Combining SAXS and XAS to study the *operando* degradation of carbon-supported Pt-nanoparticle fuel cell catalysts

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Abstract: In the last two decades, small angle X-ray scattering (SAXS) and X-ray absorption spectroscopy (XAS) have evolved into two well-established techniques capable of providing complementary and *operando* information about a sample's morphology and composition, respectively. Considering that operation conditions can often lead to simultaneous and related changes in a catalyst's speciation and shape, herein we introduce a setup that combines SAXS and XAS in a configuration that allows optimum acquisition and corresponding data quality for both techniques. To determine the reliability of this setup, the latter was used to study the *operando* degradation of two carbon-supported Pt-nanoparticle (Pt/C) catalysts customarily used in polymer electrolyte fuel cells. The model used for the fitting of the SAXS curves unveiled the fractal nature of the Pt/C-electrodes and their evolution during the *operando* tests, and both X-ray techniques were complemented with control, *ex situ* transmission electron microscopy and standard electrochemical measurements. Ultimately, the results obtained with this combined setup quantitatively agree with those reported in previous studies, successfully validating this apparatus and highlighting its potential to study the *operando* changes undergone by worse-understood (electro)catalytic systems.

Keywords: energy conversion, electrochemistry, *in situ*, synchrotron, X-ray absorption spectroscopy, small angle X-ray scattering.

Introduction

Understanding the changes in a material's physico-chemical properties induced by the operative conditions intrinsic to its application remains the ultimate challenge in materials' characterization.¹⁻³ *Ex situ*, *post mortem* techniques sometimes lead to a good understanding of a material's formation, operation and/or degradation mechanisms, but are ill-fitted to assess properties that are prone to change upon sample transfer from the experiment to the characterization technique of interest, and/or in the course of its characterization.⁴ These limitations have motivated an ever-increasing surge of interest in the use of *operando* techniques that can provide insight hardly accessible with standard methods and that can also be greatly advantageous regarding time requirements.^{5,6} Moreover, the processes of interest often imply simultaneous and related changes in more than one parameter that can only be assessed by combining several characterization techniques, possibly leading to differences in experimental setups that can affect the comparability among results and increase measurement time requirements.^{7,8} Thus, the combination of techniques into a common setup can be of great appeal,^{9,10} and is becoming increasingly extended among the synchrotron facilities in which such *operando* measurements are often performed owing to the need for X-rays with energies > 5 keV to attain the penetration depth required to characterize materials in a realistic reaction environment.^{5,7,8,11}

Within this context, the simultaneous changes in morphology and composition inherent to a nanomaterial's initial synthesis or to its operation-related degradation (e.g., corrosion) can be studied *in situ* using small angle X-ray scattering (SAXS) and X-ray absorption spectroscopy (XAS), respectively. Specifically, SAXS can be used to infer a sample's particle size distribution, average particle diameter and specific surface area, whereas in XAS the X-ray

absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) provide information about its unoccupied density of states and local geometric arrangement, respectively. Despite this complementarity, the number of experimental setups combining both techniques remains relatively scant. In their pioneering efforts at the JUSIFA beamline of the DORIS Photon Source (Germany), Haubold and collaborators¹²⁻¹⁴ used a photodiode placed in the position of the SAXS detector beam stopper to quantify the transmitted X-ray intensity – an approach that limited XAS-acquisition to the XANES energy range due to the low signal-to-noise ratio of diode detectors, which compromises XAS-data quality at high energies (i.e., in the EXAFS regime). The operative setup at the Dutch-Belgian beamline of the European Synchrotron Radiation Facility (France) suffers from the same shortcoming,¹⁵ while the one at the Structural Material Science station of the Kurchatov Centre for Synchrotron Radiation and Nanotechnology (Russia) is equipped with a linear scattering detector that leads to a high noise level in the acquired SAXS data.¹⁶ Moreover, while the MPW6.2 and BioCAT 18ID beamlines originally developed at the now defunct Synchrotron Radiation Source (UK)¹⁷ and at the Advanced Photon Source (USA)¹⁸ have displayed their capability to conduct both XAS and SAXS measurements, we are not aware of any studies originated from these stations in which both of these techniques were combined.

Thus, to the best of our knowledge, at the current time there is no combined XAS and SAXS setup including a detection system with the sufficient signal-to-noise ratio required for a rigorous assessment of the EXAFS regime, which can provide key insight on the analyte's coordination environment.¹⁹ This limitation could be circumvented by implementing the gas ionization detectors customarily used in XAS-specific beamlines, which feature a superior signal-to-noise ratio when compared to the diodes applied in Refs. 12 to 15. Additionally, such a configuration

would allow the simultaneous collection of the XAS spectrum of a reference sample, needed for the precise energy calibration required for the absorbent's XANES, from which one can derive its oxidation state²⁰ and/or information about surface adsorbates (if applicable).²¹ As suggested in Ref. 15, this approach would pass by setting the SAXS flight tube and XAS ion chambers (including the above-mentioned reference) parallel to each other and on a movable stage, as to transition among techniques within a few minutes. Even if such a configuration would not allow for a fast transition (requiring $\ll 1$ min) among measurement techniques and may therefore be ill-suited to investigate processes occurring within a short time interval, it would be valid for studies in which the overall measurement time is significantly longer than the delay required to transition among techniques (i.e., for experiments spanning over the course of several hours).

A fitting example of such a process extending over several hours / days would be the degradation of noble-metal nanoparticle (NP) electrocatalysts under operation-relevant conditions, whereby extended, potential-induced oxidation and reduction cycles lead to metal dissolution,²² re-deposition and particle growth.²³⁻²⁶ Among these metals, platinum is of special relevance due to its extended use as an electrocatalyst for the hydrogen oxidation and oxygen reduction reactions (HOR and ORR, respectively) in polymer electrolyte fuel cells (PEFCs), which are regarded as promising energy conversion devices for electric vehicles.^{27,28} Specifically, the limited activity and durability of the carbon-supported Pt-nanoparticle (Pt/C) catalysts customarily used to speed up the ORR-kinetics translate in the need for PEFC cathode loadings of $\approx 0.3 \text{ mg}_{\text{Pt}} \cdot \text{cm}_{\text{geom}}^{-2}$, that account for ≈ 50 % of the stack cost and should be decreased ≥ 3 -fold in order to render this technology cost competitive.^{27,28} To fulfill these requirements, an extensive body of work has been devoted to study the mechanisms that cause this degradation, and that can be categorized among two groups according to their corresponding potential

regimes. First, upon standard PEFC operation within potentials between ≈ 0.6 and ≈ 1.0 V vs. the reversible hydrogen electrode (RHE), surface Pt-oxidation leads to the formation of $\text{Pt}^{\text{X}+}$ ions that diffuse within the perfluorosulfonic ionomer phase. In doing so, these species can (i) re-deposit on other Pt-NPs, causing their overall growth and a loss of catalytically active surface (i.e., the so-called electrochemical Ostwald ripening);^{23,29} or (ii) get reduced upon contact with crossover H_2 permeating from the anode, which results in large Pt-nanoparticles that precipitate within the electronically insulating ionomer and that therefore are catalytically inactive.^{29,30} In the second mechanism, PEFC-startup and -shutdown can momentarily lead to cathode potentials in excess of ≈ 1.5 V vs. RHE that trigger the corrosion of the carbon support to CO_2 , causing NP-detachment and coalescence/agglomeration^{23,31,32} and drastically impacting the catalyst layer's integrity, which in turn leads to a deterioration of its mass transport properties and corresponding losses in the high current density performance.³³⁻³⁵

This understanding of its degradation mechanisms renders the Pt/C system an excellent choice to validate the combined SAXS and XAS setup discussed above, whereby flight tube and ion chambers are mounted on a movable stage allowing to transition among techniques within minutes. Thus, in this work we present the results derived from the use of such a setup to study the *operando* degradation of two commercial Pt/C catalysts, using a XAS- and SAXS-compatible liquid electrolyte flow cell to mimic the harsh electrochemical conditions encountered in a PEFC cathode.³⁶ The novel inclusion of a SAXS-derived electrode mass fractal analysis provides unprecedented insight on the evolution of the Pt-NPs' agglomeration, while the agreement among our results and previous literature reports on this well-established system and degradation mechanisms provides a successful proof-of-concept for the combined setup.

Experimental Section

Materials and working electrodes' preparation.— The catalysts used for the *operando* measurements were 30 wt. % Pt on Vulcan XC-72 carbon (Pt/V) and 30 wt. % Pt on graphitized Black Pearls 2000 carbon (Pt/BP-g), both purchased from Tanaka Kikinzoku Kogyo Co. (product codes TEC10V30E and TEC10BA30E, respectively). We note that the carbon supports in these two catalysts display very similar surface areas of 240 vs. 210 m²·g⁻¹ for V vs. BP-g, respectively,³⁷ as determined on the basis of N₂-sorption measurements using the BET equation, and thus any dissimilar corrosion behaviors of the corresponding Pt/C catalysts should mostly be related to differences in their degree of graphitization.

To process these catalysts into working electrodes implementable in our liquid electrolyte *operando* flow cell,³⁶ weighed amounts of each powder were diluted in a mixture of ultrapure water (18.2 MΩ·cm, ELGA Purelab[®] Ultra), isopropanol (99.9% Chromasolv Plus[®] for HPLC, Sigma Aldrich) and ionomer (≈ 5% Nafion[®] 117 dispersion, Sigma Aldrich), whereby the volume of the latter was set to correspond to an ionomer-to-carbon mass ratio of 1:3. These components were subsequently mixed in glass vials and placed for 15 minutes in an ultrasonication unit in order to produce an ink for spray coating. Electrode substrates consisted of pre-cut pieces of 50 μm thick conductive Kapton foil (i.e., including a thin layer of conductive carbon on one of their sides – DuPont Kapton 200RS100) which were additionally sputter-coated in-house with a ≈ 100 nm layer of gold on their carbon side to further enhance their conductivity. After placing these substrates on a mask that only exposes a circular, 4 mm diameter (i.e., 0.126 cm²) area at the center of each electrode that had not been sputtered with Au, Pt/C catalyst inks were spray-coated manually and stepwise, aiming at a Pt-loading of ≈ 1.6 mg_{Pt}·cm_{geom}⁻² (or ≈ 4.5 mg_{catalyst}·cm_{geom}⁻²). This corresponds to an overall mass increase of

≈ 500-1000 μg, which in turn accounts for ≈ 1 % of the initial substrate mass and renders the quantification of the electrode loading highly prone to imprecisions. Thus, to account for changes in the substrate mass related, like time-dependent differences in the uptake of humidity by the Kapton[®] foil, each working electrode substrate was first weighed (using a Mettler Toledo XPE206DR microbalance) along with an equivalent dummy, yielding the masses $m_{\text{substrate},t0}$ and $m_{\text{dummy},t0}$, respectively. The electrode substrate was then sprayed and left to dry and equilibrate for ≥ 12 hours, after which the resulting working electrode and the non-sprayed dummy were weighed again, resulting in $m_{\text{electrode},t1}$ and $m_{\text{dummy},t1}$. The mass of catalyst ($m_{\text{catalyst},t1}$) was then estimated using the following Equation:

$$m_{\text{catalyst},t1} = \frac{1}{1+ICR} \cdot \left[m_{\text{electrode},t1} - m_{\text{substrate},t0} \cdot \left(\frac{m_{\text{dummy},t1}}{m_{\text{dummy},t0}} \right) \right] \quad [1]$$

where *ICR* refers to the ionomer-to-catalyst ratio, with a value of 0.23 (on the basis of the ionomer-to-carbon ratio and the catalysts' Pt-content values of 1/3 and 30 wt. %, respectively, discussed above). Finally, to minimize contact resistance along the thick catalyst layers (CLs) ensuing from these high catalyst loadings, the electrodes were calendered down to ≈ 50 % of their initial thickness (determined with a profilometer) using a calendering machine developed in-house.

Electrochemical Tests.— All *operando* electrochemical experiments were performed using the liquid electrolyte flow cell developed by Binniger *et al.*,³⁶ using 0.1 M HClO₄ prepared from 60 % HClO₄ (Kanto Chemical Co., Inc.) diluted in ultrapure water (18.2 MΩ·cm, ELGA Purelab[®] Ultra) and saturated with N₂ (5.0, Messer AG) as the electrolyte. In brief, a low leak, 2

mm diameter Ag/AgCl electrode (Harvard Apparatus) was used as the reference, whereas carbon-based counter electrodes were prepared using the same procedures described above, spray-coating an ink of Black Pearls 2000 carbon (Cabot) on pre-cut, Au-sputtered Kapton[®] substrates (for details, the reader is referred to Ref. 36). Following assembly, the cell was placed in a specifically designed holder and its bottom and upper ends were connected through PTFE tubes (1 mm diameter) to the electrolyte reservoir and syringe pump (Legato 110 by Kd Scientific) operated at a withdrawal flow rate of 50 $\mu\text{L}\cdot\text{min}^{-1}$. After connecting the cell to the potentiostat (BioLogic SP-300), it was covered with a poly(methyl methacrylate) (PMMA) box with two slits for the incoming and outgoing X-ray beam / scattered signal; the same PMMA box has two more, lateral holes used to blow warm air by a Steinel HL1910E heat gun inside the box and to fit the tubes and cables connected to the cell. These include a contact thermocouple (tin-plated copper alloy by Minco) attached to the flow cell at a location next to the beam window, which is connected to an *in-house*-built control unit that tunes the heat gun power to a steady, set temperature. Furthermore, during measurements at increased temperature, a vacuum degassing device (Separel PF-3 T-S, by Dic Corporation) was used in order to remove dissolved gases from the electrolyte before reaching the heated chamber and cell. This degassing was necessary in order to prevent the formation of gas bubbles due to the decreased solubility of gases in the electrolyte at increased temperatures. Thus, unless otherwise specified, the electrochemical measurements and their corresponding *operando* XAS and SAXS measurements were performed at 60 °C – a temperature relatively close to the 80 °C at which PEFCs customarily operate.

Following the assembly of the electrochemical cell and its filling with electrolyte, the air embedded in the CL porosity was evacuated by holding a reductive potential of ≈ 0.1 V vs. RHE for the time needed to reach a quasi-negligible reduction current ($\ll 100$ μA ; typically, ≈ 5 min

were needed for this). This step proved crucial to reach the high CL utilization values discussed below. Next, the working electrode was conditioned by recording 25 cyclic voltammograms (CVs) between ≈ 0.01 and ≈ 1.2 V vs. RHE at $50 \text{ mV}\cdot\text{s}^{-1}$. This was followed by the recording (at $10 \text{ mV}\cdot\text{s}^{-1}$) of 3 more CVs between ≈ 0.03 and ≈ 1.0 V vs. RHE, which were subsequently used to quantify the catalyst's electrochemical surface area (ECSA) by integrating the area of the CVs corresponding to the charge of the underpotential deposition of hydrogen (H_{upd} , extending between ≈ 0.45 and ≈ 0.05 V vs. RHE), and using a conversion factor of $210 \mu\text{C}\cdot\text{cm}_{\text{Pt}}^{-2}$.³⁸

The electrochemical degradation protocol consisted of recording 250 CVs between 0.5 and 1.5 V vs RHE at $50 \text{ mV}\cdot\text{s}^{-1}$, whereby the potential boundaries of choice are a combination of those suggested by the US Department of Energy for load cycle vs. support stability testing (0.6-1.0 vs. 1.0-1.5 V vs RHE, respectively).³⁹ XAS and SAXS measurements were performed just after electrochemical conditioning and after 25, 50, 100 and 250 degradation cycles, in all cases while holding the working electrode at 0.45 V vs. RHE during XAS/SAXS acquisition. In the case of Pt/V, additional SAXS and XAS measurements were also performed while holding the potential at 0.95 V vs. RHE.

To estimate the utilization of the CLs in the *operando* cell (*vide infra*), we also performed complementing electrochemical measurements in a standard glass cell in which the ≈ 100 -fold lower working electrode loadings lead to ultra-thin catalyst layers for which full utilization has been previously demonstrated.⁴⁰ In brief, both Pt/C catalysts were processed into inks with an ionomer-to-carbon ratio of 1:3; after sonicating, the volume of each ink required for a Pt-loading of $\approx 17 \mu\text{g}_{\text{Pt}}\cdot\text{cm}_{\text{geom}}^{-2}$ was pipetted atop a mirror-polished, 5 mm diameter glassy carbon disc (0.196 cm^2 ; HTW Hochtemperatur-Werkstoffe GmbH) embedded in a PTFE rotating disc electrode (RDE – Pine Research Instrumentation, Inc.) After drying, the electrode was vertically

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3 mounted on a rotating shaft and immersed under potential control in a glass cell partially filled
4 with N₂-deaerated 0.1 M HClO₄ (see details above). The counter electrode was an Au-mesh
5 (99.99 % metals basis, Alfa Aesar) held in a separate compartment which ended in a #3 porous
6 glass frit, and an *in-house* developed RHE connected through a glass Luggin capillary was used
7 as the reference. The procedures applied to electrochemically condition the working electrode
8 and to subsequently estimate its ECSA were identical to those described above for the *operando*
9 cell (with the exception of the initial, long potential hold, which is not needed to evacuate the air
10 trapped in these thin CLs).
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24 *High resolution transmission electron microscopy (HR-TEM) measurements.*— HR-TEM images
25 were collected using a TECNAI F30 operating at 300kV. Unprocessed catalyst powders and
26 samples scratched from the catalytic layers after 250 degradation potential cycles (Supporting
27 Information Figs. S7 and S8), were dispersed in a 1:1 volume solution made of water and
28 isopropanol. The dispersion was sonicated for 5 min and the final solution was drop-casted on a
29 TEM grid (Agar Scientific, holey carbon film - copper, 400 mesh).
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40 *Description of the combined SAXS and XAS setup.*— All combined SAXS and XAS experiments
41 were performed at the SuperXAS beamline of the Swiss Light Source (SLS – Villigen,
42 Switzerland). The polychromatic beam resulting from the 2.9 Tesla superbend was first
43 collimated by a 1 m long Rh-coated mirror at 2.5 mrad, and the energy was collected using a
44 channel-cut Si (111) monochromator. Finally, the beam was focused on the beam stop (100 x
45 100 μm²) using a Rh-coated thoroidal mirror. Figure 1 features a schematic representation of the
46 setup; following the X-ray beam path from left to right, the first ionization chamber (*i*₀, filled
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with N₂ at 2 bars) measures the incident beam intensity during the SAXS and XAS measurements, and is followed by the *operando* electrochemical cell. Next, the SAXS flight tube and two remaining ion chambers (also filled with N₂ at 2 bars) are mounted in parallel on a table that can be moved perpendicularly to the beam direction. Specifically, a second ion chamber is placed just after the analyte / electrochemical cell (*i*₁), and is followed by a reference sample (in this case, a piece of Pt-foil of one absorption length) and a third ion chamber (*i*₂) – a configuration that allows for a precise energy calibration by assigning the first inflection point in the Pt-foil reference XANES to the Pt *L*₃ absorption energy at 11,564 eV. Complementarily, the SAXS flight tube is evacuated to $\approx 10^{-3}$ mbar using a Pfeiffer dry scroll pump, and has an internal circular section of 120 mm and a length of 580 mm, whereby both of its ends are closed with 100 μ m thick pieces of Mylar foil. This is followed by a 3.5 mm diameter steel beam stopper and the 2D detector (Pilatus 100K, active area 83.7 x 33.54 mm², pixel size 172 x 172 μ m²). The sample-to-detector-distance was quantified using an Ag-behenate standard, and accounted to 900 mm; considering this, along with the detector and beam stopper sizes, the 2 θ range available for the SAXS measurement was 0.14-5.3°. This combination of energies and angle range allow to access information from particles with diameters within the range of 1.2 to 45 nm.

XAS data treatment.— X-ray absorption spectra were collected at the Pt-*L*₃ absorption edge, and all data were treated with the Demeter software package.⁴¹ Spectra were first background-corrected and normalized using linear and spline functions for the pre- and post-edge energy regions (extending 150-20 eV below and 150-890 eV above the absorption edge, respectively), while calibrating the energy scale on the basis of the 1st derivative in the Pt-foil reference

spectrum (whereby its first maximum was assigned to 11,564 eV, *vide supra*). After conversion to the k -space, spectra within the range of 1 to 12 Å⁻¹ were Fourier-transformed and fitted in the R-range of 1-3.4 Å, using the Pt-Pt first scattering shell obtained from the ideal model of metallic-Pt within a Fm3m space group. The amplitude reduction factor values required for the fitting of the Pt/C-samples' EXAFS were estimated from the fittings of the corresponding reference Pt-foil spectra (assuming a coordination number of 12), and accounted to 0.76. All fitting results are reported in the Supporting Information (see Figures S9/S10 and Tables S1/S2).

SAXS data treatment.— The X-ray energy values employed for the acquisition of SAXS data were 11.300 and 11.545 keV (i.e., well below and close to the Pt- L_3 absorption edge) , corresponding to wavelength (λ) values of 0.10972 and 0.10739 nm, respectively. The 2D-detector collected three images per energy with an exposure time of 0.4 s·image⁻¹, resulting in a total acquisition time of ≈ 2 s per SAXS measurement, including monochromator movement. All images collected at the same energy were radially integrated and averaged using Matlab routines developed by the coherent X-ray scattering group at PSI. Using these routines, each image is converted into a scattering profile $i_{\text{scat}}(q)$, whereby the intensity (measured in counts) is reported as function of the module of the scattering vector, q :

$$q = \frac{4\pi}{\lambda} \sin(\theta) \quad [2]$$

where θ is half of the angle between the incident X-ray beam and each detector pixel measuring the scattered intensity.

The scattering cross section of photons with matter, $d\sigma/d\Omega$, is defined as the ratio of the photon flux, (Φ_{scat} – the number of photons per time unit) scattered in a solid angle $\Delta\Omega$ and the product of the irradiance of the incoming beam (E_e , or the number of photons per time and area) and the transmittance of the entire system (i.e., apparatus and sample, τ), as indicated by Equation 3:

$$\frac{d\sigma}{d\Omega} = \frac{\Phi_{\text{scat}}}{E_e \tau \Delta\Omega} \quad [3]$$

The lack of a calibrated photodiode in our combined SAXS and XAS setup prevents a direct measurement of $d\sigma/d\Omega$; however, using a pre-calibrated glassy carbon (GC) reference to calibrate the 2D-detector,⁴² the acquired data can be transformed into a scattering cross section per area by normalizing the scattering cross section in Eq. 3 with respect to the irradiated area, A :

$$\frac{d\sigma}{d\Omega} \frac{1}{A} = \frac{1}{A} \frac{\Phi_{\text{scat}}}{E_e \tau \Delta\Omega} \quad [4]$$

The detailed procedure followed to calculate this cross section per area is included in the Supporting Information, whereby Equation S8 allows estimating the sample's cross section per area for the two different energies of the probing X-rays. The so-called Anomalous SAXS (A-SAXS) curve corresponds to the difference of the scattering cross sections at each SAXS-acquisition energy (E_1 , E_2), and is proportional to the scattering by the Pt-nanoparticles in the catalysts, as extensively explained in Refs. 43 and 44:

$$\left(\frac{d\sigma}{d\Omega} \frac{1}{A}\right)_{E1}^{\text{sample}} - \left(\frac{d\sigma}{d\Omega} \frac{1}{A}\right)_{E2}^{\text{sample}} \propto \left(\frac{d\sigma}{d\Omega} \frac{1}{A}\right)^{\text{Pt-NPs}} \quad [5]$$

We must highlight here that the data treatment presented in the Supporting Information is required for a rigorous calculation of an A-SAXS curve, which should not be directly performed on the basis of raw $i_{\text{scat}}(q)$ values (since these would have to be corrected for the energy-dependent transmittance and detectors' responses).

Moreover, the estimated A-SAXS curve is directly proportional to the product of the form and structure factors ($P(q)$ and $S(q)$, respectively):

$$\left(\frac{d\sigma}{d\Omega A}\right)^{\text{Pt-NPs}} \propto P(q) S(q) \quad [6]$$

whereby $P(q)$ is related to the particle shape and size and $S(q)$ contains information regarding the interaction among Pt-particles; note that a more detailed version of this Equation (allowing to estimate the absorbent's loading, *vide infra*) is provided in the Supporting Information (cf. Eq. S19). Regarding the structure factor, if the particles in a material are far from each other (i.e., in a diluted sample), $S(q)=1$, while its value becomes larger (especially at low q -values) when the distance among scattering objects is in the order of magnitude of the incident photon's wavelength.⁴⁵ Thus, the A-SAXS curves were fitted with the SASfit software⁴⁶ including both $P(q)$ and $S(q)$ in the fitting model. The form factor was modelled assuming that Pt-NPs are spherical in shape and that their diameters follow a log-normal distribution. The structure factor was a Gaussian mass fractal function, because the Pt-particles agglomerate forming clusters that resemble larger, single nanoparticles – a condition in which the samples have the characteristics of a fractal structure. The structure factor is the Fourier transform of the density auto correlation function, $g(R)$:⁴⁷

$$S(q) = \int e^{i\vec{q}\cdot\vec{R}} g(R) dR \quad [7]$$

Additionally, for a fractal system:⁴⁸

$$g(R) = \frac{D_f}{4\pi R_0^{D_f}} R^{D_f-d} h\left(\frac{R}{\xi}\right) \quad [8]$$

where R is a variable related to the cluster size, d is the spatial dimension, D_f is the fractal dimension, R_0 is the characteristic size of the monomer forming the fractal aggregate, ξ is the characteristic size of the aggregate (correlated to the gyration radius, R_g) and $h(r/\xi)$ is the cut-off function. While different forms of this cut-off function are reported in the literature, most fractals follow the expression:⁴⁸

$$h\left(\frac{R}{\xi}\right) = e^{\left(\frac{-R}{\xi}\right)^\alpha} \quad [9]$$

which was then used as a first approximation for the fit of the A-SAXS curves, initially including α as a fitting parameter. These initial fits led to values of α that were systematically close to 2, and thus the fits were repeated imposing $\alpha=2$ to allow for a better estimate of the error. Equation 9 then becomes a Gaussian cut-off, and consequently:⁴⁷

$$\xi^2 = \frac{4}{D} R_g^2 \quad [10]$$

and the average number of particles in each cluster ($\langle N \rangle$) can be estimated with the Equation:⁴⁷

$$\langle N \rangle = \left(\frac{R_g}{R_0} \right)^{D_f} \quad [11]$$

where the value of R_0 corresponds to the mode of the log-normal NP distribution at each corresponding step of the degradation protocol.

Results and Discussion

Verification of the A-SAXS fitting approach.— As briefly discussed above, the subtraction of two SAXS curves acquired at energies close to and far below the absorption edge of a given scatterer / analyte (i.e., as to tune its form factor, $P(q)$ in Eq. 6) leads to an A-SAXS curve exclusively corresponding to the scattering arising from the element of interest (in our case, the Pt-NPs in these catalysts).^{44,45} Thus, while in a conventional SAXS measurement the different components in the cell and catalyst sample (e.g., support material) would need to be individually measured and normalized prior to the subtraction needed to isolate this component-specific scattering,⁴⁹ this approach yields the same result on the exclusive basis of one measurement at two different energies. To illustrate this method, Figure 2a displays the SAXS curves recorded at X-ray energies of 11.300 and 11.545 keV on the Pt/BP-g electrode prior to its mounting on the electrochemical cell for subsequent *operando* measurements (*vide infra*). The same Figure also includes the background scattering of the SAXS-setup (i.e., of the i_0 -to-detector path schematized in Fig. S1b), which is virtually identical at both probing X-ray energies and features two peaks at ≈ 2.3 and $\approx 4 \text{ nm}^{-1}$ that we assign to the flight tube's Mylar windows placed close to the sample.

Figure 2b features the A-SAXS curves resulting from the subtraction of the energy-dependent SAXS recorded on the dry electrodes of both catalysts (Pt/V, Pt/BP-g), and includes their corresponding fits (in the q -range of $0.3 - 3 \text{ nm}^{-1}$ – see the experimental section for details) assuming that the scattering Pt-NPs are spherical and with their diameters distributed along a log-normal trend. Note that all other A-SAXS curves and corresponding fits are reported in the Supporting Information (Figs. S4 and S5) As in previous studies in which Pt/C A-SAXS curves were fitted through a similar approach,⁵⁰⁻⁵³ its validity was verified by comparing the particle size distributions (PSDs) derived from such fits to the ones obtained by counting > 200 spherical-shaped nanoparticles in transmission electron microscopy (TEM) measurements of the raw catalyst powders (cf. Supporting Information Figure S6 and S7). The good agreement among the PSDs derived from these two approaches is illustrated in Figures 3a and 3b (for Pt/BP-g and Pt/V, respectively), and additionally implies that the processing of the catalysts into electrodes for *operando* measurements did not significantly alter the size and distribution of their Pt-NPs (estimated on the basis of the SAXS measurements). Moreover, the comparison among A-SAXS-derived PSDs for the dry electrodes of both catalysts (cf. Fig. 3c) unveils that the Pt/V catalyst features a narrower distribution and smaller average diameter than the Pt/BP-g sample, from which one would expect this Pt/V catalysts to display a greater (electrochemical) surface area (see discussion below).

Catalyst layer utilization in the operando electrochemical cell.— Prior to the *operando* SAXS and XAS measurements, we quantified the extent of utilization of the catalyst layers (CLs) in the electrochemical flow cell used for this purpose – a crucial aspect to assure that all subsequent spectroscopic results are fully representative of the catalyst's behavior, but that to the best of our

knowledge is often overlooked in *operando* electrochemical studies despite the frequent need for high loading (i.e., thick) electrodes for which full utilization is far from trivial. For the Pt/C catalysts used herein,⁵⁴ the utilization in the *operando* flow cell can be estimated by comparing their electrochemical surface area (ECSA, see Experimental Section) in this electrode configuration with the one determined in separate electrochemical measurements with an ultra-thin catalyst layer for which full utilization can be assumed, e.g., in thin-film RDE measurements in which the catalyst layer thickness (t_{CL}) remains $\ll 1 \mu\text{m}$.³⁸

With this motivation, we performed preliminary voltammetric measurements (at room temperature) on both Pt/C catalysts in the flow cell and thin-film RDE configurations (with loadings of ≈ 1000 vs. $\approx 17 \mu\text{g}_{\text{Pt}} \cdot \text{cm}_{\text{geom}}^{-2}$, respectively) and compared the cyclic voltammograms (CVs) and derived ECSA values in each electrochemical setup. Interestingly, the overlay of the CVs normalized with respect to the catalyst mass (differing ≈ 60 -fold between thick CLs flow cell and thin film RDE measurements) provides a first, qualitative confirmation of the excellent utilization of both catalysts when processed into high-loading CLs and implemented in the *operando* flow cell (see Figures 4a and 4b). This extent is quantitatively confirmed upon comparison of the ECSA values averaged on the basis of several independent measurements (cf. Table 1), which reveal that both catalysts display similar electrochemical areas of ≈ 65 vs. $\approx 70 \text{ m}_{\text{Pt}}^2 \cdot \text{g}_{\text{Pt}}^{-1}$ (for Pt/V vs. Pt/PB-g, respectively). Moreover, the agreement between flow cell- and RDE-derived ECSA values validates the procedures followed to quantify the catalyst loading in our electrodes (further discussed below) and for their initial electrochemical conditioning in the flow cell (detailed in the Experimental Section).

On the other hand, these similar ECSA values contradict the A-SAXS-derived particle size distributions discussed above (see Fig. 3c), whereby Pt/V displays a narrower NP-size

distribution from which one would also expect a larger, specific Pt surface area (SA). Analogously to the expression used to derive SA on the basis of PSDs derived from multiple nanoparticle counts in TEM measurements,^{29,30} the specific surface area corresponding to the NP-distributions estimated through the A-SAXS fits can be calculated with the Equation:

$$SA = \frac{6 \langle D^2 \rangle}{\rho \langle D^3 \rangle} \quad [12]$$

where ρ is the density of platinum ($21.45 \text{ g}\cdot\text{cm}^{-3}$), and $\langle D^2 \rangle$ and $\langle D^3 \rangle$ are the second and third-moments of the log-normal PSD, respectively. The corresponding SAs are listed in Table 1, and account to 92 vs. $107 \text{ m}_{\text{Pt}}^2\cdot\text{g}_{\text{Pt}}^{-1}$ for Pt/BP-g vs. Pt/V, thus confirming that the latter catalyst with a narrower PSD and smaller $\langle D \rangle$ also displays a greater specific surface area. As we will discuss below, the combination of similar ECSA values with differing SAs for these two catalysts leads to a mismatch in the proportionality among these variables (whereby ECSA/SA accounts to ≈ 0.8 vs. ≈ 0.6 for Pt/BP-g vs. Pt/V) that is related to their differing extents of NP-agglomeration.

Verification of the CLs' initial Pt-content and operando changes in the PSD.— Having validated our A-SAXS fitting procedure and the complete utilization of the CLs in the electrochemical cell, we proceeded to study the *operando* potential stability of Pt/V and Pt/BP-g by combining SAXS and XAS. As described in the Experimental Section, the degradation protocol consisted of 250 potential cycles between 0.5 and 1.5 V vs. RHE, whereby XAS, SAXS and ECSA-derivation voltammetric measurements were performed at various stages. Combined measurements were completed on one electrode of each catalyst (i.e., Pt/V, Pt/BP-g) with the electrochemical cell thermostated at a temperature of 60 °C, close to the customary operative

condition of PEFCs ($\approx 80\text{ }^{\circ}\text{C}$) and that should maximize the chances for potential-induced corrosion of the carbon support.⁵⁵

At this stage we must note that, while the electrochemical tests used to validate the CL-conditioning procedure and to estimate its utilization were conducted using flow cell electrode catalyst loadings of $\approx 1000\text{ }\mu\text{g}_{\text{Pt}}\cdot\text{cm}_{\text{geom}}^{-2}$ (see the section above), the *in situ* XAS and SAXS measurements described in the following were performed with larger loadings of $\approx 1600\text{ }\mu\text{g}_{\text{Pt}}\cdot\text{cm}_{\text{geom}}^{-2}$ that should result in higher-quality XAS-data (whereby all masses were estimated through the microbalance method described in the Experimental section). As discussed in the Supporting Information, this Pt-loading can also be inferred from the XAS and SAXS data (cf. Eqs. S18 and S24, respectively), and the corresponding values estimated through each technique for the two Pt/C electrodes tested with the combined setup are listed in Table 2. Upon averaging of the values calculated through each of these three approaches, the Pt-loadings amount to 1.6 vs. 1.4 $\text{mg}_{\text{Pt}}\cdot\text{cm}_{\text{geom}}^{-2}$ for Pt/BP-g vs. Pt/V, respectively, and the standard deviations only constitute ≈ 10 vs. $\approx 20\%$ of the corresponding average values. Additionally considering that the combined, overall masses of catalyst and ionomer ($\approx 0.7\text{ mg}$) account for $\approx 1/100^{\text{th}}$ of the electrode substrate's weight ($\approx 60\text{ mg}$), the excellent agreement among the values estimated through these three approaches validates the procedure used to estimate the Pt-loading on the basis of the electrode weighing described in the Experimental section (see Eq. 1). Moreover, this consistency among loading-determination approaches further endorses the fractal aggregate model used for the fitting of the A-SAXS curves, since the absolute value of the Pt-loading is the most sensitive parameter extracted from A-SAXS analysis, which is highly dependent on the precision of the A-SAXS fitting model.

Having verified the electrodes' loadings, the subsequent evolution of the A-SAXS-derived PSDs upon potential cycling is displayed in Figures 5a and 5b (for Pt/BP-g and Pt/V, respectively); in agreement with previous studies in which the changes in the Pt-NPs distribution were assessed using *in situ* A-SAXS^{50-52,56,57} or *post mortem* TEM,²⁹⁻³² the PSDs for both Pt/C materials become broader and shift towards larger average diameters as the number of potential cycles increases – a result of the potential-induced dissolution of surface Pt atoms in smaller NPs and their re-deposition onto larger ones, often referred to as electrochemical Ostwald ripening.^{23,26} Moreover, upon comparing the cycle-dependent evolution of the $\langle D \rangle$ values extracted from these PSDs and plotted in Fig. 5c, the average NP-growth rate over the first 50 cycles is significantly faster for the catalyst with the smaller initial particle size, i.e., $\approx 11 \cdot 10^{-3}$ vs. $\approx 7 \cdot 10^{-3}$ nm·cycle⁻¹ for Pt/V vs. for Pt/BP-g (with initial average diameters of 2.4 vs. 2.7 nm, respectively). This observation is qualitatively consistent with previous results on platinum NPs^{56,58} and single crystals,⁵⁹ for which the dissolution rates leading to this NP-growth can be up to two orders of magnitude greater for low-coordinated surfaces (more abundant in smaller particles) than for Pt{111}. On the other hand, resembling voltammetric degradation experiments in a liquid electrolyte cell⁵⁰ have reported a growth rate of $\approx 8 \cdot 10^{-3}$ nm·cycle⁻¹ (in the first 40 degradation cycles at room temperature) for a Pt/C catalyst with a smaller initial average diameter ($\langle D \rangle_0$) of 2.2 nm, which is lower than the $\approx 11 \cdot 10^{-3}$ nm·cycle⁻¹ observed herein for Pt/V with $\langle D \rangle_0 = 2.4$ nm – an apparent inconsistency that can be related to the higher temperature at which our measurements were conducted, and/or to the higher upper inversion potential used in this study (1.5 V vs. RHE, vs. 1.1 V vs. RHE in Ref. 50), since both of these variables are known to accelerate Pt-dissolution and -growth.^{50,51,60,61}

Following these initial 50-100 potential cycles, $\langle D \rangle$ reaches values ≥ 3.1 nm for both catalysts and their corresponding NP-growth rate decreases to $\approx 2 \cdot 10^{-3}$ nm $\cdot$ cycle $^{-1}$. As above, this slowing of the NP-growth is consistent with previous *in situ* A-SAXS results,⁵¹ whereby the size increase in liquid electrolyte was in the order of $\approx 0.4 \cdot 10^{-3}$ to $\approx 0.6 \cdot 10^{-3}$ nm $\cdot$ cycle $^{-1}$ (at room temperature vs. 80°C, respectively, and cycling the potential between 0.6 and 1.0 V vs. RHE). Moreover, the growth rate in this second regime agrees even better with the value of $\approx 1 \cdot 10^{-3}$ nm $\cdot$ cycle $^{-1}$ derived from *in situ* pair distribution function measurements of a Pt/C catalyst with $\langle D \rangle_0 \approx 3$ nm in an operative PEFC at 80 °C (cycling in the 0.6-1.2 V vs. RHE range at 100 mV $\cdot$ s $^{-1}$).⁶² As before, the ≈ 2 -to-4-fold differences among growth rate values in the above studies^{51,62} and our measurements are assigned to the higher upper potential window and/or the greater temperature at which these experiments were conducted, which favor Pt-dissolution and concomitant NP-growth.

Potential-dependent evolution of the ECSA and of the extent of NP-agglomeration.— Having used A-SAXS and XAS to estimate the CLs' initial Pt-contents, PSDs and $\langle D \rangle$ s, we now focus our attention on the cycle-dependent evolution of the electrochemical surface area, which can be estimated on the basis of the CVs recorded at different stages of the degradation protocol and plotted in Figures S8a and S8b (for Pt/BP-g and Pt/V, respectively). At this stage, we must note in passing that the initial (i.e., 0 cycles) voltammograms for both catalysts are not fully developed and, in the case of Pt/BP-g, the corresponding ECSA listed in Table 1 and Figure 6a is ≈ 15 % below the value measured by the RDE measurement where the electrodes were fully-utilized (i.e., the initial utilization for the Pt/BP-g electrode remains at a very respectable ≈ 85 %). On the other hand, both catalysts undergo further conditioning in the course of the first

25 degradation cycles and, as a result, all subsequent CVs display the characteristic features expected for Pt/C electrodes within this potential window and electrolyte. Following this concomitant increase of the ECSA, in the course of the subsequent 225 cycles the catalysts' electrochemical surface area drops to $\approx 50 \text{ m}_{\text{Pt}}^2 \cdot \text{g}_{\text{Pt}}^{-1}$, which is fully consistent with the $\approx 25 \%$ ECSA-loss observed for a similar Pt/C catalyst with an initial surface area of $\approx 70 \text{ m}_{\text{Pt}}^2 \cdot \text{g}_{\text{Pt}}^{-1}$ in Ref. 57. Interestingly, these matching trends are insensitive to the ≈ 5 -fold difference in electrode Pt-loadings (and corresponding CL-thicknesses) among studies, implying that the mechanism of ECSA decrease is not affected by microscopic diffusion (which would be slower for a thicker CL, *vide supra*) and instead corresponds to nanoscale-relevant Ostwald ripening, as previously concluded in the above study.⁵⁷

Complementarily to these ECSA-change trends, the catalysts' specific surface areas (i.e., derived from the A-SAXS PSDs) can be estimated using Eq. 12 and appear plotted in Figure 6b, where the cycle-dependent SA-losses appear to mirror those observed for the corresponding ECSA-values. As briefly discussed above, the differences between the Pt-NPs' electrochemical and specific (i.e., A-SAXS-derived) surface areas stem from the fractions of these nanoparticles that cannot contribute to the electrochemical measurement from which the ECSA is derived. This effect is in terms related to facets of these NPs' surfaces that are unexposed to the electrolyte, either because they act as the anchoring interfaces among the nanoparticles and the carbon support, or because they are in contact with other NPs when these form agglomerates. In this respect, extended potential cycling is expected to aid crystal migration and concomitant Pt-NP agglomeration (i.e., coalescence)²³ – an ECSA-loss mechanism for which the occurrence in the PEFC environment remains under debate,²³ but that has been confirmed to take place in aqueous medium using identical-location TEM.^{31,32}

To verify the impact of such agglomeration effects on our results, we used the quotient between the ECSA and the A-SAXS-derived surface area as a quantitative indicator of the extent to which the geometrically-available surface area is electrochemically utilized. This quotient is therefore denoted as “Utilized SA” in Figure 6c, whereby its evolution along the potential cycling protocol is plotted for both Pt/C catalysts. Interestingly, the fraction of this electrochemically-available SA increases upon cycling for both catalysts, indicating a net decrease of the fraction of Pt-surface used to anchor NPs or as contact points within NP-agglomerates – thus, while these trends do not discard the possible migration of NPs and formation of new agglomerates discussed above,^{23,31} the impact of this mechanism on the ECSA is outweighed by the overall fade in anchoring and inter-agglomerate contact surfaces. In fact, the increase of utilized SA with potential cycling could result from Ostwald ripening-induced coalescence of initial Pt-NP agglomerates into compact, single and large Pt-NPs due to dissolution/redeposition cycles. Whereas in each initial agglomerates, all the Pt-NPs constituting it are separately and individually resolved within the spherical particle model used for A-SAXS data fitting, the final, single and large Pt-NP resulting from this dissolution and re-deposition process is only counted as one spherical particle in the A-SAXS data fitting, resulting in a larger utilized SA. Moreover, the increase in the SA-utilization in the initial 50-100 cycles is significantly steeper for Pt/V vs. Pt/BP-g, which is in line with the trends in average NP-diameter growth presented in Figure 5c and points at Pt-dissolution as the common origin for $\langle D \rangle$ -increase and this reduction in NP-agglomeration / surface anchoring extent.

Furthermore, the specific role of NP-deagglomeration due to coalescence into single, large Pt-NPs hinted by this analysis can be further studied on the basis of the A-SAXS results, taking advantage of the structure factor related parameters (defined in Eqs. 6 to 11) and derived from

the fitting of the anomalous scattering curves. These are plotted in Figure 7, whereby the electrochemically conditioned catalysts (i.e., at 0 degradation cycles) display ≈ 2 -fold differences in their initial gyration radius values (of ≈ 3 vs. ≈ 5.5 nm for Pt/BP-g vs. Pt/V, cf. Fig. 7a). To contextualize these values, Fig. 7b displays the initial and cycle-dependent fractal dimensions of both catalysts; for Pt/BP-g (for which $D_{f,initial}=1.75$), the agglomerates are first arranged in *quasi*-bidimensional patterns (e.g., as n^2 NPs distributed along an $n \times n$ planar arrangement that would correspond to a D_f value of 2), whereas Pt/V's initial fractal dimension close to unit ($D_{f,initial}=1.3$) points at a preponderance of *quasi*-1D, linear aggregates. Equation 11 then allows deriving the average number of individual NPs forming each cluster, which is ≈ 4 -5 for the planar agglomerates in Pt/BP-g and ≈ 6 -7 for the linear ones in Pt/V (see Fig. 7c). This analysis agrees well with the two distinct kinds of cluster geometries (i.e., planar vs. linear) observed by TEM in each of these Pt/C catalysts and displayed in Supporting Information Figures S6 and S7.

Looking at the effect of potential cycling on these variables, the slight decrease of D_f observed for Pt/V (Fig. 7b) implies that the clusters in this catalyst remain linear, if undergoing a ≈ 2 -to-3-fold decrease in the number of nanoparticles that constitute them (Fig. 7c). On the other hand, the fractal dimension decreases to ≈ 1.5 for Pt/BP-g, indicating that a fraction of the catalyst's clusters evolve from their initially planar morphology into a linear shape. This is also accompanied by a slighter $\langle N \rangle$ -decrease, which reaches a final value of ≈ 2 NPs per cluster that would explain the evolution into a linear agglomerate morphology. Most importantly, the overall decrease of the NP agglomeration extent inferred from these A-SAXS-fitting variables (see A-SAXS curves and corresponding fittings in Figs. S4 and S5) is in excellent agreement with the above discussion of the SA-utilization (cf. Fig. 6c) which, unlike this analysis, did not allow

discriminating the partial contributions of NP-to-support vs. NP-to-NP contact interfaces to the estimated utilization values.

Relating A-SAXS-derived average NP-diameters and XAS-inferred Pt-Pt bond distances.— In principle, the $\langle D \rangle$ values derived from the A-SAXS curves fitting presented above could also be inferred from complementing XAS measurements by taking advantage of the number of nearest neighbors (NNs) derived from the fitting of the Fourier-transformed EXAFS spectra. More precisely, for spherical NPs like the ones in these Pt/C catalysts,^{63,64} their shape can be approximated to a truncated cuboctahedron for which the NP-diameter-dependent NN can be estimated using, e.g., the equation sets formulated by Benfield.⁶⁵ Practically speaking, though, the sensitivity of XAS to all Pt atoms and the approximate proportionality among the number of these and $\langle D \rangle^3$ implies that the larger particles in a given size distribution have a greater weight on this EXAFS-derived NN, which as a result leads to overestimated $\langle D \rangle$ values.⁶⁶ Additionally, the EXAFS equation displays a large correlation between NN and the amplitude reduction and Debye Waller factors that leads to large errors upon determination of the number of nearest neighbors.

Alternatively, several studies have reported a greater accuracy correlation between the average NP-sizes and the Pt-Pt bond distances that can also be obtained from EXAFS-fitting⁶⁷⁻⁶⁹ (or, e.g., through electron diffraction measurements).^{70,71} Inspired by such works, we proceeded to fit the Fourier-transformed *operando* EXAFS acquired for both Pt/C catalysts along the potential-cycling protocol; an exemplary fit is shown in Fig. 8a, while all other results and corresponding fitting parameters are displayed and summarized in the Supporting Information (see Figures S9/S10 and Tables S1/S2, respectively). When the resulting Pt-Pt bond distances are plotted

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3 against the A-SAXS-derived $\langle D \rangle$ values (cf. Fig. 8b), the data sets for both catalysts display a
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5 similar, *quasi*-linear trend, whereby the lattice parameter increases by $\approx 9 \cdot 10^{-3} \text{ \AA} \cdot \text{nm}^{-1}$ within the
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7 2.4-3.8 nm diameter range covered by the voltammetrically conditioned and degraded NPs
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9 considered herein. Moreover, when considering the above-cited studies (in which $\langle D \rangle$ was
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11 estimated through TEM measurements),⁶⁷⁻⁷¹ our results match the diameter vs. bond length trend
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13 established over a significantly wider $\langle D \rangle$ range of ≈ 1 to ≈ 9 nm (see Fig. 8c), further
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15 confirming the validity of this correlation among variables and the applicability of the lattice
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17 parameter/bond length to predict the average NP diameter.
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24 *Particle size effect on CV- and XAS-derived surface Pt-oxide coverage.*— To finalize our study,
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26 we highlight the complementary information provided by these *operando* techniques by
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28 attempting to correlate the cycle-dependent, A-SAXS derived particle size with the extent of Pt-
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30 surface oxidation, which can be inferred from fine differences in the shape of the XANES' white
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32 line (*vide infra*) and further verified using the electrochemical data. In this context, previous
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34 electrochemical studies^{54,72} have established that the onset in the formation of surface Pt-oxides
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36 shifts towards higher potentials as the nanoparticle size increases (i.e., for a given potential, the
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38 extent of oxide coverage is lower for larger vs. smaller Pt-NPs). Chiefly, surface blockage by
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40 these oxides hinders the reactivity of the reduced Pt-surface for the O_2 -reduction reaction⁷³
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42 (which constitutes a major bottleneck for PEFC development),^{27,28,39} and the above discussed
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44 NP-size vs. coverage relation leads to a particle size effect on the ORR-kinetics, whereby larger
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46 particles and extended surfaces are up to ≈ 10 -fold more active (per Pt-surface area) than NPs
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48 ≤ 2 nm in diameter.^{54,72,74}
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Interestingly, previous *operando* A-SAXS studies have attempted to establish the extent of Pt-surface oxidation by comparing the differences in PSDs and corresponding $\langle D \rangle$ values induced by holding the potential at values at which the surface should remain reduced or (partially) oxidized;^{12,50} specifically, potential holds at 1.1. or 1.3 V vs. RHE reportedly led to particle growths by ≈ 7 vs. ≈ 4 Å induced by the formation of surface Pt-oxides in References 12 vs. 50, respectively. Leaving aside the inconsistencies among potentials and oxide layer thicknesses between these studies,^{12,50} we did not observe a significant shift of the PSDs and $\langle D \rangle$ s derived from A-SAXS measurements performed at reductive and oxidative potentials of 0.45 vs. 0.95 V vs. RHE (see Experimental Section for details). To explain these results, one must consider that the change in the Pt-NPs scattering reported in Refs. 12 and 50 is likely a result of a place exchange between Pt- and O-atoms, whereby the former substitute the latter in the sub-surface, and Pt segregates to the immediate surface.^{75,76} This would be consistent with the potentials ≥ 1.1 V vs. RHE needed in order to trigger place exchange among surface Pt- and O-atoms,^{77,78} which would lead to the changes in Pt-specific A-SAXS scattering reported in Refs. 12 and 50 (at 1.1. vs. 1.3 V vs. RHE, respectively), and justify the lack of changes in our own experiments (at a potential of 0.95 V vs. RHE at which place exchange is irrelevant).

Alternatively, the extent of surface oxidation can be inferred from the Pt L_3 -XANES, which results from electron transitions from occupied $2p_{3/2}$ core states to empty ones in the 5d shell, and for which the white line intensity is therefore proportional to the number of unoccupied 5d states (i.e., it increases with the sample's extent of oxidation).⁷⁹ This effect is observed in Figure 9a, which features a comparison of the normalized XANES spectra recorded while holding the electrochemically conditioned (i.e., "0 cycles") Pt/V electrode at 0.45 vs. 0.95 V vs. RHE – as better resolved in the magnification in Fig. 9b, the white line maximum at $\approx 11,567$ eV is up-

shifted for the spectrum recorded at 0.95 V vs. RHE, confirming the sample's greater oxidation extent at this potential. Moreover, taking advantage of this sensitivity, Ramaker and collaborators proposed to use the difference between Pt L₃-XANES recorded at potentials at which the Pt-surface should remain reduced or oxidized (customarily referred to as “ $\Delta\mu$ ”) as an indicator of the extent of surface oxidation.^{63,80-82} Following this approach, Supporting Information Figure S11 displays the result of this subtraction (i.e., on the basis of the XANES recorded at 0.45 and 0.95 V vs. RHE) at different stages along the degradation protocol, and the maxima of these $\Delta\mu$ XANES spectra ($\Delta\mu_m$) appear plotted against the corresponding cycle number in Fig. 9c. Interestingly, the magnitude of $\Delta\mu_m$ for the conditioned sample (≈ 0.06) is slightly below the values of ≈ 0.08 , ≈ 0.1 and ≈ 0.13 reported in Refs. 81, 82 and 83, possibly due to the higher applied potentials and/or greater catalyst's ECSAs in the above-cited studies, which should translate into larger oxide coverages (*vide infra*). Beyond this point, the decrease of $\Delta\mu_m$ with the cycle number seemingly confirms the above discussed relation between oxide coverage and $\langle D \rangle$,^{54,74} whereby larger particle sizes (i.e., higher cycle numbers, cf. Fig. 5c) lead to a lower oxidation extent for a given potential. However, one must bear in mind that, due to the great penetration depth of the X-rays used, the sensitivity of XAS to surface processes like this passivation becomes poorer as the size of the probed NPs increases, and thus a part of the decrease of the magnitude of $\Delta\mu_m$ is caused by the larger particle sizes.⁸⁴ To account for this effect, $\Delta\mu_m$ can be regarded as a combination of a surface-sensitive magnitude ($\Delta\mu_{\text{surface}}$) exclusively proportional to the adsorbate's (i.e., oxide) coverage, and an r function corresponding to the ratio between the surface- and total-number of Pt-atoms:

$$\Delta\mu_m = \Delta\mu_{\text{surface}} \cdot r \quad [13]$$

whereby the value of r at different stages of the degradation protocol can be estimated on the basis of the corresponding $\langle D \rangle$ (cf. Fig. 5c), assuming a truncated cuboctahedron morphology to estimate the surface-to-total number of atoms using the equation sets in Ref. 65 (see Supporting Information Figure S12 and Table S3 for details). The surface-specific values of $\Delta\mu_{\text{surface}}$ estimated with this approach are also plotted in Fig. 9c, and confirm the expected decrease of the oxide coverage at larger particle sizes reported in the literature (cf. Fig. 9d).^{53,72}

Finally, the surface specificity of $\Delta\mu_{\text{surface}}$ can be verified by comparing this magnitude to the electrochemical oxide coverage extent estimated on the basis of the oxide reduction charge between 0.95 and ≈ 0.5 V vs. RHE in the CVs in Fig. S8b. Assuming that the oxides formed up to this potential preponderantly correspond to PtOH (i.e., a one-electron oxidation process),⁸⁵ this charge can be transformed into an oxide coverage value (θ_{ox} in Fig. 9e) by normalizing it with respect to the corresponding H_{upd} charge derived from the same voltammograms. Figure 9e confirms the expected relation between θ_{ox} and $\Delta\mu_{\text{surface}}$, whereby small deviations from linearity are likely caused by differences in the nature of these surface oxides (e.g., partial PtO formation), which likely depend on the surface coverage and particle size (*vide supra*) and, due to their different XANES spectra,⁸⁶ can in terms affect the magnitude of $\Delta\mu$. Most importantly, this relation validates the use of this particle-size corrected, surface-specific $\Delta\mu_{\text{surface}}$ parameter as a quantitative indicator of surface coverage, which can be extremely useful for other systems for which this property cannot be verified under *operando* conditions taking advantage of standard electrochemical tools (e.g., for metallic oxides for which their CVs are absent of features relatable to their degree of dispersion and oxidation state).⁸⁴

Conclusions

In this manuscript, we presented a novel, combined A-SAXS and XAS setup in which flight tube and ion chambers are mounted on a movable stage, which allows (to the best of our knowledge, for the first time) to acquire both XAS and A-SAXS within a couple of minutes and without compromising signal quality in either of these techniques. The validity of this combined setup was verified by studying the potential cycling induced degradation of two different kinds of Pt/C catalysts, extensively discussed in the literature and crucial to PEFC development. *Ex situ* HRTEM and standard electrochemical measurements allowed to validate the A-SAXS data treatment approach used to determine the particle size distributions, and confirmed the complete utilization of the highly loaded Pt/C electrodes used in the *operando* measurements. The cycle-dependent trends in particle growth and ECSA decrease are in excellent agreement with previous literature reports; moreover, the novel introduction of a Gaussian mass fractal structure factor in the modeling of the A-SAXS curves allowed to study the evolution of the Pt-clusters, which undergo a decrease of their agglomeration extent in the course of the degradation protocol. Additionally, the observed relation between the average diameters derived from the A-SAXS fits and the corresponding Pt-Pt bond distances estimated from the EXAFS fits also agree with previous reports, and validate the use of the latter XAS-derived parameter as an indicator of the average NP-size. Finally, the extent of surface oxidation derived from the changes in the shape of the XANES spectra (i.e., $\Delta\mu$) was shown to be inversely correlated with the A-SAXS-derived particle diameter, and to follow a quasi-linear relation with the oxide coverage estimated on the basis of *operando* electrochemical measurements.

Ultimately, the results derived from this work highlight the complementary information that can be inferred by combining these two techniques, and render this setup particularly attractive

for the study of (electro)catalytic systems in which the changes in NP-morphology and dispersion cannot be inferred in the course of the *operando* measurements (e.g., for the metal oxides extensively studied for the electrocatalysis of the O₂-evolution reaction).

Supporting Information

Detailed description of the procedure followed to report the scattering curves as cross sections per area using a glassy carbon standard (Figures S1 and S2), as well as the calculation of the solid angle correction (Figure S3). Full sets of *in situ* A-SAXS curves and corresponding fits for both catalysts (Figures S4 and S5). Determination of the electrodes' initial loadings on the basis of the A-SAXS and XAS results. High-resolution transmission electron microscopy images of both catalyst powders and of samples of the corresponding electrodes at the end of the *operando* degradation tests (Figures S6 and S7). Cyclic voltammograms in the course of the degradation protocols for both catalysts (Figure S8). *In situ*, Fourier-transformed EXAFS and corresponding fits during the degradation tests for both catalysts (Figures S9 and S10), along with the tabulated parameters derived from these fits (Tables S1 and S2). Difference XANES ($\Delta\mu$) spectra for the Pt/V electrode in the course of the degradation test (Fig. S11). Detailed procedure followed to estimate the surface-to-total-number of atoms as a function of the nanoparticle diameter (Figure S12 and Table S3).

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Table 1. Summary of the catalysts' electrochemical surface area (ECSA) values derived from cyclic voltammetry measurements (cf. Fig. 4) in a standard glass cell (with $\approx 17 \mu\text{g}_{\text{Pt}} \cdot \text{cm}_{\text{geom}}^{-2}$) or in the flow cell used for *operando* XAS and SAXS measurements (with ≈ 1000 vs. $\approx 1500 \mu\text{g}_{\text{Pt}} \cdot \text{cm}_{\text{geom}}^{-2}$ for the tests at room temperature vs. 60°C , respectively – cf. Table 2 for detailed loadings in the latter condition). Numbers between parentheses refer to the repetitions (i.e., independent measurements on different electrodes) that were performed to derive the (averaged) ECSA values. The *operando* ECSAs at 60°C are the values at the beginning of the XAS and SAXS degradation experiments (i.e., after electrochemical conditioning – referred below as “0 cycles”), and are calculated using the average loadings listed in Table 2.

		ECSA [#] ($\text{m}_{\text{Pt}}^2 \cdot \text{g}_{\text{Pt}}^{-1}$)		
	SA* ($\text{m}_{\text{Pt}}^2 \cdot \text{g}_{\text{Pt}}^{-1}$)	Standard electrochemical cell	<i>Operando</i> flow cell	
		Room temperature	Room temperature	60°C
Pt/BP-g	92	70 ± 8 (3)	71 ± 4 (2)	58 (1)
Pt/V	107	63 ± 13 (3)	65 ± 3 (2)	68 (1)

*Estimated on the basis of the A-SAXS-derived particle size distributions of the dry electrodes (cf. Fig. 3) using Eq. 12. [#]Calculated on the basis of the hydrogen underpotential deposition charge in cyclic voltammograms recorded in the specified cell configurations and temperatures, and the corresponding electrode Pt-masses estimated through the electrode weighing method presented in the Experimental section (for measurements at room temperature; cf. Eq. 1), or additionally averaged on the basis of the XAS- and SAXS-derived values listed in Table 2 (for 60°C measurements).

Table 2. Initial Pt-loadings of the flow cell electrodes used in the *operando* SAXS and XAS measurements at 60 °C, estimated using the microbalance method described in the Experimental section (cf. Eq. 1) or on the basis of the XAS and A-SAXS results (see Equation S18 and S24 in the Supporting Information, respectively).

Pt-loading [$\mu\text{g}_{\text{Pt}}\cdot\text{cm}_{\text{geom}}^{-2}$]				
	Microbalance	XAS	A-SAXS	Average
Pt/BP-g	1620	1320	1750	1600 ± 200
Pt/V	1620	1120	1520	1400 ± 300

Figure 1. Schematic representation of the combined SAXS and XAS setup, whereby the gas ionization detectors i_1 and i_2 and an energy-calibration standard (*Reference* – herein, a piece of Pt-foil) are mounted parallel to the flight tube, and all four elements are set on a motorized stage that can be moved perpendicular to the beam direction as to transition among techniques in ≈ 2 min. For the XAS part of the experiments, and following the X-ray beam-path from left to right, the incident X-ray intensity is first determined in a gas ionization detector (i_0), followed by the absorbent /scatterer analyte accessorially mounted in an electrochemical flow cell for *operando* measurements and gas ionization detectors i_1 and i_2 , which quantify the intensity of the attenuated beam prior to and after absorption through the Pt-foil reference, respectively. For SAXS, the table is moved perpendicular to the beam direction and the scattered signal travels through a 580 mm long flight tube (evacuated to $\approx 10^{-3}$ mbar) and is projected on a planar, 2D-detector protected by a beam-stopper. To maximize the detection area, the incoming beam and stopper are placed close to one of the 2D-detector's lateral edges (see schematic representation and scattering profile of a silver behenate standard in the right-hand insert).

Figure 2. SAXS curves of the dry Pt/BP-g electrode (i.e., prior to mounting in the electrochemical flow cell) acquired at X-ray energies of 11.300 and 11.545 keV (solid vs. dashed blue lines, respectively), along with their subtraction (i.e., A-SAXS profile corresponding to the scattering contribution of the catalyst’s Pt nanoparticles alone, solid black line), and the setup background measurement (orange solid line) (a). A-SAXS profiles for dry Pt/BP-g and Pt/V electrodes, whereby the hollow circles represent the results of the A-SAXS subtraction and the solid lines are the corresponding fits to a log-normal nanoparticle distribution (b).

Figure 3. Particle size distributions (PSDs) of the dry Pt/BP-g and Pt/V electrodes (a vs. b), determined from the fittings to a log-normal distribution of the A-SAXS curves in Figure 2b (solid lines), or on the basis of transmission electron microscopy images (> 200 particle counts) of the raw, non-processed catalyst powders (dashed lines). The insert graph (c) displays a comparison of the A-SAXS derived PSDs for both catalyst electrodes.

Figure 4. Comparison of the cyclic voltammograms (CVs) recorded at 10 mV·s⁻¹ on Pt/BP-g or Pt/V electrodes (a vs. b) in a standard three-electrode electrochemical cell (RDE with a loading of $\approx 17 \mu\text{g}_{\text{Pt}}\cdot\text{cm}_{\text{geom}}^{-2}$) or in the flow cell used in the *operando* SAXS and XAS measurements (flow cell with $\approx 1000 \mu\text{g}_{\text{Pt}}\cdot\text{cm}_{\text{geom}}^{-2}$ for both catalysts). All measurements were performed at room temperature and using N₂-saturated 0.1 M HClO₄ as the electrolyte; in the flow cell measurements, electrolyte was circulated at 50 $\mu\text{L}\cdot\text{min}^{-1}$. Currents are normalized on the basis of the Pt-loadings to illustrate the electrode's utilization in the *operando* flow cell.

Figure 5. Effect of the electrochemical potential cycles (0.5 - 1.5 V vs. RHE, $50 \text{ mV}\cdot\text{s}^{-1}$) on the catalysts' PSDs, derived from the fitting of *operando* A-SAXS curves to a log-normal distribution, for Pt/BP-g or Pt/V (a vs. b, respectively). Comparative increase of the catalysts' average nanoparticle diameter (derived from the PSDs in a and b) with the electrochemical cycle number (c).

Figure 6. Evolution of the surface area values derived from electrochemical (ESCA) and SAXS measurements (A-SAXS SA – a vs. b, respectively). The ECSA values in the upper panel are calculated on the basis of the H_{upd} charges of the CVs in Figs. S8a and S8b (within the potential range of ≈ 0.05 to ≈ 0.45 V vs. RHE) and the average mass values in Table 2, while the surface areas in the lower panel are calculated using the log-normal distributions of the particle size in Figs. 5a and 5b. The Utilized SA in (c) is estimated as the quotient between ESCA and corresponding A-SAXS SA values, and represents the fraction of the Pt-NPs’ total surface actually utilized during the electrochemical processes.

Figure 7. Effect of the electrochemical cycle number on the gyration radius (R_g) of the Pt-nanoparticle clusters for both catalysts (a). Corresponding change along the electrochemical cycles of the fractal dimension (D_f) and of the average number of particles per cluster $\langle N \rangle$ (b vs. c, respectively).

Figure 8. Fitting of the k^3 -weighed Fourier transformed EXAFS (R-space uncorrected for phase shifts) of the Pt/BP-g catalyst after electrochemical conditioning and prior to the start of the degradation protocol (a). Change of the 1st shell Pt-Pt bond length derived from the fitting of the EXAFS spectra of both catalysts recorded along the corresponding degradation protocols, as a

function of the average nanoparticle diameter derived from the corresponding A-SAXS measurements (b). In (c), these results are compared to those of Frenkel *et al.* (grey dots) and Lei *et al.* (green dots), who used XAS to derive the bond distance of Pt-based catalysts on various supports and estimated the average particle diameter using transmission electron microscopy,⁶⁶⁻⁶⁸ as well as to the values reported by Wasserman and Vermaak (orange triangle) and Solliard and Flueli (blue triangle), who used TEM to estimate the particle size and electron diffraction to determine the bond distance.^{69,70}

Figure 9. Normalized XANES after electrochemical conditioning and prior to the start of the degradation protocol for the Pt/V catalyst, at two different potentials of 0.45 or 0.95 V vs. RHE (a). The inset in (b) displays a magnification of the white line, illustrating the effect of the potential (i.e., Pt-surface oxidation state) on its magnitude. Effect of the electrochemical cycle number on the magnitude of the subtracted XANES at the spectra's maximum ($\Delta\mu_m$), whereby the data on the right-hand axis are additionally corrected for an r function that accounts for the

change of the ratio of surface-to-total-number of Pt atoms with the average nanoparticle diameter ($\Delta\mu_{\text{surface}}$ – cf. Fig. S12) (c). Evolution of $\Delta\mu_{\text{surface}}$ as a function of the average particle diameter $\langle D \rangle$ (d) and oxide coverage derived from the CVs recorded at each stage of the electrochemical degradation protocol (e), illustrating the decrease in the surface oxide coverage with increasing nanoparticle size.

TOC Abstract Graphic

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