

Supporting Information

Regulating the Electronic Structure of CoMoO₄ Microrod by Phosphorus Doping as an Efficient Electrocatalyst for Hydrogen Evolution Reaction

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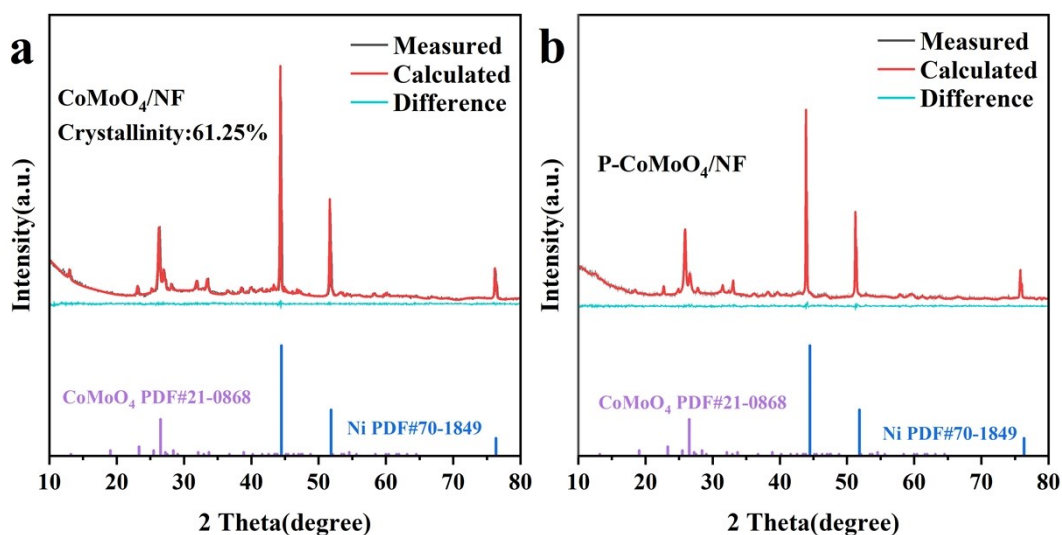


Fig. S1 Rietveld refinement results of XRD data of (a) CoMoO₄/NF and (b) P-CoMoO₄/NF.

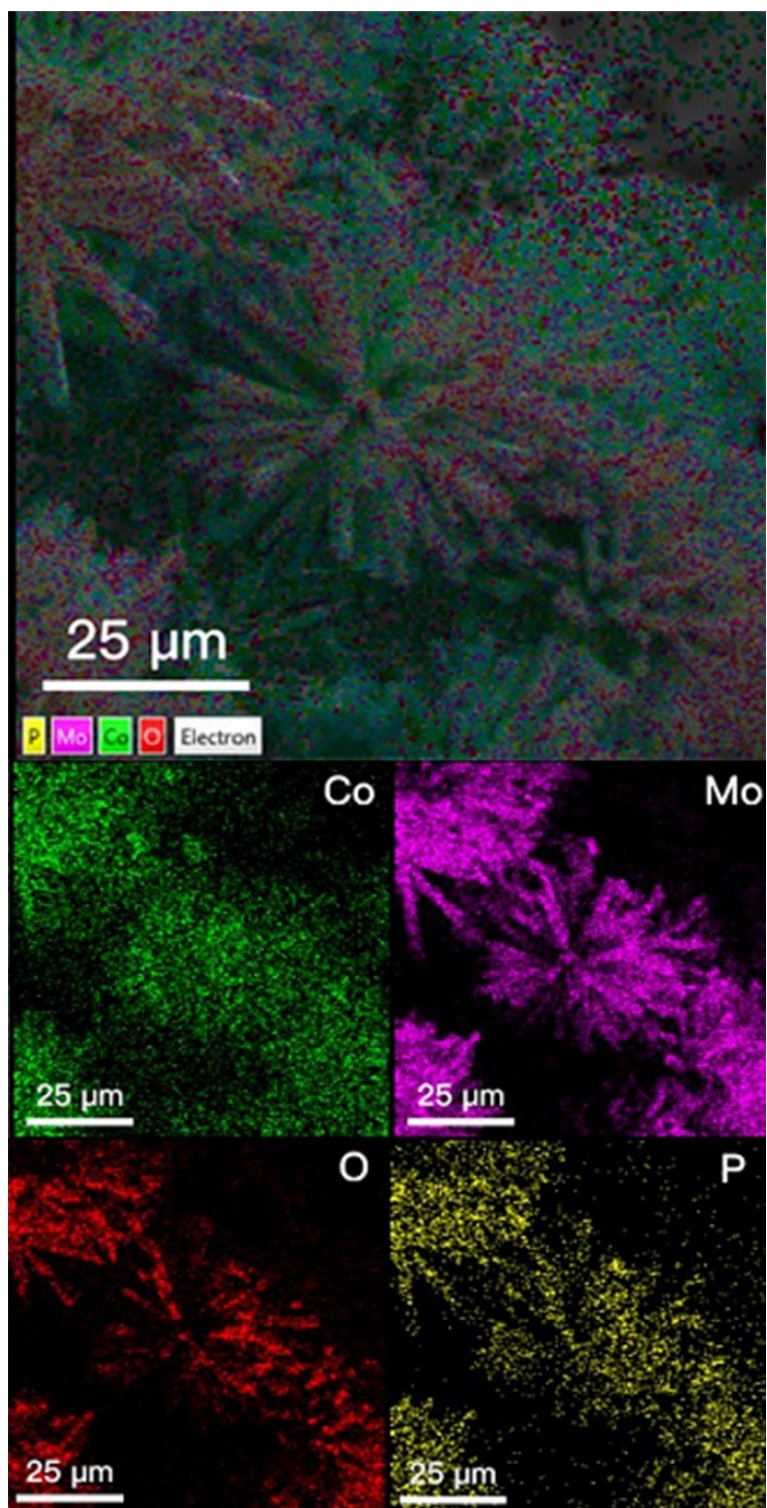


Fig. S2 EDS element mapping images of P-CoMoO₄/NF for SEM.

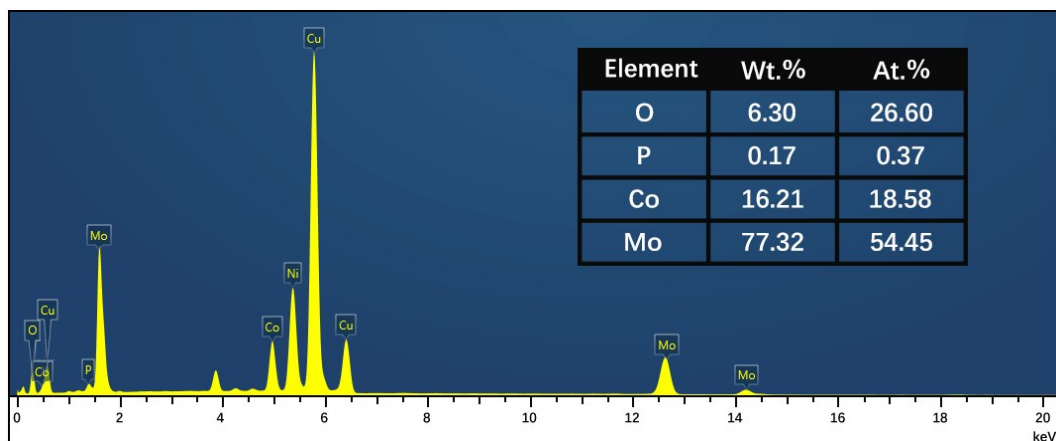


Fig. S3 TEM-EDX spectrum of P-CoMo₄/NF.

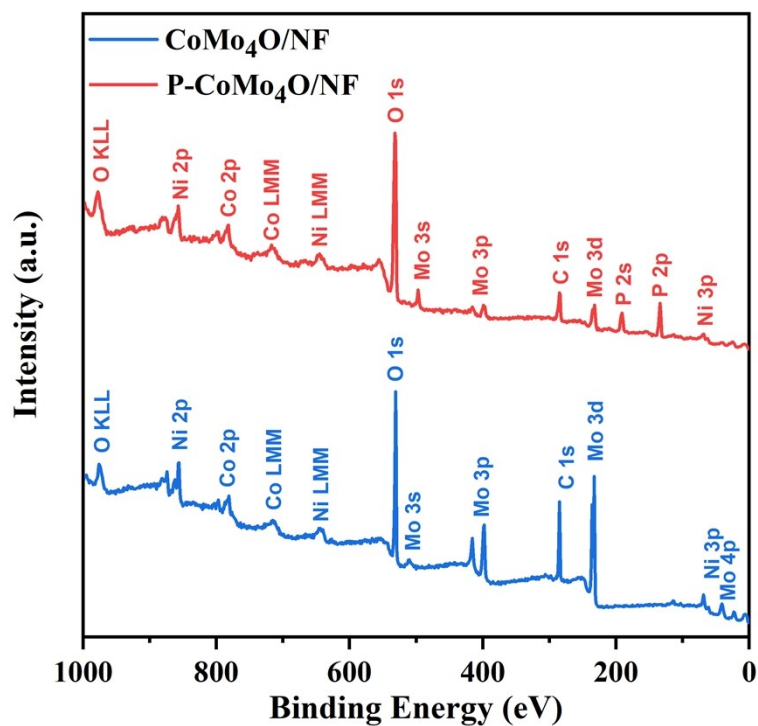


Fig. S4 XPS survey spectrum of P-CoMo₄/NF and CoMo₄/NF.

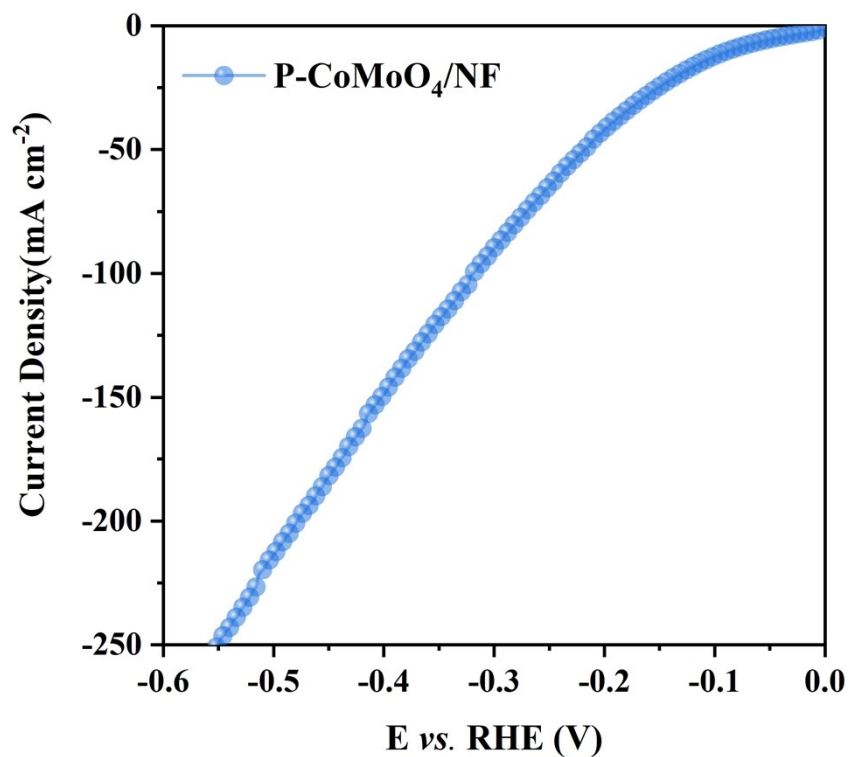


Fig. S5 LSV polarization curves of P-CoMoO₄/NF at a scan rate of 5 mV·s⁻¹ in 1 M KOH.

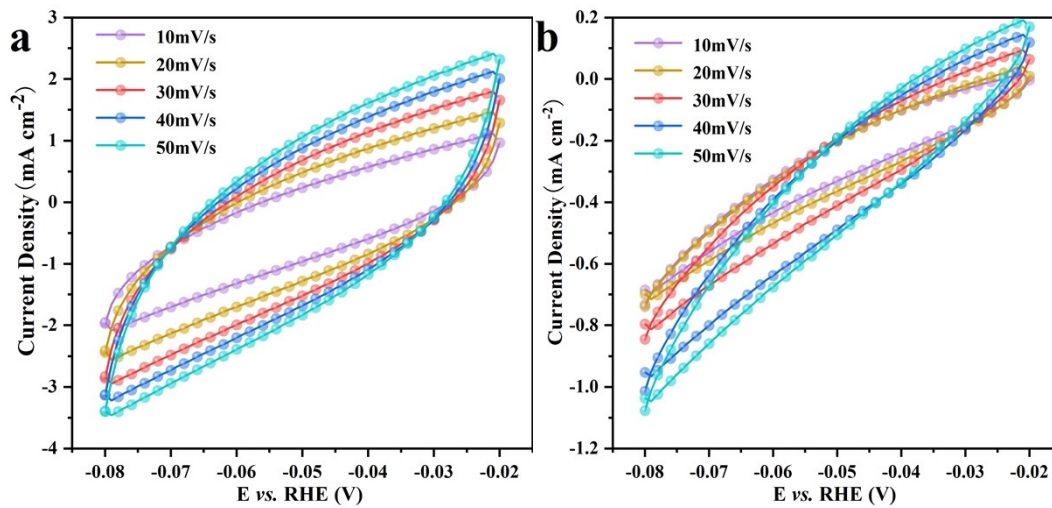


Fig. S6 CVs for HER of (a) P-CoMoO₄/NF; (b) CoMoO₄/NF with different scan rates (10-50 mV s⁻¹) in the region from -0.08 to -0.02 vs RHE.

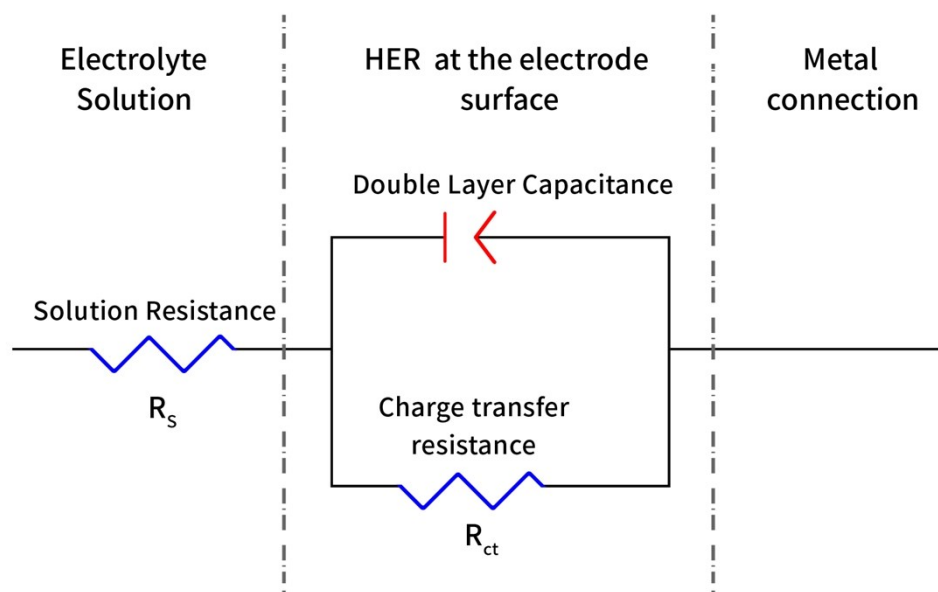


Fig. S7 A typical simplified Randles circuit for the metal oxides catalyzing HER.

In this simplified Randles circuit, R_s and R_{ct} represent the solution resistance and charge transfer resistance, respectively. C_{dl} element models the double-layer capacitance. The kinetics for Faradaic HER is determined by charge transfer resistance (R_{ct}).

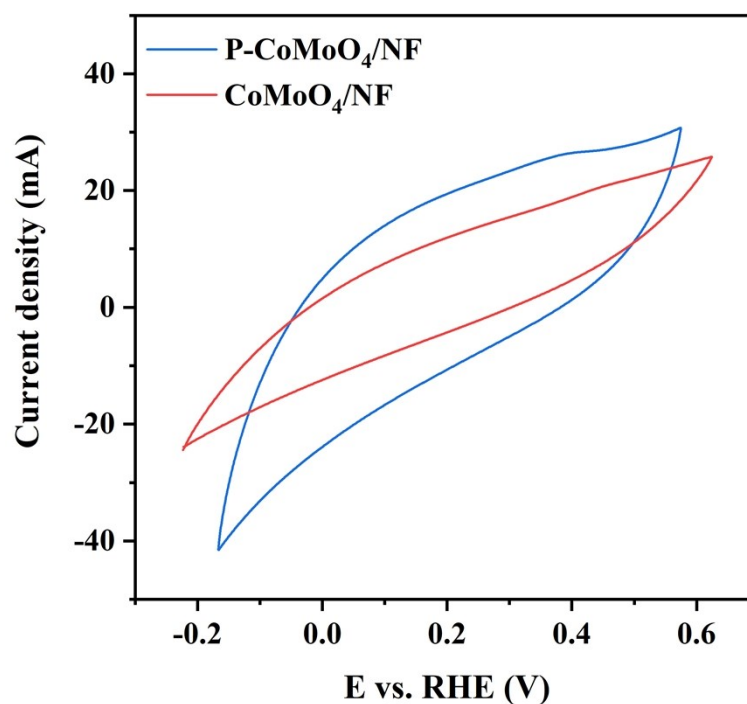


Fig. S8 CV curves for recorded between -0.2 V and 0.6 V vs. RHE in 1.0 M phosphate buffer saline (PBS) (pH=7) at a scan rate of 50 mV s⁻¹.

Calculation of TOF¹

The TOF (in s⁻¹) were calculated with the following equation:

$$\text{TOF} = \frac{JA}{2Fm}$$

J: current density (in A) during the linear sweep measurement.

A: geometrical electrode area in real.

The factor ½ arrives by taking into account that one hydrogen molecule formed by the required two protons.

m: number of active sites (in mol): the absolute components of the voltammetric charges (cathodic and anodic) tested during one CV cycle (**Fig. S5**) were calculated. Assuming a one electron redox process, this absolute charge was divided by two. The obtained value was then divided by the Faraday constant to get the number of active sites of the catalysts.

F: Faraday constant (in C/mol).

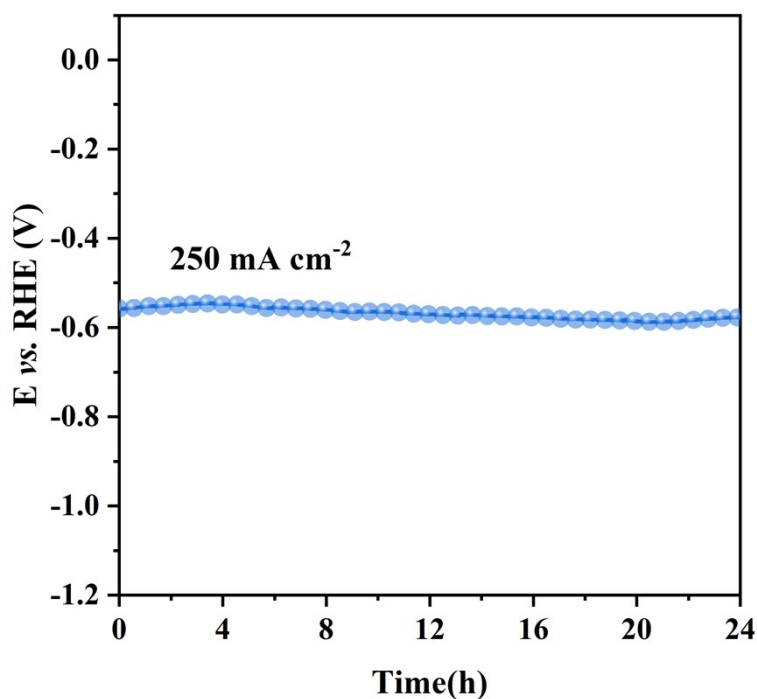


Fig. S9 Chronopotentiometric curve of P-CoMoO₄/NF under a constant current density of 250 mA cm⁻² for 24 h in 1 M KOH.

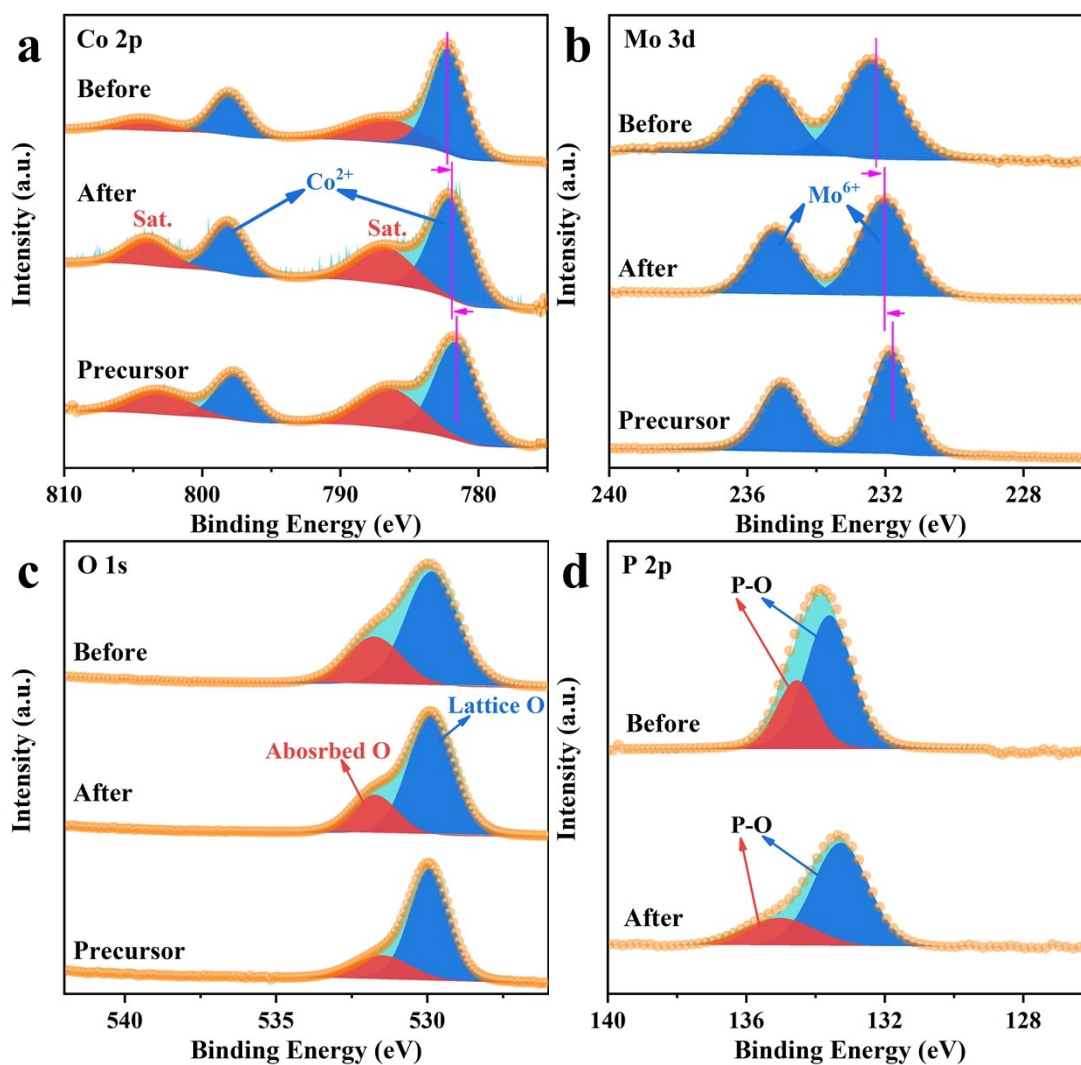


Fig. S10 XPS spectra of P-CoMoO₄/NF before and after stability test: (a) Co 2p, (b) Mo 3d, (c) O 1s, (d) P 2p.

Table S1 Elemental composition of Co, Mo and P determined by ICP-OES.

Element	Mass Fraction%	Atom%	Mass content (mg g ⁻¹)
Co	21.16	29.12	94.72
Mo	76.46	64.64	342.28
P	2.38	6.24	10.67

The ratio of Co, Mo and P is ca. 4.7: 10.4: 1.

Table S2 Comparison of HER performance of the reported and studied samples

Electrocatalyst	η_{10} (mV vs. RHE)	b (mV dec ⁻¹)	j_0 (mA cm ⁻²)	Electrolyte	Ref
P-CoMoO ₄ /NF	89	59	0.31	1 M KOH	this work
CoP	101	62	—	1 M KOH	2
S-MoP NPL	104	56	0.14	1 M KOH	3
Co/CoP	138	64	—	1 M KOH	4
CoP _x	94	49.2	0.123	1 M KOH	5
N, P-Mo _x C NF	135	57.1	0.047	1 M KOH	6
CoS P/NCNT	101	59	0.19	1 M KOH	7
CoP/CC	209	129	—	1 M KOH	8
O-CoP-2	98	59.9	0.231	1 M KOH	9
Co/Co ₃ O ₄ core/shell nanosheets	95	44	—	1 M KOH	10
MoP nanosheets	100	56.4	—	0.5 M H ₂ SO ₄	11
MoO ₂ P _x /Mo	135	62	—	0.5 M H ₂ SO ₄	12
P-Mo ₂ C@C	89	42	0.18	0.5 M H ₂ SO ₄	13
MoDCA-5	78	41	0.178	0.5 M H ₂ SO ₄	14
Co-Mo ₂ C-0.020	140	39	0.0051	0.5 M H ₂ SO ₄	15

η_{10} : the overpotential at a current density of 10 mA cm⁻².

Calculation of j_0 ¹⁶

The exchange current density (j_0) is another crucial kinetic parameter in electrocatalysis that is correlated to the rate of electron transfer under reversible conditions (that is, at zero overpotential). The magnitude of the exchange current density influences the rate of the electrochemical reaction at other potentials. The Tafel equation can be used to describe the current-potential relationship at a significant overpotential (η):

$$\eta = b \log(j/j_0)$$

where j is the current density, j_0 is the exchange current density and b is the Tafel slope.

Reference

1. J. Zhang, T. Wang, P. Liu, Z. Q. Liao, S. H. Liu, X. D. Zhuang, M. W. Chen, Ehrenfried Zschech, X. L. Feng, *Nat. Commun.*, 2017, **8**, 15437-15444.
2. X. K. Huang, X. P. Xu, X. X. Luan, D. J. Cheng, *Nano Energy*, 2020, **68**, 104332-104340.
3. K. Liang, S. Pakhira, Z. Z. Yang, A. Nijamudheen, L. C. Ju, M. Y. Wang, C. I. A. Velez, G. E. Sterbinsky, Y. G. Du, Z. X. Feng, J. L. M. Cortes and Y. Yang, *ACS Catal.*, 2018, **9**(1), 651-659.
4. H. Wang, S. X. Min, Q. Wang, D. B. Li, G. Casillas, C. Ma, Y. Y. Li, Z. X. Liu, L. J. Li, J. Y. Yuan, M. Antonietti, T. Wu, *ACS Nano*, 2017, **11**, 4358-4364.
5. R. Zhang, X. X. Wang, S. J. Yu, T. Wen, X. W. Zhu, F. X. Yang, X. N. Sun, X. K. Wang and W. P. Hu, *Adv. Mater.*, 2017, **29**(9), 1605502-1605507.
6. Y. Y. Chen, Y. Zhang, W. J. Jiang, X. Zhang, Z. H. Dai, L. J. Wan, J. S. Hu, *ACS Nano*, 2016, 8851-8860.
7. D. J. Li, J. Kang, H. J. Lee, D. S. Choi, S. H. Koo, B. C. Han and S. O. Kim, *Adv. Energy Mater.*, 2018, **8**(13), 1702806-1702812.
8. J. Q. Tian, Q. Liu, A. M. Asiri, X. P. Sun, *J. Am. Chem. Soc.*, 2014, **136**(21), 7587-7590.

9. G. Y. Zhou, M. Li, Y. L. Li, H. Dong, D. M. Sun, X. E. Liu, L. Xu, Z. Q. Tian and Y. W. Tang, *Adv. Funct. Mater.*, 2019, **30**(7), 1905252-1905259.
10. X. D. Yan, L. H. Tian, M. He, X. B. Chen, *Nano Lett.*, 2015, **15**(9), 6015-6021.
11. W. Cui, N. Y. Cheng, Q. Liu, C. J. Ge, A. M. Asiri, X. P. Sun, *ACS Catal.*, 2014, **4**(8), 2658-2661.
12. X. Xie, R. J. jin Yu, N. Xue, A. B. Yousaf, Hong Du, Kuang Liang, Nan Jianga, An-Wu Xu, *J. Mater. Chem. A*, 2016, **4**(5), 1647-1652.
13. Z. P. Shi, K. Q. Nie, Z. J. Shao, B. X. Gao, H. L. Lin, H. B. Zhang, B. L. Liu, Y. X. Wang, Y. H. Zhang, X. H. Sun, X. M. Cao, P. Hu, Q. S. Gao, Y. Tang, *Energy Environ. Sci.*, 2017, **10**(5), 1262-1271.
14. R. G. Ma, Y. Zhou, Y. F. Chen, P. X. L, Q. Liu, J. C. Wang, *Angew. Chem. Int. Ed.*, 2015, **54**(49), 14723-14727.
15. H. L. Lin, N. Liu, Z. P. Shi, Y. L. Guo, Y. Tang, Q. S. Gao, *Adv. Funct. Mater.*, 2016, **26**(31), 5590-5598.
16. C. G. M. Guio, L. A. Stern and X. L. Hu, *Chem. Soc. Rev.*, 2014, **43**(18), 6555-6569.