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Hydrogen Oxidation and Evolution Reaction Kinetics on Carbon Supported Pt, Ir, Rh, and Pd Electrocatalysts in Acidic Media

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The hydrogen oxidation and evolution reaction (HOR/HER) behavior of carbon supported metal (Pt, Ir, Rh, Pd) nanoparticle electrocatalysts is studied using the H2 pump approach, in a proton exchange membrane fuel cell (PEMFC) setup. After describing the best method for normalizing the net faradic currents to the active surface area of the electrodes, we measure the HOR/HER kinetic parameters (exchange current densities and transfer coefficients) in a temperature range from 313 K to 353 K and calculate the activation energy for the HOR/HER process. We compare the measured kinetic parameters with those extracted from different mass-transport limitation free setups in literature, to evaluate the hydrogen electrocatalysis on these most active surfaces. The HOR/HER activity scales with the following: Pt > Ir > Rh > Pd. The anodic and cathodic transfer coefficients are similar for all metals (ca. 0.5), leading to Tafel slopes of ca. 140 mV/decade at 353 K (except for the anodic branch of Pd and the cathodic branch of Rh). The lowest activation energies are found for Pt and Ir (≈20 kJ/mol). For Rh and Pd, higher activation energies are found (≈30 kJ/mol), and attributed to the formation of surface oxides and hydride phase, respectively.

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In the current view of energy conversion based on the use of fuel cells and electrolyzers, the hydrogen electrocatalysis plays a central role. H2 is used as a fuel in proton exchange membrane fuel cells (PEMFCs), where it is electrochemically oxidized at the anode electrode according to:

\[ H_2 \rightarrow 2H^+ + 2e^- \]  

In PEMFC anode electrode, only small amounts of Pt (ca. 0.05 mgPt/cm2geo) are required to catalyze the hydrogen oxidation, without contributing to any efficiency loss of the overall fuel cell performance. The same would hold true for the hydrogen evolution reaction – HER – at the cathode side of water electrolyzer systems. Moreover, except when considering contamination issues e.g. due to the presence of CO in reformate hydrogen, or stability issues e.g. due to hydrogen starvation events mode, a replacement of the current carbon supported platinum (Pt/C) based electrode technology is not contemplated in PEMFC. The drawback of both PEM-based fuel cells and electrolyzer systems arise from the large amounts of noble metal (ca. 0.4–0.9 mgmetal/cm2geo) required to catalyze at acceptable rates the sluggish oxygen reduction reaction (ORR) in fuel cell cathodes, and the oxygen evolution reaction (OER) in electrolyzer anodes.

Contrary to the acidic PEM-based technologies, anion exchange membrane (AEM) based devices, which are operating at high pH, offer the use of cost-effective non-noble metal electrodes to catalyze the ORR, and OER at almost similar rates than on noble metal electrodes in acidic electrolytes. As a result, a replacement of PEM-based devices by AEM ones will be advantageous if and only if AEM conductivities will be further increased to the level of PEM, and their sensitivity to CO2 significantly reduced. However, getting rid of the noble metal contents in AEM-device electrodes would be feasible only in the case of similar hydrogen oxidation and evolution reaction (HOR/HER) rates in AEMs versus PEM-based conversion devices. Unfortunately, recent studies have shown that the HOR/HER rates of noble metal electrodes in the alkaline environment are much slower than in acidic electrolytes by about two orders of magnitude, but still remain a few order of magnitude higher than the latest noble metal free HOR catalyst systems. Even if the reasons for this activity increase on noble metal electrodes remain not yet fully understood, these studies have highlighted the lack of fundamental understanding at a mechanistic level of the HOR/HER. Thus, the challenges in the field of hydrogen electrocatalysis over the next coming years will be to (i) have an accepted mechanistic understanding for the HOR/HER process over the entire pH-scale, which will be a prerequisite for (ii) understanding the origin of activity decrease along the pH-scale, and will help to (iii) develop HOR/HER electrocatalysts with increased reactivity in alkaline electrolytes.

From a mechanistic point of view, Eq. 1 is composed of two out of three following microscopic steps:

 condiciones en los que el hidrógeno, en su estado gaseoso, se convierte en hidrógeno iónica y viceversa.

\[ \text{Tafel step:} \quad H_2 \rightarrow 2H_{\text{ad}} \]

\[ \text{Heyrovsky step:} \quad H_{\text{ad}} + e^- + H^+ \]

\[ \text{Volmer step:} \quad H_{\text{ad}} + H^+ + e^- \]

Knowing the kinetic parameters of an electrochemical reaction, which include rate or exchange current density \( i_0 \) in A/cm2metal at given temperature/pressure and its corresponding activation energy \( E_A \) in kJ/mol, plus anodic and cathodic transfer coefficients \( \alpha, \gamma \), Tafel slopes in mV/decade, is a prerequisite to unveil the overall reaction mechanism. For instance, these parameters would allow to determine which among the Tafel, Volmer and Heyrovsky reactions constitute the HOR/HOR equilibrium, and which is the rate determining step. Kinetic parameters for the HOR/HOR have been evaluated, historically more often in acidic electrolytes, on well-defined single or polycrystalline electrode surfaces mounted in a rotating disk electrode (RDE) configuration. Using this approach, it has been demonstrated that Pt-group metal surfaces (Pt, Pd, Rh, Re and Ir) have the highest HOR/HOR activity, without any clear distinction between the reactivity of these metals. Exhaustive reviews of RDE extracted parameters can be found in Refs. 24–27. More specifically, on Pt, there was a general agreement that \( i_0 \)-values fall into the range of \( \approx 1 \text{mA/cm}^2 \), with anodic and cathodic Tafel slopes of 30 mV/decade. For Pd, since the absorption of hydrogen in its lattice competes with the electrocatalytic HOR/HOR process and prevents from a proper kinetic study on single or polycrystalline electrode surfaces, model studies have historically been performed on Pd monolayers deposited on a non-absorbing substrate such e.g. Re, Ru, Ir, Pt, Pt-Ru, Au or Ag. In these studies, the number of Pd monolayers is usually kept very small (even below 1), always in order to prevent from residual absorption to occur in the deposited Pd layers. It is questionable when using a HOR/HOR active substrate (e.g. Pt, Ir, Pt-Ru), whether the substrate might actually not contribute to the catalytic activity of the system, in parallel to surface Pd layers. Nevertheless, none of these systems had \( i_0 \)-values (evaluated using the Butler-Volmer without indicating fitted transfer coefficients) exceeding 1 mA/cm2. According to Tafel slope on Pd, Schmidt et al.
reported an anodic value slope of 220 mV/decade for a PdML/Au (111) system,\textsuperscript{34} which remains one of the only values reported so far. For Ir and Rh surfaces, fewer studies reporting HOR/HER data have been published\textsuperscript{18,59} and 41 and besides the values reported by Trasatti\textsuperscript{42} citing the results obtained in two PhD theses,\textsuperscript{43,44} sputtered Ir\textsuperscript{45} or Rh films\textsuperscript{46} and Ir-Rh alloys\textsuperscript{47} show all \textit{i}_0-values of \approx 1 mA/cm\textsuperscript{2}metal.

The \textit{i}_0-values, known for all these surfaces since the late 50’s, have been used to compute the first Volcano plot for the HER reaction in the seminal work of Trasatti, but also more recent ones,\textsuperscript{42,46-53} which provided insights about the HOR/HER mechanism. However, over the last decade, there have been several hints that Pt-group metal surfaces might proceed at much faster rates in acidic electrolytes. In particular, several electrochemical setups with reduced mass transport resistances, including H\textsubscript{2} pumping in a fuel cell setup,\textsuperscript{18,24-25} scanning electron microscopy (SECM),\textsuperscript{55,56} micro-electrodes,\textsuperscript{57} and floating electrodes,\textsuperscript{58} have shown that the \textit{i}_0-values of Pt\textsubscript{AC} and Pt/C surfaces lie in the range 20–80 mA/cm\textsuperscript{2} at \textit{T} = 293 K,\textsuperscript{55,56} 200 mA/cm\textsuperscript{2} at \textit{T} = 313 K\textsuperscript{18} and 200 to 600 mA/cm\textsuperscript{2} at \textit{T} = 353 K.\textsuperscript{24} Even though there is one order of magnitude scatter between these values, which will be discussed in the present study, these values are additionally well above the predictions from conventional RDE measurements. The transfer coefficients reported in these studies differ also from those evaluated in RDE. Thus, using kinetic parameters extracted from setup working under high mass transport conditions would provide completely different insights about reaction mechanism.\textsuperscript{18} Nevertheless, despite these recent hints, RDE kinetic parameters are still erroneously in use nowadays and are the basis of the most recent computational studies.\textsuperscript{46-50}

In this study, after explaining the discrepancy in RDE-extracted kinetic parameters, we will refine HOR/HER kinetic parameters for carbon supported Pt, Ir, Pd and Rh nanoparticles using the H\textsubscript{2} pump approach described by Neyerlin et al.\textsuperscript{24} We will quantify \textit{i}_0-values at different temperatures in order to extract activation energies. Transfer coefficients will also be determined. These values will then be critically discussed in the lights of the findings on other setups working under high mass transport conditions. These kinetic parameters were extracted between 313 K, which is the lowest temperature at which the operating conditions of a PEMFC can be accurately regulated and where electrochemical measurement in liquid electrolyte can be performed, and 353 K, the practical operating temperature of a PEMFC.

**Experimental**

**Materials.**— HOR/HER activities were evaluated on Pt/C (4.7 wt %, ref. TEC10V05E, Tanaka), Ir/C (20 wt %, ref. P40A200, Premetek), Rh/C (5 wt %, ref. 206164, Sigma Aldrich) and Pd/C (10 wt %, ref. P30A100, Premetek) catalysts. These materials were used as working electrodes in the H\textsubscript{2} pump configuration. All the metal nanoparticles are supported on a Vulcan type of carbon. The counter/reference electrodes were made of a Pt/C catalyst (50 wt %, ref. TEC10V05E, Tanaka).

**Transmission electron microscopy (TEM) measurements.**— TEM measurements of the catalysts were performed with a JEOL 2010 TEM operated at an accelerating voltage of 200 kV. The particle size distributions of the catalysts were reconstructed by measuring the diameter of at least 200 individual particles from TEM images obtained at high magnifications (\times 150–200 k) with the software ImageJ.

**Rotating disk electrode (RDE) measurements in 0.1 M HClO\textsubscript{4}.**— To demonstrate that the RDE approach would fail at quantifying HOR/HER kinetics on very active surfaces, the carbon supported catalysts used in this study were first evaluated using this technique. A heated glass jacketed cell was used in a three electrode configuration (gold as counter and a daily prepared reversible hydrogen electrode (RHE) as reference electrodes). The cleaning procedure of the cell included several boiling steps in ultrapure water (18.2 M\textsubscript{2} cm and 3 TOC, Millipore). The electrolyte solution was prepared from a 70 wt % double distilled HClO\textsubscript{4} (99.999% purity, GFS) stock solution and ultrapure water. The catalyst loadings on the polished glassy carbon disk (0.196 cm\textsuperscript{2}geo) were 5 μg/cm\textsuperscript{2}geo for the Pt/C and Rh/C catalyst, and 10 μg/cm\textsuperscript{2}geo for the Pd/C and Ir/C catalysts. The loadings were adjusted by pipetting a 10 μL aliquot of a sonicated suspension consisting of catalyst powder, a mixture of 2-propanol/ultrapure water (3/7 vol.) and 5 wt % ionomer solution (targeted ionomer to carbon I/C ratio of ca. 0.5/1). It should be noted that Rh and Ir surfaces might catalyze the reduction of Cl\textsubscript{O\textsubscript{4}}\textsuperscript{-} ions into Cl\textsuperscript{-} ions in a potential region where Cl\textsubscript{O\textsubscript{4}}\textsuperscript{-} ions adsorb on the catalyst surface.\textsuperscript{58} In this study, RDE measurements were performed within less 2–3 hours, and a potential of 0.4 V\textsubscript{RHE} was imposed during all the holding periods. Doing so, the formation of chloride species will be kept at a reasonably small level, and will not be considered in the analysis of our results.

**Membrane electrode assembly (MEA) preparation and cell assembly.**— 5 cm\textsuperscript{2} MEAs were prepared by the decal transfer method. Suspensions were first prepared by mixing a known amount of catalyst, 2-propanol, ultrapure water and ionomer solution (20 wt %, ref. D2021, Ion Power) over 24 h using a roller mixer. 5 mm ZrO\textsubscript{2} grinding media were added to the mixture to achieve a complete homogenization of the suspension, which was then coated with an automatic Mayer-rod coater on ETTE films (25 μm thick, Goodfellow), which were used as electrode decalcs. Working and counter/reference electrodes were then hot-pressed on a Nafion XL membrane (28 μm thick, Quintech) for 10 min at 155 °C and ~22 bar. The electrode loadings were deducted from the weights of the decals before and after hot-pressing, using a microbalance (ref. XP6, Metler Toledo) with an accuracy of ± 1 μg. The nominal loading of the working electrodes were 2.15, 4.5 and 6 μgmetal/cm\textsuperscript{2}geo for the Pt/C, Ir/C, Rh/C and Pd/C catalysts, respectively, leading to electrode thicknesses of 2–3 μm. The ionomer to carbon weight ratio in the electrodes was fixed to 0.8/1. For the cell assembly, 210 μm thick gas diffusion media (GDL 25 BC, SGL Carbon) were used. The sealing of the cell and the compression rate of the GDL materials (fixed to 25% of their initial thickness) was ensured using incompressible fiber glass coated PTFE gaskets. The 5 cm\textsuperscript{2} cell hardware and single serpentine flow fields were purchased from Fuel Cell Technologies and the tests were performed on an automated test station from Greenlight Innovation (ref. G60).

**Surface area measurements using cyclic and CO-stripping voltammograms.**— Prior to each HOR/HER kinetic measurement, cyclic voltammograms (CV) were recorded at room temperature and ambient pressure with the counter/reference electrode flushed with 50 nccm of 5 vol.% H\textsubscript{2} in N\textsubscript{2} and the working electrode with 5 nccm N\textsubscript{2}. In this configuration, 20 “cleaning” CV’s were first recorded between 0.08 V and 1.10 V, scan rate 100 mV/s, with a 3 A potentiotstat (Reference 3000, Gamry) using the so-called surface mode (equivalent to a linear ramp). For CO-stripping measurements, a cell voltage of 0.1 V was held for 30 min while the working electrode was successively flushed with 50 nccm 10 vol.% CO in N\textsubscript{2} during the first 3 min, then with 300 nccm N\textsubscript{2} during 25 min and finally with 5 nccm N\textsubscript{2}. Three voltammograms were then recorded at a scan rate of 100 mV/s between 0.06 V and 1.10 V. Hydrogen under-potential deposition (H-UPD) charge densities were measured on the third CV, and using the average between adsorption and desorption charges.

**Hydrogen oxidation and evolution (HOR/HER) polarization curves.**— For H\textsubscript{2} pump measurements, the fuel cell was flushed with 500 nccm of over-humidified (~110% RH) H\textsubscript{2} from the working electrode inlet to the counter/reference electrode outlet using a gas by-pass between the working electrode outlet and the counter/reference electrode inlet. The temperature dependence of the HOR/HER kinetics was investigated by increasing the cell temperature from \textit{T} = 313 K to 353 K while adjusting the inlet hydrogen partial pressure to \textit{p}_{\text{H}_2} \approx 100 kPa, at each temperature. After steady state conditions in cell/dew point temperatures and pressures were reached, HOR/HER polarization curves were recorded between –0.3 V and 0.9 V at 2 mV/s with a 30 A booster potentiotstat (30k booster, Gamry) until steady
state curves were obtained. In this study, kinetic parameters were all extracted from positive-going polarization curves. No differences were observed with kinetic parameters extracted from negative-going scans.

**Ohmic loss corrections.**—HOR/HER overpotentials \( \eta \) in V were obtained by correcting the measured potentials first from the high frequency resistance \( R_{\text{Hi}} \) in \( \Omega \ cm^2_{\text{geo}} \) measured by impedance spectroscopy after each polarization curve. This correction takes into account losses arising from proton transporting through the membrane, and contact resistances. An additional correction, introduced by Neyerlin et al., was applied to take into account the proton transport losses through the electrode thickness. The temperature-dependent ionomer conductivity is roughly 0.08 and 0.12 S/cm at 313 and 353 K, respectively. For 2 \( \mu \)m thick electrodes, this yields to effective electrode resistances of \( \approx 4 \) and \( \approx 3 \) m\( \Omega \) cm\(^2\) at 313 and 353 K, respectively.

**Table 1.** Number-averaged \( \bar{\eta}_s \) and surface-averaged \( \bar{\eta}_s \) diameters of the Pt/C, Ir/C, Rh/C and Pd/C catalysts. Electrochemical active surface area (ECSA) evaluated from TEM (ECSA\(_{\text{TEM}}\)), as well as from electrochemical methods i.e., from the H-UPD (ECSA\(_{\text{H-UPD}}\)) and CO-stripping voltammograms (ECSA\(_{\text{CO-stripping}}\)) in a rotating disc electrode 0.1 M HClO\(_4\) (RDE) and fuel cell (PEMFC) setup, recorded at \( T = 293 \) K and \( v = 0.1 \) V/s. H-UPD charge densities of 210 \( \mu \)C/cm\(^2\) for Pt and 120, 205 \( \mu \)C/cm\(^2\) for Pd and 220 \( \mu \)C/cm\(^2\) for Rh were taken. The CO-stripping reference charge densities are twice that of the H-UPD. The ECSA values in bold should be used by the interested reader to turn all surface normalized \( \bar{\eta}_s \)-values from this manuscript into mass normalized ones.

<table>
<thead>
<tr>
<th></th>
<th>Pt/C</th>
<th>Ir/C</th>
<th>Rh/C</th>
<th>Pd/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \bar{\eta}_s ) [nm]</td>
<td>2.2 \pm 0.7</td>
<td>3.3 \pm 0.9</td>
<td>3.7 \pm 0.7</td>
<td>2.8 \pm 0.5</td>
</tr>
<tr>
<td>ECSA(<em>{\text{TEM}}) ([m^2</em>{\text{metal}}/g_{\text{metal}}])</td>
<td>110</td>
<td>68</td>
<td>120</td>
<td>170</td>
</tr>
<tr>
<td>ECSA(<em>{\text{H-UPD}}) RDE ([m^2</em>{\text{metal}}/g_{\text{metal}}])</td>
<td>90</td>
<td>35</td>
<td>–</td>
<td>100</td>
</tr>
<tr>
<td>ECSA(<em>{\text{H-UPD}}) PEMFC ([m^2</em>{\text{metal}}/g_{\text{metal}}])</td>
<td>50 \pm 10</td>
<td>15 \pm 4</td>
<td>–</td>
<td>75 \pm 25</td>
</tr>
<tr>
<td>ECSA(<em>{\text{CO-stripping}}) RDE ([m^2</em>{\text{metal}}/g_{\text{metal}}])</td>
<td>120</td>
<td>55</td>
<td>150</td>
<td>170</td>
</tr>
<tr>
<td>ECSA(<em>{\text{CO-stripping}}) PEMFC ([m^2</em>{\text{metal}}/g_{\text{metal}}])</td>
<td>110 \pm 10</td>
<td>60 \pm 10</td>
<td>90 \pm 10</td>
<td>150 \pm 40</td>
</tr>
</tbody>
</table>

**Results and Discussion**

**Electrochemical active surface area (ECSA) normalization.**—One of the most critical aspects in electrocatalysis is to relate net faradaic currents to the active surface area on which the electrochemical reaction proceeds. The method for determining net HOR/HER faradaic currents using the H\(_2\) pump method has already been well detailed by Neyerlin et al. However, the method for determining in situ the electrochemical active surface area (ECSA in m\(^2\) metal/g metal) of electrodes used in the H\(_2\) pump approach remains undocumented. These electrodes consist of low metal loadings, ca. typically <2-10 \( \mu \)g metal/cm\(^2\) geo. To report rigorous HOR/HER rates, we will first start to describe the determination of the ECSA of the respective electrocatalysts using different methods. All determined ECSA values, which could be used by the reader to turn all surface normalized \( \bar{\eta}_s \)-values from this manuscript into mass normalized ones, are summarized in Table 1 as well as discussed and compared in the following section.

**Ex situ ECSA determination via transmission electron microscopy (TEM) analysis.**—For carbon supported metal electrodes, where the electrochemically active area is fixed by the dispersion, particle size and loading of the metal nanoparticles, it is common to rely in a first approach on the total weighted metal loading in the electrode \( L_{\text{metal}} \) in \( g_{\text{metal}}/cm^2_{\text{geo}} \), and use the ECSA, derived from an ex situ analysis (by microscopy, gas-phase such as Brunauer–Emmett–Teller, or X-ray diffraction), to obtain the total metal surface area of the electrode. This approach supposes an accurate determination of the metal loadings within the electrodes, which in the case of fuel cell electrodes with very low metal loadings in the range of a few \( \mu \)g/g geo very delicate. Taking the 4.7 wt % Pt/C electrode with a targeted metal loading of 2 \( \mu \)g/g geo as an example, the total loading of the electrode, including carbon and ionomer phases, is \( \approx 110 \) \( \mu \)g/g geo, i.e., \( \approx 550 \) \( \mu \)g over 5 cm\(^2\). With a \pm 1 \( \mu \)g accuracy microbalance (see the experimental section), the experimental error when determining the metal loadings of the electrodes should be less than 5%.

**Figure 1.** Representative TEM images of the A) Pt/C, B) Ir/C, C) Rh/C and D) Pd/C catalysts. The scale bar represents 20 nm.
is attributed to the low metal loadings of the catalysts, between 4.7 and 20 wt %, required to perform H2 pump measurements. Based on the analysis of at least 200 individual metal particles, particle size distributions follow convoluted Gaussian and Lorentzian distributions. Figure 2. Particle size distribution of the A) Pt/C, B) Ir/C, C) Pd/C and D) Rh/C catalysts derived by counting at least 200 particles on TEM images taken at × 150–200 k magnification.

From these particle size distributions the number-averaged diameters ($\bar{d}_N$) and the surface-averaged diameters ($\bar{d}_S$) were determined:

$$\bar{d}_N = \frac{\sum_{i=1}^{n} l_i d_i}{\sum_{i=1}^{n} l_i}$$  

$$\bar{d}_S = \frac{\sum_{i=1}^{n} l_i d_i^2}{\sum_{i=1}^{n} l_i}$$

$l_i$ stands for the number of particles having a diameter $d_i$. The number-averaged diameter ($\bar{d}_N$) is the average mathematical diameter, while the surface-averaged diameter ($\bar{d}_S$) is the diameter reported to the average surface area of the particle. The surface-averaged diameter is the most relevant diameter in electrocatalysis, and can be converted in an electrochemical active surface area (ECSA\textsubscript{TEM}) by assuming spherical particles and using the density ($\rho$) of each element for the various catalysts.

Based on this analysis the surface-averaged diameters are 2.6 nm, 3.9 nm, 2.9 nm and 4.0 nm for the Pt/C, Ir/C, Pd/C and Rh/C catalysts, which yield to ECSA\textsubscript{TEM} values of 110, 68, 170 and 120 m\textsuperscript{2}\textsubscript{metal}/g\textsubscript{metal}, respectively. Table I summarizes the diameters and ECSA\textsubscript{TEM} values for the various catalysts.

In situ ECSA determination via rotating disc electrode (RDE) and fuel cell (PEMFC) experiments.— Which fraction of the total surface area will be electrochemically active in the electrode, a key parameter in fuel cell electrodes and precluded by the optimal and maximal distribution of triple phase boundaries, is of course not predicted by ex situ ECSA values. Thus, in situ electrochemical methods, based on the oxidation of adsorbed molecular probes such as H or CO during cyclic voltammograms (CV), have been developed to determine the real active surface area of electrodes.\textsuperscript{62,63} In low temperature fuel cell, CVs can be recorded in a H2/N2 configuration (gases flushed in the anode/cathode compartments, respectively). In absence of reacting molecules in the cathode compartment and with a defined anode potential of 0 V\textsubscript{RHE} (used as reference/counter electrode), the hydrogen under-potential deposition, H-UPD, charge density of the cathode electrode can be evaluated.\textsuperscript{54} In classical fuel cell experiments, with metal loading in the electrodes of >0.1 mg\textsubscript{metal}/cm\textsuperscript{2}\textsubscript{geo},\textsuperscript{64,65} there is a good agreement with the H-UPD charge densities evaluated on the same catalyst using the thin-film rotating disc electrode (RDE) method approach in liquid electrolytes.\textsuperscript{66,67} However, when characterizing low metal loading electrodes (<0.1 mg\textsubscript{metal}/cm\textsuperscript{2}\textsubscript{geo}) some artifacts can arise. In particular, the H-UPD process on Pt is characterized by a capacitance of ~1 mF/cm\textsuperscript{2}\textsubscript{Pt}. Assuming an electrode loading of 2 mg\textsubscript{metal}/cm\textsuperscript{2}\textsubscript{geo} and a catalyst surface area of 100 m\textsuperscript{2}\textsubscript{metal}/g\textsubscript{metal} (this would be the case for the 4.7 wt % Pt/C electrodes used in this study), this yields to an electrode roughness factor of 2 cm\textsuperscript{2}\textsubscript{Pt}/cm\textsuperscript{2}\textsubscript{geo} and a H-UPD capacity of 2 mC/cm\textsuperscript{2}\textsubscript{geo}. At $v=0.02$ V/s, the resulting H-UPD currents ca. 0.04 mA/cm\textsuperscript{2}\textsubscript{geo} would be completely masked by hydrogen crossover currents, typically in the range of ~1 mA/cm\textsuperscript{2}\textsubscript{geo} with pure H\textsubscript{2} in the anode compartment. Therefore, recording CVs on a low loaded electrode with distinguishable pseudo-capacitive features, implies to (i) use fast scan rates ($v=0.1$ V/s) and (ii) use diluted hydrogen in the anode compartment since the extent of hydrogen crossover scales with the partial pressure of hydrogen (p\textsubscript{H2}) in the anode. For CVs recorded at fast scan rates it is known that, at least for Pt, the H-UPD in acid environments is a fast process, characterized by a small charge transfer resistance.\textsuperscript{68,69} As a result, it is possible to measure CVs at scan rates up to $v=1–10$ V/s without destabilizing the H-UPD adsorption isotherm.\textsuperscript{70} Admittedly, this has only been demonstrated on Pt\textsuperscript{68} and Ir\textsuperscript{71} electrodes. For metal surfaces such as Rh or Pd, characterized by two orders of magnitudes slower H-UPD rates\textsuperscript{72,73} than Pt,\textsuperscript{68,69} higher scan rates than 0.1 V/s could already lead to lower H-UPD coverages reached during CVs, and ultimately to underestimated H-UPD charge densities. Regarding now the use of diluted hydrogen in the anode compartment, 5 vol.% H\textsubscript{2} in N\textsubscript{2} induces a fixed thermodynamical shift of the anode potential by ca. –0.039 V at $T=298$ K. Working electrode potentials were corrected by this potential shift in order to yield potentials calibrated on an RHE scale for 100 kPa H\textsubscript{2}.

On top of these experimental considerations, it has been observed by Maillard et al. that "the traditional method of surface evaluation based on H-UPD coulometry results in dramatic underestimation of the surface area of Pt nanoparticles (factor of 2 for ca 1.5 nm), and is inappropriate for the measurement of the surface areas of particles with the size below 3.5 nm."\textsuperscript{74} Despite the fact that the rationale for such observation has not been commented by the authors, they have proposed to use the charge from CO-stripping measurement for the ECSA determination of small nanoparticles. This latter value should yield better agreements with ECSA\textsubscript{TEM} values over the whole range of Pt nanoparticle diameters.\textsuperscript{75} Since the particle sizes of the supported metal catalysts used in this study are all in the range of 2 to 4 nm (Table I), H-UPD and CO-stripping charge densities were recorded using the experimental parameters discussed above on the low loading Pt/C-based, Ir/C-based Rh/C-based and Pd/C-based MEAs, and will be compared in order to find the best estimate of the surface area of each electrode.

Table I. ECSA\textsubscript{TEM} values for supported metal catalysts used in this study.
Pt/C electrodes: Characteristic CVs and CO-stripping voltammograms of the Pt/C-based fuel cell electrodes are reported in Figure 3 (solid and dashed black lines). These voltammograms are compared to those recorded using the thin-film RDE method in 0.1 M HClO₄ (solid and dashed gray lines in Figure 3). These CVs, recorded at the same scan rate, were normalized to the metal loadings of the electrodes. Thus, the ECSA of the tested catalyst directly scales with the magnitude of the H-UPD and CO-stripping currents in Figure 3. The surface area determined from the H-UPD in 0.1 M HClO₄ is 90 m²/μgPt, i.e., only 75% of the surface area probe with the CO-stripping technique of 120 m²Pt/gPt. This H-UPD/CO-stripping ratio is in excellent agreement with the findings of Maillard et al. for 2.5 nm Pt/C catalyst. When comparing now the H-UPD recorded in RDE and PEMFC, it appears clearly that HER currents appear at approximately 50 mV higher potential in the fuel cell experiment compared to RDE experiment. This yields to a lower measurable H-UPD coverage in the fuel cell experiment. Similar shifts of the HER currents toward high potentials were previously discussed by Carter et al. and attributed to a low H₂ partial pressure in the cathode compartment, which thermodynamically shifts the hydrogen evolution currents to higher potentials. As pointed out by Carter et al., this effect, even when counterbalanced by using the preconized nitrogen cathode gas flux of 1 sccm/cm²geo (also used in this study), yields a lower H-UPD coverage reached under fuel cell conditions of ca. 15% compared to RDE. This was however demonstrated on a 0.4 mgPt/cm²geo loading cathode electrode. With a two orders of magnitude lower metal loading in the cathode electrode, even when using fast scan rates, HER currents reach the same magnitude than H-UPD currents at a much higher potential. In conclusion, on top of the destabilized hydrogen adsorption isotherm on small nanoparticles, the H-UPD in fuel cell underestimates by approximately 50% the ex situ ECSATEM value of low loading 2 nm Pt/C fuel cell electrodes.

Comparing now the CO-stripping voltammograms recorded in RDE and PEMFC, first, both CO-stripping peaks, which position scales primarily with the size of the Pt nanoparticles and the scan rate, appear to be centered on the same potential in both RDE and PEMFC experiments. The same charge density is probed in the two environments, leading to similar ECSA on-stripping values of 120 m²/μg Ir in RDE and 110 m²/μg Ir in the fuel cell, both in agreement with the TEM analysis (ECSATEM = 110 m²/μgIr). The latter ECSA on-stripping value determined in fuel cell will be used to normalize in the following HOR/HER currents.

Ir/C electrodes: Following the same approach than on the Pt/C catalyst, CVs and CO-stripping voltammograms were recorded on the Ir/C-MEAs. Characteristic voltammograms are reported in Figure 4 (red lines), and compared to those recorded using the RDE method in 0.1 M HClO₄ (light red lines in Figure 4). Similar to Pt, Ir forms a H-UPD layer, starting at 0.35 V_RHE. Using a charge density of 210 μC/cm²Ir, the H-UPD process yields an ECSA of 35 and 15 m²/μgIr measured using the RDE and PEMFC techniques, respectively. Compared to the ECSA estimated from the TEM analysis of 68 m²/μgIr, the H-UPD underestimates the electrochemical surface area in both the RDE and PEMFC approaches. The same arguments used to rationalize this behavior on Pt/C would also apply to Ir/C. However, the effect seen on the Ir/C catalysts is even more marked than on the Pt/C catalyst, which is likely to be attributed to the presence of surface oxides competing with the H-UPD process. Indeed, Ir is a more oxophilic surface than Pt, with surface oxides forming already at ≈0.4 V_RHE under both RDE and PEMFC conditions (Figure 4), it is therefore more than likely that these species are still present in the H-UPD region during the negative-going sweep, especially due to the fast scan rates and the high potential limit used in this study.

Looking now at the RDE and PEMFC CO-stripping voltammograms (dashed lines in Figure 4), these voltammograms are characterized by CO stripping currents starting at ≈0.8 V_RHE, a much higher potential than the formation of surface oxides on the base CV. Interestingly, it is usually observed on Pt that the CO stripping oxidation is triggered at the potential where surface oxides start to form during CV. Since the stripping of CO species starts at a much higher potential than the formation of surface oxides, this implies that the true charge associated to the CO-stripping is obtained by subtracting the charges obtained on the cyclic voltammogram for the oxides formed at potentials below the beginning of CO-stripping formation, to the actual apparent CO-stripping peak. Using this approach, and a charge density of 420 μC/cm²Ir, the ECSAs obtained with the CO-stripping technique are 55 and 60 m²/μgIr for RDE and PEMFC, respectively. These values are in very good agreement with the value predicted from the TEM analysis of 68 m²/μgIr. In the following, the surface areas determined with the CO-stripping in PEMFC will be used to normalize the HOR/HER kinetic currents.

Rh/C electrodes: CVs (solid line) and CO-stripping voltammograms (dashed line) were recorded on the Rh/C-MEA (Figure 5, green lines) and compared to those recorded in 0.1 M HClO₄ (light green lines in Figure 5). Rhodium has an electrochemical behavior similar to that of iridium, with surface oxides forming at low potentials. From measurements on polycrystalline electrodes, the oxides are known to form already at 0.3 V_RHE. When using high potential limits in CVs, significant amounts of surface oxides are formed and further reduced.
in the negative-going potential sweep, down to the H-UPD potential region, affecting this process.\textsuperscript{72} Even given the very low metal loading of rhodium on carbon (5 wt %), leading to difficulties to distinguish between pseudo-capacitive (from Rh) and double layer currents (from carbon support), the Rh/C catalyst reproduces the behavior observed on Rh\textsubscript{BC} electrodes.\textsuperscript{76-80} The H-UPD region can be resolved in the RDE experiment, with an onset at 0.1 \textit{V}_{\text{RHE}}, but not in fuel cell due to the high onset potential of the HER (already discussed above). For these reasons, the H-UPD charge density cannot be used for the determination of the surface area of the Rh/C catalyst. CO-stripping remains the only tool to determine the surface area of rhodium electrodes. Similar CO-stripping voltammograms are obtained under both PEMFC and RDE experiments, with the oxidation of the CO\textsubscript{ad} layer starting at 0.75 \textit{V}_{\text{RHE}}, 0.4 \textit{V} higher than the formation of surface oxides on the base CV. Thus, to access the charge associated to only the CO oxidation reaction, the same approach than the one used for the case-study of the iridium electrode was used, with the subtraction of the charge for oxide formed below 0.75 \textit{V}_{\text{RHE}} recorded in the base CV to the actual CO-stripping peak. Using a charge density of 440 \text{\mu}C/cm\textsuperscript{2} for the oxidation of one monolayer of adsorbed CO, the obtained ECSA on the Rh/C in the RDE and PEMFC experiments catalyst are respectively 150 and 90 m\textsuperscript{2}/g\textsubscript{Rh}, in agreement with the TEM measurement of 120 m\textsuperscript{2}/g\textsubscript{Rh}.\textsuperscript{79}

\textbf{Pd/C electrodes:} Cyclic voltammograms (solid line) and CO-stripping voltammograms (dashed line) were recorded on the Pd/C- MEAs and shown in Figure 6 (blue lines). These voltammograms, normalized to the loadings of the electrodes, are compared to those recorded in 0.1 M HClO\textsubscript{4} (light blue lines). Palladium forms a H-UPD layer, with the deposition starting at \approx 0.25 \textit{V}_{\text{RHE}} under acidic conditions, in agreement with studies on single crystal electrodes.\textsuperscript{81} The ECSA of the Pd/C catalysts was determined to 100 and 75 m\textsuperscript{2}/g\textsubscript{Pd} from the RDE and PEMFC techniques, using the H-UPD charge density with a reference charge of 205 \text{\mu}C/cm\textsuperscript{2}.\textsuperscript{81} Compared to the ECSA estimated from the TEM analysis of 170 m\textsuperscript{2}/g\textsubscript{Pd}, the H-UPD underestimates the geometric surface area in both the RDE and PEMFC approaches, and the same arguments used to rationalize this behavior on Pt/C can be invoked here. The specificity of Pd, however, is its ability to absorb hydrogen into its lattice in the same potential region as where the H-UPD process occurs. This specificity could also interfere with the determination of the ECSA. This hydrogen absorption, which has received considerable attention in the literature (see the introduction), leads ultimately to a pure palladium hydride phase, often referred as the \beta-hydride phase, characterized by a larger Pd-Pd bond distance (ca. 4\% higher with respect to a pure palladium phase).\textsuperscript{82} The formation of \beta-hydride should appear only at 0.05 \textit{V}_{\text{RHE}}, or lower potentials,\textsuperscript{83} and thus should not be considered a priori in the analysis of the voltammograms in Figure 6. When looking now more carefully at the H-UPD on Pd/C, this process appears to be less reversible, compared to the features recorded on the Pt/C (Figure 3) and Ir/C (Figure 4) electrodes at the same scan rate. This is characterized by the main H-UPD adsorption peak at \approx 0.18 \textit{V}_{\text{RHE}} and its counterpart in the desorption scan at \approx 0.28 \textit{V}_{\text{RHE}}, and which we attribute to a reduced H-UPD rate on Pd compared \textit{e.g.} to Pt (2 orders of magnitude difference in the H-UPD charge transfer resistance between these metals).\textsuperscript{69,84} The low H-UPD rate on Pd electrodes might have as a consequence that a low scan rate is required for the H-UPD process to become reversible, and reach higher H-UPD coverages during CVs.

Looking now at the CO-stripping experiments on Pd, the CO monolayer oxidation proceeds is similar manner in both RDE and PEMFC experiments. Therefore, in the RDE experiment, the true charge associated to only the stripping of adsorbed CO is obtained by subtracting the charge related to formation of oxide (between 0.65 - 0.90 \textit{V}_{\text{RHE}}) to the actual CO stripping peak starting at 0.9 \textit{V}_{\text{RHE}}. The ECSA values obtained from the CO-stripping charges are 170 and 150 m\textsuperscript{2}/g\textsubscript{Pd} for RDE and PEMFC data, respectively, and in very good agreement the value predicted from the TEM analysis of 170 m\textsuperscript{2}/g\textsubscript{Pd}. It should be noted that previous studies performed on Pd single crystal electrodes have shown that CO would adsorb preferentially on bridge sites.\textsuperscript{85,86} Interestingly, the good agreement between the surface area values evaluated by CO-stripping (using 410 \text{\mu}C/cm\textsuperscript{2} i.e. twice the charge reference used for the H-UPD process) and estimated by TEM on the Pd catalyst points at the fact that it is possible to reach a high coverage of adsorbed CO on Pd nanoparticles. In the following, surface areas determined in situ with the CO-stripping technique will be used to normalize the HOR/HER kinetic currents.

\textbf{Hydrogen Oxidation and Evolution Reaction (HOR/HER) Kinetic Parameters}

\textit{Determination via rotating disk electrode (RDE).}— Figure 7 displays HOR voltammograms (positive-going scans) recorded via the RDE technique in H\textsubscript{2}-saturated 0.1 M HClO\textsubscript{4} (\textit{v} = 20 mV/s, \textit{T} = 313 K and \omega = 1600 rpm) on Pt/C (black squares), Ir/C (red up triangles), Pd/C (blue down triangles) and Rh/C (green circles) electrocatalysts. The currents have been normalized to the geometric area of the glassy carbon electrode, and the potentials corrected by the ohmic drop (\Delta \textit{E}_\text{G} = \textit{i} \cdot \textit{R}_{\text{OHM}}) in the solution. For all the surfaces,
the HOR currents show a fast increase at small overpotentials, with the diffusion limiting current density \( i_{\text{lim}} \) of \( \approx 2.4 \text{ mA/cm}^2_{\text{geo}} \) being reached already at \( \eta \approx 50 \text{ mV} \). One singularity occurs on the Pd/C voltammogram, with an extra peak appearing on top of the diffusion limiting current at \( \eta = +70 \text{ mV} \). This superimposed current contribution can be attributed to oxidation of absorbed hydrogen (inserted in the Pd lattice), known to affect not only bulk materials but also nanosized materials.87,21

It is now well established that the HOR/HER kinetics of Pt electrodes in acid electrolytes are too fast to be evaluated using the RDE approach.19 Taking Pt as a case study, it has been shown that owing to the fast HOR/HER kinetics, the HOR branch of the voltammogram follows the predicted Nernstian diffusion overpotential term, \( \eta_{\text{diff}} \), describing the Nernstian potential shift caused by a change of the hydrogen surface concentration:19

\[
\eta_{\text{diff}} = -\frac{R \eta}{2F} \ln \left( 1 - \frac{i}{i_{\text{lim}}} \right) \quad [11]
\]

with \( i \) the measured current and \( i_{\text{lim}} \) the diffusion limiting current. For RDE experiments this implies that the kinetic currents free from diffusion contributions must be plotted versus the potential corrected for both the \( iR \)-drop (\( \Delta E_{\text{eq}} \)) and for \( \eta_{\text{diff}} \) in the HOR branch.59 The Nernstian diffusion overpotential (Eq. 11) can be rewritten to express the maximum HOR current (\( i_{\text{diff}} \)) recorded under pure diffusion conditions:

\[
i_{\text{diff}} = i_{\text{lim}} \left( 1 - e^{-\frac{R \eta}{2F}} \right) \quad [12]
\]

The diffusion current, calculated for \( T = 313 \text{ K} \) and \( i_{\text{lim}} = 2.4 \text{ mA/cm}^2_{\text{geo}} \), is added to Figure 7 (gray line). As expected, the HOR voltammogram on the Pt/C electrode follows \( i_{\text{diff}} \) throughout the entire \( +\eta \)-region, which also holds true for the Ir/C, Pd/C and Rh/C electrodes. Zooming into the micropolarization region (Figure 7B), only Pd does actually deviate from the \( i_{\text{diff}} \) curve. Therefore, Ir and Rh surfaces must have, in the same way as Pt, HOR/HER \( i_0 \)-values that are too high to be quantifiable by RDE measurements, while Pd seems to be at the limit of what could still be quantified by RDE.

As already detailed in the introduction, \( i_0 \)-values and Tafel slopes determined for these active surfaces, i.e., from voltammograms which very closely follow the Nernstian diffusion overpotential line, fall in the range of \( \approx 1 \text{ mA/cm}^2_{\text{metal}} \) and \( \approx 30 \text{ mV/decade} \), respectively. If we now were to assume that the HOR/HER kinetics would indeed be so fast that they are quasi reversible (i.e., following the Nernst equation) within the current densities accessible by RDE, one would conventionally (but erroneously) extract the kinetic currents from such RDE data using the Koutecky-Levich correction for a first order reaction:

\[
i_{\text{kin,diff}} = i_{\text{diff}} \left( \frac{i_{\text{lim}}}{i_{\text{lim}} - i} \right) \quad [13]
\]

Combining Eq. 12 and Eq. 13 would then yield:

\[
i_{\text{kin,diff}} = i_{\text{lim}} e^\frac{R \eta}{2F} \approx i_{\text{lim}} - 1 \quad [14]
\]

Eq. 14 should be regarded as a general expression describing pseudo-kinetic HOR currents, i.e., currents determined from voltammograms which closely follow the Nernstian diffusion overpotential. Thus, if RDE potentials are not corrected by the \( \eta_{\text{geo}} \)-term (a so far neglected but necessary correction)59 and if the exchange current density is far above the diffusion-limited current density, one would obtain a “kinetically-corrected” Tafel plot described by Eq. 14 and plotted in Figure 8 for a diffusion-limited current density of \( 2.4 \text{ mA/cm}^2_{\text{geo}} \); it would yield an apparent Tafel slope of \( \approx 30 \text{ mV/decade} \) and an extrapolated “exchange current density” of \( 2.4 \text{ mA/cm}^2_{\text{geo}} \), i.e., corresponding to the diffusion limited current density. Taking into account that polycrystalline electrodes typically have roughness factors of \( \approx 2 \text{ cm}^2_{\text{metal/cm}^2_{\text{geo}}} \) (or even higher roughness factors for thin-film RDE electrodes with supported catalysts), this case study rationalizes why the reported \( i_0 \)-values obtained for Pt, Ir, and Rh in RDE experiments normally range around of \( \approx 1 \text{ mA/cm}^2_{\text{metal}} \), even though much higher values are obtained with experimental methods which facilitate faster mass transport rates (e.g., in hydrogen pump experiments). It is important to consider that this artefact also applies to the micropolarization region, since at small overpotentials Eq. 14 also approximates to a linear \( i \) vs. \( \eta \) relationship (viz., \( i_{\text{kin,diff}} = 2 \cdot i_{\text{lim}} \cdot F[R/T] \)) as the Butler-Volmer equation (viz., \( i_0 = (a_a + a_\alpha) \cdot i_0 \cdot F[R/T] \)). As a consequence, the apparent exchange current density extracted from \( \eta_{\text{diff}} \)-limited voltammograms would be \( i_{\text{app}} = i_{\text{lim}} \cdot (a_a + a_\alpha) \), i.e., again on the order of \( i_{\text{lim}} \).

Determination via fuel cell, \( H_2 \) pump technique.— In the following, the kinetic parameters determined using a fuel cell approach, the so-called \( H_2 \) pump technique, will be discussed for the various carbon supported metal electrodes and are summarized in Table II.

Pt/C electrodes: HOR/HER voltammograms were recorded in the \( H_2 \) pump setup, on the Pt/C catalyst, from 313 to 353 K in 10 K steps at \( v = 2 \text{ mV/s} \). Characteristic voltammograms for the two extreme

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**Figure 7.** A) Hydrogen oxidation voltammograms recorded on Pt/C (black squares), Ir/C (red up triangles), Rh/C (green circles) and Pd/C (blue down triangles) in H₂-saturated 0.1 M HClO₄, \( v = 20 \text{ mV/s} \), \( T = 313 \text{ K} \) and \( \omega = 1600 \text{ rpm} \). The theoretical diffusion current, calculated according to Eq. 12 for \( T = 313 \text{ K} \) and \( i_{\text{lim}} = 2.4 \text{ mA/cm}^2_{\text{geo}} \), is also reported (gray line). B) Inset shows a zoom in the micropolarization region (between -2 and +5 mVRHE).

**Figure 8.** Theoretical Tafel representation of hydrogen oxidation currents extracted from diffusion limited voltammograms recorded with rotating disk electrode (assumed diffusion limited current density of 2.4 mA/cm²geo). The dashed lines represent construction lines for the visual determination of \( i_0 \) and Tafel slope.
and show a marked decrease at higher overpotentials. At specific surface area normalized voltammograms are shown in Figure 9. A) Hydrogen oxidation and evolution polarization curves in terms of geometric current densities (left-hand y-axis), at 353 K between 0.1 and 0.4 V_RHE (negative scan currents being smaller than positive going scan currents). This behavior is in agreement with the recent findings of Zalitis et al.,57 and will be commented in the last part of this study. At small overpotentials where kinetic parameters are determined (±0.05 V), both positive going and negative going scans superimpose perfectly. In Figure 9B, HOR/HER kinetic currents from Figure 9A are transposed in a Tafel representation, and the Butler-Volmer equation was fitted in the overpotential region within ±50 mV. The maximum currents reached at these potentials are ≈1 A/cm²geo, or ≈0.6 A/cm²Pt, at 353 K. Figure 9B also shows the Butler-Volmer fits, obtained in this case for sums of anodic and cathodic transfer coefficients of 1. The HOR/HER polarization curves are symmetric in this potential range, corresponding to the similar transfer coefficients α_a and α_c (0.47 ±0.06 and 0.53 ±0.06, Table II), which equate to anodic and cathodic Tafel slopes of 149 ±19 and 135 ±15 mV/decade at T = 353 K, respectively.

It should be noted that the diminishing rate of increase of the HER currents with increasing negative overpotential (below ~0.05 V_RHE, s. Fig. 9) is inconsistent with what would be predicted by a Butler-Volmer type behavior for which a rapid increase in the HER current with increasingly negative overpotentials would be expected. Since this cannot be due to electrode shielding effects which can occur in the case of gas evolving reactions in liquid electrolytes, this observed behavior likely points toward the transition to a different rate-limiting reaction mechanism, viz., a rate limitation imposed by the Tafel reaction (see below). While we do not consider it very likely, this behavior might also be ascribed to additional voltage losses due to uncompensated mass transport effects at ultra-high specific current densities, along the lines to what has been claimed for the oxygen reduction reaction in fuel cell electrodes with ultra-low loadings.88,89

Regarding the determination of i_0-values, for consistency reasons with the more oxophilic catalysts (Ir/C and Rh/C) on which HOR branches are altered by the formation of surface oxides already at low overpotentials, i_0-values extracted from the micropolarization region (η = ±10 mV) offer a more rigorous comparison between all the surfaces tested in this study. The equation of the micropolarization region is obtained by linearizing the Butler-Volmer equation for small overpotentials:

\[ i_0 (\alpha_a + \alpha_c) = \frac{RT}{F} \frac{i}{\eta} \]  

The uncertainty in the quantification of i_0 exclusively from the micropolarization region is the choice of the value of (α_a + α_c). Practically speaking, however, this term ranges between ≈0.75 and 4 and can at least be estimated within a factor of 2 to 3 from the Butler-Volmer fit, so that in the absence of any indication of the Tafel slopes, the
mental data, it was not possible to identify the true value of the anodic
potential region is definitively too small to accurately fit the experi-
mentally.

hence, only minor presence of surface oxide species at the RHE
potential.

overpotentials below 20 mV, currents from
associated with the formation of surface oxides on Ir, acting as HOR
inhibitors. Nevertheless, at overpotentials below 20 mV, currents from
positive and negative going scans perfectly superimpose, indicating
that the HOR/HOR activity is the same in both scan directions and
hence, only minor presence of surface oxide species at the RHE
potential.

transfer coefficient. HOR/HOR exchange current densities were deter-
mined by fitting the micropolarization region (±10 mV). Since the use
of the micropolarization equation requires to know the sum of anodic
and cathodic transfer coefficients (s. above), we will first assume that
this sum is ∼1. This assumption will be discussed in more detail in
the discussion part of the paper. The fitted i0-values at T = 313 K
and 353 K are 40 ±10 and 16.5 ±4.0 mA/cm2Rh, respectively (Table II).

Ir/C electrodes: Figure 10A displays geometric and specific surface
area normalized positive going HOR/HOR voltammograms recorded
on the Ir/C catalyst at 313 K and 353 K. At positive overpotentials
of ∼0.1 V, the HOR currents show a peak maximum of
≈1 A/cm2geo, or ≈0.1 A/cm2Rh at 353 K, and a fast decrease at higher
overpotentials. This early decrease of the HOR currents can be asso-
ciated with the formation of surface oxides on Ir, acting as HOR
inhibitors. Nevertheless, at overpotentials below 20 mV, currents from
positive and negative going scans perfectly superimpose, indicating
that the HOR/HOR activity is the same in both scan directions and
hence, only minor presence of surface oxide species at the RHE
potential.

The fitting of the Butler-Volmer equation was performed in the
overpotential region of −75/+20 mV (Figure 10B). Because the early
formation of surface oxides hinders the HOR even at low overpoten-
tials <50 mV, the upper limit was reduced to 20 mV, where the
Butler-Volmer fitting shows a good agreement with the kinetic data.
Since the HER region was limited, the HER region was extended to
overpotentials of −75 mV in an attempt to keep the fitted potential range constant.
The HER region displays unambiguously a fitted Tafel slope of
145 ±17 mV/decade (αH = 0.5). In the HER region, since the fitted
potential region is definitively too small to accurately fit the experi-
mental data, it was not possible to identify the true value of the anodic

Figure 10. A) Hydrogen oxidation and evolution polarization curves in terms of
gеometric current densities (left-hand y-axis) and specific current densities
(right-hand y-axis) on Ir/C in a PEMFC at 313 K (light red lines) and 353 K
(red lines). Positive going scans (solid lines) and negative going scans (dashed
lines) are included. B) Kinetic current densities (positive going scans only)
and their fit to the Butler–Volmer equation (gray dashed lines). Data collected
in H2-saturated (100 kPaH2) fully humidified conditions, and v = 2 mV/s.

Figure 11. A) Hydrogen oxidation and evolution polarization curves in terms of
gеometric current densities (left-hand y-axis) and specific current densities
(right-hand y-axis) on Rh/C in a PEMFC at 313 K (light green lines) and
353 K (green lines). Positive-going scans (solid lines) and negative-going
scans (dashed lines) are included. B) Kinetic current densities (positive-going
scans only) and their fit to the Butler–Volmer equation (gray dashed lines).
Data collected in H2-saturated (100 kPaH2) fully humidified conditions, and
v = 2 mV/s.
fro. The high anodic Tafel slope is in line with the findings of Schmidt et al. for a PdAu/Au(111) system of ca. 220 mV/decade at 293 K.\textsuperscript{34} HOR/HER \( i_0 \)-values were determined by fitting the micropolarization region (±10 mV), with a sum of anodic and cathodic transfer coefficients of 0.75. The fitted exchange current densities at 313 K and 353 K are 2.7 ±0.8 and 11.0 ±2.6 mA/cm\(^2\)Pt, respectively (Table II).

Temperature Dependence and Comparison of \( i_0 \)-values with Other Mass-Transport Limitation Free Setups

It is established that the evaluation of HOR/HER kinetic parameters using a conventional RDE approach in acidic electrolytes is definitely not possible for Pt, Ir, and Rh surfaces, since these surfaces possess \( i_0 \)-values higher than typical \( H_2 \) mass-transport limited currents in liquid electrolytes (Figure 7). It may be marginally possible for Pd surfaces. Therefore, there have been several attempts to quantify the HOR/HER kinetics, especially on Pt, using different experimental setups with much lower mass transport resistances. The \( H_2 \) pump configuration is one possible option. Nevertheless, since \( i_0 \)-values have been quantified with these setups at different temperatures and electrode structures, there is still no agreement whether these techniques yield similar activities, i.e., whether they are sufficiently free from mass transport contributions. Also, to the best of our knowledge, no experimentally reliable values for the activation energy of the HOR/HER have ever been reported to facilitate comparison of all the literature. It should be noted that activation energies based on RDE experiments have been previously reported in the literature, but since the reported kinetics are far too low, these reported activation energies are not meaningful,\textsuperscript{90,91} or, more in line with activation of physical (diffusivity and solubility of \( H_2 \)) rather than chemical (HOR/HER), processes. To obtain activation energies for the HOR/HER on the different catalysts, polarization curves were recorded for all catalysts from 313 K to 353 K in 10 K steps in a range where the fuel cell temperatures and hydrogen and water activities can be controlled with accuracy.

**Pt/C electrode:** Due to the abundance of HOR/HER data reported for Pt electrodes, motivated by the use of this catalyst in fuel cell anodes and water electrolyzer cathodes,\textsuperscript{26,27,92} we will start discussing the rates on this catalyst. All the \( i_0 \)-values measured on the Pt/C catalyst are reported in an Arrhenius plot (black line in Figure 13), from which an activation energy of 16 ±2 kJ/mol can be obtained. Exchange current densities were extrapolated to lower temperatures (dashed line in Figure 13), which would give \( i_0 \approx 75 \text{ mA/cm}^2\text{Pt} \) at 293 K. The most relevant HOR/HER \( i_0 \)-values reported for Pt-electrodes in the literature are also included in Figure 13 to facilitate a straightforward comparison of our values with those obtained with different “mass-transport limitation free” approaches. For this comparative analysis, apparent rate constants (\( k_{\text{app}} \)) in cm/s) reported in some studies\textsuperscript{25,56,81} were converted into \( i_0 \)-values using:

\[
    i_0 = 2 \cdot F \cdot k_{\text{app}} \cdot C_{H_2}
\]

where \( C_{H_2} \) is the concentration of hydrogen (e.g., \( \approx 0.7 \times10^{-6} \text{ mol/cm}^3 \) in dilute \( H_2\text{SO}_4 \)).\textsuperscript{30}

First, our exchange current densities fall within the same order of magnitude as those in a previously reported \( H_2 \) pump study,\textsuperscript{24} although they are ≈2-fold lower. In the study of Neyerlin et al. on 2 nm particle size Pt/C catalyst (\( i_0 \approx 535 \pm65 \text{ mA/cm}^2\text{Pt} \)) at 353 K using a sum of transfer coefficients of 1, this can be attributed to an imprecise surface normalization approach, which relied on the ECSA calculated from ex situ H-UPD charge densities in 0.1 M \( H_2\text{SO}_4 \) and the weight of a very light electrode.\textsuperscript{33} Using a similar \( H_2 \) pump approach, Wang et al. evaluated HOR/HER kinetic parameters on nanostructured thin film (NSTF) Pt and Pt-alloy electrodes.\textsuperscript{54} However, due to the high roughness factors of their electrodes, leading to kinetic overpotentials of only ≈5–10 mV at the highest currents, and due to the fact that the loading of their reference/counter electrode was only ≈2-fold higher than their working electrodes, leading to non-negligible kinetic losses at the reference/counter electrode which thus added to the working electrode losses, the error on the reported \( i_0 \)-value of...
500–3000 mA/cm² at 353 K is expected to be substantial and these values should be taken with care (these values are not reported in Figure 13). It is for instance very unlikely that the $i_0$-values and activation energies change by a factor of 2 and 5, respectively, depending on the pretreatment of the electrode. This study emphasizes the need to follow the approach described by Neyerlin et al. when using the H₂ pump method, viz., to use sufficiently small metal loadings on the working electrode and very high platinum loadings on the counter/reference electrode.

Kucernak and collaborators have developed several electrochemical techniques working under high mass transport rate conditions over the last decade, mostly to study ORR but also HOR kinetics. Chronologically, using a single sub-micron Pt particle supported on a micro-electrode, or Pt/C nanoparticles supported on a gold grid in contact with a perfluorsulfonic acid membrane, 2 to 5 times lower $i_0$-values compared to our findings were obtained, with Tafel slopes of $\approx 30$ mV/decade suggesting residual H₂ mass transport limitations (s. “Low loading RDE-Pt/C” in Figure 13). In part, the discrepancies in the reported exchange current densities by Chen and Kucernak, could also be attributed to errors in the surface area normalization (pseudo-capacitive currents during CV measurements were only in the range of picoamps at 1 V/s), or a high rate of sulfate adsorption (or of other contaminants) on the microelectrode in 0.1 M H₂SO₄. In the case of (bi-)sulphates poisoning, even though it is known that such species adsorb strongly on Pt and destabilize the H-UPD isotherm, their impact on the HOR/HER rates remains poorly studied with low mass transport resistance electrochemical setups. More recently, this group reported a “vacuum filtered catalyst” (VFC) method to deposit catalyst layers with ultra-low metal loadings onto a porous substrate (made conductive by a sputtered gold film) which then is let float on the surface of an aqueous electrolyte, allowing fast gas transport through the gas-phase to the partially immersed catalyst particles. Using this approach, the authors reported very similar Pt/C HOR/HER voltammograms as in our study. Even if it is not explicitly reported, their $i_0$-value can be estimated: with a current density of $27 \pm 9$ mA/cm² at $\eta = 0.01$ V, the slope of the micropolarization can be calculated and, assuming a sum of transfer coefficients of 1, would yield an $i_0$-value of $70 \pm 20$ mA/cm² at 298 K (referred as “Floating VCF Electrode-Pt/C” method in Figure 13).

Exchange current densities on Pt/C electrodes extracted from measurements using scanning electrochemical microscopy configurations in 0.01 M HClO₄, amounting to $i_0 \approx 60 \pm 20$ mA/cm² at 293 K (referred as SECM method in Figure 13), yield also similarly excellent agreement with our H₂ pump $i_0$-values. From a mechanistic point of view, SECM measurements yield also similar Tafel slopes (117 mV/decade, i.e., transfer coefficients of ca. $\approx 0.5$) as those found here. The same holds true for Ir and Rh surfaces and will be discussed latter. Although pH conditions differ slightly in these studies, the good agreement between H₂ pump, SECM and floating electrode $i_0$-values, as well as the fact that these are the highest reported $i_0$-values in the literature, lead to the conclusion that these gas-diffusion (H₂ pump) and liquid-diffusion (SECM) or mixed gas/liquid-diffusion (Floating VCF Electrode) techniques offer sufficiently low hydrogen transport limitations to enable an accurate determination of the true HOR/HER kinetics. Since these measurements have been performed on different electrode structures (from nanoparticles to extended surfaces), this would also hint at a surface insensitivity of the HOR/HER process.

To complete this comparative analysis, it can be said that Pt micro-electrode mounted in a thin electrolyte film configuration yields $i_0 \approx 50$ mA/cm² at 298 K and channel flow electrolyte cells are working under similar limited mass transport conditions than typical RDE experiments ($i_0 = 0.25$ mA/cm²). Moreover, using the thin-film RDE approach where a Pt/C catalyst is highly diluted with non-catalyzed carbon (Sun et al.), so that the kinetic currents become low compared to the current which can be sustained by mass transport, higher $i_0$-values are obtained compared to conventional RDE measurements, but some uncompensated mass transport resistances remain (s. “Low loading RDE-Pt/C” in Fig. 13).
Regarding the HOR current plateau found at small positive overpotentials (Figure 9A), with a current maximum of ca. \(0.4-0.5 \text{ A/cm}^2\) Pt at 313 K, the Floating VCF Electrode\(^{57}\) method applied to Pt/C in 4 M HClO\(_4\) reproduces qualitatively the same HOR/HER voltammograms. First, since this current plateau is 3- to 4-fold above our \(i_0\)-value, this implies that any phenomena causing this limitation (diffusion or a Tafel/Volmer/Heyrovsky limiting step) is not limiting \(i_0\). Now, assuming that the Volmer (rds)-Tafel mechanism demonstrated in alkaline electrolytes also holds true in acidic electrolytes, we hypothesize that this maximum current reached at positive overpotentials and low hydrogen coverage (\(\theta_H\)), reflects the limited ability of the Pt electrode to dissociate \(H_2\), i.e., the Tafel step. From a mechanistic point of view, having a Tafel limiting step is the only kinetics-based rationale for reaching a more or less potential-independent current plateau.\(^{23}\) Given the rate of the dissociative hydrogen adsorption (equivalent to the Tafel dissociation step: \(H_2 \rightarrow 2 \text{H}_\text{ad}\)) of 2.4 cm/s measured by Vogel et al. in H\(_2\)-D\(_2\) gas phase experiments at 295 K,\(^{100}\) and using a gas solubility of \(\approx 1 \times 10^{-6} \text{mol/cm}^3\) at 293 K in Nafion membranes\(^{101}\) (H\(_2\) solubility in strong acid liquid electrolytes being slightly lower \(\approx 0.7 \times 10^{-6} \text{mol/cm}^3\)), this would yield to a Tafel current of 0.5 A/cm\(^2\) Pt which is in excellent agreement with the current plateau found on the HOR at 313 K (s. Fig. 9A). At this point, it is also not clear whether a \(\theta_H\)-term needs to be included in Eq. 16, when calculating the Tafel rate, though this would actually be expected for a dissociative step.\(^{23}\) The fact that no current plateau is observed at current densities as low as \(-1 \text{ A/cm}^2\) Pt in the HER region (s. Fig. 9A) might either be related to the \(\theta_H\)-dependence of the Tafel reaction (\(\theta_H \approx 1 \text{ under HER conditions, while } \theta_H \ll 1 \text{ under HOR conditions) or to a higher binding energy of adsorbed hydrogen (\(H_\text{ad}\)) at these different potentials and coverages, leading to a faster Tafel recombination rate in the HER-brançh (2 \(H_\text{ad} \rightarrow H_2\)) versus the above discussed Tafel-dissociation rate in the HOR branch. Nevertheless, the HER current densities below \(-0.1 \text{ V}_{\text{RHE}}\) do display some curvature, which suggests a deviation from the Butler-Volmer reaction (i.e., slower increase in cathodic currents with increasing negative overpotential than would be expected). It should be mentioned, however, that no HER current plateau was observed at current densities as low as \(-8 \text{ A/cm}^2\) Pt in the measurements reported by Zalitis et al.\(^{95}\) in 4 M HClO\(_4\). This result suggests that the rate of the Tafel recombination step in the HER is either substantially above this current density, or that a Volmer-Heyrovsky mechanism might come into play at very negative overpotentials.

To conclude this analysis on Pt, even though it is not the aim of the present study, an analogy with the HOR/HER process in alkaline electrolytes can be drawn. In alkaline electrolytes, \(i_0\)-values are approximately two orders of magnitude lower than in acid electrolytes, implying that kinetics can be evaluated accurately using a conventional RDE approach. There, the lack of structure-sensitivity for the HOR/HER between carbon supported and polycrystalline Pt electrodes, and the anodic and cathodic branches having transfer coefficients of ca. 0.5, have already been reported\(^{9,37}\) (see also the discussion in Ref. 87 regarding single crystal \(i_0\)-values obtained by Schmidt et al.\(^{82}\)) and would confirm the findings in acidic electrolytes. As demonstrated in our previous kinetic studies, comparing acid and alkaline \(i_0\)-values on several metals, these similarities support the idea that the reaction mechanism remains the same over the entire pH-scale (a Tafel-Volmer series with the latter being the rate limiting step),\(^{18,87}\) with only the rate of the limiting step being affected by the local pH environment.\(^{18}\) Moreover, the activation energy reported in 0.1 M KOH for Pt/C and \(P_{\text{Pt}}\) surfaces is ca. \(30 \text{kJ/mol}\).\(^{18}\) There is therefore an additional \(\approx 10-15 \text{kJ/mol}\) activation barrier to overcome in alkaline electrolytes for the HOR/HER to proceed. As predicted in our earlier findings, the positive-shift of the H-UPD (formally the Volmer reaction) isotherm with increasing pH, observed on Pt(hkl),\(^{103}\) \(P_{\text{Pt}}\)\(^{104}\) and Pt/C\(^{105}\) surfaces, would cause a H-binding energy difference \((\Delta E_{\text{Hbinding}}) \approx 12.5 - 13.5 \text{kJ/mol from pH } 0 \text{ to pH } 13\) (see the detailed calculation in Durst et al.).\(^{18}\) These findings underline that the change in the H-binding energy might be, at least in part, at the origin of the HOR/HER activity decrease when going from low to high pH electrolytes.

Figure 14. Arrhenius plot for the hydrogen oxidation and evolution reaction determined with the H\(_2\) pump setup for Pt/C (black squares), Ir/C (red squares), Pd/C (blue squares) and Rh/C (green squares).
clarify this structural dependency. From a practical point of view, however, the low abundance and annual production of Ir (more than an order of magnitude lower than Pt) will limit its use in large-scale applications.105

**Rh/C electrode:** Rhodium is the third most active surface for the HOR/HER, with an approximately 10-15 times lower activity than Pt. The cathodic transfer coefficient of Rh is found to be 0.7, while the anodic transfer coefficient cannot be determined accurately because surface oxides are already present at \( \eta = 0 \) V. As with Ir, the only high mass transport approach applied to study the HOR kinetics on Rh/C electrodes is SECM.55 In that study, an anodic transfer coefficient of 0.5 has been reported and a deviation from a Butler-Volmer behavior at already \( \approx 75 \) mV (due to surface oxides) observed. Using this previously reported anodic transfer coefficient of 0.5 and the unambiguously determined cathodic transfer coefficient of 0.7 in this study, the micropolarization equation can be applied to extract \( i_0 \)-values on Rh (using a sum of transfer coefficients of 1.2). Our thus determined \( i_0 \)-value on the 4 nm particle size Rh/C catalyst is 2.5 mA/cm\(^2\)Rh at 293 K, in line with the \( i_0 \)-value reported on polycrystalline Rh\(_{x8}\), of 2 mA/cm\(^2\)Rh.55 Although this again attests to the good agreement between the activities evaluated in H\(_2\)-pump and SECM, it might question the above discussed hypothesis that oxophilic surfaces could have different HOR/HER activities depending on whether they present as nanoparticles or extended surfaces. Again, only a study looking at the HOR/HER particle size dependency on rhodium nanoparticles could answer this open question. The apparent activation barrier found for the HOR/HER on Rh/C is 28 \( \pm 1 \) kJ/mol, which is substantially larger than that of the most active Pt and Ir surfaces. This might be regarded as an additional barrier in the HOR/HER kinetics related to the presence of surface oxides already at the RHE potential.

**Pd/C electrode:** Finally, palladium is the least active catalyst amongst the noble metal electrodes studied here. At 293 K, its extrapolated activity is 1.3 mA/cm\(^2\)Pd, which is approximately 30 to 50 times lower than the activity of Pt (s. Fig. 14). This result indicates that Pd is actually at the limit of what could be quantified using a conventional RDE approach, as expected from Figure 7. As already detailed, however, due to hydrogen absorption issues, no literature data are available regarding the reactivity of bulk Pd crystals. When looking at the reactivity of Pd/C or Pd\(_{505}\)/Au systems (in the latter case, the substrate might also affect the Pd HOR/HER activity), the reported \( i_0 \)-values using conventional RDE measurements are in the range of 0.22 \( \pm 0.06 \) mA/cm\(^2\)Pd,31-33,106,107 which is in a reasonably good agreement with our findings. The apparent activation energy for the HOR/HER found in this study on the 3 nm particle size Pd/C catalyst is 31 \( \pm 2 \) kJ/mol, which is substantially larger than that obtained for Pt and Ir. A possible explanation for the higher activation energy on Pd than Pt could be the presence of an additional kinetic barrier due to the presence of the hydride phase at the RHE potential. If the hydride phase were to affect the HOR/HER kinetics, it might explain the large difference between the anodic and cathodic transfer coefficients for Pd (strikingly different from Pt, Ir, and even Rh). This question could possibly be clarified by looking at kinetics at higher temperatures (>353 K), where hydride absorption is expected to vanish.108 From a fundamental point of view, it would be interesting to examine the HOR/HER activity of Pd/C at temperatures where no absorption occurs at 0 V\(_{\text{RHE}}\) in order to determine the effect of H absorption on the HOR/HER kinetics.

**Conclusions**

In this study, the hydrogen oxidation and evolution reaction behavior in acidic media of carbon supported Pt, Ir, Rh and Pd electrodes has been studied. On all these surfaces, kinetic parameters including exchange current density, transfer coefficient and activation energy cannot be extracted using a classical RDE approach, since typical limiting diffusion currents in RDE are smaller than the \( i_0 \)-rates of these surfaces. Instead, when characterizing these surfaces using a H\(_2\)-pump setup, such as in this work, HOR/HER \( i_0 \)-values follow the order Pt > Ir > Rh > Pd. Taking Pt as a case study, the surface with the faster kinetics and thus the more complicated to evaluate, we have shown that the only methods allowing for low enough mass transport resistances to accurately access kinetic parameters are the H\(_2\)-pump, the scanning electrochemical microscopy and the floating vacuum carbon filtered electrode approaches.

On Pt, the transfer coefficients found at small overpotentials would point out at a Volmer reaction as rate limiting step. The HOR rate is limited at already small positive overpotentials by the Tafel step albeit no limitation of the HER by the same Tafel rate has been found. With this study, we provide a general guideline for the experimental evaluation of active HOR/HER electrocatalysts, as well as a data base for benchmarking commonly used carbon supported metal nanoparticle electrocatalysts. We will report in future communications the impact of computing mass-transport free \( i_0 \)-values (instead of RDE values) on the HOR/HER mechanism and Volcano-relationships.98,109

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