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Palladium electrodisolution from model surfaces and nanoparticles

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25 **Abstract**

26 Palladium (Pd) is considered as a possible candidate as catalyst for proton exchange
27 membrane fuel cells (PEMFCs) due to its high activity and affordable price compared
28 to platinum (Pt). However, the stability of Pd is known to be limited, yet still not fully
29 understood. In this work, Pd dissolution is studied in acidic media using an online
30 inductively coupled plasma mass spectrometry (ICP-MS) in combination with an
31 electrochemical scanning flow cell (SFC). Crucial parameters influencing dissolution
32 like potential scan rate, upper potential limit (UPL) and electrolyte composition are
33 studied on a bulk polycrystalline Pd (poly-Pd). Furthermore, a comparison with a
34 supported high-surface area catalyst is carried out for its potential use in industrial
35 applications. For this aim, a carbon supported Pd nanocatalyst (Pd/C) is synthesized
36 and its performance is compared with that of bulk poly-Pd. Our results evidence that
37 the transient dissolution is promoted by three main contributions (one anodic and
38 two cathodic). At potentials below 1.5 V_{RHE} the anodic dissolution is the dominating
39 mechanism, whereas at higher potentials the cathodic mechanisms prevail. On the
40 basis of the obtained results, a model is thereafter proposed to explain the transient
41 Pd dissolution.

42

43 Keywords: palladium, dissolution, ORR catalyst, ICP-MS, PEMFC

44 **1 Introduction**

45 Pd is a commonly used transition metal that exhibits high catalytic activity towards
46 several electrochemical processes, such as formic acid oxidation [1-3], alcohols
47 oxidation [4-6], hydrogen evolution/oxidation reactions (HER/HOR) [7-9] and
48 oxygen reduction reaction (ORR) [2, 7, 10-12]. Therefore, it is an interesting

49 candidate for low temperature fuel cells both in alkaline (alkaline fuel cell, AFC) and
50 acidic media (polymer electrolyte membrane based fuel cells, PEMFCs) [13].
51 Particularly PEMFCs are considered nowadays as attractive and efficient energy-
52 conversion devices for emission-free stationary and mobile applications, which may
53 play a primary role in the future of sustainable energy solutions [14]. However,
54 crucial issues like the high costs and rarity of catalysts for the sluggish oxygen
55 reduction reaction (ORR), for which platinum (Pt) represents the state of the art
56 catalyst, delay the commercialization on a large scale [15-17]. Great efforts have been
57 recently made to reduce the amount of Pt (i.e. via alloying) or to replace it with less
58 costly and/or more abundant non-Pt-based material [18, 19]. Pd along with Pt, stands
59 out as the metal with the smallest overpotential, i.e. highest activity, for the ORR [20].
60 Indeed, while slightly less active than Pt [7, 21], the costs are around 50% lower than
61 for Pt [10]. Furthermore, binary Pd-M (M=Cu, Co, Ni, Fe) and ternary alloys showed
62 higher activities compared to pure Pt [12, 22-27].

63 Beside activity, catalyst stability is essential to meet industrial and economical
64 requirements. Metal dissolution (along with the eventual successive re-deposition)
65 was demonstrated to be of primary importance in the course of PEMFC catalyst
66 degradation[28]. Yet, the mechanisms of noble metal dissolution processes are still
67 largely unknown, and contradictory results on the amount of dissolved metal under
68 various operation conditions and on the exact metal dissolution onset potentials are
69 often reported [29, 30].

70 The Pourbaix diagram suggests that Pd can be thermodynamically oxidized and even
71 dissolved at pH values and potentials relevant for PEMFCs[31]. However, despite the
72 similarity with Pt, Pd exhibits important differences in its electrochemical behavior.

73 Indeed, at high anodic potentials it is more prone to the formation of higher oxides
74 (i.e. PdO₂), hydrous oxide growth and oxygen absorption into the outer layers of the
75 Pd lattice, thus resulting in a higher dissolution rate compared to Pt [32, 33].

76 The nature of the oxide species formed on the Pd surface and the relation to its
77 dissolution are still under debate [30]. Contradictory results are also reported on the
78 Pd dissolution mechanism. Rand and Woods, studying the dissolution by cyclic
79 voltammetry and calculating the difference between the charge associated with
80 anodic oxidation and cathodic reduction, firstly concluded that Pd dissolution is
81 mainly an anodic mechanism [33], which was successively supported by other
82 authors [34, 35]. Vracar *et al.* proposed that the anodic dissolution is determined by
83 the transfer of a second electron to Pd(OH) species yielding PdO/Pd(OH)₂ [36]. Many
84 authors, argue instead that the Pd electrodisolution is mainly a consequence of
85 reduction of Pd oxides [30], such as Pd(OH) [34, 37-39], PdO and PdO₂ [30, 37, 40-
86 44], thus resulting in a dominant cathodic process. The electrodisolution of Pd is
87 influenced by several factors, including: (i) nature of anions and cations [30, 45, 46],
88 (ii) H absorption accompanied with formation of α and β hydrides [47, 48], (iii) pH
89 and the electrolyte concentration [30, 49, 50], (iv) high temperature by influencing
90 the solubility product [33], (v) scan rate, applied potential protocol [30, 50] and
91 surface morphology/composition [50].

92 While most of these studies suggest Pd dissolution under potential cycling, only few
93 works report time-resolved data on dissolution of Pd, which can provide a better
94 insight on the dissolution mechanisms by relating the dissolution rates with the
95 surface oxidation state. Cadle [44] and Bolzàn *et al.* [34] used a rotating ring disk
96 electrode (RRDE) to collect the dissolved Pd species (Pd²⁺ was suggested), thus they
97 were the first to study the time-resolved anodic and cathodic Pd dissolution in

98 sulfuric acid. Recently, Shrestha *et al.* [43] used a channel flow double electrode
99 (CFDE) to study Pd dissolution. CFDE is in principle similar to RRDE: gold collectors
100 in a flow configuration follow a Pd working electrode. Their system is efficacious in
101 relating the surface transitions with the dissolution in a time-resolved manner;
102 however, the direct quantitative measurement of the dissolved mass was not done.
103 Furthermore, studies at high potentials, where higher oxidation states might occur,
104 are challenging since the oxygen evolved at the working electrode causes a high
105 reduction current at the working electrode [43], thus masking the contribution of
106 dissolution. The use of a quartz crystal microbalance is also a useful approach to
107 relate online surface processes like also Pd dissolution in a quantitative way as shown
108 by Grdeń *et al.* and Łukaszewski *et al.* [51, 52]. Nevertheless, a study of the dissolution
109 also in the oxygen evolution potential region has not been done despite its
110 fundamental interest, as it is known that these two processes are closely related [53].
111 Additionally, the vast majority of these works only deal with bulk Pd, whereas the
112 stability of high-surface-area catalysts used in real applications has not been studied
113 thoroughly so far [54, 55].

114 In recent years, the implementation of an electrochemical scanning flow cell (SFC)
115 combined with time-resolved monitoring of the dissolved species present in the
116 electrolyte by using an on-line inductively coupled plasma mass spectrometer (ICP-
117 MS) provided new insights on the dissolution of noble metals like Pt [56, 57] and Au
118 [58, 59]. Nevertheless, even if perceived to be of paramount importance [43], a
119 detailed study of the dissolution mechanism of Pd and the influence of the applied
120 operational conditions has not been done with this technique yet.

121 In this context, we present here a first investigation on Pd dissolution with the
122 coupled SFC/ICP-MS approach. In particular, we analyze the influence of fundamental
123 parameters such as the upper potential limit (UPL), the scan rate and the anions in
124 commonly used acid electrolytes (sulfuric and perchloric) on the dissolution process.
125 Additionally, we compare the dissolution of bulk poly-Pd with a supported Pd/C
126 catalyst, to validate the results for high-surface area catalysts. Based on the
127 experimental outcome of this comprehensive study we suggest a mechanism for Pd
128 dissolution, even though the exact chemistry of the Pd oxidation is not yet completely
129 resolved.

130 **2 Experimental**

131 **2.1 Nanoparticles synthesis, characterization**

132 The carbon supported Pd was prepared via a colloidal immobilization method
133 described in a previous publication [60]. Initially, the desired amount of a PdCl₂
134 aqueous solution (from Johnson Matthey) was used to prepare a Pd colloidal
135 suspension. Separately, an aqueous solution of NaBH₄ (0.1 M) and Poly(vinyl alcohol)
136 (PVA) (1 wt% aqueous solution, Aldrich, MW=10 000, 80% hydrolyzed) were
137 prepared as well, and a precise amount of which was then mixed with the PdCl₂
138 solution: for the PVA solution (1 wt%) was needed (PVA/(Pd) (w/w)=1.2), whereas
139 for the NaBH₄ solution (0.1 M, NaBH₄/(Pd) (mol/mol)=5) was added. After 30 min, a
140 dark-brown sol is generated. To immobilize the formed colloid an activated carbon
141 (XC72R Vulcan carbon) was added to the colloidal solution and acidified at pH 1 by
142 sulfuric acid (the amount of carbon was calculated to yield a final 10 wt% of final
143 metal/carbon loading). After 2 h of vigorous stirring, the slurry was filtered and

144 washed with distilled water thoroughly. Finally, the catalyst was dried at 120 C for
145 16 h obtaining a dry catalyst powder.

146 The synthesized Pd/C powder was thereafter dispersed in ultrapure water (UPW,
147 PureLab Plus system, Elga, 18 M Ω ·cm) obtaining a black homogeneous ink suspension
148 that was easily printed into glassy carbon (GC) plates or RDE tip. Prior to any
149 electrochemical measurement, a small droplet of ink was deposited onto a TEM grid
150 (lacey carbon film supported by a gold grip from Plano GmbH) and examined by
151 transmission electron microscopy (TEM, JEOL JEM-2200FS operated at 200 kV in
152 STEM mode). From the bright field TEM micrograph obtained, the particle size
153 distribution was determined.

154 **2.2 Electrode preparation**

155 Before each experiment, the poly-Pd disk electrode was polished thoroughly with 0.3
156 and 1 μ m alumina on a polishing cloth (Strueurs, MD Mol), followed by washing in
157 ultrapure water and drying in argon, obtaining a shiny Pd surface.

158 To prepare the high-surface-area Pd/C electrodes the catalyst ink was printed onto
159 freshly mirror-polished GC plates by mean of a drop-on-demand printer (Nano-
160 PlotterTM 2.0, GeSim). The Nano-Plotter allows the printing in rapid succession of
161 catalyst layers using a piezoelectric pipette. Each layer consisted of 100 drops whose
162 volume was estimated during the measurement (250 pL) and it consist of a circular
163 deposits of a Pd/C catalyst. Two layers were used for all experiments corresponding
164 to approximately 5 ng of metal.

165 **2.3 Electrochemical characterization**

166 The majority of the results on the Pd electrochemical dissolution experiments were
167 obtained using a scanning flow cell (SFC) described in our previous works [57, 58].

168 The electrolytes employed were gas (Ar) purged 0.1 M H₂SO₄ and 0.1 M HClO₄. These
169 were prepared from concentrated acid (Suprapur®, Merck) diluted in UPW (PureLab
170 Plus system, Elga, 18 MΩ·cm). A poly-Pd disk (5 mm diameter from MaTeck) and the
171 synthesized Pd/C catalyst deposited onto the GC plate were used as working
172 electrodes (WE). The aperture of the SFC cell is 0.01 cm², slightly larger than the size
173 of the printed spots, thus the SFC was approached easily to the single spot.
174 Dissolution results for poly-Pd in the two considered electrolytes are normalized with
175 the geometrical surface area (S_{geo} in cm_{geo}⁻²). For the comparison between poly-Pd
176 and Pd/C, instead, dissolution is normalized to the real surface area (S_{real} in cm_{real}⁻²).
177 The S_{real} is obtained using the Pd-oxide reduction charge of the last activation CV with
178 an UPL of 1.4 V_{RHE} with the surface charge of 424 μC cm⁻² [30]. The three-electrode
179 configuration was completed with a graphite rod as counter electrode and an Ag/AgCl
180 as reference electrode. A LabVIEW-based, in-house developed, software controlled
181 the potentiostat (Gamry Reference 600, USA) and all experimental parameters. The
182 chosen electrolyte was flowing through the SFC (flow rate of 180 μL min⁻¹) and then
183 downstream to an inductively-coupled plasma mass spectrometer (ICP-MS, NexION
184 300X, Perkin Elmer) where the dissolved element is detected. The quantitative
185 evaluation of the dissolved ¹⁰⁶Pd was achieved using as internal standard ¹⁰³Rh.

186 The poly-Pd cyclic voltammograms in the two electrolytes were also studied with a
187 rotating disk electrode (RDE) method, for an initial comparison to validate the SFC
188 system. A in-house-built three electrode electrochemical cell with separate
189 compartment made of Teflon® was employed (for details see ref. [61]). The working
190 electrode was a Pd disk of 5 mm diameter (from MaTeck), whereas, as for the SFC,
191 graphite rod and an Ag/AgCl were used as counter and reference electrode,
192 respectively.

193 The experiments were carried out only at room temperature ($\approx 24^\circ\text{C}$) and all the
194 potentials reported in this work are referred to the reversible hydrogen electrode
195 (RHE), which was measured prior to each single experiment.

196

197 **3 Results**

198 **3.1 Oxidation and reduction of poly-Pd in acidic media**

199

200 Pd cyclic voltammograms in deaerated solution (Figure 1) are recorded using the
201 SFC with perchloric and sulfuric acid as electrolytes. The curves show typical profiles
202 for a poly-Pd electrode in the aqueous acidic solutions. The Pd electro-oxidation in
203 0.1M HClO_4 commences in the anodic scan at approximately $0.7 V_{\text{RHE}}$ (A_1 peak). A
204 well-defined oxide reduction peak with a maximum around $0.64 V_{\text{RHE}}$ is visible below
205 $0.8 V_{\text{RHE}}$ (C_1 peak) in the cathodic scan direction, in agreement with other works [30,
206 48, 62, 63]. Typically a second poorly defined peak for oxide-reduction around $1.2\text{-}1.3$
207 V_{RHE} is reported in literature (here, C_2 peak), which is thought to correspond to the
208 reduction of Pd(IV)-oxide formed at high potentials [30, 63]. In the CVs in Figure this
209 broad peak, though labelled, is not visible due to the low upper potential limit (UPL)
210 applied. However, it will be important in the following sections, where the dissolution
211 at higher UPLs (up to $1.8 V_{\text{RHE}}$) is presented and discussed.

212 Interestingly the CVs show a distinct difference in the Pd oxidation/reduction in the
213 two different electrolytes. Indeed, the onset potential for the electro-oxidation of Pd
214 in sulfuric acid (ca. $0.75 V_{\text{RHE}}$) is slightly shifted compared to perchloric acid (Figure
215 1). This is consistent with the difference in anion adsorption strength, which is known
216 to influence the Pd electro-oxidation [30]. According to Solomun, perchlorate anions

217 (ClO₄⁻) do not undergo specific adsorption so that only weak (electrostatic)
218 interactions occur between the anions of the electrolyte and the Pd electrode surface,
219 while the interaction of other anions such as the (bi-)sulfate anion (HSO₄⁻/SO₄²⁻) is
220 stronger [40-42]. Furthermore, in sulfuric acid, the Pd reduction peak is slightly
221 shifted to higher anodic potentials (0.67 V_{RHE}) and the associated charge is slightly
222 higher. A more detailed discussion on Pd oxidation will be provided in the final part
223 of the present work and the interested reader is also referred to the critical review on
224 Pd literature of Grdeń et al. [30].

225 Pd voltammograms with a lower potential limit (LPL) of 0.05 V_{RHE} are also recorded
226 in an SFC and compared with RDE measurements to validate the results (SI). At low
227 potentials (E<0.3 V_{RHE}) a large cathodic current originates from the concurrent H
228 adsorption and bulk absorption, with the formation of Pd hydride. Indeed, unlike Pt,
229 Pd absorbs hydrogen in a potential range where the under potential deposition of H
230 (H_{UPD}) as well as the hydrogen evolution (HER) occurs [30, 64]. At higher potentials
231 than HER, the desorption of the absorbed hydrogen (H_{abs}) in the poly-Pd bulk
232 structure takes place. This results in a large anodic current, which overlaps with other
233 anodic processes at the surface.

234 **3.2 Poly-Pd electrodisolution in different acidic media: influence of UPL**

235 Potential sweeps to increasing upper potential limits (UPL) in two different acidic
236 media (perchloric and sulfuric acid) are applied to poly-Pd electrode. The potential
237 program and the corresponding dissolution profile are presented in Figure 2 a-b,
238 respectively.

239 The cleaning cycles (30 CVs at 200 mV s⁻¹) are characterized by an initially higher Pd
240 dissolution signal, which is probably due to the contribution of initially present

241 surface defects. After approximately 10 CVs a constant Pd dissolution signal and a
242 stable CV is measured, indicating that a clean, steady surface state for this potential
243 window is obtained.

244 During the slow potential cycling (10 mV s^{-1}), Pd dissolution is observed at potentials
245 where Pd oxidizes ($E > 0.7 V_{\text{RHE}}$) and a small deviation from the background signal is
246 observable first with an UPL above $0.8\text{-}0.85 V_{\text{RHE}}$, in line with the onset potential
247 shown by Łukaszewski *et al.* obtained with the quartz microbalance [52]. The amount
248 of formed Pd oxide and thus the dissolution increase with the applied UPL. In fact, the
249 charge associated to the reduction peaks increases gradually with potential (Figure 2
250 c-d and SI). Furthermore, the hysteresis between anodic and cathodic scan increases
251 as the C_1 reduction peak shifts to lower potentials. A similar behavior was observed
252 also for Pt [57], and its origin is not fully understood at present [30]. At different UPL
253 up to three different peaks in the Pd dissolution profile (corresponding to the peak
254 anodic A_1 and cathodic C_2 , C_1 respectively) can be observed. A comparison of the mass
255 dissolved during the anodic and the two cathodic contributions to the transient
256 dissolutions in the two acids are shown in Figure 3.

257 The cathodic dissolution peaks (C_2 and C_1) increase constantly (Figure 3 a-b) with
258 increasing UPL as more oxide is formed, with C_2 becoming the dominating
259 contribution at high potential. Instead, the anodic contribution (A_1) to the transient
260 dissolution behaves differently (Figure 3 c). Indeed, it is possible to identify different
261 stages in the anodic transient dissolution behavior: (i) A first immune region at
262 potentials lower than Pd oxidation; (ii) a region between 0.8 and $1.4 V_{\text{RHE}}$ where the
263 transient anodic dissolution is increasing with the UPL; (iii) a region in the $1.4\text{-}1.7$
264 V_{RHE} potential range, where the transient anodic dissolution is constant

265 (independently of the UPL), due probably to the oxide coverage that lead to
 266 passivation and (iv) a region for potential higher than 1.7-1.8 V_{RHE} , where the
 267 transient anodic dissolution increases again and could be attributed to the surface
 268 change in the OER potentials. Anodic passivation is also confirmed by the decay in the
 269 dissolution signal during potentiostatic (steady-state) experiment (SI).

270 The quantitative total dissolution of Pd per cycle is reported in Table 1, along with the
 271 measured dissolution of Pt and Au under similar conditions. Comparing the
 272 dissolution in the same medium (sulfuric acid), it turns out that Pd is dissolving at a
 273 much higher rate than the other noble metals considered. Furthermore, Pd in sulfuric
 274 acid dissolves 5 times more than in perchloric acid. Similar trends were reported in
 275 other works [30, 33, 52] and it was attributed to the formation of different complexes
 276 between the dissolved species and the anion in the electrolyte (see discussion).

277 **Table 1 Comparison of the amount of Au, Pt [58], Pd in 0.1M H₂SO₄ and Pd* in**
 278 **0.1M HClO₄ dissolved per cycle depending on the applied UPL as derived from**
 279 **potential sweep experiments at 10 mV s⁻¹. BDL stands for below the detection**
 280 **limit.**

UPL / V_{RHE}	Au / ng cm _{geo} ⁻² cycle ⁻¹	Pt / ng cm _{geo} ⁻² cycle ⁻¹	Pd / ng cm _{geo} ⁻² cycle ⁻¹	Pd* / ng cm _{geo} ⁻² cycle ⁻¹
0.9	BDL	BDL	0.36	0.02
1.0	BDL	BDL	5.1	0.8
1.1	BDL	0.4	21.3	4.8
1.2	BDL	1.3	51.5	12.9
1.3	BDL	2.7	83.6	18.9
1.4	1.6	4.4	114.2	22.3

1.5	4.4	5.8	149.9	26.6
1.6	7.4	7.0	185.8	32
1.7	12.5	8.0	224.4	39
1.8	20	9.0	271.7	50

281

282 Note that until 1.1 V_{RHE} only a single dissolution peak is visible in both electrolytes,
 283 while at more positive potentials two to three peaks are observed. However, the
 284 applied scan rate (10 mV s^{-1}) does not allow a clear separation between the individual
 285 dissolution peaks. Therefore, some measurements at selected UPLs with a slower
 286 scan rate (2 mV s^{-1}) are presented in the next paragraph.

287 **3.3 Poly-Pd electro dissolution in different acidic media: slower scan rate**

288 Potential sweeps to increasing UPL (0.9, 1.2, 1.5, 1.8 V_{RHE}) in the two different acidic
 289 media (perchloric and sulfuric acid) with a 2 mV s^{-1} scan rate are applied to a poly-Pd
 290 electrode (Figure 4 a-b). At this slow scan rate the different dissolution processes
 291 occurring during cyclic voltammetry can be clearly distinguished. As expected, due to
 292 the slower scan rate, the dissolution per cycle is higher; furthermore, the observed
 293 quantitative difference between dissolution in perchloric and sulfuric acid is
 294 confirmed (see values in SI).

295 Colored arrows mark the positions of the peaks: red corresponding to the anodic
 296 oxidation/dissolution (A_1), grey and blue corresponding to the two cathodic
 297 reduction/dissolution peaks (C_2 and C_1 respectively). For the sake of clarity, the single
 298 dissolution profiles are shown separately in SI.

299 The UPLs are chosen in order to distinguish dissolution processes occurring at
 300 different potentials. (i) At a potential lower than 1.1 V_{RHE} only one peak is present as a

301 combined minor anodic and cathodic peak. (ii) In the potential range between 1.1 and
302 1.4 V_{RHE} a shoulder peak related to the cathodic dissolution due to the C_1 reduction
303 starts to appear (blue arrow). With the measured UPL of 1.2 V_{RHE} the maximum of
304 this second peak is measured at 0.8 V_{RHE} during the cathodic scan, which well
305 corresponds to the C_1 peak observed in CV with the same UPL. (iii) At more positive
306 potentials a third dissolution peak between the two is appearing (gray arrow) and is
307 increasing dramatically. With an UPL of 1.5 V_{RHE} the maximum of this third peak is
308 measured at 1.1-1.2 V_{RHE} during the cathodic scan, which matches the broad
309 reduction peak C_2 observed in the CVs.

310 The mass cyclic voltammograms of these 4 CVs in perchloric and sulfuric acid are
311 shown in Figure 4 c-d, indicating the trend of the three different contributions (one
312 anodic and two cathodic) to the dissolution more clearly. At potentials up to 1.5 V_{RHE}
313 the three peaks are not perfectly separated, despite the very low scan rate (2 mV s^{-1}),
314 while at 1.8 V_{RHE} the anodic dissolution and the first cathodic dissolution peaks
315 appear nicely distinguished. Furthermore, the anodic dissolution maxima appear to
316 be at the same potential for all the four cycles, whereas the cathodic dissolution
317 maxima shift to lower potentials in accordance with the shifts of the reduction peaks
318 (Figure 2 c-d). These shifts are attributed to the irreversibility of the oxide formation
319 [30] and are reported also for other noble metals [57, 65]. Interestingly, in sulfuric
320 acid the dissolution maximum appears to be before the reduction maximum (the
321 former is approximately 30 mV higher; see SI). Similar findings were also obtained for
322 Pt cathodic dissolution in sulfuric acid [66]. In perchloric acid, instead, the two peak
323 potentials correspond well. This difference is not well understood at present and it
324 might derive from the different interactions of the electrolyte anion with Pd. Along

325 with the change in the maxima, also the cathodic dissolution onset potentials are
326 shifting to lower potentials with increasing UPL.

327 These results allow us already to dissipate some controversy about the nature of Pd
328 dissolution. As discussed in the introduction, there is an ongoing debate whether Pd
329 dissolution is an anodic process or not. The relative contribution to the dissolution of
330 the three different peaks is shown in the inset of Figure 4 c-d. At low UPL the process
331 is predominantly anodic (note that however below 1.1 V_{RHE} only one peak is
332 appearing and is not possible to distinguish between anodic and cathodic
333 dissolution). Increasing the UPL it first appear the peak C_1 and above 1.4 V_{RHE} the
334 peak C_2 . In perchloric acid with an UPL of 1.8 V_{RHE} the anodic contribution is reduced
335 to around 37% (A_1) and the cathodic rises up to 63% (52 and 11% for C_2 and C_1
336 respectively). Thus, with increasing UPL the transient dissolution of Pd switches from
337 an anodic process to a process dominated by Pd-oxide reduction. Moreover, at
338 potentials where the OER becomes relevant the C_2 reduction/dissolution process
339 becomes dominant.

340

341 **3.4 Comparison of poly-Pd and Pd/C electrodisolution**

342 In order to estimate the value of the previous results obtained on poly-Pd for real
343 application, carbon supported Pd nanoparticles (Pd/C) are synthesized and analyzed.
344 Firstly, representative bright field TEM micrographs are acquired and the statistical
345 size distribution is evaluated (Figure 5 a). The average particle size is ca. 4.0 nm,
346 which corresponds to an electrocatalytic surface area (ECSA) of 124 $m^2 g^{-1}$ (see SI for
347 calculation). The synthesized Pd/C catalyst powder is dispersed through sonication in

- 348 ultrapure water (UPW) and the prepared ink is printed on a glassy carbon (GC) plate
- 349 obtaining spots that are measured using the SFC.

350 The Pd/C dissolution measurement (Figure 5 b-c) follows the same protocol reported
351 in Figure 4 and is performed only in perchloric acid with two printed catalyst layers
352 (ca. 5 ng). This corresponds to an initial Pd/C catalyst surface area of 0.0062 cm²
353 (estimated from the TEM size distribution and the loading in SI). Electrochemical
354 evaluation from the Pd-oxide reduction charge of the first CV [0.1-1.4 V_{RHE}] of freshly
355 prepared Pd/C electrode, yields a surface area of 0.0054 cm² (see SI). The
356 electrochemical determination of the surface area through Pd-oxide reduction is
357 convenient but not straightforward as it requires a precise knowledge of the potential
358 formation of 1 oxide monolayer (ML). In the literature, this is indicated to be for
359 polycrystalline Pd in the range 1.4-1.5 V_{RHE}, even though lower values are also
360 reported [30, 67]. To compare the electrochemical dissolution of two different
361 systems like bulk and nanoparticulate Pd, the dissolution data shown in Figure 5 b-c
362 are normalized by the real surface area (S_{real}), which is 0.0109 and 0.0035 cm² for
363 poly-Pd and Pd/C respectively. This is determined from the Pd-oxide reduction of the
364 last activation cycle ([0.1-1.4] V_{RHE}), which directly precede the dissolution
365 measurement. Pd-oxide reduction and thus S_{real} during activation of Pd/C decrease by
366 ca. 35% indicating a surface area change due to catalyst degradation. At low
367 potentials, the poly-Pd and Pd/C CVs show one interesting difference between
368 catalysts: unlike poly-Pd, Pd/C does not show a large cathodic current and anodic
369 peak corresponding to the H bulk absorption (inlet in Figure 5 b). This behavior was
370 already known in literature and was reported to be size dependent [68, 69].

371 Potential sweeps to increasing UPL (0.9, 1.2, 1.5 V_{RHE}) in perchloric acid with a 2 mV
372 s⁻¹ scan rate are applied to poly-Pd and Pd/C (Figure 5 b-c). The same feature for
373 poly-Pd, namely the presence of up to three peaks in the dissolution profile are also
374 observed for Pd/C. While the anodic peak A₁ and cathodic peak C₂ well correspond,

375 the cathodic dissolution C_1 is shifted for Pd/C to lower potentials (time delay in
376 Figure 5 c). The peak position generally depends on different parameters such as the
377 mass transfer of dissolved species out of the carbon matrix, the flow rate and scan
378 rate. While the last two are the same in both measurements, the amount of printed
379 Pd/C catalyst is so low that the mass transfer limitation can be neglected. A more
380 valuable explanation relates to the shift of the reduction to lower potential for Pd/C
381 (see inlet CVs in Figure 5 b).

382 Considering the quantitative dissolution, it is observed a slightly higher dissolution
383 per electrochemical real surface area in the case of nanoparticulate Pd/C catalyst
384 (Figure 5 c) at all considered potentials. Only few works are reported in the literature
385 of nanoparticulate palladium dissolution and to the knowledge of the author no on-
386 line detection of dissolved Pd from nanoparticles is reported. Generally they indicate
387 influence of surface morphology, geometry and particle sizes [54, 55]. Kumar *et al.*
388 studying the anodic oxidation onset potential in presence of chlorides suggested a
389 size dependent destabilization of the nanoparticles compared to bulk Pd [55]. In our
390 case, we do not see any significant difference in dissolution onset potential between
391 the two electrode systems, but the dissolution profiles suggest a small difference in
392 their behavior. Note however that a precise quantitative evaluation is rather
393 challenging especially when dealing with nanoparticulate catalyst. Indeed, (i) the S_{real}
394 is determined with the same electrochemical method for both catalyst even though
395 the precise potential of formation of 1 oxide ML can slightly change with surface
396 morphology and geometry. Indeed, with same UPL the oxide formation and reduction
397 might be different from nanoparticles and bulk Pd [55]. Furthermore, (ii) S_{real} of Pd/C
398 might change during measurement in consequence of dissolution and catalyst
399 degradation (even though measurements are limited to 3 cycles to minimize

400 degradation). Furthermore, (iii) remaining PVA from synthesis might influence the
401 dissolution (even though the washing step is expected to remove it). Finally, (iv) for
402 carbon supported nanoparticles the catalyst loading in the experiment might also
403 play a role as shown recently by Keeley *et al.* [29]. Indeed, the authors showed for
404 Pt/C that the specific dissolution (normalized per surface area) is decreasing when
405 the loading increases. This phenomenon was attributed to the decreased diffusion of
406 Pt ions into bulk solution as ions remain trapped in the porous catalyst deposit when
407 loading is higher.

408 **4 Discussion**

409 The major experimental findings of this work can be summarized as follow:

- 410 (i) The Pd dissolution is strictly correlated to the oxide formation and
411 reduction. However, no simple correlation could be established between
412 the two processes. Indeed, the dissolution onset potential in perchloric acid
413 appears to be around 50 mV higher than in sulfuric acid, whereas the
414 oxidation onset potential in perchloric acid is slightly lower (Figure 1);
- 415 (ii) Below 1.1 V_{RHE} it was not possible to differentiate between anodic and
416 cathodic processes. Between 1.1 and 1.4 V_{RHE} a cathodic dissolution related
417 to the C_1 reduction is observed. At more positive potentials a third
418 dissolution peak, corresponding to the broad C_2 reduction, appears and it
419 increases dramatically with the UPL (Figure 2-4).
- 420 (iii) Increasing the UPL, the oxide coverage increases. Therefore, while
421 transient anodic dissolution initially increases with UPL, in the 1.4-1.7 V_{RHE}
422 potential range the formed oxide protects Pd from increasing dissolution.

423 Beyond 1.7-1.8 V_{RHE} anodic dissolution increases again in correspondence
424 to the OER region (Figure 3);

425 (iv) Unlike for anodic dissolution the cathodic dissolution increases almost
426 linearly with UPL (Figure 3), becoming the dominant process for potential
427 higher than 1.7 V_{RHE} . Furthermore, its onset and maxima shifts to lower
428 potentials with increasing UPL (Figure 4), in accordance with the shift of
429 the cathodic C_1 and C_2 reduction peaks (Figure 2);

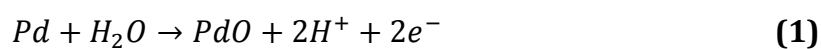
430 (v) Pd dissolves much more than Pt and Au and the dissolution depends
431 strongly on the scan rate. Pd dissolution in sulfuric acid was found to be 5
432 times higher than in perchloric acid (Table 1);

433 (vi) In potentiostatic experiments below 1.6 V_{RHE} the dissolution rate decreases
434 with time, indicating the passivation of the surface (SI);

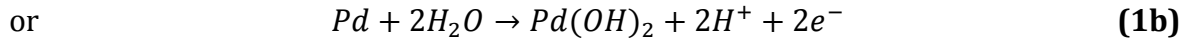
435 (vii) All these findings were additionally validated for a carbon supported high-
436 surface area Pd/C nanocatalyst, which is more interesting for application. A
437 slightly small increase in dissolution per real surface area is observed for
438 Pd/C (Figure 5).

439

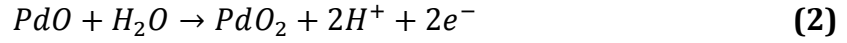
440 With our findings we confirmed the close connection between the Pd oxidation states
441 and its transient dissolution, which was already observed for Au and Pt electrode
442 materials [59]. Indeed, the electrochemical oxidation and the dissolution of Pd have
443 similar standard potentials. Pourbaix expressed the oxidation of Pd as [31]:



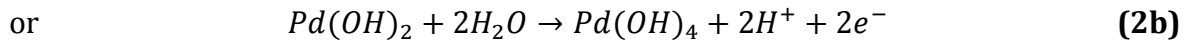
$$E^o = 0.917 + 0.0591 \log[H^+]$$



$$E^o = 0.897 + 0.0591 \log[H^+]$$



$$E^o = 1.263 + 0.0591 \log[H^+]$$



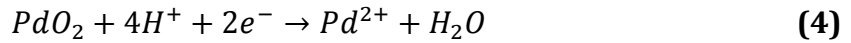
$$E^o = 1.283 + 0.0591 \log[H^+]$$

444

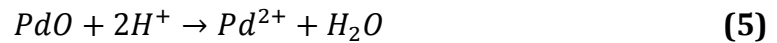
445 And the dissolution of Pd can be described as [31]:



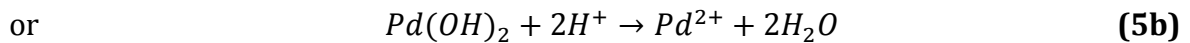
$$E^o = 0.987 + 0.0295 \log[Pd^{2+}]$$



$$E^o = 1.194 + 0.1182 \log[H^+] - 0.0295 [Pd^{2+}]$$



$$\log[Pd^{2+}] = -3.02 + 2 \log[H^+]$$



$$\log[Pd^{2+}] = -2.35 + 2 \log[H^+]$$

446

447 As anticipated, despite the large amount of literature and the variety of methods

448 applied, several aspects of Pd electro-oxidation are still poorly understood, such as

449 the chemical composition, thickness and adsorption behavior of Pd oxide layers [30].
450 In particular, there are some relevant issues in the literature that require additional
451 research [30]: (i) the first product formed during oxidation was considered by several
452 authors to be Pd(OH_{ads}) [34, 38, 39, 48, 63, 70], while other authors suggested the
453 formation of Pd(II)-oxide/hydroxide species such as PdO [30, 71] or Pd(OH)₂ [31]; (ii)
454 the potential for the formation of an oxide monolayer (generally reported to occur
455 around 1.45-1.5 V_{RHE}) is unclear, as is (iii) the onset potential for the formation of
456 higher oxidation species (i.e Pd(IV)-oxide, thicker β Pd(IV)-oxide in the OER region);
457 (iv) the presence of subsurface oxygen is claimed by some groups to play an
458 important role in the reactivity and stability of the metal [32, 41, 72] and (vi) it is not
459 obvious if anhydrous/hydrous oxide is present or not at different potentials.
460 Concerning the last point, we will consider both reactions (equations 1-1b and 2-2b),
461 but in the following discussion we will rather talk of Pd(II)- and Pd(IV)-oxides.

462 In the literature two Pd reduction peaks are reported: (i) a well-defined reduction
463 peak at lower potentials labeled here as C₁ (Figure 1) that corresponds to the
464 reduction of Pd(II)-oxide (equation 1-1b) and (ii) a second broad reduction peak
465 around 1.2-1.3 V_{RHE} (here, C₂), which is thought to correspond to the reduction of
466 Pd(IV)-oxide formed at high potentials (>1.3 V_{RHE}), slightly below the OER onset [30,
467 63] (equation 2-2b). This higher oxidation state was confirmed with XPS
468 measurement by Chausse *et al.* [73]. Zhang *et al.* and Birrs *et al.* showed
469 independently that a thick Pd “β hydrous oxide” [62, 65, 74] is only formed at very
470 large anodic polarization (higher than the OER onset) and its reduction is correlated
471 to several peaks in the low potential region, around H_{UPD} [30, 32, 65]. In our
472 experimental results no peaks of this kind are observed up to 1.8 V_{RHE}, therefore the
473 presence of a thicker hydrous oxide layer (elsewhere referred as β oxide [30]) can be

474 safely excluded from the following considerations, at least for potentials up to 1.7
475 V_{RHE} .

476 According to the literature and to cyclic voltammetry one would expect already some
477 Pd dissolution in parallel with the initial Pd oxidation, namely around 0.7 V_{RHE} and
478 0.75 V_{RHE} in perchloric and sulfuric acid respectively (Figure 1). However, a small
479 deviation from the background signal is only observable first with an UPL above 0.8-
480 0.85 V_{RHE} , close to the thermodynamically predicted standard potential for Pd metal
481 electro-dissolution ($E^0(\text{Pd}/\text{Pd}^{2+}) = 0.987 \text{ V} + 0.0295 \log(\text{Pd}^{2+})$), which assuming a
482 reasonable Pd^{2+} concentration of 1 nmol dm^{-3} would be approximately 0.72 V_{SHE} (0.78
483 V_{RHE} at $\text{pH}=1$). Experimentally, there is a more than 100 mV shift for the dissolution
484 onset in comparison to oxidation. A similar difference was already observed for Pt
485 dissolution and it was tentatively related to the ICP-MS detection limit. Recently, a
486 modified scanning flow cell configuration allowed the accumulation of dissolved Pt.
487 Thus, dissolution was measured also at potential, close to the Pt oxidation onset [56].
488 In the case of Pd this difference could be attributed either to the ICP-MS detection
489 limit (as for Pt) or to the higher standard potential of the Pd electro-dissolution
490 compared to the Pd oxidation. Furthermore, the dissolution onset potential in
491 perchloric acid appeared to be around 50 mV higher than in sulfuric acid. This is
492 somehow contradictory with the oxidation onset potential which in perchloric acid is
493 lower (Figure 1). Therefore, no simple correlation between oxidation and dissolution
494 is established, as previously observed for Au in perchloric and sulfuric acid [75].

495 Interestingly, despite exhibiting similar features, the actual measured Pd dissolution
496 in the two different electrolytes is quantitatively very different. Indeed, Pd in sulfuric
497 acid is dissolving at rates approximately 5 times higher than in perchloric media
498 (Table 1). Furthermore, comparing the dissolution in the same medium (sulfuric

499 acid), it turns out that Pd is dissolving at a much higher rate than other noble metals
500 like Pt and Au. Already Rand and Woods [33] reported Pd dissolution to be
501 approximately 30 times higher than Pt in sulfuric acid, in good agreement to our
502 results. Much higher dissolution of Pd compared to Pt was also observed by
503 Łukaszewski *et al.* [52]. Burke *et al.* [32] affirmed that this marked behavior is related
504 to the ionic radii difference of the respective cations. In fact, the electrostatic field
505 around smaller Pd cations is stronger, which leads to more stable Pd complexes and a
506 stronger solvation shell [30], resulting in the observed enhancement in Pd electro-
507 dissolution. The observed Pd dissolution difference in the two acidic electrolytes
508 could be attributed to a difference in the amount of oxide formed in the considered
509 media. Effectively, the UPL being equal, the measured Pd reduction charge in sulfuric
510 acid (Figure 2 c) is visibly higher than in perchloric (Figure 2 d), suggesting less oxide
511 formation with the latter. However, the difference in the reduction charges is only up
512 to ca. 20% (SI). Therefore, different dissolution behavior could be originated by the
513 different nature of the anions in the electrolyte. In the literature, many works
514 reported enhanced electro-dissolution in presence of chlorides and iodides [30, 37,
515 38], however only few works reported differences between perchloric and sulfuric
516 acid, the latter being the sole choice of electrolyte for most of the experimental
517 studies. Recently, Grdeń *et al.* [30] reviewed several Pd studies and classified anions
518 on the basis of their Pd electro-dissolution promotional effect as follows: $\text{ClO}_4^- <$
519 $\text{HSO}_4^-/\text{SO}_4^{2-} < \text{Cl}^- < \text{I}^-$. Anions like Cl^- and I^- form stable Pd-anion complexes that can
520 lead to an increase in dissolution [30]. Solomun, studying the role of anions in H_2SO_4
521 and HClO_4 with LEED and XPS, suggested that the adsorbed anion can weaken the Pd-
522 Pd surface bonds [30, 42]. They also proposed that the adsorption of $\text{HSO}_4^-/\text{SO}_4^{2-}$ in
523 the early stages of surface oxidation facilitates the interfacial place exchange [40-42],

524 thus resulting in enhanced Pd dissolution in the case of $\text{HSO}_4^-/\text{SO}_4^{2-}$, as confirmed
525 with our experimental findings. Furthermore, the dissolved Pd^{2+} can form in acidic
526 electrolytes stable complexes, that if on the one hand can explain the enhanced
527 electro-dissolution of Pd compared to Au and Pt, on the other hand can be at the
528 origin of the different electro-dissolution in HClO_4 and H_2SO_4 .

529 Even though the absolute amount of dissolved Pd per cycle is quite different in the
530 two electrolytes (see Table 1), the percentage contribution of the different dissolution
531 peaks follow qualitatively the same trend. (i) Below $1.1 V_{\text{RHE}}$ only one peak is present,
532 as at these low potentials it is not possible to distinguish between anodic and
533 cathodic dissolution. (ii) Between $1.1\text{-}1.4 V_{\text{RHE}}$ a dissolution peak corresponding to
534 the cathodic reduction C_1 is appearing and becoming more and more important. This
535 dissolution peak is observed in the literature with different techniques as RRDE [34,
536 44], CFDE [43] and quartz microbalance [51, 52] referred in the literature to Pd(II)-
537 oxide reduction [30]. However, the Pd(II)-oxide can only undergo chemical
538 dissolution (equations 5-5b), which is generally disregarded for other metals like Pt.
539 The Pd solubility is higher than that of Pt and this could mean that, unlike for Pt, the
540 chemical dissolution might play a role for Pd. Nevertheless, the experimental results
541 indicate an existing correlation between the Pd(II)-oxide reduction (C_1) and the
542 dissolution peak, which cannot be easily explained only with chemical dissolution.
543 Therefore, the dissolution has been often attributed to the reduction and desorption
544 of adsorbed oxygen species that causes de-passivation (equation 3). (iii) At $1.4 V_{\text{RHE}}$ a
545 second cathodic dissolution peak corresponding to the broad Pd(IV)-oxide reduction
546 (C_2) is observed (equations 2-2b). Even though the integration of such a broad peak is
547 not easy, we can safely say that even at high UPL the amount of Pd(IV)-oxide formed
548 is less than the amount of Pd(II)-oxide formed (C_2 reduction charge density is much

549 smaller than C_1 reduction charge density as shown in SI). On the other hand, the
550 amount of dissolved Pd related to Pd(IV)-oxide reduction (C_2) is much larger than the
551 dissolved Pd related to Pd(II)-oxide reduction (C_1) (Figure 3). (iv) Above 1.7 V_{RHE} the
552 cathodic dissolution overall exceeds the anodic dissolution. In particular, at 1.8 V_{RHE}
553 the cathodic dissolution associated to the Pd(IV)-oxide reduction (C_2) becomes the
554 dominant dissolution mechanism.

555 Interesting is the trend of the transient anodic Pd dissolution with different UPLs as
556 shown in Figure 3, where different potential regions can be observed in the two
557 electrolytes. Above 0.9 V_{RHE} Pd oxidation to Pd(II)-oxide (equations 1-1b) and Pd
558 metal dissolution to Pd^{2+} (equation 3) are proceeding in parallel and upon an increase
559 in UPL the transient anodic dissolution increases. Between 1.4 and 1.7 V_{RHE} no
560 increase in transient anodic dissolution is observed. This can have two reasons: (i)
561 Around 1.3-1.4 V_{RHE} a complete monolayer of Pd(II)-oxide is formed, thus preventing
562 further Pd metallic dissolution (through equation 3). In the literature, different
563 studies generally agree that the complete formation of a monolayer occurs between
564 1.4-1.5 V_{RHE} [30]. However, in this case the chemical dissolution of Pd(II)-oxide
565 (equations 5-5b) would still be present in contrast to the observed passivation.
566 Therefore, either the chemical dissolution can be disregarded (as for Pt), or the
567 passivation arises from (ii) the formation of a top layer of chemically stable Pd(IV)-
568 oxide, which is reported to start, as mentioned above, also around 1.3-1.4 V_{RHE} .
569 However, if the Pd(IV)-oxide would cover completely the Pd surface one would
570 expect much higher Pd(IV)-oxide reduction charges (peak C_2). Therefore, we suggest
571 that the kinetics of the Pd(II)-oxide chemical dissolution (equations 5-5b) is too slow
572 and the associated dissolution products are below the ICP-MS detection limit. In this
573 sense, the contribution of equations 5-5b is neglected in the following mechanistic

574 discussion and the observed passivation between 1.4 and 1.7 V_{RHE} can be explained
575 with the formation of a complete monolayer of Pd(II)-oxide. At more positive
576 potentials the amount of anodically dissolved Pd increases again. The origin of this
577 behavior is not clear yet and should be further investigated. However, this could be
578 attributed to (i) evolution of oxygen (as observed for different metals [76]) and/or to
579 (ii) changes in the oxide structure from a thin α Pd oxide to a thick, hydrous, porous β
580 Pd oxide [37, 65, 74] and/or to (iii) formation of Pd(VI)-oxides [30, 31]. Indeed, the
581 last two are reported to take place above the OER in acidic media.

582 Even though the precise nature of Pd oxide is still unresolved, we showed that its
583 dissolution process can be safely ascribed to surface processes involving different
584 oxidation states and the changes between them. Additional work needs to be done to
585 describe precisely the transient Pd dissolution. Nevertheless, a tentative mechanism
586 can be derived from our experimental observations (Scheme 1).

587 The main contribution to the **anodic dissolution** (related to oxidation peak **A₁**)
588 comes from metal Pd dissolution to Pd²⁺ (equation 3)(3), that is proceeding in parallel
589 with surface oxidation to Pd(II)-oxide (equations 1-1b). The formed Pd(II)-oxide can
590 be chemically dissolved (equations 5-5b), yielding other Pd²⁺, however as discussed
591 earlier its contribution is neglected. As the potential increases Pd(II)-oxide oxidizes to
592 Pd (IV)-oxide (equations 2-2b). Pd passivates (geometrically and/or
593 electrochemically) once the first oxide monolayer is formed (no increase in transient
594 anodic dissolution). The formed Pd-oxide film is rather complex and depends strongly
595 on the UPL. Nevertheless, we suggest a possible general composition. For UPLs in the
596 0.7-1.4 V_{RHE} potential range, the formation of more Pd(II)-oxide (equations 1-1b) is
597 favored over the formation of Pd(IV)-oxide and a monolayer Pd(II)-oxide is obtained

598 around 1.4 V_{RHE} . Once the potential is raised above 1.4 V_{RHE} the formation of Pd(IV)-
599 oxide becomes thermodynamically favorable and a layer of surface Pd_s(IV)-oxide
600 forms on top.

601 During the cathodic scan, first the Pd_s(IV)-oxide is reduced back to Pd(II) (equations
602 2-2b) (**C₂** reduction peak) or dissolved to Pd²⁺ through the electrochemical reaction
603 (equation 4) yielding the **first cathodic dissolution** peak. This peak is only obtained
604 when the UPL is high enough that Pd_s(IV)-oxide is formed (equations 2-2b).
605 Furthermore, (equation 4) is dependent on both the pH and the amount of oxide
606 formed. Thus, it can nicely explain the steep increase with the UPL of the amount of
607 dissolved Pd related to this first cathodic dissolution peak. Indeed, it becomes the
608 dominant dissolution mechanism above 1.7 V_{RHE} , where more Pd(IV)-oxide is formed.

609

610 A **second cathodic dissolution** (related to the reduction peak **C₁**) is observed at
611 lower potentials where Pd(II)-oxide reduction (equation 1-1b) takes place. During
612 transient conditions the mechanism of Pd ions production is not well understood. In
613 many past and recent works, this dissolution was related to Pd(II)-oxide reduction
614 yielding Pd²⁺ [43]. Based on electrochemical equilibria [31] Pd(II)-oxide could
615 dissolve in a chemical reduction, which as discussed earlier can be disregarded. It has
616 been suggested elsewhere for Au and other noble metals that the dissolution during
617 the negative direction scan is due to the de-passivation of the oxide, resulting in the
618 dissolution of the exposed metal ion [59]. Effectively, assuming a reasonable Pd²⁺
619 concentration of 1 nmol dm⁻³, from the dissolved amount of Pd, the equilibrium
620 potential for the Pd metal electro-oxidation ($E^0(\text{Pd}/\text{Pd}^{2+}) = 0.987 \text{ V} + 0.0295$
621 $\log(\text{Pd}^{2+})$, in equation 3) would be approximately 0.72 V_{SHE} (0.78 V_{RHE}). At such

622 potential of the Pd(II)-oxide would be already partially reduced and thus free Pd
623 metal would be exposed to the electrolyte and be available for dissolution. Still, the
624 estimated equilibrium potential of (equation 3) is higher compared to the lowest
625 potential at which dissolution was detected. This could be simply an effect of (i) mass
626 transport limitation and/or (ii) due to the presence of defects and adatoms formed
627 during the oxide reduction whose equilibrium potential can differs from that of the
628 bulk. As another possible contribution to this second cathodic dissolution peak we
629 suggest that some remaining small amount of bulk Pd_b(IV)-oxide embedded in the
630 Pd(II)-oxide layer might play a role. Indeed, when Pd(II)-oxide is reduced back to Pd
631 metal the remaining Pd_b(IV)-oxide can dissolve in a non-reversible process through
632 (equation 4). In summary, this second cathodic dissolution peak can be explained by
633 assuming a direct dissolution of the Pd metal and/or a dissolution of a remaining
634 Pd(IV)-oxide. Both explanations well match the correspondence of the Pd(II)-oxide
635 reduction peak C₁ and the dissolution measured with ICP-MS.

636 **5 Conclusion**

637 In conclusion, despite the uncertainty and complexity of the Pd oxidation states and
638 mechanism, in this work we have proposed a model for the transient Pd dissolution
639 based on our unique experimental results. This model is not only suitable for ideal
640 bulk polycrystalline Pd, but our experimental results confirmed its validity also for
641 supported high-surface-area catalysts, which despite their major interests for
642 application were not studied previously. Therefore, our findings will be of interest
643 for future studies on Pd and Pd-based alloys degradation in real applications.

644 While the proposed mechanism explains the dissolution trends of the presented
645 results, still some unresolved questions remain open and will need further

646 investigations. First, the lack of a precise knowledge of the chemical species formed at
647 the Pd surface represents an obstacle for a full understanding of Pd dissolution.
648 Secondly, the role of the transition between thin α oxide and thick β hydrous oxide
649 formed at very high anodic polarization or the formation of Pd(VI) oxide and its
650 relevance for the transpassive region could not be clarified. Finally, the influence of
651 parameters such as temperature, the presence of anions and cations in different
652 electrolytes and the nanoparticle size needs further investigation.

653

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658

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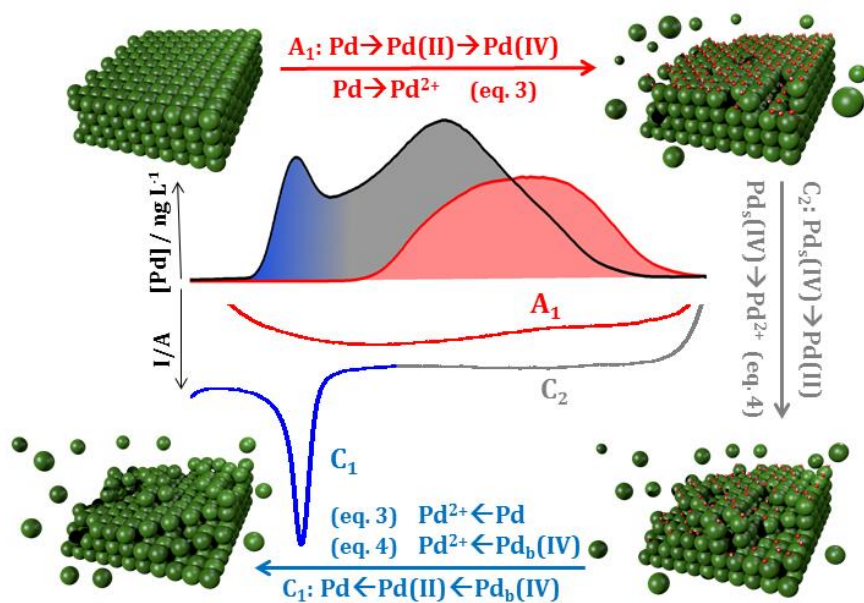
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871 **Graphical abstract**

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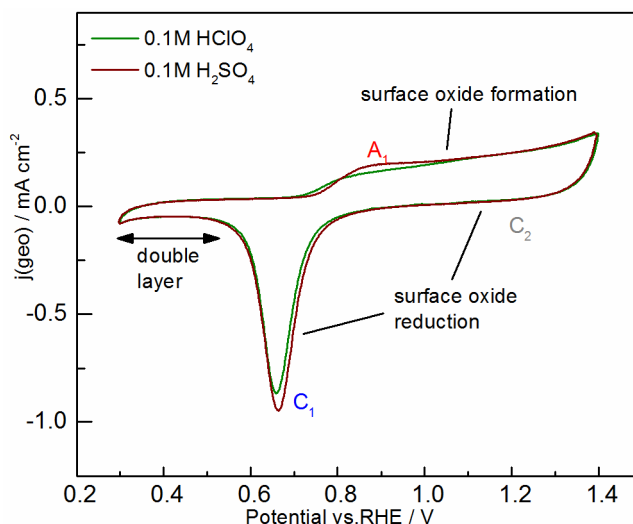
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882 **Figure 1 CVs recorded for a poly-Pd electrode in the SFC setup in 0.1M HClO₄**
 883 **and in 0.1M H₂SO₄. Scan rate: 200 mV s⁻¹. The position of the anodic oxidation**
 884 **peak and two cathodic reduction peaks are indicated with A₁, C₂ and C₁**
 885 **respectively. The complete cycle voltammogram (including hydrogen**
 886 **adsorption/absorption and desorption) and the comparison with RDE are**
 887 **reported in the SI.**

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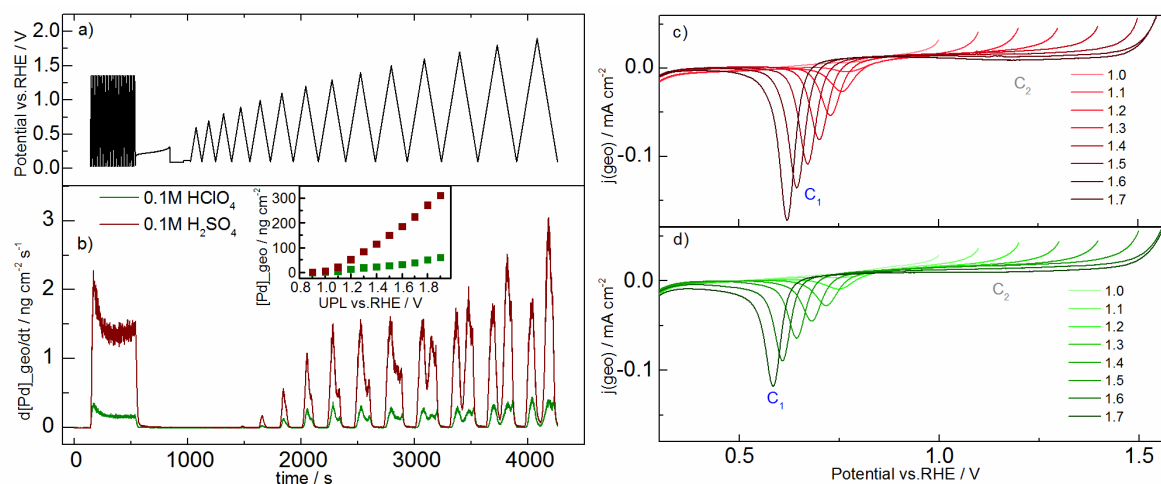
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899 **Figure 2 (a) The potential program applied to the poly-Pd electrode consisted**
 900 **of 30 scans (200 mV s^{-1}) for cleaning, an open circuit potential (OCP) phase and**
 901 **several scans (10 mV s^{-1}) with increasing UPL. The measured poly-Pd**
 902 **dissolution profiles are shown in (b). The inset in (b) corresponds to the**
 903 **integrated dissolved mass of Pd per cycle at different UPL. The corresponding**
 904 **cathodic sweeps for different UPL in $0.1\text{M H}_2\text{SO}_4$ and HClO_4 are shown in (c) and**
 905 **(d) respectively. The charge densities associated to the reduction peaks C_1 and**
 906 **C_2 are shown in the SI.**

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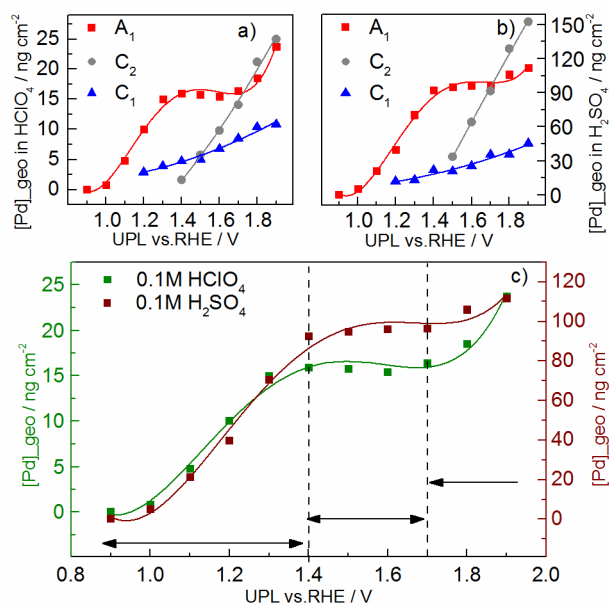
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923 **Figure 3 Integrated mass of dissolved Pd corresponding to the anodic**
 924 **dissolution peak (A₁) and the two cathodic peaks (C₂ and C₁) are reported in**
 925 **HClO₄ (a) and H₂SO₄ (b) at different UPL during the protocol shown in Figure 2.**
 926 **(c) Comparison of the anodic (A₁) dissolution peak in the two acids.**

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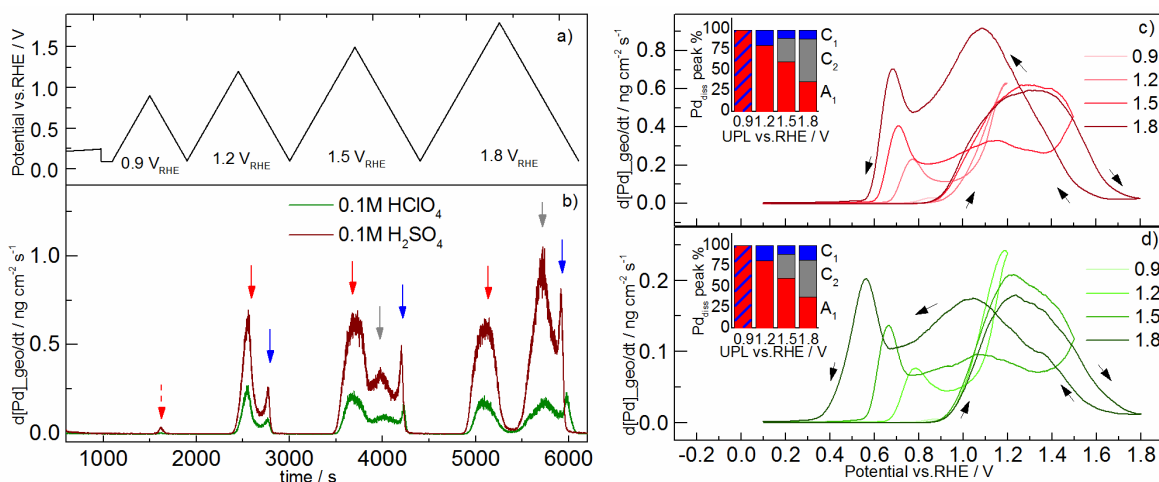
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943 **Figure 4 (a) 4 slow scans (2 mV s^{-1}) with increasing UPL (0.9, 1.2, 1.5, 1.8 V_{RHE})**
 944 **and the corresponding measured poly-Pd dissolution profiles in 0.1M HClO_4**
 945 **and H_2SO_4 (b). The position of the first (anodic: A_1) dissolution peak and the**
 946 **two cathodic (C_2 and C_1) are marked by red, grey and blue arrows respectively.**
 947 **The corresponding mass cyclic voltammograms in (c) sulphuric and (d)**
 948 **perchloric acid. The percentage of anodic (A_1) and cathodic dissolution (C_2 and**
 949 **C_1) are shown for the respective acid in the inlet of (c) and (d).**

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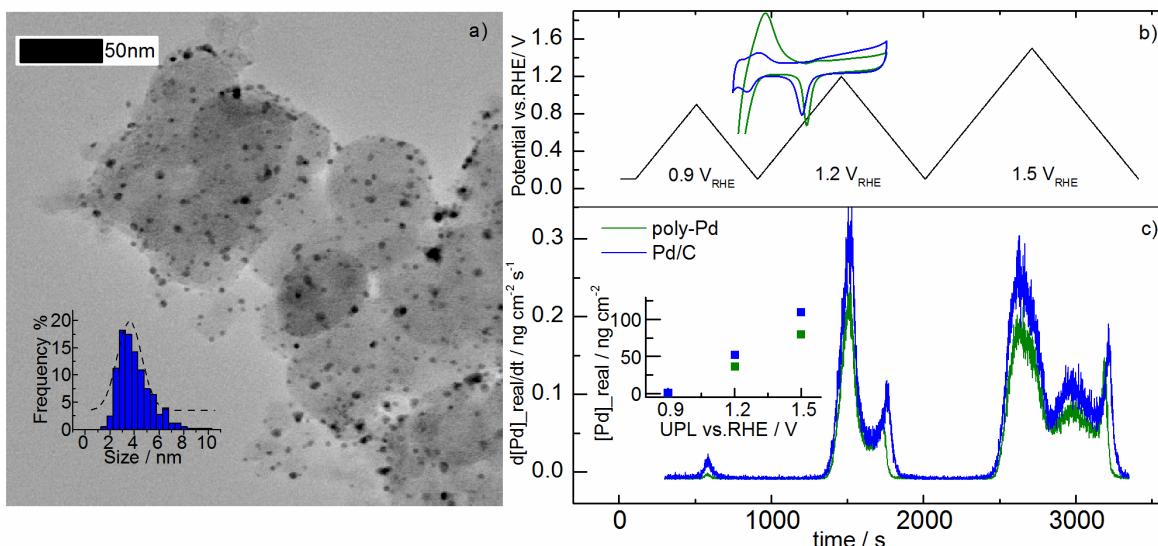
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963 **Figure 5 (a) Bright field TEM micrographs showing Pd/C nanocatalyst**
 964 **deposited on a lacey carbon TEM grid, and their particle size distribution**
 965 **(inset). (b) slow scans (2 mV s^{-1}) with increasing UPL and the corresponding**
 966 **measured poly-Pd and Pd/C dissolution profiles normalized by the real surface**
 967 **are (for Pd/C estimated after the activation) (c). Normalized CVs (b-inset) and**
 968 **the normalized mass dissolved per cycle (c-inset) are also shown. Electrolyte:**
 969 **0.1 M HClO_4 .**

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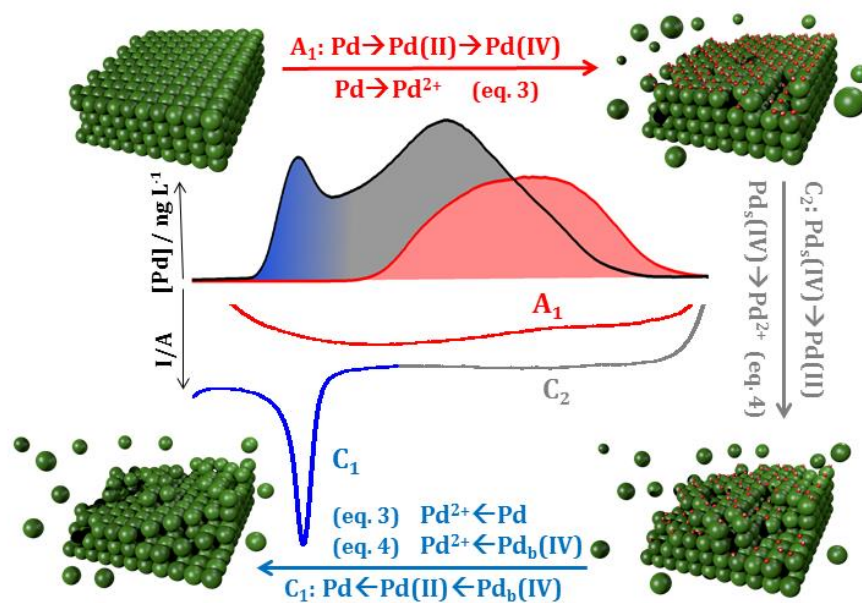
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984 **Scheme 1 Proposed model of the transient dissolution of Pd. A₁: from double**
 985 **layer region to Pd-oxide (both Pd(II) and Pd(IV) oxidation states depending on**
 986 **the UPL). C₂: reduction of Pd(IV)-oxide to Pd(II)-oxide and Pd metal (with**
 987 **dissolution). C₁: reduction of Pd(II)-oxide to Pd metal.**

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