CHAPTER 1

INTRODUCTION AND BACKGROUND

1.1 HISTORY OF FUEL CELL

Energy crisis in the 21st century as well as the increase in oil cost emphasizes the need for alternative sources of energy worldwide. Environmental concerns demand an efficient and clean energy source and also an energy conversion device which produces clean energy and do not contribute to green house gas emission. Hydrogen is a clean energy vector that can be stored and feed as fuel in fuel cells. Fuel cell is an electrochemical device which converts chemical energy from a fuel such as hydrogen in to an electrical energy.

The origin of the fuel cell dates back to the early 19th century, in 1802, from the discovery of water electrolysis by English chemists William Nicholson, Anthony Carlisle and experimented by Humphry Davy (Bagotsky et al 2015). The discovery of ozone and the hydrogen, oxygen reaction by Christian Friedrich Schönbein in 1838 (Wand 2006) led to the principle behind the fuel cell. Followed by this, William Grove constructed his “gas voltaic battery” in 1893 (Grove 1839). Grove used two compartments having porous Platinum (Pt) dipped in sulphuric acid and fed by hydrogen and oxygen gas. Therefore, the year 1839 is explicitly considered as the birth year of the fuel cell. But he could not prove the speculation on surface of actions between electrode, electrolyte and gas for the reaction to happen. The term fuel cell did not emerge until 50 years later in 1889, when Ludwig Mond and
Charles Langer, two chemists, adopted the name fuel cell; they tried to build the first practical ‘gas battery’ device using air and industrial coal gas (Mond & Langer 1889). Mond and Langer understood the Grove’s thought of larger electrode surface for the reaction and made significant changes in the experimental design of fuel cells. They found that the Pt black lost its conductivity during its long term use in the liquid electrolyte. They have adopted a method in which, diaphragm of a porous non conducting material dipped in liquid electrolyte and covered both sides by thin leaf of gold(Au) or Pt along with a thin leaf of Pt black and used hydrogen and air as gases. They obtained a current density of of 6 A.ft$^{-2}$ at a voltage of 0.73 V for their fabricated fuel cell but the voltage drop was 10% per hour of operation. Followed by this, J.H. Reid described the first alkaline fuel cell (AFC) in 1902 (Reid 1902) and Noel in 1904 (Noel 1904) obtained the patents for their concept.

However, there arose a hiatus on the development of fuel cell due to tremendous explosion of internal combustion engines during that time. After a gap, Francis Tomas Bacon, an English engineer, revisited Mond/Langer fuel cell and made numerous changes to the design by replacing Pt gauze and sulphuric acid with activated nickel electrode and Potassium hydroxide electrolyte. The Bacon Cell developed in 1932, was the predecessor of the AFC (Bacon 1969). It took almost 30 more years (1959) for Bacon to develop a 6kW 40-cell unit, with an operating efficiency of 60%. In 1959 a team led by Harry Ihrig built a 15 kW fuel cell tractor (Kreuer 2013) by using potassium hydroxide as the electrolyte and compressed hydrogen and oxygen as the reactants. In 1955, Willard Thomas Grubb filed a patent for the discovery of sulphonated Polystyrene ion-exchange resin as the electrolyte for gaseous fuel cell (Grubb & Schenectady 1959); it is now referred to as Proton Exchange Membrane and Leonard Niedrach, formulated a way of depositing Pt onto this membrane and paved a way to the modern
fuel cell system. The improvements made through the combined efforts of Grubb and Niedrach ultimately produced the "Grubb-Niedrach fuel cell" (Grubb & Niedrach 1960). In 1962, General Electrical (GE) and the National Aeronautics and Space Administration (NASA) developed this technology together, using the fuel cell in the Gemini space project; this was one of the first commercial uses of a fuel cell and from then fuel cells started getting commercial interest (Warshay & Prokopius 1989). The patents for the fuel cell were licensed by Pratt and Whitney, in 1965 as part of successful implementation of fuel cell to provide electrical power for Project Apollo. Alkali cells have since been used for space shuttles (Perry & Fuller 2002).

Throughout 1970s and 1980s, as a consequence of oil crisis, enormous research effort was dedicated to fuel cells including materials, gas sources and cost reduction. Gradually in 1980s fuel cell technology started and fuel cells were tested by automobile manufacturers. Using PEM technology, Canadian company Ballard developed the first marketable fuel cell in 1993 which was a breakthrough during that decade (Howard & Greenhill 1993). Since then, fuel cell became one of the main areas of research across the world. For the past two decades fossil fuels being vastly exploited by the human actions which in turn increased the emission of GHG reminded us the need for alternative energy technologies around the globe. There has been a large volume of R&D work in developing various renewable energy technologies to address the issue of clean energy and green energy. During the last couple of decades, hydrogen gas is being projected as an ideal energy vector which could address the issues of GHG and air pollution. Hydrogen can be produced by different techniques from multiple sources, can be stored in different forms (gas, liquid and solid in metal hydrides, porous materials etc.,) and can be used in power generation by different routes. Although the use of hydrogen in internal combustion engines is a well established technology, the efficiency of such conversion is low. Higher
efficiency of conversion can be realized in fuel Cells with the help of an electrochemical conversion device which converts the chemical energy of the fuel such as hydrogen into electricity directly.

1.2 THE BASIC PRINCIPLE OF A FUEL CELL

Basically, a fuel cell is an electrochemical device that converts the chemical energy stored in gaseous molecules of a fuel and oxidant into electrical energy. The overall process is the reverse of water electrolysis. In electrolysis, an electric current applied to water splits it into hydrogen and oxygen; by reversing the process, hydrogen and oxygen are combined to produce electricity, water and heat (Atkins 1986). Fuel cell is similar to a battery in construction but does not store the energy in the electrodes. It works like an internal combustion engine (ICE) in producing energy as long as the fuel is supplied.

The fuel cell structure unit consists of one negative electrode (anode), one positive electrode (cathode) and electrolyte, which is in contact with anode on one side and the cathode on the other side. Fuel is continuously fed in to the anode side and oxidant is continuously fed in to the cathode side. In a typical hydrogen oxygen acidic fuel cell, the reactions are as follows.

At the anode: \( \text{H}_2 \rightarrow 2\text{H}^+ + 2e^- \) \hspace{1cm} (1.1)

At cathode: \( \frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O} \) \hspace{1cm} (1.2)

Overall: \( \text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} \) \hspace{1cm} (1.3)

Figure 1.1 is a schematic representation a typical H\(_2\)/O\(_2\) fuel cell, where the hydrogen is oxidized at the anode, releasing protons and electrons, the protons pass through the electrolyte towards cathode, where the oxygen gets reduced and forms a water molecule. The electrons travel through the
external circuit which can be collected as the direct current. Hence the electrolytes must be proton conductors and electron insulators.

![Schematic representation of a H₂/O₂ Fuel cell](image)

**Figure 1.1** Schematic representation of a H₂/O₂ Fuel cell

### 1.2.1 Thermodynamic Aspects of Fuel Cell

As an electrochemical system, fuel cell operation is governed by certain thermodynamics, kinetics and operational parameters. Consider the net reaction for the H₂/O₂ fuel cell: The product is one mole of H₂O and the reactants are one mole of H₂ and half a mole of O₂.

\[ \text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} + \text{heat} \quad (1.4) \]

According to the first law of thermodynamics, the enthalpy is the difference between the heat and the work involved.

\[ \Delta H = Q - W \quad (1.5) \]
Where ΔH is the change in enthalpy, Q is the amount of heat and W is the work done.

If the change in enthalpy is negative, heat is liberated and the reaction occurs spontaneously. So according to the reaction,

In the anode: \( \text{H}_2 \rightarrow 2\text{H}^+ + 2e^- \) \( \Delta H = 0 \text{ kJ} \) (1.6)

In the cathode: \( \frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O} \) \( \Delta H = -285.8 \text{ kJ/mol} \) (1.7)

Thus, in a PEMFC, 285 kJ.mol\(^{-1}\) are converted into heat (Q) and electricity (w). Analyzing from a thermodynamic point of view, the maximum work output from the above reaction is related to the free-energy change of the reaction. Hence, for fuel cells, the work in the form of electrical energy represents the Gibbs free energy. So the maximum possible energy conversion efficiency can be,

\[ \eta_{\text{max}} = \frac{\Delta G}{\Delta H} \] (1.8)

Where \( \Delta G \) is the free energy change

At the anode: \( \text{H}_2 \rightarrow 2\text{H}^+ + 2e^- \) \( \Delta G = 0 \text{ kJ} \) (1.9)

At cathode: \( \frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O} \) \( \Delta G = -237.2 \text{ kJ/mol} \) (1.10)

The above reaction is spontaneous and thermodynamically favored because the free energy of the products is less than that of the reactants. The Gibbs free energy can also be used to calculate the output voltage of an ideal fuel cell. Since the Gibbs free energy equals the electrical work, and the electrical work equals the product of the charge and voltage, then,

\[ W = \Delta G = -nFE \] (1.11)
Where \( n \) is the number of moles of electrons involved, \( E \) is the reversible potential, and \( F \) is Faraday’s constant. If the reactants and the products are in their standard states, the equation can be represented as

\[
\Delta G_0 = -nFE_0
\]  

(1.12)

Thus

\[
E_0 = -\frac{\Delta G_0}{nF}
\]  

(1.13)

Where \( \Delta G \) is -237.2 kJ/mole, \( n = 2 \), \( F = 96500 \) C/mole. Therefore the calculated value of \( E \) is 1.229 V. This is the voltage that can be obtained in a single ideal Polymer Electrolyte Membrane Fuel Cell (PEMFC) when the thermodynamic reaction limitations are taken into account (Srinivasan 2006).

### 1.2.2 Efficiency of a Fuel Cell

The thermal efficiency of an ideal fuel cell operating reversibly on pure hydrogen and oxygen at standard conditions would be

\[
\eta_{\text{max}} = \frac{\text{Useful output energy}}{\Delta H} = \frac{\Delta G}{\Delta H} = \frac{237.2}{285.8} = 0.83
\]  

(1.14)

The efficiency of a fuel cell can be expressed in terms of the ratio of the operating cell voltage to the ideal cell voltage. The actual cell voltage is less than the ideal cell voltage because of the losses associated with cell polarization. The thermal efficiency of the fuel cell can then be written in terms of the actual cell voltage,

\[
\eta_{\text{max}} = \frac{\text{Useful output energy}}{\Delta H} = \frac{\text{useful output power}/(\Delta G/0.83)}{V_{\text{cell}} * I / (V_{\text{ideal}} * 0.83)} = V_{\text{cell}} * 0.83 / V_{\text{ideal}}
\]  

(1.15)

The ideal voltage of a fuel cell operating reversibly with pure hydrogen and oxygen in standard conditions is 1.229 V. Thus, the thermal efficiency of an actual fuel cell operating at a voltage of \( V_{\text{cell}} \) is given by
\[ \eta_e = V_{\text{cell}} \times 0.83 / 1.229 = 0.675 \ V_{\text{cell}} \] (1.16)

A fuel cell can be operated at different current densities; the corresponding cell voltage then determines the fuel cell efficiency. The standard potential in a fuel cell varies with temperature. Hence the ideal potential is less than 1.229 V when considering the gaseous water product in a fuel cell. The influence of temperature on the fuel cell voltage is shown schematically in Figure 1.2, where the fuel cell performance data from typical operating cells and the dependence of the reversible potential of \( \text{H}_2/\text{O}_2 \) fuel cells on temperature are given. The cell voltages of PEMFC, phosphoric acid fuel cell (PAFC), and molten carbonate fuel cell (MCFC) show a strong dependence on temperature (Hirschenhofer et al 1998).

\[ \text{Cell voltage (V)} \]

\[ \text{Temperature (K)} \]

**Figure 1.2 Influence of temperature on the operating voltage of different fuel cells**

The open cell potential (OCP) for a fuel cell is 1.229V, but in the non-ideal case the actual operating voltage is less than the ideal voltage because of the irreversible losses associated with the fuel cell electrochemistry (Cairns & Liebhafsky 1969; Hirschenhofer et al 1998). Several factors contribute to the irreversible losses in a practical fuel cell. The
losses which were originally termed as polarization or over potential, mainly originated from three losses: Activation loss, ohmic loss and concentration or mass transfer loss.

**Activation loss**: These are caused by the slow reaction kinetics takes place on the surface of the electrode. A portion of the voltage generated is lost in driving the chemical reaction that transfers the electrons to or from the electrode. The activation loss is dominant at low current density and increases marginally with an increase in current density.

**Ohmic loss**: The origin of ohmic polarization comes from the resistance to the flow of ions in the electrolyte and flow of electrons through the electrodes and the external circuit. This loss is proportional to the current density. It can be represented as

\[
\eta_{\text{ohm}} = iR_c
\]  

(1.17)

Where \( \eta_{\text{ohm}} \) is the ohmic polarization and \( R_c \) is the cell resistance. The dominant ohmic loss is in the electrolyte, which is reduced by decreasing the electrode separation, enhancing the ionic conductivity of the electrolyte and by modification of the electrolyte properties.

**Concentration loss**: It is also known as mass transfer loss, which is caused by the loss of concentration of fuel or oxidant on the surface of the electrode. This loss occur over the entire range of current density and become prominent at high limiting currents where it becomes difficult for the reactant gas to flow to reach the fuel cell reaction sites.

Apart from these three main losses, fuel cross over and internal energy can occur to a lesser extent. Fuel cross over mainly takes place in liquid fuel cell such as methanol and ethanol fuel cell through the electrolyte.
The electron conduction through the electrolyte can also happen rarely and its effect is usually not very important. However, these two does have a marked effect on the OCP of low-temperature cells. Figure 1.3 displays the ideal and actual current response of a fuel cell.

![Figure 1.3 Ideal and actual current-voltage response of a typical fuel cell](image)

1.3 CLASSIFICATION OF FUEL CELLS

Fuel Cells can be mainly classified into three categories, depending on their operation temperature. Low temperature fuel cell which operates below 100°C, medium temperature fuel cells, that operate below 250°C and high temperature fuel cell, operates at a temperature above 600°C. The naming of fuel cell is based on the electrolyte present except liquid fuel cells such as direct methanol fuel cell (DMFC), direct ethanol fuel cell (DEFC) etc.

Low temperature Fuel Cell consists of PEMFC and AFC which can operate below 100°C. MCFC operates in medium temperature and SOFC can be categorized as high temperature fuel cell (Hirschenhofer et al 1998).
Table 1.1 provides the characteristics of various fuel cells. Low temperature and medium temperature fuel cells are mainly used for automotive and portable applications, but PGMs as catalyst is required for the electrochemical reaction and thus commercialization is constrained by the availability of noble metals. On the other hand, high temperature fuel cells do not require noble metal catalyst, but require materials which can withstand the high temperature thermal cycles.

Table 1.1 Classification of five major types of fuel cells

<table>
<thead>
<tr>
<th>Fuel Cell Type</th>
<th>Electrodes</th>
<th>Electrolyte</th>
<th>Charge carriers</th>
<th>Operating temperature</th>
<th>Fuel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer Electrolyte Membrane Fuel cell (PEMFC)</td>
<td>Pt on carbon</td>
<td>Proton exchange membrane</td>
<td>H⁺</td>
<td>60-80°C</td>
<td>H₂</td>
</tr>
<tr>
<td>Alkaline fuel cell (AFC)</td>
<td>Ni/Ag (Pt/Pt) on porous Ni</td>
<td>Concentrated KOH in porous matrix</td>
<td>OH⁻</td>
<td>70-120°C</td>
<td>H₂</td>
</tr>
<tr>
<td>Phosphoric acid fuel cell (PAFC)</td>
<td>Pt/Pt</td>
<td>Liquid phosphoric acid</td>
<td>H⁺</td>
<td>160-200°C</td>
<td>H₂</td>
</tr>
<tr>
<td>Molten carbonate fuel cell (MCFC)</td>
<td>Ni/NiO</td>
<td>Molten Li and K carbonate in porous matrix</td>
<td>CO₃²⁻</td>
<td>650°C</td>
<td>H₂, CH₄</td>
</tr>
<tr>
<td>Solid oxide fuel cell (SOFC)</td>
<td>Ni cermets, SrLaMnO₃, other perovskites</td>
<td>Yttrium stabilized zirconia ZrO₂(Y₂O₃)</td>
<td>O²⁻</td>
<td>1000°C</td>
<td>H₂, CH₄, CO</td>
</tr>
</tbody>
</table>
1.3.1 Polymer Electrolyte Membrane Fuel cell (PEMFC)

PEMFCs are also known as proton exchange membrane fuel cell (PEFCs), solid polymer electrolyte fuel cell (SPEFCs) and ion exchange membrane fuel cell (IEMFCs). $\text{H}_2$ or small organic molecules (SOMs) can be used as fuel at the anode side and air/$\text{O}_2$ can be used as oxidant at the cathode side. The electro chemical reactions occur between $\text{H}_2$/SOMs and $\text{O}_2$ produces water, carbon dioxide ($\text{CO}_2$) and electricity. The overall reaction in a typical PEMFC is given in Equation (1.1)-(1.3) (Ladewig et al 2015).

Nano structured Pt or Pt based alloys supported on carbon (Pt/C) are the conventional electro catalysts in PEMFCs. The PEMFC performance depends on the electro chemical reaction that occurs in the three phase boundary (electrode-electrolyte-fuel/air). The electrode consists of a porous carbon cloth, in which Pt coated on one side is known as catalyst layer and the other side consists of a mixture of carbon black and 35% polytetrafluoroethylene (PTFE), known as gas diffusion layer (GDL) or backing layer. The hydrophobic GDL allows better gas transport to the catalyst layer. The electrodes are pressed on the membrane to have a better contact by reducing the contact resistance. Nafion® (DuPont) is commonly used as the solid polymer membrane which is a perfluorinated polymer with pendant sulphonic acid group. These polymer electrolytes are good electric insulators and very good proton conductors. Humidification is required to ensure better proton conduction through the membrane.

A stack is a combination of individual PEMFCs arranged in series. Each cell is separated from a neighboring cell by bipolar plates, which serve as current collectors and function as interconnectors between individual cells. Flow fields are designed with different geometrical patterns in order to provide a better gas transport to the electrodes and product water removal.
from the cell. Normal working temperature of a PEMFC is 80°C with a conversion efficiency of 50-60%.

### 1.3.2 Direct Alcohol Fuel Cells

Direct alcohol fuel cells are typically PEMFCs, which feed an aqueous hydrocarbon fuel on the anode side without any fuel reformation. The proton released by the liquid can travel through the membrane and react with O₂ forming water. The most commonly used liquid fuel cells are DMFC, DEFC and direct formic acid fuel cells (DFAFCs). Liquid fuels usually have much higher energy density and it is easy to store, transport and refill compared to H₂ (Qian et al 2006).

#### 1.3.2.1 Direct Methanol Fuel Cell (DMFC)

DMFC as the name implies uses methanol as a fuel (source of H₂) and O₂ or air as an oxidant. Nafion ® membrane is used as electrolyte as in PEMFCs. Pt-Ru alloy catalyst is more favorable for the methanol electro oxidation forming CO₂, H⁺ and electrons. This catalyst has shown the maximum tolerance to the carbon monoxide (CO) formed in this oxidation reaction as an intermediate.

The overall reaction in DMFC is as follows

At anode:

\[
\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \quad \text{E}_0 = 0.02\text{V} \quad (1.18)
\]

At cathode:

\[
3/2 \text{O}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow 3\text{H}_2\text{O} \quad \text{E}_0 = 1.23\text{V} \quad (1.19)
\]
Overall

\[ \text{CH}_3\text{OH} + \frac{3}{2} \text{O}_2 \rightarrow \text{CO}_2 + 3\text{H}_2\text{O} \quad E_0 = 1.21 \text{V} \quad (1.20) \]

Two major challenges observed in DMFCs are the sluggish kinetics of the methanol electro oxidation and crossover of methanol through the electrolyte. The oxidation of methanol occurs in several steps with the formation of intermediates like-CHO, -CO on the catalysts. The enhanced activity of Pt-Ru binary alloy catalyst over Pt attribute to both bifunctional mechanism and an electronic effect (Watanabe & Motoo 1975; Frelink et al 1995). A bifunctional mechanism involves the adsorption of oxygen containing species on Ru at lower potential and promotes the oxidation of CO to CO\(_2\). This mechanism can be summarized as:

\[ \text{Pt} + \text{CH}_3\text{OH} \rightarrow \text{PtCO}_{\text{ads}} + 4\text{H}^+ + 4e^- \quad (1.21) \]
\[ \text{Ru} + \text{H}_2\text{O} \rightarrow \text{Ru(OH)}_{\text{ads}} + \text{H}^+ + e^- \quad (1.22) \]
\[ \text{PtCO}_{\text{ads}} + \text{Ru(OH)}_{\text{ads}} \rightarrow \text{CO}_2 + \text{Pt} + \text{Ru} + \text{H}^+ + e^- \quad (1.23) \]

DMFC can work at 80\(^0\)C with liquid methanol-water mixture; depending on electrolyte it can operate at higher temperature with gaseous mixture with a conversion efficiency of 60%.

1.3.2.2 Direct Ethanol Fuel Cell (DEFC)

DEFC is another kind of liquid fuel cell in which the cheap and non-toxic ethanol is fed as fuel. High energy density and ease of availability makes ethanol an attractive alternative to methanol. Pt and tin (Sn) or rhodium (Rh) or ruthenium (Ru) based binary alloy catalysts (Pt-Sn/C, Pt-Rh/C, Pt-Ru/C) are good choices for the oxidation of ethanol at anode side
compared to Pt/C catalyst for the formation of CO$_2$ and H$_2$O. The Overall reaction in DEFC is as follows

At anode:
\[ \text{CH}_3\text{CH}_2\text{OH} + 3\text{H}_2\text{O} \rightarrow \text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \quad E_o = 0.02\text{V} \quad (1.24) \]

At cathode:
\[ 3\text{O}_2 + 12\text{H}^+ + 12\text{e}^- \rightarrow 6\text{H}_2\text{O} \quad E_o = 1.23\text{V} \quad (1.25) \]

Overall
\[ \text{CH}_3\text{CH}_2\text{OH} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O} \quad E_o = 1.21\text{V} \quad (1.26) \]

The main challenges DEFCs faces are incomplete oxidation of ethanol and crossover of fuel across the membrane but the crossover rate is less compared to methanol. There is no clear understanding regarding the adsorbed intermediates on the Pt during ethanol oxidation. It is believed that high yields of acetaldehyde (CH$_3$CHO) at lower potential and acetic acid (CH$_3$COOH) at higher potential are formed as the reaction intermediates in acidic medium (Soloveichik 2014). So the breaking of C-C bond for the complete oxidation to form CO$_2$ is a major problem in DEFCs. Pt and Sn based binary catalysts showed the highest power density for ethanol oxidation reaction (EOR) where Sn is able to adsorb OH species and can allow the formation of CO$_2$ and CH$_3$COOH at lower potential compared to Pt. The proposed mechanism is given below.

\[ \text{Pt-CO}_{\text{ads}} + \text{Sn-OH}_{\text{ads}} \rightarrow \text{CO}_2 + \text{H}^+ + \text{e}^- \quad (1.27) \]

Moderate working temperature of DEFCs is 80$^\circ$C with a conversion efficiency of around 50%.
1.3.3 Alkaline Fuel Cell (AFC)

AFCs also known as Bacon fuel cells, use 30-35wt% of potassium hydroxide as electrolyte. The basic electrochemical reactions inside AFCs are

At anode:

\[ 2H_2 + 4OH^- \rightarrow 4H_2O + 4e^- \quad E_0 = 0.83V \]  

(1.28)

At cathode:

\[ O_2 + 4e^- + 2H_2O \rightarrow 4OH^- \quad E_0 = 0.40V \]  

(1.29)

Overall:

\[ 2H_2 + O_2 \rightarrow 2H_2O \quad E_0 = 1.23V \]  

(1.30)

The reaction occurs when the hydroxyl ions (OH\(^-\)) diffuse from the cathode to anode, and H\(_2\)O diffuses in the opposite way. Figure 1.4 shows the schematic of typical AFCs. The electrodes in AFCs consist of a double layer structure, an active catalyst layer and a hydrophobic layer. Teflon coated semi permeable carbon materials or porous graphite materials can be used as electrodes. Pt/C or Pt based alloys are good choice for catalysts but then the faster kinetics of oxygen reduction reaction (ORR) at alkaline medium permits the use of non- noble metal catalysts. Potassium hydroxide solution retained in a porous stabilized matrix is the electrolyte. AFC also operates well at room temperature and have a good cold start capability. One of the major operating constraints of AFCs is the sensitivity of CO\(_2\) which in turn will convert into carbonates which are capable of blocking electrolyte pathways and electrode pores. It is assumed that the poisoning may occur by the following reactions (Al-Saleh et al 1994)
\[ \text{CO}_2 + 2\text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} \text{ and or} \]  
\[ \text{CO}_2 + 2\text{KOH} \rightarrow \text{K}_2\text{CO}_3 + \text{H}_2\text{O} \]  
(1.31)  
(1.32)

As a consequence, the operation of AFC is limited to some application where the oxidant is only pure \( \text{O}_2 \) such that no \( \text{CO}_2 \) formation will occur. AFCs can operate with an optimum temperature of 80\(^\circ\)C, with an efficiency of 60-70%.

**Figure 1.4 Schematic representation of an alkaline fuel cell**

### 1.3.4 Phosphoric Acid Fuel Cell (PAFC)

PAFC is developed in the mid-1960s and was used as a candidate for early stationary applications. Anode and cathode reactions are similar to PEMFCs but since operating temperatures are high (150-200\(^\circ\)C), PAFCs are more tolerant to fuel impurities. It uses phosphoric acid (\( \text{H}_3\text{PO}_4 \)) immobilized in a silicon carbide matrix (SiC–poly (tetrafluoroethylene) (PTFE)). The electrode consists of a porous carbon material coated with Pt/C electro catalysts. Air is used as an oxidant and reformate \( \text{H}_2 \) as fuel. The electro chemical reactions consist of
At anode: \( \text{H}_2 \rightarrow 2\text{H}^+ + 2e^- \) \( E_0 = 0\text{V} \) (1.33)

At cathode: \( \frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O} \) \( E_0 = 1.23\text{V} \) (1.34)

Overall: \( 2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O} \) \( E_0 = 1.23\text{V} \) (1.35)

The main advantages of PAFCs are that, CO contamination of the catalysts is slow between 160 and 220 \( ^\circ\text{C} \) operation temperature; up to 1% CO can be tolerated in the feed gas. And concentrated phosphoric acid electrolyte can be operated above the boiling point of water. However at lower temperatures, CO poisoning of the Pt electrocatalyst in the anode becomes severe. But, they are much less sensitive to CO than PEMFCs and AFCs. The conversion efficiency of PAFCs is around 40-45%.

1.3.5 Molten Carbonate Fuel Cell (MCFC)

MCFCs use the electrolyte which typically consists of a combination of alkali (Na and K) carbonates suspended in a porous ceramic matrix of LiAlO\(_2\). MCFCs are high temperature fuel cells that operate at temperatures above 600\(^\circ\text{C}\). The mobile ions are CO\(_3^{2-}\) which move from cathode to anode through the electrolyte and H\(_2\)O which is produced at the anode. The electrodes consist of Ni anode and NiO cathode. The electrochemical reactions consist of

At anode: \( \text{H}_2 + \text{CO}_3^{2-} \rightarrow \text{H}_2\text{O} + \text{CO}_2 + 2e^- \) (1.36)

At cathode: \( \frac{1}{2} \text{O}_2 + \text{CO}_2 + 2e^- \rightarrow \text{CO}_3^{2-} \) (1.37)

Overall: \( \text{H}_2 + \frac{1}{2} \text{O}_2 + \text{CO}_2 \rightarrow \text{H}_2\text{O} + \text{CO}_2 \) (1.38)

Since MCFC is not affected by CO, it can operate on a variety of fuels including H\(_2\), reformed alcohols or hydrocarbons, eliminating the need
for the external reformers. The MCFCs also have good thermal efficiencies, where the exhaust heat can be used to generate steam. The conversion efficiency of MCFCs is about 60%.

1.3.6 Solid Oxide Fuel Cell (SOFC)

SOFCs, a type of high temperature fuel cell uses a solid oxide material as electrolyte. The solid oxide is a mixture of zirconia and yttria (Y$_2$O$_3$-stabilized ZrO$_2$, (YSZ)) and it consists of 8-10mol% yttrium. SOFCs require no precious metals, corrosive acids, or molten materials unlike other types of fuel cells. The solid oxide electrolyte is an oxide (O$^{2-}$) ion conductor with a sufficiently high conductivity around 1000°C. The anodes of SOFC consist of Ni cermet, a composite of metallic Ni and YSZ. Strontium (Sr) doped lanthanum manganite, a mixed conductive oxide, with perovskites crystalline structure is used as the cathode material. The mobile O$^{2-}$ ions in YSZ move from the cathode to the anode and water is produced at the anode.

The electro chemical reactions consist of:

At anode:  \[ \text{H}_2 + \text{O}^{2-} \rightarrow \text{H}_2\text{O} + 2\text{e}^- \]  
\hspace{1cm} (1.39)

At cathode: \[ \frac{1}{2} \text{O}_2 + 2\text{e}^- \rightarrow \text{O}^{2-} \]  
\hspace{1cm} (1.40)

Overall: \[ \text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} \]  
\hspace{1cm} (1.41)

For SOFCs, Any kind of fuels and oxidants are suitable and no reformer is needed if methane is the fuel where anode will act as the catalyst for steam reformation to convert the fuel to H$_2$. High efficiency is one of the attractive qualities of SOFCs. The conversion efficiency of SOFCs is around 60%.
1.4 CHALLENGES IN LOW TEMPERATURE FUEL CELLS

Cost, performance and durability are the three major challenges, restricting the commercialization of PEMFCs. The PGM catalysts act as one of the most expensive components of the fuel cell. So much of the research is focused on the effective utilization of state of the art PGM catalysts for increased activity as well as stability. There is however much scope on the development of more active Pt based catalysts or non precious metal catalysts for the commercialization of low temperature fuel cells. Lowering the Pt loading, achieving higher mass activity and long term stability are the main challenges for the development of an electro catalyst. One strategy of boosting up the electro catalytic activity is to make an alloy of Pt with various transition metals (PtM). These PtM based binary, ternary alloys and/or intermetallics in PEMFCs are reported to enhance the kinetics of ORR. Alloying is also probably a rational method to reduce the Pt loading (Gasteiger et al 2005). Recent studies (Stamenkovic et al 2007) on Pt$_3$Ni (111) reported 10-fold higher ORR activity when compared to Pt (111) and 90 fold more activity compared to state of the art Pt/C electro catalysts. There are also studies reported on controlling the shape of the catalyst e.g., Pt$_3$Ni (111) for the improved ORR activity (Zhang et al 2010). There are several reports devoted to the development of Pt based alloys and intermetallics for the improved activity and stability of PEMFCs (Wang et al 2013; Oezaslan et al 2012). Apart from alloying of Pt with other metals, Fe based non precious metal catalysts have also been introduced as a replacement to Pt based catalysts for both acidic and alkaline fuel cells (Lefèvre et al 2009) to lower the costs. Despite all these findings, work on the improvement of ORR kinetics with different alloys, intermetallics and non Pt based catalysts is continuing.
The type of ion exchange membrane electrolytes plays a crucial role in the performance improvement of low temperature fuel cell. There are several publications focused on enhancing the efficiency, durability and reducing cost of ion exchange membranes for both acidic as well as alkaline fuel cells. Some properties such as 1) good proton conduction, 2) good mechanical, chemical and thermal strength, 3) low gas permeability and 4) less crossover effect in case of liquid fuels are being addressed for the development of a polymeric membrane for use in fuel cells (Siroma 2004). Though the cost is high, the perfluorinated backbone and relatively low equivalent weight makes Nafion® and related materials, a favorable choice for membranes and are commonly used in fuel cell MEA’s. In one such effort (Savinell et al 1994) a phosphoric acid equilibrated Nafion® has been developed which showed high temperature operation with good proton conductivity and reduced methanol permeability. Polybenzimidazole (PBI) impregnated with phosphoric acid has been the choice of high temperature polymer electrolyte investigated by many workers. This has led to using several other high temperature polymers for fuel cell application e.g., sulfonated polysulfones (SPSF) blended with PBI and doped with phosphoric acid has exhibited much improved mechanical strength and conductivity compared to the pure PBI membranes at higher temperatures (Hasiotis et al 2001). More attention is still necessary to optimize and develop new membranes with reduced costs for the commercialization of fuel cells.

Durability is another key issue relevant to the commercialization of fuel cells. To offer a reliable power source for both stationary and transportation, the department of energy (DOE) durability targets are 40,000 h for stationary applications and 5000 h for transportation applications respectively (DOE 2010). The degradation problem in fuel cells are complex
since many factors cause fuel cell degradation. Operational conditions such as impurity effects including fuel and air impurities can affect the durability of the fuel cells. Effect of subfreezing temperature at the start-up of fuel cells, fuel starvation, start-stop cycling, relative humidity and load cycles can results in stresses on the mechanical and chemical stability of the fuel cell components and materials. Chemical degradation on the membrane was recognized during operation (LaConti et al 2003) where $O_2$ molecule permeates through the membrane from the cathode side and reduced at the anode to form hydrogen peroxide ($H_2O_2$). It is also known that $H_2O_2$ formation is possible during ORR as an intermediate. A study by using rotating ring-disk electrode (RRDE) showed that $H_2O_2$ yield was around 80% on Pt/C catalyst deposited on a glassy carbon (GC) in the anode potential of 0V (LaConti et al 2003). Chemical degradation on fuel cells has received considerable attention whereas physical degradation such as membrane creeps and structural change of fuel cell components also play a role in the stability. Electro catalyst degradation is also one of the most important parameters which affect the overall stability of a fuel cell. Performance loss of PEMFC under steady state operation has been attributed to the loss in electro chemical surface area (ECSA) of the carbon supported electro catalysts. Corrosion of the catalyst supported carbon may lead to Pt dissolution or agglomeration while operating continuously in a start-stop cycles, which is a major factor that affects the ECSA (Fowler et al 2003). Though Pt based alloys show enhanced performance, still the stability of alloys under fuel cell operation conditions are a key challenge to look into. Enormous work is under progress to understand the degradation mechanism and to develop strategies and materials, which can mitigate the stability issues.
1.5 DEVELOPMENT OF ELECTRO CATALYST SUPPORTS FOR PEMFC’s

An electro catalyst support plays a major role by providing a surface to disperse Pt nanoparticles, by achieving high surface area. Fuel cell catalysts are generally heterogeneous where the catalysts (solid) and reactants (liquid or gas) are in different phases. Unlike homogeneous catalysts, heterogeneous catalysts require an active site to adsorb the reactant molecules to help them react. Pt and Ni act as active metals among various catalysts since they adsorb the reactant molecules strongly and activate the reaction, but not so strongly as the products should not desorb from the active site. The fuel cell electro catalysts in both anode and cathode usually dispersed on a porous carbon based materials. Pt nano particles on carbon (Pt/C) are one of the states of the art electro catalysts for low temperature fuel cell as Pt offers highest catalytic activity, chemical stability, high exchange current density and superior work function. The conductive porous support materials provide a physical surface for dispersion of small metal particles which is necessary for attaining high surface area. Carbon supports also allows significant decrease of metal loading in different fuel cells. However the lifetime of carbon supports are limited to the kinetically slow yet thermodynamically favorable oxidation reaction at fuel cell cathode.

Electrochemical corrosion of carbon in PAFC’s has been reported since 1970s and 1980s. Carbon can electrochemically oxidize to CO₂ at quite low potentials (Gruver 1978).

\[ C + 2H_2O \rightarrow CO_2 +4H^+ + 4e^- \quad E_0 = 0.118 \text{ V vs RHE} \quad (1.42) \]

Even though the corrosion kinetics of carbon is very slow, it may affect the long term durability of PEMFC’s. Studies by Kinoshita & Bett 1974 observed that the concentration of electro active carbon species such as
quinone and hydroquinone formation is higher in platinized Vulcan carbon XC 72 carbon compared to non platinized carbon samples. And the redox couples are forming at a potential of around 0.625V vs normal hydrogen electrode (NHE) in 1M H$_2$SO$_4$. Some reports on carbon corrosion showed that vulcan XC 72 carbon showed surface oxidation at potentials $\geq$ 0.8 V at 65°C and $\geq$ 1.0 V at room temperature (Kangasniemi et al 2004). A significant increase in the rate of surface oxide formation is observed at PEM fuel cell operating temperature, compared to that observed at room temperature. Increased wettability with surface oxidation also suggests that the corrosion may affect the hydrophobicity which could affect water transport in PEMFC’s by potentially contributing to its performance loss.

Differential electrochemical mass spectroscopy (DEMS) analysis to evaluate the effect of Pt to catalyze the oxidation of carbon has been reported, where the Pt activates the corrosion of carbon at lower potential resulting in a CO surface layer between 0.6-0.8V vs RHE, which leads to the loss of Pt active sites. The mechanism consists of:

Formation of a CO-surface layer at $E > 0.3$ V (RHE)

$$C + H_2O \rightarrow CO_{surf} + 2H^+ + 2e^- \quad (1.43)$$

Oxidation of CO$_{surf}$ on Pt at $E = 0.8$ V (RHE)

$$CO_{surf} + H_2O \rightarrow CO_2 + 2H^+ + 2e^- \quad (1.44)$$

When the CO surface is bound to carbon, its oxidation will occur only in areas near Pt particles by weakening the contact between Pt and carbon. Therefore, the amount of CO$_2$ formed is directly proportional to the length of grain boundaries between Pt and carbon supports (Willsau et al 1984). These analyses were confirmed by Roen et al (2004) who studied the
effect of Pt on the rate of carbon support corrosion. PEM with carbon only electrode shows less CO₂ emission at higher potential compare to Pt/C as electrode in MEA at temperature lower than ~50°C. The magnitude of CO₂ peaks with respect to cell potentials depends on the Pt mass fraction and the type of catalysts. When PtRu/C catalyst was used, CO₂ emission occurred at ~0.1V negative potential compare to Pt/C, suggesting that the CO adsorbed on the surface of the catalyst is oxidized to CO₂.

During start up–shut down process, there might be hydrogen starvation at anode side that makes the anode partially exposed to hydrogen and partially exposed to air. This phenomenon raises the cathode interfacial potential difference to 1.44V. At this high potential, the carbon in the catalyst layer can be corroded within few hours (Reiser et al 2005). It is also observed that the oxygen crossover from the cathode side is sufficient to cause the reverse current condition i.e, the anode potential will increase to oxidize water or carbon support at the anode. This also leads to the thinning of cathode electrode confirmed by the electron probe micro analysis (EPMA).

The electro chemical corrosion of carbon surface leads to change in surface chemistry of carbon by increasing hydrophilicity of the catalyst layer and GDL which results in a decrease in the gas permeability and also may affect the water transport mechanisms which will lead to flooding of pores (Siroma et al 2014). The oxidation of carbon may also increase the interface resistance by decreasing the thickness of the catalyst layer (Guilminot et al 2007). Figure 1.5 shows how the carbon oxidation affects the catalytic activity via agglomeration followed by leaching of Pt. It is essential, therefore to have an alternating support material for Pt that is more stable than carbon under fuel cell operation condition. One of the main focuses of this thesis will be on evaluating non carbon based supports for PEMFCs in acidic medium.
Intensive research has not been performed on the development of non carbon supports for PEMFCs. Some oxides, carbides and nitrides have been examined as Pt supports in some fuel cells. Out of that, oxides attract enormous interest by considering its oxidative stability in the harsh fuel cell operation condition. Metal oxides as co-catalyst or supports have strong interaction with metal nanoparticles (Tauster 1987), which could prevent the agglomeration of metal particles. The electronic structure of semiconducting metal oxides helps to modify it as catalyst supports. Then the bi-functional mechanism exhibited by some metal oxides could also help it to use as co-catalyst or catalyst supports for noble metals for reactions which have CO as adsorbates (Watanabe & Motoo 1975). Because of their outstanding properties, metal oxides have been used as independent electro catalysts, co-catalysts and supports for low temperature fuel cells in acidic and alkaline electrolytes.
1.6 METAL OXIDE BASED NON PRECIOUS ELECTROCATALYSTS FOR AFC’s

Until the early work in 1964 on cobalt phthalocyanine (Jasinski 1964), to reduce oxygen in alkaline medium, it was known that only precious metals were active for ORR. Followed by this, some studies (Meadowcroft 1970; Matsumoto et al 1977) demonstrated the oxygen reduction activity of various transition metal oxides. Since then oxides have been emerged as ORR catalysts for fuel cell applications (Cheng et al 2010; Liang et al 2011) and the idea of using non precious metal catalysts for ORR has drawn a lot of attention and there has been a significant progress in the development of non-precious metals as electro catalysts in AFCs. The rich electro chemistry due to the variable valency and abundant structures of transition metal oxides provided vast opportunity for the search and development of precious metal free catalysts. A wide variety of non-precious metals such as nitrogen doped carbon materials, different transition metals, macro cyclic compounds, various metal oxides including perovskites and spinel oxides have been explored as oxygen electrodes in AFCs (Wu et al 2009). The main criteria for choosing an appropriate electro catalyst involves, electro catalytic activity, corrosion resistance and fabrication cost.

Among them spinel oxides, having the general formula $\text{AB}_2\text{X}_4$ with a cubic close packed arrangements where $\text{A}^{2+}$ and $\text{B}^{3+}$ occupying tetrahedral and octahedral sites are promising class of materials to replace the precious Pt based electro catalysts for ORR in alkaline medium (Trasatti 1994). Mixed metal oxides with spinel structures are superior to the corresponding single oxides. Some of these oxides tend to exhibit rather high electrical conductivity by electron transfer between cations of different valencies (Chen et al 2004). Despite the abundant experiments carried out on this class of
materials, it is still unclear as to which type of spinel oxide is more active as ORR catalysts. But in terms of low cost, high abundance and multiple valencies, Mn based spinel oxides have prominent advantages over other spinel oxides for ORR.

Co and Fe substituted, Mn based spinel metal oxides as non-precious metal catalysts for ORR in AFC’s will be discussed as a part of this thesis. The substitutions by other metal oxides have been proven to improve the intrinsic electro catalytic activity because of the increase in ratio of Mn$^{3+}$/Mn$^{4+}$ in octahedral sites due to the partial substitution (Chen et al 2004). Structure tailored spinel metal oxides with high conductivity have been synthesized in most viable method. The emphasis is placed on controlling and optimizing the size, shape and structure of the mixed metal oxides towards the improved ORR activity and stability. The efficiency of structure tailored CoMn$_2$O$_4$ and FeMn$_2$O$_4$ graphene hybrid nano structures on the performance enhancement of ORR compared to other spinel oxides and stability improvement compared to the state of art catalysts have been explained.

1.7 LITERATURE REVIEW

1.7.1 Titanium Oxides (TiO$_x$)

TiO$_2$ or Titania has been considered as electrocatalyst support for PEMFCs due to its stability in fuel cell operation atmosphere, low cost, commercial availability, non-toxicity and the ease to control size and structure. Apart from the stability in acidic environment (Fovet et al 2001), another most important advantage of using TiO$_2$ is the strong metal support interaction between TiO$_2$ and metal nanoparticles (Tauster et al 1978). This in turn could avoid the agglomeration of metal nanoparticles by providing increased dispersion and could also change the electronic property of metal nanocatalysts.
TiO$_2$ was used for the reduction of oxygen in acidic and alkaline solution during 1980’s and 1990’s (Parkinson et al 1980; Baez et al 1992). Kim et.al (2007) used TiO$_2$ as catalyst, exhibited an onset potential of 0.65V vs. NHE for ORR by heat treating the Ti-sheets at 900$^\circ$C. The catalytic activity of Ti-oxides depends on the structure growth direction and work function and they found that the activity increased with (110) plane of the rutile TiO$_2$ structure. Hepel et al (2007) studied the effect of metal-support interactions and surface diffusivity of the adsorbed intermediates on bimetallic catalyst supported on nano porous TiO$_2$ by applying quantum mechanical calculations. They illustrated the surface electronic effect when Pt is added to (TiO$_2$)$_6$. When there is no bond formation between Pt atoms with O atoms of TiO$_2$, a small charge transferred from TiO$_2$ to Pt that leads to slight lowering of the HOMO energy level. When there is bond formation between Pt atom with O atoms of TiO$_2$, the charge transfers from Pt to TiO$_2$ results in dramatic changes in both HOMO and LUMO levels. When a Pt atom forms bonds with Ti atoms of TiO$_2$, the electron cloud may spread on all the surface atoms. The strong metal-support interaction lowers the activation energy for CO$_{ad}$ surface mobility, which leads to a facile diffusion of CO$_{ad}$ from Pt sites to Ru and TiO$_2$, by lowering poisoning effect for PtRu on a TiO$_2$ support compared to an unsupported PtRu or bare Pt catalysts.

Pt deposited TiO$_2$ thin films on Nafion$^\circledR$ membrane by a thermal evaporation technique and its ORR activity was studied by Gustavsson et al (2007). He found that the TiO$_2$ layer between Pt and Nafion$^\circledR$ increases the ORR performance compared to only Pt film deposited directly on Nafion$^\circledR$. The performance improvement might be due to the better dispersion of Pt on TiO$_2$ and its substantial proton conduction through the thin TiO$_2$ layer. Rajalakshmi et al (2008) reported that Pt/TiO$_2$ has better thermal stability, electro catalytic activity and corrosion resistance compared to Pt/C. The presence of TiO$_2$ provided well dispersion of Pt particles on support, which
could avoid the coalescence of Pt nanoparticles and offer better stability in fuel cell operation conditions. Mesoporous TiO$_2$ has been synthesized by template-assisted route and used as a catalyst support for PEMFC (Huang et al 2009). The performance enhancement attributed to the low mass transport limitations and high stability of Pt nanoparticles due to the strong metal support interactions. Huang et al (2012) synthesized Pt-Ir/TiO$_2$ catalysts and investigated their catalytic activity for ORR. The energy conversion efficiency of the supported Pt-Ir/TiO$_2$ (42%) is significantly higher than that of unsupported Pt-Ir black (30%).

Though TiO$_2$ as support or catalyst exhibits some catalytic performance, its low electronic conductivity and surface area still restrain its widespread applications in fuel cells. Upto certain extent, such problems could be resolved by the change of composition and morphology of TiO$_2$. Sub-stoichiometric titanium oxides known as Magnéli phase have a general formula of Ti$_n$O$_{2n-1}$ (4 < n < 10) that exhibit high conductivity compared to that of graphite (Graves et al 1991), in addition, there was no oxidation peaks observed between 0 and 2.0 V vs. NHE for Magnéli phase titanium oxides in 1 M sulfuric acid (Bartholomew & Frankl 1969) High conductivity and strong oxidation resistance make Magnéli phase titanium oxides as good catalyst supports for PEMFCs. Several studies (Chen et al 2002; Ioroi et al 2005; Ioroi et al 2007; Ioroi et al 2008; Ioroi et al 2011; Zhang et al 2013) have been carried out on various sub-stoichiometric TiO$_2$ materials including Ti$_4$O$_7$ and Ti$_5$O$_9$ as catalyst supports.

Sub-stoichiometric titanium oxides show co-catalytic performance for Pt in PEMFCs. However, it must be mentioned that they tend to be oxidized to stoichiometric TiO$_2$ in continuous operation which causes a degradation of electronic conductivity and thus electro catalytic performance.
Therefore, it is still a challenge to enhance the durability of sub-stoichiometric titanium oxides in long-time fuel cell operation.

The low electrical conductivity problem of TiO$_2$ can be solved by doping with some other metals. Niobium (Nb) doped TiO$_2$ is the most studied material which has an electrical conductivity of 0.2 -1.5 S cm$^{-1}$. Initial attempts on doped TiO$_2$ as catalyst support reported by Chen et al (2002), employed Nb doped on Ti$_4$O$_7$ (Ebonex), forming Ti$_0.9$Nb$_{0.1}$O$_2$. Electro catalytic performance of Ti$_0.9$Nb$_{0.1}$O$_2$ supported PtRuIr was compared with Ti$_4$O$_7$ supported PtRuIr. The stability for water oxidation as well as ORR is better for doped TiO$_2$ supported electro catalyst compared to the undoped one. In continuation to this, there were various reports came up with metal doping by different methods and used as catalyst supports. Nb-TiO$_2$ supported Pt by hydrothermal method (Park & Seol 2007) and Nb-TiO$_2$ supported Pt-Ru by sol gel method (Fuentes et al 2008) exhibited enhanced ORR and MOR performances compared to Pt/C and PtRu/C respectively due to the improved conductivity of supports, strong interaction and better dispersion in catalysts. Other than Nb, Molybdenum (Mb) doped TiO$_2$ was also reported by Ho et al (2011). The non-carbon Ti$_{0.7}$Mo$_{0.3}$O$_2$ support demonstrated very high activity and stability for ORR compared to commercial Pt/C and PtCo/C. The electronic structure changes of Pt due to its synergistic interaction with Ti$_{0.7}$Mo$_{0.3}$O$_2$ attributed to the enhanced activity and chemical stability in acidic and oxidative environments. Since doping can either create Ti vacancies or can donate electrons to Pt, developing TiO$_2$ is encouraged, as catalyst support in fuel cells.

Mixing carbon (C) with TiO$_2$ found to be an effective method to enhance the conductivity as well as surface area of catalyst support. C or carbon nano tubes (CNT) mixed TiO$_2$ have been synthesized by various researchers. The DMFC performance reported by Selvarani et al (2009) with
Pt/TiO$_2$-C exhibited a peak power density of 180mW cm$^{-2}$ compared to 80mWcm$^{-2}$ for Pt/C. Better formic acid oxidation reaction (FAOR) (Wang et al 2011; Qu et al 2012) and EOR (Song et al 2007) performances were observed when TiO$_2$ has been mixed with C or CNT or multi-walled carbon nanotubes (MWCNTs) (Akalework et al 2012). Morphological effects of TiO$_2$ also play a vital role on its physical properties and electrochemical performance. TiO$_2$ nanotube arrays are expected to have higher electron mobility compared to sintered TiO$_2$ nanoparticle films (Varghese et al 2009). TiO$_2$ nanotubes and nanotube arrays were used as catalyst supports for various electrochemical reactions such as EOR and methanol oxidation reaction (MOR) and with better CO tolerance. Guo et al (2009) prepared Pt nanocatalyst supported on porous anatase TiO$_2$ nanorods. The catalyst exhibited better electro catalytic activity and stability for MOR attributing to the excellent dispersion of Pt nanoparticles and the high CO tolerance of TiO$_2$ support. TiO$_2$ nanotube arrays (Rettew et al 2011), TiO$_2$ nanorod arrays (He & Hu 2011) TiO$_2$ nanofibers (Long et al 2011) and TiO$_2$ nanosheets (Saida et al 2010) were explored as electro catalyst supports for different electrochemical reactions.

Research is ongoing with the aim of using TiO$_2$ based catalyst support with better stability and activity for different fuel cell reactions. Doping and structure tailoring of TiO$_2$ nanoparticles were found to be more effective to enhance the catalytic activity. There are no reports on the morphological effects on catalytic performance so far. Herein, we have studied the morphological effect of TiO$_2$ nanotubes with surface defects for its application as electro catalyst support for ORR as well as MOR. Unlike previous studies, the Pt loading has been optimized and a detailed study on the synthesis, catalytic activity and oxidative stability of TiO$_2$ nanotube arrays supported Pt electrocatalyst is discussed in this work.
1.7.2 Tin Oxides (SnO$_x$)

SnO$_2$, a wide band gap semiconductor with high electronic conductivity and good corrosion resistance in acidic medium can also be used as catalyst support for fuel cell applications. The abundant hydroxyl groups present on the surface of SnO$_2$ have a strong influence on the suppression of CO poisoning based on the bifunctional mechanism as follows (Ye et al 2008).

SnO$_2$+H$_2$O $\rightarrow$ SnO$_2$-$\text{OH}_{\text{ads}}$+H$^+$+e$^-$  \hspace{1cm} (1.45)

Pt-CO$_{\text{ads}}$+SnO$_2$-$\text{OH}_{\text{ads}}$ $\rightarrow$ Pt+SnO$_2$+CO$_2$ + H$^+$+ e$^-$  \hspace{1cm} (1.46)

Pt/SnO$_2$C and PdSn/C was evaluated for their excellent electro catalytic activity for both MOR and FAOR in PEMFCs (Ye et al 2008; Zhang et al 2009). It is considered that the electronic effect between the metal and support could weaken its bond energy between metal and the adsorbed poisons. In case of PdSn, addition of Sn leads to the lowering of Pd (3d) binding energy which changes the electronic structure of Pd. Lower onset potential for CO oxidation compared to Pt/C was observed for Pt-SnO$_2$/MWCNTs and Pt/SnO$_2$ with different pre heat treatments (Waki et al 2005; Matsui et al 2006). The size controllable SnO$_2$ nanoparticles have been synthesized by hydrolysis of SnCl$_2$ and employed to prepare the carbon supported Pt/SnO$_2$ catalyst (Jiang et al 2005). The same researchers on another study (Jiang et al 2007) elucidated that the improved EOR performance of Pt/SnO$_2$/C comes from the available active ensembles for ethanol dehydrogenation and C-C bond splitting and also from the OH formation due to SnO$_2$ content. This catalyst exhibited surprisingly high performance for EOR compared to Pt/C.
Silva et al (2010) synthesized core–shell SnO$_2$@Pt/C and Pt/C nanoparticle electrocatalysts by a salt reduction process. Ethanol electrooxidation has been tested and the performance was compared with commercial PtSn/C. SnO$_2$@Pt system is capable of modifying the electronic structure of Pt with better activity towards EOR by reducing the amount of Pt in the electrocatalysts. Sandoval-González et al. prepared Pt-SnO$_2$/C by microwave assisted polyol method. The catalyst showed better catalytic activity and stability for MOR than commercial PtRu/C catalyst, which results from the bifunctional property of Pt and SnO$_2$ (González et al 2012).

CNT has been mixed with SnO$_2$ instead of carbon to further increase the conductivity. SnO$_2$ coated single-walled carbon nanotube (SWNT) bundles supporting Pt (Pt/SnO$_2$–SWNT) electrocatalyst was synthesized with varying SnO$_2$ loading (Hsu et al 2010) and its activity for EOR was analyzed. The electrocatalyst with the mass ratio of 50:1 of precursor salt (SnCl$_2$.2H$_2$O) to SWNTs exhibited highest current density for EOR. The proper ratio allowed for the optimization of bifunctional mechanism to increase the specific activity on Pt/SnO$_2$–SWNT surface. SnO$_2$ and Pt nanoparticles were deposited on nitrogen-doped CNT (CNx) to construct a PtSnO$_2$/CNx hybrid electrocatalyst for PEMFCs (Chen et al 2013). They demonstrated that the electrochemical durability of Pt can be enhanced by using SnO$_2$ as support. The crystalline SnO$_2$ has influence on the stability of Pt, which is more effective than the amorphous SnO$_2$.

Zhou et al (2012) did a detailed investigation on the effect of size of SnO$_2$ nanoparticles and the interface sites between Pt and SnO$_2$ on the electrocatalytic activity of MOR. They found that the 2nm size SnO$_2$ NPs on Pt electrode surfaces at ~ 50% coverage resulted ~ 40 times more active over bare Pt electrode. Their density functional theory (DFT) study suggests that the interaction between Pt and small SnO$_2$ NPs results in a weaker binding of
adsorbed OH species than that of bulk SnO\textsubscript{2}. The easy release of OH species on Pt supported SnO\textsubscript{2} NPs leads to more effective oxidation of chemisorbed CO at Pt-Sn interface making this surface an excellent catalyst for the MOR. Ternary catalyst such as Pt-Rh-SnO\textsubscript{2}/C has been synthesized for EOR in acidic medium (Kowal et al 2009 (a); Kowal et al 2009 (b)). This Pt-Rh-SnO\textsubscript{2}/C exhibit considerably higher activity than Pt-SnO\textsubscript{2}/C due to the addition of Rh component. Unusually high catalytic performance of the composite catalyst is attributed to the interaction among three components: Pt for adsorption of ethanol molecules, Rh for ease of C–C bond splitting, and SnO\textsubscript{2} for the oxidative removal of CO\textsubscript{ad} produced because of C–C bond splitting.

Even though SnO\textsubscript{2} act as a good co-catalyst, enhancing conductivity and stability by doping could further improve its catalytic performance. Pt supported Sb doped SnO\textsubscript{2} was synthesized by Lee et al (2008) for both MOR and EOR reactions. Better dispersion of Pt particles on the Sb-SnO\textsubscript{2} support and the bifunctional effect of SnO\textsubscript{2} resulted in higher electrocatalytic activity for both MOR and EOR. Pt nanoparticles were deposited on commercial Sb doped SnO\textsubscript{2} and carbon black by an alcohol-reduction process by Neto et al (2010). The presence of Pt nanoparticles, Sb-SnO\textsubscript{2} and carbon supports in close contact of Pt/Sb-SnO\textsubscript{2}-C resulted in good catalytic activity compared to Pt/C, Pt/Sb-SnO\textsubscript{2} and Pt/SnO\textsubscript{2}-C. Hypervalent (Nb\textsuperscript{5+}) or hypovalent (Al\textsuperscript{3+}) ions doped SnO\textsubscript{2} was synthesized and its electrocatalytic activity and stability towards ORR has been evaluated (Takasakiet al 2009). It was found that Pt/Sn\textsubscript{0.95}Nb\textsubscript{0.05}O\textsubscript{2} exhibited higher kinetic current than Pt/SnO\textsubscript{2}, while Pt/Sn\textsubscript{0.95}Al\textsubscript{0.05}O\textsubscript{2} is inactive for ORR. Pt/doped SnO\textsubscript{2} show better durability due to their high anticorrosion ability compared to Pt/C. But the catalytic activity of Pt/doped SnO\textsubscript{2} catalysts was lower than that of Pt/C. Kakinuma et al. synthesized the Pt/Sn\textsubscript{0.96}Nb\textsubscript{0.04}O\textsubscript{2} and Pt/Sn\textsubscript{0.96}Sb\textsubscript{0.04}O\textsubscript{2} catalysts by the colloidal method and tested for ORR activity.
and stability (Kakinuma et al 2013). The ORR mass activity value for Pt/Sn$_{0.96}$Nb$_{0.04}$O$_2$ was superior to that of Pt/Sn$_{0.96}$Sb$_{0.04}$O$_2$ and Pt/CB. The high durability and high catalytic activity rely both on the significant Pt-support interaction and stability of these supports. Sb-doped SnO$_2$ nanoparticles of around 5nm size were prepared and used as highly stable catalyst support for PEMFC's (Dou et al 2014). Electrochemical measurements show that Pt/Sb-SnO$_2$ has a comparable ORR activity to Pt/C but demonstrates significantly improved electrochemical durability. The enhanced durability of Pt/Sb-SnO$_2$ is attributed to the high stability of the Sb doped SnO$_2$ support and the strong interaction between Pt and Sb-SnO$_2$. Therefore, Sb doped SnO$_2$ can be used as a promising durable ORR catalyst support for PEMFCs. Metal oxide nanoparticles have a marked influence on its shape and size dependent physical, chemical, electronic, and catalytic properties (Wang & Rogach 2014). Various morphologies of SnO$_2$ nanomaterials have been reported including one-dimensional (1D) nanorods (Zhang et al 2003), nanobelts (Pan et al 2001), nanowires (Wang et al 2003) and nanotubes (Wang et al 2006) and two-dimensional (2D) nanosheets (Wang et al 2009).

Saha et al (2007 (a)) directly grew SnO$_2$ nanowires on carbon paper by a thermal evaporation method and deposited Pt and PtRu nanoparticles on the nanowires by potentiostatic electrodeposition method (Saha et al (2007 (b))). The composite electrodes of Pt/SnO$_2$ nanowires/carbon paper and PtRu/SnO$_2$ nanowires/carbon paper show higher mass and specific activity for MOR and better CO tolerance than Pt and PtRu deposited on glassy carbon, respectively, attributed to the unique 3D structure and bifunctional and/or electronic properties of SnO$_2$ nanowires. Mesoporous SnO$_2$ synthesized via a surfactant-template assisted method was used as Pt support and tested its activity as cathode catalyst in PEMFCs (Zhang et al 2010). The Pt/SnO$_2$ catalyst showed good electrochemical activity for ORR and more importantly much better stability in CV cycling tests than the commercial
Pt/C catalyst. The high stability is attributed to the strong interaction between Pt metal and SnO₂.

Electrochemical study of the EOR on Pt (111) deposited on to SnOₓ nanoislands by reactive layer assisted deposition was studied by Zhou et al (2011). After exposing the SnOₓ/Pt (111) surface to H₂O or an electrolyte solution, XPS provides evidence for a significant amount of H₂O/OH adsorbed on the reduced SnOₓ surfaces. Electrochemical testing for EOR revealed that the catalytic performance of Pt (111) is significantly enhanced by SnOₓ islands addition onto the surface. The enhanced EOR activity is tentatively attributed to the efficient removal of CO_ads-like poisoning species on Pt sites by oxygen-containing species that are readily formed on the SnOₓ nanoislands. The SnO₂ nanocluster supported Pt exhibited comparable catalytic activity to Pt/C and superior electrochemical stability for PEMFC’s which results from the high surface area and co-catalytic effect of SnO₂ nanoclusters (Dou et al 2013).

SnO₂ has demonstrated its considerable role in alcohol oxidation based on a bifunctional mechanism and/or an electronic effect. Research is further focused on the stability enhancement and specific surface area improvement to bring SnO₂ as a potential candidate in fuel cells. In this thesis (in chapter 4) investigations on structure tailored SnO₂ and its influence on the improved activity and stability towards EOR is described. Pt on SnO₂ nanofacets (Pt/SnO₂NFs) with oxygen defect is used as a model system to evaluate its effect on the fuel cell reactions. A detailed analysis is carried out on the physical and chemical structure of SnO₂ NFs with oxygen defects before and after Pt deposition. ORR activity and stability of the Pt/SnO₂ NFs is briefly explained in as a part of this work.
1.7.3 Cobalt Manganese Oxide and Graphene (CoMn$_2$O$_4$/G)

Transition metals of group VII and VIII elements (e.g., Mn, Fe, Co and Ni) possess multiple valences, resulting in a variety of oxides, chalcogenides and carbides. For example, manganese may exist in different valence states as Mn (II), Mn (III) and Mn (IV) corresponding to abundant manganese oxides ranging from MnO, Mn$_3$O$_4$ to Mn$_2$O$_3$ and MnO$_2$ (Post 1999). Manganese oxides play a crucial role in oxygen electrochemistry due to catalytic active centers present in Mn-Ca-O complex cluster for the oxygen evolution reaction (OER) in natural photosynthesis II (Najafpour et al 2010). But the mechanisms of both ORR and OER on manganese oxides is still unclear due to the complex redox chemistry and different crystallographic structures.

It is believed that the electrochemical activity towards the ORR in alkaline medium results from the presence of H atoms and OH groups at the manganese oxide surface (Brenet 1979). Various studies by Kozawa and Yeager (1965); Mao et al (2003); Fabio et al (2007) reported that the manganese oxides such as MnOOH, MnO$_2$, Mn$_2$O$_3$, Mn$_3$O$_4$ and Mn$_5$O$_8$ exhibited catalytic activity towards the ORR in alkaline electrolyte. Oxygen adsorption behavior on the surface of manganese oxide by Mao et al (2003) concluded that initially hydrogen peroxide ions HO$_2^-$ will be formed as partial reduction with 2 electrons followed by the disproportionation reaction of HO$_2^-$ into O$_2$ and OH$^-$. There were different mechanisms proposed for the oxygen reduction takes place on manganese oxide including end-on O$_2$ adsorption and bidentate O$_2$ adsorption (Cheng and Chen 2012). Regardless of the ambiguity, the multivalent Mn species synergically contribute to the reduction process in both two as well as four electron pathway. In situ X-ray absorption near edge structure (XANES) study revealed the involvement of Mn (III)/Mn (IV) species on the ORR electro catalysis (Fabio et al 2007).
Moreover, combining manganese oxide with another electrocatalytic compound seems to be an efficient strategy in enhancing the ORR activity. The research on composite catalysts such as manganese oxide nanoparticles electrodeposited on Pt substrate (El-Deab and Ohsaka 2006) and palladium (Pd) nanoparticles deposited on MnO$_2$ nanorods (Sun et al 2011) showed superior electrocatalytic activity to both pristine noble metals and uncoated manganese oxide. Partial substitutions of transition metals with manganese oxides have attracted extensive interests (Cheng and Chen 2012). Figure 1.6 given below presents the structure of Mn based spinels AMn$_2$O$_4$ (A=Co, Ni, Zn and Mg) representing cubic and tetragonal phases.

![Figure 1.6 Crystal structures of cubic (c-AMn$_2$O$_4$) and tetragonal (t-AMn$_2$O$_4$) Mn-based spinels (A=Co, Zn, Mg) (Cheng et al 2010)](image)

Cobalt substituted manganese spinels are potential candidate for electrocatalysts for bifunctional oxygen electrodes because of high catalytic activity and good corrosion stability of this compounds in alkaline solutions (Rios et al 2005; Koninck et al 2006; Nikolova et al 2008). The cationic distributions on the both tetrahedral and octahedral sites of spinel structure play a crucial role in ORR activity. Depends on the synthetic method, different cationic distribution was proposed for CoMn$_2$O$_4$ (Chen et al 2004).
It should also be noted that the preparation method of a spinel oxide significantly influences its physical as well as chemical properties and electrochemical characteristics. Solid state route is the conventional method for synthesis of spinel compounds, but it requires high temperature (Armijo1969). Though these types of compounds having higher crystallinity, it exhibit only limited electro catalytic activity due to the large particle size and low surface area. As the ORR in fuel cells occurs at three-phase boundaries of oxygen, catalyst and electrolyte, this requires larger active interface areas. Thus the research focus has been shifted towards nanostructured spinels as they can provide high surface areas to overcome the challenges of conventional non-precious metal oxide electrocatalysts.

Recently a facile and rapid room temperature synthetic route has been developed for the highly active Co-Mn-O spinel compounds of high specific surface areas with defects (Cheng et al 2010). They also observed that the cubic Co-Mn-O exhibited better catalytic activity for ORR compared to its tetragonal counterpart. From both experimental and computational analysis, it is evidenced that the different oxygen binding ability on the surface of the two phases attributed to the phase dependent catalytic activity. These findings demonstrate the feasibility of controllable synthesis and design of spinel-based electrocatalysts for ORR.

Manganese based oxides, when incorporated with multivalent transition-metal, should be promising alternative to Pt-based catalysts in alkaline medium but it should be worth noting that spinel metal oxides, owing to their semiconducting character, cannot provide high electrical conductivity as in the cases of metal and carbon-based catalysts. Thus carbon powders are added mechanically to metal oxides to fabricate electrodes with low resistance. However, mechanical addition of conductive materials may hinder the interface contact and also may lower the effective loading level of active
component. An alternative way is to synthesis hybrid materials combines an oxide with highly conducting carbon based materials (Hu et al 2005; Wie et al 2011). The synergistic coupling of nanomaterials found interest in order to develop spinel oxides with much improved electrocatalytic activity. Some studies on Co-Mn-O nanoparticles/graphene hybrid system showed bifunctional activity for lithium-air batteries (Wang et al 2011). Followed to this, there are some reports on the structure tailored CoMn$_2$O$_4$ and its electro chemical activity in lithium ion battery (Zhou et al 2005) where CoMn$_2$O$_4$ hollow micro cubes and mesoporous microspheres (Hu et al 2012) were synthesized. In another study (Zhai et al 2013) CoMn$_2$O$_4$ spinel nanocrystals were grown on poly (diallyldimethylammonium chloride) functionalized carbon nanotubes (PDDA-CNTs). CoMn$_2$O$_4$/PDDA-CNT catalyst showed high current densities for the ORR in alkaline and neutral conditions which outperformed the Co$_3$O$_4$/PDDA-CNT and Pt/C catalyst.

Chowdhury et al (2014) developed a nanocomposite material comprising CoMn$_2$O$_4$-PEDOT by in-situ polymerization method, exhibited high performance for both ORR and OER in alkaline solution using rotating disk electrode (RDE). Another study by Prabu et al (2014) showed improved bifunctional activity for zinc-air battery by hybrid mixture of CoMn$_2$O$_4$ nanoparticles dispersed on nitrogen doped reduced graphene oxide (N-rGO). The coupling effect between CoMn$_2$O$_4$ and graphene could attribute to the improved battery performance. Still no detailed study has been conducted on the effect of structure tailored CoMn$_2$O$_4$/G hybrid nanostructures on the performance improvement of ORR in AFCs. A detailed study comprising synthesis, structural analysis and its electro catalytic activity is discussed as a part of this thesis. The effect of nanostructure spinel oxides and its coupling effect with graphene on the catalytic performance are explained in detail.
1.7.4 **Iron Manganese Oxide and Graphene (FeMn$_2$O$_4$/G)**

Iron (Fe) based compounds are attracted wide attention as electro catalysts in both acidic as well as alkaline medium. As in case of Co and Mn, Fe based spinel compounds also found interest in lithium ion batteries, AFCs etc, but not many studies have been conducted on the Fe substituted manganese spinel compounds unlike Co-Mn-O based spinel oxides. One of these kinds was reported by Patrice et al (2004), studied the electrochemical properties of Fe substituted MnO$_2$. Fe substitution on $\gamma$-MnO$_2$ found to affect the electrochemical behavior. Most of the reports were on Fe based oxides as electro catalysts in alkaline electrolyte. A study on Pt-Fe$_3$O$_4$ NPs with Pt tunable from 2 to 8 nm and Fe$_3$O$_4$ from 6 to 20 nm was synthesized and its electro catalytic activity has been studied. The epitaxially grown Fe on Pt nanoparticles offers much enhanced ORR activity in both alkaline and acidic medium due to the electron rich nature of Pt due to the conjunction between Pt and Fe$_3$O$_4$ (Wang et al 2009).

To study the effect of carbon supported Fe$_3$O$_4$, Wu et al (2012) demonstrated 3D N-doped graphene aerogels (N-GAs) supported Fe$_3$O$_4$ via a combined hydrothermal self assembly, freeze-drying, and thermal treatment process. Because of the 3D macroporous structure and high specific surface area, the Fe$_3$O$_4$/N-GAs show excellent electrocatalytic activity for the ORR in alkaline electrolytes, including a higher current density, lower H$_2$O$_2$ yield, higher electron transfer number 4, and better durability.

Xiao et al (2013) reported lithium storage capacity on MnFe$_2$O$_4$-Graphene nanocomposites (MnFe$_2$O$_4$/GNS) which exhibited a remarkably high storage capacity. They also observed that MnFe$_2$O$_4$ could transform into a nanosized hybrid of Fe$_3$O$_4$–MnO with a size of about 20 nm after the discharge–charge process. The in-situ formed hybrid of Fe$_3$O$_4$–MnO with GNS could further improve the electro chemical performances. Another
literature on the hydrothermal synthesis of composites of reduced graphene oxide/Iron oxide (RGO/Fe₃O₄), RGO/Fe₅O₄/Fe₂O₃, and RGO/Fe₂O₃ was used as anode material for Li-ion batteries. RGO/Fe₅O₄/Fe₂O₃ showed higher specific capacity than those of the single-material counterparts due to the advantage of bi-component metal oxides (Dong et al 2014).

Recent studies on various hybrid materials such as Fe encapsulated CNT (Deng et al 2013), Iron nitride and nitrogen doped graphene (Yin et al 2014), Fe₃C on functionalized graphene (Hu et al 2014) and nitrogen-doped core-shell-structured porous Fe/Fe₃C@C nanoboxes supported on reduced graphene (Hou et al 2014) oxide gave an insight into the enhanced activity and stability of Fe based materials for the ORR in AFCs. However FeMn₂O₄ nanomaterial has not been reported previously as a novel electrocatalyst for ORR. Therefore FeMn₂O₄ coupled with graphene (FeMn₂O₄/G) is used as a candidate material for ORR in alkaline medium. A detailed study on the structure FeMn₂O₄/G hybrid nanostructure and its electrocatalytic activity is discussed as a part of this work.

1.8 ORGANIZATION OF THESIS

Chapter 2 of this thesis describes some of the characterization techniques used in this work, including pXRD, different spectroscopy analysis, microscopy analysis, surface area measurements and electrochemical measurements. Chapter 3 reports the synthesis, characterization and electrocatalytic activities of Pt deposited titanium dioxide nanotubes (Pt/TiO₂-NTs). Chapter 4 explains the role of surface oxygen defects on the metal oxide surface. Tin dioxide nanofacets (SnO₂ NFs) was used as the model support. Electrocatalytic activity for EOR has been evaluated on this Pt deposited SnO₂ NFs (Pt/SnO₂ NFs). Chapter 5 describes the oxygen reduction (ORR) activity of Pt/SnO₂ NFs. Chapter 6 discusses the ORR activity of cobalt manganese oxide and graphene hybrid nanostructure
(CoMn$_2$O$_4$/G) as non-noble electrocatalyst in AFCs. Chapter 7 investigates a new material, iron manganese oxide and graphene hybrid nanostructure (FeMn$_2$O$_4$/G) as non-noble electrocatalyst for ORR in AFCs. A depth analysis of the synthesis, characterization and electrocatalytic activity of FeMn$_2$O$_4$/G is explained. Chapter 8 concludes with a summary and suggestions for future work.