

Initiative to Evaluate Effects of Atmospheric Impurities on PEM Fuel Cell Performance

Keiko YOSHIDA* Ryu OKANO*

ABSTRACT

The effect of atmospheric impurity concentrations on fuel cell performance when a fuel cell vehicle runs in a real-life environment was evaluated by bench tests using an actual automotive cell.

The effect of the concentrations of the gaseous atmospheric impurities SO_2 , H_2S , NO_2 , and NH_3 on fuel cell power over time was clarified. Comparison of nitrogen-based and sulfur-based impurities at the same concentrations revealed that sulfur-based impurities have a larger effect on power.

Regarding the non-gaseous impurity NaCl , as sea salt also scatters in aerosol form, these evaluation results were compared with the results for the conventionally used aqueous solution. The results showed that the effect on power differs according to the injection format. Therefore, when performing bench evaluation of NaCl -based impurities, it is necessary to select an appropriate NaCl form that conforms to the assumed environment.

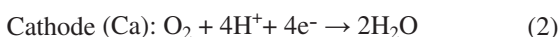
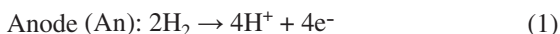
1. Introduction

Development of clean and fuel efficient vehicles is proceeding in order to address various issues such as suppression of global warming due to greenhouse gases (GHG), depletion of fossil resources, and reduction of environmental pollutants included in vehicle exhaust gas. Fuel cell vehicles (FCV) are gathering attention as a means of addressing the above issues as FCV do not emit CO_2 while running and have a driving range, refueling time, and cold start performance equal to that of gasoline vehicles⁽¹⁾.

Figure 1 shows a schematic image of a polymer electrolyte fuel cell (hereafter, “fuel cell”). The fuel cell (hereafter, “cell”) structure consists of a membrane electrode assembly (MEA) sandwiched between separators that form gas flow-fields, and a stack of multiple cells is called a fuel cell stack (hereafter, “stack”).

The MEA consists of a polymer electrolyte membrane (PEM), catalyst layers (CL), and gas diffusion layers (GDL).

The fuel cell reactions are the hydrogen oxidation reaction at the anode shown by Eq. (1) and the oxygen reduction reaction at the cathode shown by Eq. (2) below.



Fuel cells generally take in the oxygen to be supplied to the cathode from the atmosphere and react it with hydrogen inside the cells. Various atmospheric impurities may flow into the stack as FCVs become more widespread and run in increasingly diverse environments. Accordingly, it is thought that these impurity components and their concentrations will affect the stack power (hereafter, “power”). This calls for clarification of the effect of

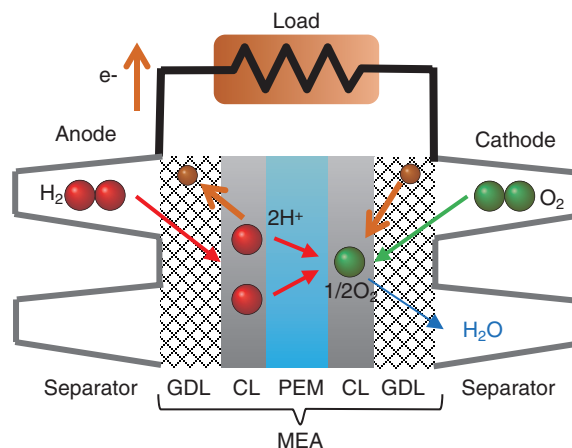


Fig. 1 Schematic image of PEM fuel cell

* Automobile R&D Center

atmospheric impurities in order to evaluate durability in real-life FCV operating environments. Under these circumstances, the effect of various atmospheric impurity types and concentrations on power is being studied in the fuel cell research field⁽²⁾. The main factor leading to reduced power is thought to be a drop in catalyst performance due to the adsorption of impurities to the surface of the Pt catalyst used in the cathode CL.

Fuel cell system costs remain high, and research is underway to reduce the amount of the precious metal Pt catalyst used as one method of reducing this cost⁽³⁾. However, simply reducing the catalyst amount reduces the Pt catalyst surface area, which is known to increase the effect to reduce power even at the same impurity concentrations⁽⁴⁾. The above demands to reduce catalyst amounts will continue to strengthen, so research to clarify the effect of impurity concentrations is important for stack development.

Most reports thus far on the effect of atmospheric impurities on power involve tests using commercial mini cells such as JARI cell⁽⁵⁾, and there are no known cases of using actual automotive cells.

Mini cells typically use a serpentine flow-field that differs from the flow-field of an actual automotive cell, so the diffusion behavior of air that contains impurities also differs. For this reason, the effect to reduce power may differ from that in an actual vehicle.

Table 1 shows typical atmospheric impurities that are thought to affect stack power⁽⁵⁾. These impurities include sulfur-based gases (H_2S , SO_2), nitrogen-based gases (NO_2 , NH_3), and the non-gaseous impurity NaCl.

Concentrations of atmospheric impurities are affected by various factors such as the geographical environment and weather conditions. For this reason it is not practical to quantitatively understand the effects of various impurities using only field trials. Therefore, this study conducted bench tests that generated power by supplying simulated atmospheric gases containing different impurity concentrations to the cathode side of an actual automotive cell.

Non-gaseous NaCl has conventionally been evaluated by the method of injecting an NaCl aqueous solution via the cell inlet⁽⁶⁾. However, in coastal areas NaCl also scatters in aerosol form⁽⁶⁾, so it is necessary to clarify the effect on fuel cell power of impurities entering in aerosol form. Therefore, this study performed bench tests using the method of aerosol injection in addition to the conventional method of injection by aqueous solution, and compared the results of both methods.

2. Bench Test Method

2.1. Gaseous Impurity Evaluation Method

2.1.1. Gas concentration settings

The assumed maximum concentration of each impurity was set as follows based on the values noted in Reference⁽⁵⁾.

Table 1 Atmospheric impurities to affect fuel cell

Impurity	Form	Concentration	Upper limit	Hot spot
H ₂ S	Gas	1700 ppb	1000 ppb	Hot spa Volcano
SO ₂	Gas	250 ppb	1000 ppb	
		19 ppb		
NO ₂	Gas	600-6000 ppb	10000 ppb	
NH ₃	Gas	21 ppb	100 ppb	Livestock Industry
		38 ppb		
NaCl	Solution Aerosol	100 µg/m ³		Coastal area

Table 1 lists these concentrations.

(1) H_2S

The main source of H_2S is volcanic gas. The measured H_2S concentration at Owakudani in Hakone is reported to have a maximum hourly average of 1700 ppb⁽⁵⁾. While higher concentrations may be observed depending on the volcanic area, the work environment management concentration for H_2S in the Industrial Safety and Health Act⁽⁷⁾ is 1000 ppb, so this study set an assumed maximum concentration of 1000 ppb.

(2) SO_2

SO_2 has the two sources of volcanic gas and fossil fuels. However, SO_2 originating from fossil fuels is tending to decrease due to advances in gasoline and factory exhaust gas desulphurization technology⁽⁸⁾. The concentration of SO_2 originating from volcanic gas was measured at 250 ppb at Owakudani in Hakone, but was 19 ppb in urban areas⁽⁵⁾. The environmental standard for SO_2 concentration established by the Ministry of the Environment⁽⁹⁾ is an hourly average of 100 ppb. Human body impact assessment results indicate that SO_2 becomes a disagreeable odor and unpleasantness increases at concentrations in excess of 1000 ppb⁽¹⁰⁾, so this study set an assumed maximum concentration of 1000 ppb.

(3) NO_2

NO_2 has various sources such as factories, thermal power plants, vehicles, and households⁽¹¹⁾. The measured value in urban areas is reported to be 600 ppb⁽⁵⁾. However, local concentrations of up to 6000 ppb at the exits of tunnels with heavy traffic in Tokyo have also been reported⁽¹²⁾. This study set an assumed maximum concentration of 10000 ppb.

(4) NH_3

Sources of NH_3 include vehicle exhaust gas and livestock manure and soil components in dairy regions. NH_3 originating from vehicle exhaust gas is reported to have a concentration of 21 ppb in areas of Tokyo with heavy traffic⁽⁵⁾. In addition, according to a report of atmospheric NH_3 concentrations originating from dairy⁽¹³⁾, a maximum

concentration of 38 ppb was observed in an area of Chiba Prefecture with a thriving livestock industry. Therefore, this study set an assumed maximum concentration of 100 ppb.

2.1.2. Experimental conditions

Evaluation used a stack consisting of ten actual automotive cells. Figure 2 shows a schematic image of the power generation evaluation apparatus. High purity hydrogen (purity 5N) was humidified and heated using a bubbling system to the same conditions as those in an actual vehicle and supplied to the stack as the fuel gas. Air with impurities removed (hereafter, “clean air”) was humidified and heated, then the specified impurity was mixed in via a T-shaped joint connected to the stack cathode gas inlet pipe and the mixture was supplied to the stack as the oxidant gas. The impurity flow rate from a gas cylinder adjusted to a constant concentration was controlled using a KOFLOC Model 3660 SERIES mass flow controller (MFC). Coolant was used to control the stack temperature to a constant temperature.

Figure 3 shows the operation mode used for evaluation. The horizontal axis shows the time, the 1st vertical axis shows the load, and the 2nd vertical axis shows the flow rate supplied to the cathode. Evaluation was performed using a mode (hereafter, “running mode”) that simulates the load variation produced by vehicle start, stop, acceleration, and deceleration. The cathode flow rate Q_{Air} changes according to the set load variation during the running mode as shown by Eq. (3).

$$Q_{Air} [\text{Nm}^3/\text{s}] = \frac{I}{4F} \times 0.0224 \times s \times \frac{1}{0.21} \quad (3)$$

I : Current [A]

F : Faraday constant [C/mol]

s : Stoichiometric number

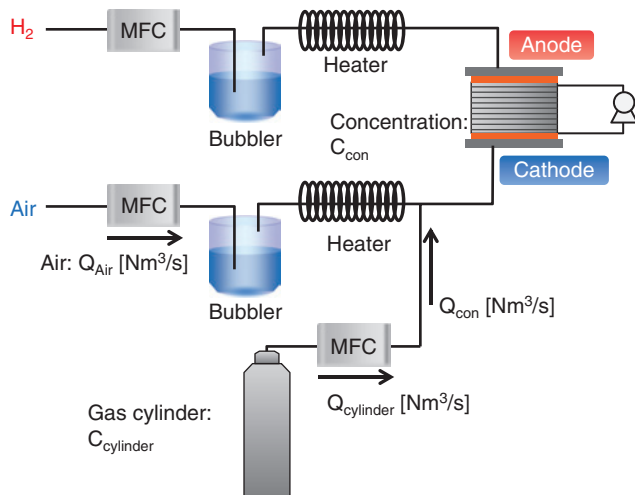


Fig. 2 Experimental scheme of gaseous impurity injection

The impurity flow rate Q_{con} entering the stack is obtained by Eq. (4) from the impurity concentration $C_{cylinder}$ of the gas cylinder and the gas flow rate $Q_{cylinder}$ [Nm³/s] supplied from the gas cylinder.

$$Q_{con} = C_{cylinder} \times Q_{cylinder} \quad (4)$$

The impurity concentration C_{con} in the air entering the stack was obtained by Eq. (5).

$$C_{con} = \frac{Q_{con}}{Q_{Air} + Q_{cylinder}} \quad (5)$$

The maximum power at the running mode during clean air supply was extracted and used as the reference for the decrease in power over time.

The difference between the power slope when various atmospheric impurities are supplied ($\Delta P_2/\Delta t$) and the power slope when clean air is supplied ($\Delta P_1/\Delta t$) was defined as the power decay rate as shown in Eq. (6) and used as the index for evaluating the effect on power when impurities are supplied (Fig. 4).

$$\text{Power decay rate [kW/h]} = \frac{\Delta P_2}{\Delta t} - \frac{\Delta P_1}{\Delta t} \quad (6)$$

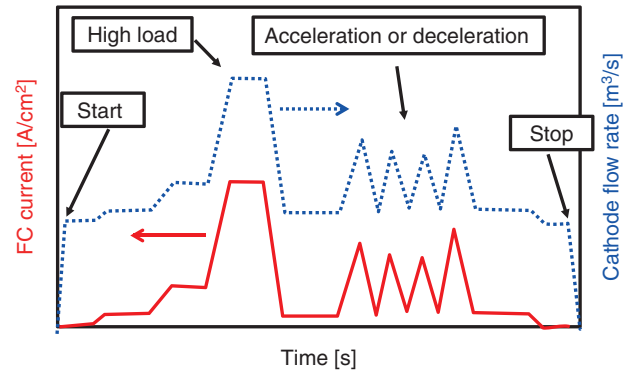


Fig. 3 Schematic drawing of evaluated operation mode

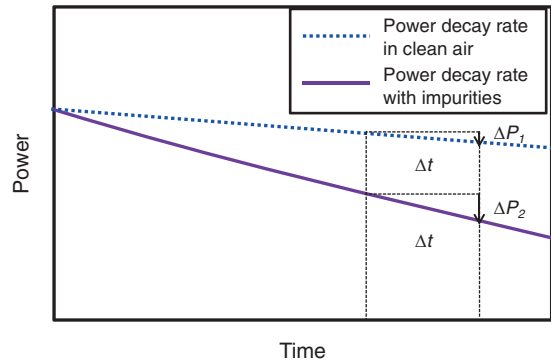


Fig. 4 Power decay rate by subtracting rate in clean air for correction

2.2. NaCl Evaluation Method

2.2.1. NaCl concentration setting

NaCl present in the atmosphere is called sea salt aerosol, and is an aerosol originating from the salinity of seawater. The sea salt aerosol concentration in the atmosphere is affected by various factors such as wind speed, wind direction, and weather, so long-term observation is needed to set the maximum value. Data released to the public could not be found, so this was measured by this study.

Preliminary investigations showed that the locations and times with the highest atmospheric sea salt aerosol concentrations in Japan are the southern islands such as Okinawa during the summer typhoon season⁽¹⁴⁾. Therefore, measurement was performed by the Japan Weathering Test Center's MIYAKOJIMA EXPOSURE TEST AND RESEARCH CENTER located in Miyako-jima, Okinawa Prefecture using a salinometer made by Electric Power Engineering Systems Co., Ltd.⁽¹⁵⁾ Figure 5 shows the frequency distribution of the NaCl concentration (4-hour average) for the one-month period from September 2 to October 2, 2016. This shows that the mode value was 20 $\mu\text{g}/\text{m}^3$, but there were also times when the concentration reached 100 $\mu\text{g}/\text{m}^3$.

Therefore, the NaCl concentration used in the tests was set to 100 $\mu\text{g}/\text{m}^3$, which was the maximum concentration measured in coastal areas.

2.2.2. NaCl test conditions

Evaluation was performed using the same stack specifications and conditions in order to clarify the difference when injecting NaCl by the aqueous solution of the conventional method and when injecting NaCl in aerosol form. Simulations were performed beforehand to investigate the vehicle power generation environment conditions that do not produce condensed water inside the flow-field, and the evaluation mode was set to the power generation mode with a fixed load of 0.1 A/cm². Evaluation used a stack consisting of ten actual automotive cells. High purity hydrogen (purity 5N) was humidified and heated using a bubbling system and supplied to the stack as the fuel gas. Clean air was humidified and heated, then NaCl

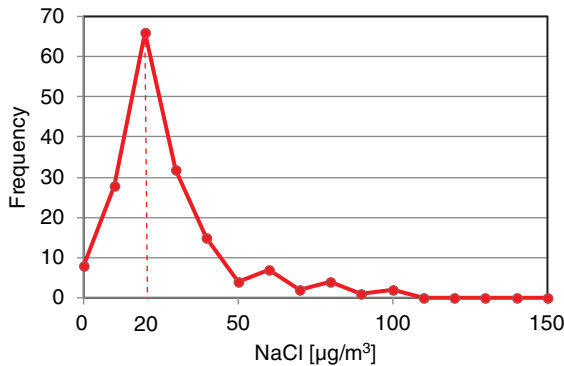


Fig. 5 Frequency distribution of sea salt aerosol

was mixed in via a T-shaped joint connected to the stack cathode gas inlet and the mixture was supplied to the stack as the oxidant gas. Coolant was used to control the stack temperature to a constant temperature.

When supplying NaCl by aqueous solution, the aqueous solution flow rate was controlled using an HPLC pump (Scientific Systems SERIES 1) to adjust the NaCl concentration in the clean air at the stack inlet to 100 $\mu\text{g}/\text{m}^3$. Figure 6 shows a schematic image of the power generation evaluation apparatus.

The NaCl flow rate Q_{NaCl} [kg/s] entering the stack was obtained by Eq. (7) from the NaCl aqueous solution concentration C_{solute} and the NaCl aqueous solution flow rate $Q_{\text{solution1}}$ [kg/s].

$$Q_{\text{NaCl}} = C_{\text{solute}} \times Q_{\text{solution1}} \quad (7)$$

The volumetric flow rate V_{Air} [m³/s] was obtained by Eq. (8) from the cathode flow rate Q_{Air} [Nm³/s], the stack inlet temperature T_{Air} [K], and the stack inlet pressure P_{Air} [kPa].

$$V_{\text{Air}} = Q_{\text{Air}} \frac{101.3}{P_{\text{Air}}} \times \frac{T_{\text{Air}}}{273} \quad (8)$$

The NaCl concentration C_{NaCl} [kg/m³] entering the stack was obtained by Eq. (9).

$$C_{\text{NaCl}} = \frac{Q_{\text{NaCl}}}{V_{\text{Air}}} \quad (9)$$

When supplying NaCl in aerosol form, the aerosol was generated using an aerosol atomizer (TSI Model 9306) and adjusted so that the NaCl concentration in the clean air at the stack inlet was 100 $\mu\text{g}/\text{m}^3$. The generated aerosol concentration was quantified according to the change in weight and the aqueous solution concentration.

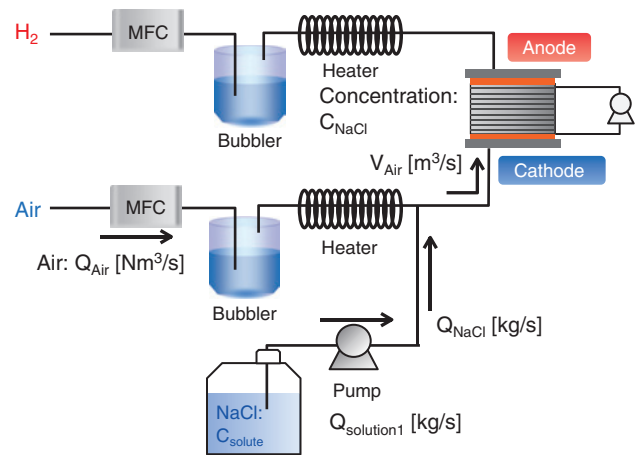


Fig. 6 Experimental scheme of salt water injection

Figure 7 shows a schematic image of the power generation evaluation apparatus.

The NaCl flow rate Q_{NaCl} [kg/s] entering the stack was obtained by Eq. (10) from the NaCl aqueous solution concentration C_{solute} and the change in NaCl aqueous solution weight $Q_{solution2}$ [kg/s].

$$Q_{NaCl} = C_{solute} \times Q_{solution2} \quad (10)$$

The total air quantity Q_t [Nm³/s] was obtained by Eq. (11) from the cathode flow rate Q_{Air} [Nm³/s] and the pressurized air flow rate Q_{pAir} [Nm³/s].

$$Q_t = Q_{Air} + Q_{pAir} \quad (11)$$

The volumetric flow rate V_t [m³/s] was obtained by Eq. (12) from the total air quantity Q_t [Nm³/s], the stack inlet temperature T_{Air} [K], and the stack inlet pressure P_{Air} [kPa].

$$V_t = Q_t \frac{101.3}{P_{Air}} \times \frac{T_{Air}}{273} \quad (12)$$

The NaCl concentration C_{NaCl} [kg/m³] entering the stack was obtained by Eq. (13).

$$C_{NaCl} = \frac{Q_{NaCl}}{V_t} \quad (13)$$

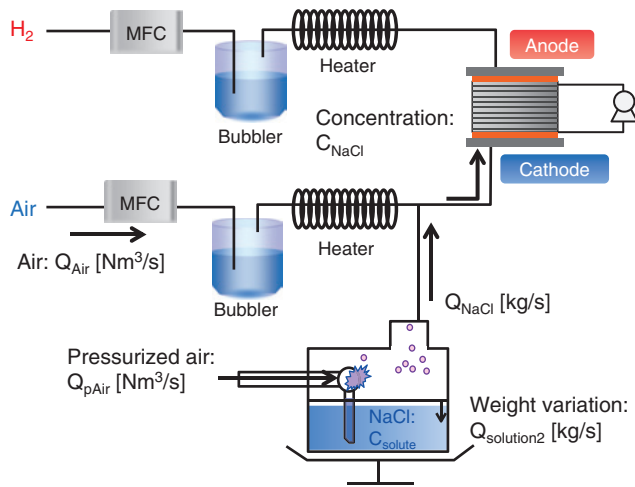


Fig. 7 Experimental scheme of salt aerosol test

3. Results and Discussion

3.1. Gaseous Impurity Results and Discussion

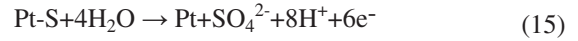
Figure 8 shows the relationship between the concentration of each impurity and the power decay rate.

The previously reported⁽⁵⁾ tendency where the drop

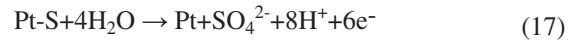
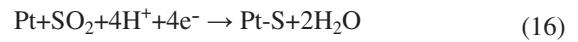
in power increases together with the concentrations of atmospheric impurities was also confirmed by this study.

Examination of the characteristics for each gas type shows that the power decay rate dependence on concentration exhibited similar behavior for the two types of sulfur-based impurities (H₂S, SO₂). The Pt catalyst surface reactions for H₂S and SO₂ proposed by Reference⁽¹⁶⁾ are as follows.

For H₂S:



For SO₂:



In both cases, the S adsorb to the Pt surface active points ultimately in the SO₄²⁻ form, so the power dependence on concentration is presumed to be similar for both H₂S and SO₂.

As described in Reference⁽⁵⁾, comparison at the same concentrations showed that NO₂ has a smaller effect on power reduction compared to sulfur-based impurities. However, Table 1 shows that whereas the maximum atmospheric concentration of sulfur-based impurities is 1000 ppb, there are some environments with a NO₂ concentration more than 1000 ppb, so it is thought that power may also be affected in regions with high NO₂ concentrations.

NH₃ did not exhibit an effect on power at the 100 ppb concentration anticipated in real-life environments. Like the previous report⁽⁵⁾, this study also confirmed that there is no effect on power as long as the concentration does not exceed 1000 ppb.

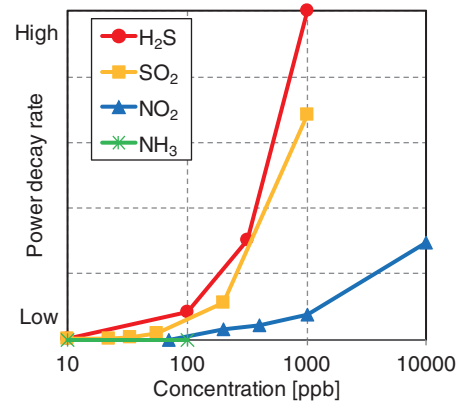


Fig. 8 Relationship between power decay rate and gaseous impurities concentration

3.2. NaCl Results and Discussion

Figure 9(a) shows the cell voltage after evaluation of NaCl injection. The difference from the beginning of life (BOL) performance indicates the degree of drop in power due to NaCl. The drop in power when NaCl is injected in aerosol form is less than that when injected by aqueous solution. Detailed analysis of the obtained values revealed a large rise in the ohmic overpotential component for cells where NaCl was injected by aqueous solution compared to cells where NaCl was injected in aerosol form, as shown in Fig. 9(b). The difference in cell voltage (ΔA) indicated by the shaded portion of the graph in Fig. 9(c) approximately matches the difference in ohmic overpotential (ΔB). Therefore, the difference in cell voltage is thought to be the difference due to this ohmic overpotential.

Reference⁽¹⁷⁾ states that the resistance increases when protons (H^+) on the PEM side chain are exchanged for Na^+ . The reason for this is thought to be that when NaCl is injected by aqueous solution, the Na^+ penetrates the electrolyte membrane and goes through a process of ion exchange with the protons (H^+) in the membrane, which increases the ohmic overpotential component.

In contrast, no increase in resistance was observed when NaCl was introduced in aerosol form. Therefore, the generation condition of condensed water inside the cathode flow-field was simulated using the Honda cell configuration and characteristics as the input to the polymer electrolyte fuel cell simulation software⁽¹⁸⁾. Figure 10 shows these results, and confirmed that condensed water is not generated in the cathode flow-field within the range of the test conditions used by this study. The reason why an increase in resistance was not observed under the test conditions used by this study is thought to be that NaCl

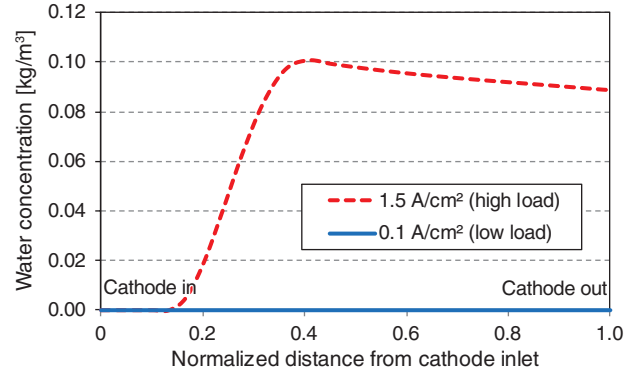


Fig. 10 Simulation of cathode channel

injected in aerosol form is not dissolved into condensed water and ionized, so Na^+ does not reach the membrane. However, consideration should also be given to cases where NaCl injected in aerosol form reaches the membrane under high load operating conditions where condensed water is generated in the cathode flow-field.

4. Conclusion

The effect of atmospheric impurity concentrations on fuel cell performance when a FCV runs in a real-life environment was evaluated by bench tests using a stack of an actual vehicle, and the following conclusions were reached.

- (1) Comparison of nitrogen-based impurities and sulfur-based impurities at the same concentrations showed that sulfur-based impurities have a larger effect on power.
- (2) Aqueous solution and aerosol were compared as the forms for injecting NaCl to the cells, and the results showed that each form affects power differently. When performing bench evaluation of NaCl-based impurities, it is considered important to select the appropriate NaCl form to be injected in accordance with the assumed environment.

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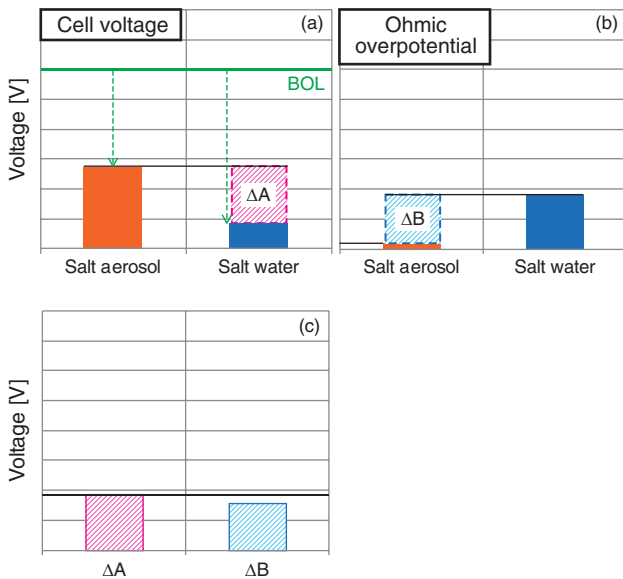


Fig. 9 Cell voltage and ohmic overpotential

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■ Author ■



Keiko YOSHIDA



Ryu OKANO