Supporting Information

Degradation Mechanisms of Supported Pt Nanocatalysts in Proton Exchange Membrane Fuel Cells: An Operando Study through Liquid Cell Transmission Electron Microscopy

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S1: Schematic representation of a liquid cell



Figure S1 – a) Schematic representation of the assembled chips, showing the gap between, the different components and the direction of the electron beam. b-c) Optical microscope image of the implemented echips. The different components are shown. d-e) e-chip with a drop of ink. The flux of the electrolyte is indicated by the blue arrows and the zone where the experiments were performed by the rectangular region.

S2 Electrochemical experiments

Before registering the CVs, the LTEM cell geometry has been validated under the flux of the electrolyte used for the study using a working electrode made of nude Pt. Results are shown below.



Figure S2. a) Evolution of the CVs as a function of the scan rate, from 200 mV/s up to 1000 mV/s. b) Description of the CVs.

The hydrogen underpotential deposition (HUPD) range was, as expected, in the range of 0.3V with more or less symmetric peaks in the negative scans. One can already see that this region was less and less determined when the peak current intensity was decreasing because the overall CVs exhibited a deviation from the horizontality. Such a deviation in liquid cells for TEM was previously reported by other researchers [1SI]. In particular, electrochemical LTEM

measurements exhibit two main differences in comparison to those obtained in a standard electrolytic cell: i) a dramatic shift of the potential range due to the use of platinum as pseudoreference electrode 38 Zimmerman et al [2SI], and ii) a non-horizontal baseline presenting a positive slope. As shown by Holtz et al [3SI] this phenomenon is associated to an Ohmic current overlaying the Faradaic component and related to the large solution resistance of the thin electrolytic liquid cell. The combination of these two effects with the weak signals when dealing with very small quantity of Pt NPs result in a broader and less defined HUDP region. Symmetrical peaks are indeed present, but difficult to integrate properly due to this deviation. A third peak should be added. However, the signal is far too weak (at least in the cathodic branch) to go further in the analysis. Besides, the cathodic peak particularly at -0,82 V, clearly corresponding to H adsorption, can be more easily qualified as the symmetric of the anodic peak present at 0,75 V. The issue is that there is an anodic electrochemical phenomenon observed which clearly evolves with time, and most probably evolves in agreement with the platinum particles modifications. This phenomenon looks to be more complex than, the sole attribution to H desorption.

Estimation of ECSA

ESCA has been estimated using the method described by Pozio et al. [4SI] by measuring the area of peaks of interest taking into account non-horizontal baseline using a built in function of the dedicated GAMRY software. Concerning the area of the broad peak which we assumed to be the desorption of the H⁺, we have used, as baseline, the line fitting the straight forward sweep segment after the H⁺ desorption peak starting between -0.2 V to -0.25 V. To take into account of the deviation from horizontality, we have tried to minimize the integration in a range not too far from 0.35V but it was definitely not appropriate and the range was effectively as large as mentioned in the publication. It may be explained by the CVs deviation when considering the projection of the distortion on the potential axis. It can be viewed as "an apparent potential range". It is the reason why we have added significant error bars in ECSA_{HUPD} to represent the uncertainty of our measurement. We did all the integrations systematically the same way for each anodic scans.

S3: EFTEM Thickness map

Investigating the thickness of the liquid layer is critical for understanding what is resolvable through liquids. EELS offers a convenient way to estimate the thickness of the layer traversed (t) in terms of the mean free path (λ) using Beer's law, which predicts an exponential decay of the unscattered incident beam: I=I₀exp(-t/ λ) [5SI]. The thickness, in terms of the inelastic mean free path (t/ λ), is measured by determining the ratio of the number of unscattered electrons (I) in the zero-loss peak (ZLP) to the total number of incident electrons (I₀). The inelastic mean free path (λ) of silicon nitride is very close to the one of water (around 225 nm). For simplicity we can consider the two the same [6SI].



Figure S3 – a) TEM image of the studied region and b) EFTEM Thickness map showing the t/λ ratio along the same area.

S4: Comparison between TEM and EFTEM modes



Figure S4: Comparison between TEM (a) and EFTEM (b) modes analyzed at the conditions mentioned in the article with the diameter of the condenser aperture set at 70 μ m

S5: Estimation of the experimental resolution



Figure S5: a) Micrograph showing two adjacent distinguishable Pt NPs. b) Gray value scan over the line in a) crossing two Pt NPs. The spatial resolution is obtained considering the FWHM of the Gaussian fit of the line scan between the two particles and using the Line Spread Function (LSF) method, [7SI]. The resolution is defined as the width within which the LSF (the dotted white line) drops to half the maximal value, i.e. the Full Width Half Maximum (FWHM).

S6: Effect of the electron beam



Figure S6a: Effect of the beam without cycling for an electron flux of about 36 e⁻/nm² sec. EFTEM images in zero loss mode of a) pristine sample, and b) sample irradiated for 30 minutes. No relevant changes are observed. c) Comparison of the calculated ECSA from the H desorption peak area, for the beam on and beam off cases. Data were normalized to initial value.

To evaluate the effect of the electron beam on the CVs, we calculated ECSA from the H desorption peak area acquired both under the electron beam irradiation (beam on) and in the absence of the electron beam (beam off). In both cases, the ECSA profile decreases to reach a

steady-state value after about 200 CVs. As for the two experimental configurations the ECSA values are within the error bars (excepts between 350 and 450 CVs), this suggests that the influence of the electron beam does not appreciably modify the observed ECSA decrease.



S7: Degradation mechanisms

Figure S7: LTEM micrographs showing several degradation mechanisms. Fig S7a) shows the detachment and diffusion of two Pt NPs (labelled as 1). b) displays snapshots corresponding to the aging respectively after 0, 400 or 500 CVs). Up to 400 CVs the system is only slightly modified during the electrochemical aging. The only detectable difference is the approaching between the two Pt NPs indicated by the black double arrow and numbered as 1. At 500 CVs, several other effects are observed: first, Pt NP labeled as 2 migrated by protruding toward the perfluorinated ionomer. Pt NP labeled as 3 is observed to detach from the C support and to diffuse within the ionomer. Besides, the appearance of isolated Pt NPs, labeled as 4 and 5 and only visible at cycle 500. Figure S7c) shows several degradation mechanisms: 1) dissolution, 2) detachment, 3) diffusion, 4) and 5) nucleation and growth.

S8: Migration of the assembly of Pt NPs within the electrolyte/ionomer phase



Figure S8a-b): Formation of Pt NPs and their diffusion within the ionomer

Figure S8a) In the zone labeled as 1, from cycle 250 we observe the appearance of a stripe of Pt NPs assembly diffusing within the electrolyte. At cycle 300, the same assembly of Pt NPs is still visible but not at the same position (label 2). The direction of the diffusion is indicated by the arrow. However, at cycle 500 the assembly disappeared, most likely diffused far away from the Pt/C agglomerate\Nafion® interface. Figure S8b) As already shown in Figure 9), at least up to 200 CVs no Pt NPs are visible within the ionomer phase. Beyond, an ensemble of isolated Pt NPs is observed which progressively diffuses away from the support of C. The position of the front of NPs is labeled as 1 and 2, and the direction of the diffusion is indicated by the arrow.

S9: Evolution of Pt NPs far from the Pt/C aggregates



Figure S9: LTEM micrographs showing the evolution of Pt NPs within the ionomer far from the carbon support

S10: Evolution of Pt/C aggregates during the cycling

The support materials for Pt-based catalysts currently used in most PEM fuel cells are porous carbon. The Vulcan XC-72 carbon black is one of the most commonly used. There are several basic requirements for an improved carbon support: high surface area, leading to the deposition of small platinum particles (maximizing catalytic surface area); low combustive reactivity under both dry and humid air conditions, improved electrochemical stability under fuel cell operating conditions, and high conductivity. However, its durability under chemically and electrochemically oxidizing conditions needs further improvement.



Figure S10: evolution of carbon support during cycling

Owing to the resolution of the LTEM technique, it is more than challenging to get information on the degradation of carbon support at the atomic level. Nonetheless, some morphological indications can be obtained at a larger scale. The first was already shown in zone 1 of Figure 8 where a *hole* in the C support is created as the result of the detachment of a Pt NP. Besides, the sub-micrometric evolution of the C support is presently shown in Figure S10. In particular, the same Pt/C agglomerate is observed at 0 cycles (Fig. S10a) and after 500 CVs (Fig. S10b). If the C support in the region labeled as A is not modified by the voltage cycles, this is not the case for the one comprised in the region labeled as B. Indeed, it is observed to shift in the direction indicated by the arrows like if a flexion of the *bridge* connecting the two regions (A and B) occurred. More interestingly is the effect shown in Figure S10c) where the two images, at 0 and 500 CVs, were superimposed and aligned taking as reference the large Pt/C agglomerate indicated by the arrow. Indeed, it is evident that not only the C support is deformed during the aging process, Figure S10b), but it also undergoes a migration within the ionomer solution. Note that the difference of contrast displayed in Fig. S10 is not significant and cannot be accounted for C degradation.

References Supporting information

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