

Supporting information

Cl⁻ - Driven Pathway Switching Enables Efficient Industrial - Current Seawater Oxidation on Dual-Atom Catalysts

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Experimental Sections

Materials Characterization: Phase identification was performed using a Rigaku SmartLab-3 kW X-ray diffractometer with Cu K α radiation. Morphological analysis was conducted on a Hitachi S4800 field-emission scanning electron microscope (FESEM). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were acquired using a JEOL JEM-2100F microscope operated at 200 kV. The nanoparticles were scraped from nickel foam for TEM analysis. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo Scientific Escalab 250 Xi system. X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra were collected at the BL10C beamline of the Pohang Light Source (PLS-II, Korea).

Seawater Treatment: The procedure for removing Ca²⁺ and Mg²⁺ from natural seawater is as follows: 2 L of raw seawater (collected from the coast of Qingdao, China) was first filtered to remove suspended particles and sediment. 120 g of KOH solid (excess) was weighed and added slowly, in small portions, to the seawater under continuous magnetic stirring. During addition, a white turbidity appeared immediately due to the formation of Ca(OH)₂ and Mg(OH)₂ precipitates. After complete dissolution of KOH, stirring was continued for another 1–2 min, then the mixture was allowed to stand for 5–10 min to allow the precipitates to settle. The supernatant was then filtered to obtain seawater depleted of Ca²⁺ and Mg²⁺. This treated seawater was used directly for the preparation of alkaline seawater electrolyte (1 M KOH + treated seawater).

Electrochemical Measurements: All electrochemical tests were performed using a Corrtest electrochemical workstation in a standard three-electrode setup. A graphite rod and a saturated Hg/HgO electrode served as the counter and reference electrodes, respectively. The catalyst grown in situ on NF (1 × 1 cm²) was used as the working electrode. All potentials were calibrated to the reversible hydrogen electrode (RHE) scale and corrected with 80% iR compensation. The electrolytes were 1 M KOH for the oxygen evolution reaction (OER) and 1 M KOH + 0.5 M NaCl

for chloride-assisted OER tests. Linear sweep voltammetry (LSV) was conducted at a scan rate of 10 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) was measured from 0.1 Hz to 100 kHz. The double-layer capacitance (C_{dl}) was determined via cyclic voltammetry at scan rates ranging from 20 to 120 mV s⁻¹. Long-term stability was evaluated by chronopotentiometry at a constant current density of 500 mA cm⁻². The flow electrolyzer system (Wuhan Zhisheng New Energy Co., Ltd.) was configured with an OER catalyst (RuCr-Ni₃P) and an HER catalyst (PtRuC), the latter being ultrasonically sprayed onto an anion exchange membrane at a loading of 2 mg cm⁻². Carbon paper served as the cathode gas diffusion layer (4 × 4 cm²), with an active area of 2 × 2 cm². A commercial PiperION-A membrane (thickness: 40 μm) was employed as the anion exchange membrane. The performance of the assembled flow electrolyzer was evaluated under flowing alkaline natural seawater solution.

All potentials measured against the Hg/HgO reference electrode were converted to the reversible hydrogen electrode (RHE) scale using the following equation:

$$E_{RHE} = E_{Hg/HgO} + 0.0977 + 0.059 \times pH$$

where: $E_{Hg/HgO}$ is the experimentally measured potential against the Hg/HgO reference electrode; 0.098 V is the standard potential of Hg/HgO reference electrode in 1 M KOH at 25 °C; pH is the pH value of the electrolyte; The conversion was performed at 25 °C (room temperature), and all electrochemical tests were conducted at this temperature.

Computational Details: It specifies that all spin-polarized DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP) with the projector-augmented wave (PAW) method. The Perdew-Burke-Ernzerhof (PBE) functional was employed for the exchange-correlation potential. The energy cutoff was set to 500 eV, and a Gamma-centered k-point grid of 3×3×1 was used for structure optimization. The slab model consisted of four atomic layers with a vacuum thickness of 15 Å to avoid interactions between periodic images. These parameters are now clearly stated to ensure reproducibility.

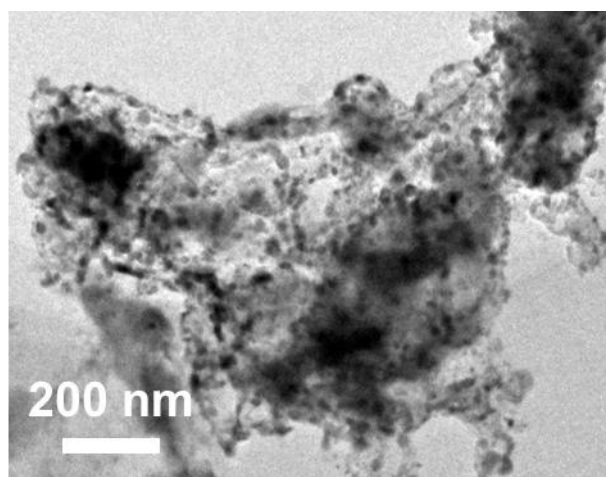


Figure S1. TEM image of synthesized RuCr-Ni₃P catalyst.

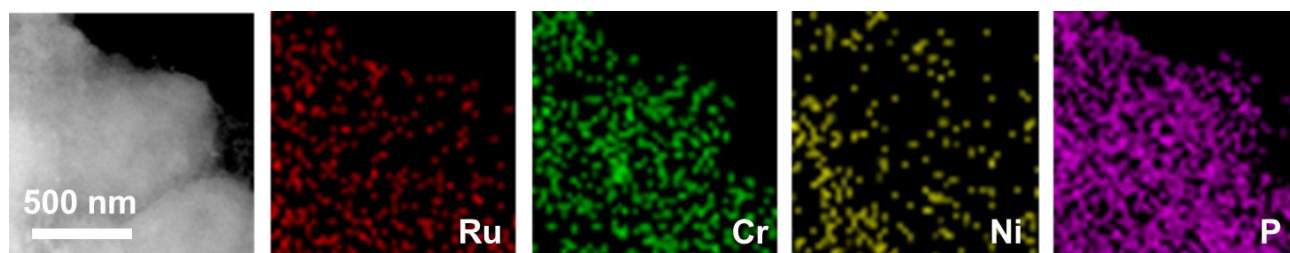


Figure S2. EDS elemental mapping of RuCr-Ni₃P catalyst.

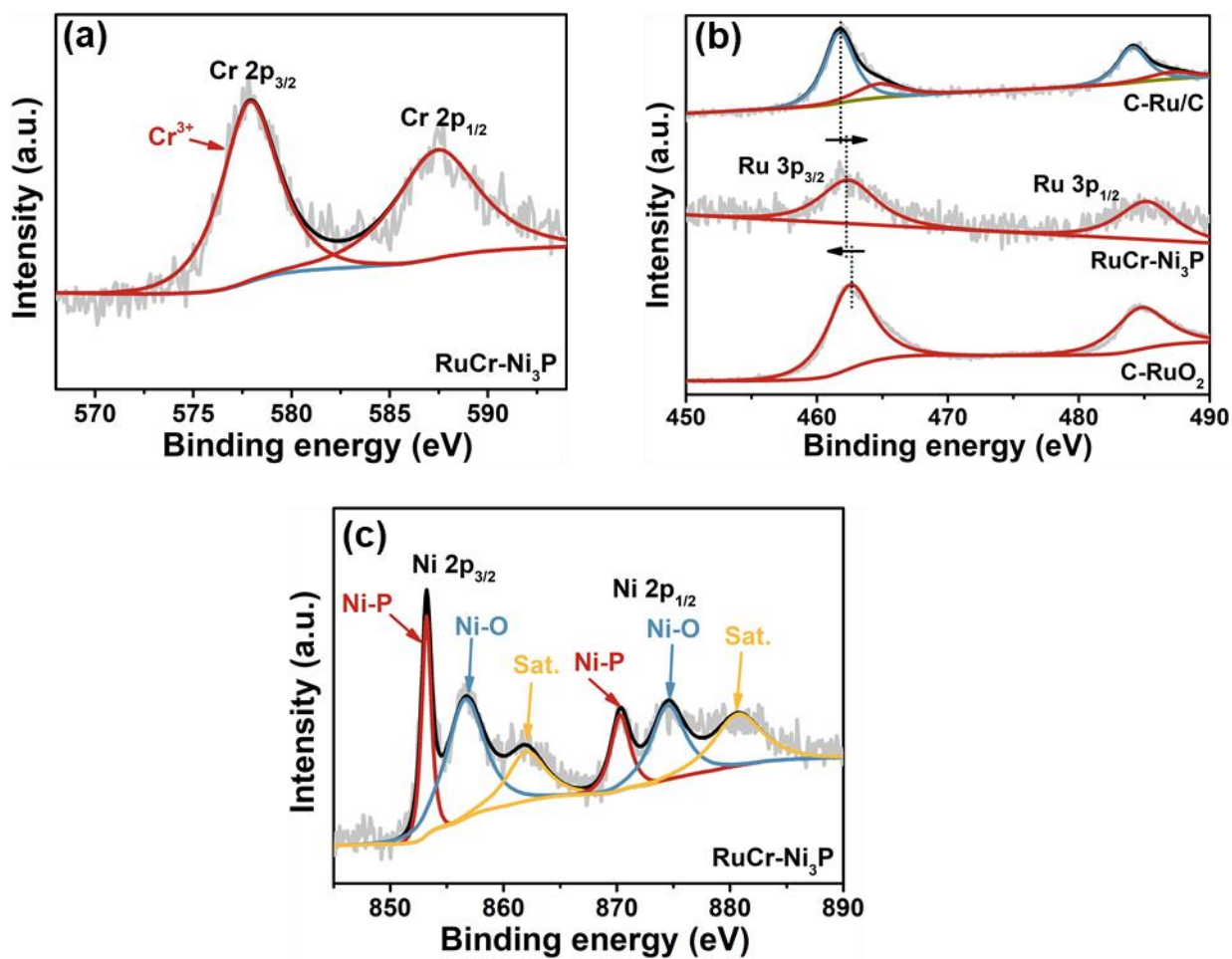


Figure S3. (a) Cr 2p, (b) Ru 3p, and (c) Ni 2p XPS spectra of RuCr-Ni₃P catalyst.

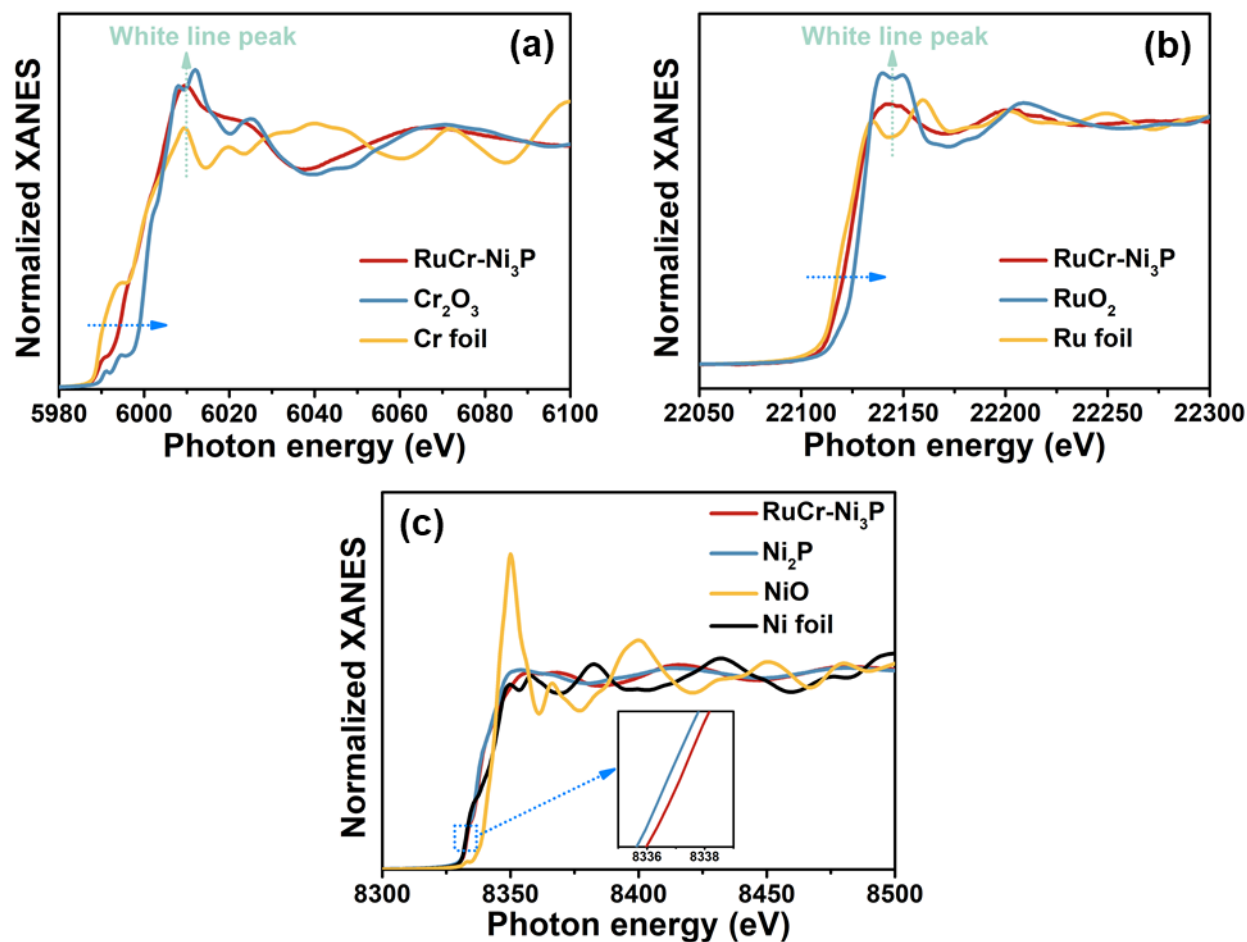


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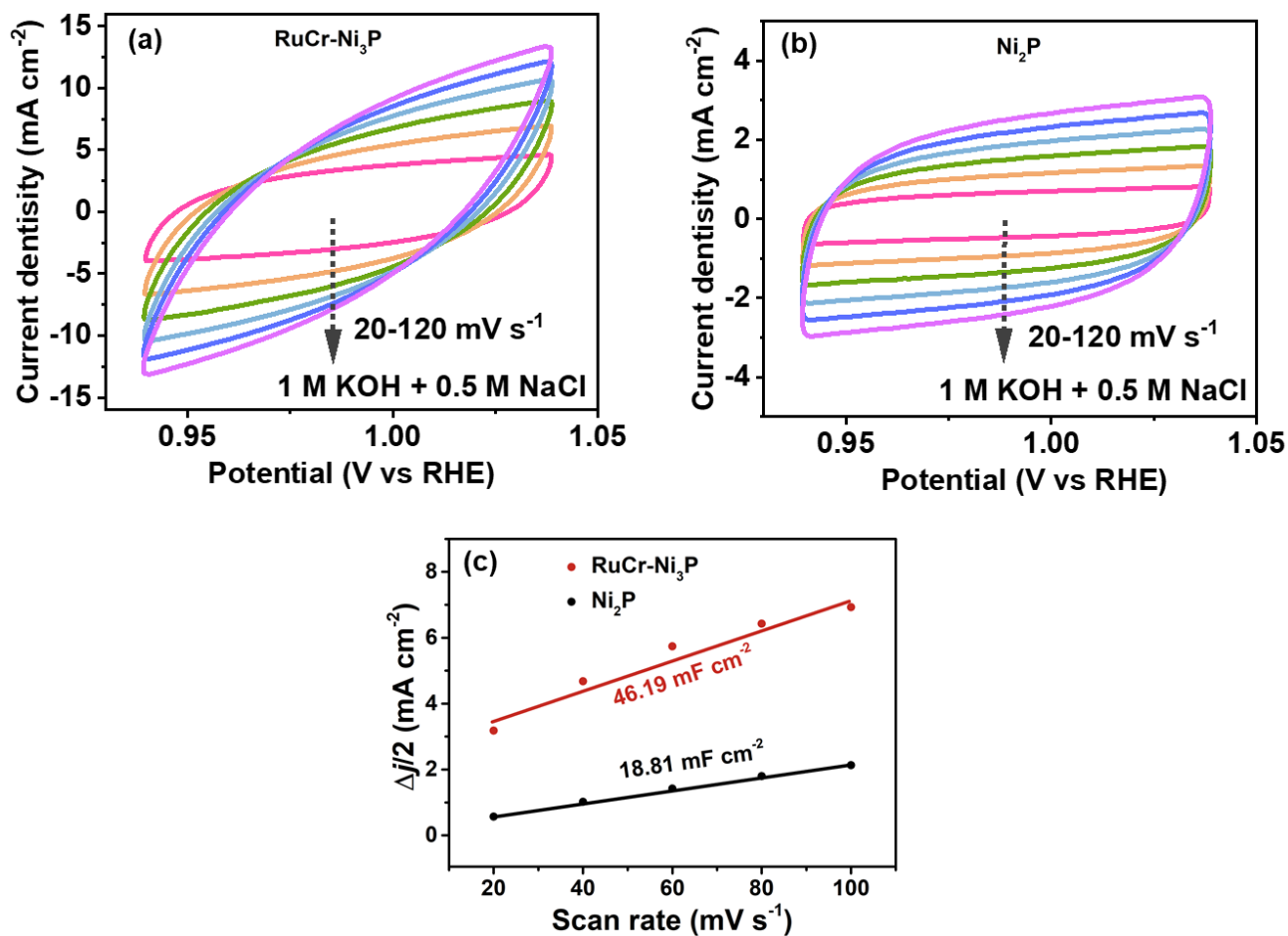


Figure S5. Cyclic voltammetry curves at various scan rates ranging from 20 to 120 mV s⁻¹ within the non-Faradaic electrode potential range for (a) RuCr-Ni₃P and (b) Ni₂P. (c) Electrochemical active surface area (ECSA).

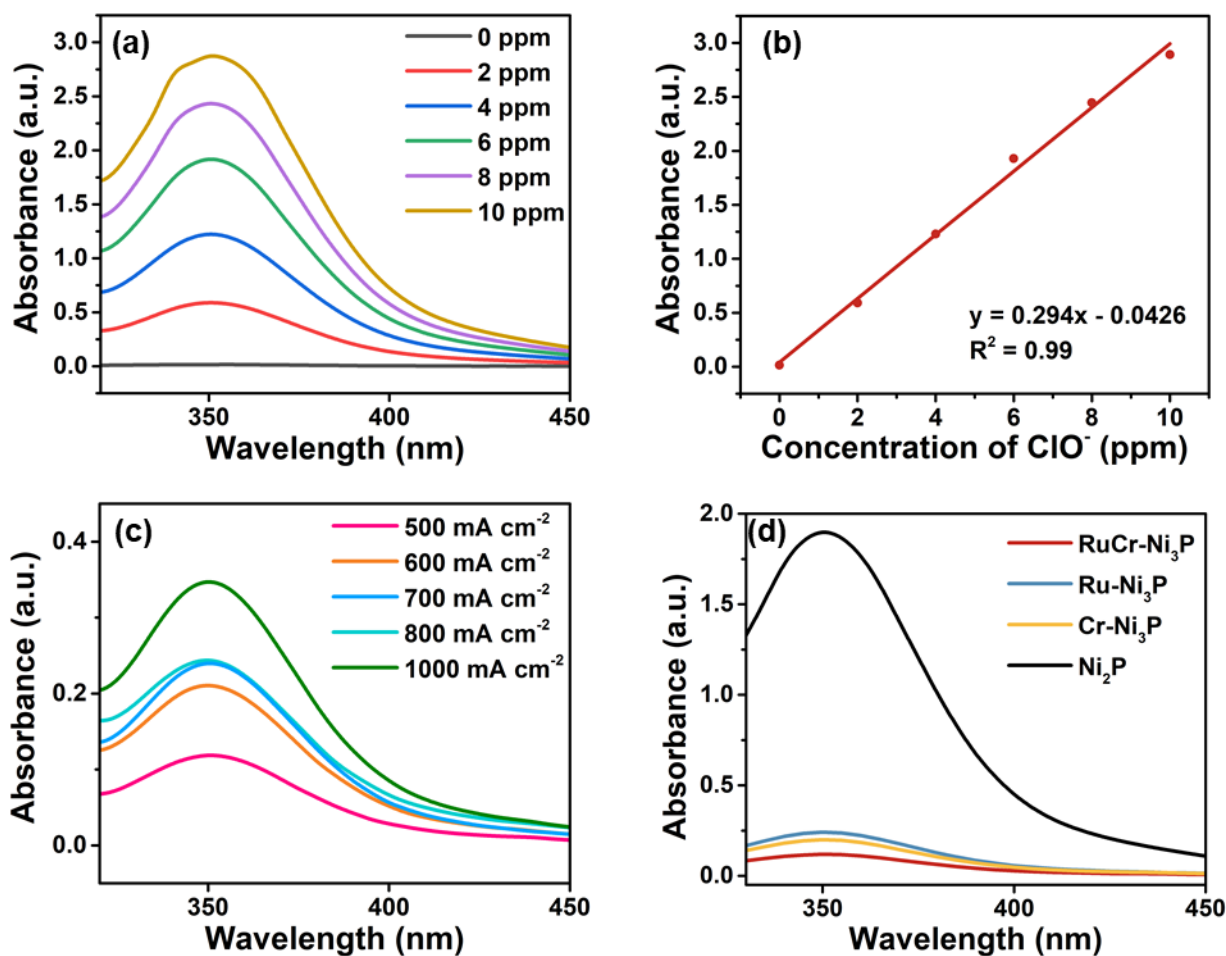


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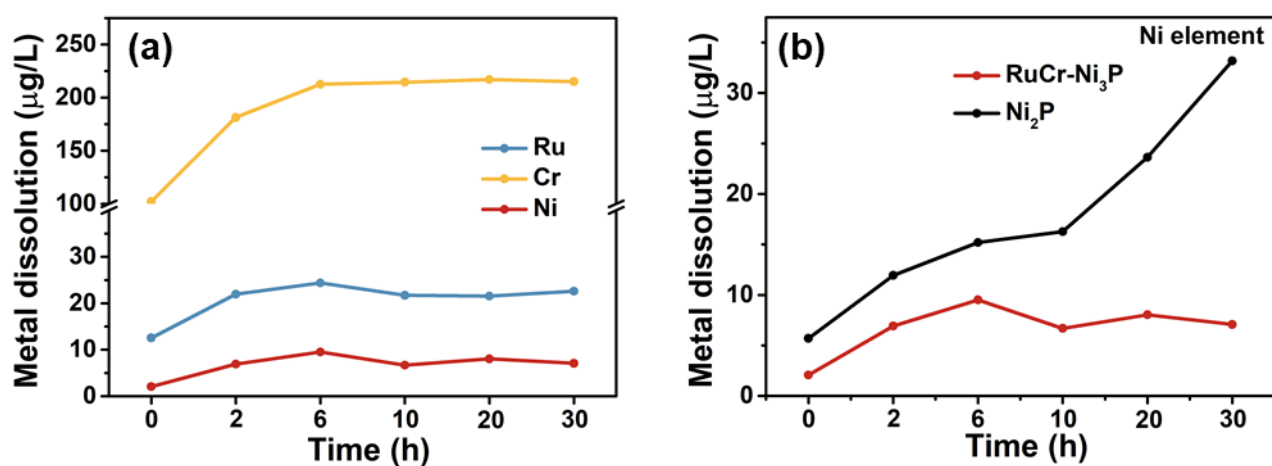


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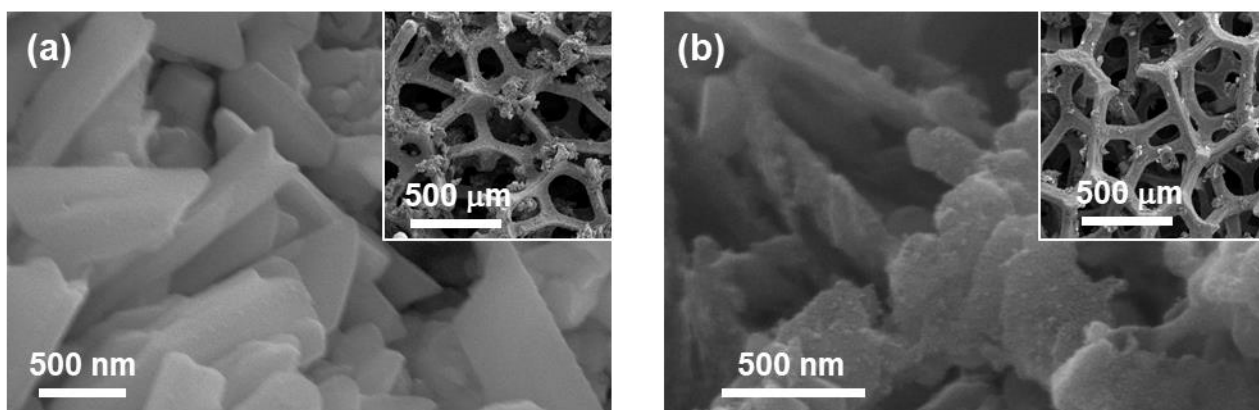


Figure S8. SEM images of RuCr-Ni₃P (a) before and (b) after testing.

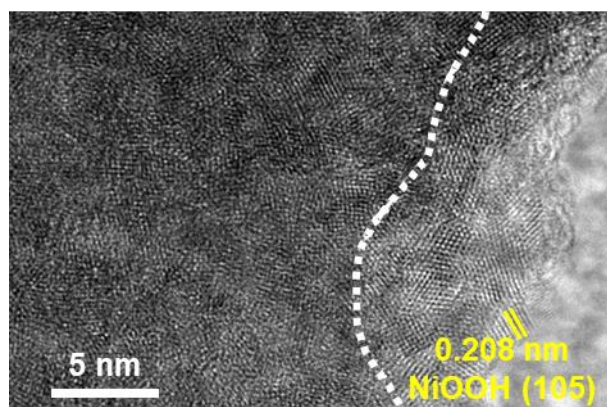


Figure S9. HRTEM image of RuCr-Ni₃P after testing.

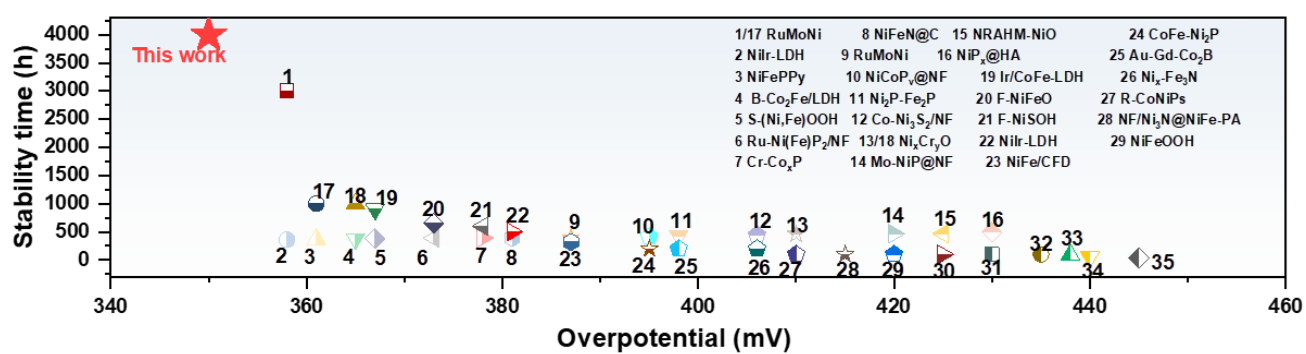


Figure S10. Benchmarking of overpotential and stability at 500 mA cm⁻² against reported OER catalysts.

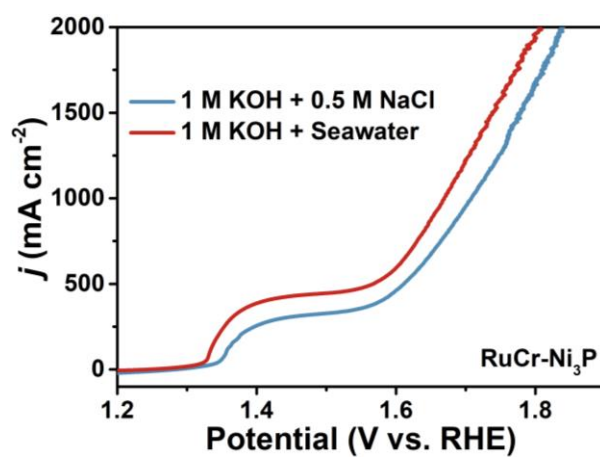


Figure S11. LSV curves of RuCr-Ni₃P and reference catalysts in 1 M KOH + 0.5 M NaCl and 1 M KOH + seawater electrolyte.

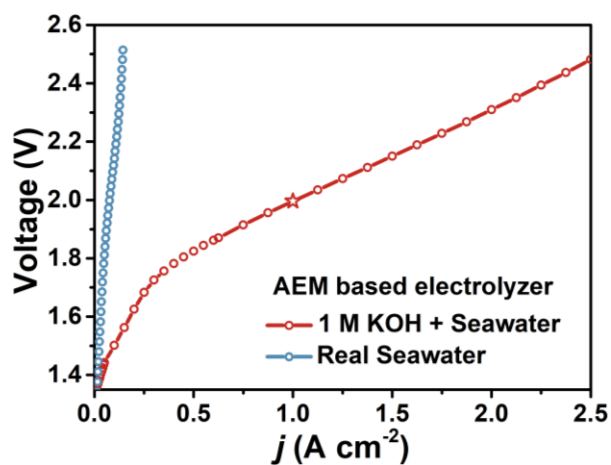


Figure S12. Polarization curves of AEM electrolyzer with RuCr-Ni₃P anode and PtRu/C cathode in different seawater electrolytes: untreated natural seawater (neutral, no KOH added) and alkaline treated seawater (1 M KOH + seawater after Ca²⁺/Mg²⁺ removal).

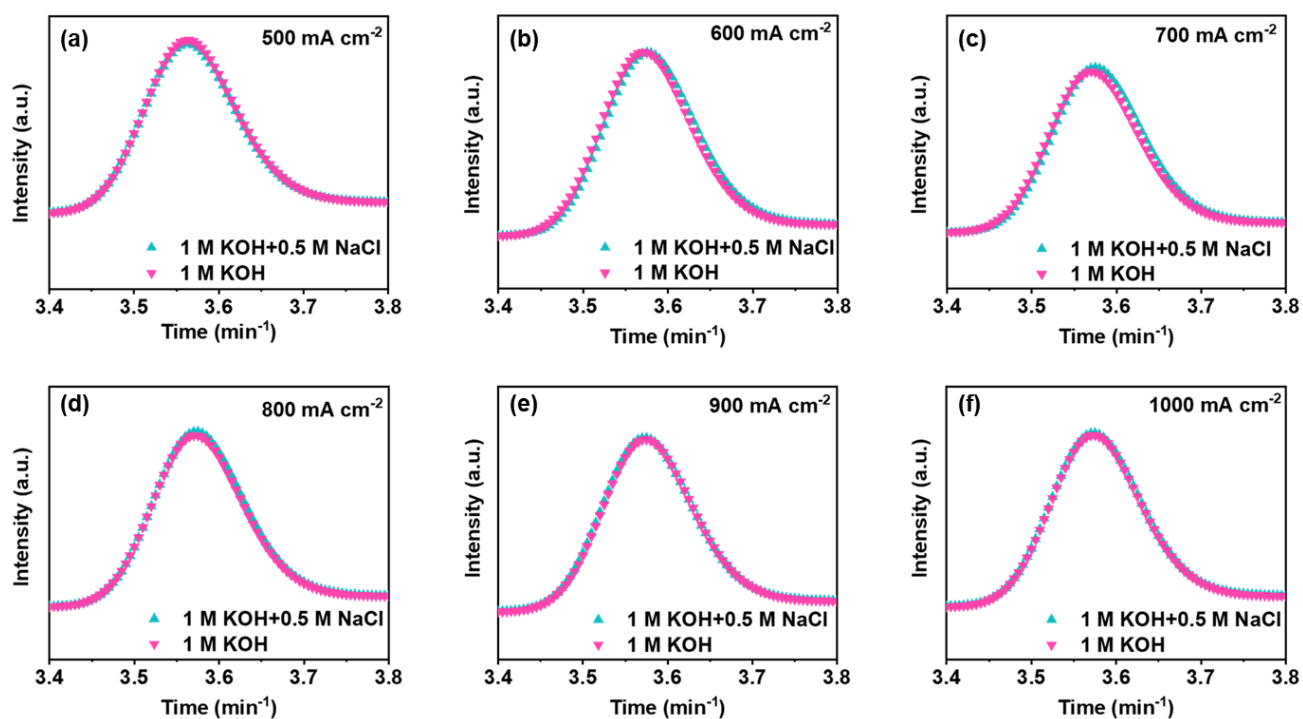


Figure S13. Gas chromatography O_2 signal collected from the electrolyzer operating at (a) 500 mA cm^{-2} , (b) 600 mA cm^{-2} , (c) 700 mA cm^{-2} , (d) 800 mA cm^{-2} , (e) 900 mA cm^{-2} , and (f) 1000 mA cm^{-2} .

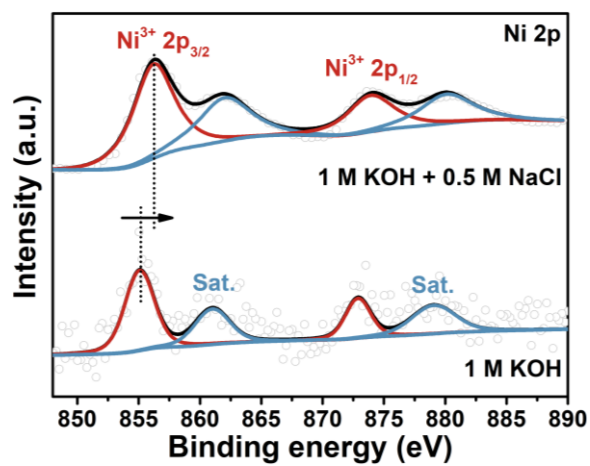


Figure S14. High-resolution Ni 2p XPS spectrum of RuCr-Ni₃P after activation.

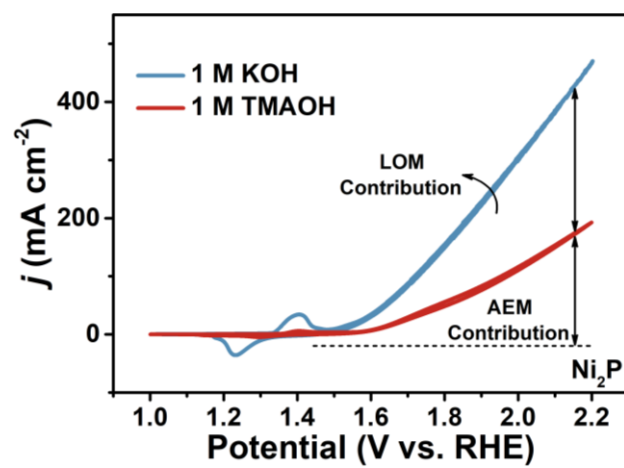


Figure S15. CV curves of Ni_2P in Cl^- -free electrolyte before and after adding TMA^+ .

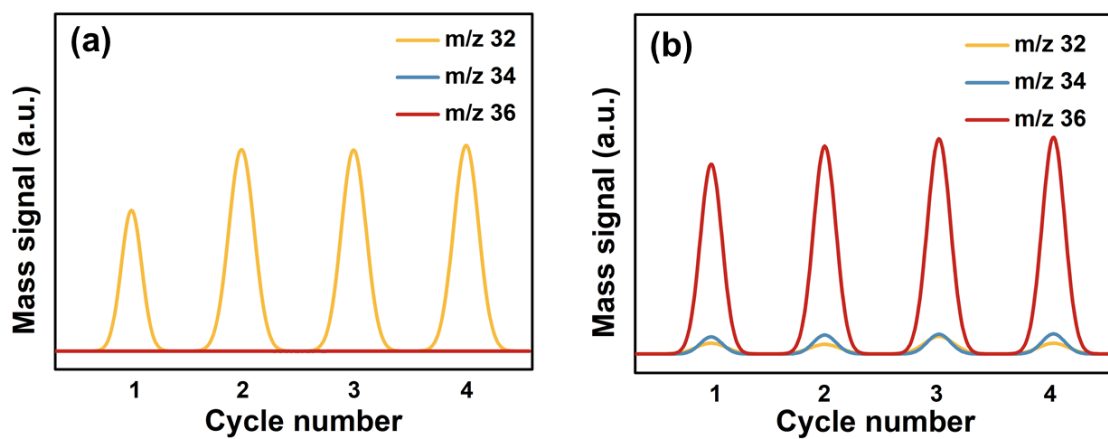


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Reference:

- [1] X. Kang, F. Yang, Z. Zhang, H. Liu, S. Ge, S. Hu, S. Li, Y. Luo, Q. Yu, Z. Liu, Q. Wang, W. Ren, C. Sun, H. M. Cheng, B. Liu, *Nat. Commun.* **2023**, *14*, 3607.
- [2] H. You, D. Wu, D. Si, M. Cao, F. Sun, H. Zhang, H. Wang, T. F. Liu, R. Cao, *J. Am. Chem. Soc.* **2022**, *144*, 9254.
- [3] X. Wang, F. Liu, H. Qin, J. Li, X. Chen, K. Liu, T. Zhao, W. Yang, M. Yu, G. Fan, F. Cheng, *Angew. Chem. Int. Ed.* **2024**, *63*, e202409628.
- [4] L. Wu, L. Yu, Q. Zhu, B. McElhenny, F. Zhang, C. Wu, X. Xing, J. Bao, S. Chen, Z. Ren, *Nano Energy* **2021**, *83*, 105838.
- [5] L. Yu, L. Wu, B. McElhenny, S. Song, D. Luo, F. Zhang, Y. Yu, S. Chen, Z. Ren, *Energy Environ. Sci.* **2020**, *13*, 3439.
- [6] D. Wu, B. Liu, R. Li, D. Chen, W. Zeng, H. Zhao, Y. Yao, R. Qin, J. Yu, L. Chen, J. Zhang, B. Li, S. Mu, *Small* **2023**, *19*, e2300030.
- [7] Y. Song, M. Sun, S. Zhang, X. Zhang, P. Yi, J. Liu, B. Huang, M. Huang, L. Zhang, *Adv. Funct. Mater.* **2023**, *33*.
- [8] B. Wang, M. Lu, D. Chen, Q. Zhang, W. Wang, Y. Kang, Z. Fang, G. Pang, S. Feng, *J. Mater. Chem. A* **2021**, *9*, 13562.
- [9] L. Guo, J. Chi, T. Cui, J. Zhu, Y. Xia, H. Guo, J. Lai, L. Wang, *Adv. Energy Mater.* **2024**, *14*, 2400975.
- [10] L. Wu, L. Yu, F. Zhang, B. McElhenny, D. Luo, A. Karim, S. Chen, Z. Ren, *Adv. Funct. Mater.* **2020**, *31*, 2006484.
- [11] M. Yue, X. He, S. Sun, Y. Sun, M. S. Hamdy, M. Benaissa, A. A. M. Salih, J. Liu, X. Sun, *Nano Res.* **2023**, *17*, 1050.
- [12] A. Malek, Y. Xue, X. Lu, *Angew. Chem. Int. Ed.* **2023**, *62*, e202309854.

- [13] W. Hao, X. Ma, L. Wang, Y. Guo, Q. Bi, J. Fan, H. Li, G. Li, *Adv. Energy Mater.* **2025**, *15*, 2403009.
- [14] K. Hemmati, A. Kumar, A. R. Jadhav, O. Moradlou, A. Z. Moshfegh, H. Lee, *ACS Catal.* **2023**, *13*, 5516.
- [15] C. Fu, W. Hao, J. Fan, Q. Zhang, Y. Guo, J. Fan, Z. Chen, G. Li, *Small* **2023**, *19*, e2205689.
- [16] Y. Zhang, W. Zhang, X. Zhang, X. Wang, J. Wang, Q. Zhao, Y. Sun, J. Li, G. Liu, X. Han, *Energy Environ. Sci.* **2024**, *17*, 3347.
- [17] L. Yu, J. Xiao, C. Huang, J. Zhou, M. Qiu, Y. Yu, Z. Ren, C. W. Chu, J. C. Yu, *PNAS* **2022**, *119*, e2202382119.
- [18] L. Liao, D. Li, Y. Zhang, Y. Zhang, F. Yu, L. Yang, X. Wang, D. Tang, H. Zhou, *Adv. Mater.* **2024**, *36*, e2405852.
- [19] C. Huang, Q. Zhou, L. Yu, D. Duan, T. Cao, S. Qiu, Z. Wang, J. Guo, Y. Xie, L. Li, Y. Yu, *Adv. Energy Mater.* **2023**, *13*, 2301475.
- [20] Y. Yu, W. Zhou, X. Zhou, J. Yuan, X. Zhang, L. Wang, J. Li, X. Meng, F. Sun, J. Gao, G. Zhao, *ACS Catal.* **2024**, *14*, 18322.
- [21] T. u. Haq, M. Pasha, Y. Tong, S. A. Mansour, Y. Haik, *Appl. Catal., B* **2022**, *301*, 120836.
- [22] G. Wang, W. Tang, Y. Chen, P. Ji, M. Lu, H. Wei, L. Cui, X. Chen, G. Wang, *Adv. Funct. Mater.* **2024**, *34*, 2404470.
- [23] F. Luo, P. Yu, J. Xiang, J. Jiang, S. Chen, *J. Energy Chem.* **2024**, *94*, 508.
- [24] P. Li, S. Zhao, Y. Huang, Q. Huang, B. Xi, X. An, S. Xiong, *Adv. Energy Mater.* **2024**, *14*, 2303360.
- [25] G. Chang, Y. Zhou, J. Wang, H. Zhang, P. Yan, H. B. Wu, X. Y. Yu, *Small* **2023**, *19*, e2206768.
- [26] L. Wu, F. Zhang, S. Song, M. Ning, Q. Zhu, J. Zhou, G. Gao, Z. Chen, Q. Zhou, X. Xing, T. Tong, Y. Yao, J. Bao, L. Yu, S. Chen, Z. Ren, *Adv. Mater.* **2022**, *34*, e2201774.

- [27] L. Yu, Q. Zhu, S. Song, B. McElhenny, D. Wang, C. Wu, Z. Qin, J. Bao, Y. Yu, S. Chen, Z. Ren, *Nat. Commun.* **2019**, *10*, 5106.
- [28] C. Huang, Q. Zhou, D. Duan, L. Yu, W. Zhang, Z. Wang, J. Liu, B. Peng, P. An, J. Zhang, L. Li, J. Yu, Y. Yu, *Energy Environ. Sci.* **2022**, *15*, 4647.
- [29] M. Ning, L. Wu, F. Zhang, D. Wang, S. Song, T. Tong, J. Bao, S. Chen, L. Yu, Z. Ren, *Mater. Today Phys.* **2021**, *19*, 100419.