

Article

Fe/N/C Catalyst Production by Collinear CO₂ Laser Pyrolysis: Toward a Specific Mass-Weighted Energy-Deposited (J.g⁻¹) Parameter Opening Discussion on FeN_x Site Formation

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Abstract

We report the synthesis of Fe/N/C ORR electrocatalysts by an original collinear CO₂ laser pyrolysis of liquid aerosol droplets in various configurations and compared them to a catalyst synthesized in the classical perpendicular one. While the precursors were always injected at the bottom side of the reactor, two collinear configurations of the laser entry into the reactor are considered: by the Top Side (T.S.) or by the Bottom Side (B.S.). The two corresponding catalysts sets show significant different ORR performances. An in-depth XPS analysis and fitting of the N1s spectra allowed for drawing the ORR performance as a function of FeN_x sites components. An original approach considering the energy delivered to a quantity of precursors in J.g⁻¹, linked to the flame temperature feature, evidenced very different conditions for perpendicular CO₂ laser pyrolysis and each of the two collinear configurations. This mass-weighted energy delivered in the classical perpendicular configuration is too low to allow for the formation of FeN_x sites and the resulting ORR performance is extremely poor, suggesting a marginal role of nitrogen species without interaction with iron atoms. In contrast, the delivered mass-weighted energies are sufficient in both collinear configurations to produce FeN_x sites. The ORR performance for catalysts produced in these both configurations is positively correlated with the amount of energy deposited on the precursors. The ORR performance in the T.S. laser configuration is positively correlated to the amount of FeN_x sites. The best performing catalysts obtained in the B.S. configuration show an opposite variation. These trends, and the ORR performance degradation of B.S. catalysts under prolonged chronoamperometry are discussed in light of the effect of temperature on the formation of the various kind of FeN_x sites. A tentative explanation is given, considering that N1s XPS fitting with a single FeN_x component may hinder the fact that Pyridinic sites components may contain a part of FeN_x sites, as suggested by theoretical calculation from the literature. The best catalysts obtained in this work by collinear configuration show similar performances to those obtained by double stage perpendicular pyrolysis previously reported with an ORR onset potential of ~860 mV.

Keywords: ORR; non-noble; catalysts; laser; pyrolysis; aerosol



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1. Introduction

M/N/C ORR electrocatalysts with M being a transition metal, typically iron, shows promising potentiality for the replacement of platinum based electrocatalysts at the cathode of proton exchange membrane fuel cells. These materials are developed using a variety of precursors containing iron, nitrogen and carbon, which are put together and converted into catalysts through at least one high temperature treatment. The latter induces precursors decomposition through relatively unknown mechanisms and results in the formation of carbon-based structures, since carbon is the majority atom in precursors, in which smaller amounts of iron and nitrogen are incorporated. To obtain ORR Fe/N/C catalyst with high performances, several features are required. The final carbon structure must be electron conductive and thus show a significant degree of graphitization. The latter point also favors the stability of the carbon backbone towards oxidative degradation. The final carbon structure should also be highly porous including macropores mesopores micropores. Macropores and mesopores favor mass transport of oxygen to ORR active sites, which are now widely accepted as being hosted in microporosity as early suggested by Jaouen et al. for catalysts prepared by high temperature treatment under ammonia [1]. A high microporosity results in high specific surface area and a high-volume density of active sites which is beneficial to high performances in fuel cell device. The consensus on the identification of the most important active sites in Fe/N/C catalyst is the result of numerous studies over a long period of time. In early 2000, analyzing Fe/N/C catalysts by Time-Of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) Lefèvre et al. evidenced the presence of FeN_xC_y fragments in the catalyst [2,3]. TOF-SIMS analysis limited the difficulties related to the presence of iron-based particles in the material in elucidating the origin of the activity in the catalyst. Progressively, the use of Mossbauer spectroscopy combined with modified synthetic approaches allowed for minimizing the formation or eliminate iron-based nanoparticles formed in the catalysts, and reinforced the evidence of the central role of so called FeN_4/C and N-FeN_{2+2} centers [4–6]. Through new synthetic approaches involving Metal Organic Framework [7,8], the last fifteen years have seen considerable progresses with the synthesis of Fe/N/C Single Atom catalysts (Free or almost-free of iron-based particles) embedded in high microporosity rich and thus high specific surface area carbon matrix. Modifying the temperature of thermal treatment with such an approach led to the formation of catalysts with one kind of FeN_x site, i.e., FeN_1 , FeN_3 , and FeN_4 sites as suggested by Extended X-Ray Absorption Fine Structure analysis [9]. These progresses not only boosted the ORR performances, by strongly increasing the amount of efficient iron involved in FeN_xC_y active site for the ORR, but also provided improved materials for deeper understanding of the structure of the most active sites [10,11] which are identified as being FeN_4 sites. Currently, the research on Metal/N/C single atom catalysts is still very active, as the latest advances, strategies and challenges, such as the performance improvement and improvement of the catalyst's stability may be found in very recent reviews [12–18].

The above evoked syntheses of Fe/N/C ORR catalysts are multistep syntheses sometimes requiring combined synthesis of specific precursors, use of templates, ball milling steps, and multiples thermal treatments. The synthesis approach involved in the present work is based on the CO_2 Laser Pyrolysis of an Aerosol of Liquid Droplet (CO_2 LP-ALD) for the synthesis of Fe/N/C catalysts that we first reported for this purpose in 2018 [19]. CO_2 laser pyrolysis of aerosol droplet is, in a way, a synthesis method related to Spray Flame Pyrolysis (SFP) for producing various kind of nanoparticles. Both methods are one step nanoparticle synthesis based on a very fast high temperature decomposition of precursors and a very fast cooling of products. The mechanisms of nanoparticle formation that have been proposed for SFP [20,21] probably holds for CO_2 LP-ALD as suggested in [19].

Over the last decades, SFP has developed considerably and an impressive variety of finely tailored nanoparticle materials that reach application in numerous fields can currently be synthesized [20–23] at laboratory, as well as on an industrial scale [23]. CO₂ LP-ALD and CO₂-LP fed with gas do not address, so far, the synthesis of such a variety of nanoparticle materials [24–28] and industrial production seems mainly related to silicon-based nanoparticles [29].

To our knowledge, only two references can be found in the literature on the subjects of synthesis of Fe/N/C ORR catalyst by SFP [30,31]. While the ORR performance in basic conditions was quite significant [30], the one in acid conditions were very poor [31], which strongly contrasts with the encouraging results recorded using one-step synthesis CO₂ LP-ALD [19]. Such a result may be related to the major difference between SFP and CO₂ LP-ALD in the way the energy is provided to decompose the aerosol liquid droplet precursors. For CO₂ LP-ALD, energy is physically delivered by the strong vibrational excitation of the laser light by an absorbing molecule present among the precursors, while for SFP, it is chemically brought by a combustion reaction. As this reaction implies the presence of oxygen, a significant oxidation of iron occurs leading to Fe₂O₃ occurs [30]. Although we demonstrated the high ORR performances in acid media which could be reached by high temperature post treatment under ammonia performed on catalyst produced by CO₂LP [32], our goal was still to produce, in a single step (i.e., without thermal post-treatment), significant amount of so called as formed performing ORR Fe/N/C. One may note that two papers [33,34] recently reported the synthesis of Fe/N/C catalysts by CO₂ LP-ALD using different liquid precursors than the ones we used. The as-prepared materials (i.e., without any thermal post treatment) in this work shows surprisingly low specific surface area compared to those we reported previously. We did not find in these reports the ORR performance of the as-formed catalysts. Only ammonia heat-treated are considered and showed much poorer performances in acid media than in basic media. Although the way we evaluate the ORR performance is different than the one used in these papers, it seems that the reported ORR performances of ammonia heat-treated catalysts do not exceed those we reported in [32]. Pursuing the goal of making performing ORR catalysts in one-step synthesis, we reported double ammonia promoted CO₂LP-ALD, with clearly improved ORR performances compared to catalysts formed by single ammonia promoted CO₂ LP-ALD [35].

The motivation of the present work was to evaluate another approach aiming at forming in one step, i.e., without thermal post treatment, improved Fe/N/C ORR catalyst using CO₂LP-ALD. It was driven by the idea that increasing the residence time of precursors and forming particles in high-temperature conditions, i.e., the flame induced by the laser driven ammonia decomposition, may improve the ORR performance. This is suggested by the strong effect of ammonia, high-temperature post treatment and by the improvement reported in our previous study [35], since in the later case the above-mentioned residence time in the high temperature region is dramatically increased compared to single CO₂LP-ALD. Thus, a collinear configuration, in which the laser and the aerosol precursors overlap along the same axe, was conceptualized [36], aiming at increasing significantly the residence time in the hot flame region compared to the classical perpendicular configuration overlap usually involved in CO₂ LP. In this paper the approach is presented and the characterization and properties of several ORR catalysts synthesized by collinear CO₂ LP are presented. The two different collinear configurations for the laser entry into the reactor (by the bottom side or by the top side), while the precursors always penetrate by the bottom side of the reactor, are evaluated. These two configurations led to catalysts with significantly different ORR performances and trends as a function of the laser power delivered. Numerous characterizations, in particular XPS analysis, were performed and are presented in Section 3.

The Section 4 is based on the overview of these results. This led us beyond the potential interest of collinear CO₂LP-ALD as a way to improve the ORR performance of as-formed catalysts, since we propose a first order quantitative evaluation of specific energy deposited on the precursors as a key to understand our results.

2. Materials and Methods

2.1. Collinear CO₂ Laser Pyrolysis Setup

Figure 1 shows an overview of the approach involved in the paper and a scheme of the experimental set-up used for collinear ammonia induced CO₂ laser pyrolysis. A picture of the pyrolysis flame obtained in this configuration is also shown. Indeed, at the preliminary stage of our study, a glass wall reactor was used in order to allow for the size of the pyrolysis flame to be evaluated. Since the glass part of the reaction is 50 cm long, the flame length obtained here at low laser power and low ammonia flow rate for safety reasons is at least 30 cm that is significantly longer than the flame length in the perpendicular CO₂LP-ALD configuration. This feature tends to prove that the collinear CO₂LP-ALD is a configuration in which the residence time of precursors and forming particles in the flame region is longer. For the catalysts studied in this paper this glass wall part of the reactor was replaced by a stainless steel component. The reactor itself is a vertical tube of 40 mm inside diameter and 450 mm length. The precursors are injected at right angle by a tube extension connection at the bottom of the reactor and are exposed to the laser radiation all along their travel from the bottom to the top of the reactor tube. In contrast to previous reports by our group [19,32,35] the laser beam was not focused, in order to overlay the total volume occupied by the precursors and the particles that have just been produced all along the reactor length. The interaction region with the laser beam then begins from the entrance of the precursors and ends at the products outlet. The final products are ejected at the top of the reactor tube from the laser interaction region by a tube extension connection at 45° from the vertical axis and directed to the powder collector. The aerosol flow always goes from the bottom to the top of the reactor. The laser beam is injected in the vertical axis of the reactor tube through ZnSe windows located at the top and at the bottom of the main tube. Two directions are investigated for the laser beam. It can be injected in the same direction as the aerosol flow (from the bottom to the top, shown in Figure 1) or in the opposite direction.

The image shows the pyrolysis flame recorded at a preliminary step of this work using a glass wall reactor. The right side of the figure provides an overview of the steps which lead from the raw powder collection to the electrode fabrication and characterizations (see Section 2.4).

2.2. Synthesis Procedure of Fe/N/C Electrocatalysts

The aerosol of precursors is composed of micron-size droplets generated by a nebulizer Pyrosol® 7901 type piezoelectric aerosol generator from RBI (RBI, Melan, France) and Ar carrier gas. The droplet size is primarily defined by the piezoelectric frequency, which is 800 kHz. The device supplier indicates an average droplet size of 8 µm for water. Toluene and iron III acetylacetonate (Fe(C₅H₇O₂)₃ referred as Fe(acac)₃) were purchased from Sigma Aldrich (Sigma Aldrich St. Louis, MO, USA), and used to prepare the liquid precursor media consisting finally in a toluene solution of Fe(acac)₃ at a concentration of 14 g.L⁻¹.

In this work, three different sets of data are provided. The first set corresponds to the use of the PRC 2200 CO₂ laser (PRC, Ladson, SC, USA) entering by the top side of the reactor, while the two other sets correspond to a bottom side laser entrance, with the PRC 2200 laser on the one hand and the PRC 2800 (PRC, Ladson, SC, USA) on the other hand. Both lasers differed from each other by their power capacity and also by slightly different

beam sections areas, $\sim 2.5 \text{ cm}^2$ and $\sim 3.1 \text{ cm}^2$ for PRC 2200 and PRC 2800, respectively. They both have the same wavelength of $10.6 \mu\text{m}$. The parameter that was systematically varied is the percentage of the maximum Laser Power (L.P.), determining the absolute laser power injected at the entrance of the reactor. Therefore, the first set of catalysts is named CatTXX-2200 where T indicates a top side entrance of the laser, XX the laser power percentage, the last indication being the type of PRC laser involved (PRC 2200). The second and third set of catalysts are named CatBXX-2200 and CatBXX-2800 where B indicates reactor Bottom window entrance of the laser and XX the laser power percentage. The gas flow rates involved in each synthesis are reported in Supplementary Materials Table S1 with other detailed conditions for all the syntheses. For the CatBXX-2800 catalysts set, the protecting argon flow of the bottom window was increased from 2500 sccm to 5000 sccm for safety reasons (see Section 3.2). As in previous work [19,32,35], the flow rates of argon and ammonia defined the so-called R parameter as the flow rate volume fraction of ammonia in argon. R was here calculated without considering the protection argon flow from the top window of the reactor, set at 8000 sccm for all the syntheses, assuming that it had no dilution effect of the ammonia flow in the reaction region.

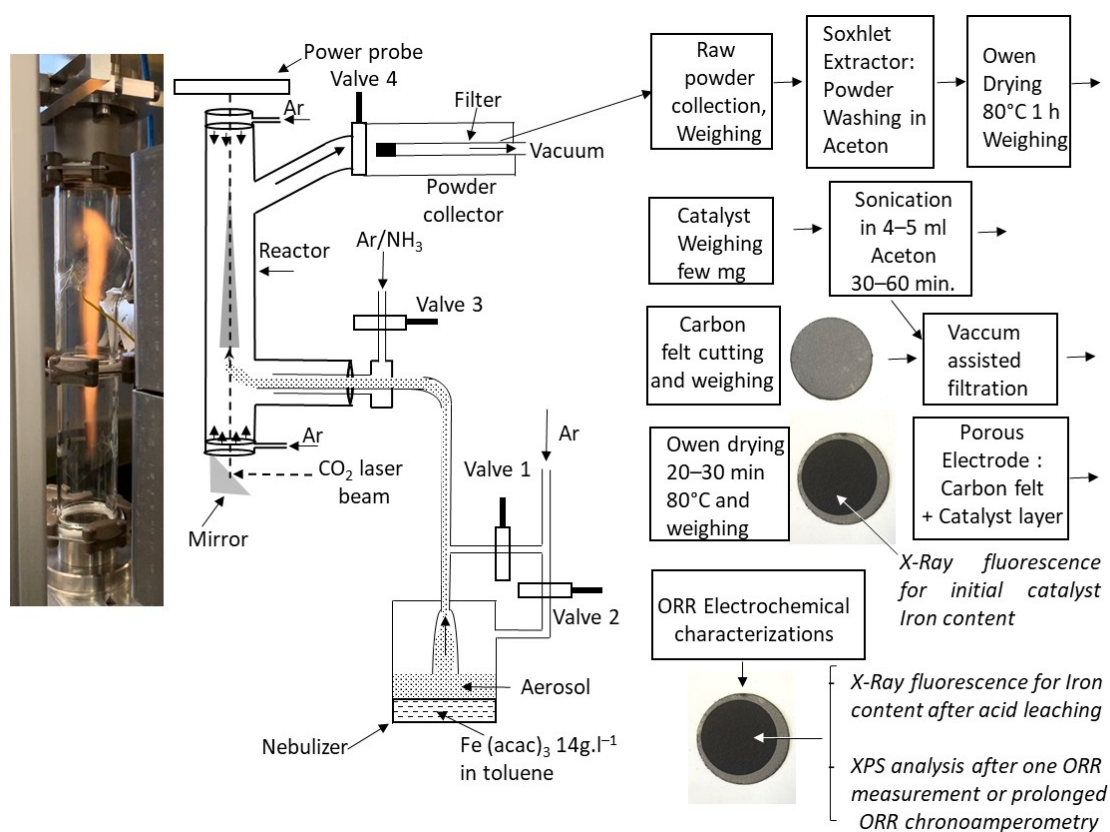


Figure 1. Experimental set up for collinear ammonia induced CO₂ laser pyrolysis illustrated in the case of the laser entering from the bottom up to the top (same direction as the aerosol flow). The arrows in the right part of the figure indicate the successive steps from the collection of the raw catalyst powders, to the fabrication of the porous electrodes, to their electrochemical characterization and their analysis by X-Fluorescence and XPS.

The following describes the way the syntheses are triggered. Thanks to a pressure regulation system, the reactor pressure is first fixed at 739 Torr while the valve 4 (powder collection) is opened, the laser entrance and exit windows of the reactor being blown with argon from the interior of the reactor in order to protect them from further powder deposition. In a first step, valve 1 is opened and valve 2 is closed in order to adjust the flow parameters in the reactor without introducing any precursor droplets. Before the

beginning of the experiment, the nebulizer, equipped by a glass-cooling coil fed with water at 15 °C, is filled with the precursor solution, turned on, and allowed for thermalizing for at least 20 min. Note that the settings of the nebulizer in term of fine power and frequency setting were previously studied in order to optimize the amount of aerosol liquid precursor delivered at the flow rate of 1185 sccm of Ar. The effective amount of liquid precursor used for each synthesis is reported in Supplementary Materials Table S1. While the valve 1 remains opened and valve 2 is closed, the aerosol cloud stays above the surface of the liquid precursor media and does not enter into the reactor.

At this step, valve 3 is opened and blown with Ar with a flow rate corresponding to the one which will be used for the ammonia flow for the synthesis (2400 sccm). After thermalization of the nebulizer, the laser is progressively set at a given ratio of its maximum power. The power detector thus indicates the incident laser power. The Ar flow rate, through valve 3, is then replaced by the same flow rate of NH₃ and the laser beam absorption by NH₃ generates a pyrolysis flame. The power detector thus indicates a new value of incident laser power, which, subtracted from the measurement recorded without ammonia allows for the power laser absorption to be calculated. The beginning of the synthesis is triggered by opening valve 2 and closing valve 1, which allows for the aerosol precursor to enter into the reactor from its bottom side. The decomposition of the aerosol produces a black powder that is harvested on a sintered tubular filter.

The next sub-sections deal with the characterization methods, electrode preparation and electrochemical characterization. The right side of Figure 1 shows an overview of the steps by which the collected powders are treated to end-up to porous electrodes used for some of the characterizations performed on it in addition to electrochemical ones.

2.3. Characterization of the Fe/N/C Electrocatalysts

All the catalysts were first washed in acetone using a Soxhlet extractor for 48 h to get rid of side products mostly consisting of polycyclic aromatic hydrocarbon. The iron content was determined directly on catalyst porous electrode samples (see below) using X-ray fluorescence as reported elsewhere [19,37]. Briefly, a collection of porous reference electrode sample was built by filtration of carbon nanotubes on H23C3 Freudenberg carbon felts. The iron content of 3.15% and 6.5% of two different set of carbon nanotubes was previously determined by thermogravimetric analysis under air. The reference electrodes with known iron loading were then prepared and used to build a calibration curve based on the iron K α line intensity as a function of the iron content in the CNT electrodes. Numerous measurements were performed in the present work and seven different calibration curves were established at different times. The slopes of the calibration curves showed a standard deviation of 7%, which was used to estimate the accuracy of the iron content determination in the catalyst materials.

The BET specific surface areas were determined using a micromeritics 3Flex apparatus (Micromeritics, Mérignac, France). The sample were outgassed at 250 °C for at least two hours before measurement.

Scanning Electron microscopy was recorded using a Zeiss 1525 Microscope (Zeiss, Marly le Roi, France) provided with a Gemini field effect gun column. Representative micrographs of the catalysts studied in this work can be found Supplementary Materials Figure S1.

Raman spectroscopy characterizations were conducted in ambient conditions using a Horiba XPLORA PLUS spectrometer (Horiba, Longjumeau, France) at an excitation wavelength of 532 nm in the range of 100–4000 cm⁻¹. Quantitative Raman parameters were obtained from the deconvolution of Raman spectra by using the Sadzky's method [38], five peaks (D, D', D3, D4, and G) and using a linear baseline and Voigt functions (a combi-

nation of Gaussian and Lorentzian functions, the proportion of which is adjusted to each spectrum). This treatment was performed using the Horiba LabSpec 6 software. Single-crystal graphite is characterized by a single band at 1581 cm^{-1} (referred to as the “G band”) in the first order region of the spectrum ($1000\text{--}2000\text{ cm}^{-1}$), attributed to the E_{2g} mode [1]. The D band at 1350 cm^{-1} as well as the D’ band at 1620 cm^{-1} are related to the presence of defects in the graphitic structure [38]. The D₃ and D₄ bands correspond respectively to the disordered carbon formed by sp² and sp³ bonds [39]. Here, the Raman data were exploited through ID/IG intensity ratio and center position of the G band.

X-Ray Diffraction was recorded on powders using a MM007HF (Rigaku®) rotating X-ray generator (Rigaku, Strasbourg, France) using a molybdenum anode. Thus, it delivered a focused monochromatic beam with a circular size of $100\text{ }\mu\text{m}$ around 17.48 keV ($\lambda = 0.70932\text{ }\text{\AA}$) using a Xenocs® (Xenocs, Grenoble, France) FOX2DMO25_25P diffraction optic. Diffraction patterns were collected through the powder samples in transmission mode during 180 s with a two-dimensional RebirX 70S hybrid pixel detector from Cegitec (Cegitec Aubagne, France). The images were then transformed into $I = f(2\theta)$ diagrams by circular integration using the open-source Python (3.10 version) library for Fast Azimuthal Integration (PyFAI). The 2θ angles were converted into $2\theta\text{ K}\alpha\text{ Cu}$.

XPS analysis was performed with a Thermo NEXSA G2 spectrometer (Thermo Fisher, Waltham, MA, USA) by recording high resolution spectra of C1s, O1s, Fe2p and N1s region. The chemical composition of the particle surface was obtained from these high-resolution data, and the feature of the N1s core level was studied by fitting (see Section 3.2.5). The monochromated K-alpha aluminum line at 1486.7 eV was used as X-ray excitation source. A low-energy electron/ion flood gun was employed to enable proper charge compensation during data acquisition. Photoelectrons were collected in constant analyzer energy (CAE) mode, using pass energies of 200 eV for survey scans and 20 eV for high-resolution core-level spectra. The detection was performed perpendicular to the sample surface. This latter consists in porous electrodes formed by filtration of a catalyst dispersion on carbon felts precoated with a 30 nm gold layer deposited by vacuum evaporation. This gold deposit prevents the unwanted collection of carbon and nitrogen photoelectrons from the carbon felt. Generally, before XPS analysis the electrode underwent an electrochemical conditioning step followed by a single ORR measurement described hereafter.

2.4. Electrode Preparation, Electrochemical Measurement and Selectivity

Perchloric acid 70%, Hydrogen peroxide 30% by wt.; Horseradish peroxidase (HRP) 25 K and 2,2’-azino-bis(3-ethylbenzothiazoline-6-sulfonate (ABTS) were obtained from Merck (Merck Darmstadt, Germany). Cyclic Voltammetry (CV) was recorded using a Bio-Logic VMP3 potentiostat (BioLogic, Seyssinet-Pariset, France). As reported previously in details [19,32,35], CVs were recorded on porous electrodes prepared by vacuum assisted filtration of catalyst liquid dispersion prepared by sonication in acetone, on Freudenberg (Freudenberg, Weinheim, Germany) carbon felt. In this work, the latter were H23C3 felts. Carbon felts were initially cut into 2.0 cm diameter circle using mechanical hole punch and weighted. Right after the catalyst filtration the porous electrodes were dried for 30 min at $80\text{ }^{\circ}\text{C}$ in air and were weighted. Subtracting the weight of carbon felt involved gave the catalyst electrode loading. Due to the cylindrical tank shape of the filtration system, the catalyst deposit was a circle of 1.6 cm diameter providing a 2.01 cm^2 catalyst area. For electrical connection to the potentiostat a gold wire was attached to a female banana crocodile clip, and the porous carbon electrode was attached to the gold wire extremity. Besides, a male banana plug was set on the three electrodes cell holder. The crocodile clips are carefully wrapped with Parafilm for protection from acid splashing. Before ORR CV recording, the porous electrode was placed on the three cells electrode frame holder and

submitted to an impregnation procedure involving successive immersion in pure ethanol, a 50/50 by volume mixture of ethanol and water, then water, for 3 to 10 min each. After the last immersion in water the electrode was rapidly immersed in the glass cell filled with HClO_4 1 M or 0.1 M. After electrolyte saturation by oxygen bubbling, the electrodes were then submitted to an extended number of scan (200 to 250) at 100 mV.s^{-1} from 1 V vs. SHE to 40 mV vs. SHE. Also described in previous works [32,35,37], since the catalysts were not acid leached before electrode preparation, the impregnation procedure gives rise to iron removal into the electrolyte. Actually, the conditioning step also serves as an acid iron leaching of the catalyst layer. The vanishing of iron related redox pics due to dilution in the bulk electrolyte provides a stable voltammogram [37]. Most of the time, the electrolyte was changed by a fresh one, although the use of the one containing the released iron give similar ORR CVs. A 20 to 30 min delay allowed for the electrode porosity to be reloaded with O_2 saturated electrolyte, then the electrode was finally polarized at 1 V vs. SHE for 4 min and the ORR CV was recorded at 5 mV.s^{-1} . The latter was background-corrected using the same measurement procedure performed under Argon-saturated electrolyte. All the potentials were measured using a sodium-saturated Calomel Electrode (SSCE radiometer analytical). On the CVs, potentials were reported versus the Standard Hydrogen Electrode (SHE, $-0.236 \text{ V vs. SSCE}$). The ORR performances of the different catalysts were compared to each other through the evaluation of the ORR onset potential or the potential at a given current expressed in mA.mg^{-1} in the kinetic region.

The selectivity of the ORR was measured using a method previously described [40] by us, involving a JASCO-570 UV-Visible spectrophotometer (JASCO, Lisses, France), and since used on various catalysts porous electrode structures [35,37,40–42]. It consists in an accurate assaying of the hydrogen peroxide produced during a chronoamperometry experiment at a determined potential in HClO_4 0.1 M under mechanical magnetic stirring. In this work, the potentials at which the selectivity was determined were 700 mV, 660 mV, 600 mV and 400 mV vs. SHE.

3. Results

3.1. Catalysts Obtained from the Top Side Entrance of the CO_2 Laser

3.1.1. Characterization of the Catalysts

In this section, the PRC 2200 laser was used. The reactor was equipped with the different powder collectors, which were successively used to synthesize three different catalysts for about 20 min duration each, using different percentages of the maximum laser power. The laser enters through the top window; therefore, this catalysts set is CatTXX-2200 (see Section 2.2). The data reported in Table 1 correspond to three syntheses in which the ammonia parameter (R) value was kept constant at 0.39. At the end of the experiments, the powders were collected and weighed, and the amount of liquid precursor consumed over the three synthesis was determined by weighing. The powders were then washed with acetone using a Soxhlet extractor for 48 h. Therefore, two different chemical yields are reported for each catalyst, a raw yield and a yield after acetone washing. It is worth noting that these low yields are only indicative since we observed that a variable amount of catalyst powder was stuck on various parts of the reactor walls along the syntheses.

The absorbed laser power and laser power densities deduced from laser beam section (Supplementary Materials Table S1) are very high for each of the synthesis and no clear correlation is observed between the chemical yield and the absorbed energy. The purified powders were characterized in term of iron content and specific surface area, providing the results shown in Table 2.

Table 1. Synthesis conditions and yields for the three catalysts obtained at different top-entrance incident laser power and a constant $R = 0.39$.

Catalyst Name	Laser % Power	Incident Power Without NH_3/W	Incident Power with NH_3/W	Laser Power Absorbed /W	Raw Chemical Yield/wt. %	Chemical Yield After Acetone Washing/wt. %
CatT40-2200	40	678	152	526	0.5	0.3
CatT55-2200	55	952	382	570	1.6	1.0
CatT70-2200	70	1228	622	606	1.4	0.9

Table 2. Iron content and specific surface area for the catalysts obtained at different top entry incident laser power and a constant $R = 0.39$.

Catalyst Name	Laser % Power	Washed Material Iron Content /wt. %	Specific Surface Area/ $\text{m}^2\cdot\text{g}^{-1}$
CatT40-2200	40	9.4 ± 0.7	127
CatT55-2200	55	3.2 ± 0.2	84
CatT70-2200	70	2.5 ± 0.2	97

The results show that the higher the laser power, the lower the iron content in the catalyst. No clear trend is observed for the specific surface area as a function of absorbed laser power. Scanning electron microscopy (see Supplementary Materials Figure S1) revealed similar particles size for the three catalysts and suggested three populations with average diameter size in the ranges of 40 nm to 60 nm, 20 nm to 40 nm, and smaller particles with diameter lower than 20 nm. Finally, the powders were characterized by X-Ray diffraction (XRD) and Raman spectroscopy (see Supplementary Materials Figure S2 for XRD and Table S2 and Figure S3 for Raman spectroscopy). Both methods point the same feature for the CatTXX-2200 set of catalysts. The XRD did not show well defined diffraction peak from which iron-based nanoparticle could be identified, while two broad structures featuring a poorly organized carbon phase are present. The 002-carbon peak is asymmetrical with a maximum shifted towards lower diffraction angles. Such characteristics suggest materials in which several graphene structures coexist (amorphous, turbostratic or graphitic-type domains). The Raman spectra fitting (Supplementary Materials Figure S3) allowed for the estimation of the intensity ratio of the D (ID) band related to defects to the intensity of the G band (IG) related to graphitic domains. Values between 1.19 and 1.22 were obtained. The position of the G band was also collected and varied between 1591 cm^{-1} and 1589 cm^{-1} . According to the three-stage model [43] these data suggest the presence of nanocrystalline graphite in the materials. Different ways to exploit Raman spectra fitting can be used to determine the size of graphitic coherent domains [44], basically with the ratio ID/IG. We observe that the laser power percentage has no influence on the size of graphitic coherent domains since the ID/IG ratio is quite the same for the CatT40XX-2200 set. Finally, Raman spectra and XRD show very similar features to those recorded on furnace carbon blacks [45].

3.1.2. Oxygen Reduction

The oxygen reduction was characterized by cyclic voltammetry in HClO_4 1 M at $5\text{ mV}\cdot\text{s}^{-1}$. The catalysts were at this step compared to each other by the onset potential recorded for the ORR (Figure 2).

It is observed that in the present top side laser entry syntheses, the ORR performance is improved when the absorbed laser power is decreased with ORR onset potentials of $\sim 780\text{ mV}$, $\sim 800\text{ mV}$ and $\sim 830\text{ mV}$ vs. SHE for CatT70-2200, CatT55-2200 and CatT40-2200, respectively. Since the catalyst powders were not acid leached, the iron content in the electrodes were measured after the conditioning step and the ORR measurements. As

mentioned previously (Section 2.2), the conditioning step, which consists in applying a CV (200 to 250 scans) at 100 mV, also serves as an iron acid leaching step of the catalyst layer. Consistently with this acid leaching, the iron content in the catalyst layer of the electrodes was found to be lower than before electrochemical characterization (Table 3). In order to check that this iron acid leaching as performed was efficient, for each material, one or two electrodes were systematically left for seven days in the acid electrolyte. Another ORR measurement was performed after replacement of the 7 days old electrolyte by a fresh one and the iron content was then measured again (Table 3). No significant modification of the iron content was observed by X-Ray fluorescence and the ORR CV overlapped with the initial one, thus suggesting that the conditioning step ensures an efficient iron acid leaching of the catalyst layers.

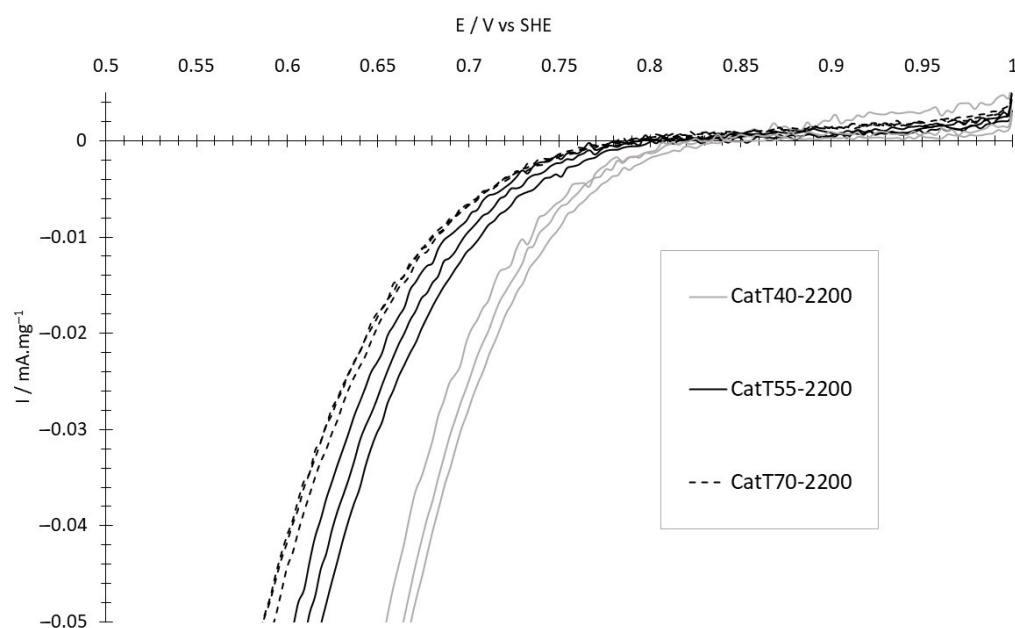


Figure 2. Background corrected ORR CVs for catalysts produced at different power laser and $R = 0.39$ with the PR2200 CO_2 laser entering in the reactor by the top of the reactor. For each laser power, three electrode samples are shown. HClO_4 1 M, 5 mV.s^{-1} .

Table 3. Iron content in the electrodes after ORR measurement.

Catalyst Name	Laser % Power	Iron Content After Electrochemistry /wt. %	Iron Content After 7 Days Immersion in the Electrolyte/wt. %
CatT40-2200	40	5.7 ± 0.4	5.7 ± 0.4
CatT55-2200	55	2.3 ± 0.2	2.3 ± 0.2
CatT70-2200	70	1.7 ± 0.1	1.9 ± 0.1

3.2. Catalysts Obtained from the Bottom Side Entrance of the CO_2 Laser

3.2.1. Characterization of the Catalysts

In this section, the catalysts were synthesized using successively the PRC 2200 and the PRC 2800 CO_2 lasers with again three different laser power percentages, but here, with the laser beam entering into the reactor by the bottom window. The two catalysts sets are CatBXX-2200 and CatBXX-2800 (see Section 2.2). As a reminder for example, CatB40-2200 is the catalyst synthesized with the PRC 2200 laser set at 40% of its maximum power and entering into the reactor by the bottom side. The first set of experiments were performed with the PRC 2200 used in the previous section with a constant value for the ammonia parameter ($R = 0.39$). After the syntheses, the reactor was dismantled and cleaned and

we found traces of catalyst powder close to the bottom laser entrance window. Because powder deposition on the window is very hazardous as it can result in local heating and strong damages to it (up to breaking), we decided to increase the protecting argon flow on it for the experiments involving the PRC 2800 CO₂ laser. Thus, for the latter experiments the ammonia flow being the same as previously (2400 sccm) the actual ammonia parameter was mechanically lowered at $R = 0.28$. Table 4 reports some of the synthesis conditions for the two sets of experiments as well as the chemical yield of the synthesis. Detailed conditions are provided in Supplementary Materials Table S1.

Table 4. Synthesis conditions and yields for the catalysts obtained at different bottom entry incident laser power with PRC 2200 laser and $R = 0.39$ and PRC 2800 laser an $R = 0.28$.

Catalyst Name	Laser % Power	Incident Power Without NH ₃ /W	Incident Power with NH ₃ /W	Laser Power Absorbed /W	Raw Chemical Yield/wt. %	Chemical Yield After Acetone Washing/wt. %
CatB40-2200	40	695	230	465	1.9	1.2
CatB55-2200	55	963	459	504	1.4	1.0
CatB70-2200	70	1250	710	540	1.0	0.8
CatB40-2800	40	786	215	571	3.3	2.6
CatB50-2800	50	995	360	635	2.7	2.2
CatB60-2800	60	1319	529	790	2.3	2.1

The absorbed laser and power densities (Supplementary Materials Table S1) for CatB40-2200, CatB55-2200 and CatB70-2200 are lower than those reported for CatTXX-2200 catalysts (Table 1) at the same L.P. percentage. This suggests that the top or bottom laser entrance strongly impact the way the laser absorption occurs (see Section 4). For CatB40-2800, CatB50-2800 and CatB60-2800 the absorbed laser powers at similar laser power percentages are higher than those reported for catalysts sets synthesized with the PRC 2200 laser. However, since the laser beam section of PRC 2800 is higher than the one of PRC 2200 laser, the power densities for similar P.L. percentage are relatively close to each other (Supplementary Materials Table S1). The data in Table 4 suggest a correlation between the (still low) chemical yields and the absorbed laser power. Lower chemical yields are obtained for higher absorbed power. The chemical yields recorded for CatBXX-2800 catalysts are higher than for CatBXX-2200 catalysts. This could be related the larger section of the PRC-2800 laser.

Table 5 reports the iron content recorded for the raw materials, as well as the specific surface areas.

Table 5. Iron content and specific surface area for the raw catalysts obtained at different bottom entry incident laser power with PRC 2200 and $R = 0.39$ and PRC 2800 and $R = 0.28$.

Catalyst Name	Laser % Power	Washed Material Iron Content /wt. %	Specific Surface Area /m ² .g ⁻¹
CatB40-2200	40	2.7 ± 0.2	89
CatB55-2200	55	3.4 ± 0.2	94
CatB70-2200	70	3.8 ± 0.3	116
CatB40-2800	40	1.7 ± 0.1	81
CatB50-2800	50	1.7 ± 0.1	96
CatB60-2800	60	1.8 ± 0.1	96

The iron contents in the catalysts formed using the PRC 2200 laser are higher than those prepared with the PRC 2800 laser and show a clear iron content increase from CatB40-2200 to CatB55-2200 taking into account the accuracy of the measurement. For the catalysts obtained from PRC 2800 laser, the iron content is not only lower but shows no significant

variation with the incident laser power percentage. The synthesis conditions do not strongly modify the specific surface areas, which lie in the same range whatever the incident laser power and the laser type involved. Scanning electron microscopy revealed similar particle sizes for the two sets of catalysts with again three populations. However, compared to CatTXX-2200 catalysts, the biggest particle diameters seem slightly lower, rarely exceeding 50 nm (Supplementary Materials Figure S1).

For both sets of catalysts CatBXX-2200 and CatBXX-2800 addressed here, XRD (Supplementary Materials Figure S2) shows the same features as those observed for the CatTXX-2200, with no diffraction peak related to iron-based phase, and a poorly organized carbon structure. The Raman spectra (Supplementary Materials Figure S3 for representative fitting) also presents similar ID/IG ratios (see Supplementary Materials Table S2) and consequently similar size of graphitic coherent domains to those of CatTXX2200 catalysts sets.

3.2.2. Oxygen Reduction

The same procedure as the one described in Section 3.1.2 was used for the ORR characterization of the catalysts. Background corrected ORR CVs recorded in fresh electrolyte are shown in Figure 3 for the catalysts of the CatBXX-2200 set. In contrast to what was observed for CatTXX-2200 catalysts, (Figure 2) it is observed that the incident laser power has no significant effect on the ORR performance since all the catalysts of this second range show quite the same ORR onset potential at ~850 to 860 mV vs. SHE. This reveals the strong impact of the laser side entrance with respect to the bottom side entrance of the precursors, which is always the bottom side of the reactor.

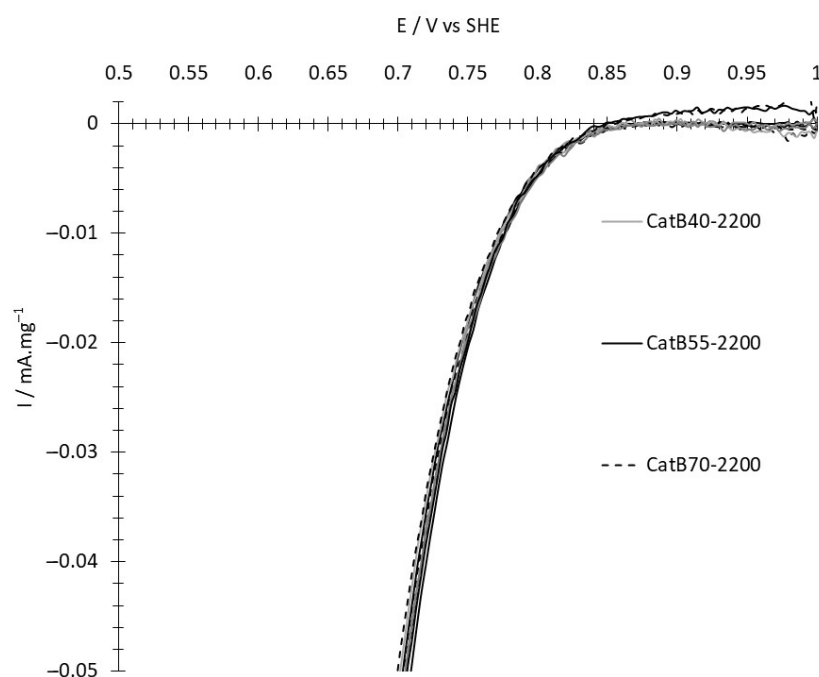


Figure 3. Background corrected ORR CVs for catalysts produced at different laser powers with the PRC 2200 entering into the reactor by the bottom side with $R = 0.39$. Three CVs recorded from three different electrodes are shown for each material. HClO_4 1 M, 5 mV.s^{-1} .

The CVs recorded on the catalysts synthesized with the PRC-2800 laser at different powers are shown in Figure 4a–d. Several electrode samples were prepared for each catalyst, which revealed a significant variability of the ORR CVs. This seems more pronounced for CatB60-2800 (Figure 4a) than for CatB50-2800 (Figure 4b) and CatB40-2800 (Figure 4c). We assume that this variability is due to inhomogeneities in the produced powders which seems more pronounced for the higher absorbed laser powers (CatB50-2800 and CatB60-2800).

The CatBXX-2200 catalysts set powders seem more homogeneous and they show lower absorbed powers. We assume that a high absorbed laser power may be responsible for a higher flame instability, which cannot be verified on our reactor at this time.

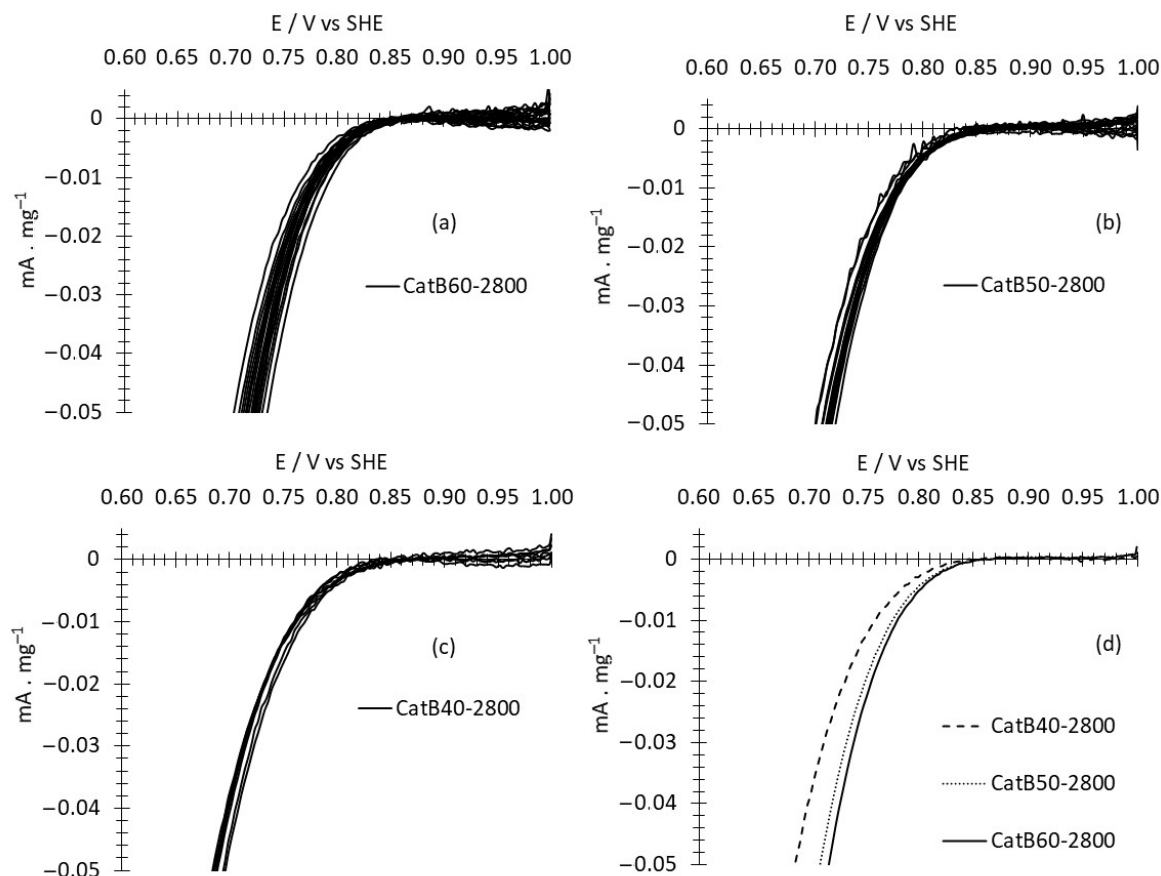


Figure 4. Background corrected ORR CVs for catalysts produced at different laser powers with the PRC 2800 laser entering in the reactor by the bottom, respectively, with $R = 0.28$. (a) ORR CVs for 20 different electrodes based on CatB60_2800. (b) ORR CVs for 15 different electrodes based on CatB50_2800. (c) ORR CVs for 7 different electrodes based on CatB40_2800. (d) Averaged ORR CVs for CatB60-2800, CatB50-2800 and CatB40-2800 obtained from (a–c). HClO_4 1 M, 5 mV.s^{-1} .

Figure 4d presents the averaged CVs obtained from the CVs shown in Figure 4a–c and allows for an easier comparison between the different materials. It appears that the catalysts synthesized with the lower laser power (CatB40-2800) is less efficient than the two others (CatB50-2800 and CatB60-2800). Actually, the CatB40-2800 catalyst shows similar ORR response than the catalysts synthesized with the PRC-2200 laser entering by the bottom side of the reactor (Figure 3). The CatBXX-2800 catalysts can also be compared using all the recorded CVs, through the averaged potential at a given current levels in the kinetic region, as for example 0.02 and 0.01 mA.mg^{-1} . The standard deviation obtained from these data allows for an evaluation of the uncertainty of the potentials (Table 6). Catalysts CatB50-2800 and CatB60-2800 have quite similar ORR performances, which are also similar to those obtained with the PRC-2200 laser of which the CVs are shown in Figure 3.

Table 6. Potential at 10 and $20 \mu\text{A mg}^{-1}$ for the catalysts synthesized with PRC 2800.

	Potential@ 0.01 mA.mg^{-1} \mV vs. SHE	Potential@ 0.020 mA.mg^{-1} \mV vs. SHE
CatB60-2800	780 ± 6	758 ± 8
CatB50-2800	776 ± 3	752 ± 6
CatB40-2800	762 ± 4	734 ± 4

Table 7 shows the iron content in the materials presented in this section after the conditioning steps and subsequent ORR measurements. Compared to the initial iron content in the catalysts (Table 5) the catalysts synthesized with PRC-2200 undergo a higher loss, retaining only between 55% and 65% of the initial iron content while the materials obtained with PRC 2800 laser retain between 77% and 82% of the initial iron content. The reason for this is unclear.

Table 7. Iron content in the electrodes after ORR measurement.

Catalyst Name	Laser % Power	Iron Content After Electrochemistry /wt. %	Iron Content After 7 Days Immersion in the Electrolyte/wt. %
CatB40-2200	40	1.5 ± 0.1	1.4 ± 0.1
CatB55-2200	55	2.0 ± 0.1	1.9 ± 0.1
CatB70-2200	70	2.5 ± 0.2	2.4 ± 0.2
CatB40-2800	40	1.4 ± 0.1	1.4 ± 0.1
CatB50-2800	50	1.4 ± 0.1	1.4 ± 0.1
CatB60-2800	60	1.4 ± 0.1	1.4 ± 0.1

As for the data shown in the previous section (laser entry by the top of the reactor), a prolonged stay of the catalysts electrodes in the electrolyte did not affect significantly the iron content, showing again the efficiency of the iron leaching during the CVs of the conditioning step of the electrode.

3.2.3. ORR Selectivity Measurements

The ORR selectivity was evaluated only on the three materials prepared using the PRC 2800 CO₂ laser entering through the bottom window of the reactor. The reason for this choice is that their oxygen reduction (ORR) performance was found to be slightly different (Figure 4), and that they were among the best performing catalysts for two of them (CatB60-2800 and CatB40-2800). Selectivities were measured directly on the porous electrodes as described in a previous report [40], by the spectrophotometric assaying of the H₂O₂ produced under chronoamperometry (CR) at a given potential in HClO₄ 0.1 M. Typical ORR CR recorded under mechanical magnetic stirring on porous electrodes can be found in [32,35,40]. Here, the ORR selectivity was investigated on electrode collections with different loadings for each of the three materials CatB40-2800, CatB50-2800 and CatB60-2800. On each electrode sample, up to four different potentials were successively explored. The whole set of data is reported for each catalyst in Supplementary Materials Table S3 for the CatB60-2800, CatB50-2800 and CatB40-2800, respectively. For measurements with the uncertainty on n higher than ±0.10, (Supplementary Materials Table S3) corresponding to a variation in percentage of H₂O₂ produced of ±5%, the data were not exploited. This was carried out to facilitate the analysis of the trends of the selectivity as a function of the potential imposed during the CR. The selectivity of the ORR is known to be dependent on the electrode catalyst loading [40,46,47]. The data shown in Supplementary Materials Table S3 consider electrodes with loads higher than 2.5 mg, which are much higher than the one for which the selectivity significantly decreases. For example, for CatB60-2800 catalysts at 400 mV and 600 mV, the selectivity decreases compared to those reported in Supplementary Materials Table S3, at respectively, 3.23 ± 0.01 and 2.75 ± 0.02 for a catalyst loading of 0.98 mg. However, despite the high electrode loading, the selectivity measured on different electrode samples of a given material, at a given potential, shows a certain variability. This probably reflects the variability observed on the CVs (Figure 4a–c) and therefore the assumed inhomogeneities in the catalyst powders.

The results of selectivity measurements are summarized in Table 8. They are calculated from the data in Supplementary Materials Table S3. It includes the average of the measurements and the corresponding standard deviation, for each potential and each material.

Table 8. Average values of selectivity for CatB40-2800, CatB50-2800S and CatB60-2800 at 700 mV, 660 mV, 600 mV and 400 mV calculated from data reported in Supplementary Materials Table S3.

Catalyst	n at 700 /mV vs. SHE	n at 660 /mV vs. SHE	n at 600 /mV vs. SHE	n at 400 /mV vs. SHE
CatB60-2800	3.21 ± 0.07	3.14 ± 0.1	3.26 ± 0.15	3.55 ± 0.12
CatB50-2800	3.30 ± 0.07	3.27 ± 0.15	3.25 ± 0.09	3.59 ± 0.04
CatB40-2800	–	3.02 ± 0.06	3.07 ± 0.04	3.39 ± 0.01

The data in Table 8 show, for each catalyst, a stable value for selectivity of the ORR at 700 mV, 660 mV and 600 mV and an increase of n at 400 mV. It can be noted that the selectivity data for each material ranks the same as the ORR performances (Figure 4d) which are very close to each other for CatB60-2800 and CatB50-2800, and significantly lower for CatB40-2800.

3.2.4. Instability of the Catalysts

The instability of the catalysts CatB40-2800, CatB50-2800 and CatB60-2800 was revealed first during selectivity measurements. Indeed, due to the variability in the selectivity measurements and despite the established robustness [35,37,40–42] of the method, we verified on several electrodes the reproducibility of the measurements. This revealed that repeated sequence measurements on the same electrode sample resulted in significant decrease of the selectivity at given potential, thus suggesting a loss of ORR activity. Since the selectivity measurement implies series of chronoamperometry measurements, it was decided to submit each catalyst to prolonged chronoamperometry at 600 mV to confirm the instability. Figure 5 gives an example of the ORR activity loss for CatB60-2800, successively induced by selectivity measurement and by further 24 h chronoamperometry at 600 mV.

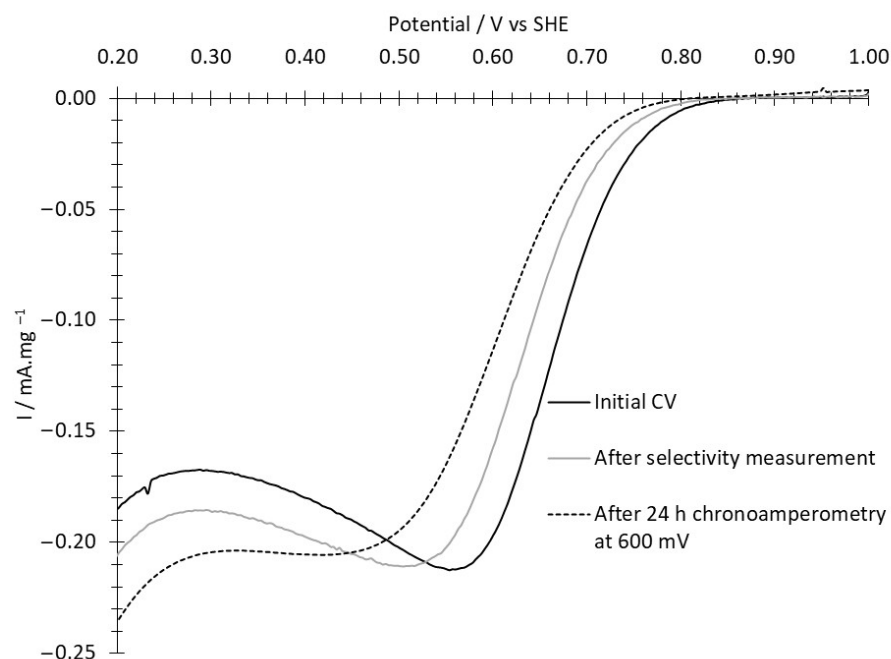


Figure 5. Illustration of the instability of the catalysts through the drop of the onset ORR potential for catalyst CatB60-2800. HClO_4 1 M, 5 mV.s^{-1} .

In an attempt to relate the drop of the ORR performance to an iron content drop in the catalysts, the latter was measured after selectivity measurement and the 24 h duration chronoamperometry at 600 mV. Again, the three different catalysts showed similar behavior with no evidence of iron drop, which could have explained the onset ORR drop. As an example, Figure 6 reports the iron content measurements at different steps of the study for CatB60-2800 i.e., before electrochemistry, after ORR CV measurement, after selectivity measurement and after CR at 600 mV for 24 h. Considering the accuracy of the determination of the iron content reflected by errors bars in Figure 6, it is seen that the loss of iron content observed after the conditioning step and the first ORR measurement is not accentuated after the selectivity measurement and the 24 h duration chronoamperometry experiment. The same behaviors were observed for CatB50-2800 and CatB40-2800 regarding the iron content. Therefore, it was not possible here to relate the ORR performance degradation illustrated in Figure 5 to a loss of iron in the catalysts.

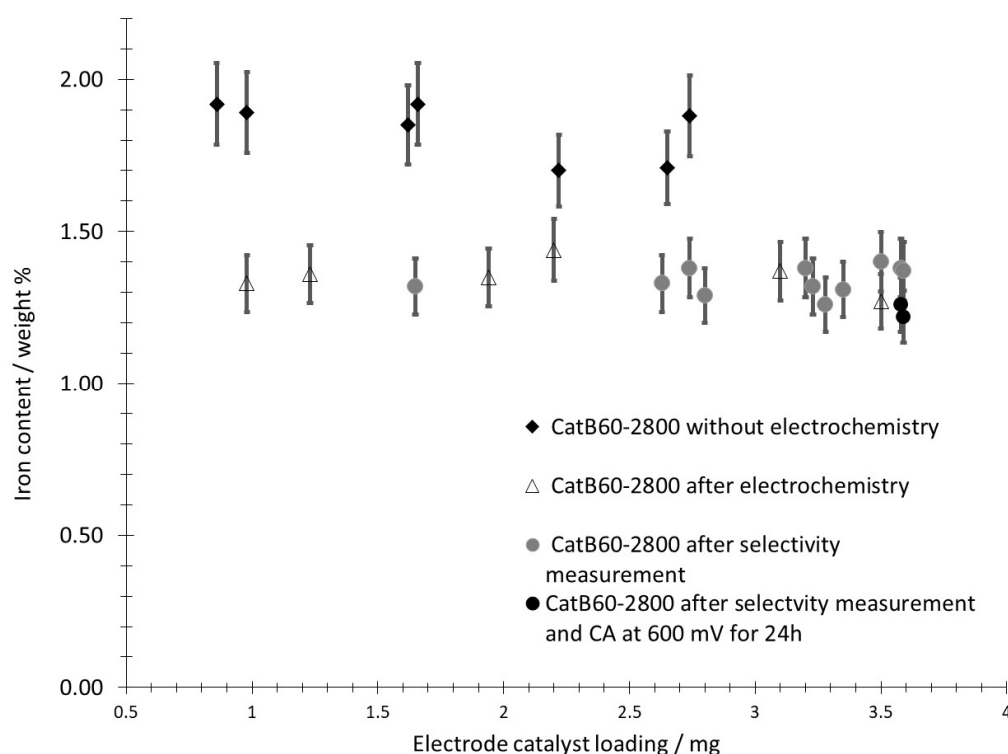


Figure 6. Iron content for the CatB60-2800 catalyst at different steps of its study for several electrode samples.

A deeper study of the instability of the catalysts is presented at the end of the next section devoted to XPS analysis.

3.2.5. XPS Characterization

The approach involving the use of porous electrodes for the ORR characterization involved here is of particular interest for XPS characterization. Indeed, numerous measurements on electrode collections can be performed easily after electrochemical measurements. An in-depth XPS study was performed on catalyst set CatTXX-2200 and, to a lesser extent, on the catalyst set CatBXX-2800. The CatBXX-2200 catalyst set was not studied because, as shown in Figure 3, all the catalysts have quite the same ORR responses. In contrast, as shown in Figure 2, the CatTXX-2200 catalyst set is the one for which the laser power percentage has the most important impact on the ORR response. In addition to the N1s core energy region, the C1s, O1s and Fe2p core regions were also recorded to allow for an atomic percent (At. %) quantification with a better accuracy ($\pm 15\%$) compared to the

exploitation of the survey spectra. Here, only the N1s binding energy regions were exploited in detail through spectra fittings. Since iron contents between 0.16 At. % and 0.34 At. % were detected in all the materials (see Supplementary Materials Figure S4), the fitting of the spectra was performed using five N1s components, i.e., pyridinic (N1), FeN_x (N2), pyrrolic (N3), graphitic (N4) and oxidized nitrogen species (N5). For N1 to N4, the fittings were performed with a Full Width at Half Maximum (FWHM) enforced between 1.4 eV and 1.5 eV, the later value being used in previous work by us [19]. For N5, which includes different oxidized nitrogen species inactive towards the ORR, the FWHM was 2.5 eV. Illustration of the N1s spectra fitting is reported in Figure 7 for the two electrodes of the CatT40-2200 catalyst that ORR CVs are reported in Figure 2. On each of these electrode sample (electrode 1 and electrode 2), the N1s spectra was recorded on two different regions of the catalysts layer. It is observed that the N1s spectra of the two regions recorded on the same electrode are quite similar, thus reflecting the good homogeneity of the catalyst layer. In contrast, the comparison of the N1s spectra of electrode 1 and electrode 2 shows clear differences which could mean that their CVs on Figure 2 do not overlap. One may assume here again that this is due to imperfect homogeneity of the catalyst powder. The quantification of each nitrogen species does not allow for detecting significant differences between both electrode samples.

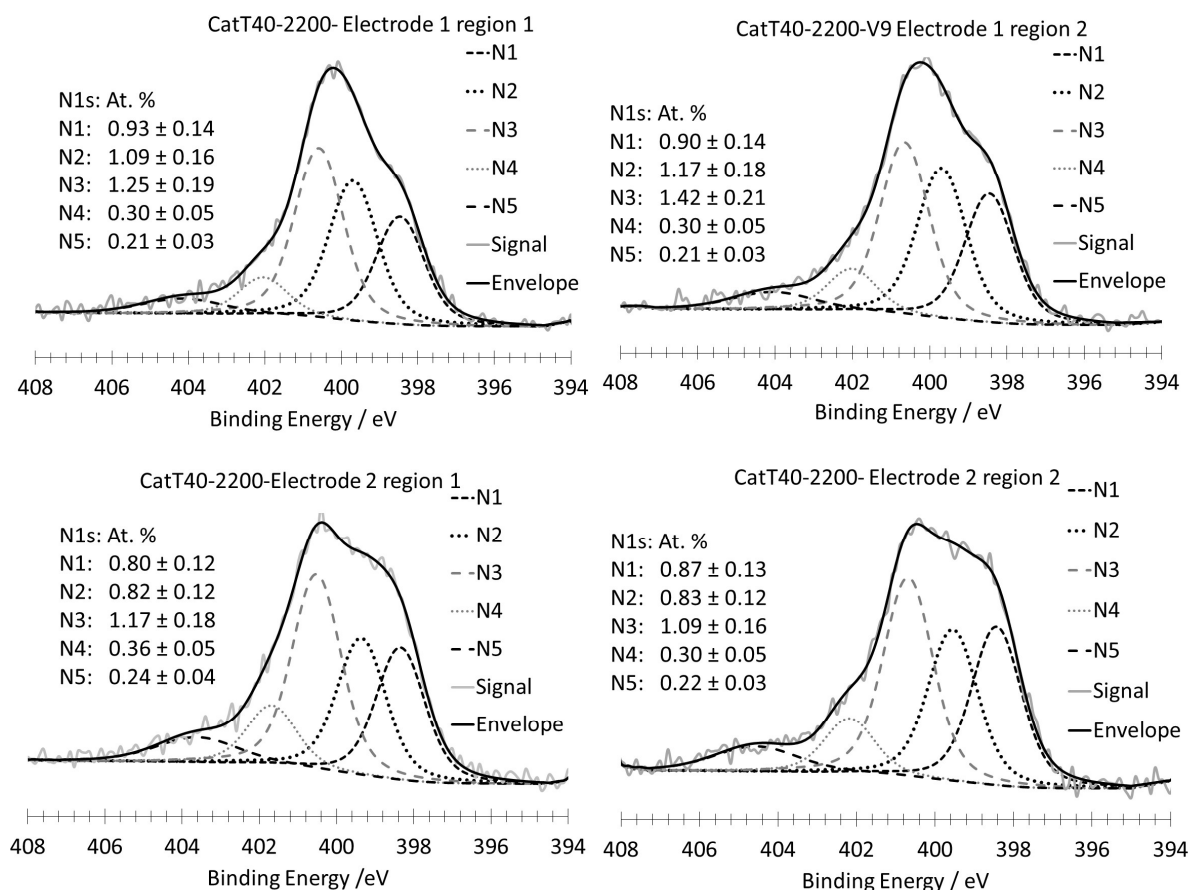


Figure 7. Illustration of fitting of the XPS N1s spectra for two electrodes of CatT40-2200 catalysts, electrode 1 (top) and electrode 2 (bottom) with two different regions of the catalyst layer analyzed.

The same fittings of the N1s spectra were performed on each electrode with CVs shown on Figure 2, respectively, for CatT40-2200, CatT55-2200 and CatT70-2200. XPS fittings of CatT55-2200 and CatT70-2200 are provided in Supplementary Materials Figure S5, and also show slightly different N1s spectra for different electrodes of the same catalysts. The total nitrogen content (oxidized nitrogen not include because ORR inactive) are reported in

Supplementary Materials Figure S6. For CatT40-2200 (three electrodes analyzed), it is found between 2.99 At. % and 3.8 At. %, for CatT55-2200 (3 electrodes analyzed), between 2.2 At. % and 2.6 At. %. For CatT70-2200 (2 electrodes analyzed), the same value of 1.9 At. % is measured. These data suggest that the lower the absorbed laser power, the higher the nitrogen content. However, only the gap between CatT40-2200 and CatT70-2200 is beyond the uncertainty of $\pm 15\%$ that is considered for measurements.

In order to compare the three types of catalyst, the potential at currents of, respectively, 0.01 mA.mg^{-1} and 0.02 mA.mg^{-1} were collected and reported as a function of the N1s atomic percent of each component of the fit (with respect to total atomic composition, including C, Fe, O), presumably active towards the ORR (N1 to N4). The results are shown in Figure 8 and reveal clear correlations: the higher the nitrogen content, the higher the ORR performance for pyridinic (N1), FeN_x (N2) and pyrrolic (N3) components. One can note that for N1 to N3, the points for which the potentials and the atomic % are the higher correspond to those of catalyst CatT40-2200 for which the three corresponding CVs in Figure 2 show the best ORR performance. No correlation is found between the ORR and the amount of graphitic component (N4) in the catalyst.

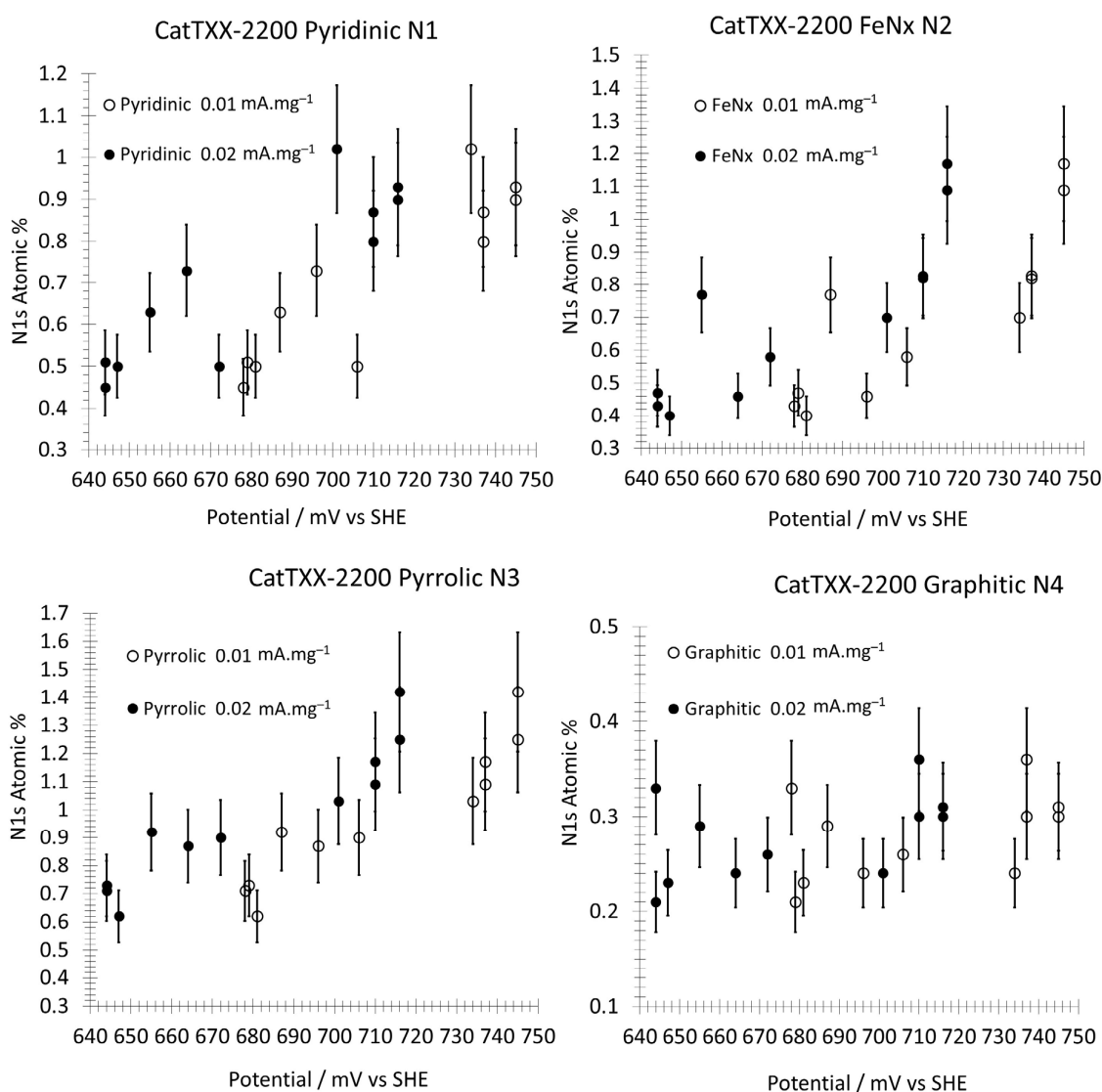


Figure 8. N1s composition obtained from spectra fitting as a function of the ORR performance reported as the potential at 0.01 mA.mg^{-1} and 0.02 mA.mg^{-1} for all the electrodes of CatTXX-2200 catalysts of which the CVs are shown in Figure 2. The data include the XPS data from Figure 7. Error bars represent $\pm 15\%$ of the N1s atomic content.

Finally, when considering each of the three catalysts, one observes that the averaged iron contents determined by the XPS analysis (see Supplementary Materials Figure S4) i.e., 0.33 At. %, 0.18 At. % and 0.17 At. % for CatT40-2200, CatT55-2200 and CatT70-2200, respectively, correlates both, with the amount of iron in the catalyst determined by x-ray fluorescence after ORR measurement (see Table 3), as well as with the At. % content of FeN_x sites obtained through the N1s peak fitting.

The catalyst CatBXX-2800 set was less extensively studied than the CatTXX-2200 one regarding the XPS analysis after a single ORR measurement. The same N1s spectra fitting procedure indicated above was used on one electrode sample of CatB40-2800, CatB50-2800 and CatB60-2800 catalysts, respectively. Indeed, as for CatTXX-2200 catalyst set, iron was detected in all the materials with the same amount for all (Supplementary Materials Figure S4). The fittings were exploited in the same way as for CatTXX-2200 catalysts (Figure 8), the results are shown in Figure 9. The N1s fitting for CatB40-2200 is shown in Supplementary Materials Figure S7 while those of CatB50-2800 and CatB60-2800 are shown below in Figure 10.

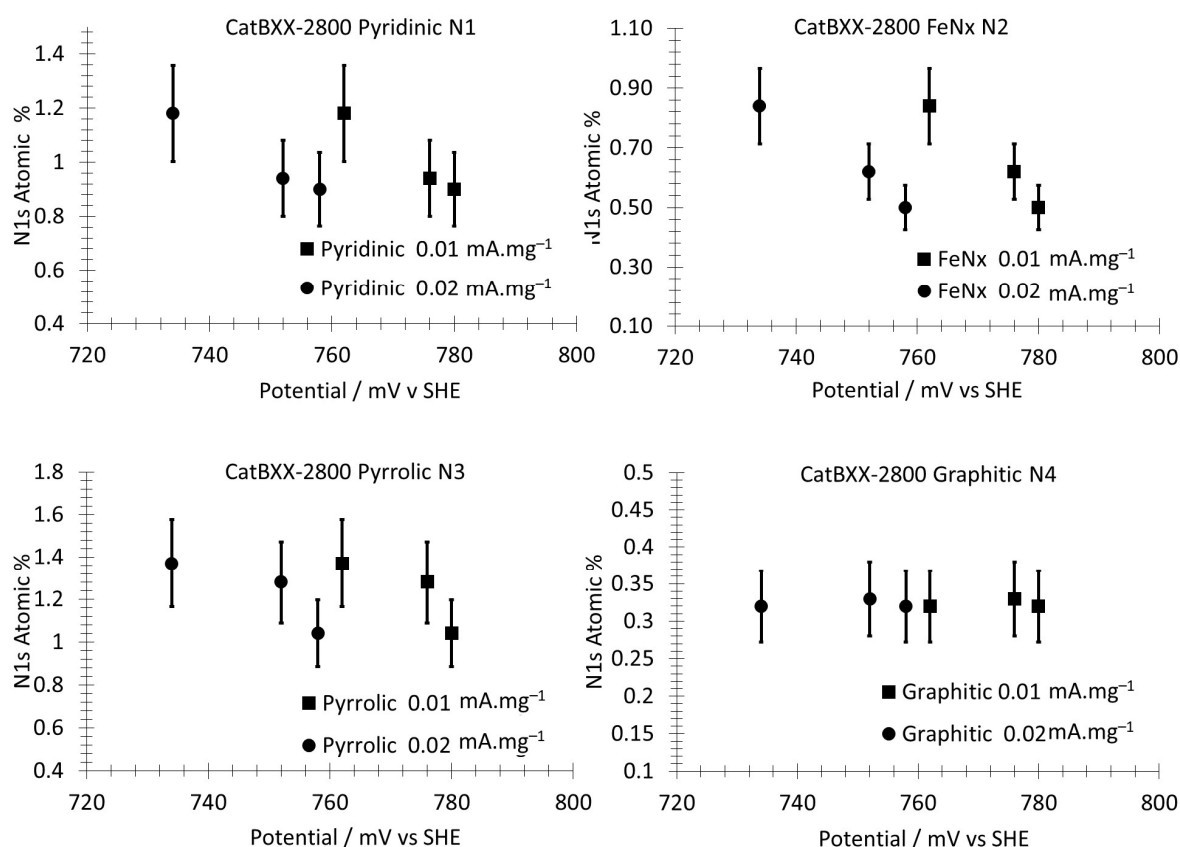


Figure 9. N1s composition obtained from spectra fitting as a function of the ORR performance reported as the potential at 0.01 mA/mg⁻¹ and 0.02 mA.mg⁻¹ for three electrode samples of each, for the CaBXX-2800 catalysts set. Error bars represent $\pm 15\%$ of the N1s atomic content of each N1s component with respect to the total atomic composition of the sample, which include C, Fe₂, and O content.

For pyridinic (N1) and pyrrolic (N3) species, a trend seems to be emerging, but the slight overlap of error bars makes it uncertain. The graphitic component content is the same for the three catalysts. For FeN_x (N2) nitrogen species FeN_x , the errors bars clearly do not overlap on the data for which the potential and atomic content are the highest and the lowest. The concerned materials are, respectively, CatB40-2800 and CatB60-2800, corresponding, respectively, to the lower performing catalyst and better performing catalyst

in Figure 4d. Therefore, the trend observed here between the ORR performance and the FeN_x atomic content is reversed compared to the one observed for the CatXX-2200 catalysts regarding N1, N3 and N3 species. In this case, the higher the atomic content, the higher the ORR performance (Figure 8). This result will be addressed in the Section 4. Regarding the total nitrogen content in the CatBXX-2800 catalyst set (see Figure S8), the same trend as for CatTXX-2200 catalysts is observed. Here again, only the gap between the lower and the higher absorbed laser powers (CatB40-2800 and CatB60-2800) is beyond the uncertainty of $\pm 15\%$ considered for measurements.

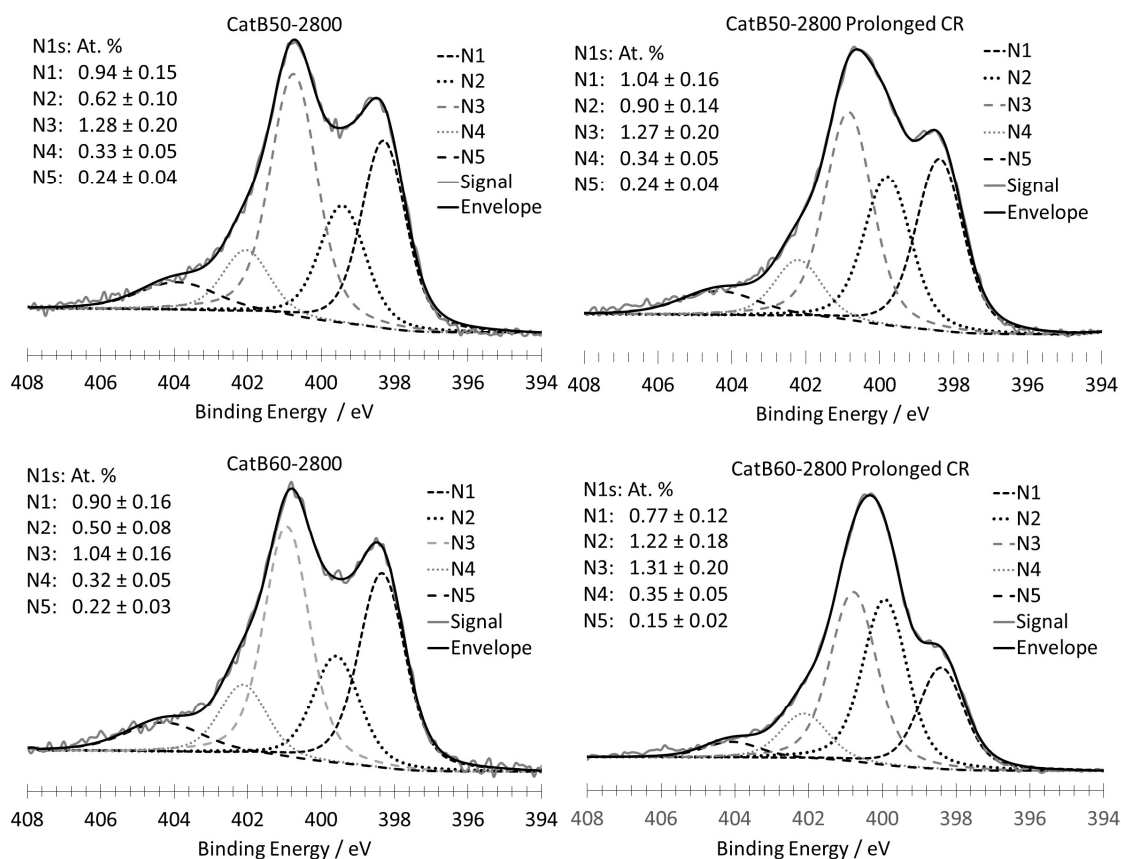


Figure 10. Fitting of the N1s spectra of catalysts CatB50-2800 (top) and CatB60-2800 (bottom) after a single ORR CV (left) and after prolonged CR at 600 mV (right).

Since the ORR instability was tested and revealed on the CatBXX-2800 catalyst set, as illustrated in Figure 5 for CatB60-2800 catalysts, we decided to submit two of them, CatB50-2800 and CatB60-2800, to a prolonged CR at 600 mV. Both materials were thus submitted to ORR at 600 mV vs. SHE for 54 h what correspond to charges of 45.1 C and 56.4 C for CatB50-2800 and CatB60-2800, respectively. After this, the XPS spectra of both electrode sample were recorded and the same N1s fitting procedure was applied.

Figure 10 compares these spectra to those recorded to the same catalysts after a single ORR CV measurement. It is clearly observed that the prolonged CR does not only degrade the ORR performance but also modifies significantly the N1s XPS spectra. One may note that XPS analysis of catalysts after ORR performance degradation is quite rare in literature. Nevertheless, strong modifications of the N1s spectra are reported in [48,49] and are related to ORR performance degradation.

The fitting was exploited in the same way as in Figures 8 and 9 to face the electrochemical performance to the quantification of N1, N2, N3 and N4 nitrogen species. Figure 11 presents the results for the XPS spectra shown in Figure 10.

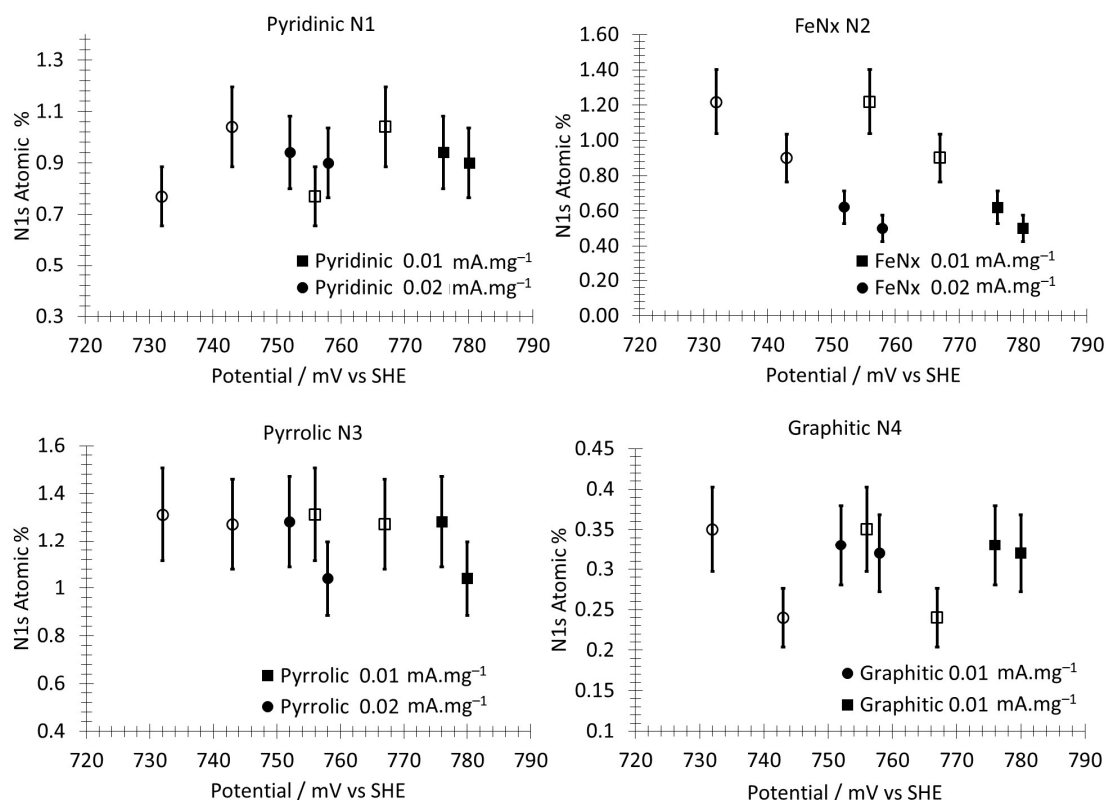


Figure 11. N1s composition obtained from spectra fitting as a function of the ORR performance reported as the potential at 0.01 mA/mg⁻¹ and 0.02 mA.mg⁻¹ CatB50-2800 and CatB60-2800 after a single ORR measurement (filled symbols) and after prolonged CR at 600 mV vs. SHE (empty symbols). Error bars represent $\pm 15\%$ of the N1s atomic content of each N1s component with respect to the total atomic composition of the sample which include C, Fe₂, and O content. Note that the data reported for the single ORR measurements are the same as those reported in Figure 9.

In a similar way to what was observed in Figure 9, a clear trend between the At. % as a function of the ORR performance is only observed for the FeN_x (N2) component. It is seen on Figure 10 that the modification observed for CatB60-2800 are more pronounced than for CatB50-2800 after the CR at 600 mV. Consistently, the lowest potential reported on the data from Figure 11 corresponds to the CatB60-2800 sample. Finally, it should be emphasized that the samples submitted to prolonged CR did not show significant modification regarding their iron content (see Supplementary Materials Figure S4). The next section considers an overview of all the results presented above, as well as additional data related to a catalyst synthesized in the classical perpendicular configuration for comparison.

4. Discussion

As a reminder for clarity of the discussion, this work investigates a new configuration, i.e., collinear laser pyrolysis, to synthesize Fe/N/C type ORR electrocatalysts using liquid aerosol droplet as precursors. The aerosol precursor was always the same and was injected from the bottom side of the reactor (Figure 1). The laser beam entered in the reactor either from the top side of the reactor or from the bottom side of the reactor. Two different lasers were involved with two different maximal power (PRC-2200 and PRC 2800). Three sets of catalysts were synthesized, CatTXX-2200, CatBXX-2200 and CatBXX-2800, where T indicates Top side laser entry into the reactor, B indicates Bottom laser entry into the reactor and XX the percentage of the maximum laser power involved. The latter parameter was systematically varied over this study. In these experiments, ammonia served both as a laser energy transfer agent through absorption of the laser beam and as a nitrogen precursor.

The amount of ammonia involved in each set of experiment was defined by R , which is the flow volume ratio of ammonia to the total flow volume, argon and ammonia, entering from the bottom side of the reactor.

Our previous works on the synthesis of Fe/N/C ORR electrocatalysts by CO_2 LP-ALD were performed in the classical orthogonal configuration, in which the laser beam and the aerosol precursors overlap perpendicularly [19,32,36]. In these reports, the CO_2 laser was focused. It is therefore of interest to compare catalysts synthesized in both configurations and similar conditions, i.e., in particular unfocused laser. This is what is reported in Figure 12, on which all the data recorded from catalysts synthesized in the collinear configuration are compared to a catalyst synthesized in perpendicular configuration with unfocused PRC-2200 laser set at 95% of its maximum laser power, with a value of R parameter of $R = 0.40$.

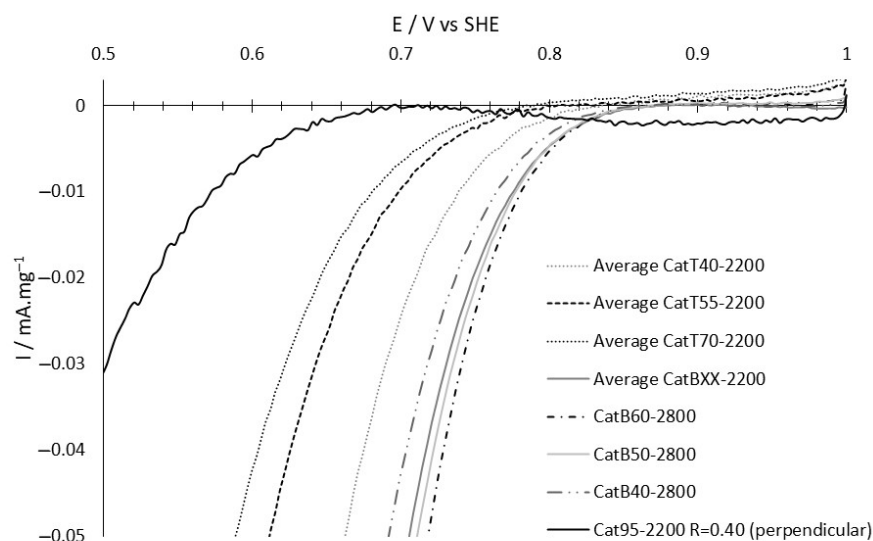


Figure 12. Comparison of ORR CVs for the catalysts synthesized in collinear configuration and two catalysts synthesized in perpendicular configuration HClO_4 1 M, 5 mV.s^{-1} . For the sake of clarity, the CVs for the catalysts synthesized in collinear configuration are average CVs of those recorded at a given laser power percentage. For the CatBXX-2200 set, since the CVs at different laser power percentage overlap (see Figure 3) an average of all the CVs is shown.

The CVs in Figure 12 clearly show that the ORR performance of the catalysts synthesized in collinear configuration outperform those of the catalyst synthesized in perpendicular configuration. The Cat95-2200 $R = 0.40$ perpendicular catalyst, which will be named Cat95-2200 in the following, was characterized in the same way as the ones synthesized in the collinear configuration. Compared to the later catalysts, the Cat95-2200 (see Supplementary Materials Table S4) is produced with a higher yield. It contains lower amount of iron (0.5 wt.%), and has a similar specific surface area. XRD feature is also similar to catalyst synthesized in collinear configuration. Raman spectra (Supplementary Materials Figure S3) is slightly different since the ID to IG ratio is slightly lower (Supplementary Materials Table S2), which corresponds to a slightly less disordered carbon structure.

Cat95-2200 was characterized by XPS by recording C1s, O1s, Fe2p and N1s core binding energies windows. Figure 13 shows the Fe2p core region, which point to an insignificant amount of iron content at the material surface in contrast to what is observed for CatTXX-22000 and CatBXX-2800 catalyst sets. Therefore, the amount of iron detected by the x-ray fluorescence is presumably deeply embedded in the carbon component of the catalyst, which prevents its detection by the surface analysis. The N1s spectra fitting of Cat95-2200 was performed with the same constraint as those mentioned above (FWHM

between 1.4 and 1.5 eV) and gave a satisfying fit quality with only four peaks, i.e., without any N2 (FeN_x) contribution (Figure 13).

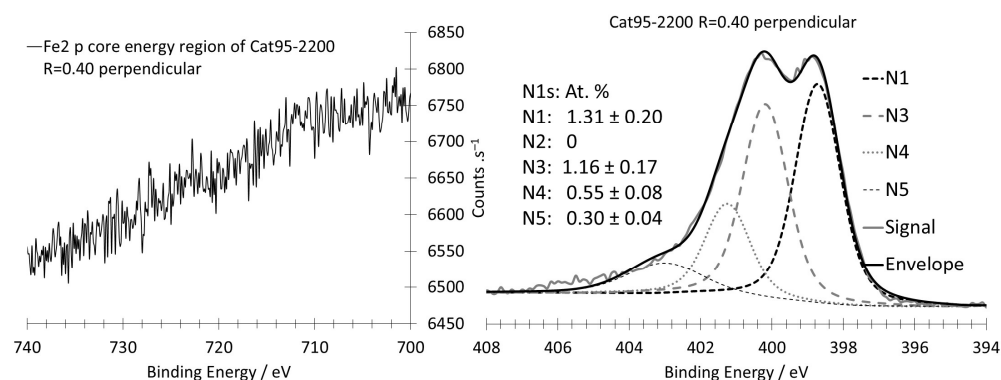


Figure 13. XPS data for catalyst Cat95-2200 R = 0.40 perpendicular. Left Fe2p core region, right N1s spectrum fitting.

The ORR performance of CatT95-2200 is very poor. The potentials at 0.01 mA.mg⁻¹ and 0.02 mA.mg⁻¹ are, respectively, 571 mV and 531 mV, much lower than those of the catalysts synthesized in collinear configuration (see Figures 8, 9 and 11). These results suggest the poor contribution of pyridinic, pyrrolic and graphitic to the ORR CatT95-2200 and point to the major role of FeN_x sites in catalysts synthesized in collinear configuration. One can note that the other features of all the catalysts recorded through XRD and Raman spectroscopy are very close to each other and therefore their role on the differences of ORR performances are presumably weak. The total nitrogen content of Cat95-2200 lies in the same range as those obtained for CatT40-2200 and CatBXX-2800 catalyst set (see Figure S8).

We address now the significant differences observed in terms of ORR performances between Cat95-2200, CatTXX-2200 and CatBXX-2800 catalysts (see Figures 8, 9 and 11). We assume that these differences are basically due to the effective conditions in which the energy is delivered to the precursors when they are injected to the reactor at its bottom side. This energy is related to the laser power absorbed by the ammonia present among the precursors. The absorbed laser power is measured with the power probe (Figure 1) which is positioned at the opposite side from the laser input into the reactor i.e., the bottom window for CatTxx2200 catalysts set and the top window for CatBXX-2800 catalysts set. A simple Beer-Lambert law is applied for the laser absorption along the reactor tube and consequently, entails an exponential decrease of the laser power along the optical path through the reactor. This means that when the laser enters by the top side of the reactor, the available laser power at the opposite side, where the precursor enters, is much lower than the values reported in Table 1. For example, for CatT70-2200, catalysts for which the absorbed power is 606 W (Table 1), the residual laser power in the precursors' entrance zone is close to zero. In contrast, for CatBXX-2800 catalyst sets, the absorbed laser power is close to its maximum in this zone (the values indicated in Table 4), since the precursors and the laser are introduced at the same location. Therefore, the amount of energy delivered on the precursors at their entry point is considerably different for both sets of catalysts. We propose here to introduce a new parameter, the mass-weighted energy given to the reaction, calculated from the energy deposited (J) per gram of precursors in a reference optical path. The reference optical pass is by convention the one estimated in the synthesis of Cat95-2200 in perpendicular configuration. It is taken as the diameter of the laser beam, i.e., 1.8 cm. The detailed calculation of the mass-weighted energy delivered to the precursors is given in Supplementary Materials Equation (S1). Basically, the distance of 1.8 cm and the gas flow rates are used to calculate a residence time. This residence time is then used to calculate both, the amount of energy deposited from the absorbed laser power as well as the amount

of precursor consumed during the residence time. This allows us to calculate a mass-weighted energy delivered to precursors ($\text{J}\cdot\text{g}^{-1}$) for the CatTXX-2200 and CatBXX-2800 catalyst sets, and for the Cat95-2200 catalysts, all for an optical path of 1.8 cm. Such a calculation is of first order. The potential modification of the gas flow rates due to the temperature is not considered. The results of the calculation are shown in Table 9, in which the residence time as defined above, the energy deposited during the residence time and the mass-weighted energy are indicated for all the syntheses.

Table 9. Residence time, laser energy deposited on precursors during residence time, and mass-weighted energy deposited on precursors during residence time, for the CatTXX-2200 and CatBXX-2800 catalyst sets and for Cat95-2200- R = 0.40 perpendicular catalyst. Detailed calculations for these data are indicated in Supplementary Materials Equation (S1).

Catalyst Name	Residence Time/s	Laser Energy Deposited During Residence Time /J	Mass-Weighted Energy/ $\text{J}\cdot\text{g}^{-1}$
CatT40-2200	0.223	29	2.1×10^4
CatT55-2200	0.223	32	1.8×10^4
CatT70-2200	0.223	34	2.0×10^4
CatB40-2800	0.158	90	7.9×10^4
CatB50-2800	0.158	100	8.8×10^4
CatB60-2800	0.158	125	1.1×10^5
Cat95-2200 perpendicular	0.021	1.89	1.9×10^3

The data shown in Table 9 reveal strong differences in the mass-weighted energy deposited on the precursors for the materials listed. Compared to the other catalysts, the Cat95-2200 catalyst this value is more than one order of magnitude lower. Between CatTXX-2200 and CatBXX-2800 catalyst sets, a significant difference by about a factor 4 to almost 6 is observed, the energy delivered in the CatBXX-2800 set being higher. It is likely that the energy deposited on the precursors as calculated here is related to the temperature value and profile at which are exposed the precursors in the pyrolysis flame. The higher the mass-weighted energy value, the higher the temperature conditions. Thus, for Cat95-2200 catalysts, we may assume that, while the temperature is high enough to decompose the precursors and produce carbon soot, it is not high enough to allow for the formation of FeN_x sites. At this point of the discussion, it is of importance to point out that the FeN_x site designation covers actually a complex variety of iron and nitrogen combinations and configurations, including carbon vacancies, in which the value of x can go from 1 to 5, as suggested by both theoretical [50–54] and experimental work [9,55]. Experimental results support that controlling the temperature is an efficient way to control the coordination number x in FeN_x based electrocatalysts [55–57]. For example, three different temperatures 300 °C, 500 °C, 1000 °C were investigated for the carbonization of the iron loaded solid precursor prepared from zinc imidazolate framework [9], leading to three catalysts with similar iron content and containing, respectively, FeN_1 , FeN_3 and FeN_4 as dominant active sites. The ORR performances were significantly different for the three catalysts with $\text{FeN}_1 < \text{FeN}_2 < \text{FeN}_4$. Similar conclusion was drawn in [55] using different precursors, i.e., relating a relatively low ORR performances to the presence of FeN_2 and FeN_3 as majority sites. These considerations may provide an explanation to the difference that we evidenced in terms of ORR performances between CatTXX-2200 catalysts and CatBXX-2800 catalyst sets. A careful look at the results shown in Figures 8 and 9 reveals that similar contents in FeN_x atomic content provide significantly different ORR performances for both materials. Since the activity in these materials is related to FeN_x sites, it suggests that the distribution of different coordination numbers in the active sites in both materials is different. This

reading is consistent with the reported effect of temperature on the coordination number distribution x , and with the mass-weighted energy deposited on precursors as calculated in Table 9, and related to a flame temperature feature. It is at least four times higher for CatBXX-2800 catalyst set than for CatTXX-2200 catalyst set. Since FeN_4 sites are reported as the most efficient sites for the ORR, it is reasonable to assume that the CatTXX-2200 catalysts contain probably a lower amount of these sites compared to CatBXX-2800 catalysts. Considering the CatTXX-2200 catalysts set, the mass-weighted energy lies in the same range for all catalysts. The differences in term of observed performances might be due to the total nitrogen content (see Figure S8). The reason for such a difference is unclear. However, in this configuration, we lack information on the length of the pyrolysis flame, which could vary as a function of the absorbed laser power and possibly impact on the nitrogen content.

In this work, the N1s XPS spectra have been fitted with a single FeN_x component, as it is extensively done in the literature. Fitting with several FeN_x components is extremely rare. Combining density functional calculation and experimental N1s spectra, Artyushkova et al. [50] reported a N1s core level fitting with several CoN_x (Cobalt analogue of FeN_x sites) components, CoN_4 and CoN_2 with 2 different configurations, for which the binding energy difference was calculated with respect to the N1s pyridine component. The same approach was used in [53], adding MN_3 sites to MN_4 and MN_2 ones (with $M = \text{Co}$ or Fe). The calculated differences in term of binding energies with respect to pyridinic nitrogen (taken at 398.8 eV) are, respectively, +0.9–0.10 eV for FeN_2 (two kinds of site) +1.5 eV and +1.2 eV (two kinds of site) for FeN_3 and 1.5 eV for FeN_4 . As pointed in [50], the pyridinic contribution contains a FeN_x contribution, and this contribution may vary depending on the distribution of FeN_x with different coordination numbers.

Attempting at fitting our N1s spectra with multiple FeN_x contributions is beyond the scope of this work. Nevertheless, this discussion may help moving forward to an interpretation of the trends observed for FeN_x as a function of the ORR performance for CatBXX-2800 catalysts both in Figures 9 and 11. In Figure 9 the trend of the ORR performance as a function of FeN_x site content is the opposite the one observed for CatTXX-2200 catalysts. In Figure 11, the FeN_x content increases despite the drop of the ORR activity due to prolonged CR at 600 mV. These trends might not take into account an underestimation of FeN_x content due to the overlap with pyridinic contribution, which results to a single FeN_x component from fitting N1s spectra.

Concerning the instability of the catalysts, which was here established, we did not find evidence for iron loss, although the X-Ray fluorescence method we used might be insufficiently accurate. Without any access to high resolution transmission electron microscopy, which is whatever a local characterization, we could not detect the presence of carbon coated iron-based particles in the material. XRD did not allow for detecting diffraction peaks from such iron-based particles, but the reason for this might be that they are too small and poorly crystalized, if they exist. Assuming such particles to be present in the catalysts means that the ratio of iron atoms involved in the formation of FeN_x is small. If the loss of ORR activity is due to the loss of FeN_x sites, this relative variation of iron content would be too small to be detected by X-Ray fluorescence or XPS analysis. The latter is the only characterization suggesting a modification of the catalysts feature due to ORR performance degradation. Despite the probable inhomogeneities we suggested above for CatBXX-2800 catalysts powders, they could have been observed by XPS analysis if these catalysts were as extensively studied as CatTXX-2200 catalysts. However, we may believe that the changes observed in the N1s spectra of CatB60-2800 in particular (Figure 10) are signs of the ORR performance degradation. In future experiments dealing with tracking XPS signature modification with ORR performance drop, the same electrode sample should be used for characterization after a single ORR measurement and prolonged chronoamperometry.

We finish now this Section 4 with comments on selectivity measurement. A point to discuss is the trends observed as a function of potential (Table 8). The general behavior shows quite stable values of n , for 700 mV 660 mV and 600 mV potentials and a clear increase at 400 mV. This means that, at such a potential, the amount of hydrogen peroxide escaping from the porous catalyst structure strongly decreases. Indeed, the ORR in all the catalysts produces a significant amount of hydrogen peroxide. A tentative explanation for the singularity observed at 400 mV is that the activation of sites able to reduce H_2O_2 into H_2O occurs, which lowers the amount of H_2O_2 detected and thus increases n .

5. Conclusions

In this paper, we reported the synthesis of different Fe/N/C ORR electrocatalysts by an original collinear CO_2 LP-ALD in two different configurations and finally compared them to a catalyst synthesized in the classical perpendicular configuration. The two different configurations were produced by keeping the precursor entry into the reactor at the bottom side, and by changing the laser entrance side i.e., top side or bottom side. This produced two sets of three catalysts for which the synthesis conditions differed from each other by the incident laser power. All the catalysts were in-depth analyzed by XPS and fittings allowed for determining the amount of the different nitrogen species which was drawn as a function of the ORR performance. Since the laser power (J.s^{-1}) involved does not reflect directly the energy (J) deposited on the precursor we proposed to evaluate the latter as a mass-weighted energy deposited on precursors and reported in J.g^{-1} . This was made basically by considering a reference optical path that stands in the perpendicular LP-ALD. From this parameter, residence time can be evaluated, taking into account the rate of precursor feeding, the mass-weighted energy is obtained. The correlations between this parameter, the kind of nitrogen and amount of nitrogen sites formed, and the ORR performances suggest the relevance of the approach. This parameter reflects probably some features of the flame temperature that is difficult to estimate. We believe therefore that it might be of interest in synthesis method such as laser pyrolysis, in which the catalyst particles are continuously formed in a dynamic mode. In this work, we did not change the precursor media, but we believe that one may assume that changing significantly the precursor media could induce modified value of the mass-weighted energy parameter with respect to given ORR performances.

The N1s XPS analysis allowed for the correlation between this parameter and the mass-weighted energy and the type and amount of nitrogen sites formed. The commonly used fitting of FeN_x sites by a single component has been discussed that points to its potential limitations due to the interplay in term of quantification between N1s pyridinic components and the different kinds of FeN_x sites formed. Theoretical calculation in literature pointed to this important aspect, and we believe that our experimental results may illustrate it.

Finally, since our goal in developing collinear pyrolysis was also to try to improve the ORR performances of the as-formed catalysts, we can mention that the best catalysts obtained here show similar performances to those obtained by double stage laser pyrolysis in which two lasers were involved and required a much higher laser power.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/c12020033/s1>, Table S1: Detailed experimental conditions for the synthesis of catalysts; Figure S1: Representative scanning electron microscopy images are shown below for all the catalysts studied in this paper; Figure S2: X-Ray diffraction analysis of catalyst powders; Table S2: ID/IG ratios and average G peak center obtained from Raman spectroscopy of catalyst powders; Figure S3: Representative Raman spectra fitting of catalyst powders; Table S3: Selectivity measurement for CatB40-2800, CatB50-2800, CatB60-2800 catalysts; Figure S4: Fe2p core XPS spectra and iron content for catalyst sets CatTXX-2200 and CatBxx-2800; Figure S5: Example

of N1s XPS spectra fitting for CatT55-2200 and CatT70-2200 catalyst electrode samples, with two electrodes each. Figure S6: Total nitrogen content determined using the XPS high-resolution spectra core regions of C1s, O1s, Fe2p and N1s for all the electrode catalyst samples analyzed. Figure S7: N1s XPS spectra fitting of CatB40-2800 catalyst electrode sample. Table S4: Synthesis conditions and characterization of Cat95-2200 R = 0.40 perpendicular catalyst. Figure S8: X-Ray diffraction analysis of Cat95-2200 R = 0.40 catalyst. Equation (S1): Calculations to produce the data shown in Table 9 of the paper for the different catalysts concerned. Table S5: Parameters used to calculate the data of Table 9 for the catalysts involved.

Author Contributions: H.P. and O.S. proposed and guided this research, and wrote the paper. P.L. conducted the laser pyrolysis syntheses with O.S. and H.P. M.F. and A.E. carried out the XPS experiments and aided interpretation and data treatment with H.P. C.D. and H.P. processed the raw materials, prepared porous electrodes and recorded electrochemical measurements. C.D. was a post-doctoral researcher back in the days within the ProCatPac project when the data were produced. H.P. recorded and exploited x-ray fluorescence measurements. C.R. performed and treated BET measurements. S.S. recorded and treated XRD. E.C. recorded and treated Raman data. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The author Claire Dazon was a post-doc at CEA when the data in this paper were produced. She left CEA and is now reachable at Olmix. Therefore, none of the authors has any conflict of interest.

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