Electrochemical Flow-Cell Setup for In Situ X-ray Investigations

II. Cell for SAXS on a Multi-Purpose Laboratory Diffractometer

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A unique electrochemical three-electrode flow-cell design is presented for in situ small-angle X-ray scattering experiments on a multi-purpose laboratory X-ray diffractometer. An electrolyte layer thickness of 2 mm enables sufficient photon transmission to acquire in situ scattering curves at high signal-to-noise ratio within less than one hour despite the restricted photon flux from a standard Cu X-ray tube. Complete tightness of the cell allows electrolyte flow with controlled gas saturation in order to guarantee constant experimental conditions even for long experimental protocols. Good electrochemical performance is achieved by a special arrangement of working and counter electrodes that are deposited on the opposing X-ray transmission windows of the cell. The functionality and reliability of the cell are demonstrated in an in situ small-angle X-ray scattering study of the degradation properties of carbon-supported Pt nanoparticles during electrochemical high-potential cycling. Careful subtraction of background scattering and absolute normalization of the scattering curves yield absolute quantitative structural information about the Pt nanoparticle phase at different stages of the degradation process, bringing insights into the real-time evolution during electrochemical characterization.

The need for high-efficiency and non-polluting energy conversion technologies for automotive applications has resulted in an increasing interest in polymer electrolyte fuel cells (PEFCs). One critical issue facing the commercialization of PEFCs is the gradual decline in performance resulting in a severe limitation of PEFC lifetime.1,2 One important cause of PEFC performance degradation is the loss of electrochemically active surface area (ECSA) of the supported platinum nanoparticles (Pt-NPs) at the cathode. This ECSA decrease of the cathode catalyst can arise from different degradation mechanisms which take place simultaneously, especially during PEFC start and stop events, when the cathode potential can reach very high transient values up to 1.4–1.5 V _{ReO}_.3 In situ analytical tools are required to gain a better understanding of the phenomena involved and to distinguish between different degradation mechanisms like platinum loss due to dissolution, nanoparticle growth resulting from electrochemical Ostwald ripening or platinum nanoparticle agglomeration due to support material corrosion.4–8

Electrochemical in situ small angle X-ray scattering (in situ SAXS) offers the unique opportunity not only to observe the evolution of the platinum nanoparticle size distribution during an electrochemical degradation experiment, but also to simultaneously monitor the evolution of the absolute platinum mass content of the electrode. In situ SAXS experiments can be conveniently performed at synchrotron X-ray sources.9–11 The high photon flux from these radiation sources yields a very good scattering signal-to-noise ratio in a short acquisition time despite the strong X-ray absorption of the electrolyte layer in transmission geometry. Furthermore, synchrotron SAXS beamlines generally offer a high degree of flexibility at the sample stage of such systems impose major challenges to the engineering of a respective electrochemical in situ cell. Furthermore, the fixed X-ray energy of laboratory X-ray diffractometers requires a different approach for the extraction of the Pt-NP scattering from the overall scattering signal. In Part I,18 we presented the design of an electrochemical three-electrode flow-cell for in situ experiments at synchrotron X-ray sources. This cell was optimized for SAXS and X-ray absorption spectroscopy (XAS) in transmission mode exploiting the high flexibility of beamline sample stages which imposed only minor restrictions on the cell geometry. The electrode geometry was adapted to the point-like cross section of focused synchrotron X-ray beams.

In Part II at hand, we present the design of an electrochemical three-electrode flow-cell for in situ SAXS experiments on a laboratory multi-purpose diffractometer PANalytical. The design was based on the same principles as the SAXS/XAS flow-cell for synchrotron facilities presented in Part I.18 However, the cell was adapted to the strong geometrical constraints defined by the sample holder and the special configuration of the diffractometer. An elongated electrode geometry was required in order to fully utilize the line-shaped X-ray beam of the device. Complete tightness of the cell enabled the usage of electrolytes with controlled gas saturation. Furthermore, the constant electrolyte flow prevented X-ray induced electrolyte degradation and heating. In this way, the system guaranteed constant experimental conditions even during long-term experiments. The in situ SAXS flow-cell was used in order to study the structural degradation of carbon-supported Pt-NPs during an electrochemical experiment that simulates the corrosive conditions during PEFC start/stop events. Extraction of the net Pt-NP scattering was achieved after suitable subtraction of all other scattering contributions. Absolute quantitative information about the structural properties of Pt-NPs was obtained after transformation of the SAXS curves to differential cross sections with the use of a glassy carbon standard.

Experimental

Multi-purpose diffractometer—The diffractometer used to perform the in situ SAXS study was a laboratory X’Pert Pro Multi-Purpose Diffractometer (MPD) PANalytical equipped with a Cu X-ray tube source which delivers 8.05 keV energy photons. SAXS measurements were carried out in transmission mode. The highly-collimated

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monochromatic X-ray beam was produced by using the Göbel mirror, low-angle slits and masks at the incident beam side. At the diffracted beam side a narrow anti-scattering slit was introduced in order to reduce the parasitic scattering. The solid-state linear 1D-detector (PIXcel) was settled in the receiving slit mode for sequential measurements. The geometry of the standard reflection-transmission spinner stage required a precise design of the electrochemical flow-cell with a maximum diameter of only 51.5 mm.

**Transmission flow-cell for laboratory diffractometer.**—The electrochemical flow-cell was designed under the geometric constraints of the sample stage with the working electrode layer precisely located at the sample plane defined by the MPD PANalytical diffractometer in transmission mode. The goal of the cell design was to find an optimum both for the SAXS performance (high signal-to-noise ratio at short acquisition times) and for the electrochemical performance (low residual ohmic resistance with homogeneous current distribution). The cell was made out of PEEK and consisted of a bottom part, a middle part, and a top part. Trimetric projections of the three parts are depicted in Figure 1. Middle and top parts were designed with a smaller diameter than the bottom part in order to allow the use of the MPD sample-holder lift to fix the electrochemical flow-cell. Similarly to the flow-cell presented in Part I, the central hole in the middle part formed the main electrochemical compartment of the cell. It was vertically confined by two X-ray windows out of Kapton foils, one placed in between middle part and top part, and one placed in between middle part and bottom part. A special type of Kapton foil was used (DuPont Kapton 200RS100) that is electrically conductive on one side. Both Kapton windows were placed with their conductive sides facing inwards into the central electrochemical compartment. The porous layer of the studied material (working electrode) was deposited by spray-coating on the conductive side of the bottom Kapton window, which was precisely located in the reference plane of the goniometer. The conductive layer of the opposite top Kapton window served as counter electrode. The thickness of the middle part precisely defined a 2 mm thickness of the electrolyte layer in the central compartment, corresponding to approximately 86% of X-ray absorption. Complete tightness of the cell assembly was guaranteed by O-rings and Teflon tape stripes sealing the central compartment both against the top part and against the bottom part. The electrolyte was flowed through the cell window by asymmetric electrolyte channels with 1 mm diameter that were precisely drilled into the middle part. The
In opposition to the SAXS/XAS flow-cell for synchrotron facilities presented in Part I,18 the size of the current flow-cell was limited with the theoretical transmission of 2 mm water (14% at 8.05 keV19). In this config-uration, the bottom working electrode was contacted via the screw contacts in the top part, and, vice versa, the top counter electrode was contacted via the screw contacts in the bottom part. Small holes in the middle part allowed the contact springs to pass through and directly contact the respective electrodes. However, this concept of contacting the electrodes from opposite sides, respectively, required a special, individual shape of both Kapton electrode substrates in order to let the spring contacts for the opposite electrode pass by (see Figures 3b and 3c). For a precise positioning of the Kapton electrode windows in the cell, landmark lines were engraved into the top part and the bottom part (see Figure 1).

With the aim of improving the electrical conductivity of the conduc-tive Kapton surface, 50–100 nm thick gold layers were sputtered on the conductive Kapton working and counter electrodes in a first step. A longitudinal central region of the electrodes was masked during the sputtering process in order to provide a gold-free window to let the X-ray beam pass without interaction with the gold layers. After the gold coating step, studied materials were spray-coated with the use of masks on top of the central gold-free region of the conductive Kapton substrate forming the working electrode (bottom window). The resulting porous electrode layer had a homogeneous thickness and a similar morphology as PEFC catalyst layers. The shape of the sprayed electrode layer was longitudinal in order to exploit the entire incident X-ray beam (see Figure 3b). The conductive Kapton substrate with the sputtered gold layer provided electrical connection between the sprayed electrode layer at the center and the contact points of the spring contacts. In order to improve the capacity of the counter electrode, two porous layer strips of high surface area carbon were sprayed on both sides of the central gold-free region of the conduc-tive Kapton counter electrode window (see Figure 3c). In this way, the two strips were not in the path of the X-ray beam, thus avoiding background scattering from the porous counter electrode layers. Consequently, the X-ray beam had to pass through the following material layers: Conductive Kapton | 2 mm electrolyte (0.1 M HClO4) | investigated material | conductive Kapton. In this configuration, the X-ray beam incident from the top was attenuated by the electrolyte layer before reaching the investigated material, thus minimizing the radiation dose and possible beam-induced degradation effects (see Results). The ohmic resistance of the overall flow-cell in an electrochemical three-electrode experiment was approximately 10 Ω (determined by high-frequency impedance). The low ohmic resistance guaranteed a good electrochemical performance despite the large loadings of active material in the working electrode layer necessary for minimizing the SAXS acquisition times. A picture of the complete in situ SAXS setup is shown in Figure 2b.

Figure 2. Pictures of the running in situ SAXS setup.

For electrical contact to the working electrode (bottom conduc-tive Kapton) and the counter electrode (top conductive Kapton), gold-coated spring contacts were first pressed into in-house designed PEEK screws (see Figure 3a). The resulting contacts were then screwed into respective holes in the top part and the bottom part. In this config-

Figure 3. Pictures of the spring contact pressed into the PEEK screw (a), the working electrode (b) and the counter electrode (c).
Materials and electrode preparation.— The investigated catalyst material consisted of Pt-NPs supported on Vulcan (Vc) XC-72R carbon (Cabot Corporation). The Pt-NPs were synthesized using a polyol method as described in Ref. 20. The obtained Pt/Vulcan catalyst had a final Pt loading of \(X_{Pt} = 14.5\text{wt} \%\) determined by thermogravimetric analysis (TGA). Electrodes were fabricated with a spray technique using an ink formulation as described for another Pt/C catalyst in Ref. 21. The sprayed porous electrode layers contained 30 wt\% of Nafion ionomer identical to the value for a typical PEFC Pt/C catalyst layer. Masses and thicknesses of the studied electrodes were determined after spray preparation using a laboratory scale and a mechanical stamp, respectively, and are summarized in Table I. These values are relevant for the subtraction of the support scattering. However, mass and thickness measurements at such low levels are relatively imprecise (20–30% relative errors) which explains the differences between the relative scaling of electrode masses and electrode thicknesses for the different Pt/Vc electrodes. The geometric area \(A_{electrode}\) of the sprayed working electrodes was 37 mm\(^2\).

The same in situ SAXS protocol was also performed with a Pt-free Vulcan carbon electrode. These measurements were necessary to realize appropriate support scattering subtraction as described in the Appendix. Also for the purpose of background scattering correction, the SAXS curve of the conductive Kapton/2 mm electrolyte/conductive Kapton stack without active material layer was measured.

Results

As described in Table I, three different Pt-Vc and one Vc electrode, respectively, were investigated. Pt-Vc 1 electrode was used to study possible beam-induced degradation effects. Detailed data analysis was performed for the in situ start/stop degradation studies of the Pt-Vc 2 and Pt-Vc 3 electrodes.

Table II summarizes the results obtained for the Pt-Vc 2 and Pt-Vc 3 electrodes in their initial states. The absolute Pt mass loadings of the electrodes determined from SAXS agree within 20–30% with the values measured by weighing the electrodes after spraying which lies within the relative error of the latter (cf. Experimental section). It can be therefore concluded that the majority of Pt in the catalyst is present in the nanoparticle phase observable by SAXS. Electrochemical Pt surface areas (given in terms of the roughness factors \(RF_{ECSA}\), cf. Appendix) are approximately 20% lower than the surface areas determined by SAXS. This is very plausible, because the surface area from SAXS must be seen as the total surface area of the Pt nanoparticles. Due to the contact with the support, a slightly reduced fraction of this total surface area is accessible for the electrolyte. The same reduction should also affect the mass-specific Pt ECSA. Given a total mass-specific Pt surface area of approximately 120 m\(^2\)/gPt determined from SAXS, a value around 100 m\(^2\)/gPt could be therefore expected from ECSA. The deviations from this value of approximately 20% for both electrodes, once up, once down, can again be explained with the large relative error on the mass value from electrode weighing (cf. Experimental section). Almost perfect agreement between the scaling of the Pt mass values determined by SAXS and the roughness factors determined by ECSA of the two electrodes is found. This shows that full electrochemical utilization of both electrodes was achieved (cf. Experimental section for electrode flooding procedure).

Figure 4a shows the raw scattering curves \(I_{meas}(q)\) acquired during the in situ degradation study of the Vulcan carbon electrode Vc. SAXS curves were measured after 0, 50, 100 and 1000 degradation cycles.
The q-dependent scattered intensities show slight changes. The top right inset reveals that the scattered intensity decreases for increasing numbers of degradation cycles in the 0.1–0.7 nm\(^{-1}\) q-range, which is relevant for the scattering of the primary particles of the Vulcan carbon material. This behavior can be related to the carbon corrosion which occurs at potentials above 0.207 V\(_{\text{SH}}\), according to the reaction:

\[
\text{C} + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{e}^- + 4\text{H}^+ \quad E^0 = 0.207 \text{ V}_{\text{SH}}.
\]

Figure 4b presents the raw scattering curves \(I_{\text{meas}}^{\text{scat}}(q)\) acquired during the beam-induced degradation study of the Pt-Vc 1 electrode. Two scattering bumps are clearly observed. The first bump situated in the 0.3–3 nm\(^{-1}\) q-range corresponds to the scattering of the Pt-NPs, which have an average diameter of 1.8 nm. The second bump located at q around 4–5 nm\(^{-1}\) tallies with the scattering peak of the Kapton foils. This was checked by measuring the scattering of the Kapton foils alone in a separate experiment. The SAXS curves recorded after different irradiation times are superimposed and reveal no changes. It can be therefore concluded that no relevant beam-induced degradation takes place during 7 hours of continuous X-ray irradiation, neither for the Pt-NPs nor for the Vulcan carbon support material.

The raw SAXS curves \(I_{\text{meas}}^{\text{scat}}(q)\) recorded during the in situ start/stop degradation study of the Pt-Vc 2 electrode are shown in Figure 5a. The Pt-NP-related scattering bumps shift to lower q-values with increasing number of degradation cycles. This behavior is a clear signature of the growth of Pt-NPs due to Pt dissolution/re-deposition cycles (electrochemical Ostwald ripening) during potential cycling between 0.5 and 1.5 V\(_{\text{RHE}}\). Net Pt scattering curves extracted from the raw data with the procedure described in the Appendix and associated data fits are plotted in Figure 5b showing that the experimental data was reproduced by the fits with good precision.

The CV curves for ECSA analysis acquired after 0, 100 and 1000 degradation cycles are presented in Figure 6a. Loss of ECSA is clearly visible from the strong decrease of the H-desorption peak in the potential region below 0.4 V\(_{\text{RHE}}\). Figure 6b shows the CV curves of the 1st, the 100th and the 1000th high-potential degradation cycles.

The relative evolutions of the roughness factors determined from SAXS and CV experiments both for the Pt-Vc 2 and for the Pt-Vc 3 electrodes are plotted in Figure 7. A high reproducibility is demonstrated by the two in situ experiments, both of the SAXS results and of the electrochemistry results. Furthermore, within each experiment a good consistency of the relative losses of roughness factors determined by SAXS on the one hand, and by ECSA analysis on the other hand is achieved. After 500 degradation cycles, a roughness factor loss around 70% is observed. Only 18% of the initial roughness factor is remaining after 1000 degradation cycles. The roughness factors after 1000 cycles are missing for the Pt-Vc 3 electrode, because in this experiment the counter electrode delaminated during the 500–1000 degradation cycle interval, most likely because of the higher CV currents due to the thicker Pt-Vc working electrode layer.
The overall decrease of roughness factor can be analyzed in further detail with the help of the evolution of the Pt-NP diameter size distribution $D_{Pt}(N_{Pt})$ together with the total number of Pt-NPs per electrode area $N_{Pt}$ and the absolute Pt mass per electrode area $m_{Pt}$. Pt-NP size distributions at different stages of the electrochemical protocol are depicted in Figure 8a for the Pt-Vc 2 electrode. As qualitatively already found from the analysis of the SAXS scattering curves, the size distributions demonstrate a particle growth with increasing number of degradation cycles. The distributions become broader and shift to larger particle sizes and the average diameter of the Pt-NPs increases from 1.8 nm in the initial state up to 4.2 nm after 1000 degradation cycles. This behavior is consistent with Pt-NP growth by the electrochemical Ostwald ripening phenomenon, where the smaller Pt-NPs are preferentially dissolved during potential cycling at high potentials and the resulting Pt ions are preferentially re-deposited on the larger Pt-NPs at low potentials.

Figure 8b presents the evolution of the average Pt-NP diameter $D_{average}^{Pt}$ (squares) together with the relative evolutions of $N_{Pt}$ (down triangles) and $m_{Pt}$ (circles). The number of Pt-NPs quickly decreases at the beginning of the in situ degradation study. In fact, $N_{Pt}$ is decreased by 50% already after 100 degradation cycles. The investigated Pt-Vc catalyst contains a significant fraction of very small Pt-NPs as the initial size distribution in Figure 8a reveals. Such small Pt nanoparticles are thermodynamically destabilized and therefore quickly dissolve at high potentials. After 1000 degradation cycles, 97% of the initial Pt-NPs have disappeared. At the same time, 53% of the absolute Pt-NP mass is lost. The Pt mass loss is most likely due to the fraction of Pt ions that are lost either into the electrolyte flow or into the Nafion phase of the porous electrode.

Nevertheless, our results suggest that the electrochemical Ostwald ripening process is predominantly responsible for the overall loss of roughness factor. This can be explained and understood from the following reasoning: If the total mass of Pt-NPs were exactly retained, the 53% of lost Pt mass would be additionally present in the final state and, consequently, the total number of Pt nanoparticles would be approximately twice as large, yielding also a hypothetical double value of approx. 36% for the final roughness factor instead of the actual value of 18%. Thus, in such a hypothetical case of preserved Pt mass, a roughness factor loss of approx. 64% would remain, which can be ascribed to electrochemical Ostwald ripening. Therefore, out of the actually observed 82% overall loss of roughness factor, approx. 64% can be interpreted to result from electrochemical Ostwald ripening, and the remaining 18% from irreversible loss of Pt mass, respectively.

The quantitative contribution of carbon support corrosion to the overall observed loss of Pt ECSA is more difficult to assess with SAXS. The reason is the model-dependency of the SAXS analysis. It can be assumed that an agglomeration of Pt nanoparticles due to detachment from the support material preserves the primary particle shape at room temperature. In such a case, agglomeration could be taken into account in the SAXS analysis by an appropriate model for an additional agglomeration structure factor. Such an analysis would require a very high precision of the net Pt SAXS data at very low q values that lies beyond the currently reached data accuracy. However, since agglomeration of Pt nanoparticles leads to a larger fraction of contact area between different particles, this process should lead to a stronger degradation of the ECSA compared to the geometric surface area of primary Pt nanoparticles determined from the spherical particle-model fit of SAXS data. The good agreement that we found between the degradation of Pt surface area values from ECSA and from SAXS indicates that Pt particle agglomeration due to carbon support corrosion plays only a minor role in the degradation mechanism of the investigated Pt/Vc catalyst during high-potential cycling at room temperature.
Figure 8. In situ degradation results of the Pt-Vc 2 electrode. Log-normal probability density distributions $P_{\text{Pt}}(D_{\text{Pt}})$ for the diameter of Pt-NPs (a). Evolutions of the average diameter of Pt-NPs $D_{\text{Pt}}^\text{average}$ (squares), the Pt mass $m_{\text{Pt}}$ (circles) and the number of Pt-NPs $N_{\text{Pt}}$ (down triangles) both relative to the initial values (b). Dashed lines are guides for the eyes.

Conclusions

An electrochemical flow-cell was developed for performing in situ SAXS experiments in transmission mode on a standard multi-purpose laboratory diffractometer. This cell is offering the advantage of high availability of the required equipment in contrast to the very limited access to synchrotron SAXS beamlines, where electrochemical in situ SAXS studies have been primarily performed so far. The cell design is optimized to provide both high-quality SAXS data within reasonable acquisition times and a good electrochemical performance with low ohmic resistance necessary to study thick porous electrode material acquisition times and a good electrochemical performance with low ohmic resistance necessary to study thick porous electrode material. Reliability of the setup and reproducibility of the results were demonstrated with an in situ SAXS experiment for the degradation properties of a Pt/Vulcan carbon PEFC cathode catalyst, emphasizing the benefit and relevance of the presented cell development. The electrochemical degradation protocol mimicked the corrosive conditions during PEFC start/stop events by potential cycles up to 1.5 V_RHE. Carbon corrosion of the Vulcan support was qualitatively established this way, different degradation mechanisms could be distinguished. Pt differential scattering cross sections at various stages during the PEFC start/stop events by potential cycles up to 1.5 V_RHE. Carbon corrosion of the Vulcan support was qualitatively established this way, different degradation mechanisms could be distinguished. Pt differential scattering cross sections at various stages during the PEFC start/stop events by potential cycles up to 1.5 V_RHE.

An absolute normalization procedure for the SAXS data yielded net Pt differential scattering cross sections at various stages during the degradation cycling that could be analyzed not only for the Pt-NP size distribution, but also for the absolute number of Pt nanoparticles and the absolute Pt mass content of the nanoparticle phase. In this way, different degradation mechanisms could be distinguished. Carbon corrosion of the Vulcan support was qualitatively established in a separate experiment for a Pt-free Vulcan carbon electrode. The quantitative analysis of the Pt nanoparticle degradation revealed electrochemical Ostwald ripening as the dominant degradation mechanism for the Pt surface area.

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Appendix

Data reduction procedure.—For an absolute quantitative analysis, the recorded SAXS curves had to be transformed to differential scattering cross sections per geometric sample area. The differential cross section $\frac{d\sigma}{d\Omega}$ is the number $I_{\text{scat}}$ of photons scattered into the solid angle $\Delta\Omega$ per unit of time, divided by the incident photon flux $j_{\text{iso}}$:

$$\frac{d\sigma}{d\Omega} = \frac{1}{\Delta\Omega} \frac{I_{\text{scat}}}{j_{\text{iso}}}$$

where $\tau$ is the X-ray transmission of the entire setup that needs to be taken into account in order to correct for X-ray absorption along the scattering path. Dividing the differential cross section by the probed sample area $A_{\text{probed}}$, the equation becomes

$$\frac{d\sigma}{d\Omega} \frac{1}{A_{\text{probed}}} = \frac{1}{\Delta\Omega} \frac{I_{\text{scat}}}{j_{\text{iso}}} = \frac{1}{\Delta\Omega} \frac{I_{\text{trans}}}{I_{\text{trans}} - I_{\text{scat}}} = \frac{1}{\Delta\Omega} \frac{I_{\text{trans}}}{I_{\text{trans}} - I_{\text{scat}}},$$

where $I_{\text{trans}}$ is the number of direct beam photons transmitted through the sample without scattering per unit of time, $I_{\text{scat}}$ is the proportionality factor between the measured photon counts per second $I_{\text{trans}}$ and the true number of photons scattered per unit of time, and $\alpha_{\text{trans}}$ is the proportionality factor between the measured photon counts per second $I_{\text{trans}}$ at $\theta = 0^\circ$ and the total number of transmitted direct beam photons per unit of time.

Thus, the differential cross section per sample area $\frac{d\sigma}{d\Omega} \frac{1}{A_{\text{probed}}}$ is directly proportional to the ratio $\frac{\alpha_{\text{trans}}}{\alpha_{\text{trans}} - \alpha_{\text{scat}}}$, that is entirely defined by the diffractometer hardware and therefore the same for different SAXS experiments with the same hardware settings. Therefore, as described below, this overall proportionality factor can be determined by a SAXS experiment with a calibrated scattering standard sample with known differential scattering cross section.

Consequently, the first step of the raw data reduction procedure was to normalize measured scattering intensities $I_{\text{trans}}$ with respect to the measured transmitted intensity $I_{\text{trans}}$ for the identical system, yielding the normalized intensities

$$i_1(q) = \frac{I_{\text{trans}}(q)}{I_{\text{trans}}(q = 0)}.$$

Then, the isotropic scattering background determined from the plateau value at large $q$ was subtracted,

$$i_2(q) = i_1(q) - i_3(q = 4.96 \text{ nm}^{-1}).$$

This data reduction procedure was first done for each scattering experiment individually: flooded flow-cell stack with Pt-Vc material (Pt-Vc), flooded flow-cell stack with Vc material (Vc) and flooded flow-cell stack without electrode material (Kaptons). Next step was to subtract the scattering of the conductive Kapton stack (Kaptons) from the scattering intensities $i_2(q)$ of each of the Pt-Vc and Vc in situ experiments,

$$i_3(q) = i_2(q) - i_2(q)_{\text{kaptons}}.$$

Subsequently, the scattering intensities $i_3(q)$ of the Vulcan carbon support were normalized in order to obtain correctly scaled support scattering intensities for subtraction from the scattering intensities $i_3(q)$ of the Pt/Vulcan catalyst samples. In principle, this support scattering scaling could be done either by using the respective electrode masses or the respective electrode thicknesses. However, due to the above-mentioned imprecisions of the measured electrode masses and thicknesses, scaling factors obtained from masses and thicknesses, respectively, were not identical. Therefore, the mean value $C_{\text{mean}}$ of the mass and thickness scale factors $C_{\text{mass}}$ and $C_{\text{thickness}}$ was used.

$$C_{\text{mean}} = \frac{1}{2} \left[ C_{\text{mass}} + C_{\text{thickness}} \right] = \frac{1}{2} \left[ \frac{m_{\text{Pt}} - m_{\text{Vc}}}{m_{\text{Pt}}} + \frac{t_{\text{Pt}} - t_{\text{Vc}}}{t_{\text{Pt}}} \right].$$
where \( m_{Pt-Vc} \) and \( m_{Vc} \) are the masses of the Pt-Vc and the Vc electrodes, respectively, and \( \Gamma_{Pt-Vc} \) and \( \Gamma_{Vc} \) are the respective thicknesses of the electrodes.

The last step of the data reduction procedure was then to subtract the scaled Vulcan carbon scattering from the scattering of the Pt/Vulcan catalyst (Pt-Vc) in order to obtain the net scattering intensity of the Pt nanoparticles,

\[
I_{Pt-NPt}(q) = I_{Pt}(q)_{Pt-Vc} - C_{mean} I_{Vc}(q)_{Vc}.
\]

As discussed above, the resulting \( I_{Pt-NPt}(q) \) is directly proportional to the Pt differential cross section per sample area \( \frac{d\sigma}{dq} \). In order to determine the \( \frac{d\sigma}{dq} \) proportionality factor of our experimental SAXS setup, a glassy carbon standard (gC) calibrated at the USAIX instrument, Advanced Photon Source, was used.\(^{12}\) The proportionality factor was obtained from the ratio of the integrated scattering data measured for this glassy carbon sample with our MPD setup and the known differential cross section per area of this sample integrated over the same \( q \)-range,

\[
\frac{1}{\Delta \Omega} \frac{d\sigma}{dq} = \frac{\int \frac{d\Omega}{\Omega} \frac{d\sigma}{dq}}{\int \frac{d\Omega}{\Omega} dR_{PD}}.
\]

**Data analysis.**—For a collection of Pt nanoparticles, the differential scattering cross section per sample area \( A \) is equal to

\[
\frac{1}{\Delta \Omega} \frac{d\sigma}{dq} = \frac{1}{A} \int_{0}^{\infty} (P_{Pt}(R_{Pt}) V(q, R_{Pt})^{2} dR_{Pt},
\]

with functions \( V(R_{Pt}) \) and \( g(q, R_{Pt}) \) as defined in Ref. 17 and the total number of Pt nanoparticles \( N_{Pt} \). A log-normal distribution \( P_{Pt}(R_{Pt}) \) of the Pt nanoparticle radius was assumed in the data fitting, \( P_{Pt}(R_{Pt}) = \frac{1}{\sigma_{Pt} R_{Pt} \sqrt{2\pi}} e^{-\frac{(\ln(R_{Pt} / R_{Pt,\text{mean}}))^{2}}{2 \sigma_{Pt}^{2}}} \).

Additional structure factors, as well as systematic errors from an insufficient subtraction of the support scattering background that become predominant at lower \( q \)-values, were approximately taken into account by an additional term \( B q^{-\eta} \) to yield the total fitting function

\[
F_{Pt-NPt}(q) = \frac{N_{Pt}}{A} \int_{0}^{\infty} (P_{Pt}(R_{Pt}) V(q, R_{Pt})^{2} dR_{Pt},
\]

Due to the absolute normalization of the scattering data to differential cross sections, results from the fit not only allowed to determine the log-normal size distribution of the Pt-NPs \( P_{Pt}(R_{Pt}) \), but also to assess the absolute number of Pt-NPs per electrode area \( \frac{m_{Pt}}{A} \). Consequently, the roughness factor \( R_{F}(SAXS) \), equal to the total Pt surface area per electrode area, and the absolute mass of Pt-NPs per electrode area \( \frac{m_{Pt}}{A} (SAXS) \) could be determined,

\[
R_{F}(SAXS) = \frac{N_{Pt}}{A} \int_{0}^{\infty} 4 \pi R_{Pt}^{2} P_{Pt}(R_{Pt}) dR_{Pt},
\]

\[
\frac{m_{Pt}}{A} (SAXS) = \frac{N_{Pt}}{A} \int_{0}^{\infty} 4 \pi R_{Pt}^{2} P_{Pt}(R_{Pt}) dR_{Pt},
\]

where \( \rho_{Pt} \) is the mass density of platinum. The ratio of these two quantities yielded the mass-specific surface area of platinum \( \frac{m_{Pt}}{A} (SAXS) \).

For comparison with the Pt surface areas determined from SAXS, the Pt ECSA values were determined from CVs by integration of the hydrogen desorption charge in the Hupd region using a value of the specific charge of 210 \( \mu \)C/cm\(^2\). From this, the electrochemical roughness factor \( R_{F}(ECSA) \) and the mass-specific electrochemical surface area \( \frac{m_{Pt}}{A} (ECSA) \) were determined, the latter with the help of the known initial Pt mass content of the sprayed electrodes.

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