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COMMUNICATION

Converting carbon black into efficient Fe-N-C single atom ORR electrocatalyst: The importance of bottom-up construction parameters

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Rui S. Ribeiro^{*abc}, Marc Florent^a, M. Fernando R. Pereira^{bc}, Teresa J. Bandoz^{*a}

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To boost an efficient energy transition, alternatives to expensive and unsustainable noble metals-based electrocatalysts for oxygen reduction reaction (ORR) are needed. Having this in mind, carbon black – Black Pearls 2000 (BP), was enriched in well-defined single-atom Fe-N active sites through a synthesis methodology employing only broadly available precursors. The methodical approach taken to optimize the synthesis conditions highlighted the importance of: (1) a proper choice of the Fe precursor; (2) melamine as an N source to limit the formation of magnetite crystals and modulate the charge density nearby the active sites, and glucose to chelate/isolate Fe atoms and thus to allow Fe-N coordination to be established, with a limiting formation of Fe⁰ clusters; and (3) a careful dosing of the Fe load. ORR on the optimized electrocatalyst (Fe_{0.06}-N@BP) proceeds mostly through a four-electron pathway, having an onset potential (0.912 V vs. RHE) and limiting current density (4.757 mA cm⁻²) above those measured on Pt/C (0.882 V and 4.657 mA cm⁻², respectively). Moreover, a current density yielded by Fe_{0.06}-N@BP after 24 h at 0.4 V vs. RHE was still above that of Pt/C at *t* = 0 (4.44 mA cm⁻²), making it a promising alternative to the use of noble metal-containing electrocatalysts in fuel cells.

Introduction

There is little doubt about the fuel cells' importance in the ongoing energy transition. It is also well known that both hydrogen oxidation (HOR) and oxygen reduction (ORR) reactions (*i.e.*, the electrochemical reactions taking place in a fuel cell) need suitable electrocatalysts to occur efficiently.^{1,2} In particular, the strong O = O bond (498 kJ mol⁻¹) renders ORR particularly challenging, leading to six orders of magnitude

slower kinetics than those of HOR.²⁻⁴ Since the most thermodynamically unfavourable reaction step dictates the overall efficiency of a given process, it comes as no surprise that a fuel cells' operation is limited by the kinetics of ORR.⁵ Conventional ORR electrocatalysts are mostly based on platinum and its alloys, which are unsustainable due to their scarcity and high prices.^{2,3,5-7} In fact, platinum-based electrocatalysts are estimated to account for over 50% of the costs associated with fuel cells under a scenario of a future massive implementation of this technology – 90% out of these costs being ascribed to a cathode electrocatalyst for ORR.⁸ Therefore, developing noble metal-free electrocatalysts for ORR has been the object of extensive research efforts.^{2,9,10} Recent research advances have focused on the preparation of single-atom catalysts. These promising materials provide active sites with higher activity than those of other metal-supported catalysts, thus opening future prospects for a new research area in electrocatalysis in general.^{11,12} However, the lack of stability often shown by the single-atom catalysts still needs to be overcome.^{11,12} In this respect, we have recently demonstrated the feasibility of designing highly active and stable single-atom Fe-N sites on hollow carbon spheres (CSs) through a synthesis methodology employing only (cheaper and more sustainable) non-noble metal precursors such as iron (III) nitrate, melamine, and glucose.¹³ However, the structural properties of CSs limited the amount of Fe introduced (0.12 wt.% only, as determined by inductively coupled plasma – optical emission spectrometry) and thus the ORR performance of the resulting electrocatalyst.¹³ Simultaneously, we have also reported an interesting ORR activity of a metal-free commercial carbon black – Black Pearls 2000 (BP).¹⁴ Moreover, the high specific surface area of BP (> 1500 m² g⁻¹)¹⁴ makes this material an ideal candidate for a support of Fe-N active sites.

Taking into account all the above, the main goal of the current study was to provide an alternative to the use of conventional noble metal-containing electrocatalysts in ORR through designing highly active and stable single-atom Fe-N active sites on a high surface area carbon black support. To reach this objective, Fe-N active sites were first introduced to the surface

^a Department of Chemistry and Biochemistry, The City College of The City University of New York, 160 Convent Avenue, New York, NY 10031, USA. E-mail: tbandosz@ccny.cuny.edu (T.J. Bandoz).

^b LSRE-LCM - Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal. E-mail: rsribeiro@fe.up.pt (R.S. Ribeiro).

^c ALICE - Associate Laboratory in Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal.

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of BP through the bottom-up construction strategy previously reported by our group.¹³ A methodical approach was then taken to optimize the synthesis conditions, focusing on the role of (1) a metal and (2) other precursors, and (3) Fe load. Standard operating conditions and ORR performance indicators were considered to evaluate the electrocatalytic activity and stability. Advanced characterization techniques were employed seeking to establish correlations between the ORR performance of the electrocatalysts and the surface properties.

Results and discussion

Effect of iron precursor

Oxygen reduction humps are clearly seen on the CV curves of all carbon black electrocatalysts, including bare BP (Figure 1a). Nevertheless, the LSV curves differ markedly (Figure 1b). All indicators of the ORR improved upon Fe-N-doping regardless of the Fe precursor employed (Table S1 of the Supplementary Information). Regarding ORR mechanisms (Text S4), pristine, highly crystalline carbon is expected to display a two-electron ORR pathway (Eq. S8, followed by the reactions described in Eq. S9 and/or Eq. S10), rather than the preferred four-electron, direct ORR pathway (Eq. S7). However, most carbon materials are amorphous. That is precisely the case of BP (as shown by the broad peak at *ca.* 20° – 26° observed in the XRD pattern given in Figure S1). Defects in the crystalline structure of carbon materials have been shown to act as active sites towards ORR.^{2,13,15} Most importantly, we have already shown that the high ORR activity of BP arises from the abundant ultramicropores in this metal-free electrocatalyst, which provide strong oxygen adsorption sites and thus enhance the ORR performance.¹⁶ Therefore, the high value of number of electrons transferred (n_e) obtained with bare BP (3.36; *cf.* Table S1), which confirms a significant contribution of the direct four-electron ORR pathway, can be ascribed to its high porosity and intrinsically defective nature. Fe-N-doping increases n_e up to values in the range 3.85 – 3.90, confirming the predominance of

S1) Nevertheless, some differences in the ORR performance of the Fe-N-doped carbon black electrocatalysts are detected (Figure 1), especially regarding onset (E_{onset}) and half-wave ($E_{1/2}$) potentials (Table S1). Specifically, these parameters follow the order $\text{Fe}_{\text{Ni}}\text{-N@BP} < \text{Fe}_{\text{Cl}}\text{-N@BP} < \text{Fe-N@BP}$, indicating the superior performance of the carbon black electrocatalyst prepared with iron (II) acetate as the metal precursor. It is also noteworthy that all Fe-N-doped carbon black electrocatalysts outperform Pt/C in terms of E_{onset} , whereas Fe-N@BP also displays an $E_{1/2}$ above that of Pt/C (Table S1). However, Pt/C has the highest limiting current density (J_L), n_e , and electrocatalytic stability.

Incorporation of single-atom Fe-N active sites: The crucial role of synthesis precursors

Additional materials were prepared to elucidate the role of each precursor (iron (II) acetate, glucose, and melamine) in incorporating single-atom Fe-N active sites on the surface of Fe-N@BP. Accordingly, Fe@BP was prepared in the absence of melamine; $\text{Fe}_{\text{no G-N@BP}}$ in the absence of glucose; and N@BP with melamine only. Both CV (Figure 2a) and LSV (Figure 2b) curves of the resulting carbon black electrocatalysts confirm their activity towards ORR. However, the differences in the ORR activity are clear (Table 1). N-doping of BP slightly improves the ORR performance indicators such as the potential needed to achieve a current density of 0.1 mA cm⁻² ($E_{0.1}$), E_{onset} , and $E_{1/2}$. This is seen in the comparison of the performance indicators of N@BP (0.816, 0.782, and 0.732 V vs. RHE, respectively) to those of bare BP (0.796, 0.772, and 0.727 V vs. RHE, respectively; *cf.* Table 1). Nevertheless, the most significant effect of N-doping is on the ORR reaction pathway, as shown when the % of H₂O₂ formation and n_e obtained on N-BP (14.1% and 3.72, respectively) are compared to those on BP (32.1% and 3.36, respectively), and also on J_L (4.239 vs. 3.480 mA cm⁻²; *cf.* Table 1). This enhancement in the ORR activity upon N-doping is ascribed to the introduction of pyridinic- (N6) and quaternary-N (NQ) species to the carbon surface.^{17,18} Likewise, Fe-doping also increases J_L and shifts the ORR reaction pathway towards the preferred direct four-electron pathway (Eq. S7) compared the performance of BP (Table

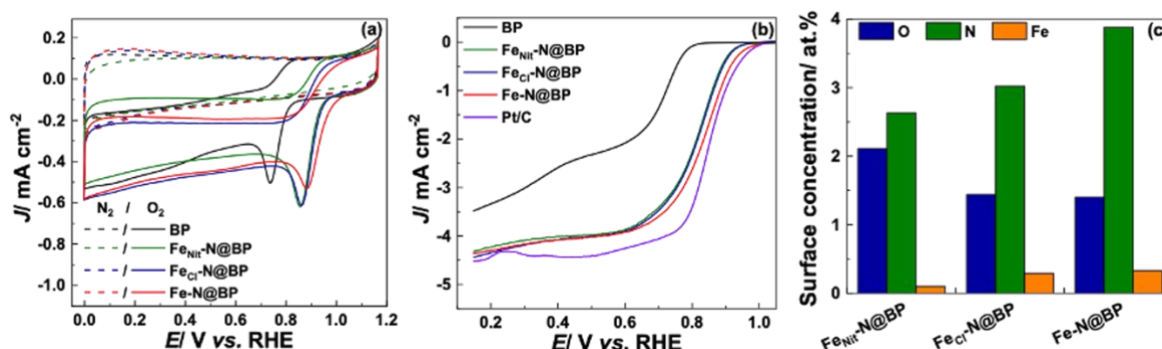


Figure 1 (a) Cyclic voltammetry (CV) curves obtained in N₂- and O₂-saturated 0.1 mol L⁻¹ KOH at 5 mV s⁻¹; (b) ORR linear sweep voltammetry (LSV) curves obtained in O₂-saturated 0.1 mol L⁻¹ KOH at 1600 rpm; and (c) amounts (in at %) of O, N, and Fe determined from X-ray photoelectron spectroscopy (XPS) analysis of carbon black electrocatalysts prepared with different iron precursors. Results obtained on commercial Pt/C are also given in (b) for comparison.

the direct four-electron ORR pathway on these electrocatalysts. Indeed, these values are already in the range of that obtained with a commercial platinum benchmark catalyst containing 20 wt.% of Pt on graphitized carbon (Pt/C, with $n_e = 3.96$; *cf.* Table

1). However, $E_{0.1}$, E_{onset} , and $E_{1/2}$ slightly decrease upon Fe-doping. A larger enhancement of the ORR activity is obtained when melamine is added as the precursor of the N species along with iron (II) acetate during the synthesis of $\text{Fe}_{\text{no G-N@BP}}$ (Figures 2a and b, and Table 1).

Taking BP as a reference, E_{onset} and $E_{1/2}$ increase by 50 and 20 mV, respectively; whereas n_e increases up to 3.86 when ORR is carried out on $\text{Fe}_{\text{no G-N}}\text{@BP}$ (Table 1). This enhancement in the ORR activity can be ascribed to the ability of N atoms to modulate the charge density nearby the active sites.^{11,19} Nevertheless, the greatest enhancement in the ORR activity occurs when glucose is added together with melamine and iron (II) acetate during the synthesis of Fe-N@BP (Figures 2a and b, and Table 1). In this case, E_{onset} and $E_{1/2}$ respectively increase by an astonishing 145 and 125 mV when compared to those obtained on BP (Table 1). In fact, the E_{onset} and $E_{1/2}$ obtained on Fe-N@BP overcome those obtained on the noble metal-containing Pt/C (20 wt.% of Pt), which is particularly relevant when taking into consideration that only earth-abundant and broadly available precursors are employed in the synthesis of Fe-N@BP . Nevertheless, Pt/C still outperforms Fe-N@BP in J_L , n_e and electrocatalytic stability (Table 1).

The data obtained in the kinetically controlled region was used to calculate two additional ORR performance indicators, Tafel slope and exchange current density (J_0). While the former provides mechanism insights, by revealing the rate determining step of ORR,²⁰ the latter can be associated to the rate constant of ORR, thus providing information on the electrocatalytic activity.²¹ The Tafel plot slope for Pt/C is *ca.* 120 mV dec^{-1} (Figure 2c), confirming that ORR on this noble metal-containing electrocatalyst proceeds mostly through the direct four-electron pathway (Eq. S7), the first electron reduction of oxygen being the rate determining step.^{22,23} The Tafel slopes of the Fe-N -doped carbon black electrocatalysts (*i.e.*, Fe-N@BP and $\text{Fe}_{\text{no G-N}}\text{@BP}$) are the same as that of Pt/C, indicating that ORR on these noble metal-free electrocatalysts also proceeds mostly

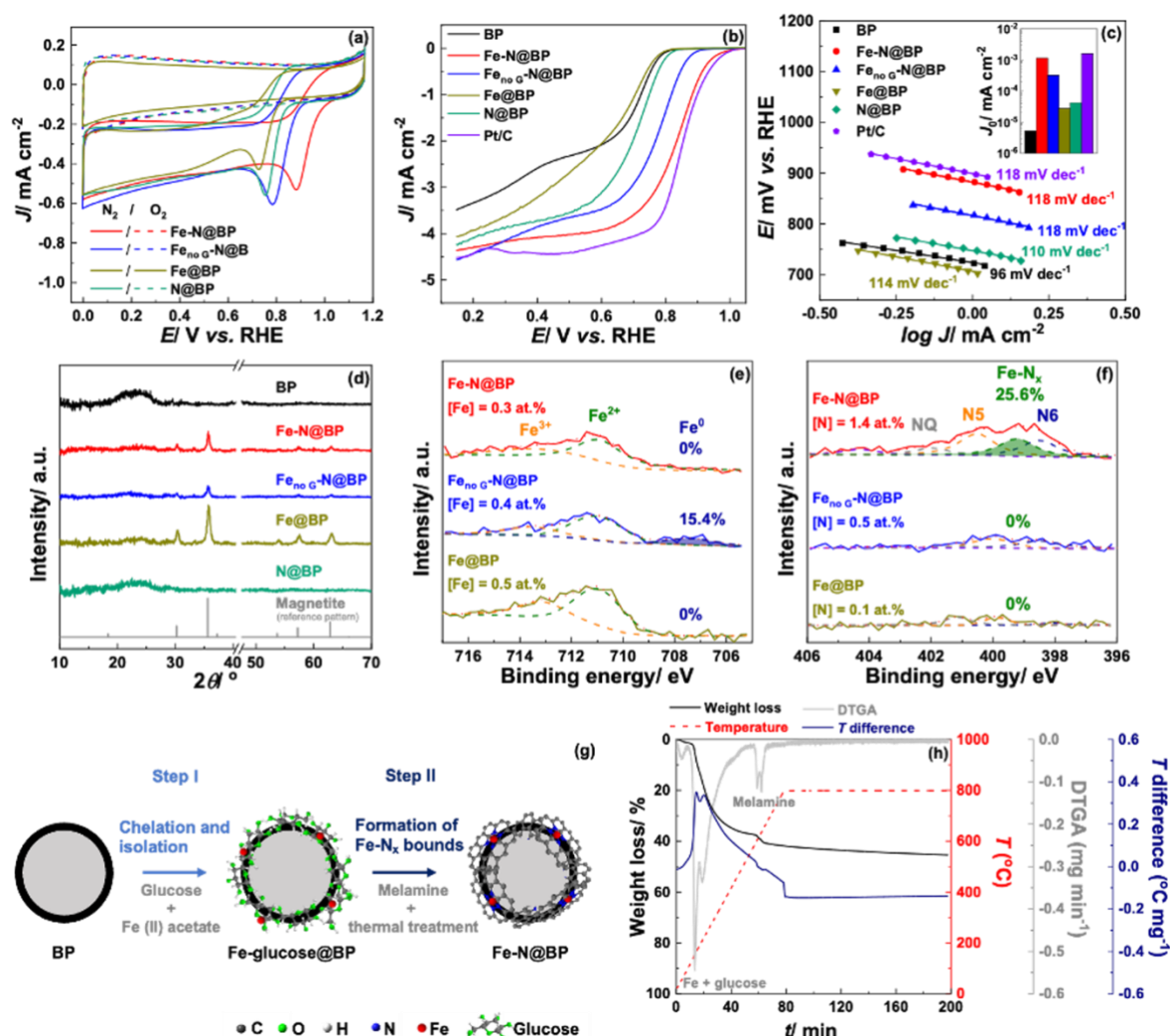


Figure 2 (a) Cyclic voltammetry (CV) curves measured in N_2 - and O_2 -saturated 0.1 mol L^{-1} KOH at 5 mV s^{-1} ; (b) ORR linear sweep voltammetry (LSV) curves measured in O_2 -saturated 0.1 mol L^{-1} KOH at 1600 rpm; (c) Tafel plot; (d) X-Ray diffraction (XRD) patterns; and deconvoluted (e) Fe 2p_{3/2} and (f) N 1s X-ray photoelectron spectroscopy (XPS) spectra of carbon black electrocatalysts prepared to study the role of the synthesis precursors. (g) Schematic representation of the synthesis methodology employed to incorporate single-atom Fe-N active sites on BP, resulting in the material denoted as Fe-N@BP . (h) Thermogravimetric analysis (TGA) carried out in argon to mimic the conditions used in the thermal treatment performed during the synthesis of Fe-N@BP . Results obtained on commercial Pt/C are also given in (b) – (c) for comparison. The X axis in (d) has a break in the range 40.5° – 47.5° due to an interferent peak arising from the XRD sample holder used for the analyses (Figure S1). Exchange current density (J_0) is given in the inset of (c).

Table 1 Summary of oxygen reduction reaction (ORR) performance markers measured on carbon black electrocatalysts prepared to study the role of the synthesis precursors: potential needed to achieve a current density of 0.1 mA cm⁻² ($E_{0.1}$), onset potential (E_{onset}), half-wave potential ($E_{1/2}$), limiting current density (J_L), % of hydrogen peroxide (H₂O₂) formation, number of electrons transferred (n_e), and stability^a

Sample	$E_{0.1}$ /V	E_{onset} /V	$E_{1/2}$ /V	J_L^b /mA cm ⁻²	H ₂ O ₂ ^c / %	n_e^c	Stability ^d / %
BP	0.796	0.772	0.727	3.480	32.1	3.36	76.3
Fe-N@BP	0.973	0.917	0.852	4.361	4.9	3.90	90.7
Fe _{noG} -N@BP	0.873	0.822	0.742	4.740	7.0	3.86	86.9
Fe@BP	0.787	0.767	0.717	4.066	6.1	3.88	90.7
N@BP	0.816	0.782	0.732	4.239	14.1	3.72	n.d.
Pt/C	0.985	0.882	0.847	4.657	2.2	3.96	98.0

^a All data refers to experiments performed at 1600 rpm; ^b Calculated at 0.15 V vs. RHE; ^c Calculated at 0.4 V vs. RHE; ^d Calculated after 24 h at 0.4 V vs. RHE. n.d.: not determined.

through the direct four-electron pathway (Eq. S7). On the contrary, Tafel slopes close to 60 mV dec⁻¹ indicate that ORR proceeds through the two-electron ORR pathway (Eq. S8, followed by the reactions described in Eq. S9 and/or Eq. S10), the pseudo-two-electron reduction reaction being the rate determining step.^{22,23} The Tafel slope obtained on BP (96 mV dec⁻¹; cf. Figure 2c) reveals that ORR on this metal-free electrocatalyst proceeds via a combination of the four- and two-electron pathways. The Tafel slopes of Fe@BP and N@BP fall within the values of BP and the Fe-N-doped carbon black electrocatalysts (Figure 2c). Regarding the ORR reaction rate, the highest value of J_0 among our carbon black electrocatalysts was for Fe-N@BP (1.1 × 10⁻³ mA cm⁻²; cf. inset of Figure 2c), which agrees with the previous discussion on the other ORR performance indicators (Table 1). In fact, this value resembles that obtained with the benchmark Pt/C (1.6 × 10⁻³ mA cm⁻²).

N₂ physisorption was carried out to determine the textural properties of the carbon black electrocatalysts prepared to study the role of each synthesis precursor used to incorporate single-atom Fe-N active sites at the surface of Fe-N@BP. As observed, BP possesses the most developed porosity (Figure S6 and Table S5). N-doping seems not to affect porosity, as observed when both the textural properties (Table S5) and pore size distribution (Figure S7) of N@BP are compared with those of BP. These results allow concluding that N-doping has a negligible effect on porosity. When Fe is added together with melamine, both the specific surface area (S_{BET}) and total pore volume (V_{total}) decrease slightly compared to these parameters for BP, as found for Fe_{noG}-N@BP (Table S5). The analysis of the data collected in Table S5 reveals that micropore volume (V_{micro}) is most affected by Fe-N-doping, leading to a decrease in the V_{micro}/V_{total} ratio from 0.182 (in BP) to 0.159 (in Fe_{noG}-N@BP). This decrease can be ascribed to the loss of micropores at ca. 0.5 – 1 nm, and just below 2 nm (Figure S7), due to pore blockage promoted by Fe species. A similar phenomenon, although more pronounced, occurs when Fe-doping is performed in the presence of glucose (Fe@BP; cf. Table S5 and Figure S7), indicating that carbonization of glucose can also lead to pore blockage. Therefore, pore blockage promoted by Fe and glucose explains the lower porosity of Fe-N@BP when compared to that of bare BP (Figure S6 and Table S5).

Thermogravimetric analysis (TGA) reveals that Fe_{noG}-N@BP is the electrocatalyst with the highest bulk Fe content (8.3 wt.%) among the carbon black electrocatalysts prepared to study the role of synthesis precursors, followed by Fe-N@BP (8.0 wt.%), and Fe@BP

(5.0 wt.%; cf. Figure S8 and Table S6). It is noteworthy that, despite having similar bulk Fe contents and ECSA (Table S6), the ORR performance of Fe-N@BP is significantly better than that of Fe_{noG}-N@BP. For instance, the $E_{1/2}$ obtained with Fe-N@BP (0.852 V vs. RHE) is 110 mV higher than that of Fe_{noG}-N@BP (0.742 V vs. RHE; cf. Table 1). These results suggest that Fe-N@BP possesses active sites with much higher electrocatalytic activity towards ORR than other catalysts addressed in this study. Despite having the lowest bulk Fe content, the XRD pattern of Fe@BP reveals shape peaks. In fact, the diffraction pattern of Fe@BP is consistent with the presence of magnetite (Figure 2d). The intensity of the peaks observed in the XRD patterns of Fe-N@BP and Fe_{noG}-N@BP is lower (Figure 2d), suggesting a decrease in the crystalline phase when Fe-doping was performed in the presence of melamine. The XRD pattern of N@BP resembles that of BP, as no crystalline phases are observed (Figure 2d).

X-ray photoelectron spectroscopy (XPS) was carried out to obtain additional insights on the surface chemical environment of the carbon black electrocatalysts prepared to study the role of synthesis precursors (Figures 2e and f, Figure S9, and Table S7). Despite not being detected through XRD, surface Fe⁰ is detected in the Fe 2p_{3/2} XPS spectrum of Fe_{noG}-N@BP (Figure 2e). On the contrary, Fe⁰ is undetected on the surface of both Fe-N@BP and Fe@BP (i.e., the Fe-doped carbon black electrocatalysts prepared in the presence of glucose). These results indicate the effectiveness of glucose to chelate and isolate Fe atoms during the synthesis of Fe-N@BP (Step I in Figure 2g), enhancing the dispersion of the active sites^{13,24} and thus avoiding the formation of Fe⁰ clusters. Only the Fe-N-doped carbon black electrocatalyst prepared in the presence of glucose reveals the Fe-N coordination (Figure 2f). Specifically, 25.6% of N at the surface of Fe-N@BP is in a chemical state like that of the Fe-N_x moiety of iron phthalocyanine.²⁴ On the contrary, no Fe-N coordination can be identified in the N 1s XPS spectrum of Fe_{noG}-N@BP (Figure 2f). These results indicate that only using glucose as the chelating agent together with the Fe and N precursors allows Fe-N coordination to be established during the synthesis of Fe-N@BP (Step II in Figure 2g).

TGA was also used to obtain additional insights on the possible mechanisms leading to the formation of Fe-N active sites on the surface of Fe-N@BP. This was achieved by mimicking the conditions used in the thermal treatment employed during the synthesis of Fe-N@BP. Two clear main weight loss regions are identified on the TGA curves, at ca. 155 – 210 °C and 590 – 650 °C (Figure 2h). The weight loss corresponding to the first of these regions can be ascribed to the decomposition of Fe-glucose complexes; whereas

that corresponding to the second region can be explained by the decomposition of melamine (Figure 2h). Glucose, a mixture containing iron (II) acetate and glucose, and melamine were also analysed by TGA (Figure S10). As observed, melamine alone completely decomposes at *ca.* 360 °C (Figure S10c). However, the decomposition temperature of melamine is increased by *ca.* 230 °C when occurring at the surface of BP (Figure 2h). This increase may be ascribed to the formation of melon (decomposition temperature $\approx$ 600 °C) due to melamine condensation reactions taking place with the release of ammonia.²⁵ The thermal decomposition temperature of glucose (*ca.* 315 °C; *cf.* Figure S10a) decreases when in the presence of iron (II) acetate (*ca.* 175 °C; *cf.* Figure S10b). In fact, the peak on the DTGA curve of the mixture containing glucose and iron (II) acetate (Figure S10b) is consistent with the weight loss observed during the synthesis of Fe-N@BP at *ca.* 155 – 210 °C (Figure 2h). More interestingly, the weight loss event occurring during the synthesis of Fe-N@BP is exothermic (Figure 2h), whereas the thermal decomposition of glucose is endothermic in the absence of BP (Figures S10a and b). This trend might be a result of the formation of the Fe-glucose@BP complex depicted in Figure 2g.

Taking all the results into consideration, the enhanced ORR performance of Fe-N@BP (Figures 2a-c and Table 1) can be ascribed to the ability of N atoms to (i) limit the agglomeration and oxidation of Fe during the synthesis (limiting the formation of magnetite crystals; *cf.* Figure 2d), and (ii) modulate the charge density of nearby carbon atoms;^{11,19} and to the ability of glucose to (iii) chelate and isolate Fe atoms, thus avoiding the formation of Fe⁰ clusters (Figure 2e) and enhancing metal-heteroatom coordination (favouring the formation of Fe-N_x moieties; *cf.* Figure 2f) during the synthesis.

To study the effect of the heteroatom precursor, urea and thiourea were employed instead of melamine. Both these electrocatalysts underperform Fe-N@BP (*i.e.*, the sample prepared employing melamine as the N precursor), and therefore were not given additional consideration (Figure S11 and Table S8).

Optimization of Fe load

Despite all positive effects arising from the inclusion of glucose as the chelating agent during Fe-N-doping of BP, the resulting electrocatalyst (Fe-N@BP) still revealed XRD peaks consistent with the presence of magnetite crystals (Figure 2d). This suggests that its Fe load might be above the optimum value. To test this hypothesis, two additional materials were prepared considering a 5- and 10-fold lower amount of iron (II) acetate (Fe_{0.06}-N@BP and Fe_{0.03}-N@BP being obtained, respectively). As observed on the CV (Figure 3a) and LSV (Figure 3b) curves, changing the Fe load affects the ORR performance of the resulting materials. Although the differences observed for $E_{0.1}$, E_{onset} , and $E_{1/2}$ are rather negligible, J_L clearly goes through a maximum, corresponding to the performance of the carbon black electrocatalyst prepared with 0.06 mmol of iron (II) acetate (Fe_{0.06}-N@BP; *cf.* Figure 3c and Table 2). Besides its better performance than those of other Fe-N-doped carbon black electrocatalysts, Fe_{0.06}-N@BP also displays higher E_{onset} and J_L than the benchmark Pt/C (Figure 3c and Table 2), and exhibits less H₂O₂ formed (Figure 3d) and higher n_e (Figure 3e) than the noble metal-containing electrocatalyst throughout the

potential window under study (0.2 – 0.6 V vs. RHE). As for the Tafel slope, the value obtained for Fe_{0.06}-N@BP is close to 120 mV dec⁻¹ (Figure 3f), confirming that ORR on this noble metal-free electrocatalysts proceeds mostly through the direct four-electron pathway (Eq. S7).^{22,23} In fact, the Tafel slopes confirm that the ORR reaction mechanism on the resulting Fe-N-doped carbon black electrocatalyst seems not to be affected by the Fe load considered in the synthesis, as values very close to 120 mV dec⁻¹ (in the range 116 – 118 mV dec⁻¹; *cf.* Figure 3f) are always obtained. These results agree with the high values of n_e (in the range 3.89 – 3.97) for the same electrocatalysts (Table 2). A similar trend is found for the ORR reaction rate. In this case, the J_0 obtained on the carbon black electrocatalysts prepared with different Fe loads falls within a narrow range (6.6×10^{-4} – 1.1×10^{-3} mA cm⁻²) and slightly below the value obtained for the benchmark Pt/C (1.6×10^{-3} mA cm⁻²; *cf.* inset of Figure 3f).

N₂ physisorption reveals similar textural properties among the Fe-N-doped carbon black electrocatalysts prepared with different Fe loads (Figure S12, Table S9, and Figure S13). Nevertheless, decreasing the metal load used in the synthesis seems to slightly limit the pore blockage by the Fe species discussed above. TGA confirms that different bulk Fe contents were effectively introduced during the syntheses, in the order: Fe_{0.03}-N@BP (1.2 wt.%) < Fe_{0.06}-N@BP (3.7 wt.%) < Fe-N@BP (8.0 wt.%; *cf.* Figure S14 and Table S10). Nevertheless, Fe_{0.06}-N@BP possesses the highest ECSA among all the carbon black electrocatalysts tested (115 cm²; *cf.* Table S10) and the best performance in ORR, despite having less than half the Fe load of Fe-N@BP (Figures 3b-d and Table 2). These results imply that the enhanced performance obtained with Fe_{0.06}-N@BP can be ascribed to the presence of active sites with an electrocatalytic activity even higher than those at Fe-N@BP. Transmission electron microscopy (TEM) micrographs, obtained both with low (Figure S15) and high (Figure 3g) magnification, reveal that Fe_{0.06}-N@BP possesses the typical morphology of carbon black materials. Regarding metal distribution, no bright spots consistent with Fe aggregates/particles are clearly identified in the high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image of Fe_{0.06}-N@BP (Figure 3h). Moreover, the energy dispersive X-ray spectrometry (EDS) elemental maps confirm the high dispersion of both Fe and N on the carbon surface (Figure 3h). In fact, overlapping the two EDS elemental maps shows that the presence of N is mostly associated with Fe (Figure S16). These results agree with those obtained by XRD (Figure 3i) and XPS (Figure 3j, Figure S17 and Table S11). Specifically, no peaks corresponding to crystalline phases were found on the XRD pattern (Figure 3i) and Fe⁰ was not detected in the Fe 2p_{3/2} XPS spectrum (Figure S17g) of Fe_{0.06}-N@BP. On the contrary, 24.1% of the surface N is in a chemical state suggesting the Fe-N_x moiety in iron phthalocyanine (Figure 3j), corresponding to an overall surface concentration of 0.7 at.% on Fe_{0.06}-N@BP. It may be argued that the absence of identifiable XRD peaks results from the low Fe load in Fe_{0.06}-N@BP. An additional material was thus prepared to assess this possibility. For that purpose, the same synthesis conditions as those used for Fe_{0.06}-N@BP were employed except for the amount of glucose,

which was reduced *ca.* 20-fold, from 6.7 to 0.3 mmol. The resulting material ($\text{Fe}_{0.06, \text{low G-N@BP}}$) possesses similar textural properties to those of bare BP (Figure S12, Table 9, and Figure S13), as the pore blockage promoted by glucose is very limited. Interestingly, despite the bulk Fe content estimated by TGA (3.1 wt.%) being similar to that of $\text{Fe}_{0.06}\text{-N@BP}$ (3.7 wt.%; *cf.* Figure 14 and Table S10), the XRD pattern of $\text{Fe}_{0.06, \text{low G-N@BP}}$ clearly depicts peaks consistent with the presence of magnetite (Figure 3i). Moreover, the N 1s XPS spectrum of $\text{Fe}_{0.06, \text{low G-N@BP}}$

reveals a smaller extent of the Fe-N_x coordination than that in $\text{Fe}_{0.06}\text{-N@BP}$, as well as the presence of oxidized-N species (Figure 3j). Thus, these results reaffirm the importance of adding glucose during Fe-N-doping of BP. On the other hand, they support the hypothesis that the enhanced ORR performance of $\text{Fe}_{0.06}\text{-N@BP}$ when compared to that obtained with Fe-N@BP (*i.e.*, the carbon black electrocatalyst with over 2-fold the Fe load of $\text{Fe}_{0.06}\text{-N@BP}$) can indeed be ascribed to the presence of well-defined single-atom Fe-N active sites and to

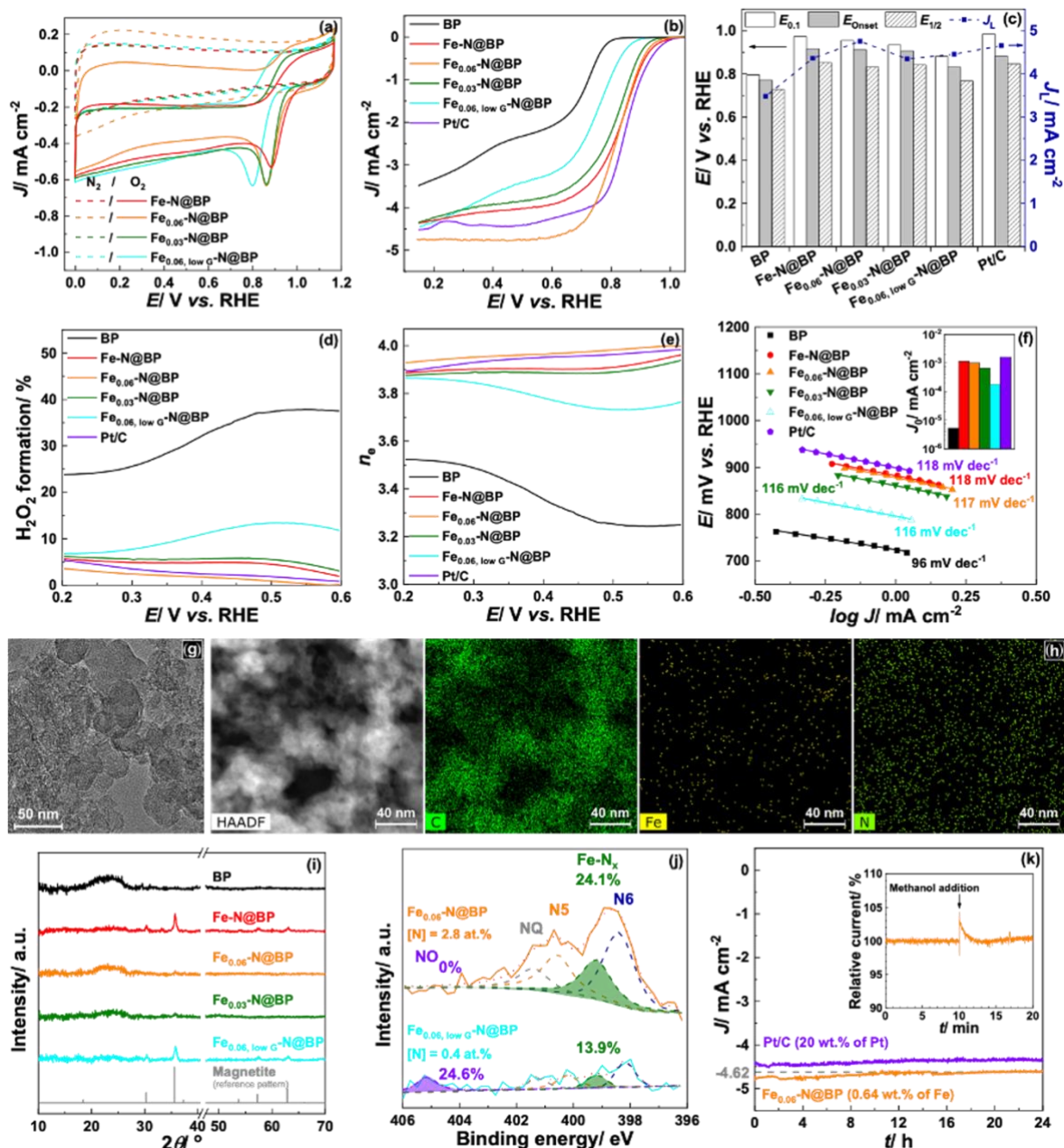


Figure 3 (a) Cyclic voltammetry (CV) curves obtained in N₂- and O₂-saturated 0.1 mol L⁻¹ KOH at 5 mV s⁻¹; (b) ORR linear sweep voltammetry (LSV) curves obtained in O₂-saturated 0.1 mol L⁻¹ KOH at 1600 rpm; (c) overview of ORR performance; (d) hydrogen peroxide (H₂O₂) formation, and (e) number of electrons transferred (n_e) during the experiments depicted in (b); and (f) Tafel plot of carbon black electrocatalysts prepared to study the effect of Fe load. (g) Transmission electron microscopy (TEM) micrograph, and (h) high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image and energy-dispersive X-ray spectroscopy (EDS) elemental maps of $\text{Fe}_{0.06}\text{-N@BP}$. (i) X-Ray diffraction (XRD) patterns of carbon black electrocatalysts prepared to study the effect of the Fe load. (j) Deconvoluted N 1s core energy level spectra of carbon black electrocatalysts prepared with different amounts of glucose. (k) Stability of $\text{Fe}_{0.06}\text{-N@BP}$ at 0.4 V vs. RHE. Results obtained on commercial Pt/C are also given in (b) – (f) and (k) for comparison. The exchange current density (J₀) is given in the inset of (f). The X axis in (i) has a break in the range 40.5° – 47.5° due to an interferent peak arising from the XRD sample holder used for the analyses (Figure S1). N6, N5, NQ, and NO in (j) represent N-pyridinic, N-pyrrolic, N-quaternary, and N-oxidized species, respectively. Inset in (k) corresponds to the stability of $\text{Fe}_{0.06}\text{-N@BP}$ to methanol cross-over at 0.4 V vs. RHE.

Table 2 Summary of ORR performance markers measured on carbon black electrocatalysts prepared to study the effect of Fe load: potential needed to achieve a current density of 0.1 mA cm⁻² ($E_{0.1}$), onset potential (E_{onset}), half-wave potential ($E_{1/2}$), limiting current density (J_L), % of hydrogen peroxide (H₂O₂) formation, number of electrons transferred (n_e), and stability^a

Sample	$E_{0.1}$ /V	E_{onset} /V	$E_{1/2}$ /V	J_L^b /mA cm ⁻²	H ₂ O ₂ ^c /%	n_e^c	Stability ^d /%
BP	0.796	0.772	0.727	3.480	32.1	3.36	76.3
Fe-N@BP	0.973	0.917	0.852	4.361	4.9	3.90	90.7
Fe _{0.06} -N@BP	0.955	0.912	0.832	4.757	1.8	3.97	95.8
Fe _{0.03} -N@BP	0.934	0.907	0.842	4.349	5.7	3.89	84.4
Fe _{0.06, low G} -N@BP	0.881	0.832	0.767	4.456	10.9	3.78	78.9
Pt/C	0.985	0.882	0.847	4.657	2.2	3.96	98.0

^a All data refer to experiments performed at 1600 rpm; ^b Calculated at 0.15 V vs. RHE; ^c Calculated at 0.4 V vs. RHE; ^d Calculated after 24 h at 0.4 V vs. RHE.

the absence of Fe aggregates/particles in the form of magnetite and/or Fe⁰. This enhanced catalyst composition also explains why Fe_{0.06}-N@BP has the highest stability for ORR (95.8% after 24 h at 0.4 V vs. RHE) among the Fe-N-doped carbon black electrocatalysts tested (in the range 84.4 – 90.7%), and similar to that obtained on the benchmark Pt/C (98.0%; cf. Table 2). In fact, despite having the slightly lower relative electrocatalytic stability, the current density yielded by Fe_{0.06}-N@BP after 24 h at 0.4 V vs. RHE (4.62 mA cm⁻²) is still above that exhibited by fresh Pt/C at $t = 0$ (4.44 mA cm⁻²; cf. Figure 3k). Moreover, Fe_{0.06}-N@BP shows an impeccable resistance to methanol cross-over (inset of Figure 3k).

Conclusions

The primary contributions of this study towards the advancement of knowledge on the design of noble metal-free carbon electrocatalysts for ORR are as follows:

- (1) The choice of the Fe precursor should be given a proper consideration. The synthesis methodology herein reported is effective for the incorporation of single-atom Fe-N active sites on BP regardless of the Fe precursor employed. Nevertheless, using iron (II) acetate as the metal precursor favours the incorporation of Fe-N active sites and prevents the formation of Fe⁰ clusters at the surface of BP, thus enhancing the ORR performance of the resulting carbon black electrocatalyst;
- (2) Understanding the role played by synthesis precursors other than the metal source is crucial to optimize the ORR electrocatalytic activity of the active sites incorporated at the surface of BP. Using melamine as the N source (i) limits the formation of magnetite crystals due to oxidation of Fe during the synthesis and (ii) modulates the charge density nearby the Fe-containing active sites. However, only the ability of glucose to (iii) chelate and isolate Fe atoms allows the Fe-N coordination to take place during the synthesis while limiting the formation of Fe⁰ clusters;
- (3) Optimization of Fe load should not be neglected. Well-defined single-atom Fe-N active sites in the absence of Fe aggregates/particles (in the form of magnetite and/or Fe⁰) can only be obtained upon carefully dosing the Fe load employed in the synthesis.

The optimized carbon black electrocatalyst (Fe_{0.06}-N@BP), obtained upon summing up the contributions described in (1) – (3), outperformed the platinum benchmark catalyst containing 20 wt.%

of Pt on graphitized carbon (Pt/C) in almost all the ORR performance indicators considered. Among these, the E_{onset} (0.912 V vs. RHE), J_L (4.757 mA cm⁻²), and n_e (3.97) obtained on Fe_{0.06}-N@BP are above those of Pt/C (0.882 V vs. RHE, 4.657 mA cm⁻², and 3.96, respectively). Despite the slightly lower relative electrocatalytic stability (95.8 vs. 98.0%), the current density yielded by Fe_{0.06}-N@BP after 24 h at 0.4 V vs. RHE is still above that produced by the fresh Pt/C at $t = 0$. Moreover, Fe_{0.06}-N@BP has a high resistance to methanol cross-over. The impressive accomplishments herein reported open a window of opportunity for the application of specifically designed carbon black electrocatalysts in fuel-cells as an alternative to the use of conventional noble metal-containing electrocatalysts.

Methods

Synthesis of carbon black electrocatalysts

The chemicals and materials employed in this study are detailed in Text S1. Fe-N active sites were incorporated at the surface of BP by optimizing the synthesis methodology previously reported by our group.¹³ For that purpose, BP (100 mg) was added to 5 mL of an aqueous solution containing iron (III) nitrate nonahydrate (0.3 mmol) and D-(+)-glucose (6.7 mmol). After sonication for 60 min, the solids were collected by vacuum filtration (qualitative paper filter), rinsed with distilled water to promote the washout of the non-adsorbed precursors, dried overnight at 60 °C, and added to 5 mL of an ethanol solution containing melamine (100 mg). After sonication for 60 min, the resulting suspension was allowed to dry at 60 °C. The solid product was then thermally annealed under an N₂ flow (100 cm³ min⁻¹) for 120 min at 800 °C (heating rate = 10 °C min⁻¹), Fe_{Nit}-N@BP being obtained. Iron (II) chloride tetrahydrate and iron (II) acetate were also used as sources on iron and resulting catalysts are referred to as Fe_{Cl}-N@BP and Fe-N@BP, respectively.

To study the role of the synthesis precursors used to obtain Fe-N@BP, additional materials were prepared in the absence of melamine (Fe@BP) and glucose (Fe_{no G}-N@BP), and with melamine only (N@BP). To evaluate the effect of the heteroatom precursor, urea and thiourea were used instead of melamine and the resulting materials are referred to as Fe-N_{Urea}@BP and Fe-N_{Thiourea}@BP, respectively. The effect of an iron load was studied upon synthesizing materials with 0.06 and 0.03 mmol of iron (II) acetate (Fe_{0.06}-N@BP and Fe_{0.03}-N@BP, respectively). An additional material was prepared considering the same synthesis conditions as those used to obtain

Fe_{0.06}-N@BP, except that the amount of glucose was decreased from 6.7 to 0.3 mmol. The resulting material is referred to as Fe_{0.06}, low G-N@BP.

Characterization techniques

N₂ physisorption and X-ray photoelectron spectroscopy (XPS) were performed as previously described.¹⁴ X-ray diffraction (XRD) analysis was performed in a PANalytical X'Pert Pro apparatus equipped with a PIXcel detector (Cu K α = 0.154 nm; data recorded at a 0.026 step size). Thermogravimetric analysis (TGA) was performed on a TA Instruments SDT Q600 thermal analyser upon heating the sample (*ca.* 10 mg) from 50 to 1000 °C at 5 °C min⁻¹ under an oxidative (air) flow. High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) imaging was performed on a FEI Titan Themis 200 microscope (operated at 200 kV), coupled to a SuperX Energy Dispersive X-ray Spectrometer (EDS) system. Additional details on the characterization techniques used in this study are described in Text S2.

Electrochemical measurements

A mixture containing 4 mg of each carbon black electrocatalyst, 160 μ L of Nafion perfluorinated resin solution, 160 μ L of ethanol, and 480 μ L of distilled water was sonicated for 60 min. A calculated volume of the resulting suspension was then drop-casted on the glassy carbon working electrode (dried at 50 °C) to obtain a catalyst load of 0.25 mg cm⁻² on the electrode surface. All electrochemical measurements were performed in an alkaline medium (0.1 mol L⁻¹ KOH), with the modified carbons as working electrodes. Please refer to Text S3 for additional details.

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Author Contributions

Rui S. Ribeiro: Conceptualization, Methodology, Investigation, Formal analysis, Writing – Original Draft, Funding acquisition; **Marc Florent:** Methodology, Writing - Review & Editing; **M. Fernando R. Pereira:** Conceptualization, Writing – Review & Editing, Supervision, Project administration, Funding acquisition; **Teresa J. Bandoz:** Conceptualization, Writing – Review & Editing, Supervision, Project administration, Funding acquisition.

Conflicts of interest

There are no conflicts to declare.

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