

A review on non-precious metal electrocatalysts for PEM fuel cells

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Received 13th October 2010, Accepted 26th May 2011

DOI: 10.1039/c0ee00558d

With the approaching commercialization of PEM fuel cell technology, developing active, inexpensive non-precious metal ORR catalyst materials to replace currently used Pt-based catalysts is a necessary and essential requirement in order to reduce the overall system cost. This review paper highlights the progress made over the past 40 years with a detailed discussion of recent works in the area of non-precious metal electrocatalysts for oxygen reduction reaction, a necessary reaction at the PEM fuel cell cathode. Several important kinds of unsupported or carbon supported non-precious metal electrocatalysts for ORR are reviewed, including non-pyrolyzed and pyrolyzed transition metal nitrogen-containing complexes, conductive polymer-based catalysts, transition metal chalcogenides, metal oxides/carbides/nitrides/oxynitrides/carbonitrides, and enzymatic compounds. Among these candidates, pyrolyzed transition metal nitrogen-containing complexes supported on carbon materials (M–N_x/C) are considered the most promising ORR catalysts because they have demonstrated some ORR activity and stability close to that of commercially available Pt/C catalysts. Although great progress has been achieved in this area of research and development, there are still some challenges in both their ORR activity and stability. Regarding the ORR activity, the actual volumetric activity of the most active non-precious metal catalyst is still well below the DOE 2015 target. Regarding the ORR stability, stability tests are generally run at low current densities or low power levels, and the lifetime is far shorter than targets set by DOE. Therefore, improving both the ORR activity and stability are the major short and long term focuses of non-precious metal catalyst research and development. Based on the results achieved in this area, several future research directions are also proposed and discussed in this paper.

1.0. Introduction

Proton exchange membrane or polymer electrolyte membrane (PEM) fuel cells, which can efficiently convert chemical energy into electricity through electrochemical reactions, are considered ideal power sources for future mobile and stationary applications due to their high energy efficiency, high power density, as well as low/zero emissions. With the approaching commercialization,

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Broader context

The approaching commercialization of polymer electrolyte membrane (PEM) fuel cells is still hindered by the high cost and limited operational stability of the Pt-based cathode catalysts traditionally utilized. Specifically, the cathode catalyst layer comprises over half of the overall cost of a fuel cell stack and the depleting global supply of platinum ensures that this price is only going to increase. Developing new catalyst materials with reduced Pt dependency, improved oxygen reduction reaction (ORR) activity and high stability is an urgent necessity. One promising approach in this field involves the development of non-precious metal catalysts. Related research efforts have become extensive, covering a broad range of non-precious metal based materials fabricated by a variety of different synthesis techniques. Until recently, the ORR activity and stability of non-precious metal catalysts were well below the required levels for application in PEM fuel cells. Several recent advances however have reduced this gap and perpetuated research and development activity towards these non-precious catalyst materials. The progress and knowledge garnered in recent years will be highlighted herein, along with insight provided regarding the remaining challenges and research directions in order to further the development of these materials and make PEM fuel cell commercialization a reality.

several challenges have been identified, including high cost and insufficient durability. Although intensive effort has been put on

both cost reduction and durability improvement, with some progress being made in recent years, major breakthroughs in PEM fuel cell technology are still necessary in order to make a sustainable commercialization feasible.

With respect to both the high cost and low durability, PEM fuel cell electrocatalysts are identified to be largely responsible. According to a United States Department of Energy's (DOE's) study in 2007, 56% of the cost in a PEM fuel cell stack comes from the platinum-based catalyst layers based on a projected cost for large scale fuel cell production.¹ This results from a significant amount of platinum-based catalysts required in (i) the anode catalyst layer to catalyze the hydrogen oxidation reaction (HOR) or liquid fuel oxidation reaction and (ii) the cathode catalyst layer to catalyze the oxygen reduction reaction (ORR). In particular, when compared to the anodic HOR, the cathode suffers from relatively sluggish ORR kinetics and therefore high overpotential, limiting the performance of a PEM fuel cell. At the current technology status, Pt-based electrocatalysts are the



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practical materials in terms of both activity and stability, although their performance is still insufficient and needs further improvement. The major drawback of these Pt-based catalysts is their limited availability and high cost, contributing to the excessive production costs of fuel cell systems. With respect to the availability of Pt materials for PEM fuel cells, some arguments indicate the importance of Pt recycling. If the Pt in the catalyst layer can be recycled at the end of the fuel cell life with an efficiency of 100%, Pt availability may not be a severe issue facing fuel cell commercialization. However, even while excluding the process costs of Pt recycling, the material loss for every full life cycle will draw heavily on global Pt supplies due to realistic recycle efficiencies being less than 100%. In addition, the price of Pt has been steadily increasing with no break in this trend expected in the near future. This will only serve to escalate this challenge facing fuel cell commercialization. Various other noble metal based catalysts (*i.e.* Pd, Ru) have been investigated as alternatives to Pt. These metals have minimal applicability however, as it involves replacing one expensive metal catalyst with another less expensive metal with diminished performance. Thus, developing inexpensive catalyst materials with both high performance and durability has emerged at the forefront of modern research and development efforts towards PEM fuel cell technology and its commercialization.

For PEM fuel cell cost reduction, the search for inexpensive, high performance electrocatalysts for PEM fuel cells has taken two different approaches. The first approach is to reduce catalyst usage through increasing Pt utilization in the catalyst layers. This can be achieved by alloying Pt with inexpensive metals (Co, Fe, *etc.*), and/or by utilizing unique support materials for Pt nanoparticle deposition. In the last two decades, the required Pt loading has been reduced significantly to approximately 0.4 mg cm⁻².² Unfortunately, the increasing Pt price during this time has totally offset the Pt loading reduction, rendering the efforts made towards Pt loading reduction in the last two decades ineffective. Therefore, it seems that this approach may not be the long-term solution for cost reduction of PEM fuel cells. The other approach is to develop non-precious metal-based electrocatalyst materials. This approach has been stimulated extensively by the recent push for PEM fuel cell commercialization. Thus, development of high performance, non-precious metal-based catalyst materials seems to be the solution for a long-term and sustainable commercialization of PEM fuel cells. Unfortunately, until today, the performance of the best non-precious metal catalysts (generally carbon supported Fe- and/or Co-N catalysts) is still inferior when compared to Pt-based catalysts in terms of both activity and stability. However, the incremental improvement in both activity and stability of non-precious metal catalysts towards their practical usage has been seen in recent years, making this approach more active and promising.

Regarding the development of non-precious metal based catalysts for PEM fuel cell applications, research efforts have become more extensive, covering a broad variety of potential materials, several of which have been reviewed in recent years.³⁻⁹ The most promising catalysts investigated thus far are carbon-supported M-N (M-N_x/C) materials (M = Co, Fe, Ni, Mn, *etc.*) formed by the pyrolysis of a variety of metal, nitrogen and carbon precursor materials.⁴ Other non-precious metal electrocatalyst materials investigated include non-pyrolyzed transition

metal macrocycles, conductive polymer based complexes (pyrolyzed and non-pyrolyzed), transition metal chalcogenides, metal oxide/carbide/nitride materials, as well as enzymatic based electrode materials, all of which will be discussed in the ensuing sections. For a practical non-precious catalyst for use in PEM fuel cells, the DOE has set up the activity and stability goals for 2015, which are: (i) the ORR activity must reach a volumetric current density of 300 A cm⁻³ at 0.8 V iR-free, and the stability must reach 5000 hours at operating temperatures below 80 °C.¹⁰ For clarity, catalyst activity refers to the electrokinetics of the ORR occurring on these materials, generally measured at high electrode potentials. The activity goal is evaluated on a volumetric basis, as non-precious metal catalysts are relatively inexpensive compared with Pt. Thus, increased loading is not a significant issue unless catalyst layers approach the thickness of ~100 μm, at which point mass transport issues will arise.² The performance of these catalysts takes into consideration the current densities produced over a broad range of potentials encountered at the cathode of fuel cells during transient conditions. Performance thus not only provides a metric of the electrokinetics of the ORR occurring in a broad potential range, but also takes into account mass transport, electronic transport and structural/chemical factors arising from the distinct catalyst configurations. Stability and durability of electrocatalyst materials comprise the activity and performance retention following accelerated degradation testing or long term operation. Despite significant progress in the field of non-precious metal electrocatalysts for PEM fuel cell applications, both the specific activity and stability requirements have not been met yet. Therefore, there is still a long way to go in order to reach the practical usage of non-precious metal catalysts in PEM fuel cell applications. In this paper, insight into the progress made on non-precious metal catalysts with a variety of different structures and properties will be provided, along with the proposed catalytically active sites and reaction mechanisms from various authors. Discussion of the factors influencing catalyst performance and strategies for future improvements will also be provided.

2.0. M-N_x/C catalysts

One of the most promising non-precious metal electrocatalysts in PEM fuel cell application is carbon-supported transition metal/nitrogen (M-N_x/C) materials (M = Co, Fe, Ni, Mn, *etc.*, and normally $x = 2$ or 4), which have gained increasing attention due to their promising catalytic activity displayed towards the ORR, along with the utilization of abundant, inexpensive precursor materials. It was initially demonstrated in 1964 that transition metal porphyrins, namely cobalt phthalocyanine (CoPc) could act as ORR electrocatalysts in alkaline conditions.¹¹ Later, the catalytic activity of various metal-N₄ complexes supported on carbon was demonstrated in acidic media. However, stability issues arose as the catalyst structures were found to decompose in the presence of acid, resulting in a loss of catalytic activity.¹² A significant breakthrough was achieved years later when high temperature heat treatment procedures (~400 to 1000 °C) were introduced to the catalyst synthesis process. This approach was demonstrated to modify the carbon supported M-N_x/C catalyst materials, increasing the concentration of available ORR active sites while at the same time improving the catalyst stability as

well.^{13–18} These structural transformations are a subject of extensive debate, where at high temperatures the atomic configuration of the macrocycle compounds was found to partially or completely decompose. These transformations have been confirmed by various methods including Mössbauer spectroscopy,^{19–22} X-ray photoelectron spectroscopy (XPS),^{20–26} extended X-ray absorption fine structure (EXAFS),^{22,27} time of flight secondary ion mass spectroscopy (ToF-SIMS)^{24,28–31} or thermogravimetric mass spectroscopy (TG-MS),^{26,32} where often these characterization techniques are coupled to provide further insight regarding the nature of surface configurations remaining following pyrolysis. Interestingly, different catalytically active site structures have been proposed from these studies including $M-N_4/C$,^{19,20,22,28,29} $M-N_2/C$ ²⁹ and $N-C^{23,26}$ species. These conflicting reports can most likely be attributed to differences in the synthesis procedures (*i.e.* type of macrocycle precursor, pyrolysis temperature and duration) and the nature and sensitivity of the characterization techniques utilized.

Due to different structures of the synthesized catalysts after high temperature decomposition, it was proposed that expensive transition metal macrocycle compounds were not actually required, and that catalytically active $M-N_x/C$ moieties could be formed with a variety of different precursor materials.^{17,33,34} The only requirement was a proper metal–nitrogen coordination occurring on a carbon support resulting from heat treatment, to achieve ORR active catalyst materials using simple metal, nitrogen and carbon precursor materials. Verifying this, in 1989, some active ORR electrocatalysts were successfully prepared using polyacrylonitrile (PAN), Co or Fe salts, and a Vulcan XC-72 carbon black support.¹⁷ This provided a new direction of research involving inexpensive precursor materials. Since then, several different types of transition metal-ion centers have been investigated, including Fe, Co, Ni and Cu, along with various non-macrocycle nitrogen source materials such as organic complexes, nitrogen containing salts and even gaseous nitrogen precursors.

In an effort to produce highly active and stable non-precious metal catalysts, ample approaches have been pursued with significant emphasis placed on elucidating the exact effect of synthesis conditions and the nature of the catalytically active sites. Progress in this field of research will be discussed in this section. Non-pyrolyzed $M-N_x/C$ catalyst materials will initially be discussed, as they provide favorable structural control in the absence of high temperature treatment procedures and are the fundamental building blocks of pyrolyzed $M-N_x/C$ catalysts, which will be discussed thereafter.

2.1. Non-pyrolyzed $M-N_x/C$ materials

Transition metal macrocycle compounds have been employed in many applications, specifically as catalysts for a variety of different processes.^{11,35} As previously mentioned, CoPc was initially demonstrated to possess ORR activity in alkaline conditions,¹¹ which opened a new direction for research in the field of fuel cell catalysis, leading to numerous investigations focusing on the use of transition metal macrocycle compounds as ORR electrocatalyst materials.^{36–52} For fuel cell applications, these catalysts are usually supported on high surface area carbon supports to create sufficient reaction surface area. The activity of these complexes has been found to be directly related to the metal

ion center and encompassing ligand structure.^{35,37,44,53–55} Simple cobalt-based complexes (*i.e.* CoPc or Co porphyrin) have catalytic activity towards the reduction of oxygen by a 2-electron process to produce H_2O_2 , whereas a 4-electron reduction process forming H_2O is commonly observed for Fe-based complexes.^{39,44,53} However, the activity and stability of these non-pyrolyzed $M-N_x/C$ catalysts are too low to be used as ORR catalyst materials in a fuel cell. As mentioned previously, a heat treatment process can improve their ORR activity to a promising level. The benefits of utilizing non-pyrolyzed macrocycle compounds, however, are important in this field of scientific research for fundamental understanding. During high temperature pyrolysis procedures in inert environments, the structures of the catalyst precursors are significantly altered, leading to uncertainty regarding the nature of the catalytically active sites and the ORR mechanism. In the case of non-pyrolyzed macrocycle complexes, the well-defined structure is preserved during simple synthesis procedures. This allows a direct correlation between the catalyst structure and the resulting ORR activity and stability. Thus, numerous studies have been aimed at these types of investigations in order to provide a relationship between the $M-N_x/C$ catalyst structures and observed electrocatalytic properties. These studies are in an attempt to elucidate the precise structural effects on the ORR activity and reaction mechanism, which will provide insight for future progress in the synthesis of high performance, non-precious metal electrocatalysts.

2.1.1. Metal-ion center effect on the ORR activity and stability. The electrochemical properties of non-pyrolyzed transition metal macrocycle compounds are dependent on a variety of factors. The metal ion center has a significant influence on the redox and electronic properties of these compounds. Fe and Co metal-ion centers have been found to display the optimal electrocatalytic properties, attributed to their distinct redox properties and have been proposed as the active site for the ORR.^{44,53} These two particular metal types have thus been the focus of the majority of investigations. The nature of the ligand–metal interaction also plays an important role in the ORR activity of these compounds, with various macrocycle structures (*i.e.* Pc or porphyrins) available, which possess significantly different chemical and electronic properties. Particularly, a high ionization potential of the metal-ion centers has been deemed an important factor influencing ORR activity.^{54,56,57} In one particular study based on density functional theory calculations, Co porphyrins were found to have a higher degree of ionization potential compared to their Fe counterparts (Fe porphyrins).⁵⁴ However, FePc was determined to possess a significantly higher ionization potential than CoPc, elucidating the effect of ligand on these materials' properties and ORR activity. In general, for all of these metal-ion centers investigated, higher ORR activity could be correlated to increased oxygen binding capabilities and higher ionization potentials.

2.1.2. Ring substituent group effect of the non-pyrolyzed transition metal macrocycles on their ORR activity and stability. Moreover, and most significantly, the presence of substituent functional groups on the outer rings of the macrocycle compounds can also serve to tailor the electrochemical and chemical properties of these materials.^{41–43,46,49–51,58} Several

interesting observations have been drawn from studies investigating substituent groups on transition metal macrocycle complexes. Recently, functional group substituents, which are attached on the outer rings of transition metal macrocycle complex materials and their effect on ORR activities were studied by Baker *et al.*⁵¹ In this study, FePc/C and FePc/C substituted with three different functional groups as illustrated in Fig. 1 were investigated. Different substituent groups were shown to have an effect on the redox behavior, the ORR activity and the stability of these complexes in acidic media at different temperatures. Furthermore, substituent groups were found to play an important role influencing the exact mechanism of the ORR, with the number of electrons transferred varying between 1 and 3 for different samples. One possible explanation is that the substituent could affect the mode of macrocycle adsorption on the carbon support which could exert an influence on the electrochemical activity. This is in agreement with earlier studies highlighting the influence that the size and shape of substituted macrocycle complexes will have on the resulting catalytic properties, due to varying alignments on the carbon support and steric effects.^{37,44} Moreover, Baker *et al.*⁵¹ further claimed that the varying ORR activities and redox properties of these substituted FePc/C complexes would be caused by altered electron densities of the metal-ion centers and ring structures resulting from the substituent groups. Previous reports have in fact indicated that the electron withdrawing or releasing properties of the substituent groups would result in lower or higher electron densities of the metal-ion center, respectively,^{59,60} which has been found by other groups to result in enhancement of the ORR activity.^{41,44} Moreover, a recent report by Li *et al.*⁶¹ indicated that functionalizing carbon supported FePc with thioether phenyl groups (Fe-SPc/C) with a structure inspired by naturally occurring ORR catalysts would lead to exemplary stability

enhancements under potentiodynamic conditions in acidic electrolyte. This is due to an electron supplying mechanism provided by the functional groups in Fe-SPc/C, reducing the lifetime of highly oxidizing intermediates. This provides indication that careful design of these non-pyrolyzed complexes can not only serve to improve the ORR activity but also have a significant impact on the operational stability of non-pyrolyzed M-N_x/C materials.

In summary, although non-pyrolyzed M-N_x/C catalyst materials may never find application in PEM fuel cells due to their modest ORR activity and stability, they provide a basis for investigations into the nature of ORR active sites and reaction mechanisms on carbon supported metal-nitrogen complexes. Fundamental understanding of these factors can provide a platform for future studies directed at the synthesis of inexpensive, stable, highly active ORR electrocatalysts.

2.2. Pyrolyzed M-N_x/C

The discovery that ORR catalytically active M-N_x/C materials could be synthesized by the simple pyrolysis of transition metal, carbon and nitrogen containing precursor materials, paved the way for ample investigations of this variety. In order to develop M-N_x/C catalysts with the highest catalytic activity and stability under fuel cell operating conditions, the main focus has been placed on systematic trial and error investigations based on optimization of synthesis conditions, precursor materials and catalytic structures. Several factors were deemed important to the activity and stability of pyrolyzed M-N_x/C electrocatalysts, including transition metal type and loading, carbon support surface properties and nitrogen content, and heat treatment conditions and duration. Although significant progress over recent years has been achieved in elucidating these factors, the overall understanding is still limited. Catalysts of this class were reviewed in detail in 2008.⁴ Herein, results obtained prior to 2008 will be highlighted, along with the progress made recently regarding the influence of precursor materials and synthesis procedures utilized on the ORR activity and operational stability of pyrolyzed M-N_x/C catalysts. This insight will provide researchers the ability to properly design synthesis procedures to adequately tailor catalytically active sites, with the goal of producing highly active and durable electrocatalyst materials for PEM fuel cell applications.

2.2.1. Non-precious metal types and source materials.

Several different non-precious transition metals have been investigated as potential active centers for M-N_x/C chelates, including Fe, Co, Mn, Ni, Cu and Cr. Preliminary investigations have indicated that for pyrolyzed M-N_x/C catalysts, Fe and Co were the most active transition metal-ion centers for ORR catalysis.^{33,37,62} Furthermore, if one catalyst contains two or more different types of metal-ion centers, its ORR activity can be enhanced notably. In an early study investigating the effect of combining metal-ion centers, Chu and Jiang⁶³ revealed that heat treatment of various binary metal macrocycles rendered ORR electrocatalysts more active than those that just had one type of metal-ion center, such as Fe, Co, Ni, or Cu. Additionally, among binary metal catalysts investigated (Co/Fe, V/Fe, Ni/Fe or Cu/Fe), heat treated Co/Fe macrocycles had significantly higher ORR activity than other

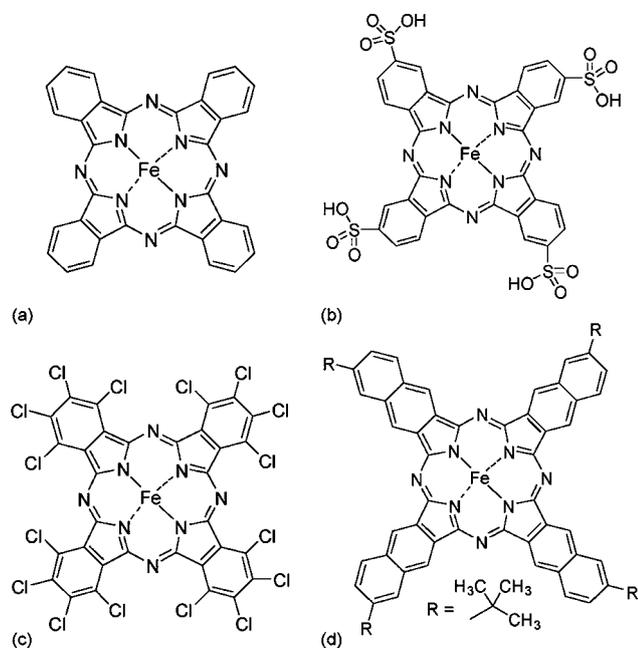


Fig. 1 Molecular structure of (a) FePc and (b, c and d) various substituted FePc molecules investigated for ORR catalytic activity and stability. Reprinted from ref. 51, with permission from Elsevier.

combinations. Considering Fe and Co centers alone possess the highest ORR activity of pyrolyzed M-N_x/C catalysts, it is understandable that a combination of the two is superior to other formulations investigated. These findings have inspired modern research on the development of pyrolyzed Fe/Co catalyst materials,^{64–71} in an attempt to couple the high ORR activity of Fe-based electrocatalysts with the significant stability of Co-based electrocatalysts. When combined, these materials have not only been observed to improve the ORR activity compared to each individual constituent,^{64–66,68–70,72} but have also been demonstrated to result in improved stability.^{65,68} In one example, Zelenay *et al.*⁶⁷ successfully synthesized heat treated CoFe-polypyrrole supported on carbon. As displayed in Fig. 2, this complex had very high ORR performance in a fuel cell setup and only 10% performance degradation after 130 h at 0.4 V, attributed primarily to catalyst layer flooding. This work was based on pyrolyzed conductive polymer materials which will be discussed specifically in Section 3.4, however adequately demonstrates the exemplary performance of mixed metal species. Despite significant work in recent years investigating the ORR activity and stability of binary Fe/Co-based M-N_x/C catalysts, the exact nature of the activity and stability enhancements remains unknown. Several authors have proposed that it is a result of some type of complementary mechanism occurring between the two metal-ion centers.^{63,69} Future work should be directed at elucidating these factors in order to insightfully tailor synthesis parameters (*i.e.* Fe : Co ratios, precursor materials, fabrication

procedures) to develop binary Fe/Co-based M-N_x/C catalysts with improved ORR performance and stability.

With respect to the nitrogen precursor materials utilized for pyrolyzed M-N_x/C materials, several different macrocycle structures have been investigated including phthalocyanines (Pc), tetramethoxyphenylporphyrin (TMPP), tetraphenylporphyrin (TPP) as well as tetraaza annulene (TAA). As previously mentioned, due to the uncertainty regarding the exact nature and specific role of the macrocycle metal-ion centers as the ORR active sites following high temperature decomposition,^{14,31,73,74} several non-macrocycle compounds such as inorganic salts and organometallic complexes have also successfully been employed as catalyst precursor materials. Highly active ORR catalysts have been developed using these simple, readily available precursor materials, which is considered a breakthrough in the targeted research area. Table 1 provides several examples of simple inorganic and organic compounds that have been used as precursor materials for Fe- and Co-based pyrolyzed M-N_x/C ORR electrocatalysts. These compounds either contain nitrogen in their structure (*i.e.* transition metal macrocycles) or require the addition of a supplementary nitrogen containing compound due to the absence of nitrogen in their inherent structure (*i.e.* various inorganic salts or organometallic complexes). Upon pyrolysis, ORR active moieties are formed, with the exact nature of these site structures a subject of debate. The most prevalent uncertainty in the literature surrounds whether or not the transition metal species are present in the active site structures, or merely facilitate the incorporation of catalytically active N-C species. This will be discussed in Section 2.2.2, although Table 1 also highlights whether or not the specific researchers indicated the presence of metal species in the active site structures.

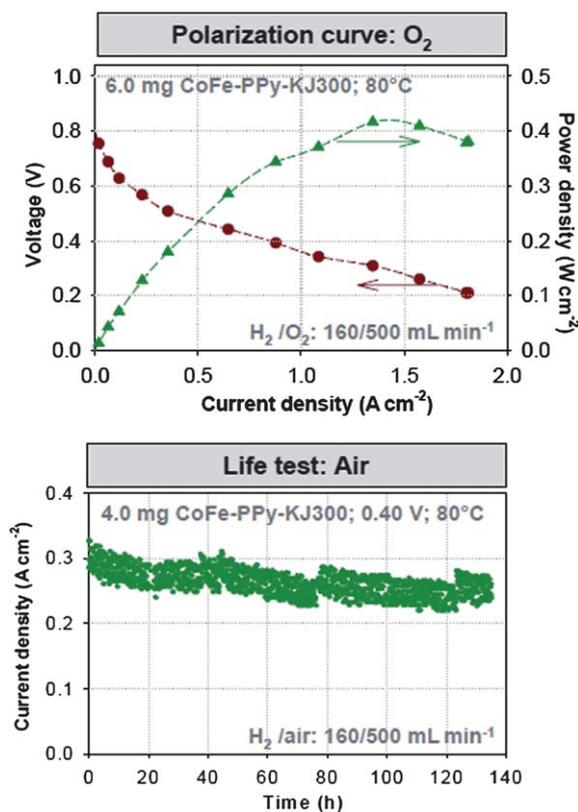


Fig. 2 Fuel cell polarization curve (top) and stability life test (bottom) of a heat treated CoFe-polypyrrole carbon catalyst material. Figure obtained from DOE Annual Review Presentation.⁶⁷

2.2.2. Proposed structures of the M-N_x/C catalytic active site for ORR. Regarding the exact nature of the ORR catalytically active site, there are several different structures and formation mechanisms that have been proposed in the literature. Through ToF-SIMS, Dodelet *et al.* initially proposed that the nature of the catalytic sites involved a coordination between the transition metal ion, nitrogen functional groups and the carbon support, in the form of MN_xC_y⁺.^{29,95} In the case of Fe based catalysts synthesized from either FeAc or ClFeTMPP, two different catalytically active sites were observed, namely FeN₂/C and FeN₄/C (Fig. 3a and b, respectively). The former was observed to have a higher ORR catalytic activity and its formation was favored at pyrolysis temperatures between 700 and 900 °C.²⁹ Recently however, Dodelet's group has revised their proposed active site configurations claiming that the majority of active site structures consist of an Fe-N₄/C (labeled by the authors as FeN₂₊₂/C) configuration bridging two adjacent graphene crystallites (Fig. 3c).⁹⁹ These are primarily hosted in the micropores of the catalyst materials and with deliberate carbon support selection and synthesis methods to obtain ideal nanostructure configurations, active site densities can be improved.¹⁰⁰ This would adequately explain previous studies correlating ORR activity to the presence of Fe ions coordinated by four nitrogens observed through Mössbauer analysis.^{19,20,22,73,144} Kramm *et al.*²⁰ have recently attributed improved ORR kinetics of these Fe-N₄ centers to Fe-ion centers with higher electron densities. This could possibly be tied back to fundamental investigations on

Table 1 Transition metal containing precursors used in the synthesis of M–N_x/C catalysts for the ORR and whether or not the corresponding authors deemed metal as part of the active site structures^{a,b}

Metal	Precursor type	Compound	Active site structures					
			Metal based	Metal free	Not specified			
Iron	Macrocycle	FePc	24	26, 75, 76	77–79			
		FePcTc	24					
		FeTPP	22, 64, 80, 81					
		FeCITPP	21, 80, 82, 83					
		FeCITMPP	19, 20, 29, 73, 84–92					
		FeTAA	13					
		FeTPTZ	93					
		Inorganic salts	FeAc			17, 29, 63, 87, 88, 91, 92, 94–106	107–114	115, 116
			FeSO ₄			33, 117, 118	23, 71, 119, 120	93, 121–124
			Fe(CN) ₆			102		121
FeCl _x				125–128				
Cobalt	Organometallic complex	Ferrocene		129				
		CoPc	31, 34	75	77			
		CoTPP	28, 64, 82, 83, 130, 131					
		CoTMPP	30, 69, 132, 133		134, 135			
		CoTAA	136	25	137			
	Macrocycle	CoTPTZ	138					
		CoTETA	139		140			
		Inorganic salts	CoAc	17, 30, 34, 141	113			
			Co(NO ₃) ₂	142	23, 71, 119, 120	128, 143		
			CoSO ₄	33		121		
CoCl _x				127				

^a Arguments regarding whether or not metal comprises the active site structures are not always exclusively confirmed. ^b Several of these references come from the same groups with multiple works supporting their hypothesis.

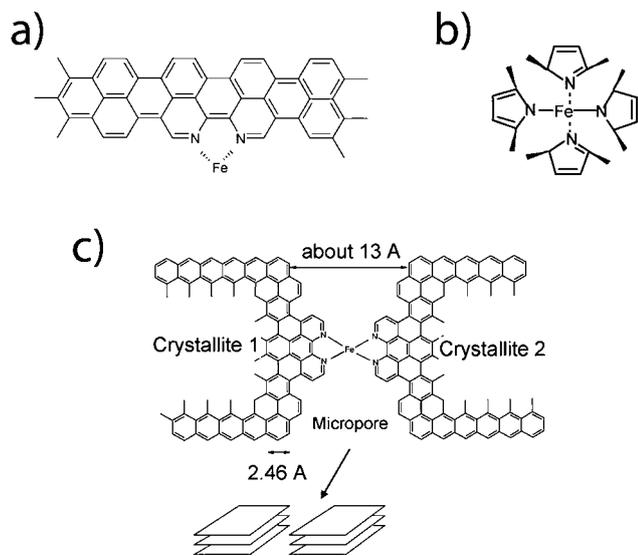


Fig. 3 (a and b) Earlier proposed catalytically active FeN₂/C and FeN₄/C structures, respectively. (c) Revised FeN₂₊₂/C (overall FeN₄/C) active site structure bridging two adjacent graphitic crystallites. Adapted and reprinted from ref. 99 with permission from Elsevier.

non-pyrolyzed M–N_x/C catalysts discussed previously, in that the distinct chemical properties of the carbon support and nitrogen ligands could exert electron releasing/withdrawing effects on the metal-ion center, influencing the catalytic activity observed. These findings reveal that while a focus should always be maintained on the development of M–N_x/C catalysts with improved active site densities, it is possible to tune the electronic

and structural properties of these active site structures in order to enhance the ORR electrokinetics.

ToF-SIMS indicated a slightly different nature of catalytically active sites for Co-based M–N_x/C catalysts synthesized from either CoAc or CoTMPP.³⁰ The presence of CoN_xC_y sites was observed, similar to those observed for Fe-based M–N_x/C catalysts; however, only the presence of CoN₄/C species could be confirmed, and there was no clear conclusion on the existence of other similar CoN_xC_y arrangements such as CoN₂/C. It was also observed that there was no dominant ORR active site and that all Co-containing groups present possessed the same degree of ORR activity. Interestingly, these findings were different from the conclusions drawn for Fe-based catalysts through ToF-SIMS, however are consistent with other studies correlating ORR activity with Co–N₄ species detected with EXAFS.^{27,141}

In the literature, some authors readily support the claims attesting the ORR activity of M–N_x/C catalysts to the existence of MN_xC_y moieties,^{14,19,20,22,88} whereas other authors had a differing opinion regarding the possible role of the transition metal towards the ORR active site. Instead of being a part of the active site structure, it has been proposed that the presence of the metal-ion center serves to catalyze the formation of N/C catalytically active sites during the pyrolysis procedures.^{76,108,110,113,119,129,145} Specifically, the ORR activity is attributed to the formation of graphitic nitrogen and/or pyridinic nitrogen functional groups, or the degree of edge plane exposure the latter represents. This claim has been supported in the literature with ORR activity being reported for metal free N/C catalyst materials.^{146,147} This further demonstrates the convoluted understanding regarding the exact nature of the catalytically active moieties with respect to ORR.

These contradicting reports likely arise due to fundamental and sensitivity variations between material characterization techniques. Insight into active site formation mechanisms and structures is still insufficient at the current technology state. It can however be concluded that the type of metal-ion center utilized for $M-N_x/C$ catalysts has a significant impact on the properties and ORR activity of these pyrolyzed materials. The exact role of the metal-ion center regarding the ORR active site as well as the structures of the active site is a controversial subject however, and future detailed investigations are required in order to provide further insight into this topic.

2.2.3. Non-precious metal loading and content. It has been recognized that not only does the type of metal and metal-precursor materials used affect the ORR activity of pyrolyzed $M-N_x/C$ catalysts, the relative metal content present in the catalyst also plays an important role in its catalytic activity. Investigations into the influence of metal content on the ORR catalytic activity are ample,^{29,74,87,95,117,122,148–150} and this phenomenon has been discussed in detail recently.⁴ Generally, the optimal metal content of pyrolyzed $M-N_x/C$ catalysts varies from study to study. For example, in one particular study,¹⁴⁹ the optimal Co loading in pyrolyzed Vulcan XC-72 carbon black supported CoPc catalyst was found to be 3.5 wt%. Conversely, another study indicated that a Co content of 7.18 wt% in pyrolyzed Co-triipyridyl triazine (CoTPTZ) supported on Black Pearls 2000 resulted in the highest ORR activity of the resultant materials.¹³⁸ These diverse results could be an effect of the varying surface areas and properties of the carbon support utilized (Black Pearl 2000 has significantly higher surface areas), the size and quality of dispersion of the metal precursor materials, or to the distinct synthesis and heat treatment procedures utilized. Commonly however, a distinct trend is observed relating metal contents to the ORR activity of pyrolyzed $M-N_x/C$ catalysts. At low relative metal contents (study dependent) the ORR activity of these materials will increase with increasing metal content up to a maximum saturation point in which a plateau of ORR activity is observed.^{117,122,148,151} This commonly observed trait is illustrated in Fig. 4, where for pyrolyzed Black Pearl 2000 supported Fe-triipyridyl triazine (TPTZ) electrocatalyst materials, an optimal Fe loading of 4.7 wt% can be observed.¹²² Beyond this plateau region, the catalytic activity can actually decrease with increasing metal loadings,^{117,148} attributed to the formation of ORR inert metal particles and/or metal oxide/carbide materials blocking reactant access to the carbon support pores and active sites.^{74,117,122,151} Further investigations indicated the effectiveness of acid leaching procedures to remove these metallic species.^{22,145,152} Improved ORR activity was observed following acid leaching, providing evidence supporting the notion of active site blockages by inert metallic species. Thus, there is no doubt that the transition metal content in pyrolyzed $M-N_x/C$ catalysts has a significant impact on the ORR activity. The optimal metal loading is material dependent and determined through systematic investigations over a broad range of values. Future investigations should be directed at determining optimal metal contents to produce the highest density of active sites in $M-N_x/C$ catalysts, without too much regard to the formation of inert metallic species. These species can readily be removed by an acid washing post-treatment procedure (which will be discussed

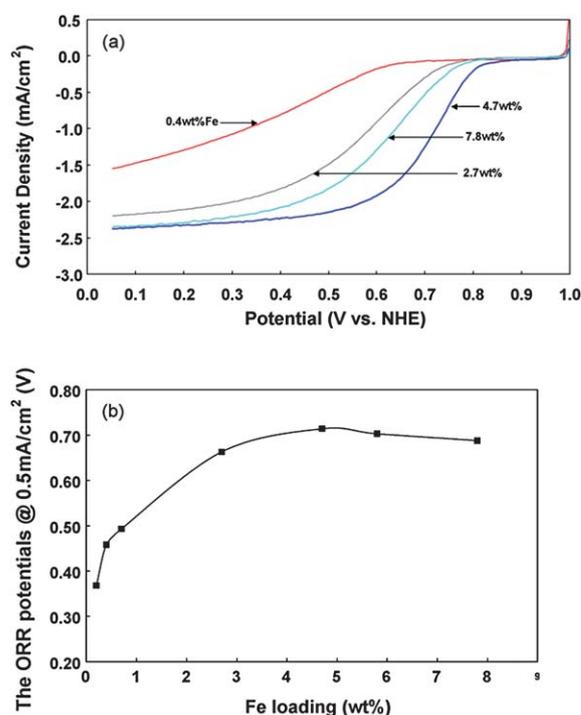


Fig. 4 (a) ORR polarization curves for pyrolyzed FeTPTZ/C catalyst obtained at a rotation speed of 400 rpm in 0.5 M H_2SO_4 solution and (b) ORR potential at a current density of 0.5 mA cm^{-2} as a function of Fe content, displaying an optimal content of 4.7 wt%. Reprinted from ref. 122, with permission from Elsevier.

further in Section 2.2.5) without deterioration or removal of the catalytically active site structures demonstrated previously.²²

2.2.4. Carbon support properties: surface nitrogen content and microporosity. The nature and surface properties of the carbon support present in pyrolyzed $M-N_x/C$ catalysts have a significant impact on the resulting ORR activity and stability. The surface nitrogen content of the catalyst materials was initially deemed the most critical factor influencing the performance, with nitrogen presence an utmost requirement for obtaining materials with ORR activity.¹⁵³ With respect to this, several reports have demonstrated that increases in the surface concentration of nitrogen can be directly linked to an increase in the ORR activity.^{75,88,95–97} Various carbon support materials have been investigated including carbon black materials,^{17,80,85,86,154} oxidized¹⁴² or activated carbons,^{13,25,101,155} as well as even carbons doped with nitrogen prior to catalyst synthesis.^{71,88,95,102} Nitrogen incorporation into the surface of the carbon support materials can be obtained by pyrolysis of various nitrogen precursors in the presence of carbon. Nitrogen precursor materials commonly used include: (i) macrocycle complexes such as Pc or TMPP, (ii) organic compounds such as ethylenediamine (EDA), (iii) nitrogen containing polymers such as PAN, and (iv) gaseous precursors such as NH_3 or CH_3CN . Furthermore, oxidizing the nitrogen-containing carbon supports prior to pyrolysis could also be effective in facilitating the formation of catalyst active sites due to the preferential adsorption of metal ions on oxidized carbon particles.^{71,96,101,117,134,142} To demonstrate the wide range of nitrogen precursor materials that can be used for synthesis of

Table 2 Nitrogen-containing compounds employed in the synthesis of pyrolyzed M–N_x/C ORR catalyst materials and whether or not the corresponding authors deemed metal as part of the active site structures^{a,b}

Precursor type	Compound	Active site structures		
		Metal based	Metal free	Not specified
Organic	Ethylenediamine	142	23, 71, 119, 120, 156	148 126 125 115 123, 124 116
	1,10-Phenanthroline	94, 117, 157		
	Nitroaniline			
	Aminosilane			
	Histidine			
	Cyanamide	118		
	2,2-Bipyridine	104		
	N-Methylpyrrole	141		
	2,5-Dimethylpyrrole	141		
	2,5-Dimethyl-3-pyrroline	141		
	Maleimide	141		
	Imidazole	141		
	Organic polymer	Polyacrylonitrile	17, 33, 34, 141	
Thiourea		141		
Inorganic salt	Ammonium iron sulfate			93, 122, 158
Gas	Ammonia	30, 87, 88, 90, 91, 95–103, 105, 106, 151, 159	147	148
	Acetonitrile		108–114	160, 161

^a Arguments regarding whether or not metal comprises the active site structures are not always exclusively confirmed. ^b Several of these references come from the same groups with multiple works supporting their hypothesis.

pyrolyzed M–N_x/C catalysts, a summary is provided in Table 2. Moreover, Table 2 is broken down to whether or not the authors attributed metal species to being part of the active site or not, in order to further highlight this extensive debate present in the literature.

It is worthwhile to point out that the use of NH₃ as a gaseous precursor for nitrogen opened up an interesting direction in the field of pyrolyzed M–N_x/C catalysts for the ORR. The use of NH₃ during pyrolysis above can not only result in the formation of nitrogen functional groups on the carbon support, but also it can lead to the partial gasification of the support during the heat treatment. This support gasification emanates from the disordered carbon phase,^{97,106,162} and is demonstrated to be an important factor enhancing the ORR activity of the NH₃ derived M–N_x/C catalysts. It was demonstrated that in the presence of NH₃, the gasification of the disordered carbon phase could occur at a rate ten times faster than on graphitized carbon¹⁰⁵ according to the following reaction mechanism:⁹⁷



It was observed that gasification of the disordered phase present in carbon supports could result in the formation of micropores. Recently, the presence of these micropores in the carbon support has been considered a critical factor in developing more active NH₃ derived M–N_x/C catalysts, as long as there is a sufficient amount of nitrogen present.^{94,97,105,106,162,163} Studies have indicated that the mass loss accompanying NH₃ etching was dependent on the heat treatment time¹⁶² and a maximum ORR activity could be usually observed for a mass loss of 30–50%.^{97,99,105,162} These catalysts were prepared first by impregnation of a carbon support with FeAc, followed by a high temperature pyrolysis treatment in NH₃. Calculated weight losses were due to NH₃ etching of the carbon support and pore

formation, thus the observed activity dependency is specific to this class of NH₃ derived catalysts. It has been demonstrated that in the presence of a transition metal, nitrogen functional groups formed on the walls of these micropores during NH₃ etching could serve to bridge metal ions in creating catalytically active sites.^{91,99,106}

The promising results observed with NH₃ etching during M–N_x/C pyrolysis have led authors to investigate various ways in order to optimize micropore formation and increase active site densities. Due to the preferential gasification of disordered carbon, the importance of a high degree of disordered carbon has been demonstrated.^{97,99,100} One particular study, based on the investigation of fifteen different carbon black support materials with varying properties, resulted in the conclusion that increases in the amount of disordered phase carbon and/or optimizing the size of the graphitic particles in the carbon support would result in an improved electrocatalytic ORR activity after NH₃ etching.⁹⁹ For further improving the catalytic activity of the M–N_x/C material, ball-milling of graphitic based carbon supports has also been investigated in order to induce a higher degree of structural disorder.^{98,103} While CO₂ can effectively be used to induce carbon support etching as well and improve ORR activity, the specific activity enhancements are inferior compared to NH₃ etching which simultaneously incorporates nitrogen groups and facilitates active site formation.¹⁵⁹ In summary, NH₃ etching during heat treatment can effectively increase the microporous volume of the carbon support through preferential gasification of disordered carbon, resulting in a higher nitrogen loading and ORR active site formation.

Utilizing this knowledge gained from previous investigations, in 2009 Lefevre *et al.*⁹⁴ synthesized the best non-precious metal catalysts to date with respect to ORR activity. Due to the recent emphasis placed on active site containing micropores, these authors utilized highly microporous Black Pearl 2000 carbon supports. As an alternative approach to active site impregnation with NH₃ pyrolysis in the presence of metal precursor, the

micropores of the carbon support were filled with 1,10-phenanthroline (phen) and iron acetate as pore fillers by planetary ball-milling. In this way, the best performing electrocatalyst was obtained by exposing this filled carbon support to pyrolysis at 1050 °C in an Ar environment in order to induce catalytically active site formation into the micropores, anchored between two adjacent graphitic crystals present in the carbon support as illustrated in Fig. 5. Subsequently, a second pyrolysis in NH₃ was carried out at 950 °C, which was found to be dramatically

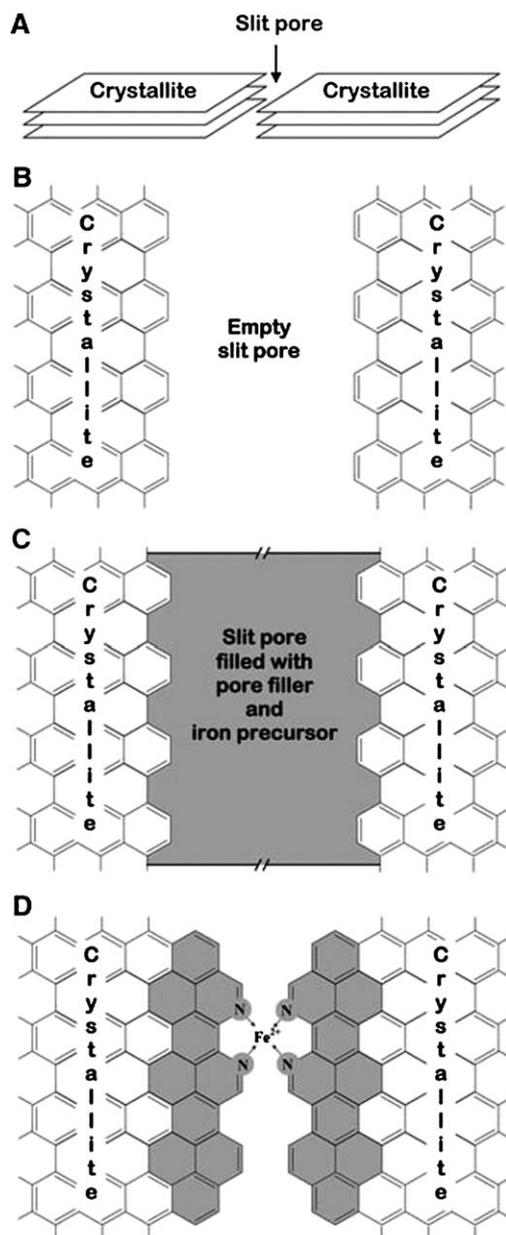


Fig. 5 Schematic of the micropore filling mechanism and active site formation displaying (a) two adjacent graphitic crystallites encompassing a slit pore, (b) cross-section of the empty slit pore, (c) the same slit pore after impregnation of pore filler and metal precursor materials and (d) active site formation and graphitic growth between graphitic crystallites after heat treatment. From ref. 94. Reprinted with permission from AAAS.

effective in improving the ORR activity of the final M-N_x/C catalyst. Additionally, in this study, two different pore filler materials were used, either nitrogen containing (phen), or nitrogen free (perylene-tetracarboxylic dianhydride). In the latter case, NH₃ was utilized during the initial pyrolysis in order to provide the required nitrogen content. The activity of the synthesized catalysts was found to be dependent on the type of pore filler and carbon support used.¹⁵⁷ As previously mentioned, this M-N_x/C catalyst displayed the highest ORR activity to date, with a volumetric current density of 99 A cm⁻³ at an iR-free cell voltage of 0.8 V, significantly higher than 2.7 A cm⁻³ determined for the previously presumed best non-precious metal catalyst as displayed in Fig. 6.⁹⁴ This ORR activity is approaching the target of 130 A cm⁻³ set by the DOE for 2010.¹⁰ Despite significant ORR activity, the stability of these materials under fuel cell operation seemed to be insufficient and needs further improvements if it is to be used as a cathode catalyst in fuel cells.

The limited stability of NH₃ pyrolyzed M-N_x/C catalysts is an ongoing issue overshadowing the promising ORR performance observed with these materials.⁹⁰ For example, one study indicated that using even small amounts of NH₃ during the pyrolysis (only 1.3% NH₃ in an NH₃/Ar mixture) of furnace grade carbon black supported CFeTMPP could result in a considerable decrease in catalyst stability when compared with that pyrolyzed in pure Ar.⁸⁹ A significant increase in ORR activity was observed however, consistent with a previous study indicating reduced activation overpotentials and enhanced kinetic current densities for carbon supported Fe phenanthroline complexes pyrolysed in NH₃ compared to Ar.¹⁴⁸ Clearly there is a trade-off between ORR activity and catalyst stability if NH₃ is used during the pyrolysis.⁸⁹ The higher stability of Ar pyrolyzed catalysts has been attributed to a higher degree of graphitization in the carbon support, a factor previously deemed important to catalyst stability.⁹⁰

Various approaches have also been investigated in order to produce M-N_x/C catalysts with a higher degree of porosity and

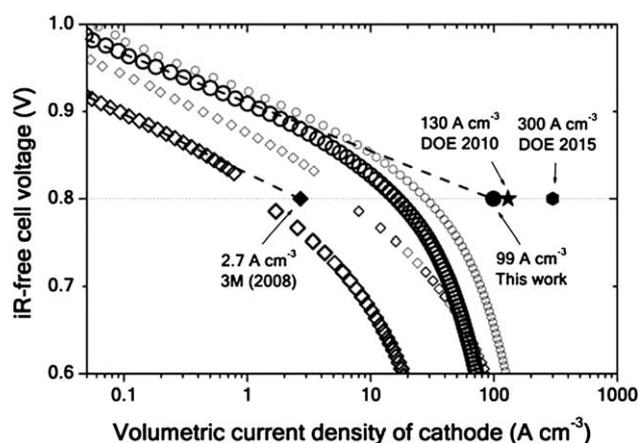


Fig. 6 ORR volumetric current densities at iR-free cell voltages. Diamonds refer to the most active M-N_x/C catalyst formed previously based on pyrolysis of metal salt-nitroaniline precursors in NH₃,¹²⁶ and circles refer to the most active M-N_x/C catalyst in the discussed work.⁹⁴ Large symbols correspond to corrected polarization curves for DOE fuel cell reference conditions. From ref. 94. Reprinted with permission from AAAS.

active site densities. Choi *et al.*¹²⁰ recently employed both Ketjen Black 600 and Ketjen Black 300 as carbon supports for pyrolyzed $M-N_x/C$ catalysts, with micropore areas of $591.9 \text{ m}^2 \text{ g}^{-1}$ and $154.2 \text{ m}^2 \text{ g}^{-1}$, respectively. Fe and Co salts were employed as the metal precursor materials and EDA as a nitrogen source. Ketjen Black 600 supported catalysts were found to display higher ORR activity after synthesis, which was attributed to the higher pore volume and surface area. The authors indicated that allowing a sufficient amount of time for polymerization of the $M-N_x$ complex in the micropores prior to pyrolyzation was a critical parameter leading to improved ORR activity. The best performing electrocatalyst reported in this work displayed a maximum power density of 0.44 W cm^{-2} in a fuel cell setup, along with no performance degradation after being held at 0.4 V vs. RHE for 100 h as displayed in Fig. 7.

The use of foaming agents such as FeC_2O_4 during transition metal macrocycle pyrolysis has also been demonstrated to result in porous carbon based catalyst particles with higher catalytic activities due to their significant surface areas.^{70,164} Moreover, another approach for developing carbon supported catalyst materials with high surface area is silica hard template synthesis methods. After heat treatment, highly porous catalyst materials formed by this method were found to display promising ORR activity either in the presence of a transition metal ($M-N_x/C$ catalysts)^{23,107,115,135} or even metal free $N-C$ catalysts.¹⁴⁷

It is obvious that the properties and surface characteristics of the carbon support have a direct influence on the resulting ORR electrocatalyst materials. In particular, it has been determined that nitrogen incorporation has a significant impact, where higher surface nitrogen contents on the carbon support produce catalysts with higher ORR performance. The significant impact of carbon support porosity should also be acknowledged, along with the high degree of nitrogen incorporation and active site formation inside the catalyst micropores.

2.2.5. Heat treatment temperature and conditions. It has been recognized that the high temperature pyrolysis of $M-N_x/C$ catalysts in an inert environment can result in heat annealing and active site formation, leading to catalytic materials with both higher ORR activity and stability when compared to their non-pyrolyzed counterparts.⁵⁵ This occurrence was reviewed in 2007,⁵ with the focal points of this review and recent advances highlighted in this section. In general, the optimal heat treatment temperature of $M-N_x/C$ catalysts is material dependent and

mainly determined by trial and error based experiments. Different pyrolysis temperatures in inert environments have varying effects on both ORR activity and stability of the synthesized catalysts. An example of the typical pyrolysis temperature effects observed is displayed in Fig. 8 for a CoTPTZ/C based catalyst pyrolyzed at temperature between 600 and 900 °C in an N_2 environment.¹³⁸ In this aspect, ample systematic investigations have been carried out on the effects of pyrolysis temperature (incomplete reference

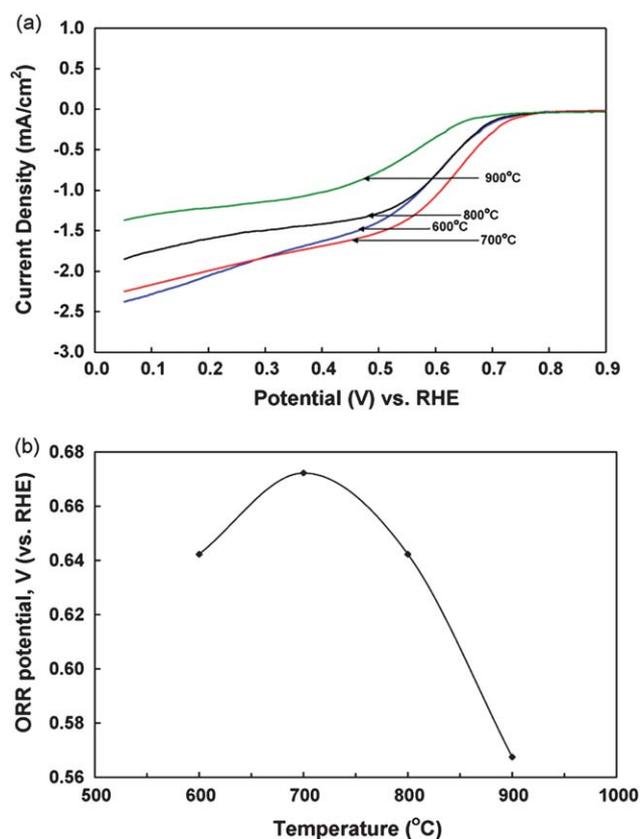


Fig. 8 (a) ORR polarization curves obtained at an electrode rotation of 400 rpm in 0.5 M H_2SO_4 for a pyrolyzed CoTPTZ/C catalyst and (b) pyrolysis temperature effect on the ORR potential obtained at a current density of 0.5 mA cm^{-2} . Reprinted from ref. 138, with permission from Elsevier.

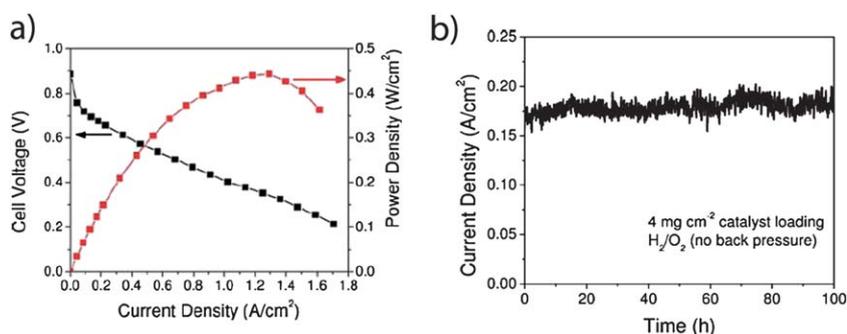


Fig. 7 (a) Fuel cell performance of a pyrolyzed FeCo-EDA complex supported on carbon black and (b) durability test at a cell voltage of 0.4 V for 100 h of operation. Adapted reprint with permission from ref. 120. Copyright 2010 American Chemical Society.

list).^{13,23–26,28,31,34,71,81,82,85,93,119,130,138,139,143,155} Due to the temperature variations observed from sample to sample, there are no generalized temperature values at this moment.

Normally, $M-N_x/C$ catalysts displaying the highest activity towards ORR can be synthesized at pyrolysis temperatures between 500 and 800 °C in inert environments (N_2 or Ar). In this temperature range, it has been proposed that a thermal annealment process occurs between the carbon, nitrogen and metal groups, creating some catalytically active sites responsible for the ORR activity observed through electrochemical measurements. This observed ORR activity is commonly attributed to the presence of coordinated metal–nitrogen chelate complexes or their remaining fragments well dispersed and annealed on the surface of the carbon support material. As previously discussed, the exact nature of the catalytically active sites formed during pyrolysis is a subject of extensive debate. At temperatures approaching and exceeding 800 °C, the metal–nitrogen chelate bonds are known to decompose and a reduction in ORR activity was commonly observed.^{13,26,29,34,81,85,93,143,151,153} Various reports have attributed this decrease in ORR activity to either: (i) formation and growth of relatively inert metallic or metal oxide/carbide particles at these excessive temperatures^{28,31,34,93,138} or (ii) a decrease in the surface nitrogen content of the pyrolyzed $M-N_x/C$ catalysts.^{23,26,119,165}

In the case of (i), inert metallic contaminants on the surface of $M-N_x/C$ catalysts can serve to block the catalytically active ORR sites themselves, or the micropores they reside in. To combat this, recent reports investigated the effect of acid leaching and repyrolysis on synthesized $M-N_x/C$ catalysts.^{79,107,119,159} In one particular investigation, an $M-N_x/C$ catalyst synthesized by pyrolyzing iron acetate with a nitrogen doped porous carbon support was developed.¹⁰⁷ The authors found that the initial pyrolysis step involved the formation of the catalytically active sites, whereas acid leaching and re-pyrolyzation could remove inactive residues (metals and/or metal oxides) and resulting contaminants, respectively. The latter observation could provide explanation for the exemplary ORR performance increment observed by Koslowski *et al.*¹⁵⁹ by exposing pyrolyzed CoTMPP/Fe oxalate based catalysts to a second pyrolysis in N_2 . This enhancement was coupled with a weight loss of 15% and higher BET surface areas, which could be attributed to the burnoff of active site/pore blocking contaminants remaining from HCl washing. This mechanism however was not discussed in detail. Referring back to the work of Liu *et al.*,¹⁰⁷ the initial post-treatment acid leaching step actually resulted in an reduced ORR activity of the sample as seen in Fig. 9 (Sample Fe– CN_x –L), however after re-pyrolysis (sample Fe– CN_x –LH), the observed ORR activity was increased slightly compared to that of the catalyst material prior to purification (Fe– CN_x). This demonstrates the benefit of the contaminant removal and re-pyrolysis procedures. A similar acid leaching procedure to remove surface metals had also been demonstrated in improving catalytic stability of a pyrolyzed CoFeN/C electrocatalyst,⁷¹ which was attributed to a lower amount of H_2O_2 generated in the absence of surface metallic particles. Wu *et al.*⁷⁹ effectively coupled acid leaching procedures in a FePc/phenolic resin pyrolyzed catalyst, followed by NH_3 pyrolysis and etching (previously discussed) to synthesize non-precious catalyst materials with exemplary performance to date, displaying a maximum power density of 560 $mW\ cm^{-2}$ in an H_2 – O_2 fuel cell setup.

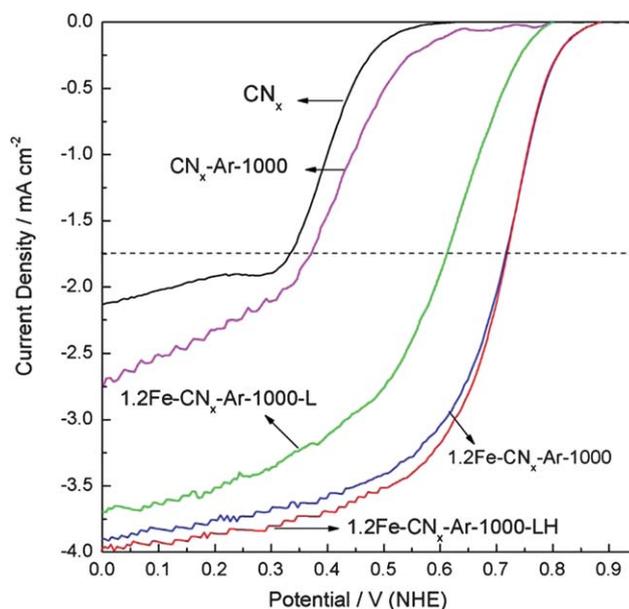


Fig. 9 ORR polarization curves for a pyrolyzed Fe-based $M-N_x/C$ catalyst indicating the effect of heat treatment, acid leaching and sample repyrolysis. Reprinted from ref. 107, with permission from Elsevier.

There also appears to be a trade-off between catalyst activity and stability as a result of the heat treatment temperature utilized in inert environments. At lower temperatures (500–800 °C), catalysts exhibiting the highest electrocatalytic activity can be created, however these catalysts were found to have limited stability. Improved stability has been observed for catalysts synthesized at higher pyrolysis temperatures in N_2 or Ar, however these catalysts displayed an initial ORR activity inferior to that resulting from lower temperature heat treatment procedures. The rationale behind these observations is debatable, due to the fact that the catalyst degradation mechanisms are inter-related to the nature and structure of the catalytically active sites, a controversial subject on its own. Therefore, most investigations could only provide empirical results pertaining to the stability of these pyrolyzed $M-N_x/C$ catalysts, with little insight provided in order to elucidate the root cause behind these observations. A recent report²³ provided new insight into this topic by attributing the ORR active sites of $M-N_x/C$ catalysts to pyridinic and graphitic nitrogen species, with the former displaying a higher degree of activity. It was observed that at elevated pyrolysis temperatures, these catalysts contain a higher amount of quaternary nitrogen and less pyridinic nitrogen. This serves to explain the decrease in ORR performance at elevated temperatures. The enhanced stability in the presence of more quaternary nitrogen functionalities could be attributed to the fact that, unlike pyridinic nitrogen groups, quaternary nitrogen functionalities do not possess a lone pair of electrons, and are thus less prone to degradation by the protonation reaction.

Non-traditional heat treatment methods have also been developed. These include chemical vapor deposition using either vapor precursor feeds or target sputtering,^{109,110,165–170} sol–gel methods,^{171–173} low temperature plasma carbonisation,^{174,175} ultrasonic spray pyrolysis,^{176,177} as well as microwave based methods.¹³⁴ These methods all provide alternative approaches to

synthesizing catalytically active $M-N_x/C$ which have shown some success. Vapor deposition and target sputtering methods provide one approach to synthesize homogeneous materials; however deliberate control of catalyst morphologies and nanostructures with this method is a challenge. Sol-gel preparation procedures allow distinct nanostructure control in synthesizing homogeneous, highly porous structures in the absence of a carbon support; however these methods must be coupled with thermal treatments and thus are more complicated multi-step approaches. Low temperature plasma carbonization is an effective method to prevent catalyst particle sintering and surface area loss accompanying traditional pyrolysis procedures; however these methods require complex equipment, are complicated and costly. With one of the major challenges for non-precious metal ORR catalysts being their low active site densities, one important approach is to develop synthesis routes for self-supported catalysts. As mentioned earlier, vapour deposition and sol-gel pyrolysis methods are effective in producing homogeneous, self-supported catalyst materials. Recently, Liu *et al.*¹⁷⁶ have also applied ultrasonic spray pyrolysis techniques toward the development of homogeneous, self-supported catalyst materials with controlled morphologies and structures. It was demonstrated that the synthesized self-supported catalysts in this work had high active site densities, with well controlled porous catalyst morphologies and structures. Fig. 10a shows a self-supported Fe-polypyrrole catalyst successfully prepared by ultrasonic spray pyrolysis, with a well-defined honeycomb-like mesoporous sphere structure, and higher active site densities than a conventional carbon-supported catalyst. This self-supported catalyst demonstrated 3.4 times higher peak power density than the carbon-supported one in an un-optimized H_2 -air fuel cell single-cell test (Fig. 10b). Note that this performance was fed with air rather than pure O_2 .

2.2.6. Stability of pyrolyzed $M-N_x/C$ catalysts. Although the ORR activities of these pyrolyzed $M-N_x/C$ catalysts are promising, compared to DOE targets, their performance with respect to stability is still insufficient and considered an ongoing challenge. The exact source of the instabilities of these materials is still a subject of controversy in the literature. Some works have reported that detrimental H_2O_2 byproducts may result in the degradation of active site structures, elucidated by treating pyrolyzed $M-N_x/C$ catalyst materials with H_2O_2 solutions. Lefevre and Dodelet⁸⁷ treated pyrolyzed $M-N_x/C$ catalysts

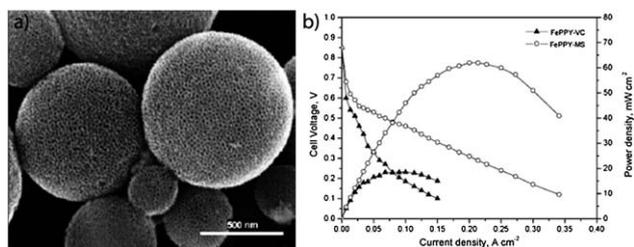


Fig. 10 (a) SEM image and (b) fuel cell polarization curve of a self-supported iron-polypyrrole catalyst synthesized by ultrasonic spray pyrolysis.¹⁷⁶ Reproduced by permission of The Royal Society of Chemistry.

(carbon supported Fe macrocycles or salts, prepared under various conditions) with a 5% H_2O_2 in H_2SO_4 . They reported a loss of ORR activity for all materials, with the magnitude of activity loss being sample dependent. This degradation was attributed to the oxidation/attack of the active site structures by H_2O_2 itself, or radical species formed by the simultaneous presence of H_2O_2 and Fe ions. Other authors have indicated similar ORR activity losses following H_2O_2 treatment procedures.^{68,73} Interestingly, Koslowski *et al.*¹⁹ obtained contradicting results for pyrolyzed N_4 -macrocycle complexes, where negligible performance loss was observed after treating $M-N_x/C$ catalyst materials in concentrated H_2O_2 for 10 minutes at room temperature. Moreover, increased H_2O_2 yield during the ORR is not always linked to catalyst stability when utilizing heat treated $M-N_x/C$ materials with different carbon supports⁶⁸ or different transition metal-ion centers¹⁷⁸ (ref. 82, unpublished). This indicates that instability issues are dependent on the type of precursor materials and synthesis method utilized and can arise due to factors other than H_2O_2 production, including catalyst surface properties (*i.e.* hydrophobic or hydrophilic, porosity and pore size distribution), the degree of graphitization, or the specific surface functional groups present. Highlighting the latter point, Popov's group has recently attributed ORR activity loss to protonation of the catalytically active pyridinic functional groups under acidic conditions.^{23,107,119} These conflicting reports highlight the necessity for future investigations regarding the instability of pyrolyzed $N-M_x/C$ catalysts.

In summary, pyrolyzed $M-N_x/C$ materials are promising non-precious metal catalysts for the ORR in fuel cell applications. It is well accepted that a high degree of graphitization is important for catalyst durability as these species comprise a very stable form of carbon. The instability issues that arise using even small amounts of NH_3 have also been demonstrated⁸⁹ as discussed previously and are reported to derive from a reduced degree of graphitization. Careful design and synthesis of these materials is very important in order to produce highly active, stable catalysts. In this section, the importance of a variety of factors has been illustrated. The type of precursor materials utilized, including the type of metal and its nominal content in the final catalyst structure are very important parameters influencing ORR activity. Furthermore, the carbon support and the resulting surface properties after pyrolysis significantly alter the ORR activity and stability of pyrolyzed $M-N_x/C$ catalysts, with the importance of a high surface nitrogen content and microporosity illustrated. Finally, the heat treatment conditions, specifically the pyrolysis temperature employed will result in performance variations, with the optimal conditions being material dependent and determined by systematic investigations. It should be noted that due to the structural changes during catalyst synthesis, the exact nature of the catalytically active ORR site and reaction mechanism are a subject of immense debate. Regardless, the best performing non-precious ORR catalyst materials reported to date are generally pyrolyzed $M-N_x/C$ complexes. A volumetric current density of $99 A cm^{-3}$ at an iR-corrected voltage of 0.8 V was reported for an iron based pyrolyzed $M-N_x/C$ catalyst, approaching the DOE 2010 target of $130 A cm^{-3}$.⁹⁴ In a fuel cell setup, maximum power densities approaching up to $450 mW cm^{-2}$ have been obtained for various binary FeCo-N/C pyrolyzed materials^{23,67,71,120} and up to $560 mW cm^{-2}$ for a multistep

FePc/phenolic resin based catalyst pyrolyzed in NH_3 .⁷⁹ These are the highest power densities obtained to date for non-precious metal ORR electrocatalyst materials. However, when comparing results of this nature, the effect of fuel cell operating conditions (temperature, gas feed rates and backpressure, anodic/cathodic catalyst loading, *etc.*) is significant and should always be taken into account. Despite promising ORR activity observed for some of these pyrolyzed $\text{M-N}_x/\text{C}$ catalysts, very little is understood regarding the stability of these materials.¹⁷⁹ This remains a considerable challenge that must be overcome if these materials are to be used as fuel cell cathode catalysts.

3.0. Conductive polymers

Conductive polymers such as polypyrrole (PPy), polyaniline (PANI), polythiophen (PTh), poly(3-methyl)thiophen (PMeT), as well as poly(3,4-ethylenedioxythiophene) (PEDOT) characteristically display mixed metal and polymer like properties and are considered ideal for many applications due to their low cost, high electronic conductivity and distinct redox properties.^{180–182} Recently, conductive polymers have been also investigated for application towards non-precious ORR electrocatalysis in three different ways: (i) utilizing conductive polymers as ORR electrocatalysts on their own,^{180,182–184} (ii) incorporating non-precious metal complexes into the conductive polymer matrix,^{180,182,184–193} and (iii) employing conductive polymers as a nitrogen/carbon precursor material for pyrolyzed $\text{M-N}_x/\text{C}$ catalysts.^{66,68,128,194–196}

3.1. Catalytic ORR activity of conductive polymer materials

In 2005, Khomenko *et al.*¹⁸³ investigated the ORR activity of PPy, PANI, PTh, PMeT as well as PEDOT. In order to provide further insight into the nature of ORR catalyzed by these conductive polymers, quantum-chemical calculations were also carried out. With the exception of PEDOT, each of these electronically conducting polymers displayed ORR activity at high overpotentials. It was argued that in order for these conducting polymers to interact with oxygen, they must be in their reduced states which normally occur at these low electrode potentials. In the case of PEDOT, in the potential range required for ORR, this polymer cannot be reduced, resulting in inertness towards the ORR. Based on calculations and consistent with experimental observations it was claimed that the presence of electron donor heteroatoms influence the catalytic activity, with nitrogen atoms (PPy and PANI) providing more activity enhancements than sulfur atoms (PTh and PMeT). The fundamental conclusions drawn from this particular study are strikingly similar to those for $\text{M-N}_x/\text{C}$ catalysts and can provide a basis for investigations focused on improving the ORR activity of conductive polymers and their composites.

Later studies reported the ORR activity of various conductive polymer materials supported on carbon. These polymers have either contained nitrogen or sulfur in their inherent structure. Martinez-Millan *et al.*^{180,184} investigated the ORR activity of carbon supported PPy, PANI, as well as PMeT. For these three carbon supported polymers, ORR occurred at very high overpotentials. The obtained ORR open circuit potentials were 0.62, 0.48 and 0.63 V vs. NHE, respectively. For ORR stability, PPy/C

was tested for 48 hours using chronoamperometry, with a steady decrease in activity observed, implying a slow degradation of the catalyst structure. Sulub *et al.*¹⁸² investigated the activity of carbon supported PTh, where an open circuit potential of 0.72 V vs. RHE was observed, along with a very low onset potential for ORR. Interestingly, the results from these studies^{180,182,184} differed from the results presented by Khomenko *et al.*,¹⁸³ where nitrogen based conductive polymers did not necessarily provide higher activity than sulfur based ones. This could indicate some sort of interaction with the carbon black support materials or different preparation techniques.

3.2. Incorporation of transition metals into conductive polymers for ORR activity improvement

Investigations on the incorporation of transition metal complexes into the conductive polymer matrices were proposed in order to further improve the activity of carbon supported conductive polymer composites. Typical examples are transition metal compounds incorporated into PANI or PPy polymers (M-N_x configuration), or incorporated into PTh or PMeT polymer composites (M-S_x configuration).^{180,182,184,185} This method was first proposed by Bashyam and Zelenay,¹⁸⁵ where they utilized a carbon supported PPy (PPy/C) to entrap Co ions. After successful incorporation, the synthesized catalyst showed steady performance increases during the initial 30 hours of fuel cell testing. During this time, the coupling between Co and adjacent nitrogen groups in the polymer was evidenced by the transition of metallic Co to ionic Co, after which promising fuel cell performance was achieved with a maximum power density of *ca.* 0.14 W cm^{-2} displayed in an $\text{H}_2\text{-O}_2$ fuel cell (2.8 atm absolute pressure of O_2). Therefore, the observed ORR activity was attributed to the strong Co-PPy interactions, possibly forming Co-N catalytically active sites with the proposed structure shown in Fig. 11. In addition, significant performance stability after 100 hours of operation was also observed using this Co-PPy

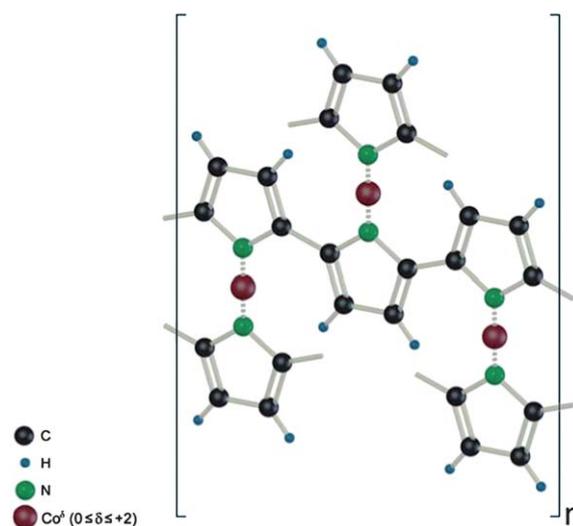


Fig. 11 Proposed structure of catalytically active Co-PPy composite formed after entrapment and reduction of the Co precursor in PPy. Reprinted by permission from Macmillan Publishers Ltd.¹⁸⁵

complex as the fuel cell cathode catalyst in an H₂-air fuel cell operating at 0.4 V.

Martinez Millan *et al.*^{180,184} also investigated the ORR activity of carbon supported PPy, PANI, as well as PMeT incorporated with Ni and Co. For all of these conductive polymers, the addition of Ni was found to improve the ORR performance (either in terms of open circuit potential or catalytic current density). In the case of PPy/C, improved stability after Ni incorporation was also observed.¹⁸⁴ When incorporated with Co, both PPy/C and PMeT/C displayed significantly improved catalytic activities towards the ORR, whereas PANI/C displayed a higher current density, but a slightly lower open circuit potential.¹⁸⁰ For PPy/C, it was demonstrated that the incorporation of Co could result in a significantly improved stability. The application of PTh as an ORR electrocatalyst was also investigated by the same group.¹⁸² Using a pure PTh material, the ORR activity observed is insignificant, but when it was supported on carbon black, an enhanced activity at high overpotentials could be observed. The addition of Ni or Co into this conductive polymer complex was also investigated, however no obvious improvement with respect to ORR activity was observed. Regarding the ORR stability, the incorporation of Co and Ni into PTh/C had less stability when compared to that of metal free PTh/C. Out of all the materials investigated by this group in a systematic fashion, including PPy/C, PANI/C, PTh/C, and PMeT/C (either pure or incorporated with Ni or Co), Co-incorporated PPy/C was found to display the most promising properties in terms of both ORR activity and stability.¹⁸⁰ This study reinforces the performance and stability of CoPPy/C catalysts demonstrated by Bashyam and Zelenay,¹⁸⁵ however does not investigate the fuel cell performance, nor the effects of electrochemical activation that were reported to have a significant impact on ORR activity of this class of catalyst. Attempts to improve the catalytic activity of CoPPy/C complexes have also been carried out through the synthesis of PPy with three different counter ions (Cl, dodecylbenzenesulfonic acid (DBS) or dodecylsulfonic acid (DS)) in order to optimize the nanostructure and properties of the synthesized polymer.¹⁸⁹ The authors observed that increasing the interchain distance of the PPy complex could allow more Co incorporation and thus a higher concentration of Co centered catalytically active sites could be obtained. For example, five times of amount of Co was incorporated into PPy synthesized using DBS, and the resulting catalyst displayed the highest ORR activity with an onset potential of 0.76 V vs. RHE. Reddy *et al.*¹⁹⁰ employed multiwalled carbon nanotubes (MWNT) as a support for CoPPy compounds. Improved catalytic ORR activity was observed compared with previously reported results in PEM, direct methanol as well as direct ethanol fuel cells. Furthermore, a high stability over 50 hours of operation in a PEM fuel cell setup was demonstrated for these materials. Clearly there are methods to tailor the activity and stability of Co-based conductive polymer complexes by chemical functionalization, utilizing different carbon supports, *etc.* and these approaches can be investigated in order to further understand and improve the ORR electrokinetics occurring on these complexes.

Simple inorganic transition metal compounds are not the only materials that have been utilized as ORR catalysts entrapped in conductive polymer matrices. A copper manganese oxide

complex was investigated, immobilized into PPy to form transition metal oxide-conductive polymer composites (Cu_{1.4}Mn_{1.6}O₄/PPy) for ORR catalysis.¹⁸⁷ The electrochemical testing showed that this Cu_{1.4}Mn_{1.6}O₄/PPy composite displayed ORR activity at low potentials. Furthermore, the effect of doping anions used during the electropolymerization of this complex was also investigated. Five different anions with the structure of KA ($A = \text{Cl}^-$, PF_6^- , ClO_4^- , NO_3^- or SO_4^{2-}) were investigated, and the use of Cl^- resulted in materials with the highest ORR activity. It was argued that these doping anions had an effect on the charge transfer properties of the catalyst complexes, resulting in the observed differences in the ORR activity. This highlights the importance of the electronic properties of conductive polymer complexes on the ORR activity and further efforts should be focused on their enhancement. Similar experiments were carried out with carbon cloth supported transition metal oxides encapsulated coated in PPy.¹⁹¹ It was found that copper manganese oxide particles could display some ORR activity with significant stability, with PPy considered a protective electron conducting shell rather than the catalytically active material.

3.3. Incorporation of transition metal macrocycles into conductive polymers for ORR activity improvement

The immobilization of various catalytically active non-precious metal macrocycle materials in a surrounding conductive polymer matrix has also been investigated. In 1995, Coutanceau *et al.*¹⁸⁸ investigated the immobilization of iron and cobalt tetrasulfonated phthalocyanines (CoTsPc or FeTsPc) into PANI and PPy. They observed an increased ORR activity for PPy entrapped Pc macrocycles, however in the case of PANI, very little differences were observed. Over ten years later, various studies have investigated the encapsulation of CoTPP macrocycles^{186,192} or CoTPPS in PPy on various supports, and some ORR activities were observed. Although these materials all showed catalytic activity towards ORR at high overpotentials, the activities were fairly low as commonly observed on non-precious macrocycle catalysts in the absence of heat treatment. With respect to ORR performance and stability, these materials offer little competition to the development of pyrolyzed M-N_x/C catalysts unless drastic performance increments are realized.

3.4. Conductive polymers used as nitrogen and carbon precursors in synthesizing pyrolyzed M-N_x/C catalysts

Conductive polymers have also been utilized as precursors in synthesizing highly active M-N_x/C catalysts to provide both carbon and nitrogen sources during high temperature pyrolysis. Despite inherent ORR activity observed on transition metal complexes immobilized in conductive polymers, their catalytic ORR activities were still inferior to that of heat treated compounds. Lee *et al.*¹⁹⁴ investigated the effect of heat treatment on Co-PPy/C catalysts, along with the influence of heat treatment temperature. It is obvious that heat treatment on their Co-PPY/C sample can effectively increase the ORR activity, as shown in Fig. 12. The authors attributed the enhanced ORR activity to the formation of catalytically active pyrolic and quaternary nitrogen functionalities generated during the heat treatment. A shift in the ORR mechanism was also observed

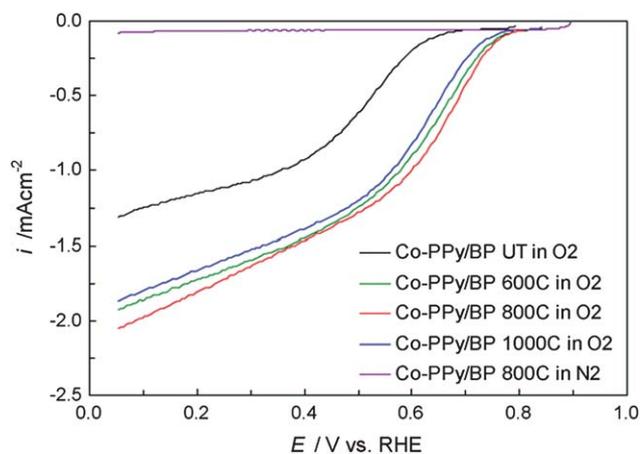


Fig. 12 Effect of heat treatment and heat treatment temperature on the ORR activity of Co-PPy/C catalyst materials. UT indicates untreated catalyst material. Note: In figure legend, O₂ refers to half-cell testing conditions; all pyrolysis was done in N₂. Reprinted from ref. 194, with permission from Elsevier.

from a 2-electron dominant pathway to a more efficient 4-electron dominant pathway as a result of heat treatment.

Wu *et al.*⁶⁶ carried out investigations on pyrolyzed PANI/C complexes, doped with Fe and/or Co. Results from this study indicated that the ORR overpotential of these complexes could be reduced significantly by the incorporation of these metals, showing an onset potential of 0.9 V vs. RHE for FeCo-PANI/C. The product selectivity was also increased dramatically, with 99.6% H₂O produced at an electrode potential of 0.4 V vs. RHE. This is a significant improvement compared to the 84% H₂O produced by pyrolyzed PANI/C. Furthermore, a high stability of this catalyst was also observed with less than a 2% activity loss during 450 hours of fuel cell lifetime testing. A later study⁶⁸ indicated superior stability of these FeCo-PANI/C ORR catalysts compared with similar PPy based materials. This enhanced stability was attributed to the aromatic nature of PANI, which has stronger interactions with the metal-ion centers. Moreover, ordered graphitic like structures could be readily formed which are important for catalyst stability. Upon further optimization, these FeCo-PANI/C materials have recently been reported to demonstrate exemplary fuel cell performance with a maximum cell power density of 550 mW cm⁻² and 700 hours of operational stability at a cell voltage of 0.4 V.¹²⁸ Yuasa *et al.*¹⁹⁶ also pyrolyzed a CoPPy/C sample and achieved an enhanced catalytic ORR activity. At a pyrolysis temperature of 700 °C, utilizing PPy as the coordinating ligand, Co ions could be entrapped to form Co-N_x active centers without metallic Co formation. In a recent study,¹⁹⁵ *p*-toluenesulfonic acid (TsOH) was incorporated into pyrolyzed CoPPy/C materials and found to result in improved ORR activity of these electrocatalyst materials, displaying a current density of 0.21 A cm⁻² at a fuel cell voltage of 0.4 V, almost double that of pure unmodified pyrolyzed CoPPy/C. Moreover, a higher product selectivity for H₂O production was also obtained. The authors attributed this improvement in ORR activity to the higher amount of nitrogen incorporation into the catalyst materials, which was facilitated by the presence of TsOH.

In summary, electron conducting polymers provide interesting metal/polymer like properties that can be beneficial in the

synthesis of non-precious metal ORR catalysts. These polymers can be used for both pyrolyzed and non-pyrolyzed catalyst materials. When used as precursors for pyrolysis, these materials display very promising ORR activity and stability, with results and electrocatalyst properties similar to the pyrolyzed M-N_x/C catalyst discussed in Section 2.2. When utilized as non-pyrolyzed catalyst materials, limited catalytic ORR activity and stability are still not sufficient for fuel cell cathode applications.

4.0. Non-precious transition metal chalcogenides for ORR catalysis

Transition metal chalcogenides are one group of ORR catalyst materials which have been studied extensively in the last several decades. There are many reports about the high ORR catalytic activity of Mo-Ru-Se chalcogenide complexes, with performances approaching that of platinum.¹⁹⁷⁻²⁰⁴ However, Ru is considered a precious metal and its high cost and scarce availability hinder its potential application as cathode catalysts in PEM fuel cells. Thus, efforts have been directed at investigating non-precious transition metal chalcogenides, with some progress being made in recent years.

Behret *et al.*²⁰⁵ initially demonstrated the potential application of non-precious transition metal chalcogenide materials as ORR electrocatalysts. These authors prepared various M^(a)₂M^(b)_{3-z}X₄ thiospinels, where M^(a) = Mn, Fe, Co, Ni, Cu or Zn, M^(b) = Ti, V, Cr, Fe, Co or Ni and X = S, Se or Te. A systematic study on ORR activity was carried out using these various thiospinel complexes in 2 M H₂SO₄ vs. a hydrogen electrode in the same solution. Co₃S₄ complexes synthesized by an aqueous precipitation reaction at moderate temperatures (~400 to 450 °C) displayed the most promising ORR activity and performance with an open circuit voltage of ~800 mV vs. RHE, and a current density of 20 mA cm⁻² at 600 mV vs. RHE. However, this activity was found to degrade rapidly when compared with other less active compounds synthesized at higher temperatures. Results from this investigation indicated that the ORR activity of the thiospinel compounds was directly related to the type of metal utilized, with an order of Co > Ni > Fe. Moreover, performance decrease was also observed when sulfur was partially replaced with O, Se or Te. This study provides insight into the activity of non-precious transition metal chalcogenides, initiating further investigations into these inexpensive materials as ORR catalysts several decades later.

This inspired theoretical investigations by Sidik and Anderson²⁰⁶ in order to explain the exemplary activity of Co sulfide species, where three different Co₉S₈ surface structures were studied. It was determined that the partially OH covered surface of Co₉S₈ (202) should be active for ORR, with an onset potential of 0.74 V vs. RHE. No investigations were carried out with respect to ORR stability, thus experimental results would be needed in order to further characterize and optimize surface structures and properties. These interesting findings led to another similar theoretical investigation carried out on Co₉Se₈ phase structure, in an attempt to explain the inferior ORR activity of this complex compared with sulfur-based chalcogenides.²⁰⁷ Results from this quantum computational approach indicated that Co₉Se₈ should in fact display a higher overpotential compared to Co₉S₈ (>0.22 V), which was consistent

with the experimental observations reported by Behret *et al.*²⁰⁵ decades earlier. To supplement the theoretical investigation, the authors synthesized CoSe electrodes with unspecified stoichiometries by refluxing dicobalt octacarbonyl ($\text{Co}_2(\text{CO})_8$) and selenium powder in a xylene solvent.²⁰⁷ The synthesized compound displayed negligible ORR activity in 0.5 M H_2SO_4 . However, after subjecting the CoSe complex to heat treatment at 900 °C in an NH_3 environment, considerable ORR activity was observed, with an onset potential of 0.5 V *vs.* RHE. While NH_3 pyrolysis of transition metals has been demonstrated to result in the formation of active site structures (Section 2.2.4), in this study there is an absence of a carbon support to anchor these functional groups and XRD analysis indicated improved crystallization as opposed to ligand coordinated ion formation. Thus, the authors attributed this increase in ORR activity to the enhanced crystallization of nonstoichiometric CoSe as a result of heat treatment. The observed ORR activity however was still significantly lower than that of Pt-based electrodes.

At around the same time, Susac *et al.*²⁰⁸ synthesized three thin films of CoSe with varying Co/Se ratios, using magnetic sputtering of different targets. For comparison, the authors also developed an XC72R carbon supported CoSe powder (CoSe/C). The ORR activity of all materials was investigated in 0.1 M H_2SO_4 . Without any optimization to the surface structure or properties of the complexes, CoSe/C displayed an open circuit potential of 0.78 V *vs.* RHE, slightly higher than the most active CoSe thin film (0.74 V *vs.* RHE). Cyclic voltammetry (CV) was carried out on these materials, and the results indicated that after initial CV sweeps, some surface Co was leached out, leaving a chalcogen rich active surface. The authors proposed that the ORR active sites consisted of a Co deficient form of CoSe surrounded by chalcogen atoms. It was also noted that during electrochemical testing, some Se–S exchange occurred between the surface of the thin films and the H_2SO_4 electrolyte, however the exact effects of this occurrence are still unknown. Due to the fundamental differences between the CoSe/C and Pt/C materials, specifically the unknown CoSe/C surface area, the authors argued that appropriate comparison with platinum based catalysts is obscured. The CoSe/C particles were also very large and non-uniform (*ca.* 10–100 nm) with numerous agglomerates observed, thus development of carbon supported CoSe nanoparticles with uniform size and proper dispersion could potentially increase the applicability of this class of catalyst.

A year later, Susac *et al.*²⁰⁹ expanded on their investigations, preparing FeS_2 and $(\text{Fe/Co})\text{S}_2$ thin films by a similar magnetic sputtering procedure. The synthesized FeS_2 thin films were found to display higher ORR activity compared to naturally occurring mineral FeS_2 (pyrite), which had previously been shown to possess ORR activity in acidic conditions.²¹⁰ The variation in ORR activity of these two materials was attributed to differing surface sulfur contents, however the exact mechanism of the activity enhancement is still unknown. In addition, the ORR activity of the synthesized thin films was compared with the ORR activity of a thin film of Pt, allowing adequate comparison based on similar reaction surface areas. Unfortunately, this FeS_2 thin film displayed a much lower open circuit potential of 0.78 V *vs.* RHE than that of the Pt electrode which had an open circuit potential of 1.02 V *vs.* RHE. Moreover, in terms of catalytic current density at 0.6 V *vs.* RHE, the Pt

electrode had a current density three orders of magnitude larger than that of the FeS_2 electrode. In addition, the cobalt containing $(\text{Fe/Co})\text{S}_2$ thin film displayed a slightly higher open circuit potential (0.8 V *vs.* RHE) and enhanced catalytic current densities than that of FeS_2 thin film electrode. Despite performance still significantly lower than a Pt thin film electrode, this work indicated the possibility of combining transition metal species for improved ORR activity and performance. Whether the observed ORR enhancement arises due to a complementary reaction mechanism occurring between Fe and Co or simply due to the addition of Co sulfide species with a higher activity is unknown. Elucidating this relationship along with investigating other binary transition metal catalysts could provide valuable information and progress towards the development of transition metal chalcogenide catalysts.

Feng *et al.*²¹¹ used a Vulcan XC-72 carbon as a dispersing agent and support material in preparing Co_3S_4 and CoSe_2 carbon supported chalcogenides ($\text{Co}_3\text{S}_4/\text{C}$ and CoSe_2/C , respectively). $\text{Co}_3\text{S}_4/\text{C}$ (20 wt%) complexes were synthesized by three different reflux methods using cobalt carbonyl and sulfur dispersed in *p*-xylene, followed by a heat annealment at 250 °C in pure nitrogen. The two samples synthesized by *in situ* surfactant free methods displayed promising ORR activity with onset potentials of ~0.66 to 0.68 V *vs.* RHE in 0.5 M H_2SO_4 . This activity was significantly higher than that of the third $\text{Co}_3\text{S}_4/\text{C}$ material synthesized by a surfactant based method (onset potential of ~0.3 V *vs.* RHE). This poor activity was attributed to the presence of surfactants blocking the ORR active sites. These materials were shown to have electrochemical stability below 0.8 V *vs.* RHE,²¹² however a later report by these authors suggested that these compounds were unstable under long term exposure to air, where phase conversion from Co_3S_4 to CoSO_4 was observed by XRD analysis.⁶ In addition, the CoSe_2/C compounds developed in this study were also synthesized by a similar organic solvent based reflux procedure.²¹¹ After slight modification of these materials, an onset potential of ~0.70 V *vs.* RHE and an open circuit potential of 0.81 V *vs.* RHE were observed through electrochemical testing.²¹³ These methods led to more uniform sized particles dispersed on the carbon support and minimal agglomerates observed compared with the work of Susac *et al.*,²⁰⁸ however these particles were still relatively large (>50 nm). Development of synthesis procedures to load carbon support materials with smaller transition metal chalcogenide nanoparticles with controlled surface morphologies and properties could provide valuable ORR activity enhancements and should be a focus of future investigations.

Lee *et al.*²¹⁴ took a novel approach, synthesizing W–Co–Se chalcogenide materials for use as ORR catalysts. W–Co–Se was synthesized by a chemical precipitation method, utilizing xylene as the solvent under reflux conditions. In this synthesis, $\text{W}(\text{CO})_6$, $\text{Co}_4(\text{CO})_{12}$ and elemental Se were used as the precursor materials. Through ORR testing in 0.5M H_2SO_4 , W–Co–Se displayed an onset potential of 0.755 V *vs.* RHE. This chalcogenide was also found to be electrochemically stable between 0.05 and 0.8 V *vs.* RHE. The electrochemical stability along with significant ORR activity were not shown when using individual W or Co, indicating that the presence of Se might serve to modify the electronic properties of the materials, enhancing the stability and rendering this W–Co–Se catalysts with an ORR activity. Unfortunately,

the ORR activity and stability of this W–Co–Se catalyst were still significantly lower than those of commercially available Pt/C. Despite this observation, investigating binary transition metal combinations offers an interesting direction for non-precious chalcogenide electrocatalysts. With improved activity of Fe/Co binary combinations previously demonstrated,²⁰⁹ other possible binary and even ternary combinations can be investigated systematically including differing formulations of transition metal and chalcogen species.

In summary, although non-precious transition metal chalcogenides have displayed some promise as alternative catalyst materials for PEM fuel cell applications, the observed ORR activity and stability are still significantly lower than those of commercially available Pt/C catalyst, and furthermore, lower than those of precious metal chalcogenide compounds. Therefore, developing novel non-precious chalcogenides (including new binary and ternary combinations) along with the optimization of bulk and surface properties should be on the forefront of research in this area. The use of a carbon support could also serve to improve the dispersion and reactive surface area of transition metal chalcogenide particles and is an attractive approach. Future work is still required directed at reducing particle sizes while enhancing their surface properties, particle morphologies and dispersion on the carbon support.

5.0. Metal oxides, carbides, nitrides, oxynitrides and carbonitrides

Non-precious metal carbides, oxides, oxynitrides and carbonitrides have been considered promising inexpensive electrocatalyst alternatives for fuel cell applications in recent years, as reviewed by Ishihara *et al.*⁸ In this field of research, significant advancements have been made in developing this class of transition metal based catalysts with steady performance improvements over recent years, as illustrated in Fig. 13.

5.1. Metal oxides

Non-precious transition metal oxides possess reasonable ORR activity and stability in alkaline media. However, despite suitable stability in acidic and oxidizing conditions, their limited ORR

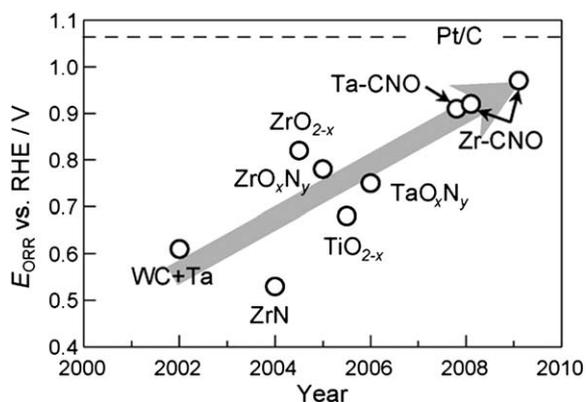


Fig. 13 Summary of the progress over recent years with respect to transition metal oxide, carbide and nitride based materials as ORR electrocatalysts. Reprinted from ref. 8, with permission from Elsevier.

activity still remains a challenge.^{215,216} The low ORR activity is attributed to the inherently large band gap (low conductivity) of these materials and arduous adsorption of oxygen on the surface suggesting they may not be suitable as cathode catalysts for acidic fuel cells such as PEM fuel cells. Regardless, numerous studies have been reported in recent years investigating the potential application of metal oxide composites as ORR electrocatalysts. For example, Liu *et al.*²¹⁷ reported that zirconium oxide (ZrO_x) thin film catalysts were shown to possess ORR activity at an electrode potential below 0.9 V vs. RHE. A later study by this group²¹⁸ explored other transition metal compounds and found that the ORR activity of these compounds had an order of $ZrO_{2-x} > Co_3O_{4-x} > TiO_{2-x} = SnO_{2-x} > NbO_{5-x}$. In their most recent study,²¹⁹ ZrO_{2-x} thin films were synthesized by radio frequency sputtering, and they found that the ORR activity of these samples could be improved if a higher radio frequency power was used during synthesis. These ORR activity increments were linked to a higher degree of oxygen defected state on the catalyst surface and improved electronic conductivity of these materials.

Tungsten oxide based materials (WO_x and M_x-WO_3 where $M = Na, K, Ba, Pb, Ti, U$ or Cd) have also been employed both as anode HOR and cathode ORR electrocatalysts.^{220–224} However, it was concluded that the electrochemical activity of these materials was too low for application as fuel cell catalysts.

Tantalum oxides, even with a high ORR onset potential, seem to be not promising as potential fuel cell catalysts due to their extremely low bulk electronic conductivity. In order to improve their electronic conductivity, Kim *et al.*²²⁵ deposited Ta_2O_5 nanoparticles onto a conducting carbon support. These composite materials were found to display an onset potential very similar to that of Pt. Unfortunately, the observed mass specific current densities were still insufficient, most likely due to poor electron transport to reaction sites. Unless this can be overcome and current densities improved significantly application of these materials as ORR catalysts may not be possible.

In summary, due to the low inherent activity and insulator properties of metal oxides, their performance is still not sufficient enough yet for practical usage as acidic fuel cell cathode catalysts. For developing more active and stable ORR catalysts, more research is necessary in order to provide facile O_2 adsorption and enhanced electronic conductivity, coupled with improved stability in acidic media. It appears as if simple metal oxides without further modification to overcome these challenges will not be suitable ORR electrocatalysts. Some of the approaches taken to overcome these challenges will be discussed in the following sections.

5.2. Metal carbides

Tungsten carbide (WC) was reported to possess a similar electronic structure to that of platinum,^{226,227} which inspired several investigations exploring this material and other metal carbide compounds as possible catalyst materials for PEM fuel cell applications. A majority of these studies were focused on the application of WC-based materials as HOR anode catalysts.^{228–233} In these studies, high HOR activity of WC materials was observed in a PEM fuel cell setup,²³³ displaying a current density of $0.9 A cm^{-2}$ at a cell voltage of $\sim 0.14 V$, temperature of

80 °C and backpressure of 3 atm. This performance was still inferior to that of commercial Pt/C.

Due to the limited stability of carbide materials in acidic and highly oxidizing environments such as those encountered during operation of a PEM fuel cell cathode, the potential application of pure WC and other carbide materials as ORR electrocatalysts seems to be unfeasible if the composition and structure of such materials are not modified. To address these composition and structure modifications, two different efforts have investigated the effect of incorporating Ta into WC materials.^{234,235} Enhanced electrocatalytic activity and stability towards the ORR were observed in the presence of Ta,²³⁵ attributed to the formation of a W–Ta alloy phase.

Ni–Ta–C compounds formed by sputtering techniques were also tested as ORR electrocatalyst materials.^{236,237} These synthesized materials were found to have significant stability which was attributed to the formation of a thin TaO protective film on the catalyst surface.²³⁶ Using this material, adequate ORR activity was also observed, indicating that this film did not hinder electron transport. The effect of heat treatment on N–Ta–C was also reported to provide an enhancement on the observed ORR activity, however the activity was still extremely low (ORR onset potential of 0.45 V vs. RHE).²³⁷

5.3. Metal nitrides

Transition metal nitrides have relatively good stability in acidic conditions and under high electrochemical potentials; therefore they could be considered as potential ORR electrocatalyst materials.⁸ For example, carbon supported tungsten nitride (W₂N/C) was investigated using a single PEM fuel cell setup, where significant stability after 100 hours of operation was observed.²³⁸ Although the ORR activity of this material was relatively low (ORR onset potential of 0.6 V vs. RHE), its high stability renders it as a promising non-precious electrocatalyst.

Molybdenum nitride materials were also investigated as ORR electrocatalysts.²³⁹ When supported on carbon black, these MoN/C catalyst materials were found to display an open circuit potential of over 0.7 V in a single fuel cell setup. Notably, significant stability of this material was observed during 60 hours of operation. Xia *et al.*²⁴⁰ further demonstrated the catalytic activity of MoN/C catalysts, synthesized using an ammonia heat treatment procedure of MoTPP/C. The effective reduction of oxygen by a 4-electron pathway to produce water was attributed to the hexagonal MoN structure formed during the synthesis. No mention was made however to the similar preparation procedures to pyrolyzed M–N_x/C catalysts. Namely, a heat treatment of a transition metal macrocycle was utilized using NH₃ treatment in the presence of a carbon support. The possibility of supplementary M–N_x/C or metal free N–C active site structures could potentially contribute to the observed ORR activity and could be probed by more sensitive characterization techniques.

Carbon supported niobium nitride complexes formed by a polymerized complex method and subsequent nitration pyrolysis under flowing NH₃ have also been investigated.^{241,242} Once again heat treatment of carbon supported transition metal species in NH₃ was utilized where ORR activity was observed, however the authors attributed it to the formation of high degree of crystallinity and surface concentration of Nb⁵⁺ ions.

Moreover, it was found that the formation of surface Nb⁵⁺ could be facilitated by the incorporation of Ba. This could serve to hinder the formation of competing Nb⁴⁺ ions, resulting in an ORR onset potential of 0.77 V vs. RHE.²⁴¹

Carbon supported Co–W (CoW/C) treated with NH₃ at high temperatures was also found to possess some catalytic activity towards the ORR.²⁴³ It was found that the catalytic ORR activity was strongly dependent on the synthesis conditions. At the optimized synthesis conditions, highly active CoW/C catalyst was obtained, which was composed of CoW nitride and CoW oxynitride as determined by XRD analysis. Through half cell testing, an onset potential of 0.749 V vs. RHE and a current density of –0.158 mA cm^{–2} at an electrode potential of 0.6 V vs. RHE were obtained for the most active catalyst treated at Co–W/C catalyst treated in NH₃ at 550 °C. The ORR activity was attributed to the metal nitrides and pyrrolic nitrogen species present in the carbon support.

5.4. Metal oxynitrides

Metal oxynitrides are another kind of materials which show some ORR activity. These kinds of materials are commonly formed by substitutionally doping nitrogen into metal oxides. It was reported that this doping could effectively reduce the high inherent band gap of metal oxides, leading to enhanced electron conducting properties important to electrocatalysis.²⁴⁴ Ta oxynitrides were investigated as ORR electrocatalysts and found to have a promising onset potential of 0.8 V vs. RHE.²¹⁶ In addition, the incorporation of carbon into this kind of material could also further enhance their ORR activity.²⁴⁵

Another example is carbon supported zirconium oxynitride [ZrO_xN_y/C] catalysts formed by pyrolyzing ZrO₂/C at a high temperature in the presence of ammonia.²⁴⁶ This catalyst material gave an ORR onset potential of 0.7 V vs. RHE. In a later study,²⁴⁷ ZrO_xN_y thin films synthesized using a reactive sputtering method displayed an ORR onset potential of 0.8 V vs. RHE. In terms of ORR activity, the most favorable catalyst structure present in these types of materials was found to be crystalline Zr₂ON₂ phase atomic structures. In these studies, utilizing ammonia did not result in improved ORR activity compared with the reactive sputtering method in an N₂/O₂ environment, indicating that the same active site formation mechanisms and ORR performance enhancements of NH₃ derived M–N_x/C catalysts are not as readily applicable to this class of materials.

5.5. Metal carbonitrides

Transition metal carbonitrides have also been explored as ORR catalyst materials in the literature. For example, a Co_xC_{1–x–y}N_y thin film was synthesized by Yang *et al.*,¹⁷⁰ using a method of magnetron sputtering coupled with heat treatment. ORR measurements showed that this thin film had some catalytic ORR activity with mainly a 2-electron pathway producing H₂O₂. This approach was further expanded to other transition metals, where one study indicated that Cr, Co and Ni carbonitrides could display ORR activity, whereas V and Mn carbonitrides' activity was negligible.²⁴⁸ In addition, Fe carbonitride materials synthesized by a similar sputtering/heat treatment procedure

were also explored, and some ORR activity was found.²⁴⁹ In the case of Fe and Co carbonitrides synthesized by this method, nitrogen content in the catalysts was found to have an effect on the corresponding ORR activity.^{170,249} ORR activity was found to improve steadily with increasing nitrogen content up to approximately 3 at.% (material dependent), after which, increments in the nitrogen content had a minimal effect as illustrated in Fig. 14. This approach and ensuing results are similar to those obtained for pyrolyzed M-N_x/C catalysts discussed in Section 2.2. The activity saturation with nitrogen content observed indicates some other limiting factors present in this type of catalyst which could potentially be low surface areas due to their thin film morphologies obtained using magnetron sputtering procedures.

It was found that the partial oxidation of various transition metal carbonitride materials, including Ta, Zr and Nb carbonitride composites, had a positive effect on their catalytic ORR activity.^{250–255} This partial oxidation could give high ORR activity with onset potentials of 0.97, 0.9 and 0.89 V vs. RHE for partially oxidized ZrCN,²⁵³ TaCN²⁵⁵ and NbCN,²⁵¹ respectively. Highly active ZrCN was obtained by pyrolysing zirconium oxide and carbon powder at 1800 °C. This material was then partially oxidized at temperatures between 1000 and 1400 °C, with maximum ORR activity obtained at 1200 °C. Moreover, the stability of this highly active partially oxidized ZrCN was also demonstrated by a 100 hour stability test at an electrode potential of 0.6 V vs. RHE.²⁵² This indicates that these materials can be considered one of the most promising non-precious metal catalysts for ORR. Future work is necessary to further optimize and improve both their ORR activity and stability which could render them very competitive candidates as electrocatalyst materials.

6.0. Enzymatic compounds

In recent years, enzyme modified electrodes have been explored in an effort to develop alternative non-precious fuel cell cathode materials. These studies were stimulated by the extremely high onset potential and ORR activity observed on several naturally occurring oxygen reducing oxidase enzymes.^{256–258} Laccase in

particular has been studied as an ORR electrocatalyst due to its high activity and astounding selectivity for the 4-electron ORR to produce water. Early investigations involved adsorbing laccase directly onto carbon based electrodes, then testing its ORR activity.^{256,259–261} In this way, a direct electron transfer between the electrode surface and enzyme molecules could occur. However, these laccase molecules were only weakly adsorbed on the electrode,²⁵⁹ and could only provide a monolayer of surface coverage, leading to both insufficient ORR activity and stability. Further improvements involved the immobilization of the enzyme in a redox active polymer hydrogel,^{262–273} such as osmium based complexes, which could be “wired” to the surface of the cathode electrode. These redox polymers allowed the effective transport of electrons, reactants and products to multiple layers of the ORR active enzyme, resulting in significantly higher active surface areas and ORR activity over the traditional monolayer approach.^{266,267,271,272} It was found that the ORR activity was strongly dependent on the redox potential of the immobilization polymer hydrogel.²⁶⁷

There are however issues when dealing with enzymatic based electrodes. Specifically, the significant ORR dependency on system temperature and pH remains a challenge.^{260,264–266} Normally, enzyme based catalysts could only give optimal activity at mildly acidic conditions.^{256,263–265,269} These materials would thus require the presence of a buffer compound, a feat that may not be feasible for PEM fuel cells. Moreover, considering their issues with stability, utilizing these types of materials as PEM fuel cell cathode catalysts may not be realistic.

Interestingly, high ORR activity and product selectivity of naturally occurring tri-nuclear copper based enzyme complexes have also been found. This inspired the synthesis of copper based materials with a similar atomic configuration in an attempt to mimic the natural rates of ORR on these complexes.^{257,258,274} Significant progress in this area has yet to be realized, however, in 2008, a copper coordinated complex supported on carbon black was reported to display high ORR activity and reduced pH dependency.²⁵⁷ Thus, this field of research offers an interesting non-traditional approach to developing ORR catalysts, with further modifications of these copper based complexes necessary in order to obtain adequate performance and stability under fuel cell operating conditions.

7.0. Conclusions

For a sustainable PEM fuel cell commercialization, developing active, inexpensive non-precious metal ORR catalyst materials to replace currently used, expensive Pt-based catalysts is a necessary and essential requirement. This review paper outlines the progress in this field of research over the past 40 years. Several important kinds of carbon-supported non-precious metal electrocatalysts for ORR are reviewed, including non-pyrolyzed and pyrolyzed transition metal nitrogen-containing complexes, conductive polymer-based catalysts, transition metal chalcogenides, metal oxides/carbides/nitrides/oxynitrides/carbonitrides, as well as enzymatic compounds. Among these candidates, pyrolyzed M-N_x/C materials are considered the most promising ORR catalysts because they have demonstrated some ORR activity and stability close to those of commercially available Pt/C catalysts. Although other types of non-precious metal catalysts

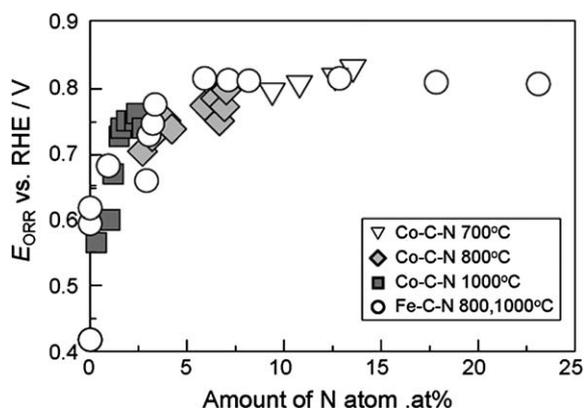


Fig. 14 Effect of nitrogen content on the ORR onset potential of Fe- and Co-based carbonitride complexes. At low nitrogen contents, an increase in onset potential with increasing nitrogen is observed, followed by a plateau in performance enhancement. Reprinted from ref. 8, with permission from Elsevier. Based on data summarized from ref. 170 and 249.

have also shown promise with respect to ORR activity and/or stability in acidic media, for PEM fuel cell applications, the observed performances are still too far away from the requirements for application. With respect to pyrolyzed M–N_x/C ORR catalysts, various challenges and opportunities for breakthroughs co-exist. In the following sections, we will focus on this type of M–N_x/C catalyst, and discuss their challenges and possible research directions.

7.1. Challenges

Obviously, to date great progress has been achieved in the area of non-precious metal catalysts for ORR. The possible application of some pyrolyzed M–N_x/C catalysts has already been demonstrated using PEM fuel cell operation conditions. For example, the most active non-precious metal catalysts is a microporous iron based catalyst developed by Lefevre *et al.*,⁹⁴ which have displayed volumetric ORR activity (99 A cm⁻³, iR corrected, cell voltage of 0.8 V) approaching the DOE 2010 target of 130 A cm⁻³. Furthermore, several authors have reported fuel cell power densities of up to 450 mW cm⁻² for pyrolyzed binary FeCo–N/C complexes^{23,67,71,120} and up to 550 and 560 mW cm⁻² for pyrolyzed FeCo–PANI/C¹²⁸ and FePc/phenolic resin materials synthesized by multi-step pyrolysis methods,⁷⁹ respectively, as ORR cathodic electrode catalysts. However, there are still many challenges with respect to both ORR activity and stability that must be overcome in this field of research. Regarding the ORR activity, the actual volumetric activity of even the most active non-precious metal catalysts still needs to be improved in order to reach the DOE 2010 target of 130 A cm⁻³, and furthermore the 2015 target of 300 A cm⁻³.¹⁰ Regarding the ORR stability, stability tests are generally run at low current density or low power level, which are not real conditions for fuel cell operation, particularly for automobile applications. Therefore, improving the ORR activity of non-precious metal catalyst is still the short term research and development priority. Only if the ORR activity successfully approaches the provided targets, research and development into improving the stability of these materials will move to the forefront of investigations.

7.2. Research directions

As discussed above, state-of-the-art non-precious metal catalysts have shown promise for meeting the DOE 2010 activity target. The short-term task is developing methods to improve the catalyst structures and optimize the catalyst layer to further increase the activity to the 2010 target level of 130 A cm⁻³ and surpass it to meet the 2015 target level of 300 A cm⁻³ under the DOE reference conditions. In the long term, fundamentally understanding active site structures is the key to further improving activity and eventually addressing the stability issue. Once we can controllably design and synthesize a non-precious metal catalyst with a high active site density and utilization, the application of these catalysts in PEM fuel cells will become a reality.

From a fundamental point of view, improving activity and stability relies on further understanding of the active site structures. At present, active site structures are still a subject of controversy, which hinders efforts to control active site formation. The difficulty in determining active site structures stems from the complexity and variety of the catalysts' surfaces. Based on previously reported results, we can divide active sites into two main types: (1) transition metal containing active sites of the form MN_xC_y. In the case of Fe, this could correlate to either (i) pyrolic nitrogen-based active sites, which are favorable to a 2-electron or a 2-step, 4-electron (slow) ORR, with a typical example being the so-called low-temperature Fe–N₄ structure in pyrolyzed metal porphyrins and Pc, or (ii) pyridinic nitrogen-based active sites, which are favorable to a direct 4-electron (fast) ORR. A typical example is the micropore hosted Fe–N₂₊₂ configuration. Most of the heat-treated catalysts benefit from the formation of this active site, with respect to ORR activity. (2) Metal free pyridinic or graphitic nitrogen-based active sites. In this case, the transition metal is not considered an integral part of the active site structure. The role of the transition metal has been attributed to catalyzing the formation of these ORR active functional groups on the surface of carbon based materials. Pyridinic and graphitic nitrogen active sites can be favourable to a 4-electron (slow or fast) ORR, depending on the nitrogen distribution in the carbon matrix and the overall material

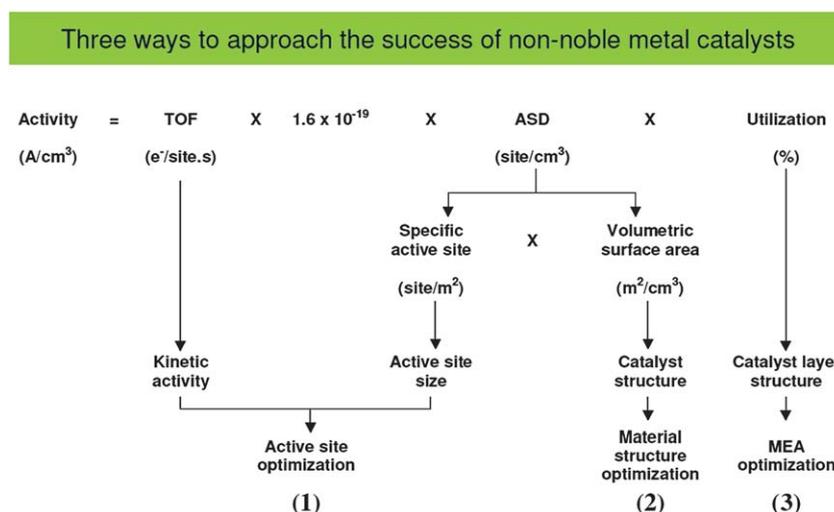


Fig. 15 Analysis of how to improve the ORR activity of non-precious metal catalysts.²⁷⁵

properties. The ORR activity of nitrogen-doped graphite or carbon nanotubes is attributed to these types of active sites.

It is interesting that most of the reported catalyst activity for $M-N_x/C$ catalysts can be attributed to these active site structures. The difficulty lies in determining the actual configurations of the active sites as well as how to distinguish the sites for each individual catalyst, as they always exist simultaneously in pyrolyzed non-precious metal catalysts. Through the extensive efforts to enhance the ORR activity of non-noble metal catalysts, most work previously has focused on seeking intrinsic activity enhancement by optimizing synthesis conditions in order to tailor the resulting structure and properties of catalyst materials. Uncertainty over the exact nature of the active sites, along with a significant amount of ambiguity surrounding the active site mechanism, limits such progress. Elucidating the exact nature of the active site structures will pave the way to controllable design and the synthesis of a non-precious metal catalyst with higher ORR activity and improved stability. In the future, more tactful approaches need to be considered to effectively increase the performance of non-precious metal catalysts.

As shown in Fig. 15, based on analysis of the volumetric activity equation, three primary factors determine the performance of non-precious metal catalysts. Basically, the kinetic volumetric activity and performance of a non-precious metal catalyst are determined by what the turnover frequency of the active site is, how many active sites are in a unit volume (active site density), and how many sites are active during the operation (utilization). Turnover frequency is the intrinsic activity toward the ORR, which may depend on the different active site structures. Active site density can be divided into two parameters: specific active site density, meaning how many active sites are in a unit of surface area; and volumetric surface area, meaning how much surface area is in a unit of volume. Obviously, the specific active site density depends on the active site size, while the volumetric surface area is related to the catalyst morphology or structure. It is still not possible to accurately determine the specific active site density however, due to uncertainty over the nature of the active sites in these kinds of catalysts. Increasing the volumetric surface area is therefore the most viable approach to improve active site densities. Another important factor is the utilization of the active sites, which is closely related to the nature of the catalyst layer or the membrane electrode assembly (MEA). It is well known that catalyst utilization is as low as 30–50% in a 10 μm catalyst layer of a Pt-based MEA. One can imagine how low the utilization will be in a 100 μm catalyst layer of non-precious metal catalyst-based MEA. Thus, alongside efforts to improve the intrinsic activity of non-precious metal ORR catalysts, working on improving the catalyst structure to achieve higher volumetric surface area, and optimizing the catalyst layer for higher active site utilization offer much more opportunity for performance improvements. These should be two important research directions for future research and development of non-precious metal catalysts.

In summary, the future research directions on non-precious metal ORR catalysts for PEM fuel cell applications would be proposed as follows:

1. To improve the ORR activity (>10 times), by overcoming the ongoing challenge of low active site densities of non-precious metal catalysts in current MEA structures;

2. To further explore new materials and optimize the catalyst synthesis conditions in order to achieve high active and stable non-precious catalysts. For example, explore new $(\text{Fe}, \text{Co})-N_x/C$ catalysts, utilizing new chemicals as nitrogen precursors and optimized heat-treatment procedures.

3. To explore high surface area carbon supports with tunable pore size to improve catalyst structures for the purpose of achieving higher volumetric surface areas. For example, explore innovative synthesis method to produce self-supported but high surface area $(\text{Fe}, \text{Co})-N-C$ and metal-free $N-C$ catalysts.

4. To optimize the catalyst layer for higher active site utilization.

5. To improve catalyst stability, for example, by exploring alternative supports other than carbon and investigating metal-free $N-C$ catalysts.

6. To fundamentally understand the ORR mechanisms and their relationship with catalyst active site structures and composition using both theoretical calculations (molecular/electronic level modeling) and experimental approaches to tailor new catalyst structures and ORR activity levels.

Acknowledgements

The authors would like to acknowledge the financial support of the Natural Sciences and Engineering Research Council of Canada (NSERC), the University of Waterloo and the National Research Council of Canada Institute for Fuel Cell Innovation.

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