



CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Fuel cells

2.1.1 Basics of Fuel Cell Technology

Fuel Cell is an electrochemical device that produces electricity by separating the fuel via a catalyst. Hydrogen gas is the basic fuel, but fuel cell required oxygen as well. Every fuel cell has two electrodes, one negative and one positive, named respectively, the cathode and anode. And every fuel cell also has an electrolyte, which conducts the ionic charges between the anode and the cathode, in other words, it allows the flow of electrons in order to create electricity, as illustrated in Figure 2.1. The electrolyte also provides a physical barrier to prevent the fuel and oxidant gas streams from directly mixing. As long as the reactants—pure hydrogen and—oxygen are supplied, the fuel cell will continue to generate power.

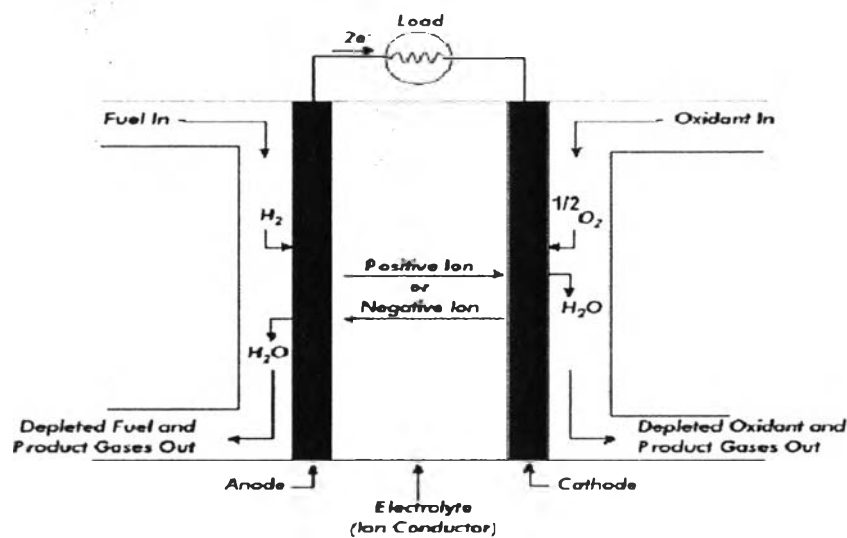


Figure 2.1 Fuel-cell unit and fuel processing (Holland *et al.*, 2007).

Fuel cells come in many varieties; still, they all function in the same general manner. They consist of three segments which are sandwiched together, that are the anode, the electrolyte, and the cathode.

There is no other energy generation technology offers the combination of advantages that a fuel cell does. The advantages include that, it can work at efficiencies two to three times of the fuel burning engine and it also needs no moving parts. Moreover, as it converts the fuel (hydrogen) and oxygen to electrical energy directly, the only by-products are heat and water. Plus, this waste heat from a fuel cell can be used to provide hot water or space heating for a home or office. Without combustion, hydrogen fuel cell systems are also virtually pollution free.

2.1.2 Type of Fuel Cells

There are a variety of fuel cells types. And each type of fuel cells is in different stages of development. Fuel cells can be separated into various categories, according to the type of electrolyte, the combination of type of fuel and oxidant, the temperature of operation, whether the fuel is processed outside (external reforming) or inside (internal reforming) the fuel cell, and etc.

The most common classification of fuel cells is by the type of electrolyte used in the fuel cells and includes Proton exchange membrane (polymer) electrolyte fuel cell (PEMFC), Alkaline fuel cell (AFC), Phosphoric acid fuel cell (PAFC), Molten carbonate fuel cell (MCFC), and Solid oxide fuel cell (SOFC), as shown in Table 2.1.

Proton exchange membrane (polymer) electrolyte fuel cells (PEMFCs) are being used in different applications, mainly for prime power for fuel cell vehicles (FCVs). As a result of the high interest in FCVs and hydrogen, PEMFC has become the most promising fuel cell compare to all other types of fuel cell in the past decade. Even though significant development of PEMFC for stationary applications has been taken place, many researchers and developers are now concentrating on automotive and portable applications.

Table 2.1 Comparison of the fuel cell technologies (Blake *et al.*, 2010)

Fuel Cell Type	Operating Temperature	Electrical Efficiency	Applications
Polymer Electrolyte membrane (PEM)	60–100°C 140–212°F	53–58%	<ul style="list-style-type: none"> • Backup power • Portable power • Transportation • Small distributed generation • Specialty vehicles
Alkaline (AFC)	90–100°C 194–212°F	60%	<ul style="list-style-type: none"> • Space • Military
Phosphoric Acid (PAFC)	175–200°C 347–392°F	>40%	<ul style="list-style-type: none"> • Distributed generation
Molten Carbonate (MCFC)	600–1000°C 1112–1832°F	45–47%	<ul style="list-style-type: none"> • Electric utility • Large distributed generation
Solid Oxide (SOFC)	600–1000°C 1112–1832°F	35–43%	<ul style="list-style-type: none"> • Auxiliary power • Electric utility • Large distributed generation

2.2 Hydrogen Fuel

In today's world, hydrogen gas is used primarily for producing chemicals, but a bright future is expected for it as a vehicle fuel in combination with fuel cells. However, to utilize hydrogen as a future alternative fuel, both the advantages and disadvantages of hydrogen fuel have to be considered.

2.2.1 Advantages and Disadvantages of Hydrogen Fuel

The advantages of hydrogen, as a fuel, are as follow:

- Hydrogen is a very clean fuel that produces minimal emissions when combusted directly or in combination with hydrocarbon fuels.
- Hydrogen can be produced anywhere in the world.
- If Hydrogen is used in place of fuel, hydrogen fuel cells will cost a lot less than filling up a tank of gasoline.
- When hydrogen is used in a fuel cell, the only byproducts are heat and water.
- There will be less dependence on foreign oil for gasoline.
- Use of hydrogen energy will cut down on atmospheric pollution.

In spite of the advantages of hydrogen fuel, there are also several disadvantages of hydrogen, as a fuel. The disadvantages of hydrogen fuel are given below.

- It costs more energy to produce Hydrogen than is earned from it.
- Now hydrogen is generally separated by a reforming process that uses fossil fuels and natural gas. Plus the supplies of natural gas are becoming harder to obtain, and coal is a major source of pollution.
- Currently, the technology to produce, store, and transport hydrogen power at an efficient cost is not available.
- The hydrogen fuel cell car has to be at a certain temperature to perform well. There might be a problem with a hydrogen fuel cell car if it is used in an area where the temperature is very low. Since these cars have water in the fuel cell system constantly, there is a risk it could freeze.
- Hydrogen is highly explosive.

2.2.2 Hydrogen Production Processes

Hydrogen fuel does not occur naturally on earth; therefore, it is not an energy source, but it is an energy vector or carrier. This suggests that it has to be produced from one of the primary energy sources, such as fossil fuels, nuclear, and renewable energy resources, as illustrated in Figure 2.2.

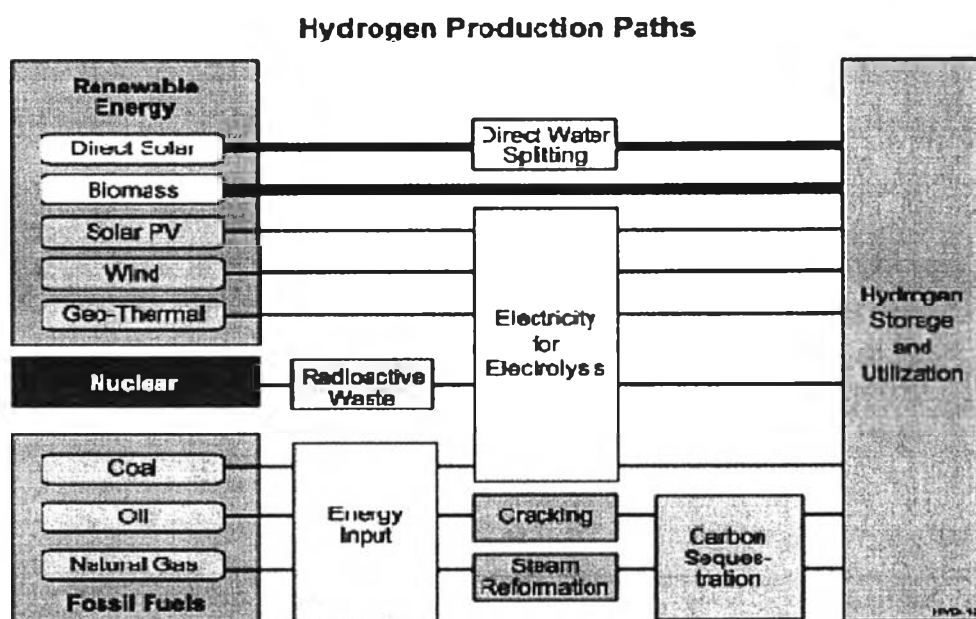


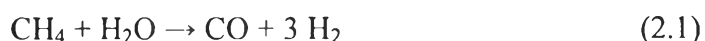
Figure 2.2 Hydrogen production path

(<http://www.fsec.ucf.edu/en/consumer/hydrogen/basics/production.htm>)

And from the figure above, we can see that hydrogen can be manufactured by a number of ways. However, the dominant technology for direct production of hydrogen is steam reforming of hydrocarbons (Methane, Methanol, Ethanol).

2.2.2.1 Steam Reforming

Steam reforming (SR) is also known as steam reforming of methane (SRM) and is the most common process to produce a commercial bulk of hydrogen. Steam reforming is a thermal process. This process allows catalytic reaction to take place that converts steam and lighter hydrocarbons such as natural gas (methane) or refinery feedstock into hydrogen and carbon monoxide (syngas) at the temperature of 700–1100°C. The chemical equation of this reaction is as shown below.



And if there is excess water in the process, syngas will react further to give more hydrogen and carbon dioxide in the secondary reaction, which is

called the water gas shift reaction. The reaction is performed at about 130°C. The reaction can be described in the following equation.



The first reaction (Equation 2.1) is strongly endothermic (consumes heat), the second reaction (Equation 2.2) is mildly exothermic (produces heat). And both of the reactions are reversible in nature.

The produced carbon dioxides are removed before use by means of pressure swing adsorption (PSA) with molecular sieves for the final purification. The PSA works by absorbing all impurities from the syngas stream to leave a pure hydrogen gas.

2.2.2.2 Partial Oxidation (POX)

Partial oxidation is used in refineries for the conversion of light gas (Methane) or residues (liquid, highly viscous hydrocarbons) into hydrogen, CO, CO₂, and water. The partial oxidation reaction occurs when the hydrocarbon is combusted with the limited amount of oxygen, in other words it is partially oxidized in a reformer. The partial oxidation reformation can be accomplished either with a burner or a catalyst. The general chemical equation of the partial oxidation can be described as follows.



The partial oxidation reaction is an exothermic (heat-producing) process. So, this reaction does not require a constant supply of additional heat, like the steam reforming reaction. Thus, this reaction has a higher overall efficiency compared to that of the steam reforming reaction.

2.2.2.3 Autothermal Reforming (ATR)

A third promising method for producing hydrogen, often referred to as autothermal reforming (ATR). This technique combines partial oxidation and steam reformation, with the partial oxidation reaction providing heat for steam.

Autothermal reforming produces syngas by using oxygen and carbon dioxide or steam in a reaction with methane. Methane is partially oxidized in a single chamber, where the reaction takes place.

When the ATR uses carbon dioxide, the H₂ to CO ratio produced is 1:1. And when the ATR uses steam, the H₂ to CO ratio produced is 2.5:1. The reactions can be explained in the chemical equations below, using CO₂:



And using steam:



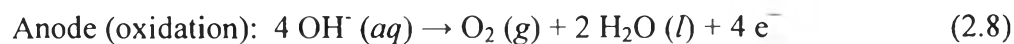
The outlet temperature of the syngas is in the range of 950–1100°C and outlet pressure can be as high as 100 bar.

ATR is different from the steam reforming process as the steam reforming process needs no oxygen but ATR require the use of oxygen. However, the advantage of ATR is that the H₂ to CO ratio can be varied. Besides this is particularly useful for manufacturing certain second generation biofuels, such as DME which needs a 1:1 H₂ to CO ratio.

2.2.2.3 *Electrolysis of Water*

The other conventional technique in producing hydrogen is electrolysis. The electrolytic process decomposes water into its two basic components, hydrogen and oxygen. Electrical current is applied or being pass through water. The current enters the electrolysis device through a negatively charged electrode, a cathode. Subsequently the current passes through the water, and leaves through a positively charged electrode, an anode. Hydrogen is then developed and collected at the cathode, whereas the oxygen is collected at the anode.

The equations of the reactions occurred at the cathode and the anode, are given below.



Combining the half reaction pair yields the overall decomposition of water into oxygen and hydrogen:



Thus, the number of the produced hydrogen molecules is twice the number of the produced oxygen molecules. And assuming at an equal temperature and pressure for both the gases, the volume of hydrogen produced is also twice the volume of the oxygen produced.

2.3 Gas Treatment

Nowadays, there are many methods used in removing impurity gases from the desired product gas, for examples, PSA (<http://www.gas-plants.com/pressure-swing-adsorption.htm>), and Preferential Oxidation.

2.3.1 Pressure Swing Adsorption (PSA)

Pressure swing adsorption (PSA) technology is commonly used in gas production and it is suitable for the many different applications in the refining, petrochemical, chemical, and iron/steel-making industry. However, one the major purpose of the PSA is to separate some gas species from accompanied gases mixture, or in other words, to purify some gas species under pressure according to the species' molecular characteristics and affinity for an adsorbent material. Different gas species are likely to get attracted to different adsorbents, more or less strongly. The higher the pressure, the more gas is adsorbed in a fix-bed. And when the pressure is reduced, the gas is released.

This process can be used for recovery and purification of hydrogen from a wide range of gases streams. The PSA process is an adiabatic process. The PSA procedure is as follows.

- The impure feedstock gas is passed into a cylinder at high pressure.
- The cylinder holds beads of adsorbent material.
- The impurities in the feed gas (for example carbon dioxide) are attracted or adsorbed onto the internal surfaces of the adsorbent beads.
- Hydrogen is left in the vessel, most of which is removed as purified hydrogen product.
- Then the pressure in the cylinder is reduced, and the impurities are released from the adsorbent material.

The main advantages of a PSA process are that it can produce primary H₂ product at a purity of 99.999% and recovery up to 90%, at the same time it also produce secondary CO₂ product at a purity of 99.4% with a recovery of 94%. Another advantage of the process is absence of large amounts of CO₂ in the waste gas (during blow down and purge steps) making it a fuel gas of high calorific value.

2.3.2 Preferential Oxidation or Selective Oxidation of CO

As well known, the research in fuel cells, especially in the portable and transportation applications, has boomed in the last few years because of their high power density and environmental friendly. The proton-exchange membrane fuel cell (PEMFC) is predicted as one of the most promising for these applications. But for their proper operation, the CO content of hydrogen stream after hydrocarbon fuel reforming and water-gas-shift reactions must not exceed 10 ppm, or else the catalyst in PEMFC can be deteriorated. This can be achieved by using the preferential oxidation method, in order to oxidize CO in the excess of hydrogen with the presence of a suitable catalyst.

A suitable catalyst, for the preferential CO oxidation reaction (PROX) in enrich-H₂ gas mixtures for the production of CO-free hydrogen for fuel cell systems, is required. High reaction rate, high selectivity with respect to the undesired side reactions, and stability towards deactivation are the most important requirements

from a catalyst (Manzoli *et al.*, 2008). And the following chemical equations are the desired and undesired reactions for PROX of CO in the presence of excess hydrogen feed.



2.4 Properties of Gold

Gold is a chemical element therefore it can only be found, not manufactured. The symbol that represents gold, in chemistry, is Au. Pure gold has a bright shiny yellow in color and still, it maintains without oxidizing in water or even air. Because of its beauty and attractiveness, it has been served as a precious metal, jewelry, as well as a symbol of wealth and a store of value throughout history.

Apart from its primarily use as a store of value, gold also has some industrial uses arising from its physical qualities. The industrial uses include the use in dentistry, which require a high degree of resistance to bacterial colonization, and in the manufacture of some electronics products, which require high corrosion resistance property of gold. The important properties of gold are shown in the following table.

Table 2.2 Properties of gold

http://www.utilisegold.com/uses_applications/properties_of_gold/

PROPERTIES

Atomic weight	196.97
Atomic number	79
Number of naturally occurring isotopes	1
Melting point (°C)	1064
Boiling point (°C)	2800
Crystal structure	FCC
Electronic configuration	$[\text{Xe}]4f^{14}5d^{10}6s^1$

Density (gcm^{-3})	19.3
Thermal conductivity ($\text{Wm}^{-1}\text{K}^{-1}$)	310
Electrical resistivity micro-ohm m at 20°C	0.022
Hardness (Hv)	25
Tensile stress (MPa)	124
Electrode potential (v)	+1.68
Energy of first ionization ($\text{kJ}\cdot\text{mol}^{-1}$)	888
Energy of second ionization ($\text{kJ}\cdot\text{mol}^{-1}$)	1974.6

Gold is the most malleable and ductile pure metal known. Gold is a good conductor of electricity and heat, like most of the metals. It is also not affected by exposure to air or to most reagents, in other words good resistance to oxidation and corrosion. Plus, it is inert and a good reflector of infrared radiation.

2.5 Deposition-precipitation (DP)

There are many techniques that can be used in preparing catalyst, such as co-precipitation, impregnation, and deposition-precipitation. However, one of the most common used techniques is deposition-precipitation method, in which high catalytic activity for oxidation of CO at a temperature as low as -73°C is observed (Haruta *et al.*, 2001). Shimada *et al.* (2010) examined the influence of the preparation methods for Pt/CeO₂ and Au/CeO₂ catalysts in CO oxidation, still the mean particle sizes of the metal particles increases in the order of deposition-precipitation > solid grinding > impregnation. And the particle shape of Au is hemispherical with the used of deposition-precipitation technique, on the other hand the particle shape of Au is spherical with the used of solid grinding and impregnation. Avgouropoulos *et al.* (2006) also pointed out that the deposition-precipitation is a suitable way to prepare catalyst for CO oxidation because it allows a larger fraction of nano sized gold and copper species to be exposed on the catalytic surface. Plus, Grisel *et al.* (2000) re-

ported that the deposition-precipitation method leads to the smallest average particles in their study.

2.6 Literature Review

The attention in using Au as a catalyst has started to increase significantly from the time when Haruta *et al.* (1989) revealed that supported gold catalysts are quite active for oxidizing CO at low temperature range. However, the activity of the Au catalyst also depended on many factors, for example, preparation method, calcination temperature, concentration of CO and H₂O, and most importantly the types of supports used.

Grisel *et al.* (2002) studied on the oxidation of CO over Au/MgO_x/Al₂O₃ multi-component catalysts in a H₂-rich environment. The result showed that Au/MO_x/Al₂O₃ was able to oxidize CO in the excess of H₂ and at the temperature appropriate for fuel cell applications. The addition of MgO improved both low temperature oxidation of CO and H₂. Plus, the presence of MnO_x and FeO_x in Au/MgO/Al₂O₃ additionally improved CO₂ selectivity and also enhanced low temperature oxidation of CO. Nevertheless, the study based on decreasing of H₂ oxidation should be focused.

Grisel *et al.* (2000) investigated the influence of the preparation of Al/Al₂O₃ on CH₄ oxidation activity. The conclusion was that the catalyst obtained from homogeneous deposition-precipitation was the best performing catalyst, for the reason that homogeneous deposition-precipitation leads to the smallest average particle size (3–5 nm). This idea is also supported by Sakurai *et al.* (2005). They found that the majority of the gold particles dispersed on the CeO₂ support, which was prepared by deposition-precipitation method, were 3 nm in size (or even smaller). The study also revealed that Au/CeO₂ was much more active than Au/TiO₂ and Pt/CeO₂. The importance of the low temperature reducibility of ceria and the promotion effect of gold particles has been suggested (Andreeva *et al.*, 2002). Consequently, this Au/CeO₂ catalyst has started to earn more interest for its high activity for oxidation reaction at low temperatures.

Centeno *et al.* (2006) have done the comparative study of Au/Al₂O₃ and Au/CeO₂-Al₂O₃ catalysts. Deposition-precipitation method was used to prepare both the two gold-containing catalysts, Au/Al₂O₃ and Au/CeO₂-Al₂O₃. Different characterization techniques were also used, i.e. XRD, FTIR and TEM. The Au/Al₂O₃ sample exhibited a much lower catalytic activity in the oxidation reaction of CO than that of the Au/CeO₂-Al₂O₃ sample. This effect was caused by the following propositions, which were the higher dispersion of gold on CeO₂/Al₂O₃ as in comparison to Al₂O₃ and a strong promoting effect of ceria in the oxidation of the Au⁰ sites for adsorption of CO. Evidence was also found that isolated Au⁺ sites were more active in oxidation of CO than metallic gold particles.

Luengnaruemitchai *et al.* (2004) investigated selective catalytic oxidation of CO in the presence of H₂ over Au/CeO₂ catalyst and have pointed out that the CO conversion and selectivity of Au/CeO₂ in the stability test were maintained for 2 days with very small loss of activity. From this result, it can be confirmed that the Au/CeO₂ was quite stable as in comparison with Au/Fe₂O₃, CuO-CeO₂, and Au/TiO₂ catalysts, as reported by Kahlich *et al.* (1999). However, the increasing in concentration of CO₂ and water vapor in feedstream had a significant negative effect on the activity of the Au/CeO₂. This effect was due to the absorption of carbonate and blocking of water on the active site (Luengnaruemitchai *et al.*, 2007).

Calcination temperature also has an effect on the activity of the supported Au catalyst in oxidation of CO, as reported by Park *et al.* (1999). It showed that the higher the calcination temperatures, the lower the activity of the catalysts. X-ray photoelectron spectroscopy and X-ray absorption fine structure (XAFS) results showed that when the calcination temperature was increased, there was a phase transition of gold from Au(OH)₃ through Au₂O₃ to metallic Au for all catalysts. This showed that oxidized gold is more active than metallic gold. Thus, the effect of calcination temperature on oxidation state of gold was proven to be important for the activity of the supported gold catalyst.

Catalytic performance and characterization of Au/doped-ceria catalysts for PROX of CO was investigated by Avgouropoulos *et al.* (2008). The ceria support was modified by the addition of various cations (i.e. Sm³⁺, La³⁺, and Zn²⁺). The result was found out that doping of ceria affected the physicochemical properties and

catalytic performance in the PROX of the catalysts. The doping of Zn^{2+} and Sm^{3+} to the Au/ceria catalyst was found to be more active than undoped ceria. However, La-doped Au/ceria catalyst had the opposite effect. The dispersion of gold depended on the nature of the dopants. The highest dispersion of gold was found on the Au/Zr-CeO₂ catalyst, while the gold particle size was ~5 nm for Au/La-CeO₂ and 3.5–4 nm for Au/Sm-CeO₂. And for undoped catalyst, both high dispersed gold clusters (~1nm) and large gold particle (>10 nm) were found. Furthermore, the presence of excess CO₂ in the reactant feed provoked a decrease in the activity of all catalysts, particularly the undoped catalyst.

Manzoli *et al.* (2008) studied the PROX of CO in H₂-rich gas mixtures over Au/doped ceria catalysts prepared by deposition-precipitation. The dopants used in this work were Sm^{3+} , La^{3+} , and Zn^{2+} . The Raman data collected along the characterization of the bare supports proved that there was a change of CeO₂ environment in the presence of dopants due to the formation of solid solutions, plus there was an increase in formation of oxygen vacancies in the lattice of ceria. The FTIR result verified the important role of metallic gold particle and also confirmed the different in concentration of metallic gold particles on the surface of Au catalysts. The following order of intensity of the band at 2103 cm⁻¹, ascribed to CO adsorption on metallic gold particles was observed: Au/Zn-CeO₂ ≈ Au/Sm-CeO₂ > Au/CeO₂ > Au/La-CeO₂. Additionally, the doping of ceria had a useful effect on CO₂ and H₂O tolerance of doped gold catalysts.