

Supporting Information

Evaluating the Stability of Co₂P Electrocatalysts

for the Hydrogen Evolution Reaction in both Acidic and Alkaline Electrolytes

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Experimental Details

Materials: Cobalt chloride (>98%, Sigma-Aldrich), sodium hypophosphite monohydrate (>99%, Aldrich), sodium acetate (>99%, Merck), acetic acid (glacial, 100%, Merck), nitric acid (>65%, Sigma-Aldrich), sulfuric acid (99.999 %, Sigma-Aldrich), potassium hydroxide (AP, max. 0.002% Na, Merck) were purchased from commercial vendors and used as received. Support material is porous carbon paper (CP, Spectracarb™ 2050A 2050GDL). Milli-Q water (18.2 M Ω ·cm) was used in all cleaning steps and for preparation of solutions.

Preparation of Co₂P on carbon paper (Co₂P@CP): Prior to electrodeposition, the carbon paper was pre-treated in concentrated nitric acid at 50 °C for 25 mins, followed by rinsing with water to remove residual organic species and to increase hydrophilicity of the carbon paper. The pre-treated electrodes were immersed in the electrodeposition solution (50 mM CoCl₂, 1 M NaH₂PO₂, and 0.1 M NaOAc in water). Nitrogen was bubbled through the electrolyte solution for at least 20 min prior to deposition and maintained during the entire deposition process. The potential of was cycled 10 times between -0.35 and -1.05 V vs. a standard calomel electrode (SCE, E_{RE} = +0.274 V) at a scan rate of 5 mV/s. After electrodeposition, the electrode was gently rinsed with copious amounts of Milli-Q water. Thermal phosphidization of the electrodeposited sample, mixture of CoP_x, CoOOH and Co₂(PO₄)₃, was carried out in a horizontal calcination tube furnace with a quartz boat containing 2.5 g of NaH₂PO₂·H₂O used as P precursor. The boat was located upstream and a 100% H₂ flow of 150 mL/min STP was introduced. The reactor was heated to 260 °C (10 °C/min) to dehydrate sodium hypophosphite followed by a further temperature increase to 350 °C with a slower heating rate (2 °C/min). The reactor was then kept at 350 °C for 3 h while maintaining H₂ flow. Upon thermal decomposition, sodium hypophosphite releases PH₃ which further reacts with the electrodeposited precursor to form cobalt phosphide Co₂P@CP. The samples were let to cool down to room temperature in the same gas composition. Thermally treated samples were rapidly transferred into a glovebox. The amount of Co₂P catalyst deposited on the substrate is around 3.2±0.1 mg/cm².

Electrochemical measurements: Electrochemical experiments were performed in a two-compartment electrochemical cell separated by a glass frit using a Metrohm Autolab PGSTAT302N. A saturated calomel electrode (SCE) (for electrodeposition) and a Red Rod electrode (Hach XR440, Radiometer Analytical, E_{RE} = +0.486 V, for stability tests) were used as reference electrode (RE) and a Pt plate (1 cm²) as counter electrode (CE). All potentials reported in this paper were converted to reversible hydrogen electrode (RHE) unless otherwise specified. The series resistance of the electrochemical cell was measured before each experiment using electrochemical impedance spectroscopy. The measured series resistance was approximately 2.1 Ω in 0.5 M H₂SO₄ and 1.6 Ω in 1 M KOH, respectively. iR-drop correction was applied in each experiment. Hydrogen was bubbled through the electrolyte solutions for at least 20 min prior to the activity test and maintained during the entire measurement. The electrochemical activity of the cobalt phosphides was measured by linear sweep voltammetry (LSV) at a scan rate of 2 mV/s.

The onset potential was chosen at open-circuit potential (OCP, +0.05 V in acid and +0.25 V in alkaline). The lower limit of the potential was selected at the geometric current density of 50 mA/cm⁻² in order to avoid influence of H₂ bubbles. The stability of the catalyst films was assessed by repeated LSV scans between 0 V and -0.20 V vs. RHE at 100 mV/s for 2000 sweeps. This potential range was chosen to avoid serious bubble formation and possible Pt leaching from the counter electrode. The total duration of the stability test including activity assessment and other electrochemical measurements was about 5 h. The bare carbon paper did not show any measurable HER activity within the investigated potential window. The electrochemical surface area (ECSA) was calculated based on the electrochemical double layer capacitance C_{dl} . To measure C_{dl} of the samples, the potential was swept with a span of 100 mV, with OCP at center (0 V vs. RHE in acid; ~0.2 V vs. RHE in alkaline), and repeated three times at each of five different scan rates (50, 100, 150, 200 and 250 mV/s). The specific capacitance (C_s) was chosen as $C_s = 0.035 \text{ mF cm}^{-2}$ in 0.5 M H₂SO₄ and $C_s = 0.040 \text{ mF cm}^{-2}$ in 1 M KOH based on reported values.¹ The number of replicates for each experiment was three to six.

Materials Characterization: X-ray photoelectron spectroscopy (XPS) measurements were carried out on a K-Alpha XP spectrometer (Thermo Scientific), equipped with a monochromatic X-ray source (Al K α = 1486.6 eV). High-resolution spectra of core levels (Co 2p, P 2p, O 1s) and wide-range survey spectra were recorded with a pass energy of 50 eV and 200 eV, respectively. Powder XRD patterns were recorded on a Bruker D2 PHASER X-ray diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). Raman spectra were recorded on a Renishaw Raman microscope equipped with a 514 nm laser, using a 1800 lines/mm grating, and a CCD detector. For each scan, 5 accumulations with acquisition time of 90 s were taken. The SEM images and EDX spectra were obtained by a FEI Quanta 3D FEG with an Oxford Instruments EDX detector. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) measurements were performed on SPECTROBLUE EOP spectrometer equipped with an axial plasma source (Ar). Sample uptake rate was set to 2 ml/min. The emission intensity of Co ions was measured at 228.6 and 238.9 nm, for P ions at 177.5 and 178.3 nm.

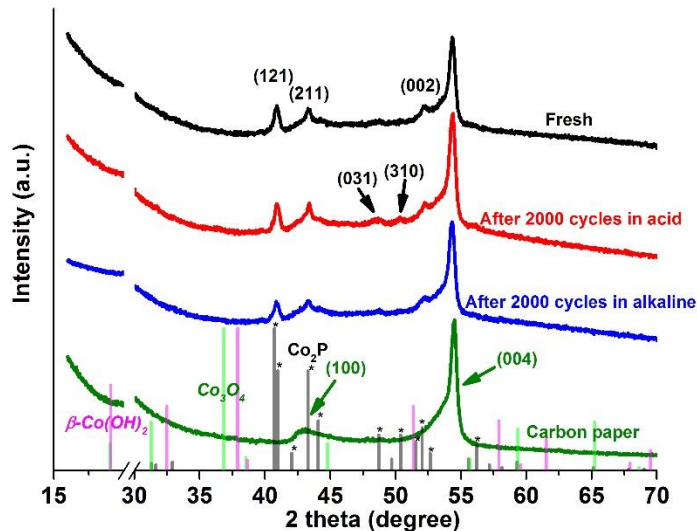


Figure S1. XRD patterns for as-synthesized $\text{Co}_2\text{P@CP}$ (black), $\text{Co}_2\text{P@CP}$ after stability test in acid (red), $\text{Co}_2\text{P@CP}$ after stability test in alkaline (blue), and carbon paper substrate (green). The 2θ range from $20\text{-}30^\circ$ was skipped to avoid the strongest peak of the carbon paper substrate. Grey bars marked with an asterisk (*) correspond to Co_2P (PDF No.: 00-032-0306), pink bars to $\beta\text{-Co(OH)}_2$ (PDF No.: 00-030-0433), and green bars to Co_3O_4 (PDF No.: 00-042-1467).

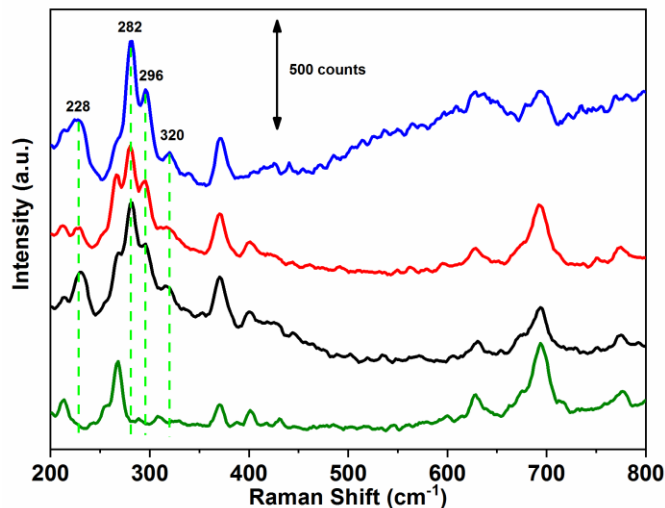


Figure S2. Raman spectra ($\lambda_{ex} = 514 \text{ nm}$) of fresh $\text{Co}_2\text{P@CP}$ (black), $\text{Co}_2\text{P@CP}$ after stability test in acid (red), $\text{Co}_2\text{P@CP}$ after stability test in alkaline (blue), and carbon paper substrate (green). The peaks at 228, 282, 296 and 320 cm^{-1} are attributed to cobalt phosphide.^{2,3}

Table S1. EDX analysis of as-synthesized $\text{Co}_2\text{P@CP}$, $\text{Co}_2\text{P@CP}$ after stability test in acid and alkaline.

Sample	Ratio of Co : P
Fresh	2.0 ± 0.1
After 2000 sweeps in acid	1.8 ± 0.1
After 2000 sweeps in alkaline	2.2 ± 0.1

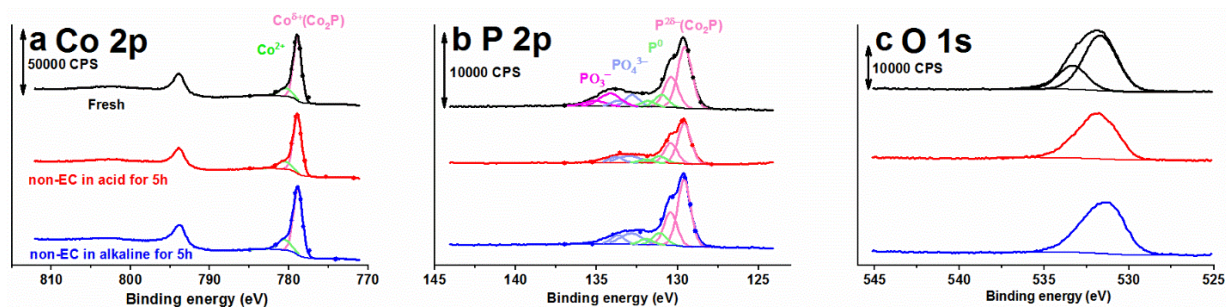


Figure S3. XPS of the a) Co 2p region, b) P 2p region and c) O 1s region of fresh $\text{Co}_2\text{P@CP}$ (black line) and after immersion for 5 h in 0.5 M H_2SO_4 (red line) and 1 M KOH (blue line) solutions.

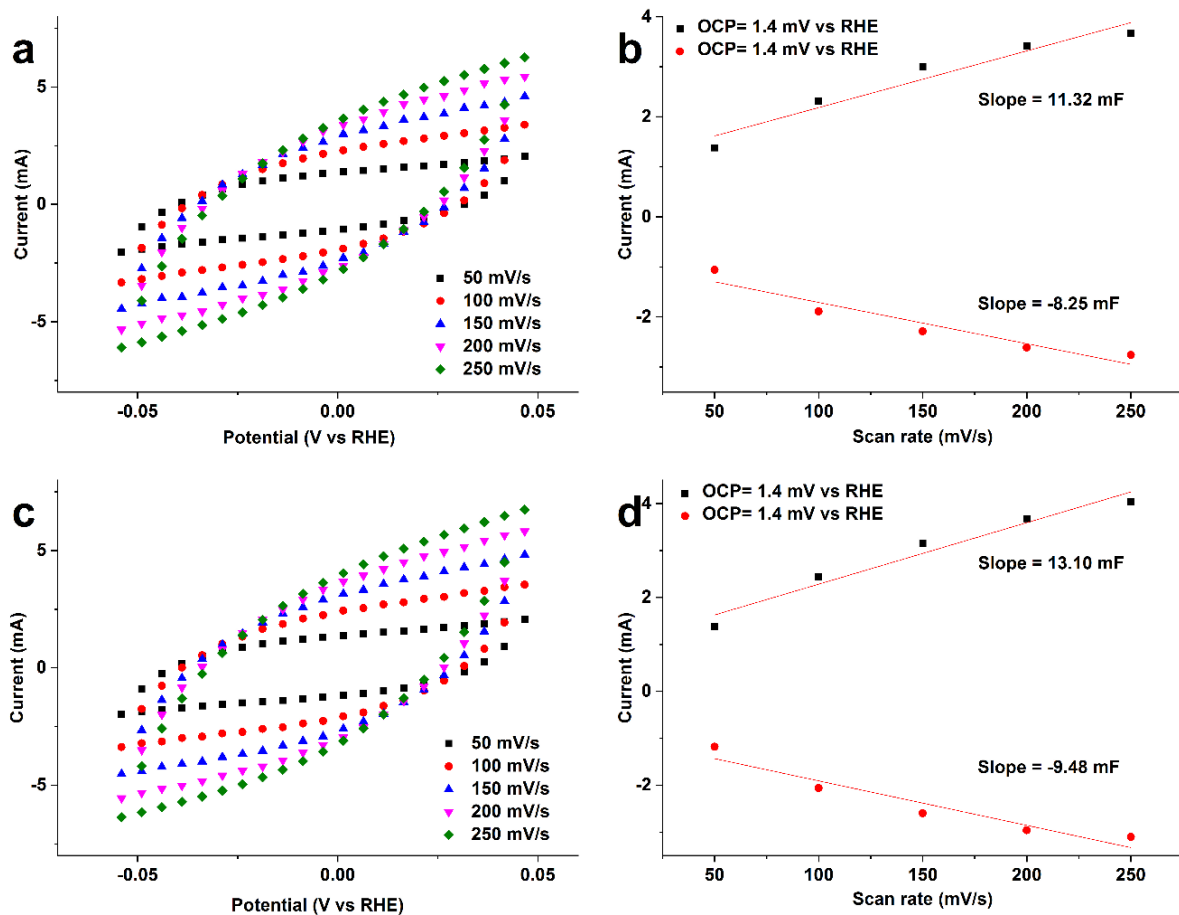


Figure S4. Double layer capacitance measurements for determining electrochemical active surface area (ECSA) for Co₂P@CP before (a, b) and after (c, d) stability tests in 0.5 M H₂SO₄. (a, c) Cyclic voltammograms were measured in a non-Faradaic region of the voltammogram at the following scan rates: 50, 100, 150, 200, 250 mV/s. (b, d) Cathodic and anodic charging currents measured at OCP vs. RHE plotted as a function of scan rate.

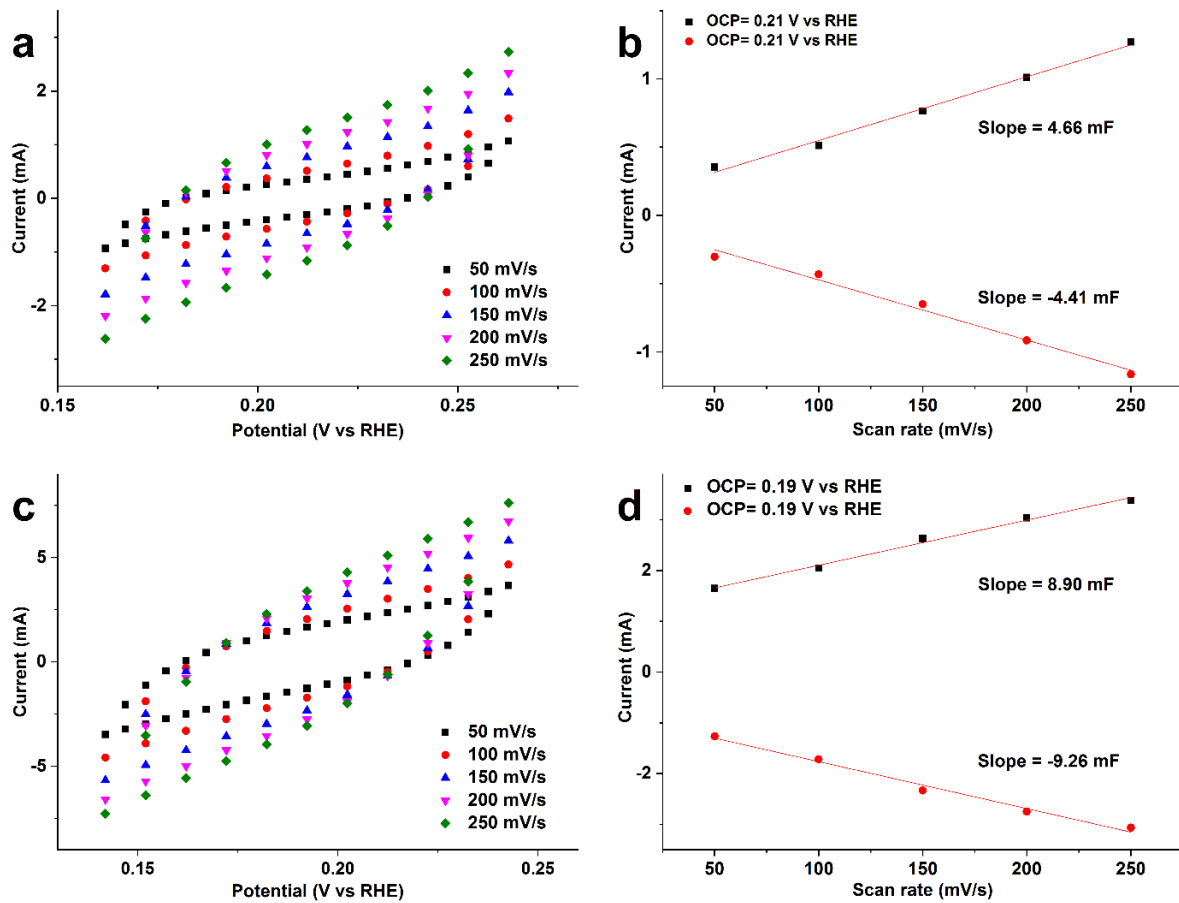


Figure S5. Double layer capacitance measurements for determining electrochemical active surface area (ECSA) for Co₂P@CP before (a, b) and after (c, d) stability tests in 1 M KOH. (a, c) Cyclic voltammograms were measured in a non-Faradaic region of the voltammogram at the following scan rates: 50, 100, 150, 200, 250 mV/s. (b, d) Cathodic and anodic charging currents measured at OCP vs. RHE plotted as a function of scan rate.

Electrochemically active surface area (ECSA) calculation

To measure the electrochemical double layer capacitance of the samples, the potential was swept with a span of 100 mV, where the OCP locates in the center (0 V vs. RHE in acid; ~ 0.2 V vs. RHE in alkaline electrolyte), and repeated three times at each of five different scan rates (50, 100, 150, 200 and 250 mV/s). In these regions, the integrated charge should be due to the charging of the electrode–electrolyte double layer. The double layer charging current i , normalized on the geometric area of the electrode, is directly proportional to the scan rate v :

$$i = vC_{dl}$$

C_{dl} was derived as the average value of linear fitted slope by plotting both the anodic and cathodic current against the scan rate. In our case, capacitive currents were measured at related OCP vs. RHE for Co₂P@CP before and after stability tests in both electrolytes (Fig. S4a, c and S5a, c). The measured capacitive currents are plotted as a function of scan rate in Fig. S4b, d and S5b, d. The specific capacitances (C_s) were chosen as $C_s = 0.035 \text{ mF cm}^{-2}$ in 0.5 M H₂SO₄ and $C_s = 0.040 \text{ mF cm}^{-2}$ in 1 M KOH based on typical reported values.¹

Hence, the ECSA of the catalyst layer can be calculated as:

$$ECSA = \frac{C_{dl}}{C_s}$$

In our case, ECSA values are determined as 279.7 and 322.6 cm² for Co₂P@CP in 0.5 M H₂SO₄ before and after the stability test, while in 1 M KOH values before and after stability test were 113.4 and 227.0 cm².

References

- (1) McCrory, C. C. L.; Jung, S.; Peters, J. C.; Jaramillo, T. F. Benchmarking Heterogeneous Electrocatalysts for the Oxygen Evolution Reaction. *J. Am. Chem. Soc.* **2013**, *135*, 16977–16987.
- (2) Saadi, F. H.; Carim, A. I.; Drisdell, W. S.; Gul, S.; Baricuatro, J. H.; Yano, J.; Soriaga, M. P.; Lewis, N. S. Operando Spectroscopic Analysis of CoP Films Electrocatalyzing the Hydrogen-Evolution Reaction. *J. Am. Chem. Soc.* **2017**, *139*, 12927–12930.
- (3) Goryachev, A.; Gao, L.; Zhang, Y.; Rohling, R. Y.; Vervuurt, R. H. J.; Bol, A. A.; Hofmann, J. P.; Hensen, E. J. M. Stability of CoP_x Electrocatalysts in Continuous and Interrupted Acidic Electrolysis of Water. *ChemElectroChem* **2018**, *5*, 1230–1239.