Development of PROX (Preferential Oxidation of CO) System for 1 kW$_e$ PEMFC

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Abstract—PROX is known as one of the most promising technologies which prevent the anode of PEMFC from being poisoned by carbon monoxide. Hence, commercialization of the PEMFC system is highly dependent on the development of the corresponding PROX system. This study is focused on the development of the PROX system for 1 kW$_e$ PEMFC, and the results can be used to predict the performance of a higher-scaled system. Pt-Ru/Al$_2$O$_3$ catalyst made by incipient wetness method has been used for the reaction, since this catalyst shows high activity and selectivity for CO oxidation over a wide range of temperature. With the catalyst, a 1 kW$_e$ proto-type PROX system was set up and its performance was evaluated for the steady state as well as the transient conditions. The outlet CO concentration of the system was below 10 ppm at its steady state. Also, even at transient conditions, in which sudden flow rate change occurred, the resulting CO concentration still remained under 10 ppm.

Key words: PEMFC, PROX, Pt-Ru, CO Oxidation, Hydrogen

INTRODUCTION

During the last decade, PEMFC (Polymer Electrolyte Membrane Fuel Cell) has been moving more towards commercialization. Especially, in vehicular and residential applications, the market and technical requirements have been delineated by various organizations. One of the issues that still hinders the fuel cell from entering into the real market is durability. The main culprit raising the durability issue is carbon monoxide. If the reformate from the hydrocarbon is used, CO in reformate severely poisons the anode of PEMFC. Therefore, CO content in the reformate should be less than 20 ppm to make the system operable [U.S. Department of Energy, 2000].

To meet this requirement, several different methods for the CO removal have been studied including metal membrane [Han et al., 2000; Nam et al., 2000], PROX (Preferential Oxidation of CO) [Inbody et al., 2000; Dudfield et al., 1998], and combinations of them [Liu et al., 2000]. PROX is usually preferred because of its compactness and fast response to the load change. Especially for the vehicular application, in which compactness and fast response are very important, PROX is sometimes regarded as the only option satisfying the severe market and technical requirements. Los Alamos National Laboratory in the United States and MERCATOX group in Europe are the frontiers in the PROX development around the world. SK Corporation also has been working on PROX as a national project funded by the Korean government. This paper describes the current results of the study and is mainly focused on the performance of catalyst and 1 kW$_e$ PROX reactor system.

EXPERIMENTAL

1. Catalyst Preparation and Activity Test

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‡This paper is dedicated to Professor Wha Young Lee on the occasion of his retirement from Seoul National University.

The mixed solution of Pt and Ru precursors was impregnated at a certain weight ratio onto γ-alumina, sized 300-600 μm. The resulting paste was dried overnight and the dried powder was then calcined in H$_2$ for 4 hours. 0.15 g of the prepared catalyst was loaded in 4 mm I.D. of quartz tube reactor and lab-scaled activity test of the catalyst was performed by using a simulated gasoline reformate. Its composition was 36% H$_2$, 17% CO$_2$, 28% N$_2$, 17% H$_2$O, 1% CO, and air was added as the oxidant. Each gas was controlled by MFC and steam generator. The total flow rate was kept at 100 ml/min (wet base). The test was performed over the range of 100-160 °C at various flow rates of inlet air.

2. Scale-Up Test

The same size of catalyst was used in 1 kW$_e$ 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. 1 depicts the schematic diagram of the proto-type PROX system for 1 kW$_e$ PEMFC. The reactor system is designed as dual stages and the catalyst developed in this study is
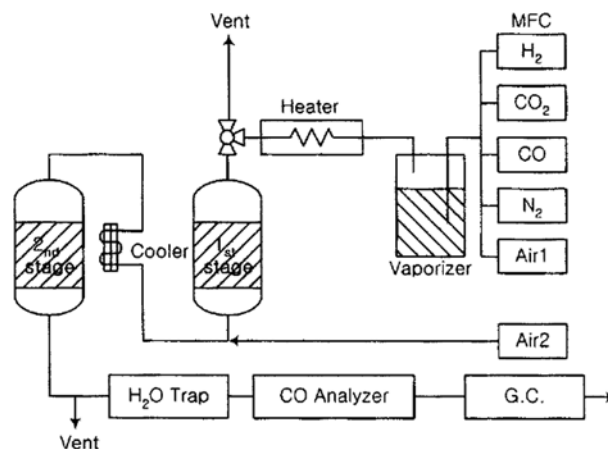

Fig. 1. Schematic diagram of the PROX system for 1 kW$_e$ PEMFC.

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% $H_2O(g)$. The mixed gas is then heated to the desired temperature by an electric heater before it enters the 1st stage. Until the gas reaches the desired temperature, it is vented out. When the temperature of the mixed gas is high enough to initiate the CO oxidation reaction on the catalysts, the flow is then switched to the 1st stage. Secondary air is added in between the 1st and 2nd stages. The gas mixed with the secondary air is cooled down to the desired temperature by the inter-stage cooler before it flows into the 2nd stage. Outlet gas from the 2nd stage is sampled and sent to CO analyzer and G.C. via an H_2O trap.

CO and H_2 concentrations in effluent gas from the reactor were analyzed by Infrared Gas Analyzer (California Analytical Instruments) and HERMOR615 (Maihak). CO_2, O_2, and CH_4 were analyzed by Gas Chromatography, in which TCD and FID detectors are equipped. Selectivity of CO oxidation was calculated by the following equation:

$$\text{Selectivity} = [(\text{moles of converted CO to } CO_2) / 2(\text{moles of total reacted } O_2)] \times 100$$

RESULTS AND DISCUSSION

The activity and the selectivity of Pt-Ru/Al_2O_3 catalyst were evaluated over the range of temperature, 100-160 °C, and shown in Fig. 2. The CO conversions and selectivities were compared for two different stoichiometric O_2/CO ratios in the reactant. When the ratio is 2.0, the CO conversion shows almost 100% at 100 °C and 98% at 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 with increasing temperature.

The conversion is lower but the selectivity is higher when the O_2/CO ratio is 1.6 than when the ratio is 2.0, regardless of the temperature in the reactor. In fuel cell applications, hydrogen loss in the PROX reactor significantly reduces the overall system efficiency; high CO selectivity of PROX catalyst is one of the major requirements together with the CO conversion. Fig. 2 clearly shows that a multi-staged reactor system, in which each stage has high CO selectivity with low O_2/CO ratio, is required to maximize the CO
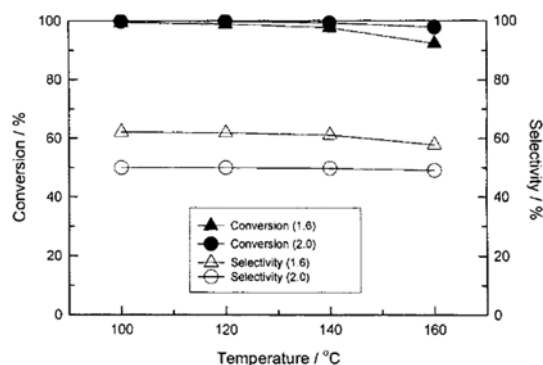

Fig. 3. Outlet CO concentration and temperature of the single stage reactor at different oxygen stoichiometries (T_{top} and T_{bott} are the catalyst temperatures at the inlet and outlet parts of the reactor, respectively).

selectivity and conversion.

Fig. 3 shows the performance of the single PROX reactor at various oxygen stoichiometry. At higher oxygen content, the CO conversion gets better but the selectivity gets worse. This is due to the fact that the excess oxygen starts to induce the undesirable hydrogen oxidation leading to increased reactor temperature in the reactor, and it in turn, contributes to lowering the selectivity. As a result, oxygen which is supposed to be used for CO oxidation gets rather insufficient. If one introduces more oxygen under this condition to complete the CO oxidation, this phenomenon propagates and gets even worse. To reduce the hydrogen loss and increase the selectivity together, a multi-staged system is required. As the number of reactor increases, however, the control becomes more complex and the cost is more expensive. This study investigated a dual stage PROX system as the simplest case.

In case of a dual stage system, the amount of air into each stage for the complete CO oxidation is very important. Also, the combined total amount of air for the reaction has to be kept as low as possible. Any excess in oxygen content is directly proportional to the hydrogen loss. The total amount of air is mostly determined by the amount into the 1st stage, since a major portion of CO is removed in that stage. Hence, minimizing the air flow to the 1st stage is desired. There is, however, a limit lowering the air flow into the 1st stage. Below a certain point, the CO content in the interstage gas

Fig. 2. Conversion and selectivity of the Pt-Ru/Al_2O_3 catalyst prepared in this study (Numbers in parenthesis are stoichiometric ratio of O_2 and CO).
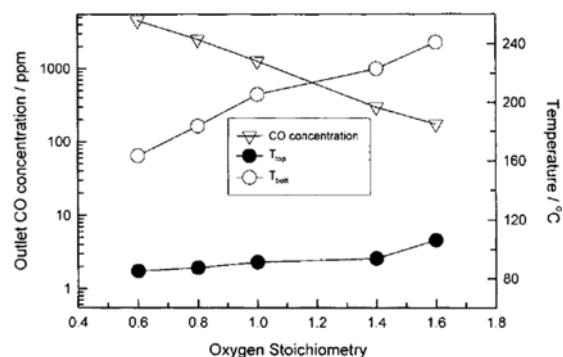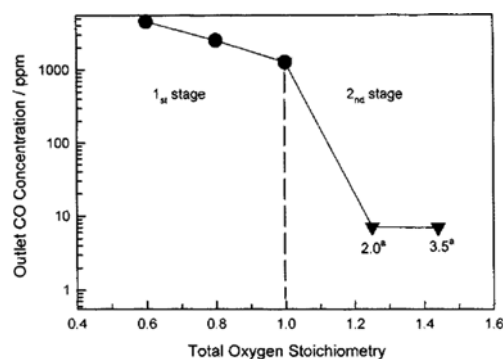

Fig. 4. The outlet CO concentration of the dual staged 1 kW$_e$ PROX at different oxygen stoichiometries (a: O_2/CO ratio for the 2nd stage alone).
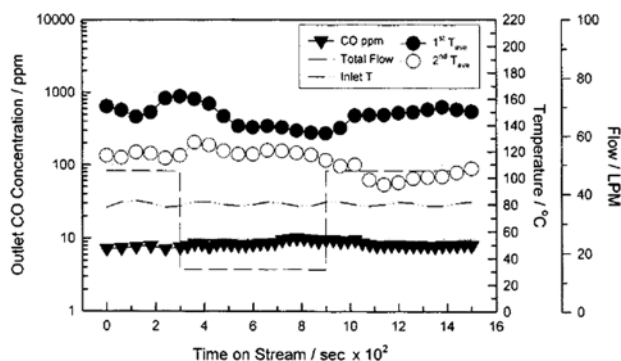
Fig. 5. The steady and the load transient performances of the dual staged 1 kW$_e$ PROX (T$_{ave}$ is the arithmetic mean of catalyst temperatures at inlet and outlet parts of each stage).

flow is so high that the CO level never goes down below 10 ppm in the 2nd stage. Therefore, there must be optimal amounts of air to the stages leading to the lowest hydrogen loss and hence highest CO selectivity.

Fig. 4 shows the result under the selected optimal amounts of inlet air. The 2nd stage can process as much as 1,200 ppm CO inlet, which is the case when O$_2$/CO ratios are 1.0 and 2.0 for the 1st and 2nd stages, respectively. Although the ratio for the 2nd stage is bigger than for the 1st stage, the actual amount of air into the 2nd stage is lower, since the CO content in the 2nd stage is much lower. At these ratios, the minimum amount of air is used in the system, meaning the highest CO selectivity. Therefore, the steady performance is determined at the optimum condition and is found to be enough to apply the PROX system to PEMFC.

Fig. 5 shows the results of load transient test in the dual stage PROX system. The total flow to the system is abruptly decreased from 100% to 35% and after 10 minutes it is returned back to 100%. During the transient change of the total flow, the outlet CO concentration still remains under 10 ppm, even though the temperatures of the 1st and 2nd stage are slightly disturbed. For fuel cell systems to be used in vehicular application, it is highly important to endure such a sudden load change. The load change is translated into the change in the amount of the reactant and it inevitably results in a temperature fluctuation in the PROX system. One can use a complex temperature control network to cope with such a disturbance and quickly return the system to the normal operating conditions. However, such a delicate temperature control adds complexity to the system as well as concerns about increased cost of the vehicle.

In this study, our PROX system shows good performance both for steady states and for transient condition without extensive temperature control. It is believed that the better performance is due to the characteristics of our PROX catalyst having high activity and selectivity over a wide range of reaction temperature.

CONCLUSION

A catalyst that has high activity and selectivity over wide range of temperature has been developed. Using the catalyst, it is confirmed that 10,000 ppm of CO can be removed by dual stage PROX system for 1 kW$_e$ fuel cell application. The steady and transient performances show good results in that the outlet CO concentration can be held at less than 10 ppm, and the hydrogen consumption is about 0.7%. For 10 kW PEMFC system, new design of scale-up PROX reactor has been developed and the performance is being evaluated.

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REFERENCES

Dudfield, C. D., Adcock, P. L. and Chen, R., "Development & Evaluation of CO Selective Oxidation Reactor," 1998 Fuel Cell Seminar Abstracts.

Han, J. S., Kim, I. S. and Choi, K. S., "Purifier-Integrated Methanol Reformer for Fuel Cell Vehicles," *J. Power Sources*, **86**, 223 (2000).

Inbody, M., Borup, R., Hedstrom, J., Morton, B., Hong, J. K. and Tafoya, J., "CO Clean-Up Development," 2000 annual Progress Report, U.S. Department of Energy, 57 (2000).

Liu, D. J., Williams, J. C., Kaiser, M. and Winstead, D. R., "Two New Approaches for CO Removal from Reformate Fuel for the PEM Fuel Cell Application," 2000 Fuel Cell Seminar Abstracts.

Nam, S. W., Yoon, S. P., Ha, H. Y., Hong, S.-A. and Maganyuk, A. P., "Methane Steam Reforming in a Pd-Ru Membrane Reactor," *Korean J. Chem. Eng.*, **17**, 288 (2000).

"Target PROX Specifications," 2000 Annual Progress Report, U.S. Department of Energy, 163 (2000).