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1 Oxygen Crossover Effect on Palladium and Platinum Based  
2 Electrocatalysts During Formic Acid Oxidation Studied by  
3 Scanning Electrochemical Microscopy

4

5 Juan V. Perales-Rondón<sup>a,b</sup>, Enrique Herrero<sup>b</sup>, José Solla-Gullón<sup>b</sup>, Carlos M. Sánchez-  
6 Sánchez<sup>\*,a</sup>, Vincent Vivier<sup>a</sup>

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8 <sup>a</sup>Sorbonne Universités, UPMC Univ Paris 06, CNRS, Laboratoire Interfaces et Systèmes  
9 Electrochimiques, 4 place Jussieu, F-75005, Paris, France.

10 <sup>b</sup>Instituto Universitario de Electroquímica, Universidad de Alicante, Ap. 99, 03080, Alicante,  
11 Spain

12

13

14 \* Corresponding author: Tel.: +33 1 44 27 41 58

15 E-mail address: carlos.sanchez@upmc.fr

16

17 **Abstract**

18 The electrocatalytic activity towards formic acid oxidation reaction (FAOR) in the  
19 presence of simultaneous oxygen reduction reaction (ORR) displayed by 5 different  
20 metallic nanoparticles (NPs) (Pt<sub>100</sub>, Pt<sub>75</sub>Pd<sub>25</sub>, Pt<sub>50</sub>Pd<sub>50</sub>, Pt<sub>25</sub>Pd<sub>75</sub> and Pd<sub>100</sub>) was studied and  
21 compared using chronoamperometry and the micropipette delivery/substrate collection  
22 (MD/SC) mode of the scanning electrochemical microscopy (SECM). This is of special  
23 interest for understanding the O<sub>2</sub> crossover effect in direct formic acid fuel cells  
24 (DFAFCs) and to search highly selective electrocatalysts useful in mixed-reactant fuel  
25 cells (MRFCs). A detailed analysis of the SECM results in comparison with  
26 chronoamperometry demonstrates, for the first time, the relevant role played by dissolved  
27 O<sub>2</sub> in solution on the Pd<sub>100</sub> NPs deactivation during FAOR, which cannot be explained  
28 neither by the specific adsorption of dichloroethane (DCE) on Pd nor by a simple addition  
29 of two opposed currents coming from simultaneous FAOR and ORR. Two main  
30 mechanistic factors are proposed for explaining the different sensitivity towards O<sub>2</sub>  
31 presence in solution during FAOR when comparing Pd- and Pt-rich catalysts. On the one  
32 hand, the relevance of H<sub>2</sub>O<sub>2</sub> production (ORR byproduct) and accumulation on Pd NPs,  
33 which alters its performance towards FAOR. On the other hand, the predominance of the  
34 poisoning pathway forming CO<sub>ads</sub> during FAOR on Pt NPs, whose oxidation is facilitated  
35 in the presence of traces of O<sub>2</sub>. Interestingly, the deactivation effect displayed on Pd<sub>100</sub>  
36 NPs during FAOR due to the H<sub>2</sub>O<sub>2</sub> generation and accumulation becomes negligible if a  
37 convective regime is applied in solution.

38 SECM is proved as a fast and powerful technique for studying O<sub>2</sub> crossover effect in  
39 different electrocatalysts and for identifying highly selective electrocatalysts candidates  
40 for MRFCs. In particular, among the samples evaluated, Pt<sub>75</sub>Pd<sub>25</sub> NPs present the highest

41 average performance for FAOR in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution in the presence of O<sub>2</sub> within the  
42 potential range under study (0.3-0.7 V vs RHE).

43

44 *Keywords:* Crossover, FAOR, ORR, fuel cells, SECM

45

46 *This article is dedicated to the memory of Prof. Antonio Aldaz Riera, a great mentor in*  
47 *science and life.*

48

49

50 *Highlights:*

51 • SECM as a proper diagnostic tool to evaluate electrocatalysts in the presence of  
52 reactants crossover.

53 • Simultaneous FAOR and ORR on Pd, Pt and Pd-Pt alloyed nanoparticles imaged  
54 by SECM.

55 • Pd electrode deactivation during FAOR due to the role of O<sub>2</sub> crossover.

56 • Pt<sub>75</sub>Pd<sub>25</sub> nanoparticles display the highest performance for FAOR in the presence  
57 of O<sub>2</sub>.

58

59

## 60 **1. Introduction**

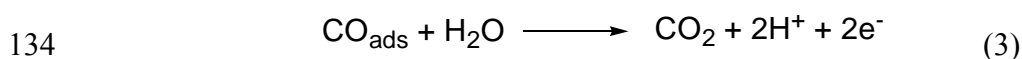
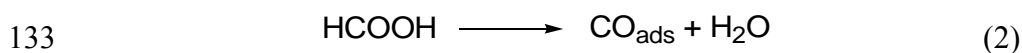
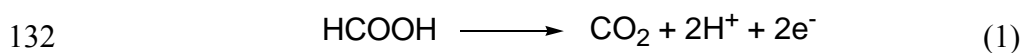
61 Fuel cells have attracted a lot of attention, from their first description as a gas voltaic  
62 battery by W.R. Grove on the 19<sup>th</sup> century [1,2]. This is because fuel cells, as well as other  
63 electrochemical devices, are able to convert chemical energy into electrical energy in one  
64 single step and they do not need to produce firstly mechanical work and secondly  
65 electrical energy as the internal combustion engine does [3]. There are many different  
66 types of fuel cells that may be classified either by their operation temperature or by the  
67 type of electrolyte used. Nevertheless, almost all low-temperature fuel cells ( $T < 200\text{ }^{\circ}\text{C}$ )  
68 use a conventional two-compartment reactor separated by an ion exchange membrane  
69 where the fuel and the oxidant flows are kept apart and directly fed into the anode and  
70 cathode chambers, respectively. However, crossover effects in different types of  
71 conventional fuel cells have been already described in the literature, since reactants  
72 crossover can lead to significant performance degradation, a non-negligible crossover  
73 current contribution and an important fuel cell voltage and power output diminution. A  
74 lot of attention has been paid to the permeation of fuels such as methanol [4], formic acid  
75 [5,6] and hydrogen [7] from the anode to the cathode side in conventional fuel cells. In  
76 particular, fuel crossover represents a major issue for direct methanol fuel cells (DMFCs)  
77 [8-10], since this problem accounts for one of their major performance losses. Moreover,  
78 this fact limits the maximum methanol concentration used at the anode side, since  
79 methanol crossover provokes cathode deactivation by CO poisoning. More recently,  
80 oxygen crossover in non-aqueous Li-air batteries, which can be considered as a reversible  
81 half-fuel cell, has also become a relevant issue limiting the market penetration of this type  
82 of technology, since one of their main limitations at present is the formation of unwanted  
83 lithium derivatives ( $\text{Li}_2\text{CO}_3$  and  $\text{LiOH}$ ) caused by  $\text{O}_2$  crossover into the anode side [11,12].  
84 Alternatively, other types of reactors eliminating the ionic membrane have been recently

85 proposed in fuel cells for avoiding high cost, degradation and ohmic losses due to the use  
86 of those membranes. For instance, the Swiss-roll mixed-reactant fuel cell (MRFC) [13,14],  
87 where the ion exchange membrane has been substituted by a highly porous separator and  
88 a single mixture of fuel and oxidant feeds simultaneously anode and cathode. The key  
89 issue for the success of those systems is to achieve high selectivity of the anode and  
90 cathode electrocatalysts to avoid mixed-potentials at both electrodes and fuel-cell voltage  
91 degradation. This means electrocatalysts with high tolerance to the presence of a high  
92 concentration of either the fuel or the oxidant, for cathode and anode, respectively.  
93 Therefore, in both cases, either to study the role of reactants crossover on the  
94 corresponding counterpart electrocatalyst activity in conventional fuel cells or to find  
95 novel highly selective electrocatalysts useful in MRFCs, it is necessary to identify a  
96 diagnostic tool, which should be able to evaluate electrocatalyst performance under those  
97 specific experimental conditions.

98 A broad range of electrochemical techniques have been already used to study  
99 different aspects present in fuel cells and batteries. For instance, impedance techniques  
100 have been widely used to determine the state-of-charge and electrodes stability in primary  
101 and secondary batteries [15,16]. More recently, new electrochemical scanning probe  
102 microscopies [17-19] have been incorporated too, since there is a significant demand of *in-*  
103 *situ* methods for simultaneous evaluation of electrodes surface properties and chemical  
104 activity. In particular, scanning electrochemical microscopy (SECM) [20,21] has become a  
105 powerful electroanalytical technique that has been already successfully applied to study  
106 Li-ion batteries [22,23] and electrocatalyst performance for different fuel cell reactions [24]  
107 such as oxygen reduction (ORR)[25-31], oxygen evolution (OER) [32-34], carbon dioxide  
108 reduction (CRR)[35], methanol oxidation (MOR)[36] and formic acid oxidation (FAOR)  
109 [36-38], as well as a high-throughput technique applied to the combinatorial screening of

110 mixed and alloyed electrocatalytic materials [39-41]. However, they are very scarce  
 111 examples where SECM have been already used to study either electrocatalysts tolerance  
 112 to the presence of the counterpart reactant or highly selective electrocatalysts useful in  
 113 MRFCs. So far, only the use of the tip generation/substrate collection (TG/SC) mode of  
 114 SECM for studying methanol tolerance of Pt and Pd-Co ORR electrocatalysts as a  
 115 function of applied potential have been reported [42]. In this context, the direct formic acid  
 116 fuel cell (DFAFC) [43,44], which is based on the electrochemical oxidation of formic acid  
 117 (HCOOH) to CO<sub>2</sub> at the anode (E° = -0.199 V or -0.25 V vs SHE depending on the  
 118 HCOOH reference state used for the thermodynamic calculation of the standard potential  
 119 (aqueous or liquid, respectively) [45]) and ORR at the cathode (E° = 1.229 V vs SHE)  
 120 represents an attractive system to study electrocatalysts selectivity and tolerance facing  
 121 reactants crossover.

122 FAOR on pure Pt may follow two main reaction routes: through a direct via, which  
 123 produces CO<sub>2</sub> as main product and represents the desirable pathway (dehydrogenation,  
 124 reaction 1) and/or through a poisoning pathway (dehydration, reaction 2) by forming CO,  
 125 which remains strongly adsorbed on the platinum surface and blocks the reaction of  
 126 interest, unless a positive enough potential is reached for desorbing and oxidizing CO  
 127 from the Pt surface (reaction 3). In contrast, FAOR on pure Pd mainly follows the active  
 128 intermediate route (reaction 1) avoiding CO formation and providing a much higher  
 129 catalytic activity at lower overpotentials than on Pt electrodes [46,47]. For this reason, Pd  
 130 and Pd-based materials are considered as the state-of-the-art anode catalysts in DFAFCs  
 131 [48-51].





135 The most studied case in DFAFCs is the HCOOH crossover effect during ORR,  
136 which has been already reported as not truly relevant for the DFAFCs performance [5,6].  
137 Nevertheless, the case of oxygen crossover effect during FAOR on Pd, Pt and Pd-Pt  
138 alloys, which we study herein is, so far, a non-described phenomenon in electrocatalysts  
139 for FAOR. Therefore, the main goal of this article is to mimic the effect of O<sub>2</sub> crossover  
140 from the cathode side towards the anode side in DFAFCs, using the micropipette  
141 delivery/substrate collection (MD/SC) mode of SECM, which is based on the transfer of  
142 a neutral species by diffusion across an immiscible liquid/liquid interface as sketched for  
143 HCOOH in Figure 1 [36,38,52]. It is worth noting that the acidic solution used as aqueous  
144 phase outside the micropipette should not be totally deaerated in order to study the effect  
145 of simultaneous reactions, FAOR and ORR, on Pd, Pt and Pd-Pt alloys.

146

## 147 **2. Experimental**

### 148 Chemicals and Electrodes

149 Most chemicals were ACS reagent grade supplied by Sigma-Aldrich and were used  
150 without further purification: 1,2-dichloroethane (CH<sub>2</sub>Cl-CH<sub>2</sub>Cl, DCE) anhydrous 99.8%,  
151 octyltriethoxysilane 97.5%, polyethylene glycol dodecyl ether (Brij<sup>®</sup> 30), n-heptane,  
152 sodium borohydride (NaBH<sub>4</sub>) 99.99%, K<sub>2</sub>PdCl<sub>4</sub> 99.99%, H<sub>2</sub>PtCl<sub>6</sub>•6H<sub>2</sub>O 99.99% (37.50%  
153 in Pt). However, H<sub>2</sub>SO<sub>4</sub> Suprapur<sup>®</sup> 96% and HCOOH 98 % were supplied by Merck,  
154 glassy carbon (GC) plates 1 mm thick (type 2) from Alfa Aesar and Ar gas ≥ 99.9998  
155 purity was supplied by Air Liquide. All aqueous solutions were prepared with ultrapure  
156 water (18.2 MΩ cm at 25 °C, Purelab Ultra system, Elga-Vivendi).

157

158 Synthesis of Pt, Pd and PtPd alloyed nanoparticles (NPs)

159 5 different types of quasi-spherical Pt-Pd NPs (Pt<sub>100</sub>, Pt<sub>75</sub>Pd<sub>25</sub>, Pt<sub>50</sub>Pd<sub>50</sub>, Pt<sub>25</sub>Pd<sub>75</sub> and  
160 Pd<sub>100</sub>) were synthesized by reduction of either H<sub>2</sub>PtCl<sub>6</sub> and/or K<sub>2</sub>PdCl<sub>4</sub> precursors with  
161 NaBH<sub>4</sub> using a water in oil (w/o) microemulsion of water/polyethylene glycol-  
162 dodecylether (BRIJ® 30)/n-heptane [47,53]. The percentage of surfactant in volume  
163 represented 16.5% of the total microemulsion volume. The concentration of H<sub>2</sub>PtCl<sub>6</sub>,  
164 K<sub>2</sub>PdCl<sub>4</sub> and NaBH<sub>4</sub> was 0.1, 0.1, 1.0 M, respectively. For preparation of PtPd alloyed  
165 NPs, an aqueous solution containing both precursors (H<sub>2</sub>PtCl<sub>6</sub> + K<sub>2</sub>PdCl<sub>4</sub>) with the proper  
166 atomic ratio of both elements was employed. In order to have micelles with the same size,  
167 the molar ratio water to surfactant was kept constant, which approximately ensures  
168 constant NP size in all cases (3 - 4 nm average NPs size). After complete reduction of the  
169 metallic precursors, which took place in a few minutes, acetone was added to the solution  
170 to cause phase separation and NPs flocculation. Finally, all metallic NPs synthesized were  
171 washed with acetone as has been described in previous works [54] in order to eliminate  
172 adsorbed surfactant and were dispersed in ultra-pure water giving as a result 5  
173 independent NPs suspensions.

174

175 Voltammetric and chronoamperometric studies

176 Cyclic voltammetry (CV) and chronoamperometry experiments were carried out in  
177 a conventional electrochemical glass cell using a three-electrode configuration at room  
178 temperature with (1000 rpm) or without electrode rotation. The counter and the reference  
179 electrodes were a Pt wire (0.5 mm diameter) and a reversible hydrogen electrode (RHE),  
180 respectively. All NPs were studied by depositing 4 µL of each NPs suspension either on  
181 a gold collector for static measurements or on a GC rotating disc electrode (RDE) for  
182 reaching a laminar convection regime. All electrode potentials in this work are quoted vs.

183 *RHE*. The electrode potential was controlled either with a CHI 760E potentiostat  
184 (CHInstruments) or with a multi-channel VMP3 potentiostat (BioLogic), working with  
185 an NStat configuration (1 counter, 1 reference and 5 simultaneous working electrodes).  
186 CVs for electrochemical surface area (ECSA) quantification were carried out in a  
187 deaerated 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. Chronoamperometries for studying the electrocatalytic  
188 activity for FAOR were carried out in: *i*) deaerated 0.01 M HCOOH and 0.5 M H<sub>2</sub>SO<sub>4</sub>  
189 solution, *ii*) deaerated 0.01 M HCOOH, 0.088 M DCE and 0.5 M H<sub>2</sub>SO<sub>4</sub> solution and *iii*)  
190 air saturated 0.01 M HCOOH and 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. An electrochemical pre-  
191 treatment for removing the CO<sub>ads</sub> accumulated at the electrode surface from previous  
192 FAOR experiments was performed before starting each new chronoamperometry. This  
193 consists in holding the electrode potential at 0.9 V for 5 s, since CO<sub>ads</sub> on the Pd surface  
194 requires a bit more positive potential than on Pt for being totally oxidized to CO<sub>2</sub> [47].

195

#### 196 Electrochemical surface area (ECSA) of Pt, Pd and PtPd alloyed NPs

197 The ECSA for all 5 types of NPs was electrochemically determined by depositing 2  
198  $\mu\text{L}$  of each NPs suspension on a gold current collector and quantifying the charge  
199 involved under the voltammetric peaks corresponding to the hydrogen desorption within  
200 the hydrogen underpotential deposition (UPD) region (between 0.05 and 0.45 V for Pt  
201 and Pt alloyed NPs and between 0.1 and 0.5 V for Pd NPs) corrected by subtracting the  
202 double-layer contribution [55]. For this purpose, the corresponding CV was performed for  
203 each type of synthesized NP in a 0.5 M H<sub>2</sub>SO<sub>4</sub> deaerated solution at scan rate 50 mV s<sup>-1</sup>,  
204 as it is shown in Figure 2. 210  $\mu\text{C cm}^{-2}$  was adopted as the calibration charge density for  
205 the desorption of a complete monolayer of H atoms on polyoriented Pt or Pd electrodes  
206 [56]. Before ECSA evaluation, an additional cleaning procedure for all 5 types of  
207 synthesized NPs was performed by adsorbing CO at the NPs surface [38,53]. After that, a

208 linear voltammetry at  $20 \text{ mV s}^{-1}$  with an upper potential limit of 0.9 V was performed for  
209 a complete electrochemical oxidation-stripping of CO from the NPs surface [57]. All 5  
210 types of NPs were suspended in water and normalized for exhibiting equal specific  
211 surface area ( $0.035 \text{ cm}^2 \mu\text{L}^{-1}$ ).

212

### 213 Preparation of electrocatalyst arrays of Pt, Pd and PtPd alloyed NPs

214 The NPs array preparation is described elsewhere [28,52] and the specific array pattern  
215 (5 spots in 2 identical rows separated by  $700 \mu\text{m}$  from center to center) used here is  
216 schematically described in Figure 3. This was prepared by dispensing all 5 metallic NPs  
217 dispersed in water using a picoliter solution dispenser CHI 1550A from CHI Instruments.  
218 All 5 types of NPs were dispensed on a conductive flat current collector of GC ( $1.5 \text{ cm} \times$   
219  $1.5 \text{ cm}$ ), which has been selected since is totally inactive for ORR and FAOR within the  
220 potential range under study. Each NPs suspension was sonicated for 2 min before  
221 charging the dispenser to avoid NPs agglomeration. A total of 160 drops of each type of  
222 metallic NPs suspension were dispensed in 8 successive series of 20 drops each, allowing  
223 the water solvent to be evaporated before each new series of drops was added. The  
224 average spot size obtained was between  $200$  and  $250 \mu\text{m}$  in diameter.

225

### 226 Glass Micropipette Fabrication

227 The micropipettes were prepared by pulling borosilicate capillaries with O.D.:  $1.5$   
228  $\text{mm}$  and I.D.:  $1.0 \text{ mm}$  and length of  $90 \text{ mm}$  using a laser-based puller P-2000 from Sutter  
229 Instrument Co. Micropipettes with an internal opening diameter of  $30 \mu\text{m}$  were routinely  
230 fabricated. Micropipettes exact diameter was checked using an optical microscope  
231 BA200 from Motic Co. The inner wall of the micropipettes was made hydrophobic to  
232 avoid aqueous solution penetration within the micropipette by filling it with

233 octyltriethoxysilane overnight and finally, drying it exhaustively by pumping air through  
234 following an standard protocol [36,52,58]. Then, those micropipettes were loaded with a  
235 liquid mixture 50:50 HCOOH:DCE (v/v) before starting electrocatalyst SECM imaging.

236

### 237 Scanning electrochemical microscopy (SECM) imaging

238 All SECM images were carried out using the MD/SC working mode of SECM using  
239 either a CHI 910B or a 920D microscope from CHInstruments and a three-electrode  
240 configuration at room temperature. The electrochemical cell employed was built in Teflon  
241 with an 8 mm diameter aperture for scanning the substrate electrode. This is an open  
242 electrochemical cell, which does not allow total suppression of O<sub>2</sub> in solution. A platinum  
243 wire, 0.5 mm diameter, was used as a counter electrode and a commercial Hg/Hg<sub>2</sub>SO<sub>4</sub>  
244 (K<sub>2</sub>SO<sub>4</sub> sat.) electrode within a Luggin capillary as reference. Nevertheless, all potential  
245 values presented herein have been referred to *RHE* ( $E_{\text{Hg}/\text{Hg}_2\text{SO}_4} = +0.64 \text{ V vs. } RHE$  for the  
246 pH value of the solutions employed). Before FAOR imaging any tilt on the electrocatalyst  
247 array substrate was eliminated in order to avoid crushing the glass micropipette while  
248 scanning. This is achieved by performing a series of approach curves using a gold  
249 ultramicroelectrode (UME) built by heat sealing under vacuum a gold wire in a flint glass  
250 capillary as described elsewhere [20]. This procedure consists in approaching a gold UME  
251 of 25 μm diameter to the array substrate surface at three different locations. The gold  
252 UME is kept at a potential negative enough to perform ORR under steady-state  
253 conditions. Controlling the ratio between the steady-state current and the final current of  
254 the gold UME when is approaching the GC surface, it is possible to establish a controlled  
255 tip-substrate distance. In particular, we select stopping the UME approach when the  
256 distance between the UME and the surface is equivalent to the UME radius (12.5 μm)  
257 [20]. This approach is repeated at three different locations on the GC surface, making a

258 triangle between these three points. The electrocatalyst array substrate tilt is considered  
259 corrected when reaches the following condition:  $\Delta z/\Delta x$ (or  $\Delta y$ ) < (1.5  $\mu\text{m}/1\text{ mm}$ ). Then,  
260 the gold UME is replaced by a glass micropipette filled with a solution of HCOOH:DCE  
261 (50:50), which is slowly approached until it touches the GC surface, but avoiding to crush  
262 it. After this, the micropipette is retracted 50  $\mu\text{m}$  in Z direction. Then, the micropipette  
263 scans at constant distance the array surface in the XY plane, meanwhile the species of  
264 interest (HCOOH) is delivered within the bulk solution by crossing the liquid-liquid  
265 interface between two immiscible phases, DCE and H<sub>2</sub>O, in this case. The current  
266 collection for FAOR (difference between the maximum oxidation current displayed at the  
267 catalyst spot location and the background current at the same scanned line in the SECM  
268 image at a given tip-substrate distance) is calculated to quantitatively compare the  
269 catalytic activity of all different materials studied by SECM [<sup>38,59</sup>] (see later Table 1).

270 All SECM images were collected after performing an electrochemical pre-treatment  
271 for removing the CO<sub>ads</sub> accumulated at the electrode surface from previous FAOR  
272 experiments (potential pulse at 0.9 V for 2 s). The electrolyte 0.5 M H<sub>2</sub>SO<sub>4</sub> was purged  
273 with Ar gas until a low concentration of O<sub>2</sub> in the bulk solution was reached (0.10 mM,  
274 40% of the initial O<sub>2</sub> concentration in air saturated solution [<sup>60</sup>]). This O<sub>2</sub> concentration  
275 in solution was experimentally determined by measuring the electrochemical steady state  
276 current for ORR at -0.05 V provided by a gold UME after purging with Ar gas the 0.5 M  
277 H<sub>2</sub>SO<sub>4</sub> solution within the SECM cell. Moreover, an Ar blanket was kept above the  
278 solution during SECM imaging. The tip scan rate was 125  $\mu\text{m s}^{-1}$ , using increments of 25  
279  $\mu\text{m}$  each 0.2 s.

280

### 281 **3. Results and discussion**

282 First of all, the catalytic activity for FAOR of all 5 metallic NPs synthesized is  
283 individually evaluated by chronoamperometry at 3 different potentials (0.3 V, 0.5 V and  
284 0.7 V) in a low concentrated HCOOH solution (0.01 M) in order to achieve a similar  
285 concentration to that found in the SECM experiment. Figure 4 shows the comparison of  
286 all 5 oxidation current densities displayed by Pt, Pd and PtPd alloyed NPs after 600 s.  
287 This comparison allows to identify the most active electrocatalyst for FAOR under  
288 steady-state conditions at each given potential. In particular, Pd<sub>100</sub> and secondly Pt<sub>25</sub>Pd<sub>75</sub>  
289 NPs exhibit the highest activity at 0.3 V (figure 4A), meanwhile Pt<sub>100</sub> NPs exhibit a  
290 negligible activity at the same potential, due to CO poisoning [61]. In contrast, Pt<sub>75</sub>Pd<sub>25</sub>  
291 and secondly Pt<sub>100</sub> NPs exhibit the maximum activity at 0.5 and 0.7 V (figures 4B and  
292 4C), meanwhile, Pd<sub>100</sub> NPs show a negligible oxidation current at those potentials. These  
293 results are in agreement with those already published in the literature [62-64]. Nevertheless,  
294 they correspond to the electrocatalysts activity towards FAOR in the total absence of any  
295 other competitive reaction.

296 In contrast, Figure 5 displays SECM images for simultaneous FAOR and ORR under  
297 steady-state conditions on the electrocatalyst array formed by Pt, Pd and PtPd alloyed  
298 NPs schematically shown in Figure 3. These SECM images are also collected at 3  
299 different potential values, namely, 0.3 V, 0.5 V and 0.7 V. Unlike the behavior observed  
300 in the chronoamperometric tests presented in Figure 4, Pt<sub>50</sub>Pd<sub>50</sub> is the most active  
301 electrocatalyst spot at 0.3 V ( $I_{\text{collected}} = 97$  nA), whereas Pt<sub>75</sub>Pd<sub>25</sub> is the most active sample  
302 at 0.5 ( $I_{\text{collected}} = 75$  nA) and 0.7 V ( $I_{\text{collected}} = 56$  nA). Table 1 summarizes the oxidation  
303 current collected on each catalytic spot from the SECM images shown in Figure 5 as a  
304 function of applied potential. As can be seen, SECM catalytic activity results at 0.3 V  
305 differ from those obtained by chronoamperometry (Figure 4A). Nevertheless, there is a  
306 common feature, Pt<sub>75</sub>Pd<sub>25</sub> and secondly Pt<sub>100</sub> electrocatalyst spots exhibit the highest

307 catalytic activity at 0.5 and 0.7 V in both cases (figures 4B, 4C and 5). Furthermore, in  
308 all 3 SECM images, the background current corresponds to a reduction current on the  
309 array. In fact, the reason for that behavior is that active electrocatalyst spots for FAOR  
310 provide some oxidation current when the micropipette fluxes HCOOH on top of them,  
311 however, this oxidation current is not large enough to overcome the initial reduction  
312 current coming from the ORR and only produces a diminution in the background  
313 reduction current. This behavior is unexpected taking into account the important  
314 difference in local concentration between both electroactive species, O<sub>2</sub> and HCOOH.  
315 Bulk O<sub>2</sub> concentration in solution is very low (0.1 mM) and local HCOOH concentration  
316 coming out from the micropipette is expected to be much more important, since HCOOH  
317 presents high affinity toward the aqueous phase. Thus, we assume a fast HCOOH transfer  
318 across the liquid-liquid interface in the micropipette, which is the case for most similar  
319 neutral molecules [<sup>36</sup>]. It means a low partition coefficient,  $K$  ( $\approx 0.01$ ), which is defined  
320 as the ratio between backward and forward rate constants ( $k_b/k_f$ ) of the molecule coming  
321 out from the micropipette. Therefore, this comparison between catalytic activity for  
322 FAOR (Figure 4) and simultaneous FAOR and ORR (Figure 5) raises up a huge impact  
323 of O<sub>2</sub> crossover effect during FAOR. However, the impact of this effect is very different  
324 on Pd- and Pt-rich electrocatalysts and this is particularly relevant on Pd-rich  
325 electrocatalysts, since Pd<sub>100</sub> and Pt<sub>25</sub>Pd<sub>75</sub> electrocatalyst spots display a much lower  
326 HCOOH oxidation current than Pt-rich electrocatalysts under the same experimental  
327 conditions (SECM image, Figure 5). In spite of the fact that HCOOH local concentration  
328 should be at least two orders of magnitude larger than that of O<sub>2</sub> under those experimental  
329 conditions and thus, an oxidation net current would be expected in the SECM images,  
330 which is not the case in Figure 5. Additionally, it is important to rule out the potential  
331 contamination effect associated with the leakage of DCE coming out from the



332 micropipette during SECM images, in order to demonstrate the relevant role of the O<sub>2</sub>  
333 presence in solution during FAOR on Pd-rich catalysts. It has been already reported in  
334 the literature a strong adsorption of DCE at Pd surface [65], which could partially hinder  
335 their catalytic response and justify lower oxidation currents obtained when the MD/SC  
336 mode of SECM is used to study those electrocatalysts. Actually, DCE presents a non-  
337 negligible solubility in water (8.7 g/L at 20°C [66], which is equivalent to 0.088 M). For  
338 this reason, it is feasible that some DCE can get across the micropipette liquid-liquid  
339 interface and reach the electrocatalysts surface. Figure 6 presents the same  
340 chronoamperometries displayed in Figure 4, but in the presence of 0.088 M DCE in  
341 solution. Then, comparing the maximum current density reached in the presence (Figure  
342 6) and absence (Figure 4) of DCE, it is evident that an important drop in catalytic current  
343 for all 5 metallic NPs studied is observed when DCE is in solution (Figure 6). Moreover,  
344 a faster catalyst deactivation effect is observed for Pd<sub>100</sub> at 0.3 V and Pt<sub>75</sub>Pd<sub>25</sub> at 0.5 V in  
345 presence of DCE, since the current decay does not stop along 600 s. Nevertheless, the  
346 most active electrocatalyst as a function of applied potential remains unchanged in all  
347 cases (Pd<sub>100</sub> at 0.3 V and Pt<sub>75</sub>Pd<sub>25</sub> at 0.5 V and 0.7V). Thus, it is demonstrated that the  
348 sole presence of DCE in solution is not enough to justify the important difference in  
349 catalytic activity reported by SECM when simultaneous FAOR and ORR take place on  
350 Pd-rich electrocatalysts. Moreover, our results prove that the accumulation of organic  
351 solvent released from the micropipette into the solution may be not negligible in long  
352 term experiments, provoking an important quantitative impact, but it does not  
353 qualitatively alter the catalytic activity results obtained by the MD/SC mode of SECM.

354 Finally, Figure 7 compares the O<sub>2</sub> crossover effect during FAOR on Pd  
355 electrocatalysts in the absence (Figure 7A,  $\omega = 0$  rpm) and in the presence (Figure 7B,  $\omega$   
356 = 1000 rpm) of convection in solution. Figure 7 displays the same chronoamperometry at

357 0.3 V performed in an air saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> solution (black plots) for evaluating  
358 ORR and a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution containing 0.01 M HCOOH saturated by either argon  
359 (green plots) or air (red plots) for evaluating FAOR and simultaneous FAOR and ORR,  
360 respectively. Thus, figure 7A proves that the O<sub>2</sub> crossover effect during FAOR on Pd  
361 cannot be explained by a simple addition of two opposed currents coming from ORR and  
362 FAOR. The current decrease (0.044 mA cm<sup>-2</sup>) observed when simultaneous ORR and  
363 FAOR occur on the Pd surface (Figure 7A, red plot) in comparison with the current  
364 exclusively provided by FAOR (Figure 7A, green plot) does not correspond to the  
365 reduction current provided by ORR (-0.009 mA cm<sup>-2</sup>, Figure 7A, black plot). Therefore,  
366 the results displayed in Figure 7A confirm the reliability of the SECM results already  
367 reported in Figure 5, where Pd<sub>100</sub> NPs show a relevant decrease in activity for FAOR in  
368 the presence of a low concentration of O<sub>2</sub> in solution. In contrast, the same  
369 chronoamperometries performed under a laminar convective regime (Figure 7B,  $\omega =$   
370 1000 rpm), which does not allow the accumulation of any reaction intermediate or product  
371 in the vicinity of the electrode surface, display a negligible O<sub>2</sub> crossover effect during  
372 FAOR on Pd, since the current decrease shown when the simultaneous ORR and FAOR  
373 occur on the Pd surface (ca. 0.032 mA cm<sup>-2</sup>, Figure 7B, red and green plots) is actually  
374 smaller than the reduction current provided by ORR (-0.08 mA cm<sup>-2</sup>, Figure 7B, black  
375 plot). In conclusion, the negative impact on FAOR due to the O<sub>2</sub> crossover effect on Pd  
376 NPs is only relevant when the products or intermediates formed in one or both reactions  
377 (FAOR and ORR) accumulate near the electrode surface.

378 Regarding the different behavior displayed by Pt- and Pd-rich catalysts, it should be  
379 noted that for both electrodes, ORR has reached diffusion limited currents at 0.5 or 0.3  
380 V. Thus, it would be expected that the effect of O<sub>2</sub> on both electrodes were similar. It  
381 should be also noted that the chronoamperometric results in Figure 4 show that the

382 currents after 600 s for Pd<sub>100</sub> at 0.3 V and Pt<sub>100</sub> at 0.5 V are almost the same, thus the mere  
383 superposition of an additional reaction, in this case the ORR, which is under diffusion  
384 control, should have resulted in a similar diminution in the currents. However, the current  
385 diminution effect during FAOR on Pd NPs is significantly higher. Thus, we propose two  
386 main factors for explaining the different sensitivity towards O<sub>2</sub> presence in solution  
387 during FAOR when comparing Pd- and Pt- rich catalysts. On the one hand, the different  
388 type of product formed during ORR on Pd and Pt, since the H<sub>2</sub>O<sub>2</sub> production on Pd is  
389 much more relevant than on Pt, being the number of electrons exchanged (*n*) during ORR  
390 between 2.85 and 3.60 on Pd and between 3.95 and 4.00 on Pt [27]. Therefore, we propose  
391 ORR byproducts (particularly H<sub>2</sub>O<sub>2</sub>) accumulation on the Pd surface as the responsible  
392 of diminishing its FAOR catalytic performance. One of the possible options is a chemical  
393 reaction producing no net electron transfer between H<sub>2</sub>O<sub>2</sub> accumulated on the Pd surface  
394 and HCOOH, which reduces the HCOOH concentration close to the surface. On the other  
395 hand, at 0.5 V on Pt, CO is still formed and accumulated on the surface [61], leading to  
396 lower currents. It is also known that traces of O<sub>2</sub> facilitate the oxidation of adsorbed CO,  
397 and, thus, in the presence of O<sub>2</sub>, CO coverage on Pt would be smaller, and higher FAOR  
398 activity could be obtained. Then, the reduction current due to the ORR would be  
399 compensated by a higher oxidation current for the FAOR, resulting in a lower diminution.  
400 This compensating mechanism is not possible on Pd electrodes, because CO is not  
401 effectively formed.

402

#### 403 **4. Conclusions**

404 The relevant role displayed by O<sub>2</sub> crossover during FAOR specially on Pd NPs is  
405 demonstrated here. Depending on the electrocatalyst material and the applied potential,  
406 O<sub>2</sub> can be reduced simultaneously with HCOOH oxidation, which in some cases produces

407 an important deactivation of FAOR and reduces the interest of that material as anode in  
408 DFAFCs. This deactivation effect displayed by O<sub>2</sub> presence in solution is proved for Pd  
409 and Pd-rich electrocatalysts by SECM imaging and it is also verified by conventional  
410 chronoamperometry. This fact diminishes the anode efficiency by reactant competition  
411 and because of ORR byproducts (particularly H<sub>2</sub>O<sub>2</sub>) accumulate and react on the anode  
412 electrocatalyst surface. However, this phenomenon is not equally evident in all types of  
413 electrocatalysts, being Pd much more sensitive to this than Pt, since the H<sub>2</sub>O<sub>2</sub> production  
414 from ORR is much more relevant on Pd than on Pt. Nevertheless, this negative impact  
415 displayed on Pd NPs becomes negligible when the hydrodynamic regime in solution does  
416 not allow H<sub>2</sub>O<sub>2</sub> accumulation on the Pd NPs surface as have been proved by the RDE  
417 measurements (Figure 7B). We believe this conclusion provides a new approach to  
418 develop future synthesis of Pd-based electrocatalysts for FAOR, since introducing a co-  
419 catalyst next to Pd for activating ORR towards H<sub>2</sub>O production ( $n = 4$ ) should provide  
420 longer-term activity for FAOR. Actually, we think this may be the reason why some  
421 recently published Pd-based electrocatalysts (Pd-Ni<sub>2</sub>P/C) outperform Pd anodes in  
422 DFAFCs [48].

423 SECM is proved as a fast and powerful technique for studying O<sub>2</sub> crossover effect in  
424 different electrocatalysts and for identifying highly selective electrocatalysts candidates  
425 for MRFCs, which represents a key issue for further development of DFAFCs and  
426 MRFCs. In particular, among the samples evaluated, Pt<sub>75</sub>Pd<sub>25</sub> NPs present the highest  
427 average performance for FAOR in presence of O<sub>2</sub> within the entire potential range under  
428 study (0.3-0.7 V) according to the SECM current collected in Table 1. The MD/SC mode  
429 of SECM is used to locally provide a constant flux of HCOOH near different  
430 electrocatalysts in a low concentrated O<sub>2</sub> aqueous solution. However, this mode of SECM

431 could be also applied to study other molecules of interest such as methanol, ethanol or  
432 glycerol.

433

#### 434 **Acknowledgements**

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437 Generalitat Valenciana (project PROMETEOII/2014/013).

438

439

440 **TABLES**

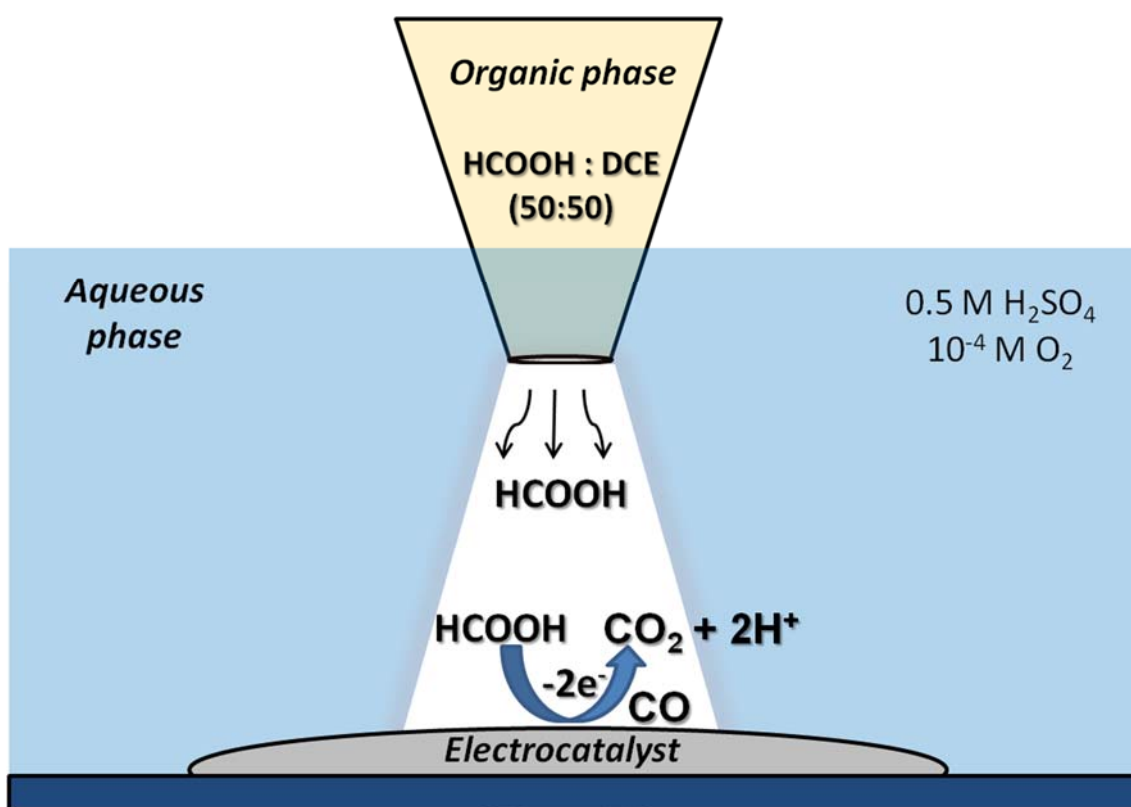
441 **Table 1.** Oxidation current collected on Pt, Pd and PtPd alloyed NPs as a function of  
 442 applied potential from SECM images shown in Figure 5

443

<b>E (V) vs RHE</b>	<b>I<sub>collected</sub> (nA)</b>	<b>I<sub>collected</sub> (nA)</b>	<b>I<sub>collected</sub> (nA)</b>	<b>I<sub>collected</sub> (nA)</b>	<b>I<sub>collected</sub> (nA)<sup>1</sup></b>
	<b>Pt<sub>100</sub></b>	<b>Pt<sub>75</sub>Pd<sub>25</sub></b>	<b>Pt<sub>50</sub>Pd<sub>50</sub></b>	<b>Pt<sub>25</sub>Pd<sub>75</sub></b>	<b>Pd<sub>100</sub></b>
<b>0.3</b>	50	92	97	65	
<b>0.5</b>	75	75	47	26	
<b>0.7</b>	51	56	44	27	

444 <sup>1</sup>Oxidation current is not different from background current

445

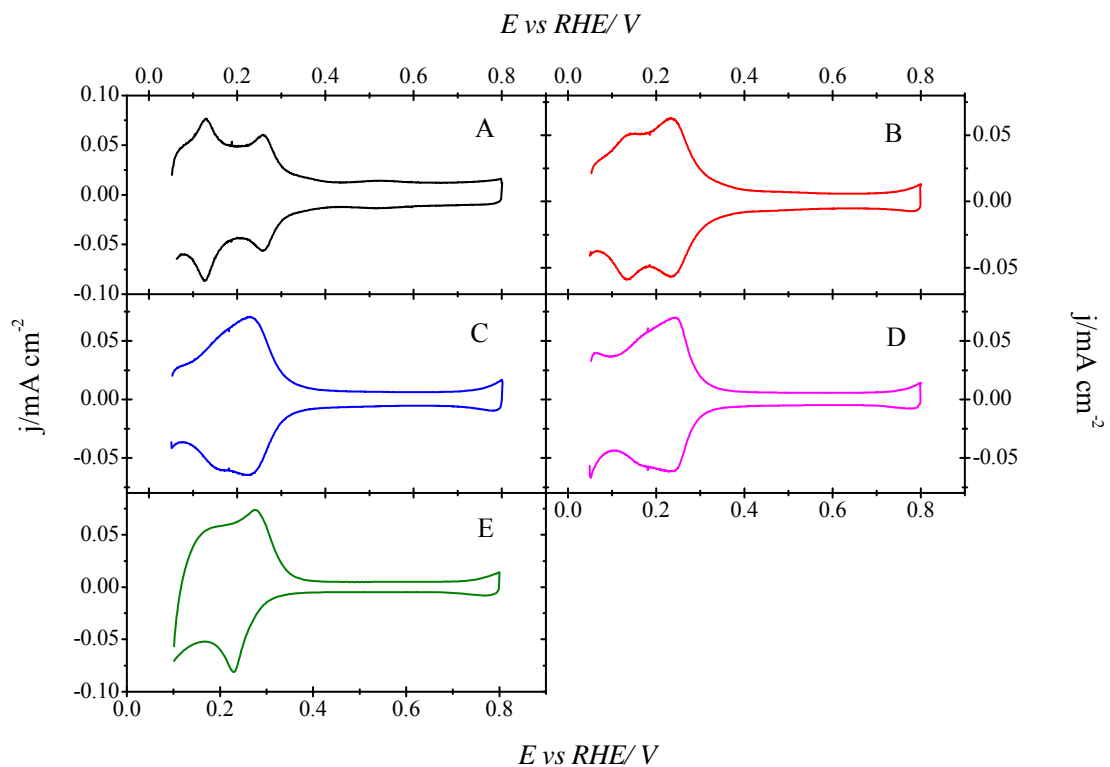


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448

449 **Figure 1.** Schematic representation of the conventional MD/SC mode of the SECM  
 450 applied to the screening of electrocatalysts for the HCOOH oxidation reaction in the  
 451 presence of  $\text{O}_2$  in aqueous solution.

452

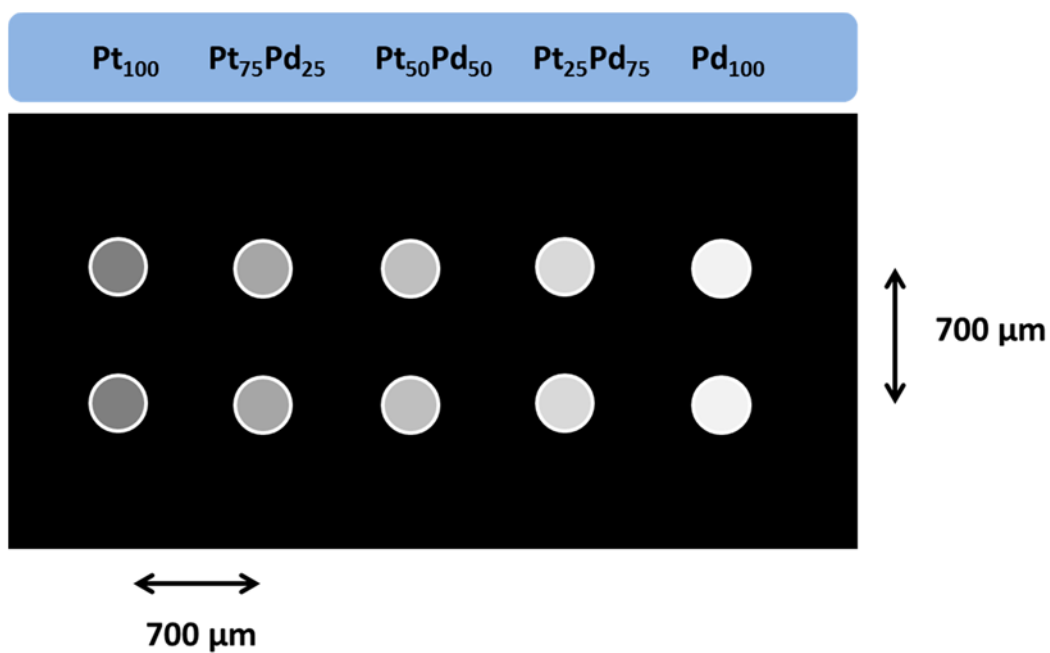


453  
 454 **Figure 2.** Cyclic voltammeteries for electrochemical surface characterization on  
 455 synthesized Pt, Pd and Pt-Pd alloyed NPs in deaerated 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. (A) Pt<sub>100</sub>;  
 456 (B) Pt<sub>75</sub>Pd<sub>25</sub>; (C) Pt<sub>50</sub>Pd<sub>50</sub>; (D) Pt<sub>25</sub>Pd<sub>25</sub> and (E) Pd<sub>100</sub>. Scan rate 50 mV s<sup>-1</sup>.

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 458  
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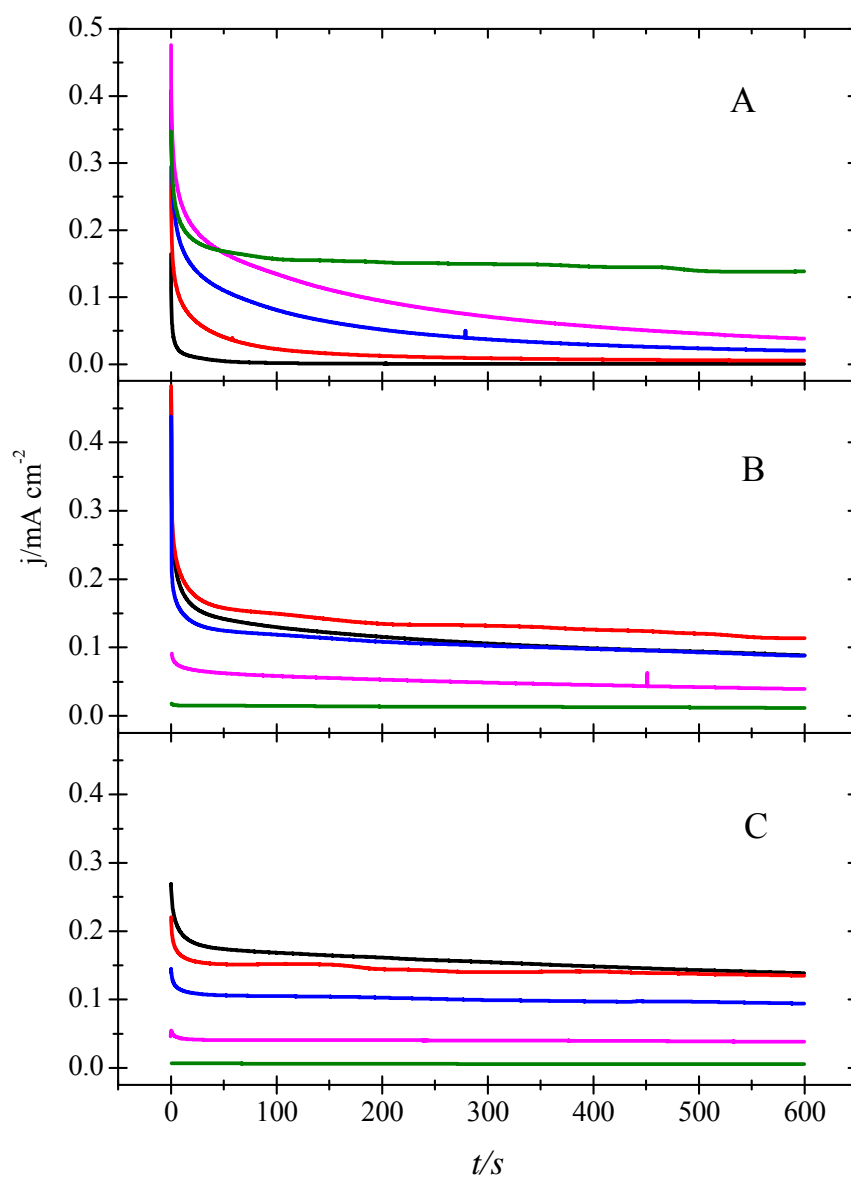
461

462 **Figure 3.** Array pattern of 2 x 5 of Pt, Pd and Pt-Pd alloyed NPs on a glassy carbon

463 substrate.

464

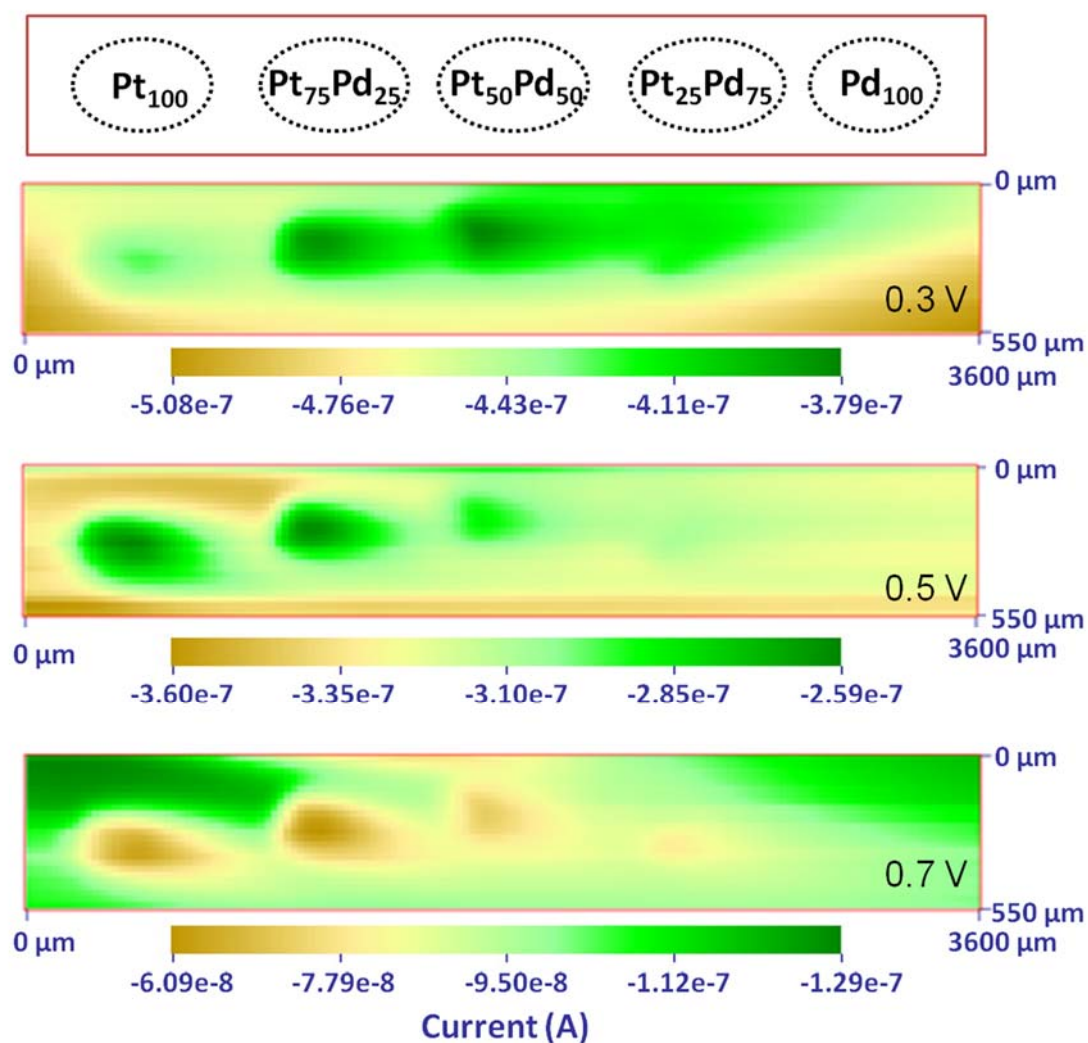
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467 **Figure 4.** Chronoamperometries of Pt<sub>100</sub> (black line), Pt<sub>75</sub>Pd<sub>25</sub> (red line), Pt<sub>50</sub>Pd<sub>50</sub> (blue  
 468 line), Pt<sub>25</sub>Pd<sub>75</sub> (purple line) and Pd<sub>100</sub> (green line) NPs in argon saturated 0.01 M HCOOH  
 469 and 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at different potentials. A) 0.3 V, B) 0.5 V and C) 0.7 V vs  
 470 RHE.

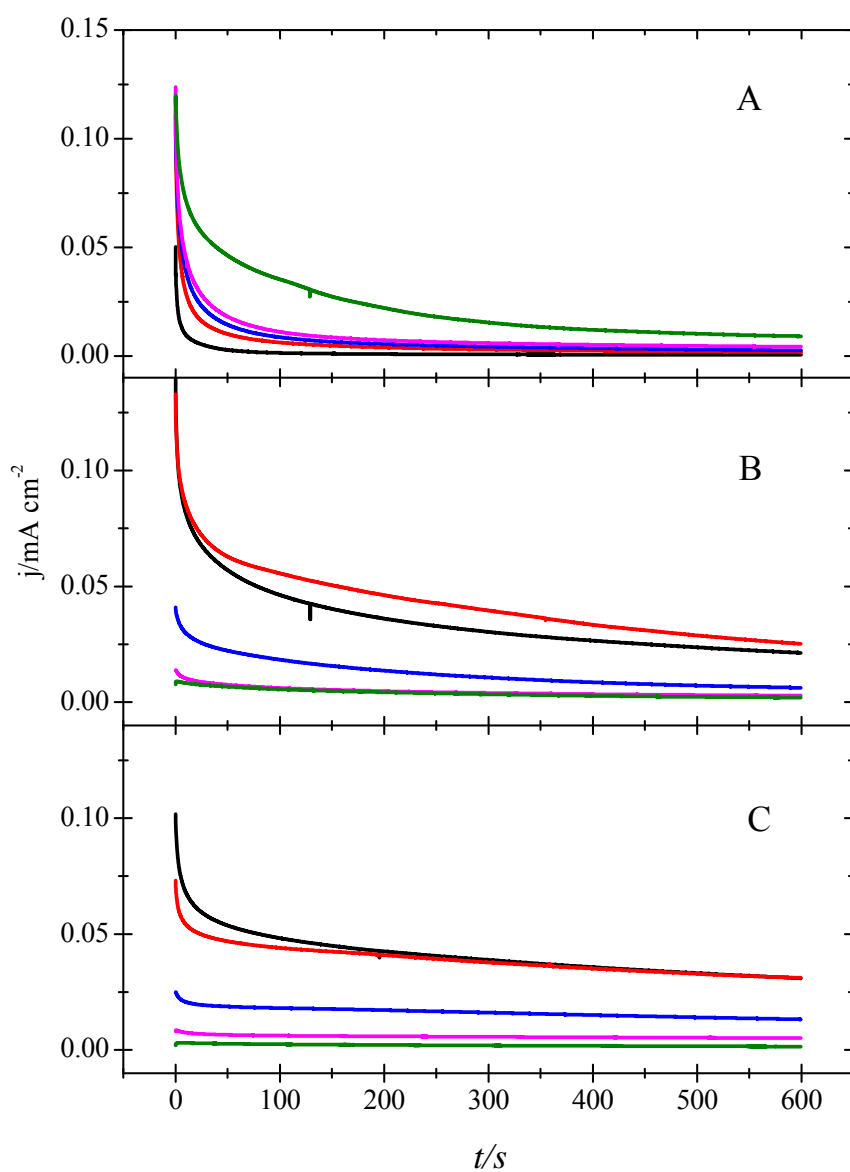
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473

474 **Figure 5.** SECM MD/SC images displaying the substrate current for simultaneous FAOR  
 475 and ORR in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 10<sup>-4</sup> M O<sub>2</sub> solution on Pt, Pd and Pt-Pd alloyed NPs. The  
 476 substrate potential is held constant at 3 different potentials (0.3, 0.5 and 0.7 V vs RHE).  
 477 The substrate array is formed by spots of 5 different NPs Pt<sub>100</sub>, Pt<sub>75</sub>Pd<sub>25</sub>, Pt<sub>50</sub>Pd<sub>50</sub>, Pt<sub>25</sub>Pd<sub>75</sub>  
 478 and Pd<sub>100</sub>. The tip scan rate was 125 μm s<sup>-1</sup>, using increments of 25 μm each 0.2 s. Tip-  
 479 substrate distance = 50 μm.

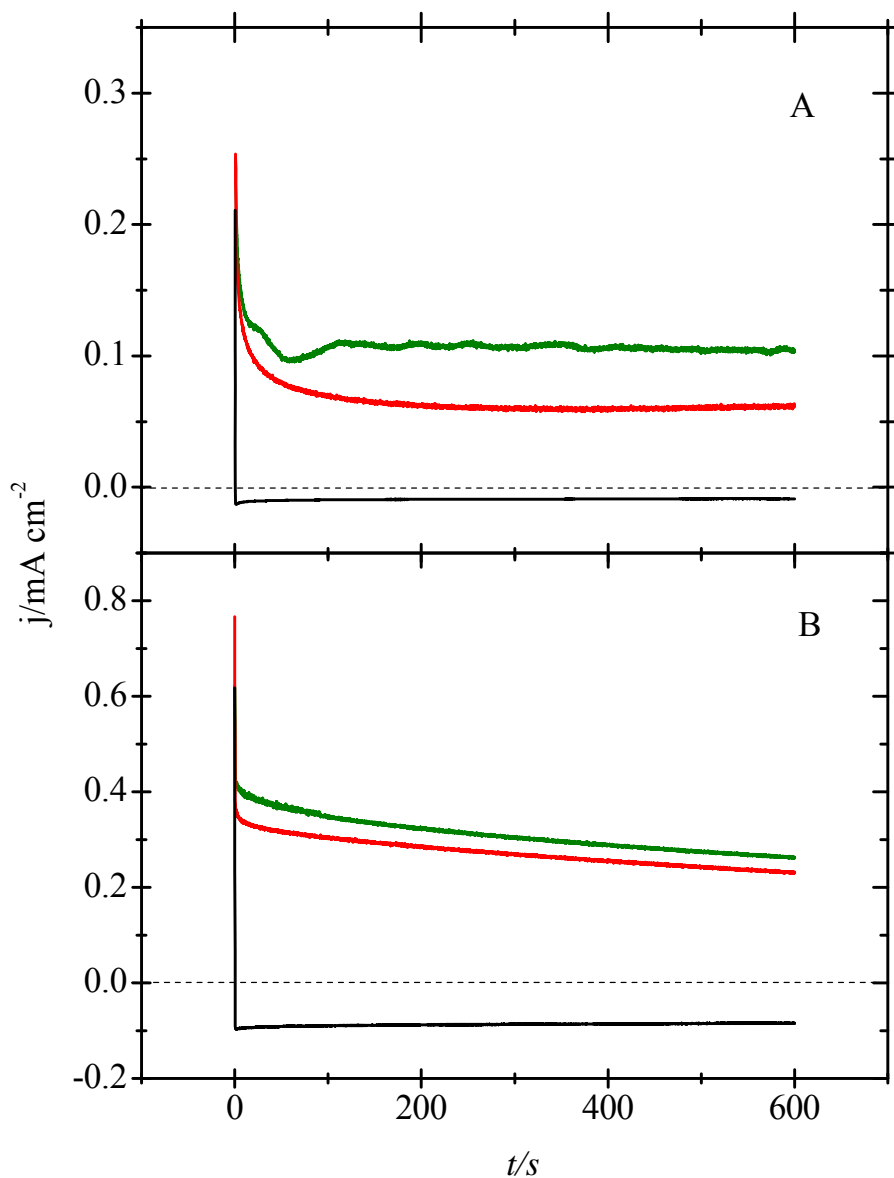
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481

482 **Figure 6.** Chronoamperometries of Pt<sub>100</sub> (black line), Pt<sub>75</sub>Pd<sub>25</sub> (red line), Pt<sub>50</sub>Pd<sub>50</sub> (blue  
 483 line), Pt<sub>25</sub>Pd<sub>75</sub> (purple line) and Pd<sub>100</sub> (green line) NPs in argon saturated 0.01 M HCOOH,  
 484 0.088 M DCE and 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at different potentials. A) 0.3 V, B) 0.5 V and  
 485 C) 0.7 V vs RHE.

486



487

488 **Figure 7.** Chronoamperometries at 0.3 V of Pd NPs using a RDE at 0 rpm (A) and 1000

489 rpm (B). Green plots correspond to an Ar saturated 0.01 M HCOOH + 0.5 M H<sub>2</sub>SO<sub>4</sub>

490 solution. Red plots correspond to non deaerated 0.01 M HCOOH + 0.5 M H<sub>2</sub>SO<sub>4</sub> solution.

491 Black plots correspond to a non deaerated 0.5 M H<sub>2</sub>SO<sub>4</sub> solution.

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