연료전지자동차용 연료변환기의 일산화탄소 정제 장치

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Catalytic CO Clean-Up Unit in the On-Board Fuel Processor

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Introduction

In vehicle application of PEMFC, the use of pure hydrogen is known to be the best option in the sense that the fuel cell engine can be made compact and the dynamic characteristics can be close to the conventional internal combustion engines [1]. Besides, the regulation of zero-emission can be achieved only by the use of pure hydrogen. The drawback is, however, that the hydrogen infrastructure does not exist at present and the storage of hydrogen on-board still requires a lot of technical improvements. Therefore, on-board reforming system is considered as the near term solution for the fuel cell powered vehicle [2]. The on-board reforming system consists of two subsystems. One is the hydrogen generating unit, in which H_2-rich gas is produced by reforming hydrocarbon fuels. The other is the CO clean-up unit which eliminates CO from the reformate gas. CO is the main culprit to reduce the performance of PEMFC, so that it must be reduced to very low concentrations, 20~100ppm depending on the anode material and operation method of PEMFC [3,4]. In general, CO is reduced by water gas shift (WGS) reaction and by preferential oxidation (PROX) reaction. Between the two, WGS reaction is easier to control since WGS ($\Delta H = -41.1$ kJ/mol_{CO}) is much weaker exothermic reaction than PROX ($\Delta H = -283$ kJ/mol_{CO}). Whereas, the volume of catalyst to oxidize a certain amount of CO is smaller for PROX since the rate of PROX reaction is faster than that of WGS. Moreover, since there is a limit of thermodynamic conversion, the CO concentration low enough to be applied to PEMFC system cannot be achieved in WGS reaction. Therefore, in reforming system for PEMFC, the volume of CO clean-up subsystem has to be distributed appropriately to WGS and PROX considering the controllability and total volume of CO clean-up system. Especially for vehicular application of fuel cells, power density [kWe/volume] and specific power [kWe/weight] of fuel processor are important factors that must be considered in the design. Therefore, to reduce the volume and weight more, it is profitable that PROX deals with much CO within the limits of its controllability. It is known that the CO concentration in reformate before PROX is 1~2% in vehicle application [5,6].

In this study, the activities of Pt-Ru catalysts with various Pt/Ru ratios were investigated over the preferential CO oxidation. The determined catalyst was applied to 10kWe and 25kWe PROX systems. Their steady and transient performances were investigated using gasoline-reformed gas. Also, non-pellet type catalyst was applied to a small-scale PROX system and the design parameter is being studied for the development of the larger-scale PROX system.

Results and Discussion

1. Pt-Ru Catalyst Study

CO conversions over the catalysts with various ratios of Pt/Ru are shown in Fig. 1. The catalyst with composition E shows the highest conversion in screened catalysts over the temperature range of 120~240^{o}C, while the catalyst with composition A shows the lowest conversion. The composition A is the Pt-rich catalyst, while the composition E is the Ru-rich catalyst. As the composition is changed from A to E, methane concentration in effluent gas rises, as shown in Fig. 2. Although the catalyst with composition E among the screened catalysts showed the best performance for the CO removal at the whole reaction temperature range, the catalyst with composition D was chosen for the PROX, since the hydrogen consumption by methanation is too high in case of the catalyst with composition E.

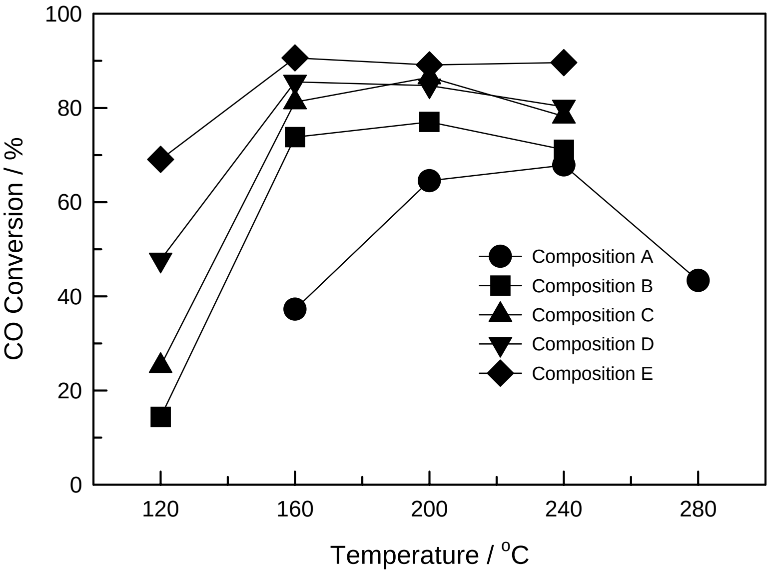

Fig. 1. The CO conversions over the catalysts with various compositions of Pt/Ru. GHSV 80,000hr^{-1}, O_2/CO = 1.0 (stoichiometric ratio)

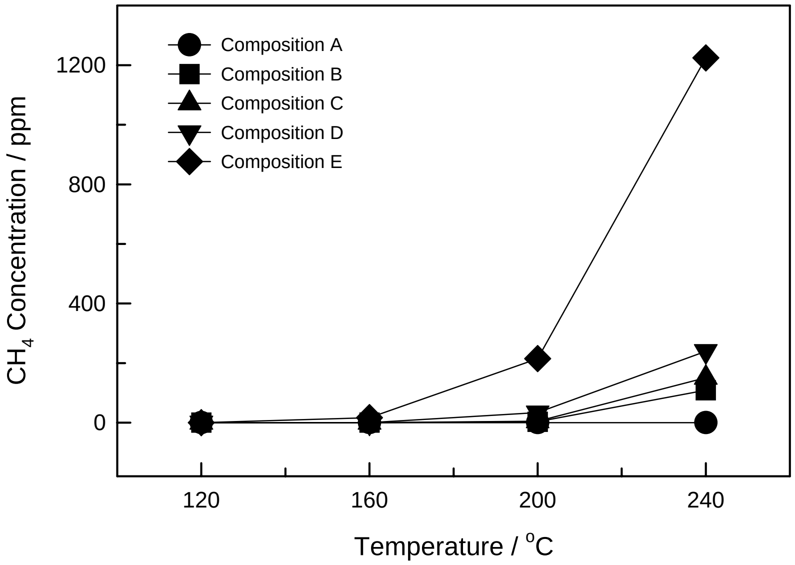

Fig. 2. The methane concentrations in the effluent gas. GHSV 80,000hr^{-1}, O_2/CO = 1.0 (stoichiometric ratio)

2. 10kWe and 25kWe PROX Development

Fig. 3 shows the 10kWe PROX systems. The reactor system was designed to minimize pressure drop even though small size of catalyst was applied. Each stage consisted of multi-tube reactors with 1/2 inch I.D. Inter-stage cooler was installed between 1st and 2nd stages. The modularized design of each stage makes it easily possible to enlarge the scale of PROX simply by inserting a stage considering pressure drop and catalyst size.

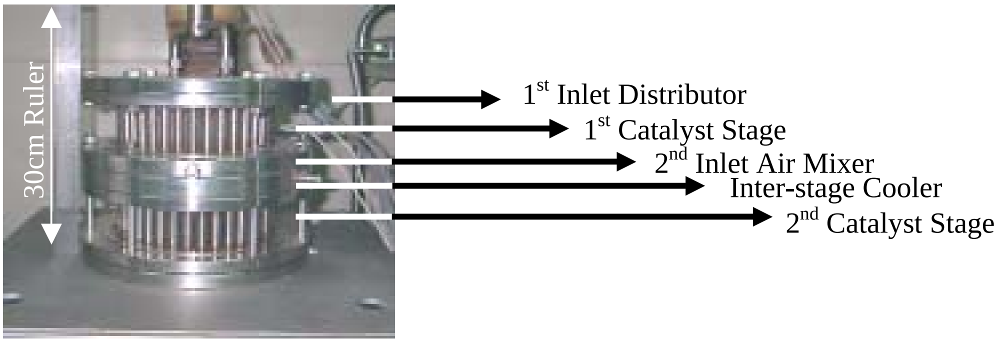

Fig. 3. 10kWe dual-staged PROX.

10kWe PROX was developed as dual-staged design. The gas distributor, which was specially designed for the homogeneous distribution of reactant to each parallel reactor, was installed in inlet part of each stage.

Fig. 4 shows 10kWe single-stage (catalyst volume, 0.06 L/kWe) and dual-stage (catalyst volume, 0.12 L/kWe) performances. Single-stage performances were evaluated using the 1st stage of 10kWe dual-staged reactor. In single-stage performance, the outlet CO concentration decreased with the increase in the inlet air. However, when the air was fed over 1.4 of stoichiometric O_2/CO ratio, the outlet CO concentration was increased on the contrary. This means that excess inlet air brought about the large extent of H_2 oxidation and hence CO selectivity became low at the elevated temperature.

Dual stage performances were evaluated adding the first and secondary air to each stage. The O_2/CO ratio of the 1st stage was held constant and the amount of the secondary air was controlled so that the outlet CO concentration of 2nd stage could be below 20ppm. The optimum steady state was determined at the condition that the total amount of inlet air was minimized and the outlet CO concentration of the 2nd stage maintained below 20ppm. When the 1st oxygen stoichiometry was in the range of 1.0~1.2, the amounts of total inlet air could be minimized as shown in Fig. 4. At the optimum condition, the outlet CO concentration was under 20ppm and the hydrogen loss was under 2%.

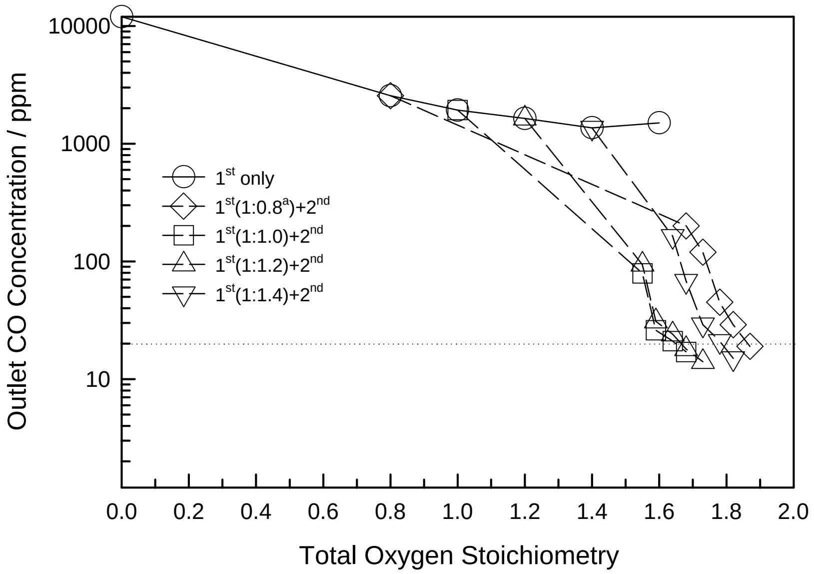

Fig. 4. 10kWe Steady Performance.
([a]:O_2/CO ratio for the first stage alone)

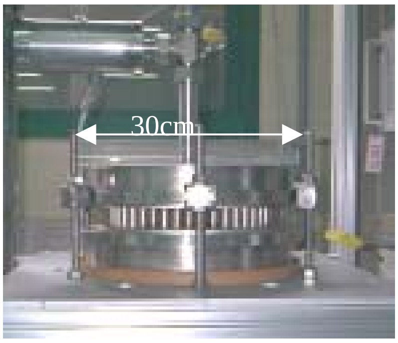

Fig. 5. 25kWe PROX Test-Set.

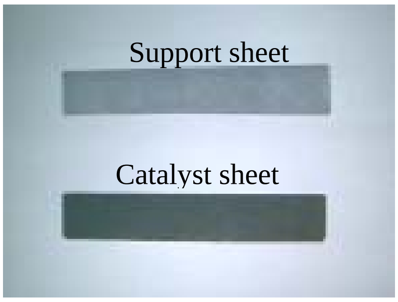

Fig. 6. Support Sheet and Catalyst–Coated Sheet.

The design of 10kWe PROX was also applied to 25kWe PROX. The design and construction of 25kWe PROX was finished and the performance is being evaluated. Fig. 5 shows the test set for the 1st stage of 25kWe PROX. Using only one stage, the steady performance of dual-staged PROX could be estimated. When the inlet CO concentration in the reformate was 10,000ppm, the outlet CO concentration was 1500ppm at 1.2 of the oxygen stoichiometric ratio. Also, when the inlet CO concentration in the reformate was 1500ppm, the outlet CO concentration could be lowered fewer than 20ppm at 2.5 of the oxygen stoichiometric ratio. For the performance confirmation of the 25kWe PROX, the dual-staged integration test will be performed.

3. Non-pellet Application

Small-scale PROX was manufactured in a type of heat exchanger using non-pellet catalyst. Fig. 6 shows the support and catalyst sheets. Pt-Ru catalyst screened in Fig. 1 and 2 was impregnated on the support sheet that γ-Al_2O_3 is coated on porous sus-mesh plate (thickness 1.0mm). The surface area of the catalyst sheet is $96m^2/g$. The catalyst sheet was applied to a heat exchanger type of PROX. Air will be applied as the coolant. The preheated air can be used efficiently in PEMFC system since the air fed into the auto-thermal reformer or cathode of PEMFC should be heated to each operating temperature for the proper operation. Moreover, the PROX can be controlled isothermally, so that the high performance of the PROX is expected as well as highly compact volume. Currently, the performance evaluation is being processed with a patent for this design.

Conclusions

10kWe PROX was developed with highly compact volume (catalyst volume 0.12L/kWe) and it showed good performances that the outlet CO concentration was under 20ppm at steady state consuming 1.8% of hydrogen. 25kWe PROX with compact volume is also being developed. The performance of 25kWe dual-staged PROX could be estimated using 1st stage only. The result was that the outlet CO concentration was 1500ppm at 1.2 of the oxygen stoichiometric ratio, when the inlet CO concentration in the reformate was 10,000ppm. Also, when the inlet CO concentration in the reformate was 1500ppm, the outlet CO concentration could be lowered fewer than 20ppm at 2.5 of the oxygen stoichiometric ratio. To meet the challenge of non-pellet application, small-scaled PROX with a heat exchanger type was manufactured and is currently being evaluated.

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