Identification of catalytic sites in cobalt-nitrogen-carbon materials for the oxygen reduction reaction

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Single-atom catalysts with full utilization of metal centers can bridge the gap between molecular and solid-state catalysis. Metal-nitrogen-carbon materials prepared via pyrolysis are promising single-atom catalysts but often also comprise metallic particles. Here, we pyrolytically synthesize a Co–N–C material only comprising atomically dispersed cobalt ions and identify with X-ray absorption spectroscopy, magnetic susceptibility measurements and density functional theory the structure and electronic state of three porphyrinic moieties, CoN4C12, CoN3C10,porp and CoN2C5. The O2 electro-reduction and operando X-ray absorption response are measured in acidic medium on Co–N–C and compared to those of a Fe–N–C catalyst prepared similarly. We show that cobalt moieties are unmodified from 0.0 to 1.0 V versus a reversible hydrogen electrode, while Fe-based moieties experience structural and electronic-state changes. On the basis of density functional theory analysis and established relationships between redox potential and O2-adsorption strength, we conclude that cobalt-based moieties bind O2 too weakly for efficient O2 reduction.

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The transition from fossil to renewable energies is necessary to meet the rising energy demand while minimizing anthropogenic climate change and urban pollution 1–3. Electrochemical energy conversion will play an increasing role for the storage of renewable electricity, production of fuels and their conversion into electricity. Hydrogen is an interesting energy vector since it can be produced via water electrolysis (hydrogen evolution reaction, HER) and later oxidized in H₂/air fuel cells to reform water and electricity on demand (hydrogen oxidation reaction, HOR). However, the electrochemical oxygen reactions (oxygen reduction reaction (ORR) and oxygen evolution reaction (OER)) are slow, limiting the roundtrip efficiency 4. While acidic electrolytes are more restrictive than alkaline ones regarding the breadth of catalysts that may be stable under ORR/OER conditions, the advent of highly conductive and stable proton exchange membranes (PEM) has hitherto favoured the development of acidic fuel cells and electrolyzers. Their major drawback is, however, the need for platinum-group metals to catalyze the ORR and OER.

Following the pioneering report of Jasinski on the ORR activity of cobalt phthalocyanine 5, advanced Metal–N–C materials have since 1989 been prepared by pyrolyzing separate metal, nitrogen and carbon precursors 6. Although the activity and durability of such catalysts have been improved 7–11, the identification of the active-site structure has lagged behind due to the non-crystallographic order of metal atoms in the most active sites and the simultaneous presence of crystalline metal phases. Metal ions coordinated with pyridinic nitrogen atoms embedded in a graphene matrix with hexagonal atomic arrangement, such as the MeN₄C₁₀ moiety, have for a long time been viewed as the most probable site structure 12–18. Other studies hypothesized moieties integrated in disordered carbon sheets involving non-hexagonal rings, such as the MeN₄C₁₂ moiety 19, 20. Calle-Vallejo et al. 21 investigated with density functional theory (DFT) the adsorption energy of oxygen intermediates on MeN₄C₁₂ and MeN₄C₁₀ moieties, revealing differences up to 0.7 eV. This highlights the importance of precisely determining the local site structures in Me–N–C materials for deciphering their reactivity.

Using X-ray absorption near-edge structure (XANES) spectroscopy we recently identified the active-site structure in pyrolyzed Fe–N–C catalysts as being a porphyrin-like FeN₄C₁₂ moiety, in contrast with FeN₄C₁₀ or FeN₂+C₄ moieties previously assumed 22. The formation of FeN₄C₁₂ moieties requires a strongly-disordered host material, in line with experimental observations 9, 23. Although moieties present in Fe–N–C materials are now better described 22, 24–26, active sites in Co–N–C materials are still poorly identified. Co–N–C catalysts are ORR-active and advantageous vs. Fe–N–C since they produce less radical oxygen...
Absence of Co–Co bonds in Co0.5 evidenced with EXAFS and TEM. We synthesized a Co–N–C catalyst with the same approach developed for preparing Fe–N–C catalysts comprising only FeN4C4 moieties, and labeled it Co0.5, with 0.5% Co in the catalyst precursor before pyrolysis (see Methods). The EXAFS spectrum of Co0.5 was analyzed assuming a variable number of nitrogen ligands in the equatorial plane and additional oxygen atoms in the axial position. The best-fit analysis is shown in Fig. 1, revealing 4- and/or 5-fold coordination structures. No Co–Co backscattering signal was needed to obtain an excellent fit. The dominant contribution to the EXAFS signal is given by the Co–N distance, while the peak at 2.44 Å is due to Co–O and/or Co–C. The structural parameters obtained from the fitting are reported in Supplementary Table 1. The Co–N distance, 1.95–1.96 Å, agrees with values determined by DFT for cobaltous-porphyrins. However, the EXAFS experimental data can be reproduced with the same accuracy by a CoN4 or an O-CoN4 structure, as reported for Fe0.5 (ref. 22). Moreover, the uncertainty on the nitrogen coordination number (Supplementary Table 1) leaves room for hypothesizing moieties with a lower coordination, as investigated later in this study. The absence of metallic Co–Co bonds in Co0.5 was independently confirmed by TEM (Supplementary Fig. 1). The selected area electron diffraction (SAED) pattern shows only broad rings, as expected for amorphous carbon. No sign of reflections originating from metallic particles was observed, and no evidence of particles was found in the images. Multiple areas of the sample were analyzed, and the
Electrocatalytic properties of Co0.5 towards the ORR. The ORR activity and selectivity of Co0.5 was then investigated with a rotating ring disk electrode (RRDE) in acid medium (Fig. 2a). The ORR current density at 0.8 V vs. a reversible hydrogen electrode (RHE) is 0.9 mA cm\(^{-2}\) for a loading of 800 µg cm\(^{-2}\) (12 µgCo cm\(^{-2}\)), which compares well with state of art Co–N–C catalysts in acid medium, in spite of low cobalt content in Co0.5 (refs 39–41). The Pt/C catalyst reaches 1.0 mA cm\(^{-2}\) at 0.91 V vs. RHE, and its higher activity is due to its higher atom-specific ORR activity (the higher Pt loading, 40 µg cm\(^{-2}\), resulting in identical number of metal atoms per cm\(^{2}\) as for cobalt, due to the 3.3 times higher molar mass of Pt vs. Co).

Regarding selectivity, the % peroxide released by Co0.5 during ORR at 0.5–0.8 V vs. RHE is 3–5 % in 0.1 M H\(_2\)SO\(_4\) at a loading of 5000 µg cm\(^{-2}\) (Fig. 2b). Co0.5 is thus less selective to water formation than Fe0.5, for which we measured <0.5 % H\(_2\)O\(_2\) in acid, at equal catalyst loading.\(^{22}\) The peroxide production was also measured at a lower loading, since it has been reported that, for some Fe–N–C catalysts, this can result in greatly increased detection of H\(_2\)O\(_2\) (ref. 43). The % H\(_2\)O\(_2\) released by Co0.5, however, only increased up to 11% at 200 µg cm\(^{-2}\) (Fig. 2b). By analogy with what is known for unpolymerized Metal-N\(_4\) macrocycles, this result may be explained by the generally higher formal potential of Metal\(^{II}\)/Metal\(^{I}\) for cobalt vs. iron macrocycles, leading to weaker interaction with oxygen intermediates, including H\(_2\)O\(_2\) (ref. 45). Square-wave-voltammetry in acid medium supports this possible explanation, identifying redox-peak positions at 1.25 V and 0.75 V vs. RHE for Co0.5 and Fe0.5, respectively (Supplementary Fig. 2). Although Co–N–C catalysts typically release more peroxide during the ORR, subsequent reactions between H\(_2\)O\(_2\) and MeN\(_x\)C\(_y\) moieties produce less radical oxygen species on cobalt- than iron-centers, which is beneficial for fuel cell durability.\(^{27}\) Also, the insigniﬁcant ORR activity in acidic medium of N–C (Fig. 2a) means that the cobalt moieties are the most active-site for ORR in Co0.5. This catalyst was then investigated in PEM fuel cell and compared to Fe0.5 and Pt/C (Fig. 2c, d). For comparison, we prepared a Pt-based cathode with similar metal-site density (1% Pt/C) and similar thickness as Co0.5 or Fe0.5 cathodes. For carbon-rich catalysts, the thickness is set by the catalyst loading, here 4 mg cm\(^{-2}\), corresponding to a moiety where the cobalt ion is coordinated in-plane by four nitrogen atoms at 1.96 Å when O\(_2\) is adsorbed end-on. A similar phenomenon occurs for Pt, switching from surface-oxidized state to a state free of oxygen adsorbates at ~0.8 V vs. RHE.\(^{44,45}\) In contrast, Co0.5 does not change oxidation state throughout the ORR region (Supplementary Fig. 2) and the TS-value of 65 mV per decade observed at high potential is, therefore, intrinsic to the ORR mechanism on CoN\(_x\)C\(_y\) moieties. Overall, and for similar cathode thickness, the gap between the curves for 1% Pt/C and Co0.5 or Fe0.5 is only a factor two at 0.6 V. A key issue is that, while Pt can be deposited as nanoparticles up to 50 wt% on carbon, the ORR activity of Metal–N–C materials levels off at 2–3 wt% metal.\(^{46}\) Further work is thus needed to (i) improve reactant transport in thick Me–N–C electrodes, (ii) increase the number of active sites or (iii) their turnover frequency. The latter two tasks require identifying the structure of active moieties, object of the present study.

Structural identification of Co-moieties in Co0.5 by XANES. To overcome the limitations of EXAFS, we resorted to XANES, which is more sensitive to the geometrical arrangement of atoms around the photo-absorber. Our XANES analysis was first validated with cobalt phthalocyanine (Co(II)Pc). The agreement between experimental and calculated spectra of Co(II)Pc is excellent in the whole energy range (Supplementary Fig. 3). For this fit, the square residual function, R\(_{sq}\) (Methods section) is 1.06. The optimized structure resulted in a Co–N distance of 1.90(2) Å, which agrees with an X-ray diffraction determination.\(^{47}\) We then calculated the Co K-edge XANES spectra of various Co\(_{x}\)C\(_y\) candidate sites for Co0.5, including structures previously investigated with DFT.\(^{20,31–34}\) Some of these clusters are depicted in Supplementary Fig. 4 together with the results of the fitting procedure. Supplementary Fig. 4a, c report the XANES fitting performed assuming a CoN\(_x\)C\(_y\) moiety enclosed in a graphene plane and a CoN\(_{2+2}\)C\(_{6+4}\) moiety bridging two graphene planes, respectively. For the calculations, only the in-plane distances between cobalt and nitrogen atoms were allowed to vary. For these hypothetical sites, the fit between experimental and calculated XANES spectra is unsatisfactory (R\(_{sq}\) = 2.97 and 2.81, respectively) and the fit quality was little improved by adding an axial oxygen (Supplementary Fig. 4b, d). The disordered arrangement of nitrogen and carbon atoms surrounding cobalt ions has been recently revealed by STEM for another Co–N–C catalyst.\(^{29}\) This suggests that the arrangement of carbon atoms around cobalt ions is different from that in graphene.

We then considered different defective sites derived from CoN\(_{10}\)–namely pyridinic CoN\(_{10}\)porp and CoN\(_{10}\) (Supplementary Fig. 5a, c) and two defective sites derived from CoN\(_{12}\)C\(_{6}\)–namely CoN\(_{2+2}\)C\(_{6+4}\) and CoN\(_{2+3}\)C\(_{6+3}\) (Supplementary Fig. 5e, g). None of these four pyridinic-defective candidate sites correctly reproduced the experimental XANES spectrum of Co0.5. Again, the addition of an O\(_2\) molecule in end-on mode did not improve much the fit quality (Supplementary Fig. 5b, d, f, h). The structural parameters obtained from these analyses are summarized in Supplementary Table 2.

We then considered a cobalt moiety based on a porphyrinic architecture, analogous to that found for the Fe-based active-site geometry in Fe0.5 (ref. 22). Fig. 3a, b show the XANES analyses performed on the square-planar CoN\(_{12}\) moiety, with and without an axial O\(_2\) adsorbed end-on. These fits show an excellent agreement between experimental and theoretical spectra and correspond to a moiety where the cobalt ion is coordinated in-plane by four nitrogen atoms at 1.96–1.97 Å, and possibly by one oxygen molecule at 2.23 Å (Table 1, rows 1 and 2). Two defective sites, derived from the porphyrinic CoN\(_{12}\) moiety by subtracting one or two nitrogen atoms (porphyrinic CoN\(_{10}\)porp and CoN\(_{10}\)G5 model sites), also correctly reproduce the experimental spectrum (Fig. 3c, e, respectively). For the CoN\(_{10}\)porp motif, the XANES analysis resulted in a Co–N bond length of 1.96 Å when O\(_2\)–free, and 1.99 Å when O\(_2\) is adsorbed end-on without out-of-plane displacement of cobalt (Table 1, rows 3 and 4). The XANES analysis also revealed the CoN\(_{10}\)G5 edge-defect, representing a halved porphyrinic moiety, binding O\(_2\) end-on with a Co–O bond length of 1.90 Å with O\(_2\) in the same plane as the CoN\(_{10}\)G5 motif (Fig. 3e, f and Table 1, rows 5 and 6). For the CoN\(_{10}\)G5 motif only, the bound O\(_2\) molecule was necessary to reach a good fit (R\(_{sq}\)– value of 1.12–1.16, Table 1). For the CoN\(_{12}\)porp and CoN\(_{10}\)porp moieties (with or without adsorbed O\(_2\)), the Co–N bond lengths determined by XANES and EXAFS are in good agreement, and so
is the case for the CoN₂C₅ moiety free of adsorbed O₂ (Table 1 and Supplementary Table 1).

The energy of formation and O₂ adsorption energy were then calculated by DFT-D approach for the possible sites identified by XANES analysis, namely CoN₄C₁₂, CoN₃C₁₀,porp and CoN₂C₅, and the results were compared to those obtained for the CoN₄C₁₀ pyridinic moiety (Supplementary Fig. 6). The optimized bond distances for the above-mentioned porphyrinic sites, with and without a dioxygen molecule adsorbed in end-on mode, follow the trends of bond distances determined by EXAFS and XANES (Supplementary Table 3). The stability of these porphyrinic defective motifs is assessed by the Co(II) binding energy, −6.8 to −7.5 eV for the ground states, comparable to −8.2 eV obtained for CoN₄C₁₀ (Supplementary Table 4). Moreover, our DFT-D results reveal that the adsorption of an O₂ molecule results in the displacement of the cobalt ion by 0.4 and 0.5 Å above the plane for CoN₃C₁₀,porp and CoN₂C₅, respectively. The O₂ adsorption energies in the ground-state structures are −0.80, −1.23 and −1.26 eV for CoN₄C₁₂, CoN₃C₁₀,porp and CoN₂C₅, respectively. This is comparable to the O₂ adsorption energies for the ground state of the CoN₄C₁₀ site, −0.97 eV. Although O₂ adsorbs on all cobalt moieties, the obtained adsorption energies are, however, significantly smaller than those of the FeN₄C₁₀ and FeN₄C₁₂ moieties in ground state, −1.83 and −1.84 eV, respectively (Supporting Information of ref. 22). This indicates that cobalt binds O₂ more weakly compared to iron-based moieties. Due to the lower experimental ORR activity of Co₀.₅ vs. Fe₀.₅ (Fig. 2d) one can unambiguously conclude that cobalt moieties are situated on the weak-binding side of a volcano plot. While no definitive conclusion can be made on the volcano-plot position of iron moieties in Fe₀.₅ only from the present work (the weak and strong binding branches being both possible), yet unpublished work on Fe₀.₅ post-treated with H₂O₂ suggests that Fe₀.₅ is also positioned on the weak binding side of a volcano plot. The weaker binding of O₂ (and thus of H₂O₂, via scaling relationships) by CoNₓCₙ moieties also explains the higher amount of peroxide detected by RRDE for Co–N–C vs. Fe–N–C, as reported above. The O₂ adsorption energy of molecular cobalt catalysts is often weaker than desired for an ideal metal-centered moiety, and the same conclusion is made from the present combined experimental and theoretical study for the pyrolyzed Co₀.₅ catalyst. Hence, cobalt-moieties with the highest calculated O₂ adsorption energy should

Fig. 3 Experiment versus theory. a-f Comparison between the K-edge XANES experimental spectrum of Co₀.₅ (black hollow circles) and the theoretical spectrum calculated with the depicted structures (solid red lines). Cobalt, nitrogen, oxygen and carbon atoms are represented in purple, blue, red and gray, respectively.
be the most active ones, which gives the following expected ORR turnover frequency ranking CoN2C5 > CoN4C12 > CoN3C10,porp. To better assess which moieties may be present in Co0.5 we measured the magnetic susceptibility of Co0.5 and N–C with superconducting quantum interference device (Supplementary Fig. 7). The plot of the inverse of the magnetic molal susceptibility \( \chi_m \) of Co0.5 is linear with temperature (inset of Supplementary Fig. 7), as expected for Curie–Weiss paramagnetism. The positive intercept at 0 K leads to a negative Curie–Weiss temperature of –0.36 K, signifying weak antiferromagnetic interaction between magnetic moments.\(^{48}\) The value of the slope \( \chi_m/\mu_B = f(T) \) yields a magnetic moment \( \mu_{\text{eff}} = 3.52 \text{ Bohr magnetons (} \mu_B \) \), averaged on all cobalt moieties in Co0.5. For the first-row transition metals, to the first approximation, only the spin contribution to the effective magnetic moment can be considered (\( \mu_{\text{eff}} = 2 \mu_B \sqrt{\langle s^2 + s \rangle} \) leading to \( s_{\text{average}} = 1.33 \) in Co0.5, where \( s_{\text{average}} \) is the spin density averaged on all cobalt moieties present in Co0.5. According to the DFT spin density analysis and selecting the three best candidates on the basis of EXAFS and XANES analysis (Supplementary Table 4, CoN2C5, CoN4C10,porp and O2–CoN2C5 in their ground state, spin density of cobalt of 0.88, 0.58 and 1.83, respectively), one can propose that Co0.5 contains for example CoN2C12 and O2–CoN4C5 in a 53%/47% distribution, or CoN4C10,porp and O2–CoN2C5 in a 40%/60% distribution. Both distributions result in a theoretical \( s_{\text{average}} \) value of 1.33, similar to the experimental value (Supplementary Table 5). Considering only these three motifs, the fraction of O2–CoN2C5 sites must be in the range of 47–60%, the remaining being split between CoN2C12 and CoN4C10,porp sites.

We recently demonstrated that the porphyrinic FeN4C12 moiety with one or two axial ligands matched the XANES experimental spectrum of Fe0.5 and other Fe-based catalysts.\(^{22}\) Since defective Fe-porphyrinic moieties were not investigated in that study, we extended here the XANES analysis of Fe0.5 in order to investigate whether such Fe-based moieties could also match the experimental XANES spectrum of Fe0.5. The analyses are shown in Supplementary Fig. 8 for FeN4C10,porp and FeN2C5. While O2–FeN4C10,porp reproduces the general features of the spectrum, the fit quality is poorer than that obtained with O2–FeN4C12 (Fig. 5e, f in ref. \(^{22}\)). Although this does not preclude the existence of FeN4C10,porp moieties in Fe0.5 they may only represent a minor iron fraction. The present study therefore suggests that the structural disparity of MeNxC5 moieties is larger in Co–N–C than Fe–N–C materials. Support for this is also provided by square-wave voltammetry (SWV) revealing a broader peak for Co0.5 (Supplementary Fig. 2).

**Operando XANES signatures of Co- and Fe-moieties during ORR.** We then investigated the behavior of Co- and Fe-based moieties in operando conditions. Figure 4a shows the normalized operando XANES spectra recorded at ORR potential range for Co0.5 in acid medium and Fig. 4b shows the same type of data for Fe0.5. Although the latter show a large change with electrochemical potential, similar to a previous report by Mukerjee’s group on other Fe catalysts\(^{43}\), the magnitude of the change is insignificant for Co0.5 in the ORR region, even on the differential \( \Delta \mu \) spectra (inset of Fig. 4a). The potential dependence of the XANES spectra observed on Fe0.5 in N2-saturated electrolyte supports the fact that the XANES variability is primarily controlled by the electrochemical potential, while the adsorption of O2 or oxygen intermediates has only a minor effect (Fig. 4d). The spectral changes observed in Fig. 4b probably result not only from a change in oxidation state, which would a priori only shift the edge position of the XANES spectra, but also from deeper structural changes and reorganization of the N (or C) ligands, as proposed in ref. \(^{26}\) and/or an Fe(II) low-to-high spin crossover.\(^{49}\) SWV (Supplementary Fig. 2) shows that, while Fe0.5 displays a clear peak at 0.75 V vs. RHE in acidic medium, Co0.5 did not show any signal in the 0–1 V region, but instead shows a redox transition at 1.25 V vs. RHE. This largely explains the different potential-dependences of the XANES spectra recorded in the ORR region for Fe0.5 and Co0.5. In addition, the redox potential observed for Fe0.5 corresponds to its onset potential for the ORR (see Fig. 3b in ref. \(^{22}\)). It is however surprising that the XANES spectra of Fe0.5 are still changing below 0.6 V vs. RHE, while most Fe ions should already be in +II oxidation state. Spin-state or conformation changes may still be occurring below 0.6 V.

The very different position of the redox peak for Fe0.5 and Co0.5 experimentally supports the fact that O2 adsorption on cobalt moieties is much weaker than on iron moieties. Linear relationships between the Me(III)/Me(II) redox potential and the adsorption energy for O2 have clearly been established for various macrocycles comprising first-row transition metals (Fig. 3 in ref. \(^{42}\)). On this basis, the experimentally-determined relative positions of the redox peak for Fe0.5 and Co0.5 (0.75 and 1.25 V vs. RHE) are in line with our DFT calculations that predict O2 adsorption energies of \(-1.8 \text{ eV for FeN2C12 and } -0.8 \text{ to } -1.2 \text{ eV for the porphyrinic Co-moieties.}"

**Comparative operando XANES spectra collected under O2 and N2 provide additional insights into the reactivity of the active sites.** Fig. 4c, d show the XANES spectra measured in O2- and N2-saturated acidic electrolyte at two representative potentials (0.2 and 0.8 V vs. RHE) for Co0.5 and Fe0.5 respectively. Although for Fe0.5 we do not observe significant spectral changes in O2-free or O2-saturated electrolyte, for Co0.5 a clear variation is observed between 7720 and 7735 eV. This effect is magnified in the experimental \( \Delta \mu_{\text{O2-N2}} \) spectra obtained by subtracting from the XANES spectrum of Co0.5 measured under O2 that measured under N2 (insets of Fig. 4c, d). A fit of the \( \Delta \mu_{\text{O2-N2}} \) spectrum of Co0.5 at 0.8 V is shown in Supplementary Fig. 9, corresponding to an active-site structure with four nitrogen atoms at 1.95 Å with or without an oxygen molecule adsorbed end-on at 2.22 Å. In N2-saturated electrolyte, oxygen comes exclusively from water activation, whereas in O2-saturated electrolyte the oxygen may come from water activation or O2 adsorption. These \( \Delta \mu \) analyses strongly suggest that, for Fe0.5, an Fe-O bond probably exists in both O2-saturated and N2-saturated electrolytes, with oxygen originating from O2 and H2O, respectively. In contrast, for Co0.5 the active sites are less oxophilic and a Co–O bond is formed only in O2-saturated electrolyte. To the best of our knowledge, this is the first direct operando evidence of molecular O2 adsorption on the cobalt centers in Co–N–C materials. The general picture that emerges from the present work supports the

### Table 1 XANES structural parameters for porphyrinic cobalt moieties

<table>
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<tr>
<th>Row nbr.</th>
<th>Moiety</th>
<th>Co-N/Å</th>
<th>Co-O/Å</th>
<th>Bending/°</th>
<th>Rsq</th>
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<td>—</td>
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<td>—</td>
<td>—</td>
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<tr>
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<td>1.86 (4)</td>
<td>32 (7)</td>
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</tr>
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<td>2.01 (4)</td>
<td>1.90 (4)</td>
<td>50 (5)</td>
<td>1.13</td>
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</table>

Abbreviation: XANES, X-ray absorption near-edge structure

Best-fit structural parameters obtained from the analysis of the XANES spectrum of Co0.5 performed on the structures proposed in this work and depicted in Fig. 3. Bending is the angle between the Co-O vector and the O-O bond and \( R_{sq} \) is the residual function. Errors are given in parentheses.
view that the active moieties formed at high temperature have a porphyrinic or defective porphyrinic architecture and also obey to the same general trends that have been reported on well-defined macrocycles comprising 3d transition-metal ions from the first row. However, while cobalt moieties in pyrolyzed materials do not change structure when catalyzing the ORR in acid medium, the iron moieties do change structure due to the change of oxidation and/or the spin state. The exact structural change induced by the redox switch will require extensive modeling work, which is beyond the scope of the present paper. The onset of OER in acidic medium on Co0.5 is not well defined but clearly situated above the redox peak associated with Co(II)/Co(III) at 1.25 V vs. RHE (Supplementary Fig. 2), suggesting Co(III)NxCy moieties could be the active-site for OER in Co0.5. The operando XANES spectra were also recorded at OER potentials, and these spectra showed only a small difference compared to the XANES spectrum recorded at 1.0 V vs. RHE (Supplementary Fig. 11), supporting the fact that CoNxCy moieties were still present at such high potential and are responsible for the OER activity of Co0.5. As for the ORR, the oxygen-binding energy of the porphyrinic CoN4C12 moiety is close to the ideal value that may be expected for a Metal-N4 moiety. OER activity has also been reported experimentally for heterogeneous Co–N2C materials in alkaline medium. These heterogeneous catalysts mostly comprised metallic cobalt or cobalt oxide while the presence of CoNxCy moieties could not be certified. The onset of OER in acidic medium on Co0.5 is not well defined but clearly situated above the redox peak associated with Co(II)/Co(III) at 1.25 V vs. RHE (Supplementary Fig. 2), suggesting Co(III)NxCy moieties could be the active-site for OER in Co0.5. The operando XANES spectra were also recorded at OER potentials, and these spectra showed only a small difference compared to the XANES spectrum recorded at 1.0 V vs. RHE (Supplementary Fig. 11), supporting the fact that CoNxCy moieties were still present at such high potential and are responsible for the OER activity of Co0.5. As for the ORR, it must be noted that the cobalt content in Co0.5 was not optimized to reach the highest activity.

In contrast, Co–N–C materials should be stable for long duration at low potentials needed to catalyze the HER. Two
recent reports demonstrated the high activity of CoN₈-C₉ moieties toward HER in acid and alkaline medium.²⁸,²⁹ The HER polarization curve of Co₉.₅ is however negatively shifted by 200 mV relative to Pt/C (Supplementary Fig. 12). In addition, Co₉.₅ did not show any activity for the HOR (Supplementary Fig. 13), highlighting an irreversible behavior between HER and HOR on cobalt moieties. This intriguing fact seems to also apply to non-precious metal solid-state materials such as Mo and W nitrides, sulfides, and carbides. Such structures lead to efficient HER catalysts but were never reported to be efficient HOR catalysts.⁵⁶,⁵⁷

**Discussion**

We identified with XANES, EXAFS, magnetic susceptibility measurements and DFT analysis the detailed structures and electronic state of single-atom catalytic sites in pyrolyzed Co–N–C materials. Three (defective) porphyrinic moieties were identified and showed some activity toward the ORR, OER and HER in acidic medium. DFT-D calculations showed that these cobalt moieties bind oxygen intermediates too weakly relative to an optimum Metal–N–C ORR catalyst, while iron moieties bind oxygen intermediates more strongly than cobalt ones. It however cannot be determined from the present study if iron moieties bind oxygen intermediates more or less strongly than optimally desired for the ORR. These insights support that the general activity descriptors for the active sites in pyrolyzed Metal–N–C catalysts are similar to those identified earlier for molecular Metal-N₄ macrocycles. For Co–N–C catalysts, modifications of the carbon matrix with nitrogen or other light elements resulting in a stronger O₂ binding energy at cobalt centers should improve their ORR activity. Generally, rational modification of the carbon matrix hosting such metal-centered moieties could be used for optimizing their activity toward a large variety of (electro)chemical reactions. These materials can bridge the gap between molecular and solid-state catalytic materials, offering perspectives for catalysts based on earth-abundant elements.

**Methods**

**Synthesis.** The catalyst precursor of Co₉.₅ was prepared from a Zn(II) zolotid imidazolate framework (Baseline Z1200 from BASF, labeled ZIF-8), Co(II) acetate and 1,10-phenanthroline. Weighed amounts of the powders of Co(II)Ac (15.97 mg), phen (200 mg) and ZIF-8 (800 mg) were ball-milled (Pulverisette 7 premium, Fritsch) at 400 rpm for 2 h (4 × 30 min with 5 min rest in-between) in a ZrO₂ crucible (45 cm³) filled with 100 ZrO₂ balls (5 mm diameter). A split-hinge oven was equilibrated at 1,050 °C under Ar flow, and the catalyst precursor was quickly introduced and pyrolyzed at 1,050 °C in Ar for 1 h (see details in ref.22). The N–C material was prepared similarly but without cobalt. Due to a mass loss of 65–70 wt% during pyrolysis in Ar (unmodified by the presence of Co or Fe at 0.5 wt%) caused by volatile products formed from ZIF-8 and phen while Co does not form volatile compounds, the cobalt content in Co₉.₅ is 1.5 wt%.

**Rotating ring disk electrode measurements.** Electrochemical activity and selectivity toward the ORR was determined using the RRDE technique. For Co₉.₅, N–C and Pt/C (5 wt% Pt/C, provided by Johnson Matthey) catalysts, an ink including 10 mg of catalyst, 109 µl of a 5C wt% Nafion® solution containing 15–20% water, 300 µl of ethanol and 36 µl of de-ionized water was sonicated and mixed using a vortex. An aliquot of 9 µl was deposited on the glassy-carbon disk (0.247 cm²) with a Pt ring (Pine Instruments, nominal collection efficiency 0.97), resulting in a loading of 818 µg cm⁻². For lower Co₉.₅ loadings (200 µg cm⁻²), the catalyst mass and Nafion solution aliquot in the ink were proportionally decreased, and the decrease in Nafion solution balanced by increased ethanol aliquot. 9 µl of ink was again deposited on glassy carbon. The working electrode with the deposited catalyst layer was used in a four-electrode cell setup connected to a bipotentiostat (BioLogic SP 300) and rotator (MSP, Pine Instruments). The counter and reference electrodes were a graphite rod and a reversible hydrogen electrode (RHE), respectively. The acetic electrolyte was an O₂-saturated aqueous solution of 0.1 M H₂SO₄ except for ORR on Pt/C (0.1 M HClO₄). For Pt/C only, the electrode was first cleaned by performing 300 cycles at 500 mV s⁻¹ between 0 and 1 V vs RHE. The RDE polarization curves were recorded with a scan rate of 10 (Fe–N–C) or 50 mV s⁻¹ (Pt/C, to avoid contamination) at 1.600 r.p.m. and corrected for the background current measured in N₂-saturated electrolyte. The second cycle was used for correction. For measuring the % H₂O₂ released during ORR, the potential of the Pt ring was held at 1.2 V vs. RHE.

**Square-wave voltammetry.** Catalysts inks were prepared by dispersing 3.1 mg catalyst in a solution prepared by mixing 150.2 µl of millipore water, 465 µl of isopropanol alcohol and 6.2 µl of 5 wt% Nafion® (Nafion to catalyst mass ratio of 10 wt%). The ink solution was then sonicated 60 min. 20 µl of the ink was pipetted on glassy-carbon disk (0.247 cm²) to reach a loading of 400 µg cm⁻². This lower loading than used for most RRDE experiments was necessary to obtain a proper balance between the signal coming from the redox peak and that due to the double layer. The electrodes were dried through a rotational drying method at 800 r.p.m. SWV experiments were carried out in 0.1 M HClO₄ aqueous electrolyte using an Autolab bipotentiostat (PGSTAT302N) with a step potential of 5 mV, potential amplitude of 20 mV and scan frequency of 10 Hz in a standard electrochemical cell (Chromel).
(core ionization threshold energy) and $S_N^2$ (amplitude reduction factor taking into account intrinsic losses).

The XANES data analysis of Co$_{0.5}$ was carried out with the MXAN code in the framework of the full MS scheme, following the same modeling approach adopted to identify the structure of the catalytic active sites in Fe–N–C materials. The MXAN method is based on the MT approximation for the shape of the potential and uses a complex optical potential, based on the local density approximation of the self-energy of the excited photoelectron. The minimization of the Co(II) XANES spectrum has been carried out starting from the X-ray structure of this compound, while in the case of Co$_{0.5}$ we tested different coordination geometries.

The cluster size used in the calculations was chosen on the basis of a convergence analysis. This fit includes a minimal number of selected parameters: the Co–N and Co–O distances, the Co-displacement, the Co-5th ligand distance and the bending angle between the Co–O vector and the O–O bond. During the fit, the outer carbon atoms of the ring rigidly followed the motion of the nitrogen atoms. Least-square fits of the experimental data in the space of the structural parameters were achieved by minimizing the residual function defined as

$$R_B = \frac{n}{N} \sum_{i=1}^{N} \left( \frac{m_i y_i^\text{th} - m_i y_i^\text{exp}}{e_i} \right)^2,$$

where $n$ is the number of independent parameters, $m$ is the number of data points, $y_i^\text{th}$ and $y_i^\text{exp}$ are the theoretical and experimental values of absorption, respectively, $e_i$ is the individual error in the experimental data set, and $w_i$ is a fitting weight. Here, we assumed a constant experimental error, $e_i = 1\%$, for the whole experimental data set. Five non-structural parameters have been optimized, namely the Fermi energy level $E_F$, the experimental resolution $\Gamma_{\text{exp}}$, the energy and amplitude of the plasmon, $E_p$ and $A_p$. The fit of the Ag XANES spectrum of Co$_{0.5}$ in O$_2$ or N$_2$-saturated electrolyte was obtained by the MXAN code with the following procedure: (1) Theoretical XANES spectrum calculation of the CoN$_4$C$_2$ moiety as reference, using the spectrum under nitrogen at 0.8 V. (2) At each step of the fitting procedure the program calculated the theoretical spectrum of a CoN$_4$C$_2$:O$_2$ moiety under oxygen. (3) The difference spectrum is calculated.

**DFT-D computation.** DFT-D computations were carried out on cluster models shown in Supplementary Fig. 6. The bonding bands were saturated with hydrogen. The computational method is based on the DFT cluster approach augmented with an empirical dispersion term as implemented in deMon2k computer program used for the present computations. For the exchange-correlation functional, the approximations of Perdew–Burke–Ernzerhof's 1996 were used. Triple-$\zeta$ basis sets were used for the C and H atoms and double-$\zeta$ bases plus polarization for Co(II) cations. Automatically generated auxiliary functions up to $l$ = 2 (for the metal atom) and $l$ = 3 (for H, C, O atoms) were used for fitting the density. A quasi-Newton method in internal redundant coordinates with analytical energy and forces was used for structure optimization. The convergence was based on the Cartesian gradient and displacement vectors with thresholds of $10^{-3}$ a.u. The energy convergence was set to $10^{-4}$ a.u. The binding energy of cobalt cation per Co–N bond (BE) and adsorption energy of end-on adsorbed O$_2$ molecule ($E_{\text{ads}}$) are obtained as

$$\text{BE} = E_{\text{tot}}(\text{complex}) - E_{\text{tot}}(\text{CoII}) - E_{\text{tot}}\left(\text{N}_2\text{C}_2\right)^-.$$

In the above formula, the total energies for the ground state triplet dioxygen with total spin $S$ = 1 (two unpaired electrons) and Co$^{2+}$ in its quartet ground state are obtained as a difference between the total energies of the higher-energy minima states and the ground state. The atomic spin density was computed for all the Co–N and Co–O distances, the Co-displacement, the Co-5th ligand distance and the bending angle between the Co–O vector and the O–O bond. During the fit, the outer carbon atoms of the ring rigidly followed the motion of the nitrogen atoms. Least-square fits of the experimental data in the space of the structural parameters were achieved by minimizing the residual function defined as

$$R_B = \frac{n}{N} \sum_{i=1}^{N} \left( \frac{m_i y_i^\text{th} - m_i y_i^\text{exp}}{e_i} \right)^2,$$

where $n$ is the number of independent parameters, $m$ is the number of data points, $y_i^\text{th}$ and $y_i^\text{exp}$ are the theoretical and experimental values of absorption, respectively, $e_i$ is the individual error in the experimental data set, and $w_i$ is a fitting weight. Here, we assumed a constant experimental error, $e_i = 1\%$, for the whole experimental data set. Five non-structural parameters have been optimized, namely the Fermi energy level $E_F$, the experimental resolution $\Gamma_{\text{exp}}$, the energy and amplitude of the plasmon, $E_p$ and $A_p$. The fit of the Ag XANES spectrum of Co$_{0.5}$ in O$_2$ or N$_2$-saturated electrolyte was obtained by the MXAN code with the following procedure: (1) Theoretical XANES spectrum calculation of the CoN$_4$C$_2$ moiety as reference, using the spectrum under nitrogen at 0.8 V. (2) At each step of the fitting procedure the program calculated the theoretical spectrum of a CoN$_4$C$_2$:O$_2$ moiety under oxygen. (3) The difference spectrum is calculated.

**References**


interpretation. G.F.H. and S.L. performed the TEM characterization. F.J. and A.Z. supervised the project, wrote and edited the manuscript, with inputs from all authors.

**Additional information**

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