Electrochemically prepared Fe: NiO thin film catalysis for oxygen evolution reaction

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ABSTRACT

The electrocatalysis-based nickel oxide (NiO) films and doped with various amount of iron were synthesized on stainless steel (SS) substrate by electrodeposition. X-ray diffraction analysis (XRD) and filed effect scanning electron microscopy (FE-SEM) utilized to investigate structural and morphological properties. The X-ray diffraction analysis polycrystalline cubic structure has confirmed. Surface morphology study revealed the grains are regularly scattered over the total surface of the substrates after doping. The oxygen evolution reaction (OER) properties of doped films more efficient than that of pure thin films. The 4% Fe: NiO films exhibited an overpotential of 320 mV at 10 mA cm$^{-2}$ current density and a Tafel slope of 89.80 mV dec$^{-1}$. The electrode shows the high durability over 5 h with small degradation.

1 Highlights (for review)

NiO and Fe: NiO thin films were electrodeposited for OER application. The OER activity highly influence on the Fe doping. The overpotential of Fe: NiO electrode is 320 mV with a Tafel slope 89.80 mV dec$^{-1}$. Fe: NiO electrode shows best durability and stability.

2 Introduction

In recent days, essential is to design efficient energy conversion devices and innovation of bulk type sources due to increase in the growing energy demand [1–10]. The alternative energy sources can be utilized as substitute in the problems of energy demand. Though, the additional energy source like solar energy retains interrupted energy due to day-time cycle [11, 12]. Subsequently, the dependency on fossil fuels is diminished by conversion of energy from renewable sources [13]. The standby promising source for fossil fuels is hydrogen (H$_2$) due to high mass-specific energy density [14–16]. Electrochemical water splitting is favorable technology for making hydrogen as a hygienic chemical energy by using sustainable energy resources [17, 18].
The electrochemical water splitting is most promising approach to achieve cost-effective production of hydrogen. Currently, in water splitting noble metals (Pt, Ru and Ir-based compounds) as an electrocatalysts are used as effective electrocatalysts having minimum overpotential and insufficiency limitations on usage [19]. Hence, need to develop highly proficient and established inexpensive electrocatalysts towards the OER application. The transition metal-based OER electrocatalysts are considered due to richness and low cost in comparison to precious metals [20–25]. From last decades, nickel (Ni) and Ni-based materials explored the best electro-catalytic activity towards OER and economically available abundant in earth crust [26–30]. The miscellaneous catalytic properties of nickel oxides (NiO) incorporated in various useful devices [31, 32]. More in recent times, metal oxides are reported with doping for the best the OER catalytic performance analogous to or even greater than pristine compound [33, 34].

Presently, more research efforts are taking on NiO and Ni-based nanostructures for energy related applications. Khan et al. reported the combustion synthesis of Fe@NiO nanocomposites for supercapacitor applications [35]. Gao Manna et al. reported Ni–Fe mixed oxide as an efficient electrocatalyst for practical overall water electrolysis [36]. Bell et al. reported the structural and electrochemical investigation of Ni–Fe catalysts for the OER in alkaline electrolyte on gold electrode by electrodeposition [37]. Gordon et al. used the microplasma-based deposition method to coat the nanostructured Fe-doped NiO oxides for OER study. It was found that incorporating Fe into the rocksalt NiO structure results in a decrease in overpotential [38]. Boettcher et al., enhanced the OER activity by increasing the conductivity of nickel hydroxide by adding the Fe impurities systematically [39]. Hence, it is clear that adding Fe impurities into Ni-based catalysts is positive for both OER and HER, although the anode and cathode possess different interface behaviors for water electrolysis [40].

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In this work, we have reported electrochemical synthesis of iron-doped nickel oxide thin film onto a stainless steel (SS) substrate and treated with 350 °C heat treatment. The prepared film can be directly used for OER without further treatment such as adding binders or conductive film. Furthermore, iron-doped nickel oxide catalyst exhibit good OER performance in an alkaline medium. The Fe-doped nickel oxide exhibits low onset potential and overpotential, small Tafel slope with decent stability.

### 3 Experimental

The electrodeposition experiment was performed, in a conventional 3-electrode cell apparatus. Stainless-steel substrates were used as a cathode, polished by a fine grade polish paper, and then washed with acetone followed by drying in the same vapors to clean oily substances from the surface. The bath solution was formed using of 1.16 and 0.64 gm for Ni (NO3)2.6H2O and FeCl3, respectively. The potentiostatic mode is used at constant potential - 1.0 V/SCE. Subsequently, the prepared thin films treated at 350 °C for 2 h. and used for further characterizations. The XRD and FE-SEM appliances employed to investigate structural and surface morphology of prepared thin films.

The investigation of electrochemical study and stability of the electrodeposited nickel oxide and iron-doped nickel oxide films finished in 1 M KOH using a CHI6002E electrochemical workstation at room-temperature. The electrode catalytic activities estimated with support of LSV, steady-state polarization (Tafel plots), and stability of the doped and undoped thin films towards the OER.

The reversible hydrogen electrode (RHE) values are obtained with measured potentials from Nernst equation (eq. (1) was used)

\[ E_{\text{RHE}} = E_{\text{SCE/SCE}} + 0.059 \text{pH} + E^0_{\text{SCE/SCE}} \]

where \( E_{\text{RHE}} \) is the converted potential vs RHE, \( E_{\text{SCE/SCE}} \) is experimentally measured potential vs. reference electrode SCE and \( E^0_{\text{SCE/SCE}} \).

A linear portion of Tafel slope resolved by fitting plot with Tafel equation as,

\[ \eta = b \log (j) + a \]

where ‘b’ is the Tafel slope, \( \eta \) is over potential, and ‘a’ is the fitting parameter. The stability investigation was done with a current density 10 mA cm \(^{-2}\) for chronopotentiometry measurement.
4 Results and discussion

The nickel oxide and iron-doped nickel (Fe:NiO) oxide thin films were characterized for structural study with the help of with the help of X-ray diffraction analysis. The X-ray diffraction graphs of the pristine and doped nickel oxide thin films deposited on stainless steel substrate are shown in Fig. 1. The leading peaks are indexed at (111), (200) are planes of NiO with cubic structure [JCPDS: 47-1049]. In addition with this, the peaks assigned as an solid cube sign were originated due to the stainless steel substrate and the similar kind of results are reported by other researchers [41]. No extra peak corresponds to the iron oxide or other impurities observed means NiO structure is unaffected by iron dopant. The cubic structure continued the same results after addition of iron which reveals that iron ions without difficulty substituted in nickel ions with insignificant lattice distortion. The average grain size (D) measured for (2 0 0) peak from Debye-Scherer equation [42]:

\[ D = \frac{0.9\lambda}{\beta \cos \theta} \]  

The average crystallite size was calculated along (200) plane found to be decreased (15-9 nm) for zero-doped nickel oxide and iron-doped nickel oxide thin films. The additional amounts of dopant probably exerting strain force on edge motion consequently reduce in crystallite size [43].

![Fig. 1 X-ray diffraction patterns of NiO and Fe:NiO thin films at different doping concentrations (2, 4, and 6 wt%)](image)

The surface morphology of pure and iron-doped nickel oxide thin film is shown in Fig. 2a, b. The pristine NiO film seems some voids with non-uniform distribution of grains shown in Fig. 2a. Amalgamation of grains into different size-shapes and cloudy overgrown splashes are observed. In 4% Fe:NiO thin films splashes converts into spherical grains with fine surface morphology represented in Fig. 2b. The process of overgrowing and coalescence is observed with uniform distribution of the grains over the entire substrate. The surface morphological results are consisted with that of presented structural results.

4.1 OER and pseudocapacitive performance

The electrochemical performance at 20 mV/s scan rate was performed for pristine and doped iron nickel oxide thin films in 1 M KOH electrolyte. The linear sweep voltammetry (LSV) measurement of pure-nickel oxide, various amounts of iron-doped-nickel thin films are shown in Fig. 3. Usually researchers have been reported the NiO as capable catalysts in water splitting applications. A feasible oxygen evolution mechanism of nickel oxide thin films presented below. The Ni\(^{2+}\) ion on nickel oxide electrode surface oxidized to Ni\(^{3+}\), and then the oxidized Ni\(^{3+}\) ions during the electrochemical reactions [44]. The possible OER reaction mechanism of NiO thin film is given below:

\[ \text{Ni}^{2+} + 3\text{OH}^- \rightarrow \text{NiOOH} + \text{H}_2\text{O} + \text{e}^- \]  
\[ \text{NiOOH} + \text{OH}^- \rightarrow \text{NiO(OH)}_2 + \text{e}^- \]  
\[ \text{NiO(OH)}_2 + 2\text{OH}^- \rightarrow \text{NiO}_2 + 2\text{H}_2\text{O} + 2\text{e}^- \]

On the complete: OER : \(4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-\)

As shown in Fig. 3 the observed LSV curve for pure NiO and 2% iron-doped-nickel oxide presented the same overpotential (350 mV). Further, by comparing 6% Fe-doped nickel oxide exhibited the small catalytic activity due to the low film quality. The 4% iron-doped-nickel oxide thin film exhibited the 320 mV overpotential value which is minimum as required by pure and other iron-doped-nickel oxide films. After iron addition, the diffusion of Ni\(^{2+}\) cations is brought by Fe\(^{2+}\) addition whereas the oxidation of Ni\(^{2+}\) from Ni\(^{3+}\) rate also becomes high and
improved catalyst efficiency [44]. The bar diagram (Fig. 4), represents lowest overpotential of 320 mV with more anodic current for 4% iron-doped-nickel oxide film.

The kinetic behavior of the electrocatalyst is evaluated from the comparative Tafel plot analysis by using LSV curves. The Tafel plots are estimated for pristine and iron-doped-nickel oxide thin films near the onset potential represented in Fig. 5. The Tafel slope significance provides mechanism of water oxidation reactions and the kinetics, the smallest value of the slope is desirable for catalyst to generate a great current feedback over a slight potential range [45]. The 4% iron-doped-nickel oxide thin film possesses the smaller Tafel slope 89.80 mV dec⁻¹, whereas other pure nickel and iron-doped-nickel oxide (2 and 6%) shows the 402.31, 222.29 and 112.20 mV dec⁻¹, respectively. The lowest Tafel slope obtained for the 4% Fe-doped NiO thin film electrode is in agreement with the LSV results suggesting superior electrochemical reaction kinetics compared with other electrodes in Table 1 [46–48]. It is well known that the Tafel slope gives information about the electronic structure of the active metal sites and electronic conductivity. Thus, it is reasonable to
believe that the superior reaction kinetics is due to enhanced electronic conductivity and alteration of the electronic structure in the catalysts. Electrochemical stability is the most important factor in developing efficient catalysts for mass production. The Fig. 6 shows the chronopotentiometry experiment graph of 4% iron-doped-nickel oxide film at 10 mA cm$^{-2}$ measured for 5 h in 1 M KOH. The stable catalytic behaviors with negligible changes in overpotential even at a high current. The current density remains nearly constant to applied overpotential for long time; this present superior operational stability of doped NiO thin film for electrochemical OER.

5 Conclusion

We have presented pure and iron-doped-nickel oxide thin film catalysis on stainless steel substrate via electrodeposition method. The prepared thin films revealed change in crystallinity and surface morphology after addition of iron in nickel oxide. There was improvement in OER performance up to 4% iron among other thin films with overpotential 320 mV at 10 mA cm$^{-2}$ current density. The 89.80 mV dec$^{-1}$ minimum value obtained for 4% iron-doped-nickel oxide thin film for the Tafel slope. The doping effect may obtain influence in OER activity in NiO thin films. Our experimental results encourage to propose and investigation for other transition metal oxides for energy conversion applications.

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Author contribution

SCB: Writing-Original draft preparation, Methodology. RJ Deokate: Writing, reviewing and editing.

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Data availability

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Declarations

Competing interest  The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Ethical approval  This article does not contain any studies with human participants or animals performed by any of the authors.

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