Supplementary Information

Elucidation of adsorption processes at Pt(331) model

electrocatalysts in acidic aqueous media

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S1. Electrochemical cell

Figure S1 shows the design of the electrochemical cell used in this work. The electrolytes were saturated in the preconditioning compartment with Argon (5.0, Air Liquide, Germany) or oxygen (4.6, Air Liquide, Germany). During the measurements, the main compartment was continuously supplied with the same gas mixture. For the experiments, the hanging meniscus configuration was used (Figure S1B). As the reference electrode (RE) and counter electrode (CE), a mercury–mercurous sulfate (MMS) electrode and a Pt wire (GoodFellow) were used, respectively. The measured potentials were converted to the RHE scale. The preparation of the Pt(111) crystals and their characterization are described in detail elsewhere [1].

(A)



Figure S1. (A) Schematics of the electrochemical cell used for the preparation and characterization of Pt(111) and Pt(331) electrodes. Abbreviations: WE, RE, CE, and DE stand for working, reference, counter and "dummy" electrodes, respectively. (B) Hanging meniscus configuration used for the characterization of the bead electrodes.

S2. Equivalent electric circuit for the surface limited reversible adsorption.

According to the approach developed by Dolin, Ershler [2] and Randles [3], a general model of the electrode/electrolyte interface consists of at least three parts (Figure S2). The first part reflects the impedance of the electrolyte Z_{el} , which can often be approximated by an uncompensated resistance as: $Z_{el} = R_U$. The second part is related to the impedance due to electrochemical processes involving the interfacial charge transfer, Z_F . Particular equations describing Z_F depend on many factors, such as the mechanism and kinetics of the electrochemical reactions, or mass transport modes [4]. The third part is the impedance of the interface itself, Z_i . Its response is of capacitive nature described by a formula given as $Z_i = C'_{DL}^{-1}(j\omega)^{-\varphi}$, where C'_{DL} is the parameter, which is proportional to the double layer capacitance, C_{DL} , and $\varphi \leq 1$. When $\varphi = 1$, $C'_{DL} = C_{DL}$. The Dolin-Ershler-Randles approach assumes the total impedance, Z_{tot} : $Z_{tot} = Z_{el} + (Z_i^{-1} + Z_F^{-1})^{-1}$, which corresponds to a general equivalent circuit as shown in Figure S2. The parallel combination of Z_F and Z_i reflects the hypothesis that the current due to electrochemical processes can be considered as a "leakage" of the interfacial "capacitor".



Figure S2. A generalized physical model describing the electrode/electrolyte interface according to the Dolin-Ershler-Randles approximation.

In the studied electrode potential region, several adsorption/desorption processes can take place: adsorption of *H, *OH and *O from water. High concentration of HClO₄ allows neglecting contributions of diffusional mass transport.

When small *AC* probing signals are applied to a system where reversible single-stage surface limited adsorption occurs, the current due to adsorption, *i*, and the fractional coverage of the adsorbate, θ , oscillate around quasi-steady-state values. The linear part of the response assigned to the adsorption process can be written as [5,6,7,8]:

$$\Delta i = \left(\frac{\partial i}{\partial E}\right) \Delta E + \left(\frac{\partial i}{\partial \theta}\right) \Delta \theta \tag{1}$$

where Δ corresponds to parameters which oscillate during *AC* probing. If the current due to adsorption and the current of double layer charging are assumed to be additive, the solution of equation 1 leads to the classical model of reversible adsorption with interfacial impedance, *Z*, given by [4,5]:

$$Z(j\omega) = R_U + \left((j\omega)^{\varphi} C_{\rm DL}' + \frac{1}{R_{\rm ads} + (j\omega C_{\rm ads})^{-1}} \right)^{-1}$$
(2)

where ω is the angular frequency; $R_{ads} = -1/(\partial i/\partial E)$ is the adsorption resistance; $C_{ads} = -q_{ads}(\partial \theta/\partial E)$ is the adsorption capacitance; q_{ads} is the charge necessary to form an adsorbate layer, and *j* is the imaginary unit. The corresponding equivalent circuit is shown in Figure S3A. The adsorption model described by equation 2 does not show any continuous pathways for the *direct* current at $\omega \rightarrow 0$. This is in agreement with the fact that the *direct* current of the surface limited adsorption (like *H or *OH adsorption) at steady state is zero. This model, however, accepts a *direct* current to flow at non-steady state conditions, for example in a potentiodynamic scan, enabling the adsorption capacitance to charge. In classical impedance experiments, the ability to distinguish between contributions of the double layer and the adsorption capacitance C_a will depend on the R_{ads} . For a very fast adsorption, R_{ads} is small and the double layer response will effectively incorporate C_{ads} (Figure S3B). If two adsorption processes with significantly different time constants occur simultaneously, the interfacial impedance can be consequently described by the following equation:

$$Z(j\omega) = R_U + \left((j\omega)^{\varphi} C_{DL}' + \frac{1}{R_{ads,1} + (j\omega C_{ads,1})^{-1}} + \frac{1}{R_{ads,2} + (j\omega C_{ads,2})^{-1}} \right)^{-1}$$
(3)

where parameters $R_{ads,1}$ and $C_{ads,1}$, and, correspondingly, the parameters $R_{ads,2}$ and $C_{ads,2}$ correspond to the two different adsorption processes. This corresponds to the equivalent circuit shown in Figure S3C.



Figure S3. Possible physical models of the Pt(331)/electrolyte interface in 0.1M HClO₄. R_U – electrolyte resistance, Z_{dl} – impedance of the double layer, $C_{ads,i}$ – adsorption capacitances, $R_{ads,i}$ – adsorption resistances.

References

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