

## Optimum operating conditions of DIR-MCFC without vapor-phase carbonate pollution

Kimihiko Sugiura<sup>a,\*</sup>, Mayumi Daimon<sup>a</sup>, Kazumi Tanimoto<sup>b</sup>

<sup>a</sup>Osaka Prefectural College of Technology, 26-12 Saiwai, Neyagawa, Osaka 572-8572, Japan

<sup>b</sup>National Institute of Advanced Industrial Science and Technology, Kansai,  
1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

### Abstract

In direct internal reforming-molten carbonate fuel cells (DIR-MCFC), deterioration of catalytic activity takes place in the anode channel due to both liquid-phase pollution and vapor-phase pollution. Although the liquid-phase pollution can be solved by installing protective barrier, an effective defense method and a reactivation method of vapor-phase polluted catalyst have not established yet. In order to study the reactivation method, the adhesion form of potassium compounds in the polluted catalyst under the various gas conditions was evaluated by using a thermogravimetric analyzer in which water vapor can feed. Additionally, the activity of the treated catalyst was also tested by a differential reactor. As a result, KOH changes to  $K_2CO_3$  under a  $CO_2$  concentration of 25% or more. KOH becomes a solid-phase from the liquid-phase when it is changed into  $K_2CO_3$ . Therefore, the catalyst can not be reactive because  $K_2CO_3$  chokes pores of the catalyst. However, the activity of the polluted catalyst is revived to 80% of the initial activity by controlling the gas species concentration, especially  $CO_2$ . Moreover, the catalytic activity can be revived under a steam-carbon ratio of 2.0 or more. Based on the results obtained by these fundamental experiments, the reactivation methods of catalyst polluted are proposed as follows: (i) catalyst should be loaded more upstream in the anode; (ii) in order to reactivate the polluted catalyst, the DIR-MCFC should maintain a steam-carbon ratio of 2.0 or more; (iii) gas conditions to activate the catalyst should be applied regularly.

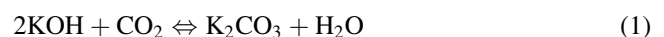
© 2003 Elsevier Science B.V. All rights reserved.

**Keywords:** DIR-MCFC; Reforming catalyst; Pollution; Mass change performance

### 1. Introduction

In direct internal reforming-molten carbonate fuel cells (DIR-MCFC), deterioration of catalytic activity takes place in the anode channel due to both liquid-phase pollution and vapor-phase pollution [1–5]. The liquid-phase pollution meant that catalytic activity is deteriorated by the molten salt's ( $62Li_2CO_3/38K_2CO_3$ ) adhering to the catalyst [6]. It can be solved by installing protective barrier in the pollutant pathway [7]. On the other hand, the vapor-phase pollution meant that that catalytic activity is deteriorated by KOH adhering to the catalyst [8]. Because the vapor-phase pollution is caused in the entire electrode, an effective defense method has not yet been established. Moreover, a reactivation method of a vapor-phase polluted catalyst has not yet been developed. In the vapor-phase pollution, the adhesion form of content potassium in the polluted catalyst is decided depending on the various gas conditions. Generally,

potassium changes the form to KOH or  $K_2CO_3$  by  $CO_2$  and  $H_2O$  concentration as shown in Eq. (1).



Though KOH is the liquid-phase at the cell temperature,  $K_2CO_3$  is the solid-phase. Although the supplying inert gas can volatilize KOH from the polluted catalyst, it can not volatilize  $K_2CO_3$ . Therefore, if the influence of the gas compositions on KOH in the polluted catalysts is evaluated, a reactivation method for the vapor-phase polluted catalyst is proposed. The adhesion form of the potassium content in the polluted catalyst was evaluated by using a thermogravimetric analyzer in which water vapor can be fed. Additionally, a differential reactor also tested the activity of the treated catalyst [9]. Moreover, the influence of the steam-carbon ratio, which is the operating condition of the DIR-MCFC, on the KOH form is examined. Finally, this paper proposes a reactivation method for catalyst polluted by vapor-phase carbonate and the optimum the conditions operating a DIR-MCFC without vapor-phase carbonate pollution.

\* Corresponding author. Tel.: +81-72-820-8537; fax: +81-72-821-0134.  
E-mail address: [sugiura@sys.osaka-pct.ac.jp](mailto:sugiura@sys.osaka-pct.ac.jp) (K. Sugiura).

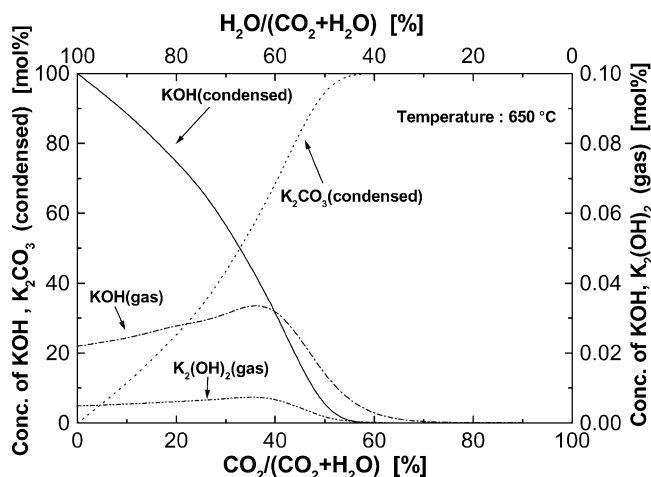


Fig. 1. Chemical equilibrium calculation of KOH–K<sub>2</sub>CO<sub>3</sub>.

## 2. Chemical equilibrium calculation of KOH–K<sub>2</sub>CO<sub>3</sub> reaction

Fig. 1 shows the result of calculating the chemical equilibrium of the KOH–CO<sub>2</sub> reaction shown in Eq. (1). The thermodynamic data was quoted from JANAF Thermo-chemical Tables [10]. Here, “condensed” means the coexistence of both of the solid-phase and the liquid-phase. A reactive temperature is the cell temperature of 650 °C. The chemical equilibrium is calculated by changing CO<sub>2</sub>/(CO<sub>2</sub> + H<sub>2</sub>O), which is arranged with the mole fractions. KOH (liquid-phase) is changed into K<sub>2</sub>CO<sub>3</sub> (solid-phase) by the addition of CO<sub>2</sub>. In the condensed-phase, the concentration of KOH and K<sub>2</sub>CO<sub>3</sub> correspond when the CO<sub>2</sub> concentration is about 33%. In the vapor-phase, KOH and K<sub>2</sub>(OH)<sub>2</sub> exist a little, and they are changed into K<sub>2</sub>CO<sub>3</sub> (solid-phase) with increasing CO<sub>2</sub>, too. Here, K<sub>2</sub>CO<sub>3</sub> (vapor-phase) is negligible under this

calculated condition because it is about  $2 \times 10^{-8}$  mol%. Therefore, if the DIR-MCFC could be operated under CO<sub>2</sub> of 33% or less, the catalytic activity may be able to be revived to volatilize KOH by supplying an inert gas. Moreover, the concentration of each gas species hardly influences the reaction temperature (range of 400–650 °C).

## 3. Experimental apparatus and procedures

From the above-mentioned chemical equilibrium calculation, steam and the CO<sub>2</sub> concentration greatly influence the form of KOH in the catalyst. If the mass change of the polluted catalyst can be measured under various gas compositions, the form of KOH in the polluted catalyst can be confirmed because the mass of KOH and K<sub>2</sub>CO<sub>3</sub> is greatly different. However, steam can not be supplied to the reactor because the sensor is in the reactor of a conventional thermogravimetric analyzer. Therefore, the thermogravimetric analyzer in which water vapor can be fed employed in this study as shown in Fig. 2. The mass change of the polluted catalyst filled to the sample basket, which is made of a stainless mesh, can be measured by being hung from an electronic balance within the reactor. The temperature of the polluted catalyst is also measured by thermocouple (type: K, diameter: 0.5 mm) that is installed in the basket so as not to interfere in the mass measurement. The computer continuously takes these data under the temperature rise with electric furnace. The supply gases, which are mixed H<sub>2</sub>, N<sub>2</sub>, and CO<sub>2</sub> by mass flow controller, are fed to the reactor through the humidifier. The supply gas temperature rises by passing the alumina ball layer that is installed within the reactor. The experimental conditions are shown in Table 1. The reactor is heated up until 800 °C at 5 °C/min of heating rate. Gas flow rate is  $4.17 \times 10^{-5}$  m<sup>3</sup>/s. In order to study the

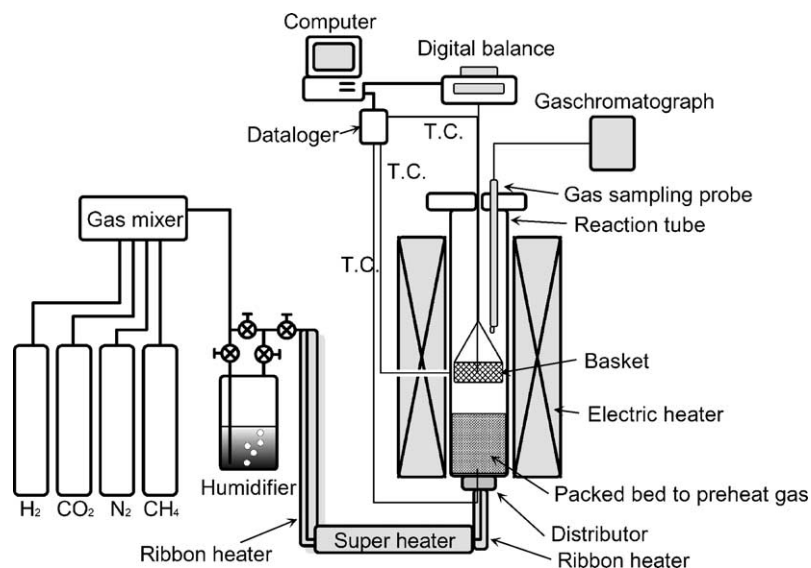


Fig. 2. Schematic diagram of experimental apparatus.

Table 1  
Experimental conditions

Concentrations (vol.%)				
N <sub>2</sub>	CO <sub>2</sub>	H <sub>2</sub> O	CH <sub>4</sub>	S/C
100	0	0		
90	10	0		
75	25	0		
50	50	0		
25	75	0		
0	100	0		
50	0	50		
25	0	75		
0	10	90		
0	20	80		
0	25	75		
0	40	60		
0	80	20		
		75	25	3.0
		67	33	2.0
		60	40	1.5
		50	50	1.0

Gas flow rate:  $4.17 \times 10^5$  m<sup>3</sup>/s; heating rate: 5.0 °C/min; final temperature: 800 °C; mass of catalyst: 5.0 g; pollution fractions : 0, 1.6, 3.0 mass%.

effect of gas species on the mass change of the polluted catalyst, gas species compositions are widely varied.

The catalyst polluted by vapor-phase carbonate is made according to the following procedures: (1) Ni/MgO catalyst (TOPSOE: type: RKNR) is soaked in the KOH solution of an arbitrary concentration; (2) The catalyst taken out of an aqueous solution is dried in N<sub>2</sub> atmosphere of 250 °C during 24 h. The catalytic activity and the specific surface area of the polluted catalyst made like this are almost the same as those of the polluted catalysts are gathered from DIR-MCFC. Therefore, the catalyst polluted made by this making procedure can imitate the polluted catalyst by vapor-phase carbonate in DIR-MCFC. Here, the pollution fraction of the polluted catalyst are 0, 1.6, 3.0 mass%.

## 4. Results and discussion

### 4.1. The effect of adsorbing water on the catalyst

In order to evaluate the effect of adsorbing water on the catalyst and on the mass change of the polluted catalyst, the mass change of the soak/dry catalyst, which is soaked in pure water and dried by furnace, and the dry catalyst, which is only dried under N<sub>2</sub> atmosphere, are measured. Fig. 3 shows the effect of H<sub>2</sub>O adsorption in mass change of catalyst. From this figure, the mass change of the dry catalyst decreases by about 2 mass% at 100 °C. On the other hand, the mass change of the soak/dry catalyst decreases by about 2 mass% at 100 °C and decreases by about 5 mass% in the temperature range from 300 to 400 °C. As the reason for these mass decrements is desorption of chemical absorption water and physical absorption water, it has to be considered

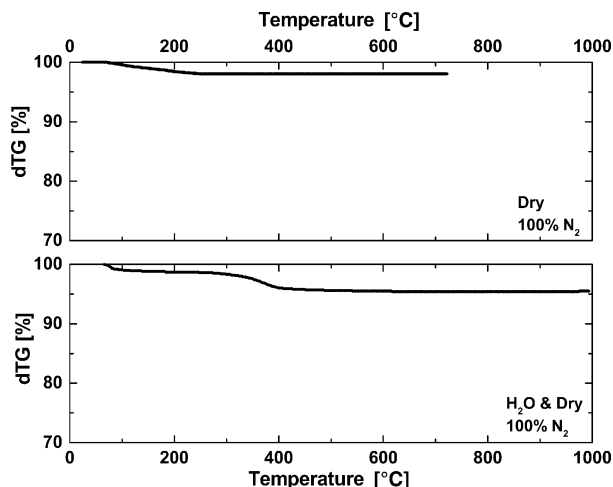


Fig. 3. Effect of H<sub>2</sub>O adsorption in mass change of catalyst.

that these mass decrements are included in the experimental data.

### 4.2. CO<sub>2</sub> concentration dependence of KOH–K<sub>2</sub>CO<sub>3</sub> reaction

Fig. 4 shows the mass change of the polluted catalyst by increasing the catalyst temperature in various CO<sub>2</sub> concentrations. The mass decreases by 2–4% at 100 °C and decreases by 10–15% in the temperature range from 300 to 400 °C. The former decrement is desorption of water, the latter decrement is the sum of: desorption of water, the volatilizing of KOH, the evaporation of the absorbed water by KOH and the mass increment to change from KOH into K<sub>2</sub>CO<sub>3</sub>. Thus, the mass decrement between 300 and 400 °C is defined to  $\Delta M$  as shown in Fig. 5. The relation between this  $\Delta M$  and CO<sub>2</sub> concentration is shown in Fig. 6. Here,  $\Delta M$  is plotted as a decrement from 100%.  $\Delta M$  decreases by increasing CO<sub>2</sub> concentration and is saturated when CO<sub>2</sub> concentration is 25% or more. In the case of the polluted catalyst of 1.6 mass% of pollution fraction, there must be only 1.6 mass% mass change when all KOH evaporates. However, the mass change is about 13 mass%. The reason is

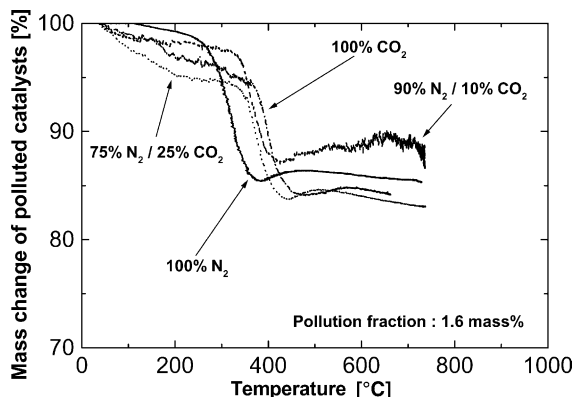


Fig. 4. Mass change of polluted catalysts in CO<sub>2</sub>/N<sub>2</sub> gas atmosphere.

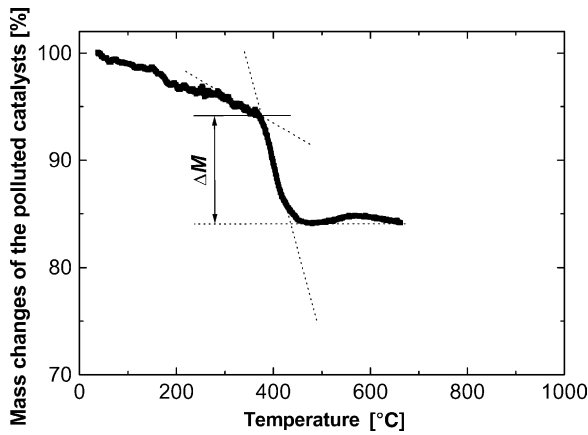


Fig. 5. The definitions of mass decrement ( $\Delta M$ ) between 300 and 400 °C.

that the mass change of 0% CO<sub>2</sub> corresponds to the sum of: the evaporation of water, the volatilizing of KOH and the evaporation of the adsorbed water by KOH. Therefore, the KOH content of  $\Delta M$  is 1.6 mass% and the remainder is water. On the other hand, all KOH is changed into K<sub>2</sub>CO<sub>3</sub> under 100% CO<sub>2</sub>. In this case, KOH of 1.6 mass% becomes K<sub>2</sub>CO<sub>3</sub> of 1.97 mass% from Eq. (2), and the mass of the polluted catalyst increases, but it decreases about 10%. The reason is that the mass change of 100% CO<sub>2</sub> corresponds to the sum of: the evaporation of water, the evaporation of water absorbed to KOH and a mass increment to change from KOH into K<sub>2</sub>CO<sub>3</sub>.

$$\frac{K_2CO_3}{2KOH} = \frac{138}{2 \times 56} \cong 1.23; 1.6 \text{ mass\%} \times 1.23 = 1.97 \text{ mass\%} \quad (2)$$

It is assumed that the water content in the polluted catalyst is the same if it is a catalyst of the same pollution fraction. Then, the difference between the mass change of 0% CO<sub>2</sub> and the mass change of 100% CO<sub>2</sub> corresponds to the sum of mass increments caused when all KOH is changed into K<sub>2</sub>CO<sub>3</sub> and water absorbed to K<sub>2</sub>CO<sub>3</sub>. The content of  $\Delta M$

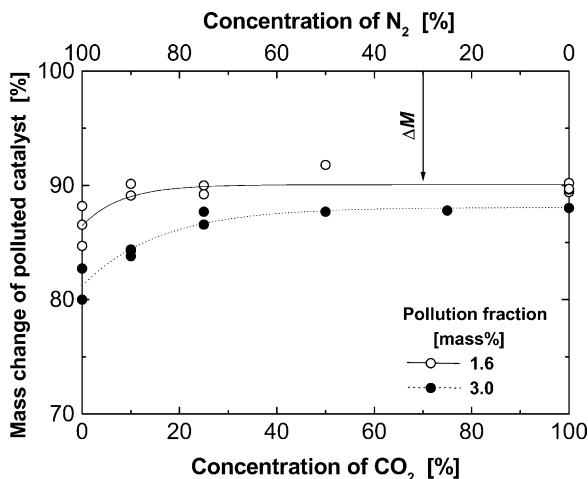


Fig. 6. Effect of CO<sub>2</sub> concentration on mass change of polluted catalysts.

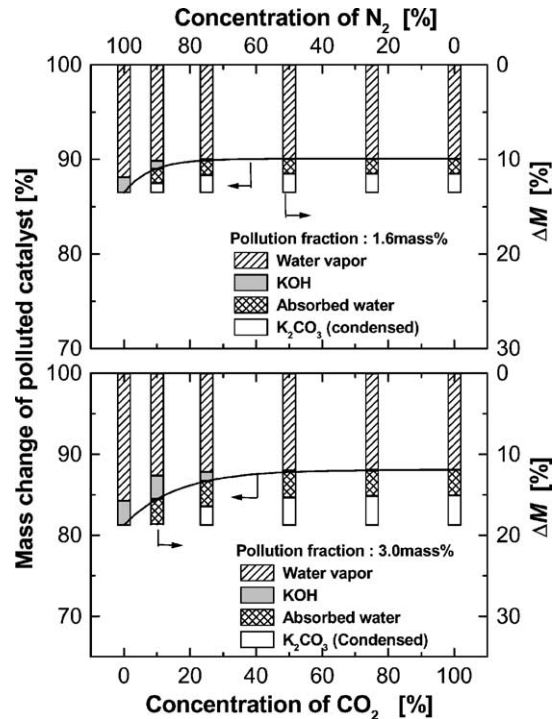


Fig. 7. Contents of the mass change in CO<sub>2</sub>/N<sub>2</sub> gas atmosphere.

was arranged based on such an idea. Fig. 7 shows the contents of  $\Delta M$ . Although the adsorbed water is evaporated with KOH in 0% CO<sub>2</sub>, it is absorbed to K<sub>2</sub>CO<sub>3</sub>, which is changed from KOH, as CO<sub>2</sub> concentration increases. When the CO<sub>2</sub> concentration becomes 25% or more, KOH has been almost changed into K<sub>2</sub>CO<sub>3</sub>. Therefore, if the CO<sub>2</sub> concentration is 25% or less, KOH can volatilize from the polluted catalyst and the catalytic activity might be able to be reactivated.

From the above-mentioned result,  $\Delta M_{100\%N_2} - \Delta M$  based on  $\Delta M$  of 100% N<sub>2</sub> is arranged to exclude these water influence from  $\Delta M$  and to be represented by the mass change of the KOH reaction only. Because  $\Delta M_{100\%N_2}$  shows the mass of KOH and the adsorbed water in the catalyst, K<sub>2</sub>CO<sub>3</sub> is hardly generated in the catalyst if  $\Delta M_{100\%N_2} - \Delta M$  is zero. On the other hand, KOH changes into K<sub>2</sub>CO<sub>3</sub> and remains in the catalyst if  $\Delta M$  is a plus value. Therefore, the data is shown as  $\Delta M_{100\%N_2} - \Delta M$ .

#### 4.3. CO<sub>2</sub>/H<sub>2</sub>O mixed gas dependence of the KOH–K<sub>2</sub>CO<sub>3</sub> reaction

The gas atmosphere around the catalyst in the DIR-MCFC is a CO<sub>2</sub>/H<sub>2</sub>O mixed gas because CO<sub>2</sub> and H<sub>2</sub>O are generated with the cell reaction. Fig. 8 shows effect of CO<sub>2</sub>/H<sub>2</sub>O gas atmosphere on the mass change of the polluted catalysts. Here,  $\Delta M_{100\%N_2} - \Delta M$  is arranged to evaluate the variation to K<sub>2</sub>CO<sub>3</sub> of KOH.  $\Delta M_{100\%N_2} - \Delta M$  is saturated when the CO<sub>2</sub> concentration is 30% or more. Although  $\Delta M_{100\%N_2} - \Delta M$  under CO<sub>2</sub>/N<sub>2</sub> atmosphere steadied with 25% or more of CO<sub>2</sub>, it under CO<sub>2</sub>/H<sub>2</sub>O atmosphere it steadied with 30% or

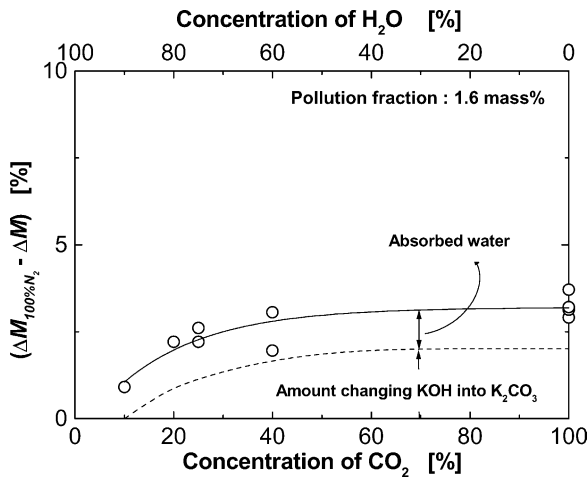


Fig. 8. Effect of CO<sub>2</sub>/H<sub>2</sub>O gas atmosphere on mass change of polluted catalysts.

more of CO<sub>2</sub>. Therefore, as water addition is effective in controlling the changing of KOH into K<sub>2</sub>CO<sub>3</sub>, the catalytic activity of the polluted catalyst might be able to be reactivated if CO<sub>2</sub> concentration can be suppressed to 30% or less under the high steam atmosphere.

4.4. Evaluation of catalytic activity of the reactivation catalysts

Until Section 4.3, it was considered that the mass reduction was due to evaporation of KOH, and a mass increment was due to a change from KOH to K<sub>2</sub>CO<sub>3</sub>. The potassium quantity in the catalyst before and after experimenting was measured by atomic absorption spectrochemical analysis to confirm these considerations. Table 2 shows the analysis result. Here, potassium quantity is converted into KOH quantity and the polluted catalyst of the pollution fraction 3.0 mass% was used for the analysis. The pollution fraction (KOH) from the polluted catalyst under the 0% CO<sub>2</sub> condition was detected as about 0.65 mass%. On the other hand, the pollution fraction in the polluted catalyst under the 100% CO<sub>2</sub> condition was detected as about 3.25 mass%; this value corresponds to the pollution fraction of the polluted catalyst before experimenting. In 100% CO<sub>2</sub> experimenting, it is judged that KOH changes into K<sub>2</sub>CO<sub>3</sub> and remains in the catalyst because the pollution fraction has hardly changed before and after the experiment. On the other hand, it can be judged that KOH evaporated from the polluted catalyst because the pollution fraction has decreased to one-fifth

Table 2  
Comparison of concentration of KOH in polluted catalyst in N<sub>2</sub> with CO<sub>2</sub> gas atmospheres

	Before experiment	After experiment	
		100% N <sub>2</sub>	100% CO <sub>2</sub>
Pollution fraction (mass%)	3.02	1.53	3.25

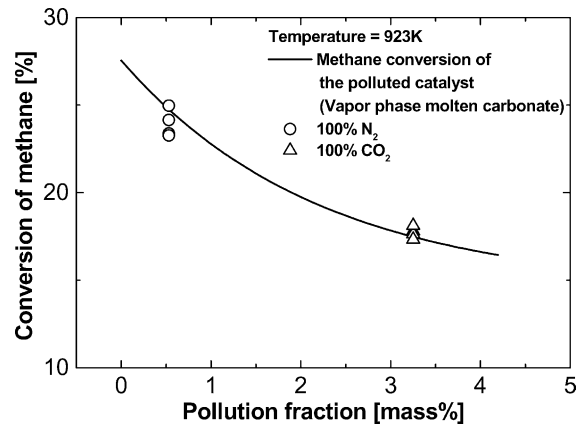


Fig. 9. Evaluation of catalytic activity of the reactivated catalysts.

of its original value after the experiment of 100% N<sub>2</sub>. Here, KOH and K<sub>2</sub>CO<sub>3</sub> in the polluted catalyst could not be identified in an X-ray structure analysis because the KOH and K<sub>2</sub>CO<sub>3</sub> in the polluted catalyst are little.

Moreover, the differential reactor evaluates the catalytic activity (methane conversion and reaction rate constant) of both catalysts after experimenting under 100% N<sub>2</sub> and 100% CO<sub>2</sub> conditions. Here, the experimental method and the analysis technique have been already published in another paper [8]. Fig. 9 shows the comparison between methane conversion of polluted catalyst by vapor-phase carbonate (solid line) from another paper and methane conversion of catalyst after experimenting. The activity of the catalyst after experimenting under the 100% CO<sub>2</sub> condition is same as catalytic activity of the polluted catalyst (3.0 mass% of pollution fraction). However, the catalytic activity of the polluted catalyst after experimenting under the 100% N<sub>2</sub> (0% CO<sub>2</sub>) condition is revived to 80% of the initial activity. Fig. 10 shows the reaction rate constant of the reactivation catalysts. Here, each lines means the reaction rate constant of the catalyst polluted by vapor-phase carbonate from another paper [8]. The catalytic activity of the catalyst after experimenting under the 100% CO<sub>2</sub> condition is not improved, but after experimenting under 100% N<sub>2</sub> condition

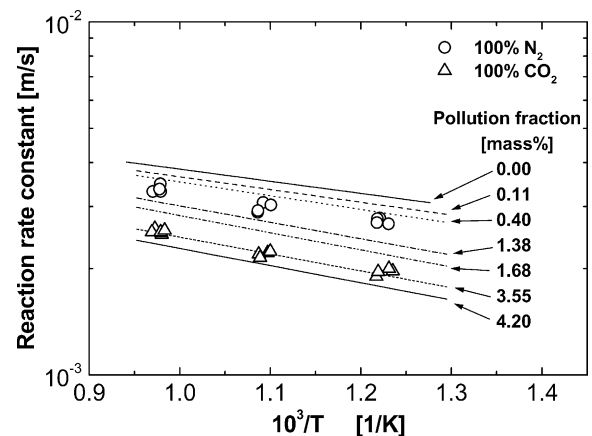


Fig. 10. Reaction rate constant of the reactivated catalysts.

it has been improved. As the slopes of these reaction rate constants are similar to the slope of the reaction rate constant of the catalyst polluted by vapor-phase carbonate, the reaction mechanism does not change even if the polluted catalyst is reactivated. Therefore, the catalytic activity of the polluted catalyst can be revived by controlling the gas composition in operating the DIR-MCFC. From the viewpoint of the catalyst loading, as CO<sub>2</sub> concentration is low and H<sub>2</sub>O concentration is high upstream at the anode catalyst is not easily polluted. However, as CO<sub>2</sub> concentration rises by generation with the cell reaction in the downstream anode catalyst is polluted easily.

4.5. Effect of the simulation gas of DIR-MCFC on KOH–K<sub>2</sub>CO<sub>3</sub> reaction

As fuel gas of DIR-MCFC is likely to be natural gas, 25CH<sub>4</sub>/75H<sub>2</sub>O has been generally adopted as a gas composition for research. Recently, ratio of steam and methane (S/C) has been decreased from about 1.5 to 2 to improve the power generation efficiency. Therefore, the effect of the simulation gas of DIR-MCFC on the KOH–K<sub>2</sub>CO<sub>3</sub> reaction is examined by changing S/C. Fig. 11 shows the mass change of the polluted catalyst by increasing the catalyst temperature in various S/C. The mass for all experimental conditions increases at about 150 °C and decreases in the temperature range from 300 to 400 °C. An increment at 150 °C is adsorption of supplied water because this increment is almost proportional to H<sub>2</sub>O concentration. Moreover, this increment is unrelated to the KOH–K<sub>2</sub>CO<sub>3</sub> reaction, because the mass change of the catalyst has returned to zero before the catalyst temperature reaches the melting temperature of KOH. On the other hand, a decrement from 300 to 400 °C is related to KOH–K<sub>2</sub>CO<sub>3</sub> reaction. Therefore, this decrement is related to ΔM as shown Fig. 12. ΔM increases by increasing S/C (H<sub>2</sub>O concentration increases) and it saturates when S/C is 1.5 or more. ΔM is the same tendency as ΔM of the methane even if the methane is replaced with nitrogen. Because the reforming reaction is not caused in the temperature range from 300 to 400 °C as shown in Table 3,

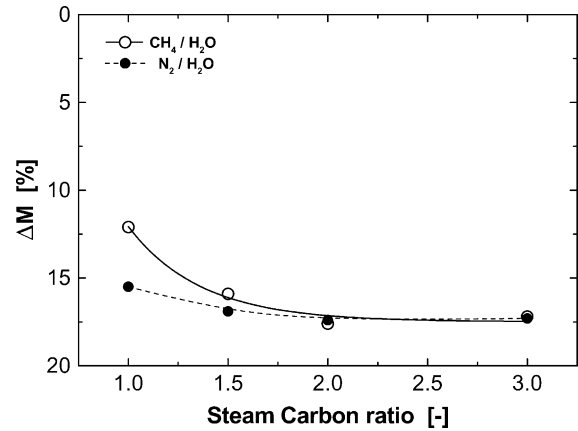


Fig. 12. Effect of CH<sub>4</sub>/H<sub>2</sub>O gas atmosphere on mass change of polluted catalysts.

Table 3  
Dry gas composition under CH<sub>4</sub>/H<sub>2</sub>O gas atmosphere

Temperature (°C)	Concentration (vol.%)								
	S/C = 3.0			S/C = 2.0			S/C = 1.5		
	CO <sub>2</sub>	H <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>	H <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>	H <sub>2</sub>	CH <sub>4</sub>
350	1.12	0	98.88	1.11	0	98.89	0.78	0.01	99.21
400	1.19	0	98.81	1.08	0.02	98.9	0.86	0.03	99.1
450	1.77	0.12	98.11	1.22	0.09	98.69	0.33	0.14	99.53
500	1.66	0.40	97.94	1.45	0.37	98.18	1.92	0.42	97.65
550	3.57	1.04	95.39	3.45	1.40	95.15	3.71	1.12	95.17

it is thought that the change in ΔM greatly influences H<sub>2</sub>O concentration. On the other hand, ΔM decreases when S/C is 1.0, because the carbon deposition occurs. Therefore, the catalytic activity might be reactivated if S/C is 1.5 or more. Moreover, the methane conversion and reaction rate constant, which are measured by the same method as in Section 4, were added to Figs. 9 and 10, respectively. These results are shown as Figs. 13 and 14, respectively. The catalytic activity of the polluted catalyst experimented on with S/C is of 3.0 almost revived to the initial activity. On the

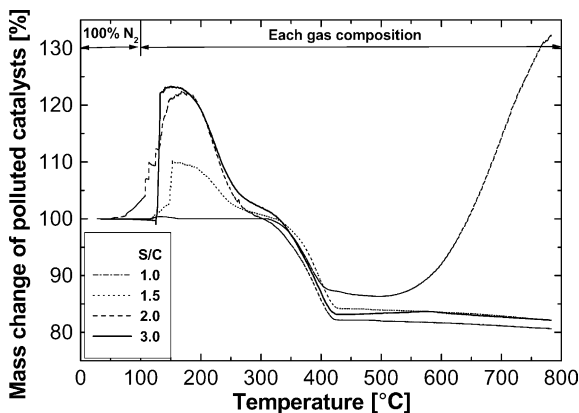


Fig. 11. Mass change of polluted catalysts in CH<sub>4</sub>/H<sub>2</sub>O gas atmosphere.

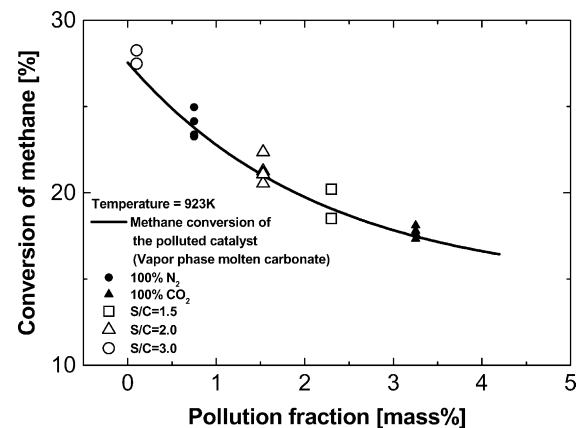


Fig. 13. Evaluation of catalytic activity of the reactivated catalysts.

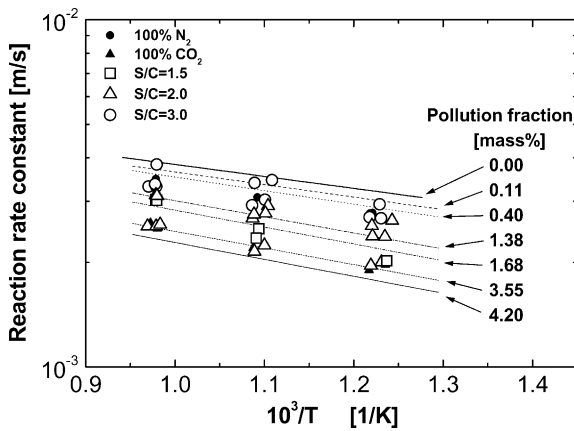


Fig. 14. Reaction rate constant of the reactivated catalysts.

other hand, the methane conversion decreases by decreasing S/C. If the catalytic activity in 100% CO<sub>2</sub> was defined a 0% and the initial activities was defined 100%, the catalytic activity when S/C is 2.0 is revived only 36% of initial activity. As the catalytic activity is revived only 16% of initial activity at 1.5 of S/C, it is difficult to reactivate the polluted catalyst if S/C is 1.5 or less. Moreover, the reaction rate constant with S/C of 3.0 is similar to the one of pollution fraction 0.11 mass%, and the reaction rate constant in with of S/C 1.5 is similar to the one of pollution fraction 3.55 mass% from which the catalytic activity can not be reactivated. Therefore, catalytic activity can be reactivated safely if S/C is two or more.

4.6. Verification of reactivation method by DIR-MCFC

The proposed reactivation method is verified by applying it to the DIR-MCFC. Evaluation method is that the polluted catalyst is loaded in anode channel of DIR-MCFC, and DIR-MCFC is supplied by various gas compositions during start-up procedure. Here, DIR-MCFC made by National Institute of Advanced Industrial Science and Technology—Kansai (AIST) is a 16 cm<sup>2</sup> single cell; the electrodes were sintered nickel as shown in Table 4. The electrolyte eutectic is a mixture of lithium carbonate (Li<sub>2</sub>CO<sub>3</sub>), by 62 mol%, and potassium carbonate (K<sub>2</sub>CO<sub>3</sub>), by 38 mol%. The electrolyte matrix is lithium aluminum oxide. A fresh catalyst, which has not been polluted, and the polluted catalyst were used for the catalyst of the DIR-MCFC. The catalyst loading density is 65 mg/cm<sup>2</sup>. The operating condition is shown in Table 4. Here, the proposed reactivation method is used as a start-up gas. Fig. 15 shows initial cell performance used by the experiment under the standard condition (STD) and DIR mode condition (DIR). In all conditions, the cell performance in the STD condition is better than cell performance in the DIR condition. Moreover, the gas in the start-up does not influence cell performance because cell performance in the STD condition is the same in most cells. Because there is an individual difference in each cell, cell performance should be arranged by the difference between voltage in

Table 4  
AIST's DIR-MCFC components and experimental conditions

Materials	
Cathode	NiO (in situ)
Anode	Ni/Al
Matrix	LiAlO <sub>2</sub>
Electrolyte	62% Li <sub>2</sub> CO <sub>3</sub> /38K <sub>2</sub> CO <sub>3</sub>
Electrode area	16 cm <sup>2</sup>
Temperature	923 K
Pressure	0.1 Mpa
Current density	0–150 mA/cm <sup>2</sup>
Gas utilization	40%
Standard gas composition	
Cathode	70% Air/30 CO <sub>2</sub>
Anode	70.4% H <sub>2</sub> /17.6CO <sub>2</sub> /12H <sub>2</sub> O
DIR mode gas composition	
Cathode	70% Air/30 CO <sub>2</sub>
Anode	25% CH <sub>4</sub> /75H <sub>2</sub> O (S/C = 3.0) 40% CH <sub>4</sub> /60H <sub>2</sub> O (S/C = 1.5)
Start-up gas composition	
RT to 220 °C	100% Air
220–650 °C	
Cathode	100% CO <sub>2</sub>
Anode	
CO <sub>2</sub>	100 ([N <sub>2</sub> ] = 0)
N <sub>2</sub>	0 ([CO <sub>2</sub> ] = 100)
CH <sub>4</sub>	25
H <sub>2</sub> O	75
S/C	3.0
CH <sub>4</sub>	40
H <sub>2</sub> O	60
S/C	1.5

STD and voltage in DIR ( $dV = V_{STD} - V_{DIR}$ ) as shown in Fig. 16. The catalytic activity in the cell will be evaluated by using this arrangement method. As  $dV$  where a fresh catalyst is installed is almost constant even if a current density increases, the catalyst is reforming the necessary hydrogen for the cell. However, as  $dV$  where the polluted catalyst is installed increases with increasing current density, there is

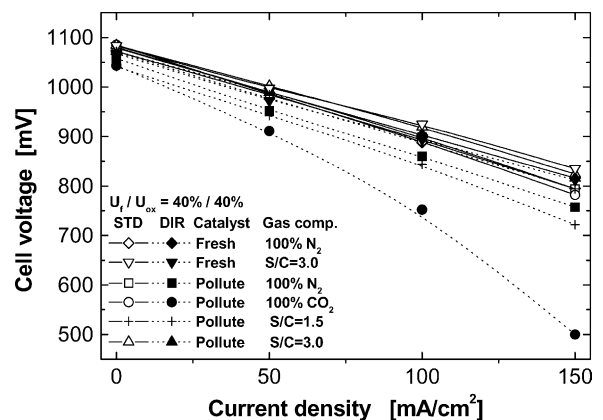


Fig. 15. Initial cell performance of AIST's DIR-MCFC.

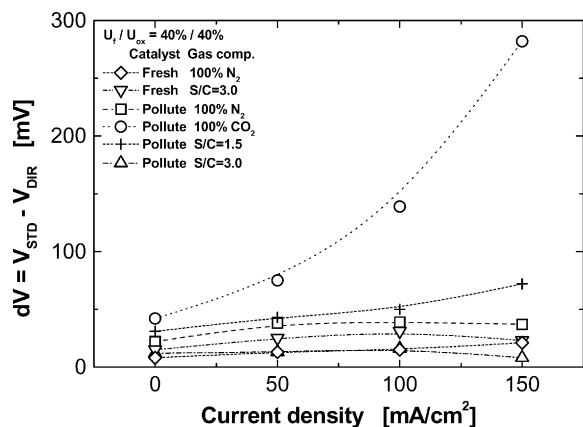


Fig. 16. DIR-MCFC performance.

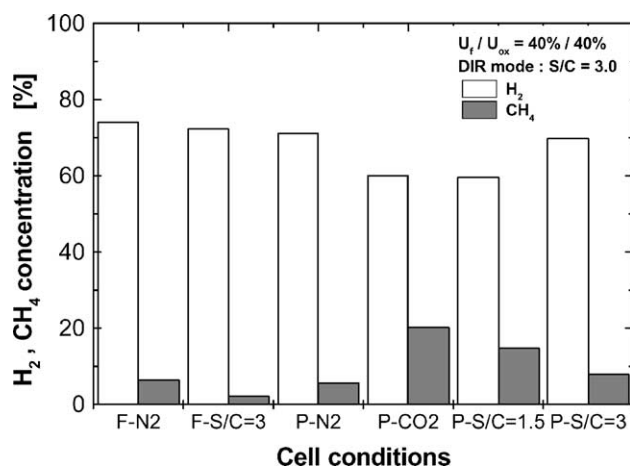


Fig. 17. Catalytic activity of the reactivated catalyst within DIR-MCFC.

the possibility that the polluted catalyst is not reforming the necessary hydrogen for the cell. Especially, as  $dV$  under 100%  $\text{CO}_2$  condition increases drastically by increasing the current density, the polluted catalyst can not be reactivated. On the other hand,  $dV$  under 100%  $\text{N}_2$  and  $dV$  under  $\text{S/C} = 3.0$  are almost the same.  $dV$  under  $\text{S/C} = 1.5$  is poor. The gas composition of the anode outlet is analyzed by gaschromatography,  $\text{H}_2$  and  $\text{CH}_4$  concentration in anode outlet at OCV are shown as Fig. 17.  $\text{H}_2$  and  $\text{CH}_4$  concentration that uses a polluted catalyst and uses 100%  $\text{N}_2$  and  $\text{S/C} = 3.0$  as a start-up gas are almost same as the one that uses a fresh catalyst. On the other hand, as  $\text{H}_2$  and  $\text{CH}_4$  concentration that uses a polluted catalyst and uses 100%  $\text{CO}_2$  as a start-up gas are considerably bad, the polluted catalyst can not be reactivated under this condition. Moreover, as  $\text{H}_2$  and  $\text{CH}_4$  concentration (a polluted catalyst;  $\text{S/C} = 1.5$ ) are almost the middle of 100%  $\text{N}_2$  condition and 100%  $\text{CO}_2$  condition, the polluted catalyst can not be reactivated enough under this condition. Therefore, as the supplied gases, which are 100%  $\text{N}_2$  and  $\text{S/C} = 3.0$ , can make  $\text{KOH}$  volatilize from the polluted catalyst in DIR-MCFC, the proposed reactivation method is appropriate. Moreover, the DIR-MCFC can be operated without vapor-

phase carbonate pollution and the polluted catalyst can be reactivated by using these reactivation methods if the DIR-MCFC is operated under the condition that the ratio of  $\text{H}_2\text{O}$  to  $\text{CH}_4$  ( $\text{S/C}$ ) in the fuel is increased.

## 5. Conclusion

A reactivation method for catalyst polluted by vapor-phase carbonate was developed by elucidating the adhesion form of potassium compounds in the polluted catalyst. Moreover, optimum-operating conditions of the DIR-MCFC without vapor-phase carbonate pollution was proposed by evaluating the reactivation method within the DIR-MCFC. The results obtained in this study are summarized as follows.

- (1) The catalytic activity of a catalyst polluted by vapor-phase carbonate is revived to 80% of the initial activity by  $\text{N}_2$  flowing into the polluted catalyst.
- (2) The catalytic activity of a catalyst polluted by vapor-phase carbonate is not revived for changing  $\text{KOH}$  into  $\text{K}_2\text{CO}_3$ , if the DIR-MCFC was operated under the condition where  $\text{CO}_2$  concentration was larger than 25%.
- (3) Catalyst should be loaded more upstream in the anode where the  $\text{H}_2\text{O}$  concentration is high and the  $\text{CO}_2$  concentration is low.
- (4) The catalytic activity can be reactivated if  $\text{S/C}$  is two or more.
- (5) The DIR-MCFC can be operated without vapor-phase carbonate pollution if the ratio of  $\text{H}_2\text{O}$  to  $\text{CH}_4$  ( $\text{S/C}$ ) in the fuel was two or more.

## Acknowledgements

This work was supported by Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan.

## References

- [1] C. Hirai, M. Matsumura, S. Tanaka, Studies on reforming catalyst for internal reforming molten carbonate fuel cell, Abstract Book of the 29th Battery Symposium in Japan, vols. 79–80, 1988.
- [2] Y. Gonjyo, M. Matsumura, S. Tanaka, Performance of internal reforming molten carbonate fuel cell—activity of internal reforming catalyst vs. cell voltage, Abstract book of the 29th Battery Symposium in Japan, vols. 81–82, 1988.
- [3] S. Tanaka, M. Matsumura, Y. Gonjyo, T. Okada, H. Ide, M. Miyazaki, Development of internal reforming molten carbonate fuel cell stacks, J. Inst. Electr. Eng. Jpn. B 112 (8) (1992) 741–747.
- [4] E. Kikuchi, S. Ueyama, A. Koyama, A. Machino, T. Matsuda, Steam reforming of hydrocarbons on noble metal catalysts. Part 8. Steam reforming of methane on supported ruthenium catalysts, Sekiyu Gakkaiishi 33 (1990) 152–157.
- [5] M. Matsumura, C. Hirai, Deterioration mechanism of direct internal reforming catalyst, J. Chem. Eng. Jpn. 31 (5) (1998) 734–740.



- [6] K. Sugiura, K. Ohtake, Deterioration of a catalyst's activity by liquid-phase MC poisoning in DIR-MCFC, *J. Chem. Eng. Jpn.* 21 (6) (1995) 1170–1178.
- [7] Y. Miyake, N. Nakanishi, T. Nakajima, Y. Itoh, T. Saitoh, A. Saii, H. Yanaru, A Study on degradation phenomena of reforming catalyst in DIR-MCFC, *J. Chem. Eng. Jpn.* 21 (6) (1995) 1104–1109.
- [8] K. Sugiura, I. Naruse, K. Ohtake, Deterioration of a catalyst's activity in direct internal reforming-molten carbonate fuel cells (effect of adsorption of vapor-phase molten carbonate), *J. Jpn. Soc. Mech. Eng. Ser. B* 65 (629) (1999) 330–336.
- [9] K. Sugiura, I. Naruse, Relationship between catalytic activity and gas-phase pollution fractions in the catalyst in DIR-MCFC (reactivation method of polluted catalyst by vapor-phase carbonate), *J. Jpn. Soc. Mech. Eng. Ser. B* 66 (641) (2000) 249–255.
- [10] JANAF Thermochemical Tables, third ed., vol. 14, 1985, pp. 606–608, 628, 1219–1222, 1273–1275.