Supplementary Information:

Is there anything better than Pt for HER?

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1 Experimental Details

1.1 Electrochemical Methods

The electrochemical measurements were performed in a three-electrode cell with a Hg|Hg$_2$SO$_4$ reference electrode (RE) placed in a Luggin capillary, an iridium wire as counter electrode, a rotating disk electrode (RDE) as working electrode (WE) and a platinum wire dummy electrode for calibrating the RE versus RHE. For all experiments, a 0.5 M H$_2$SO$_4$ (Merck, Suprapur) electrolyte was used. All samples were deposited on new and freshly cleaned glassy carbon electrodes (GCE) ($\varnothing=5.0$ mm, Sigradur® G). Commercially available (HiSPEC 9100) Pt/C catalyst was deposited on GCEs with various loadings by drop casting a fixed amount of ink diluted appropriately. The deposition of mass selected nanoparticles will be described in the following. The RE was calibrated versus the RHE by measuring the open circuit potential of the platinum dummy while continuously purging the electrolyte with H$_2$. All cyclic voltammograms (CVs) measuring the HER activity were performed with continuous H$_2$ purging of the electrolyte at a scan speed of $\nu=50$ mV s$^{-1}$ (except two highest loading samples scanned with $\nu=10$ mV s$^{-1}$ to minimize non-faradaic currents due to high roughness) and a rotation rate of $\omega=1600$ rpm. The CVs are compensated for ohmic drop, which was measured via impedance spectroscopy at the high frequency limit of the spectrum. The amount of catalytically active sites on the platinum nanoparticles was measured for each sample by electrochemical oxidation of adsorbed CO (i.e. CO-stripping), see section 1.6 for description.

1.2 Nanoparticle Deposition

The physical deposition process described in this section allows for the deposition of highly precise loadings of a well-defined particle mass. Size-uniformity, dispersion, morphology etc. of nanoparticles, comparable to the ones in this study, has previously been characterized and reported for this method$^1$–$^3$. Cleaned glassy carbon electrodes (see section 1.4 for details) were loaded into our UHV system (Omicron Technologies, base pressure $\approx 10^{-10}$ mbar) and then submitted to 1 keV Ar$^+$ sputtering at $\approx 1$ µA sample current for 10 minutes to remove the outer atomic layers and ensure a clean electrode surface. The glassy carbon stubs were then characterized by ion scattering spectroscopy (ISS) to verify the cleanliness of the sample surface (Figure S7). The deposition of mass selected nanoparticles was done using a magnetron based cluster source combined with a time of flight mass filter. The production and deposition of mass selected Pt nanoparticles can be described by a five step process as summarized in$^3$. (1) Small Pt entities are ejected from a Pt target by Ar$^+$ sputtering, (2) the Pt entities agglomerate to nanoparticles within an ‘aggregation zone’, (3) the Pt nanoparticles exit the aggregation zone by supersonic expansion caused by a pressure gradient, (4) the Pt nanoparticles are focused into a narrow beam using electrostatic lenses and subsequently filtered by a time-of-flight mass filter, (5) soft landing (< 0.1 eV per atom) the mass selected nanoparticles on the glassy carbon electrode. The vast majority of the deposited nanoparticles are singly ionized, which makes it possible to measure the discharge current and correlate this current directly to the number of particles. Using this method, precise loadings of a known nanoparticle mass can be obtained. Pt nanoparticles of mass 370 k amu (3.8 nm) were deposited on the glassy carbon electrodes with calculated loadings between 13 ng cm$^{-2}$ and 5000 ng cm$^{-2}$. After deposition of Pt nanoparticles, the electrodes were characterized with ion scattering spectroscopy to confirm the presence of Pt on the surface (see Figure S7).
1.2.1 Rastering details
During the deposition of the nanoparticles, the glassy carbon electrode was moved in a raster pattern to promote a homogenous coverage of nanoparticles. A small and large raster area was used to facilitate a small and large final deposition area. The small raster area was made by moving the electrode in a (1 x 1) mm$^2$ raster pattern, which yielded a final deposition area of ≈ 6.2 mm$^2$ due to the width of the nanoparticle beam. This final deposition area is well within the confines of the glassy carbon electrode and thereby the measured discharge current corresponds directly to the number of particles. In order to fully utilize the entire electrode surface, a large raster area was made by moving the electrode in a (4 x 4) mm$^2$ raster pattern during deposition yielding a final deposition area of ≈ 30 mm$^2$. This caused a fraction of the deposited particles to land on the sample holder, meaning there was no longer a 1:1 correspondence between discharge current and number of particles. This was corrected by simulating the beam profile and calculating the fraction of particles beyond the electrode surface.

1.2.2 Calculating Loading of Particles Produced with the Cluster Source
The physical deposition method used will cause an error in loading, which can be determined by the finite resolution of the time of flight mass filter. For the deposited particles in this work, the minimal resolution (maximum transmission) was chosen, such that the error in particle mass is given by

$$\Delta m = \frac{m_{\text{dep}}}{20}$$

where $\Delta m$ is the error on the deposited mass and $m_{\text{dep}}$ is the mass of the deposited particle. For 370k amu (3.8 nm diameter) Pt nanoparticles (spherical approximation) this error corresponds to 18.5k amu. The loading and error thereof is then

$$\text{Loading} = (m_{\text{dep}} \pm \Delta m) N_{\text{NP}}$$

where $N_{\text{NP}}$ is the number of nanoparticles as measured by the discharge current. This is then normalized by the area of the electrode surface to obtain the values in Table S6. Thereby the error in loading will scale linearly with the number of particles and thus the loading itself.

The precision of the actual loading values wrt. the target loading value is the same for all samples (around 3 ng cm$^{-2}$ disk) and is directly related to the time at which the ion particle beam is blanked.

1.3 General Preparations
The electrochemical cell was cleaned with a freshly prepared piranha solution (3:1 volumetric mixture of concentrated H$_2$SO$_4$ and 30% H$_2$O$_2$) and a freshly prepared aqua regia solution (3:1 volumetric mixture of concentrated HCl and HNO$_3$). The cell was rinsed with ultrapure water (Merck Milli-Q® 18.2 MΩ·cm) in between and after. Using a combined heater/pump system, 90 °C deionized water was circulated through the cell jacket while the cell was filled with ultrapure water (Merck Milli-Q® 18.2 MΩ·cm). After 15 minutes the cell was emptied, rinsed and filled with fresh ultrapure water. This was repeated three times.

Following additional items used for experiments have also been cleaned in piranha, aqua regia (when applicable) and heated ultrapure water: RDE head, u-cups, tweezers (PTFE), mounting block (PTFE), solution flasks, counter electrode and dummy electrode.
1.4 Electrode Preparation

New glassy carbon electrodes (GCEs) (Ø=5.0 mm, surface Ra < 50 nm, SIGRADUR G, HTW Hochtemperatur-Werkstoffe GmbH) were cleaned by following procedure:

i. 10 minutes sonication in isopropyl alcohol
ii. 3 times rinse, then 10 minutes sonication, then 3 times rinse in ultrapure water (Merck Milli-Q® 18.2 MΩ cm)
iii. Submersion of GCE’s in concentrated nitric acid (Merck Suprapur® 65 %) for 1 hour
iv. Repeat step ii.

The cleaned electrodes were subsequently transferred to the UHV system for deposition of mass selected Pt nanoparticles (details in section 1.2) or a commercially available Pt/C catalyst was deposited via dropcasting (details below).

1.5 Preparation and Drop Casting of Pt/C ink

A blank ink was made by mixing 7 mL Milli-Q H₂O, 18 mL isopropyl alcohol, 10 mL ethanol and 10 µL Nafion perfluorinated resin solution 5 wt. % into a clean vial and sonicating for 10 minutes. A concentrated catalyst ink was made by weighing out and mixing a commercially available Pt/C catalyst powder (HiSPEC 9100 Pt 60%, Johnson Matthey Fuel Cells) in a portion of the blank ink. The concentrated catalyst ink was sonicated for 30 min. to get a homogeneous suspension of the catalyst powder. A series of aliquots from this concentrated ink were diluted with the blank ink to produce one diluted ink for every sample loading in the range 500–10⁵ ng Pt cm⁻², the high limit being that corresponding to the concentrated ink without further dilution. The concentration of the inks were made so that the desired Pt loading would be achieved by drop casting 7 µL for every sample. A 7 µL portion of each ink was then drop casted onto a series of new and freshly cleaned GCEs.

1.6 Characterization of Catalyst Surface Area via CO-stripping

CO-strip measurements were performed on all samples as follows: A few cycles were performed in Ar-staurated electrolyte to observe the expected CV. Then the WE potential was held at +50 mV vs. RHE for 15 minutes. CO was dosed into the electrolyte (for 2 min) and adsorbed on the platinum nanoparticles. The electrolyte was then purged with Ar for the remaining 13 minutes allowing excess CO in the electrolyte to escape. Consecutively, CVs were recorded while scanning the potential between 0.05 and 1.0 V vs. RHE (v=10 mV s⁻¹, ω=200 rpm) in the Ar purged electrolyte. On the first anodic sweep the CO was oxidized giving a distinct peak. Upon integrating the charge under the peak (with non-faradaic current subtracted), the amount of CO oxidized and hence the number of platinum sites were calculated. For background subtraction the cycle after an additional potential-hold period (at +50 mV vs. RHE for 15 minutes, only Ar-purging) was used. A typical oxidation peak and a background cycle can be seen in Figure S1 (left) and the same oxidation peak with background subtracted (right). The integrated charges (Q_{CO}) from CO-stripping experiments on each sample are given in Table S6 and plotted in Figure S2 versus the Pt loading. The lower estimate of Q_{CO} is assumed to be the most accurate value (light green peak area) and the estimated error is bounded by the upper value of Q_{CO} (sum of light green peak area and dark green area). The two estimates are close for all samples and for most cases fall within the marker size on the plot. In addition to the number of sites, the electrochemically active surface area (ECSA) may be found by normalizing the
obtained \( Q_{CO} \) with the surface charge density \( \sigma_{CO-stripe} \) for CO on platinum. The theoretical \( \sigma_{CO-stripe} = 420 \, \mu \text{C cm}^{-2} \) is commonly used\(^5\) although it may vary somewhat with the potential under which CO adsorbs, electrolyte, surface structure etc.\(^7\)

1.6.1 CO-stripe Charge vs. Loading: Spherical Approximation

The net charge associated with a CO-stripe \( (Q_{CO}) \) on Pt nanoparticles of uniform size with a mass loading per area of \( L \) dispersed over an area \( A_{geo} \) can be approximated by:

\[
Q_{CO}(L) = \sigma_{CO, Pt} \, A_{particle} \, N_{particle} = 4 \pi \sigma_{CO, Pt} r_{particle}^2 L A_{geo} \, m_{particle}^{-1} = \frac{3 \sigma_{CO, Pt} L A_{geo}}{\rho_{Pt} r_{particle}}
\]

where \( \sigma_{CO, Pt} \) is the surface charge density [charge per area] associated with CO on Pt (generally coverage and facet dependent) and \( \rho_{Pt} \) is the mass density of platinum. \( A, m, r \) (particle subscript) denotes, surface area, mass and radius of each particle, respectively. The total number of particles is given by \( N_{particle} \). The underlying assumption is that the particles are well dispersed and act as hard spheres, meaning loss of surface area due to particle-particle overlap or particle-substrate interaction is negligible and that particle roughness or faceting does not significantly increase the area of an individual particle. This spherical approximation is used as an upper bound of \( (Q_{CO}) \) vs. \( L \) in Figure S2 to compare and validate the observed CO-stripe charges with the deposited loading.

1.6.2 Simulation of Nanoparticle Overlap

In addition to the spherical approximation, a simulation assessing particle overlap was performed to validate the experimentally observed strip-charges with the Pt loadings deposited. The simulation of the particle overlap is based on two assumptions: random particle positions and that the particles do not agglomerate significantly when in contact. From the sample coverage, the number of particles per area is found and an equivalent number of random particle positions \((x,y)\) are generated per area with all particles beginning at \((z=0)\). The simulation then loops through the particles and finds the overlapping particles based on the positions and the particle size. If the edge-to-edge distance is found to be lower than -0.3 nm the particle (i.e. the particles overlap more than 0.3 nm) one of the particles is shifted upwards until the edge-to-edge distance is 0. This simulates the line of sight landing process of a cluster source under our approximations. This is reiterated for all overlaps until...
there are no longer overlapping particles. Next the simulation counts all particles that are in contact with or within 0.5 nm of another particle \((N_{\text{contact}})\). The particles that are still placed on the carbon support with \(z=0\) are also counted \((N_{\text{base}})\). To translate these numbers into area losses, the simulation designates a set amount of area to be lost per particle-support contact \((z=0)\) \(A_{\text{base}}\) and per particle-particle contact \(A_{\text{contact}}\).

By multiplying the number of contacts and particles on the support with the respective area losses \((A_{\text{base}}\) or \(A_{\text{contact}}\)), the simulation accounts for the total area loss. This is converted to a relative area loss by using the total particle surface area, calculated from the number of particles \((N_{\text{total}})\) and the surface area per particle \((A_{\text{surface}})\) and the equation:

\[
\frac{N_{\text{total}} \times A_{\text{surface}} - (N_{\text{contact}} \times A_{\text{contact}} + N_{\text{base}} \times A_{\text{base}})}{N_{\text{total}} \times A_{\text{surface}}}
\]

Thus, the result of the simulation is the relative surface area \((A_{\text{rel}})\) of the nanoparticles of a specific size at the given coverage. This can be multiplied by any measure of surface area (such as CO strip charge) to give an estimate of the expected result, accounting for particle overlap. Specifically, one could calculate the expected CO strip charge from the surface area \(A_{\text{surface}}\) and multiply it by \(A_{\text{rel}}\) to obtain the CO strip charge that would be expected from nanoparticles of the size and coverage that was simulated.

To acquire a reasonable estimate for the loss \(A_{\text{base}}\), the value was fitted such that the resulting CO strip charge agreed with the measured CO strip charges at coverages below 100 ng cm\(^{-2}\), where this loss dominates the area loss due to very few particle-particle contacts. Likewise, an estimate for \(A_{\text{contact}}\) was found by fitting to CO strip charges at coverages above 500 ng cm\(^{-2}\), where this loss effect dominates. The resulting simulation can be seen in Figure S2.

### 2 Additional Experimental Results

Figure S2 shows the integrated charge of CO-strip peaks for the different samples as a function of the loading. The left plot in S2 gives an overview of mass selected particles with within the loading range up to 5000 ng cm\(^{-2}\). The inset displays a smaller range of points, which is used for the linear fit, since the particle-particle overlap is negligible at these low coverages. Evidently, the trend is quite linear up to 1000 ng cm\(^{-2}\), and at 5000 ng cm\(^{-2}\) the deviation from linearity is moderate. A simulation of nanoparticle overlap was performed on the mass-selected nanoparticles with small raster pattern (blue points): As shown in the left Figure, the deviation from linearity is essentially captured by the model and ascribed to particle-particle overlap. A spherical approximation (assuming \(\sigma_{\text{CO,Pt}} = 420 \mu\text{C cm}^{-2}\)) is co-plotted. In general all points are below this trend line, attributable to 420 \(\mu\text{C cm}^{-2}\) overestimating the actual coverage of the adsorbed CO adlayer under experimental conditions as well as loss of ECSA due to overlap. Note the three samples with larger raster patterns (green) display a larger integrated charge than their counterparts (blue), consistent with the higher dispersion leading to less overlap. Since the commercial Pt/C (red points) don’t have a single well-defined size but rather a distribution, these points are not directly comparable with the mass-selected nanoparticles (blue and green) nor is the spherical approximation or the simulation expected to match. The right plot in S2 shows the full range of loadings up to \(10^5\) ng cm\(^{-2}\): At these high loadings, the dispersion of the commercial Pt/C most likely varies significantly in between samples, owing to the high concentration of the dropcasted ink creating a non-uniform film. The general strip-charge observed is, however, generally higher than for mass-selected particles of
similar loading. This is most likely due to the dispersion on high surface area carbon-substrate and that the average Pt crystallite size of Pt/C is smaller and thus has higher surface/mass-ratio.

**Figure S2**: Integrated CO-strip charge vs. loading deposited by cluster source or via dropcasting. Blue and green dots are 3.8 nm nanoparticles (small and large raster pattern, respectively) deposited with the cluster source whereas red dots denote the dropcasted samples of commercially available Pt/C.

**Figure S3**: Mass activity of all samples at a fixed geometric current density (10 mA cm\(^{-2}\)) vs. the measured overpotential. CVs were recorded in H\(_2\)-saturated 0.5 M H\(_2\)SO\(_4\) with a rotation rate of \(\omega=1600\) rpm and are post-corrected for 100% of the Ohmic drop as measured by EIS. A potential scan rate of \(v=50\) mV s\(^{-1}\) was used for all samples except for the two highest loadings (50000 and 100000 ng cm\(^{-2}\)) in which case 10 mV s\(^{-1}\) was used to minimize the influence of double layer charging current arising from the relative high roughness. Blue and green denotes 3.8 nm Pt nanoparticles deposited with the cluster source with small and large raster patterns respectively and red denotes commercially available Pt/C catalyst. All error bars are within the size of markers.
Figure S4: Comparison of mass-normalized activities for two different samples made of the same catalyst (i.e., 3.8 nm mass-selected Pt nanoparticles). The higher loading sample leads to a drastically lower estimate of $j_{\text{mass}}$ compared to the lowest loading sample due to mass transport limitations, illustrating the common pitfall of comparing with “reference” measurements. CVs were recorded in H$_2$-saturated 0.5 M H$_2$SO$_4$ with a rotation of $\omega=1600$ rpm and are post-corrected for 100% of the Ohmic drop as measured by EIS. A potential scan rate of $\nu$=50 mV s$^{-1}$ was used. Cathodic sweep shown for both samples, hence the negligible shift from (0,0).

Figure S5: CVs of ultra-low loadings of 3.8 nm Pt NPs showing hysteresis on the HER branch. Arrows indicate direction of scan, showing that the return (anodic) scan is notably less active than the forward scan (cathodic). CVs were recorded with a potential scan rate of $\nu$=50 mV s$^{-1}$ in H$_2$-saturated 0.5 M H$_2$SO$_4$ with a rotation of $\omega=1600$ rpm and are post-corrected for 100% of the Ohmic drop as measured by EIS. Note that here the current density is normalized by the disk area and thus underestimates the real current density on the raster pattern area on which the nanoparticles are dispersed.
### Table 6: Overview of loading values and other selected metrics for all the samples studied

Blue and green sections pertain to the 3.8 nm Pt nanoparticle samples deposited with small and large raster pattern, respectively, using the cluster source w. time of flight mass filter. The red section pertains to drop casted samples of commercial Pt/C.

| Loading [ng cm\(^{-2}\)] | TOF at \(\eta = 15\) mV [\(\#H_2\) site\(^{-1}\) s\(^{-1}\)] | CO-strip charge [C] | \(\eta\) [mV] | mass activity [A mg\(^{-1}\)] | TOF at 10 mA cm\(^{-2}\) [\(\#H_2\) site\(^{-1}\) s\(^{-1}\)] |
|---------------------------|---------------------------------|-------------------|----------|-----------------|----------------------------------|
| **small raster pattern**  |                                 |                   |          |                 |                                  |
| 13±1                      | 3.1E+02                         | 3.0E-07           | 133      | 7.6E+02         | 6.6E+03                          |
| 19±1                      | 2.6E+02                         | 4.6E-07           | 115      | 5.2E+02         | 4.2E+03                          |
| 50±3                      | 1.1E+02                         | 1.4E-06           | 85       | 2.1E+02         | 1.4E+03                          |
| 100±5                     | 7.9E+01                         | 2.6E-06           | 61       | 1.0E+02         | 7.5E+02                          |
| 17±1                      | 2.4E+02                         | 4.2E-07           | 120      | 5.9E+02         | 4.6E+03                          |
| 50±3                      | 9.8E+01                         | 1.6E-06           | 83       | 2.0E+02         | 1.2E+03                          |
| 100±5                     | 7.3E+01                         | 3.1E-06           | 54       | 1.0E+02         | 6.3E+02                          |
| 200±10                    | 4.8E+01                         | 6.7E-06           | 41       | 5.0E+01         | 3.0E+02                          |
| 200±10                    | 5.8E+01                         | 5.0E-06           | 48       | 5.1E+01         | 3.9E+02                          |
| 500±25                    | 2.8E+01                         | 1.6E-05           | 35       | 2.0E+01         | 1.2E+02                          |
| 500±25                    | 3.6E+01                         | 1.5E-05           | 34       | 2.0E+01         | 1.3E+02                          |
| 1000±50                   | 2.2E+01                         | 2.8E-05           | 29       | 1.0E+01         | 7.1E+01                          |
| 5000±250                  | 9.0E+00                         | 1.1E-04           | 20       | 2.0E+00         | 1.8E+01                          |
| **large raster pattern**  |                                 |                   |          |                 |                                  |
| 565±28                    | 4.7E+01                         | 1.9E-05           | 24       | 1.8E+01         | 1.0E+02                          |
| 1000±50                   | 2.4E+01                         | 4.5E-05           | 21       | 1.0E+01         | 4.4E+01                          |
| 5000±250                  | 1.3E+01                         | 1.5E-04           | 16       | 2.0E+00         | 1.3E+01                          |
| **Commercial Pt/C**       |                                 |                   |          |                 |                                  |
| 500±34                    | 4.0E+01                         | 1.5E-05           | 30       | 2.0E+01         | 1.3E+02                          |
| 1000±67                   | 1.7E+01                         | 3.6E-05           | 30       | 1.0E+01         | 5.5E+01                          |
| 5000±276                  | 5.0E+00                         | 2.2E-04           | 21       | 2.0E+00         | 8.8E+00                          |
| 50000±2875                | 3.0E-01                         | 2.8E-03           | 21       | 2.0E-01         | 6.9E-01                          |
| 100000±5150               | 4.0E-01                         | 3.3E-03           | 18       | 1.0E-01         | 6.0E-01                          |
3 Characterization

3.1 Ion Scattering Spectroscopy (ISS)

Ion scattering spectroscopy is a surface sensitive technique capable of detecting ppm levels of surface species. An ion beam of inert gas is accelerated towards a surface and the backscattered ions are detected at a known angle; giving information of outermost atomic layers of the sample\(^8\). This technique was employed before and after deposition of Pt nanoparticles to ensure a clean glassy carbon surface as well as a successful deposition of Pt. Figure S7 shows representative spectra for all the different loadings made using the cluster source and the inset shows ISS of the clean glassy carbon surface. The broad peak at low energy (inset) stems from secondary ions ripped of the surface. Due to the extreme sensitivity of this technique, trace amounts of either inherent or atmospheric oxygen is detected as well as miniscule amounts of argon still present on the surface after sputter cleaning. Finally, the Pt signal is seen to scale with the loading (main plot).

\[\text{Figure S7: Ion scattering spectroscopy of selected samples after deposition of mass selected Pt nanoparticles. The ion beam used was 1 keV He}^+\text{ and the scattering angle was 146.7}^\circ.\text{ The inset shows a representative spectrum of a clean glassy carbon electrode prior to the deposition of nanoparticles, also represented by the red curve in the main plot. Larger Pt loading causes a larger fraction of the incident He}^+\text{ ion beam to scatter from the surface Pt atoms, confirming the presence of Pt on the surface of the electrode.}\]
3.2 STEM of commercial Pt/C catalyst

![STEM images](image)

**Figure S8**: 300 kV STEM images of the commercially available catalyst (HiSPEC 9100). The images display the bright platinum nanoparticles on a non-visible carbon support.

4 Definitions & Metrics

**Turnover frequency** (TOF): number of $\text{H}_2$ molecules consumed (HOR) or evolved (HER) per catalytically active site per unit time:

$$\text{TOF} = \frac{\# \text{H}_2}{\text{site} \times \text{time}} = \frac{i/q_{\text{HOR/HER}}}{Q_{\text{CO-strip}}/q_{\text{CO-strip}}} = \frac{i}{Q_{\text{CO-strip}}}$$

where $i$ is the HOR/HER current and $Q_{\text{CO-strip}}$ is the integrate charge found from a CO-strip experiment. The charge transferred during each HOR/HER and CO-strip reaction, $q_{\text{HOR/HER}}$ and $q_{\text{CO-strip}}$ respectively, are both $2e^-$ and thus cancel out.

**Specific activity**: Current normalized by ECSA.

$$j_{\text{ECSA}} = \frac{i}{A_{\text{Pt}}} = \frac{i}{Q_{\text{CO-strip}}/\sigma_{\text{CO-strip}}}$$

Using this relation, $j_{\text{ECSA}}$ from the floating electrode$^9$ and $\text{H}_2$-pump techniques$^{10}$ was converted to TOF for Figure 2B in the main text using $\sigma_{\text{CO-strip}} = 420 \ \mu\text{C cm}^{-2}\text{Pt}$. 

**Mass activity**: Current normalized by amount (mass, $M_{\text{Pt}}$) of catalyst on sample

$$j_{\text{mass}} = \frac{i}{M_{\text{Pt}}}$$
**Geometric current density:** Current normalized by geometric area of sample ($A_{geo}$):

$$j_{geo} = \frac{i}{A_{geo}}$$

The samples displaying hysteresis (and hence investigated with the simulation) are deposited with a raster pattern smaller than the GCE disk and loadings below 5000 ng cm$^{-2}$ even have sub-monolayer coverage within this pattern. Thus, the disk area is not a reasonable estimate of $A_{geo}$. The latter, however, can be estimated from the HOR current measured at a high overpotential (i.e., 0.2 V) using the following relationship:

$$A_{geo} = \frac{i_{0.2V}}{j_{l,a}}$$

where $j_{l,a}$ is the limiting anodic current density. This method provides a reliable estimate, since at very anodic overpotentials the HOR reaction is completely limited by $H_2$ transport and the measured current is proportional to $A_{geo}$. The limiting anodic current density is calculated from the mass transport coefficient for $H_2$, $k_{d,H_2}$, and the bulk concentration of $H_2$:

$$j_{l,a} = 2Fk_{d,H_2}[H_2]^{\alpha}$$

For a RDE setup, $k_{d,H_2}$ is calculated using the Levich equation$^{11}$:

$$k_{d,H_2} = \frac{D_{H_2}}{\delta_{H_2}} = 0.62D_{H_2}^{2/3}v_k^{-1/6}\omega^{1/2}$$

where $D_{H_2}$ is the diffusion coefficient of $H_2$ (in m$^2$·s$^{-1}$), $\delta_{H_2}$ is the length of the diffusion layer for $H_2$ (in m), $v_k$ is the kinematic viscosity of the solvent (in m$^2$·s$^{-1}$), and $\omega$ is the rotation rate (in rad·s$^{-1}$). The high accuracy of the Levich equation to estimate $j_{l,a}$ in RDE measurements has been reported elsewhere$^{12,13}$.

5 Numerical Model of the Hysteresis in the CVs of HER

5.1 Governing equations

The present model accounts for the change in the surface concentrations of $H_2$ and $H^+$ with time due to electrochemical reaction and mass transport. Since the net flux of species diffusing to or from the interface is proportional to $A_{geo}$, the model simulates the geometric current ($j_{geo}$, in A·m$^{-2}$) for a given sample in a cyclic voltammetry (CV) experiment. The HOR/HER kinetics are described by using the Butler-Volmer equation:

$$j_{geo} = nFk^0_{geo} \left( e^{\beta F(E-E^0_{eq})/RT[H_2]} - e^{(\beta-1)F(E-E^0_{eq})/RT[H^+]} \right)$$

where $n$ is the total number of transferred electrons (for HOR/HER, $n = 2$), $F$ is the Faraday constant (in s·A·mol$^{-1}$), $k^0_{geo}$ is the standard rate constant per geometric area (in m·s$^{-1}$), $\beta$ is the symmetry factor of the rate-determining step, $E$ and $E^0_{eq}$ are the electrode potential and the standard equilibrium potential, respectively (in V), $R$ is the standard gas constant (in J·K$^{-1}$·mol$^{-1}$), $T$ is the temperature (in K), and finally $[H_2]$ and $[H^+]$ are the surface concentrations of hydrogen molecules and protons, respectively (in mol·m$^{-3}$).
The relation between $j_{geo}$ and the change in the surface concentrations of $H_2$ and $H^+$ due to electrochemical reaction (i.e., $d[H_2]^{\text{reac}}/dt$ and $d[H^+]^{\text{reac}}/dt$, respectively) is given by Faraday's law of electrolysis:

$$j_{geo} = -h_{H_2} 2F \frac{d[H_2]^{\text{reac}}}{dt} = h_{H^+} F \frac{d[H^+]^{\text{reac}}}{dt}$$

where $h_{H_2}$ and $h_{H^+}$ are the characteristic lengths for $H_2$ and $H^+$, respectively (in m, see below). The change in surface concentrations of $H_2$ and $H^+$ due to mass transport (i.e., $d[H_2]^{\text{diff}}/dt$ and $d[H^+]^{\text{diff}}/dt$, respectively) is given by the total fluxes of $H_2$ and $H^+$ along the diffusion layer:

$$\frac{d[H_2]}{dt} = \frac{j_{H_2}}{h_{H_2}} = -\frac{k_{d,H_2}}{h_{H_2}} ([H_2] - [H_2]^{\infty})$$

$$\frac{d[H^+]}{dt} = \frac{j_{H^+}}{h_{H^+}} = -\frac{k_{d,H^+}}{h_{H^+}} ([H^+] - [H^+]^{\infty})$$

where $j_{H_2}$ and $j_{H^+}$ are the total fluxes of $H_2$ and $H^+$ (in mol·s$^{-1}$·m$^{-2}$), respectively, $k_{d,H_2}$ and $k_{d,H^+}$ are the mass transport coefficients for $H_2$ and $H^+$ (in m·s$^{-1}$), respectively, and $[H_2]^{\infty}$ and $[H^+]^{\infty}$ are the bulk concentrations of $H_2$ and $H^+$, respectively. The mass transport coefficients can be obtained from the Levich equation as shown in the previous section.

The total change in the surface concentrations of $H_2$ and $H^+$ due to electrochemical reaction and mass transport (i.e., $d[H_2]/dt = d[H_2]^{\text{reac}}/dt + d[H_2]^{\text{diff}}/dt$ and $d[H^+]/dt = d[H^+]^{\text{reac}}/dt + d[H^+]^{\text{diff}}/dt$) is given by the following governing equations:

$$\frac{d[H_2]}{dt} = \frac{1}{h_{H_2}} [\frac{j_{geo}}{2F} - \frac{k_{d,H_2}}{h_{H_2}} ([H_2] - [H_2]^{\infty})]$$

$$\frac{d[H^+]}{dt} = \frac{1}{h_{H^+}} [\frac{j_{geo}}{F} - \frac{k_{d,H^+}}{h_{H^+}} ([H^+] - [H^+]^{\infty})]$$

Our model numerically solves the system of coupled differential equations above using a Python code, with the following initial conditions:

$$[H_2]_{t=0} = [H_2]^{\infty}$$

$$[H^+]_{t=0} = [H^+]^{\infty}$$

$$E_{t=0} = 0$$

where $[H_2]_{t=0}$, $[H^+]_{t=0}$ and $E_{t=0}$ are the values of the surface concentrations of $H_2$ and $H^+$ and the electrode potential at $t = 0$. Then, a cathodic-going potential sweep to $E = E_{\text{switch}}$ followed by an anodic-going sweep from $E = E_{\text{switch}}$ back to $E = 0$ is applied to simulate the CV experiment:

$$0 < t \leq t_{\text{switch}}: \quad E(t) = -v_{\text{scan}} t$$

$$t > t_{\text{switch}}: \quad E(t) = -v_{\text{scan}} t + v_{\text{scan}} (t - t_{\text{switch}})$$

where $v_{\text{scan}}$ is the scan rate (in V·s$^{-1}$) and $t_{\text{switch}} = E_{\text{switch}}/v_{\text{scan}}$.

In practice, $h_i$ only affects the degree of hysteresis of the simulated polarization curves, which originates from the finite rate of mass transport of $H_2$ and $H^+$. Indeed, when a physical system governed by diffusive transport of species $i$ is disturbed from an initial state of equilibrium by a sudden change in boundary conditions (e.g., change of $E$), it takes a finite amount of time $\tau_{\text{dif},i}$ for
the system to effectively reach a new equilibrium state. In planar diffusion, the most common approximation of the critical time $\tau_{dif,i}$, which is also known as characteristic time scale for diffusion, is given by:

$$\tau_{dif,i} = \frac{\delta_i^2}{6D_i}$$

An advantage of this simple model is that, by choosing the appropriate values of $h_i$, it accounts for the critical time it takes for the diffusion layers of $H_2$ and $H^+$ to equilibrate each time $E$ changes without computing their transient solutions (i.e., without having to numerically solve the diffusion equations for $H_2$ and $H^+$ along their corresponding diffusion layers) and, therefore, with an almost negligible computational cost. In the present model, we chose $h_i = \delta_i/6$, so that:

$$\frac{k_{d,i}}{h_i} = \frac{1}{\tau_{dif,i}}$$

### 5.2 Determination of Rate Constant

The accurate determination of the intrinsic rate constant is not possible, as mass transport still limits our determination of the intrinsic activity of acidic HOR/HER on Pt, even for the lowest loading samples. However, it is possible to determine a lower bound for the intrinsic rate constant by fitting the slope of the micropolarization region (i.e., from -10 to 10 mV) using the following relations:

$$j_{geo} = \frac{j_{0,geo}F}{RT} \eta$$

$$j_{0,geo} = 2Fk_{geo}^0(c_R^\infty)^{1-\beta}(c_O^\infty)^\beta$$

For the case of the lowest loading sample (i.e., 13 ng·cm$^{-2}$, roughness factor = 0.015), the apparent exchange current density at room temperature is $j_{0,geo} \approx 2$ mA·cm$^{-2}$. Normalizing to the active area, the lower bound for $j_{0,ECSA}$ at room temperature determined in the present study is $j_{0,ECSA} \approx 140$ mA·cm$^{-2}$, which is close to the value of 135 mA·cm$^{-2}$ determined by H$_2$-pump experiments at 313 K using also the equation above, and higher than their extrapolated value to 293 K of 75 mA·cm$^{-2}$.

The exchange current density determined in the present study corresponds to an apparent rate constant of $k_{geo}^0 \approx 1.5\cdot10^{-2}$ m·s$^{-1}$ ($k_{ECSA}^0 \approx 1$ m·s$^{-1}$).

### 5.3 Benchmark

In order to check the quality of the model, we have benchmarked it against the RDE measurements by Zheng et al.$^{13}$. In this study, the authors reported the polarization curves for HOR/HER on a full-sized Pt disk in 0.1M HClO$_4$ at different rotation rates, ranging from 100 to 3600 rpm. The degree of hysteresis increases as the rotation rate is decreased. As shown in Figure S9, the agreement between the simulated and the experimental polarization curves is excellent, even in the degree of hysteresis. The small differences in the absolute values of the currents are due to uncertainties in the values used for $[H_2]^\infty$, $v_{kin}$, $D_{H_2}$ and $D_{H^+}$, as no data for 0.1M HClO$_4$ is available.
Figure S9. (A) HOR/HER polarization curves (iR-corrected) at different rotation speeds on a polycrystalline Pt disk in H₂-saturated 0.1 M HClO₄ at a scanning rate of 10 mV s⁻¹ adapted from 15. Dashed grey lines are the concentration overpotential curves at different rotation speeds. (B) Simulated HOR/HER polarization curves at different rotation speeds using the time-dependent model described in this section. The parameters used in the model are reported in Table S10.

Table S10. Parameters used in the numerical simulations. [H⁺]₀ is calculated from the bulk pH. For [H₂]₀, D_H₂ and v_kin we chose the values reported by Mello et al. 15 and Markovic et al. 16 for 0.5 M H₂SO₄ and assume that their values in 0.1 M HClO₄ are very similar, as no data for 0.1 M HClO₄ is available. For D_H⁺ we chose the values reported for pure water and assume that their values under acidic conditions are very similar, as no data for H₂SO₄ nor HClO₄ is available.

| Parameter                        | Symbol | Full-sized Pt disk, 0.1 M HClO₄, Zheng et al. | Pt nanoparticles, 0.5 M H₂SO₄, this work |
|----------------------------------|--------|-----------------------------------------------|------------------------------------------|
| Temperature                      | T      | 293 K                                          | 298 K                                    |
| Scan rate                        | v_scan | 10 mV s⁻¹                                      | 50 mV s⁻¹                                 |
| Symmetry factor                  | α      | 0.5                                            | 0.5                                      |
| Rate constant                    | k₀     | 1.5·10⁻² m s⁻¹                                 | 1.5·10⁻² m s⁻¹                           |
| Bulk concentration of H₂         | [H₂]₀  | 0.59 mmol L⁻¹                                  | 0.59 mmol L⁻¹                            |
| Bulk concentration of H⁺         | [H⁺]₀  | 100 mmol L⁻¹                                   | 501 mmol L⁻¹                             |
| Kinematic viscosity of the solvent | v_kin | 1.07·10⁻⁶ m² s⁻¹                               | 1.07·10⁻⁶ m² s⁻¹                        |
| Rotation rate                    | ω_rot | 100—3600 rpm                                  | 1600 rpm                                 |
| Diffusion coefficient for H₂     | D_H₂  | 3.70·10⁻⁹ m² s⁻¹                               | 3.70·10⁻⁹ m² s⁻¹                        |
| Diffusion coefficient for H⁺     | D_H⁺  | 9.31·10⁻⁹ m² s⁻¹                               | 9.31·10⁻⁹ m² s⁻¹                        |
5.4 Parametric Study

Figures S11 B-D show the effect of the scan rate, the rotation rate, and the diffusion coefficients of \( H_2 \) and \( H^+ \) on the simulated polarization curves for HER. The hysteresis is more pronounced if the scan rate is increased, if the rotation rate is slowed, or if the diffusion coefficients decrease. Indeed, when a system is governed by diffusion, the degree of hysteresis on the CV depends on the relative values between the rate of mass transport—in this case determined by the RDE rotation rate and the diffusion coefficients—and the scan rate: if the former is very fast compared to the latter, the degree of hysteresis is negligible, and vice versa.

\[ D_i = k[H_2]^{-b}D_i^{bulk} \]

where \( b \) and \( k \) are constant parameters. The values these parameters are obtained as
where \([H_2]^{max}\) is the maximum \([H_2]\) reached at the lowest potential (i.e., when \(E = E_{\text{switch}}\)) and \(a\) is the constant scaling factor that was used in the original model. In this way, \(D_i\) decreases from \(D_i^{\text{bulk}}\) to \(aD_i^{\text{bulk}}\) in a smooth way when scanning to more negative potentials instead of having the down-scaled \(aD_i\) artificially imposed from the onset (see Figure S12 B). The value of \([H_2]^{max}\) has been calculated from the concentration overpotential curve, as shown in Section S6.

![Figure S12](image.png)

Figure S12. (A) Simulated polarization curves (solid lines) using a power law model for the variation of diffusion coefficients with \([H_2]\). The concentration overpotential curves for bulk diffusion coefficients is shown in black dashed line. (B) \(D_i\) relative to \(D_i^{\text{bulk}}\) as a function of \([H_2]\) for the different samples (same legend as left plot).

| Loading (ng·cm\(^{-2}\)) | \(E_{\text{switch}}\) (V) | \(a\) | \([H_2]^{max}\) (mmol·L\(^{-1}\)) |
|--------------------------|-----------------|------|---------------------|
| 13                       | -0.23           | 0.01 | 464                |
| 48                       | -0.21           | 0.03 | 464                |
| 100                      | -0.07           | 0.1  | 106                |
| 498                      | -0.045          | 0.4  | 19                 |
| 5000                     | -0.03           | 1    | 6                  |

Table S13. Parameters used in the numerical simulations for 5 selected samples.

6 On the H\(_2\) Oversaturation

Due to the facile kinetics of HER on Pt at low pH values, the concentration of \(H^+\) species at the surface decreases causing diffusion in order to maintain the balance of consumption and delivery of that species. At the same time, \(H_2\) molecules evolve at a faster rate than the mass transport can take it away, resulting in \(H_2\) oversaturation. This phenomenon has previously been reported for RDE measurements at \(j_{geo} > 2\) mA cm\(^{-2}\).\(^{12,13,17}\)
In this section, we show that $H_2$ oversaturation at the interface can be 3 orders of magnitude higher than the saturation concentration at room temperature and pressure (i.e., 0.59 mmol L$^{-1}$) at very negative overpotentials. Moreover, we show that the concentration of $H_2$ at the interface depends not only on the electrode potential, but also on the pH (i.e., $[H^+]^\infty$) and the relative magnitudes of the mass transport coefficients of $H_2$ and $H^+$.

We begin by considering HOR/HER under diffusion control in the limiting case of infinitely slow scan rate (i.e., steady-state). Such a process is called a Nernstian reaction and the relation between the diffusion limited current $j_d$ and the overpotential $\eta$ is given by the concentration overpotential curve (Figure S14 A):

$$j_d = \frac{1 - e^{-2F\eta/RT}}{j_{l,a} - j_{l,c}}$$

where $j_{l,a}$ and $j_{l,c}$ are the anodic and cathodic limiting currents, respectively. $j_d$ can also be expressed as a function of the concentration gradients along the diffusion layers:

$$j_d = 2Fk_d[H_2]^\infty([H_2]^\infty - [H_2]) = -Fk_d[H^+][H^+]^\infty - [H^+]^\infty$$

The anodic and cathodic limiting currents are reached when $[H_2]$ or $[H^+]$ become zero, respectively:

$$j_{l,a} = 2Fk_d[H_2]^\infty$$

$$j_{l,c} = -Fk_d[H^+]^\infty$$

Combining the previous equations, the following relations are obtained (Figures S14 B and C):

$$[H_2] = [H_2]^\infty \left(1 - \frac{j_d}{j_{l,a}}\right)$$

$$[H^+] = [H^+]^\infty \left(1 - \frac{j_d}{j_{l,c}}\right)$$

Thus, for HOR/HER under diffusion control and at steady state, $[H_2]$ and $[H^+]$ depend on the electrode potential, the mass transfer coefficients, and the bulk concentrations $[H_2]^\infty$ and $[H^+]^\infty$.

Particularly, a large $H_2$ oversaturation is predicted at very cathodic potentials when $[H^+]^\infty$ is high. Figure S14 C shows that, for HOR/HER in 0.5 M H$_2$SO$_4$ and using a RDE operating at 1600 rpm, $[H_2]$ increases from a saturation value of $[H_2]^\infty = 0.59$ mmol L$^{-1}$ at the equilibrium potential to $[H_2] = 28$ mmol L$^{-1}$ at $-0.05$ V, $[H_2] = 350$ mmol L$^{-1}$ at $-0.1$ V, and $[H_2] > 450$ mmol L$^{-1}$ at $-0.15$ V or lower. This increase of 3 orders of magnitude is a consequence of the huge concentration of $H^+$ that exist in 0.5 M H$_2$SO$_4$ and the fact that the transport coefficients of $H_2$ and $H^+$ are similar, as shown in the scheme of the concentration profiles along the diffusion layers at three different potentials in Figures S14 D-E. Also, note that the $[H_2]$ values predicted by the concentration overpotential curve corresponds to the average surface concentration of $H_2$ per geometric area. For low loading samples, where the ECSA might be much lower than $A_{geo}$, the local concentration of $H_2$ at the actual interfaces can be even higher.
Although the previous results correspond to the limit of infinitely slow scan rate (i.e., steady-state), the \([H_2]\) values predicted by our model when using a finite scan rate show practically the same \([H_2]\) at a given potential. These results are shown in Figure S15, where it can be seen that the predicted \([H_2]\) for a very slow (5 mV s\(^{-1}\)) and a very fast (100 mV s\(^{-1}\)) scan rates are equal. Therefore, the \(H_2\) oversaturation in the HER branch is not just an exclusive peculiarity of Nernstian reactions, and also occurs in more realistic experiments with hysteresis.

Figure S15. Simulated polarization curves for HOR/HER reaction in 0.5 M H\(_2\)SO\(_4\) and using a RDE operating at 1600 rpm and several scan rates (A). Surface concentration of \(H_2\) predicted by the model as a function of the electrode potential (B) and simulated time (C). Dashed black lines corresponds to the limit of infinitely slow scan rate (i.e., Nernstian reaction).
Finally, the $[H_2]$ vs. time plots for the simulations of the samples used in the present study are not affected by the scaling of the diffusion coefficients. The reason is that $[H_2]$ depends on the ratio $D_{H_2}/D_{H^+}$, but if both coefficients are scaled by the same amount, then $[H_2]$ remains the same. Figure S16 shows $[H_2]$ as a function of time when using the scaling factors for the diffusion coefficients, while the corresponding plot for bulk diffusion coefficients is shown in the inset of Figure 3B in the main text.

![Figure S16](image_url)

**Figure S16.** The average surface concentration of $H_2$ as a function of time during the simulation where traces a, b, c, d, e correspond to simulations for 13, 48, 100, 498 and 5000 ng cm$^{-2}$, respectively.

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