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Communication

Fe-substituted cobalt-phosphate polyoxometalates as enhanced oxygen evolution catalysts in acidic media

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ABSTRACT

All-inorganic and earth-abundant bi-/trimetallic hydr(oxy)oxides are widely used as oxygen evolution electrocatalysts owing to their remarkable performance. However, their atomically precise structures remain undefined, complicating their optimization and limiting the understanding of their enhanced performance. Here, the underlying structure-property correlation is explored by using a well-defined cobalt-phosphate polyoxometalate cluster $[\{Co_4(OH)_3(PO_4)\}_4(SiW_9O_{34})_4]^{32-}$ (**1**), which may serve as a molecular model of multimetal hydr(oxy)oxides. The catalytic activity is enhanced upon replacing Co by Fe in **1**, resulting in a reduced overpotential (385 mV) for oxygen evolution (by 66 mV) compared to that of the parent **1** at 10 mA cm⁻² in an acidic medium; this overpotential is comparable to that for the IrO₂ catalyst. These abundant-metal-based polyoxometalates exhibit high stability, with no evidence of degradation even after 24 h of operation.

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The oxygen evolution reaction (OER) is the key half-reaction for many renewable energy conversion and storage technologies, including electrocatalytic water splitting and CO₂ reduction. The sluggish kinetics of the OER have long been the bottleneck hindering the widespread use of such technologies [1–3]. Ru- and Ir-based materials are the state-of-the-art OER catalysts, but they suffer from disadvantages such as scarcity, high cost, and low intrinsic activity [4,5]. In the past decades, the development of all-inorganic and earth-abundant bi-/tri-metallic hydr(oxy)oxides as OER catalysts for alkaline

media (metal oxides [6,7], hydr(oxy)oxides [8,9], cobalt-phosphate composites [10,11], etc.) has been successful, and these materials exhibit excellent activity. Unfortunately, the lack of in-depth knowledge about the relationship between their atomically precise structures and the origin of their enhanced performance has hindered further design of active, stable, and cost-effective OER electrocatalysts. Metal-organic frameworks (MOFs), which have a well-defined atomic architecture, could per se be used to reveal the structure-property relationship at the molecular level [12,13]. However, MOFs are

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composed of metal ions (or clusters) and organic linkers, and therefore, are less suitable as model systems for hydr(oxy)oxides.

Polyoxometalates (POMs) constitute a class of well-defined metal-oxo clusters. They feature well-defined and unique structural motifs, and can be seen as an intermediate between molecular complexes and extended oxides [14]. In addition, all-inorganic, oxidatively-resistant, and earth-abundant POMs with excellent OER activity have been produced [15–26]. Therefore, POMs are ideal candidates for a molecular model of bi-/tri-metallic hydr(oxy)oxides to explore the origin of the improved catalytic activity in the OER and to gain a clearer insight into the structure-property correlation.

For the OER, acidic media are preferred because of numerous advantages over alkaline media, such as high energy efficiency, low Ohmic losses, and easy product separation or carbonation [23,27]. Unfortunately, earth-abundant OER electrocatalysts are unstable toward dissolution in acidic media and are typically inferior to noble-metal-based catalysts [1,23,28]. Developing highly active and stable earth-abundant OER catalysts in acidic media remains a great challenge in this area. Herein we show that by substitution of a parent POM cluster, $\{\text{Co}_4(\text{OH})_3(\text{PO}_4)_4(\text{SiW}_9\text{O}_{34})_4\}^{32-}$ (**1**), with Fe into two isostructurally analogous POM clusters $\{\{\text{Fe}_2\text{Co}_2(\text{OH})_3\text{PO}_4\}_4(\text{SiW}_9\text{O}_{34})_4\}^{24-}$ (**2**) and $\{\{\text{FeCo}_3(\text{OH})_3\text{PO}_4\}_4(\text{SiW}_9\text{O}_{34})_4\}^{28-}$ (**3**), we can achieve significantly enhanced OER performance. The insoluble barium salt of **3** (Ba[**3**]) is the best catalyst, with an overpotential of 385 mV at 10 mA cm⁻² in 0.5 M H₂SO₄; this overpotential is 66 mV lower than that of the barium salt of **1** (Ba[**1**]) and comparable to that of the commercial IrO₂ catalyst under similar conditions (393 mV). These catalysts exhibit negligible activity decay and retain their structural integrity even after 2000 cyclic voltammetry (CV) cycles and 24 h of long-term electrolysis.

The synthetic routes to **1**, **2**, and **3** and the structures of these compounds are shown in Fig. 1. Single-crystal X-ray diffraction (SCXRD) analysis confirms their isostructural characteristics [18,29]. The water-insoluble barium salts of

Fig. 1. Synthetic routes to $\{[\text{Co}_x\text{Fe}_{4-x}(\text{OH})_3(\text{PO}_4)_4(\text{SiW}_9\text{O}_{34})_4]^{n-}\}$ ($x = 4, 2$, or 1 ; $n = 32, 24$, or 28). Polyhedral and ball-and-stick representations of the structure of $\{[\text{Co}_x\text{Fe}_{4-x}(\text{OH})_3(\text{PO}_4)_4(\text{SiW}_9\text{O}_{34})_4]^{n-}\}$. WO₆, green octahedra; SiO₄, blue tetrahedra; PO₄, yellow tetrahedra; O, gray spheres; Co violet spheres; P, yellow spheres.

Ba₁₆ $\{[\text{Co}_4(\text{OH})_3(\text{PO}_4)_4(\text{SiW}_9\text{O}_{34})_4]\}$ (Ba[**1**]), Ba₁₂ $\{[\text{Fe}_2\text{Co}_2(\text{OH})_3\text{PO}_4]_4(\text{SiW}_9\text{O}_{34})_4\}$ (Ba[**2**]), and Ba₁₄ $\{[\text{FeCo}_3(\text{OH})_3\text{PO}_4]_4(\text{SiW}_9\text{O}_{34})_4\}$ (Ba[**3**]) were prepared by simple metathesis of the corresponding counteranions Na⁺ or K⁺ into Ba²⁺. The FT-IR bands provide a reliable fingerprint for the POM structures [23,30,31]. The presence of **1** in Ba[**1**], **2** in Ba[**2**], and **3** in Ba[**3**] was confirmed by FT-IR spectroscopy (Fig. S1 in SI). Besides, the corresponding signature FT-IR spectra of Fe-substituted Ba[**2**] and Ba[**3**] were consistent with that of the parent Ba[**1**], due to the isostructural nature of **1**, **2**, and **3**.

The OER activities of Ba[**1**], Ba[**2**], and Ba[**3**] were measured using a typical three-electrode system in O₂-saturated 0.5 mol L⁻¹ H₂SO₄ solution at 25 °C. Linear sweep voltammetry (LSV) experiments were performed at a scan rate of 5 mV s⁻¹ after the system reached equilibrium. The electrodes were prepared by mixing Ba[**1**], Ba[**2**], or Ba[**3**] with commercial carbon paste oil (CPO) at 40% content by weight [23]. As shown in Figure 2a, both Ba[**2**]/CPO and Ba[**3**]/CPO electrodes showed significantly enhanced electrocatalytic activity as compared with the Fe-free Ba[**1**]/CPO electrode. Ba[**2**]/CPO showed an overpotential of 406 mV at 10 mA cm⁻² (Table 1), which was 45 mV smaller than that of Ba[**1**]/CPO (451 mV). With a decrease in the Fe substitution ratio, the corresponding overpotential decreased to 385 mV for Ba[**3**]/CPO (66 mV smaller than that of Ba[**1**]/CPO). Because of the isostructural nature of **1**, **2**, and **3**, the enhanced OER catalysis was attributed solely to the Fe substitution, which gives us a well-defined model for substitution effects on the catalytic enhancement. It is also noteworthy that excess Fe, as in the case of Ba[**2**], can lead to an increase in the OER overpotential. These results are consistent with those of previous studies using W₂₃Co_wFe_xO_y(OH)_z transition-metal clusters (TMCs) [29], where the lower Fe content favored low adsorption energies ($\Delta G_0 - \Delta G_{\text{OH}} > 1.6$ eV) for the OER intermediates, while a larger Fe content was associated with large adsorption energies ($\Delta G_0 - \Delta G_{\text{OH}} < 1.6$ eV). In this case, an optimum catalyst would exhibit a free-energy difference ($\Delta G_0 - \Delta G_{\text{OH}}$) of around 1.6 eV, resulting in the well-known volcano-like behavior [32,33].

A modified electrode of 40% IrO₂/CPO was prepared for comparison, and its OER performance was examined under the same conditions. At 10 mA cm⁻², the IrO₂/CPO electrode produced an overpotential of 393 mV (Fig. 2b and Table 1), which was 8 mV higher than that of Ba[**3**]/CPO. In 1.0 M H₂SO₄, the

Fig. 2. (a) LSV curves of Ba[**1**]/CPO, Ba[**2**]/CPO, Ba[**3**]/CPO, and pure CPO electrodes in 0.5 mol L⁻¹ H₂SO₄, no *iR* correction. (b) LSV curves of Ba[**3**]/CPO, IrO₂/CPO, and pure CPO electrodes in 0.5 mol L⁻¹ H₂SO₄, no *iR* correction.

Table 1

Overpotential (η) of different catalysts at 10 mA cm⁻² in acidic electrolyte.

Catalyst	Electrolyte	η (mV)	Ref.
Ba[1]/CPO	0.5 mol L ⁻¹ H ₂ SO ₄	451 ^a	This work
Ba[2]/CPO	0.5 mol L ⁻¹ H ₂ SO ₄	406 ^a	This work
Ba[3]/CPO	0.5 mol L ⁻¹ H ₂ SO ₄	385 ^a	This work
IrO ₂ /CPO	0.5 mol L ⁻¹ H ₂ SO ₄	393 ^a	This work
Co ₃ O ₄ /FTO	0.5 mol L ⁻¹ H ₂ SO ₄	570 ^b	[34]
γ -MnO ₂ /FTO	1.0 mol L ⁻¹ H ₂ SO ₄	489 ± 5 ^b	[35]
Ni _{0.5} Mn _{0.5} Sb _{1.7} O ₇	1.0 mol L ⁻¹ H ₂ SO ₄	672 ± 9 ^b	[7]
IrO ₂ /FTO	0.5 mol L ⁻¹ H ₂ SO ₄	330 ^b	[34]
Ba[Co-POM]/CP	1.0 mol L ⁻¹ H ₂ SO ₄	361 ^b	[23]
Ba[3]/CPO	1.0 mol L ⁻¹ H ₂ SO ₄	398 ^a	This work

^a Overpotentials were obtained without *iR* correction.

^b Overpotentials were obtained with *iR* correction.

Ba[3]/CPO electrode generated an overpotential of 398 mV at 10 mA cm⁻² (Table 1 and Fig. S2 in SI), which is comparable to the remarkable example of the Ba[Co-POM] catalyst [23]. To the best of our knowledge, Ba[3] is also one of the best non-noble metal-based OER electrocatalysts in acidic media (Table 1).

To gain better insight into the superior performance of Ba[3]/CPO, we estimated the available active sites in the modified electrodes by evaluating the total amounts of Fe and Co, assuming that both are active during the OER. This approach imposes an upper limit on the available active sites. In comparison, the IrO₂/CPO mixture contains almost 3.4 times more active sites than does the corresponding Ba[3]/CPO mixture (Table S1 in SI). For comparison, a modified electrode of 12% IrO₂/CPO with a similar mass of active sites as 40% Ba[3]/CPO was prepared, and its OER performance was examined under the same conditions. As shown in Table S1 and Fig. S3, 12% IrO₂/CPO exhibits an overpotential of 528 mV at 10 mA cm⁻², which is greater than that of Ba[1]/CPO (385 mV) by 143 mV. These results suggest that Ba[3] may show better intrinsic activity than the state-of-the-art IrO₂ at 10 mA cm⁻² in acidic media, but its activity might be limited by other parameters such as electron transfer, as indicated by the magnitude of the Tafel slope. The Tafel slopes of all the catalysts are depicted in Fig. S4 in SI. Ba[1] (194 mV dec⁻¹) and Ba[2] (189 mV dec⁻¹) exhibit a larger Tafel slope than does Ba[3], suggesting that the OER is kinetically favored on Ba[3] (181 mV dec⁻¹). Similar large Tafel slopes have been reported for other POM-based OER electrocatalysts [23–25], possibly due to the competition between a chemical step and an electron-transfer limiting step [23]. In the case of IrO₂, a smaller Tafel slope was observed (96 mV dec⁻¹).

The operational stability of the Ba[1], Ba[2], and Ba[3] catalysts was evaluated by a long-term cycling test in 0.5 M aqueous H₂SO₄ solution. Satisfactorily, the LSV curves after 2000 CV cycles practically overlapped with the original ones, displaying a very small change in overpotential (< 8 mV) at 10 mA cm⁻² (Fig. 3a and Figs. S5 and S6 in SI). Chronoamperometric response (*i-t*) tests further showed that all the three catalysts maintained their activity for at least 24 h of electrolysis (Fig. 3b and Figs. S7 and S8 in SI). In particular, the LSV curves of Ba[3]/CPO showed only a minimal overpotential change (< 25

Fig. 3. (a) LSV curves of Ba[3]/CPO electrode before and after 2000 CV cycles. (b) Chronoamperometric response of Ba[3]/CPO for 24 h at a constant applied potential of 1.48 V vs. RHE. (c) LSV curves of Ba[3]/CPO electrode before and after 24 h of long-term electrolysis. (d) FT-IR spectra of Ba[3] before and after long-term operation.

mV, Fig. 3c) at 10 mA cm⁻² after 24 h of electrolysis.

To evaluate the structural integrity under operation, the FT-IR spectra of the POM catalysts after the stability test were measured [21,22,36]. The FT-IR spectra of Ba[1] (Fig. S9 in SI), Ba[2] (Fig. S10 in SI), and Ba[3] (Fig. 3d) after 2000 CV cycles were largely identical to those of the as-synthesized catalysts. Inductively coupled plasma-mass spectrometry (ICP-MS) analysis was carried out to quantify the metal (Ba, Co, Fe, or W) content in the 0.5 mol L⁻¹ H₂SO₄ mother liquor after 2000 CV cycles. The ICP-MS data demonstrated that quite a few amount (around 2%) of metal may leach out of the prepared catalysts (Table S2 in SI). These results collectively suggested the superior stability of these three bi-/trimetallic earth-abundant electrocatalysts.

In summary, the OER performance of an earth-abundant POM-based cobalt-phosphate cluster is largely improved by isostructural Fe substitution. The best catalyst Ba[3] exhibits an overpotential of 385 mV at 10 mA cm⁻² in 0.5 mol L⁻¹ H₂SO₄ solution, which is comparable to that observed for the IrO₂ catalyst. Multiple experiments collectively confirmed the good operational stability of Ba[3]. Our “in situ isostructural substitution” approach affords a synthetic route to well-defined multimetallic catalysts with enhanced performance. This also offers the ideal model for future experimental or theoretical work to study the structure-property correlation in detail, with the aim of developing more efficient molecular-based heterogeneous catalysts beyond OERs and understanding the related catalytic mechanisms.

Supporting Information. Electrocatalytic experiments, ICP-MS analysis and IR spectra.

References

- [1] C. C. L. McCrory, S. Jung, I. M. Ferrer, S. M. Chatman, J. C. Peters, T. F. Jaramillo, *J. Am. Chem. Soc.*, **2015**, 137, 4347–4357.
- [2] B. M. Hunter, H. B. Gray, A. M. Müller, *Chem. Rev.*, **2016**, 116, 14120–14136.
- [3] N.-T. Suen, S.-F. Hung, Q. Quan, N. Zhang, Y.-J. Xu, H. M. Chen, *Chem. Soc. Rev.*, **2017**, 46, 337–365.
- [4] Y. Pi, Q. Shao, P. Wang, F. Lv, S. Guo, J. Guo, X. Huang, *Angew. Chem. Int. Ed.*, **2017**, 56, 4502–4506.
- [5] I. A. Moreno-Hernandez, C. A. MacFarland, C. G. Read, K. M. Papadantonakis, B. S. Brunschwig, N. S. Lewis, *Energy Environ. Sci.*, **2017**, 10, 2103–2108.
- [6] J. Suntivich, K. J. May, H. A. Gasteiger, J. B. Goodenough, Y. Shao-Horn, *Science*, **2011**, 334, 1383–1385.
- [7] R. D. L. Smith, M. S. Prévot, R. D. Fagan, Z. Z. Zhang, P. A. Sedach, M. K. J. Siu, S. Trudel, C. P. Berlinguette, *Science*, **2013**, 340, 60–63.
- [8] M. Gong, Y. Li, H. Wang, Y. Liang, J. Wu, J. Zhou, J. Wang, T. Regier, F. Wei, H. Dai, *J. Am. Chem. Soc.*, **2013**, 135, 8452–8455.
- [9] B. Zhang, X. Zheng, O. Voznyy, R. Comin, M. Bajdich, M. García-Melchor, L. Han, J. Xu, M. Liu, L. Zheng, F. P. G. D. Arquer, C. T. Dinh, F. Fan, M. Yuan, E. Yassitepe, N. Chen, T. Regier, P. Liu, Y. Li, P. D. Luna, A. Janmohamed, H. L. Xin, H. Yang, A. Vojvodic, E. H. Sargent, *Science*, **2016**, 352, 333–337.
- [10] M. W. Kanan, D. G. Nocera, *Science*, **2008**, 321, 1072–1075.
- [11] K. Jin, J. Park, J. Lee, K. D. Yang, G. K. Pradhan, U. Sim, D. Jeong, H. L. Jang, S. Park, D. Kim, N.-E. Sung, S. H. Kim, S. Han, K. T. Nam, *J. Am. Chem. Soc.*, **2014**, 136, 7435–7443.
- [12] 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, *Nat. Energy*, **2016**, 1, 16184.
- [13] W. Cheng, X. Zhao, H. Su, F. Tang, W. Che, H. Zhang, Q. Liu, *Nat. Energy*, **2019**, 4, 115–122.
- [14] M. Carraro, A. Sartorel, F. M. Toma, F. Puntoriero, F. Scandola, S. Campagna, M. Prato, M. Bonchio, *Top. Curr. Chem.*, **2011**, 303, 121–150.
- [15] Q. S. Yin, J. M. Tan, C. Besson, Y. V. Geletii, D. G. Musaev, A. E. Kuznetsov, Z. Luo, K. I. Hardcastle, C. L. Hill, *Science*, **2010**, 328, 342–345.
- [16] S. Tanaka, M. Annaka, K. Sakai, *Chem. Commun.*, **2012**, 48, 1653–1655.
- [17] F. Song, Y. Ding, B. Ma, C. Wang, Q. Wang, X. Du, S. Fu, J. Song, *Energy Environ. Sci.*, **2013**, 6, 1170–1184.
- [18] X.-B. Han, Z.-M. Zhang, Y.-G. Li, W. Lin, W.-S. You, Z.-M. Su, E.-B. Wang, *J. Am. Chem. Soc.*, **2014**, 136, 5359–5366.
- [19] X.-B. Han, Y.-G. Li, Z.-M. Zhang, H.-Q. Tan, Y. Lu, E.-B. Wang, *J. Am. Chem. Soc.*, **2015**, 137, 5486–5493.
- [20] L. Yu, X. Du, Y. Ding, H. Chen, P. Zhou, *Chem. Commun.*, **2015**, 51, 17443–17446.
- [21] L. Yu, Y. Ding, M. Zheng, *Appl. Catal. B-Environ.*, **2017**, 209, 45–52.
- [22] M. Zheng, Y. Ding, X. Cao, T. Tian, J. Lin, *Appl. Catal. B-Environ.*, **2018**, 237, 1091–1100.
- [23] M. Blasco-Ahicart, J. Soriano-López, J. J. Carbó, J. M. Poblet, J. R. Galán-Mascaros, *Nat. Chem.*, **2018**, 10, 24–30.
- [24] M. Martin-Sabi, J. Soriano-López, R. S. Winter, J.-J. Chen, L. Vilà-Nadal, D.-L. Long, J. R. Galán-Mascaros, L. Cronin, *Nat. Catal.*, **2018**, 1, 208–213.
- [25] W. Luo, J. Hu, H. Diao, B. Schwarz, C. Streb, Y.-F. Song, *Angew. Chem. Int. Ed.*, **2017**, 56, 4941–4944.
- [26] Q. Han, D. Sun, J. Zhao, X. Liang, Y. Ding, *Chin. J. Catal.*, **2019**, 40, 953–958.

Graphical Abstract

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Fe-substituted cobalt-phosphate polyoxometalates as enhanced oxygen evolution catalysts in acidic media

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Fe-substituted cobalt-phosphate polyoxometalates with enhanced oxygen evolution activity and good stability in acidic media are reported, which are among the best non-noble metal-based acidic water oxidation catalysts that may serve as a molecular model of multi-metallic hydr(oxy)oxides.

- [27] C. Shang, C. Cao, D. Yu, Y. Yan, Y. Lin, H. Li, T. Zheng, X. Yan, W. Yu, S. Zhou, J. Zeng, *Adv. Mater.*, **2019**, 31, 1805104.
- [28] C. Lei, H. Chen, J. Cao, J. Yang, M. Qiu, Y. Xia, C. Yuan, B. Yang, Z. Li, X. Zhang, L. Lei, J. Abbott, Y. Zhong, X. Xia, G. Wu, Q. He, Y. Hou, *Adv. Energy Mater.*, **2018**, 8, 1801912.
- [29] X.-B. Han, X.-Y. Tang, Y. Lin, E. Gracia-Espino, S.-G. Liu, H.-W. Liang, G.-Z. Hu, X.-J. Zhao, H.-G. Liao, Y.-Z. Tan, T. Wagberg, S.-Y. Xie, L.-S. Zheng, *J. Am. Chem. Soc.*, **2019**, 141, 232–239.
- [30] L. Ruhlmann, C. Costa-Coquelard, J. Canny, R. Thouvenot, *Eur. J. Inorg. Chem.*, **2007**, 11, 1493–1500.
- [31] M. Pope, *Heteropoly and Isopoly Oxometalates*, Springer, Berlin, **1983**.
- [32] I. C. Man, H.-Y. Su, F. Calle-Vallejo, H. A. Hansen, J. I. Martínez, N. G. Inoglu, J. Kitchin, T. F. Jaramillo, J. K. Nørskov, J. Rossmeisl, *ChemCatChem*, **2011**, 3, 1159–1165.
- [33] E. M. Fernández, P. G. Moses, A. Toftelund, H. A. Hansen, J. I. Martínez, F. Abild-Pedersen, J. Kleis, B. Hinnemann, J. Rossmeisl, T. Bligaard, J. K. Nørskov, *Angew. Chem. Int. Ed.*, **2008**, 47, 4683–4686.
- [34] J. S. Mondschein, J. F. Callejas, C. G. Read, J. Y. C. Chen, C. F. Holder, C. K. Badding, R. E. Schaak, *Chem. Mater.*, **2017**, 29, 950–957.
- [35] A. Li, H. Ooka, N. Bonnet, T. Hayashi, Y. Sun, Q. Jiang, C. Li, H. Han, R. Nakamura, *Angew. Chem. Int. Ed.*, **2019**, 58, 5054–5058.
- [36] R. Al-Oweini, A. Sartorel, B. S. Bassil, M. Natali, S. Berardi, F. Scandola, U. Kortz, M. Bonchio, *Angew. Chem. Int. Ed.*, **2014**, 53, 11182–11185.

铁取代的钴-磷多酸作为酸性介质中性能增强的析氧催化剂

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摘要: 纯无机的非贵金属基双/三金属氢氧(氧)化物因其优异的析氧反应(OER)性能而得到广泛关注及研究。但这些催化剂的原子精度的结构表征较为困难, 阻碍了人们对其构效关系的认识, 从而影响了进一步对催化性能的精确调控。金属有机框架(MOFs)材料因具有明确的结构及化学组成可调等优点, 可以作为一类结构确定的OER电催化剂, 但是MOFs为有机配体和金属离子配位形成的框架材料, 与金属氢氧(氧)化物结构类型不同。

多酸是由高氧化态的Mo^{VI}, W^{VI}, V^{V/IV}, Nb^V和Ta^V等组成的金属-氧簇。多酸尺寸介于分子与块体氧化物之间, 可以被看作一种具有明确结构的分子氧化物。因此, 多酸可用作模型体系从分子水平上探究金属氢氧(氧)化物催化剂的反应机理。此外, 多酸已被证明是很有前景的非贵金属水氧化催化剂。

对于OER, 酸性介质更具优势, 因为它与碱性介质相比具有高效率、低欧姆损耗、易于产物分离等优点。但是, 非贵金属OER电催化剂在酸性介质中很难稳定且性能通常不如贵金属催化剂。制备酸性介质中高效和稳定的非贵金属OER电催化剂仍然是一大挑战。

在本论文中, 我们首先采用“原位同构取代”策略, 将结构明确的[Co₄(OH)₃PO₄]₄(SiW₉O₃₄)₄]³²⁻ (1)钴-磷多酸阴离子中的Co原子替换成Fe原子, 合成了不同Fe含量的[Fe₂Co₂(OH)₃PO₄]₄(SiW₉O₃₄)₄]²⁴⁻ (2)和[FeCo₃(OH)₃PO₄]₄(SiW₉O₃₄)₄]²⁸⁻ (3)。然后通过离子交换, 向1, 2和3中引入Ba²⁺, 成功合成了不溶于水的多酸阴离子结构维持的多相催化剂Ba[1], Ba[2]和Ba[3]。性能最好的Ba[3]在0.5 mol L⁻¹ H₂SO₄溶液中的电流密度仅需要385 mV过电位(无*iR*校正), 比相同条件下无Fe取代的Ba[1]和商业IrO₂催化剂的过电位分别低66 mV和8 mV。经过2000圈的循环伏安测试和24 h的长时间电解测试, Ba[1], Ba[2]和Ba[3]均表现出较高的稳定性。另外, 采用红外光谱(FT-IR)以及电感耦合等离子体质谱(ICP-MS)等多种表征测试手段进一步确认了它们的稳定性。

本文采用的“原位同构取代”策略为合成更高效的结构明确的多金属催化剂提供了新思路, 同时也为进一步从分子水平上探索相关催化机理提供了难得的模型。

关键词: 钴-磷; 多酸; 析氧反应; 同构取代

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