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Synthesis and Electrocatalytic Oxygen Evolution Performance of P@Fe-MOF/NF

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Abstract

The significance of developing efficient electrocatalysts based on non-precious and abundantly available elements on Earth for achieving sustainable energy conversion and storage is highlighted. We present a straightforward and effective approach to fabricate an integrated catalyst, P@Fe-MOF/NF, loaded on nickel foam (NF) with exceptional electrochemical water-splitting performance. This catalyst was successfully synthesized through a simple hydrothermal process followed by a phosphorization heat treatment. The P@Fe-MOF/NF catalyst demonstrated superior oxygen evolution reaction (OER) catalytic performance, achieving a current density of 10 mA cm^{-2} at a low overpotential of 248 mV and exhibiting a Tafel slope of 68.75 mV dec^{-1}. This work not only provides a robust strategy for developing new, efficient, and cost-effective electrocatalysts but also holds significant implications for advancing sustainable energy technologies.

Keywords

Metal-organic Frameworks; Electrocatalysis; Oxygen Evolution Reaction; Hydrogen Evolution Reaction.

1. Introduction

Within the framework of sustainable energy, humanity must meet current demands while protecting the interests of future generations, making energy issues, especially energy storage technology, a critical global strategic topic [1]. With the depletion of fossil fuels and the rising demand for clean energy, electrocatalytic water splitting for H_2 and O_2 generation becomes crucial, where the oxygen evolution reaction (OER) serves as a key limiting step [2]. Although iridium- and ruthenium-based materials are excellent OER catalysts, their high cost and scarce availability limit their use. Concurrently, excessive use of coal and fossil fuels not only emits harmful pollutants, damaging the environment, but is also unsustainable [3]. Therefore, developing carbon-neutral, eco-friendly renewable energy technologies, such as electrochemical water splitting to produce green H_2 fuel, reducing energy demand, and overcoming the critical challenges of catalysts, becomes a vital pathway to balance environmental protection and energy requirements [4].

Iron-based materials exhibit significant advantages as electrocatalysts, including their high abundance, low cost, exceptional chemical activity, and good long-term stability. These characteristics, stemming from iron's inherent low electrical resistivity, abundant natural reserves, and economic viability as a metallic element, have led to extensive research and interest in iron-based materials in the field of electrocatalysis [5]. On another front, metal-organic frameworks (MOFs), a class of porous materials formed by periodic connections of metal nodes (or clusters) and organic linking ligands, have garnered widespread attention [6]. With their unique porosity, ease of molecular-level modification, and tunable structural properties, MOFs have demonstrated their potential value in various domains, including catalysis, energy storage, gas adsorption and separation,

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and drug delivery, particularly in electrocatalysis, where they exhibit significant catalytic activity in reactions such as oxygen reduction (ORR), OER, and HER [7].

Phosphide-modified catalysts, with their array of advantages including enhanced catalytic activity, electronic structure modulation, improved thermal stability and corrosion resistance, better dispersion and stability, increased selectivity, and reduced cost, exhibit outstanding performance in various catalytic applications. These characteristics not only facilitate effective adsorption and conversion of reactants and optimize the electronic properties of the catalysts but also enhance the catalysts' stability and activity under harsh conditions, providing cost-effective catalytic solutions [8,9]. Hence, phosphide-modified catalysts demonstrate immense potential in fields such as energy conversion, environmental protection, and chemical synthesis. In this study, Fe-MOF/NF was successfully synthesized via a one-step hydrothermal method, and further modified by phosphidation to prepare the P@Fe-MOF/NF catalyst, while investigating the impact of secondary sodium phosphate addition during the phosphidation process. This catalyst exhibited exceptional catalytic performance in the OER, achieving a significant current density of 10 mA cm^{-2} at an overpotential of just 248 mV and showcasing a low Tafel slope of 68.75 mV dec^{-1}. These results highlight the efficiency and potential application value of P@Fe-MOF/NF as an electrocatalyst.

2. Experimental

2.1 Synthesis of Fe-MOF/NF-140, 160, 180

To synthesize the Fe-MOF/NF electrodes, nickel foam (NF) with dimensions of 20×20 mm^2 was first trimmed and then ultrasonically cleaned in hydrochloric acid, anhydrous ethanol, and deionized water, respectively, followed by drying to obtain a clean nickel foam substrate. Subsequently, 0.2 mmol of ferric chloride and an equimolar amount of terephthalic acid were dissolved in 10 mL of ethanol solvent. The solution was treated under ultrasonication for 30 minutes to ensure thorough mixing. Afterward, the resulting solution was transferred to a reactor and reacted at 140°C, 160°C, and 180°C for 20 hours, respectively, to complete the growth of Fe-MOF. After the reaction, the obtained electrodes were thoroughly washed and dried, resulting in the Fe-MOF/NF-140, 160, 180 electrodes. This synthesis method aims to optimize the growth of Fe-MOF on nickel foam, thereby enhancing its performance in relevant electrochemical applications.

2.2 Synthesis of P@Fe-MOF/NF-200, 300, 400

The prepared Fe-MOF/NF-140 electrodes were placed at two ends of an alumina crucible separately with sodium hypophosphite (200 mg, 300 mg, 400 mg) ensuring that the electrodes did not directly contact the sodium hypophosphite. In a nitrogen atmosphere, the temperature was raised to 350°C and maintained for 2 hours for heat treatment, where the rate of temperature increase was set to 5°C/min. This process yielded the P@Fe-MOF/NF-200, 300, 400 catalysts.

2.3 Electrochemical Characterizations

Electrochemical characterizations were conducted using a CHI660 electrochemical workstation, where experiments were performed in a conventional three-electrode system. Specifically, a Hg/HgO electrode was used as the reference electrode, which is the preferred choice for alkaline media. A 1.5 cm × 1.5 cm platinum sheet was selected as the electrode for OER testing, while a carbon rod was chosen as the counter electrode for HER. The prepared Cu-MOF/NF electrode was utilized as the working electrode for the experiments. The alkaline electrolyte used was a 1.0 M KOH solution. All electrochemical tests were conducted at room temperature and the electrodes were activated prior to testing through 10 cyclic voltammetry (CV) scans to ensure the reliability of the data. Linear sweep voltammetry (LSV) data were collected at a scan rate of 10 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) measurements were performed within a frequency range of 10^6 to 10^{-2} Hz, with an amplitude of 0.68 V and a potential bias of 5 mV. The electrochemical double-layer capacitance (C_{dl}) was measured in the non-faradaic region using CV at various scan rates (20-100 mV s^{-1}).

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3. Result and Discussion

3.1 OER Performance of Fe-MOF/NF-140, 160, 180

The OER electrocatalytic performance of the prepared Fe-MOF/NF-140, 160, 180 was measured in a 1.0 M KOH electrolyte using a typical three-electrode system. Thanks to the strong conductivity, large specific surface area, and three-dimensional porous structure, the NFs as substrates demonstrated their superiority. The LSV curves of these samples are shown in Figure 1(a), where Fe-MOF/NF-140 exhibited the best OER catalytic activity. To achieve a current density of 10 mA cm^{-2}, Fe-MOF/NF-140 required an overpotential (η) of only 264.4 mV, while Fe-MOF/NF-160 and Fe-MOF/NF-180 required overpotentials (η) of 288.4 mV and 319.4 mV, respectively, as shown in Figure 1(b).

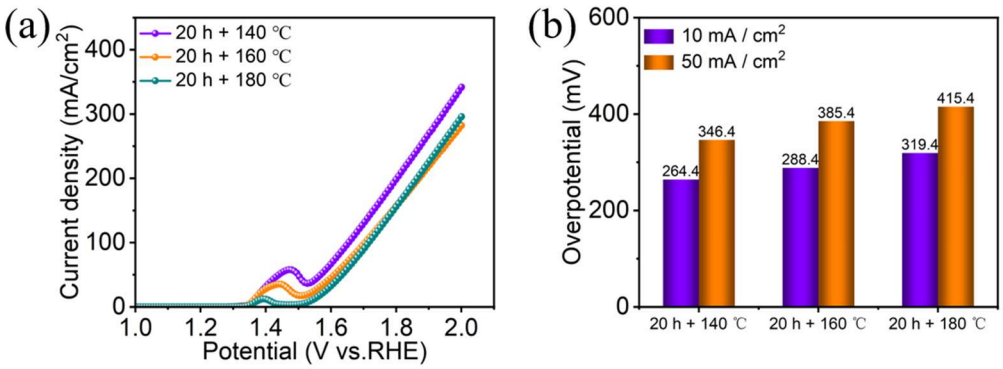

Figure 1. OER activity of Fe-MOF/NF-140, 160, 180 electrodes in 1.0 M KOH electrolyte: (a) LSV curves, (b) corresponding η

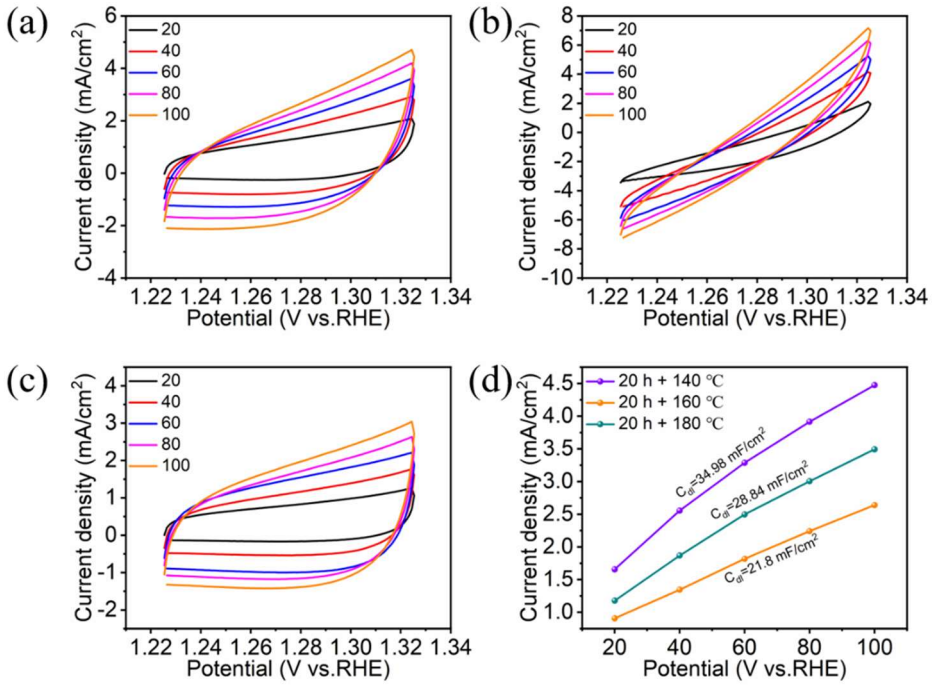

Figure 2. CV curves of (a) Fe-MOF/NF-140, (b) Fe-MOF/NF-160, (c) Fe-MOF/NF-180, and (d) C_{dl} of Fe-MOF/NF-140, 160, 180

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The electrochemical active surface area (ECSA) plays a decisive role in the electrocatalytic activity. The Cdl value at the solid-liquid interface is directly proportional to the effective ECSA, and the ECSA of the catalyst can be estimated through the C_{dl} value. C_{dl} was measured by conducting CV in the non-faradaic region at scan rates of 20-100 mV s^{-1} (Figure 2(a)-(c)). As shown in Figure 2(d), the C_{dl} values for Fe-MOF/NF-140, Fe-MOF/NF-160, and Fe-MOF/NF-180 were calculated to be 34.89 mF cm^{-2}, 28.84 mF cm^{-2}, and 21.8 mF cm^{-2}, respectively. The largest C_{dl} value of Fe-MOF/NF-140 indicates that it has the largest ECSA, implying the greatest number of surface active sites.

3.2 HER Performance of Fe-MOF/NF-140, 160, 180

In a 1 M KOH solution, the HER performance of the catalysts was investigated using a standard three-electrode system. Figure 3(a) displays the LSV curves for Fe-MOF/NF-140, Fe-MOF/NF-160, and Fe-MOF/NF-180. The results reveal that the HER activity of these catalysts is essentially consistent. The overpotentials of the catalysts were calculated from the LSV curves. As shown in Figure 3(b), at a current density of 10 mA cm^{-2}, the overpotential required for Fe-MOF/NF-140 is 236.6 mV, and for Fe-MOF/NF-160 and Fe-MOF/NF-180, it is 235.6 mV and 264.6 mV, respectively. This indicates that the hydrothermal temperature has a minimal impact on the HER performance of Fe-MOF/NF catalysts and that the overall HER performance is relatively poor, hence the focus will be on studying their OER performance after subsequent phosphidation modification.

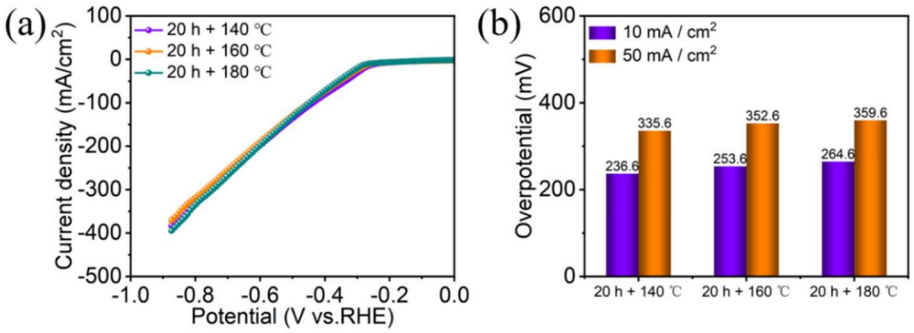

Figure 3. HER activity of Fe-MOF/NF-140, 160, 180 electrodes in 1.0 M KOH electrolyte: (a) LSV curves, (b) corresponding η

3.3 OER Performance of P@Fe-MOF/NF-200, 300, 400

As shown in Figures 4(a)-(b), P@Fe-MOF/NF-300 requires the lowest overpotential of 248.4 mV to reach 10 mA cm^{-2}. The Tafel slope, an important parameter for estimating OER kinetics, derived from the LSV curves, is shown in Figure 4(c). The Tafel slope for P@Fe-MOF/NF-300 is 68.75 mV dec^{-1}, which is lower than those for P@Fe-MOF/NF-200 and P@Fe-MOF/NF-400, at 116.5 and 132.8 mV dec^{-1}, respectively, indicating good OER kinetics for P@Fe-MOF/NF-300. Electrochemical impedance spectroscopy (EIS) was also used to further elucidate the OER catalytic kinetics corresponding to the charge transfer process, as shown in Figure 4(d). The small semicircle in the high-frequency region of the Nyquist plots represents low charge transfer resistance (Rct), and the smallest semicircle diameter for P@Fe-MOF/NF-300 indicates its lowest charge transfer resistance.

The C_{dl} values shown in Figure 5 were calculated based on cyclic voltammetry graphs (Figures 5(a)-(c)), indicating the size of the active electrochemical surface area. The calculated Cdl values for P@Fe-MOF/NF-200, P@Fe-MOF/NF-300, and P@Fe-MOF/NF-400 samples are 23.74, 18.54, and 47.35 mF cm^{-2} (Figures 5(d)), respectively, suggesting that P@Fe-MOF/NF-300 has the largest ECSA. From these results, it is evident that P@Fe-MOF/NF synthesized with 300 mg of sodium hypophosphite during the thermal phosphidation process exhibits the optimal OER performance. Furthermore, after phosphidation, the OER performance of Fe-MOF/NF-140 is significantly enhanced, with the overpotential required to reach 10 mA cm^{-2} reduced from 264.4 mV to 248.4 mV.

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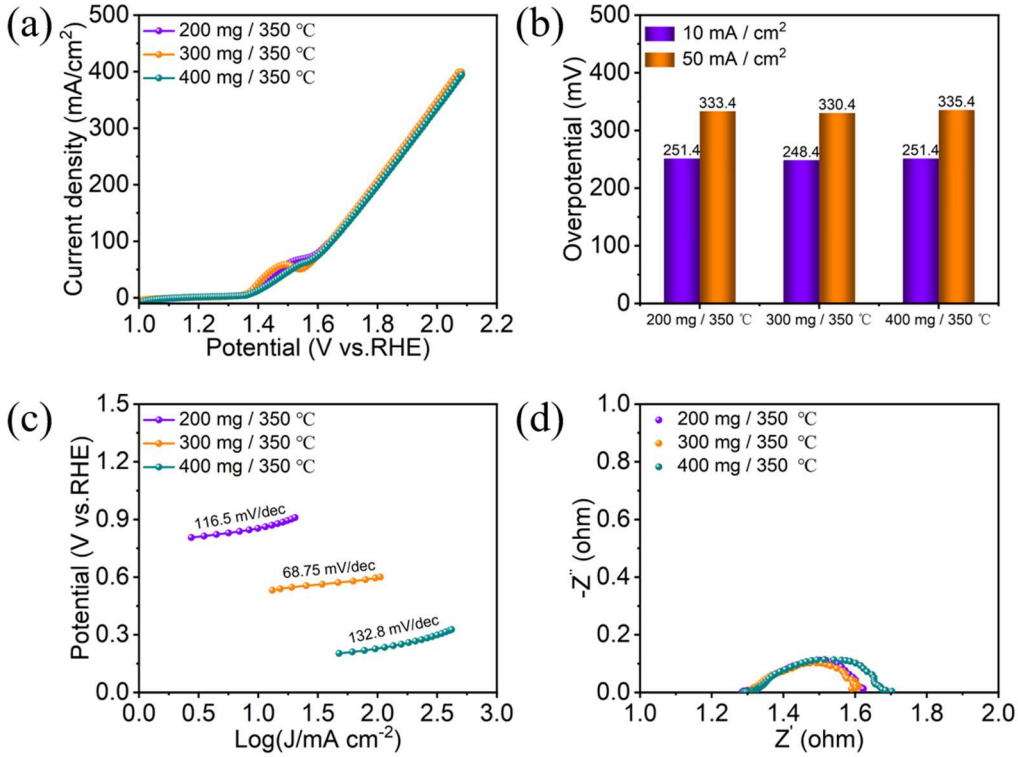

Figure 4. OER activity of P@Fe-MOF/NF-200, 300, 400 electrodes in 1.0 M KOH electrolyte: (a) LSV curves, (b) corresponding η, (c) Tafel plots, (d) Nyquist plots

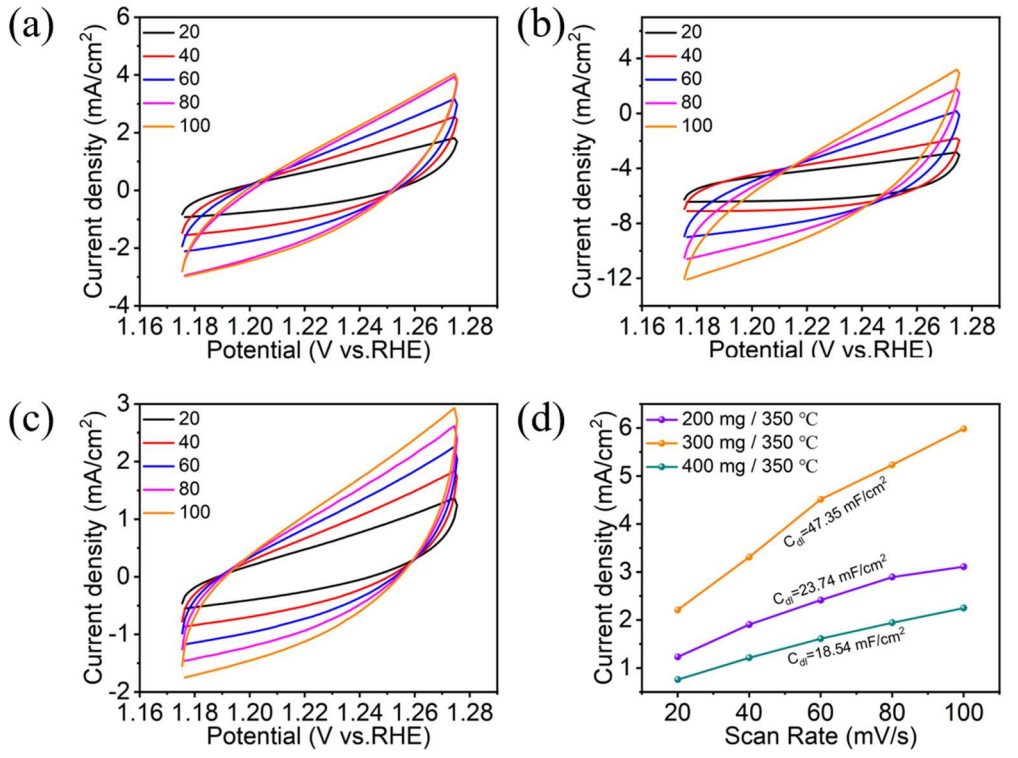

Figure 5. CV curves of (a) P@Fe-MOF/NF-200, (b) P@Fe-MOF/NF-300, (c) P@Fe-MOF/NF-400, and (d) C_{dl} of P@Fe-MOF/NF-200, 300, 400

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4. Conclusion

We successfully synthesized the Fe-MOF/NF material and identified 140°C as the optimal synthesis temperature. Using Fe-MOF/NF-140 as a precursor and undergoing thermal treatment and phosphidation modification with 300 mg of sodium hypophosphite, the resulting P@Fe-MOF/NF catalyst exhibited optimal OER performance. This strategy is not only environmentally friendly but also endows P@Fe-MOF/NF with a high specific surface area and excellent OER electrocatalytic activity. In a 1.0 M KOH electrolyte, the P@Fe-MOF/NF electrode demonstrated an OER overpotential of only 248.4 mV at a current density of 10 mA cm^{-2} and a Tafel slope of 68.75 mV dec^{-1}, showcasing its potential application in the field of electrocatalysis.

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