CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Fuel Cell

Nowadays, there are five main types of fuel cells, which convert chemical energy directly into electrochemical energy with high efficiency and low emission of pollutants, namely the alkaline fuel cell (AFC), the polymer electrolyte membrane fuel cell (PEMFC), the phosphoric acid fuel cell (PAFC), the molten carbonate fuel cell (MCFC), and the solid oxide fuel cell (SOFC).

2.1.1 Phosphoric Acid Fuel Cell (PAFC)

PAFC is in the first stages of commercialization since it shows relative tolerance for widely applications. Concentrated phosphoric acid (H_3PO_4) in liquid form is used as the electrolyte in this fuel cell. The electrolyte is retained in a small pore matrix made from Teflon boned silicon carbide. Addition of electrolyte may be required after operate for many hours because some of it can be entrained in the fuel streams. The operating temperatures of PAFC is typically around 200°C and can be operates up to 220 °C (Hirschenhofer *et al.*, 1998).

2.1.2 Alkaline Fuel Cell (AFC)

AFC can be operated at higher temperature than PAFC (up to 250°C) by using concentrated potassium hydroxide (KOH) aqueous solution as the electrolyte. A solid matrix, which usually made from asbestos, is used as an electrolyte container and a various types of catalyst can be used such as noble metal, nickel, spinels, and metal oxide (Song, 2002). The advantage of this fuel cell is simple in design and cheap. However, there are two major factors limiting the AFC, which are pure hydrogen requirement and carbon dioxide sensitivity.

2.1.3 Molten Carbonate Fuel Cell (MCFC)

The MCFC has been developed to a high degree of sophistication for running on fuels e.g. natural gas since it offers high fuel-to-electricity efficiency. This fuel cell operates at high temperature (about 650°C) and the cell performance is very sensitive to operating temperature. The salt mixture, usually consists of lithium carbonate (Li_2CO_3) and potassium carbonate (K_2CO_3), is used as electrolyte and can be a good ionic conductor when it melted. On the other hand, mobile and corrosive electrolyte is the main disadvantage of MCFC.

2.1.4 Solid Oxide Fuel Cell (SOFC)

Ceramic is used as a solid-phase electrolyte in SOFC to overcome the electrolyte corrosion problem in MCFC. The operating temperature of SOFC is typically in the range of 800 - 1,000 °C to achieve adequate ionic conductivity. However, it has drawbacks because of the materials including the sealants requirement and the longer start-up time.

2.1.5 Polymer Electrolyte Membrane Fuel Cell (PEMFC)

PEMFC have been extensively studied over the last decade because they provide clean energy and good commercial viability. A solid polymer membrane is used as the electrolyte in the cell. An order of magnitude higher power density than any other fuel cell is the outstanding properties of PEMFC. Moreover, the corrosion and the electrolyte management problems are eliminated by the use of a solid polymer electrolyte. On the other side, they still suffer from high-cost of the catalyst used in membrane electrode assembly (MEA).

2.2 Polymer Electrolyte Membrane Fuel Cell

In the 1960s, a polymer electrolyte membrane (PEM) or proton exchange membrane was firstly used in a fuel cell as an auxiliary power source in the space aviation. A PEMFC is an electrochemical cell that is fed hydrogen and oxygen. The oxidation of hydrogen occurs at the anode and releases the protons, which is conducted through the polymer electrolyte membrane to the cathode. The electrons released from hydrogen travel along the electrical detour to the cathode and generate an electrical current. The reduction of oxygen occurs at the cathode and then water is produced. Figure 2.1 schematically shows the described reactions.

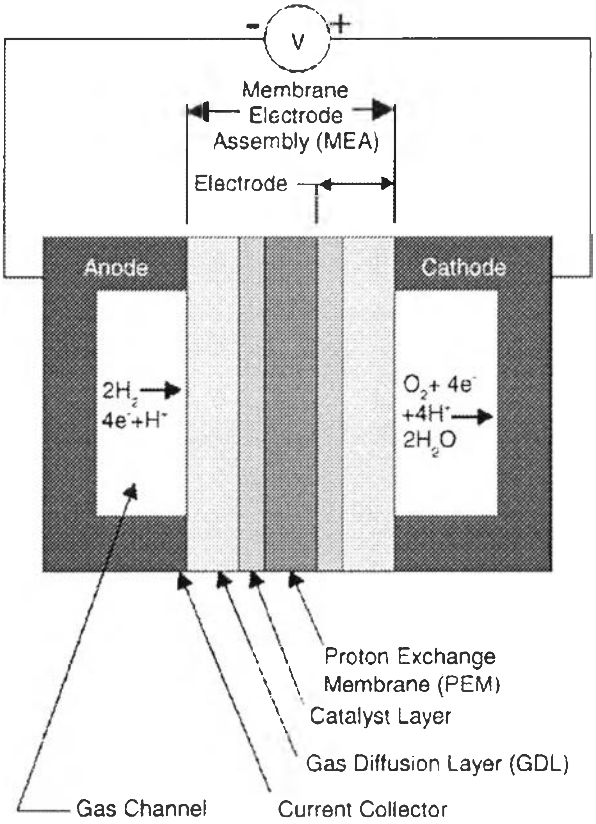

Figure 2.1 Schematic of a single typical PEMFC (Litster and McLean, 2004).

The important part is membrane electrode assembly (MEA), which is mounted at the core of PEMFC as shown in figure 2.1. There are three components in MEA consist a polymer electrolyte membrane, catalyst layer, and gas diffusion layer (GDL).

2.2.1 Catalyst Layer

The catalyst layer or active layer is located between PEM and GDL. The most commonly used catalysts in PEMFC are platinum (Pt) and platinum based alloys due to their high catalytic activity, chemical stability and exchange current density (Sharma and Pollet, 2012). However, the high cost of platinum make it not available commercially. To decrease platinum usage in PEMFC, supported metal catalysts become an excellence option.

2.2.2 Gas Diffusion Layer

The porous gas diffusion layers in PEMFC are made of porous carbon paper or woven carbon cloth, with a thickness in the range of 100 - 300 micrometer, and located on the back of the catalyst layers. The GDL provide not only the electrical conductor that transports electrons to and from the catalyst layer, but also structural support for the electrodes (Dicks, 2006)

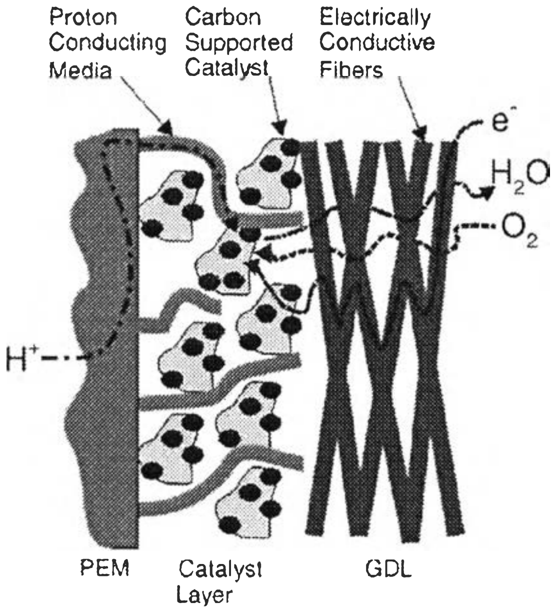

Figure 2.2 Transport of protons, electrons, and gases in the PEMFC (Litster and McLean, 2004).

The transport in MEA consists of

- the transport of protons form the polymer electrolyte membrane to the catalyst
- the transport of electrons from the current collector (trough the gas diffusion layer) to the catalyst
- the transport of the reactant and gases to and from the catalyst layer and the gas diffusion layer

2.3 Carbon Monoxide Removal

Because only small amounts of carbon monoxide (CO) in hydrogen (H_2) stream causes decreasing in efficiency of PEMFC, CO should be eliminated to a trace-level. Different method can be used to remove CO including selective diffusion, selective methanation, and preferential oxidation (Park *et al.*, 2009).

2.3.1 Selective Diffusion

Various types of membranes such as metal alloys and porous ceramic have been applied to remove CO by selective diffusion of the H_2 through the membrane. The major requirements of membrane properties are high selectivity to H_2 and high H_2 permeability. The palladium (Pd) metal has been well known as the representative material for H_2 separation because of its high H_2 permeability, good mechanical characteristics and highly catalytic surface. The permeation of H_2 through Pd involves following three steps (Ockwig and Nenoff, 2007).

(1) Reversible dissociative chemisorption of hydrogen on the Pd surface.

(2) Reversible dissolution of surface atomic hydrogen in the bulk layers of the Pd.

(3) Diffusion of atomic hydrogen in the membrane.

2.3.2 Selective Methanation

The main gaseous components exit from water-gas shift reactor are CO, CO_2 and H_2. The following reactions can be carried out over the hydrogenation catalyst in the selective CO methanation.

$$CO(g) + 3H_2(g) \rightarrow CH_4(g) + H_2O(g) \qquad \Delta H^o_{298} = -206 \text{ kJ/mol}$$

$$CO_2(g) + 4H_2(g) \rightarrow CH_4(g) + 2H_2O(g) \qquad \Delta H^o_{298} = -165 \text{ kJ/mol}$$

The advantage of selective CO methanation is this reaction does not require any gases such as air in the PROX reaction.

2.3.3 Preferential Oxidation (PROX)

Preferential oxidation (PROX) has been developed during the last decade and become an interesting reaction for removing very small amounts of CO from the gaseous stream to a parts-per-million (ppm) level. The following reactions can be carried out over the oxidation catalyst in the PROX system.

$$CO(g) + \tfrac{1}{2}O_2(g) \rightarrow CO_2(g) \qquad \Delta H^o_{298} = -283 \text{ kJ/mol}$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow 2H_2O(g) \qquad \Delta H^o_{298} = -242 \text{ kJ/mol}$$

Although this PROX system requires the introduction of air or oxygen, the smaller amounts of hydrogen can be consumed compared with those of the selective methanation.

2.4 Metal Catalysts for Carbon Monoxide Oxidation

In 1993, Oh and Sinkevitch compared various alumina-supported catalysts for the preferential CO oxidation (PROX) and found that Ru/Al_2O_3 and Rh/Al_2O_3 were more selective than Pt/Al_2O_3. After that, a number of more active catalysts for CO oxidation have been reported, such as metal oxide, supported gold catalysts, supported Pt-based and supported noble metal catalysts. Taylor *et al.* (1999) presented the first results showing that copper zinc oxide catalysts, prepared by co-precipitation, were effective for the ambient temperature carbon monoxide oxidation and displayed much higher activity for reaction than the commercial hopcalite catalysts which was the most widely used catalyst at that time.

Pillai and Deevi (2006) studied on ceria-supported gold catalysts for room temperature oxidation of CO to CO_2. Au/CeO_2 catalysts containing as low as 1 wt.% Au, prepared by deposition-precipitation technique, was found to be a highly active catalyst with complete CO conversion and high activity for a prolonged period. They suggested that the presence of highly dispersed gold particles in close contact with the ceria surface defects was vital for the superior performance of the catalyst.

Scirè *et al.* (2010) reported a comparative study on ceria supported group IB metal catalysts (Au/CeO_2, Cu/CeO_2 and Ag/CeO_2) and proposed that a higher atomic radius of the IB metal and the presence of smaller crystallites of both IB metal and ceria resulted in a larger enhancement of reactivity of surface oxygen on ceria.

Horvath *et al.* (2011) promoted 0.04-7.4 wt.% CeO_2 into SiO_2-supported Au catalyst and resulted in CeO_2 decoration of 1-3 nm over Au nanoparticles, which induced high CO oxidation activity.

Recently, Sakwarathorn *et al.* (2011) prepared Au/CeO_2 catalysts via modified deposition-precipitation for preferential oxidation (PROX) of CO in H_2-rich stream. The highest catalytic activity was obtained by using NaOH as a precipitating agent at pH 7 because of well-dispersed of Au nanoparticles on the support surface.

Silver received much attention recently because of their large surface areas and unique physio-chemical and biological properties. Silver is an excellent catalyst for many catalytic oxidation reactions include ammonia oxidation and oxidation of methane, organic volatile compounds and carbon monoxide. In industrial, it is used for oxi-dehydrogenation of methanol to formaldehyde and for epoxidation of ethylene to ethylene epoxide. NO_x abatement is one of applications which Ag has remarkable performances. Miyadera and Yoshida (1993) were one of the first to observed high selectivity of NO_x to nitrogen and high resistance to SO_2 poisoning over 2 wt.% silver doped alumina catalysts. Brosius *et al.* (2005) reported that the Ag/Al_2O_3 is an active catalyst for selective catalytic reduction (SCR) of NO_x. Moreover, Park and Boyer (2005) also found that the lean-NO_x performance of $Ag/\gamma\text{-}Al_2O_3$ catalysts for NO_x reduction was dependent on the Ag loading.

Frey *et al.* (2008) prepared Ag/TiO_2 catalysts with different Ag loadings by oxalate co-precipitation using $AgNO_3$ and $Ti(OCH(CH_3)_2)_4$ as precursors. They reported that 10% (w/w) Ag/TiO_2 catalyst exhibited low-temperature CO oxidation activity with $T_{50} = 333$ K.

The highly dispersed Ag nanoparticles on modified carbon nanotubes (MCNs) was prepared by Dai and co-workers (2011). They reported that smaller particle size of Ag nanoparticles showed higher activity for CO oxidation at low reaction temperatures.

Yu *et al.* (2011) prepared the ultrasmall Ag nanoparticles supported on silica by introduce the functional monomer salicylaldimine Schiff base into a SiO_2 matrix and tested it for CO oxidation. The activity of ultrasmall silica-supported Ag nanoparticles catalyst was depended on the particle size of Ag. The suitable Ag particle size for CO oxidation was in the range of 3-5 nm.

Many researchers have studied on ceria, which has been used as a support in catalytic CO oxidation, due to its remarkable oxygen storage capacity (OSC) and redox ability. Imamura *et al.* (2000) investigated the behavior of the lattice oxygen of silver on silver/ceria composite oxide, prepared by co-precipitation, in methane and carbon monoxide oxidation. In the high temperature oxidation of methane, silver (I) oxide decomposed and aggregated to large particles of metallic silver and rapidly deactivated. On the other hand, silver retained high activity during the low temperature oxidation of carbon monoxide. It was found, however, that ceria accelerated the desorption of the lattice oxygen of silver, which was assumed to be related to the well-known oxygen storage function of ceria. Although silver tends to be converted more easily to metallic state in the presence of ceria, the function of ceria of sustaining the dispersed state of silver will help to maintain the high activity of the latter in the oxidation of carbon monoxide.

The possible mechanisms of soot oxidation over Ag/CeO_2 catalyst were proposed by Shimizu *et al.* (2010). One is that carbon was oxidized by a reactive oxygen species as atomic oxygen species and CO intermediate reacts immediately with another reactive oxygen species to produce CO_2. The other mechanism is that carbon was oxidized by the reactive molecular species such as O_2^- to produce CO_2. Thus, they tentatively denote O_n^{x} (n = 1 or 2, x = 1 or 2) as a possible reactive oxygen species in Figure 2.3.

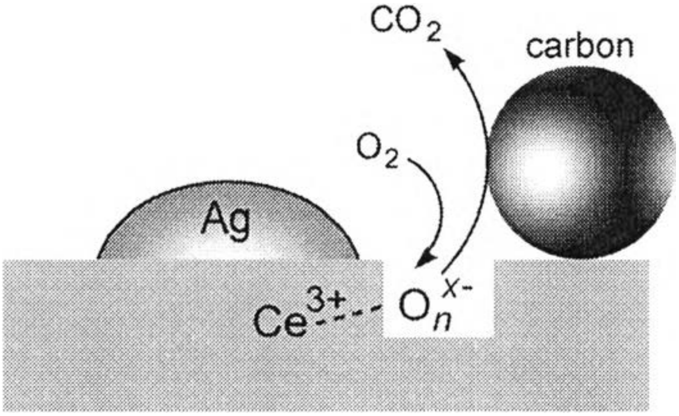

Figure 2.3 Schematic mechanism of soot oxidation over Ag/CeO_2 catalyst (Shimizu *et al.*, 2010).

Kang *et al.* (2012) investigated CO oxidation over Ag/CeO_2 and CeO_2 catalysts prepared by sol-gel method. They found that the CO conversions no significantly increased with reaction temperature on the CeO_2 (from room temperature to 300 °C). In contrast, a significant increase of CO conversion on Ag/CeO_2 was observed up to 180 °C and the complete conversion was achieved at 250 °C. Kang and coworkers suggested that a part of Ag incorporated into the fluorite lattice of CeO_2 and aroused the expansion of the lattice. The inserted Ag increased the crystal defects of CeO_2, which might accelerate the activation of lattice oxygen and formation of oxygen vacancies. Moreover, the presence of Ag also improved the reducibility of surface oxygen on CeO_2 and promoted the oxygen transfer in the CO oxidation.

2.5 Ceria and Ceria-supported Catalysts

Ceria and ceria-supported catalysts are very popular in preferential oxidation (PROX) reaction to remove carbon monoxide (CO) due to its high oxygen storage capacity and redox capability, according to the reactions:

$$2\,CeO_2 + CO \rightarrow CO_2 + Ce_2O_3$$

$$Ce_2O_3 + \tfrac{1}{2}\,O_2 \rightarrow 2\,CeO_2$$

2.5.1 Outstanding Characteristics of Ceria

Ceria is one of the interesting metal oxides because of their high oxygen storage capacity and the capacity of cerium (Ce) to switch between the two oxidation states of Ce^{3+} and Ce^{4+}. Under oxidizing conditions, Ce^{3+} can take up oxygen and switch to Ce^{4+} (CeO2). When they are under reducing conditions, they can release O_2 to the surrounding and then switch to Ce^{3+} again. So, this process is a redox cycle that can repeat many times. Moreover, ceria also has been found to increase the reaction rate of CO oxidation by lower the activation energy. (Shalabi *et al.*, 1996).

2.5.2 Methods of Ceria Synthesis

There are several methods to synthesize nanosized ceria powders.

2.5.2.1 Solid-state Reaction

In 2000, Xin *et al.* developed a novel method, solid-state reaction, to synthesize ceria ultrafine particles (around 3 nm). Ammonium cerium(IV) nitrate $[(NH_4)_2Ce(NO_3)_6]$ or cerium(III) nitrate hexahydrate $[Ce(NO_3)_3.6H_2O]$ can be use to prepare ceria by mixing with sodium hydroxide (NaOH). The advantages of the solid-state-reaction method are simple, cheap and convenient. In addition, this method also give high yields of products and diminish contaminate due to involving a few solvents.

2.5.2.2 Mechanochemical Processing

The synthesis of ceria nanoparticles via mechanochemical processing was reported by Tsuzuki and McCormick (2001). The ultrafine ceria were obtain by calcined the as-milled powders of cerium(III) hydroxide [$Ce(OH)_3$], which were formed by a solid-state reaction between cerium(III) chloride ($CeCl_3$) and sodium hydroxide (NaOH) in a sodium chloride (NaCl) matrix.

2.5.2.3 Sol-gel

In 2006, Parinyaswan *et al.* reported that the ceria support was successfully prepared by sol-gel method. An aqueous solution of urea [$CO(NH_2)_2$] was mixed with a $Ce(NO_3)_3.6H_2O$ solution and aged at 100°C for 50h. The sol-gel ceria supported catalysts showed higher CO conversion and selectivity than commercial ceria. However, the maximum CO conversion and selectivity of ceria that synthesized via sol-gel method (41% at 130°C and 65% at 50°C, respectively) still much lower than other synthesis methods.

2.5.2.4 Precipitation

Precipitation method is the simple one for ceria synthesis because this method requires only cerium precursor and precipitating agent. Different precipitating agents are used to prepared ceria powder under basic conditions e.g. NH_3 (Zhang *et al.*, 2009), NaOH (Pinjari and Pandit, 2011), Na_2CO_3 (Sakwarathorn *et al.*, 2011). Moreover, some of the additives or surfactants can be added to modify the properties of ceria such as crystalline structure, porosity and pore size (Terribile *et al.*, 1998).

2.6 Polyelectrolytes

Polyelectrolyte has been used in various purposes, one of its interesting advantages is to use as a capping agent for nanoparticle synthesis. In 2006, Limsavarn *et al.* synthesized silver nanoparticles by using a copolymer of styrene sulfonate and maleic monomers. The formation of silver nanoparticle was confirmed by the silver plasmon absorbance (400 nm) in UV-Vis spectra.

The silver nanoparticle was also successfully prepared by the chemical reduction of silver nitrate in the presence of humic acid. Humic acid was used as a capping agent because it has carboxylate group that can stabilized silver ions. (Dubas and Pimpan, 2008)

Dubas *et al.* (2011) also studied on surgical sutures coating for antimicrobial properties. Using the LbL technique, the silver nanoparticles capped with sodium alginate (1 : 0.1 mM) were deposited on the polyamide surgical sutures and showed the highest antimicrobial efficiency.

The molecular structures of most common used polyelectrolytes are showed in Figure 2.4.

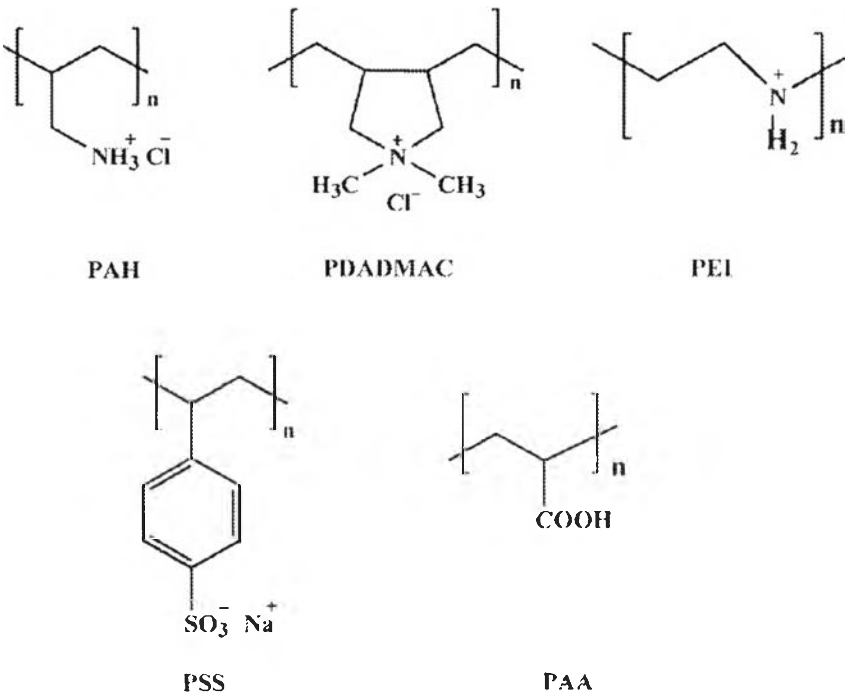

Figure 2.4 Structures of most commonly used polyelectrolytes (Shi *et al.*, 2004).