

Supporting Information

Sulfuric Acid Electrolyte Impacts Palladium Chemistry at Reductive Potentials

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DESIGN OF TPD CHAMBER TO MEASURE PALLADIUM ELECTRODES

Modelling of TPD spectra to find optimum carrier gas flow

ESS CatalySys gas mass spectrometer detector used for the AP-TPD experiments incorporates inlets controlling the inlet flow to be 5, 10 or 20 mL min⁻¹. The detection limit (LOD) reported by the provider for H₂ is 0.5 ppm. TPD spectra were then modelled considering a single desorption event corresponding to a H:Pd = 0.01 (for the worst case scenario) from a 3 mg Pd thin film (0.28 µg H₂) when using 5, 10 and 20 mL min⁻¹ carrier gas flows. As observed in Figure S1, a carrier gas flow of 10 mL min⁻¹ was low enough for the technique to have sufficient sensitivity to detect small H_{abs} desorption events from a Pd thin film. Using lower flow rate of 5 mL min⁻¹ would yield a more intense peak but other complications such as diffusion of the desorbed H₂ (diffusion is not considered in the modelling of Figure S1) would broaden signals and in the end will result in lower sensitivity.

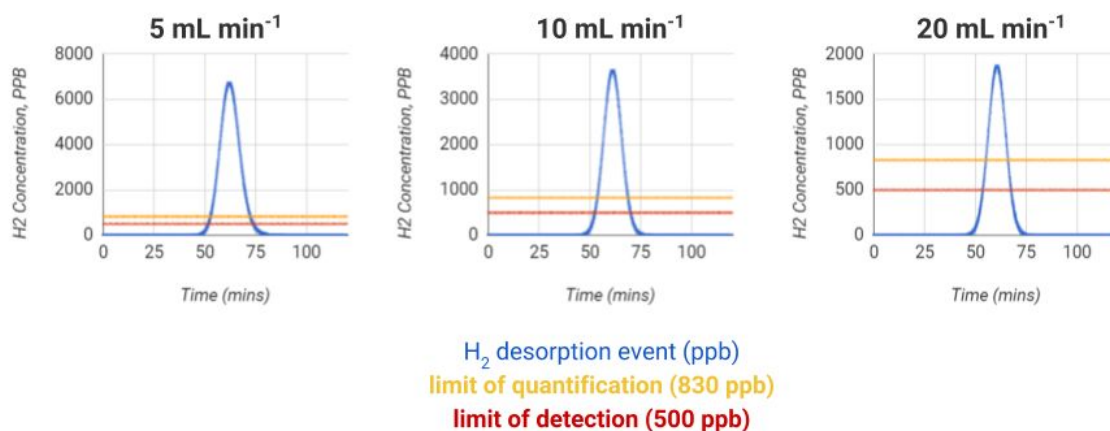


Figure S1. Modelling of TPD spectra depending on the carrier gas flow used in the experiment. The model considers a 3 mg Pd thin film and a single H-desorption event corresponding to H:Pd ~ 0.01 (or 0.28 µg H₂). Flows of 5, 10 and 20 mL min⁻¹ of carrier gas were modelled. No other processes such as diffusion of H₂ were considered in the modelling.

Calculation of the TPD chamber dimensions needed to avoid diffusion

The effective transport of H₂ (or other desorbed species) by the bulk motion of the carrier gas will depend on both diffusion and advection phenomena. Diffusion of H₂ in Ar gas (carrier gas in this study) will spread the analyte throughout the chamber yielding signal broadening in the TPD spectra. Advection phenomena, on the other hand, would drag the desorbed H₂ molecules towards the detector. Peclet Number (Pe) is a dimensionless number that quantitatively compares advection vs. diffusion for a given system. Pe number is defined as the advective transport rate divided by the diffusive transport rate, so that roughly $Pe \gg 1$ indicates that advection prevails over diffusion, while at $Pe \ll 1$ diffusion prevails. Pe can be calculated from eq (S1):

$$Pe = \frac{Q}{\varnothing D} \quad (S1)$$

where Q is gas flow (i.e. 10 cm³ s⁻¹, see above), D is the diffusion coefficient of a given gas in the carrier gas used (i.e. $D_{H_2/Ar} = 0.828$ cm² s⁻¹ at 15 °C)¹ and \varnothing is the internal diameter of the pipe where the transport of matter is being studied (i.e. internal diameter of a hypothetical cylindrical TPD chamber). TPD experiments are usually carried out at temperatures between 25 - 600 °C, so the diffusivity of H₂ in Ar was taken at an intermediate temperature of 300 °C ($D_{H_2/Ar, 300\text{ }^\circ\text{C}} = 2.324$ cm² s⁻¹). From the application of eq (S1) to our system, $Pe \geq 1$ (advection prevails over diffusion) is only attained for a cylindrical chamber with a diameter $\varnothing \leq 0.9$ mm. This diameter is physically impossible when the aim is to measure thin film samples. Therefore, different geometries other than a cylinder were considered and the chamber depicted in Figure 3 was designed. The equivalent Pe number calculated for the designed chamber on Figure 3 is $Pe \sim 0.01$ (at an intermediate temperature of 300 °C). It can be seen how challenging it is to achieve $Pe > 1$ and some broadening coming from H₂ diffusion especially at high temperatures is unavoidable and inherent of AP-TPD experiments.

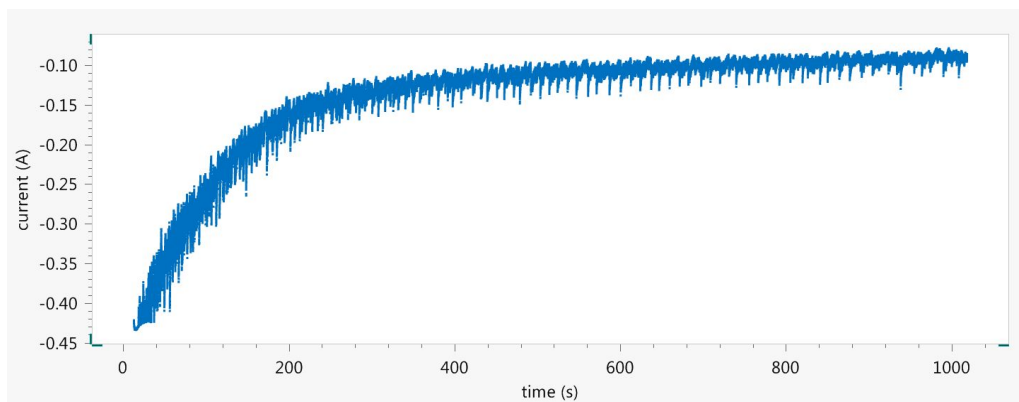


Figure S2. Absorption of hydrogen in Pd_{foil} in 1 M H_2SO_4 by chronoamperometry: samples were held at -0.4 V (vs. RHE) until the applied current trace reached a constant value, then held for further 400 s to ensure saturation.

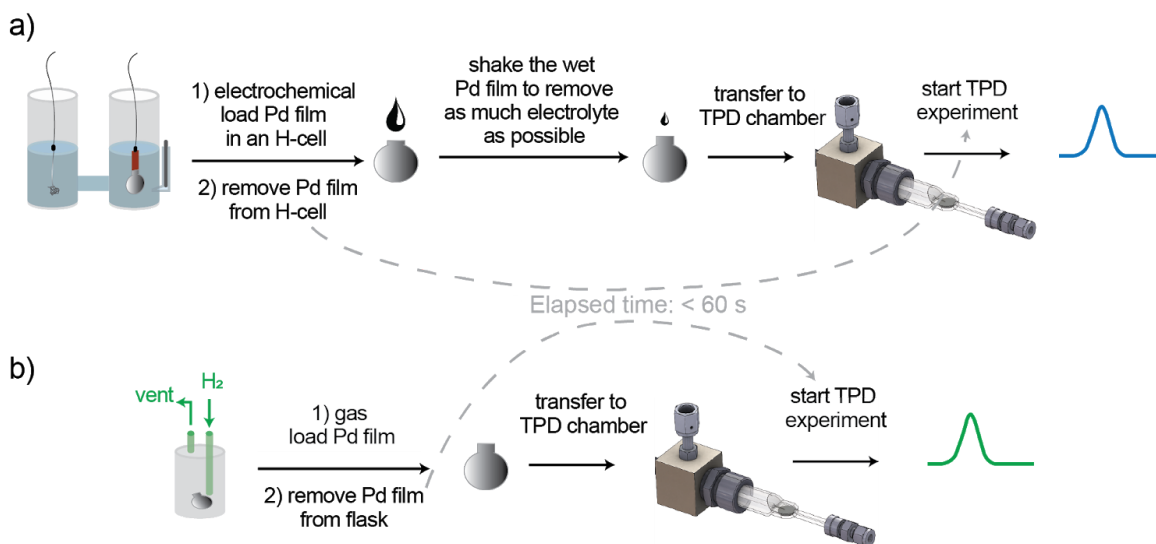


Figure S3. Experimental procedure used to measure the *in situ* TPD spectra of palladium films loaded with hydrogen by: (a) electrochemical means and (b) gas means.

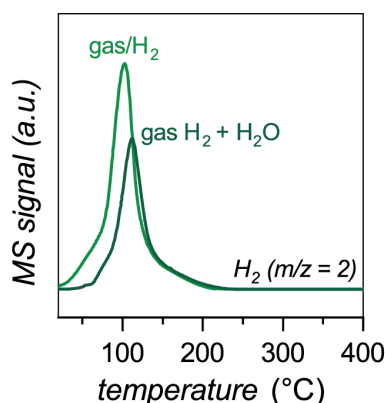


Figure S4. TPD spectra of H_2 ($m/z = 2$) for a palladium foil hydrided by gas means (by applying a flow of H_2 gas: **gas/ H_2** , light green); and for a similar **gas/ H_2** palladium submerged in deionized water for 5 seconds right after the loading (**gas/ $\text{H}_2 + \text{H}_2\text{O}$** , dark green). Both samples are similar with the only difference that the **gas/ H_2** is “dry” whereas the **gas/ $\text{H}_2 + \text{H}_2\text{O}$** is “wet”, i.e. it is introduced in the TPD chamber with water remnants on top of the palladium hydride. The temperature of the main H_2 -desorption event is similar for both “dry” and “wet” palladium hydride samples. This indicates that the remnant of water (or electrolyte) on top of Pd_{foil} for “wet” samples does not impact the kinetics of hydrogen desorption on the TPD experiments of this work. Consequently the upward shift in desorption temperature observed for **echem/ H_2SO_4** and **gas/ $\text{H}_2 + \text{H}_2\text{SO}_4$** samples relative to both **gas/ H_2** and **gas/ $\text{H}_2 + \text{H}_2\text{O}$** is attributed to the presence of adsorbates derived from the H_2SO_4 -electrolyte.

The slight upward shift in the desorption temperature observed for **gas/ $\text{H}_2 + \text{H}_2\text{O}$** vs. **gas/ H_2** is probably due to the lower initial H_{abs} -content in the “wet” sample (see lower area under the main peak), possibly originated from the desorption of some of the H_{abs} during the additional H_2O -submersion step. It is known that for a second-order desorption the temperature of desorption in the TPD spectra increase with decreasing initial surface coverage.²

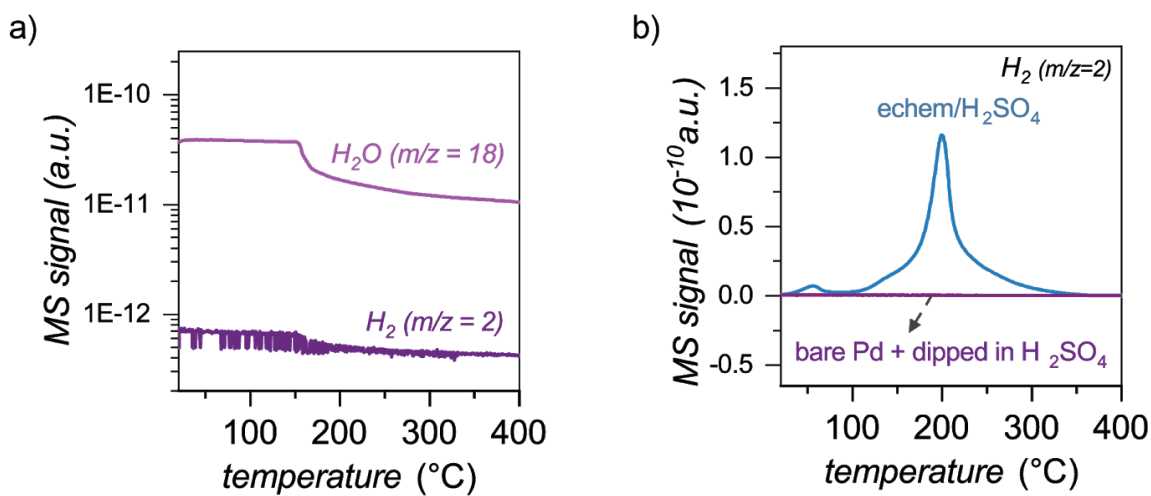


Figure S5. (a) TPD spectra of H_2O ($m/z = 18$) and of H_2 ($m/z = 2$) for a bare palladium foil (with no H_{ads}/H_{abs}) dipped in H_2SO_4 for 5 sec. (b) Comparison of the H_2 -TPD spectrum of the bare Pd_{foil} dipped in H_2SO_4 with that of **echem/ H_2SO_4** (palladium loaded with hydrogen by electrochemical means in 1M H_2SO_4). The artifactual H_2 -background from water in the electrolyte remnants is negligible compared to the H_2 signal from the desorption of H_{abs} from palladium.

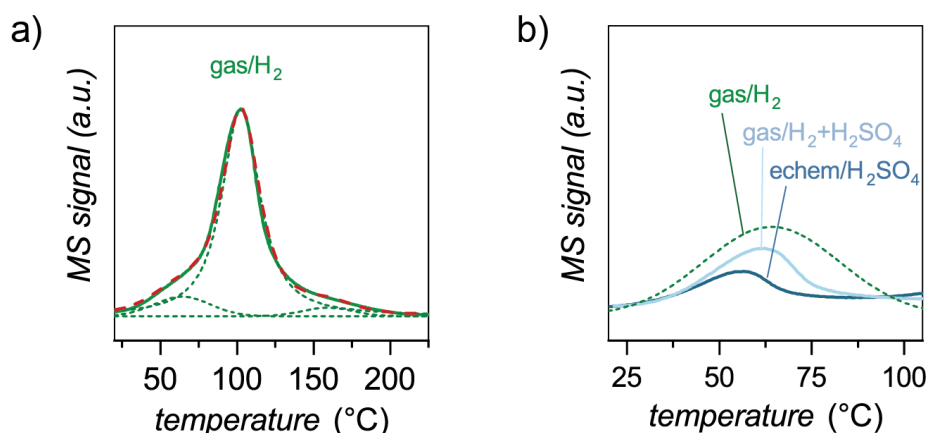


Figure S6. (a) H₂-TPD spectra of **gas/H₂** (a pristine **Pd_{foil}** where H_{abs} was previously absorbed by passing a flow of H₂ gas; solid green line) deconvoluted in three peaks (green dashed lines): at 63 °C of H_{abs} desorbing from β -PdH_x; at 102 °C of H_{abs} desorbing from the bulk of $(\alpha + \beta)$ -PdH_x; and a third peak at 160 °C that was included solely to fit the high-temperature tail of the main H₂-desorption peak (no physical meaning is attributed to this peak). The sum of deconvoluted peaks is also shown as a red dashed line. (b) Comparison of the H₂-peak at 50 – 70 °C for the three samples under study in this work: **gas/H₂** (from the deconvoluted spectra on (a)), **gas/H₂+H₂SO₄** and **echem/H₂SO₄**. The intensity of the H₂-peak from β -PdH_x follows the trend: **gas/H₂** > **gas/H₂+H₂SO₄** > **echem/H₂SO₄**.

SEMI-QUANTITATIVE ANALYSIS OF H₂ SIGNALS OF TPD SPECTRA

LiAlH₄ was chosen as a reference substance to quantify the mass fragment m/z = 2 signal from H₂ in the TPD spectra. Upon heating in an inert atmosphere, LiAlH₄ decomposes in two different steps following reactions:^{3,4}



Accordingly, TPD spectrum (measured in the same conditions as spectra on Figure 4a: 20 °C min⁻¹, 15 mL min⁻¹ of Ar carrier gas flow, from 20 to 400 °C) of the prepared LiAlH₄ sample showed two peaks of H₂ coming from reactions (1) and (2). As the amount of LiAlH₄ was known, so was the amount of H₂ detected in the TPD with an integral value of $(1.5 \pm 0.7) \cdot 10^{-6}$ a.u. per mmol of H₂ yielded from the calibration. Accordingly, the amount of H₂ detected in the spectra of Figure 4a corresponds to initial palladium hydrides with the H_{abs} content indicated on Table S1. This semi-quantification cannot be taken as accurate (a partial hydrolysis of the LiAlH₄ during quick transfer to the TPD chamber may be unavoidable, and would yield in slight over-estimation of the H₂ amount), but indicates that we are indeed measuring the desorption of H_{abs} from a fully H_{abs}-saturated **Pd_{foil}**, rather than being detecting only some residual H_{abs} or H_{ads} (which would yield H: Pd or x several orders of magnitude smaller).

Table S1. Semi-quantitative analysis of H₂ signals from TPD spectra in Figure 4a.

Sample	<i>x</i> (<i>PdH_x</i>)
gas/H₂	1.5 ± 0.7
gas/H₂+H₂SO₄	1.4 ± 0.7
echem/H₂SO₄	1.3 ± 0.6

Preparation of the LiAlH₄ reference sample: Samples were prepared by drop casting a 1 M LiAlH₄ solution in diethyl ether on a Kapton/Cr/Au substrate inside an Ar glove box. The sample was then dried out at room temperature under an Ar atmosphere for 4 days.

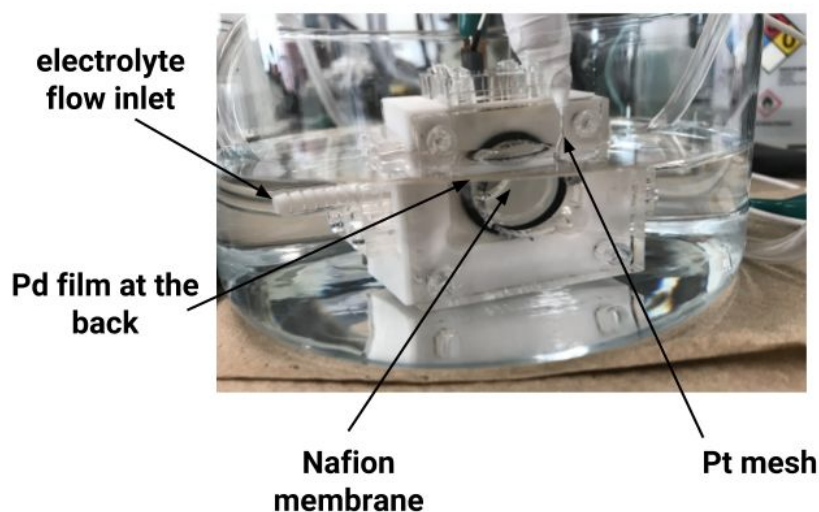


Figure S7. Photo of the flow cell set up employed for the accurate quantification of hydrogen absorbed in palladium films and for the HER electrocatalytic tests. The flow cell is similar to the one reported previously⁵ but adapted to separate working (Pd film) from counter (Pt mesh) electrode. For this purpose, one of the cell's windows is sealed with a Nafion membrane instead of with a glass slide, the cell is immersed in a flask with the electrolyte and the counter electrode is placed close to the Nafion membrane but outside the cell. Similar to the previously reported cell, the palladium film supported on glass is sealed into the back of the cell with an O-ring. The electrolyte is flowing constantly inside the cell towards the surface of the sample to remove H₂ bubbles and the electrolyte from the outlet goes to a reservoir to be recirculated. A port for the reference electrode is included at the top of the cell. This configuration allows the accurate quantification of hydrogen by eliminating any interferences from H₂ bubbles or electrolyte species formed on the counter electrode.

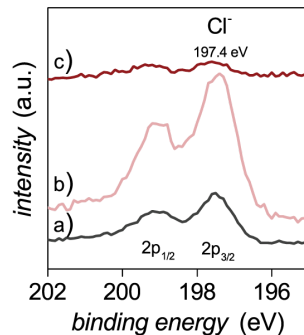


Figure S8. XPS spectra of Cl 2p binding energy region of (a) as-prepared **Pd_{foil}**, (b) **Pd_{foil}** submerged in 1M HCl for 15 min and (c) **Pd_{foil}** treated electrochemically in 1M HCl at -0.4 V vs. RHE for 15 min. All samples were rinsed with deionized water and dried out at 50 °C for 1 h before the XPS measurement. The amount of chloride observed on **echem/HCl** is even smaller than the chloride observed on the as-prepared **Pd_{foil}** (coming from contamination).

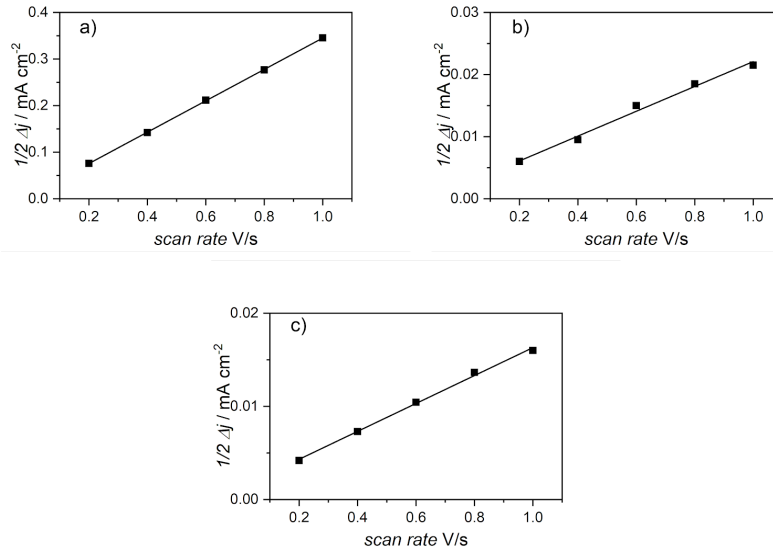


Figure S9. Electrochemically-active surface area (ECSA) measurements derived from double layer capacitance obtained in 1M H₂SO₄ for the three palladium samples used in this work (a) **Pd_{edep}** measurements were made between 0.4 and 0.6 V vs. RHE and current was taken at 0.5 V; (b) **Pd_{foil}** measurements were made between 0.15 and 0.25 V vs. RHE and current was taken at 0.21 V; and (c) **Pd_{film}** measurements were made between 0.4 and 0.6 V vs. RHE and current was taken at 0.51 V.

Table S2. Electrochemically-active surface area (ECSA) measured as capacitance (mF cm^{-2}) and the estimated roughness factor for each sample type.

Sample	ECSA (mF cm^{-2})	roughness factor*
Pd_{foil}	0.020	1.3
Pd_{edep}	0.337	22
Pd_{film}	0.015	1.0

*Relative roughness factors were calculated considering **Pd_{film}** had a roughness factor of 1. Roughness factors are calculated only for comparison purposes among the three samples.

ESTIMATION OF THE $\text{H}_{\text{ads}}:\text{Pd}$ FOR **Pd_{edep}**

Assuming **Pd_{edep}** has a roughness factor of 22 from ECSA measurements (see Figure S9 and Table S2, considering **Pd_{film}** and **Pd_{foil}** have similar roughness factor of ~ 1), the real surface area of the **Pd_{edep}** was 39 cm^2 (geometrical surface area 1.77 cm^2). **Pd_{edep}** weighed $\sim 18 \text{ mg}$ (0.169 mmol Pd). Considering the surface atom density of palladium to be $2.19196 \cdot 10^{-6} \text{ mmol cm}^{-2}$,⁶ there are $8.5 \cdot 10^{-5} \text{ mmol}$ of Pd on the surface that are equivalent to the mmol of H_{ads} . Then dividing mmol of H_{ads} by the total mmol of Pd yields a $\text{H}_{\text{ads}}:\text{Pd} = 0.0005$.

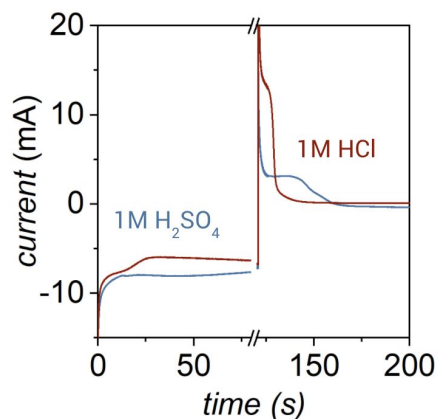


Figure S10. Chronoamperometric data for Pd_{film} samples in 1 M HCl (red) and 1 M H_2SO_4 (blue) electrolytes prepared with TraceSELECT® HCl and 99.999% H_2SO_4 reagents. Measurements were conducted in a flow cell with an applied potential of -0.20 V and +0.46 V (vs. RHE) for absorption and desorption respectively. This graph shows that the lesser absorption and desorption of H_{abs} in H_2SO_4 relative to HCl electrolyte is not due to trace inorganic contaminants in the former. The lesser absorption and desorption of H_{abs} is due to the sulfate adsorbates formed in sulfuric acid at reductive potentials.

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