We are IntechOpen, the world’s leading publisher of Open Access books
Built by scientists, for scientists

6,500 Open access books available
177,000 International authors and editors
195M Downloads

154 Countries delivered to
TOP 1% Our authors are among the most cited scientists
12.2% Contributors from top 500 universities

WEB OF SCIENCE™
Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com
Chapter 2

Oxygen Reduction Reaction

Lindiwe Khotseng

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.79098

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 chalogenides, 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 \( \text{O}_2 \) to \( \text{H}_2\text{O} \) or a two-electron pathway from \( \text{O}_2 \) to \( \text{H}_2\text{O}_2 \). 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]:

$$\text{O}_2 + 2 \text{H}_2\text{O} + 4 \text{e}^- \rightarrow 4 \text{OH}^- \quad E^\circ = 0.401 \text{ V} \quad (1)$$

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

$$\text{O}_2 + \text{H}_2\text{O} + 2 \text{e}^- \rightarrow \text{HO}_2^- + \text{OH}^- \quad E^\circ = 0.080 \text{ V} \quad (2)$$

$$\text{HO}_2^- + \text{H}_2\text{O} + 2 \text{e}^- \rightarrow 3 \text{OH}^- \quad E^\circ = 0.880 \text{ V} \quad (3)$$

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

Direct four-electron reduction:

$$\text{O}_2 + 4 \text{H}^+ + 4 \text{e}^- \rightarrow 2 \text{H}_2\text{O} \quad E^\circ = 1.230 \text{ V} \quad (4)$$

Indirect reduction:

$$\text{O}_2 + 2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2\text{O}_2 \quad E^\circ = 0.680 \text{ V} \quad (5)$$

$$\text{H}_2\text{O}_2 + 2 \text{H}^+ + 2 \text{e}^- \rightarrow 2 \text{H}_2\text{O} \quad E^\circ = 1.776 \text{ V} \quad (6a)$$

Or chemical decomposition:

$$2 \text{H}_2\text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{O}_2 \quad E^\circ = 1.776 \text{ V} \quad (6b)$$

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 $\eta$ 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):

$$\eta = \eta_{act} + \eta_{conc} + iR$$  \hspace{1cm} (8)

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

$\eta_{conc}$ is the concentration over-potential, a function describing the mass transport limitations associated with electrochemical processes. $\eta_{conc}$ 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, $\eta$, and the net current is known as the Butler-Volmer equation and is given as follows [13]:

$$i = \dot{i}_o \left\{ \exp \left( \beta \frac{nF}{RT} \eta \right) - \exp \left( -[1-\beta] \frac{nF}{RT} \eta \right) \right\}$$  \hspace{1cm} (9)

where $i$ is the ORR current density, $\dot{i}_o$ is the exchange current density, $n$ is the number of electrons transferred in the rate-determining step, $\beta$ is the transfer coefficient, $\beta$ is the

![Figure 1](http://dx.doi.org/10.5772/intechopen.79098)
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]

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

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

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

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

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

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

$$b_a = 2.303 \frac{RT}{\beta nF}$$ (15)
A plot of $\eta$ versus log $i_c$ also known as the Tafel plot and gives a linear relationship, with slope $2.303 \frac{RT}{\beta nF}$ known as the Tafel slope and the intercept yielding the $i_0$. 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: Pt > Pd > Ir > Rh [27]. Wang [18] reports that Ru can undergo a four-electron reduction reaction. Ag is reported
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 contracting 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]. Kuan et al. [50] report on uniform, high-yield icosaedral 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 Bonnemann 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 Bonnemann 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
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.

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$_2$SO$_4$ at a scan rate of 20 mV [51].
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 (N₂, Ar or He) or reducing H₂ 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 RuSeₙ and Pt for ORR has shown that the performance of RuSeₙ 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 RuSeₙ is not changed, while for Pt, the potential shifts to the negative direction (120–150 mV). A similar behaviour was observed when RuSeₙ was embedded in a polymeric 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 macrocyclizing 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 N₄, 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 PtTiO$_2$/CNT synthesised using metal organic chemical vapour deposition. The PtTiO$_2$/CNT was more electrocatalytically active compared to PtTiO$_2$, while good stability was observed for both PtTiO$_2$ and PtTiO$_2$/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. Pt/TiO$_2$/C showed improvement in activity and thermal stability for ORR compared to Pt/C [69]. Khotseeng 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$_2$O$_4$ 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
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/TiO$_2$ and PtRu/MoO$_2$. 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/TiO$_2$, PtRu/MoO$_2$ with the highest current density towards ORR.

![Figure 6](image_url)

*Figure 6*. ORR polarisation curves of PtRu/MWCNT PtRu/MWCNT compared to Pt/C, PtRu/C PtRu/TiO$_2$ and PtRu/MoO$_2$ commercial catalysts in O$_2$-saturated 0.1 M HClO$_4$ at 20 m V/s and 1600 rpm [70].
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].

### Table 1.

| Catalyst          | 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\(_2\)    | 997                  | 17.82                |

The study of the activity of electrocatalysts towards ORR in comparison with commercial Pt/C, PtRu/C and PtRu/TiO\(_2\).
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\textsubscript{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\textsubscript{2}O, which can directly form through a four-electron reduction with the rate constant k\textsubscript{1}, or adsorbed hydrogen peroxide (H\textsubscript{2}O\textsubscript{2,ads}), which is through a two-electron process with the rate constant k\textsubscript{2}, which can be reduced further by another two-electron process to form water with rate constant k\textsubscript{3}. The simplified schematic pathway of oxygen reduction reaction for both acidic and alkaline media is shown in Figure 7.

![Figure 7. A simplified schematic pathway of oxygen reduction reaction for both acidic and alkaline media](source)
constant $k_0$ or be chemically decomposed on the electrode surface ($k_0$), or be desorbed in the electrolyte solution ($k_d$). 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:**

$$1/2O_2 + Pt \rightarrow PtO$$  \hspace{1cm} (16)

$$PtO + H^+ + e^- \rightarrow Pt - OH$$  \hspace{1cm} (17)

$$Pt - OH + H^+ + e^- \rightarrow H_2O + Pt$$  \hspace{1cm} (18)

In this mechanism, no $H_2O_2$ is formed. On the Pt surface, the $O_2$ adsorption breaks the $O\equiv O$ 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:**

$$O_2 + 2Pt \rightarrow Pt_2O_2$$  \hspace{1cm} (19)

$$Pt_2O_2 + H^+ + e^- \rightarrow Pt_2 - O_2H$$  \hspace{1cm} (20)

$$Pt_2 - O_2H \rightarrow Pt - OH + Pt - O$$  \hspace{1cm} (21)

$$Pt - OH + Pt - O + H^+ + e^- \rightarrow Pt - OH + Pt - OH$$  \hspace{1cm} (22)

$$Pt - OH + Pt - OH + 2H^+ + 2e^- \rightarrow 2Pt + 2H_2O$$  \hspace{1cm} (23)

In this mechanism, no $H_2O_2$ is involved as well. Because there is adsorbed $O_2$ on the surface, $O\equiv O$ 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 $O_{ad}$, $OH_{ad}$, and $HO_2_{ad}$ [98, 99].

The rate expression under Temkin conditions of adsorption is

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

where $k$ is the rate constant and $\eta$ 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$_2$O 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

$$j = k \left[ O_2 \right] \exp \left[ -\beta \eta F/RT \right]$$

(25)

where $\beta$ is the symmetry factor.

The reaction is of the first order with respect to O$_2$ in solutions. It was found that the H$_2$O$_2$ 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$_2$O$_2$, 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 $\Pi^*$ and $\Pi$ orbital combination on O$_2$ [101]. This gives rise to a singlet or a triplet nature of di-oxygen orbitals
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 \( d^2 \) 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 \( d^2 \) 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.

Acknowledgements

I thank ESKOM (TESP), NRF (THUTHUKA), Ithemba Labs, Physics Department (UWC), Chemical Engineering Department (UCT) and Chemistry Department (UWC).

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

Author details

Lindiwe Khotseng

Address all correspondence to: lkhotseng@uwc.ac.za

Department of Chemistry, University of the Western Cape, South Africa
References

[1] Liu B, Bard AJ. Scanning electrochemical microscopy. 45. Study of the kinetics of oxygen reduction on platinum with potential programming on tip. Journal of Physical Chemistry B. 2002;106(49):12801-12806. DOI: 10.1021/jp026824f

[2] Song C, Zhang J. Electrocatalytic oxygen reduction reaction. In: Zhang J, editor. PEM Fuel Cell Electro催化剂: Fundamentals and Applications. London: Springer; 2008. pp. 89-134. DOI: 10.1007/978-1-84800-936-3

[3] Raghuveer V, Kumar K, Viswanathan B. Nanocrystalline lead ruthenium pyrochlore as oxygen reduction electrode. Indian Journal of Engineering and Material Science. 2002;9:137-140

[4] Meng H, Zeng D, Xie F. Pd based electrocatalysts for proton exchange membrane fuel cells. Catalysts. 2015;5:1221-1274. DOI: 10.3390/catal5031221

[5] Damjanovic A, Genshaw MA, Bockris JOM. The mechanism of oxygen reduction at platinum in alkaline solutions with special reference to H₂O₂. Journal of the Electrochemical Society. 1967;114:1107-1112. DOI: 10.1149/1.2426425

[6] Damjanovic A, Sepa DB, Vojnovic MV. New evidence supports the proposed mechanism of O₂ reduction at oxide free platinum-electrodes. Electrochimica Acta. 1979;24:87-89. DOI: 10.1016/0013-4686(79)87013-9

[7] Wroblowa HS, Pan YC, Razumney G. Electro-reduction of oxygen: A new mechanistic criterion. Journal of Electroanalytical Chemistry. 1976;69(2):195-201. DOI: 10.1016/S0022-0728(76)80250-1

[8] Ozoemen KI. Nanostructured platinum free electrocatalysts in alkaline direct alcohol fuel cells: Catalyst design, principles and applications. RCS Advances. 2016;6:89523-89549. DOI: 10.1039/C6RA15057H

[9] Yuan XZ, Song C, Wang H, Zhang J. EIS diagnosis for PEM fuel cell performance. In: Electrochemical Impedance Spectroscopy in PEM Fuel Cells: Fundamentals and Applications. London: Springer; 2010. pp. 193-262. DOI: 10.1007/978-1-84882-845-2

[10] Roquet L, Belgsir EM, Léger JM, Lamy C. Kinetics and mechanisms of the electrocatalytic oxidation of glycerol as investigated by chromatographic analysis of the reaction products: Potential and pH effects. Electrochimica Acta. 1994;39:237-2394. DOI: 10.1016/0013-4686(94)E0190-Y

[11] Corrosion: Impact, Principles and Practical Solutions. What is Overpotential [Internet]. 1999. Available from: http://corrosion-doctors.org/Corrosion-Kinetics/Overpotential-definition.htm [Accessed: 2018-01-06]

[12] Fuel Cell Technology. Hydrogen Fuel Cell Engines and Related Technologies [Internet]. 2001. Available from: https://energy.gov/sites/prod/files/2014/03/f9/fcm00r0.pdf [Accessed: 2018-12-28]
[13] Corrosion for Engineers. Corrosion current. [Internet]. 2005. Available from: https://can-teach.candu.org/Content%20Library/20053213.pdf [Accessed: 2018-01-6]

[14] Lim B, Kim JW, Hwang SJ, Yoo SJ, Cho EA, Lim TH, Kim SK. Fabrication and characterization of high activity Pt/C electrocatalysts for oxygen reduction. Bulletin of the Korean Chemical Society. 2010;31(6):1577-1582. DOI: 10.5012/bkcs.2010.31.6.1577

[15] Kongkanand A, Kuwabata S, Girishkumar G, Kamat P. Single wall carbon nanotubes supported platinum nanoparticles with improved electrocatalytic activity for oxygen reduction reaction. Langmuir. 2006;22(5):2392-2398. DOI: 10.1021/la052122g

[16] Yu EH, Kremer U, Scott UK. Principles and materials aspects of direct alkaline alcohol fuel cells. Energies. 2010;3:1499-1528. DOI: 10.3390/en3081499

[17] Yuan W, Scott K, Cheng H. Fabrication and evaluation of Pt-Fe alloys as methanol tolerant cathode materials for direct methanol fuel cells. Journal of Power Sources. 2006;163:323-329. DOI: 10.1016/j.jpowsour.2006.09.005

[18] Wang B. Recent developments of non-platinum catalysts for oxygen reduction reaction. Journal of Power Sources. 2005;152. DOI: 10.1016/j.jpowsour.2005.05.098

[19] Modibedi RM, Mathe MK, Motsoeneng RG, Khotse L, Ozoemena KI, Louw EK. Electro-deposition of Pd on carbon paper and Ni foam via surface limited redox replacement reaction for oxygen reduction reaction. Electrochimica Acta. 2014;128:406-411. DOI: 10.1016/j.electacta.2013.11.062

[20] Wang XM, Wang ME, Zhou DD, Xia YY. Structural design and facile synthesis of a highly efficient catalyst for formic acid electro-oxidation. Physical Chemistry Chemical Physics. 2011;13:13594-13597. DOI: 10.1039/C1CP21680E

[21] Thompsett D. Catalysts for proton exchange membrane fuel cell. In: Hoogers G, editor. Fuel Cell Technology Handbook. Taylor & Francis Group: CRC Press LLC; 2003. p. 6.1-6.23

[22] Choi HJ, Jung SM, Seo JM, Chang DW, Dai L, Baek JB. Graphene for energy conversion and storage in fuel cells and supercapacitors. Nano. 2012;1:534-551. DOI: 10.1016/j.nanoen.2012.05.001

[23] Nishanth KG, Sridhar P, Pitchumani S, Shukla AK. Carbon supported Pt-Pd alloy as methanol-tolerant-oxygen-reduction electrocatalyst for DMFC. ECS Transactions. 2010;28(23):273-281. DOI: 10.1149/1.3502358

[24] Motsoeneng RG, Modibedi RM, Mathe MK, Khotse L, Ozoemena KI. The synthesis of PdPt/carbon paper via surface limited redox replacement reactions for oxygen reduction reaction. International Journal of Hydrogen Energy. 2015;40:16734-16744. DOI: org/10.1016/j.ijhydene.2015.08.060

[25] Li W, Zhao X, Manthiram A. Room temperature synthesis of Pd/C cathode catalysts with superior performance of direct methanol fuel cell. Journal of Materials Chemistry A. 2014;2:3468-3476. DOI: 10.1039/C3TA14193D
[26] Antolini E. Effect of structural characteristics of binary palladium-cobalt fuel cell catalysts on the activity for oxygen reduction. ChemPlusChem. 2014;79:765-775. DOI: 10.1002/cplu.201402034

[27] Norskov JK, Rossmeis L, Logadotir A, Lindqvist L, Kitchin JR, Bligaard T. Origin of the overpotential for oxygen reduction at a fuel cell cathode. Journal of Physical Chemistry B. 2004;108:17886-17892. DOI: 10.1021/jp047349j

[28] Antolini E. Palladium in fuel cell catalysis. Energy and Environmental Science. 2009;2:915-931. DOI: 10.1039/B820837A

[29] Li W, Xin Q, Yan Y. Nanostructured Pt-Fe/C cathode catalysts for direct methanol fuel cell: The effect of catalyst composition. International Journal of Hydrogen Energy. 2010;35:25-30. DOI: 10.1016/j.ijhydene.2010.01.013

[30] Zhang Z, Li M, Wu Z, Li W. Ultra-thin PtFe-nanowires as durable electrocatalysts for fuel cells. Nanotechnology. 2011;22:15602 (5 pp). DOI: 10.1088/0957-4484/22/1/015602

[31] Yang H, Vogel W, Lamy C, Alonso-Vante N. Structure and electrocatalytic activity of carbon supported Pt-Ni alloy nanoparticles toward the oxygen reduction reaction. Journal of Physical Chemistry B. 2004;108(30):11024-11034. DOI: 10.1021/jp049034

[32] Remona AM, Phani KLN. Study of methanol tolerant oxygen reduction reaction at Pt/Bi/C bimetallic nanostructured catalysts. Fuel Cells. 2011;11(3):385-393. DOI: 10.1002/fuce.201000082

[33] Lim B, Jiang M, Camargo PHC, Cho EC, Tao J, Lu X, Zhu Y, Xia Y. Pd-Pt bimetallic nanodendrites with high activity for oxygen reduction. Science. 2009;324:1302-1305. DOI: 10.1126/science.1170377

[34] Paulus UA, Wokaun A, Scherer GG, Schmidt TJ, Stamenkovic V, Markovic NM, Ross PN. Oxygen reduction on high surface area Pt based alloy catalysts in comparison to well defined bulk alloy electrodes. Electrochimica Acta. 2002;47(22-23):3787-3798. DOI: 10.1016/S0013-4686(02)00349-3

[35] Zhang J, Vukmirovic MB, Klie R, Sasaki K, Adzic RR. Platinum monolayer electrocatalysts for O2 reduction: Pt monolayer on Pd (111) and on carbon supported Pd nanoparticles. Journal of Physical Chemistry B. 2004;108:10955-10964. DOI: 10.1021/jp0379953

[36] Chang SH, Su WN, Yeh MH, Pan CJ, Yu GK, Liu DG, Lee JF, Hwang BJ. Structural and electronic effects of carbon supported Pt/Pd nanoparticles on the electrocatalytic activity of the oxygen reduction reaction and on methanol tolerance. Chemistry — A European Journal. 2010;16(36):11064-11071. DOI: 10.1002/chem.201000458

[37] Tiwari JN, Tiwari RN, Singh G, Kim KS. Review: Recent progress in the development of anode and cathode catalysts for direct methanol fuel cells. Nano Energy. 2013;2(5):553-578. DOI: 10.1016/j.nanoen.2013.06.009

[38] Xu JB, Zhao TS, Li YS, Yang WW. Synthesis and characterization of the Au modified Pd cathode catalyst for alkaline direct ethanol fuel cells. International Journal of Hydrogen Energy. 2010;35:9693-9700. DOI: 10.1016/j.ijhydene.2010.06.074
[39] Xu JB, Zhao TS, Yang WW, Shen SY. Effect of surface composition of Pt-Au alloy cathode catalyst on the performance of direct methanol fuel cells. International Journal of Hydrogen Energy. 2010;35:8699-8706. DOI: 10.1016/j.ijhydene.2010.05.008

[40] Kim Y, Hong JW, Lee YW, Kim M, Kim D, Yun WS, Han SW. Synthesis of AuPt heteronanostructures with enhanced electrocatalytic activity toward oxygen reduction. Angewandte Chemie International Edition. 2010;49:10197-10201. DOI: 10.1002/anie.201005839

[41] Fu G, Liu Z, Chen Y, Lin J, Tang Y, Lu T. Synthesis and electrocatalytic activity of Au@Pd core-shell nanothorns for the oxygen reduction reaction. Nano Research. 2014;7(8):1205-1214. DOI: 10.1021/nr400544p

[42] Kim J, Momma T, Osaka T. Cell performance of Pd-Sn catalysts in passive direct methanol alkaline fuel cell using anion exchange membrane. Journal of Power Sources. 2009;189:999-1002. DOI: 10.1016/j.jpowsour.2008.12.108

[43] Stassi AD, Urso C, Baglio V, Di Blasi A, Antonucci V, Arico AS. Electrocatalytic behaviour for oxygen reduction reaction of small nanostructured crystalline bimetallic Pt-M supported catalysts. Journal of Applied Electrochemistry. 2006;36:1143-1149. DOI: 10.1007/s10800-006-9197-9

[44] Elzing A, Van der Putten A, Visscher W, Barendrecht E. The cathodic reduction of oxygen at cobalt phthalocyanine. Influence of electrode preparation on electrocatalysis. Journal of Electroanalytical Chemistry. 1986;200:313-322. DOI: 10.1016/0022-0728(86)90063-X

[45] Greeley J, Stephens IEL, Bondarenk AS, Johansson TP, Hansen HA, Jaramillo TF, Rossmeissl J, Chorkendorff I, Norskov JK. Alloys of platinum and early transition metals as oxygen reduction electrocatalysts. Nature Chemistry. 2009;1:552-556. DOI: 10.1038/nchem.367

[46] Shao M, Peles A, Shoemaker K. Electrocatalysis on platinum nanoparticles: Size effect on oxygen reduction reaction activity. Nano. 2011;11:3714-3719. DOI: 10.1021/nl2017459

[47] Subbaramananna M, Pillai VK. Shape dependent electrocatalytic activity of Pt nanostructures. Journal of Materials Chemistry. 2008;18:5858-5870. DOI: 10.1039/B811149A

[48] Hao D, Xue-Zhao S, Cheng-Min S, Chao H, Chuan X, Chen L, Yuan T, Deng-Ke W, Hong-Jun G. Synthesis on monodisperse palladium nanocubes and their catalytic activity for methanol electro-oxidation. Chinese Physics B. 2010;19:106104 (3pp). DOI: 10.1088/1674-1056/19/10/106104

[49] Narayanan R, El-Sayed MA. Shape dependent catalytic activity of platinum nanoparticles in colloidal solution. Nano Letters. 2004;4:1343-1348. DOI: 10.1021/nl0495256

[50] Kuai L, Geng B, Wang S, Zhao Y, Luo Y, Jiang H. Silver and gold icosahedra one-pot water-based synthesis and their superior performance in the electrocatalysis for oxygen reduction reactions in alkaline media. Chemistry—A European Journal. 2011;17:3482-3489. DOI: 10.1002/chem.201002949

[51] Adonis T. Electrochemical characterization of platinum based catalysts for fuel cell applications [thesis]. Bellville: University of the Western Cape; 2012
[52] Bezerra CWB, Zhang L, Marques ALB, Zhang J. A review of heat treatment effect on activity and stability of PEM fuel cells for oxygen reduction reaction. Journal of Power Sources. 2007;173:891-908. DOI: 10.1016/j.jpowsour.2007.08.028

[53] Koh S, Strasser P. Electrocatalysis on bimetallic surfaces modifying catalytic reactivity of oxygen reduction by voltammetric surface dealloying. Journal of the American Chemical Society. 2007;129:12624-12625. DOI: 10.1021/ja0742784

[54] Jeyabharathi C, Venkateshkumar P, Mathiyasaraj J, Phani KLN. Platinum-tin bimetallic nanoparticles for methanol tolerant oxygen-reduction activity. Electrochimica Acta. 2008;54(2):448-454. DOI: /10.1016/j.electacta.2008.07.053

[55] Easton EB. Chemical modification of fuel cell catalysts and electrochemistry of proton exchange membrane fuel cell electrode [thesis]. St. John’s: Memorial University of Newfoundland; 2003

[56] Lamy A, Lima V, LeRhun F, Delime C, Coutanceau C, Leger JM. Recent advances in the development of direct alcohol fuel cells (DAFC). Journal of Power Sources. 2002;105:283-296. DOI: 10.1016/S0378-7753(01)00954-5

[57] Martin LG. Synthesis and characterization of Pt-Sn/C cathode catalysts via polyl reduction method for use in direct methanol fuel cell [thesis]. Bellville: University of the Western Cape; 2013

[58] Jahnke H, Schonbron M, Zimmerman G. Organic dyestuffs as catalysts for fuel cells. In: Boschke FL, editor. Physical and Chemical Applications of Dye Stuff. 61. Berlin: Springer-Verlag; 1976. pp. 133-181. DOI: 10.1007/BFb0046059

[59] Zagal J, Bindra P, Yeager E. A mechanistic study of O₂ reduction on water soluble phthalocyanines adsorbed on graphite electrodes. Journal of the Electrochemical Society. 1980;127:1506-15017. DOI: 10.1149/1.2129940

[60] Lefèvre M, Proietti E, Jaouen F, Dodelet JP. Iron based catalysts with improved oxygen reduction activity in polymer electrolyte fuel cells. Science. 2009;324:71-74. DOI: 10.1126/science.1170051

[61] Zhong HX, Zhang HM, Liu G, Liang YM, Hu JW, Yi BL. A novel non-noble electrocatalyst for oxygen reduction in proton exchange membrane fuel cells. Electrochemistry Communications. 2006;8:707-712. DOI: 10.1016/j.jpowsour.2006.11.080

[62] Matsuki K, Kamada H. Oxygen reduction electrocatalysis on some manganese oxides. Electrochimica Acta. 1986;31:13-18. DOI: 10.1016/0013-4686(86)80054-8

[63] Chang CC, Wen TC, Tien HJ. Kinetics of oxygen reduction at oxide derived Pd electrodes in alkaline solution. Electrochimica Acta. 1997;42:557-565. DOI: 10.1016/S0013-4686(96)00195-8

[64] Vago ER, Calvo EF. Oxygen electro-reduction on iron oxide electrodes: iii. Heterogenous catalytic H₂O₂ decomposition. Journal of Electroanalytical Chemistry. 1995;388:161-165. DOI: 10.1016/0022-0728(95)03860-J
[65] Kim J, Ishihara A, Mitsushima S, Kamiya N, Ota K. Catalytic activity of titanium oxide for oxygen reduction reaction as a non-platinum catalyst for PEFC. Electrochimica Acta. 2007;52:2492-2497. DOI: 10.1016/j.electacta.2006.08.059

[66] Shurma S, Pollet BG. Review: Support materials for PEMFC and DMFC electrocatalysts. Journal of Power Sources. 2012;208:96-119. DOI: 10.1016/j.jpowsour.2012.02.011

[67] Wang YJ, Wilkinson DP, Zhang J. Review: Noncarbon support materials for polymer electrolyte membrane fuel cell electrocatalysts. Chemical Reviews. 2011;111(12):7625-7651. DOI: 10.1021/cr100060r

[68] Montero-Ocampo C, Garcia JRV, Estrada EA. Comparison of TiO₂ and TiO₂-CNT as cathode catalyst supports for ORR. International Journal of Electrochemical Science. 2013;8:12780-11280

[69] Ruiz-Camacho B, Valenzuela MA, Alonso-Vante N. The effect of metal oxide-carbon support on electrocatalysts for fuel cell reactions. World Journal of Engineering. 2002:973-974

[70] Khotseng L, Bangisa B, Mobedi M, Linkov V. Electrochemical evaluation of Pt based binary catalysts on various supports for direct methanol fuel cells. Electrocatalysis. 2016;7:1-12. DOI: 10.1007/s12678-015-0282-x

[71] Li J, Zhou H, Zhuo H, Wei Z, Zhuang G, Zhong X, Deng S, Lia X, Wang J. Oxygen vacancies on TiO2 promoted the activity and stability of supported Pd nanoparticles for the oxygen reduction reaction. Journal of Materials Chemistry A. 2018;6:2264-2272. DOI: 10.1039/C7TA09831F

[72] Singh RN, Lal B, Malyiya M. Electrocatalytic activity of electrodeposited composite of polypyrrole and CoFe₂O₄ nanoparticles towards oxygen reduction reaction. Electrochimica Acta. 2004;49:4605-4612. DOI: 10.1016/j.electacta.2004.05.015

[73] Usgaocar AR, Chong Harold MH, De Groot CH. Modulation of carbon nanotube metal contacts in gaseous hydrogen environment. Journal of Nanoscience. 2014:1-7. DOI: 10.1155/2014/404519

[74] Villiers D, Sun SH, Serventi AM, Dodelet JP, Dsilets S. Characterization of Pt nanoparticles deposited onto carbon nanotubes grown on carbon paper and evaluation of this electrode for the reduction of oxygen. Journal of Physical Chemistry B. 2006;110(51):25916-25925. DOI: 10.1021/jp065923g

[75] Khotseng L. Electrocatalysts for direct methanol fuel cells. In: Merhandez R, Dunning C, editors. Direct Methanol Fuel Cells: Applications, Performance and Technology. Hauppauge: Nova Science Publishers; 2017. pp. 1-50

[76] Yaldagard M, Jahanshahi M, Seghatoleslami N. Carbonaceous nanostructured support materials for low temperature fuel cell electrocatalysts. World Journal of Nanoscience and Engineering. 2013;3:121-153. DOI: 10.4236/wjne.2013.34017

[77] Li D, Lv H, Kang Y, Markovic NM, Vojislav R. Progress in the development of oxygen reduction reaction catalysts for low-temperature fuel cells. Annual Review of Chemical Biomolecular Engineering. 2016;7:509-532. DOI: 10.1146/annurev-chembioeng-080615-034526
[78] Xing Y. Synthesis and electrochemical characterization of uniformly dispersed high loading of Pt nanoparticles on sonochemically treated carbon nanotubes. Journal of Physical Chemistry B. 2004;108(51):19255-19259. DOI: 10.1021/jp046697i

[79] Sevjidsuren G, Zils S, Kaserer S, Wolz A, Ettingshausen F, Dixon D, Schoekel A, Roth C, Altantsog P, Sangaad D, Ganzorig CH. Effect of different support morphologies and Pt particle sizes in electrocatalysts for fuel cell application. Hindawi Publishing Cooperation, Journal of Nanomaterials. 2010:Article ID 852786 (9 pp). DOI: 10.1155/2010/0852786

[80] Jukk K, Alexeyeva N, Johans C, Kontturi K, Tammeveski K. Oxygen reduction on Pd nanoparticle/multi-walled carbon nanotube composites. Journal of Electroanalytical Chemistry. 2012;666:67-75. DOI: doi.org/10.1016/j.jelechem.2011.12.003

[81] Wang S, Jiang SP, White TJ, Guo J, Wang X. Electrocatalytic activity and interconnectivity of Pt nanoparticles on multi-walled carbon nanotubes for fuel cells. Journal of Physical Chemistry C. 2009;113:18935-18945. DOI: 10.1021/jp906923z

[82] Nagaiah TC, Kundu S, Bron M, Muhler M, Schumann W. Nitrogen doped carbon nanotubes as a cathode catalyst for the oxygen reduction reaction in alkaline medium. Electrochemistry Communications. 2010;12:338-341. DOI: 10.1016/j.elecom.2009.12.021

[83] Gong K, Du F, Xia Z, Durstock M, Dai L. Nitrogen doped carbon nanotube arrays with high electrocatalytic activity for oxygen reduction. Science. 2009;323:760-763. DOI: 10.1126/science.1168049

[84] Ghosh S, Raj CR. Facile in situ synthesis of multiwall carbon nanotube supported flower-like Pt nanostructures: An efficient electrocatalyst for fuel cell application. Journal of Physical Chemistry C. 2010;114:10843-10849. DOI: 10.1021/jp100551e

[85] Wang H, Wang W, Key J, Ji S, Ma Y, Khoetseng L, Lv W, Wang R. Sponge like carbon containing nitrogen and iron provides a non-precious oxygen reduction catalyst. Journal of Solid State Electrochemistry. 2005;19(4):1181-1186. DOI: 10.1007/s1000

[86] Yang W, Yang S, Guo J, Sun G, Xin Q. Comparison of CNF and XC-72 carbon supported platinum catalysts for direct methanol fuel cell. Carbon. 2007;45(2):397-401. DOI: 10.1016/j.carbon.2006.09.003

[87] Goth K, Kawabata K, Fujii E, Morishige K, Kinumoto T, Miyazaki Y, Ishida H. The use of graphite oxide to produce mesoporous carbon supporting Pt, Ru or Pd nanoparticles. Carbon. 2009;47(8):2120-2124. DOI: 10.1016/j.carbon.2009.03.052

[88] Du SF, Lu YX, Steinberger-Wilckens R. PtPd nanowire arrays supported on reduced graphene oxide as advanced electrocatalysts for methanol oxidation. Carbon. 2014;79:346-353. DOI: 10.1016/j.carbon.2009.03.052

[89] Kou R, Shao YY, Wang J, Wu H, Liu J, Akasay IA, Lin Y. Enhanced activity and stability of Pt catalysts on functionalized graphene sheets for electrocatalytic oxygen reduction. Electrochemistry Communications. 2009;11:954-957. DOI: 10.1016/j.elecom.2009.02.033

[90] Osmieria L, Pezzolatob L, Specchia S. Recent trends on the application of PGM-free catalysts at the cathode of anion exchange membrane fuel cells. Current Opinion in Electrochemistry. 2018;4:9-25. DOI: 10.1016/j.coelec.2018.05.011
[91] Lu ZJ, Xu MW, Bao SJ, Tan K, Chai H, Ji CC, Chang Q, Cai CJ. Facile preparation of nitrogen-doped reduced graphene oxide as a meta-free catalyst for oxygen reduction reaction. Journal of Materials Science. 2013;48(23):8101-8107. DOI: 10.1007/s10853-013-7622-0

[92] Jurzinsky T, Cremers C, Jung F, Pinkwart K, Tubke J. Development of materials for anion exchange membrane direct alcohol fuel cells. International Journal of Hydrogen Energy. 2015;40(35):11569-11576. DOI: 10.1016/j.ijhydene.2015.02.056

[93] Rivera LM, Gonzalo G, Pastor E. Novel graphene materials for the oxygen reduction reaction. Current Opinion in Electrochemistry. 2018;18:23-29. DOI: 10.1016/j.coelec.2018.05.009

[94] Damjanovic A, Genshaw MA, Bockris JOM. The role of hydrogen peroxide in oxygen reduction at platinum in H$_2$SO$_4$ solution. Journal of the Electrochemical Society. 1967;114:466-472. DOI: 10.1149/1.2426629

[95] Maa L, He H, Hsu A, Chen R. PdRu/C catalysts for ethanol oxidation in anion-exchange membrane direct fuel cells. Journal of Power Sources. 2013;241:696-702. DOI: 10.1016/j.jpowsour.2013.04.051

[96] He Q, Cairns J. Review: Recent progress in electrocatalysts for oxygen reduction suitable for alkaline anion exchange membrane fuel cells. Journal of the Electrochemical Society. 2015;162(14):F1504-F1539. DOI: 10.1149/2.055151es

[97] Hsueh LK, Gonzalez ER, Srinivasan S, Chin DT. Effects of phosphoric acid on oxygen reduction kinetics at platinum. Journal of the Electrochemical Society. 1984;131(4):823-828. DOI: 10.1149/1.2115707

[98] Damjanovic A, Brusci V. Electrode kinetics of oxygen reduction on oxide-free platinum electrodes. Electrochimica Acta. 2008;12:615-628. DOI: 10.1016/j.electacta.2008.10.034

[99] Liang ZX, Zhao TS, Xu JB, Zhu LD. Mechanism study of ethanol oxidation reaction on palladium in alkaline media. Electrochimica Acta. 2009;54:2203-2208. DOI: 10.1016/j.electacta.2008.10.034

[100] Toda T, Igarashi H, Uchida H, Watanabe M. Role of electronic property of Pt and Pt alloys on electrocatalytic reduction of oxygen. Journal of the Electrochemical Society. 1998;145(12):4185-4188. DOI: 10.1149/1.1835934

[101] Tatsumi K, Hoffman R. Metalloporphyrins with unusual geometries. 1. Mono-, di-, tri atom-bridged porphyrin dimers. Journal of the American Chemical Society. 1981;103:3328-3341. DOI: 10.1021/ja00402a018

[102] Griffith JS. On the magnetic properties of some haemoglobin complexes. Proceedings of the Royal Society of London. 1956;A235:23-36. DOI: 10.1098/rspa.1956.0062

[103] Pauling L. Nature of the iron-oxygen bond in oxyhaemoglobin. Nature. 1964;203:182-183. DOI: 10.1038/203182b0