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1 **Electrocatalytic synthesis of hydrogen peroxide on Au-**
2 **Pd nanoparticles: from fundamentals to continuous**
3 **production**

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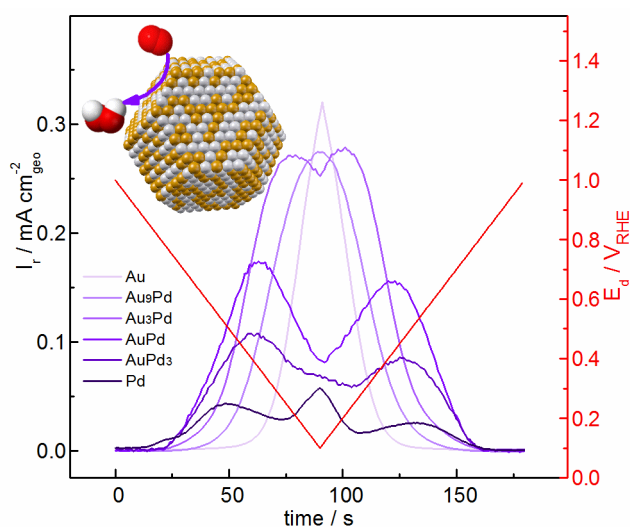
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28 **Abstract**

29 The electrochemical synthesis of hydrogen peroxide (H_2O_2) represents a promising
30 alternative to the anthraquinone process, as it combines on-site chemical and electrical
31 production. The design of selective electrocatalysts is challenging and is commonly
32 based on the alloying of elements to generate a synergistic effects and increase activity.
33 In the present work, we report the electrochemical activity of Au-Pd nanoparticles
34 immobilized directly onto an electrode as a model to study H_2O_2 electrochemical
35 synthesis from fundamentals to continuous production. The impact of composition on
36 the oxygen reduction (ORR), on the selectivity, as well as the peroxide reduction and
37 oxidation (PROR) are studied.



38

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40 Keywords: gold, palladium, hydrogen peroxide, electrocatalyst

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42

43 **1 Introduction**

44 Hydrogen peroxide (H₂O₂) is an excellent green oxidant applied in several important
45 processes, for instance pulp and paper bleaching, water-cleaning, disinfection and
46 industrial synthesis of consumer goods [1, 2]. At present, H₂O₂ is manufactured almost
47 exclusively through the anthraquinone process in centralized reactors, where it is often
48 concentrated up to 70 wt% to reduce costs [3]. However, as typical end-users require
49 concentrations of 2-8 wt% [2], local production by means of a less energy demanding
50 synthetic technology is desirable [4].

51 Electrochemical reactors represent an attractive alternative for the production of H₂O₂
52 via O₂ reduction on-site. Intensive research has been carried out over recent years both
53 in alkaline [5, 6] and acidic medium [7-9]. However, as H₂O₂ degradation can be base
54 catalysed, more promising is the synthesis in acidic medium [10]. In acid, H₂O₂ is
55 synthesized from O₂ and protons in a 2-electron ORR pathway ($\text{O}_{2(\text{g})} + 2\text{H}^{+}_{(\text{aq})} + 2\text{e}^{-} \rightarrow$
56 $\text{H}_2\text{O}_{2(\text{aq})}$) [11]; its standard potential is 0.69 V [12]. The well-developed technology of
57 proton exchange membrane fuel cells (PEM-FC) could be directly utilized for eventual
58 H₂O₂ production and collection of electrical current on a larger scale.

59 Noble metals such as Pt and Pd are the most promising PEM-FC catalysts, due to their
60 high stability at potentials of operational interest in acidic environments [12]. However,
61 both tend to reduce O₂ to H₂O in a 4-electron pathway with high faradaic efficiencies
62 [11]. Recently, the addition of mercury to Pt or Pd led to the discovery of
63 unprecedentedly active electrocatalyst for the H₂O₂ synthesis, which was ascribed to the
64 synergetic presence of two metals with different oxygen binding energies [8, 13].
65 However, the toxicity of Hg might ultimately limit the application of these alloys. Au and
66 Au-Pd catalysts were shown to have the lowest overpotential besides Hg-based catalysts
67 [8]. Au and Pd are safe and, thanks to their high dissolution onset-potential, also
68 promising candidates in acidic media [14]. In addition AuPd nanoparticles supported on
69 carbon and oxide materials have been extensively studied as heterogeneous catalysts for
70 direct H₂O₂ synthesis from molecular H₂ and O₂ [15].

71 Pd binds oxygen intermediates strongly and has a low ORR overpotential close to Pt
72 [16]. Au shows remarkable variation in the kinetics and the mechanism of the ORR
73 varying between 2- and 4-electrons process, depending on support, crystallographic
74 orientation, size and pH [17-19]. Such behavior is common to all electrodes that interact
75 weakly with O₂ (i.e. Au, Ag, Hg) [17, 20]. The alloy of Au and Pd, has been shown to
76 influence activity and selectivity for the ORR [7, 21, 22]. Jirkovsky *et al.* studied the
77 influence of carbon supported Au-Pd catalysts (Pd < 50%) and showed that the addition
78 of a small fraction (8%) of Pd leads to an increase in H₂O₂ selectivity compared to pure
79 Au [7]. This was attributed to the ensemble (or geometric) effect caused by the presence
80 of finely dispersed Pd in Au, influencing the O₂ adsorption on the catalyst surface [23].
81 Erikson *et al.* studied the ORR behavior of Au-Pd electrodeposited catalysts with higher
82 Pd% (only Pd > 50%) however particle size distributions were variable between
83 samples [22].

84 In this context, we studied the performance of colloidal AuPd nanoparticles immobilized
85 directly onto an electrode over a wide range between pure Au and Pd (Au, Au₉Pd, Au₃Pd,
86 AuPd, AuPd₃, Pd) and with controlled particle size distributions around 3-4 nm
87 (statistical size from TEM micrographs). In particular, we present their ORR activity,
88 H₂O₂ selectivity and the PROR in an acidic environment with the rotating ring-disc
89 electrode (RRDE). Finally, potentiostatic production of H₂O₂ (2 and 30 min) provides us
90 additional information on the catalyst behavior in real systems.

91 **2 Materials and Methods**

92 **2.1 Nanoparticle synthesis and characterization**

93 For the preparation of Au-Pd nanoparticles a colloidal synthesis method described
94 elsewhere was followed [24]. An aqueous solution (800 ml, HPLC grade water)
95 containing metal precursors in the desired ratio was prepared from stock solutions of
96 PdCl₂ (6 mg_{Pd} ml⁻¹, Sigma Aldrich, Reagent Plus® 99%) and HAuCl₄ · 3H₂O (12.5 mg_{Au} ml⁻¹
97 Sigma Aldrich, Au assay ≥49.0%) with a total metal content of 20 mg metal in 800 ml.
98 Separately aqueous solutions of NaBH₄ (Sigma Aldrich, 0.1 M) and Poly(vinyl alcohol)
99 (PVA) (1 wt% aqueous solution, Sigma Aldrich, MW=10,000, 80% hydrolyzed) were also
100 prepared. PVA addition to the metal solution (PVA/(Au + Pd) (w/w)=1.2) was followed
101 by addition of a freshly prepared solution of NaBH₄ (0.1 M, NaBH₄/(Au + Pd)
102 (mol/mol)=5) to form a dark-brown sol which is generated in 30 min. The obtained
103 solutions were finally concentrated with the help of a rotary evaporator to 0.1 mg ml⁻¹.

104 For examination by scanning transmission electron microscopy (STEM), to determine
105 the particle size distributions, a JEOL 2200FS TEM operating at 200 kV was used. The
106 prepared solutions were dispersed onto a lacey carbon film supported by a gold TEM
107 grid and then subjected to bright field contrast.

108 The Au:Pd molar ratios were measured by ICP-MS (NexION 300X, Perkin Elmer) by
109 dissolving the AuPd samples in boiling aqua regia (4 ml solution, Merck Suprapur acids).

110 XPS measurements were performed applying a monochromatic Al K α X-ray source
111 (1486.6 eV) operating at 15 kV and 25 W (Quantera II, Physical Electronics,
112 Chanhassen). Analysis of the spectra was carried out using Casa XPS
113 (<http://www.casaxps.com/>).

114 **2.2 Electrochemical characterization**

115

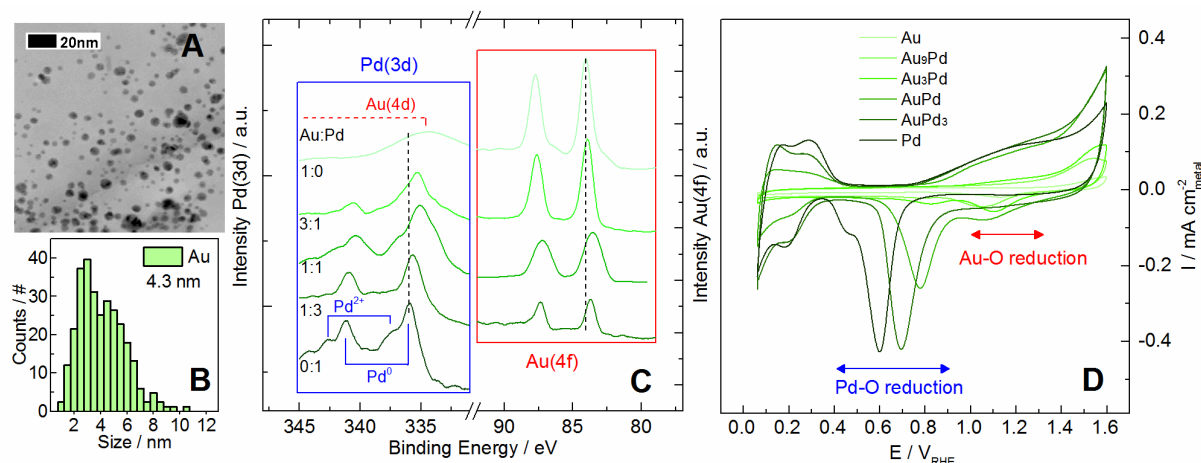
116 All electrochemical results were obtained via thin-film technique either on a rotating
117 disc electrode (RDE, Ar background and PROR) or rotating ring-disc electrode (RRDE)
118 method. Experiments were carried out at room temperature ($\approx 24^\circ\text{C}$) in a three electrode
119 Teflon cell and potentials refers to the reversible hydrogen electrode (RHE), measured
120 prior to experiments. Mirror polished poly-Pt, poly-Au, poly-Pd (5 mm, MaTeck) and Au-
121 Pd catalysts (10 $\mu\text{g}_{\text{metal}} \text{cm}^{-2}$) on glassy carbon (GC) with an area of 0.196 cm² were
122 alternated as working electrodes. Both the counter electrode, a graphite rod, and the
123 reference electrode, a saturated Ag/AgCl electrode (Metrohm), were separated by a
124 Nafion membrane (Tschurl modification). Potentiostat (Gamry Reference 600) and
125 rotator (MSR Pine Rotator System) were controlled with a Gamry V6 Software. The
126 supporting electrolyte was gas (Ar or O₂) purged 0.1 M HClO₄, prepared by dilution of

127 concentrated perchloric acid (Suprapur®, Merck) in ultrapure water (PureLab Plus
 128 system, Elga, 18 MΩ-cm). For PROR, 10 mM H₂O₂ (AnalaR NORMAPUR) were added to
 129 the Ar purged electrolyte. More details about the single electrochemical method are
 130 available in the SI.

131

132 3 Results and discussion

133 3.1 TEM and Surface Characterization



134

135 **Figure 1 (a) Representative bright field TEM micrograph and (b) statistic particle size distribution of Au**
 136 **colloidal nanoparticles deposited on a lacey carbon TEM grid. The micrographs of the other prepared**
 137 **catalysts are shown in the SI. (c) XPS spectra for the series of freshly prepared Au-Pd catalysts and (d)**
 138 **corresponding initial cyclic voltammograms [0.1-1.6] V_{RHE} in Ar purged 0.1M HClO₄. Scan rate: 200 mV s⁻¹.**

139

140 The Au-Pd nanoparticles (Au, Au₉Pd, Au₃Pd, AuPd, AuPd₃, Pd) are prepared through a
 141 sol-immobilization method yielding the presence of a face-centered cubic (fcc) structure,
 142 as recently described [24]. The average particle size and size distribution are estimated
 143 statistically from bright field STEM micrographs (Figure 1a-b and Figure S1.1-5). The
 144 sizes are summarized in Table 1 along with the Au:Pd molar ratios estimated with ICP-
 145 MS and XPS (Figure 1c). XPS spectra (Figure 1c) show a shift in Au 4f photoelectron peak
 146 towards lower binding energies once Pd is present, which is a typical feature observed
 147 for Au-Pd alloys [25]. The molar ratio of the Au₉Pd estimated by XPS differs slightly
 148 from the value obtained via ICPMS. For low Pd content the estimation of the molar ratio
 149 with XPS is less accurate owing to direct overlap between Pd(3d) and Au(4d) peaks.

150 **Table 1 Particle size and Au:Pd molar ratios estimated via ICP-MS and XPS of the prepared catalysts.**

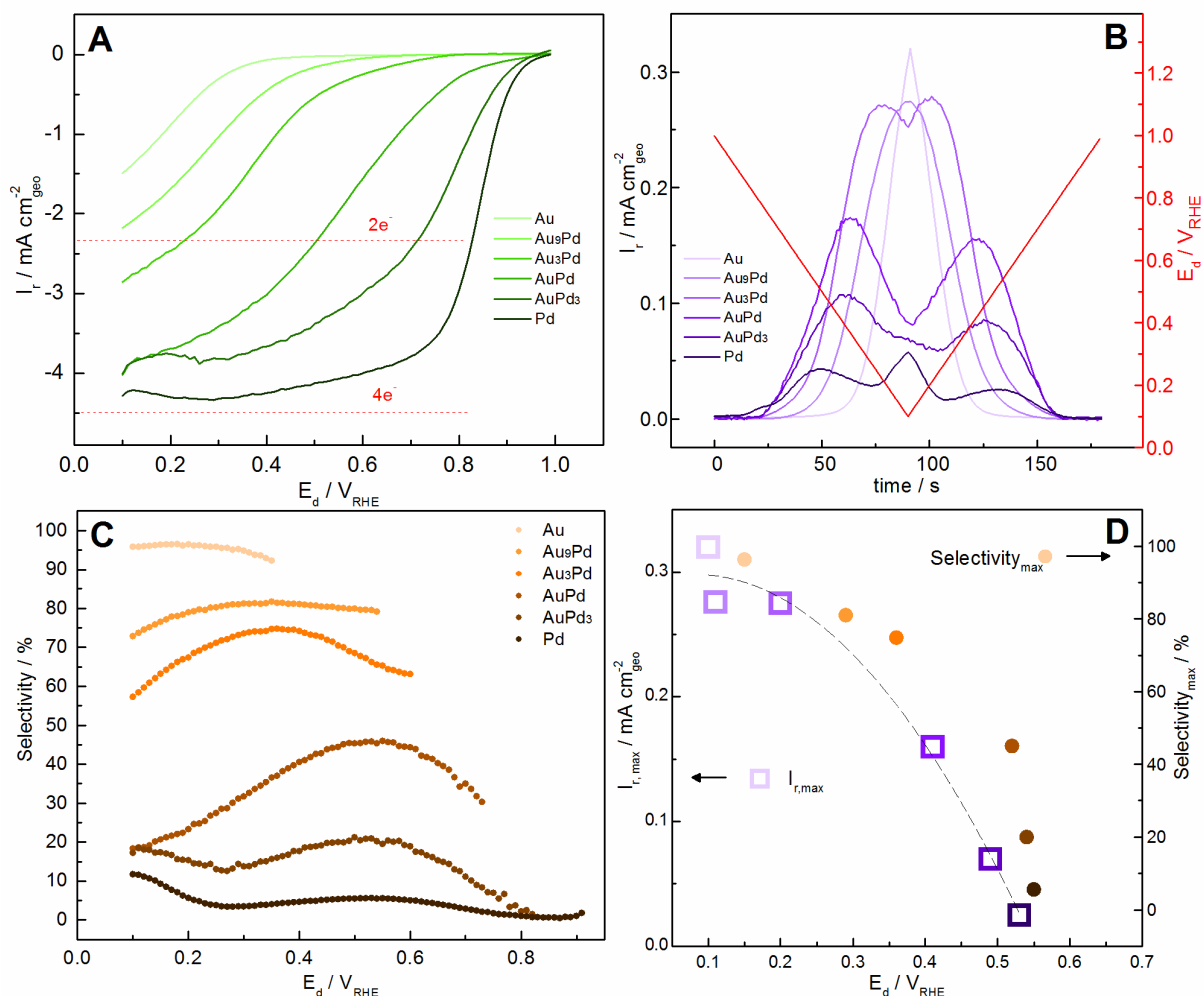
	N of particle	median / nm	st. dev.	Au:Pd ratio ICPMS	Au:Pd ratio XPS
Au	298	4.3	±1.3	100:0	100:0
Au₉Pd	362	2.7	±1.0	91:9	98:2
Au₃Pd	322	3.5	±1.1	77:23	74:26
AuPd	251	4.1	±0.8	46:54	48:52
AuPd₃	285	3.7	±1.1	26:74	27:73
Pd	277	3.2	±1.2	0:100	0:100

151

152 The shape of the initial Ar background cyclic voltammograms (CVs) (Figure 1d and as
153 reference poly-Au and poly-Pd electrodes in Figure S2.1-2) are related to the surface
154 state and composition. The upper potential limit (UPL) of $1.6 V_{RHE}$ is chosen in order to
155 measure the Au oxide (denoted as Au-O due to lack of information about stoichiometry)
156 reduction peak which is only distinguishable with high UPLs [26]. Typical features of Au
157 and Pd vary with the composition. Hydrogen under potential deposition (H_{UPD}) is only
158 present in samples with high Pd content (from 1:1 molar ratio Au:Pd onwards).
159 Furthermore, two peaks in the H_{UPD} are observed for $AuPd_3$ and Pd in accordance with
160 previous literature [27]. Proceeding anodically, the onset potential for the Pd oxide (Pd-
161 O is used as exact composition is not known) and Au-O formation are around $0.7 V_{RHE}$
162 and $1.3 V_{RHE}$ respectively. The cathodic scan is dominated by two main features, namely
163 Au-O and Pd-O reductions. For pure Pd and Au catalysts the maxima of the respective
164 reduction peak were measured at $0.6 V_{RHE}$ and $1.1 V_{RHE}$. The presence of one or two
165 reduction peaks reflects the composition: (i) for low Pd content (Au_9Pd) only the Au-O
166 reduction is visible (as in [7]), whereas (ii) for high Pd content ($AuPd_3$) only the Pd-O
167 reduction is present (as in [28]); (iii) for intermediate compositions (Au_3Pd and $AuPd$),
168 instead, two peaks are observed. Interestingly, the Pd-O peak position shifts significantly
169 when Pd is mixed to Au. Such a shift has been attributed to alloying [7, 22, 28] and was
170 exploited by Rand and Woods to define the surface composition based on a linear
171 dependence with the reduction potential [29]. However, this approach was shown to be
172 limited only to high Pd content ($> 40\%$) [28, 30] and for Au-Pd non-polarized to H_{UPD}
173 where H absorption might take place [28]. Even though quantification is difficult, the
174 position and the associated charges are good indicators of surface composition changes.
175 Note, that also potential cycling might cause minor changes in surface composition due
176 to metal segregation [21].

177 **3.2 Oxygen Reduction Reaction (ORR)**

178 The ORR on Au-Pd nanoparticles is studied with the RRDE (calibration in Figures S3.1-2)
179 with simultaneous H_2O_2 monitoring at the ring during the ORR. From the detected
180 currents, disc (I_d) and ring (I_r), the H_2O_2 selectivity ($S_{H_2O_2}$) is derived.



181

182 **Figure 2 RRDE results obtained for ORR on different Au-Pd catalyst compositions in O₂ saturated 0.1M HClO₄.**
 183 **Rotation: 900 rpm. Scan rate: 50 mV s⁻¹. E_r: 1.28 V_{RHE}. The colors (green for I_d, violet for I_r, brown for S_{H₂O₂}) are**
 184 **graded with the change in composition. (a) Disc anodic polarization current (I_d) (b) Ring current (I_r) profiles**
 185 **during one cycle [0.1-1.0] V_{RHE}. (c) Calculated values of S_{H₂O₂}. (d) S_{H₂O₂} and I_r maxima vs. disc potential.**

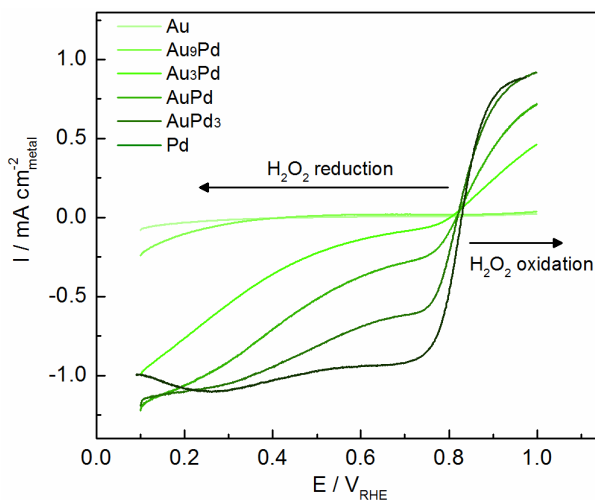
186 The results are summarized in Figure 2 (Au and Pd polycrystals are reported in Figures
 187 S4.1-4). The ORR data collected at the disc (I_d in Figure 2a) show at a glance, how the
 188 composition significantly affects the ORR onset potentials: from 0.4 V_{RHE} for Au it shifts
 189 positively, until 0.9 V_{RHE} for Pd. The theoretical diffusion limited currents (dashed lines
 190 in Figure 2a) calculated from the Levich equation [31] suggest a mechanism change from
 191 a 2 (dominant H₂O₂ production) to a 4-electrons process with increasing Pd content.

192 The presence of H₂O₂ is confirmed by the I_r profiles (Figure 2b), corresponding to H₂O₂
 193 oxidation ($\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^+ + 2\text{e}^-$). The total H₂O₂ current (I_{per}) can be estimated from
 194 correcting I_r by the collection efficiency N and compared to I_d (Figure S4.5). As observed
 195 from the I_d and the I_r , H₂O₂ production is considerably influenced by composition. In
 196 particular, the highest I_r is measured for pure Au ($\sim 0.32 \text{ mA cm}_{\text{geo}}^{-2}$ @ 0.1 V_{RHE}) and the
 197 lowest for Pd ($< 0.05 \text{ mA cm}_{\text{geo}}^{-2}$). Interestingly, for low Pd contents (Au, Au₉Pd, Au₃Pd)
 198 the onset potentials at the ring and the disc coincide, while for the remaining
 199 composition (AuPd, AuPd₃, Pd) the I_r onset potential remains constant at a value close to
 200 the standard potential (0.69 V). Note that, in a 2-electron process the peak of the volcano

201 plot coincides with the standard potential. Thus, a catalyst for the H_2O_2 production can
202 have zero overpotential [32]. Tentatively, the lack of overpotential can explain the fact
203 that the I_r onset potential for active catalyst coincide. Interestingly, for AuPd_3 and Pd an
204 I_r peak is observed at low potential ($<0.2-0.3 V_{\text{RHE}}$) where Pd is covered with hydrogen.
205 This is well known also for Pt-based catalysts [33].

206 As I_r , the $S_{\text{H}_2\text{O}_2}$ (Figure 2c) decreases with Pd content from a $S_{\text{H}_2\text{O}_2, \text{max}}$ of $\sim 95\%$ to less
207 than 10% for pure Au and Pd respectively. As also observed elsewhere, both $S_{\text{H}_2\text{O}_2}$ and I_r
208 exhibit a maximum [7, 8, 13]. Tentatively, this can be attributed to a mechanism change
209 with increasing overpotential. As for the onset-potential also the maxima of I_r and $S_{\text{H}_2\text{O}_2}$
210 are shifting similarly with the composition (Figure 2d). The high $S_{\text{H}_2\text{O}_2}$ of Au is confirmed
211 also with poly-Au (see Figure S4.4). Both show similar onset potentials and $S_{\text{H}_2\text{O}_2}$ around
212 95-98%. In a recent publication on carbon supported Au-Pd catalysts, Jirkovsky *et al.*
213 observed a $S_{\text{H}_2\text{O}_2}$ enhancement for low Pd concentration ($<15\%$) with a maximum for 8%
214 Pd [7], whose $S_{\text{H}_2\text{O}_2}$ approached 95%. This was attributed to geometric effect due the
215 presence of single Pd atoms surrounded by Au. Our Au_9Pd does not show improvement
216 in terms of $S_{\text{H}_2\text{O}_2}$ compared to the pure Au sample, whose $S_{\text{H}_2\text{O}_2}$ is already approaching
217 95%. The influence of the support and of isolated Pd needs to be further addressed in
218 future studies. Indeed, first principles calculation suggests an influence on $S_{\text{H}_2\text{O}_2}$ due to
219 geometric effect [34], that could correspond to a shift in onset potential while
220 maintaining a high $S_{\text{H}_2\text{O}_2}$.

221 3.3 Peroxide Reduction and Oxidation Reaction (PROR)

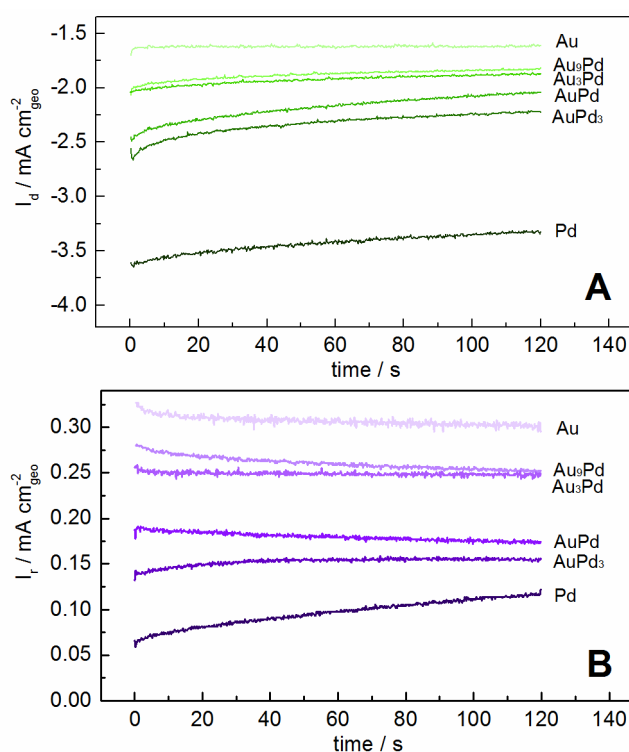


222
223 **Figure 3 Anodic sweep of the PROR on various Au-Pd catalyst compositions in Ar saturated 0.1M HClO_4 +**
224 **10mM H_2O_2 . Rotation: 900 rpm. Scan rate : 50 mV s^{-1} .**

225 Once produced, H_2O_2 can “degrade” through: (i) electrochemical peroxide reduction
226 (PRR) ($\text{H}_2\text{O}_2 + 2\text{e}^- + 2\text{H}^+ \rightarrow 2\text{H}_2\text{O}$), (ii) electrochemical peroxide oxidation (POR)
227 ($\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{e}^- + 2\text{H}^+$) and (iii) chemical disproportionation ($2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$). The
228 latter is influenced by the reaction environment, whereas the others are mainly related
229 to the catalyst surface and presence of impurities [35, 36]. It is therefore of utmost
230 importance to answer the question of whether the produced H_2O_2 would be further

231 reduced in a fuel cell at operational potentials, dominated by PRR. PROR was studied in
 232 Ar-saturated 0.1M HClO₄ containing 10 mM of H₂O₂ (Figure 3). Interestingly, the
 233 polarization curves match around 0.8 V_{RHE}. At such potential, the dominating reaction
 234 (PRR to POR) changes with the surface state (reduced to oxidized), as observed for poly-
 235 Pt [36]. The Pd oxidation onset is ~0.7 V_{RHE}, which is indeed when the PRR current starts
 236 to decrease (see also poly-Pd in Figure S5.1). Inactive metals for ORR are also less active
 237 for PRR: an increase in Au content corresponds to a proportional decrease in both ORR
 238 (Figure 2) and PRR (Figure 3). This trend is also confirmed by previous literature on co-
 239 electrodeposited Au-Pd [22, 37]. Already at 10% Pd content an undesired (even though
 240 limited) increase in the H₂O₂ reduction current was observed. As Au is selective and not
 241 active for the PRR, it can be indicated as the best candidate for applications that require
 242 high S_{H2O2}.

243 3.4 Potentiostatic H₂O₂ production



244

245 **Figure 4 Measured I_d (a) and I_r (b) during 2 min potentiostatic experiment in O₂ saturated 0.1M HClO₄.**
 246 **Rotation: 900 rpm. E_d corresponds to the potential of $I_{r,max}$ (see Table 2). E_r : 1.28 V_{RHE}.**

247 To finally bridge the gap between possible “real application” and our fundamental
 248 studies we need to understand how the catalysts behave during demanding continuous
 249 H₂O₂ production. RRDE data (Figure 4 and Figure S6.1) during 2 min potentiostatic
 250 condition (potential of $I_{r,max}$ for each composition) confirms the activity and S_{H2O2} trend
 251 observed in the previous sections. Interestingly, the I_r (and thus S_{H2O2}) slightly increases
 252 with time for Pd rich catalysts (AuPd₃, Pd). This is even more evident during the 30
 253 minutes measurements (see Figure S6.1) and can be tentatively attributed to the
 254 presence of either impurities or spectator species that initially poison active sites
 255 favoring the H₂O₂ production, as observed for Pt [38]. Such spectator species can be

256 easily removed with a simple CV [13]; indeed, the ORR behavior before and after the
257 measurement is not affected (see Figure S6.2).

258 The productivity (Table 2) of the catalyst after 2 and 30 minutes is determined from the
259 POR limiting current on Pt (see calibration in Figure S6.3). In line with the high $S_{H_2O_2}$ and
260 low PRR activity of Au, its productivity is the highest. Thus, the measurement on Au was
261 extended to 1 and 2 h yielding 12.3 and 22.9 mol $g_{metal}^{-1} cm^{-2}_{geo}$. Increasing the Pd
262 content, the $S_{H_2O_2}$ decreases and PRR activity increases, resulting in a proportional
263 productivity decrease. Despite the low productivity expected for 4-electron catalysts
264 with low $S_{H_2O_2}$ as Pd, it yields ~ 2.40 mol $g_{metal}^{-1} cm^{-2}_{geo}$ after 30 min. This can be again
265 attributed to a poisoning of the active sites for complete reduction, favoring a 2-electron
266 process.

267 **Table 2 H₂O₂ productivity after 2 and 30 mins of measurement.**

	Potential hold (V _{RHE})	Productivity 2 min (mol g_{metal}^{-1} cm^{-2}_{geo})	Productivity 30 min (mol g_{metal}^{-1} cm^{-2}_{geo})
Au	0.10	0.46	6.79
Au ₉ Pd	0.15	0.39	5.46
Au ₃ Pd	0.25	0.40	5.87
AuPd	0.40	0.29	3.37
AuPd ₃	0.45	0.24	3.42
Pd	0.50	0.14	2.40

268

269 4 Conclusions

270 A set of Au-Pd nanocatalysts are synthesized as model catalysts to study the
271 electrocatalytic behaviour for H₂O₂ synthesis from fundamental perspectives and for
272 continuous H₂O₂ production.

273 The ORR and the PROR behavior are significantly affected by the composition: upon an
274 increase in Au content we observe an increase in I_r and $S_{H_2O_2}$, whereas the onset is
275 shifting to lower potentials. The $S_{H_2O_2}$ of Au is the highest (95%) at the price of low
276 activity. Previous theoretical studies as well as experimental works suggest that
277 geometrical effects (triggered by the presence of atomically dispersed Pd in Au) might
278 enhance the activity whereas maintaining high $S_{H_2O_2}$, which are however not observed in
279 this work. For Au₉Pd and Au₃Pd, the activity is indeed higher (i.e. H₂O₂ formation onset
280 potential already close to nominal for Au₃Pd), but the $S_{H_2O_2}$ decreases while remaining
281 relatively high (between 60 and 80%). With an eye on applications, these compositions
282 might still be interesting where a compromise between $S_{H_2O_2}$ and energy output is
283 allowed, as the typical end-user requires H₂O₂ concentration in the range 2-8 wt%. On
284 the other hand, if high H₂O₂ concentration and high $S_{H_2O_2}$ is required, pure Au would
285 potentially be the catalyst of choice, as the productivity during a potentiostatic
286 measurement indicates (highest productivity that steadily increases up to 2h).

287 Our observations on a spectrum of compositions between elements with contrasting O₂
288 adsorption energy can be extended to other alloys with similar characteristic. The

289 fundamental studies help to forecast the ORR behavior and reaction selectivity for
290 potential applications. Furthermore, future investigations on fuel cells, the stability of
291 catalysts, as well as on the effect of support are of particular importance to understand
292 how these catalysts will perform in real applications.

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