CHAPTER 1

INTRODUCTION

1.1 FUEL CELLS: AN OVERVIEW

The setback of global climate change caused by greenhouse gases and environmental pollution has enforced manufacturers and researchers to find an alternative source of energy. During the last two decades continuous efforts in research and development were made to find a clean energy source. The new energy source must be efficient and almost zero emission of hazardous produces. Among the existing options viz., solar power, wind power, tidal power and geothermal power, fuel cells are the most promising source of clean energy.

The development of fuel cell is an emerging technology for the production of energy and that can meet the demand in the energy sector. A fuel cell is an electrochemical system, which continuously as well as directly converts chemical energy into electrical energy (Viswanathan and Scibioh 2009). Fuel cells are flow battery, which does not store energy and produce current continuously (Van et al 2006). However, the continuous supply of the fuels and the removal of by-products are an important issue in the fuel cell technology.

In fuel cell, hydrogen and oxygen gases are used as fuel in the presence of acidic/alkaline electrolytic medium. The cell reaction is as follows:
Anode: \( \text{H}_2 \rightarrow 2 \text{H}^+ + 2 \text{e}^- \)  \hspace{1cm} (1.1)

Cathode: \( \text{O}_2 + 4 \text{H}^+ + 4 \text{e}^- \rightarrow 2 \text{H}_2\text{O} \)  \hspace{1cm} (1.2)

Here hydrogen gas is consumed at anode and oxygen gas is consumed at cathode.

Some salient features of Fuel cells are,

- Simple direct conversion of chemical energy into electrical energy
- Exhibits higher efficiencies than the existing fuel burning engines
- Works silently without any rotating or moving components
- They do not generate toxic gases like SOx or NOx

Figure 1.1 Schematic diagram of fuel cell
Because of these advantages, fuel cells are being developed for automobiles, portable electronic devices and military applications (Viswanathan and Scibioh 2009).

Sir William Grove invented first fuel cell as Gas batteries around 1839. Continued efforts were made by the number of researchers to improve their efficacy and working conditions. Nowadays the fuel cells are being developed for the commercial applications such as automobiles and space applications. Their design and properties made the system suitable for the specific applications (Viswanathan and Scibioh 2009).

Since, the efficiency of electrochemical energy conversion by fuel cells are high, the interest has gone in front of an intensive development of components and of better cell designs. Therefore, it is expected that the performance would be improved significantly in the near future (Appleby 1992).

However, to commercialize these fuel cell numbers of hurdles must be overcome. Among the hurdles, cost is the main factor. The fuel cell membrane and anode/cathode catalyst used in the fuel cells are costlier. Thus alternative materials with same efficiency are required in the present scenario.

### 1.2 FUEL CELL: A PROMISING SOURCE OF ENERGY

Fuel cells are promising energy source that generates current instantaneously and will be used for the specific applications. Compared to conventional internal combustion engine, fuel cell has an efficient energy conversion process. Internal combustion engine converts chemical energy into thermal energy and subsequently into mechanical energy. Whereas fuel cell
operated engines starts instantaneously and there would be no combustion involved in it. In fuel cells, choice of fuel is an important parameter for the specific applications.

1.3 CHOICE OF FUELS

The technical characteristics and economic feasibility of the fuel is an important for the application. For transportation application hydrogen, methanol, and gasoline or related products were tried.

Table 1.1 Chemical and Electrochemical energy conversion data of the different fuels

<table>
<thead>
<tr>
<th>Fuel</th>
<th>ΔG°/ kcal/mol</th>
<th>E° (V)</th>
<th>Energy density (kWh/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>-56</td>
<td>1.15</td>
<td>32.67</td>
</tr>
<tr>
<td>Methanol</td>
<td>-166</td>
<td>0.98</td>
<td>6.13</td>
</tr>
<tr>
<td>Ammonia</td>
<td>-80</td>
<td>0.62</td>
<td>5.52</td>
</tr>
<tr>
<td>Hydrazine</td>
<td>-143</td>
<td>1.28</td>
<td>5.22</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>-124</td>
<td>1.15</td>
<td>4.82</td>
</tr>
<tr>
<td>Formic acid</td>
<td>-68</td>
<td>1.14</td>
<td>1.72</td>
</tr>
</tbody>
</table>

Recently, motor manufacturing companies like Honda, Toyota, Tata and Ford have introduced the electric vehicles in the market operated in the hydrogen as fuel. The Table 1.1 briefly explains the type of fuel and their energy conversion efficiencies.

Among different fuels, hydrogen stand up first in its category, because the theoretical current density of 32.67 kWh/kg. But lack of fuel infrastructure, bulk storage system and safety concerns have prompted fuel
cell developers to search for an alternative fuel. Indeed, various car manufacturers tried to introduce the fuel cell based electric vehicles in urban areas. Thus the developers have shifted from hydrogen gas to methanol for the commercial applications.

The manufacturers believe that the direct alcohol fuel cell (DAFC) is one of the most suitable and promising options. In DAFC, the alcohol used directly in the fuel cell anode without any reforming process. It can be operated at low temperature and has high energy conversion efficiencies, above all it emits only a low amount of by-products. The liquid fuels used in DAFC are an important source of energy (Lamy et al 2009, Zainoodin et al 2010).

Oorja Protonics a California based company has received CE safety certification for its primary OorjaPac product, a portable direct methanol fuel cell (DMFC) for commercial usage. The company’s first product, OorjaPac, is designed for forklifts, using a 13 L (3.4 gallon) storage tank of methanol to provide power to the vehicle for 10 h. The company has got an initial market by producing forklifts and pallet trucks using DMFC (CE report, Zainoodin et al 2010).

1.4 CLASSIFICATION OF FUEL CELLS

Fuel cells are generally classified on the basis of three various parameters which includes the type of fuel used for energy conversion, the process i.e., either inside or outside reforming and the operating temperature.
1.5 DIRECT ALCOHOL FUEL CELLS (DAFC)

DAFCs are attracting and increasing interest as power sources for portable applications due to certain advantages over analogous devices fed with hydrogen. Alcohols, such as methanol, ethanol, ethylene glycol, and glycerol, exhibit high energy density, and their storage and transport are much easier as compared to hydrogen.

Table 1.2 Typical classifications of various fuel cells and their operating temperature

<table>
<thead>
<tr>
<th>Type of Fuel cell</th>
<th>Fuel used</th>
<th>Operating temp (K)</th>
<th>Current Efficacy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkaline Fuel Cell [AFC]</td>
<td>Hydrogen, methanol etc.,</td>
<td>53 – 573</td>
<td>High</td>
</tr>
<tr>
<td>Phosphoric acid Fuel Cell [PAFC]</td>
<td>Phosphoric acid</td>
<td>373 – 493</td>
<td>Moderate</td>
</tr>
<tr>
<td>Molten Carbonate Fuel Cell [MCFC]</td>
<td>Molten Carbonates</td>
<td>923 – 1123</td>
<td>Moderate</td>
</tr>
<tr>
<td>Solid Acid Fuel Cell [SOFC]</td>
<td>Air / Oxygen</td>
<td>973 – 1273</td>
<td>High</td>
</tr>
</tbody>
</table>

1.5.1 Direct Methanol Fuel Cell (DMFC)

In DAFC, Methanol fed fuel cells have the many attentions in the recent years in the low temperature operated PEMFCs. Because the fuel i.e., methanol is relatively cost effective, abundant, can be stored and transported very easily. Methanol can be derived from the agricultural products. Due to its
simple structure, low molecular weight and very high energy density (6.1 kWh/kg), the research on the DMFC has been widened. Since DMFC can operate with the feeding of methanol directly i.e., reforming is not required and since the system is compact and it is suitable for portable power sources. To be competitive in the market, the DMFCs have to be able to operate in conditions close to ambient conditions and to deliver a high power density at low costs (Lamy et al 2001).

A scheme of the overall reaction process occurred in protonic electrolyte based DMFC is outlined below.

\[
\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ 6\text{e}^- \quad \text{(anode)}  \quad (1.3)
\]

\[
3/2 \text{O}_2 + 6 \text{H}^+ + 6 \text{e}^- \rightarrow 3\text{H}_2\text{O} \quad \text{(cathode)}  \quad (1.4)
\]

\[
\text{CH}_3\text{OH} + 3/2 \text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad \text{(overall)}  \quad (1.5)
\]

In the alkaline electrolyte medium the reaction will be

\[
\text{CH}_3\text{OH} + 6\text{OH}^- \rightarrow \text{CO}_2 + 5\text{H}_2\text{O} + 6\text{e}^- \quad \text{(anode)}  \quad (1.6)
\]

\[
3/2 \text{O}_2 + 3\text{H}_2\text{O} + 6 \text{e}^- \rightarrow 6\text{OH}^- \quad \text{(cathode)}  \quad (1.7)
\]

\[
\text{CH}_3\text{OH} + 3/2 \text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad \text{(overall)}  \quad (1.8)
\]

In both the electrolytic medium the overall reaction will be the same one but the reaction pathways were different.

1.5.2 Direct Ethylene Glycol Fuel Cell (DEGFC)

Analysis of the current status of research in this field reveals that DMFCs are ready to reach the market. Even though DMFC are well developed with direct liquid fuel fed power source, DMFCs have a number of
disadvantages. One among is the cost which is very high due to the usage of platinum based compounds as catalysts and second one is the toxicity of methanol.

During the last few years, researchers are working to find an alternative liquid fuel to replace methanol, which is to be non toxic with equal current efficiency. Several research groups have published their achievements in developing a new type of liquid fuel cell that uses ethylene glycol i.e., Direct ethylene glycol fuel cells (DEGFCs). EG have a number of advantages that makes it superior to methanol for fuel cell applications viz.,

- EG has a theoretical capacity of 17% higher than that of methanol in terms of Ah m\textsuperscript{-1}.
- The boiling point of ethylene glycol (198°C) is higher than that of methanol (64.7°C), which makes EG safer to work with wide applications.
- It is widely used in the automobile industry, the supply chain is already established, which is not applicable for methanol.

All these benefits make EG based fuel cells a promising source of alternative energy (Serov and Kwak 2010, Yu et al 2010).

Apart from these fuels, small organic molecules such as ethanol, n-butanol and some poly hydric alcohols etc., were also used as direct alcohol fuels.

In the direct liquid fed fuel cells, however, it is worth to be mentioned, the fuel should be oxidized completely (or close to 100%), which is still challenging task for DMFC and DEGFCs. On the other hand the catalytic poisoning by the by products formed during the electrooxidation
reaction could be removed by the suitable method. Hence, a suitable catalyst is required for the complete oxidation of the fuel extremely important. This makes the fuel cell activity in the long term usage.

The electrooxidation of alcohols follows different reaction pathways. In this section the mechanism of electrooxidation of alcohols such as methanol, ethylene glycol and glycerol were discussed.

1.5.3 Electrooxidation of Methanol

The electro-oxidation of methanol is a subject of intensive research in the context of FC research for the development of the direct methanol fuel cell. Electrocatalyst such as Pd, that is inactive in the acidic medium and highly active in alkaline medium. Pd electrocatalyst are highly active for the alcohol and hydrogen electrooxidation exclusively studied in the alkaline medium (Bianchini and Shen 2009). Furthermore, the corrosion constraints are less significant in alkaline media and the reaction rate is faster in alkaline electrolytic medium compared to acidic medium (Arico et al 2009).

In a typical design of a DMFC, at anode methanol was fed which gets oxidized to CO$_2$ as given below.

$$\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \quad E^\circ = 0.016 \text{ V/SHE} \quad (1.3)$$

At the cathode the oxygen (air) gets reduced into water and the reaction is as follows

$$3/2 \text{O}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow 3\text{H}_2\text{O} \quad E^\circ = 1.229 \text{ V/SHE} \quad (1.4)$$

The overall reaction yields about 1.18 V to 1.23 V, depends on their catalyst and the stack design. The DMFC operation at slightly higher temperature 100 – 120°C can be realized due to the high water content at the
anode, which keeps the membrane in well-humidified state. Hence, liquid water/methanol mixture will be the better feed to cool stack.

The general reaction mechanism of methanol electrooxidation at the Pd catalyst in alkaline medium as follows

\[
Pd + \text{H}_2\text{O} \rightarrow Pd(\text{OH})_{\text{ads}} + \text{H}^+ + e^- \quad (1.9)
\]

\[
Pd + \text{CH}_3\text{OH} \rightarrow Pd(\text{CH}_3\text{OH})_{\text{ads}} \quad (1.10)
\]

\[
Pd(\text{CH}_3\text{OH})_{\text{ads}} \rightarrow Pd(:\text{COH}) \quad (1.11)
\]

\[
Pd(:\text{COH}) + \text{H}_2\text{O} \rightarrow Pd(\text{HCOOH})_{\text{ads}} + \text{H}^+ + e^- \quad (1.12)
\]

\[
Pd(\text{HCOOH})_{\text{ads}} \rightarrow Pd(\text{CO})_{\text{ads}} + \text{H}_2\text{O} \quad (1.13)
\]

\[
Pd(\text{CO})_{\text{ads}} + Pd(\text{OH})_{\text{ads}} \rightarrow 2Pd + \text{CO}_2 + \text{H}_2\text{O} \quad (1.14)
\]

The formation of Pd-CO$_{\text{ads}}$ would be the strongest bond the proper catalyst design is needed in the recent scenario to remove the CO as CO$_2$.

1.5.4 Electrooxidation of Ethylene glycol and Glycerol

The electrooxidation of EG on Pt surface in the acidic medium and the complete oxidation of EG to CO$_2$ produce 10 electrons per glycol molecule and can be written as follows

\[
(\text{CH}_2\text{OH})_2 + 2\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 10 \text{H}^+ + 10 e^- \quad (1.15)
\]

The EG oxidation in acidic medium is complicated, the kinetics of oxidation is slow and performance of the catalysts is not still optimized. These issues can be overcome by carrying out the reaction in the alkaline medium. Pt based catalyst shows an improved catalytic activity for EG in
alkaline medium. Pd also exhibits improved catalytic activity in the EG electrooxidation in alkaline medium. The electrooxidation yields numbers of intermediate products and these intermediates have to be oxidized completely by an active catalyst.

The general reaction mechanisms for the electrooxidation of EG/glycerol in acidic or alkaline medium is as follows (Lamy et al 2001).

\[(\text{CH}_2\text{-OH})_2 \rightarrow \text{OH-C-CH}_2\text{-OH} \quad (1.16)\]

\[\text{OH-C-CH}_2\text{-OH} \rightarrow \text{OH-C-C-OH} \quad (1.17)\]

\[\text{OH-C-CH}_2\text{-OH} \rightarrow \text{HOO-C-CH}_2\text{-OH} \quad (1.18)\]

\[\text{OH-C-C-OH} \rightarrow \text{OH-C-C-OOH} \quad (1.19)\]

\[\text{HOO-C-CH}_2\text{-OH} \rightarrow \text{HO-C-C-OOH} \quad (1.20)\]

\[\text{HO-C-C-OOH} \rightarrow \text{HOO-C-C-OOH} \quad (1.21)\]

Complete oxidation of EG/Glycerol into CO\(_2\) is not possible. Hence the proper design of catalyst is required for complete oxidation.

1.6 ELECTROCATALYST FOR DAFCs

1.6.1 Issues in DAFCs

In the last decade researchers and fuel cell developers have concentrated to develop a non-platinum catalyst for fuel cells. The high cost of the Pt catalyst makes the researchers to find an alternative non-platinum based catalyst for fuel cells. Before developing a catalyst for the DAFCs, it has to fulfill the following properties:
The catalytic activity of the anode must be improved by identifying the suitable catalyst.

The catalyst must show improved activity at ambient conditions i.e., corrosive nature in acidic and basic medium at operating temperature.

The amount of precious noble metal content has to be reduced by adopting a suitable method.

1.6.2 Slow kinetics of electrooxidation reaction

Up to date, Platinum (Pt) and platinum group metals is the best candidate for the anode catalyst for the DAFCs. DAFCs are working in lower operating temperatures in an acidic environment. During the oxidation of alcohols number of byproducts were formed. For an example in methanol electrooxidation the byproducts are $\text{HCOOH}_{\text{ads}}$, $\text{CHO}_{\text{ads}}$, $\text{CO}_{\text{ads}}$ etc., which could adsorbed on the active sites of the catalyst and led to reduce the catalytic activity. The carbon monoxide (CO), a poisonous intermediate formed during the methanol electrooxidation reaction, which forms a strong bond with catalyst (Pt/Pd-CO$_{\text{ads}}$) block the fuel to reach the catalytic site results the reduced catalytic activity. Hence, a suitable method has to be identified to overcome this problem.

In order to overcome these issues, several methods were adopted. Some of the known methods are as follows:

- Designing the catalyst in the nano scale.
- Using bimetallic or alloy catalyst.
- Placing the noble metal catalyst on a suitable support.
- Using an alkaline medium in which the kinetics of the electrochemical reactions is faster than in an acidic medium.
1.6.3 Palladium as an electrocatalyst for DMFCs

Palladium is a chemical element with the chemical symbol Pd and an atomic number of 46. It is a rare and slustrous silvery-white metal. Palladium, platinum, rhodium, ruthenium, iridium and osmium form a group of elements referred to as the platinum group metals. These have similar chemical properties, but palladium has the lowest melting point and is the least dense of them. Palladium is a soft silver-white metal that resembles platinum. It is the least dense and has the lowest melting point of the platinum group metals. Common oxidation states of palladium are 0, +1, +2 and +4. Although originally +3 was thought of as one of the fundamental oxidation states of palladium. Melting point of 1554°C, Boiling Point of 2963°C. Pt and Pd have very similar properties (same group in the periodic table, similar FCC crystal structure, similar atomic size). The cost of Pd, however, is comparably lower than that of Pt, so Pd could be a good substitute for Pt as the catalyst in fuel cells. Pd is interesting as it is at least fifty times more abundant on the earth than Pt. For these reasons, Pd has been tested in fuel cells as a Pt-free catalyst (as anode material in alkaline media and in direct formic acid fuel cells, and as cathode material) and Pt cocatalyst (as anode and cathode material in acid media) (Antolini 2010)

Currently various methods were used for the preparation of Pd based electrodes which include chemical reduction, microemulsions, or reversed micelles. Depending on the type and number of the metal precursors or on the specific synthetic protocol, alloys or composite materials can also be obtained. In general, the catalysts are used as metal support in the form of metal particles or thin films, to provide the best performance for alcohol oxidation. Because nano particles provide more active centers through the improved surface area. Hence, the more particles participated in the reaction, results enhanced the activity many fold.
Due to the surface forces the nano/micro particles are getting agglomerated, resulting in the loss of catalytic activity. To overcome this problem, a number of methods were adopted, one among is the placing of catalyst on the suitable support.

1.7 SUPPORTED Pd AS ELECTROCATALYST FOR DAFCs

Isolated micro/nano particles of noble metals supported on high surface area materials are of considerable interest in catalysis. This is in part due to their unique physical and chemical properties (Shukla et al 1999, Watanabe and Motto 1975).

Compared to pure metal, supported noble metal catalyst shows distantly superior activity. This is due to the maximum utilization of catalyst. Compared to pure metal catalyst the support provides high surface area, which can act as a platform for the metal catalyst, hence the maximum portion of the catalyst would take part in the electrocatalytic reaction.

There are many other factors to be taken into account for the design of an effective and stable Pd electrocatalyst for alcohol oxidation in fuel cells. In particular the morphology, shape, dispersion of the metal particles and the nature of the support material are to be considered. This is generally comprised of a carbon black (CB), which plays a vital role by different nano structured carbon materials (tubes, wires, fibers, etc.,). Not only pure CB, this can be a composite with other materials such as metal and metal oxides, which may also promote the alcohol oxidation on Pd.

In terms of low durability of PEM fuel cell catalysts, the corrosion of carbon in the catalyst (Pd/C) has been identified to be the major reason for the failure of catalyst particularly in Pd based catalysts. Although other failure
modes such as Pt dissolution, sintering, as well as agglomeration. Oxidation of the carbon support to produce CO$_2$ can occur, resulting in the separation of Pd particles from the carbon support and loss of performance. This results a low Pd utilization as well as less performance in the fuel cell operations. For the anode catalyst, the carbon support can also be oxidized in the situation of fuel (hydrogen) starvation. With respect to the instability of carbon materials in fuel cell environments, the carbon materials (Vulcan XC-72R) currently used with fuel cell catalysts do not meet the durability requirements for automotive applications. Therefore, it is necessary to explore the stable alternatives to replace carbon materials for the catalyst support to improve the catalytic activity (Wang et al. 2011).

To redress these issues, some alternative support materials rather than the carbon based supporting materials in PEMFCs have been explored. In addition, the noncarbon supporting materials should have a strong physicochemical and electronic interaction with catalytic metals to improve their catalytic activity and durability. With respect to the examination of noncarbon support materials for fuel cell catalysts, considerable work has been done in the past decades. The materials developed include metal oxides, (Su et al. 2009, Xu et al. 2008ab.), carbides (Hu et al. 2006), conducting polymers (Pandey and Lakshminarayanan 2009, 2010, Selvaraj and Alagar 2007) were studied.

The detailed study and their advantages as supports were discussed in the forthcoming section.

The carbon catalyst support is converted to CO$_2$, and Pt and/or Ru particles may be lost from the electrode, resulting in loss of performance. Besides carbon oxidation, catalyst agglomeration is another problem for the reduction of a PEM fuel cell’s durability (Garland 2008). When operated at
higher temperatures. The catalyst sintering could reduce the electro-active surface area of the Pt catalyst, lower the Pt utilization, and degrade its catalytic activity. In particular, carbon supports oxidation lead to catalyst agglomeration.

To avoid this problem, the usage of a non-carbon support such as metal oxides or other materials has proved to be very important and significant to obtain good PEM fuel cell performance (Chen et al 2005, Garland et al 2008, Shim et al 2001, Wang et al 2011, Xiong and Manthiram 2004). The use of noncarbon supports can not only reduce the amount of noble metal like Pt but also enhance catalytic activity and stability. To further improve catalytic activity, developing promising noncarbon catalyst supports is necessary in the design and synthesis of new electrocatalyst.

To reduce the usage of expensive catalyst (Pd/Pt) and at the same time to improve the catalyst activity toward fuel cell reactions, one of the approaches is to develop some cost-effective metal oxide supported catalysts. A typical metal oxide supported catalyst contains metal oxide support particles and the metal catalyst particles. In the ability, the metal support particles offer a high physical surface area for dispersion of smaller catalyst particles to achieve a high surface area. In some synthesis cases, the formed catalysts might be sintered at high temperatures to increase the attachment between the support and the catalyst particles. The strong physicochemical and electronic interaction between the metal support and the catalyst particles can generate a bifunctional mechanism for catalytic reaction, benefiting the reaction kinetics (Wang et al 2011).

Conducting metal oxides are considered to be emerging candidates for catalyst support in fuel cell applications. With high surface area, mechanical, thermal, and hydrothermal stabilities, some conducting metal oxides have been demonstrated as catalyst supports (Hu et al 2006, Wang
et al 2011, Xu et al 2008). They have resulted in uniform dispersion of catalyst particles, effective metal support interactions, as well as reasonable catalytic activities for fuel cell performance.

![Figure 1.2](image)

**Figure 1.2  Schematic representation of (a) pure and (b) supported metal catalyst (Pt/Pd)**

It is well-known that inorganic metal oxide materials with a one-dimensional structure (i.e., nanowire, nanorod, nanotube, and nanofibers) have unique physicochemical properties structural stability, crystallinity, unique optical, quantum size effects, hollow core structures, very large specific surface areas, narrow inner pores, and active catalytic surfaces (Adachi and Lockwood 2006, Bae et al 2008, Liang et al 2010).

Other materials with nanostructured morphology have been successfully employed to prepare Pd-based electrocatalyst for DAFCs. Li et al (2000) have described the synthesis of Pd particles supported on a large variety of nanotubes, including MWCNTs, (Sun et al 2008). TiO$_2$ nanotubes, (Hu et al 2006) vanadium oxide nanotubes (Maiyalagan et al 2008) and MnO$_2$ nanotubes (Xu et al 2008) and used them as electrocatalyst for alcohol oxidation.
Various alcohols, including methanol, ethanol, glycerol, and ethylene glycol, are effectively oxidized on Pd-oxide/C electrodes. Out of all the electrocatalyst investigated, Pd-Co$_3$O$_4$ (2:1, w:w)/C shows the highest activity for the electrooxidation of methanol, ethylene glycol, and glycerol. Pd-NiO (6:1, w:w)/C shows improved electrocatalytic activity towards ethanol electrooxidation reactions. On the other hand, Pd-Mn$_3$O$_4$/C shows considerably better performance and high stability than any other oxide-promoted Pd/C for the alcohol electrooxidation. It has been observed that the amount of metal oxide affects the catalytic activity as well as the electrode stability. In general, high contents of metal oxides reduce the electronic conductivity due to their semiconductor behavior, while, in some cases, the solubility of the metal oxides in alkaline solution can decrease the electrode stability, as is the case of the Pd-Co$_3$O$_4$/C electrocatalyst (Xu et al 2008).

Shen and co-workers have observed that the onset potential for ethanol oxidation on a Pd-NiO/C electrode is more negative and also provides a higher peak current density as compared to the case for a similar Pt-NiO/C electrode. Also, it was found that the oxidation of CO on Pd-NiO/C exhibits a higher overpotential than that on Pt-NiO/C, whereas the peak area of CO oxidation on Pd-NiO/C is much smaller. Extensive potential oscillation occurs on Pt-NiO/C already at relatively low current densities and increases with the current density, which is a typical phenomenon of catalyst poisoning. Consistently, this electrode exhibits a much larger potential polarization as compared to the Pd-NiO/C electrode, which is stable even at relatively high current densities. Apparently, no strongly adsorbed species is formed on the Pd-NiO/C surface to block the active sites for ethanol oxidation. The drastic potential increase, up to the oxygen discharge, exhibited by the Pd-NiO/C electrode at 12 mA/cm$^2$ has been credited to a concentration polarization effect (Hu et al 2006).
Similar results, in terms of both electrochemical activity and stability, have been reported for the ethanol oxidation on Pd/TiO$_2$C. This electrocatalyst shows a higher surface area as well as higher electrochemical activity and stability as compared to Pd/C with the same metal loading. The best performance is provided by the Pd/TiO$_2$C catalyst with a Pd to TiO$_2$C ratio of 1:1. The onset potential of the ethanol oxidation on the Pd/TiO$_2$C electrocatalyst shows a negative shift of about 150 mV and a 3-fold peak current density as compared to Pd/C (Hu et al 2006).

Tungsten oxide was also used as a catalyst support in DMFCs, (Cuoi et al 2008), the formed Pt/WOx catalyst showed much higher catalytic activity toward methanol oxidation. This activity enhancement was believed to be due to the formation of tungsten bronzes, which favor the dehydrogenation of methanol. In addition, the oxophilic nature of the oxide support may also help in removing the adsorbed intermediates during the methanol oxidation (Tseung et al 1997).

The enhancement effect in methanol electrooxidation was believed to be due to the synergistic interaction between Pt and WOx because this interaction can lead to the best CO$_{ads}$ tolerance. To evaluate CO tolerance of the Pt/WOx catalyst, Micoud et al (2009) prepared a well-defined WO$_3$ supported platinum catalyst (Pt/WOx) using the impregnation followed reduction method in which a Pt salt was reduced to Pt nanoparticles and then dispersed onto commercially available monoclinic WO$_3$ support.

By monitoring CO$_{ads}$ electrooxidation currents at potentials as low as 0.1 V vs. RHE, they demonstrated that Pt/WOx catalyst had a higher CO tolerance than that of carbon supported Pt or PtRu catalysts. In addition, it has also been found that tungsten oxides can help the proton transfer process during methanol electrooxidation due to the formation of tungsten trioxide
hydrates. Park et al (2004) observed these effects for methanol electrooxidation catalyzed by a PtRu/WO$_3$ catalyst.

Other metal oxides such as VO$_x$, ZrO$_2$, RuO$_x$, SiO$_2$, In$_2$O$_3$ have been used as support for noble metal catalyst (Nakajima and Honma 2002, Park et al 2004, Yu et al 2001, Chhina et al 2009, Maiyalagan 2009, Ishikawa et al 1994, Bang et al 2007).

Electronically conducting polymers are best known as conducting polymers are important materials because of their unique optical, electronic, chemical, and mechanical properties, easy preparation, and feasible application in electrochemical energy conversion. Some polymers such as polyaniline, polypyrrole, and polythiophene have been extensively studied as supports to disperse metallic particles. The physical and chemical properties of these polymers are well-known and allow the preparation of electronic conductive polymer-supported electrocatalyst. These polymer supports provide the possibility of higher surface areas and higher conductivity in the potential range where the organic polymer molecule can be oxidized. Pt/Pd dispersion onto and inside such a polymer support to form supported catalysts can reduce the amount of noble metals used and improve the catalytic activity for the oxidation of hydrogen, small organic molecules such as methanol, ethanol, formic acid etc. (Selvaraj and Alagar 2007, Wang et al 2011).

The use of conducting polymers as catalyst supports for metal nanoparticles was first attempted by Pickup and group using electronically and ionically conducting polypyrrole/polystyrenesulfonate particles as support for Pt and Pt oxide nanoparticles (Qi 1998). Later, other conducting polymers and their composites such as poly(3,4-ethylenedioxythiophene)--poly(styrene sulfonic acid) or PEDOT-PSS (Kuo et al 2006, Lefebvre et al 1999, Tintula et al 2010), PEDOT (Choi et al 2005, 2003, Drillet et al 2006, 2007, Kuo et al 2006), poly(N-vinyl carbazole), poly(9-(4-vinylphenyl) carbazole) (Choi
et al 2005), polyaniline (PANI), Nafion® (Choi et al 2005), Polymer with metal composites were also studied (Lofrano et al 2000, 2004), such as poly(diallyldimethylammonium chloride) (Jiang 2007), and poly(N-acetylaniline) (Jiang 2007). PPy/MWCNT/Pt nanocomposite exhibits enhanced catalytic activity (Selvaraj and Alagar 2007). Pt dispersed PEDOT-V$_2$O$_5$ as novel catalyst exhibits superior catalytic activity (Maiyalagan and Viswanathan 2010).

1.8 REVIEW OF LITERATURE

In this section the recent studies on the supported Pd nanocatalyst for the electrocatalysis of methanol, ethylene glycol, glycerol in the alkaline medium were reviewed.

The main requirement of the suitable support for fuel cells electrocatalyst are high surface area, good electrical, thermal stability, suitable porosity to allow good flow, and high stability in the fuel cell environment. Conductive carbon black (CB) meets most of these characteristics, yet they exhibit low stability to corrosion, especially in acidic media at high potential and high temperature (>90°C). Vulcan – type carbon material, are the suitable material for the low temperature fuel cell applications.

The large variety of carbon supported Pd metal nanoparticles are prepared by reduction of physical or chemical adsorbed modified precursors including acetate, nitrate and chloride salts of palladium with a chemical reducing agents such as NaBH$_4$, hydrazine, formaldehyde, hydrogen gas etc. That may also act as template to stabilize the nanoparticles and these reagents yield the nanoparticles in the range of 3 to 25 nm.
Pattabiraman (1997) has investigated the electrooxidation of hydrogen, methanol, formaldehyde and ethylene glycol at carbon supported palladium. The Pd dispersed catalyst on carbon supports exhibit high activity for the oxidation of hydrogen and ethylene glycol in alkaline medium.

Xu et al (2007) have studied the electrooxidation of methanol on Pt and Pd supported carbon microspheres. The current density at - 0.3 V (Hg/HgO) was 11.4 and 2.5 mA cm², respectively, while the current density for EG oxidation was 22.8 and 3.6 mA cm², respectively. The catalytic activity order of alcohol oxidation on Pd/C and Pd/Carbon microspheres was methanol > EG > ethanol.

Liu et al (2008) have compared the electrocatalytic activity of Pd for methanol and propanol oxidation in alkaline media. They found that the current densities of 1-propanol and 2-propanol oxidation on Pd electrode are much higher at corresponding potentials than that of methanol oxidation, and the onset potentials of 1-propanol and 2-propanol oxidation on Pd electrode are more negative compared to that of methanol oxidation. The activity of Pd for propanol oxidation was higher than that of Pt.

Xu et al (2008) observed that addition of Au can significantly increase the electrocatalytic activity and stability of palladium for 2-propanol oxidation. PdAu/C in the Pd:Au atomic ratio of 4 : 1 has higher electrocatalytic activity and better stability for electrooxidation of 2-propanol than Pd/C. Pd possesses remarkably higher activity for ethanol oxidation in alkaline media than Pt, and is a promising material for the direct ethanol alkaline fuel cells.

Bianchini and Shen (2008) have evaluated the performance of Pd/MWCNT for the oxidation of methanol, ethanol, and glycerol in 2.0 mol/L
KOH solutions. Among the other alcohols, glycerol shows improved current density and ethanol shows lower onset potential.

Instead of pure Pd/C or Pt/C, the electrocatalytic activity was very minimum. In order to enhance the activity, metal oxides supported on the Pd/C or Pt/C was introduced and studied by a number of research groups.

The effect of the addition of various oxides CeO$_2$, NiO, Co$_3$O$_4$ and Mn$_3$O$_4$ to Pd/C and Pt/C catalysts for alcohol oxidation was investigated by Xu et al (2008). The addition of these metal oxides significantly promoted catalytic activity, and stability of the Pd/C electrocatalyst for alcohol electrooxidation. The results suggest that the addition of oxide to Pd/C significantly promotes the catalytic activity and stability for the electrooxidation reactions of methanol, ethanol, EG and glycerol. This is indicated by the negatively shifted onset potential and by the significantly higher current densities for the reaction on Pd-oxide/C than that on pure Pd/C or Pt/C. Co$_3$O$_4$ influence the electrocatalytic activity and it shows the highest electrooxidation activity of methanol, EG and glycerol. NiO exhibits improved catalytic activity towards ethanol and Pd-Mn$_3$O$_4$/C shows significantly better performance stability than any other oxide-promoted Pd/C for the alcohol electrooxidation.

Shen et al (2006) have studied the electrocatalytic influence of NiO on PdNiO/C electrode towards ethanol oxidation. They observed that the negative onset potential with higher peak current. And the electrode exhibits lower CO oxidation peak current density. The drastic potential increase, up to the oxygen discharge, exhibited by the Pd-NiO/C electrode at 12 mA cm$^{-2}$ has been attributed to a concentration polarization effect.
Indium oxide support has the greatest influence on the electrochemical activity of Pd nanoparticles mainly in conjunction with multi walled carbon nano tubes (MWCNTs) as conductive support material. In particular, it has been reported that a composite electrode with a mass ratio of Pd to In$_2$O$_3$ of 10:3 (Pd loading of 0.2 mg cm$^{-2}$) is twice as much more active than Pd/MWCNT (Chu et al 2008).

C/TiO$_2$ shows mass transfer is much faster than Pd/C, and the shows a negative onset potential of 150 mV and 3 fold peak current density compared to Pd/C (Hu et al 2006).

Su et al (2009) have reported the enhanced electrochemical performance of Pd coated on the TiO$_2$ nanofibers prepared by electro spinning method. The electrocatalytic activity for the electrooxidation of methanol, ethanol, EG and glycerol at Pd/TiO$_2$ in alkaline medium was studied. The electrode (Pd/TiO$_2$) exhibits an excellent electrocatalytic activity towards glycerol electrooxidation.

Wen et al (2010) have reported the enhanced electrooxidation of ethanol at Pd on graphene/Tin oxide support. The presence of tin oxide would absorb more OH ion, hence the intermediates were getting oxidized more easily and at the same time the intermediates do not block the Pd active sites.

Demarconny et al (2007) have investigated the EG oxidation on PtPd, PtPdBi, and PtBi catalysts in alkaline media. On these electrocatalyst, EG is converted into mixtures of glycolic acid, glyoxylic acid, oxalic acid, and formic acid, but the relative composition depends on the catalyst. It has been proposed that Bi favors the adsorption of OH species and also affects the product distribution by depressing C-C bond cleavage, like Pd.
Yan et al (2010) have studied the Pd on hollow carbon hemisphere supported catalyst for the electrooxidation of ethanol and isopropanol.

Becerik et al (1999) found that both Pt and Pd supported on PPY showed high catalytic activity for the electrooxidation of D-glucose in neutral media and could reduce the poisoning effect of CO as well.

Andreev et al (2006) have studied the electrocatalytic properties of Pd/Pani nanocomposite, followed by Liao et al (2009) have also studied the electrochemical behavior of formic acid electrooxidation and concluded that the composite material shows an improved stability and current response.

Pandey and Lakshminarayana (2009) have studied the electrooxidation of Pd nano particles dispersed in polyaniline matrix exhibits an excellent catalytic activity towards formic acid electrooxidation at acidic medium, methanol and ethanol at alkaline medium. The same group (Pandey and Lakshminarayanan 2010) studied the polyethylene dioxy thiophene [PEDOT] /Pd nanocomposite and reported an excellent electro catalytic activity towards ethanol electrooxidation in alkaline medium.

Selvaraj and Alagar (2007) have studied the electro oxidation of alcohol at PPy/MWCNT/Pt-Ru nanocomposite electrode and revealed that the electrocatalytic activity was enhanced by the PPy polymer.

Ding et al (2011) have demonstrated the Pd/PPy/Pd sandwich type complex have been successfully utilized for the electrocatalytic oxidation of formic acid.
Table 1.3: Various catalysts and supports towards alcohol electrooxidation

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Support</th>
<th>Fuel</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>Ni-Zn</td>
<td>Ethanol</td>
<td>Bambagioni et al 2009</td>
</tr>
<tr>
<td>Pd</td>
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<td>Methanol</td>
<td>Chen et al 2005</td>
</tr>
<tr>
<td>Pd</td>
<td>TiO$_2$</td>
<td>Ethanol</td>
<td>Hu et al 2006</td>
</tr>
<tr>
<td>Pd</td>
<td>TiO$_2$</td>
<td>Glycerol</td>
<td>Su 2009</td>
</tr>
<tr>
<td>Pd</td>
<td>In$_2$O$_3$/CNt</td>
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<td>Chu et al 2008</td>
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<tr>
<td>Pd</td>
<td>Poly(pyrrrole)</td>
<td>Formic acid</td>
<td>Ding et al 2011</td>
</tr>
<tr>
<td>Pd</td>
<td>NiO/C</td>
<td>Ethanol</td>
<td>Hu et al 2006</td>
</tr>
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<td>Ethanol</td>
<td>Liang et al 2009</td>
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<td>Poly(aniline)</td>
<td>Formic acid</td>
<td>Pandey et al 2009</td>
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<td>Poly(aniline)</td>
<td>Methanol</td>
<td>Pandey et al 2009</td>
</tr>
<tr>
<td>Pd</td>
<td>PEDOT</td>
<td>Ethanol</td>
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<tr>
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<td>PEDOT</td>
<td>Methanol</td>
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<td>Pd</td>
<td>Poly(pyrrrole)</td>
<td>Methanol</td>
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<td>Carbon</td>
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<td>Alcohol</td>
<td>Xu et al 2007</td>
</tr>
<tr>
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<td>C/Mn$_3$O$_4$, NiO$_2$, Co$_2$O$_2$CeO$_2$</td>
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<td>Xu et al 2008</td>
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</tr>
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<td>Zhao et al 2012</td>
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<td>Pd/Pt-Ru</td>
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<tr>
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<td>MWCNTt</td>
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<td>Support</td>
<td>Fuel</td>
<td>Reference</td>
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<tr>
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<tr>
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<tr>
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<td>Ethanol</td>
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<td>Pt</td>
<td>WO₃</td>
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<td>Cui et al 2008</td>
</tr>
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<td>EG</td>
<td>Drillet et al 2007</td>
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<td>Methanol</td>
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<td>TiO₂</td>
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</tr>
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<td>MnO₂</td>
<td>Formic acid</td>
<td>Mohammed et al 2011</td>
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<td>PPy</td>
<td>Glucose</td>
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<td>Carbon/CMK-5</td>
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<td>PtRu &amp; Pd</td>
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<td>Pt</td>
<td>PEDOT/PSS</td>
<td>Methanol</td>
<td>Kuo et al 2006</td>
</tr>
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</table>

Recently, Antolini et al (2010) has presented an overview of these hybrid materials as low-temperature fuel cell catalyst supports. In the hybrid ceramic–carbon materials, the ceramic material supplies co-catalytic properties and increases the corrosion resistance, and the carbon supplies a high electron conductivity to the mixed composite. Finally, in the hybrid polymer–ceramic materials, the polymer confers a high surface area and proton conductivity, and the inorganic high corrosion resistance and co-catalytic activity to the composite. The improved characteristics of the mixed supports with respect to the individual component and their effect on the electrochemical activity were reviewed.

Chun et al (2011) have studied the electrocatalytic activity of Pd-Ni/CMK-15 catalyst towards electrooxidation of methanol. The results revealed that the support (CMK-15) has more resistance to CO poisoning.
Zhao et al (2012) have fabricated a nano catalyst of Pd/Mn$_3$O$_4$/MWCNT for methanol electrooxidation reaction. The electrode exhibits higher catalytic activity as well as the higher stability compared to pure Pd/MWCNT.

1.9 OBJECTIVE OF THE PRESENT WORK

The objective of the present study is to synthesize the nano structured manganese oxide materials as a support for Palladium to study the electrochemical properties towards electrooxidation of alcohols.

The effect of support, supporting electrolyte for the electrooxidation of alcohols such as methanol, ethylene glycol, glycerol and Xylitol are reported.

The main objectives of the present study include:

i) Manganite nano rods supported Pd as an electrocatalyst for the electrooxidation of ethylene glycol.

ii) PdNi coated Manganite nano rods as catalyst for the electrooxidation of methanol, ethylene glycol and glycerol in strong alkaline medium.

iii) Electrooxidation of xylitol at Pd/C and Pd/CNT electrodes in neutral, acidic and alkaline medium.

iv) Synthesis of Poly ortho phenylene diamine (PPD)/MN nano composite as a novel support for Pd towards electrooxidation of methanol, ethylene glycol, glycerol, and xylitol.
v) Facile synthesis of Poly pyrrole (PPy)/MN – a novel nanocomposite supportive material for Pd towards the electrooxidation of methanol, ethylene glycol and xylitol.

vi) Development of Pd/γ–Mn₂O₃ nano catalyst for the electrooxidation of methanol, ethylene glycol and xylitol in alkaline medium.

vii) Development of TiO₂/Mn₅O₈ supported Pd – A facile electrocatalyst for the electrooxidation of Methanol, Ethylene glycol and xylitol.