

**A step forward: Hydrogen production on cobalt molybdenum sulfide
electrocatalyst in anion exchange membrane water electrolyzer**

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Supporting Information

Transition metal sulfides synthesis procedure:

Initially, an aqueous solution of the metallic precursor was prepared and let stirring. The cobalt and molybdenum precursors employed herein were cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$, Alfa Aesar) and ammonium heptamolybdate tetrahydrate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$, Alfa Aesar), respectively. Simultaneously, sodium diethyldithiocarbamate trihydrate ($\text{C}_5\text{H}_{10}\text{NNaS}_2 \cdot 3 \text{H}_2\text{O}$, Alfa Aesar) was added to 20 mL of ultrapure water (Milli-Q, $18.2 \text{ M}\Omega \text{ cm}$ at $20 \text{ }^\circ\text{C}$) and the solution was stirred until the complete dissolution of the sulfur precursor. In the sequence, the sulfur precursor solution was slowly dripped (about one droplet per second) into the metallic one, which was under vigorous stirring. During this dripping, solids started emerging in the metallic solution. For CoS_x synthesis, it was evidenced the appearance of green solids, while for MoS_x yellow solids were seen initially, but it started becoming orange as more droplets were added. The final mixture was then transferred to Teflon-lined stainless-steel autoclave which was posteriorly heated at $240 \text{ }^\circ\text{C}$ during 24 h. Afterwards, the autoclave was let cooling down naturally before opening until a temperature close to ambient one was achieved. The material was collected after various centrifugation (six times applying 9000 rpm during 20 min) and washing steps. The first centrifugation was done with the mixture resulting from hydrothermal reaction. The two subsequent steps and last three ones were performed after water and absolute ethanol (VWR Chemicals) washing, respectively. Resulting solids were then dried at $50 \text{ }^\circ\text{C}$ in vacuum (50-200 mbar) overnight. Finally, they were collected and stocked to be applied in the characterizations thereafter. Particularly, during the bimetallic sulfide ($\text{Co}_{0.5}\text{Mo}_{0.5}\text{S}_x$) synthesis, the metallic solution was prepared by the direct addition of 20 mL of cobalt chloride solution to 20 mL of ammonium heptamolybdate (AHM) solution, followed by vigorous stirring. Once the solution containing the sulfur precursor was dripped into the metallic solution containing both metals, green solids started appearing as well as in CoS_x synthesis. The precursor amounts and volumes applied in the synthesis of each catalyst are evidenced in **Table S1**.

Table S1. Quantities of precursors and volumes applied in the synthesis of the unsupported transition metal sulfides.

Catalyst	CoS_x	MoS_x	Co_{0.5}Mo_{0.5}S_x
n_{CC} (mmol)	2.00	0	1.00
n_{AHM} (mmol)	0	0.28	0.14
n_{SDEDTC} (mmol)	2.00	2.00	2.00
V_{CC} (mL)	40	0	20
V_{AHM} (mL)	0	40	20
V_{SDEDTC} (mL)	20	20	20

*n_x = quantity of compound "X", V_x = volume of solution "X", CC = cobalt chloride, AHM = ammonium heptamolybdate and SDEDTC = sodium diethyldithiocarbamate.

ICP-OES and XPS procedure:

Inductively coupled plasma-optical emission spectrometry (ICP-OES) analysis was performed with an Agilent 5110 VDV device. Catalyst powder was first submitted to a mineralization procedure, which consisted in the addition of 5 mL of HNO₃ solution (> 68 %) and 3 mL of HCl solution (34-37 %), and further heating in an Anton-Paar Multiwave PRO microwave reaction system. Ultrapure water was added to the resultant solution until a final volume of 50 mL was achieved. The final solution was sampled five times to be used in the analysis in order to obtain a good precision of the results.

X-ray photoelectron spectroscopy (XPS) analysis was carried out with a Kratos Axis Ultra DLD spectrometer using a monochromatic Al K α source (1486.6 eV) operating at 180 W (12 mA, 15 kV). The device was operated at 9×10^{-8} Pa and the charge neutralizer system was applied. High-resolution spectrum was recorded using an analysis area of 300 $\mu\text{m} \times 700 \mu\text{m}$, step size of 0.1 eV and 40 eV pass energy, which corresponds to Ag 3d_{5/2} full width at half maximum (FWHM) of 0.55 eV. The binding energy was calibrated using C 1s binding energy fixed at 284.8 eV as an internal reference. Data were treated with Casa XPS software (version 2.3.24).

Raman spectrum of $\text{Co}_{0.5}\text{Mo}_{0.5}\text{S}_x$ catalyst powder:

Raman spectroscopy measurement of catalyst powder was carried out at room temperature using a Horiba Jobin Yvon LabRAM HR 800 UV Raman confocal microscope, specifically an Olympus BXM confocal microscope which enabled the operation in backscattering mode, equipped with a CCD detector cooled by the Peltier effect. It was applied the excitation wavelength of 532 nm, supplied by a diode-pumped solid state (DPSS) green laser from Oxxius, and the laser power delivered to the samples was 0.2 mW, aided by an optical density filter. In addition, 600 grooves mm^{-1} grating and the confocal pinhole diameter of 200 μm were used, resulting in a spectral resolution of 1.5 cm^{-1} . Finally, the spectrometer was calibrated with a silicon standard and the LabSpec v.5 software was used for the acquisition and treatment of data.

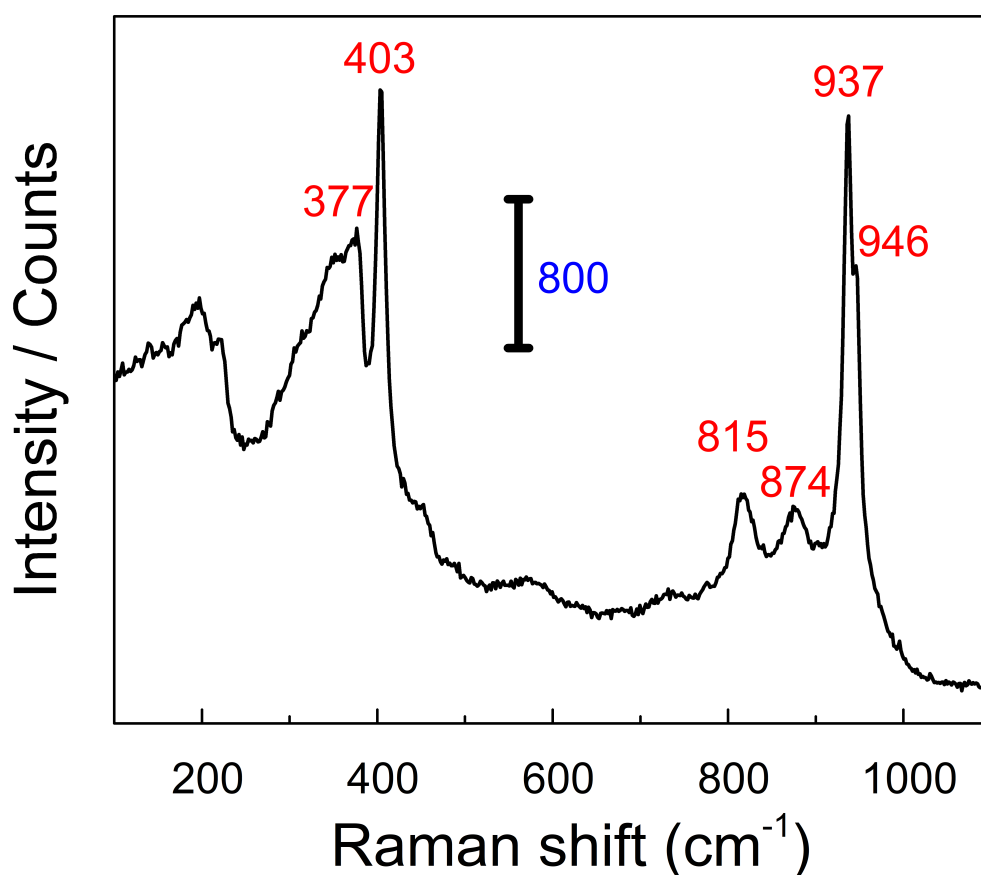


Figure S1. Raman spectrum of $\text{Co}_{0.5}\text{Mo}_{0.5}\text{S}_x$ powder.

Three-electrode cell configuration:

Potentiostat device (Autolab, PGSTAT 302N) was connected to a three-electrode cell composed of Kel-F® material, due to the use of alkaline electrolyte, containing a PTFE top (**Figure S2**). Glassy carbon slab and Hg/HgO (RE-61AP Reference electrode, ALS Co., Ltd) filled with 1 M KOH (Sigma-Aldrich) solution, were applied as counter- and reference electrodes, respectively, for all measurements. The working electrode was composed of a commercial rotating disk electrode (RDE) system (Metrohm Autolab) containing 5 mm diameter glassy carbon as substrate, which served as surface for the deposition of the evaluated electrocatalysts. Linear sweep voltammetry (LSV) analyses were performed in 1 M KOH by scanning the potential between 0.14 V and -0.56 V vs RHE at 10 mV s⁻¹, besides applying a rotation speed of 1600 rpm in the working electrode.



Figure S2. Electrochemical cell designed with Kel-F® and PTFE top.

Catalytic ink preparation for three-electrode cell tests:

The materials were attached to the electrode by preparing a catalytic ink, which was deposited onto the glassy carbon substrate and let drying for some minutes, while the electrode was stirred at 700 rpm. The ink composition consisted of 475 μL of ultrapure water, 475 μL of isopropanol (VWR Chemicals), 50 μL of Nafion® perfluorinated resin suspension (5 wt. % in lower aliphatic alcohols and water, containing 15-20 % water, Sigma-Aldrich) and 14 mg of the catalyst analyzed. As methodology adopted to the ink production, initially, only water, isopropanol and Nafion® were added to a sample vial, which was ultrasonicated in a bath for 15 min. Subsequently, the solid material was added to the produced suspension, which was further put in ultrasound bath once more until the homogenization of the ink was achieved (approximately, 30 min). To perform the electrochemical analyses, 7 μL of ink was added to the glassy carbon substrate, therefore, the theoretical mass loading applied in this study was 0.5 mg cm^{-2} for all other materials. Noteworthy, these values consider the geometrical surface area of the electrode.

Reference electrode (Hg/HgO) calibration:

Initially, 40% Pt/C was deposited on the working electrode glassy carbon substrate with a mass loading of 0.28 mg cm^{-2} . Then CV analysis was performed between -0.93 and 0.40 V vs Hg/HgO in H_2 -saturated 1 M KOH at 100 mV s^{-1} until a reproducible profile in current density vs potential plot was achieved. Consecutively, a new CV analysis was performed between -1.03 and -0.83 V vs Hg/HgO at 10 mV s^{-1} ; the result is presented in **Figure S3**. The average of potentials in which the curve crosses the value of 0 mA cm^{-2} in both anodic and cathodic directions was considered the theoretical potential of HOR/HER (0 V vs RHE). Based on this analysis, it was stated that for the reference electrode used during three-electrode cell measurements, -0.940 V vs Hg/HgO is equivalent to 0 V vs RHE. Therefore, such value was used for all potential conversions towards V vs RHE unit.

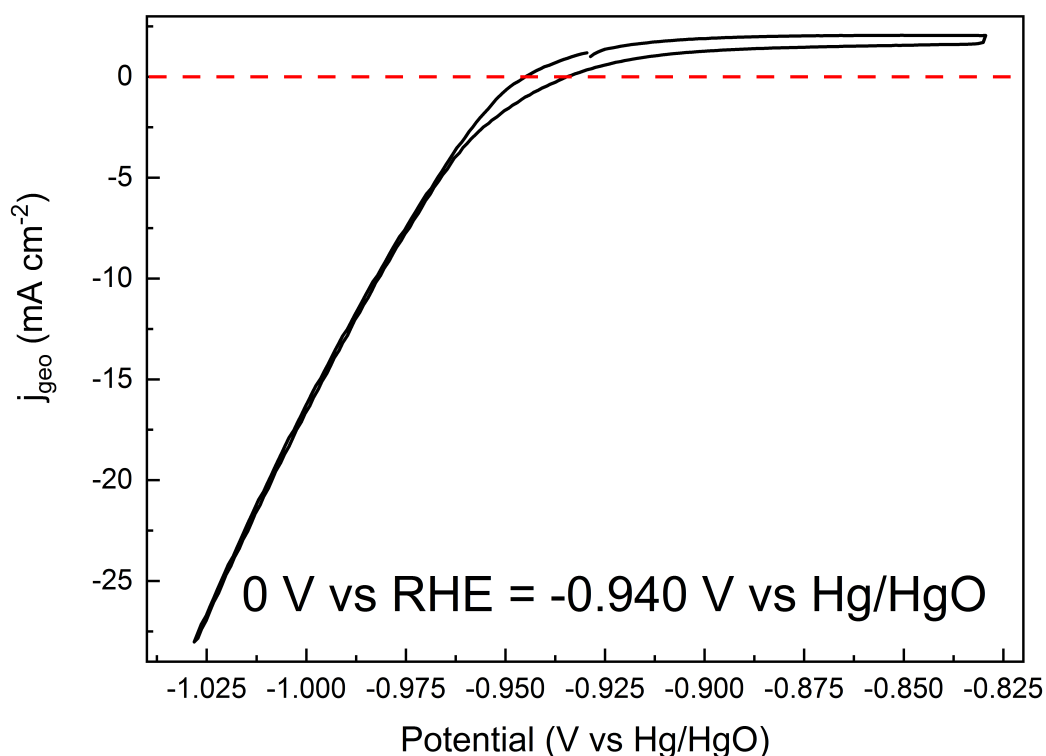


Figure S3. CV of 40% Pt/C in H_2 -saturated 1 M KOH at 10 mV s^{-1} in a potential window of HER/HOR.

AEMWE configuration:

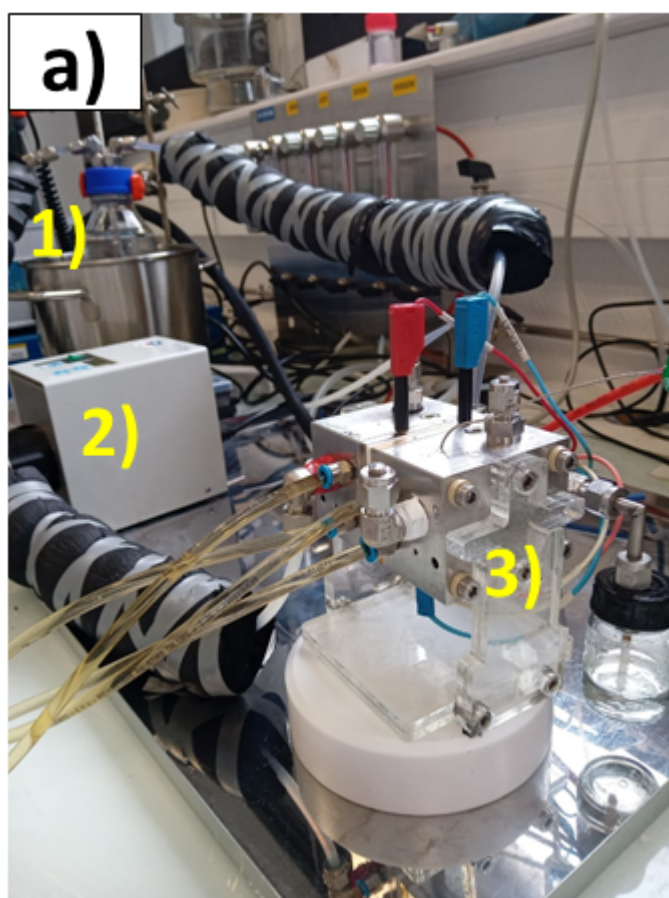
A BioLogic VSP Potentiostat (20 V/4 A) was connected to a single AEMWE cell composed of two titanium-based polar plates containing three parallel straight channels each (length, width, and depth equal 15, 2 and 2 mm, respectively), two porous titanium, which plays a role as porous transport layer (PTL) and was applied in both anodic and cathodic compartments, besides the membrane electrode assembly (MEA). This last one comprised a Sustainion® X37-50 Grade RT (Dioxide Material™) membrane sandwiched by two gas diffusion electrodes (GDE) of 1.8 cm², which were directly assembled in the cell. However, before being inserted in the cell, the membrane was soaked in 1 M KOH overnight and the electrodes were soaked in 0.1 M KOH for 1 h, followed by vigorous rinsing. The anode GDE was obtained by depositing 2 mg cm⁻² of commercial Iridium black (Sigma-Aldrich) onto Bekaert Bekipor® ST 40 BL3 stainless steel (alloy: 316 L, thickness = 0.23 mm, and porosity = 84 %), while each cathode GDE was obtained by depositing the transition metal sulfide onto AvCarb® MGL370 (thickness = 0.37 mm, and porosity = 78 %) carbon paper with a mass loading target of 3.5 mg cm⁻². All catalysts were in a powder form and, therefore, to deposit them on the gas diffusion layers (GDL) by spray-coating method, catalytic inks were prepared. Inks were produced by mixing the catalyst with Sustainion® XB-7 ionomer and solvent (50 % v/v ethanol in water). The homogenization was obtained by the application of pulsed sonication, i.e., 1 s of sonication followed by 4 s of ultrasound absence repeated during 5 min, with an ultrasonic probe (power = 280 W) from Qsonica. When it came to the anode, a proportion of 97 and 3 wt.% of Ir black and XB-7, respectively was respected, while for the cathodes such proportion was altered to 90 and 10 wt.%; the catalyst was maintained as major component though. As previously mentioned, the mass loading target was 3.5 mg cm⁻² for each TMS, however, real mass loading, presented in **Table S2**, was obtained by the mass difference of AvCarb® MGL370 before and after catalysts deposition.

Table S2. Mass loading obtained for each GDE cathode.

Catalyst	Mass loading (mg cm ⁻²)
CoS _x	3.6
MoS _x	3.4
Co _{0.5} Mo _{0.5} S _x	3.9* / 3.4#

Mass loadings in the activity* (represented by **Figure 2**) and stability# (represented by **Figures 3** and **SX**) tests.

During analysis, the cell, maintained at 50 °C, was fed only in the anodic compartment by 2 mL min⁻¹ of 0.1 M KOH solution, also stocked at 50 °C, in a closed loop. **Figure S4** presents images of AEMWE setup. For performance tests, the LSV curves were registered at 10 mV s⁻¹. The stability test was divided in many steps. Initially, a LSV was recorded at 5 mV s⁻¹ between OCV and 2 V, then the cell was maintained at 2 V during 10 h. Thereafter, it was repeated three more times until achieve 40 h of chronoamperometry analysis.



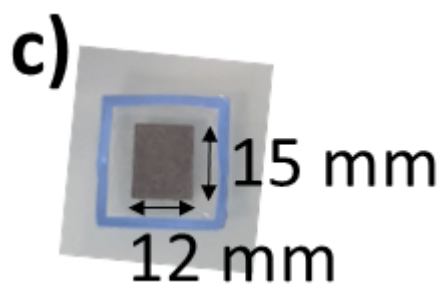
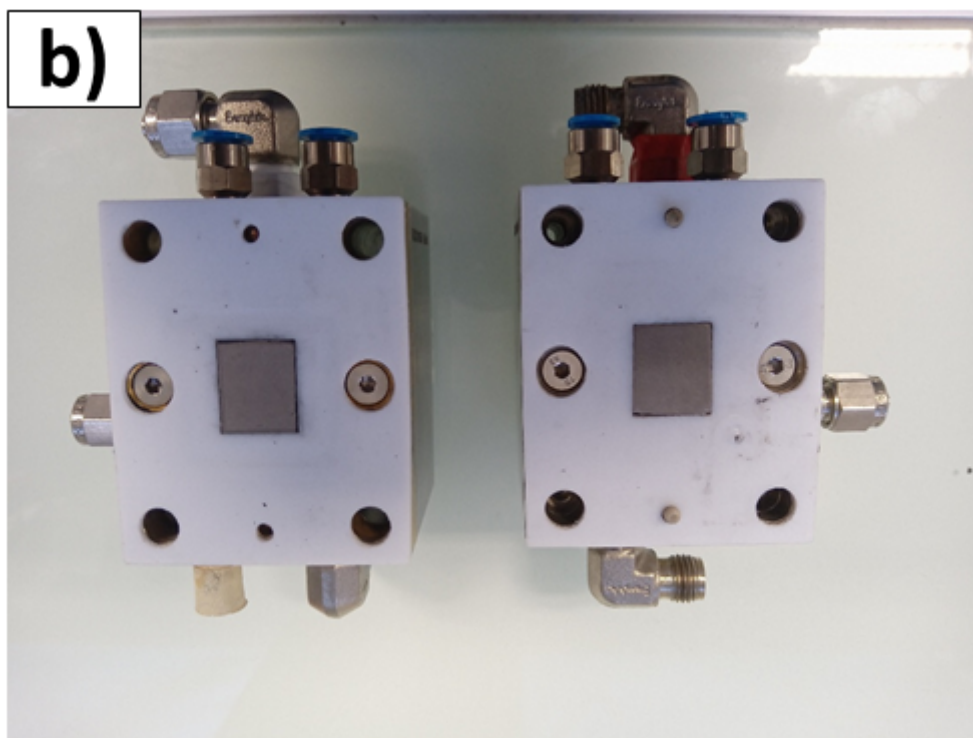


Figure S4. Anion exchange membrane water electrolysis setup used for the obtained results reported herein. **a)** Image of complete setup comprising 1) oil bath with temperature controlled by thermostat for electrolyte heating, 2) pump for electrolyte recirculation and 3) AEMWE cell. **b)** Cell gaskets and **c)** MEA images.

Performance test result with mass loading normalization:

Although the aim during cathode deposition was to obtain a mass loading equal 3.5 mg cm^{-2} , this value can suffer experimental deviation, which is natural in the spray-coating method. As verified in **Table S2**, each GDE cathode had a different mass loading. Once $\text{Co}_{0.5}\text{Mo}_{0.5}\text{S}_x$ mass loading was the highest one, **Figure 2** was replotted but with mass loading normalization, as may be seen in **Figure S5**, in order to elucidate that its highest activity does not accrue from its higher quantity in the analysis.

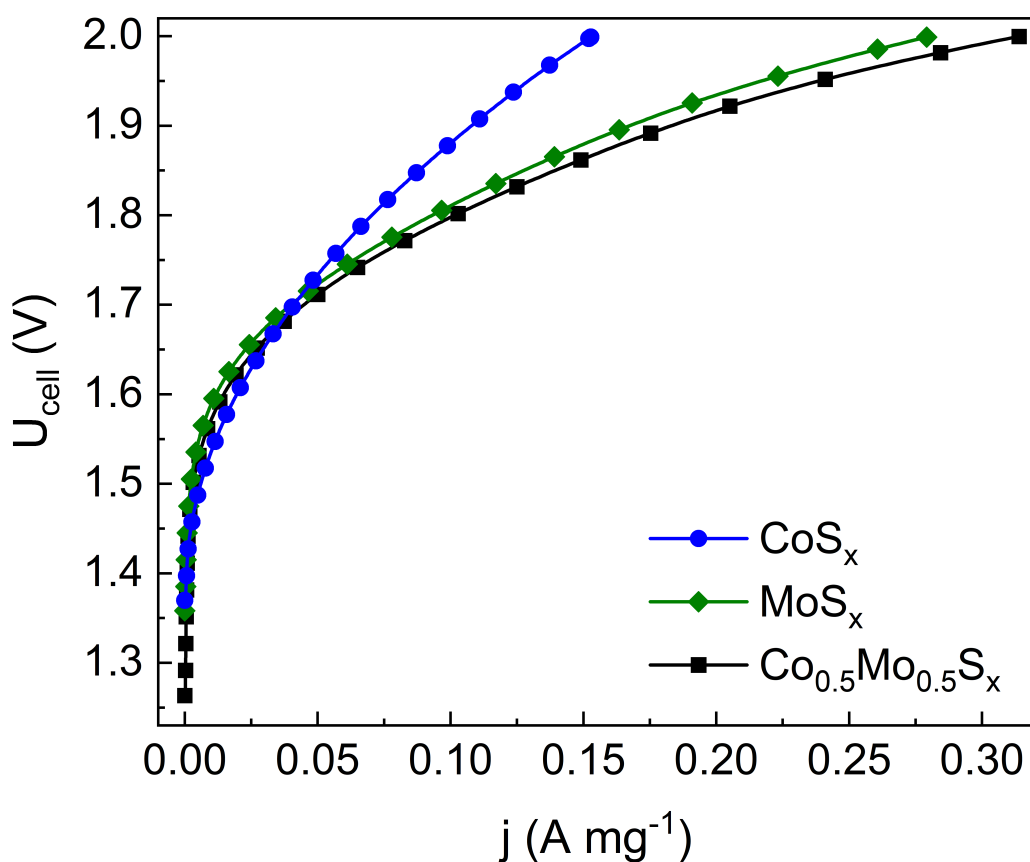


Figure S5. Mass loading normalized polarization curves obtained from analysis in AEMWE device at $50 \text{ }^\circ\text{C}$ fed by 0.1 M KOH . Ir black and Sustainion® X37-50 were applied as anode catalyst and membrane, respectively, for all measurements.

Specific energy consumption calculation:

The value of specific energy consumption is given by **Equation S1**.

$$\varepsilon \text{ (kWh Nm}^{-3}\text{)} = \frac{2 \times F}{3600 \times V_m \text{ (m}^3 \text{ mol}^{-1}\text{)} \times 10^3} \times U \text{ (j)} \quad \text{Equation S1}$$

And assuming that H₂ behaves as ideal gas, V_m can be calculated by **Equation S2**.

$$V_m = \frac{R \times T}{P} \quad \text{Equation S2}$$

Therefore, by combining **Equations S1** and **S2**, the **Equation S3**, which was used to plot curves of **Figure 2**, was obtained.

$$\varepsilon \text{ (kWh Nm}^{-3}\text{)} = \frac{2 \times F \times P}{3600 \times R \times T \times 10^3} \times U \text{ (j)} \quad \text{Equation S3}$$

For the calculations, voltage unit adopted was Volt. Furthermore, all parameters' values applied are presented below.

- F = 96,485 C mol⁻¹;
- P = 101,325 Pa;
- R = 8.314 Pa m³ mol⁻¹ K⁻¹;
- T = 323.15 K.

Calculation of the current decay percentages

The calculation of reversible current decay, irreversible current decay, and current decay rate were done according to the **Equations S4, S5 and S6**, respectively.

$$\text{Reversible current decay of } n^{\text{th}} \text{ interval (\%)} = \frac{j_b^{n+1} - j_f^n}{j_b^n - j_f^n} \times 100 \quad \text{Equation S4}$$

$$\text{Irreversible current decay of } n^{\text{th}} \text{ interval (\%)} = \frac{j_b^n - j_b^{n+1}}{j_b^n - j_f^n} \times 100 \quad \text{Equation S5}$$

$$\text{Current decay rate (\% h}^{-1}\text{)} = \frac{\left(\sum_{i=1}^n \frac{j_b^i - j_f^i}{j_b^i} \right) \times \frac{100}{10}}{n} \quad \text{Equation S6}$$

For the calculations, the meaning of the variables is presented below.

- **j** corresponds to current density;
- **n** corresponds to the number of the interval;
- **b** corresponds to the beginning of the interval, i.e., first value in the interval;
- **f** corresponds to the final of the interval, i.e., last value in the interval.

Performance test result with mass loading normalization:

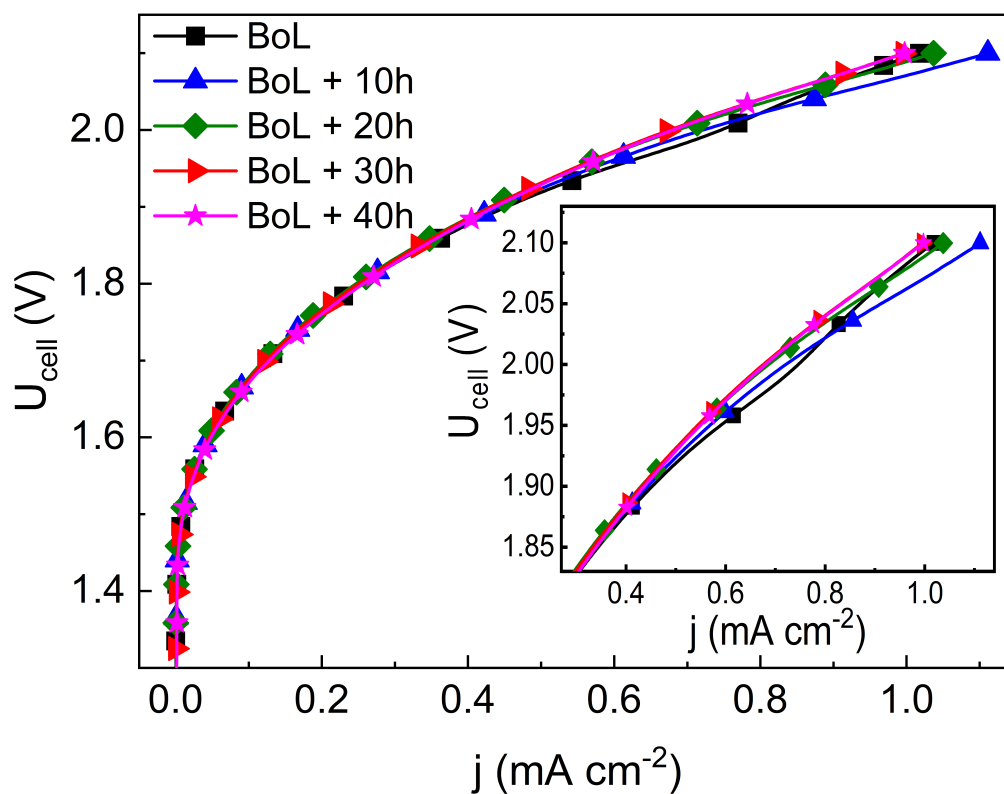


Figure S6. Polarization curves, at 5 mV s^{-1} , obtained before and after each chronoamperometry interval of stability test. BoL = "Beginning of life", i.e., fresh $\text{Co}_{0.5}\text{Mo}_{0.5}\text{S}_x$.

Raman spectroscopy for GDE analyzes:

Raman spectroscopy measurements of GDE materials were carried out at room temperature using a Horiba Jobin Yvon LabRAM HR 800 UV Raman confocal microscope, specifically an Olympus BXM confocal microscope which enabled the operation in backscattering mode, equipped with a CCD detector cooled by the Peltier effect. For all measurements, it was applied the excitation wavelength of 532 nm, supplied by a diode-pumped solid state (DPSS) green laser from Oxxius, and the laser power delivered to the samples was 0.2 mW, aided by an optical density filter; it was focused to a spot size corresponding to $2 \mu\text{m}^2$ of the sample. In addition, 1800 grooves mm^{-1} grating and the confocal pinhole diameter of 200 μm were used, resulting in a spectral resolution of 0.5 cm^{-1} . The spectrometer was calibrated with a silicon standard. Finally, the MEA samples were directly placed under the microscope objective and many spectra were registered at different points of cathode GDE surface. LabSpec v.5 software was used for the acquisition and treatment of data.

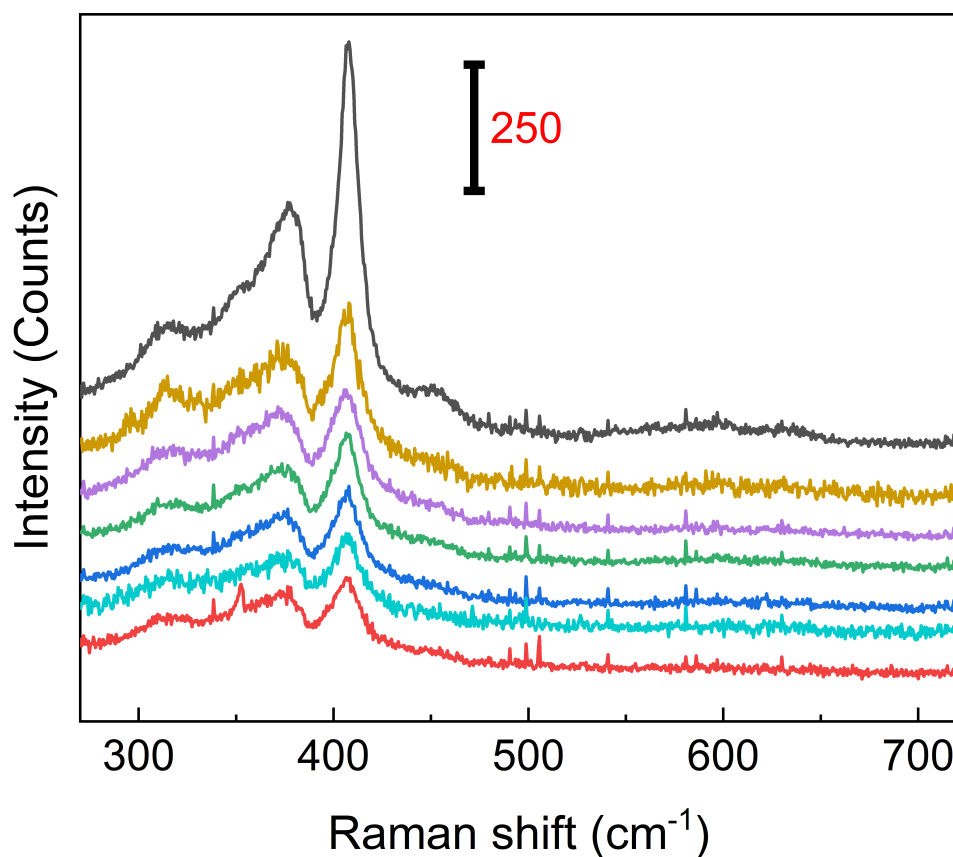
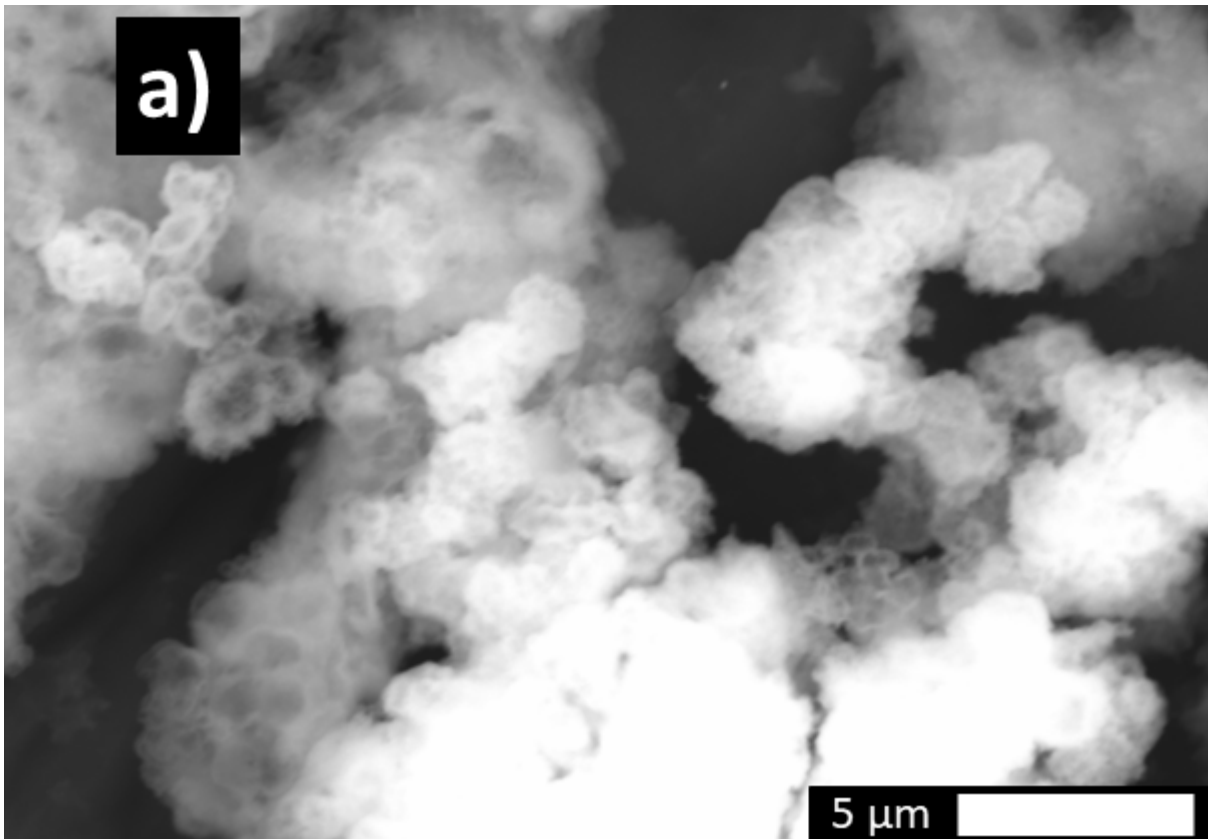


Figure S7. Raman spectra of fresh $\text{Co}_{0.5}\text{Mo}_{0.5}\text{S}_x$ GDE probed at both center and corner of MEA.

Cobalt and molybdenum elemental mapping for a fresh $\text{Co}_{0.5}\text{Mo}_{0.5}\text{S}_x$ GDE:

Field emission gun scanning electron microscopy (FEG-SEM) analyzes were performed in a JEOL 7900F microscope, equipped with Bruker QUANTAX FlatQUAD energy dispersive X-ray spectroscopy (EDS) microanalysis system. Samples were directly observed in the microscope without any particular preparation.



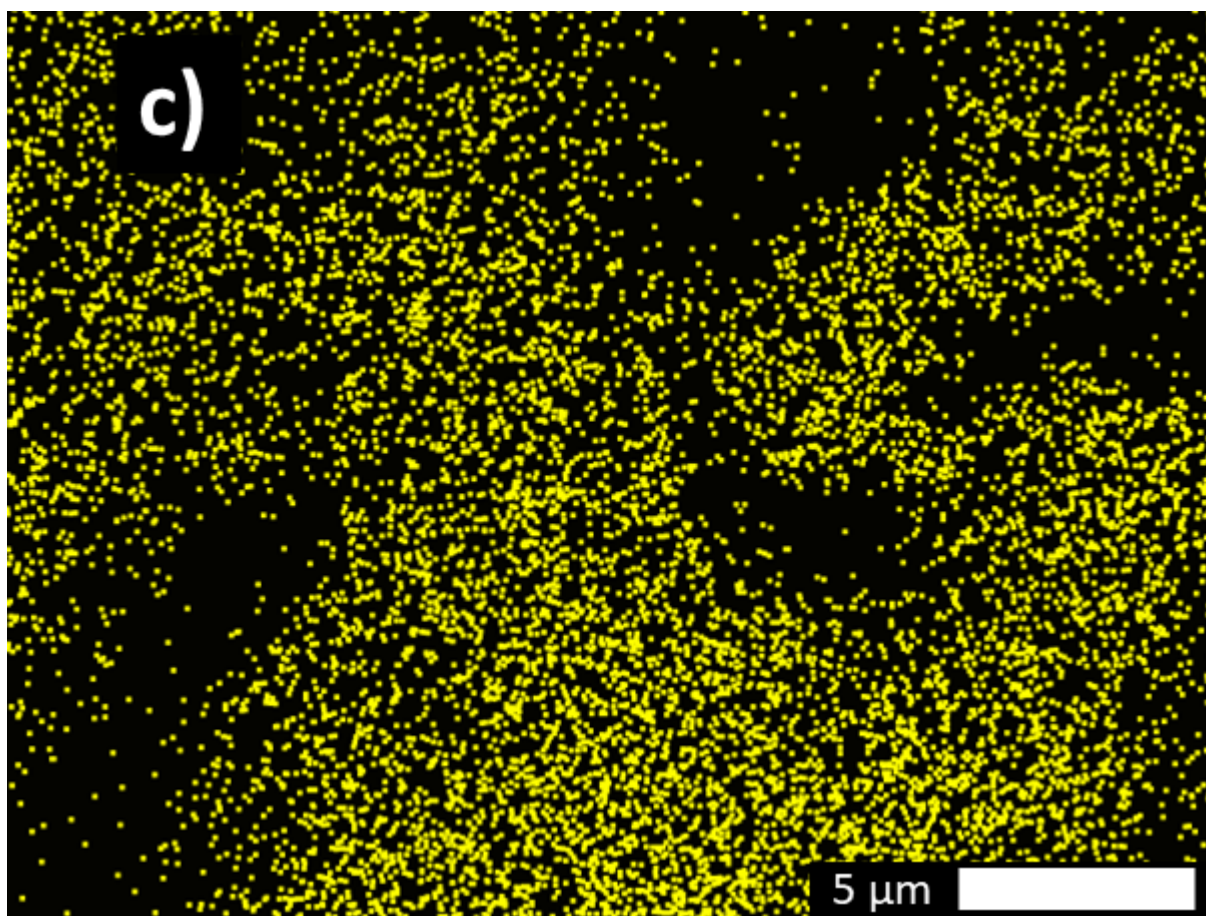
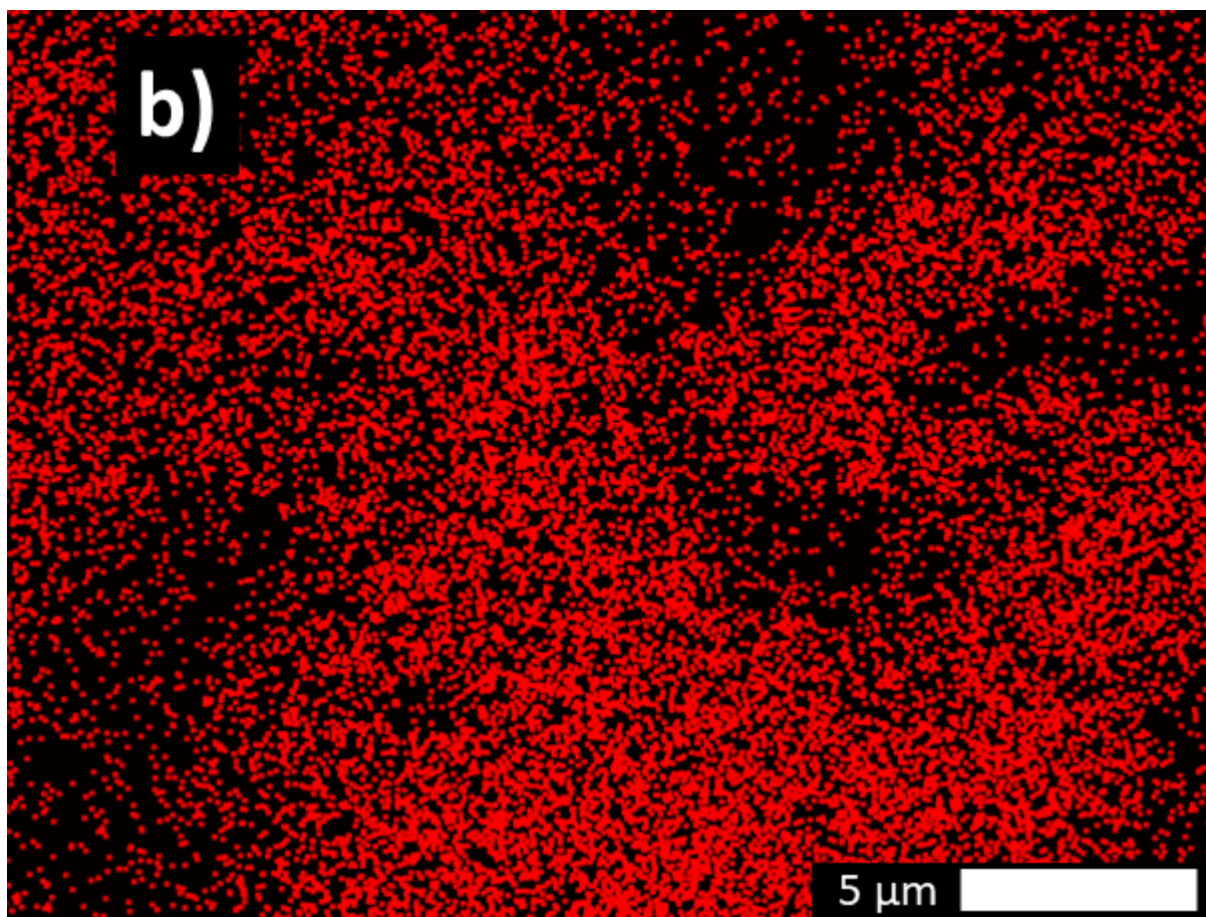


Figure S8. a) FEG-SEM image of a fresh $\text{Co}_{0.5}\text{Mo}_{0.5}\text{S}_x$ recorded in backscattered electron mode. b) Cobalt and c) Molybdenum elemental mapping obtained by the application of EDS analysis.