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1 Structure Dynamics of Carbon-Supported Platinum-  
2 Neodymium Nanoalloys during the Oxygen  
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21 **KEYWORDS:** Pt alloys, Rare Earth Metals, Operando measurements, Oxygen Reduction  
22 Reaction, Proton Exchange Membrane Fuel cells.

## 23 **ABSTRACT**

24 Platinum-rare earth nanoalloys have been predicted to be promising proton exchange membrane  
25 fuel cell (PEMFC) electrocatalysts for the cathodic oxygen reduction reaction (ORR). However,  
26 their implementation in PEMFCs is limited by the challenge of their preparation as carbon-  
27 supported nanostructures. Consequently, the practical structure-activity-stability trends for this  
28 class of nanoalloys remain largely unexplored. Herein, carbon-supported Pt-Nd nanoalloys as  
29 ORR electrocatalysts are described. The physical chemistry of selected electrocatalysts was  
30 extensively investigated by means of combined *ex situ* and *operando* techniques, which reveal the  
31 unique structural dynamics of Pt-Nd nanoalloys in a simulated PEMFC cathode environment. The  
32 experimental observations, supported by theoretical calculations, indicate that after initial  
33 significant structural modification in the early stage of operation, the ORR activity is mediated in  
34 the longer-term by surface compressive strain rather than charge transfer between Pt and Nd. Such  
35 key *operando* structure-activity-stability relations underpin further optimization of carbon-  
36 supported Pt-rare earth nanoalloys as fuel cell cathode catalysts.

37

## 38 **1. INTRODUCTION**

39 Proton-exchange membrane fuel cells (PEMFCs) are considered as suitable devices to contribute  
40 to the CO<sub>2</sub> neutrality targets,<sup>1</sup> and have gained much attention for use in heavy-duty and long-  
41 distance transportation due to the high gravimetric energy density of hydrogen.<sup>2</sup> Notwithstanding,  
42 the massive implementation of PEMFCs is still hindered by technical barriers that need to be  
43 overcome, including performance, durability, cost and fuel efficiency.<sup>3,4</sup> In fact, the performance  
44 of a PEMFC has an important dependency on the catalyst layers,<sup>5</sup> which usually possess high Pt

45 loadings specially at the cathode, where the sluggish oxygen reduction reaction (ORR) takes place.  
46 Therefore, tailoring high-performance Pt-based electrocatalysts for the ORR is of paramount  
47 importance, which current target is to use 0.1 g<sub>PGM</sub>/kW (platinum-group metal, PGM) for  
48 automotive and 0.3 g<sub>PGM</sub>/kW for heavy-duty transport applications.<sup>2</sup>

49

50 A widely used strategy to increase the activity of ORR electrocatalysts is by alloying Pt with late  
51 transition metals (usually Ni, Co, Fe, Cu, *etc*), which also decreases simultaneously the amount of  
52 Pt.<sup>5</sup> However, the long-term stability of these materials represents a crucial issue that must be  
53 overcome.<sup>6, 7</sup> In this context, Pt-rare earth metal (Pt-REM) alloys have been proposed as a  
54 promising family of highly active/stable electrocatalysts for the ORR.<sup>8</sup> Theoretical studies  
55 suggested that the exceptionally negative formation energy of Pt-REM alloys represents a kinetic  
56 barrier to diffusion of the REM atom, and impedes the alloy degradation.<sup>8,9</sup> Experimental evidence  
57 with bulk sputter-cleaned polycrystalline electrodes<sup>10-13</sup> and unsupported nanoparticles (NPs)<sup>14, 15</sup>  
58 revealed that the high activity of these alloys (including the cubic structure Pt<sub>3</sub>Y system) stems  
59 from the formation of a specific structure, in which the Pt-REM alloy is protected by a Pt-rich  
60 overlayer,<sup>16</sup> which experiences a lateral compressive strain.<sup>11, 16</sup> Indeed, the surface specific ORR  
61 activity showed an exponential dependence on the degree of compressive strain in the Pt-REM  
62 alloys.<sup>14, 15</sup>

63

64 Escudero-Escribano *et al.*<sup>13</sup> correlated the ORR specific activity of Pt<sub>5</sub>REM sputter-cleaned  
65 polycrystalline electrodes (REM = La, Ce, Sm, Gd, Tb, Dy, Tm) to the *ex situ* measured Pt lattice  
66 parameter. Pt<sub>5</sub>REM forms a hexagonal crystalline structure, the atomic arrangement of which

67 stabilizes the so-called *kagome* layer.<sup>16</sup> This particular configuration presents an unusual CaCu<sub>5</sub>-  
68 like structure that accommodates the alloying elements of different atomic radius in a different  
69 way from face centered cubic (FCC) or hexagonal close packed (HCP) alloys, to form uniform  
70 bond lengths between Pt-Pt, Pt-REM and REM-REM:<sup>16</sup> the CaCu<sub>5</sub> structure consists of alternating  
71 layers of Pt<sub>2</sub>REM and Pt<sub>3</sub> layers. The pure Pt layers in bulk Pt<sub>5</sub>M alloys have hollow vacancy-like  
72 spaces at positions below and above the REM atoms. This results in a compressed Pt overlayer  
73 despite alloying Pt with larger REM atoms, which can be explained by the hexagonal symmetry  
74 of both the Pt(111) surface and the Pt<sub>5</sub>REM bulk structure. In fact, the lattice parameter *a* in the  
75 hexagonal structure continues its contraction while moving towards the so-called lanthanide  
76 contraction, but the *b* and *c* lattice parameters are considerably different due to the different re-  
77 organization of the atoms. Namely, for Pt-REM alloys with the CaCu<sub>5</sub>-like structure, the unit cell  
78 *a* will contract (shorter Pt-Pt distances) as the REM covalent radii decreases (lanthanide  
79 contraction).<sup>13</sup> *Ex situ* measurements of the imposed compressive strain in the Pt lattice revealed  
80 that the specific ORR activity is highest at a contraction of -3 %, respect to Pt bulk.<sup>13</sup>

81

82 Nevertheless, the limited availability of carbon-supported Pt-REM nanostructures has restricted  
83 the transposition of the results obtained on model extended surfaces to practical PEMFCs. Indeed,  
84 synthesis of nanoparticle Pt-REM alloys is challenging due to the highly negative standard redox  
85 potential of rare earth metals (far beyond the stability range of water) and their high oxophilicity,  
86 which favours formation of REM oxygen-containing species instead of alloys.<sup>17</sup> Although recent  
87 synthesis approaches<sup>17-20</sup> have enabled the preparation of carbon-supported Pt-REM nanoalloys,  
88 their reported ORR mass activity (between 0.3 - 0.7 A mg<sub>Pt</sub><sup>-1</sup>)<sup>21-23</sup> is far below that of unsupported

89 9 nm Pt<sub>x</sub>Y<sup>14</sup> NPs (3.05 A mg<sub>Pt</sub><sup>-1</sup>) or 8 nm Pt<sub>x</sub>Gd<sup>15</sup> NPs (3.60 A mg<sub>Pt</sub><sup>-1</sup>). Therefore, further  
90 understanding and optimization of Pt-REM/C nanoalloys are still needed.

91  
92 *In situ* and/or *operando* techniques, such as X-ray diffraction (XRD), X-ray absorption  
93 spectroscopy (XAS), *online* inductively coupled plasma mass spectrometry (ICP-MS), *etc.*, are  
94 essential tools to understand electrocatalyst behaviour in real or simulated electrochemical  
95 environments of the application device. Indeed, it is largely accepted that fundamental reactivity  
96 descriptors (*e.g.* surface strain, chemistry and/or crystallinity) of Pt-based electrocatalysts  
97 measured and tailored *ex situ* are not necessarily conserved *in situ*<sup>24-27</sup> due to surface reconstruction  
98 in the particular environment of the PEMFC cathode on operation.<sup>24, 28</sup> Indeed, to the best of our  
99 knowledge, such *In situ* and/or *operando* techniques has never been used to investigate this  
100 promising novel class of Pt-REM/C nanoalloys.

101  
102 In this contribution, we describe the synthesis and extensive characterization of carbon-supported  
103 Pt-Nd nanoalloys. By adjusting the quantity of the Nd chemical precursor during the synthesis, the  
104 Pt:Nd composition in the final electrocatalyst was systematically modulated and the ORR activity  
105 was tailored. Two Pt-Nd/C electrocatalysts of different crystal structure were selected on the basis  
106 of their high ORR activity, and were investigated by means of an extensive range of combined *ex*  
107 *situ* (WAXS, XAS, HRTEM, STEM/EELS, ICP-MS) and *operando* (WAXS) techniques. The *ex*  
108 *situ* and *operando* structural properties of the selected materials were rationalized and compared,  
109 to shed new light on the *operando* structure-activity-stability relationships of carbon-supported Pt-  
110 REM nanoalloys.

111

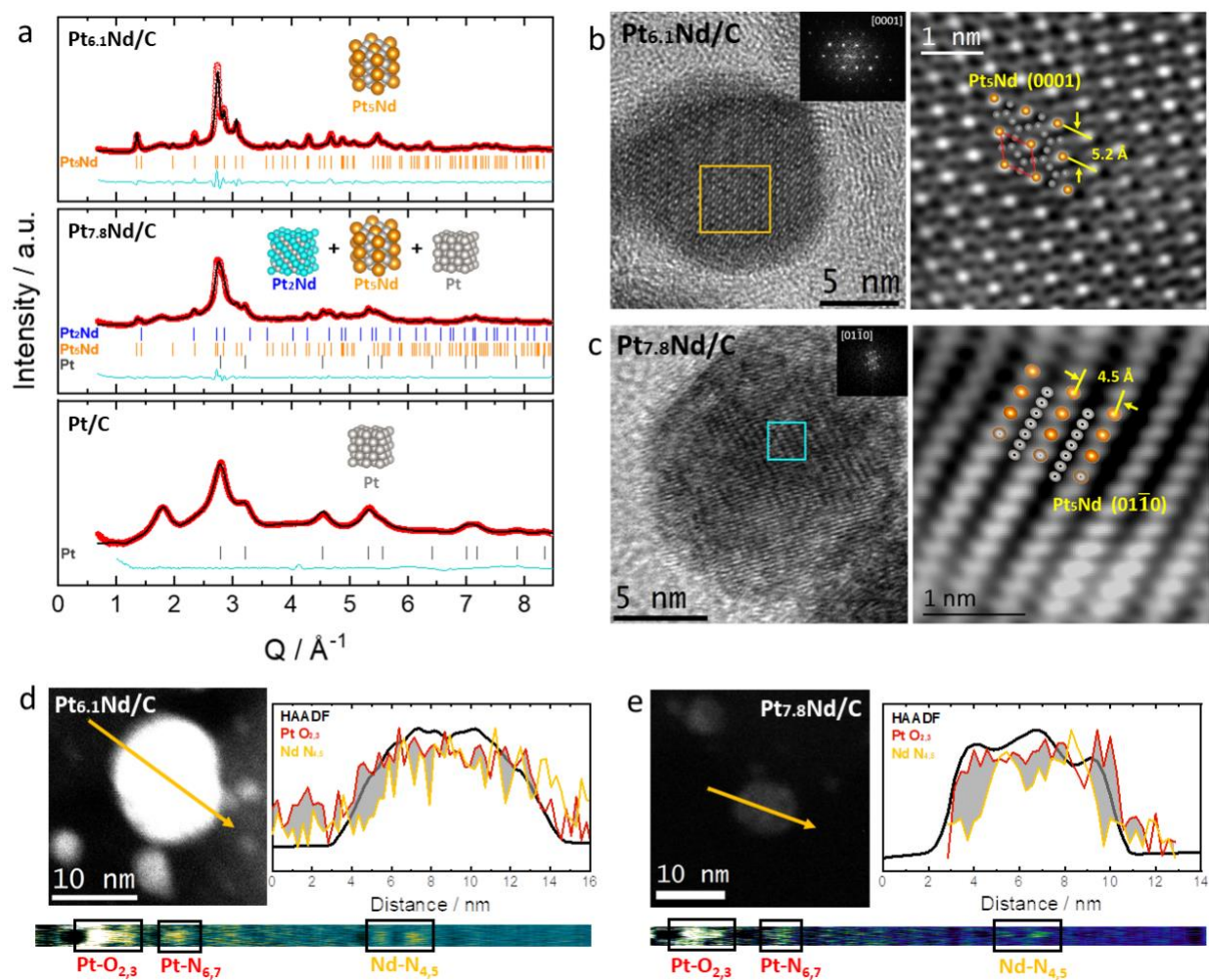
### 112 3. RESULTS AND DISCUSSION

113 We have prepared Pt-Nd/C nanoalloys using the carbodiimide complex route proposed by Hu *et*  
114 *al.*<sup>18</sup> with some modifications<sup>29, 30</sup> (see Supplementary Information S1). Firstly, five Pt:Nd atomic  
115 ratios (16.5:1, 7.8:1, 6.1:1, 5.7:1 and 5.4:1) were obtained by systematically varying the Nd  
116 precursor content in the synthesis. The Pt<sub>x</sub>Nd/C catalyst series prepared was subsequently  
117 characterized by means of XRD, ICP-MS and electron microscopy, and their electrocatalytic  
118 activity was investigated using the RDE technique in 0.1 M HClO<sub>4</sub> electrolyte (see Supplementary  
119 Information S6). This preliminary screening revealed that the Pt<sub>7.8</sub>Nd/C and Pt<sub>6.1</sub>Nd/C  
120 electrocatalysts present the highest activity for the ORR among the series (0.55 A mg<sub>Pt</sub><sup>-1</sup> and 0.63  
121 A mg<sub>Pt</sub><sup>-1</sup> at 0.9 V<sub>RHE</sub>, respectively), surpassing the reference Pt/C material from Johnson-Matthey  
122 (0.24 A mg<sub>Pt</sub><sup>-1</sup>). Interestingly, and despite relatively close overall chemical composition and ORR  
123 activity, the crystalline structures of these two materials revealed by XRD are different, with  
124 Pt<sub>6.1</sub>Nd/C presenting only the Pt<sub>5</sub>Nd hexagonal phase and Pt<sub>7.8</sub>Nd/C a mixture of cubic Pt, cubic  
125 Pt<sub>2</sub>Nd and hexagonal Pt<sub>5</sub>Nd phases. These two electrocatalysts were selected as model samples for  
126 a more comprehensive understanding of the structure-activity-stability trends in this class of  
127 nanoalloys.

128 Rietveld full profile refinement of the wide-angle synchrotron X-ray scattering (WAXS) patterns  
129 of Pt<sub>7.8</sub>Nd/C and Pt<sub>6.1</sub>Nd/C collected *ex situ*, see Figure 1a, confirms the above results obtained  
130 from laboratory-source XRD. Quantitative phase analysis indicates that the Pt<sub>7.8</sub>Nd/C sample  
131 comprises 51 wt.% hexagonal Pt<sub>5</sub>Nd, 37 wt.% FCC Pt and 12 wt.% cubic Pt<sub>2</sub>Nd crystalline phases,  
132 and that the Pt<sub>6.1</sub>Nd/C sample is 100 wt.% hexagonal Pt<sub>5</sub>Nd crystal structure. Further

133 microstructural parameters, such as the lattice constants of these phases and their associated  
 134 coherent domain sizes, were extracted from the Rietveld refinement, and are shown in Table 1.  
 135 Compared to the reference Pt/C electrocatalyst, the nearest neighbour Pt-Pt distances are shorter  
 136 in the Pt<sub>2</sub>Nd and Pt<sub>5</sub>Nd crystalline arrangements, corresponding to a compressive strain of *ca.* -2%  
 137 and -3%, respectively.

138



139  
 140 **Figure 1.** (a) Refined *ex situ* WAXS patterns (vertical bars represent the theoretical diffraction  
 141 pattern of each crystalline phase, and the cyan line represents the residual from the refinement);  
 142 representative HRTEM micrographs of (b) Pt<sub>6.1</sub>Nd/C and (c) Pt<sub>7.8</sub>Nd/C; and (c) representative  
 143 HAADF-STEM/EELS analysis of (d) Pt<sub>6.1</sub>Nd/C and (e) Pt<sub>7.8</sub>Nd/C. Pt/C is used as reference in (a).



144 **Table 1.** Chemical composition, particle size and refined structural data of Pt<sub>6.1</sub>Nd/C and  
 145 Pt<sub>7.8</sub>Nd/C. Pt/C is used as reference.

	<sup>a</sup> Metal content (%wt.)	<sup>a</sup> Pt:Nd ratio	<sup>b</sup> Mean particle size (nm)	Crystalline phase weight fraction (%)	Lattice parameter a (Å)	<sup>c</sup> Lattice parameter c (Å)	Coherent domain size (nm)	Pt – Pt distance (Å)	<sup>d</sup> ε (%)
Pt <sub>7.8</sub> Nd/C	Pt: 26.67 Nd: 2.52	7.8 : 1	6.1 ± 1.6 *12.8 ± 1.7	Pt <sub>5</sub> Nd: 51 Pt <sub>2</sub> Nd: 12 Pt: 37	Pt <sub>5</sub> Nd: 5.357 Pt <sub>2</sub> Nd: 7.644 Pt: 3.914	Pt <sub>5</sub> Nd: 4.421	Pt <sub>5</sub> Nd: 4.0 Pt <sub>2</sub> Nd: 5.3 Pt: 3.2	Pt <sub>5</sub> Nd: 2.678 Pt <sub>2</sub> Nd: 2.702 Pt: 2.767	Pt <sub>5</sub> Nd: -3.1 Pt <sub>2</sub> Nd: -2.2 Pt: 0.1
Pt <sub>6.1</sub> Nd/C	Pt: 27.04 Nd: 3.29	6.1 : 1	6.8 ± 1.5 *13.1 ± 2.1	Pt <sub>5</sub> Nd: 100	Pt <sub>5</sub> Nd: 5.364	Pt <sub>5</sub> Nd: 4.408	Pt <sub>5</sub> Nd: 9.5	Pt <sub>5</sub> Nd: 2.682	Pt <sub>5</sub> Nd: -3.0
Pt/C	Pt: 47.2	--	3.7 ± 0.9	Pt: 100	Pt: 3.909	--	Pt: 1.6	Pt: 2.764	0

146 a: Determined by ICP-MS; b: Determined by TEM; c: in a hexagonal structure a=b≠c; d: Relative  
 147 to Pt/C. \* Average size of agglomerates.

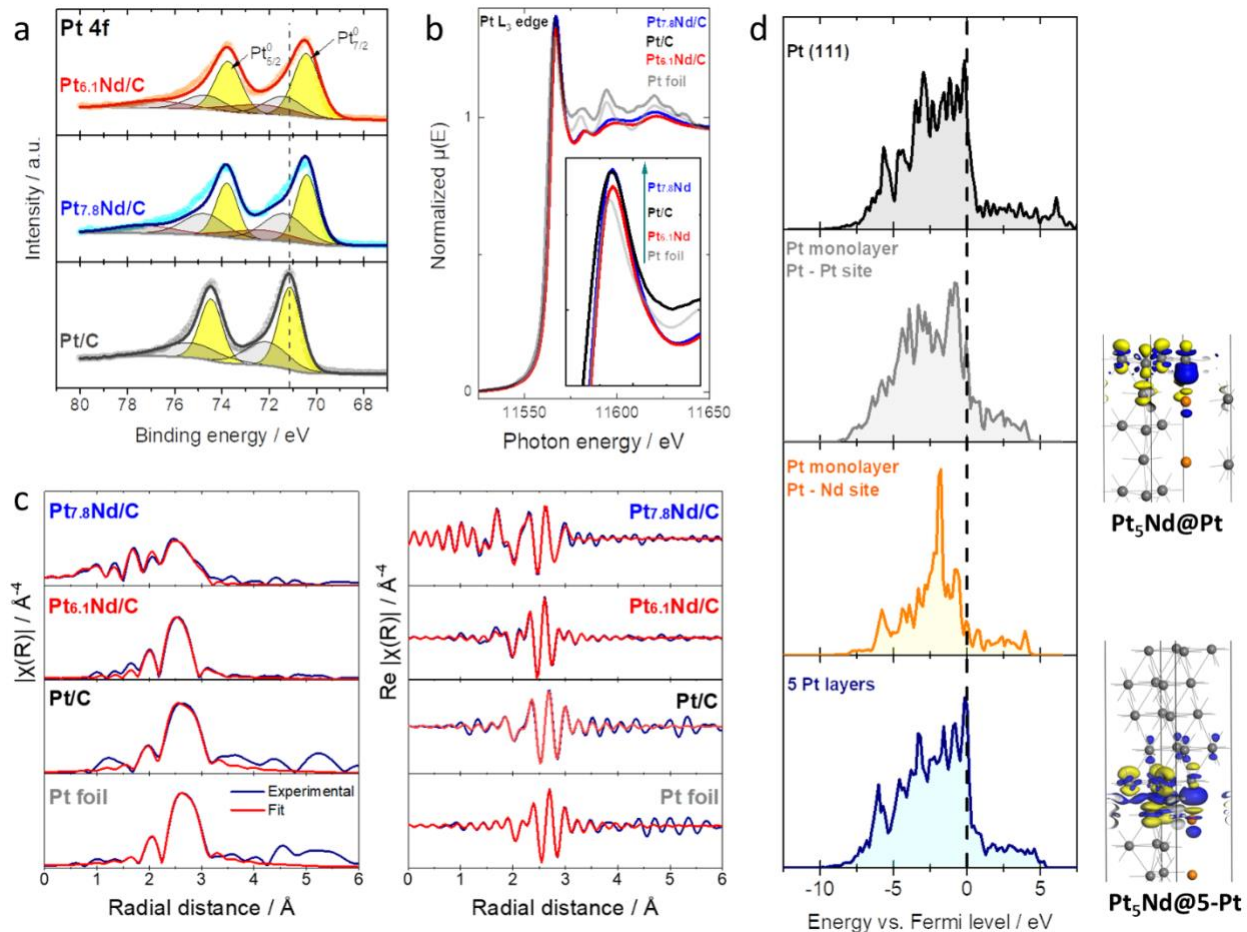
148

149 High resolution TEM overviews and the corresponding power spectrum on isolated NPs, Figure  
 150 1b and c, resolve the atomic arrangements in both materials, where the Pt<sub>5</sub>Nd (0001) and the Pt<sub>5</sub>Nd  
 151 (01 $\bar{1}$ 0) crystalline planes are observed for Pt<sub>6.1</sub>Nd/C and Pt<sub>7.8</sub>Nd/C, respectively. For both  
 152 electrocatalysts, the results of combined HAADF-STEM and EELS analyses, Figure 1d and 1e,  
 153 also confirm the presence of both Pt and Nd in the NPs. Due to the difference between the Pt and  
 154 Nd dissolution potentials and the post-synthesis acidic wash (4 h in N<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub>), it  
 155 is expected the stabilization of a Pt-rich shell surrounded the alloy structure.<sup>31</sup> Based on the  
 156 computed phase diagram of the possible structures and their associated stabilities (see the  
 157 Supplementary Information S9), a pure Pt monolayer over the Pt<sub>5</sub>Nd alloy (Pt<sub>5</sub>Nd@Pt) is a quite  
 158 stable structure. Considering that the thickness of an atomic monolayer of Pt is ~ 0.2 nm, and that  
 159 the probe size and the probe step in the HAADF-STEM/EELS were 0.5 nm and 0.4 nm  
 160 respectively, the detection of one atomic Pt monolayer is clearly below the detection limit of the

161 microscope used. Therefore, the presence of Pt<sub>5</sub>Nd@Pt with a thinner Pt overlayer or structures  
162 with Pt-rich multilayers cannot be ruled out.

163 The near-surface composition was investigated by XPS. Figure 2a shows the Pt 4*f* photoemission  
164 lines, which indicates the predominance of the Pt metallic state at the near-surface region in all  
165 cases (the survey spectra and the Nd 3*d* photoemission lines are given in the Supplementary  
166 Information S7). However, the binding energy position of the Pt metallic doublet in Pt<sub>7.8</sub>Nd/C and  
167 Pt<sub>6.1</sub>Nd/C is downshifted with respect to that of the Pt/C reference, suggesting a modification of  
168 the Pt electronic structure. The alloy formation energy ( $\Delta H^{\circ}_{\text{Pt5Nd}} = -55 \text{ kJ g}^{-1} \text{ atom}^{-1}$ )<sup>32</sup> correlates  
169 with the difference in electronegativity between the alloying metals,<sup>33</sup> leading to charge transfer  
170 from Nd ( $\chi_{\text{Nd}} = 1.14$ ) to Pt ( $\chi_{\text{Pt}} = 2.28$ ) and increased electron density around Pt. Besides,  
171 compressive strain, *i.e.*, shorter Pt-Pt interatomic distances, might also modify the electronic states  
172 of Pt due to the overlapping of the electron conduction bands.<sup>34</sup>

173



174

175 **Figure 2.** (a) Pt 4f photoemission lines (Pt/C is used as reference); *ex situ* Pt L<sub>3</sub> edge (b) XANES  
 176 and (c) fitted FT EXAFS spectra (Pt foil and Pt/C are used as reference) of Pt<sub>6.1</sub>Nd/C and Pt<sub>7.8</sub>Nd/C.  
 177 (d) Projected density of states (PDOS) of Pt surface atoms from Pt (111) surface, Pt<sub>5</sub>Nd@Pt or  
 178 Pt<sub>5</sub>Nd@5-Pt. To show the effect of sub-surface Nd on the electronic structure of surface Pt in  
 179 Pt<sub>5</sub>Nd@Pt, the PDOS on different surface Pt atom either on top of a subsurface Nd atom or above  
 180 3 subsurface Pt atoms are represented.

181

182 The local electronic structure and coordination environment of Pt in the electrocatalysts was  
 183 studied using X-ray absorption spectroscopy (XAS). The *ex situ* X-ray absorption near-edge  
 184 structure (XANES) at the Pt L<sub>3</sub> edge are shown in Figure 2b for Pt<sub>7.8</sub>Nd/C and Pt<sub>6.1</sub>Nd/C. As  
 185 reference, Pt/C and the Pt foil were used. The white line intensity in the XANES spectra indicates

186 the transition from occupied Pt  $2p$  electrons to empty Pt  $5d$  states. Therefore, this parameter is  
187 indicative of the Pt  $5d$  band occupancy,<sup>24</sup> with a higher white line intensity suggesting higher  
188 density of unoccupied valence states at Pt sites (more vacancies) respect to the Pt foil. As seen in  
189 Figure 2b, the white line intensity follows the trend Pt foil < Pt<sub>6.1</sub>Nd/C < Pt/C ≤ Pt<sub>7.8</sub>Nd/C. The  
190 average first-shell Pt-Pt bond lengths were determined by fitting the filtered Fourier Transform X-  
191 ray absorption fine structure (EXAFS) spectra, shown in Figure 2c and Supplementary Information  
192 S8 respectively. The nearest neighbor Pt-Pt interatomic distances are shorter for Pt<sub>6.1</sub>Nd/C and  
193 Pt<sub>7.8</sub>Nd/C than in the reference Pt/C and Pt foil, which reflects a compressive strain of *ca.* -3 %  
194 and -1.6 % respectively, in agreement with the refined WAXS parameters.

195

196 Density functional theory (DFT) calculations were carried out to gain more information on the  
197 electronic structure of the Pt-Nd electrocatalysts. As was mentioned above, the optimization of  
198 several alloyed Pt<sub>5</sub>Nd systems, through the calculation of their grand potential as a function of the  
199 Pt chemical potential (see details in the Supplementary Information S9), predicts the stability of a  
200 slab with a pure Pt monolayer (Pt<sub>5</sub>Nd@Pt) and the metastability of thicker Pt-covered slabs with  
201 5 Pt overlayers (Pt<sub>5</sub>Nd@5-Pt), which agrees with the experimental data shown in Figure 1. Such  
202 structures are compressively strained relative to the Pt (111) reference, with shorter Pt-Pt  
203 interatomic distances in the  $x$ - $y$  plane, of average value of 2.67 Å (2.75 Å for the Pt reference), in  
204 line with the experimental results.

205

206 Interestingly, in the Pt<sub>5</sub>Nd@Pt structure model, the Pt atom of the monolayer just above the Nd  
207 atom appears to be electron-enriched, while Nd undergoes an electron loss (Figure 2d), suggesting

208 a strongly polarized bond between  $\text{Pt}^{\delta-}$  and  $\text{Nd}^{\delta+}$ . In fact, the surface work function of  $\text{Pt}_5\text{Nd@Pt}$   
209 (5.53 eV) is computed to be lower than that of Pt (111) (5.70 eV), which confirms electronic  
210 enrichment of the surface. This increased electron density on Pt might be reflected in the downshift  
211 observed by XPS in the Pt 4f region (Figure 2a). The computed projected densities of states  
212 (PDOS), *c.f.* Figure 2d, exhibits a strong narrow peak for the Pt located on top of the subsurface  
213 Nd (associated with the Pt- $d_{z^2}$  orbital), which suggests a decrease of its orbital overlaps with the  
214 surrounding atoms, in agreement with the formation of a Pt-Nd partially ionic bond. Thus, this Pt  
215 site on  $\text{Pt}_5\text{Nd@Pt}$  has a specific reactivity between a delocalized surface and an isolated atomic  
216 structure.

217

218 In the case of the  $\text{Pt}_5\text{Nd@5-Pt}$  structure, although the Pt atoms at the interface with  $\text{Pt}_5\text{Nd}$  create  
219 similar bonding associated with a charge transfer from Nd toward the closest Pt atoms as for the  
220 case of  $\text{Pt}_5\text{Nd@Pt}$ , no significant charge transfer from Nd is found to occur beyond the two first  
221 neighboring Pt layers. However, the Pt atoms at the surface still experience compressive strain,  
222 induced by the epitaxy on the  $\text{Pt}_5\text{Nd}$  alloy. Thus, the modification of the surface electronic  
223 properties is due to an increase of the  $d$ -band width compared to Pt (111), which results from the  
224 stronger  $d$ -orbital overlapping,<sup>35</sup> as is confirmed by the corresponding PDOS shown in Figure 2d.  
225 In both cases, the electronic modifications close to the Fermi level will induce changes in the  
226 surface reactivity, and modulate the adsorption energies of adsorbates.<sup>36, 37</sup>

227

228 At this point and based on the *ex situ* characterization of  $\text{Pt}_{6.1}\text{Nd/C}$  and  $\text{Pt}_{7.8}\text{Nd/C}$ , it might be  
229 expected that both electrocatalysts are particular active for the ORR. However, the observed

230 activity enhancement, in terms of mass activity, is only *ca.* 3-fold respect to the Pt/C benchmark.  
231 *Operando* WAXS measurements were carried out to follow any modification of the electrocatalyst  
232 structure during the electrochemical operating conditions. Conventional thin-film electrodes (20  
233  $\mu\text{g}_{\text{Pt}} \text{cm}^{-2}_{\text{geo}}$ ) on glassy carbon substrates were mounted in a dedicated X-ray-transparent  
234 electrochemical flow cell described in a previous contribution<sup>26</sup> filled with N<sub>2</sub>-saturated 0.1 M  
235 HClO<sub>4</sub> electrolyte and kept at the open circuit potential (OCP) prior to any measurement (see  
236 Supplementary Information S4 for more details). The electrochemical test protocol started with  
237 electrode preconditioning (or electrochemical activation) procedure, consisting of potential  
238 cycling between 0.05 and 0.95 V<sub>RHE</sub> at 100 mV s<sup>-1</sup> for 20 cycles. WAXS patterns were collected  
239 with 1 s temporal resolution. For both Pt<sub>6.1</sub>Nd/C and Pt<sub>7.8</sub>Nd/C electrocatalysts, significant  
240 structural changes were observed even upon the early electrochemical activation, which are shown  
241 in Figures 3 and 4, respectively.

242

243 In the case of Pt<sub>6.1</sub>Nd/C, Figures 3a-b show that the first cathodic scan (from the OCP to 0.05  
244 V<sub>RHE</sub>) triggers the sudden growth of a pure Pt FCC phase. This crystalline phase (initially absent  
245 from the pristine sample) further evolves as soon as the electrode potential passes below 0.32 V<sub>RHE</sub>  
246 (Figure 3b) and reaches a stable weight fraction of *ca.* 20 wt.% after only one second. For  
247 Pt<sub>7.8</sub>Nd/C, Figures 4a-b show that, during the first cathodic scan, the pure Pt FCC phase (already  
248 present in the pristine sample) further increases once the electrode potential passes below 0.80  
249 V<sub>RHE</sub> and reaches a stable weight fraction of *ca.* 65 wt.% after *ca.* 10 seconds. The Pt<sub>2</sub>Nd cubic  
250 phase that was detected in the pristine Pt<sub>7.8</sub>Nd/C sample was not observed *operando*, but rather an  
251 increased fraction of the Pt FCC instead. This suggests the Pt<sub>2</sub>Nd phase converted to Pt FCC during  
252 the hold of the electrode at OCP (*ca.* 20 min during cell alignment with the X-ray beam),

253 highlighting the low stability of the Pt<sub>2</sub>Nd crystalline structure under the electrochemical  
254 conditions.

255

256 For both samples, the origin of the Pt atoms constituting the growing Pt FCC phase might be  
257 correlated with the evolution of the individual phase intensities or scale factors (Figure 3c and 4c).

258 However, the appearance of the Pt FCC phase is not correlated to the change in the intensity of

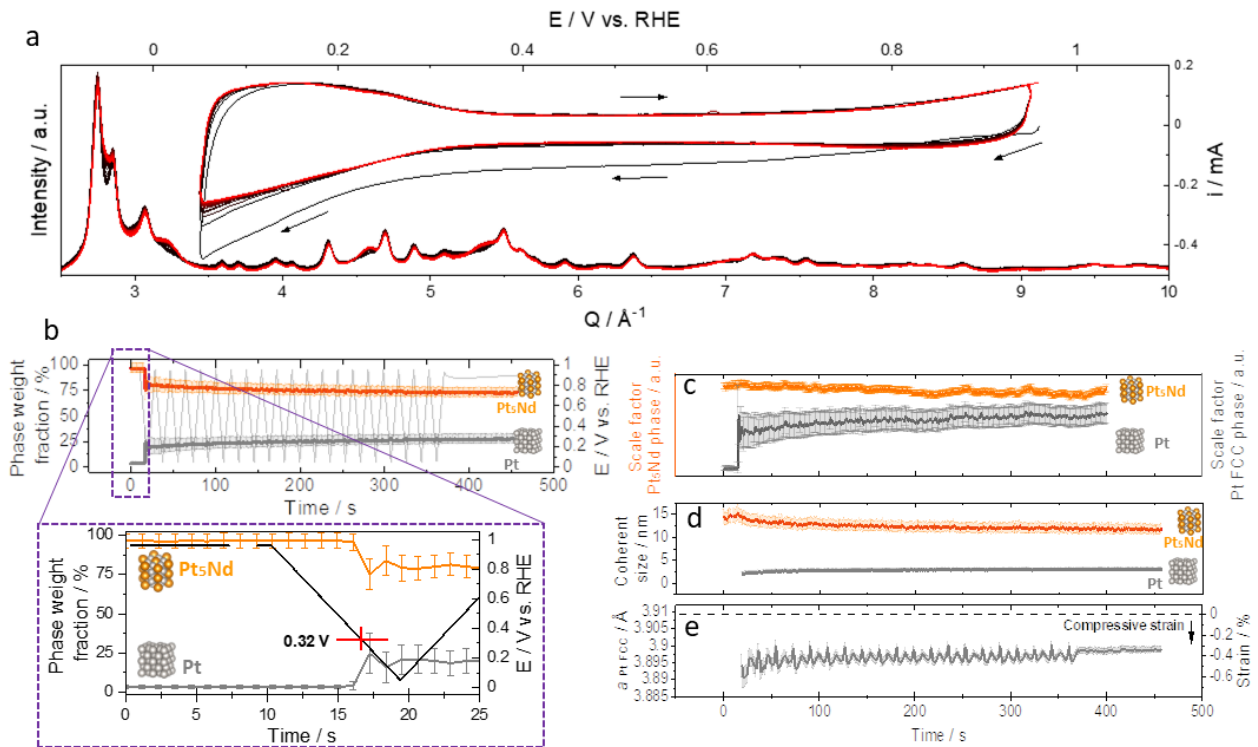
259 Pt<sub>5</sub>Nd, which suggests that the origin of the Pt FCC comes from the electrochemical reduction of

260 an amorphous phase containing Pt (*e.g.*, amorphous Pt oxides). The slight decrease of the Pt<sub>5</sub>Nd

261 phase intensity during the subsequent electrochemical activation suggests, in both cases, possible

262 phase conversion from the hexagonal Pt<sub>5</sub>Nd to Pt FCC, but only to a minor extent.

263



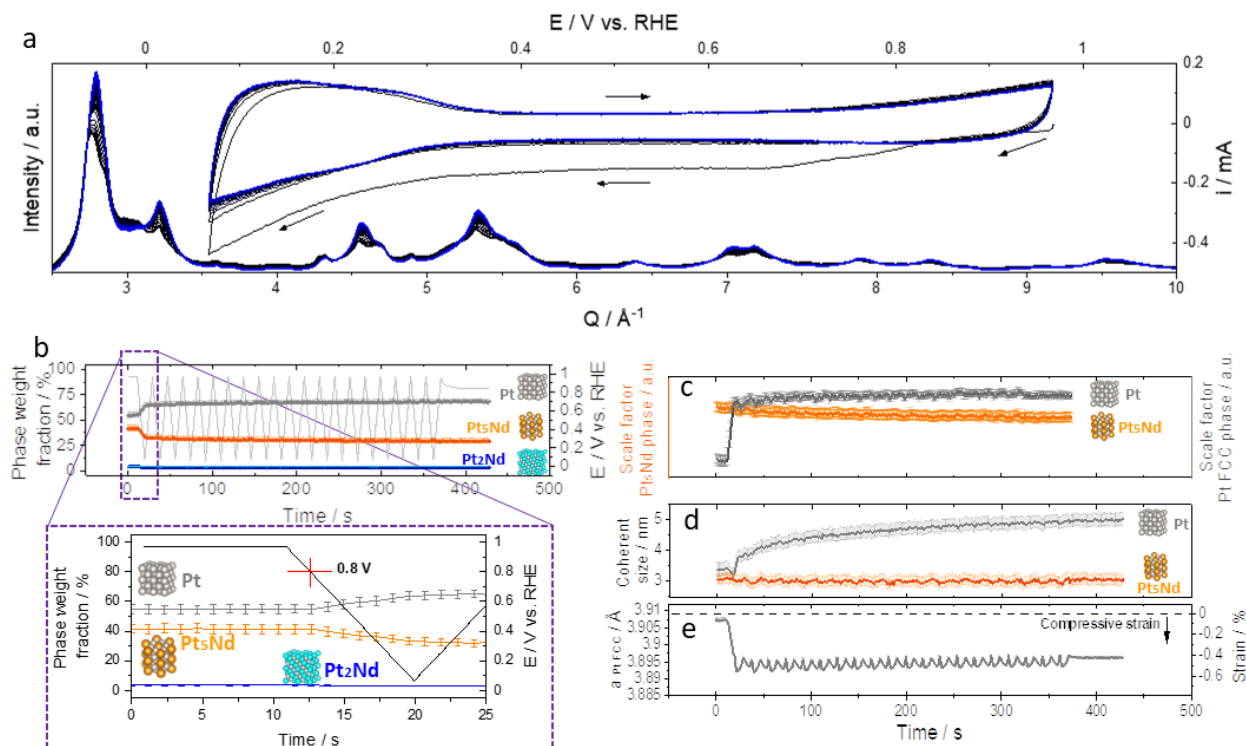
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265 **Figure 3.** *Operando* WAXS analysis during the electrochemical activation of Pt<sub>6.1</sub>Nd/C: (a) cyclic  
266 voltammogram and *operando* WAXS patterns (the arrows indicate the polarization direction); and  
267 refined microstructural parameters extracted from the WAXS patterns: (b) phase weight fractions,  
268 (c) scale factors, (d) coherent domain sizes, and (e) lattice parameter and relative strain.

269  
270 For Pt<sub>6.1</sub>Nd/C, further analysis reveals that the average coherent domain size of the Pt<sub>5</sub>Nd phase  
271 decreases from 15 nm to 10 nm at the end of the electrochemical activation, and that the coherent  
272 domain size of the Pt FCC phase increases to *ca.* 3 nm, Figure 3d. This behaviour is consistent  
273 both with the partial phase transition from Pt<sub>5</sub>Nd to Pt FCC triggering the formation of thicker Pt  
274 overlayers, and/or small pure Pt NPs are formed. The computed phase diagram (see the  
275 Supplementary Information S9) predicts that Pt multilayer deposits on the Pt<sub>5</sub>Nd phase could  
276 remain kinetically stable as slow Pt diffusion should impair the nucleation of pure Pt NPs.  
277 Otherwise, the multilayer deposits could nucleate into pure Pt NPs. For Pt<sub>7.8</sub>Nd/C, the results of  
278 Figure 4d indicate that during the electrochemical activation the average coherent domain size of  
279 the Pt<sub>5</sub>Nd phase seems almost constant (*ca.* 3 nm), however, the coherent domain size of the Pt  
280 FCC phase seems to increase from *ca.* 3 nm to *ca.* 5 nm. This increase in size might also be related  
281 to the conversion of Pt<sub>2</sub>Nd to Pt FCC.

282





283  
 284 **Figure 4.** *Operando* WAXS analysis during the electrochemical activation of Pt<sub>7.8</sub>Nd/C: (a) cyclic  
 285 voltammogram and *operando* WAXS patterns (the arrows indicate the polarization direction); and  
 286 refined microstructural parameters extracted from the WAXS patterns: (b) phase weight fractions,  
 287 (c) scale factors, (d) coherent domain sizes, and (e) lattice parameter and relative strain.

288  
 289 For both electrocatalysts, the refined average lattice parameter of the Pt FCC phase,  $a_{\text{PtFCC}}$ , is  
 290 smaller relative to the reference Pt/C (dashed black line in Figures 3e and 4e), indicating that this  
 291 crystalline phase is under compressive strain. The compressive strain in both cases reaches *ca.* -  
 292 0.4 % at the end of the electrochemical activation. Notwithstanding, the *operando* average strain  
 293 is significantly lower than that measured *ex situ*. The model derived from DFT proposes that as  
 294 the Pt shell thickness increases (higher number of Pt layers over the Pt<sub>5</sub>Nd structure) the Pt-Pt  
 295 interatomic distances through the *z*-axis increase (lattice dilation, see Figure S11 in the  
 296 Supplementary Information S9), while the surface Pt atoms experience lateral compressive strain

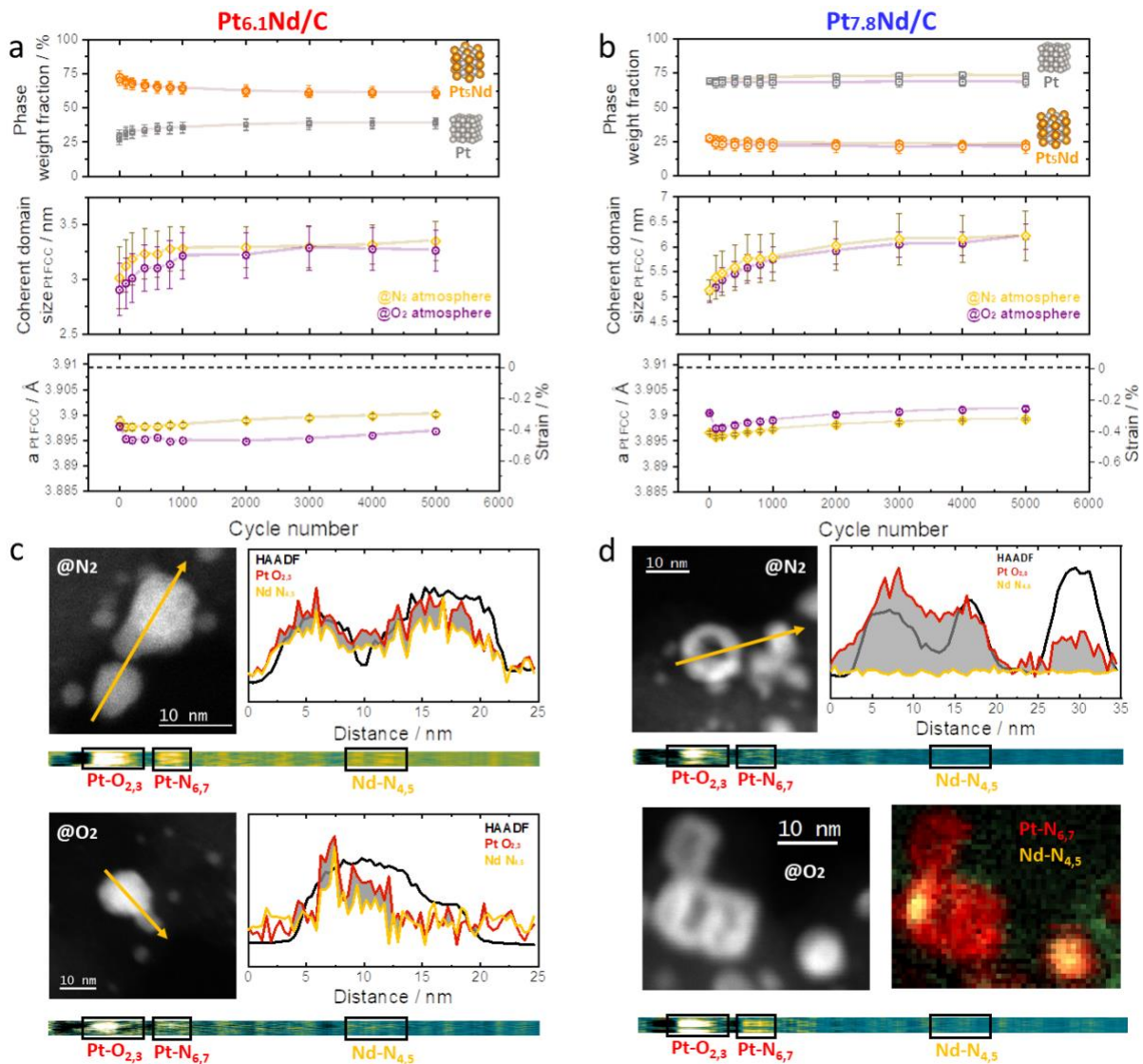
297 along the  $x$ - $y$  plane. The average residual strain is approximately -0.89 %, suggesting a  
298 counterbalance between compressive and tensile strain.

299

300 The structural evolution of the  $\text{Pt}_x\text{Nd}/\text{C}$  electrocatalysts was followed through an accelerated  
301 degradation test (ADT), *c.f.* Figure 5, that used 5,000 square-wave potential cycles between 0.6-  
302 0.95  $V_{\text{RHE}}$ <sup>38</sup> (see the Figure S1 in the Supplementary Information S3). The ADT was carried out  
303 under both  $\text{N}_2$ - and  $\text{O}_2$ - saturated 0.1 M  $\text{HClO}_4$ , although no significant structural difference was  
304 observed for catalysts aged in these different atmospheres over 5,000 cycles.

305

306 For  $\text{Pt}_{6.1}\text{Nd}/\text{C}$ , the phase weight fraction of the  $\text{Pt}_5\text{Nd}$  alloy decreases slightly from *ca.* 75 % to 70  
307 % after 5,000 cycles, and the FCC Pt phase weight fraction increases from *ca.* 25 % to 30 % after  
308 the ADT. The most pronounced phase transitions take place during the first 500 electrochemical  
309 cycles, little further modification occurring thereafter. The average coherent domain size of the Pt  
310 FCC phase grew during the ADT from *ca.* 3 nm to 3.25 nm. The  $a_{\text{PtFCC}}$  is shorter respect to the Pt  
311 reference during the ADT, pointing out a compressive strain, which is gently relaxed at the end of  
312 the ADT. The HAADF-STEM micrographs and the EELS chemical profiles after the ADT, *c.f.*  
313 Figure 5c and Supplementary Information S10, indicate the predominance of dense NPs, the  
314 chemical composition of which comprises both Pt and Nd. Even though the thickening of the Pt  
315 overlayer might be expected, this feature does not fully explain the increase of the average Pt FCC  
316 phase weight fraction nor its increased average coherent domain size. If we assume the presence  
317 of solid NPs with a Pt-rich overlayer thickness of 1 nm ( $\sim 5$  Pt atomic layers, see below), the  
318 remaining contribution of the Pt FCC is probably related to the presence of pure Pt NPs.



320

321 **Figure 5.** Refined WAXS parameters (weight fraction, coherent domain size, lattice parameter  
 322 and relative strain) of the crystalline phases detected during the applied ADT of (a) Pt<sub>6.1</sub>Nd/C and  
 323 (b) Pt<sub>7.8</sub>Nd/C. Representative STEM/EELS chemical mapping of (d) Pt<sub>6.1</sub>Nd/C and (c) Pt<sub>7.8</sub>Nd/C  
 324 after the ADT.

325

326 In contrast, in the case of Pt<sub>7.8</sub>Nd/C, the Pt FCC phase is clearly predominant (*ca.* 75 %*wt.*) relative  
 327 to the Pt<sub>5</sub>Nd alloy (*ca.* 25 %*wt.*). This behaviour is constant along the whole ADT. The average

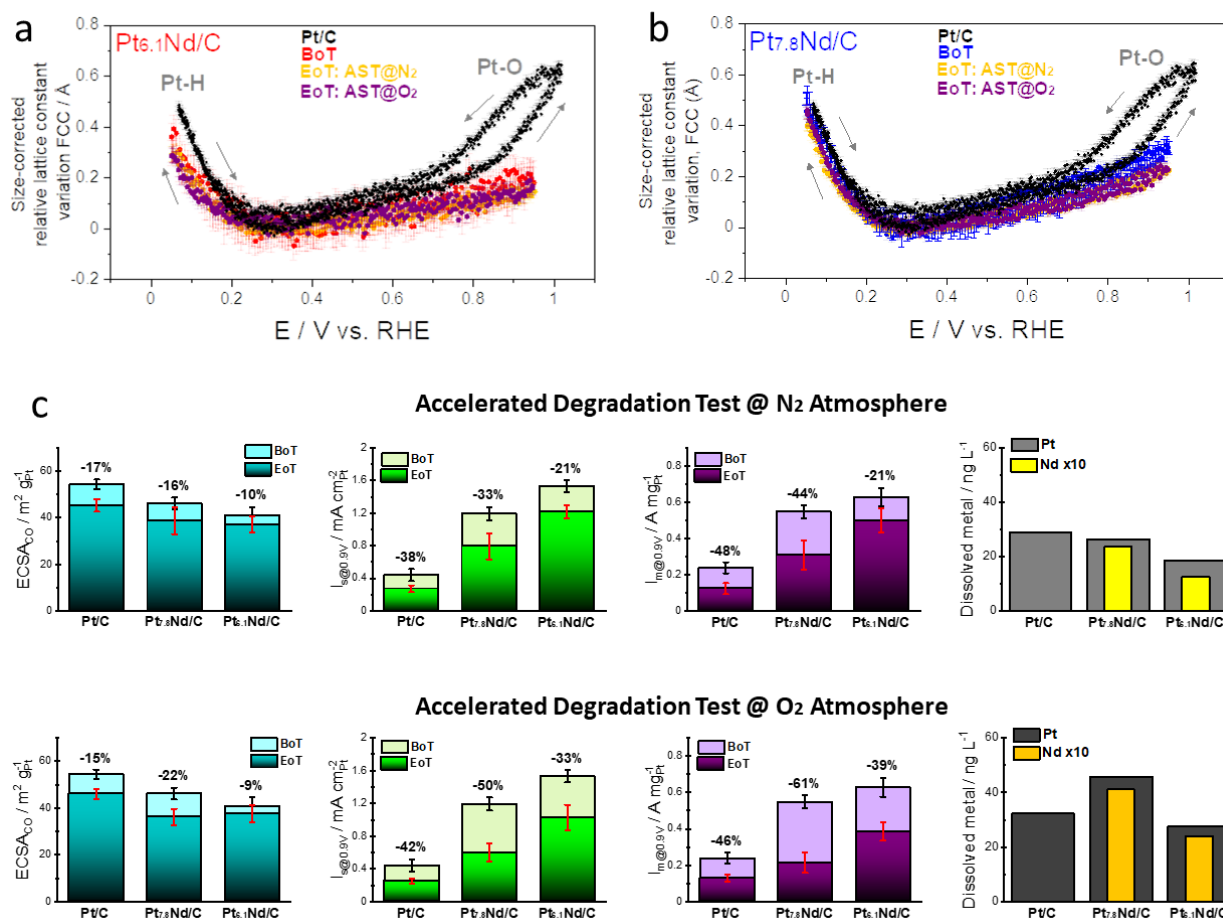
328 coherent domain size of the Pt FCC phase, indeed, increases with the cycle number, indicating the  
329 formation of bigger Pt crystalline domains during the ADT, from  $\sim 5$  nm to  $\sim 6.5$  nm. At the end  
330 of the ADT, the trend follows an upward behaviour, suggesting the continuous increment of the Pt  
331 crystalline domains. Meanwhile, the lattice parameter  $a_{\text{PtFCC}}$  indicates a trend towards lattice  
332 relaxation as the cycle number increases. The STEM micrographs and the EELS chemical profiles  
333 after the ADT shown in Figure 5d and Supplementary Information S10 reveal the predominance  
334 of hollow Pt structures, these architectures corresponding to the dominant Pt FCC phase. Clearly,  
335 the growing coherent domain size trend testifies to the loss of the Pt-Nd alloy, and the stabilization  
336 of Pt hollow architectures. Interestingly, the EELS mapping shown in Figure 5d (ADT@O<sub>2</sub>)  
337 reveals the presence of solid core/shell NPs with a Pt-rich shell of *ca.* 1 nm thick ( $\sim 5$  Pt atomic  
338 layers, see Supplementary Information S10), and some domains of the hollow structures  
339 maintained the Pt-Nd alloy, supporting the *operando* WAXS results.

340

341 In addition to the structure/morphological evolution in the Pt-Nd electrocatalysts, the  
342 electrochemical strain dynamics were followed throughout the ADT, see Figure 6a and b. It has  
343 been reported that the origin of the electrochemical strain dynamics in NPs comes from the  
344 adsorption processes that take place at the electrode/electrolyte interphase,<sup>26</sup> whereby the  
345 adsorption/desorption events induce NP lattice expansion/contraction at the electrochemical  
346 interphase. For the Pt/C benchmark (black profile in Figure 6a and b), in the potential range of  
347  $0.05 \leq E \leq 0.30$  V<sub>RHE</sub>, the hydrogen underpotential deposition (H<sub>upd</sub>) region (denoted as Pt-H in  
348 Figure 6a and b), one can appreciate a reversible lattice expansion, *i.e.*, no hysteresis. In contrast,  
349 at  $E > 0.5$  V<sub>RHE</sub>, *i.e.*, the oxygenated species adsorption/desorption region (denoted as Pt-O in  
350 Figure 6a and b), the pronounced hysteresis indicates an irreversible structural change due to the

351 Pt oxidation dynamics.<sup>39</sup> The results of Figure 6a indicate that, strikingly, the lattice expansion is  
352 attenuated in both the Pt-H and Pt-O regions for Pt<sub>6.1</sub>Nd/C vs. the Pt/C reference, in agreement  
353 with a lower H and OH surface coverage, respectively, evoking weaker adsorption energy of both  
354 species. This tendency is maintained at the end of the ADT, so confirming by *operando*  
355 measurements the benefit of the Pt-Nd alloy. For Pt<sub>7.8</sub>Nd/C, even though the strain dynamics in  
356 the Pt-H region are Pt-like, it seems that there is lower oxide surface coverage, relative to Pt/C,  
357 and less intense hysteresis at the Pt-O region is observed. Although the Pt-like behaviour might be  
358 explained by the presence of pure Pt architectures, the lower hysteresis (related to the oxide  
359 dynamics) in this electrocatalyst could also be linked to an effect on the local morphology,  
360 decreasing its local oxophilicity.

361



362

363 **Figure 6.** Potential-dependency of the relative lattice constant variation of (a) Pt<sub>6.1</sub>Nd/C and (b)  
 364 Pt<sub>7.8</sub>Nd/C. (c) Electrochemical active surface area (EC<sub>SA</sub>, determined by CO-stripping), specific  
 365 surface activity ( $I_s$ ), mass activity ( $I_m$ ) and detected dissolved Pt and Nd in the electrolyte, at the  
 366 beginning (BoT) and at the end (EoT) of the 30,00 cycles ADT under nitrogen or oxygen  
 367 atmosphere of Pt<sub>6.1</sub>Nd/C and Pt<sub>7.8</sub>Nd/C. Pt/C is used as reference.

368

369 Enhanced kinetics of the sluggish ORR in acidic medium require the binding energies ( $\Delta E$ ) of the  
 370 key reaction intermediates, *i.e.*, O\* and OH\*, to be weaker than with Pt (111) by  $\sim 0.2$  eV and  
 371  $\sim 0.1$  eV, respectively.<sup>40</sup> The DFT computations performed in this work predict a weaker  
 372 adsorption energy change,  $\Delta E_{O^*}$  and  $\Delta E_{OH^*}$ , of 0.248 and 0.063 eV *vs.* Pt (111), respectively,  
 373 using the Pt<sub>5</sub>Nd@5-Pt structure (this model matches better the *operando* experimental results). It

374 may be inferred that the enhanced adsorption properties shown in Figure 6 come from the surface  
375 compressive strain rather than the strong Pt-Nd charge transfer, since this electronic perturbation  
376 does not go beyond the two first Pt layers. In this work, the DFT results aim at guiding the  
377 interpretation of experimental observations rather than strictly predicting the behavior of the  
378 complex practical system.

379 The electrochemical activity-stability towards the ORR of the Pt<sub>x</sub>Nd/C electrocatalysts was  
380 evaluated using the RDE technique in 0.1 M HClO<sub>4</sub> electrolyte. The ADT consisted of 30,000  
381 square-wave potential cycles between 0.6-0.95 V<sub>RHE</sub><sup>38</sup> (see the Figure S1 in the Supplementary  
382 Information S3). To visualize the possible oxygen adsorption-induced segregation effects, the  
383 ADT was carried out in N<sub>2</sub>- and O<sub>2</sub>-saturated electrolyte, when notable performance differences  
384 were observed after 30,000 cycles. The cyclic voltammograms in N<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub>, at  
385 the beginning (BoT) and at the end (EoT) of the ADT of Figure S15 in the Supplementary  
386 Information S11 display the features typical of Pt in acidic medium. While the cyclic  
387 voltammograms of Pt<sub>6.1</sub>Nd/C, at BoT and EoT, are characterized by a distorted H<sub>upd</sub> region due to  
388 the modified Pt-H interaction on Pt-REM alloys,<sup>13</sup> the cyclic voltammograms of Pt<sub>7.8</sub>Nd/C present  
389 an intermediate Pt/Pt-alloy behaviour, in full agreement with the results discussed above.

390

391 As was mentioned above, in terms of specific ORR activity (I<sub>s</sub>), the results of Figure 6c confirm  
392 that the synthesized Pt-Nd electrocatalysts are intrinsically more active than the Pt/C benchmark,  
393 as improvement factors at BoT of 2.7 (Pt<sub>7.8</sub>Nd/C) and 3.4 (Pt<sub>6.1</sub>Nd/C) are observed. These features  
394 might be directly related to the enhanced adsorption properties shown in Figure 6a and b.  
395 Nonetheless, the ORR polarization curves shown in Figure S15 in the Supplementary Information

396 S11 reveal evident degradation after the ADT and highlight a stronger activity loss after the ADT  
 397 under O<sub>2</sub> atmosphere. This behavior is reflected in the mass-transport-corrected ORR polarization  
 398 curves (normalized by Pt mass, Figure S16 in the Supplementary Information S11), demonstrating  
 399 that Pt<sub>7.8</sub>Nd/C and Pt<sub>6.1</sub>Nd/C experienced stronger degradation after the ADT under O<sub>2</sub> atmosphere.  
 400 *Ex situ* ICP-MS measurements of the electrolyte at EoT corroborate these conclusions since higher  
 401 concentration of dissolved metal was detected after electrochemical cycling in O<sub>2</sub> atmosphere,  
 402 suggesting higher metal dissolution under these conditions. Although we have shown indirect  
 403 evidence of the metal dissolution through the ADT, this *ex situ* approach is insufficiently precise,  
 404 since it is not possible to disentangle the transient dissolution events that take place or quantify the  
 405 metal dissolution. The ECSA, I<sub>s</sub> and I<sub>m</sub> values, at the BoT and EoT under both atmospheres, are  
 406 exposed in Figure 6c and Table 2, with the concentration of dissolved Pt and Nd in the electrolyte.

407

408 **Table 2.** Electrochemical kinetic parameters of Pt<sub>6.1</sub>Nd/C and Pt<sub>7.8</sub>Nd/C at BoT and EoT.  
 409 Commercial Pt/C is used as reference.

	Condition	<sup>a</sup> ECSA (m <sup>2</sup> g <sub>Pt</sub> <sup>-1</sup> )	I <sub>s@0.9 V</sub> (mA cm <sub>Pt</sub> <sup>-2</sup> )	I <sub>m@0.9 V</sub> (A mg <sub>Pt</sub> <sup>-1</sup> )	<sup>b</sup> Dissolved metal (ng L <sup>-1</sup> )
Pt <sub>7.8</sub> Nd/C	BoT	46.19 ± 2.5	1.19 ± 0.08	0.54 ± 0.04	--
	EoT@N <sub>2</sub>	38.85 ± 2.7	0.79 ± 0.15	0.31 ± 0.08	Pt: 26.4; Nd: 235.4
	EoT@O <sub>2</sub>	36.17 ± 3.5	0.59 ± 0.11	0.21 ± 0.05	Pt: 45.8; Nd: 411.3
Pt <sub>6.1</sub> Nd/C	BoT	41.00 ± 3.6	1.53 ± 0.07	0.62 ± 0.05	--
	EoT@N <sub>2</sub>	37.01 ± 3.4	1.21 ± 0.08	0.49 ± 0.06	Pt: 18.5; Nd: 127.1
	EoT@O <sub>2</sub>	37.59 ± 3.7	1.02 ± 0.15	0.38 ± 0.05	Pt: 27.6; Nd: 240.6
	BoT	54.41 ± 2.1	0.44 ± 0.07	0.23 ± 0.03	--



Pt/C	EoT@N <sub>2</sub>	45.30 ± 2.7	0.27 ± 0.04	0.12 ± 0.03	Pt: 28.7
	EoT@O <sub>2</sub>	46.02 ± 2.0	0.26 ± 0.03	0.13 ± 0.02	Pt: 32.3

410 a: Determined by CO-stripping; b: Determined by ICP-MS on the electrolyte recovered at EoT.

411

412 From Figure 6c and Table 2 it is concluded that the Pt/C benchmark suffered similar degradation  
413 after the ADT under both atmospheres. However, it seems that the degradation of Pt<sub>7.8</sub>Nd/C and  
414 Pt<sub>6.1</sub>Nd/C is more pronounced after the ADT under O<sub>2</sub> atmosphere. The ECSA variations might be  
415 related to the slight particle size changes and morphological transitions provided in the  
416 Supplementary Information S11; meanwhile, the activity attenuation of the Pt-Nd electrocatalysts  
417 is related to their compositional segregation, and decrease of the kinetic benefit from the alloying  
418 effect.

419

420 Theoretical works have suggested that in Pt-based alloys the presence of adsorbed oxygen induces  
421 segregation of the non-precious metal to the surface.<sup>41</sup> In fact, due to the larger atomic radii and  
422 lower surface energy of REMs relative to Pt, it is expected that the Nd atom tends to segregate to  
423 the surface. To obtain insights concerning oxygen-induced segregation of Nd in Pt-Nd alloys, we  
424 have performed DFT calculations of the segregation energies ( $E_{\text{seg}}$ ) of the Nd atom on the Pt (111)  
425 surface in the presence and absence of oxygen. Figure S20 in the Supplementary Information S12  
426 illustrates how the  $E_{\text{seg}}$  of one Nd atom evolves as a function of its position in the Pt slab in the  
427 presence and in the absence of adsorbed oxygen, revealing the strong oxygen-induced segregation  
428 of Nd towards the topmost surface layer of Pt (the more negative  $E_{\text{seg}}$  value, the greater the  
429 segregation). The segregation energy of a Nd atom located on the first surface layer interacting  
430 with oxygen is more than double that in the absence of oxygen ( $E_{\text{seg}} = -4.7$  eV vs.  $-2.1$  eV).

431 Furthermore, the effect of oxygen seems to be limited to the Nd atoms located in the two top layers;  
432 the Nd atoms located in the third and fourth layers are found to have a bulk-like behaviour and the  
433 presence of oxygen does not induce their segregation. This result is in line with the reported  
434 isosurfaces in Pt<sub>5</sub>Nd@5-Pt, suggesting the strong segregation of Nd atoms located in the upper  
435 surface layers and their dissolution during the ADT under oxygen atmosphere, resulting in Pt-Nd  
436 alloy system with constrained Pt outer surface layers.

437

#### 438 **4. CONCLUSION**

439 The Pt<sub>6.1</sub>Nd composition has the highest ORR activity among the carbon-supported Pt-Nd  
440 nanoalloy series. Even though the *ex situ* characterization techniques revealed surface compressive  
441 strain and electronic modifications due to the strong charge transfer between Pt and Nd, at the  
442 electrochemical operating conditions, the structure of the electrocatalysts underwent significant  
443 transformation. The strongest of these were observed during the early electrode conditioning  
444 (electrochemical surface activation) rather than through ADT of 5,000 cycles. The *operando*  
445 determined electrochemical strain dynamics and DFT predictions provided evidence for enhanced  
446 adsorption properties of Pt<sub>6.1</sub>Nd/C before and after the electrochemical cycling, which are reflected  
447 in the ORR activity in the RDE. No significant structural changes were detected during the 5,000  
448 cycles ADT under inert (N<sub>2</sub>) or reactive (O<sub>2</sub>) atmosphere. However, after a 30,000 cycle ADT, the  
449 O<sub>2</sub> atmosphere induces higher electrocatalytic activity decay relative to that observed under N<sub>2</sub>  
450 atmosphere. This behaviour is consistent with Nd segregation induced by oxygen adsorption, and  
451 diminished ORR kinetic benefit from the Pt-Nd alloy. Even though the expected high  
452 activity/stability on this Pt-REM/C nanoalloys was not observed, the *operando* structure-activity-

453 stability relations described underpin further optimization/understanding of carbon-supported Pt-  
454 rare earth nanoalloys as fuel cell cathode catalysts.

455 This study is a contribution to the understanding of the structure-activity-stability relationships of  
456 carbon-supported Pt-rare earth nanoalloys under electrochemical conditions.

457

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473

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475 The manuscript was written through contributions of all authors. All authors have given approval  
476 to the final version of the manuscript.

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488

#### 489 **ASSOCIATED CONTENT**

490 The following files are available free of charge.

491 **Supporting Information**: Experimental methodology, electrocatalysts optimization and  
492 selection, supplementary spectroscopy information, phase stability diagram, characterization  
493 after the ADT, and oxygen-induced segregation diagram. are available in the Supporting  
494 Information.

495

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506

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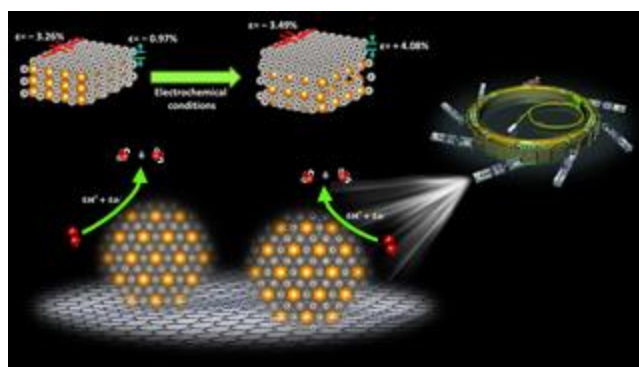
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641 **TOC graphic**



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