Iron/Nitrogen co-doped mesoporous carbon synthesized by an endo-templating approach as an efficient electrocatalyst for the oxygen reduction reaction

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Abstract

Iron/Nitrogen-doped carbon catalysts are considered to be one of the most promising candidates to replace platinum-based catalysts for the oxygen reduction reaction in the cathode of the fuel cell. Herein, we demonstrate a simple and cost-effective strategy for the fabrication of Fe-N-C-mesoporous-carbons involving the carbonization of calcium citrate followed by a post-treatment with urea and ammonium sulfate iron (II). The synthesized materials exhibit high values of surface area, large nitrogen and iron contents. The iron is present in two configurations: i) γ -iron phase and ii) iron coordinated to nitrogen (Fe-N_x). When used as an electrocatalyst in basic electrolyte, the Fe-N-C material predominantly catalyzes the four-electron pathway with an onset potential of 0.91 V and a half-wave potential of 0.81 V. In acidic electrolyte, the optimized catalyst exhibits an onset potential of 0.73 V. The experimental results show that the N-functionalities and the Fe-N coordination sites play a major role in catalytic performance in both kinds of electrolytes and that the γ -

iron phase has little or no catalytic effect. In this regard, pure N-doped carbon shows to be better catalyst than pure Fe-doped carbon. Hence, these results provide useful guidelines for the development of highly active and cost-effective ORR catalysts.

Keywords: carbon nanomaterial, Fe-N-C catalyst, non-noble metal catalysts, Fe-N coordination, oxygen reduction reaction.

1. Introduction

The commercialization of fuel cells is greatly dependent on the design and synthesis of active electrocatalysts that trigger the oxygen reduction reaction (ORR) occurring in the cathode [1-3]. Up to now, platinum-based materials have been considered as the most efficient electrocatalysts for the ORR [4]. However, despite its high catalytic activity, platinum is not suitable as a cathode catalyst due to its low tolerance to fuel crossover, degradation with time and especially high cost and scarcity [5, 6]. For this reason much effort has been devoted to developing new efficient, cost-effective and stable electrocatalysts that can replace those based on platinum. Of these, non-precious metal and metal-free N-doped carbon catalysts have attracted a great deal of attention due to their excellent ORR performance and low cost [7, 8]. However, metal-free carbon materials in acid media have suffered from their poor catalytic performance and limited stability [9-11]. Consequently, N-doped carbons loaded with non-precious metals (*i.e.* iron or cobalt) are considered as the most promising candidates for the ORR [7, 12].

In order to produce an efficient electrocatalyst able to replace the commercial platinum catalyst, the following conditions have to be met, namely: i) the presence of a high density of active centers and ii) a large specific surface area with a porosity made up of fully accessible pores that facilitate the transport of the reactants and products towards and away from the active sites [13-18]. Considerable effort has been made to identify these active centers and to determine their catalytic effect on the ORR process [19-21]. The incorporation of nitrogen groups into the carbon framework has proven to

enhance not only electrocatalytic activity but also electrical conductivity and resistance to oxidation [22, 23]. More specifically, the quaternary and pyridinic functional groups are considered to be the most active catalytic centers for the ORR [13, 23-25]. In addition, the introduction of iron in N-doped carbons (Fe-N-C catalysts) provides more active sites that can be distributed on different moieties. For instance, some authors have reported the fabrication of Fe-based electrocatalysts with a high activity derived from the existence of Fe and Fe₃C nanoparticles [26-32]. Fe-N_x coordination sites have also been demonstrated to be catalytic active centers that lead to materials with a remarkable catalytic activity [25, 33-36]. Moreover, several authors have shown that when both types of iron species are present, the catalytic activity is due to the synergetic effect between these active sites [32, 37-39]. Therefore, an understanding of the influence of the different functionalities in the Fe-N-C materials is required to allow a rational design of non-precious metal catalysts.

In general, the fabrication of Fe-N-C catalysts is achieved through high-temperature treatment of carbon precursors that contain nitrogen (e.g., 1,10-phenanthroline, aniline, carbendazim, pyrrole) and iron species (e.g., iron(II) acetate, tris(acetylacetonato)iron(III), Iron(III) chloride) [25, 35, 36, 40-46]. Several strategies for synthesizing these catalysts such as, hard-templating, soft-templating, endo-templating strategies, etc have been investigated [25, 35, 36, 40-46]. However, in spite of the well-controlled properties of the synthesized materials [47], these methodologies are expensive, tedious and time-consuming, which hampers the large-scale production and limits their use as potential platinum substitutes. Recently we presented a simple methodology for

producing nitrogen-doped mesoporous carbons consisting in the direct carbonization of citrate salts (*i.e.* calcium, iron and zinc) followed by an additional thermal treatment with melamine [23, 48]. The synthesized materials were tested as electrodes for supercapacitors [48] and as electrocatalysts for the ORR [23]. Although they show an excellent electrocatalytic activity in basic electrolyte, their performance is very low in an acid medium in spite of their good durability. Herein, we present novel Fe-N mesoporous carbon catalysts based on the simple carbonization of calcium citrate that is used as the carbon precursor. In this case, we employed urea and ammonium iron (II) sulfate as the nitrogen and iron precursors, respectively. The resulting material possesses a high specific surface area, a porosity made up of mesopores and a high number of active sites as a result of the presence of nitrogen and iron. The as-prepared electrocatalysts exhibit a catalytic activity comparable to that of commercial platinum, catalyzing the preferential 4-electron pathway with a better durability. In addition, a series of experiments was performed in which the amount of iron and nitrogen introduced was varied in order to gain an insight into the influence of the different active sites on the enhancement of ORR activity in both basic and acid media.

2. Experimental Section

2.1. Preparation of Fe-N-doped mesoporous carbon

In a typical synthesis, a predetermined amount of calcium citrate salt (*Aldrich*) was heat-treated in a quartz reactor under nitrogen up to 600 °C at a heating rate of 3 °C min⁻¹ and held at this temperature for 1 hour. The resulting black solid was washed with diluted HCl (10 %), then with abundant distilled

water and dried at 120 °C for several hours. Afterwards, the resulting mesoporous carbon (CCa) was impregnated using the drop-wise technique with ammonium iron (II) sulfate dissolved in ethanol. Different weight ratios of ammonium iron (II) sulfate/CCa were used (0, 0.07, 0.37 and 0.78). The dried impregnated sample was then mixed with urea (Urea/CCa weight ratio = 0, 5, 10) and heat treated under nitrogen up to 800 °C (heating rate of 3 °C min⁻¹) for 2 hours. The resulting black solid was washed with HCl (15 %) for 2 days, then with abundant distilled water and dried at 120 °C for several hours. The as-obtained Fe-N-C samples were labelled CCa-x-y, where x indicates the ammonium iron (II) sulfate /CCa weight ratio and y the Urea /CCa weight ratio.

2.2. Characterization of materials

The morphology of the powders was examined by scanning (SEM, *Zeiss DSM 942*) and transmission (HRTEM, *JEOL (JEM 2100)* and *JEOL (JEM 2100-F)*) electron microscopy. Nitrogen sorption isotherms were obtained at -196 °C using a *Micromeritics ASAP 2020* volumetric adsorption system. The Brunauer-Emmett-Teller (BET) surface area was deduced from an analysis of the isotherm in the relative pressure range of 0.04-0.20. The total pore volume was calculated from the amount of nitrogen adsorbed at a relative pressure of 0.90. The mesopore size distribution was calculated by means of the Kruk-Jaroniec-Sayari (KJS) method [49]. The primary mesopore volume (V_m) and external surface area (S_{ext}) were estimated using the α_s -plot method. The reference adsorption data used for the α_s analysis of the carbon sample correspond to a non-graphitized carbon black sample [50].

X-ray photoelectron spectroscopy (XPS) was performed on a *Specs* spectrometer, using Mg K α (1253.6 eV) radiation from a double anode at 150 W. The binding energies for the high resolution spectra were calibrated by setting C 1s to 284.4 eV. X-ray diffraction (XRD) patterns were obtained on a *Siemens D5000* instrument operating at 40 kV and 20 mA and using Cu K α radiation ($\lambda=0.15406$ nm). Bulk elemental analysis (C, H, N and O) of the samples was carried out on a *LECO CHN-932* microanalyzer. The bulk Fe content in the catalysts was obtained by ICP-MS analysis on a *7700x equipment (Agilent)*.

2.3. Electrochemical measurements

Electrochemical measurements were conducted using a computer-controlled potentiostat (*Biologic VMP3* multichannel generator). The catalyst inks were prepared by ultrasonically dispersing 1.5 mg of the C_{Ca}-x-y sample in a solution containing 100 μ L Nafion (5 wt %) solution and 900 μ L deionized water. For comparison purposes, the Pt/C catalyst (20 wt % Pt on carbon black, *HiSPEC 3000, Alfa Aesar*) ink was prepared in the same way, using the same amount of catalyst (*i.e.* 1.5 mg). The mass loading of both catalysts was the same, *i.e.* 0.1 mg cm⁻². The catalyst inks were deposited onto a polished glassy carbon electrode (α -Al₂O₃ slurry, 50 nm) and dried at room temperature. A conventional three-electrode cell was employed, incorporating a rotating disk electrode (RDE) or rotating ring-disk electrode (RRDE) coated with the catalyst film as the working electrode and a saturated calomel electrode (SCE) or Ag/AgCl (3 M KCl) as the reference electrodes for the 0.1 M KOH solution or the 0.1 M HClO₄ solution, respectively. A Pt wire or a graphite rod was

employed as the counter electrodes. It is worth mentioning that no contribution of platinum to the catalytic activity of the synthesized carbon materials was confirmed by the electrochemical measurements. All the experiments were carried out at 20 °C. Before testing, O₂/N₂ gas was bubbled through the electrolyte in the cell for 30 min to saturate it with O₂/N₂. The measured potentials vs. SCE or Ag/AgCl (3 M KCl) were converted to the reversible hydrogen electrode (RHE) scale by means of the Nernst equation:

$$E_{\text{RHE}} = E_{\text{Ref}} + E^{\circ}_{\text{Ref}} + 0.059 \text{ pH} \quad (1)$$

where E_{Ref} is the experimentally measured potential vs. SCE or Ag/AgCl reference and E°_{Ref} values are: $E^{\circ}_{\text{SCE}} = 0.241 \text{ V}$ and $E^{\circ}_{\text{Ag/AgCl}} = 0.21 \text{ V}$ at 20 °C. The potential values provided throughout the text are referenced against RHE unless otherwise stated.

RDE linear sweep voltammetry (LSV) measurements were conducted from 1.2 to 0 V vs. RHE in O₂-saturated 0.1 M KOH and 0.1 M HClO₄ electrolytes at a scan rate of 10 mV s⁻¹ at disk rotation rates of 400, 800, 1200, 1600, 2000 and 2400 rpm. The working electrode was a 3.0 mm diameter GC rotating disk electrode.

The apparent number of electrons transferred during the ORR on the carbon catalysts was determined by the Koutechy-Levich equation:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K} \quad (2)$$

$$B = 0.62nFC_0(D_0)^{2/3}\nu^{1/6} \quad (3)$$

where J is the measured current density, J_K is the kinetic current density, J_L is the diffusion-limited current density, ω is the electrode rotation rate, F is the Faraday constant (96485 C mol⁻¹), C_0 is the bulk concentration of O₂ (1.1 × 10⁻³

mol L⁻¹ for 0.1 M HClO₄ solution and 1.2 × 10⁻³ mol L⁻¹ 0.1 M KOH solution), D_0 is the diffusion coefficient of O₂ (1.4 × 10⁻⁵ cm² s⁻¹ for 0.1 M HClO₄ solution and 1.93 × 10⁻⁵ cm² s⁻¹ for 0.1 M KOH solution) and ν is the kinetic viscosity of the electrolyte (0.01 cm² s⁻¹ for both the 0.1 M HClO₄ solution and the 0.1 M KOH solution) [51-53].

For the RRDE tests, the disk potential was scanned at 10 mV s⁻¹, while the ring potential was held at 1.5 V vs. RHE in order to oxidize any H₂O₂ produced [26, 54]. The working electrode was a 4 mm GC disk electrode and a Pt ring electrode (500 µm gap). The H₂O₂ collection efficiency at the ring ($N=0.424$) was provided by the manufacturer. The following equations were used to calculate n (the apparent number of electrons transferred during the ORR) and % H₂O₂ (the percentage of H₂O₂ released during the ORR) [55]:

$$n = \frac{4 I_D}{I_D + (I_R/N)} \quad (4)$$

$$\% H_2O_2 = 100 \frac{2 I_R/N}{I_D + (I_R/N)} \quad (5)$$

where I_D is the Faradaic current at the disk, I_R is the Faradaic current at the ring, N is the H₂O₂ collection coefficient at the ring.

The stability of the catalyst was assessed by means of an US Department of Energy's accelerated durability test protocol by cycling the catalysts between 0.6 and 1.0 V (vs. RHE) at 50 mV s⁻¹ under a N₂ atmosphere in 0.1 M HClO₄ [56, 57].

3. Results and discussion

3.1. Structural and textural properties of the Fe-N-C mesoporous carbons

As we have previously shown, the carbonization of calcium citrate results in a mixture formed by carbonaceous matter and embedded CaO nanoparticles [48]. These nanoparticles act as an endotemplate, so that once removed by acid washing, a highly porous carbon with a porosity made up of mesopores of ~ 10 nm is obtained [48]. In this work, the mesoporous carbon is doped by varying the amounts of nitrogen and iron by thermal treatment with urea and ammonium iron (II) sulfate. In this way, a Fe-N-doped mesoporous carbon is obtained, as illustrated in Scheme 1.

The SEM image in Figure 1a reveals that the carbon samples are made up of particles with an irregular morphology. The porosity of the Fe-N-doped carbons was investigated by means of nitrogen physisorption analysis. It can be seen that all the samples exhibit a type IV isotherm characteristic of mesoporous materials (Figure 1b). The Fe-N-doped carbons have high specific surface areas in the $900\text{-}1100\text{ m}^2\text{ g}^{-1}$ range and large pore volumes ($1.59\text{-}1.13\text{ cm}^3\text{ g}^{-1}$), as can be seen from the data in Table 1. The incorporation of nitrogen groups results in a small decrease in the specific surface area and pore volume from $1610\text{ m}^2\text{ g}^{-1}$ and $2.6\text{ cm}^3\text{ g}^{-1}$ in the case of the un-doped carbon to $1290\text{ m}^2\text{ g}^{-1}$ and $2.1\text{ cm}^3\text{ g}^{-1}$ in the N-doped sample (CCa-0-10). Similarly, the introduction of iron causes a reduction in the specific surface area compared to the un-doped sample ($1430\text{ m}^2\text{ g}^{-1}$ for CCa-0.37-0 sample). On the other hand, the simultaneous incorporation of iron and nitrogen groups produces a decrease both in the specific surface area and pore volume, which becomes more pronounced as the amounts of iron and nitrogen are increased (see Figure 1c and Table 1). Indeed, the sample with the highest iron content

exhibits a BET surface area of only $910 \text{ m}^2 \text{ g}^{-1}$ and a pore volume of $1.13 \text{ cm}^3 \text{ g}^{-1}$. The porosity of these materials is made up almost exclusively of mesopores, which represent $> 95\%$ of the total pore volume (see Table 1). These mesopores have sizes in the 9.5-11 nm range, as can be deduced from the pore size distributions represented in Figure 1d. This mesoporous structure is highly favorable for the ORR since the wide mesopores allow easy access to the active sites, which enhances mass transfer kinetics [13].

By applying the synthesis procedure described above, it was possible to prepare a variety of carbon catalysts with different iron contents in the 0.08-2.85 wt % range (see Table 1). It was observed that iron is distributed in two kinds of configurations: i) an γ -iron phase and ii) iron coordinate to nitrogen (Fe-N_x). High resolution TEM images of the CCa-0.37-10 sample reveal the presence of iron nanoparticles inserted within the carbon framework in sizes in the 15-40 nm range (see Figure 2a). As can be seen, some of the iron nanoparticles were eliminated as a result of acid leaching, leaving hollow nanocages formed by a carbon graphitic layer. The high resolution image in Figure 2b confirms the encapsulation of these nanoparticles by a graphitic layer of around 4 nm. Closer inspection of one of these nanoparticles (Figure 2c) shows a crystalline lattice spacing of 0.336 nm corresponding to graphite (see inset Figure 2c). Furthermore, additional patterns of 0.21 nm and 0.18 nm are also present, which correspond to the (111) and (200) planes of γ -iron (austenite). The presence of the γ -iron phase was also detected by XRD analysis (Pattern: 00-023-0298) in the case of the Fe-N-C samples with the highest iron contents (CCa-0.78-10), as shown in Figure 2d. In addition to γ -iron, the XRD pattern

also exhibits a weak signal that can be attributed to Fe_3C (*vide infra*). Besides the iron nanoparticles, an additional iron configuration was evidenced by HRTEM inspection. For example, in the case of the CCa-0.37-10 sample, the line concentration profile obtained by TEM-EDX analysis shows that the concentrations of carbon, nitrogen and iron correlate well (Figure S1a-b). This would appear to suggest the existence of some type of coordination between the nitrogen and iron (Fe-N_x). The mapping images for carbon, nitrogen and iron clearly corroborate the homogenous distribution of the different elements (Figure S1c-f). Interestingly, when no nitrogen precursor was added (*i.e.*, CCa-0.37-0), only a small fraction of iron was incorporated (0.08 wt % for CCa-0.37-0). By contrast, when the carbonaceous material was pyrolyzed in the presence of urea, a large amount of iron was incorporated (1.12 wt % for CCa-0.37-10). This suggests that the presence of nitrogen groups is crucial for the incorporation of homogeneously distributed iron atoms and supports the existence of a Fe-N_x configuration.

The amount of nitrogen incorporated into the carbon sample increases with the amount of urea added from 0.72 wt % for the CCa-0.37-0 sample to 6.86 wt % for CCa-0.37-10 (Table 1). In addition, it was observed that the fixed nitrogen diminishes as the amount of Fe precursor increases (CCa-0.07-10 > CCa-0.37-10 > CCa-0.78-10). This behavior can be ascribed to the reduction of the iron ions by defective N-doped carbons during the carbonization step, leading to higher iron but lower nitrogen contents [58].

In order to evaluate the chemical nature of the nitrogen functional groups, X-ray photoelectron spectroscopy (XPS) analysis was applied (Figure 3). The

XPS general spectrum does not exhibit any signal corresponding to iron which should appear at 706-711 eV (see Figure 3a). Its absence might be due to the fact that the iron nanoparticles go undetected due to their encasement by the graphitic layers, while at the same time the amount of Fe-N_x coordination sites remains below the detection limit of the technique. The high-resolution N 1s XPS spectra for the CCa-0.37-10 sample can be deconvoluted into three main peaks at 398.4 eV, 400.2 eV and 401.4 eV which are assigned to pyridinic-N (44.7 %), pyrrolic-N (35.4 %) and quaternary-N (12.3 %) respectively, and two minor peaks at 399.3 eV 403.3 eV, which are attributed to Fe-N (3.4 %) and pyridine-N-oxide (4.3 %) respectively (Figure 3b) [58-60]. Considering that the amount of nitrogen in CCa-0.37-10 is 5.64 at % (6.86 wt %) and that the Fe-N contribution represents around 3.4 % (as demonstrated previously on the high-resolution N 1s XPS spectrum), it can be inferred that around 0.19 at % of the iron is coordinated to nitrogen (Fe-N). This value represents more than half of the total amount of iron, confirming that an important fraction of iron is coordinated to nitrogen, as previously indicated by the HRTEM concentration profiles. In addition, on the basis of the HRTEM images that prove the existence of an iron phase, it can be assumed that the remaining iron is in the crystalline form of γ -iron (~ 0.04 at %). Likewise, the other Fe-N-C samples containing different iron amounts (CCa-0.07-10 and CCa-0.78-10), exhibit a similar distribution of nitrogen functionalities (see Figure S2 and Table S1).

It is important to point out that the iron coordinated with nitrogen is present even in the Fe-N-C sample with the lowest iron content, as can be deduced from the EDX-TEM analysis of the CCa-0.07-10 sample (Figure S3).

Moreover, the mapping images reveal that the iron is homogeneously distributed among the carbon and nitrogen groups (Figure S3c-f). The amount of nitrogen coordinated to iron (Fe-N), as deduced from the high-resolution N 1s XPS spectrum (see Figure S2b and Table S1), is around 0.6 % of the total amount of nitrogen in CCa-0.07-10. On the basis of this result, it is inferred that the amount of iron in Fe-N is ~ 0.042 at %, which is close to the amount of iron obtained by ICP analysis (0.049 at % corresponding to 0.23 wt %, see Table 1). It can therefore be concluded that, in this sample, the iron is mostly coordinated with nitrogen atoms. In addition, no iron was found in the form of any isolated nanoparticle by HRTEM inspection, as is shown in Figure S4. By contrast, the sample with the highest iron content (*i.e.*, CCa-0.78-10, 2.85 wt %), exhibits a high amount of iron nanoparticles (Figure S5a). As in the CCa-0.37-10 sample, these iron nanoparticles are encapsulated by a graphitic layer (Figure S5b). A close inspection of one of these nanoparticles shows crystalline lattice spacings of 0.21 nm and 0.336 nm that correspond to γ -iron and graphite, respectively (Figures S5c and S5d). In addition, there is another crystalline lattice spacing of 0.24 nm that can be assigned to the (210) plane of Fe_3C , which coexists together with the γ -iron phase. The presence of both phases is also evidenced in the XRD patterns (*vide infra*). Besides the substantial fraction of iron-forming nanoparticles, there is also a fraction of iron coordinated to nitrogen (see Table S1), which is uniformly distributed as evidenced by TEM-EDX inspection (Figures S6). These results indicate that the Fe-N-C material will exhibit an excellent ORR activity due to the combination of an easily accessible mesoporous structure with a large amount of active sites. What is more, carbon material with catalytic active sites (*i.e.*, N-quaternary, N-pyridinic and Fe-N)

could be synthesized by heat-treating a carbonaceous material with urea and an iron precursor.

3.2. ORR measurements

Analysis of the catalytic activity was performed by using a rotating disk (RDE) and rotating ring-disk (RRDE) electrodes in a three-electrode electrochemical cell in 0.1 M KOH and 0.1 M HClO₄. In a first step, for comparison purposes, the catalytic activity of the un-doped mesoporous carbon (CCa-0-0), Fe-doped mesoporous carbon (CCa-0.37-0) and N-doped mesoporous carbon (CCa-0-10) was analyzed in 0.1 M KOH. The lineal sweep voltammetry curves (LSVs) in Figure 4a show that the incorporation of iron (CCa-0.37-0 sample) up-shifts the onset potential by 40 mV and increases the limiting current density. However, the catalytic activity of the catalyst doped exclusively with iron is still far from that of commercial Pt/C. On the other hand, the incorporation of N-groups significantly enhances catalytic activity by positively shifting the onset and half-wave potentials (40 and 50 mV, respectively) and increasing the limiting current density (4.29 mA cm⁻² vs. 3.72 mA cm⁻² for the un-doped mesoporous carbon). These results demonstrate that nitrogen functionalities enhance catalytic activity more than iron species. The kinetic current density (J_K), which is another parameter normally used to characterize the activity of ORR catalysts, was determined from the RDE measurements at different rotating speeds (Figure S7) and calculated on the basis of the Koutecky-Levich analysis (Figure S8) [61]. As expected, the J_K values calculated at 0.7 V for CCa-0.37-0 (7.1 mA cm⁻²) and CCa-0-10 (7.15 mA cm⁻²) are superior to those of the un-doped carbon catalyst (4.6 mA cm⁻²).

More importantly, these results suggest that doping with pure iron enhances the ORR reaction less than doping with pure nitrogen.

In order to assess the influence of nitrogen upon catalytic activity in the Fe-N-doped carbons, we prepared several samples with different nitrogen contents in the 0-6.86 wt % range, maintaining the iron precursor:carbon ratio of 0.37. The LSV curves corresponding to various Fe-N-C samples with different nitrogen contents are shown in Figure 4b. It can be seen that electrocatalytic activity improves with the nitrogen content, so that the CCa-0.37-10 sample (6.86 wt % N) exhibits the best electrocatalytic performance. This can be ascribed to its large nitrogen content and greater number of iron active sites compared to the other Fe-N-doped mesoporous carbon materials (see below). In addition, the CCa-0.37-10 sample exhibits a higher limiting current density than commercial Pt/C and a slightly lower kinetic current density (4.68 mA cm^{-2} vs. 7 mA cm^{-2} for Pt/C calculated at 0.8 V).

The influence of the amount of iron incorporated into the Fe-N-C samples upon the electrocatalytic activity was also examined. As shown in Figure 4c, when the iron content rises, there is a shift to higher values of both the onset potentials (from 0.88 V for CCa-0-10 to 0.91 V for CCa-0.37-10) and the half-wave potentials (from 0.76 V for CCa-0-10 to 0.814 V for CCa-0.37-10). The onset potential value of the CCa-0.37-10 sample is comparable to those of the Fe-N-doped carbon catalysts reported to date in the literature [57, 62-66] and it is only 39 mV lower than that of commercial platinum. In addition, The remarkable value of the half-wave potential is comparable to some of the best reported in the literature [25, 62, 64, 67-71] and similar to that of commercial

Pt/C. The onset and half-wave potentials values corresponding to these catalysts are summarized in Figure 4d and compared to those of Pt/C. In addition, the limiting and kinetic current densities of the CCa-0.37-10 sample (4.64 mA cm^{-2} and 13.6 mA cm^{-2} , respectively) are superior to those of the N-doped mesoporous carbon (4.3 mA cm^{-2} and 6.8 mA cm^{-2} (calculated at 0.7 V), respectively). What is more, Figure 4d shows that the amount of iron introduced into the Fe-N-C samples hardly influences the catalytic activity when the iron precursor:carbon ratio is in the 0.07-0.37 range. Indeed, CCa-0.37-10 (1.12 wt % Fe) and CCa-0.07-10 (0.23 wt % Fe) exhibit very similar onset/half-wave potential values. This result can be attributed to the fact that CCa-0.07-10 sample exhibits a higher amount of nitrogen functional groups and a slightly superior specific surface area. Interestingly, the carbon material with the highest Fe-doping (CCa-0.78-10) exhibits the lowest limiting and kinetic current density values (4.3 mA cm^{-2} and 4.25 mA cm^{-2} (calculated at 0.8 V), respectively; vs 4.75 mA cm^{-2} and 4.6 mA cm^{-2} for the CCa-0.07-10 catalyst and 4.64 mA cm^{-2} and 4.68 mA cm^{-2} for the CCa-0.37-10 sample). This result can be ascribed to the fact that CCa-0.78-10 has lower amounts of N-quaternary, N-pyridinic and Fe-N and higher amounts of γ -iron nanoparticles, suggesting that there is an optimum iron load that governs their ability to combine with nitrogen atoms (see Table S1).

A more in-depth study of the reaction pathway was performed by using a RRDE system to gain a more accurate assessment of the amount of HO_2^- present. Figure 4e compares the peroxide yield corresponding to the mesoporous carbon catalysts and Pt/C in 0.1 M KOH. It can be seen that the

CCa-0.37-10 catalyst exhibits the lowest HO_2^- yield, *i.e.*, $\sim 10\%$ over the whole range of potentials. In addition, for CCa-0.37-10 the number of electrons transferred is greater than 3.7 and close to that of Pt/C (Figure 4f), which demonstrates its excellent electrocatalytic selectivity. The good electrocatalytic performance of the CCa-0.37-10 sample is ascribed to a combination of: i) its high specific surface area and its porosity which is made up of large mesopores that reduces mass-transport resistance [13, 72, 73], and ii) its large number of active centers (*i.e.*, N-quaternary, N-pyridinic and Fe-N) for catalyzing the oxygen reduction reaction [25, 74, 75]. Furthermore, its improved electrocatalytic activity depends not only on the amount of nitrogen, but also on the nature of the nitrogen functional groups. Thus, the sample with the highest proportion of Fe-N groups (CCa-0.37-10), shows the best electrocatalytic performance. We believe that because their textural properties are similar, these active sites, along with N-quaternary and N-pyridinic, are the main contributors to the ORR activity. The durability of the CCa-0.37-10 sample was also tested by means of chronoamperometric experiments. The results shown in Figure S9 demonstrate its excellent stability, as it is able to retain *ca.* 87 % of the initial current after 3 hours, whereas the current retention of the commercial Pt/C is much lower ($\sim 70\%$).

The electrocatalytic activity of the synthesized materials was also investigated in an acid medium (0.1 M HClO_4). It was mentioned above that, in basic electrolyte, it is more effective to incorporate nitrogen groups than to employ pure iron doping to enhance catalytic activity. A similar claim can be made for acid electrolyte. Hence, as can be seen in Figure 5a, the catalytic activity of the N-doped carbon catalyst (*i.e.*, CCa-0-10) is superior to that of the

sample only doped with iron (*i.e.*, CCa-0.37-0). Moreover, Figure 5b shows that the samples co-doped with nitrogen and iron undergo a notable improvement in their catalytic activity, as can be inferred from the increase in the onset and half-wave potentials, and in the limiting current density. In short, these results confirm that the simultaneous incorporation of both nitrogen and iron species into the carbon framework is essential in order to achieve a significant enhancement of the ORR activity. In particular, the CCa-0.37-10 sample (6.86 wt % N and 1.12 wt % Fe) exhibits the best performance, with onset and half-wave potentials of 0.74 V and 0.5 V, respectively (see Figures 5c and 5d), similar to the results obtained in basic electrolyte. In view of the higher proportion of Fe-N sites in the CCa-0.37-10 sample (see Table S1), it can be deduced that these functionalities are the main contributors to catalytic performance. The results obtained indicate that, in comparison to N-doped samples, these active centers enhance the catalytic activity in acid electrolyte to a greater extent than in basic electrolyte. On the other hand, it can be seen that the sample with the largest amount of iron (CCa-0.78-10) exhibits lower onset and half-wave potentials and also lower limiting current densities than those of the CCa-0.37-10 catalyst. Since the majority of the iron is in the form of γ -iron, the results demonstrate that these nanoparticles do not have a significant influence on electrocatalytic activity. Their contribution to catalytic activity can also be discarded due to the encasement of the metallic particles by the graphitic layer which prevents the diffusion of the electrolyte. In addition, this sample possesses the lowest amount of N-pyridinic and N-quaternary among the Fe-N-C samples, confirming the importance of these contributions to the catalytic activity. At this point, it is worth mentioning that the CCa-0.37-10

catalyst is not as active in an acidic as in an alkaline medium and its catalytic performance is inferior to that of commercial platinum. Nevertheless, its activity is still significant compared to other Fe-N-C catalysts reported in the literature [25, 63, 64]. The calculated electrochemical kinetic current density (J_k) (obtained from the different LSVs at various rotating speeds, Figure S10; and calculated on the basis of the Koutecky-Levich analysis, Figure S11) has a value of 4.92 mA cm^{-2} at 0.45 V. This value is superior to that of the N-doped catalyst (CCa-0-10 catalyst, 1.83 mA cm^{-2}) and also to that of some advanced Fe-N-catalysts reported in the literature [25, 76]. We also analyzed the ORR mechanism for the optimized catalyst CCa-0.37-10 by means of RRDE measurements. Figure 5e shows that the peroxide yield does not exceed 15 %, which confirms the high selectivity of this catalyst and that the oxygen reduction reaction takes place predominantly via the four-electron pathway (Figure 5f).

The long-term stability of the electrocatalysts is another major concern in fuel-cell technology [77]. Consequently, the durability of the CCa-0.37-10 catalyst was tested following a US Department of Energy's accelerated durability test protocol based on cycling the catalysts between 0.6 and 1.0 V (vs. RHE) at 50 mV s^{-1} under N_2 atmosphere in 0.1 M HClO_4 [56, 57]. Figure S12 compares the LSVs recorded at a rotation speed of 1600 rpm in an O_2 -saturated electrolyte before and after the accelerated durability test in 0.1 M HClO_4 electrolytes. As can be seen, the CCa-0.37-10 catalyst shows a remarkable stability performance, with the onset potential decreasing by only ~ 35 mV and the half-wave potential varying by only ~ 50 mV after 4000 cycles. What is most interesting is that after the 4000 cycles, the Fe-N-C catalyst

exhibits an onset potential comparable to that of Pt/C and a similar limiting current density. In addition, the difference in half-wave potential between both electrocatalysts is been reduced by ~ 50 %. Therefore, the initially less active Fe-N-C catalyst (Figure S12a), is able to match the activity of Pt/C after the long-term cycling operation (Figure S12b).

4. Conclusions

To conclude, we have presented a simple strategy for the fabrication of a Fe-N-C catalyst involving the use of calcium citrate as carbon precursor and urea and ammonium sulfate iron (II) as nitrogen and iron precursors, respectively. The resulting carbons possess iron distributed in the form of Fe-N coordination and γ -iron species, and a high content in nitrogen moieties (5-8 wt %). In addition, the Fe-N carbon samples have a mesoporous structure with high specific surface areas. The non-precious metal catalysts exhibited a high ORR performance in both basic and acid electrolytes with high onset (0.91 V and 0.74 V, respectively) and kinetic current densities (13.6 mA cm^{-2} and 4.92 mA cm^{-2} , respectively). Their good electrocatalytic performance was ascribed to a combination of optimized textural properties and a large number of active centers (*i.e.*, N-quaternary, N-pyridinic and Fe-N). In this sense, these functionalities were identified as the main contributors to the catalytic activity on both electrolytes. On the contrary, the γ -iron phase encapsulated by a graphitic carbon layer showed little or no catalytic contribution to the ORR activity. In addition, the effective Fe-N-C catalyst shows an excellent long-term durability that surpasses that of commercially available platinum.

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Figures and Tables

Scheme 1. Schematic illustration of the synthesis procedure: (1) Carbonization of the calcium citrate; (2) acid washing of the carbon/CaO composite; (3) urea and ammonium iron (II) sulfate infiltration and (4) thermal treatment of the Fe/N impregnated carbon.

Table 1. Physico-chemical properties of the mesoporous carbons.

Sample Code	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{p} ($\text{cm}^3 \text{g}^{-1}$) ^a	V_{micro} ($\text{cm}^3 \text{g}^{-1}$) ^b	V_{meso} ($\text{cm}^3 \text{g}^{-1}$) ^c	N (wt %)	Fe (wt %)
CCa-0-0	1610	2.57	0.04	2.53	0.54	-
CCa-0-10	1290	2.098	0.028	2.07	6.97	-
CCa-0.07-10	1100	1.588	0.031	1.557	7.96	0.23
CCa-0.37-10	1030	1.384	0.036	1.348	6.86	1.12
CCa-0.78-10	910	1.128	0.024	1.104	4.72	2.85
CCa-0.37-0	1430	2.645	0.013	2.632	0.72	0.08

^a Pore volume at $p/p_0 \sim 0.95$. ^b The micropore volume was determined by using the α_s -plot method applied to the N_2 adsorption branch. ^c Mesopore volume obtained from the difference between pore volume (V_{p}) and micropore volume (V_{micro}).

Figure 1. a) SEM image of the CCa-0.37-10 sample, b) and c) nitrogen sorption isotherms and d) pore size distributions of the mesoporous carbon materials.

Figure 2. a) TEM image of the CCa-0.37-10 sample in a random region, b) HRTEM image of an iron nanoparticle, c) an enlarged HRTEM image of an iron nanoparticle (inset: SAED pattern corresponding to this image) and d) XRD patterns of the CCa-0.07-10, CCa-0.37-10 and CCa-0.78-10 carbon samples.

Figure 3. a) XPS general spectrum and b) high-resolution N 1s core level spectrum corresponding to the CCa-0.37-10 sample.

Figure 4. Comparison of the RDE polarization curves at 1600 rpm for a) catalysts CCa-0-0, CCa-0-10, CCa-0.37-0 and Pt/C, b) catalysts CCa-0-10, CCa-0.07-10, CCa-0.37-10, CCa-0.78-10 and Pt/C, c) catalysts CCa-0.37-0, CCa-0.37-5, CCa-0.37-10, CCa-0.37-20 and Pt/C, d) comparison of the onset and half-wave potentials, e) number of electrons transferred and f) peroxide yields for the CCa-0.07-10, CCa-0.37-10, CCa-0.78-10 and Pt/C catalysts. Electrolyte: 0.1 M KOH.

Figure 5. Comparison of the RDE polarization curves at 1600 rpm for a) catalysts CCa-0-0, CCa-0-10, CCa-0.37-0 and Pt/C, b) catalysts CCa-0-10, CCa-0.07-10, CCa-0.37-10, CCa-0.78-10 and Pt/C, and c) catalysts CCa-0.37-0, CCa-0.37-5, CCa-0.37-10, CCa-0.37-20 and Pt/C, d) comparison of the onset and half-wave potentials, e) number of electrons transferred and f) peroxide yields for the CCa-0.07-10, CCa-0.37-10, CCa-0.78-10 and Pt/C catalysts. Electrolyte: 0.1 M HClO₄.