Supplementary Information (SI) for Journal of Materials Chemistry A.

Polymerized Tungstate-Molybdenum Sulfide Electrocatalysts for Hydrogen Evolution Reaction under acidic conditions

Maria El Khoueiry,[a,b,c] Nathalie Leclerc,[a] Haitham Maslouh,[b,c,d] Mikhael Bechelany,[d] Emmanuel Cadot,[a] Clément Falaise[a*] and Loïc Assaud[b,c*]

[a] *Institut Lavoisier de Versailles, CNRS, UVSQ, Université Paris-Saclay, 45 avenue des Etats-Unis, 78035 Versailles (France).*
[b] *Institut de Chimie Moléculaire et des Matériaux d'Orsay, CNRS, Université Paris-Saclay, 7 Av. des Sciences, 91400 Orsay (France).*
[c] *Institut des Matériaux Poreux de Paris, ENS, ESPCI Paris, CNRS, PSL University, 75005 Paris (France).*
[d] *Institut Européen des Membranes de Montpellier, Université de Montpellier, CNRS, Ecole Nationale Supérieure de Chimie de Montpellier, 300 avenue du Professeur Jeanbrau, 34090 Montpellier, (France).*

Table of contents

1. **Materials and methods**
a. Preparation of W_x-Mo_3S_4-CNT compounds
b. Time-resolved Small Angle X-ray Scattering
c. Vibrational spectroscopies
d. SEM/TEM analyses
e. Electrochemical characterizations
f. Atomic Force Microscopy characterizations
g. Implementation in PEM electrolyser

2. **Additional figures**
a. Figure S1
b. Figure S2
c. Figure S3
d. Figure S4
e. Figure S5
f. Figure S6
g. Figure S7
h. Figure S8
i. Figure S9
j. Figure S10
k. Figure S11
l. Figure S12

1. Materials and methods

a. Preparation of W_x-Mo_3S_4 and W_x-Mo_3S_4-CNT

Sodium tungstate dihydrate was purchased from Chempur Feinchemikalien und Forschungsbedarf GmbH (99+%). Multi-walled carbon nanotubes carboxylic acid-functionalized were purchased from Sigma-Aldrich. Nafion perfluorinated resin 5 wt% was also obtained from Sigma-Aldrich. Sulfuric acid 96% was purchased from VWR Chemicals. Hydrochloric acid 37% was obtained from Sigma-Aldrich. Ethanol was acquired from VWR Chemicals. Milli-Q ultrapure water with 18.2 MΩ.cm resistivity was used. $Mo_3S_4(H_2O)_9Cl_6.2NH_4Cl.2H_2O$ was synthesized as described in the literature (G. Sakane; T. Shibahara *Inorg. Synth*. **2002**, 33, 144).

General procedure for the preparation of the W_x-Mo_3S_4 materials. The systems W_x-Mo_3S_4 were synthesized from mixing a solution of tungstate ions and an acidified solution of aqua cluster $[Mo_3S_4(H_2O)_9]^{4+}$. The tungstate solution was prepared by dissolution of 4.9 g of sodium tungstate ($Na_2WO_4.2H_2O$; 14.8 mmol) in 15 mL of distilled water. In a separate beaker, $Mo_3S_4(H_2O)_9Cl_6.2NH_4Cl.2H_2O$ (0.384 g; 0.41 mmol) was dissolved in 2 mL of diluted HCl. At room temperature, the solution of aqua cluster is added dropwise to the preformed tungstate solution under rigorous agitation. The pH of the resulting solution is adjusted to the desired pH value (1, 4 or 8) by adding HCl (1M). An instant precipitation is observed leading to the formation of W_x-Mo_3S_4 aggregates. The stirring of resulting dark solution is maintained for two hours. Dark powder of W_x-Mo_3S_4 polymers was isolated by filtration, washed by cold water, and dried in air. Typical yields: >80 % (based on Mo_3S_4 cluster).

General procedure for the preparation of the W_x-Mo_3S_4-CNT materials. These carbon-supported systems were synthetized using the same procedure detailed previously. The only difference is the addition of carbon nanotubes to the tungstate solution. Then all the consecutive steps remain the same.

b. Time-resolved Small Angle X-ray Scattering

Small angle X-ray scattering (SAXS) measurements were performed on the high brilliance SWING beam line at the Soleil synchrotron facility, with monochromators set at 12 KeV (λ = 1.0332 Å). Using a CCD detector (EIGER-4M) at 795 mm from the capillary, diffraction patterns were recorded for reciprocal spacing $q = 4\pi \sin(\theta)/\lambda$ varying between 0.01 and 1.4 $Å^{-1}$. Fixed 1.5 mm quartz capillaries were used as sample containers for the solutions. Usual corrections for background subtractions (empty cell and detector noise) and intensity normalization, using water as a standard, were applied.

The reaction solutions have been prepared by dissolution of sodium tungstate, and aqua cluster $[Mo_3S_4(H_2O)_9]^{4+}$ in acidified water (diluted HCl). To slow-down the polymerization of W_x-Mo_3S_4, we used concentration of reactants much lower than those used for the large-scale preparation of W_x-Mo_3S_4. The mixing of the solution was performed using two-syringe pumps in order to measure SAXS data quickly after the mixing the reactant. A solution of 20 mM of sodium tungstate was placed in a syringe while the acidified Mo_3S_4 solution (1.6 mM in diluted HCl) is place in another syringe. The estimated time between the mixing the reactants and the first measurement was about 30 seconds. SAXS data were collected every 10 seconds during the first 30 minutes.

c. Vibrational spectroscopies

Infrared spectroscopy. FT-IR Nicolet spectrophotometer with diamond crystal was used to measure all spectra. Attenuated Total Reflectance (ATR) corrections and spectra analysis were done through Omnic software.

Raman spectroscopy. Raman spectra were acquired using a Renishaw inVia Raman microscope with a 532 nm excitation wavelength and a ×50 objective lens. The W_5-Mo_3S_4 compound was prepared as a catalytic ink by mixing 10 mg of the catalyst with 20 µL of Nafion™ solution (5 wt%), 1 mL of isopropanol and 0.1 mL of water, followed by sonication for 4 h. The resulting suspension was deposited by drop casting onto a 5% wet-proofed Toray 120 carbon paper gas diffusion layer (GDL) serving as the working electrode, to achieve a catalyst loading of approximately 2 $mg.cm^{-2}$. Operando Raman measurements were performed both on dry electrodes and under applied electrochemical potential in a homemade H-cell filled with a 0.5 M H_2SO_4 solution, using an Ag/AgCl electrode as the reference and a platinum foil aw the counter electrode. The electrochemical measurements were controlled by an EmStat4S potentiostat/galvanostat.

d. SEM/TEM Analysis

JSM 7001-F Jeol SEM-FEG was used for Energy Dispersive X-ray Spectroscopy. MET Jeol 2100 Plus and MEB ZEISS Sigma HD was used for all recorded TEM and SEM images respectively.

e. Electrochemical characterizations

The electrochemical tests were performed using Solartron ModuLab XM ECS Analytical potentiostat. All electrochemical tests were carried out in a three-electrode cell, under argon/nitrogen atmosphere in 0.5 M H_2SO_4. A graphite rod was used as counter electrode and Ag/AgCl reference electrode was used from radiometer analytical (XR110). The working electrode used is a surface modified glassy carbon disk with 3 mm diameter. The ink was prepared using a catalyst mass of 8 mg in 400 µL of ethanol and Nafion. The prepared ink was left under sonication for 15 min. 2 µL were drop casted onto the glassy carbon electrode and left to dry under air overnight. Linear sweep voltammograms were registered in the faradaic region (0 till 0.4 *vs* RHE) to study Hydrogen Evolution Reaction occurring at the cathode. Tafel slopes were obtained through plotting $\eta = b \log|j| + a$; where b is the Tafel slope and j is the current density. Galvanostatic Electrochemical Impedance Spectroscopy (GEIS) was used to measure the charge-transfer resistance. Frequencies ranged from 10^{-1} Hz till 10^{5} Hz and current densities ranged from 1 $mA.cm^{-2}$ till 10 $mA.cm^{-2}$. Represented Nyquist plots were measured at 10 $mA.cm^{-2}$. The charge transfer resistance was obtained through fitting Nyquist and Bode plots using ZView software. To estimate the electrochemically active surface area (ECSA), cyclic voltammetry was performed in the non-faradaic region (0.065 till 0.16 *vs* RHE). Scan rates ranged between 200 and 5 $mV.s^{-1}$. The double layer capacitance Cdl (µF) was obtained through the linear fit of the geometric surface of the CVs plotted against the square root of the scan rates. Then EASA (m^2) is estimated following the equation EASA=Cdl/Cs. Cs is the specific capacitance of the material. Based on literature, Cs = 40 $\mu F.cm^2$ will be used. ECSA ($m^2.g^{-1}$) is then calculated by dividing EASA by the catalyst mass.

f. Atomic Force Microscopy (AFM) Characterizations

Atomic Force Microscopy (AFM) was used to measure the topography, nanomechanical and electrochemical properties. AFM Bruker Dimension Icon was used under different modes. PeakForce Tapping mode was applied for all measurements. To investigate nanomechanical properties, Quantitative Nanomechanical Mode (PF-QNM) was used. Bruker Scanasyst-Air tips were used with a silicon nitride cantilever and a spring constant of 0.4 N/m. The scan size was 600 nm x 600 nm. The frequency was fixed at 2 KHz and the scan rate at 0.2. The peakforce amplitude was 60 nm and the peakforce setpoint was set at 1.6 nN. Nanoscope Analysis 1.9 software was used for image analysis.

Scanning electrochemical microscopy (SECM) measurements were performed in liquid media (10 mM H_2SO_4, 100 mM KCl) using a PF-SECM probe supplied by Bruker with a ~50 nm Pt-glass-apex tip. The scan size was 5 µm x 5 µm. The catalyst layer was deposited via drop-casting (catalytic ink consisting of a mixture of the catalyst combined with Nafion® /ethanol) onto a glassy carbon substrate, previously polished. For the hydrogen evolution reaction (HER) investigation, the Substrate Generation–Tip Collection mode was used. Using a bipotentiostat (CHI 700F series), both the tip and the sample were polarized to promote HER at the substrate and hydrogen oxidation at the probe. A Pt wire was employed as counter electrode and a Ag/AgCl wire as a pseudo reference electrode. The oxidation current was measured at the tip. In this configuration, a potential of -50 mV was applied to the substrate, while a potential of 150 mV was applied to the tip.

g. Implementation in PEM electrolyser

A custom-built proton exchange membrane (PEM) water electrolyzer was operated as a single cell with an active area of 25 cm^2 (Figure S0) (T. Srour et al. *Int. J. Hydrogen Energy* **2024**, *58*, 351-361). Catalyst layers were prepared via a spraying technique using a Sono-Tek ExactaCoat inkjet system, which deposited the catalysts directly onto a PTFE inert substrate and subsequently transferred onto Nafion™ 115 membranes via the so-called decal transfer process (X. Liang et al. *Fuel* **2015**, *139*, 393) to form catalyst-coated membranes (CCMs).

The CCMs were then integrated with an IrO_2 anode catalyst and either a W_5-Mo_3S_4-CNT/C or a Pt/C cathode catalyst, the latter serving as a benchmark reference. The full assembly included a titanium porous transport layer (PTL) (Sintered Ti Gr. 1, 1 mm thick, 40% porosity, powder size 75 µm, size pores of 10 µm) and a gas diffusion layer (GDL) (Toray 120 carbon paper, 370 µm, 5% wet-proofed, Fuel Cell Store). Catalyst loadings were set to 3 mg.cm^{-2} for IrO_2 (Surepure Chemetals) at the anode, and either 2.5 mg.cm^{-2} for W_5-Mo_3S_4-CNT (10wt%)/C (40 wt%) Vulcan® XC 72) or 0.5 mg.cm^{-2} for Pt/C (60 wt%) at the cathode. The catalyst ink for W_5–Mo_3S_4–CNT/C (40 wt%) Vulcan® XC 72 was prepared by dispersing 110 mg of catalyst with 250 mg of Nafion™ solution (20 wt%), 12 mL of deionized water, and 12 mL of isopropanol. The mixture was ultrasonicated for 8 h to ensure homogeneous dispersion. The final catalyst loading was calculated based on the actual surface area of the transferred layer on the Nafion™ 115 membrane, as determined by the deposited mass and image analysis. Electrochemical performance was assessed through polarization curves recorded for a total duration of 45 h alternatively at a current density of 400 mA.cm^{-2} for 16 h and 600 mA.cm^{-2} for 4 h, as well as through electrochemical impedance spectroscopy (EIS) from 100 kHz to 0.1 Hz at various current densities, using an electrochemical workstation (VSP 300 potentiostat Bio-Logic Science Instruments). All experiments were conducted at 80°C under a total applied compression of 15 kN. Ultrapure water (from Veolia) with a resistivity of 18.2 MΩ.cm at 25 °C was used throughout the tests.

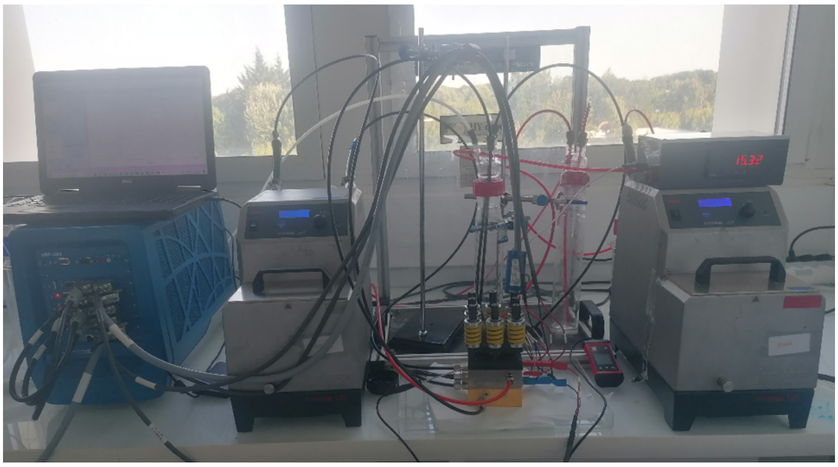


Figure S0. Photograph of the custom-built PEM water electrolyzer.

2. Additional figures

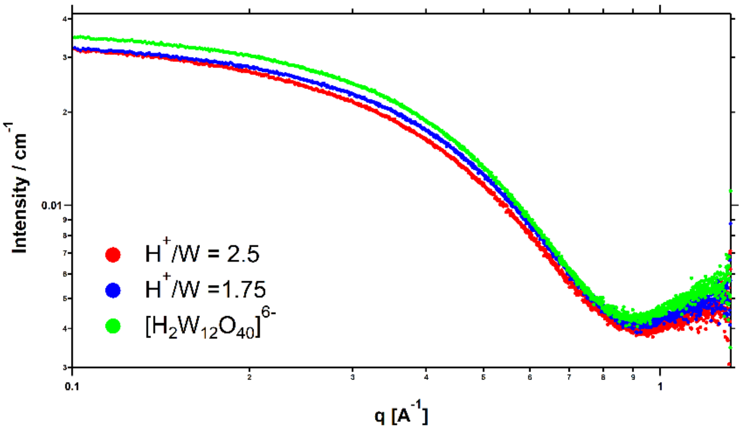


Figure S1. Comparison of the log(q)–log(I(q)) scattering curves of tungstate solution (10 mM) with h value (H^+/WO_4^{2-} ratio = 2.5 and 1.75, measured after one day) with the log(*q*)–log(I(*q*)) scattering curve of an aqueous solution containing 0.8 mM $[H_2W_{12}O_{40}]^{6-}$ (rubidium salt).

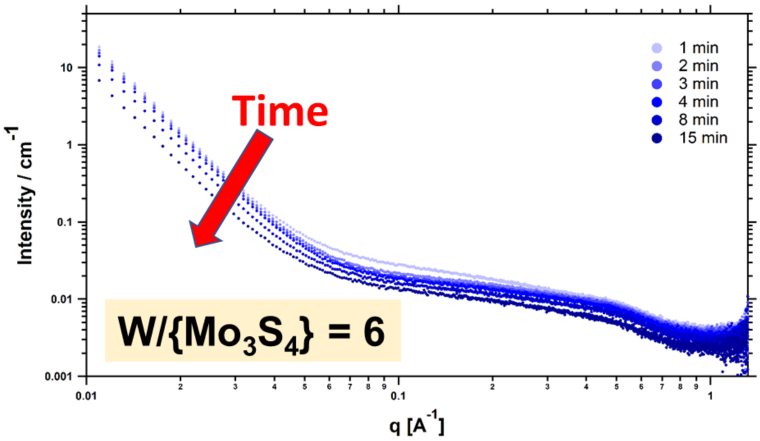


Figure S2. Time-resolved SAXS curves of a solution containing 10 mM of tungstate ions and 1.6 mM of $\{Mo_3S_4\}$ cluster, with h value of 2.5.

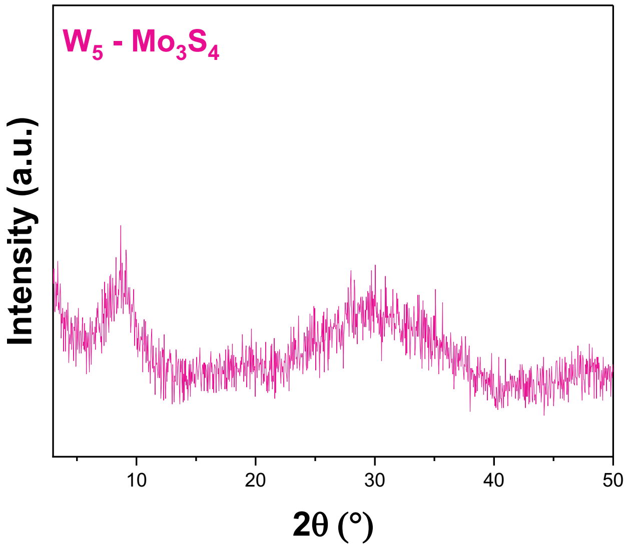
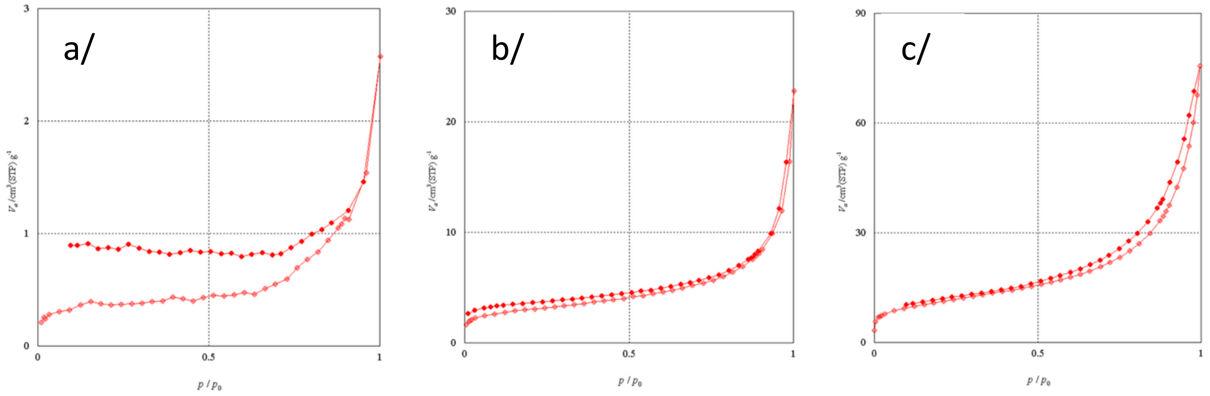


Figure S3. Powder X-ray pattern (copper radiation) of the inorganic polymer notated **W_5-Mo_3S_4**, indicating the material is amorphous. Powder X-ray diffraction analysis of all others prepared inorganic polymers does not show any Bragg peaks.



W_8-Mo_3S_4, 1.41 $m^2.g^{-1}$

W_5-Mo_3S_4, 10.6 $m^2.g^{-1}$

W_2-Mo_3S_4, 38.9 $m^2.g^{-1}$

Figure S4. Specific surface area measurement performed by BET for the different compounds.

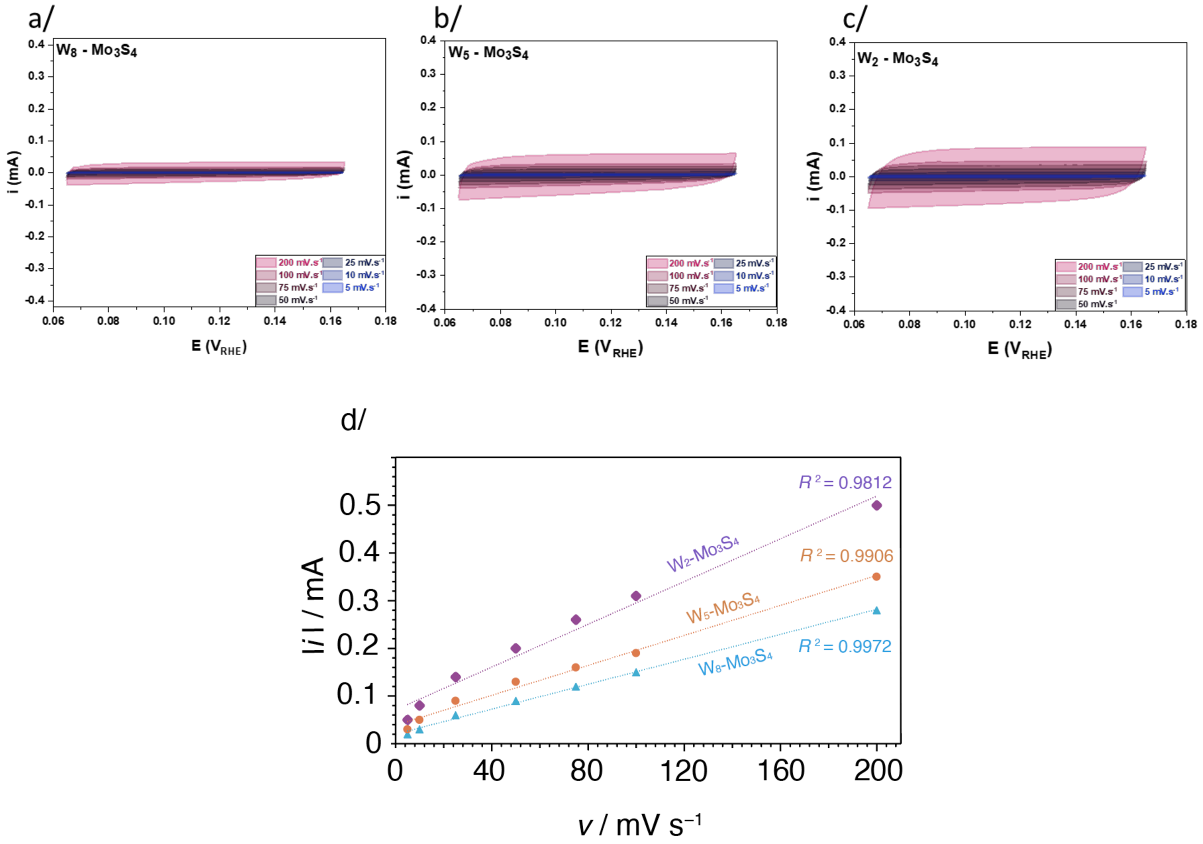


Figure S5. Cyclic voltammograms in the non-faradaic region used to estimate the electrochemically active surface area for the three catalysts: a/ W_8–Mo_3S_4, b/ W_5–Mo_3S_4, and c/ W_2-Mo_3S_4. d/ Capacitive current vs. scan rate plot for the three samples.

The average capacitive current (|i|) measured at 0.12 V vs RHE scales linearly with scan rate ($R^2 > 0.98$ for all samples; see Figure S2), confirming the capacitive nature of the current response. The extracted slopes indicate an increasing electrochemically active surface area in the order $W_8 < W_5 < W_2$-Mo_3S_4.

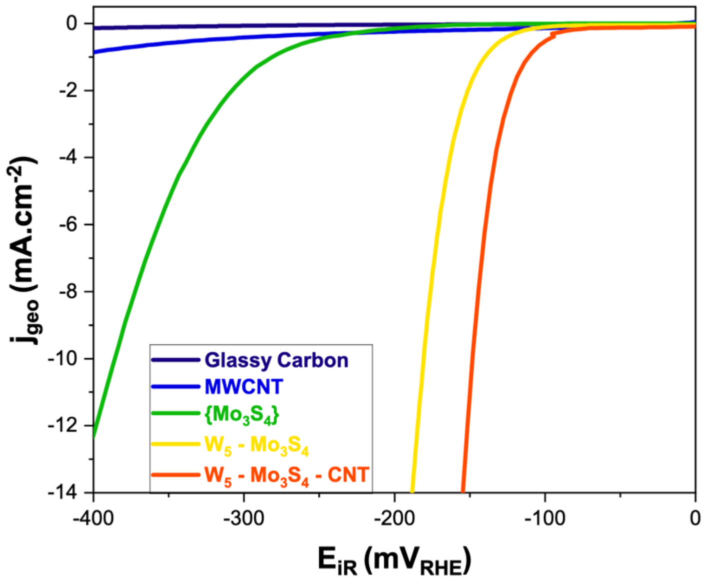


Figure S6. 10th cycle of LSV curves of control experiments: Glassy carbon, CNT-only, Mo_3S_4-only, W_5-Mo_3S_4 and W_5-Mo_3S_4 -CNT.

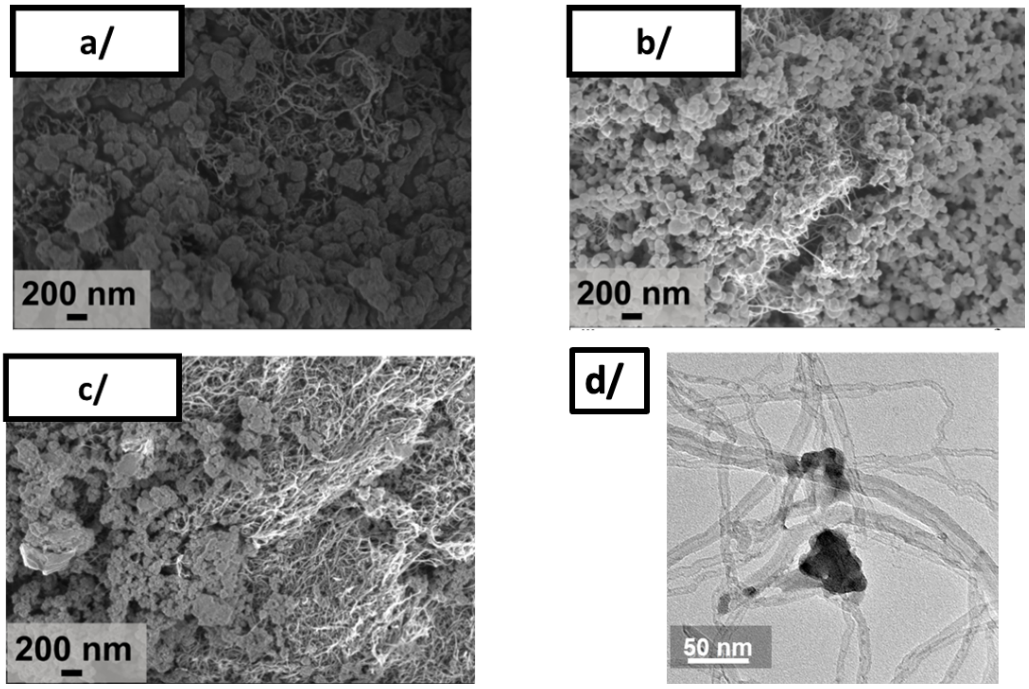


Figure S7. a/ SEM images of W_8-Mo_3S_4-CNT. b/ SEM images of W_5-Mo_3S_4-CNT. c/ TEM images of W_2-Mo_3S_4-CNT. d/ TEM image of W_2-Mo_3S_4-CNT.

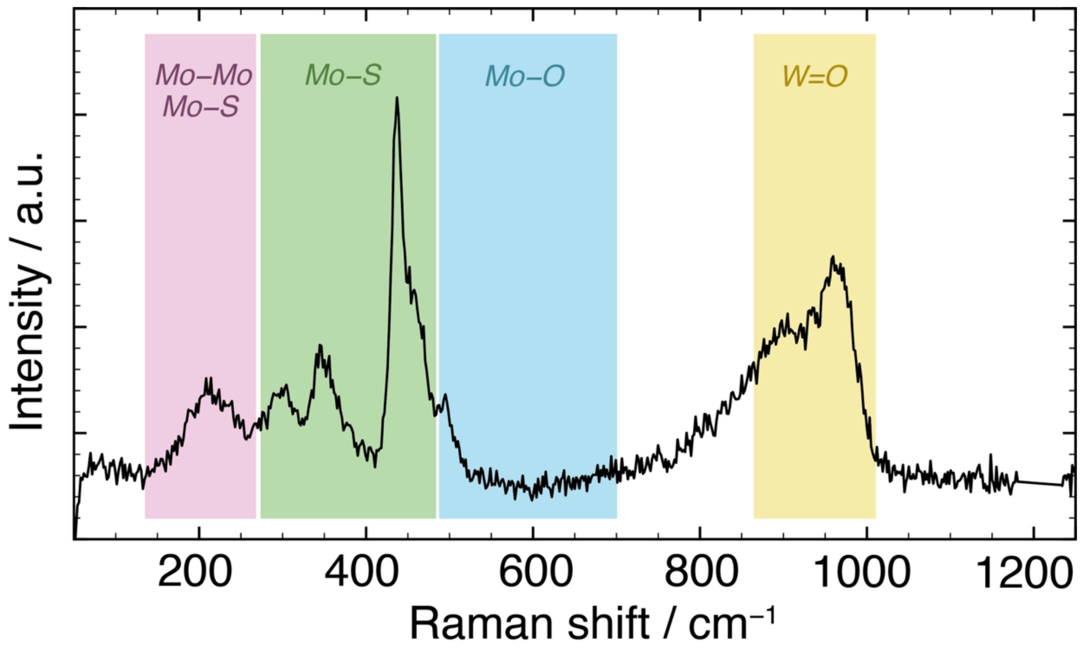


Figure S8. Raman spectrum of the W_5-Mo_3S_4 powder, showing band assignments for the main vibrational modes of the crystal structure.

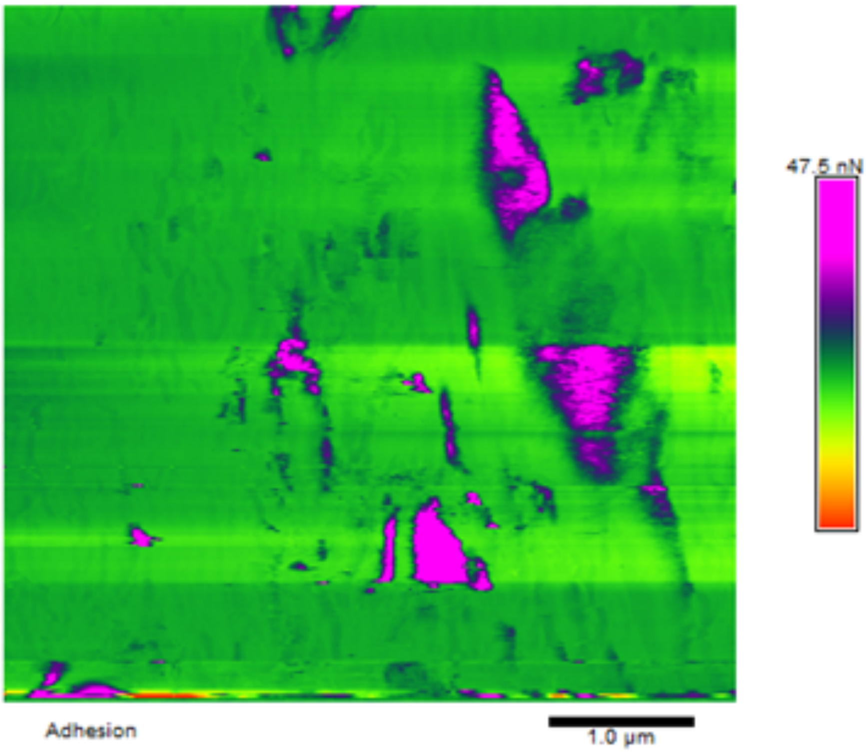


Figure S9. Nanomechanical properties of the substrate.

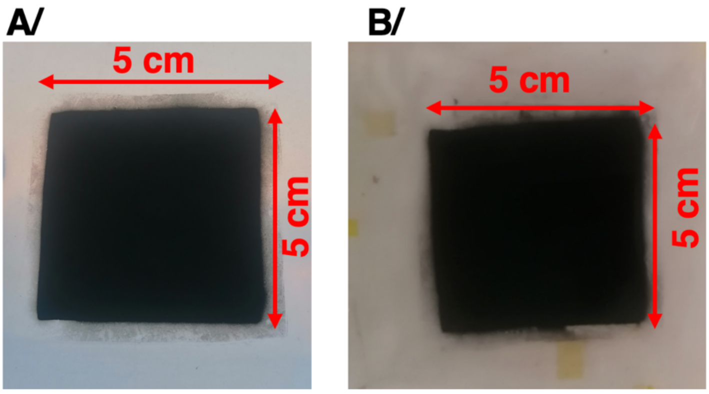


Figure S10. A/ Photograph of the W_5-Mo_3S_4-CNT/C catalyst layer deposited on PTFE via spray coating; B/ Photograph of the resulting catalyst-coated membrane obtained after the decal transfer process.

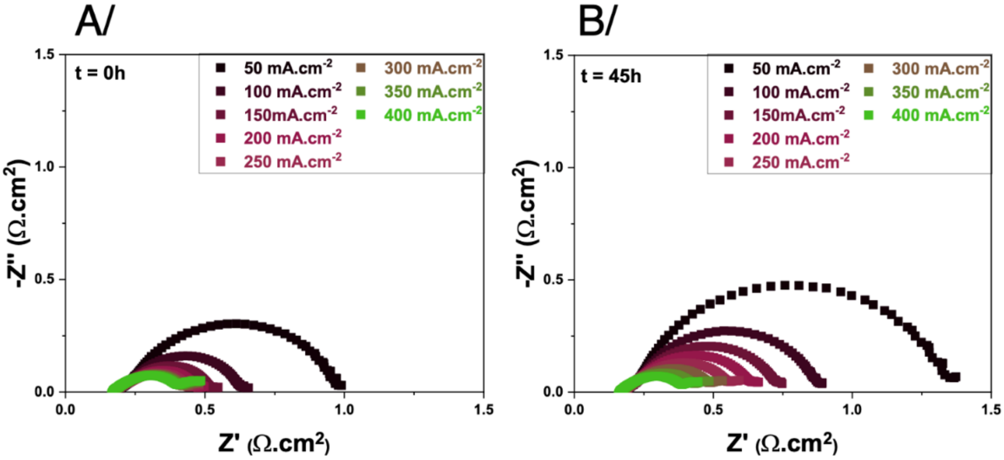


Figure S11. A/ Nyquist plots of a PEM electrolyzer recorded at initial time (t = 0 h) under different applied current densities ranging from 50 to 400 mA·cm^{-2}. B/ Nyquist plots of a PEM electrolyzer recorded after 45 h of operation under different applied current densities ranging from 50 to 400 mA·cm^{-2}. The Nyquist plots display the electrochemical impedance spectra of a proton exchange membrane (PEM) electrolyzer measured at the initial time (t = 0 h) and after 45 hours of operation under various applied current densities ranging from 50 to 400 mA.cm^{-2}. The spectra show semi-circles that are characteristic of electrochemical systems, typically representing charge transfer resistance and double layer capacitance effects. The general trend indicates a decrease in the diameter of the semicircles as the current density increases. This suggests a strong dependence of the interfacial resistance on the operating current density. The shrinking arc radius with increasing current density reflects a reduction in polarization resistance, likely due to enhanced electrode kinetics, and/or better membrane conductivity during electrolysis. However, at very high current densities, although resistance continues to decrease, the system may begin to experience mass transport limitations (not clearly visible at t = 0 h but clearly observed at t = 45 h), particularly due to bubble formation. Overall, the impedance analysis highlights a clear correlation between current density and interfacial resistance, with higher current operation leading to improved charge-transfer dynamics. These results provide insights into the electrochemical performance and durability of the system, particularly in relation to electrode activation and possible transport limitations.

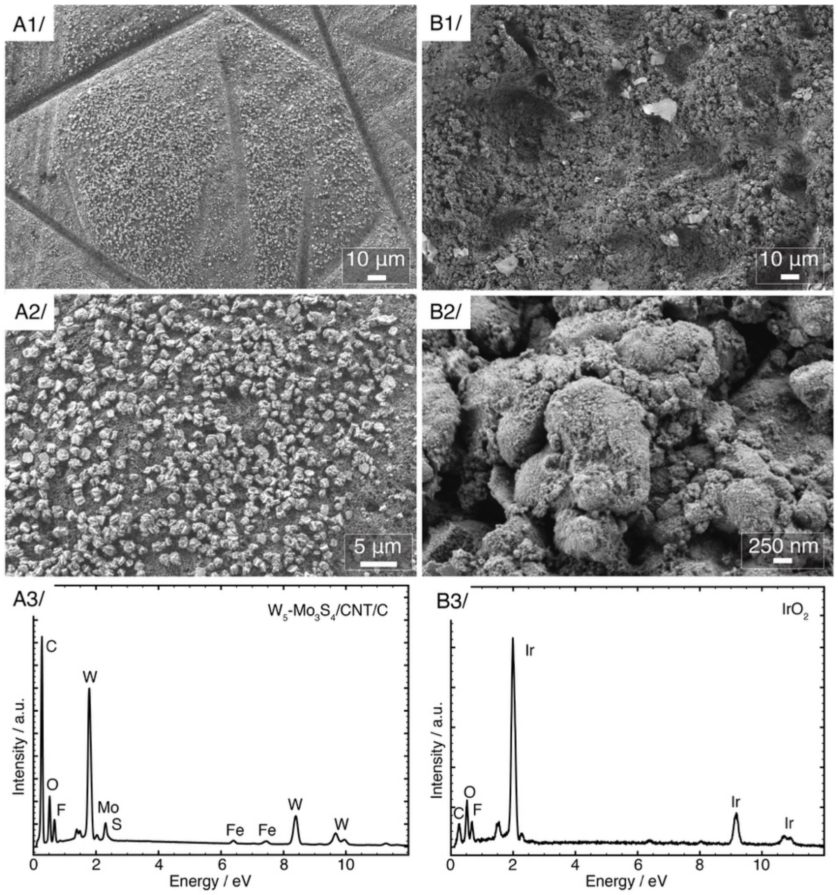


Figure S12. SEM micrographs of W_5-Mo_3S_4 cathode side (A1, A2) and IrO_2 anode side (B1, B2) of the CCM after 45 h under electrolysis operating conditions at 80°C, and the corresponding elemental analyses performed by EDS (A3, B3).