Electrocatalytic properties of spinel type Ni$_x$Fe$_{3-x}$O$_4$ synthesized at low temperature for oxygen evolution in KOH solutions

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Some nickel-substituted ferrites (Ni$_x$Fe$_{3-x}$O$_4$, where x = 0.25, 0.5, 1.0, 1.5) obtained at low temperature in the form of films on nickel supports have been investigated as electrocatalysts for the oxygen evolution reaction in alkaline solution. The true electrocatalytic activity of the oxide is greatly increased by increasing the nickel substitution, being highest with 1.0 mole Ni. The electrocatalytic evolution of O$_2$ follows approximately second-order kinetics in OH$^-$ ion concentration. The Tafel slope values for the reaction at different catalytic films are approximately the same (i.e., 41-47 mV decade$^{-1}$). The catalysts prepared in situ have been observed to be electrocatalytically much more active than those of similar oxides prepared by other methods.

Ferrosplines, M$_x$Fe$_{3-x}$O$_4$ (M = a bivalent metal ion), are technologically important materials owing to their remarkable structural, electronic, magnetic and catalytic properties$^1$. They have been used as heterogeneous catalysts in a number of reactions such as highly selective oxidation of butene to butadiene$^2$, synthesis of ammonia$^3$, decomposition$^4$ of H$_2$O$_2$ etc. Nickel ferrite and substituted nickel ferrites find applications in electronic technology and also in devices for telecommunication measurements$^5$. The use of cast magnetite (Fe$_3$O$_4$) as anodes for chlorine and chlorate production is well-known$^6$. There are very few studies on the use of this spinel family of oxides as oxygen anodes$^7-9$ probably because of relatively high overpotential$^{10}$.

Very recently we have studied$^{11}$ the electrocatalytic properties of pure and Mn-substituted ferrites, synthesized at 70°C by a precipitation method, for oxygen evolution in alkaline solution. Results showed that the catalysts prepared by this method are many times more active than those prepared by ceramic method. In the present paper we report the preparation of Ni-substituted ferrites and their use as oxygen anodes in alkaline medium.

Experimental

The nickel-substituted products of cast magnetite (Fe$_3$O$_4$) were obtained at 70°C as precipitates by adding the required amount of 5M NaOH to O$_2$-saturated mixed aqueous solutions of nickel sulphate (LR, BDH, nickel 21-23%) and iron (II) ammonium sulphate (AR, BDH, 99%) in stoichiometric ratio as described elsewhere$^{11,12}$. The formation of the spinel was checked by recording XRD powder patterns.

The electrode was prepared in the film form by painting a slurry containing the oxide and Triton X-100 onto one side of the pretreated nickel support (1.5 x 1.0 cm$^2$). After painting, the plate was annealed at 400°C for 1.5 hr. To obtain a good adherent oxide film the sample was removed from the furnace when it attained a temperature <80°C. Morphology of the film was examined by a scanning electron microscope (SEM, JEOL). The pretreatment of the support and electrical contacts with the oxide film were made as described earlier$^{11,13}$.

Electrochemical studies, viz., cyclic voltammetry AC impedance and Tafel polarization were carried out in a conventional three-electrodes single compartment Pyrex glass cell using electrochemical impedance system (Model 273A, EG and G, PARC). The procedural details are given in our previous paper$^{11}$. A bright Pt-foil was used as counter electrode. The reference electrode was Hg/HgO/KOH(1 M). All potential values in the text are given with respect to the reversible potential for this reference, which is +0.099 V/SHE.

The electrochemically active area of the oxide electrode was determined by AC-impedance measurements in 1 M KOH over the frequency range of 0.01 Hz to 100 kHz at three different DC potentials between 0 -0.2 V. The data were displayed as Bode plot (i.e. log $|Z|$ versus log $f$ and $\theta$ vs log $f$) and the double layer capacitance ($C_{dl} = 1/|Z|$) was estimated by extrapolating the linear capacitance region to the log $|Z|$ axis at $\omega = 1$ (or $f = 0.16$ Hz) as reported elsewhere$^{14}$. 

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Results and discussion

Morphology of the films appeared to be similar regardless of the nickel substitution in the oxide. Four representative scanning electron micrographs, two for the pure and the other two for 1.0 mole Ni-substituted ferrite are shown in Fig. 1(a-d). At low magnification the films exhibited some cracks with the maximum width, 7-10 μm (Fig. 1c & d).

Cyclic voltammetry

Cyclic voltammograms of the oxide electrodes (Ni/Ni₃FeₓO₄) at the potential scan rate of 20 mV sec⁻¹ at 25°C indicate almost similar features (Fig. 2), regardless of the presence or absence of the Ni in the Fe₃O₄ lattice. Each voltammogram exhibited a pair of redox peaks before the onset of oxygen evolution. The formal redox potential for the redox couple formed on different catalysts was found to range between 0.412 and 0.470 V. It is noteworthy that cyclic voltammogram of nickel substituted ferrite films on Pt did not show any redox peaks before the commencement of O₂ evolution. Thus the redox peaks produced on the Ni₃FeₓO₄ films on Ni in 1M KOH during anodic cycling conditions originated from the nickel support and not from the oxidation-reduction of the oxide film. Similar results were also obtained for manganese-substituted ferrite films on Ni²⁺.

Double layer capacitance/roughness factor

In electrocatalysis dealing with different electrode materials, the knowledge of electrochemically active surface area (or roughness, \( R_F \)) of the catalysts is important. In the present work, \( R_F \) was estimated from the double layer capacitance (\( C_{dl} \)) value of the oxide/1M KOH interface, determined by impedance measurements. AC impedance data were taken over a frequency range of 0.01 Hz - 100 kHz at varying potentials and corresponding to each potential the data were plotted as Bode curves. These plots were quite similar to each other and demonstrated a single capacitive region over the frequency range used. A typical Bode plot for Ni₀.₅ Fe₂.₅O₄ are shown in Fig. 3.

To minimize the contribution of any faradaic process, the \( C_{dl} \), determined in the potential region 0-200 mV were considered for the estimation of the oxide roughness.
Electrocatalytic activity

The electrocatalytic activity of oxides was determined by recording the IR-free Tafel plots (i.e., $E$ versus log $i$) for oxygen evolution at the potential scan rate of 0.2 mV s$^{-1}$ in $1 \text{M KOH}$ solution at 25°C (Fig. 4). The Tafel polarization curves shown in Fig. 4 are similar and indicate little influence of the nickel substitution on the nature of the curve. At low overpotential, the Tafel slope for O$_2$ evolution on different nickel substituted oxides was approximately the same (41-47 mV decade$^{-1}$), indicating that the O$_2$ evolution reaction follows similar mechanistic paths on all the catalysts. Figure 4 further shows that amongst all the catalysts, Ni$_{0.5}$Fe$_{2.5}$O$_4$ is the electrocatalytically most active oxide while Ni$_{0.25}$Fe$_{2.75}$O$_4$ is the least active one. Based on the oxygen overpotential values at the current density of 300 mA cm$^{-2}$ (on geometrical scale) in $1 \text{M KOH}$ at 25°C (Table 1), the electrocatalytic activity of oxides followed the order as:

$$\begin{align*}
\text{Ni}_0.5\text{Fe}_{2.5}\text{O}_4 (\eta_{O_2}=420 \text{ mV}) & \quad \text{NiFe}_2\text{O}_4 (\eta_{O_2}=431 \text{ mV}) \\
\text{Ni}_1.5\text{Fe}_{1.5}\text{O}_4 (\eta_{O_2}=482 \text{ mV}) & \quad \text{Ni}_{0.25}\text{Fe}_{2.75}\text{O}_4 (\eta_{O_2}=520 \text{ mV})
\end{align*}$$

The apparent electrocatalytic activity for the nickel-substituted ferrite electrodes, particularly Ni$_{0.3}$Fe$_{2.3}$O$_4$, has been observed to be very high as compared to the similar electrodes prepared by Iwakura et al.$^7$ by thermal decomposition of metal nitrates and Orehotskey et al.$^8$ by a freeze-drying method. At a current density of 10 mA cm$^{-2}$ (on a geometrical scale) Iwakura et al. observed $\eta_{O_2}$ =440 mV on CoFe$_2$O$_4$ and $\eta_{O_2}$ =580 mV on MnFe$_2$O$_4$ in $1 \text{M KOH}$ at 30°C. Orehotskey et al. found $\eta_{O_2}$ =340 mV on NiFe$_2$O$_4$ in 30 wt% KOH at 25°C, while our electrode (NiFe$_2$O$_4$) in $1 \text{M KOH}$ at 25°C gave $\eta_{O_2}$ 330 mV only. Overpotential data for electrodes other than those under studies are not available at high current densities.

The true electrocatalytic activity has also been estimated at different overpotentials. Based on values of the true current density at $\eta_{O_2}$ =400 mV in $1 \text{M KOH}$ at 25°C, the different catalysts showed the following order:

$$\begin{align*}
\text{NiFe}_2\text{O}_4 (37.3 \text{ mA cm}^{-2}) & \quad \text{Ni}_{0.5}\text{Fe}_{2.5}\text{O}_4 (24.8 \text{ mA cm}^{-2}) \\
\text{Ni}_{1.5}\text{Fe}_{1.5}\text{O}_4 (17.5 \text{ mA cm}^{-2}) & \quad \text{Ni}_{0.25}\text{Fe}_{2.75}\text{O}_4 (14.2 \text{ mA cm}^{-2}) \\
\text{Fe}_3\text{O}_4 (6.2 \text{ mA cm}^{-2})
\end{align*}$$

This indicates that the nickel substitution in the Fe$_2$O$_4$ lattice increases the true catalytic activity of the oxide exhibiting a maximum with 1.0 mole Ni (i.e. NiFe$_2$O$_4$). The room temperature saturation magnetization value for the oxides has also been observed to follow a similar trend.$^7$. Thus, the change in the electrocatalytic properties with change in nickel-substitution can be ascribed to the variation in the magnetic properties of the oxide. Iwakura et al. also observed an increase in electrocatalytic activity with increase in effective Bohr magneton in the case of spinel-type ferrite films electrodes of MFe$_2$O$_4$ (M = Mg, Cu, Ni, Co, and Mn) on Fe substrate.$^7$. In contrast, Orehotskey et al.$^8$ did not observe any influence of the variation in the room temperature saturation magnetization on the electrocatalytic activity of the
Table 1 — Electrode kinetic parameters on Ni/Ni$_x$Fe$_{3-x}$O$_4$ ($0 \leq x \leq 1.5$) in 1 M KOH at 25°C

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Tafel slope (mV dec$^{-1}$)</th>
<th>Order $(p)$</th>
<th>$\eta_{o2}$ (mV) at $I$ (mA cm$^{-2}$)</th>
<th>$I$(mA cm$^{-2}$) at $\eta_{o2}$(mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>100</td>
<td>300</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>66</td>
<td>-</td>
<td>472</td>
<td>651</td>
</tr>
<tr>
<td>Ni$<em>{0.25}$Fe$</em>{2.75}$O$_4$</td>
<td>41</td>
<td>-</td>
<td>414</td>
<td>520</td>
</tr>
<tr>
<td>Ni$<em>{0.5}$Fe$</em>{2.5}$O$_4$</td>
<td>42</td>
<td>2.3</td>
<td>371</td>
<td>420</td>
</tr>
<tr>
<td>NiFe$_2$O$_4$</td>
<td>45</td>
<td>1.7</td>
<td>379</td>
<td>431</td>
</tr>
<tr>
<td>Ni$<em>{1.5}$Fe$</em>{1.5}$O$_4$</td>
<td>47</td>
<td>-</td>
<td>390</td>
<td>482</td>
</tr>
</tbody>
</table>

Ref. 11

Fig. 4 — IR-compensated Tafel plots for nickel ferrite film electrodes on Ni in 1 M KOH at 25°C [A; Ni$_{0.5}$Fe$_{2.5}$O$_4$; B; NiFe$_2$O$_4$; C; Ni$_{1.5}$Fe$_{1.5}$O$_4$; and D; Ni$_{0.25}$Fe$_{2.75}$O$_4$].

Ni$_x$Fe$_{3-x}$O$_4$ spinel series prepared by a freeze-drying technique for oxygen evolution in base.

The reaction order $(p)$ with respect to [OH$^-$] was determined by recording the Tafel polarization curves at different KOH concentrations (0.1-1.0 M), keeping the ionic strength of the solution constant ($\mu = 1.5$). For this purpose only the active catalysts 0.5 and 1.0 mole Ni-substituted ferrites, were chosen. The value of $p$ was estimated from the slope of the linear plot of log $i$ versus log [OH$^-$] at a constant potential across the oxide film/KOH interface and found to be $p = 2$. For the determination of the order, the first linear region of the Tafel polarization curves was chosen.

As has been observed by us, Orehotskey $et$ $al.$ also found similar low Tafel slope values (37-47 mV decade$^{-1}$) for O$_2$ evolution on Ni$_x$Fe$_{3-x}$O$_4$ (0.49 $\leq x \leq 1.68$) prepared by a freeze-drying technique. Also, the MnFe$_2$O$_4$ and Mn$_{1.5}$Fe$_{1.5}$O$_4$ electrodes, obtained by the method, similar to that employed in situ showed$^{11}$ low Tafel slope (36-47 mV decade$^{-1}$) and second-order kinetics in OH$^-$ concentration for O$_2$ evolution. In contrast, Iwakura $et$ $al.$ observed a considerably higher Tafel slope (110-115 mV decade$^{-1}$) on the catalytic film of the same oxide (NiFe$_2$O$_4$) prepared by the thermal decomposition of metal nitrates at 1150°C on a Pt-substrate. The observed higher Tafel slope may be attributed to the presence of phase inhomogeneity in the oxides.

As the observed values of the electrode kinetic parameters for the O$_2$ evolution reaction on Ni$_x$Fe$_{3-x}$O$_4$ were very similar to those found$^{11}$ on MnFe$_2$O$_4$ and Mn$_{1.5}$Fe$_{1.5}$O$_4$, a similar reaction mechanism could also be used to explain the results of the present investigation.

The study shows that the low temperature precipitation method is suitable for obtaining highly active nickel ferrites for electrolytic evolution of oxygen in KOH solutions. The substitution of Ni for Fe in the Fe$_3$O$_4$ lattice increases the true electrocatalytic activity significantly, the activity being highest with 1.0 mole Ni. The oxide roughness is also enhanced in the presence of nickel.

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References


