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Degradation Phenomena of Reforming Catalyst in DIR-MCFC

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1. Introduction

1.1 Background

Recently, energy consumption is increasing with the population growth of developed countries and developing countries, and an exhausting of petroleum resources has become a big problem worldwide. In addition, CO₂, SO_x and NO_x which are toxic substances emitted when these resources are used, cause environmental polluting problem such as global warming and acid rain, etc. From these situations, high efficiency, energy-saving and environmental-saving power source is needed in recent years, and fuel cell can solve these problems. Therefore, researching, developing and commercializing on fuel cell are promoted in many countries. Fuel cell is categorized by the difference of its electrolyte and operating temperature. In this research, we use Molten Carbonate Fuel Cells (MCFC) which uses a molten carbonate as the liquid electrolyte. MCFC is expected as a distributed power station and the CO₂ concentrator. Generally, fuel cell performances are evaluated by I-V performance, cell resistance and gas chromatography, etc. for which fuel cell only generate by supplying fuel gas and oxidant gas to cell. Generally, although gas chromatography is utilized only to detect the gas crossover (it is gas leakage phenomenon between two poles through electrolyte) on fuel cell development, the performance of reforming catalyst in the anode channel in operation is evaluated by gas chromatography on R&D of Direct Internal Reforming-Molten Carbonate Fuel Cell (DIR-MCFC). Moreover, MCFC installed the segmented electrode is evaluated about the gas crossover and the utility of the segmented electrode by a gas chromatography and the image measurement technique. This chapter introduces the use method of a gas chromatograph through the degradation factor of reforming catalyst in DIR-MCFC.

1.2 Kind of fuel cell, power generation principle and Issues of DIR-MCFC

From above-mentioned, the kind of fuel cell is decided by the electrolyte used, and the operating temperature, the fuel used and the system structure are decided as shown in Table 1. For example, although Phosphoric Acid Fuel Cell (AFC) and Polymer Electrolyte Fuel Cell (PEFC) exhaust the produced water to the cathode side, MCFC, Solid Oxide Fuel Cell (SOFC) and Alkaline Fuel Cell (AFC) exhaust it to the anode side. Therefore, the system structure is different by fuel cell used. On the fuel gas, the high temperature operation type fuel cell such as MCFC and SOFC can use various fuels, because they do not use an

electrode catalyst and they can use CO as a fuel. However, the low temperature operation type fuel cell such as PAFC and PEFC use only hydrogen because CO becomes a catalyst poison, and AFC can only, moreover, pure hydrogen because CO₂ makes the electrolyte be deteriorated. Therefore, the low temperature operation type fuel cell needs an addition facility such as the shift convertor.

	AFC	PAFC	MCFC	SOFC	PEFC
Electrolyte	Potassium hydroxide	Phosphoric acid	Molten carbonate	Stabilized zirconium	Ion-exchange membrane
Ionic conductor	OH ⁻	H ⁺	CO ₃ ²⁻	O ²⁻	H ⁺
Specific resistance	< 1Ωcm	< 1Ωcm	< 1Ωcm	< 1Ωcm	< 20Ωcm
Operating temperature	50 - 150°C	190 - 220°C	600 - 700°C	- 1000°C	80 - 120°C
Corrosively	Medium	Strong	Strong	non	Medium
Electrode catalyst	Nickel/silver	Platinum	Not need	Not need	Platinum
Fuel	Pure H ₂ without CO ₂	H ₂ (CO ₂ content; OK)	H ₂ & CO	H ₂ & CO	H ₂ (CO ₂ content; OK)
Fuel source	By-product hydrogen of electrolytic industry, Water electrolysis	Natural gas, Light oil, Methanol	Oil, Natural gas, Methanol, Coal gas	Oil, Natural gas, Methanol, Coal gas	Natural gas, Methanol
Generating efficiency	60%	40 - 50%	40 - 60%	50 - 65%	40 - 50%

Table 1. Kind and feature of fuel cell

Because this study targets MCFC, the power generation principle of MCFC is shown in Fig.1. The fuel of MCFC is hydrogen obtained by reforming the natural gas and the coal gasification gas, and CO₂ that stabilizes the molten salt and steam that prevents the carbon deposition are contained in the fuel gas. Hydrogen supplied to the cell is separated to the proton and the electron with the anode catalyst ($H_2 \rightarrow 2H^+ + 2e^-$). This proton and carbonate ion, which has been transmitted in electrolyte, generate steam and CO₂ with the electrochemical reaction ($2H^+ + CO_3^{2-} \rightarrow H_2O + CO_2$).

On the other hand, oxygen supplied to the cell and electrons transmitted from external circuit react into oxygen ion with the cathode catalyst ($0.5 O_2 + 2e^- \rightarrow O^{2-}$). Carbon dioxide supplied to the cell deliquesces to the electrolyte on the cathode electrode, and it becomes carbonate ion as this CO₂ reacts with oxygen ion ($CO_2 + O^{2-} \rightarrow CO_3^{2-}$). Here, the carbonate ion generated is the electrolyte, and it moves toward the anode electrode. Overall reaction is an evolution reaction of water.

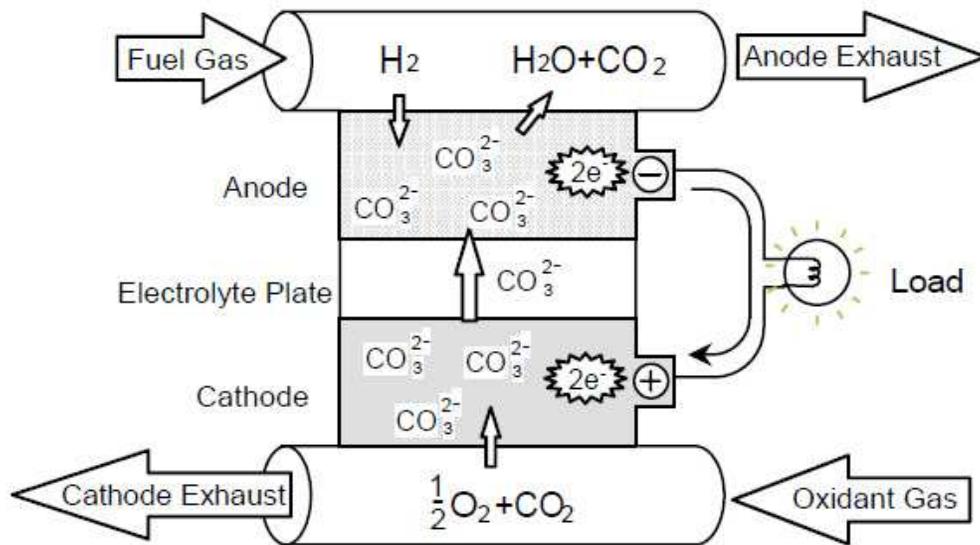


Fig. 1. Schematic diagram of power generation principle of MCFC

MCFC has three reforming type to obtain hydrogen from various fuel as shown in Fig.2. The kinds of reforming type on MCFC are classified into the external reforming type, which has the reformer outside the cell as shown in Fig.2 (a), and the internal reforming type, which

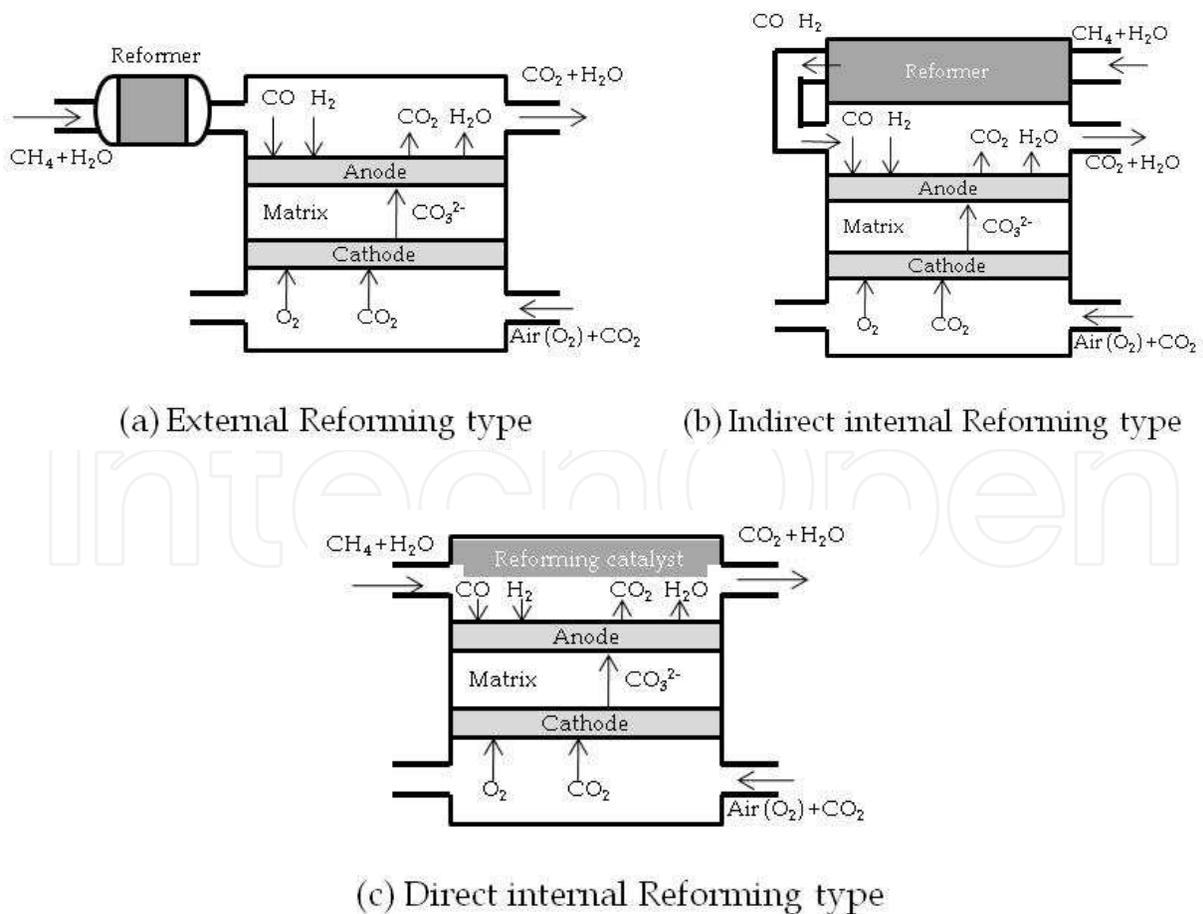


Fig. 2. Schematic diagram of comparison of reforming type

has the reformer inside the cell. Moreover, the internal reforming type is classified into the indirect reforming type, which sets up the reformer among cells as shown in Fig.2 (b), and the direct internal reforming type, which fills the reforming catalyst directly to the anode channel as shown in Fig.2 (c). Although the merits of ER-MCFC (Fig.2 (a)) are a simple structure and the enlargement of MCFC is easy, the demerits are that a big space required for installation and heat supply to reformer are necessary. The merits of IIR-MCFC (Fig.2 (b)) can make the system compact by stacking the reformer of one every five cells, and can control the cell temperature by the endothermic reaction of the reformer. However, as a demerit, the system and the cell structure of IIR-MCFC become more complex than that of ER-MCFC, and the height of IIR-MCFC stack becomes taller than ER-MCFC only by the thickness of the reformer. On the other hand, because DIR-MCFC (Fig.2 (c)) has a reforming catalyst in the anode channel, the system size of DIR-MCFC is smaller than that of ER-MCFC, and the cell structure is simple as well as ER-MCFC. Moreover, the reforming reaction is promoted from the chemical equilibrium value because MCFC consumes hydrogen to which the reforming catalyst reforms by the cell reaction. Therefore, the generation efficiency of DIR-MCFC is larger than that of ER-MCFC and IIR-MCFC.

Because MCFC uses the electrolyte of liquid phase, it has the problem that the electrolyte decrease as the operating time passes (Tanimoto, K. et al., 1998). However, because the reforming catalyst is loaded in the anode gas channel, the possibility that it is polluted by the molten salts of liquid phase and vapour phase is high as shown in Fig.3. The liquid phase pollution is caused by which the molten salt leak through the cell component such as separators and adhere to the catalyst (Sugiura et al., 1999). The vapour phase pollution is caused by which the vaporised electrolyte disperse to the gas channel with the steam generated by the cell reaction and adhere to the catalyst. The reforming catalyst is polluted by adhering of these molten salts, and the performance of the reforming catalyst deteriorates

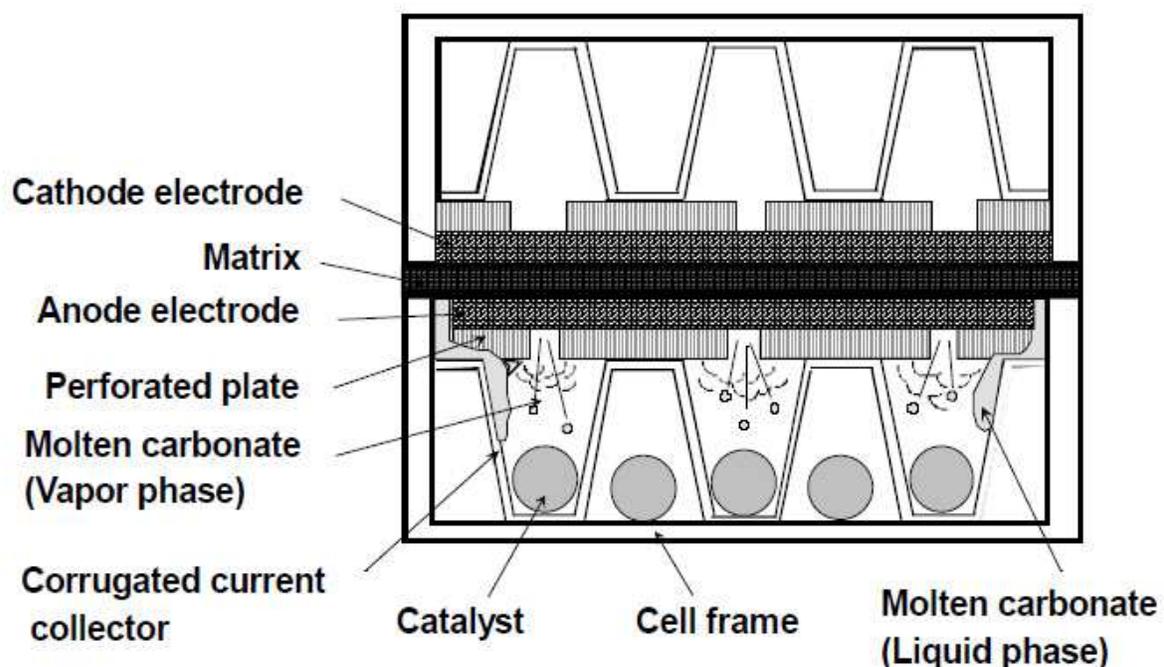


Fig. 3. Schematic diagram of catalyst pollution mechanism by molten salts in DIR-MCFC

and DIR-MCFC cannot generate electricity finally. Therefore, these pollution phenomena of the reforming catalyst should be confirmed by the DIR-MCFC single cell, and the prevention method of the catalyst pollution should be proposed.

2. Experimental

2.1 Experimental apparatus and conditions

Figure 4 shows the schematic diagram of the experimental apparatus. The heater plate was set up in the top and bottom of the DIR-MCFC single cell, and the cell temperature was maintained at 650°C by which the DIR-MCFC single cell be blanketed by the insulation using the thermo-regulator (E5T@Omron, Japan). The reduction of the cell contact resistance and the gas sealing in the cell were carried out by compressing the single cell, the heater plates and the insulation by air press. H₂ and CO₂ as anode gases were adjusted by the mass flow controller (3660@Kofloc, Japan) and mixed with the mixer that is contained glass ball, and were humidified by passing through a humidifier and being supplied to DIR-MCFC. To prevent the dew formation of the supply gas, the piping between the humidifier and the cell was made shorter, and the piping temperature was maintained by a ribbon heater at 120°C. On the other hand, air from the compressor and CO₂ as cathode gas were also adjusted by the mass flow controller and mixed with the mixer, and were supplied to DIR-MCFC. Cell voltage was measured and recorded by a data logger (DR130@Yokogawa Electric Co. Ltd, Japan). Cell resistance was measured by a milliohm meter with AC 4 probes (3566@Turuga Electric Co. Ltd, Japan).

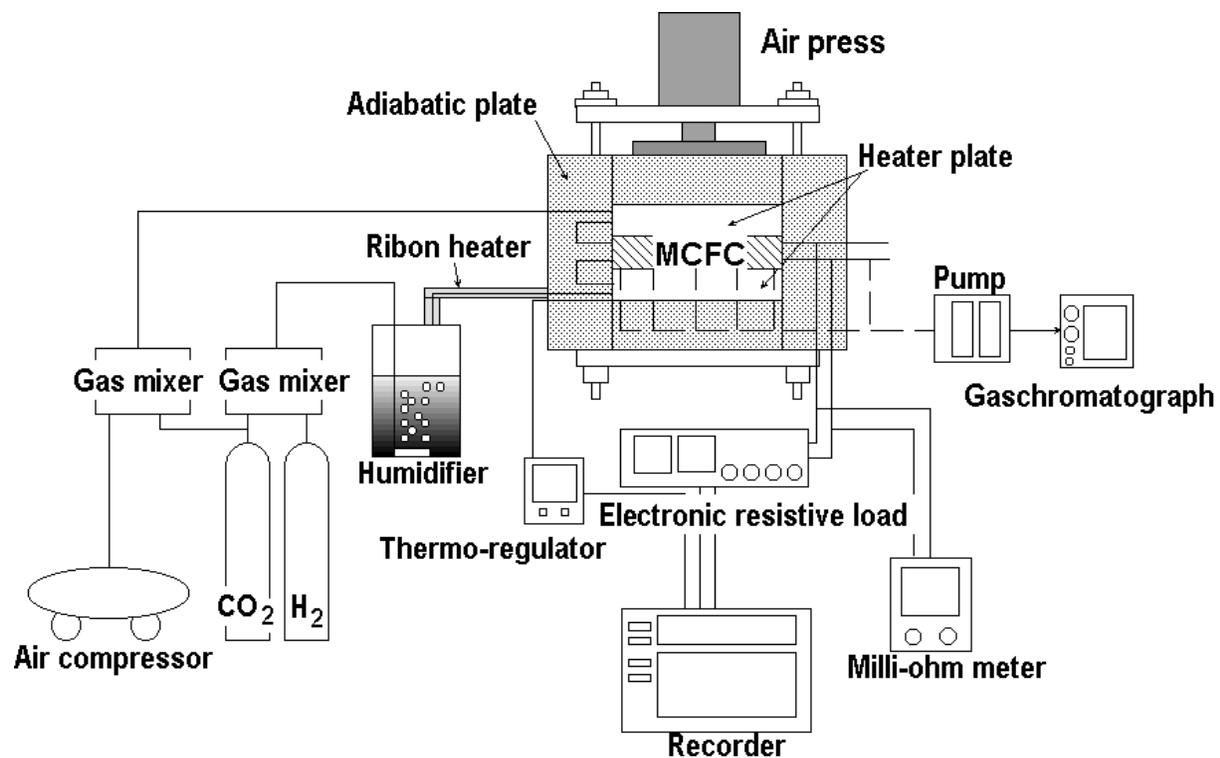


Fig. 4. Schematic diagram of experimental apparatus

The DIR-MCFC single cell had five sampling port for measuring the gas composition distribution in the cell as shown in Fig.5, and the sampling gas was collected by the pump through these ports, and analyzed with the gas chromatograph (GC-8AIT@Shimazu Co., Japan; the detector was the thermal conductivity detector). The locations of each sampling port were 3, 25, 50, 75 and 97% against the direction of flow, respectively. The reforming catalyst was loaded into the valley of the anode corrugated current collector as shown in Fig.6. Here, the corrugated current collector of anode side was made of Inconel steel, and that of cathode side was made of SUS316L, respectively. The standard gas condition was called ER mode; anode gas composition was $72\text{H}_2/18\text{CO}_2/10\text{H}_2\text{O}$ (Volume %), cathode gas composition was $70\text{Air}/30\text{CO}_2$, and the gas utilization of both sides was 40%, respectively. The standard condition of DIR-MCFC was called DIR mode; anode gas composition was $25\text{CH}_4/75\text{H}_2\text{O}$ (steam carbon ratio is 3.0), and cathode composition was same as ER mode. The operating atmosphere was 0.1MPa. As shown in Fig 3, general MCFC single cell was composed of anode cell frame (SUS316L), anode corrugated current collector (Inconel), anode current collector (Ni), anode electrode, matrix, cathode electrode (NiO), cathode

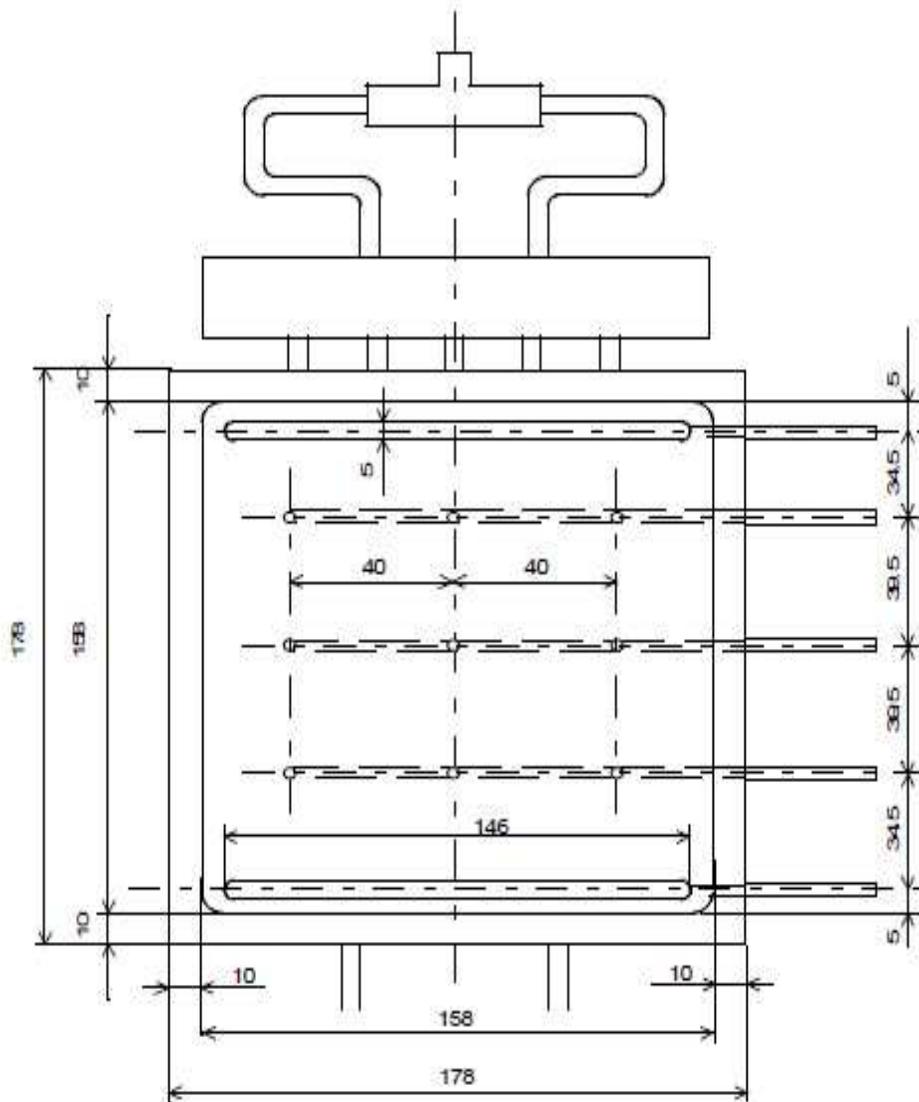


Fig. 5. Location of sampling port of anode cell frame in DIR-MCFC

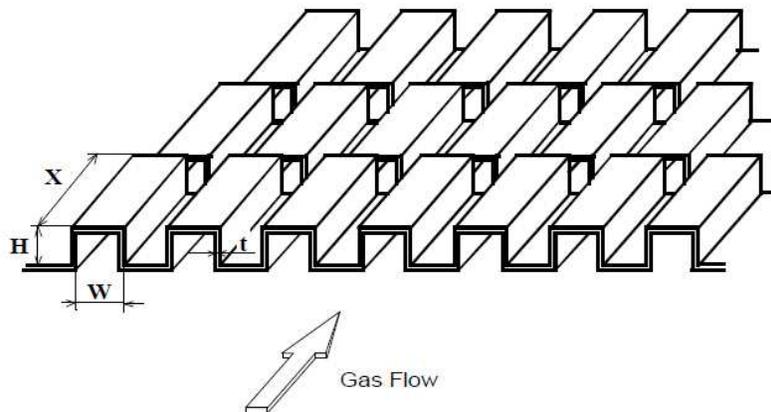


Fig. 6. Structure of corrugated current collector

current collector (SUS316L), cathode corrugated current collector (SUS316L) and cathode cell frame (SUS316L). Table 2 shows the specification of each cell component. All cell components such as anode electrode, cathode electrode, matrix and electrolyte sheet were made by a doctor blade method. The anode electrode was made of Ni-3wt%Al powder. The cathode electrode was made of Ni powder as a green sheet, and this green sheet was changed to NiO in the cell while the start up procedure. The matrix was made of LiAlO_2 . The electrolyte was made of $62\text{Li}_2\text{CO}_3/38\text{K}_2\text{CO}_3$.

	Anode	Cathode	Matrix
Materials	Ni-3wt%Al	NiO (in situ)	LiAlO_2
Thickness [mm]	0.75-0.85	0.75-0.85	0.50
Porosity [%]	50	55	50
Mean pore diameter [micron]	3	1-4, 0.2-0.4	0.1

Table 2. Specification of cell components

2.2 Setting of gas chromatograph

In fuel cell research, the crossover between anode and cathode through the electrolyte and the activation of the reforming catalyst are evaluated by the gas analysis. Especially, because CH_4 is reformed to H_2 in the anode channel of DIR-MCFC, H_2 , CH_4 , CO and CO_2 concentration become the index of the catalytic activity. Moreover, because neither N_2 nor O_2 exist in the anode gas, N_2 and O_2 become the index of the crossover. To analyse these gases in short time, the column diverged to two passages, one passage was composed by 0.5m of the shimalite Q 100/180 and 1.5m of the porapak Q 80/100, and another passage was composed by 2.5m of the molecular sieve 5A 60/80 as shown in Fig.7. The carrier gas was Argon gas, the flow rate of the carrier gas was 50ml/min, and the inlet pressure was 121.6kPa, respectively. The temperature of the column, the detector and the injection temperature were 90°C , 100°C and 100°C , respectively. Figure 8 shows the chromatogram obtained by this column. The peak of CO_2 does not overlap with that of air because air is hardly contained in the anode gas though the peak of air appears immediately after the analysis beginning. Because the desorption of CO is slow, the analysis time is about 20 minutes.

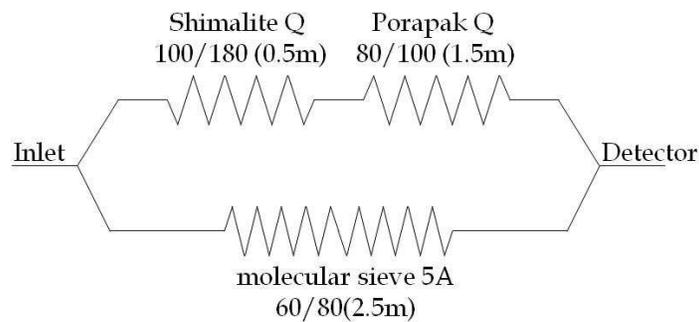


Fig. 7. Schematic diagram of the column structure for DIR-MCFC

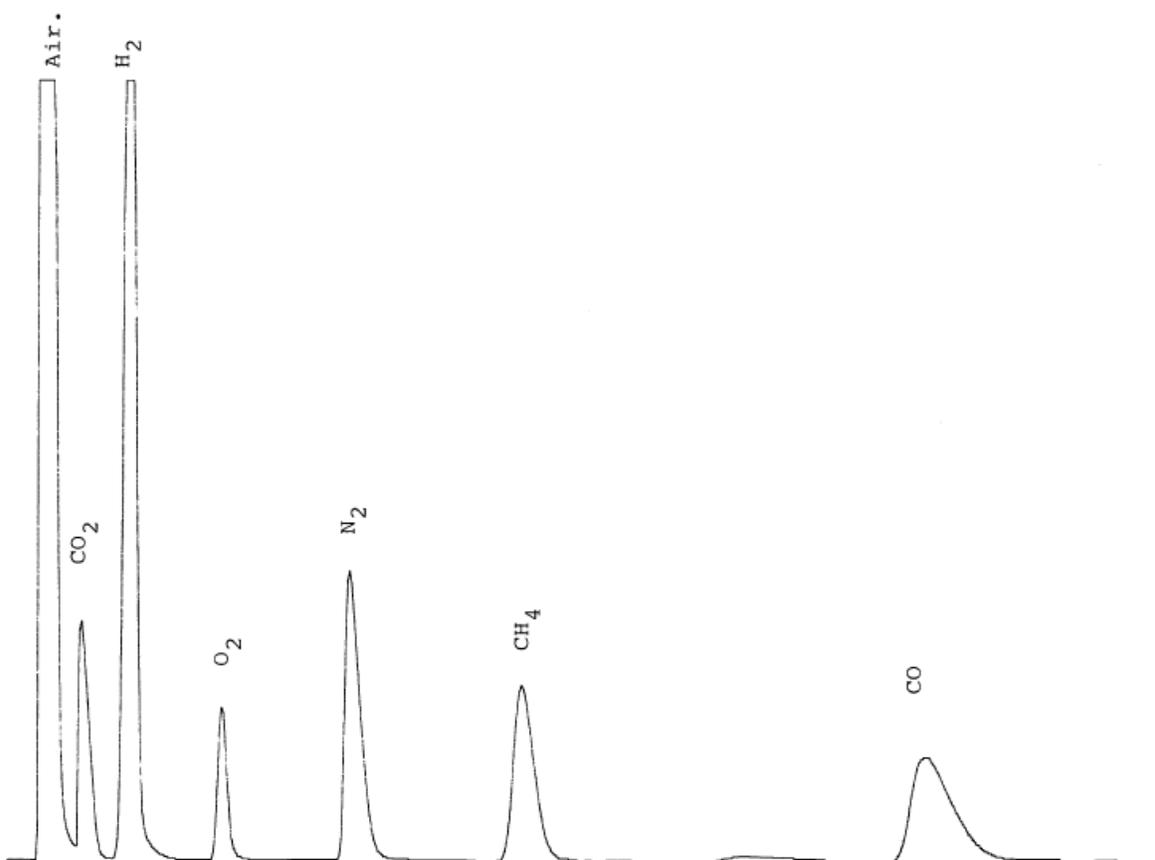


Fig. 8. Example of chromatogram using the column for DIR-MCFC

2.3 Loading method of reforming catalyst in the anode channel

The influence of the loading method of the reforming catalyst on the cell performance is examined by four loading methods as shown in Fig.8. Here, the reforming catalyst was the commercially available nickel catalyst (25wt%Ni/MgO; Type RKNR@ Haldor Topsoe, Denmark), and is 1.2mmO.D.x1.4mmL of the cylinder type.

- a. "Frame side" means that the reforming catalyst was loaded into only the frame side of the corrugated current collector to keep away the catalyst from the electrode that contains the carbonate as shown in Fig.9 (a). The catalyst loading density was 48mg/cm².

- b. "Electrode side" means that the reforming catalyst was loaded into only the electrode side of the corrugated current collector to improve the reforming rate by making the reforming reaction adjoin the cell reaction as shown in Fig.9 (b). The catalyst loading density was $78\text{mg}/\text{cm}^2$.
- c. "Upper stream" means that the reforming catalyst was loaded into both side of the upper stream part and the frame side of the downstream part of the corrugated current collector to cool the vicinity of the cathode outlet locally as shown in Fig.9 (c). The catalyst loading density of the frame side and the electrode side were $60\text{mg}/\text{cm}^2$ and $30\text{mg}/\text{cm}^2$, respectively.
- d. "Downstream" means that the reforming catalyst was loaded into both side of the downstream part and the frame side of the upper stream part of the corrugated current collector to cause the reforming reaction uniformly with the entire anode electrode as shown in Fig.9 (d). The catalyst loading density of the frame side and the electrode side were $60\text{mg}/\text{cm}^2$ and $30\text{mg}/\text{cm}^2$, respectively.

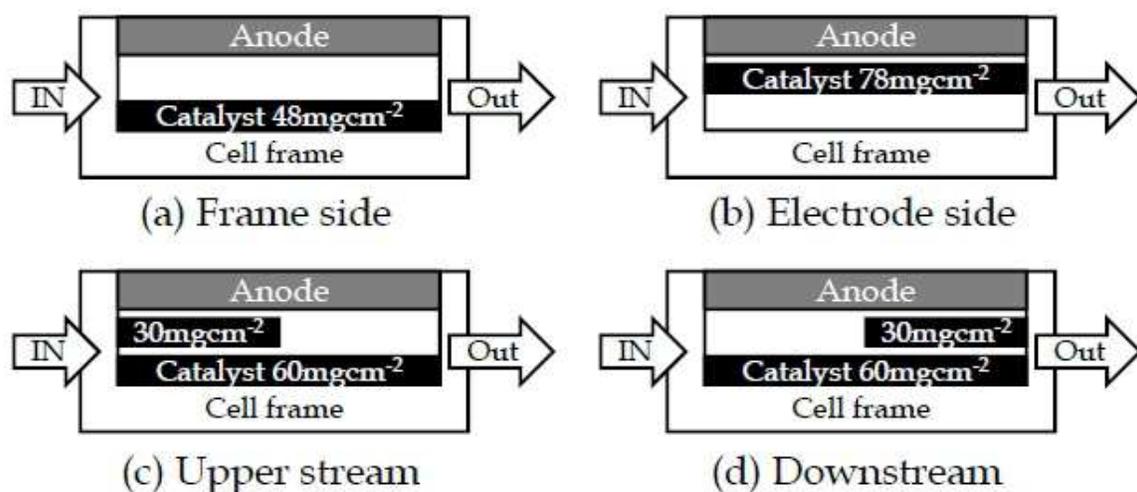


Fig. 9. Schematic diagram of loading method of the reforming catalyst and loading amount

3. Results and discussion

3.1 Cell performance

Figure 10 shows the initial performance comparison between the ER mode (the reforming catalyst does not work) and the DIR mode under the downstream of loading condition. Because the difference of both modes is little, the reforming catalyst works correctly at the initial period. Figure 11 shows the influence of the loading method of the reforming catalyst on the life performance. Here, this result is the cell performance under DIR mode. Although all cell voltages are almost same until 300 hours of the operating time, the cell performances other than the cell of "downstream" are rapidly deteriorated. Moreover, the cell performance of "downstream" is also deteriorated when the operating time exceeds 600 hours. This deteriorating reason should be judged the catalyst pollution originating or the cell deteriorating originating. Therefore, the deteriorating reason is evaluated by comparing of the performance under ER mode with that of the "Downstream" cell under DIR mode as shown in Fig.12. Although the cell performance under ER mode is good, the cell performance under DIR mode deteriorates gradually from 100 hours to 600 hours of

operating time, and deteriorates rapidly when the operating time exceeds 600 hours. It is a peculiar problem to DIR-MCFC (Miyake et al., 1995).

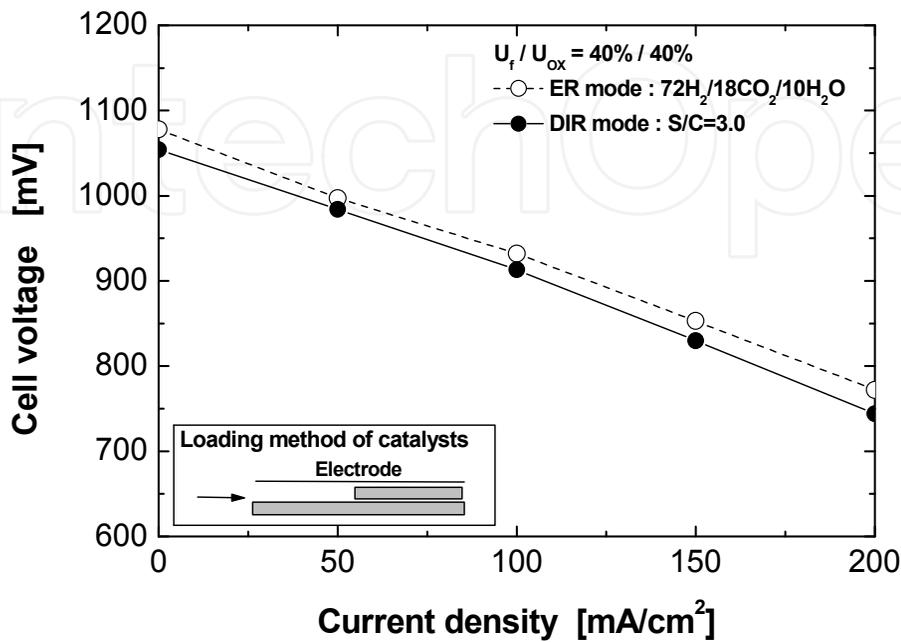


Fig. 10. Initial I-V performance of 250cm² DIR-MCFC single cell

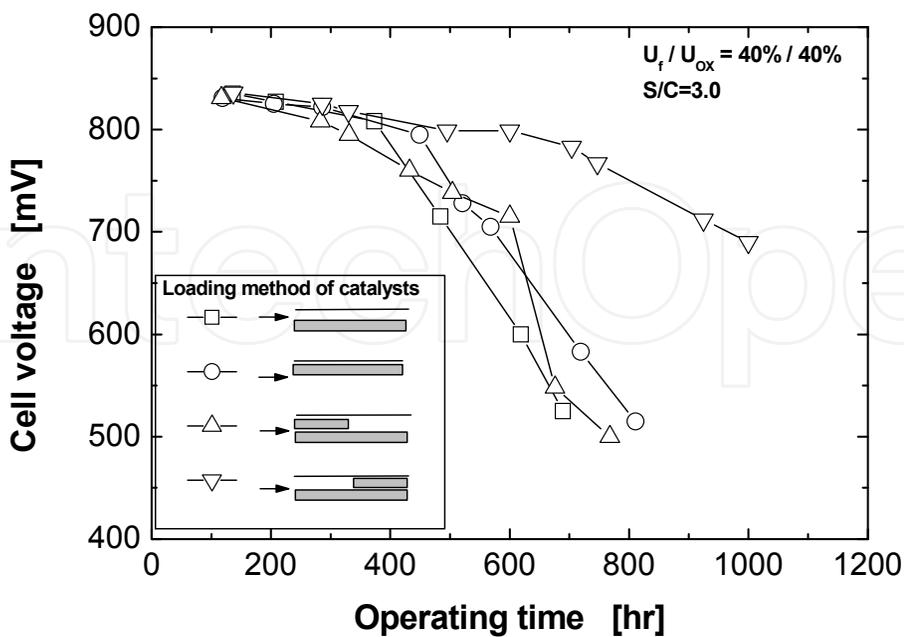


Fig. 11. Influence of the loading method of the reforming catalyst on the life performance

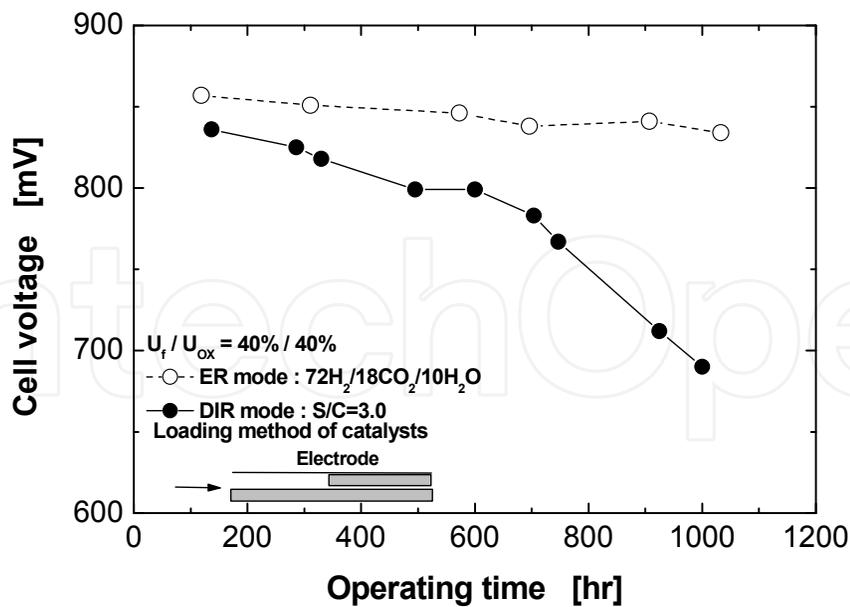


Fig. 12. Comparison of the cell performance between ER mode and DIR mode

Figure 13 shows comparison of the gas composition change in the cell according to operating time between “Upper stream” and “Downstream”. Here, these results are that gases that collected at OCV (because the cell reaction does not occur, the ability of the catalyst is purely evaluated.) are analyzed by gas chromatograph. From the result of Fig.12 (a), because the hydrogen concentration of “Upper stream” is almost corresponding to the chemical equilibrium, the ability of the reforming catalyst is good. However, the hydrogen

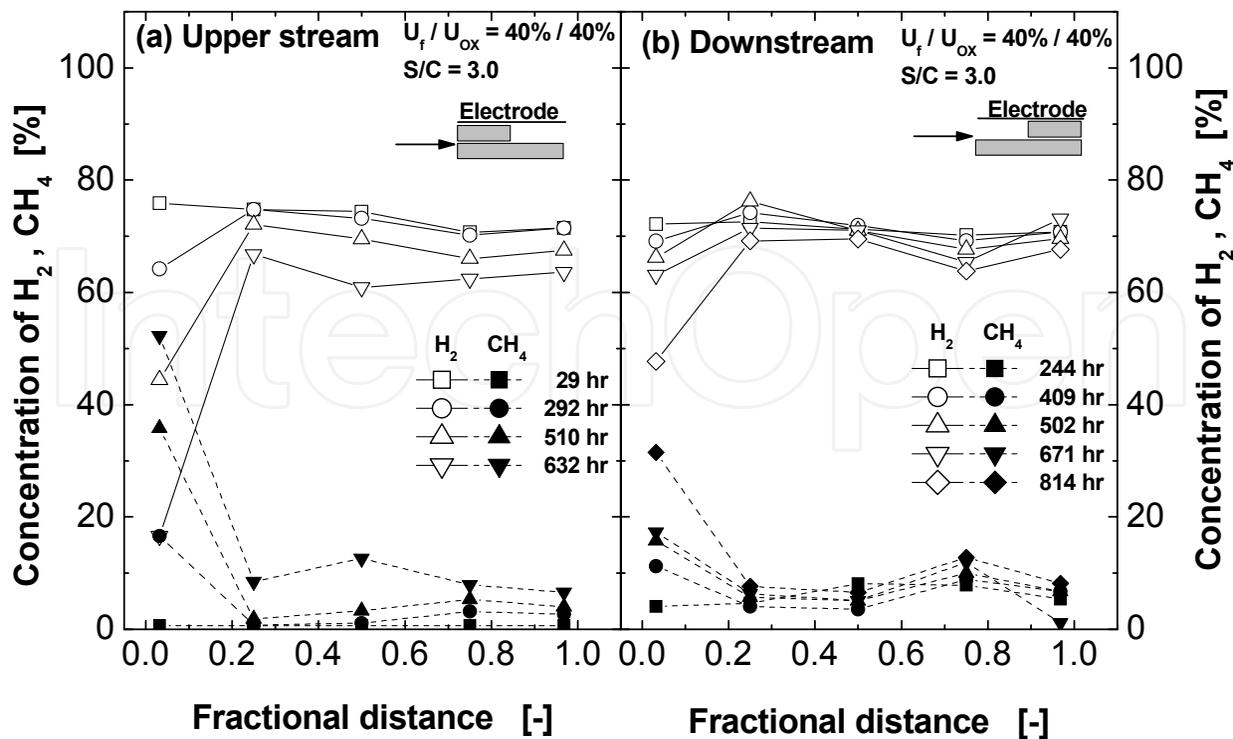


Fig. 13. Gas composition change in the cell according to operating time

concentration decreases and the methane concentration increases near the inlet when the operating time exceeds 292 hours. These concentration changes become large and progress toward the downstream side at 632 hours of the operating time. Therefore, the cell performance of "Upper stream" deteriorates for which the necessary hydrogen content cannot be secured by the catalyst pollution.

On the other hand, although the hydrogen concentration decreases and the methane concentration of "Downstream" increases near the inlet with the lapse of time, they are corresponding to the chemical equilibrium in 80% region of the entire cell. Moreover, they change rapidly at 814 hours of the operating time, and this change is corresponding to the drastic descent of the cell voltage. Therefore, the deterioration factor of the cell of "Downstream" is the pollution of catalyst loaded into the inlet as well as the cell of "Upper stream". Although the electrode of the downstream can use the hydrogen not used for the cell reaction of the hydrogen reformed in the upper stream part, the electrode of the upper stream cannot use the hydrogen if the catalyst of the upper stream cannot make the hydrogen by the catalyst pollution. Consequently, because the electrode of the upper stream hardly works when the operating time exceeds about 600 hours, the effective reaction area of the electrode decreases and the DIR-MCFC cannot generate electricity finally.

3.2 Analysis of the polluted catalyst

These four cells are disassembled to confirm the deterioration factor of DIR-MCFC, and are observed. Moreover, the polluted catalyst collected from the cell after experiment ends is analyzed by ICP for which it confirm that the molten salts make the reforming catalyst pollute. Figure 14 shows the sketch drawing of anode in each cell disassembled. All anode electrodes have discoloured from the parabolic and the gray to the black toward the exits from the inlet. There was no difference of these compositional variations though these different colours of electrodes were analyzed by an X-ray structure analysis.

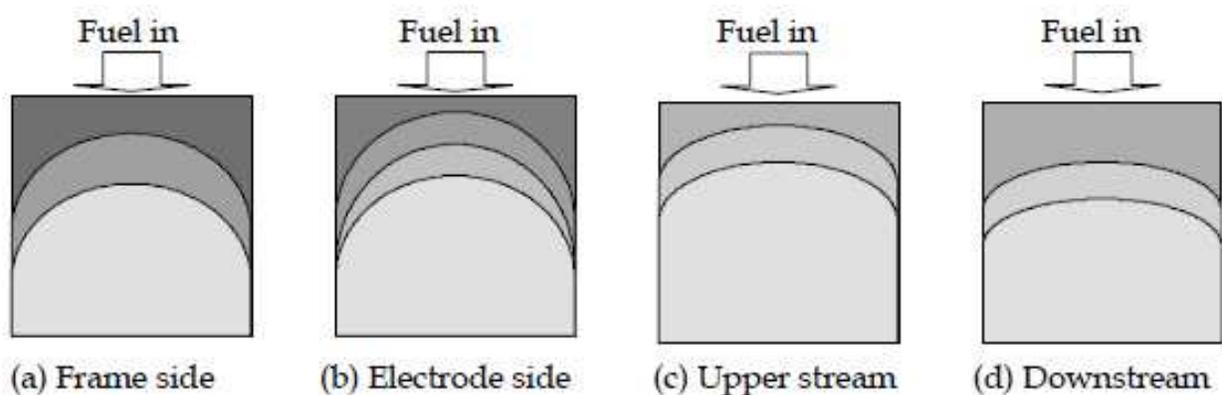


Fig. 14. Sketch drawing of anode in each cell disassembled

The reforming catalysts were collected according to this discoloration of each electrode after about 1000 hours of operating, and the amount of lithium and potassium in the catalyst were analyzed by ICP. Figure 15 shows the carbonate content in the collected catalyst from each cell. Here, amount of Li_2CO_3 and K_2CO_3 are converted from the results of lithium and potassium by ICP, and the location number means that it is a catalyst collected from the

place shown in the number of the sketch of the electrode in each figure. Moreover, #4 and #5 of “Upper stream” and #6 and #7 of #Downstream” mean that the catalyst is collected from the electrode side of the corrugated current collector. The frame of electrode such as #1 of “Frame side”, #5 of “Electrode side”, #6 of “Upper stream” and #5, #7 of “Downstream” means that the catalyst is collected from near the wet seal part. Moreover, the colours of the catalysts collected from each location are corresponding to the colour of each electrode. Although the catalysts collected from the wet seal part and the upper stream part include much carbonate, the carbonate content of the catalysts collected from the centre of the cell and the downstream part are comparatively few. The carbonate content of the catalyst collected from “Downstream” is fewer than others. MCFC adopts the wet seal method that prevents the gas leakage by forming the liquid film with the molten salt between the matrix and the electrode. Therefore, a little molten salt begins to leak from the wet seal part into the cell. Especially, because the wet seal part of the upper stream is orthogonal to the gas flow, the leakage amount of the molten salts is much. However, because the wet seal part of the cell side is parallel to the gas flow, the leaked molten salt flows along the cell frame. The leaked molten salt doesn't, therefore, penetrate the catalytic layer easily. From these results, we understand that the discoloration of the parabolic in anode is signs where the electrolyte flows in the anode channel.

On the other hand, when the amount of lithium is compared with potassium, the amount of potassium is much. It can guess that potassium that is more than this composition is the molten salts of vapour phase because the molten salt of liquid phase is the same as the composition ratio of the electrolyte (47Li₂CO₃/53K₂CO₃; wt%). Therefore, Figure 15 was arranged to the ratio of the liquid phase molten salt and the vapour phase molten salt as shown in Fig.16. The liquid phase molten salt is more than the vapour phase molten salt in all location, and the vapour phase molten salt is distributed in the entire cell almost

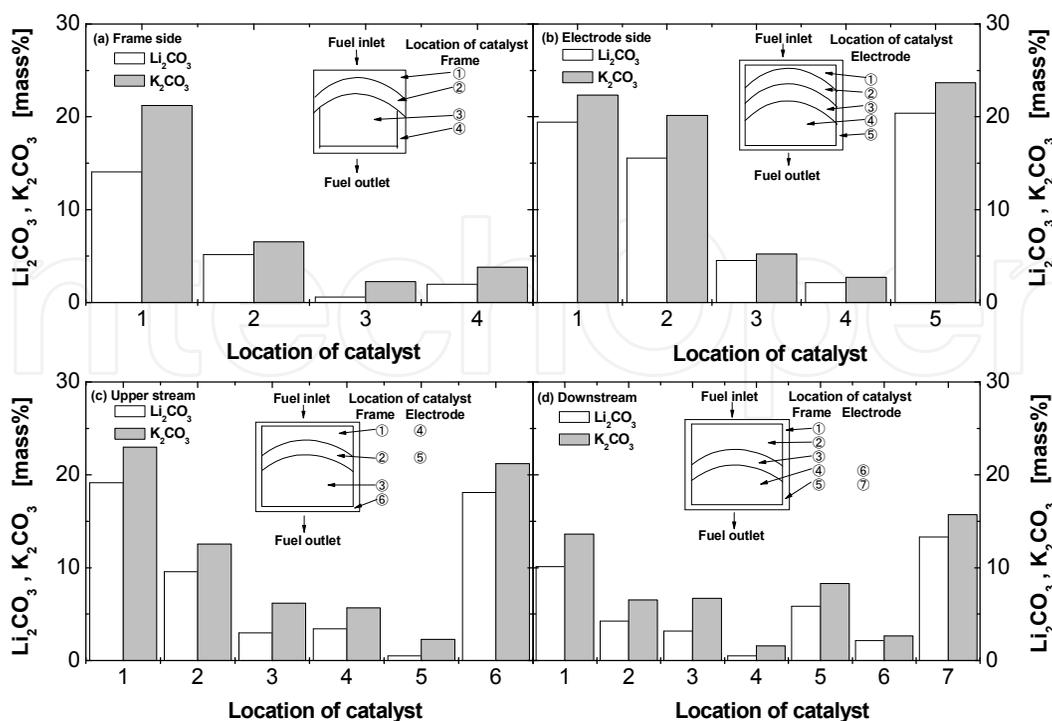


Fig. 15. Carbonate content in the collected catalyst from each cell

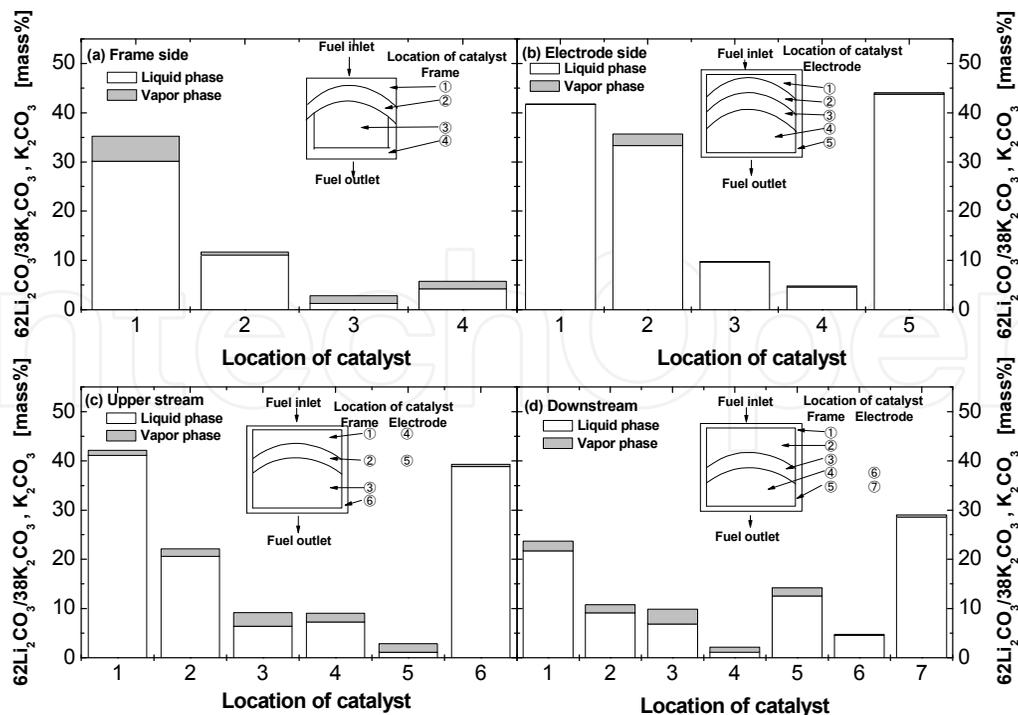


Fig. 16. Ratio of the liquid phase molten salt and the vapour phase molten salt in the polluted catalyst

uniformly. Generally, as for potassium, the deliquescence is stronger than lithium's, and the vapour partial pressure is also higher. Therefore, we elucidate the electrolyte volatile behaviour in MCFC using a visualization technique (Sugiura et al., 2008). The influence of electrolyte leakage from the wet seal section on the electrolyte volatile behaviour is evaluated by visualizing the wet seal. Here, because the Li/Na electrolyte is less volatile than the Li/K electrolyte, it is possible to pay attention to the electrolyte leakage from the wet seal part by excluding the influence of the volatilizing phenomenon if $52\text{Li}_2\text{CO}_3/48\text{Na}_2\text{CO}_3$ electrolyte is used as the electrolyte. The volatilization phenomenon of the wet seal section is elucidated by observing a wet seal section via a visualization cell. Figure 17 shows the measurement image of the wet seal section in the anode gas channel immediately after operation. Figure 17 (a) shows the measurement image under OCV conditions, and Figure 17 (b) shows the measurement image under 125 mA/cm^2 of current density, respectively. Here, the electrode is supported only on one side because there is not the support for the cell frame side to observe the wet seal section. Therefore, this cell uses the current collector to prevent the electrode curving. From Fig.17 (a), we can see that volatile matter gushes from the wet seal section, which is a part of the anode and cell frame, and this gush is promoted by the increase of the current density, as shown in Fig.17 (b). This gush originates because the electrolyte of the wet seal section flows as a mist, with steam and CO_2 generated in the anode cell reaction. Moreover, this mist electrolyte volatilizes in the gas, is changed into a powder of Na_2CO_3 by reacting with CO_2 , and it furthermore becomes a smaller mist by the gas flow. We understand that the gap of the wet seal part grows when the elasticity of the corrugated current collector decreases by the endothermic reaction of the catalyst, and the leakage of the molten salt from this grown gap is promoted, and the reforming catalyst is polluted by this leaked molten salt as shown in Fig.18. The catalytic activity of the reforming catalyst decreases by which the specific surface area

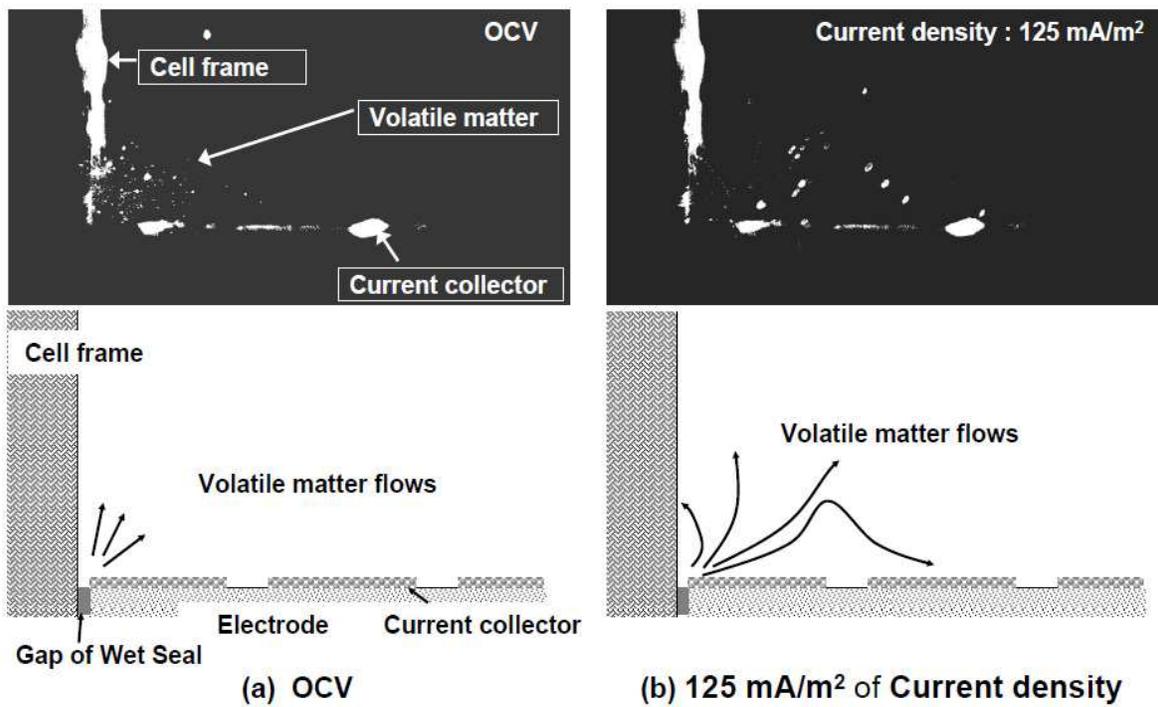


Fig. 17. Measurement image of wet seal part in the anode gas channel

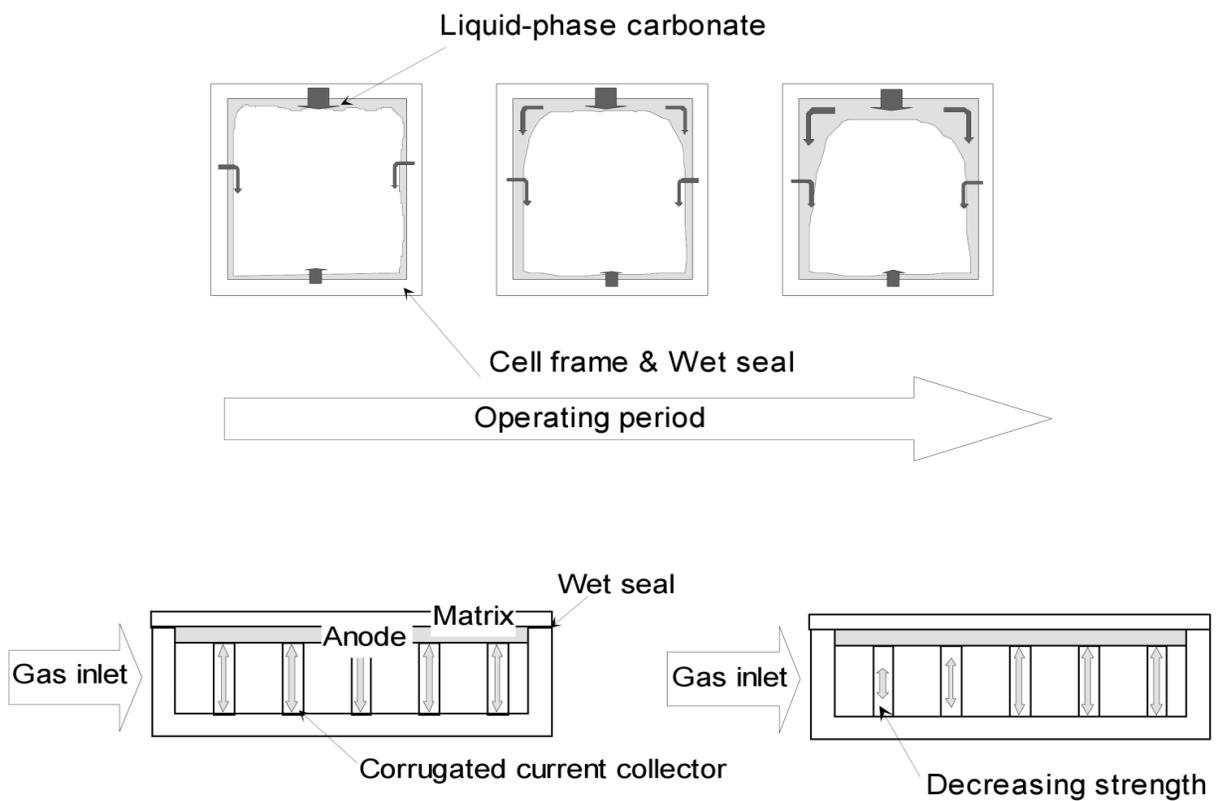


Fig. 18. Mechanism of the liquid phase pollution of reforming catalyst

decrease by adhering the leaked electrolyte to the reforming catalyst. The electrolyte that adheres to the reforming catalyst cannot be easily removed because the reforming catalyst

has a micro pore structure (Sugiura & Ohtake, 1995). Moreover, the potassium in the leaked molten salt easily changes into KOH with the steam produced by the cell reaction, and disperses with the produced gas in the catalytic layer. Therefore, the catalyst pollution is divided into the liquid phase pollution and the vapour phase pollution. Though it is difficult to defend the catalyst from the vapour phase pollution, the catalyst can be defended from the liquid phase pollution for which the catalyst be covered by the material with large contact angle with the molten salt.

3.3 Prevention method of the liquid phase pollution

The corrugated current collector is plated by nickel which has large contact angle with molten salt to defend the catalyst from the liquid phase pollution. Figure 19 shows the effect of Ni plating on the cell performance. Here, the operating condition is DIR mode ($U_f/U_{ox}=75\%/50\%$; $S/C=3.0$), and the catalyst loading method adopted "Downstream" whose performance was the best in a current experiment. Moreover, Ni plating was applied to the corrugated current collector by the electrolytic process, and the thickness of Ni plating was about 100 microns. It is clear that the performance of the cell with the corrugated current collector with Ni plating is better than that of non plating. Moreover, the catalyst is collected after about 1000 hours of operating, and the carbonate content of the collected catalyst is analysed.

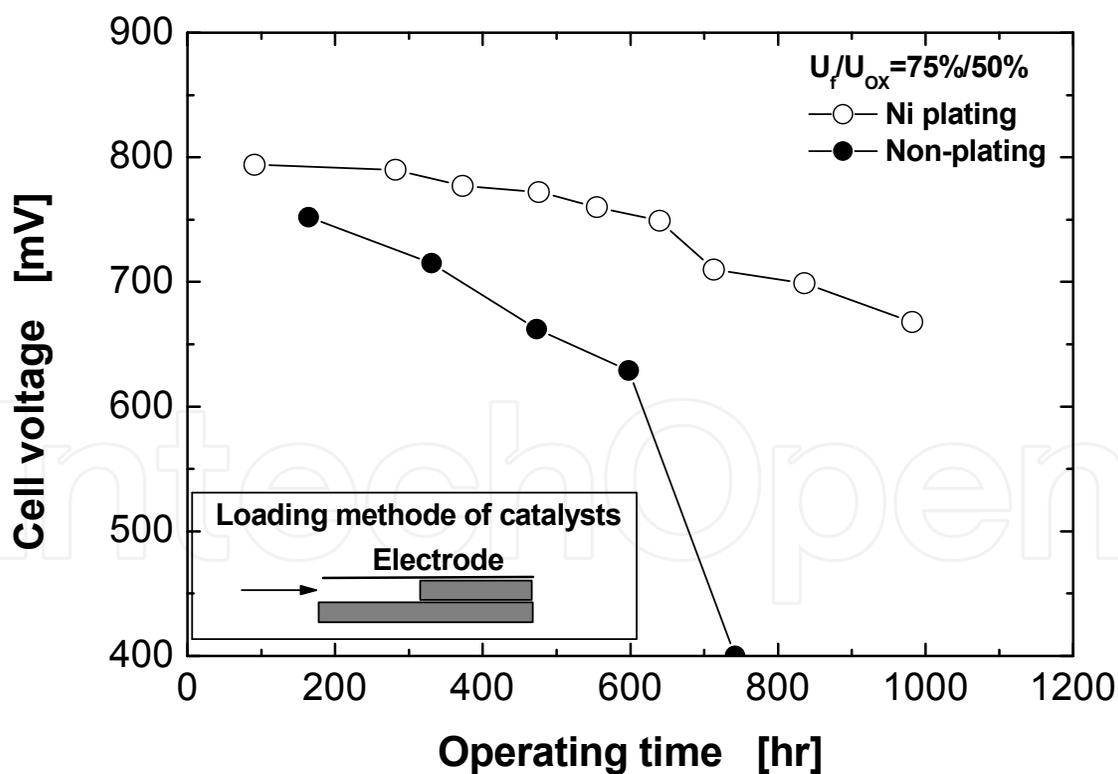


Fig. 19. Effect of Ni plating on the cell performance

Figure 20 shows the carbonate contents and the ratio of the liquid phase molten salt and the vapour phase molten salt in the polluted catalyst. Here, (a) and (b) are the carbonate content

n the polluted catalyst, and (c) and (d) are the ratio of the liquid phase molten salt and the vapour phase molten salt in the polluted catalyst, respectively. It is clear that the carbonate content of the catalyst of the cell frame side by Ni plating decreases from that of non-plating. Therefore, the effect of Ni plating on the liquid phase pollution is able to be confirmed. However, the carbonate content of the catalyst of the electrode side has hardly changed though Ni plating was applied to the corrugated current collector. This reason is that because the catalyst of the electrode side is faced with the electrode, the path for the molten salt to reach the catalyst layer is different from the catalyst of the frame side, and there is a possibility that the catalyst contacts to the electrode. Therefore, the effect of Ni plating on the liquid phase pollution is small. From these results, it is clear that the liquid phase pollution can be controlled by applying Ni plating to the corrugated current collector.

On the other hand, the ratio of the vapour phase pollution of most catalysts in the cell is higher than that of the liquid phase pollution by controlling the liquid phase pollution. Because the vapour phase pollution is caused in the entire cell, the control of the vapour phase pollution is not easy like the liquid phase pollution. However, we elucidated that the vapour phase pollution originates in volatilizing of the molten salt that leaks from the wet seal part. Moreover, because this molten salt leakage from the wet seal part stops within one week after the operating temperature reaches, we understand that the catalyst pollution does not occur if this molten salt leakage can be controlled (Sugiura et al., 2010).

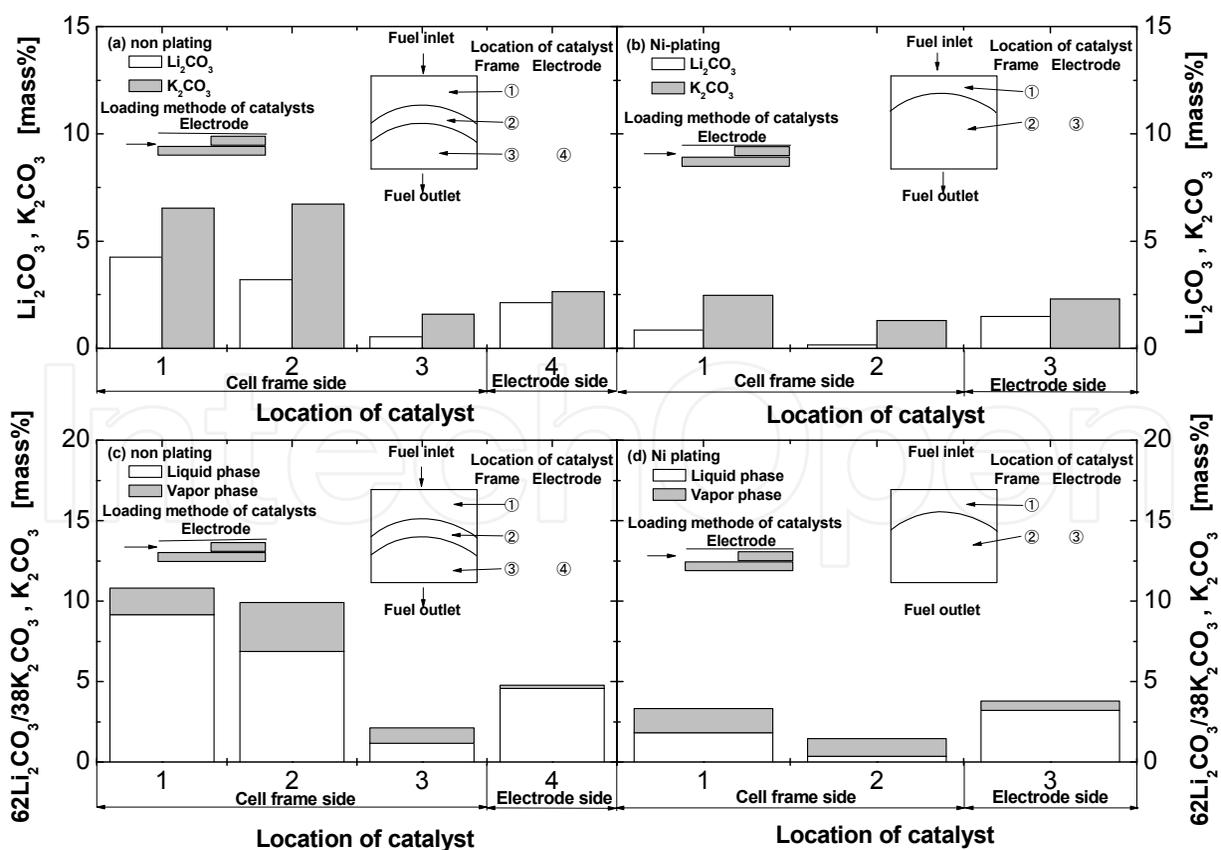


Fig. 20. Effect of Ni plating on the pollution ratio

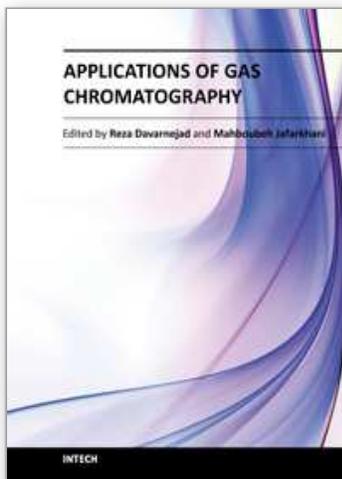
4. Conclusion

The catalyst pollution in DIR-MCFC was elucidated from the cell test. The gas chromatograph is profitable for the evaluation of DIR-MCFC. The degradation factor of DIR-MCFC was the catalyst pollution by electrolyte, and the catalyst pollution is classified into the liquid phase pollution and the vapour phase pollution. The liquid phase pollution is the leaked electrolyte from the wet seal part, and the leaked electrolyte flows with the gas supplied along the cell frame and into the catalyst loading area. The gap of the wet seal part grows when the elasticity of the corrugated current collector decreases by the endothermic reaction of the catalyst, and the leakage of the molten salt from this grown gap is promoted, and the reforming catalyst is polluted by this leaked molten salt. The catalytic activity of the reforming catalyst decreases by which the specific surface area decrease by adhering the leaked electrolyte to the reforming catalyst. The electrolyte that adheres to the reforming catalyst cannot be easily removed because the reforming catalyst has a micro pore structure. Therefore, because the liquid phase pollution has to be controlled physically, the catalyst was covered by the nickel with large contact angle with the molten salt. The performance of DIR-MCFC was improved using the corrugated current collector with Ni plating, which repels molten salts.

From the visualization experiment, because the electrolyte that polluted the reforming catalyst dispersed from wet seal section, DIR-MCFC can operate for long time if the reforming catalyst was protected from the electrolyte gush for 7 days from the operation-start. Moreover, though the most of the volatile matter of anode side was the electrolyte that gushed from the wet seal part, the part of volatile matter was KOH generated as the water generated by the cell reaction reacts with the electrolyte, and as the generated KOH returns to K_2CO_3 in the region where the concentration rose by the CO_2 generated by the cell reaction.

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This valuable book aims to provide a connection between various chromatography techniques and different processes. Authors applied these techniques in supercritical technology, medical, environmental, physique and chemical processes. Most of them prepared mathematical support (such as correlation) for their original results obtained from the chromatography techniques. Since chromatography techniques (such as GC, HPLC & etc) are separating and analyzing methods, this chapters will help other researchers and young scientists to choose a suitable chromatography technique. Furthermore, this book illustrates the newest challenges in this area.

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