Anodic Oxidation Modulation of W-MOF/NF Microstructures and Electrocatalytic OER Performance

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Abstract

Electrocatalytic decomposition of water is an effective technology for hydrogen energy production, and the development of an efficient, highly stable and cost-effective non-noble metal-based electrocatalyst for the oxygen extraction reaction (OER) of alkaline electrolytes is essential for the wide application of OER. Here, nickel foam-loaded W-MOF nanoparticles (W-MOF/NF) were prepared by a one-step hydrothermal method, and the microstructure of W-MOF/NF was tuned by anodic oxidation. The overpotential of the prepared W-MOF/NF electrode was 449.4 mV in 1.0 M KOH electrolyte at 10 mA cm^{-2} current density.After anodizing W-MOF/NF@Et The overpotential of the electrode decreased to 419.4 mV.

Keywords

Metal-organic Framworks; Anodic Oxidation; Oxygen Evolution Reaction.

1. Introduction

The electrochemical decomposition of water, which is critical to the overall green and sustainable energy blueprint, has attracted extensive research due to the potential of its pure and clean products to address environmental degradation and energy crisis [1]. However, the actual achievable electrolysis efficiency is still far from satisfactory due to the slow kinetics of the oxygen evolution reaction (OER) due to the multistep proton-coupled electron transfer and the high energy barriers for the destruction of strong O-H bonds and the formation of O-O bonds [2, 3]. The noble metals Pt and Ir/Ru are considered as benchmark catalysts for hydrogen and oxygen removal reactions (HER) and OER, respectively, but it is difficult to promote the overall water decomposition effectively due to their high overpotentials and inability to adapt to the full PH environment [4].Meanwhile, the high price of precious metals also limits their practical application. Due to their low cost and abundant resources, transition metal oxides and sulfides have received widespread attention and are considered as promising alternatives to precious metal-based catalysts. However, obtaining efficient bifunctional catalysts for alkaline total water decomposition is still a great challenge due to their low activity and poor stability [5, 6].MOFs are coordination polymers with a structure of metal ions linked to organic ligands, and MOFs have emerged as promising catalysts for water electrolysis due to their structural advantages such as abundant active sites, chemical compositions, and structural modifiability [7, 8]. However, W-MOFs still suffer from poor electrical conductivity, acid intolerance, as well as poor stability, resulting in poor electrocatalytic decomposition of water, which hinders their practical application [9]. Therefore, the use of strategies such as constructing different nanostructures, optimizing ligands, and designing metal sites and defect structures can effectively regulate the local electronic structure such as coordination environment, binding energy, conductivity, and charge transfer efficiency to achieve efficient electrocatalytic decomposition of water performance [10, 11].

Therefore, in this work, V-MOF/NF electrodes were synthesized by a simple one-step hydrothermal method, and the effects of different hydrothermal solution ratios on the OER performance of the electrodes were investigated. Meanwhile, the microstructure of W-MOF/NF was modified by anodic oxidation. The effects of different anodizing solution conditions on the engine performance were investigated. As a result, an extraordinary OER activity was realized with an overpotential of 449.4 mV in 1.0 M KOH electrolyte at 10 mA cm^{-2} current density.After anodizing W-MOF/NF@Et The overpotential of the electrode decreased to 419.4 mV.

2. Sample Preparation

2.1 Preparation of W-MOF/NF

The nickel foam was cut into 20×20 mm2 and placed in hydrochloric acid, anhydrous ethanol (Et) and deionized water (DI), respectively, ultrasonically cleaned and dried to obtain the cleaned nickel foam. The cleaned nickel foam, WCl6 (31.72 mg, 0.08 mmol) and 2,6-naphthalenedicarboxylic acid dipotassium salt (20 mg, 0.08 mmol) were dissolved in a mixture of 10 mL of DI and Et (DI : Et 1 : 0, 4:1, 3 : 2) and ultrasonicated for 30 min to obtain a homogeneous mixed solution. Then, the above mixed solution was transferred to a reactor and reacted at 180 ℃ for 20 h. The electrode obtained after the reaction was cleaned and dried to obtain the W-MOF/NF electrode.

2.2 Anodic Oxidation Modification of W-MOF/NF

The W-MOF/NF electrodes were anodized using W-MOF/NF electrodes as anodes, platinum sheets as cathodes, and deionized water and ethanol as electrolytes. The treatment conditions were 30 V and 2 min. The electrodes obtained after the anodic oxidation treatment in deionized water and ethanol electrolyte were named W-MOF/NF@DI and W-MOF/NF@Et.

3. Results and Discussion

The OER activities of W-MOF/NF electrodes with different water and ethanol solution ratios were tested in N$_2$ saturated 1.0 M KOH electrolyte, respectively, as shown in Fig. 1(a,b). Hydrothermal heating in different water and ethanol ratio solutions had an effect on the OER activity of W-MOF/NF. The overpotential of the hydrothermal W-MOF/NF electrode in 10 mL DI was 449.4 mV at 10 mA cm^{-2}. It was significantly enhanced compared to that in DI : Et= 4 : 1 (491.4 mV) and DI : Et = 3:2 (482.4 mV).
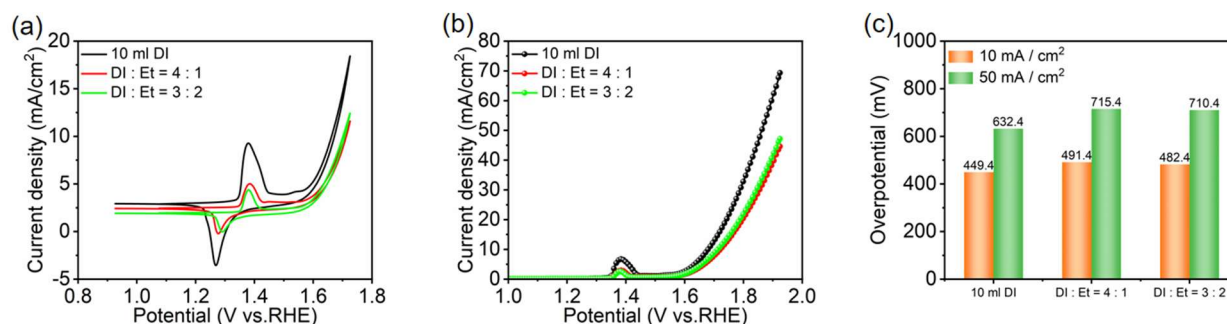

Fig. 1 OER electrochemical activity of W-MOF/NF electrode in 1.0 M KOH electrolyte: (a) CV; (a) LSV, (b) corresponding η at 10 mA cm^{-2} and 50 mA cm^{-2}

The Tafel curve can be used to study the kinetic process of the OER-catalyzed reaction at the electrode, which can be obtained from the LSV polarization curve as shown in Fig. 2(a). The Tafel slopes of the W-MOF/NF electrode at DI : Et = 1 :0 in the hydrothermal process, at DI : Et = 4 : 1 and at DI : Et = 3 : 2 were 24.8 mV dec-1, 147.1 mV dec-1 and 130.1 mV dec-1, respectively. To explore the electrocatalytic enhancement mechanism, electrochemical impedance spectroscopy was investigated. Electrochemical impedance spectroscopy (EIS) can be used to investigate the charge transfer

efficiency of the electrodes. Fig 2(b) shows the impedance spectra of the hydrothermal W-MOF/NF electrode under the conditions of deionized water and ethanol ratio. The radius value of the semicircle in the high frequency region indicates the charge transfer resistance (R_{ct}), and the smaller the radius of the semicircle, the smaller the value of R_{ct} [12]. The W-MOF/NF electrode hydrothermally heated in DI has the smallest R_{ct} value, indicating the highest charge transfer efficiency at the electrode surface. It is consistent with the results of the electrocatalytic activity test.
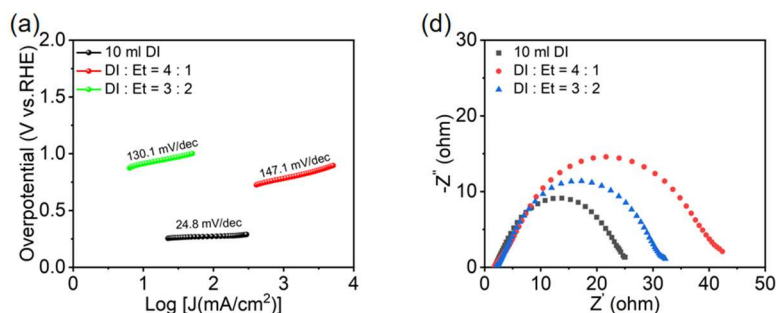

Fig. 2 (a) Tafel graph (b) AC impedance plot of W-MOF/NF electrode

The best performing W-MOF/NF hydrothermally treated under DI conditions was selected for further investigation. The W-MOF/NF was modified in terms of microstructure by anodic oxidation. As shown in Fig. 3(a-c), the electrocatalytic activity of the W-MOF/NF@Et electrode was significantly enhanced after the anodic oxidation treatment, which was attributed to the increase of catalytic active sites after anodic oxidation, as well as the anodic oxidation leading to the generation of W-unsaturated coordination sites. The overpotentials of the W-MOF/NF@DI and W-MOF/NF@Et electrodes at 10 mA cm^{-2} were 461.4 mV and 419.4 mV.
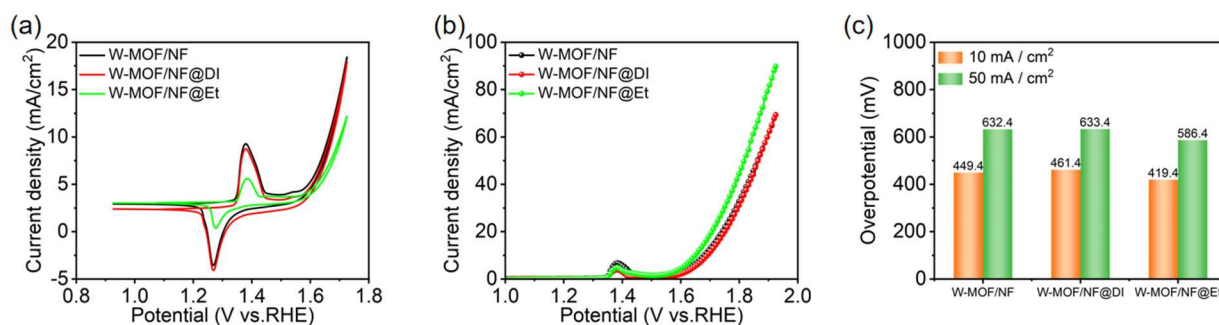

Fig. 3 OER electrochemical activity of W-MOF/NF, W-MOF/NF@DI and W-MOF/NF@Et electrode in 1.0 M KOH electrolyte: (a) CV; (a) LSV, (b) corresponding η at 10 mA cm^{-2} and 50 mA cm^{-2}

Fig 4(a) shows the Tafel curves of W-MOF/NF, W-MOF/NF@DI and W-MOF/NF@Et with Tafel slopes of 24.8 mV dec^{-1}, 30.2 mV dec^{-1} and 21 mV dec^{-1}, respectively, where the W-MOF/NF@Et electrode shows better performance with a significantly lower Tafel slope. Fig 2(b) shows the impedance profiles of W-MOF/NF electrodes anodized in deionized water and ethanol solutions. The W-MOF/NF@Et electrode has the smallest R_{ct} value, indicating the highest charge transfer efficiency on the electrode surface. It is consistent with the results of the electrocatalytic activity test.
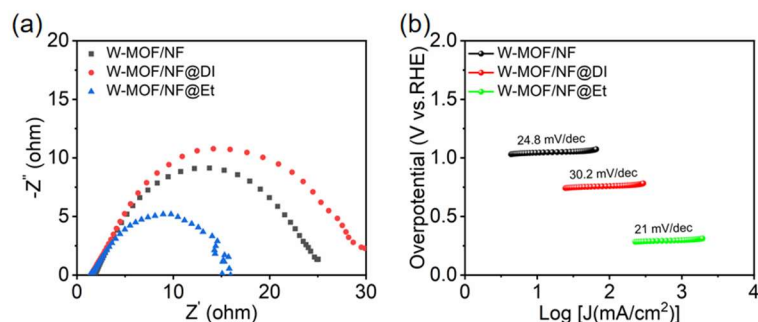
Fig. 4 (a) Tafel graph (b) AC impedance plot of W-MOF/NF, W-MOF/NF@DI and W-MOF/NF@Et electrode

The surface morphology of the electrode was characterized by SEM, and Fig 5(a) shows the SEM image of the W-MOF/NF electrode hydrothermally prepared in DI. The W-MOF/NF electrode synthesized using deionized water was obtained as a nanoflower particle-like structure with a diameter of about 100 nm.Fig 5(b) shows the SEM image of the W-MOF/NF@Et electrode after anodic oxidation treatment in ethanol solution. After the anodic oxidation treatment, the W-MOF/NF@Et electrode still retains the nanoparticle structure, indicating that the anodic oxidation hardly changes the morphology of the electrode. However, the surface roughness of the anodized W-MOF/NF@Et electrode increased, which would be favorable for the adsorption of water molecules and the electrocatalytic reaction.
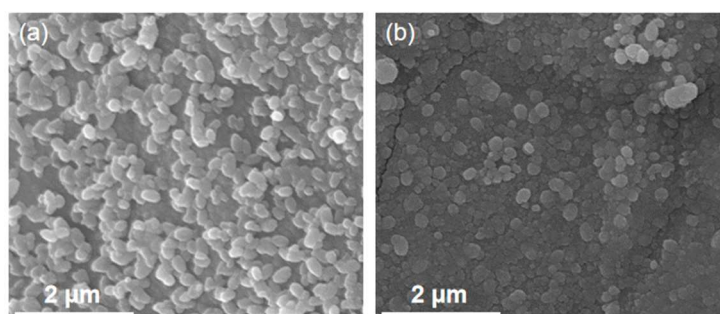

Fig. 5 SEM images of W-MOF/NF, and W-MOF/NF@Et electrodes

4. Conclusion

In summary, we successfully prepared W-MOF/NF electrodes with excellent OER performance by hydrothermal integrated synthesis with an overpotential of 449.4 mV in 1.0 M KOH electrolyte at a current density of 10 mA cm^{-2}. Meanwhile, the microstructure of the electrodes was tuned by anodic oxidation, and the W-MOF/NF electrodes were further modified, and the performance of the obtained W-MOF/NF@Et electrodes was further improved. The NF@Et electrode had a further improved performance with an overpotential of 449.4 mV in 1.0 M KOH electrolyte at 10 mA cm-2 current density.

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