Long-term operation of small-sized single molten carbonate fuel cells

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Abstract

Single molten carbonate fuel cells (MCFCs), with an effective electrode area of 256 cm^2 and state-of-the-art components, are run at 150 mA cm^{-2} under atmospheric pressure for 15 000 and 40 000 h, then the components are analyzed for material degradation. Cell output is reduced due to a short-circuit induced by dissolution of the NiO cathode, increase of IR-drop, and increase of anode and cathode polarization. It is concluded that the main factors that limit the life of the materials are dissolution of the NiO cathode and the degradation of LiAlO$_2$ matrix. © 1998 Elsevier Science S.A. All rights reserved.

1. Introduction

Molten carbonate fuel cells (MCFCs) have many attractive features for power generation, namely, high energy-conversion efficiency, low emissions, and multi-fuel capabilities. A mega-watt class of MCFC power-generation system will be demonstrated within several years in Japan and the USA [1–3].

It is widely agreed that the target endurance of the MCFC system is maintenance-free operation for 40 000 h [4,5]. It has been reported that a small-sized, single MCFC was run for up to 20 000 h [6]. The key issues of MCFC technology for long-term operation have been discussed. The operation of a MCFC for 40 000 h has not been reported and the stability of conventional MCFC materials for 40 000-h operation has not been confirmed; it is not known how degradation of the MCFC materials affects cell performance.

In the study reported here, two small-sized, single MCFCs assembled with conventional materials have been operated for 15 000 and 40 000 h, respectively. After the endurance test, the cells were disassembled and the cell components were analyzed to identify the extent of degradation of the cell materials during 40 000 h of operation.

2. Experimental

2.1. Cell operation

The tested MCFC was a single cell with an effective electrode area of 256 cm^2. The anode was porous Ni–Al plaque, while the cathode was porous Ni plaque, oxidized in situ and lithiated to NiO(Li$^+$). The matrix was made of LiAlO$_2$ of thickness 1.2 mm. Molten carbonate was used as the electrolyte and was impregnated into the matrix when the assembled cell was heated. The carbonate was a lithium-rich eutectic carbonate of Li$_2$CO$_3$/K$_2$CO$_3$ (62/36 mol%). The anode current-collector was a perforated nickel plate, while the cathode current-collector was a perforated plate made of stainless-steel type 316L. The bipolar plate was a clad plate of nickel and stainless steel type 316L.

Two cells were assembled; one was operated for 15 000 h and the other for 40 000 h. Both cells were operated at 650°C and atmospheric pressure. The anode gas was a mixture of H$_2$/CO$_2$ (80/20%) humidified at 50°C; the cathode gas was a mixture of air/CO$_2$ (70/30%). Gas utilization of the anode and the cathode was 40% at 150 mA cm^{-2}, which was the normal load. For the cell operated for 40 000 h, the cathode gas was diluted by the addition of nitrogen after 16 000 h of operation. The gas composition of the cathode after the dilution was O$_2$/CO$_2$/N$_2$ = 11/22/67. The electric resistance of the

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cell was measured using a milliohm meter (Yokogawa Hewlett-Packard, HP-4776). The gas composition at the anode outlet was measured using a gas chromatograph at 0 mA cm^{-2}. Since it was observed that some of the molten carbonate electrolyte was lost during lengthy operation, carbonate was added to the cell periodically.

2.2. Post-test analysis of components

After operation of the MCFC, the cells were disassembled. Electron micrographs were taken of the anode, cathode, matrix and cathode current-collector and used to examine the degradation of the materials. The changes in thickness of the anode and cathode before and after operation were calculated by measuring the electrode thickness from the electron micrographs. The particle sizes of NiO in the cathode and LiAlO$_2$ in the matrix were measured from cathode electron micrographs. The matrix was ground to powder and X-ray diffraction was taken. The other matrix sample was soaked in 6 M hydrochloric acid. After filtration, the nickel concentration in the filtrate was analyzed by ICP spectroscopic analysis.

3. Results and discussions

3.1. Long-term operation of MCFC

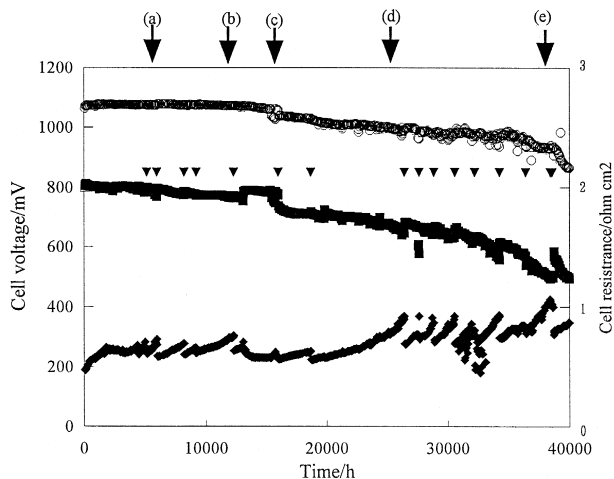The histories of the cells operated at 40 000 and 15 000 h are shown in Figs. 1 and 2, respectively. The supply of
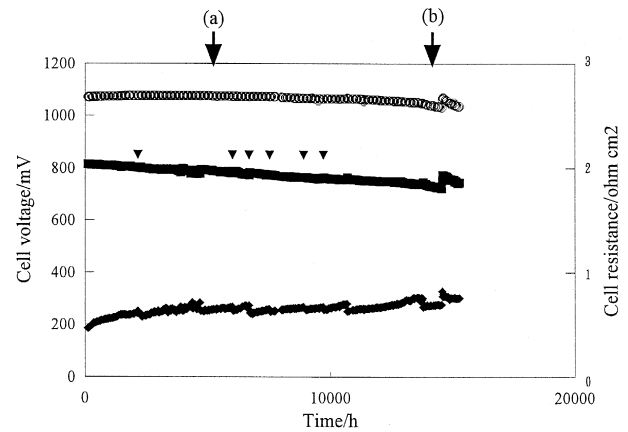

Fig. 2. Long-term cell performance for 15 000 h: (○) open-circuit voltage; (■) cell voltage at 150 mA cm^{-2}; (♦) cell resistance; (▼) additional point of carbonate. $T = 650°C$, atmospheric pressure. Anode gas is H$_2$/CO$_2$ = 80/20 (dry base) humidified at 50°C and its utilization is 40% at 150 mA cm^{-2}. Cathode gas is air/CO$_2$ = 70/30 (O$_2$/N$_2$/CO$_2$ = 14/56/30) and its utilization is 40% at 150 mA cm^{-2}. The supply of CO$_2$ gas is interrupted at (a) and (b).

CO$_2$ to the test facilities was interrupted for periods of 5 or 6 h for three times during the 40 000 h and twice during 15 000 h due to failure of the gas supply. The first interruption of CO$_2$ did not influence the cell performance of either cell. The second interruption of CO$_2$ caused a rise in the output voltages of both cells. The third interruption of CO$_2$ to the 40 000-h cell also increased the output voltage.

The NiO cathode dissolved into the electrolyte during long-term operation. The dissolved nickel cation was reduced to nickel metal by hydrogen that migrated from the anode side. As a consequence, nickel metal was precipitated in the matrix. Ota et al. [7] have reported that the solubility of NiO is proportional to the partial pressure of CO$_2$; the low partial pressure of CO$_2$ is the likely cause of the reduction of the dissolved NiO. The cathode gas composition of the 40 000-h cell was changed from CO$_2$/O$_2$/N$_2$ = 30/14/56 to CO$_2$/O$_2$/N$_2$ = 22/11/67 at 16 000 h. This affected the open-circuit voltage (OCV) and the output voltage drop at 16 000 h, as shown in Fig. 1.

During long-term operation, the electrolyte was gradually lost due to vaporization, creep, and consumption by the corrosion reaction. Consequently, the amount of electrolyte in the matrix became insufficient to fill the matrix. Thus, electrolyte should be added to the matrix during operation to keep the matrix completely filled with electrolyte. The carbonate electrolyte was added 16 times during the 40 000-h operation and six times during the 15 000-h operation, as shown in Figs. 1 and 2. The latter show that the ohmic cell resistance is restored immediately after the addition of carbonate. The total amount of electrolyte added to the 40 000-h cell was almost the same as

Fig. 1. Long-term cell performance for 40 000 h: (○) open-circuit voltage; (■) cell voltage at 150 mA cm^{-2}; (♦) cell resistance; (▼) additional point of carbonate. $T = 650°C$, atmospheric pressure. Anode gas is H$_2$/CO$_2$ = 80/20 (dry base) humidified at 50°C and its utilization is 40% at 150 mA cm^{-2}. Cathode gas is air/CO$_2$ = 70/30 (O$_2$/N$_2$/CO$_2$ = 14/56/30) up to 16 000 h, O$_2$/N$_2$/CO$_2$ = 11/67/22 from 16 000 to 40 000 h and its utilization is 40% at 150 mA cm^{-2}. The supply of CO$_2$ gas is interrupted at (a), (b) and (d). Cathode gas was changed (c).
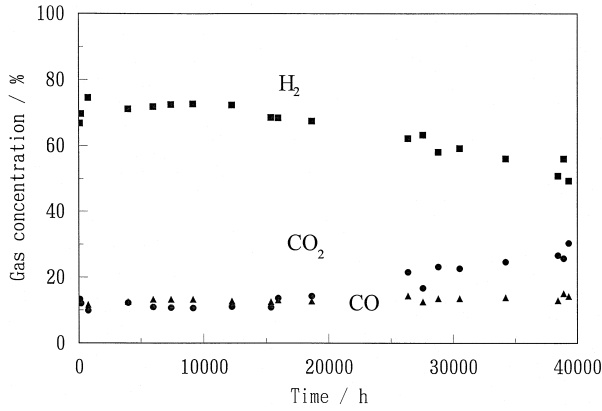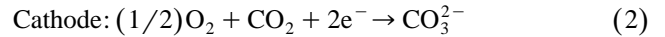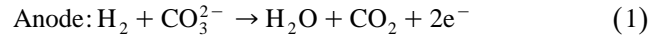
Fig. 3. Gas composition of tested MCFC for 40 000 h of anode outlet gas at 0 mA cm^{-2}. (■) H$_2$, (●) CO$_2$ and (▲) CO.

that loaded initially to the matrix. This means that a large amount of electrolyte was removed from the cell during operation.

Although the OCV is generally constant under uniform conditions, the value for the 40 000-h cell decreased slightly with time after 12 000 h, as shown in Fig. 1. In particular, a decay in the OCV was observed after 16 000 h. The OCV of the 15 000-h cell also slightly decreased with time after 10 000 h, as shown in Fig. 2. The gas composition at the anode outlet of the 40 000-h cell was measured by gas chromatography, as shown in Fig. 3. The H$_2$ concentration decreased slightly with time. Simultaneously, the concentration of CO$_2$ increased due to the formation of a short-circuit in the cell. When the deposited nickel metal created an electrical path through the matrix between the anode

and cathode, the electrochemical reaction on the anode and cathode sides proceeded as follows:

$$\text{Anode}: H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^- \tag{1}$$

$$\text{Cathode}: (1/2)O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-} \tag{2}$$

Thus, in the anode, hydrogen was consumed and carbon dioxide was produced. Gas-analysis results (Fig. 3) agreed with the explanation of the short-circuit.

3.2. Decline of cell output

The cell voltage, which depends on time and current density, is given by

$$E(t,I) = E_0 - \Delta E_{n.1} - \Delta E_{NiO}(t) - (R_a(t) + R_c(t)$$
$$+ R_{ohm}(t))I \tag{3}$$

where: E_0 = theoretical cell voltage; $\Delta E_{n.1}$ = Nernst loss; $\Delta E_{NiO}(t)$ = reduction in OCV due to the short-circuit; $R_a(t) + R_c(t)$ = non-ohmic polarization; $R_{ohm}(t)$ = ohmic cell resistance. The parameters $\Delta E_{NiO}(t)$, $(R_a(t) + R_c(t))I$ and $R_{ohm}(t)I$ are all dependent on time. The decline of cell output arises from these parameters. $\Delta E_{NiO}(t)$ is calculated from the difference between the theoretical and observed OCV, $R_{ohm}(t)$ is measured from the ohmic cell resistance, and $(R_a(t) + R_c(t))I$ is estimated by rearranging Eq. (3). The values of $\Delta E_{NiO}(t)$, $(R_a(t) + R_c(t))I$ and $R_{ohm}(t)I$ for the 40 000-h cell are given in Fig. 4.

The rate of the decay in cell output during the 15 000-h operation was 8 mV kh^{-1}. By contrast, the decay during the 40 000-h operation was not constant. The rate of the
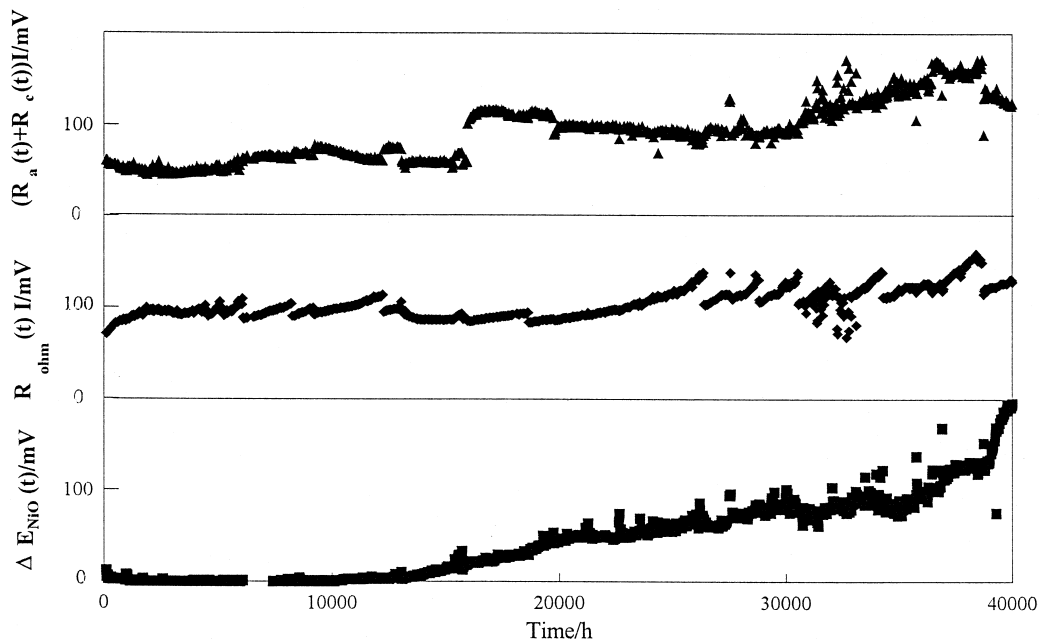

Fig. 4. Decline in cell performance at 150 mA cm^{-2}. The histories of $\Delta E_{NiO}(t)$ (lower), $R_{ohm}(t)I$ (middle) and $(R_a(t) + R_c(t))I$ (upper) are shown. The change of cathode gas composition after 16 000 h influenced $(R_a(t) + R_c(t))I$.

Table 1
Thickness change of electrode after long-term operation

Operating time (h)	Anode thickness change (%)	Cathode thickness change (%)
15 000	1.4	0.5–5.0
40 000	2.5–4.2	13.6–20.5

decay of cell output after 30 000 h became larger than that up to 12 000 h (Fig. 4). The OCV reduction caused by the short-circuit began at 13 000 h. The rate of decay of $\Delta E_{NiO}(t)$ was almost constant at 4.4 mV kh^{-1} until 35 000 h. After 35 000 h, the rate of decay became large. The decline of $(R_a(t) + R_c(t))I$ was observed after 30 000 h. By comparison, the $R_{ohm}(t)I$ did not increase in comparison with the others, since electrolyte was added to the cell.

3.3. Post-test analysis

After operation for 15 000 and 40 000 h, the cells were disassembled, and the anode, cathode, matrix and cathode-current collector were examined in order to investigate the life-limiting factors.

The change in thickness of the electrode during the test is presented in Table 1. Compressive deformation of the anode was relatively low, i.e., up to 4.2%, after 40 000 h; it is clear that the Ni–Al anode has effective resistance to compressive deformation. By contrast, the change in thickness of the cathode was larger than that of the anode.

Table 2 lists the particle size in the NiO cathode before and after testing. The diameter of the NiO particles increased with time. Since the solubility of NiO in molten carbonate is very low [7], it is suggested that the growth of the particles of NiO developed via an Ostwald ripening process. The large particles of NiO contained large pores. Since the pore distribution of the cathode in the initial state is optimized, the increase in NiO particle size influences the performance of the cell.

The amount of nickel detected in the matrix is given in Table 3. The amount in the initial NiO cathode was 293 mg cm^{-2}. The losses of the NiO cathode corresponded to 9 and 16% after 15 000 and 40 000 h of operation, respectively. These values are similar to the thickness change observed in the cathode (Table 1). It is thought that these losses were responsible for the change in thickness of cathode. The NiO cathode was dissolved into the electrolyte, the nickel cations were reduced by hydrogen that

migrated from the anode to yield nickel metal, and the precipitated nickel in the matrix caused a short-circuit. The shape of the precipitated nickel appears to be spherical, as shown in Fig. 5. The nickel precipitates were connected and yielded a nickel chain, which had a three-dimensional structure. The mechanism of growth of nickel particles and chains has not yet been elucidated in detail. It is thought that the short-circuit occurred by electrical connection of the anode and cathode through nickel chains in the matrix.

Table 4 shows the characterization of LiAlO$_2$ both before and after testing. The particle size of LiAlO$_2$ increased with operating time. Although the specific surface area of LiAlO$_2$ was suitable, it was not possible to measure the value. It was difficult to separate LiAlO$_2$ from the carbonate in the matrix. Assuming the particle shape to be spherical, the specific surface area is proportional to the square of the radius. The present data show that the particle radius increased. It is suggested that there is a decreased in both the specific surface area and the electrolyte supporting force of the LiAlO$_2$. In spite of the addition of carbonate, the ohmic cell resistance was not restored to the initial value after 20 000 h. Thus, it would appear that particle growth of LiAlO$_2$ occurred after 20 000 h. The crystal phase of LiAlO$_2$ in the matrix was transformed from the γ- to the α-phase with time; 31 and 80% of γ-LiAlO$_2$ was transformed to the α-phase after 15 000 and 40 000 h, respectively. The density of α-LiAlO$_2$ and γ-LiAlO$_2$ is 3.40 and 2.61 g cm^{-3}, respectively [8]. It is thought that the transformation of γ-LiAlO2 to the α-phase occurred simultaneously as the volume was reduced. The results of the long-term operation indicated that the thickness of the matrix did not change, and the counter effect is thought to be that the precipitated nickel in the matrix increased the matrix thickness. It has been reported that γ-LiAlO$_2$ is a stable phase in MCFC operations in comparison with the α- and β- phases [8]. This knowledge about the crystal phase stability of LiAlO$_2$ is inconsistent with the present data shown in Table 4. The behaviour of the phase transformation of LiAlO$_2$ needs to be clarified.

Table 2
Particle growth of NiO cathode

Operating time	Particle growth (μm)
Start of test	1
15 000 h	2.5
40 000 h	2.4

Table 3
Amount of dissolved nickel in the matrix

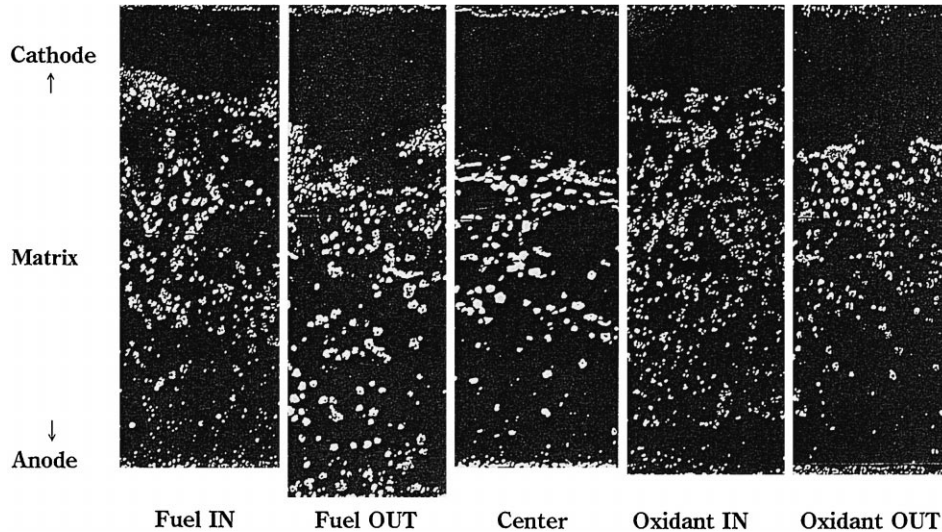| Operating time (h)	Precipitated nickel (mg cm^{-2})
15 000	26
40 000	45.9

Fig. 5. Electron micrograph of cross-section of the matrix in the 40 000-h MCFC. The upper side is the anode and the lower side is the cathode. The white area is precipitated Ni.

Table 5 shows the metal loss due to corrosion of the cathode current-collectors made from stainless steel type 316L. Since the thickness of the corrosion layer was estimated from electron micrographs of the cross-section of the corrosion layer, there is a range between the maximum and minimum thickness.

3.4. Material degradation and cell performance

The decline in cell performance is found to be the result of three factors, namely: (i) the short-circuit, (ii) the increase in the anode and cathode polarization; (iii) the increase in the ohmic cell resistance. The degradation in these components reduces the cell performance. We tried to match these three causes of cell performance decline to the component degradation. The time dependency of the amount of deposited nickel, $M(t)$, in the matrix is considered to be as follows.

$$\frac{M(t_1)}{M(t_2)} = \left(\frac{t_1}{t_2}\right)^{\alpha} \tag{4}$$

α is estimated to be 0.58 from the data given in Table 3. This suggests that the amount of deposited nickel in the matrix is proportional to the square root of time. The mechanism of nickel precipitation in the matrix remains unclear. Although the relation between the time and the amount of deposited nickel in the matrix has been reported

[6,9], the results differ among MCFC researchers. From the present results, the behaviour of nickel deposition in the matrix apparently obeys a parabolic rate law. The decline of cell performance due to the short-circuit becomes large after 35 000 h, as shown in Fig. 4. The amount of dissolved nickel is thought not to be simply related to the cell performance.

The thickness of the cathode changed, as shown in Table 1, as the NiO cathode dissolved into the electrolyte and, simultaneously, the NiO particles of the cathode grew during cell operation. It is concluded that the particle growth of NiO changes the micropore structure of the cathode, which affects the electrochemical reaction in the cathode. The deterioration of the pore structure of the cathode influences cell performance. In Fig. 4, the polarization of the anode and cathode begins to increase at 30 000 h. Although 16% of the NiO cathode is dissolved at 40 000 h, the polarization of the anode and the cathode remains almost constant until 30 000 h. The amount of dissolved NiO in the carbonate at 30 000 h is the threshold value for the cell to produce an acceptable output for long-term operation. If the dissolution of the NiO cathode obeys a parabolic rate law, then the threshold for the constant polarization of the anode and the cathode is estimated to be 38 mg cm^{-2}. The inflection point of $\Delta E_{NiO}(t)$ is 35 000 h and 42 mg cm^{-2}, as shown in Fig. 4. The present results indicate that the dissolution of the NiO

Table 4

Characteristics of LiAlO2 in the matrix

Operating time	Particle growth (μm)	Content of a phase (%)
Start of test	0.1–0.5	0
15 000 h	0.4–4.0	31
40 000 h	0.5–8.0	80

Table 5

Metal loss of corrosion of cathode current-collector

Operating time (h)	Metal loss (μm)
15 000	35–48
40 000	43–86

cathode influences severely the decline of cell performance due to the deterioration of the cathode pore structure.

The causes of the rise in ohmic cell resistance during operation are the development of corrosion layers and the electrolyte loss. When the electrolyte was added into the cell at 25 000 h, the ohmic cell resistance was restored and held for 4000 or 2000 h. After 25 000 h, the ohmic cell resistance increased for 1000 h whenever the electrolyte was added. This suggests that the electrolyte supporting force of $LiAlO_2$ decreases due to deterioration of the $LiAlO_2$, see Table 4. The data given in Table 5 shows how the corrosion layer of the cathode current-collector develops.

In summary, it is concluded that the cause of the decline in cell performance in the 40 000-h MCFC is material degradation. The key factors of material degradation that affect cell performance for long-term operation are dissolution of the NiO cathode and deterioration of the $LiAlO_2$. Further research on these issues is needed in order to achieve a high-performance MCFC.

References

[1] E.H. Camara, Proceedings of the 2nd International Fuel Cell Conference, Kobe, Japan, 1996, p. 17.

[2] H.C. Maru, B.S. Baker, Proceedings of the 2nd International Fuel Cell Conference, Kobe, Japan, 1996, p. 115.

[3] M. Fukai, M. Ooue, H. Yamazaki, K. Ito, Proceedings of the 3rd FCDIC Fuel Cell Symposium Proceedings, Tokyo, Japan, June 10–11, 1996, p. 133.

[4] J.R. Selman, Proceedings of the 2nd International Fuel Cell Conference, Kobe, Japan, February 5–8, 1996, p. 103.

[5] A.J. Appleby, F.R. Foulkes, Fuel Cell Handbook, Van Nostrand-Reinhold, New York, 1989, p. 555.

[6] H. Urushibata, T. Murahashi, Proceedings of the International Fuel Cell Conference, Makuhari, Japan, 1992, p. 223.

[7] K. Ota, S. Mitsushima, K. Kato, S. Asano, H. Yoshitake, N. Kamiya, J. Electrochem. Soc. 139 (3) (1992) 667.

[8] H.C. Maru, L. Paetsch, B.S. Baker, Proceedings of the Symposium on Molten Carbonate Fuel Cell Technology, USA, 1984, Proc. Vol. 84-13, The Electrochemical Society, Pennington, NJ, USA, p. 20.

[9] H. Kasai, A. Suzuki, Proceedings of the 3rd International Symposium Carbonate Fuel Cell Technology, Honolulu, HI, USA, May 1993, Proc. Vol. 93-3, The Electrochemical Society, Pennington, NJ, USA, p. 290.