A CoV₂O₄ Precatalyst for the Oxygen Evolution Reaction: Highlighting the Importance of Postmortem Electrocatalyst Characterization

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Experimental Information

Materials.

Unless otherwise noted, all commercial chemicals were used as received without further purification. Cobalt (II) Oxide (CoO, 99+%) was purchased from Acros Organics. Vanadium (III) Oxide (V₂O₃, 97%) was purchased from Alfa Asear. Sodium hydroxide (NaOH, BioUltra), ferrocenecarboxylic acid (C₁₁H₁₀FeO₂, 97%), sodium phosphate monobasic dihydrate (NaH₂PO₄·2H₂O, ACS grade) and 5 wt % Nafion 117 solution (in a mixture of lower aliphatic alcohols and water) were purchased from Sigma Aldrich. Nafion 117 solid membranes were purchased from Fuel Cell Store. Nitric Acid (HNO₃, Trace Metal) was purchased from Thermo Fisher Scientific. Isopropyl alcohol (C₃H₈O, ACS) was purchased from EMD Millipore. Nitrogen (N₂) was boil-off gas from a liquid nitrogen source. Oxygen (O₂, industrial grade) was purchased from Cryogenic Gases. All water used in this study was ultrapure water (18.2 MΩ cm resistivity) purified using a Thermo Scientific BarnsteadTM Nanopure water purification system.

Synthesis and Deposition of CoV₂O₄

 CoV_2O_4 was prepared by solid state synthesis from CoO and V_2O_3 metal precursors. A 1:1 molar ratio of CoO (1 mmol, 0.075 g) and V_2O_3 (1 mmol, 0.150 g) were ground and mixed with an agate mortar and pestle, and then compressed into a pellet with a hydraulic press die at an applied pressure of 12,000 psi. The resulting pellet was heated under Ar first to 500 °C with a heat ramp of 5 °C/min, and then to 800 °C with a heat ramp of 2 °C/min. The pellet was then held at 800 °C for 20 h under Ar. The resulting material was then ground in an agate mortar and pestle to obtain a powder form.

5 mm diameter glassy carbon disks (4 mm thick, 0.196 cm^2 surface area, Sigradur G, HTW Hochtemperatur-Werkstoffe GmbH) or 1.6 cm × 3.2 cm glassy carbon plates (0.1 mm thick, 5.1 cm² surface area, HTW Hochtemperatur-Werkstoffe GmbH) were used as working electrodes. The glassy carbon disks were lapped with silicon carbide abrasive papers (CarbiMet 2, 600/P1200, Buehler), followed by sequential polishing with diamond abrasive slurries (MetaDi Supreme, Buehler) in an order of 9 μ m, 6 μ m, 3 μ m, 1 μ m, and 0.1 μ m diameter particle slurries (1 min polishing each) on synthetic nap based polishing pads (MD Floc, Struers). Between each lapping and polishing step, the disks were sonicated for ~30 s in isopropyl alcohol. The lapping and polishing were performed using a Struers LaboPol-5 polisher with a LaboForce-1 specimen mover. The disks were held in the LaboForce-1 specimen mover with 5 psi of applied pressure per disk, and during lapping and polishing the platen speed was held at 200 rpm and the head speed at 8 rpm in the opposite rotation direction from the platen. The glassy carbon plates were polished by hand using the same polishing order as the disks: first grinding by hand on the silicon carbide abrasive paper followed by sequential polishing by hand with diamond abrasive slurries sequentially from from 9 μ m to 0.1 μ m on the synthetic nap polishing pad. Between each lapping and polishing step, the

plates were sonicated for \sim 30 s in isopropyl alcohol. After the final polishing step, the glassy carbon disks were sonicated in an 1M nitric acid solution for 10 min, followed by sequential 3 min sonications in acetone and then ultrapure water, and finally dried in an N₂ stream.

CoV₂O₄ was deposited onto the polished glassy carbon surfaces via dropcasting of a catalyst ink suspension. Catalyst ink suspensions were prepared by adding 80mg of the CoV₂O₄ powder into a solution of 3.8 mL H₂O, 1 mL isopropyl alcohol, and 40 μ L 5 wt % Nafion 117 solution. The resulting suspension was sonicated for 30 minutes immediately prior to dropcasting. For the glassy carbon disk working electrodes, 2 x 5 μ L of the catalyst ink suspension was dropcast directly onto the disk surface using a calibrated micropipetter. Electrodes were allowed ten minutes to dry in an gravity oven at 60°C between additions. For the glassy carbon plate working electrode, 2 x 25 μ L of the catalyst ink suspension was dropcast directly onto the disk surface using a calibrated micropipetter. Electrodes were allowed ten minutes to dry in a gravity oven at 60°C between additions. For the glassy carbon plate working electrode, 2 x 25 μ L of the catalyst ink suspension was dropcast directly onto the disk surface using a calibrated micropipetter coating approximately 1 cm² of the plate. Electrodes were allowed ten minutes to dry in a gravity oven at 60 °C between additions. Electrodes were dried in a gravity oven at 60°C for 10 minutes prior to use. The mass loading of as-synthesized catalyst on the surface was the same for every electrode prepared at 0.84 mg cm⁻². V₂O₃ was deposited in an identical manner to that described above for comparative measurements of pre-activation and OER measurements.

Materials Characterization of As-Synthesized CoV₂O₄ and Prepared Films

The phase of the as-synthesized CoV_2O_4 powder was confirmed by powder X-ray diffraction (PXRD). PXRD data was collected using a Rigaku Miniflex 600 X-ray diffractometer with a Cu K α radiation source (40 kV/15 mA). Peak matching was performed using the Jade software with reference materials collected from the ICSD-FIZ Karlsruhe. The BET (Brunaeur-Emmet-Teller) surface areas of the CoV₂O₄ material was estimated from N₂ adsorption/desorption isotherms in powder forms using a Micromeritics ASAP 2020 surface area and porosimetry analyzer. Prior to surface area measurements, the CoV₂O₄ samples heated at 150°C for 8-12 h, then immediately weighed and transferred to the sample tube for the measurement. The surface area was calculated with the Brunauer-Emmett-Teller (BET) method in the relative pressure range of 0.005 to 0.25 of adsorption data.

The metal composition of the as-synthesized CoV_2O_4 material was determined using inductivelycoupled plasma—mass spectrometry (ICP-MS) and X-ray photoelectron spectroscopy (XPS). For ICP-MS measurements, 10 mg of the as-synthesized CoV_2O_4 samples were added to 10 mL of concentrated HNO₃ and the mixture was left to sit at 60°C for ~2 hr until the particle fully dissolved. This solution was diluted then used to analyze the Co and V content in the solution using a Perkin-Elmer Nexion 2000 ICP-MS. Calibration standards for cobalt (Ricca Chemical, 1000 ppm in 10% HNO₃) and vanadium (Sigma Aldrich, 1000 ppm in 10% HNO₃) were prepared by diluting the as received standard with 1M trace metal grade HNO₃ to create calibration standards at the 1, 5, 10, 20, and 50 ppm level. All samples were run against a Bi internal standard.

XPS measurements were conducted on the dropcast films on glassy carbon electrodes. The XPS spectra were acquired on a Kratos Axis Ultra XPS with a monochromatic Al x-ray source operating at 8 mA and 14 kV. High-resolution spectra were collected with a pass energy of 20 eV and a step size of 0.1 eV. The XPS peak positions were calibrated according to the $sp^2 C$ 1s for adventitious carbon at 284.8 eV. XPS data analysis was processed using CasaXPS version 2.3.17 (Casa Software Ltd). To quantify elemental ratios, peaks in the XPS high-resolution were fit to symmetric Voight line shapes comprised of 10% Gaussian and 90% Lorentzian functions with a Shirley background. Elemental ratios were calculated by quantifying the total peak areas in the Co $2p_{3/2}$ peak and V $2p_{3/2}$ peak and then dividing by their respective relative sensitivity factors (as tabulated for the Kratos Ultra XPS instrument).

Transmission Electron Microscopy (TEM) measurements of the as-synthesized CoV_2O_4 were conducted by first suspending a small amount (>1 mg) of the as-synthesized CoV_2O_4 in ~5mL isopropanol. The sample was added to a Cu TEM grid with 10 additions of ~50 µL drops of the suspension dropcast from a glass pipette. The grid was dried for 5 minutes at room temperature between each addition. The catalyst-modified TEM grid was then inserted into a JEOL 3100R05 Double Cs Corrected TEM/STEM equipped with Gatan Ultrascan 1000 CCD TV camera for image processing and a JEOL SDD X-ray detector for elemental detection. Measurements were taken with an acceleration voltage of 200 kV. Images were processed using Gatan Microscopy Suite. HRTEM and SAED measurements were also conducted on the same instrument using the same sample preparation techniques.

Average particle sizes were estimated pre- and post-electrolysis for 30 particles each from TEM images in Figure 1. The particle areas were calculated using ImageJ to process the figures based on the TEM scale bars. The measured parameters were converted to particle volumes by assuming cubic particles due to the cubic lattice of CoV₂O₄ and Co₃O₄. The particle areas and volumes are summarized in Table S1. The average (and median) particle size pre-electrolysis is average = 1.04×10^7 nm³ (median = 7.08×10^5 nm³) and post-electrolysis is average = 4.23×10^5 nm³ (median = 2.74×10^5 nm³). Note that the average particle sizes should be considered very rough approximations due to the large variance in measured particle areas and the assumptions made in the particle size calculations.

| | Pre Ele | ctrolysis | Post Electrolysis | | |
|--------------------|---------------------------------|--|---|--|--|
| Particle Number | Measured Area / nm ² | Calculated Volume / nm ³ | Measured Area / 10 ³ nm ² | Calculated Volume / nm ³ | |
| 1 | 1.74×10^5 | $7.25 	imes 10^7$ | $1.30 	imes 10^4$ | $1.48 	imes 10^6$ | |
| 2 | 1.71×10^{5} | $7.05 	imes 10^7$ | $1.09 	imes 10^4$ | $1.14	imes10^6$ | |
| 3 | 1.66×10^{5} | 6.75×10^{7} | 9.71×10^{3} | $9.56 	imes 10^5$ | |
| 4 | 1.63×10^{5} | 6.57×10^{7} | 9.05×10^{3} | 8.61×10^{5} | |
| 5 | $4.41 	imes 10^4$ | $9.26	imes10^6$ | 8.91×10^{3} | $8.41 	imes 10^5$ | |
| 6 | $2.37 	imes 10^4$ | $3.66	imes10^6$ | 8.31×10^{3} | $7.57 	imes 10^5$ | |
| 7 | $2.14 	imes 10^4$ | $3.13	imes10^6$ | 7.83×10^{3} | $6.92 	imes 10^5$ | |
| 8 | $2.10 	imes 10^4$ | $3.04	imes10^6$ | 7.69×10^{3} | 6.74×10^{5} | |
| 9 | $1.99 	imes 10^4$ | $2.80	imes10^6$ | 7.43×10^{3} | 6.40×10^{5} | |
| 10 | $1.82 	imes 10^4$ | $2.45	imes10^6$ | 6.91×10^{3} | $5.74 	imes 10^5$ | |
| 11 | 9.40×10^{3} | $9.12 	imes 10^5$ | 6.67×10^{3} | $5.44 	imes 10^5$ | |
| 12 | 9.16×10^{3} | $8.77 	imes 10^5$ | 4.72×10^{3} | 3.25×10^5 | |
| 13 | 9.00×10^{3} | $8.53 	imes 10^5$ | 4.68×10^{3} | 3.21×10^5 | |
| 14 | 8.19×10^{3} | 7.41×10^{5} | 4.36×10^{3} | $2.88 	imes 10^5$ | |
| 15 | 8.02×10^3 | $7.19 	imes 10^5$ | 4.28×10^3 | $2.80 	imes 10^5$ | |
| 16 | 7.86×10^{3} | $6.97 	imes 10^5$ | 4.14×10^{3} | $2.67 	imes 10^5$ | |
| 17 | 7.05×10^{3} | $5.92 	imes 10^5$ | 4.00×10^{3} | $2.53 	imes 10^5$ | |
| 18 | 6.97×10^{3} | $5.82 	imes 10^5$ | 4.00×10^{3} | $2.53 	imes 10^5$ | |
| 19 | 6.73×10^{3} | $5.52 	imes 10^5$ | 3.76×10^{3} | 2.31×10^5 | |
| 20 | 6.57×10^{3} | $5.32 	imes 10^5$ | 3.44×10^{3} | $2.02 	imes 10^5$ | |
| 21 | 5.92×10^{3} | $4.55 	imes 10^5$ | 2.80×10^3 | $1.48 	imes 10^5$ | |
| 22 | 5.59×10^{3} | $4.18	imes10^5$ | 2.76×10^{3} | $1.45 	imes 10^5$ | |
| 23 | 5.27×10^{3} | $3.82 	imes 10^5$ | 2.74×10^3 | 1.44×10^5 | |
| 24 | 5.11×10^{3} | $3.65 	imes 10^5$ | 2.68×10^{3} | $1.39 	imes 10^5$ | |
| 25 | 5.03×10^{3} | $3.56 	imes 10^5$ | 2.66×10^{3} | 1.37×10^5 | |
| 26 | 4.46×10^{3} | $2.98 	imes 10^5$ | 2.58×10^3 | 1.31×10^5 | |
| 27 | 4.21×10^{3} | $2.74 	imes 10^5$ | 2.20×10^3 | $1.03 	imes 10^5$ | |
| 28 | 4.21×10^{3} | $2.74 	imes 10^5$ | $2.18 	imes 10^3$ | 1.02×10^5 | |
| 29 | 3.08×10^{3} | $1.71 	imes 10^5$ | 1.10×10^{3} | $3.65 	imes 10^4$ | |
| 30 | 2.92×10^{3} | $1.58 	imes 10^5$ | 1.04×10^{3} | $3.36 	imes 10^4$ | |
| Average | 3.16×10^{4} | 1.04 × 10 ⁷ | 5.22×10^{3} | 4.23 × 10 ⁵ | |
| Standard Deviation | $5.53 	imes 10^4$ | 2.35×10^7 | 3.08×10^3 | 3.63×10^5 | |
| Median | 7.94×10^{3} | 7.08 $\times 10^{5}$ | 4.21×10^3 | $2.74 	imes 10^5$ | |

Table S1: Particle size estimates from TEM images shown in Figure 1 showing the before and after measured size and calculated particle volume.

Electrochemical Analysis

Rotating Disk Electrode Voltammetry and Controlled Current Electrolysis. Electrochemical measurements were conducted with a Bio-Logic SP200 or SP300 potentiostat/galvanostat. Catalystmodified glassy carbon working electrodes were mounted into a Pine Instrument Company E6-series ChangeDisk RDE assembly and affixed to an MSR rotator (AFMSRCE, Pine Instrument Company). The reference electrode was a commercial Ag/AgCl/KCl(sat.) electrode (CH instruments) externally referenced to ferrocenecarboxylic acid in 0.2 M phosphate buffer at pH 7 (0.329 V vs Ag/AgCl_{sat}) prior to each set of The auxiliary electrodes were graphitic carbon rods (99.999%, Strem Chemicals). experiments. Measurements were conducted in custom two-compartment H-cells where the working and reference electrodes were submerged in the first chamber in ~120 mL of 1 M NaOH, and the second chamber held the auxiliary electrode in ~18 mL of 1 M NaOH solution. Prior to each set of measurements, the electrolyte solution was sparged with O_2 for at least 30 min, and the solution was continuously blanketed with O_2 during rotating disk electrode voltammetry (RDEV), controlled-current electrolysis (CCE) stability measurements, and potential cycling measurements. Note that each electrochemical measurement was conducted at least three times, and reported values are averages of these runs with standard deviations as reported errors. Prior to each set of experiments, the uncompensated solution resistance (Ru) was measured with a high-frequency single point impedance measurement at 100 kHz with a 20 mV amplitude about the open-circuit potential (OCP), and RDEV measurements were corrected for iR drop at 85% through positive feedback using the Bio-Logic ECLab software. Our typical electrochemical setup resulted in Ru $\approx 10 \Omega$ in 1 M NaOH.

For the CCE stability measurements, CCE experiments were conducted at 10 mA cm⁻²_{geo} current density for 28 h at 1600 rpm rotation rate. Throughout the measurement, the solution was continuously sparged with O₂ that was pre-saturated with H₂O by first bubbling through a gas-washing bottle filled with H₂O. The pre-saturation of the sparge gas with H₂O helped prevent evaporation of the electrolyte solution during the measurement. For the cycling stability measurements, cyclic RDEV experiments were conducted at a constant 1600 rpm rotation rate between the potential range between $\eta = 0$ V to 0.4 V at 0.1 V s⁻¹. After every 50 cycles, a slow scan rate measurement between $\eta = 0$ V to 0.4 V at 0.01 V s⁻¹ followed by a 30 second static measurement at $j_{geo}=10$ mA/cm². The potential from each of these static measurements were used to determine activity metrics.

Oxygen Product Detection. O_2 evolved during OER measurements was quantified using a Unisense Microsensor Monometer equipped with an Ox-500 oxygen probe. The probe was quantified using a three point calibration curve with N₂-sparged (0 % O_2), air-saturated (20.8 % O_2) and O_2 -sparged (100 % O_2) solutions (Figure S3a). The dissolved O_2 concentration in solution at 20 °C was determined from a linear

interpolation of solubility data reported at 15 and 25 °C: $[O_2]_{saturated} = 0.83 \text{ mM}$ in 1 M NaOH.^{S1, 2} O₂ measurements were conducted in a sealed two-compartment H-cell. The first compartment was gastight and contained the glassy carbon disk working electrode, the Ag/AgCl/KCl(sat.) reference electrode, and the Ox-500 oxygen probe in a total compartment volume of 28 mL. The second compartment contained the carbon rod auxiliary electrode. The two compartment were separated by Nafion 117 membrane. Both compartments were filled with 1 M NaOH solutions, and the first compartment was filled such that there was no appreciable headspace. The solution was air-saturated prior to use, and the concentration of dissolved O₂ was monitored for 10 min at open circuit potential (OCP), followed by a controlled current electrolysis where the current density was held at 10 mA/cm² for 20 min passing a total charge of 2.35 C. The concentration of the dissolved O₂ was monitored in real time, and the total amount of O₂ produced was determined by determining the difference between the measured O₂ minus the background O₂ (at OCP). The Faradaic efficiency was calculated by dividing the amount of O₂ produced by the theoretical value calculated from the total charge passed.

Electrochemical Measurements on Glassy Carbon Plates. In order to collect enough CoV₂O₄ sample for post-OER analysis using PXRD, it was necessary to perform stability measurements on larger surface area glassy carbon plates. Measurements were conducted in custom two-compartment H-cells where the working and reference electrodes were submerged in the first chamber in ~120 mL of 1 M NaOH, and the second chamber held the auxiliary electrode in ~18 mL of 1 M NaOH solution. The catalyst-modified glassy carbon plates were held in the working electrode chamber such that ~ 1 cm² of the electrode was submerged in the electrolyte. The samples were then held at a constant potential of $\eta = 0.35$ V for 28 h in a controlled-potential electrolysis (CPE) experiment.

Post-OER Materials Characterization

Post-OER XPS analysis was conducted directly on catalyst-modified glassy carbon disks after CCE or cycling stability measurements. After the stability measurements, the electrodes were rinsed in ultrapure water and dried in air. The dried disks were analyzed directly using XPS as described above.

Post-OER TEM-EDX measurements were measured on catalyst particles removed from glassy carbon disk electrodes. After stability measurements, the disk electrode was sonicated in isopropanol for 2 hrs to dissolve the Nafion binder and remove the catalyst. The resulting suspension of catalyst particles in isopropanol was centrifuged at 7000 rpm for 15 min at room temperature. The supernatant was decanted, and the powder was collected and dried by heating in air at 60°C. The dried powder was suspended in isopropanol and loaded onto a Cu TEM grid and analyzed using TEM-EDX as described above.

Post-OER PXRD measurements were conducted on catalyst material from the 28-h CPE measurements on catalyst-modified glassy carbon plate electrodes. After electrolysis, the catalyst-modified glassy carbon

plates were sonicated in isopropanol for ~ 2 h to dissolve the Nafion binder and resulted in a suspension of catalyst particles in isopropanol. The resulting suspension of catalyst particles in isopropanol was centrifuged at 7000 rpm for 15 min at room temperature. The supernatant was decanted, and the powder was collected and dried by heating in air at 60°C. To obtain enough catalyst sample for PXRD measurements, the catalyst samples from 10 independent glassy carbon plates post-electrolysis were combined into a single PXRD sample.

Post ICP-MS measurements were conducted on catalyst material from the 28-h CPE measurements on catalyst-modified glassy carbon plate electrodes. After electrolysis, the catalyst-modified glassy carbon plates were sonicated in isopropanol for ~ 2 h to dissolve the Nafion binder and resulted in a suspension of catalyst particles in isopropanol. The resulting suspension of catalyst particles in isopropanol was centrifuged at 7000 rpm for 15 min at room temperature. The supernatant was decanted, and the powder was collected and dried by heating in air at 60°C. Approximately 1 mg of catalyst was removed and dissolved in 10 mL HNO₃ by heating at 60°C. The solution was diluted with 1M HNO₃ and analyzed using ICP-MS as described above.

Table S2. Metal Contents, Lattice Parameters, and BET Surface Areas of as-synthesized Co_3O_4 and CoV_2O_4 , and metal content of post-electrolysis CoV_2O_4 (in red).

| Catalyst | Calculated V (atom %) ^a | V (atom %) (ICP-MS) | V (atom %) (XPS) | Lattice parameter (Å) ^b | Grain size (nm) ^b | S _{BET} (m ² /g) | V (atom %) (ICP-MS) Post- electrolysis |
|-----------------------------|---------------------------------------|------------------------|---------------------|--|------------------------------------|--------------------------------------|---|
| $\text{Co}_3\text{O}_4{}^c$ | - | - | - | 8.080 ^c | 16.68 ^c | 41.54 ± 0.94^{c} | - |
| CoV_2O_4 | 66.7% | 64.9% | 63.3% | 8.380 | > 100 | 0.80 ± 0.13 | 0.04% |

^{*a*}V atom % ratio = $\frac{n_V}{n_{C0}+n_V}$ × 100%. ^{*b*}Calculated from PXRD (311) peak. ^{*c*}Data for Co₃O₄ from Reference ^{S3}



Figure S1. Representative cyclic RDEV of V_2O_3 in 1 M NaOH in the potential window used for the OER studies in this report. The V_2O_3 system shows no evidence of OER activity under the conditions used in this study. The RDEVs shown is the 2nd cycle for V_2O_3 .



Figure S2. High resolution XPS spectra of CoV_2O_4 both as-synthesized and after 28-h electrolysis in the C 1s region.



Figure S3. Representative Tafel plot of CoV_2O_4 in O₂-purged 1 M NaOH with rotation rate of 1600 rpm. The linear regression region was chosen near the j = 10 mA/cm²_{geo}. The Tafel slope is 52 ± 3.



Figure S4. (a) Three-point calibration curve for the oxygen meter and (b) the time-dependent measurement of O_2 evolved by CoV_2O_4 . The dashed red line is the expected amount of O_2 evolved based on charge passed, and the solid black line is the amount of O_2 measured. The Faradaic efficiency was calculated based on the total O_2 produced at the end of the experiment divided by the expected amount of O_2 based on total charge passed.

| Catalyst | $\eta_{j=10mA/cm^2_{geo}} \ (\mathrm{V})^a$ | $j_{s,\eta=350mV,geo}$ (mA/cm ²) ^a | $j_{s,\eta=350mV,BET}$ $(\mu A/cm^{2}BET)^{a}$ | $ \begin{array}{c} j_{s,\eta=350mV,mass} \\ (A/g) \end{array} $ | Tafel Slope | Ref |
|---|---|--|---|---|----------------|--------------|
| CoV2O4 | 0.37 ± 0.01 | 2.44 ± 0.48 | 368 ± 73 | 2.90 ± 0.57 | 52 ± 3 | This Work |
| Co ₃ O ₄ | 0.42 ± 0.01 | 0.42 ± 0.11 | 1.20 ± 0.31 | 0.5 ± 0.1 | 52 ± 3 | S3 |
| Co _{2.25} Cr _{0.75} O ₄ | 0.35 ± 0.01 | 8.84 ± 2.7 | 14.06 ± 4.28 | 10.6 ± 3.2 | 60 ± 3 | S3 |
| $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ | N.R. | ~20 ^b | ~40 ^b | ~10 ^b | N.R. | S4 |
| Exfoliated NiFe LDH | ~0.3 | ~9 ^c | N.R. | ~29 ^c | ~40 | S5 |
| Ni _{0.9} Fe _{0.1} O _x | 0.336 | 1.24 ± 0.04 | N.R. | 1065 ± 129^{c} | 30 | S6 |
| V-doped Co ₃ O ₄ ^d | 0.29 | ~90 | N.R. | ~160 | 53.3 | S7 |
| V-doped NiFe ₂ O ₄ ^e | 0.27 | ~110 ^c | N.R. | ~200 | 42.08 | S7 |
| a-CoVOx | 0.35 | ~10 | N.R. | 69.5 | 51 | S8 |
| Ni ₃ Fe _{0.5} V _{0.5} | ~0.2 | ~1000 ^c | N.R. | ~4000 ^c | 39 | S9 |
| Co ₄ V ₃ Fe ₃ O _x | 0.307 | 98.1 | N.R. | N.R. | 36 | S10 |
| NF@Co _{1-x} V _x -HNN | 0.268 | 100 | N.R. | N.R. | 80 | S11 |
| CoMoV LDH | 0.15 | N.R. | N.R. | N.R. | 106 | S12 |
| Co _{0.8} V _{0.2} OOH | 0.19 | N.R. | N.R. | N.R. | 39.6 | S13 |
| CoV _{1.5} Fe _{0.5} O ₄ | ~0.3 | N.R. | N.R. | N.R. | 38 | S14 |

Table S3. OER activity of as-synthesized CoV_2O_4 compared to other OER catalysts. Note that activitymetrics are based on the characterization of the as-synthesized CoV_2O_4 material.

^{*a*}Metrics were determined and reported primarily from RDEVs or other voltammetric measurements. ^{*b*}Reported at 400 mV note CoV₂O₄ shows $j_{s,\eta=400mV,geo}$ of 18.4 ± 3.4 (mA/cm²), $j_{s,\eta=400mV,BET}$ of 2770 ± 511 and $j_{s,\eta=400mV,mass}$ of 21.9 ± 4.0 (A/g). ^{*c*}Reported at 300 mV note CoV₂O₄ shows $j_{s,\eta=300mV,geo}$ of 1.88 ± 0.60 (mA/cm²), $j_{s,\eta=300mV,BET}$ of 283 ± 90 (µA/cm²_{BET}) and $j_{s,\eta=300mV,mass}$ of 2.24 ± 0.71 (A/g). ^{*d*}Reported for system with V doping at 7.7 atom %. ^{*e*}V doping atom % was not specified in manuscript.



Figure S5. The first six RDEVs measured for V_2O_3 at in O_2 -saturated 1 M NaOH at 1600 rpm and 0.1 V/s scan rate. There is a large oxidative peak at $\eta \approx 0.05$ V that decreases substantially in current after the first cycle. This voltammetric behavior is qualitatively similar to that observed in the first six scans of CoV_2O_4 (see Figure 2 in the manuscript), and we attribute it to oxidative vanadium etching.



Figure S6. High resolution XPS spectra of CoV_2O_4 both as-synthesized and after 10,000 cycle stability measurements in the (a) Co 2p region, (b) V 2p region, (c) O 1s region, and (d) C 1s regions.



Figure S7: Zoom in of Figure 1c. showing CoV_2O_4 after long term stability measurements. Inset shows crystals with lattice fringes measured about 0.24 nm in *d*-spacing.



Figure S8: Representative SAED patterns of CoV_2O_4 before (left) and after (right) constant current measurement showing a transition from a highly crystalline system before electrolysis to a more amorphous material after constant current electrolysis.

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