

# CHAPTER I

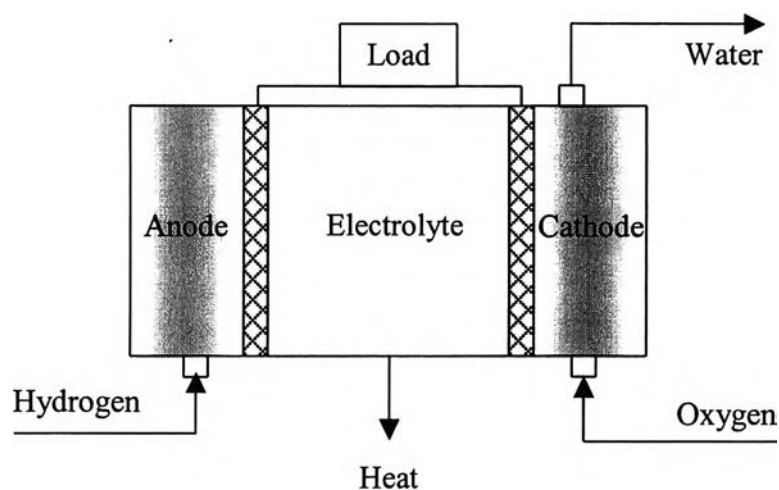
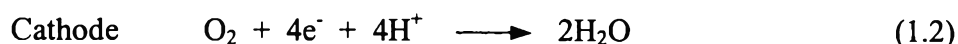
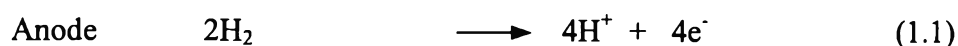
## INTRODUCTION

### 1.1 Introduction

Fuel cells will certainly play a key role in the future world energy perspective. Basically relying on electrochemical reactions, it can directly and continuously convert up to 90% of the energy contained in the fuels into usable electricity, which is far higher than the conventional indirect technology. That high efficiency not only makes it economical but also significant in the near future when the fossil fuel sources run down. In addition, substitution of fuel cells for conventional power plants will definitely improve air quality, reduce water consumption and wastewater discharge and eliminate many of the sources of noise associated with conventional steam, gasoline, and diesel-powered systems. The conventional generation of electricity discharges remarkably high amounts of particulates, sulphur oxides and nitrogen oxides while fuel cell power plant emissions are ten times less than those specified by the most stringent environmental regulations. Low water usage in fuel cells is obviously contrary to the massive water demand for cooling in steam power plants and no pretreatment is required prior to disposal in communities. Fuel cell utilization also slows down the greenhouse effect since its CO<sub>2</sub> production is less than that of the conventional power generation methods based on direct combustion. Besides, fuel cells have such a small size that makes them most compact means of electric power generation. Although fuel cells are based on the same principles as those of the widely used batteries, electrical power can be produced as long as the cells are supplied with fuel while the batteries must be thrown away (primary batteries) or recharged properly (secondary batteries).

Such unique characteristics of fuel cells offer the opportunity to respond to the future energy projects in an environmentally friendly way. Among the various applications, fuel cell powered electric vehicles are one of the most important applications since replacing the conventional engine with a fuel cell will eliminate the pollution problems and double the distance that can be driven for the same

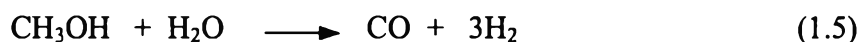
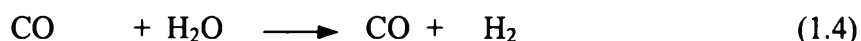
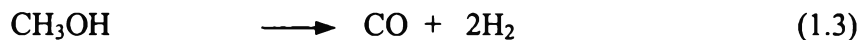
amount of gasoline. Fuel cell is a device converting hydrogen and oxygen to water and generating electricity without combustion. A fuel cell consists of two electrodes sandwiched around an electrolyte as shown in Figure 1.1.  $H_2$  is fed into the anode where it is split into a proton and an electron by the anode catalyst. The membrane is impermeable to the electrons as a result the electrons are forced to travel through the external circuit while the protons pass through the electrolyte to the cathode where they combine with  $O_2$  coming from the air and electrons from the external circuit to form water. Equations 1.1 and 1.2 illustrate the fuel cell operation.



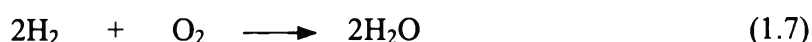
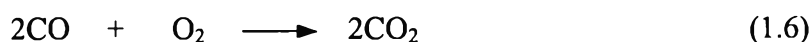
**Figure 1.1** Schematic drawing of a Proton Exchange Membrane (PEM) fuel cell.

$H_2$  is the most suitable fuel for the fuel cell technology in comparison with hydrocarbons, alcohols or coal because of its highly electrochemical reactivity. Furthermore, the mechanism of  $H_2$  reaction is well understood and there are no undesirable side products like the others. However, in order to use  $H_2$  as fuel for fuel cells it is necessary to integrate  $H_2$  production unit with fuel cells because of the  $H_2$  explosion risk and the limitations of  $H_2$  onboard storage.

Steam reforming is an efficient, economical, and widely used process for H<sub>2</sub> production. The reactions taken place in the reformer are illustrated in Equations 1.3, 1.4, and 1.5.



However, reforming not only produces H<sub>2</sub> as a main product but also has a side product namely CO (~6-8%) which is reduced to ~1% after a water gas shift reactor. CO levels as low as 100 ppm quickly poison fuel cell Pt anodes reducing the overall fuel cell performance. Thus, in order to obtain the maximum performance, the CO concentration in the reformed gas has to be reduced to less than 10 ppm. There are basically four methods of eliminating the CO: adsorption, membrane filtration, methanation, and selective oxidation. However, CO removal by adsorption requires large amounts of adsorbent. Using Pressure Swing Adsorption needs expensive compressors and methanation is inefficient because for each mole of CO three moles of hydrogen are used. Furthermore, most CO methanation catalysts will also methanate CO<sub>2</sub> reducing the overall efficiency of the process significantly. Filtration through Pd membranes is slow, needs a lot of Pd and requires compression to high pressures. Therefore, selective oxidation of CO is the simplest and most efficient choice. However, oxidation of ~1% CO in a stream containing 50% or greater hydrogen requires a very selective catalyst to prevent extensive oxidation of hydrogen and thus reducing the overall efficiency. Once O<sub>2</sub> is introduced into the H<sub>2</sub> stream containing CO, two competitive reactions take place as shown in Equations 1.6 and 1.7. O<sub>2</sub> can oxidize both CO and H<sub>2</sub> to form CO<sub>2</sub> and H<sub>2</sub>O, respectively. The challenge is to find the kind of catalyst that can selectively promote CO oxidation rather than H<sub>2</sub> oxidation. Moreover, very high CO conversion is necessary in order to reduce the CO amount down to 10 ppm as desired for fuel cell use.



Several studies about these processes have been conducted and numerous catalysts have been considered. However, further study is still needed since no catalyst that meets the very high conversion and high selectivity requirement has been found. Although cobalt oxide catalyst gave high selectivity with high conversion, it was not so stable in normal condition (Teng *et al.*, 1999). Being used as electrodes, Pt is not only expensive but also is in short supply. Operating temperature is also critical. Most of catalysts investigated are active in a relatively high temperature range 200-250°C, which is not suitable for proton exchange membrane (PEM) fuel cells of interest for transportation.

Supported Au catalysts have been previously investigated as one of the best candidates for selective CO oxidation. Torres Sanchez *et al.* (1997) reported that supported Au catalysts are, in contrast to Pt-group metal catalysts, substantially more active for CO oxidation than for H<sub>2</sub> oxidation resulting in the higher selectivity. Furthermore, its catalytic activity is enhanced by moisture and almost insensitive to CO<sub>2</sub> (Torres Sanchez *et al.*, 1997).

Although CO oxidation on Au/MnO<sub>x</sub> and Au/α-Fe<sub>2</sub>O<sub>3</sub> have been studied since 1997, these previous studies did not study selective oxidation using a fully simulated reformed gas. Depending on whether partial oxidation, steam reforming or a combination of the two is used for reforming the hydrocarbons, the composition of the reformed gas after the water gas shift reactor is approximately 40-60% H<sub>2</sub>, 10-20% CO<sub>2</sub>, 10-20% H<sub>2</sub>O, and 0.5-2% CO. The important components in this mixture are H<sub>2</sub>O and CO<sub>2</sub> in terms of their effect on the catalyst.

## 1.2 Research Objectives

The purpose of this thesis is to develop new catalysts, which can replace the currently used catalysts for CO oxidation in the presence of H<sub>2</sub> for fuel cell applications. The thesis is limited to the study of MnO<sub>x</sub> and FeO<sub>x</sub> supported Au catalysts prepared by the co-precipitation method. In order to understand the relationship between the catalyst properties and its activity and selectivity, several different characterization methods were used.