Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Power Sources 145 (2005) 515–525
JOURNAL OF POWER SOURCES
www.elsevier.com/locate/jpowsour

MCFC performance diagnosis by using the current-pulse method

Kimihiko Sugiura [a,*], Hironori Matsuoka [a], Kazumi Tanimoto [b]

[a] *Osaka Prefectural College of Technology, 26-12 Saiwai, Neyagawa, Osaka 572-8572, Japan*
[b] *National Institutes of Advanced Industrial Science and Technology, Kansai, 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan*

Accepted 1 January 2005
Available online 25 July 2005

Abstract

Several problems prevent molten carbonate fuel cells (MCFC) operation for an extended period. However, if the degradation factors can be identified and resolved in a timely manner, MCFC could become a valuable technology. Therefore, a performance diagnosis should be developed which enables the simple and instantaneous determination of MCFC degradation factors. A suitable six parameter equation obtained by a current-pulse method, obtainable from MCFC's transient response in 100 ms, is expressible in an equivalent circuit composed of three sub-circuits. The relationship between these parameters and each degradation factor is evaluated by a single MCFC cell, the electrode area of which is 16 cm^2. Degradation factors include cross-leakage, electrolytic loss, cell temperature distribution and gas composition/flow rate. As a result, each of six parameters in the MCFC transient response corresponds to an ohmic potential drop, anode/cathode gas diffusion resistance, reactive resistance, three-phase interfacial resistance and electrolyte properties, respectively. The proposed performance diagnosis specifies the degradation factors by combining the six parameters. Performance diagnosis was applied to a single MCFC cell of an electrode area of 81 cm in extended operations, and the degradation factor diagnosed. As a result, the diagnosis was able to specify the cell degradation factors from the degradation factor ratio, corresponding to cell voltage, cell resistance and the N_2 concentration of MCFC single cell performance. Therefore, the proposed performance diagnosis is able to easily specify the driven MCFC degradation factors in a timely manner.

Keywords: MCFC; Current-interrupted method; Current-pulse method; Transient response; Degradation factor

1. Introduction

Molten carbonate fuel cells (MCFC) potentially provide high-efficiency power generation, and their development has progressed to the extent that prototype demonstration power plant testing has already been conducted. However, some MCFC related problems must be overcome for the purpose of commercialization. These include the problems of cathode dissolution, separator/current collector corrosion, cross-leakage and electrolytic loss, etc., reflected in cell voltage loss. If these degradation factors can be readily obtained by means of a performance diagnosis in a timely manner, they can be overcome and the MCFC can be operated for an extended period. Our objective is to develop a performance diagnosis that can determine MCFC degradation factors instantaneously and easily by using the current-pulse method. This paper reports on the applicability of performance diagnosis to MCFC transient response. Fig. 1 shows the transient response when a step current-pulse is impressed for 100 ms. Generally, the cell voltage is expressed by the following formula:

$$V = V_0 - \eta_{IR} - \eta_R - \eta_{NE} \quad (1)$$

where V is the output voltage of MCFC, V_0 the standard potential, η_{NE}, η_{IR} and η_R are Nernst loss, ohmic loss, the anode and the cathode over potential, respectively. The η_{IR} is attributed to the ohmic resistance through the cell components. The η_R is attributed to the charge and mass transfer resistance of electrode reactions [1]. The η_{NE} is decided from the Nernst potential difference between gas inlet and outlet during current load. However, because Nernst loss does not occur until 100 ms [2], it can be neglected in the proposed diagnosis. Therefore, transient response used in the diagnosis shown in Fig. 1 is determined by reactive

* Corresponding author.

0378-7753/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jpowsour.2005.01.086

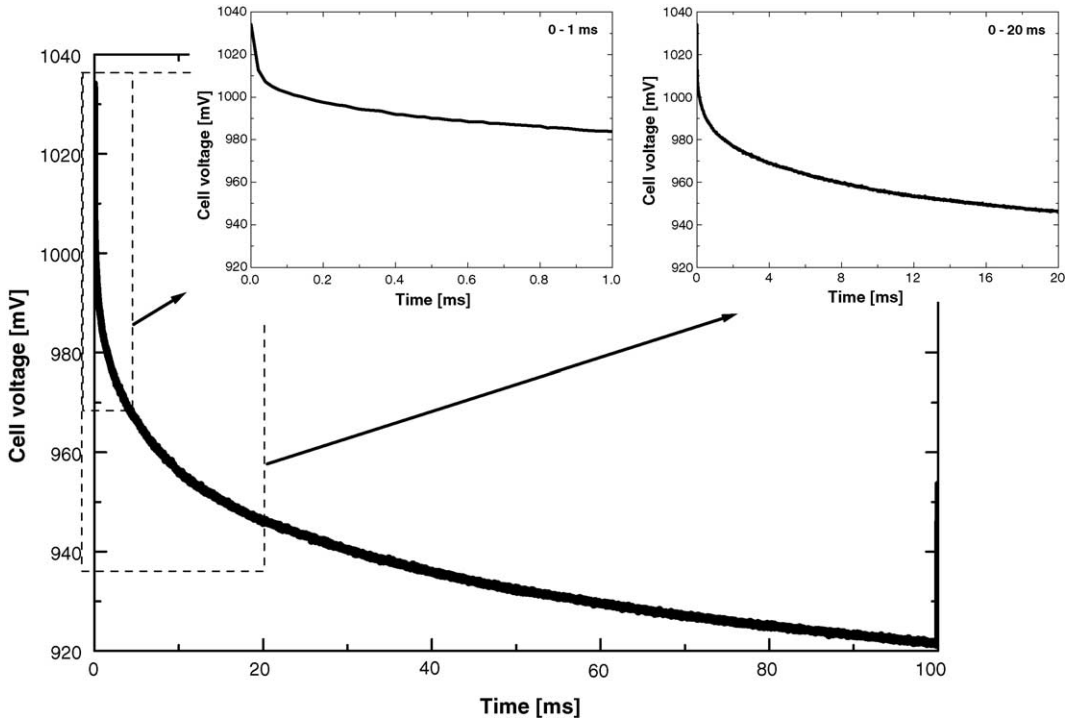

Fig. 1. The transient response of MCFC.

resistance and ohmic loss. Each time the transient response is divided, it is composed of three exponential functions. Generally, the equivalent circuit of the exponential function is shown with a single resistance and a parallel single resistance, and one capacitor. The MCFC transient response is composed of the three sub-circuits shown in Fig. 2, and the voltage related Eq. (2) is derived from an equivalent circuit:

$$V_{\text{out}}(t) = E_0 - (R_0 + R_1 + R_2 + R_3)I_0 + R_1 I_0\, \mathrm{e}^{-(t/C_1R_1)} + R_2 I_0\, \mathrm{e}^{-(t/C_2R_2)} + R_3 I_0\, \mathrm{e}^{-(t/C_3R_3)} \quad (2)$$

Here, Eq. (2) is rearranged to Eq. (3) by substituting $y_0 = E_0 - (R_0 + R_1 + R_2 + R_3)I_0$, $A_1 = R_1 I_0$, $A_2 = R_2 I_0$, $A_3 = R_3 I_0$, $t_1 = C_1R_1$, $t_2 = C_2R_2$, $t_3 = C_3R_3$ into Eq. (2).

$$V_{\text{out}}(t) = y_0 + A_1\, \mathrm{e}^{-(t/t_1)} + A_2\, \mathrm{e}^{-(t/t_2)} + A_3\, \mathrm{e}^{-(t/t_3)} \quad (3)$$

Ultimately, this equation is composed of three exponential functions as shown in Fig. 1. Here, y_0 means cell voltage at 100 ms, and A_1–A_3, t_1–t_3 are parameters of the proposed diagnosis, respectively. Eq. (3) means that cell performance stabilizes early if the value of the parameters is small. The proposed diagnosis, diagnoses the MCFC degradation factor by evaluating changes in the six parameters in operation. First, the correlation of various degradation factors and each parameter is experimentally clarified to create the standard of the diagnosis. The degradation factor of the cell is diagnosed by evaluating the difference between each parameter of the cell in operation and this standard.

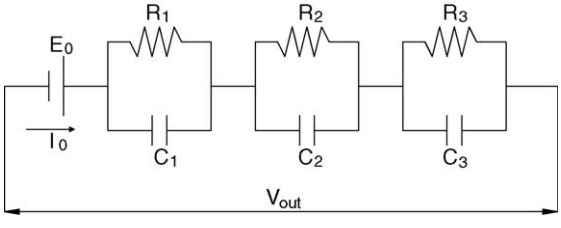

Fig. 2. The equivalent circuit of MCFC.

2. Experimental apparatus and procedure

Fig. 3 shows a schematic diagram of experimental apparatus. MCFC made by the National Institute of Advanced Industrial Science and Technology, Kansai (AIST) is a 16 cm single cell. Anode and cathode materials are conventional, and the electrolyte is (52 + 48) mol% (Li + Na)/CO_3 melts. The electrolyte matrix is lithium aluminium oxide. The fuel cell is installed in the electric furnace to maintain isothermal conditions. Anode gas is humidified by passing through a humidifier and is supplied to the MCFC. Cell voltage is measured and recorded by data logger, and cell resistance measured by a milliohm–meter with AC four probes. The pulsed current of 150 mAcm^{-2} is periodically removed from the MCFC with a pulse oscillator and the transient response is recorded with a digital oscilloscope.

Experimental conditions are shown in Table 1. The anode standard gas is 70.4H_2/17.6CO_2/12H_2O, and the cathode standard gas is 70air/30CO_2, with a usage of 40% for each use. The single cell, which imitated the three degradation factors is made and operated under conditions for identifying

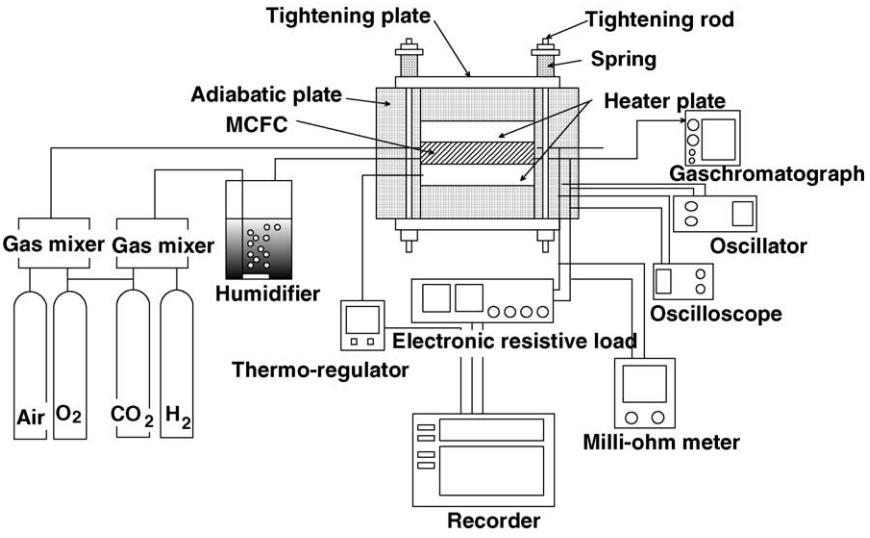

Fig. 3. Schematic diagram of experimental apparatus.

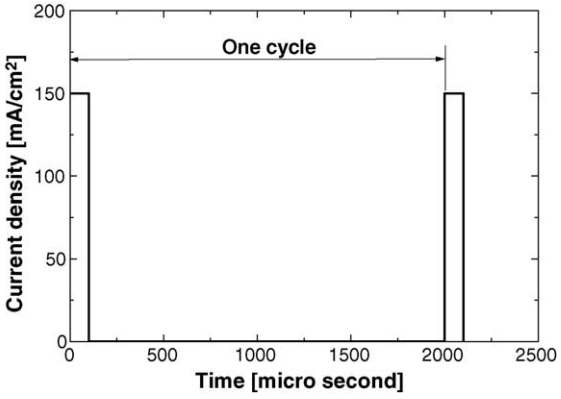

Fig. 4. Current-pulse to obtain transient response.

the parameter originating in each degradation factor. In this instance, three degradation factors refer to electrolytic loss, mass transfer resistance and cross-leakage. For electrolytic loss, the electrolyte loading ratio is varied from 110 to 150%. In this instance the loading ratio of 100% refers to an electrolyte volume corresponding to the matrix pore volume. The cathode gas composition is changed to $33O_2/67CO_2$ to select parameters originating in cathode mass transfer resistance, and the parameter which originates in the anode mass transfer resistance identified by adding 40% nitrogen to anode gas. In addition, the parameter, which originates in each reaction resistance is identified by changing cell temperature from 600 to 650 °C. Moreover, the MCFC single cell is made of a cracking electrode and cracking matrix to cause cross-leakage. Nitrogen concentrations of these cells are 1.6, 4.33 and 4.72%. The current density is 150 mA cm^{-2} when the experiment is carried out to identify parameters relating to various degradation factors. The mean transient response when the electric current shown in Fig. 4 impressed 30 times is used by the performance diagnosis.

3. Results and discussion

3.1. Identification of parameters relating to each degradation factor and the physical significance of each parameter

Several cells with a different electrolyte loading ratios were made to imitate electrolytic loss. The cells were then

Table 1
Experimental conditions

	Anode		Cathode
Standard condition			
Gas utilization (%)		40	
Standard gas composition (%)	$70.4H_2/17.6CO_2/12H_2O$		$70Air/30CO_2$
Current density (mA cm^{-2})		150	
Temperature (°C)		650	
Electrolyte loading ratio (%)		125	
Experimental condition			
Parameter selection for the diagnostics			
(1) Electrolyte loss (%)		110, 117, 125, 129,132.5, 133.5, 140,150	
(2) Mass transfer resistance	40% N_2 add		$33O_2/67CO_2$
(3) Cross-leak	1.6, 4.33, 4.72% N_2		
Reactive resistance (temperature dependence) (°C)		600, 610, 620, 630, 640, 650	

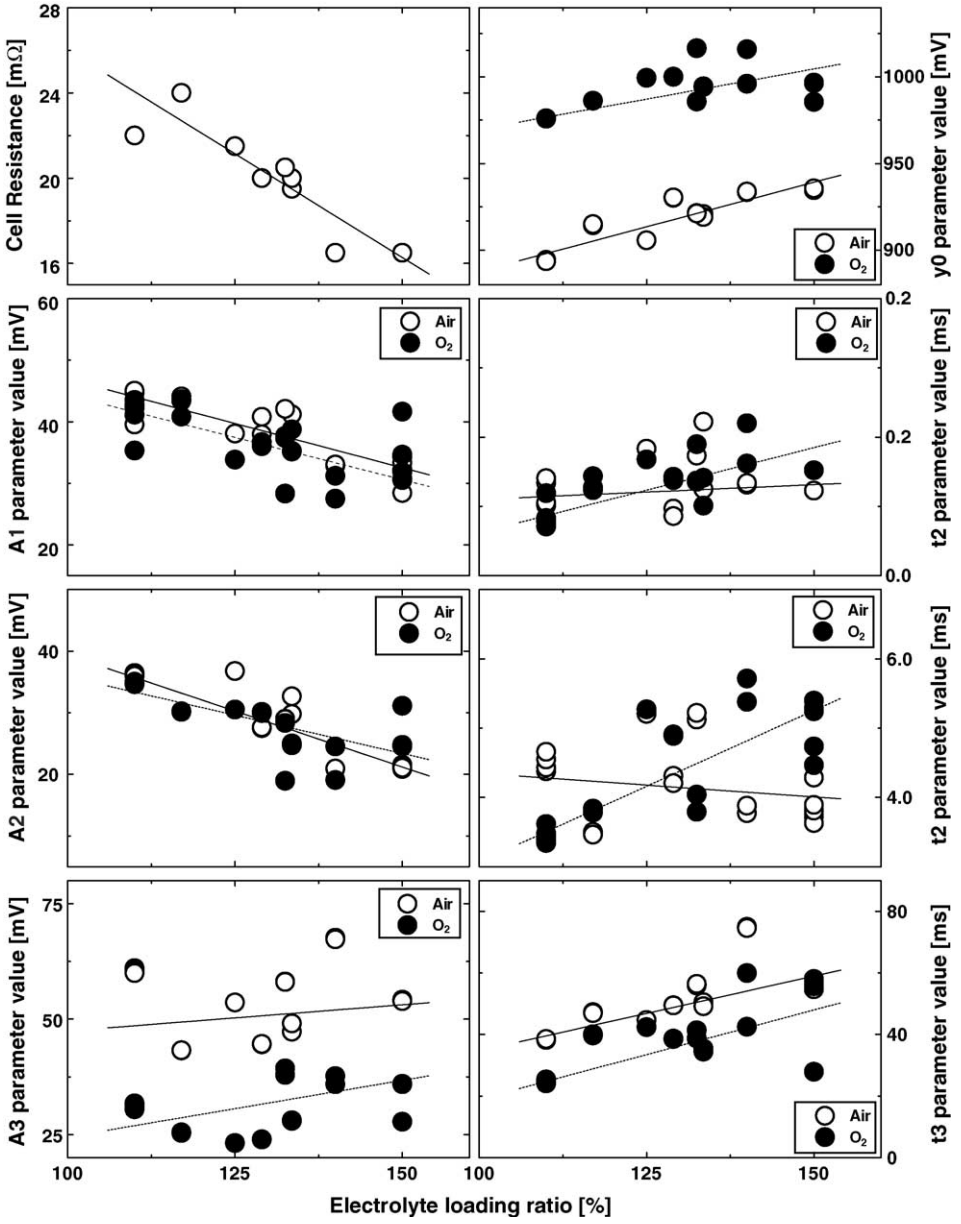

Fig. 5. Parameter of the electrolyte loss and cathode mass transfer resistance.

evaluated to identify the parameters relating to electrolytic loss. The structural change of the cathode electrode and the stat transition of the three-phase interface are reflected in cathode mass transfer resistance. These changes are imitated by changing the cathode gas composition, because the diffusion of O_2 and CO_2 to the three-phase interface of the cathode electrode is disturbed by N_2. Therefore, the cathode mass transfer resistance is evaluated by removing nitrogen from the cathode gas. Because the gas composition is not changed in actual cell operation, this experiment, which changes the gas composition, evaluates the decrease in the three-phase interface and the change in the electrode structure. Fig. 5 shows the relationship between each parameter and the electrolytic loss and cathode mass transfer resistance. Here, gas chromatography is used to confirm that the cells used by this experiment do not cause cross-leakage. Regarding electrolytic loss, the cell resistance increases by decreasing the electrolyte load ratio. The cell resistance increases and, according to the y_0 parameter the cell voltage decreases with a decrease in the electrolyte load ratio. This is because the ceramic-based matrix becomes bare where there are few electrolytes. Regarding the identification of parameters, because there are few changes in the t_1 and t_2 parameters with a decrease in the electrolyte loading ratio, these parameters are unrelated to electrolytic loss. On the other hand, because the A_1–A_3 and t_3 parameters change with a decrease in the electrolyte load ratio, these parameters are related to electrolytic loss. If the amount of electrolyte decreases during MCFC operation, the cell resistance increases by exposing the matrix comprising the insulator and the A_1 and A_2 parameters increase, and the A_3

Table 2
Parameter of the anode reactiveness

	y_0	A_1	t_1	A_2	t_2	A_3	t_3
Standard	0.940	0.0167	0.000387	0.0279	0.00612	0.0244	0.0686
40% N_2 add in anode	0.940	0.0160	0.000522	0.0294	0.00627	0.0326	0.0730
Ratio	1.000	0.960	1.349	1.057	1.025	1.334	1.065

and t_3 parameters decrease. Therefore, the generation of the electrolytic loss can be diagnosed by observing the A_1–A_3 and t_3 parameters during cell operation. Moreover, to find the parameters, which relate to cathode mass transfer resistance, the parameter, which changes depending on the difference in the cathode gas composition is evaluated without regard to the electrolyte load ratio. A_3 and t_3 parameters decrease with a gas composition, which removes nitrogen from cathode gas, and the behaviour of the t_2 parameter is obviously different with changes in the gas composition. Therefore, these parameters relate to cathode mass transfer resistance. If the A_3, t_2 and t_3 parameters change, there is a possibility that the structure and the three-phase interface area of the cathode electrode have changed.

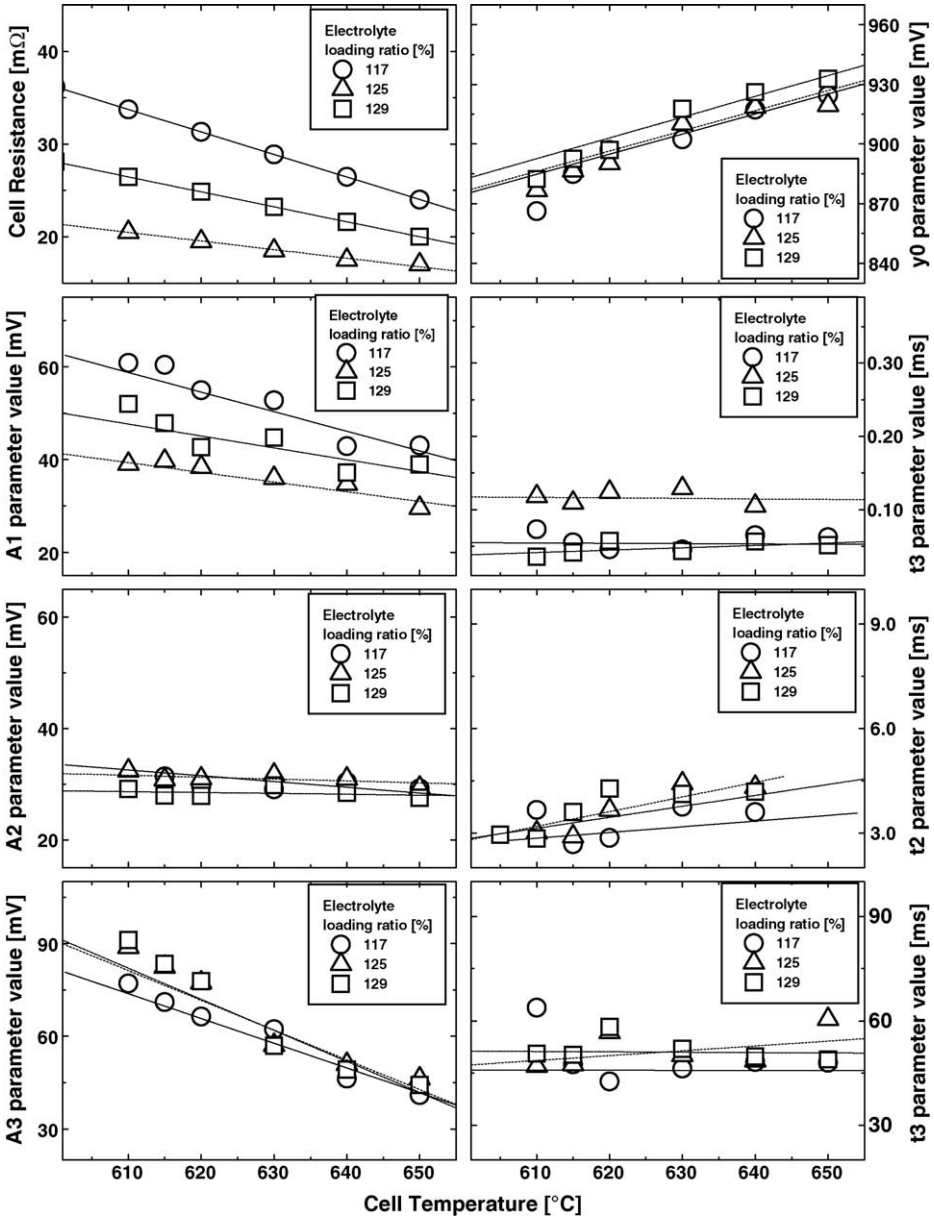

Fig. 6. The relation between each parameter and cell temperature.

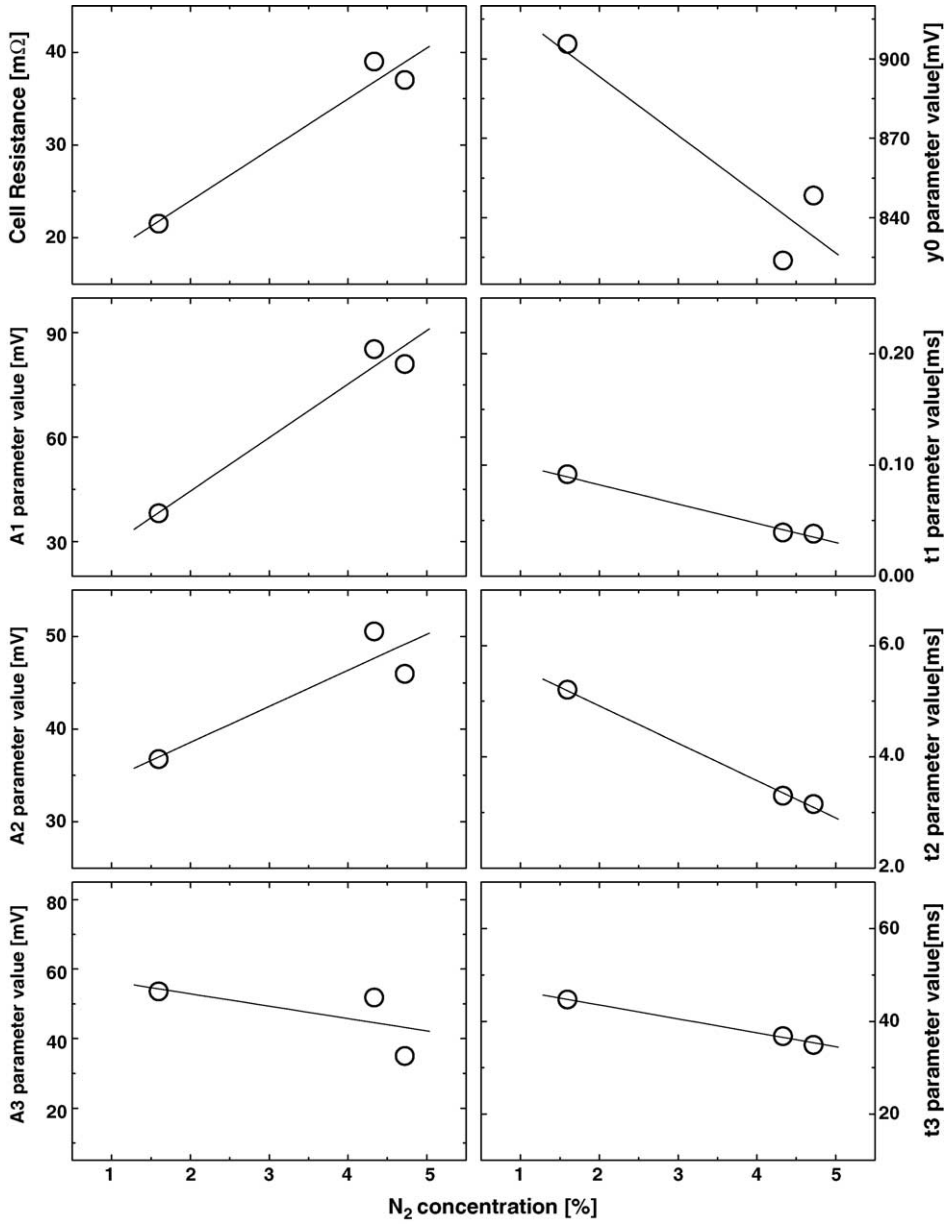

Fig. 7. Parameter of the cross-leak.

The physical meaning of each parameter can be found by evaluating the behaviour of each parameter when the cell temperature changes. Fig. 6 shows the relationship between each parameter and the cell temperature. Here, the experimental parameter relates to the electrolyte load ratio. As the cell resistance increases and y_0 decreases with a decreasing cell temperature, the electric conductivity of the electrolyte decreases. The A_1, A_3 and t_2 parameters change with a decreasing cell temperature. Because A_3 and t_3 parameters related to the electrolyte load ratio are similar to the cell resistance behaviour, it is understood that A_3 and t_3 parameters are related in terms of electrolyte conductivity.

Because the A_1 parameter closely resembles the cell resistance behaviour, it is understood that the A_1 parameter is involved in the resistance of all of the cell components. Because the t_2 parameter changes with changes in cell temperature and cathode gas composition, it is understood that the t_2 parameter is involved in cathode reactivity. As it is not clear from the results of these experiments, parameters, which relate to the anode reaction cannot be easily identified. When nitrogen was supplied in the amount of 40% in the anode gas to improve the hydrogen transport capacity to the electrode, the change in each parameter was evaluated. As a result, other parameters have hardly changed though the A_3 and t_1 parameters have changed greatly, as shown in Table 2. As the A_3 parameter relates to electrolyte conductivity, it is understood that the t_1 parameter is related to anode reactivity.

Table 3
Parameter for cell performance diagnostics and the physical meanings of each parameter

	Cell performance degradation	Electrolyte loss	Cross-leak	Cathode reaction resistance	Anode reaction resistance	Physical meaning
y_0	Decrease	Decrease (slightly)	Decrease (rapidly)	Decrease (slightly)	–	Output voltage
A_1	Increase	Increase (slightly)	Increase (rapidly)	–	–	All cell components resistance
t_1	Decrease	–	Decrease (slightly)	–	Decrease (rapidly)	Anode reactiveness
A_2	Increase	Increase (slightly)	Increase (rapidly)	–	–	Both electrode reaction resistance
t_2	Decrease	–	Decrease (slightly)	Decrease (rapidly)	–	Cathode reactiveness
A_3	Increase	Decrease (slightly)	Decrease (slightly)	Increase (rapidly)	Increase (slightly)	Electrolyte interfacial resistance
t_3	Increase	Decrease (slightly)	Decrease (slightly)	Increase (rapidly)	Increase (slightly)	Electrolyte interfacial reactiveness

Finally, parameters relating to cross-leakage have been identified. In our earlier research, cross-leakage was imitated by supplying nitrogen to the anode side; however, this method was not capable of completely imitating cross-leakage because of the inability to deteriorate the cell components, such as electrodes and electrolytes. Therefore, an MCFC single cell comprises a cracking electrode and cracking matrix to cause cross-leakage. The nitrogen concentrations of these

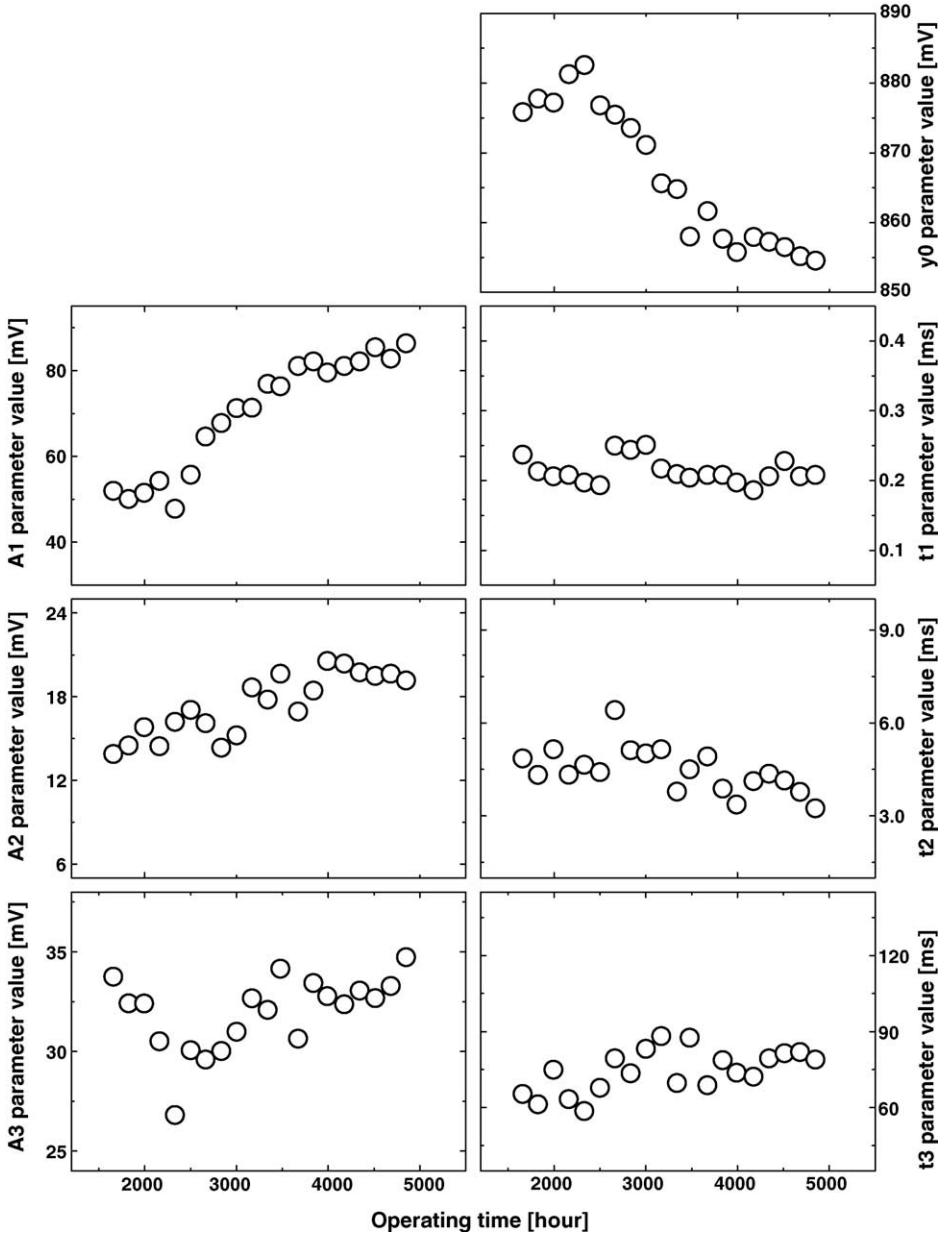

Fig. 8. Application of diagnostics to cell-I.

cells are 1.6, 4.33 and 4.72%. Fig. 7 shows the relationship between each parameter and the N_2 concentration in anode gas, where an increase in the N_2 concentration means there is a cross-leakage progression. All parameters change as the cross-leakage is promoted. A_1 and A_2 have been especially changed. This is because when cross-leakage occurs in a cell, all of the electrochemical reactions, including electrode reactions and electrolyte conductivity, etc., are influenced. Therefore, it is necessary for the diagnosis to detect the occurrence of cross-leakage, and to treat the cell appropriately.

The parameters used to diagnose cell performance and the physical meaning of each parameter is summarized in Table 3. Parameters, which diagnose electrolytic loss and cross-leakage are almost the same, but two degradation factors can be distinguished by the behaviour of t_1 and t_2, and the changing magnitude of A_1 and A_2. Here, because the A_2 parameter relates to both electrolytic loss and cross-leakage, it is understood that the physical meaning of the A_2 parameter is dual electrode reaction resistance. Therefore, the degradation factor is determined by observing the parameters of the cell under operating conditions.

3.2. Application of performance diagnosis to the 81 cm^2 MCFC in extended operations

The developed diagnoses are applied to the diagnosis of cell performance in extended operations. The specifications of the two cells, which apply diagnosis are summarized in Table 4. Cell-I is operated at a cell temperature of 720 °C, and the electrolyte load ratio is 5% greater than that of a conventional cell. Although cell-II, which has a standard electrolyte load ratio, is operated at a standard cell temperature, the cathode gas composition is $33O_2/67CO_2$ for decreasing the cathode mass transfer resistance.

Fig. 8 shows the change in each parameter during the operating hours of the cell-I. From the behaviour of each parameter that the cell-I condition changed at three periods, the period until 2500 h (period I), the period from 2500 to 4000 h (period II) and the period of 4000 h or more (period III) can be determined. Changes in each parameter are summarized in Table 5 for these three periods. An index is proposed which shows the degradation factor ratio during these three

Table 4
Specifications of two MCFC single cells to apply diagnostics

	Cell-I	Cell-II
Electrolyte	$52Li_2CO_3/48Na_2CO_3$	
Electrolyte loading ratio (%)	130	125
Cell temperature (°C)	720	650
Cathode gas composition (%)	$70Air/30CO_2$	$33O_2/67CO_2$
Anode gas composition (%)	$70.4H_2/17.6CO_2/12H_2O$	
Operation time (h)	5330	13816

Table 5
Diagnosis results of two MCFC single cells

Operation time (h)	y_0	A_1	t_1	A_2	t_2	A_3	t_3	Degradation factor ratio [%]			
								Electrolyte loss	Cross-leak	Cathode reaction resistance	Anode reaction resistance
Cell-1											
I $1500 \leqq t < 2500$	Increase (slightly)	Constant	Decrease (slightly)	Increase (slightly)	Constant	Decrease (slightly)	Decrease (slightly)	30.0	32.1	0.0	25.0
II $2500 \leqq t < 4000$	Decrease (rapidly)	Increase (rapidly)	Decrease (slightly)	Increase (rapidly)	Decrease (slightly)	Increase (rapidly)	Increase (rapidly)	45.0	57.1	87.5	50.0
III $4000 \leqq t < 5000$	Decrease (slightly)	Increase (slightly)	Increase (slightly)	Decrease (slightly)	Decrease (slightly)	Increase (slightly)	Increase (slightly)	20.0	21.4	75.0	33.3
Cell-II											
I $6500 \leqq t < 8000$	Constant	Increase (slightly)	Increase (slightly)	Constant	Constant	Constant	Constant	10.0	10.7	0.0	0.0
II $8000 \leqq t < 10000$	Decrease (slightly)	Increase (slightly)	Constant	Increase (slightly)	Decrease (slightly)	Constant	Constant	30.0	39.3	31.3	0.0
III $10000 \leqq t < 12000$	Decrease (rapidly)	Increase (slightly)	Decrease (slightly)	Increase (rapidly)	Decrease (rapidly)	Increase (slightly)	Constant	40.0	57.1	62.5	41.7

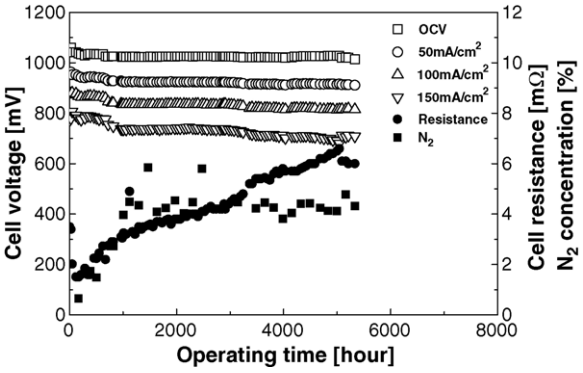

Fig. 9. Life performance of cell-I.

periods. The behaviour of the six parameters obtained from the cell is compared with the behaviour of the six parameters of each degradation factor shown in Table 3. If both parameters correspond to a "rapid increase", the weight index is 1.0. If one parameter corresponds to a "rapid increase" and another corresponds to an "increase", the weight index is 0.75. If both parameters correspond to an "increase", the weight index is 0.5. If neither parameter corresponds, the weight index is assumed to be 0. For example, the degradation factor ratio (δ_{DF}) of the cathode reaction during period is calculated as follows by the use of these weight indices. Here, n refers to the number of corresponding parameters, n_{DF}

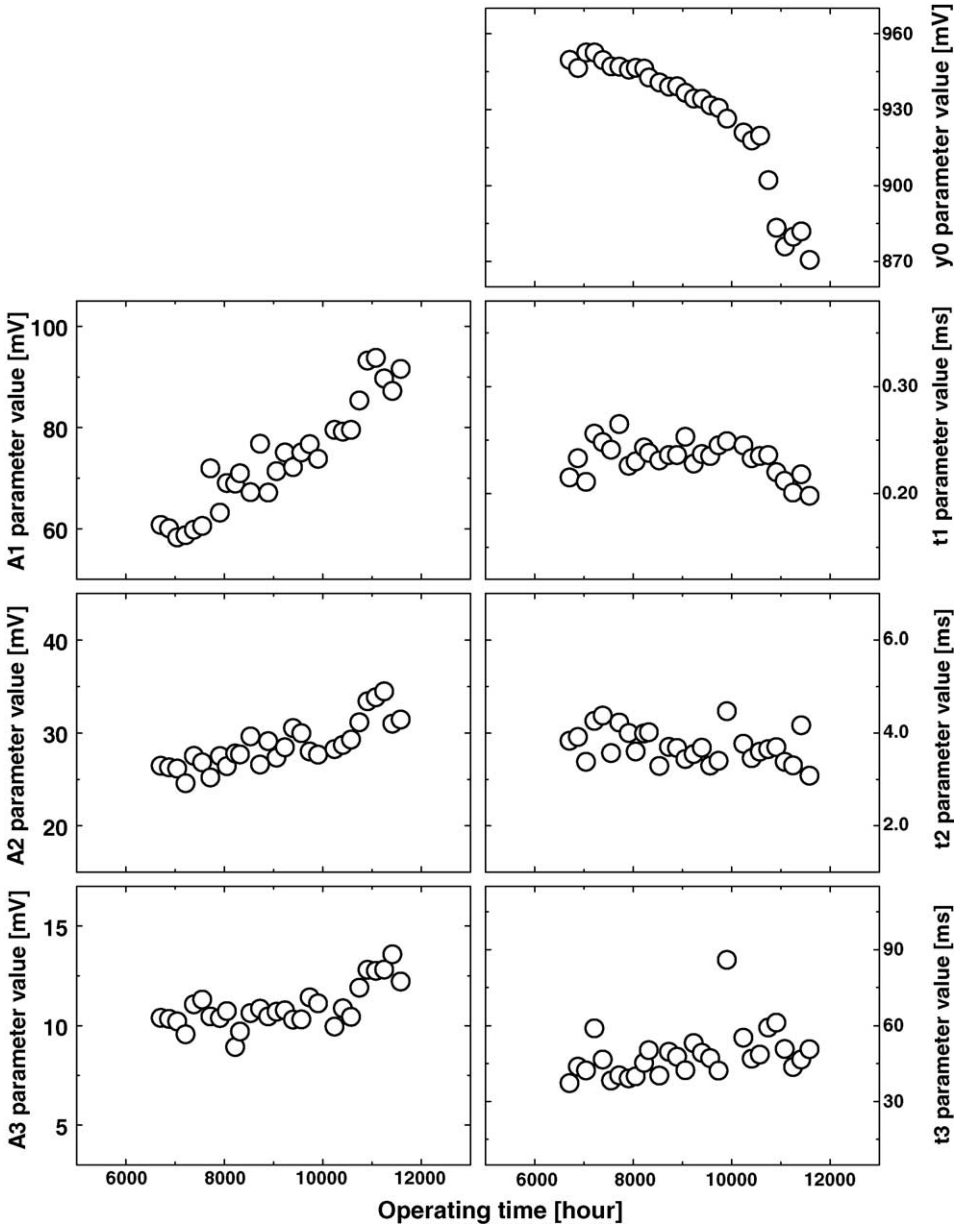

Fig. 10. Application of diagnostics to cell-II.

refers to the number of parameters to which each degradation factor relates and ϕ_i refers to the weight index, respectively. Both the A_3 and the t_3 parameter are "rapid increases", and the t_2 parameter is a combination of a "rapid increase" and an "increase".

$$\delta_{\mathrm{DF}} = \sum \left(\frac{n}{n_{\mathrm{DF}}} \right) \varphi_i = \frac{2}{4} \times 1 + \frac{1}{4} \times 0.75 = 0.69 \qquad (4)$$

Therefore, the degradation factor ratio of cell-I during the three periods is also shown in Table 5. Electrolytic loss commences during period 1, along with the commencement of cross-leakage. However, there is only a small amount of cathode mass transfer resistance and anode mass transfer resistance is also small. Therefore, it can be determined that hydrogen has been consumed by the entry of air into a cell, not from the cross-leakage passing an electrode but from a wet seal. In period *n*, there is continued electrolytic loss and considerable progression of cross-leakage. Because there is a rapid increase in the cathode mass transfer resistance, we can determine that cross-leakage passing the electrode takes place during this period. During period III, the cathode mass transfer resistance progresses considerably and the anode mass transfer resistance progresses a little though electrolytic loss and the slight abatement of cross-leakage. It can be understood from this diagnosis that the cathode electrode structure in the part where the cross-leakage occurred has broken, and that electrolytic loss has occurred in this part. Moreover, in the anode electrode, an oxide film was formed in the part where the cross-leakage occurred and the cross-leakage was suppressed on the basis of these results. The results of comparing the conventional operating data as shown in Fig. 9 with the diagnosis results are as follows: because the nitrogen concentration in the anode gas comprising the cross-leakage index was maintained at about 4%, it had been determined from the conventional data that there was cross-leakage from the outset. However, cell performance was good, notwithstanding the occurrence of cross-leakage. Moreover, cell performance decreased slowly with increasing cell resistance after exceeding 3000 h, though the nitrogen concentration in the anode gas was constant. It was difficult to understand the reason for this degradation. However, the diagnosis determined that the 4% nitrogen concentration until the passage of 2500 h is due to the inflow of air from a wet seal, caused by cross-leakage after operating hours exceeded 2500 h. Thus, the cause of a 4% nitrogen concentration until 2500 h and the cause of a 4% nitrogen concentration after 2500 h are different, although the nitrogen concentration remained nearly steady at 4%. Therefore, the diagnosis does a good job of explaining the operating data, and is effective in the detailed diagnosis of cell performance. Fig. 10 shows the change in each parameter during the operating hours of the cell-II. It can be determined from the behaviour of each parameter that the cell-II condition also changed during the three periods, including the period from 6500 to 8000 h (period I), the period from 8000 to 10,000 h (period II) and the period of 10,000 h or more (period III). The change in each parameter and the degradation factor ratio during these three periods are also summarized in Table 5. In period I, the cell sustained electrolytic loss and the cross-leakage did not influence the cell performance. Because the cathode gas of the cell is O_2/CO_2, nitrogen in the anode gas is not attributable to cross-leakage from the cathode, but is rather due to the inflow of air from a wet seal. Electrolytic loss and the cross-leakage were promoted in period II. Moreover, because of the increase in cathode mass transfer resistance, there is a strong possibility of cross-leakage passing the electrode. In period III, electrolytic loss and the cross-leakage were promoted rapidly after the operating hours exceeded 10,000 h. In addition, the cathode mass transfer resistance and the anode mass transfer resistance increased drastically. The t_1 parameter, which is the index of anode reactivity and the t_2 parameter, which is the index of cathode reactivity, decreased rapidly. Therefore, there is a cell resistance increase and an electrolytic loss accelerated by the cross-leakage related oxidation of the anode electrode and the current collector. Conversely, the following results were obtained from the conventional operating data, as shown in Fig. 11 and the diagnosis results: though the N_2 concentration in an anode gas is about 4% from its initial state, it decreases after 10,000 h of operation, after which there is a rapid increase in cell resistance and cell performance deteriorates rapidly. Therefore, a conventional determination was that the degradation was caused by metal corrosion. However, this diagnosis can determine a decrease in the nitrogen concentration because the airflow insertion from a wet seal is suppressed by the formation of oxide film, and that cell resistance has increased because the anode electrode and the current collector have become oxidized by cross-leakage. Therefore, if the cell electrolytes were refilled at 7000 h, cross-leakage would not occur and cell life performance would be improved. As the performance diagnosis can obtain more information than through a conventional determination, the cell degradation factor is adequately obtained by combining the diagnosis with conventional operating data. If the cell is appropriately treated to evade the degradation factor, the cell can be operated for an extended period.

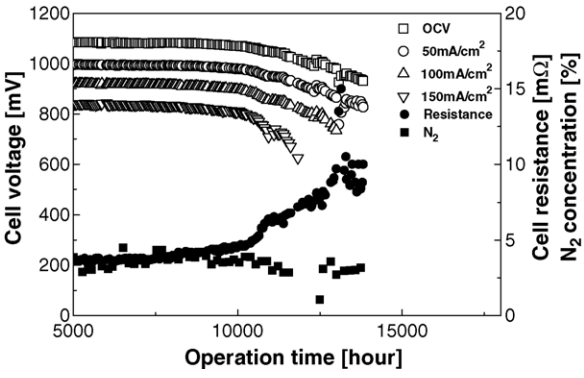

Fig. 11. Life performance of cell-II.

4. Conclusion

The objective of the study is to develop cell performance diagnosis by using a transient response. The obtained results in this study are summarized as follows:

(1) parameters relating to electrolytic loss include A_1–A_3 and t_3;
(2) parameters relating to cross-leakage include A_1–A_3 and t_1–t_3;
(3) parameters relating to cathode mass transfer resistance include A_3, t_2 and t_3;
(4) parameters relating to anode mass transfer resistance include A_3, t_1 and t_3;
(5) the proposed diagnosis of the degradation factors of an actual cell, by using the transient response was effective.

References

[1] C.-G. Lee, H. Nakano, T. Nishina, I. Uchida, S. Kuroe, Characterization of a 100 cm^2 class molten carbonate fuel cell with current interruption, J. Electrochem. Soc. 145 (8) (1998) 2747–2751.
[2] X. Xu, K. Tanimoto, K. Sugiura, Analysis of transient voltage response on 4 cm × 4 cm molten carbonate fuel cell by a current pulse method, J. Electrochem. Soc. 149 (8) (2002) 1025–1029.