

CHAPTER II LITERATURE REVIEW

2.1 Background of Fuel Cell

Fuel cell, an electrochemical device, converts chemical energy between a fuel and an oxidant directly to electrical and thermal energy. In addition, fuel cells have the potential to be reliable, inexpensive and environmentally friendly sources of energy. Generally, fuel cell operates like a battery. Unlike a battery, it does not run down or require recharging. However, it will produce energy in the form of electricity and heat as long as fuel, hydrogen, is supplied.

Fuel cell is composed of two electrodes sandwiched around an electrolyte as shown in Figure 2.1.

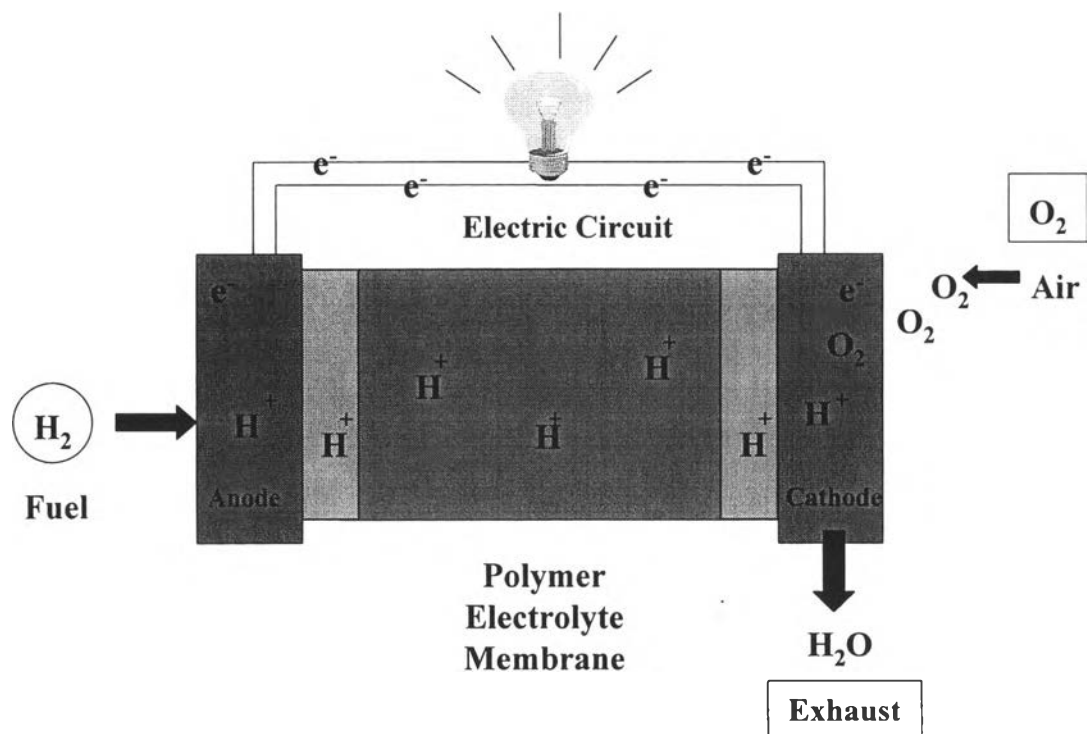


Figure 2.1 The simple diagram of the fuel cell.

H₂ fuel is fed into the anode of the fuel cell, whereas O₂ from air enters the fuel cell through the cathode. The H₂ atom splits into a proton and an electron taking different paths to the cathode. The protons pass through the electrolyte. The membrane is impermeable to the electron and thus the electron travels through the external electrical circuit to the cathode. At the cathode the proton, the electron and the oxygen atom are reunited to produce a water molecule as shown in equations 1-3 below.



Generally, there are six main fuel cell systems that are in various stages of development. These fuel cell systems are given in Table 2.1. Polymer electrolyte fuel cell (PEFC) technology, as used in electric vehicles operates at low temperatures between 50 and 125°C, seems to be the most appropriate for terrestrial transport applications. There are many advantages of PEFC which are high efficiency, solid non-corrosive electrolyte, low temperature, rapid start-up, high power density, insensitive to differential pressure and insensitive to CO₂.

Although H₂ can be used as a fuel, it is not suitable for transportation as a compressed gas or a liquid due to its low boiling point. Consequently, on board-conversion of carbonaceous fuel to H₂ is necessary. CH₃OH not only is regarded as the most desirable chemical existing as liquid at ambient temperatures but also is used for fuel cell-powered vehicles due to its high energy density, ease of transport, absence of sulfur contamination, and possibility of conversion at moderate temperatures (200-400°C). Steam reforming of CH₃OH is a well-established technology for H₂ production. However, a small amount of CO in the reformed fuel deteriorates the Pt electrode and the cell performance in the application to PEFC. Trace amount of CO in reformed gas must be reduced to less than 10 ppm before entering to fuel cell.

Table 2.1 Main types of fuel cell (Acres *et al.*, 1997)

Fuel cell type	Electrolyte	Operating temperature (°C)
1. Alkaline (AFC)	Potassium hydroxide	50-90
2. Proton exchange membrane or Polymer electrolyte (PEMFC) or (PEFC)	Solid proton conducting polymer	50-125
3. Phosphoric acid (PAFC)	Orthophosphoric acid	190-210
4. Molten carbonate (MCFC)	Lithium/potassium carbonate mixture	630-650
5. Solid oxide (SOFC)	Stabilized zirconia	900-1000
6. Direct methanol (DMFC)	Sulphuric acid or solid polymer	50-120

2.2 Selective CO Oxidation

Selective CO oxidation has been studied by many researchers because of its importance in fuel cell applications.

Oh and Sinkevitch (1993) observed activity and selectivity of Ruthenium (Ru), Rhodium (Rh) and Platinum (Pt) supported on alumina (Al_2O_3) catalyst for selective CO oxidation in H_2 rich stream. They discovered that $\text{Ru}/\text{Al}_2\text{O}_3$ and $\text{Rh}/\text{Al}_2\text{O}_3$ gave the best result of CO oxidation with nearly 100% CO conversion at temperatures as low as 100°C while $\text{Pt}/\text{Al}_2\text{O}_3$ gave 90% CO conversion at temperature 180°C . However, the gas reaction mixtures, which were different from

the reformed gas consisted of 900 ppm CO, 800 ppm O₂, 0.85% H₂ and balance with N₂.

The Cu/Cr/Ba and Cu/Cr/Ba/Si catalysts were studied for the selective CO oxidation with a mixed gas of 80%H₂, 2%CO, and 18%air. It was found that the Cu/Cr/Ba/Si catalyst appeared to have a higher CO conversion and slightly lower H₂ conversion than Cu/Cr/Ba catalyst of 85% and 67% at 140°C (Cheng, 1996).

Pt supported on zeolite catalysts have higher selectivity than conventional Pt/Al₂O₃ catalyst. Especially, Pt supported on mordenite showed the highest selectivity with high conversion from CO to CO₂ at 200°C. The composition of gaseous mixture used was 1%CO, 500 ppm or 2%O₂ and H₂ balance (Igarashi *et al.*, 1997).

Torres Sanchez *et al.* (1997) reported that Au/MnO_x catalyst was one of the best catalysts for removal of CO from H₂ rich fuel gases. They found that CO oxidation over Au/MnO_x catalyst reached 100% CO conversion at temperatures below 0°C while H₂ oxidation took place only at temperatures above 0°C. However, the gas composition used in this work was far away from realistic gas composition that was 1%CO, 1%O₂ and balance with H₂.

Kahlich *et al.* (1997) studied the kinetics of the selective CO oxidation in H₂ rich gas on Pt/Al₂O₃ with 1%CO, 1%O₂, 75%H₂ and balance with N₂ in the gas stream. The selectivity was about 40% at maximum CO conversion of 80% in the temperature range of 200 to 250°C.

The kinetics of selective CO oxidation was studied by using 3.15%Au/ α -Fe₂O₃ catalyst at temperature 80°C in simulated reformed gas. A high selectivity of 75% was reached at large CO partial pressures but decreased considerably with reducing partial pressure of CO (Kahlich *et al.*, 1999).

Ito *et al.* (2000) studied the strong rhodium–niobia interaction in niobia-supported Rh (Rh/Nb₂O₅), niobia-promoted Rh/SiO₂ (Nb₂O₅-Rh/SiO₂) and RhNbO₄/SiO₂ catalysts in selective CO oxidation. They found that niobia (NbO_x) increased the activity and selectivity for selective CO oxidation.

Bethke and Kung (2000) investigated the supported Au catalyst that focused on a series of Au/ γ -Al₂O₃ catalyst. They discovered that the presence of Mg citrate

in the preparation solution had an important effect on the properties of the catalyst. In order to obtain the best activity and selectivity, there appeared to be an optimal average Au particle size about 5-10 nm. The selectivity of this catalyst of 50% was obtained at 100°C with the reactant gas of 48% H_2 , 1% CO , 0.5% O_2 and 50.5% He at near atmospheric pressure.

Furthermore, three different catalysts, namely $Pt/\gamma-Al_2O_3$, $Au/\alpha-Fe_2O_3$ and $CuO-CeO_2$ were evaluated and compared for their catalytic performance. Among the three catalysts tested, the $Au/\alpha-Fe_2O_3$ sample was the most active while the $CuO-CeO_2$ was the most selective. Regardless of whether CO_2 or both CO_2 and H_2O were presented in the reactant feed, the maximum CO conversion achieved over the $Au/\alpha-Fe_2O_3$ sample was 99% with 40% selectivity at 110°C. The $CuO-CeO_2$ and $Pt/\gamma-Al_2O_3$ were reached maximum CO conversion of 99% with 66% and 41% selectivity at 200°C, respectively. The effects of the presence of CO_2 and H_2O in the reactant gas were also investigated. The presence of 10% H_2O caused a significant decrease on their activity, while the presence of both CO_2 and H_2O had a beneficial effect on the activity of this sample at lower reaction temperatures. (Avgouropoulos *et al.*, 2002).

2.3 Properties of Gold

Gold (Au) is unique among metallic elements. It has high resistance to oxidation and corrosion. Au ($Z=79$) has the atomic configuration $[Xe]4f^{14}5d^{10}6s^1$, and lies in Group 11 (IB) of the periodic classification of the elements with copper (Cu) and silver (Ag). The three metals are often being referred to as the “coinage metals” and Au lies between Pt in Group 10 and Hg in Group 12. Common oxidation states are 0, 1, and 3. Au exhibits all the expected properties of a metal in terms of luster, hardness, ductility (ability to be drawn into wire), malleability (ability to be beaten or rolled into sheets), high thermal and electrical conductance, having the highest electronegativity especially when compared to selenium (Se), and being only slightly more electropositive than sulfur (S) and iodine (I). The high electronegativity of Au gives rise to another unique feature of its chemistry. Au does

not react directly with other electronegative elements such as sulfur and oxygen, and it is only dissolved in hydrochloric acid when a strong oxidizing agent such as nitrate ion is present (Bond and Thompson, 1999).

2.4 Catalyst Preparation Method

Heterogeneous catalysts are often prepared by wet chemistry methods such as, co-precipitation, deposition-precipitation, hydrothermal synthesis or sol-gel process (Livage, 1998). The catalytic properties are strongly affected by every step of preparation together with the quality of the raw materials. The choice of a laboratory method for preparing a given catalyst depends on the physical and chemical characteristics desired in the final composition. It is easily understood that the preparation methods are also dependent on the choice of the base materials and experience shows that several ways of preparation can be considered, even for a given selection of the base material (Perego and Villa, 1997). Deposition-precipitation and impregnation on sol-gel methods are concentrated in this work.

2.4.1 Deposition-precipitation Method (DP)

This procedure is, in principle, similar to the co-precipitation method. The precipitation of a metal hydroxide or carbonate is formed on the particles of a powder support through the reaction of a base with the Au precursor. The main challenge is to bring about the precipitation of the metal hydroxide particles inside the pores of the support. Therefore, the nucleation and growth on the support surface will result in a uniform distribution of small particles on the support. On the contrary, rapid nucleation and growth in bulk solution will lead to large crystallites and inhomogeneous distribution, since the last particles will be unable to enter into the pores, but will deposit only on the external surface. In order to obtain the best results, an efficient mixing method should be used together with a slow addition of the alkali solution to avoid the build up of local concentration. It has been found that the best base is urea, which is usually added at room temperature, by raising the temperature to 90°C, urea is slowly hydrolyzed to generate ammonium hydroxide homogeneously through the solution. The pH of the solution remained practically

constant and the rate of precipitation being higher than that of hydrolysis. The best result in terms of homogeneous distribution was also obtained when an interaction between the support and the active precursor took place (Pinna, 1998).

Au showed a unique catalytic nature and action when it was deposited as nanoparticles on variety of metal oxides. Most reactions were noticeably structure sensitive over such supported Au catalysts. Deposition-precipitation was effective to deposit Au with high dispersion on TiO_2 . This method was applicable to any forms of support including beads, honeycombs, and thin films. An important requirement was the support materials should have high surface areas, preferably higher than $50 \text{ m}^2/\text{g}$. Since gold hydroxide could not be deposited at low pH, this method was useless for metal oxides having low point of zero charge, for example, $\text{SiO}_2\text{-Al}_2\text{O}_3$ support (Haruta, 1997^c).

Gold hydroxide precipitates with high homogeneous dispersion on TiO_2 , most probably on specific surface sites, in the pH range 6 to 10. The calcination of TiO_2 with $\text{Au}(\text{OH})_3$ in a reducing gas atmosphere, such as H_2 and CO led to smaller Au particles than in air. An increase in calcination temperature not only caused particle coagulation but also brought about stronger interaction with the TiO_2 support (Tsubota *et al.*, 1995).

The catalytic activity of supported Au catalysts has been investigated by Haruta *et al.* (1996), activity of Au/TiO_2 , strongly depended on the pH of a starting solution, metal loading, the addition of Mg citrate and calcination atmosphere. The unique role of Mg citrate might be, firstly, to prevent coagulation during calcination due to blockage by citrate anions sticking on TiO_2 surface. The second role can be assumed to suppress earthquake effect caused by crystallization of $\text{Ti}(\text{OH})_4$ to TiO_2 because Mg^{2+} ion was found to retard the crystallization of amorphous TiO_2 , and finally, it can reduce the particle size of Au for preparation of Au/TiO_2 (Sakurai and Haruta, 1996).

2.4.2 Impregnation on Sol-gel Method (ISG)

Support prepared by sol-gel method has several promising advantages over precipitation method. In general, sol-gel synthesis offers better control over

surface area, pore volume, and pore size distribution. Moreover, sol–gel method allows the formulation of quite a number of gel with high uniformity and stability (Perego and Villa, 1997).

Ko (1994) found that the single most important characteristic of sol–gel preparation of catalytic materials is its ease of control that refers to the following advantages: (i) the ability to maintain high purity because of purity of starting materials; (ii) the ability of change physical characteristics such as pore size distribution and pore volume; (iii) the ability to vary compositional homogeneity at a molecular level; (iv) the ability to prepare samples at low temperatures; (v) the ability to introduce several components in a single step; and (vi) the ability to produce samples in different physical forms.

The sol–gel process involves first formation of a sol followed by that a gel. The hydrolysis and partial condensation of a precursor can obtain a sol, which is a liquid suspension of solid particles ranging in size from 1 nm to 1 μ m. The further condensation of sol particles into a three-dimensional network produces a gel. Sol-gel chemistry with metal alkoxides can be described in term of two classes of reactions.



where:

M = metal corresponding to the alkoxide

X = H or R (an alkyl group)

The relative rates of hydrolysis and condensation determine the extent of branching of the inorganic polymer and colloidal aggregation in the gelation mixture. These relative rates are functions of many parameters, such as temperature, pH and concentration of the metal ion precursors. In addition, drying and calcination conditions also affect the extent of branching and cross-linking, and the properties of the final oxide (Kung and Ko, 1996).

Finally, this procedure requires that the support is contacted with a certain amount of solution of metal precursor, then it is dried and calcined. The

volume of the solution containing the precursor does not exceed the pore volume of the support. In the simplest way, the impregnation solution is sprayed on the support, which is maintained under stirring and has been previously evacuated. In principle this method appears to be simple, economical (especially when using solutions of costly active components) and able to give a reproducible metal loading which is limited by the solubility of the metal precursor (Pinna, 1998). Furthermore, this method is to deposit Au particles on a preformed support by soaking the support in a solution of gold salt, followed by drying and calcination. This may be done either by just filling the pores of the support with the solution or by suspending the support in a larger volume of solution, from which the solvent is then removed.

Impregnation is the simplest classical method to make supported Au catalysts. The generally used salt is either chloroauric acid or hydrogen tetrachloroaurate. Impregnation usually leads to the formation of somewhat large Au particles, due to the need to apply calcination or reduction in order to achieve the metallic state, and to the low melting point of Au (1337 K) which allows atomic mobility at quite low temperatures (Bond and Thompson, 1999).