

A Facile MOF Based Iron-Molybdenum Bimetallic Electrode Material Preparation for Hydrogen Evolution

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Abstract: Hydrogen energy has become the most potential energy source due to its high calorific value and environment-friendly combustion products. However, there are huge economic problems in hydrogen storage and transportation. Hydrogen can be prepared by catalysis in a way of reducing cost and speeding up speed which is the core idea of electrocatalytic water decomposition for hydrogen production. In this work, we developed an electrode material for Hydrogen evolution reaction (HER) bimetallic catalyst, and achieved that the hydrogen overpotential produced by acidic non-precious metal catalyst under acidic environment was only 275mV. More importantly, a good idea was provided for bimetallic co-catalysis of HER.

Keywords: Hydrogen evolution, Bimetallic catalyst, Synergic catalytic effect.

1. Introduction

The world is faced with a serious energy and environmental crisis with the continuous growth of population and the continuous development of industry which promotes the development and exploration of future energy sources. Hydrogen energy has attracted more and more researcher's attention as one of the most potential clean energy in the future [1]. The fact that hydrogen is a by-product of most processes in the oil industry means that some countries have no shortage of hydrogen [2]. However, hydrogen storage and transportation are still facing great difficulties at the current stage of development both in terms of safety and cost [3, 4]. This means that it is more economical and convenient to use hydrogen on the spot than to transport it remotely.

The simplest way to prepare it is by cracking water to produce hydrogen: $2\text{H}_2\text{O}(\text{l}) = 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$ but this reaction is difficult to occur under normal conditions. Accelerating water decomposition by electrochemical method has gradually become one of the effective methods for hydrogen production. According to theoretical calculation, the theoretical minimum voltage of water decomposition into hydrogen and oxygen is 1.23V [5, 6]. But in fact, it is difficult to reduce the voltage reach to this value due to the existence of various polarization effects. Thus, the researchers began to develop appropriate electrode materials to catalyze the water decomposition [7, 8, 9]. Most of the experimental results showed that the d-band orbit level of transition metal could enhance the catalytic capacity of hydrogen evolution [10, 11, 12]. Therefore, the fourth cycle transition metal element has gradually become a suitable choice for hydrogen evolution reaction (HER) catalysis due to its advantages of cheap and easy availability and excellent catalytic performance.

The catalytic reaction requires not only suitable catalytic element but also large specific surface area [13, 14]. The larger the specific surface area is, the more active centers can be supported, and the stronger the catalytic capacity will be displayed, which is reflected in HER as lower hydrogen

precipitate drive overpotential. Metal-organic frame materials (MOFs) are considered as potential electrocatalytic electrode materials due to their large specific surface area and regular structure. There are metal atoms in the center of each MOF monomer, that is, they can provide metal catalytic active central sites, and when multiple metal sites are catalyzed as active centers at the same time, they usually play a synergistic catalytic role on HER [15]. In this work, MIL-88B MOF was used as the base and the metal organic frame was calcined on the chemical compound of molybdenum acetyl acetone. Then the metal organic frame was burned into the carbon skeleton with good conductivity so a carbon skeleton bimetallic composite electrode derived from MOF was prepared.

2. Materials and Instrument

2.1. Materials

Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ Tianjin Guangfu fine chemical institute, China), sodium hydroxide (NaOH , Beijing Chemical Works, China), terephthalic acid (H_2BDC , Aladdin), molybdenum acetylacetonate ($\text{C}_{10}\text{H}_{14}\text{MoO}_6$, Aladdin), dimethylformamide ($\text{C}_3\text{H}_7\text{NO}$, DMF, Beijing Chemical Works, China), Nafion (5.0 wt%, Dupont), deionized water (resistivity of $18.25 \text{ M}\Omega \cdot \text{cm}$) was produced by a high purity water dispenser. All reagents were analytical grade and used without further purification.

2.2. Synthesis and preparation

4.32g (0.016mol) $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ mixed with 1.992g (0.012mol) H_2BDC was dissolved separately in 80mL DMF and 6.4mL 2M NaOH , stirred to solve in reaction still and put in an oven with 100°C for 12h, centrifuged and washed with deionized water and acetone three times then intermediate MOF MIL-88B was gained after dried. 200mg MIL-88B was dispersed in 20mL DMF to gain solution A and 200mL molybdenum acetylacetonate was solved in 20mL DMF to gain solution B. Mix A with B and the mixture was centrifuged and washed according to the above

method, then the production was purified by 800°C burning for 4h with a 3°C/min heating rate at N₂ atmosphere to obtain the FeMo@C which is based on carbon skeleton derivative of MIL-88B/Mo(acac)₂.

2.3. Structural characterization

The crystal structure of materials was characterized by X-ray diffraction (XRD, Rigaku) with Cu K α scanned from 5 to 50 degree with 5 degree·min⁻¹. Scanning electron microscopy (SEM) was performed on a HITACHI SU020 microscope. Transmission electron microscopy (TEM) was performed on a FEI Tecnai G20/JEM2010 microscope.

2.4. Properties characterization

The properties of electrode material were mainly tested on CHI660E electrochemical workstation through a three-electrode system while glassy carbon electrode (GCE) is used as the working electrode, platinum plate electrode as the counter electrode, Hg/Hg₂SO₄ (saturated K₂SO₄ electrolyte) electrode or Hg/HgO (1 M KOH electrolyte)

electrode is used as the working electrode when the electrolytic liquid system is 0.5M H₂SO₄ (acid environment) or 1M KOH (alkaline environment) respectively. The actual experimental potential values were derived from the following equation:

$$E_{vs. RHE} = E_{vs. Hg/HgO} + 0.098 + 0.059pH$$

$$E_{vs. RHE} = E_{vs. Hg/Hg_2SO_4} + 0.616 + 0.059pH$$

2.5. Results

The XRD of the synthesized sample is shown below (Figure 1), the mainly peaks of MIL-88B and Mo(acac)₂ was corresponded to the standard JCPDS card or simulated result. High signal-to-noise ratio demonstrate that the synthesized sample has good crystallinity, With the addition of Mo(acac)₂, the peak of 8.9° widened and became stronger.

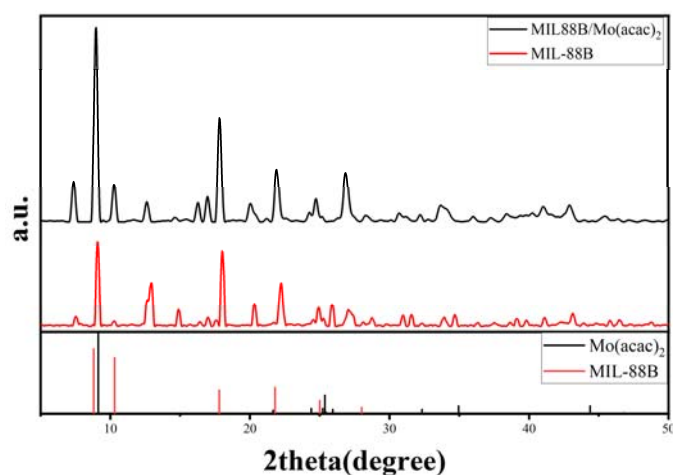


Figure 1. XRD of MIL-88B and MIL-88B/Mo(acac)₂

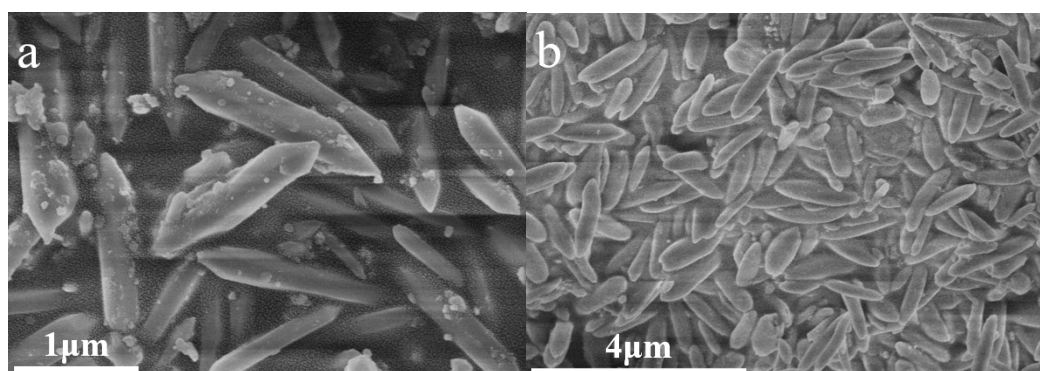


Figure 2. SEM of MIL-88B(a) and MIL-88B/Mo(acac)₂(b)

The SEM was used to observe the morphologies of the samples before carbonization. As shown in the figure above (Figure 2), depict a segregate rod-like morphology which is consistent with that of MIL-88B, further prove the reliability of the sample synthesis method.

The TEM (Figure 3) of the final product after burning

shown an overall structure that has barely changed compared with unburning, but the porosity was demonstrated clearly on the image. The porous structure can greatly improve the ion transport efficiency and electrochemical performance of the material.

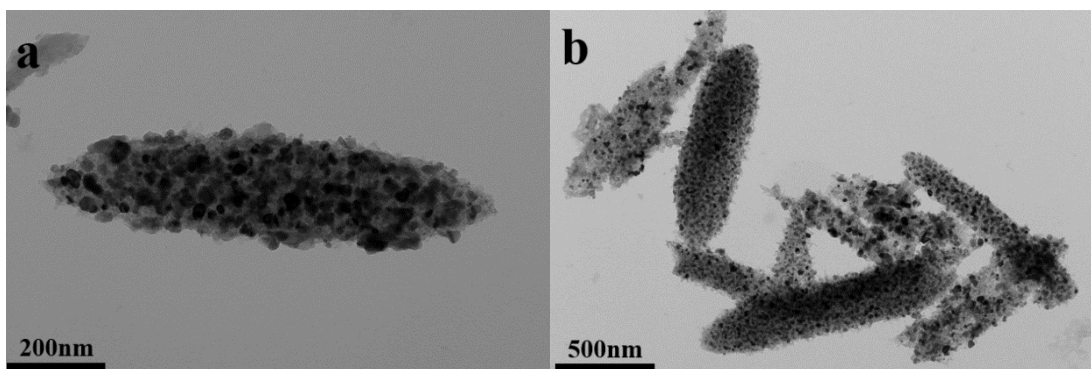


Figure 3. TEM of FeMo@C

Three electrode systems are used for the electrochemical performance test, 5mg (burned MIL-88B, FeMo@C) was dispersed in a mixture of 4.5mL ethyl alcohol and 50 μ L 5%wt Nafion and ultrasonicated for 30min.

The linear sweep voltammetry (LSV) experiments were performed at a scan rate of 10 $\text{mV}\cdot\text{s}^{-1}$ from 0 to -0.6 V (vs. RHE) in 0.5 M H_2SO_4 or from 0 to -0.5 (vs. RHE) in 1 M KOH solution, respectively. The result of LSV was depicted (Figure 4) and shown that the doping of Mo element greatly improves the electrochemical performance of electrode materials reduce the overpotential from 471mV (vs. RHE) to 275mV (vs. RHE) in an acidic environment (**Figure 4a**). In fact, this overpotential value is very promising for bimetallic non-noble metal catalysts under acidic conditions. When HER is catalyzed in an acidic environment, the former has a small oxidation peak when hydrogen is not precipitated, which is inferred to be from the oxidation of molybdenum element. At the same time, it has been proved that, compared

with mono-metal catalysis, the catalytic effect of bimetal interaction on HER is significantly enhanced. The mechanism may be that the d-band orbital electron clouds of the two metals have a synergistic effect on each other, which enhances the positive effect in the process of hydrogen adsorption and desorption, thus improving the catalytic efficiency compared with the pure Fe metal element. The overpotential value in alkaline environment is relatively ordinary compared with most studies (Figure 4b), which shown 480mV for burned MIL-88B and 269mV for FeMo@C. But the improvement of its catalytic performance after doping Mo still indicates that the incorporation of Mo has a great promotion effect on the catalysis of Fe, which indicates that the incorporation of Mo has a positive effect on the catalysis of HER by Fe in both acidic and alkaline environments. The difference is that the Mo is oxidized in an acidic environment.

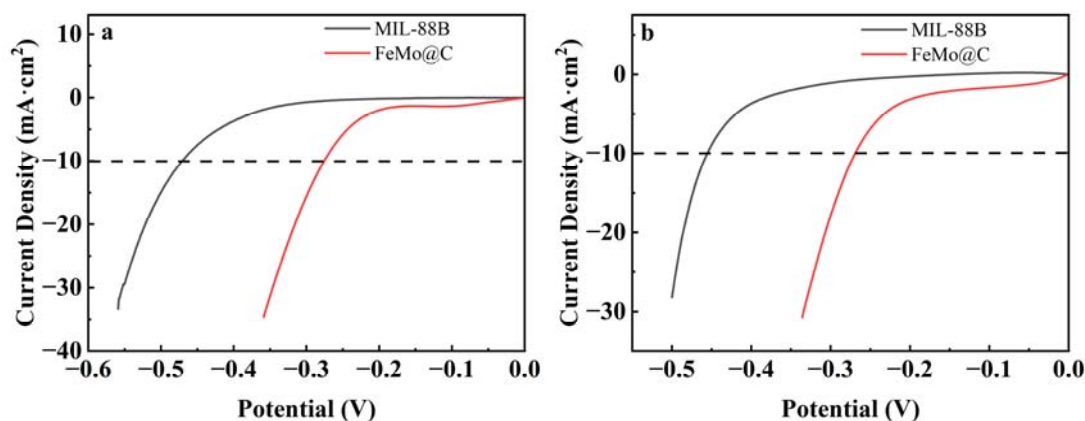


Figure 4. LSV of MIL-88B (burned) and FeMo@C in 0.5M H_2SO_4 (a) and 1M KOH(b).

Electrochemical impedance spectroscopy (EIS) was scanned from 10kHz to 1Hz with a 5mV amplitude at the working voltage of electrode. The electrode impedance was shown as Figure 5. Charge transfer resistance (R_{ct}) is an important indicator to measure HER catalytic efficiency. The larger the charge transfer resistance is, the slower the reduction rate of hydrogen ions in water into hydrogen, that is, the lower the current density. The magnitude of the charge

transfer resistance in the electrochemical impedance diagram is proportional to the radius of the semicircle in the diagram so it is clearly the pictures demonstrate that the R_{ct} of FeMo@C are less than MIL-88B in both acidic and alkaline environments. The R_{ct} of FeMo@C in acid environment is only 13 Ω obtained by fitting impedance spectrum software and expected to be an efficient catalyst for hydrogen evolution.

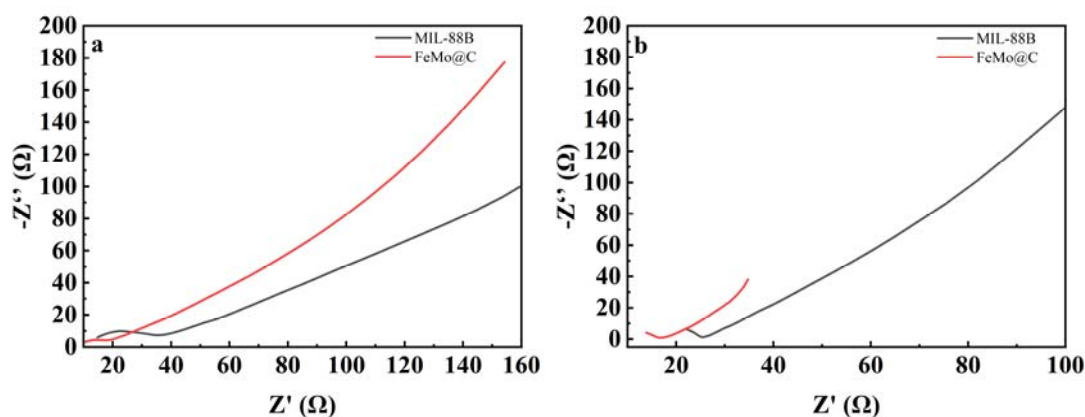


Figure 5. EIS of MIL-88B (burned) and FeMo@C in 0.5M H₂SO₄(a) and 1M KOH(b).

3. Conclusion

To sum up this work, a non-noble bimetallic catalyst is synthesized for hydrogen evolution derived from MIL-88B (Fe) MOF composited with organo-molybdenum by a mixed co-hydrothermal method between AB aqueous. Compared to HER catalyzed by iron element, the doping of molybdenum improves the catalytic efficiency of HER in aqueous solution. Especially when the current density was 10mA·cm⁻¹ in acidic solution, the catalytic overpotential of FeMo@C reached 275mV and R_{ct} comes to 13Ω. This work provides a simple synthesis idea for efficient hydrogen evolution bimetallic catalysts.

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