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Review Article

Recent advances of Fe–N–C pyrolyzed catalysts for the oxygen reduction reaction



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Abstract

This review summarizes recent advances in the development of pyrolyzed M–N–C catalysts for the oxygen reduction reaction, focusing on activity, stability, and the reactivity descriptors proposed for the rational design of pyrolyzed M–N–C catalysts. We discuss the last advances in achieving high catalytic activity and stability and the new insights into the characterization of FeN₄ active sites by Mössbauer spectroscopy in combination with Density Functional Theory (DFT) calculations of the Fe–N–C catalysts. In addition, we present the different reactivity descriptors proposed in the literature for the rational design of Fe–N–C pyrolyzed materials: (i) structural descriptors determined by X-Ray Photoelectron Spectroscopy (XPS) and Mössbauer spectroscopy and (ii) the redox potential of the active center MN_x .

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Introduction

Electrochemical reactions such as hydrogen evolution and hydrogen oxidation reaction, oxygen reduction reaction (ORR), and the oxygen evolution reaction are the basis of industrial processes such as water electrolysis,

fuel cells, and rechargeable metal-air batteries. The need for noble metals, such as Pt-based electrocatalysts for the ORR and hydrogen evolution reaction/hydrogen oxidation reaction and RuO₂/IrO₂ for the oxygen evolution reaction, is one of the major obstacles for their commercialization owing to the high price and scarcity of the noble metals [1-3]. The design and synthesis of low-cost, efficient, and durable electrocatalysts for energy conversion is one of the main challenges of the present research study. The ORR is well studied because it is crucial for the widespread use of fuel cells. Two main alternatives have been presented for reducing the presence of noble metals in fuel cells: (i) enhancing noble metal mass activity via alloying or core-shell nanostructures and (ii) replacement of noble metal by nonprecious metal catalysts based on earth-abundant elements [4]. This review is focused on the second alternative, specifically on pyrolyzed Fe–N–C catalysts, active sites of which in most cases seem to involve an FeN₄ structure, similar to intact molecular catalysts such as metal porphyrins and phthalocyanines. MN₄ molecular catalysts have been widely studied owing to the excellent electrocatalytic activity for many reactions [5-12]. Since the pioneering work of Jasinski [13] that reported the catalytic activity of cobalt phthalocyanine for the ORR in alkaline media, a considerable effort has been made to use these molecular catalysts for the ORR. Despite the excellent catalytic activity in basic media, there is a critical lack of stability in acidic media owing to the degradation of the active centers and metal loss to the electrolyte. Several strategies have been proposed to increase the activity and durability in MN₄ molecular catalysts in both acidic and alkaline media [14,15]. However, the low stability in acidic media prevents the practical applications of these catalysts [16].

Heat treatment of different metals, salts, and carbon and nitrogen precursors is one of the most successful synthetic routes to increase the activity and stability for the ORR. The performance of the M–N–C materials depends on the temperature of heat treatment and the nature of precursors. The hieratically structured metal– organic framework (MOF) has shown good catalytic activity [17,18]. Besides, the MOF can also act as a C– N precursor and as an autotemplate for pyrolyzed M– N–C catalysts. MOF-derived M–N–C catalysts seem

to be the most active for the ORR [19-22]. The control over the porosity and the distribution of the precursors (metal, nitrogen, and carbon in the MOF structure) generates M-N-C catalysts with tunable catalytic activity [23]. Durable M-N-C materials are obtained when aromatic polymers are used as C-N precursors adsorbed in carbon support and in the presence of metal salts (Fe or Co) [24]. The high durability in acidic media (more than 700 h at 0.4 V in a fuel cell) is associated with the high level of graphitization of the carbon matrix developed during pyrolysis. The use of hard templates has also been explored [25,26]. These catalysts present high activity, a high electroactive area, and respectable durability for ORR at all pH values [27]. The use of a template induces an increase in the area and hence increases the active sites exposed to the electrolyte, increasing mass transport.

Several reviews have been published on M-N-C pyrolyzed catalysts for ORR [28–33]. This review presents a summary of the last advances in catalytic activity, stability, active site characterization, and development of reactivity descriptors described in the literature, which are the basis for the design of pyrolyzed Fe–N–C catalysts.

Catalytic activity and stability of M-N-C

Despite efforts using new synthetic routes, the onset potentials of the ORR in acidic media remain in the range of 0.80-0.95 V vs. Reversible Hydrogen Electrode (RHE) and close to 1 V vs RHE in basic media [34]. The goal is to selectively insert high-density homogeneously distributed single MN₄ atomic sites over a highly graphitized matrix. Local electron density of MN₄ active sites can be modulated by doping with N heteroatoms [33,35,36]. The catalytic activity of FeN₄ active sites depends on the ratio of the amount of pyridinic to pyrrolic nitrogen functionalities because the former (i) is related to a higher exposure of edge defects on the carbon layer, (ii) is related to the formation of FeN_x moieties, and (iii) acts as secondary active sites promoting the reduction of H₂O₂ to H₂O [37].

The inclusion of S atoms has been also studied to modulate the catalytic activity of the FeN₄ active sites. Mun et al. [38] explored the modulation of the FeN₄ activity by the inclusion of S in the graphitic layer as oxidized electron-withdrawing S functionalities (C-SO_x) or electron-donating thiophene—like S, increasing the activity with electron-withdrawing groups. Choi et al. [39] demonstrated by the evaluation of the O₂— FeN₄ binding energy that the inclusion of hydroxyl and epoxy groups in the carbon lattices could decrease the activity in FeN₄ sites. This inclusion strongly modifies the E_b because it alters the local iron electronic structure influenced by the variation of the π -electron delocalization over the C matrix.

Although the Fe–N–C exhibits good performance in ORR, the main challenge for practical applications is to increase their long-term activity and stability in acidic media under *operando* conditions. Among all the degradation hypotheses proposed in the literature [40], there is a consensus about degradation mechanisms that cause activity loss: (i) the FeN₄ demetallation and (ii) the carbon oxidation reaction [32]. Demetallation of the active centers depends on the applied potential and is mainly induced by the carbon oxidation caused by H_2O_2 or reactive oxygen species by-products from the ORR or by leaching under acidic conditions [30,32,33,39,41–43].

Kumar et al. [44] suggested that the activity loss of M– N–C catalysts (Fe or Co) containing metal-based nanoparticles under simulated operando conditions (0.6–1.0 V vs. RHE) is associated with an imperfect graphene coverage of the metallic particles that leads to the leaching of the metallic content. However, during the start-up/shutdown test (1.0–1.5 V vs. RHE), an important activity loss was detected even for catalysts having only MN₄ atomically dispersed sites. This was attributed to the carbon oxidation reaction that occurred over the graphitic surface (CO and CO₂ releasing), reflecting on a conductivity reduction (Figure 1a).

Kumar et al. [43] found that significant FeN_x moieties were lost when load-cycling accelerated stress tests (AST) were conducted under O_2 compared with those conducted under Ar atmosphere, evidenced by the formation of iron oxide particles at 80 °C (Figure 1a). The authors attribute that corrosion observed is induced by the reactive oxygen species by-products from ORR. Recently, Santori et al. [45] demonstrated that a Fe-N-C catalyst containing only FeN_x sites pyrolyzed under NH₃ atmosphere presents similar activity to that of the Ar-pyrolyzed ones, but they differ in their stability because the NH₃-treated ones suffer from major leaching in acidic media and, hence, higher demetallation than the Ar-treated ones. The presence of highly basic N atoms inserted during the NH₃ pyrolysis that suffer protonation in acidic media leads to a weakening or breaking of the Fe-N bond, leading to the loss of Fe ions.

Active site characterization

During the last decade, a great deal of effort has been put into the characterization of the active sites in the Fe-N-C pyrolyzed catalysts [46-48]. The main handicap is the high number of active sites generated during the pyrolysis processes [37]. The Fe-N-C cat-





Degradation models, and structural assignation of Mössbauer parameters. **(a)** Representation of the demetallation produced under load-cycling Accelerated Stress Test (AST) in saturated Ar and O_2 acidic electrolyte, and of the COR mechanism at high potential values (E vs. Reversible Hydrogen Electrode, RHE (V)). Reproduced from the study by Kumar et al [43] with permission. Copyright 2019, John Wiley & Sons, Ltd. In this work, the influence of O_2 on the demetallation and the formation of oxide iron particles was reported. **(b)** Experimental isomer shift (IS) and quadrupolar splitting (QS) values (mm s⁻¹) for D1, D2, and D3 Mössbauer signals (orange, green, and blue symbols, respectively) [20,49,52–64] and theoretical QS values (at the PBE/DZVP2 level) for Fe(III) and Fe(II) FeN₄C_x (x = 10 and 12) models with different spin states (included as bars) [66]. The experimental assignation for D1* as Fe(III)N₄-HS moieties is included as red stars [43,64,65]. COR, carbon oxidation reaction.

alysts contain a variety of different active site structures with different turnover numbers. The active sites can be divided into three groups: (i) N-doped carbon functionalities, (ii) FeN_x active species hosting in micropores or imbedded in the graphitic matrix, and (iii) ironbased oxide/carbide/nitride particles encapsulated in Ndoped carbon shells. Among all the active sites, the FeN₄ moieties are able to reduce O₂ to H₂O and are considered the most active structures for the ORR in acidic and basic media [37,48].

⁵⁷Fe Mössbauer spectroscopy differentiates the local iron environment, oxidation state, and spin configuration of iron in the active sites. Mössbauer signals show at least two or three doublets accompanied by singlets or sextets. The signals have been interpreted considering the previous literature of iron-based inorganic species such as carbides, oxides and nitrides, as well as data of FeN₄ macrocycles [49-51]. The singlets and sextets have been attributed to iron-based inorganic species formed during the pyrolysis (α -Fe and γ -Fe as singlets and Fe_xO_wFe₃C, Fe_xN as sextets). The doublets are assigned to D1, D2, and D3, which correspond to similar iron coordination environment of nonpyrolyzed FeN4 active sites. Figure 1b summarizes experimental isomer shift (IS) and quadrupolar splitting (QS) values (mm s^{-1}) for quadrupolar doublets D1, D2, and D3 extracted from the literature that characterize different Fe–N–C catalysts [52-64]. However, these traditional assignments have been recently questioned. A study of Wagner et al. [65] showed the dependence of the doublet signals, with the temperature and applied field for FeTMPPCl-pyrolyzed catalysts. In addition, some

authors have proposed different assignations based on a link between Mössbauer spectroscopy and other spectroscopic techniques with theoretical DFT calculations [43,65,66]. Mineva et al. [66] proposed a different description for D1 and D2 signals. The study involved pyrolyzed catalysts with only FeN4 actives sites, with D1 and D2 signals reported previously (with IS values between 0.30 and 0.45 mm s⁻¹) [20], and attributes the D1 signal to high-spin $Fe(III)N_4C_{12}$ (S = 5/2) porphyrinic sites (D1* in Figure 1b) and the D2 signal to the presence of low-spin Fe(II)N₄C₁₀ pyridinic units (S = 0). The calculated QS values for Fe(III)N₄C_{10/12} (1a, 1d, 1e, and 1f, S = 5/2) and Fe(II)N₄C_{10/12} models (1a, 1d, 1e, and 1f, S = 0 and 1) are included in Figure 1b. In this figure, the filled red and green zones represent the coincidence of the theoretical data for Fe(III)N₄C₁₂-HS, with experimental IS and QS values previously assigned as D1 sites, whereas those obtained for Fe(II)N₄C₁₀-LS and Fe(II)N₄C₁₀-MS match with the IS and QS values previously assigned as D2 sites. Mineva et al. [66] that D1* units are inserted as superficial sites in the graphitic matrices, fact that suggests the Fe(III) oxidation state and its superior availability for the catalysis in comparison with D2 bulk sites, protected from exposure to the atmosphere. Besides, a recent study supported by in situ Mössbauer spectroscopy confirmed the aforementioned D1* assignation, as the superior durability of D2 bulk sites over the D1* moieties under ORR in acidic media, which suffer demetallation forming iron(III) oxide particles [67]. Reported experimental assignations for D1^{*} as Fe(III)N₄-HS moieties for Fe–N–C catalysts are also included in Figure 1b [43,64,65].

The search for activity descriptors in Fe-N-C pyrolvzed materials is of fundamental importance for the rational design of active catalysts for the ORR. The representation of the adsorption energy versus the experimental catalytic activity shows volcano correlations [68–70], which follow the Sabatier principle [71]. For molecular type MN₄ catalysts, there are several reactivity descriptors [72], such as the number of delectrons in the metal [73,74], the donor-acceptor intermolecular hardness [75,76], the binding energy of intermediates [72,77], and the M(n+)/(n) redox potential [5,6,72,78,79]. In M-N-C catalysts, the reactivity descriptors were focused on structural parameters determined by XPS and Mössbauer spectroscopy of the catalysts. Artyushkova et al. [37] presented a complete study of 45 catalysts synthesized from different precursors for the ORR in acidic media. They found different relationships between the amount and type of active sites determined by XPS versus the total reduction to H₂O or partial reduction to H₂O₂. The four-

Figure 2

electron reduction to water seems to be related to the presence of FeN_x active centers in the catalysts. In addition, there is a linear trend of the activity with the ratio of pyridinic and Fe-N to the pyrrolic functionalities [37]. Ramaswamy et al. [35] explained this dependence because the nitrogen atoms induce a perturbation in the delocalized π -electron of the carbon matrix that affects the electron density on the metal center and then modifies the adsorption of O₂ on the Fe-N_x active site. In addition, a connection between D1 doublet signals (Fe(II)N₄, S = 0), quantified by Mössbauer spectroscopy with the catalytic activity, has been reported (Figure 2a) [50,51,54]. The activity for D1 was explained by Kramm et al. [54] based on its orbital availability compared with that of middle- or high-spin states of FeN₄ sites, which is expected to favor the interaction with O₂ enhancing the ORR activity. In Figure 2b, the reassigned D1* signal likewise shows a linear dependency with the activity that diminishes as the D1* sites dissolve in O2-acid media, while less activity influence by the D2 is observed [67]. The



Different reactivity descriptors for M-N-C pyrolyzed catalysts. (a) Linear dependence of the D1 sites assigned to Fe^{II}N₄-sites from Mössbauer spectroscopy data with the ORR activity for the FeTMPPCI-pyrolyzed catalyst. Reproduced from the study by Kramm et al [51] with permission. Copyright 2019, John Wiley & Sons, Ltd. (b) Linear correlation between the quantified D1* sites by Mössbauer spectroscopy (assigned as Fe(II)N₄C₁₂-HS sites) and the D1:D2 ratio (D2 assigned as Fe(II)N₄C₁₀-LS or Fe(II)N₄C₁₀-MS sites) with the ORR activity of a previous Fe–N–C catalyst reported in the study by Zitolo et al [20]. Figure reproduced with permission from Li et al [67]. Copyright 2020, Creative Commons license. (c) Linear correlation between the formal potential (E vs. Reversible Hydrogen Electrode, RHE (V)) and ORR activity of a series of nonpyrolyzed and pyrolyzed iron and cobalt porphyrine derivatives, reproduced from the study by Venegas et al [81]. Copyright 2020, Elsevier. (d) Tafel slopes for nonpyrolyzed (FeP) and pyrolyzed (Fep-HT) 4PhFeP. Reproduced with permission from Zúñiga et al [84]. Copyright 2019, Elsevier, Creative Commons license. ORR, oxygen reduction reaction.

relations of the structural parameters previously mentioned, supported by XPS and Mössbauer spectroscopy, present a good correlation with the activity in acidic media. However, owing to the protonation of the different types of nitrogen present in the catalysts at low pH, the electron-withdrawing effect on the Fe $-N_x$ active site changes with pH [27].

The redox potential is usually described in MN_4 molecular complexes as the reactivity descriptor for a myriad of reactions [5–12,79]. Zagal et al. [80] showed a linear correlation of the redox potential of several M–N–C catalysts with the activity in acidic media using data from the literature. Venegas et al. [81] established a correlation between the redox potential of iron and cobalt porphyrins before and after the pyrolysis process, with the activity reported for the ORR both in acidic and alkaline media (Figure 2c).

The pH changes the mechanism of the ORR from an inner-sphere mechanism in acidic media to outer-sphere one in basic media because in basic media, the Fe(III) species are strongly coordinated to OH⁻ species avoiding the presence of active Fe(II) [37,82,83]. However, Zúñiga et al. [84] proposed an inner-sphere mechanism in basic media based on the connection between the redox potential and the onset of the polarization curves. In addition, the Tafel plot analysis showed two Tafel slopes, 0.060 and 0.120 Vat low and high overpotentials, respectively, which change around the redox potential Fe(III)OH/(II) of the FeN₄ active site (Figure 2d). Two Tafel slopes imply a change of the inner-sphere mechanism from a region of potential-dependent surface concentration of Fe(II) (low overpotentials) to a region where this concentration is constant (high overpotentials) in both acidic [85,86] and basic media [87].

Conclusions

In this article, we have presented a short review of the recent literature of Fe-N-C pyrolyzed catalysts. The work has been focused on the advances in the activity and stability and in the characterization by Mössbauer spectroscopy and the new reactivity descriptors proposed in the last years. We summarize the new characterization of FeN₄ active sites present in Fe-N-C catalysts, by Mössbauer spectroscopy, and compared with the traditional assignations. We also summarize the degradation mechanism under operando conditions, and the advances to increase the catalytic activity of the Fe-N-C catalyst. We discuss the new advancements in the use of reactivity descriptors for the rational design of these catalysts. We have divided the activity descriptors into two groups: (i) structural descriptors, which are mainly focused on the amount of MN₄ active sites in M-N-C catalysts characterized by XPS and Mössbauer spectroscopy, and (ii) the redox potential of M-N-C. The redox potential of M-N-C can be a good activity

predictor because it can be related to the binding energy of O_2 to the metal center of the active sites in M–N–C catalysts.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

Papers of particular interest, published within the period of review, have been highlighted as:

- * of special interest
- * * of outstanding interest
- Shao M, Chang Q, Dodelet JP, Chenitz R: Recent advances in electrocatalysts for oxygen reduction reaction. *Chem Rev* 2016, 116:3594–3657, https://doi.org/10.1021/ acs.chemrev.5b00462.
- Wang HF, Tang C, Zhang Q: A review of precious-metal-free bifunctional oxygen electrocatalysts: rational design and applications in Zn-Air batteries. Adv Funct Mater 2018, 488: 1803329, https://doi.org/10.1002/adfm.201803329.
- Zhu YP, Guo C, Zheng Y, Qiao SZ: Surface and interface engineering of noble-metal-free electrocatalysts for efficient energy conversion processes. Acc Chem Res 2017, 50: 915–923, https://doi.org/10.1021/acs.accounts.6b00635.
- Kulkarni A, Siahrostami S, Patel A, Nørskov JK: Understanding catalytic activity trends in the oxygen reduction reaction. *Chem Rev* 2018, 118:2302–2312, https://doi.org/10.1021/ acs.chemrev.7b00488.
- Zagal JH: Metallophthalocyanines as catalysts in electrochemical reactions. *Coord Chem Rev* 1992, 119:89–136, https://doi.org/10.1016/0010-8545(92)80031-L.
- Zagal JH, Griveau S, Silva JF, Nyokong T, Bedioui F: Metallophthalocyanine-based molecular materials as catalysts for electrochemical reactions. *Coord Chem Rev* 2010, 254: 2755–2791, https://doi.org/10.1016/j.ccr.2010.05.001.
- Venegas R, Recio FJ, Zúñiga C, Viera M, Oyarzún MP, Neira K, Marco JF, Zagal JH, Tasca F: Comparison of the catalytic activity for O₂ reduction of Fe and Co MN₄ adsorbed on graphite electrodes and on carbon nanotubes. Phys Chem Chem Phys 2017, 19:20441–20450, https://doi.org/10.1039/C7CP03172F.
- Tasca F, Recio FJ, Venegas R, Geraldo DA, Sancy M, Zagal JH: Linear versus volcano correlations for the electrocatalytic oxidation of hydrazine on graphite electrodes modified with MN₄ macrocyclic complexes. *Electrochim Acta* 2014, 140: 314–319, https://doi.org/10.1016/j.electacta.2014.04.059.
- Gulppi MA, Recio FJ, Tasca F, Ochoa G, Silva JF, Pavez J, Zagal JH: Optimizing the reactivity of surface confined cobalt N₄-macrocyclics for the electrocatalytic oxidation of Icysteine by tuning the Co(II)/(I) formal potential of the catalyst. *Electrochim Acta* 2014, 126:37–41, https://doi.org/10.1016/ j.electacta.2013.07.230.
- Gutiérrez CA, Silva JF, Recio FJ, Griveau S, Bedioui F, Caro CA, Zagal JH: In search of the best iron N₄-macrocyclic catalysts adsorbed on graphite electrodes and on multi-walled carbon nanotubes for the oxidation of I-cysteine by adjusting the

Fe(II)/(I) formal potential of the complex. *Electrocatalysis* 2014, 5:426–437, https://doi.org/10.1007/s12678-014-0209-y.

- Recio FJ, Gutierrez CA, Venegas R, Linares-Flores C, Caro CA, Zagal JH: Optimization of the electrocatalytic activity of MN₄macrocyclics adsorbed on graphite electrodes for the electrochemical oxidation of L-cysteine by tuning the M (II)/(I) formal potential of the catalyst: an overview. *Electrochim Acta* 2014, 140:482–488, https://doi.org/10.1016/ j.electacta.2014.04.098.
- Zúňiga C, Tasca F, Calderón S, Farías D, Recio FJ, Zagal JH: Reactivity indexes for the electrocatalytic oxidation of hydrogen peroxide promoted by several ligand-substituted and unsubstituted Co phthalocyanines adsorbed on graphite. *J Electroanal Chem* 2016, **765**:22–29, https://doi.org/10.1016/ j.jelechem.2015.11.007.
- 13. Jasinski R: A new fuel cell cathode catalyst. *Nature* 1964, 201: 1212–1213, https://doi.org/10.1038/2011212a0.
- Venegas R, Recio FJ, Riquelme J, Neira K, Marco JF, Ponce I, Zagal JH, Tasca F: Biomimetic reduction of O₂ in an acid medium on iron phthalocyanines axially coordinated to pyridine anchored on carbon nanotubes. J Mater Chem 2017, 5: 12054–12059. https://doi.org/10.1039/C7TA02381B.
- Abarca G, Viera M, Aliaga C, Marco JF, Orellana W, Zagal JH, Tasca F: In search of the most active MN₄ catalyst for the oxygen reduction reaction. The case of perfluorinated Fe phthalocyanine. J Mater Chem 2019, 7:24776–24783, https:// doi.org/10.1039/C9TA09125D.
- Tammeveski K, Zagal JH: Electrocatalytic oxygen reduction on transition metal macrocyclic complexes for anion exchange membrane fuel cell application. *Curr Opin Electrochem* 2018, 9: 207–2013, https://doi.org/10.1016/j.coelec.2018.04.001.
- Aiyappa HB, Masa J, Andronescu C, Muhler M, Fischer RA, Schuhmann W: MOFs for electrocatalysis: from serendipity to design strategies. *Small Methods* 2019, 3:1800415, https:// doi.org/10.1002/smtd.201800415.
- Gonen S, Elbaz L: Metal organic frameworks as catalysts for oxygen reduction. Curr Opin Electrochem 2018, 9:179–188, https://doi.org/10.1016/j.coelec.2018.03.035.
- Proietti E, Jaouen F, Lefèvre M, Larouche L, Tian J, Herranz J, Dodelet JP: Iron-based cathode catalyst with enhanced power density in polymer electrolyte membrane fuel cells. Nat Commun 2011, 2:416, https://doi.org/10.1038/ncomms1427.
- Zitolo A, Goellner V, Armel V, Sougrati MT, Mineva T, Stievano L, Fonda E, Jaouen F: Identification of catalytic sites for oxygen reduction in iron- and nitrogen-doped graphene materials. Nat Mater 2015, 14:937–942, https://doi.org/10.1038/nmat4367.
- Strickland K, Miner E, Jia Q, Tylus U, Ramaswamy N, Liang W, Sougrati MT, Jaouen F, Mukerjee S: Highly active oxygen reduction non-platinum group metal electrocatalyst without direct metal-nitrogen coordination. Nat Commun 2015, 6: 7343, https://doi.org/10.1038/ncomms8343.
- Wang HF, Chen L, Pang H, Kaskel S, Xu O: MOF-derived electrocatalysts for oxygen reduction, oxygen evolution and hydrogen evolution reactions. *Chem Soc Rev* 2020, 49: 1414–1448, https://doi.org/10.1039/C9CS00906J.
- Armel V, Hindocha S, Salles F, Bennet S, Jones D, Jaouen F: Structural descriptors of zeolitic-imidazolate frameworks are keys to the activity of Fe-N-C catalysts. J Am Chem Soc 2017, 139:453-464, https://doi.org/10.1021/jacs.6b11248.
- Wu G, More KL, Johnston CM, Zelenay P: High-performance electrocatalysts for oxygen reduction derived from polyaniline, iron, and cobalt. *Science* 2011, 332:443–447, https:// doi.org/10.1126/science.1200832.
- Serov A, Artyushkova K, Niangar E, Wang C, Dale N, Jaouen F, Sougrati MT, Jia Q, Mukerjee S, Atanassov P: Nano-structured non-platinum catalysts for automotive fuel cell application. Nanomater Energy 2015, 16:293–300, https://doi.org/10.1016/ j.nanoen.2015.07.002.
- 26. Serov A, Robson MH, Smolnik M, Atanassov P: Tri-metallic transition metal-nitrogen-carbon catalysts derived by

sacrificial support method synthesis. *Electrochim Acta* 2013, 109:433–439, https://doi.org/10.1016/j.electacta.2013.07.104.

 Rojas-Carbonell S, Artyushkova K, Serov A, Santoro C,
 ** Matanovic I, Atanassov P: Effect of pH on the activity of platinum group metal-free catalysts in oxygen reduction reaction. ACS Catal 2018, 8:3041–3053, https://doi.org/10.1021/ acscatal.7b03991.

This study establishes the critical role of the multitude of surface functional groups in mechanism of oxygen reduction reaction as function of the pH.

 Matanovic I, Artyushkova K, Atanassov P: Understanding PGM- ^{**} free catalysts by linking density functional theory calcula- tions and structural analysis: perspectives and challenges. *Curr Opin Electrochem* 2018, 9:137–144, https://doi.org/10.1016/ i.coelec.2018.03.009.

This review discusses the advances in the DFT calculations of corelevel shifts in binding energies of N 1s electrons as measured by Xray photoelectron spectroscopy.

- Li J, Jaouen F: Structure and activity of metal-centered coordination sites in pyrolyzed metal-nitrogen-carbon catalysts for the electrochemical reduction of O₂. Curr Opin Electrochem 2018, 9:198–206, https://doi.org/10.1016/j.coelec.2018.03.039.
- Martinez U, Babu SK, Holby EF, Zelenay P: Durability challenges and perspective in the development of PGM-free electrocatalysts for the oxygen reduction reaction. *Curr Opin Electrochem* 2018, 9:224–232, https://doi.org/10.1016/ j.coelec.2018.04.010.
- Liu J, Zhang H, Qiu M, Peng Z, Leung MKH, Lin WF, Xuan J:
 ** A review of non-precious metal single atom confined nanomaterials in different structural dimensions (1D-3D) as highly active oxygen redox reaction electrocatalysts. J Mater Chem 2020, 8:2222-2245, https://doi.org/10.1039/ C9TA11852G.

This review discusses the recent advances in non-precious metal catalysts such as synthesis, characterization, performance in catalyzing oxygen redox reactions.

- Martinez U, Babu SK, Holby EF, Chung HT, Yin X, Zelenay P: Progress in the development of Fe-Based PGM-free electrocatalysts for the oxygen reduction reaction. Adv Mater 2019, 31:1806545, https://doi.org/10.1002/adma.201806545.
- Jaouen F, Charreteur F, Dodelet JP: Fe-Based catalysts for oxygen reduction in PEMFCs: importance of the disordered phase of the carbon support. J Electrochem Soc 2006, 153: A689–A698, https://doi.org/10.1149/1.2168418.
- He Y, Liu S, Priest C, Shi Q, Wu G: Atomically dispersed metal-nitrogen-carbon catalysts for fuel cells: advances in catalyst design, electrode performance, and durability improvement. *Chem Soc Rev* 2020, 49:3484–3524, https:// doi.org/10.1039/C9CS00903E.
- Ramaswamy N, Tylus U, Jia Q, Mukerjee S: Activity descriptor identification for oxygen reduction on nonprecious electrocatalysts: linking Surface Science to Coordination Chemistry. J Am Chem Soc 2013, 135:15443–15449, https://doi.org/ 10.1021/ja405149m.
- Wang DW, Su D: Heterogeneous nanocarbon materials for oxygen reduction reaction. Energy Environ Sci 2014, 7: 576–591, https://doi.org/10.1039/C3EE43463J.
- Artyushkova K, Serov A, Rojas-Carbonell S, Atanassov P: Chemistry of multitudinous active sites for oxygen reduction reaction in transition metal-nitrogen-carbon electrocatalysts. J Phys Chem C 2015, 119:25917–25928, https:// doi.org/10.1021/acs.jpcc.5b07653.
- Mun Y, Lee S, Kim K, Kim S, Lee S, Han JW, Lee J: Versatile strategy for tuning ORR activity of a single Fe-N₄ site by controlling electron-withdrawing/donating properties of a carbon plane. J Am Chem Soc 2019, 141:6254–6262, https:// doi.org/10.1021/jacs.8b13543.
- Choi CH, Lim HK, Chung MW, Ghon G, Ranjbar S, Altin A, Sougrati MT, Stievano L, Oh HS, Park ES, Luo F, Strasser P, Drazic G, Mayrhofer KJJ, Kim H, Jaouen F: The Achilles' heel of iron-based catalysts during oxygen reduction in an acidic medium. *Energy Environ Sci* 2018, 11:3176–3182, https:// doi.org/10.1039/C8EE01855C.

- Shao Y, Dodelet JP, Wu G, Zelenay P: PGM-Free cathode catalysts for PEM fuel cells: a mini-review on stability challenges. Adv Mater 2019, 31:1807615, https://doi.org/10.1002/ adma.201807615.
- Choi CH, Baldizzone C, Grote JP, Schuppert AK, Jaouen F, Mayrhofer KJJ: Stability of Fe-N-C catalysts in acidic medium studied by operando spectroscopy. *Angew Chem Int Ed Engl* 2015, 54:12753–12757, https://doi.org/10.1002/anie.201504903.
- 42. Yang N, Peng L, Li L, Wei Z: Theoretical research on the oxidation mechanism of doped carbon based catalysts for oxygen reduction reaction. *Phys Chem Chem Phys* 2019, **21**: 26102–26110, https://doi.org/10.1039/C9CP04691G.
- Kumar K, Dubau L, Mermoux M, Li J, Zitolo A, Nelayah J, Jaouen F, Maillard F: On the influence of oxygen on the degradation of Fe-N-C catalysts. *Angew Chem Int Ed* 2019, 132:3261–3269, https://doi.org/10.1002/ange.201912451.
- Kumar K, Gairola P, Lions M, Ranjbar-Sahraie N, Mermoux M, Dubau L, Zitolo A, Jaouen F, Maillard F: Physical and chemical considerations for improving catalytic activity and stability of non-precious-metal oxygen reduction reaction catalysts. *ACS Catal* 2018, 8:11264–11276, https://doi.org/10.1021/ acscatal.8b02934.
- Santori P, Speck FD, Li J, Zitolo A, Jia Q, Mukerjee S, Cherevko S, Jaouen F: Effect of pyrolysis atmosphere and electrolyte pH on the oxygen reduction activity, stability and spectroscopic signature of FeNx moieties in Fe-N-C catalysts. J Electrochem Soc 2019, 166:F3311-F3320, https:// doi.org/10.1149/2.0371907jes.
- Masa J, Xia W, Muhler M, Schuhmann W: On the role of metals in nitrogen-doped carbon electrocatalysts for oxygen reduction. Angew Chem Int Ed 2015, 54:10102–10120, https:// doi.org/10.1002/anie.201500569.
- 47. Jia Q, Ramaswamy N, Tylus U, Strickland K, Li J, Serov A, Artyushkova K, Atanassov P, Anibal J, Gumeci C, Barton SC, Sougrati MT, Jaouen F, Halevi B, Mukerjee S: Spectroscopic insights into the nature of active sites in iron-nitrogencarbon electrocatalysts for oxygen reduction in acid. Nanomater Energy 2016, 29:65–82, https://doi.org/10.1016/ j.nanoen.2016.03.025.
- Jia Q, Ramaswamy N, Hafiz H, Tylus U, Strickland K, Wu G, Barbiellini B, Bansil A, Holby EF, Zelenay P, Mukerjee S: Experimental observation of redox-induced Fe–N switching behavior as a determinant role for oxygen reduction activity. *ACS Nano* 2015, 9:12496–12505, https://doi.org/10.1021/ acsnano.5b05984.
- Kramm UI, Abs-Wurmbach I, Herrmann-Geppert I, Radnik J, Fiechter S, Bogdanoff P: Influence of the electron-density of FeN4-centers towards the catalytic activity of pyrolyzed FeTMPPCI-based ORR-electrocatalysts. J Electrochem Soc 2011, 158:b69-b78, https://doi.org/10.1149/1.3499621.
- Morozan A, Sougrati MT, Goellner V, Jones D, Stievano L, Jaouen F: Effect of furfuryl alcohol on metal organic framework-based Fe/N/c electrocatalysts for polymer electrolyte membrane fuel cells. *Electrochim Acta* 2014, 119: 192–205, https://doi.org/10.1016/j.electacta.2013.12.022.
- Kramm UI, Ni L, Wagner S: 57Fe Mössbauer spectroscopy characterization of electrocatalysts. Adv Mater 2019, 31: 1805623, https://doi.org/10.1002/adma.201805623.

This work reviews the dependence of the formed species in M-N-C catalysts identified by Mössbauer spectroscopy with synthetic conditions and their link with ORR activity. A summary of Mössbauer parameters of MN4 and inorganic species used to interpret the fingerprints of M-N-C catalysts is included.

 Koslowski UI, Abs-Wurmbach I, Fiechter S, Bogdanoff P: Nature of the catalytic centers of porphyrin-based electrocatalysts for the ORR: a correlation of kinetic current density with the site density of Fe-N4 centers. J Phys Chem C 2008, 112: 15356-15366, https://doi.org/10.1021/jp802456e.

- Tributsch H, Koslowski UI, Dorbandt I: Experimental and theoretical modeling of Fe-, Co-, Cu, Mn-based electrocatalysts for oxygen reduction. *Electrochim Acta* 2008, 53:2198–2209, https://doi.org/10.1016/j.electacta.2007.09.027.
- Kramm UI, Herrmann-Geppert I, Bogdanoff P, Fiechter S: Effect of an ammonia treatment on structure, composition, and oxygen reduction reaction activity of Fe-N-C Catalysts. *J Phys Chem C* 2011, 115:23417–23427, https://doi.org/10.1021/ jp207417y.
- 55. Kramm UI, Herranz J, Larouche N, Arruda TM, Lefèvre M, Jaouen F, Bogdanoff P, Fiechter S, Abs-Wurmbach I, Mukerjee S, Dodelet JP: Structure of the catalytic sites in Fe/N/C-catalysts for O₂-reduction in PEMfuel cells. *Phys Chem Chem Phys* 2012, 14:11673–11688, https://doi.org/10.1039/C2CP41957B.
- Ferrandon M, Kropf AJ, Myers DJ, Artyushkova K, Kramm U, Bogdanoff P, Wu G, Johnston CM, Zelenay P: Multitechnique characterization of a polyaniline-iron-carbon oxygen reduction catalyst. J Phys Chem C 2012, 116:16001–16013, https://doi.org/10.1021/jp302396g.
- 57. Kramm UI, Lefèvre M, Larouche N, Schmeisser D, Dodelet JP: Correlations between mass activity and physicochemical properties of Fe/N/C catalysts for the ORR in PEM fuel cell via ⁵⁷Fe Mössbauer spectroscopy and other techniques. *J Am Chem Soc* 2014, **136**:978–985, https://doi.org/10.1021/ ja410076f.
- Kramm UI, Lefèvre M, Bogdanoff P, Schmeißer D, Dodelet JP: Analyzing structural changes of Fe–N–C cathode catalysts in PEM fuel cell by Mößbauer spectroscopy of complete membrane electrode assemblies. J Phys Chem Lett 2014, 5: 3750–3756, https://doi.org/10.1021/jz501955g.
- Brüller S, Liang HW, Kramm UI, Krumpfer JW, Feng X, Müllen K: Bimetallic porous porphyrin polymer-derived non-precious metal electrocatalysts for oxygen reduction reactions. *J Mater Chem* 2015, 3:23799–23808, https://doi.org/10.1039/ C5TA06309D.
- Sahraie NR, Kramm UI, Steinberg J, Zhang Y, Thomas A, Reier T, Paraknowitsch JP, Strasser P: Quantifying the density and utilization of active sites in non-precious metal oxygen electroreduction catalysts. Nat Commun 2015, 6:8618, https:// doi.org/10.1038/ncomms9618.
- Sougrati MT, Goellner V, Schuppert AK, Stievano L, Jaouen F: Probing active sites in iron-based catalysts for oxygen electro-reduction: a temperature-dependent ⁵⁷Fe Mössbauer spectroscopy study. Catal Today 2016, 262:110–120, https:// doi.org/10.1016/j.cattod.2015.10.017.
- Kramm UI, Herrmann-Geppert I, Behrends J, Lips K, Fiechter S, Bogdanoff P: On an easy way to prepare metal-nitrogen doped carbon with exclusive presence of MeN4-type sites active for the ORR. J Am Chem Soc 2016, 138:635-640, https:// doi.org/10.1021/jacs.5b11015.
- Leonard ND, Wagner S, Luo F, Steinberg J, Ju W, Weidler N, * Wang H, Kramm UI, Strasser P: Deconvolution of utilization, site density, and turnover frequency of Fe-nitrogen-carbon oxygen reduction reaction catalysts prepared with secondary N-precursors. ACS Catal 2018, 8:1640-1647, https://doi.org/ 10.1021/acscatal.7b02897.

This paper studies M-N-C catalysts with a variety of secondary nitrogen precursors. This analysis provides a more fundamental description and understanding of the origin of the catalytic reactivity in M-N-C catalysts.

- Zhong L, Frandsen C, Mørup S, Hua Y, Pan C, Cleemanna LN, Jensen J, Li Q: ⁵⁷Fe-Mössbauer spectroscopy and electrochemical activities of graphitic layer encapsulated iron electrocatalysts for the oxygen reduction reaction. *Appl Catal, B* 2018, **221**:406–412, https://doi.org/10.1016/ j.apcatb.2017.09.014.
- Wagner S, Auerbach H, Tait CE, Martinaiou I, Kumar SCN,
 Kübel C, Sergeev I, Wille HC, Behrends J, Wolny JA, Schünemann V, Kramm UI: Elucidating the structural composition of an Fe–N–C catalyst by nuclear- and electron-

resonance techniques. Angew Chem Int Ed 2019, 58:

10486-10492, https://doi.org/10.1002/anie.201903753. The dependence of the D1 Mössbauer signal with the temperature and applied field for a FeTMPPCI pyrolyzed catalyst is reported. The presence of Fe(III)N₄ HS entities was probed by EPR spectroscopy.

Mineva T, Matanovic I, Atanassov P, Sougrati MT, Stievano L, Clémancey M, Kochem A, Latour JM, Jaouen F: **Understanding** 66. active sites in pyrolyzed Fe-N-C catalysts for fuel cell cathodes by bridging density functional theory calculations and ⁵⁷Fe Mössbauer spectroscopy. *ACS Catal* 2019 9: Fe Mössbauer spectroscopy. ACS Catal 2019, 9: 9359–9371, https://doi.org/10.1021/acscatal.9b02586. Through the link between DFT calculation of QS values for FeN₄-Cx

(x = 10 or 12) models with spectroscopic characterization (Mössbauer,)EPR, and magnetization) of a previous reported Fe-N-C catalyst is reported. They re-assign D1* as Fe(III)N₄C₁₂ (S = 5/2) sites, and D2 as $Fe(II)N_4C_{10}$ (S = 0) units.

 Li J, Sougrati MT, Zitolo A, Ablett J, Oguz IC, Mineva T,
 Atanassov P, di Cicco A, Kumar K, Dubau L, Maillard F, Jaouen F: Identification of Durable and Non-Durable FeNx Sites in Fe-N-C Materials for Proton Exchange Membrane Fuel Cells. ChemRxiv 2020, https://doi.org/10.26434/chemrxiv.11842431.v1. Preprint.

A stability and durability study for D1* and D2 sites for a previously reported Fe-N-C catalyst though *in-situ* Mössbauer spectroscopy is informed

- 68. Koper MTM: Theory of multiple proton-electron transfer reactions and its implications for electrocatalysis. Chem Sci 2013, 4:2710-2723, https://doi.org/10.1039/C3SC50205H.
- Koper MTM: Thermodynamic theory of multi-electron transfer 69. reactions: implications for electrocatalysis. J Electroanal Chem 2011, 660:254-260, https://doi.org/10.1016/ j.jelechem.2010.10.004.
- Norksov JK, Rossmeisl J, Logadottir A, Lindqvist L, Kitchin JR, 70. Bligaard T, Jonnson H: Origin of the overpotential for oxygen reduction at a fuel-cell cathode. J Phys Chem B 2004, 108: 17886-17892, https://doi.org/10.1021/jp047349j
- 71. Sabatier P: Hydrogénations et déshydrogénations par catalyse. Ber Dtsch Chem Ges 1911, 44:1984-2001, https://doi.org/ 10.1002/cber.19110440303.
- 72. Zagal JH, Koper MTM: Reactivity descriptors for the activity of molecular MN4 catalysts for the oxygen reduction reaction. Angew Chem Int Ed 2016, 55:14510-14521, https://doi.org/ 10.1002/anie.201604311.
- 73. Zagal J, Paez M, Tanaka AA, dos Santos Jr JR, Linkous CA: Electrocatalytic activity of metal phthalocyanines for oxygen reduction. J Electroanal Chem 1992, 339:13-30, https://doi.org/ 10.1016/0022-0728(92)80442-7.
- 74. Zagal JH, Paez M: Catalytic electrooxidation of 2mercaptoethanol on a graphite electrode modified with metal-phthalocyanines. Electrochim Acta 1989, 34:243-247, https://doi.org/10.1016/0013-4686(89)87092-6
- Cardenas-Jiron GI, Gulppi MA, Caro CA, del Río R, Páez M, 75. Zagal JH: Reactivity of electrodes modified with substituted metallophthalocyanines. Correlations with redox potentials, Hammett parameters and donor-acceptor intermolecular hardness. Electrochim Acta 2001, 46:3227-3235, https://doi.org/ 10.1016/S0013-4686(01)00614-4
- 76. Cardenas-Jiron GI, Zagal JH: Donor-acceptor intermolecular hardness on charge transfer reactions of substituted cobalt phthalocyanines. J Electroanal Chem 2001, 497:55-60, https:// doi.org/10.1016/S0022-0728(00)00434-4.

- 77. He H, Lei Y, Xiao C, Chu D, Chen R, Wang G: Molecular and electronic structures of transition-metal macrocyclic complexes as related to catalyzing oxygen reduction reactions: a density functional theory study. J Phys Chem C 2012, 116: 16038-16046, https://doi.org/10.1021/jp303312r.
- 78. Randin JP: Interpretation of the relative electrochemical activity of various metal phthalocyanines for the oxygen reduction reaction. Electrochim Acta 1974, 19:83-85, https:// doi.org/10.1016/0013-4686(74)85060-7.
- 79. Beck F: The redox mechanism of the chelate-catalysed oxygen cathode. J Appl Electrochem 1977, 7:239-245, https:// doi.ora/10.1007/BF00618991.
- 80. Zagal JH, Ponce I, Baez D, Venegas R, Pavez J, Paez M, Gulppi N: A possible interpretation for the high catalytic ac-tivity of heat-treated non-precious metal Nx/C catalysts for O2 reduction in terms of their formal potentials electrochem. Solid State Lett 2012, 15:B90-B92, https://doi.org/10.1149 2 032206esl
- 81. Venegas R, Muñoz-Becerra K, Candia-Onfray C, Marco JF, Zagal JH, Recio FJ: Experimental reactivity descriptors of M-N-C catalysts for the oxygen reduction reaction. Electrochim Acta 2020, 332:15340, https://doi.org/10.1016/ j.electacta.2019.135340

This paper shows the electrocatalytic trend using the redox potential as reactivity descriptor for the ORR in M-N-C pyrolyzed catalysts.

- Workman MJ, Serov A, Tsui LK, Atanassov P, Artyushkova K: Fe-N-C Catalyst graphitic layer structure and fuel cell per-formance. *ACS Energy Lett* 2017, 2:1489–1493, https://doi.org/ 10.1021/acsenergylett.7b00391.
- 83. Ramaswamy N, Mukerjee S: Influence of inner- and outersphere electron transfer mechanisms during electrocatalysis of oxygen reduction in alkaline media. J Phys Chem C 2011, 115:18015-18026, https://doi.org/10.1021/jp204680p.
- 84. Zúñiga C, Candia-Onfray C, Venegas R, Muñoz K, Urra J, Sánchez-Arenillas M, Marco JF, Zagal JH, Recio FJ: Elucidating the mechanism of the oxygen reduction reaction for pyrolyzed Fe-N-C catalysts in basic media. Electrochem Commun 2019, 102:78-82, https://doi.org/10.1016/j.elecom.2019.04.0

This paper proposes an inner-sphere mechanism for pyrolyzed MN4 complexes in basic media.

- Chlistunoff J: RRDE and voltammetric study of ORR on pyrolyzed Fe/polyaniline catalyst. On the origins of variable tafel slopes. J Phys Chem C 2011, 115:6496–6507, https://doi.org/ 10.1021/jp108350t.
- Osmieri L, Escudero-Cid R, Monteverde AHA, Ocón P, Specchia S: **Performance of a Fe-N-C catalyst for the oxygen** 86. reduction reaction in direct methanol fuel cell: cathode formulation optimization and short-term durability. Appl Catal, *B* 2017, **201**:253–265, https://doi.org/10.1016/ j.apcatb.2016.08.043.
- 87. García A, Retuerto M, Dominguez C, Pascual L, Ferrer P Gianolio D, Serrano A, Aßmann A, Sanchez DG, Peña MA Rojas S: Fe doped porous triazine as efficient electrocatalysts for the oxygen reduction reaction in acid electrolyte. Appl Catal, B 2020, 332:15340, https://doi.org/10.1016/ j.apcatb.2019.118507.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.coelec.2020.08.006.