Supporting Material for:
Soft X-ray Operando Spectroscopy for Gas-Evolving Electrocatalysis at 100mA/cm^2

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1- Electrochemical high Flow cell design and manufacturing details.

The EC- flow cell, as described in the main text, is a reactor chamber housing the working electrode (WE) and the counter electrode (CE), positioned 5 mm apart. The WE is an Au-coated Si_3N_4 membrane, while the CE is a Pt flat plate. The reference electrode (RE) is a 1 mm diameter Pt wire**,** placed along the flow channel before the reactor chamber (see Figure 1**,** main text**)**. The potential of the quasi-RE was calibrated, at the beginning of every experiment, with an Ag/AgCl (3M KCl) electrode placed in electrical contact in the external electrolyte reservoir.
The WE is mounted with the gold-plated side facing the reactor chamber, where it interacts with the electrolyte (for details see Section 4 - Material and Methods, SI). The electrical contact with the WE is established through four retractable gold-plated pins connected to the external contacts in the back chamber of the cell. The WE is sealed with an O-ring pressed by the front lid of the cell, ensuring that the electrode contacts remain isolated from the electrolyte chamber and preventing liquid leakage from the cell reactor.

Structural design:
The EC- flow cell consists of three main components: the cell body and two lids. Technical sketches of the main body and the lids are reported in Figure S3 (spans several pages).
The front lid, holding in place the WE Au-coated Si_3N_4 window, features a conical groove (90° wide angle) that terminates with a 2 mm diam. hole which allows the WE window to be exposed to the incoming X-ray beam while ensuring the outgoing photons exit at the 45° angle.
The back lid covers the electrode compartment, where the wire connections/soldering are made. All electrical connections exit from the back compartment of the cell and are routed through a hollow steel tube to enable connection to an external potentiostat. The steel tube holding the cell is positioned vertically within the experimental chamber on a four-degree-of-

freedom manipulator, enabling precise positioning and alignment (see Section 3 – Cell-beam alignment).
Both the front and back lids are fastened with four M2 bolts each, which screw into embedded nuts in the cell body, facilitating easy assembly (see Figure S3). The back lid is sealed with an O-ring, while the feedthroughs for the WE pins and CE are sealed with epoxy glue and an O-ring, respectively.
A continuous electrolyte flow inside the cell is ensured through two silicon tubes with an inner diameter of 3 mm: one serving as the inlet and the other as the outlet. The inlet is connected to a DG10-BT103S peristaltic pump, which offers a speed range of 0.1 to 100 rpm with a speed accuracy of ±0.2%. The pump has a single-channel flow rate range of 0.0017 to 21 ml/s. Both inlet-outlet tubes are equipped with 24 V whisper safety microvalves (Bürkert Magnetventil Type 6724, Article No. 20071064), which are interlocked with the chamber pressure gauge. If the pressure in the experimental chamber exceeds 1×10^{-6} mbar, the valves automatically close, stopping the liquid flow and thereby limiting the leaking liquid volume.

The main body and the two lids were fabricated using stereo-lithography performed by Sectris AB with a Formlabs Form 3+ printer. A Rigid 10K resin, which is based on a polyamide precursor reinforced with glass fiber to enhance mechanical rigidity, was used for this purpose. After printing, the components were washed in isopropanol and subsequently cured at 60° C for 60 min using the Form Cure machine to ensure full polymerization and mechanical stability.
Pictures of the 3D-printed components of the cell and the assembled cell including the fluidic inlet/outlet tubes with the connected safety microvalves, and all the electrical contacts are reported in Figure S1.

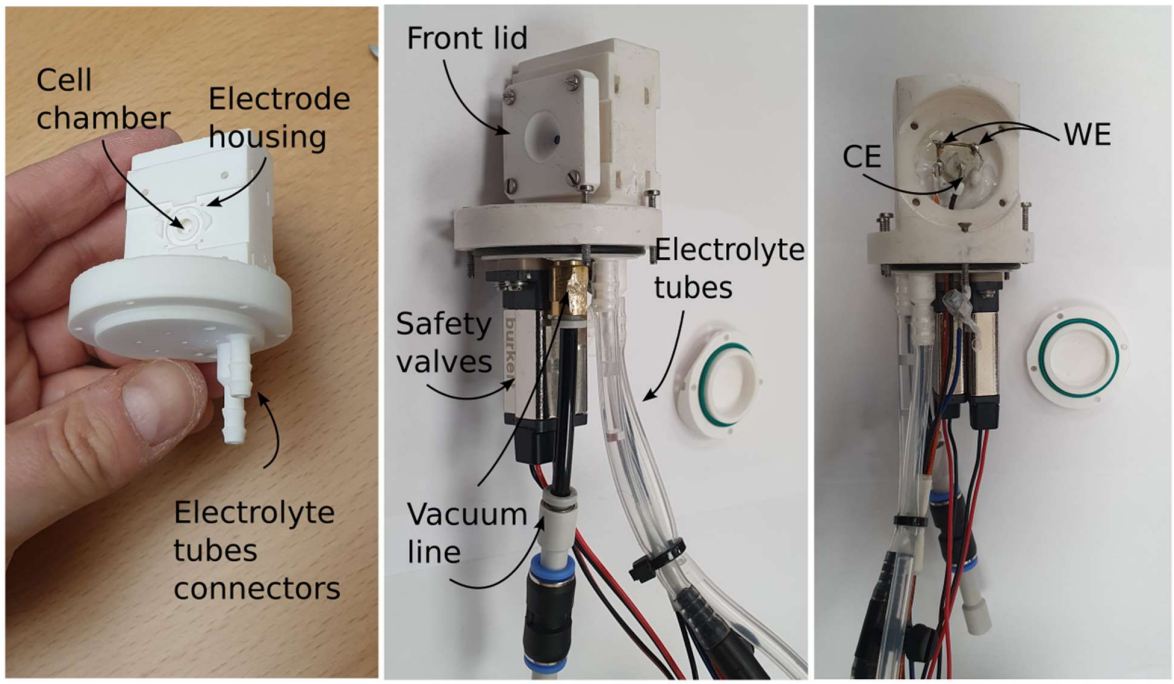

Figure S1. Picture of the EC- flow cell with details of all the attachments highlighted.

Finally, an external safety capsule (see Section 2-External protective capsule, SI) mounted around the EC-flow cell is differentially pumped to 10^{-5} mbar through a 4mm pipe attached to the bottom of the cell via a Swagelock connector (this 4 mm pipe is converted to a 6mm one after 10 cm to reduce vacuum induction). The pipe, which passes through the hollow steel tube, is connected to a scroll pump used to evacuate both the safety capsule and the experimental chamber of the beamline end-station.

2- External protective capsule.

As described in the main paper, the external capsule serves as a containment barrier, ensuring no loss of beamline vacuum in the event of rupture of the Au-coated Si_3N_4 membrane (WE). The capsule consists of a stainless-steel main body equipped with two lids that secure the Si_3N_4 grid windows in place (windows details in Section 4 – Materials and methods, SI). Images of the fully assembled protective capsule and the corresponding technical schematics are provided in Figure S3.
The capsule and its lids were machined from polished stainless steel. The Si_3N_4 grid windows, positioned at a 45° angle relative to each other, are securely mounted using the two holding lids, which incorporate O-ring seals and are fastened to the capsule with four screws each.
The fully assembled capsule is then mounted onto the EC-flow cell holder (with the EC-flow cell pre-positioned) by aligning it with the holder and securing it with three screws at the bottom of the capsule.
The capsule maintains a vacuum seal through an O-ring at its base. The angle of the capsule windows relative to the WE surface of the EC-flow cell is fixed at 22.5°.

3- Cell-beam alignment.

As already mentioned, the dimension of the WE Si_3N_4 window is 1mm x 1mm. Considering that the X-ray beam has a diameter of 340 µm (horizontal) x 170 µm (vertical) and it should pass through two windows before reaching the detector, a precise alignment of the cell is critical. This issue was addressed using an optical LASER (633nm, CW) as alignment tool, placed collinear to the X-ray beam, outside the sample chamber. A copper foil (1cm x 1cm), used as reflective surface, was positioned in place of the WE in the flow cell. The flow cell was then inserted in its holder but rotated 180° to directly face the LASER. Alignment was achieved by adjusting the cell position until the laser beam directly struck the reflective surface. The external capsule was mounted and its orientation was adjusted so that the laser beam could enter through the capsule entrance window, reflect off the copper foil, and exit through the capsule exit window. The X-Y-Z position and angle were then set as rotation center for the flow cell. Finally, the detector was positioned at the appropriate angle, aligned with the capsule exit window, to ensure optimal data acquisition.
Images of the safety capsule and the cell-beam alignment procedure using the laser are shown in Figure S2.

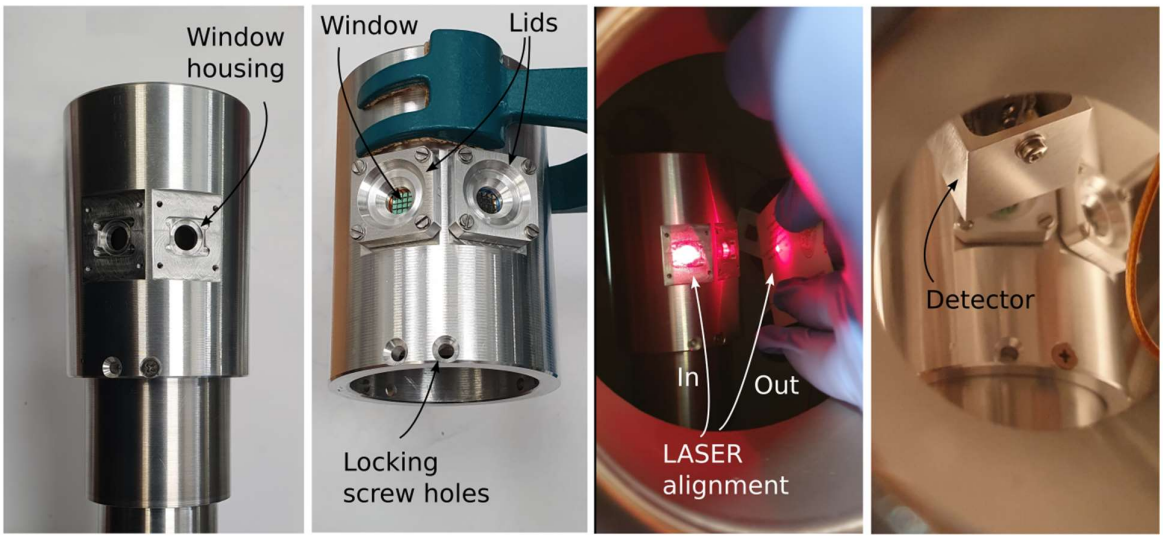

Figure S2. Images of the assembled safety capsule and its alignment with the cell using an optical laser.

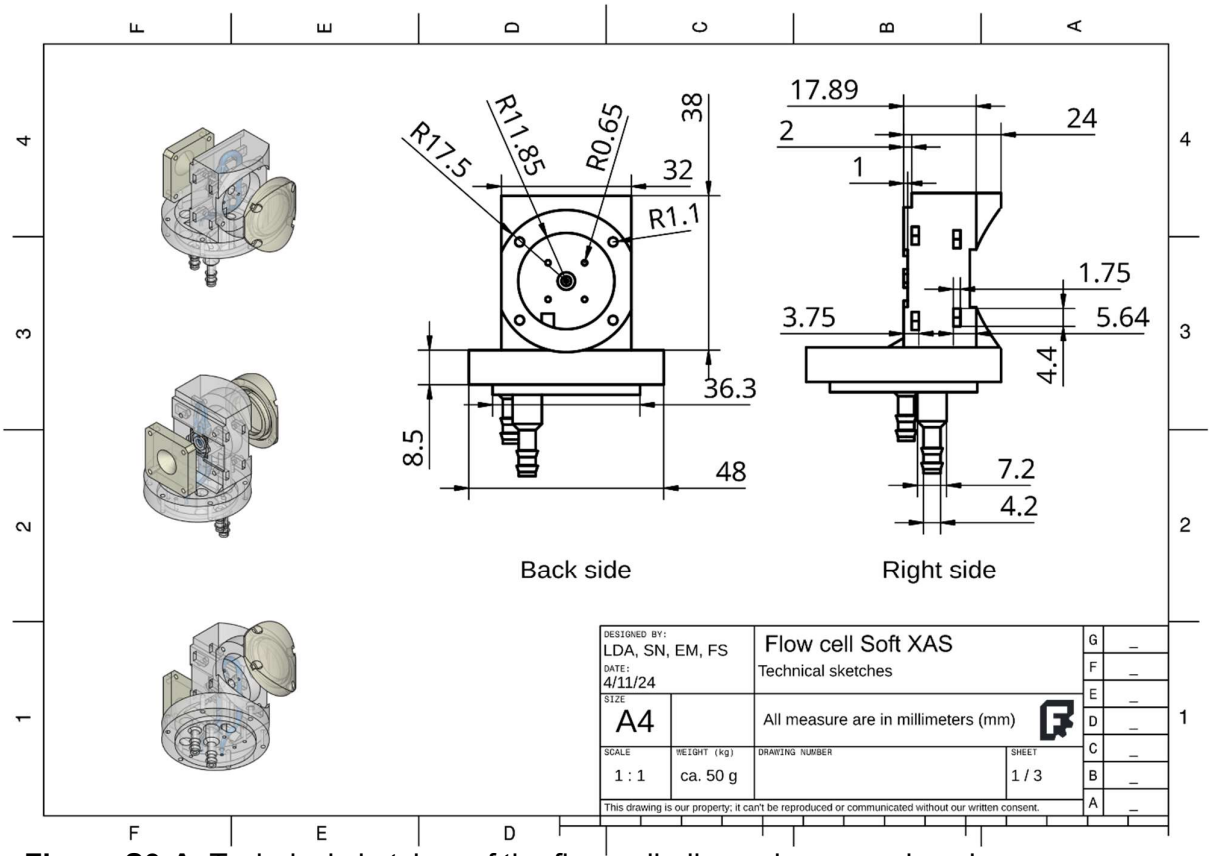

Figure S3-A. Technical sketches of the flow cell, dimensions are given in mm.

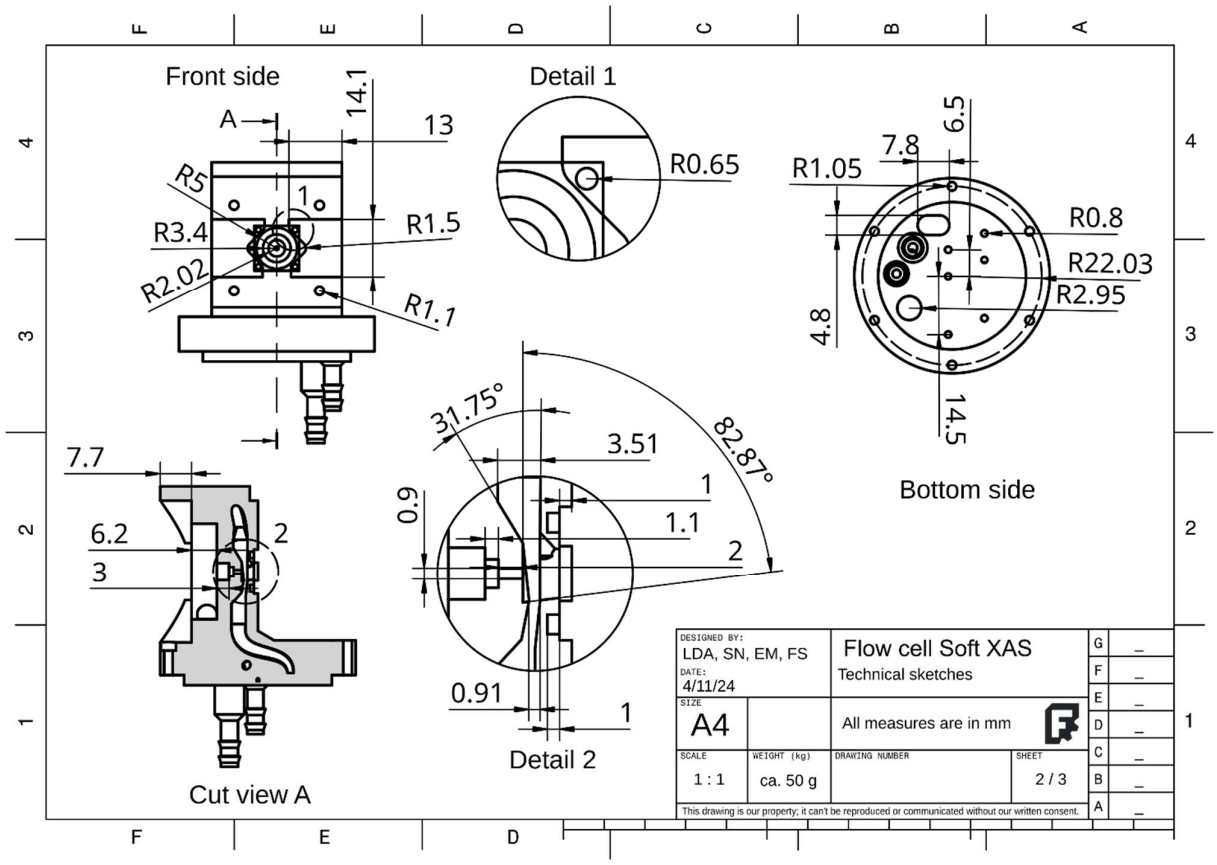

Figure S3-B. Technical sketches of the flow cell and its sections and magnifications on the e-chem reactor, dimensions are given in mm.

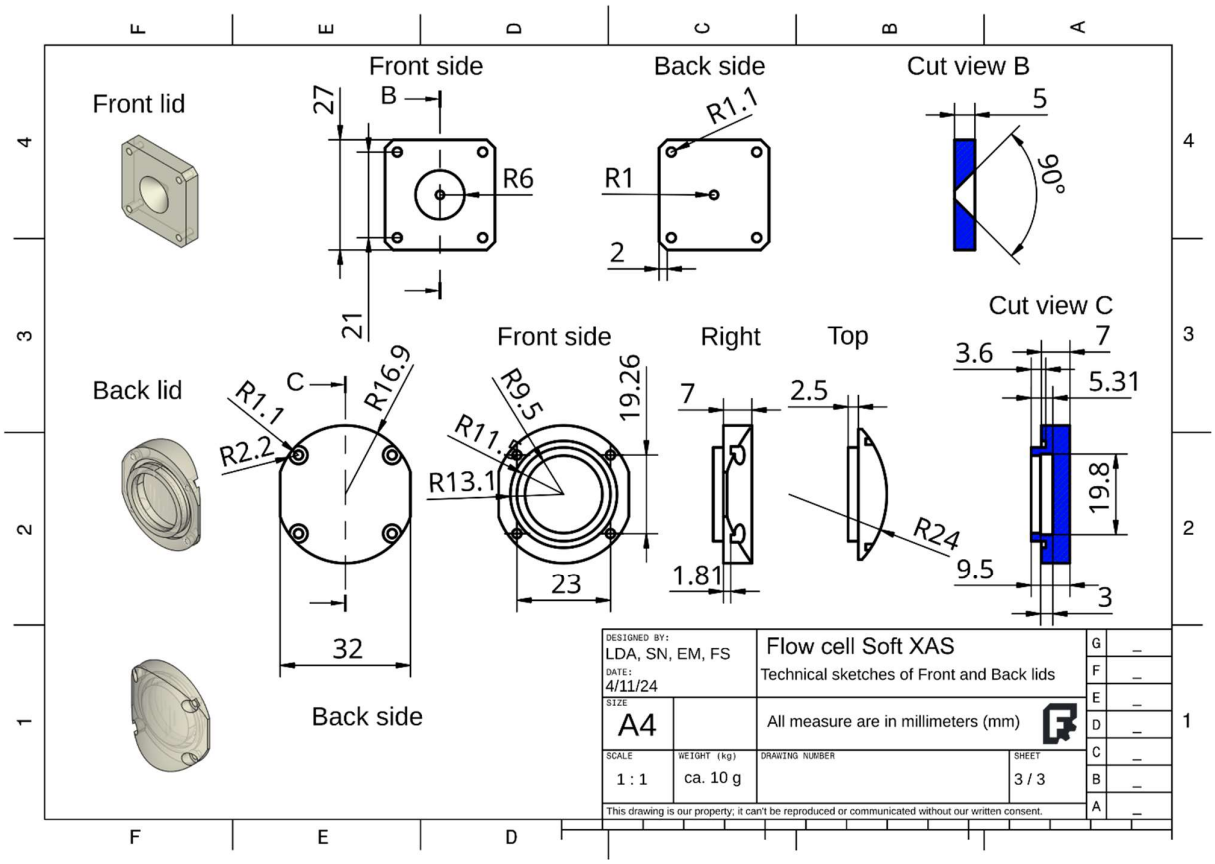

Figure S3-C. Technical sketches of the flow cell lids, dimensions are given in mm.

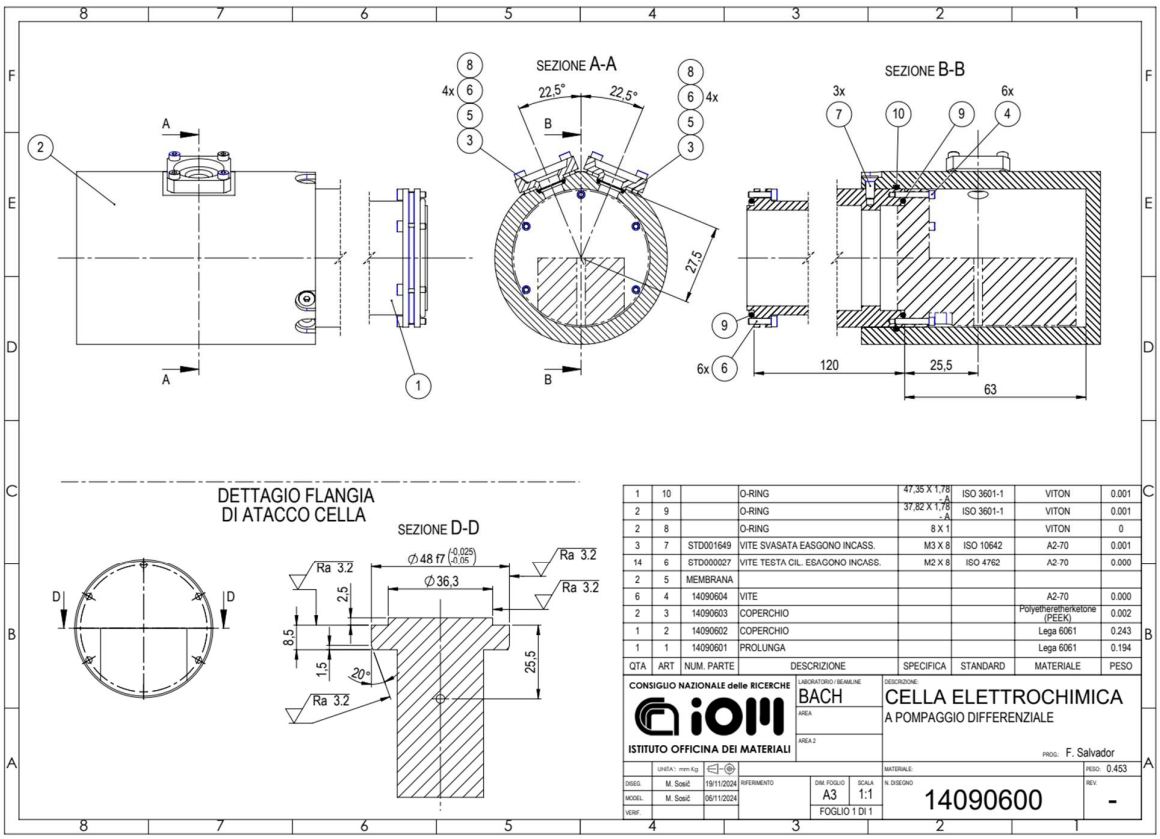

Figure S3-D. Technical sketches of the safety capsule body.

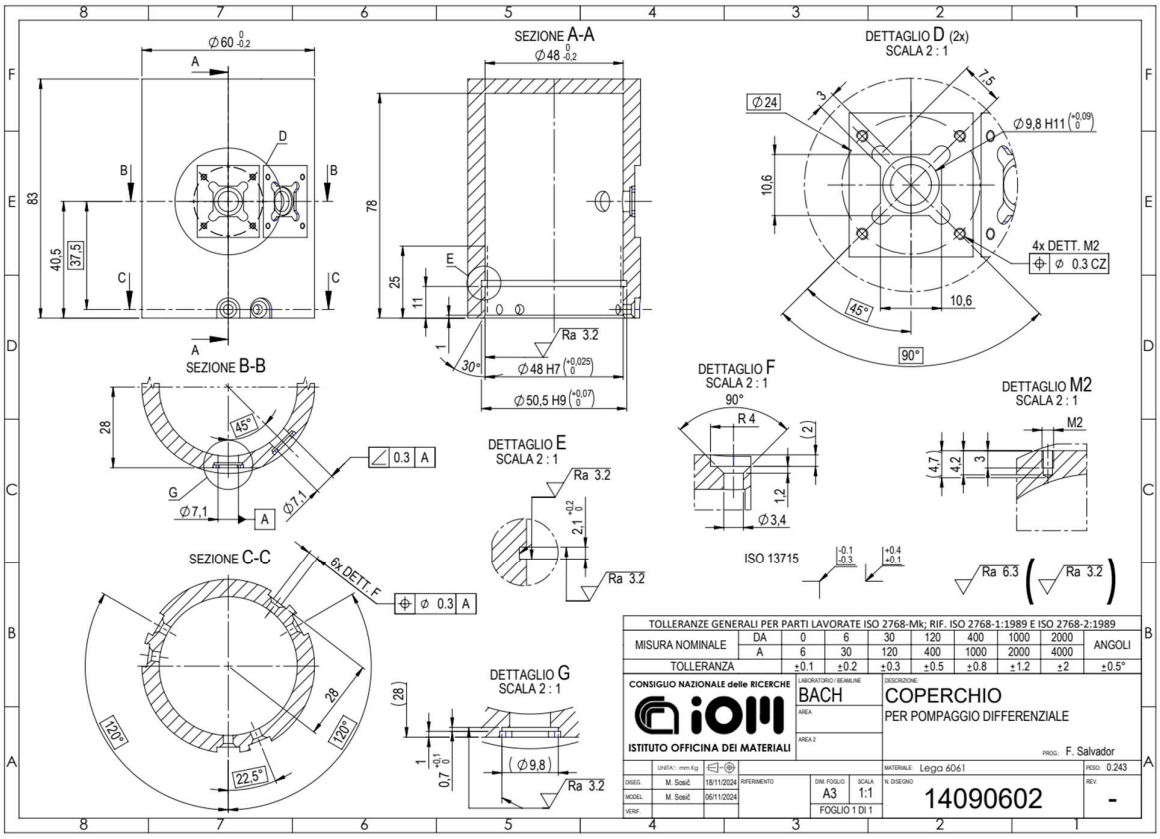

Figure S3-E. Technical sketches of the safety capsule body.

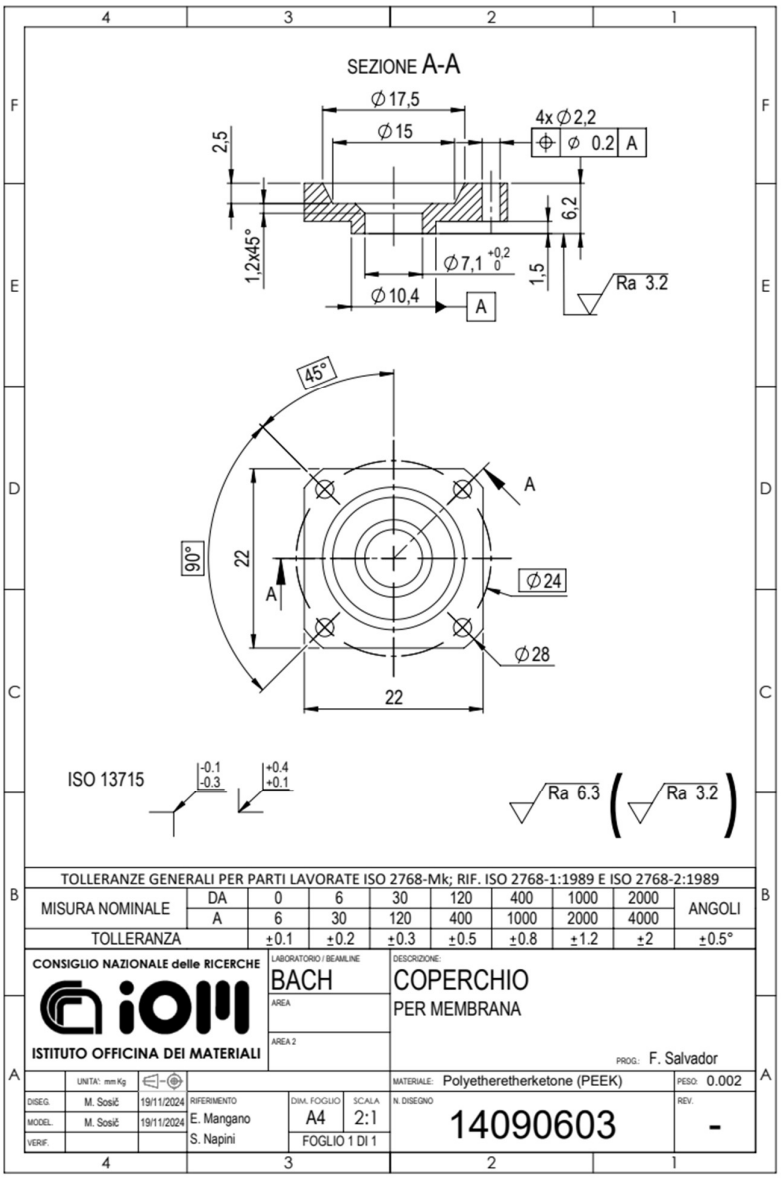

Figure S3-F. Technical sketches of the safety capsule lid.

4- Materials and methods

The chemicals used in this work, $Ni(NO_3)_2$ and KOH (99.99% trace mental basis), were purchased by Sigma Aldrich and used as obtained. Pure water was obtained by a MilliQ system from Millipore. The Si_3N_4 100 nm thick 1x1 mm^2 windows were purchased by TedPella (Prod # 21905**,** Square, 10mm frame, frame thickness 200µm).
Si_3N_4 100 nm thick multi-windows consisting of a 4 x 4 array of 1.0mm x 1.0mm membranes with a 0.5 mm support rib between each adjacent membrane were purchased by Silson Ltd. The overall window size is then 5 mm x 5 mm.
The Si_3N_4 windows, used as WE in the high-flow EC-cell, were made conductive by sequentially depositing 5 nm of metallic Ti followed by 15 nm of metallic Au via electron beam evaporation. The Ti layer was used to improve the adhesion of the Au layer to Si_3N_4. The resulting Ti/Au conductive film covers uniformly the entire surface of the Si_3N_4 layer (see schematic picture in Figure S4). The window was used without further alteration for the electrochemical deposition.

Figure S4. Schematic representation of a Ti/Au coated Si_3N_4 membrane used both as WE and soft-X ray transparent window of the high-flow EC-cell

NiOOH catalyst preparation

NiOOH electrocatalyst was prepared by electrochemical activation of a $Ni(OH)_2$ film deposited on the flat gold-coated side of the Si_3N_4 window via cathodic electrodeposition from a $(Ni(NO_3)_2$ 100 mM solution. A “drop electrodeposition” method was used, which consists in creating a two-electrode setup using an electrolyte drop as electrochemical “cell” (see scheme in Figure S5).

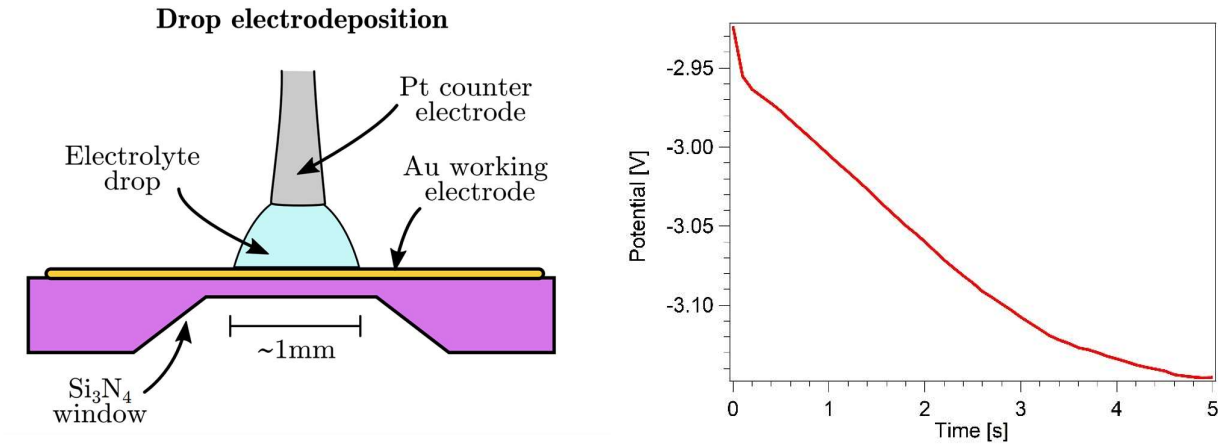

Figure S5. a) Scheme of the two-electrode electrochemical cell created using the Au-coated Si_3N_4 window, a Pt wire and an electrolyte drop. The confinement of the cell corresponds the electrolyte drop surface. b) Potential evolution during 5 s electrodeposition time applying a cathodic current density of -20 mA/cm^2.

A drop of deposition solution was carefully positioned on the center of the WE, i.e. on the Au-coated Si_3N_4 window, see Figure S5(a). The counter electrode (CE), made of a Pt wire, was carefully immersed in the solution drop and gently pulled up, until the desired surface area of the drop was in contact with the WE. A cathodic current density of -20 mA/cm^2 was applied for 5 s. The solution drop was then removed by gentle rinse of the window in deionized water. The potential evolution during the 5 s-deposition time is shown in Figure S5(b). The catalytic NiOOH material was generated in-situ upon introducing the 1M KOH electrolyte into the cell, following an activation CV cycle (Fig. 2A in the main text). To ensure the stabilization of the active NiOOH catalyst and prevent its reduction to the unstable $Ni(OH)_2$ phase in highly alkaline 1M KOH environment, the potential was maintained at 0.69 V vs NHE.

In-situ/operando soft X-Ray absorption spectroscopy

In-situ/operando soft X-ray absorption spectroscopy (sXAS) experiments were conducted at the BACH beamline (IOM - CNR) of the Elettra synchrotron facility in Trieste (Italy) to study the evolution of the NiOOH electrocatalyst at the Ni L- and O K-edges during the oxygen evolution reaction (OER). The in-situ sXAS spectra were recorded using synchrotron radiation linearly polarized in the horizontal plane and detected in fluorescence yield (FY) mode with a photodiode (IRD, AXUV100G) placed at 45° with respect to the incoming X-ray radiation, achieving an energy resolution better than 250 meV.
The electronic structure evolution of the $Ni(OH)_2$/NiOOH catalytic system was then monitored at the Ni L- and O K-edges at selected applied voltages (0.69 V, 0.8 V, 1.1 V and 0.4 V vs NHE). Each voltage was applied for 650 sec during which Ni L and O K-edges were measured in FY mode. The corresponding Chronoamperometry curves recorded during the

operando XAS experiment at the selected applied potentials (vs NHE) are reported in Figure S6.

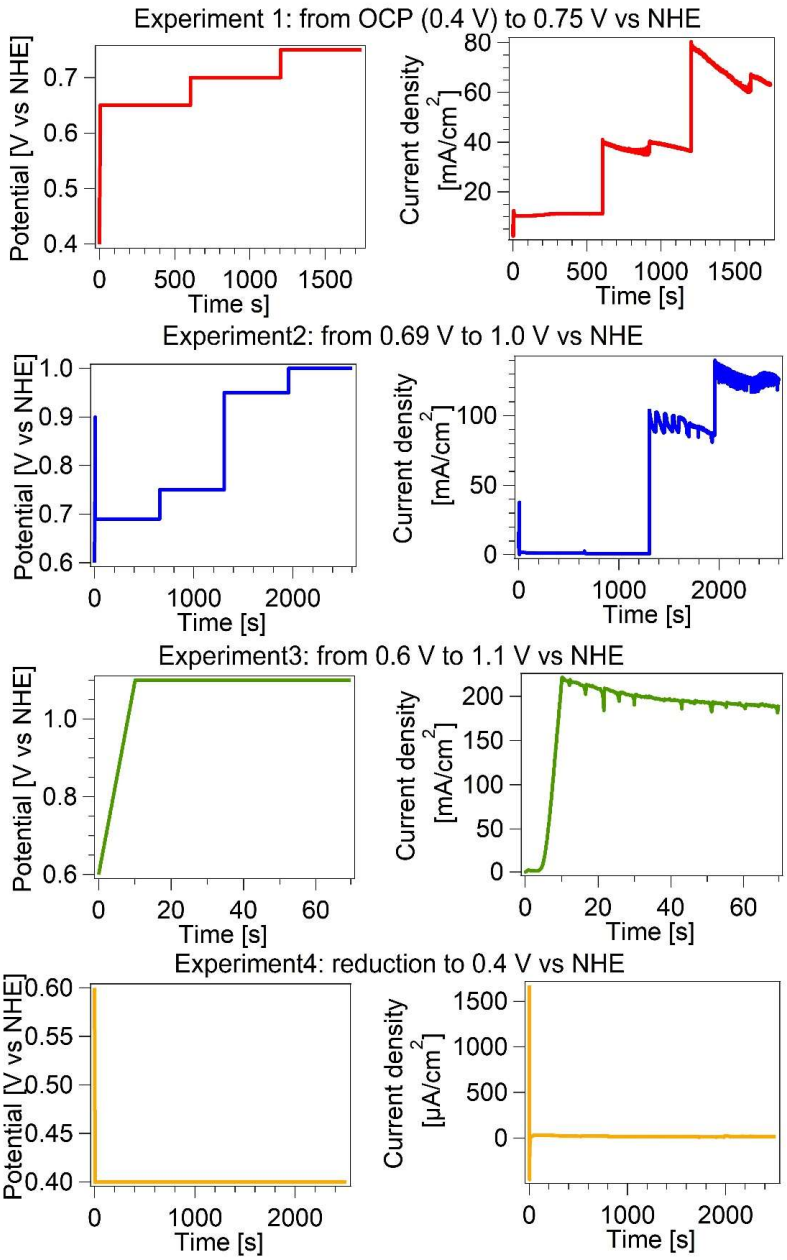

Figure S6. Chronoamperometry measurements during operando XAS experiments. The left panel shows the applied potentials (vs. NHE), while the right panel displays the current density evolution over time.

Under OER conditions, a high current density of 200 mA/cm² was reached at 1.1 V, demonstrating a complete transition from Ni(II) to Ni(III)/Ni(IV), corresponding to the

formation of the catalytically active NiOOH phase. The system's reversibility was confirmed by measuring the sample at 0.4 V, where it was fully reduced to Ni(II), representing the inactive OER phase. These measurements were conducted using the described high-flow EC- cell, which was mounted on the BACH branch line, fully dedicated to in-situ and operando sXAS experiments under electrocatalytic conditions. During the operando experiment a continuous electrolyte flow was maintained at a rate of 5 ml/min using a DG10-BT103S peristaltic pump. The electrochemical measurements, including electrodeposition, cyclic voltammetry (CV), and chronoamperometry, were conducted using a PalmSens4 potentiostat, capable of operating within a wide potential range (-5V to 5V) and current range (100 pA to 10 mA) with a good resolution and low noise.

Fittings

In order to estimate the Ni^{2+} contribution in the oxidized NiOOH, we performed a component analysis on the Ni L-edge (bands 853-856 eV) at the oxidized potentials, as shown in Fig.2D. in the main paper. First, the component of the reference spectra of the reduced catalyst, attributable to Ni^{2+}, and the fully oxidized, attributable to Ni^{3+}, have been determined (top spectra). Then, these fittings have been used to extract the amplitudes of these two components in the operando spectra. The results are represented in Fig. S7.

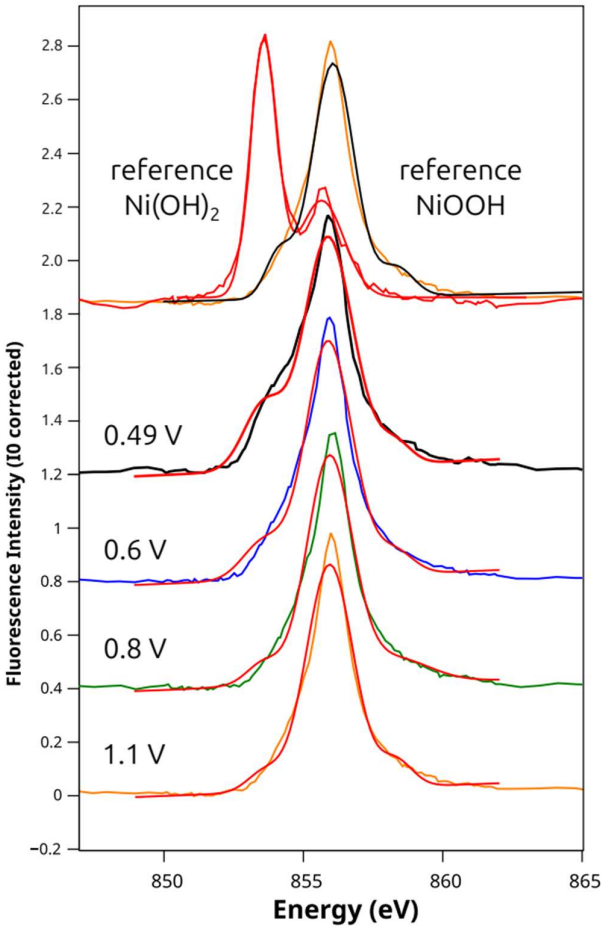

Figure S7. Results of the fitting for the component analysis relative to Fig.2D. The reference spectra have been taken from the data of the most reduced spectrum collected (corresponding to $Ni(OH)_2$) and the most oxidized spectrum, the NiOOH oxidized at 1.1 V. The references have been fitted with a sum of Gaussians, 2 for the $Ni(OH)_2$ and 3 for the NiOOH. These reference spectra have been used to extract the amplitude ratio plotted in Figure 2D.

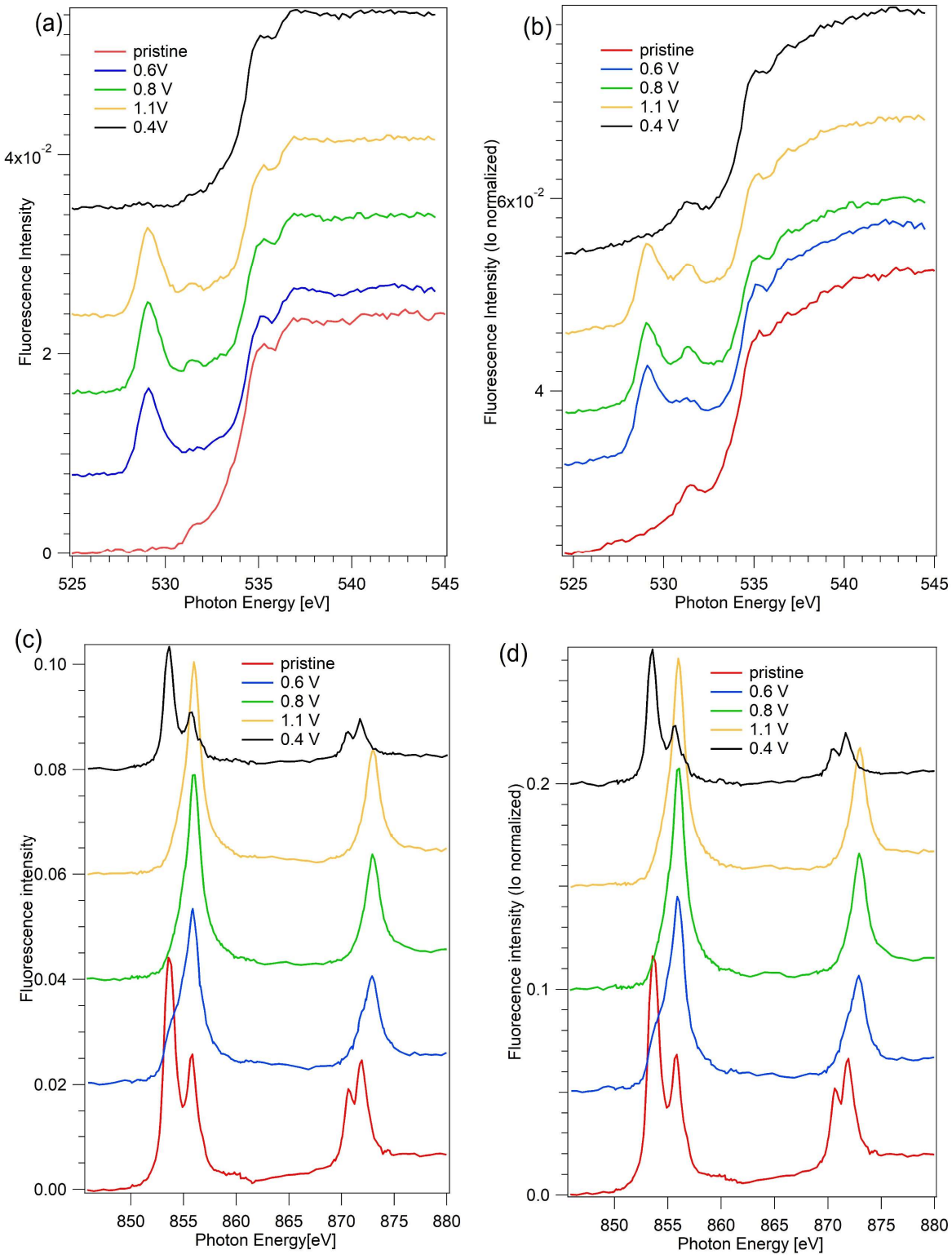

Figure S8. As-measured fluorescence signal (left panel) and fluorescence normalized by the incident intensity measured on a mirror before the experimental chamber (right panel) at the O K-edge (a, b) and Ni L-edge (c, d).