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Oxygen Reduction Reaction

Lindiwe Khotseng

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Abstract

In this chapter, the oxygen reduction reaction (ORR), which is one of the most important reactions in energy conversion systems such as fuel cells, including its reaction kinetics, is presented. Recent developments in electrocatalysts for ORR in fuel cells, including low and non-Pt electrocatalysts, metal oxides, transition metal macrocycles and chalcogenides, are discussed. Understanding of the interdependence of size, shape and activity of the electrocatalysts is evaluated. The recent development of ORR electrocatalysts with novel nanostructures is also reported. The mechanism catalysed by these electrocatalysts is presented. Finally, the perspectives of future trends for ORR are discussed.

Keywords: oxygen reduction reaction, electrocatalysts, reaction kinetics, mechanism, novel nanostructures, polymer membrane fuel cells

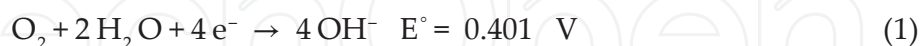
1. Introduction

Oxygen reduction reaction (ORR) has been the subject of extensive investigation over the last century [1]. This is largely because ORR is of major importance to energy conversion, in particular in the field of fuel cells and metal-air batteries [1–3]. ORR is the most important cathodic process in polymer electrolyte membrane fuel cells (PEMFCs) [4]. Among all catalysts evaluated, Pt is still the best catalyst for ORR. The major obstacle with Pt is that it belongs to the platinum group of metals, which are rare metals, hence too expensive for feasible commercialisation of fuel cells. This has led to more research being conducted in an effort to find alternate electrocatalysts that can be used.

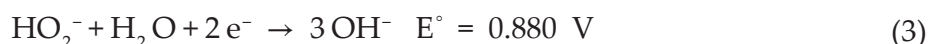
Oxygen reduction in aqueous solutions occurs mainly through two different pathways: either a four-electron reduction pathway from O_2 to H_2O or a two-electron pathway from O_2 to H_2O_2 . The most accepted mechanism of ORR was first proposed by Damjanovic et al. [5, 6]

and later modified by Wroblowa et al. [7], making it easier to understand the complicated reaction pathway of oxygen on the metal surface. They suggest that ORR proceeds along two parallel reaction pathways with rates that are comparable. In PEMFCs, a four-electron transfer is preferred.

The ORR is alkaline media versus reversible hydrogen electrode (RHE) at 25°, and its thermodynamic potentials at standard conditions are presented as follows [3, 8, 9]:

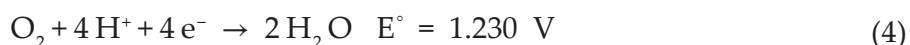


The pathway involving the hydrogen peroxide is expressed as follows [10]:

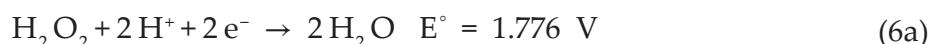


The ORR is acidic media versus RHE at 25°, and its thermodynamic potentials at standard conditions are presented as follows:

Direct four-electron reduction:



Indirect reduction:



Or chemical decomposition:



2. Kinetics of ORR

It is desirable for the ORR to occur at potentials close to thermodynamic potentials as much as possible. For the thermodynamic potentials to be obtained, the charge transfer kinetics of the ORR must be quick. It has been reported that the kinetics of fuel cells at cathode are slow, hence show over-potential η as in Eq. (7) [3, 11]:

$$\eta = E - E_{eq} \quad (7)$$

E is the resultant potential and E_{eq} is the equilibrium potential.

The difference between E and E_{eq} is called polarisation.

There are three distinct types of polarisation expressed in Eq. (8):

$$\eta = \eta_{act} + \eta_{conc} + iR \quad (8)$$

η_{act} is the activation over-potential, a function describing the charge transfer kinetics of an electrochemical reaction. η_{act} is always present and mostly dominant at small polarisation currents.

η_{conc} is the concentration over-potential, a function describing the mass transport limitations associated with electrochemical processes. η_{conc} is predominant at larger polarisation currents.

iR is the ohmic drop. This function takes into account the electrolytic resistivity of an environment when the anodic and cathodic elements of a corrosion reaction are separated by this environment while still electrically coupled.

The graph in **Figure 1** depicts a polarisation curve showing the electrochemical efficiency of a fuel cell.

The expression relating the over-potential, η , and the net current is known as the Butler-Volmer equation and is given as follows [13]:

$$i = i_o \left\{ \exp \left(\beta \frac{nF}{RT} \eta \right) - \exp \left(-[1 - \beta] \frac{nF}{RT} \eta \right) \right\} \quad (9)$$

where i is the ORR current density, i_o is the exchange current density, n is the number of electrons transferred in the rate-determining step, β is the transfer coefficient, β is the

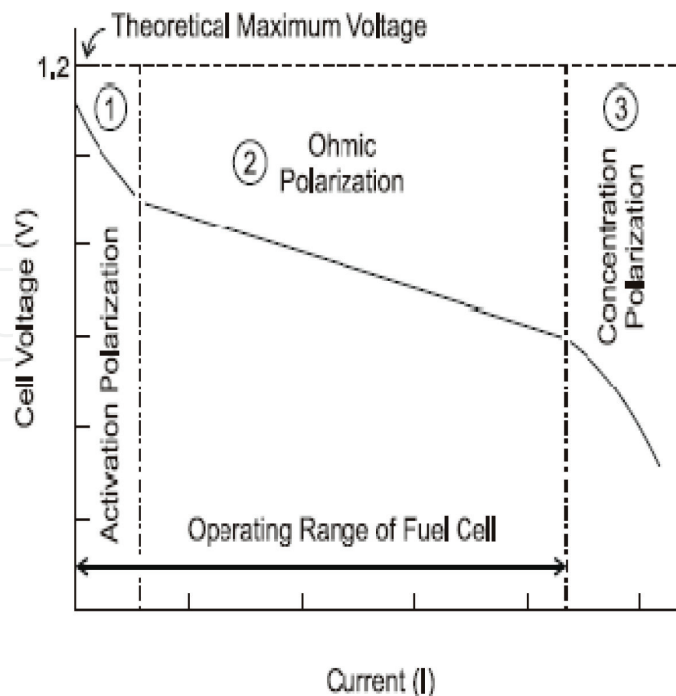


Figure 1. The polarisation curve shows the electrochemical efficiency of the PEMFC at any operating current [12].

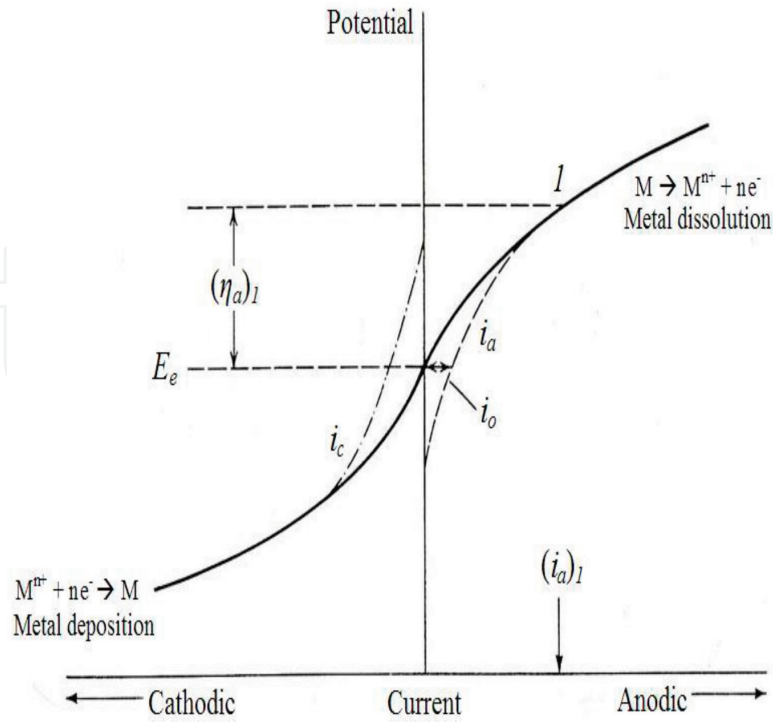


Figure 2. Current-potential relationship of a metal dissolution ($M \rightarrow M^{n+}$)/deposition ($M^{n+} \rightarrow M$) process [13].

over-potential of ORR, F is the Faraday constant, R is the gas constant and T is the temperature in K. The first term in the Butler-Volmer equation represents the anodic reaction/metal dissolution, while the second term represents the cathodic reaction/metal deposition. A plot of the Butler-Volmer equation gives the polarisation curve as shown in **Figure 2**.

There are two limitations in the Butler-Volmer equation.

1. A low over-potential region, also known as polarisation resistance/charge transfer resistance, where the Butler-Volmer equation simplifies to [13]

$$i = i_c = i_o \exp \left\{ (1 - \beta) \frac{nF}{RT} \eta \right\} \quad (10)$$

$$\eta_c = b_c \log \left(\frac{i_c}{i_o} \right) \quad (11)$$

$$b_c = -2.303 \frac{RT}{(1 - \beta)nF} \quad (12)$$

2. At high over-potentials region, the Butler-Volmer equation simplifies to Tafel equation

$$i_a = i_o \exp \left(\beta \frac{nF}{RT} \eta \right) \quad (13)$$

$$\eta_a = b_a \log \left(\frac{i_a}{i_o} \right) \quad (14)$$

$$b_a = 2.303 \frac{RT}{\beta nF} \quad (15)$$

A plot of η versus $\log i_c$ also known as the Tafel plot and gives a linear relationship, with slope $2.303 \frac{RT}{\beta_{\text{H}^+} F}$, known as the Tafel slope and the intercept yielding the i_o . The Tafel slope gives the information about the mechanism of the ORR. The higher the Tafel slope, the faster the over-potential increases with current density. With a low Tafel slope, the electrochemical reaction is able to obtain a high current density, at low over-potential. For ORR, two Tafel slopes, 60 mV dec^{-1} and 120 mV dec^{-1} , respectively, are obtained, depending on the potential range and the electrode material used.

3. Electrocatalysts for ORR

The kinetics of the ORR at the cathode are very important, as they are the factors for the performance of PEMFCs [14, 15]. There are several issues that need to be addressed, including slow reaction kinetics at the cathode, which are due to highly irreversible ORR, and fuel crossover in the cathode, which causes a mixed potential, leading to potential loss and 25% reduction in efficiency, hence reducing the ORR performance [16–19]. An electrocatalyst is used to induce a four-electron reduction of O_2 to water by utilising the protons that permeate from the anode. Pt is the electrocatalyst that is currently used for ORR reactions, as it is the only commercially available catalyst with sensible activity and stability for PEMFCs, although it offers limited commercialisation of fuel cells due to its limited availability and high cost [4, 20]. It is also reported that Pt still shows over-potentials of over 400 mV from the equilibrium reversible potentials (1.19 V at 80°C) [21]. These high potentials result in the formation of adsorbed species on a platinum surface that restrain the ORR and hence result in performance loss [2]. Considerable research has been conducted to try to (1) reduce the costs of fuel cells, which is one of the stumbling blocks in fuel cell commercialisation using low-cost non-Pt catalysts such as supported platinum group metals Pd, Ir and Ru; (2) improve the electrocatalytic activity of the cathode catalyst, which includes using bimetallic alloy catalysts, transition metal macrocyanides, transition metal chalcogenides and metal oxides in order to improve the ORR kinetics on the new catalyst; and (3) fabricate Pt with novel nanostructures such as nanotubes, graphene and carbon nanofibres (CNFs), as it is known that supports may significantly affect the performance of the catalyst. However, these efforts are still in the research stage, as their activity and stability are still lower than that of the Pt catalyst.

3.1. Single-metal catalyst

Other noble metals, such as Pd, Ag, Rh, Ir and Ru, have also been used as cathode materials for ORR [22]. Among these, Pd, which has the same electron configuration and lattice constant as Pt, as they belong to the same row in the periodic table, showed the most improved ORR towards alcohol in an alkaline medium, while it is reported to be inactive in an acid medium [4, 23]. It has been showed that Pd/C is less sensitive to alcohol contamination compared to Pt/C, hence more tolerant to alcohol crossover [16, 24, 25]. However, when comparing the ORR activity of Pd/C to Pt/C, the former has less activity and high potentials of amount 0.8 V versus NHE, hence less stability, which prevents its replacement as the preferred ORR catalyst over Pt/C [26]. The noble metals in terms of ORR activity follow the trend: $\text{Pt} > \text{Pd} > \text{Ir} > \text{Rh}$ [27]. Wang [18] reports that Ru can undergo a four-electron reduction reaction. Ag is reported

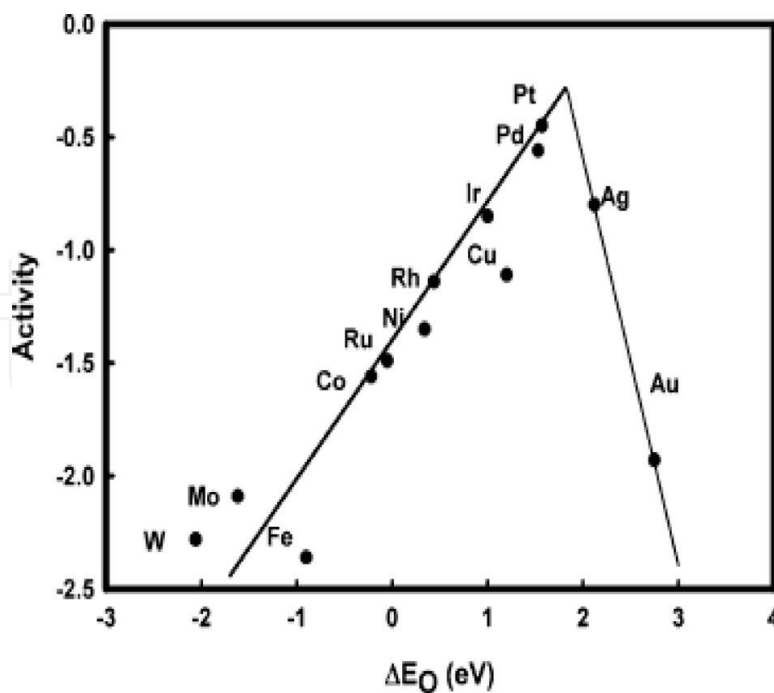


Figure 3. Oxygen reduction activities as a function of oxygen-binding energy [27].

to show less electrocatalytic activity towards ORR compared to Pt, but is more stable than Pt cathodes during long-term operations [4].

There are several metals other than noble metals that were also evaluated as cathode catalysts for ORR. **Figure 3** shows a comparison of the activities of various catalysts as a function of binding energy. These catalysts showed less catalytic activity towards ORR compared to Pt, with less electrochemical stability [28].

3.2. Bimetallic-alloyed catalysts

Transition metals such as Fe, Ni, Co and Cr have been extensively studied due to their improved ORR electrocatalytic activity as alloys for Pt in the presence of a support [17, 28]. Yuan et al. [17] prepared PtFe/C using the impregnation method. Current densities of PtFe/C for ORR in methanol were higher (78.6 mA cm^{-2}) than in Pt/C (65.0 mA cm^{-2}), but was lower in methanol-free solutions, indicating that PtFe/C is a better methanol-tolerant catalyst compared to Pt/C. In terms of power density, the PtFe/C showed an improvement of 20–30% compared to Pt/C [17]. Other researchers [29, 30] also reported better performance of PtFe/C for ORR. Yang et al. [31] report on PtNi/C prepared via the carbonyl complex route an improved mass and specific activity of PtNi/C compared to Pt/C with an improved electrocatalytic activity towards ORR. Pt-Bi/C showed improved methanol tolerance for ORR compared to Pt/C [3]. Remona and Phani [32] synthesised PtBi/C by micro-emulsion. The PtBi/C displayed a higher methanol tolerance compared to mass activity (1.5 times higher) for ORR compared to Pt/C. The high ORR activity of PtBi/C was due to distortion (internal stress) of three Pt sites by Bi.

The effect of Pd on Pt catalysts has been reported by various researchers [33–36], who all reported an improved electrocatalytic activity towards ORR. The improved electrocatalytic activity of Pt alloys has been ascribed to geometric effect, namely a decreased Pt-Pt bond distance, the dissolution of more oxidisable alloying components, a change in surface structure and electronic effect, that is, an increase in Pt d-band vacancy [31, 37]. Other noble metals (Au, Ir, Rh and Ru) were also studied as Pt alloys. PtAu/CNT (carbon nanotubes) was reported to show an improved electrocatalytic activity in an alkaline membrane compared to Pt/CNT [38–40]. Pd-Pt alloy had the highest electrocatalytic activity towards ORR compared to other Pt-alloyed noble metals. Fu et al. [41] report on an improved ORR electrocatalytic activity and a larger diffusion-limiting current density compared to commercial Pd black. The improvement of Pt with noble metals (Pd, Ag and Au) is attributed to these metals having a fully occupied d-orbital. The d-orbital coupling effect between metals decreases the Gibbs free energy for the electron-free steps in ORR, resulting in improved ORR kinetics [37].

Binary Pd catalysts (Cu, Ni, Fe, Co, W and Mo) have been identified as promising cathode catalysts for ORR with an improved electrocatalytic activity and stability compared to Pd alone due to changes in Pd-Pd bond length, modification of the electron configuration and change of surface species and compositions [4, 25]. Kim et al. [42] used PdSn/C as a cathode for direct methanol fuel cells. Their results exhibited a high performance in high methanol concentrations compared to commercial Pt/C. Wang [18] reports on PdCo catalysts tested for ORR. The results showed improved activities towards ORR, with PdCo improvement only observed when less than 20% Co was used. Meng et al. [4] report on PdFe, PdCu, PdAg and PdCo, which all showed an improved electrocatalytic activity compared to Pd alone. In the presence of alcohol, the binary Pd catalysts showed an improved electrocatalytic performance for ORR compared to Pt.

Although bimetallic catalysts (Pt with Fe, Ni, Co, etc.) have shown improvement in the performance of the ORR compared to Pt [27], the lack of preparation methods to control large synthesis has limited its use in commercial devices [33]. In addition, the dissolution of transition metals alloyed in the Pt-M catalyst is a major drawback, because these transition metals are electrochemically soluble at a potential range between 0.3 and 1.0 V versus NHE in acidic media [43].

One possible way to overcome the dissolution of transition metals and improve stability of catalysts is by preparing multi-component catalysts (three and more electrocatalyst alloys). The multi-component catalysts are able to shift the d-band centre by a strain effect (caused by the lattice mismatch in the multi-component system) and lower the adsorption energy of surface oxygenated intermediates, thereby enhancing the surface catalytic activity.

Tiwari et al. [37] report on various multi-component catalysts that have been synthesised over the years with either Pt or Pd, including PtTiM (M = Co, Cr, Cu, Fe, Mn, Mo, Ni, Pd, Ta, V, W and Za), PtCuCo, PtCoSe₂, PtIrCo, PdFePt, PtCuCoNi, PdSnPt and PdCoPt. From the multi-component catalysts, they reported an improved electrocatalytic activity towards ORR compared to pure Pt and the possibility of reducing the costs of the electrocatalysts for PEMFCs.

More research is also done on trying to improve the kinetics of Pt catalysts through the development of new and the optimisation of existing synthesis methods that can control the shape and surface structure of the electrocatalyst in order to improve its performance [8, 33, 44, 45]. There has been contrasting reports on particle size and specific activity. Some researchers report a decrease in specific activity with a decrease in particle size, while other researchers report an increase in specific activity with a decrease in particle size. The discrepancy may be the result of different electrocatalysts with different shapes and degree of agglomeration [46]. It has been reported that metallic nanostructures with different shapes display unique chemical and physical properties [47]. Significant progress has been made for size-controlled spherical nanostructures, but only limited progress has been made with non-spherical nanostructures, which are reported to show more improved ORR electrocatalytic activity for fuel cells compared to spherical-shaped electrocatalysts, the reason being that the highly symmetric face-centred cubic crystal structure of Pt-based catalysts makes it not easy to obtain a non-spherical shape, which involves a competition over the desire to minimise the surface energy through the formation of thermodynamically stable spherical shapes. Hao et al. [48] report that cubic Pd nanocrystals exhibit better performance in methanol compared to the spherical Pd catalyst of a similar size. The improvement was attributed to cubic nanocrystals that contain a more electroactive surface area compared to its spherical counterpart. It has also been reported that Pt electrocatalysts with a tetrahedral shape showed much improved reaction kinetics compared to the spherical Pt nanoparticles. It has been reported that low-index crystal planes give poor electrocatalytic properties, while high-index planes give a high electrocatalytic activity and stability [47, 49]. Pt nanocubes have been reported to have much improved specific activity for ORR compared to commercial Pt catalysts (spherical) [47, 50]. Kuai et al. [50] report on uniform, high-yield icosahedral Ag and Au nanoparticles prepared using a hydrothermal system in the presence of polyvinylpyrrolidone and ammonia. The prepared Au and Ag nanoparticles showed an improved ORR electrocatalytic activity and excellent stability compared to spherical Pt/C nanoparticles.

The form or shape of the electrocatalysts depends on the synthesis method and the various parameters used. **Figure 4** shows the formation of various forms of Pt nanocubes using different strategies based on the polyol method [47]. The formation of Pt tubes can be obtained through two different routes, either galvanic displacement or using selected templates [47]. Researchers have synthesised metal nanoparticles with various shapes [32].

Researchers are reporting an improved electrocatalytic activity of ORR using various synthesis methods focusing on surface structure. Lim et al. [14] report on the synthesis of Pt/C using the modified polyol method using ethylene glycol as the reducing agent. The prepared catalyst had the highest mass activity, which was 1.7 times higher than the commercial Pt/C [14]. The improvement was attributed to small and uniform particle size and better dispersion. Adonisi et al. [51] report on various Pt-based catalysts synthesised using the Bonnemenn method. Some of those catalysts showed an improved ORR electrocatalytic activity compared to commercial Pt/C. **Figure 5** shows a graph depicting 20% Pt/C commercial compared to 20% Pt/C synthesised catalysts using the Bonnemenn method. From the graph, it can be observed that the 20% Pt/C commercial catalyst was found at lower current densities than the prepared 20% Pt/C catalyst. The mass activities of the 20% Pt/C commercial and 20% Pt/C prepared catalysts were found to be 12.6 and 15.8 A/g, respectively, and the specific activities were

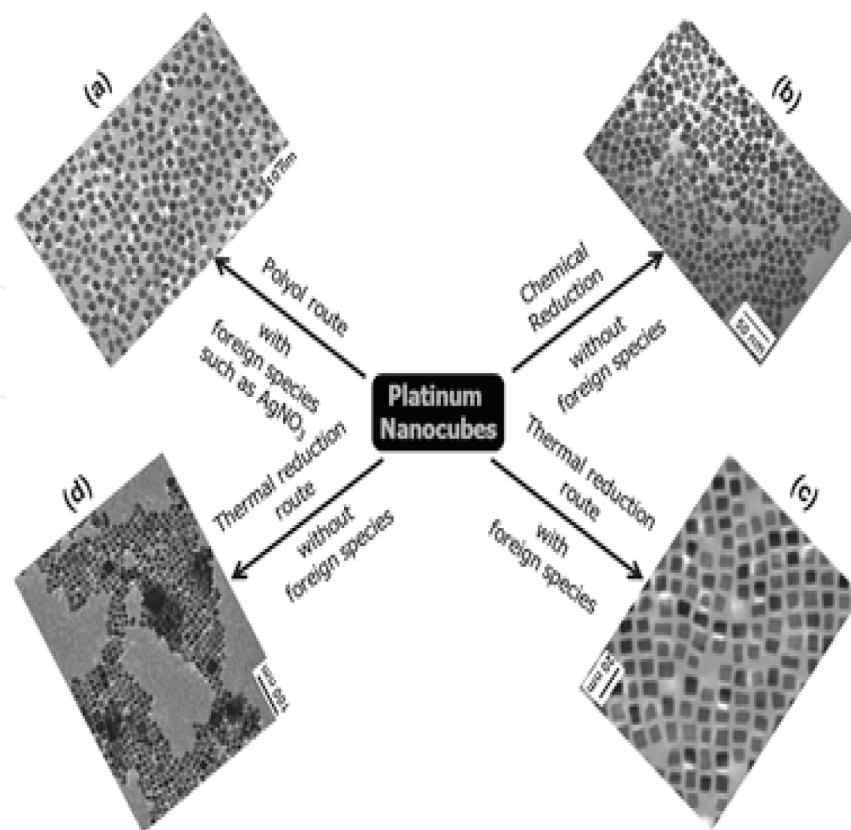


Figure 4. Different routes for the synthesis of Pt nanocubes along with their electron micrographs [47].

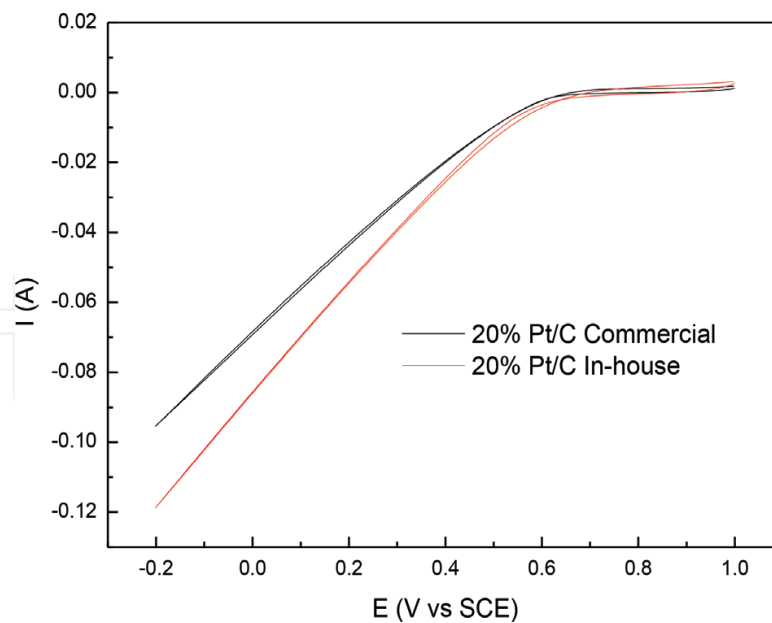


Figure 5. Cyclic voltammograms for ORR of 20% Pt/C commercial and prepared electrocatalysts in O_2 -saturated 0.5 M H_2SO_4 at a scan rate of 20 mV [51].

found to be 0.060 and 0.063 A cm^{-2} , respectively. This improvement was attributed to the particle size of the prepared catalysts, which was smaller than the particle size for the commercial Pt/C catalyst.

Post-treatment after synthesis has been reported to change the physicochemical properties of the electrocatalysts. Heat treatment is considered as one of the important and sometimes necessary steps to improve the activity of the catalysts [52]. Heat treatment involves heating the catalyst under inert (N_2 , Ar or He) or reducing H_2 atmosphere in the temperature range of 80–900°C for 1–4 h [52]. The benefit of heat treatment is the removal of impurities resulting from the preparation stages, allowing uniform dispersion and stable distribution of the catalyst on the support, thereby improving the electrocatalytic activity of the prepared catalyst. It has been determined that the electrocatalytic reduction of oxygen on the catalyst can be influenced by the particle size and surface structure, and hence treatment can have an effect on ORR activity and stability by altering the surface structure of the catalyst [32]. Various researchers have worked on heat treatment of mono and bimetallic catalysts for ORR [50]. They all concluded that heat treatment improves alloying of the catalysts, which decreases the Pt-Pt distance and hence d-band vacancy of the Pt and thus improves the electroactivity of the catalyst [53]. Jeyabharathi et al. [54] report on improved methanol tolerance of PtSn/C after heat treatment, while the ORR activity remained intact. Sarkar et al. report on PdW synthesised using thermal composition followed by annealing at 800°C with an improved electrocatalytic activity for ORR and catalyst durability with an improved methanol tolerance compared to Pt [32].

3.3. Transition metal macrocycles and chalcogenides

Transition metals such as macrocycles and chalcogenides have been used as ORR catalysts since the 1960s due to their inactivity towards the oxidation of methanol [55]. Other than noble metals, they are the most-studied electrocatalysts for oxygen reduction. The study of ruthenium chalcogenides Ru_xSe_y and Pt for ORR has shown that the performance of Ru_xSe_y is slightly weaker than Pt and that the difference was their behaviour in the presence or absence of methanol. Under these conditions, the electroactivity of Ru_xSe_y is not changed, while for Pt, the potential shifts to the negative direction (120–150 mV). A similar behaviour was observed when Ru_xSe_y was embedded in a polymetric matrix, such as polyaniline. RuSM (M = Rh, Re, Mo, etc.) when used as catalysts, methanol oxidation on the cathode was suppressed or avoided leading to a reduced mixed potential. The results confirm that the chalcogenide of Ru is insensitive to methanol, in contrast to the Pt catalyst [56]. The main concern with this approach was the low power output due to low activity of these catalysts for ORR, compared to the Pt catalyst [17]. Cobalt and iron phthalocyanide are the most-studied transition metals as centres for macrocycling rings as catalysts for ORR in fuel cells [56, 57]. These ORR catalysts have shown that a number of metal chelates will chemisorb oxygen [58]. A fuel cell with an iron phthalocyanide cathode can only be stable for up to 10 h [17], but has shown improved activity towards ORR in alkaline media [44]. Zagal et al. [59] report that when Fe chelates with N_4 , a four-electron ORR occurs. Co phthalocyanide has demonstrated similar ORR kinetics as commercial Pt/C, as it also leads to a four-electron process per oxygen molecule, that is, to water, but at lower potentials (0.25 and –0.25 versus RHE) [44, 56]. However, these compounds are not completely stable under strong acid conditions [17, 56]. They decompose via hydrolysis in the electrolyte and attack the macrocyanide via peroxide, causing poor performance and stability [58, 60, 61]. Transition metal chalcogenides are more stable and show an improved electrocatalytic activity at temperatures above 800°C.

3.4. Metal oxides

Another route to stabilising nanoparticles is the development of metal oxide composite supports. Metal oxides such as IrO_2 , NiO , CeO_2 , ZrO_2 , TiO_2 and SnO_2 have also been studied as ORR catalysts in basic acidic media [62–66]. Nanoparticles on metal oxides are not able to improve the electrocatalytic activity due to their limited electron conductivity, but are reported to have excellent corrosion resistance in various electrolyte media [66, 67]. Researchers use metal oxides in combination with carbon supports that have desirable properties such as a high surface area and a high electric conductivity. The metal oxides combined with carbon supports are reported to improve the stability and the electrocatalytic activity of the electrode material. Carbon surfaces are functionalised before they are used as supports for catalysts in order to improve their surface properties, but the disadvantage of functionalisation is that it accelerates the degradation process of the support material. The presence of the metal oxide delays the corrosion process. Montero-Ocampo et al. [68] report on PtTiO_2 and $\text{PtTiO}_2/\text{CNT}$ synthesised using metal organic chemical vapour deposition. The $\text{PtTiO}_2/\text{CNT}$ was more electrocatalytically active compared to PtTiO_2 , while good stability was observed for both PtTiO_2 and $\text{PtTiO}_2/\text{CNT}$ that was provided by the TiO_2 support. This was attributed to the high conductivity of CNT compared to TiO_2 , which has limited electron conductivity. $\text{Pt}/\text{TiO}_2/\text{C}$ showed improvement in activity and thermal stability for ORR compared to Pt/C [69]. Khotseng et al. [70] compared the activity for PtRu/TiO_2 to commercial PtRu/C and Pt/C . They reported a high electroactive surface area and activity of commercial Pt/C and PtRu/C compared to PtRu/TiO_2 towards ORR. When durability studies were performed for the same catalysts, the PtRu/TiO_2 recorded a loss of 29% compared to Pt/C and PtRu/C , which recorded a loss of 64 and 32%, respectively. Li et al. [71] reported an improved oxygen reduction activity, a better durability and a higher methanol tolerance capability in alkaline solution compared to Pt/C .

Most metal oxides were found to be unstable in acidic media. To overcome this instability, conducting polymer polypyrrole (Ppy) was used against the dissolution of metal oxides. During synthesis, the metal oxides were sandwiched between the Ppy layers. Through this research, an improved electrochemical stability of the metal oxides was achieved [18]. Singh et al. [72] report on CoFe_2O_4 oxides sandwiched between Ppy layers. A high electrocatalytic activity towards ORR at high cathodic potentials was obtained with stability in acidic media [72].

3.5. Novel nanostructures with electrocatalysts

Although Pt-based catalysts have been widely studied due to their high current density and low over-potential, when used as cathode catalysts, their activity is lowered due to slow reaction kinetics. More research is required to try to improve the catalyst activity. One of the focus areas is looking into loading Pt nanostructures with a high activity on the surface of supporting materials with (1) low cost, (2) good electrical conductivity, (3) strong catalyst-support interaction that is influenced by its surface functionalities to limit the possible deactivation of the electrocatalyst and allow for efficient charge transport, (4) large surface area and (5) good resistance to corrosion to allow high stability [8, 22, 24, 73–75]. Carbon black (CB) is the most-used support for Pt and Pt alloy catalysts. CB is thermochemically unstable and hence suffers from corrosion, leading to performance degradation and durability issues and high potential

[66, 76]. Nanostructured carbon materials, for example, mesoporous carbon, CNFs, CNTs and graphene, have been studied extensively as support materials for electrocatalysts, as they have been identified as some of the most promising materials for PEMFCs due to their high chemical stabilities, high electric conductivities and improved mass transport capabilities [32, 77].

CNTs are attractive support materials in fuel cell applications and are by far the most-explored carbon nanostructures as catalyst supports in fuel cells due to their excellent mechanical strength, a high surface area and a high electric conductivity and because they have reported to show an improved catalytic activity [22, 32, 78] compared to CB. The carbon surface is functionalised to provide oxygen-binding groups for the growth of metal catalyst ions [79]. CNTs can be single-walled (SWCNT) or multi-walled (MWCNT), depending on the structure. Both SWCNT and MWCNT have been used as support materials to disperse the electrocatalyst and have been reported to show an enhanced electrocatalytic activity towards ORR. SWCNTs have unique electrical and electronic properties, a wide electrochemical stability and high surface areas [9]. When compared to commercial Pt/C (from ETEK) in acidic media, the SWCNT showed an improved electrocatalytic activity performance, with the negative shift of onset potential by 10 mV compared to Pt/C, whose onset potential moved to a higher potential by 15 mV [15, 73]. Jukk et al. [80] report on Pd/MWCNT having an enhanced electrocatalytic activity compared to Pd/C for ORR. Wang et al. [81] reported on Pt/MWCNT, which showed an improved electrocatalytic activity for ORR compared to Pt/C. Khotseng et al. [70] compared PtRu/MWCNT with commercial Pt/C, PtRu/C and prepared PtRu/TiO₂ and PtRu/MoO₂. From **Figure 6** and **Table 1**, it is observed that PtRu/MWCNT has the highest mass and specific activity at 0.9 V compared to commercial Pt/C, PtRu/C and prepared PtRu/TiO₂ PtRu/MoO₂ with the highest current density towards ORR.

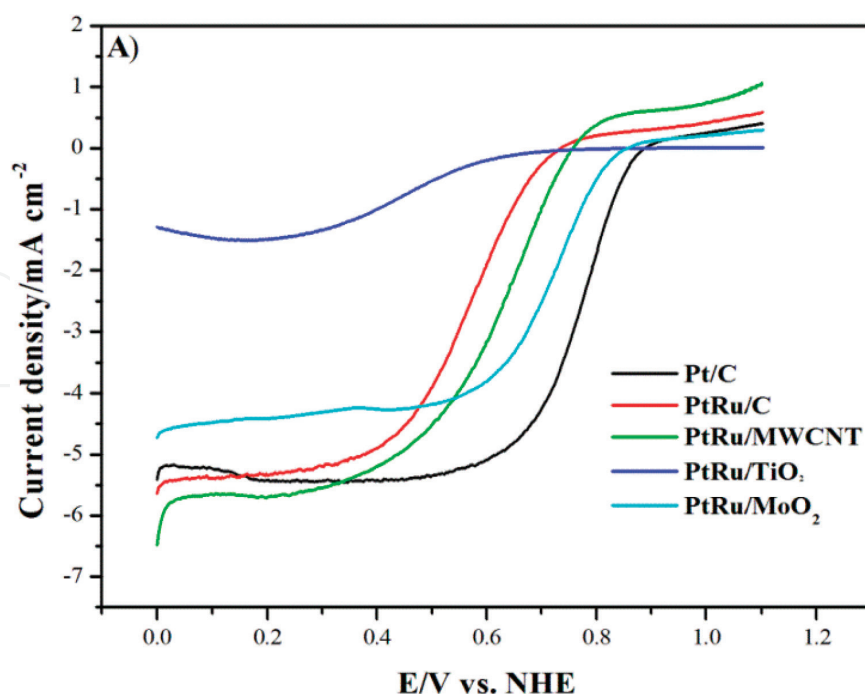


Figure 6. ORR polarisation curves of PtRu/MWCNT compared to Pt/C, PtRu/C, PtRu/TiO₂ and PtRu/MoO₂ commercial catalysts in O₂-saturated 0.1 M HClO₄ at 20 mV/s and 1600 rpm [70].

Catalyst	ORR catalytic activity at 0.9 V	
	MA (mA mg ⁻¹)	SA (mA cm ⁻²)
Pt/C	85.85	0.188
PtRu/C	463	1.66
PtRu/MWCNT	35.6 × 10 ³	111
PtRu/TiO ₂	18.94	1.04
PtRu/MoO ₃	997	17.82

Table 1. Studying the activity of electrocatalysts towards ORR in comparison with commercial Pt/C, PtRu/C and PtRu/TiO₂.

The two main functionalities are oxygen, namely carboxyl (—COOH), hydroxyl (—OH) and carbonyl (—C=O), and nitrogen groups. Modified CNTs with nitrogen functional groups have been reported to show a much improved electrocatalytic activity towards ORR through forming thermally stable structures during heat treatment [82, 83]. Nitrogen is known to efficiently create defects on carbon materials, which might increase the edge plane exposure and thus improve the ORR activity [29]. Ghosh and Raj [84] report on an improved electrocatalytic activity towards ORR for N-doped CNTs. Wang et al. [85] report on a sponge-like nitrogen containing carbon with a high electrocatalytic ORR activity compared to commercial Pt/C with a considerably higher methanol tolerance. One distinct advantage offered by CNTs is their high resistance towards corrosion compared to CB, and hence they have an enhanced electrochemical stability compared to CB [66, 84].

CNFs have been reported to show an improved electrocatalytic activity towards ORR compared to CB [66]. Yang et al. [86] report on an improved electrocatalytic activity for ORR for Pd/CNF. The biggest difference between CNTs and CNFs is their exposure of active edge planes. For CNTs, the basal planes are exposed, while for CNFs, edge planes are exposed [66].

Graphene and graphene oxide (GRO) have also been investigated as another support material for electrocatalysts in fuel cells due to their high electron transfer rate, a large surface area and a high conductivity [64]. When compared to CNTs, they have a higher surface area and a similar electric conductivity for electrochemical applications and can also be produced at a lower cost compared to CNTs [21]. In graphene, both basal and edge planes interact with the electrocatalysts, while for CNTs, only basal planes are exposed [66]. A surface built up only of basal planes is said to have a homogeneous surface, while a surface built up of both basal and edge planes is said to have a heterogeneous surface. Heterogeneous surfaces are reported to better stabilise the metal in a highly dispersed state. It has been reported that Pd/GRO shows a better ORR activity and forms a four-electron oxygen-reduction process compared to Pt [87–89]. N-doped graphene has been reported to show an improved electrocatalytic activity towards ORR compared to graphene in acidic and alkaline media [90]. Lu et al. [91] report a superior electrocatalytic activity of N-GRO compared to GRO. The fast electron transfer rate of graphene can particularly facilitate ORR much quicker in fuel cells [66].

Other nanostructured carbon supports such as mesoporous carbon, carbon nanocoils and carbon aerogel have also been used as support material for cathode catalysts and have been reported to show an improved ORR electrocatalytic activity [76].

Although carbon supports have been reported to show an improved ORR electrocatalytic activity, carbon oxidation or corrosion due to the presence of O_2 and/or high electrode potential has been identified as one of the major causes of failure for PEMFC degradation [67]. Non-carbon supports such as electrically conducting polymers, for example, polyaniline, Ppy and mesoporous silica, have also been used as supports to improve the stability of the electrode materials. Shurma and Pollet [66] and Wang et al. [67] report on various non-carbon supports for electrocatalysts for fuel cells. However, it is reported that with non-carbon supports, no major breakthrough has been achieved as yet [66].

3.6. Anion exchange membranes

ORR is also studied in alkaline media using anion exchange membranes (AEMs) [92]. The significant reason for the change in electrolyte membrane from acid to alkaline is the improved electrokinetics of ORR in alkaline [93]. Pd is emerging as an alternative catalyst compared to Pt in alkaline. It is reported that more ORR catalysts are available for alkaline solutions compared to acidic solutions, due to excessive corrosion in acidic media. Pt/C in basic media is said to enhance ORR towards alcohol [94, 95], while non-Pt catalysts also showed an improved ORR when employed. In addition, in alkaline media, Pt/C is more tolerant to alcohol crossover due to its inactivity in alcohol oxidation reaction. Pd alloys are reported to be comparable or slightly better than Pt/C [4]. Kim et al. reported on PdSn using anion exchange membrane (AEM) which showed an improved ORR electrocatalytic activity with a high methanol tolerance compared to commercial Pt/C tested in proton exchange membrane [42]. He and Cairns [96] report on various electrocatalysts for ORR in AEM.

4. Mechanisms for ORR in the presence of an electrocatalyst

Oxygen reduction on Pt is one of the most extensively studied mechanisms [3]. It involves a multi-electron process with a number of elementary steps, involving different reaction intermediates. The mechanism can be shown schematically as follows [97] (Figure 7).

From the mechanism, only two products are observed with ORR on Pt, either H_2O , which can directly form through a four-electron reduction with the rate constant k_1 , or adsorbed hydrogen peroxide ($H_2O_{2,ads}$), which is through a two-electron process with the rate constant k_2 , which can be reduced further by another two-electron process to form water with rate

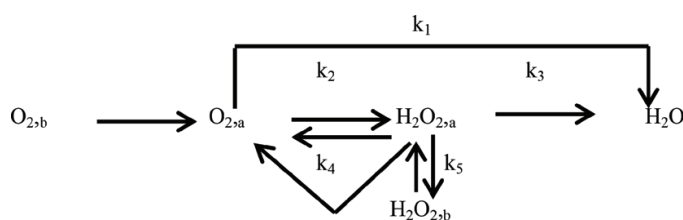


Figure 7. A simplified schematic pathway of oxygen reduction reaction for both acidic and alkaline media [7].

constant k_3 , or be chemically decomposed on the electrode surface (k_4), or be desorbed in the electrolyte solution (k_5). For ORR in fuel cells, the direct four-electron process is required.

Oxygen reduction on a Pt catalyst in acid media occurs via dissociative adsorption of O_2 followed by the protonation of the adsorbed species, with the former being the rate-determining step [55].

The main steps in the mechanism of ORR are given subsequently. One is known as dissociative mechanism for a low current density range and the other associative mechanism for a high current density range:

Dissociative mechanism:



In this mechanism, no H_2O_2 is formed. On the Pt surface, the O_2 adsorption breaks the $O-O$ bond and forms adsorbed atomic O with further gain of two electrons, in the two consecutive steps, forming H_2O . Because there is no adsorption of O_2 on the surface, no H_2O_2 can be formed. This mechanism can be considered as the direct four-electron reduction reaction.

Associative mechanism:



In this mechanism, no H_2O_2 is involved as well. Because there is adsorbed O_2 on the surface, $O-O$ may not be broken down in the following steps, resulting in the formation of H_2O_2 , which can be reduced further to form water.

Pt shows two Tafel slope regions. At a high potential, low current density (>0.8 V), the electrode surface is a mixture of Pt and PtO with the Tafel slope of 60 mV dec^{-1} and the reaction order 0.5 with respect to pH in alkaline media. The fractional reaction order was represented in terms of the first electrochemical step as a rate-determining step under the Temkin isotherm, that is, the adsorption of reaction intermediates O_{ads} , OH_{ads} and HO_{2ads} [98, 99].

The rate expression under Temkin conditions of adsorption is

$$j = k [O_2] [H^+]^{1/2} \exp [-\eta F/RT] = 374 k [O_2] [OH^-]^{1/2} \exp [-\eta F/RT] \quad (24)$$

where k is the rate constant and η is the over-potential.

At a low potential, high current density (<0.8 V), the electrode surface is a pure Pt with the Tafel slope of 120 mV dec^{-1} and the reaction order 0 with respect to pH in alkaline media, with H_2O as the reacting species. The adsorption of intermediate species to a Langmuir isotherm under Temkin conditions no longer holds.

The rate expression under Langmuir conditions is

$$j = k [\text{O}_2] \exp [-\beta \eta F/RT] \quad (25)$$

where β is the symmetry factor.

The reaction is of the first order with respect to O_2 in solutions. It was found that the H_2O_2 formed was greater in an alkaline solution than in an acidic one [4, 94]. In alkaline solutions, about 80% of the reduction current is through the direct reduction and the other current forms H_2O_2 , which leads to a complicated mechanism.

Various models representing the adsorbed states of oxygen are represented in **Figure 8**.

Figure 8(a) is known as the bridge model. It is a 2:2 complex of metal oxygen where the bonding arises from the interaction between the d-orbital on the metal with a Π^* and Π orbital combination on O_2 [101]. This gives rise to a singlet or a triplet nature of di-oxygen orbitals

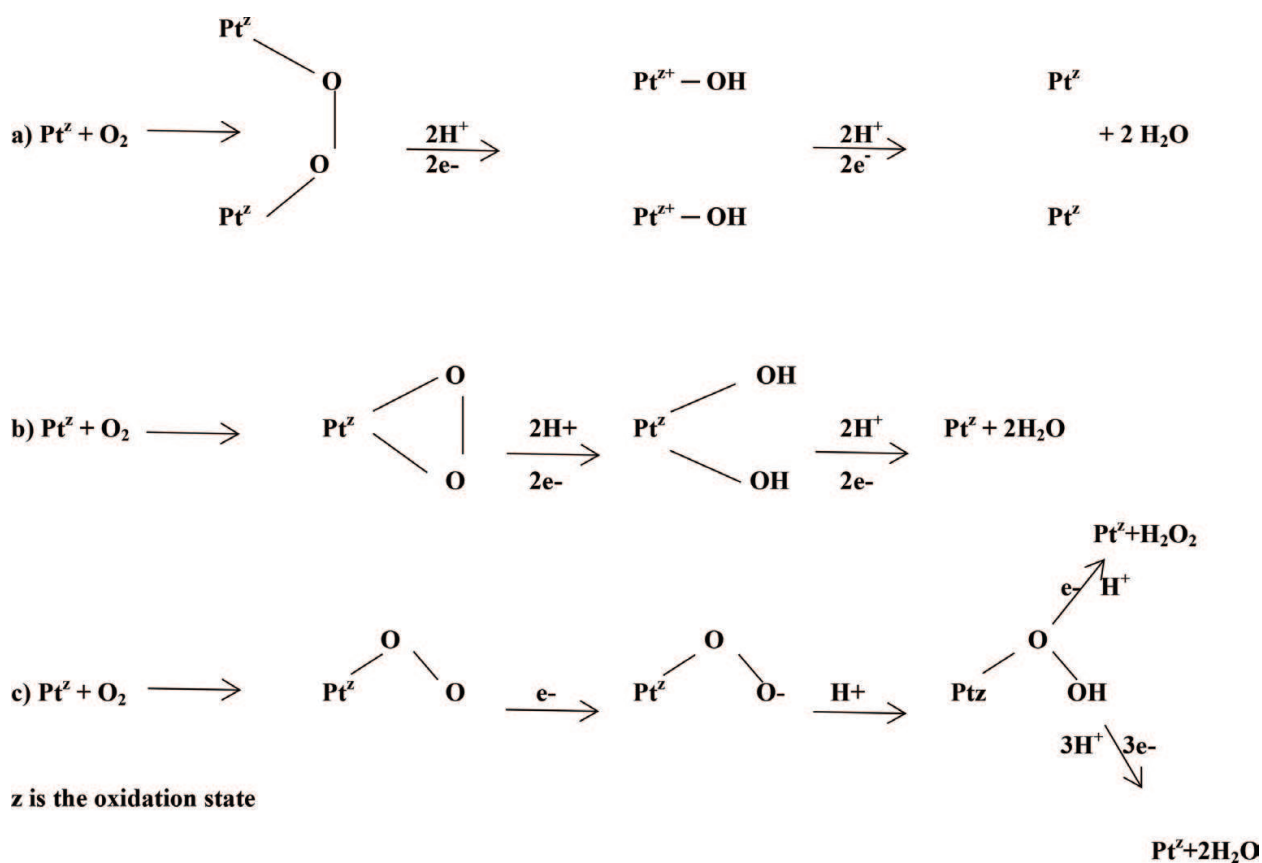


Figure 8. Oxygen reduction on Pt from the (a) bridge model, (b) Griffiths model and (c) Pauling model [100].

and determines the bridge or a transmode of interaction of di-oxygen with the metal [101]. **Figure 8(b)** is known as the Griffiths model. It is a 2:1 metal-di-oxygen complex structure, which involves a side on the interaction of oxygen with metal. This type of bonding can be viewed as rising from two contributions: (1) σ -type bonding is formed by overlapping between the Π orbitals of oxygen and the d_z^2 orbitals on the metal; (2) Π back-bond interaction between the metal d Π orbitals and partially occupied Π^* antibonding orbital on O_2 arises [102]. **Figure 8(c)** is known as the Pauling model. It is a 1:1 metal-oxygen complex structure, which is an end-on interaction of O_2 with metal. In this model, the σ bond is formed by the donation of electron density from the σ -rich orbital of di-oxygen to the acceptor d_z^2 orbital on the metal. The metal's two d -orbitals, namely d_{xz} and d_{yz} , then interact with the Π^* orbitals of di-oxygen, with the corresponding charge transfer from the metal to the O_2 molecule. The Griffiths and Pauling models are the preferred models due to the donating abilities of the filled Π and σ orbitals of the di-oxygen molecule, respectively [103].

5. Conclusion

ORR has a huge role to play in fuel cell development. Comparing the ORR electrocatalytic activity of Pt with other single metals, Pt shows the most improved electrocatalytic activity, but its large-scale applications are limited by its high cost and scarcity. The addition of a second metal to a metal electrocatalyst decreases its particle size (large surface area), which leads to an increased lattice strain and hence an increased electrocatalytic activity [28]. It has been concluded that multi-component catalysts improve ORR activity, although it is not conclusive on which multi-catalyst shows the most improved ORR activity, as various researchers report on different multi-component catalysts as the most improved. Although improvement has been obtained, the Pt loading required is still too high to produce PEMFCs at commercially viable prices [22]. The transition metal phthalocyanine is offering reasonable performance as an ORR catalyst, although it suffers from lack of long-term stability.

The challenge remaining is optimising the synthesis method in order to control the shape and the surface structure of especially non-spherical electrocatalysts, which are reported to show the most improved ORR electrocatalytic activity with most stable electrocatalysts, while they contribute to the lowering of Pt usage and hence cost reduction of the PEMFC.

Catalyst support is one of the critical components in improving the electrocatalytic activity of PEMFCs, as they are responsible for parameters that govern the performance of the fuel cell, that is, particle size, catalyst dispersion and stability [8]. Comparison of the carbon supports, CNTs and graphene supports provides considerable advantages concerning mass and charge transport. The disadvantage of using these supports is the costs [25]. In addition, the deposition, distribution and crystallite size of metal nanoparticles are affected by the synthesis method and oxidation treatment of carbon supports.

Using an alkaline medium, Pt-free nanoparticles can be used as electrocatalysts for fuel cells, with a reduced alcohol crossover, an improved ORR kinetics and limited risks of corrosion.

Recently, research has been focused on using AEMs. The main advantage of using AEM fuel cells over PEMFCs is that it allows for the use of less expensive, Pt-free electrocatalysts. AEM fuel cells promise to solve the cost barriers of PEMFCs.

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Conflict of interest

I have no conflict of interest to declare.

Nomenclature

AEM	anion exchange membrane
CB	carbon black
CNF	carbon nanofibre
CNT	carbon nanotube
GRO	graphene oxide
MWCNT	multi-walled carbon nanotube
NHE	normal hydrogen electrode
ORR	oxygen reduction reaction
PEMFC	polymer electrolyte membrane fuel cell
Ppy	polypyrrole
RHE	reversible hydrogen electrode
SWCNT	single-walled carbon nanotube

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