

Short communication

# Performance of a unit cell equipped with a modified catalytic reformer in direct internal reforming-molten carbonate fuel cell

Jung-Ho Wee\*

*Department of Chemical and Biological Engineering, Korea University, 1, 5-Ka, Anam-Dong, Sungbuk-Ku, Seoul 136-701, South Korea*

Received 14 March 2005; accepted 6 June 2005

Available online 22 July 2005

## Abstract

The performance of a unit cell (50 mm × 50 mm) equipped with a modified direct internal reformer is investigated by comparison with that of a traditional reformer in which the reforming catalyst is loaded constantly throughout the cell. The channel depth ratio of the inlet and outlet in the modified reformer is 1:2, and the depth of the channel increases linearly to the outlet position. Half the amount of the reforming catalyst in the outlet position is loaded in the inlet position. The unit cell with a modified reformer shows good stability in terms of open-circuit voltage and its overall electrical resistance is 94% that of a unit cell equipped with a traditional reformer. In long-term cell performance tests with a cell utilization of 40%, the modified reformer unit cell shows greater durability; it provides 40 more hours of performance than the cell with a traditional reformer. Furthermore, the average temperature of the outlet gases from the modified reformer unit cell over the course of 200 h is lower than that of a traditional reformer unit cell by 8 °C. The potassium and lithium poisoning levels of catalysts in the modified reformer are respectively, 54 and 45% of those in a traditional reformer.

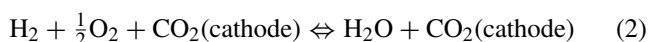
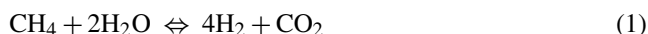
The results might be attributed to the different loading amount of the reforming catalyst, leading to a more uniform dispersion of the reforming reaction throughout the cell. This dispersion of the reforming reaction may also lead to the uniform dispersion of other reactions throughout the cell, improving the overall cell performance.

© 2005 Elsevier B.V. All rights reserved.

*Keywords:* Direct internal reforming; MCFC; Modified reformer; Anode compartment; Reforming reaction

## 1. Introduction

In a direct internal reforming molten carbonate fuel cell (DIR-MCFC), hydrogen is directly and continuously produced from methane by a combination of steam reforming and the water–gas shift reaction in the anode compartment of the catalytic reformer. The overall reaction is shown in Eq. (1). The electrochemical reaction in the fuel cell, as shown in Eq. (2), provides the heat that is essential for the endothermic catalytic reforming reaction.



In practice, the heat needed for the endothermic reforming reaction could be provided by an exothermic electrochemical reaction, which would also help to control the temperature of the stack. This would not, however, be sufficient to offset completely the excess heat produced by the electrochemical reaction and would make management of the temperature within the cell to be an issue [1–6].

Traditional methods of controlling cell temperature are to pass excess gas or to apply a high rate of gas flow throughout the cathode channel. The latter lowers the stack temperature and helps to create a somewhat more uniform temperature gradient throughout the cell. This method depends, however, on the temperature of the oxidant gases fed into the cathode. It also rests upon the assumption that convective heat transfer is dominant in the MCFC. Furthermore, applying this method presents the problem of a potentially unnecessary loss of cathode gases.

\* Tel.: +82 2 923 3105; fax: +82 2 926 6102.  
E-mail address: [jhwee@korea.ac.kr](mailto:jhwee@korea.ac.kr).

One of the most important factors leading to deterioration in cell performance is a non-uniform reaction rate throughout the cell as this causes non-uniform heat transfer and an uneven distribution of temperature. When the DIR-MCFC is operating properly, the first reaction carried out in the cell is the methane reforming reaction. Therefore, a better-dispersed reforming reaction could be a key factor in facilitating the efficient dispersal of other reactions throughout the cell. In the case of a DIR-MCFC equipped with a traditional reformer, in which the catalyst is uniformly loaded at a constant channel depth within the reformer, the reforming reaction may not be well dispersed due to the amount of catalyst being predetermined and loaded irrespective of the position of the cell. This may give rise to the non-uniformity of all other reactions and an uneven temperature distribution throughout the cell. Accordingly, the performance of such fuel cells decreases rapidly [7–9].

Many simulation-based studies [2–6,9–10] have investigated the local reactions and the temperature distribution in MCFCs and have found local heated areas or cold spots in the cells [6]. According to these reports, the extent of the reactions in the inlet position of a unit cell, including reforming and electrochemical reactions, is much greater than that of reactions in the outlet position. This causes uneven temperature distribution, e.g., a 15 °C difference between the inlet and outlet positions in a 50 mm × 50 mm cell.

Various means of achieving an efficient dispersion of reactions and a uniform temperature distribution in cells have been suggested in previous studies. For example, simulation results have evaluated modifications to the reformer and the cell configuration [1,6], while others have considered modifications to the unit cell [11], stack [12–13] and reformer [14]. There have also been investigations of the effects of system configuration and operating conditions that include changes in gas flow rates and advanced reforming catalysts [15–18]. Despite these efforts, however, most proposed solutions have been deemed too expensive, too complicated, or only achievable under simulated conditions. Importantly, there have as yet been no studies conducted on the actual performance of a unit cell equipped with a simple, modified internal reformer in which there are differing amounts of reforming catalyst loaded throughout the cell.

This paper suggests that even greater reforming and electrochemical reactions in the inlet position can be dispersed to the outlet position by setting up a modified catalytic reformer in the anode compartment. The modified direct reformer is designed for much greater reactions in the outlet position than in the inlet position by controlling the loading amount of the reforming catalyst. In such a situation, half the amount of the reforming catalyst in the outlet position is loaded in the inlet position. The performance of a unit cell equipped with a modified direct internal reformer is investigated in terms of its performance relative to that of a cell with a traditional reformer, i.e., one in which the reforming catalyst is loaded evenly throughout the cell.

## 2. Experimental

A 50 mm × 50 mm unit cell equipped with two different reformers is shown schematically in Fig. 1. A traditional catalyst reformer (named TR), in which 6.25 g of reforming catalyst were uniformly loaded into the channel at a constant depth of 3 mm, see Fig. 1(a). The modified reformer (named MR) is shown in Fig. 1(b). Half the amount of catalyst in the outlet channel was loaded into the inlet channel at a depth of 2 mm. As well, the catalyst amount in the outlet channel was loaded at a depth of 4 mm. The total amount of catalyst was also 6.25 g. The catalyst bed was loaded with reforming catalysts and covered with the perforated current collector. Following this, two types of unit cells, each equipped with one of the reformers, were assembled with identical components, including current-collectors, anodes, cathodes and electrolytes. The characteristics of the two unit cells are listed in Table 1.

The reforming Ni catalyst used in this study was a cylindrical-type (diameter = 1.23 mm; Length = 1.80 mm) obtained from Haldor Topsoe (see [9] for more details). The two 50 mm × 50 mm unit cells were equipped with the experimental apparatus for measuring cell performance illustrated in Fig. 2.

During operation of the unit cells, an air cylinder applied an absolute pressure of 2.48 bar to cause the cell components to stick together. Anode gases and cathode gases flowed perpendicular to each other. The steam-to-carbon ratio was 2.5, and the operating temperature remained steady at 650 °C.

Details of the operating time and temperature for each step in the cell performance test are given in Fig. 3. A total of 140 h were required to approach a steady state. The specifications and operating conditions, including gas flow rates and compositions for each step are given in Table 2.

When the unit cells reached a steady state, the open-circuit voltage (OCV) for each cell was measured for 150 h. The volt-

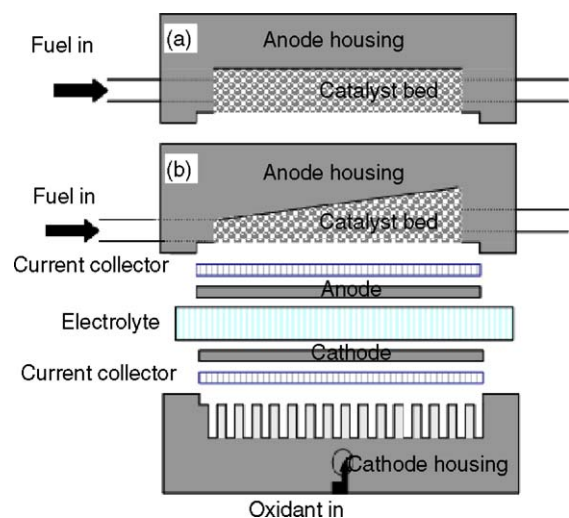


Fig. 1. Configuration of disassembled unit cell of DIR-MCFC: (a) traditional reformer; (b) modified reformer.

Table 1  
Unit cell characteristics

Unit cell component	Characteristics
<b>Anode compartments</b>	
Anode housing	
Size (width × length × height; mm × mm × mm)	70 × 70 × 20
Material	SUS-316
Catalysis bed (traditional reformer)	
Size (width × length × depth; mm × mm × mm)	50 × 50 × 3
Catalysis bed (modified reformer)	
Size	
Inlet (width × length × depth; mm × mm × mm)	50 × 50 × 2
Outlet (width × length × depth; mm × mm × mm)	50 × 50 × 4
Catalysts	
Loaded amount (g)	6.25
Anode electrode	
Size (width × length × thickness; mm × mm × mm)	50 × 50 × 0.8
Material	Ni
<b>Cathode compartments</b>	
Cathode housing	
Size (width × length × height; mm × mm × mm)	70 × 70 × 20
Material	SUS-316
Cathode electrode	
Size (width × length × thickness; mm × mm × mm)	50 × 50 × 1
Material	NiO
<b>Electrolyte</b>	
Matrix (thickness; mm)	$\gamma$ -LiAlO <sub>2</sub> ; (0.18)
Li (Li <sub>2</sub> CO <sub>3</sub> )/K (K <sub>2</sub> CO <sub>3</sub> ) mole ratio	62/38

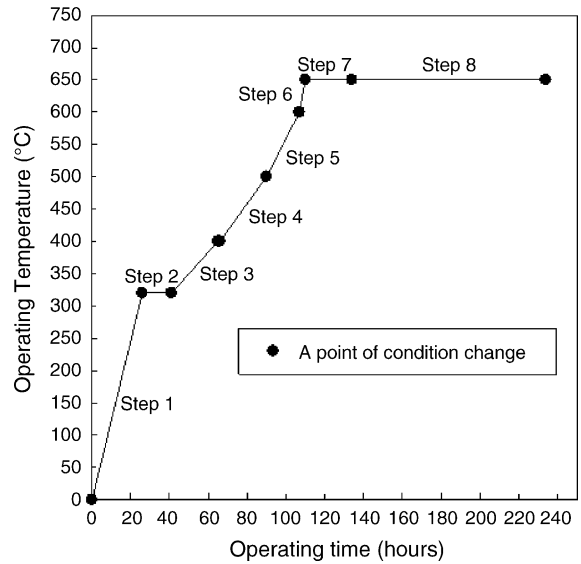


Fig. 3. Detailed changes in operating conditions of unit cell.

age at varying current density (*I*–*V* curve) was then measured with an electric load tester. After that, in order to determine the endurance of each unit, the voltages were recorded over 200 h at a constant current density of 140.4 mA cm<sup>-2</sup> (utilization = 40%). At that time, the temperature of the outlet gases was determined with a calibrated thermocouple.

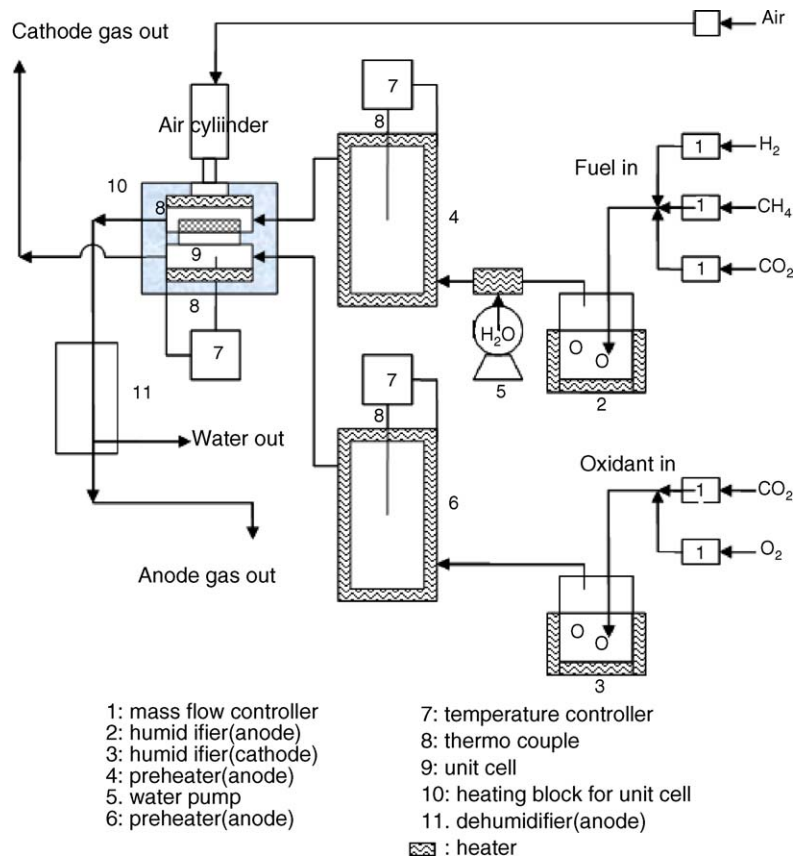


Fig. 2. Schematic diagram of experimental apparatus for measuring the performance of a unit cell.

Table 2  
Specifications and operating conditions for each step of performance test for unit cells in DIR-MCFC

Steps	Specifications	Flow-rate of anode gases (ml min <sup>-1</sup> )	Flow-rate of cathode gases (ml min <sup>-1</sup> )
Step 1	Pre-heat and burn out binder in electrolyte	Air: 250	O <sub>2</sub> : 200
Step 2	Burn out the binder in electrolyte and purge	Air: 250 N <sub>2</sub> : purging	O <sub>2</sub> : 200
Step 3	Reduce and activate reforming catalyst and anode electrode	H <sub>2</sub> : 100–150; CO <sub>2</sub> : 30–50	O <sub>2</sub> : 200
Step 4	Electrolyte dissolution and wet in matrix	H <sub>2</sub> : 100–150; CO <sub>2</sub> : 30–50	O <sub>2</sub> : 200; CO <sub>2</sub> : 50
Step 5	Electrolyte dissolution and wet in matrix	H <sub>2</sub> : 100–150; CO <sub>2</sub> : 30–50	O <sub>2</sub> : 200; CO <sub>2</sub> : 50
Step 6	Set the operating temperature	H <sub>2</sub> : 100–150; CO <sub>2</sub> : 30–50	O <sub>2</sub> : 100; CO <sub>2</sub> : 200
Step 7	Stabilize the condition	H <sub>2</sub> : 71.3; CO <sub>2</sub> : 17.8	O <sub>2</sub> : 35.6; CO <sub>2</sub> : 71.3
Step 8	Normal operation for performance of unit cell	CH <sub>4</sub> : 17.8 (S/C ratio = 2.5); CO <sub>2</sub> : 17.8	O <sub>2</sub> : 35.6; CO <sub>2</sub> : 71.3

In order to investigate the relative amounts of catalyst poisoning in the reforming catalysts, the two unit cells were carefully disassembled and the loaded catalysts sampled after having been operating for 200 h at a steady state. The deposited amounts of carbon, potassium and lithium were then determined with a carbon analyzer (Shimadzu, TOC-5000) and ICP-AES (Jobin yvon emission instrument, JY138 ULTRACE). In order to ensure exact results for the experiments, the cell performance test and analysis of the reforming catalyst were each repeated five times. All results listed represent the average values of these experiments.

### 3. Results and discussion

#### 3.1. OCV and *I*-*V* curve

The starting OCV of each cell and its variation over 150 h, which indicate the initial stabilization and the endurance of the cell without utilization, are shown in Fig. 4.

Although the OCV of the TR-unit cell, at 1.058 V is slightly higher than that of the MR-unit cell, VB., 1.055 V, the

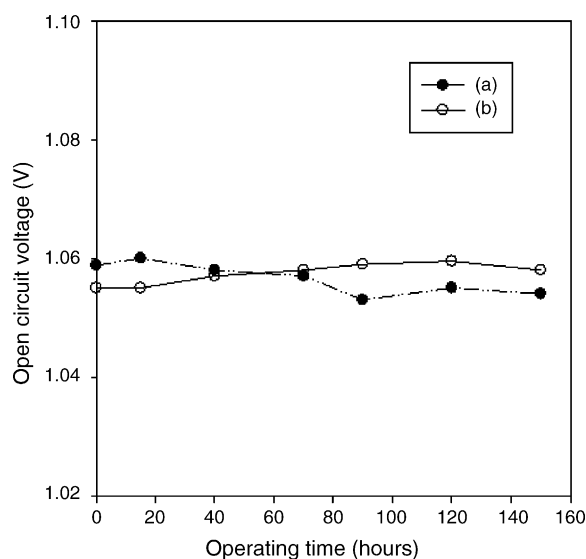


Fig. 4. Open-circuit voltages in unit cell performance test: (a) traditional reformer; (b) modified reformer.

OCV of the MR-unit cell is maintained at its initial value with greater stability and actually increases to 1.058 V after 150 h. The OCV of the TR-unit cell, on the other hand, decreases to 1.054 V after 150 h. These results show that the modified reformer structure has a positive influence on overall cell stability.

The effect of the modified reformer structure on the electrical resistance of the cell is demonstrated in the *I*-*V* curves of the two unit cells (Fig. 5). The change in cell voltage for each cell is observed by varying the current density from 0 to 200 mA cm<sup>-2</sup>, as shown in Fig. 5. The slope of each plot represents the respective electrical resistance. The slope of the MR-unit cell is  $2.253 \times 10^{-3}$  mΩ, which is lower than that of the TR-unit, namely,  $2.398 \times 10^{-3}$  mΩ. Therefore, the overall electrical resistance of the MR-unit cell is 94% of that of the TR-unit cell.

Considering the above two results, it is evident that the cell performance of the MR-unit cell differs from that of the TR-unit cell under the same conditions. In other words, the reaction rates in the MR-unit cell are different from those in the TR-unit cell under the same conditions. The TR-unit cell experiences variations in the anode gas composition because,

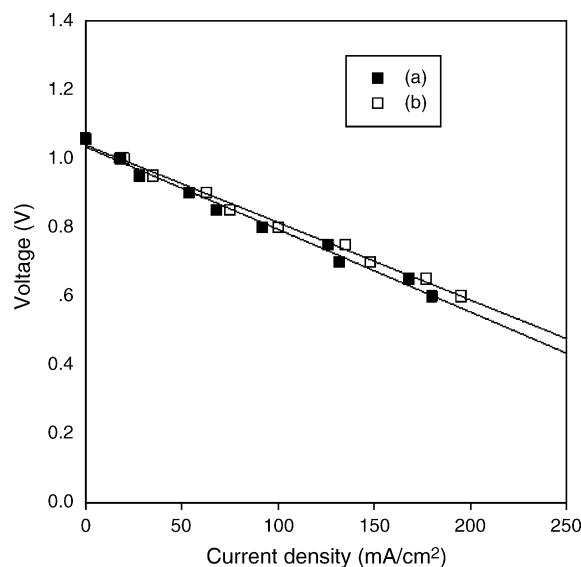


Fig. 5. *I*-*V* curves from unit cell performance test: (a) traditional reformer; (b) modified reformer.

compared with a MR-unit cell, a smaller amount of unreacted  $\text{CH}_4$  and a larger amount of hydrogen remain in the front region of the cell. In the rear region, less unreacted methane but more hydrogen also remains, due to the relatively large amount of catalyst (note that the local composition of gases in the unit cell could not be investigated in this experiment). This effect causes the dispersion of gases to be more uniform throughout the MR-unit cell than throughout the TR-unit cell. The uniform reforming reaction rate might be the key factor in maintaining uniform gas distribution. Therefore, this effect of the MR might improve the maintenance of the OCV and its electrical resistance.

### 3.2. Endurance of cell performance with cell utilization

The endurance of the two unit cells at 40% utilization is shown in Fig. 6. The cell voltages were measured while maintaining a current density of  $140.4 \text{ mA cm}^{-2}$  over during 200 h. The cell voltage of the TR-unit cell remains at about 0.69 V, for 100 h, after which it decreases to 0.54 V. By contrast, there is little change in cell voltage over a longer period of time with the MR-unit cell, i.e., about 0.72 V for 140 h. Finally, the voltage decreases to 0.66 V at 200 h.

The MR-unit cell provides 40 more hours of performance. In other words, when the unit cell is operated over a long-term at a cell utilization of 40%, the outstanding effects of the modified reformer are displayed. In the long-term cell performance test, the reforming reaction rate is more actively carried out over 100 h than without utilization. In this case, a more balanced reforming reaction rate throughout the MR-unit cell might lead to dominant control over every other chemical reaction rate and thus lead to the maintenance of a more uniform gas dispersion and composition. As a result, the MR-unit cell might show

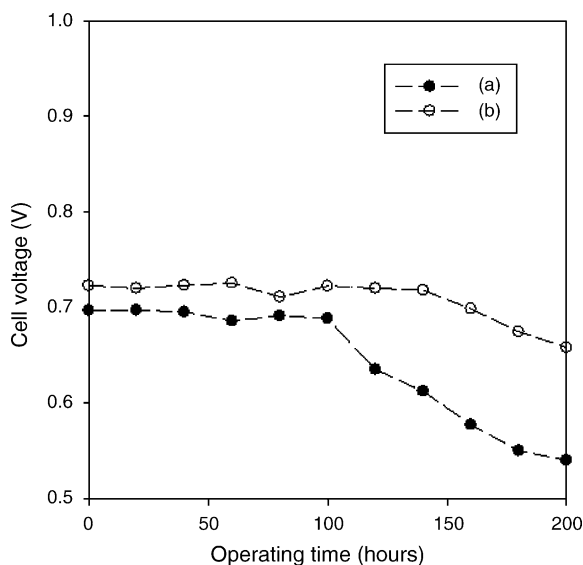


Fig. 6. Endurance of unit cell performance during 200 h at  $140.4 \text{ mA cm}^{-2}$ : (a) traditional reformer; (b) modified reformer.

more stability and a sustained performance with utilization.

The average temperature of the outlet gases from the MR-unit cell over 200 h is  $659^\circ\text{C}$ , which is  $8^\circ\text{C}$  lower than the value of  $667^\circ\text{C}$  for the TR-unit cell. This temperature difference between the two cells is very important. In spite of a lack of information regarding temperature throughout the cell, this difference shows that the temperature distribution in the MR-unit is more uniform than that in the TR-unit cell. The lower outlet gas temperature of the MR-unit cell might also be evidence for a more balanced reforming reaction rate throughout the MR-unit cell, as mentioned before, that would cause the electrochemical reactions to be carried out more uniformly.

### 3.3. Catalyst poisoning

The amount of catalyst poisoning of each unit cell, including carbon deposition and alkalis from the electrolytes, after 200 h of operation is presented in Fig. 7.

This study used a Ni reforming catalyst (28.74 wt.%) on a MgO substrate, with potassium (0.17 wt.%) added as a promoter. The level of carbon deposition in the MR-unit cell is 4.18 wt.%, which is slightly higher than the 4.07 wt.% of the TR-unit cell.

The levels of potassium and lithium poisoning in the MR-unit cell were, respectively, 54 and 45% of those of the TR-unit cell. These differing amounts might be attributed mainly to the low temperature of the gases (or of the cell) at the anode gas outlet. The lower temperatures may increase carbon deposition and decrease evaporation of electrolyte. Furthermore, in the MR-unit cell, the catalysts are more deeply loaded in the channel of the reformer and thus possibly prevent the diffusion of the evaporative electrolytes. These findings show

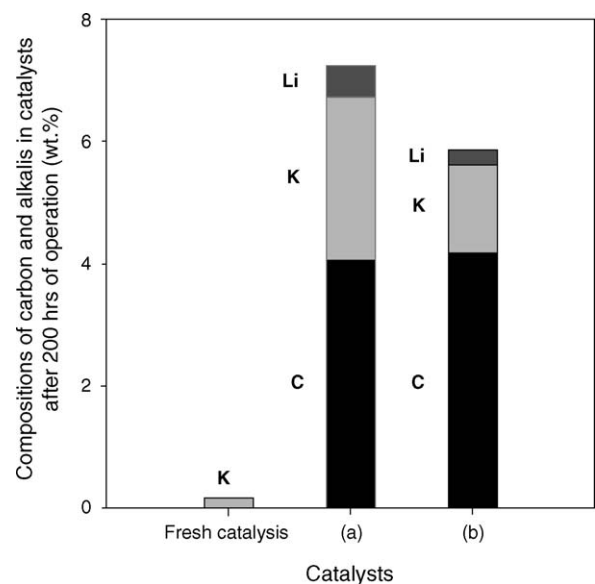


Fig. 7. Compositions of carbon deposits and alkali poisons in catalysts after 200 h of operation: (a) traditional reformer; (b) modified reformer.

that the MR-unit cell has an advantage in terms of less poisoning of the catalysts.

#### 4. Conclusions

For two DIR-MCFC unit cells, one equipped with a modified reformer (MR) and the other with a traditional reformer (TR), the effects of modified catalyst reformer on the cell performance are as follows:

1. The modified structure of the reformer has a positive influence on cell stability (endurance time) and the overall electrical resistance of the MR-unit cell is 94% that of the TR-unit cell.
2. In a long-term cell performance tests with a cell utilization of 40%, the outstanding effects of MR are displayed. The MR-unit cell is more durable; deterioration is delayed by over 40 h compared with a TR-unit cell. Furthermore, the average temperature of the outlet gases of the MR-unit cell over 200 h is 8 °C less than of the TR-unit cell.
3. The levels of potassium and lithium poisoning in the MR-unit cell are, respectively, 54 and 45% those in the TR-unit cell.

In the MR-unit cell, the above results can be attributed to the different loading amounts of the reforming catalyst, with less in the front region and more in the rear region. This feature possibly leads to a change in the reforming reaction rate, which becomes more uniform than that in the TR-unit cell under the same conditions. This greater balance of the reforming reaction rate leads to variations in the gas compositions as the gases are more uniformly dispersed throughout the cell. This effect might improve the cell performance, decrease the anode gas temperature and reduce the poisoning of catalysts in the MR-unit cell.

#### Acknowledgement

The author is grateful for the support from research grants awarded by the Korea Research Foundation (KRF) and the Korea University.

#### References

- [1] S. Freni, G. Maggio, *Int. J. Energ. Res.* 21 (1997) 253–264.
- [2] J.-H. Koh, B.-S. Kang, H.-C. Lim, *J. Power Sources* 91 (2000) 161–171.
- [3] A.L. Dicks, *J. Power Sources* 71 (1998) 111–122.
- [4] F. Yoshiba, N. Ono, Y. Izaki, T. Watanabe, T. Abe, *J. Power Sources* 71 (1998) 328–336.
- [5] B. Bosio, P. Costamagna, F. Parodi, *Chem. Eng. Sci.* 54 (1999) 2907–2916.
- [6] H.-K. Park, Y.-R. Lee, M.-H. Kim, G.-Y. Chung, S.-W. Nam, S.-A. Hong, T.-H. Lim, H.-C. Lim, *J. Power Sources* 104 (2002) 140–147.
- [7] S.H. Clarke, A.L. Dicks, K. Pointon, T.A. Smith, A. Swann, *Catal. Today* 38 (1997) 411–423.
- [8] A.L. Dicks, *J. Power Sources* 61 (1996) 113–124.
- [9] J.-H. Wee, K.-Y. Lee, *J. Appl. Electrochem.* 35 (2005) 521–528.
- [10] P. Heidebrecht, P.K. Sundmacher, *Chem. Eng. Sci.* 58 (2003) 1029–1036.
- [11] K. Sugiura, I. Naruse, *J. Power Sources* 106 (2002) 51–59.
- [12] R. Fellows, *J. Power Sources* 71 (1998) 281–287.
- [13] T. Tagawa, M. Ito, S. Goto, *Appl. Organomet. Chem.* 15 (2001) 127–134.
- [14] S. Cavallaro, N. Mondello, S. Freni, *J. Power Sources* 102 (2001) 198–204.
- [15] K. Sugiura, M. Daimon, K. Tanimoto, *J. Power Sources* 118 (2003) 228–236.
- [16] F. Yoshiba, Y. Izaki, T. Watanabe, *J. Power Sources* 137 (2004) 196–205.
- [17] B.-S. Kang, J.-H. Koh, H.-C. Lim, *J. Power Sources* 108 (2002) 232–238.
- [18] T. Takeguchi, Y. Kani, T. Yano, R. Kikuchi, K. Eguchi, K. Tsujimoto, Y. Uchida, A. Ueno, K. Omoshiki, M. Aizawa, *J. Power Sources* 112 (2002) 588–595.