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Pt alloys, Rare Earth Metals, *In situ*/*operando* measurements, Oxygen Reduction Reaction, Proton Exchange Membrane Fuel cells.

ABSTRACT

Platinum-yttrium alloys are considered promising candidates to satisfy the challenging requirements for the cathodic oxygen reduction reaction (ORR) in proton exchange membrane fuel cells (PEMFCs). Nevertheless, the practical structure-activity-stability trends of these electrocatalysts in the form of carbon-supported nanostructures are poorly understood, especially under the operating conditions. Herein, carbon-supported Pt_xY nanoalloys were explored during the electrochemical ORR environment, following the atomic-scale degradation steps that the nanoalloys experience during operation. Our results reveal that Pt_xY/C nanoalloys undergo considerable structural modification during the early stage of electrochemical cycling. Moreover, *operando* techniques identify that, during accelerated stress testing under O_2 atmosphere, the majority of nanoalloy degradation occurs during the initial 1,000 electrochemical cycles, and is accompanied by a diminished ORR performance. The observed *operando* structure-activity-stability trends guide further optimization routes for carbon-supported Pt-Y nanoalloys as PEMFC cathode electrocatalysts.

1. INTRODUCTION

Current decarbonization targets are priority in our society, and proton-exchange membrane fuel cells (PEMFCs) have gained attention as energy conversion devices that can contribute importantly to fulfilling these objectives.[1] Nevertheless, their massive production and commercialization are still hindered by technical barriers that need to be overcome, including performance, durability, cost and fuel efficiency,[2, 3] and one particular bottleneck is the electrocatalyst activity and long term durability for the sluggish oxygen reduction reaction (ORR). A well-known approach to enhance the ORR electrocatalytic activity is by alloying Pt with late transition metals (usually Ni, Co, Fe, Cu, *etc*), which also decreases simultaneously the amount of Pt and, therefore, the cost.[4] The long-term stability of Pt-based nanoalloys during the ORR, however, represents a crucial issue that must be tackled.[5-7]

Since their introduction as ORR electrocatalysts in 2009,[8] platinum-yttrium (Pt-Y) alloys have been considered as promising candidates to satisfy the demanding ORR requirements from their predicted high activity and long-term stability. Pioneering theoretical studies[8] concluded that the exceptionally high negative alloy formation energy (-1.02 eV/atom for Pt_3Y)[9] represents a partial thermodynamic barrier for yttrium diffusion through the alloy lattice, which should provide high electrochemical stability. Further research on bulk sputter-cleaned Pt_3Y polycrystalline electrodes[8, 10, 11] and unsupported Pt_xY nanoparticles (NPs)[12] revealed that the high electrocatalytic activity of these alloys stems from the formation of a specific structure, in which the Pt-Y alloy is protected by a thin Pt-rich overlayer, which induces a lateral compressive strain in the Pt-rich shell.[13] Indeed, the surface specific ORR activity showed an exponential dependence on the degree of *ex situ* measured compressive strain of the Pt-rich shell.[12] In the particular case of unsupported Pt_xY NPs, a particle size dependency was also identified, and an

66   outstanding ORR mass activity of 3.05 A mg_{Pt}^{-1} was obtained for NPs of *ca.* 9 nm.[12]

67   Nevertheless, after the applied accelerated stress test (AST), which consisted of 9,000 potential

68   cycles from 0.6 to 1.0 V_{RHE} (triangular potential wave at 100 mV s^{-1}) in O_2-saturated 0.1 M

69   $HClO_4$, the unsupported Pt_xY NPs lost *ca.* 64 % of their initial mass activity.

70   Inspired by the contributions discussed above, further research focused on the challenging

71   production of carbon-supported Pt_xY nanoalloys,[14-17] the practical and desired form for an ORR

72   electrocatalyst. Even though several studies claimed the formation of carbon-supported Pt-Y

73   nanoalloys (more usually yttrium (hydr)oxide-decorated Pt NPs instead of the actual alloy),[18] the

74   first solid evidence was reported in 2016[17] and 2018[15]. However, the measured ORR mass

75   activity of the Pt-Y/C nanoalloys reported so far is in the range between 0.1 and 0.6 A mg_{Pt}^{-1},[14,

76   15, 17, 19-21] which is still far below that of the reference value of 3.05 A mg_{Pt}^{-1} of unsupported 9 nm

77   Pt_xY NPs,[12] *c.f.* **Figure S1** and **Table S1**. This discouraging trend raises critical questions for the

78   viability of Pt_xY/C as ORR electrocatalyst, such as 1) the discrepancy between the theoretically

79   predicted high stability and the experimentally observed high activity loss; 2) the reason for the

80   activity gap between unsupported NPs and carbon-supported NPs; 3) the electrochemical

81   threshold and driving force for alloy degradation under the reaction environment; 4) the

82   electrochemically induced metal dissolution structural transitions during operation, and so on.

83   Of huge potential in this context, the development of *in situ* and *operando* techniques, such as

84   wide-angle synchrotron X-ray scattering (WAXS),[22] X-ray absorption spectroscopy (XAS),[23]

85   *online* inductively coupled plasma mass spectrometry (ICP-MS),[24] *etc.*, has provided

86   fundamental insights at the atomic scale on the degradation of Pt-based electrocatalysts in real or

87   simulated PEMFC electrochemical environments. Nevertheless, the studies that have used these

88   advanced techniques for the characterization of Pt-Y nanoalloys are scarce. For instance,

89   Escudero-Escribano *et al.* have used *in situ* grazing incident X-ray diffraction (GIXRD) to study

90   the formation, induced strain and correlation lengths of the Pt-rich overlayer on Gd/Pt(111)

91   single-crystal electrodes, reporting that the induced compressive strain that the Pt overlayer

92   experiences is relaxed upon repeated electrochemical cycling in the potential range 0.6-1.0 V_{RHE}.

93   This strain relaxion effect is stronger as the upper potential limit increases. To the best of our

94   knowledge, the only publication concerning the *in situ* characterization of Pt-Y nanoalloys is

95   given by Malacrida *et al.*[25] *In situ* ambient pressure X-ray photoelectron spectroscopy (APXPS)

96   was used to investigate the dealloying mechanism of unsupported Pt_xY NPs under near PEMFC

97   operating conditions, when the nature of oxygenated near-surface species was observed as a

98   function of the applied potential.[25] From this study, the authors concluded that a post-synthesis

99   acidic wash is needed to form a protective Pt-rich overlayer, and to avoid the presence/leaching

100   of Y^{3+} cations that may compromise the conduction properties of the PEMFC membrane.

101   Nevertheless, there is still a need for a deeper understanding of the relatively novel Pt_xY/C

102   nanoalloys during the ORR operating conditions.

103   For this purpose, we have synthesized carbon-supported Pt_xY nanoalloys *via* a solid-state

104   approach, and have used advanced techniques for their characterization, *i.e.*, *operando* WAXS,

105   *online* ICP-MS, atomic resolution HAADF-STEM, and have interpreted the results with the

106   assistance of DFT calculations. We have followed, from the early electrochemical activation to

107   the end of the applied AST, the time- and potential-resolved metal dissolution, the variations in

108   crystal structure, the evolution of the local chemical composition and the morphology of Pt_xY/C

109   nanoalloys as ORR electrocatalysts. The extracted results are rationalized and critically

110   discussed, shedding light for the first time on the *operando* relationship between physico-

111   chemical properties, ORR activity and stability of carbon-supported Pt-Y nanoalloys.

112

3. RESULTS AND DISCUSSION

Pt_xY/C nanoalloys were synthesized using the carbodiimide complex route developed by Hu *et al.*[14] using carbon Ketjenblack EC-300J as a support. The resulting powder was treated *via* an acidic wash in N_2-saturated 0.5 M H_2SO_4[21, 26] (see **Supplementary Information S2**). The as-prepared electrocatalyst crystalline structure, morphology and chemical properties were characterized *ex situ*, and reported in our previous contribution.[21] Briefly, the chemical analysis, determined by ICP-MS, sets a Pt content of *ca.* 27 % *wt.* and an Y content of *ca.* 3 % *wt*. The higher atomic Pt:Y obtained by ICP-MS relative to the Pt_3Y crystalline structure stoichiometry could be related to the formation of the Pt-rich shell and the possible presence of small pure Pt NPs. Besides, the *ex situ* characterization confirms the formation of Pt_3Y nanoalloy, and the presence of a dominant population of NPs of *ca.* 5 nm was observed, as well as some agglomerates of *ca.* 12 nm dispersed over the carbon support.

The ORR electrocatalytic activity and long-term stability were investigated using the rotating disk electrode (RDE) technique in 0.1 M $HClO_4$ electrolyte at 25 °C (**Supplementary Information S2**). These screenings attest that Pt_xY/C surpasses the initial ORR mass activity of the Pt/C reference (0.58 A mg_{Pt}^{-1} *vs.* 0.23 A mg_{Pt}^{-1} at 0.9 V_{RHE}, respectively). The electrocatalysts' stability was evaluated using an AST inspired from the Fuel Cell Technical Team of the U.S Department of Energy (DoE/FCTT) protocol, which consists of 30,000 potential cycles from 0.60 to 0.95 V_{RHE} (square potential wave, 3 s at each potential limit with a transition of 0.5 s in between)[27] in O_2-saturated 0.1 M $HClO_4$. After the AST, the Pt_xY/C and the reference Pt/C lost, respectively, *ca.* 35 % and *ca.* 44 % of their initial mass activity (see **Figure**

134 **S3**). Even though these results clearly show an enhanced performance of Pt_xY/C with respect to

135 the Pt/C reference, the activity value and retention of Pt_xY/C do not correlate with the expected

136 trend.

137 Previously, we have reported that Pt-rare earth nanoalloys undergo significant structure

138 transitions during the early surface conditioning step, namely, the electrochemical activation.[28, 29]

139 Such transitions, often not investigated or underestimated, do induce a considerable effect on the

140 electrocatalyst activity and its retention.[30, 31] Therefore, *online* ICP-MS and *operando* WAXS

141 measurements were conducted to follow any possible degradation of Pt_xY/C during the

142 electrochemical activation, see **Figure 1**.

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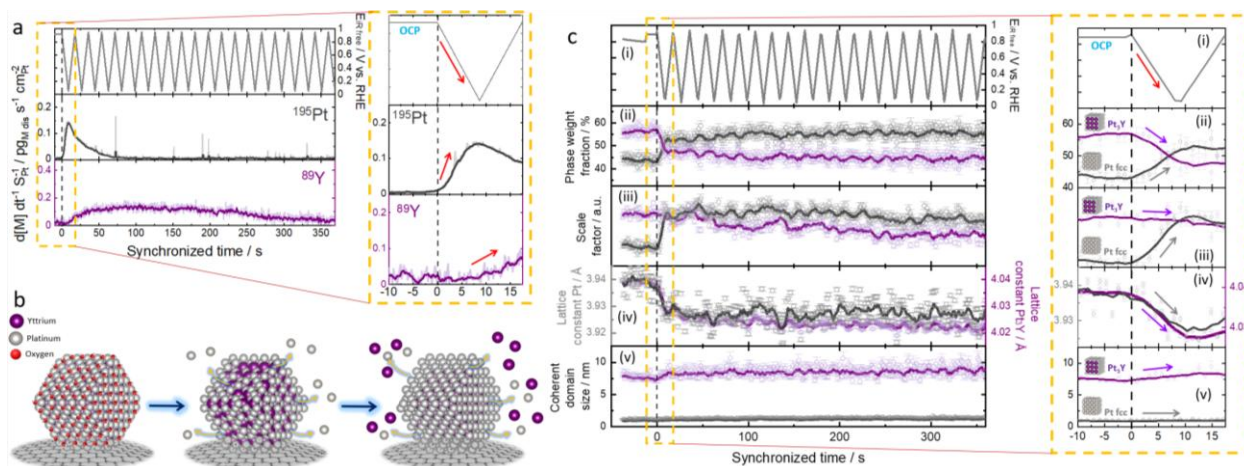
145 **Figure 1.** (a) Specific dissolution profiles extracted from *online* ICP-MS measurements; (b)
146 schematic representation of the Pt_xY nanoalloy dissolution and stabilization; and (c)
147 microstructural refined parameters extracted from *operando* WAXS measurements [where (i)
148 indicates the electrode potential wave profile used, (ii) the phase weight fraction, (iii) scale
149 factor, (iv) lattice constant and (v) coherent domain size of the Pt_3Y alloy and Pt phases] of
150 Pt_xY/C during the electrochemical activation. The highlighted region in (a) and (c) indicates the
151 first polarization scan. The arrows serve as a guide to the eye.

152

153 A sharp peak is observed in the specific dissolution profiles, *c.f.* **Figure 1a**, for Pt and a broad

154 peak for Y, which decay through the potential cycling until the signals are stabilized, revealing

155 that the first cathodic scan (first polarization from the open circuit potential, OCP, to 0.05 V_{RHE})

156 induces metal dissolution. It may be noticed that Pt dissolution starts before Y dissolution, which

157 suggests that the partial or the total dissolution of the protective Pt overlayer formed *ex situ* (after

158 the post-synthesis acidic wash) exposes the Y atoms to the acidic electrolyte, see **Figure 1b**.

159 These Y atoms are quickly oxidized into Y^{3+} ($E^0_{Y^{3+}/Y^0} = -2.38$ V_{SHE}), which represents a strong

160 segregation driving force toward the surface and, eventually, the Y atoms are dissolved. This

161 process might proceed until Pt is sufficiently available to form a thicker protective overlayer,

162 reconstructing the surface and stabilizing the NP structure, see **Figure 1b**. In line with the

163 specific dissolution profiles, the refined parameters extracted from *operando* WAXS

164 measurements, **Figure 1c**, also reveal that as soon as the electrode potential goes from the OCP

165 to 0.05 V_{RHE}, evolution of the structure of the Pt_xY nanoalloys is triggered. Quantitatively, the

166 metallic phase weight fraction of the Pt_3Y alloy decreases from *ca.* 60 % to 45 %, and a Pt face-

167 centered cubic (*fcc*) phase increases from *ca.* 40 % to 55 %. This trend might be linked to the Y

168 dissolution observed in **Figure 1a**. The scale factor intensities, however, seem to be independent

169 from each other, namely, the steady decrease of the Pt_3Y scale factor (related to the Y

170 dissolution) is not correlated to the sudden growth of the *fcc* Pt scale factor. This behavior

171 suggests that the increase of the *fcc* Pt phase might originate from the electrochemical reduction

172 of an amorphous phase containing Pt, even at such low electrode potential.[32] Besides, we do not

173 rule out the probability that the dissolved Pt species might redeposit forming pure Pt crystalline

174 domains during the potential cycling.[33] Furthermore, during the electrochemical activation, the

175 lattice constant of both Pt$_3$Y and *fcc* Pt phases experienced a contraction of *ca.* -0.4 % and -0.5

176 %, respectively. Finally, while the average coherent domain size of the Pt$_3$Y phase slightly grows

177 from *ca.* 7.5 nm to 8 nm, that of the *fcc* Pt phase seems to be almost constant (*ca.* 1.2 nm).

178 After the electrochemical activation, three potentiodynamic cycles at 5 mV s^{-1}, from 0.05 to 0.95

179 V$_{RHE}$, were performed to clearly resolve the transient dissolution behavior of Pt and Y. **Figure**

180 **2a** shows the specific dissolution profiles of Pt$_x$Y/C under these conditions. In agreement with

181 the literature,[24, 33-37] the predominant Pt dissolution signal is located at the cathodic scan. This

182 feature is related to the electrochemical reduction of the formed Pt oxides.[35] Besides, the specific

183 Pt dissolution profile also reveals the presence of an additional anodic dissolution peak during

184 the first potential cycle. This signal could be associated with the dissolution of low-coordinated

185 sites through the surface oxidation.[24] Moreover, the Y dissolution follows the first anodic Pt

186 dissolution, and low-intense broad signals appear during the cathodic Pt dissolution, suggesting

187 the stabilization of a protective Pt-rich shell after the electrochemical activation.

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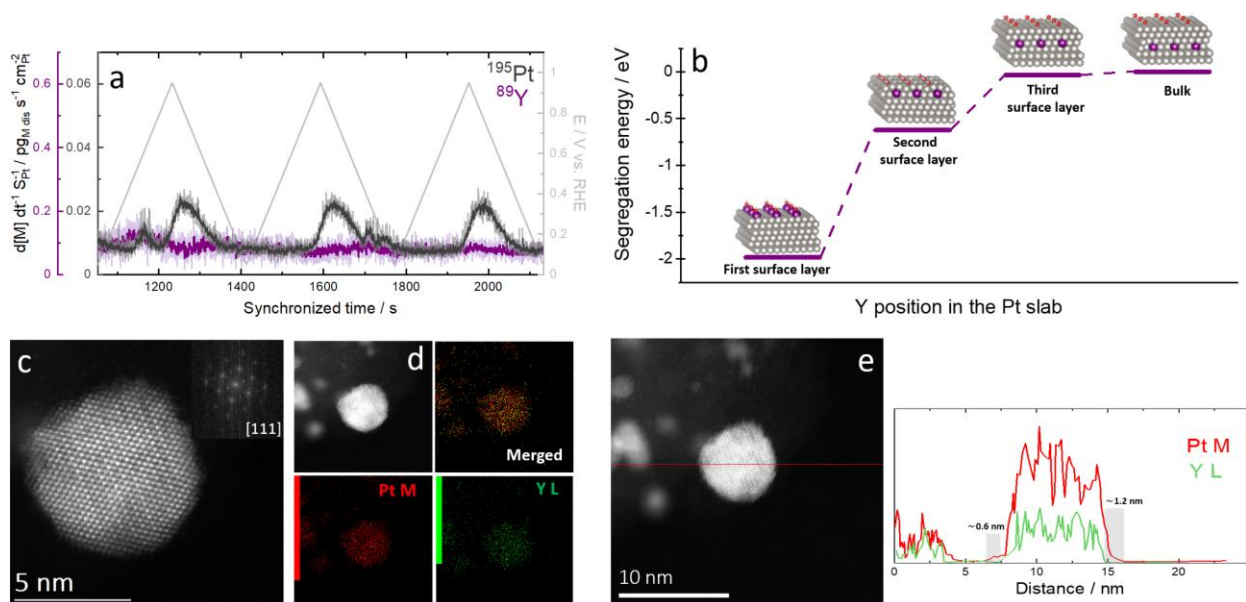
Figure 2. (a) Specific dissolution profiles of Pt_xY/C acquired during slow potentiodynamic cycles (3 cycles at 5 mV s^{-1}); (b) OH-adsorption induced segregation energy as function of the Y position in the Pt slab. The negative values of segregation energies indicate the preference of Y to migrate toward the surface. Representative HAADF-STEM analysis after the electrochemical activation of Pt_xY/C: (c) atomic resolution micrograph (the insert shows the corresponding SAED); (d) EDX elemental mapping; and (e) EDX line scan chemical analysis.

For the sake of clarity, **Figure 2b** exhibits the OH-adsorption induced segregation energy diagram as function of the Y atom position in the Pt slab, *i.e.,* Y atoms exposed at the surface (first surface layer) and protected by *n* Pt monolayers (*n* =1, 2 or 3). This diagram unveils that Y atoms present a strong affinity for OH, which favors their segregation towards the surface and eventually their dissolution (the more negative the segregation energy, the easier the segregation), in line with previous reports on Pt_3Y alloys covered by a Pt monolayer.[38] Notwithstanding, this trend is suppressed once Y atoms are protected by at least 3 Pt monolayers, stabilizing a core/shell (Pt-Y alloy/Pt-rich overlayer) structure. To gain more insights, high resolution HAADF-STEM analyses were carried out after the electrochemical activation, and are presented in **Figure 2c-e** and **Supplementary Information S3**. The average particle size measured *ex situ* is not affected by the electrochemical activation (see below). Besides, the atomic-resolution micrographs and their respective EDX chemical mapping/profiles clearly confirm the presence of the Pt-Y nanoalloy after the electrochemical activation, as NPs presenting a Pt enrichment of 0.6-1.2 nm at the surface. Considering that the thickness of an atomic monolayer of Pt is ~ 0.2 nm,[39] the observed Pt-rich overlayer is 3-6 atom thick, in agreement with the diagram shown in **Figure 2b**.

213 Following the Pt_xY/C nanoalloy stabilization after electrochemical activation, the effect of the

214 square potential wave used in the AST on compositional degradation was investigated by

215 electrochemical *online* ICP-MS. To clearly deconvolute and resolve the dissolution events during

216 the square potential wave, we have held the lower and upper potential limits (0.60 and 0.95 V_{RHE}

217 respectively) for 3 min, following a slow transition between them at 5 mV s^{-1}. **Figure 3a** shows

218 the acquired specific dissolution profiles using three cycles under the aforementioned conditions.

219 Looking at the Pt specific dissolution profile, the anodic dissolution signal through the surface

220 oxidation (yellow arrows in **Figure 3a-b**) peaks as soon as the electrode potential reaches 0.95

221 V_{RHE}, followed by a slow decay. This anodic dissolution event could be associated with the

222 formation and dissolution of metastable Pt species (*e.g.*, amorphous surface oxides,[40] $Pt-O_xH_y$[41]),

223 the origin of which comes from the slow Pt oxidation kinetics.[40] After the formation of a stable

224 Pt oxide, signal decay is observed indicating that the surface is passivated. Meanwhile, the

225 cathodic dissolution event through the reduction of the stabilized Pt oxides (red arrows in **Figure**

226 **3a-b**) takes place, and results in a more intense single peak. This signal has been largely

227 attributed to the oxide place-exchange mechanism, *i.e.*, the exchange of the original lattice sites

228 of surface Pt atoms by O atoms. Simultaneously, the Y specific dissolution profile presents

229 signals during the first cycle at both anodic and cathodic regimes, which are attenuated during

230 the second and third cycles. Based on **Figure 2b,** it might be expected that once the stabilized Pt

231 shell is partially dissolved, its thickness eventually decreases, leading to higher segregation

232 driving force of the previously protected Y atoms, and to the subsequent dissolution of Y until Pt

233 diffusion re-stabilizes the NP structure. This observation might suggest that the stabilization of

234 the Pt-rich shell is critical in hampering Pt-Y segregation.

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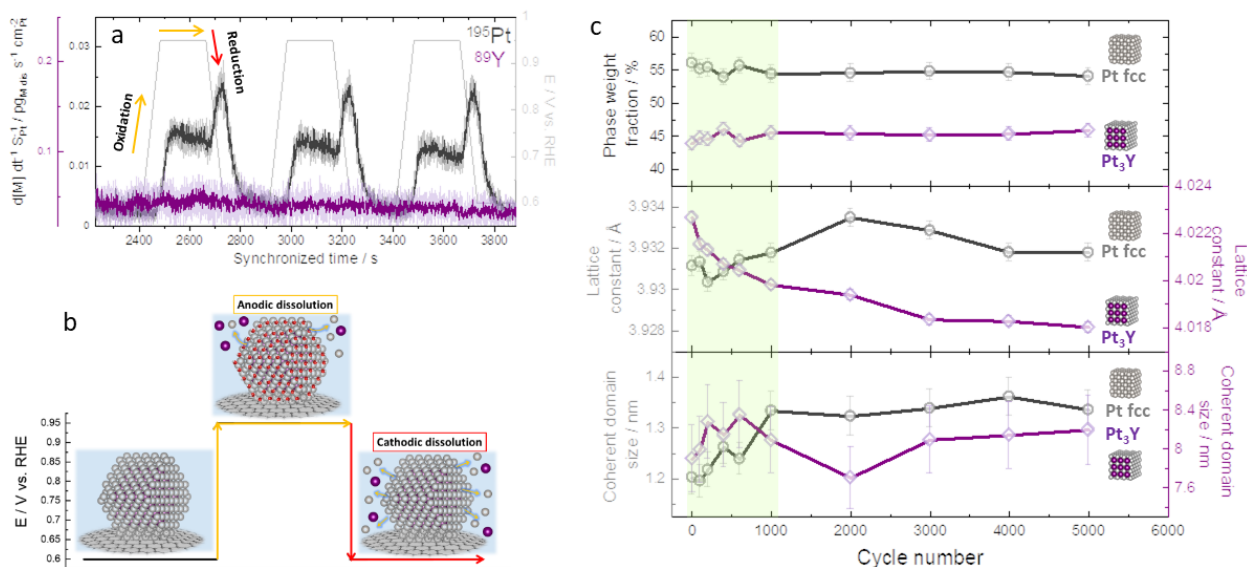
Figure 3. (a) Specific dissolution profiles of Pt_xY/C acquired during simulated AST potential cycles (square-like wave, $0.60 - 0.95\ V_{RHE}$, 3 min at each potential limit with a transition between them at 5 mV s^{-1}). The yellow and red arrows (oxidation and reduction, respectively) serve as a guide to the eye. (b) schematic representation of the Pt_xY/C dissolution during the AST potential cycles; (c) microstructural refined parameters extracted from *operando* WAXS measurements (metallic weight phase fraction, lattice constant and coherent domain size) of the Pt_3Y alloy and Pt phases detected during the applied AST (square-like wave, $0.60 - 0.95\ V_{RHE}$, 3 s at each potential limit with a transition between them of 0.5 s).

Furthermore, the degradation of the Pt_xY/C nanoalloys during the AST (square potential wave, 3 s at each potential limit with a transition of 0.5 s between) was followed by means of *operando* WAXS and *online* ICP-MS in O_2-saturated 0.1 M $HClO_4$ at 25 °C. The evolution of the WAXS refined microstructural parameters during the AST (5,000 cycles) are shown in **Figure 3c.** The metal phase weight fraction of the Pt_3Y alloy lies between 43 - 48 % during the first 1,000 cycles, and reaches an almost constant value of *ca.* 45 % afterwards. Moreover, during the first 1,000 cycles, the metal phase weight fraction of the *fcc* Pt phase fluctuates between 57 - 52 %, and stabilizes *ca.* 55 % afterwards. While the lattice constant of the *fcc* Pt phases underwent an

254 increasing trend (lattice constant expansion), the Pt_3Y phase follows a decreasing behavior

255 (lattice constant contraction). This trend clearly reflects the expected steady loss of the

256 compressive strain effect, with negative effect on the electrocatalytic ORR performance. Finally,

257 the average coherent domain size trend of the Pt_3Y phase revealed a slight increase from *ca.* 7.8

258 nm to 8.4 nm during the first 600 cycles, continuing to *ca.* 8 nm (1,000 cycles), *ca.*7.7 nm (2,000

259 cycles) and *ca.* 8 nm thereafter. Besides, the *fcc* Pt phase slight grew during the first 1,000 cycles

260 from *ca.* 1.20 nm to 1.35 nm, achieving an almost constant value of *ca.* 1.37 nm thenceforth.

261 Therefore, the strongest structural degradation during the AST takes place during the first 1000

262 cycles, in line with previous results on Gd/Pt(111) single-crystal electrodes.

263 Owing to the fact that the most pronounced microstructural variations are discernible during the

264 first 1,000 cycles, the Pt and Y dissolution were monitored by *online* ICP-MS during the first

265 1,000 cycles of the AST (**Supplementary Information S4**). The total dissolved Pt and Y under

266 these conditions, *i.e.*, the integrated specific dissolution rates, are *ca.* 155 pg and 201 pg,

267 respectively, which represent a loss of 0.01 % and 0.13 % of the initial electrode loading after

268 1,000 AST cycles.

269 Enhanced kinetics of the sluggish ORR in acidic medium require the binding energies (ΔE) of

270 the key reaction intermediates, *i.e.*, O* and OH*, to be weaker than those with Pt (111) by ~0.2

271 eV and ~0.1 eV, respectively.[42] DFT computations were performed to track the ΔE_{O*} and ΔE_{OH*}

272 as a function of the Pt-Pt interatomic distance, *c.f.* **Figure 4 and Supplementary Information**

273 **S5**. The Pt-Pt interatomic distances of Pt_xY/C nanoalloys during the AST were extracted from

274 the *operando* WAXS measurements and are plotted in **Figure 4**, from which a modest

275 weakening of ΔE_{O*} (~ 0.02 eV) and ΔE_{OH*} (~ 0.001 eV) respect to Pt (111) may be observed.

13

276 This result indicates that the induced compressive strain is attenuated by the thickening of the Pt

277 overlayer, which leads to lower ORR activity.
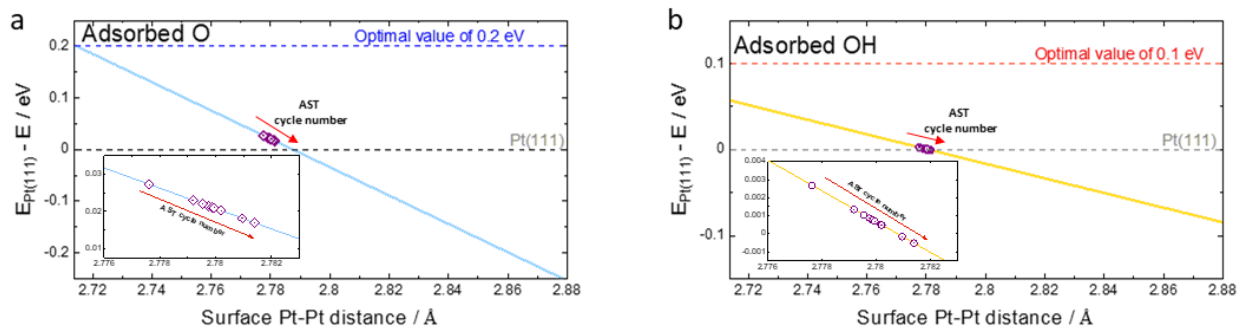
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279 **Figure 4.** DFT calculated binding energies, with respect to Pt (111) surface, of (a) adsorbed O,

280 and (b) adsorbed OH as function of the Pt-Pt interatomic distance. Purple points represent the

281 experimental average Pt-Pt interatomic distance of Pt$_x$Y/C nanoalloys during the AST (5000

282 square-like wave, $0.60 - 0.95$ V_{RHE}, 3 s at each potential limit with a transition between them of

283 0.5 s).

284

285 With this knowledge, the local morphology and chemical composition of the Pt$_x$Y/C

286 electrocatalyst were investigated after the AST in the RDE setup (30,000 square potential wave,

287 3 s at each potential limit with a transition of 0.5 s between in O_2-saturated 0.1 M $HClO_4$ at 25

288 °C) using high resolution HAADF-STEM analyses, *c.f.* **Figure 5** and **Supplementary**

289 **Information S6**. **Figure 5a** shows the evolution of the average particle size from the *ex situ* state

290 to the end of the AST: while the electrochemical activation does not strongly affect the average

291 particle size, the potential cycling of the AST causes a growth of the electrocatalyst particles

292 from 5.4 nm to 6.6 nm, in line with the average coherent domain size trend in **Figure 3c**. The

293 ECSA variations shown in **Figure S3** might be related to this particle size evolution. Although

294 the acquired micrographs indicate the predominance of dense NPs, the presence of porous

295 structures after the AST was also observed (**Supplementary Information S6**), which are

296 expected due to the dealloying process occurring on potential cycling.[7, 39] The atomic-resolution

297 micrographs and their respective EDX chemical mapping/profiles, **Figure 5b-d,** clearly confirm

298 the presence of the Pt-Y nanoalloy after the AST, with a thicker Pt enrichment at the border of

299 the NPs of *ca.* 1.2-1.6 nm, being equivalent to a Pt shell of 6-8 atom thick.

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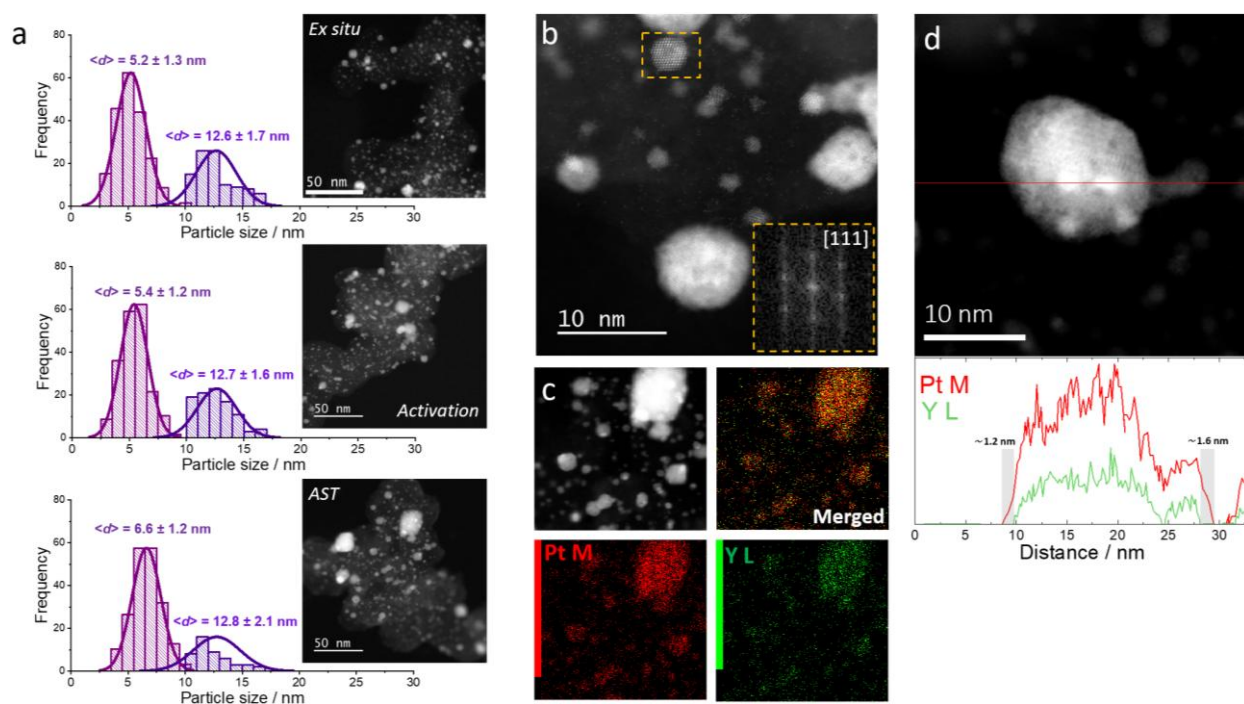
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302 **Figure 5.** Representative HAADF-STEM analysis of Pt$_x$Y/C after the AST: (a) evolution of the

303 average particle size, from the *ex situ* state, the electrochemical activation and at the end of the

304 AST; (b) atomic resolution micrograph (the insert shows the corresponding SAED); (c) EDX

305 elemental mapping; and (d) EDX line scan chemical analysis.

306

307 **4. CONCLUSION**

15

308 Carbon-supported Pt_xY nanoalloys were extensively studied, for the first time, under the

309 electrochemical conditions for the ORR by means of *operando* WAXS, *online* ICP-MS, atomic

310 resolution HAADF-STEM and DFT calculations. This allowed monitoring of the atomic-scale

311 degradation steps undergone by the electrocatalyst from the early electrode surface conditioning

312 (or electrochemical activation) to the end of the applied AST. Such results clearly revealed that

313 the Pt_xY/C nanoalloys underwent considerable degradation during the early operation steps

314 (electrochemical activation), with metal dissolution and crystalline structure evolution being

315 observed, and surface reconstruction.

316 Furthermore, *operando* measurements identified that the strongest nanoalloy degradation, in

317 terms of metal dissolution and structural evolution, takes place during the first AST 1,000 cycles

318 under O_2 atmosphere, which eventually diminished the ORR kinetic benefit from the Pt-Y alloy.

319 Although the expected high ORR performance of Pt_xY/C was not observed, the proposed

320 *operando* structure-activity-stability trends guides further optimization of the delicate

321 activity/stability trade-off of this system. Besides, we believe that this work might inspire further

322 in-depth understanding of the degradation of carbon-supported Pt-based nanoalloys during the

323 harsh ORR electrochemical environment.

324

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343

Author Contributions

345 The manuscript was written through contributions of all authors. All authors have given approval

346 to the final version of the manuscript.

Author Contributions

348 **Carlos A. Campos-Roldán** : Conceptualization, writing-original draft, formal analysis,

349 investigation, **Raphaël Chattot** : Conceptualization, writing-review & editing, formal analysis,

350 investigation, **Jean-Sébastien Filhol** : Writing-review & editing, formal analysis, methodology,

351 **Hazar Guesmi** : Writing-review & editing, formal analysis, methodology, **Nuria Romero** :

352 Methodology, investigation, writing-review & editing, **Rémi Bacabe** : Investigation, **Pierre-**

353 **Yves Blanchard** : Writing-review & editing, supervision, **Valentin Vinci** : Writing-review &

354 editing, investigation, **Jakub Drnec** : Writing-review & editing, formal analysis, investigation,

355 **Jacques Rozière:** Funding acquisition, conceptualization, writing-original draft, supervision,

356 **Deborah J. Jones** : Funding acquisition, conceptualization, writing-original draft, supervision,

357 **Sara Cavaliere** : Funding acquisition, conceptualization, writing-original draft, supervision.

358 **ASSOCIATED CONTENT**

359 The following files are available free of charge.

360 **Supporting Information**: Comparison of the current state-of-the-art, experimental

361 methodology, computational details, *ex situ* complementary characterization, complementary

362 HAADF-STEM analyses after the electrochemical activation and after the AST, and *online* ICP-

363 MS dissolution profile during the first AST 1,000 cycles are available in the Supporting

364 Information.

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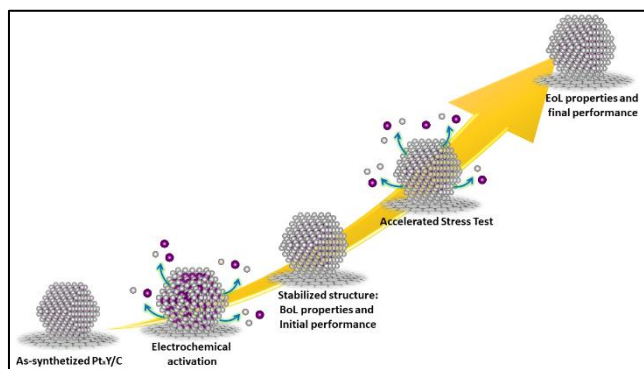
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519 **TOC graphic**

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