

Development of PROX (Preferential Oxidation of CO) System  
for 1kW<sub>e</sub> PEMFC  
1kW<sub>e</sub> 급 PEMFC 용 CO 선택 산화반응 시스템의 개발

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To generate hydrogen for PEMFC, reforming of hydrocarbon is usually used. However, without complete removal of CO, which is produced as a byproduct of the reformation, the PEMFC is severely poisoned by the adsorption of CO on the surface of the anode. PROX is known as one of the most promising technologies which prevent the anode from being poisoned by CO. The purpose of this study is to develop PROX catalyst operating relatively wide range of temperature conditions. This selected catalyst has been applied to 1kW<sub>e</sub> proto-type system. The concentration of CO in the effluent gas was below 10 ppm at its steady state condition. Also, even at transient conditions, in which sudden flow rate change has occurred, the resulted CO concentration still remained under 10 ppm.

## 1. Introduction

During the last decade, PEMFC (Polymer Electrolyte Membrane Fuel Cell) has moved towards commercialization. Especially, in transportation and residential application, the market and technical requirements have been delineated by various organizations. One of the issues that still hinder the fuel cell from entering into the real market, is durability. The main culprit raising durability issue is carbon monoxide. If the reformat from the hydrocarbon is used, CO in reformat severely poisons the anode of PEMFC. Therefore, it is required that the reformat into the stack should contain CO concentration less than 20 ppm [1]. To meet the requirement, many organizations and companies have researched CO removal system. It is known that several methods of CO removal can be applied to fuel cell systems. They are PSA(Pressure Swing Absorption), methanation, metal membrane, PROX(Preferential Oxidation of CO) and so on. Among them, PROX is usually selected, since it is compact and responses fast to changes in load. The compactness and fast response is more important in fuel cell vehicle. Hence, PROX is in general regarded as the most promising option, satisfying the severe market and technical requirements. Los Alamos National Laboratory in America and MERCATOX program in Europe are the frontiers in the PROX development over the world. Some studies by them had been published based on the performance data from their own prototypes [2,3]. SK corporation also has been working on PROX since last year as a national project funded by Korean government. This paper describes interim results of the project and is mainly focused on the development of catalyst and 1kW<sub>e</sub> PROX reactor system.

## 2. Experimental

### 2-1. Catalyst preparation and activity test

1.5wt % of Pt and Ru mixture was impregnated onto  $\gamma$ -alumina, sized 300~600  $\mu\text{m}$ , and the resulted paste was dried over night. The dried powder was calcined in  $\text{H}_2$  for 4 hours. Lab-scaled activity test of the prepared catalyst was performed using the simulated gasoline reformat. The composition of it was 36%  $\text{H}_2$ , 17%  $\text{CO}_2$ , 28%  $\text{N}_2$ , 17%  $\text{H}_2\text{O}$ , and 1%  $\text{CO}$ . Air was used as the oxidant. Each gas was controlled by MFC and the total flow rate was maintained at 100 ml/min (wet base). 0.15g of the catalyst was loaded in 4mm I.D. of quartz tube reactor for the activity test. The test was performed over the range of 100~160  $^\circ\text{C}$  at various flow rates of air.

### 2-2. Scale-up test

The same size of catalyst was used in 1kW<sub>e</sub> PROX reactor. The reactor was designed so as to minimize pressure drop and to enable efficient heat transfer. Inter-stage cooling of gas was applied to control gas temperature. Fig. 2 depicts the schematic diagram of the proto-type PROX system for 1kW<sub>e</sub> PEMFC. The reactor system was designed as two stages and the catalyst developed in this study was loaded into each stage. The volume of catalyst in each bed is 100 ml. The flow of reactant is controlled by MFC and the mixed gas passes through a water vaporizer which makes gas contain 17%  $\text{H}_2\text{O}(\text{g})$ . The mixed gas is then heated to a desired temperature by an electric heater before the inlet of the first reactor. Until the gas reaches the desired temperature, it is vented out by 3-way valve. Secondary air is added to outlet gas from the first reactor and the gas is cooled to desired temperature by cooler just before the inlet of second reactor. Outlet gas from the second reactor is sampled and sent to CO analyzer and G.C. via an  $\text{H}_2\text{O}$  trap.

$\text{CO}$  and  $\text{H}_2$  concentrations in effluent gas from the reactor were analyzed by Infrared Gas Analyzer (California Analytical Instruments) and HERMOR615 (Maihak).  $\text{CO}_2$ ,  $\text{O}_2$ , and  $\text{CH}_4$  were analyzed by Gas Chromatography, in which TCD and FID detectors are equipped.

Selectivity of  $\text{CO}$  oxidation was calculated by the followed equation,

$$\text{Selectivity} = \left[ \frac{\text{moles of converted CO to CO}_2}{2 \text{ (moles of total reacted O}_2\text{)}} \right] \times 100$$

## 3. Results and discussion

The activity and the selectivity of Pt-Ru/ $\text{Al}_2\text{O}_3$  catalyst were evaluated over the range of temperature, 100~160  $^\circ\text{C}$ , and shown in Fig. 1. The  $\text{CO}$  conversions and selectivities were compared for two different stoichiometric  $\text{O}_2/\text{CO}$  ratios in the reactant,. When the ratio is 2.0, the

CO conversion shows almost 100% at 100°C and decreases to 98% when the reaction temperature increases to 160°C. The CO selectivity decreases slightly from about 50%, to 48% by the temperature increase in the reactor. When the ratio is 1.6, the CO conversion and the selectivity at 100°C are 99% and 62%, respectively, and also decreased by the temperature increase.

The conversion is lower but the selectivity is higher when the O<sub>2</sub>/CO ratio is 1.6 than those when the ratio is 2.0 regardless the temperature in the reactor. In fuel cell application, since the hydrogen consumption of PROX is one of factors that reduce system efficiency, the high CO selectivity of PROX catalyst is one of the major requirements together with the CO conversion. Therefore, It is believed that multi-staged reactor system is required to maximize the CO selectivity and conversion, in which every stage has high CO selectivity with low O<sub>2</sub>/CO ratio.

Fig. 3 shows the performance of 1<sup>st</sup> reactor at various oxygen stoichiometry. At higher oxygen content, the CO conversion gets better. The excess oxygen, however, reacts with hydrogen heating up the reactor and consequently resulting in poorer selectivity. This implies that single reactor system would need much more oxygen to completely remove 1% of CO to less than 10 ppm. Such a high oxygen input would deteriorate the selectivity and hence sharply increase hydrogen loss. To reduce the burden of CO and increase the selectivity in the single reactor, multi-staged reactor system is required. However, as the number of reactors increases, the control gets more complex and the cost is more expensive in fuel cell application. This study investigated a two staged PROX system.

The inlet CO concentration to the 2<sup>nd</sup> stage is desired to be as high as possible in order to reduce the burden of the 1<sup>st</sup> stage. There is, however, a limit in it, since beyond a certain point, the final CO concentration from the 2<sup>nd</sup> stage can not be guaranteed under 10 ppm. The combined test of 1<sup>st</sup> stage and 2<sup>nd</sup> stage was performed at decreasing air inlet to the 1<sup>st</sup> stage, while the air inlet into 2<sup>nd</sup> stage was adjusted so that the outlet CO from the 2<sup>nd</sup> stage maintains under 10 ppm. Fig. 4 shows that 2<sup>nd</sup> stage can process as much as 1,200 ppm CO inlet, which is the case when O<sub>2</sub>/CO ratio to the 1<sup>st</sup> stage is 1.0. At that time, O<sub>2</sub>/CO ratio of 2<sup>nd</sup> stage is 2.0. At the ratios lower than 1.0 at 1<sup>st</sup> and 2.0 at 2<sup>nd</sup> stage, the outlet CO concentration of 2<sup>nd</sup> stage can't be held under 10 ppm.

Fig. 5 is the results of load transient test in two stages' PROX system. The total flow to the system is abruptly decreased from 100% to 35% and after 10 minutes it was returned back to 100%. During the transient change of the total flow, the outlet CO concentration is still remained under 10 ppm even though the temperatures of 1<sup>st</sup> and 2<sup>nd</sup> stage are changed. It is believed that the improved performance is due to the use of PROX catalyst that has high selectivity over a wide range of reaction temperature.

#### 4. Conclusion

The catalyst, which has high activity and selectivity over wide range of temperature, was developed. Using the catalyst, it is confirmed that 10,000 ppm of CO can be removed by two stages' PROX system for 1kW<sub>e</sub> fuel cell application. The steady and transient performance showed

good results that the outlet CO concentration could be held less than 10 ppm and the hydrogen consumption was about 1.4%. For 10kW PEMFC system, new design of scale-up PROX reactor is being developed. The catalyst with the higher selectivity at the wide temperature range will be developed continuously.

## References

1. Target PROX Specifications, 2000 Annual Progress Report, U.S. Department of Energy, p 163.
2. CO Clean-Up Development, M. Inbody *et al.*, 2000 annual Progress Report, U.S. Department of Energy, p 57.
3. Development & Evaluation of CO Selective Oxidation Reactor, C.D. Dudfield *et al.*, 1998 Fuel Cell Seminar Abstracts.

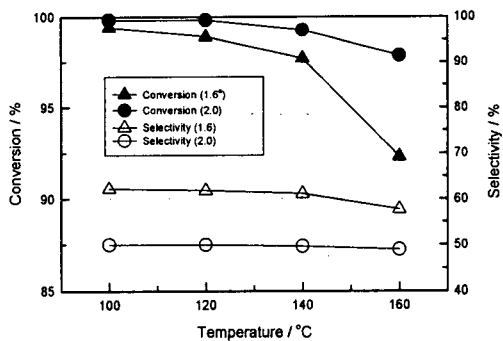


Fig. 1. Activity test of developed catalyst with the temperature.  
1.6<sup>a</sup>: O<sub>2</sub>/CO stoichiometry

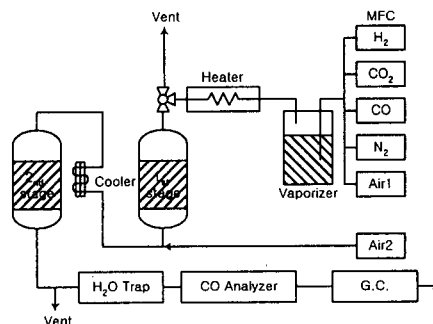


Fig. 2. Schematics of proto-type PROX system for 1kW<sub>e</sub> PEMFC

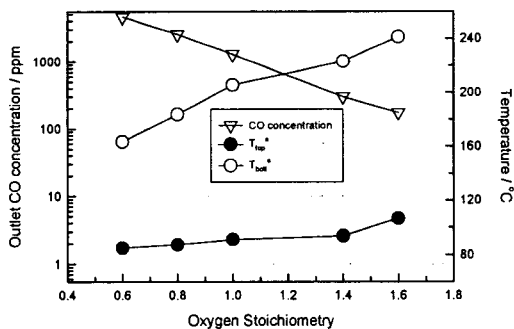


Fig. 3. The outlet CO concentration and temperature of single stage reactor with the oxygen stoichiometry.  
a: bed temperatures of gas inlet (T<sub>top</sub>) and outlet part (T<sub>bot</sub>)

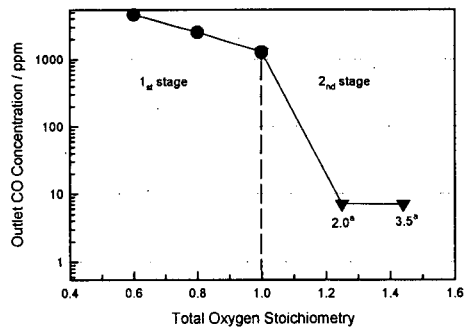


Fig. 4. The outlet CO concentration of two stages' system with oxygen stoichiometry.  
a: Inlet O<sub>2</sub>/CO ratio to 2<sup>nd</sup> stage

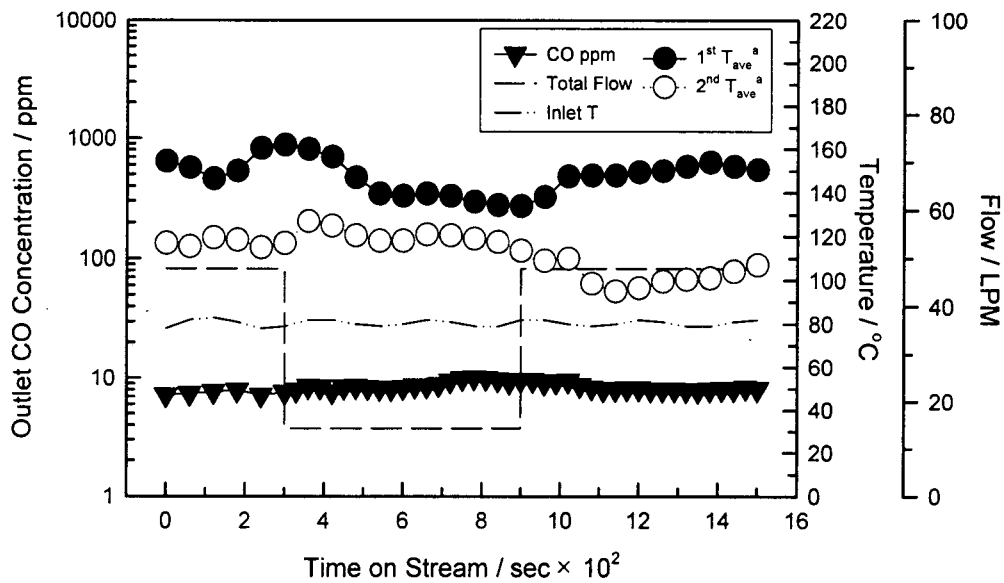


Fig. 5. The steady and load transient performance of proto-type two stages' PROX system for  $1\text{kW}_e$  PEMFC.

a: Arithmetic mean of bed temperatures at inlet part and outlet part in each stage.