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Article

Iron-based binary metal-organic framework nanorods as an efficient catalyst for the oxygen evolution reaction

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ABSTRACT

First-row transition metal compounds have been widely explored as oxygen evolution reaction (OER) electrocatalysts due to their impressive performance in this application. However, the activity trends of these electrocatalysts remain elusive due to the effect of inevitable iron impurities in alkaline electrolytes on the OER; the inhomogeneous structure of iron-based (oxy)hydroxides further complicates this situation. Bimetallic metal-organic frameworks (MOFs) have the advantages of well-defined and uniform atomic structures and the tunable coordination environments, allowing the structure-activity relationships of bimetallic sites to be precisely explored. Therefore, we prepared a series of iron-based bimetallic MOFs (denoted as Fe₂M-MIL-88B, M = Mn, Co, or Ni) and systematically compared their electrocatalytic performance in the OER in this work. All the bimetallic MOFs exhibited higher OER activity than their monometallic iron-based counterpart, with their activity following the order FeNi > FeCo > FeMn. In an alkaline electrolyte, Fe₂Ni-MIL-88B showed the lowest overpotential to achieve a current density of 10 mA cm⁻² (307 mV) and the smallest Tafel slope (38 mV dec⁻¹). The experimental and calculated results demonstrated that iron and nickel exhibited the strongest coupling effect in the series, leading to modification of the electronic structure, which is crucial for tuning the electrocatalytic activity.

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1. Introduction

Hydrogen is a clean and flexible fuel for future energy applications, and can be produced via electrochemical water splitting process in conjunction with renewable but intermit-

tent energy sources, such as solar or wind power. However, the oxygen evolution reaction (OER) on the anode is a complex four-electron process that involves O–H bond breakage and O–O bond formation, and therefore, a high overpotential is required to drive the anode reaction [1]. Thus, the development

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of efficient, stable, and economical OER electrocatalysts to reduce the overpotential and energy losses of the anode reaction would be highly desirable.

Recent research in alkaline electrolytes has mainly focused on the electrocatalytic performance and underlying mechanism of OER electrocatalysts based on first-row transition metal compounds, especially oxides, layered double hydroxides, chalcogenides, phosphides, and nitrides based on Mn, Fe, Co, and Ni [2–15]. Among these non-precious transition metal electrocatalysts, iron-based materials are noteworthy in two aspects. Firstly, monometallic iron-based compounds are generally considered to possess inferior electrocatalytic activity for the OER. For example, early work reported that the OER activity of transition metal oxides followed the order $\text{RuO}_2 > \text{IrO}_2 > \text{MnO}_2 > \text{NiO} > \text{Co}_3\text{O}_4 \gg \text{Fe}_3\text{O}_4$; this trend was explained in terms of the enthalpy of the reactions $\text{MO}_x + 1/2\text{O}_2 \rightarrow \text{MO}_{x+1}$ and the related trend in the M–O bond strength [16,17]. A comparative study of nickel, cobalt, and iron oxide electrodes in 1 M NaOH also showed that iron electrodes display the poorest OER performance [18]. Subbaraman et al. reported that the OER activity of well-characterized metal (oxy)hydroxide films on a Pt (111) surface followed the trend $\text{Ni} > \text{Co} > \text{Fe} > \text{Mn}$ [5]. Additionally, density functional theory (DFT) calculations conducted by Calle-Vallejo et al. [19] revealed that the OER activity of FeO is comparable to that of CoO, but much poorer than that of NiO. However, research by Corrigan [20] and others has shown that alkaline electrolytes inevitably contain iron impurities, which will be incorporated into non-iron catalysts, particularly nickel and cobalt-based materials, and significantly affect their OER performance. Since many early researchers did not recognize the presence and potential influence of the iron impurities, the activity trends discussed above may be inaccurate. Utilizing high-purity alkaline electrolytes, Boettcher et al. reported the revised activity trend $\text{FeO}_x\text{H}_y > \text{CoO}_x\text{H}_y > \text{NiO}_x\text{H}_y > \text{MnO}_x\text{H}_y$ in an alkaline electrolyte; they explained that the instability and insulating properties of iron-based (oxy)hydroxide mask its OER activity [4,21,22]. Based on the above discussion, iron species are unavoidable in alkaline electrolytes, and monometallic iron catalyst exhibit unsatisfactory OER catalytic activity. Hence, the development of bimetallic iron-based materials and the exploration of the underlying factors that regulate their OER activity is of great theoretical and practical significance.

Compared to monometallic systems, binary catalysts often exhibit enhanced catalytic performance. This enhancement is usually attributed to synergetic effects, which are defined as cooperation between different components and/or active sites in a catalyst that results in significantly enhanced catalytic performance relative to the sum of the performance of the individual components [23]. Unfortunately, the synthesis of bimetal oxides and (oxy)hydroxides based on iron requires significant effort. Taking NiFe (oxy)hydroxides as an example, Bell et al. revealed that Fe^{3+} shows limited solubility in nickel hydroxides and that increasing the iron concentrations above 50% leads to the appearance of a mixture of FeOOH and Fe_2O_3 [24,25]. The resulting heterogeneity in the surface composition and structure complicates the evaluation of the OER performance of the catalysts. Recently, metal-organic frameworks (MOFs) have

received great attention for their potential as (electro)catalysts [26–33], which originates from the well-defined microstructures that are formed by the coordination of organic ligands and metal-ion nodes. Among the various MOFs, iron-based MILs (named for the Materials Institute Lavoisier) show excellent stability due to the strong bonds between their trivalent metal ions and oxygen-anion-terminated linkers [34–36]. More interestingly, iron-based MILs show structural flexibility. One of the metal atoms in the trinuclear iron-cluster can be replaced by an atom of a second metal to produce Fe_2M cluster nodes that resemble bimetallic electrocatalysts [37]. Therefore, based on their well-defined and uniform microstructures and adjustable coordination environments, iron-based bimetallic MILs show promise for the investigation of the OER electrocatalytic performance of bimetallic catalysts.

Herein, we focused on a series of bimetallic MOFs with MIL-88B structure (Fe_2M -MIL-88B, M = Mn, Fe, Co, or Ni; the abbreviations of Fe_2Mn , Fe, Fe_2Co , and Fe_2Ni are also used in this work for brevity) and investigated their electrocatalytic performance for the OER in alkaline electrolyte, as shown in Scheme 1. Compared with the monometallic Fe-MIL-88B, the incorporation of Mn, Co, and Ni enhance the catalytic activity. Fe_2Ni -MIL-88B clearly outperforms the other bimetallic MOFs, exhibiting a low overpotential of 307 mV to achieve 10 mA cm^{-2} and a small Tafel slope of 38 mV dec^{-1} . Further investigation demonstrated that introducing a second metal could induce a coupling effect between the different metal sites and modify their electronic structure, thereby expediting the OER process.

2. Experimental

2.1. Synthesis of materials

All reagents and solvents were obtained from commercial sources and used directly without further purification.

The Fe-MIL-88B framework was prepared according a previous reported method with slight modifications [38]. Briefly, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.90 mmol) and terephthalic acid (1.0 mmol) were dissolved in 10 mL *N,N*-dimethylformamide (DMF). 2 mL of 0.2 M NaOH was quickly added to the above homogeneous solution, and the resulting mixture was stirred constantly for 1 h. The mixture was then transferred into a Teflon-lined autoclave (40 mL) and heated without agitation at 100°C for 15 h. Sub-

Scheme 1. Scheme of the preparation and structure of Fe_2M -MIL-88B (Orange, blue, gray, red, and white spheres represent Fe, M, C, O, and H atoms, respectively).

sequently, the products were centrifuged, washed sequentially with DMF and methanol, and dried under vacuum at 80 °C overnight prior to further characterization.

The Fe₂Mn-MIL-88B framework was prepared using a process similar to that used to prepare Fe-MIL-88B, except that FeCl₃·6H₂O (0.47 mmol) and Mn(NO₃)₂ (solution, 50 wt%, 0.53 mmol) were used as the metal salts.

The Fe₂Co-MIL-88B framework was prepared using a process similar to that used to prepare Fe-MIL-88B, except that FeCl₃·6H₂O (0.57 mmol) and Co(NO₃)₂·6H₂O (0.43 mmol) were used as the metal salts.

The Fe₂Ni-MIL-88B framework was prepared using a process similar to that used to prepare Fe-MIL-88B, except that FeCl₃·6H₂O (0.57 mmol) and Ni(NO₃)₂·6H₂O (0.43 mmol) were used as the metal salts.

2.2. Physical characterization

The morphologies of the frameworks were analyzed using scanning electron microscopy (SEM, field-emission JSM-7800F microscope) and transmission electron microscopy (TEM, JEM-2100 field emission electron microscope); energy-dispersive X-ray spectroscopy (EDX) mapping was recorded using a FEI Tecnai G2 F20. Powder X-ray diffraction (XRD) studies were performed using a RIGAKU Miniflex600 diffractometer with Cu K_α radiation ($\lambda = 1.54178 \text{ \AA}$). Fourier-transform infrared (FT-IR) spectra were collected with a Thermo Nicolet 6700 Spectrometer using KBr pellets; the region below 750 cm⁻¹ was recorded in greater detail using a Nicolet iS50 Spectrometer. The elemental compositions of the materials were analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES, ICP-OES 7300DV). N₂ adsorption-desorption isotherms were recorded using a Quantachrome Autosorb-iQ instrument at 77 K. Before analysis, all samples were degassed at 150 °C for 6 h. X-ray photoelectron spectra (XPS) were collected using a Thermo ESCALAB 250Xi spectrometer with Al K_α radiation ($h\nu = 1486.6 \text{ eV}$), and the C 1s binding energy at 284.5 eV was used to correct all the measured binding energy values.

2.3. Electrochemical measurements

All electrochemical measurements were conducted using a three-electrode cell setup and a computer-controlled bipotentiostat (Pine Company). A saturated calomel electrode was used as the reference electrode, and the electrode potential was calibrated and converted to that of the reversible hydrogen electrode (RHE). The counter electrode was a carbon rod electrode. To prepare the working electrodes, samples (2.5 mg) of the MOFs were mixed with Vulcan XC-72 (Cabot) (2.5 mg) and dispersed in 2 mL ethanol containing 30 μL of Nafion solution (5 wt%, Dupont). After 3 h of sonication, 30 μL of the resulting homogeneous ink was deposited onto a pre-cleaned glassy carbon rotating disk electrode (GC-RDE, 0.196 cm²). Commercial iridium black (Johnson Matthey) and Vulcan XC-72 were physically mixed to produce an Ir/C composite containing 20 wt% of iridium. The obtained Ir/C, which was oxidized to

IrO_x/C under the anodic working conditions, was used as a benchmark catalyst for comparison. RDE measurements of the samples were performed in O₂ or N₂-purged 0.1 M KOH electrolyte at a scan rate of 10 mV s⁻¹ at 1600 rpm. Unless otherwise noted, all curves were iR-corrected. Electrochemical impedance spectra (EIS) were collected using a Solartron 1287A potentiostat in combination with a 1260 FRA unit at an amplitude of 10 mV and a frequency scan range of 10 kHz to 100 mHz, and were conducted at either open circuit potential or 1.580 V vs RHE. The stability investigation was performed in N₂-purged 0.1 M KOH using carbon cloth on which a 1 mg cm⁻² loading of the catalyst had been deposited as the working electrode. Chronoamperometry was conducted for 10 h at a potential of 1.703 V (vs RHE, without iR-correction), and OER polarization curves before and after the stability test were recorded at a scan rate of 50 mV s⁻¹.

2.4. DFT calculation

All calculations were conducted using the DMol³ code embedded in Materials Studio (Accelrys, San Diego, CA) [39], and considered both spin polarization and long-range dispersion correction via Grimme's scheme [40]. Exchange and correlation effects were described using the generalized gradient approximation with the Perdew-Burke-Ernzerhof (PBE) functional [41]. All electrons core treat method was implemented and the double numerical atomic orbital augmented by a polarization function was chosen as the basis set [42]. During geometrical optimization, the basis set cut-off was set at 5.2 $\text{\AA}$. The convergence tolerances for the geometry optimization were set to 10⁻⁵ Ha for energy, 0.002 Ha/ $\text{\AA}$ for force, and 0.005 $\text{\AA}$ for displacement. The electronic SCF tolerance was set to 10⁻⁶ Ha. A Fermi smearing parameter of 0.005 Ha was used in the calculations. The reciprocal space was sampled with Gamma points for the relaxation calculations and electronic structure computations. A vacuum region with a thickness of greater than 15 $\text{\AA}$ was added to avoid artificial interactions between Fe₂M-MIL-88B and its images.

3. Results and discussion

Fe₂M-MIL-88B (M = Mn, Fe, Co, or Ni) frameworks were synthesized via the solvothermal reaction of the appropriate metal ions and terephthalic acid; their hexagonal structure was obtained through the connection of the trinuclear oxo-centered metal clusters (Fe₂MO) to the 1,4-benzenedicarboxylate (BDC) ligands [35,43]. The chemical formula of the frameworks can be expressed as [Fe₂MO(BDC)₃(H₂O)₂(X)]_n, where X is the anion coordinated to the metal ions of the Fe₂MO unit [36]. The morphologies of the samples were characterized using SEM and TEM as shown in Fig. 1. All the MOFs showed a well-defined elongated hexagonal bipyramidal morphology, which is typical of MIL-88B structures [44,45]. The size distributions obtained from the SEM images indicated that Fe-MIL-88B was much thinner and longer than the other MOFs, with a length of $763 \pm 66.5 \text{ nm}$ and a diameter of $83.6 \pm 13.5 \text{ nm}$, while Fe₂Mn-MIL-88B was the shortest and thickest, with a length of

Fig. 1. SEM and TEM images of Fe₂Mn-MIL-88B (a,e), Fe-MIL-88B (b,f), Fe₂Co-MIL-88B (c,g), and Fe₂Ni-MIL-88B (d,h) (inset: distributions of the length of the samples). TEM images of Fe₂Ni-MIL-88B (i) and the corresponding elemental mapping of oxygen (j), iron (k), and nickel (l), along with the corresponding EDX spectra (m) in the selected region.

562.9 ± 37.2 nm and a diameter of 136.8 ± 13.6 nm. Fe₂Ni-MIL-88B and Fe₂Co-MIL-88B were very similar in size, with lengths of 677.3 ± 77.4 and 674.9 ± 60.2 nm and diameters of 127.3 ± 19.0 and 120.7 ± 15.9 nm, respectively. In addition, in the EDX elemental mapping images of Fe₂Ni-MIL-88B (Fig. 1), Fe, Ni, and O are all clearly observed, and no obvious elemental segregation was found in the selected region.

The structure of Fe₂M-MIL-88B was further characterized using XRD and FT-IR. The XRD patterns shown in Fig. 2(a) demonstrate that the diffraction peaks of the as-prepared Fe₂M-MIL-88B were almost identical to those attributed to MIL-88B structures [38,46,47]. The slight differences in the peak positions and intensities of the XRD patterns of the other frameworks were attributed to the different host-guest interactions of the flexible MIL-88B framework when Fe³⁺ was partially replaced by another metal ion. Analysis of the FT-IR spectra provided information about the functional groups of Fe₂M-MIL-88B. For comparison, the FT-IR spectrum of terephthalic acid, which was consistent with published reports [48], is also shown in Fig. 2(b). The adsorption peak of ν_{as}(-COO-) for pure terephthalic acid appeared at 1684 cm⁻¹, but in the spectrum of Fe₂M-MIL-88B, no obvious peak was observed at this

position. Instead, ν_{as}(-COO-) and ν_s(-COO-) adsorption bands corresponding to the coordination bonds between the ligands and the trinuclear oxo-centered metal clusters were present at 1583 and 1397 cm⁻¹, indicating the absence of free ligand in the as-prepared materials and the coordination of all the ligands to metal clusters [48,49]. Additionally, the peak at 751 cm⁻¹, which is attributed to the vibration of the C-H bonds of benzene rings, further demonstrated the presence of coordinated organic ligands [44,49]. Detailed analysis of the vibration of the trinuclear clusters in the frameworks was conducted based on the peaks at wavelengths below 750 cm⁻¹ shown in Fig. 2(c). For Fe-MIL-88B, the vibration of the central oxygen in the planar Fe₃O cluster with D_{3h} symmetry produced an adsorption peak at approximately 613 cm⁻¹. However, when one iron in the trinuclear metal cluster was replaced with another metal ion, the symmetry was reduced from D_{3h} to C_{2v} [49]. For this reason, the intensity of this band was obviously lower in the mixed-metal cluster samples, while the band corresponding to Fe₂MO (M = Mn, Co, or Ni) at 695 cm⁻¹ was prominent. Additionally, the peaks from 540 to 550 cm⁻¹ correspond to bonds between the metal ions and the carboxylic groups of the BDC ligands [44,47,48]. The positions of these peaks varied de-

Fig. 2. XRD patterns (a) and FT-IR spectra (b,c) of Fe₂M-MIL-88B.

Fig. 3. OER polarization curves (a) and Tafel plots (b) calculated from the polarization curves of Fe₂M-MIL-88B and 20% Ir/C in O₂-saturated 0.1 M KOH; (c) EIS spectra of Fe₂M-MIL-88B at an overpotential of 350 mV with an inset showing the equivalent circuit model (symbols: raw data; lines: linear fit results); (d) Chronoamperometry results of Fe₂Ni-MIL-88B/CC and OER polarization curves before (dashed curve) and after (solid curve) the stability test (without iR-correction); (e) ECSA of Fe₂M-MIL-88B calculated from LSV measurements performed in a non-faradaic region at different scan rates.

pending on the metal ions in the framework, indicating successful coordination between the linkers and the different metal ions. All the above results clearly prove the formation of the MIL-88B structure in all the materials and confirm the successful synthesis of Fe₂MO clusters in Fe₂M-MIL-88B.

The electrocatalytic performance of the synthesized Fe₂M-MIL-88B catalysts toward the OER was directly measured in O₂-purged 0.1 M KOH using a standard three-electrode system; Vulcan XC-72 carbon powder was mixed with the MOFs to increase their conductivity. Since iron was the main constituent of all the catalysts, the possible influence of iron impurities in the electrolyte could be ignored; thus, the KOH electrolyte was used without further purification. For comparison, 20 wt% Ir/C, which is oxidized to IrO_x/C at high anodic potential, was utilized as a benchmark catalyst. The electrocatalytic performance of Fe₂M-MIL-88B was investigated using linear sweep voltammetry (LSV), and the results are shown in Fig. 3(a). A typical anodic peak from 1.400 to 1.470 V vs RHE, which could correspond to the oxidation of Ni²⁺ [50,51], appeared in the LSV curve of Fe₂Ni-MIL-88B, while no significant anodic peaks were observed for the other catalysts in the examined potential range. Compared to the OER onset overpotential of Fe-MIL-88B (396 mV), the values of Fe₂Mn-MIL-88B, Fe₂Co-MIL-88B, and Fe₂Ni-MIL-88B were reduced (363, 273, and 248 mV, respectively). The incorporation of the second metal obviously enhanced the electrocatalytic activity to different degrees. At low current density (< 5 mA cm⁻²), Fe₂Mn-MIL-88B could drive the OER with a lower overpotential than that of Fe-MIL-88B. However, both these catalysts exhibited poor OER electrocatalytic activities and required overpotentials of greater than 470 mV

at 10 mA cm⁻², which is the approximate current density of the anode in a solar water-splitting device with an efficiency of 10% under 1 sun illumination [52]. When nickel or cobalt was introduced in the samples, their OER electrocatalytic performance was significantly enhanced. Fe₂Co-MIL-88B and Fe₂Ni-MIL-88B exhibited overpotentials of 348 and 307 mV, respectively, which were superior to that of the benchmark Ir/C electrocatalyst (376 mV). Fe₂Ni-MIL-88B clearly outperformed the other tested samples, and its catalytic activity was comparable to that of other reported MOF OER electrocatalysts (Table 1).

To further investigate the OER catalytic properties of these samples, the Tafel slopes were calculated from the polarization plots. As shown in Fig. 3(b), Fe₂Ni-MIL-88B exhibited a Tafel slope of 38 mV dec⁻¹, which was much smaller than those of the

Table 1

Comparison of the electrocatalytic OER performance of Fe₂M-MIL-88B with that of other reported MOF electrocatalysts tested in 0.1 M KOH on a GC-RDE.

Catalyst	Loading (mg cm ⁻²)	η (mV) @10 mA cm ⁻²	Tafel slope (mV dec ⁻¹)	Ref.
Fe ₂ Ni-MIL-88B	0.191	307	38	This work
Fe ₂ Co-MIL-88B	0.191	348	47	This work
MAF-X27-OH	0.18	461	66	[28]
NiFe-MOF	0.3	406	—	[27]
Ti ₃ C ₂ T _x -CoBDC	0.208	410	48.2	[30]
Fe ₃ -Co ₂	0.2	283	43	[29]
Fe:2D-Co-NS	0.2	282	59	[31]
FeCo-MNS-1.0	0.36	298	21.6	[65]
CTGU-10c2	0.14	240	58	[32]

Fig. 4. N₂ adsorption-desorption isotherms (a) and pore size distributions (b) of Fe₂M-MIL-88B.

other materials (Fe, 52 mV dec⁻¹; Fe₂Mn, 80 mV dec⁻¹; Fe₂Co, 47 mV dec⁻¹; Ir/C, 78 mV dec⁻¹) and further demonstrated its faster OER catalytic kinetics. To study the OER kinetics, EIS analyses of the catalysts were performed at an electrode potential of 1.580 V vs RHE; the results are displayed in Fig. 3(c). The trend in the charge transfer resistance R_{ct} (Fe₂Ni, 2.096 $\Omega \text{ cm}^2$; Fe₂Co, 6.478 $\Omega \text{ cm}^2$; Fe₂Mn, 3003 $\Omega \text{ cm}^2$; Fe, 5325 $\Omega \text{ cm}^2$) was clearly consistent with the trend in the catalytic activity shown in Fig. 3(a). Fe₂Ni-MIL-88B exhibited the lowest charge transfer resistance, clearly indicating its more efficient charge transfer in the OER.

The short-term electrochemical stability of Fe₂Ni-MIL-88B was also examined using chronoamperometry and is presented in Fig. 3(d). Only a slight change in the OER activity was observed, thus substantiating the durability of Fe₂Ni-MIL-88B in alkaline solutions.

To reveal the underlying reasons for the improved performance of the bimetallic Fe₂M-MIL-88B catalysts, we carefully investigated several possible factors that might affect their electrochemical performance. First, ICP-OES was conducted to investigate the relative proportions of metal in each catalyst. The Fe:M molar ratios (M = Mn, Co, Ni) were 2.00, 2.29, and 2.02 for Fe₂Mn-MIL-88B, Fe₂Co-MIL-88B, and Fe₂Ni-MIL-88B, respectively, indicating similar metal contents. We then evalu-

ated the electrochemical active surface area (ECSA) of the Fe₂M-MIL-88B catalysts by calculating their double-layer capacitance (C_{dl}) values from polarization curves measured in the non-Faradaic region. The slopes of the curves in Fig. 3(e), which represent the C_{dl} values, reveal that Fe₂Ni-MIL-88B (C_{dl} : 1.65 mF cm⁻²) and Fe₂Co-MIL-88B (C_{dl} : 1.79 mF cm⁻²) had slightly larger ECSAs than monometallic Fe-MIL-88B (C_{dl} : 1.55 mF cm⁻²). These results indicated that the incorporation of the second metal slightly increased the surface area of the MOFs, which would afford more active sites and promote the OER process. However, the C_{dl} value doubled to 3.37 mF cm⁻² for Fe₂Mn-MIL-88B, which was in agreement with the specific surface area results of the N₂ adsorption-desorption isotherms (Fe-MIL-88B: 35.2 m² g⁻¹; Fe₂Mn-MIL-88B: 116.4 m² g⁻¹; Fe₂Co-MIL-88B: 47.9 m² g⁻¹; Fe₂Ni-MIL-88B: 35.7 m² g⁻¹) in Fig. 4. Based on the poor OER catalytic activity of Fe₂Mn-MIL-88B, it was concluded that the ECSA was not the principal factor responsible for the performance enhancement.

To further explore the OER reaction mechanism for Fe-MIL-88B, we measured the OER current density of Fe₂M-MIL-88B in alkaline electrolytes with different pH values (from 12.57 to 13.98) using LSV; the results are shown in Fig. 5(a). The OER reaction order of pH illustrates how the proton activity affects the OER kinetics of the rate-determining step

Fig. 5. (a) LSV measurements of the catalysts in O₂-purged 0.0316 M KOH (pH 12.57, ■), 0.1 M KOH (pH 13.12, ●), 0.316 M KOH (pH 13.54, ▲), and 1 M KOH (pH 13.98, ▼). OER current density at (b) 1.550 V vs. RHE and the indicated potential (c) after iR-correction at the investigated pH values.

(RDS). Thus, important information about the reaction process can be obtained from the reaction order $\rho = (\partial \log(i) / \partial \text{pH})_E$ [53]. The reaction order ρ is zero for the traditional proton-electron coupled mechanistic routes when RHE is used as the reference electrode; as a result, the OER activity should be pH-independent under these conditions. However, on the RHE scale, all four catalysts exhibited pH-dependent OER activity at a potential of 1.550 V, which is a commonly used potential value in the literature [54,55] (For Fe₂Ni-MIL-88B, the measured activities at pH values of 13.54 and 13.98 were very similar. A similar phenomenon has been reported by other researchers. This phenomenon might be related to the accelerating effect of higher-pH electrolytes on the oxidation of nickel centers [56]. However, in the pH range we focused upon, namely, the region near 13.12 in 0.1 M KOH, the slope of the linear fitting is obviously non-zero. Thus, pH-dependence of the OER activity of Fe₂Ni-MIL-88B is conceivable). For Fe-MIL88B and Fe₂Mn-MIL88B, which showed poor electrocatalytic perfor-

mance, the potential of 1.550 V may have been too low for detectable OER current to be produced. Thus, measurements were also conducted at the potential required to achieve a current density of 2 mA cm⁻² in 1 M KOH; these results are shown in Fig. 5(c). All four catalysts exhibited pH-dependent OER activity. This dependence indicated the existence of decoupled proton and electron transfer steps in the catalytic process [57], in which the RDS may be a proton transfer step or an acid/base equilibrium prior to the proton transfer step [53]. Therefore, the acid dissociation constant K_a is important for the transfer of protons, which is the equilibrium constant of a surface active site under deprotonation [53,55,58]. Thus, investigation of the electronic structure of the Fe₂M-MIL-88B materials was necessary.

The chemical composition and electronic properties of the as-obtained Fe₂M-MIL-88B materials were examined by XPS analysis; the results are shown in Fig. 6. The full survey patterns in Fig. 6(a) demonstrate the existence of Fe, O, C, and the

Fig. 6. (a) XPS survey patterns of all the samples; (b) Mn 2p high-resolution spectrum of Fe₂Mn-MIL-88B; (c) Fe 2p high-resolution spectra of all samples (Dashes: raw data. Gray line: fitting results); (d) Mn 3s high-resolution XPS spectrum of Fe₂Mn-MIL-88B; (e) Co 2p and (f) Ni 2p high-resolution spectra of Fe₂Co-MIL-88B and Fe₂Ni-MIL-88B, respectively; (g) Fe³⁺ content calculated from the fitting results of Fe₂M-MIL-88B.

expected metal elements in the bimetallic MOFs. Detailed information regarding the oxidation states of the metal elements was obtained from the high-resolution XPS spectra. As shown in Fig. 6(b), the Mn 2*p* spectrum of Fe₂Mn-MIL-88B contained spin-orbit-split 2*p*_{1/2} and 2*p*_{3/2} peaks with binding energies of 641.5 and 653.3 eV, respectively. Two satellite peaks were observed at approximately ~4.8 eV higher binding energy than the 2*p* peaks; such satellites are a feature of the Mn²⁺ state [59]. To identify the Mn oxidation state in a straightforward manner, the Mn 3*s* peaks resulting from the coupling of the non-ionized 3*s* electrons with 3*d* valence electrons were also investigated, as the magnitude of the splitting of these peaks is diagnostic of the oxidation state [59–61]. The measured energy separation of ~6.3 eV in Fig. 6(d) further confirmed that the Mn oxidation state was 2. For Fe₂Co-MIL-88B, the Co 2*p* XPS spectrum in Fig. 6(e) exhibited two characteristic peaks at 796.7 and 781.2 eV, along with strong satellite peaks at 802.0 and 785.6 eV, indicating that the main oxidation state of cobalt was 2 [26,29]. From the two characteristic peaks at 873.8 and 856.1 eV in the Ni 2*p* spectrum of Fe₂Ni-MIL-88B in Fig. 6(f), it was concluded that the predominant oxidation state of the Ni ions was Ni²⁺ [62,63].

The iron oxidation states were analyzed in great detail. As shown in Fig. 6(c), all four Fe 2*p*_{3/2} spectra were fitted using Gupta and Sen (GS) multiplets, high-binding-energy surface structures, and satellite peaks [64]. Based on the GS multiplet model, the series of peaks at 710.4, 711.4, 712.4, and 713.5 eV were assigned to the Fe³⁺ oxidation state, and the peaks at 708.3, 709.2, and 710.4 eV were attributed to Fe²⁺. The main oxidation state of iron was clearly 3. However, when a second metal was incorporated to the MOFs, the peaks shifted to lower binding energy and the Fe³⁺/Fe²⁺ intensity ratio decreased, indicating the altered electronic properties of the iron ions as well as the interactions between iron and the second metal. The most distinct change was observed for Fe₂Ni-MIL-88B. As shown in Fig. 6(g), Fe₂Ni-MIL-88B had an Fe³⁺/(Fe³⁺ + Fe²⁺) peak area ratio of 82.72%, which was lower than those of Fe-MIL-88B (91.39%), Fe₂Mn-MIL-88B (91.24%), and Fe₂Co-MIL-88B (89.65%). This suggests a relatively strong coupling effect between iron and nickel, which may explain the major improvement in the OER electrochemical activity of Fe₂Ni-MIL-88B compared with that of monometallic Fe-MIL-88B.

The charge transfer phenomenon can be well explained by the electronic structure of the MOFs (Fig. 7). The valence electron configuration of Fe³⁺ is 3*d*⁵ with a high-spin state, which

Fig. 7. Schematic representation of the electronic coupling between Fe and Ni in Fe₂Ni-MIL-88B.

means that Fe³⁺ has unpaired electrons in the π -symmetry (t_{2g}) *d*-orbitals that interact with the bridging O²⁻ via π -donation [26]. Mn²⁺ has a similar valence electronic configuration of 3*d*⁵ and a high-spin state; thus, its influence on the electronic structure of Fe³⁺ was expected to be slight, which agreed with the electrochemical experiment results. In contrast, the electronic structure of Ni²⁺ is 3*d*⁸, with fully occupied π -symmetry (t_{2g}) *d*-orbitals. For this reason, the main interaction between the bridging O²⁻ and Ni²⁺ is $e-e^-$ repulsion. When Ni is doped into the Fe-based MOF, the π -donation via Fe³⁺ and the bridging O²⁻ could be enhanced by the $e-e^-$ repulsion between the bridging O²⁻ and Ni²⁺. Electron would be partially transferred from Ni²⁺ to Fe³⁺ via the bridging O²⁻, creating a strong coupling effect between Fe³⁺ and Ni²⁺. A similar coupling phenomenon would be expected between Fe³⁺ and Co²⁺ due to the 3*d*⁷ electronic structure of Co²⁺ with low spin [65], as suggested by the results of the DFT calculations of the spin states of the metals (Table 2). The XPS results also demonstrated a positive shift in the Fe 2*p* peak after doping with nickel and cobalt. The larger shift observed for nickel indicates that the coupling effect between Fe³⁺ and Ni²⁺ was much stronger than that of Fe³⁺ with the other metal atoms, which explains the superior OER activity of Fe₂Ni-MIL-88B. These results clearly illustrate the coupling effect between iron and different metal atoms in the well-defined MOF structure. The strong synergy between the metal sites modifies the electronic structure, endowing the

Table 2

Energies of Fe₂M-MIL-88B with varied Mulliken spin states.

Initial spin multiplicity		1	2	3
Fe ₂ Mn	Final spin	3.82×2, ~3.45 ^{Mn}	−3.77, 1.52, 3.68 ^{Mn}	−3.80, 3.01, 3.28 ^{Mn}
	Energy (Ha)	−4887.845132	−4887.833044	−4887.818988
Fe	Final spin	3.83×2; 3.81	3.78, −3.82, 1.10	3.75, −3.80, 2.08
	Energy (Ha)	−5000.539747	−5000.531345	−5000.533114
Fe ₂ Co	Final spin	1.72, −1.40, 0.69 ^{Co}	1.72, −1.37, 0.70 ^{Co}	1.87, −0.70, 0.82 ^{Co}
	Energy (Ha)	−5119.585567	−5119.585562	−5119.582236
Fe ₂ Ni	Final spin	1.90, −1.86, 1.35 ^{Ni}	1.66, −2.13, 1.23 ^{Ni}	1.97, −1.67, 1.39 ^{Ni}
	Energy (Ha)	−5245.130615	−5245.129398	−5245.130189

catalysts with enhanced OER electrocatalytic performance.

4. Conclusions

In summary, a series of iron-based bimetallic MOFs with MIL-88B structure were developed and employed as OER electrocatalysts in alkaline electrolyte due to the tunable structure characteristics of this framework. The well-defined structure of MOFs on the molecular scale makes them useful in the systematic investigation of structure-activity relationships. Notably, the OER activity of the framework was enhanced after doping with a second metal, with the activity following the order $\text{Fe}_2\text{Ni-MIL-88B} > \text{Fe}_2\text{Co-MIL-88B} > \text{Fe}_2\text{Mn-MIL-88B}$. Among them, $\text{Fe}_2\text{Ni-MIL-88B}$ exhibited the best catalytic performance, requiring only 307 mV of overpotential to achieve an OER current density of 10 mA cm^{-2} and exhibiting a small Tafel slope of 38 mV dec^{-1} in 0.1 M KOH , making it superior to the commercial Ir/C electrocatalyst. XPS analysis and DFT calculations revealed that partial electron was transferred from Ni^{2+} to Fe^{3+} via the bridging O^{2-} , resulting in strong coupling between them and modifying their electronic structure, which in turn improved the OER performance.

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Graphical Abstract

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Iron-based binary metal–organic framework nanorods as an efficient catalyst for the oxygen evolution reaction

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The electronic coupling effect induced by the introduction of a second metal into iron-based MOFs significantly enhances their electrocatalytic performance toward the oxygen evolution reaction.

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具有高效析氧催化性能的铁基双元金属有机框架纳米棒研究

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摘要: 析氧反应(OER)是电解水制氢的关键步骤, 开发高效、稳定、廉价的OER电催化剂是目前该领域的研究热点。碱性电解液中的OER电催化剂成分以Mn、Fe、Co、Ni等为主, 其中单一组分的Fe基化合物催化活性不高, 但碱性电解液中的痕量铁杂质极易掺入Ni、Co等非Fe基材料的结构中, 极大影响其OER催化性能, 即现有大部分非Fe基化合物无法回避Fe的影响。为探究Fe基多金属电催化剂的活性规律, 本文以结构清晰、组分可控的Fe基金属有机框架材料为基底, 通过掺入Mn、Co、Ni等元素构建双元金属化合物Fe₂M-MIL-88B(M = Mn, Co, Ni), 并围绕上述Fe基双金属电催化剂的构效关系展开研究。

扫描电镜、透射电镜、X射线衍射光谱、红外光谱等表征结果表明, 所制备的Fe基双金属材料均为具有MIL-88B构型的纳米棒, 其特征三核金属簇Fe₃O中的一个铁原子被第二元金属所替代, 从而形成相应的三核混合金属簇Fe₂MO。上述Fe

基双金属催化剂的析氧催化活性顺序为: $\text{Fe}_2\text{Ni} > \text{Fe}_2\text{Co} > \text{Fe}_2\text{Mn} > \text{Fe}$ (0.1 M KOH电解液). 其中, $\text{Fe}_2\text{Ni-MIL-88B}$ 电催化剂在 10 mA cm^{-2} 析氧电流对应的过电位仅需307 mV, 明显低于OER基准电催化剂20 wt% Ir/C(376 mV).

结合材料的元素组成、电化学活性比表面积(ECSA)及金属价态分析发现, 第二元金属的引入会在不同程度上降低Fe的价态, 其中Ni的影响程度最大, Co次之, Mn的影响最小. 借助分子轨道理论对上述实验现象进行了解释. 处于低自旋态的 Ni^{2+} 与邻近桥氧 O^{2-} 之间存在电子排斥作用, 因此部分电子将从 Ni^{2+} 经 O^{2-} 转移至高自旋态的 Fe^{3+} , 从而在 Ni^{2+} 和 Fe^{3+} 之间形成了较强的电子耦合作用. Co^{2+} 具有和 Ni^{2+} 相似的构型, 但影响稍小. 而 Mn^{2+} 和 Fe^{3+} 同为高自旋态, 对 Fe^{3+} 的电子结构影响最小, 导致活性改善程度最低. 密度泛函理论计算得到的自旋态变化情况印证了上述推测. 该系列Fe基双金属材料的催化性能主要受金属活性位点的电子结构影响, Fe与邻近金属间形成的电子耦合作用修饰了金属活性位点的电子结构, 从而提高了材料的OER本征催化活性.

关键词: 析氧反应; 金属有机框架; 电催化; 电子耦合作用; 水氧化

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