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Development of residential PEFC cogeneration systems: Ru catalyst for CO preferential oxidation in reformed gas

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Abstract

The performance of the novel Ru catalyst in a single-stage CO preferential oxidation removal reactor was investigated for residential polymer electrolyte fuel cell (PEFC) cogeneration systems. The outlet CO concentration of the CO removal reactor was reduced to less than 1 ppm even at $[O_2]/[CO] = 1.5$. The natural gas fuel processor equipped with the CO removal reactor achieved the target thermal efficiency of 77% (LHV). Moreover, the durability of the Ru catalyst has been confirmed for more than 16,000 h at a micro-reactor and for more than 8000 h at an actual CO removal reactor. Because of the low O_2/CO molar ratio, the high CO removal conversion and the long-term durability, the Ru catalyst contributes to the development of residential PEFC cogeneration systems.

Keywords: CO preferential oxidation; Ru catalyst; Fuel processor; Natural gas; Reformed gas; Polymer electrolyte fuel cell; Residential use

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1. Introduction

Fuel cells have been anticipated as high efficiency and clean power generation devices. Recently, polymer electrolyte fuel cell (PEFC) systems have increasingly been developed for transportation and stationary power sources applications, especially for vehicle and residential use. From a feasibility study for residential energy demand in Japan, Osaka Gas has been developing 0.5–1 kW class PEFC cogeneration systems for residential use. The target specifications of the residential PEFC cogeneration systems are shown in Table 1. An AC power generation efficiency of not less than 35% (LHV) and a heat recovery efficiency of not less than 30% (LHV) are required for these systems in order to save energy. Moreover, 90,000 h durability is required for these systems. Natural gas provided as city gas is thought to be a promising fuel for residential use in terms of infrastructure.

The natural gas reforming process, comprising desulfurization, steam reforming and CO shift reactors, has already been established for phosphoric acid fuel cell (PAFC) systems [1–3]. However, for the PEFC system using hydrocarbons as the raw fuel, a CO removal process is required in addition to the reforming process established for the PAFC. That is because the anode catalyst of the PEFC is poisoned by small amounts of CO in the reformed gas [4–8]. Considering long-term durability, the acceptable CO concentration appears to be about 10 ppm, even if a CO tolerant anode catalyst is adopted and bleed air

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Table 1
Target specifications of the residential PEFC cogeneration systems

Nominal output	500 W	1 kW
Net AC power generation efficiency	≥35% (LHV)	≥35% (LHV)
Heat recovery efficiency (hot water)	≥30% (LHV) at 60 °C	≥35% (LHV) at 70 °C
Durability	90,000 h (10 years)	90,000 h (10 years)
Turn down	50/100%	30/50/75/100%
Operation mode	Grid connected continuous	Grid connected continuous

is supplied to the anode [8]. As the inlet CO concentration of the anode is increased, the cell voltage decreases [4,5,7]. The cell voltage determines the power generation efficiency of the cell stack. Therefore, the outlet CO concentration in the CO removal process is an important parameter governing the power generation efficiency of the PEFC system.

A CO preferential oxidation process using a noble metal catalyst has generally been used for the CO removal process. It has been reported that CO was reduced to ca. 100 ppm on a Pt/Al_2O_3 catalyst with the addition of air corresponding to $[O_2]/[CO] = 2$ (molar ratio) [4]. It has been also reported that the additive air corresponding to $[O_2]/[CO] \geq 3$ was needed to remove CO to below the detection limit from H_2 containing 1.0 vol.% CO on a conventional Pt/Al_2O_3 catalyst [9]. The excess O_2 wastes H_2 fuel in the reformed gas by combustion. Therefore, the O_2/CO molar ratio in the CO preferential oxidation removal process is also an important parameter governing the power generation efficiency of the PEFC system. Moreover, when the large amount of air is added to the CO removal reactor, it becomes difficult to control the temperature of the CO removal reactor due to the reaction heat evolution. Thus, several kinds of noble metal catalysts have been studied to improve CO preferential oxidation removal [7,9–16]. Some reports show that Ru catalyst has wider temperature window for CO preferential oxidation removal than Pt catalyst [7,11,12]. It has been reported that CO was reduced below 100 ppm at ca. 195–230 °C on a Ru catalyst, while at ca. 190–200 °C on a Pt catalyst under the experimental conditions of $H_2/CO/CO_2/O_2 = 75/1/25/1.5$ and $SV = 6500\,h^{-1}$. The minimum outlet CO concentration of the Ru catalyst appeared to be ca. 50 ppm [12]. On the other hand, some reports show that zeolite-supported noble metal catalysts has higher selectivity for CO preferential oxidation removal than Pt catalyst [9,10,16]. It has been reported that 100% and ca. 90% CO conversions were achieved in the reaction mixture consisted of 1.0% CO, 0.5% O_2, and H_2 balance on Ru/Mordenite and Pt–Ru/Mordenite, respectively. CO_2 and H_2O were not contained in the reaction mixture. It was described that there is room for the improvement of the Ru/Mordenite due to the narrow temperature window, and the Pt–Ru/Mordenite is a promising catalyst [16].

Recently, multi-stage CO preferential oxidation has been repeatedly proposed for the CO removal process [9,14,17–20]. In multi-stage CO preferential oxidation, the total amount of additive air can be reduced by optimizing the additive air at each stage. Moreover, temperature control at each stage becomes easier because there is less reaction heat evolution for each stage. Therefore, CO is removed to less than 10 ppm successfully by the multi-stage CO preferential oxidation process in the actual reactors. It has been reported that CO was reduced to less than 10 ppm by a two-stage reactor at a total additive air corresponding to $[O_2]/[CO] > 2$ [17]. However, complex hardware is required to control temperatures and oxidant injections along the multi-stage catalytic layer. Hence, the single-stage CO removal process is preferable for residential use.

A simulation of the natural gas steam reforming process shows that the O_2/CO molar ratio should be reduced to 1.5 in order to achieve the target fuel processor efficiency of 77% (LHV) when the fuel utilization rate of the cell stack is assumed to be 75%. The target fuel processor efficiency is obtained by inverse calculation on the assumption that the AC power generation efficiency = 35%, the cell stack efficiency = 56%, the inverter efficiency = 90% and the AC power consumption of auxiliaries = 10%. Consequently, it is essential to develop a CO preferential oxidation catalyst, on which CO can be removed to below 10 ppm at $[O_2]/[CO] \leq 1.5$ in the single-stage process in order to develop the residential PEFC cogeneration systems.

Moreover, the establishment of the durability of the CO preferential oxidation catalyst is very important for the residential system because the long-term durability of the catalyst has never been reported.

In this paper, the performance, including the long-term durability, of the novel Ru catalyst in a single-stage CO preferential oxidation removal reactor for residential PEFC cogeneration systems is reported.

2. Experimental

The novel Ru catalyst was prepared by an impregnation method. The precursors were obtained by the impregnation of aqueous solution of $RuCl_3$ into γ-Al_2O_3 (2–4 mm Ø spheres). They were washed and dried followed by reduction in N_2H_4 aqueous solution. Then, the novel Ru catalyst was obtained by a pre-treatment of the Ru/Al_2O_3 in N_2 containing H_2 flow before the use. The pre-treatment improves CO preferential oxidation activity of the catalyst [21]. Ru loading on the catalyst was 1.0 wt.%. The specific surface area of the Ru catalyst was 174 m^2/g by BET one point method using N_2 adsorption. A conventional Pt/Al_2O_3 catalyst was prepared by an impregnation method as a reference. Pt loading on the catalyst was 1.0 wt.%.

Catalytic activity was measured in a conventional fixed bed flow reactor made of stainless steel tube under almost atmospheric pressure. 8 mm (5.6 g) of the catalyst was placed at the center of reactor. To measure the CO preferential oxidation activity, the temperature of the reactor was increased to the test temperature under a N_2 flow. The test gas, generated from the standard gas by mass flow controllers, was fed at a flow rate of 1000 ml/min corresponding to GHSV = 7500 h^{-1}. The GHSV value was shown in dry base. Water was added to all the test gas by a pump through a vaporizer before the reactor. The test gas composition is simulated to resemble the reformed gas after the CO shift converter with additive air. Reaction temperatures were measured by a thermocouple located along the centerline of the reactor. The maximum temperature of the catalyst layer, which was always at the top of the catalyst layer, was shown in the table and figures as the reaction temperature.

The gas composition at the inlet and the outlet of the reactor at a stationary state was analyzed by a gas chromatograph equipped with TCD and FID. The results are shown in dry base. The detection limit of both CO and CH_4 was 1 ppm, while the detection limit of O_2 was 20 ppm. The concentration below the detection limit was plotted as 0 ppm in the figures.

The fuel processor efficiency was defined as (heat of H_2 consumed at the cell stack)/(total natural gas input to the fuel processor).

3. Results and discussion

3.1. Comparison of the CO preferential oxidation activities on the conventional Pt catalyst and the novel Ru catalyst

Table 2 shows the comparison of CO preferential oxidation activity on the conventional Pt catalyst and of the novel Ru catalyst at $[O_2]/[CO] = 1.5$. In the case of the Pt catalyst, 1226 ppm CO and 2782 ppm O_2 remained in the outlet gas at 100 °C. As the reaction temperature was increased to 160 °C, the outlet CO concentration decreased to 23 ppm with the increase in O_2 consumption. Although additive O_2 was consumed sufficiently at 180 °C, the outlet CO concentration increased to 77 ppm. Thus, on the Pt catalyst, CO was not removed to below 10 ppm

Table 2
Comparison of the activities on the conventional Pt catalyst and the novel Ru catalyst[a]

Reaction temperature (°C)	Conventional Pt catalyst Outlet gas composition			Novel Ru catalyst Outlet gas composition		
	CO (ppm)	O_2 (ppm)	CH_4 (ppm)	CO (ppm)	O_2 (ppm)	CH_4 (ppm)
100	1226	2782	N.D.	N.D.	N.D.	49
120	575	1518	N.D.	N.D.	N.D.	147
140	114	443	N.D.	2.7	N.D.	387
160	23	103	N.D.	5.3	N.D.	1060
180	77	N.D.	N.D.	12	N.D.	3039

[a] Reaction conditions: 0.5 vol.% CO, 20 vol.% CO_2, 0.75 vol.% O_2, 3 vol.% N_2, H_2 balance (dry base), 11 vol.% H_2O (wet base), GHSV = 7500 h^{-1} (dry base).

from the simulated reformed gas at $[O_2]/[CO] = 1.5$. Concerning methanation as a side reaction, the outlet CH_4 concentration was less than the detection limit between 100 and 180 °C.

On the other hand, in the case of the Ru catalyst, CO was removed to less than 1 ppm (the detection limit) at 100 °C. As the reaction temperature was increased to 180 °C, the outlet CO concentration increased to 12 ppm. Additive O_2 was completely consumed at all the reaction temperatures. Thus, on the Ru catalyst, CO was removed to below 10 ppm at least between 100 °C and ca. 170 °C even at $[O_2]/[CO] = 1.5$. In particular, the outlet CO concentration of the catalyst layer was less than 1 ppm between 100 and 120 °C. As for methanation, the outlet CH_4 concentration was increased with increasing reaction temperature.

It is generally considered that the selectivity for CO oxidation is high at lower temperatures. However, the O_2 oxidation activity of the Pt catalyst was low in the low temperature range, so that the outlet O_2 of the catalyst, which failed to react, increased with decreasing reaction temperature below 180 °C. Therefore, even if selectivity for CO oxidation was high at the lower temperatures, the amount of O_2 used for CO oxidation was limited on the Pt catalyst. Consequently, high CO removal conversion was not achieved at the low O_2/CO molar ratio on the Pt catalyst. On the other hand, the additive O_2 was consumed completely on the Ru catalyst even at 100 °C. Because CO was oxidized effectively by the small amount of O_2, CO removal at the low O_2/CO molar ratio became possible on the Ru catalyst in the low temperature range. It can be explained that the CO preferential oxidation activity is dominated not by the selectivity but by the O_2 oxidation activity in the low temperature range. Moreover, there is a possibility that the methanation of CO contributes to CO removal on the Ru catalyst. CH_4 generated by the methanation during the CO removal process can be finally used as the fuel at the reformer burner through the cell stack in the natural gas steam reforming process. Further studies are required in order to clarify the effect of the CO methanation on the CO removal over the Ru catalyst.

It is calculated that CH_4 generation of 500 ppm by the side reaction reduced the fuel processor efficiency in ca. 0.1%. And, the natural gas fuel processor efficiency of 77% (LHV) can be achieved even if several hundreds ppm CH_4 is generated as the methanation side reaction in the CO preferential oxidation process at $[O_2]/[CO] = 1.5$. Therefore, the Ru catalyst can satisfy the requirement to achieve the target fuel processor efficiency for a residential PEFC cogeneration system. Furthermore, the temperature window, where CO is removed to below 10 ppm at $[O_2]/[CO] = 1.5$, is sufficiently wide, so that temperature control of the catalyst layer becomes easy. As for size, the volume of catalyst corresponding to GHSV $= 7500\,h^{-1}$, which is much less than that of the steam reforming catalyst, is reasonably acceptable in a CO removal reactor for residential use. Thus, the Ru catalyst makes possible single-stage CO preferential oxidation removal at $[O_2]/[CO] = 1.5$ with simple temperature control for a residential PEFC system.

3.2. *Long-term durability of the Ru catalyst*

A long-term durability test result of a CO preferential oxidation catalyst has not been reported, so that it is very important to establish the durability of the catalyst for a residential PEFC system, which requires 90,000 h durability.

Fig. 1 shows the durability test result of the CO preferential oxidation on the Ru catalyst at $[O_2]/[CO] = 2.0$. CO has been removed to below 2 ppm stably on the Ru catalyst for more than 16,000 h, except for an experimental error at around 10,600 h. The dependence of the CO preferential oxidation activity on reaction temperature was investigated after 10,000 h of operation at $[O_2]/[CO] = 1.5$ and 2.0. The results are shown in Fig. 2. The outlet CO concentration of the catalyst layer was below 10 ppm at least between ca. 100 and 170 °C at $[O_2]/[CO] = 1.5$. There were few differences in the outlet CO concentration between those two conditions. Thus, the temperature window of the Ru catalyst, where CO was removed to below 10 ppm, was sufficiently wide even at the low O_2/CO molar ratio after 10,000 h of operation. It was confirmed that the remarkable degradation of the CO preferential oxidation activity of the catalyst did not appear under long-term operation.

3.3. *Performance of the Ru catalyst in natural gas fuel processors*

High efficiency and low cost natural gas fuel processors have been developed for the 500 W and 1 kW

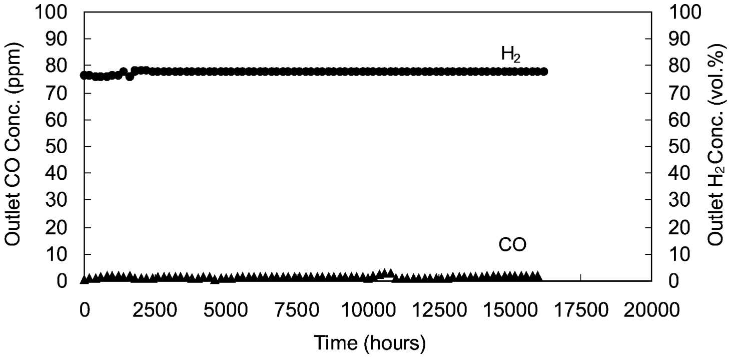

Fig. 1. Durability test result of the CO preferential oxidation on the novel Ru catalyst. Reaction conditions: 0.5 vol.% CO, 19 vol.% CO_2, 1 vol.% O_2, 4 vol.% N_2, H_2 balance (dry base), 20 vol.% H_2O (wet base), temperature = 120 °C, GHSV = 7500 h^{-1} (dry base).

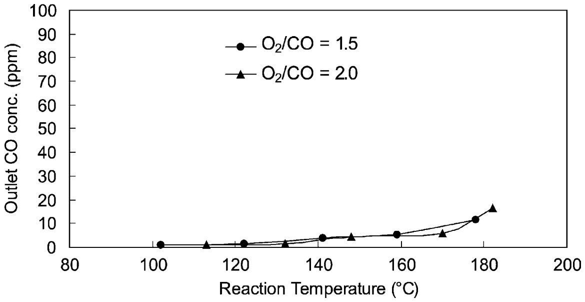

Fig. 2. CO preferential oxidation activity of the novel Ru catalyst after 10,000 h of operation. Reaction conditions: 0.5 vol.% CO, 19 vol.% CO_2, 0.75 or 1.0 vol.% O_2, 3 or 4 vol.% N_2, H_2 balance (dry base), 20 vol.% H_2O (wet base), GHSV = 7500 h^{-1} (dry base); (●) $[O_2]/[CO] = 1.5$, (▲) $[O_2]/[CO] = 2.0$.

residential PEFC cogeneration systems [22]. These fuel processors contain desulfurizers, steam reformers, CO shift reactors, and CO removal reactors, with steam generators, burners and heat exchangers. The single-stage CO preferential oxidation is adopted for the CO removal process. The CO removal reactor is filled with the Ru catalyst, and the O_2/CO molar ratio is set at 1.5. The size of the fuel processor for the 1 kW PEFC system was $280(W) \times 440(L) \times 395(H)$, including thermal insulation. Table 3 shows the recent performance data of the fuel processors. In the case of the 1 kW class fuel processor, the thermal efficiency reached 77% (LHV) under the condition of $S/C = 2.5$, $[O_2]/[CO] = 1.5$, on the assumption of fuel utilization rate at the cell stack of 75%. The outlet CO concentration was stably less than 1 ppm. Thus, the CO removal at $[O_2]/[CO] = 1.5$ using the Ru catalyst contributes to achieving the target fuel processor efficiency.

The durability test of the fuel processor for the 1 kW PEFC system was carried out at $S/C = 3.0$. In the test, the nominal output operation and the half load operation were repeated alternately every hour, because continuous operation with a fluctuating load control is presumed for an early commercial PEFC system for residential use. Fig. 3 shows the change of the outlet gas composition of the fuel processor at the nominal output operation. The outlet gas composition hardly changed over more than 8000 h. Thus, it was confirmed that the fuel processor is satisfactorily reliable

Table 3
Initial performance data of the natural gas fuel processors[a]

Class	S/C	O_2/CO	Thermal efficiency (LHV) (%)	Composition of product gas (dry base)				
				H_2 (vol.%)	N_2 (vol.%)	CH_4 (vol.%)	CO_2 (vol.%)	CO (ppm)
500 W	2.5	1.5	75	75.36	2.76	1.77	20.1	<1
1 kW	2.5	1.5	77	75.39	2.77	1.77	20.07	<1

[a] Composition of natural gas: $CH_4 = 88\%$, $C_2H_6 = 6\%$, $C_3H_8 = 3\%$, $C_4H_{10} = 3\%$, assumption of H_2 utilization rate in cell stack: 75%.

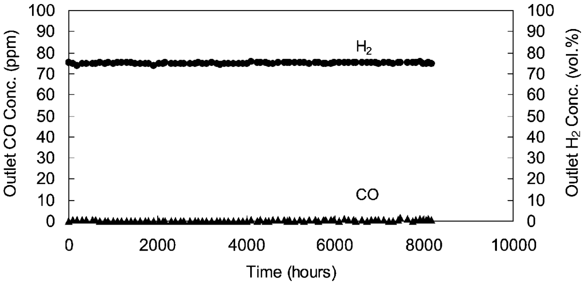

Fig. 3. Durability test result of the natural gas fuel processor.

for long-term operation, even if there were frequent changes in the load. Moreover, the outlet CO concentration of the fuel processor was stably less than 1 ppm for more than 8000 h. CO was also stably removed to less than 1 ppm despite changes in the load. Thus, it was also confirmed that the Ru catalyst has sufficient activity, usability and durability in an actual CO removal reactor for a residential PEFC system.

Moreover, the power generation tests have been conducted on the natural gas fuel processors with cell stacks in trial residential PEFC cogeneration systems. The cell stack can be operated stably without bleed air to the anode, because CO in the reformed gas provided to the anode is reduced to less than 1 ppm in the fuel processor. Therefore, the H_2 combustion loss by bleed air on the anode catalyst is prevented. Consequently, the Ru catalyst contributes to an increase in the power generation efficiency of the residential PEFC cogeneration system thanks to the low outlet CO concentration as well as the low O_2/CO molar ratio.

4. Conclusion

The CO preferential oxidation activities of the novel Ru catalyst and the conventional Pt catalyst were investigated for a residential PEFC cogeneration system. At $[O_2]/[CO] = 1.5$, CO was removed to below 10 ppm at least between ca. 100 and 170 °C on the Ru catalyst, while CO was not reduced to below 10 ppm on the Pt catalyst. In particular, the outlet CO concentration of the Ru catalyst was less than 1 ppm between 100 and 120 °C. The performance of the Ru catalyst satisfies the requirements of the target fuel processor efficiency and the single-stage CO removal reactor for a residential PEFC cogeneration system. As for durability, the CO preferential oxidation activity of the Ru catalyst has hardly changed over more than 16,000 h.

Moreover, natural gas fuel processors equipped with single-stage CO preferential oxidation removal reactors using the Ru catalyst have been developed for residential PEFC cogeneration systems. The 1 kW class fuel processor showed the target thermal efficiency of 77% (LHV) under the condition that the S/C ratio at the steam reformer was 2.5, the O_2/CO ratio at the CO removal reactor was 1.5, assuming fuel utilization in the cell stack of 75%. The outlet CO concentration of the fuel processor was reduced to less than 1 ppm for more than 8000 h. Thus, the Ru catalyst makes possible single-stage CO preferential oxidation removal at $[O_2]/[CO] = 1.5$ at the target fuel processor efficiency for a residential PEFC cogeneration system.

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