CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Preparation of Platinum and Ruthenium Nanoparticles

Platinum and Ruthenium nanoparticles can be prepared via various methods

2.1.1 Ion Exchange

Ion exchange is a reversible chemical reaction which an ion from solution is exchanged for a similarly charged ion attached to an immobile solid particle. These solid ion exchange particles are either naturally occurring inorganic zeolites or synthetically produced organic resins. The synthetic organic resins are the predominant type used today because their characteristics can be tailored to specific applications. An organic ion exchange resin is composed of high-molecular-weight polyelectrolytes that can exchange their mobile ions for ions of similar charge from the surrounding medium. Each resin has a distinct number of mobile ion sites that set the maximum quantity of exchanges per unit of resin.

Table 2.1 Selectivity of ion exchange resins in order of decreasing preference

Strong acid cation exchanger	Strong base anion exchanger
Barium	Iodide
Lead	Nitrate
Calcium	Bisulfite
Nickel	Chloride
Cadmium	Cyanide
Copper	Bicarbonate
Zinc	Hydroxide
Magnesium	Fluoride
Potassium	Sulfate

2.1.2 Incipient Wet Impregnation (IWI)

Impregnation is one of the best known methods of producing catalysts. The principle is to impregnate porous supports with solutions of active components. It is used to produce especially with expensive active component; for instance, noble metals are employed as supported catalysts. Alumina is a widely use support for such technique. After the impregnation, catalyst particles are dried. Also the metal salts added are decomposed to the corresponding oxides by heating. The process is shown as followed:
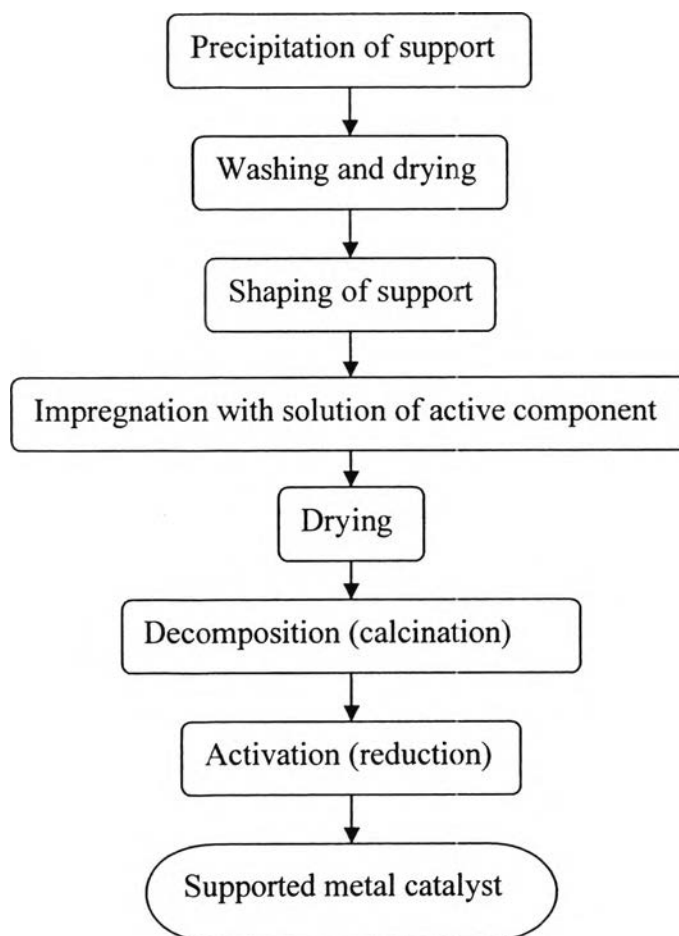
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┌─────────────────────────────┐
│   Precipitation of support  │
└─────────────────────────────┘
              │
              ▼
┌─────────────────────────────┐
│     Washing and drying      │
└─────────────────────────────┘
              │
              ▼
┌─────────────────────────────┐
│      Shaping of support     │
└─────────────────────────────┘
              │
              ▼
┌──────────────────────────────────────────────┐
│  Impregnation with solution of active component │
└──────────────────────────────────────────────┘
              │
              ▼
┌─────────────┐
│   Drying    │
└─────────────┘
              │
              ▼
┌─────────────────────────────┐
│  Decomposition (calcination) │
└─────────────────────────────┘
              │
              ▼
┌─────────────────────────────┐
│    Activation (reduction)   │
└─────────────────────────────┘
              │
              ▼
(    Supported metal catalyst   )
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Figure 2.1 Production of supported metal catalysts by impregnation.

During the impregnation process, the active components having unstable anions (e.g. nitrates, acetates, carbonates, and hydroxides) are used. The support is then immersed in a solution of the active component under specific

conditions. The selective adsorption of the active component either on the surface or inside of the support depends on the production condition applied. In order to obtain a good impregnation, air in pores of the support needs to be removed by evacuation or treated with carbon dioxide or ammonia gas prior to impregnation. And after the impregnation process, catalyst is dried and calcined.

IWI or incipient wetness impregnation is for large scale manufacture. It is the most advantageous method because the support is brought into contact with a solution, the volume of which corresponds to the total pore volume of the solid and which contains the appropriate amount of precursor. Figure 2.2 demonstrates the principle of the IWI:
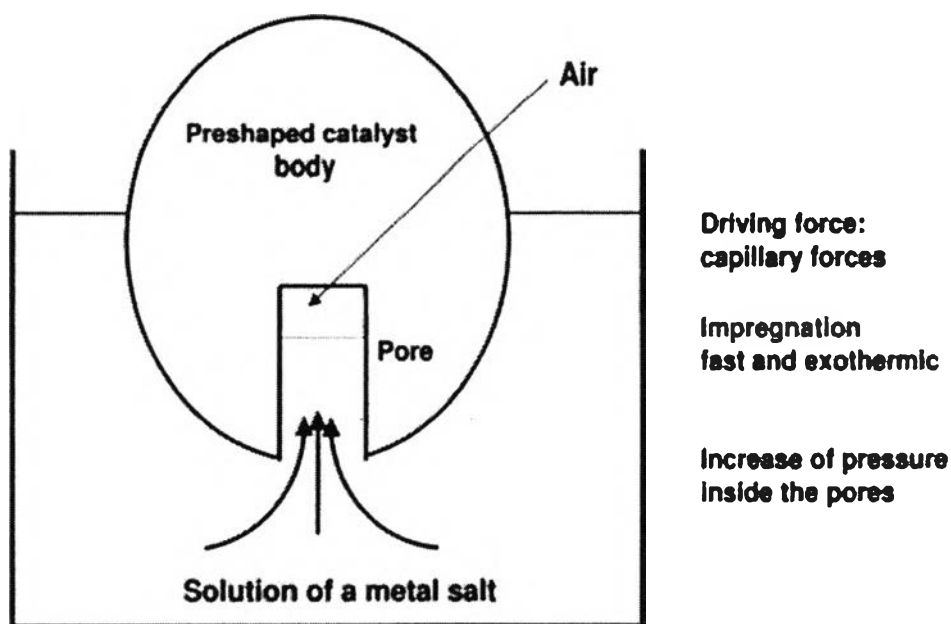
Figure 2.2 Principle of catalyst prepared by incipient wetness impregnation.

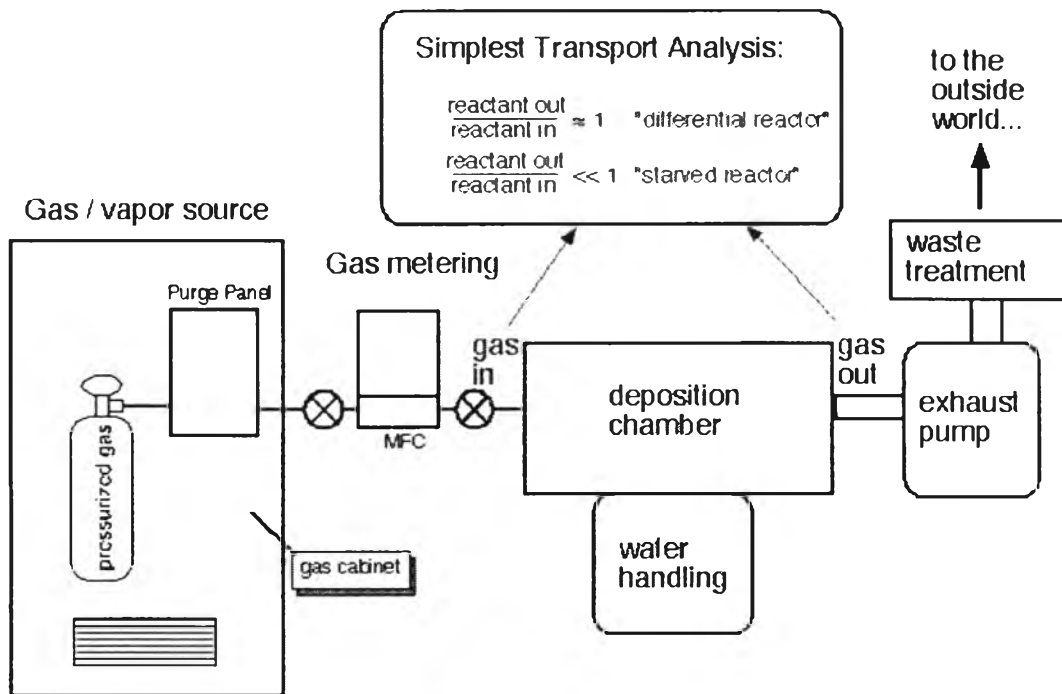### 2.1.3 Chemical Vapor Deposition (CVD)

Figure 2.3 General CVD reactor.

Chemical vapor deposition (CVD) is a chemical reaction which transforms gaseous molecules called precursor, into a solid material in the form of thin film or powder, on the surface of a substrate. Typical reactor used for CVD operation is illustrated in figure 2.3. The process is widely used to produce semiconductor devices. A step-by-step fundamental chemical vapor deposition process is as follows:

- Vaporization and transportation of precursor molecules into a reactor
- Diffusion of precursor molecules to surface
- Adsorption of precursor molecules to surface
- Decomposition of precursor molecules on surface and incorporation into solid films
- Recombination of molecular by-products and desorption into gas phase

2.1.4 <u>Chemical Reduction</u>

Chemical reduction is a simple method of preparing Pt and Ru nanoparticles. Chemical reduction process is carried out under high temperature. Conductive heating (reflux and stir) is often used, but microwave dielectric loss heating may be a better synthesis option in view of its energy efficiency, speed, uniformity and simplicity in execution (Chen *et al.*, 2004). In this process, a solution containing the metal precursor salts, reducing agent, and a stabilizer are refluxed at 393–443 K, where the reducing agent decomposes for metal ion reduction.

2.1.4.1 Reducing Agent

<u>Alcohol</u>

The preparation of Pt nanoparticles by alcohol reduction in the presence of polymer stabilizers is widely practiced. The reaction of H_2PtCl_6 with methanol may take place in two steps:

$$PtCl_2^{-6} + CH_3OH \rightarrow PtCl_2^{-4} + HCHO + 2H^+ + 2Cl^- \qquad (2.1)$$

$$PtCl_2^{-4} + 2CH_3OH \rightarrow Pt^0 + HCHO + 4H^+ + 4Cl^- \qquad (2.2)$$

Methanol as the reducing agent has the advantages in generating uniformly distributed nanoparticles. Polymers such as poly (*N*-vinyl-2-pyrrolidone), Carbowax-20 M, poly (*N*-isopropylacrilamide), sodium polyacrylate, etc., are used almost exclusively with respect to the stabilization for colloidal metal nanoparticles.

The polyol process is a proven technique for preparing colloidal metal particles. In this process, a polyol (most commonly ethylene glycol) solution containing the metal precursor salts is refluxed at 393–443 K, where the polyol decomposes homogeneously to release the reducing agent for metal ion reduction. Conductive heating (reflux and stir) is often used, but microwave dielectric loss heating may be a better synthesis option in view of its energy efficiency, speed, uniformity and simplicity in execution (Chen *et al.*, 2004).

It is well known that the catalytic activity of the metal is strongly dependent on the particle shape, size and size distribution. Conventional preparation techniques based on wet impregnation and chemical reduction of the metal

precursors often do not provide adequate control of particle shape and size. There is continuing effort to develop alternative synthesis methods based on microemulsions, sonochemistry, and microwave irradiation; all of which are in principle more conducive to generating colloids and clusters on the nanoscale, and with greater uniformity.

Lee *et al.* (2006) obtained PtRu(1:1)/C electrocatalysts by polyol method for polymer electrolyte fuel cells. They prepared electrocatalyst using $H_2PtCl_6.6H_2O$ and $RuCl_3.3H_2O$ as precursors for Pt and Ru, respectively. They applied ethylene glycol as a reducing agent, then stirred and reflux the system at 195°C. Product obtained on carbon substrate was observed to show better distribution of nanoparticles, whereas without carbon as a substrate, nanoparticles seemed to agglomerate.

The synthesis of highly dispersed supported and unsupported PtRu with uniform nanoparticle size remains challenges, especially for unsupported and supported electrocatalysts with high metal loading. Recently, the polyol process is widely used to prepare Pt based supported electrocatalysts. For example, Wang *et al.* (2007), Zhao *et al.* (2006) and Liu *et al.* (2005, 2006) have reported that a microwave radiation is an efficient method in view of its energy efficiency, speed, uniformity and simplicity in execution to produce Pt/C materials using ethylene glycol as a reducing agent.

Citrate salts

In 2005, Lin *et al.* performed the reduction of hexachloroplatinic acid in solution by citrate. The overall reaction for the reduction of $PtCl2^{-6}$ by citrate takes place as follows:
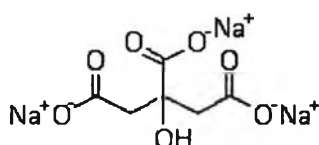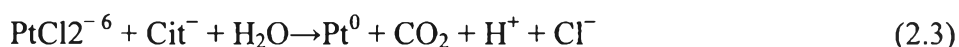
$$PtCl2^{-6} + Cit^- + H_2O \rightarrow Pt^0 + CO_2 + H^+ + Cl^- \qquad (2.3)$$

Figure 2.4 The molecular structure of trisodium citrate.

2.1.4.2 Stabilizer or Protective Agent

Protective agent is applied to avoid metal particles agglomeration. Good protective agents are removed from the metal nanoparticles easily. There are various chemicals used as protective agents to synthesize Pt nanoparticles were reported, polymer (Jiang *et al.*, 2006 and Zuo et al., 1999) and carboxylic anion (Zhao *et al.*, 2006).

Lin *et al.* (2006) prepared platinum nanoparticles of 2–3 nm average size by methanol reduction while using sodium citrate as the stabilizer. Because of the relatively small size of citrate, it hardly can function as a steric stabilizer like polymers. It is probably stabilizing nanoparticles via electrostatic interaction. When a few drops of sulfuric acid were added to the methanol–citrate sol, immediate precipitation of Pt was observed.

Tian *et al.* (2007) has synthesized Pt nanoparticles via polyol process in the presence of ionic polyelectrolyes such as poly(diallyldimethyl-ammonium chloride) (PDDA), poly(allylamine hydrochloride) (PAH), poly (sodium 4-styrenesulfonate) (PSS), Nafion, poly(acrylic acid) (PAA), poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMP) and non-ionic polymer, poly(vinyl-pyrrolidone) (PVP). Polyelectrolyte-stabilized Pt NPs have a particle size range of 2–4 nmThe best electrocatalytic activities were observed on PDDA–Pt and PSS–Pt NPs which also showed better electrocatalytic activity than that of the commercial Pt black catalysts.
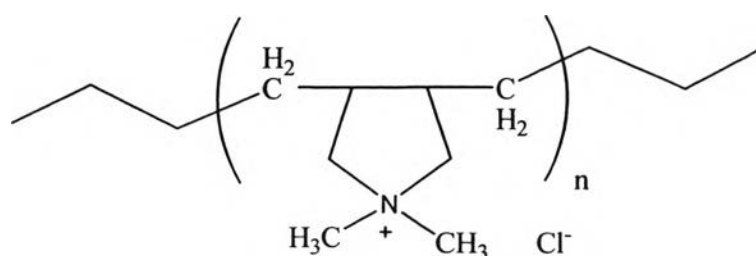

Figure 2.5 Molecular structure of PDDA

Lou *et al.* (2007) has shown that 3-thiophenemalonic acid can reduce platinum precursor and stabilize Pt nanoparticles obtained simultaneously

during microwave radiation. The particle size was between 1-5 nm depends on molar ratio between 3-thiophenemalonic acid and H_2PtCl_6.

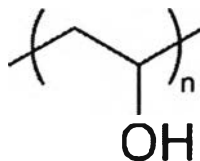## 2.2 Poly(vinyl alcohol) (PVA)

Figure 2.6 Molecular structure of PVA.

Poly(vinyl alcohol) is a hydrophilic polymer which is also water-soluble due to hydroxyl side groups along the polymer chains shown in figure 2.6; hence, it absorbs water and swell easily, but swelling behavior can be inhibited by adding salts (Li *et al.*,2008). Koski *et al.* suggested that, the dissolution of PVA varies due to type of solvent, temperature, and degree of hydrolysis. In Aqueous phase, water, there is hydrogen bonding between inter- and intramolecular chains, among hydroxyl groups on PVA themselves and hydroxyl groups on PVA with hydroxyl groups of water molecules. Therefore, to overcome such attractive force which might cause gel formation, heating over 80 °C is necessary. Moreover, chemical and physical properties of PVA depend on degree of hydrolysis because water acts as a plasticizer, more water absorbed causes higher elongation and flexibility, whereas tensile strength is reduced. PVA is fully degradable and is a quick dissolver. It is odorless and is non toxic PVA has a melting point of 230°C and 180–190°C for the fully hydrolyzed and partially hydrolyzed grades. It decomposes rapidly above 200°C as it can undergo pyrolysis at high temperatures. The preparation of PVA is via hydrolysis of poly(vinyl acetate) partially or completely in order to remove acetate groups from the polymer chains

Li *et al.* (2008) have reported that in fabrication of PVA via electrospinning technique, adding salts promoted smoother and thinner jet. The addition of ionic salt improves jet surface charge density and jet conductivity. It is considered that the

solution with a higher amount of LiCl has a higher net surface charge density. As jet conductivity increased, higher elongation forces are imposed to the jet under the electrical field. Thus smooth and thin jet was obtained when electrospun PVA solutions with the addition of LiCl. The addition of the salt was found to be relatively more effective on the fiber diameter than other parameters.

There have been many researches focused on electrospun PVA recently. Most studies involve incorporating the second component into PVA solution and directly fabricate nanofiber by electrospinning since the electrospinning process is cheap and simple. Jin *et al.* (2007) have successfully prepared PVA containing silver nanoparticles for anti-microbial applications using electrospinning technique. Two pathways were reported. Firstly, they applied $AgNO_3$ in 12% PVA solution and refluxed the mixture at various temperatures, 50-80 °C and then directly electrospinned the solution. Secondly, they electrospinnined $PVA/AgNO_3$ and annealed the as-spun fibers, the silver ions remained in the fiber were reduced during annealing process.

Bai *et al.* (2006) studied about the preparation of poly(vinylalcohol) (PVA) nanofibers containing gold nanoparticles by electrospinning method. Composite nanofibers of PVA and gold nanoparticle were synthesized by an electrospinning method. Morphology and distribution of nanoparticles were characterized by TEM. The average diameter of composite fibers decreased obviously with the added amount of Au nanoparticles increasing, and the average diameters of the Au particles increased. The band of Au–O-interaction was confirmed by FTIR spectra.

Shan *et al.* (2007) Poly(vinyl alcohol) (PVA) nanofiber mats were collected on indium tin oxide (ITO) substrate by electrospinning method. They collected electrospun PVA nanofibers on ITO to obtain nanofiber mats-modified electrode after crosslinking treatment. Because of the high surface area and the presence of – OH groups in PVA nanofibers, the electrode could be further modified by self assembly technique. Most of the reported layer-by-layer self-assembly techniques were based on the electrostatic attraction between polycations and polyanions.

2.3 Electrospinning

Electrospinning is one of technique that produces polymer fibers with nanometer-sized diameters with the use electrostatic forces. The standard setup for electrospinning consists of a spinneret with a metallic needle, a syringe pump, a high-voltage power supply, and a grounded collector. A polymer, sol-gel, composite solution (or melt) is loaded into the syringe and this liquid is driven to the needle tip by a syringe pump, forming a droplet at the tip. When a voltage is applied to the needle, the droplet is first stretched into a structure called the "Taylor cone". Above a critical voltage, electrostatic forces overcome the surface tension of the solution, and an electrified polymer jet is formed. The jet is then elongated and whipped continuously by electrostatic repulsion until it is deposited on the grounded collector in the form of a randomly interconnected fibrous mat (Smit *et al.*, 2005). The electrospinning process is given below
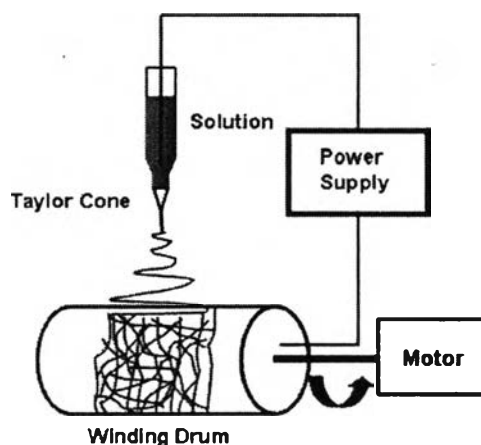

Figure 2.7 Schematic diagram of electrospinning set up.

The fiber formation by electrospinning depends on the polymer solution properties and the spinning parameters. Similar to traditional fiber spinning processes (e.g., melt spinning), electrospinning also requires a proper viscosity (i.e., sufficient chain entanglement) of the polymer solution to form fibers. Therefore, in addition to

having the proper polymer solution concentration, polymers with linear or lightly branched structures are usually desired, while those with highly branched or star-shaped architectures should be avoided. Unlike other fiber spinning processes, the electrostatic driving force in electrospinning indicates that the conductivity of the polymer solution is another important factor for spinning performance (Hong *et al.*, 2007).

Electrospinning of polymer solutions is a novel and efficient fabrication method of preparing microporous membranes that are composed of ultra-fine fibers with diameters in the range of several micrometers to tens of nanometers. Control of the processing parameters can easily produce the electrospun fibrous membranes with porosities in the range of 30–90% and pore sizes in the range of sub-micrometers to a few micrometers. In addition, a fully interconnected open pore structure offers a good ion conduction channel and a large specific surface area.

The random orientations of the electrospun fibers in the typically obtained non-woven webs are acceptable in some applications such as filters, wound dressings and tissue scaffolds. The fiber morphology is controlled by the experimental parameters and is dependent upon solution conductivity, concentration, viscosity, polymer molecular weight, applied voltage, etc. Much work has been done on the effect of parameters on the electrospinning process and morphology of fibers (Gu *et al.*, 2005). During the last 10 years extensive research has been conducted on various aspects of electrospinning. These efforts include spinning in any different polymer and solvent pairs, varying fiber forming conditions, fiber characterization and process modeling. Many improvements of the electrospinning process have been patented or proposed. But almost all of the improvements are involved in either how to spin more fibers during a short time by increasing the number of nozzles or how to collect continuous fibers or yarns through altering collecting set-up or how to change solution properties by simply adding some additives. No literature brings in improvement fixings on changing the electrospinning set-up device which can directly act on any solution prepared for spinning, so that the spinning can become easier and thinner fibers can be produced under the same condition (Wan *et al.*, 2006).

2.4 Fuel Cell

A fuel cell is an electrochemical energy conversion device. It consists of anode and cathode sides. On the anode side, hydrogen diffuses to the anode catalyst where it later dissociates into protons and electrons. These protons often react with oxidants causing them to become what is commonly referred to as multi-facilitated proton membranes (MFPM). The protons are conducted through the membrane to the cathode, but the electrons are forced to travel in an external circuit (supplying power) because the membrane is electrically insulating. On the cathode catalyst, oxygen molecules react with the electrons (which have traveled through the external circuit) and protons to form water.

The materials used in fuel cells differ by type. The electrode–bipolar plates are usually made of metal, nickel or carbon nanotubes, and are coated with a catalyst (like platinum, nano iron powders or palladium) for higher efficiency. Carbon paper separates them from the electrolyte. The electrolyte could be ceramic or a membrane. There are several different types of fuel cells, each using a different chemistry.

Fuel cells are usually classified by their operating temperature and the type of electrolyte they use. Some types of fuel cells work well for use in stationary power generation plants. Others may be useful for small portable applications or for powering cars. The interesting types of fuel cell include:

2.4.1 Proton Exchange Membrane Fuel Cell (PEMFC)

Proton exchange membrane fuel cells, also known as proton electrolyte membrane fuel cells (PEMFC), are a type of fuel cell being developed for transport applications as well as for stationary and portable applications. The PEMFC has a high power density and a relatively low operating temperature (ranging from 60 to 80 degrees Celsius) the low operating temperature means that it doesn't take very long for the fuel cell to warm up and begin generating electricity. But its fuel must be purified, and a platinum catalyst is used on both sides of the membrane. There are four basic elements in the PEM fuel cell:

- The anode, the negative post of the fuel cell, has several jobs. It conducts the electrons that are freed from the hydrogen molecules so that they can be used

in an external circuit. It has channels etched into it that disperse the hydrogen gas equally over the surface of the catalyst. This oxidation half-cell reaction is represented by:

Anode side: $H_2 \longrightarrow 2H^+ + 2\,e^-$ $E^o = 0\ V_{SHE}$ (2.4)
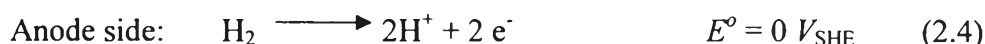
- The cathode, the positive post of the fuel cell, has channels etched into it that distribute the oxygen to the surface of the catalyst. The oxygen molecules react with the protons permeating through the polymer electrolyte membrane and the electrons arriving through the external circuit to form water molecules. This reduction half-cell reaction is represented by:

Cathode side: $4\,H^+ + 4\,e^- + O_2 \longrightarrow 2H_2O$ $E^o = 1.229\ V_{SHE}$ (2.5)

Overall Cell Reaction: $2H_2 + O_2 \longrightarrow 2H_2O$ $E^o = 1.229\ V_{SHE}$ (2.6)
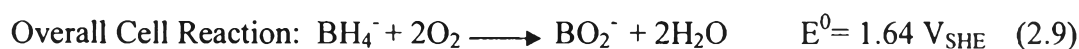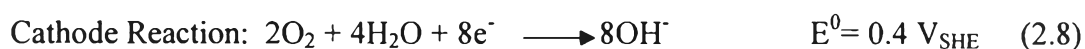
- The electrolyte is the proton exchange membrane. This membrane only conducts positively charged ions and blocks electrons. For a PEMFC, Nafion is commonly used as a source for proton exchange membrane.

- The catalyst is a special material that facilitates the reaction of oxygen and hydrogen. It is usually made of platinum nanoparticles coated onto carbon supports. The catalyst is rough and porous so that the maximum surface area of the platinum can be exposed to the hydrogen or oxygen. The platinum-coated side of the catalytic membrane on both anode and cathode sides of the PEM.

2.4.2 Direct Borohydride Fuel Cell

Direct borohydride fuel cells (DBFCs) are a subcategory of alkaline fuel cells that Borohydride resolved into an aqueous solution as fuel. The method of using Borohydride instead of gaseous hydrogen, has many advantages over conventional hydrogen in an alkaline fuel cell. First of all the storage problem has been solved. The highly alkaline fuel and waste borax prevents poisoning of the fuel

cell from carbon dioxide (CO_2) in the air. For mobile applications no special devices such as dangerous high pressure chlinders or an energy consuming apparatus which chill down to liquid hydrogen state are needed.
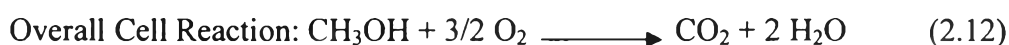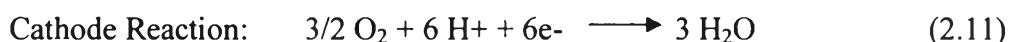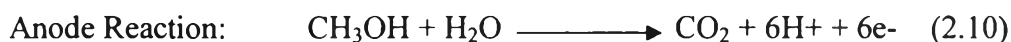
The DBFCs are quite novel fuel cells that based on the borohydride oxidation and the oxygen reduction. These fuel cells decompose and oxidize the borohydride directly, side-stepping hydrogen production and even producing slightly higher energy yields (Dermirci, 2007). Theoretical electrode reactions of DBFC are presented by (Cheng *et al.*, 2007):

Anode Reaction: $NaBH_4 + 8OH^- \longrightarrow NaBO_2 + 6H_2O + 8e^-$ $E^0 = -1.24\ V_{SHE}$ (2.7)

Cathode Reaction: $2O_2 + 4H_2O + 8e^- \longrightarrow 8OH^-$ $E^0 = 0.4\ V_{SHE}$ (2.8)

Overall Cell Reaction: $BH_4^- + 2O_2 \longrightarrow BO_2^- + 2H_2O$ $E^0 = 1.64\ V_{SHE}$ (2.9)

Borohydride fuel is safe, operates at low temperature, contains a high H-capacity of hydrogen and is as easy to handle as gasoline. Furthermore our DBFC has a higher performance and is cheaper than any other fuel cells because It does not need expensive platinum catalysts. Unfortunately, DBFCs do produce some hydrogen from a side step reaction of $NaBH_4$ with water heated by the fuel cell. This hydrogen can either be piped out to the exhaust or piped to a conventional hydrogen fuel cell. Either fuel cell will produce water or the water can be recycled to allow for higher concentrations of $NaBH_4$.

2.4.3 Direct Methanol Fuel Cells (DMFC)

DMFC is electrochemical device that convert high energy density fuel (liquid methanol) directly to electricity. It is similar to the PEMFC in that the electrolyte is a polymer and the charge carrier is the hydrogen ion (proton). For the DMFC, The liquid methanol (CH_3OH) is oxidized in the presence of water at the anode generating CO_2, hydrogen ions and the electrons that travel through the external circuit as the electric output of the fuel cell. The hydrogen ions travel through the electrolyte and react with oxygen from the air and the electrons from the external circuit to form water at the anode completing the circuit. At the anode and cathode sides, the half-cell reactions are presented by:

Anode Reaction: $CH_3OH + H_2O \longrightarrow CO_2 + 6H+ + 6e-$ (2.10)

Cathode Reaction: $3/2\ O_2 + 6\ H+ + 6e- \longrightarrow 3\ H_2O$ (2.11)

Overall Cell Reaction: $CH_3OH + 3/2\ O_2 \longrightarrow CO_2 + 2\ H_2O$ (2.12)

Thermodynamically, the reversible potentials for the overall reaction at 25 °C are 1.214 V for DMFC and 1.23 V for the hydrogen fuel cell. Nevertheless, the storage of methanol is much easier than that of hydrogen because it does not need to be done at high pressures or low temperatures. These cells have been tested in a temperature range from about 50°C-120°C. This means they can operate at the low temperature. However, the efficiency of current direct-methanol fuel cells is low due to the high permeation of methanol through the membrane materials used, which is known as methanol crossover, and the dynamic behavior is sluggish. Other problems include the management of carbon dioxide created at the anode. Current DMFCs are limited in the power they can produce, but can still store high energy content in a small space. This means they can produce a small amount of power over a long period of time. This makes them presently ill-suited for powering vehicles (at least directly), but ideal for consumer goods such as cellular phones, digital cameras, laptops and other consumer products.
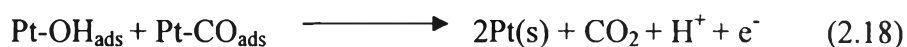
2.4.3.1 Anode catalyst for DMFC

Parson *et al.* (1988) investigated about methanol oxidation. It was found that the oxidation would possibly involve two main processs:

(i) Electrosorption of methanol onto a substrate

(ii) addition of oxygen to absorbed carbon-containing intermediates to generate carbon dioxide

The adsorption and subsequent reaction of methanol on Pt take place by the follow steps (Hamnett , 1997)

$CH_3OH + Pt_{(s)} \longrightarrow Pt\text{-}CH_2OH_{ads} + H^+ + e^-$ (2.13)

$Pt\text{-}CH_2OH_{ads} + Pt_{(s)} \longrightarrow Pt_2\text{-}CHOH_{ads} + H^+ + e^-$ (2.14)

$Pt_2\text{-}CHOH_{ads} + Pt_{(s)} \longrightarrow Pt_3\text{-}Coh_{ads} + H^+ + e^-$ (2.15)

$Pt_3\text{-}COH_{ads} \longrightarrow Pt\text{-}CO_{ads} + 2Pt_{(s)} + H^+ + e^-$ (2.16)
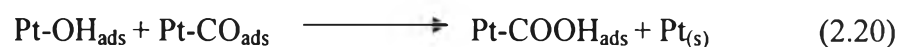
The extension of the potential may include the formation of platinum hydroxide (Pt-OH) and oxidation of CO to CO_2, as shown in equation (2.17) to (2.21)
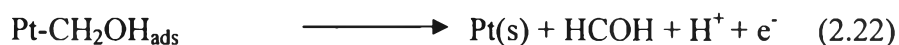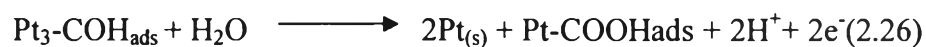
$$Pt_{(s)} + H_2O \longrightarrow Pt\text{-}OH_{ads} + H^+ + e^- \qquad (2.17)$$

$$Pt\text{-}OH_{ads} + Pt\text{-}CO_{ads} \longrightarrow 2Pt(s) + CO_2 + H^+ + e^- \qquad (2.18)$$

or

$$Pt\text{-}CO_{ads} + H_2O \longrightarrow Pt\text{-}COOH_{ads} + H^+ + e^- \qquad (2.19)$$

or $$Pt\text{-}OH_{ads} + Pt\text{-}CO_{ads} \longrightarrow Pt\text{-}COOH_{ads} + Pt_{(s)} \qquad (2.20)$$

$$Pt\text{-}COOH_{ads} \longrightarrow Pt(s) + CO_2 + H^+ + e^- \qquad (2.21)$$

Addition reaction that have been suggested are:

$$Pt\text{-}CH_2OH_{ads} \longrightarrow Pt(s) + HCOH + H^+ + e^- \qquad (2.22)$$

$$Pt_2\text{-}CHOH_{ads} + Pt\text{-}OH_{ads} \longrightarrow 3Pt_{(s)} + HCOOH + H^+ + e^- \qquad (2.23)$$

or

$$Pt_2\text{-}CHOH_{ads} + H_2O \longrightarrow 2Pt_{(s)} + HCOOH + 2H^+ + e^- \qquad (2.24)$$

$$Pt_3\text{-}COH_{ads} + Pt\text{-}H_2O \longrightarrow 3Pt_{(s)} + Pt\text{-}COOHads + H^+ + e^- \qquad (2.25)$$

or

$$Pt_3\text{-}COH_{ads} + H_2O \longrightarrow 2Pt_{(s)} + Pt\text{-}COOHads + 2H^+ + 2e^- \qquad (2.26)$$

Equation (2.13)-(2.16) show the electrosorption process whereas subsequent reaction involve oxygen transfer or oxidation of surface-bonded intermediates. Arising from the equation (2.16), the stable $Pt\text{-}CO_{ads}$ species might possibly poison the Pt catalyst. $Pt\text{-}CO_{ads}$ can mostly be removed by the oxygenated species, $Pt\text{-}OH_{ads}$, as described in equation (2..18). Since the dissociative adsoption of water (equation (2.19)) occur slowly at the normal operating potentials of DMFC. Therefore, on a pure Pt surface, the dissociative chemisorption of water has become the rate-determining step when the applied potential is below 0.70 V. This result has led to the investigation of any catalyst that can dissociate water at relatively lower

potentials than 0.70 V and high reactivity toward oxidation of CO as well as high stability for DMFC anodic reaction.

2.4.3.2 Cathode Catalyst for DMFC

In addition, the reduction of O_2 at the cathode is another important factor in operation of DMFC.

$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O \quad E^0 = 1.23\ V$$

The most familiar catalyst for oxygen reduction are the noble and coinage metals, especially Pt and gold (Au).

Zaragoza-Martin *et al.*, (2007) studied about Pt/carbon nanofibers electrocatalysts for hydrogen oxidation in fuel cells Effect of the support oxidizing treatment. Different Pt-based electrocatalysts supported on carbon nanofibers and carbon black (Vulcan XC-72R) have been prepared using a polymermediated synthesis. The effect of carbon nanofibers treatment with HNO_3 solution on Pt particle size and electroactive area has been analyzed. This synthesis method produces highly dispersed Pt nanoparticles on the carbon nanofibers with an average diameter around 2.5 nm. Highly dispersed Pt with homogeneous particle size and an electroactive area around of 100m2 g−1 is obtained in raw carbon nanofibers. Moreover, the oxidizing treatment favours the aggregation of the platinum nanoparticles considerably reducing the electroactive surface area. Electrocatalysts supported on carbon nanofibers exhibits a stability at 1.2V in sulfuric acid solution similar to Pt/Vulcan XC-72R. The slight decrease in the electroactive surface area results from Pt particle aggregation that can be produced by the effect of the applied potential and the electrochemical oxidation of the carbon support.

Huang et al., (2007) investigated about Platinum nanoparticles supported on activated carbon fiber as catalyst for methanol oxidation. Activated carbon fiber (ACF) with high specific surface area has been used as support in the preparation of Pt nanoparticles electrocatalyst (Pt/ACF) for direct alcohol fuel cells. It is found that the Pt nanoparticles on ACF are highly and homogeneously dispersed with a narrow size distribution in the range of 1.5–3.5 nm with an average size of 2.4 nm. In comparison with the commercial E-TEK Pt/C catalyst, the Pt/ACF catalyst

exhibits much higher catalytic activity for methanol, ethanol and isopropanol oxidation, which are about 2.4 times as high as that of the former. The fibrous support, with abundant functional groups and plentiful micropore on the surface, offers the advantages of a short diffusion distance and a strong interaction between Pt particles and carbon support, which efficiently resist the agglomeration of Pt particles and the loss in active surface area of the catalyst during continuous cycling. This might be the reason why the Pt/ACF catalyst performs significantly better electrochemical stability than commercial Pt/C catalyst.