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Are Fe-N-Cs An Alternative to Pt-based Electrocatalysts for the Next Generation of Proton Exchange Membrane Fuel Cells?

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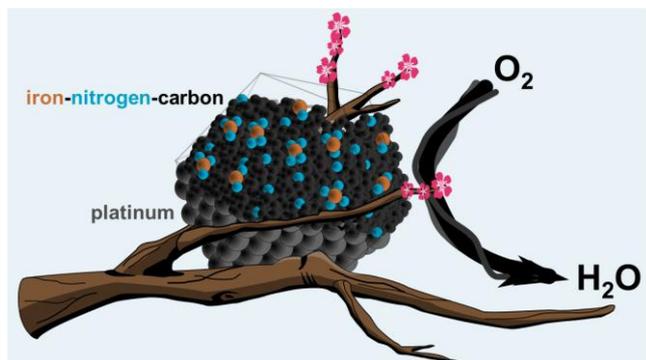
ABSTRACT

Notable progresses have been made for low Pt-based and Fe-N-C electrocatalysts for proton exchange membrane fuel cells (PEMFCs) applications. Particularly, the research and development of cost-effective Fe-N-Cs have witnessed significant improvements in the recent years, due to the need of an alternative candidate to the scarce, and expensive, platinum. Numerous studies have been exploring the design and optimization of Fe-N-Cs and generally make simple performance comparison with commercial Pt/C catalysts on the basis of rotating disk electrode (RDE) and/or membrane electrode assembly (MEA), thus arguing that said materials are comparable, or could even surpass, Pt/C electrocatalysts. The resulting question, *i.e.* ‘are Fe-N-Cs an alternative to Pt-based electrocatalysts in PEMFCs?’ is the centerpiece of this review. Here, the

interconnectedness and differences between Fe-N-Cs and Pt-based materials are discussed from fundamental insights to applications in PEMFCs, covering the oxygen reduction reaction (ORR) mechanism, the nature of active sites and its effect on the intrinsic activity, the rational design of catalyst layer, the electrocatalysts performances in PEMFCs and their durability in operating conditions. This review provides a global picture of the current research state in the field of PEMFCs electrocatalysts, focusing onto the two most important types of cathode materials and aiming to shed light on the potential of Fe-N-Cs as replacement for Pt-based catalysts along with pointing out the research directions toward the next generation of PEMFCs.

KEYWORDS: Fe-N-C electrocatalysts, Pt-based electrocatalysts, oxygen reduction reaction, proton exchange membrane fuel cells, durability, catalytic layer.

Graphical abstract



1. Introduction

Addressing the challenges related to the climate change requires the development of green and sustainable energy conversion or storage systems,¹ such as fuel cells. The latter has attracted great research interest throughout the past decades, with one of the key objectives of said research being to meet the energy requirements needed to become an alternative to fossil energy-based systems.² Proton exchange membrane fuel cells (PEMFCs) operates through two half-cell reactions, namely the hydrogen oxidation reaction (HOR), and the oxygen reduction reaction (ORR), with electric energy output and pure water as products. The ORR exhibits six or more orders of magnitude slower kinetics than the HOR, hence being the limiting reaction.³ Nowadays, platinum-based catalysts are generally regarded as the state-of-the-art electrocatalysts for ORR. Loadings as high as 0.4 mg_{Pt}/cm² are required to promote the ORR while meeting the requirements for automotive practical application. However, the high cost and scarcity of Pt significantly impede the development of PEMFCs.⁴⁻⁵ As such, a target of reducing the Pt usage down to 0.1 mg_{Pt}/cm² without compromising the PEMFC activity or durability was proposed by United States Department of Energy (DOE) for 2025.⁶ Strategies such as alloying Pt with a second, less expensive, metal have been put forward to decrease the Pt loading. This incidentally decreases the cost of the electrocatalyst in the PEMFCs stacks while achieving the enhanced activity owing to the optimized binding energy of the ORR intermediates.⁷⁻⁸ To date, the DOE 2025 target has been fulfilled (*i.e.* activity of 1.08 A/mg_{Pt}@0.9V_{IR-free} with 0.033 mg_{Pt}/cm² and 36 % losses in mass activity after 30k cycles *vs.* DOE target being an activity of 0.44 A/mg_{Pt}@0.9V_{IR-free} with

0.1 mg_{Pt}/cm² and a durability of < 40 % losses in mass activity after 30k cycles⁹), but long term, large-scale deployment of PEMFCs in the field of automotive production might require the use of elements that are far less scarce than Pt. As such, earth-abundant platinum-group metal free (PGM-free) based electrocatalysts and more specifically, metal-nitrogen-carbon (M-N-C) electrocatalysts have been of growing interest, due to their low cost, CO-tolerance and high intrinsic activity toward the ORR.¹⁰⁻¹²

Cobalt phthalocyanine has been proposed in 1964 by Jasinski as an active phase for the ORR.¹³ Following this pioneering work, M-N-C electrocatalysts prepared by high temperature pyrolysis of metal-macrocycle complexes adsorbed on carbon substrate were investigated and showed promising ORR activity.¹⁴⁻¹⁵ In 1989, it was reported by Yeager *et al.* that M-N-C electrocatalysts could be synthesized through pyrolysis of separated metal, carbon and nitrogen sources which enabled better flexibility and control of the electrocatalysts physico-chemical properties.¹⁶ To date, tremendous progresses have been achieved for the preparation of Fe-N-C electrocatalysts (iron being considered as the best 3d-transition metal for M-N-C applied to the ORR) leading to high performances in fuel cells. Very recently, the catalytic activity (0.0442 A/cm²@0.9 V_{IR-free}) or durability (30 mV losses at 0.8 A/cm² after 30k cycles) of Fe-N-C-containing PEMFCs reached the DOE targets (0.044 A/cm²@0.9 V_{IR-free}, ≤ 30 mV losses at 0.8 A/cm² after 30k cycles) for 2025¹⁷, although not simultaneously. In the light of those exciting achievements for both Fe-N-Cs and Pt-based catalysts, getting a comparison statement between both electrocatalysts' families is of extreme interest. Such is the aim of this review that will cover, on both Pt-based electrocatalysts and Fe-

N-Cs (1) the ORR mechanism; (2) the nature of active sites and their plurality; (3) the intrinsic activity regulation; (4) the structural engineering of cathode catalyst layer in PEMFCs; (5) the degradation mechanisms. Finally, outlooks and challenges are addressed to answer the question brought forth in this review, *i.e.* the alternatives to Pt-based electrocatalysts provided by Fe-N-Cs.

2. The ORR mechanism of Pt/C vs. Fe-N-C

One must first clarify fundamental mechanistic insights for the ORR mechanism on both Fe-N-Cs and Pt based electrocatalysts to be able to establish a meaningful comparison. The ORR proceeds by either four-electron ($4e^-$) pathway with H_2O (acidic media) and OH^- (alkaline media) as primary reduction products or two-electron ($2e^-$) pathway with H_2O_2 (in acid) and HO_2^- (in alkaline) as main products.¹⁸⁻¹⁹ The detailed mechanism in acidic media can be divided into three pathways as shown in **Figure 1A**. Typically, the oxygen molecule is first adsorbed and activated on the surface of catalyst to form O_2^* (herein the $*$ is denoted as active site of catalyst), followed by O-O bond cleavage in three different manners, (1) dissociative pathway: the O-O bond in O_2^* is cleaved directly into two O^* intermediates, which are then successively reduced to OH^* and H_2O^* and eventually end up with desorption of H_2O^* , (2) associative-dissociative pathway: OOH^* is first generated from O_2^* , then the O-O bond in OOH^* is cleaved into O^* and OH^* , followed by their successive reductions to form H_2O , (3) the associative pathway: the O_2^* is sequentially reduced to OOH^* and $HOOH^*$, then 2 OH^* can be generated and finally reduced to H_2O^* . For most catalysts (*e.g.* Pt (111) and four

electron-dominated Fe-N-Cs), the associative-dissociative pathway is considered as dominant.²⁰⁻²¹

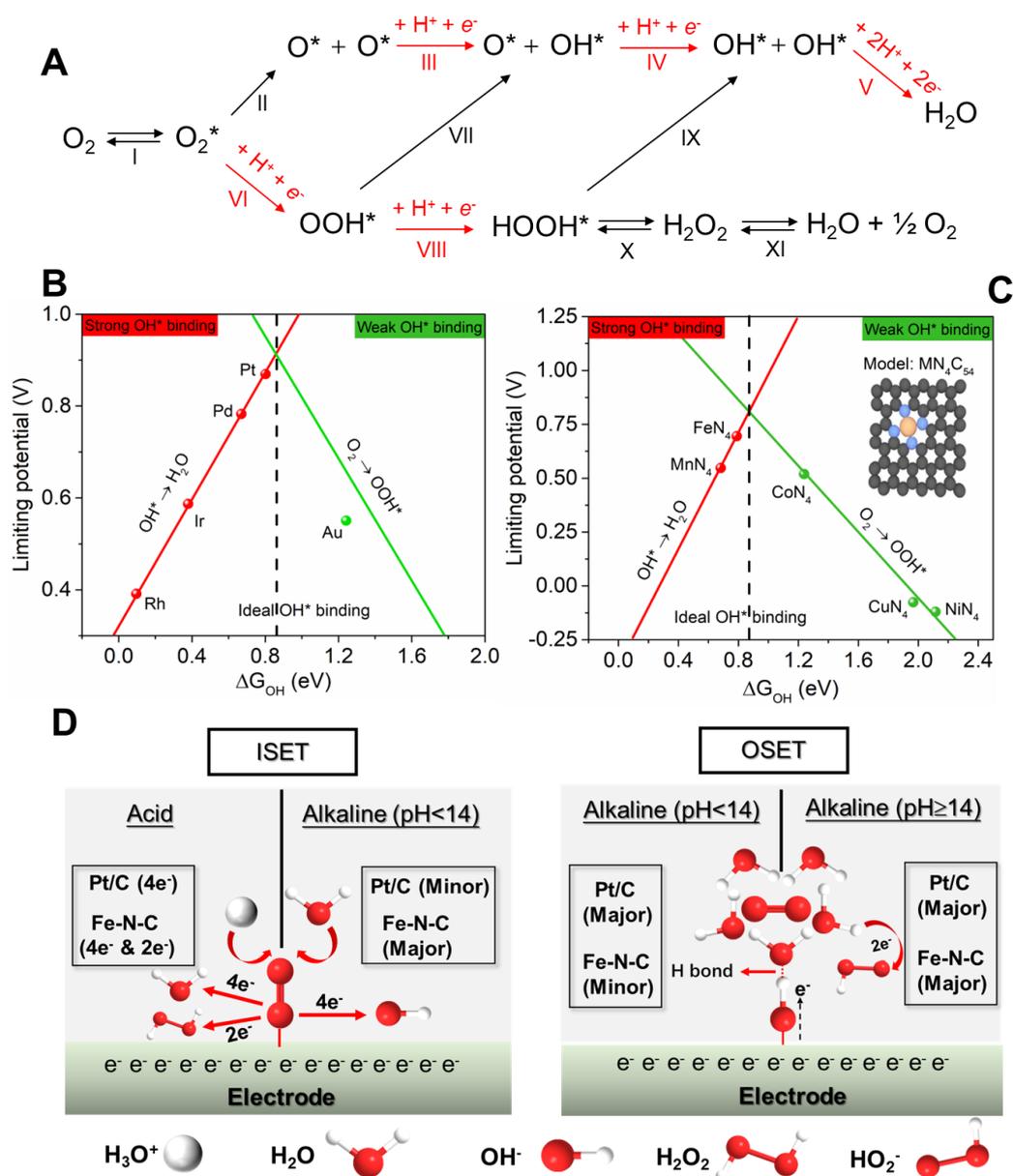


Figure 1. (A) The generalized reaction pathway toward ORR; the red lines correspond to steps involving a proton and an electron (*i.e.* either proton coupled electron transfer or sequential electron transfer/proton transfer); (B) the limiting potential plot for various metal catalysts as a function of OH* Gibbs free energy (ΔG_{OH}), adapted from Ref. 21; (C) the limiting potential plot for various M-N-Cs (M = Fe, Co, Mn, Cu, Ni) catalysts as a function of ΔG_{OH} , adapted

from Ref. 22; (D) The ISET (inner sphere electron transfer) and OSET (outer sphere electron transfer) mechanisms comparison between Pt/C and Fe-N-C. For the ISET, in the case of acid media, the unstable binding of generated H_2O_2 intermediate onto Fe(II)- N_4 leads to partial desorption of H_2O_2 and thus, an incomplete $2e^-$ reduction. In sharp contrast, under mild ($\text{pH} < 14$) alkaline medium, the stable adducts HO_2^- -Fe(II)- N_4 lead to a complete reduction of the HO_2^- to OH^- , whereas an OEST begins to dominate in ORR for Pt/C. Notably, OSET is observed for both Pt/C and Fe-N-C at $\text{pH} \geq 14$ due to full OH^- coverage on the electrode surface.

The association-dissociative pathway typically involves three oxygen intermediates, *i.e.* OOH^* , O^* , OH^* (**Figure 1A**) and the theoretical electrocatalytic activity is strongly dependent of their binding free energies. Nørskov's group^{21, 23-24} proposed the following scaling relations between each of the aforementioned intermediates, *i.e.* $\Delta G_{\text{OH}^*} = 1/2 \Delta G_{\text{O}^*}$ and $\Delta G_{\text{OH}^*} = \Delta G_{\text{OOH}^*} - 3.2 \text{ eV}$, thus implying that the catalyst surface reactivity can be quantified as the function of one binding energy, *e.g.* OH^* . According to the Sabatier principle, the ideal ORR electrocatalyst should bind its intermediates species neither too strong nor too weak.²⁵ This results in the existence of volcano-plot like correlation between the activity and the binding energy of the intermediates (**Figure 1B** and **1C**). Among all investigated elements, Pt exhibits the closest-to-optimum OH^* binding energy, being only 0.1 – 0.2 eV too strong. This can be further improved through modulation of its electronic structure (*e.g.* downshifting the 5d-band center of the Pt surface) to decrease its affinity toward OH^* species. A similar volcano plot is also established for several 3d-transition metal-N-C catalysts, as shown in **Figure 1C**. Fe-N-C appears as the most active M-N-C, owing to its FeN_4 active site and binds OH^* slightly too strongly as well, thus implying that modifying its 3d-band structure might

also results in activity enhancement. Interestingly, the apex potential for extended metallic surfaces is *ca.* 100 mV higher than for M-N-Cs (**Figure 1B** and **1C**), hinting toward an intrinsically inferior activity for Fe-N-Cs *vs.* Pt-based catalysts.

The ORR selectivity (H_2O_2 *vs.* H_2O) mainly depends on the dissociation energy barrier of absorbed O_2 molecule on the surface of the active site. The O_2 dissociation energy barrier on pure carbon materials surface is relatively high due to the weak oxygen adsorption, thus favoring H_2O_2 generation.^{21,26} On the contrary, the O_2 dissociation energy barrier (dominated by associative-dissociative pathway as previously mentioned) on metal surfaces or metal-doped nitrogen-carbon surface is much lower, thus greatly favoring the $4e^-$ pathway for both Pt and Fe-N-C catalysts.²⁷⁻²⁸ The first charge transfer (Step VI in **Figure 1A**) is considered as the determining step (RDS) for both Pt and Fe-N-C electrocatalysts.²⁹⁻³¹ Tse *et al.*³² evidenced the RDS of Pt does not involve a proton transfer step, *i.e.* $\text{Pt} + \text{O}_2 + e^- \rightarrow \text{Pt-OO}^*$, which was later confirmed by George *et al.* and Talarposhti *et al.* in acidic media, owing a high density of Pt nanoparticles onto the carbon surface.³³⁻³⁴ In opposition to Pt catalyst, the RDS of Fe-N-C involves a proton-coupled electron transfer (PCET), *i.e.* $\text{N}_x\text{-Fe} + \text{O}_2 + \text{H}^+ + e^- \rightarrow \text{N}_x\text{-Fe-OOH}^*$.³² This would suggest that in acidic media, the ORR performance of Fe-N-C electrocatalyst is intrinsically inferior to that of Pt catalyst due to the increased complexity of the PCET on the Fe-N-C. Chen *et al.*³⁰ proposed that the PCET was arising from the $2e^-$, H_2O_2 generating pathway, thus implying that the $4e^-$ transfer was proton-independent. Such independence would underline that (i) minimizing the $2e^-$ pathway selectivity on Fe-N-C is critical and (ii) owing that the proton independency is upheld, the Fe-N-Cs would

not be limited by the slow PCET and therefore could potentially compete with Pt-based electrocatalysts.

The ORR process is complicated not only because of multiple electron and proton transfer steps, but also due to the pH dependence of its mechanism. Here, the ORR mechanism as a function of pH is elucidated for both Pt and Fe-N-C. To understand the mechanism, one must first understand the chemical state of the double-layer, which has been discussed in details in the pivotal works of Ramaswamy and Mukerjee:³⁵⁻³⁶ (i) in acidic media and operating ORR conditions, the inner-Helmholtz plane (IHP) consists of chemisorbed O_2 , OH^* and H_2O dipoles, whereas the outer-Helmholtz plane (OHP) consists of solvated O_2 , electrolyte anions and H_3O^+ ; (ii) in alkaline media and operating ORR conditions, the double-layer chemistry is similar, the notable differences being the alkali metal ions replacing the protons from the acidic environment and the fact that the OH^* now arises from direct OH^- adsorption rather than H_2O activation at high potentials. This directly impacts both the Pt and Fe-N-C reactivity: (i) for Pt, in acidic media, the ORR occurs through reduction of the adsorbed O_2 in the IHP, in concert with proton transfers from the OHP to the IHP, leading to a $4e^-$ reduction without desorption of the intermediate (**Figure 1D**); (ii) in alkaline environment, two mechanisms are observed, owing to the partial formation of an oxide layer onto the Pt surface: an inner sphere electron transfer (ISET) on oxide-free Pt-sites where O_2 can chemisorb, which leads to a $4e^-$ transfer, similarly to (i); a non-surface specific outer sphere electron transfer (OSET) on the Pt-oxide, where the solvated O_2 forms an hydrogen bond with the OH^* that ultimately leads to a $2e^-$ pathway and HO_2^- generation (**Figure 1D**). Logically,

the OSET contribution increases with the OH* coverage and, thus, dominates in strong alkaline environment on Pt ($\text{pH} \geq 14$), as illustrated in **Figure 1D**. The domination of the $2e^-$ pathway at $\text{pH} \geq 14$ also occurs on Fe-N-C. On the latter, (i) little to no contribution of the $2e^-$ pathway is observed in mild alkaline solution (at $\text{pH} < 14$), indicating that O_2 adsorption on the Fe-N_x center is favored over OH* formation, leading to the formation of HO₂⁻. Said reduction is (ii) not favorable in acidic environment, owing to the weak H₂O₂ binding on the active sites, thus leading to a mix of H₂O₂ and H₂O being generated on Fe-N-C (see **Figure 1D**).³⁶⁻³⁷ In summary, in alkaline environment, the Pt surface gradually becomes (with the pH increases) non-specific and dominated by $2e^-$ pathway, whereas Fe-N-C electrocatalysts mainly follow a $4e^-$ pathway. In acidic environment, the ORR on Pt/C occurs through the $4e^-$ pathway, whereas lower selectivity and H₂O₂ generation is observed on Fe-N-C. The pH variation induced by the alkaline vs. acid environment also indirectly impacts the Fe-N-Cs by modifying the chemistry of the nitrogen³⁸⁻³⁹ neighboring the Fe-N_x active sites (*e.g.* stronger withdrawing electron effect from N-H respect to N⁻ induced by protonation of pyridinic N from alkaline to acidic media, thus affecting the 3d-band density of iron atoms).

In this section, we underlined that (i) both Fe-N-C (through its Fe-N₄ moiety) and Pt are respectively the best M-N-C and best element for the ORR, although they bind the oxygen intermediates slightly too strongly; (ii) both electrocatalysts families follow a dissociative-associative pathway (or associative for the Fe-N-Cs with low selectivity). The low selectivity of the Fe-N-Cs in acidic media, along with a PCET being the rate determining step on the $2e^-$ pathway, are here identified as two of the key limiting

aspects of the Fe-N-Cs when being compared to Pt-based electrocatalysts. To overcome them, one direction would be to finely tune the electronic properties of the active sites, along with the chemical surface properties of the Fe-N-Cs, to slightly decrease the OH* binding energy and to increase the ORR selectivity toward a 4e⁻ pathway. However, before proposing structural modifications, one must understand the nature, and plurality, of the Fe-N-Cs active sites, which diversity is equal to the one of Pt-based electrocatalysts.

3. The nature of active sites for Pt-based electrocatalysts and Fe-N-Cs

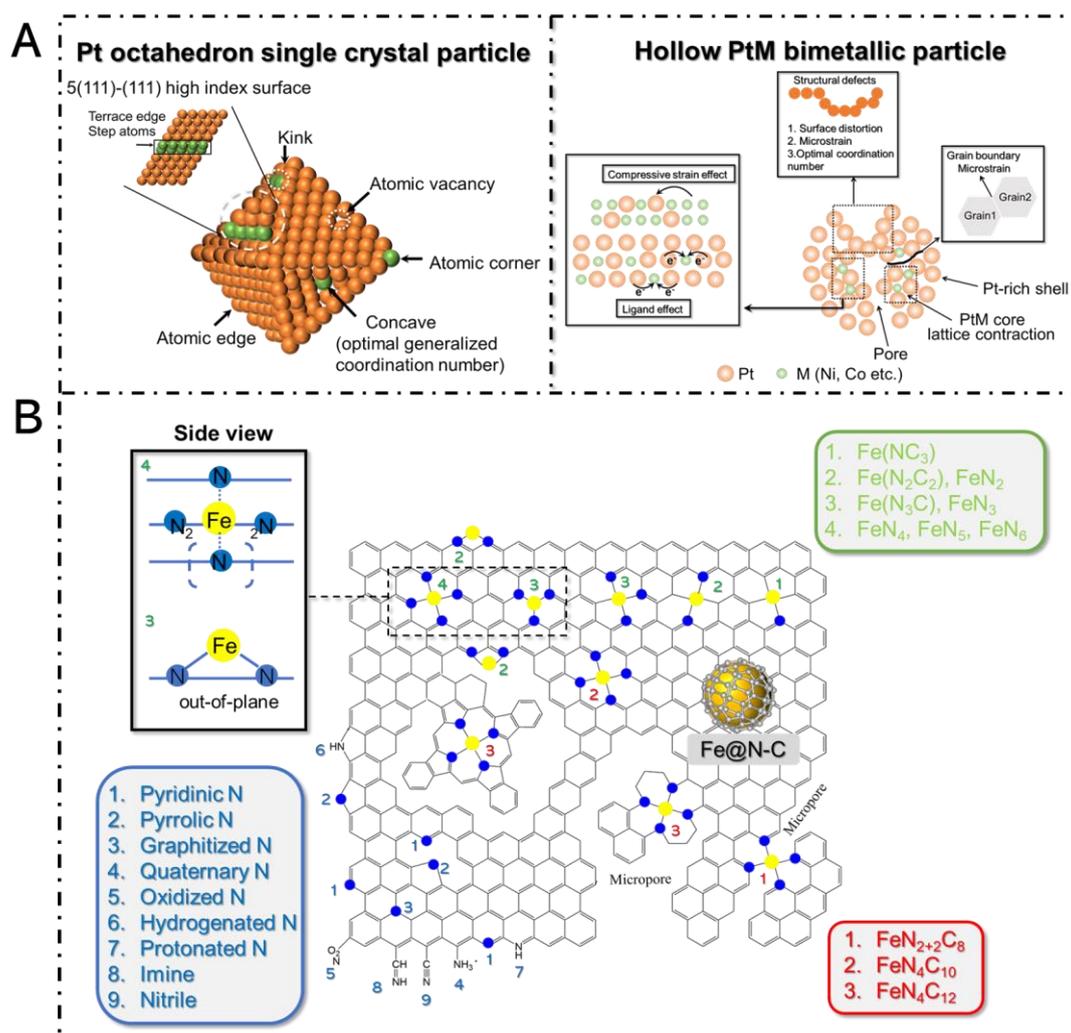


Figure 2. The nature of active sites (A) of Pt-based electrocatalysts (using a Pt octahedron single crystal (111) particles (left) and hollow PtM bimetallic particle (right) as example); and (B) of the various FeN_x -containing, N-containing and metallic nanoparticles discussed in the literatures on Fe-N-C electrocatalysts.

Each accessible platinum atom contributes, to a certain extent, to the ORR. For Pt-based nanoparticles, the activity strongly depends on (i) the Pt atom coordination and (ii) its average distance with its closest neighbors. Both strongly impact the Pt electronic structure and, thus, the OH^* binding strength. This was the first observed on

monocrystalline surfaces, by investigating different crystalline orientations and showing that Pt (110) > Pt (111) > Pt (100) in terms of activity.⁴⁰ This order changes when switching from Pt to Pt₃Ni, *i.e.* Pt₃Ni (111) > Pt₃Ni (110) > Pt₃Ni (100), hence explaining the interest for Pt_xNi structures with high (111) facets density, *e.g.* octahedra⁴¹. Interestingly, the activity of the basal planes is modified in presence of steps, atomic vacancy, *etc.*⁴²⁻⁴⁷ (see **Figure 2A** left). Specifically, it appears that the high-coordinated ‘bottom-of-the-step’ site is key for the ORR on Pt extended surfaces. Further investigation by Calle-Vallejo and Tymoczko *et al.*⁴⁸ evidenced that an optimal active site should exhibit a generalized coordination number (*i.e.* a coordination number considering the first and second row of neighbors) of 8.3, whereas Le Bacq *et al.*⁴⁹ underlined the key role played by the interatomic distance of a given active site onto its activity. Those aspects play a fundamental role in the design of Pt-based ORR electrocatalysts: (i) the optimized mass activity for Pt nanoparticles is observed in the size of 2-3 nm.⁵⁰⁻⁵¹ Further downsize of the Pt nanoparticles results in inferior intrinsic specific activity due to dominating low-coordinated steps and kinks leading to too strong oxygen binding.⁵⁰ Incidentally, this explains why single Pt atoms or Pt nanoclusters (albeit promising in terms of Pt utilization⁵²⁻⁵³) present a low intrinsic activity for the ORR, *i.e.* because of their extremely low coordination and the resulting too strong binding of the intermediates species;⁴⁸ (ii) as observed in **Figure 1B**, Pt (111) shows a slightly too strong adsorption strength of the oxygen intermediates, which can be optimized by following three approaches, namely (a) designing PtM (M = 3d-transition metals^{40, 54} or rare-earth elements⁵⁵⁻⁵⁶) without modifying the coordination or nanoparticle size, leading

to an activity improvement through strain⁵⁷⁻⁵⁹ and ligand⁶⁰ effects (for the 3d-transition metal) along with more complex structural modifications (*e.g.* Kagome layer for the rare-earth elements,⁵⁵ grain boundary,⁶¹ structural defects,⁶¹⁻⁶² surface distortion⁶³ *etc.*) (see **Figure 2A** right). Indeed, those effects result in the alteration of the Pt 5d-band electronic structure and, as such, a near-optimal oxygen-based adsorbates binding energy (b) optimizing the structure through the design of shape-controlled nanostructures, aiming to expose preferential facets of Pt to maximize the catalytic activity.⁶⁴⁻⁶⁵ (*e.g.* Pt₃Ni octahedra dominated by (111) facets, see **Figure 2A** left) (c) implementing structural defects into the Pt-based nanostructures, aiming to design active sites with an optimal generalized coordination number and optimal atomic distance with the nearest neighbors and, therefore, an optimal binding energy for the ORR intermediates.^{48, 61} Those different approaches led to a wide range of highly performing, innovative Pt-based electrocatalysts, that are discussed in further extent in Ref.^{47, 61, 66}.

Similarly to Pt-based electrocatalysts, the Fe-N-C electrocatalysts derived from separated iron, carbon/nitrogen precursors present a wide diversity of active sites. However, where the Pt-based electrocatalysts active sites diversity arises from the distance, and coordination, with other platinum atoms, the Fe-N-Cs diversity arises from the presence or absence of Fe, along with the coordination with nitrogen. Specifically, as shown in **Figure 2B**, three type of active sites are observed: (1) atomically dispersed iron moiety (FeN_xC_y), (2) N-doped carbon moiety (C-N), (3) iron-based nanoparticles. The precise identification of FeN_xC_y coordination shells (x, y values) remains challenging and is conventionally extrapolated from Mössbauer spectroscopy⁶⁷ and X-ray

adsorption spectroscopy, more specifically, extended X-ray adsorption fine structure (EXAFS).⁶⁸ The possible Fe-N_x coordination number in the first shell is proposed to be $x = 1 - 4$, based on experimental and theoretical calculation findings⁶⁹⁻⁷⁶ (**Figure 2B**). Notably, on the basis of EXAFS and Mössbauer findings, recent works have been discussing higher coordination numbers, including the presence of a nitrogen atom below the plane, thus leading to a N-FeN₄⁷⁷⁻⁸⁰ or N-FeN₄-N⁸¹⁻⁸² structure (left inset in **Figure 2B**). The chemistry and relative abundancy of the Fe-containing moieties are usually controlled by two parameters, *i.e.* (i) the pyrolysis temperature^{69, 82} and (ii) their position in the carbon structure, *i.e.* FeN₂ is commonly observed on the edge of the carbon crystallite⁸³ while FeN₃ and FeN_xC_{4-x} (where C is located at first coordination shell with $x \leq 4$) moieties are observed in-plane (Figure 2B).^{74, 83} The first and second coordination shell of the moiety most often considered as best for the ORR, the FeN₄, is widely debated,⁸⁴ and often established from a combination of Mössbauer and EXAFS findings combined with modelling. Hence, it is essential to look to this discussion with a critical eye, *i.e.* (i) the fitting of the Mössbauer/EXAFS data can often correspond to several geometries and (ii) the pyrolytic methods undergone to synthesize the Fe-N-Cs lead to the presence of a wide variety of coordination/chemistry, *i.e.* that there is not one type of active site in a given electrocatalyst. Unfortunately, obtaining a direct proof of the existence of a given coordination (*e.g.* by high resolution electron microscopy combined by elemental mapping) is extremely challenging on Fe-N-Cs synthesized by pyrolytic methods, leaving the exact nature of the active sites as hypotheses, albeit strongly backed with indirect evidences. Furthermore, inadequate characterization

procedure can also affect the obtained data and, thus, the interpretation. For example, for Mössbauer spectroscopy, low temperature is required for a precise identification of the different moieties, as α -Fe₂O₃ nanoparticles share similar Mössbauer parameters to FeN₄C₁₂ sites at room temperature.⁸⁵⁻⁸⁶

On the basis of Mössbauer spectrum results, Kramm *et al.*⁷⁹⁻⁸⁰ originally proposed that the Fe-containing moieties consisted of low spin (here referred as D1, and considered as a Fe(II)-N₄ moiety), intermediate spin (D2, Fe(II)-N₂₊₂, Fe situated between two carbon crystallites) and high spin (D3, N-Fe(II)-N₂₊₂, Fe situated between two carbon crystallites with N-graphitic in the plane underneath the Fe atom or FeN₄₊₁ with adjacent protonated nitrogen). Only D1 and D3 sites were deemed to exhibit high ORR activity while D2 was considered as inactive due to the Fe fully occupied 3d orbital failing to bind O₂ in a non-bent conformation. Although the D3 sites are proposed to be most active site for ORR,⁷⁹⁻⁸⁰ they are preferentially hosted in micropores,⁸⁷ which compromises their performance in PEMFC operating conditions due to their inaccessibility to ionomer,⁸⁸ flooding and demetallation⁸⁹⁻⁹⁰. In recent studies, Mukerjee's group⁹¹⁻⁹³ provided further insights on the D1 moiety and its variations as a function of potential, ascribing it to high spin 'in-plane' OH-Fe(III)-N₄ sites (axially coordinated to oxygen from water activation) at high potential and 'out-of-the-plane' Fe(II)-N₄ sites at low potential, the latter being considered as the active site⁹⁴ while the site-blocking effect resulted from water activation was viewed as detrimental.^{85, 94-95} In this end, intrinsic activity could be significantly improved by increasing the Fe(III)/Fe(II) redox transition potential.^{94, 96} The local carbon structure in the second shell surrounding the

FeN₄ moiety also varies on distinct FeN₄C_y sites: 'y' values are found to be eight (*i.e.* FeN₂₊₂C₈, micropore sites, bridging two carbon crystallite)⁹⁷⁻⁹⁹, ten (*i.e.* FeN₄C₁₀, bound to pyridinic N),⁸⁵ or twelve (*i.e.* FeN₄C₁₂, bound to pyrrolic N)^{68, 85, 100}. The FeN₄C₁₂ moieties, surface accessible, correspond to the D1 doublet¹⁰⁰⁻¹⁰¹. The moiety location is also of critical importance when addressing the material stability, *e.g.* FeN₂, FeN₂₊₂C_y moieties are edge sites while FeN₄C_y, FeN₃ and FeN_xC_{4-x} moieties are more likely 'plane-exposed' sites (*i.e.* situated in the carbon basal plane facing the mesopore, **Figure 2B**).^{83, 102-103} Hence a mesoporous carbon favors FeN₄₊₁, FeN₄C_y, FeN₃, FeN_xC_{4-x} as main active sites, whereas more 'edge-exposed' (*e.g.* armchair, zig-zag edge of carbon basal plane and micropores) lead to FeN₂ and FeN₂₊₂C_y as main active sites. Noteworthy, the carbon edges are preferentially corroded, thus suggesting that, from a durability standpoint, the development of 'plane-exposed' sites should be favored.

Assessing the reactivity of Fe-based nanoparticles (metallic Fe, iron oxides, carbides and nitrides) observed in highly loaded Fe-N-Cs remains challenging, due to the simultaneous presence of FeN_xC_y sites. Extensive studies have revealed that they act as the main ORR active site in alkaline medium.¹⁰⁴⁻¹¹¹ Specifically, a synergetic effect between Fe-nanoparticles and FeN_xC_y moieties has been widely proposed.¹¹²⁻¹²⁰ For instance, in alkaline media, Wei's group¹²¹ proposed that Fe/Fe₃C nanoparticles could dramatically improve the activity of the adjacent Fe-N_x by modifying the electronic structure of the latter, which favored the O₂ adsorption. In acidic media, the Fe-based nanoparticles (Fe/Fe₃C) encapsulated into thin graphitic N-doped carbon layer (Fe@N-C, see **Figure 2B**) usually present an excellent ORR activity and durability.¹²²⁻¹²⁹

However, the encapsulated Fe-based nanoparticles are not involved in the ORR process, but exert a positive electronic effect on the outer surface of graphitic carbon layer that favors the stabilization of the H_2O_2 intermediates and enables full $4e^-$ ORR.^{124-125, 128} More importantly, they are protected from direct contact with the electrolyte and H_2O_2 intermediates, thus exhibiting high stability.^{124, 128} Indeed, Choi *et al.*¹³⁰ recently confirmed that these carbon-encapsulated Fe nanoparticles (Fe@N-C) electrocatalysts presented a high ORR activity leading to $4e^-$ reduction, dominated by the indirect four electron oxygen reduction (S^* , see **Figure 3**, $\text{O}_2 \rightarrow \text{H}_2\text{O}_2$ and $\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O}$) associative pathway. However, ‘electrolyte-exposed’ iron-based nanoparticles are ORR inactive in acidic environment, as revealed by the independence of the ORR activity on their presence.¹³⁰⁻¹³² As such, the latter should be avoided in acidic environment as it also contributes, through its corrosion during operation, to the poisoning of membrane and the formation of strong oxidative radical HO^\bullet by Fenton reaction.¹³¹⁻¹³² Mitigation methods, such as the use of sulfur-based precursors, have been recently introduced to prevent their excessive formation.¹³³⁻¹³⁵ Overall, the contribution to the catalytic activity of the iron-based nanoparticles in acidic environment strongly depends on the thickness of the N-doped carbon shell surrounding them, which itself depends of the synthesis procedure (*e.g.* pyrolysis temperature and type of carbon, nitrogen precursors).¹³⁶⁻¹³⁷ Altogether, the improved ORR performance can be achieved through (1) increasing the sites density of atomic, D1, FeN_xC_y sites or rational design of Fe@N-C site with proper coated N-doped carbon layer; (2) removing the naked Fe-based nanoparticles to prevent the poisoning of membrane or the formation of high corrosive reaction radical species

(ROS) induced by Fenton reaction due to the dissolution of Fe nanoparticles during ageing.¹³¹⁻¹³²

Nitrogen atoms are also incorporated into carbon matrix during pyrolysis as iron-free, nitrogen-containing functionalities. Such nitrogen species in carbon matrices have been assigned by X-ray photoelectron spectroscopy and density functional theory (DFT) calculations, including imine or nitrile groups (≤ 398.0 eV),¹³⁸ pyridinic N (398.3 – 398.8 eV),¹³⁹ amine group (399.5 – 399.8 eV),¹³⁸⁻¹³⁹ pyrrolic N or hydrogenated N (400.6 – 400.9 eV),¹³⁹⁻¹⁴⁰ and a mixture of quaternary N, graphitic N and protonated pyridinic N (401.5 – 403.0 eV),^{138, 141-142}. The nitrogen-based moieties are highly sensitive to their chemical environment, with different binding energies observed for chemically identical moieties (*e.g.* pyridinic) if they are found in the basal plane or on the carbon edge.¹³⁹ The N-containing functionalities only catalyze part of the ORR: in acidic media, whereas FeN_xC_y and Fe@N-C sites are S or S* with direct four electron reduction or single site series 2×2 e⁻ electron reduction processes (see **Figure 3**); the pyrrolic N, protonated or hydrogenated N, quaternary N (N⁺) and graphitic N are S1 sites (O₂ → H₂O₂, **Figure 3**) and pyridinic N is a S2 site (H₂O₂ → H₂O, **Figure 3**).^{130, 138-139, 142-143} The exact nature of the pyridinic N site is still controversial, with Guo *et al.*¹⁴⁴ suggesting that the latter is responsible for a Lewis-basic behavior of the neighboring carbon atoms, but Kondo *et al.*¹⁴⁵ arguing that the lone pair on the pyridinic nitrogen implies a negatively charged nitrogen and thus that the surrounding carbon atoms should be positively charged, rendering them inadequate as a Lewis base. This should be also considered in the prism of the pH variations, as the phenomena changes

in acidic environment, with the protonation of the pyridinic N ($pK_a = 6.5$)^{37-39, 146-147} that modify its charge delocalization and thus, in theory, the Lewis basicity of the adjacent carbon atoms. Notably, N-containing moieties exhibit nearly no activity or far lower ORR activity in acidic environment, with respect to FeN_xC_y moieties.^{83, 130, 146} Furthermore, they act as defects in the carbon structure and, therefore, starting points for degradations during operation in acidic environment, although this defectivity can be positively used to tune the electronic structure of the iron, as explored in the following section.

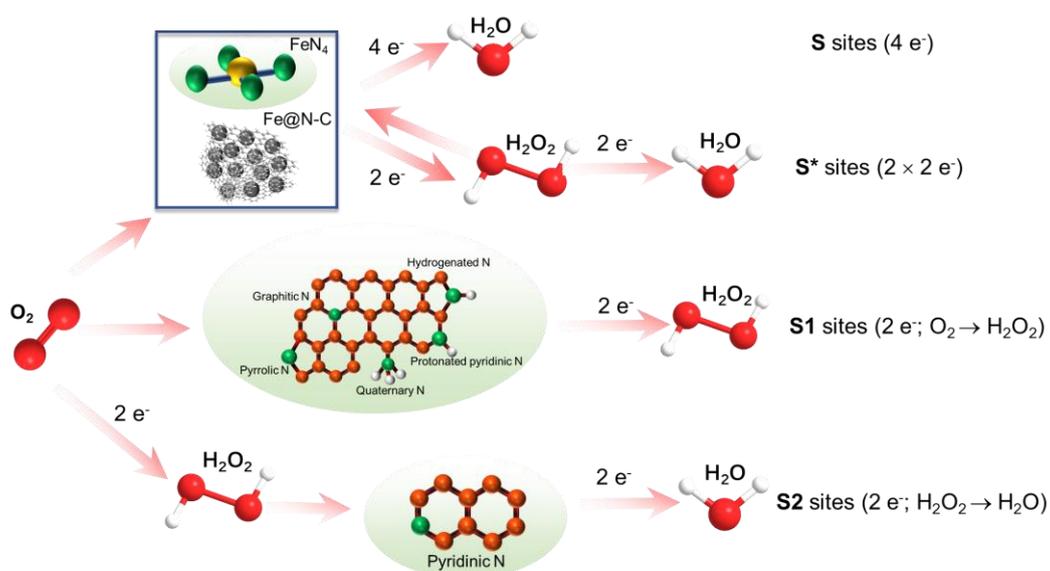


Figure 3. The ORR reaction pathway on the distinct active sites in the Fe-N-Cs electrocatalysts.

The quantification of the active sites in both Pt-based and Fe-N-C electrocatalysts is also of critical importance. CO as a molecular probe has been widely applied to quantify the active site for Pt-based catalysts by means of chemisorption or CO electrochemical stripping,¹⁴⁸⁻¹⁴⁹ whilst no or extremely weak adsorption of CO at room temperature

or under potential was observed on Fe-N-C electrocatalysts.¹⁵⁰⁻¹⁵¹ A variety of probe molecules (*e.g.* CN^- ,¹⁵²⁻¹⁵⁴ H_2S ,¹⁵⁵ SCN^- ,¹⁵⁶ SO_2 ,¹⁵⁶ NO ,⁶⁷ *etc.*) thus has been extensively employed as poisoning agents to quantify the active sites in Fe-N-Cs. Sahraie *et al.*¹⁵⁷ have successfully quantified the bulk and surface-based density of Fe-N_x sites using low-temperature CO pulse chemisorption, and the positive correlation between CO uptake and kinetic current density in acidic medium evidenced that CO molecule was predominantly adsorbed on surface sites. Kucernak *et al.*¹⁵⁸ developed a protocol that allowed the quantification of the Fe-N_x sites by means of nitrite adsorption followed by reductive stripping operated at pH = 5.2. Such strategy represents the most advanced methodology for quantification of Fe-N_x active sites to date.¹⁵⁹ It is worth noting that the interaction between nitrite ion and iron center can be significantly impacted by the FeN_x sites surroundings (*e.g.* the presence of basic groups neighboring the FeN_x sites exert an electron-donating effect on Fe thus weakening the chemisorption of the nitrite anion on the Fe center), which limits the its application in some certain catalysts, as revealed by Kumar and Asset *et al.*¹⁶⁰ Furthermore, these methods only apply to FeN_x moieties, *i.e.* Fe-based nanoparticles and Fe-free moieties cannot be assessed by such means. Interestingly, both Fe-N-Cs and Pt-based electrocatalyst show some similarities in terms of active sites: (i) both present a wide variety of potential active sites for the ORR, for which structure-activity relationships will be established in the next section and (ii) structural defects in the electrocatalysts structure are interesting, as they either lead to the formation of ideally coordinated active sites, with optimal nearest-neighbor distance (for Pt-based), or to a higher density of iron, nitrogen-

based moieties that are crucial for the oxygen reduction activity. Furthermore, the atomically dispersed nature of the iron site, vs. the mandatory minimal size of the Pt nanoparticles to access a relevant intrinsic activity, imply a far higher utilization of the former, which, owing an optimal loading and dispersion, could lead to extremely high activity, comparable to platinum electrocatalysts.

4. The regulation of ORR intrinsic activity on Fe-N-Cs and Pt-based electrocatalysts

4.1. π -electron delocalization of carbon basal plane on Fe-N-Cs

According to the previous analysis, the Fe(II)-N₄ site is deemed to be the most important Fe-N-C's site for the ORR. It is located on the strong adsorption side of the volcano plot (**Figure 1C**). When addressing this sole moiety, it appears that its catalytic activity is governed by d-electron density of iron, as the alteration of d-band center greatly affects the type, and strength, of the bonding between the Fe center (d_{z^2} orbital) and molecular O₂ or oxygenated intermediate (π^* anti-bonding orbital).¹⁶¹⁻¹⁶³ The d-electron density of the iron center can be regulated by the surrounding π -conjugated ligand or carbon basal plane with various donating- or withdrawing-electron properties.¹⁶⁴⁻¹⁶⁵ Ramaswamy *et al.*¹⁶⁵ observed that, during the pyrolysis of iron macrocyclic complex, the Fe-N₄ active site switched from a π -electron rich macrocyclic ligand environment to a relatively π -electron deficient graphitic carbon environment, which resulted in a decreased electron density at the Fe center and a downshifted d-band center of Fe, thus optimizing the adsorption strength of ORR intermediates and leading to an

higher turnover number. Further optimization of OH* binding energy on FeN₄ moieties can be performed through modification of the carbon basal plane: increasing the density of structural defects (edge, hole, heteroatom-doping) or disorder degree (lower graphitization degree) disrupt the π -electron delocalization, which further increases the electron withdrawing nature of the carbon plane, thus downshifting the d-band center and enhancing the ORR (see **Figure 4A**). On the contrary, a highly graphitized carbon surface with fewer defects results in an increased electron donating property and a stronger OH* binding, therefore compromising the ORR activity (**Figure 4A**). It is worth noting that, although increasing the structural defects density can potentially optimize the ORR activity, highly defective carbon planes ('overshooting') will not only result in too weak OH* binding energy (shift to the right side of volcanic plot, **Figure 4A**) but also reduce their durability due to large number of preferential corrosion sites.^{17, 83} Taken together, a trade-off between graphitization degree and structural defects should be carefully considered for optimization of both intrinsic activity and durability.

4.2. Ligand effect surrounding FeN₄ site.

In addition to the effect of π -electron delocalization of carbon basal plane on d-electron density of Fe center, the so-called ligand effect also plays an important role in tuning the ORR activity.¹⁶⁶ A variety of element dopants with distinct electronegativity have been investigated, with sulfur-doping being the most commonly studied.¹⁶⁷⁻¹⁷³ Generally, the S-doping does not affect the coordination of Fe center: the sulfur atom is either adjacent or away from the nitrogen atoms in the FeN₄ site.¹⁷⁴⁻¹⁷⁵ Two forms of S dopants with electron-withdrawing oxidized S (C-SO_x)¹⁷⁶ and electron-donating

thiophene-like S (C-S-C)¹⁷⁵⁻¹⁷⁸ are proposed to tune the electron structure of the FeN₄ moiety. Specifically, the introduction of oxidized sulfur (-C-SO_x)¹⁷⁶ on the neighboring FeN₄ sites significantly decreases the d-band center of Fe by an electron-withdrawing effect, which shifts OH* binding energy toward the apex direction of the volcano plot (**Figure 4A**). On the contrary, the thiophene-like C-S-C increases the electron density of the Fe center due to a strong electron-donating effect thus brings the electrocatalyst toward the stronger adsorption energy side (Figure 4A). Besides S-doping, other elements such as B,¹⁷⁹⁻¹⁸⁰ P,¹⁸¹⁻¹⁸³ and O¹⁸⁴ with different withdrawing/donating groups are also documented. Independently of the dopant nature, it is important to note that (1) the effect on the d-band center strongly depends on the distance between the dopant and the FeN₄ moiety;¹⁷⁸ (2) as aforementioned for the structural defects, the content of dopants should be carefully controlled so as to obtain optimal binding energy on Fe center (*e.g.* excessive amount of C-SO_x or electron-withdrawing groups resulting in too weak OH* binding on FeN₄ sites-right side of volcano plot, **Figure 4A**).

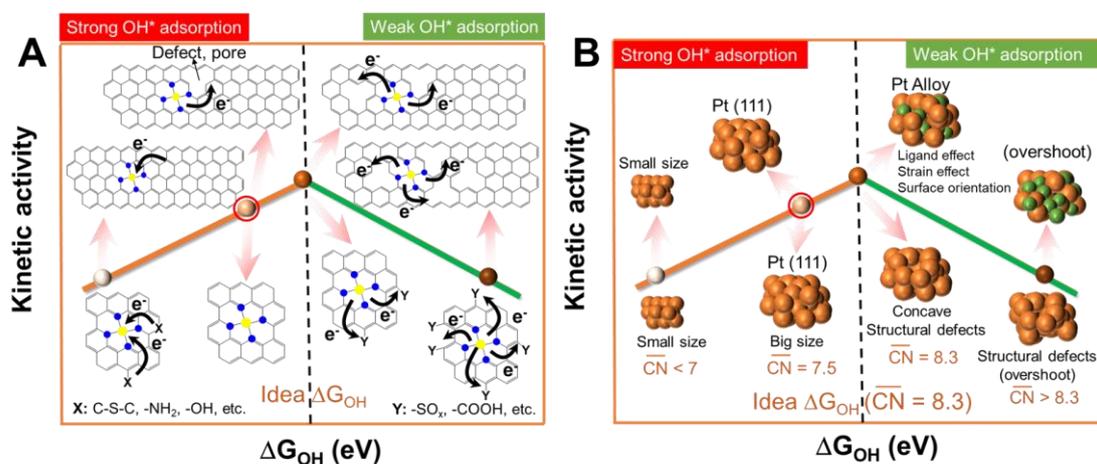


Figure 4. Schematic illustration of activity regulation by the modification of the electronic structure of the active site on Fe-N-C electrocatalysts (A), and Pt-based electrocatalysts (B)

aiming to improve the ORR intrinsic activity.

4.3 The regulation of intrinsic activity of Pt-based catalysts

Tuning the surroundings of a given active site echoes with the recent efforts undergone to design innovative Pt-based electrocatalysts, as touched upon in Section 3, and that Sabatier-driven, volcano-shaped activity is easily applied to this family of electrocatalysts as well. Indeed, considering Pt (111) as the 'Fe(II)-N₄ like' site, binding OH* 0.1 - 0.2 eV too strongly, it appears that, as illustrated on **Figure 4B**: (1) the addition of 3d-transition metals and/or the use of clearly defined crystalline orientations (*e.g.* Pt₃Ni(111), octahedra, nanoframes) lead to a downshifting of the Pt 5d orbital and the resulting weakening of the OH* adsorption strength, thus greatly increasing the ORR activity.^{40-41, 185} But such modification also impacts the nanostructure durability, as well-organized facets and 3d transition metals both exhibit low stability in highly acidic environment;^{63, 186} (2) properly decreasing the Pt nanoparticles size enables more exposure of active sites, but excessive downsizing exposes a large density of edges sites with decreased coordination number (**Figure 4B**). This negatively impacts the ORR activity due to too strong OH* adsorption as well as decreasing the nanoparticles durability due to the easier aggregation of small particles induced by large surface energy; (3) the addition of localized structural defects (*e.g.* platinum adatoms, concavities) modifies the local environment of a given platinum atom and, through the changes in its microstrain and local coordination, thus its OH* binding strength (Figure 4B).^{48-49,}

⁶³ However, in a similar fashion, structural defects such as inner cavities are prone to

collapse when exposed to harsh environmental conditions.¹⁸⁷ Those aspects bring forth similar conclusions than those presented for the Fe(II)-N₄ site, *i.e.* that an excess in structural defects or alloying elements would be detrimental for the ORR activity, by ‘over-shooting’ the optimal OH* binding strength, and that such modified nanostructures would, in addition, show depreciated electrocatalytic activity (**Figure 4B**).

5. Engineering of cathode catalyst layer (CL) for Pt-based and Fe-N-C electrocatalysts and applications in PEMFCs

Although high ORR activity is usually obtained in 3-electrode cell rotating disk electrode (RDE) measurements, the experimental conditions widely differ from those into which the electrocatalysts are meant to operate, *i.e.* PEMFCs, the activities obtained in the latter being far more meaningful than those obtained in liquid electrolyte. In PEMFCs, several challenges arise from the mass transport limitations (*e.g.* O₂ and H⁺ transport to the interface, H₂O removal). The ORR in PEMFCs occurs at the triple-phase boundary (catalyst-electrolyte-gas) and involves (i) the electrocatalyst and (ii) H⁺, and O₂ circulating through the ionomer and/or the electrode porosities to/from said electrocatalyst and (iii) the provisioning/removal of H₂O.¹⁸⁸ Therefore, apart from the rational design of electrocatalysts with high ORR performance, the engineering of catalytic layers with a well-designed triple-phase boundary is of great importance for practical application, as illustrated in **Figure 5**. First, a good ionomer coverage of the carbon support must be achieved, as to ensure optimal active site accessibility to the charged species. For example, Ott *et al.*¹⁸⁹ modified carbon black surfaces by nitrogen doping,

enhancing the interaction between the ionomer and the carbon surface and leading to an even ionomer coverage, thus significantly reducing the oxygen transport resistance and improving the fuel cell power density for Pt-based electrocatalysts. Likewise, Huang's group¹⁹⁰ also reported the chemical modification of carbon support with surface oxidation, identifying an optimal surface oxygen loading to create favorable carbon-ionomer interaction and to balance hydrophobic and hydrophilic properties on the catalytic layer, favoring the water management. The thickness of the ionomer layer, should also be considered carefully, as Harada *et al.*¹⁹¹ showed that a dense ionomer layer (> 3 nm) on the top of the active sites resulted in limited local O₂ diffusion. In the presence of Pt-based nanostructures, the interactions between the latter and the ionomer have to be considered, owing to the poisoning of the Pt surface by the side chain of perfluorosulfonated ionomers (*e.g.* -SO₃⁻).¹⁹² A recent study to address this challenge consisted in depositing a thin layer of carbon (< 1 nm) on the Pt nanoparticles surface to prevent poisoning without compromising gas/proton permeability.¹⁹³ Another way to address the Pt poisoning is to optimize the pore structure of the carbon support, which tunes the location of the Pt-based nanoparticles: exposure of the Pt nanoparticles on the carbon support outer surface is favorable, as it eases the O₂ accessibility, but increase the ionomer poisoning effect. Contrarily, the deposition of Pt particles in the carbon inner porosities can efficiently prevent the poisoning effect and particles aggregation during ageing,¹⁹⁴ at the cost of depreciated gas transport (see **Figure 5A**). To this end, Yarlagadda *et al.*⁸⁸ identified a perfect trade-off through porous carbon design with a bottleneck pore size of 4 -7 nm, in which Pt particles located inside pore did not suffer

from poisoning by the ionomer (contactless with ionomer) nor high gas transport resistance (**Figure 5A**).

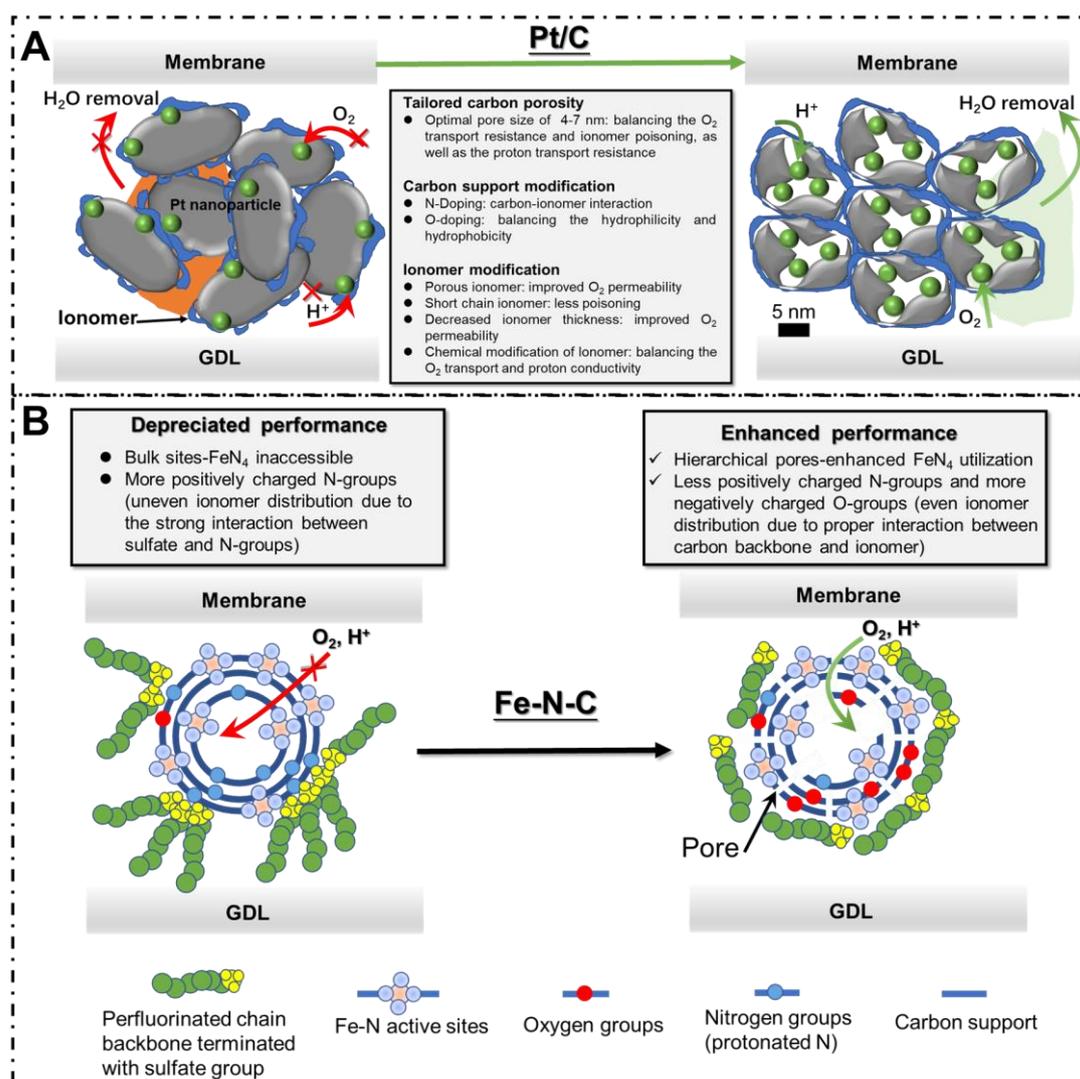


Figure 5. Schematic illustration of cathode catalyst layer and triple-phase boundary engineering on Pt-based (A) and Fe-N-C (B) electrocatalysts.

Inferior intrinsic activity and limited active sites density usually result in thicker catalytic layers for Fe-N-Cs with respect to that of Pt-based catalysts (60-100 μm of CL for Fe-N-Cs vs. 10 μm for identical performance for Pt-based catalyst).¹⁹⁵⁻¹⁹⁷ However,

the increased thickness of the Fe-N-Cs catalytic layer not only increases the mass transport limitation,¹⁹⁸ but decreases the utilization of the catalyst located within the catalytic layer and increases the possibility for its detachment and flooding during operation.^{196, 199-200} In this end, two strategies are employed for the optimization of Fe-N-Cs performances in PEMFCs as shown in the **Figure 5B**: (1) increasing the accessibility of FeN₄ sites and rationalizing the design of the Fe-N-Cs porous structure. Very recently, Jiao *et al.*²⁰¹ proposed an innovative approach to bring the percentage of utilized active sites near 100%, by first pyrolyzing a nanosized zeolitic imidazolate framework (ZIF-8) and then using chemical vapor deposition of FeCl₃ to replace the ‘vapor-accessible’ ZnN₄ moieties originally present in ZIF-8 by FeN₄. An activity in PEMFC of 33 mA/cm_{geo}² at 0.9 V(IR-free) was reached, close to target of 2025 set by DOE. The design of an optimized, hierarchical, porous structure would also greatly increase the FeN₄ accessibility, by exposing inaccessible or buried FeN₄ sites, along with favoring the mass transport of reactants and products.^{159, 202} However, an overly complex porous network could ultimately be detrimental, by increasing the structure defectivity (thus lowering its stability and compromising the intrinsic activity of FeN₄ sites, see **Figure 4A**) as well as rendering some sites non-accessible to the ionomer; (2) optimizing the catalytic layer structure. Similar to Pt-based systems, the ionomer content plays an important role in facilitating, or limiting, gas transportation and ionic species conductivity. Thus, trade-off between gas transport and proton conductivity should be achieved,²⁰³ in the form of a uniform coverage of the Fe-N-C electrocatalyst by a thin layer of ionomer (< 3 nm).²⁰⁴ As far as the catalyst-ionomer interactions are concerned, Artyushkova

*et al.*²⁰⁵ revealed the pivotal role played by the nitrogen species within the carbon network: the hydrogenated N and positively charged protonated N interact strongly with negatively charged sulfonated groups of perfluorosulfonated ionomers (*e.g.* Nafion®), hence disrupting the ionomer network and limiting the proton transport. On the contrary, surface oxides with a negative charge were deemed responsible for an even distribution of ionomer and optimal interaction between the Fe-N-C and ionomer (**Figure 5B**).

To provide a clear insight into the current state of the Fe-N-Cs as PEMFCs electrocatalysts vs. Pt-based systems, a list of some of the most promising Fe-N-Cs and Pt-based systems is provided in **Table 1** and **Table 2**. To allow for a meaningful comparison, the technical details (*e.g.* pressure, gas atmosphere, flow rate, *etc.*) are also provided. It is worth noting that the lack of unified durability test protocols for Fe-N-Cs make the data comparison on that specific aspect meaningless.

Table 1 The MEA-based PEMFC performances of ‘state-of-the-art’ Fe-N-Cs

Entry ^a	L ^b mg/cm ²	P ^c kPa _{abs}	T °C	FR ^d (H ₂ /O ₂) sccm	RH ^e %	j _{0.9V} ^f O ₂ mA/cm ²	P _{max} ^g O ₂ mW/cm ²	FR ^d (H ₂ /Air) sccm	j _{0.8V} ^f Air mA/cm ²	P _{max} ^g Air mW/cm ²	Ref.	Year
DOE	4.0	150	80	-	100	44	1000	-	150	500	6	
S-doped Fe-N-C	4.0	150 (250)	80	200/200	100	-	940* (1030*)	-	-	-	206	2015
Metal Organic Framework (MOF)-derived Fe-N-C	3.5-4.0	150	80	-	100	-	603	-	-	-	207	2015
Polyamide + cyanamide derived Fe-N-C	4.0	100	80	200/200	100	-	870	200/200	90	390*	208	2017
Carbon black + Phenanthroline + polyaniline derived Fe-N-C	4.0	238	80	300/400	100	-	1060*	300/400	120	380*	209	2017
MOF-derived Fe-N-C	2.8	250	80	300/400	100	35*	1141	-	-	-	210	2017
Fe-N-C	2.0	450	80	300/400	100	-	823*	-	-	-	10	2018

Fe-N-C (50 cm _{geo} ²)	4.0	173	75	-	100	-	750	-	-	570	196	2018
MOF-derived Fe-N-C (pyrolyzed at 700°C under N ₂)	4.3	203	80	200/200	100	30	-	200/200	75*	320*	211	2019
MOF-derived, templated Fe-N-C	2.7(O ₂) 2.0(Air)	100	80	300/400	100	22	-	300/500	129	420*	159	2019
MOF-derived Fe-N-C	4.0	100	80	200/200	100	-	-	200/200	75*	360*	212	2019
Chemical Vapor Deposition (CVD)-synthesized Fe-N-C	4.0	200	80	300/500	100	27	-	300/500	117*	-	213	2020
MOF-derived Fe-N-C	4.0	200	80	200/200	100	35	750	200/200	64	340*	214	2020
MOF-derived Fe-N-C	4.0	150	80	200/200	100	28.5	-	-	-	-	204	2020
CVD-synthesized Fe-N-C	6.0	150	80	200/1000	100	33	-	500/2000	-	370*	201	2021
MOF-derived, NaCl-assisted Fe-N-C	4.0	100	80	150/200	100	-	890*	150/200	-	390*	215	2021
NH ₄ Cl-treated Fe-N-C	4.0	150	80	700/1700	100	44.2	-	200/400	151*	601*	17	2022
NH ₄ Cl-treated + CVD Fe-N-C	4.0	150	80	700/1700	100	33	-	200/400	85*	535*		
MOF-derived Fe-N-C	3.9	203	80	200/200	100	41.3	>1200	300/1000	199	429	216	2022

^a DOE: 2025 performance target of department of energy, US; ^b loading of catalyst. ^c total outlet pressure (absolute) for a fully humidified H₂ and O₂/air. ^d flow rate of H₂ and O₂/air. ^e relative humidity. ^f current density (IR-corrected) at applied voltage and gas atmosphere (0.9 V under O₂ or 0.8 V under air). ^g rated power under O₂ or air. * indicates that IR correction is not specified or no IR-correction is applied.

Table 2 The MEA-based PEMFC performances ranking the best among reported Pt-based electrocatalysts

Entry ^a	L ^b mg _{Pt} /cm ²	P ^c kPa _{abs}	T (°C)	FR ^d (H ₂ /O ₂) sccm	RH ^e %	j _{0.9V} ^f O ₂ A/mg _{Pt}	j _{0.9V} ^f O ₂ mA/cm ²	AST ^g Condition (V)	AST ^h MA(Volt) loss (% or mV)	Ref.	year
DOE	0.1	150	80	-	100	0.44	44	0.6 - 0.95	< 40 % < 30 mV	6	
PtNi/C	0.1	150	80		100	0.62	62	0.6 – 1.0	20 %	217	2014
PtNi/C	0.11	150	80	696/1654	65	1.34	147.4	0.6 – 1.3	43% (5000 cycles)	218	2016
Co@Pt/Co-N-C	0.033	150	80	200/200	100	1.08	35.6	0.6 – 1.0	36 % 6 mV	9	2018
Octahedral PtNi/C	0.1	50	80	-	100	0.57	57	-	-	219	2019
PtCo/C	0.1	150	80		100	0.79	79	0.6 – 0.95	37 % 31 mV	220	2019
CoPt/C	0.105	150	80	500/1000	100	0.56	58.8	0.6 – 0.95	19 %	221	2019

^a DOE: 2025 performance target of department of energy, US; ^b loading of Pt; ^c total outlet pressure (absolute) fully humidified for H₂ and O₂/air; ^d flow rate of H₂ and O₂; ^e relative humidity; ^f current density (IR-corrected) at applied voltage under O₂ (0.9 V); ^g Accelerated stress test (AST) at given potential range according to DOE catalyst durability evaluation protocols ⁶; ^h mass activity loss at 0.9 V (IR-corrected), and voltage loss at 0.8 A/cm² after 30000 cycles (unless other stated).

In the case of Pt-based catalyst, great accomplishments on both activity and durability have been achieved, even surpassing the performance target set by DOE 2025. (**Table 2**). Hence, it appears that the electrocatalytic performance of Pt-based electrocatalysts is not decisive for the commercial success, the limitations rather arising from the scarcity and cost of platinum, requiring either 100% efficiency in terms of Pt recycling ²²² for further utilization or greater advances in terms of catalytic improvement. Although innovative structures far outperforming PtCo have been identified, owing to the directions discussed in Section 3 and 4, translating them from the laboratory-scale to large-scale industry level remains extremely difficult.⁶⁶ Fe-N-C electrocatalysts present lower performance with respect to Pt-based electrocatalyst in both activity and durability. The MOF-derived Fe-N-Cs are the most promising, *e.g.* very recently, Wu's group ¹⁷ reported a MOF-derived NH₄Cl treated Fe-N-C electrocatalyst that reached the 2025 DOE target in terms of activity (**Table 1**), through the successful implementation of structural defects in the vicinity of the FeN₄ sites. However, those materials showed poor durability (up to 94 % activity loss after 30,000 potential cycles between 0.6 V and open circuit potential). By post-deposition of a N-doped carbon layer onto the Fe-N-C surface, the durability was found to meet the U.S 2025 DOE target, while exhibiting decreased activity. This indicates that both parameters are often correlated, as discussed in Section 4, and that designs that are not bound by the Volcano plot presented

in **Figure 4A** are needed to go ‘beyond’ those limitations.

By opposition, Fe-N-Cs are better performing than Pt-based electrocatalysts in alkaline environment, as reported in liquid electrolyte^{135, 223-225}, and benefit from the less corrosive environment. This highlights their potential application as anion exchange membrane fuel cells (AEMFCs) cathode electrocatalysts. However, the design of an AEMFC has to consider several challenges that are cathode catalytic layer independent, *i.e.* (i) carbonation is usually encountered in the presence of CO₂ (from the air feed), which dramatically decreases the ionic conductivity of the AEM, the pH and greatly impacts the performances;²²⁶⁻²²⁸ (ii) water management is required to maintain membrane hydration, as water serves as both as a reactant and as a product at the cathode and anode, respectively, while avoiding flooding;²²⁹⁻²³¹ (iii) the alkaline environment decreases the HOR kinetics at the anode, thus requiring the identification of adapted electrocatalysts for said reaction.²³² As such, the research and development of AEMFCs has lagged far behind the one of PEMFCs. However, recent years have witnessed significant advancements, and high peak power density (*e.g.* > 1 W/cm² in H₂/O₂) using Fe-N-C catalysts at the cathode have been reported.²³³⁻²³⁶ Specifically, Mustain’ group²³⁷ recently developed an AEMFC with a state-of-the-art Fe-N-C electrocatalyst, which achieved a peak power density of > 2 W/cm² under H₂/O₂, while > 1 W/cm² of power density was still obtained under H₂/Air (CO₂-free).

Here, two critical points were evidenced: (i) the gap between the Pt-based electrocatalysts and Fe-N-C electrocatalysts has been steadily decreasing throughout the years. Fe-N-C are now close to achieve the 2025 DOE target in terms of durability and activity

¹⁷. The latter has been reached for Pt-based electrocatalysts, and even surpassed (by *ca.* 3 times in terms of $j_{0.9V}$ in A/g^{-1}_{Pt} and mA/cm^2_{geo} , see **Table 2**), the main objective being now to even further decrease the Pt content by implementing advanced Pt-based nanostructures in PEMFCs; (ii) hence, for both Fe-N-C and Pt-based electrocatalysts, the transition from liquid electrolyte to PEMFCs is not trivial. Notably, advanced-Pt nanostructures designed around porosity, structural defects or preferential crystallite orientation have yet to be successfully implemented in PEMFCs. The final application should be kept in mind when designing the electrocatalyst, and the iron sites should be excluded from domains where the ionomer/gases cannot access (*e.g.* micropores, *etc.*). The functionalization of the carbon support (or, in the Fe-N-C case, the iron-free moieties) is also pivotal, as it controls the ionomer dispersion over the catalyst layer. Drastically increasing the density of iron sites would be a direction to even further increase the Fe-N-Cs competitiveness, but, as evidenced by Wu's group, obtaining an active and stable Fe-N-C electrocatalyst is extremely challenging. Furthermore, (i) the Fe-N-Cs perform remarkably well in AEMFCs, implying that, owing that the membrane and anode limitations of those systems are addressed, they would be of extreme interest; (ii) M-N-C as supports for Pt-based electrocatalysts have recently encountered interest,⁹ in the light of a synergy between the Co@Pt core@shell nanoparticles and a Co-N-C electrocatalyst, the former reducing any H_2O_2 generated on the latter, thus increasing the selectivity, activity and durability while decreasing the Pt loading.

6. Degradation mechanism of Pt-based and Fe-N-C electrocatalysts

As a result of the promises hold by their activity, the durability of Pt-based and Fe-N-C electrocatalysts should be carefully addressed. For both families, at the micrometer scale, the thinning of cathode catalyst layer (the decomposition of carbon support and ionomer) is often observed during ageing, which results in cracking or detachment of the catalytic layer.^{196, 238} In consequence, the overall activity suffers a dramatic decrease, especially in the high current region as it is there controlled by the mass transport properties. The catalyst layer corrosion is strongly accelerated by start-up/shut-down events, during which the local heterogeneity on the feed gas concentration also leads to extreme degradation.²³⁹⁻²⁴² The changes observed at the micrometer scale are direct consequences of phenomena occurring at the atomic/nanometric level, which will be discussed in detail in this section.

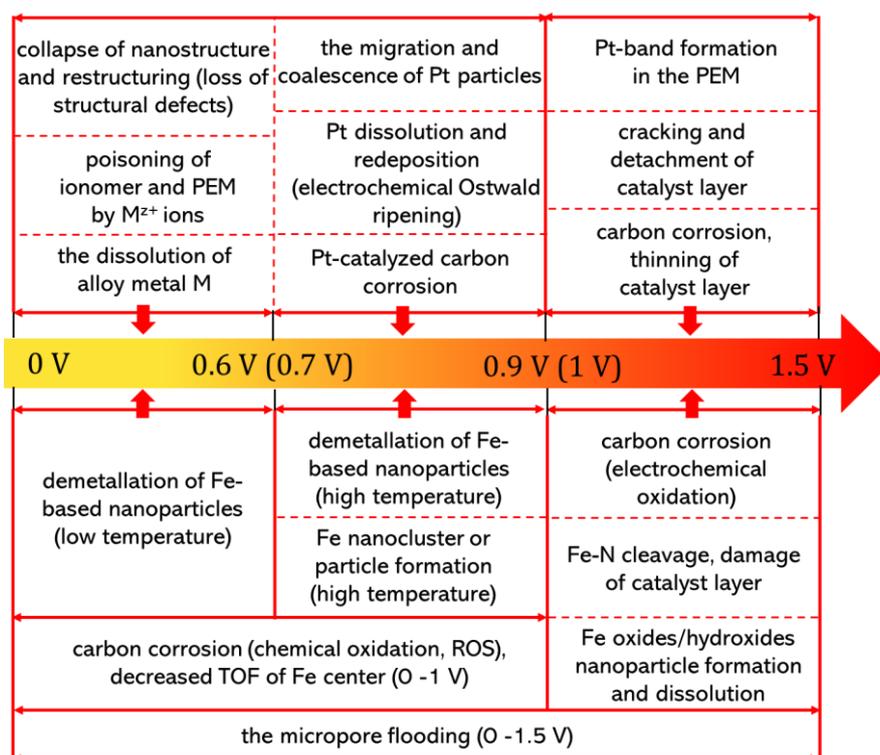


Figure 6. The degradation mechanism of Pt-based (above arrow) and Fe-N-Cs (below arrow) electrocatalysts as a function of potential (given vs. RHE).

An overview of the mechanisms as a function of the potential at which the catalytic layer is exposed is presented in **Figure 6**. For Pt-based electrocatalysts, the corrosion of the carbon support occurs in a wide potential range, forming CO/CO₂ or carbon surface oxygen groups.²⁴³ It preferentially occurs on amorphous carbon or carbon-edge defects, thus highlighting the importance of carbon support nature.²⁴⁴⁻²⁴⁵ The corrosion rate is significantly enhanced in the presence of Pt nanoparticles.²⁴⁶ During accelerated stress tests (ASTs) at high potentials (*i.e.* 1.0 – 1.5 V vs. RHE, simulating start-up/shut-down events on real PEMFCs operation), the collapse of the carbon structure is observed, impeding mass-transport of reactant gas and water removal from catalyst layer.²⁴⁷⁻²⁴⁹ Furthermore, the carbon partial oxidation (*i.e.* generation of surface oxygen groups) also improves the surface hydrophilicity, thus leading to water management issue.²⁴⁹⁻²⁵⁰ Besides the carbon support itself degradation, the support corrosion usually induces the loss of electrochemical surface area (ECSA) owing to the detachment of Pt-based nanoparticles and subsequent agglomeration on the support^{247, 251} while the crystallite migration and Pt nanoparticle coalescence at high potential was proposed to be dependent on the Pt nanoparticles-support interactions and, especially, to the surface oxygen group coverage.²⁵²

The dissolution rate of platinum is strongly dependent on the initial particle size, with the smaller ones showing faster dissolution rate compared to the larger ones (Gibbs-Thompson equation).²⁵³ The dissolution phenomenon are usually enhanced at

higher potentials.²⁵⁴⁻²⁵⁵ When exposed to ASTs, the Pt dissolution can be subdivided into anodic scan and cathodic scan dissolution, with the former being less affected by the upper/lower potential limit (UPL/LPL) and showing slower dissolution rate compared to the cathodic sweep. Topalov *et al.*²⁵⁶ used the place exchange mechanism to justify this phenomenon, with Pt exchanging its place with O at > 1.1 V vs. RHE and being subsequently dissolved during the cathodic scan. It is noteworthy that the Pt^{z+} ions generated from the dissolution of platinum are not only redeposited within catalyst layer, but diffusing into the PEM where Pt^{z+} can be reduced by H₂ crossing-over from anode side, leading to the formation of a Pt-band inside the PEM.^{250, 257-259} Crystallite growth is also commonly observed during platinum nanoparticles ageing, and is mainly attributed to (a) the coalescence of nanoparticles and (b) the dissolution of small Pt nanoparticles into Pt²⁺, followed by redeposition on the larger size Pt nanoparticles (electrochemical Ostwald ripening).²⁶⁰ The operating conditions (*e.g.* the UPL,²⁶¹ relative humidity,²⁶² temperature,²⁶³ *etc.*) and physicochemical properties of electrocatalyst itself (*e.g.* the initial particles size and shape,²⁶⁴ pore size distribution,²⁶⁴ *etc.*) play a crucial role for the stability of Pt nanoparticles during ageing.

PtM/C (M = Co, Ni) suffers from additional ageing mechanisms due to the preferential dissolution of the transition metal during operation.²⁶⁵ Asset *et al.*¹⁸⁷ emphasized that the lower UPL was crucial to prevent substantial dissolution of Ni, the growth of crystallites size and the loss of structural defects. Sneed *et al.*²⁶⁶ evidenced that Pt-rich, small size, PtM nanoparticles are stable while larger ones, with higher content of 3d transition metal, are continuously leaching the 3d-transition metal during the operation,

which leads to the formation of hollowed-out shells. This dissolution incidentally leads to the loss of the strain effect induced by the presence of the alloying element,²⁶⁷⁻²⁶⁸ although it might under specific ageing conditions, lead to the formation of hollow Pt-rich nanoparticles with enhanced activity.¹⁸⁶ Owing to their smaller initial ECSA (low Pt loading, larger nanostructures), the PtM often exhibit enhanced local O₂ transport resistance, which is magnified during ASTs, thus dramatically decreasing the performance at high current density.^{88, 269} The dissolved transition metal M^{Z+} cations are not reduced in PEMFCs operation condition, thus still existing as M^{Z+} ions in the catalytic layer,²⁷⁰⁻²⁷¹ where they can significantly decrease the proton transport property through strong interaction with the sulfonic acid groups in the perfluorosulfonated membrane and ionomer,²⁷²⁻²⁷³ alongside decreasing the oxygen permeability.^{248, 274}

The durability of Fe-N-Cs, especially in PEMFC condition, is far below the target of DOE in 2025⁶ and results of numerous mechanisms. Similarly to Pt, the degradation mechanisms are (i) potential dependent and (ii) chemistry dependent (*e.g.* Fe-based nanoparticle, FeN_xC_y moiety). They include, as illustrated in **Figure 6**, (i) micropore flooding, (ii) demetallation, including the dissolution of Fe-based nanoparticles and disintegration of the FeN_x moiety, (iii) carbon corrosion, including electrochemical oxidation and chemical oxidation. The first mechanism would lead to the “deactivation” of the active sites induced by its inaccessibility to the reactants. Such deactivation might be reversible, through water management or catalyst regeneration, while the latter two result in the “loss” of performance due to destruction of active site (*i.e.* irreversible oxidation of carbon surface and disintegration of FeN_x sites).

Dodelet *et al.*^{89, 275} proposed that the electro-oxidation of the carbon transformed the hydrophobic surface to hydrophilic one, which led to easier micropores water flooding where most of the active FeN_x sites were hosted. As such, the micropores water filling impedes the O₂ transport to the FeN_x active sites, along with leading to their demetallation through Le Chatelier principle,⁹⁰ inducing dramatic performance drop. Synthesizing the Fe-N-C at high pyrolysis temperature usually lead to an higher graphitization degree and lower heteroatoms doping content, which makes the carbonaceous surface more hydrophobic, hence preventing the flooding.⁸⁹

Demetallation of Fe-N-Cs can be subdivided into (i) dissolution of Fe-based nanoparticles and (ii) disintegration of FeN_x moieties, depending on applied potential and operation temperature in PEMFCs. Choi *et al.*¹³¹ proposed that the demetallation of Fe-based nanoparticles occurred only below 0.7 V *vs.* RHE at low temperature (20 °C), with the potential range extending to 1 V *vs.* RHE at 80 °C.¹²⁹ The generated Fe²⁺ can readily diffuse into the membrane and subsequently decrease the proton conductivity. In addition, the presence of Fe²⁺ also leads to a Fenton reaction, favoring the formation of high oxidative radical oxygen species (ROS), which will be discussed in the following paragraphs. The demetallation of Fe-based nanoparticles, *e.g.* low valence Fe metal or iron carbide is also observed at high potential range (*i.e.* above 1 V *vs.* RHE) accompanied with the post-formation of high valence iron compounds (*e.g.* Fe(OH)₃).²⁷⁶ Atomic FeN_xC_y moiety is believed to be highly stable and its destruction mainly occurs at high potential range (*i.e.* 1 V - 1.5 V *vs.* RHE), probably arising from the cleavage of Fe-N bond induced by severe carbon corrosion.^{11, 131, 276} The destruction of the FeN_xC_y

moiety generally results in the formation of Fe-based nano-cluster or particles and their subsequent dissolution. Besides, the surface mobility and possible transformations of FeN_xC_y edge and in-plane sites at medium potential range (0.6 - 1 V vs. RHE) during ageing at 80 °C have also been recently reported, resulting in the formation of 2D Fe cluster.¹⁶⁰

Similar to the case of Pt-based electrocatalysts, carbon corrosion is also prevalent in the Fe-N-Cs during ageing, but it is not catalyzed by the presence of Fe-based moieties. The dramatic carbon support degradation during start-up/shut-down events also holds true, leading to similar consequences (*i.e.* loss of active sites, mass-transport limitation, water management issues). The carbon corrosion is believed to exert more severe effects on the Fe-N-Cs since the active sites (*i.e.* FeN_xC_y) are embedded into carbon matrix and thus are disintegrated with the corrosion of the carbon. The carbon corrosion is also caused by carbon oxidation reaction (COR), which can be classified into two mechanisms, *i.e.* electrochemical oxidation (carbon electrooxidation to CO and CO_2) and chemical oxidation. Choi *et al.*¹³¹ proposed the potential range for CO_2 and CO formation to be above 0.9 V vs. RHE at 50 °C. The COR rate strongly increases at higher temperature/potential.²⁷⁷ On the other hand, the performance losses during ageing at low potential range (*i.e.* 0.6 V - 1 V vs. RHE) are usually governed by chemical oxidation of carbon surface, where the ROS formed from H_2O_2 by the Fenton reaction are responsible for the carbon corrosion. Such oxidation phenomena is particularly true in PEMFC operation condition (O_2 feed, high current density) since the generated amount of H_2O_2 is far higher in comparison to the one detected in an RDE

measurement.¹²⁹ Choi *et al.*²⁷⁸ observed that, although the FeN_xC_y moiety was structurally stable at low potential range, its turnover frequency (TOF) was also dependent of partial chemical carbon oxidation induced by the ROS, which modified the electronic structure of the carbon backbone and, thus, the binding strength of oxygen-based species on the Fe atom center. In addition, CO/CO₂ gas evolution is observed at low potential range (< 0.9 V vs. RHE) and the degradation extent is independent of operation temperature and potential range, implying that the chemical oxidation of the carbon surface also plays a vital role in the Fe-N cleavage. Owing to the points aforementioned, it appears that increasing the Fe-N-Cs durability goes through (i) the decrease of Fe-based nanoparticles (to reduce Fe²⁺-induced membrane poisoning and Fenton reaction); (ii) a highly favored 4e⁻ reactive pathway, to limit the H₂O₂ generation and (iii) an adequate graphitization of the support, to achieve an acceptable trade-off between durability and activity. Interestingly, this last point is not only critical for Fe-N-C electrocatalysts, but also for Pt-based electrocatalysts, as the degradation of the carbon support also leads to the active phase detachment, agglomeration, *etc.* However, going in the direction of highly graphitized supports usually results in low carbon specific surface, *i.e.* low dispersion of the Pt-based nanoparticles and decreased ECSA. Nevertheless, to the advantage of the Fe-N-C electrocatalysts, the carbon-related corrosion ought to be weaker on the latter, owing that a 4e⁻ pathway is favored and Fe-based nanoparticles are removed, since the FeN_x moieties do not catalyze the COR, by opposition to Pt-based nanoparticles.

7. Conclusion and perspectives

Over the past years, considerable progresses have been achieved in developing efficient Pt-based and Fe-N-C electrocatalysts for PEMFCs applications. Here, we compare those two families of electrocatalysts on the basis of (i) their structural properties and ORR mechanism; (ii) their intrinsic ORR activity and (iii) performances in PEMFCs and durability, to assess the potential of Fe-N-Cs as replacement for Pt-based electrocatalysts in PEMFCs applications. Both families of electrocatalysts benefit from a wide variety of active sites and of means to control the latter's activities. Indeed, Pt-based electrocatalysts activity can be finely tuned by the addition of structural defects, alloying elements and/or morphological changes to expose crystallites with preferential orientation, whereas the Fe-N-Cs active site nature, density, localization and carbon backbone defectivity play a crucial role in the electrocatalyst activity and selectivity. For both families of electrocatalysts, the design approaches are currently governed by the Sabatier principle, *i.e.* the reaction is occurring on a given active site (Pt-atom *vs.* FeN_x) that should bind the oxygen intermediate neither too strongly nor too weakly. Hence, they are limited by the scaling relationships between the different oxygen intermediates, which ultimately limits their improvement. Going 'beyond' the top of the volcano plot discussed in Section 4 would require a true paradigm shift in terms of electrocatalyst design, by using, for example, co-catalysis (*i.e.* an ORR mechanism where the different reaction steps are undergone onto different active sites of the electrocatalyst, *e.g.* **evidenced** bi-metallic center for M-N-Cs). Freeing the electrocatalyst design from the scaling relationships is especially crucial for Fe-N-C electrocatalysts,

as the means of tuning their activity (*i.e.* by adding a controlled density of structural defects to modify the d-band of iron) impact their stability. **In the current design landscape, however, the Fe-N-Cs more and more appear as a credible alternative to Pt-based electrocatalysts**, as their performances are now reaching the DOE 2025 target. This point comes with several additional positive features for Fe-N-C electrocatalysts: (i) although still behind for PEMFCs applications, Fe-N-Cs are more interesting than Pt-based electrocatalysts as AEMFCs cathodes; (ii) the Fe-N-Cs, especially in the current economical, and geopolitical context, benefit of being only composed of earth-abundant elements, thus being free of the strain that currently exists on the platinum resources; (iii) durability wise, owing that the design of Fe-N-Cs is greatly improved (limitation of the density of active sites in micropores, removal of the exposed Fe-based nanoparticles, enhanced selectivity for the $4e^-$ pathway, proper graphitization degree), the Fe-N-Cs should exhibit excellent stability in operating ORR conditions, as they should not suffer from Pt-induced carbon corrosion. In conclusion, and considering the challenges related to the implementation of the more complex Pt-based nanostructures in PEMFCs, the Fe-N-Cs hold great promises. However, further improvements in the intrinsic activity should imply new design approaches, as achieving both activity and durability objectives would be challenging by simply moving on the volcano plot branches (see Figure 4). Such new approaches are numerous, ranging from the design of bi-metallic active sites to break the scaling relationships, to functionalizing the carbon backbone with heteroatoms that would not decrease its stability (*e.g.* fluorine²⁴⁷) while adequately modifying the iron electronic structure.

Several other points of interest arise from this review, that apply for both Pt-based electrocatalysts and Fe-N-Cs: (i) electrocatalysts should always be designed with the catalytic layer in mind, as numerous promising electrocatalysts cannot be yet implemented in PEMFCs owing to poor ionomer distribution around/within the catalyst, unproper morphology for solid electrolyte applications, *etc*; (ii) especially for Fe-N-Cs, the use of rigorous, and standardized, characterization protocols for the activity and durability is essential, as a proper comparison of those materials stability in their own family, and with Pt-based electrocatalysts, is challenging.

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