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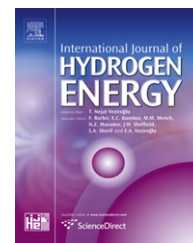
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Review

Non precious metal catalysts for the PEM fuel cell cathode

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ABSTRACT

Low temperature fuel cells, such as the proton exchange membrane (PEM) fuel cell, have required the use of highly active catalysts to promote both the fuel oxidation at the anode and oxygen reduction at the cathode. Attention has been particularly given to the oxygen reduction reaction (ORR) since this appears to be responsible for major voltage losses within the cell. To provide the requisite activity and minimise losses, precious metal catalysts (containing Pt) continue to be used for the cathode catalyst. At the same time, much research is in progress to reduce the costs associated with Pt cathode catalysts, by identifying and developing non-precious metal alternatives. This review outlines classes of non-precious metal systems that have been investigated over the past 10 years. Whilst none of these so far have provided the performance and durability of Pt systems some, such as transition metals supported on porous carbons, have demonstrated reasonable electrocatalytic activity. Of the newer catalysts, iron-based nanostructures on nitrogen-functionalised mesoporous carbons are beginning to emerge as possible contenders for future commercial PEMFC systems.

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1. Introduction

Fuel cells produce electricity from the energy of a fuel through a highly efficient direct electrochemical conversion process, resulting in low emissions and low environmental impact. Of the different types of fuel cell under development at the present time, the Proton Electrolyte Membrane Fuel Cell (PEMFC) is attracting the most attention. This can start up fast and easily and operates at near ambient temperatures. It offers the prospect of a highly efficient, low pollution power source for fuel cell vehicles, stationary power generation and cogeneration applications and portable power devices [1]. However, the PEMFC has a long way to go to become commercially viable for applications other than in niche markets. The use of the noble metal platinum as the preferred catalyst for the anode

and cathode is one of the impediments to widespread PEMFC commercialisation on account of its high cost and scarcity [2]. On the cathode side of the fuel cell, the sluggish reaction kinetics for the oxygen reduction reaction (ORR), that leads to high voltage losses within the fuel cell and therefore low conversion efficiency, has stimulated researchers around the world to look for alternative materials that are cheaper and yet perform better or equivalent to the Pt standard.

PEMFCs also suffer from inadequate performance and durability arising mainly from cathode catalyst oxidation, catalyst migration, loss of electrode active surface area, membrane degradation and corrosion of the carbon support [3]. In their review of activity benchmarks and requirements for oxygen reduction catalysts, Gasteiger et al. [4] have highlighted the performance requirements for potential non-Pt

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electrocatalysts in terms of their catalytic activity and durability. This review also discussed the mechanisms of oxygen reduction on non-Pt catalysts. Wang [5] has also reviewed a few likely candidates in the recent development of non-platinum catalyst for the oxygen reduction reaction. Both reviews have highlighted the importance of producing ORR catalysts for fuel cells in large numbers for applications such as fuel cell vehicles [5]. Regardless of their applications, the production of lower cost ORR catalysts by developing a better understanding of electrocatalysis for the ORR is vital for continuous improvement and further development of PEMFC technology.

For the purpose of this review precious metals are the platinum group metals comprising two sub-groups: platinum-iridium-osmium and palladium-rhodium-ruthenium. To these may be added gold and silver. All of these elements are regarded as precious metals because of their beauty, excellent physical properties and resistance to corrosion and oxidation [6]. They all commend high prices in international markets. Of the precious metals, platinum has currently demonstrated the highest electrocatalytic activity for oxygen reduction at the cathode of PEMFC. Pd, Ru and various Pt group alloyed with non-precious metals have also been investigated as ORR catalysts, but they are not reviewed here.

Other transition metal elements in the periodic table are referred to as non-precious metals (NPMs). This includes nickel, iron, cobalt, chromium, copper, tungsten, selenium and tin which have all been found to have some activity for catalysis of the ORR reaction. These non-precious metals are often employed in catalysts in the form of transitional metal complexes such as chalcogenides, transition metal oxides or nitrides and macrocycles (porphyrins or phthalocyanines). Note that some transition metals have also been incorporated into precious metal containing catalysts, for example the Ru-Se catalysts prepared recently by Rao et al. [7]. Such catalysts are also not included in this review.

This paper reviews progress in the development of non-precious metal catalysts solely for the PEM fuel cell cathode carried out over the past 10 years. By way of background, section 2 describes the state of the art supported Pt catalyst preparation and characterization. Section 3 focuses on the oxygen reduction reaction (ORR), its mechanism and the methods used to investigate the electrocatalysis. In the following sections, five non-precious metal catalyst groups are reviewed, each having received the most attention by researchers in recent years. These are: - NPM-based macrocycles, NPM-based chalcogenides, NPM-based electroconductive polymers, NPM-based nitrides and NPM-Carbon. The review ends with a brief discussion of the leading contenders of carbon-based catalysts.

2. Conventional ORR catalysts

In the PEM fuel cell platinum supported on carbon has been the preferred catalyst for both the hydrogen oxidation reaction and ORR at the anode and cathode, respectively. The slow reactions at the cathode, involving the splitting of oxygen molecules, generally requires a higher loading of Pt on the cathode catalyst, compared to the relatively facile activation

and splitting of hydrogen molecules at the anode. This has led researchers to focus more on cathode catalyst development.

The carbon used as the catalyst support serves not only to disperse the active metal, but also to provide good electronic conductivity to enable a high current to be drawn from the fuel cell. Supported platinum catalyst has been traditionally prepared by a wet chemistry approach that starts with a Pt containing precursor that is absorbed on high surface area carbon blacks. Suitable carbons, such as can be obtained from Cabot Corporation (Vulcan XC-72R, Black Pearls BP 2000), Ketjen Black International, Chevron (Shawinigan), Erachem and Denka, are produced by the pyrolysis of hydrocarbons [8]. The absorbed compound yields finely dispersed Pt particles when thermally decomposed. Examples are shown in Fig. 1 for Pt on a range of different supports with different loadings.

The Pt/Carbon material is sandwiched between the electrolyte and a thicker porous carbon which acts as a gas diffusion layer (GDL). To do this the material is first deposited onto either the electrolyte or the GDL e.g. by screen printing. To fabricate a complete planar fuel cell, the electrolyte and the two electrodes including catalyst layers are bonded together by hot pressing. This method of assembling a PEM fuel cell, whilst being low-cost and amenable to volume production, has the disadvantage of producing a relatively thick layer of catalyst in which Pt is under-utilised. More recently other methods of depositing the active metal onto carbon have been investigated with a view to improving its utilisation and good reviews have been given by Viswanathan and Scibioh [9] and Wee et al. [10]. Emerging methods of depositing Pt include various modified thin-film methods, electrodeposition and sputter deposition, dual ion-beam assisted deposition, electroless deposition, electro-spray method and direct Pt sols deposition. Recently Caillard et al. [11] have prepared catalyst with a Pt loading of between 0.01 and 0.1 mg_{Pt} cm⁻² by plasma sputtering <5 nm Pt directly onto carbon nanofibres. Fig. 2 shows the microporous carbon nanofibre layer before and after plasma nano-cluster deposition.

The electrocatalytic activity of Pt catalysts very much depends on the catalytic active surface area, i.e. on the degree of dispersion and the Pt particle sizes. The exact figure is yet to be established but the typical optimum Pt particle size for ORR, in terms of mass activity, has been reported to be in the range from 2 to 4 nm [12]. In the early days of PEM fuel cell development, the catalyst loading was typically 28 mg/cm² of platinum. In recent years, by controlling the Pt particle size and dispersion, the usage has been reduced commonly to around 0.2 mg/cm² in the fuel cell. Using this figure, the basic raw-material cost of the platinum in a 1 kW PEMFC at such loadings would be about \$10, a small portion of the total cost [1]. Thus capital cost may not be such an issue for PEMFCs as was once perceived. Nevertheless, issues of Pt degradation, its recovery and global availability for widespread vehicle use continue to stimulate research on non-Pt catalysts.

3. Kinetics and mechanism of the ORR

The reduction of the oxygen molecule in aqueous solutions particularly in acidic media is accepted to proceed through either of the two major pathways:-

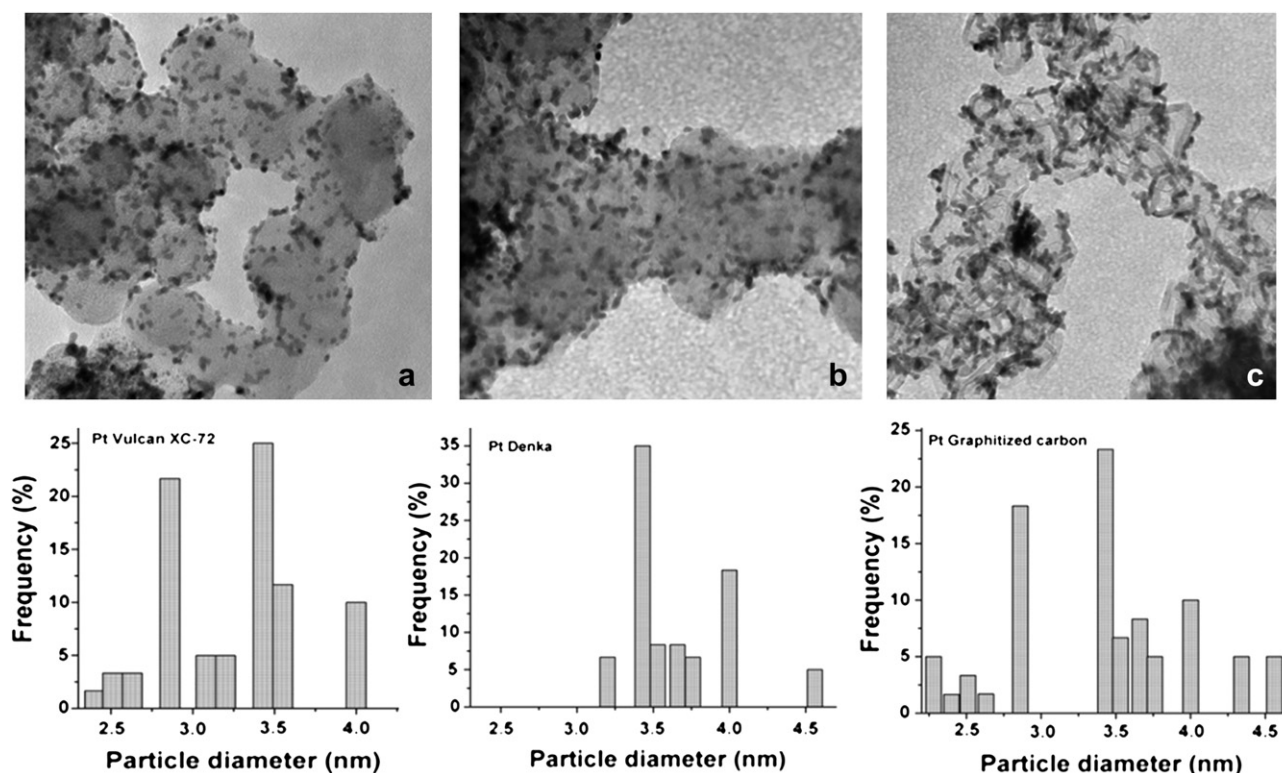
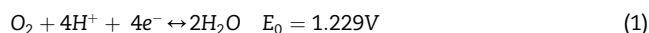
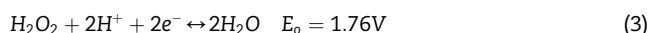
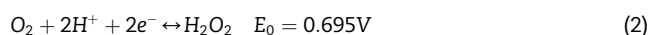


Fig. 1 – TEM images of Pt/C catalysts with histograms of Pt particle size distribution: (a) Pt/Vulcan XC-72R (40 wt%) (b) Pt/Denka (40 wt%) (c) Pt/graphitized carbon (50 wt%) [8].

i) The direct 4-electron reduction reaction to H_2O .



ii) The parallel pathway, the 2-electron reduction reaction to hydrogen peroxide, H_2O_2 , the adsorbed peroxide being reduced to H_2O .



Where E_0 is the thermodynamic potentials at standard conditions.

For pathway (ii), two products are possible - either the reaction stops with the production of H_2O_2 or it proceeds also to produce H_2O . The extent of reaction appears to depend on the chosen catalyst material. The 4-electron route should be the mostly favoured reaction pathway since it produces a high voltage for a H_2/O_2 fuel cell. However, the slow rate of ORR even on platinum typically reduces the working voltage near to 0.8 V compared with the theoretical open circuit potential given by peroxide reduction [13].

Characterisation of the ORR is commonly carried out by electrochemical techniques such as Cyclic Voltammetry (CV), measurements using a Rotating Disk Electrode (RDE) or Rotating Ring Disk Electrode (RRDE) and Electrochemical Impedance Spectroscopy (EIS). CV records the current drawn from the electrode as it is cycled between chosen high and low

potentials. From the resulting voltammogram the electrochemical surface area and mass- and area-specific activities of oxygen reduction catalysts can be obtained [14]. For example Fig. 3 shows the voltammograms of thin-film Pt electrodes of various thicknesses in perchloric acid (HClO_4) and sulphuric acid (H_2SO_4), respectively. From these it can be seen that the thinner the catalyst film, the lower is the peak current density. Also the peak potential for the ORR does not vary much between films of different thickness and even with the thinnest film this peak potential is only 50 mV less than that exhibited by bulk platinum. No significant differences are observed between the activities of the same catalyst when measured in each electrolyte.

The RDE technique has been used extensively to study electrode kinetics variety of oxidation and reduction reactions. The electrochemical reduction of oxygen on thin film Pt electrodes is no exception and example curves of potential vs. current density obtained using a RDE are shown in Fig. 4.

Analysis of data from the RDE is commonly done by applying the Koutecky-Levich equation [15], which for the oxygen reduction may be written in this functionally useful form [16]:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} = \frac{1}{nFkC_{\text{O}_2}} - \frac{1}{0.62nFD_{\text{O}_2}^{2/3}v^{-1}C_{\text{O}_2}^b\omega^{1/2}}$$

where j is the measured current density, j_k is kinetic current density, j_d is the diffusion current density, n is the number of electrons transferred per O_2 molecule, k is the rate constant

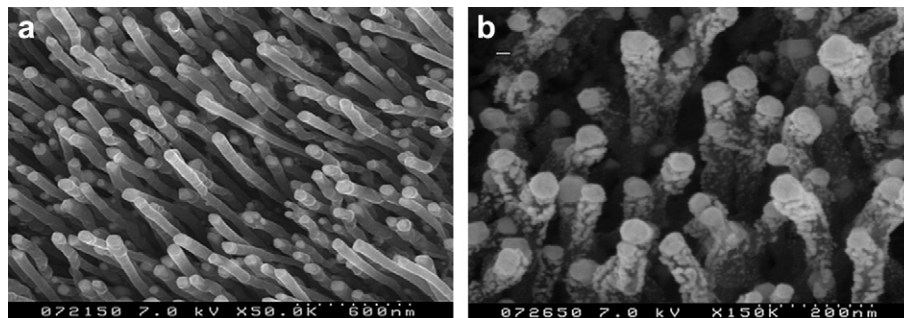


Fig. 2 – SEM micrograph of the microporous CNF layer (a) before (b) after Pt nano-clusters deposition ($0.02 \text{ mg}_{\text{Pt}}\text{cm}^{-2}$) [12].

for O_2 reduction, F is the Faraday constant, ω is the disk rotation speed, $C_{\text{O}_2}^b$ is the bulk O_2 concentration, D_{O_2} is the O_2 diffusion coefficient, and ν is the solution kinematic viscosity. For cathodic reactions governed by mixed transport-kinetic control, plots of $1/j$ vs $1/\omega^{1/2}$ (see insert in Fig. 5) for constant values of k are predicted to generate straight lines having slopes proportional to $1/n$ and intercepts proportional to $1/k$. Note that the slope of the plots are independent of applied overpotential, but the rate constant may be dependent on potential. The derivation of n and k from experimentally measured Koutecky-Levich plots appears to be viable when the plots are linear but care needs to be exercised when the plot is more complex [15]. The importance of the Koutecky-Levich plots will become relevant in the following sections of this paper where we consider non-Pt ORR catalysts.

A variation of the RDE is a rotating ring disk electrode (RRDE) in which a central ring disk electrode is surrounded by a concentric ring, separated by a coaxial insulating ring. The advantage that the RRDE offers over the RDE, for the ORR, is the ability to detect H_2O_2 produced in the reaction using the outer ring.

Among the proposed mechanisms for ORR on Pt, an early publication by Yeager et al. [17] considered the dissociation of the adsorbed O_2 to be the RDS as follows:



The adsorbed O atom then reacts electrochemically via reactions (5) and (6), and these reactions are considered to be quasi-reversible.



Other elementary steps may occur:



Recent studies demonstrate that the nature of bonding of the adsorbed O_2 to the Pt surface affects the overall reduction kinetics and reaction pathway [18]. At low current density, reaction (4) could become the RDS, as confirmed by work of Wang et al. [19]. This is given credence by the Tafel slope changing from 120 mV per decade at high current densities to 60 mV per decade at low current densities [20]. The change in slope is commonly observed with ORR catalysts and Wang predicted, and experimentally confirmed, that it occurs at about 0.77 V which is the reversible potential for the transition between adsorbed O and OH on Pt/C.

4. NPM-based macrocycles

Transition metal macrocyclic compounds have been investigated as potential ORR catalysts since the early 1960s. For example the groups of Yeager et al. [21] and Jasinski [22] pioneered extensive work on phthalocyanines supported on carbon. By the time Appleby published his seminal Fuel Cell

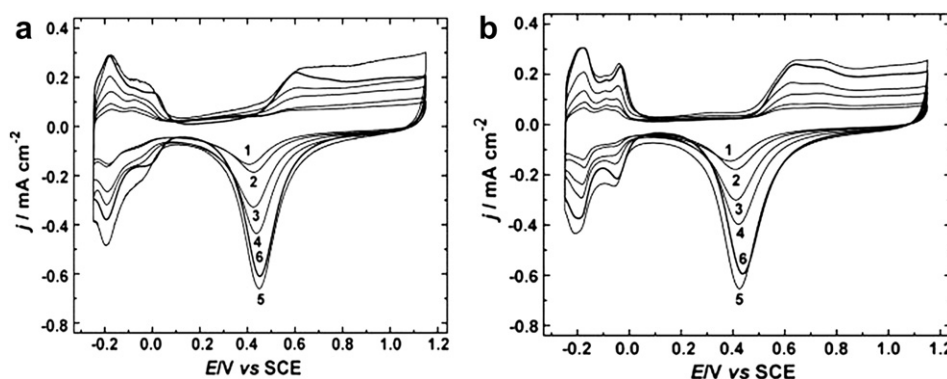


Fig. 3 – Cyclic voltammograms for thin-film Pt electrodes (curves 1–5) and bulk Pt (curve 6) in (a) Ar-saturated 0.1M HClO_4 and (b) 0.05M H_2SO_4 . Pt film thickness (1) 0.25 nm (2) 0.5 nm (3) 1 nm (4) 2 nm (5) 10 nm. $\nu = 100 \text{ mVs}^{-1}$ [13].

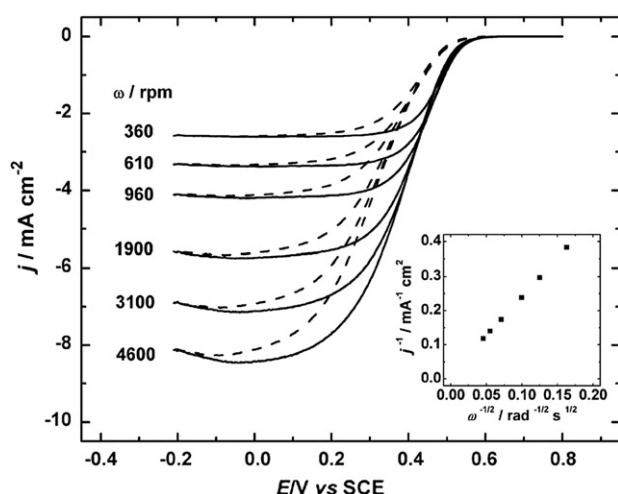
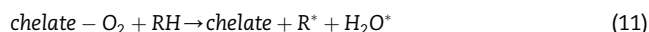


Fig. 4 – RDE voltammetry results for O_2 reduction on 0.5 nm Pt/GC in O_2 -saturated 0.1 M HClO_4 (solid lines) and 0.05 M H_2SO_4 (dashed lines), $\nu = 10 \text{ mV s}^{-1}$. Insets: Koutecky–Levich plots for O_2 reduction on 0.5 nm Pt/GC in 0.1 M HClO_4 at 0 V vs. SCE [14].

Handbook [23] such transition metal macrocyclic compounds had been identified as a specific class of compounds containing metal chelates that are able to catalyse the ORR on both acid and alkaline media. The general mechanism may be represented as:



where RH is a proton source and R^* , H_2O^* are radicals. Metal chelates are relatively stable in acid media and a common feature of these compounds is the MN_4 structure, where M is the central metal atom, which is coordinated in a planar configuration to four nitrogen atoms that are part of a stable cyclic aromatic structure.

Among the many series of macrocyclics, phthalocyanines (Pc) complexed with various transition metals such as iron,

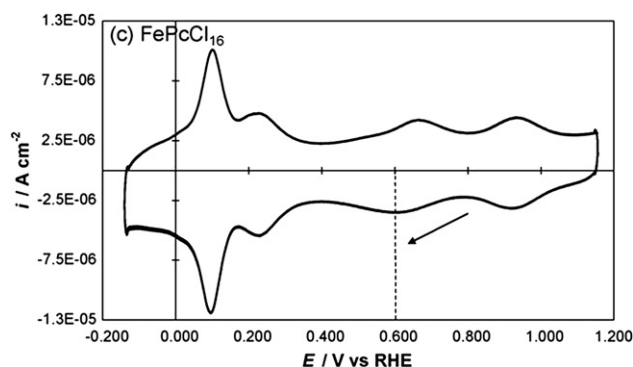


Fig. 5 – The CV of the FePcCl_{16} adsorbed on a pyrolytic graphite electrode at a scan rate, 100 mVs^{-1} . Peak potential for the $\text{Fe}^{\text{III/II}}$ reduction wave indicated with a dotted line. Scan performed at 20°C and 1 atm in a N_2 in 0.1M H_2SO_4 [22].

cobalt, nickel and copper have been thoroughly investigated as oxygen reduction catalysts. Of the various phthalocyanines evaluated for the reduction of oxygen for fuel cells, the complexes with cobalt and copper appear to be the most stable, while those with iron and cobalt seem to have the best combination of activity and stability. In acid solutions, the initial step of the ORR on iron phthalocyanine complexes is believed to be the chemisorption of the oxygen molecule by the central transition metal atom [24].

In 1964 Jasinski [22] began his work with cobalt phthalocyanine on carbon electrodes that resulted in a promising non precious catalyst for the ORR in alkaline media. Jahnke [25] subsequently found this catalyst was also active in acid electrolytes. Over the decades since this work, many studies have been carried out with NPM macrocycles and it appears that Fe- and Co- macrocyclic complexes have exhibited the highest electrocatalytic activity, especially for PEMFC applications. In 1975, Meier et al. [26] reported that carbon–Teflon supported iron phthalocyanine in 3 M H_2SO_4 produced $20\text{--}80 \text{ mA/cm}^2$ at $0.85\text{--}0.65 \text{ V}$, with less than 100 mV degradation for 1000 h at 20 mA/cm^2 . More recent investigation of iron phthalocyanines particularly for PEMFCs has been carried by Baker et al [27] who prepared four types of FePcs: iron (III) phthalocyanine (FePc), iron (III) phthalocyanine -4,4',4'',4'''-tetrasulfonic acid ($\text{FePc}(\text{SO}_3)_4$), iron (II) 1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-hexadecachloro-29H, 31H-phthalocyanine (FePcCl_{16}) and 2,11,20,29-tetra-*tert*-butyl-2,3-naphthalocyanine ($\text{NpPc}(\text{tBu})_4$). These four types of FePcs represent different types of substituent on the Fe. The study found that the substituent had a strong effect on the mode of adsorption of the FePcs species. Each of the synthesized catalysts was tested at ambient pressure and in the temperature range of $20\text{--}80^\circ\text{C}$ in 0.1 M H_2SO_4 . The results showed that in addition to substituent, the temperature also had an influence on the ORR mechanism. Of the four FePcs tested, FePcCl_{16} was the most stable in an acidic ORR environment where it showed the lowest kinetic overpotential. Fig. 5 shows the CV of the FePcCl_{16} adsorbed on a pyrolytic graphite electrode.

In the range between 20°C – 60°C and at 80°C , the number of electrons transferred for FePcCl_{16} are $n = 2$ and $n = 1$, respectively. This can be seen from the Koutecky-Levich Plot in Fig. 6.

Another class of macrocyclic complex that show a good potential for ORR catalysis is the chelates of 5,14-dihydro-5,9,14,18-dibenzotetraaza [14]annulene, or tetraazaannulene (TAA) [28]. Contamin et al. [29] prepared CoTAA catalyst supported on a mixture of an active charcoal and sulphur in the form of thiourea, with S/Co ratios of either 1 or 0. The prepared CoTAA samples were heated at 600°C and 800°C . RDE tests on the resulting materials were carried out in 0.25 M H_2SO_4 and 0.5 M HClO_4 . It appeared that the CoTAA heated at 600°C showed particularly good activity and stability compared with the sample heated to 800°C and X-ray photoelectron spectroscopy (XPS) indicated that the presence of sulphur enhances the reduction of oxygen by the active cobalt ion.

Porphyrins are the second major class or group of macrocyclics investigated as non-precious metal catalysts, examples being tetramethoxyphenyl-porphyrin (TMPP) and tetraphenylporphyrin (TPP). The recent review by Feng

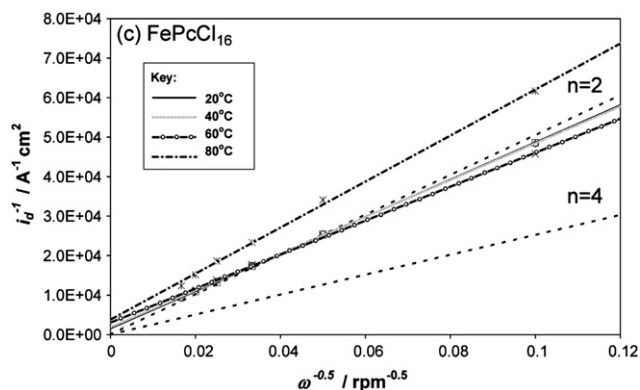


Fig. 6 – The Koutecky-Levich Plot for FePcCl₁₆, adsorbed on a pyrolytic graphite electrode at different temperatures. Theoretical lines for the 2 \bar{e} and 4 \bar{e} O₂ reduction process are as marked [22].

and Alonso-Vante [2] has summarized the development of Fe- and Co- based TMPP, TPP, Pc and TAA.

Carbon-supported Fe–Co catalyst, produced by pyrolysis of CoTMPP in the presence of iron oxalate has been reported and patented by Hilgendorff et al. [30,31]. They claim that the catalytic activity is almost identical to that of a conventional standard catalyst material employing platinum.

Polylenko and colleagues also studied pyrolyzed Fe- and Co-based TPP as well as the mixture of Co/FeTPP (1:1 atomic weight ratio) for ORR catalysts [32]. The catalysts were prepared by pyrolyzing the Co and FeTPP at temperatures between 500 °C and 800 °C. In their preparation procedure, amorphous fumed silica was added to the Co and FeTPP and sonicated to provide a good dispersion of silica in the matrix. The solution was then dried and pyrolyzed and finally the silica was etched out using Potassium Hydroxide (KOH). The etching out of silica particles resulted in a hollow spherical structure that provided a high surface area for the dispersion of catalytically active sites. X-ray diffraction revealed the presence of metal crystallites which increased in size as the temperature of pyrolysis increased, and XPS indicated the presence of about 7 types of N in the pyrolyzed TPP. They were pyridinic, Me-N_x, pyrrollics at 2 different binding energies, graphitic, quaternary amine and pyridine N-oxide. Upon pyrolysis at 700 °C, only 15% of N in CoTPP and 16% of N in FeTPP remained as Me-N_x centres. Pyrolysis at 600 °C yielded the most active catalysts as confirmed by electrochemical studies in a 3 compartment cell. Steady state polarization curves for material pyrolysed at 600 °C are given in Fig. 7 which shows that the pyrolyzed Co/FeTPP catalyst has the highest activity compared with single Fe- and Co- based TPP.

Gojkovic et al. [33] found that a Fe-based TMPP chloride that was heat treated from 200 °C to 1000 °C revealed hydrogen peroxide (H₂O₂) formation during the ORR which was detected using RRDE at potential of 0.8 V at the limiting current in 0.1 M H₂SO₄. It seems that when the heat treatment temperature is greater than 600 °C, the ORR occurs at between 0.90 V and 0.83 V. Fig. 8 shows the polarization curves of H₂O₂ oxidation and reduction. It appeared that the oxidation occurs faster than reduction reaction. This is

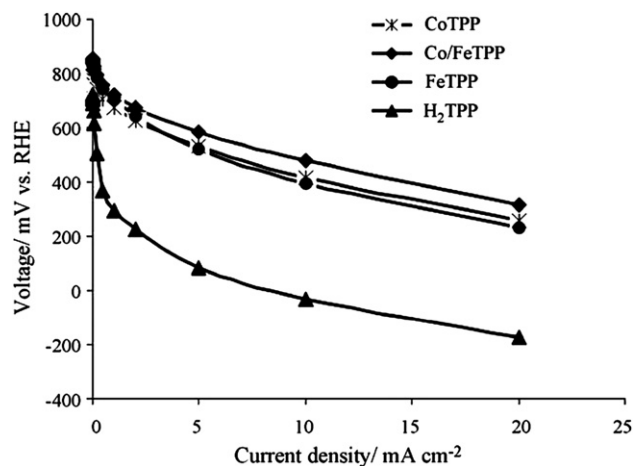


Fig. 7 – The steady state polarization curves for CoTPP, FeTPP, Co/FeTPP and H₂TPP pyrolyzed at 600°C in 0.5 M H₂SO₄ [27].

possibly the reason that the H₂O₂ cannot be detected at potentials greater than 0.8 V.

However, the ORR on this catalyst appeared to progress by both the direct and series reaction paths with the number of electrons transferred being between 3.45 and 4 depending on the electrode potential, regardless of the heat treatment temperature [33].

Using similar preparation methods as Gojkovic et al., Schulenberg et al. [34] prepared FeTMPP chloride catalyst that was pyrolyzed at 900 °C for 1 h in Ar atmosphere. They also confirmed the presence of H₂O₂ and found that the porphyrin decomposed during heat treatment with nitrogen atoms of the heat treated porphyrin becoming bonded at the edge of graphene layers as pyridine- and pyrrole- type nitrogen. They suggested that a 6-fold coordinated Fe³⁺ was responsible for the catalytic activity and that the active sites degrade in the presence of H₂O₂. Fig. 9 shows the proposed structure of

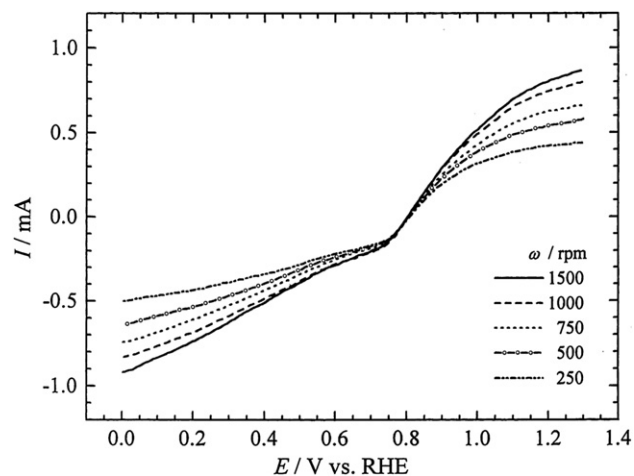


Fig. 8 – Oxidation and reduction of H₂O₂ on FeTMPPCl/BP heat treated at 800°C. Electrolyte: Ar saturated 0.1 M H₂SO₄ solution containing 3 × 10⁻⁴ M H₂O₂. Sweep rate 5 mV s⁻¹. Rotation rate: 1000 rpm.

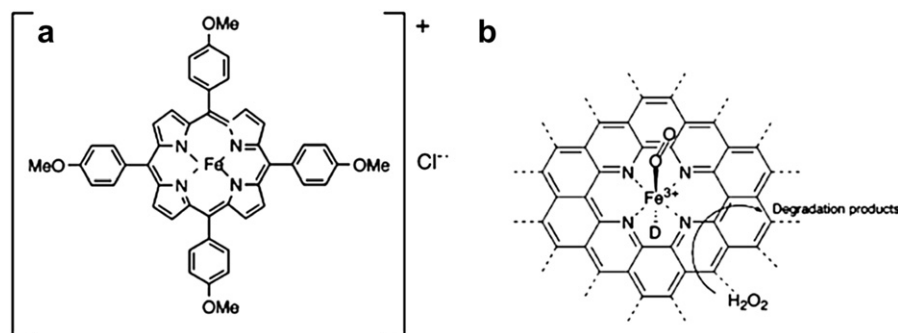


Fig. 9 – The FeTMPPCl structure (a), and (b) the proposed model of the active sites that could be destroyed with the presence of H_2O_2 [29].

FeTMPPCl and the proposed model of degraded active sites caused by H_2O_2 .

In a later study, Medard et al. [35] prepared two types of catalysts using two different Fe precursors: iron acetate (FeAc) and FeTMPP chloride. Two procedures were used in the catalyst preparation. The first started with the adsorption of the Fe precursor onto the carbon powder which was then pyrolyzed at 900°C in $\text{NH}_3/\text{H}_2/\text{Ar}$. The second procedure began with the pyrolysis of the carbon alone at 900°C in $\text{NH}_3/\text{H}_2/\text{Ar}$ followed by the adsorption of the Fe precursor onto the pyrolyzed carbon, followed once again with a pyrolysis step. The ORR catalytic activity of the catalysts was determined using the RDE in H_2SO_4 saturated with O_2 . The nitrogen content on the catalyst surface was found to have the most influence on the ORR with high nitrogen content improving activity towards the ORR and selectivity to the reduction of oxygen to water via the $4e^-$ pathway. Increasing the relative amount of $\text{Fe-N}_2/\text{C}$ improved both activity and selectivity of the catalysts towards the $4e^-$ reaction, while most of the H_2O_2 formation could be attributed to $\text{Fe-N}_4/\text{C}$.

Herrmann et al. [36] have modified Co-based TMPP by adding various metal oxalates. The oxalates added prior to the pyrolysis of CoTMPP behaved as a structure forming agent to provide a nano-scaled template for the carbonisation of the CoTMPP. The oxalates were removed by an etching step after pyrolysis, the argument being that the removal of template would produce highly porous carbon particles with different morphologies, and that the decomposition of oxalate would enhance the catalyst specific surface area. Crystalline tin that arose, for example, from the pyrolysis of tin oxalate is accessible to the acid etchant in which it is highly soluble. The particle size of the tin crystallites determines the morphology of the final catalyst. It was suggested that the thin film of pyrolyzed CoTMPP that formed onto the surface of the carbon support would decrease the catalyst specific surface area as the CoTMPP loading increased. This is because the pyrolysis of porphyrin yields a compact and glassy material structure rather than a porous one. The catalysts all received a heat treatment under continuous Ar flow at 450°C and 850°C and were characterised using RDE in $0.5\text{ M H}_2\text{SO}_4$. The group found that $\text{SnC}_2\text{O}_4\text{-CoTMPP}$ catalyst had the highest specific surface area ($857\text{ m}^2/\text{g}$) with 50% of the area attributed to micropores and mainly in the form of amorphous carbon. In RDE tests, the

current density for $\text{SnC}_2\text{O}_4\text{-CoTMPP}$ and $\text{FeC}_2\text{O}_4\text{-CoTMPP}$ were higher than those of $\text{NiC}_2\text{O}_4\text{-CoTMPP}$ and $\text{CoC}_2\text{O}_4\text{-CoTMPP}$ catalysts. Fig. 10 shows the Tafel-plots of various metal oxalates-CoTMPP prepared by Herman et al.

Kosłowski et al. [37] have investigated the influence of porphyrin structure on the ability to directly or indirectly catalyse the ORR. They prepared various FeTMPP and H_2TMPP -based catalysts using a Foaming Agent Technique (FAT). Both iron (II) oxalate and sulphur were used in the synthesis and the prepared catalyst materials were heat treated under N_2 at 800°C . To modify the structure of the catalysts as well as their composition, various post-treatments using HNO_3 , H_2O_2 , N_2 and CO_2 were carried out on the prepared catalyst. This allowed the influence of structure and composition on catalytic activity to be investigated. The structural changes were investigated using ^{57}Fe Mossbauer spectroscopy and their influences on catalyst activity were studied by using the RRDE. They found that the generic catalysts that went through a few post-treatments had a number of atomic Fe centres that correlated well with kinetic current density as measured in the RRDE. Specifically Kosłowski found that the total number of in- plane Fe-N_4 moieties implanted in a graphene type

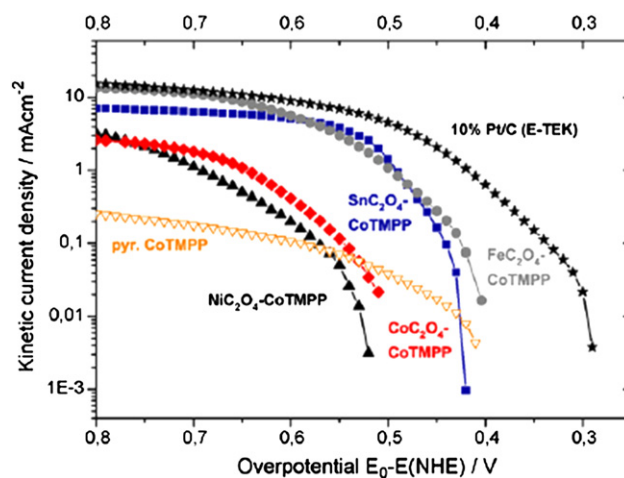


Fig. 10 – Tafel-plots of the investigated catalysts determined from RDE in O_2 saturated H_2SO_4 (0.3 V/min , 0.071 cm^2) [31].

matrix relates directly to the current density for a given potential for the reduction of oxygen to water. They also proposed a linear correlation between the number of CFeN₂ centres and rate of H₂O₂ formation.

A review of progress in the role of macrocyclic complexes in the preparation of non noble electrocatalysts for PEM fuel cell reactions by Zhang, et al. [38] has discussed how their syntheses, heat treatment, carbon support and catalyst layer structure significantly influences the catalytic activity and stability for ORR. Rao et al. [39] has also shown that functionalisation of carbon with nitrogen helps to increase the activity of catalyst subsequently prepared by incorporation of FeTMPP.

5. NPM-based Chalcogenides

Non precious metal chalcogenides first received the attention of researches to replace Pt in the 1970s when various transitional metals showed a distinctive oxygen reduction reaction at the cathode. Baresel [40] was one of the first to find that Co-S had a high electrocatalytic activity for ORR, and research on transition metal sulphides and selenides has continued to today. For example, Feng [2] has successfully prepared nanoparticles of Co₃S₄ and CoSe₂ supported on carbon by in situ synthesis methods under mild conditions without any surfactant preventing particle aggregation. The catalysts showed ORR electrocatalytic activity in 0.5 M H₂SO₄ with the onset potential at ca. 0.7 V vs RHE. In the review by Zhang et al. [38] the unique feature of chalcogenides is reported to be their high stability in an acidic environment, especially if employed in combination with other transition metals.

A group of researchers in 2006 found that Co_{1-x}Se, FeS₂ and (Co, Fe)S₂ prepared using magnetron sputtering on to glassy carbon were electrochemically active for ORR though their OCP was still lower than Pt [41]. The activity of Co_{1-x}Se alone for ORR depended on the amount of Se in the composition and a kinetically controlled process was observed in the potential range 0.5–0.7 V vs RHE. The equivalent OCP and Tafel region were found in Co-Se supported on Vulcan XC72R. The authors suggested that some extra chalcogen surrounding a Co-deficient nanocrystalline form of CoSe may contribute to the active site, and some Se to S exchange occurs in the H₂SO₄ electrolyte during the cyclic voltammetry and the RDE measurement [2].

The activity of noble metal chalcogenides catalysts for ORR has been enhanced by Lee and colleagues [42]. They developed novel ternary non precious metal chalcogenides W-Co-Se. It is believed that the chalcogen Se would enhance the catalytic activity and stability of W and Co by modifying their electronic structures. To verify this, the electronic structure of catalysts were analysed using XPS. The chemical shifted binding energies for W 4f_{7/2} and Co 2p_{3/2} in the W-Co-Se chalcogenide were found to be 0.6 and 1.6 eV higher, respectively, than those of their highest oxidation-state oxides such as WO₃ (35.4 eV) [43] and CoO (780.4 eV). These binding energies are also much higher than those of their binary chalcogenides such as WSe₂ (W 4f_{7/2} = 32.2 eV) [43] and CoSe (Co 2p_{3/2} = 778.7 eV) [44]. The changes in binding energies for these

elements can be explained by the fact that selenium is more electronegative than tungsten or cobalt. Charge transfer from tungsten and cobalt to selenium may cause the chemical shift of core-level peaks for metals to positive binding energy, and for selenium to a negative one, indicating that they are a complete ternary chalcogenide.

Lee's group synthesized their catalysts by a chemical precipitation reaction using tungsten carbonyl, cobalt carbonyl and selenium powder. The material was heated at 140 °C for 20 h under argon. The CV was carried out in 0.5 M H₂SO₄ in saturated N₂ and the results revealed that the formation of W-Co-Se chalcogenides is electrochemically stable in the potential range between 0.05 and 0.8 V vs NHE since no anodic oxidation currents could be seen. The polarization of the W-Co-Se chalcogenides catalyst under saturated O₂ shows a larger cathodic current than under saturated N₂. As seen in Fig. 11, the onset potential for ORR was observed at 0.755 V and it can be seen that when the electrode potential is more negative than 0.4 V, the diffusion limited current appeared and a significant dependence on rotating rate indicates that the ORR is limited by mass transport. This ternary chalcogenides catalyst was claimed to have much higher ORR catalytic activity than that the binary chalcogenides as studied by Susac et al. [41].

6. NPM-based electroconductive polymer

Another group of non-precious metal catalysts that has drawn the attention of researchers recently is that of catalyst synthesized with conjugated heterocyclic polymers such as polyaniline (pani), polypyrrole (Ppy) and poly(3-methylthiophene (P3MT)).

Martinez et al. [45] have studied cobalt composite electroconductive polymers. The catalysts produced via chemical method were carbon/polyaniline/cobalt (C-Pani-Co), carbon/polypyrrole/cobalt (C-Ppy-Co), and carbon/poly(3-methylthiophene)/cobalt (C-P3MT-Co). In the case of the pani and ppy materials, the modification with Co was intended to imitate the atomic configuration of cobalt-containing porphyrins, thus allowing the formation of Co-N bonds without destroying the

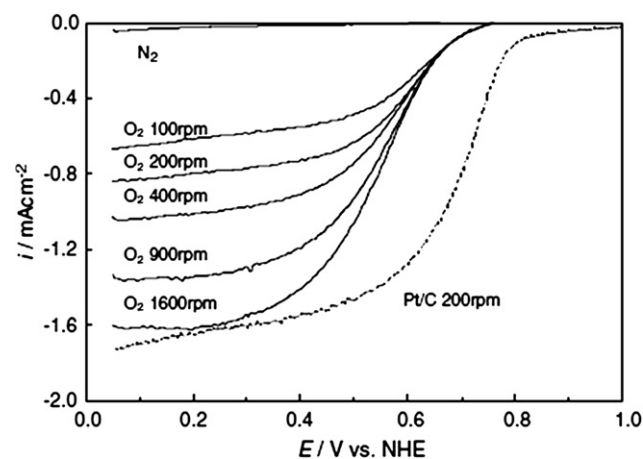


Fig. 11 – ORR polarization curves for W-Co-Se in 0.5 M H₂SO₄ at 25°C. Scan rate: 5 mV s⁻¹ [36].

initial polymer structure. In the case of Co-P3MT, Co atoms are bonded to sulphur atoms. Cyclic voltammetry (CV) of all three materials under nitrogen and oxygen atmosphere showed that all catalysts had electrocatalytic activity for ORR. The potentials at which the maximum current density occurred in CV was used to rank the performance of these materials as ORR catalysts, and the highest potential attained was in the order of C-Ppy-Co > C-Ppy > C-P3MT-Co. The potential generated by C-Ppy-Co catalyst was 325 mV at maximum current density of $2.01 \times 10^{-5} \text{ mA cm}^{-2}$ Fig. 12 shows the CV for C-Ppy and C-Ppy-Co.

A stability test conducted with C-Ppy Co revealed that this material was stable for 48 h after an initial decrease in activity during the first 2 h in a 0.5 M H_2SO_4 and O_2 environment [45]. The dominant activity of the C-Ppy-Co catalyst later was thoroughly investigated by Lee et al. [46] through a study of pyrolyzed and unpyrolyzed Co-Ppy-C synthesized using a chemical method of polymerization at 80 °C. The Co-Ppy-C that had been pyrolyzed at 800 °C and then heat treated at various temperatures from 600 °C–1000 °C showed better ORR catalyst activity compared with catalysts that had other heat treatment temperatures. The polarization curves of unpyrolyzed and pyrolyzed Co-Ppy-C are shown in Fig. 13.

Results of RRDE measurements show that the ORR mechanism is strongly potential-dependent for both pyrolyzed and unpyrolysed catalysts. At low overpotential >0.5 V, it is likely that the pyrolyzed Co-Ppy-C at 800 °C proceeds predominantly via 4-electron transfer ORR whereas unpyrolyzed Co-Ppy-C shows a dominant 2-electron transfer process to H_2O_2 . The heat treatment certainly increased the ORR activity and XPS results suggested that pyrrolic type nitrogen and graphitic nitrogen may be responsible for this improvement [46]. The behaviour and performance of this catalyst had been investigated earlier by Bashyam and Zelenay [3], but without pyrolysis during its preparation. The catalysts that were synthesized via a simple chemical method, with Co loading $6.0 \times 10^{-2} \text{ mg cm}^{-2}$ and 16 wt% Ppy content in the composite, generated 0.2 A cm^{-2} at 0.50 V and maximum power density of 0.14 W cm^{-2} in $\text{H}_2\text{-O}_2$ fuel cell test. The catalyst polarization is shown in Fig. 14.

Though the energy generated in a H_2 -air fuel cell using a Co-Ppy-C composite cathode was half of that produced in

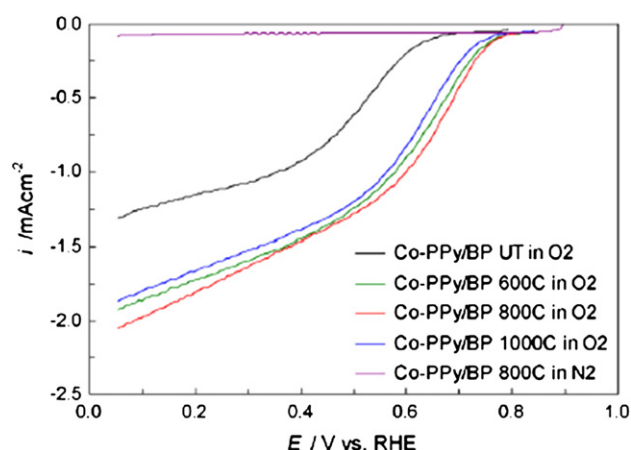


Fig. 13 – The polarization curves of unpyrolyzed and pyrolyzed Co-PpyC catalyst at 5 mVs^{-1} , 25°C in $0.5\text{M H}_2\text{SO}_4$ under saturated N_2 and O_2 .

a $\text{H}_2\text{-O}_2$ fuel cell, interestingly the cell performance with the Co-Ppy-C composite cathode was very stable, and showed no appreciable drop over 100 h of operation [3]. This kind of observation offers some hope of a stable non-precious metal catalyst being developed for the ORR in PEMFCs.

The activities of three heterocyclic conjugated polymers modified with nickel have been studied by Martinez and Smit [47]. These were C-Pani-Ni, C-Ppy-Ni, C-P3MT-Ni and their precursors, which were all synthesized and tested. The SEM images showed no significant change for the carbon/polymer and carbon/polymer/nickel samples as compared to carbon black morphology. The FTIR bands suggested the existence of Ni-N bonds (for Pani and Ppy) and Ni-S bonds (for P3MT). TGA result revealed that the thermal stability in an intermediate range had been reduced by adding the nickel to the presence of nickel oxides, or hydroxides, carboxylic acid groups but improves stability at high temperature, suggesting modification of the carbon support. Cyclic voltammetry revealed that all materials have electrocatalytic activity for the ORR but of the materials tested, C-Ppy-Ni had the highest ORR activity producing a current density 2.4 mA/cm^{-2} . This value was

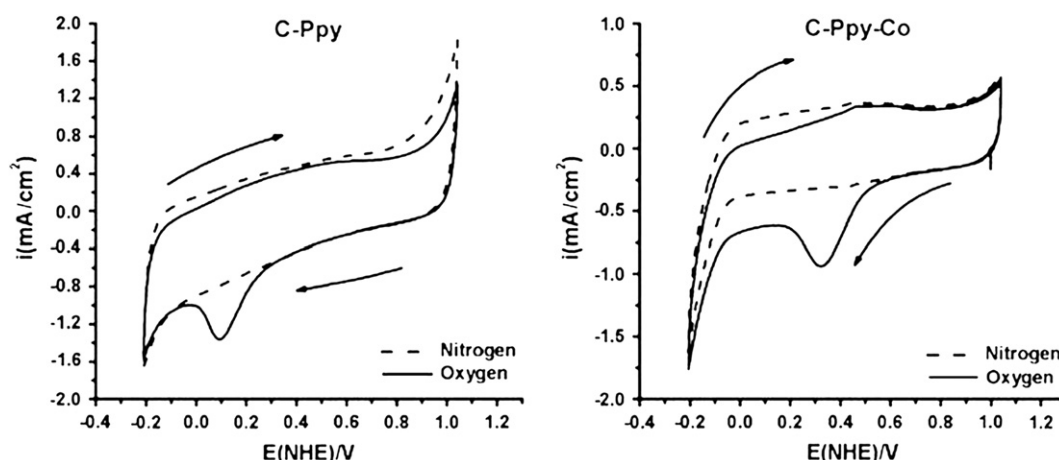


Fig. 12 – The CV for C-Ppy and C-Ppy-Co carried out at room temperature in $0.5 \text{ M H}_2\text{SO}_4$ at 20 mV/s [39].

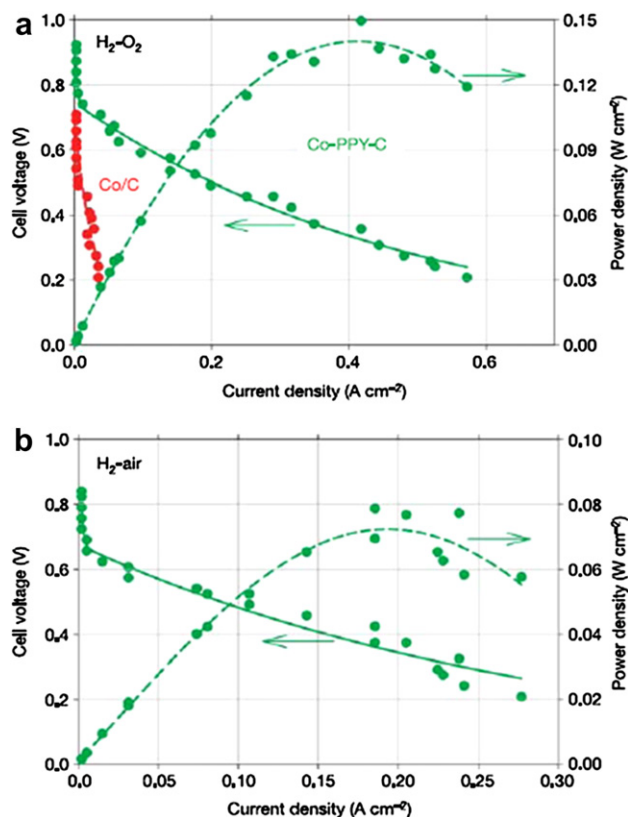


Fig. 14 – The polarization and power density of CoPPyC plots for (a) H₂-O₂ fuel cells (b) H₂-air fuel cells. The cell temperature is at 80°C[3].

calculated by subtracting the maximum current density on the ORR peak in the O₂ with the current density in the N₂. This can be seen in Fig. 15.

Among the heterocyclic polymers modified with Ni by Martinez and Smit, it was found that the C-Ppy-Ni has the highest exchange current density at 4×10^{-5} mA cm⁻² and was the best electrocatalyst for ORR. This material also showed a significant stability for 2 days in 0.5 M H₂SO₄, under O₂ [47]. The additions of Co- and Ni- into heterocyclic polymers have been shown to have remarkable ORR

electrocatalytic activity. The researchers of these materials have claimed that the addition of Co to polypyrrole shifted the ORR towards positive potential, and on the other hand, the Ni shifted the ORR peak towards negative potentials.

In addition to Co and Ni modified polymers, an iron-Polypyrrole has also been investigated. Liu et al. [48] synthesized pyrolyzed FePpy mesoporous spheres (FePpy-MS) using a template-assisted ultrasonic spray pyrolysis method. This resulted in a self-supported catalyst with a high volumetric surface area. It was believed that the high surface area would enhance the specific activity of the catalyst. The pyrolyzed FePpy was prepared by polymerizing the polypyrrole into polypyrrole colloids. This was subsequently fed through a high temperature furnace. The FePpy mesoporous sphere catalyst was obtained after etching with HF. For comparison, the group prepared a catalyst using conventional impregnation method yielding FePpy supported on Vulcan carbon (FePpy-VC). The BET method revealed that the specific surface areas calculated were 1263 m² g⁻¹ and 168 m² g⁻¹ for FePpy-MS and FePpy-VC, respectively. By dividing the specific surface area by the total volume of bulk carbon, the volumetric surface areas found were 780 m² cm⁻³ and 313 m² cm⁻³ for FePpy-MS and FePpy-MS, respectively and they claimed that the higher iron content for a larger volumetric surface area would lead to high active density for FePpy-MS. Moreover, the mesoporous structure of the FePpy-MS catalyst would have a benefit for mass transport. In a CV test, FePpy-MS catalyst shows 7 times higher capacitive current density than that of FePpy-VC. In a real H₂-air PEM fuel cell test, both catalysts start at similar open circuit potential (OCP) of about 0.83 V but at 0.40 V, the FePpy-MS catalyst produced 0.14 A cm⁻² of current density and a maximum power density of 62 mW cm⁻² as shown in Fig. 16. Long term catalyst stability has so far not been reported by the researchers.

In this section it is worth mentioning that N-doped ordered porous carbon (CN_x) has been synthesized recently via a nanocasting process using polyacrylonitrile (PAN) as the carbon and nitrogen precursor [49]. To engineer a suitable pore structure for the carbon, mesoporous silica was used as a hard template. Nitrogen adsorption/desorption, X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) were used to characterize the synthesized CN_x and the derived Fe oxygen reduction

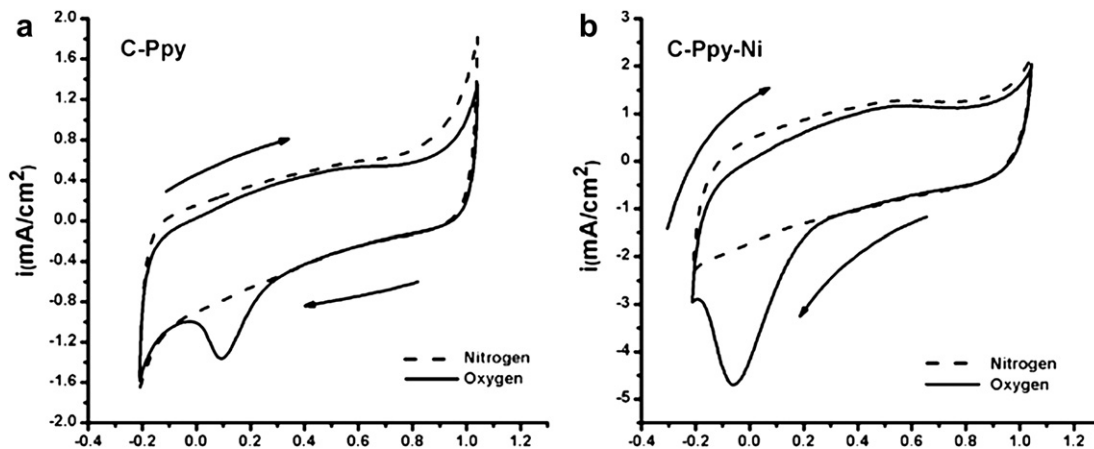


Fig. 15 – The CV for (a) C-Ppy and (b) C-Ppy-Ni carried out at room temperature in 0.5 M H₂SO₄ at 20 mV/s [41].

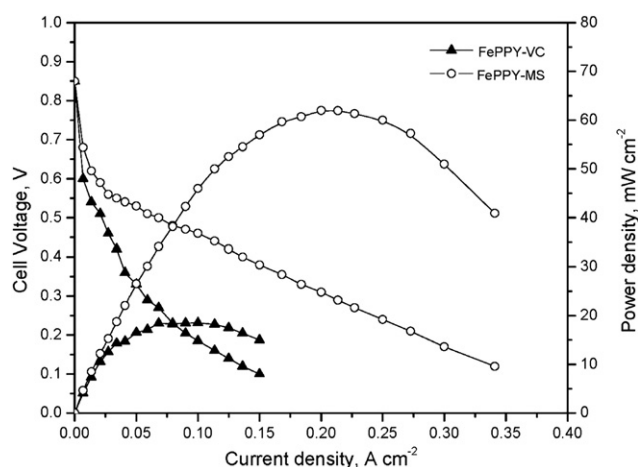


Fig. 16 – Polarization and power density curves for H_2 -air PEM fuel cells [42].

catalysts. The CN_x exhibited a highly ordered porosity and high graphitization with a surface area of $1132 \text{ m}^2 \text{ g}^{-1}$ and a nitrogen content of 6.88 at.%. The NPM ORR catalysts were prepared by pyrolyzing iron acetate-impregnated CN_x in argon, followed by post-treatments. An impressive current density as high as $600 \text{ mA } 0.6 \text{ A cm}^{-2}$ at 0.5 V was obtained in an H_2/O_2 PEMFC using a catalyst loading of 2 mg cm^{-2} .

7. NPM-based nitrides

It is only recently that nitrides modified by non precious metals have been investigated as potential ORR catalysts. In this regard, molybdenum nitride ($\text{Mo}_2\text{N/C}$) and tungsten nitride ($\text{W}_2\text{N/C}$) have been studied by Zhong et al. [50,51]. A temperature-programmed reaction (TPR) strategy was used to prepare $\text{Mo}_2\text{N/C}$. The electrocatalytic activity of this material was investigated using Linear Sweep Voltammetry (LSV) in $0.5 \text{ M H}_2\text{SO}_4$ saturated under N_2 or O_2 . The ORR on the electrode occurred at a relatively positive potential of about 0.46 V . The RDE technique was used to measure the kinetics of the ORR on the prepared catalysts. Using the Levich equation, the rate of the ORR on $\text{Mo}_2\text{N/C}$ was calculated and corresponded to an electron transfer of 3.8, suggesting that the reaction mechanism followed a 4-electron pathway. In a single cell test, the $\text{Mo}_2\text{N/C}$ electrode demonstrated a low open circuit potential (OCP) in the range $0.6\text{--}0.8 \text{ V}$. Despite this, the catalyst showed no deterioration during a 60 h cell test at 200 mA cm^{-2} . The same group proceeded to measure the ORR activity of tungsten nitride catalyst. The same preparation and test method were applied to $\text{W}_2\text{N/C}$ as for the $\text{Mo}_2\text{N/C}$. In this case, the LSV curves in N_2 atmosphere showed no apparent reduction current, which demonstrated a high stability of the catalyst in N_2 , but, the reduction current of the $\text{W}_2\text{N/C}$ in O_2 saturated solution significantly increased as the potential was scanned. The difference between the N_2 and O_2 cases showed that the catalyst has significant electrocatalytic activity for the ORR which started at a relatively positive potential of about 0.6 V vs SHE. In a single fuel cell test, the

catalyst exhibit relatively good performance which improved when the temperature was increased. At a current density of 100 mA cm^{-2} , the cell voltage at 80°C is 0.367 V , which is about 146 mV and 223 mV higher than that at 70°C and 60°C respectively. The maximum power densities of the single cell was found to be 39.2 mW cm^{-2} at the higher temperature of 70°C . A stability test at 120 mA cm^{-2} found that the output voltage of a single cell remained constant over test of approximately 90 h .

8. Carbons and NPM-carbon catalysts

This section highlights progress in catalyst materials comprising functionalised carbons, or metals supported either directly on carbon or carbon activated with nitrogen. The rationale behind using a carbon support functionalised with nitrogen is to synthesise the macrocyclic-like structures that features metal-nitrogen bonding that are known to catalyse the ORR. The preparation of catalyst directly supported on carbon involves the impregnation of a solution of a transition metal salt into a microporous carbon. The functionalisation of carbon with nitrogen can be achieved in many ways. One method is to deposit the transition metals as a compound which already contains nitrogen atoms such as the TPTZ ligand (2, 4, 6-Tris (2-pyridyl)-1, 3, 5-triazine). Another method is to heat up the transition metal deposited via impregnation of a salt solution in the carbon in the presence of a nitrogen containing gas (N_2 or NH_3).

Much has been discussed in the literature regarding the activation of carbon for use as a support for NPM catalysts. Indeed, work has been carried out to investigate if carbon itself can be so activated that it can act as a catalyst in its own right. Charretre et al. [52] have investigated the influence of the structural parameters of pristine commercial carbon blacks on their activity for oxygen reduction. They found best catalytic activities were obtained with materials that have (i) the smallest particle diameters (obtained from BET measurements); (ii) the amount of disordered phase which is proportional to W_D , the width at half maximum of the D peak in the Raman spectrum of the pristine carbon; and (iii) the mean size of the graphene layers characterizing the graphitic crystallites in the carbon black. Optimizing these three parameters appeared to maximizes the fraction of the pristine carbon black that becomes microporous upon reaction with NH_3 and, therefore enables the formation of Fe/N/C catalytic sites. A $\text{FeN}_{2+2}/\text{C}$ structure bridging two adjacent graphitic crystallites was proposed as a potential model for most of the catalytic sites present in such Fe/N/C type catalysts.

More recently Wang et al. [53] prepared a range of mesoporous carbon treated with ammonia which was shown to have some activity for catalysis of the ORR. The materials were prepared using a soft-template to generate micropores within the walls of a two dimensional hexagonal ordered mesoporous carbon. This was heated in NH_3 for 1 h at various temperatures from 950 to 1050°C . The material treated at the highest temperature gave an onset potential of 0.72 V , which is just 80 mV below that of a commercial $20\text{wt}\%$ Pt/Vulcan carbon (a benchmark material from Electrochem Inc.). Nitrogen adsorption measurements suggested that heat

treatment had given rise to degradation of the ordered structure but at the same time the material retains its mesoporous structural component. The activity for ORR is attributed to the large percentages of both pyridinic type (~ 398.5 eV) and graphitic type (~ 401.3 eV) carbons as determined by narrow scan N1s XPS analyses.

Various metals supported on carbon or carbon-nitrogen structures have been proposed as ORR catalysts. Cr-based electrocatalysts have been prepared using R.F magnetic sputtering at 343 K (no heat treatment) and 1073 K (during heat treatment) [54]. The Cr=C and Cr=C=N catalysts were deposited under argon (Ar) and Ar + N₂, respectively at a pressure 4.7×10^{-1} Pa. Electrochemical measurements carried out at 303 K in 0.1 mol dm⁻³ H₂SO₄ showed that both catalyst had high electrochemical stability in the potential range of 0.05–1.0 V. The potential–current density curves showed that both Cr=C and Cr=C=N prepared at 1073 K had higher catalytic activity for ORR than the same materials prepared at 343 K. This indicated that the heating of material during the sputtering process served to enhance catalytic activity for the ORR. The Cr=C=N was found to have a higher surface area than Cr=C, which is believed to be responsible for the increase in the catalytic activity. The ORR for catalyst obtained by sputtering under gas atmosphere containing N₂ occurred at 0.72 V [54].

Iron catalysts on functionalised carbons have been studied intensively in recent years. Bezerra et al. [55] studied carbon supported Fe-N electrocatalysts derived from an N-containing ligand 2, 4, 6-Tris (2-pyridyl)-1, 3, 5-triazine (TPTZ). The TPTZ ligand contains 5 nitrogens per molecule which is able to produce a particularly active catalytic site when bonded with Fe. In their modelling calculations, it was confirmed that the Fe could bond to N on the central aromatic ring of TPTZ with a Fe-N bond length 2.08 Å. Experimentally the Fe-TPTZ/C that had undergone heat treatment at 800 °C showed good activity for the ORR. From CV characterization, the ORR catalytic activity is at a high onset reduction potential of 0.88 V and proceeds predominantly by 4-electron process from oxygen to water. The polarization curves obtained from a PEM fuel cell test at 80 °C revealed that the open circuit potential is around 0.83 V. At voltage of 0.30 V, this fuel cell able to produce a current density of 0.23 A cm⁻² with a maximum MEA power density of 0.070 W cm⁻² [55]. Fig. 17 shows the structure and the CV of heat treated Fe-TPTZ catalyst.

Zhang et al. [56] further investigated the performance of the fuel cell catalyzed by Fe-TPTZ/C using EIS combined with steady-state polarization in the temperature range 23–80 °C. The results showed that the cell performance increases as temperature increases. The EIS measurement could distinguish the individual contributions to cell resistance made by proton transport and reaction kinetics.

The degradation of N₄ macrocycles that occurs during a heat treatment at very high temperatures has opened up an opportunity for researchers to look for alternative methods of producing metal chelate catalysts. One approach has been to produce metal chelates using a method, similar to that just described, using ligands such as TPTX, but without the N₄ macrocycles. For example, the impregnation of a Fe or Co precursor on a mesoporous carbon support which later undergoes a heat treatment in N₂ has successfully created

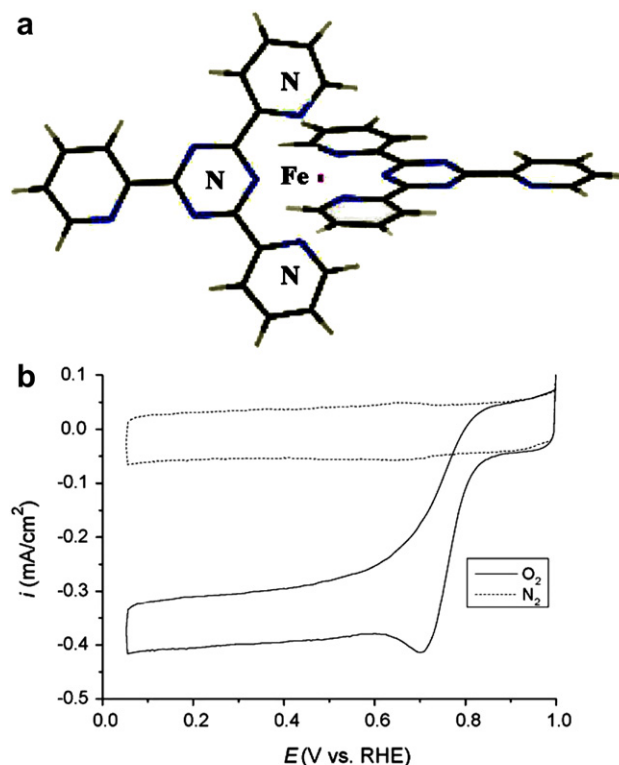


Fig. 17 – (a) The proposed structure of Fe-TPTZ complex and (b) The CV of 800°C heat treated Fe-TPTZ in N₂ and O₂ saturated 0.5 M H₂SO₄. Potential scan rate: 5 mVs⁻¹. Fe-N/C loading in the catalyst layer: 0.10 mg cm⁻² [46].

metal-N ligands that are able to catalyse the ORR. An example of this approach is the catalyst of iron-based N-C investigated by Lefevre et al. [57]. This group reported on a Fe-N-C produced by impregnating iron acetate (FeAc) onto a microporous carbon black that is subsequently pyrolyzed in ammonia (NH₃) thereby creating activated micropores during the treatment that may host catalytic sites. These sites form on carbon with a disordered structure. To capitalize on the high micropore content of microporous carbon blacks and to overcome the limitations resulting from their lack of disordered carbon, a mixture of pore filler and iron precursor was introduced into the micropores. Planetary ball-milling was used to fill in the pore-filler/iron precursor mixture to prevent limitations of solubility and adsorbability normally associated with simple impregnation. Lefevre et al. found that the N-bearing, 1, 10-phenanthroline (phen) pore filler after being pyrolyzed firstly with Ar at 1050 °C and secondly with NH₃ at 950 °C resulted in a very high catalytic activity. With a nominal 1 wt% Fe content, the phen-based catalyst generated 99 A cm⁻³. The achieved volumetric activities were found after the group optimized the mass loss during pyrolysis in NH₃ at $\sim 30\%$ and used a Nafion to catalyst ratio of ~ 1.5 . Note that Lefevre and colleagues are using volumetric activity for ORR because its product with electrode thickness predicts the kinetic current density of the cathode. The latest contribution by this group has almost reached the breakthrough required for practical ORR catalysts but Levi [58] has argued that there

are two major issues with the proposed catalysts. These are insufficient diffusion of oxygen molecules and protons to the catalytic sites and the instability of the catalysts that downgrade with time [58].

The investigation of Fe-based catalyst by Herranz et al. [59] has focused on determining the limit of catalytic activity resulting from either the maximum numbers of available micropores in the support or the maximum number of Fe ions that can be adsorbed on the support. The group used two different precursors; the cations Fe^{2+} [Iron (II) Acetate] and the anions $\text{Fe}(\text{CN})$ [potassium hexacyanoferrate (II)] adsorbed on a carbon black. The carbon support was pyrolyzed in Air (at 550 °C) or NH_3 (950 °C) beforehand. The air- pyrolyzed carbon support possessed carboxylic functionalities that were able to adsorb Fe^{2+} whilst the NH_3 -pyrolyzed carbon contained pyridinic as well as carboxylic functionalities that able to adsorb both Fe^{2+} and $\text{Fe}(\text{CN})$. As a result, they found that the adsorption of Fe ions is not a limiting factor to the ORR activity and rather that the catalytic activity of the catalysts prepared by heat treatment in pure NH_3 is governed mainly by the number of available micropores to host the catalytic sites.

At this point we should mention that most carbons investigated to date for cathode catalysts have been pyrolytic materials of the type used for Pt-metal catalysts. Less work has been done on mesoporous carbons and even less work on catalysts supported by carbon nanotubes (CNT). Exceptions to the latter is the work recently reported by Rao et al. [60] and Geng et al. [61] who have independently synthesized CNTs functionalised with nitrogen. Rao prepared N-CNT composites via template technique using polymer precursors such as polyphenylacetylene (PPA), poly(4-vinylpyridine) (P4VP), poly(3-methylpyrrole)(PMPy), poly(2-methyl-1-vinylimidazole)(PMVI) and poly(p-pyridazine-3,6-diyl) (PPP). Each of these gave rise to a range of nitrogen contents in the subsequent catalyst, and the influence of nitrogen level on the electrochemistry was determined experimentally. The CNT_{PMVI} that contains the surface nitrogen of 8.4 atom %, showed the highest onset potential (0.46 V) among all catalyst in a single reduction peak. Furthermore XPS confirmed that high atom % of pyridinic-type nitrogen functionalities in this catalyst has significantly contributed to a high ORR activity. Gen et al. used a more common chemical vapour deposition method to prepare catalyst in which ethylene which was pyrolysed at 850 °C with ferrocene and different amounts of melamine (a source of nitrogen). XPS showed that between 0.2 at.% and 0.4 at.% Fe was incorporated in all CN_x . As expected the nitrogen content increased in proportion to the amount of melamine added (up to 7.7% N). Increasing the nitrogen shifted the onset potential of the ORR up to +0.705 V vs SHE. Thus both studies have shown that activation by nitrogen significantly increases the activity of the CNT-supported Fe catalyst.

The kinetics and mechanism of the oxygen reduction reaction on Pt catalysts have been studied for several decades [17,19,62–64]. By comparison, the mechanism of the O_2 reduction reaction on non precious metal catalysts is still relatively unclear. It is significant therefore that a study of the mechanism of the ORR on Fe catalysts has been carried out recently by Jaouen and Dodelet [65]. They have examined the experimental rates of O_2 and H_2O_2 electroreduction and H_2O_2 disproportionation produced by Fe-N-C catalyst. A 0.2 wt% Fe

catalyst was prepared by impregnating iron acetate (FeAc) into a non-microporous carbon black (BET area is $71 \text{ m}^2 \text{ g}^{-1}$) which was subsequently heat treated at 950 °C in NH_3 . The catalytic activity of O_2 reduction followed by H_2O_2 disproportionation on the Fe-N-C catalyst was studied using a RDE in H_2SO_4 at pH 1. It turned out that the Fe-N-C catalyst for this study demonstrated that the O_2 reduction proceeds via a direct 4-electron pathway. The percent of H_2O_2 formed on the Fe-N-C catalyst was very low and almost independent of catalyst loading ($50\text{--}960 \mu\text{g cm}^{-2}$) and rotation rate ($100\text{--}1600 \text{ rpm}$). The observations showed a sluggish linear E-I kinetics for the electroreduction of H_2O_2 on the Fe-N-C catalyst. The H_2O_2 disproportionates very slowly to H_2O and $1/2 \text{ O}_2$.

9. Discussion

It is clear from this brief review that several classes of NPM catalysts for PEM fuel cell cathodes have been under intensive investigation for the past 10 years. The NPM materials based on chalcogenides, nitrides and of various carbons have all demonstrated an ability to catalyse the ORR but studies of their electrocatalytic activities have not been reported as widely as those of the macrocyclic NPM catalysts. All candidate materials that have been reviewed are stable in an acidic environment and have the capacity for the charge transfer to take effect. The nature of metal chelates that consist of a central metal atom surrounded by four nitrogen atoms make them unique candidates for non platinum metal cathode catalysts. The use of transition metals (Co- and Fe- are currently favoured) at the centre of N_4 -ligands creates an opportunity for interaction between metal ions and oxygen for ORR. Over the past 10 years researchers have reported a relatively high electrocatalytic activity for Co/Fe-TMPP catalysts as compared to CoTAA and CoPc. The outstanding performance of Co/Fe-TMPP catalysts is believed to be due to the inner ring π -electrons cyclic conjugations of the closed macrocyclic N_4 chelates. To catalyse the oxygen reduction, the central metal ions need empty d_z^2 orbitals for the purpose of bonding the oxygen molecule to the metal ion and at the same time, d_{xz} , d_{yz} orbitals require to be filled or partly filled for attaining back-bonding with the π -electrons of the oxygen [66,67]. These circumstances are well suited to Fe^{2+} , Fe^{3+} and Co^{2+} [68]. There appears to be general agreement that heat treatment of pyrolyzed metal N_4 chelates in an inert atmosphere on high surface area carbon support in the range temperature of 500 °C–900 °C improves the activity and stability of the catalysts. However, the mechanism by which heat treatment affects the catalytic activity of the N_4 macrocycles still remains unclear [69]. Bezerra et al. [70] in a review of Fe-N/C and Co-N/C catalyst for the ORR also emphasized that the heat treatment is one of the factors that affect the activity of the catalyst, but that there are other factors that needs to be taken into consideration in developing highly active catalysts. These include the type of metal precursor and ligands, metal loading, carbon support and also the method of catalyst preparation. From these observations we may conclude that there is still much work to be done to elucidate why N_4 systems do exhibit ORR activity and what can be done to improve catalyst effectiveness either in its preparation or

pretreatment, or in the incorporation of catalyst between the GDL and electrolyte of the PEMF. The latter aspect appears to be significant by its absence from recent literature.

The degradation of macrocyclic structures during heat treatment has inspired the development of remarkable alternatives such Fe- and Co- precursors (metal salts) impregnated on various carbon which are subsequently heat treated in N precursors (N₂, NH₃ or Acetonitril). Catalyst prepared by this method seem to show significant performance in PEM fuel cell environments although research has focused on electrochemical performance rather than long-term activity in working fuel cells. For this reason lifetime has not been established and the real breakthrough has therefore not yet been achieved.

The development of non-precious metal catalysts that are based on a microporous carbon structure in which the metal (Fe) is finely dispersed may lead to material that has high intrinsic reaction kinetics for the oxygen reduction reaction. In this regard, the influence of individual nitrogen precursors may be a significant factor, as may be the structure of the carbon itself. Recent work using carbon nanotubes may hold the key to increasing the dispersion of Fe within the carbon at the nano-scale. If the Fe atoms can be activated by N-functionalised carbons in the same way as N₄ macrocyclics then this could provide substantially improved catalytic activity. At the same time the accessibility of the catalyst sites in carbon nanotubes, to the large oxygen molecule may limit its real effectiveness as a catalyst support and therefore not reduce the high overpotential that continues to limit the performance of PEM fuel cells. Management of the water produced at the cathode/electrolyte surface in materials with a fine pore structure may also be a challenge. The GDL and cathode catalyst layer in PEM fuel cells usually incorporate a hydrophilic material (such as Nafion™) that helps the egress of water produced by the fuel cell and without which the cathode becomes flooded. This has been studied extensively for Pt/C catalyst [71] but the issue of water management from NPM catalysts has yet to be investigated seriously. As with long term catalyst performance, this is something that can only be done by carrying out long term fuel cell tests. Such issues are sure to stimulate further research in the development of non-precious metal catalysts for the PEM fuel cells of the future.

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