CHAPTER II
BACKGROUND AND LITERATURE SURVEY

2.1 Fuel Cell

A fuel cell is an electrochemical energy conversion device, which continuously converts the chemical energy of a fuel directly into electrical energy. In principle, a fuel cell operates like a battery. Unlike a battery, however, a battery stores the energy in a substance inside and after the use it has to be thrown away for the primary type or recharged appropriately for the secondary type. On the other hand, a fuel cell will harvest the electrochemical energy from a fuel that is fed from outside the cell and directly transformed to the electricity. In addition, a fuel cell can operate continuously as long as fuel and an oxidant are available.

Fuel cell consists of two electrodes (anode and cathode) that are separated by an electrolyte, as shown in Figure 2.1. In an operation, the fuel and the oxidant will be charged to the anode and cathode, respectively. At the anode, the fuel will diffuse into the porous electrode to the reaction zone, where the Pt-catalyst is located, and dissociated into electrons and ions there. Then, the electrons are forced to travel and do work through an external circuit; while the ions will go pass through the electrolyte to the cathode where the oxidant reduction occurs. The oxidant at the cathode will be reduced by the electrons from the external circuit to combine with the ions from the anode.

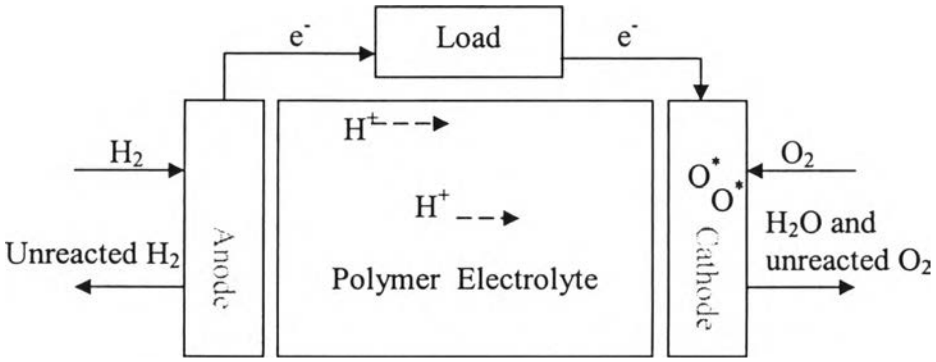

Figure 2.1 Drawing diagram of proton exchange membrane fuel cell.

Fuel cell systems can be categorized according to the working temperature, the operating pressure and the type of electrolyte, etc. The most common and practical one is classified by the type of the electrolyte used. By this mean, fuel cell systems were divided into, Alkaline Fuel cell (AFC), Proton Exchange Membrane Fuel Cell (PEMFC), Phosphoric Acid Fuel Cell (PAFC), Molten Carbonate Fuel Cell (MCFC) and Solid Oxide Fuel Cell (SOFC).

Table 2.1 Fuel cell types distinguished by the electrolyte (Kordesch *et al.*, 1996)

Fuel Cell System	**Operating Temp. (°C)**	**Electrolyte**
Alkaline Fuel Cell (AFC)	60 – 90	35 – 50 % KOH
Proton Exchange Membrane Fuel Cell (PEMFC)	50 – 80	Polymer membrane
Phosphoric Acid Fuel Cell (PAFC)	160 – 220	Concentrated Phosphoric acid
Molten Carbonate Fuel Cell (MCFC)	620 – 660	Li_2CO_3/Na_2CO_3
Solid Oxide Fuel Cell (SOFC)	800 – 1,000	ZrO_2/Y_2O_3

Compared to other types of fuel cells, PEMFC generates more power for given volume or weight of fuel cell. This high-power density characteristic makes them compact and light weight which is suitable for several daily-life applications, such as, computer notebook, cell phone, and automobile. Moreover, it will certainly come to replace the conventional ways of generating and storing energy like combustion engine and battery. Fuel cell system was first to be used in Gemini space program in the 1960s as auxiliary power source and it also provided drinking water for the astronauts. PEMFC has many unique characteristics that makes it appropriates for a portable application and an automobile, such as, quick startup, transient response, long life, and low operating temperature. However, there are some disadvantages as well; for example, water-management problem, expensive electrode catalyst and polymer membrane, and poor CO tolerance. PEMFC requires pure H_2 to be an ideal fuel, especially CO-free H_2 because only a trace amount of CO can significantly decrease the performance of the PEMFC.

2.2 Fuel Processing

Hydrogen is an ideal fuel for the fuel cell, but its storage, distribution and safety constrains are the major issues. The exist infrastructure that being used for oil can not handle the hydrogen. Therefore, the research and development activity are focused on hydrogen production and storage system. Hydrogen can be stored in compressed tank or in materials, such as nanotube, metal hydrides, and a number of chemical compounds. However, in practice storing gaseous hydrogen on-board has many problems, for example, high risk to explode, requirement of big space to reach efficient amount and refilling problem. Therefore, the idea of on-board hydrogen production was very concerned.

Hydrogen is also stored in alcohols or hydrocarbons, such as, methanol, gasoline and methane gas. The hydrogen rich synthesis gas can be obtained by reforming such hydrocarbons and alcohols. The liquid form of alcohol, specifically methanol, and gasoline made them easy to handle and convenient for being used. It can easily be transported and stored by using the exist infrastructure. Moreover, it needs lesser safety constrains than an instance gaseous hydrogen storage.

The concept of the reformer for hydrogen generation from hydrocarbons and alcohol prefers catalytic steam reforming over other methods (partial oxidation, autothermal reforming, propane cracking, etc.) because it is more effective for hydrogen production and gives higher overall system performance. The steam reforming of hydrocarbon produces a mixture of hydrogen and carbon monoxide (syngas) (Equation 8). It is an endothermic reaction ($\Delta H^\circ > 0$) and occurs at high temperatures (> 700 °C) which heat transfer is typically a limiting factor rather than the reaction kinetic. The appropriate catalysts are always required for the steam reforming of most hydrocarbons, and Ni has been proved to be the most active catalyst (Carrette *et al.*, 2001). Normally, the water gas shift reaction (Equation 9) is a further process where CO is converted into CO_2 and H_2.

$$C_nH_m + nH_2O \longleftrightarrow nCO + (n+0.5m)H_2 \qquad (8)$$

$$CO + H_2O \longleftrightarrow CO_2 + H_2 \qquad (9)$$

The reformate from reforming of hydrocarbon always contains some amounts of CO. It has nothing to do with this CO if it is high temperature fuel cells (MCFC or SOFC), which CO can be used as fuel as well. In contrast, for low temperature fuel cells (AFC, PEMFC, and PAFC) only a few ppm of CO is allowed to be in the fuel. There are several ways to remove CO from the reformate stream. The water gas shift reaction (WGSR) is used in the first step to convert CO to CO_2 hereby producing more hydrogen. With the WGSR the left CO would be in a range of 1%, the next CO removal process has to be very efficient because it needs to remove CO down to only few ppm in which PEMFC can be tolerate. Variety of strategies can be used in this step, for examples, Pd-membrane filtration, methanation (Equation 10) and selective CO oxidation (Equation 11).

$$CO + 3H_2 \longleftrightarrow CH_4 + H_2O \qquad (10)$$

$$CO + 0.5O_2 \longleftrightarrow CO_2 \qquad (11)$$

Pd alloy membrane is very effective for removal of CO from the reformate stream, but it requires rather high pressure difference and a relatively high temperature which reduces the performance of the overall system (Carrette *et al.*, 2001). The reduction strategy or methanation is another approach for CO removal. In this process hydrogen is reacted with CO to form methane and water. The main disadvantage of this method is that every mole of removed CO needs three mole of hydrogen which leading to reduction of the overall efficiency as well. Therefore, the selective CO oxidation seems to be the most practical and economical way for CO removal. This can be achieved by selective oxidizing CO to CO_2. In addition to preventing H_2 loss, opposed to the methanation process, it still achieves complete conversion at relatively low temperature with two stage reactor. (Dudfield *et al.*, 2001)

2.3 Zeolites

Zeolite is a microporous crystalline aluminosilicate material. The zeolite structure is made up of TO_4 where T represents Si or Al with oxygen atoms connecting neighboring atoms. If there are only Si atoms in T positions, the structure of this kind is silica (SiO_2) which is an uncharged structure. Once the Al is incorporated into the Si framework, the +3 charge of Al made the framework negatively charged, and the extraframework cations are required in order to keep the overall framework neutral. (Equation 12)

$$M^{m+}_{n/m} \;\bullet\; [Si_{1-n}Al_nO_2] \;\bullet\; nH_2O \qquad (12)$$

(extraframework cation) (framework) (sorbed phase)

The Si/Al ratio can vary from 1 to infinity, the completely siliceous form being polymorphs of SiO_2. The lower limit of Si/Al is 1 because any two AlO^-_4 tetrahedra do not favor to sit next to each other due to electrostatic repulsion between them. In this work we focused on a Zeolite A, which is one of the most important industrial zeolite and has a void volume fraction of 0.47, with a Si/Al ratio of 1. Zeolite A is widely used in variety of applications, for examples, using as water softening in detergents or as additive in polyvinyl chloride (PVC) thermoplastic in industrial gas drying or in separation of linear and branched hydrocarbons, etc. The Composite Building Units (CBUs) of the zeolite A (LTA) are the double 4-ring, β cage and α cage (Figure 2.2), which is formally a cavity known as an α cage for historical reasons.

Generally, zeolite A has a three dimensional pore system. Molecules can diffuse into the cage in all three directions through an eight member oxygen ring windows (Figure 2.3). Zeolite A is available in three different grades, which are types 3A, 4A and 5A. These grades are unique from one another due to their chemical composition and aperture size. Type 3A is the potassium form of the zeolite that has aperture size of 3 Å and will adsorb those molecules which have a critical diameter of less than 3 Å. For type 4A and 5A are sodium and calcium forms of zeolite A, respectivly. Similar to 3A zeolite, 4A and 5A zeolites have 4 and 5 Å aperture size which can adsorb molecules with critical diameter less than 4 and 5 Å, respectively.

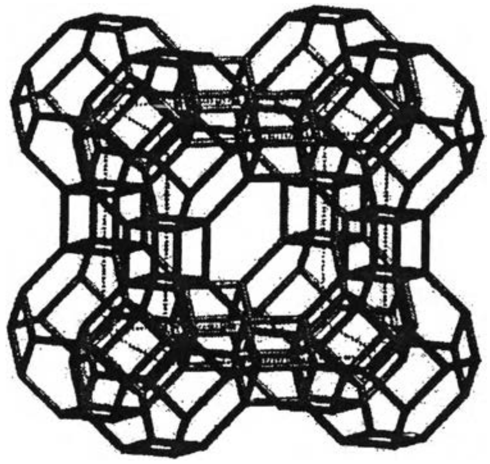

Figure 2.2 Structure of zeolite A.

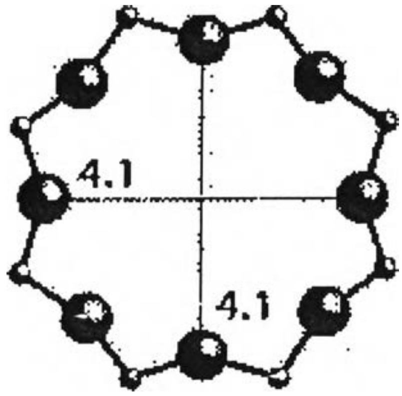

Figure 2.3 8-ring window viewed along <100> plan.

Zeolite A is normally synthesized in a gelling process. Sources of alumina (usually sodium aluminate) and silica (usually sodium silicate) are mixed in basic aqueous solution to give a gel. Then the gel will be heated by hydrothermal heating technique to let the gel transform to zeolite. Besides the conventional hydrothermal heating technique, the microwave heating technique can be used, as well. It provides many advantages over the conventional technique, such as, short synthesis time, narrow particle sized distribution, broad synthesis composition and high purity (Xu *et al.*, 2001). Moreover, any types of alumina and silica can also be used as starting materials for zeolite synthesis. By using these silatrane and alumatrane as the precursors, zeolite was successfully developed via sol-gel process and microwave heating technique (Sathupanya *et al.*, 2003).

2.4 Selectivity of CO Oxidation Catalysts

It is well known that only a trace amount of CO can severely depress the efficiency of PEMFC by poisoning the Pt electrode. Thus, the CO content in H_2-rich stream has to be got rid prior to PEMFC down to <100 ppm for the state-of-art Pt-Ru electrode. In order to achieve that goal, water gas shift reactor (WGSR) connected with preferential oxidation of CO (PROX) or selective CO oxidation reaction in series has been used. The effluent from WGSR contains about 0.5-1% CO, will be further reduced to ppm level at the PROX unit. Where needing a very active catalyst to selective by oxidize CO because the catalyst has to oxidize about 1% CO to less than 100 ppm without oxidizing large amounts of H_2.

Several catalysts for PROX have been developed. In general, theses catalysts involve high loading of precious metal on high surface area support, especially alumina (Al_2O_3). The most extensively studied metal is Pt and Pt/Al_2O_3 catalyst has tentatively been investigated by many authors, and used as a reference for newly synthesized catalysts.

Oh and Sinkevitch (1993) reported that they can achieved 100% conversion of CO with 0.5% Pt/Al_2O_3 at 180 °C. Kahlich *et al.* (1997) claimed that with 0.5% Pt/Al_2O_3 catalyst, it is not possible to have more than 80% conversion of 1% CO with 1% O_2 in the presence of H_2 even at temperature as high as 250 °C. On the other hand, Manasilp and Gulari (2001) reported the results consistent with Kahlich *et al.* (1997). They examined 1 and 2% Pt/Al_2O_3 prepared by sol-gel method and found that the 2% sol-gel Pt/Al_2O_3 gave maximum CO conversion of 80% at 170 °C with constant selectivity around 45-50% at temperature below 170 °C. Furthermore, at temperature about 170 °C both conversion and selectivity drastically drop to 10% and 5% at 210 °C.

In addition to Pt catalysts, Rh and Ru were found to be the most appropriate catalyst for the PROX. Rh/Al_2O_3 and Ru/Al_2O_3 can completely oxidize CO at as low temperature as 100 °C with high selectivity (Oh and Sinkevitch, 1993). Moreover, 99.9% CO conversion was obtained by Ru/Subunit (porous carbonaceous material) catalyst at temperature range of 105 – 120 °C (Snytnikov *et al.*, 2003).

Besides alumina, another materials were also used as support for Pt. Pt/Sibunit (porous carbonaceous material) was found to oxidize CO at lower temperatures compared to Pt/Al_2O_3. It showed 99.8% CO conversion at temperature from 135° to 160 °C (Snytnikov *et al.*, 2003). In addition, it has been considered that CeO_2, ZrO_2 and CeO_2-ZrO_2 mixed oxide are the active supports for oxygen storage (Liu *et al.*, 2002). Therefore, Pt/$Ce_xZr_{x-1}O_2$ (x=0, 0.15, 0.5, 0.68, 1) catalysts have been examined for the selective CO oxidation reaction by Wootch *et al.*, 2004. It turned out that Pt/CeO_2 displayed the highest CO conversion and selectivity of 78 and 80%, respectively, at temperatures around 100 °C and at λ=1. Whereas Pt/$Ce_{0.15}Zr_{0.85}O_2$ catalyst reported by Marino *et al.,* 2000, showed the best performance.

Variety of zeolites, including A type zeolite, mordenite and X type zeolite, were examined as a catalyst support. It was found that Pt supported on zeolite catalysts show better selectivity than the conventional Pt supported alumina catalyst, in the order of A type zeolite>mordenite>X type zeolite>alumina (Igarashi *et al.*, 1997). Pt supported on 3, 4, and 5 A zeolites were further examined and the Pt-3A showed the best selectivity. It completely oxidized CO to CO_2 in a wide range of temperature, from 185°-220 °C; in contrast, at this range of temperature the Pt-4A and Pt-5A could reduce CO concentration down to 1300 and 675 ppm, respectively (Rosso *et al.*, 2004).

Furthermore, some promoters have been used for the supported Pt catalysts. Özkara and Aksoylu (1999) investigated the selective oxidation of CO in a H_2-rich gas stream over a series of Pt-Ce and Pt-Sn catalysts supported on activated carbon. Three types of activated carbons including grinded and HCl washed activated carbon (AC1), air-oxidized form of activated carbon (AC2) and HNO_3 oxidized form of activated carbon (AC3) were used as catalyst supports. They found that among these catalysts, the 0.25 % SnO_x - 1 % Pt/AC2 gave stable activity during the reaction due to their alloy content providing sites for O_2 adsorption and displaying the highest activity of 80 % CO conversion.

Many spectroscopic techniques, which are Fourier-Transform Infrared spectroscopy (FT-IR), X-ray Photon Spectroscopy (XPS), High-Resolution Transmission Electron Microscope (HRTEM), Energy Dispersive X-ray analysis (EDAX) and Diffuse reflectance Fourier-transform Infrared Spectroscopy (DRIFTS), were used to study the structural characteristics and mechanisms of the Fe oxide promoted Pt/alumina catalyst compared to an un-promoted one in the selective CO oxidation.

Using a TEM and a HRTEM techniques it was found that the Pt particles, both of promoted and un-promoted catalysts, were highly dispersed with particle size about 2 nm. These were confirmed by XRD where the Pt metal particle size of 1.9 nm was observed for both catalysts. Moreover, no separated phase of Fe oxide was observed by XRD and/or HRTEM, which suggested high distribution of Fe oxide in the catalyst. All those implied that the presence of Fe oxide in the catalyst did not have effect on the Pt metal particle size and distribution. Moreover, Fe oxide preferred to associate only with Pt metal, evidenced by EDX mapping results. In order to check the valence state of the Fe, the XPS technique was used. The results showed that only oxide state of Fe was present and no Pt-Fe alloy was observed.

By comparing the DRIFTS spectra of CO chemisorbed of promoted and un-promoted catalysts, some information were obtained, those were;

1. CO was less uptake by promoted catalysts, about 75% of the un-promoted catalysts.
2. The promoted catalysts had less adsorbed bridge CO.
3. The surface of the support in the promoted catalysts had more carbonate-like species.
4. The IR spectrum of the sample without Fe oxide did not show CO_2 bands.
5. No CO bands on Fe^{2+} or Fe^{3+} was observed.

In addition, the CO band shift (~ 3 cm^{-1}) toward lower wave number indicated the electron-rich property of the promoted catalysts comparing to the un-promoted one. All of those results could be understood that:

1. The Fe oxide was located on the surface of Pt metal particle and partially covered the surface, and as a consequence, it decreased the amount of

CO adsorbed.

2. The Fe oxide strongly interacted with the Pt metal and modified an electronic property of the Pt, which was evidenced by the further elongation of the CO adsorbed band.
3. CO did not adsorb on Fe oxide.
4. Fe oxide had provided active oxygen for CO oxidation, hence, the promoted catalyst was more active for CO oxidation.

Moreover, most of Fe oxide was presented together with the Pt. The Fe oxide preferred to sit on the Pt particle and covered some area of the Pt particles. In order to check the state of the Fe in promoted catalysts, XPS and TOF-SIMS studies were conducted. The results suggested that only oxide phase of Fe was presented and no Fe-Pt alloy was formed.

It has been reported that the presence of Fe oxide in the promoted catalyst provides active oxygen for CO oxidation (Liu *et al.*, 2002). New Pt-Fe/mordenite (M) catalysts have been proposed by Watanabe *et al.*, (2003). Pt-Fe/M with 2:1 Pt/Fe ratio revealed the best performance, 100 % CO conversion and selectivity were achieved at temperatures below 200 °C. Normally, the reformate gases contain CO_2 and H_2O, therefore the effect of them on the catalytic performance with 1%CO, 0.5% O_2, 25% CO_2, 20% H_2O, H_2 balance were carried out. The complete CO removal without H_2 loss was obtained again with narrower temperature window (80° – 150 °C). The reason for this has not yet provided. However, the Temperature Programming Desorption (TPD) and Fourier Transform Infrared Spectroscopy (FTIR) measurements were measured, and revealed that CO adsorption on the Pt site was weakened, probably allowing the adsorbed CO to react with adsorbed O_2 easier.

Korotkikh and Farrauto (2000) had investigated the catalytic activity of promoted Pt by base metal oxide supported on γ-Al_2O_3 (promoted Pt/Al_2O_3). They found that this promotion enhanced conversion of both CO and H_2. As a result, the CO conversion was significantly increased from 13.2% to 68.0% at 90 °C and at stoichiometric condition while the selectivity did not change much (78 and 82 %). They claimed that this was a consequence of providing sufficient dissociated oxygen by the base metal oxide. Moreover, they also displayed the effect of some reaction conditions, such as, temperature, space velocity and the effects of H_2O and CO_2, as well. In the presence of CO_2 the reactant gas slightly increased the CO conversion while the selectivity remained unchanged. In addition, 3% of H_2O decreased the CO conversion from 75% to 68%, but when adding more H_2O to 10%, it did not change the catalyst activity and selectivity.

In most of those studies, however, the composition of reaformate was simplified by using H_2/CO mixture. Therefore, the realistic reformate containing CO_2 and H_2O has been considered in this work. This includes the preliminary results of Pt/A type zeolite (LTA) and the conventional Pt/Al_2O_3. Further study is the investigation of the Fe promoted Pt/LTA catalytic activity. Pt-Fe/LTA with different Pt/Fe ratio is tested in the temperature range from 80° to 300 $^{\circ}C$. The effect of CO_2 and H_2O is also studied.