

In-plane Visualization of Oxygen Partial Pressure Distribution on Cathode Side during Fuel Cell Operation

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ABSTRACT

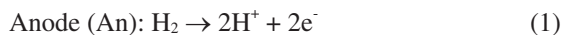
A system capable of visualizing and measuring the distribution of oxygen partial pressure in fuel cells during vehicle operation at a high level of resolution has been developed in order to help enable the creation of a method of control that would ameliorate the decline in fuel cell performance. Changes in the fluorescent intensity of an oxygen-sensitive reagent coating the gas flow paths of an acrylic plate designed for the visualization of generation were used to measure oxygen partial pressure.

The research discussed in this paper made it possible to predict the distribution of increases in the resistance of the materials employed in the fuel cell, which is the main cause of performance declines at high current densities. In addition, the research verified the effectiveness of applying control to reduce the partial pressure of the residual oxygen in the cathode tubes in reducing this increase in resistance, making it possible to develop a method of control that ameliorated the decline in output displayed by fuel cell vehicles.

1. Introduction

The development of clean, high-fuel-efficiency vehicles is an urgent issue in terms of responding to the global environmental impact of pollutants such as CO₂ and NO_x in automotive exhaust gas and the future depletion of fossil fuels. Aiming for the realization of a society based on renewable energy, Honda is advancing the development of fuel cell vehicles, which use hydrogen as a fuel rather than fossil fuels.

Fuel cells are generation devices that produce electricity from the chemical reaction between hydrogen and oxygen. The actual reaction comprises a hydrogen oxidation reaction at the anode (Equation (1)) and an oxygen reduction reaction at the cathode (Equation (2)). Water is produced as a by-product of the reaction at the cathode.



Honda is proceeding with the development of vehicles using lightweight and compact polymer electrolyte fuel cells (PEFC), which are able to be started even at low temperatures⁽¹⁾.

Figure 1 shows a schematic image of a PEFC. PEFC comprise a membrane electrode assembly (MEA), which positions catalyst layers (CAT) and gas diffusion layers

(GDL) on each side of a polymer electrolyte membrane (PEM), and separators that form flow paths for gases and coolant.

The smallest unit formed by these elements is termed a cell. Multiple cells arranged in layers are termed a stack. The PEM promotes the transfer of protons (H⁺) produced in the hydrogen oxidation reaction shown in Eq. (1). The CAT positioned on both sides of the PEM promote the reactions shown as Eqs. (1) and (2). The GDL function to disperse reaction gases to the CAT and to supply power. The separators supply reaction gases to the anode and cathode

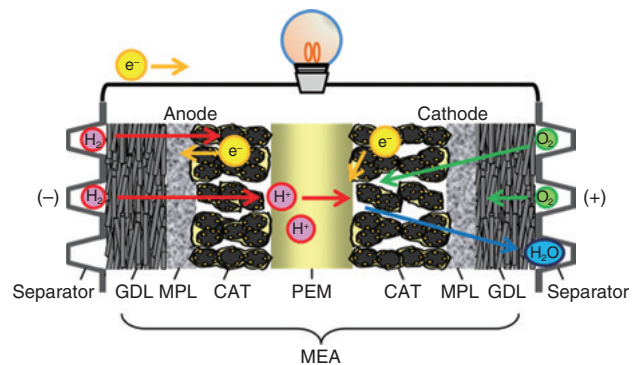


Fig. 1 Schematic image of PEFC

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electrodes, isolate reaction gases from neighboring cells, provide a cooling function through the supply of coolant, and supply power from the CAT.

Technologies for the realization of higher-power and higher-efficiency generation are necessary for the achievement of compactness and light weight in fuel cell systems for fitting in vehicles.

Figure 2 shows the energy loss that occurs during generation in fuel cells due to three forms of polarization loss.

The three forms of polarization are activation polarization originating in activation of the catalyst, ohmic polarization originating in proton and electron transfer, and concentration polarization originating in the transport resistance of the reaction gases. Ohmic polarization and concentration polarization in particular increase significantly under conditions of high current density, making it necessary to reduce these forms of polarization in order to realize high-efficiency operation at high current densities.

The design of cathode electrode materials and oxygen concentration control are necessary for the reduction of concentration polarization. Sensors for the measurement of oxygen at the electrode are necessary in turn for the study of these factors. MEA with inbuilt optic fiber oxygen sensors⁽²⁾ are suitable for this task, meaning that a measurement method is already available. This paper will focus on the remaining issue, the method of reduction of ohmic polarization; it is necessary to control the increase in the resistance of the PEM, which is the major factor in this form of polarization. It is known that when the PEM is exposed to the fuel cell environment, in which both hydrogen and oxygen are present, the sulfone groups that promote proton transfer are eliminated, and resistance increases⁽³⁾. Vehicle lifespan is taken into consideration in the development of fuel cell vehicles, and the development process incorporates system control targeting the increase in the resistance of the PEM. Realizing an accurate understanding of the mixed gas environment in the fuel cell stack is an important factor in the creation of this control.

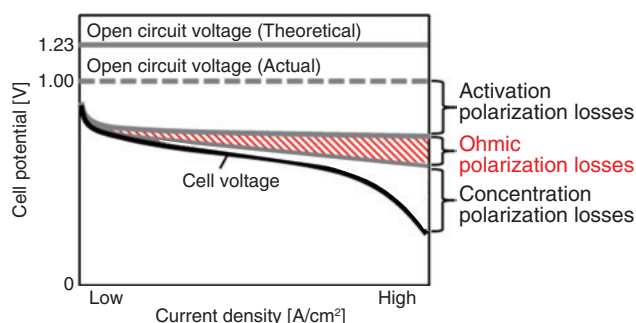


Fig. 2 I-V curve and various polarization losses of operating fuel cell

2. Necessity for Visualization of Oxygen Partial Pressure

2.1. Increase in PEM Resistance due to Hydrogen and Oxygen Combustion Reaction

Figure 3 shows the mechanism of increase in the resistance of the PEM that is generally known. Because the material of the PEM contains water, miniscule amounts of gas are transmitted inside the PEM. When this happens, some hydrogen and oxygen directly combust on the CAT, and OH radicals are produced as a by-product⁽⁴⁾. When these OH radicals make contact with the polymer covalent bonds of the PEM and produce a substitution reaction, molecular structures including the sulfone groups that promote proton transfer are eliminated, and the resistance of the PEM increases⁽⁵⁾.

Determining the quantity of the hydrogen/oxygen combustion reaction and taking the various factors that accelerate the reaction into consideration makes it possible to predict the increase in the resistance of the PEM. In this paper, the quantity of hydrogen consumed in the combustion reaction is defined as the quantity of the combustion reaction. Because the relationship between the quantity of the combustion reaction and the increase in the resistance of the PEM differs with the molecular structure of the polymer materials employed in the PEM, the relationship is determined by experiment. Figure 4 shows the relationship between the quantity of the combustion reaction and the resistance of the PEM obtained from durability tests in which hydrogen and oxygen are supplied and only the chemical degradation of the PEM is evaluated. The resistance of the PEM increases with the quantity of the combustion reaction.

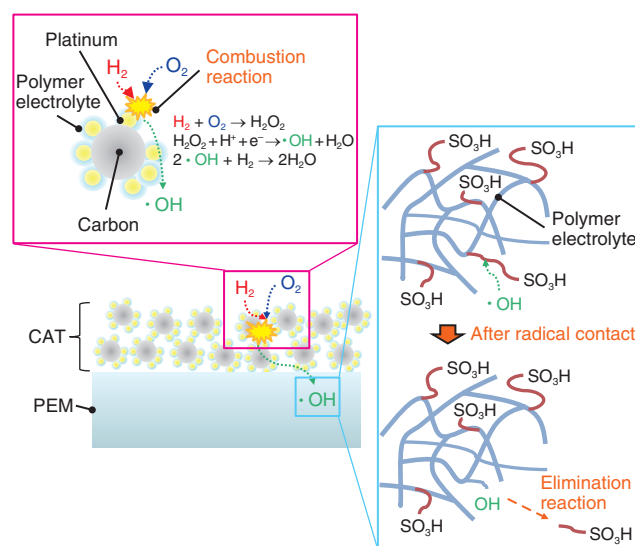


Fig. 3 Mechanism of increase in PEM resistance following combustion reaction of hydrogen and oxygen

The quantity of the combustion reaction is determined by integrating the speed of the reaction at each point in time. The speed of the combustion reaction is chiefly dependent on hydrogen partial pressure, oxygen partial pressure, and temperature, and mapping these parameters makes it possible to understand the quantity of the combustion reaction during operation of the fuel cell vehicle. Data concerning the speed of the combustion reaction is obtained using actual cells. Figure 5 shows an example of actual maps. The theory of the speed of chemical reactions indicates that the combustion reaction will become faster

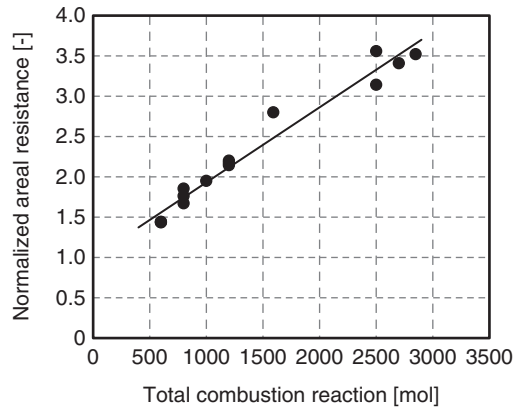


Fig. 4 Relationship between combustion reaction and PEM areal resistance

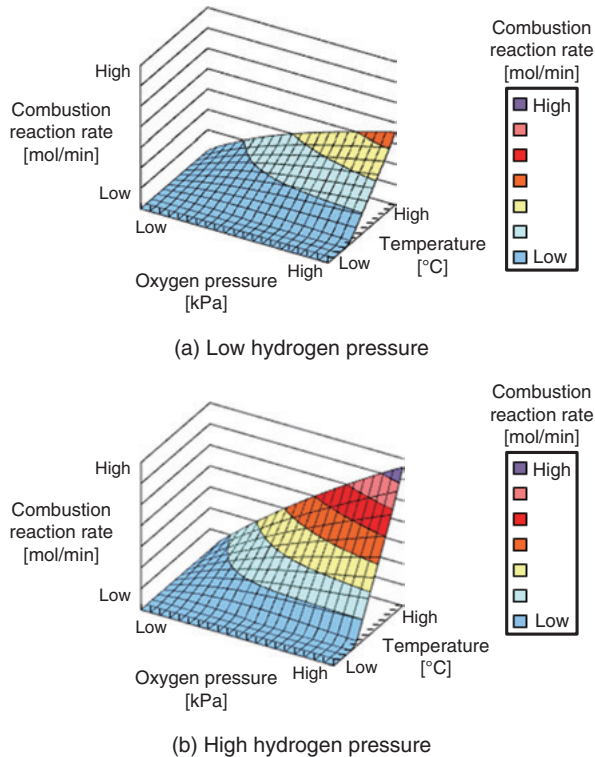


Fig. 5 Examples of combustion reaction rate maps

the higher the partial pressure of the reaction species and the temperature of the reaction system. By determining the hydrogen partial pressure, oxygen partial pressure, and temperature during the operation of a fuel cell vehicle and obtaining the quantity of the combustion reaction from a map of its rate, it is possible to predict the increase in the resistance of the PEM.

2.2. Frequency Durability Tests and Quantity of Combustion Reaction in Fuel Cell Vehicles

During the development of fuel cell vehicles, frequency durability tests modeling the frequency of operation of the vehicle in a normal use environment are conducted in order to help ensure stack performance with consideration of the vehicle's lifespan. These frequency durability tests employ high-accuracy simulations that make it possible to understand the stack environment under various control conditions, such as at start-up and during generation, and incorporate technologies for the determination of the quantity of the combustion reaction. By contrast, when control is suspended (the soak state), which represents the greater part of normal vehicle operation, it is necessary to solve nonlinear simulations incorporating complex reaction diffusion equations in order to understand the stack environment, and the accuracy of determination of the quantity of the combustion reaction is low. In the soak state, because hydrogen, which has a high coefficient of membrane permeability, instantaneously arrives at the cathode generating surface from the anode, while the residual oxygen at the cathode generating surface is simultaneously consumed, the cathode surface is uniformly filled with hydrogen and nitrogen. Following this, the oxygen remaining in the cathode tube gradually arrives at the cathode generating surface. The behavior of the distribution of oxygen partial pressure at this time is complex, affected by the influx and dispersion of the oxygen remaining in the cathode tube and the consumption of the gases on the CAT, and the prediction of the quantity of the combustion reaction represents a challenge. A technology making it possible to measure the oxygen partial pressure at the generating surfaces of the cells is therefore necessary to realizing an accurate grasp of the quantity of the combustion reaction during frequency durability tests.

3. Goals

The research discussed in this paper set two goals in order to reduce performance decline in fuel cell stacks. One of these was to develop a system for the measurement of the distribution of oxygen partial pressure at the generating surfaces in an actual cell, and to determine the distribution of the quantity of the combustion reaction in the soak state based on the actual distribution of oxygen partial pressure. The other was to focus on the distribution of oxygen partial pressure in the soak state in order to create a method of controlling the increase in the resistance of the PEM.

4. Principle of Oxygen Partial Pressure Measurement using LED-Induced Fluorescence

4.1. Selection of Method of Measurement of Oxygen Partial Pressure

Standard methods of measurement of oxygen concentration include zirconia sensors using electromotive force produced by a concentration cell, magnetic methods using the paramagnetism of oxygen, and mass analysis methods using differences in mass numbers. The present research defined the system performance factors necessary to measuring the distribution of oxygen partial pressure at the generating surfaces under actual operating conditions. These factors were that high-resolution image measurement would be possible, that gas would not be consumed by sampling, that measurements would be possible in high-humidity environments, that electrical insulation was possible and the method would not result in explosions, and that it displayed a rapid transient response. A system for the visualization of oxygen partial pressure employing LED Induced Fluorescence (LED-IF), based on the use of oxygen-sensitive reagents, was selected as a method satisfying these performance demands⁽⁶⁾. Photon density was reduced by using an LED light source rather than a laser light source. This made it possible to direct a more uniform light on samples modeling actual cells with high surface areas, and to conduct measurements in a safe environment.

4.2. Oxygen-sensitive Reagent

A Pt-porphyrin complex was used as the oxygen-sensitive reagent. Pt-porphyrin complexes become excited and fluoresce when they absorb light corresponding to their band gaps. When oxygen molecules are present in the vicinity of a Pt-porphyrin complex, part of the fluorescent energy is used as excitation energy for the oxygen molecules. Because of this, the intensity of the fluorescence declines the greater the oxygen partial pressure⁽⁷⁾. Figure 6 shows the relationship between the absorption wavelength region and the fluorescence wavelength region for the

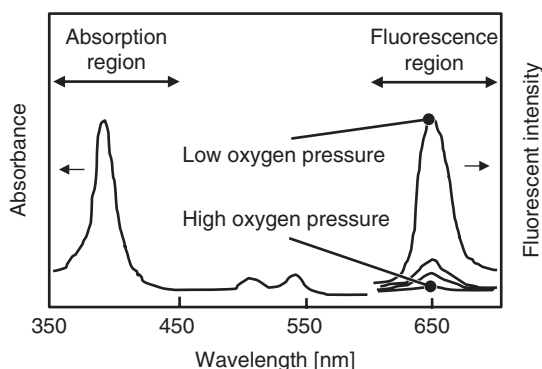


Fig. 6 Luminescence property of oxygen-sensitive reagent

oxygen-sensitive reagent selected for use in the present research. Because the absorption wavelength region and the fluorescence wavelength region are separated, it is possible to remove the effect of reflected and scattered light and selectively focus only on fluorescence originating in the reagent by restricting the measurement wavelength region⁽⁷⁾.

A calibration curve is obtained by shining an excitation light on a surface coated with the oxygen-sensitive reagent and measuring fluorescent intensity under various oxygen partial pressure conditions. Using this curve, it is possible to convert fluorescent intensity into oxygen partial pressure. Figure 7 shows an example of an actual calibration curve.

Because water is produced in the fuel cell generating environment, it is necessary to fix the reagent to help ensure that it will not be washed away by water. The oxygen-sensitive reagent selected for use in the present research contained an organic binder. The application of an annealing treatment to this organic binder strongly fixed the reagent to the coated surface, rendering it suitable for use in the fuel cell generating environment. Under high-humidity operating conditions there were cases in which the surface coated with the reagent became fogged due to condensation and the effect of scattered reflection caused deviations in the measurement results. To help avoid this, the surface coated with the reagent was further coated with a hydrophilic agent.

4.3. Configuration of Measurement Equipment

The developed LED-IF oxygen partial pressure measurement system was employed in a darkroom environment in order to help avoid any effect from external light. Figure 8 shows a schematic image of the system.

An LED light with a wavelength of 405 nm is trained on a sample coated with the oxygen-sensitive reagent. The dimensions of the LED light to be shone on the surface are adjusted using a lens. When excited, the oxygen-sensitive pigment emits fluorescent light of a wavelength

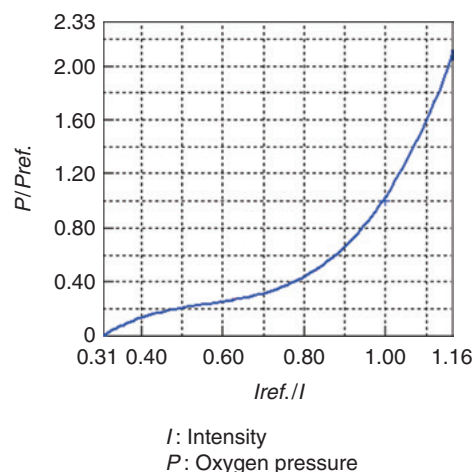


Fig. 7 Example of calibration curve

of 650 nm. At the same time, reflected light and scattered light originating in the LED light are produced around the sample. Because oxygen partial pressure is measured using fluorescent intensity, an optical filter is employed to help ensure that only the fluorescent wavelength region is captured by the camera.

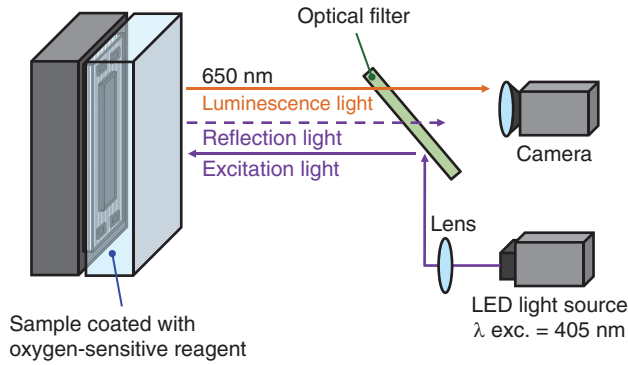


Fig. 8 Oxygen partial pressure distribution measurement system

5. Tests and Results

5.1. Acrylic Plate for Visualization of Generation

The configuration of the evaluation cell was identical to that of the cells employed in the Honda FCX Clarity. Figure 9 shows a schematic image of the cell structure.

In order to visualize oxygen partial pressure in the cathode flow paths using LED-IF, it was necessary to coat the cathode flow paths with the oxygen-sensitive reagent and capture the fluorescence emitted by the reagent using a camera. An acrylic plate for the visualization of generation was created based on the shape of an actual cathode flow path to help enable this. A high-transparency acrylic with no fluorescent agents that would affect the measurements was selected as the material for the plate. Figure 10 shows a schematic image of the plate.

The thickness of the acrylic plate and the structure of its couplings were designed with consideration of heat expansion and mechanical stress in order to make it possible to reproduce the actual high-temperature and high-voltage generating environment.

The use of comb-shaped collectors made it possible to realize uniform generation at the cathode surfaces, as in actual cells. The side of the comb-shaped electrodes for visualization was not part of the target region for measurement of oxygen partial pressure, and in this area scattered reflection affected the intensity of fluorescence when the LED light was shone on the surface. In order to respond to this effect of scattered reflection, parts other than the collecting surfaces were coated in a black pigment.

Spray coating was used to coat the areas of the acrylic plate in the cathode flow paths with the oxygen-sensitive reagent.

5.2. Verification of Operation of LED-IF Oxygen Partial Pressure Visualization System

In order to verify the ability of the LED-IF oxygen partial pressure visualization system and the acrylic plate employed for visualization of generation to determine the distribution of oxygen partial pressure, the stoichiometry-dependence of oxygen partial pressure during generation was studied.

Stoichiometry was given by Eq. (3), and was a relative value against the state in which neither too much nor too little gas was supplied for the reaction in the fuel cell, considered as 1.

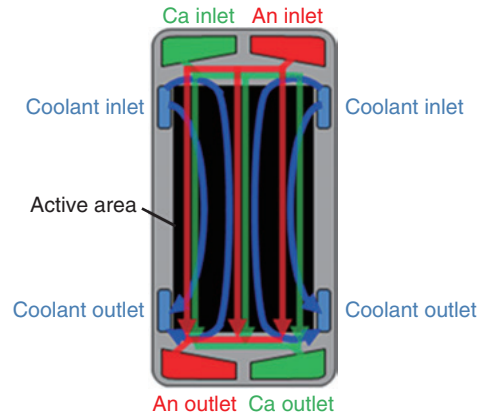


Fig. 9 Schematic image of cell structure

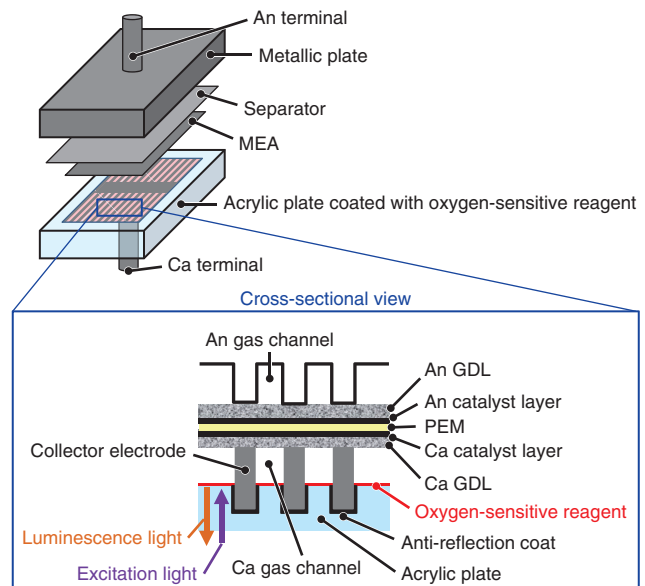


Fig. 10 Transparent acrylic plate for visualization of oxygen pressure

$$\text{Stoichiometry} = \text{Quantity of supplied gas} / \text{Quantity of gas necessary for reaction} \quad (3)$$

When stoichiometry is low, oxygen partial pressure is low due to the fact that there is little residual oxygen downstream in the cathode flow paths. The residual gas is chiefly made up of nitrogen at this time. When stoichiometry is high, oxygen partial pressure is high downstream in the cathode flow paths. Figure 11 shows calculation results.

The results demonstrate that oxygen partial pressure declines from the entrance of the cathode to its outlet. They also indicate that oxygen partial pressure at the cathode outlet increases with stoichiometry.

In order to verify the facts suggested by the calculation results, oxygen partial pressure at the cathode outlet was focused on, and the results of calculations taking oxygen consumption, working pressure, and pressure loss into consideration were compared with measurement results for oxygen partial pressure. Figure 12 shows the results.

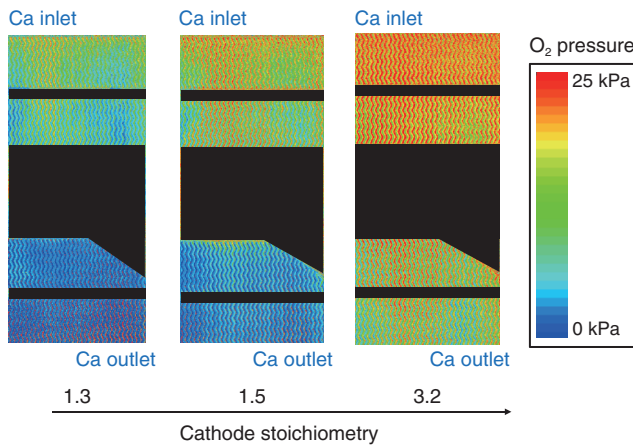


Fig. 11 Change in oxygen pressure distribution with cathode stoichiometry

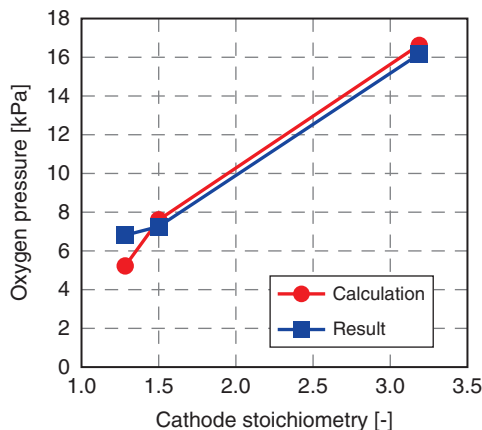


Fig. 12 Comparison of calculation and measurement results for Ca outlet oxygen pressure during generation with cathode stoichiometry

There was a good correlation between the calculation and measurement results, verifying that sufficient accuracy for the purposes of the present research had been achieved. It could also be expected that measurement accuracy would be further increased by modification of the methods of obtaining the calibration curve and of processing noise in the images.

The results discussed here verified that it was possible to measure the distribution of oxygen partial pressure during generation in a fuel cell using the developed LED-IF oxygen partial pressure visualization system.

5.3. Measurement of Oxygen Partial Pressure in Soak State

A vehicle operating environment was reproduced and measurements of oxygen partial pressure were conducted to make it possible to understand the distribution of the quantity of the combustion reaction in a soak state, when the accuracy of calculation of the quantity is low, based on actual measurements. Figure 13 shows the procedure employed in the experiment.

The quantity of water in the MEA was adjusted by means of generation. At this time, the area within the cathode was filled with air [Fig. 13(1)]. The oxygen partial pressure in the cathode tubes was adjusted in order to reproduce the application of control to stop the operation of the fuel cells. At this time, the area within the cathode displayed a uniform, predetermined oxygen partial pressure [Fig. 13(2)]. The supply of gas to the anode and cathode was stopped in order to reproduce a soak state. Because hydrogen has a high

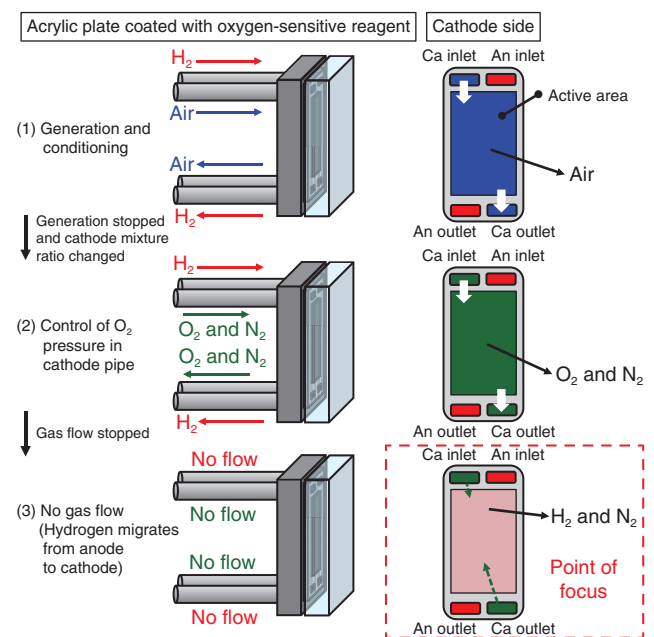


Fig. 13 Experimental procedure for measurement of oxygen pressure distribution after cessation of fuel cell operation

coefficient of membrane permeability, it migrated to the cathode side and immediately began reacting with oxygen following the commencement of the soak. The area within the cathode was therefore filled with a mixed gas composed of hydrogen and nitrogen directly after the commencement of the soak. Following this, due to the effect of buoyancy, oxygen flowed chiefly from the connecting holes at the cathode outlets, producing a mixture of hydrogen and oxygen. The distribution of Oxygen partial pressure was measured in this mixed gas environment [Fig. 13(3)]. Using the method described above, the application of control to stop fuel cell operation was modeled, and the distribution of oxygen partial pressure in the subsequent soak state was examined. Figure 14 shows the results.

It was possible to study the distribution of partial pressure in the oxygen flowing from the connecting holes at the cathode outlet at a high degree of resolution. It was predicted that at this time, hydrogen and oxygen would both be present on the CAT close to the cathode outlet connecting holes, and that the resistance of the PEM would increase simultaneously with the production of radicals by the combustion reaction. It was also predicted that the quantity of the combustion reaction would be greater and that there would be a significant increase in the resistance of the PEM in areas in which oxygen partial pressure was high.

In order to verify these predictions, the quantity of the combustion reaction in each area of the cathode was calculated from a map of the speed of the combustion reaction, using the results of measurements of oxygen partial pressure, hydrogen partial pressure, and temperature. Figure 15 shows the relationship between these results and those for the increase in the resistance of the PEM in each area of the cathode obtained from a durability test modeling a soak state.

These results verify that it is possible to predict the distribution of the increase in the resistance of the PEM using data concerning the distribution of oxygen partial pressure.

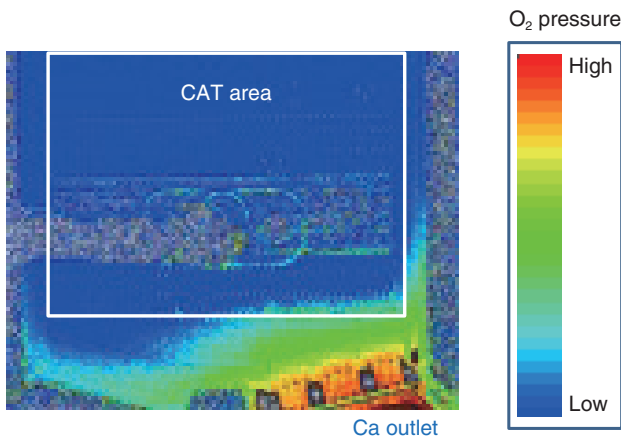


Fig. 14 Oxygen pressure distribution following cessation of fuel cell operation

5.4. Optimization of Control to Stop Fuel Cell Operation and Results of Frequency Durability Tests

Based on the results discussed in Section 5.3, it was conjectured that the main cause of the increase in the resistance of the PEM was the diffusion of oxygen through the connecting holes at the cathode outlets. In order to verify this theory, control was applied to reduce the partial pressure of the residual oxygen in the cathode tubes, and the distribution of oxygen partial pressure in the soak state was measured. Figure 16 shows the results, demonstrating that the partial pressure of the oxygen arriving at the CAT declines as the partial pressure of the residual oxygen in the cathode pipes declines.

Based on these results, it can be predicted that it would be possible to reduce the quantity of the combustion reaction and control the increase in the resistance of the PEM by creating a control that reduced the partial pressure of the residual oxygen in the cathode tubes during frequency durability tests. In order to verify this prediction, frequency durability tests were conducted using conventional control and the newly developed

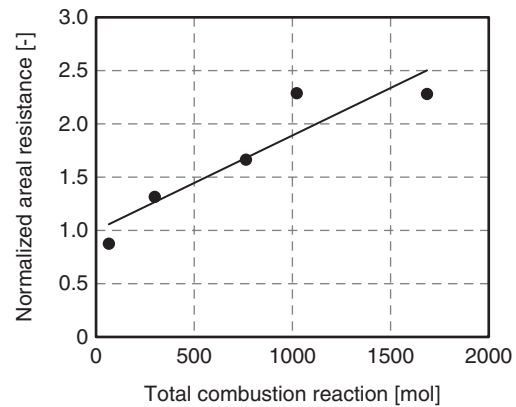


Fig. 15 Relationship between combustion reaction and PEM areal resistance derived from oxygen pressure distribution

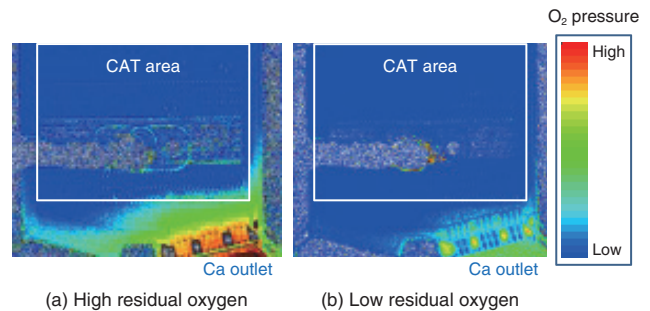


Fig. 16 Comparison of oxygen pressure distribution due to residual oxygen pressure in cathode pipe

control designed to reduce the partial pressure of the residual oxygen in the cathode tubes, and the distribution of the increase in the resistance of the PEM following the tests was compared. Figure 17 shows the results, which correspond well with the prediction that the resistance of the PEM would increase in areas at which oxygen arrives at the CAT, as indicated by the LED-IF oxygen partial pressure measurement system.

These results indicate that by using the developed system it is possible to predict the distribution of increase in the resistance of the PEM in a soak state, and to reduce the increase in PEM resistance by applying control to reduce the partial pressure of residual oxygen in the cathode tubes.

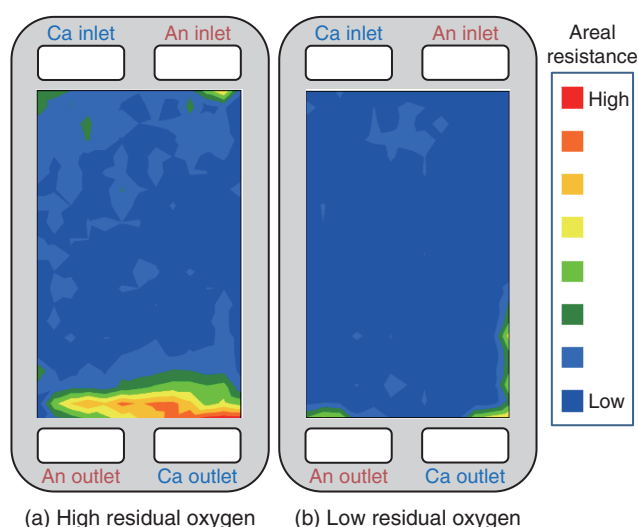


Fig. 17 Comparison of distribution of increase in PEM resistance due to residual oxygen pressure in cathode pipe

6. Conclusion

The LED-IF oxygen partial pressure measurement system developed in the research discussed in this paper was applied in the development of control to stop operation of a fuel cell vehicle, with the following results:

- (1) It was possible to measure the distribution of oxygen partial pressure in the generating environment in a cell of the same size as those used in an actual fuel cell vehicle, increasing the accuracy of determination of the distribution of the quantity of the combustion reaction.
- (2) The application of control to reduce the partial pressure of the residual oxygen in the cathode tubes at the commencement of soak in a fuel cell vehicle made it possible to control the increase in the resistance of the PEM.

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