Rotating Disk Electrode measurements on low and high loading catalyst layers: diffusion limitations and application to Pt catalysts supported on porous micrometric carbon xerogel particles designed for Proton Exchange Membrane Fuel Cells

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Abstract

Innovative fuel cell catalysts are now often being supported on nanostructured materials in order to improve mass transport, contact with the ionomer and active phase distribution. However, to maintain their inner structure, these supports are used as µm-sized particles, which hampers to perform accurate kinetic experiments on rotating disk electrode since a thin layer of catalyst is in principle required. The present study thus aims at checking if accurate measurements remain possible for thick layers of large particles. To do so, oxygen reduction was first performed on a commercial Pt catalyst supported on carbon black; both a typical thin and a thick layer (37 and 370 μg_{Pt} cm^{-2}) were used. The impact of the diffusion limitations on the kinetic current was determined. The same measurement protocol was then performed with a catalyst supported on 5 µm particles of a nanostructured carbon (~15 µm layer thickness, 370 $\mu g_{Pt}.cm^{-2}$). Results and calculation show that, for both thick layers, the kinetic current should be measured at higher potential (1.00 or 1.05 $V_{/ESH}$) than usual to avoid diffusion limitations. Also, the voltage scanning rate should be lowered to 0.5 or 1 $mV.s^{-1}$ to decrease the impact of the double layer capacity on the measurements.

Keywords: Pt/C catalyst, carbon xerogel, PEMFC catalysts, RDE measurements, Catalyst layer calibration, PEMFC diffusion-kinetics

1. Introduction

In order to provide alternative energies for fossil fuels, many routes are explored including the use of solar, wind, hydrothermal energy, *etc.* Hydrogen, which can be obtained *via* the electrolysis of water, is an interesting way to store the energy produced by intermittent sources as it can be further consumed in fuel cells to produce electricity for various applications. Several types of fuel cells exist on the market [1,2]. As part of this work, we will focus on the Proton Exchange Membrane Fuel Cell type (PEMFC). Its principle relies on the oxidation of hydrogen (at the anode) and the reduction of oxygen (at the cathode), while a proton-conducting membrane (Nafion®, usually) allows for the charge transport in-between.

Under the conditions of temperature, pressure and acidity of a PEM fuel cell, the oxygen reduction reaction is an intrinsically very slow reaction, requiring the use of a catalyst to limit the kinetic

overpotential [3–7], i.e. the voltage loss due to the reaction sluggishness. As such, a PEMFC cathodic catalytic layer is generally composed of a mixture of a solid catalyst and a proton conducting polymer, such as Nafion®. The catalyst itself is made of platinum (or platinum-based alloy) nanoparticles deposited on a carbon support [8]. While other materials with catalytic properties are envisaged in order to limit or eliminate the platinum used at the cathode, their commercial use is still limited owing to their poor performance or durability [9–11]. Therefore, the large-scale application of PEMFCs in vehicles is conditioned by a decrease in the quantities of used noble metals in PEMFCs or, at least, by the optimized use of all the particles present in the electrodes [12]. This is where the carbon support plays a key role. Indeed, for all the Pt particles to be active, it should provide sufficient electrical conductivity, and its porosity should be adequate for ensuring (i) a proper contact between the Nafion® and the Pt particles, (ii) a sufficient feed of oxygen and (iii) the evacuation of the produced water. The surface state of the carbon, as well as its crystallographic structure or composition, also have an impact on the stability of the platinum particles [13]. Finally, one must note that the carbon support is not thermodynamically stable in the oxidizing conditions of a PEMFC cathode. Indeed, the potential of the electrode is systematically higher than the oxidation potential of carbon ($E^0_{CO_2/C} = 0.207\ V_{/ENH}$ at 298 K), leading to a progressive degradation of the support over time and so decreasing the activity of the Pt particles [14–16]. Despite this drawback, at present, carbonaceous materials remain prime candidates, as other materials such as titanium or tungsten oxides still suffer from lower performance [17,18].

Carbon blacks are the most commonly used carbon carriers in fuel cells today, with Vulcan® XC-72 from Cabot remaining the reference material [18,19]. In addition to carbon blacks, other synthetic carbon materials are under study [17,20,21]. The main objectives are the optimization of the electrode architecture, the improvement of the carbon/Pt/Nafion® interaction and the decrease of carbon degradation during operation. The main materials studied are carbon nanotubes, nanospheres or nanofibers, graphene, ordered mesoporous carbons (OMC) and carbon gels [17,20–22]. As an example, carbon xerogels are considered owing to their controlled architecture: by choosing an appropriate pore texture, one can decrease the diffusion limitations at the cathode [23]. Indeed, such materials are composed of amorphous carbon nodules, made of small graphitic domains [24], strongly linked to each other by covalent bonds between carbon atoms. The obtained material can be pictured as a porous monolith with meso- or macropores corresponding to voids between the microporous nodules, the size of the latter being controlled by the gel synthesis conditions. Unlike catalyst layers based on carbon blacks, where the porosity depends on the space between the aggregates, and thus on the coating preparation mode [25], the pore texture of carbon xerogel-based catalyst layers is directly related to that of the pristine monolith. Indeed, µ-sized particles obtained by grinding display the same pore texture, which is maintained in the final electrode owing to the incompressibility of the carbon fragments. However, the use of meso- or macroporous carbon xerogels as catalyst support inevitably implies the obtaining of relatively thick catalyst layers. First, it is difficult to grind carbon xerogels below *ca.* 5 µm. Second, decreasing too much the particle size would lead to the disappearance of the controlled pore texture. The unavoidable use of large carbon particles can in turn bring some issues in terms of catalytic activity measurement.

Indeed, the activity of catalysts for PEMFC applications is usually studied *via* measurements in Rotating Disk Electrode (RDE) configuration in liquid acidic medium [26,27], in order to get rid of the problems of contact between the Pt nanoparticles and the solid ionomer (Nafion®). The measured activity values for the Oxygen Reduction Reaction (ORR) vary frequently from one research team to another [27] since this characterization technique is very sensitive to the operating variables, such as the electrolyte used

[26] or the presence of impurities [28]. In addition, the platinum loading [29], the homogeneity [29] and the composition [29,30] of the catalyst layer can strongly impact the measured values of activity. Finally, the thickness of the catalyst layer could result in more or less severe diffusion limitations, impacting the apparent kinetics measured by RDE characterization[31]. In that respect, the Pt loading and the thickness of the studied layer must remain low enough. It is for example recommended to keep the Pt loading in the 5-20 $\mu g_{Pt}/cm^2$ range, and layer thickness as low as possible (< 5 µm).
However, as mentioned earlier, it is usually not possible to comply with these recommendations when nanostructured carbons are used. Thus, the objective of this work is to determine the influence of a high thickness, and thus high Pt loading on the accuracy of RDE measurements for a catalyst layer based on either a carbon black or a carbon xerogel, the latter being made of micrometric porous particles (*ca.* 5 µm). Starting from moderate Pt catalyst content (34 or 37 wt.%), the chosen electrode Pt loading (370 $\mu g_{Pt}\ cm^{-2}$) corresponds to the minimum possible to obtain a continuous coating using micrometric porous particles as catalyst support, but this inevitably leads to thick layers on RDE: around three times the average particle size (*ca.* 15 µm) is necessary to obtain a homogeneous coating. In order to highlight the impact of high thickness and high Pt loading, the following methodology was developed. First, comparative RDE measurements were performed on a conventional (*ca.* 37 $\mu g_{Pt}\ cm^{-2}$) layer of a commercial Pt/carbon black catalyst, then on a 10 times thicker layer of the same composition, thus displaying a higher Pt loading (*ca.* 370 $\mu g_{Pt}\ cm^{-2}$). Second, identical characterizations were repeated on a home-made, fully characterized porous catalyst, composed of Pt/carbon xerogel micrometric fragments prepared following a well-known method [32]: in that case, due to the large particle size of the carbon support, only catalyst layers with high Pt loading (*ca.* 370 $\mu g_{Pt}\ cm^{-2}$) were prepared and the characterization data were compared with those obtained on the thick commercial catalyst layer of equivalent loading. This study sheds some light on the experimental difficulties arising when characterizing catalyst layers made of nonconventional supports and suggests solutions for the obtaining of accurate results.

2. Materials and Methods

2.1. Catalysts used in this study

Materials. The reagents used to produce the catalysts were resorcinol $C_6H_6O_2$ (Merck, for synthesis), sodium carbonate Na_2CO_3 (Acros Organics, 99.5% extrapure, anhydrous), dihydrogen hexachloroplatinate (IV) hexahydrate $H_2PtCl_6{\cdot}6H_2O$ (Alfa Aesar, 99.9% metal basis, crystalline), sodium hydroxide NaOH (Acros Organics, extrapure, pellets), sodium borohydride $NaBH_4$ (Merck, fine granular for synthesis), and tri-sodium citrate dihydrate $Na_3C_6H_5O_7{\cdot}2H_2O$ (Merck, EMSURE® for analysis).

The two catalysts chosen for this study were (i) a commercial Pt/carbon catalyst (Tanaka TEC10E40E 37 wt.% Pt) and (ii) a home-made Pt/carbon xerogel catalyst prepared following the procedure described by Job *et al*. [32]. The complete method is available in the Supplementary Materials. The Pt deposition on the carbon xerogel was achieved according to reference [33] with the SEA method [34–37]. The protocol is detailed in the Supplementary Materials and Figure S1 schematizes the different steps of the catalyst preparation.

The physico-chemical characterizations performed on the two catalysts are detailed in the Supplementary Materials. The following properties are summarized in Table 1: the specific surface area (S_{BET}), the micropore volume (V_{DUB}), the specific macropore volume (V_{Hg}), the mean pore size measured by mercury porosimetry (d_p), the mean diameter of Pt particles measured by TEM (d_{TEM}), the surface-weighted average diameter of particles (d_s), the volume-weighted average diameter of particles (d_v), and the mean diameter of Pt crystallites (d_{XRD}) measured by X-ray diffraction.

Concerning the home-made carbon xerogel, the textural properties on the monolith and the powder were similar (Table 1). As expected from the synthesis conditions, the carbon xerogel is a micro-macroporous solid with an average macropore size of *ca.* 85 nm. The mean particle size, as determined by laser granulometry (details in the supplementary information), was close to 5 µm (Figure S2). The details about the measurements by N_2 adsorption-desorption as well as mercury intrusion porosimetry are given in the supplementary materials (Figures S3-S4).

In order to estimate the Pt nanoparticle size, both catalysts were observed by TEM (Figures 1a and 1c). As seen from these images, the dispersion is better for the commercial catalyst as aggregates are formed in the case of the carbon xerogel-based sample. The size distribution of about 200 nanoparticles is represented on Figure 1b and 1d for both catalysts. The distribution is centered on 2.0-2.5 nm for the commercial catalyst (Figure 1b) and around 4.0-4.5 nm for the carbon xerogel catalyst (Figure 1d). The corresponding surface-weighted average diameter of particles, d_s, and the volume-weighted average diameter of particles, d_v, can be calculated with the d_{TEM} is order to compare these values with diameters obtained with other techniques, and all the values are reported in Table 1. Indeed, the CO stripping technique in RDE measures the total surface of the platinum sample S_{co} and an average diameter d_{co} is calculated using S_{co} and the platinum mass of the sample. A comparison between d_s and d_{co} is more relevant, CO stripping being a surface-sensitive technique.

The samples have been also characterized by XRD (Figure S5). The diffraction peaks of Pt are observed at 39° and 46° and, by application of the Scherrer equation (Eq. S3 from Supplementary Materials), the crystallite sizes were calculated (Table 1). The crystallite sizes are 2.7 and 5.4 nm for the commercial and the carbon xerogel-supported samples respectively. In the case of diameter measured by XRD, a comparison between d_v, calculated from TEM images, and d_{XRD} is also more relevant because XRD is sensitive to the volume of the particles.

2.2. Electrochemical characterization

Material. All the glassware was cleaned by immersion in a H_2SO_4:H_2O_2 solution (sulfuric acid H_2SO_4, Merck, 98% EMSURE®, for analysis and hydrogen peroxide H_2O_2, Merck, 30% Perhydrol®, EMSURE®, stabilized for higher storage temperature, for analysis) overnight and thoroughly rinsed with ultrapure water (Millipore, 18 MΩ cm), and finally boiled for 15 min in ultrapure water. The electrolytic solutions were prepared from ultrapure water and $HClO_4$ (70% Suprapur®, Merck).

Equipment. For measuring the electrochemical properties of the catalysts, a three electrodes setup is used with a potentiostat Metrohm Autolab PGSTAT204. It is composed of the following elements: (i) a glass cell; (ii) a glassy carbon EDT type working electrode; (iii) a couter-electrode composed of a platinum grid allowing the oxidation of water or the reduction of protons in an acid medium; (iv) a commercial Hydroflex® hydrogen relative electrode (ERH) from Gaskatel, usedas a reference; (v) a gas inlet allowing O_2, Ar, or CO to bubble in solution; (vi) a gas outlet.

The concentration of the electrolyte is 0.1 M of $HClO_4$.

Catalytic layer preparation. To measure the electrochemical properties of the catalysts, inks of samples were prepared [33]. For the Pt-carbon xerogel (34 wt.% Pt), a Pt amount of 370 μg_{Pt} cm^{-2} was chosen to obtain a continuous and relatively homogeneous coating of approximately 15 µm, corresponding to three times the average diameter of the carbon xerogel particles. In the case of the commercial catalyst, two amounts of Pt were chosen: 370 and 37 μg_{Pt} cm^{-2}, corresponding respectively to the same Pt amount than the carbon xerogel sample and a ten times lower loading (and thickness). The thin layer corresponds to commonly prepared layers when carbon black-supported catalysts are investigated in RDE configuration as PEMFC cathode catalyst. The composition of the 5 mL inks was conditioned by the platinum weight fraction of the catalyst and the desired Pt loading of the electrode in three steps. (i) The mass of catalyst in the ink was calculated in order to obtain the desired mass of platinum on the electrode (37 or 370 μg_{Pt} cm^{-2}) when a drop of 10 µL of this ink is deposited on the electrode; (ii) The amount of Nafion® was set to obtain a Nafion®/Carbon mass ratio of 0.295 using a dispersion of Nafion® LQ 1105 at 5 wt.%; (iii) the quantity of water (MilliQ 18 MΩ) was set to obtain a total volume of 3.6 mL including the water contained in the Nafion® dispersion; (iv) the quantity of isopropanol (99.5 %, Acros) was set to obtain a total volume of 1.4 mL including the amount contained in the dispersion of Nafion®. The desired amounts of water, isopropanol, catalyst and Nafion® were stirred together (see the precise amount in Table S1 in Supplementary Materials). In order to blend it homogeneously, the mixture was further processed in an ultrasonic bath for 15 min. Once the ink was homogeneous, 10 µL of ink were deposited on a glassy carbon (GC) disk (5 mm in diameter), rotating at 500 rpm and the layer was dried by a hot air flux parallel to the electrode surface while rotating at 500 rpm. This procedure should ensure homogeneity of the layer thickness [31]. An estimation of the catalyst layer thickness was obtained by profilometry (Veeco Dektak 8 Stylus Profile). At least three samples were prepared and characterized in RDE measurements for reproducibility purposes.

High frequency impedance spectroscopy. The cell atmosphere was purged by an Ar flow for 20 min. The high frequency resistance was measured thanks to an impedance measurement performed between 100 Hz and 100 kHz with an amplitude of 10 mV in open circuit voltage. The cyclic voltammetry during activation and the CO-stripping were performed with an ohmic drop correction of 85% of the impedance-measured high frequency resistance to be sure that this correction is not higher than the real value.

Activation of catalysts. Prior to any measurement, the electrolyte was de-aerated by Ar bubbling. Then, 50 voltammetry cycles were performed between 0.05 $V_{/RHE}$ (potential *vs.* Relative Hydrogen Electrode) and 1.23 $V_{/RHE}$ at a scanning rate of 0.5 V s^{-1}. Moreover, three voltammetry cycles with a scanning rate of 0.02 V s^{-1} and same potential boundaries were recorded in order to monitor the three-electrode setup and check for any disturbance of the catalyst state (*e.g.* loss of powder on the GC electrode).

CO stripping voltammetry. The Pt specific surface area was measured by CO stripping voltammetry [38,39]. The procedure was initiated by the application of a steady potential of 0.1 $V_{/RHE}$ to the working electrode, while gaseous CO (Air Liquide N47 grade, CO ≥ 99.997%) was bubbled in the electrolyte solution for 10 min. The bubbling time was increased compared to [33] in order to ensure complete CO coverage of the Pt particles in the case of a thick layer. After an Ar purge of 30 min to remove the CO dissolved in the electrolyte (still at 0.1 $V_{/RHE}$), the CO chemisorbed at the surface of the Pt particles was electro-oxidized into CO_2 by increasing the electrode potential from 0.05 to 1.23 $V_{/RHE}$ at 0.02 V s^{-1}. The electrode was then cycled between 0.05 and 1.23 $V_{/RHE}$ at the same scan rate for two more cycles. The third cycle representing the background of the CO stripping measurement was subtracted from the first one in order to isolate the CO electro-oxidation peak. The Pt specific surface area, S_{CO} (m^2 g_{Pt}^{-1}),

was calculated from the CO oxidation peak current (~ 0.8 V), assuming that the electro-oxidation of a full monolayer of CO_{ad} requires 420 µC cm_{Pt}^{-2} [40].

The CO equivalent particle diameter, d_{CO}, was calculated from CO stripping results by [38,39,41]:

$$d_{\mathrm{co}} = \frac{6 \text{ x } 10^{-3}}{\rho_{\mathrm{Pt}}\, S_{\mathrm{CO}}} \quad (1)$$

where ρ_{Pt} is the density of Pt (21.4×10^3 kg m^{-3}). As CO stripping voltammetry is a surface-sensitive method, d_{CO} corresponds to a surface-weighted average diameter and can be compared to d_s (Table 1).

Activity for the oxygen reduction reaction. The activity of the catalysts for the oxygen reduction reaction (ORR) was measured after saturation of the electrolyte by oxygen bubbling during 20 min. The electrode potential was set at 0.2 $V_{/RHE}$, then increased to 1.05 $V_{/RHE}$ at a scan rate of 5 mV s^{-1} and finally decreased back to 0.2 $V_{/RHE}$ at the same scan rate, while measuring the reduction current. This measurement was repeated at various rotation speeds of the electrode (400, 400, 900, 1600, 2500 and 400 rpm again). The first and last trials at 400 rpm allow to check for the reproducibility of the measurements and the non-degradation of the catalyst during the experiment.

Chronoamperometry under oxygen. The measurement consisted in imposing a potential of 0.4 $V_{/RHE}$ for 5 min and then stabilizing the system at the desired potential for 10 min. These measurements were performed for different potentials (0.90 $V_{/RHE}$, 0.90 $V_{/RHE}$, 0.93 $V_{/RHE}$, 0.95 $V_{/RHE}$, 0.98 $V_{/RHE}$ and 0.90 $V_{/RHE}$). The stabilization at 0.4 $V_{/RHE}$ before each measurement allowed for the reduction of the platinum surface, leading presumably to the same reduced state before starting the stabilization at high potential.

3. Results and discussion

3.1. Commercial Pt/carbon black catalyst (Tanaka): Influence of the catalyst layer loading on the RDE characterization

As the catalyst layer produced from the Pt-carbon xerogel catalyst (particle size of 5 µm) will be thicker than those usually used in RDE characterizations [17], it is important to understand the influence of the layer thickness on the catalytic activity and to determine whether the obtained results are representative of the Pt surface and the intrinsic Pt activity. To cope with this issue, the commercial catalyst has been processed into a thin and a thick layer. The latter was produced such as to bear the same amount of platinum (370 μg_{Pt} cm^{-2}) on the electrode as the Pt-carbon xerogel catalyst layer (see section 3.4) and a similar platinum mass fraction, respectively 37 and 34 wt.%, whereas the thin layer contains 10 times less Pt (37 μg_{Pt} cm^{-2}). The high roughness of the coatings makes the measurements with profilometry poorly accurate. Nevertheless, the highly-loaded layer was measured to be 20 µm thick. It was not possible to measure the thickness of the thin layer by profilometry. However, the composition of the two deposits being identical, the average thickness of the deposit should be 10 times smaller, *i.e.* ~ 2 µm.

3.1.1. CO stripping and cyclic voltammetry under Ar

The first and the third voltammetry cycles under Ar for CO stripping are depicted in Figure 2 for catalytic layers with loadings of 37 and 370 $\mu g_{Pt}\ cm^{-2}$. At least three samples were characterized in each case to assess the reproducibility of the measurements. The double layer current (I_{dlc}) during a cyclic voltammetry is measured for potential values around 0.4-0.5 $V_{/RHE}$ on Figure 2b and 2d. It allows to directly deduce the electrochemical double layer capacity with Eq. 2.

$$I_{dlc} = C_{dl}\frac{dU}{dt} \quad (2)$$

where I_{dlc} is the double layer current (A), C_{dl} is the double layer capacity (F), U is the potential (V) and t is the time (s). $\frac{dU}{dt}$ can be approximated by the scan rate (5 mV s^{-1}). The corresponding values of double layer capacity, C_{dl}, are reported in Table 2.

On the one hand, Figures 2b, 2d and Table 2 show that the double layer capacities are very close for measurements performed several times in the same conditions (standard deviation of 5.5 and 4.3 % respectively), which seems to show a good reproducibility of the catalyst mass deposited on the electrode, whatever the Pt loading. Indeed, the double layer capacity is theoretically proportional to the amount of catalyst support present. On the other hand, the calculation of the double layer capacity gives an average value of 99 F g_{carbon}^{-1} and 180 F g_{carbon}^{-1} for the low and high Pt loadings, respectively. The measured double layer capacitance values are thus not proportional to the deposited mass when increased 10 folds.

Figures 2a and 2c compare the first voltammetry cycle of the CO stripping measurement for the commercial catalyst with the two Pt loadings. The oxidation peaks of CO (around 0.8 $V_{/RHE}$) are much more reproducible in the case of the layers with 37 $\mu g_{Pt}\ cm^{-2}$ compared to those with 370 $\mu g_{Pt}\ cm^{-2}$. The reason for reproducibility issues in the case of layers with high loading has not yet been elucidated, and does not result from a variation in the mass deposited on the electrode since the associated double-layer capacities (Table 2 and Figure 2d) are almost identical for the four same electrodes. In addition, Figures 2a and 2c show that the oxidation peak of CO starts at the same potential for both Pt loadings, but spreads to higher potentials for higher Pt loadings. This potential spreading could be due to diffusion limitations, resulting in a higher concentration of species produced (CO_2) in the layer, induced by the increased layer thickness: the CO_2 concentration increase could possibly slow down the kinetics of the oxidation reaction of CO into CO_2.

The area of the CO peak is calculated by subtracting the third voltammetry cycle (Figures 2b and 2d) from the first one (Figures 2a and 2c), in order to remove the effects of both the carbon support and the oxidation of the platinum surface. The charge of the CO oxidation peak (~0.8 V) is related to the electrochemically active platinum surface S_{CO} (Table 2): average values obtained are 105 (± 2.1%) and 70 (± 17.0%) $m^2\ g_{Pt}^{-1}$ for the samples loaded at 37 $\mu g_{Pt}\ cm^{-2}$ and 370 $\mu g_{Pt}\ cm^{-2}$, respectively (Table 2). Theoretically, these values should be identical if the measurements conditions were the same for Pt particles contained in both layers. It could be interesting to also perform the CO stripping measurements at lower scan rate in order to check if the difference between the two values are still the same.

From the S_{CO} values (Table 2), a mean diameter of platinum particles, d_{CO}, can be calculated (Eq. 1) assuming that the entire platinum surface corresponds to spheres of the same diameter. Equation 1 allows to calculate an average particle diameter of 2.7 nm and 4.0 nm for the layers with 37 $\mu g_{Pt}\ cm^{-2}$ and 370 $\mu g_{Pt}\ cm^{-2}$, respectively. These values can be compared to the surface-weighted average

diameter of particles (Eq. S1 from the Supplementary Materials), d_s (2.7 nm), calculated from TEM images (Table 1); the comparison confirms the better accuracy of the measurements performed at low Pt loading.

3.1.2. Activity for the oxygen reduction reaction (ORR)

The cyclic voltammetries under O_2 at different rotating speeds of the electrode for the layers of commercial catalyst, with low and high Pt loading, are represented in Figures 3a and 3c. These curves are corrected for the ohmic drop measured by electrochemical impedance spectroscopy. For the low loading (37 $\mu g_{Pt}\,cm^{-2}$, Figure 3a), the back and forth diffusion-convection plateaus (*i.e.* at low potential) are identical because the current is controlled only by the supply of reagents to the surface of the sample by diffusion-convection. For the high loading (370 $\mu g_{Pt}\,cm^{-2}$) (Figure 3c), the forward and backward diffusion plateaus are not superimposed anymore. This is mainly due to two phenomena. First, the absolute capacitive current is increased (Figures 2b and 2d) because of the higher capacitance (3.7×10^{-3} *vs.* 67×10^{-3} F cm^{-2}, respectively). Indeed, this capacitance is calculated from Table 2 by multiplying C_{dl} by the mass of the carbon and dividing by the surface of the electrode. Second, the oxidation/reduction current of the platinum surface is not negligible compared to the diffusion convection plateau. For both layers, the increase in the diffusion limiting current at low potential is proportional to the square root of the electrode rotation speed (see Figure S6) as described by the Levich equation (Eq. 3) [42]:

$$i_l = 0.62nFSD_O^{2/3}\omega^{1/2}v^{-1/6}C_O^* \quad (3)$$

where i_l is the limiting current (A), n is the number of exchanged electrons, F is the Faraday constant (C mol^{-1}), S is the geometric area of the electrode (cm^2), D_o is the oxygen diffusion coefficient ($cm^2\ s^{-1}$), ω the angular frequency rotation (rad s^{-1}), v is the cinematic viscosity ($cm^2\ s^{-1}$) and C_O* is the oxygen concentration in the solution (mol cm^{-3}).

The cyclic voltammetry curves at 1600 rpm under O_2 for the electrodes loaded with 37 $\mu g_{Pt}\,cm^{-2}$ and 370 $\mu g_{Pt}\,cm^{-2}$ are depicted in Figure 3b and 3d, respectively. The current values at 0.90 and 0.95 $V_{/RHE}$ are reported in Table 2. After correction for the ohmic drop, these voltammetry curves under O_2 (in red) can be further corrected to account for the capacitive effect of the carbon support as well as the current resulting from the oxidation of the platinum surface. This second correction can be made by subtracting a voltammetry cycle performed under the same conditions, but under Ar (in blue). For the electrode with low Pt loading (Figure 3b), the correction has almost no impact because the absolute double layer capacity is very low (3.7×10^{-3} F cm^{-2}); it nevertheless improves the accuracy of the activity measurement at 0.95 $V_{/RHE}$. However, in the case of the electrode with high loading, the capacitive effect is very marked (67×10^{-3} F cm^{-2}). Without correction (Figure 3d, in red), the diffusion plateaus at low potential (forth and back) are not equal, the hysteresis normally observed between 0.8 and 1.0 $V_{/RHE}$ is strongly modified, and the current measured at very high potential is positive. After correction, the curve displays a shape closer to that observed for the thin layer. However, between 0.2 and 0.4 $V_{/RHE}$, the correction results in the presence of a peak arising from the proton adsorption/desorption under argon. In addition, at very high potential, the current does not tend to 0 mA cm^{-2}. Very high potential values are therefore always partially affected by the capacitive phenomena and/or the

current produced during the oxidation of the platinum surface, despite the correction. A slower scan rate at 1.0 or 0.5 mV s^{-1} could possibly eliminate this problem.

Chronoamperometries at 0.90 $V_{/RHE}$, 0.93 $V_{/RHE}$, 0.95 $V_{/RHE}$ and 0.98 $V_{/RHE}$, performed under O_2 for 10 min to stabilize the current, are shown in Figure 4. The current density values measured by chronoamperometry (Figure 4 and Table 3) allow to overcome the capacitive effect by stabilizing the system at a given potential. It should be mentioned however that the current does not stabilize completely because the platinum surface is slowly oxidized, even after several hours of chronoamperometry. Despite this, the oxidation state of both samples should normally be identical after 10 min at the same potential. The values obtained by chronoamperometry (Figure 4) can therefore be compared with the back curves (decreasing potentials) of the cyclic voltammetries after correction (black curves, from Figures 3b and 3d). The results obtained here show that lower currents are obtained after stabilization for 10 min in comparison with the values resulting from voltammetry at the same potential. In addition, the divergence between the two series of data is increased for the sample containing more Pt, probably due to the higher capacitive effect.

For two layers made from the same catalyst, but with different Pt loadings, the current at a given potential is theoretically proportional to the platinum amount present on the electrode, if the current is limited by the kinetics of the reaction only. Indeed, in this case, the current produced can be described by the Tafel equation (Eq. 4) [43,44]:

$$i = Sj_0 e^{-\frac{\propto F}{RT}\eta} \quad (4)$$

where i is the current (A), S is the active Pt surface (cm^2), j_0 is the exchange current density (A cm^{-2}), α is the transfer coefficient (dimensionless), F is the Faraday constant (C mol^{-1}), R is the perfect gas constant (J mol^{-1} K^{-1}), T is the temperature (K), and η is the kinetic overpotential (V).

The only variable that changes between the two cases (the low and high Pt loadings) is the surface S, which should be proportional to the platinum amount deposited assuming that the contact between platinum and the electrolyte are the same. The intensity values per gram of platinum resulting from the chronoamperometry are used for the following calculations since, at high Pt loading (*i.e.* thick catalytic layer), the values determined by cyclic voltammetry are tainted by errors due to the double layer capacity of the carbon support. The intensity per gram of platinum should be the same regardless the platinum amount if the currents are limited by kinetics only (Eq. 4). However, as seen from Table 3, this is not the case at the potential values generally used to compare the activity of different catalysts (0.90 $V_{/RHE}$ or 0.95 $V_{/RHE}$). Indeed, at these potentials, the current is also limited by diffusion for the layer with high Pt loading. These results agree with previous works [44], which showed that, from 50 to 100 μg_{Pt} cm^{-2}, the intensity per gram of platinum at 0.90 $V_{/RHE}$ strongly decreases. Indeed, if the Pt loading on the electrode becomes higher, the thickness of the catalyst layer to be crossed by O_2 becomes larger, the consumption of O_2 increases, ending up with the appearance of diffusion limitations. If, however, the data are taken at a potential of 0.98 $V_{/RHE}$, the intensity values per gram of platinum become similar for both samples (Table 3), indicating that the diffusion limitations appear to be negligible under these conditions.

Diffusion limitations under O_2 in RDE for catalysts are often partially corrected by the Koutecki-Levich equation [44] to decrease the impact of diffusion phenomena:

$$I_k = \frac{I_{lim} \times I}{I_{lim} - I} \quad (5)$$

where I_k is the kinetic current (A), I_{lim} is the limit current (A) and I is the measured current (A). This correction allows, in some cases, to correct the diffusion limitations from the diffusion-convection limit current [44]. This method has been applied to the chronoamperometry values under O_2. The values obtained by Eq. 5 (Table 4) show that the differences in activity per unit mass between the two layers are only partially corrected. For example, at 0.95 $V_{/ERH}$, the ratio of currents per mass unit of Pt still equals 1.27 after correction (*vs.* 1.49 before correction), whereas it should be equal to 1.

The measurement of catalyst activity with 20 µm thickness and/or a high platinum amount (370 μg_{Pt} cm^{-2}) seems therefore possible, but the reference potential needs to be adjusted in order to ensure the relevance of the results.

3.1.3. Diffusion-convection limitations: impact of the layer thickness

Measurements of catalyst activity should be made under conditions such that the oxygen concentration in the whole layer equals the oxygen concentration in the electrolyte. The electrochemical measurements have shown that limitations appear when a catalyst layer with high Pt loading is used in RDE measurements; these limitations can originate from several phenomena. In activity measurements, the limitations may first be due to insufficient oxygen renewal at the surface of the electrode due to a slow rotation rate. This is why a high rotation speed (1600 rpm) is used for these measurements. At this speed, the diffusion-convection stage is reached for a value of 6 mA cm^{-2} (Figure 3). Below 10 % of this value (0.6 mA cm^{-2}), diffusion-convection limitations on the surface of the electrode can be assumed to be low. From Figure 4, one can deduce that, during chronoamperometry measurements, diffusion-convection limitations can be considered negligible for minimum potential values of 0.98 $V_{/RHE}$ only in the case of the layer with high Pt loading; the minimum potential range can be lowered to 0.93 $V_{/RHE}$ for the layer with the lowest loading. It should be reminded here that the high Pt loading samples correspond to thick coatings, around 15 µm, and the low Pt loading samples have thinner coatings, around 2 µm.

A second type of diffusion limitation may occur within the catalyst layer. By assuming that only diffusive phenomena take place, mass transport is described by Fick's law (Eq. 6):

$$J = -D\nabla C \quad (6)$$

where J is the oxygen flux (mol cm^{-2} s^{-1}), D is the diffusion coefficient of oxygen in water (cm^2 s^{-1}) and C is the concentration of the diffusing species, *i.e.* oxygen (mol cm^{-3}).

By applying this equation to a mono-dimensional catalyst layer, one obtains:

$$J = D_{eff}\frac{C^* - C_0}{h} \quad (7)$$

where J is the flux (mol cm^{-2} s^{-1}), D_{eff} is the effective diffusion coefficient in the porous medium (cm^2 s^{-1}), C^* is the concentration of reactant at the catalytic layer surface (mol cm^{-3}), C_0 is the concentration at the vitreous carbon/catalyst layer interface (mol cm^{-3}) and h is the catalyst layer thickness (cm). The effective diffusion coefficient takes into account the void fraction of the catalyst, such as [45]:

$$D_{eff} = \frac{\varepsilon}{\tau} D \tag{8}$$

where ε is the void fraction (dimensionless) and τ is the tortuosity of the porous material (dimensionless). The tortuosity can be approximated as the inverse of the void fraction [45]. Eq. 8 becomes:

$$D_{eff} = \varepsilon^2 D \tag{9}$$

The void fraction of the catalytic layer can easily be estimated from the thickness, the mass of the constituents and the densities of the latter:

$$\varepsilon = \frac{V_{layer} - V_{solid}}{V_{layer}} \tag{10}$$

$$V_{solid} = \frac{m_{c/cm^2}}{\rho_c} + \frac{m_{Pt/cm^2}}{\rho_{Pt}} + \frac{m_{Naf/cm^2}}{\rho_{Naf}} \tag{11}$$

where V_{layer} is the total volume of the layer (cm³), V_{solid} is the volume of solid material that constitutes the layer (cm³), m_{C/cm^2}, m_{Pt/cm^2} and m_{Naf/cm^2} correspond to the masses of carbon, platinum and Nafion® in the layer (g) respectively, ρ_c, ρ_{Pt}, and ρ_{Naf} are platinum, carbon and Nafion® densities (g cm^{-3}).

ε is calculated equal to 0.78 for the two Pt loadings using densities of 2 g cm^{-3} for carbon [46], 1.97 g cm^{-3} for Nafion® [47] and 21.5 g cm^{-3} for platinum. Considering an oxygen diffusion coefficient value of 2.1×10^{-5} cm² s^{-1} [48], the effective diffusion coefficient is calculated equal to 1.3×10^{-5} cm² s^{-1}.

The diffusion limitations in the layer can be neglected if the relative difference between C^* and C_0 is low. In the following, a value of 0.1 will be considered small enough to neglect internal diffusion limitations. Indeed, it corresponds to a difference between C^* and C_0 of 10 %:

$$\frac{C^* - C_0}{C^*} < 0.1 \tag{12}$$

Using Eq. 7, Eq. 13 can be written as follow:

$$\frac{Jh}{C^* D_{eff}} = \frac{C^* - C_0}{C^*} \tag{13}$$

So, diffusion limitations are neglected if:

$$\frac{Jh}{C^* D_{eff}} < 0.1 \tag{14}$$

In that equation:

(i) J is imposed by the current produced per surface unit of electrode (oxygen consumption) and can be connected to the current produced using Faraday's law (Eq. 15):

$$Q = nFe \tag{15}$$

where Q is the reaction charge (C), n is the number of reacted moles (mol), F is the Faraday constant (C mol^{-1}), and e is the number of exchanged electrons per reacted molecule. By dividing Q and n by time, Eq. (16) is obtained:

$$J = \frac{I_{/cm^2}}{Fe} \quad (16)$$

(ii) h corresponds to the thickness of the layer estimated by profilometry, which is not very accurate due to the deposit roughness. The thickness of the layer with high loading is measured ~ 20 µm while that of the layer with low loading is estimated close to 2 µm;

(iii) C^* corresponds to the oxygen concentration in the electrolyte at saturation, *i.e.* 1.35 µmol cm^{-3} at 20°C and 1 bar [49];

(iv) D_{eff} is the effective diffusion coefficient in the porous medium (Eq. 8) [45].

All values in Eq. 13 are known except for J (Eq. 16), which depends on the produced current. For both catalyst layer loadings, the minimum current at which diffusion limitations are no longer negligible can be calculated by combining Eqs. (16), (9) and (14):

$$I_{/cm^2} = \frac{0.1C^*\varepsilon^2 DFe}{h} \quad (17)$$

The number of electrons exchanged per reacted molecule, e, is close to 4 for Pt catalysts [50-54], even though the mechanism may proceed through a 4-electron or (2+2)-electron mechanism, depending on the voltage [51]. In any case, the approach proposed here does not require a complex correction of the ORR curves to account for the internal mass transfer impact, as sometimes performed in the literature [55]. On the contrary, the goal is to determine the current below which the system works in chemical regime, e.g. without any mass transport limitations, despite the layer thickness and porosity, and to consider currents below that limit for the determination of the catalyst activity.
With e = 4, Eq. (17) leads to a value of 3.4 mA cm^{-2} (*i.e.* 90 A g_{Pt}^{-1}) for the thin layer (loading of 37 μg_{Pt} cm^{-2}), and a value of 0.34 mA cm^{-2} (*i.e.* 0.90 A g_{Pt}^{-1}) for the thick layer (loading of 370 μg_{Pt} cm^{-2}).

In Table 3, for the layer with low Pt loading, diffusion limitations can be neglected, with all the values of measured current being lower than 90 A g_{Pt}^{-1}. For the layer with high Pt loading, only the measurement performed at 0.98 $V_{/RHE}$ just reaches the 0.90 A g_{Pt}^{-1} limit. This explains why the two layers tend to reach the same current per mass unit of platinum from 0.98 $V_{/RHE}$ only, while they have the same composition. This is furthermore confirmed by Figure 4: for the layer with low Pt loading, the current measured at different potentials remains below the 3.4 mA cm^{-2} limit (blue curve), whereas, for the layer with high Pt loading, only the current measured at 0.98 $V_{/RHE}$ can be considered limitation-free since it (barely) reaches the limit of 0.34 mA cm^{-2} (red curve).

3.1.4. Summary concerning the commercial catalyst characterization

The RDE measurements of highly loaded layers of a commercial catalyst, containing thus high Pt amounts (370 μg_{Pt} cm^{-2}), seem possible, although some differences in comparison to lowly loaded layers (Pt loading of 37 μg_{Pt} cm^{-2}) have been highlighted: (i) the platinum surface S_{CO} is underestimated

by about 33 % and less reproducible; (ii) the beginning of the oxidation peak of CO is at the same potential but spreads towards higher voltages; (iii) the shape of the voltammetric curves under O_2 is strongly modified by the double layer current (I_{cdc}) and the oxidation/reduction current of the platinum surface, which makes the kinetic measurements difficult to exploit during the cyclic voltammetry at 5 mV s^{-1} for the highly-loaded sample; and (iv) the oxygen reduction current measured at a potential below 0.98 $V_{/RHE}$ is limited by internal and external diffusion for the thick layers.

In order to obtain accurate values of kinetic currents for the highly loaded sample (370 μg_{Pt} cm^{-2}) during the ORR measurements, the scanning rate should be decreased to 0.5 or 1 mV s^{-1} and a cyclic voltammetry under argon should be performed and subtracted to this ORR measurement to decrease I_{cdc} and the oxidation/reduction current of the platinum surface. The reference potential for kinetic current measurements should be increased to approximately 1.0 or 1.05 $V_{/RHE}$, in order to overcome the external (to the surface) diffusion-convection limitations and internal (within the catalyst layer) diffusion limitations. It must be mentioned that increasing the reference potential to 1.00 $V_{/RHE}$ for measurements of the kinetic current with thick layers is feasible. Indeed, for the thick layer, the maximum current to avoid internal mass transfer issues is ~0.34 mA/cm², which is not a problem given the detection limit of the setup – one could easily decrease the current down to 0.05 mA/cm², like in the case of the thin layer at 0.98 V/RHE (Figure 4). It is why we recommend a voltage around 1 or 1.05 V/RHE for future similar measurements.

The goal of this part was only to verify if measurements with high loading (370 μg_{Pt} cm^{-2}), thus high thickness, are possible and what modifications must be made to obtain accurate measurements. The final goal is to be able to characterize catalysts supported on porous particles of large diameter (5 µm in diameter), which automatically implies the preparation of thick coatings, as performed in the next section.

3.2. Electrochemical characterizations of the Pt/carbon xerogel catalytic layer

In this part, the homemade Pt/carbon xerogel catalyst is characterized by the same RDE measurements, as mentioned in section 2.4. The Pt amount deposited onto the electrode is 370 μg_{Pt} cm^{-2} as for the layer with high Pt loading made from the commercial catalyst. The aim of these measurements is to check if similar and/or other problems occur with the Pt-carbon xerogel catalyst compared to the commercial one. The thickness of the Pt-carbon xerogel layer measured by profilometry is ~ 17 µm.

3.2.1. CO stripping and cyclic voltammetry under Ar

Figure 5a shows the CO stripping voltammetry curves for three layers of Pt/carbon xerogel catalyst prepared in the same way for reproducibility. The third voltammetry cycle (after CO electrooxidation) is represented in Figure 5b for each sample. The double layer capacity is very reproducible, indicating that the deposited catalyst amounts are very close (standard deviation of 5.3%, Table 2). However, its value is more than twice that observed using the same amount of commercial catalyst (Table 2).

The areas of the CO peaks (Figure 5a) are more reproducible than in the case of the commercial catalyst layers with high Pt loading (Figure 2c). As explained in section 3.3.1., an average particle size d_{CO} of 3.9 nm can be calculated (Eq. 1) from the CO oxidation peak area, S_{CO}. This value (Table 2) is lower than that obtained *via* TEM images (5.3 nm, Table 1). This may be due to the middling quality of the TEM micrographs, which may have underestimated the proportion of particles smaller than 1 nm.

The position of the CO electrooxidation peak (Figure 5a) is shifted to higher potential compared to layers of commercial catalyst with lower loading (37 μg_{Pt} cm^{-2}), as shown previously in Figure 2a and

2c. Additionally, the peak around 0.67 $V_{/RHE}$ comes from the significant presence of Pt particles aggregates [41]. This conclusion is confirmed by TEM images, where aggregates are indeed visible (Figure 1c).

3.2.2. Activity of the catalysts for the oxygen reduction reaction (ORR)

The voltammetry cycles under O_2 are depicted in Figure 6a. The double-layer capacity being higher than for the commercial catalyst, its impact on the voltammetry cycles (Figure 6a) are even more acute. The back and forth diffusion stages are very different, but the average values are proportional to the square roots of the scanning speeds (see Figure S6), as for the layers made of commercial catalyst (Eq. 3).

Figure 6b shows that the correction (by subtracting the blank measurement under Ar to the voltammetry cycle under O_2) allows to mitigate a large part of the capacitive effect and the oxidation/reduction of the platinum surface. The correction is however incomplete, unlike in the case of the commercial catalyst layer with high loading (Figures 3b and 3d). Indeed, the current does not tend exactly to 0 mA cm^{-2} at very high potential. Currents measured at high voltage remain flawed. A slower scan rate (0.5 or 1 mV s^{-1}) could limit the impact of the double-layer capacity.
The current values at 0.90 and 0.95 $V_{/RHE}$ in voltammetry cycles under O_2 (Table 2) are very similar between the carbon xerogel and the commercial catalyst with the same platinum loading. However, despite corrections, these values still deviate from the true kinetic current due to (i) diffusion limitations, (ii) the double layer capacity and (iii) the oxidation/reduction current of the platinum surface.

3.2.3. Diffusion limitations in the Pt-carbon xerogel catalyst

Concerning the diffusion limitations, the same calculations (Eq. 6 to 17) as is section 3.3.3 can be made. The diffusion-convection limitation on the surface of the catalyst layer resulting from the rotational speed of the electrode does not depend on the catalytic layer. Since the diffusion-convection limit current is approximately 6 mA cm^{-2} at 1600 rpm, at 0.6 mA cm^{-2}, the diffusion-convection limitations at the surface of the electrode can be considered low enough to be neglected. This situation corresponds to a current of 1.6 A g_{Pt}^{-1} for electrodes containing 370 μg_{Pt} cm^{-2}. All the intensities described in Table 2 are therefore tainted with diffusion-convection limitations due to an insufficient replenishment of O_2 at the surface of the catalyst layer.

Concerning the diffusion limitations within the catalyst layer, the same calculation from Eq. 14, allowing to estimate the current from which the diffusion limitations become significant leads to a value of 0.33 mA cm^{-2} (0.87 A g_{Pt}^{-1}) for the carbon xerogel layer. For these calculations, a thickness of 17 µm was considered and the void fraction of the layer, ε, was calculated to be 0.72 from the density of its various components and its thickness (Equations 10 and 11).

The intensities measured at 0.90 and 0.95 $V_{/RHE}$ (Table 2) are therefore impacted by diffusion phenomena in the catalyst layer and by diffusion-convection limitations in the fluid phase close to the catalyst layer surface. These results show that it is necessary to compare the measurements at a higher potential than is generally considered in the literature (about 1.0 $V_{/ERH}$ instead of 0.90 or 0.95 $V_{/ERH}$).

3.2.4. Extrapolation to a thin carbon xerogel based catalyst

In order to decrease the diffusion limitations during the study of catalysts supported on carbon xerogels or other types of porous large particles (a few microns in diameter), a layer corresponding to particles isolated on the surface of the vitreous carbon has been envisaged from a theoretical point of view. In this case, one can check for the existence of diffusion limitations on an isolated particle. For this, the Weisz modulus Φ (Eq. 18) is the equivalent of Eq. 13, but applied to a porous particle and not to a layer:

$$\Phi = \frac{r L_p^2}{C^* D_{eff}} \tag{18}$$

where r is the observed reaction rate per volume unit of the particle (mol cm^{-3} s^{-1}), L_p is the characteristic length of the particle (cm), C^* is the reactant concentration outside the particle (mol cm^{-3}), and D_{eff} (Eq. 8) is the effective diffusion coefficient in the particle (cm^2 s^{-1}). If the Weisz modulus is less than 0.1, the effect of the internal matter transfer can be considered small enough to be neglected.

The parameters of the equations are similar to those of Eq. (13). The differences come from the thickness of the layer that corresponds to the characteristic length, L_p (*i.e*. to the volume/surface ratio of the isolated particle, Eq. 19), and from the molar flux, J, which corresponds to rL_p.

In the case of spherical particles:

$$L_p = \frac{d}{6} \tag{19}$$

where d is the particle diameter (cm).

Finally, the effective diffusion coefficient in the particle was calculated from Eq. (20) by adding the micropore and meso-macropore volume of the particle to calculate a global void fraction (Equation 21), without distinguishing the two porosity levels of the particle. Thus:

$$D_{eff} = \varepsilon^2 D \tag{20}$$

where ε is the void fraction of the carbon particle (dimensionless) and D is the diffusion coefficient (cm^2 s^{-1}) of oxygen in the electrolyte (considered to be water). The void fraction of the particle, ε, can be calculated as:

$$\varepsilon = \frac{V_{Hg} + V_{DUB}}{V_{Hg} + V_{DUB} + \frac{1}{\rho_{carbon}}} \tag{21}$$

where V_{Hg} is the meso-macropore volume determined by mercury porosimetry (cm^3 g^{-1}), V_{DUB} is the micropore volume determined by nitrogen adsorption-desorption (cm^3 g^{-1}), and ρ_{carbon} is taken equal to 2 g cm^{-3} [24, 56]. The platinum volume is neglected because it has a very high density (21.5 g cm^{-3}). The volume of Nafion® is neglected as well since the ratio between the amount of Nafion® inside the pores of the carbon xerogel and outside the particles is not known. The obtained void fraction is equal to 0.68.

In the case of a particle of 5 µm in diameter, with a void fraction of 0.68, a current of 60 A g_{Pt}^{-1} is obtained for a Weisz modulus equal to 0.1. In other words, in the case of a 5-µm isolated particle of Pt/carbon xerogel catalyst, the internal diffusion limitations for currents below 60 A g_{Pt}^{-1} can be considered as low enough to be neglected. This value is much higher than the calculated current value leading to mass transfer limitations in the case of a layer of approximately 17 µm of carbon xerogel (0.33 mA cm^{-2}, or 0.87 A g^{-1}, section 3.4.3). This value of 60 A g^{-1} is however overestimated for several reasons.

First, the calculation of the Weisz modulus assumes a perfectly mixed medium outside the particle, whatever the direction. But, in reality, the particle is in contact with the vitreous carbon, and other particles may be close or agglomerated, thus greatly limiting the convection. This renders the assumption of a perfectly mixed medium doubtful.
Second, since the particle size distribution (centered on 5 µm) is rather wide (Figure S2), the influence of the presence of larger carbon xerogel particles needs to be considered. In that respect, particles larger than 5 µm suffer much severe diffusion limitations because the Weisz modulus varies with the square of the particle size.

The use of isolated particles, and not of homogeneous layers, would nevertheless allow to reduce the impact of mass transfer. However, experiments should be carried out to study the impact of such modifications on the homogeneity and reproducibility of deposits. In addition, the diffusion-convective plateau may not be reached if the amount of carbon xerogel particles is too small or if the vitreous carbon surface is not fully covered [57]. This plateau allows to check the oxygen concentration in the solution because the limiting current varies only as a function of the rotation speed of the electrode and the oxygen concentration in the solution (Equation 5). Determining the plateau value is however not directly necessary for the measurement of the kinetic current.

Finally, the characterization of the Pt-carbon xerogel catalyst did not bring additional issues compared to the commercial catalyst with the same platinum amount. The reproducibility of the results is even better.

4. Conclusion

The goal of this work was to understand the impact of the layer thickness (and consequently high Pt loading) on RDE measurements, when unconventional catalyst supports are used. In particular, the study aimed at determining if classical protocols need to be modified in order to characterize Pt/C catalysts made of µm-sized nanostructured carbon supports, now widely studied in literature. To do so, RDE measurements were first performed on layers made of a commercial catalyst (37 wt.% Pt) with a common Pt loading (37 $\mu g_{Pt}\ cm^{-2}$ – conventional thin layer) and a high Pt loading (370 $\mu g_{Pt}\ cm^{-2}$ – thick layer). Then, similar characterization procedures were applied to a layer made of Pt supported on 5 µm carbon xerogel particles, with a thickness of about 15 µm, corresponding to the minimum requested to get a homogeneous coating; given the catalyst Pt content (34 wt.%), the electrode loading was also equal to 370 $\mu g_{Pt}\ cm^{-2}$.
The study on commercial catalysts showed that measurements of catalyst activity and electrochemical surface area are possible in the case of high Pt loading (*i.e.* thick layer) even if some differences remain unclear: (i) lower reproducibility and value of the S_{CO}, (ii) higher double layer capacity per gram of carbon. However, modifications to conventional measurement protocols need to be made by reducing the scanning rate to 0.5 or 1 mV s^{-1} and by increasing the reference potential to 1.00 or 1.05 $V_{/RHE}$ for relevant measurements of the kinetic current. This was necessary in order to reduce the impact of the double-layer capacity and to lower the impact of diffusion limitations. In the case of Pt/carbon xerogel catalysts, no specific problems due to the pore texture were detected and the reproducibility was even better. However, the same modifications to conventional measurement protocols are needed (decrease of scanning rate and increase of the reference potential for ORR measurements). Indeed, calculations showed that similar diffusion limitations were present in both samples. Note also that RDE measurements on partially isolated carbon xerogel particles could also be considered to reduce the impact of these limitations.

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Compliance with ethical standards

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