Experimental Methods

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## Experimental Methods

# Electrodes preparation

Gold single crystal electrodes were purchased from Mateck GmbH. All the electrodes have a cylindrical shape (different diameters) with a groove on the side, which was used to make electrical contact by means of Au wire. The diameter of the polished (exposed) surface was 6mm for Au (110), 8 mm for Au (111) and Au (100) and 10mm for Au (211). The nominal orientation accuracy was < 0.1° and the polishing roughness <10 nm. Prior to each experiment the electrodes were flamed annealed to red heat with a propane-air burner and cooled down in an argon stream.

After the experiments the electrodes were carefully rinsed in mQ H2O and dried in a Ar stream. If the electrodes were put in contact with Pb containing electrolytes (i.e, for Pb under-potential measurement and selective Pb poisoning experiments), the electrodes were lifted under potential control under anodic conditions to avoid the adventitious deposition of Pb ions, they were electrochemically cleaned in 0.1M HClO4 (∼15 cycles 0.2-1.2 VRHE) and thoroughly rinsed with mQ H2O before being flame annealed for the following experiment.

The polycrystalline Au electrode was prepared by cutting a 0.5 cm x 0.5 cm piece (total exposed area = 0.5 cm2) from an Au foil (*Alfa Aesar,* 0.25 mm thickness, 99.9975+ %). A gold wire was employed as current collector. The electrode was degreased in concentrated HNO3 solution and thoroughly rinsed with mQ H2O (including an ultra-sonication treatment). Prior to each experiment the electrode was electrochemically cleaned applying five potential cycles (0.1-1.65 VRHE, 50mVs-1) in the same electrolyte used for the tests (e.g., CO2 sat 0.1 M KHCO3 for bulk CO2 electrolysis experiments). The electrode was rinsed in mQ H2O in between the experiments.

# Lead Under Potential Deposition (Pb-UPD)

The Pb-UPD characterization was conducted in a single compartment three-electrodes glass cell at ambient temperature. A gold mesh and a Hg/HgSO4/sat. K2SO4 electrode were employed as counter and reference electrodes, respectively. Pb-UPD curves were recorded in a Ar saturated 0.01 M HClO4 solution containing 1mM Pb(ClO4)2. The single crystals were positioned in a hanging meniscus configuration (height ~3-5 mm) under potential control (E = 0.6 VSHE) and the headspace volume was blanketed with Ar. Cyclic voltammetry (CV) curves were recorded between 0.6 VSHE and -0.2 VSHE (+0.814 V and +0.014 V vs. Pb2+/Pb scale, respectively). The cathodic sweep was recorded first. For single crystals the first cycle is reported and used for the ensuing analyses.

# Bulk CO2 electrolysis experiments.

All the electrochemical measurements throughout this study were carried out with a BioLogic VMP2 potentiostat controlled through the EC-Lab software.

Bulk CO2 electrolysis experiments were carried out in a custom-made three-electrodes glass H-cell (Scheme in Figure S1). The working electrode (WE) and CE compartments were separated by a Nafion® 117 proton conducting membrane, while the reference compartment was separated by a glass frit. A gold mesh (GoodFellow 99.9%) was always used as counter electrode. The WE compartment was encased in a glass thermostat jacket connected to a heated circulating bath (Grant Instruments, TC120) equipped with a refrigerator unit (Grant Instruments, C1G). The temperature of the WE compartment was always kept constant at 25°C.

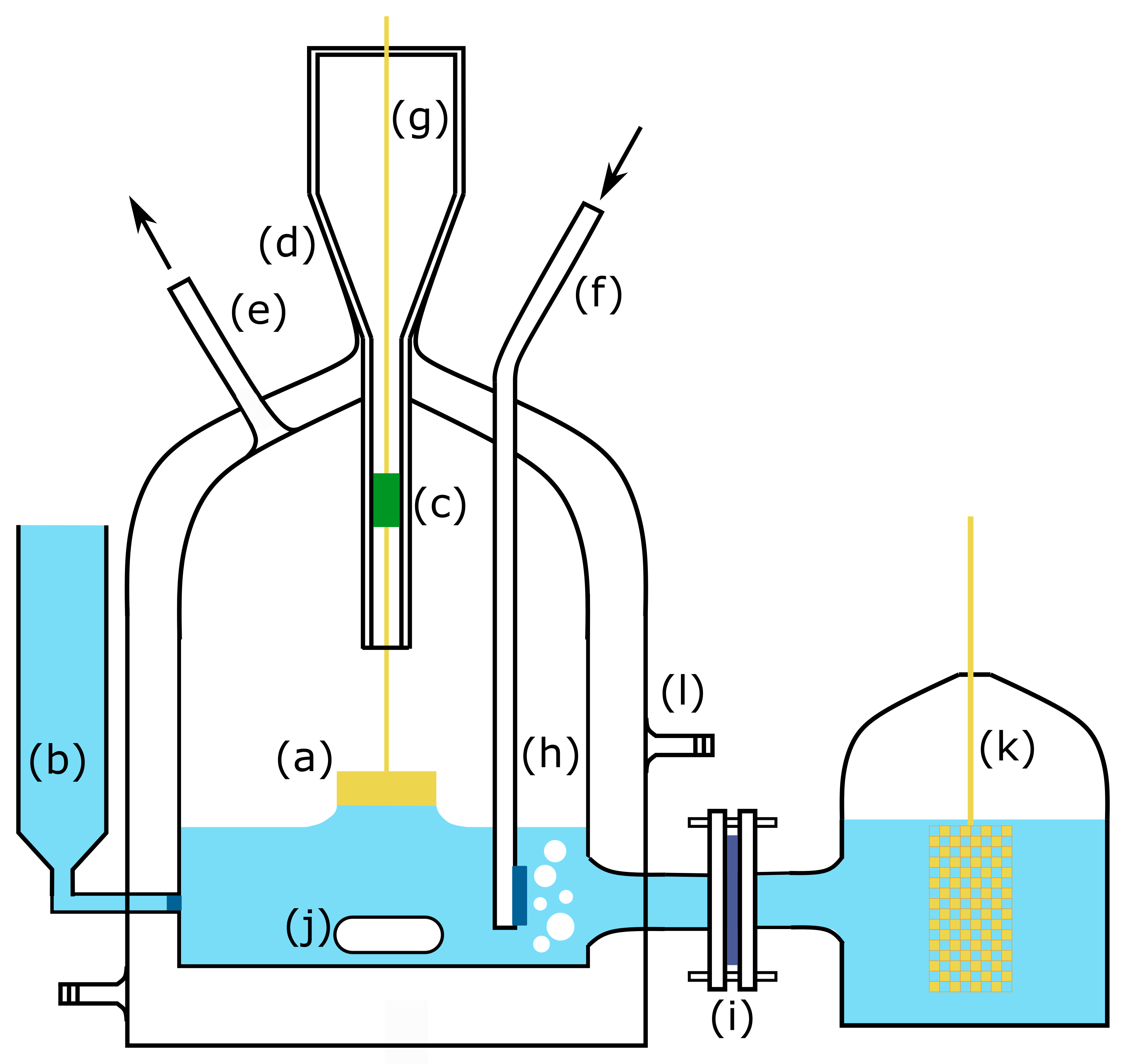


Figure S 1. (left)Scheme of the setup used for CO2 electrolysis experiments with Au single crystals. (a) working electrode (WE) in hanging meniscus configuration; (b)reference electrode compartment; (c) septum; (d) WE shaft; (e) gas outlet to pump/GC;(f) gas inlet; (g) current collector (Au wire); (h) bubbler with frit; (i) Nafion membrane; (j) stirring bar; (k)counter electrode (Au mesh); (l)outer glass jacket (for temperature control). (right) Photo of a single crystal electrode in the hanging meniscus configuration.

The headspace of the WE compartment was connected to a gas-circulating loop (setup-loop, 1/8” stainless steel tubing) feeding the gas chromatograph sample loops before reaching again the WE compartment. A detailed description of the setup is given in ref. 1. During the experiments the gas in the headspace and in the setup-loop was continuously circulated by means of a diaphragm liquid pump (*KNF*, NF1.5TTDCB-4 10-28V). The electrical contact with the working electrode (pcAu/single crystals) was achieved via a Au wire. The wire was passed through a septum located in the WE shaft (see Figure S1) in order to maintain an optimal sealing of the headspace. The immersion of the single crystals was carried out under potential control using a dummy electrode (Au wire). Once contact was established, the electrode was retracted gently pulling the wire until a proper hanging meniscus configuration was achieved. The height of the meniscus was kept at ~3-5 mm (see Figure S1).

CO2 bulk electrolysis experiments were carried out potentiostatically (chronoamperometry, CA) in a CO2 saturated 0.1 M KHCO3 electrolyte (pH 6.8), which was prepared purging CO2 (AGA, Carbon Dioxide 5.2 Scientific,) in a 0.1 M KOH aqueous solution (prepared from KOH·1H2O Fluka, TraceSELECT®, ≥ 99.995 %, solid pellets). The pressure of the headspace gas was kept at 1.1 bar. CO2 was constantly purged in the electrolyte through a bubbler equipped with a glass frit. The bubbler faced toward the cell wall opposite to the WE to avoid disturbances to the hanging meniscus. During the measurements the electrolyte was continuously stirred (~1000 RPM) using a Teflon coated stirring bar. The electrolyte was replaced after each measurement and the electrodes were re-prepared as described in section 1. The duration of the CA experiments was set to 1000s. During this time the gaseous products were continuously accumulated in the gas loop. At the end of the CA, after 5 min of equilibration time, an aliquot of the gas present in the headspace was injected in the GC. At least three independent measurements (i.e., fresh electrolyte and flame annealed electrodes) were carried out for each potential (-0.6, -0.7 and -0.8 VRHE).

The working electrode potential (EWE) was referenced against a Hg/HgSO4/sat. K2SO4 reference electrode (SI analytics) and converted to the reversible hydrogen (RHE) scale according to:

ERHE (V) = EWE + EMSE + 0.059 \* pH

Where EWE and EMSE are the set potential at the WE (vs. Hg/HgSO4) and the reference electrode potential (typically 0.664 V ± 5mV vs. ESHE), respectively. The pH of the CO2 saturated 0.1M KHCO3 electrolyte was 6.8 ± 0.1 (verified with pH meter). The reference electrode potential (EMSE) was regularly checked by measuring the equilibrium potential against a Pt|H2(1atm) |H+(0.1 M) electrode in 0.1 M HClO4 at 25°C.

Potentiostatic Electrochemical Impedance Spectroscopy (PEIS) measurements were carried out at +0.1 VRHE (ΔV = 10 mV, from 100 kHz to 1 Hz) immediately after the appropriate hanging meniscus height was achieved. The resulting spectra were fitted using a modified Randles equivalent electrical circuit (with a constant phase element) to extrapolate the Ohmic resistance of the electrochemical cell (Ru) and the double layer capacitance (CDL). Without losing potential control, the uncompensated Ohmic resistance was correct for via positive feedback (85% of Ru) before the CO2 electrolysis experiment started. Typical Ru values fluctuated between 80 Ω and 100 Ω depending on the quality of the electrical contact between the crystal and the Au wire. The remaining 15% of the Ru was corrected for after the measurement (based on the average current registered at the WE).

# Product Detection and Analysis

Gaseous reaction products were detected and quantified via in-line gas chromatography (GC). The products were accumulated in the setup-loop/headspace during CO2 electrolysis experiments. The setup-loop fed two GC sample loops (0.5 mL each) placed in series before returning to the WE compartment. At the completion of the CA experiments the sample loop aliquots were injected in the GC and detected by a thermal conductivity detectors (TCD) and a flame ionization detector (FID) placed in parallel (one for each sample loop). The separation of the products was achieved with a HP-PLOT Molesieve-5A column (L: 30 m, ID: 0.53 mm) for permanent gases (TCD detector) and a HP-PLOT Q column (L: 45 m, ID: 0.53 mm) for light hydrocarbons (FID detector). The FID detector is preceded by a methanizer (Ni cat., 350 °C) for CO detection and quantification. Calibration of the GC was carried out according to the procedure reported by Jovanov et al.1

The concentration of each product, moli, was calculated as follows:

Where Ai is the signal measured after the CA, Ki is the signal measured with standard calibration gas mixture and ci is the concentration of each gas in the calibration mixture. A mixture containing CO (1.01%), CH4, C2H6, C2H4, C3H8, C3H6 was used for light hydrocarbons and CO. A 5% H2/Ar mixture was used for H2. The volume of the setup-loop (Vl, 61 mL) was measured via hydrogen evolution measurements with a Ti electrode in 0.1 M KOH. The full details of the procedure are reported in the supporting information file of reference 1. The partial current density (ji) and Faradic Efficiency (FEi) for each product were calculated using the following relationships:

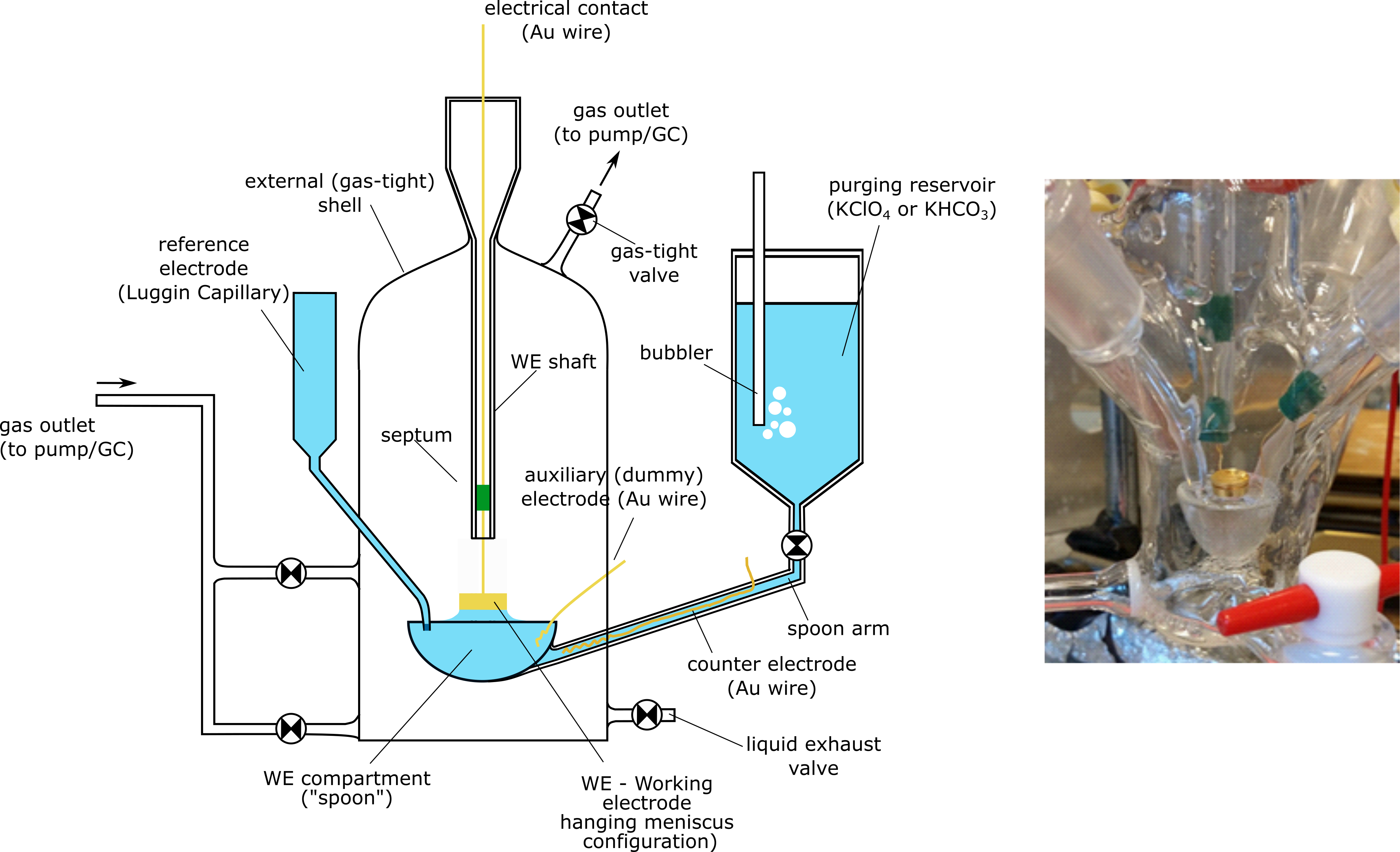
where [moli] is the concentration of the product as measured via GC, ni the number of e- transferred per mol of each product, t the duration of the measurement (1000s) and Q is the total charge passed through the WE. The concentration of formate was determined via HPLC (Agilent 1200 series) equipped with autosampler. A 30µL aliquot was injected and separated in a BIORAD (Aminex HPX-87H) column (50 °C). An aqueous diluted H2SO4 solution (5 mM) was used as mobile phase (0.6 mLmin-1). The elute was detected and quantified with a photodiode array detector (wavelength = 210 nm). The typical retention time for formate was ca. 13 min.

# Hydrogen Evolution Reaction

Sweep voltammetries were recorded in H2 saturated 0.1 M HClO4 (Merck Suprapur 70%), 0.1 M KOH and 0.1 M phosphate buffer (pH 7). The phosphate buffer was prepared from 0.5 M KH2PO4 and K2HPO4 stock solutions, in turn prepared mixing the appropriate equivalents of H3PO4 (Suprapur, 85%) and KOH (0.5M, prepared from KOH·1H2O *Fluka,* TraceSELECT®, ≥ 99.995 %, solid salt). The influence of the ionic strength on the activity coefficients of the ions was corrected for using the extended Debye–Hückel law.2 The pH of the buffer was verified to be 7 ± 0.1 with a standard pH meter. A single compartment three-electrodes glass cell was used for the tests (ambient temperature). A gold mesh and a Hg/HgSO4/sat. K2SO4 electrode were employed as counter and reference electrodes, respectively. The reference electrode was calibrated *in situ* against a Pt|H2|H+ electrode (RHE electrode) prior to each set of measurements (i.e., at every change of electrolyte). Single crystal electrodes were immersed under potential control (+0.2 VRHE) using a dummy electrode (Au wire). The height of the meniscus was adjusted to be ~3-5 mm. The headspace of the cell was blanketed with H2 gas. Sweep voltammograms were recorded cathodically starting from 0.1 VRHE with a scan rate of 20mVs-1. The Ohmic resistance of the electrochemical cell was measured via EIS (at +0.1VRHE, ΔV = 10 mV, from 100 kHz to 1 Hz) after the sweep voltammetry. The first sweep was considered for subsequent analyses and the uncompensated resistance was corrected for (100%) after the tests. Multiple experiments (at least two for each electrode) were conducted to assure the reproducibility of the results.

# Selective Poisoning Experiments

Selective poisoning experiments were carried out in a custom-made glass cell (scheme in Figure S 2). The WE compartment consisted of a small “spoon” cup (~4.5 mL) connected through an empty “arm” to an external reservoir. The WE was enclosed in a cylindrical larger shell equipped with multiple necks to accommodate auxiliary electrodes and the reference electrode lugging capillary structure. A Au gold wire placed in the arm of the spoon cup (see scheme in Figure S 2) was used as counter electrode. The position of the CE is crucial to minimize the oxidation of the reaction products. Ideally the electrode should be located as far away as possible from the WE. A liquid exhaust valve was present at the bottom of the external shell. The WE (single crystals and Au foils) were lowered into the WE cup through a cylindrical shaft (with a septum-wire configuration as for standard CO2 electrolysis experiments) from the top neck of the external shell. The cell was connected to the same setup used for the standard CO2 electrolysis experiments allowing for the circulation of the gas headspace and product quantification. Multiple valves (equipped with Teflon stopcocks) allowed the sealing of the external cell during the experiments.



*Figure S 2 (left) Scheme of the setup used for selective Pb poisoning experiments with Au single crystals and polycrystalline electrodes. (right) Photo of the cell and electrode in hanging meniscus configuration in the “spoon” compartment. The arm of the spoon is visible in the background.*

The poisoning experiments we carried out according to the following procedure:

1. Pb was deposited via a Pb-UPD procedure with the WE placed in the “spoon” cup. The cup was filled with a Ar saturated 0.01M KClO4 solution (pH 7) containing 1mM of Pb(ClO4)2 before the single crystal (or pcAu) were lowered into the WE compartment. The single crystal was put in contact with the electrolyte under potential control (E = 0.65 VSHE). The reference electrode lugging capillary compartment was filled with CO2 sat KHCO3 (pH 6.8). A Hg/HgSO4/sat. K2SO4 reference electrode was used for all the experiments. The deposition of Pb was carried out sweeping the potential cathodically (20 mVs-1) from 0.65 VSHE to the desired potential (see main manuscript). At this point the potential was hold for the ensuing electrolyte exchange steps.
2. The excess of Pb2+ ions present in the cup was removed by purging the cup with Pb-free, Ar saturated 0.01M KClO4 electrolyte, which was fed from the external reservoir through the arm of the spoon. During this exchange phase the electrolyte overflew at the edges of the cup and was removed through the bottom liquid exhaust valve. Typically, an excess of 300-400 mL of Pb-free electrolyte was used (ca. 100 times the volume of the cup) to ensure the complete removal of Pb2+ ions. During the deposition and first exchange phases the headspace volume of the external cell was saturated with Ar. Note that during this phase the electrode was kept in contact with the electrolyte under potential control to avoid the removal of the Pb atoms previously deposited on the surface.
3. Once the excess of Pb2+ ions was removed, the potential was swept to -0.2 VSHE and the electrolyte was exchanged to CO2 saturated 0.1M KHCO3 using the same procedure described in step 2. About 100-200 mL of CO2 saturated KHCO3 was used for the exchange. During this phase the headspace of the external cell was saturated with CO2, which was continuously purged through the setup-loop in preparation for CO2 electrolysis experiment. Note that a direct exchange from Pb-containing KClO4 to KHCO3 is not possible because Pb2+ is not soluble in (bi)carbonate solutions and it would precipitate forming carbonate salts.
4. Once the cell was saturated with CO2, the external cell and the setup-loop were sealed off (Teflon valves) and the CO2 electrolysis experiment was initiated. Chronoamperometries were carried out at -0.7 VRHE with varying amounts of Pb present on the surface (see main text). The duration and quantification procedure were identical to what described in section 3. Because of the limited volume of the “spoon”, it was not possible neither to stir the electrolyte nor purge directy CO2 in the cup during the CO2 electrolysis experiments. Consequently, the results obtained with this electrochemical configuration are not directly comparable to the ones acquired with the standard cell. Consequently, in order to have a fair term of comparison for Pb-poisoned electrodes, CO2 electrolysis blank tests were carried out with the same electrodes in the spoon cell without any Pb adsorbed on the surface.

# References

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(2) Atkins, P. W.; De Paula, J. *Atkins’ Physical Chemistry*, 9th ed.; Oxford University Press: Oxford ; New York, 2010.