

Real-time Measurement of Water Content of CCM in On-board Fuel Cell Stack System

Toru IWANARI*

Kazuyoshi MIYAJIMA*

Koichiro FURUSAWA*

Masajiro INOUE*

ABSTRACT

In order to increase the durability of fuel cell stacks, the in-plane water content of the catalyst-coated membranes (CCM) in the cells is controlled within the proper range using stack impedance.

Setting out to elucidate the status of the in-plane water content of the CCM, the research discussed in this paper employed a water content distribution measurement system to conduct real-time measurements of the in-plane water content of the cells in a fuel cell stack forming part of an on-board generation system. The use of the system makes it possible to determine the in-plane water content of the CCM during both constant current generation and transient current generation. The results of this study verified the effectiveness of the in-plane CCM water content control employed in the 2016 model FCV. In addition, optimization of the control of in-plane water content of the CCM has also had an effect in further increasing the durability of the fuel cell stacks.

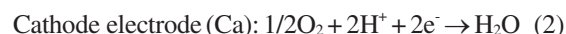
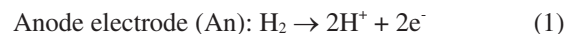
1. Introduction

The environmental effects of CO₂, NO_x and other pollutants in automotive exhaust gases and the future depletion of fossil fuels make the development of clean, high-fuel-efficiency vehicles an urgent task. Seeking to realize a sustainable society based on energy circulation, Honda is engaged in research and development efforts in relation to fuel cell vehicles (FCV), which use hydrogen rather than fossil fuels, and fuel cell technologies⁽¹⁾.

Figure 1 shows an image of the structure of a fuel cell and its internal chemical reactions. The fuel cell (simply termed “cell” below) is made up of a membrane electrode assembly (MEA) and separators that form gas channels. A fuel cell stack (termed “stack” below) is created by layering multiple cells together.

The MEA is made up of a polymer electrolyte membrane (PEM), a catalyst layer (CL), and a gas diffusion layer (GDL). The PEM making up the CL are also called catalyst-coated membranes (CCM).

In the cell, a hydrogen oxidation reaction occurs at the anode electrode as shown by Eq. (1), and an oxygen reduction reaction occurs at the cathode electrode as shown by Eq. (2). These chemical reactions between hydrogen and oxygen produce electricity and water.



In addition to seeking increased compactness and weight reductions, and realizing high-efficiency-generation performance with higher output, it is also necessary for the stacks fitted in FCV to display durability in relation to the fluctuations in current load to which cells used in automotive environments are subjected. To help

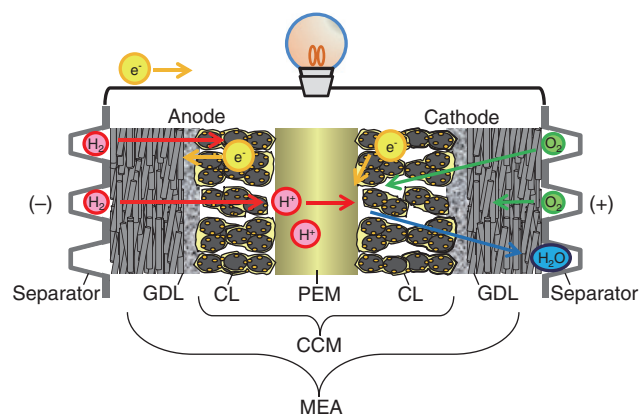


Fig. 1 Schematic image of fuel cell

* Automobile R&D Center

ensure durability in cells, it is necessary to maintain the surface area of the electrode catalysts, which contributes significantly to the output of the cell, and to maintain the thickness of the PEM, which functions both to separate the oxygen and the hydrogen that serves as fuel, and to electrically insulate the anode and the cathode.

The ability to maintain the surface area of the electrode catalysts and the thickness of the PEM is closely related to the in-plane water content of the CCM in the cell. Generally, when the water content is high, the electrode catalysts become coagulated due to dissolution, agglomeration, and redeposition, and the decline in the catalyst surface area accelerates. It has also been reported that when the water content is low, impurities and hydrogen peroxide accumulate in the PEM, promoting chemical degradation and reducing the thickness of the PEM⁽²⁾.

In order to increase the durability of automotive fuel cells, it is therefore necessary to identify the in-plane distribution of the water content of the CCM and control it to within the proper range.

2. Development Goals

The development of the stack for the 2016 model FCV therefore sought to realize increased stack durability through the development of multi-segment impedance sensors⁽³⁾ to identify the in-plane distribution of water content of the CCM in the cells and the calculation of the optimum in-plane water content distribution using simulations⁽⁴⁾.

The research discussed in this paper set out to use the developed impedance distribution measurement system (IDMS) in order to conduct real-time test bench measurements of the in-plane distribution of water content of the CCM of the cells in a stack used in an actual on-board generation system, and to verify that the in-plane water content was within the proper range. The outcomes of the research would be reflected in the control method employed in actual on-board generation systems.

3. Necessity for Measurements

The in-plane distribution of water content of the CCM in the cells displays a range of variation due to instantaneous changes in operating conditions, including the flow rate and pressure of the gases supplied to the stack, the temperature of the stack, and the current being generated. However, in order to increase the durability of the cells, it is essential to constantly maintain the in-plane water content of the CCM to a range within upper and lower limits. Upper and lower limit values for in-plane water content of the CCM were set based on the results of CCM durability tests using miniature cells, as shown in Fig. 2.

In the actual on-board generation system, the in-plane water content of the CCM in the cells is controlled within upper and lower limits using the measured stack impedance, based on the relationship between in-plane water content

and stack impedance shown in Fig. 3.

While a variety of factors affect the in-plane water content of the CCM, in the on-board generation system used in the 2016 model FCV, the method applied to control water content is control of the level of humidity of the air supplied to the stack. A humidifier bypass control valve connected in parallel to a humidifier adjusts the quantity of airflow through the humidifier, controlling the in-plane water content of the CCM in the cells (Fig. 4).

The range for control of stack impedance ("Target impedance" in Fig. 3) is affected by the uneven in-plane distribution of water content of the CCM ("Distribution of water content" in Fig. 3) and measurement error. The optimization of the uneven in-plane distribution of water content of the CCM by means of simulation of constant current generation contributed to expanding the range for control of stack impedance.

However, despite the fact that the uneven in-plane distribution of water content of the CCM was taken into consideration in setting the range for control of stack impedance, it was predicted using a simulation of constant

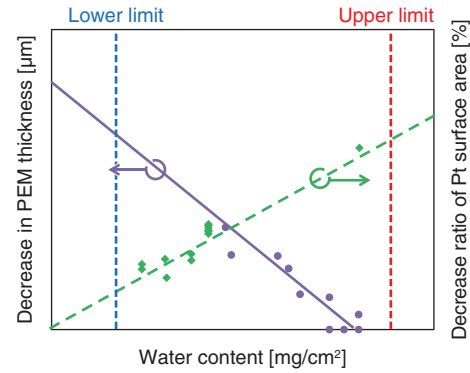


Fig. 2 Upper and lower limits for water content to maintain PEM thickness and Pt surface area

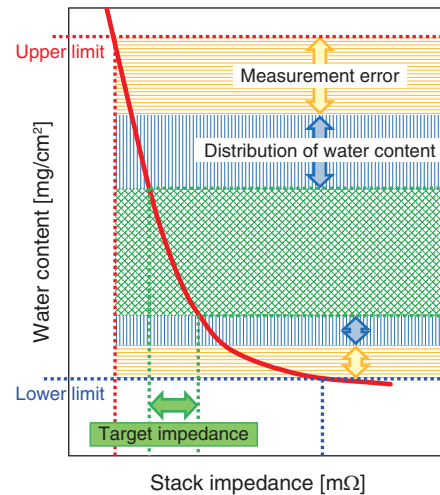


Fig. 3 Relationship between stack impedance and water content

current generation. Because of this, it was necessary to verify whether the in-plane water content of the CCM was maintained within the scope of the upper and lower limit values during transient current generation in an actual on-board generation system.

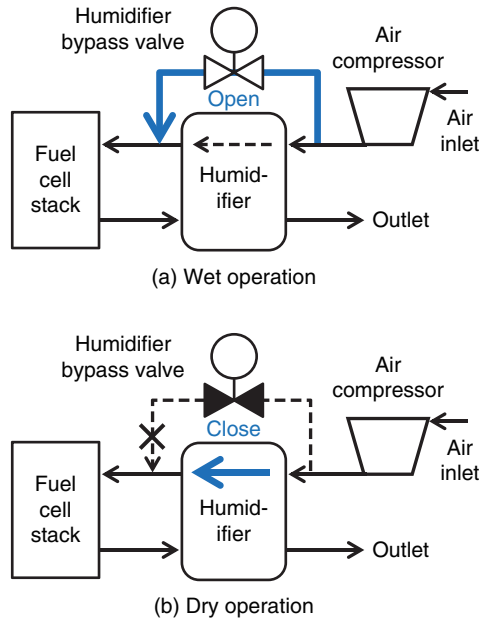


Fig. 4 Schematic image of humidity control of supplied air

4. Issues of Conventional Measurement Method

Conventionally, the dry weight method (Fig. 5) or the nuclear magnetic resonance (NMR)⁽⁵⁾ method have been used to measure the in-plane distribution of water content of the CCM.

The dry weight method takes the difference in weight between objects when they contain water and when they do not as the weight of the water. When employing this measurement method, the cells are operated for a set period of time under the conditions for which it is desired to take measurements of the in-plane water content of the CCM, following which they are dismantled. The CCM is then cut into a set number of segments, which are placed in bags from which their water content cannot evaporate, and then weighed. Following this, they are dried, and weighed once again. The difference in weight between the two measurements is considered to be the in-plane water content of the CCM. Given the potential for evaporation of the water content during the dismantling of the cells and the cutting of the CCM, it is necessary to perform the operations quickly in a high-humidity environment. In addition, because the in-plane water content of the CCM can only be measured under fixed generating conditions, the facts that it is necessary to

take repeated measurements for each operating condition, and that it is not possible to conduct measurements under transient conditions, have represented issues for the method.

In the NMR method, a test specimen is placed in a magnetic field, and is bombarded by a high-frequency magnetic field in order to excite nuclear spin resonance. The NMR signal produced by the test specimen is received and its atomic state is measured, enabling measurement of the local amount of water in the CCM in real time. Because this method necessitates exposing the stack and the actual on-board generation system to a strong magnetic field, the large size of the measurement apparatus and the potential for malfunctioning of the system have represented issues.

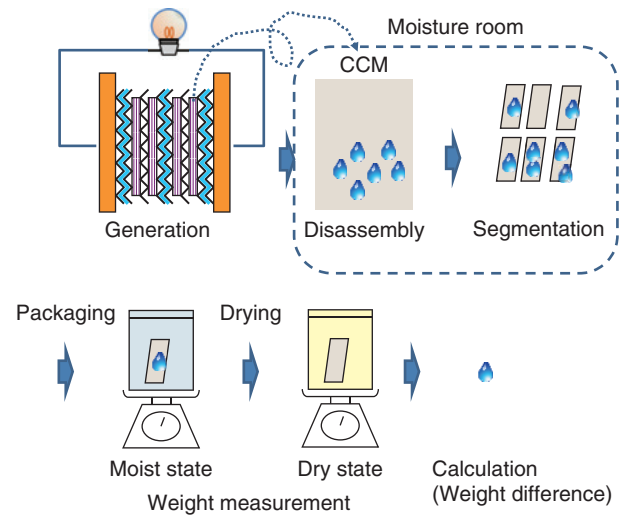


Fig. 5 Dry weight method for measurement of water content of CCM

5. Method of Addressing Issues

An IDMS for the test bench measurement of the distribution of water content of the cells through measurement of impedance in the stacks used in actual on-board generation systems was introduced in order to measure water content of the CCM, as shown in Fig. 6. The current superimposed for measurement is measured as a current signal (V_2) by means of the shunt resistor of a terminal pad with split sensors [shown in Fig. 6(b)]. At the same time, the cell voltage signal (V_1) is measured [Fig. 6(c)]. This makes it possible to calculate impedance, and thus to calculate in-plane water content of the CCM. It can then be verified whether the in-plane water content of the CCM remains within the upper and lower limit values during constant current generation and transient current generation. Because these measurements are conducted in a high-voltage and high-frequency environment, adequate consideration is given to insulation of devices and measures to respond to noise.

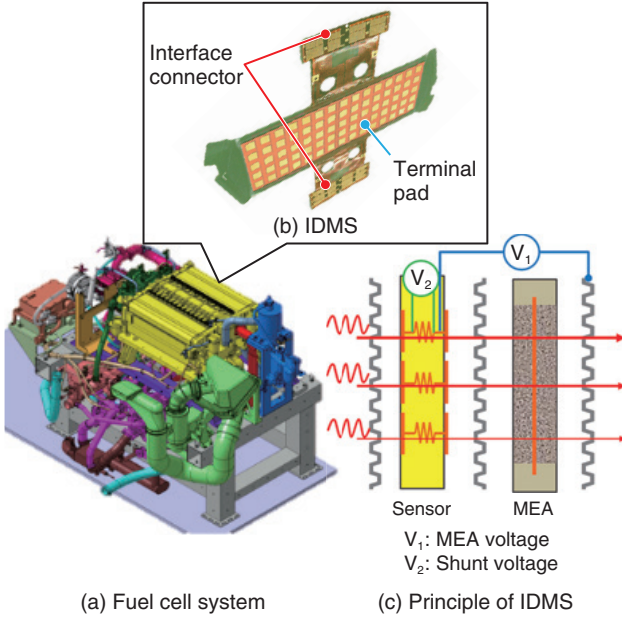


Fig. 6 Fuel cell system with IDMS for bench use

6. Results of Bench Test

6.1. Constant-speed Running Mode

The first verification measurements focused on whether the in-plane water content of the CCM remained within the upper and lower limit values in constant-speed running mode (constant current generation).

Figure 7 shows results for the in-plane distribution of water content of the CCM for different current ranges. In the low-current range, as shown in Fig. 7(a), because the water produced on the cathode side flows towards the outlet (Ca OUT), the amount of in-plane water in the CCM increases the closer the CCM are to the outlet. Because of this, it is possible for the amount of in-plane water in the CCM on the cathode inlet side (Ca IN) to drop below the lower limit value. It is considered that the slight decline in the amount of in-plane water in the CCM on the cathode outlet side (Ca OUT), as shown in Fig. 8, is due to water flowing to the opposite anode side via the CCM. By contrast, in the high-current range, the highest amount of in-plane water in the CCM shifts from the cathode outlet side (Ca OUT) to the cathode inlet side (Ca IN). It is considered that this is because, with the increase in current, the area of generation shifts to the cathode inlet side (Ca IN), which has a high concentration of oxygen. Because generation produces a high amount of water, it is possible that the in-plane water content of the CCM in the central area of the cell could increase above the upper limit value.

Figure 9 shows results for the in-plane water content of the CCM for different current ranges. The results make it possible to confirm that the stack impedance value is appropriately controlled within the upper and lower limit

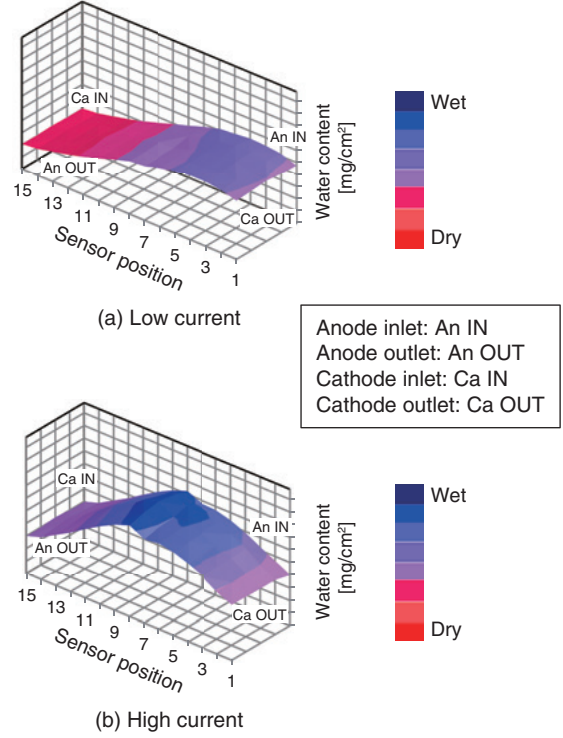


Fig. 7 Water content distribution under conditions of constant current generation

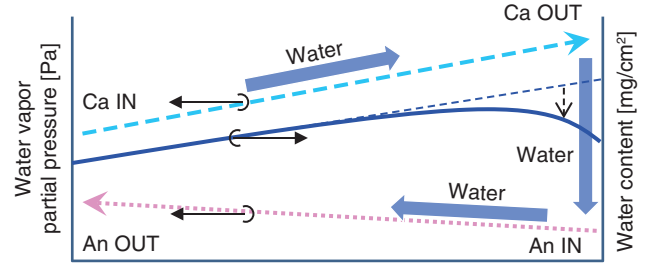


Fig. 8 Schematic image of movement of water in CCM

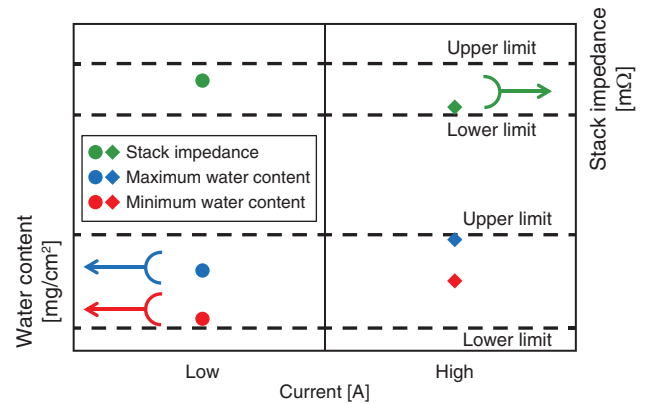


Fig. 9 Results for water content under conditions of constant current generation

values. It was also confirmed that the in-plane water content of the CCM remained within the upper and lower limit values in the cases of the lower limit value on the cathode inlet side in the low-current range and the upper limit value for the CCM in the central area of the cell in the high-current range.

6.2. Stack Evaluation Running Mode

Figure 10 shows a schematic image of stack evaluation modes (transient current generation) and stack impedance values employed during development. Using the water content distribution measurement system, it was possible to measure the in-plane distribution of water content of the CCM in real time during running mode.

The in-plane water content of the CCM varies considerably during running mode, increasing (the impedance value declines) during acceleration, and decreasing (the impedance value increases) during deceleration and idling. The study therefore focused on whether or not the in-plane water content of the CCM remained within the upper and lower limit values in all areas of the cell. The results of verification for each operating mode will be discussed below.

6.2.1. During acceleration and deceleration

Figure 11 shows time series data for the maximum and minimum values for in-plane water content of the CCM during acceleration and deceleration. Figure 12(a) shows results for the measurement of the in-plane distribution of water content of the CCM in the direction of the length of the cell, where the in-plane water content reaches its maximum during acceleration. The blue and red circles within the figure show maximum and minimum values for the in-plane water content of the CCM in the width direction of the cell. As in the case of the high-current range during constant-speed running operation [Fig. 7(b)], during acceleration the in-plane water content of the CCM reaches its maximum value in the center of the cell in the direction of gas flow but remains below the upper limit value.

Figure 12(b) shows the results of measurements of the

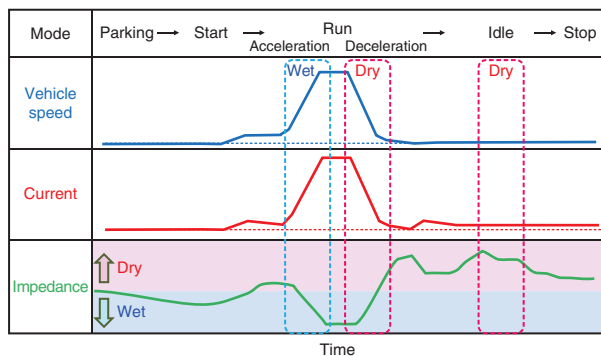


Fig. 10 Schematic image of evaluation running mode for fuel cell vehicle

in-plane water content of the CCM during deceleration, when water content reaches its minimum. In the transition from acceleration to deceleration, the in-plane water content of the CCM at the cathode inlet declines to close to the lower limit value. In the high-current range, as shown in Fig. 12(a), the in-plane water content of the CCM is high because the amount of water produced by generation is high, but during deceleration, the amount of water produced

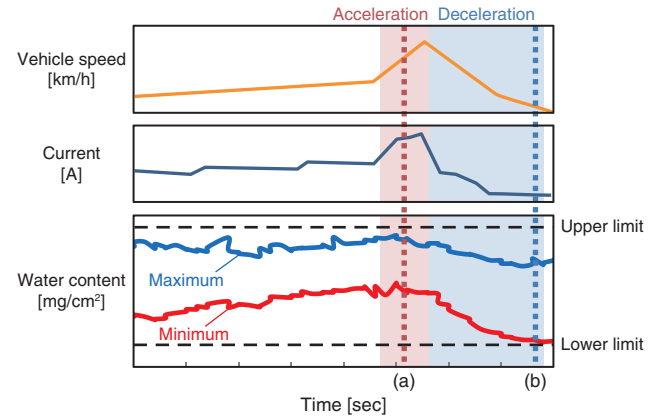
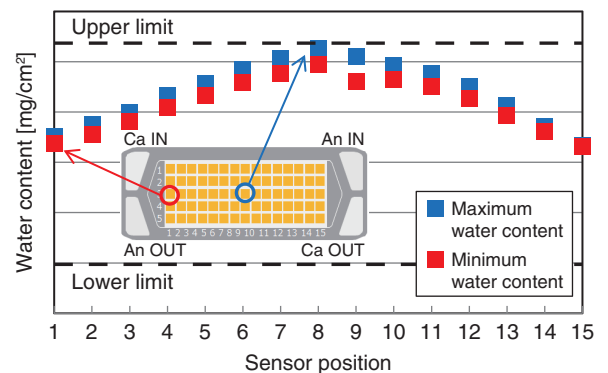
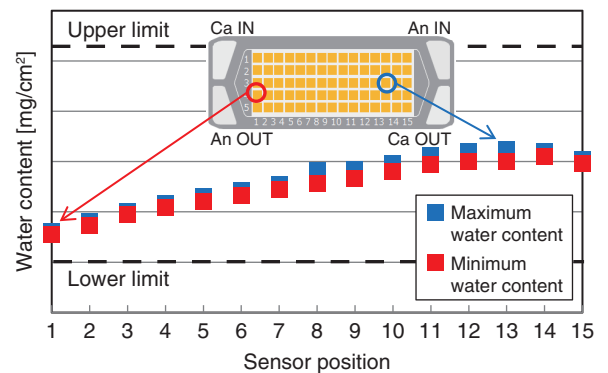


Fig. 11 Time-series results for water content in acceleration mode and deceleration mode



(a) In acceleration mode



(b) In deceleration mode

Fig. 12 Results for water content distribution in acceleration mode and deceleration mode

by generation declines in response to the current. In addition, because the high-current generation immediately preceding deceleration increases the temperature of the stack, the amount of saturation vapor in the gases increases, and more water is discharged outside the stack. In addition, during deceleration the quantity of airflow becomes excessive because of a lag in the response of air supply control. It is considered that the synergistic effect of these factors reduces the in-plane water content of the CCM close to the cathode inlet. It was verified, however, that the in-plane water content of the CCM during deceleration remained within the upper and lower limit values.

6.2.2. During idling

Figures 13 and 14 show the results of measurement of the in-plane water content of the CCM during idling. As the results show, the in-plane water content of the CCM at the cathode inlet declines with time, until it drops below the lower limit value. Despite the fact that stack impedance is controlled within the desired range, during idling the amount of water produced by generation is low, and dry air is supplied to the stack, with the result that the decline in the in-plane water content of the CCM close to the cathode inlet is greater than initially projected.

In response, in addition to adjusting the total quantity of air supplied to the stack, the ratio of supplied air passing through the humidifier was increased during idling, when very little water is produced by generation, increasing the water content of the CCM close to the cathode inlet.

It was verified that this change in control was effective, with the results shown in Fig. 15 demonstrating that the water content of the CCM at the cathode inlet no longer declines below the lower limit value during idling.

Real-time measurement of the in-plane distribution of water content of the CCM in cells employed in actual on-board generation systems has made it possible to verify that the water content is controlled within upper and lower limit values even in stack evaluation running mode.

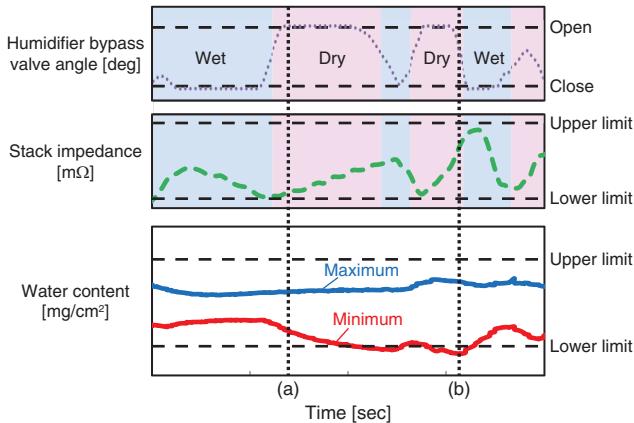
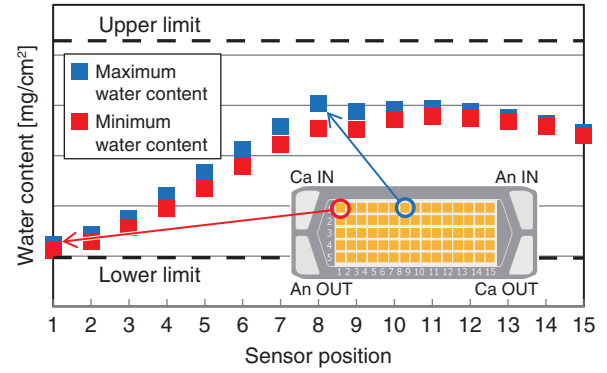
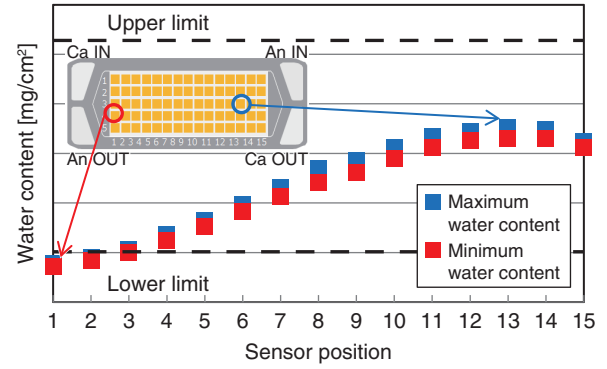


Fig. 13 Time-series results for water content in idling mode



(a) Immediately after idling



(b) During idling

Fig. 14 Results for water content distribution in idling mode

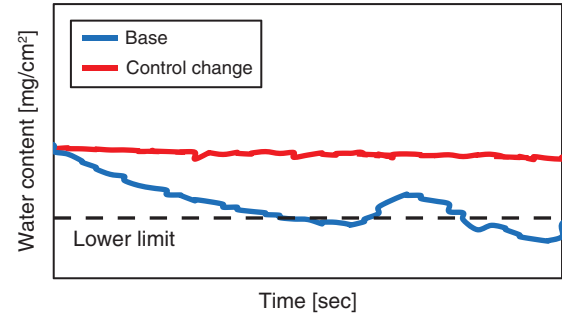


Fig. 15 Effect of change in control on water content at cathode inlet

7. Conclusion

Verification of the control of the in-plane water content of the CCM in cells employed in the 2016 model FCV generation system produced the following results:

- (1) It was verified that during constant current generation, stack impedance control maintained the in-plane water content of the CCM within the upper and lower limit values.

- (2) It was verified that the in-plane water content of the CCM was maintained within the upper and lower limit values during acceleration and deceleration, when transient current generation is occurring.
- (3) The causes of a reduction in the in-plane water content of the CCM below the lower limit value during idling were identified, and measures introduced in response were verified to be effective.

These results demonstrate the effectiveness of control of the in-plane water content of the CCM in cells using stack impedance. In addition, the optimization of control has also had an effect in increasing the durability of the fuel cell stack.

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■ Author ■



Toru IWANARI



Kazuyoshi MIYAJIMA



Koichiro FURUSAWA



Masajiro INOUE