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Elucidation of Degradation Factor Distribution by the Improved Diagnostics

Y. Takeuchi†*, K. Sugiura†, Y. Yoshitani†, K. Kumano‡ & T. Murakami‡

†Department of Technological Systems, Mechanical Engineering Course, Osaka Prefecture University College of Technology, Neyagawa, Osaka 5728572, Japan

‡Tsuruga Electric Corporation, Sumiyoshi, Osaka 558-0041, Japan

f18012@osaka-pct.ac.jp

ABSTRACT: Our diagnostics evaluates the PEFC's transient response with a resistance polarization, an activation polarization and a diffusion polarization, and derives diagnostics parameters by analyzing this transient response. We have clarified the degradation factors (the three polarizations) and distribution by applying this diagnostics system to PEFC short stack or PEFC single cell with a quadrisection separator. Finally, Tsuruga Electric Corporation has sold maintenance equipment as PEFC Performance Diagnostics System (PPSD) "356 TD" using this diagnostic method. Conventional diagnostics equipment is too expensive, and an analyzing time is too long. However, our equipment, the 356TD is able to diagnose deterioration factors as well as impedance analysis by measuring the transient response for about one minute and is dramatically cheaper than conventional one. However, because the reflection of each deterioration factor in each parameter is small, it is necessary to diagnose the parameters strictly. Therefore, as there is a possibility of causing the diagnostic error, it should be improved. We have developed a new algorithm for PEFC performance diagnostics that solves the transient response by the third differential equation directly to satisfy the demand mentioned above last year. A new diagnostic approximates the transient response of PEFC directly using the on-line algorithm of the method of least squares and obtains three diagnostic parameters sequentially. The adequacy of a new algorithm was verified by evaluating the cell inner heat flux distribution using a special separator that can measure heat flux distribution and a 25cm2 PEFC single cell. As a result, the special separator was able to obtain a corresponding heat flux distribution to a past temperature distributed data. Moreover, our new algorithm was able to derive corresponding three parameters to previous diagnostics parameters though it has to be verified further.

INTRODUCTION

Recently, Polymer Electrolyte Fuel Cell (PEFC) begins to be used to a lot of fields such as automotive industry, household power generation etc. because it can be operated at the low temperature, and a good handling ability and hardly emits air pollutants. However, PEFC has still some problems such as cost of the fuel cell products, the improvement of a life performance and a development of simple maintenance equipment and so on. Our laboratory has researched about fuel cell and hydrogen production technology for long time. In order to reduce the cost of PEFC system, one group has developed a catalyst layer with a self-water-management since 2015, and other group has developed a separator with a self-water management since 2003. Our group focus on a fuel cell maintenance equipment to enhance the life performance of a fuel cell. We are considering that if the degradation of the fuel cell was able to be diagnosed at the early stage, we can enhance the life performance by applying appropriate treatment to fuel cell. We have proposed a fuel cell performance diagnostic that diagnoses the degradation factor of MCFC instantaneously using a current interruption method since 2003. Thereafter, we have applied it to PEFC, and the PPDS (PEFC Performance Diagnose System) installed this diagnostic was launched by Turuga Electric Corporation in 2004. Our diagnostics evaluates three parameters, the resistance polarization, the activation polarization and the diffusion polarization by analyzing a transient response at a current interruption, and decided the degradation factor. Although our first model used an equivalent circuit composed of an anode, cathode and electrolyte polarization, we neglected an equivalent circuit of anode side to improve a diagnostics accuracy and to short an analyzing time because an anode polarization is much smaller than a cathode polarization since 2013. After this improvement, as the diagnostics accuracy was improved, the diagnostics was able to judge most of degradation factor that originated in cathode polarization on PEFC single cell, and the diagnostic results were also corresponding to that of the Cole-Cole plot [1, 2]. This diagnostic was applied to a short stack composed of four cells and a PEFC single cell with a quadrisection separator as shown in Figure 1 and 2, and it found the deteriorated cell in the short stack, and it also obtained the degradation distribution in the same cell [3, 4]. However, because the reflection of each deterioration factor in each parameter was small, there is a possibility of causing the diagnostic error. Therefore, a new algorithm for PEFC performance diagnostics has been developed by solving the transient response using the third differential equation directly. A new diagnostic approximates the transient response of PEFC directly using the on-line algorithm of the method of least squares, and obtains three diagnostic parameters sequentially. The adequacy of a new algorithm is verified by evaluating the cell inner heat flux distribution using heat flux sensors and a special separator that can measure heat flux distribution as shown in Figure 3 and 4, respectively. the separator has four spaces for installing the heat flux sensor to the back of each electrode as shown in Figure 4 (b). After installing each heat flux sensor as shown in Figure 4 (c), each space was buried so that there was no gap by the carbon block as shown in Figure 4 (d). By installing the sensors close to the reaction area, the sensors could measure how much heat flows from inside to outside and from outside to inside. Figure 5 shows Cross diagram of PEFC.

Figure 1. Photograph of PEFC short stack

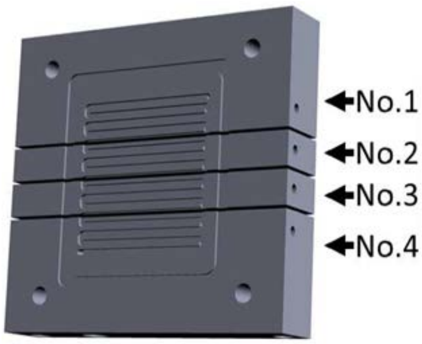
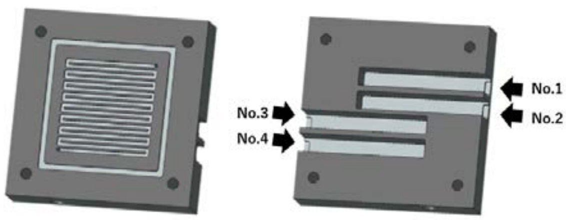
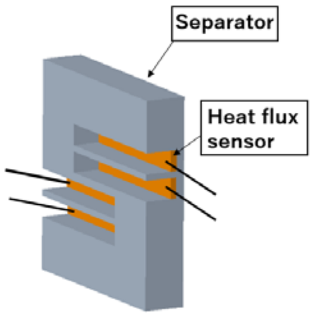


Figure 2. Schematic diagram of four segmented separator

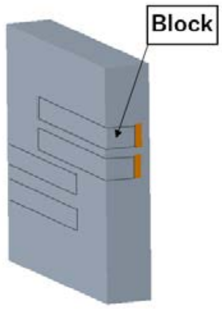
Figure 3. Heat flux sensor



(a) front view (b) back view



(c) Separator installed heat flux sensors



(d) Separator installed heat flux sensors and blocks

Figure 4. Schematic diagram of separator for measuring heat flux

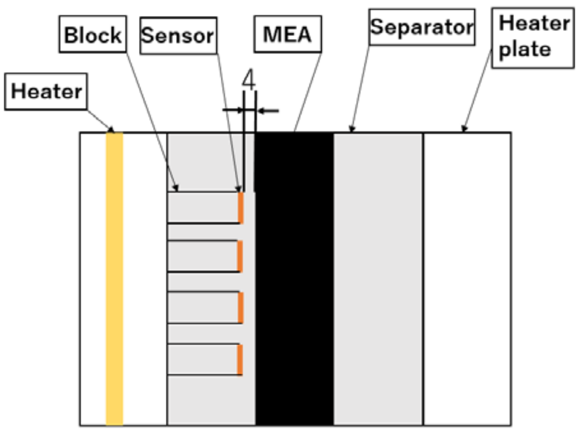
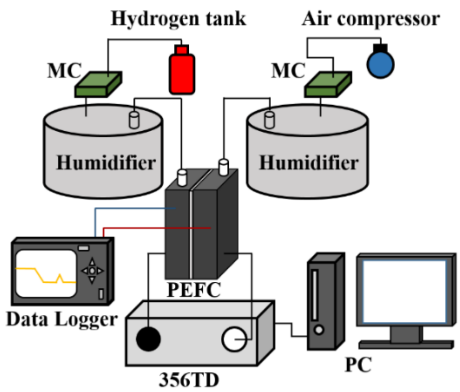


Figure 5. Cross diagram of PEFC

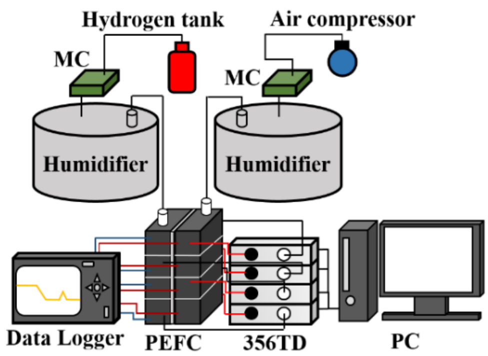
EXPERIMENT

Figure 6 shows the experimental apparatus for the evaluation of the cell performance. Figure 6 (a) and (b) show the experimental apparatus for a single cell and a short stuck respectively. The separator was made of carbon and have an effective electrode area of 25cm^2 and a serpentine gas channel of 1mm×1mm. Here, each portion of separator used this paper from the top end was numbered from No.1 to No.4. Anode gas and cathode gas were humidified by passing through the humidifier and were supplied to the cell. In order to prevent dew formation in the supply pipe, the piping between the humidifier and the cell was made shorter and was maintained to 80℃with a ribbon heater. A cell temperature, a cell voltage and four heat flux were recorded in a computer online by a data logger. A milliohm meter with AC 4 probes was used to measure a cell resistance. The PEFC Performance Diagnostic System (PPDS; 356TD) composed of an A/D converter and a pulse generator measured a transient response of PEFC during 28.2msec. The obtained transient response was converted to CSV data and sent to the PC by USB cable, and each fitting parameter was delivered by analyzing this CSV data. Here, because it was clarified that the cell voltage drop from the current interruption to 0.04msec in a transient response means a resistance polarization, the PPDS analyzed transient response that subtracted voltage drop in this section, and derived parameters of an activation and a diffusion polarizations [5]. This paper changed a new analytic algorithm.

The experimental conditions were prepared two humidified conditions and an influence of air utilization ratio as shown in Table 1 and 2, respectively. The standard condition was worked under the full humidifying that the temperature of the cell and the humidifier is set at 80℃. On the other hand, the non-humidifying condition was worked without humidifying and the cell temperature was set at 30℃. Here, the cell current density was 0.08A/cm^2. In the experiment that examines the influence of humidifying, the fuel utilization was 70%, and the air utilization was 40%, respectively. In the experiment that examines the influence of oxidant gas utilization, the fuel utilization was fixed at 70%, and the air utilization was varied from 40% to 90% every 10%. The operating pressure was atmosphere.



(a) for single cell



(b) for quadrisection separator

Figure 6. Schematic diagram of experimental apparatus

Table 1. Experimental conditions that examines the influence of humidifying

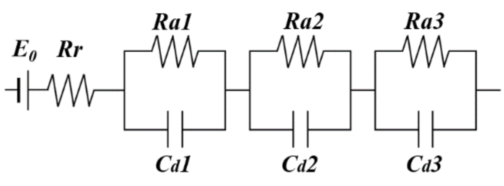
	Standard	Non-humidifying
Fuel Utilization [%]	70	
Air Utilization [%]	40	
Standard Current Density [A/cm^2]	0.08	
Cell Temperature [℃]	80	30
Humidifier Temperature (AN) [℃]	80	Not use
Humidifier Temperature (CA) [℃]	80	Not use

Table 2. Experimental conditions that examines the influence of oxidant gas utilization

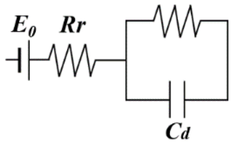
Operating Condition	
Fuel Utilization [%]	70
Air Utilization [%]	40,50,60,70,80,90
Standard Current Density[A/cm^2]	0.08
Cell Temperature[°C]	80
Humidifier Temperature[°C]	80

Diagnostic principle

Generally, although the PEFC performance is diagnosed by an I-V curve and a Cole-Cole plot, each method has both merits and demerits. The former diagnostics cannot identify the degradation factor though can diagnose a deterioration of a cell performance easily. On the other hand, although the latter diagnostics can identify the degradation factor, its diagnostic time is longer than the former one. The PPDS developed by us can diagnose the degradation factor of PEFC instantaneously by evaluating the transient response. At the first stage of this study, the transient response was expressed by the equivalent circuit composed of three RC circuits where anode reaction, cathode reaction and electrolyte resistance are imitated as shown in Figure 7 (a). At first, an evaluating equation was derived from this equivalent circuit by Laplace transforming. In Eq. (1), each parameter stands for the following: E_0, Rr, Ra, and Cd mean the open circuit voltage, the resistance of ions in an electrolyte, a diffusion resistance, an activation loss and an electric double layer capacity generated at the interface between the electrode and electrolyte, respectively. Generally, it is well known that the anode polarization is very small compared with the cathode polarization, and the resistance polarization is also reflected in voltage drop to 0 – 1msec in the transient response. Therefore, in the second stage, we changed to the equivalent circuit shown only in cathode electrode as shown in Figure 7 (b), and the fitting equation was also changed to Eq. (2). Moreover, the resistance polarization is derived by Eq. (3). As a result of deterioration diagnosis under various conditions by this method, the correlation between each parameter and each polarization was clarified as following: ΔV parameter, A_1 parameter and t_1 parameter mean the resistance polarization, the activation polarization and the diffusion polarization, respectively. The conventional diagnostics had been diagnosing the deteriorating situation of various cells using these parameters (ΔV, A_1 and t_1) as diagnostic parameters [6]. However, because the reflection of each deterioration factor in each parameter was small, it was necessary to diagnose the parameters strictly. Therefore, as there was a possibility of causing the diagnostic error, it should be improved. We have developed a new algorithm for PEFC performance diagnostics that solves the transient response by the third differential equation as shown in Eq. (4) directly to satisfy the demand mentioned above last year. The third differential Eq. (4) was discretize by the difference method and was converted into Eq. (5). The model Eq. (6) was obtained by simplifying Eq. (5). Each parameter (a, b, c) was obtained by fitting the transient response by Eq. (6) using on-line algorithm. Here, e_t on the right side of Eq. (6) means error in measurement. although the initial value of each parameter was replaced with the convergence value obtained from this online algorithm sequentially, an increase in the repetition processing lengthens the analytical time. the time variance of the parameter mentioned above should be checked to confirm the applicability to PEFC's transient response of the third differential equation. Figure 8 shows the transition of varying of each parameter by repetitive processing. As you can see, the result stabilized in the third, and the time variance of each parameter stabilizes with an increase in an analytical frequency. Therefore, we were able to confirm that the application for third differential equation to transient response is appropriate [7-10].



(a) equivalent circuit at the beginning of study



(b) equivalent circuit only on the cathode side

Figure 7. Equivalent circuit of PEFC

$$V_{out}(t) = y_0 + A_1 e^{-\frac{t}{t_1}} + A_2 e^{-\frac{t}{t_2}} + A_3 e^{-\frac{t}{t_3}} \quad (1)$$

$$V_{out}(t) = y_0 + A_1 e^{-\frac{t}{t_1}} \quad (2)$$

$$\Delta V = V_{out}(0) - V_{out}(100\mu sec) \quad (3)$$

$$V_{out}(t) = \frac{d^3 y(t)}{dx^3} + a\frac{d^2 y(t)}{dx^2} + b\frac{dy(t)}{dx} + cy(t) \quad (4)$$

$$y(t + 3 \cdot \Delta t) + ay(t + 2 \cdot \Delta t)$$

$$+by(t + \Delta t) + cy(t) = e_t \quad (5)$$

$$y_{t+3} + ay_{t+2} + by_{t+1} + cy_t = e_t \quad (6)$$

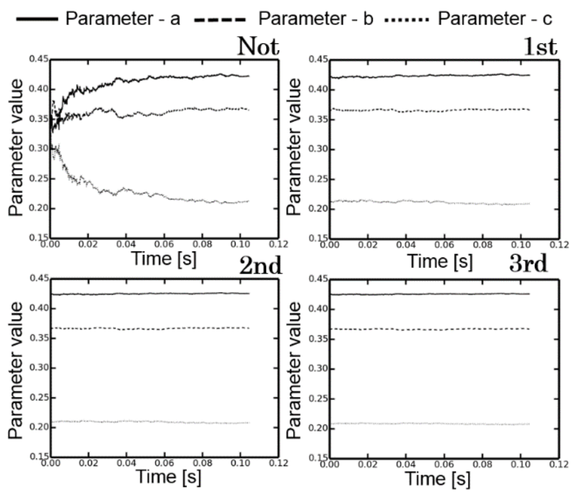


Figure 8. Validation of application for the third differential equation to transient response

RESULT AND DISCUSSION

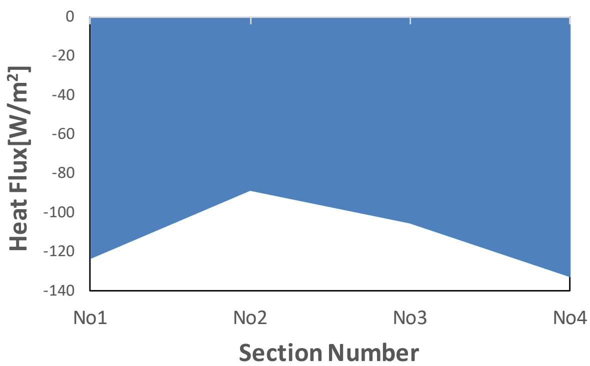
Verifying the heat flux distribution by presence of humidifying

We aim to confirm the validity of the new diagnostics by comparing with the conventional diagnostics under condition of examining influence by presence of humidifying. In order to verify the correlation, firstly the heat flux distribution of each humidifying condition was measured by the separator as shown in Figure 4. Figure 9 shows the heat flux distribution in direction of gas flow. Here, the heat flow from the cell to the separator side was defined as a positive. From Figure 9 (a), the heat flux becomes negative by heating with the heater plate because the cell temperature is maintained by the heater plate at 80°C. However, the heat flux at the center part of the cell (No.2) is smaller than other positions because the cell is heated by emitting the latent heat when the steam generated by the cell reaction condenses. Moreover, because the current density at the cell midrange is generally high, the cell temperature becomes higher than other parts in the cell by heating with the cell reaction. In previous study [4], It was confirmed that midrange has the highest current density, as shown in Fig 10. It shows heat distribution in the same electrode. Consequently, the heat flux at the center part of the cell becomes smaller. Therefore, we think that a weak flooding phenomenon is caused from the center part of the cell to gas outlet under the standard operating condition, and the cell reaction at the center part is more active than other position. From Figure 9 (b), the change of the heat flux originates in only the cell reaction because the cell is not heated by the heater plate under the non-humidifying condition. Because the steam generated by the reaction is added to the supplied gas with the heat of reaction, the heat flux is accumulated from the center part of the cell to gas outlet. Based on these findings, we verified two degradation factor distributions obtained by the conventional diagnostics and the new diagnostics.

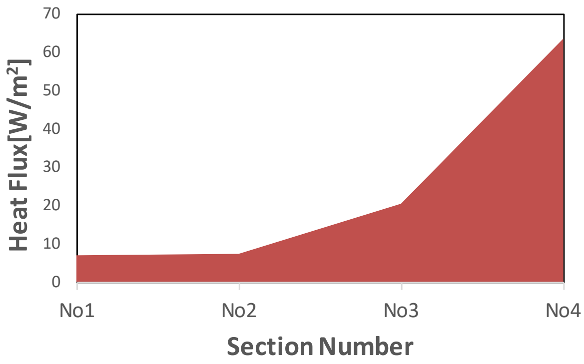
Confirmation of correlation between former diagnostics parameter and new diagnostics parameter

Figure 11 shows polarization distribution obtained using the conventional diagnostics by presence of humidifying. In both conditions, A_1 (the activation polarization) and t_1 parameter (the diffusion polarization) grow toward the gas outlet (No.4) from the gas inlet (No.1) in all current density region though ΔV parameter (the resistance polarization) decreases. This reason is that the flooding/plugging phenomena is caused by flowing as steam generated by cell reaction condensing to the gas downstream, and consequently A_1 and t_1 parameter of the downstream increase. Oppositely, because this excess water wets the membrane, ΔV parameter decreases toward the gas outlet from the gas inlet. Especially, this tendency is remarkable in the condition without heating and humidifying. However, the difference of the parameter under the same condition by each place is small though the difference of the parameter by presence of humidifying is great. On the other hand, the diagnostics result by the new diagnostics is shown in Fig.12. The change of parameter-c on the current density is the largest, and because the increase of parameter-c means the improvement of the cell performance as shown in Eq. (6), the behavior of parameter-c becomes opposite of A_1 in the previous diagnostics. Therefore, parameter-c may be corresponding to A_1 (activation polarization). On the other hand, the change of parameter-b on the current density is the smallest, and the behavior of parameter-b and ΔV parameter under non-humidifying condition resembles closely. Therefore, parameter-b may be corresponding to ΔV (resistance polarization). Finally, the change of parameter-a decreases with the increase of current density, and especially it decreases drastically under non-humidifying condition. If the parameter-a decreases, it means there are few voltage variations to an electric current density increase. Moreover, if the parameter-a became minus, it means the cell voltage decreases. Therefore, because this behavior and the flooding/plugging phenomena are similar, we are considering that parameter-a is corresponding t1 (diffusion polarization) at present.

From these results, because the correlation between each parameter by the new algorithm and each polarization cannot be identified enough, it should be verified furthermore in the condition that each polarization is greatly reflected. However, because the new diagnostics can greatly reflect the difference of the humidifying conditions in each parameter as well as the conventional diagnostics and it was able to shorten the diagnosing time, we are considering that its validity was verified.

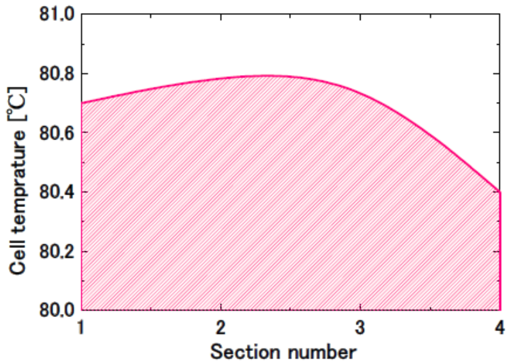


(a) Standard operating condition

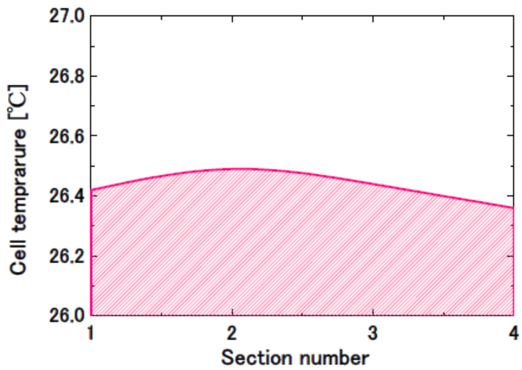


(b) Non-humidifying condition

Figure 9. Heat flux distribution in direction of gas flow



(a) Standard operating condition



(b) Non-humidifying operating condition

Figure 10. Heat distribution in the same Electrode

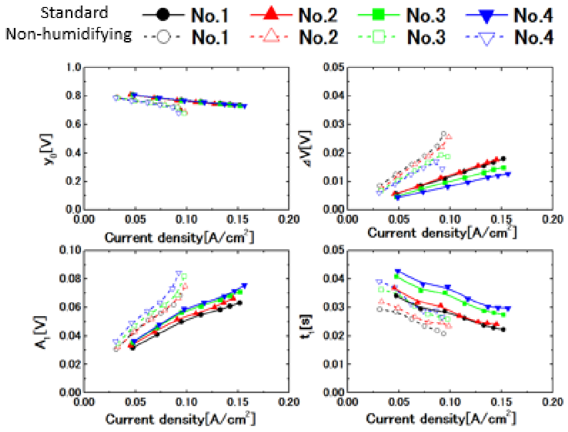


Figure 11. Polarization distribution obtained by the conventional diagnostics

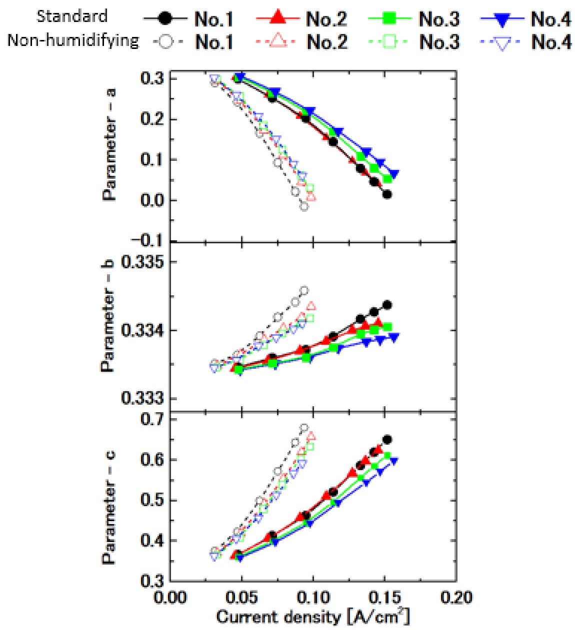


Figure 12. Diagnostics result by the new diagnostics

CONCLUSIONS

The results obtained in this study are summarized as follows.

- By measuring heat flux inside the PEFC, we verified the degradation factor for PEFC.
- We verified the degradation factors in each part by comparing with the conventional data.
- The new algorithm was able to greatly reflect the difference of the humidifying conditions in each parameter as well as the conventional algorithm.

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