

## CHAPTER II

### LITERATURE REVIEW

#### 2.1 Background

Fuel cell can be classified according to the working temperature, the operating pressure, and the type of electrolyte, etc. Referring to the electrolyte type however, is the most common method. Following this classification, there are five types of fuel cell as listed in Table 2.1.

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

Fuel cell system	Temperature range (°C)	Electrolyte
Alkaline Fuel Cell (AFC)	60-90	35-50 % KOH
Polymer Electrolyte Fuel Cell (PEM)	50-80	Polymer membrane
Phosphoric Acid Fuel Cell (PAFC)	160-220	Conc. phosphoric acid
Molten Carbonate Fuel Cell (MCFC)	620-660	$\text{Li}_2\text{CO}_3/\text{Na}_2\text{CO}_3$
Solid Oxide Fuel Cell (SOFC)	800-1000	$\text{ZrO}_2/\text{Y}_2\text{O}_3$

Reactions taken place in a fuel cell are different depending on the type of fuel cell. In each case, there is one net ion flow transferred through the electrolyte in order to make the continuous operation. All reactions are mentioned in Table 2.2.

Each type of fuel cell requires different kind of electrodes which is not only stable under the working environment but also can be able to catalyze the reactions at two electrodes. Furthermore, the materials of the electrodes should be as cheap as possible for economic consideration. Table 2.3 shows the currently used electrodes for all kinds of fuel cell.

**Table 2.2** Typical electrochemical reactions in fuel cells

Fuel cell	Anode reaction	Cathode reaction
AFC	$\text{H}_2 + 2\text{OH}^- \longrightarrow 2\text{H}_2\text{O} + 2\text{e}^-$	$\frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \longrightarrow 2\text{OH}^-$
PEM	$\text{H}_2 \longrightarrow 2\text{H}^+ + 2\text{e}^-$	$\frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2\text{O}$
PAFC	$\text{H}_2 \longrightarrow 2\text{H}^+ + 2\text{e}^-$	$\frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2\text{O}$
MCFC	$\text{H}_2 + \text{CO}_3^{2-} \longrightarrow \text{H}_2\text{O} + \text{CO}_2 + 2\text{e}^-$	$\frac{1}{2} \text{O}_2 + \text{CO}_2 + 2\text{e}^- \longrightarrow \text{CO}_3^{2-}$
SOFC	$\text{H}_2 + \text{O}^{2-} \longrightarrow \text{H}_2\text{O} + 2\text{e}^-$	$\frac{1}{2} \text{O}_2 + 2\text{e}^- \longrightarrow \text{O}^{2-}$

**Table 2.3** Preferred electrocatalysts for the main fuel cells

Fuel cell	Anode catalyst	Cathode catalyst
AFC	Pt, Ag	Pt, Ag
PEM	Pt	Pt/Ru
PAFC	Pt	Pt/Cr/Co, Pt/Ni
MCFC	Ni, Ni/Cr	Li/NiO
SOFC	Ni/ZrO <sub>2</sub>	LaSrMnO <sub>3</sub>

Having different structures, five types of fuel cell are responsible for different tasks. Compared to the others, PEM is expected to be the primary power source in electric vehicles, because of its low temperature of operation and rapid startup and transient response. The electrolyte in PEM is an ion exchange membrane, which is a good proton conductor. The advantages of PEM are:

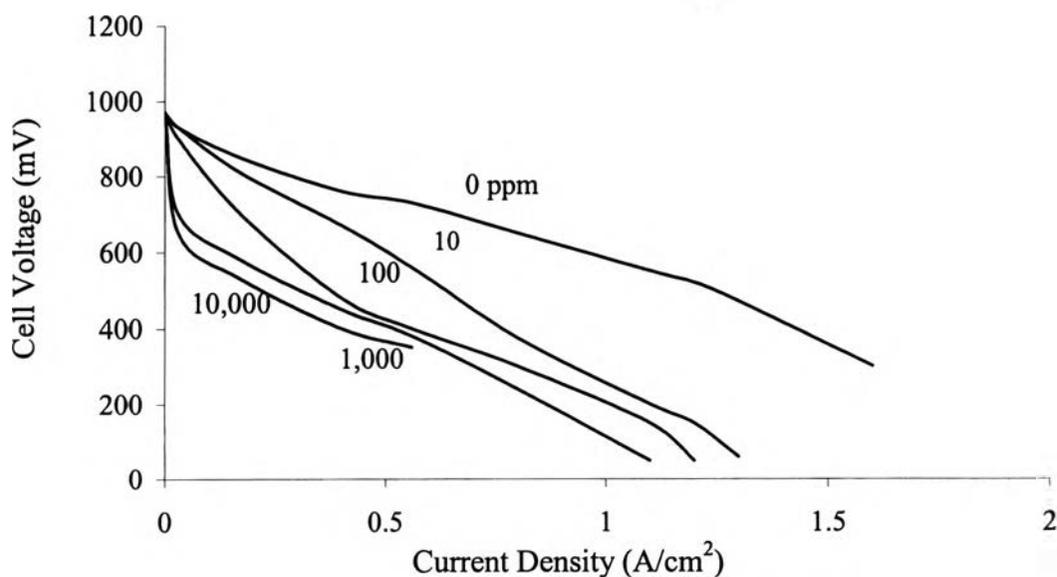
- Less corrosion since the only liquid in this fuel cell is water,
- Simple fabrication,
- Ability to withstand large pressure differentials,
- Long life.

However, there are still some disadvantages that are:

- High cost of the electrolyte,
- Water-management problem,

- Poor CO tolerance,
- High cost of catalyst at the electrodes,
- Difficulty in thermally integrating with a reformer.

One of the most important things needed to overcome is the poor CO tolerance. Fuel cell basically runs on pure H<sub>2</sub>. However, there are no current methods of storage of hydrogen in adequate amounts because of the risk of explosion and the difficulty of refilling at high pressures. Metal hydrides such as borohydride can store a few percent of their total weight in hydrogen but the hydrogen is given up only at elevated temperatures and lifetime under cyclic operation conditions is problematic. As a result the only viable option for mobile applications of fuel cells is on board generation of hydrogen on demand by reforming of a liquid hydrocarbon such as gasoline rich in hydrogen. However, the product of the reforming reaction contains ~6-10% CO which is reduced by the water gas shift reaction to ~1% in the effluent stream. At 1% CO concentration the Pt anode of a PEM is poisoned in seconds and at 100 ppm after an hour or two decreasing the fuel cell performance, especially at high current densities. The substantial degradation of fuel cell performance can be seen in Figure 2.1 (Kordesch *et al.*, 1996).



**Figure 2.1** Fuel cells poisoning by CO (PEM Fuel cell performance). Temperature: 89°C, hydrogen: 0.2 MPa<sub>abs</sub>, oxygen: 0.2 MPa<sub>abs</sub>, electrolyte: Nafion 117, catalyst loading: 4 mg/cm<sup>2</sup>.

There are two approaches to prevent the poisoning of the fuel cell catalysts. The first way is to decrease the CO concentration in the reformed gas to below 10 ppm. The second way is developing less CO sensitive catalysts at the electrodes. This is rather difficult because Pt has proven to be the best catalyst for both the H<sub>2</sub> oxidation and the O<sub>2</sub> reduction reactions (Kordesch *et al.*, 1996). Thus, CO removal from reformed gas is the more practical means in preventing fuel cell performance poisoning.

Au catalyst has long been regarded as catalytically far less active than the others because of its filled d-band. However, recent research has clearly shown that supported gold catalyst is intrinsically more active for CO oxidation than for H<sub>2</sub> oxidation (Torres Sanchez *et al.*, 1997). And since the catalytic activity of this kind of catalyst is enhanced by moisture and almost insensitive to CO<sub>2</sub>, it becomes a very promising candidate for selective CO oxidation for fuel cell applications.

Au has become active not because of itself but because it has the interaction with the support carrying it on. A good support for this reaction should have the capacity to dissociate O<sub>2</sub>. This characterization is required since the support will generate active oxygen from O<sub>2</sub> molecule by changing their oxidation state. Active oxygen is the oxidizing agent for oxidation reaction. There are several supports having the O<sub>2</sub> storage as well as dissociation capacity such as CeO<sub>2</sub>, ZrO<sub>2</sub>, MnO<sub>x</sub>, FeO<sub>x</sub>, etc. In addition, the catalyst should be active for CO oxidation while for the activity for H<sub>2</sub> oxidation should be poor.

Through the screening of support materials, which give the largest difference in catalytic activity between the oxidation of CO and H<sub>2</sub>, Au/MnO<sub>x</sub> and Au/FeO<sub>x</sub> were found to be the best candidates for selective CO oxidation (Torres Sanchez *et al.*, 1997).

## 2.2. Literature Review

A variety of alumina-supported noble metals (Pt/Al<sub>2</sub>O<sub>3</sub>, Pd/Al<sub>2</sub>O<sub>3</sub>, Rh/Al<sub>2</sub>O<sub>3</sub>, Ru/Al<sub>2</sub>O<sub>3</sub>) were examined in selective oxidizing CO in the presence of excess H<sub>2</sub>. The feed stream contained CO, H<sub>2</sub>, and O<sub>2</sub>. The catalysts were prepared by impregnation method. Pd/Al<sub>2</sub>O<sub>3</sub> gave the lowest activity while Rh/Al<sub>2</sub>O<sub>3</sub> and

Ru/Al<sub>2</sub>O<sub>3</sub> gave the highest activity. In order to give complete CO conversion Pt/Al<sub>2</sub>O<sub>3</sub> required temperature as high as 200°C but only 100°C for Rh/Al<sub>2</sub>O<sub>3</sub> and Ru/Al<sub>2</sub>O<sub>3</sub>. Moreover, alumina-supported Rh or Ru had excellent selectivity for CO oxidation promising an ability to be a good candidate for purifying the fuel cell feed stream with a minimum loss of the energy content (Oh and Sinkevitch, 1993).

Au catalyst has long been considered as a far less catalytically active than the others because of its d filled band. However, Hoflund *et al.* (1995) started working on manganese oxide-supported Au catalyst for low-temperature oxidation. Interestingly, even with no pretreatment this catalyst was superior to the best, pretreated platinumized tin oxide catalyst under the same condition. Co-precipitation was used to prepare the catalyst. The reactant gas consisted of 1% CO, 0.5% O<sub>2</sub> and in He. Deactivation test showed that the activity of Au/MnO<sub>x</sub> slightly decreased due to CO<sub>2</sub> retention on the catalyst surface.

Pt/Al<sub>2</sub>O<sub>3</sub> was less selective for CO oxidation so that in order to oxidize 1% CO in the H<sub>2</sub> rich fuels it required more than 2% O<sub>2</sub>. This not only caused the fuel loss by H<sub>2</sub> combustion but also led to a risk of explosion at such a high temperature of 200°C. To overcome this weakness, zeolite-supported Pt catalysts were proposed. The reaction mixture consisted of CO, O<sub>2</sub> and H<sub>2</sub>. Igarashi *et al.* (1997) even got 100 % selectivity with Pt/zeolite catalysts implying that the O<sub>2</sub> addition can be minimized to the stoichiometric amount for 100% conversion of CO. The selectivity depends on kinds of support by the following order: A-type zeolite > mordenite > X-type zeolite > alumina. The highest selectivity with high conversion of CO catalyst was Pt supported on mordenite. This catalyst was a good alternative for a conventional alumina- supported Pt catalyst.

Torres Sanchez *et al.* (1997) found that supported Au catalyst is extremely more active for CO oxidation than for H<sub>2</sub> oxidation. Besides, moisture enhances the catalytic activity of Au and CO<sub>2</sub> has no effect on it. The supported Au catalyst has been investigated whether Au/MnO<sub>x</sub> is still stable in H<sub>2</sub> atmosphere although it prefers oxidizing pretreatment. This type of catalyst was also operated at much lower temperature (127°C) comparing to Pt/zeolite catalyst (200°C).

Metal oxides have been studied for competitive oxidation of H<sub>2</sub> and CO in an oxidative atmosphere. Teng *et al.* (1999) discovered that this catalyst could also

be effectively utilized in CO removal for fuel cell applications. CoO was considered the best among metal oxide catalysts. However, the selectivity of these catalysts decrease under H<sub>2</sub> pressure at high temperature and amount of water in feed also affects to their catalytic performance. Furthermore, study is needed to investigate the stability of this kind of catalyst in the practical environment.

Kahlich *et al.* (1999) found that the kinetics of selective CO oxidation on Au/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> catalyst seems to be very simple. The reaction orders with respect to partial pressure of CO and O<sub>2</sub> were 0.55 and 0.27 in which the first one was strongly temperature dependent. Increasing temperature was more favorable to H<sub>2</sub> oxidation thus decreased the selectivity. The most superior characteristic of this catalyst was giving high activity and selectivity at considerably low temperature of 80°C in comparison with Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

Ito *et al.* (2000) studied the interaction between Rhodium (Rh) and Niobia (Nb) in Niobia-supported Rh (Rh/Nb<sub>2</sub>O<sub>5</sub>), Niobia-promoted Rh/SiO<sub>2</sub> (Nb<sub>2</sub>O<sub>5</sub>-Rh/SiO<sub>2</sub>) and RhNbO<sub>4</sub>/SiO<sub>2</sub> catalysts in selective CO oxidation. Niobia (NbO<sub>x</sub>) increased the activity and selectivity for CO oxidation.

The Selectoxo™ catalyst was commercialized in 1960s for H<sub>2</sub> production in ammonia synthesis. The catalyst contained 5% Pt supported on  $\gamma$ -alumina promoted with a base metal oxide. The feed also contained 10% H<sub>2</sub>O besides CO, O<sub>2</sub> and H<sub>2</sub>. It was found that base metal oxide promoted Pt/Al<sub>2</sub>O<sub>3</sub> to overcome the low activity by providing sites for O<sub>2</sub> adsorption and dissociation (Korotkikh and Farrauto, 2000).

Utaka *et al.* (2000) studied the CO removal from H<sub>2</sub>-rich gas by considering both CO oxidation and water gas shift reactions. The catalyst was supported Cu and prepared by co-precipitation method and the test gas contained H<sub>2</sub>, CO, H<sub>2</sub>O and CO<sub>2</sub> as methanol steam reformed gas. At a relatively low temperature of 100-150°C Cu/Al<sub>2</sub>O<sub>3</sub>-ZnO performed an excellent activity among several supported Cu catalysts. Low space velocity was preferred in order to get high conversion.

Supported Au catalysts seem to be one of the best promising candidates for selective CO oxidation because of their excellent properties. However, there is only a narrow range of Au particle size of about 5-10 nm for the best activity and selectivity. Bethke and Kung (2000) tried to find the way to prepare Au/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

with a desired Au particle size. However, their feed gas consisted of H<sub>2</sub>, CO and O<sub>2</sub> only. Mg citrate was found to have a significant effect on the properties of the catalyst. Without citrate the average Au particle size was larger leading to the lower conversion and selectivity.

Guczi *et al.* (2002) continued playing with Au nanoparticles catalysts for CO oxidation. The iron oxide-supported Au catalyst was their interest. They found that the catalytic activity of this catalyst came from the changes in morphology and electronic structure and the reaction occurred at the metal-oxide interface along the perimeter of the metal particle.

Multi-component-supported Au catalyst has also been investigated for selective CO oxidation. Grisel *et al.* (2002) showed that in case of Au/MgO-Al<sub>2</sub>O<sub>3</sub> the presence of MgO enables the preparation of small, stable Au particles on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> leading to the improvement of both low-temperature CO and H<sub>2</sub> oxidation. Adding MnO<sub>x</sub> and FeO<sub>x</sub> to Au/MgO-Al<sub>2</sub>O<sub>3</sub> further enhanced low-temperature CO oxidation with improved CO<sub>2</sub> selectivity.