INTRODUCTION

The increased industrializations vis-à-vis the energy demand in people’s daily life have caused not only the rapid depletion of fossil fuel resources but, the increase of the environmental pollution also. The latter adversely affects our life quality and the climate. In view of these, research on new environmental-friendly energy sources and their practical applications have attracted increasing attention in past decades (Antolini 2006; Blomen et al., 1993; Lanninie et al., 2003). So, ensuring clean and efficient energy sources is one of the biggest challenges of the 21st century. Among the proposed clean energy sources, fuel cells, such as proton exchange membrane fuel cells (PEMFCs), direct methanol fuel cells (DMFCs), direct formic acid fuel cells (DFAFCs), etc., have been considered as the most promising power sources with high energy density and high efficiency (Singh et al., 2013; Bianchini et al., 2009; Scott et al., 2007).

1.1 Fuel Cell

A fuel cell is an electrochemical device that can convert the chemical energy of a fuel into electrical energy. In fact, a fuel cell has two electrodes, an anode and a cathode (Fig.1.1). The main reactions in a fuel cell include a fuel oxidation at anode and oxygen reduction at cathode. Thus, fuel cells function like a battery. However, unlike a battery, fuel (hydrogen, alcohol, etc.) and oxidant (oxygen or air) are not integral part of the fuel cell, but they are supplied from outside during the operation. When the power is not needed, the supply of fuel and oxygen /air is stopped.

A single cell is composed of an anode where fuel is supplied and its oxidation takes place, an electrolyte which conducts ions but not electrons, and a cathode where the oxidant is supplied and reduction takes place. An external circuit connects the anode to the cathode to allow the electron flow from the anode to the cathode and hence the current flow from the cathode to the anode. A block diagram of a single fuel cell is shown in shown in Fig.1.1.
Fig. 1.1. Block diagram of a Fuel Cell.

A single cell will generally produce around 0.75 Volts at 2 Amps, thus generating around 1.5 Watts of DC power (Lanninie and Dicks 2003). DC electricity is widely applicable in industries such as chloroalkali and aluminium industries (Shukla et al., 1986), etc.

At present, there are mainly three technologies, which are used as micro combined heat and power generator for domestics as well as commercial and technological applications. The three technologies are the Internal combustion engine, Stirling engine and fuel cells. Their comparative performances and operational characteristics are shown in Table 1.1:

**Table 1.1:** Domestic micro combined heat and power technologies (Wu et al., 2006a; Hawkes et al., 2009)

<table>
<thead>
<tr>
<th>Features</th>
<th>Internal Combustion Engine</th>
<th>Stirling Engine</th>
<th>Fuel Cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity (electrical)</td>
<td>1 kW+</td>
<td>1 kW+</td>
<td>1 kW+</td>
</tr>
<tr>
<td>Electrical efficiency</td>
<td>20%</td>
<td>10%</td>
<td>35-60%</td>
</tr>
<tr>
<td>Overall efficiency</td>
<td>85%</td>
<td>90%</td>
<td>85%</td>
</tr>
<tr>
<td>Heat to Power ratio</td>
<td>3:1</td>
<td>10:1</td>
<td>1:1</td>
</tr>
<tr>
<td>Able to vary output</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Fuel used</td>
<td>Gas, biogas, liquid fuels</td>
<td>Gas, biogas, butane</td>
<td>Hydrocarbon fuel</td>
</tr>
<tr>
<td>Noise</td>
<td>Loud</td>
<td>Fair</td>
<td>Quiet</td>
</tr>
<tr>
<td>Maturity</td>
<td>High</td>
<td>Fair</td>
<td>Low</td>
</tr>
<tr>
<td>Companies producing</td>
<td>Baxi</td>
<td>Whispergen</td>
<td>Baxi, Bluegen (CFCL)</td>
</tr>
</tbody>
</table>
As fuel cells are not governed by the thermodynamic law of heat engine and so, they can achieve much higher operational electrical efficiencies (i.e. greater than Carnot) compared to traditional ones such as internal combustion engine, diesel engine, gas turbines, etc. The comparative efficiencies of different energy converting devices are given in Table 1.2.

Table 1.2: Efficiencies of direct energy devices (Shukla et al., 1986).

<table>
<thead>
<tr>
<th>Energy converter</th>
<th>% efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermoelectric</td>
<td>10</td>
</tr>
<tr>
<td>Thermionic</td>
<td>22</td>
</tr>
<tr>
<td>Photovoltaic</td>
<td>18</td>
</tr>
<tr>
<td>Low Temperature fuel cell</td>
<td>60</td>
</tr>
<tr>
<td>High Temperature fuel cell</td>
<td>60</td>
</tr>
<tr>
<td>Gas turbines</td>
<td>30</td>
</tr>
<tr>
<td>Internal combustion engine</td>
<td>30</td>
</tr>
<tr>
<td>Diesel engines</td>
<td>40</td>
</tr>
</tbody>
</table>

Hydrogen is the preferred fuel in fuel cells as it produces higher electrochemical performance and reduced cell degradation. Hydrogen fed in at the anode gets oxidized giving an electron to the anode and H\(^+\) ion to the electrolyte. The H\(^+\) ion passes through a conductive electrolyte and comes near the cathode. When an external load is connected between the two electrodes a potential is generated and current flow in the external circuit.

**Brief historical background**

In nineteenth century, a German Scientist C. F. Schönbein discovered the principle of Fuel Cell (1838) and after one year in 1839, a British judge and scientist, Sir William Robert Groove for the first time, displayed the demonstration of a fuel cell. For the purpose, he used the principle of reverse of electrolysis i.e. the reaction of oxygen and hydrogen generating electricity. A block diagram of the cell is shown in Fig.1.2.
Fig.1.2. (a) Water is being electrolysed into hydrogen and oxygen by passing an electric current through it, and (b), the power supply has been replaced with an ammeter, and a small current is flow. → The electrolysis is reversed – the hydrogen and oxygen are recombining, and an electric current is being produced.

Later, the chemist Ludwig Mond and Charles Langer in 1889 attempted to build the first practical device using air and hydrogen (Platinum metal as catalyst and sulphuric acid as electrolyte). As early as in 1932, Bacon resurrected the machine developed by Mond and Langer with certain modifications like replacing platinum electrodes with nickel gauze and sulphuric acid with alkali potassium hydroxide. This modified device (also named Bacon Cell) was, in fact, the first alkaline fuel cell (AFC). After a lapse of nearly 20 years (i.e. in 1952), Bacon and his coworker constructed a fuel cell capable of producing the maximum output power of 5 kW, enough to power a welding machine (Blomen and Mugerwa, 1993; Hoogers, 2002). In the beginning of 1960s, the US government agency, the National Aeronautics and Space Administration (NASA) considered the fuel cells to power upcoming manned space flights as they are relatively light weights and highly efficient. Thereafter, NASA soon proceeded to develop fuel cells suitable for spacecraft. As a result of such efforts, both alkaline and polymer electrolyte fuel cells were developed and demonstrated their capabilities in a series of manned space flights such as the Apollo, Gemini and Space Shuttle successfully. The alkaline fuel cell (AFC) developed by Pratt and Whitney for the Apollo programme operated at a higher temperature (260ºC), higher KOH concentration (~ 85%) and lower pressure (near atmospheric) than the Bacon Cell.
### 1.1.1 Types of Fuel Cell

Based on the operational temperature and the type of the electrolyte used, there are several types of fuel cells, of these most important ones are shown in Table 1.3: (Carrette et al., 2001).

**Table 1.3: Characteristics of fuel cells (WADE and Alanne et al., 2004)**

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Proton exchange membrane fuel cell (PEMFC)</th>
<th>Alkaline fuel cell (AFC)</th>
<th>Phosphoric acid fuel cell (PAFC)</th>
<th>Molten carbonate fuel cell (MCFC)</th>
<th>Solid oxide fuel cell (SOFC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge carrier</td>
<td>H⁺ ions</td>
<td>OH⁻ ions</td>
<td>H⁺ ions</td>
<td>CO₃⁻ ions</td>
<td>O⁻ ions</td>
</tr>
<tr>
<td>Type of electrolyte</td>
<td>Polymeric membrane (perfluoro sulphonic acid)</td>
<td>Aqueous KOH soaked in a matrix</td>
<td>Phosphoric acid solutions</td>
<td>Phosphoric acid (immobilized liquid)</td>
<td>Stabilized zirconia ceramic matrix with free oxide ions</td>
</tr>
<tr>
<td>Typical construction</td>
<td>Plastic, metal or carbon</td>
<td>Plastic, metal</td>
<td>Carbon, porous ceramics</td>
<td>High temp. metals, porous ceramic</td>
<td>Ceramic, high temp metals</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Platinum</td>
<td>Platinum</td>
<td>Platinum</td>
<td>Nickel</td>
<td>Parasites</td>
</tr>
<tr>
<td>Oxidant</td>
<td>Air or O₂</td>
<td>Purified air or O₂</td>
<td>Air or O₂ – enriched air</td>
<td>Air</td>
<td>Air</td>
</tr>
<tr>
<td>Fuel</td>
<td>Hydrocarbons or methanol</td>
<td>Clean hydrogen or hydrazine</td>
<td>Hydrocarbons or alcohols</td>
<td>Clean hydrogen, natural gas, propane, diesel</td>
<td>Natural gas or propane</td>
</tr>
<tr>
<td>Operational Temperature</td>
<td>50 - 100ºC</td>
<td>60 - 80ºC</td>
<td>100 - 200ºC</td>
<td>600 - 700ºC</td>
<td>600 - 1000ºC</td>
</tr>
<tr>
<td>Size range</td>
<td>3 – 250 kW</td>
<td>10 – 200 kW</td>
<td>100 – 200 kW</td>
<td>250 – 5 MW</td>
<td>1 – 10 MW</td>
</tr>
<tr>
<td>Electrical efficiency</td>
<td>30 – 50%</td>
<td>32 – 70%</td>
<td>40 – 55%</td>
<td>55 – 57%</td>
<td>50 – 60%</td>
</tr>
<tr>
<td>Primary contaminants</td>
<td>CO, sulfur and NH₃</td>
<td>CO, CO₂ and sulfur</td>
<td>CO &gt; 1%, sulfur</td>
<td>sulfur</td>
<td>sulfur</td>
</tr>
<tr>
<td>Advantage</td>
<td>Solid electrolyte reduces corrosion and electrolyte management problems -low temp -Quick start-up</td>
<td>Faster cathode reaction leads to high performance and Low cost components</td>
<td>Higher temp enables CHP -Increased tolerance to fuel impurities</td>
<td>High efficiency -Fuel flexibility -Can use a variety of catalysts -Suitable for CHP</td>
<td>High temp corrosion and breakdown of cell components -Long start-up -Low power density</td>
</tr>
<tr>
<td>Disadvantage</td>
<td>Expensive catalyst -Sensitive to fuel impurities -Low temp waste heat</td>
<td>Sensitive to CO₂ in fuel and air and Electrolyte management</td>
<td>Pt catalyst -Long start-up -Low current and power</td>
<td>High efficiency -Fuel flexibility -Can use a variety of catalysts -Suitable for CHP -Solid electrolyte</td>
<td>High temp corrosion and breakdown of cell components -Long start-up</td>
</tr>
</tbody>
</table>
Among different categories of fuel cells, alkaline fuel cells (especially Direct methanol fuel cell, (DMFC)) have drawn considerable attention during recent years. However, alkaline electrolytes (e.g. KOH, NaOH) are associated with a drawback, that is, they do not reject CO₂, which is produced as product during alcohol oxidation. Therefore, application is restricted to operation on fuel and oxidant that do not produce CO₂. So, the use of hydrogen as fuel is a good choice, but being the gaseous nature it has low energy density (~0.49 kWh kg⁻¹ for 1.5% dilute hydrogen) and requires highly pressurized tanks, metal hydride, carbon nanotubes or other hydrogen storage materials to achieve higher energy density. Besides, it is highly flammable gas and so, its transportation is rather not easy. In comparison to hydrogen, alcohols such as methanol (energy density = 6.1 kWh kg⁻¹), ethanol (energy density = 8.0 kWh kg⁻¹), ethylene glycol (energy density = 5.2 kWh kg⁻¹) and glycerol (energy density = 5.0 kWh kg⁻¹) exhibit high volumetric energy density (Larminie and Dicks, 2003) and their storage and transportation are much easier to hydrogen. The most common direct alcohol fuel cell (DAFC) is DMFC wherein, methanol is used as fuel without being reformed. Methanol is readily available and a low-cost liquid fuel (Lamy et al., 2002; Antolini, 2007a). DMFCs give the low output power and so it can be used where a low power but a high energy density is required such as ‘always on’ mobile telephones, personal digital assistants, remote monitoring and sensing equipments (Selvaraj et al., 2008). However, for successful application of alkaline DAFCs, the electrolyte carbonation issue must be resolved.

In DMFC, a mixture of methanol and water is allowed to flow over anode where methanol is directly oxidized to CO₂, however, the formation of possible other compounds, such as formaldehyde, formic acid or other organic molecules cannot be ruled out (Lamy et al., 2002).

### 1.1.2 Thermodynamics of DMFCs

Electrode reactions occurring at anode as well as on cathode in a DMFC, equipped with a proton conducting electrolyte can be written as:

At anode

\[
CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \quad E_1^0 = 0.02 \text{ V vs. SHE} \quad (1)
\]

At cathode,

\[
\frac{3}{2} O_2 + 6H^+ + 6e^- \rightarrow 3H_2O \quad E_2^0 = 1.23 \text{ V vs. SHE} \quad (2)
\]
And in alkaline medium the above reaction can be represented as

At anode,

\[ \text{CH}_3\text{OH} + 6\text{OH}^- \rightarrow \text{CO}_2 + 5\text{H}_2\text{O} + 6e^- \quad E_1^o = -0.81 \text{ V vs. SHE} \quad (3) \]

At cathode,

\[ \frac{3}{2} \text{O}_2 + 3\text{H}_2\text{O} + 6e^- \rightarrow 6\text{OH}^- \quad E_2^o = 0.40 \text{ V vs. SHE} \quad (4) \]

The overall reaction for acidic as well as alkaline electrolytes

\[ \text{CH}_3\text{OH} + \frac{3}{2}\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad (E^o_{\text{cell}} = 1.21 \text{ V}) \quad (5) \]

Under standard conditions when the overall cell reaction is at equilibrium, one can write

\[ -\Delta G^0 = nFE_{\text{cell}}^0 \quad (6) \]

Where, \( \Delta G^0 = -702 \text{ kJ mol}^{-1} \) and \( \Delta H^0 = -726 \text{ kJ mol}^{-1} \) in the complete oxidation of per molecule of methanol

\[ E_{\text{cell}}^0 = \frac{-\Delta G^0}{nF} = \frac{702 \times 10^3}{6 \times 96,485} = E_2^o - E_1^o = 1.213 \text{ V} \quad (7) \]

Where, \( F = \text{Faraday constant} = 96,485 \text{ C mol}^{-1} \) and \( n = \text{number of electron exchanged} \)

Thus, the theoretical energy efficiency \( (\varepsilon_{\text{eq}}) \) becomes,

\[ \varepsilon_{\text{eq}} = \frac{-\Delta G^0}{-\Delta H^0} = \frac{702 \times 10^3}{726 \times 10^3} = 96.7\% \quad (8) \]

However, the practical cell efficiency is always lower than the theoretical one.

There are three factors that are responsible for the loss of practical efficiency under working conditions with current density \( j \) and the cell voltage \( E_j \). These are: (i) overpotentials for the anodic \( (\eta_a) \) and cathodic \( (\eta_c) \) charge transfer reaction at the two electrodes (ii) ohmic drop \( (jR_e) \) and (iii) the mass transfer limitations.

Considering these factors the cell voltage \( (E_j) \) at the current density of \( j \) flowing in the external circuit can be represented as,

\[ E_j = E_2^o(|jj|) - E_1^o(|jj|) = (E_2^o + \eta_c) - (E_1^o + \eta_a) - R_e|jj| \quad (9) \]

\[ E(|jj|) = E_{\text{eq}} - [(|\eta_a| - |\eta_c| + R_e|jj|)], \quad (10) \]

(\( E_2^o - E_1^o \)) being equilibrium potential \( (E^o_{\text{eq}}) \)

where, \( \eta_a > 0 \) for an anodic, i.e., oxidation reaction and \( \eta_c < 0 \) for a cathodic i.e. reduction reaction) take into account both the slow rates of the electrochemical reaction
(activation polarization) and the limiting rate of mass transfer (concentration polarization), thus, the practical energy efficiency of the cell \( \varepsilon_{cell}^{CH_3OH/O_2} \) can be expressed as,

\[
\varepsilon_{cell}^{CH_3OH/O_2} = \frac{n_{exp} \cdot FE(j)}{-\Delta H^\circ} = \frac{n_{exp} \cdot FE(j) \cdot nE_{eq}^\circ}{-n(E_{eq} \Delta H^\circ)} = \frac{n_{exp} \cdot E(j) \cdot \Delta G^\circ}{nE_{eq} \Delta H^\circ}
\]

(11)

\[
\therefore \quad \varepsilon_{cell}^{CH_3OH/O_2} = \frac{n_{exp} \cdot E(j) \cdot \Delta G^\circ}{nE_{eq} \Delta H^\circ}
\]

(12)

Thus, the practical energy efficiency depends upon the number of electrons exchanged in the oxidation of a molecule of methanol.

Three paths are known (Bagotzki et al., 1977) for the methanol oxidation in DMFC: (i) the complete oxidation through \( CO_2 \) pathway, (ii) the complete oxidation through formaldehyde pathway and (iii) the complete oxidation through formic acid pathways. These mechanisms are schematically represented in Fig. 1.3.

![Fig.1.3. Schematic representation of mechanisms for methanol oxidation.](image)

In each oxidation path the number of electrons exchanged are different and hence the efficiencies are also different. This can be shown as follows:

For a DMFC working at, say, +0.5 V and 50 mA cm\(^{-2}\), the number of electrons exchanged and the corresponding efficiencies are as follows:

\[
(1) \quad CO_2 (n = 6): \quad \varepsilon_{cell}^{CH_3OH/O_2} = \frac{6 \times 0.5}{1.213} \times 96.7\% = 40\%
\]
(2) HCHO \( (n = 2) \): \[
\frac{\text{CH}_3\text{OH}}{\varepsilon_{\text{cell}}} = \frac{2}{6} \times \frac{0.5}{1.213} \times 96.7\% = 13\%
\]

(3) HCOOH \( (n = 4) \): \[
\frac{\text{CH}_3\text{OH}}{\varepsilon_{\text{cell}}} = \frac{4}{6} \times \frac{0.5}{1.213} \times 96.7\% = 27\%
\]

Thus, to increase the overall efficiency significantly, it is essential to decrease overpotential \( \eta \) and the ohmic drop \( R_{\text{e}} \) and to increase faradaic efficiency \( (\varepsilon_F) \), i.e. to favour the complete oxidation of methanol to \( \text{CO}_2 \) (avoiding the formation of aldehyde and formic acid).

1.1.3 Electrocatalysis

The decrease in \( |\eta| \) is directly related to the increase in the rate of the electrochemical reactions occurring at both electrodes. This is typical in electrocatalysis, where the actions of the electrode potential and the catalytic electrode material will synergistically increase the reaction rate. The current density \( j \) is proportional to the rate of reaction \( \nu \) (under zero field condition), i.e.

\[
j = nF\nu \\
j = \tilde{j} + \bar{j}
\]

Based on the Butler-Volmer equation for multielectron transfer reaction,

\[
j = j_0 [\exp \left( \frac{\tilde{a}F\eta}{RT} \right) - \exp \left( -\frac{\tilde{a}F\eta}{RT} \right)]
\]

Where,

\( \tilde{a} = \text{transfer coefficient for de- electronation reaction} = \tilde{v}/\nu + r(1 - \beta) \)

\( \tilde{a} = \text{transfer coefficient for electronation reaction} = \tilde{v}/\nu + r\beta \)

\( \nu = \text{stoichiometry number}, \beta = \text{symmetry factor} \sim 0.5 \)

\( \tilde{v} = \text{number of electron transferred before the rate determining step (rds)} \)

\( \bar{v} = \text{number of electron transferred after the rate determining step (rds)} \)

\( j_0 = \text{exchange current density}, r = \text{number of electrons involved in the rds} \)

\( j_0 \) value depends upon the nature and structure of the electrode material and is used to compare the electrocatalytic activities of different electrode materials towards a particular reaction. Higher the \( j_0 \) the greater is the electrocatalytic activity of the electrode material. Thus, the development of new electrode materials with greatly enhanced specific/chemical surface area by suitable methods and investigation of their electrocatalytic activities towards technologically important reactions are the main task of electrocatalysis.
1.1.4 Electrocatalytic Scale

As the electrochemical rate constant depends upon the nature of the electrode materials under the given reaction conditions, it is, therefore, worthwhile to know the relative activities of electrode materials for a particular reaction under identical experimental conditions. To compare the electrocatalytic activities the following three scales have been used in literature:

(1) Based on the exchange current density.
(2) Based on the overpotential (or potential).
(3) Based on the current density.

The electrocatalyst with the higher exchange current density for a particular reaction is considered as more active. However, this scale is meaningful only when the reaction has the same Tafel slopes on different electrodes chosen for the investigation. The electrocatalytic activities of the electrocatalysts can be best compared by knowledge of values of overpotential (or current density) at a fixed current density (or overpotential). The electrode which shows the least overpotential for the considered reaction at a fixed current density is said to be the highest active. Similarly, the electrode which produces a higher current density (compared to others) at a fixed overpotential (or potential) is considered as more active.

In the above comparison, the term “current density” can be defined as.

\[ \text{Current density} \ (j) = \frac{\text{Observed current (in A or mA)}}{\text{Geometrical area of the electrode (cm}^2\text{)}} \]  

(16)

The current density, so obtained, is known as the apparent current density (\(j_a\)).

But, for the same geometrical area, one can have materials of different electrochemically active areas (EASAs) and that the rate of electrochemical reaction increases with increasing EASAs of the electrode. Therefore, before making a comparison between activities of electrodes, the apparent current (or observed current) of electrodes should be normalized with respect to EASA, the resulting current is called as the true current density (\(j_t\)) and is defined as:

\[ \text{True current density} \ (j_t) = \frac{\text{Apparent current (A or mA)}}{\text{EASA (cm}^2\text{)}} \]  

(17)

1.1.5 Methanol oxidation reaction

Mechanisms of MOR on Pt have been widely studied experimentally in the 70’s and the 80’s of the past century and are reviewed comprehensively by Parsons et al. (1988), Aricò et al. (2001) and Hogarth et al. (2002). Most important experimental facts suggested the following three basic stages for the methanol oxidation reaction:
$\text{CH}_3\text{OH} + \text{Pt} \rightarrow \text{Pt-CO} + 4\text{H}^+ + 4\text{e}^- \quad \text{……………………(a)}$

$\text{H}_2\text{O} + \text{Pt} \rightarrow \text{Pt-OH} + \text{H}^+ + \text{e}^- \quad \text{……………………(b)}$

$\text{Pt-CO} + \text{Pt-OH} \rightarrow \text{CO}_2 + 2\text{Pt} + \text{H}^+ + \text{e}^- \quad \text{…………………(c)}$

Reaction (a) requires almost no overpotential to proceed being fast even at 0.1 V vs. RHE. It is the reason, why methanol spontaneously adsorbs on a piece of Pt dipped in an acidified methanol solution with formation of a high coverage by CO\text{ads}, because reaction (a) can couple with hydrogen evolution. Reaction (b) is the rate determining step up to the potential value of about 0.660 V vs. RHE in 0.5 M $\text{H}_2\text{SO}_4$. Above that potential, reaction (c) becomes slower than reaction (b). At sufficiently high potential (above ca. 0.7 V vs. RHE in 0.5 M $\text{H}_2\text{SO}_4$), the formation of surface PtO occurs simultaneously with the reactions (a)-(c):

$\text{Pt} + \text{H}_2\text{O} \rightarrow \text{PtO} + 2\text{H}^+ + 2\text{e}^- \quad \text{…………………(d)}$

The extent of this reaction is potential- and time-dependent and can ultimately lead to two monolayers of PtO. Reaction (d) prevents reaction (a) from occurring at all, i.e., it shuts down methanol oxidation, because methanol cannot adsorb on PtO.

1.1.6 Oxygen reduction reaction

The cathodic reaction in direct methanol fuel cell is the oxygen reduction reaction (ORR) and it is heart of several renewable energy technologies such as water electrolysis, metal – air batteries, fuel cell and other industrial applications (Lee et al., 2013) (see Fig.1.4).

![Fig.1.4. Taken from Lee et al. (2013).](image)

The electrocatalysis for $\text{O}_2$ reduction reaction has less been studied in comparison with other reactions such as hydrogen evolution, oxygen evolution etc. It is because of the fact that the study involves several difficulties such as stability of electrode materials, solubility of oxygen, sensitivity of the reaction to presence of small impurities in solution etc.
The solubility of oxygen in water is $10^{-4}$ mol/L or less which decreases further in presence of the electrolyte.

Further, the reaction has highly positive thermodynamic reduction potential ($E^\circ$=1.23V vs SHE). Due to this only Platinum and other noble metals (Pd, Ru etc.), and their alloys are stable which are pretty costly and have limited abundance. So, researches are now being carried out to search out Pt-free electrode materials that can efficiently reduces oxygen even at higher potentials (Liang et al., 2011 & 2012; Sharma et al., 2013a; Poux et al.; 2012).

The ORR kinetics is known to depend on the binding strength of hydroxide (OH) ion to the surface of the catalyst and is governed by Sabatier’s principle which states that the catalytic activity maximizes when the binding of the reaction intermediates to the surface is neither too strong nor too weak. Sepa et al. (1981) reported that the ORR mechanism on the Pt surface takes place in a similar manner as on the Pt surface. The steps involved in ORR mechanism can be given as follows.

\[
\begin{align*}
2 \text{Pt} + \text{O}_2 & \rightarrow \text{Pt}_2\text{O}_2 \\
\text{Pt}_2\text{O}_2 + \text{H}^+ + e^- & \rightarrow \text{Pt}_2\text{O}_2\text{H} & \text{(rate determining step)} \\
\text{Pt}_2\text{O}_2\text{H} & \rightarrow \text{Pt-OH} + \text{Pt-O} \\
\text{Pt-OH} + \text{Pt-O} + \text{H}^+ + e^- & \rightarrow \text{Pt-OH} + \text{Pt-OH} \\
\text{Pt-OH} + \text{Pt-OH} + 2\text{H}^+ + 2e^- & \rightarrow 2\text{Pt} + 2\text{H}_2\text{O}
\end{align*}
\]

It has already been established that the reduction of oxygen takes place either by direct 4e$^-$ path or by 2e$^-$ path giving H$_2$O and H$_2$O$_2$, respectively. (Shukla et al., 2003; Kordesch et al., 1994; Sharma et al., 2013a & 2014):

The important steps involved in two reaction paths (i.e. 4-electrone and 2-electron) in acid as well as alkaline medium along with their respective thermodynamic potentials are briefly shown in Fig.1.5.
1.1.7 Drawbacks and remedial measures of DMFCs

1.1.7.1 Drawbacks of DMFCs

There are two important drawbacks which are as follows:

1. Both the electrode reactions, the oxidation of alcohol at anode and the reduction of oxygen at cathode, are sluggish ones and require more active catalysts. Pt is used as an active electrocatalyst for both MOR and ORR which is costly and has limited abundance in nature. Also, it is poisoned by the alcohol oxidation intermediate species, particularly CO, formed during the methanol oxidation reaction MOR.

2. In a DMFC there is a crossover of methanol from the anode compartment to the cathode compartment through polymer membrane which is used to separate the two compartments. In fact, the methanol molecule diffuses through the membrane from the anode compartment to the cathode one. This methanol crossover, depolarizes the cathode due to the establishment of a competition between methanol oxidation ($E^{\circ}_{\text{CH}_3\text{OH/H}^+} = 0.02$ V vs SHE) and oxygen reduction ($E^{\circ}_{\text{O}_2/\text{H}_2\text{O}} = 1.23$ V vs SHE) at the cathode surface. The methanol oxidation at the fuel cell cathode is thermodynamically highly feasible and therefore, the presence of any methanol molecule in the neighbourhood of the cathode in the cathode compartment would undergo oxidation which thereby results decrease in the cathode efficiency and hence the overall cell efficiency.

1.1.7.2 Remedial measures

In order to minimize the above drawback, the research work has been carried out in following directions:

(a) To reduce the mass and improve CO poisoning tolerance of Pt
(b) To develop low cost novel polymer membranes with high chemical, thermal and mechanical stability and low permeability to reactant (methanol).
(c) To develop Pt-free new anode materials with reduced cost and CO poisoning tolerance
(d) To develop Pt-free new cathode materials with reduced cost.
(e) To develop methanol tolerance cathode materials.
1.1.7.3 Research work carried out

In order to reduce mass and hence the cost, Pt is obtained in highly dispersed form on high surface areas support materials. Generally carbon materials of varying form such as Vulcan carbon (Sharma & Pollet, 2012; Rajesh et al., 2002 & 2003), carbon nanopowder (Singh et al., 2009b), carbon nanotube (single wall (Wu et al., 2007; Girishkumar et al., 2004) carbon nanotubes (SWCNTs) and multiwalled (Li et al., 2002, 2003 & 2004), carbon nanotubes (MWCNTs)), carbon microspheres (CMSs) (Xu et al., 2007), nanowire arrays (NWAs) (Wang et al., 2008), graphene (Shang, 2010 and Sharma et al., 2010), etc. Various carbon support used for Pt-based catalysts have already been reviewed by Antolini (2009).

To improve the catalytic activity and CO poisoning tolerance, Pt has also been alloyed with several non Pt metals such as Pd (Limpattayanate et al., 2014), Ni (Antolini et al., 2006), Cu (Xia et al., 2012), Fe (Guo et al., 2014; Chen et al., 2014a), and investigated their influence on the catalytic activity towards methanol oxidation and oxygen reduction reaction.


A great deal of attention was paid to the use of graphene as catalyst support material because it is of low cost and has considerably higher specific surface area as well as conductivity in comparison to other carbon supports. Graphene is an allotrope of carbon, whose structure is one-atom-thick planar sheets of sp² bonded carbon atoms that are densely packed in a 2D honeycomb crystal lattice. It possesses high specific surface area (~ 2630 m² g⁻¹) (Brownson et al., 2011), excellent electronic mobility (~2,50,000 cm² V⁻¹ s⁻¹) (Novoselov et al., 2005), exceptional thermal conductivity (~5,000 Wm⁻¹ K⁻¹) (Balandin et al., 2008) super mechanical properties with theoretical Young’s modulus of 1TPa (Lee et al., 2008), which enable it a promising material for use in electrochemical devices, such as fuel cells, supercapacitors, batteries, sensors, etc.

Li et al. (2010) reported that during deposition of Pt nanoparticles on GO by ethylene glycol method, a majority of oxygenated functional groups on GO gets removed resulting in Pt/chemically converted graphene (CCG), which shows better tolerance to CO and much more enhanced catalytic activity for MOR compared to Pt/MWCNT. The MOR and EOR study on Pt/GNS, PtRu/GNS, Pt/CB and PtRu/CB electrodes shows that both methanol and ethanol electrooxidations have enhanced greatly on GNS compared to those on CB.
Galal et al. (2012) prepared graphene supported-Pt-M (M = Ru or Pd) for methanol oxidation. They reported both Pt-Pd and Pt-Ru co-catalysts are good co-catalysts for methanol oxidation but Pt-Ru is more favorable due to its high electrocatalytic behavior even with its lower loading which indicates that Ru has higher ability for removing carbonaceous species. Also the Pt-Ru catalyst graphene sub-micron composite prepared by this method gives higher current density 133 mA/cm$^2$ compared to the other methods of preparation.

Zhu et al. (2012) reported Hollow composite of Pt and CoSn(OH)$_6$ electrocatalysts supported on graphene nanosheets (HPt&CoSn(OH)$_6$/GNSs) prepared by using cobalt metal nanoparticles as sacrificial templates. The catalyst HPt&CoSn(OH)$_6$/GNSs exhibited improvement of electrooxidation activity for CH$_3$OH in comparison to solid composite of Pt and CoSn(OH)$_6$ catalyst supported on GNSs, pure Pt catalyst supported on GNSs, HPt&CoSn(OH)$_6$ supported on carbon black catalyst, and commercial E-tek PtRu/C catalyst.

Gao et al. (2013) prepared graphene-Pd (G-Pd) and Pt (G-Pt) composite for alcohol oxidation in alkaline condition. The peak current of graphene-Pt decreased by about 27% after 100 cycles, while that of Vulcan carbon supported-Pt decreased by 73%. Further, the onset potentials of methanol oxidation were $\sim$0.5 and $\sim$0.35 V for graphene-Pt obtained by thermal reduction and electrochemical reduction, while the onset potential was $\sim$0.08 V for G-Pt, even slightly lower than those for graphene-Pt ($\sim$0.10 and $\sim$0.20 V) obtained by chemical reduction.

Qian et al. (2013) prepared Pt and Pt-M (M=Pd and Co) based composites supported on graphene and found improvement in electrocatalyst tolerance to carbon monoxide poisoning (Pt/graphene, $I/I_b$=1.197) than commercial Pt/C ($I/I_b$=0.893) catalyst. Also EASA improved 4 and 3.3 times for PtPd/graphene and PtCo/graphene, respectively, in relation to commercial Pt/C.

Rajesh et al. (2013) prepared the vertically grown multiwalled carbon nanotubes (MWCNTs) on single layer graphene floor (G-MWCNTs) is synthesized by one step chemical vapour deposition (CVD) method as supporting material for Pt. The high performance of G-MWCNT as catalyst support for methanol electrooxidation regard to EASA, forward anodic peak current density, onset oxidation potential, diffusion efficiency and the ratio of $I/I_b$.

Lu et al. (2014) reported graphene oxide (GO) as a structure-directing agent for the formation of PtPd alloy concave nanocubes enclosed by high index facets. Compared to the unsupported PtPd nanocubes, the composition ratio of Pt to Pd changed significantly from 1 : 1 to 3 : 1. Due to the exposed high-index facets and the strong interaction between catalysts and
graphene support, the as-synthesized PtPd concave nanocubes exhibited enhanced electrocatalytic activity and high durability toward methanol oxidation.

Chen et al. (2014b) prepared bimetallic PtPd nanocubes supported on graphene nanosheets (PtPdNCs/GNs) by a rapid, one-pot and surfactant-free method, for the methanol electrooxidation, wherein N,N-dimethylformamide (DMF) was used as a bi-functional solvent for the reduction of both metal precursors and graphene oxide (GO) and for the surface confining growth of PtPdNCs. The PtPdNCs/GNs composites exhibited higher electrocatalytic activity ($j_p = 0.48 \text{ A mg}^{-1}$) and better tolerance to CO poisoning ($I_f/I_b = 1.27$) compared with PtPd nanoparticles supported on carbon black (PtPdNPs/C) ($j_p = 0.28 \text{ A mg}^{-1}$; $I_f/I_b = 1.01$) and PtNPs/GNs ($j_p = 0.33 \text{ A mg}^{-1}$; $I_f/I_b = 0.95$).

Cai et al. (2014) proposed a green synthesis of Pt on Pd bimetallic nanodendrites supported on graphene (GPtPdNDs) with a Pd interior and a dendrite like Pt exterior was achieved using a two step preparation, mixing graphene and PdCl$_4^{2-}$ first, then adding PtCl$_4^{2-}$ and ethanol without any other solvent. Because no halide ions (refer in particular to Br$^-$, I$^-$) or surfactant was involved in the synthesis, the prepared GPtPdNDs were directly modified onto a glassy carbon electrode and showed excellent electrocatalytic performance in methanol oxidation without any pretreatments. Moreover, with the special structure of PtPdNDs and the synergetic effects of Pt and Pd and the enhanced electron transfer by graphene, the GPtPdNDs composites exhibited higher electrocatalytic activity and better tolerance to Pt nanoparticles supported on graphene (GPtNPs) and Pt/C for methanol oxidation.

Zhong et al. (2013) reported a facile and effective ultrasonication method to non-covalently functionalize graphene with copper phthalocyanine-3,4′,4″,4‴-tetrasulfonic acid tetrasodium salt (TSCuPc) as a promising catalyst support for Pt nanoparticles. They found that, TSCuPc, Pt nanoparticles are homogeneously deposited on the surface of graphene, and their dispersivity and electrochemical active surface area (ECSA) are obviously enhanced. The activity and stability of Pt/TSCuPc-graphene was much higher than the Pt/graphene and commercial Pt/C catalysts for methanol oxidation.

Li et al. (2014a) prepared hollow Pt-Pd nanospheres (Pt-Pd HNSs) supported on reduced graphene oxide for methanol oxidation. For the preparation of composite a rapid and simple route is adopted. For large-scale synthesis also in the preparation, no surfactant, seed, or template is involved. The cyclic voltammograms (CVs) of the RGOs/Pt-Pd HNSs were recorded in 1.0 M
NaOH containing 1.0 M methanol. The onset potential and forward peak potential negatively shift. The forward peak current density \( (j_F) \) is ca. 28 mA cm\(^{-2}\), which is much higher than those of the RGOs/Pt (0.88 mA cm\(^{-2}\)), RGOs/Pd (0.38 mA cm\(^{-2}\)), Pt black (24 mA cm\(^{-2}\)) and Pd black (15 mA cm\(^{-2}\)) catalysts under the same conditions.

Sun et al. (2014) prepared size-selected Pt colloidal nanoparticles on high-surface-area graphene powders for methanol oxidation. Pt-graphene (Pt–G) catalyst synthesized through the high-concentration solution system. The mixing process exhibits the densely-packed Pt NPs on graphene surfaces with non-flat wrinkles. Moreover, the high-density Pt NPs in the catalyst give rise to the high methanol oxidation current in its forward scan. This catalyst outperforms all the other catalysts synthesized in the low-concentration solution systems in terms of the MOR current and electrochemical surface area (ECSA). The mass activity of Pt–G-1 catalyst reached up to 489.66 mA/mg\(_{Pt}\).

Zhang et al. (2014) synthesize Pt-Pd bimetallic nanoparticles anchored on graphene by one-step reduction route for methanol electro-oxidation. The peak current densities of different Pt-PdNPs/G catalysts changed with the Pt/Pd ratio, and showed a maximum current density for the Pt-PdNPs/G catalyst with a nominal Pt/Pd ratio of 1/3. The Pt1Pd\(_3\)NPs/G catalyst showed higher current density (2.727 mA cm\(^{-2}\)) than PtNPs/G (1.688 mA cm\(^{-2}\)) and PdNPs/G (1.157 mA cm\(^{-2}\)).

To improve the ORR kinetics, Pt-bimetallic and trimetallic alloys with different structures such as core-shell (Ma et al., 2010), cage bell (Qu et al., 2012), hollow Pt nanosphere (Chen et al., 2008) etc, have recently been designed and these studies are comprehensively reviewed by Singh et al. (2014).

Antolini et al. (2008) have recently presented a comprehensive review of Pt based catalysts as methanol resistant oxygen reduction materials for direct methanol fuel cells.

Recently, it is observed that the Pt surface modified with nitrogen (PtN\(_x\)/C) shows significant methanol tolerance as compared to commercial Pt/C while maintaining their high activity towards ORR (Oh et al., 2007). The high methanol tolerance may be attributed to the modification of the surface with nitrogen which prevents methanol from adsorbing on the active sites while oxygen is not disturbed for the reduction reaction. Later, Oh and Kim (2008) reported that the heat treatment temperature and the molar ratio of Pt to N play important roles in the
performance of the catalyst. The heat treatment higher than 500 °C is effective to modify the Pt surface.

Hwang et al. (2007) prepared Pt-Co/C bimetallic NPs via a modified Watanabe process by employing microwave heating to correlate the structure-catalytic activity relationship for Pt-Co/C bimetallic NPs toward the ORR. As compared to the Pt/C catalyst, the bimetallic Pt-Co/C catalysts exhibited an enhancement factor of 3 in the mass activity at 0.95 V toward ORR. The activity enhancement might originate from the favourable electronic effects of a well mixed alloy underneath a thin “Pt-rich skin” structure of the Pt-Co bimetallic NPs. This “Pt-rich skin” is created by the dissolution of Co-oxide on Pt-Co bimetallic NPs while washing in acidic electrolyte before being subjected to the ORR study.

Qian et al. (2008) prepared PtM/C (M = Co, Cr, or Fe) for ORR analysis in acidic medium. The PtM/C catalysts in 1 M HClO₄ followed the ORR activity order: \( \text{PtCo/C(T, 500)} > \text{PtCr/C(S)} > \text{PtFe/C(S)} > \text{Pt/C} > \text{PtFe/C(T, 500)} \), showing that PtCo/C-type catalysts had a higher catalytic activity for ORR. The number of exchanged electron in the ORR was found to increase from 3.4 to 4.2 when the sintering temperature increased from 200 to 500 °C.

Nesselberger et al. (2011) reported the influence of particle size on the ORR activity of Pt in three different electrolytes: HClO₄, H₂SO₄ and KOH. The activity trend for the ORR with increasing particle size is independent of the electrolyte and it rapidly decreases going from polycrystalline Pt, to unsupported Pt black particles and high surface area (HSA) carbon supported Pt NPs.

Carpenter et al. (2012) also obtained well-faceted cubic and octahedral nanocrystals of Pt₃Ni, and octahedral and truncated octahedral nanocrystals of PtNi through the solvothermal method using DMF as both solvent and reductant. These Pt alloy nanocrystals were found to have ORR specific activities 3-5 times greater than that of a Pt standard catalyst.

Guo et al. (2013a) reported a new seed-mediated synthesis of core/shell FePtM/FePt (M = Pd, Au) nanowires (NWs) and their electrocatalysis for ORR in 0.1 M HClO₄. These FePtM/FePt NWs show shell thickness and core composition-dependent electrocatalytic activity for ORR. They are generally more active and durable than the corresponding alloy NW. The FePtM/FePt (0.8 nm shell) NWs are also stable in the ORR condition and show no activity
decrease after 50000 potential sweeps between 0.4 and 0.8 V (vs. Ag/AgCl). Authors have claimed that these are the most efficient catalysts ever reported for ORR.

Seo et al. (2011) obtained GNS-supported Pt (Pt/GNS) and Pd (Pd/GNS) NPs and observed superior ORR activity of Pd/GNS compared to Pt/GNS in alkaline media. Kou et al. (2009) studied the ORR on Pt NPs supported on functionalized graphene sheets (f-GNS) in 0.5 M H\textsubscript{2}SO\textsubscript{4}. This electrode showed a higher electrochemical surface area and oxygen reduction activity with improved stability as compared with the commercial catalyst. The improved performance can be attributed to smaller particle size (~2 nm) and less aggregation of Pt NPs on the functionalized graphene sheets.

Xin et al. (2011) deposited the Pt NPs onto graphene sheets via synchronous reduction of H\textsubscript{2}PtCl\textsubscript{6} and graphene oxide (GO) suspension using NaBH\textsubscript{4}. Lyophilization is introduced to avoid irreversible aggregation of GNS, which happens during conventional drying process. Pt/GNS catalysts revealed a high catalytic activity for both methanol oxidation and oxygen reduction reaction compared to Pt supported on carbon black (Pt/C). The performance of the catalytic film is further improved after heat treatment in N\textsubscript{2} atmosphere at 300 ºC for 2h. In fact, the interaction between GNS and Pt NPs is enhanced during annealing.

Rao et al. (2011) prepared graphene-supported Pt and Pt\textsubscript{3}M (M = Co and Cr) alloy NPs by ethylene glycol reduction method. The ORR activity of Pt\textsubscript{3}M/GNS electrode is found to be 3-4 times higher than that of Pt/GNS. In addition, Pt\textsubscript{3}M/GNS electrodes exhibited overpotential 45-70 mV lower than that of Pt/GNS. The high catalytic performance of Pt\textsubscript{3}M alloys is ascribed to the inhibition of formation of (hydr)oxy species on Pt surface by the alloying elements.

He et al. (2012) synthesized graphene nano-sheets supporting Pt NPs using perfluorosulfonic acid (PFSA) as a functionalized anchoring agent. The prepared Pt NPs are uniformly deposited on GNS with a narrow particle size ranging from 1-4 nm in diameter. The novel catalyst exhibited a higher catalytic activity for ORR. The PFSA/functionalyzed Pt/GNS (PFSA-Pt/GNS) catalyst revealed a better CO-oxidation and lower loss rate of electrochemical area in comparison with that of the plain Pt/GNS and conventional Pt/C catalyst. The PtCo NP catalysts on hexadecyltrimethylammonium bromide (CTAB)-functionalized graphene support (Nam et al., 2012), Pt NPs-dispersed GNS-wrapped MWCNT composites (Arvind et al., 2012), and Pt/GNS/CB composite structure (Li et al., 2012), recently investigated have also shown
considerably enhanced ORR activities, specific surface areas and long term durabilities compared to commercial catalysts.

1.2 Modification of conductive membrane

The crucial part in a fuel cell is the polymer membrane having the essential function of a H⁺/OH⁻ conductive medium as well as a barrier to prevent direct contact between fuel and oxidant. The polymer membrane should maintain high proton conductivity; have reasonable chemical, thermal and mechanical stability; a low permeability to reactants; low cost; and ready availability.

A lot of research work toward the development of membrane technology have been carried out and were reported in the literature (Zhang et al., 2012; Merle et al., 2011; Thiam et al., 2011).

The most employed proton-conductive membrane is currently Nafion, which is a perfluorinated polymeric membrane developed by DuPont in the late 1960s (Kim et al., 2006). The advantages associated with Nafion membrane is its chemical stability, high proton conductivity, and high mechanical strength but its high methanol permeability (~10⁻⁶ cm²/s), high cost and lower operational temperature (~100 °C or lower) limited its application (Ahmad et al., 2010).

The commercial Nafion membranes, such as the fluorinated membrane from DuPont (Kim et al., 2006; Fu et al., 2008), Flemion from Asahi Glass and Neosepta from Tokuyama Soda (Wirguin, 1996), have been intensively used as proton-conducting electrolyte membranes in DMFC due to their chemical stability and high proton conductivity (~0.1 S/cm) in the fully hydrated state. In addition, this unique polymer also possesses high mechanical strength (Sadrabadi et al., 2009) and elevated thermal stability (Kumar et al., 2009).

Recently, inexpensive engineering thermoplastics, such as poly (etheretherketone) (PEEK) (Kim et al., 2006; Xing et al., 2004), polysulfone (PSF) (Kim et al., 2006; Karlsson et al., 2004) and polybenzimidazole (PBI) (Zhai et al., 2007) as alternative for the commercial Nafion membrane (a proton-conductive membrane) applicable in DMFCs, as they shows very high mechanical and thermal stability in high temperature operation and also their cost is lower than Nafion.

The extensive researches have been carried out to modified Nafion membrane or produce other comparable polymer or composite membrane since Nafion is a very expensive material. In the last decade, there was so many materials or filler had been tried to develop a new hybrid
membrane with better quality such as silica (Kim et al., 2006), montmorillonite (MMT) (Sadrabadi et al., 2009), polyvinyl alcohol (Kumar et al., 2009), SiO$_2$ (Xi et al., 2007), ZrO$_2$ (Rodgers et al., 2008), zeolite (Wang et al., 2008d), zirconium phosphate (Helen et al., 2006), poly(propylenoxide) (Lin et al., 2007), SPEEK (Helen et al., 2006), PBI (Ainla et al., 2007), PSF (Karlsson et al., 2004), etc.

The commercially available anion-exchange membranes (AEMs) are typically based on crosslinked polystyrene and are not very stable in alkaline or electrochemical environments. In addition, the aminated crosslinked polystyrene is blended with other polymers and with fabric supports that limit the ionic conductivity and may decrease the chemical stability of the membrane. (Merle et al., 2011).

The first AEM was developed by Japanese scientists from the Tokuyama Soda Company using polychloropropene crosslinked by divinylbenzene. It was then functionalized with quaternary ammonium groups via triethylamine (Wang et al., 1997). In recent years efforts have been made in direction to remove the shortcoming associated with AEM. Merle et al. (2011) reported a lot of studies carried out on anion exchange membrane, such as AEM from Poly vinyl alcohol (PVA) and poly (acrylic acid) PAA (Wu et al., 2006b), having ionic conductivity of $30 \times 10^{-2}$ S cm$^{-2}$ at room temperature, stable at a wide temperature range (25-90°C) and has excellent thermal and mechanical properties, chitosan (Barbara 2001), alkaline-blend polymer electrolyte based on PVA/tetraethyl ammonium chloride (TEAC) (Yang et al., 2005) etc. Some hybrid based membrane were also reported such as, copolymer of glycidylmethacrylate (GMA) and $\gamma$- methacryloxypropyl trimethoxy silane ($\gamma$-MPS) (Yonghui et al., 2006) having anion exchange capacities in the range of 0.83–1.36 $\times 10^{-3}$ eq g$^{-1}$, copolymer based on vinyl benzyl chloride and called poly(VBC-$\gamma$-MPS) (Wu et al., 2008a), plomer electrolyte based on PVA polymer matrix, titanium dioxide (TiO$_2$) ceramic fillers, KOH, and H$_2$O (Wu et al., 2008b), PVA/ZrO$_2$ polymer electrolytes (Yang et al., 2006), etc.

Yan et al. (2012) prepared a series of imidazolium-functionalized polysulfones (PSf-ImOHs) successfully by chloromethylation-Menshutkin two-step method. PSf-ImOH possesses very high thermal stability (TOD: 258 °C), higher than quaternary ammonium and quaternary phosphonium functionalized polysulfones (TOD: 120 °C and 186 °C, respectively). Ion exchange capacity (IEC) of PSf-ImOH membranes ranges from 0.78 to 2.19 mmol g$^{-1}$ with degree of chloromethylation from 42% to 132% of original chloromethylated polysulfone. PSf-
ImOH membranes have low methanol permeability of $0.8-4.7 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, one order of magnitude smaller than that of Nafion 212 membrane.

1.3 Novel Pt-free new electrode materials

As the literature is quite vast and it is not possible to describe all the research work carried out to improve the overall efficiency of the cell in the present dissertation. It is therefore decided to describe the important work carried out to discover new Pt-free electrode materials to improve the efficiency of methanol oxidation and oxygen reduction reaction in alkaline solution. The work improvement carried out in this direction can be grouped as follows:

1.3.1 Methanol oxidation reaction

1.3.1.1 Pure Ni and Ni-based metal composites and alloy

Transition metals were also studied as electrode materials for methanol oxidation in alkaline medium. Among which, nickel is the most investigated electrocatalyst. It is considered that when Ni is placed in contact with an aqueous alkali solution, it gets covered with a layer of Ni(OH)$_2$ (Fleischmann et al., 1971).

Under anodic potential condition, the Ni(OH)$_2$ surface normally changes in the following manner:

$$\text{Ni(OH)}_2 \rightarrow \text{NiOOH} + \text{H}^+ + e^- \quad (a)$$

The oxidation of primary alcohols at Ni/NiOOH electrodes in alkaline medium leads to the formation of organic acids as shown below:

$$\text{RCH}_2\text{OH} + \text{NiOOH} \rightarrow \text{RCOOH} + \text{Ni(OH)}_2 \quad (b)$$

It is reported that the MOR commences in the potential region where multi-layers of NiOOH are formed on the electrode surface, and occurs in two stages (Kowal et al., 1997): (i) methanol is firstly oxidized to formate in the potential window 0.36–0.44V (vs. SCE) and (ii) formate is then oxidized further to carbonate at potentials above ~ 0.45 V vs. SCE. The MOR has been investigated on dispersed Ni, nickel alloy and nickel complex modified CNTs in alkaline medium. The MOR activity of Ni is found to enhance by alloying with Ru and Cu (Kim and Park, 2003; Kazakov et al., 2004; Danaee et al., 2008; Jafarian et al., 2006). According to Shen et al. (2010) and Bambagioni et al. (2009), Ni species are oxophilic like Ru and have the capacity to generate OH$_{ads}$ at a lower potential, and facilitate the oxidative desorption of the intermediate products, thus enhancing both the catalytic activity and stability of noble and non-noble catalysts. Singh et al. (2008 a, & 2008 b) studied the MOR on electrodeposited films of Ni
on graphite, glassy carbon and Ti electrodes in 1M KOH + 1M CH₃OH. Results showed a strong influence of the nature of support on the activity of the Ni over layer. They further observed that the MOR activity of Ni improved greatly when it was obtained in highly dispersed form on high surface-area La₂₋ₓSrₓNiO₄ (0≤ₓ≤1) electrodes. It is claimed that similar MOR current densities have not been found on any other non platinum electrodes in alkaline solutions. It is noteworthy that modified electrodes are not poisoned during the MOR. Thus, these oxide catalysts can be used as a support in alkaline DMFCs.

Barakat et al. (2014) reported CoₓNiₓ-decorated graphene as novel, super effective and stable non-precious electro-catalyst for methanol oxidation. The obtained results have indicated that utilizing graphene as a support strongly enhances the electro-catalytic activity as the current density was nearly ten times. A negative onset potential (−40 mV vs. Ag/AgCl) was obtained which is considered as a distinct progress in the non-precious electro-catalysts research field. The electronic structure which is controlled by the alloy composition showed strong influence on the electro-catalytic activity; Co₀.₂Ni₀.₂ alloy nanoparticles revealed the best performance while Co₀.₁Ni₀.₃ nanoparticles were the worst.

1.3.1.2 Transition metal complex oxide

The complex oxides of Transition metals belonging to perovskite and spinel families have also been investigated for electrocatalysis of MOR. Among the transition metal oxides, the perovskite oxides of the general compositions ABO₃ and A₂BO₄ with excellent electrical conductivities and catalytic activity were considered as possible materials for the application as anodes in DMFCs.

Raghuveer et al., (2001), has tested a series of rare earth cuprates with compositional formulae Ln₂₋ₓMₓₖCu₁₋ₐMₙ₋₉'O₄₋₅ (where Ln = La and Nd; M= Sr, Ca and Ba; M’ = Ru and Sb: 0.0 ≤ x ≤ 0.4 and y = 0.1) as anode electrocatalysts for MOR in alkaline media. These materials showed significant activity for the MOR at higher potentials. The linear correlation between Cu³⁺ content and MOR activity suggested that the active sites for adsorption of methanol are Cu³⁺ ions. These materials showed better tolerance against the poisoning compared to that of conventional noble metal electrocatalysts. The lattice oxygen in these oxides has been considered as active oxygen to remove CO intermediates of MOR. The methanol oxidation onset potential for La₁₋ₓSrₓCoO₃₋₅ was 0.03 V lowers than that for La₁₋ₓSrₓCuO₃₋₅. However, the electrocatalytic activity for MOR on La₁₋ₓSrₓCuO₃₋₅ was much higher than that of
La$_{1-x}$Sr$_x$CoO$_{3-\delta}$. The results showed the higher electrocatalytic activities of La$_{1-x}$Sr$_x$CuO$_{3-\delta}$ are due to the capability of Cu ions for the adsorption of methanol and the existence of a large amount of oxygen vacancies facilitating oxygen ion (O$^{2-}$) transport into the proximity of adsorbed methanol oxidation intermediates at the reaction sites.

_Biswas et al. (1992)_ investigated Perovskites, La$_{1-x}$Sr$_x$CoO$_3$ and La$_{1-x}$Sr$_x$MnO$_3$, as promoters of the MOR on Pt in alkaline medium.

_Singh et al. (2008 a, b; 2007)_ investigated the MOR activities of La$_{2-x}$Sr$_x$NiO$_4$ (0 $\leq$ x $\leq$ 1), LaSrNi$_{1-x}$Ru$_x$O$_4$ (0.1 $\leq$ x $\leq$ 1) and Cu$_x$Co$_{3-x}$O$_4$ (0 $\leq$ x $\leq$ 1) in an alkaline solution at 25 °C. The results demonstrate that all the three series of oxide electrodes are CO poisoning tolerant and quite active for the MOR. The electrocatalytic activity is observed to increase with x in the case of oxides without containing Ru. The onset potential for MOR on Pt was significantly lower than that on La$_{2-x}$Sr$_x$NiO$_4$, however, the observed apparent current densities are considerably low at Pt compared to that on La$_{2-x}$Sr$_x$NiO$_4$.

_Ding et al. (2013)_ prepared porous nickel cobaltite (NiCo$_2$O$_4$) by a facile chemical deposition route. The NiCo$_2$O$_4$ material is found to exhibit typical agglomerate porous nanostructures with the specific surface area (SSA) and pore volume of ~190 m$^2$ g$^{-1}$ and 1.136 cm$^3$ g$^{-1}$. NiCo$_2$O$_4$ exhibited higher electrocatalytic activity, lower overpotential, better stability and greater tolerance compared to those of NiO and Co$_3$O$_4$ materials synthesized by the same procedure. The impressive electrocatalytic activity is largely attributable to the binary electroactive sites of Co and Ni species, intrinsic high electronic conductivity and superior porous nanostructures of the NiCo$_2$O$_4$ electrode.

### 1.3.1.3 Pure Pd or Pd-based metal composites and alloys

With regard to new fuel cell anode electrocatalysts, there are two major concerns: performance, including activity, reliability and durability, and cost reduction. As on till date no any Pt based electrocatalyst is reported which can produce acceptable power densities in direct alcohol fuel cell (DAFCs). According to the annual report of the U.S. Department of Energy (DOE) in 2008, the Pt-based catalyst ink accounts for 27–43% of the cost of a direct H$_2$ PEM fuel cell stack (James, B. D.; Kalinoski, J. A. Mass Production Cost Estimation for Direct H$_2$ PEM Fuel Cell System for Automotive Applications: 2008 Update, 2009). The total cost of a fuel cell stack can be largely reduced by lowering the catalyst loading and using low- or non-Pt-based
electrocatalysts. Therefore, how to improve the catalytic activities and lower the costs of anode and cathode catalysts are the critical issues to realize the real commercialization of fuel cells.

Considerable efforts are, therefore, being carried out to design new catalytic structures for DAFC anodes that do not contain platinum or contain tiny amounts of this rare metal and, most are able to oxidize primary and secondary alcohols with fast kinetics and tolerable deactivation. Within this context, palladium is emerging as an attractive replacement for platinum in DAFCs. Palladium is more abundant in nature (15 parts per billion by weight, www.Chemicool.com a) and less expensive (cost of pure Pd: $ 5833 per 100 g, www.Chemicool.com a) than platinum (abundance of Pt: 5 parts per billion by weight and cost of pure Pt: $ 13000 per 100 g, www.Chemicool.com b) but cost-associated issues are not the main driving force behind the increasing interest in palladium, the real attraction for Pd-based electrocatalysts is originated by the fact that, unlike Pt-based electrocatalysts, they can be highly active for the oxidation of a large variety of substrates in alkaline environment wherein non-noble metals are sufficiently stable for electrochemical applications. Not only this, the substitution of Pd with suitable non-noble metals (transition metal or their oxides) can decrease the cost of the membrane electrode assemblies (MEAs) so as to boost the commercialization of DAFCs.

Shen et al., (2006) prepared nanocrystalline oxides (CeO$_2$, Co$_3$O$_4$, Mn$_3$O$_4$ or NiO) incorporated Pd/C electrocatalysts by intermittent microwave heating. All the four Pd-oxide/C electrocatalysts exhibited the higher MOR activities and poisoning tolerance than that of Pt/C or PtRu/C electrocatalysts, the activity, however, being the greatest with the Pd-NiO/C electrode. The electrocatalytic activity of the Pd–NiO/C electrocatalyst towards alcohol oxidations at E = -0.20 V vs Hg/HgO, followed the order: ethanol (266.67 mA mg$^{-1}$) > ethylene glycol (150 mA mg$^{-1}$) > methanol (103.7 mA mg$^{-1}$) > glycerol (50.0 mA mg$^{-1}$).

Xu et al., (2008a) performed similar studies of oxidation of methanol, ethanol, ethylene glycol (EG) and glycerol on Pt/C, Pd/C and oxide (CeO$_2$, NiO, Co$_3$O$_4$ and Mn$_3$O$_4$)-promoted Pd/C in 1M KOH + 1M alcohol.

Results indicated that Pd/C electrocatalysts alone had low activity and very poor stability for the alcohol electro-oxidation. However, addition of oxides like CeO$_2$, NiO, Co$_3$O$_4$ and Mn$_3$O$_4$ improved significantly the catalytic activity and stability of the Pd/C electrocatalysts for the alcohol electrooxidation. The Pd-Co$_3$O$_4$ (2:1, w:w)/C exhibited the highest activity for the electrooxidation of methanol, j being 80, 100.3 and 39.7 mA mg$^{-1}$ at E = -0.30 V vs. Hg/HgO,
for methanol, EG and glycerol oxidations, respectively. While the most active catalyst for the ethanol electrooxidation is Pd-NiO (6:1, w:w)/C ($j=189.0$ mA mg$^{-1}$ at $E=-0.3$ V vs. Hg/HgO). On the other hand, Pd-Mn$_3$O$_4$/C shows significantly better performance ($j=54.3$ mA mg$^{-1}$ at $E=-0.3$ V vs. Hg/HgO) for ethanol oxidation reaction.

Zhang et al., (2006) prepared well-dispersed Pd NPs on the surface of vanadium oxide nanotubes (VO$_x$-NTs) through a simple reductive process. The morphology and structure of the resulting Pd/VO$_x$-NTs composites were characterized by TEM, electron diffraction (ED) and XRD. The MOR study carried out in 1M CH$_3$OH + 0.1M NaOH indicated that the prepared Pd/VO$_x$-NTs composites had an excellent electrocatalytic activity ($I_p = 0.09$ mA) and stability in comparison to the VO$_x$-NTs electrode. The peak currents were linearly proportional to the square root of scan rates, which suggested the electrocatalytic oxidation of methanol on Pd/VO$_x$-NTs is a diffusion controlled process.

Wang et al., (2008) prepared highly ordered Pd/Pt core–shell nanowire arrays (Pd/Pt NWAs) by anodized aluminum oxide (AAO) template-electrodeposition and magnetron sputtering methods. Pd/Pt NWA electrode showed a very high electrochemical active surface area and high electrocatalytic activity for the methanol electrooxidation in acid medium. The mass specific anodic peak current density was 756.7 mA mg$^{-1}$ Pt for the methanol oxidation on the Pd/Pt NWA electrode. This is higher by a factor of four as compared to conventional E-TEK PtRu/C electrocatalysts.

Cheng et al., (2008) have synthesized highly ordered Pd nanowire arrays (NWAs) using a porous aluminum oxide template by pulse electrodeposition. The study indicated excellent electrocatalytic activities for Pd NWAs electrodes for methanol and isopropanol oxidation in alkaline media; the peak current densities being 111 and 65 mA cm$^{-2}$, in methanol and isopropanol, respectively.

Liu et al., (2008) reported the oxidation of methanol, 1-propanol, and 2-propanol on electrodes constituted by Pt and Pd disks, in alkaline media, and suggested that Pd is a much better catalyst for the oxidation of 2-propanol and 1-propanol as compared to Pt.

Xu et al., (2008b) demonstrated a completely new, simple and effective strategy for preparing catalysts by using β-MnO$_2$ nanotubes as the supporting materials. The Pd nanoparticles were coated onto β-MnO$_2$ nanotubes through a simple reductive process. The study indicated that
the Pd nanoparticles were homogeneously dispersed and well separated from one another on the β-MnO₂ nanotubes surfaces. In the case of methanol oxidation in 1M CH₃OH + 0.1M NaOH, the Pd/β-MnO₂ nanotubes electrodes have a lower onset potential and higher catalytic activity than the one on Pd/C electrode. The long term stability of the electrode was checked by recording 500 cycles of CV at 100 mV s⁻¹ and found that after 500 scan, the peak current was still about 82% of that of the first scan.

The largest number of half cell studies is concerned with nanostructured Pd, alone or alloyed with other metals, supported on carbon materials such as C, CMSs, CHCs, HCSs, CNTs, and nanofibers (NFs) (Bianchini, and Shen, 2009).

Lee et al., (2009) have synthesized Pd nanoparticles on Vulcan XC-72R (Pd/C) by means of polyl process in poly(vinyl pyrrolidone) and NO₃⁻ ion. Cyclic voltammogram (CV) analyses showed higher catalytic activity (2.32 mA cm⁻²) and higher stability of the synthesized Pd/C nanoparticles than commercial Pd/C (1.33 mA cm⁻²) at 20 µg cm⁻² Pd loading for methanol electrooxidation in 0.1M NaOH + 2M CH₃OH. However, the EASA value for the new electrode (3.69 m² g⁻¹) was considerably low compared to that for commercial Pd/C (32.35 m² g⁻¹).

Wang et al., (2009a) prepared nanoporous palladium (NPPd) with ultrafine ligament size of 3–6 nm by de-alloying of an Al–Pd alloy in an alkaline solution and investigated their electrocatalytic activity for electro-oxidation of methanol, ethanol, and formic acid in 1M KOH + 1M alcohol solution. The mass activities were quite high; values were 149, 148, 262 mA mg⁻¹ for the oxidation of methanol, ethanol and formic acid, respectively.

Bambagionia et al., (2009) have prepared palladium and platinum–ruthenium nanoparticles supported on MWCNT by the impregnation-reduction procedure. The performance of materials so obtained, were investigated for the oxidation of methanol, ethanol, and glycerol in 2M KOH solutions. The Pd/MWCNT electrode exhibited the high activity for the oxidation reaction of all alcohols even at metal loadings as low as 17-20 µg cm⁻² in comparison to that of the Pt-Ru/MWCNT electrode. Such a remarkable electrocatalytic activity of Pd/MWCNT can be associated to both the high dispersion of the metal particles and the intrinsic properties of the MWCNTs. Notably, the Pd/MWCNT electrode is electrochemically stable only for the oxidation of ethanol, while the oxidation reactions of methanol and glycerol are featured by a fast increase of the overpotential.
Liu et al., (2009) prepared Pd and PdNi nanoparticles supported on Vulcan XC-72 carbon by a chemical reduction with formic acid process. The catalysts were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), cyclic voltammetry, and chronoamperometry for the oxidation of methanol in 1M NaOH + 1M CH₃OH solution. The results showed that the PdNi/C catalyst has higher electrocatalytic activity (520 A g⁻¹ Pd) than the Pd/C (460 A g⁻¹ Pt) catalyst.

Singh et al., (2009 a & 2009 b) obtained the nanocomposite films of Pd and MWCNTs and of Pd and NC for use as electrocatalysts for MOR in alkaline medium. Results have demonstrated that a low content of MWCNTs/NC in the composite improves the electrocatalytic activity of the electrode greatly. In contrast, its higher contents (> 1wt% MWCNT or 0.5%NC) decreased the activity. The electrocatalytic activity of the composite electrode was the greatest with 1% MWCNT (jₚ ≈ 607.73 mAmg⁻¹ Pd, Ep ≈ 65 mV vs. Hg/HgO and 0.5% NC (jₚ ≈ 258.67 mAmg⁻¹ Pd, Ep ≈ -5 mV vs. Hg/HgO) in 1M KOH + 1M MeOH. Introduction of 1% Ni to the active Pd-1wt%MWCNT electrode improves the apparent electrocatalytic activity further.

Zhao et al., (2010) have prepared MnO₂-modified MWCNTs (MnO₂/MWCNTs) supported Pd-nanoparticles (NPs) by wet impregnation method and studied their electrocatalytic activity towards methanol electrooxidation reaction. Pd-MnO₂/MWCNTs exhibited higher electrocatalytic activity and stability than Pd/MWCNTs and Pd/carbon black. The synergetic effect between Pd and MnO₂ on MWCNTs is considered to be the main reason for the enhanced performance of Pd- MnO₂/MWCNTs toward methanol electrooxidation.

Anindita et al., (2011) prepared ternary nanocomposites of Pd, Ru and NC by the sodium borohydride reduction method and investigated as electrocatalyst for MOR in alkaline medium. The study have shown that with the increase of weight percent of Ru, from 1 to 50 wt%, in the Pd-0.5wt%C-Ru composite, the rate of MOR initially increases, attains a maximum and declines thereafter. Among the electrocatalysts investigated, the Pd-0.5wt%C-20wt% Ru electrode exhibited the greatest electrocatalytic activity. This active electrode was approximately three times more active than the base electrode (Pd-0.5wt% C).

Wang et al., (2011) prepared bimetallic Pd-Ag/C catalysts with different Ag loadings by the borohydride reduction method and investigated for methanol electrooxidation. The Pd-Ag(1:1)/C catalyst exhibited the greatest catalytic activity among the series.
Qi et al., (2011) prepared PdNi alloy from dealloying a ternary Al$_{7.5}$Pd$_{10}$Ni$_{15}$ alloy in an aqueous solution of 20 wt% NaOH under free corrosion condition. The alloy catalyst, Pd$_{40}$Ni$_{60}$, so obtained, exhibited an enhanced electrocatalytic performance towards MOR.

Alcaide et al., (2011) studied the electrochemical behavior of carbon supported Pd-Pt electrocatalysts toward MOR and reported that 25:75 atomic ratio of Pd:Pt gives the best performance in direct methanol single fuel cell test.

Zhang et al., (2011a) prepared Pd/GNS by a microwave-assisted one-pot method with the use of tannic acid as a reducing agent. They reported much higher electrocatalytic activity and stability than that of commercial Pd/C catalyst towards MOR in alkaline medium.

Zhao et al., (2011) synthesized Pd nanoparticles supported on polypyrrole (ppy)-functionalized graphene (Pd/PPy-GNS). The electrochemical test indicated that the electrocatalytic activity of Pd/PPy-GNS is much better than that of the commercial catalyst for methanol oxidation.

Guo et al. (2010) demonstrated a wet-chemical approach for the synthesis of high quality 3D Pt-on-Pd bimetallic nanodendrites supported on GNS (TP-BNGN). The electrochemical data indicated that the as-prepared graphene/bimetallic nanodendrite hybrids exhibited much higher electrocatalytic activity towards MOR than the platinum black (PB) and commercial E-TEK Pt/CB catalysts.

Zhang et al. (2011c) prepared graphene-supported Pd$_1$Pt$_3$ electrocatalyst by fast one-step microwave heating method. They observed an increase in electrochemically active area of the Pd$_1$Pt$_3$ nanostructures with introduction of graphene. The graphene supported Pd$_1$Pt$_3$ electrocatalyst exhibited 80% enhancement of the electrocatalytic specific mass current for the oxidation of methanol than unsupported Pd$_1$Pt$_3$.

Zhang et al. (2011d) obtained well-dispersed PtPdAu ternary alloy nanoparticles on GNS via a simple one-step chemical reduction method in ethylene glycol and water system. Electrochemical experiments demonstrated that the synthesized PtPdAu catalyst/GNS exhibited much better catalytic activity and stability for MOR compared to PtPd/GNS, PtAu/GNS and Pt/GNS catalysts in alkaline solutions.

Li et al. (2012) prepared Pd/GNS by a photocatalytic method and investigated as electrocatalyst for MOR in alkaline medium. Pd/GNS electrocatalyst exhibited 3.4 times higher catalytic activity than that of commercial Pd/C catalyst.
Ye et al. (2013) investigated the effect of oxide (CeO$_2$, NiO, Co$_3$O$_4$, and Mn$_3$O$_4$) on stability of Pd/C for methanol oxidation in alkaline medium. Results showed that the Pd–Mn$_3$O$_4$/C is the best stable catalyst and gives the best stable performance of methanol oxidation. The Pd–Co$_3$O$_4$/C and Pd–NiO/C give much higher catalytic activities than the other Pd-oxide/C electrocatalysts, however, they did not show the stable performance toward methanol oxidation.

An et al. (2013) prepared Pd/SnO$_2$–TiO$_2$/MWCNT by a facile and controllable in situ chemical method and evaluated their performances in methanol and ethanol oxidation reactions evaluated. The results revealed that the composite provided excellent and superior levels of performance in terms of their electrocatalytic activity, electrochemical active surface (EAS), carbon monoxide (CO) tolerance and stability for both methanol and ethanol oxidations in alkaline solutions.

Kannan et al. (2013) adopted one-pot synthesis of chain like palladium nano cube and studied their MOR activity. The cubic chain-like Pd nanostructures show ~11.5 times more activity on the basis of an equivalent noble metal mass for methanol oxidation than the spherical shaped Pd nanoparticles and commercial Pd/C catalysts. Also the electrocatalytic performance of anisotropic cubic chain-like Pd nanostructures toward the alcohol oxidation is superior than the rest of catalysts.

Cui et al. (2014) prepared mesoporous Ti$_{0.5}$Cr$_{0.5}$N supported PdAg nanoalloy by solid-solid phase separation method. This ternary nitride exhibits highly porous, sintered, and random network structure with a crystallite size of 20-40 nm, resulting in a high specific surface area. Bimetallic PdAg nanoparticles (~ 4 nm) act as anode catalysts for the methanol oxidation but PdAg/Ti$_{0.5}$Cr$_{0.5}$N exhibits much higher mass activity and durability for MOR than PdAg/C and Pd/C.

Zhao et al. (2014) synthesized size-controlled amorphous Pd–Ni–P NPs. Differential scanning calorimetry identified typical MG (metallic glass) properties of the unsupported Pd–Ni–P NPs with a wide supercooling region of 55 K (602–657 K). The supported MG-NPs showed remarkable catalytic properties in methanol electro-oxidation in an alkaline medium. After 400 voltammetry cycles, the loss of current density was only 3.5% when Pd–Ni–P NPs on Vulcan XC-72 were used as a catalyst.

Zheng et al. (2014a) prepared core-shell gold-palladium @palladiumnanocrystals (AuPd@Pd) by a simple and green wet-chemical method at 25ºC. Buffer, 2-[4-(2-hydroxyethyl)-
1-piperazinyl] ethanesulfonic acid (HEPES), is used as a reducing agent and a shape-directing agent, while there is no template, seed, organic solvent, or surfactant involved. The as-prepared nanocomposites exhibited good methanol oxidation activity in alkaline medium compare to the G-Pd and commercial Pd black catalysts. The G-AuPd@Pd shows the specific activity of 0.401 mA cm$^{-2}$Pd, which is 3.8 and 1.1 times higher than those of the G-Pd (0.105 mA cm$^{-2}$Pd) and Pd black (0.368 mA cm$^{-2}$Pd) catalysts.

Amin et al. (2014) prepared Pd, Ni and Pd–Ni nanoparticles uniformly dispersed on Vulcan XC72R carbon black by microwave irradiation using NaBH$_4$ as a reducing agent. The electrocatalysts were examined for methanol oxidation in alkaline medium (0.6 M MeOH + 0.5 M KOH). Two methanol oxidation peaks were observed at Pd–Ni/C at 0 and +913 mV. Their current density values are higher than those at Pd/C and Ni/C electrocatalysts by 3.84 and 1.43 times, respectively. The catalytic rate constant at Ni/C and Pd–Ni/C was estimated using double-step chronoamperometry as $1.80 \times 10^3$ and $5.88 \times 10^3$ cm$^3$ mol$^{-1}$ s$^{-1}$, respectively. Pd–Ni/C showed better stability performance when compared to Pd/C and Ni/C electrocatalysts.

Zhang et al. (2013a) prepared well-dispersed Pd nanoparticles (PdNPs) supported on graphene (PdNPs/PVP-graphene) sheets by a simple one-pot process, in which the reduction of Poly Vinyl Pyrrolidone-functionalized graphite oxide and Pd precursor was carried out simultaneously using ascorbic acid as a soft reductant. The peak current density of PdNPs/PVP-graphene is about 1.08 mA cm$^{-2}$, which is 1.93 times that of PdNPs/Vulcan (0.563 mA cm$^{-2}$). In the presence of 1.0 M NaOH and 0.5 M CH$_3$CH$_2$OH, the onset potential of ethanol oxidation on PdNPs/PVP-graphene (~0.75 V) is lower than on PdNPs/Vulcan (~0.65 V). And the peak current density of PdNPs/PVP-graphene is about 1.876 mA cm$^{-2}$, which is 1.25 times that of PdNPs/Vulcan (1.504 mA cm$^{-2}$).

Guo et al. (2013b) prepared Pd nanoparticle decorated on graphene by electrostatic self assembly method. Graphene nanosheets (GS) are non-covalently functionalized with novel N,N-bis-(n-butylimidazoliumbromide salt)-3,4,9,10-perylene tetracarboxylic acid diimide (PTCDI-ILs) via the π–π stacking, and then employed as the support of Pd nanoparticles. Pd nanoparticles with an average size of 2.7 nm are uniformly dispersed on GS surface. The Pd/PTCDIILs/GS exhibits unexpectedly high activity toward methanol oxidation reaction, probably due to the large electrochemical surface area of Pd nanoparticles. It also shows enhanced electrochemical stability due to the structural integrity of PTCDI-ILs/GS.
Huang et al. (2013) demonstrates a ternary nanocomposite based on Pd/MnO$_2$ nanolamella–graphene sheets (Pd/MNL/GS) applicable in direct methanol fuel cell (DMFC). Graphene has been used as both a green reducing agent in the synthesis of MnO$_2$ nanolamella as well as a superior supporting material for growing and supporting Pd nanoparticles (NPs). For MOR, Pd/MNL/GS hybrids showed extremely large electrochemically active surface areas (ECSAs) and significantly high forward peak current densities, than those of the Pd/GS and Pd/Vulcan XC-72 catalysts.

Wang et al. (2014) prepared the graphene-supported Pd-Co bimetallic composite for alcohol oxidation. At the same Pd loadings on graphene, the current densities corresponding to the forward anodic peak of the different Pd-Co/RGO catalysts were found to decrease by about 25% when compared with that of the pure Pd nanoparticles supported on reduced graphene oxide for both methanol. However, chronoamperometry tests confirmed that the stability was increased by up to 240% for methanol oxidation.

Wang et al. (2013a) investigated the electrocatalytic activities of Pd-NPs supported on reduced graphene oxide for methanol oxidation. They prepared several well-dispersed palladium nanoparticles with a diameter of around 5 nm, decorated on reduced graphene oxide sheets by a facile in-situ reduction where bivalent tin ions were used as reducing agent, in order to fabricate electrocatalyst for methanol oxidation. The EASA of Pd-RGO was found 31.12 m$^2$ g$^{-1}$ which exhibited excellent electrocatalytic activity and superior stability toward methanol oxidation reaction.

Li et al. (2014b) prepared high dispersion Pd nano-particles on a graphene-like carbon (GLC) surface functionalized by 9-amino-1-azabenzanthrone (AABZ). They found that the forward peak current density of the Pd-AABZ/GLC catalyst is 770 A g$^{-1}$Pd, which is 1.9 and 1.2 times higher than that of the Pd on commercial carbon black and reduced graphene oxide. The current at 3600 s of the chronoamperometric experiments for the Pd-AABZ/GLC catalysts is 230 A g$^{-1}$Pd, which is 2.54 times higher than that of Pd/XC-72 (Pd/commercial Vulcan XC-72 carbon black).

Bimetallic palladium-silver nanoparticles (NPs) supported on reduced oxide graphene (RGO) with different Pd/Ag ratios (Pd-Ag/RGO) were prepared by an easy green method which did not use any additional reducing agents or a dispersing agent (Li et al., 2014c). The Pd-Ag/RGO hybrids exhibited good electrochemical catalytic activity towards methanol and ethanol
electro-oxidations and Pd-Ag (1:1)/RGO had the best catalytic activity with peak current densities of 630 and 1601 mA mg\(^{-1}\text{Pd}\) for methanol and ethanol electro-oxidation, respectively. In addition, the Pd-Ag (1:1)/RGO showed high catalytic stability. Among the different Pd/Ag ratios, the Pd-Ag (1:1)/RGO had the best catalytic activity and stability.

Zheng et al. (2014b) prepared Pd/MgO-reduced graphene oxide hybrid for methanol oxidation. They studied effect of MgO content in the catalyst with Pd loading of 0.028 mg cm\(^{-2}\) on the electrocatalytic activity of Pd/MgO-RGO. The catalytic activity of the catalyst for methanol oxidation changes with the content of MgO. The best result was found on the Pd/MgO-RGO electrode with Pd to MgO weight ratio of 5:4. The \(I/I_b\) on Pd/MgO-RGO is 2.48 times as large as that on Pd/RGO, suggesting that Pd/MgO-RGO has less carbonaceous species accumulation and is much more tolerant toward CO poisoning.

Safavi et al. (2014) reported in situ electrodeposition of graphene/nano-palladium on carbon cloth (G-Pd/CC) for methanol oxidation in alkaline media. The ECSAs of G-Pd/CC and Pd/CC were 24.2 and 7.8 cm\(^2\), and the onset potentials for the oxidation of methanol on the G-Pd/CC and Pd/CC were about -0.63 and -0.35 V, (vs. SCE), respectively. The onset potential for the methanol oxidation on the G-Pd/CC electrode is 280 mV more negative than that observed on the Pd/CC electrode.

1.3.2 Oxygen reduction reaction
The oxygen electrode is highly irreversible in aqueous electrolyte and takes place at a high positive potential (\(E^o=1.23\) V vs. SHE) in acid medium. At a such high potential most of the metal electrodes will undergo dissolution, only noble metals and their alloys are stable. Both noble and non-noble metal based electrocatalysts have been investigated for ORR. Among the noble metals Pt and Pd metals and their alloys appears to be the best ones (Shukla & Raman, 2003; Markovic et al., 2001; Gasteiger et al., 2005; Viswanathan et al., 2006; Shao et al., 2011; Antolini et al., 2008). Other classes of electrocatalysts studied for ORR are transition metal chalcogenides (based on noble and non-noble metals) (Shukla & Raman, 2003; Viswanathan et al., 2006; Lee et al., 2007a; Othman et al., 2012); pyrolyzed macrocyclic compounds (Shukla & Raman, 2003; Viswanathan et al., 2006; Othman et al., 2012; Wang, 2005; Bezerra et al., 2007) and metallic oxides (Shukla & Raman, 2003; Viswanathan et al., 2006). The literature for ORR is very vast and it is not easy to discuss all the papers here, so, the literature review presented here is based on only some important and relevant papers.
1.3.2.1 Pd and Pd based catalysts

In acidic media, Pd has a higher ORR activity than any other noble metals, except for Pt, but Pd is more sensitive to anion adsorption than Pt due to stronger interaction between the Pd surface and anion (Cl\(^-\), ClO\(_4^-\), SO\(_4^{2-}\) etc.) (Climent et al., 2000; Arenz et al., 2003). While in alkaline media Pd exhibits higher ORR activity than in acidic solution due to decrease in the anion poisoning effect in alkaline solution. Indeed, many studies have shown that the ORR activity of Pd/C in alkaline solution is comparable to that of Pt/C (Shao et al., 2007; Jiang et al., 2009). On Pd the ORR takes place in the same manner as on Pt (Sepa et al., 1981; Vracer et al., 1987), however, it has lesser ORR activity and poorer stability than Pt, particularly at high cathodic potentials (Shao, 2011). To improve the activity and stability, a number of alloys of Pd with transition metals such as Pd–Fe (Zhang et al., 2011b), Pd–Co (Wang et al., 2012a; Lee et al., 2012), Pd–Ni (Sanchez et al., 2008), Pd–Cu (Kariuki et al., 2010), Pd–Ag (Slanac et al., 2012; Liu et al., 2013a), Pd–Mo (Sarkar et al., 2008), Pd–W (Sarkar et al., 2009), have been prepared and investigated.

According to Fernandez et al (2005a), the ORR on bimetallic electrocatalysts proceeds through a mechanism wherein one metal breaks the oxygen-oxygen bond of molecular oxygen and the other one acts to reduce the resulting adsorbed atomic oxygen as follows:

\[
2M + O_2 \rightarrow 2MO \\
2MO + 4H^+ + 4e^- \rightarrow 2M + 2H_2O
\]

Incorporation of more active metals (e.g., Co) into Pd facilitates the dissociative adsorption of O\(_2\) forming adsorbed oxygen atoms (O\(_{ads}\)). The latter (O\(_{ads}\)) atoms then migrate from the Co site to Pd site where the electroreduction reaction occurs with less polarization. Based on Gibbs free energy considerations, Pd-Co, Pd-Ti, Pd-Co-Au and Pd-Co-Mo are good ORR catalysts. Investigations of Pd-Co-Au (7:2:1)/C and Pd-Co-Mo(7:2:1)/C ternary catalysts and Pd-Ti binary catalyst as cathode materials in PEMFCs showed the comparable ORR performance to that of commercial Pt/C but good methanol tolerance and stability than Pt/C (Fernandez et al., 2005b; Raguveer et al., 2005; 2006). Similar results with Pd-Co alloys dispersed on C were also found by others (Shao et al., 2006a; Mustain et al., 2006; Wang et al., 2007). After high temperature annealing (900 °C) the Pd atom tends to migrate to the surface of the alloy nanoparticle forming a Pd rich ‘skin’ (Shao et al., 2006a). The origin of enhanced ORR kinetics on the Pd-Co catalyst is due to the combination of the compressive strain effect and
ligand effect which reduces the adsorption energy of the adsorbates by the d band center of the Pd skin.

For the Pd-M alloy system, Wang and Balbuena (2005) have proposed a thermodynamic guideline. According to them when a catalyst consists of two metals, one with a low occupancy of d-orbitals (Co, Ni, Cr or V) and the other with fully occupied d-orbitals (Pd, Au and Ag); the d orbital coupling decreases the Gibbs free energy of the electron transfer steps in ORR, resulting in an enhanced ORR kinetics.

The effect of particle size and degree of alloying were also studied by Liu and Manthiram (2008) on the Pd$_{70}$Co$_{30}$ catalyst. Results showed that an increase of the annealing temperature from 350 °C to 500 °C decreased the catalytic activity due to the enhanced degree of alloying and particle size. In the case of carbon-supported Pd-Co-Mo alloy, Rao and Viswanathan (2010) also observed the higher ORR activity with the catalyst heat treated at 700 °C compared to that heat treated at higher temperatures. The alloy catalyst showed considerably higher ethanol tolerance and stability and comparable ORR activity to commercial Pt/C in 0.5M H$_2$SO$_4$ containing ethanol, and the ORR follows the four electron reaction pathway leading to water formation. Wang et al., (2007) obtained the highest ORR activity for Pd:Co with atomic ratio of 2:1 and heat treated at 500 °C, whereas, Zhang et al., (2007) reported the optimal heat treatment temperature of 300°C for Pd-Co/C alloy electrocatalyst.

Xu et al., (2009) prepared a novel nanotubular mesoporous (NM), PdCu (NM-PdCu) bimetallic nanocomposite with a nanoporous shell, which showed superior ORR activity and methanol tolerance than commercial Pt/C and Pd/C catalysts. They suggested that the trimodal hollow bimetallic structure of the NM-PdCu plays crucial role for the enhancement of the ORR activity.

Shao et al., (2006b; 2007) demonstrated that the ORR activity of Pd$_3$Fe/C prepared by the hydrogen reduction and deposition methods is comparable to that of the Pt/C. They found good parallelism between specific activity and Pd-Pd interatomic distance which is expressed as a function of Fe content.

Incorporation of carbon atoms in the PdFe/C clusters and high temperature annealing facilitate the formation of Pd-Fe-C alloy and homogenous solid solution (Yeh et al., 2009). The Fe site on the surface act as oxygen adsorption site and that increasing the Fe site on the surface reduces the Gibbs energy of oxygen adsorption. The adsorption of oxygen is not the only factor
that increases the activity but the interaction between non-noble metal and palladium can also influence the geometric structure including the Pd-Pd bond distance, i.e. increasing the Fe content increases the probability on the surface of PdCFe electrocatalyst which increases the density of effective adsorption sites on the surface of electrocatalyst and thus increases the activity. The lattice contraction caused by the addition of Fe may also be responsible for the increased activity. The Pd-Pd bond distance can be adjusted by alloying Pd with Fe₅C species to optimize the activity in ORR. The methanol crossover test yielded the strong resistance of the PdCFe/C electrocatalyst towards MOR, which therefore have great potential as cathode electrocatalyst in DMFCs.

LI and Halder (2009) synthesized PdFe nanorods with a diameter of 3 nm and length 10-50 nm and were found to show better performance than commercial Pt/C. They could be next generation of Pd based catalysts because of the higher stability and activity of nanorods in comparison to small nanoparticles.

Yang et al., (2010 a & b) prepared carbon supported Pt decorated PdFe and PdCo (PdFe@PdPt/C and PdCo@PdPt/C) electrocatalysts, by the galvanic reaction. These catalysts consisted of a PdPt surface and PdM (M = Fe, Co) core. There were no discrete Pt nanoparticles and the M has been fully incorporated into Pd and PdPt as an alloying element. PdFe@PdPt/C was four times and PdCo@PdPt/C was six times more active than Pt/C. The enhancement in the ORR activity could be explained in terms of the weaker OH_ads binding on the Pt and Pd sites in the near surface region and favourable strain effect between the PdPt shell and PdM core which arise due to the addition of M to the core and the methanol tolerance could be attributed to the presence of Pd on the catalyst surface.

It has theoretically hypothesized and experimentally verified that Pt monolayer on Pd offers electrocatalytic activity several times higher than that of Pt (Zhang et al., 2005; 2004). Sarkar et al., (2010) synthesized multimetallic nanoalloy Pt₇₅Co₂₅, Pt₇₅Pd₂₀Co₁₀ and Pt₅₀Pd₃₀Co₂₀ by microwave assisted solvothermal method at low temperature (300 °C). This synthesis process produced a seed mediated growth of multimetallic Pt-Pd-Co nanoalloy electrocatalyst with a high degree of alloying and controlled particle size within a short reaction time. The multimetallic alloy, thus obtained, exhibited much higher ORR activity compared to the same electrocatalyst synthesized by borohydride reduction method. The enhancement in ORR activity may be due to ‘surface strain effect’ developed on the outermost Pt and Pd atomic layers due to
the low concentration of Co on the surface compared to that in the alloy core as facilitated by the pressure effect under the MW-ST condition.

The catalytic activity of the Pd for ORR is improved significantly by adding elements like Co, Fe Cu etc. However, these non noble metal elements might tend to leach out under electrochemical conditions. Consequently, the dissolution of the nonnoble metal components within the Pd alloys under DMFC operating conditions would lead to a limited lifetime of a DMFC. Joo et al., (2008) reported that the ORR activity of carbon supported Pd-based PdPt catalyst is significantly higher than Pd/C but slightly lower than Pt/C in terms of onset potential.

Wang et al., (2008c) prepared Pd₃Ptₓ/C alloy of different Pd/Pt atomic ratios by one step reduction route and reported that the Pd₃Pt/C exhibits the highest ORR activity among all the catalyst prepared and shows a comparable ORR activity with the commercial Pt/C. Later they (Wang et al., 2009b) tuned the surface and structure of Pd₃Pt/C alloy during synthesis with the use or no use of trisodium citrate (TC) as a complexing agent which lead to Pd enrichment on the surface layer of the Pd₃Pt/C catalyst and no lattice expansion. Nishanth et al., (2011) reported the optimum atomic ratio of Pt:Pd in Pt-Pd/C is 2:1 and the DMFC with it as cathode delivers peak power density of 115 mW cm⁻² at 70 °C as compared to 60 mW cm⁻² obtained with Pt/C. Alvarez et al., (2011) carried out a comparative study of Pd prepared by the ethylene glycol reduction method, and Pt in DMFC using different methanol concentrations (1, 3, 5, 7 M) and operating temperatures (20, 40, 60 °C). They observed that Pd performed better than Pt at methanol concentration 5M and at 60 °C with air.

Wei et al. (2011) reported the synergistic effect of Co alloying and oxidation treatment induced progressive enhancement on ORR activities of Pd/C catalyst. They observed the electrocatalytic properties of alloy NPs toward ORR greatly dependent on their particle sizes, morphologies, structure and surface compositions (Hwang et al. 2007, Wang et al. 2009e and Wei et al. 2010), and concluded that the modification of Pd-Co catalysts, and the oxidative thermal treatment are promising techniques to achieve high ORR activity and durability.

Takenaka et al. (2011) reported highly durable carbon nanotube-supported Pd catalysts covered with silica layers for the ORR in HClO₄. The silica-coated Pd/CNT cathode catalyst showed the ORR activity similar to Pd/CNT, regardless of the Pd metal with a silica insulator. The silica-coated Pd/CNT was highly durable during potential cycling between 0.05 and 1.20 V vs. RHE in aqueous HClO₄ while Pd/CNT suffered serious deactivation under the same
conditions. The silica layers in the silica-coated Pd/CNT prevent the diffusion of dissolved Pd species from the Pd metal out of the layers. Therefore, silica-coated Pd/CNT was highly durable under the cathode conditions. Furthermore, coverage of Pd/CNT with silica layers inhibited the two-electron reduction of oxygen to H$_2$O$_2$.

*Mentus et al. (2012)* reported the ORR study on potentiodynamically formed Pd/TiO$_2$ composite electrodes. By multiple potentiodynamic polarization of polished titanium surface in an aqueous PdCl$_2$ solution, a thin composite Pd/TiO$_2$ layer was formed. The ORR study of the Pd/TiO$_2$ layer were investigated in 0.1 mol dm$^{-3}$ KOH and 0.1 mol dm$^{-3}$ HClO$_4$ solutions. In alkali a single Tafel slope of 65 mV was found in the whole ORR region while in acidic condition it showed two Tafel slopes: a low (b$\approx$−79 mV) and the other high ones (b$\approx$−290 mV).

*Hong et al. (2012)* adopted galvanic replacement method for the preparation of Pd-Pt alloy nanocrystals (NCs) with hollow structures such as nanocages with porous walls and dendritic hollow structures and Pd@Pt core-shell dendritic NCs with uniform Pd octahedral and cubic NCs as sacrificial templates. The synthesized hollow NCs exhibited considerably enhanced ORR activities compared to those of Pd@Pt core-shell NCs and a commercial Pt/C catalyst, and their electrocatalytic activities were highly dependent on their morphologies.

*Erikson et al. (2012)* prepared palladium nanocubes for oxygen reduction reaction in acid and alkaline medium and compared the ORR activities with spherical nanoparticles and bulk Pd. The study showed the enhanced electrocatalytic activity of Pd nanocubes in both acid and alkaline solutions, which was attributed to predominance of Pd (100) facets. The mechanism of ORR on Pd NPs was similar to that on bulk Pd, the first electron transfer being the rate-limiting step, and the reaction predominantly followed a four-electron pathway in both solutions.

*Noto et al. (2012)* prepared two Pd-based carbon nitride (N content being ~ 13 wt%) electrocatalysts for the ORR for application in polymer electrolyte membrane fuel cells (PEMFCs). They investigated two different metal combinations in the multimetal clusters, Pd–Ni and Pd–Co–Au for PdNi-CNh 900 and PdCoAu-CNh 600, respectively. 0.75 and 0.51 g of Pd were required for the PdNi-CNh 900 and PdCoAu-CNh 600 materials, respectively, to produce the same electrical power as 1.12 g of platinum mounted in a reference fuel cell.

*Xiong et al. (2013)* developed three-dimensional bimetallic Pd–Cu nanodendrites by using a facile double-template fabrication process for ORR applicable in both chemical and microbial fuel cells. They reported an electrochemically active surface area of 80.2 m$^2$/g$_{Pd}$, a
peak current of 17.4 mA/cm² and an unusual limiting current density of 12 mA/cm² for this catalyst. Also, the fabricated bimetallic catalyst displayed a better long-term stability than the state-of-the-art Pt/C catalyst.

Erikson et al. (2013) electrodeposited (deposited at a constant potential varying the deposition time) Pd coatings on glassy carbon. In alkaline media the Pd/GC electrodes show a high specific activity toward ORR and it does not depend on the deposition time. In acidic solution a little dependence on deposition time was observed. The specific activities values determined at 0.8 V were rather similar, but some increase with longer deposition time was found. For 600 and 900 s deposited Pd, the specific activities were comparable with that of bulk palladium. The ORR on electrodeposited Pd proceeds mainly through a four-electron pathway in both solutions and the reduction mechanism is similar to that on bulk Pd. The Tafel slope values determined in the potential regions of 0.85 V > E > 0.8 V and 0.75 V > E > 0.7 V were close to −60 mV and −120 mV that are typical for ORR on palladium catalysts, showing the rate determining step as the transfer of the first electron to O₂ molecule.

Zhang et al. (2013b) prepared PdPt nanocages (NCs) for ORR by applying potential cycling treatment on core–shell Pd@Pt nanodendrites (NDs) in 0.5 M sulfuric acid, during which Pd core was dissolved and the Pd@Pt structure was transformed to hollow nanocages. They observed that Pd@Pt NDs/C has higher ORR activity than that of Pt/C, and the activity was further improved when the Pd@Pt NDs were transformed to PdPt NCs. At E= 0.85 V, the Pt mass activities of PdPt NCs/C, Pd@Pt NDs/C and Pt/C were 230.9, 158.8 and 136.1 mA mg⁻¹Pt, respectively.

Jukk et al. (2013) prepared PdNP/MWCNT nanocomposites by sputter-deposition of palladium onto MWCNTs. Two Tafel regions with different slopes can be distinguished. At low overpotentials the Tafel slope is close to -60 mV dec⁻¹ and at higher overpotentials the slope is approximately -100 mV dec⁻¹. The SA values for PdNP/MWCNT catalysts and bulk Pd were comparable. A higher ORR specific activity in alkaline solution than in acid one was found for the electrodeposited Pd/GC electrodes (Erikson et al. 2013).

Cho et al. (2013) prepared a series of hollow (h) Pd nanoshells (hPd–X) by employing Co nanoparticles as sacrificial templates with different concentrations (X=1-40 mM K₂PdCl₄) of a Pd precursor. These catalysts were investigated for ORR in alkaline medium. The onset potentials obtained were positive and followed the order: hPd-20 > Pt-20/C > Pd-20/C > hPd-40 > hPd-12
> hPd-6 > hPd-1. The n values for hPd-6, hPd-12, hPd-20, hPd-40, Pd-20/C, and Pt-20/C calculated from the slopes in the K–L plots were 3.27, 3.42, 3.98, 3.72, 3.93, and 3.87, respectively. The obtained jk value of hPd-20 (93.5 mA cm$^{-2}$) was higher than that of Pd-20/C (51.5 mA cm$^{-2}$) but slightly lower than that of Pt-20/C (123 mA cm$^{-2}$) at -0.6 V vs. SCE. hPd-20 showed the highest ORR activity among the hPd-X series (X = 1, 6, 12, 40) with a reasonable stability.

Xue et al. (2014) prepared Pd nanoparticles supported on PDDA (Poly(diallyldimethylammoniumchloride))-functionalized carbon black which exhibited enhanced ORR activity and 4e$^{-}$ pathway in alkaline medium. The catalyst was prepared by simple aqueous phase reduction method. Stability test displayed a loss of 18% current after 2000 sec while it was ~68% for platinum under similar experimental condition.

Seo et al. (2013) prepared graphene nanosheet (GNS) -supported Pd and Pd$_3$Y nanoscale-alloy (Pd/GNS and Pd$_3$Y/GNS) electrocatalysts by impregnation method. They combined the experimental measurements with ab initio density functional theory (DFT) calculations to identify the d-band center position of Pd atom in the pure Pd and Pd$_3$Y alloys as a function of site on near the surface. Both approaches clearly have shown that alloying the Pd with Y significantly modifies the electronic structures of Pd atoms. For the Pd/GNS and Pd$_3$Y/GNS, the kinetic current density, j$_k$, at a potential of 0.85 V vs. RHE were 0.093 and 0.001 mA cm$^{-2}$ in acidic media, and 1.50 and 0.89 mA cm$^{-2}$ in alkaline media, respectively. The j$_k$ of Pd$_3$Y/GNS was lower than that of the Pd/GNS under both alkaline and acidic conditions.

Liu et al. (2012) investigated the impact of graphene substrate–Pd nanoparticle interaction on the O, OH, and OOH adsorption that is directly related to the electrocatalytic performance of these composites in oxygen reduction reaction (ORR) by first-principles-based calculations. Doping the single vacancy graphene with B or N will tune the average d-band center and also the activity of the composite toward O, OH, and OOH adsorption. The adsorption energies of O, OH, and OOH are reduced from $-4.78$, $-4.38$, and $-1.56$ eV on the freestanding Pd$_{13}$ nanoparticle to $-4.57$, $-2.66$, and $-1.39$ eV on Pd$_{13}$/single vacancy graphene composites, showing that the defective graphene substrate will not only stabilize the Pd nanoparticles but also reduce the adsorption energies of the O-containing species to the Pd particle, and so as the poisoning of the ORR active sites.
Vinayan et al. (2013) reported triangular shaped palladium nanoparticles (Pd NPs) decorated nitrogen doped graphene as good catalyst for ORR as well as hydrogen storage. Nitrogen doped graphene (N-G) is synthesized by uniform coating of polyelectrolyte modified graphene surface with a nitrogen containing polymer followed by their pyrolysis. They found the specific surface area, 146.4 m$^2$g$^{-1}$ for nitrogen doped graphene. The N-G sample exhibits a mesoporous volume (0.64 cm$^3$ g$^{-1}$) with an average pore radius 5 nm. The Pd/N-G gives an electrochemical surface area of 88.9 m$^2$g$^{-1}$ for the initial cycle and it was reduced to 73.9 m$^2$g$^{-1}$ and 70.3 m$^2$g$^{-1}$ after 100$^{th}$ and 500$^{th}$ cycles, respectively. RDE study shows good ORR activity along with methanol tolerance nature of the catalysts. Hydrogen storage study of N-G and Pd/N-G give a storage capacity of 1.1 wt% and 1.9 wt%, respectively at 25 °C and 2 MPa hydrogen equilibrium pressure. The single cell PEMFCs performance gives a maximum power density of 305 mWcm$^{-2}$ at 60 °C.

Kakaei et al. (2014) prepared graphene supported Pd in sodium dodecyl sulfate for ORR in 0.5M H$_2$SO$_4$. They found conductivity of graphene on carbon paper is of 66 mS cm$^{-1}$ by using a four-point probe technique, which is approximately 1.2 and 1.65 times better than that of graphite coated carbon paper and carbon paper. After that palladium is electro-reduced onto the carbon paper based electrodes (with or without graphene) in absence or presence of different concentrations of sodium dodecyl sulfate (SDS), that are used in oxygen reduction reaction (ORR) for direct methanol fuel cells. The catalytic activities of graphene-supported Pd nanoparticles and Pd-carbon paper electro-catalysts for ORR were 112 and 2 Ag$^{-1}$Pd, which can reveal the particular properties of the exfoliated graphene supports and SDS media.

Zheng et al. (2014a) demonstrated green synthesis (wet-chemical method) of core-shell gold-palladium@palladium nanocrystals dispersed on graphene for ORR and MOR in alkaline media. Buffer, 2-[4-(2-hydroxyethyl)-1-piperazinyl] ethanesulfonic acid (HEPES) was used as a reducing agent and a shape-directing agent (Xie et al. 2007), while no template, seed, organic solvent, or surfactant was used. The ORR study indicated the specific activity of the G-AuPd@Pd catalyst as 0.401 mA cm$^{-2}$Pd, which was 3.8 and 1.1 times higher than those of the G-Pd (0.105 mA cm$^{-2}$Pd) and Pd black (0.368 mA cm$^{-2}$Pd) catalysts. Furthermore, the specific activity of the G-AuPd@Pd was also higher than the nanoporous PdNi alloys (0.210 mA cm$^{-2}$) (Xu et al. 2013) and Pt-on-Pd nanodendrites (0.307 mA cm$^{-2}$) (Peng et al. 2009). Similarly, the
mass activity of the G-AuPd@Pd is 0.174 mA mg\(^{-1}\)Pd, which is 2.2 and 8.9 times larger than those of the G-Pd (0.080 mg\(^{-1}\)Pd) and Pd black (0.195 mg\(^{-1}\)Pd) catalysts.

_Yin et al. (2014)_ synthesized a series of well-coupled graphene (G) and MPd\(_3\) (M = Fe, Cu, Ag, Au, Cr, Mo, W) nanocrystals nanocomposites (G-MPd\(_3\) NCPs) via a versatile electrostatic assembly and hydrogen reduction strategy, i.e., sequential assembly of coordination anions and cations on excess cationic polymer modified graphene oxide to form composite precursors and then thermal treating under H\(_2\)/Ar gases atmosphere. Compared with single component, monometallic, and some reported non-Pt catalysts, greatly enhanced ORR performances are observed in those NCPs due to strong synergistic or coupling of their constituents. Among them, G-FePd\(_3\) NCPs exhibit the highest catalytic activity.

_Jukk et al. (2014)_ investigated electrochemical reduction of oxygen on Pd nanoparticle-decorated nitrogen-doped graphene (Pd/NG). The specific activity of the prepared Pd/NG catalyst was 0.015 mA cm\(^{-2}\) in acid media, which is almost twice to that observed for polycrystalline Pd (0.009 mA cm\(^{-2}\)). In alkaline electrolyte, the value of SA of Pd/NG was significantly higher than that observed in acid solution. The Pd/NG catalyst exhibited excellent electrocatalytic activity towards the ORR in alkaline media.

_Carrera-Cerritos et al. (2014)_ prepared Pd supported on reduced graphene oxide (rGO) by polypyrrole supported Cu\(_x\)Mn\(_{3-x}\)O\(_4\) (1.0 ≤x ≤1.4) by thermal decomposition method and investigated its catalytic properties towards ORR alkaline medium. They observed that substitution of Mn by Cu increases the catalytic activity, the activity being maximum with Cu\(_{1.4}\)Mn\(_{1.6}\)O\(_4\). Cationic distribution computation showed the presence of Mn\(^{3+}\) and Mn\(^{4+}\) ions at octahedral sites while Cu\(^+\) ion, at tetrahedral sites. ORR catalysis is correlated to the increase of Mn\(^{4+}\) ion. The ORR study was performed in the electrolyte, 2.5×10\(^{-3}\) M KOH + 0.8M KCl solution (pH=11). The composite electrodes followed the activity order: Cu\(_{1.4}\)Mn\(_{1.6}\)O\(_4\)> Cu\(_{1.3}\)Mn\(_{1.7}\)O\(_4\)> Cu\(_{1.2}\)Mn\(_{1.8}\)O\(_4\)> Cu\(_{1.1}\)Mn\(_{1.9}\)O\(_4\)> CuMn\(_2\)O\(_4\).
Co$_{1-x}$S-GNS hybrid synthesized by a low temperature (80˚C) solution-phase reaction (Wang et al., 2011a) showed the ORR current density 1.1 mAcm$^{-2}$ at 0.7 V vs. RHE (1600 rpm) and the onset potential, 0.8 V vs. RHE in acidic medium, The ORR followed 4e$^-$ pathway.

Cheng et al. (2011) reported M$_x$Mn$_{3-x}$O$_4$ (M = Co, Mg and Zn) oxides as bifunctional catalysts for both ORR and OER. Result have shown that the cubic Co-Mn-O spinel outperforms the tetragonal phase in intrinsic ORR catalytic activity but tetragonal spinel surpasses the cubic phase for OER which is probably due to dissimilar binding energies of oxygen adsorption on cobalt and manganese defect sites. The catalytic activities of metal cobaltites, in 0.1 M KOH ORR followed the activity order: Co$_x$Mn$_{3-x}$O$_4$ (NaH$_2$PO$_2$ reductant) > Co$_x$Mn$_{3-x}$O$_4$ (NaBH$_4$ reductant) > Cubic CoMn$_2$O$_4$ > Tetragonal CoMn$_2$O$_4$ Spinel. The ORR activities of all the four spinel samples were comparable to Pt/C. Phase dependent ORR studied were carried out with the help of XPS (X-ray photoelectron spectroscopy) and TPD (Temperature programmed desorption) analysis. Results suggest that the cubic phase has a stronger oxygen binding ability than the tetragonal phase.

Liang et al. (2011) investigated the catalytic activity of Co$_3$O$_4$ nanoparticles supported on reduced graphene oxide towards ORR and OER in an alkaline solution (KOH). The ORR activity was observed to enhance on nitrogen doping of graphene and that the Co$_3$O$_4$/N-rGO electrode showed similar ORR activity but superior stability to Pt. Whereas, Physical mixtures of Co$_3$O$_4$ and rmGO and either free Co$_3$O$_4$ nanoparticle (size ~ 4-8 nm) or rmGO exhibited very poor ORR activities while Co$_3$O$_4$/N-rmGO showed enhanced activity with the onset potential of ~0.88 V vs. RHE and the Tafel slope of 42 mV/decade (in 0.1M KOH). Only ~6% yield of HO$_2^-$ in the RRDE study and 4 e$^-$ path observed in the ORR study demonstrated the synergistic effect of Co$_3$O$_4$ and rmGO in the hybrid on the ORR reactivity. Durability test (10000-25000 sec.) showed little decay in the ORR activity in the case of Co$_3$O$_4$/N-rmGO while that Pt/C (50 wt% Pt on Vulcan XC72) and Pd/C (10 wt%Pd on activated carbon) underwent respectively 30% and 20% decay in the ORR activity. In 1M KOH, Co$_3$O$_4$/N-rmGO produced the lowest Tafel slope of 37 mV/decade among the spinel oxide reported ever. Such a low Tafel slope for ORR on spinel oxides are scarce in literature.

Graphene supported composites MnCo$_2$O$_4$/N-rmGO and Co$_3$O$_4$/N-rmGO were prepared by two step solvothermal method by Liang et al. (2012) and studied their catalytic activity toward both ORR and OER in 1M KOH. The ORR onset and peak potentials for MnCo$_2$O$_4$/N-
rmGO and Co₃O₄/N-rmGO were 0.95 & 0.88 and 0.93 & 0.86 V vs. RHE respectively. While in case of 20wt%Pt/C peak potential is on 0.90 V vs. RHE. The RRDE study showed 4 e⁻ path for ORR with Tafel slope of 36 mV/decade on MnCo₂O₄/N-rmGO. The stability test for 20000 sec displayed only 3.5% decay in current density in the case of MnCo₂O₄/N-rmGO while it was 25% and 33% in case of binary physical mixtures of MnCo₂O₄ with N-rmGO and Pt/C. BET measurements indicated that Mn doping increases the electrochemically active surface area of the hybrid. Tetragonal spinel exhibited lower intrinsic ORR activity than the cubic phase (Cheng et al., 2011).

Poux et al. (2012) studied the ORR activity of carbon supported perovskites like LaCoO₃ or La₀.₈Sr₀.₂MnO₃ in 1M NaOH. At 0.9V vs. RHE for electrode containing 60% of carbon the current density observed for LaCoO₃ and La₀.₈Sr₀.₂MnO₃ were 3.3 and 8.6 μA cm⁻²oxide, respectively. It was observed that the ORR activity of the perovskite/C electrode approaches to Pt/C on addition of perovskite. They considered the oxide/C as bifunctional catalyst with carbon catalyzing the ORR in to H₂O₂ and perovskite catalyzing further H₂O₂ following chemical/electrochemical transformation to H₂O, while carbon alone is only capable to support the reduction to H₂O₂. (Sun et al., 2011; Hermann et al., 2000).

Wu et al. (2012) reported the Fe₃O₄ supported on N-doped graphene aerogel (Fe₃O₄/N-GAs) as efficient electrocatalysts for the ORR in 0.1M KOH. In comparison to carbon supported oxide (Fe₃O₄/N-CB), Fe₃O₄/N-GAs exhibited a more positive onset potential (-0.19V vs. Ag/AgCl), higher cathodic current density (-2.56 mA/cm²), lower H₂O₂ yield, and higher electron transfer number (3.72-3.95). The durability test showed ~79.3% current retention in the case of Fe₃O₄/N-GAs while only ~61.0% retention in the case of Pt/C. The higher activity of Fe₃O₄/N-GAs can be attributed to the effect of macropores on the diffusion rate of the electrolyte.

Wu et al. (2012b) studied the ORR at the MnOₓ-graphene composite in 0.1M KOH and found the activity order – α-MnO₂ nanowire>amorphous MnOₓ nanoparticle>β-MnO₂ microprism. 4e⁻ reduction occurs on MnOx-graphene composite.

Wang et al. (2013) investigated the ORR using Co₃O₄/C and MnOₓ-Co₃O₄/C as methanol tolerant catalysts in alkaline medium. The SA of MnOₓ-Co₃O₄/C was higher than that of Co₃O₄/C and the mass activity of the former was 1.4 times higher than that of the latter. The ORR on MnOₓ-Co₃O₄/C proceeds by 4e⁻ (~3.9) pathway. In the electrolyte, 1M KOH +
1MCH$_3$OH 91% current density retained by MnO$_x$-Co$_3$O$_4$/C whereas it decreased by 54% for Pt/C. Wang et al. (2013c) also synthesized Co$_3$O$_4$ nano-rod decorated on reduced graphene oxide composite by one pot hydrothermal procedure. The ORR activity and stability of Co$_3$O$_4$/rGO nanocomposite was much superior to Pt/C.

Liu et al. (2013b) reported NiCo$_2$S$_4$ nanoparticles grown on graphene as an effective bifunctional nonprecious electrocatalyst for ORR and OER in an alkaline medium. NiCo$_2$S$_4$@N/S-rGO was synthesized by a one-pot solvothermal strategy using Co(OAc)$_2$, Ni(OAc)$_2$, thiourea, and graphene oxide as precursors and ethylene glycol as the dispersing agent. In comparison to commercial Pt/C catalyst, NiCo$_2$S$_4$@N/S-rGO showed less reduction activity, much better durability, and superior methanol tolerance toward ORR in 0.1 M KOH; it revealed higher activity toward OER in both KOH electrolyte and phosphate buffer at pH 7.0.

Chowdhary et al. (2014) reported the CoMn$_2$O$_4$ supported on conducting polymer, PEDOT (ploy (3, 4-ethylenedioxythiophene) as efficient electrocatalysts for ORR & OER in alkaline medium 0.1 M KOH. CoMn$_2$O$_4$-PEDOT nanocomposite were prepared by α – Mn$_2$O$_4$ nanorod and dodecyl benzene sulphonic acid (DBSA). Although α – Mn$_2$O$_4$ nanorod did not show any ORR/OER activity but the spinel CoMn$_2$O$_4$-PEDOT composites with optimised weight ratio of 25 mg exhibited enhanced ORR activity comparable to the commercial Pt/c catalyst, due to synergistic chemical coupling effect between PEDOT and CoMn$_2$O$_4$. The RDE study exhibited ~ 3.9 electron involved in ORR process with a Tafel slope of 70 mV/decade at low and 129 mV/decade at high overpotentials.

1.3.2.3 Transition metal chalcogenides

For the first time Alonso-Vante and Tributsch (1986), reported application of the chevrel compounds (prepared by solid state reaction) as electrocatalysts for the ORR in an acid medium, they observed an enhancement in the ORR activity when Mo was partially substituted by Ru. The compounds containing non-substituted octahedral Mo showed the metallic behavior while Ru substituted Mo octahedral (Mo$_{6-x}$M$_x$X$_8$, where X = S, Se, Te) systems showed the semiconducting behavior (Alonso-Vante et al., 1987). The significant change observed in the overpotential for the ORR on metal, metal clusters and mixed metal clusters has been explained in terms of modification in geometrical and electronic properties of materials (Alonso-Vante et al., 2003). The compound Mo$_{4.2}$Ru$_{1.8}$Se$_8$ displayed catalytic behaviour comparable to that of Pt.
The ORR overpotentials on catalysts of the Mo₆X₈ series followed the trend Te < Se < S (Alonso-Vante et al., 1989; Fischer et al., 1995).

Later, a variety of compounds, MoₓRuᵧSₜ, MoₓOsₜSₚ, WₓRuᵧSₜ, RhₓRuᵧSₜ and ReₓRuᵧSₜ were prepared on various surface functionalized carbon blacks (Reeve et al., 1998a & b). The compounds, RhₓRuᵧSₜ, ReₓRuᵧSₜ and MoₓRuᵧSₜ exhibited the best ORR activities but lower than that of Pt. However, their activities were significantly higher than Pt in methanol containing electrolytes.

The catalytic activity of Ru-chalcogenide matrix has been observed to improve by incorporation of second transition metal (Cr, W, Mo or Rh). The introduction of W increased the current densities and power densities upto 30% and 25% than that obtained with Ru-Se alone with only minor loss in methanol tolerance (Cheng et al., 2007a). This increase in activity can be ascribed to the Co-catalytic effect of W. Cheng et al., (2007b) reported maximum power density of 40 mA cm⁻² and current density of 79 mA cm⁻² at -0.5V vs. Hg/Hg₂SO₄ reference electrode with RuSe₀.₂₀W₀.₂₉. But, they observed minor loss in the methanol tolerance, by the addition of W. Surarez-Alcantara & Solorza-Feria, (2009) reported that in the charge transfer coefficient the entropy turnover play an important role in the electrocatalytic process.

The thermally treated RuSe/C catalysts show the better performance for ORR by maintaining the methanol tolerance (Cheng et al., 2007c). The crystallinity of the RuSe/C changes from amorphous to the highly crystalline form and the Se:Ru ratio decreases after heat treatment at 300-600 °C. The ORR study has shown that on increasing temperature, the ORR activity increases upto 400°C and decreases thereafter. At higher temperatures, the decrease in the activity might be due to the loss of an optimum Se:Ru ratio and bi-functionality of RuSe. Thermal treatment leads to a stable cathode because combination of Ru and Se effectively suppresses the blocking sites at which the reaction causing catalyst degradation can take place but the thermally treated RuSe/C catalyst is not as good as Pt/C in activity but the former one has high methanol tolerance. Serov et al. (2008) observed the highest catalytic activity (power density = 62 mW cm⁻²) for RuSe/C calcined at 300°C. RuSe/CNT (Ru:Se = 1:0.2) synthesized by the modified polyol reduction method and calcined at 400°C, exhibits good oxygen reduction activity and methanol tolerance (Jeng et al., 2011).
Lee and Woo, (2010) observed that as the amount of Se increases in Ru-Se, metallic Ru on the catalyst surface increases and thereby the ORR activity. The Ru$_{80}$Se$_{20}$/C catalyst exhibited the maximum ORR activity as well as significantly high methanol tolerance property.

Serov et al., (2007) reported that Palladium based chalcogenides (PdS$_x$/C and PdSe$_x$/C) prepared by refluxing the palladium acetylacetonate in xylene with S/Se and carbon are highly methanol tolerant. S addition to the Pd reduces the ORR activity due to the formation of semi-amorphous Pd phase, while the addition of Se promotes the ORR due to the modification of the Pd surface but preserving the bulk structure of crystalline Pd.

Madhu et al. (2011 and 2013) prepared metal selenides (PdSe and RuSe) by hydrothermal method and investigated their activity toward ORR in acidic medium. Results show that, in case of both, PdSe and RuSe, the maximum ORR activity was observed with 1:1 ratio of metal (Pd or Ru) and Se.

1.3.2.4 Transition metal macrocycles

Transition metal macrocycles (TMMC) is another kind of fuel cell catalysts which has been extensively studied as a potential substituent of Pt for ORR catalysis. The molecules of TMMC are having square planer structure with the metal ion symmetrically surrounded by 4N atoms. These N atoms are from each member of ring systems, which in turn are connected by C atoms (Porphyrins) or N atoms (Phthalocyanins). These TMMC are inert to MOR, while show reasonable activity and remarkable selectivity towards ORR. They can catalyze a direct 4e$^-$ reduction of O$_2$ to H$_2$O (Wang, 2005). The major drawback of this kind of catalysts is their low stability in acidic medium (Bezerra et al., 2007). Heat treatment considerably improves the ORR activity and stability.

Jasinski (1964) reported for the first time that transition metal porphyrins and phthalocyanines show electrocatalytic activity toward ORR. Most of these complexes, particularly cobalt and iron porphyrins, showed ORR in two consecutive two-electron reduction processes involving hydrogen peroxide as the intermediate. Thereafter Jhanke et al., (1976) examined polymeric metal phthalocyanin and discovered that the heat treatment in an inert atmosphere can significantly improve the ORR activity as well as stability.

Macrocyclic MN$_4$ complexes of a great variety of metals have been tested including, Fe, Co, Ru, Pd, Pt, Ir, VCr, Ni, Cu, Zn, Mo, Au, Sn, Sb, Ga, Na, Ag. Among these macrocyclic
complexes of Fe and Co appeared to be the best ones. The ORR on the Co chelates gives H₂O₂ as the main product of the reaction (Zagal et al., 1980; 1992).

The performance (activity, stability, selectivity) of the catalysts based on TMMC is directly related to the catalyst structure, which varies greatly with the preparation conditions (Bezerra et al., 2008). Furthermore, N is a necessary component of the catalyst site (Fournier et. al., 1997) and its high content improves both ORR activity and selectivity towards 4e⁻ reduction of O₂ (Medard et al., 2006). The surface concentration of N changes with the heat treatment. The most common N sources are NH₃, acetonitrile, pyrrole, N-containnig polymer and carbon modified with N. The nature of the N source (Wei et al., 2000) and the catalyst loadings are found to influence the ORR activity greatly (Cote et al., 1998).

The activity of MN₄ with different supports has been observed to follow the order: MWCNT (treated with HNO₃ for 12 h) > MWCNT > SWCNT > DWCNT (Morozan et al., 2011). The MWCNT supported cobalt phthalocyanin shows two steps, 2e⁻ process whereas CoTAP and CoPT₃pz exhibit one step, 4e⁻ pathway for ORR in alkaline medium. It indicates that the N atoms in the backbone of the compound strongly affect the catalytic activity (Xu et al., 2011). Nanoshell carbon which itself active for ORR when improved by transition metal phthalocyanin show enhancement in the catalytic activity for ORR due to the coexistence of N atom on the surface of nanoshell carbon (Ozaki et al., 2010).

Yuasa et al., (2005; 2006; 2007) synthesized metal-macrocycle compound catalyst by using a new polymeric ligand, polypyrrole (PPy). ORR analyses show that the pyrolyzed Co-PPy/C delivers enhanced catalytic activity and stability, and the heat treatment changes the mechanism from 2e⁻ to 4e⁻ transfer process i.e. from the indirect (peroxide) to direct pathway. The Co site forms four coordinate bonds with the N of the PPy rings (Co-N₄). During the pyrolysis the Co-Co distance is shortened, which enhanced the catalytic activity (Yuasa et al., 2005). Lee et al., (2009) also reported that the heat treatment is the necessary step to improve the catalytic activity. They found the improvement in the activity, stability and mechanism from 2e⁻ to 4e⁻ with pyrolyzed Co-PPy/C than unpyrolyzed Co-PPy/C. PPy-based electrocatalysts used in the ORR study have recently been reviewed by Singh et al., (2011a).

Oh et al., (2011) prepared novel nitrogen-modified carbon nanofibers by pyrolysis of Co, PPy and ethylenediamine (Co-ED/PPy-CNF). This novel electrode showed significantly
improved ORR activity and stability; only 5% performance degradation was observed after 100 h. The improvement in the performance has been caused due to the synergistic effect of ED and PPy.

*Walter et al.,* (2011) prepared Co-PPy samples by plasma and chemical methods. The plasma produced sample exhibited the higher catalytic activity than one prepared by the chemical method. The activity was further improved by tuning of the plasma parameters such as gas composition, substrate bias, etc.

*Nasini et al. (2013)* prepared cobalt (III) complexes of macrocyclic ligands supported on multiwalled carbon nanotubes for ORR. It was observed that MWCNTs-supported catalysts showed higher ORR activity and current density due to p–p stacking interactions with nanotubes. RDE and RRDE analyses show that these complexes reduce oxygen via four-electron reduction process in a mild acidic solution and two steps two-electron reduction process in a basic solution, with negligible amount of hydrogen peroxide generation.

*You et al. (2014)* reported enhanced ORR on cobalt-porphyrin functionalized with graphene oxide in an alkaline solution. Cobalt [5,15-(p-aminophenyl)-10,20-(pentafluorophenyl) porphyrin](CoAPFP) functionalized with graphene oxide (GO) by N-(3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDC hydrochloride) used as an amide-coupling reagent (GO-CoAPFP). Electrochemical investigation revealed that the ORR performance of ERGO-CoAPFP is much better than GO-CoAPFP. The ORR on ERGO-CoAPFP followed four-electron pathway.