Co-doping NiP_2 as efficient and robust bifunctional electrocatalyst for overall water splitting in alkali and seawater

Xiaoyu Hao,[†a,b] Qian Sun,[†a] Tianyi Zhang,[a] Panpan Song,[c] Jinglun Guo,[a] Svetlana Peshayad,[d] Longlong Chen, [e] Xiaolei Huang,[*c] Xuqing Liu[*a,b]

[a] State Key Laboratory of Solidification Processing, Centre of Advanced Lubrication and Seal Materials, Northwestern Polytechnical University, Xi'an 710072, China

[b] Shandong Laboratory of Advanced Materials and Green Manufacturing at Yantai, Yantai 264006, China

[c] Key Laboratory of Rare Earths, Ganjiang Innovation Academy, Chinese Academy of Sciences, Ganzhou 710043, China.

[d] al-Farabi Kazakh National University, Faculty of Physics and Technology, Almaty 050040, Kazakh.

[e] China National Petroleum Corporation Qinghai Oilfield Branch, Qinghai 817500, China

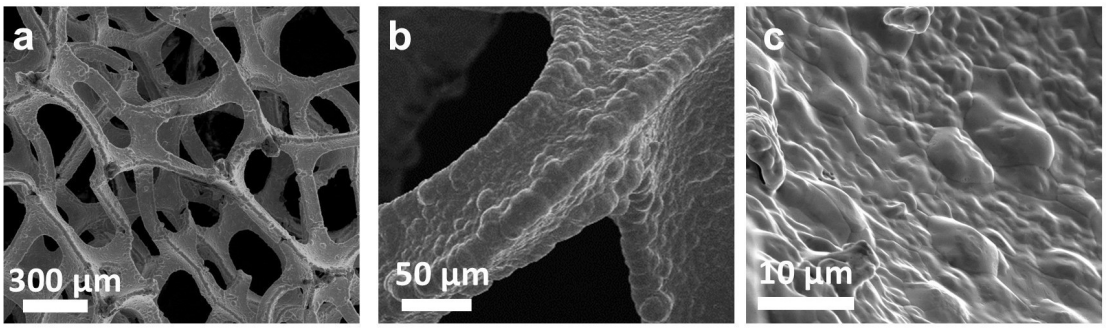

Fig.S1 SEM images of NF.

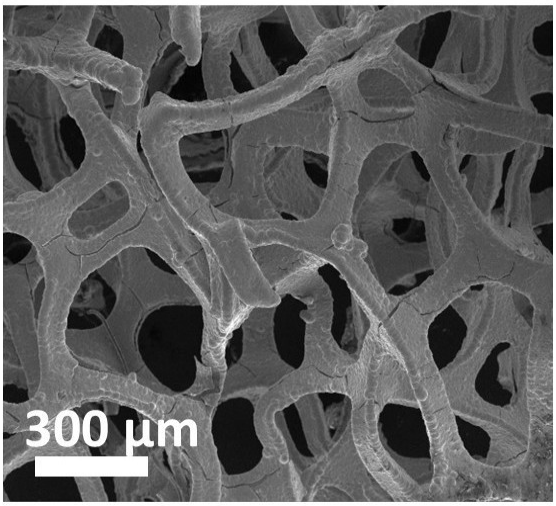

Fig.S2 SEM of Co_8-NiP_2.

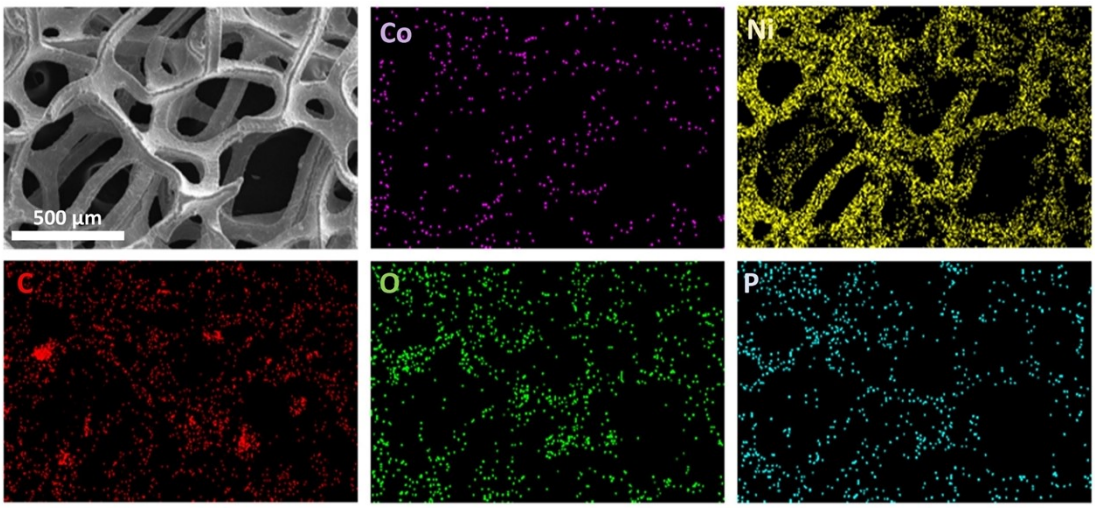

Fig.S3 EDS mapping of Co_8-NiP_2.

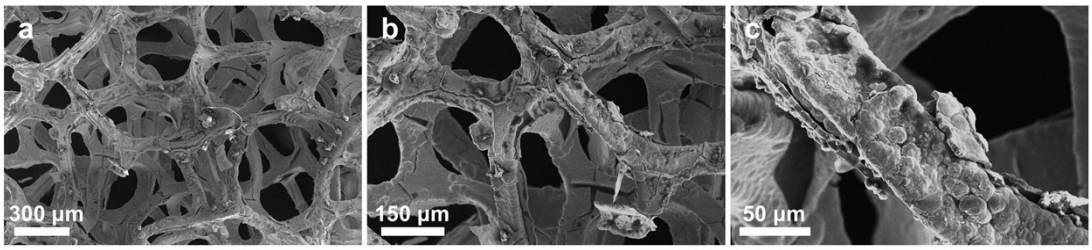

Fig.S4 SEM images of NiP_2.

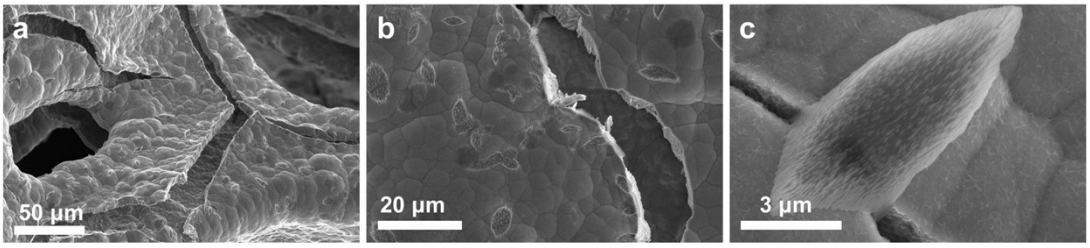

Fig.S5 SEM images of Co_2-NiP_2.

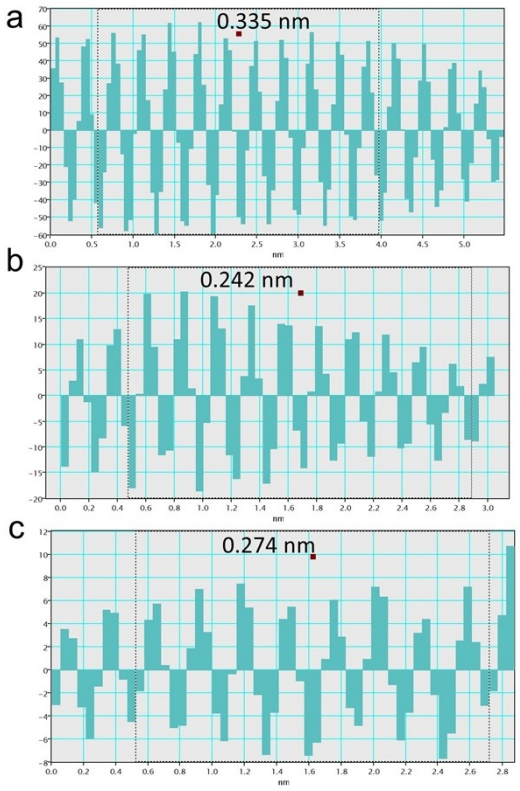

Fig.S6 Calculation of lattice spacing of Co_8-NiP_2.

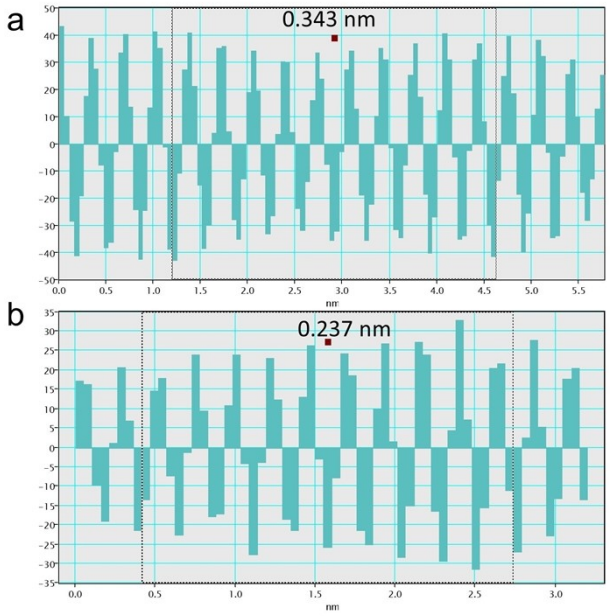

Fig.S7 Calculation of lattice spacing of NiP_2.

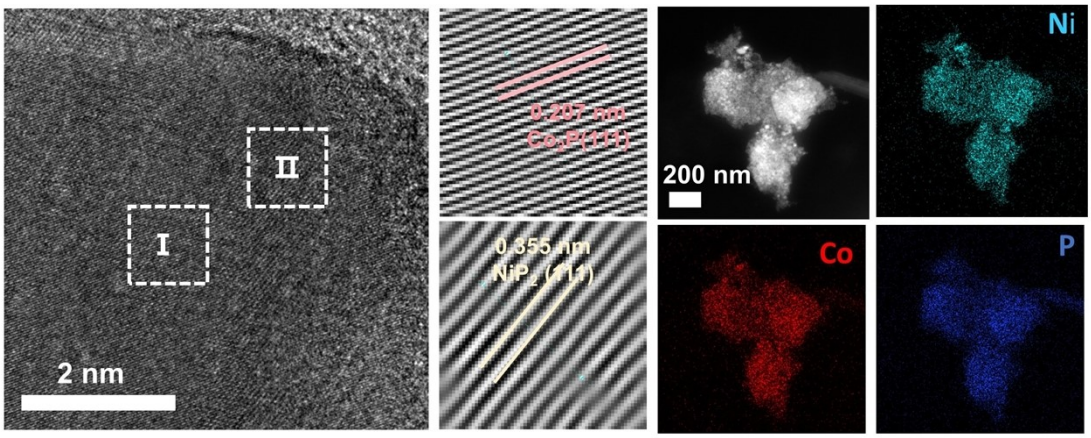

Fig.S8 HRTEM image and SAED patterns of Co_2-NiP_2.

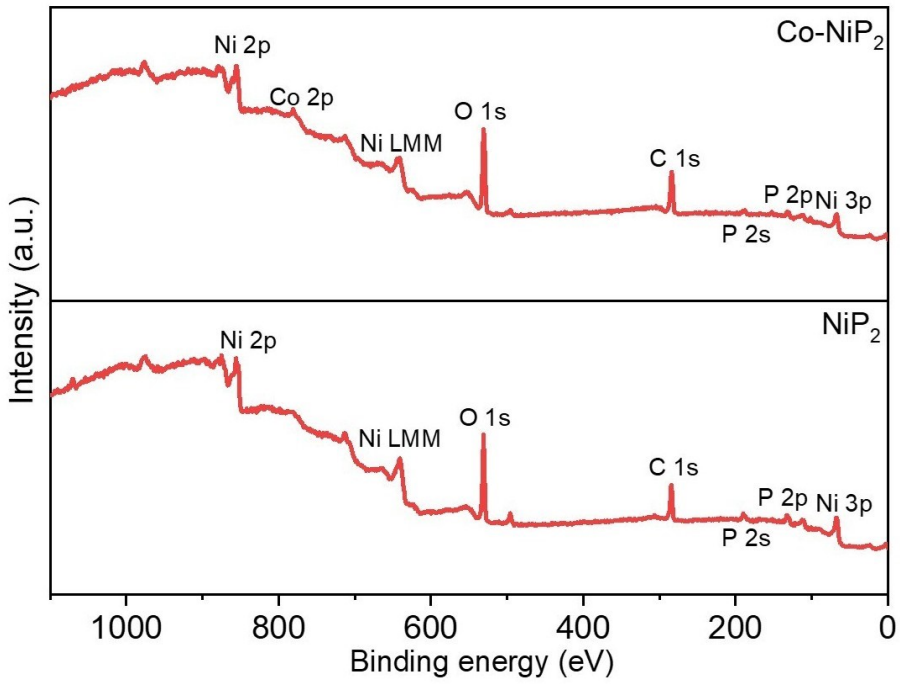

Fig.S9 XPS spectra of NiP_2 and Co_8-NiP_2

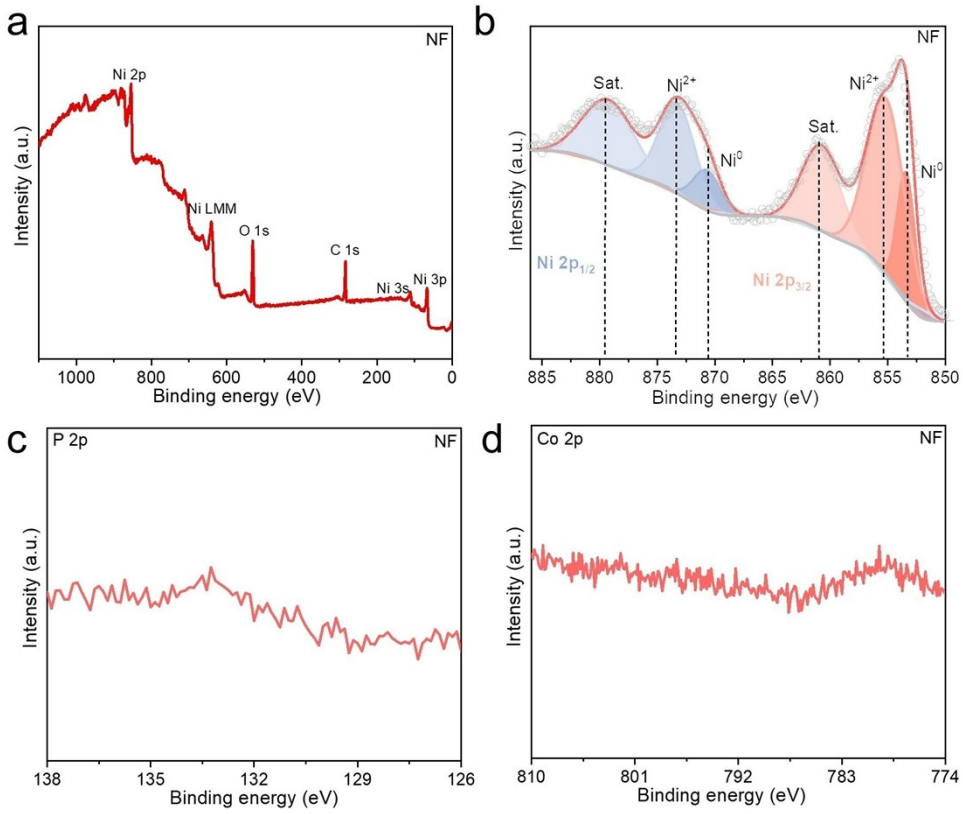

Fig.S10 (a) XPS spectra of NF. High resolution of (b) Ni 2p, (c) P 2p, (d) Co 2p.

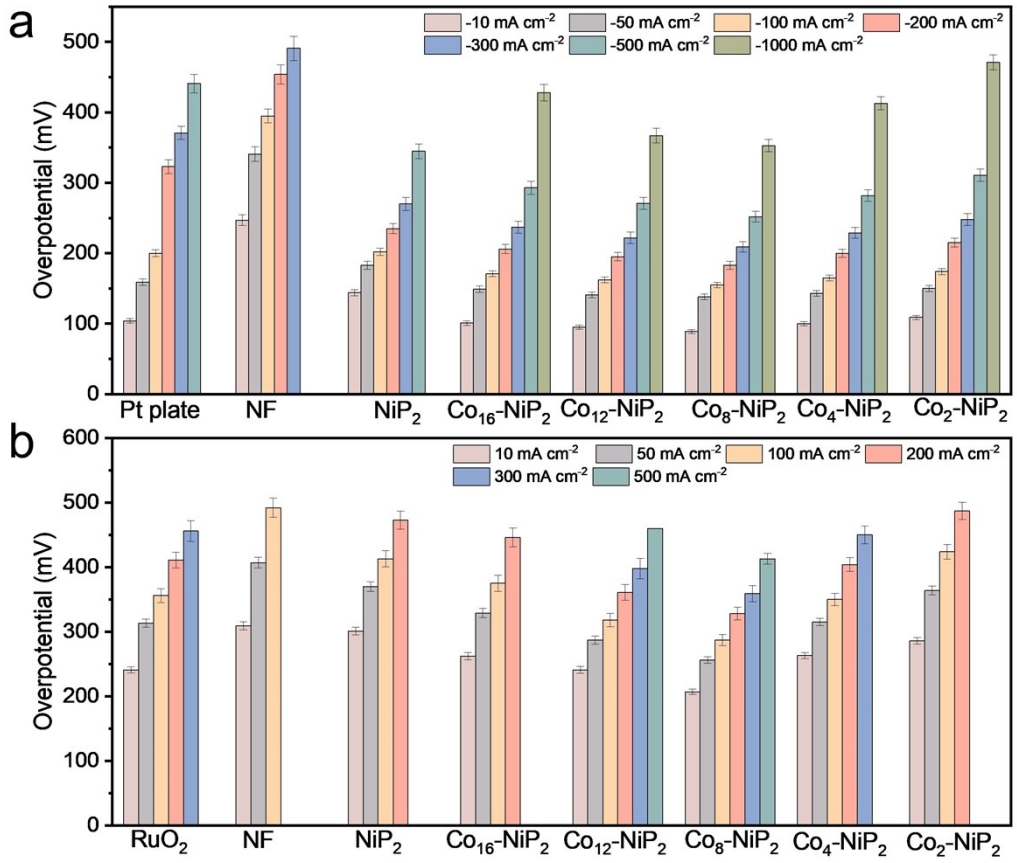

Fig.S11 Overpotential comparison of (a) HER and (b) OER in 1 M KOH.

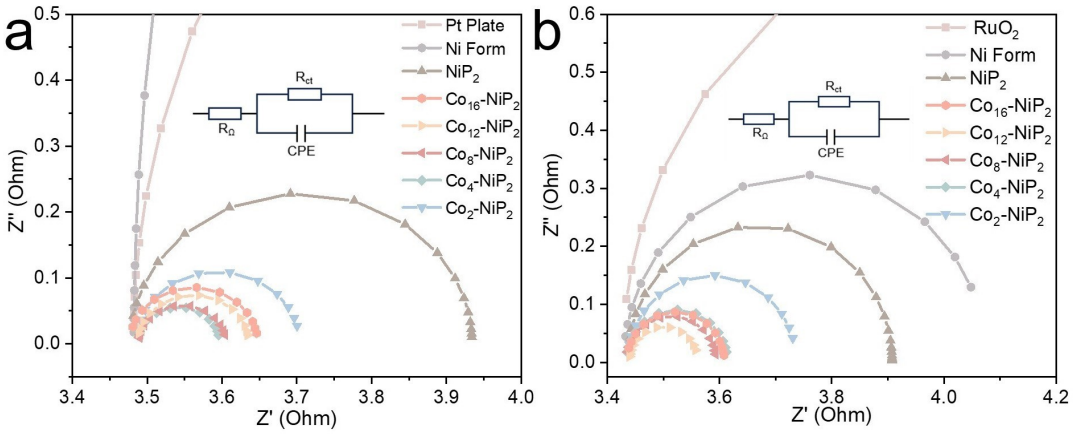

Fig.S12 Nyquist plot of (a)HER and (b) OER.

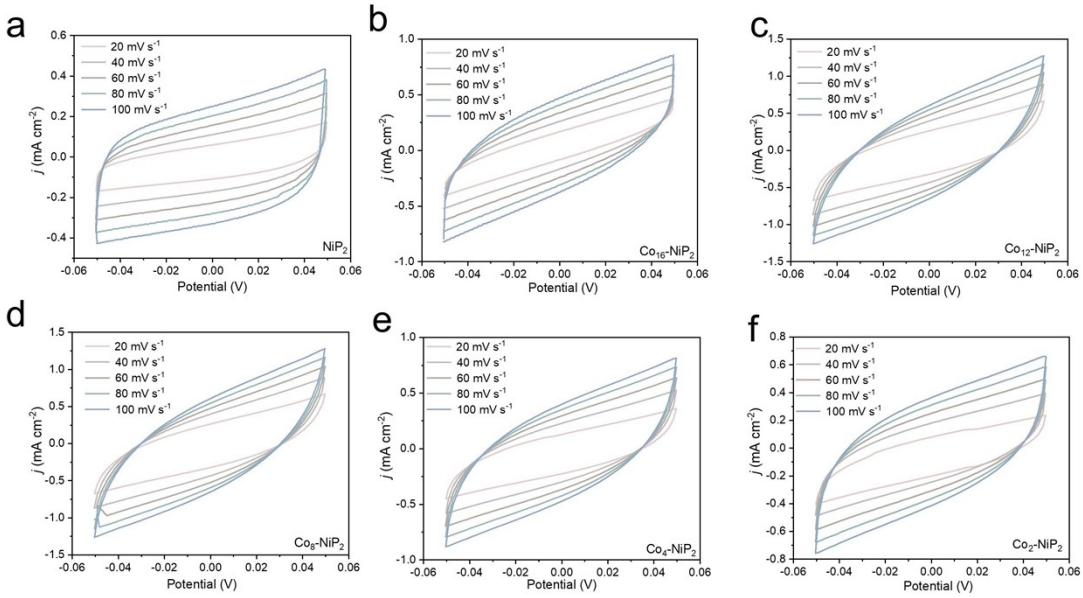

Fig.S13 CV curves at the scan rate of 20, 40, 60, 80, 100 mV s^{-1} of HER process.

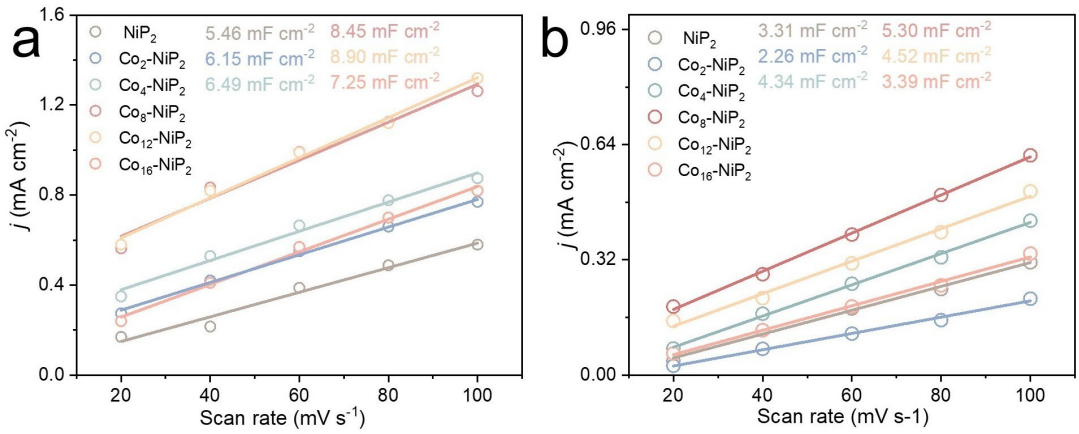

Fig.S14 C_{dl} values of (a) HER catalysts and (b) OER catalysts.

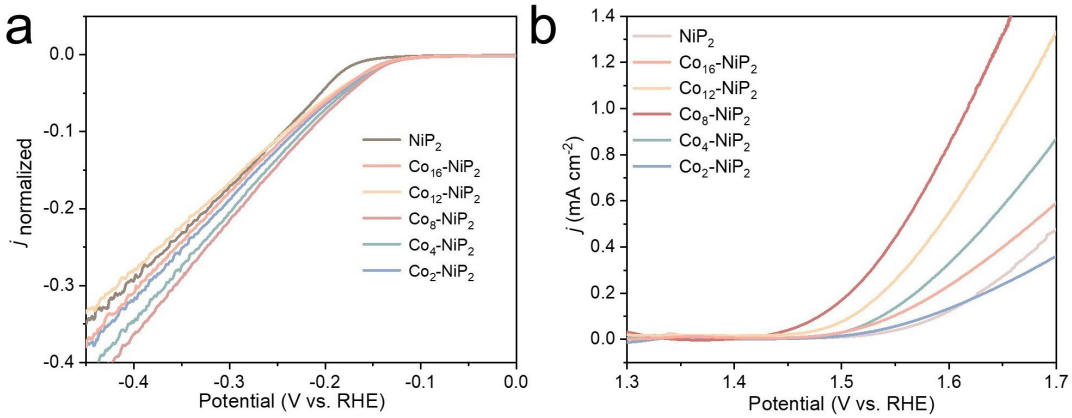

Fig.S15 The normalized polarization curves of ECSA of (a) HER and (b) OER.

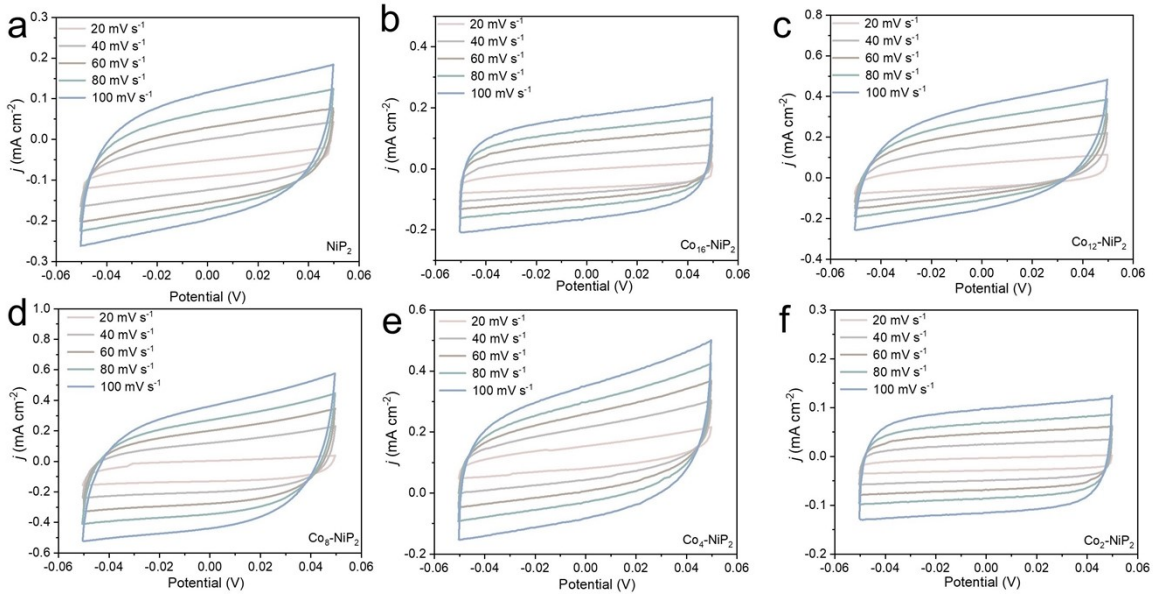

Fig.S16 CV curves at the scan rate of 20, 40, 60, 80, 100 mV s-1 of OER process.

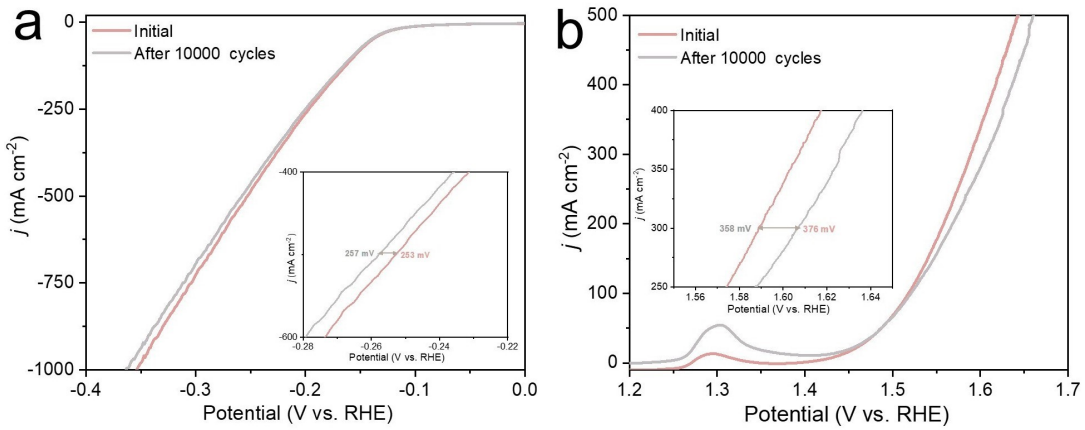

Fig.S17 Polarization curve of (a) HER and (b) OER before and after 10000 cycles.

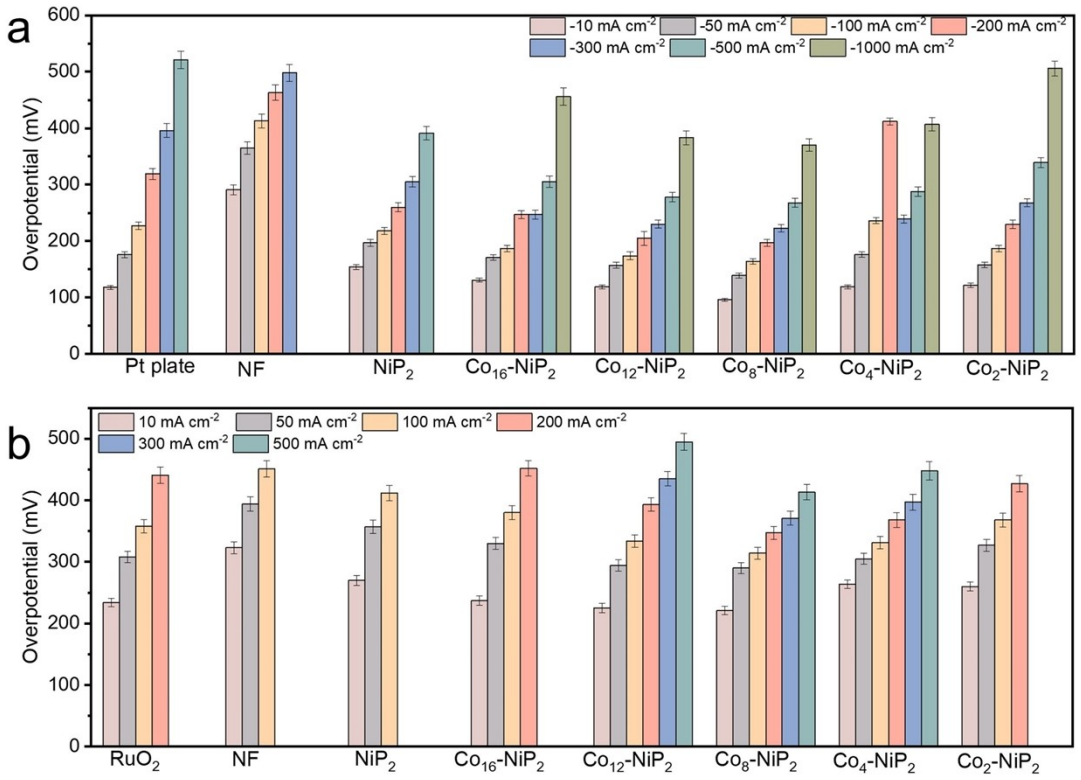

Fig.S18 Overpotential comparison of (a) HER and (b) OER in alkaline seawater.

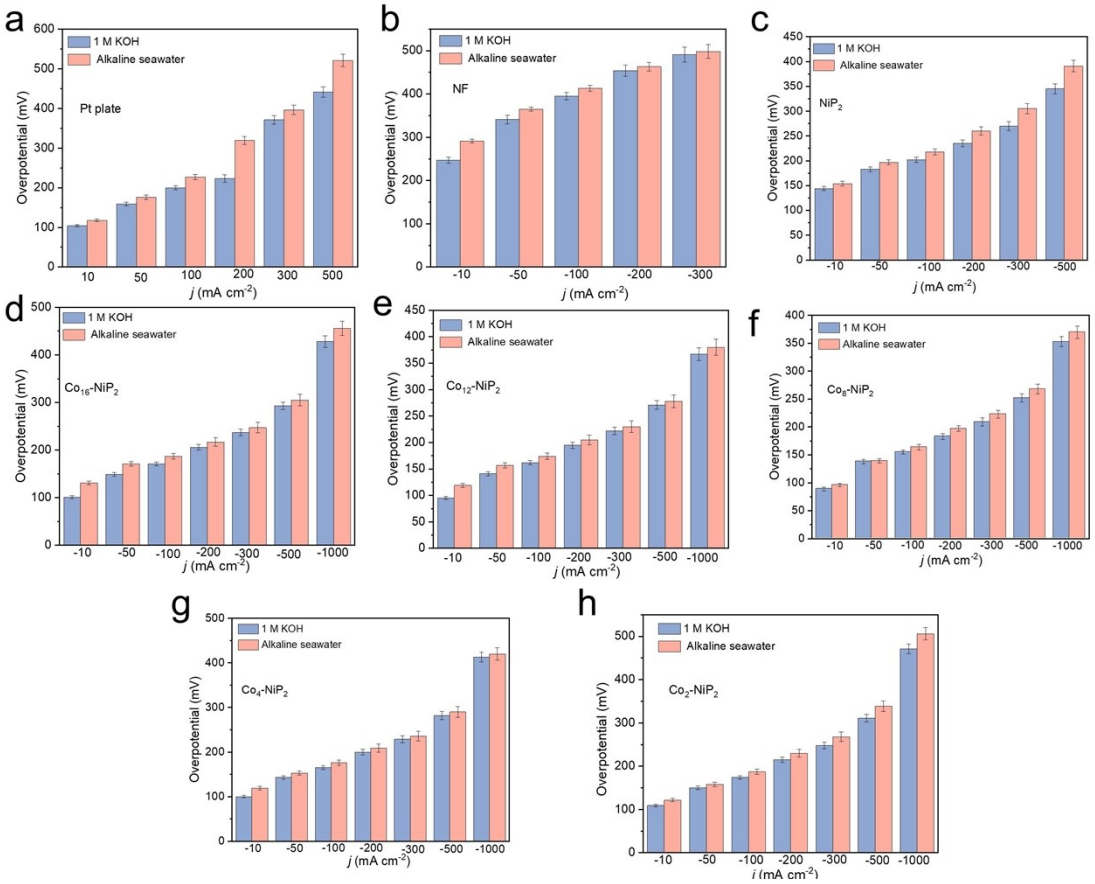

Fig.S19 Overpotential comparison of (a) Pt plate, (b) NF, (c) NiP_2, (d) Co_{16}-NiP_2, (e) Co_{12}-NiP_2, (f) Co_8-NiP_2, (g) Co_4-NiP_2, (h)Co_2-NiP_2 in 1 M KOH and alkaline seawater for HER.

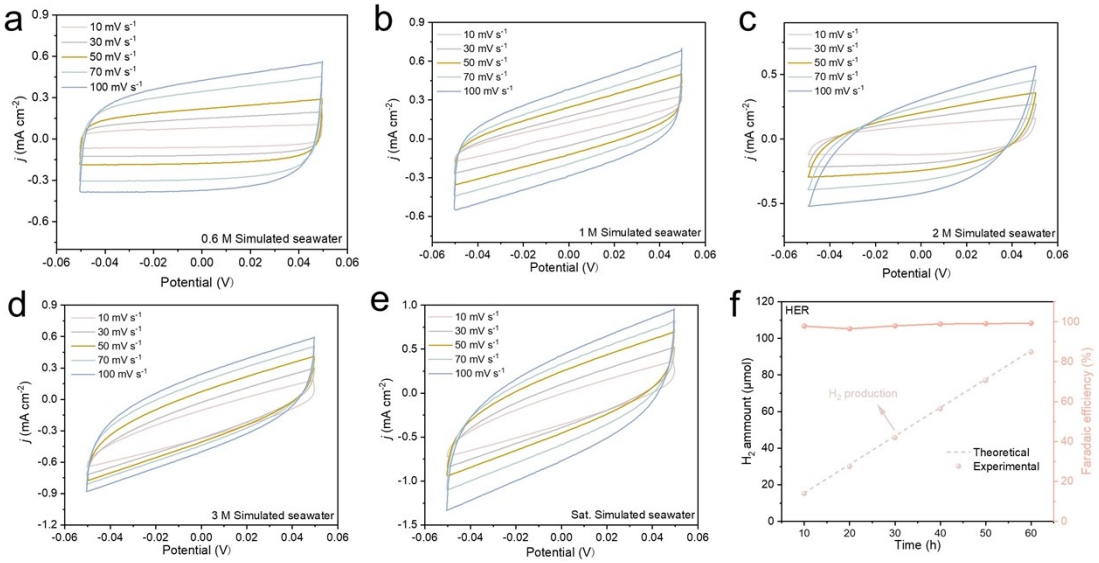

Fig.S20 CV curves at the scan rate of 20, 40, 60, 80, 100 mV s^{-1} of Co_8-NiP_2 for HER in (a) 0.6 M, (b) 1 M, (c) 2 M, (d) 3 M, (e) saturated simulated seawater. (f) Faraday efficiency.

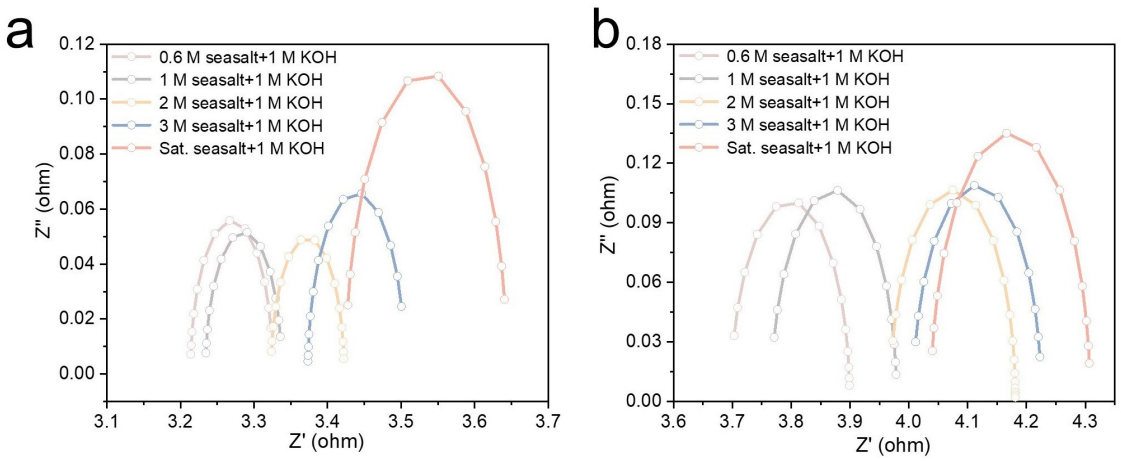

Fig.S21 Nyquist plot of (a)HER and (b) OER at simulated seawater of different concentrations.

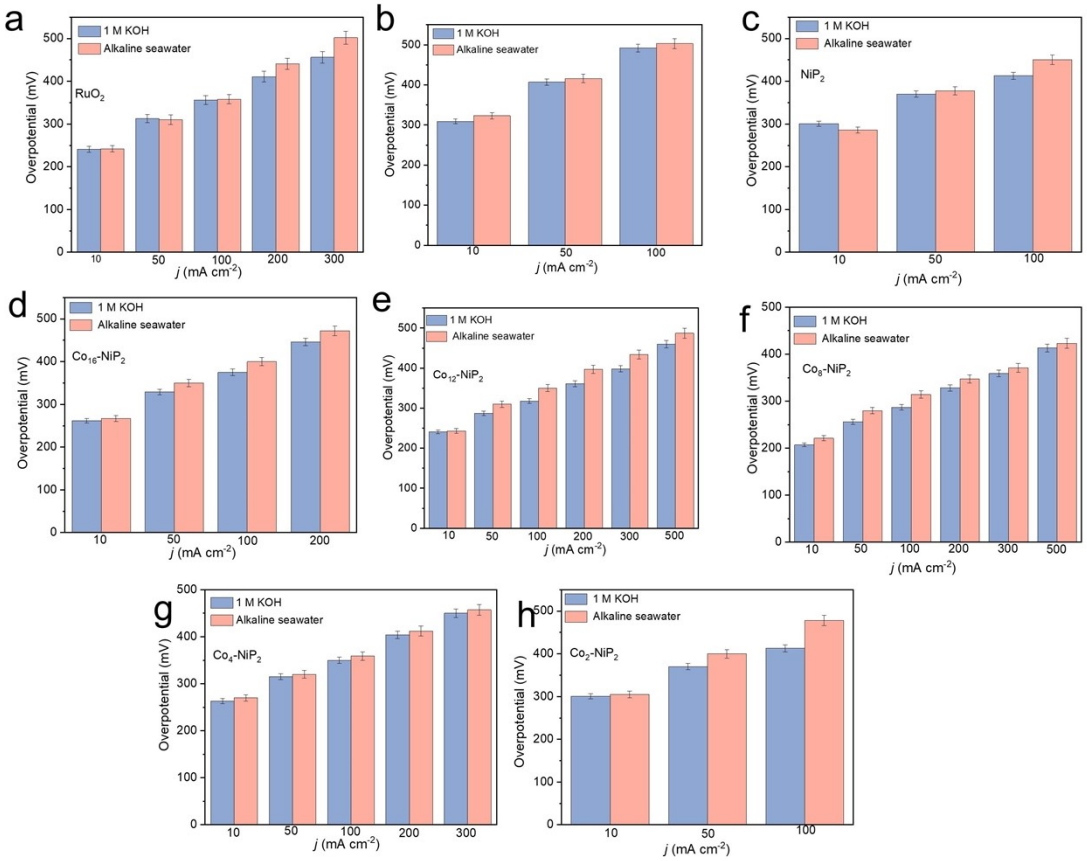

Fig.S22 Overpotential comparison of (a) RuO_2, (b) NF, (c) NiP_2, (d) Co_{16}-NiP_2, (e) Co_{12}-NiP_2, (f) Co_8-NiP_2, (g) Co_4-NiP_2, (h) Co_2-NiP_2 in 1 M KOH and alkaline seawater for OER.

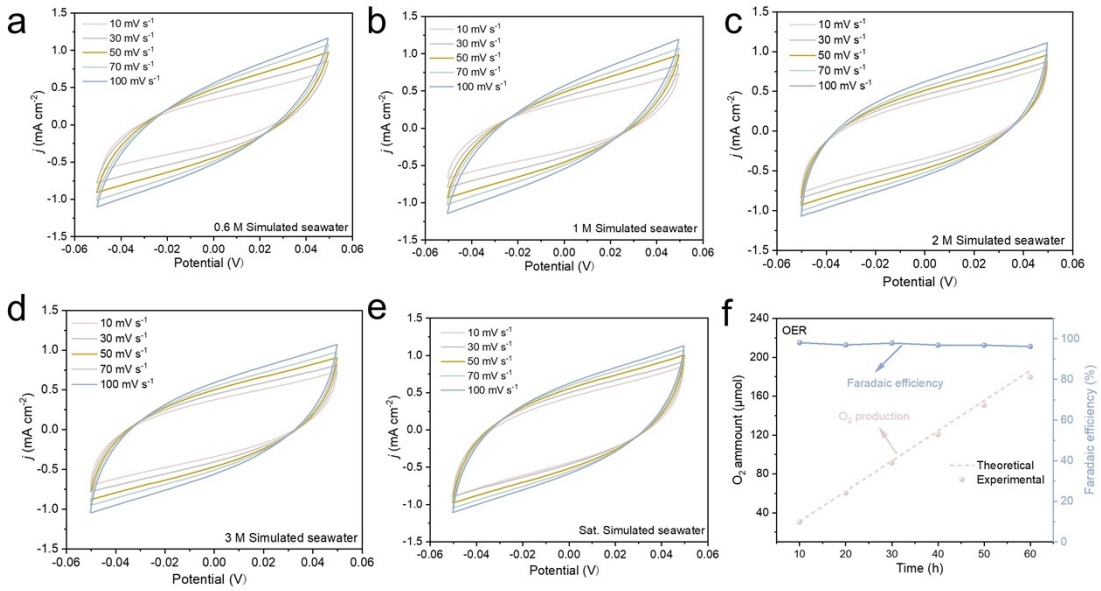

Fig.S23 CV curves at the scan rate of 20,40,60,80,100 mV s^{-1} of Co_8-NiP_2 for OER in (a) 0.6M, (b) 1M, (c) 2M, (d) 3M, (e) saturated simulated seawater. (f) Faraday efficiency.

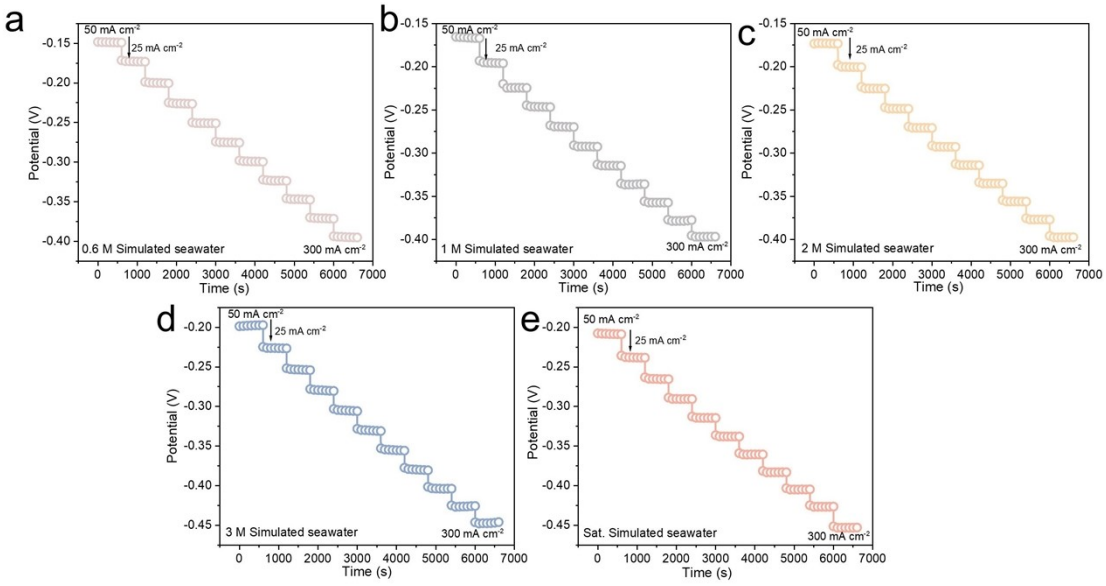

Fig.S24 Multi-step CP tests of Co_8-NiP_2 for HER in (a) 0.6 M, (b) 1 M, (c) 2 M, (d) 3 M, (e) saturated simulated seawater.

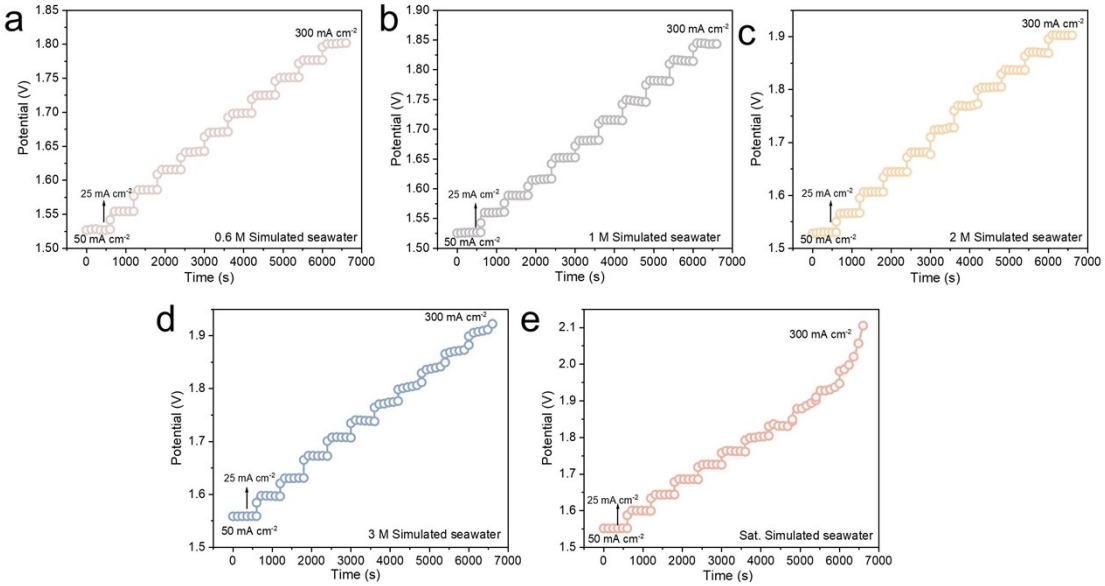

Fig.S25 Multi-step CP tests of Co_8-NiP_2 for OER in (a) 0.6 M, (b) 1 M, (c) 2 M, (d) 3 M, (e) saturated simulated seawater.

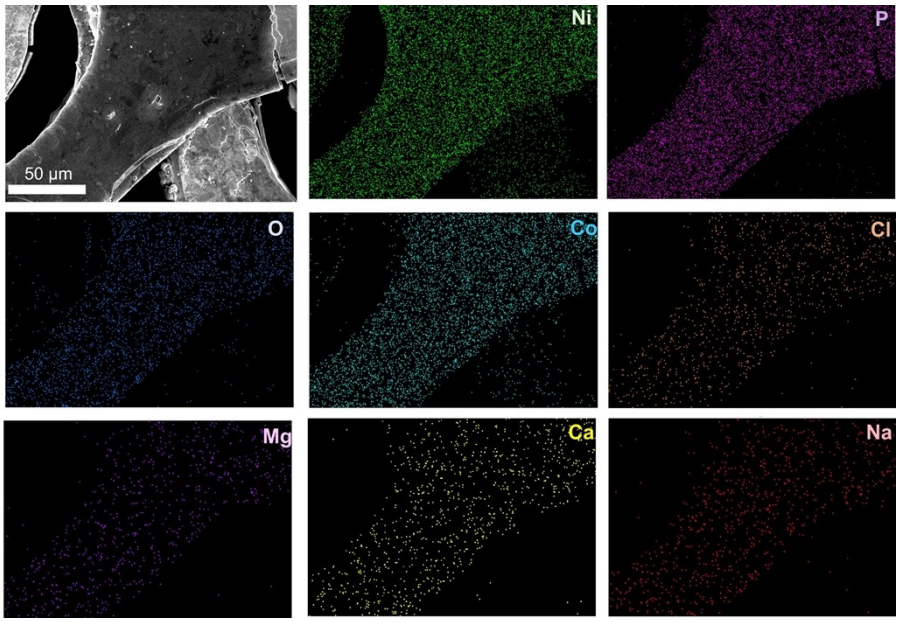

Fig.S26 SEM image and EDS element mapping of Co_8-NiP_2 after long-term HER in seawater.

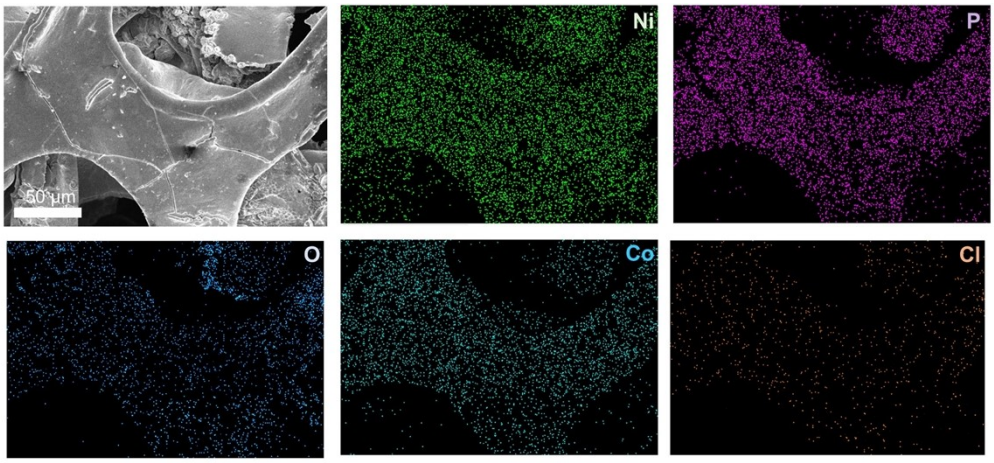

Fig.S27 SEM image and EDS element mapping of Co_8-NiP_2 after long-term OER in seawater.

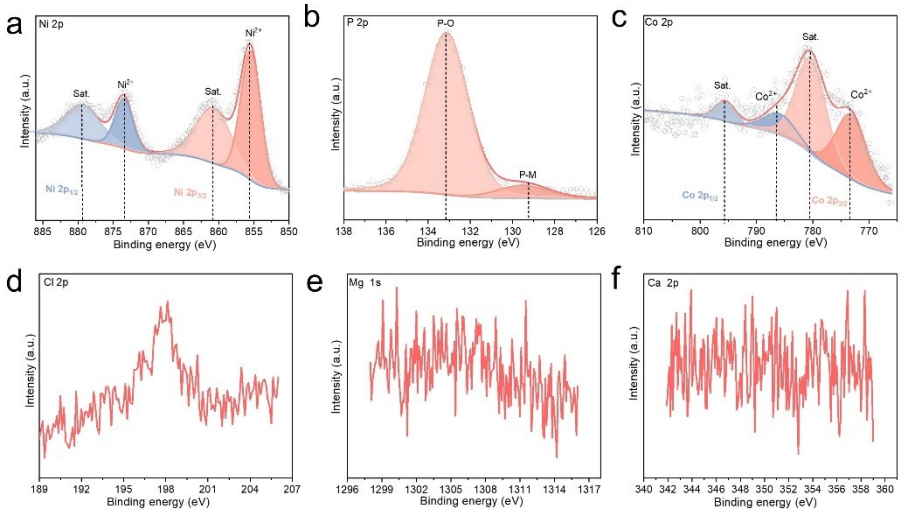

Fig. S28 (a) Ni 2p, (b) P 2p, (c) Co 2p, (c) Cl 2p, (e) Mg 1s and (h) Ca 2p spectrum of Co_8-NiP_2 after long-term HER in seawater.

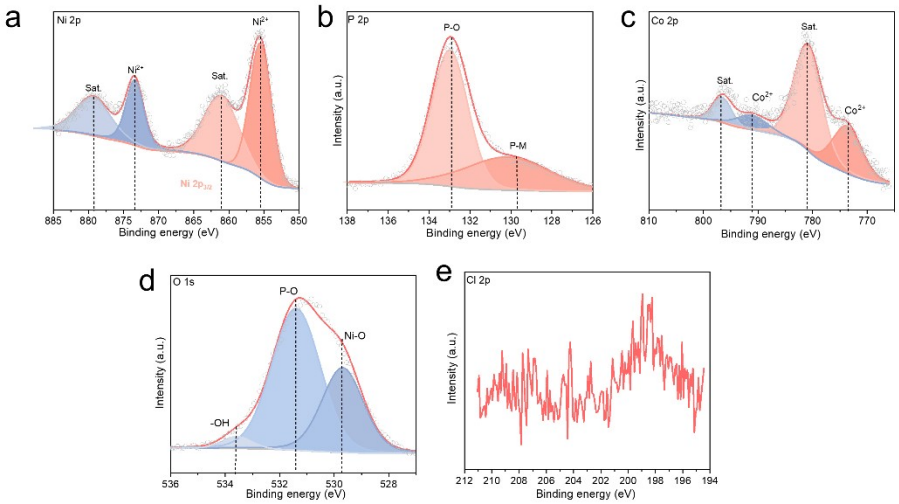

Fig. S29 (a) Ni 2p, (b) P 2p, (c) Co 2p, (c) O 1s and (h) Cl 2p spectrum of Co_8-NiP_2 after long-term OER in seawater.

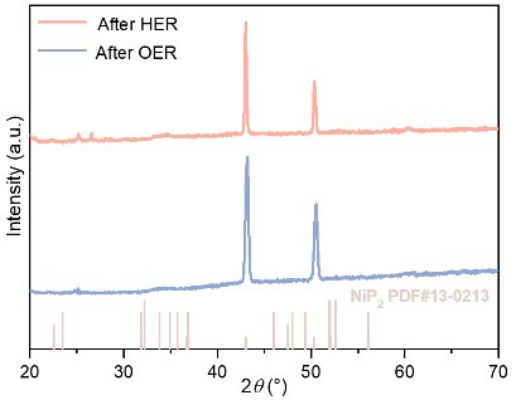

Fig. S30 XRD spectra of Co_8-NiP_2 after long-term HER and OER in seawater.

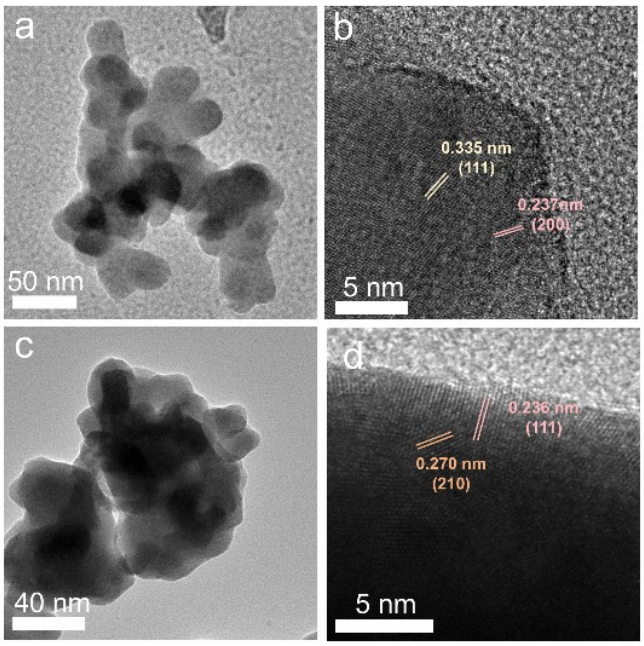

Fig. S31 (a, b) TEM images of Co_8-NiP_2 after long-term HER in seawater. (c, d) TEM images of Co_8-NiP_2 after long-term OER in seawater.

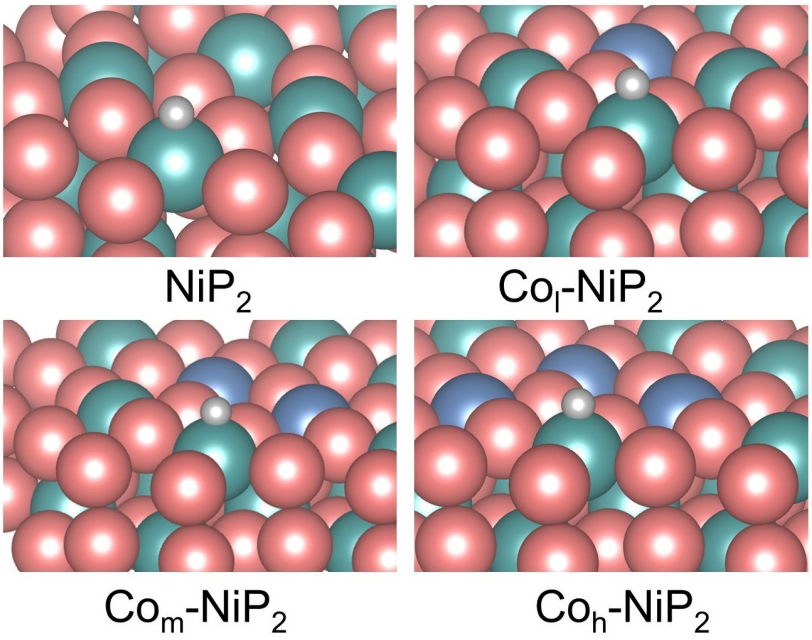

Fig.S32 HER intermediate adsorption model.

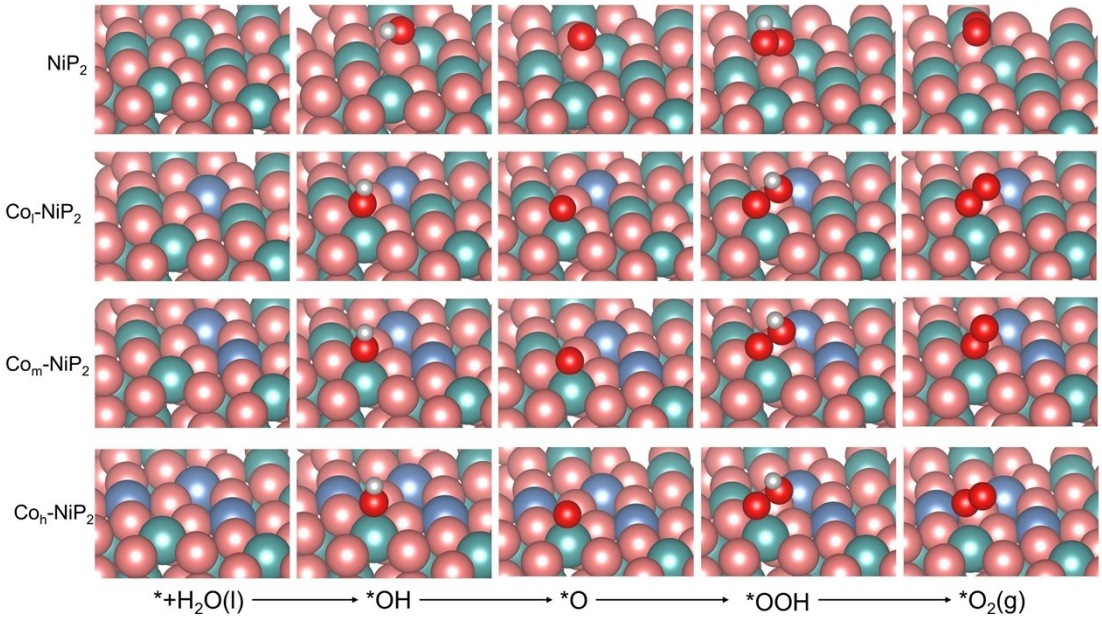

Fig.S33 OER intermediate adsorption model.

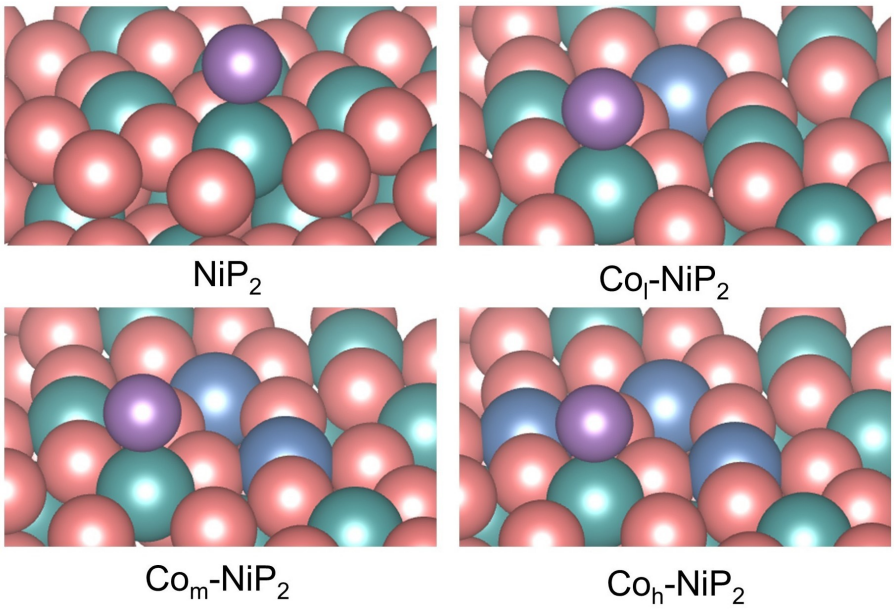

Fig.S34 Cl* adsorption model.

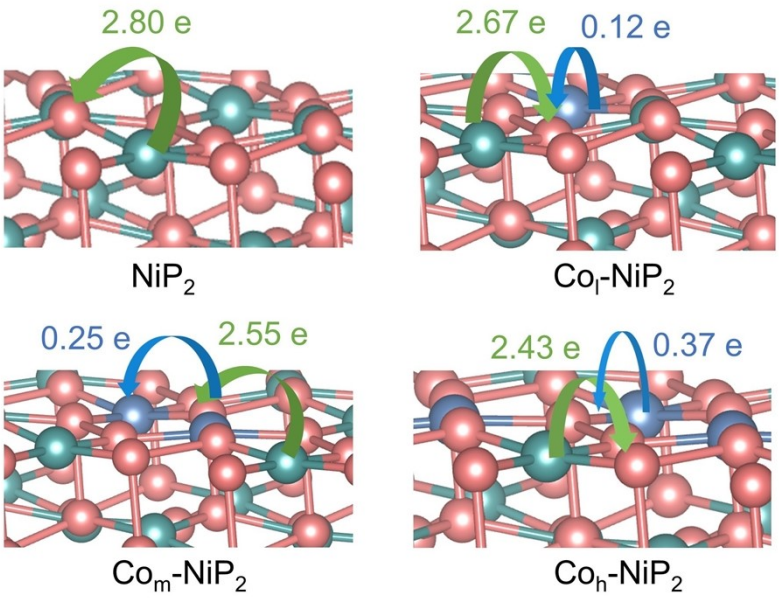

Fig.S35 Average Bader charge transfer quantity of Ni, Co, P (blue: Co→P, green: Ni→P).

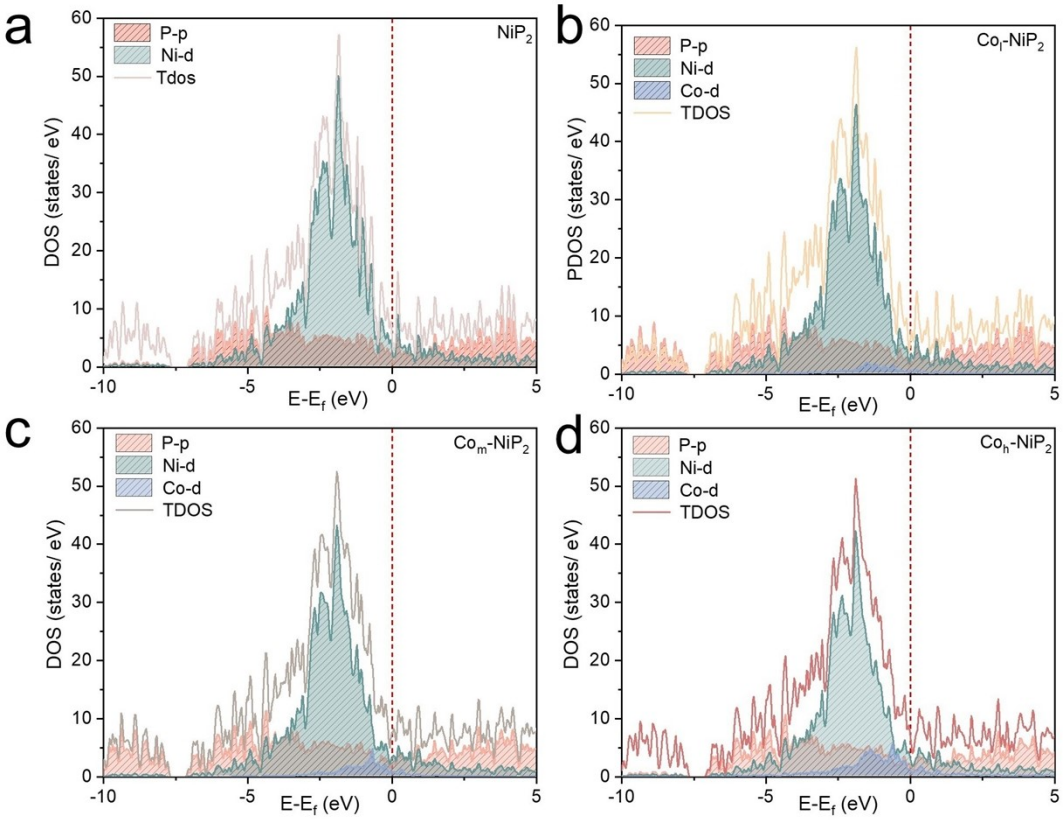

Fig.S36 DOS of (a) NiP_2, (b) Co_l-NiP_2, (c) Co_m-NiP_2, (d) Co_h-NiP_2

Table S1 The performance of TMP-based HER catalysts reported in recent literature.

Material	electrolyte	electrode	Current density	Overpotential (mV)	Tafel slope (mV dec−1)	Reference
This work	1 M KOH	NF	10	89.7	53.0	
			100	155.2		
			500	252.0		
			1000	352.8		
V-NiP/NiP	1 M KOH	NF	100	211	103	S1
			500	293		
			1000	334		
CoO-Co_3O_4/rGO@NiP	1 M NaOH	Mild steel	10	106.2	107.9	S2
Ag-AgP/Ni_2P	1 M KOH	NF	10	78	68.9	S3
Ni_2P	1.M KOH	NF	10	159	99.8	
Ni_2P@C	1.M KOH	NF	10	132	56.29	S4
Cu-NiP_2	1.M KOH	NF	10	248	108	S5
Mn-NiP_2				233	108	
NPO/NiP	1.M KOH	NF	10	76	213	S6
NiP_x	1 M KOH	Ti	10	82	42	S7
		CC		94	49	
		stainless steel		97	56	
Por-NiP-Cr	1 M KOH	BDD	50	234	66.72	S8
			100	252		

Ni_2P/Ni_5P_4	1 M KOH	CC	10 100	139 170	62	S9
$Ce_{0.10}$-NiCoP	1 M KOH	NF	10	96	94.75	S10
Ni_2P/Co_2P	1 M KOH	NF	10	66	48	S11
Ce-NiP	1 M KOH	NF	10 100	116 235	305.9	S12
Fe-Ni_2P@C	1 M KOH	NF	10 1000	75 313	45	S13
Y-NiP	1 M KOH	GP	10 500	50.6 160	55	S14
FeCoP/TiN	1 M KOH	CP	500	129	44.9	S15
Co/NiCoP	1 M KOH	-	50 300	295 361	92	S16
NiFeP@Ni_2P/MoO_x	1 M KOH	-	10 100 500 1000	80 232 332 390	131.04	S17

Table S2 The performance of TMP-based OER catalysts reported in recent literature

Material	electrolyte	electrode	Current density	Overpotential (mV)	Tafel slope (mV dec−1)	Reference
This work	1 M KOH	NF	10 100 300 500	207.2 287.0 359 413	67.7	
Ni_2P@C	1 M KOH	NF	10	279	79	S4
Cu-NiP_2	1 M KOH	NF	10	276	113	S5
Mn-NiP_2				271	129	
NPO/NiP	1 M KOH	NF	10	240	116	S6
$Ce_{0.10}$-NiCoP	1 M KOH	NF	10	218	72.12	S10
Ni_2P-R	1 M KOH	NF	50	379	27.41	S18
MnCr-NiCoP	1 M KOH	NF	10	234.8	50.4	S19
Fe-Ni2P	1 M KOH	NF	10	214	36.95	S20
Ce-NiP	1 M KOH	NF	10 50	276 337	96 93.9	S12
Ni_7Fe_3-Pi	1 M KOH	NF	10 100	189 286	46.37	S21
Fe-Ni_xP/RGO-M	1 M KOH	GCE	20 100	242 275	44.87	S22
Ni_2P/Fe(	1 M KOH	NF	10	240	57.25	S23

O)OH-40						
$(Ni_{0.83}Fe_{0.17})2P$	1 M KOH	NF	10	215	31.84	S24
P-NiCo-LDH	1 M KOH	NF	10	290	55.05	S25
NiFe:SSP	1 M KOH	FTO	10	248	31	S26
		NF	10	195	31	
Co/NiCoP	1 M KOH	-	300	430	64	S16
P-CoFe LDH	1 M KOH	NF	300	347	48.8	S27
P-CoO_X/NiFe LDH	1 M KOH	NF	300	265	38.7	S28
$Ni_2P/FePO_x$/RGO	1 M KOH	GC	100	291	53.8	S29
			500	367		
			1000	421		
Fe-Ni_2P-S/C	1 M KOH	GC	100	266	52.9	S30
			500	323		
			1000	357		
$Ce_{0.1}$-Fe_2P/NiCoP	1 M KOH	NF	500	280	55.3	S31
$NiCo_2S_4$@Fe_2P	1 M KOH	-	500	322	44	S32

Table S3 The performance of TMP-based catalysts in seawater electrolysis reported in recent literature.

Material	electrolyte	Reaction	Current density	Time (h)	Reference
This work	1 M KOH + seawater	seawater splitting	10 300	500	
V-$Ni_2P/Ni_{12}P_5$	Simulated seawater	HER	100	10	S1
Ni_3S_2/NiP_x	1 M KOH + 0.5 M NaCl	seawater splitting	100	200	S33
NiFeP/NiP	Alkaline seawater	seawater splitting	10	500	S34
CoP/Co2P	1 M KOH + 0.5 M NaCl	HER	10	25	S35
Ru-Co2P	Alkaline seawater	HER	50	30	S36
CNFMPO	1 M KOH + 0.5 M NaCl	seawater splitting	50	15	S37
Ru/C/NiCoP/NF	1 M KOH+0.5 M NaCl	seawater splitting	100	150	S38
Co2P-R	1 0 M KOH + seawater	seawater splitting	100	200	S39
Mn-FePV	Alkaline seawater	OER	100	100	S40
$Ni_2P/Co(PO_3)_2$	Alkaline seawater	HER	600	60	S41

Reference

S1. D. He, L. Cao, J. Huang, X. Zhang, C. Wang, K. Li, K. Kajiyoshi and L. Feng, Mol. Catal. 2024, **558**, 114046.

S2. M. S. Meera, S. Sasidharan, S. George and S. M. A. Shibli, Appl. Energy Mater. 2025, **8**, 6001-6015.

S3. J. Wang, F. Tian, L. Zhang, H. Zhang, J. Fan, L. Zhang, T. Xu and X. Cui, J. Colloid Interface Sci. 2024, **673**, 284-290.

S4. K. Yang, X. Liu, J. Xu, Y. Gong, S. Shen, J. Fan, X. Zhang and Y. Xue, P Prog. Nat. Sci. Mater. Int. 2024, **34**, 102-107.

S5. G. E. Ayom, M. D. Khan, F. M. de Souza, W. Lin, R. K. Gupta and N. Revaprasadu, J. Energy Storage 2024, **97**, 112882.

S6. P. Jiang, B. Zhou, R. He, Y. Li, N. Xu, J. Qiao and D. Ruan, J. Colloid Interface Sci. 2024, **669**, 927-934.

S7. Q. Sun, X. Hao, D. Zhang, T. Zhang, Y. Zhao, X. Huang and X. Liu, Energy Environ. Mater. 2024, **7**, e12726.

S8. R. Zhu, J. Zang, L. Dong, X. Tian, F. Sun, Q. Fu, Z. Zhuang and Y. Wang, Carbon, 2025, 120392.

S9. L. Huang, X. Wei, Y. Yu, D. Sun, Y. Qu, J. Wen, X. Yuan, Q. Su, F. Meng and G. Du, J. Mater. Sci. Technol. 2026, 242: 306-316.

S10. M. Zhang, H. Xu, H. Yang, X. Shang, M. Yuan, Y. Fu, Y. Xiao, S. Wang, X. Wang and B. Jia, Small, 2025, 2504837.

S11. T. Xu, D. Jiao, J. Fan, Y. Dong, Z. Jin, L. Zhang, W. Zhang, J. Zhao, W. Zheng and X. Cui, Carbon Energy, 2025, **7**, e668.

S12. S. Liu, Y. Ye, L. Gao, Z. Yan, H. Pan, Z. Wang, G. Zhang and X. Huang, Green Chem. 2025, **27**, 7307-7318.

S13. D. Li, Z. Li, R. Zou, G. Shi, Y. Huang, W. Yang, W. Yang, C. Liu and X. Peng, Appl. Catal. B Environ. Energy 2022, **307**, 121170.

S14. L. Yang, W. Gou, C. Cheng, Y. Tian, K. Qu, H. Sun, J. Chen, J. Sun and C.-P. Li, Appl. Surf. Sci. 2024, **654**, 159505.

S15. X. Yang, W. Guo, H. Xi, H. Pang, Y. Ma, X. Leng, C. Hou, L. Li, X. Huang and F. Meng, Adv. Funct. Mater. 2025, 2505078.

S16. Y. Lin, X. Cui, Y. Zhao, Z. Liu, G. Zhang and Y. Pan, Nano Res. 2023, **16**, 8765-8772.

S17. Y. Luo, S. Wu, P. Wang, H. Ranganathan and Z. Shi, J. Colloid Interface Sci. 2023, **648**, 551-557.

S18. X. Yu, X. Wang, P. He, G. Yang, F. Qin, Y. Yao, X. Cui and L. Ren, Energy Environ. Mater. 2025, e70101.

S19. Y. Zhang, M. Zhang, H. Zhang, D. Han, J. Wang, R. Yang, C. Zuo and X. Chen, Fuel, 2025, **396**, 135348.

S20. M. Yan, W. Liu, K. Xiang, Y. Li, Y. Zhang, J. Zhang, Y. Ren, Y. Sun, Y. Li and J. Liu, Inorg. Chem. 2025, **64**, 9807-9816.

S21. Y. Zhu, Q. Li, N. Li, M. Lv, F. Xue, M. Dong, K. Lin, J. Deng, J. Zeng and Q. Li, ACS Sustain. Chem. Eng. 2025, **13**, 12910-12919.

S22. Q. Ye, J. Wang, P. Guan, Y. Liu, D. Xu, Y. Zhao and Y. Cheng, J. Mater. Chem. A, 2025, **13**, 14293-14303.

S23. Y. Xing, S. Liu, Y. Liu, X. Xiao, Y. Li, Z. Wang, Y. Hu, B. Xin, H. Wang and C. Wang, Nano Energy, 2024, **123**, 109402.

S24. Z. Wang, S. Liu, J. Du, Y. Xing, Y. Hu, Y. Ma, X. Lu and C. Wang, Green Chem. 2024, **26**, 7779-7788.

S25. J. Zhang, E. Weatherspoon, A. S. Alsubaie, E. Burcar, A. DeMerle, Z. M. El-Bahy and Z. Wang, Adv. Compos. Hybrid Mater. 2025, **8**, 72.

S26. I. Mondal, J. N. Hausmann, S. Mebs, S. Kalra, G. Vijaykumar, K. Laun, I. Zebger, S. Selve, H. Dau and M. Driess, Adv. Energ. Mater. 2024, **14**, 2400809.

S27. G. Huang, Y. Wang, X. Ma, Y. Cao, B. Wei, L. Zhang, W. Chen, F. Ye, C. Xu and X. Du, J. Taiwan Inst. Chem. Eng. 2024, **163**, 105664.

S28. H. M. Xu, C. J. Huang, H. R. Zhu, Z. J. Zhang, T. Y. Shuai, Q. N. Zhan, V. Y. Fominski and G. R. Li, Small, 2024, **20**, 2400201.

S29. Y. Liu, L. Ji, D. Xu, Q. Ye, Y. Zhao and Y. Cheng, J. Colloid Interface Sci. 2025, **683**, 474-483.

S30. Z. Wang, K. Wang, Y. Pan, Q. Ye, C. Zhang, D. Zhang, Y. Zhao and Y. Cheng, J. Colloid

Interface Sci. 2025, **678**, 886-896.

S31. F. Zhang, K. Wang, H. Zhang, S. Yang, M. Xu, Y. He, L. Lei, P. Xie and X. Zhang, Adv. Funct. Mater. 2025, 2500861.

S32. A. B. Ali, T. A. Ahmed, F. Alimova, R. Jhala, P. R. Rao, J. Nanda, A. Painuly, A. Singh, A. S. Shaik and S. Islam, Synth. Met. 2025, 117962.

S33. J. Zhang, M. Sun, Y. Jiang, Y. Su, T. Zhao, Q. Lu and G. Yin, Chin. J. Chem. 2025, **43**, 3109-3118.

S34. S.-Y. Lu, L. Wang, C. Wu, J. Zhang, W. Dou, T. Hu, R. Wang, Y. Liu, Q. Yang and M. Jin, Inorg. Chem. Front. 2024, **11**, 3187-3199.

S35. J.-B. Chen, H. Wang, Y.-X. Xiao and J. Ying, Chem. Mater. 2025, **37**, 2145-2154.

S36. B. Jiang, H. Xiao, J. Li, H. Tang, H. Chen, S. Deng, Y. Tan, C. Yu, J. Wang and A. Huang, Small, 2025, **21**, 2406900.

S37. H.-M. Zhang, L. Zuo, Y. Gao, J. Guo, C. Zhu, J. Xu and J. Sun, J. Mater. Sci. Technol. 2024, **173**, 1-10.

S38. Z. Liu, X. Ning, A. Hao, M. F. Khan and S. Rehman, ChemSusChem, 2025, **18**, e202401197.

S39. X. Wang, T. Su, Z. Lu, L. Yu, N. Sha, C. Lv, Y. Xie and K. Ye, J J. Colloid Interface Sci. 2025, **691**, 137389.

S40. K. Wang, X. Liu, Q. Yu, X. Wang, J. Zhu, Y. Li, J. Chi, H. Lin and L. Wang, Small, 2024, **20**, 2308613.

S41. M. Zhang, W.-Z. Chen, Z. Liu, J. He and Y.-Q. Wang, Int. J. Hydrog. Energy. 2023, **48**, 17783-17800.