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Electrochemical Studies of Iron-doped Nickel Oxide Electrode for Oxygen Evolution Reaction

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Abstract: In this paper, the iron-doped nickel oxide thin film as anode catalyst was prepared by RF reactive sputtering method. The oxygen evolution reaction (OER) on the iron-doped nickel oxide was investigated with cyclic voltammetry, linear sweep voltammetry, polarization curves and electrochemical impedance spectroscopy. Results show that the iron acts as active site in the film which makes the overpotential lower, and changes the rate-limiting from primary discharge of OH⁻ ions to the recombination of oxygen atom. With the increasing of oxygen content in flu ratio during sputtering, the electrocatalytic activities of the film increase. Iron-doped nickel oxide thin film is promising material as OER electrocatalyst for hydrogen production than the nickel electrode. The oxygen overpotential on the film was over 500 mV lower than the overpotential with nickel at 50 mA/cm².

Key words: Iron-doped nickel oxide, Electrocatalytic, Hydrogen energy

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1 Introduction

In recent years, there has been a lot of public interest in our environment and energy, especially new energy source. Due to the fact that increasing environment pollution is resulting from the increasing application of fossil fuels and man fears their shortage occurring in the future. Hydrogen energy is considered an efficient energy, low pollution fuel. It is one of the most promising energy carriers for the future^[1-5]. Hydrogen production from solar energy is the best way to solve the energy crisis and air pollution, so it is necessary to develop highly active and stable

electrocatalysts for hydrogen production^[6].

Besides being an unavoidable side effect in numerous electrolytic systems, the oxygen evolution reaction is basic anodic reaction because of its relationship with most important electrochemical processes such as hydrogen production in water electrolysis^[7]. One of the major shortages of traditional anodic materials is the high overpotential associated with the OER, which leads to low efficiency. So the choice of anodic material is an essential prerequisite for the optimization of the electrolytic processes^[8-9]. In order to be used for technological application, such materials

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have to be endowed manifold characteristics, such as high electronic conductivity, good electrocatalytic properties, long-term chemical and corrosion resistance in concentrated alkaline solutions

Nickel and nickel oxide are considered the most suitable anode material for the OER in concentrated alkaline solution, because of their electrocatalytic properties and corrosion resistance in concentrated alkaline solutions, and because it is relatively cheap^[10-13].

Several studies have reported increased activities for the evolution of oxygen on nickel oxide electrode when iron is present^[13-14]. Iron-doped nickel oxide thin film can be fabricated by reactive magnetron sputtering, cathodic electrodeposition etc.

In this paper, the electrocatalytic properties of iron-doped nickel oxide thin films prepared by sputtering method for OER were investigated by cyclic voltammetry, linear sweep voltammetry, Tafel polarization curves and electrochemical impedance spectroscopy.

2 Experimental Details

The Iron-doped nickel oxide thin films were prepared by RF magnetron sputtering from a Fe-Ni alloy target which is 76.4 mm in diameter, 3 mm in thickness and 99.99% in pure. The atom content of Fe, Ni is 21% and 79% respectively. The sputtering parameter of oxygen content in flue ratio during sputtering (from 10% to 40%) was changed for studying their effects on the electrochemical properties of the film. The deposition chamber was pumped to a pressure of less than 4×10^{-3} Pa with diffusion pump before sputtering was started. Then a pre-sputtering process was followed for 10 min to clean the target surface and remove any possible contamination.

The electrochemical measurements were carried out at CH1660 electrochemical workstation (CH Instruments Corp., USA) in a conventional three-electrode cylindrical electrochemical cell which has a saturated calomel reference electrode (SCE) and a large area Pt counter electrode. All tests were conducted with a well defined electrode area of 1 cm^2 in 1 mol/L potassium hydroxide (KOH) prepared using deionized water. The reference electrode was brought into

contact with the cell bath through a Luggin capillary (KCl agar-agar salt bridge) in order to minimize the IR drop of the solution resistance (Fig 1).

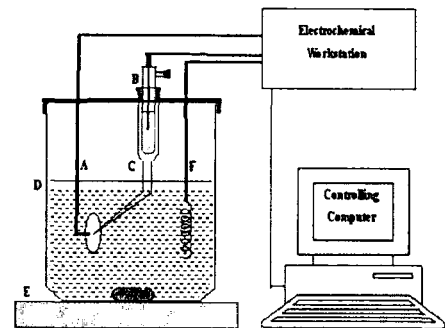


Fig 1 Schematic diagram of the experimental set-up
A: working electrode, B: reference electrode,
C: Luggin capillary, D: electrochemical cell,
E: magnetic stirrer, F: counter electrode

3 Results and Discussion

3.1 Cyclic Voltammetry

Electrochemical properties of the film and nickel were studied by cyclic voltammetry (Fig 2). The scan rate is 0.1 V/s . The cyclic voltammograms show only one anodic peak and one reduction peak in the range of potential from 0.1 V to 0.5 V. The reduction peak potential towards the positive direction, and the difference in potential between two peaks lowers than pure nickel. Most obvious was the large increase in OER current which is the anodic peak in the Fig 2.

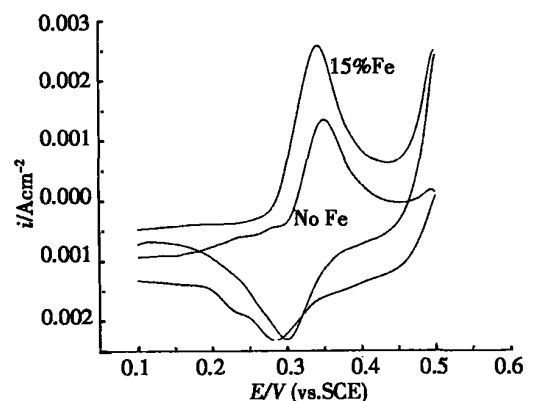


Fig 2 Effect of iron in the film on cyclic voltammograms

A shift of anodic peak potential towards the positive direction and lowering of the potential difference

between the anodic and cathodic peak indicates that shift of equilibrium potential for OER to more negative values and a decrease in the overpotential for OER which occurred on the iron-doped nickel oxide thin film (Table 1). The increase of peak current suggests that more active site is present in the electrode, and the iron may acts as active site.

3.2 Linear Sweep Voltammetry

Fig 3 shows liner sweep voltammetry plots for the films which were deposited under different oxygen content and nickel electrode. The electrodes were maintained at an anodic potential 0.6 V for 15 mins prior to the polarization. The curves were performed using a linear sweep at 1 mV/s. The results indicate that better electrocatalytic activity for OER is obtained with 40% oxygen content. The results (Tab 1) show that iron-doped nickel oxide thin films are suitable materials for OER applications than the Ni electrode.

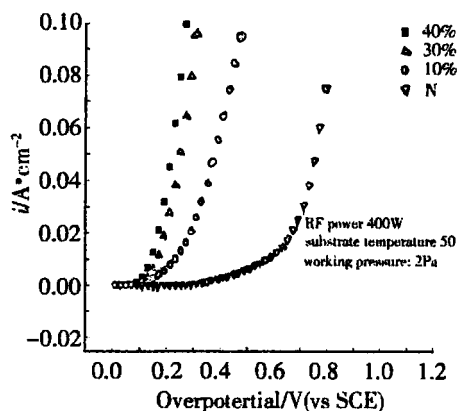


Fig 3 Linear sweep voltammetry plots of different electrode

3.3 Tafel Polarization

In order to investigate the electrocatalytic activity of the prepared films, Tafel polarization measurements were performed (Fig 4), and the corresponding electrochemical parameters (Tafel slope, exchange current density) were derived from the recorded curves and summarized in Table 1.

Tafel equation,

$$\eta = a + b \lg i \tag{1}$$

where η represents the overpotential, i the measured current, b the Tafel slope, and a the intercept related to the exchange current density i_0 through

equation $a = (2.3RT) / (nF) \times \lg i_0$. The other parameter of interest is b , the symmetry factor, which can be calculated from the Tafel slope as $b = (2.3RT) / (nF)$, and n represents the number of electrons exchanged, F is the Faraday constant, and R is the gas constant

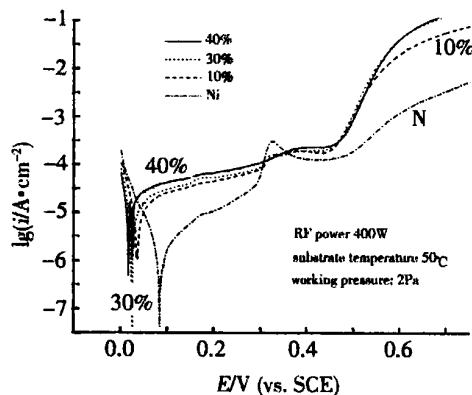
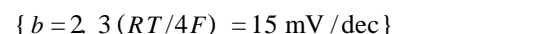
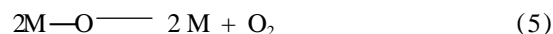
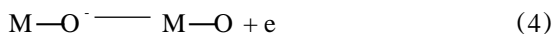
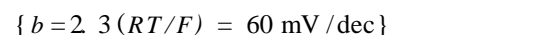
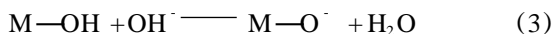
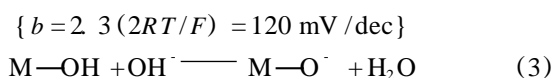
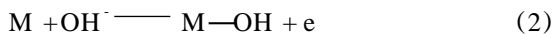


Fig 4 Tafel polarization curves recorded on the different electrode

A significant change in the Tafel slope is usually interpreted as a change in the rate-limiting step. One commonly accepted reaction way for oxygen evolution reaction in alkaline solution is shown in Eq 2 to 5.



Where, M is an active site in the catalyst. $M-OH$ and $M-O$ are two adsorption intermediates. Which step is the rate-limiting step depends on the strength of the adsorption of the intermediates. The results are consistent with reaction 3 being the rate-limiting step, when iron or oxygen content is relatively high. The overpotential is sensitive to iron or oxygen content, comparing 10% sample with the 40% one, both of the difference for iron and oxygen content in the sample were less than 1%, but the difference for oxygen overpotential is significant (Tab 1).

Tab 1 Summary of film characterization

Electrode	Fe/% (by mass)	Oxygen/% (by mass)	Tafel slope/ mV/dec	lg(i_0 /A)	Ovepotential/V at 50 mA/cm ²	R_{ct} / · cm ²
10%	14.00	25.67	51.20	-13.20	372	3.67
30%	14.59	26.24	49.30	-12.70	251	1.85
40%	15.00	26.46	37.70	-8.25	219	0.62
Ni	0	0	111.01	-13.70	756	-

The addition of iron makes a change in the rate-limiting from primary discharge of OH⁻ ions to the recombination of oxygen atom. This is reasonable if the iron impurities were to provide more favorable site for the adsorption of the intermediates

3.4 Electrochemical Impedance Spectroscopy

The electrochemical impedance spectroscopy (EIS) technique was applied to further investigate the electrode/electrolyte interface and the corresponding processes that occur at the electrode surface. To ensure a complete characterization of the electrode /electrolyte interface and corresponding processes, EIS measurements were made over five frequency decades, from 5 kHz to 0.01Hz

EIS measurements were carried out at potential of 600 mV which were shown in Fig 5. The model of the equivalent circuit includes the constant phase element (C_{pe}) in parallel with the charge transfer resistance R_{ct} (insertion in the Fig 5). The values of the R_{ct} (· cm²) are 3.67, 1.85, 0.62 for 10%, 30%, 40% sample, respectively. The lowest R_{ct} (0.62), was observed on 40% sample. The result is in agreement with the experimental data obtained by liner sweep voltammetry measurements (Fig 2).

4 Conclusions

The Iron-doped nickel oxide thin films were prepared by RF magnetron sputtering. The cyclic voltammetry experiment shows the iron may acts as active site in the electrode. The addition of iron makes a change in the rate-limiting from primary discharge of OH⁻ ions to the recombination of oxygen atom. EIS measurement results are in agreement with the experimental data obtained by liner sweep voltammetry

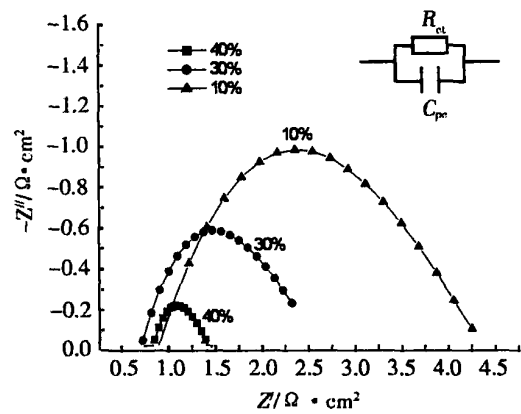


Fig 5 Electrochemical impedance spectroscopy of different electrode

measurements. These results mentioned above indicate that iron-doped nickel oxide is promising as an oxygen catalyst.

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氧化铁镍电极上析氧反应的电化学研究

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摘要: 应用射频反应磁控溅射法制备阳极催化氧化铁镍薄膜, 由循环伏安、线性扫描伏安、极化曲线和电化学交流阻抗谱等研究发生在该电极上的氧化反应. 结果表明, 作为活化中心的铁能使过电势降低, 并且随着溅射过程氧流量的增加催化性能增强, 铁的掺入使得速率限定步骤由 OH^- 的释放变为氧原子的结合. 与镍相比, 氧化铁镍是更理想的催化阳极材料, 当电流密度为 $50 \text{ mA}/\text{cm}^2$ 时, 其氧的过电势比镍的下降了 500 mV .

关键词: 氧化铁镍; 电催化; 氢能