

Supporting Information

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

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Materials & Methods

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Materials and Methods

Reference Electrocatalysts

A 20 wt. % Pt/Vulcan XC72 catalyst was purchased from E-TEK and used as reference material without any treatment. The number-averaged Pt nanoparticle size was 2.9 ± 0.6 nm. A solid PtNi/C catalyst was prepared by a modified polyol method according to the protocol described in Ref. ¹ under the name ‘A-PtNi/C’.

Synthesis of the porous hollow PtNi/C nanoparticles

The porous hollow PtNi/C NPs were synthesized by a ‘one-pot’ method extensively described by our group in Ref. ¹⁻⁴ and others. As in Ref. ⁴, the electrocatalysts were synthesized at $T = 278, 393, 313, 333$ and 353 K, with a ratio between the Pt precursor ($\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$ – Alfa Aesar Premion 99.995% metal basis) and the Ni precursor (NiCl_2 – Alfa Aesar anhydrous 99.99% metal basis) of 1 : 3.

X-Ray Diffraction

The XRD patterns of the catalysts before ageing were determined with a PANalytical X’Pert Pro MPD vertical goniometer/diffractometer with a diffracted-beam monochromator ($\text{CuK}\alpha$ radiation, $\lambda = 0.15406$ nm) operating at 45 kV and 40 mA, the technical details being provided in Ref. ⁴.

Synchrotron X-Ray Diffraction and Rietveld Analysis

X-ray Diffraction (XRD) measurements were performed at ID31 beamline of the European Synchrotron Radiation facility (ESRF) in Grenoble, France to determine the microstrain of the electrocatalysts before ageing and their structural properties after ageing. The high-energy X-ray radiation (60 keV or $0.207 \text{ \AA}$) was focused on a Kapton capillary of $d = 1$ mm, containing the sample powder for the electrocatalysts before ageing. The electrocatalysts after ageing and electrochemical analysis (‘Fresh + ORR’) were

characterised on the glassy carbon electrode. The electrode was positioned parallel to the beam and adjusted so that the beam only passed through the electrocatalyst deposit. The scattered signal was collected with Dectris Pilatus CdTe 2M detector positioned 300 mm behind the sample. The size of the beam at the sample position was $4\text{ }\mu\text{m} \times 30\text{ }\mu\text{m}$ (vertical $\times$ horizontal). The energy, the detector distance and the tilts were calibrated using a standard CeO_2 powder. The 2D diffraction patterns were reduced to the presented 1D curves using pyFAI software package. The Rietveld refinements were carried using the Fullprof software, using the $Fm-3m$ structure of a cubic closed-packed metal ($a \approx 3.9\text{ }\text{\AA}$). The instrumental resolution function was determined by the refinement of the CeO_2 standard sample. The Thomson-Cox-Hastings profile function was adopted with possibility for uniaxial anisotropic broadening from size origin.

Transmission Electron Microscopy and STEM-EDX mapping

The particle size distribution was determined from TEM images obtained at low/medium magnification ($\times 80000/150000$) with a JEOL 2010 transmission electron microscope operating at 200 kV with a point-to-point resolution of 0.19 nm. To consider the irregular shape of the NPs, the inner and external Feret diameter were determined, according to Ref. ^{2,4}. The X-EDS spectra were recorded on individual nanoparticles by scanning the beam in a square region adjusted to the particle size. The quantitative analyses were performed on Pt L and Ni K lines using the K-factor provided by the JEOL software.

Atomic Absorption Spectrometry

The Ni and Pt content of each electrocatalyst were established by AAS (PinAACLE 900F, PerkinElmer) according to the procedure described in Ref. ⁴

Electrochemical Measurements in Liquid Electrolyte

The preparation of the electrochemical glassware, of the electrocatalyst ink, the electrochemical cell and the parameters used for characterisation of the electrocatalysts activity for the ORR, the CO_{ads} stripping and the reactivity in Ar-saturated electrolyte have been standardized by our group and are extensively

discussed in Ref. ¹⁻⁴. All the experiments were performed in 0.1 M HClO₄, with a Pt loading onto the working electrode surface of 20 μg cm⁻². The accelerated stress test of the electrocatalysts involved 20,000 potential cycles between 0.60 and 1 V vs. RHE at a potential sweep rate of $\nu = 0.050 \text{ V s}^{-1}$ at $T = 353 \text{ K}$. The electrolyte was replaced with fresh solution after 5,000 and 20,000 cycles to perform CO_{ads} stripping and ORR measurements.

Table S1. Physical properties of the porous hollow PtNi/C nanoparticles synthesized at $T = 278, 293, 313, 333$ and 353 K. The platinum wt. % loading and the nickel atomic content were determined by the Atomic Absorption Spectroscopy (AAS). The external (d_{ext}) and inner (d_{int}) diameters of the nanoparticles were estimated from the Transmission Electron Microscopy (TEM) micrographs, while the crystallite size (d_{XRD}) and the lattice parameter (a) were established from X-Ray Diffraction (XRD) patterns.

	Pt wt. %	Ni at. %	d_{ext} (nm)	d_{int} (nm)	d_{XRD} (nm)	a (nm)
$T = 278$ K	14.8	20	9.4 ± 2.6	5.6 ± 1.7	1.5 ± 0.1	0.385
$T = 293$ K	16.6	23	9.7 ± 2.8	6.3 ± 2.3	1.8 ± 0.1	0.384
$T = 313$ K	20	14	11.5 ± 3.5	7.6 ± 2.8	3.2 ± 0.1	0.387
$T = 333$ K	17.5	18	10.3 ± 2.9	5.7 ± 2.0	3.2 ± 0.2	0.386
$T = 353$ K	18.2	19	6.8 ± 2.0		3.5 ± 0.2	0.3865

Table S2. Activity for the oxygen reduction reaction – corrected from the ohmic losses and the diffusion in solution – at $E = 0.95$ V and $E = 0.9$ vs. RHE for the porous hollow PtNi/C electrocatalysts synthesized at $T = 278, 293, 313, 333$ and 353 K and the Pt/C and PtNi/C benchmark materials. The activities were either given with respect to the electrochemically active surface area of the electrocatalysts (specific activity, SA) or to the mass of platinum (Pt) in the electrocatalyst (mass activity, MA). The Pt specific surface area of the electrocatalysts (in $\text{m}^2 \text{g}_{\text{Pt}}^{-1}$) is also provided.

	$\text{SA}_{0.95}$ ($\mu\text{A cm}_{\text{Pt}}^{-2}$)	$\text{MA}_{0.95}$ ($\text{A g}_{\text{Pt}}^{-1}$)	$\text{SA}_{0.90}$ ($\mu\text{A cm}_{\text{Pt}}^{-2}$)	$\text{MA}_{0.90}$ ($\text{A g}_{\text{Pt}}^{-1}$)	Pt Specific Surface Area ($\text{m}^2 \text{g}_{\text{Pt}}^{-1}$)
Pt/C	26 ± 3	21 ± 2	209 ± 32	166 ± 30	83 ± 7
PtNi/C	70 ± 20	26 ± 5	575 ± 157	215 ± 41	42 ± 6
$T = 278$ K	108 ± 18	60 ± 11	1000 ± 111	580 ± 72	56 ± 8
$T = 293$ K	119 ± 31	62 ± 10	1328 ± 146	699 ± 110	51 ± 7
$T = 313$ K	140 ± 29	53 ± 6	1247 ± 139	496 ± 40	42 ± 5
$T = 333$ K	179 ± 41	77 ± 12	1677 ± 204	695 ± 89	41 ± 3
$T = 353$ K	170 ± 48	62 ± 13	1498 ± 148	550 ± 50	37 ± 2

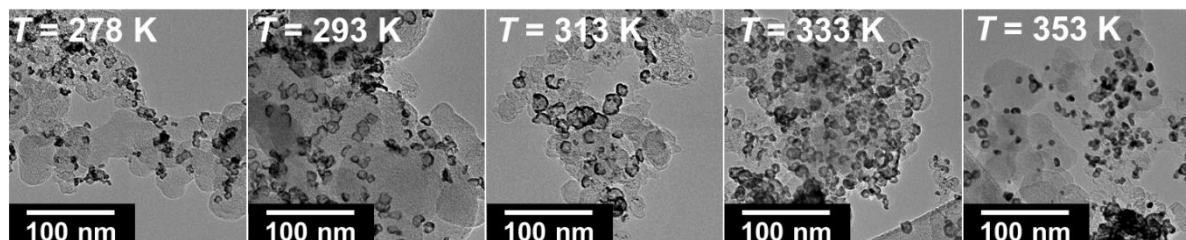


Figure S1. Transmission Electron Microscopy (TEM) micrographs of the different porous hollow PtNi/C electrocatalysts synthesized in this work.

Table S3. Descriptors of the Ni-induced strain and of the density of structural defects for the porous hollow PtNi/C electrocatalysts discussed in this work and the Pt/C and PtNi/C benchmark materials. (i) The ratio between the electrical charge under the ‘pre-peak’ of the CO_{ads} stripping and the total electrical charge of the CO_{ads} stripping ($Q_{pp,CO} / Q_{T,CO}$); (ii) The potential of the second peak of the CO_{ads} stripping ($E_{p,CO}$); (iii) The first moment of the potential weight of the CO_{ads} stripping (μ_1^{CO}), the microstrain determined from the Rietveld analysis of the electrocatalysts WAXS patterns (μ_ϵ , which was taken from Chattot *et al.*¹ work for the Pt/C and PtNi/C references) and the microstrain corrected from the crystallite diameter (Corrected μ_ϵ).

	$Q_{pp,CO} / Q_{T,CO}$	$E_{p,CO}$ (mV vs. RHE)	μ_1^{CO} (mV vs. RHE)	μ_ϵ (% %)	Corrected μ_ϵ (%)
Pt/C	0	797	811.8	17	0.3
PtNi/C	0.23	788	765.0	90	3.0
T = 278 K	0.58	784	738.2	204	3.4
T = 293 K	0.6	782	735.5	211	3.8
T = 313 K	0.76	794	718.7	136	3.8
T = 333 K	0.72	790	715.1	147	4.1
T = 353 K	0.68	793	717.6	166	5.0

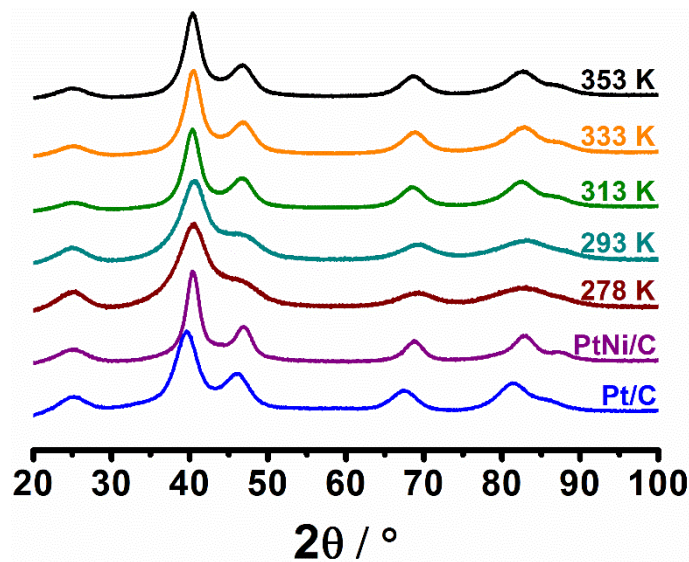


Figure S2. X-Ray Diffraction (XRD) patterns of the electrocatalysts discussed in this work and of the Pt/C and PtNi/C references.

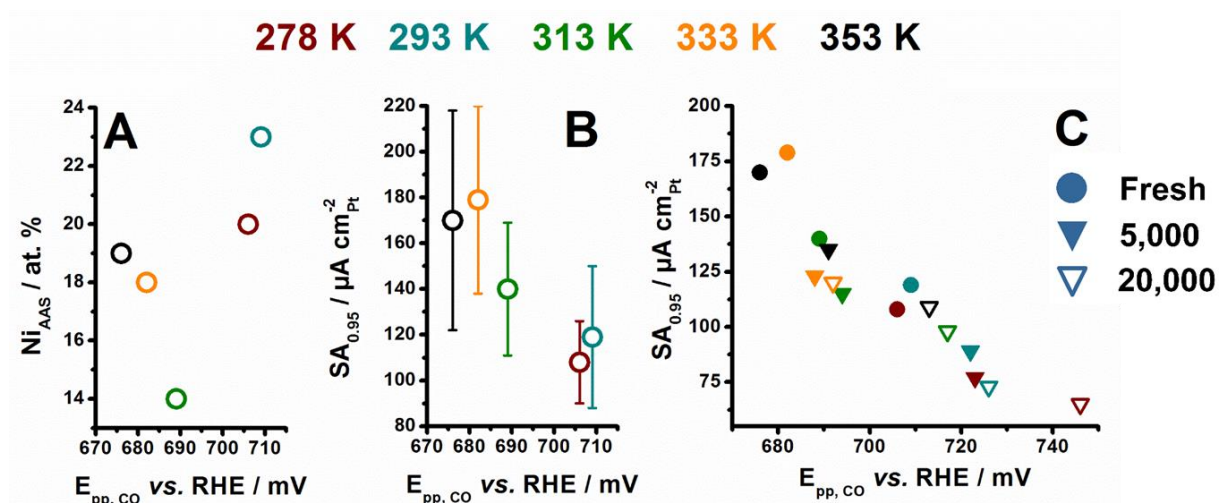


Figure S3. (A) Variation of the Ni atomic content determined by atomic absorption spectroscopy (AAS) vs. the potential of the 'pre-peak' of the CO_{ads} stripping. (B – C) Evolution of the specific activity for the oxygen reduction reaction – corrected from the ohmic losses and the diffusion in solution – 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 (B) and after (A) 5,000 and 20,000 cycles between $E = 0.6$ V vs. RHE and $E = 1.0$ V vs. RHE at $\nu = 0.05$ V s^{-1} at $T = 353$ K in an Ar-saturated 0.1 M HClO_4 electrolyte vs. the potential of the 'pre-peak' of the CO_{ads} stripping voltammogram.

Table S4. Activity for the oxygen reduction reaction – corrected for the ohmic losses and the diffusion in solution – measured at $E = 0.95$ V vs. RHE and $E = 0.90$ vs. RHE for the porous hollow PtNi/C electrocatalysts synthesized at $T = 278, 293, 313, 333$ and 353 K and the benchmark Pt/C electrocatalyst after 5,000 cycles 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 an Ar-saturated 0.1 M HClO₄ electrolyte. The activities were either given with respect to the electrochemically active surface area of the electrocatalysts (specific activity, SA) or to the mass of platinum Pt in the electrocatalyst (mass activity, MA).

	SA_{0.95} ($\mu\text{A cm}_{\text{Pt}}^{-2}$)	MA_{0.95} (A g_{Pt}⁻¹)	SA_{0.90} ($\mu\text{A cm}_{\text{Pt}}^{-2}$)	MA_{0.90} (A g_{Pt}⁻¹)
Pt/C	27 ± 2	20 ± 2	183 ± 10	127 ± 8
$T = 278$ K	77 ± 15	29 ± 2	438 ± 33	159 ± 6
$T = 293$ K	89 ± 9	38 ± 2	532 ± 8	222 ± 37
$T = 313$ K	115 ± 18	41 ± 3	561 ± 24	227 ± 9
$T = 333$ K	123 ± 12	40 ± 5	687 ± 202	223 ± 73
$T = 353$ K	135 ± 23	35 ± 1	640 ± 108	168 ± 7

Table S5. Activity for the oxygen reduction reaction – corrected for the ohmic losses and the diffusion in solution – measured at $E = 0.95$ V vs. RHE and $E = 0.90$ vs. RHE for the porous hollow PtNi/C electrocatalysts synthesized at $T = 278, 293, 313, 333$ and 353 K and the benchmark Pt/C electrocatalyst after 20,000 cycles 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 an Ar-saturated 0.1 M HClO₄ electrolyte. The activities were either given with respect to the electrochemically active surface area of the electrocatalysts (specific activity, SA) or to the mass of platinum Pt in the electrocatalyst (mass activity, MA).

	SA 0.95 ($\mu\text{A cm}_{\text{Pt}}^{-2}$)	MA 0.95 (A g_{Pt}⁻¹)	SA 0.9 ($\mu\text{A cm}_{\text{Pt}}^{-2}$)	MA 0.9 (A g_{Pt}⁻¹)
Pt/C	37 ± 3	27 ± 2	218 ± 15	159 ± 9
$T = 278$ K	65 ± 5	23 ± 1	341 ± 36	123 ± 3
$T = 293$ K	73 ± 13	30 ± 3	398 ± 70	163 ± 14
$T = 313$ K	98 ± 20	32 ± 5	395 ± 45	154 ± 30
$T = 333$ K	120 ± 7	39 ± 5	604 ± 143	195 ± 57
$T = 353$ K	109 ± 4	31 ± 1	517 ± 30	147 ± 5

Table S6. Mean external diameter determined from the TEM images of the porous hollow PtNi/C electrocatalysts discussed in this work, after 20,000 cycles between $E = 0.6$ V vs. RHE and $E = 1.0$ V vs. RHE in Ar-saturated 0.1 HClO₄ at $\nu = 0.05$ V s⁻¹.

External diameter (nm)	
$T = 278$ K	8.0 ± 2.8
$T = 293$ K	7.8 ± 2.8
$T = 313$ K	10.7 ± 3.6
$T = 333$ K	7.8 ± 2.5
$T = 353$ K	6.7 ± 2.5

Table S7. Evolution of the position of the second peak of the CO_{ads} stripping ($E_{p,CO}$) during the ageing of the porous hollow PtNi/C electrocatalysts discussed in this work – 5,000 and 20,000 potential cycles 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 an Ar-saturated 0.1 M HClO₄ electrolyte.

	$E_{p,CO}$ (mV vs. RHE) (Before ageing)	$E_{p,CO}$ (mV vs. RHE) (After 5,000 cycles)	$E_{p,CO}$ (mV vs. RHE) (After 20,000 cycles)
$T = 278$ K	784	792	807
$T = 293$ K	782	799	807
$T = 313$ K	794	807	824
$T = 333$ K	790	807	807
$T = 353$ K	793	805	815
<i>Average</i>	789	802	812

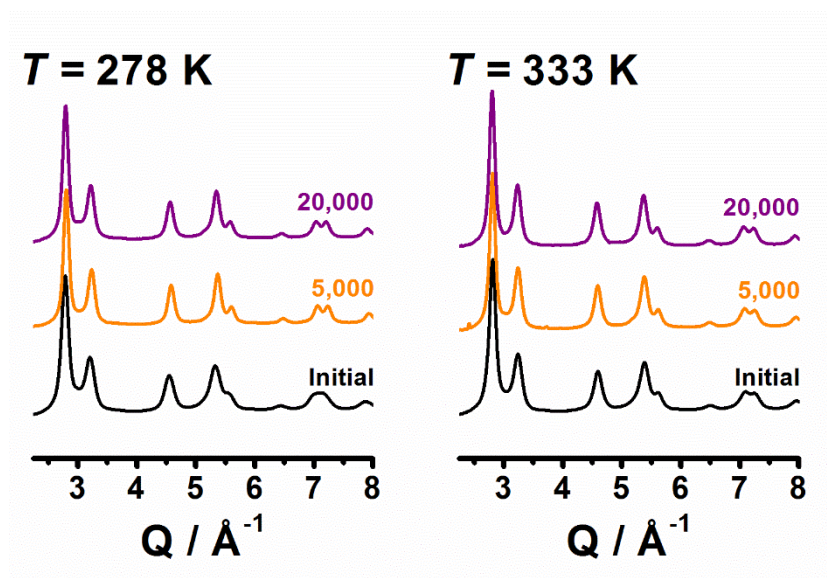


Figure S4. X-Ray Diffraction (XRD) patterns of the electrocatalysts synthesized at $T = 278$ K and $T = 333$ K before (but after electrochemical characterisation) and after 5,000 and 20,000 cycles between $E = 0.6$ V vs. RHE and $E = 1.0$ V vs. RHE at $\nu = 0.05$ V s⁻¹, $T = 353$ K in an Ar-saturated 0.1 M HClO₄ electrolyte.

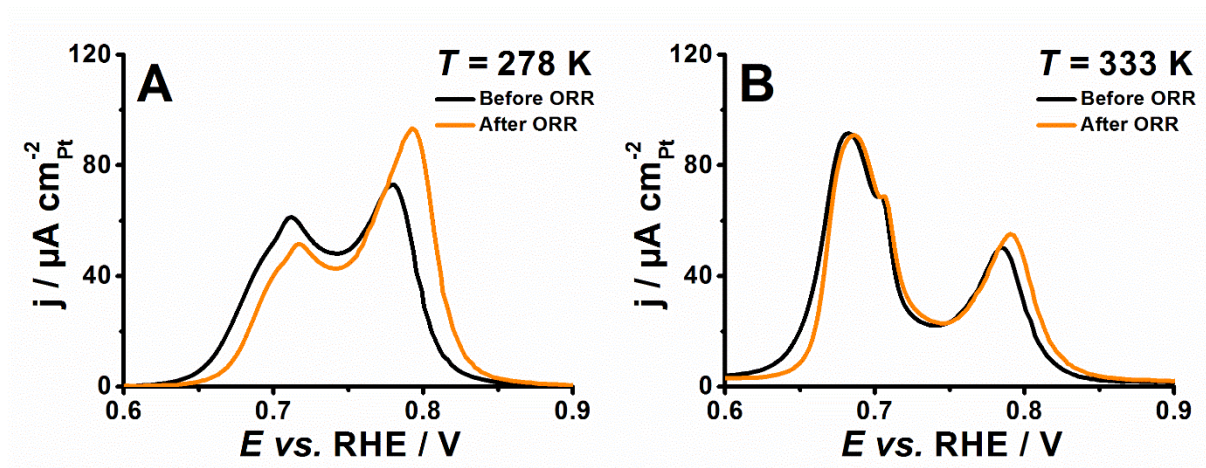


Figure S5. Evolution of the CO_{ads} stripping performed in an Ar-saturated 0.1 M HClO_4 electrolyte ($\nu = 0.02 \text{ V s}^{-1}$, $T = 298 \text{ K}$) before and after the ORR for the porous hollow PtNi/C electrocatalysts synthesized at (A) $T = 298 \text{ K}$ and (B) $T = 333 \text{ K}$.

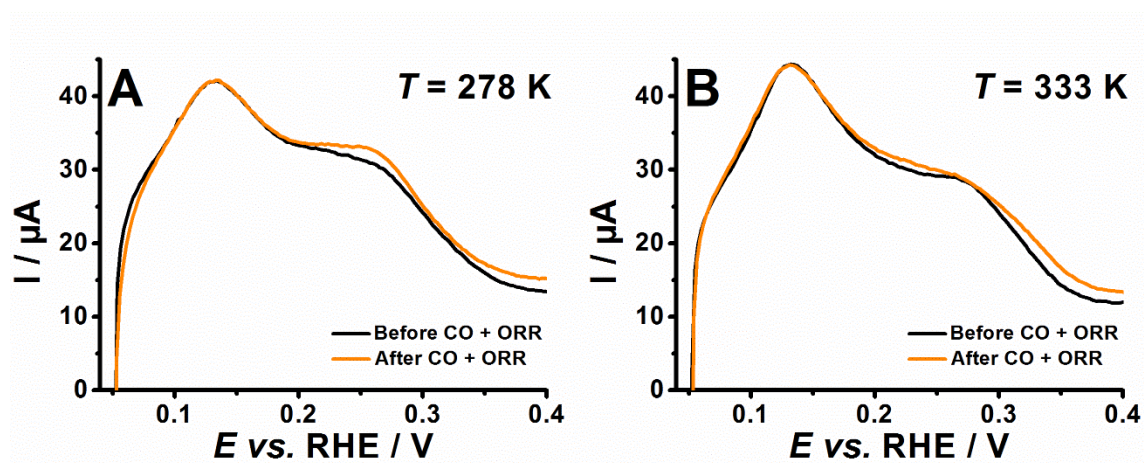


Figure S6. Evolution of the base voltammograms performed in an Ar-saturated 0.1 M HClO_4 electrolyte ($\nu = 0.02 \text{ V s}^{-1}$, $T = 298 \text{ K}$) before and after the electrochemical characterisation (CO_{ads} stripping + ORR) for the porous hollow PtNi/C electrocatalysts synthesized at (A) $T = 298 \text{ K}$ and (B) $T = 333 \text{ K}$. For comparison purposes, the voltammograms were normalized to the intensity of the highest H_{upd} peak.

Table S8. Evolution of the theoretical Ni atomic content, determined from the position of the second peak of the CO_{ads} stripping voltammogram ($E_{p,CO}$) during the ageing of the porous hollow PtNi/C electrocatalysts introduced in this work – 5,000 and 20,000 cycles 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 an Ar-saturated 0.1 M HClO₄ electrolyte.

	Ni at. % (from AAS) (Before ageing)	Ni at. % (from $E_{p,CO}$) (After 5,000 cycles)	Ni at. % (from $E_{p,CO}$) (After 20,000 cycles)
$T = 278$ K	20	16 ± 1	6 ± 1
$T = 293$ K	23	11 ± 1	6 ± 1
$T = 313$ K	14	6 ± 1	0 ± 1
$T = 333$ K	18	6 ± 1	6 ± 1
$T = 353$ K	19	7 ± 1	2 ± 1

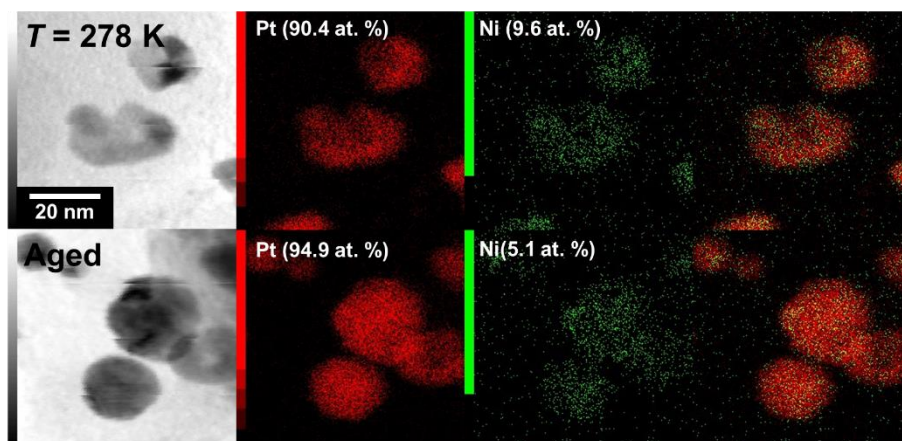


Figure S7. Evolution of the chemical composition measured by STEM-EDX of the porous hollow PtNi/C electrocatalysts synthesized at $T = 278$ K before and after 20,000 potential cycles between $E = 0.6$ V vs. RHE and $E = 1.0$ V vs. RHE at $v = 0.05$ V s⁻¹ and $T = 353$ K in an Ar-saturated 0.1 M HClO₄ electrolyte.

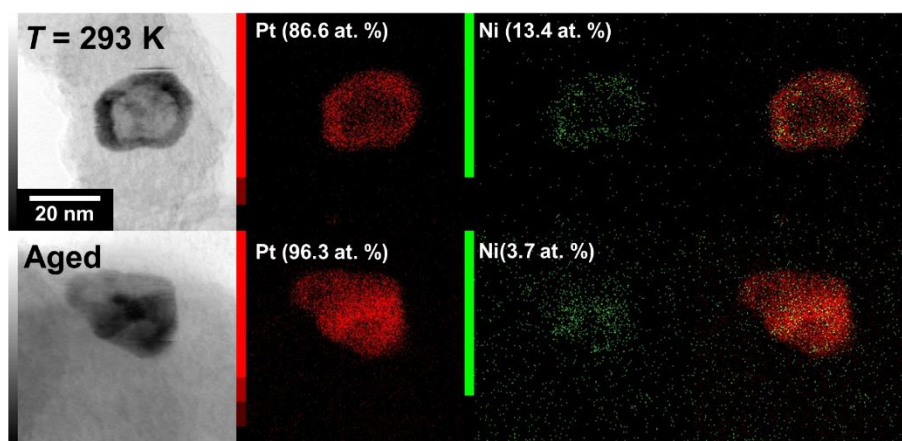


Figure S8. Evolution of the composition measured by STEM-EDX of the porous hollow PtNi/C electrocatalysts synthesized at $T = 293$ K before and after 20,000 potential cycles between $E = 0.6$ V vs. RHE and $E = 1.0$ V vs. RHE at $v = 0.05$ V s⁻¹ and $T = 353$ K in an Ar-saturated 0.1 M HClO₄ electrolyte.

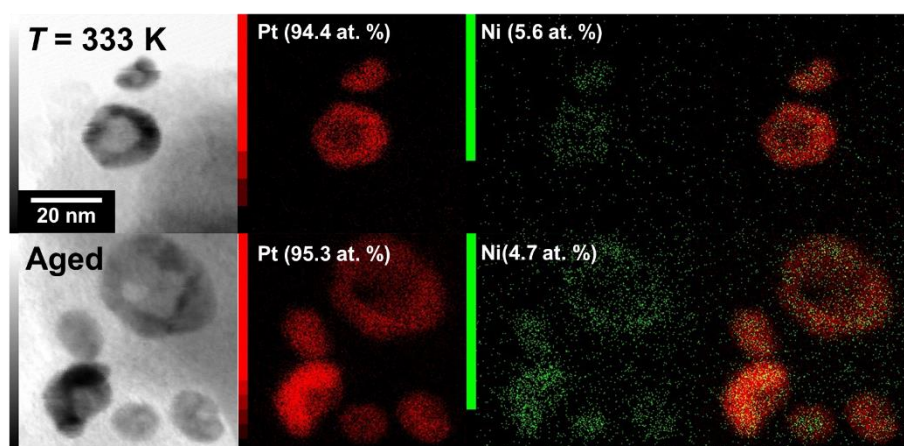


Figure S9. Evolution of the composition measured by STEM-EDX of the porous hollow PtNi/C electrocatalysts synthesized at $T = 333$ K before and after 20,000 potential cycles between $E = 0.6$ V vs. RHE and $E = 1.0$ V vs. RHE at $\nu = 0.05$ V s⁻¹ and $T = 353$ K in an Ar-saturated 0.1 M HClO₄ electrolyte.

Table S9. Evolution of the ratio of the charge under the ‘pre-peak’ of the CO_{ads} stripping to the total charge of the CO_{ads} stripping ($Q_{pp,CO} / Q_{T,CO}$) during the ageing of the porous hollow PtNi/C electrocatalysts discussed in this work – 5,000 and 20,000 potential cycles 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 an Ar-saturated 0.1 M HClO₄ electrolyte.

	$Q_{pp,CO} / Q_{T,CO}$ (Before ageing)	$Q_{pp,CO} / Q_{T,CO}$ (After 5,000 cycles)	$Q_{pp,CO} / Q_{T,CO}$ (After 20,000 cycles)
$T = 278$ K	0.58	0.33	0.17
$T = 293$ K	0.6	0.39	0.30
$T = 313$ K	0.76	0.61	0.43
$T = 333$ K	0.72	0.59	0.55
$T = 353$ K	0.68	0.64	0.57

Table S10. Evolution of the first moment of the potential weight (μ_1^{CO}) during the ageing of the porous hollow PtNi/C electrocatalysts discussed in this work – 5,000 and 20,000 cycles between $E = 0.6$ V vs. RHE and $E = 1$ V vs. RHE at $\nu = 0.05$ V s⁻¹ and $T = 353$ K in an Ar-saturated 0.1 M HClO₄ electrolyte.

	μ_1^{CO} (mV vs. RHE) (Before ageing)	μ_1^{CO} (mV vs. RHE) (After 5,000 cycles)	μ_1^{CO} (mV vs. RHE) (After 20,000 cycles)
$T = 278$ K	738	772	801
$T = 293$ K	735	779	791
$T = 313$ K	718	748	776
$T = 333$ K	715	740	751
$T = 353$ K	717	738	763

References

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