

– SUPPORTING INFORMATION –

The Effect of Surface Conditions on the Electrochemical CO₂ Reduction Performance of Bimetallic AuPd Electrocatalysts

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S.1 – Materials

All solutions were prepared using ultrapure water (Millipore Milli-Q IQ 7000 system, 18 mΩ cm) and reagents of trace metal purity. Electrolytes were prepared from KH₂PO₄ (99.995%, Supelco), K₂HPO₄ (99.99%, Supelco) and KHCO₃ (≥99.95%, Sigma-Aldrich). Polycrystalline gold foils (25x25x1 mm, 99.995%) were obtained from MaTeck GmbH, while glassy carbon electrodes (25x25x1 mm) were purchased from HTW (Sigradur ®, polished). As counter electrode either a platinum foil (MaTeck GmbH, 25x25x0.1 mm, 99.995%) or glassy carbon electrode (HTW, Sigradur ®, polished) was used.

S.2 – Electrochemical Measurements

Prior to all measurements, the resistance of the system was determined using potentiostatic electrochemical impedance spectroscopy (PEIS) at open circuit potential on a Biologic 200 SP potentiostat. The potentiostat corrected for 85% of the ohmic drop during the measurement, while the remaining 15% was manually compensated. All potentials were converted to the RHE scale, unless mentioned otherwise, using $V_{RHE} = V_{Ag/AgCl} + 0.197 + 0.059 \cdot pH_{bulk}$.

Chronoamperometry measurements were performed for 1 hour to determine the electrocatalytic performance. The measurements were carried out in a custom-made electrochemical cell made of PEEK consisting of a cathodic and anodic compartment separated by a Selemion membrane (ForBlue Selemion AMVN, AGC Engineering, Japan), following the design from Lobacarro et al. [1]. The cell compartments were stored in 20 vol. % HNO₃ (Sigma, ACS reagent, 70%) overnight and washed with ultrapure water prior to each experiment. The electrode of interest was used as working electrode, while platinum foil (25x25x0.1 mm, 99.995 %, MaTeck GmbH) was used as a counter electrode. The electrodes were held in place by copper tape (AT528, Advance Tapes), which also provided electrical connection to the potentiostat. A leak-free Ag/AgCl electrode (LF-1.6-48, Innovative Instruments) was used as a reference electrode. The leak-free electrode was stored in 3.0 M KCl saturated with silver chloride (Supelco).

Prior to the experiment, each cell compartment was filled with 1.8 mL of the electrolyte. Humidified CO₂ gas (4.5N, Linde Benelux B.V., The Netherlands) was flown through the cathodic compartment with a flow rate of 8 mL_n min⁻¹ for at least 15 minutes to remove any other (dissolved) gasses and to saturate the electrolyte. The CO₂ gas flow was maintained over

the duration of the chronoamperometry measurement to supply fresh CO₂ and remove any formed gaseous products from the cathode compartment headspace. The outgoing gas stream was sampled every 2 minutes by an inline gas chromatograph (Compact GC 4.0, GAS). The GC was calibrated with a series of calibration gasses containing product gasses with concentrations in the range of 50 ppm – 8000 ppm, balanced with CO₂ (Linde Benelux B.V., The Netherlands). The faradaic efficiencies and partial currents for gaseous products during chronoamperometry measurements were determined by averaging the measured values between 34 min and 55 min after the start of the chronoamperometry measurement. After the experiment, the electrolyte in the cathodic chamber was collected and 100 µl was injected into a high-performance liquid chromatograph (HPLC, Agilent Technologies 1260 Infinity, USA) to quantify the formed liquid products. The HPLC was calibrated with a dilution series in the range of 0.01 mM to 5 mM of formic acid (95%, Sigma–Aldrich). The flowrate of the eluent (1 mM H₂SO₄ (aq)) was set to 0.6 mL min⁻¹ and the measurement ran for one hour. The HPLC used two Aminex HPX-87H columns (Biorad) in series heated to 60 °C. A refractive index detector (RID) was used for the detection of products.

S.3 – Electrode preparation

Three electrodes were examined as working electrode: polycrystalline gold (Au), palladium electrodeposited on polycrystalline gold foil (AuPd) and palladium electrodeposited on glassy carbon (Pd/C).

Prior to every measurement, the platinum counter electrode was washed with ultrapure water and flame annealed until the surface glowed red-hot. Polycrystalline gold foil was first wetted and manually sanded using ultrafine sandpaper (2000, Struers, USA) for one to two minutes to make sure any contaminants were removed from the surface. After sanding, the electrode was washed using ultrapure water, subsequently dried using compressed air, and flame annealed to the point that the electrode glowed red hot to remove any organics left on the surface. Glassy carbon electrodes were first cleaned using acetone to remove any left-over glue on the surface from the copper tape used in the previous experiments. Next, the electrode was ultrasonicated using ultrapure water for at least 15 minutes and manually polished for one to two minutes using undiluted alumina paste and a microfiber cloth (DP-floc, Struers, USA). After another washing step with ultrapure water, the electrode was ultrasonicated in water for 15 minutes to remove any

residual alumina particles from the surface. Subsequently, the electrodes were ultrasonicated for 15 min in 20 vol.% HNO₃ (aq) (Sigma-Aldrich, ACS reagent grade, 70%) solution to make sure all leftover alumina dissolved from the electrode surface. Then, the electrode was washed and ultrasonicated for at least 15 minutes using ultrapure water to ensure all acid was removed from the electrode. Finally, the electrodes were dried using compressed air.

The AuPd and Pd/C electrodes were prepared using the cleaned gold foil or glassy carbon electrode respectively, following the procedure of Kortlever et al. [9]. In short, the freshly cleaned electrode was placed in a single compartment cell with one side of the electrode exposed to electrolyte. A glassy carbon counter electrode was placed perpendicular to the working electrode. A leakless Ag/AgCl electrode (LF-1.6-100, Innovative Instruments) was used as reference electrode and the electrolyte chamber was filled with a 0.1 M H₂SO₄ (Sigma-Aldrich, ACS reagent grade, 95.0-98.0%) + 1 mM PdCl₂ (Alfa Aesar, Premion, 99.999%) solution. After performing potentiostatic electrochemical impedance spectroscopy (PEIS) at open circuit potential to determine the resistance of the setup, chronoamperometry was performed at 0.315 V vs. Ag/AgCl for 60 seconds. During the process, palladium ions from the solution were reduced and deposited on the surface of the electrode.

S.4 – Material analysis

X-ray photoemission spectroscopy (XPS) spectra were obtained using a Thermo Scientific K α spectrometer utilizing a monochromatic Al K α excitation source. The base pressure inside the analysis chamber was about 2·10⁻⁹ mbar. High resolution XPS spectra were recorded using 400 μ m spot size, 0.1 eV step size and 50 eV pass energy (200 eV for the survey). All spectra were charge-corrected to the C 1s adventitious carbon (284.8 eV). The obtained XPS spectra were deconvoluted with CasaXPS v2.3 software. Scanning electron microscopy (SEM) images were obtained using JEOL 6500F microscope at an acceleration voltage of 15 kV, coupled with an energy dispersed X-ray analysis detector (Ultradry, Thermo Scientific).

S.5 – SEM-EDX results

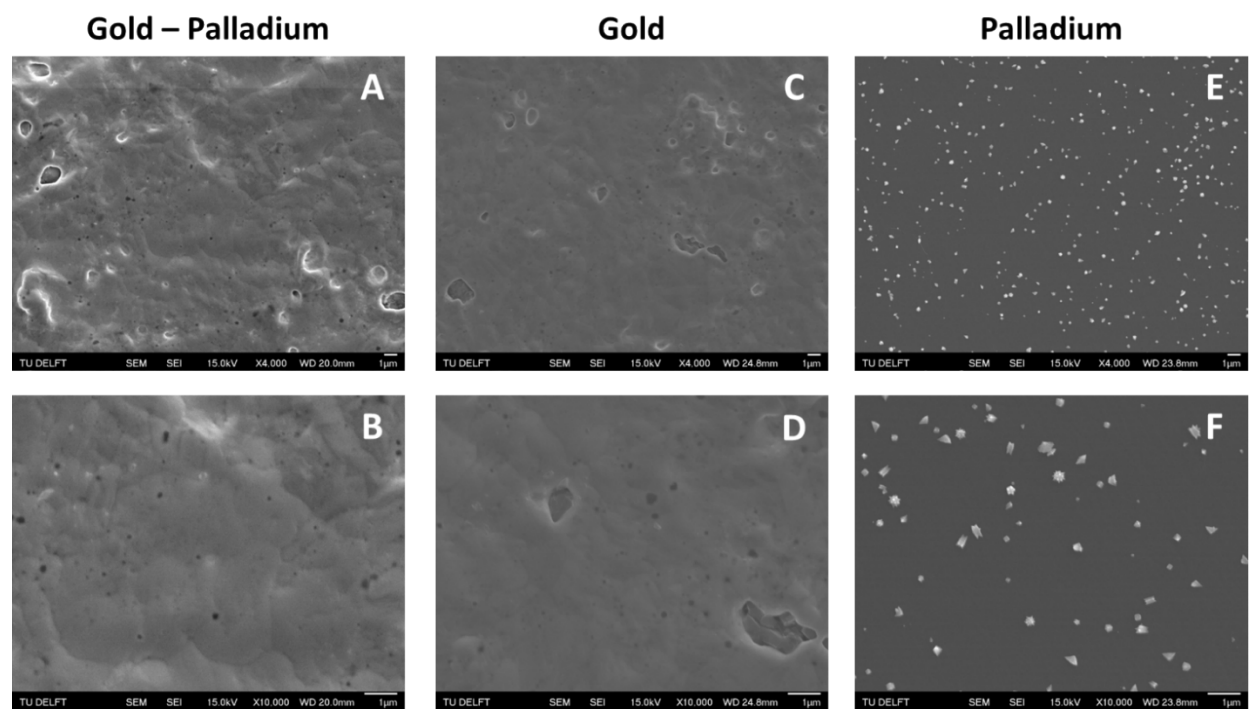


Figure S1. Scanning electron microscopy (SEM) images of electrodeposited palladium on a gold electrode (A & B), pure gold electrode (C & D), and electrodeposited palladium on a glassy carbon electrode (E & F) at different magnifications.

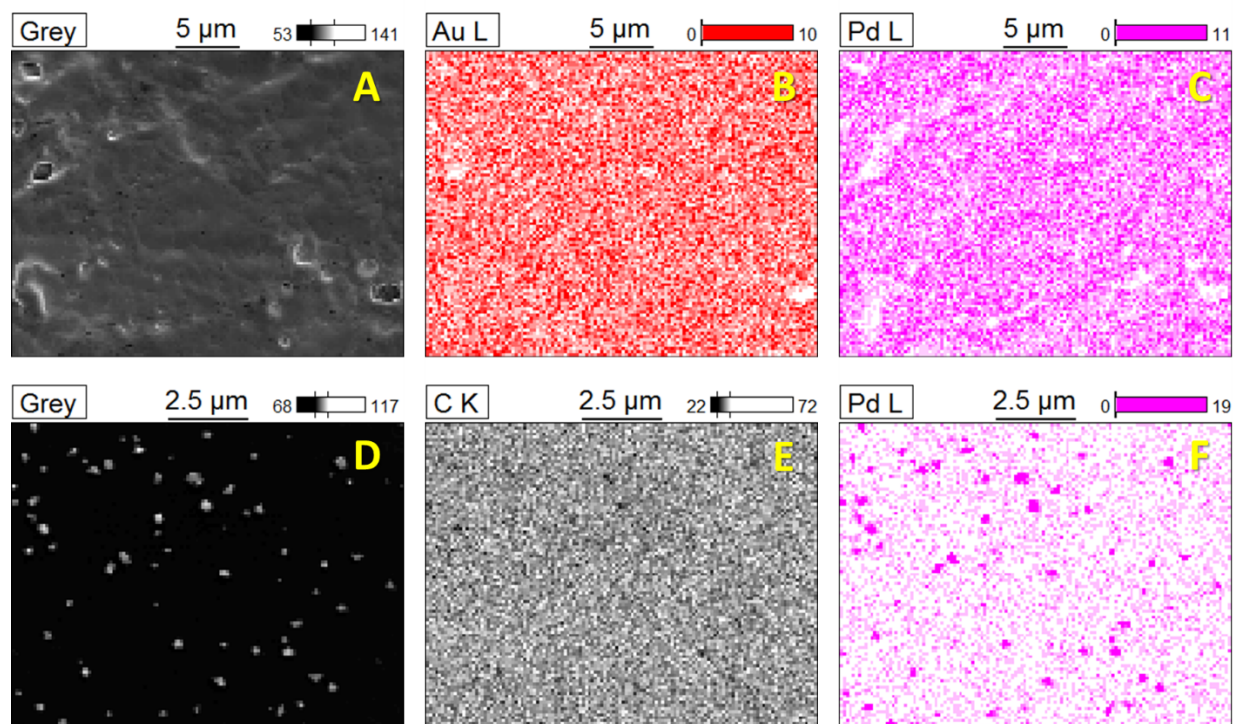


Figure S2. Elemental mapping of the gold-palladium electrode surface (A-C) and electrodeposited palladium on a glassy carbon electrode (D-F) using energy-dispersive X-ray spectroscopy (EDX)

Full scale counts: 36363

ML28(79)

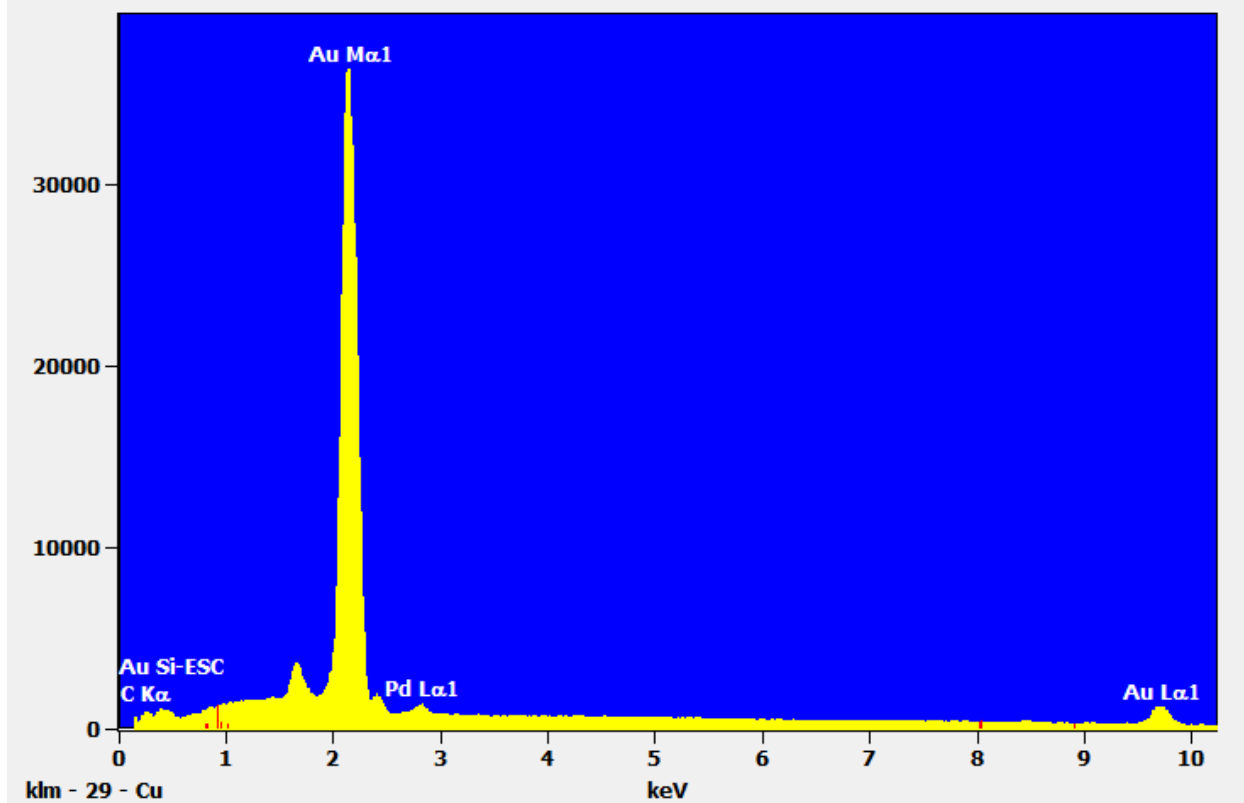


Figure S3. EDX spectrum of the gold-palladium electrode surface.

S.6 – XPS results

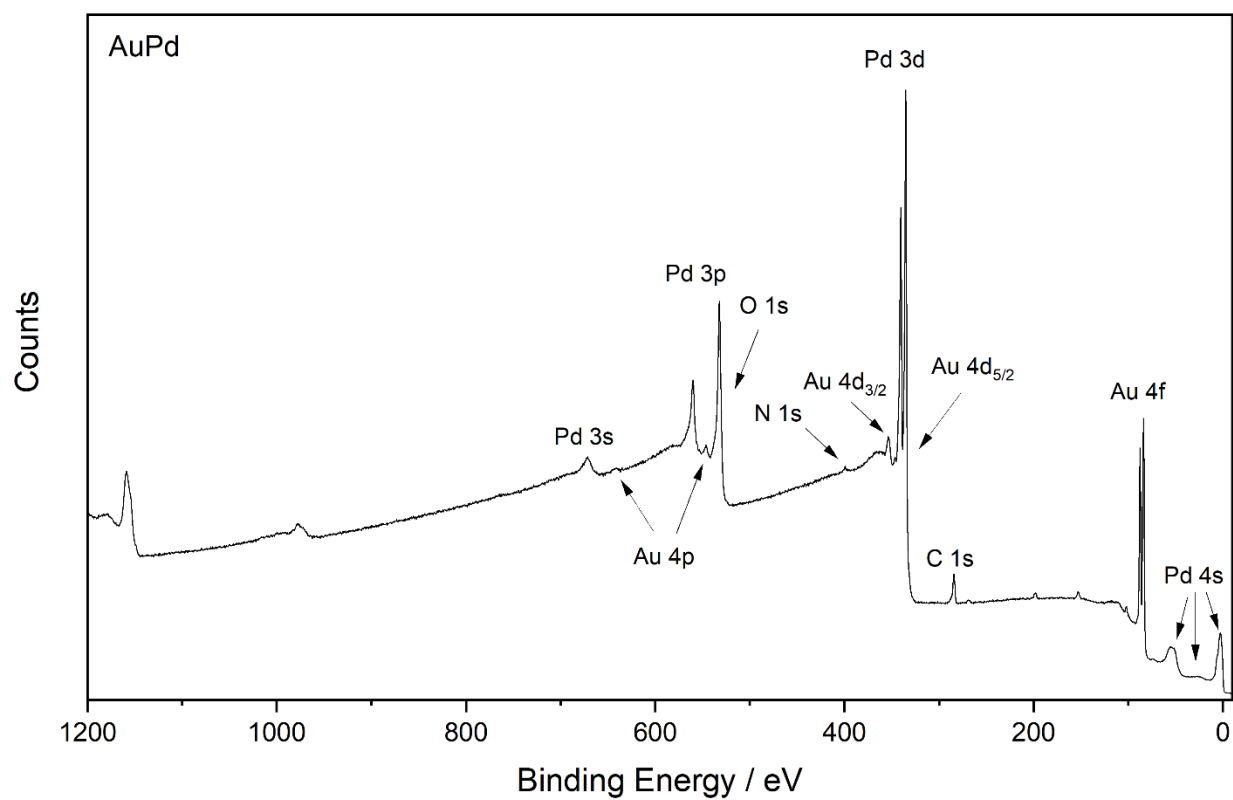


Figure S4. XPS survey spectrum from -10 eV to 1200 eV of a Pd-Au electrode. Pass energy is 200 eV with step size 0.1 eV.

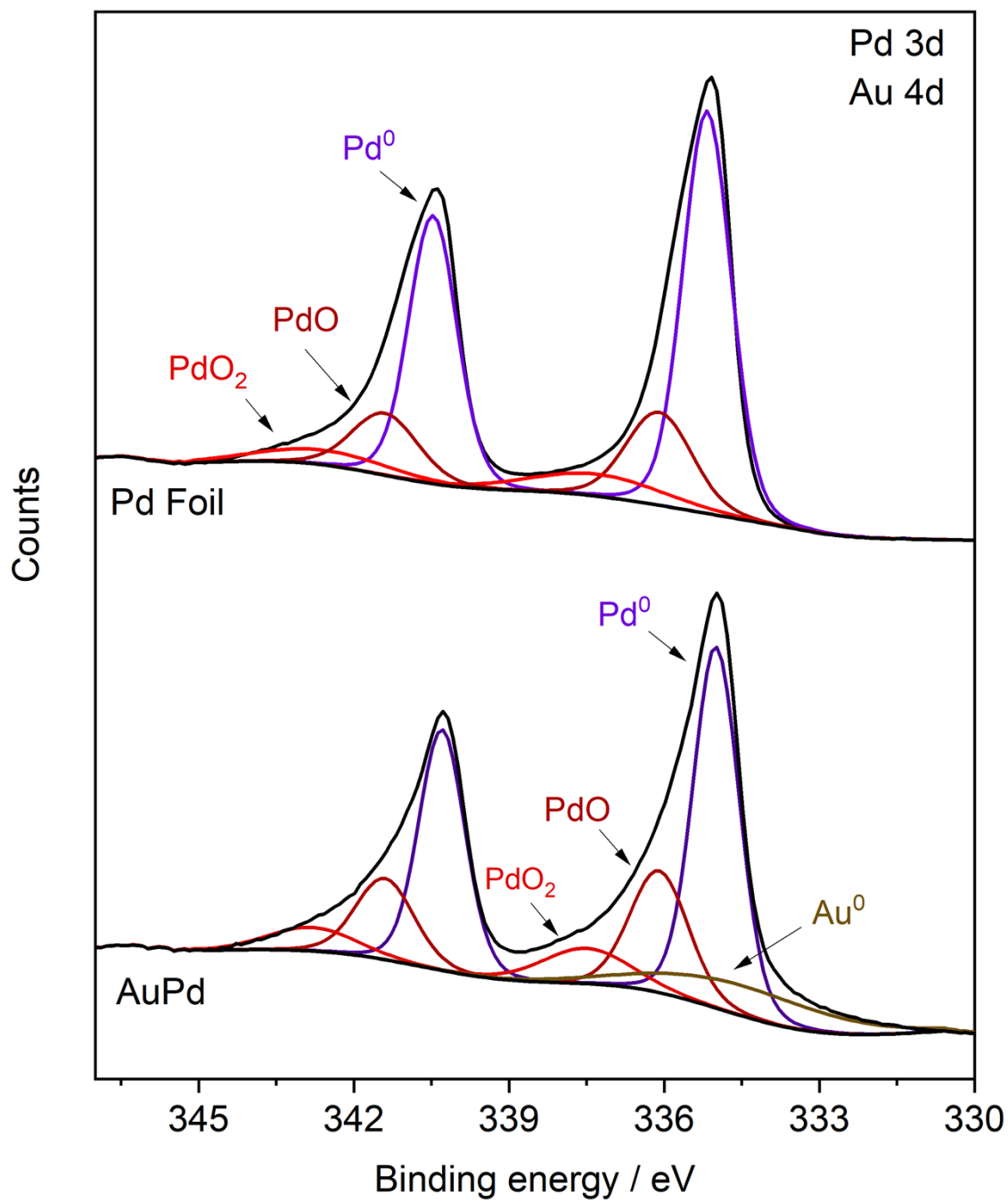


Figure S5. XPS high resolution Pd 3d and Au 4d spectral region for a Pd foil and AuPd electrode.

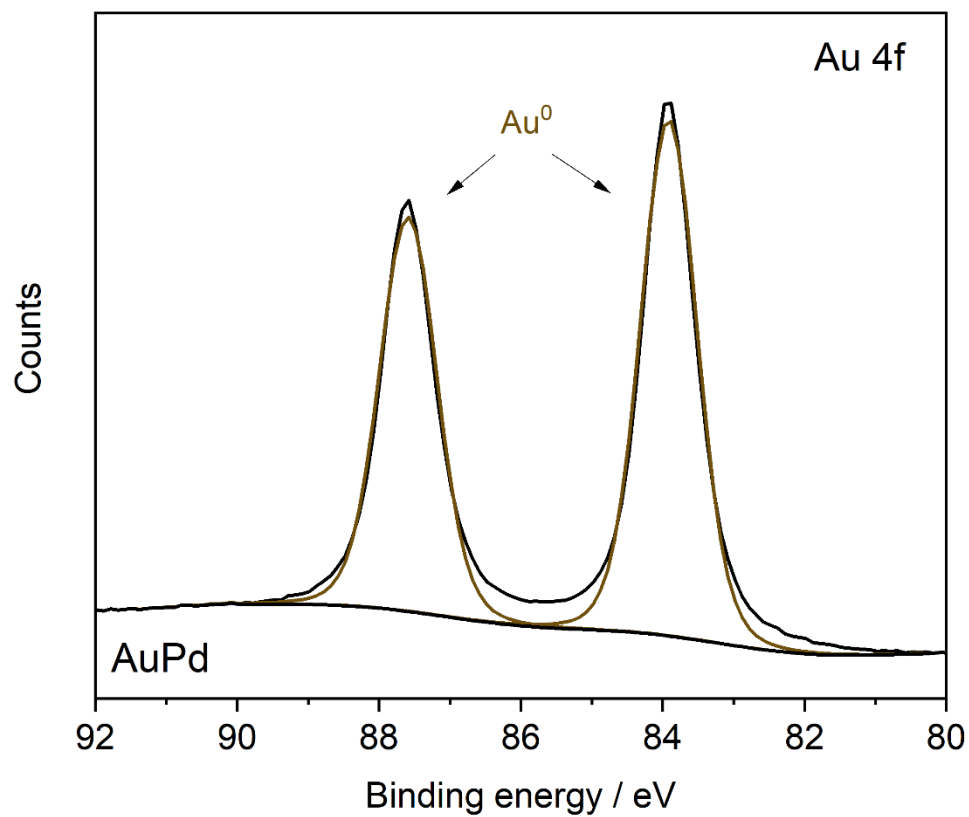


Figure S6. XPS high resolution Au 4f spectrum for a AuPd electrode.

| Name | AuPd | | Pd Foil | |
|----------------------------|----------|------|----------|------|
| | Position | FWHM | Position | FWHM |
| Pd⁰ 5/2 | 335 | 1.05 | 335.17 | 1.1 |
| Pd⁰ 3/2 | 340.3 | 1.05 | 340.47 | 1.1 |
| PdO 5/2 | 336.1 | 1.33 | 336.1 | 1.5 |
| PdO 3/2 | 341.4 | 1.33 | 341.4 | 1.5 |
| PdO₂ 5/2 | 337.5 | 2 | 337.3 | 3 |
| PdO₂ 3/2 | 342.8 | 2 | 342.6 | 3 |
| Au 4d 5/2 | 334.5 | 4 | | |
| Au 4f 7/2 | 83.91 | 0.94 | | |
| Au 4f 5/2 | 87.59 | 0.96 | | |

Table S1. AuPd and Pd foil XPS fitting parameters.

S.7 – Ferro/ferricyanide experiments

Ferro-/ferricyanide redox couple was used to determine the hydrodynamics of the flow within the cell. A buffer of 0.1 M KHCO_3 (99.95%, Sigma Aldrich) + 5 mM $\text{K}_3\text{Fe}(\text{CN})_6 \cdot \text{H}_2\text{O}$ (99.9%, Sigma Aldrich) + 5 mM $\text{K}_4\text{Fe}(\text{CN})_6$ (99.9%, Sigma Aldrich) was made and inserted through the cell, using polished glassy carbon (HTW) as both the working and counter electrode, since unpolished glassy carbon or metal surfaces could lead to unwanted side reactions [4]. Furthermore, Argon was bubbled through the electrolyte to simulate the CO_2 bubbles during the experiment and to remove any dissolved oxygen to prevent ferrocyanide oxidation [5]. Lastly, all experiments were performed in the dark to prevent photolysis of the cyanide complexes through photo dissociation under UV light leading to cyanide formation [6]. Linear sweep voltammetry was performed between open circuit potential to + 0.7 V vs E_{oc} at a sweep rate of 1 mV/s and maintaining an Argon flowrate of 8 ml_n/min . The sweep rate was kept low to limit the contribution of double layer charging. Cell resistance could not be determined using PEIS since at any potential faradaic reactions occur. Therefore, these results are shown without ohmic drop compensation.

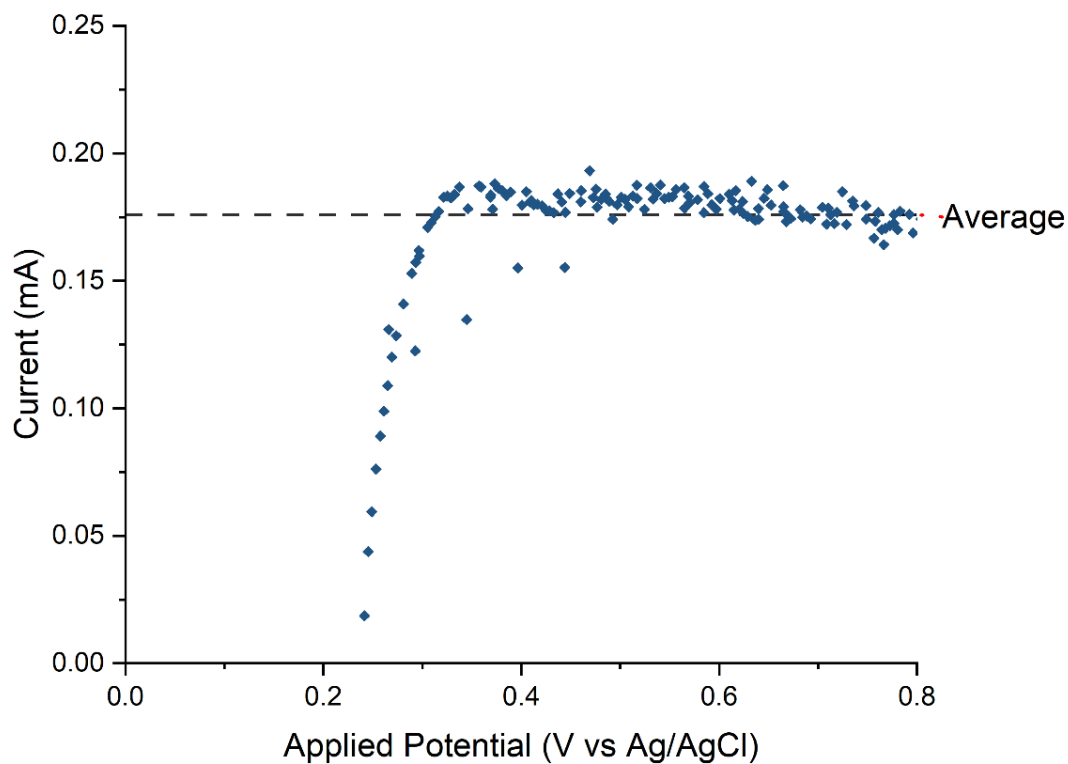


Figure S7. Reversible ferrocyanide oxidation during a LSV of 0.1 mV/s from open circuit potential to $E_{OC} + 0.7$ V. Results shown are the average of eight consecutive LSVs. The potential is shown up until 0.8 V. The average oxidation current is shown as a dashed line in the figure and the average of the current between 0.6 V vs. Ag/AgCl and 0.8 V vs. Ag/AgCl.

| Applied potential vs. RHE | CO ₂ consumption (nmol/s) | |
|---------------------------|---|--|
| | Phosphate buffer (0.1 M KH ₂ PO ₄ +0.1 M K ₂ HPO ₄) | Bicarbonate buffer (0.1 M KHCO ₃) |
| -0.8 | 4.6 | 10.5 |
| -0.9 | 12.8 | 11.1 |
| -1 | 22.7 | 19.5 |
| -1.1 | 25.1 | 24.5 |
| -1.2 | 22.9 | 23.6 |

Table S2. CO₂ consumption rates on a polycrystalline gold electrode in both a phosphate and bicarbonate buffer at a potential range between -0.8 V vs. RHE and -1.2 V vs. RHE. The consumption rates are calculated from the sum of average partial current densities of all CO₂ reduction products at each respective potential.

References

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