

Supporting Information

Interfacial Co–O–Fe Bonding in Novel Amorphous NiCo–ZIF@MIL –100 as Efficient Active Sites Enabling Electrocatalytic Water Oxidation

Tianhao Yu,^a Peng Gao,^a Hong Du^{*ab} and Ling Dong^{*a}

^a*College of Chemistry and Chemical Engineering, Xinjiang Normal University,
Urumqi, 830054, China.*

^b*Xinjiang Key Laboratory of Energy Storage and Photoelectrocatalytic Materials,
Urumqi, 830054, China.*

***Corresponding Authors**

*Email: 175790509@qq.com

*Email: 1057618470@qq.com

Fig. S1 XRD pattern of catalyst (a)NiCo-ZIF and stimulated ZIF-67; (b) MIL-100 and stimulated MIL-100.

Fig. S2 DTG of (a)NiCo-ZIF; (b)MIL-100; (c) NiCo-ZIF@MIL (1:2).

Fig. S3 Full XPS spectra (a) NiCo-ZIF and MIL-100; (b) C 1s of NiCo-ZIF and MIL-100; (c) O 1s of NiCo-ZIF; (d) Ni 2p of NiCo-ZIF and NiCo-ZIF@MIL (1:2).

Table S1 Catalyst based ZIF-67, reaction condition, and OER performances.

Catalysts	Electrolyte	Substrate	η_{10} (mV)	Ref.
EG/Co(OH) ₂ /ZIF-67	1.0 M KOH	EG	280	1
CoP ₂ /Fe-CoP ₂ YSBs	1.0 M KOH	GC	266	2
Co ₃ O ₄ /Co-Fe DSNBs	1.0 M KOH	GC	297	3
Mo-CoOOH	1.0 M KOH	GC	249	4
Co@NCS/NHCP@CC	1.0 M KOH	CC	248	5
NiCoFeHO@NiCoLDH YSMRs	1.0 M KOH	GC	278	6
IrCo(OH) ₂ @ZIF67/NF	1.0 M KOH	NF	198	7
NiFe-LDH/ZIF-67	1.0 M KOH	GC	222	8
Cu(OH) ₂ @ZIF-67/CF	1.0 M KOH	CF	205	9
NiCoZnP/NC	1.0 M KOH	CC	238	10

Fig. S4 (a) LSV (b) Tafel slopes (c) EIS and (d) C_{dl} of NiCo-ZIF@MIL(2:1), NiCo-ZIF@MIL(1:1), NiCo-ZIF@MIL(1:2), and NiCo-ZIF@MIL(1:3).

Fig. S5 (a)-(f) are ECSA of NiCo-ZIF, MIL-100, NiCo-ZIF@MIL (2:1), NiCo-ZIF@MIL (1:1), NiCo-ZIF@MIL (1:2), and NiCo-ZIF@MIL (1:3).

The calculation process of C_{dl} as follow: First, we measured CV in a range of 1.47 V to 1.58 V vs. Ag/AgCl (1.0 M KOH solution) at different scan rates (20, 40, 60, 80 and

100 mV/s). Under each scan rate, the measurements were repeated ten cycles to reduce errors. The measured CV results are presented in Fig. S5a. Second, the double-layer capacitance C_{dl} was estimated by plotting the Δj (Y-axis in Fig. S5a) $= (j_a - j_c)$ at 1.53 V (where j_c and j_a are the cathodic and anodic current densities, respectively) against the scan rate (X-axis in Fig. S5a), in which the slope was twice that of C_{dl} .

Take NiCo-ZIF as an example :

The following are the j_a and j_c values for NiCo-ZIF (at 1.53 V and different scan rates 20, 100 mV/s.):

$$j_a(20) = 0.0730 \text{ mA/cm}^2, j_a(100) = 0.3060 \text{ mA/cm}^2;$$

$$j_c(20) = -0.0690 \text{ mA/cm}^2, j_c(100) = -0.2876 \text{ mA/cm}^2;$$

$$\Delta j = (j_a - j_c) \text{ values : } \Delta j(20) = 0.142 \text{ mA/cm}^2, \Delta j(100) = 0.5936 \text{ mA/cm}^2 ,$$

$$\Delta j = \frac{\Delta j(100) - \Delta j(20)}{100 - 20} \times 2 = 0.0028225 \text{ mF cm}^{-2}$$

$$C_{dl} = 0.0028225 \text{ mF cm}^{-2} \times 1000 \approx 2.82 \text{ mF cm}^{-2}$$

Fig. S6 (a) XRD (b) HRTEM (c) O 1s, (d) Fe 2p, (e) Co 2p and (f) Raman spectra of NiCo-ZIF@MIL (1:2) after the OER measurement.

After OER, the XRD peak positions showed no significant change (Fig. S6a). It could be found from Fig. S6b that the morphology of catalyst NiCo-ZIF@MIL (1:2) still maintains polyhedral morphology after OER process. The above results fully indicate that the superior stability of the synthesized electrocatalyst.¹¹ After the OER process, there are two new peaks at 535.19 eV and 532.06 eV appeared in the O 1s spectrum, which can be attributed to the satellite peak and the metal-OOH species, respectively (Fig. S6c).^{12,13} Comparing the XPS spectra Fe 2p before and after OER, there is a positive shift in the overall peak position (Fig. S6d). In addition, the appearance of Fe_0 (720.56 eV/707.79 eV) in NiCo-ZIF@MIL could prove that the metallicity of NiCo-ZIF@MIL.¹⁴⁻¹⁶ Comparing the XPS spectra Co 2p before and after OER, there is a negative shift in the overall peak position (Fig. S6e). This is due to the fact that cobalt is oxidised in the oxygen-rich environment of the OER, which increases the electron cloud density and charge transfer around the cobalt. As shown in Fig. S6f of Raman spectrum, after the OER process, the peaks are attributed to M-O at 470, 519, 599, 616,

and 680 cm^{-1} , respectively.^{17 18} In addition, the peak area of M-O in the O1s of high-resolution XPS spectra is also significantly increased (Fig.S6c). The above results indicate that there is a strong synergistic interaction between Co and Fe during the OER process, which promotes the formation of Co-O-Fe bridge bonds and accelerates the adsorption of OH^- , thus lowering the energy barrier.

Table S2 The dissolved quantity of Fe, Co, Ni in KOH

NiCo-ZIF@MIL	Fe	Co	Ni
dissolved quantity	0.059 mg L^{-1}	0.019 mg L^{-1}	0.006 mg L^{-1}

The structural models of NiCo-ZIF and MIL-100 are firstly constructed separately (Fig. S7a and Fig. S7b), and then the unit-cluster models are extracted from the bulk-phase structures of NiCo-ZIF-67 and MIL-100, which are then combined and de-computed and optimised to obtain a stable NiCo-ZIF@MIL structure (Fig. S7c).

Fig. S7 The calculation model of (a) NiCo-ZIF, (b) MIL-100 and (c) NiCo-ZIF@MIL.

Fig. S8 The geometric configuration of (a) NiCo-ZIF and (b) MIL-100; The mechanism cycle diagram of OER (c) NiCo-ZIF and (d) MIL-100.

Refernce

1. J. Cao, C. Lei, J. Yang, X. Cheng, Z. Li, B. Yang, X. Zhang, L. Lei, Y. Hou and K. Ostrikov, *J. Mater. Chem. A*, 2018, **6**, 18877-18883.
2. V. Ganesan, J. Son and J. Kim, *Nanoscale*, 2021, **13**, 4569-4575.

3. X. Wang, L. Yu, B. Y. Guan, S. Song and X. W. Lou, *Adv. Mater.*, 2018, **30**, 1801211-1801216.
4. L. Tang, L. Yu, C. Ma, Y. Song, Y. Tu, Y. Zhang, X. Bo and D. Deng, *J. Mater. Chem. A*, 2022, **10**, 6242-6250.
5. Z. Chen, Y. Ha, H. Jia, X. Yan, M. Chen, M. Liu and R. Wu, *Adv. Energy Mater.*, 2019, **9**, 1803918-1803931.
6. Q. Niu, M. Yang, D. Luan, N. W. Li, L. Yu and X. W. Lou, *Angew. Chem. Int. Ed.*, 2022, **61**, e202213049.
7. Y. Gao, J. Bai, T. Zhou and Y. Gong, *Dalton Trans.*, 2022, **51**, 8832-8839.
8. W. Wu, J. Liu, G. Chen, Y. Chen and C. Xu, *Int. J. Hydrogen Energy*, 2020, **45**, 1948-1958.
9. L. Ye, Y. Zhang, L. Wang, L. Zhao and Y. Gong, *Dalton Trans.*, 2021, **50**, 7256-7264.
10. B. Chen, D. Kim, Z. Zhang, M. Lee and K. Yong, *Chem Eng J*, 2021, **422**, 130533-130544.
11. L. Wang, Y. Pan, D. Wu, X. Liu, L. Cao, W. Zhang, H. Chen, T. Liu, D. Liu, T. Chen, T. Ding, Y. Wang, C. Ding, C. Kang, C. Li, J. He and T. Yao, *J. Mater. Chem. A*, 2022, **10**, 20011-20017.
12. M. Egyir, D. Luyima, S.-J. Park, K. S. Lee and T.-K. Oh, *Sci. Total Environ.*, 2022, **835**, 155453-155459.
13. R. Hou, X. Yang, L. Su, W. Cen, L. Ye and D. Sun, *Nanoscale*, 2023, **15**, 18858-18863.
14. Y. Zhang, T. Zhu, Q. Zhong and H. Qu, *J. Alloys Compd.*, 2023, **958**, 170447-170473.
15. Yueqi Zhanga, Xinghang Liua, Zhenwei Wana, Zeyuan Wanga, Fengquan Gaob, Cuijuan Xuan. 10.2139/ssrn.4728250.
16. Q. Liu, Q. Su, W. Cheng, J. Ding, W. Zhang, J. Wang, Y. Wang, X. Wang and Y. Huang, *Appl. Catal., B*, 2024, **340**, 123188 -123198.
17. H. L. Jing Yang, Wayde N. Martens, and Ray L. Frost, *J. Phys. Chem. C* 2010, **114**, 111–119.
18. O. Bøckman, T. Østvold, G. A. Voyiatzis and G. N. Papatheodorou, *Hydrometallurgy*, 2000, **55**, 93–105.