Bulk-Palladium and Palladium-on-Gold Electrocatalysts for the Oxidation of Hydrogen in Alkaline Electrolyte

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The commercial feasibility of alkaline-exchange membrane fuel cells and electrolyzers passes by the development of hydrogen oxidation and evolution reaction (HOR/HER) catalysts featuring an activity and/or cost advantage over platinum, which remains the most active metal for these processes. Among these alternatives, Pd appears as a promising candidate, since its price is typically 2–3 fold lower than that of Pt. With this motivation, the first section of this study displays our attempts at quantifying the kinetic parameters of the HOR/HER on bulk Pd in 0.1 M NaOH, which were prevented by the simultaneous absorption of hydrogen into bulk palladium. We succeeded at circumventing this issue by depositing Pd-adlayers on a polycrystalline Au-substrate by galvanic displacement of underpotentially-deposited Cu or by electrochemical plating of Pd. The resulting surfaces appear to consist of three-dimensional Pd-structures of an unknown thickness that we believe to scale with the palladium coverage, \( \theta \). This last parameter is inversely proportional to the HOR/HER-activity of the Pd-on-Au surfaces, in agreement with numerous theoretical and experimental studies in acid media that correlate this effect to the tensile strain induced by the Au-substrate on the Pd-lattice.

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Proton-exchange membrane fuel cells (PEMFCs) fueled with hydrogen stored at 700 bar can attain energy densities in excess of 200 Wh·kg\(^{-1}\) (on a PEMFC system basis), making them excellent candidates for the propulsion of environmentally-benign, full range (≥300 miles) vehicles. However, the actual commercialization of PEMFC powered cars has been deterred by the lack of a hydrogen infrastructure and the high cost of the PEMFC. In this last respect, a significant fraction of the system’s price is related to the costly platinum-based catalysts needed to catalyze the oxidation of hydrogen and the reduction of oxygen taking place at the FC anode and cathode, respectively. The kinetics of the oxygen reduction reaction (ORR) on Pt\(^{4}\) are \( \approx 7 \) orders of magnitude slower than those of the hydrogen oxidation reaction (HOR),\(^5\) in agreement with the HOR- and ORR\(^{−}\)-exchange-current density (\( i_0 \)) values of 4 ± 2·10\(^{−2}\) mA·cm\(^{−2}\) vs. 2.5·10\(^{−5}\) mA·cm\(^{−2}\) estimated by Neyerlin and coworkers (at 80°C and 100 kPa H\(_2\)/air partial pressure). As such, the Pt-loading at the PEMFC’s cathode (\( \approx 0.2–0.4 \) mg·cm\(^{−2}\)) is well above the \( \leq 0.05 \) mg·cm\(^{−2}\) required for the anodic HOR, and thus much research is being devoted to the development of more active and/or less expensive ORR catalysts.\(^6,10\) These include alloys of Pt with non-noble metals like Ni, Co or Cu (as well as their de-alloyed derivatives), and catalysts consisting of non-noble metal nanoparticles covered by one or a few monolayers of Pt (i.e., the so-called “core-shell” catalysts).

Alternatively, operating a fuel cell in alkaline environment allows for the use a wider variety of potentially inexpensive, noble-metal free ORR-catalysts. Among these, certain materials based on Fe-, Co- and/or Cu-N\(_4\) chelates (or equivalent non-noble metal salts combined with a nitrogen precursor) show the greatest potential,\(^11–13\) having demonstrated ORR-activities comparable to that of Pt and reasonable short-term durability. This potential cost advantage, along with the advent of hydroxide-exchange membranes and ionomers with promising ionic conductivities,\(^14,15\) has resulted in a surge of interest to develop alkaline membrane fuel cells (AMFCs). On the other hand, Shen and coworkers\(^16\) have recently shown that the oxidation of hydrogen on Pt in alkaline electrolyte is \( \approx 100\)-fold slower than in acid (projected \( i_0 \) of \( \approx 4 \) mA·cm\(^{−2}\) in H\(_2\)-saturated 0.1 M KOH at 80°C, vs. the 2.4 ± 0.4 mA·cm\(^{−2}\) measured in a PEM hydrogen pump in Ref. 5). Consequently, AMFCs would require Pt-loadings comparable to those used in PEMFC cathodes to compensate for the sluggish HOR-kinetics in alkaline electrolyte.

For this reason, more active and/or less expensive HOR-catalysts need to be developed for AMFCs. However, very few studies have dealt with the factors that control the kinetics of the HOR in alkaline medium. A number of works combining modeling and electrochemistry have suggested that intermediate hydrogen-metal bond energies result in improved hydrogen-oxidation/evolution kinetics\(^8,10,17–19\) in agreement with the so-called “Sabatier principle”. However, the binding energies and corresponding exchange current densities featured in those works were systematically estimated at a reference pH of 0, and thus do not account for the detrimental effect of the solution alkalinity on the reaction kinetics.\(^15–19\) Indeed, the implementation of this pH effect on the modeling of the electrochemical interface is only in its initial stage,\(^20,21\) but should prove crucial for unveiling the fundamental reasons for these differing behaviors in a near future. In the meantime, Strmcnik et al. have recently demonstrated a remarkable improvement of the HOR-kinetics on Pt in 0.1 M KOH following the addition of an oxophilic metal component,\(^22\) either as an alloy (e.g., Pd\(_{0.1}\)Ru\(_{0.9}\)) or through decoration of the Pt-surface with Ni(OH)\(_2\)-adislants.

Inspired by this work, some recent studies have further explored the kinetics of the HOR on Ir\(^{23}\) and Ru,\(^23,24\) which are typically more affordable than Pt\(^{25}\) but also 1–2 orders of magnitude less abundant.\(^26\) Alternatively, palladium mining resources are comparable to those for platinum,\(^26\) while typically remaining 2–3 fold less expensive than Pt\(^{25,27}\) Moreover, some of the modeling-based works discussed above\(^17–19\) have suggested that the HOR/HER exchange current density on Pd is close to that on Pt, rendering palladium a potential candidate for the catalysis of the HOR in alkaline medium. Despite this premise, we are not aware of any works having dealt with the electrochemistry of hydrogen on palladium in alkaline electrolyte. In an attempt to fill this void, we report here our efforts at quantifying the HOR-activity of polycrystalline Pd using rotating disc electrode (RDE) voltammetry in 0.1 M NaOH. As we will show in the following, quantification of the HOR-activity on bulk palladium is not possible due to the interference by the fast hydrogen adsorption reaction. Therefore, we have instead determined the HOR-activity of palladium (sub-)monolayers deposited onto a polycrystalline gold substrate. Interestingly, these palladium-on-gold surfaces display improved HOR-activities as their palladium coverage decreases; a behavior that we relate to a change in the strength of hydrogen-adsorption, in turn caused by the tensile strain on the Pd-lattice induced by the gold substrate.
Experimental

Chemicals and gases.—Electrolyte solutions were prepared from NaOH·H2O pellets (99.95% purity, TraceSELECT, Sigma Aldrich) or 96% H2SO4 (Ultrapur, Merck) diluted in ultrapure water (18.2 MΩ·cm, Millipore). The use of high-purity NaOH pellets instead of the KOH (99.99%, Emsure, Merck) used in our previous work was motivated by a recent report according to which this NaOH has less 3d-transition metal impurities, which would contaminate the Pt surface at low potentials. Furthermore, H2SO4-based electrolytes containing given concentrations of CuSO4·5 H2O (99.99% purity, Sigma Aldrich) or PbCl2 (99.999% purity, Sigma Aldrich) were also used. High purity argon (6.0-grade), hydrogen (6.0-grade) and CO (4.7-grade) were purchased from Westfalen AG (Münster, Germany).

Electrochemical setup.—The electrochemical measurements in acid and alkaline electrolytes were performed in a standard glass cell or a house-made polytetrafluoroethylene (PTFE) cell, respectively. The choice of PTFE as opposed to glass for the measurements in alkaline media was motivated by the detrimental effects of glass corrosion products on the HOR/HER-kinetics of Pt. The PTFE cell was embedded in a stainless steel jacket connected to a calibrated thermostat (Julabo Labortechnik GmbH, Seelbach, Germany) at 293 K, and it was closed with a four-necked glass cover which has no contact to electrolyte. The glass cell used with acid electrolytes also had four necks, and thus both setups consisted of similar working, reference and counter electrodes, along with a gas bubbler that allowed for gas blanketing above the surface of the electrolyte or direct bubbling through a fluorinated ethylene propylene (FEP) tube. The counter electrode was a Pt-wire (99.99%-4%, Advent, Oxford, England) embedded in a PTFE-stopper. The Ag/AgCl reference electrode consisted of a glass tube ended in a porous glass frit (Vycor 7930, Advanced Glass & Ceramics, Holden, MA) and filled with water saturated in AgCl (99.999%, Sigma Aldrich) and KCl (99.999%, Sigma Aldrich); its opposite end was covered with a plastic stopper with a silver wire embedded in it (Ametek) and immersed in this electrolyte. This reference electrode was kept in a separated glass holder filled with the electrolyte of choice and connected to the main electrolyte compartment through a Luggin capillary consisting of a FEP tube with an AFCBP1 bipotentiostat (Pine Research Instrumentation). Counter electrodes were a Pt-wire (99.99%, Advent, Oxford, England) or a house-made polytetrafluoroethylene (PTFE) cell, respectively. Finally, the clean working electrode was immersed under potential control in the electrolyte solution of choice (in the case of RRDEs, after mounting on a polyetheretherketone (PEEK) shaft (Pine Research Instrumentation)). More precisely, the measurements with PdPC and AuPC were systematically started in Ar-saturated 0.1 M H2SO4, recording voltammograms between 0.4–1.1 V RHE or 0.0–1.5 V RHE at 200 or 500 mV·s−1, respectively, until stable CVs were obtained.

Results and Discussion

Roughness factor and hydrogen-oxidation activity of polycrystalline palladium.—The HOR/HER-activity of a given catalyst is often assessed on the basis of the so-called exchange current density, , which corresponds to the current flowing at the electrode/solution interface at the equilibrium potential. Moreover, in order to provide a meaningful comparison between materials with different compositions, morphologies and degrees of dispersion (from model surfaces to carbon-supported nanoparticles), is typically normalized by the catalyst’s electrochemically active surface area (ECSA). Several different electrochemical methods can be applied to estimate this ECSA, with all of them relying on a number of assumptions that ultimately compromise their precision to different extents.

In the case of metal surfaces onto which hydrogen can adsorb at potentials positive of the H2-evolution onset, their ECSA can be derived from the charge related to this hydrogen underpotential deposition (Hupd) process. This approach is particularly applicable on Pt-based catalysts, for which the cyclic voltammograms (CVs) recorded in aqueous electrolytes feature a well-defined separation between the potentials corresponding to the formation and reduction of Pt(hydro)oxides (at > 0.55 V RHE) and the (at < 0.4 V RHE). The Pt-ECSA is then estimated by integrating the charge down to the HER-onset (≈0.05 V RHE) and dividing the resulting value by 210 μC·cm−2. This customary Pt-ECSA estimation approach is close to the 197 μC·cm−2 estimated by averaging the Pt-ECSA-charges calculated for low-index Pt single crystals (i.e. 240, 147 and 205 μC·cm−2 for Pt(111), Pt(110) and Pt(100), respectively). However, this normalization value remains highly arbitrary, since it is not possible to quantitatively determine the crystallographic composition of non-single crystalline Pt-surfaces, and it additionally relies on the false assumption that the Pt surface is fully covered with Pt-hydride at the HER-onset potential used as the lower integration boundary. On the other hand, the Hupd on the polycrystalline palladium (PdPC) that first attracted our interest is accompanied by the absorption of hydrogen into the metal lattice, which in turn prevents the evaluation of the ECSA using this approach. Alternatively, the Pd-ECSA can also be derived from the charge required to oxidize a (sub)monolayer of potentiostatically adsorbed carbon monoxide, using the so-called CO-stripping method. However, to use this approach one must know the surface CO-coverage and adsorption mode (i.e., linear vs. bridged), which in terms depend on the CO-deposition potential and the surface crystallographic
composition. Hara and coworkers\textsuperscript{35} performed CO-stripping experiments on Pd single crystals in 0.1 M H\textsubscript{2}SO\textsubscript{4} using a CO-dosing potential of 0.4 V\textsubscript{RHE} in order to avoid any interference from hydrogen absorption on the CO-adsorption process. The authors compared the measured CO-oxidation charges to those expected for the fully covered crystals (i.e., \( \approx 490, \approx 300 \) and \( \approx 430 \) \( \mu \)C \( \cdot \) cm\textsuperscript{-2} for Pd(111), Pd(110) and Pd(100), respectively) and estimated \( \theta_{\text{CO}} \)-values of 0.67, 1.1 and 0.75 for Pd(111), Pd(110) and Pd(100). Under the arbitrary assumption that Pd\textsubscript{EC} were to consist of a linear combination of these low index planes in equal proportions, these CO-stripping charges and \( \theta_{\text{CO}} \)-values could be averaged to yield an ECSA normalization charge of 330 \( \mu \)C \( \cdot \) cm\textsuperscript{-2}, with an implicit error of \( \pm 40\% \).

Finally, the electrochemical surface area can also be derived from the charge under the peak associated with the reduction of palladium (hydr)oxide on CVs recorded using positive inversion potentials (\( E_{\text{inv}} \)) of \( \geq 1.0 \) V\textsubscript{RHE}. Nevertheless, this approach is probably the most imprecise out of these three, since the definition of an integration baseline free of pseudo-capacitive contributions is highly ambiguous, and the stoichiometry of these (hydr)oxides changes with the potential. While several works\textsuperscript{36–38} have reported the dependency of this (hydr)oxide reduction charge with \( E_{\text{inv}} \) for CVs in acidic electrolytes (i.e., 0.5 M HClO\textsubscript{4} in Ref. 37, vs. 1 M H\textsubscript{2}SO\textsubscript{4} in Refs. 36 and 38), none of those studies specified whether those charges took into consideration the electrode's ECSA. The latter was only quantified by Chierchie and coworkers\textsuperscript{37} who estimated a roughness factor (RF) of 1.2 cm\textsuperscript{2}Pd \( \cdot \) cm\textsuperscript{-2geom} from capacitance measurements. Additionally, we are not aware of any work in the literature reporting the same sort of correlation in the alkaline electrolyte of interest to this study. Nevertheless, Burke and coworkers\textsuperscript{40} showed that the onset of palladium oxidation in this basic medium takes place at lower potentials than in acid, suggesting that for a given \( E_{\text{inv}} \)-value the Pd-oxidation/reduction charge could be larger in alkaline electrolyte than in acid.

In sight of these possibilities, our measurements started by recording CVs on a polycrystalline palladium (Pd\textsubscript{PC}) disc immersed in Ar-saturated 0.1 M H\textsubscript{2}SO\textsubscript{4} between 0.4 V\textsubscript{RHE} and \( \approx 0.85 \) V\textsubscript{RHE} and the oxide reduction currents in the negative-going scans become larger and peak at lower potentials as \( E_{\text{inv}} \) increases.

Next, we proceeded to estimate the ECSA of the Pd\textsubscript{PC}-surface by CO-stripping, dosing carbon monoxide in the 0.1 M H\textsubscript{2}SO\textsubscript{4} electrolyte at the 0.4 V\textsubscript{RHE} used in Ref. 35 for 10 minutes and then re-saturating it with argon for 30 minutes. Following the subtraction of the oxidation charge in the positive-going branch of the stable CV from that observed in the first scan (solid vs. dashed lines in Fig. 1b, respectively), the charge corresponding to the oxidation of CO was 654 \( \mu \)C \( \cdot \) cm\textsuperscript{-2}geom. Considering the conversion charge of \( \approx 330 \) \( \mu \)C \( \cdot \) cm\textsuperscript{-2} discussed above, this CO-stripping charge yields a Pd-roughness factor of \( \approx 2 \) cm\textsuperscript{2}Pd \( \cdot \) cm\textsuperscript{-2geom}, an RF-value unexpectedly high for a well-polished polycrystalline surface that is probably caused by the partial dissolution of Pd during the excursions to high potentials presented in Fig. 1a.\textsuperscript{41,42}

Having quantified the Pd\textsubscript{PC}-RF in acid medium, the same electrode was transferred to a solution of Ar-saturated 0.1 M NaOH, where we proceeded to record new CVs between \( \approx 0.4 \) and \( \approx 1.0–1.3 \) V\textsubscript{RHE}. The resulting voltammograms with different \( E_{\text{inv}} \) values appear plotted in Figure 2a, where Figure 1d shows a direct comparison between the individual CVs recorded in both electrolytes using an inversion potential of \( \approx 1.0 \) V\textsubscript{RHE}. Transferring the electrode from acid to alkaline medium resulted in an earlier onset of the Pd-(hydr)oxide formation on the CVs' positive-going scans (in good agreement with Ref. 40), along with a broader (hydr)oxide-reduction peak in the negative-going sweeps. Despite these differences, the overall charge integrated from the oxide reduction peaks did turn out to be virtually the same in both acid and alkaline media, as shown in Figure 1e, whereby the Pd-surface normalized charges increase linearly from \( \approx 170 \) to \( \approx 375 \) \( \mu \)C \( \cdot \) cm\textsuperscript{-2} when increasing \( E_{\text{inv}} \) from 1.0 to 1.3 V\textsubscript{RHE}. These values are in very good agreement with those reported in Ref. 37 and, while being less precise than those derived from lengthy CO-stripping measurements, they provided us with a fast means of quantifying the Pd-ECSA of the unstable model surfaces presented below.

Following the recording of these CVs between \( \approx 0.4 \) and 1.0–1.3 V\textsubscript{RHE} in 0.1 M NaOH, we proceeded to study the behavior of bulk palladium in the vicinity of the reversible hydrogen potential by opening the lower potential boundary to a value of \( \approx 0.1 \) V\textsubscript{RHE}. The resulting stable voltammogram appears plotted in Figure 2a, and is characterized by a lack of symmetry between the negative- and positive-going potential scans, in good agreement with previous CVs recorded on bulk\textsuperscript{43–45} and nano-sized\textsuperscript{46,47} Pd-structures. The reduction currents observed at potentials \( \leq 0.4 \) V\textsubscript{RHE} have been assigned to the simultaneous H\textsubscript{upd}-reaction on the Pd-surface and the absorption of hydrogen in the Pd-lattice, as formulated in Equations 1 and 2.
be magnified by the triggering of the $H_{upd}$-process and the subsequent evolution of $H_2$. These possibly cause the oxidation currents of $\approx 8 \, mA \cdot cm^{-2}_{geom}$ at $\approx 0.6 \, V_{RHE}$ observed in the first positive-going scan following potential excursions down to $-0.1 \, V_{RHE}$ (cf. dashed black line in Fig. 2b).

Besides the unexpectedly high current densities, a closer look at the micropolarization region in the vicinity of the reversible hydrogen potential (see Fig. 2c) unveils that continuous cathodic currents are observed on Pd at potentials below $\approx +0.1 \, V_{RHE}$ (whereby the RHE scale was calibrated in a separate measurement with a PtPC-ring), i.e., above the reversible potential for the HER. This clearly proves that this current must arise from the continuous absorption of hydrogen into the Pd bulk, which unfortunately makes it impossible to quantify the exchange current density for the HOR/HER on bulk-PdPC. In a recent study, Sheng and coworkers,\textsuperscript{21} attempted to circumvent this interference from H-absorption by directly immersing the PtPC-electrode at 0 \, V_{RHE} and immediately recording HOR/HER-polarization curves (first scans only) in the negative-going direction. Interestingly, their HER-$i_0$ value of $\approx 100 \, mA \cdot cm^{-2}_{geom}$ at 298 K is $\approx 2$-fold larger than the $\approx 60 \, mA \cdot cm^{-2}_{geom}$ at 313 K recently determined by our group\textsuperscript{37} for carbon-supported Pd-nanoparticles (2–4 nm in diameter). Whether this difference is due to a structure-sensitivity of the HOR/HER on Pd surfaces or it results from interference by some H-absorption is not yet known.

**Preparation of a palladium-on-gold surface by galvanic replacement of Cu upd**—Alternatively, the absorption of hydrogen into the Pd-lattice has been successfully circumvented by depositing thin Pd-overlayers onto non-absorbing substrates as Pt,\textsuperscript{48–50} Rh,\textsuperscript{49,50} and Au-single crystals\textsuperscript{52–55} as well as other materials.\textsuperscript{49,50} In the beginning of the 2000’s, the group of Radoslav Adžić developed a novel method for the preparation of such metal monolayers on foreign substrates, as mediated by the underpotential deposition and galvanic replacement of copper.\textsuperscript{56} In brief, the process typically starts with the aforesaid copper underpotential deposition (Cu upd) on the substrate of choice, which can consist of a well-defined surface (e.g., an Au(111) single crystal\textsuperscript{50,53} or, for practical FC-applications, of carbon-supported nanoparticles.\textsuperscript{54,55} This Cu-covered substrate is then transferred to a different solution containing the desired overlayer metal in its cationic form (e.g., Pd$^{2+}$); the latter then presumably place-exchanges with the adsorbed copper to yield an adlayer of monoatomic thickness, as schematized in Figure 3a.

Motivated by this possibility of suppressing the interference of H-absorption on our HOR/HER-measurements, we set to extend this methodology to the preparation of a Pd-monolayer on polycrystalline gold (AuPC), directly followed by the determination of the adlayer’s HOR/HER-activity in H$_2$-saturated 0.1 M NaOH. The choice of an AuPC-substrate was motivated by its poor catalytic behavior for the oxidation of hydrogen, well documented in the literature\textsuperscript{22,56} and further confirmed by our measurements (see below). Moreover, the polycrystalline surface consists of a combination of planar domains with different orientations, somehow analogous to the (100), (110) and (111) facets present on the carbon-supported nanoparticles that constitute the majority of FC-relevant catalysts.\textsuperscript{57–59} This particularity renders this surface somehow closer to this application than in the single crystal case. On the other hand, while Cu upd on well-defined gold single crystals has been abundantly discussed in the literature (e.g., on Au(111), Au(110) or stepped Au-crystals)\textsuperscript{50,52–55} fewer works have dealt with the deposition of copper on polycrystalline Au.\textsuperscript{53–55} Most importantly, to the best of our knowledge, none of the above-mentioned studies unambiguously clarified whether it is possible to reach a complete coverage of the AuPC-surface with underpotentially deposited copper. Therefore, prior to performing the galvanic replacement experiments, we decided to first study the underpotential deposition of copper on polycrystalline gold.

Our experiments started by potential-cycling the AuPC-disc immersed in argon-saturated 0.1 M H$_2$SO$_4$ between $\approx 0.0$ and $\approx 1.6 \, V_{RHE}$ until a stable voltammogram was obtained (see Experimental section for details). The latter is plotted in...
Filho and coworkers\textsuperscript{66} for the inversion potential of approx. 1.6 cm\(^2\) is remarkably larger than the figures reported in the literature (e.g., 0.0 and \(\approx 1.5–1.6\) V\(_{RHE}\) required to attain a well-developed, stable CV. Such excursions to high potentials reportedly result in significant gold-dissolution and re-deposition following the oxidation and reduction of the disc’s surface, respectively.\textsuperscript{66,67}

Having attained a stable AuPC-surface state and quantified its RF, we proceeded to transfer the electrode to a deaerated solution of 0.1 M H\(_2\)SO\(_4\) with \(\approx 1\) mM CuSO\(_4\), holding the potential at \(\approx 0.75\) V\(_{RHE}\) in order to prevent uncontrolled copper-deposition on its surface. The Cu upd Process was first studied by recording CVs between this positive potential limit and different negative inversion potentials of \(\approx 0.31\), \(\approx 0.29\), \(\approx 0.27\), \(\approx 0.25\) and \(\approx 0.23\) V\(_{RHE}\). The stable voltammograms, plotted in Figure 5a, superimpose at potentials \(\geq 0.31\) V\(_{RHE}\) and are again in good agreement with other CVs reported in the literature.\textsuperscript{64} Moreover, their oxidation and reduction peaks can be related to the adsorption and desorption of Cu upd on Au-planes with certain crystallographic orientations.\textsuperscript{60,61} More precisely, the oxidation currents at \(\approx 0.4\) and \(\approx 0.6\) V\(_{RHE}\) (and corresponding reduction shoulders at \(\approx 0.35\) and \(\approx 0.6\) V\(_{RHE}\)) can be assigned to Au(111), while all three Au(100), Au(110) and Au(111) domains possibly contribute to the broader redox process at \(\approx 0.65\) V\(_{RHE}\). The sharply decreasing reduction currents at \(\leq 0.27\) V\(_{RHE}\); on the other hand, are due to copper bulk-deposition.

In an effort to determine the negative potential limit up to which the copper-deposition process is limited to upd (sub)monolayer formation (i.e., excluding Cu-plating), we performed a second set of experiments in which the electrode was held at \(\approx 0.31\), \(\approx 0.29\), \(\approx 0.27\) or \(\approx 0.25\) V\(_{RHE}\) for a time period ranging between 10 and 200 seconds, followed by the stripping of the deposited copper by scanning the potential from the holding value up to \(\approx 0.75\) V\(_{RHE}\). The conversion charge of \(Q_{\text{ox-red}}\) was then integrated and a surface coverage \(\theta\) was calculated from the known thickness of the Pd deposit, using the following expression:

\[
\theta = \frac{Q_{\text{ox-red}}}{Q_{\text{Pd-plating}}}
\]

Table I. Summary of the roughness factor (RF) values for the polycrystalline gold (AuPC) substrate used in each Pd/AuPC surface preparation experiment. RF was estimated from the charge under the peak related to the reduction of Au-oxide \(Q_{\text{ox-red}}\) on CVs recorded in Ar-saturated 0.1 M NaOH with a positive potential limit of 1.6 V\(_{RHE}\) (see Fig. 4), by dividing each \(Q_{\text{ox-red}}\) value by the conversion charge of Cu upd reported by Tremiliosi-Filho and coworkers.\textsuperscript{66}

![Figure 3.](image)

Figure 3. (Color online) Schematic representation of the possible mechanisms of copper underpotential deposition (Cu upd) and its subsequent galvanic replacement with palladium on a polycrystalline gold substrate. In (a), the entire AuPC substrate gets covered with Cu upd atoms, which then place-exchange with Pd\(^2+\) to yield a complete, continuous monolayer of Pd on AuPC. In (b) and (c), the copper-coverge during the upd process is not complete; moreover, in (b) the replacement process still happens in an atom-by-atom manner and the resulting Pd-deposit has monoatomic height, in (c) the Pd\(^2+\) atoms do not get preferentially reduced on the positions occupied by Cu upd, leading to non-planar Pd-deposits.

![Figure 4.](image)

Figure 4. Cyclic voltammograms recorded in Ar-saturated 0.1 M H\(_2\)SO\(_4\), on an AuPC disc scanned at 50 mV.s\(^{-1}\). The overlapping black and gray lines correspond to CVs recorded with the gold-disc embedded in a polytetrafluoroethylene-holder (‘PTFE’) or in hanging meniscus configuration (‘HM’), respectively. The patterned area represents the charge used to estimate the electrode’s roughness factor listed in Table I.

| Surface preparation procedure | \(Q_{\text{ox-red}}\) \(\mu\text{C} \cdot \text{cm}^{-2}\) | RF\(_{\text{Au}}\) \(\mu\text{C} \cdot \text{cm}^{-2}\) |
|-----------------------------|-----------------|-----------------|
| Cu upd + galvanic replacement | 666             | 2.47             |
| Pd-plating, low \(\theta\)   | 628             | 2.33             |
| Pd-plating, high \(\theta\)  | 710             | 2.63             |
the charges related to the stripping of Cu potentiostatically-deposited at various $E$-values and -holding periods to conclude that it is indeed possible to reach a full Cu upd-coverage on an AuPC substrate held at 0.18 V RHE. However, careful observation of the Cu-stripping scans in that work unveils that, at this holding-potential, the peaks at ≈0.45 and ≈0.55 V RHE that the authors relate exclusively to Cu upd become larger with the $E$-holding time, possibly indicating contributions from the plating of Cu 2+. On the other hand, in Ref. 64 Motheo et al. reported Cu upd-CVs remarkably similar to those in Figure 5a, along with a corresponding Cu upd-charge of ≈210 μC·cm$^{-2}$ at a negative inversion potential just positive of the Cu-plating onset. While the authors mistakenly related this excessively low charge to the full coverage of the AuPC-surface, the striking similarities with our results reinforce the validity of our conclusion that Cu upd on polycrystalline gold is only partial, and limited to a θCu-value of ≈0.7.

Following this quantification of the extent of copper coverage, we proceeded to verify other aspects of the Pd/Au-surface preparation procedure that may affect its outcome. To start with, we examined whether a partial stripping of the Cu-adlayer might occur during the initial contact of the copper-covered substrate with the Pd 2+-solution, caused by the brief interruption of potential control during this step. To test this possibility, an AuPC electrode with underpotentially deposited copper produced by holding the potential at 0.31 V RHE for 150 seconds (cf. Fig. 5b) was emersed from the Cu 2+-containing solution for 10 seconds, which we considered as a delay representative of the time required to transfer the electrode between the Cuupd- and the Pd 2+-solutions. The electrode was then re-immersed in the Cu upd-electrolyte, whereby the copper remaining on its surface was promptly stripped by scanning the potential up to 0.75 V RHE (not shown). As it turned out, the stripped charge accounted for ≈220 μC·cm$^{-2}$, which is ≈10% lower than the original Cu upd-charge of ≈250 μC·cm$^{-2}$. This result indicates that ≈10% of the original Cu upd is lost during this 10 second emersion period. Emphasizing the importance of a fast transfer, as it was described previously for Cu upd on single-crystal Au electrodes.69

Next, we wondered whether the galvanic replacement time of 3 minutes first suggested by Brankovic et al. in Ref. 53 (that has ever since been adopted by other workgroups66,70 would grant a sufficient supply of Pd 2+-ions to allow for their stoichiometric exchange with Cu upd. In an attempt to reproducibly evaluate the diffusion rate of Pd 2+ to the gold substrate, we performed a separate experiment in which we recorded polarization curves at different rotation rates on an AuPC-disc immersed in Ar-saturated 0.1 M H 2SO 4 containing 0.5 mM PdCl 2. The curves, plotted in Figure 6, feature Pd 2+-reduction currents at all potentials below ≈0.85 V RHE, while the plated palladium gets stripped at potentials positive of this value. Moreover, assuming that the

Figure 5. (Color online) Voltammetric study of the copper underpotential deposition (Cu upd) on polycrystalline gold (AuPC) in 0.1 M H 2SO 4 with 1 mM CuSO 4. (a) Cyclic voltammograms at 10 mV·s$^{-1}$ with negative inversion potentials between 0.31 and 0.23 V RHE. (b) Cu-stripping charges upon holding of the potential at values between 0.25 and 0.31 V RHE for the time indicated on the x-axis, followed by scanning the potential at 10 mV·s$^{-1}$ up to 0.75 V RHE. All charges are normalized by the roughness factor of the AuPC-disc, derived from Figure 4 and listed in Table 1: the horizontal dashed line at ≈370 μC·cm$^{-2}$ represents the charge corresponding to the stripping of a full Cu upd-monolayer on AuPC (see discussion).

Figure 6. (Color online) Polarization curves (20 mV·s$^{-1}$) showing the plating and stripping of palladium on AuPC in Ar-saturated 0.1 M H 2SO 4 with 0.5 mM PdCl 2. The Koutecky-Levich plot in the inset displays the linear relation between the reciprocal of the Pd-plating current at 0.5 VRHE and the inverse square root of electrode rotation speed, whereby the zero-intercept confirms that the current at this potential is exclusively diffusion-limited.
Pd-plating process is a first order reaction, the current values measured at a given potential (\(i_{\text{meas,E}}\)) can be related to the corresponding diffusion-limited and kinetic currents (\(i_{\text{lim}}\) and \(i_{\text{kin,E}}\), respectively) using the Koutecký-Levich equation:

\[
\frac{1}{i_{\text{meas,E}}} = \frac{1}{i_{\text{lim}}} + \frac{1}{i_{\text{kin,E}}} = \frac{1}{i_{\text{lim}}} + \frac{1}{i_{\text{kin,E}}} = \frac{1}{B \cdot C^* \cdot \omega^{1/2}}
\]

whereby \(i_{\text{meas,E}}\) corresponds to the current that one would observe in the absence of concentration gradients between the bulk of the electrolyte and the electrode’s surface. As for \(i_{\text{lim}}\), its value depends on the concentration of Pd\(^{2+}\) in the bulk of the plating solution (\(C^*\)), the electrode’s rotation speed (\(\omega\)), and a constant \(B\) set by the electrolyte’s kinematic viscosity and Pd\(^{2+}\) diffusivity. In this respect, the inset of Figure 6 demonstrates the linear relation between the inverse square root of \(\omega\) and the reciprocal of the corresponding currents measured at 0.5 V\text{RHE} expected from Equation 6. Moreover, the line’s intercept at the origin (whereby \(1/i_{\text{lim}}\approx 0\)) confirms that the kinetic current at this potential is infinitely large. Therefore, the currents measured at 0.5 V\text{RHE} are exclusively under diffusion-control (\(i_{\text{meas,0.5V}}\approx i_{\text{lim}}\)).

As discussed above, the diffusion-limited currents in Figure 6 can be used to estimate the minimum (i.e., the diffusion-limited) time required to quantitatively exchange the Cu\text{upd} layer on the AuPC-electrode surface with palladium. More precisely, the \(i_{\text{lim}}\)-value of \(\approx 0.4\) mA·cm\(^{-2}\) at 900 rpm measured in the 0.5 mM PdCl\(_2\) electrolyte would translate into a diffusion-limited current of \(\approx 40\) μA·cm\(^{-2}\) (at the same \(\omega\)) in the more dilute 50 μM PdCl\(_2\) solution used in the galvanic replacement experiments. Additionally considering the AuPC-roughness factor of \(\approx 2.5\) cm\(^3\)\(\cdot\)cm\(^{-2}\), the Cu\text{upd}-coverage of \(\approx 0.7\) and the monolayer-equivalent charge of \(\approx 370\) μC·cm\(^{-2}\) estimated above, \(\approx 20\) seconds of immersion in the 50 μM PdCl\(_2\) solution at 900 rpm would be the minimum time necessary to provide the required amount of palladium to substitute all of the surface copper atoms. To allow for kinetic limitations, we chose a \(\approx 10\)-fold longer deposition time (three minutes); this is the same time as was proposed by Brankovic and coworkers,\(^53\) except that in our work, the conversion charge of \(\approx 170\) μC·cm\(^{-2}\) expected from our previous Cu\text{upd}-experiments was increased to \(\approx 250\) μC·cm\(^{-2}\) when the conversion charge of \(\approx 170\) μC·cm\(^{-2}\) derived from Figure 1e is taken into account. Additionally considering the AuPC-RF of \(\approx 2.5\) Au\text{A}_{\text{geom}}\(\cdot\)cm\(^{-2}\) (Table I), the palladium coverage on the gold substrate (\(\theta_{\text{Pd/Au}}\)) reached in the galvanic replacement step accounts for \(\theta_{\text{Pd/Au}}\approx 0.4\) cm\(^3\)\(\cdot\)cm\(^{-2}\), which is \(\approx 40\%\) short of the \(\approx 0.7\) cm\(^3\)\(\cdot\)cm\(^{-2}\) expected from our previous Cu\text{upd}-experiments (see discussion above). Nevertheless, this higher, predicted \(\theta_{\text{Pd/Au}}\) value is estimated on the assumption that the galvanic replacement proceeds through the place-exchange of every Cu\text{upd}-atom on the gold substrate with Pd, as schematized in Figure 3b. Instead, the lower \(\theta_{\text{Pd/Au}}\) found herein points at a galvanic replacement mechanism whereby the reduction of Pd\(^{2+}\) and the complementing oxidation of a Cu\text{upd}-atom occur at different locations via the donation

| Table II. Pd-roughness factor (RF) values of the Pd/AuPC surfaces prepared in this work. The RFs were derived from the charge under the Pd-(hydr)oxide reduction peak (\(Q_{\text{ox,-red}}\)) in CVs recorded in Ar-saturated 0.1 M NaOH with a positive potential limit of 1.0 V\text{RHE}, following their normalization by a charge of \(170\) μC·cm\(^{-2}\) (cf. Figure 1e). The corresponding palladium-on-gold coverage terms (\(\theta_{\text{Pd/Au}}\)) were estimated by dividing these RF\(\cdot\)Pd-values by the roughness factors of the AuPC-substrate (RF\(\cdot\)Au) summarized in Table I. For each cell, the figures on the left- and right-hand sides of the vertical line correspond to the values estimated prior to and after the HOR/HER-activity test in H\(_2\)-saturated 0.1 M NaOH, respectively.

| Surface preparation procedure | \(Q_{\text{ox,-red}}\) [μC·cm\(^{-2}\)\(\cdot\)Au\text{A}_{\text{geom}}] | RF\(\cdot\)Pd [cm\(^3\)\(\cdot\)Pd\(\cdot\)cm\(^{-2}\)\(\cdot\)Au\text{A}_{\text{geom}}] | \(\theta_{\text{Pd/Au}}\) [cm\(^3\)\(\cdot\)Pd\(\cdot\)cm\(^{-2}\)\(\cdot\)Au\text{A}_{\text{geom}}] |
|--------------------------------|---------------------------|-------------------------------|---------------------|
| Cu\text{upd} + galvanic replacement | 162 | 116 | 0.95 | 0.68 | 0.39 | 0.28 |
| Pd-plating, low \(\theta_{\text{Pd}}\) | 91 | 55 | 0.54 | 0.32 | 0.23 | 0.14 |
| Pd-plating, high \(\theta_{\text{Pd}}\) | 278 | 222 | 1.64 | 1.31 | 0.62 | 0.50 |
of electrons through the Au_{PC}-substrate and/or neighboring Pd-atoms already reduced. This alternative mechanism is depicted in Figure 3c, and would result in the formation of three-dimensional Pd-islands similar to those obtained upon galvanic replacement of Cu_{Au} with platinum atop Rh(111) single crystals.\textsuperscript{71,72} Here it is important to note that the formation of these Pd-islands is not incompatible with the above discussed absence of H-absorption, since the latter is believed to require Pd-thicknesses of $\geq 3$ monolayers.\textsuperscript{51}

Keeping our focus on Figure 7a, the subsequent decrease of the negative potential limit to 0.1 V_{RHE} caused the appearance of reduction currents at $\leq 0.3$ V_{RHE} that can be related to the H_{upd} on the Pd-surface, analogous with the behavior observed for Pd_{PC} (cf. Fig. 2a). On the other hand, while the voltammogram recorded on polycrystalline palladium displayed several oxidation peaks between $\approx 0.4$ and $\approx 0.6$ V_{RHE} (Fig. 2a), the CV for the Pd/Au_{PC} surface in Figure 7a only features one well-defined oxidation maximum at $\approx 0.7$ V_{RHE}. Resembling oxidation peaks at potentials $> 0.6$ V_{RHE} have already been reported in the literature for palladized palladium,\textsuperscript{43} mesoporous Pd-films\textsuperscript{73} or palladium-nanoparticles supported on glassy carbon,\textsuperscript{46} and were related to the desorption of underpotentially deposited hydrogen.\textsuperscript{46,74} Moreover, the small shoulder extending between $\approx 0.4$ and $\approx 0.6$ V_{RHE} on the solid-line CV in Figure 7a has been assigned to H_{upd}-desorption\textsuperscript{45} or to the oxidation of absorbed hydrogen.\textsuperscript{46} In the latter case, the small charge related to the shoulder would suggest that hydrogen adsorption on this Pd/Au_{PC}-surface is indeed very minor.

Next, we proceeded to H$_2$-saturate the 0.1 M NaOH electrolyte while holding the Pd/Au_{PC}-electrode at 0.6 V_{RHE}, as we had done in the measurement on Pd_{PC} (see above). The first positive and negative going polarization curves recorded in this hydrogen-saturated electrolyte are plotted as black lines in Figure 7b; the latter also displays the corresponding stable curves recorded on Pd_{PC} and Au_{PC}-electrodes for the sake of comparison. While we will only quantify and discuss the HOR/HER-kinetic parameters associated with this Pd/Au_{PC}-surface below, it is worth noting that it is remarkably more active than the initial one (solid blue vs. black lines, respectively).

In an effort to better understand this activity loss, we re-saturated the electrolyte with argon while holding the disc at 0.6 V_{RHE} and then proceeded to record new voltammograms between 0.1 and 1.0 V_{RHE}. Figure 7c displays a comparison between this CV and the one recorded prior to the HOR/HER-activity measurement (cf. Fig. 7a), and unveils a loss of Pd ECSA within the course of the measurement. More precisely, the integration of the Pd-(hydr)oxide reduction peak following the approach described above and depicted in Figure 7a yields $\theta_{Pd/Au} = 0.28 \text{ cm}^2 \cdot \text{ cm}_{Au}^{-2}$ (Table II), $\approx 30\%$ lower than the 0.39 cm$^2$·cm$^{-2}$ estimated before the HOR/HER-activity test. This loss of Pd-ECSA is probably caused by the well-known diffusion of Pd into Au and the subsequent formation of a Pd-Au alloy at room temperature,\textsuperscript{52,74} resulting in a loss of electrochemically active palladium surface. In addition, the loss of Pd-surface atoms would agree well with the $\approx 30\%$ increase of the average particle size observed by Di Vece and coworkers\textsuperscript{52} upon hydrogenation of Pd-nanoclusters at room temperature, which they explained by the formation of Pd-hydrides that promote atom detachment and re-deposition onto larger clusters. Finally, surface rearrangement\textsuperscript{52} and/or the irreversible adsorption of impurities in the alkaline electrolyte\textsuperscript{51,65} may also contribute to this loss of Pd-ECSA.

Preparation of palladium-on-gold surfaces by Pd-plating on Au_{PC}.— Based on our findings in the previous section, the galvanic replacement of the Cu_{Au} deposited on Au_{PC} with palladium does not result in the expected full-coverage of the gold substrate with a Pd-monolayer. Interestingly, the formation of pseudomorphic monolayers has been demonstrated for Pd/Au-surfaces prepared by electrochemical deposition of Pd$^{2+}$ atop an Au(111) single crystal,\textsuperscript{51,77} as schematized in Figure 8a. However, this growth mode could not be reproduced on Au(100)\textsuperscript{78} and Au(110),\textsuperscript{79} whereby a second Pd-adlayer started growing prior to the complete coverage of the Au-substrate with palladium (cf. Fig. 8b), and clear indications of alloy formation were observed. Inspired by these works, we proceeded to prepare Pd/Au surfaces by direct Pd-plating on the Au_{PC}-substrate. Different, however, to these previous studies,\textsuperscript{51,77-79} in which Pd-deposition was performed from stagnant electrode by scanning the potential until a certain charge was attained, we examined an approach where the electrode is rotated at a constant potential (0.5 V_{RHE}) at which Pd-deposition from Pd$^{2+}$ occurs at a diffusion-limited rate (cf. Fig. 6).

In the first of these experiments, we sought to reach a full coverage of the Au_{PC}-surface with palladium ($\theta_{Pd/Au} = 1$) by aiming at a Pd$^{2+}$-reduction charge equal to the one required for the layer-by-layer deposition of four Pd-monolayers. Considering the Au_{PC}-substrate's roughness factor for this experiment ($\approx 2.3$ cm$^2$·cm$^{-2}$, s. 2nd row of Table I) and the deposition charge of $\approx 370 \mu$C·cm$^{-2}$, four Pd-monolayers would require a deposition charge of $\approx 3.4$ mC·cm$^{-2}$·geom. The actual plating of palladium was again performed in an Ar-saturated solution of 0.1 M H$_2$SO$_4$ with 50 $\mu$M PdCl$_2$, which is 10-fold smaller than the 500 $\mu$M PdCl$_2$ used in Figure 6, Considering the direct proportionality between $i_{lim}$ and reactant concentration (s. Equation 6), the diffusion-limited current at 900 rpm and 0.5 V_{RHE} in this 50 $\mu$M PdCl$_2$ solution amounts to $\approx 40 \mu$A·cm$^{-2}$·geom., and the desired coverage should be obtained
expected diffusion-limited current of the alloying, aggregation and/or contamination effects discussed above. 

After ≈80 seconds. The Pd-deposition charge attained with this approach was ≈3.4 mC·cm⁻², in excellent agreement with the expected value. On the other hand, when the electrode was rinsed with water and transferred to a new cell containing 0.1 M NaOH, the initial voltammogram resembled the one recorded on the previous surface (compare Figs. 9a and 7a), and the RF_Pd-value derived from it was only ≈0.5 cm²·cm⁻²geom (or θ_Pd/Au ≈0.23 cm²·cm⁻², see Table II). This is well below the ≈2.3 cm²·cm⁻²geom (i.e., the AuPC-substrate’s RF) expected from layer-by-layer deposition, pointing at a non-pseudomorphic growth mechanism similar to the one described by Kibler and coworkers for Pd-adlayers deposited on Au(100) and Au(110).

Using the same approach as above, the initial CVs in the deaerated electrolyte were followed by its saturation with H₂ (while holding the electrode at 0.6 V_RHE), after which we proceeded to record the polarization curves displayed in Figure 9b. While the kinetic parameters derived from these measurements will be discussed in the following section, we note that the surface again did not exceed the expected diffusion-limited current of ≈2.5 mA·cm⁻²geom, and also suffered from a slight loss of HOR/HER activity upon cycling like the surface derived from galvanic replacement (see Fig. 7b). In this respect, the voltammograms recorded in the same electrolyte after its re-saturation with argon (gray line in Figure 9c) point at a RF_Pd of only ≈0.3 cm²·cm⁻²geom (or θ_Pd/Au ≈0.14 cm²·cm⁻², corresponding to the loss of ≈50% of the palladium initially present on the surface due to the alloying, aggregation and/or contamination effects discussed above.

In a second experiment, the targeted Pd-deposition charge was further increased to that required for the pseudomorphic plating of six Pd-monolayers which, considering the substrate’s RF of ≈2.6 cm²·cm⁻²geom (Table I, 3rd row), corresponds to ≈5.8 mC·cm⁻²geom. The plating conditions remained unchanged (i.e., 900 rpm and 0.5 V_RHE), except that the deposition time was set to ≈150 seconds, during which a somewhat higher charge of ≈8.1 mC·cm⁻²geom was passed, probably due to imprecisions in the electrolyte’s Pd²⁺-concentration. Once again, the Pd/Au-surface was transferred into the Ar-saturated, 0.1 M NaOH electrolyte, in which we recorded the CVs plotted in Figure 10a. Interestingly, this initial voltammogram is strikingly different from those obtained for the previous Pd/Au-surfaces, and instead resembles the CV recorded on the PdPC-disc (Fig. 2a) or others reported for nano-sized Pd-structures. This difference may result from the higher RF_Pd-value estimated for this third surface (≈1.6 cm²·cm⁻²geom or θ_Pd/Au ≈0.62 cm²·cm⁻², see Table II), which points at a non-pseudomorphic growth mechanism resulting in a larger degree of coverage of the AuPC-substrate by a Pd-deposit consisting of a larger number of adlayers. The latter appear to have an electrochemical behavior closer to that of bulk palladium, since in the subsequent HOR/HER-activity measurements plotted in Figure 10b (discussed in further detail below) the positive-going polarization curves display an oxidation peak at ≈0.7 V_RHE that extends beyond the diffusion-limited current values. If in a much smaller extent, this behavior is analogous to what was previously observed for PdPC (cf. Fig. 2b), that we related to the oxidation of absorbed hydrogen.
Finally, new CVs were recorded in 0.1 M NaOH electrolyte re-saturated with argon, yielding a reduced RFPd-value of \( \approx 1.3 \text{ cm}^2_{\text{Pd}} \cdot \text{cm}^2_{\text{geom}} \) or \( \theta_{\text{Pd/Au}} \approx 0.5 \text{ cm}^2_{\text{Pd}} \cdot \text{cm}^2_{\text{geom}} \) (see Fig. 10c and Table II) which again is consistent with the loss of palladium in the course of the measurement. To verify the accuracy of the coverage determination, we transferred the electrode into a cell filled with deaerated 0.1 M H\(_2\)SO\(_4\), in which we recorded the voltammogram of the baseline for the integration of the (hydr)oxide-reduction charge. This difference is possibly related to the inaccurate definition of the baseline for the integration of the (hydr)oxide-reduction charge. This difference is possibly related to the inaccurate definition of the baseline for the integration of the (hydr)oxide-reduction charge discussed above, which tends to underestimate RF-values. On the other hand, Gossner and Mizera\(^{54}\) have proposed that the CO-coverage on a Pd-rich PdAu-alloy surface may be larger than that on pure Pd. As such, the CO-stripping conversion charge of \( \approx 330 \text{ \mu C} \cdot \text{cm}^2_{\text{Pd}} \) arbitrarily averaged from palladium single-crystal values\(^{55}\) and used herein may be too low and thus slightly overestimate the RFPd-value.

Quantification of the HOR/HER-activity of all palladium-on-gold surfaces.— To finalize this study, we proceeded to correct the HOR/HER-currents measured for all three Pd/AuPC-surfaces (\( i_{\text{meas},E} \)) for diffusion limitations, using the approach recently described by our group for PdPC in the same electrolyte.\(^{47}\) In brief, following the \( iR \)-correction of the polarization curves, the HER-currents were considered as being kinetically controlled, while the HOR-branches were additionally corrected for the diffusion overpotential (\( \eta_{\text{diff}} \)) and transformed into kinetic currents (\( i_{\text{kin},E} \)) using Equations 7 and 8, respectively:\(^{82}\)

\[
\eta_{\text{diff}} = \frac{RT}{nF} \ln \left( \frac{1 - i_{\text{meas},E}}{i_{\text{lim}}} \right) \quad [7]
\]

\[
i_{\text{kin},E} = \frac{i_{\text{meas},E}}{1 - \frac{i_{\text{meas},E}}{i_{\text{lim}}}} \quad [8]
\]

where \( i_{\text{lim}} \) represents the diffusion-limited HOR-current that, for the conditions applied in our measurements (i.e., in 0.1 M NaOH at 293 K and with \( \omega = 1600 \text{ rpm} \)) amounts to \( \approx 2.5 \text{ mA} \cdot \text{cm}^{-2}_{\text{geom}} \) (see the polarization curve for PtPC in Figs. 2b and 7b). The resulting Tafel plots for the initial negative-going scans and normalized to the initial RFPd-values (s. Table II) are shown in Figure 12a. Interestingly, the two lower Pd-coverages yield HOR Tafel slopes of \( \approx 240 \text{ mV} \cdot \text{dec}^{-1} \), consistent with the \( \approx 220 \text{ mV} \cdot \text{dec}^{-1} \) reported by Schmidt and coworkers\(^{52}\) for well-characterized Pd-on-Au(111) surface alloys in 0.1 M HClO\(_4\). On the other hand, the surface with the highest \( \theta_{\text{Pd/Au}} \) features a Tafel slope of \( \approx 150 \text{ mV} \cdot \text{dec}^{-1} \), closer to the \( \approx 120 \text{ mV} \cdot \text{dec}^{-1} \) observed for PtPC\(^{56}\) or Pd/C,\(^{47}\) respectively. The HOR/HER-mechanism on these monometallic surfaces has been ascribed\(^{52}\) to a fast Tafel reaction followed by a rate-determining Volmer step (cf. Eq. 5), which in terms can be described by the Butler–Volmer equation:

\[
i_{\text{kin},E} = i_0 \exp \left[ \frac{F \eta}{RT} - \frac{1}{n} \left( \frac{1}{\alpha} - \frac{1}{2} \right) \right] \quad [9]
\]
where α is the transfer coefficient, T is the temperature (293 K), η is the overpotential, and F and R are the Faraday and ideal gas constants (96,485 A · s · mol⁻¹ and 8.314 J · mol⁻¹ · K⁻¹, respectively). More precisely, Equation 9 can be applied to all combinations of the Tafel, Heyrovsky and Volmer reactions (Eqs. 3-5) with the only exception of the Tafel-RDS mechanism, for which a much lower Tafel slope of ≈ 30 mV · dec⁻¹ would be expected.

Unfortunately, unlike in previous studies,47,82 we were unable to fit our results to Eq. 9. This possibly results from the fact that the Butler-Volmer equation presented above is a simplified version of a more complex expression that also takes the hydrogen-coverage (θH) into consideration.63,83 Thus, Eq. 9 is only valid over a potential region in which changes in θH are small (i.e., typically between ≈ 0.05 and ≈ 0.05 V_RHE).64,82 In the case of Figure 12a, however, the HER- and HOR-branches extend between −0.1 and > +0.5 V_RHE, concomitant with a large variation in the H-coverage, so that Eq. 9 cannot describe the overall kinetics. Nevertheless, for small overpotentials (i.e., in the micropolarization region), Eq. 9 should be valid and can be linearized to:

\[ i_{\text{kin}} = i_0 \cdot \frac{\eta F}{RT} \]  

The micropolarization region within ± 20 mV of the reversible hydrogen potential is shown in Figure 12b, whereby the HOR/HER-currents do display the linear dependency with η expected from Equation 10. The η₀-values derived from the linear fits and summarized in Table III appear plotted as a function of the Pd-coverage of the AuPC-substrate in Figure 12c, which unveils a marked, quasi-linear decrease of the catalytic activity with increasing θPd/AuPC.

At this point, it is useful to briefly summarize our limited knowledge of the morphology and composition of these Pd surfaces. First, all surfaces appear to consist of three-dimensional Pd-adlayers supported on an AuPC-, or surface-alloyed PdAu-substrate. While the exact thickness of these Pd-adlayers remains unknown, the CVs and polarization curves recorded on the two surfaces with the lower θPd/AuPC values show no signs of hydrogen absorption. On the contrary, there are clear indications of hydrogen absorption for the surface with the highest θPd/AuPC, which therefore appears to consist of thicker Pd-adlayers.

On the basis of these observations, we now revert to the literature to find an explanation for the HOR/HER-activity trends observed in our measurements, which point at a decrease of the catalytic performance with the increased thickness of the Pd-adlayers. Luckily, the H₂-reaction on Pd-multilayers of various thicknesses and supported on Au-native crystal has been addressed in a number of computational44-88 and experimental85-88 studies that have reported qualitatively similar reactivity trends, if only in acid electrolyte. More precisely, the larger size of the Au-substrate atoms when compared to Pd is known to cause a tensile strain on the palladium adlayer with a decrease of the HER activity.90 This effect reaches a maximum upon deposition of 2–5 Pd-monolayers44,88 (depending on the crystallographic orientation of the Au-substrate) and explains the lower HOR/HER i₀-values observed for all of our bimetallic surfaces (3.2–22.7 μA · cm⁻² at 298 K, s. Table III) when compared to pure Pd reported by Sheng et al.31 (i₀ ≈ 100 μA · cm⁻² at 298 K) or to 3 nm Pd nanoparticles on carbon reported by Durst et al.45 (i₀ ≈ 60 μA · cm⁻² at 313 K).

Finally, our results hint at directions for the design of Pd-based catalysts with an improved HOR/HER-activity, possibly accessible by deposition of Pd on a metal substrate with a smaller lattice parameter.46 This should result in a compressed Pd-adlayer characterized by a lower H-adsorption and a catalytic performance correspondingly better than that of Pd, in contrast to the less active surfaces obtained herein by Pd-deposition on larger Au, which induces tensile strain and an excessive strength of H-adsorption. Nevertheless, this hypothesis remains only tentative, and further experimental studies should be devoted to the verification of its validity.

## Conclusions

In summary, our attempts at quantifying the HOR/HER-activity of PdPC were impeded by the unavoidable H-adsorption on the kinematic measurements. We managed to minimize this effect by depositing adlayers of palladium on a polycrystalline Au-substrate, either by galvanic replacement of underpotentially-deposited copper or by electrochemical plating from a Pd²⁺-solution under defined transport limited deposition rates using a rotating disk electrode. Interestingly, none of these approaches resulted in the intended complete palladium coverage of the underlying gold disc. Instead, the surfaces appear to consist of three-dimensional Pd-structures of an unknown thickness that we believe to scale with the palladium coverage, θPd/Au. Moreover, this last parameter is inversely proportional to the HOR/HER-activity of the Pd/AuPC-surfaces, in agreement with numerous theoretical and experimental studies that correlate this effect to the tensile strain on the Pd-lattice induced by the Au-substrate. This explanation is consistent with recent experimental observations that point at the strength of H-adsorption as the main HOR/HER-activity descriptor in alkaline electrolyte, as previously established for acid media.

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