for OER on electrocatalysts suggest that the electroformation of oxygen on the oxide catalysts follows almost similar mechanistic paths, regardless of the Ni-substitution in CoO₄ matrix.

The influence of temperature on the OER has also been investigated on some oxide catalysts (viz., CoO₄, Ni₈₂₅Co₂₇O₄ and NiCoO₄) at different temperatures 30, 40, 50, 60 and 70 °C. The standard apparent electrochemical activation energy (ΔH°FE,app) was determined by constructing the Arrhenius plot (log j vs 1/T) at constant applied potential (640 mV) in first Tafel region and shown in Fig. 8. The electrochemical activation energy (ΔH°FE,app) was calculated by measuring the slope of the plot. The charge transfer coefficient (α) and standard activation energy (ΔH°FE,app) were estimated from b values at different temperatures and by using the relation ΔH°FE,app = ΔH°FE + αFE, respectively. The average values of electrochemical activation energy (ΔH°FE,app), charge transfer coefficient (α) and standard activation energy (ΔH°FE,app) are given in Table 4.

The standard entropy of reaction (ΔS°⁰) has also been calculated by using the following relation [33].

$$\Delta S^0 = 2.303R \left[ \frac{\Delta H^0}{2.303RT} + \log j - \log n\text{F} \text{O}_\text{OH}^- \right]$$

where ω = kT/h and n = 2 and other terms involved in the

![Figure 6. iR-free Tafel plots on the cobaltite film electrode on Ni in 1M KOH at 25 °C (scan rate 0.2 mV sec⁻¹); (a) CoO₄ and (b) NiCoO₄](image)

Table 2. Values of equivalent circuit parameter for OER on pure and Ni-substituted cobaltite matrix in 1M KOH at 25°C.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Loading (mg cm⁻²)</th>
<th>L × 10⁶ (heneri)</th>
<th>R (ohm)</th>
<th>Q × 10⁻¹ (FS⁻¹)</th>
<th>n</th>
<th>C × 10³ (mF)</th>
<th>Rₑ</th>
<th>Rₑ (mg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoO₄</td>
<td>5.4±1.0</td>
<td>1.04±0.2</td>
<td>2.4±0.5</td>
<td>0.87±0.11</td>
<td>0.6±0.1</td>
<td>61.8±1.8</td>
<td>1030±30</td>
<td>~191</td>
</tr>
<tr>
<td>Ni₈₂₅Co₂₇O₄</td>
<td>4.8±0.1</td>
<td>0.89±0.01</td>
<td>2.3±0.1</td>
<td>3.14±0.16</td>
<td>0.7±0.1</td>
<td>122.6±4.1</td>
<td>2042±68</td>
<td>~425</td>
</tr>
<tr>
<td>Ni₈₂₅Co₂₇O₄</td>
<td>5.5±0.1</td>
<td>0.89±0.04</td>
<td>2.0±0.1</td>
<td>6.92±0.98</td>
<td>0.5±0.1</td>
<td>135.3±6.1</td>
<td>2254±101</td>
<td>~410</td>
</tr>
<tr>
<td>NiCoO₄</td>
<td>5.5±0.1</td>
<td>0.73±0.03</td>
<td>2.7±0.2</td>
<td>4.41±0.77</td>
<td>0.4±0.1</td>
<td>97.9±1.2</td>
<td>1631±21</td>
<td>~297</td>
</tr>
<tr>
<td>Ni₈₂₅Co₂₇O₄</td>
<td>5.1±0.4</td>
<td>0.95±0.11</td>
<td>1.7±0.1</td>
<td>2.41±0.13</td>
<td>0.3±0.1</td>
<td>112.0±1.8</td>
<td>1867±30</td>
<td>~366</td>
</tr>
<tr>
<td>Ni₈₂₅Co₂₇O₄</td>
<td>5.5±1.0</td>
<td>0.61±0.11</td>
<td>1.9±0.2</td>
<td>5.96±0.14</td>
<td>0.2±0.1</td>
<td>89.6±1.9</td>
<td>1494±33</td>
<td>~272</td>
</tr>
</tbody>
</table>

Table 3. Values of electrode kinetic parameter for OER on pure and Ni-substituted cobaltite 1M KOH at 25°C.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Loading (mg cm⁻²)</th>
<th>Tafel slope /mV decade⁻¹</th>
<th>Order (p)</th>
<th>j/mA cm⁻² at E/mV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>b₁</td>
<td>b₂</td>
<td></td>
<td>650</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>jₛ</td>
</tr>
<tr>
<td>CoO₄</td>
<td>5.4±0.2</td>
<td>66</td>
<td>134</td>
<td>1.2</td>
</tr>
<tr>
<td>Ni₈₂₅Co₂₇O₄</td>
<td>4.8±0.1</td>
<td>72</td>
<td>101</td>
<td>-</td>
</tr>
<tr>
<td>Ni₈₂₅Co₂₇O₄</td>
<td>5.5±0.1</td>
<td>74</td>
<td>114</td>
<td>-</td>
</tr>
<tr>
<td>NiCoO₄</td>
<td>5.5±0.2</td>
<td>63</td>
<td>101</td>
<td>1.0</td>
</tr>
<tr>
<td>Ni₈₂₅Co₂₇O₄</td>
<td>5.1±0.4</td>
<td>71</td>
<td>98</td>
<td>-</td>
</tr>
<tr>
<td>Ni₈₂₅Co₂₇O₄</td>
<td>5.5±0.5</td>
<td>68</td>
<td>104</td>
<td>-</td>
</tr>
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</table>
equation have their usual meaning. Table 4 shows that 0.25, 0.5 and 1.0 mol Ni-substitution in Co$_3$O$_4$ matrix decrease the $\Delta H^\#_{0}$ and $\Delta H^{10}$-values for OER, the magnitude of reduction being the greatest in 0.5 mol Ni in both the cases. Value of Tafel slope ($b_1$) increased slightly with rise in temperature from 30 to 70°C. The increase in $b_1$ values were 50 to 59, 72 to 78 and 64 to 72 mV decade$^{-1}$ for Co$_3$O$_4$, Ni$_{0.25}$Co$_{2.75}$O$_4$ and NiCo$_2$O$_4$, respectively. The increase in the $b_1$ value with rise in temperature is not usual but it is demanded as per its definition, $b = \frac{2.303RT}{F \Delta S_{0}}$. The charge transfer coefficient ($\alpha$) value was observed to be almost constant with each electrocatalyst. The values of the standard entropy of activation ($\Delta S^{0}$) for OER on Co$_3$O$_4$ and its Ni-substituted derivatives were found to be highly negative and not much different also, regardless of nature of catalysts. The highly negative value of $\Delta S^{0}$ indicate that the reaction of oxygen evolution is followed through formation of similar adsorption intermediate.

4. CONCLUSION

The result showed that co-precipitation method produces single phase nano-sized spinel type oxides with enhanced surface area and hence high electrocatalytic activity. The Ni-substitution in Co$_3$O$_4$ matrix considerably improves the oxide roughness factor and found to be greatest with the 0.5 mol Ni-substitution. However, the substitution of nickel did not affect the electrocatalytic activity of the material significantly.

5. ACKNOWLEDGEMENTS

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REFERENCES


Table 4. Values of thermodynamic parameter for OER on pure and Ni-substituted cobaltites 1M KOH.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Charge transfer coefficient ($\alpha$)</th>
<th>$\Delta H^{\#}_{2}$ /kJ mol$^{-1}$ at E = 0.58 V</th>
<th>$\Delta H^{10}$ /kJ mol$^{-1}$ calculated from $b$-value</th>
<th>$-\Delta S^{0}$ /J deg$^{-1}$mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co$_3$O$_4$</td>
<td>1.13</td>
<td>58.1</td>
<td>120.2</td>
<td>182.4</td>
</tr>
<tr>
<td>Ni$<em>{0.25}$Co$</em>{2.75}$O$_4$</td>
<td>0.86</td>
<td>48.2</td>
<td>97.2</td>
<td>200.8</td>
</tr>
<tr>
<td>Ni$<em>{0.5}$Co$</em>{2.5}$O$_4$</td>
<td>0.76</td>
<td>46.9</td>
<td>88.9</td>
<td>205.0</td>
</tr>
<tr>
<td>NiCo$_2$O$_4$</td>
<td>0.93</td>
<td>54.6</td>
<td>107.4</td>
<td>184.9</td>
</tr>
</tbody>
</table>