CHAPTER II

LITERATURE SURVEY

2.1 Background

Fuel cell is an electrochemical device that converts chemical energy to electrical and thermal energy. Currently, there are six main fuel cell systems in various stages of development. These fuel cell systems are listed in Table 2.1.

Table 2.1 Main types of fuel cell classified according to the electrolyte (Acres *et al.*, 1997).

Fuel cell type	Common abbreviation	Electrolyte	Operating temperature,^{o}C
Alkaline	AFC	Potassium hydroxide	50-90
Proton exchange membrane (Polymer electrolyte)	PEMFC (PEFC)	Solid proton conducting polymer	50-125
Phosphoric acid	PAFC	Orthophosphoric acid	190-210
Molten carbonate	MCFC	Lithium/potassium carbonate mixture	630-650
Solid oxide	SOFC	Stabilised zirconia	900-1000
Direct methanol	DMFC	Sulphuric acid or solid polymer	50-120

With the exception of the direct methanol fuel cell (DMFC), characterization and nomenclature of these is by the electrolyte and associated operating temperature. These features also govern the requirements of the

electrocatalysts, which control the reactions. The DMFC stands alone involving a carbonaceous fuel (methanol) fed directly to the anode; all others use hydrogen as the anode fuel, either as a pure gas, or as a hydrogen-rich gas mixture. A catalytic steam reformer, or partial oxidation reactor, fed with methanol, is sometimes referred to as the indirect methanol fuel cell, since in contrast to the DMFC, it is still hydrogen that is ultimately oxidized on the fuel cell anode. The nature of the electrolyte in any fuel cell, and the associated operating temperature, are crucial features of consideration for effective catalysts. The nature of the electrolyte also determines the identity of the dominant migrating ion, as listed in Table 2.2.

Table 2.2 Fuel cell systems showing anodic and cathodic reactions, and the dominant of ion transport in the electrolyte.

Fuel cell	Anode reaction	Net ion transport	Cathode reaction
AFC	$H_2+2OH^- \longrightarrow 2H_2O+2e^-$	$\leftarrow OH^-$	$O_2+2H_2O+4e^- \longrightarrow 4OH^-$
PEMFC (PEFC)	$H_2 \longrightarrow 2H^++2e^-$	$H^+\rightarrow$	$O_2+4H^++4e^- \longrightarrow 2H_2O$
PAFC	$H_2 \longrightarrow 2H^++2e^-$	$H^+\rightarrow$	$O_2+4H^++4e^- \longrightarrow 2H_2O$
MCFC	$H_2+CO_3^{2-} \longrightarrow H_2O+CO_2+2e^-$ $CO+CO_3^{2-} \longrightarrow 2CO_2+2e^-$	$\leftarrow CO_3^{2-}$	$O_2+2CO_2+4e^- \longrightarrow CO_3^{2-}$
SOFC	$H_2+O^{2-} \longrightarrow H_2O+2e^-$ $CO+O^{2-} \longrightarrow CO_2+2e^-$ $CH_4+4O^{2-} \longrightarrow 2H_2O+CO_2+8e^-$	$\leftarrow O^{2-}$	$O_2+4e^- \longrightarrow 2 O^{2-}$

Many electrocatalysts have been examined over many years for their applications to fuel cells; the nature of preferred electrocatalysis is critically dependent on the nature of the fuel cell. Currently preferred electrocatalysts for the various cells are listed in Table 2.3.

Table 2.3 Preferred electrocatalysts for the main fuel cell systems.

Fuel cell	Anode catalyst	Cathode catalyst
AFC	Pt/Au, Pt, Ag	Pt/Au, Pt, Ag
PEMFC	Pt, Pt/Ru	Pt
PAFC	Pt	Pt/Cr/Co, Pt/Ni
MCFC	Ni, Ni/Cr	Li/NiO
SOFC	Ni/ZrO_2	$LaSrMnO_3$

Hydrogen is regarded as one of the most important energy sources to produce heat, electricity, power energy and industries in the near future. Hydrogen energy can be efficiently converted into mechanical or electrical energy with production of only water by combustion. Hydrogen, though promising as a fuel, is not suitable for transportation as a compressed gas or a liquid due to its low boiling point. Therefore, on board-conversion of carbonaceous fuel to hydrogen is suggested and has been extensively investigated. Methanol is regarded as the most desirable chemical existing as liquid at ambient temperatures.

Methanol is used for fuel cell-powered vehicles and as a source of chemical products 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 methanol is one important method for on-site hydrogen generation systems. In addition, the reformed gas is benign for the environment because no NO_x, SO_x and dust have been produced in the

process. One efficient utilization of methanol is an application to polymer electrolyte fuel cells (PEFCs) with a proton exchange membrane after catalytic conversion into hydrogen. PEFC has been studied as an ideal on-site power source for vehicles and/or small facilities because of some advantages, such as compact size, operation at low temperature (<120°C) and high pressure, and a high power density, Steam reforming of methanol is a well-established technology for hydrogen production. However, in case of the application to PEFC, a small amount of CO in the reformed fuel strongly adsorbs on active site, deteriorates the Pt electrode and the cell performance, and inhibits the hydrogen oxidation reaction at the anode. Although CO-tolerant electrodes such as Pt-Ru electrode have been developed, the allowable level of CO concentration is still low. It is thus necessary to remove trace amount of CO in the reformed gas to less than 10 ppm before it enters the fuel cell. Many researchers have struggled to solve this problem over noble metals and/or base metals.

Pd (Palladium) metal is known to have a better resistance to thermal sintering, lower price than Pt (Platinum) and Rh (Rhodium), and a good selectivity for the oxidation of hydrocarbon and carbon monoxide.

CeO_2 (Ceria) is the most significant oxide of rare earth elements, which has been widely investigated in a catalytic converter as structural and electronic promoters to improve the activity, selectivity and thermal stability of the catalysts (Alessandro *et al.*, 1999). CeO_2 is used due to the capacity of Ce to switch between the two-oxidation states Ce^{3+} and Ce^{4+}, which gives an oxygen-storing capacity to the oxide. Moreover, CeO_2 promotes water gas shift reaction and the steam reforming reactions. It stabilizes supports and keeps high surface area, prevents sintering of metals, and thus, stabilizes their dispersed state and promotes CO oxidation.

The mixed oxide between CeO_2 and other rare earth oxides were investigated by some authors who believed that the oxygen atoms are from

bulk. Amount of oxygen given off by the mixed oxide is higher than that of the pure CeO_2. An addition of the rare earth oxide is believed to induce the oxygen vacancies in bulk, which accelerates the movement of oxygen atoms through the lattice. Fornasiero *et al.* (1995) incorporated the ZrO_2 (Zirconia) into a solid solution with CeO_2. The TPR indicates that the OSC (Oxygen Storage Capacity) of Rh loaded solid solution is higher than Rh/CeO_2 sample.

One of the methods used to stabilize CeO_2 is through the addition of ZrO_2, an oxide that is itself not reducible. It has been found that mixtures of CeO_2 and ZrO_2 exhibit high oxygen storage capacity, higher than that of CeO_2 alone. ZrO_2 also prevents sintering of the CeO_2 crystallites and is capable of directing CeO_2 structure. Therefore this research focused on Pd (Palladium) supported on CeO_2, ZrO_2 and mixed CeO_2-ZrO_2.

Several methods have been used to prepare the above mixed oxides, which are loaded with metal. This work focused on co-precipitation and impregnation on sol-gel technique.

In co-precipitation method, one more soluble salt, which contains the metal of interest, are neutralized through the addition of base to form a co-precipitate of the corresponding metal oxide. This method is applied when the catalysts with mixed-support are prepared.

Sol-gel method was chosen to be an interesting route for preparing the catalyst. The term of sol-gel describes the technique fairly accurately, with sol meaning a colloidal solution. A colloid is an intermediate state between being a solution and a suspension, in which particles of the solute are large enough to scatter light, but to small to settle, generally in the range of between one and one thousand nanometers (Purcell, 1997). Also, the word of gel means a dispersion of a solid substance in a fluid medium that behaves like elastic solid or a semi-solid rather than a liquid. This technique has several promising advantages (i) superior homogeneity and purity; (ii) better microstructural control of metallic particles; (iii) higher BET surface area; (iv) improved

thermal stability of the supported metals; (v) well-defined pore size distributions; (vi) the ease with which additional elements can be added. Moreover, the interesting advantages of the sol-gel methods are the occurring of non-agglomerated, nanometer-sized particles (Cauqui and Rodriquez-Izquierdo, 1992).

The conditions employed for activating the catalyst have an enormous effect on its subsequent performance, because this variation may be related to the oxidation state of the metal oxide surface (Tanielyan and Augustine, 1992). A remarkable property of Pt/CeO_2 catalysts is that they have been found to have considerable activity at low temperatures after certain-pretreatment. There have been observed that an improved activity after a reduction in CO at $300^{\circ}C$ for the oxidation of CO with either Pt, Pd, or Rh supported on CeO_2. It is believed that an improved low-temperature activity of Pt/CeO_2 for oxidation of CO after a reductive pre-treatment in a rich synthetic exhaust gas mixture at $450^{\circ}C$. The same observation has been made with other reducing agents: H_2 at $600^{\circ}C$ (Golunski et al., 1995) and at $300^{\circ}C$ and CO at $490^{\circ}C$ (Serre et al., 1993). Holmgrena et al. (1999a) found that the activity is higher after reduction at $200^{\circ}C$ and $300^{\circ}C$ on Pt/CeO_2 than after reduction at $500^{\circ}C$.

2.2 Literature Review

The selective carbon monoxide oxidation has been studied by a large number of researchers because of its significance in fuel cell applications. Polymer electrolyte fuel cells (PEFCs) have received much attention because of characteristics essential for transportation applications. They are light in weight, small in size, and have high power density at a relatively low operating temperature (e.g. about $80^{o}C$). PEFCs require platinum electrocatalysis for the hydrogen oxidation and the oxygen reduction at such a low temperature. It is desirable in the case of electric vehicles to operate the PEFC with reformed fuels from methanol or natural gas, but the performance of the PEFC with conventional Pt catalyst operating on reformates is shown to be seriously depressed by carbon monoxide poisoning.

Consequently, the development of selective carbon monoxide oxidation catalyst has received attention. There remains a need for development of catalysts, which exhibit higher activities for prolonged periods. Numerous materials are known to oxidize carbon monoxide in the presence of hydrogen but they are very active at higher temperature, which are not suitable for PEFC applications.

Cu/Cr/Ba based catalysts were found to selectively oxidize CO in a H_2-containing stream. Cu/Cr/Ba and Cu/Cr/Ba/Si (listed composition $CuO/Cr_2O_3/BaO$ 33/38/9) were prepared by precipitation method and calcined in CO_2 at $300^{o}C$ before use. A mixed gas of H_2, CO and air was used as a feed. The result shows that Cu/Cr/Ba/Si catalyst appears to have a higher CO conversion and slightly lower H_2 conversion than the Cu/Cr/Ba catalyst (Cheng, 1996).

Kahlich *et al.* (1997) have developed the selective carbon monoxide oxidation reaction on Pt/Al_2O_3 in simulated reformer gas (75%H_2, rest N_2) over a wide range of carbon monoxide concentrations (0.021-5%). The result

shows that the optimum temperature for the PROX (preferential oxidation) is 200°C and significantly loses in selectivity at high temperature.

Igarashi *et al.* (1997) have studied the selective oxidation of carbon monoxide in reformed fuels from methanol or natural gas by Pt/A type zeolite, Pt/modernite, Pt/X type zeolite and conventional Pt/Al_2O_3. Their types of zeolite were prepared by ion exchange in an aqueous solution of [Pt $(NH_3)_4$] $Cl_2.H_2O$. The catalytic activity was tested by using 1%CO, O_2 (500 ppm and 2%) balance in H_2 under the reaction temperature of 150-350°C. They found that Pt supported on zeolite catalysts can oxidize carbon monoxide much more selectively than conventional Pt/Al_2O_3 catalysts. Pt/modernite shows the highest selectivity, with high conversion from carbon to carbon dioxide and has resistance to the water addition in the feedstream.

Hutchings *et al.* (1998) reported the effect of preparation conditions on the catalytic performance of copper manganese oxide catalysts for CO oxidation. Copper-manganese oxides were prepared by using a co-precipitation procedure and studied by using the mixture of 5%CO in He, 5ml/min and O_2, 50 ml/min as a reactant gas. The variables include the precipitate aging time, pH and temperature of precipitation, the [Cu]/[Mn] ratio of the precipitation solution and the catalyst calcination temperature. The optimum preparation conditions are 1/2 [Cu]/[Mn] ratio at pH 8.3 and 80°C for 12 hours aging time, followed by calcination at 500°C for 17 hours.

Kahlich *et al.* (1999) studied kinetics of selective low-temperature oxidation of CO on $Au/\alpha\text{-}Fe_2O_3$ in simulated reform gas at atmospheric pressure. They found that carbon monoxide oxidation rate as a function of CO and O_2 partial pressure at 80°C yields reaction orders with respect to CO and O_2 of 0.55 and 0.27, respectively.

Holmgrena *et al.* (1999a) investigated the influence of oxidative and reductive pre-treatments in the temperature range 40-230°C on the isothermal carbon monoxide oxidation activity of CeO_2 and Pt/CeO_2. The result of this

study is that reduction at 200°C or 300°C was higher activity than reduction at 500°C. XPS measurements show that Pt is not completely reduced at 200°C.

Holmgrena et al. (1999b) studied the interaction between CO and Pt/CeO$_2$ catalysts by oxygen storage capacity measurements, CO and CO$_2$ isotope exchange and FT-IR measurements. The result shows that the presence of Cl from the Pt precursor has no significant effect on the oxygen storage capacity. This indicates that Cl does not hinder the oxygen transport from CeO$_2$ to Pt.

Cu/Al$_2$O$_3$-ZnO demonstrates an excellent activity for catalytic removal of CO by oxygen-assisted water gas shift reaction. The addition of a small amount of O$_2$ greatly promotes CO removal especially at 150°C. Further addition of O$_2$ only lead to H$_2$ conversion without promoting CO removal. CO conversion is improved with a decrease in a space velocity (Utaka et al., 2000).

The low temperature CO oxidation activity of three monolith catalysts (Pt/Al$_2$O$_3$, CoO$_x$/Al$_2$O$_3$ and Pt/CoO$_x$/Al$_2$O$_3$) has been studied by using different temperature-programmed methods: CO-TPD (desorption), TPO (oxidation), TPR (reduction), and CO light-off. Preoxidized cobalt-oxide-containing catalysts are found highly active for CO oxidation at temperature as low as 200 K, and at this low temperature the activity is independent of the presence of Pt (Thormählen et al., 2000).

Ito et al. (2000) have studied strong rhodium-niobia interaction in Rh/Nb$_2$O$_5$, Nb$_2$O$_5$-Rh/SiO$_2$, and Rh/NbO$_4$/SiO$_2$ catalysts applied to selective CO oxidation. The feed stream contains 3% H$_2$, 0.2%CO and 1%O$_2$ balance in He. It has been found that niobia (NbO$_x$) increases the activity and selectivity for selective CO oxidation in H$_2$. However, there is no direct relation between the H$_2$ and CO chemisorption ability and the activity and selectivity.

The catalytic activity of CO oxidation by O$_2$ has been investigated by Pt/C, Ru/C and Pt-Ru/C for anodic catalysts for polymer electrolyte fuel cells

catalysis. Experiments were run using a mixture of 0.4% CO, 0.2%O_2 with He as balance. Pt-Ru/C alloys perform better than pure Pt/C. The addition of water vapor to the reactant mixture leaves the catalytic performance of Pt/C and Pt-Ru/C virtually unchange (Bracchini *et al.*, 2000).

Activity of Ag/CeO$_2$ composite catalyst has been studied by oxidation of methane and carbon monoxide. Ag/CeO$_2$ composite oxide was prepared by co-precipitation method. Oxidation of CO was carried out in the reactant gas of 1.04%CO, 8.96%He, and 90.0%air at a space velocity of 6000h^{-1}. Ag/Ce catalysts have higher activity and durability than Ag (100) catalyst because CeO$_2$ has an effect of dispersing Ag metal and preventing its aggregation to large particles (Imamura *et al.*, 2000).