CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Fuel Cells

Fuel cells are electrochemical devices that directly convert a fuel's energy to electrical energy without combustion. They provide a very clean energy, high reliability, very little noise, high quality electricity, highly efficient source of electrical energy and potentially to power electric vehicles. Their goals are cost reduction and pollutant minimization keeping a high efficiency.

Fuel cells are primarily classified by a kind of electrolyte they employed, which also determines the kind of chemical reactions that take place in the cell, the kind of catalysts required, the temperature range in which the cell operates, the fuel required, and other factors. These characteristics also affect the applications for which these cells are most suitable. There are several types of fuel cells currently under development, each with their own advantages, limitations, and potential applications. A few of the most promising types are included Polymer Electrolyte Membrane (PEM), Phosphoric Acid (PA), Molten Carbonate (MC) and Solid Oxide (SO) as shown in Table 2.1. PEM fuel cells are primarily used for transportation and some stationary applications. Due to their fast startup time, low sensitivity to orientation, and favorable power-to-weight ratio, PEM fuel cells are particularly suitable for using in passenger vehicles, such as cars and buses.

In the polymer electrolyte membrane (PEM) fuel cell, also known as a proton-exchange membrane cell and illustrated in Figure 2.1, H_2 gas is used as a fuel. A catalyst in the anode separates hydrogen atoms into protons and electrons. The membrane in the center transports the protons to the cathode while leaving the electrons behind. The electrons flow through a circuit to the cathode, forming an electric current to do useful work. In the cathode, another catalyst helps the electrons, hydrogen nuclei and oxygen from the air recombine. The main exhaust of fuel cell is water vapor when utilizing pure H_2 as a fuel, and H_2O-CO_2 mixture when H_2 fuels are used.
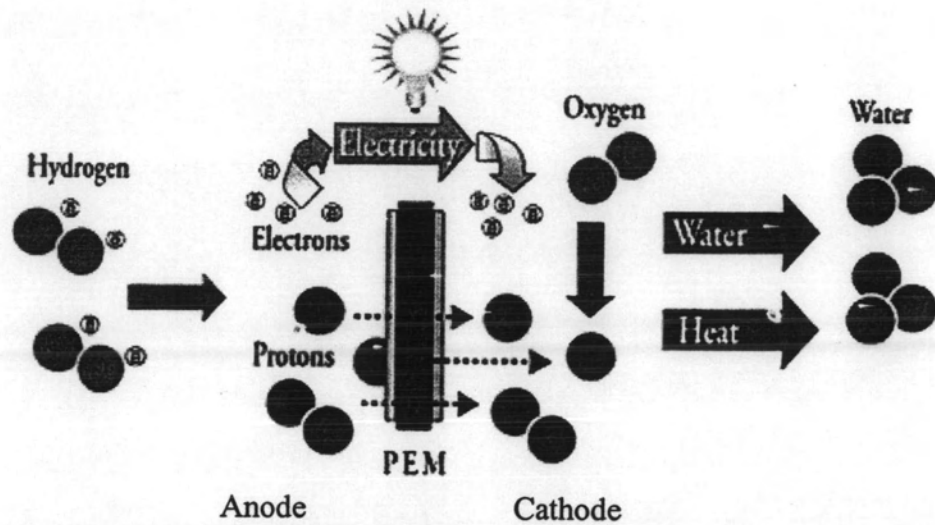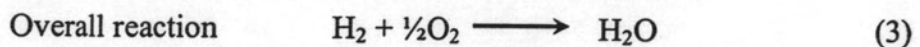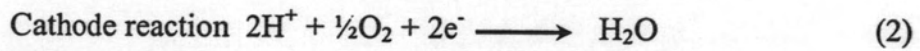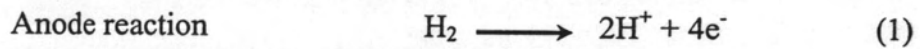
Figure 2.1 Diagram of Polymer Electrolyte Membrane (PEM) fuel cell.

Anode reaction $\qquad$ $H_2 \longrightarrow 2H^+ + 4e^-$ $\qquad$ (1)

Cathode reaction $\quad 2H^+ + \frac{1}{2}O_2 + 2e^- \longrightarrow H_2O$ $\qquad$ (2)

Overall reaction $\qquad H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$ $\qquad$ (3)

PEM fuel cells operate at relatively low temperatures of around 60-100°C. Low temperature operation allows them to quickly start (less warm-up time) resulting in less wear on system components and better durability. However, a requirement of noble-metal catalyst (typically Pt) for separating the hydrogen's electrons and protons at the anode cell also increase the system cost. Moreover, the Pt catalyst is also extremely sensitive to CO poisoning. Thus, it requires an additional reactor to abate CO in the H_2 stream, particularly for the derived from alcohols or hydrocarbon fuels (commercial gasoline), before feeding to PEM fuel cells.

Table 2.1 Fuel Cell Comparisons

|	PEMFC	MCFC	PAFC	SOFC
Electrolyte	Ion exchange membrane	Molten carbonate salt	Liquid phosphoric acid	Solid metal oxide
Operating Temp. (^{o}C)	60-100	600-1000	150-200	600-1000
Oxidant	O_2/Air	CO_2/O_2/Air	O_2/Air	O_2/Air
Maximum Efficiency (%)	60	85	80	85
Maximum Power Output Range (size)	250 kW	2 MW	1 MW	220 kW
Waste heat uses	Space heating or water heating	Excess heat can produce high-pressure steam	Space heating or water heating	Excess heat can be used to heat water or produce steam
Applications	Vehicle applications, medium to large scale stationary power generation	Large-scale power generation	Medium to large scale power generation	Medium to large scale power generation

2.2 Hydrogen Production Processes

H_2 is the most common base material in the universe. On earth, practically all H_2 is in a compound formed with other elements. It reacts very readily with O_2 to create H_2O. Under H_2 production processes, the water molecule and the raw material are split, and the result is H_2, CO and CO_2. In other words, the H_2 gas comes from both steam and hydrocarbon compounds.
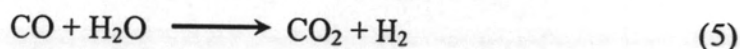
2.2.1 Steam Reforming

Steam reforming is a reaction between a hydrocarbon fuel and water to create H_2. Steam reforming of natural gas is currently the cheapest process to produce H_2, and accounts for about half of the world's hydrogen production. In the process, steam at a temperature of 700-1000 °C is fed to be heterogeneously reacted with methane in a reactor over a catalyst. Natural gas mainly consists of methane, mixed with some heavier hydrocarbons and CO_2. By applying high temperature steam to methane, H_2 and CO_2 are created. Even more H_2 can be produced from the same amount of fuel when compared with auto thermal reforming or partial oxidation, the process requires much more heat input to continue the reaction.

The reaction that is involved is:
$$CH_4 + H_2O \longrightarrow CO + 3H_2 \tag{4}$$
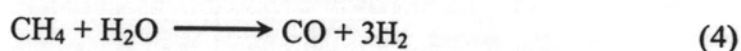
And for the following "Water gas shift reaction" is:
$$CO + H_2O \longrightarrow CO_2 + H_2 \tag{5}$$

Steam reforming is the most common method of producing H_2 nowadays.

2.2.2 Partial Oxidation

Partial oxidation reaction is a process that partially oxidizes the fuel to CO and H_2 rather than fully oxidizes to CO_2 and H_2O. This is accomplished by injecting air with the fuel stream prior to the reformer. The advantage of partial oxidation over steam reforming is that it is an exothermic reaction rather than an

endothermic reaction and therefore generates its own heat. An example reaction for this process is:

$$C_8H_{18} + H_2O + 9/2O_2 \longrightarrow 6CO + 2CO_2 + 10H_2 \qquad (6)$$
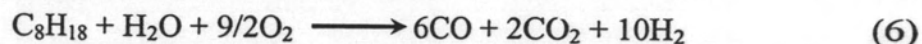
2.2.3 Carbon Dioxide Reforming

Because the fuel supplying is CH_4, the reforming reaction between CH_4 and CO is as shown below. With an approximate 10-15% CO_2 fed, approximate 10-15% CO are being generated. An example reaction for this process is:

$$CH_4 + H_2O \longrightarrow 3H_2 + CO \qquad (7)$$

2.2.4 Autothermal

Autothermal is a combination of partial oxidation and steam reforming. The term reflects the heat exchanging between the endothermic steam reforming process and the exothermic partial oxidation, which also creates a sufficient heat to drive itself and generates more hydrogen than only partial oxidation alone. The hydrocarbons react with a mixture of O_2 and steam in a "thermo reactor" over a catalyst surface.

Generally, the production of clean H_2 for the PEMFC from hydrocarbon feeds is accomplished by a series of catalytic steps including steam reforming, desulfurization, water gas shift and CO removal by preferential CO oxidation as shown in Figure 2.2.
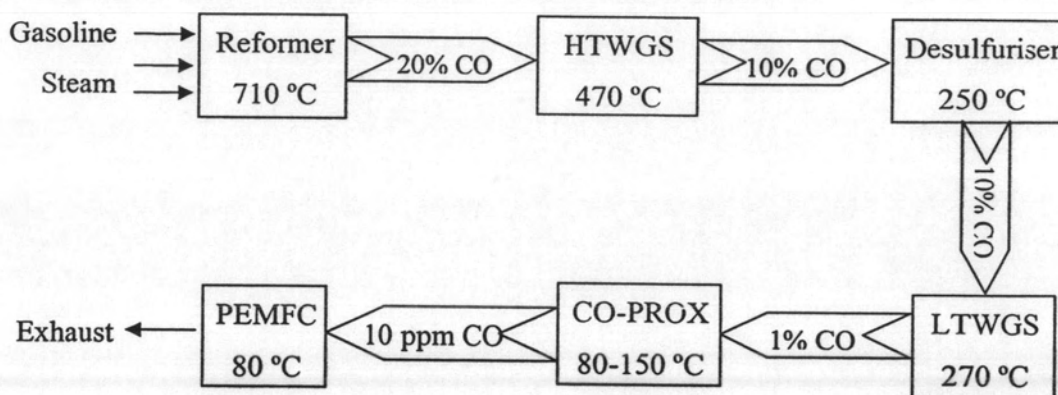
Figure 2.2 Schematic description of a gasoline processor for hydrogen production.

2.3 CO Removing Method

2.3.1 Pressure Swing Adsorption (PSA)

Pressure Swing Adsorption (PSA) is an adiabatic process applying for purification of gases by removing the accompanied impurities using fixed bed adsorption under high pressure. The advantages of the process are high purity of hydrogen (99.9 – 99.999% mol), high efficiency of hydrogen recovery up to 90% and low investment and operational costs. PSA may be used for treatment of most common gases.

2.3.2 Membrane Filtration

Membrane separation involves partially separating a feed containing a mixture of two or more components by using a semipermeable barrier (the membrane) through which one or more of the species moves faster than another or other species. Although the majority of time the feed, retentate, and permeate are usually liquid or gas, they may also be solid.

2.3.3 Methanation

The methanation reactor converts any residual CO_2 back to CH_4 using a small part of the H_2 product to effect the reactions.

$$CO + 2H_2 \longleftrightarrow CH_4 + \frac{1}{2}O_2 \qquad (8)$$
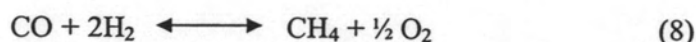
2.3.4 Preferential Oxidation or Selective Oxidation of CO

Preferential or selective oxidation of CO is a reaction that oxidizes one chemical rather than another. In fuel cells, the reaction is used to preferentially oxidize CO to CO_2 from the reformate stream after the water-gas shift reactor and before the fuel cell. This may require a catalyst. This technique is the simplest and high efficiency.

$$CO + 1/2O_2 \longrightarrow CO_2 \qquad (9)$$

The literature report several studies on the catalyst for the preferential CO oxidation including noble metal generally supported on alumina as catalyst support. In 1993, Oh and Sinkevith have investigated the variety of noble metals (Ru, Rh, Pd and Pt) supported on alumina. They found that Ru and Rh gave the highest CO conversion. On the other hand, Pd gave the lowest CO conversion and to achieve the complete CO conversion the Pt requires high temperature of 200°C while the Rh requires heating up only to 100°C. After that, Igarashi et al. (1997) have investigated the Pt supported on zeolites for preferential oxidation of CO. Varieties of zeolite were used as a support, which are A zeolite, mordenite, X zeolite, and alumina. The effect of support has been investigated on the selectivity for CO oxidation versus H_2 oxidation follows the order of A zeolite > mordenite > X zeolite > alumina. In addition, the highest conversion of CO to CO_2 was achieved by Pt/mordenite. With the Pt/mordenite, CO can be oxidized completely by using two stages reactor. Then, Rosso et al. (2004) have developed the noble metal supported A zeolite catalysts, which employed 1 % of Pt, Pd and Ru as active metals and 3, 4 and 5-A as catalyst supports. The Pt catalysts showed a complete CO conversion and a comparatively high selectivity. Otherwise, the 1 % Pt supported on 3A zeolite catalyst showed the

best performance. It can completely oxidize CO to CO_2 at a wide range of temperatures, from 185-220 °C. In contrast, at this range of temperature, the Pt/4A zeolite and Pt/5A zeolite could only reduce CO concentration down to 1300 and 675 ppm, respectively. Therefore, the 1 % Pt/3A catalyst was the best since it can give the highest selectivity for CO oxidation with minimal facilitating side reactions, e.g. H_2 oxidation, RWGS reaction. In the same year, Watanabe et al. (2003) proposed the new Pt-Fe/mordenite catalysts for the PROX, which has a superior activity than the conventional Pt/Al$_2$O$_3$ catalysts. The Pt-Fe/mordenite was investigated for the catalytic performance at various conditions compared to the Pt/mordenite. It was found that a complete removal of CO with 100% selectivity was achieved at 80-150°C. Moreover, the selective CO oxidation on gold catalysts was studied by Kandoi et al. (2004). Their results showed that Au and Cu provided more selective on CO than Pt at low temperatures. However, at higher temperature, Pt and Cu lose some of their selectivity to CO oxidation, whereas the selectivity on Au decreases substantially primarily because of the significantly weaker CO adsorption.

Haruta and Daté (2001) studied the Au nanoparticles catalysts for many catalysis reactions such as the epoxidation of propylene, water-gas-shift reaction and CO oxidation. Moreover, for CO oxidation it is indicated that CO is adsorbed only on steps, edges and corner sites. Thus, smaller metallic Au particles are preferable (Mavrikakis et al., 2000).

Varieties of material support catalysts for selective CO oxidation that use Au as metal active site were determined by several research groups as follows, Rossignol et al. (2005) investigated the support effects of Au/Al$_2$O$_3$, Au/ZrO$_2$, Au/TiO$_2$. All of catalysts were prepared by laser vaporization of a metallic Au rod followed by deposition of the formed clusters onto the support powders. With this method, they managed to get highly dispersed small Au particles (2-3 nm) on the surface of all supports with a narrow size distribution. It was found that no significant effect of the supports. By contrast, Arrii et al. (2004) discovered that TiO$_2$ is the best support for Au nanoparticles in the catalytic oxidation since it can convert more CO than that of ZrO$_2$ and Al$_2$O$_3$.

Avgouropoulos et al. (2002) reported that, at low-temperature, Au/α-Fe$_2$O$_3$ showed higher preferential oxidation selectivity than a commercial Pt/γ-Al$_2$O$_3$

catalyst. But it has been previously studied on the kinetics of CO selective low-temperature oxidation in H_2-rich stream over $Au/\alpha\text{-}Fe_2O_3$ and found that the reaction orders respected to the partial pressure of CO and O_2 were 0.55 and 0.27, respectively. The activity of catalyst was observed to strongly depend on temperature. Increasing temperature also facilitates H_2 oxidation and decreases the selectivity. When comparing $Au/\ \alpha\text{-}Fe_2O_3$ with $Pt/\gamma\text{-}Al_2O_3$, the Au catalyst seems to be a superior catalyst for this process. This catalyst can give a higher activity and selectivity at lower temperature of $80°C$ and requires lower excess O_2 for achieving a 99 % conversion of 1.5 % CO in a simulated reformer gas. (Kahlich *et al.*, 1999) Otherwise, Schubert *et al.* (2004) studied the influence of H_2O and CO_2 on the selective CO oxidation in H_2-rich gases over $Au/\ \alpha\text{-}Fe_2O_3$. They found that the addition of CO_2 reduced the CO oxidation rate and the selectivity. In contrast, the addition of H_2O resulted in the selectivity increment by suppressing the competitive H_2 oxidation reaction and deactivation of the catalyst was accelerated due to the increasing of carbonate formation on catalyst surface.

Bethke and Kung (2000) studied the $Au/\gamma\text{-}Al_2O_3$ catalysts for selective CO oxidation in a H_2-rich stream. They discovered that only a narrow range of Au particle size (about 5-10 nm) the can provide the best activity and selectivity. Besides, they found that the particle size of Au could be made smaller by the addition of Mg citrate during the deposition/precipitation of chlorohydroxy gold clusters. Without citrate, the average Au particle size was larger, which subsequently was leading to the lower conversion and selectivity. At relative low temperature of 100 °C, $Au/\gamma\text{-}Al_2O_3$ catalysts gave the selectivity of about 50 % with the reactant gas of 48 % H_2, 1 % CO, 0.5 % O_2 balanced He. Then, Grisel *et al.* (2002) studied multi-component catalysts for oxidation of CO in H_2-rich environment by adding metal oxide (MO_x) on Au/Al_2O_3. They showed that in case of $Au/MgO\text{-}Al_2O_3$, the presence of MgO enables the preparation of small and stable Au particles on $\gamma\text{-}Al_2O_3$, which leading to the improvements of both low-temperature CO and H_2 oxidation. Moreover, further addition of MnO_x and FeO_x to $Au/MgO\text{-}Al_2O_3$ enhanced low temperature CO oxidation and improved CO_2 selectivity.

Luengnaruemitchai *et al.* (2004) studied the effects of preparation methods (impregnation, co-precipitation and sol-gel) on PROX of CO in a simulated

reforming gas to CO_2 over Au/CeO_2 catalysts. They found that the activity of Au catalyst depended very strongly upon the preparation method. Co-precipitation 1 % Au/CeO_2 catalyst exhibited the highest activity and good selectivity at $110^{\circ}C$.

Zhang *et al.* (2003) showed that adding small amount of Pt (1.0 wt. %) on Au supported on ZnO leading to improved stability and the optimum content of Au in Au/ZnO was 1.5 wt. %

2.4 Properties of Gold

Gold (Z = 79) has the atomic configuration as $[Xe]4f^{14}5d^{10}6s^1$, and therefore lies in Group 11(IB) of the periodic classification of elements. It is a congener of Cu and Ag, which often being referred to as the "coinage metals", and lies between Pt in group 10 and mercury in group 12. Concerning our area of specific interest, Pt is a versatile catalytic metal and is widely used in commercial applications for both chemical processing and pollution control, notably in automobile exhaust catalytic systems. But, Au exhibits all the properties expected of a metal in term of lustre, hardness, ductility, malleability, high thermal and electrical conductance, high resistance to oxidation and corrosion. A comparison of physical properties between Au and Pt as shown in Table 2.2.

Table 2.2 Physical Properties of Au Compared to Pt

Property	Pt	Au
Atomic number	78	79
Atomic mass	195.08	196.97
Electronic configuration	$[Xe]4f^{14}5d^{9}6s^{1}$	$[Xe]4f^{14}5d^{10}6s^{1}$
Structure	fcc	fcc
Metallic radius(nm)	0.1385	0.1442
Melting temperature (°C)	1769	1064
Boiling temperature (°C)	4170	2808

2.5 Structure and Properties of Zeolite

As before, in 1997 Igarashi *et al.* have investigated the Pt supported zeolites for the preferential oxidation of CO. Varieties of zeolite were used as a support. A supported A-type zeolite catalyst has also been reported for its higher selectivity for preferential CO oxidation than supported mordenite, X-type zeolite and alumina catalysts (where mordenite > X-type zeolite > alumina). Zeolite molecular sieves are crystalline, highly porous materials, which belong to the class of aluminosilicates. The corresponding crystallographic structure is formed by tetrahedrons of (AlO_4) and (SiO_4). These tetrahedrons are the basic building blocks for various zeolite structures, such as zeolites A and X. For instance, the sodium form of zeolite A has a pore opening of approximately 4 Angstroms (4×10^{-10} m), called 4A molecular sieve. If the sodium ion is exchanged with the larger potassium ion, the pore opening is reduced to be approximately 3 Angstroms (3A molecular sieve). On ion exchange with calcium, one calcium ion replaces two sodium ions. Thus, the pore opening increases to be approximately 5 Angstroms (5A molecular sieve). Ion exchange with other cations is sometimes used for particular separation purposes.
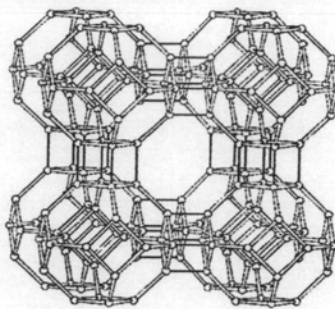
Figure 2.3 Structure of A-Type Zeolite.

Additionally, A-type zeolite was synthesized by conventional and microwave heating techniques and mostly silicates and aluminates were used as starting materials. In 2003, Sathupunya *et al.* directly synthesized A-type zeolite via sol-gel process and microwave heating technique by using silatrane and alumatrane as starting materials. That process has many advantages compare to conventional process such as a higher uniform crystallinity and a narrower particle size distribution.