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1 Stabilization of Carbon-Supported Platinum-Rare 2 Earth Nanoalloys during Electrochemical Activation

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20 **KEYWORDS:** Pt alloys, Rare earth metal, *Operando* measurements, Electrochemical
21 activation, Oxygen reduction reaction, Proton exchange membrane fuel cell
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25 ABSTRACT

26 Carbon-supported platinum-rare earth nanoalloys are promising electrocatalysts for the oxygen
27 reduction reaction. However, their structure-activity-stability trends are poorly understood.
28 Herein, we followed the evolution of Pt-Nd/C nanoalloys during the electrochemical surface
29 conditioning, *i.e.*, prior to the initial evaluation of electrocatalytic activity, and observed that
30 their compositional, morphological and structural *ex situ* properties are considerably modified by
31 the electrochemical activation step. It is these stabilized properties, therefore, that should be
32 considered when discussing the electrocatalyst beginning of life state for the structure-activity-
33 stability relationships rather than those determined *ex situ* on the as-synthesized electrocatalyst.

34

35 Proton-exchange membrane fuel cells (PEMFCs) are a promising technology that are set to
36 contribute to achieving the current net carbon-emission neutrality targets.¹ If performance, cost
37 and durability must be improved, one particular focus is on the electrocatalyst activity and long
38 term durability for the sluggish oxygen reduction reaction (ORR). Platinum-rare earth metal
39 alloys (Pt-REM) have been considered as suitable candidates to satisfy the ORR requirements,²
40 and research on carbon-supported Pt-REM nanostructures has considerably increased in recent
41 years.³⁻¹¹ Notwithstanding, their reported ORR activity is still lower than state-of-the-art carbon-
42 supported PtNi and PtCo nanoalloys.^{12, 13} Therefore, there is a need for a deeper understanding,
43 especially during operation, of the relatively novel Pt-REM/C nanoalloys.

44 Recent studies using the rotating-disk electrode (RDE)¹⁴⁻¹⁷ have indicated that the impact of
45 early surface conditioning, *i.e.* electrochemical activation (ECA), has been hitherto
46 underestimated, and is an important factor contributing to the performance of Pt-based

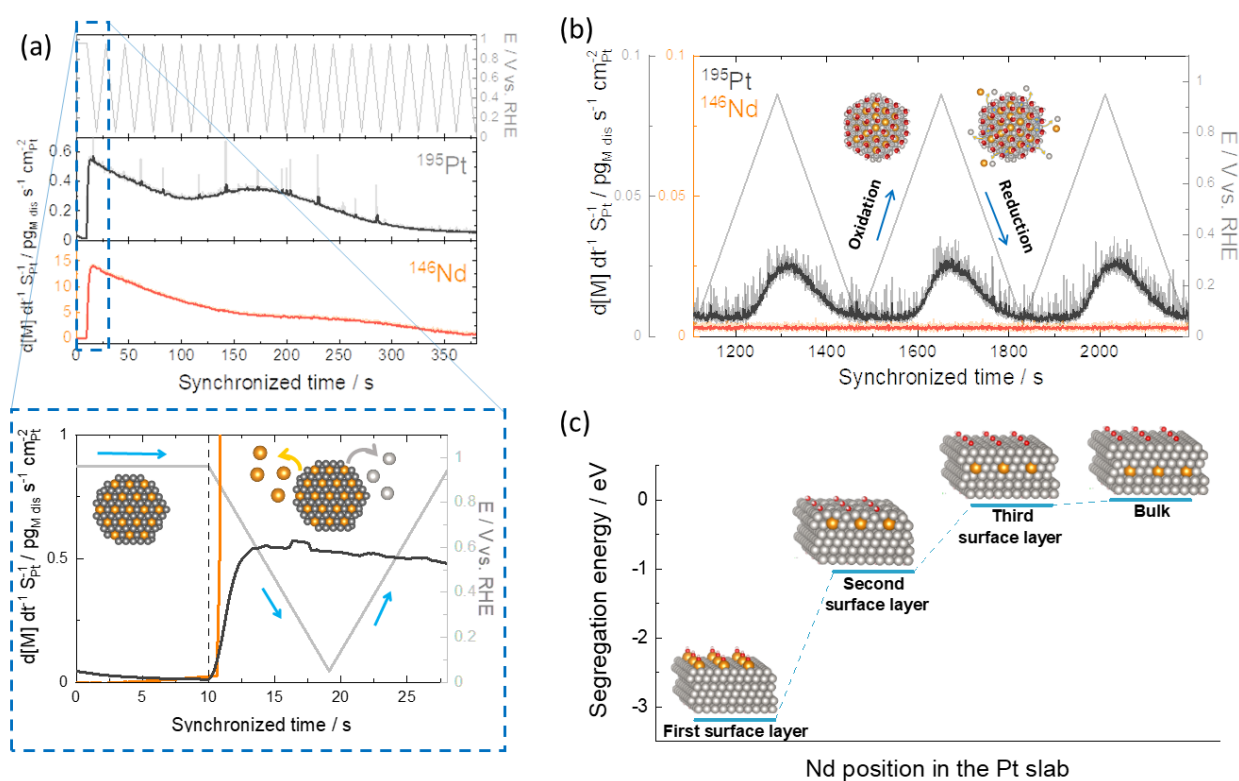
47 nanoalloys. For instance, Danisman *et al.*¹⁷ have recently reported important activity changes of
48 PtNiMo/C depending on the initial electrochemical surface pretreatment. Similar results have
49 been reported for PtNi/C¹⁵, PtCo/C¹⁴ and PtCu/C^{14, 16} nanocatalysts, Therefore, one might
50 conclude that further studies are needed to understand the effect of the ECA on the ORR
51 performance in more detail. Indeed, in our previous contribution¹⁸, evolution of the crystal
52 structure of hexagonal Pt-Nd/C nanoalloys during the ECA was observed for the first time for Pt-
53 REM/C nanoalloys using *operando* wide-angle synchrotron X-ray scattering (WAXS)
54 measurements. Briefly, the structural characterization of the as-prepared Pt-Nd/C electrocatalyst
55 revealed that the crystal structure is *ca.* 100 wt.% the hexagonal Pt₅Nd phase, with compressive
56 strain of *ca.* -3.7% relative to the Pt/C reference. However, it was determined from *operando*
57 WAXS measurements that the first cathodic scan during the ECA (from open circuit potential to
58 0.05 V_{RHE}) triggers the growth of a Pt face-centred cubic (fcc) phase that reaches a stable weight
59 fraction of *ca.* 20 wt.% (**Figure S4a**). From the trends of the individual scale factors and the
60 average coherent domain sizes of these two components (hexagonal and fcc), **Figure S4b and**
61 **S4c** respectively, it was surmised that the origin of the Pt fcc component might come from the
62 electrochemical reduction of a Pt-containing amorphous phase. These striking results raised new
63 questions concerning the origin and nature of the *actual* properties (structure, local coordination
64 environment, chemical composition, morphology, particle size) of the stabilized electrocatalyst
65 which describe the *real* beginning of life (BoL) state and are clearly different from the *ex situ*
66 properties determined on the as-prepared nanomaterial. Furthermore, the characterization of the
67 electrocatalyst properties after the ECA and before the ORR electrocatalytic evaluation is
68 paramount for the understanding of the structure-activity-stability relationships of carbon
69 supported Pt-REM nanoalloys as ORR electrocatalysts.

70 In this work, using the Pt-Nd/C nanocatalyst, the evolution of the structure, local
71 electronic/coordination environment, and metal dissolution before, during and after the ECA (see
72 **Supplementary Information S2**) were extracted from *in situ* X-ray absorption spectroscopy
73 (XAS), *online* inductively coupled plasma mass spectrometry (ICP-MS), electron microscopy
74 techniques (HAADF-STEM/EDX) and density functional theory (DFT), aiming to understand
75 and properly characterize the *actual* BoL state of Pt-Nd/C before its electrocatalytic evaluation.

76 Firstly, the transient metal dissolution during the ECA protocol (**Supplementary Information**
77 **S2**) was assessed using an electrochemical flow cell coupled with an ICP-MS¹⁹ (**Supplementary**
78 **Information S4**). The acquired specific dissolution profiles are shown in **Figure 1**. During the
79 ECA, the results of **Figure 1a** indicate that the metal dissolution starts after polarizing the
80 electrode from the open circuit potential (OCP) to the lower limit potential (0.05 V_{RHE}). One can
81 also observe in **Figure 1a** that Pt dissolution starts slightly before than Nd dissolution,
82 suggesting that the partial or total dissolution of the protective Pt layer triggers the Nd
83 dissolution, with the most intense signal observed during the first cathodic scan. After that, the
84 dissolution signal seems to be stabilized for both metals. The specific dissolution rate of Pt (pg_{dis}
85 s⁻¹ cm⁻²_{Pt}) at the most intense dissolution peak is *ca.* 25-fold lower than that of Nd, despite Pt is 5
86 times greater abundant in the alloy stoichiometry. Indeed, after the partial or total dissolution of
87 the protective smooth Pt layer at the surface and due to the larger atomic radii and surface energy
88 of REM relative to Pt, it is expected that Nd atoms exposed at the surface/electrolyte interface
89 are quickly oxidized into Nd³⁺ (E⁰_{Nd³⁺/Nd⁰} = -2.323 V/SHE) and dissolve once in contact with the
90 acidic electrolyte, giving a strong thermodynamic driving force for the Nd segregation from the
91 bulk of the alloy towards the surface. However, this process eventually induces the surface
92 reconstruction and the expected thickening of the protective Pt-rich shell. Furthermore, the

93 dissolved Pt species might redeposit back through Oswald ripening,¹⁹ forming longer Pt
 94 crystalline domains. These observations might suggest that the structural changes detected by
 95 WAXS are, until a certain extent, related to dissolution events. The total dissolved mass during
 96 the ECA, relative to the initial metal loading at the electrode, of Pt and Nd are $0.0029 \pm 0.001 \%$
 97 and $1.78 \pm 0.46 \%$, respectively.

98



99

100 **Figure 1.** Transient dissolution profiles acquired from *online* ICP-MS analysis (a) during the
 101 electrochemical activation (20 cycles at 100 mV s^{-1} , the zoomed section shows the first
 102 dissolution events during the first potential cycle), and (b) during slow potentiodynamic cycles (3
 103 cycles at 5 mV s^{-1}). (c) OH-adsorption induced segregation energy as function of the Nd position
 104 in the Pt slab. The negative values of segregation energies indicate the preference of Nd to
 105 segregate toward the surface.

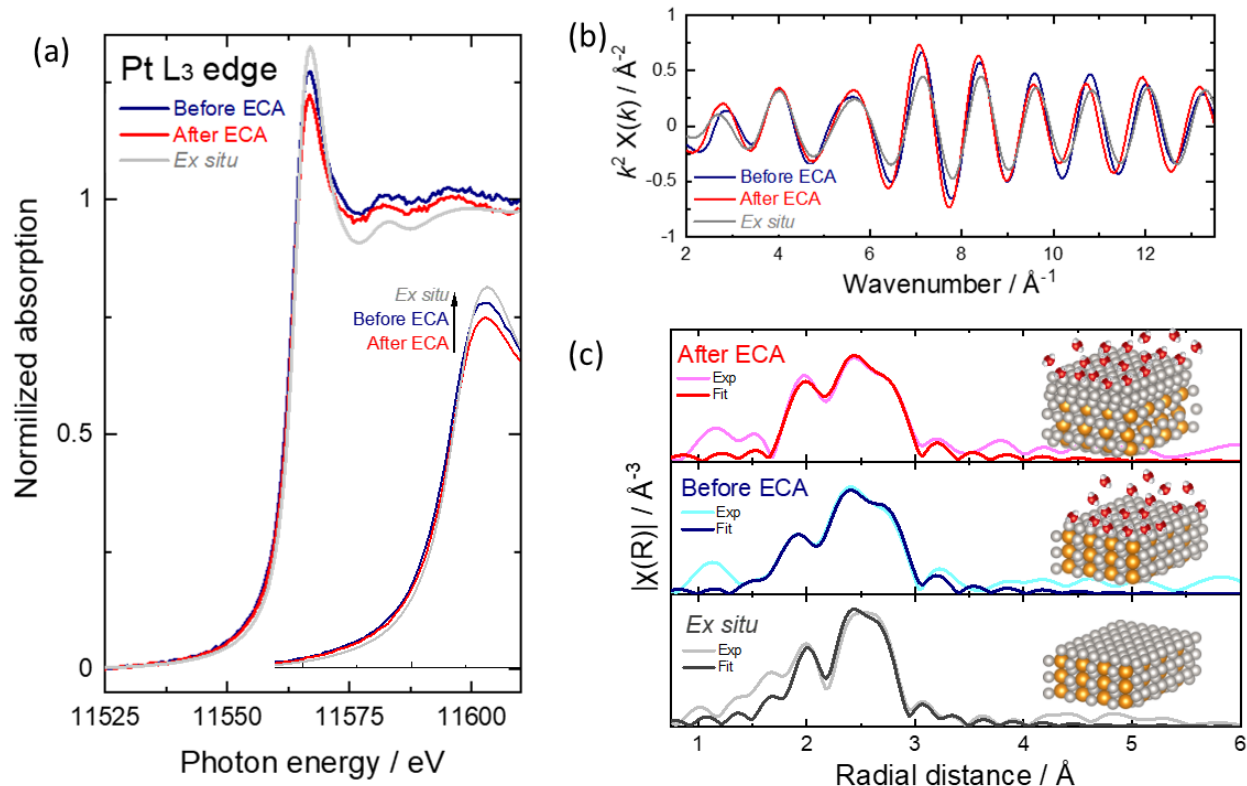
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107 It is known that the Pt dissolution is a transient process, *i.e.*, it depends on the potential scan rate
108 (timescale).²⁰ To gain more information on the transient dissolution behaviour of Pt and Nd,
109 three potentiodynamic cycles with slower potential scan rates (0.05 to 0.95 V_{RHE} at 5 mV s⁻¹)
110 were applied following the ECA, see **Figure 1b**. The predominant Pt dissolution signal is centred
111 in the cathodic scan, in agreement with the literature.^{14, 19-23} This feature is a consequence of the
112 reduction of the formed Pt oxide which induces a surface and sub-surface re-structuring *via* the
113 place exchange mechanism,¹⁴ being expected to gradually start at a critical coverage around or
114 slightly below the potential of full coverage of chemisorbed oxygenated species.²⁰ Furthermore,
115 dissolution of Nd seems to be suppressed. It may be concluded from this result that the surface
116 and sub-surface re-structuring during the ECA triggers the stabilization of a thick protective Pt-
117 rich shell, which prevents further Nd dissolution. With this knowledge, the OH-adsorption
118 induced segregation energy was calculated as function of the Nd position in the Pt slab, *c.f.*
119 **Figure 1c**, starting from Nd atoms exposed at the surface (first surface layer), Nd atoms
120 protected by 1 Pt monolayer (second surface layer), Nd atoms protected by 2 Pt monolayers
121 (third surface layer), and Nd atoms protected by 3 Pt monolayers (bulk). The aforementioned
122 diagram clearly shows that, in presence of OH, Nd atoms located near the surface have strong
123 tendency to segregate toward the top surface layer (the more negative the energy, the easier the
124 segregation). However, the segregation of Nd atoms could be attenuated if they are protected by
125 at least 3 Pt overlayers, resulting in a core/shell (Pt₅Nd alloy@Pt layers) system with a
126 compressively strained Pt outer surface layer.¹⁸

127

128 Surface reconstruction is expected to modify the local electronic and coordination environments,
129 and *in situ* XAS measurements were performed to investigate the local properties before and
130 after the ECA, see **Figure 2a-c**. The spectra recorded *ex situ* were used for comparative
131 purposes. It may be observed from the X-ray absorption near-edge structure (XANES) spectra at
132 the Pt L₃ edge, *c.f.* **Figure 2a**, that the white line intensity follows the trend *ex situ* > before ECA
133 > after ECA. This observation might indicate that the local electronic structure before and after
134 the ECA differs from that in the as-prepared nanocatalyst, since the white line intensity is
135 proportional to the number of empty Pt 5*d* states. Thus, the as-prepared sample is characterized
136 by a higher density of unoccupied valence states (more vacancies) than the sample before and
137 after the electrochemical conditioning. Nevertheless, the ECA also induces a lowering of the
138 white line intensity, inferring a decreased surface oxidation state. This result might suggest that
139 the surface oxides produced by the contact with air in the *ex situ* sample are reduced during
140 operation, increasing the scale factor of the fcc phase observed in **Figure S4**. However, the
141 redeposition of the dissolved Pt species *via* Oswald ripening might also occur simultaneously.¹⁹
142 Therefore, the growing of the Pt fcc component could be related to the electrochemical reduction
143 of the *ex situ* formed Pt oxides and the redeposition of dissolved Pt species.

144



145

146 **Figure 2.** *In situ* Pt L₃ edge XAS measurements before (blue line) and after (red line) the
 147 electrochemical activation at the OCP: (a) XANES region and EXAFS fitting (b) in the *k*-space
 148 and (c) in the *R*-space. The *ex situ* spectra (grey line) is used as reference.

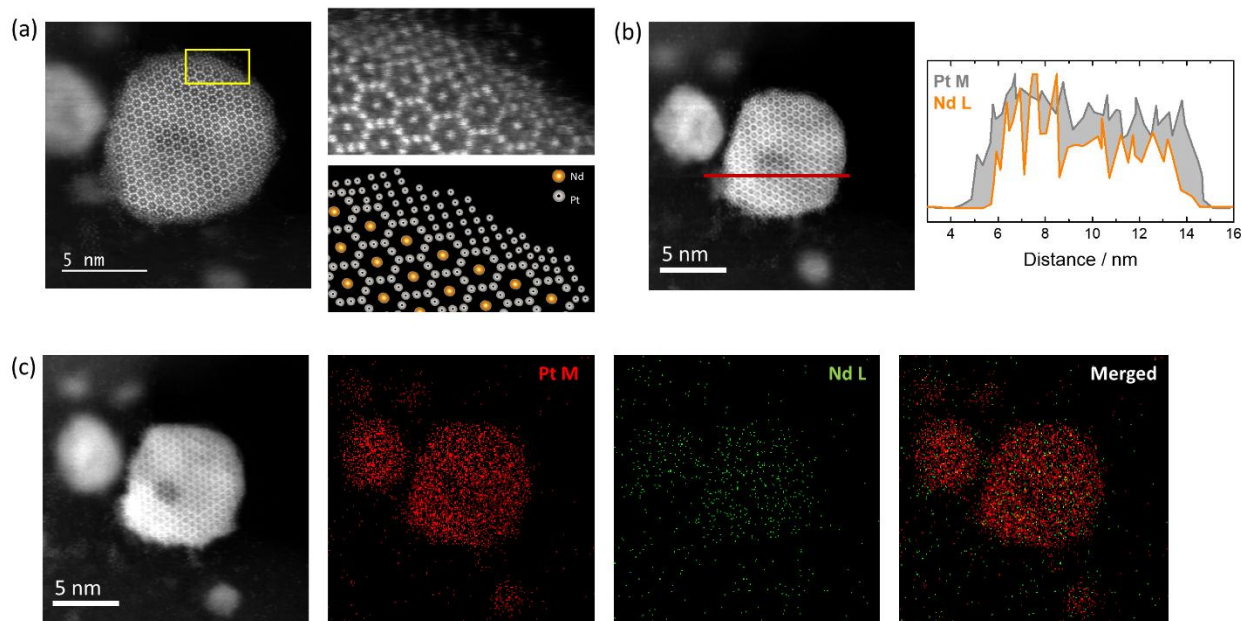
149

150 In the extended X-ray absorption fine structure (EXAFS) region in *k*-space, **Figure 2b**, the
 151 oscillations of the *ex situ* measurement are slightly modified before the ECA, and even stronger
 152 after the ECA. This feature could be related to adsorbates at the electrode/electrolyte interface²⁴
 153 and surface re-structuring induced by the ECA, modifying the local coordination environment.
 154 The average first-shell Pt-Pt coordination number ($N_{\text{Pt-Pt}}$) and the average Pt-Pt bond lengths
 155 ($R_{\text{Pt-Pt}}$) were determined by fitting the filtered Fourier Transformed EXAFS spectra in the *R*-
 156 space shown in **Figure 2c** (fitting details are given in the **Supplementary Information S6**).
 157 When the Pt-Nd/C is in the electrochemical environment, *i.e.*, before and after the ECA, the N_{Pt} .

158 r_{Pt} increases from 5.6 (*ex situ*) to 7.6 (before ECA) and 8.05 (after ECA). This result might
159 indicate the formation of larger Pt domains before and after the ECA, in line with the growth of
160 the Pt fcc phase observed by WAXS. The average R_{Pt-Pt} before the ECA is larger than in the *ex*
161 *situ* as- prepared catalyst, increasing from 2.66 Å to 2.69 Å. This observation is consistent with
162 the slight increase in coordination number and might also be related to the effect of adsorbates on
163 the crystal lattice expansion.²⁵ After the ECA, the R_{Pt-Pt} decreases to 2.67 Å, which still reflects
164 an expansion with respect to the measured *ex situ* value, being in line with our previous WAXS
165 results.¹⁸ Owing to the fact that the specific ORR activity of Pt-REM presents an exponential
166 dependence on the surface compressive strain,^{26, 27} these results clearly underpin that an
167 overestimated *ex situ* strain magnitude might not properly describe the ORR electrochemical
168 activity, since the induced strain evolves during operation.²⁵

169 After the ECA in the *online* ICP-MS set up, the catalyst layer was recovered to examine the
170 nanocatalyst structure and its chemical profile by HAADF-STEM/EDX, *c.f.* **Figure 3**. In fact,
171 the average size of the NPs and agglomerates after the ECA, shown in the **Supplementary**
172 **Information S8**, is *ca.* 7 nm and 13 nm, *i.e.* no significant difference to the values in the as-
173 prepared electrocatalyst.

174



175
 176 **Figure 3.** HAADF-STEM analysis after the electrochemical activation: (a) representative
 177 atomic-resolution micrograph with an overview at the NP border and its respective atomic
 178 simulation, (b) chemical line scan by EDX, and (c) chemical mapping by EDX.

179

180 The atomic-resolution micrograph of the electrocatalyst shown in **Figure 3a** clearly confirms the
 181 presence of the hexagonal Pt₅Nd alloy after the ECA, in agreement with the previous WAXS
 182 results. However, a Pt-rich atomic shell, which is ~ 5-6 atoms thick, is clearly observed for the
 183 isolated NP (**Figure 3a**), in agreement with the EDX line scan (**Figure 3b**) and EDX chemical
 184 mapping (**Figure 3c**) of the NP. These results support the thickening of the protective Pt
 185 overlayers after ECA due to the surface reconstruction. Different regions of the sample were
 186 analyzed by EDX, observing higher Pt:Nd ratios (**Supplementary Information S8**). Our
 187 proposed model derived from DFT¹⁸ suggests that as the Pt shell thickness increases (higher
 188 number of Pt layers over the Pt₅Nd core) the Pt-Pt interatomic distances through the z-axis
 189 increase (lattice dilatation), while the surface Pt atoms are compressively strained laterally, along
 190 the x-y plane. The average residual strain is approximately -0.89 %, suggesting a counterbalance

191 between compressive and tensile strain. Indeed, the projected density of states (PDOS) of a Pt
192 monolayer onto the Pt₅Nd alloy (Pt₅Nd@Pt) presents more empty states than the structure with 5
193 Pt layers onto the Pt₅Nd alloy (Pt₅Nd@5-Pt), see **Supplementary Information S10**. This result,
194 supported by the XANES and HAADF-STEM studies, clearly suggests that the electronic
195 structure of the as-prepared catalyst evolves once the surface conditioning is performed,
196 modifying its electrocatalytic properties.

197 In conclusion, the transition of the properties of carbon-supported hexagonal Pt-Nd
198 nanoalloys occurring during the electrochemical activation was studied by *online* ICP-
199 MS, *in situ* XAS and atomic-resolution HAADF-STEM combined with DFT calculations.
200 The results of the study suggest that the structural transitions during the early
201 electrochemical activation are consequence of the electrochemical reduction of the *ex situ*
202 formed oxides and metal dissolution. This metal dissolution promotes surface
203 restructuring, and thickening of the initial protective Pt-rich shell to 5-6 atoms thick.
204 However, the compressive strain in the restructured surface is attenuated compared to that
205 determined in the *ex situ* measurement. The *ex situ* strain magnitude does not properly
206 describe the ORR electrochemical activity, since the induced strain evolves during activation.

207 Therefore, the stabilized properties after the electrochemical activation should be taken into
208 consideration when discussing the electrocatalyst beginning of life state for the structure-
209 activity-stability relationships rather than those measured *ex situ* on the as-synthesized
210 electrocatalyst, as well as in the analysis of long-term *in situ/operando* accelerated degradation
211 tests.

212

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231 **Author Contributions**

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

234 **Author Contributions**

235 **Carlos A. Campos-Roldán**: Conceptualization, methodology, writing-original draft, formal
236 analysis, investigation, **Jean-Sébastien Filhol**: Writing-review & editing, formal analysis,
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238 **Mickaël Bigot**: Investigation, **Raphaël Chattot**: Writing-review & editing, conceptualization,
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240 Writing-review & editing, supervision, **Jacques Rozière**: Writing-review & editing,
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243 editing, conceptualization, funding acquisition, supervision

244

245 **ASSOCIATED CONTENT**

246 The following files are available free of charge.

247 **Supporting Information**: Synthesis procedure, electrochemical protocol, details regarding the
248 measurements, comparison of the electrochemical signal between the used setups, supplementary
249 methodology information are available in the Supporting Information.

250

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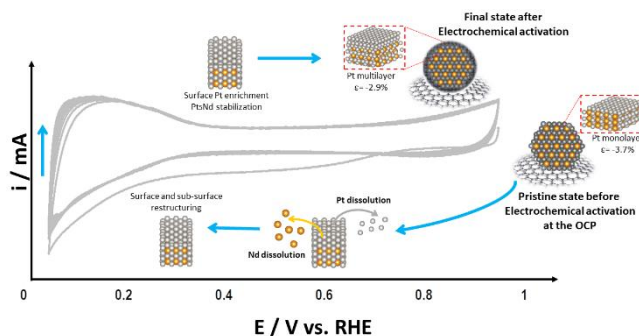
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362 **TOC graphic**



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