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Performance diagnostics of PEFC by current-pulse method

K. Sugiura [a,*], M. Yamamoto [a], Y. Yoshitani [a], K. Tanimoto [b], A. Daigo [c], T. Murakami [c]

[a] *Osaka Prefectural College of Technology, 26-12 Saiwai, Neyagawa, Osaka 572-8572, Japan*
[b] *National Institute of Advanced Industrial Science and Technology, Kansai, 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan*
[c] *Tsuruga Electric Corporation,1-3-23 Minamisumiyoshi, Sumiyoshi-ku, Osaka 558-0041, Japan*

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Abstract

PEFC cannot be operated for extended periods because it has some problems. However, if the deterioration factors can identified on time, PEFC can be operated for extended periods by overcoming these problems. Therefore, performance diagnostics needs to be developed to judge the PEFC deterioration factors instantaneously and simply. MCFC performance diagnostic has now been developed by the current-pulse method. Therefore, a thesis was examined relating to the applicability of the diagnostic to a PEFC characteristic diagnosis. The diagnostic evaluates changes in the seven parameters of the fitting equation led from PEFC's transient response between 100 ms obtained by the current-pulse method. The relationship between these parameters and each deterioration factor is evaluated using a PEFC single cell whose electrode area is 25 cm^2. In this case, deterioration factors include cell temperature, the flooding phenomenon and the gas composition/flow rate. As a result, each of seven parameters in the transient response of PEFC corresponds to an ohmic potential drop, anode/cathode gas diffusion resistance, reactive resistance, three-phase interfacial resistance and electrolyte properties, respectively. When the flooding phenomenon is caused in the cathode channel, the transient response of the PEFC obviously differs from the standard value. The change in each parameter is examined by gradually raising the humidity of the cathode supply gas (flooding gradually being caused in the cathode channel). The influence of the flooding phenomenon clearly appeared in three parameters, and in the same way, the temperature dependency of each parameter is confirmed. Therefore, the proposed performance diagnostic will be able to specify the PEFC deterioration factors while driven, easily and on time.

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

1. Introduction

In the future, the polymer electrolyte fuel cell (PEFC) is expected to become a distributed power station and power unit for cars and the like because of its high efficiency and low temperature operation and the like. Therefore, researchers in every country in the world have been conducting research on improving PEFC performance. However, for the purpose of commercialization, some PEFC related problems, such as the problem of drying the polymer electrolyte, flooding the GDL and gas channel by generated water, cross-leakage and CO poisoning of electrodes, etc., reflected in cell voltage loss must be overcome. Because degradations are reflected only in voltage variation, degradation factors by which the voltage changes cannot be confirmed. If the degradation factors can be readily obtained by means of performance diagnosis in a timely manner, they can be overcome and a PEFC can be operated for extended periods. Performance diagnosis that can determine MCFC degradation factors instantaneously and easily by the current-pulse method yet [1,2] has been developed, and is expressed as an equivalent circuit, the transient response of which is shown in Fig. 1. This equivalent circuit is composed of a single resistance, a parallel single resistance and a single capacitor, with the voltage related Eq. (1) being derived from an equivalent circuit:

$$V_{out}(t) = E_0 - (R_0 + R_1 + R_2 + R_3)I_0 + R_1 I_0 \, e^{-t/C_1R_1} + R_2 I_0 \, e^{-t/C_2R_2} + R_3 I_0 \, e^{-t/C_3R_3} \quad (1)$$

Here, Eq. (1) is rearranged to Eq. (2) by substituting $y_0 = E_0 - (R_0 + R_1 + R_2 + R_3)I_0$, $A_1 = R_1 I_0$, $A_2 = R_2 I_0$, $A_3 = R_3 I_0$, $t_1 = C_1 R_1$, $t_2 = C_2 R_2$, $t_3 = C_3 R_3$ into Eq. (1)

$$V_{out}(t) = y_0 + A_1 \, e^{-t/t_1} + A_2 \, e^{-t/t_2} + A_3 \, e^{-t/t_3} \quad (2)$$

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

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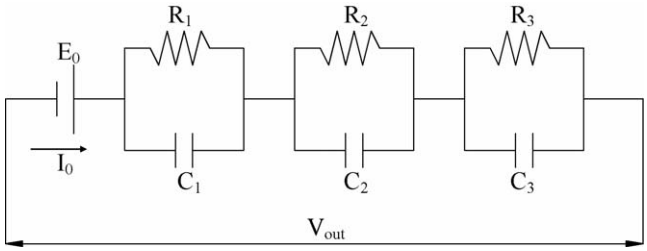

Fig. 1. The equivalent circuit for PEFC performance diagnostics.

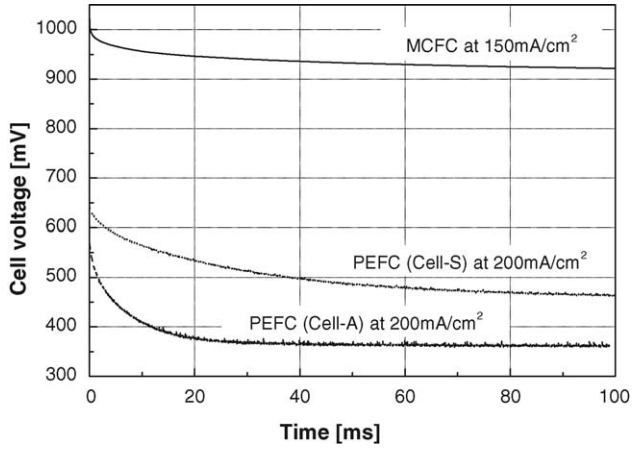

Fig. 2. Comparison between the transient response of MCFC and PEFC.

Here, y_0 refers to cell voltage at 100 ms, and A_1, A_2, A_3, t_1, t_2 and t_3 are respective diagnostic parameters. Eq. (2) suggests that cell performance stabilizes early if the value of the parameters is small, and diagnosis of the MCFC degradation factor is accomplished by evaluating changes in the six parameters during operation, by which it is easy to specify the driven MCFC degradation factors in a timely manner. The present paper examines the applicability of this diagnostic to PEFC characteristic diagnosis.

Fig. 2 shows a comparison between the transient responses of MCFC and PEFC. The voltage drop of PEFC to 1 μs is greater than that of the MCFC, and the voltage stability of PEFC in about 20 ms is slower than that of the MCFC. Therefore, the PEFC parameters has different possibilities than the behaviour of parameters used for MCFC performance diagnosis because the PEFC time constant is assumed to be larger than that of the MCFC.

2. Experimental apparatus and procedure

Fig. 3 shows a schematic diagram of the experimental apparatus. The temperature of the PEFC is maintained at 80 °C by means of a temperature controller. Anode gas and cathode gas are humidified by passing through the humidifier and being supplied to the PEFC. To prevent the supply gas from condensing, the piping between the humidifier and the cell is shortened, and the piping temperature is maintained by a ribbon heater at 85 °C. The cell voltage is measured and recorded by a data logger. Cell resistance is measured by a milliohm-meter with ac 4 probes.

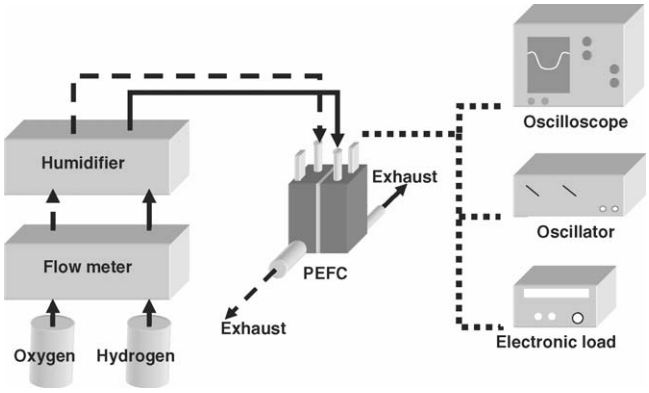

Fig. 3. Schematic diagram of experimental apparatus.

Diagnostics is examined by two kinds of cells of A and S. Each cell is a 25 cm^2 single cell, and the electrolyte membrane of both cells is Nafion® 112. The both electrode catalyst of cell-A is Pt/C (HiSPEC 4000, Johnson Matthey). Carbon paper (TGP-H-060, Toray) and carbon clothe (ELAT/SSNC/V3.1: water repellency is processed) are attached using hot press as gas diffusion backing to anode and cathode, respectively. On the other hand, the anode catalyst of cell-S is Pt–Ru/C, and the cathode catalyst is Pt/C, respectively. The GDL for both electrodes of cell-S is similar to GDL for anode of cell-A. Therefore, the GDL for cathode of cell-S is not given the treatment of water-repellent. In both cells, both gas channel geometries are Serpentine. The differences of these two cells are (1) an easiness of flooding by difference of GDL on cathode side and (2) a reactiveness of anode electrode by difference of anode electrode catalyst.

The pulsed current of 200 mA cm^{-2} is periodically removed from the PEFC using a pulse oscillator, and the transient response is recorded by means of a digital oscilloscope. The experimental conditions are shown in Table 1. Anode gas is supplied to the cell as humidifying gas ($51H_2/49H_2O$) made by passing 100% H_2 into the humidifier at 80 °C. Cathode gas is also supplied to the cell as humidifying gas ($51air/49H_2O$),

Table 1
Experimental conditions

	Anode	Cathode
Standard condition		
Gas utilization (%)	70	40
Standard gas composition (%)	$51H_2/49H_2O$	$51air/49H_2O$
Current density (mA cm^{-2})	300	
Cell temperature (°C)	80	
Humidifier temperature (°C)	80	
Experimental condition		
Parameter selection for the diagnostics		
(1) Reactivity	65, 70, 75, 80 °C	
(2) Mass transfer resistance	Gas utilization: 90% (or 100%)	Gas utilization: 70%
(3) Flooding of cathode gas		Humidifier temperature: 70 °C

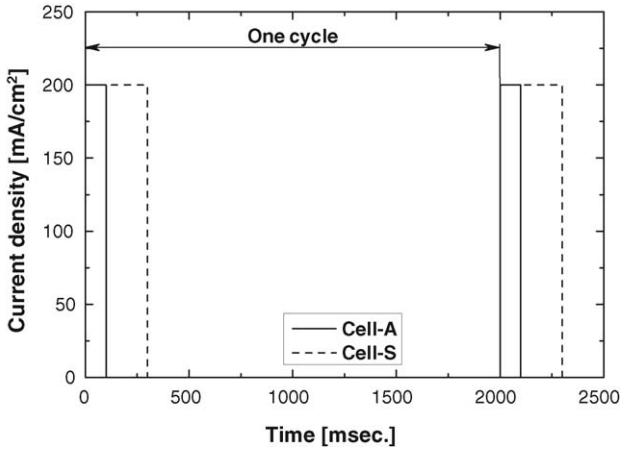

Fig. 4. Current-pulse to obtain transient response.

made by passing 100% air into the humidifier at 80 °C. The fuel gas utilization rate is 70%, and oxidant gas utilization rate is 40%, respectively. The current density of standard condition is 300 mA cm^{-2}, and the operating pressure is atmospheric. Single cells that imitate the three degradation factors are made and operated under conditions for identifying the parameters originating in each degradation factor. In this instance, three degradation factors refer to reactivity, mass transfer resistance and flooding in a cathode gas channel:

(1) Reactivity influences the degradation of MEA properties by CO poisoning and the degradation of polymer electrolytes etc. Because the maximum parameter that verifies reactivity is cell temperature, the parameter that originates in each reaction resistance is identified by changing the cell temperature from 80 to 65 °C.
(2) Because the parameter that verifies mass transfer resistance is the flow rate, both gas utilizations are changed to select parameters originating in mass transfer resistance. Fuel gas utilization is changed to 70%, 90% (or 100%), and oxidant gas utilization is changed to 40% and 70%.
(3) In the flooding phenomenon, if the dew point of steam generated by an electrochemical reaction and steam supplied to the cell raises more than the cell temperature, steam supersaturated in the channel becomes dew condensation. Because dew condensation clogs the channel and disturbs the diffusion of the gas, the PEFC performance deteriorates, making it difficult to find parameters originating in

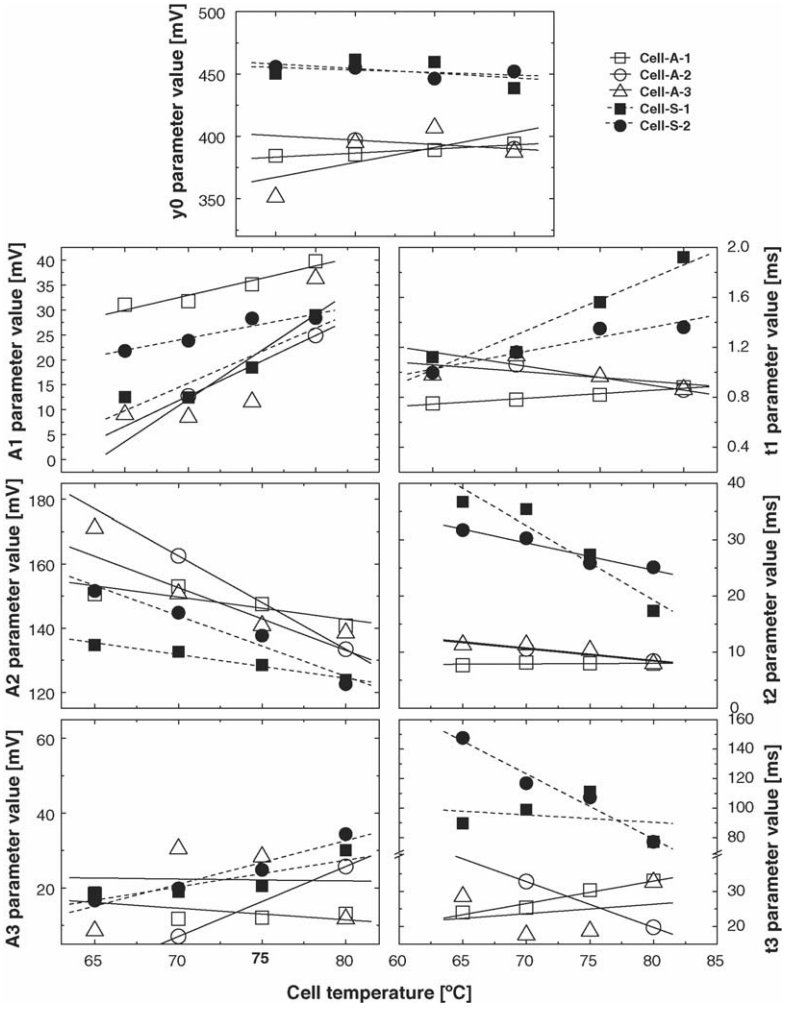

Fig. 5. Relation between each parameter and cell temperature.

the flooding phenomenon. However, if the above-mentioned parameters are found, parameters relating to flooding can be selected. Therefore, the parameters that originate in the flooding phenomenon are identified by decreasing the humidifier temperature of the cathode side at 10 °C and changing the steam supersaturated in the channel to dew condensation. To verify the influence of flooding in each parameter, the time variation of each parameter is measured immediately after the temperature of the humidifier is lowered.

The current density is 200 mA cm^{-2} when experiments are carried out to identify parameters relating to various degradation factors. The mean transient response when the electric current shown in Fig. 4 is impressed 30 times is used in the performance diagnosis. The sampling frequency of each cell is 500 kHz, and changes with each experimental condition, with the transient response being measured with a stable cell voltage. Here, the reaction rate differs by the difference of the anode electrode catalyst, and the time until the voltage becomes steady is also different. Therefore, the time to impressing electric current to each cell is different. As the electric current impression time of the cell-S is 300 ms, and that of cell-A is 100 ms, the parameter of time constant of cell-S is larger than that of cell-A. The difference of the absolute amount of the parameter is a difference of each cell specification, and it is unrelated to the degradation factor that is verified by this paper. Therefore, it is necessary to verify the change in each parameter into each degradation factor.

3. Results and discussion

3.1. Identification of parameters relating to reactivity

Because PEFC does not cause great temperature distribution in the cell under operating conditions, the identification of parameters that relate to the cell temperature appear to be meaningless. However, the cell temperature greatly influences activation energy of the electrode and the ionic conductivity of the membrane. Therefore, if parameters that relate to cell temperature can be found, the electrode and membrane conditions of PEFC are diagnosed by monitoring these parameters. Fig. 5 shows the relationship between each parameter and cell temperature. Here, a blank plot is data of the cell-A, and a solid plot is data of the cell-S, respectively. Experiments were undertaken

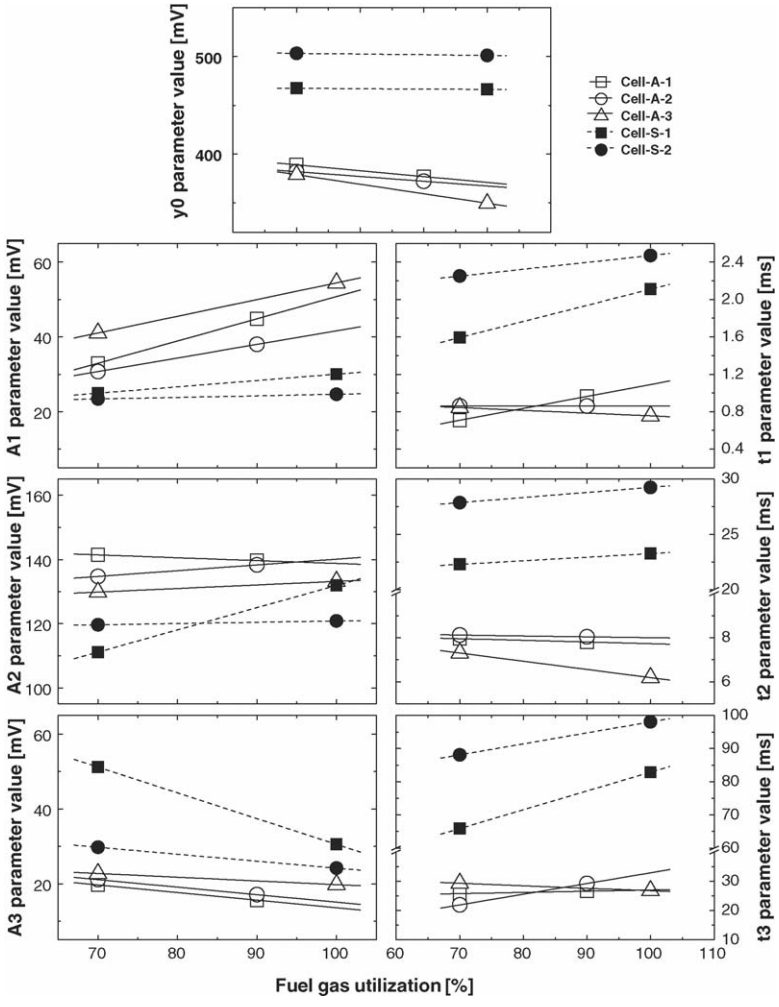

Fig. 6. Relation between each parameter and fuel gas utilization.

using two cells S with three cells A to improve the reliability of the data. As the y_0 parameter is difficult to change into a temperature change, this parameter cannot be used to diagnose cell reactivity. The A_1, A_2, t_1 and t_2 parameters change with decreasing cell temperature. Generally, the activation energy of the electrode in the fuel cell rises with increasing cell temperature. Especially, as the change in parameter t_2 of cell-S with the Ruthenium catalyst with high temperature dependency is large, it is understood that the A_2 and t_2 parameters are involved in the anodic reaction. This tendency corresponds to the case of MCFC. Conversely, as ionic conductivity of the membrane lowers with increasing cell temperature, it is understood that the A_1 and t_1 parameters are involved in ionic conductivity.

On the other hand, with the A_3 and t_3 parameters, the results were different in cell-A and cell-S. The difference between cell-A and cell-S lies in whether or not there is water repellency relative to the gas diffusion layer. This is confirmed by the visual experimental results showing that flooding is caused easily in cell-S, with hardly any flooding in cell-A. Therefore, it is understood that the A_3 and t_3 parameters are involved in the flooding phenomenon. However, the participation of these parameters in the cell cannot be judged from this stage.

3.2. Identification of parameters relating to mass transfer resistance

Generally, because the PEFC Reynold's number is low by operating at low temperature, mass transfer resistance is large. Therefore, the gas channel of PEFC adopts a serpentine type to increase the supply gas pressure and Reynold's number, and mass transfer resistance of the reactant gas is lowered. However, if the flooding phenomenon is caused in the gas channel, reactant gas cannot be transported to the electrode. The mass transfer resistance change is imitated by changing the gas utilization (as changing flow rate). Therefore, the mass transfer resistance to each electrode is evaluated by changing gas utilization. Fig. 6 shows the relationship between each parameter and the fuel gas utilization. The A_1 parameter of both the cell-A and the cell-S increases with an increase in fuel gas utilization, and cell-A of the increase ratio is larger than that of cell-S. As the difference between the cell-A and the cell-S lies in whether or not there are water repellency relative to the gas diffusion layer and anode catalyst, and the difference of the behaviour of parameter A_1 by the fuel gas utilization presence of the water in the reaction field. We understand that PEFC reaction fields are a three-phase

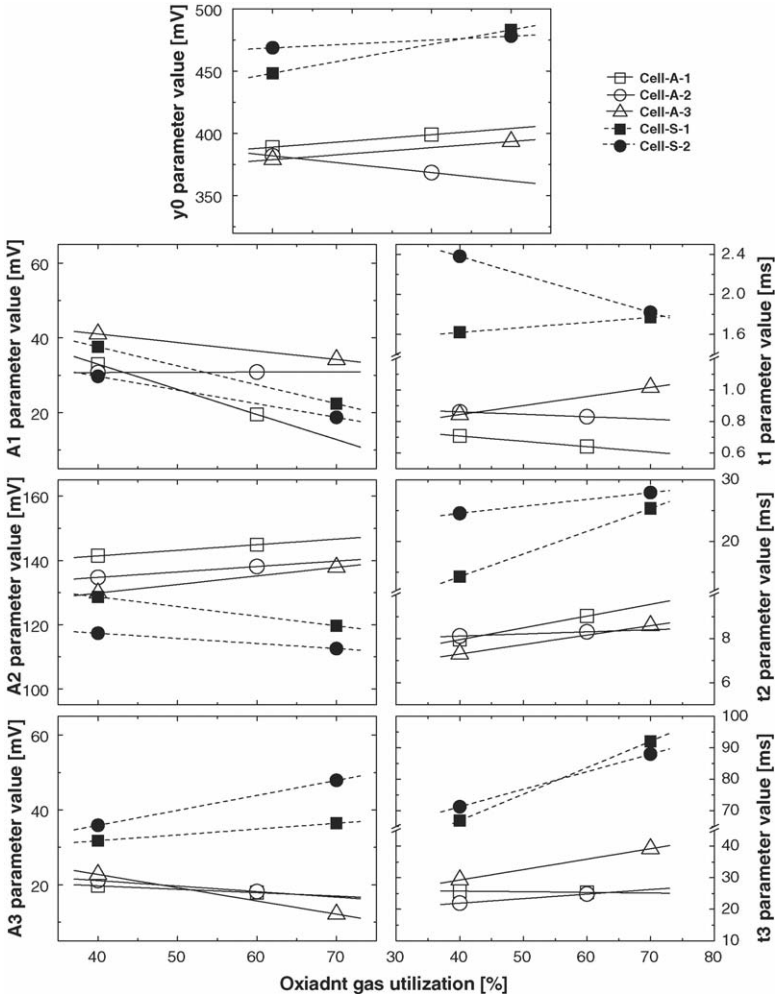

Fig. 7. Relation between each parameter and oxidant gas utilization.

interface composed of the membrane, the electrode, and water, and water in the membrane and the electrode plays the role of an electrolyte. As described in Section 3.1, it is confirmed by visual experimental results that flooding is caused easily in cell-S, and hardly any flooding is caused in the cell-A. The three-phase interface of cell-S is made large by the existence of water in the reaction field but that of cell-A is small because the supplied water is exhausted by the gas diffusion layer of the water-repellent treatment. Therefore, it is understood that the A_1 parameter relates to the three-phase interface including the ionic conductivity of the membrane. On the other hand, parameters A_3, t_1 and t_3 influence of the fuel gas utilization appears only in cell-S. One of the reasons the t_1 and t_3 parameters become high with a decrease of hydrogen as a reactant gas is the difference of the anode electrode catalyst. Moreover, the reason the A_3 parameter becomes small is due to an increase of the three-phase interface of the anode side by which the flooding water transports from cathode to anode through the membrane because of the growing differential pressure between the anode and cathode caused by a decrease of the anode flow rate. However, because there was hardly any flooding caused on cell-A, this effect was small.

Fig. 7 shows the relationship between each parameter and the oxidant gas utilization. The tendency of the t_1 and t_3 parameters is almost the same as that of the influence of the fuel gas utilization, because the oxygen transport capacity to the electrode is decreased. The behaviour of the A_1 and A_3 parameter of both cells are opposite to the case of fuel gas utilization, and cell-S of this tendency is especially larger than that of cell-A. The reason the A_1 parameter is decreased by a decrease in the oxygen flow rate is because the water not exhausted by the flow rate decrease wet the membrane, and ionic conductivity is improved. Conversely, the A_3 parameter of cell-A hardly changes at all but that of cell-S changes greatly. Moreover, because there was no temperature dependency of the A_3 parameter in both cells, a single cell that does not provide water repellency relates to the change in the A_3 parameter. Therefore, the relation of the A_3 parameter to the flooding phenomenon will be strong or the A_3 parameter might relate to an increase of mass transfer resistance with the flooding phenomenon.

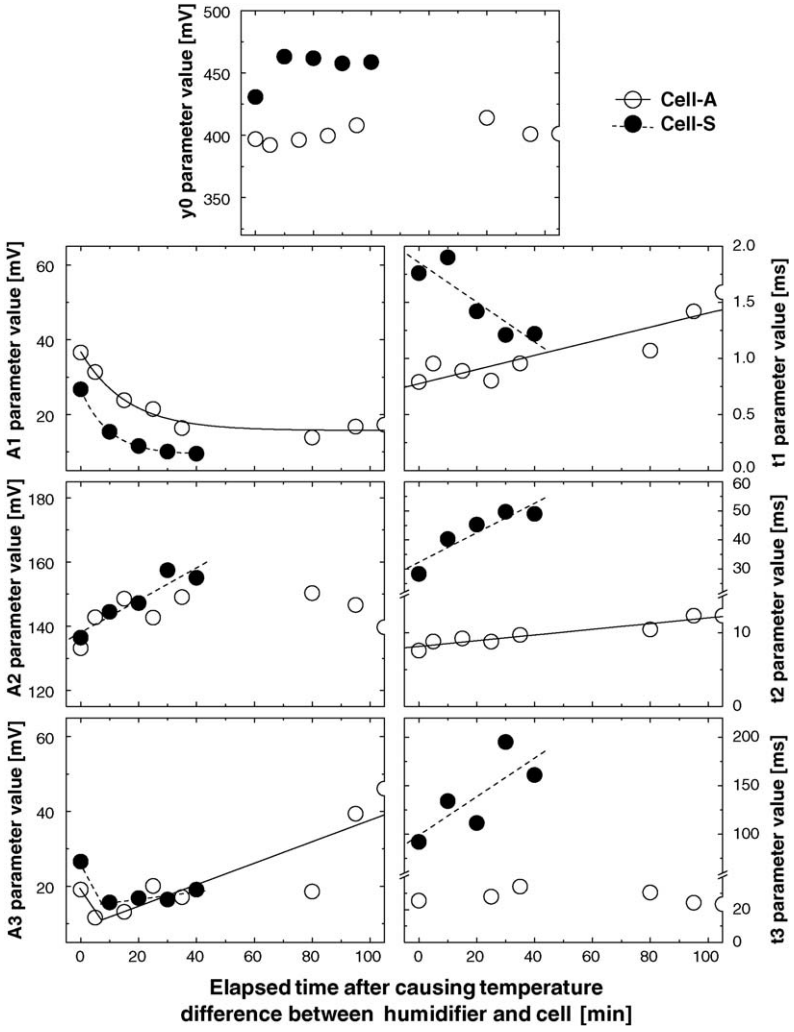

Fig. 8. Parameter of the flooding phenomenon of cathode gas channel.

3.3. Identification of parameters relating to the flooding phenomenon and the physical significance of each parameter

As described in Section 3.2, it is understood that there is a difference of transient response caused by the easiness of flooding. Therefore, the parameter that originates in the flooding phenomenon is identified by decreasing the humidifier temperature of cathode side by 10 °C and changing steam supersaturated in the channel to dew condensation. To verify the influence of the flooding for each parameter, the time variation of each parameter is measured immediately after the temperature of the humidifier is lowered. The results are as shown in Fig. 8. Here, the measurement time of cell-A is about 2 h, and that of cell-S is about 1 h, respectively. The A_1 parameter of both cells decreases with the progression of flooding. It is understand that the ionic conductivity of both cells is improved because the membrane is enriched with the water caused by the flooding. Therefore, as these results achieve the above-mentioned results, it is understand that the A_1 parameter relates to the ionic conductivity of the membrane. The A_2 parameter of both cells increases with progressive flooding because oxygen is disturbed to transport to electrode with water caused by the flooding. This result almost corresponds to the results of the cell-temperature dependency in which the relationship of the A_2 parameter to the electrode reaction resistance is strong. Moreover, although the A_2 parameter relates to oxygen gas utilization, it does not relate to fuel gas utilization. Therefore, it is understand that the A_2 parameter relates to cathodic reaction resistance. In the case of the A_3 parameter, the A_3 parameter of both cells decreases immediately after the commencement of flooding, there is an increase of the three-phase interface by which the flooding water is transported from cathode to the anode through the membrane. However, it is understood that as the anode electrode is covered with water moved from cathode progressive flooding, the A_3 parameter increases by disturbing the transport of hydrogen to the anode. Because the water repellency occurs relative to cell-A, a decrease in cell temperature and a decrease of the anode supply steam with increasing fuel gas utilization are hardly reflected in the A_3 parameter. However, in the flooding phenomenon to cover the electrode with water directly, even the A_3 parameter of cell-A is changed because water that has passed the membrane from cathode influences the anodic reaction. Therefore, it is understood that the A_3 parameter relates to anodic reaction resistance.

On the other hand, because the t_2 parameter of both cells increases with the progression of flooding, reactivity of both cells worsens. From the results of cell temperature dependency and oxygen gas utilization dependency, the t_2 parameter changes on the condition that the flooding is caused easily. Therefore, it is understood that the t_2 parameter relates to the reactivity of cathodic reaction. Although the t_1 parameter of cell-A increases with progressive flooding, that of cell-S decreases. From the results of cell temperature dependency, the t_1 parameter is assumed to relate to ionic conductivity of the membrane. The condition of the three-phase interface is assumed to be different because the GDL of each cell is different. Therefore, the behaviour of the t_1 parameter of each cell is different, but this cannot be determined from these data. It is understood that the t_1 parameter is related to the three-phase interface including the ionic conductivity of the membrane.

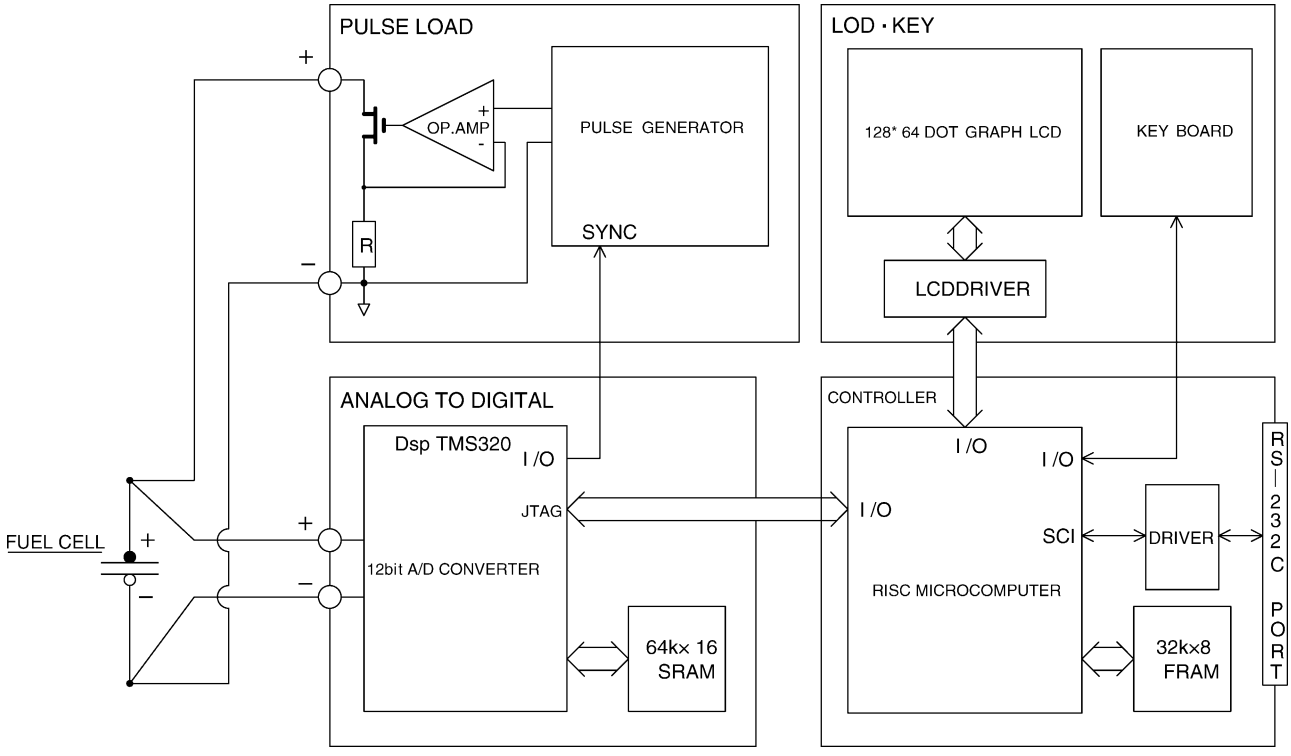

Fig. 9. Schematic diagram of the MCFC performance diagnostics device.

It is only in cell-S that the t_3 parameter changed the progression of flooding. Ultimately, the t_3 parameter relates to only cell-S that installs conventional carbon paper as GDL. Therefore, although the t_3 parameter can be assumed to relate to the flooding phenomenon, it is not possible to conclude it from the data.

The parameter that influences the cell temperature, mass transfer, and the flooding of the cathode side to diagnose the PEFC characteristic has been identified, as a result of which it was clarified that a variety of degradation factors are reflected in the transient response of the PEFC and the concept of the MCFC characteristic diagnostics can be used to diagnose the PEFC characteristics. However, to improve the accuracy of diagnosis, transient response in various conditions should still be analyzed.

3.4. Development of PEFC performance diagnostics prototype

The MCFC performance diagnosis device shown in Fig. 9 is being developed by collaboration between our laboratory and the Tsuruga Electric Corporation. The device is composed of a pulse generator, a controller, an A/D converter, and a display. The device currently is used to verify MCFC characteristic diagnosis, and obtains excellent results. From the above-mentioned results, the concept of MCFC performance diagnostics can be used to diagnose PEFC characteristics. Therefore, the device is improved for PEFC and is used in various experiments to improve the accuracy of the diagnosis. The device will be put into commercial service in the future.

4. Conclusion

The objective of the study is the verification of MCFC characteristic application diagnostics to the PEFC. The obtained results in this study are summarized as follows:

(1) Parameters relating to ionic conductivity of the membrane include A_1 and t_1.
(2) Parameters relating to cathodic reaction resistance include A_2 and t_2.
(3) Parameters relating to anodic reaction resistance include A_3.
(4) Parameters relating to the flooding phenomenon include A_3 and t_3.
(5) The MCFC performance diagnostics is effective to diagnose the performance of PEFC.

References

[1] K. Sugiura, H. Matsuoka, K. Tanimoto, Performance diagnostics of MCFC by using a current-pulse method, J. Power Sources 145 (2005) 515–525.
[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) A1025–A1029.