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Ricardo Sgarbi, Kavita Kumar, Frederic Jaouen, Andrea Zitolo, Edson Ticianelli, et al.. Oxygen Reduction Reaction Mechanism and Kinetics on M-N_xC_y and M@N-C Active Sites Present in Model M-N-C Catalysts Under Alkaline and Acidic Conditions. *Journal of Solid State Electrochemistry*, 2021, 25 (1), pp.45-56. 10.1007/s10008-019-04436-w . hal-02397015

HAL Id: hal-02397015

<https://hal.science/hal-02397015>

Submitted on 6 Dec 2019

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Oxygen Reduction Reaction Mechanism and Kinetics on $M-N_xC_y$ and $M@N-C$ Active Sites Present in Model M-N-C Catalysts Under Alkaline and Acidic Conditions

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Abstract

M-N-C electrocatalysts (where M is Fe or Co) have been investigated for mitigating the dependence on noble metals when catalyzing the oxygen reduction reaction (ORR) for fuel cell technologies in acidic or alkaline conditions. Rotating disc and rotating ring-disk electrodes measurements for Fe-N-C and Co-N-C catalysts demonstrate promising performances and stability for the ORR, while the activity of main suspected active sites ($M-N_xC_y$ and $M@N-C$) has been discussed on the basis of the known physical-chemical properties of the catalysts in acid and alkaline media. Thereupon, it is observed that atomically-dispersed $Fe-N_xC_y$ sites reach the highest ORR activity in acid media when amplified by an adequate energy binding between the metallic center and the oxygenated reaction intermediates. In contrast, $Fe@N-C$ core-shell sites reach a maximum ORR mass activity in alkaline media through a synergistic effect involving catalyst particles with metallic iron in the core and nitrogen-doped carbon in the shell.

Keywords: Fe-N-C catalyst, Co-N-C catalyst, PGM-free catalysts, alkaline exchange membrane fuel cell, proton exchange membrane fuel cell.

Introduction

The oxygen reduction reaction (ORR) electrocatalysis plays a key role in the development of sustainable and clean energy technologies, particularly when related to energy storage and conversion devices. Among these devices, fuel cells that convert the chemical energy of a fuel into electricity rely on air-reducing cathodes. Depending on the choice of electrolyte, fuel cells are operated in a broad range of pH, from acidic to neutral and alkaline conditions, as represented by the proton exchange membrane (PEMFC), microbial (MFC) and alkaline exchange membrane (AEMFC) fuel cells, respectively [1, 2]. Catalysts based on platinum (Pt) and platinum-group-metals (PGM) reach high activity and selectivity for ORR to water in acidic conditions [3], in the same way as several PGM catalysts exhibit good performances for ORR, with relative tolerance to fuel contamination, in alkaline media [4]. However, the high cost and the CO poisoning of PGM-based catalysts have been pointed out as unsolved problems for the wide-scale implementation of these devices [2, 5, 6].

Two classes of PGM-free catalysts have been widely investigated focusing on eliminating PGM for the ORR electrocatalysis: i) metal-free carbon-nitrogen (N-C) composites and ii) transition metal-incorporated carbon-nitrogen matrices (referred to as M-N-C, with M = Fe or Co) [7–9]. Recently, an extraordinary expectation towards the use of M-N-C catalysts for ORR electrocatalysis has grown, due to the recent and rapid progress in the field over the past 10 years, regarding improvement in the electrocatalytic activity, power performance, tolerance to CO and, although more challenging, improvements in stability and durability as well, observed in both high and low pH conditions [10–14]. However, a better understanding of the nature and the number of the different active sites in pyrolyzed M-N-C materials and correlations with the ORR electrocatalysis at different pH values is still required for an optimized choice of such catalysts as a function of the operating conditions, in particular regarding the operating pH of the fuel cell device.

When the pH changes from acidic (PEMFC, pH~1) to alkaline (AEMFC, pH~13) conditions, the overall four-electron O₂ reduction changes from $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ to $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$, in acid and alkaline conditions, respectively, with implications on the mechanism, selectivity and intrinsic activity of different catalytic sites. The ORR mechanism can also proceed indirectly, first involving 2 electrons leading to H₂O₂ or HO₂⁻ peroxide intermediate, release ($O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ and $O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$) followed by a second sequential 2-electron transfer, whereby H₂O₂ or HO₂⁻ are reduced to H₂O or OH⁻, at

1 the same or at a different active site ($\text{H}_2\text{O}_2 + 2 \text{H}^+ + 2\text{e}^- \rightarrow 2 \text{H}_2\text{O}$ and $\text{HO}_2^- + \text{H}_2\text{O} + 2 \text{e}^- \rightarrow 3$
2 OH^-). Chemical disproportionation of H_2O_2 and HO_2^- may also be considered in both media [1,
3 15]. In addition to the different role of H^+ and OH^- species and different intermediates species
4 in the two different electrolytes, the pH difference can also modify the double layer structure,
5 resulting in different possibilities of electron-transfer mechanisms: inner- and outer-sphere [16,
6 17].
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11 Many studies have investigated the nature of the different ORR active sites in M-N-C
12 catalysts [18–20], and three main types of active sites have been proposed: N_xC_y , $\text{M-N}_x\text{C}_y$ and
13 M@N-C [7], where N_xC_y sites are nitrogen functional groups in a carbon matrix, $\text{M-N}_x\text{C}_y$ are
14 atomically-dispersed nitrogen-bonded metal centers embedded in a N-doped carbon matrix and
15 M@N-C sites are a nanoparticulated metallic centers surrounded by a N-doped carbon shell
16 (itself free of $\text{M-N}_x\text{C}_y$ sites). In tuning the intrinsic ORR activity of these structurally and
17 chemically different active sites, another important parameter is the nature of the metal (M),
18 with all works reported since the 1990's pointing to iron (Fe) and cobalt (Co) as universally
19 leading to the most active PGM-free metals, regardless of the nature of the metal-based sites,
20 $\text{M-N}_x\text{C}_y$ or M@N-C [21–23].
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31 Regarding Co-N-C catalysts, $\text{Co-N}_x\text{C}_y$ moieties have been pointed as the main active
32 centers that catalyze the ORR, either in alkaline or acidic conditions [24–26]. Meanwhile,
33 Co@N-C sites have shown ORR activity, with the N-C matrix providing protection of the
34 metallic core, that would otherwise be rapidly leached out in acidic medium [26]. Along the
35 same lines, the high ORR activity of Fe-N-C catalysts has been clearly linked to the content of
36 Fe- N_xC_y sites, especially in low pH conditions [7, 27]. However, it has been recently reported
37 that Fe-N-C catalysts containing Fe@N-C core-shell structures (without Fe- N_xC_y moieties) also
38 can exhibit good ORR activity, either in high or low pH conditions [19, 28, 29]. In summary, it
39 is well-established that optimized M-N-C catalysts can achieve high activities towards ORR
40 electrocatalysis, sometimes approaching those of PGM-based materials. However, it is still
41 unclear which are the truthful activities of $\text{M-N}_x\text{C}_y$ and M@N-C sites, when the catalysts are
42 used in different pH conditions.
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53 Herein, we study the ORR electrocatalytic activity and mechanism of two M-N-C
54 catalysts exclusively comprising metal as $\text{M-N}_x\text{C}_y$ sites (Fe or Co), two other M-N-C catalysts
55 exclusively comprising metal as M@N-C core-shell structures (Fe or Co), and one N-C baseline
56 material synthesized similarly as the other four materials but without addition of Fe or Co
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precursor under both acidic and alkaline conditions. The catalysts were characterized by transmission electron microscopy (TEM) and X-ray absorption spectroscopy (XAS). Their electrochemical activity was evaluated in acidic (0.1 mol L⁻¹ H₂SO₄) and alkaline (0.1 mol L⁻¹ NaOH) conditions using rotating ring-disk electrode (R(R)DE). This study demonstrates that changing the pH from acidic to alkaline results in a switch of the ability of Ar-pyrolized M-N_xC_y and M@N-C sites to reduce O₂; while M-N_xC_y sites (Fe-N_xC_y > Co-N_xC_y) are most active in acidic conditions, M@N-C (Fe@N-C > Co@N-C) reach a higher mass activity (powder mass) in alkaline conditions.

Experimental Section

Electrocatalysts synthesis

The electrocatalysts were synthesized using the method described by Zitolo *et al.* [24], in which the zinc(II) zeolitic imidazolate framework ZIF-8 (purchased from BASF, Basolite Z1200), metal(II) acetate (Fe or Co) and 1,10-phenanthroline were mixed via dry planetary ball milling in optimized ratio of 200 mg phenanthroline, 800 mg ZIF-8 and either 0.5 wt. % or 5.0 wt. % of metal (Fe or Co) to the overall mass of the three precursors. The dry mixed powder of the catalyst precursor was then heated under Ar flow with a ramp rate of 5 °C min⁻¹ to 1050 °C, and held at that temperature for 1 h, at which point the split-hinge oven was opened and the quartz tube and boat quenched to room temperature while still flowing Ar. The amount of Fe or Co before pyrolysis was either 0 (for N-C), 0.5 or 5.0 wt.% in relation to the total mass of metal salt, phenanthroline and ZIF-8. Due to about 2/3 mass loss of phenanthroline and ZIF-8 during the pyrolysis, the Fe or Co content after pyrolysis is *circa* three-times higher than in the catalyst precursor before pyrolysis. The catalysts are labeled as M_x, where M is Fe or Co and *x* is the wt. % metal in the catalyst precursor before pyrolysis, either 0.5 or 5.0. As a benchmark catalyst, Pt nanoparticles (40 wt.%) supported on graphitized carbon (TEC10EA40E) was utilized, purchased from Tanaka Kikinzoku Kogyo (TKK).

Preparation of inks and layers

Inks for the formation of PGM-free catalyst layers were prepared by dispersing the catalytic powders (10 mg) with a 5 wt.% Nafion solution (50 µL, Sigma-Aldrich), isopropanol (854 µL, Carl Roth) and ultrapure water (372 µL, Millipore, 18.2 MΩ cm), followed by ultrasonic homogenization, as described by Kumar *et al.* [30]. For the benchmark catalyst, the

1 ink was prepared in a similar way, consisting of Pt/C powder (5 mg), 5 wt.% Nafion solution
2 (54 μL), isopropanol (1446 μL) and ultrapure water (3600 μL). Then, the desired aliquot of
3 each prepared ink was dropped onto glassy carbon disc substrate of the RDE or RRDE (0.196
4 cm^2 for both), followed by drying with hot air under controlled rotation speed. The total
5 loadings were in the range of 0.1 to 0.8 mg cm^{-2} for PGM-free catalysts and 20 $\mu\text{g}_{\text{Pt/C}} \text{cm}^{-2}$ (on
6 RDE) or 10 $\mu\text{g}_{\text{Pt/C}} \text{cm}^{-2}$ (on RRDE) for the Pt/C benchmark catalyst.
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10 11 **Electrochemical measurements**

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14 Before any electrochemical experiment, the glassware, polytetrafluoroethylene (PTFE)-
15 based materials and electrodes were cleaned with a 50% v/v solution of H_2SO_4 (Merck,
16 Suprapur 96 wt.%) / H_2O_2 (Carl Roth, 30% w/w) followed by rinsing in ultrapure water (MQ
17 grade, 18.2 $\text{M}\Omega \text{ cm}$, 1–3 ppm TOC) and hot ultrapure water. All glassy carbon discs were
18 polished with 3 and 1 microns diamond polishing paste (Presi). Fresh Ar-saturated electrolytes
19 were prepared from NaOH (Alfa Aesar, 50% w/w aq. soln.), H_2SO_4 and ultrapure water to
20 obtain an electrolyte concentration of 0.1 mol L^{-1} .
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28 The electrochemical measurements were performed using three-electrode
29 electrochemical cells with the temperature controlled at 25 $^\circ\text{C}$. A glass cell was used for acid
30 medium and PTFE cell for alkaline medium. A commercial reversible hydrogen electrode
31 (RHE, Gaskatel GmbH) coupled to the cell by Luggin capillary was used as the reference
32 electrode. To filter the high-frequency electrical noise, a Pt-wire immersed in the electrolyte
33 was connected to the reference electrode. In each electrolyte, the counter electrode was a carbon
34 sheet and the working electrode was glassy carbon coated with the investigated catalyst, with
35 loading varying depending whether RDE or RRDE measurements were performed, as described
36 below.
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45 RRDE or RDE measurements were performed with Autolab PGSTAT302N and
46 PGSTAT12 potentiostat, respectively. For RDE measurements, a homemade glassy carbon
47 cylinder (glassy carbon Sigradur[®] from Hochttemperatur-Werkstoffe GmbH) embedded in a
48 PTFE cylinder, coupled to a commercial system for controlling the rotation rate (Orignalys), was
49 utilized as the working electrode. For RRDE measurements, a Pt-ring and a glassy carbon disc
50 tip (Pine Research) embedded in a PTFE rod was used.
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57 For both RDE and RRDE measurements, electrochemical break-in of the thin-film
58 electrodes was performed by applying 50 cyclic voltammograms (CVs) between 0.0 and 1.0 V
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1 vs. RHE at 100 mV s⁻¹ in Ar-saturated 0.1 mol L⁻¹ H₂SO₄ or 0.1 mol L⁻¹ NaOH. Then, the CVs
 2 of the thin films were recorded in the same conditions at 10 and 5 mV s⁻¹. The ORR polarization
 3 curves were recorded at 5 mV s⁻¹ in O₂-saturated electrolyte at 1600 rpm. All measurements
 4 were dynamically corrected from Ohmic drop.
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7 The kinetic current density for ORR (*i_k*) was determined according to Koutecky Levich
 8 (Equation 1):
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$$10 \quad i_k = -\frac{(i_L \cdot i)}{(i_L - i)} \quad (1)$$

11 where *i_L* is the oxygen-diffusion limited current density at 0.2 V and *i* is the Faradaic current
 12 after Ohmic drop correction and capacitive current subtraction.
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16 Consequently, the mass activity (*i_{MA}*) was calculated using the equation below:
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$$20 \quad i_{MA} = \frac{i_k}{m} \quad (2)$$

21 where *m* is the catalyst loading on the glassy carbon electrode.
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25 For RRDE measurements, the same initial steps as described for RDE measurements
 26 were followed. Additionally, the catalyst loading was 0.1 mg cm⁻² except for the Pt catalyst for
 27 which 10 μg_{Pt} cm⁻² was utilized. To detect H₂O₂ or HO₂⁻ produced during ORR, the Pt-ring was
 28 polarized at 1.2 V vs. RHE. The peroxide quantification further requires the value of the
 29 collection efficiency (*N*), which was determined experimentally using the Fe³⁺/Fe²⁺ redox
 30 couple from K₃Fe(CN)₆ salt, as described before [31]. The experimental value was found to be
 31 *N* = 0.24. The equations below was utilized for determining the number of electrons transferred
 32 along the ORR (*n_{e-}*, Equation 3) and the peroxide percentage (Equation 4):
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$$44 \quad n_{e-} = \frac{4i_d}{i_d + (\frac{i_r}{N})} \quad (3)$$

$$45 \quad \%H_2O_2 \text{ or } \%HO_2^- = \frac{2\frac{i_r}{N}}{(\frac{i_r}{N}) + i_d} \times 100 \quad (4)$$

46 where *i_d* and *i_r* are the currents at the disk and Pt-ring, respectively.
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53 Physicochemical characterizations

1 TEM images of the electrocatalysts were recorded using a JEOL 2010 TEM instrument
2 operated at 200 kV with a point-to-point resolution of 0.19 nm. Acquisition of Co and Fe K-
3 edge X-ray absorption spectra were made at room temperature, in transmission mode at
4 SAMBA beamline of the Synchrotron SOLEIL (Gif-sur-Yvette, France), with a focusing
5 Si(220) monochromator. Pellets were prepared by mixing an adequate catalyst amount with
6 PTFE powder so as to get an optimal absorption signal. The Athena software was employed for
7 XAS data analysis, comprising the XANES (X-ray absorption near edge structure) spectra and
8 the Fourier Transforms of the EXAFS (Extended X-ray absorption fine structures) signals [32].
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18 **Results and discussion**

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21 Detailed physicochemical characterization of the catalysts using XAS, Raman and ^{57}Fe
22 Mössbauer Spectroscopy, TEM, X-EDS and XRD analyses [30, 33] have been presented in
23 previous studies published by Zitolo *et al.* [33] and Kumar *et al.* [30]. In brief, the important
24 observations previously reported are that the catalysts with 5 wt. % metal contents ($M_{5.0}$)
25 comprise metallic or metal carbide nanoparticles surrounded by a shell of N-doped graphitic
26 carbon (here referred to as M@N-C), while catalysts with low metal content ($M_{0.5}$) comprise
27 metal cations that are atomically dispersed in the N-doped carbon matrix and coordinated by
28 nitrogen atoms (here referred to as M-N_xC_y). Moreover, metal-based particles in the Fe_{5.0} and
29 Co_{5.0} catalysts were found to be exclusively Fe₃C and metallic Co, respectively. Other important
30 findings are related to the presence of more graphitic carbon structure in the neighborhood of
31 the metal-based nanoparticles for $M_{5.0}$ catalysts, as well as the presence of smaller graphite
32 crystallites in $M_{0.5}$.
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44 Fig. 1 displays physicochemical characterizations of Fe_{0.5}, Fe_{5.0}, Co_{0.5} and Co_{5.0}. TEM
45 images shown in Fig. 1a-d evidence that the synthesized catalysts exhibit two different carbon
46 nanostructures: stacked graphitic layers (mainly for Fe_{5.0} and Co_{5.0}) and sheet-like layers with
47 poorly structured carbon, for both metals contents. This indicates that the initial highly
48 structured and organized ZIF-8 carbon and nitrogen precursor was significantly modified
49 during pyrolysis. As reported previously [26, 29], these results confirm that the catalysts present
50 particular characteristics denoting the existence of two distinct zones: i) in one case, the
51 presence of segregated metallic-based nanoparticles (10-100 nm) is seen, as confirmed by the
52 dark spots in the images of the higher metal load materials (Fe_{5.0} and Co_{5.0}) and ii) a zone
53 containing the metals atomically dispersed over the carbon-nitrogen matrix (Fe_{0.5} and Co_{0.5}).
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Fig. 1e and 1f show XANES spectra for both types of catalysts at the Fe (energy = 7112 eV) and Co (energy = 7709 eV) K-edges, respectively, where reference spectra for Fe and Co foils and Fe₃C, were included for comparison. The high similarities between the XANES signals obtained for Fe_{5.0} and Co_{5.0} with those shown for Fe₃C and metallic Co foils, respectively, clearly indicate that the black spots in Fig. 1b and 1d for these samples are essentially zero-valent Fe and Co species [30]. In the cases of Fe_{0.5} and Co_{0.5}, the shift toward higher energy of the edge with respect to that of the metal foil and the large hump peaking at *ca.* 20 eV above the energy of the metal edge is unequivocally evidencing that the Co and Fe atoms are present in oxidized states [24, 30, 33].

Fig. 1 Physical and chemical properties of metal-N_xC_y and metal@N-C catalysts. **a-d** representative transmission electron microscopy images and **e, f** XANES and **g, h** Fourier transforms of the EXAFS spectra measured at Co or Fe K-edge. Adapted from Ref. [30] with permission from The American Chemical Society.

Fourier transforms of the EXAFS signals, either for the samples as well as for the metallic standards, are shown in Fig. 1g and 1h. First, it should be noted that the *x*-axis positions of the several peaks are related to the distance between the X-ray absorbing metal atoms and neighboring atoms present in the different coordination shells surrounding the element under investigation. However, the radial distances do not exactly correspond to the atomic distances, since a phase shift correction must be applied to precisely estimate the interatomic distance and this correction depends on the nature of the backscattering elements [33]. Here, in the case of the Fe-containing materials (Fig. 1g), the presence of the Fe-Fe coordination (peak next to 2.1-2.2 Å) is only detected for Fe_{5.0}, as concluded from comparisons with the features of the Fe₃C [34] and results reported by Zitolo *et al.* [33]. In this case, a weak shoulder is also observed at radial distance near to 1.6-1.7 Å, and this may be related to the existence of some Fe-C or Fe-N interatomic distances in the second coordination sphere, possibly assigned to Fe-C interatomic distance in Fe₃C or to Fe-C interatomic distance from a small amount of Fe-N_xC_y moieties. However, ⁵⁷Fe Mössbauer transmission spectra for the same material (catalyst named as Fe_{5.0}RP in that work) performed in our former work [30] revealed the presence of only one sextet component with Mössbauer parameters exactly matching those of Fe₃C. The ⁵⁷Fe Mössbauer spectra confirmed the conclusions drawn from XANES and EXAFS signals, and,

1 thus it may be concluded that Fe_{5.0} does not contain Fe-N bonds from Fe-N_xC_y moieties. This is
2 also in line with the absence of EXAFS signal for Fe_{5.0} at a radial distance of *ca* 1.0 Å, typical
3 for Fe-N distance in FeN_xC_y moieties. For the Fe_{0.5} material, the main peak located at 1.4 Å and
4 the less intense peak at 2.4 Å might be assigned to Fe-N and Fe-C backscatterings, respectively
5 [33]. It should be also noted that the signals for more distant shells are only clearly observed
6 for the Fe foil, indicating the absence of long-distance ordered coordination shells in Fe-
7 containing samples, particularly for Fe_{0.5}. This observation is in agreement with usual
8 propositions that, for these kind of systems, metal species are atomically dispersed in the
9 carbon-nitrogen matrix for Fe_{0.5} and, mainly as Fe₃C for Fe_{5.0}. Finally, the EXAFS of the Co-
10 based catalysts evidence two main differences with respect to the Fe-based catalysts: (i) in the
11 case of Co_{5.0}, the Co-Co coordination extends to much longer shells resembling that of the Co
12 foil, confirming that metallic Co is present as a principal species; (ii) in the case of Co_{0.5}, the
13 XANES is similar to that of Fe_{0.5} and calculations of XANES spectra for different model sites
14 showed that a good match could be obtained with either porphyrinic (CoN₄C₁₂) or defective
15 porphyrinic structures (*e.g.* CoN₃C₁₀) [24].
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28 Fig. 2a and 2b show Ohmic-drop corrected CVs for all four catalysts at a fixed loading
29 in the thin-film electrode in acid and alkaline electrolytes, respectively. Results for a Fe- and
30 Co-free N-doped carbon prepared otherwise similarly (labelled M₀) are included for
31 comparison. For the M_{5.0} and M₀ catalysts and either in acid or alkaline electrolytes, the CV
32 features are those typically found for large capacitance systems, so that the currents are mostly
33 related to charge accumulation in the double layer (non-faradic and non-redox process) at the
34 catalyst | electrolyte interface. This general trend differs in the case of Fe_{0.5} in acid medium, for
35 which a redox pair, consistent with the Fe³⁺/Fe²⁺ couple, is apparent at *ca.* 0.7 V *vs.* RHE.
36 Results in Fig. 2a also show that the CV profiles exhibit similar current intensities, except for
37 the Fe_{0.5} catalyst, for which the intensities are unequivocally higher than the others, which we
38 relate to a larger carbon specific surface area [30], and/or features associated to the presence of
39 surface defects, as compared to the other cases. Another aspect is that Co_{0.5} has a larger surface
40 area than Fe_{0.5} [30], yet results in a CV that is distinct from that of Fe_{0.5} and more similar to
41 those of the other catalysts with lower BET area. This may be explained by the presence of too
42 narrow micropores in this case, which do not effectively contribute to the charge accumulation
43 in the double layer, and/or to the more organized structure of the carbon phase, leading to a
44 lower content of surface groups (N or O) and thereby decreased capacitive currents [35]. The
45 absence of redox peak assigned to Co cations in Co_{0.5} is explained by the fact that the Co²⁺/Co³⁺
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1 redox in a similar Co-N-C catalyst (flash pyrolyzed) was found at potentials well above the
2 upper limit of the CVs presented here [24]. However, we noticed anodic current at high potential
3 values for Co_{5.0} in alkaline electrolyte, which indicates that Co nanoparticles are progressively
4 covered by a thin passivating layer of Co(OH)₂ followed by the oxidation of Co(OH)₂ to Co₂O₃
5 and CoOOH species, in agreement with the literature [36, 37]. Finally, the absence of Fe redox
6 features for the Fe_{5.0} catalyst in acidic conditions is consistent with previous results showing
7 that in this case all Fe is present as encapsulated metal carbide nanoparticles [30]. This implies
8 that these species, even when present in the catalyst, have no direct contact with the electrolyte.
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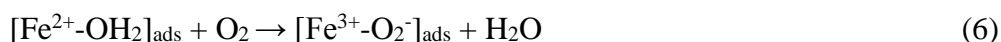
18 **Fig. 2** Electrochemical properties of Fe-N-C and Co-N-C catalysts in alkaline and acid media.
19 CVs in Ar-saturated electrolyte 0.1 mol L⁻¹ **a** H₂SO₄ and **b** NaOH at 10 mV s⁻¹; ORR
20 polarization curves in O₂-saturated electrolyte 0.1 mol L⁻¹ **c** H₂SO₄ and **d** NaOH at 5 mV s⁻¹ and
21 1600 rpm. For all measurements: 0.8 mg_{powder} cm⁻² and 25 °C. For comparison, Pt/C (20 μg_{Pt/C}
22 cm⁻²) and M₀ (N-C without Fe or Co) catalysts were utilized. Measurements were repeated at
23 least three times leading to the same results (all results and errors are tabulated in Supporting
24 Information).
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34 Polarization curves for the ORR were constructed by subtracting the capacitive currents
35 of CV (at 5 mV s⁻¹) in Ar-saturated electrolytes from those related to the ORR, and employed
36 to evaluate the ORR activity of the catalysts (M₀, M_{0.5} and M_{5.0}). These results are shown in
37 Fig. 2c and 2d, for the acid and alkaline electrolytes, respectively, while results obtained for a
38 Pt/C catalyst were included for comparison. Generally, results show that all onset potentials are
39 higher for Fe-N-C than for Co-N-C catalysts, denoting the higher activity of Fe-N-C materials
40 for the ORR electrocatalysis. Following previous descriptors for the ORR activity on M-N-C
41 catalysts, these differences in activity can be discussed in terms of the possibility that the
42 reaction may occur involving inner- and outer-sphere electron transfer processes in alkaline
43 media [16, 17], and also in terms of the binding energy of O₂ on M²⁺ active metal species in
44 acid media [21], as detailed below.
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55 In alkaline conditions, both outer- and inner-sphere electron transfer processes can co-
56 exist in the same electrocatalyst at different potentials [16, 17]. At more positive potentials (>
57 0.8 V vs. RHE), the outer-sphere electron transfer is essentially inoperant and the reaction can
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occurs by the direct adsorption of desolvated O₂ on the active sites, thus following the inner-sphere electron transfer [17]. In this case, the onset potential for the ORR is dependent on the binding energy between O₂ and the active metallic center (M²⁺), which in turn is directly related to the M³⁺/M²⁺ redox potential [17, 18, 21, 38]. Based on the fact that the redox potential of Co³⁺/Co²⁺ ($E^{\circ} = 1.92$ V) is much higher than that of Fe³⁺/Fe²⁺ ($E^{\circ} = 0.77$ V) [39], the O₂ molecule adsorbs much weakly and/or to a lesser extent on Co²⁺, and in this way, the ORR onset potential for Co-N-C would be smaller than for Fe-N-C catalysts, as observed in Fig. 2d. In acidic conditions, inner-sphere electron transfer is the only possibility for the ORR electrocatalysis [16, 17]. Therefore, the causes of the differences in the ORR onset potentials on different metallic centers is explained similarly to the alkaline medium.

Fig. 2c shows that in acidic conditions, Fe_{0.5} reaches the highest onset potential among all catalysts (0.92 ± 0.01 V), being only 0.04 V smaller than that of Pt/C (see details in Supporting Information). The behavior of this catalyst confirms the high importance of having atomically dispersed Fe-N_xC_y active sites for allowing the occurrence of the Fe³⁺/Fe²⁺ oxidation process, as detected by CV. This couple seems to be the cause of the enhanced ORR electrocatalysis [40, 41] compared to the other catalysts. As already discussed in the literature [5, 17, 21], the active sites first generate Fe²⁺ from the reduction of Fe³⁺ (Equation 5), which next promotes the displacement of adsorbed H₂O by O₂, accompanied by an electron transfer of Fe²⁺ to O₂ (Equation 6); the [Fe³⁺-OH]⁻_{ads} species would be regenerated in the following reaction step, so that the process becomes cyclically repeated:



In acid media, other studies have shown that the onset potential for the ORR is directly related to the redox potential of the metal in the M-N_xC_y sites [17, 21, 28]. Here, such a redox process was only evident for Fe_{0.5}; it was not seen for Fe_{5.0} because in this case the only catalyst metal phase is formed by Fe₃C particles surrounded by a nitrogen-carbon shell (Fe@N-C). Finally, in the case of the Co-N-C catalysts in acid media, although results in Fig. 1 show that Co_{0.5} presents the same atomic distribution as Fe_{0.5}, the corresponding CV does not evidence the occurrence of redox processes. This is because the presence of redox features of Co only appears at potentials well above the onset of the ORR, as is the case of Co³⁺/Co²⁺. From the results in Fig. 2c, it is seen that the activity of the Co-N-C catalysts for the ORR is in fact not

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2 so much superior to that of M_0 , which demonstrates the smaller role of $Co-N_xC_y$ and $Co@N-C$
3 for the promotion of the ORR electrocatalysis.

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5 In alkaline medium, for the Fe-N-C catalysts (Fig. 2d), results show that the ORR onset
6 potentials are very close (or equal, in the case of $Fe_{5.0}$) to that of Pt/C (0.97 ± 0.01 V), that is,
7 0.97 ± 0.01 V for $Fe_{5.0}$ and 0.95 ± 0.01 V for $Fe_{0.5}$. This high catalytic activity of $Fe_{5.0}$ evidences
8 that in this medium, the Fe@N-C sites are active for the ORR, in contrast to the acid medium.
9 Although substantially smaller than those of the Fe-N-C materials, the same catalytic
10 phenomena are seen for the $Co@N-C$ and $Co-N_xC_y$ materials, for which the values of onset
11 potential are 0.84 ± 0.01 V and 0.82 ± 0.01 V, respectively. In fact, a similar enhancement of
12 catalytic activity is also seen in the absence of metallic centers (M_0). The higher activity of the
13 Fe@N-C active sites in alkaline medium can be assigned to the enhancement of electrical
14 conductivity of nitrogen-carbon and a synergistic effect between the metallic centers and the
15 nitrogen-carbon shell. This is in line with recent results demonstrating that a higher degree of
16 graphitization of carbon is beneficial to the electrical conductivity [42], and that synergies
17 between the nitrogen-carbon shell and metallic centers contribute to efficient ORR
18 electrocatalysis [19, 28, 43–46].

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20 Another aspect to be discussed is the cause of the positive shift on the onset potential
21 when the pH is changed from low to high values. This fact may be related to the OH_{ads} coverage
22 and its desorption to regenerate the active metallic center M^{2+} [5, 18, 21]. Thus, a higher
23 concentration of OH^- species in the electrolyte (alkaline media) seems to favor high coverages
24 of OH_{ads} . In contrast, the effective OH_{ads} coverage in acidic conditions requires more energy
25 due to the much smaller OH^- availability to generate and regenerate the M^{2+} active center, as
26 shown above (Equations 5-6); also Fe^{3+} species can be poisoned by strong adsorption of H_2O ,
27 blocking the generation of Fe^{2+} species active for ORR [47].

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29 Interestingly, the change in pH from acid to alkaline leads to a lower increase of the
30 onset (half-wave) potentials by 30 mV (30 mV) for $Fe_{0.5}$ and 100 mV (70 mV) for $Fe_{5.0}$. This
31 indicates that the activity of the Fe- N_xC_y sites in the present case is little affected by the pH, so
32 that the $Fe_{0.5}$ catalyst can promote the ORR electrocatalysis with similar efficiency, either at
33 high or low H^+/OH^- concentrations. In contrast, results for Fe@N-C sites denote larger
34 variations of onset/half-wave potentials, but the shift is smaller in the case of the half-wave
35 potential, possibly indicating some occurrence of inner- and outer-sphere electron transfer
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1 mechanisms in alkaline medium, depending on the electrode potential. These behaviors were
2 not found in Co-N-C catalysts, and, then this feature is exclusively related to Fe-N-C catalysts.
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4 For the investigation of PGM-free catalyst loading effects on the mass activity for ORR
5 electrocatalysis was selected the Fe_{0.5} catalyst in both pH conditions. Then, that catalyst loading
6 effect was evaluated for Fe_{0.5} in the range of 0.1 to 0.8 mg_{powder} cm⁻² in 0.1 mol L⁻¹ H₂SO₄ and
7 0.1 mol L⁻¹ NaOH electrolytes, and the results are shown in Fig. 3. CV profiles in Fig. 3a and
8 3b exhibit the expected proportional increase of the capacitive currents from low to high catalyst
9 loadings in both pH conditions. For example, at 0.4 V, the capacitive currents increase linearly
10 with the catalyst loading (see Fig. 1 – Supporting Information). This is mainly caused by the
11 increase in the electrochemically available area, which is more pronounced in acidic conditions
12 due to some contributions of currents related to redox processes of Fe³⁺/Fe²⁺ and of oxygen
13 functional groups present in the carbon matrix. As described in the literature [48], the oxidative
14 process of carbon causes changes in the magnitude of the capacitive current at low pHs, while
15 in alkaline media the graphitic structures are less functionalized because they become
16 hydrophilic enough for releasing some carbon functional groups.
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31 **Fig. 3** Electrochemical properties of different Fe_{0.5} catalyst loadings. CVs in Ar-saturated
32 electrolyte 0.1 mol L⁻¹ **a** H₂SO₄ and **b** NaOH at 10 mV s⁻¹; ORR polarization curves in O₂-
33 saturated electrolyte 0.1 mol L⁻¹ **c** H₂SO₄ and **d** NaOH at 5 mV s⁻¹ and 1600 rpm. All
34 measurements were performed at 25 °C. Measurements were repeated at least three times
35 leading to the same results (all results and errors are tabulated in Supporting Information).
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42 In Fig. 3c and 3d, the results evidence a displacement of the ORR onset and half-wave
43 potentials to higher values and increased oxygen diffusion limited current densities (in the range
44 of 0.0 V to 0.55 V) with the increase of the catalyst loading, with the effects being higher in the
45 acid medium. This increase in the oxygen diffusion limited current densities with the increase
46 of the catalyst loading is probably related to the increased residence time of
47 reactant/intermediate species [49, 50], like OH⁻, O₂, H₂O₂ or HO₂⁻ inside the catalyst layer,
48 enhancing their further reduction to complete the 4-electron process. Moreover, a sufficient
49 number of active sites is necessary to catalyze the ORR efficiently [49, 50], otherwise no
50 oxygen diffusion limited currents appear, which in acid media, seems to be the case for loadings
51 ≤ 0.2 mg_{powder} cm⁻². In alkaline electrolytes, this effect may be minimized by the electrostatic
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2 interaction of anionic HO_2^- species with the Fe^{2+} cation from $\text{Fe-N}_x\text{C}_y$ active sites [16, 17, 40],
3 thus driving the ORR to OH^- even in thin catalyst layers (as also observed in Fig. 4) [51].
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7 **Fig. 4** RRDE measurements of Fe-N-C and Co-N-C catalysts. Peroxide percentage produced
8 from ORR electrocatalysis in O_2 -saturated electrolyte 0.1 mol L^{-1} **a** H_2SO_4 and **b** NaOH at 5
9 mV s^{-1} and 1600 rpm. For all measurements: $0.1 \text{ mg}_{\text{powder}} \text{ cm}^{-2}$ and $25 \text{ }^\circ\text{C}$. For comparison, Pt/C
10 ($10 \text{ } \mu\text{g}_{\text{Pt/C}} \text{ cm}^{-2}$) and M_0 (without Fe or Co) catalysts were utilized (all results are tabulated in
11 Supporting Information).
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20 The oxygen diffusion limited currents for the M-N-C catalysts are all smaller than that
21 observed for Pt/C (Fig. 2c and 2d), that is known to lead to a predominant 4-electron ORR
22 mechanism (O_2 is mostly reduced to H_2O in acid or OH^- in alkaline electrolytes). To discuss
23 these issues, the percentages of $\text{H}_2\text{O}_2/\text{HO}_2^-$ formation and the number of electrons involved in
24 the ORR were obtained from rotating ring-disk measurements and these results are shown in
25 Fig. 4. Generally speaking, the n_{e^-} values for the M-N-C catalysts, and more specifically Fe-N-
26 C, are not so different from that of Pt/C, either in acid or alkaline media, but this is more evident
27 in the alkaline medium (see Tables 1-2 – Supporting Information). Results related to the
28 $\text{H}_2\text{O}_2/\text{HO}_2^-$ formation are consistent with the above observations related to the number of
29 transferred electrons in the ORR, as would be expected because the same data and principles
30 are used in the calculations of n_{e^-} and $\% \text{H}_2\text{O}_2/\text{HO}_2^-$. These aspects regarding the number of
31 electrons/percentages of $\text{H}_2\text{O}_2/\text{HO}_2^-$ formation confirm that in the alkaline medium $\text{Fe-N}_x\text{C}_y$
32 and Fe@N-C sites perform the reaction involving similar pathways and provide additional
33 evidence that the Fe@N-C sites stabilize the HO_2^- intermediate as efficiently as $\text{Fe-N}_x\text{C}_y$.
34 Therefore, synergistic effects in the Fe@N-C catalyst can provide an adequate energy binding
35 between HO_2^- and the nitrogen-carbon shell, even without the direct contact between the Fe
36 metallic center and the reactants or intermediates. In the cases of the Co-N-C materials, inferior
37 n_{e^-} values regularly ranging from 3 to 2 are observed in Fig. 4 and Tables 1-2 (Supporting
38 Information).
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56 Adequate adsorption energies of oxygenated intermediates species has been pointed to
57 be essential for achieving high n_{e^-} values in the ORR, and in this sense the anionic HO_2^- species
58 formed along the ORR in alkaline conditions seems to be more strongly bound to the catalyst
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1 compared to the H_2O_2 species in acidic media, ensuring larger occurrence of the complete ORR
2 electrocatalysis to OH^- . However, the higher amounts of $\text{H}_2\text{O}_2/\text{HO}_2^-$ detected by the ring for the
3 Co-catalysts, compared to the Fe-catalysts, may mean that the binding energies of $\text{H}_2\text{O}_2/\text{HO}_2^-$
4 on Co- N_xC_y sites are small [21, 24, 52], as it would be also expected for the Co@N-C sites. In
5 fact, trends observed here regarding the onset potentials, oxygen diffusion-limited currents, and
6 number of electrons transferred in the ORR were similar to those observed in other studies of
7 the ORR electrocatalysis in other Fe-N-C and Co-N-C catalysts [24, 53–55].

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13 Further information about the reaction mechanism was obtained from Tafel plots
14 constructed in the high-potential region of the ORR polarization curves and expressed in terms
15 of the mass activity of the catalysts (i_{MA}), calculated as described in the experimental section.
16 Results are shown in Fig. 5. The slopes of the resulting lines (Tafel slopes) were calculated, and
17 the values are summarized in Table S1 and Table S2 (see Supporting Information). First, it is
18 noted that $\text{Fe}_{0.5}$ and $\text{Fe}_{5.0}$ exhibit higher Tafel slopes as compared to $\text{Co}_{0.5}$ and $\text{Co}_{5.0}$ in both
19 media (Fig. 5a and 5b), and this is consistent with the occurrence of distinct ORR mechanisms
20 and/or rate-determining steps in the two class of investigated materials. This observation is
21 similar to those reported in published works when comparing Fe- vs. Co-based catalysts [22,
22 24, 53, 56].

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33 The Tafel slopes for $\text{Fe}_{0.5}$ and $\text{Fe}_{5.0}$ catalysts are essentially the same in acid or alkaline
34 media, demonstrating that the rate determining step of the ORR mechanism may be the same
35 in both cases, although involving different active sites and for $\text{Fe}_{0.5}$ in acid medium
36 corresponding to a direct redox-mediated process. This implies that the different ORR activities
37 seen for $\text{Fe}_{0.5}$ and $\text{Fe}_{5.0}$ in acid media (as evidenced for the different reaction overpotentials at a
38 given mass activity) may be related to the different catalyst specific active areas and/or different
39 synergistic phenomena related to the different nature of the active centers. In alkaline media,
40 since no redox features are detected but the activities are also close, one may conclude that the
41 rate determining step, the ORR mechanism and eventually the specific active area are very
42 similar for both catalysts. Finally, the results evidence the absence of mass-transport and
43 conductivity problems related to the thickness/structure of catalytic layers, so that the
44 magnitude of Tafel slopes is only related to the ORR mechanism [57].

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58 **Fig. 5** Mass-transport-corrected Tafel plots of Fe-N-C and Co-N-C catalysts at fixed loading,
59 and for $\text{Fe}_{0.5}$ on different catalyst loadings. Performed in O_2 -saturated electrolyte 0.1 mol L^{-1} **a**,

1 **c** H₂SO₄ and **b, d** NaOH at 5 mV s⁻¹, 1600 rpm and 25 °C. For **a, b** measurements: 0.8 mg_{powder}
2 cm⁻², Pt/C (10 μg_{Pt/C} cm⁻²) and M₀ (without Fe or Co) catalysts were utilized. Measurements
3 were repeated at least three times leading to the same results (all results and errors are tabulated
4 in Supporting Information). In **c, d** panels, different Fe_{0.5} loadings were used.
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10 For easier comparisons of the mass activity towards the ORR of materials, the
11 previously calculated values at 0.85 V were plotted for each set of catalyst in both
12 electrolytes (Fig. 6). Analyzing the results in acidic conditions (Fig. 6a), it is concluded that
13 among all M-N-C catalysts, Fe_{0.5} presents the highest mass activity for the ORR, followed by
14 Fe_{5.0}, Co_{0.5} and Co_{5.0}, as shown in Fig. 5a and 6a. This superior activity of Fe_{0.5} compared to
15 that of Fe_{5.0} indicates a superior activity of Fe-N_xC_y sites compared to Fe@N-C; this trend is
16 maintained for Co_{0.5} with respect to Co_{5.0}. Therefore, we conclude that M-N_xC_y sites provide
17 higher mass activity than M@N-C in acid conditions.
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29 **Fig. 6** Mass activity towards the ORR (*i*_{MA}) measured at 0.85 V for **a** all catalysts investigated
30 in this study and **b** for different Fe_{0.5} catalyst loadings. All ORR experiments conducted at 1600
31 rpm, 5 mV s⁻¹, 25 °C in O₂-saturated 0.1 mol L⁻¹ (**red**) H₂SO₄ or (**blue**) NaOH electrolytes.
32 Catalyst loadings of 0.8 mg_{powder} cm⁻² were employed in **a**. Measurements were repeated at least
33 three times leading to the same results (all results and errors are tabulated in Supporting
34 Information).
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44 In alkaline solution, results show that Fe_{5.0} presents the highest mass activity for the
45 ORR, followed by Fe_{0.5}, Co_{5.0}, and Co_{0.5}. Therefore, generally speaking, it is seen that a high
46 number of M@N-C sites (present in the catalysts with high metal content) can provide higher
47 mass activity in alkaline medium as compared to a low number of M-N_xC_y sites, that is
48 predominant in catalysts with low metal content. These results show that, in alkaline media, the
49 presence of atomically-dispersed M-N_xC_y sites is not mandatory for the promotion of the ORR
50 electrocatalysis with good efficiency. However, this mass activity distinction for materials
51 containing M@N-C and M-N_xC_y sites seems to be evident only for Ar-pyrolyzed catalysts (or
52 another inert gas). Indeed, recently, Santori *et al.*[58] have shown that other factors can lead to
53 increased mass activity when switching from Ar- to NH₃-treated catalysts containing
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atomically-dispersed Fe-N_xC_y sites. Further, another important aspect is that the catalyst without a metallic center (M₀) resulted in the poorest mass activity towards the ORR, stressing the crucial importance of having the metallic M@N-C or M-N_xC_y active sites for catalyzing the ORR, particularly in the case of iron. This is in agreement with the observation above reported, confirming that synergistic effects between the M²⁺ active metallic center and nitrogen-carbon shell (M@N-C) enhance the ORR mass activity, more than M-N_xC_y sites in high OH⁻ concentrations. Previous experimental studies provide support for the high activities found for Fe@N-C sites in alkaline media [10, 28, 44, 46, 59–61].

Fig. 6b allows discussing the mass activity as a function of the Fe_{0.5} catalyst loading for the two pH conditions. It is first noted that the mass activities are higher in alkaline than in acid media (except for 0.8 mg_{powder} cm⁻²), following the same trends found in Fig. 6a. Also, it is noted that there is an increase of the ORR mass activity with increased catalyst loading in acidic conditions, while the opposite occurs in alkaline media. These results confirm the need of longer residence time of reactants and/or intermediates inside the catalyst layer, as well as of the amount of Fe-N_xC_y sites in acid medium, while this is not the case in alkaline medium. These results have strong implications for the design of PGM-free catalysts layers in the cathodes of PEMFC and AEMFC.

Conclusions

In conclusion, we investigated the pH-effect towards ORR electrocatalytic activities using a library of M-N-C catalysts featuring either M-N_xC_y or M@N-C active sites. The change in the pH of the electrolyte resulted in a switch of the ability of the active sites to reduce O₂, however, the higher performance for Fe-N-C compared with Co-N-C catalysts was maintained. Therefore, we reported there are two factors that alter the ORR activity: i) the nature of the metallic center and ii) the nature of the active sites. It is found that M-N_xC_y sites are more active when the ORR is performed in acidic conditions. For the most active center (Fe-N_xC_y), this property was assigned to the formation of Fe²⁺ from Fe³⁺/Fe²⁺ redox couple in direct contact with the electrolyte, reactants, OH_{ads} and intermediates due to their adequate energy binding with the surface. Conversely, M@N-C present better performances for ORR electrocatalysis in the alkaline conditions when normalized by powder mass. Fe@N-C led to the highest activity for Ar-pyrolyzed catalysts, displaying an effective synergistic effect between the iron as a metallic core with the nitrogen-carbon shells. It is emphasized that the indirect contact of the

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metallic center with surface hydroxyl and other intermediates drives the ORR electrocatalysis more effectively. Finally, Fe@N-C stabilizes HO₂⁻ intermediates adequately resulting in predominance of 4-electron transfer per oxygen molecule.

Acknowledgments

The authors thank the French National Research Agency through the CAT2CAT and ANIMA projects (Grant No. ANR-16-CE05-0007-03), the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), Brazil (process number: 1614344), CAPES/COFECUB program (process numbers: 88887-187755/2018-00 and Ph-C 914/18) and the São Paulo State Research Foundation (FAPESP – process number: 2013/16930-7) for financial supports. The Synchrotron SOLEIL (Gif-sur Yvette, France) is acknowledged for provision of synchrotron radiation facilities at beamline SAMBA (Proposal No. 20171318). We also acknowledge Qingying Jia (Northeastern University, Boston, USA) for providing the EXAFS spectrum of Fe₃C.

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