Iron-Nitrogen-doped Dendritic Carbon Nanostructures for an Efficient Oxygen Reduction Reaction

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Abstract

A novel Fe-N-doped carbon with a dendritic structure is analyzed as an electrocatalyst for the oxygen reduction reaction. The synthesis of the material was accomplished through a nanocasting approach using pyrrole as the nitrogen and carbon source, and iron chloride as the iron dopant. The Fe-N-C thus synthesized consists of small nanoparticles with a diameter of ~ 240 nm and a pom-pom-like morphology. They exhibit a relatively high specific surface area combined with a very accessible porosity and a high nitrogen (~ 11 wt %) and iron (~ 5 wt %) content. With respect to electrocatalytic activity, in basic electrolyte the Fe-N-doped carbon nano-pompoms exhibited high onset (0.94 V) and half-wave potentials (0.82 V), and a large kinetic current density (19 mA cm^{-2}), higher than commercial platinum catalysts. The electrocatalysts were also tested in acid electrolyte, giving an onset potential of 0.75 V and a peroxide yield lower than 10 % over a wide range of potentials. Furthermore, the newly developed carbon nanostructures exhibit excellent durability, better than commercially available platinum in both media. The excellent electrocatalytic activity is attributed to a combination of a high specific surface area with very

accessible porosity and the presence of numerous active centers (*i.e.* iron coordinated to nitrogen and nitrogen functional groups).

Keywords: carbon material, nitrogen-doping, oxygen reduction reaction, non-noble metal catalysts, nano-pompom.

Introduction

Fuel cells and metal-air batteries have recently attracted much attention for advanced energy storage and conversion technologies.¹⁻² However, the sluggish kinetics of the oxygen reduction reaction (ORR) at the cathode limits widespread commercialization.³ Although platinum-based catalysts are considered the most efficient electrocatalysts for the oxygen reduction reaction, their scarcity, limited durability, and above all, their high cost hinder large-scale practical use.⁴

Porous carbon materials have been widely investigated as ORR electrocatalysts because of their high electrical conductivity, resistance against corrosion, good thermal and chemical stability, wide availability and above all, their low cost.⁵⁻⁸ However, un-doped carbon materials cannot catalyze the 4 electron pathway in the ORR process, which is associated with high current densities and a high onset potential, and which allows the production of hydrogen peroxide.^{6, 9} N-doped carbons with small amounts of non-noble metals such as cobalt or iron have been shown to be an excellent alternative to state-of-the-art platinum-based catalysts.¹⁰⁻¹¹ In particular, the active sites in Fe-N-C catalysts are believed to be iron coordinated to nitrogen,¹²⁻¹⁴ along with the various nitrogen functional groups (*i.e.* N-quaternary and N-pyridinic) that enhance not only the catalytic activity but also electrical conductivity, surface wettability and resistance to oxidation.¹⁵⁻¹⁶

The design of carbon-based catalysts for the ORR process requires not only the presence of numerous active catalytic sites, but also the dispersion of these active centers over an easily accessible surface area.¹⁷⁻¹⁸ Thus, in order to guarantee fast mass transport of the species to the reaction sites, the catalyst

should combine accessible porosity, made up of wide pores in the mesopore range (> 2 nm) that reduce diffusional resistance¹⁶, with small particle sizes that ensure short diffusional paths.¹⁹⁻²⁰ It is not easy to design catalysts that meet both requirements, so a literature review yields only few examples. Brun *et al.* designed carbon aerogels with interlinked nanoparticles of about 15-20 nm and pore width in the mesopore range.²¹ Similarly, Chan *et al.* fabricated iron nitrogen-doped carbon with a core-shell geometry, a uniform pore size of 8 nm and a particle diameter of around 600 nm.²² Other morphologies have been reported such as carbon nanosheets and nanotubes with good catalytic activity.²³⁻²⁴ Our group recently reported the synthesis of iron-nitrogen doped carbon capsules with particle diameter of around 600 nm.²⁵ The material consisted of hollow carbon particles with a curved thin layer (~ 50 nm) that exhibited excellent catalytic activity in both basic and acid electrolytes.

In this paper we report the fabrication of a novel Fe-N-carbon material with dendritic morphology by using pyrrole as the N-rich carbon precursor, FeCl_3 as the iron source, and silica particles as the sacrificial template. The carbon material obtained in this way is made up of small nanoparticles (of around 240 nm), which exhibit very open porosity (pores > 3 nm) and more importantly contain numerous, uniformly distributed nitrogen and iron functional groups. Recently, Huang *et al.* analyzed the use of a N-doped carbon with a similar morphology for the ORR process in a basic medium.²⁶ However, such metal-free N-doped carbons are only appropriate for use in basic electrolytes as in acid electrolytes they suffer from very low catalytic activity and limited stability.²⁷⁻²⁹ The Fe-N carbon catalysts developed in this research were tested

in acid and basic media and the results show that they exhibit high ORR activity, comparable to commercial platinum, and excellent durability.

Experimental Section

Preparation of the Fe-N-doped carbon nano-pompoms

The Fe-N-doped carbon pompoms were produced by using dendritic silica nanoparticles as sacrificial template and pyrrole monomer (Aldrich, 99%) as the N-containing carbon precursor. The silica used as the template was synthesized as reported by Yang *et al.*³⁰ The silica particles were first impregnated by the drop-wise addition of a 2 M FeCl₃ ethanol solution (around 0.27 g FeCl₃/g silica). Then the impregnated sample was exposed to pyrrole vapor at 25 °C for 22 h in a closed vessel. Afterwards, the dark impregnated sample was heated under N₂ up to 600 °C (at 3 °C min⁻¹) and held at that temperature for 1 h. The silica framework was removed by etching with hydrofluoric acid. The carbon residue was collected by filtration, washed with distilled water, and dried at 120 °C for several hours.

In order to incorporate iron, the carbon product was impregnated with a solution of FeCl₃ in ethanol (up to 0.15 g FeCl₃ per gram of carbon). Then it was heat-treated to the desired temperature (*i.e.* 800, 850 and 900 °C) at 3 °C min⁻¹ and held at that temperature for 1 h. To remove unstable iron species, the carbonized product was washed in 0.5 M H₂SO₄ solution at 80 °C for 8 h. Then the catalyst was purified with abundant distilled water, collected by centrifugation and dried. Finally, the solid product was heat-treated for a second time at the same temperature as the first treatment for 1 hour. In this way, a Fe-

N-C catalyst was finally obtained. This material was denoted as *CNP-x*, where *x* indicates the temperature of treatment, in °C.

Characterization of materials

The morphology of the powders was examined by scanning (SEM, Zeiss DSM 942) and transmission (HRTEM, JEOL (JEM 2100-F)) electron microscopy. The particle size distribution for all the materials was obtained from several SEM pictures by measuring 100-150 particles. Nitrogen sorption isotherms were performed at -196 °C in 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.³¹ 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.³²

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. 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 in a 7700x unit (Agilent).

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 *CNP-x* sample in a solution containing 100 μL Nafion solution (5 wt %) and 900 μL 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 for all the catalysts was the same, *i.e.* 0.1 mg cm^{-2} . The catalyst inks were deposited onto a polished glassy carbon electrode ($\alpha\text{-Al}_2\text{O}_3$ 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 HClO_4 solution, respectively. A Pt wire or a graphite rod was employed as the counter electrodes. All the experiments were carried out at 20 $^\circ\text{C}$. Before testing, O_2/N_2 gas was bubbled through the electrolyte in the cell for 30 min to saturate it with O_2/N_2 . 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:

$$E_{\text{RHE}} = E_{\text{Ref}} + E_{\text{Ref}}^0 + 0.059 \text{ pH} \quad (1)$$

where E_{Ref} is the experimentally measured potential vs. SCE or Ag/AgCl reference and E_{Ref}^0 values are: $E_{\text{SCE}}^0 = 0.241 \text{ V}$ and $E_{\text{Ag/AgCl}}^0 = 0.21 \text{ V}$ at 20 $^\circ\text{C}$. The potential values provided in 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 Koutecky-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 x 10⁻³ mol L⁻¹ for 0.1 M HClO₄ solution and 1.2 x 10⁻³ mol L⁻¹ 0.1 M KOH solution), D_0 is the diffusion coefficient of O₂ (1.4 x 10⁻⁵ cm² s⁻¹ for 0.1 M HClO₄ solution and 1.93 x 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).³³⁻³⁵

Cyclic voltammetry (CV) was performed from 0 to 1.2 V vs. RHE in 0.1 M KOH and 0.1 M HClO₄, with a sweep rate of 50 mV s⁻¹.

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.³⁶⁻³⁷ 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 % H_2O_2 (the percentage of H_2O_2 released during the ORR):³

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

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

where I_D is the Faradaic current at the disk, I_R is the Faradaic current at the ring, N is the H_2O_2 collection coefficient at the ring.

The stability of the catalyst was assessed by means of a US Department of Energy accelerated durability test protocol by cycling the catalysts between 0.6 and 1.0 V (vs. RHE) at 50 mV s^{-1} under a N_2 atmosphere in 0.1 M $HClO_4$ for 4000 cycles.³⁸⁻³⁹

Results and discussions

Structural characteristics of the Fe-N-doped carbon nano-pompoms

The synthesis procedure of the carbon nano-pompom electrocatalysts (CNP) is illustrated in Scheme 1. The synthesis is based on a nanocasting approach using silica particles with a dendritic structure (diameter $\sim 300 \text{ nm}$) and pyrrole as the N-rich carbon precursor. The silica particles were first impregnated with $FeCl_3$ in order to polymerize the pyrrole which was added to the silica template by vapor phase deposition. Once the pyrrole was polymerized, the composite was carbonized up to the desired temperature and the carbon nano-pompoms were collected after silica and iron etching. The iron doping of the N-doped carbon nano-pompoms was accomplished by impregnation with $FeCl_3$ followed by a thermal treatment. The iron electroactive centers were obtained once the non-reactive or unstable iron nanoparticles had

been removed by acid washing and the sample had been subjected to an additional thermal treatment.

The morphology of the carbon materials was first examined by SEM analysis. As Figure 1a shows, the carbon particles have a dendritic morphology, with a diameter of 250 ± 30 nm in the case of the sample pyrolyzed at 800 °C (see inset). The magnified SEM image in Figure 1b shows that the dendritic structure of the template is preserved in the carbon, which exhibits a very open structure made up of interconnected thin layers (size ~ 10 nm). The morphology of the carbon materials is retained (Figure S2) regardless of the carbonization temperature. In contrast, at higher temperatures the carbon nanoparticles are smaller, with particle sizes of 235 ± 30 nm and 215 ± 30 nm for the samples produced at 850 °C and 900 °C respectively (see insets in Figure S2a and S2c). Further structural characterization by transmission electron microscopy confirms the morphology of the CNPs, as shown in Figure 1c. Furthermore, the TEM images in Figures 1c and 1d reveal the existence of well-developed porosity made up of numerous meso- and macropores creating a crumpled radial configuration. The textural properties of the CNPs were analyzed by nitrogen physisorption. The nitrogen sorption isotherms displayed in Figure 2a show large nitrogen uptakes for $p/p_0 > 0.8$ which is indicative of the existence of large cavities (macropores and interparticle voids). The pore size distributions in Figure 2b show that the meso-macroporous structure is made up of two pore systems, one of 4 nm and one in the 50-75 nm range, confirming the observations in the TEM inspection. The textural properties of these carbon samples are listed in Table 1. They have a similar BET surface area in the 430-520 m² g⁻¹ range and a pore volume in the 0.54-0.62 cm³ g⁻¹ range.

The microstructure of the carbonaceous materials was examined by XRD analysis. The X-ray diffraction patterns in Figure 2c of the carbon samples obtained at 800 °C or 850 °C exhibit a broad diffraction peak at $2\theta = 24^\circ$ that corresponds to amorphous carbon. However, the carbon pyrolyzed at 900 °C (CNP-900) exhibits a sharp peak at $2\theta = 26^\circ$, which shows the presence of well-organized graphitic domains. This result indicates that at the high temperature (900 °C) used for the synthesis of the CNP-900 sample, a certain amount of amorphous carbon is converted into graphitic carbon due to the catalytic effect of inserted iron nanoparticles.⁴⁰⁻⁴¹ The XRD patterns show no peaks attributable to any Fe or Fe₃C phases. However, the as-prepared carbon samples have small peaks of Fe₃C and Fe₅C₂ that are completely removed once they are washed with H₂SO₄, as shown by the results in Figure S3 which give the XRD patterns for the CNP-800 sample before and after acid washing.

The thermal treatment of N-doped carbon nano-pompoms impregnated with FeCl₃ gave rise to Fe-N-C samples that have a significant amount of iron. The iron content was determined by ICP analysis and the results are listed in Table 1. The amount of iron decreases with temperature from 5.4 % (800 °C) to 2.6 wt % (900 °C). The presence of iron in the CNP samples is evidenced by the XPS general spectra in Figure S4. In order to analyze the type of iron configurations, HRTEM studies were carried out. HRTEM inspection found no evidence of iron or iron carbide nanoparticles in the CNP samples (see Figures 1c-d and 3). Moreover, the EDX-TEM analysis in Figure 3 shows that the iron is uniformly distributed along with the carbon and nitrogen in the carbon framework. By comparing the EDX concentration profiles of iron and nitrogen in Figure S5, we can deduce that the two elements are well-correlated which

suggests the existence of a certain Fe-N coordination. The presence of this Fe-N configuration was further confirmed by X-ray photoelectron spectroscopy analysis (XPS). The high resolution N 1s XPS spectra in Figure 2d exhibited three peaks that can be assigned to N-pyridinic (398.4 eV), N-quaternary (401.1 eV) and Fe-N (399.1 eV).^{14, 42-43} These results confirm the existence of atomically dispersed Fe-N coordination sites and prove that iron is mostly coordinated to nitrogen. As we would expect, higher N content leads to a greater proportion of Fe-N coordination sites (Table 2), which allows the introduction of more active sites. In addition, the N1s spectra exhibited two additional peaks that corresponded to N-pyrrolic (400.1 eV) and pyridine-N-oxides (402.3 eV). The Fe-N contribution along with the pyridinic and quaternary nitrogen groups are believed to be highly active for the ORR and their contribution represents > 80 % of the total amount of nitrogen.^{25, 44-46} An increase in synthesis temperature is associated with a decrease in the least stable species (N-pyrrolic) and an increase in the amount of the most stable species (N-pyridinic and N-quaternary) (see Table 2). The bulk nitrogen content of the CNP samples was determined by elemental analysis (Table 1). The materials exhibit a high nitrogen content and, as we would expect, nitrogen content is lower, the higher the carbonization temperature, going from 11 wt % (800 °C) to 3.54 wt % (900 °C).

ORR performance of the Fe-N-doped carbon nano-pompoms

The electrocatalytic activity of the CNP samples was examined in 0.1 M KOH and 0.1 M HClO₄. The ORR activity was first studied in both electrolytes by using a rotating disk electrode (RDE). The corresponding polarization curves at 1600 rpm are displayed in Figures 4a and 4c for the different materials along

with that of commercial Pt/C. In 0.1 M KOH, the Fe-N-C samples exhibit high catalytic activity. The CNP-800 electrocatalyst demonstrates the best catalytic performance (see Figure 4a) with high onset (0.94 V) and half-wave potentials (0.82 V) similar to those of commercial platinum (0.95 V and 0.83 V, respectively) with the same mass loading (0.1 mg cm^{-2}). The values of the onset and half-wave potentials are comparable to those of the top-performing Fe-N-doped carbon materials reported in the literature.^{25, 39, 47-54} In addition, the CNP-800 catalyst has a diffusion-limited current density of 4.6 mA cm^{-2} , which is higher than that of commercial platinum (Figure 4a). Especially remarkable is the value of the kinetic current density at 0.7 V for CNP-800 (19.1 mA cm^{-2}), which is 20 % higher than that for commercial platinum and higher than those reported in the literature for Fe-N-carbon catalysts.^{25, 50, 54-55} This parameter was calculated on the basis of the Koutecky-Levich analysis (Figure S6) from the RDE measurements at different rotating speeds (Figure S7).⁵⁶ The values of the onset and half-wave potentials along with the kinetic current densities at 0.7 V for the Fe-N-doped carbon materials and commercial platinum are displayed in Figure 4b. The sample pyrolyzed at the lowest temperature (*i.e.* 800 °C) demonstrates the best electrocatalytic performance with more positive onset and half-wave potentials and higher kinetic current density. Since all the carbon materials have similar textural properties with respect to specific surface area and the pore size distribution, the differences in catalytic performance can be ascribed to the chemical properties. The lower heat-treatment temperature leads to a material with a higher iron content and more nitrogen functional groups.

The electrochemical performance of the CNP catalysts was also evaluated in 0.1 M HClO₄ electrolyte. As in the basic electrolyte, the CNP-800 sample exhibited the highest electrocatalytic activity, shown in Figure 4c. As Figure 4d shows, the onset and half-wave potentials of CNP-800 are higher than those of the Fe-N-doped carbons pyrolyzed at higher temperatures (0.75 V and 0.54 V vs. 0.67 V and 0.39 V for CNP-850, and 0.71 V and 0.48 V for CNP-900). The well-defined plateau in the diffusion-limited current region in the linear sweep voltammetry in the basic medium compared to the acidic shows that the CNP catalysts are more active in basic electrolyte, which is common.⁵⁷ The catalytic activity of the synthesized Fe-N-C electrocatalysts in 0.1 M HClO₄ compares well with that of some of the best performing Fe-N-C catalysts found in the literature in terms of onset and half-wave potentials.^{25, 48-49} Although these values are lower than those for commercial platinum (see Figure 4d), the kinetic current density for CNP-800 is similar to that of Pt/C. The values of the kinetic current density were calculated from the Koutecky-Levich plots in Figure S8, which were obtained from RDE measurements at different rotating speeds (Figure S9). The Koutecky-Levich plots were also used to calculate the number of electrons involved in the ORR process. Figures S10a-b, provide a comparison of the slopes from the Koutecky-Levich plots for the Fe-N-C catalysts with those expected for the ideal four-electron and two-electron processes. The Fe-N-C catalysts exhibit slopes similar to an ideal four-electron process, suggesting that the material catalyzes the efficient four-electron pathway. The enhanced electrocatalytic activity of the CNP-800 is also corroborated by performing cyclic voltammetry and comparing the results with those for CNP-850 and CNP-900. CNP-800 displays a more positive and more

pronounced reduction peak in both electrolytes (see Figures S11a-b). At this point, it is important to mention that a possible contribution of the platinum counter electrode to the catalytic activity of the synthesized carbon materials was discarded in both electrolytes (see Figure S12).

In order to gain a better understanding of the reaction pathway, a rotating ring-disk electrode (RRDE) was used to accurately quantify the amount of H_2O_2 generated. Figure 5a provides a comparison of the peroxide yield along with the number of electrons transferred for the CNP-800 sample with those of commercial platinum in 0.1 M KOH. In the case of the CNP-800 catalyst, the proportion of HO_2^- formed is lower than 5 % and the number of electrons is higher than 3.9. In contrast, the Pt/C catalyst performs worse with a higher peroxide yield and the number of electrons < 3.9. Therefore, the developed CNP-800 electrocatalyst is more selective than commercial Pt. In 0.1 M HClO_4 , the CNP-800 sample exhibits a number of electrons transferred close to 4 (at potentials ≤ 0.6) and a H_2O_2 yield of ~ 2 % for low overpotentials increasing to over 10 % for high overpotentials (see Figure 5b). CNP-800 exhibited slightly lower electrocatalytic selectivity than Pt/C, which agrees with the results from RDE.

These results confirm the good electrocatalytic activity demonstrated by the RDE measurements, and the excellent electrocatalytic selectivity of the CNP electrocatalysts in both electrolytes. In particular, the CNP-800 catalyst exhibits the best electrocatalytic performance mainly due to its high amount of nitrogen and iron functional groups. In addition, the majority of its nitrogen is present in the form of highly active ORR centers (*i.e.* N-quaternary, N-pyridinic) and the iron is coordinated to nitrogen atoms in the form of Fe-N, instead of

elemental iron or iron oxides/carbides, whose contribution to the catalytic activity in the ORR process is still open to debate.^{25, 58-60} Furthermore, these active sites are atomically dispersed and well-distributed throughout the carbon particles with a high surface area and optimized morphology, with a dendritic structure and very open porosity that minimizes mass-transport limitations.^{16, 61-62} Interestingly, the sample heat-treated at an intermediate temperature of 850 °C shows the worst performance. This result can be ascribed to its lower amount of nitrogen (11 wt % for CNP-800 vs. 9.5 wt % for CNP-850) and iron functionalities (5.4 wt % for CNP-800 vs. 3.3 wt % for CNP-850), as well as its minor content of Fe-N coordination sites (see Table 2). In addition, CNP-850 has a lower electronic conductivity than CNP-900 as a result of the removal of oxygen functionalities with the increase of temperature^{2, 63} and the lower amount of quaternary-N.⁶⁴⁻⁶⁵ In order to confirm the important role of iron in the catalytic activity, we examined the electrocatalytic performance of an iron-free N-doped carbon CNP sample (850 °C). Figure S13 compares the catalytic activity of this sample with that of the Fe-N-C catalysts. Comparing the samples heat-treated at the same temperature, the iron-free CNP showed a similar onset potential to that of CNP-850. However, the Fe-doped catalyst exhibited a 30 mV higher half-wave potential and a higher limiting current density (15 %). The results show that the presence of iron enhances overall catalytic activity, decreasing the overpotential for the reaction and increasing the limiting current density.

The durability of the Fe-N-C materials was examined by means of chronoamperometric experiments in O₂-saturated 0.1 M KOH. Figure 5c shows that after 13 000 s the CNP-800 catalyst retains > 85 % of its initial current,

whereas commercial platinum is able to retain < 70 %. In 0.1 M HClO₄, the durability was assessed by performing an accelerated durability test protocol consisting of several cyclic voltammetry cycles between 0.6 V and 1 V.³⁸⁻³⁹ After 4000 cycles (see Figure 5d), CNP-800 shows slightly decreased catalytic activity, with a shift of only 40 and 60 mV in the onset and half-wave potentials, and a 4 % loss in the value of limiting current density. On the contrary, the loss in activity in the case of commercial platinum is so high that it becomes comparable to that of CNP-800. These results demonstrate the excellent stability of the Fe-N-C catalyst, superior to commercial platinum in both electrolytes.

Conclusions

In summary, we have presented the synthesis of a dendritic iron/nitrogen co-doped carbon electrocatalyst by means of a templating approach that involves the use of pyrrole as the nitrogen and carbon source, and FeCl₃ for iron doping. The resulting carbon material has high amounts of iron (~ 5 wt %) coordinated to nitrogen, and nitrogen functional groups (~ 11 wt %). This Fe-N-C catalyst exhibits a dendritic pompom-like structure and a very open porosity made up of interconnected, mesoporous, thin carbon layers with a high specific surface area (~ 500 m² g⁻¹). The combination of these structural and chemical properties gives rise to an active electrocatalyst with numerous and accessible active sites. The as-prepared Fe-N-C catalysts exhibited excellent activity in both acidic and basic electrolyte with high onset potentials (0.94 V in 0.1 M KOH and 0.75 V in 0.1 HClO₄) and high selectivity towards the preferential 4-electron process. Moreover, these Fe-N doped carbon catalysts have excellent long term stability, better than commercial platinum in both media.

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Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

SEM and TEM images of the dendritic silica particles used as template; SEM images of the Fe-N-doped carbon nano-pompoms; XRD patterns before (black trace) and after (blue trace) acid washing for the CNP-800 sample; XPS general spectra of the Fe-N-doped carbon nano-pompoms CNP-800, CNP-850 and CNP-900; TEM image of the CNP-800 sample and the line profile concentration for nitrogen and iron; Koutecky–Levich plots at different potentials for CNP-800, CNP-850 and CNP-900 electrocatalysts in 0.1 M KOH and 0.1 M HClO₄; lineal sweep voltammetries at different rotating speeds for CNP-800, CNP-850 and CNP-900 electrocatalysts in 0.1 M KOH and 0.1 M HClO₄; Koutecky-Levich plots for the Fe-N-doped carbon nano-pompoms in 0.1 M KOH (at 0.7 V) and 0.1 M HClO₄ (at 0.35 V); Cyclic voltammetries at 50 mV s⁻¹ for the Fe-N-doped carbon nano-pompoms in 0.1 M KOH and 0.1 M HClO₄ electrolytes; lineal sweep voltammetries at 1600 rpm for the carbon nano-pompoms and the iron-free carbon nano-pompoms in 0.1 M KOH.

List of Tables and Figures

Scheme 1. Schematic illustration of the synthesis procedure.

Table 1. Physico-chemical properties of the Fe-N doped carbon nano-pompoms.

Sample Code	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_p ($\text{cm}^3 \text{g}^{-1}$) ^[a]	N (wt %)	Fe (wt %)
CNP-800	480	0.57	11.0	5.4
CNP-850	520	0.62	9.5	3.3
CNP-900	430	0.54	3.5	2.6

^[a] Pore volume was determined at $p/p_0=0.90$.

Table 2. Distribution of the nitrogen functional groups in the Fe-N doped porous carbon nano-pompoms.

Sample Code	Nitrogen functional groups (%)				
	N-pyridinic	N-pyrrolic	N-quaternary	Fe-N	Pyridine-N-oxide
CNP-800	34.7	11.9	32.1	16.2	5.0
CNP-850	35.7	10.5	33.7	15.4	4.7
CNP-900	33.5	-	47.8	10.2	8.4

Figure 1. (a, b) SEM and (c, d) TEM images of the Fe-N-doped carbon nanopompoms (sample: CNP-800). The inset in (a) displays the particle size distribution.

Figure 2. (a) Nitrogen sorption isotherms, (b) pore size distributions, (c) XRD patterns and (d) XPS N 1s core level spectra of the CNP-800, CNP-850 and CNP-900 carbon samples.

Figure 3. (a) TEM image and the EDX mappings for (b) carbon, (c) nitrogen, (d) oxygen, (e) iron and (f) integration of all the elements. (Sample: CNP-800)

Figure 4. Comparison of linear sweep voltammetry at 1600 rpm in (a) 0.1 M KOH and (c) 0.1 M HClO₄ and comparison of the onset and half-wave potentials and kinetic current densities (at 0.7 V in 0.1 M KOH and 0.35 V in 0.1 M HClO₄) in (b) 0.1 M KOH and (d) 0.1 M HClO₄ for Fe-N-doped carbon nano-pompoms and Pt/C.

Figure 5. Number of electrons and peroxide yield at 1600 rpm in O₂-saturated: (a) 0.1 M KOH and (b) 0.1 M HClO₄. (c) Chronoamperometric responses at a constant rotation speed of 1600 rpm in an O₂-saturated 0.1 M KOH solution during 13500 s at 0.7 V and (d) linear sweep voltammograms at 1600 rpm in 0.1 M HClO₄ before and after 4000 voltammetry cycles for the CNP-800 and Pt/C catalysts.

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