Oxygen Reduction Reactions on Single- or Few-Atom Discrete Active Sites for Heterogeneous Catalysis

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The oxygen reduction reaction (ORR) is of great importance in energy-converting processes such as fuel cells and metal–air batteries and is vital to facilitate the transition toward a nonfossil dependent society. The ORR has been associated with expensive noble metal catalysts that facilitate the O₂ adsorption, dissociation, and subsequent electron transfer. Single- or few-atom motifs based on earth-abundant transition metals, such as Fe, Co, and Mo, combined with nonmetallic elements, such as P, S, and N, embedded in a carbon-based matrix represent one of the most promising alternatives. Often these are referred to as single atom catalysts; however, the coordination number of the metal atom as well as the type and nearest neighbor configuration has a strong influence on the function of the active sites, and a more adequate term to describe them is metal-coordinated motifs. Despite intense research, their function and catalytic mechanism still puzzle researchers. They are not molecular systems with discrete energy states; neither can they fully be described by theories that are adapted for heterogeneous bulk catalysts. Here, recent results on single- and few-atom electrocatalyst motifs are reviewed with an emphasis on reports discussing the function and the mechanism of the active sites.

1. Introduction

The sluggish kinetics of oxygen reduction reaction (ORR) is often the decisive factor when implementing energy conversion and storage processes such as fuel cells, and metal–air batteries.[1–8] Researchers have struggled for decades to find efficient, stable catalysts to speed up the kinetics and to minimize energy losses, but so far catalytic efficiency and long-term stability is unfortunately still commercial fuel cell catalysts contain high ratios of noble metals such as Pt, Pd, and Ru.[9–25] So far, the cost of a catalyst from the Pt group in fuel cell stacks is projected by the US. Department of Energy to make up about half the cost of the stack, clearly limiting its commercial viability.[26,27] Hence, if we ever expect fuel cells and metal–air batteries to be true competitive fossil-free alternatives, we need to improve the exploration of catalysts based on cheap and abundant elements, even approaching the so-called “no-cost catalysts,” if required. In the last ten year, research in this field has been intense, and several promising alternatives are now coming forward.[28–40] Among the best approaches, ORR catalysts based on nonprecious metal, such as Ni, Fe, or Co correlated to nonmetallic elements such as P, S, N, Si, or C represent one of the most viable systems.[41–49] Nowadays, it is well known that size and shape of metal nanoparticles and substrate materials are very important factors in determining the activity of catalysts,[50–52] and decreasing the metal particle size leads to a larger free surface, lower coordination number, and constrained spatial configuration, resulting, among other things, in better accessibility to empty d atomic orbitals from the metal species.[53–56]

Accordingly, in recent years, there has been an increasing attention devoted to downsizing the transition metal particles into clusters or ultimately into single atoms supported in matrices consisting of non-noble-metal materials.[57–60] Such single- or few-atom motifs embedded in a conductive matrix have the potential to both deliver a low overpotential at each active site and concurrently be present in large quantities to provide an overall high turnover number and thus a high current density at low potential. These systems are however not only technically interesting, they are also scientifically intriguing as they represent a kind of middle state between molecular catalysts and heterogeneous bulk catalysts. The catalytic mechanism and the role and nature of the active sites in single- or few-atom catalyst motifs is still being explored and continue to puzzle researchers. Here we review recent findings with emphasis on reports from the last 5 years that describe synthesis and performance, but most importantly, those that describe catalytic mechanisms and the role of metal atom and other surrounding elements. We are aware of reviews on ORR catalysis focused on single active metal catalysts[61–72] but there are very few[73,74] that focus on ORR catalysis based on such discrete catalyst motifs, we therefore review both theoretical and experimental reports, and

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end by giving an outlook into the possibilities and limitations of such catalysts to be implemented in real practical applications.

The review is outlined in chapters where atomic motifs based on specific metals are separated, followed by an individual chapter where fully nonmetallic electrocatalysts are reviewed. We note that to a very large extent the single or few atomic motifs means a coordination of a single metal atom to other nonmetallic atoms such as nitrogen, carbon, sulfur, or phosphorus. In some few reports however, the catalyst motifs comprise neighboring metal atoms coordinated to nonmetallic atoms. We refer to these works in the below sections and categorize them according to the metal with the highest concentration. In addition, since the ORR proceeds differently and might involve different adsorbates, intermediates, and ions depending on the electrolyte and pH, the comparison is made by indicating the ORR conditions. Lastly, we finish each subchapter with a table presenting electrochemical performance data for ORR.

2. Iron-Based Electrocatalysts

Among current nonprecious catalysts based on single active transition metal atom sites, Fe-based catalysts are by far the most extensively studied. The main reason for this popularity is of course the high, abundance, environmentally benign properties and low price of the raw material, but also the fact that they exhibit a very good catalytic efficiency and stability when coordinated in a matrix comprising for example carbon, nitrogen and sulfur. It is easy to draw an analogy to natural catalysts, enzymes, which in many cases contain coordinated iron atoms as the active part. At least in part, the high chemical and thermal stability concurrent with high activity can be explained by a beneficial charge relocation around the iron–heteroatom nanoparticles. Furthermore, because of the strong Fe–heteroatom bonds the degradation and agglomeration of neighboring metal nanoparticles are mitigated. Since Fe-coordinated motifs, such as Fe–N, Fe–S, Fe–C, and Fe–P, generally exhibit good electron transfer properties as well as excellent chemical stability in most solvents such systems can also be attractive supports for other heterogeneous electrocatalysts and some of these have already shown good synergy effects. A common strategy to achieve iron coordinated motifs is by using macrocyclic molecules and or metal organic frameworks containing Fe–N2, Fe–N4, Fe–S, and Fe–P motifs. These systems are summarized in the following subchapters.

However before continuing, we consider it important to emphasize a crucial point in the characterization of metal-coordinated motifs, namely to ensure that the catalytic performance is not originating from metal clusters or metal nanoparticles that might have aggregated in the support or are remnant from the synthesis process. Unambiguous evidence for atomically dispersed catalysts is normally achieved by a combination of techniques, where high-resolution electron microscopy techniques such as high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), Cs-corrected electron microscopy and X-ray photoelectron spectroscopy (XPS) lay the foundations, but X-ray absorption fine structure spectroscopy (XAFS) is normally needed to fully support the presence of single metal atoms, and the absence strong metal-metal coordination. XAFS is a technique that probes the oscillatory structure in the X-ray absorption coefficient close to the X-ray absorption edge. It is therefore highly sensitive to the local coordination of the specific element that is probed, which usually is the specific metal atom. XAFS is usually divided into...
two separate but related subclasses, extended X-ray absorption fine spectroscopy (EXAFS), and X-ray absorption near-edge structure spectroscopy (XANES). Although the physical origin of these two techniques are the same, they are sensitive for different properties, where XANES are more suited to reveal the coordination chemistry and oxidation state, and EXAFS can give information on coordination number, atomic bond distances and therefore are better suited to reveal the coordination environment of the metal atoms. These techniques are vital for the understanding of the catalytic activity of metal coordinated motifs, and we briefly refer to them in the following chapters; however we do not expand further on the interpretation of these techniques in this review, but refer to more specialized publications.[94] In the case of iron-containing species, we note however that 57Fe Mössbauer spectroscopy also can be particularly useful and aid to elucidate the coordination environment of the iron atom.[95–97]

2.1. Iron–Carbon-Based Catalysts

Transition metal–carbon-based catalysts show promising properties for ORR in both alkaline and acidic condition based on their excellent corrosion resistance, good electrical conductivity and a flexibility in choice of doping elements (e.g., Fe, Co, or Ni).[98–101] Being one of the most potential cost-effective non-noble-metal catalysts, Fe-based catalysts are likely to play a pivotal role in the transition to a sustainable society. One of the key aspects for Fe-based catalysts is to ensure a high conductivity by improving charge-carrier concentrations.[53,102–104] This can be achieved by the doping of carbon by Fe atoms to obtain optimal electronic and geometric structures, and strategies for this are summarized below. Concurrently, a vital aspect for single or few-atom motifs to improve the ORR efficiency is to obtain a structural design of the catalysts that enhances the selectivity toward 4e\(^{−}\) reduction of O\(_2\) by suppressing the production of H\(_2\)O\(_2\). It has been shown that under alkaline solutions, the Lewis acidic Fe\(^{2+}\) active sites can efficiently adsorb and immediately reduce the Lewis basic HO\(_2\)\(^{−}\) intermediates through a 4e\(^{−}\) process.[55,57,105–107] However in very strong alkaline electrolytes, the active sites from the iron center are fully covered by adsorbed hydroxy species in the inner Helmholtz plane and the solvated O\(_2\) is localized in the outer Helmholtz plane.[108–110] As a result, the active iron center in Fe–C catalysts is not easily accessible in strong alkaline solutions. In acidic medium, a different reaction path occurs ensuring that the active site is directly accessible to the reactants (O\(_2\), H\(^{+}\)) and other intermediate products (e.g., H\(_2\)O\(_2\)), while finally in neutral electrolytes H\(_2\)O\(_2\) negates its Lewis basic character and undermines its stabilization on Fe\(^{2+}\) active sites, leading to a 2e\(^{−}\) ORR pathway, generating H\(_2\)O\(_2\).[57,75,100] Precise control over the structural parameter of Fe–carbon-based catalysts with homogeneously distributed single atomic sites can be used to fine-tune the properties of the active center and optimize the catalytic ORR efficiency and simultaneously unveil the catalytic mechanism. However, obtaining such precise control, and to get experimental insight is challenging. A successful attempt was however presented by Rümmeli and co-workers who were able to examine individual Fe atoms residing at graphene edges using Cs aberration-corrected TEM in situ investigations (Figure 1).[111] Although their results do not directly connect to ORR catalysts, their study points to two important issues; the diffusion of single Fe atoms at graphene edges is edge-dependent (zigzag and armchair), indicating the

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**Figure 1.** Identification of hexagonal and pentagonal carbon rings. a–c) High-resolution TEM (HRTEM) images (false color), magnified regions of HRTEM with overlaps of the density functional theory (DFT)-calculated atomic structures, and DFT-derived structures (top and side views) of a pentagon including an Fe atom. Gray ball, carbon atom; orange ball, Fe atom. d–f) HRTEM images (false color), magnified regions of HRTEM with overlaps of the DFT-calculated atomic structures, and DFT-derived structures (top and side views) of a distorted hexagon including an Fe atom, Scale bars: b,e) 0.5 nm. Reproduced with permission.[111] Copyright 2014, United States National Academy of Sciences.
need of strong anchoring, and in line with other studies they also show that electronic trap states at edges are highly affected by nearby transition metals.\[112,113\]

### 2.2. Iron–Nitrogen-Based Catalysts

The activity of many transition metal-based catalysts suffers from low stability in acidic media due to leaching, and many also exhibit rather large overpotential and low selectivity for 4e\(^-\) ORR pathway, and hence most transition metal compounds are not as competitive as Pt.\[67,95\] In contrast, Fe–N catalysts exhibit encouraging ORR activities and stabilities in both alkaline and acidic conditions, where the latter often is explained by the firm attachment of transition metals to nitrogen functionalities.\[114,115\]

The good catalytic efficiency in acidic media is explained by the ability of the active iron site to directly adsorb O\(_2\) and catalyze the subsequent O=O bond breaking.\[116,117\] However, not all Fe–N\(_x\) moieties can be referred to as active sites due to their location within the catalyst material, and fast mass transportation and low charge injection/extraction barrier are important factors since it affects both kinetics and the energy conversion efficiency. Kucernak et al. found that the effective utilization of Fe–N\(_x\) moieties by a Fe–N–C single atom catalysts (SAC) was only about 4.5% since only the moieties at the triple-phase boundary (TPB) of the carbon (e\(^-\)), the ionomer (H\(^+\)) and the O\(_2\) can be involved in the ORR.\[118,119\]

To increase catalytic ORR efficiency various strategies have been used to achieve both i) a high-density of Fe–N\(_x\) moieties and ii) ensure that as many as possible are residing at the TPB. Typical examples of nitrogen sources are, e.g., cyanamide, melamine, and phenanthroline (Figure 2a). A striking example of a successful strategy to achieve (ii) is the study by Wan et al.\[118\] who synthesized a concave catalyst with highly dispersed Fe–N\(_4\) moieties. The hybrid catalyst possesses a mesoporous structure, with a large surface area and concurrently the concave structure means a high ratio of Fe-coordinated moieties at the TPB (Figure 2a–d). The good
mass transport is manifested by a power density of 1.18 W cm\(^{-2}\) under 2.5 bar H\(_2\)-O\(_2\), and an activity of 129 mA cm\(^{-2}\) at 0.8 V\(_{\text{IR-free}}\) under 1.0 bar H\(_2\)-air (Figure 2e).\(^{[118]}\)

A strategy to address (i) has been to ally a so-called cascade anchoring strategy, which has shown the ability to balance both single-atomic dispersion and high metal loading (up to 12.1 wt\%).\(^{[120]}\) The procedure is briefly shown in Figure 3, where the metal ions are chelated and anchored onto O-rich carbon support by a chelating agent, which can effectively sequester metal ions and physically isolate the metal complex. M–N\(_x\) moieties formed from decomposed carbon nitrogen species (CN\(_x\)) can bind with metal atoms and thereby prevent metal atoms from aggregation.

This sequential protecting strategy efficiently stabilizes the Fe atoms and hinders them from agglomeration even after pyrolysis, and the coordination polymer and the abundant repeating units significantly increase the atomic density of iron. Also the relieved passivation effect of OH\(^*\) on Fe–N\(_4\)/C structure leads to its superior ORR activity to Pt/C in alkaline solution as shown in reports using similar strategies.\(^{[108,110,116]}\)

2.3. Iron–Sulfur-Based Catalysts

The introduction of sulfur into a carbon matrix induce structural defects that can improve the ability for oxygen adsorption and change the bandgap of the host material.\(^{[121,122]}\) It has also been shown that protonation of sulfur is not as severe as that of nitrogen,\(^{[123]}\) and thus S-species can be used to significantly improve the ORR efficiency of the active site due to a synergistic effect as shown by Shen et al.\(^{[57]}\) Chen et al. presented an efficient strategy to achieve atomically dispersed Fe–N\(_y\) on N, S codecorated hierarchical carbon layers by coating carbon nanotubes (CNTs) with 2,2-bipyridine and Fe salt precursor.\(^{[124]}\) By a similar strategy, Hoque et al. realized in situ formation of Fe\(^{\text{II}}\)N bonds in the N, S codoped carbons via the suitability of the precursors and silica template.\(^{[125]}\) Mesoporous architecture and in situ formation is an effective method to improve the efficiency and durability of Fe–S based catalysts. However, the size of the carbon supporting plane is the main factor governing the kinetic activity of the Fe–N\(_4\) site since it affects the electron-rich \(\pi\)-band with the degree of delocalization.\(^{[126]}\) The high electron density of the \(\pi\)-band increases the \(\eta\)-orbital energy level of the active site, which in turn induces an intermolecular hardness factor \((\eta\text{Dmol})\) of the bond between the ORR intermediates and the Fe–N\(_4\) sites, resulting in strong adsorption of the ORR intermediates.\(^{[127]}\) Mun et al. report a versatile strategy to incorporate electron-withdrawing/donating functionalities on the carbon plane by S-doping (Figure 4). The strength of the electronic effect, derived from
the delocalized π-band of the carbon plane on the d-orbital of the Fe ion in the Fe–N₄ site results in a beneficial change of ORR activity of the Fe–N₄ site.[128]

2.4. Iron–Phosphorus-Based Catalysts

Fe–P-based catalysts are considered a new class of promising composites that so far are less studied. Phosphorus hold some interesting features for ORR since its lower electronegativity compared to carbon can change the charge distribution on neighboring atoms and increases the affinity toward electron acceptor molecules.[89,129] Its larger covalent radius compared to nitrogen has been seen as a difficulty when doping carbon nanostrucctures with phosphorus,[130] explaining the reduced amount of experimental reports for such catalysts. Recently, an Fe-coordinated motif on a carbon matrix codoped with nitrogen and phosphorus was synthesized by an impregnation method followed by pyrolysis of different renewable woody biomass.[131] In this study, density functional theory (DFT) calculations indicated that Fe–P bonds were able to effectively activate the O₂ molecule and promote a subsequent 4e⁻ ORR under alkaline conditions. It was also shown by DFT that the main effective sites were single N–P–O–Fe–O centers, where the associated P–O–Fe bond could significantly lower the adsorption energy of strongly adsorbed intermediates (O₆ and OH₉) and thus give rise to enhanced ORR performance.[132] This is in line with other reports showing that a secondary co-coped heteroatom (P, S, or B) of N-doped nanocarbons are able to break the electro-neutrality of carbon and thereby boost the ORR catalytic activities.[129,133]

3. Cobalt-Based Electrocatalysts

Given many similarities of cobalt and iron, it is natural that many strategies developed for Fe-based catalysts hold also for Co-based catalysts, and synthesis schemes for designing single- and few-atom Fe-based catalysts can usually be adopted for their respective Co-based counterparts. However, compared to iron, cobalt has one advantage. When used as catalyst in proton exchange membrane cells (PEMC), leakage of Fe leads to solvated Fe²⁺ or Fe³⁺ close to the membrane. These ions risk to react with H₂O₂ to produce hydroxyl and hydroperoxyl radical species in the so-called Fenton’s reaction and such radical species are known to be detrimental for PEMs leading to poor long-term stability of PEMCs.[139,140] In the following subsections, we review diverse Co-coordinated motifs.

3.1. Cobalt–Nitrogen-Based Catalysts

The overall ORR performance of M–N–C catalysts is reported to follow the general efficiency trend Fe > Co > Mn > Cu > Ni in both acid and alkaline electrolytes.[141,142] Although this trend generally seems to hold when comparing the catalytic performance for single atomic catalysts (Tables 1–4), it is clear that the coordination number as well as catalyst support significantly affect the performance data and that several catalysts diverge from the general trend. A common problem when preparing atomically dispersed metal catalysts is that the high surface energy of single atoms often leads to aggregation and/or being lost from the support.[143] Incorporation of nitrogen into a carbon support has shown to be an effective method to increase the stability of single metal catalysts and there are numerous reports on such strategies.[55,144–147] Similar to iron, the coordination of Co to nitrogen has furthermore shown to be an excellent strategy to enhance the ORR activity and the ideal single-atom catalysts should have a high density of atomically dispersed sites. Wu et al. used salt template to scalable synthesize highly dense and monodispersed Co single atoms on nitrogen-doped 2D carbon nanosheets, where the site fraction of single Co atoms in the carbon matrix reaches ~15.3% resulting in high electrochemical surface area (ECSA) of ~105.6 m² g⁻¹.[148] Also by a template method, Sun et al. used a dual-template pyrolysis method to prepare Co-coordinated motifs embedded in hierarchically ordered porous N-doped carbon. XAFS studies were used to support the presence of single Co atoms coordinated to nitrogen in a Co–N₄–C configuration, and that there are practi-
cally no Co–Co interactions, excluding the presence of larger clusters or particles (Figure 5). They further showed the excellent performance for ORR in alkaline medium (0.1 M KOH) with an $E_{1/2}$ of 0.892 V, which is 53 mV more positive than that of Pt/C, in addition the catalysts showed good stability, electron transfer number close to 4 (3.9) and fast kinetics, manifested by a Tafel slope of 58 mV decade$^{-1}$ and five times higher current density than Pt/C at 0.9 V.

By preparing reference samples comprising Co-nanoparticles, Sun et al. showed that the catalytic effect indeed is correlated to the Co-N$_4$ sites. From DFT studies it is revealed that the active site for the oxygen reduction in both acidic and alkaline medium is the central metal atom. In alkaline medium the ORR process is represented by the scheme$^{[5,152]}$

\[ \text{H}_2\text{O}_2 + 4e^- + \text{H}_2\text{O} \rightarrow 2\text{OH}^- + \text{H}_2 \]

I) $^*\text{O}_2(\text{g}) + \text{H}_2\text{O}_2(\text{l}) + \text{e}^- \rightarrow ^*\text{OOH} + \text{OH}^-$

II) $^*\text{OOH} + \text{e}^- \rightarrow ^*\text{O} + \text{OH}^-$

III) $^*\text{O} + \text{H}_2\text{O}_2(\text{l}) + \text{e}^- \rightarrow ^*\text{OH} + \text{OH}^- + ^*$

IV) $\text{OH}^- + \text{e}^- \rightarrow \text{OH}^- + ^*\text{O}$

where the $^*$ represents the active site (cobalt). It was shown that the rate limiting steps in the scheme above were the formation of $^*\text{OOH}$ and $\text{OH}^-$ (steps I and IV). Zhang et al.$^{[153]}$ synthesized Co–N$_4$ catalysts embedded in multichannel carbon matrix with a different methods using Co–porphyrin as a precursor. Similarly, they established an active site comprising a central Co atom coordinated to four nitrogen. More specifically

| Electrocatalyst type | $E_{\text{onset}}$ (vs RHE) | $E_{1/2}$ (vs RHE) | Ref. |
|---------------------|--------------------------|------------------|-----|
| Fe–C | 0.21 V (vs NH$_3$) | 0.1 V (vs NH$_3$, 0.1 M KOH) (0) | [134] |
| Fe–C | 0 V (vs Ag/AgCl) | NA | [78] |
| Fe–C | 1.050 V | 0.874 V (0.1 M KOH) (40) | [131] |
| Fe–C | 0.97 V | 0.88 V (0.1 M KOH) (20) | [135] |
| Fe–C–N | NA | 0.891 V (0.1 M KOH) (43) | [93] |
| Fe–N$_x$ | 0.98 V | 0.90 V (0.1 M KOH) (50) | [120] |
| Fe–N$_x$ | NA | 0.89 V (0.1 M KOH) (NA) | [136] |
| Fe–N$_x$ | NA | 0.900 V (0.1 M KOH) (58) | [137] |
| Fe–N$_x$–Co | 1.06 | 0.863 V (0.1 M HClO$_4$) (NA) | [75] |
| Fe–N$_x$ | 0.968 V | 0.888 V (0.1 M KOH) (NA) | [121] |
| Fe–S | NA | 0.85 V (0.1 M KOH) (30) | [125] |
| Fe–S | 0.95 V | 0.83 V (0.1 M KOH) (20) | [138] |
| Fe–P | 0.884 V | 0.815 V (0.1 M KOH) (6) | [129] |
| Fe–N$_x$ | 0.941 V | 0.814 V (0.5 M H$_2$SO$_4$) (30) | [116] |
| Fe–S$_x$ | 0.821 V | 0.729 V (0.1 M HClO$_4$) (NA) | [122] |

Table 2. ORR performance of single- and few-atom motifs. The onset ($E_{\text{onset}}$) and half-wave potential ($E_{1/2}$) are reported versus RHE, unless otherwise specified. In all cases, values are reported as given in specific respective references, without formatting number of digits.

| Electrocatalyst type | $E_{\text{onset}}$ (vs RHE) | $E_{1/2}$ (vs RHE) | Ref. |
|---------------------|--------------------------|------------------|-----|
| Co–N$_x$, $x = 1–4$ | NA | 0.892 V (0.1 M KOH) (53) | [149] |
| Co–N$_x$ | NA | 0.838 V (0.1 M KOH) (4) | [151] |
| Co–N$_x$ | 0.95 V (0.1 KOH) | 0.86 V (0.1 M KOH) | [153] |
| Co–N$_x$ | 0.982 V (0.1 KOH) | 0.881 V (0.1 M KOH) (70) | [55] |
| Co–N$_x$ | 0.990 V (0.1 KOH) | 0.84 V (0.1 M KOH) (0.10) | [155] |
| Co–N$_x$ | 0.970 V (0.1 KOH) | 0.87 V (0.1 M KOH) (50) | [163] |
| Co–N$_x$ | NA | 0.846 V (0.1 M KOH) | [164] |
| Co–N$_x$ | 0.956 V (0.1 KOH) | 0.851 V (0.1 M KOH) (20) | [165] |
| Co–N$_x$ | NA | 0.878 V (0.1 M KOH) (6) | [60] |
| Co–N$_x$ | NA | 0.80 V (0.5 M H$_2$SO$_4$) (–60) | [54] |
| ZnCoN$_x$ | 0.91 V (0.1 M HClO$_4$) | 0.76 V (0.1 M HClO$_4$) (–60) | [155] |
| ZnCoN$_x$ | 0.92 V (0.1 M HClO$_4$) | 0.76 V (0.1 M HClO$_4$) (–100) | [76] |
| ZnCoN$_x$ | 1.004 V (0.1 M KOH) | 0.861 V (0.1 M KOH) (35) | [77] |
| ZnCoN$_x$ | 0.97 V (0.1 M HClO$_4$) | 0.796 V (0.1 M HClO$_4$) (77) | [77] |
| Co–N$_{3+2}$ | 0.93 V (0.5 M H$_2$SO$_4$) | 0.84 V (0.5 M H$_2$SO$_4$) (NA) | [158] |
| Co–N$_x$ | 0.76 V (0.5 M H$_2$SO$_4$) (–70) | 0.69 V (0.5 M H$_2$SO$_4$) (–70) | [163] |
| Co–N$_x$ | NA | 0.778 V (0.5 M H$_2$SO$_4$) (NA) | [166] |
Table 3. ORR performance of single- and few-atom motifs. The onset ($E_{\text{onset}}$) and half-wave potential ($E_{1/2}$) are reported versus RHE, unless otherwise specified. In all cases, values are reported as given in specific respective references, without formatting number of digits.

| Electrocatalyst type | $E_{\text{onset}}$ (vs RHE) | $E_{1/2}$ (vs RHE) | Ref. |
|----------------------|-----------------------------|-------------------|------|
|                       | $E_{\text{onset}}$ (vs RHE) | $E_{1/2}$ (vs RHE) | Shift versus Pt/C ref. [mV] |
| **Noble metals**      |                             |                   |      |
| O=Rh—N$_4$           | 0.89 V (0.1 M HClO$_4$)     | 0.75 V (0.1 M HClO$_4$) (NA) | [167] |
| O=Ir—N$_4$           | 0.97 V (0.1 M HClO$_4$)     | 0.864 V (0.1 M HClO$_4$) (44) | [166] |
| Pt—N$_6$             | NA                          | 0.76 V (0.1 M HClO$_4$) (NA) | [149] |
| **Transition metals** |                             |                   |      |
| Mn—N$_6$             | NA                          | 0.80 V (0.5 M H$_2$SO$_4$) (~60) | [171] |
| Mn—N$_2$O            | NA                          | 0.86 V (0.1 M KOH) (40) | [172] |
| Mn—N$_2$P$_2$        | 0.97 V (0.1 M KOH)          | 0.84 V (0.1 M KOH) (0, NA) | [179] |
| Cu—N$_4$             | 0.99 V (0.1 M KOH)          | 0.895 V (0.1 M KOH) (25) | [182] |
| Cu—N$_2$, Cu—N$_4$   | 0.97 V (0.1 M KOH)          | 0.81 V (0.1 M KOH) (NA) | [181] |
| Cu—N$_4$, Cu—N$_4$   | NA                          | 0.869 V (0.1 M KOH) (NA) | [181] |
| Nb—C$_6$             | −0.13 V (vs Ag/AgCl, 0.1 M KOH) | NA | [182] |
| W—N$_5$              | NA                          | 0.88 V (0.1 M KOH) (NA) | [185] |
| W—C$_6$              | −0.23 V (vs Ag/AgCl, 0.1 M KOH) | NA | [184] |
| **Post-transition metals** |                         |                   |      |
| Zn—N$_4$             | 0.00 V (vs SCE, 0.1 M KOH)  | −0.175 V (vs SCE, 0.1 M KOH) (NA) | [187] |
| Zn—N$_4$             | NA                          | 0.873 V (0.1 M KOH) (15) | [188] |

Luo et al. showed support from XANES and EXAFS data for well-defined Co—N$_4$ motifs in a slightly distorted square-pyramidal configuration with D$_{4h}$ symmetry and a strong EXAFS-peak at 1.34 Å that indicated the absence of a Co—Co coordination. In addition a Co—N coordination number (CN) close to 4 was reported in the XANES spectra at 7714 eV arising from a so-called 1s—4p$_z$ shake-down transition was reported, in line with other works. The Co—N$_4$ catalysts prepared by Luo et al. performed similar to the material prepared by Sun et al. (Table 2) but with a distinctly higher Tafel slope, indicative of slower kinetics. Although both Luo et al. and Sun et al. also reported that their Co—N$_4$ catalysts performed relatively well in acidic conditions with decent stability, their main focus did not lie in this pH range. Wang et al. proposed on the other hand, focused on the performance of similar Co—N$_4$ catalysts in acidic electrolyte and presented impressive ORR performance for such conditions (Table 2). Even though the active center seemed to be similar to previous Co—N$_4$ sites, they reported an oxidation state that is slightly higher than the observed under alkaline conditions (slightly above Co$^{3+}$). In acidic conditions, Zhao et al. also reported strong performance of Co—N$_4$ moieties embedded in a carbon matrix. Interestingly and in line with other reports, the authors showed that when going from Co nanoparticles toward homogeneously dispersed Co—N$_4$ sites the catalytic performance improved and the catalytic mechanism approached a full 4e$-$ process with very low yield of H$_2$O$_2$.[155] Theoretical calculations show that both Co—N$_4$ and Co—N$_5$ moieties embedded in a carbon matrix are thermodynamically stable.[156,157] From the reports available at present date, only few experimental support for Co—N$_2$ moieties are however reported in all other cases EXAFS is shown to give a Co—N coordination close to four, although some reports identify their active centers as Co—N$_2$. For most of the Co—N$_x$ reports, there is however, a lack of XAFS, and the x should rather be seen as being a value not fully determined. From Table 2, it is also clear that the ORR performance of Co—N$_x$, Co—N$_2$, and Co—N$_4$ moieties are very similar. It is interesting to note however that Sun et al. propose that Co—N$_4$ and Co—N$_2$ sites are complementing each other in the ORR, in such way that the dissociation of O$_2$ only proceeds until the adsorption of HOOH on the Co—N$_4$ site and that the further dissociation of HOOH only proceeds on neighboring Co—N$_2$ sites.[156] Other studies indicate however that ORR could proceed with good efficiency from start to beginning (from (I) to (IV) in Equation (I) on both Co—N$_4$ and Co—N$_2$ sites.[158] The conclusion on this matter could also be a sort of a middle way. In a detailed work, He et al.[158] present experimental support for the presence of a slightly different active site, which they refer to as Co—N$_{2+2}$ in line with earlier theoretical studies.[159] By using a surfactant (Pluronic F127 block copolymer) assisted approach in combination with zeolitic imidazolate framework they achieved highly dispersed single Co-atomic sites. Different from most other studies, they showed support from EXAFS data for an average coordination number 3.6. Whether this unambiguously support the presence of Co—N$_{2+2}$ sites, seen as Co—N$_4$ moieties bridging over two adjacent armchair graphitic edges (Figure 6), is not fully clear. Nonetheless, it is interesting to note that Liu et al.[159] proposed that these type of sites can only form for highly porous supports such as that used by He et al. It is also interesting that the catalyst by He et al. so far exhibits the best ORR performance in acidic conditions among the platinum group metal-free and Fe-free catalysts (Table 2).
to on Zn–N₄, and Co–N₄ manifested by half wave potentials of 0.861 V in 0.1 M KOH, and 0.796 V in 0.1 M HClO₄. Few studies have also focused on noncarbon supports for atomically dispersed Co–N catalysts. Deng et al. studied the anchoring of Co on a boron nitride support by DFT calculations and concluded that both bonding mechanism and rate limiting step are very similar to those of Co–N motifs on carbon supports.[158]

3.2. Cobalt–Sulfur-Based Catalysts

So far there are, to our knowledge, no documented work of dispersed single Co atoms coordinated to sulfur atoms. This could originate partly from the fact that metal organic frameworks (MOFs) often are sensitive to one of the most common sulfur precursor, H₂S. However, many works points toward the possibility of achieving good ORR performance with sulfur-coordinated Co atoms,[160,161] especially when synergy effects of nitrogen coordination are included.[162]

4. Non-Cobalt- or Iron-Based Electrocatalysts

In this section we review the use of single-metal catalysts based on elements other than Co and Fe. These are divided into noble metals, transition metals, and post-transition metals. For noble

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**Table 4.** ORR performance of single- and few-atom motifs. The onset (\(E_{\text{onset}}\)) and half-wave potential (\(E_{1/2}\)) are reported versus RHE, unless otherwise specified. In all cases, values are reported as given in specific respective references, without formatting number of digits.

| Electrocatalyst type                        | \(E_{\text{onset}}\) (vs RHE) | \(E_{1/2}\) (vs RHE) | Shift versus Pt/C ref. [mV] | Ref. |
|--------------------------------------------|--------------------------------|----------------------|-----------------------------|------|
| N–graphene                                 | 0.035 V (vs NHE)               | NA                   | (vs NHE, 0.1 M KOH)         | [190]|
| B–graphene                                 | 0.029 V                        |                      |                             |      |
| P–graphene                                 | −0.011 V                       |                      |                             |      |
| O–graphene                                 | −0.017 V                       |                      |                             |      |
| S–graphene                                 | −0.058 V                       |                      |                             |      |
| Graphene                                   | −0.145                         |                      |                             |      |
| Pyridinic-N-doped hydrogen substituted graphdiyne | 1.02 V                      | 0.85 V (0.1 M KOH)   |                             | [227]|
| N-doped carbon black                       | 0.97 V                         | 0.82 V (0.1 M KOH)   |                             | [241]|
| Zigzag-edged graphene nanoribbons on CNTs  | 0.960 V                        | 0.819 V (0.1 M KOH)  |                             | [242]|
| B-doped graphitic quantum dots             | −0.05 V (vs SHE)               | NA                   | (vs SHE, 0.1 M KOH)         | [243]|
| B–N–nanocarbon                             | 0.98 V                         | 0.84 V (0.1 M KOH)   |                             | [244]|
| (N, P-doped) porous carbon materials       | NA                             | −0.19 V (0.1 M KOH)  |                             | [245]|
| B- and N-substituted graphene nanoribbons  | 1.09 V                         | 0.96 V (0.1 M KOH)   |                             | [221]|
| P–N-codoped graphene framework            | NA                             | 0.845 V (0.1 M KOH)  |                             | [229]|
| Si–N–CNTs                                  | −0.02 V (vs Ag/AgCl)           | NA                   | (vs Ag/AgCl, 0.1 M KOH)     | [246]|
| N–S–codoped hallow carbon                  | 0.93 V                         | 0.81 V (0.1 M KOH)   |                             | [247]|
| N–P–ordered mesoporous carbon             | 0.88 V                         | NA                   | (0.1 M KOH)                 | [234]|
| N- and l-codoped carbon material           | 0.944 V                        | 0.828 V (0.1 M KOH)  |                             | [248]|
| B–N–P–ternary doped graphene               | −0.06 V (vs Ag/AgCl)           | NA                   | (vs Ag/AgCl, 0.1 M KOH)     | [249]|
| N–S–B–CNTs                                 | −0.05 V (vs Ag/AgCl)           | −0.2 V (vs Ag/AgCl, 0.1 M KOH) | [198]|
| N–S–CNTs                                   | −0.06 V                        | −0.2 V               |                             |      |
| N–B–CNTs                                   | −0.06 V                        | −0.2 V               |                             |      |
| N–S–B–rGO                                  | −0.06 V                        | −0.2 V               |                             |      |
| N/S/P/O 2D carbon                          | 0.98 V                         | 0.82 V (0.1 M KOH)   |                             | [199]|
| N–P–S porous carbon                        | −0.006 V (vs Ag/AgCl)          | NA                   | (vs Ag/AgCl, 0.1 M KOH)     | [205]|
| B–N–P–S–graphene                           | −0.03 V (vs Ag/AgCl)           | NA                   | (vs Ag/AgCl, 0.1 M KOH)     | [206]|
| Ternary (P, S, N)-doped graphene           | −0.007 V (vs SHE)              | −0.109 V (vs SHE, 0.1 M KOH) | [250]|
| C-doped BN                                  | 0.83 V                         | NA                   | (0.1 M KOH)                 | [251]|
| X-doped CₓNₓ on macroporous carbon X = B   | −0.17 V (vs Ag/AgCl)           | NA                   | (vs Ag/AgCl, 0.1 M KOH)     | [219]|
| X = P                                      | −0.10 V                        |                      |                             |      |
| X = S                                      | −0.07 V                        |                      |                             |      |
| Pyridinic-N grafted graphene                | 0.7 V                          | NA                   | (0.1 M H₂SO₄)               | [210]|
| N-doped graphene                            | 0.77 V                         | NA                   | (0.1 M H₂SO₄)               | [10]  |
| Nitrogen content                           | 0.91 V                         |                      |                             |      |
| 1.7 at%                                     |                               |                      |                             |      |
| 8.1 at%                                     |                               |                      |                             |      |
metals, we could only find studies using Ru, Pd, Ag, Ir, Pt, and Au. In the case of transition metals, we found that only Mn, Cu, Nb, and W have been used as single- or few-atom catalyst for ORR. As discussed later, catalyst based on the aforementioned elements shows a remarkable tolerance again methanol, ethanol, and carbon monoxide poisoning; even those reported using Pt as single-atom catalyst. In most cases, the production of H\textsubscript{2}O\textsubscript{2} is limited, and mostly a complete 4e⁻ ORR is observed. Additionally, a common ground, but not always, is the use of nitrogen to efficiently trap single metals into the lattice of a graphitic-like substrate. Although the synthesis processes differ, the resulting metal-coordinated motifs interactions occur with similar configurations, such as M–N\textsubscript{4}, M–N\textsubscript{2}, O=M–N\textsubscript{4}, or M–C\textsubscript{x} if no nitrogen is present.

4.1. Precious Metal-Based Catalysts

Among the noble metals' family, we only found reports describing Ru, Pd, Ag, Ir, Pt, and Au as single-metal catalyst for ORR. Pt is still to be the most popular metal, but not necessary the most successful, while the others are relatively unexplored since only one report could be found. They are divided in sections corresponding to the element, and are presented in order of atomic number.

Figure 5. Structural analysis of single-atomic Co sites embedded in hierarchically ordered porous N-doped carbon (Co-SAS/HOPNC). a) XANES spectra and b) FT-EXAFS curves of Co-SAS/HOPNC, CoO, Co\textsubscript{3}O\textsubscript{4}, and Co foil at the Co K edge. c) WT-EXAFS of Co-SAS/HOPNC, Co foil, CoO, and Co\textsubscript{3}O\textsubscript{4}. d) The corresponding EXAFS fitting curves of Co-SAS/HOPNC at k space. e) The corresponding EXAFS fitting curves of Co-SAS/HOPNC at r space. Inset: Schematic model of Co-SAS/HOPNC: Co (orange), N (blue), and C (gray). Adapted with permission.\textsuperscript{[149]} Copyright 2018, United States National Academy of Sciences.
4.1.1. Ruthenium-Based Catalysts

A catalyst containing \( \text{O} = \text{Ru} - \text{N}_4 \) moieties embedded into nitrogen-doped graphene oxide (GO) was reported by the group of James M. Tour in 2017.\(^{167}\) The catalysts was prepared by pyrolysis of a mixture of \( \text{Ru(NH}_3)_6\text{Cl}_3 \) and GO, under an \( \text{Ar}/\text{NH}_3 \) atmosphere at 750 °C, achieving a Ru loading of 1.7 wt%. The catalyst shown in Figure 7a exhibited uniformly distributed Ru atoms as observed by aberration-corrected HAADF-STEM (Figure 7b). The oxidation state of Ru was identified as \( \text{Ru}^{4+} / \text{Ru}^{5+} \) with a configuration of \( \text{O} = \text{Ru} - \text{N}_4 \) by means of XAFS studies and extensive DFT simulations. The authors found that the enclosed \( \text{Ru} - \text{N}_4 \) moieties having one oxygen molecule ligand, as depicted in Figure 7c, could reproduce all the features (marked as a, b, ..., f in Figure 7c) of the experimental spectrum. The ORR performance was studied in acidic conditions (0.1 M HClO\(_4\)) where the Ru-coordinated motifs exhibited a half-wave potential \( (E_{\text{1/2}}) \) of 0.75 V (vs RHE), and only a negative shift of 18 mV and a loss of 7% of the initial current were observed after 10 000 CV cycles (0.6 – 1.0 vs RHE). In particular, this \( \text{O} = \text{Ru} - \text{N}_4 \) motif exhibited a mass activity at 0.70 V (vs RHE) 7.5 times greater than that of commercial \( \text{Pt}/\text{C} \) (20 wt%), as well as high tolerance toward methanol and carbon monoxide poisoning. However, a high Tafel slope of 134 mV decade\(^{-1} \) (Pt/C Tafel slope = 85 mV decade\(^{-1} \)) indicated a rather slow kinetics, and suggest that the first electron-transfer step is the rate-determining step during the ORR. The activity is attributed to the higher oxidation state of Ru centers, and the role of the \( \text{O} = \text{Ru} - \text{N}_4 \) moiety is to reduce the adsorption free energies of ORR intermediates, decreasing the activation barrier for the first electron transfer reaction, which was identified as the rate-limiting step.

4.1.2. Silver-Based Catalysts

For the case of Ag single-atom catalyst, Sun and co-workers reported in 2019 the use of \( \alpha \)-MnO\(_2\) nanowires as a substrate to incorporate Ag atoms through a hydrothermal process.\(^{168}\) The presence of Ag atoms on \( \alpha \)-MnO\(_2\) resulted in improved conductivity and significant lattice distortion, in addition to a large amount of oxygen vacancies, causing an increase up to three times in the kinetic current density for oxygen electrocatalysis. The Ag-coordinated motif on \( \alpha \)-MnO\(_2\) was used in \( \text{Zn} \)-air batteries achieving a high discharge peak power of 273.2 mW cm\(^{-2}\), and an energy density of 915.4 Wh kg\(^{-1}\)\(_{\text{Zn}}\). The \( \text{Zn} \)-air battery had a stable operation for up to 3200 cycles of charge–discharge. The excellent rechargeability was attributed to a crystal phase transformation from \( \alpha \)-MnO\(_2\) to \( \delta \)-MnO\(_2\) due to the presence of atomic Ag.

4.1.3. Iridium-Based Catalysts

A popular methodology to prepare single-metal catalysts consist in using molecular sieves, such as the zeolite imidazolate framework-8 (ZIF-8). Its high nitrogen content allows to easily retain single-metal atoms. This synthesis process was used by Chen and co-workers\(^{169}\) to produce O=Ir–N\(_4\) moieties into a carbon-based support by using an Ir-impregnated ZIF-8 (Ir-ZIF-8) followed by a pyrolysis under \( \text{Ar}/\text{H}_2 \) (10% \( \text{H}_2 \)) atmosphere at 950 °C (see Figure 7d). The resulting material contained atomically disperse Ir atoms (Figure f–h) as observed by high-resolution HAADF-STEM studies. The presence of Ir–N and Ir–O was demonstrated by EXAFS studies, suggesting that a square-pyramidal configuration \( \text{O} = \text{Ir} - \text{N}_4 \) was favorable (see the inset Figure 7d), resembling that of Co–N\(_4\).\(^{170}\) This configuration showed to be beneficial for ORR in acidic conditions (0.1 m HClO\(_4\)), where an \( E_{\text{onset}} \) of 0.97 and \( E_{1/2} \) of 0.864 V (vs RHE) were observed. The Ir-coordinated motif showed excellent ORR performance with a turn over frequency (TOF) of 24.3e− site\(^{-1}\) s\(^{-1}\) and a mass activity of 12.2 A mg\(^{-1}\)\(_{\text{Ir}}\) at 0.85 V (vs RHE) with minimal \( \text{H}_2\text{O}_2 \) production (≈3.5%). In addition no observable changes on the current density after 5000 CV cycles were reported.

Figure 6. a) Atomistic structure of Co–N\(_{2+2}\) and Co–N\(_4\) active sites of the Co–N–C catalysts. b) Calculated free energy evolution diagram for 4e\(^{-}\) ORR pathway on the Co–N\(_{2+2}\) site under a limiting electrode potential of \( U = 0.73 \) V and on Co–N\(_4\) site under a limiting electrode potential of \( U = 0.67 \) V. c) Atomistic structure of the initial state (left), transition state (middle), and final state (right) for OOH dissociation reaction on the Co–N\(_{2+2}\) site. In this figure, the gray, blue, yellow, red and white balls represent C, N, Co, O, and H atoms, respectively. Adapted with permission.\(^{158}\) Copyright 2018, RSC.
attributed the observed activity to a reduced electron density at the Ir center facilitating the desorption of oxygenated species. This was supported by the presence of Ir$^{3+}$ species and theoretical simulations, where clear differences in charge density of O\(\text{Ir}^\text{N_4}\) sites shows the electron transfer from Ir atoms to nearby N atoms (Figure 7e), decreasing its adsorption energy to OH-intermediates.

4.1.4. Platinum-Based Catalysts

Generally, carbon-based materials are used as substrate for single- or few-atom catalysts due its feasibility to introduce nitrogen and easily trap single-metal atoms, nevertheless metal nitrides or carbides, such as TiN or TiC, are occasionally used. A report in 2015 by the group of Lee used TiN nanoparticles in which single atom Pt were anchored by a simple impregnation method using chloroplatinic acid$^{[171]}$ Through EXAFS studies, it was observed that Pt atoms were primarily stabilized by chlorine ligands (Pt–Cl) with an optimal Pt loading of 0.35 wt\%. However the ORR performance for this particular catalyst is far from the desired 4e–, actually it is highly selective toward the 2e– process with 65% selectivity in acidic conditions (0.1 M HClO$_4$). According to the authors, the high H$_2$O$_2$ selectivity was attributed to the isolated single Pt-sites, since these would not be able to dissociate the O=O bonds, following then a preferentially 2e– pathway. Overall, the catalyst achieved a mass activity of 78 A g$^{-1}$ at 0.05 V overpotential. A higher selectivity for the 2e– process was observed when using TiC$^{[172]}$ instead of TiN, with a loading of 0.45 wt\% of Pt and similar Pt–Cl configuration.

Regarding carbon-based supports, a report in 2017 by Sun and co-workers$^{[152]}$ showed the production of single-atom Pt catalyst onto carbon black support by pyrolysis of urea,
chloroplatinic acid and carbon black. An optimal loading of 0.4 wt% of Pt was reported. As usual for carbon supports, nitrogen played a key role in the metal anchoring. EXAFS studies showed that nitrogen not only reduces Pt agglomeration, but also minimizes the oxidation of Pt atoms avoiding the formation of PtO2. In addition, the ORR activity in acidic conditions (0.1 M HClO4) revealed that the formation of PtO2 in the absence of nitrogen significantly reduces the ORR activity (E1/2 0.44 V vs RHE), while the synergetic effect of N and Pt are easily observed with an E1/2 0.76 (vs RHE), and a full 4e− ORR process, in sharp contrast to the results shown by Lee et al. on TiC and TiN substrates. In addition, a high tolerance to methanol and carbon monoxide were reported, in striking difference to what is normally observed in bulk Pt-based catalysts. The strong interaction of Pt with the N atoms was evidenced by the enhanced durability with only a 3 mV negative shift of E1/2 after 10 000 CV cycles. Similar results have been observed on Pt-SAC prepared on purely defective carbon black without nitrogen precursors involved, where Pt–C4 moieties were identified as ORR active sites. This was reported in 2018 by Liu et al.[173] where Pt–C4 sites (1.1 wt% of Pt) on carbon black were produced by a hydrothermal method followed by a pyrolysis at 900 °C under Ar atmosphere. The Pt-SAC exhibited enhanced operational stability (9 mV negative shift for E1/2 after 10 000 CV cycles), high methanol tolerance, and an excellent E1/2 of 0.835 V (vs RHE) with a Tafel slope of 93 mV decade−1 under acidic conditions (0.1 M HClO4).

Also in 2018, a work by Wang and co-workers reported a peculiar Pt-SAC using a nitrogen-doped porous carbon support fabricated through the pyrolysis of cattle bone.[174] Although the process consisted in several steps, the final carbonaceous material was obtained by heat treatment at 1000 °C under ammonia atmosphere. The Pt atoms were attached by a photochemical solid-phase reduction method, where a carbon paste impregnated with H2PtCl6 was irradiated with ultraviolet light to finally produce single Pt atoms homogeneously dispersed into the carbon matrix. XANES and EXAFS studies, in conjunction with DFT calculations, indicated the presence of Pt–N4 moieties. The ORR activity was evaluated in alkaline conditions (0.1 M KOH) where an optimal Pt loading was found at 3.8 wt% with a jk of 3.23 mA cm−2 and a mass activity of 0.17 A mg−1Pt, which is a significant improvement in comparison with commercial Pt/C (jk of 0.77 mA cm−2 and mass activity of 0.04 A mg−1Pt) at 0.9 V (vs RHE). However, the ORR performance under acidic conditions (0.1 M HClO4) was unfavorable, where a high selectivity toward the 2e− ORR process was observed, in contrast to the studies mentioned earlier.[152,173]

4.1.5. Gold-Based Catalysts

In 2019, Han and co-workers[175] used density functional theory to evaluate the ORR activity of different single-atom catalyst based metals (Au, Pd, and Pt for ORR) supported on TiC, and based on the these predictions, they produced Au-coordinated motifs on TiC particles by an incipient wetness method followed by reduction under hydrogen atmosphere. Other single-atom catalysts were also produced, however the Au-based catalyst exhibited the best ORR performance. The ORR activity was studied in acidic conditions (0.1 M HClO4), however as in the case of Pt–TiC and Pt–TiN studies by Lee et al.[171,172] the 2e− ORR pathway was significantly favored, with an H2O2 yields of 87%. A mass activity of 4.16 A mg−1Au, and a TOF of 1.57 s−1 at 0.2 V (vs RHE).

4.2. Transition Metal-Based Electrocatalysts

In this section, we review other transition metals besides Fe and Co, and we could only find reports of single-metal catalyst for ORR based on Mn, Cu, Nb, and W, with Mn and Cu being the most studied and manifesting the best ORR performance.

4.2.1. Manganese-Based Catalysts

Wu and co-workers[176] synthesized Mn-N4 moieties into a graphic substrate by pyrolysis and acid leaching of Mn-doped ZIF-8, this initial step already produces Mn-N4 sites, however only a low density was achieved. Thus a secondary adsorption process was necessary in which the carbonized Mn-doped ZIF-8 was immerse in a solution containing Mn(II) chloride and nitrogen precursors followed by a thermal annealing at 1100 °C under N2 atmosphere. This process is exemplified in Figure 8a. HRTEM studies (Figure 8b) revealed the characteristic morphology of pyrolyzed ZIF-8, and STEM analysis shows the presence of Mn homogeneously distributed along the ZIF-8 (Figure 8c,d), while aberration-corrected MAADF-STEM depicts the atomic dispersion of Mn (Figure 8e). A composition of 3.03 wt% of Mn resulted in the highest ORR activity with a full 4e− reaction under acidic conditions (0.5 M H2SO4) with an E1/2 of 0.80 V (vs RHE). Spectroscopy studies showed that Mn2+ species had a coordination number (CNMn-N) of 4±0.4, suggesting the presence of Mn–N4 sites. These Mn-N4 moieties were identified as the active sites and not only the free CN4 groups; however, an optimal nitrogen doping level and configuration seems to be crucial to achieve a maximum ORR activity. In this case, it was reported that cyanamide as N source produced large amounts of pyridinic-N and exhibited the best ORR performance. In line with other M–N4 catalysts (M being a metal), the Mn–N4 sites exhibit excellent stability with only a loss of 17 mV in E1/2 after 30 000 CV cycles. A 100 h long durability tests at 0.7 V (vs RHE) resulted in a loss of only 12% of the initial current and a shift of 29 mV of E1/2 after 5000 CV cycles. In this case, the metal–N4 configuration seems to be crucial to achieve a maximum ORR activity. In this case, it was reported that cyanamide as N source produced large amounts of pyridinic-N and exhibited the best ORR performance. In line with other M–N4 catalysts (M being a metal), the Mn–N4 sites exhibit excellent stability with only a loss of 17 mV in E1/2 after 30 000 CV cycles. A 100 h long durability tests at 0.7 V (vs RHE) resulted in a loss of only 12% of the initial current and a shift of 29 mV of E1/2 after 5000 CV cycles. In this case, the metal–N4 configuration seems to be crucial to achieve a maximum ORR activity.

Using a different strategy, Chen and co-workers[177] produced in 2018 atmospherically dispersed Mn–N3O4 sites within a graphitic framework through pyrolysis of a Mn-based MOF consisting of Mn2+ ions and oxygen-containing trimesic acid linkers (Mn-1,3,5-benzenetricarboxylic acid). The resulting material consisted mostly of Mn atoms with a valence state between Mn0 and Mn2+ coordinated with O and N forming a Mn–N3O4 configuration. The ORR under alkaline conditions (0.1 M KOH) resulted in an E1/2 of 0.86 V (vs RHE), with a high stability with no obvious decay in E1/2 after 5000 CV cycles. In this case, the authors attributed the ORR activity to the shift in the position of the d-band center, according to the d-band model.[178]
DFT simulations showed beneficial d-band center shifts from ~0.95 to ~2.79 eV from a bulk MnO system compared to the single-atom Mn–N₃O configuration. Another study involving Mn as single-atom catalyst was published by Lu’s group in 2019.[179] In this occasion, Mn–NₓPᵧ moieties were embedded on a mesoporous carbon composite after polymerization of o-phenylenediamine followed by calcination. The resulting composite mostly had Mn²⁺ species in coordination with N and P, such coordination favored electron delocalization in the 3d-band of Mn which enhanced the conductivity. The ORR activity was studied under alkaline conditions (0.1 m KOH) where the optimum Mn-N₃Pᵧ composite (0.39 wt% of Mn) exhibited an E_{onset} of 0.97 V and an E_{1/2} of 0.84 V (vs RHE). The authors found that both P and Mn played a key role in the observed activity, and that the formation of P–C bonds, not phosphate groups, were beneficial for ORR.

4.2.2. Copper-Based Catalysts

Single-atom Cu moieties produced in combination with MOFs seems to exhibit the best performance toward ORR. A work using MOF was reported in 2018 by Baek and co-workers,[181] where Cu–Nₓ moieties were formed onto a nitrogenated 2D carbon matrix. The catalyst was produced by pyrolysis of a nitrogen-free Cu-based MOF (Cu(BTC)(H₂O)₃) with...
dicyandiamide as N source. In this case, the dicyandiamide was the key for the formation of highly stable single Cu atoms, where an optimal Cu content of 20.9 wt% was achieved. Spectroscopy studies revealed the presence of Cu$^+$ and Cu$^{2+}$ species forming Cu–N$_2$ and Cu–N$_4$. The authors investigated the effect of nitrogen by removing the dicyandiamide, which resulted on large (200–300 nm) Cu particles with no sign if single Cu atom integration into the carbon support. A four electron reaction and a $E_{1/2}$ of 0.869 V (vs RHE) were observed under alkaline conditions (0.1 M KOH) with no current loss after methanol and CO injection, and a robust performance was maintained for at least 10 000 s at 0.865 V with a decrease of only 0.2% of the original current. The observed mass activity was over 54 times larger for the Cu–N$_2$ material compared to the Cu nanoparticles at 0.85 V (vs RHE).

In another study, Li and co-workers$^{[182]}$ reported in 2018 the production of Cu–N$_x$ sites on graphitic-like substrates based on the ZIF-8, a common molecular sieve used also for other single-atom catalysts. The authors used a gas migration strategy, which transfer single-atoms from bulk materials onto a support. In this case, they achieved the production of volatile Cu(NH$_3$)$_x$ species under an ammonia atmosphere, ammonia molecules hauled the surface copper atoms out of a Cu foam. The resulting Cu(NH$_3$)$_x$ species were trapped by the defects on the pyrolyzed ZIF-8, where the optimum Cu content was found at 0.54 wt% with a surface coverage of $\approx$0.06 Cu atoms nm$^{-2}$. The oxidation state of Cu was identified to be between Cu$^+$ and Cu$^{2+}$, similarly to other single-metal catalysts. The ORR performance was studied under alkaline (0.1 M KOH) conditions were an $E_{1/2}$ of 0.895 V (vs RHE) with a TOF of 0.68 Hz was observed, no obvious activity decay was noticed in $E_{1/2}$ after 5000 CV cycles, and no changes in the Cu–N$_4$ structure were detected. Here the authors studied the effect of the substrate by using nitrogen-doped graphene as a substrate. The resulting Cu–N$_4$ sites on graphene exhibited a lower ORR activity with an $E_{1/2}$ of 0.74 V (vs RHE). Recently, similar half-wave potential on graphene was reported by Yao’s group in 2019,$^{[183]}$ where Cu–N$_4$ and Cu–N$_x$ sites on N-doped graphene had an $E_{\text{onset}}$ of 0.869 V and $E_{1/2}$ of 0.779 V (vs RHE). These results highlight the importance to select the appropriate substrate.

Carbon nanotubes have also been used as a substrate for single-atom Cu catalyst, for example in 2019 Xiang and co-workers$^{[184]}$ pyrolyzed Cu phthalocyanine in combination with oxidized carbon nanotubes producing Cu–N$_x$ moieties. The observed Cu species were in line with other publications, where Cu$^+$ and Cu$^{2+}$ forms Cu–N$_2$ or Cu–N$_4$ sites. In this occasion, a total of 0.2 wt% of Cu was introduced, with an average separation distance of 0.6 nm between Cu–N$_x$ sites. The ORR performance was reported under alkaline conditions (0.1 M KOH) with an $E_{1/2}$ of 0.81 V (vs RHE) and a TOF of 1.03 s$^{-1}$ at 0.8 V. In this particular case, the increase of Cu$^{2+}$ species resulted in a decrease ORR activity, suggesting that Cu$^+$–N$_x$ moieties are the main active site, this is in contrast to the results reported by Baek and co-workers,$^{[181]}$ clearly indicating the need for more studies.

4.2.3. Niobium-Based Catalysts

In 2013, Chisholm and co-workers$^{[180]}$ reported the production of Nb–C moieties incorporated into onion-like carbon shells through an arc-discharge method using Nb rods as cathode and C rods as anode under a methane atmosphere. In this particular case, no nitrogen was necessary to achieve a single Nb atom dispersion into the carbon-based support. The catalyst had a unique configuration composed of an NbC core surrounded by several graphitic but highly defective layers as depicted in Figure 8f. The single Nb–C moieties, located at the graphitic shell (see Figure 8g, h), exhibited an $E_{\text{onset}}$ of $-0.13$ V (vs Ag/AgCl) under alkaline (0.1 M KOH) conditions, an electron transfer number of 3.2–3.8, and a reduction in the initial current of 8% at $-0.40$ V (vs Ag/AgCl) after 30 000 s of continuous operation. The ORR activity was attributed to the Nb–C complexes rather than the oxide, which is normally associated with Nb$_2$O$_5$ species on bulk Nb carbides. In addition, the strong Nb–O interaction facilitates the O$_2$ dissociation and promotes a 4e$^-$ ORR pathway. The authors performed theoretical studies where they observed a strong interaction of Nb with oxygenated species, the latter is attributed to an increase in the density of states near the Fermi surface and an enhanced charge transfer from Nb to the O$_2$ molecule due to the filling of $\pi^*$ antibonding states, resulting in a decreased O–O dissociation energy barrier.

4.2.4. Tungsten-Based Catalysts

Tungsten is a metal not commonly seen in the ORR field, at least not as catalyst. However, recently in 2019, Zhao’s group$^{[185]}$ reported the production of atomically dispersed tungsten on nitrogen-doped carbon nanosheets forming a W–N$_x$ configuration with remarkable activity in both acidic and alkaline conditions, in contrast with other ORR-inert W-based catalysts. In alkaline conditions (0.1 M KOH), the single-atom W catalyst exhibited an impressive $E_{\text{onset}}$ of 1.01 V (vs RHE), $E_{1/2}$ of 0.88 V (vs RHE) and a mass activity of 0.69 A mg$^{-1}$ (at 0.9 V vs RHE). The W–N$_3$ catalyst also exhibited a good performance in acidic conditions (0.1 M HClO$_4$), with $E_{\text{onset}}$ of 0.87 V (vs RHE) and $E_{1/2}$ of 0.77 V (vs RHE), respectively. In contrast, sites with W–N$_1$ or W–N$_4$ configurations exhibited relatively poor ORR activity in both acidic and alkaline electrolytes. The observed ORR activity is attributed to the moderate interaction between OH$^-$ and the single W atoms, as identified from theoretical calculations.

Other study involving W as a single-atom catalyst was reported earlier in 2016 by Guo et al.$^{[186]}$ They used the arc-discharging method with a methane atmosphere to produce WC nanoparticles covered by several graphitic layers (WC@C), where these onion-like graphitic layers hosted the W–N$_x$ moieties. A similar configuration was reported by Chisholm and co-workers$^{[180]}$ for Nb–C$_x$ catalyst. The carbon shells were composed with a mixture of amorphous phase and distorted graphitic layers containing high density of single W atoms. The catalyst exhibited an $E_{\text{onset}}$ of $-0.23$ V (vs Ag/AgCl) for the ORR in alkaline conditions (0.1 M KOH) with a complete 4e$^-$ ORR process. Similar to other metal-coordinated motifs, no noticeable current change was observed after the addition of methanol or ethanol. Additionally, a reduction of only 20% in current density was observed after 30 000 s at $-0.40$ V (vs Ag/AgCl). The ORR activity was attributed to an increased
density of states near the Fermi surface for the single-atom W incorporated into the graphitic layers, resulting in a stronger O\textsubscript{2} adsorption and thereby a weakening of the O–O bond.

4.3. Post-Transition-Metal-Based Electrocatalysts

4.3.1. Zinc-Based Catalysts

Among the nontransition metals, Zn is the only one that have been reported as single-metal catalyst for ORR. Zn is interesting as ORR catalyst because it has a fully filled 3d band, as a result it does not form species with high valence state, thus being harmless to the electrode and membrane. A report in 2017 by Gu and co-workers\cite{187} showed the production of Zn–N\textsubscript{4} sites onto a carbon support by pyrolysis of urea, zinc acetate and carbon black. The concentration of 0.30 wt% of Zn resulted in the best ORR activity, where the presence of Zn\textsuperscript{2+} was identified forming Zn–N\textsubscript{4} sites. The ORR was evaluated under alkaline conditions (0.1 M KOH) with an $E_{1/2}$ of $-175$ mV (vs SCE), and similar to other non-noble metal catalyst, a high tolerance toward methanol and CO were observed. The observed activity was partially attributed to the highly defective carbon black support containing large amounts of pyridine- and pyrrole-like nitrogen dopants forming several Zn–N\textsubscript{4} active sites. Another report using Zn as single-metal catalyst was published in 2019 by the group of Wei\cite{188}. In this occasion, the formation of Zn–N\textsubscript{4} moieties onto a carbon support was carried out by pyrolysis of poly(o-phenylenediamine) and ZnCl\textsubscript{2}. They found that a concentration of 9.33 wt% of Zn exhibited the best ORR performance with an $E_{1/2}$ of 0.746 V (vs RHE) under acidic conditions, and an $E_{1/2}$ of 0.873 V (vs RHE) under alkaline media. A low H\textsubscript{2}O yield of less than 5% was observed in both acidic and alkaline solutions. Spectroscopy studies revealed a Zn–N\textsubscript{4} configuration formed with Zn\textsuperscript{2+} species. The authors also reported a high stability under both acidic and alkaline conditions, mainly attributed to a low susceptibility for protonation and a large formation energy of Zn(OH)\textsubscript{2}, respectively.

5. Nonmetallic Electrocatalysts

Inspired by the first report on the ORR activity of nitrogen-doped CNT arrays,\cite{189} carbon-based metal-free nanostructures have attracted tremendous attention as low cost and durable electrocatalysts, in particular under alkaline medium. Due to charge neutrality, the surface of sp\textsuperscript{2}-hybridized graphene and carbon nanotubes are chemically inert. However, they are an excellent support to host compatible elements and form stable catalytic active motifs. It is well demonstrated that introducing nonmetals into graphitic carbon framework possess the potential to surpass the ORR performance of the state-of-the-art Pt catalyst.\cite{190} Despite the great progress in development of highly efficient metal-free electrocatalyst for ORR, the principal guidelines for electrocatalysts design cannot be fully described yet. The problem originates from the difficulty in defining the actual activity descriptors for the catalytic motifs at the experimental level. For carbon-based nonmetal electrocatalyst, two main reason can be distinguished: i) the geometric structure of the motif, the density and configuration of heteroatoms within the motif, and chemical environment of the heteroatom highly influence the ORR activity and cannot be easily controlled during the synthesis, and ii) since the comprising elements of catalytic motifs are carbon and its nonmetal neighboring elements in periodic table, it is extremely difficult to directly detect the catalytic steps during the reaction by currently available characterization techniques, including various electron-based, spectroscopy, and electrochemical technologies.

Taking nitrogen-doped carbon nanostructures as an example, nitrogen usually incorporate into the carbon framework in different configurations described by the hybridization outline and number of carbon neighbors/vacancies. The most known configurations are pyrrolic-N, pyridic-N, and graphitic-N and combined nitrogen clusters. Nitrogen-doped carbon nanostructures have been extensively studied and many interesting papers and reviews are published about the formation mechanism and characterization of N-doped carbon nanostructures. It is shown that, different nitrogen configurations contribute differently to the electrocatalytic reaction and hence have dissimilar activities\cite{10,191–194} While it is practically possible to control the nitrogen content and even to some extent the configuration during the synthesis process, it is a difficult task to identify which type of nitrogen is responsible or more active than others for catalytic performance. Hence, the underlying universal mechanism of the ORR on the active centers is usually understood through theoretical calculations. In most of computational approaches, the most energetically stable configuration of the motif is first established and then used for further analysis of the ORR mechanism. However, from practical perspective, selective incorporation of heteroatoms cannot be easily achieved and more importantly with the current characterization techniques, there is a significant level of uncertainty about the formed configuration within the catalytic motif. Such vague information to begin with makes it difficult to define the design principles for active ORR catalysts.

From the computational research perspective, uneven charge and spin densities as a result of the electronegativity differences between the comprising elements of the catalytic motif is the main descriptor for ORR activity. Hence, the ORR activity can be triggered or enhanced by introducing curvature and defects, doping, and alloying.\cite{195,196} Binding energies with the intermediates species during the reaction is another important activity descriptor which has been emphasized for many nonmetal electrocatalysts. Band structural modification due to the assembly of heteroatoms within the carbon framework is another widely studied mechanism to describe the catalytic performance of the materials.\cite{197}

The simplest catalytic motif in metal-free catalysts can be formed from a single heteroatom and its carbon neighbors. However, in most cases the catalytic motif has more complicated configuration comprising several similar or different heteroatoms, vacancies and their neighboring carbon atoms. Apart from nitrogen as the most investigated nonmetal heteroatom, group II and III p-block elements including B, S, P, Si, Sb, and also F in individual and multinary configurations have been theoretically and experimentally examined for ORR.\cite{198–203} Dissimilar from isotropic Pt-based catalysts in which all similar
surface atoms contribute equally to catalytic reaction, the active sites are confined to the close vicinity of the heteroatoms in metal-free catalysts. Therefore, increasing the number of heteroatoms increase the number of active sites and results in improving the catalytic efficiency. Furthermore, it is shown that the distribution of the catalytic active sites in a more discrete manner inhibit the localization of electronic states on the active site and improve the catalytic performance.\(^{1924}\) In many studies, the Sabatier principle is very well confirmed, meaning that too strong or too weak interaction of active sites with intermediate adsorbates reduces the catalytic activity. In alkaline ORR, the OH adsorption is often shown to be the rate limiting step and catalysts with \(E_b(\text{OH})\) values in the range of 2.2–3.0 eV is likely to perform as good catalysts regardless of the type of the heteroatom.\(^{197}\) Based on this argument, some of the X–N–C (X = B, P, S) multinary heteroatom motifs show superior activities compared to the nitrogen alone. The rationality of this prediction is elucidated experimentally showing considerably high ORR activity of N–P–C nanostructures.\(^{9,205,206}\) To present a more constructive review, we have divided this section to nitrogen and non-nitrogen containing motifs for ORR.

5.1. Nitrogen–Carbon-Containing Motifs (N–C and X–N–C Systems, X = B, P, S)

Nitrogen-doped carbon structures are the most experimentally investigated nonmetal electrocatalyst for ORR. One reason is that nitrogen atoms sitting at the zigzag edges of a carbon framework, which are among those configurations that have higher chances to be formed during synthesis,\(^{207}\) are shown to be more catalytically active.\(^{208,209}\) Unlike most other heteroatoms, nitrogen itself does not directly involve in the catalytic process but rather the neighboring carbon atoms, even up to several atoms away that become catalytically active. This is experimentally demonstrated by investigating the catalytic activity of nitrogen containing carbon structures in which either N or adjacent C sites are chemically blocked by grafting to acetyl group. It is observed that while presence of N-acetyl functional group does not affect the ORR activity, grafting acetyl group to the neighboring C suppresses the activity completely.\(^{210}\) Therefore, the catalytic motif (N–C) involves either single atom nitrogen or several of them in addition to several surrounding carbon atoms. An ex situ post-ORR XPS measurements on the N-containing highly oriented pyrolytic graphite model system after half-cell ORR reaction in acidic medium, confirmed this hypothesis by revealing the transformation of the pyridinic-N to pyridonic-N suggesting that it is the adjacent carbon atom to the pyridinic-N that adsorb the OH species.\(^{110}\) Some preferential directions around the nitrogen atom are recognized by ab initio study for which the C atoms exhibit lower ORR overpotential. This is the first direct calculation to demonstrate the configuration of the catalytically active N–C motif showing an upside-down triangle shape around the central nitrogen. The vertices of the triangle are shown to be along the armchair directions of the graphene sheet with a distance of around 4.3 Å from the N atom which is inline with the topography studies by STM.\(^{204,211,212}\)

As previously stated, different descriptors, individually or in in combination with each other, are used to illustrate the mechanism of ORR on metal-free catalysts. The difference between electronegativity of the elements within the motif is one of the main activity descriptors. Nitrogen possess larger electronegativity than carbon and once it replaces carbon, its unpaired electrons delocalize to its adjacent carbon atoms. Such electron delocalization increases the charge density on neighboring carbon atoms depending on the distance from nitrogen and also configuration of nitrogen atom and hence they behave differently during the catalytic process. Interestingly, In B–N codoped graphene quantum dots (BN-GQDs), B atoms (and not C atoms) become the adsorption site within the catalytic motif which is explained by accumulation of positive charges on B atoms due to the electron withdrawing properties of N. This is further confirmed by analysis of the photoemission peak of B in B- and BN-GQDs, showing that in the presence of nitrogen the binding energy of boron is up-shifted which clearly indicates an average higher positive charge accumulation on B.\(^{213}\) However, it is shown by Zou et al. that charge density alone cannot explain the differences in the adsorption affinities within the motif. Both the B-site and its nearest C-site possess similar charge density at the edge of B–C (for B-doped graphene nanoribbons) and B–N–C motifs (for B–N codoped graphene nanoribbons) and hence it is expected that they behave similarly for \(\text{O}_2\) adsorption. However, the higher spin charge density at the edge of B–N–C compared to the B–C turn it to a more catalytic active site for ORR.\(^{214}\) Similarly, while there is no direct interaction in the form of bonding between S and the coming oxygen molecule, \(\text{O}_2\) directly adsorb on S in S–N–C motif. The theoretical spin density analysis clearly indicates that the spin density on S significantly increases in the presence of nitrogen.\(^{215}\) Song et al. have another explanation for the higher activity of S atoms within S–N–C motifs. According to their calculation, the sulfur and nitrogen atoms adopt a specific configuration in the motif which causes different activities of the comprising elements. S and N remain nonbonded while replacing C–C bond which causes N atom to adopts a pyridinic configuration and the S atom an edge-like bonding. Such specific arrangement facilitates the formation of \(\text{SO}_2\) functionalities in the first place. Further, the migration of the oxygen atoms to neighboring carbon atoms is possible due to high spin and positive charge densities.\(^{216}\)

With a closely related argument, the coordination environment of the heteroatom is understood to have a key role on the activity of the catalytic motif and mechanism of the ORR. Calculation of the adsorption energy of the ORR intermediate species on graphitic B–N–C motifs (G-BCxNy) showed that while G-BC3, G-BC2N, and G-BCN2 are unable to adsorb \(\text{O}_2\) and hence initiate ORR, \(\text{O}_2\) can be chemisorbed on the G-BN3 motif. The largest polarization of B (B\(^{+}\)) is achieved in G-BN3 and hence the electronegative oxygen is attracted to B\(^{+}\). Increasing N/B ratio is shown to favorably affect the band structure with respect to an increasing number of donor states which facilitates the electron transfer and hence turns this motif to a highly active ORR electrocatalyst candidate.\(^{217}\) It is shown that, the energy barriers for the formation of different reaction intermediates on B–N–C motif in boron-doped C\(_2\)N monolayer is highly correlated to the coordination structure of B- sites which causes different distribution of the 2p states near the Fermi level. Therefore, even though the formation energy of B–N and B–C bonding is
pretty close, the motif in which B is replacing N atoms is more catalytically active than those where B replaces C atoms and they perform different rate determining step for ORR.[218] In an interesting approach overpotential mapping from ab initio calculation is used to demonstrate the effect of the spatial distribution of N and P within the motif on the availability and nature of active sites for ORR. It is shown that the electronic properties and hence the catalytic performance of P–N–C motif is strongly affected by the relative position of the N and P atoms within the motif. Locating three nitrogen atoms in the close vicinity around a central P or away from it results from the creation of highly localized states associated with the neighboring C atoms and hence a strong interaction with the oxygenated species. A P–N separation distance of at least 4 Å is hence suggested to improve the quantity and distribution of active sites.[204] The effect of coordination environment is emphasized by varying the type of additional heteroatom (X) within the X–N–C motif. For example, by replacing either C or N atoms in graphitic C3N4 with B, P, or S atoms, Pei et al. were able to experimentally investigate the ORR catalytic performance and explain the mechanism of reaction by theoretical calculations. In line with their experimental observation, the following trend for catalytic activity was achieved by DFT calculation: S-doped > P-doped > pristine > B-doped C3N4. The rate determining steps on these motifs were different being the \( \text{OH} \) to \( \text{OH}^- \) transformation with a 0.61 eV for S–N–C and formation of \( \text{OH}^- \) for pristine C3N4 highlighting the importance of the coordination structure of the heteroatoms within the motif which alter charge transfer property.[219] However, this result is in contradiction with many previous publications pointing toward the synergistic effect of B and N atoms on the catalytic activity of the motif compared to N–C motif.[214,220] In another study, the chemical reactivity of dual doped graphene is investigated for motifs containing one 2p element (B, N, or O) and one 3p element (Al, Si, P, or S) along with carbon. 2p elements can fit much easier than 3p elements are shown to alter the flat structure of graphene and hence the catalytic performance of P–N–C motif is strongly dependent and increases by increasing the size of N-doped GQDs (increasing the number of atoms within the catalytic motif). Hence keeping the number of nitrogen atoms within the GQDs constant, smaller QDs exhibit smaller free energy of rate-determining step involved in the ORR and consequently a smaller overpotential.[222] However, due to the large portion of active edges, presence of oxygen functional groups cannot be avoided in QDs. Hence the mechanism and selectivity of ORR is shown to be related to the presence of the oxygen functional groups. A mild chemical reduction of doped GQDs with NaBH4 is shown to not only modify the catalytic activity (reducing the overpotential) but also increase the selectivity toward four-electron oxygen reduction pathway.[213]

In addition, since electron transfer is an important final step of ORR, the electron conductivity is also considered as an important activity descriptor.[223] The B–N content within the B–N–C motif in B–N substituted graphene nanoribbons is observed to influence the catalytic performance originating from the variation of the electron conductivity. While an electron transfer number of 3.9 is achieved with a B–N content of 5–9.7 at%, it reduces to 3.2 at the B–N content of 24.2 at% and hence performing a mixed two-electron and four-electron transfer pathway during the ORR process.[221]

While in most studies a carbon matrix hosts the heteroatoms, Zhao et al. have comprehensively investigated the activation of hexagonal boron nitride (h-BN) sheets for ORR upon carbon doping. They have well demonstrated, by DFT calculations, that substituting N by C in h-BN creates high spin and charge densities and in turn enhances the \( \text{O}_2 \) adsorption on C-site. Differently, substitution of boron with carbon turns the B atom into the \( \text{O}_2 \) adsorption site due to higher charge density on B compared to adjacent C atoms for this particular configuration. Investigation of reaction pathway nevertheless shows the former to be more catalytically active configuration promoting the subsequent ORR steps to take place through a four-electron pathway.[224] In another study, the catalytic activity of graphene islands embedded into h-BN was investigated from a first-principles perspective (Figure 9c–f).[225] The graphene islands covering unequal number of B and N sites perform magnetic properties while those covering equal numbers are nonmagnetic. The optimum level of activation for C atoms is achieved at the zigzag interface of embedded islands, and hence magnetic islands in which smaller number of N sites (compared to...
Figure 9. a) Schematic structural representations of different configurations of B and N sites at graphene nanoribbon and b) its corresponding free energy diagram for ORR on different motifs at pH = 13. Reproduced with permission.[221] Copyright 2015, ACS. c–h) Free energy diagrams of ORR on carbon doped h-BN for different substitution configurations (shown as inset) in acidic condition. Blue boxes pointing out the rate limiting steps and red circle represents the catalytic site. Reproduced with permission.[225] Copyright 2019, ACS. i) Schematic illustration of the preparation process and the final configuration of hydrogen-substituted graphdiyne (HsGDY) from the monomer triethynylbenzene possessing only pyridinic-N configuration. Reproduced with permission.[227] Copyright 2018, Springer Nature.
B sites) are replaced by C atoms are shown to be catalytically more active. The reason is the higher O₂ adsorption strength on C at B-sites compared to the C at N-sites. It is argued that due to back transfer of electrons from the lone pairs of N atoms to C at B-site, it has lower effective electronegativity than those C atoms replacing N-sites. Hence, since O has higher electronegativity than C, it tends to chemisorb at the less electronegative site.\[223\] The criteria are a bit different in the case of introducing P- and S-sites into h-BN. The theoretical analysis reveals that the minimum ORR overpotential is achieved when catalytic motifs are constructed by S replacing N-sites and P replacing C-sites. However, in the case of P–S doping, the highest activity is achieved when both P- and S-sites substitute C atoms, respectively. Here, the O₂ adsorption energy introduced as the key descriptor. Presence of S- and P-sites changes the hybridization of the adjacent site from sp² to sp³ which consequently improve the stability of intermediates.\[226\]

Nevertheless, selectivity toward synthesis of certain motifs with certain coordination configurations is the main bottleneck toward design of active electrocatalysts. In this regard, researchers often correlate the findings from theoretical simulation with the synthesis protocol to achieve an effective strategy in which the desired configuration has a higher probability to form. Etching graphene and introducing defects prior to nitrogen doping for example is shown to be successful in promoting pyridinic-N formation.\[228\] By associating the computational prediction with the synthesis method, highly effective P–N–C frameworks were designed and the theoretically identified active P–N sites were intensified during the synthesis.\[229\] Lv et al. have chemically designed hexagonal N–C framework named as hydrogen-substituted graphdiyne which solely contain pyridinic-N (Figure 9i).\[227\]

5.2. Nonnitrogen Containing Motifs

5.2.1. Phosphorus–Carbon-Based Catalysts

Due to the similarity in the chemical properties of nitrogen and phosphorus, phosphorus is another widely investigated heteroatom for ORR reaction by forming P–C motifs.\[9\] Similar to nitrogen, coordination and chemical bonding of P is an important descriptor for ORR activity. It is speculated by DFT calculations that the adsorption of intermediate ORR species occur within a small region around P, pointing toward a small catalytic motif size of few atoms.\[230\] However, the binding configuration of phosphorus in carbon matrix is not fully understood and interpretation of XPS results regarding the number of bonds is not straightforward. Phosphorus is able to form two types of hybridization (sp³ and sp³ d) and hence three to five bonds as shown in Figure 10a–e. It is shown that the replacement of C with P in a monovacancy state (graphitic configuration PC₃G) is energetically preferable and formation of P=O bonding in the same configuration (OPC₃G) reduces the formation energy even further to form the most stable and hence experimentally most feasible configuration. Another favorite configuration is the integration of P within the motif as a result of a divacancy formation in the graphene matrix (PC₄G). The formation energy also reduces for this configuration after P–O bond formation (OPC₄G).\[231\] The catalytic active site varies with the configuration of P within the motif; while the P site has the strongest interaction with *OH in PC₃G sheets due to its large spin and high positive charge, the adjacent C sites are the active sites in OPC₃G due to the saturation of the dangling bond of P by O atom. The scenario is different for PC₄G and OPC₄G motifs in which both the P- and C-sites can similarly attract *OH and effectively contribute to the ORR process. For PC₄G, the kinetically most favorable reaction pathway is shown to be the hydrogenation of O₂ molecule to form OOH followed by a further hydrogenation of OOH, resulting in H₂O + O formation.\[232\]

Silicon can be introduced to P–C motifs with a preferential location closest to the P-site. The catalytic reaction on SiPC₄ motif is shown to start with oxygen adsorption on the Si-site with the bonding exchange between Si and P sites and electron transfer through carbon atoms (Figure 10f). For this motif, the detailed kinetic and thermodynamic behaviors analysis demonstrates its capability for oxygen reduction via a two-electrode pathway and H₂O₂ formation.\[233\] Furthermore, the order of introducing P- and N-site to the motif is shown to alter the performance of N–P–C catalysts. The introduction of P atoms promote the formation of graphitic-N in their vicinity. Interestingly, after N–C bond formation, the former P–C bonds weaken and consequently the graphitic-P will be replaced by graphitic-N with a “self-sacrifice” behavior.\[234\] However, the higher activity of this structure compared to P-sites on N–C motifs is explained on the basis of high ORR activity of graphitic-N which is a matter of doubt.

5.2.2. Sulfur–Carbon-Based Catalysts

To investigate the active site within S–C motifs, different configurations have been modeled and studied from first principles perspective. Sulfur can be stabilized on the graphene surface either by replacing C atom (graphitic-S) or by bonding to two carbon atoms forming out of plane configuration. It can also substitute carbon atoms at the graphene edges either as pyridinic-S/pyrrolic-S or sulfur oxide. Additionally it is capable of connecting two graphene sheets by forming a sulfur cluster ring and also in the form of pyridinic-S cluster in bulk of graphene.\[235,236\] Similar to nitrogen, the ORR catalytic activity is closely related to the charge and spin density distributions as a result of the configuration of S atoms within the motif.\[237\]

It is shown that the presence of Stone–Wales defects facilitate the integration of sulfur into the graphene lattice, the newly created S–C motifs activates the graphene zigzag edges which are, otherwise, fully inactive. In addition Stone–Wales defects increase the polarity of the motif and hence more atoms with higher spin and charge density, meaning more active sites, are present.\[235\] It is worth highlighting that, while sulfur atoms are shown to facilitate two-electron reaction mechanism, carbon atoms with high charge or spin density promote four-electron transfer pathway. In another study, clustered S–C motifs (more than one S atom within the motif) were shown to be catalytically more active than those with single S-sites. The latter is rationalized by the optimized O₂ adsorption strength due to limited accumulation space for the approaching O₂.
molecules toward the cluster. However, it is difficult to correlate these theoretical results with experimental observations due to inherent differences in S-C motifs produced by various synthesis strategies. These rather unique materials exhibit their own functionalities and structural characteristics that complicates the interpretation of XPS data, hiding the true nature of the S-sites and the origin the enhanced activities.\[238\]

5.2.3. Silicon–Carbon-Based Catalysts

Silicon is a p-block element from the carbon group which has been investigated as a component of metal-free catalytic motifs for ORR. An O—O bond elongation of 0.29 Å is observed for \( \text{O}_2 \) by approaching SiC surface indicating that \( \text{O}_2 \) can be dissociated easily on the surface due to electronic charge transfer...
from SiC to the 2p₈. Even though lower number of adsorption sites for O₂ can be distinguished on SiC compared to Pt(111), the remaining sites favorably adsorb the intermediate species throughout the reaction and thereby the whole surface contributes to the catalytic process which is shown to result in better ORR performance compared to Pt(111).[239] In the case of SiCₓ, chemisorption of O₂ molecules occurs by simultaneous bonding with two adjacent Si atoms in the motif with the Si–O bond length of 1.76 Å and adsorption energy of 1.09 eV. Dong et al. have shown that there is a larger adsorption affinity for ORR intermediate on SiCₓ than SiC, which is attributed to the higher positive charge density on Si atoms for SiC. In addition, SiCₓ is shown to have higher electron conductivity due to its narrower bandgap (2.52 eV for SiC and 0.65 eV for SiCₓ), 6, which promotes a faster charge transfer.[240]

6. Perspectives and Outlook

It is clear from the previous chapters that many catalysts based on transition single or few metal-coordinated motifs or even metal free catalysts demonstrate performance values that are in line or better then Pt-based reference catalysts. Yet, despite these strong performance data, platinum group metals are fully dominating commercial applications in ubiquitous life. It is also clear that electrochemical performance data based on cyclic voltammetry and linear sweep voltammetry do not always correlate linearly with fuel cell performance, and that full evaluation of catalyst performance should ideally be tested as components in membrane electrode assemblies (MEAs) integrated in fuel cells. Different from many earlier studies which evaluated the catalysts under relatively low voltages,[252,253] Wang et al. imposed realistic fuel cell conditions[54] and evaluated a Co–N₄-based catalysts at a viable voltage of 0.7 V for 100 h using air feed to the cathode. By monitoring the voltage–current (VI) polarization plots were recorded during the durability test to monitor the possible degradation evolution. At initial stage up to 30 h, there are insigniﬁcant losses (less than 15 mV) at all current density ranges, and a 100 h continuous operation eventually results in a loss around 60 mV at 1.0 A cm⁻² (corresponding to an overall decrease in performance of about 10%). The authors speculate that the performance loss likely is related to unstable active site or instabilities in electrode structure. Similarly, Li and co-workers tested singly dispersed Fe–Co catalyst motifs coordinated to nitrogen under very realistic automotive fuel cell conditions (1 A cm⁻²) and demonstrated a very good stability with negligible performance loss under cycling conditions for 100 h.[73] It should be noted that optimization of the MEAs is highly delicate, and that commercially used catalysts take advantage from highly optimized processes that are yet to be accomplished for new catalysts such as those presented in this review. Another aspect with few atom catalyst sites usually embedded in a carbon-rich matrix is the risk of carbon corrosion,[254] especially at the harsh conditions of fuel cells operating in cars.[255] In summary it is clear that more studies need to be done regarding long-term stability under practical conditions in fuel cells for platinum free catalysts but that all in all performance data on metal coordinated few atom motifs are encouraging and likely will play an important role in future energy conversion technologies.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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