

Supporting Information:

**Growth and Activation of an Amorphous Molybdenum Sulfide Hydrogen Evolving
Catalyst**

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Experimental Section

Physical measurements

Electrochemical measurements were recorded on an EG&G Princeton Applied Research Potentiostat/Galvanostat model 273. EQCM measurements were performed with home-made equipment using a home-made potentiostat (Wenking-type). The home-made potentiostat was connected to an EG&G 175 Universal Programmer or a TTI Function/Arbitrary/Pulse generator model TG2511. A three-electrode configuration was used. For polarization and electrolysis measurements, a platinum wire was used as the counter electrode and a home-made Ag/AgCl (KCl saturated) electrode was used as the reference electrode. The reference electrode was placed in a position very close to the working electrode, often with the aid of a Luggin tube. In case of electrochemical film deposition, a fresh titanium wire was used as the counter electrode. Potentials were referenced to a standard hydrogen electrode (SHE) or reversible hydrogen electrode (RHE), respectively, by adding a value of $(0.197+0.059 \cdot \text{pH})$ V. Gas chromatography measurements were conducted on a Perkin-Elmer Clarus 400 GC with a TCD detector and a 5 Å molecular sieves packed column or on a home-made gas analyzer equipped with a Valco microvolume dual filament TCD detector and a HayeSep DB 100/120 mesh, 30 ft. long, 2mm internal diameter, stainless steel packed column (part number G3591-80088 – Agilent Technologies). UV-Vis spectra were recorded using an Ocean Optics USB 2000+ spectrophotometer connected to a home-built dual lamp (D_2 and tungsten filament lamps) optic fiber light source. X-ray photoelectron spectroscopy (XPS) data were collected by an Axis Ultra (Kratos Analytical, Manchester, UK) under ultra-high vacuum condition ($>10^{-8}$ Torr), using a monochromatic Al K_α X-ray source (1486.6 eV), in the Surface Analysis Laboratory of CIME at EPFL. The source power was maintained at 150W (10 mA, 15 kV) Gold (Au $4f_{7/2}$) and copper (Cu $2p_{3/2}$) lines at 84.0 and 932.6 eV, respectively, were used for calibration, and the adventitious carbon 1s peak at 284.8 eV as an internal standard to compensate for any charging effects. After a Shirley background subtraction, the spectra were fitted with Gaussian/Lorentzian product functions. For quantification, integrated intensities were compared using relative sensitivity factors from the recommendations of the supplier. Ohmic drop was corrected by current interrupt technique on the PAR 273 equipment.

Electrodes fabrication

The 6 MHz AT-cut quartz crystals coated with gold were purchased from XTRONIX and manipulated at all times using nitrile gloves to avoid transfer of grease from the hands to the resonator. 0.1 mm polyurethane-coated copper wires were prepared to be glued by removing the polyurethane layer at the tips by burning them with a flame. The oxide formed at the surface of the copper was removed with 6.0 M hydrochloric acid and the wires washed with water. A very small amount of silver epoxy resin was prepared and used to glue the copper wire to one side of the resonator. After it, the resonators were transferred to an oven heated at 90 °C for 15 minutes. The same procedure was applied again to glue the second wire to the opposite side of the resonator. The resonators were stored in a closed box and cleaned briefly with analytical grade acetone prior to be assembled in the EQCM cell.

Initially, porous Vycor[®] was used as a bridge for the fabrication of the reference electrodes. Since its shortage on the market, it was successfully replaced by porous silica gel spheres, typically used for desiccation. Type II silica gel of 3.5 mm bead size (Aldrich, catalog n. S7500-1KG) was first soaked in pure acetone for an hour. Acetone was removed and replaced by water. After 24 hours the water solution was replaced by saturated KCl solution and the solution renewed each day for 3 consecutive days. The spheres can be stored under saturated KCl solution for months and are ready to use. Direct addition of water to the dry spheres will cause them to break.

Ag/AgCl reference electrodes were built using a 4 mm external diameter glass tube with an inner diameter of 3 mm. The desired length was cut and the tips heated briefly with an Oxygen / Propane burner. A pure silver wire (0.5 mm diameter, 99.9 %, Aldrich) was wound around a 0.5 mm supporting copper wire to yield a silver coil. The silver coil was transferred to a branch of a U-shape glass tube filled with 6.0 M HCl. The silver wire was connected to the positive pole of a laboratory power supply and the negative pole was connected to a small platinum wire on the other branch of the U-tube. A constant current of 3 mA was applied during 30 minutes to oxidize the surface of the silver to silver chloride. A previously prepared silica gel sphere filled with saturated KCl solution was fixed to the tip of the glass tube using a transparent heat-shrink polyolefin tube by heating it inside a boiling solution of saturated aqueous KCl. The tube was filled with saturated KCl/AgCl mixture and the coiled silver wire added. The top of the tube was sealed with hot glue to ensure no leaks

or evaporation of the filling solution. The electrode was kept immersed in saturated aqueous KCl when not in use. The potential of the reference electrodes was periodically checked using a standard reference electrode from Metrohm. To verify the potential of the electrode, both electrodes were dipped into concentrated KCl solution, and the potential difference between them measured using a high precision digital voltmeter (Fluke 87V). If the difference between the electrodes was bigger than 5 mV the home-made electrode was discarded and a new electrode was built.

FTO-coated glass electrodes were prepared from plates cut down to rectangular plates of 9 x 25 mm. The plates were thoroughly washed with ethanol and then with acetone. An adhesive tape with a hole of 5 mm diameter was attached on each plate in such a way that a circle of 5 mm diameter on the bottom part and a small strip at the top remained uncovered. The 5 mm circle is the only active area of the electrode and the small strip used for electrical contact.

Home-made EQCM cell

The electrochemical cell designed for use with our EQCM apparatus was built from polyester/styrene cross-linked resin, and differs from the major commercial cells by the fact that the quartz disc is held in a vertical position, with the counter electrode facing the surface of the working electrode. This design prevents materials formed close to the counter electrode from falling onto the surface of the working electrode. Another improvement lies in the minimal area of solution that is in contact with the atmosphere. Waves propagating on the surface of the solution caused noise during the measurements; this noise is minimized in our current design (Figure S1).

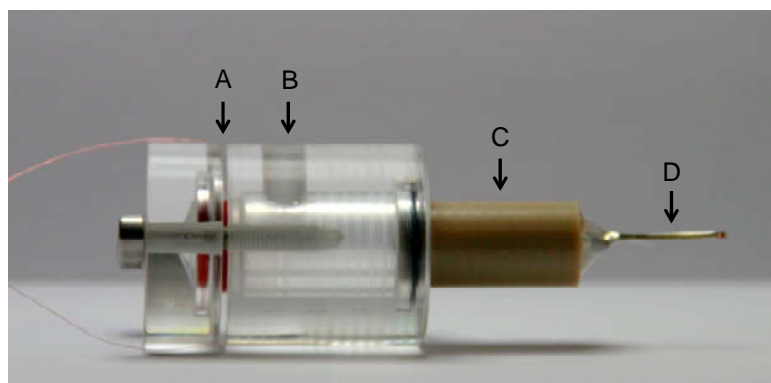


Figure S1. Photograph of our home-made EQCM cell. Quartz disc location (**A**), access for the reference electrode (**B**), PEEK compartment containing Pt counter electrode (**C**) and electrical contact of the Pt counter electrode (**D**).

Potential and electrolyte calibration

To ensure a correct calibration of the overpotentials measured during LSV experiments, the reversible hydrogen electrode potential in our experimental conditions was measured as follows: A small spherical Pt electrode was obtained by melting a Pt wire using a propane/oxygen torch. This small spherical electrode was fixed in a glass body and used as a working electrode. Pt was activated by oxidation at high anodic potentials (+1.8 V *vs.* Ag/AgCl) prior to the measurement.

1.0 M H₂SO₄ was degassed with H₂ for 15 minutes and a small flow of H₂ was kept flowing on the headspace of the cell. A home-made saturated KCl, Ag/AgCl electrode was used as a reference in a similar way as during LSV studies. The starting potential of the cyclic voltammetry experiment was set to 220 mV *vs.* Ag/AgCl for 5 seconds followed by the potential scan at 1.0 mV·s⁻¹. After the experiment, the potential of the reference electrode was measured against a master electrode (Metrohm, part. number 6.0726.100) and determined to be 200.6 mV *vs.* SHE.

The potential scale of the data obtained was referenced against SHE (Figure S2). The anodic scan crosses the zero current axes at -4.88 mV *vs.* SHE while the cathodic wave crosses the same axes at -1.23 mV. The mean value of -3.05 mV was considered as 0 V *vs.* RHE. In this work, at 1.0 M H₂SO₄, RHE was considered as having the same value as SHE, and thus, the pH of 1.0 M H₂SO₄ considered as being equal to 0.

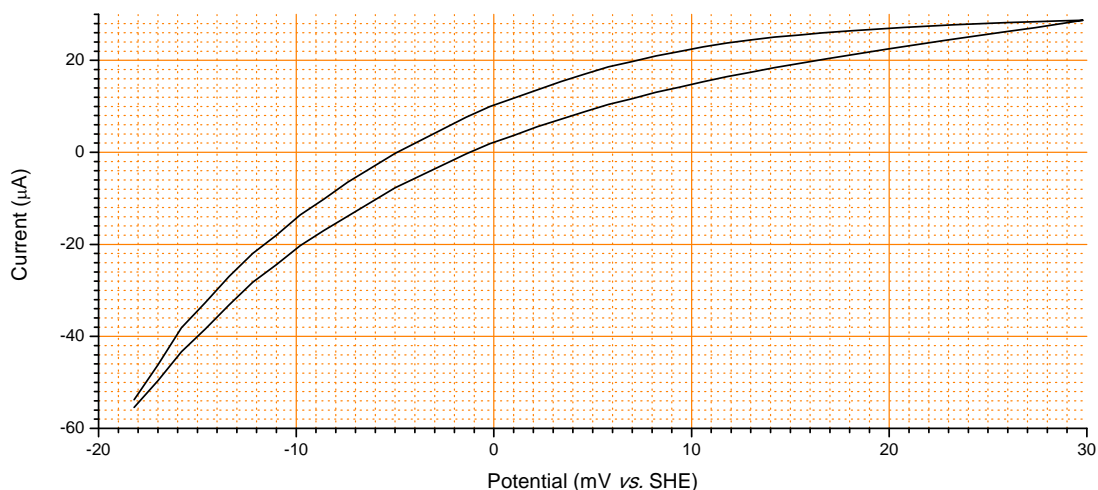


Figure S2. Cyclic voltammogram for the H_2/H^+ couple measured on Pt electrode at $\text{pH}=0$.

Molar absorptivity of MoS_4^{2-}

$(\text{NH}_4)_2\text{MoS}_4$ (100 mg, 0.384 mmol) was dissolved in 50 mL of water with the help of an ultrasonic bath. The dark red solution was filtered through a syringe Nylon membrane filter (0.22 μm) directly into a 100 mL volumetric flask. The flask was filled with pure deionized water and three aliquots of 1.000 mL were transferred to three different 10 mL volumetric flask. One drop of a concentrated solution of NaClO (13 %, by weight) was added to each flask to oxidize the MoS_4^{2-} ions to stable MoO_4^{2-} species. The volumetric flasks were filled and homogenized. The concentrations of these solutions were determined by ICP-OES. The concentration of the mother solution was calculated to be $3.1795 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$.

Eight solutions with different concentrations of MoS_4^{2-} were prepared by diluting aliquots of 50, 100, 150, 200, 250, 300, 400 and 500 μL of the mother solution into 8 different 10 mL volumetric flasks. The electronic spectra of these solutions were recorded (Figure S3). The absorbances at 316.5, 467.2 and 529.5 were plotted against the concentration of their respective solutions, calculated from the concentration of the mother solution and the dilution factor. The ϵ are 873 (529 nm), 12049 (467 nm) and 16783 (316 nm) $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$.

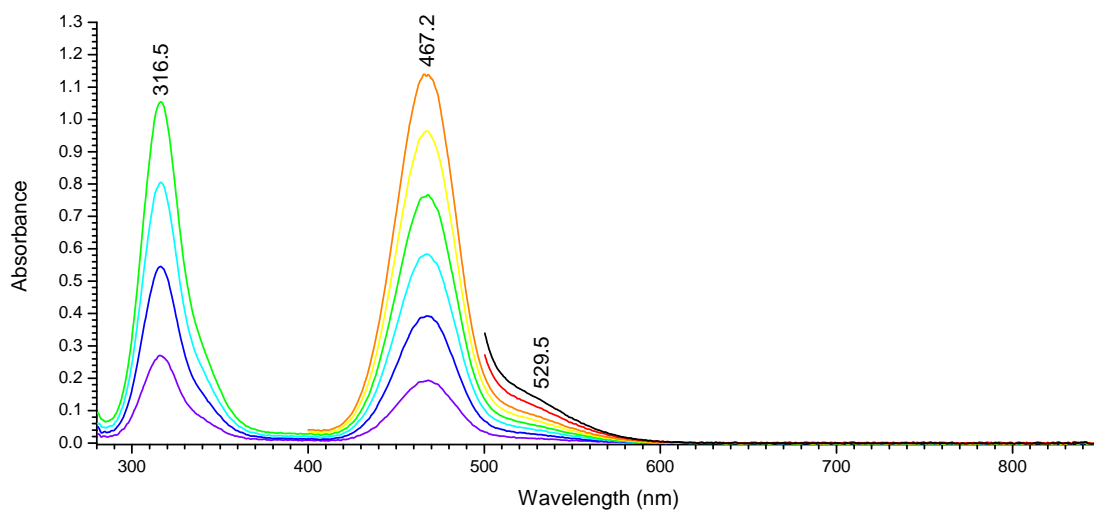


Figure S3. Electronic spectra of $(\text{NH}_4)_2\text{MoS}_4$ recorded at different concentrations in water.

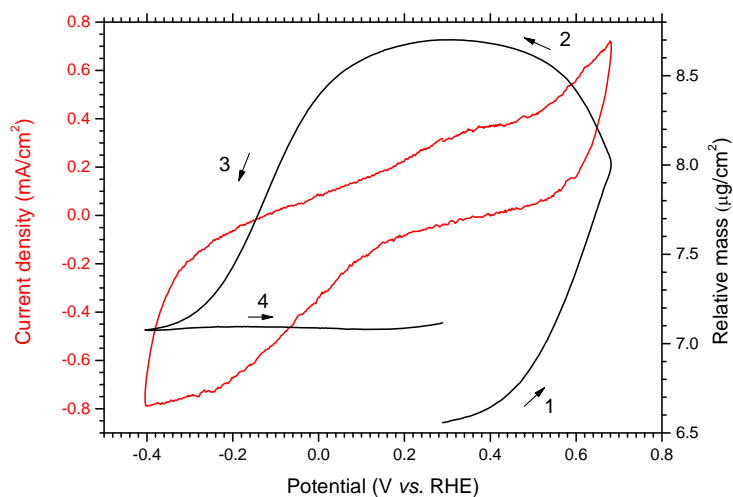


Figure S4. The evolution of current (red line) and film mass (black line) during the 16th potential cycle.

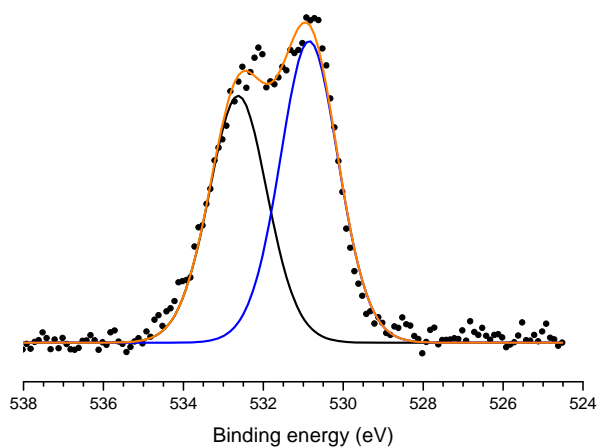


Figure S5. O 1s XPS spectrum for a MoS₂-CE film. experimental data (•••), fitting envelope (—), O from MoO₃ (—).

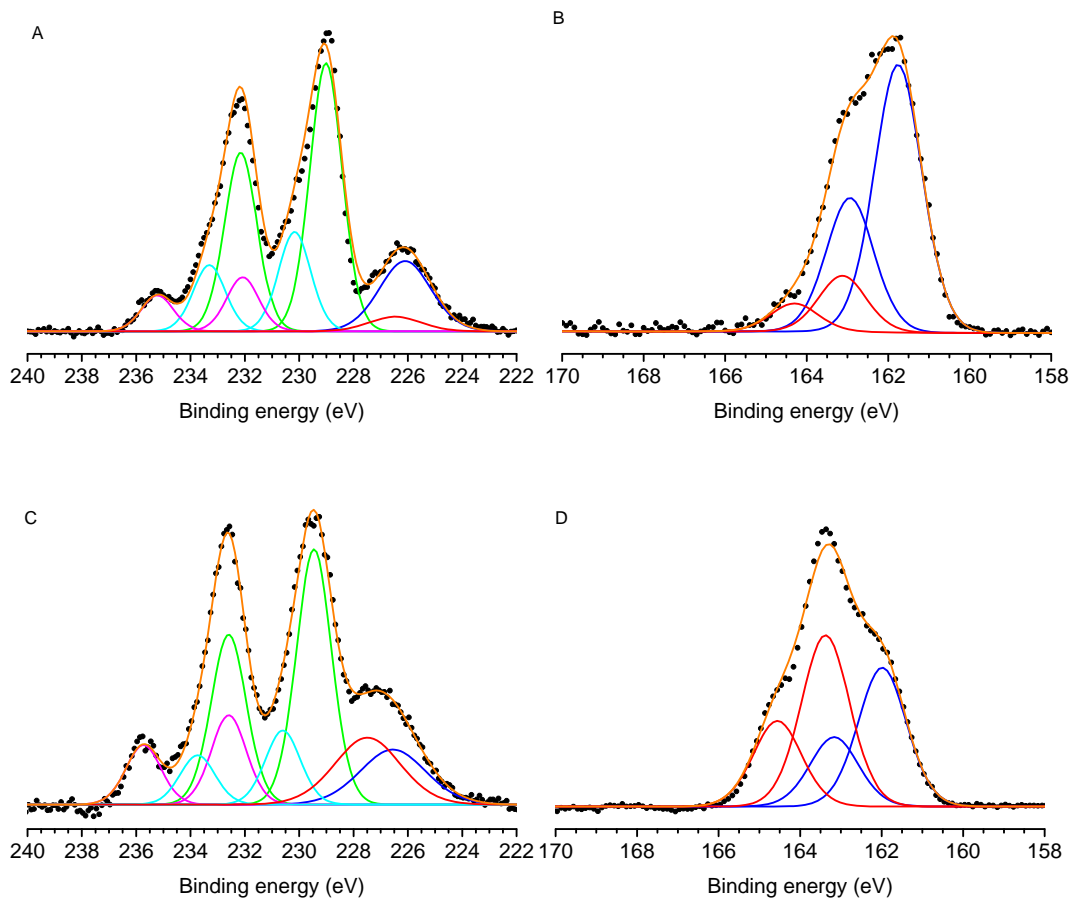


Figure S6. XPS spectra for a molybdenum sulfide film deposited by potential cycling from -0.4 to 0.7 V (A and B), or by potential cycling from 0.7 and -0.4 V (C and D). (A, C) Mo 3d region, experimental data ($\bullet\bullet\bullet$), fitting envelope (---), $\text{Mo}^{\text{A}}\text{S}_n$ (---), $\text{Mo}^{\text{B}}\text{S}_n$ (---), MoO_3 (---), S_2^{2-} 2s (---), S^{2-} 2s (---). (B, D) S 2p region, experimental data ($\bullet\bullet\bullet$), fitting envelope (---), S_2^{2-} (---), S^{2-} (---).

Table S1. Binding energies for the S 2s components.

Material	S ¹ 2s (eV)	S ² 2s (eV)	S ⁰ 2s (eV)	S ¹ :S ² :S ⁰ ratio
Crystalline MoS ₂	-	226.7	-	-
MoS ₃ -AE	227.3	225.9	229.7	2.2:1:0.6
MoS ₂ -CE	226.8	226.4	-	0.4:1:0
MoS ₃ -AE after acid wash	227.3	226.9	-	1.5:1:0
MoS ₃ -AE after activation	226.8	226.5	-	0.4:1:0
MoS _x -CV-A ^a	227.4	226.6	-	1.2:1:0
MoS _x -CV-C ^b	226.5	226.1	-	0.2:1:0

^afrom 0.7 to -0.4 V; ^bfrom -0.4 to 0.7 V.