

Elucidating the mechanisms driving the ageing of porous hollow PtNi/C nanoparticles by the means of CO_{ads} stripping

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Abstract

The specific activity for the oxygen reduction reaction (ORR) of Pt-alloy electrocatalysts depends on (i) strain/ligand effects induced by the non-noble metal (3d transition metal or a rare-Earth element) alloyed to Pt, (ii) the orientation of the catalytic surfaces and (iii) the density of structural defects (such as vacancies, voids and grain boundaries). The latter impacts on the ‘generalized’ coordination number of the active sites for the ORR, on the contraction of the lattice parameter and on the adsorption strength of the intermediate species (O^* , OH^* , OOH^*), resulting in enhanced ORR specific activity. Here, we discuss a set of parameters derived from CO_{ads} stripping measurements and the Rietveld refinement of the X-Ray Diffraction (XRD) patterns, aiming to separate the contribution of the leaching of the non-noble metal and of the structural defects on the reactivity of porous hollow PtNi/C nanoparticles. Porous hollow PtNi/C nanoparticles were aged at $T = 353$ K, in an Ar-saturated 0.1 M $HClO_4$ electrolyte, during 20,000 cycles between $E = 0.6$ V vs. RHE and $E = 1.0$ V vs. the reversible hydrogen electrode (RHE), with an intermediate characterization after 5,000 cycles. The losses in ORR specific activity were attributed to the dissolution of Ni atoms (modifying strain/ligand effects) and to the increase of the crystallite size (d_{XRD}), resulting in a diminution of the density of grain boundaries. In agreement with the Gibbs-Thompson equation, the electrocatalysts that presented larger crystallites ($d_{XRD} > 3$ nm) were far more stable than the ones with the smallest crystallites ($d_{XRD} < 2$ nm). We also observed that performing intermediate characterizations (in an O_2 -saturated electrolyte) results in activity losses for the ORR.

Keywords: CO_{ads} stripping, X-ray diffraction, Oxygen Reduction Reaction, Proton Exchange Membrane Fuel Cells, Durability.

Introduction

The activity of Pt-alloy and Pd-alloy for various electrochemical reactions, such as the alcohols oxidation ¹⁻⁶ (MOR, EOR, *etc.*), the borohydride oxidation ⁷ (BOR) or the oxygen reduction reaction (ORR) ⁸⁻¹⁰ is governed by their structural properties, composition and morphology. Thus, tuning the activity of Pt for the ORR can be achieved by nanostructuring the electrocatalysts, *i.e.* by controlling the size ¹¹, shape ^{8,10,12-16}, noble metal content ¹⁷⁻²², preferential crystallite orientation ^{13,23} and density of structural defects of the nanoparticles.

As rationalized by Nørskov and Hammer ²⁴, alloying Pt with a 3d transition metal modifies the density of states of the Pt 5d-band, and thus impacts on the adsorption strength of oxygenated species ²⁵⁻²⁸ (O*, OH*, OOH*) leading to a volcano-plot relationship between the specific activity for the ORR and the chemisorption energy of oxygenated species. The latter can be rationalized in the frame of the Sabatier principle, *i.e.* the ideal electrocatalyst should bind the adsorbate species neither too strongly nor too weakly. By controlling the nature of the alloying element, and especially by using 3d-transition metals (or rare-Earth elements ²⁹⁻³¹), significant enhancement of the specific activity for the ORR can be reached.

As evidenced by Stamenkovic *et al.* ²³, the specific activity of the PtM electrocatalysts also depends on the crystallographic orientation of the facets. Indeed, on Pt₃Ni (hkl) surfaces, the ORR specific activity varies as Pt₃Ni (111) > Pt₃Ni (110) > Pt₃Ni (100), due to the modification of the Pt 5d-band center on the different facets ²³. Accordingly, electrocatalysts with a preferential crystallite orientation were synthesized, as PtNi octahedra ^{13,21}. However, preferential

crystallite orientation and faceting cannot be observed on highly defective catalysts, which are composed of small interconnected crystallites and highly disordered surfaces^{9,32}.

As recently introduced by Calle-Vallejo *et al.*^{33,34} the electrocatalytic activity for the ORR of a given catalytic site depends on its ‘generalized’ coordination number, *i.e.* the coordination number determined by considering its 1st and 2nd neighbours. A theoretical ‘generalized’ coordination number of 8.3 (obtained by introducing atomic vacancies) has been found optimal for the ORR, which is slightly higher than 7.5 for a Pt atom on a (111) facet in a face-centered cubic structure. Therefore, concave catalytic sites (as those present at the inner surface of porous hollow nanoparticles or in open pores present at the surface^{9,16}) feature a higher ‘generalized’ coordination number, resulting in a higher activity for the ORR. Hitotsuyanagi *et al.*³⁵, Kuzume *et al.*³⁶ and Bandarenka *et al.*^{37–39} also evidenced the crucial role of steps on Pt single crystals. An optimal density of steps of $n = 3$ has been found for Pt₃Ni [n(111) × (100)] surfaces resulting in a 3.5 fold improvement in specific activity for the ORR vs. Pt(111)³⁹. Note that Le Bacq *et al.*⁴⁰ recently showed that highly-defective Pt surfaces are composed of sites featuring relaxed (that strongly bind ORR intermediates) and contracted lattice parameter (that weakly bind ORR intermediates). The combination of domains featuring contracted and expanded lattice parameter renders highly defective Pt surfaces active both for eletrooxidation and electroreduction reactions.

Our recent works^{41–44} discussed the effect of structural defects on the activity of various nanostructures (such as porous hollow PtNi nanoparticles^{41,42}, commercial Pt/C, solid PtNi with various dispersions, core@shell PNi and PtNi sea-sponges⁴³) and the characterization tools used to correlate the density of structural defects and the electrocatalytic activity for the ORR. In this paper, we present an experimental methodology to disentangle the role of

structural defects and the role of Ni on the ORR activity of porous hollow PtNi/C nanoparticles by combining X-Ray Diffraction (XRD) measurements and electrochemistry. This methodology has been further applied to study the robustness of highly defective porous PtNi/C electrocatalysts in simulated proton-exchange membrane fuel cell (PEMFC) conditions.

Results and Discussion

I. Descriptors of the porous hollow PtNi/C NPs morphology.

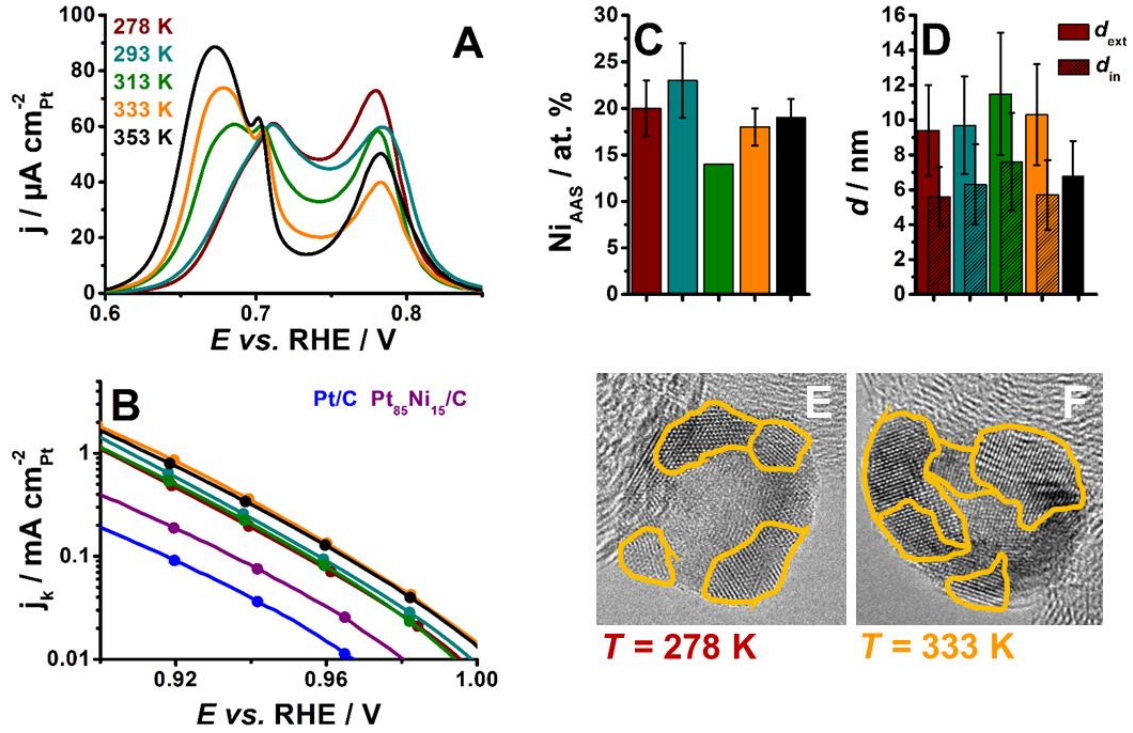


Figure 1. Electrochemical and physico-chemical properties of the electrocatalysts introduced in Ref. ⁴². (A) CO_{ads} stripping measurements on the electrocatalysts synthesized at $T = 278, 293, 313, 333$ and 353 K in Ar-saturated 0.1 M HClO₄ at $v = 0.02$ V s⁻¹; (B) Tafel plot of ohmic drop and mass-transport corrected linear sweep voltammograms in O₂-saturated 0.1 M HClO₄ at $v = 0.005$ V s⁻¹ and $\omega = 1600$ rotation per minute (rpm) ($T = 298$ K, Pt loading = $20 \mu\text{g cm}^{-2}$); (C) Nickel atomic content determined by atomic absorption spectroscopy (AAS); (D) External (d_{ext}) and inner (d_{in}) diameter of the porous hollow PtNi/C nanoparticles synthesized at different temperatures – due to its dual morphology, *i.e.* agglomerates + isolated nanoparticles, only the diameter of the isolated nanoparticles was given for the electrocatalyst synthesized at $T = 353$ K; (E) High-Resolution Transmission Electron Microscopy (HR-TEM) micrograph of the electrocatalyst synthesized at $T = 278$ K. The grain boundaries are highlighted

in orange; (F) HR-TEM micrograph of the electrocatalyst synthesized at $T = 333$ K. The grain boundaries are highlighted in orange.

In a recent study⁴², we studied the effect of several parameters, *i.e.* (i) the Ni atomic content, (ii) the crystallite size, (iii) the lattice parameter, (iv) the texturation⁴⁵ and (v) the density of structural defects on the specific activity for the ORR of porous hollow PtNi/C nanoparticles. The electrochemical and the physico-chemical properties of these electrocatalysts are presented in **Figure 1**, as well as in **Figure S1**, **Figure S2** and **Table S1**, **Table S2** and **Table S3**. They were synthesized at different temperatures, *i.e.* $T = 278, 293, 313, 333$ and 353 K using a one-pot synthesis first introduced by Bae *et al.*⁴⁶ and widely discussed in other works^{9,32,41,47}. The fine nanostructure of the porous hollow PtNi/C nanoparticles was assessed in the light of CO_{ads} stripping measurements. Two peaks of variable intensity and potential were observed: a ‘pre-peak’ from $E = 0.55$ V vs. RHE to $E = 0.73$ V vs. RHE and a main peak from $E = 0.73$ V vs. RHE to $E = 0.90$ V vs. RHE, see **Figure 1A**. The specific activity for the ORR measured at $E = 0.95$ V vs. RHE of the porous hollow PtNi/C nanoparticles synthesized at $T = 333$ K was 7-fold higher compared to a commercial Pt/C and 2.5-fold higher compared to a solid PtNi/C electrocatalyst with identical crystallite size, Ni atomic content and lattice parameter (see **Figure 1B** and **Table S2**). The electrocatalysts synthesized at different temperatures feature a similar Ni atomic content (**Figure 1C**), similar external and internal diameters (**Figure 1D**) and are composed of 1.5 – 3.5 nm crystallites interconnected to form the shell of the hollow structure (**Figure 1E – 1F** and **Table S1**). The electrocatalyst synthesized at $T = 333$ K shows an enhancement factor of 1.7 in specific activity for the ORR at $E = 0.95$ V vs. RHE with respect to the electrocatalyst synthesized at $T = 278$ K. Interestingly, this higher activity is associated to a predominance of the CO_{ads} stripping ‘pre-peak’, *i.e.* a higher ratio of the electrical charge under the CO_{ads} stripping ‘pre-peak’ ($Q_{pp,CO}$) to the total electrical charge of the CO_{ads} stripping ($Q_{T,CO}$) (see **Figure 2**).

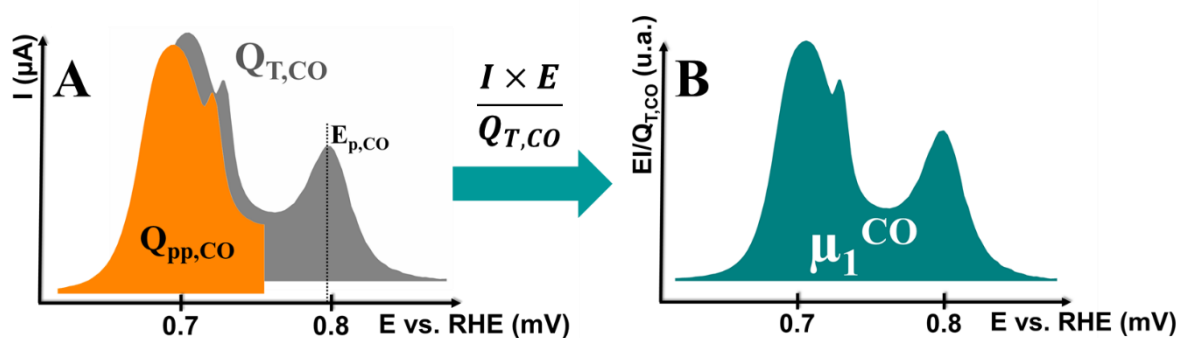


Figure 2. Parameters describing the physico-chemical properties of a nanostructured, low Ni atomic content, electrocatalyst extracted from CO_{ads} stripping measurements: (A) The electrical charge under the CO_{ads} stripping pre-peak ($Q_{\text{pp,CO}}$), the total electrical charge of the CO_{ads} stripping ($Q_{\text{T,CO}}$) and the position of the main peak ($E_{\text{p,CO}}$) ; (B) The first moment of the potential weight of the CO_{ads} stripping voltammogram determined as the integral of $(EI)/Q_{\text{T,CO}}$ (μ_1^{CO}).

Some physico-chemical properties of an electrocatalyst, such as the density of structural defects, the Ni atomic content or the Ni-induced strain, can be determined from the CO_{ads} stripping voltammograms^{42,43}. This is especially true for electrocatalysts with low Ni atomic content, similar crystallite size and Pt-enriched surface, as discussed in Refs.⁴² and ⁴³. The CO_{ads} electrooxidation mechanism is rather complex (see Lebedeva *et al.*^{48–51} for stepped Pt single crystals, Maillard *et al.*^{52–55} for carbon-supported Pt nanoparticles). Maillard *et al.*^{52,55} have shown that the formation of agglomerated nanoparticles, *i.e.* nanocrystallites (NCs) interconnected by grain boundaries, induced the appearance of a CO_{ads} stripping ‘pre-peak’ at much lower potential than the main peak. This pre-peak can be observed at $E = 0.55 – 0.73$ V vs. RHE in **Figure 1A** and **Figure 2**. It is representative of the electrooxidation of CO_{ads} on nanocrystallites interconnected by grain boundaries (which favours OH nucleation and facilitate CO oxidation at lower potential) and, *lato sensu*, of the density of structural defects present onto the electrocatalyst surface. The main peak at $E = 0.73 – 0.90$ V vs. RHE (**Figure 1A** and **Figure 2**) was ascribed to the electrooxidation of CO_{ads} molecules on isolated nanocrystallites, *i.e.* either non-

connected via grain boundaries, non-defective or monocrystalline Pt-rich NPs. Therefore, the density of structural defects on the electrocatalysts surface is proportional to the ratio of the electrical charge under the CO_{ads} stripping ‘pre-peak’ ($Q_{\text{pp,CO}}$) to the total charge of the CO_{ads} stripping ($Q_{\text{T,CO}}$). As shown previously,⁴² a straightforward relationship exists between the density of structural defects ($Q_{\text{pp,CO}} / Q_{\text{T,CO}}$) and the specific activity for the ORR of porous hollow PtNi/C NPs.

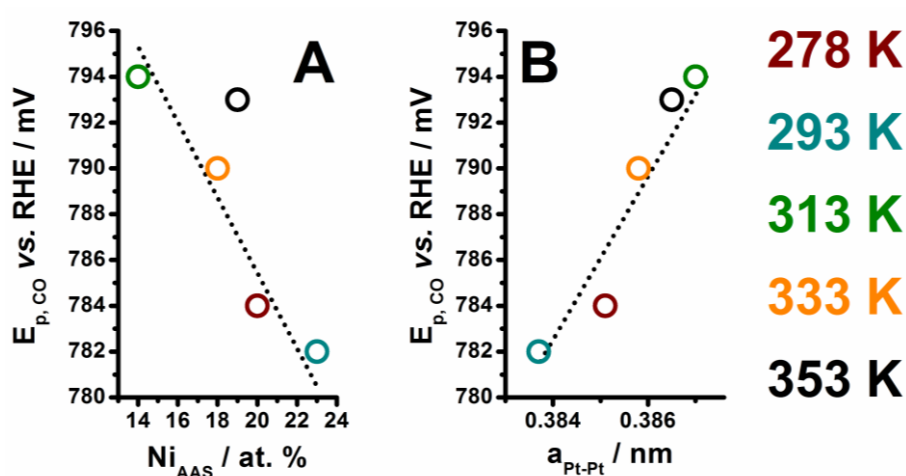


Figure 3. Variation of (A) the potential of the high-potential peak of the CO_{ads} stripping voltammogram ($E_{\text{p,CO}}$) on the porous hollow PtNi/C electrocatalysts synthesized at $T = 278, 293, 313, 333$ and 353 K vs. the Ni atomic content determined by Atomic Absorption Spectroscopy (AAS) and (B) potential of the high-potential peak of the CO_{ads} stripping ($E_{\text{p,CO}}$) vs. the lattice parameter of the electrocatalysts discussed in this work.

The presence of a non-noble metal (PtM, $M = \text{Fe}, \text{Ni}, \text{Co}, \text{etc.}$) in the Pt NCs influences CO_{ads} stripping measurements. Recent works from van der Vliet *et al.*⁵⁶ and Bandarenka *et al.*⁵⁷ have shown that Pt_3Ni skin surfaces and Cu/Pt near surface alloys present a lower overpotential for the CO_{ads} oxidation than pure Pt surfaces. This trend is widely observed in the literature (PdM@PtPd/C core-shell⁵⁸, PtCo and PtNi ribbons¹ or PtNi hollow nanoparticles⁹). **Figure 3A** and **Figure 3B** represent the evolution of the potential of the high-potential peak of the

CO_{ads} stripping ($E_{p,CO}$) vs. the Ni atomic content and vs. the lattice parameter, respectively. The evolution of the potential of the ‘pre-peak’ of the CO_{ads} stripping ($E_{pp,CO}$) shows no direct relationship with the Ni atomic content (see **Figure S3A**). In contrast, a linear relationship is observed between the high-potential peak of the CO_{ads} stripping ($E_{p,CO}$) and the Ni atomic content (**Figure 3A**). This linear relationship is even better between $E_{p,CO}$ and the lattice parameter of the electrocatalyst (**Figure 3B**). In conclusion, $E_{p,CO}$ appears to be a relevant marker to approximate the Ni at. % content and the Ni-induced contraction of the lattice parameter for porous hollow PtNi/C electrocatalysts (and, therefore, the modification of the Pt 5d-band centre by the strain and ligand effects^{59–62}).

As previously stated^{41–44}, the specific activity for the ORR of porous hollow PtNi/C nanoparticles is controlled by a combination of two aspects of the electrocatalyst morphology, *i.e.* the Ni-induced contraction of the lattice parameter and the density of structural defects. It has been recently shown by Density Functional Theory calculations and verified experimentally by Le Bacq *et al.*⁴⁰ that the surface of the porous hollow PtNi/C nanoparticles is composed of a combination of (i) domains with contracted and relaxed lattice constant and (ii) atoms with high and low coordination number. In consequence, the Pt 5d-band centre not only depends on the Ni content, but also of the density of structural defects. $E_{p,CO}$ and $Q_{pp,CO} / Q_{T,CO}$ consider these two aspects separately (see **Figure 4A** and **Figure 4B**). Thus, it is essential to use a parameter which describes their synergetic effect on the electrocatalyst specific activity (**Figure 4C**). The first moment of the potential weight is ideally suited to this purpose. It was introduced by Chatot *et al.*⁴³ (μ_1^{CO} , mV vs. RHE) and determines the mean potential of the CO_{ads} stripping weighted from the intensity of the ‘pre-peak’ and the high-potential peak, as described in **Figure 2** and in **Equation 1**.

$$\mu_1^{CO} = \int_{0.55}^1 \frac{E \times I}{\int_{0.55}^1 I \times dE} \times dE = \int_{0.55}^1 \frac{E \times I}{Q_{T,CO}} \times dE \quad (Eq. 1)$$

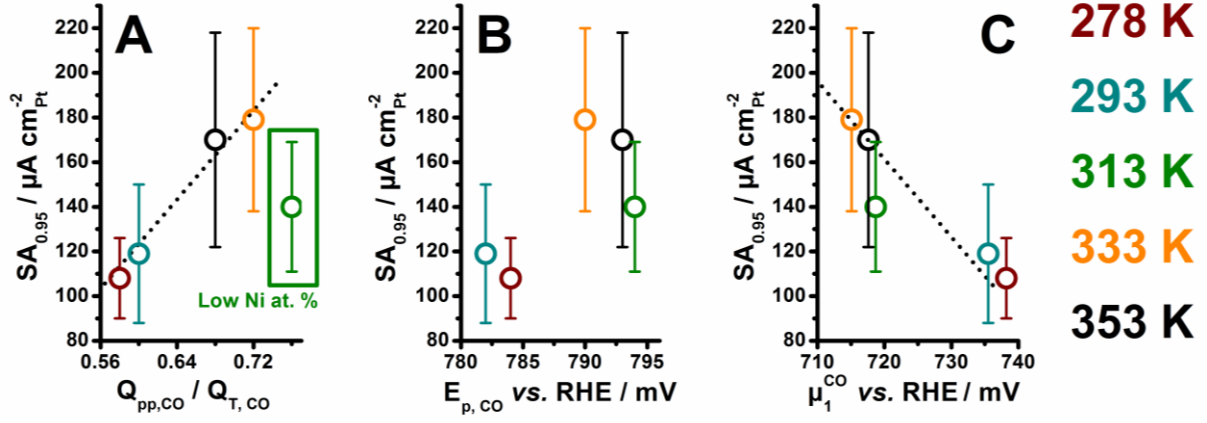


Figure 4. Variation of the specific activity for the ORR measured at $E = 0.95$ V vs. RHE on the porous hollow PtNi/C electrocatalysts synthesized at $T = 278, 293, 313, 333$ and 353 K vs. (A) the ratio of the electrical charge under the ‘pre-peak’ ($Q_{pp,CO}$) to the total CO_{ads} stripping charge ($Q_{T,CO}$); (B) the potential of the high-potential peak of the CO_{ads} stripping ($E_{p,CO}$); (C) the first moment of the potential weight of the CO_{ads} stripping (μ_1^{CO}).

As shown recently, the density of structural defects in an electrocatalyst can also be approximated by the microstrain (μ_e) derived from Rietveld analysis of X-ray diffraction patterns^{41,43}. The microstrain reflects local variation of the lattice parameter around the mean ($\mu_e \propto \Delta a/a$).

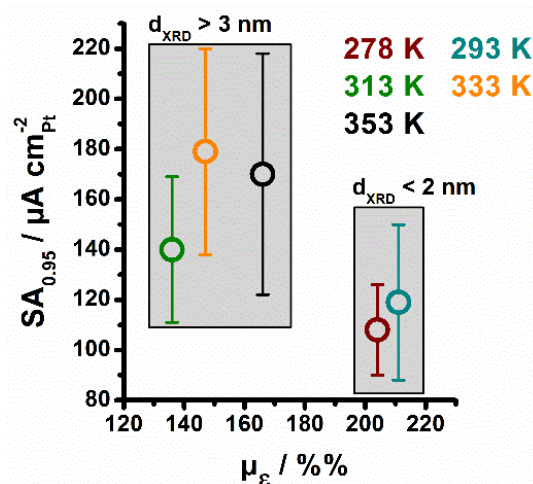


Figure 5. Variation of the specific activity for the ORR measured at $E = 0.95$ V vs. RHE on the porous hollow PtNi/C electrocatalysts synthesized at $T = 278, 293, 313, 333$ and 353 K, vs. the microstrain determined by Rietveld refinement from XRD patterns (μ_ϵ).

Table 1. Crystallite size and anisotropy determined by Rietveld refinement from XRD patterns for the porous hollow PtNi/C electrocatalysts synthesized at $T = 278, 293, 313, 333$ and 353 K.

	Crystallite size / nm	Anisotropy / nm
$T = 278$ K	1.5 ± 0.1	0.32 ± 0.01
$T = 293$ K	1.8 ± 0.1	0.36 ± 0.02
$T = 313$ K	3.2 ± 0.1	0.40 ± 0.02
$T = 333$ K	3.2 ± 0.1	0.44 ± 0.02
$T = 353$ K	3.5 ± 0.2	0.48 ± 0.03

According to the works of Qin *et al.*^{63,64}, the microstrain is mostly due to grain boundaries. Thus, the electrocatalysts with the smallest nanocrystallites, *i.e.* with the highest density of grain boundaries, present the highest microstrain value (see **Figure 5** and **Table 1**. The microstrain corrected from the crystallite size⁴³ is provided in **Table S3**). However, the ‘high-microstrain’ / ‘small-crystallites’ porous hollow PtNi/C electrocatalysts, which contain a high density of grain boundaries, are also the worst-performing for the ORR (at $E = 0.95$ V vs. RHE, $j_k = 108 \pm 18 \mu A cm_{Pt}^{-2}$ for the electrocatalyst synthesized at $T = 278$ K and $j_k = 119 \pm 31 \mu A cm_{Pt}^{-2}$ for

the electrocatalyst synthesized at $T = 293$ K, see **Table S2**), as a result of their small crystallite size ($d_{\text{XRD}} < 2$ nm) that increases the proportion of low coordinated atoms^{11,65}.

Thus, as observed in **Figure 5**, the surface density of grain boundaries (*i.e.* the microstrain) cannot solely explain the increase in ORR activity induced by the structural defects, confirming that other defects, such as vacancies, steps, *etc.* impact on the specific activity (and contribute to the CO_{ads} stripping ‘pre-peak’).

II. Ageing of the porous hollow PtNi/C NPs.

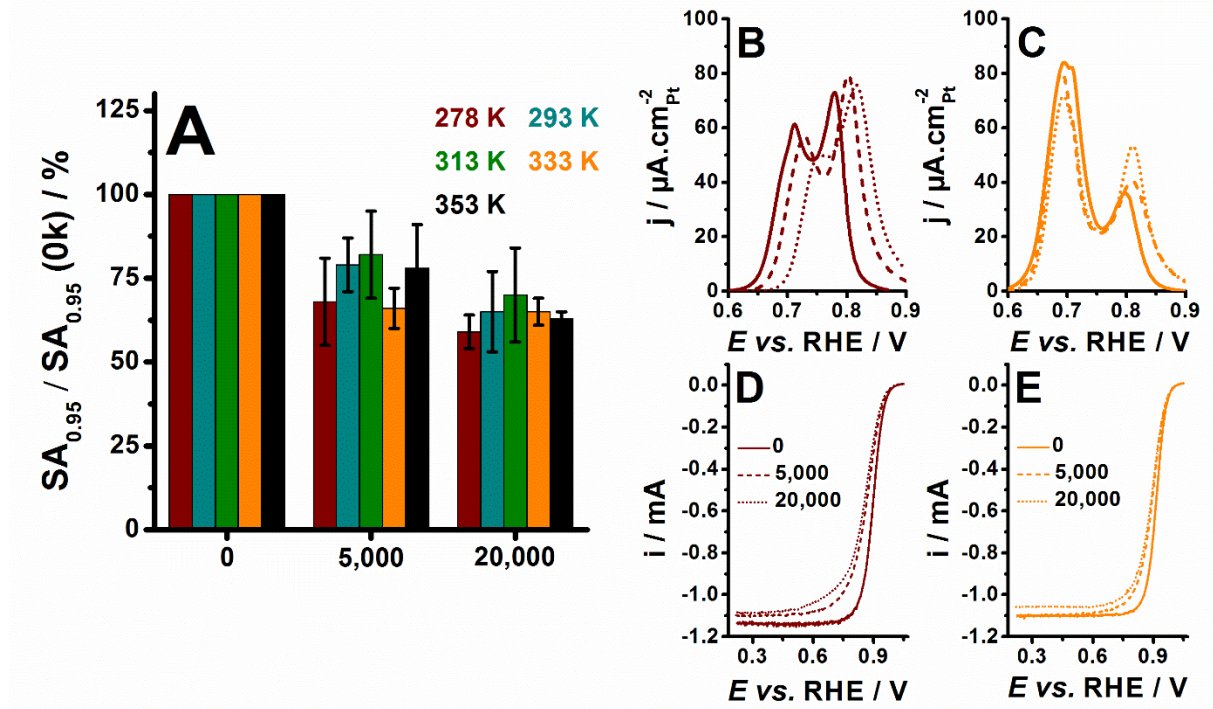


Figure 6. (A) Ratio of the specific activity for the ORR measured at $E = 0.95$ V vs. RHE for the electrocatalysts synthesized at $T = 278, 293, 313, 333$ and 353 K before ($SA_{0.95}(0k)$) and after ($SA_{0.95}$) 0, 5,000 and 20,000 potential cycles with linear profile between $E = 0.6$ V vs. RHE and $E = 1.0$ V vs. RHE at $\nu = 0.05$ V s⁻¹ and $T = 353$ K in Ar-saturated 0.1 M HClO₄; (B – C) Background-subtracted CO_{ads} stripping voltammograms measured before and after 5,000 and 20,000 potential cycles with linear profile for the porous hollow PtNi/C electrocatalysts synthesized at (B) $T = 278$ K and (C) $T = 333$ K; (D – E) Ohmic drop corrected polarization curves in O₂ saturated 0.1 M HClO₄ before and after 5,000 and 20,000 potential cycles with linear profile for the porous hollow PtNi/C electrocatalysts synthesized at (D) $T = 278$ K and (E) $T = 333$ K.

Figure 6, Table S4 and Table S5 summarize the changes of the electrocatalytic properties of the porous hollow PtNi/C nanoparticles synthesized at $T = 278, 293, 313, 333$ and 353 K after 20,000 potential cycles with linear profile between $E = 0.6$ V vs. RHE and $E = 1.0$ V vs. RHE (Ar-saturated 0.1 M HClO₄, $T = 353$ K and $\nu = 0.05$ V s⁻¹), with an intermediate characterisation

after 5,000 potential cycles. After 20,000 potential cycles, a 30 to 40 % loss of the specific activity for the ORR is reported at $E = 0.95$ V vs. RHE (**Figure 6A**), the most stable electrocatalyst being that synthesized at $T = 313$ K ($j_k = 140 \pm 29 \mu\text{A cm}_{\text{Pt}}^{-2}$ before ageing and $98 \pm 20 \mu\text{A cm}_{\text{Pt}}^{-2}$ after 20,000 potential cycles) and the least stable that synthesized at $T = 278$ K ($j_k = 108 \pm 18 \mu\text{A cm}_{\text{Pt}}^{-2}$ before ageing and $73 \pm 13 \mu\text{A cm}_{\text{Pt}}^{-2}$ after 20,000 potential cycles, see **Table S4** and **Table S5**). A mass activity loss approaching 60 % is also observed for the electrocatalyst synthesized at $T = 278$ K after 20,000 potential cycles (**Table S5**). For comparison purposes, the mass and specific activity for the ORR measured at $E = 0.9$ V vs. RHE after 5,000 and 20,000 potential cycles are provided in **Table S4** and **Table S5**, respectively.

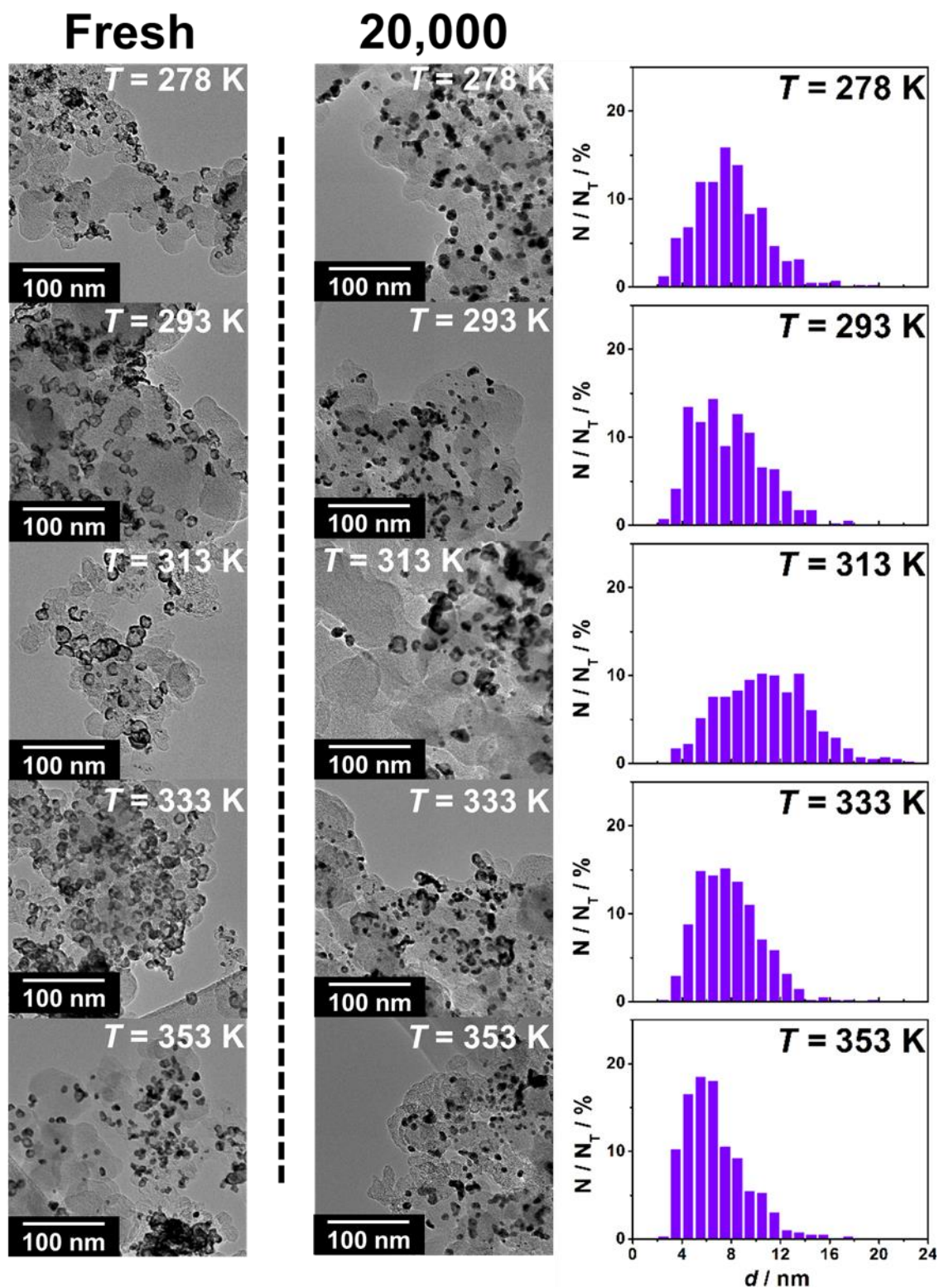


Figure 7. Representative TEM micrographs of the porous hollow PtNi/C electrocatalysts studied in this work before (Fresh – extracted from **Figure S1**) and after 20,000 cycles between $E = 0.6$ V vs. RHE and $E = 1.0$ V vs. RHE at $v = 0.05$ V s⁻¹ and $T = 353$ K in an Ar-saturated 0.1 M HClO₄ electrolyte. The particle size distributions are provided for the nanoparticles obtained after 20,000 cycles (see **Figure 1**

and Ref. ⁴² for the external / inner diameter and the particle size distribution of the electrocatalysts before ageing).

As observed in **Figure 7**, the hollow nanostructure is not maintained upon ageing, with the notable exception of the electrocatalyst synthesized at $T = 313$ K which remains partly hollow-shaped. The central cavity collapses, leading to the formation of 7 – 10 nm solid nanoparticles (see **Table S6**). The losses in ORR specific activity can be correlated to the changes of the CO_{ads} stripping voltammograms. As observed in **Figure 6B** and **Figure 6C** for the electrocatalysts synthesized at $T = 278$ K and $T = 333$ K, the losses in ORR specific activity (see **Figure 6D** and **Figure 6E**) are associated with a decrease in intensity of the CO_{ads} stripping ‘pre-peak’ (*i.e.* a diminution of $Q_{\text{pp,CO}} / Q_{\text{T,CO}}$) and an increase in potential of the CO_{ads} stripping peaks (*i.e.* an increase of $E_{\text{pp,CO}}$ and $E_{\text{p,CO}}$ and, thus, a decrease of μ_1^{CO} , see **Figure 7**).

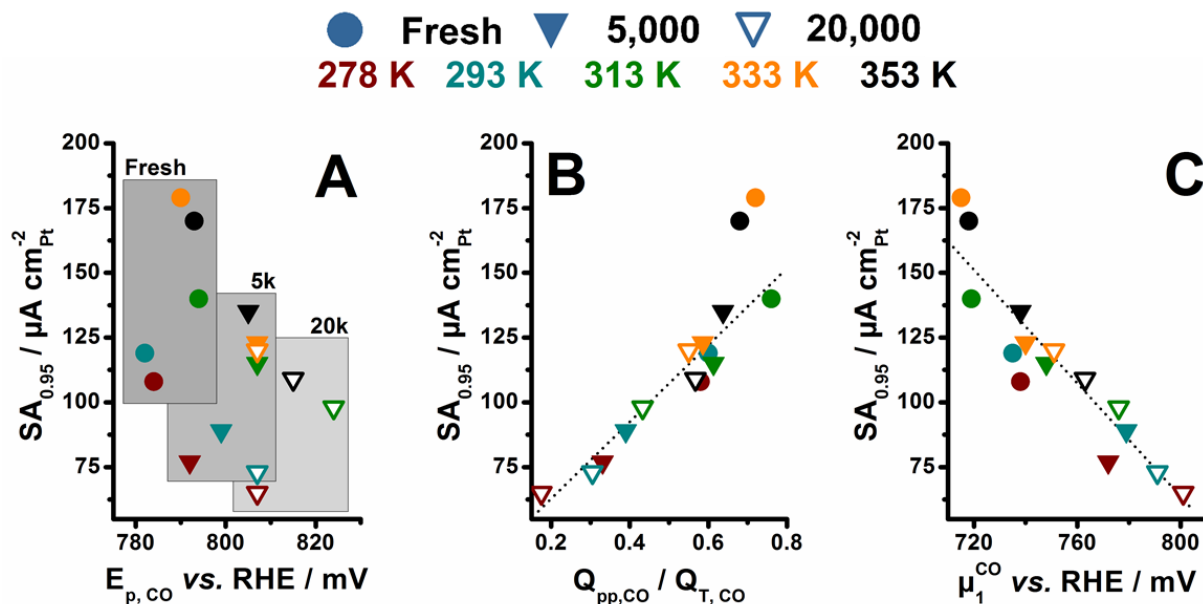


Figure 8. Variation of the specific activity for the ORR measured at $E = 0.95$ V vs. RHE for the porous hollow PtNi/C electrocatalysts synthesized at $T = 278, 293, 313, 333$ and 353 K before (Fresh) and after 5,000 and 20,000 potential cycles with linear profile between $E = 0.6$ V vs. RHE and $E = 1.0$ V vs. RHE in Ar-saturated 0.1 M HClO_4 at $\nu = 0.05$ V s^{-1} and $T = 353$ K vs. (A) the potential of the high-potential

peak in CO_{ads} stripping voltammograms ($E_{p,CO}$); (B) the ratio of the electrical charge under the ‘pre-peak’ ($Q_{pp,CO}$) to the total electrical charge of the CO_{ads} stripping voltammogram ; (C) the first moment of the potential weight of the CO_{ads} stripping (μ_1^{CO}).

The average value of $E_{p,CO}$ shifts from $E_{p,CO} = 789$ mV vs. RHE before ageing to $E_{p,CO} = 802$ mV vs. RHE and $E_{p,CO} = 812$ mV vs. RHE after 5,000 and 20,000 potential cycles, respectively (see **Table S7** and **Figure 8A**). This relaxation is associated with a diminution of the Ni atomic content of the electrocatalysts synthesized at $T = 278$ K and $T = 333$ K as determined from the Scanning Transmission Electron Microscopy – Energy Dispersive X-ray (STEM-EDX) micrographs (see **Figure S7**, **Figure S8** and **Figure S9**). In contrast to AAS analyses, STEM-EDX analyses are performed on single nanoparticles therefore explaining the difference between the values reported in **Figure 8C** and **Figure 1**. The depletion in Ni and the subsequent relaxation of the lattice parameter, predicted by the evolution of $E_{p,CO}$, (*i.e.* disappearance of the Ni-induced lattice parameter contraction) is in agreement with in the literature for PtM electrocatalysts^{44,66–69}.

Table 2. Variation of the microstrain (μ_ϵ) the mean crystallite size (d_{XRD}) for the electrocatalysts synthesized at $T = 278$ and 333 K before (prior to the electrochemical characterisation, *i.e.* ‘Fresh’) and after electrochemical characterisation (‘Fresh + ORR’) and after 5,000 and 20,000 potential cycles between $E = 0.6$ V vs. RHE and $E = 1.0$ V vs. RHE in Ar-saturated 0.1 M HClO₄ at $\nu = 0.05$ V s⁻¹ and $T = 353$ K

		μ_ϵ / % %	d_{XRD} (nm)
$T = 278$ K	Fresh	204	1.5 ± 0.1
	Fresh + ORR	91	3.5 ± 0.2
	5,000	16	4.2 ± 0.3
	20,000	19	3.9 ± 0.3
$T = 333$ K	Fresh	147	3.2 ± 0.1

Fresh + ORR	81	4.0 ± 0.3
5,000	65	5.2 ± 0.7
20,000	44	4.6 ± 0.6

The physical properties of the electrocatalysts synthesized at $T = 298$ K and $T = 333$ K after electrochemical characterisation (*i.e.* CO_{ads} stripping + 6 cycles between $E = 0.2$ V vs. RHE and $E = 1.0$ V vs. RHE at $v = 0.005$ V s⁻¹ in an O₂-saturated 0.1 M HClO₄ electrolyte) but before ageing are provided in **Table 2** as ‘Fresh + ORR’. Interestingly, the electrocatalysts suffer from dramatic structural modification after the initial electrochemical characterisation. For the electrocatalyst synthesized at $T = 278$ K, the microstrain shifts from $\mu_\epsilon = 204$ %% to $\mu_\epsilon = 91$ %% and the crystallite size shifts from $d_{\text{XRD}} = 1.5$ nm to $d_{\text{XRD}} = 3.5$ nm. Castanheira *et al.*⁷⁰ underlined the impact of the intermediate characterizations of a Pt/HSAC electrocatalyst during its ageing in an Ar-saturated electrolyte, focusing on the impact of CO_{ads} stripping and cyclic voltammograms. They showed that the intermediate characterizations intensify the degradation of the Pt/HSAC Electrochemical Surface Area (ECSA)⁷⁰. Here, it appears that the measurement of the ORR activity in O₂-saturated electrolyte also results in modification of the electrocatalysts morphology, likely because of the shift between a reductive atmosphere (CO) and an oxidant atmosphere (O₂). This is further confirmed by the changes of the base and the CO_{ads} stripping voltammograms before and after the ORR (see **Figure S5** and **Figure S6**). A diminution of the contribution of the pre-peak of the CO_{ads} stripping is observed for the electrocatalyst synthesized at $T = 278$ K (while being less visible for the electrocatalyst synthesized at $T = 333$ K) concomitantly with a shift of the $E_{\text{p,CO}}$ toward higher potentials accounting for the diminution of both the density of structural defects and the nickel atomic content in the electrocatalyst.

Simultaneously to the increase of $E_{\text{p,CO}}$, a decrease of ratio of the electrical charges ($Q_{\text{pp,CO}} / Q_{\text{T,CO}}$) is observed during the ageing of the electrocatalysts (see **Figure 8B**) that correspond to

a dramatic decrease of the microstrain (μ_ϵ), as observed for the electrocatalysts synthesized at $T = 278$ K and $T = 333$ K (**Table 2**). This is in agreement with the increase of the average crystallite size (d_{XRD}) determined from the XRD patterns (**Table 2**) resulting from Oswald ripening and/or crystallite migration/coalescence⁷¹. The variation of the PtNi crystallite size evolution in crystallite size observed between 5,000 and 20,000 cycles ($d_{\text{XRD}} = 4.2 \pm 0.3$ nm at 5,000 cycles and $d_{\text{XRD}} = 3.9 \pm 0.3$ nm at 20,000 cycles for the electrocatalyst synthesized at $T = 278$ K) remains in the standard deviation and was thus considered as non-significant. Depending on their initial morphology ('NCs < 2nm' / 'high-microstrain' or 'NCs > 3 nm' / 'low-microstrain'), the NPs suffer different fates. For the electrocatalysts where the density of structural defects mainly results of a high density of grain boundaries (*i.e.* the electrocatalysts synthesized at $T = 278$ K and $T = 293$ K), the increase of the crystallite size results in a dramatic decrease of the grain boundaries density and, therefore, of the microstrain (see **Table 2** for the electrocatalyst synthesized at $T = 278$ K), the ratio of the electrical charges (**Figure 8B**) and the ORR specific activity at $E = 0.95$ V vs. RHE. However, for the electrocatalysts that presented a NCs diameter > 3 nm and an initial $Q_{\text{pp,CO}} / Q_{\text{T,CO}} > 0.68$, *i.e.* the electrocatalysts where the grain boundaries are not the main type of structural defects, the losses in specific activity for the ORR are far less severe (with the exception of the electrocatalyst synthesized at $T = 313$ K, which, according to the evolution of $E_{\text{p,CO}}$ might have lost all its Ni atomic content, see **Table S8**). Consequently, on electrocatalysts where the initial ORR activity is controlled by the density of structural defects, a $d_{\text{XRD}} > 3$ nm (and therefore, stable structural defects) is a pre-requisite to stable ORR activity during ageing. The morphological and structural changes of the electrocatalysts (*i.e.* μ_ϵ , d_{XRD} , a , *etc.*) slow down between 5,000 and 20,000 potential cycles (see **Figure 8**). Therefore, (i) most of the electrocatalysts degradation occurs during the 5,000 first cycles between $E = 0.6$ V and $E = 1.0$ V vs. RHE at $T = 353$ K and (ii) the losses in the density of structural defects which occurs between 5,000 and 20,000 cycles do not impact the NCs size.

The density of grain boundaries remains identical and other types of structural defects are likely impacted (such as the concavity of the internal surface during the collapsing of the nanoparticles, see **Figure 7**).

Combining high-resolution TEM and electrochemistry, Dubau *et al.*⁴⁴ recently reported that the ageing of porous hollow and solid PtNi/C NPs was primarily driven by the nickel depletion. The electrocatalysts discussed by Dubau *et al.*⁴⁴ presented a $d_{\text{XRD}} > 3 \text{ nm}$ ⁴¹, therefore supporting the results discussed in this manuscript, *i.e.* porous hollow and solid PtNi/C structures with a $d_{\text{XRD}} > 3 \text{ nm}$ do not suffer dramatic losses in structural defects density during their ageing. Most of their ORR activity losses are resulting from the dissolution of the Ni atoms from the PtNi shell (see **Figure 8**, **Figure S7**, **Figure S8**, **Figure S9** and Ref.⁴⁴).

Figure 8C shows that the first moment of the potential weight of the electrocatalysts discussed in this work (μ_1^{CO}) is directly correlated to the changes of ORR specific activity at $E = 0.95 \text{ V vs. RHE}$. This nicely confirms that the losses in ORR specific activity for the ORR are induced by the combination of the relaxation of the lattice parameter, *i.e.* the diminution of the Ni-induced lattice contraction, and a decrease of the density of structural defects.

Conclusion

In this paper, we present a set of parameters extracted from CO_{ads} stripping voltammograms, which allow an accurate description of the porous hollow PtNi/C electrocatalysts structural properties : (i) the ratio of the electrical charges of the CO_{ads} stripping ($Q_{pp,CO} / Q_{T,CO}$) provides insights on the density of structural defects on the electrocatalyst surface (for an electrocatalyst with a low Ni content, close crystallite size and Pt-rich surface, such as the porous hollow PtNi/C nanoparticles); (ii) the position of the high-potential peak of the CO_{ads} stripping ($E_{p,CO}$) provides insights on the Ni content of the electrocatalyst and (iii) the first moment of the potential weight summarizes all the contributions of the structural defects and of the Ni-induced contraction of the lattice parameter, therefore showing that these two contributions fully describe the activity of porous hollow PtNi/C nanoparticles in the conditions discussed in this manuscript. Using these tools, we investigated the electrochemical stability of the porous hollow PtNi/C nanoparticles and observed that the losses in ORR specific activity were induced by a combination of losses in Ni-induced lattice contraction and an increase of the crystallite size, resulting in a diminution of the density of grain boundaries. The electrocatalysts that presented an initial nanocrystallite size $d_{XRD} > 3$ nm presented a higher stability than the one with the smallest nanocrystallites. We also noticed that the intermediate characterisations in O₂-saturated electrolyte resulted in much more aggravated changes of the electrocatalyst morphology and ORR activity than simple cyclic voltammograms in Ar-saturated electrolyte.

Supporting Information

The materials and methods, the physico-chemical properties (energy dispersive X-ray maps, X-ray diffraction patterns) and the electrocatalytic activity for the ORR of the different electrocatalysts before and after an accelerated stress test composed of 20,000 potential cycles, the transmission electron micrographs of the fresh PtNi/C electrocatalysts, the evolution of physico-chemical and electrochemical parameters as a function of the potential of the first peak of the CO_{ads} stripping and the evolution of the base and of the CO_{ads} stripping voltammograms before and after electrochemical characterization are provided in Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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