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Article

Cobalt/iron bimetal-organic frameworks as efficient electrocatalysts for the oxygen evolution reaction

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ABSTRACT

The development of high efficiency and stable electrocatalysts for oxygen evolution is critical for energy storage and conversion systems. Herein, a series of Co/Fe bimetal-organic frameworks (MOFs) were fabricated using a facile ultrasonic method at room temperature, as electrocatalysts for the oxygen evolution reaction (OER) in alkaline solution. The Co₂Fe-MOF exhibited an overpotential of 280 mV at a current density of 10 mA cm⁻², a low Tafel slope of 44.7 mV dec⁻¹, and long-term stability over 12000 s in 1 mol L⁻¹ KOH. This impressive performance was attributed to the high charge transfer rate, large specific surface area, and synergistic effects of the cobalt and iron centers.

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1. Introduction

The energy crisis and environmental pollution are serious issues caused by the continuous consumption of fossil fuels [1]. Developing renewable and clean sources of energy to replace traditional fossil fuels has become increasingly necessary [2–4]. Hydrogen production via electrochemical water splitting is considered to be an ideal method to solve these issues. The oxygen evolution reaction (OER) is a bottleneck for overall water splitting due to its sluggish reaction kinetics [5–7]. Therefore, efficient electrocatalysts should be developed for the OER to decrease the overpotential and increase the reaction rate. Although some state-of-the-art noble metal catalysts (e.g., IrO₂ or RuO₂) exhibit high electrocatalytic performance, their high cost and scarcity prohibit large-scale application [2,8,9]. Therefore, significant efforts have been devoted to developing

low cost and earth-abundant electrocatalysts, including non-noble transition metal-based oxides [10], (oxy)hydroxides [11,12], phosphides [13–15], nitrides [16], sulfides [17–20], and selenides [21–23]. Among them, Co-based materials have exhibited promising performance for the OER because oxidized cobalt centers can promote the formation of OOH species and subsequent deprotonation to form O₂ [24]. In addition, when Fe is doped into Co-based catalysts, the OER performance can be further improved [25,26].

Metal-organic frameworks (MOFs), also known as porous coordination polymers, have been widely applied to medicine delivery [27], gas storage and separation [28,29], catalysis [30], and sensing [31] due to their large specific surface areas, tunable pore sizes, periodic structures, and diversity of metal centers and organic linkers. For electrochemical water splitting, MOFs have been used as precursors and templates for synthe-

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sizing oxide/carbon composites with high OER activity [32–35]. However, tedious fabrication processes and high pyrolysis temperatures are generally required, which is unsuitable for practical applications. Consequently, the direct use of MOFs as electrocatalysts toward OER is desirable.

Herein, we report a facile ultrasonic method for fabricating Co/Fe-based bimetal-organic frameworks as highly efficient water oxidation catalysts in alkaline solution. The OER performance of the Co_xFe -MOFs followed a volcano-type pattern with increasing Fe content. The optimized Co_xFe -MOFs exhibited high catalytic activity with an overpotential of 280 mV at 10 mA cm^{-2} and a Tafel slope of 44.7 mV dec^{-1} . This performance can be ascribed to the large specific surface area, excellent conductivity, and synergistic effects of Co and Fe.

2. Experimental

2.1. Materials

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was purchased from Tianjin Guangfu Technology Development Co., Ltd. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, trimesic acid (H_3BTC), and RuO_2 were purchased from Aladdin. Triethylamine ($(\text{C}_2\text{H}_5)_3\text{N}$) and N,N -dimethylformamide (DMF) were purchased from Tianjin Fuyu Fine Chemical Co. Nafion (5%) was obtained from Sigma Aldrich. All reagents were used without further purification, and deionized water was used throughout the experiments.

2.2. Synthesis of the Co_xFe -MOFs

The Co_xFe -MOFs were synthesized according to a previously reported method with some modifications [36]. In a typical synthesis, H_3BTC (0.75 mmol), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.5 mmol), and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.25 mmol) were dissolved in a mixed solution of DMF (32 mL), ethanol (2 mL), and deionized water (2 mL) under vigorous stirring. Subsequently, triethylamine (0.8 mL) was added rapidly to the above solution. The mixture was stirred for 5 min and continuously ultrasonicated for 8 h at room temperature. Finally, the products were collected via centrifugation, washed with ethanol three times, and dried at 60 °C overnight. A similar procedure was adopted for the preparation of the Co-, Co_3Fe -, Co_1Fe -, and Fe-MOFs using different molar ratios of Co/Fe chloride salts (1:0, 3:1, 1:1, 0:1) at the beginning with the total amount of metal salt held constant at 0.75 mmol.

2.3. Characterization

Field-emission scanning electron microscopy (FESEM) was performed using a NOVA NanoSEM 450 instrument at 10 kV. Transmission electron microscopy (TEM), HRTEM, and EDS were performed using a JEM2100F TEM instrument at an acceleration voltage of 200 kV. X-ray diffraction (XRD) was performed using a D/max-2400 diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 154.1 \text{ nm}$). X-ray photoelectron spectroscopy (XPS) was recorded on an ESCALAB 250Xi spectrometer with a monochromated Al $\text{K}\alpha$ radiation source. Fourier transform infrared spectra (FT-IR) were collected using a NEXUS EURO instru-

ment. Inductively coupled plasma-atomic emission spectrometry (ICP-AES) was performed with an Optima2000DV instrument from PerkinElmer company. The BET specific surface area was determined using an AUTO SORB-1-MP apparatus.

2.4. Electrochemical measurements

To prepare the working electrode, 5 mg of the prepared catalysts were added into a mixed solution containing 480 μL of water, 480 μL of ethanol, and 40 μL of a 5% Nafion solution. Subsequently, the mixed solution was sonicated for 30 min to obtain a homogeneous catalyst ink. Finally, 5 μL of the catalyst ink was immobilized on glassy carbon by drop-casting and dried at room temperature. All electrochemical measurements were performed using a standard three-electrode system (CHI 760E electrochemical station) at room temperature. The electrolyte was a 1 mol L^{-1} KOH solution. A glass carbon electrode was utilized as the working electrode, and Hg/HgO and Pt wire were used as the reference and counter electrodes, respectively. All potentials were calibrated to the reversible hydrogen electrode (RHE) using the following equation: $E(\text{RHE}) = E(\text{Hg}/\text{HgO}) + 0.098 \text{ V} + 0.059\text{pH}$. Linear sweep voltammetry (LSV) was recorded at a scan rate of 5 mV s^{-1} with 95% iR-compensation. Electrochemical impedance spectroscopy (EIS) was performed at a frequency ranging from 10 kHz to 0.1 Hz at 1.53 V vs. RHE. The durability test was conducted by cyclic voltammetry (CV) from 1.1 to 1.7 V vs. RHE at a scan rate of 100 mV s^{-1} for 500 cycles. The chronopotentiometry was measured at a current density of 10 mA cm^{-2} . To estimate the electrochemical active surface area (ECSA) of the catalyst, the electrochemical double layer capacitance (C_{dl}) was measured via CV in the non-Faradaic potential range of 0.1 to 0.2 V vs. Hg/HgO with scan rates of 10–50 mV s^{-1} . The turnover frequency (TOF) was calculated using the following formula: $\text{TOF} = jA/4nF$, where j is the current density at an overpotential of 280 mV, A is the geometric area of the GC electrode, 4 is the number of electrons transferred to produce one molecule of oxygen, n is the number of moles of active sites, and F is Faraday constant (96485 C mol^{-1}).

3. Results and discussion

The fabrication process of the Co_xFe -MOFs is illustrated in Scheme 1. Triethylamine was used to accelerate the deprotonation of the organic ligands under ultrasonic conditions [37]. The Co_xFe -MOFs were formed by the coordination reaction of $\text{Co}^{2+}/\text{Fe}^{3+}$ with deprotonated trimesic acid (H_3BTC). The structural information of the as-prepared Co-, Co_xFe -, and Fe-MOFs was obtained by XRD, as shown in Fig. 1a. With increasing Fe content, the crystal structure of the Co_xFe -MOFs gradually changed from Co-MOF to Fe-MOF. FT-IR spectroscopy was performed to characterize the functional groups in the Co_2Fe -MOF (Fig. 1b). The free trimesic acid ligand was also analyzed by FT-IR for comparison. In the Co_2Fe -MOF, the absorption band at 3426 cm^{-1} was attributed to the stretching vibration of the O–H motifs. The bands between 1300 and 1650 cm^{-1} arose from the stretching vibrations of C=O and C–C

Scheme 1. Schematic illustration of the fabrication procedure of the $\text{Co}_2\text{Fe-MOFs}$.

bonds, respectively, on the benzene rings [38]. In particular, the bands at 1622 and 1371 cm^{-1} can be ascribed to the respective asymmetric and symmetric stretching vibration bands of the carboxyl groups bound to metal ions. For comparison, the free trimesic acid ligand showed a stretching vibration of the carboxyl group at 1721 cm^{-1} . The difference in asymmetric vibration indicates that no free carboxylic groups were present in $\text{Co}_2\text{Fe-MOF}$ [39].

The morphology and microstructure of $\text{Co}_2\text{Fe-MOF}$ were characterized by SEM and TEM. The SEM images (Fig. 2a and 2b) indicate that $\text{Co}_2\text{Fe-MOF}$ is composed of nanoparticles with an average size of approximately $50\text{--}100\text{ nm}$. These nanoparticles were loosely packed into a porous structure, which is favorable for exposing more active sites for the OER. In the high-resolution TEM image of $\text{Co}_2\text{Fe-MOF}$ (Fig. 2d), no obvious lattice fringes were observed due to the easily damaged MOF structure under high energy electron beam irradiation [40]. This result is consistent with the observation of weak circle rings shown at the top-right selected area electron diffraction (SAED) pattern. As shown by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM; Fig. 2e), the EDS element mapping revealed a uniform distribution of Co, Fe, C, and O throughout the entire catalyst without impurities. EDS elemental analysis confirmed a molar ratio of $2:1$ for Co: Fe (Fig. S1), consistent with the inductively coupled plasma (ICP) analysis (Table S1).

XPS measurements were obtained to investigate the surface composition and chemical valance states of the as-obtained $\text{Co}_2\text{Fe-MOF}$. The XPS survey spectra verified the coexistence of

Fig. 2. (a, b) SEM images of $\text{Co}_2\text{Fe-MOF}$. (c) TEM and (d) HRTEM images (inset: SAED pattern) of $\text{Co}_2\text{Fe-MOF}$; (e) HAADF-STEM image and STEM-EDS element mapping of $\text{Co}_2\text{Fe-MOF}$ (Co: pink; Fe: yellow; C: red; O green).

Co, Fe, C, and O (Fig. S2). In the Co $2p$ region (Fig. 3a), the binding energies of 781.9 and 797.7 eV can be ascribed to Co $2p_{3/2}$ and $2p_{1/2}$ peaks, respectively. In addition, two satellite peaks corresponding to Co $2p_{3/2}$ and Co $2p_{1/2}$ were observed at 786.5 and 803.2 eV , respectively. These results suggest the presence of Co^{2+} bound to oxygen [41]. The Fe $2p$ region shown in Fig. 3b exhibited two peaks at 711.5 and 725.3 eV , which were assigned to Fe $2p_{3/2}$ and Fe $2p_{1/2}$, respectively. Moreover, a satellite peak at 716.2 eV was observed, indicating the $+3$ valance

Fig. 1. (a) XRD patterns of the Co-MOF, $\text{Co}_2\text{Fe-MOF}$, and Fe-MOF samples; (b) FT-IR spectra of $\text{Co}_2\text{Fe-MOF}$ and H_3BTC .

Fig. 3. (a–d) High-resolution XPS spectra of Co 2p, Fe 2p, C 1s, and O 1s for the Co₂Fe-MOF electrocatalyst.

state for iron [42]. The C 1s spectrum was deconvoluted into three peaks (Fig. 3c). The peak at 284.8 eV was attributed to C=C bond of the benzoic ring, the 288.4 eV peak arose from the carboxyl group (O=C–O) of BTC^{3−}, and the 286.0 eV peak was assigned to C–O [39,43]. In the high-resolution XPS spectrum of O 1s (Fig. 3d), three peaks at 530.8, 531.6 and 532.7 eV were observed, arising from the coordinated oxygen, carbonyl group, and absorbed water, respectively [39]. Compared to those of the Co-MOF, the binding energies of the Co 2p_{3/2} and Co 2p_{1/2} spectra of Co₂Fe-MOF were positively shifted by 0.3 eV, indicating decreasing electron density at the Co centers. Furthermore, the Fe 2p_{3/2} and Fe 2p_{1/2} peaks were negatively shifted by 0.3 eV compared to those of Fe-MOF, suggesting an electron donation effect from Co to Fe (Fig. S3). The above results indicate that Fe incorporation can regulate the electronic environment of the Co centers. N₂ adsorption-desorption isotherms were recorded to calculate the specific surface area of Co₂Fe-MOF (Fig. S4). A IV-type isotherm with H3-type hysteresis loop indicated the existence of mesopores in Co₂Fe-MOF [44]. The specific surface area of Co₂Fe-MOF was determined to be 36.6 m² g^{−1} based on the Brunauer-Emmett-Teller (BET) method. Large surface areas and mesoporous structures are favorable for the improved OER activity.

The electrocatalytic activities of the Co_xFe-MOFs toward the OER were evaluated by LSV in a typical three-electrode electrochemical cell with 1 mol L^{−1} KOH as the electrolyte. A GC electrode with drop-casted catalysts was used as the working

electrode and Hg/HgO and Pt wire were used as the reference and counter electrodes, respectively. Unless otherwise stated, the ohmic potential drop (*iR*) arising from solution resistance compensation was applied to all experimental data and all potentials were calibrated against the reversible hydrogen electrode (RHE). For comparison, bare GC and commercial RuO₂ electrodes were tested under the same conditions. As shown in Fig. 4a, the bare GC and Fe-MOF exhibited negligible OER activity. In contrast, the bimetal MOFs showed a significantly enhanced catalytic activity, unlike single metal materials. For the optimized Co₂Fe-MOF activity, an overpotential of 280 mV is required to reach a current density of 10 mA cm^{−2}, which is lower than those required for Co₁Fe-MOF (297 mV), RuO₂ (307 mV), and Co₃Fe-MOF (314 mV). This value is also lower than most recently reported Co/Fe-based OER electrocatalysts (Table S2). Meanwhile, Co₂Fe-MOF exhibited a lower Tafel slope of 44.7 mV dec^{−1} than those of the Co₁Fe-MOF (48.9 mV dec^{−1}), Co₃Fe-MOF (55.6 mV dec^{−1}), Co-MOF (69.9 mV dec^{−1}), RuO₂ (82.0 mV dec^{−1}), and Fe-MOF (176.2 mV dec^{−1}) samples, reflecting the favorable kinetics of Co₂Fe-MOF toward the OER.

EIS analysis was conducted to investigate the electrochemical behavior of the prepared electrodes. The Co₂Fe-MOF exhibited a smallest semicircle diameter among these catalysts, as shown in the Nyquist plots (Fig. 4c), indicating that it possessed the lowest charge transfer resistance (*R*_{ct}). Additionally, the ECSAs were evaluated by calculating *Cdl* based on CV in the non-Faradaic region (Figs. S5 and S6). The Co₂Fe-MOF exhibit-

Fig. 4. (a) LSV curves of the Co_xFe-MOFs, Co-MOF, Fe-MOF, GC, and RuO₂; (b) Tafel plots derived from the LSV curves; (c) Nyquist plots at an overpotential of 300 mV; (d) TOF values of the Co_xFe-MOFs ($x = 1, 2, 3$), Fe-MOF, and Co-MOF at an overpotential of 280 mV.

ed a lower Cdl value (2.33 mF cm⁻²) compared to those of the Co-MOF (6.28 mF cm⁻²) and Co₃Fe-MOF (3.96 mF cm⁻²), indicating a superior intrinsic OER activity for the Co₂Fe-MOF. We further calculate the TOF to evaluate the intrinsic activity of the catalysts. Assuming all Co and Fe atoms are involved in the OER, the TOF value of Co₂Fe-MOF was 0.032 s⁻¹, higher than those of Co₁Fe-MOF (0.011 s⁻¹), Co₃Fe-MOF (0.008 s⁻¹), Co-MOF (0.002 s⁻¹), and Fe-MOF (0.0007 s⁻¹).

Stability is another important parameter for the practical application of electrocatalysts. Fig. 5a shows the LSV curves of

the Co₂Fe-MOF before and after 500 CV scans at a scan rate of 100 mV s⁻¹. Only slight current density attenuation was observed for the polarization curves after 500 cycles, indicating the superior stability of Co₂Fe-MOF for the OER. From the chronopotentiometric curve in Fig. 5b, only a slight increase in the applied potential was required for the Co₂Fe-MOF to maintain a current density of 10 mA cm⁻² for a duration of 12000 s. The I - t curve of the Co₂Fe-MOF at an applied potential of 1.58 V vs. RHE is provided in Fig. S7. The observed slight decrease in catalytic activity was attributed to the oxygen bubble that was

Fig. 5. (a) polarization curves of the Co₂Fe-MOF before and after 500 cycles in 1.0 mol L⁻¹ KOH; (b) Associated chronopotentiometric curve at a current density of 10 mA cm⁻².

adsorbed on the electrode, preventing the intimate contact between the catalyst and electrolyte and detachment of the catalyst from the working electrode surface.

4. Conclusions

We synthesized a series of Co_xFe -MOFs with different Co/Fe molar ratios, using a simple ultrasonic method, as efficient electrocatalysts for the OER. The Co_2Fe -MOF showed the best catalytic performance among the prepared catalysts with a low overpotential of 280 mV at 10 mA cm^{-2} and a Tafel slope of 44.7 mV dec^{-1} . Moreover, the Co_2Fe -MOF exhibited long-term durability for at least 12000 s. Its high OER performance can be attributed to the synergistic effects of Co^{2+} and Fe^{3+} , mesoporous structure, and enhanced charge transfer rate. This study provides a promising method for examining highly active MOF materials for water splitting applications.

References

- [1] X. Q. Du, Z. Yang, Y. Li, Y. Q. Gong, M. Zhao, *J. Mater. Chem. A*, **2018**, 6, 6938–6946.
- [2] P. W. Menezes, C. Panda, S. Loos, F. Bunschei-Bruns, C. Walter, M. Schwarze, X. H. Deng, H. Dau, M. Driess, *Energy Environ. Sci.*, **2018**, 11, 1287–1298.
- [3] Y. Gou, Q. Liu, X. F. Shi, A. M. Asiri, J. M. Hu, X. P. Sun, *Chem. Commun.*, **2018**, 54, 5066–5069.
- [4] Y. N. Guo, J. Tang, Z. L. Wang, Y. M. Kang, Y. Bando, Y. Yamauchi, *Nano Energy*, **2018**, 47, 494–502.
- [5] B. Zhang, X. L. Zhang, O. Voznyy, R. Comin, M. Bajdich, M. G. Melchor, L. L. Han, J. X. Xu, M. Liu, L. R. Zheng, F. G. Arquer, C. T. Dinh, F. J. Fan, M. J. Yuan, E. Yassitepe, N. Chen, T. Regier, P. F. Liu, Y. H. Li, P. Luna, A. Janmohamed, H. L. Xin, H. G. Yang, A. Vojvodic, E. H. Sargent, *Science*, **2016**, 352, 333–337.
- [6] H. B. Yang, J. W. Miao, S. F. Hung, J. Z. Chen, H. B. Tao, X. Z. Wang, L. P. Zhang, R. Chen, J. J. Gao, H. M. Chen, L. M. Dai, B. Liu, *Sci. Adv.*, **2016**, 2, e1501122.
- [7] Q. Qin, H. Jang, L. L. Chen, G. Nam, X. E. Liu, J. Cho, *Adv. Energy Mater.*, **2018**, 8, 1801478.
- [8] K. Xiao, L. Zhou, M. Shao, M. Wei, *J. Mater. Chem. A*, **2018**, 6, 7585–7591.
- [9] C. J. Xuan, J. Wang, W. W. Xia, J. Zhu, Z. K. Peng, K. D. Xia, W. P. Xiao, H. L. Xin, D. Wang, *J. Mater. Chem. A*, **2018**, 6, 7062–7069.
- [10] Z. Li, W. H. Niu, L. Zhou, Y. Yang, *ACS Energy Lett.*, **2018**, 3, 892–898.
- [11] D. Wu, Y. C. Wei, X. Ren, X. Q. Ji, Y. W. Liu, X. D. Guo, Z. A. Liu, A. M. Asiri, Q. Wei, X. P. Sun, *Adv. Mater.*, **2018**, 30, 1705366.
- [12] Q. He, H. Xie, Z. U. Rehman, C. D. Wang, P. Wan, H. L. Jiang, W. S. Chu, L. Song, *ACS Energy Lett.*, **2018**, 3, 861–868.
- [13] C. Guan, H. J. Wu, W. Xiao, X. M. Liu, W. J. Zang, H. Zhang, J. Ding, Y. P. Feng, S. J. Pennycook, J. Wang, *Nano Energy*, **2018**, 48, 73–80.
- [14] B. W. Zhang, Y. H. Lui, A. P. S. Gaur, B. L. Chen, X. H. Tang, Z. Y. Qi, S. Hu, *ACS Appl. Mater. Interfaces*, **2018**, 10, 8739–8748.
- [15] Q. Qin, H. Jang, P. Li, B. Yuan, X. E. Liu, J. Cho, *Adv. Energy Mater.*, **2018**, 9, 1803312.
- [16] P. Z. Chen, K. Xu, Z. W. Fang, Y. Tong, J. C. Wu, X. L. Lu, X. Peng, H. Ding, C. Z. Wu, Y. Xie, *Angew. Chem. Int. Ed.*, **2015**, 54, 14710–14714.
- [17] B. Q. Li, S. Y. Zhang, C. Tang, X. Y. Cui, Q. Zhang, *Small*, **2017**, 13, 1700610.
- [18] Y. X. Li, J. Yin, L. An, M. Lu, K. Sun, Y. Q. Zhao, F. Y. Cheng, P. X. Xi, *Nanoscale*, **2018**, 10, 6581–6588.
- [19] J. W. Li, Q. N. Zhuang, P. M. Xu, D. W. Zhang, L. C. Wei, D. S. Yuan, *Chin. J. Catal.*, **2018**, 39, 1403–1410.
- [20] J. Jin, J. Yin, H. W. Liu, P. X. Xi, *Chin. J. Catal.*, **2019**, 40, 43–51.
- [21] Y. S. Du, G. Z. Cheng, W. Luo, *Nanoscale*, **2017**, 9, 6821–6825.
- [22] C. Xia, Q. Jiang, C. Zhao, M. N. Hedhili, H. N. Alshareef, *Adv. Mater.*, **2016**, 28, 77–85.
- [23] G. L. Chai, K. P. Qiu, M. Qiao, M. M. Titirici, C. X. Shang, Z. X. Guo, *Energy Environ. Sci.*, **2017**, 10, 1186–1195.
- [24] B. S. Yeo, A. T. Bell, *J. Am. Chem. Soc.*, **2011**, 133, 5587–5593.
- [25] K. W. Liu, C. L. Zhang, Y. D. Sun, G. H. Zhang, X. C. Shen, F. Zou, H. C. Zhang, Z. W. Wu, E. C. Wegener, C. J. Taubert, J. T. Miller, Z. M. Peng, Y. Zhu, *ACS Nano*, **2018**, 12, 158–167.
- [26] X. F. Lu, L. F. Gu, J. W. Wang, J. X. Wu, P. Q. Liao, G. R. Li, *Adv. Mater.*, **2017**, 29, 1604437.
- [27] P. Pei, Z. F. Tian, Y. F. Zhu, *Microporous Mesoporous Mater.*, **2018**, 272, 24–30.
- [28] L. K. Meng, K. Liu, S. Fu, L. Wang, C. Liang, G. H. Li, C. G. Li, Z. Shi, *J. Solid State Chem.*, **2018**, 265, 285–290.
- [29] J. N. Joshi, G. H. Zhu, J. J. Lee, E. A. Carter, C. W. Jones, R. P. Lively, K. S. Walton, *Langmuir*, **2018**, 34, 8443–8450.
- [30] R. Yan, Y. Zhao, H. Yang, X. J. Kang, C. Wang, L. L. Wen, Z. D. Lu, *Adv. Funct. Mater.*, **2018**, 28, 1802021.
- [31] M. Sohail, M. Altaf, N. Baig, R. Jamil, M. Sher, A. Fazal, *New J. Chem.*, **2018**, 42, 12486–12491.

Graphical Abstract

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Co/Fe -based bimetal-organic frameworks were synthesized, using a facile ultrasonic method, as efficient electrocatalysts for the OER. The optimized Co_2Fe -MOF exhibited high performance toward the OER.

- [32] X. Wang, L. Yu, B. Y. Guan, S. Y. Song, X. W. Lou, *Adv. Mater.*, **2018**, 30, 1801211.
- [33] X. L. Wang, H. Xiao, A. Li, Z. Li, S. J. Liu, Q. H. Zhang, Y. Gong, L. R. Zheng, Y. Q. Zhu, C. Chen, D. S. Wang, Q. Peng, L. Gu, X. D. Han, J. Li, Y. D. Li, *J. Am. Chem. Soc.*, **2018**, 140, 15336–15341.
- [34] L. M. Cao, Y. W. Hu, S. F. Tang, A. Llin, J. W. Wang, Z. M. Zhang, T. B. Lu, *Adv. Sci.*, **2018**, 5, 1800949.
- [35] M. M. Wang, M. T. Lin, J. T. Li, L. Huang, Z. C. Zhuang, C. Lin, L. Zhou, L. Q. Mai, *Chem. Commun.*, **2017**, 53, 8372.
- [36] S. L. Zhao, Y. Wang, J. C. Dong, C. T. He, H. J. Yin, P. F. An, K. Zhao, X. F. Zhang, C. Gao, L. J. Zhang, J. W. Lv, J. X. Wang, J. Q. Zhang, A. M. Khattak, N. A. Khan, Z. X. Wei, J. Zhang, S. Q. Liu, H. J. Zhao, Z. Y. Tang, *Nature Energy*, **2016**, 1, 16184.
- [37] D. A. Yang, H. Y. Cho, J. Kim, S. T. Yang, W. S. Ahn, *Energy Environ. Sci.*, **2012**, 5, 6465–6473.
- [38] X. J. Zheng, X. Y. Song, X. M. Wang, Z. H. Zhang, Z. M. Sun, Y. S. Guo, *New J. Chem.*, **2018**, 42, 8346–8350.
- [39] F. Z. Sun, G. Wang, Y. Q. Ding, C. Wang, B. B. Yuan, Y. Q. Lin, *Adv. Energy Mater.*, **2018**, 8, 1800584.
- [40] X. P. Dai, M. Z. Liu, Z. Z. Li, A. X. Jin, Y. D. Ma, X. L. Huang, H. Sun, H. Wang, X. Zhang, *J. Phys. Chem. C*, **2016**, 120, 12539–12548.
- [41] P. Guo, J. Wu, X. B. Li, J. Luo, W. M. Lau, H. Liu, X. L. Sun, L. M. Liu, *Nano Energy*, **2018**, 47, 96–104.
- [42] H. Wang, F. X. Yin, G. R. Li, B. H. Chen, Z. Q. Wang, *Int. J. Hydrogen Energy*, **2014**, 39, 16179–16186.
- [43] S. H. Liu, Z. Y. Wang, S. Zhou, F. J. Yu, M. Z. Yu, C. Y. Chiang, W. Z. Zhou, J. J. Zhao, J. S. Qiu, *Adv. Mater.*, **2017**, 29, 1700874.
- [44] J. Zhou, Y. B. Dou, A. W. Zhou, R. M. Guo, M. J. Zhao, J. R. Li, *Adv. Energy Mater.*, **2017**, 7, 1602643.

钴/铁双金属有机框架材料用于电催化析氧反应

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摘要: 开发高效且稳定的电催化剂用于水氧化反应对于能源存储与转化系统至关重要。目前商业贵金属材料(如IrO₂和RuO₂)拥有最好的电催化析氧性能, 但其稀缺性和高成本阻碍了它们的实际应用。金属有机框架材料(MOFs)由于具有比表面积大、周期性结构、孔径可调、金属中心和有机配体多样性等特点, 已经广泛应用于药物输送、气体存储、催化、传感等领域。在电催化领域, MOFs通常作为前驱体或模板在高温下热解来制备金属氧化物/多孔碳复合材料, 虽然它们显示出较高的催化活性, 但是往往需要复杂的制备工艺和高温条件。因此, 利用MOFs的固有活性不经过热解处理直接使用MOFs作为析氧反应(OER)电催化剂是非常有意义的。由于氧化态的钴中心有利于OOH物种的形成并可促进OOH脱质子形成氧气, 钴基材料已经显示出很好的OER性能。尤其是当Fe掺杂进钴基催化剂时, OER性能可得到进一步提高。因此, 开发一种高效的Co/Fe双金属MOFs用于电催化析氧反应是很好的选择。

本文以Co²⁺和Fe³⁺为金属离子, 以均苯三甲酸为有机配体, 在三乙胺存在条件下通过简单的超声法合成了一系列不同Co/Fe比的双金属MOFs。以电催化性能最好的Co₂Fe-MOF为研究对象, 从扫描电子显微镜和透射电子显微镜图可以看出Co₂Fe-MOF由松散堆积的纳米粒子组成, 这种结构具有较大的比表面积, 从而可以暴露更多的催化活性位点。电化学测试结果表明, 在所有的Co_xFe-MOFs中, Co₂Fe-MOF达到10 mA cm⁻²的电流密度需要的过电位(280 mV)最低, 且低于大部分文献报道的钴/铁双金属催化剂。而且Co₂Fe-MOF的Tafel斜率低至44.7 mV dec⁻¹, 表明在电催化过程中有较快的反应动力学。电化学阻抗分析表明, Co₂Fe-MOF有较小的电荷转移电阻, 有利于电子从电解液到电极表面的传递。XPS测试分析表明, Fe的加入可以调节Co金属中心周围的电子环境, 有利于提升催化剂的电催化性能。总之, Co₂Fe-MOF优良的电催化性能可归因于其具有较大的比表面积、较高的电子传输速率以及Co和Fe金属中心的协同效应。本研究为直接利用MOFs材料作为低成本析氧反应电催化剂提供了新策略。

关键词: 双金属有机框架材料; 析氧反应; 电催化剂; 协同效应; 超声法

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