

Control Method to Reduce Degradation in Fuel Cell System at Start-up

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ABSTRACT

In the fuel cell system, the anode electrode is supplied with sufficient hydrogen during generation, but when the system is stopped, the inflow of air from the exterior replaces the hydrogen with air. When the system is started with air replacing hydrogen at the anode electrode, corrosion of the catalyst at the cathode electrode occurs.

This paper proposes a method that helps to prevent corrosion of the catalyst by discharging corrosion current to external circuits at start-up. New measurement tools including measurements of electrical potential, corrosion current, and gas analysis were applied to the fuel cell system in developing the control system. Using these tools, the internal environment of the fuel cell stack was clarified, and a method of discharge at the optimal timing with consideration of hydrogen starvation was developed. The ability of the developed start-up discharge method to control corrosion at the cathode electrode was verified by measurements of potential, corrosion current, and quantity of CO₂ generated, and durability tests using an actual fuel cell system confirmed the effectiveness of the system.

1. Introduction

Today, efforts are being made to move away from fossil fuels as a result of air pollution originating in automotive exhausts, climate change due to CO₂ emissions, spiraling oil costs, and other energy-related issues. In order to resolve these issues, Honda is engaged in the development of the fuel cell electric vehicle, the ultimate environmentally responsible vehicle.

Polymer electrolyte fuel cells are the standard cells employed in fuel cell vehicles. These cells are able to operate at low temperatures, are compact, and offer a high level of energy efficiency.

Figure 1 shows a schematic diagram of the structure of a fuel cell. The cell is made up of separators to provide flow channels for gases and coolant, gas diffusion layers to diffuse gases and discharge the water produced by the reaction, catalyst layers to promote catalytic reactions, and a Proton Exchange Membrane (PEM). In the catalyst layers, several nm of platinum nano-particles are supported at high dispersion on a high-specific surface area carbon carrier of several tens of nm.

Looking at the chemical reactions taking place in a fuel cell, first, hydrogen supplied to the anode is divided into protons (H⁺) and electrons by the catalyst layer. The protons migrate to the cathode through the electrolytic membrane. On the cathode side, oxygen supplied to the

cathode combines with electrons that have migrated from the anode side to the exterior and protons that have crossed the electrolytic membrane, producing water. At this time, an oxygen reduction reaction occurs in the catalyst layer on the cathode side, generating electromotive force. The cathode electrode catalyst layer therefore plays an important role in fuel cell performance.

Because the catalyst layer on the anode side becomes degraded when the cell generates electricity with insufficient

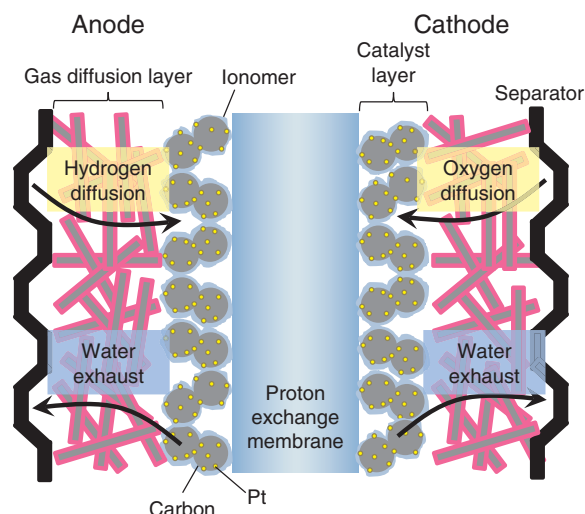


Fig. 1 Schematic of fuel cell

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fuel (termed “hydrogen starvation” below), it is essential to pay careful attention to the status of fuel during generation.

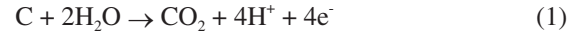
Figure 2 shows the gas and coolant flow in a fuel cell stack. Gases flow to the generating areas from the upper sections of the separators, and electricity is produced. Following this, the remaining unconsumed gases and the water produced by the reaction are discharged from the lower sections of the separators.

When a fuel cell system stops generating electricity, hydrogen is present on the anode side, and air is present on the cathode side. After a certain period of time has elapsed, air inflows from outside the system. Air inflows into the anode side, and ultimately air replaces the hydrogen on the anode side. When the system is started with air on both the anode and cathode sides (termed “air-air start” below), gas mixing occurs when hydrogen fuel is introduced to the anode side because of the presence of air on this side. Because variations occur in the gas supply to the electrodes, as Fig. 3 shows, in downstream areas of the flow channels, which hydrogen does not reach efficiently, the potential of the anode electrode tends not to decline, and corrosion current flows due to the difference in potential in the electrode. In addition, the potential of the opposite cathode

electrode becomes prone to increase. This exposes the cathode to high potentials of 1V or more⁽¹⁾.

At this time, a reaction of the type described by Eq. (1) occurs downstream from the high-potential cathode. Because the electrons released in this reaction pass through the cathode due to the difference in potential, corrosion current is generated. The high potential results in a decline in generation performance due to corrosion of the carbon supporting the catalyst and reduction of the effective surface area of the catalyst through elution of the platinum⁽¹⁾. In addition, the corrosion of the carbon at the electrode results in changes to its water retention ability, and the ability of the catalyst layer to discharge water declines.

This is known to result in a decline in gas diffusion performance, with a consequent decline in the generation performance of the fuel cell⁽²⁾.



The results of potential cycle tests indicate that the repeated exposure of the cathode catalyst to high potentials results in corrosion of the carbon support and elution of the platinum⁽³⁾.

A variety of materials-based measures have been proposed as means of reducing the corrosion of cathode materials due to air-air starts⁽⁴⁾. Standard measures might, for example, involve increasing the corrosion resistance of the platinum-supported carbon. A system-based measure being employed is the sealing of the space around the anode and cathode in order to help prevent the inflow of air.

This paper considers a control-based approach to the reduction of corrosion, and proposes a start-up discharge control method.

2. Methods of Reducing Corrosion of Electrode Materials

“Start-up discharge” refers to the release to external circuits of the corrosion current generated downstream from the anode when gas is supplied at fuel cell start-up, as shown in Fig. 4. The electrons that flow to the external circuit would be transferred to the cathode and used in normal fuel cell reactions. This would help to prevent

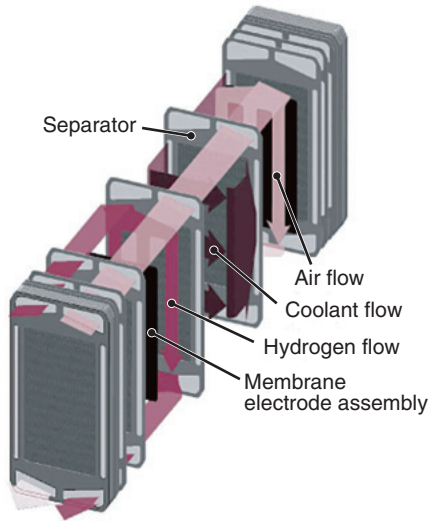


Fig. 2 Fuel cell stack configuration

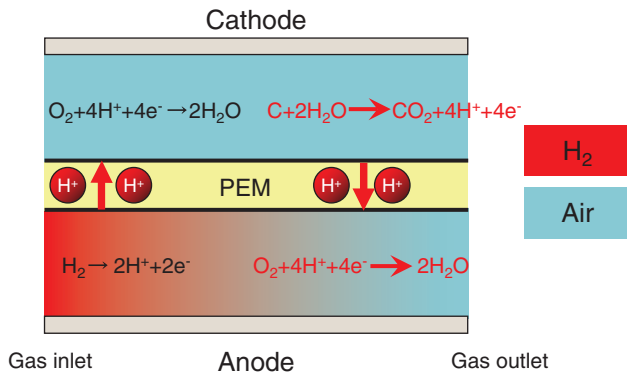


Fig. 3 Model of carbon corrosion at Air-Air start-up

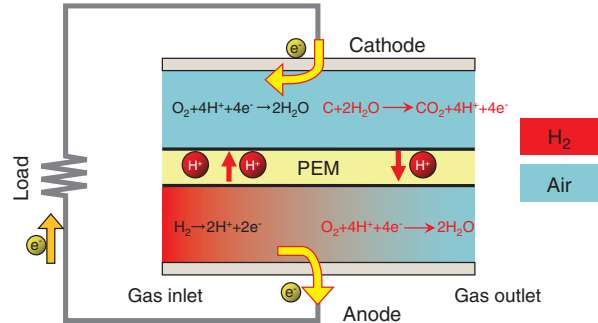


Fig. 4 Model of start-up discharge

reactions such as the one shown in Eq. (1) from occurring downstream in the flow channels. It was also considered that the discharge of electricity would reduce the voltage of the cell and lower the potential of the cathode, helping to prevent the cathode from being exposed to a high potential.

Figure 5 shows a timing chart for start-up discharge control.

Directly after the commencement of start-up of the fuel cell system, hydrogen is supplied to the anode and air is supplied to the cathode. At this time, the voltage of the fuel cell stack begins to increase. Conventional control begins discharging after open-circuit voltage has been reached, but start-up discharge control begins discharging while voltage is increasing. There is no change in the method of introducing gases at this time between the two control methods. Tests were conducted using two patterns for discharging: commencement of discharge simultaneously with the introduction of the gases (current control); and commencement of discharge after voltage had risen to a certain degree (voltage control).

One point to which it was necessary to give particular attention in constructing a system for start-up discharge control was attempting to ensure that discharge did not commence before hydrogen had been substituted at the anode. As Figure 6 shows, commencing discharge with insufficient hydrogen at the anode results in hydrogen starvation due to the reaction described by Eq. (1), leading to corrosion of the catalyst at the anode electrode⁽⁵⁾. Because the activation energy necessary to promote a reaction at the anode is lower than that at the cathode, the amount of catalyst material used at the anode is generally lower than that used at the cathode. This means that corrosion of the anode catalyst has a significant effect in reducing the performance of the fuel cell.

By contrast, insufficient oxygen at the cathode does not result in corrosion, but simply produces a decline in voltage.

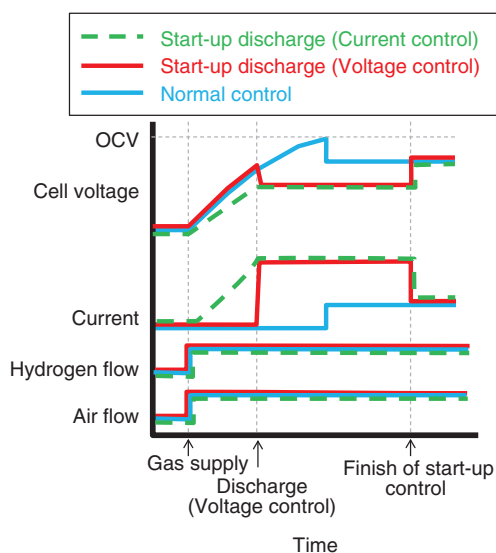


Fig. 5 Timing chart for start-up discharge

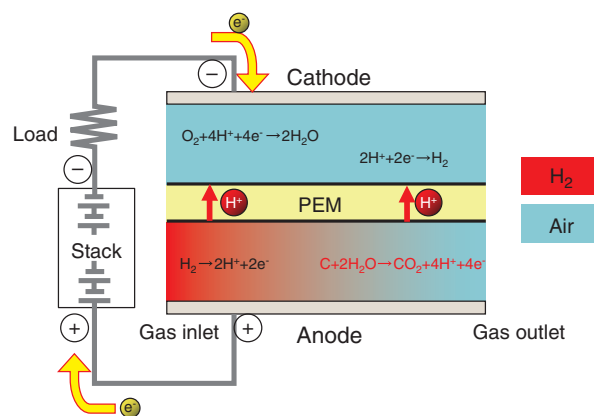


Fig. 6 Model of H₂ starvation

3. Measurement Methods

As indicated in Chapter 2, in order to implement start-up discharge control, it was necessary to obtain a detailed understanding of the reactions taking place in the fuel cells at start-up. It was necessary to conduct the measurements in a fuel cell system, because it was difficult to test transient occurring at start-up with only stack equipment. Therefore, potential and current density sensors were positioned in a fuel cell stack, and measurements of the internal environment of the cells were conducted with the stack fitted in a fuel cell system (a generating system incorporating the fuel cell stack, a gas supply system, and a cooling system).

Using the measurement methods discussed below, the internal reactions in the fuel cells were elucidated, helping to enable the development of a control system.

3.1. Measurements of Potential

Generation with insufficient hydrogen present at the anode would result in an increase in potential at the anode; in order to determine the effectiveness of the control, the study examined whether or not generation was occurring under such a condition of hydrogen starvation, and whether or not potential increase at the cathode had been controlled.

Cell voltage can be used as a parameter for understanding fuel cell performance, but the behavior of voltage alone is not sufficient to provide an accurate understanding of the reactions occurring within the cells. Cell voltage is a function of the difference in potential between the cathode and anode sides, and an accurate grasp of the reactions occurring at each electrode can be obtained by measuring the potential of each electrode. Potential measurements were therefore conducted using a small, thin-film electric potential sensor developed by Honda⁽⁶⁾. Figure 7 shows the positioning of the sensor. The potential sensor was a self-hydrogen-generating type. A voltage of 1.4 V was impressed in the sensor's voltage impression section, generating hydrogen at a reference electrode positioned on

the anode side. With the reference electrode providing the reference potential, the anode potential was considered as the difference between anode potential and the reference potential, and the cathode potential was considered as the difference between cathode potential and the reference potential. Using this method, it was possible to measure potential even in the case of an internal cell environment with no hydrogen present, as at air-air start.

Discharge timings were determined while conducting measurements of the potential at the anode and cathode at start-up using this sensor.

3.2. Corrosion Current Measurements

Corrosion current flowing into the electrodes at start-up was measured using a current density sensor inserted in a fuel cell stack. As shown in Fig. 8, a divided electrode was used for the anode, and oxidation-reduction current produced at start-up was measured. The corrosion current flowing through the entire electrode was calculated by integration of the figures obtained. Because corrosion of the carbon at the cathode at start-up would produce the phenomenon described by Eq. (1), the analysis was conducted with a particular focus on oxidation current.

3.3. Gas Analysis

Measurements of the CO_2 generated by corrosion of electrode materials at start-up were conducted using a mass spectrometer, Hx-07i⁽⁷⁾ (manufactured by Nohmi Bosai,

Ltd.). Using the highly responsive measurement device, the gases for measurement were narrowed down to specific gas species, and the amount of gas taken in was reduced. Corrosion of the carbon that supports the platinum used as a catalyst in fuel cells generates CO_2 , and measurements of this CO_2 were conducted to quantify carbon corrosion.

4. Measurement Results

4.1. Before start-up discharge

Potential and corrosion current were measured at air-air start. Results for potential are shown in Fig. 9, and results for corrosion current are shown in Fig. 10.

The image on the right-hand side of Fig. 9 shows a fuel cell seen from the orientation of the electrodes. At air-air start, the potential of both the anode and the cathode prior to start-up is 1V. At start-up, hydrogen is supplied to the electrodes, and the potential of the anode declines to 0V. The results of potential measurements show that because the anode potential does not readily decline to 0V in the vicinity of the cathode outlet (position 4), where the substitution of the gases is delayed, the opposite cathode potential increases, and the cathode is exposed to a high potential. Factors such as the speed of gas substitution and the status of corrosion of electrode materials can be confirmed from these changes in potential.

The results of measurements of the corrosion current in the electrodes, shown in Fig. 10, indicate that there is a significant flow of oxidation current downstream of the electrodes directly after start-up. These results also demonstrate that at air-air start, because the cathodes are exposed to high potentials and corrosion of the cathode

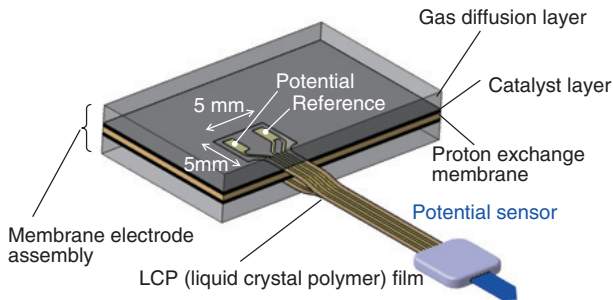


Fig. 7 Configuration of potential sensor

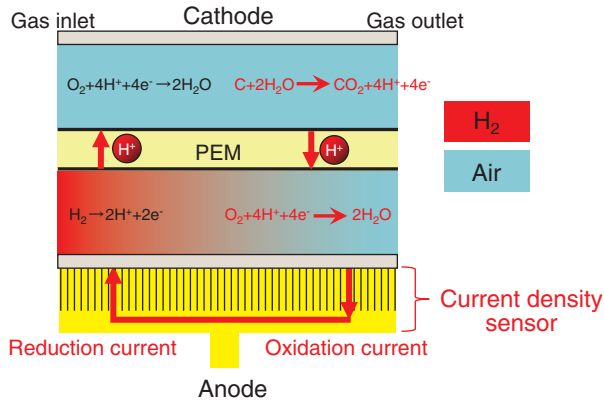


Fig. 8 Current density sensor

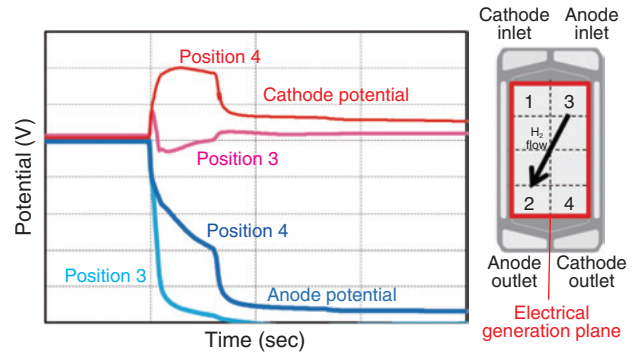


Fig. 9 Potential measurement at start-up

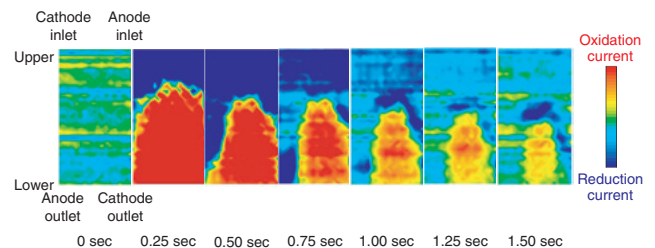


Fig. 10 Comparison of corrosion current

catalyst occurs, corrosion current flows downstream in the flow channels of the stack.

4.2. Study of Effect of Start-up Discharge

From data including potential, corrosion current, and gas concentration, the effectiveness of the start-up discharge method was confirmed. The study results for each control method are described below.

4.2.1. Current control

A fuel cell was connected to a load resistance prior to start-up in order to discharge current immediately after gas supply (current control). Figure 11 shows the results of CO₂ measurements conducted during start-up discharge under these conditions. These results show that despite the fact that CO₂ declines at the cathode, CO₂ is generated at the anode.

This indicates that because there is insufficient replacement of hydrogen at the anode electrode when discharge is commenced immediately when the gases are introduced, and reactions occur in which carbon, platinum or other substances release electrons in place of the hydrogen, the volume of CO₂ generated at the anode increases. Because CO₂ generated at the anode at start-up has a greater effect on cell performance than CO₂ generated at the cathode at start-up, the results demonstrate that current control is not sufficient to control performance declines.

In addition, with regard to the allocation of gas, the cell voltage changes polarity at points that are distant from the gas manifold because of the effect of the direction of layering. Because corrosion of the anode materials occurs when start-up discharge is conducted immediately after start-up despite the fact that the corrosion of the cathode materials is controlled, this form of control was judged as not being sufficiently effective.

4.2.2. Voltage Control

To continue the study, start-up discharge was conducted after start-up before the fuel cell reached open circuit

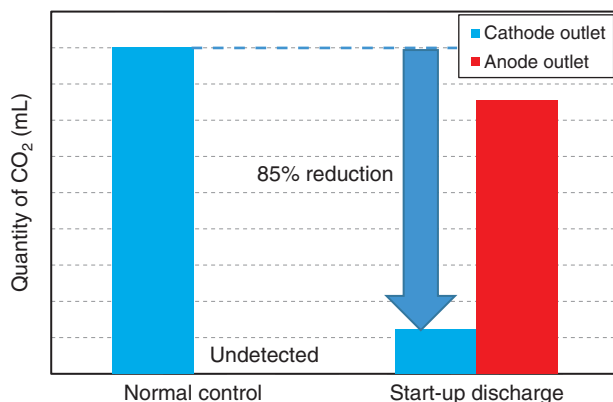


Fig. 11 Quantity of CO₂ at normal control and start-up discharge (Current control)

voltage (voltage control), and potential, corrosion current, and quantity of CO₂ generated were measured.

Figure 12 shows the behavior of potential close to the cathode outlet, where potential is most prone to increase. Start-up discharge produced little effect in reducing the peak value of cathode potential, but the period for which the electrode was exposed to high potential was reduced. Based on this, it is considered that corrosion current continued to flow while the cathode was exposed to high potential, and it was possible to reduce corrosion current in areas in which the cathode potential was controlled. In addition, because no increase in anode potential was observed, it was concluded that start-up discharge did not result in hydrogen starvation, and inhibited the degradation of the anode catalyst.

Figure 13 shows the integrated values for corrosion current at the electrodes for normal control (Fig. 13(a)) and start-up discharge control (voltage control) (Fig. 13(b)). These results demonstrate that start-up discharge results in an overall reduction in the value of oxidation current. Under normal start-up conditions, a significant oxidation current flows at the cathode outlet, and the application of start-up

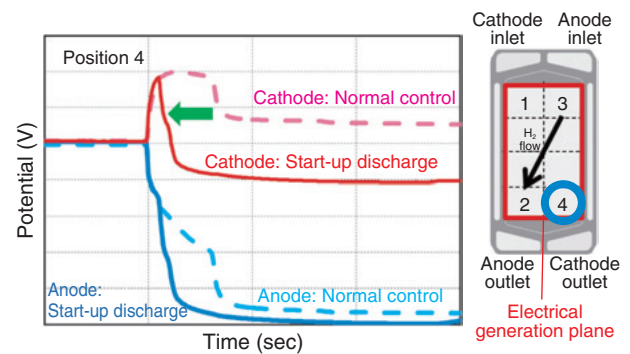


Fig. 12 Potential measurement at start-up with and without start-up discharge (Position 4)

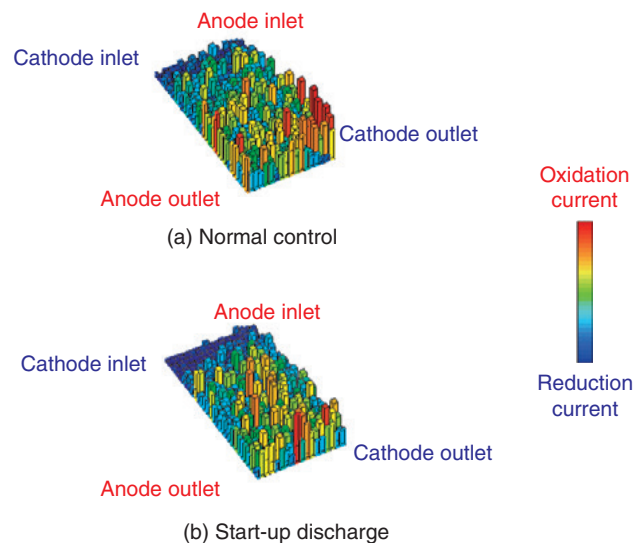


Fig. 13 Comparison of integrated oxidation current for normal control and start-up discharge (Voltage control)

discharge control (voltage control) results in a reduction of this oxidation current.

Figure 14 shows the results of measurements of CO_2 at the cathode outlet. The results show that while the overall reduction in CO_2 is lower than the reduction for current control, voltage control reduces the quantity of CO_2 generated at the cathode. The CO_2 measurements therefore also demonstrate the effectiveness of this control method, indicating a reduction in the level of corrosion of the cathode catalyst.

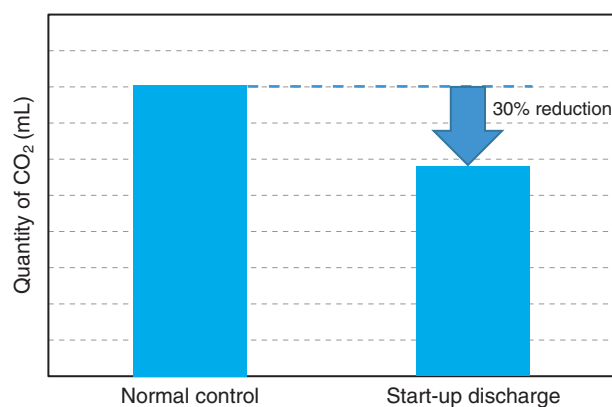


Fig. 14 Quantity of CO_2 at cathode outlet (Voltage control)

5. Verification Tests

The developed voltage control start-up discharge method was applied to an actual fuel cell stack and durability tests were conducted. The start-up durability modes were tested in the following order: soak, scavenging, air-air start, generation, and shutdown.

Figure 15 shows the level of decline in performance measured over start-up-shutdown cycles with and without start-up discharge, converted to correspond to a single cycle.

These results indicate that the use of discharge control

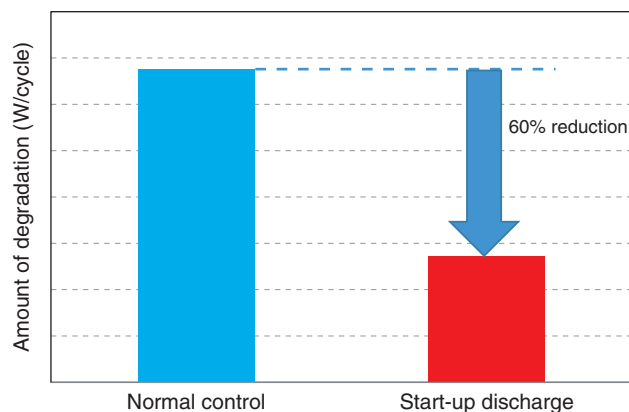


Fig. 15 Amount of degradation for normal control and start-up discharge (Voltage control)

at air-air start not only reduces the generation of CO_2 due to corrosion on the cathode side, controls potential and reduces corrosion current, but also reduces the decline in cell performance resulting from these multiple effects to less than half of previous levels, demonstrating the effectiveness of the control method.

6. Conclusion

Measurements of electrical potential and corrosion current and gas analyses were conducted in the fuel cell system, and a start-up discharge control method was developed to reduce the corrosion of electrode materials.

- (1) Setting an earlier timing for start-up discharge (current control) resulted in hydrogen starvation at the anode, and the method was ineffective as an electrode corrosion control measure.
- (2) Measurements of potential, corrosion current and the quantity of CO_2 generated indicated that the use of the developed start-up discharge (voltage control) method reduced the level of corrosion of the cathode, and verification tests using an actual fuel cell system confirmed the method's effectiveness.

7. Afterword

The development of the control method discussed here was made possible by advances in technologies for conducting detailed studies of the internal environment of fuel cells. Potential, corrosion current, gas analysis and other internal cell conditions measured in the course of this study will be fed back into evaluations of a fuel cell and materials, and thus assist in enhancing the development of fuel cells and materials.

The measurement methods described here has being applied to coming research for extending the long life of fuel cells, by developing optimal control methods for the power generation, shutdown, etc. while studying the actual internal environment of the cells.

In addition, the authors believe that the reduction of materials corrosion by the optimal system control will allow substitution of lower cost materials, making it possible to reduce the cost of fuel cells in the future.

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