

Disentangling the Degradation Pathways of Highly Defective PtNi/C Nanostructures – An Operando Wide and Small Angle X-Ray Scattering Study

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ABSTRACT

Hollow bimetallic nanostructures are perfect systems to unravel the ageing mechanisms of both Pt-based alloys and highly defective nanostructures used in proton-exchange membrane fuel cells (PEMFC) cathodes, since the mobility of their surface and bulk atoms leads to detectable chemical (i.e. Ni dissolution) and physical (i.e. decrease of the density of structural defects, collapse of the nanostructure, etc.) changes. In this study, we precisely and dynamically monitored these physicochemical changes on porous hollow PtNi/C nanoparticles during an ageing procedure composed of 5,000 potential cycles with linear ramp between 0.6 and 1.0 or 1.1 V vs. RHE by using (i) synchrotron operando wide and small angle X-ray scattering (WAXS and SAXS), (ii) scanning transmission electron microscopy (STEM) in combination with X-ray energy dispersive spectroscopy (X-EDS) and (iii) electrochemical measurements. The synchrotron operando WAXS and SAXS results dynamically correlated the structural changes of the hollow NPs both at the atomic (Ni depletion, lattice parameter relaxation, variation in the density of structural defects, etc.) and nanometric (restructuring of the nanoparticles/collapse of the hollow nanostructure) level. They revealed that the collapse of the hollow nanostructure was always accompanied by a significant loss of the Ni content. The 0.6 – 1.1 V vs. RHE ageing protocol resulted in a more severe depreciation of the ORR associated with a larger restructuring

of the nanoparticles than the 0.6 – 1.0 V vs. RHE ageing protocol, thus providing evidence that a critical potential exists for the stability of highly defective nanoalloys.

KEYWORDS

Oxygen Reduction Reaction, Porous-Hollow PtNi/C Nanoparticles, Structural Defects, Durability, Operando Wide and Small Angle X-Ray Scattering.

TEXT

Introduction

Two equally important properties of electrocatalysts are their initial activity and their long-term stability after several thousand hours of operation. In the case of the oxygen reduction reaction (ORR), a wide variety of sophisticated Pt-based nanostructures with high initial electrocatalytic activity has been synthesized: PtNi octahedra ^{1,2}, PtNi nanoframes ³, PtNi porous nanoparticles (NPs) ^{4,5}, and porous hollow PtNi NPs ^{6–15}. However, accelerated stress tests (AST e.g. Ref. ^{2,3,16–18}) mimicking real-life proton exchange membrane fuel cell (PEMFC) conditions show that many of these out-of-equilibrium nanostructures are metastable and deactivate extremely fast. This considerably reduces their practical interest as electrocatalysts in low-pH or high-potential harsh environments. In PEMFC cathodes, the main degradation mechanism of PtM nanocrystallites (M being a 3d transition metal) is the continuous dissolution of M into the highly oxidizing environment of the cathode ^{19,20}. This process is driven by the fast corrosion of M into M^{Z+} at the surface of the NPs, and results in the decrease of strain and ligand effects ^{19–24}. In parallel, PtM nanocrystallites undergo classical degradation mechanisms, i.e.

dissolution/redeposition of $\text{Pt}^{\text{Z}+}$ ions by electrochemical Ostwald ripening, as well as crystallite migration, agglomeration and coalescence^{25–28}.

Among the many nanocatalysts displaying high ORR activity, porous hollow PtNi/C NPs are particularly interesting. They exhibit 9-fold enhancement in specific activity (SA) and 6-fold enhancement in mass activity (MA) compared to solid Pt/C⁷. This enhancement has been associated to (i) their open-porous architecture and the presence of an inner cavity, i.e. the contribution to the ORR of both the inner and the outer surface, along with the porosity of the walls; (ii) the presence of ca. 10 – 15 at. % of Ni in the NPs shell, thus inducing the contraction of the lattice parameter and the resulting modification of the Pt electronic structure (i.e. strain effect^{29,30}) and (iii) a positive contribution of structural defects/polycrystallinity (grain boundaries^{8,9,31} and highly coordinated atoms^{10,32,33} manifesting experimentally through high microstrain values, the microstrain, μ_{ϵ} , being the variation of the lattice parameter, $a_{\text{Pt-Pt}}$, around its average value, i.e. μ_{ϵ} is proportional to $\Delta a_{\text{Pt-Pt}}/a_{\text{Pt-Pt}}$ ^{10,31,34,35}). Because of their peculiar morphology, the porous hollow PtNi/C NPs provide insights onto the activity and stability of both (i) alloyed and (ii) defect-rich nanostructures.

The beneficial effect of the structural defects onto the ORR activity arises from the unique character of each active site in a highly defective nanostructure. In highly ordered nanostructures (e.g. octahedra¹⁶), the surrounding of each platinum active site is similar (i.e. generalized coordination number³², same distance with nearest neighbouring atoms¹⁰, no surface distortion, etc.) and, therefore, the activity of each platinum active site are approximately the same. By opposition, highly disordered nanostructures (e.g. porous hollow PtNi/C NPs⁷, PtNi sponges³¹,

Pt nanowires ³⁶, etc.) present extremely different surroundings for their active sites. As recently evidenced by Calle-Vallejo et al. ³² and Le Bacq et al. ¹⁰, the activity of a given active site is highly dependent of (i) its generalized coordination number (i.e. the coordination number calculated with consideration for the first and second neighbours ³²) and (ii) the distance with their first neighbours. These parameters influence the active site oxophilicity and, thus, reactivity. An optimal defect-rich electrocatalyst then presents a non-negligible proportion of active sites with an optimal oxophilicity (i.e. with an optimal generalized coordination number and distances with the first neighbours) and, thus, a tremendous activity for the ORR.

The stability of porous hollow PtNi/C nanostructures during an ageing test simulating potential variations at a PEMFC cathode was recently investigated by Dubau et al. ¹⁵ and Asset et al. ¹¹. Results showed that, in the 0.6 – 1.0 V vs. RHE, window often used to investigate the stability of an electrocatalyst, the dissolution of Ni atoms is mostly responsible for the observed drop of ORR activity. In addition, the combined beneficial effect of structural defects and hollow nanostructure were partially maintained even after 20,000 potential cycles. However, the kinetics of restructuring and the effect of the potential range investigated remains poorly understood. Recently, Li et al. ³⁷ investigated the ageing of complex, nanoporous nanostructures (i.e. highly defective) in liquid electrolyte by IL-TEM. They performed up to 10,000 cycles between 0.6 and 1.0 to 1.2 V vs. the reversible hydrogen electrode (RHE) and evidenced that the increase of the upper potential limit resulted in (i) a more important **restructuring** of the nanostructure (i.e. losses of porosities, etc.) and (ii) a higher dissolution of the non-noble element (e.g. Ni). In this manuscript, we provide further insights into the degradation mechanisms of porous hollow PtNi/C NPs (and, **as such**, of the degradation mechanisms of highly defective nanostructures) using operando wide and small angle X-ray scattering (WAXS and SAXS). We used two

different AST conditions consisting of potential cycling in an electrochemical flow cell (Ar-saturated 0.1 M HClO₄ at T = 353 ± 1 K, v = 0.050 V s⁻¹, 5,000 potential cycles) between 0.6 and 1.0 V vs. RHE or between 0.6 and 1.1 V vs. RHE. In the rest of the paper, we refer to the former and latter conditions as mild and harsh AST, respectively. To correlate structure, chemistry and electrocatalytic properties, the fresh and aged porous hollow PtNi/C nanoparticles were analysed using electrochemistry (rotating disk electrode – RDE), X-ray energy dispersive spectroscopy (X-EDS) elemental maps and high-resolution transmission electron microscopy (HR-TEM), thus providing a global picture of the degradation mechanisms.

Results & Discussion

Figure 1 presents the *ex-situ* electrocatalytic properties of the porous hollow PtNi/C nanostructures before and after the mild and harsh ageing tests (more detailed graphs of the electrochemical measurements are provided in **Figure S2**). The values of the corresponding physicochemical and electrochemical properties (extracted from X-ray diffraction, TEM, CO_{ads} stripping and linear sweep voltammetry in O₂ saturated 0.1 M HClO₄) of the porous hollow PtNi/C NPs are provided in **Table S1**.

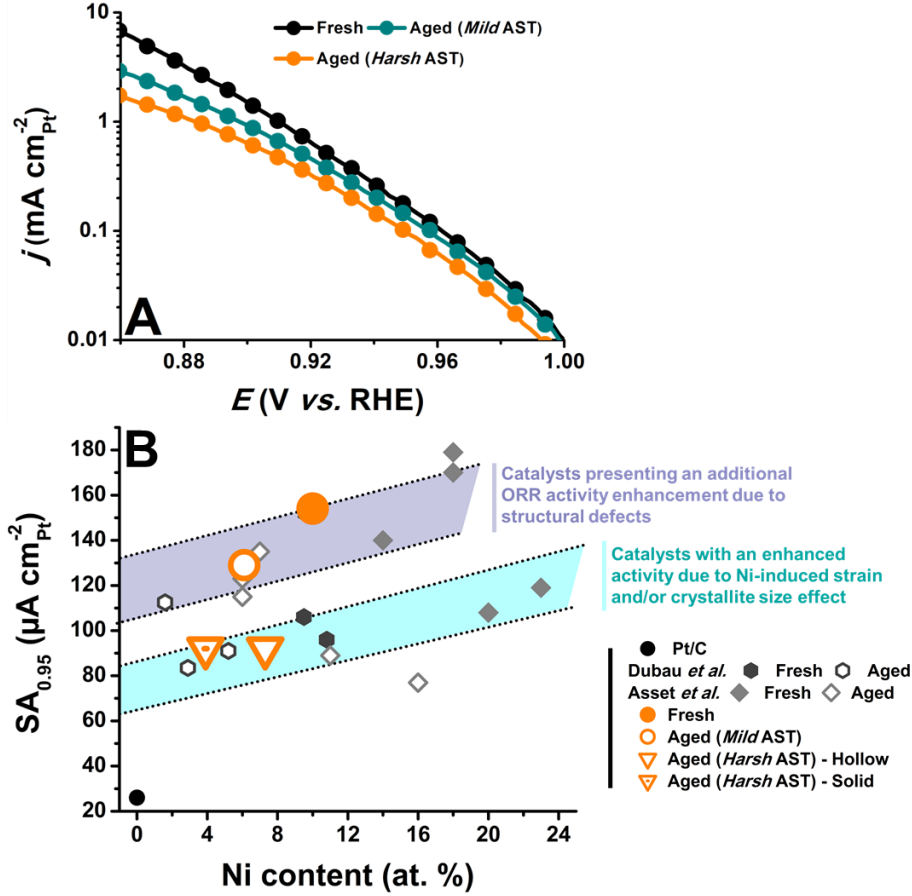


Figure 1. Electrocatalytic properties of the porous hollow PtNi/C electrocatalyst before and after *ex-situ* mild and harsh AST. **(A)** Linear sweep voltammograms in O₂-saturated 0.1 M HClO₄ in Tafel representation, corrected from the oxygen diffusion in solution and the Ohmic drop ($\nu = 0.005 \text{ V s}^{-1}$, $\omega = 1600 \text{ rpm}$). **(B)** Relationship between the specific activity ($SA_{0.95}$) for the ORR measured at $E = 0.95 \text{ V vs. RHE}$ and the Ni content for the fresh and aged porous hollow PtNi/C electrocatalysts discussed in this work and for references samples published in Dubau *et al.*¹⁵ and Asset *et al.*¹¹. The catalysts from Ref.^{11,15} presented were aged up to 5,000 potential cycles (in Ar-saturated 0.1 M HClO₄ between 0.6 and 1.0 V vs. RHE or 1.1 V vs. RHE, $\nu = 0.05 \text{ V s}^{-1}$ and $T = 353 \pm 1 \text{ K}$).

Figure 1A shows that the loss of ORR activity upon ageing is much more severe after the *harsh* than the *mild* ageing, as assessed by the lower values of specific ($SA_{0.95}$) and mass ($MA_{0.95}$) activities for the ORR, and specific surface area measured by CO_{ads} stripping coulometry ($S_{Pt,CO}$, see **Table S1** and **Figure S2**). The extracted values of the specific activity for the ORR measured at $E = 0.95$ V vs. RHE ($SA_{0.95}$) are represented as a function of the Ni content determined by STEM-X-EDS in **Figure 1B**. For the sake of generalizing our findings, **Figure 1B** also gathers data collected on (i) porous hollow PtNi/C electrocatalysts that underwent heat treatment under various atmosphere (N_2 , H_2 , air and without heat treatment) before and after a *mild* ageing test ('fresh' and 'aged', respectively) ¹⁵ and on (ii) porous hollow PtNi/C electrocatalysts that were synthesized at different temperatures ($T = 278, 293, 313, 333$ and 353 K) before and after a *mild* ageing test ('fresh' and 'aged', respectively) ¹¹. Those results are extracted from:

- (i) the works of Dubau *et al.* ^{8,15} where porous hollow PtNi/C NPs were heat-treated and their physicochemical (*i.e.* polycrystallinity, density of structural defects, Ni content) and electrochemical properties were investigated. Reducing the polycrystallinity of the NPs dramatically reduced their activity, hence underlining the essential role played by the structural defects.
- (ii) the works of Asset *et al.* ^{9,11}, where the synthesis temperature effect onto the morphology, activity and stability of the porous hollow PtNi/C NPs was investigated. It was observed that increasing the synthesis temperature resulted in an increase of the crystallite size, but also in a higher specific activity for the ORR. Hence, if the grain boundaries (and the resulting microstrain ^{34,35}) are essential to obtain highly active

structural defects, other structural defects (*e.g.* nanovoids, cavities and overcoordinated atoms) are also contributing to the ORR activity.

The catalysts can be sorted into two distinct groups: (i) those located in the purple region of **Figure 1B** feature a highly defective nanostructure where the structural defects are highly beneficial for the ORR and (ii) those located in the blue region of **Figure 1B** are either solid nanostructures, almost monocrystalline with a lower ORR activity ⁸ or polycrystalline structures where the structural defects are not beneficial for the ORR ^{9,11}. As already documented by Dubau *et al.* ¹⁵, porous hollow PtNi/C NPs remain in the defective domain in *mild* AST conditions. In contrast, the same catalysts shift from the ‘defective’ (*i.e.* the purple region of **Figure 1B**) to the ‘non-defective’ (*i.e.* the blue region) group after *harsh* AST conditions.

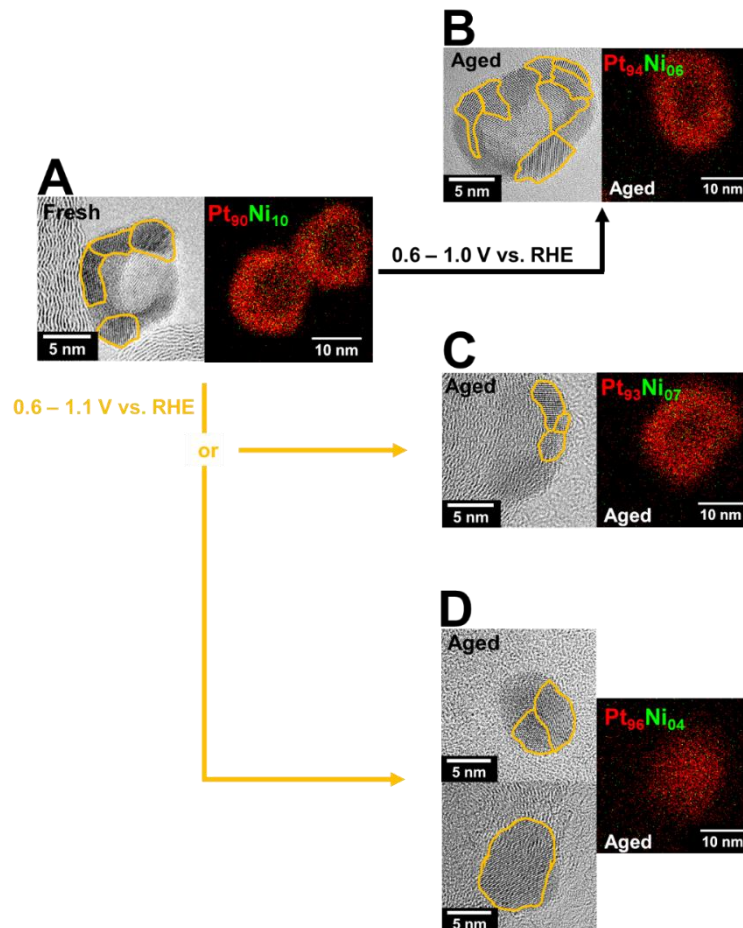


Figure 2. Initial and *post mortem* STEM/X-EDS elemental maps and HR-TEM of the porous hollow PtNi/C electrocatalysts scrapped from the gas diffusion electrode analysed in this work (A) before and after the (B) *mild* and (C - D) *harsh* ASTs (see **Table S1** for the error bars onto the Ni content). The yellow lines in HR-TEM micrographs highlight grain boundaries.

The structural stability of the catalyst during the *mild* AST is confirmed by HR-TEM micrographs presented in **Figure 2B**, which show that the NPs remained hollow and polycrystalline with minimal deviation of the inner (d_{in}) and outer (d_{ext}) diameters compared to the fresh catalyst (see **Table S1**). The STEM/X-EDS elemental maps however show that the Ni

content dropped during the AST. After the *harsh* AST, two distinct types of nanostructures, namely hollow (see **Figure 2C**) and collapsed PtNi/C NPs (see **Figure 2D**), are observed both in STEM-X-EDS elemental maps and in lower resolution TEM images (see **Figure S3**). Presumably, the existence of two types of nanostructures after *harsh* ageing originates from the poly-dispersity of the fresh catalyst, with smaller NPs collapsing and larger NPs remaining hollow in agreement with our former findings³⁸. The HR-TEM micrographs indicate that, after the *harsh* AST, the hollow particles remained polycrystalline while the collapsed particles partially became single crystals (reduction of the density of structural defects, see **Figure 2D**). Moreover, STEM/X-EDS measurements indicate that the two types of aged NPs differ also by their Ni-content. **Figure 2** clearly shows that, while collapsed NPs are strongly depleted in Ni (3.9 ± 0.9 at. % Ni compared to 9.8 ± 0.8 at. % before ageing), hollow NPs remain Ni-rich (7.3 ± 0.6 at. % Ni and 6.3 ± 0.7 at. % Ni after *harsh* and *mild* AST, respectively). In addition to a lower density of grains boundaries (*i.e.* losses in structural defects) and to the lower Ni content, the very disappearance of the inner surface of the collapsed particles contributes to further reduce their electrocatalytic activity.

Time-resolved SAXS/WAXS measurements enabled the monitoring of the ageing of the NPs in *operando* conditions, using the custom-made cell presented in **Figure S1** (the variations of the electrochemical signal throughout the *mild* and *harsh* ageing are provided in **Figure S4**). Care was taken to avoid beam damage by minimizing the duration of exposure of the carbon coated backing (CCB) to the X-rays (*i.e.* the exposure length was $t = 10$ s every $t = 20$ min). The position of the Bragg peaks in the WAXS patterns (see **Figure S5**) provided the lattice parameter ($a_{\text{Pt-Pt}}$), indicative of the degree of Pt and Ni alloying. Moreover, the Rietveld refinement of the

WAXS patterns provided an average value for both the crystallite size (d_{XRD}) and the microstrain (μ_e , *i.e.* the shift of the lattice parameter from its average value, proportional to $\Delta a_{\text{Pt-Pt}}/a_{\text{Pt-Pt}}$). Complementary to WAXS, the SAXS patterns (see **Figure S6** and **Figure S7**) were fitted with a model fully described in the Supporting Information assuming polydispersed hollow NPs homogeneously distributed onto a porous material. The structural parameters derived from the analysis are (i) the inner (d_{in}) and outer (d_{ext}) average diameters of the NPs, (ii) the platinum specific surface and (iii) the shape parameter k of the gamma distribution (*i.e.* a two-parameter distribution of the NPs inner diameter defined by the shape parameter k and the mean NPs inner diameter). A high k value (*e.g.* 50) corresponds to a narrow Gaussian distribution of the inner diameters of the NPs around the average value; in that case, all the NPs are hollow and have similar inner diameters. By contrast, for values of k close to 1, the size distribution is skewed towards particles with vanishingly small inner diameters (see **Figure S9**), *i.e.* towards collapsed NPs. From the averages values of d_{in} , d_{ext} and the value of k , a geometric calculation allowed estimating the specific surface area of the NPs (S_{Pt}). The time evolution of all the structural parameters derived from the *in situ* SAXS/WAXS patterns analysis/refinement in both *mild* and *harsh* ageing conditions is gathered in **Figure 3**. The experimentally-challenging conditions of the *operando* measurements (*i.e.* variation of the cell thickness due to the electrolyte flow and formation H_2 bubbles at the counter-electrode, poly-dispersity of the electrocatalyst, etc.) led to discrepancies in the Rietveld analysis of the WAXS patterns. For example, (i) the initial lattice parameter and microstrain are different for the *mild* and *harsh* ageing (see **Figure S7**) and (ii) the crystallite size estimated by Rietveld refinement ($d_{\text{XRD}} \approx 5.2 - 6.4$ nm at $t = 0$ min, see **Figure S7**) was much larger than the shell thickness of the NPs determined from TEM (volume-averaged $e = 2.4$ nm) or by analysis of the *operando* SAXS patterns (*ca.* 2.3 – 3.2 nm). The

CCBs being made of the same ink and electrocatalyst, this likely results from (i) slight changes in the distance between the CCBs and the detector (although the cell itself was replaced at the same position, the CCBs might have moved inside the cell) and (ii) the difference between the CCBs thicknesses and the calibration sample (CeO_2) thickness. The samples thickness impacts the width of the Bragg peaks (*i.e.* a parallel beam was used in these experiments, with a beam size smaller than the sample size) and, as such, the microstrain and crystallite size absolute values. Thus, only the normalized parameters are presented in **Figure 3A to 3C**. In addition, the experimental conditions resulted in a non-negligible noise; thus, a statistical analysis was carried out to determine the trend followed by the parameters during the *mild* and *harsh* ageing (see Supporting Information). Three different models were chosen: (i) a plateau, (ii) a linear dependence and (iii) a linear dependence followed by a plateau. A statistical χ^2 test (see Supporting Information and **Figure S13 to S19**) was then carried out to assess the most relevant model to describe each parameter, during the *mild* and *harsh* ageing. In short, the p -value was calculated for each model and the selected model was the one with the lowest number of parameters and a p -value ≤ 0.9 (see Supporting Information). A few exceptions were made to this selection, *i.e.*

- (i) a linear dependence was chosen instead of a plateau for the evolution of crystallite size ratio during the harsh ageing (see **Figure 3B**), as the plateau is less accurate (higher p -value) and the experimental points, in average, increase throughout the experiment (see **Figure S14**);
- (ii) a linear dependence + plateau was chosen instead of a plateau for the evolution of the platinum specific surface and of the shape parameter k during the harsh ageing (see **Figure 3E and 3F**) as it is the most accurate model (lowest p -value) and is consistent

with the observations of **Figure 1** and **Figure 2** (*i.e.* the nanostructure is not stable during the *harsh* ageing).

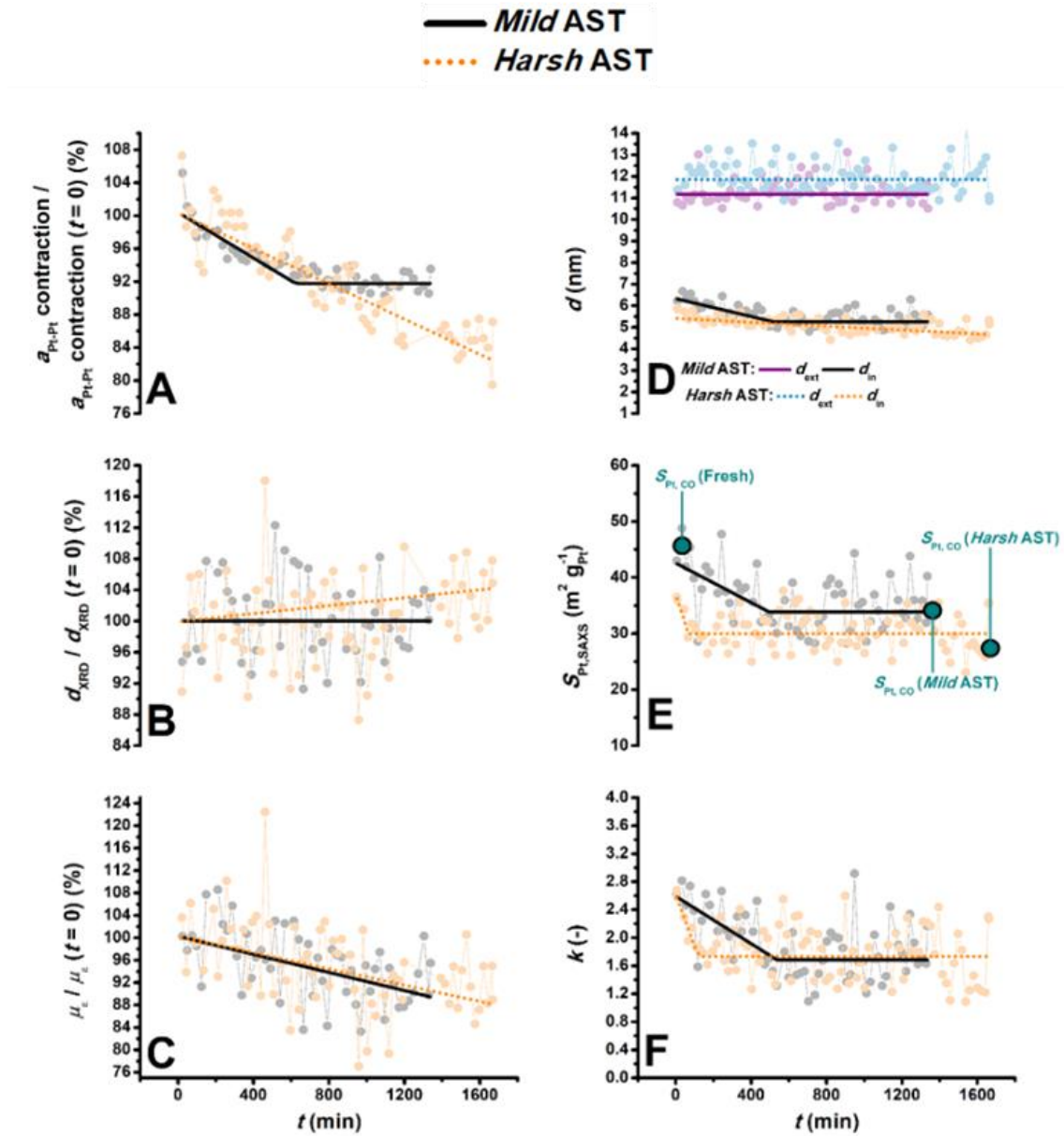


Figure 3. Structural parameters extracted from Rietveld refinement of *operando* (A, B, C) WAXS and (D, E, F) SAXS patterns measured on the porous hollow PtNi/C electrocatalyst during the *mild* and *harsh* ageing ($v = 0.050 \text{ V s}^{-1}$ and $T = 353 \pm 1 \text{ K}$). (A) Normalized variation

of the degree of contraction of the lattice parameter $a_{\text{Pt-Pt}}$ with respect to the Pt lattice parameter, **(B)** normalized variation of the average crystallite size, d_{XRD} , **(C)** normalized variation of the microstrain value, μ_{ε} , **(D)** variation of the external and inner diameters of the NPs, **(E)** variation of the specific surface area of the electrocatalyst (in dark-cyan, the Pt specific surface area determined from the *ex-situ* CO_{ads} stripping measurements) and **(F)** variation of the dimensionless shape parameter k (see **Figure S9**). Since the number of potential cycles was kept constant, the *harsh* ageing was 20% longer than the *mild* ageing.

The main structural changes detected *operando* by SAXS/WAXS measurements are the following: (i) the lattice parameter contraction (with respect to the lattice parameter of Pt/C, *i.e.* $a_{\text{Pt-Pt}} = 0.393$ nm) decreased by 8 % and 18 % in *mild* and *harsh* AST conditions, respectively (see **Figure 3A**); (ii) the crystallite size slightly increased in *harsh* AST conditions, while it remained unchanged in *mild* AST conditions (see **Figure 3B**); (iii) the microstrain values decreased by 11 % in *mild* AST conditions and by 12 % in *harsh* AST conditions (see **Figure 3C**). The relative constancy with time of the microstrain and of the crystallite size values in *mild* ageing conditions confirms that the loss of Ni atoms (and the associated relaxation of the lattice parameter, see **Figure 3A**) is one of the main reason for the ORR catalytic activity losses^{11,15}. This situation contrasts with ageing in *harsh* conditions, where the more pronounced relaxation of the lattice parameter occurs concomitantly with an increase of the crystallite size (see **Figure 3B**) and a slightly higher decrease in the density of structural defects (*i.e.* the decrease of the microstrain, μ_{ε} , see **Figure 3C**), in adequation with the findings of Li *et al.*³⁷. Interestingly, the Ni losses were not proportional to the normalized variations of the lattice parameter: for instance, a 10% decrease of the lattice parameter contraction was observed during the *mild* AST, while 40

at. % of the Ni atoms were lost during the *harsh* AST (see **Figure 2B**). This means that a non-negligible part of the lattice contraction, *i.e.* the strain, in the fresh electrocatalyst is not due to the alloying of Pt with Ni and comes from the structural defects (*e.g.* missing atoms, nanovoids, *etc.*).

Before analysing the SAXS results, it is useful to ascertain their robustness by cross-correlating them with independent characterization data. For that purpose, the specific surface area of the NPs ($S_{\text{Pt,SAXS}}$, see **Figure 3E**) was determined from structural parameters d_{in} , d_{ext} and k extracted from the SAXS patterns (see **Figure 3D** and **3F**). The same quantity was determined using CO_{ads} stripping measurements before and after *mild* and *harsh* ageing ($S_{\text{Pt,CO}}$, see dark-cyan points overlaid to **Figure 3E**). Although minor discrepancies are noticed between these two techniques, most likely in reason of experimental noise or because of the slightly different experimental conditions ^{11,39} (namely rotating disk electrode *vs.* the gas-diffusion layer configuration imposed by the *in situ* measurements), the similar experimental trend provides strong support to the robustness of our analysis. The SAXS data point to very different ageing kinetics in *mild* and *harsh* AST conditions. In *harsh* AST conditions, the NPs undergo first a fast process that rapidly brings their specific surface area close to their final value (most likely NPs partial collapse, which alone accounts for a *ca.* $15 \text{ m}^2 \text{ gPt}^{-1}$ drop in $S_{\text{Pt,CO}}$ and $S_{\text{Pt,SAXS}}$ see **Figure 2D**). In *mild* conditions, no collapse of the hollow nanostructure is observed (see **Figure 2B**), and the structural evolution takes place over the same timescale as Ni depletion. During the first 500 minutes, the shell of the hollow NPs progressively thickens, as assessed by the decrease of d_{in} . The observed decrease of k points to a statistical size distribution that is increasingly skewed towards small NP sizes. Interestingly, k , $S_{\text{Pt,SAXS}}$ and $a_{\text{Pt-Pt}}$ stabilize for $t > 500 \text{ s}$, strongly

suggesting a slowing down of the degradation kinetics. Note that, according to the observations of Asset *et al.*¹¹, the NPs undergoing the *mild* ageing conditions ultimately partially collapse after 20,000 potential cycles. This suggests that the degradation mechanisms are similar at 1.0 V and 1.1 V vs. RHE but that its kinetics is slower at lower electrode potential, **in accordance with the decrease in the driving force.** This likely resulted from:

- (i) the so-called place exchange mechanism (*i.e.* at $E > 1.0$ V vs. RHE, the oxygen diffuses in the first Pt monolayers of the NPs, thus destabilizing the Pt atoms and resulting in their dissolution^{40–43})
- (ii) the reorganization of the nanostructure. Like monocrystalline Pt nanoparticles of *ca.* 2 – 3 nm^{25–28}, the porous hollow PtNi/C NP (*i.e.* a polycrystalline shell with an active inner and external surface) is an *out-of-equilibrium* structure with a high surface energy. During ageing, the nanostructure tends to diminish its surface energy by restructuring itself, *i.e.* by crystallite growth and re-orientation, *etc.* This phenomenon is accelerated by the higher potential limit during the *harsh* ageing, which facilitate the Pt and Ni atoms dissolution/Pt^{Z+} redeposition.

Conclusions

In summary, this manuscript provides *operando* insights into the degradation mechanism/kinetics of porous hollow PtNi/C NPs in simulated PEMFC cathode conditions. In a more general perspective, our study describes a methodology to monitor structural changes in *operando* conditions of all types of bimetallic Pt-based/C nanocatalysts for the ORR. We have demonstrated that the upper potential limit of the AST ($E = 1.0$ V vs. 1.1 V vs. RHE) largely impacts the extent of degradation of bimetallic PtNi/C NPs. The *mild* ageing conditions (upper

potential limit = 1.0 V *vs.* RHE) cause depletion in Ni content and limited losses of structural defects density. The *harsh* ageing conditions (upper potential limit = 1.1 V *vs.* RHE) result in a more severe degradation of the nanostructure as revealed by the substantial Ni content drop, the increase of the crystallite size and a more severe diminution of the structural defects density resulting ultimately in higher ORR specific and mass activity losses. Thus, studying the stability of electrocatalysts out of the 0.6 – 1.0 V *vs.* RHE potential range (*i.e.* the conventional load-cycle protocol) appears to be fundamental. Indeed, increasing the upper potential greatly facilitates the NPs restructuring. Moreover, if the load-cycle protocol is adequately mimicking the operating range of a PEMFC cathode, it does not consider potential increases observed during start and stop events (where the potential can increase up to *ca.* 1.5 V *vs.* RHE), essential in the prospect of designing PEMFC for vehicle applications. This manuscript also underlines the interest of using wide and small angle X-ray scattering as tools to monitor electrochemical devices *operando* and gain reliable insights on the durability trends close to the operating conditions of the applications. WAXS provides clear and direct insights into the variation of the nanostructure at an atomic level while SAXS unveils the morphological changes and the intermediate structures formed during the ageing process. In combination, these methods provide a global picture of the structural changes the bimetallic nanoparticles.

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Notes

The authors declare no competing financial interest.

ASSOCIATED CONTENT

The supporting information contains the materials and methods (including the scheme of the *operando* cell), a table summarizing the physico-chemical properties of the electrocatalysts, details onto the electrochemical measurments, the transmission electron microscopy micrographs of the electrocatalysts, the WAXS & SAXS patterns, the technical and calculation details of the SAXS fitting and the statistical analysis of the data obtained by WAXS and SAXS.

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