Oscillation mechanism in polymer electrolyte membrane fuel cell studied by *operando* monitoring of oxygen partial pressure using optical probes

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The stability of polymer electrolyte fuel cells (PEFCs) during power generation is one of the most important issues, especially at high current densities. A new oscillation phenomenon was observed in a PEFC with 10-straight channels operated at the temperature of 60 °C and the relative humidity of 60% using a gas diffusion layer (GDL) without a micro porous layer at the cathode. The cell voltage oscillated periodically under a constant-current operation. The period and amplitude were approximately 2 s and 20 mV, respectively, but changed at different gas flow rates and current densities. An *operando* system was developed for detecting the oxygen partial pressure (pO₂) using optical probes. pO₂ during the oscillation synchronized with the cell voltage. During the oscillation, the generated water was proposed to increase and accumulate in the catalyst layer (CL), accordingly lowering the transport and thus reduction reaction of oxygen. The larger overvoltage resulted in the heat in the CL, by which the liquid water having accumulated in the CL was removed as water vapor to the GDL. This oscillation could be more pronounced at higher current density.

**Keywords**: PEFC, Oscillation, *Operando* measurement, Oxygen partial pressure, Gas diffusion layer

1. Introduction

Polymer electrolyte fuel cells (PEFCs) are used for the residential, transportation, and portable applications as energy conversion devices with no emission of carbon dioxide. Besides the cell performance, the durability and stability during power generation are major concerns 1-3. Under certain conditions, the cell voltage and the current density become unstable and even fluctuated because of the instability of the reactions inside PEFCs. Since the excess liquid water in a cell is one of the main sources of instability, the water management during power generation has been extensively studied 4,5.

The water generated by the power generation is continuously removed outside the fuel cell through the gas diffusion layers (GDLs). However, when the water generation is too large, the flooding is inevitable. Therefore, a proper water management is of paramount importance for PEFCs. Materials must be developed, and the operating conditions and the cell components must be optimized. Barbir et al. investigated unexpected increases in pressure and cell resistance of a PEFC stack during power generation 6. They pointed out that the increase in pressure could be indicative of the increased liquid water in the stack, while the increase in cell resistance of a membrane dry-out. Hirakata et al. investigated the effect of pore size of GDL on the periodic instability of the cell voltage accompanied by the synchronized change in gas pressure, concluded to be caused by the water droplets blocking/releasing the cathode flow channel 7.

Recently, the oscillation phenomena during power generation have been reported in running PEFCs. Sanchez and coworkers reported an oscillatory fluctuation when the cathode was dry and the anode was wet at a nominal humidity of 152% with the cell temperature of 70 °C 8. The current density first decreased slowly from 650 to 610 mA cm⁻² within 1000 s at a constant cell voltage of 500 mV. Subsequently, a fluctuation in current density started, followed by a continuous oscillation between 600 and 60 mA cm⁻² accompanied by a gradual decrease in current density resulting in the decrease in cell performance. During the oscillation, the transition from the lowest current to the highest current took place in 20 s, and the transition from the highest to the lowest slightly longer than 20 s. The change of the coefficient of the electro-osmotic drag accompanied by that of the liquid-vapor permeation at the interface of the membrane was suggested as a major feedback mechanism for the oscillatory behavior 8,9. The change in the properties at the membrane interface was visualized by current-sensing atomic force microscopy showing the oscillatory behaviors 10. The fluctuations were found to be also related to the water shortage at the anode. A combination of the limited water available at the anode, the electroosmotic
drag transporting water from the anode to the cathode, and the insufficient water back diffusion from the cathode to the anode was proposed to cause the anode to dehydrate. The cell ohmic resistance decreased and the performance recovered by the anode re-humidification. Atkins et al. found periodic oscillations in current and cell resistance at a fixed cell potential of 500 mV. From the initial conditions using sparger bottles for the feed-stream humidification (cell temperature = 100 °C, sparger temperatures at the anode/cathode = 115 °C /110 °C), the temperatures of the sparger bottles were lowered to 80 °C. Large fluctuations and a significant decrease of the current density, approximately by 0.5 A cm⁻², were observed. The oscillation period of current was several hundreds of seconds and become larger when the sparger temperature was kept at 80 °C. The ohmic resistance also oscillated between 50 and 250 mΩ.

We found a new oscillation phenomenon during power generation at 0.6 A cm⁻² using a GDL without a micro porous layer (MPL) at 60 °C and 60% RH. The differential pressure between the cathode inlet and outlet was 0 kPa during the oscillation. This phenomenon is very different from the cell voltage fluctuation previously reported to be synchronized with the differential pressure caused by the plugging of flow channels. A different mechanism should have caused this new oscillation without the excess liquid water in the gas flow channel. The amplitude and period of this newly-found oscillation were approximately 20 mV and 2 s, respectively, whereas the oscillation or fluctuation of the cell voltage previously reported at the dried cathode showed a period significant longer than ours, about tens of seconds to hours after power generation. The oscillation amplitudes of the current density at constant voltages in previous studies were large, too: 0.05 – 0.55 A cm⁻², 0.5 – 1.1 A cm⁻², and 0.55 – 0.83 A cm⁻². According to Nernst equation (Equation (1)), the oxygen partial pressure (pO₂) is directly related to the fuel cell overvoltage.

\[ E = \frac{-\Delta G(T)}{2F} + \frac{RT}{2F} \cdot \ln \left( \frac{p(O_2)^{1/2}}{p(O_2)} \right) \]  
where \( \Delta G \) is the molar Gibbs free energy (J mol⁻¹), T temperature (K), F Faraday constant (96485 C mol⁻¹), R universal gas constant (J mol⁻¹ K⁻¹), and \( p \) partial pressure. To elucidate the mechanism of this new oscillation phenomenon, we focused on p(O₂) inside the GDLs during power generation.

For the oscillation studies, "operando measurements", or direct analytical methods in operation (during power generation), are very important. William et al. developed an operando measurement system of the O₂ concentration using a commercially-available micro oxygen-concentration sensor 25 µm in diameter inserted into the GDL at the cathode of an operating PEFC. The O₂ concentrations were measured at different current densities and relative humidities (RHs). By X-ray computed tomography (CT), the GDL structure was also analyzed to be related to the O₂ transport resistance. In their system, similar to an current interrupt method for measuring an ohmic resistance, the current of the PEFC was interrupted. When the current was interrupted, the oxygen concentration returned to the channel level in milliseconds, while the sensor behavior related to RH and temperature changed over many seconds. Therefore, for monitoring p(O₂), at least 5 s was needed. In addition, the measurements at multiple locations were not easy due to the shape and strength of the O₂ sensors made with glass capillaries. Previously, our group developed a 2-dimensional visualization system of p(O₂) on the GDL surfaces and the flow-channel walls inside running PEFCs using an oxygen-sensitive dye film. To monitor p(O₂) inside a GDL, we have developed a new apparatus using 5 optical fibers with diameter of 50 µm. The probes can be precisely located with a spatial resolution of 1 µm in depth, and p(O₂) can be simultaneously measured at 5 points both under the flow channel and under the ribs with the time resolution of 100 ms. With using this operando monitoring system, the voltage oscillation was found to be synchronized with the p(O₂) oscillation at all the locations inside the GDL. With using this newly-developed apparatus, the voltage oscillation was studied.

2. Instrumental
2.1 Oxygen-sensitive dye film
Pt(II)tetrakis-pentafluorophenylporphyrin (PtTFPP), an oxygen-sensitive dye, was used as an oxygen sensor. PtTFPP was mixed with poly(1-trimethylsilyl-1-propyne) (polyTMSP) and toluene, and the concentration of the dye solution was adjusted to 25 wt% with respect to PtTFPP. PtTFPP has absorption peaks at 320 (blue light) and 530 nm (green light), and an emission peak of at 650 nm (red light). In this study, green light was used for the detection of p(O₂) because of the excitation of Si in an optical fiber by blue light. The emission intensity of the oxygen sensitive dye monotonically decreased as p(O₂) increased.

2.2 Optical fiber
A single-mode optical fiber with a clad diameter of 125 µm and a core diameter of 10 µm was used. The fibers were immersed in HF solution (pH = 2.9) and etched until the diameter became approximately 50 µm. Subsequently, the top of the optical fiber was trimmed flat perpendicular to the fiber axis. On the apex of a fiber, an oxygen-sensitive dye film was coated with a thickness of 2 µm. The change in emission intensity as a function of temperature was small, -0.5% K⁻¹. The influence of the humidity on the oxygen partial pressure in air was negligibly small, too. When the dye film at the apex of a probe was wet with liquid droplets, the emission intensity much increased. Under the conditions for the power generation in this study, the apex of the probe was never wet, and the intensity of the emission was steadily monitored.

2.3 Oxygen monitoring system
Figure 1(a) shows a schematic representation of the p(O₂) monitoring system, briefly described in a previous report. In the cathode side of a GDL, 5 holes were created down to the catalyst layer (CL) both under the flow channels and the ribs. The optical probes were inserted directly into a PEFC through the holes. The distance between the probe apex and the CL surface was controlled by a micrometer.

The effect of inserting the probe into the manufactured hole on the mass fraction of O₂ was numerically estimated using X-ray CT images experimentally obtained. A hole with a diameter of 90 µm was computationally created and an artificial probe with a diameter of 50 µm was virtually inserted into the hole. The O₂ concentration on both surfaces of the GDL was calculated at the current density of 1 A cm⁻², only the gas diffusion being considered. The O₂ mass fraction was calculated inside the GDL, and the difference was estimated to be less than 1% with/without a virtual hole and a probe.

For measuring the distance between the probe apex and the CL, a super luminescent diode light with a wavelength of 830 nm was introduced to the probe to obtain an interference light from the CL and the probe apex (Fig. 1(b)). The spectrum of reflection

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light out from the optical probe was Fourier-transformed to measure the distance within an accuracy of 1 μm.

2.4 Cell for oxygen monitoring

Figure 2(a) shows the structure of a cell with 10 straight flow channels for p(O2) monitoring. At the cathode side of a stainless endplate, a window was created for the insertion of the optical probes. An acrylic insulator plate with 5 holes was located between the endplate and the current collector for the probe positioning. The cathode and the anode gases were supplied as parallel flows. The channel length was 30 mm. The ribs at the cathode and the anode overlapped each other. The active catalyst area was 20 mm × 20 mm. Figure 2(b) shows the positions of the holes created through the GDLs under the central rib, located at 2.5, 10.0, and 17.5 mm from the edge of the CL, and those under the flow channels at 5.0 and 15.0 mm from the edge of the CL.

2.5 Optical settings

A 532 nm diode laser light was divided into five beams by beam splitters. The power of each beam was 2 μW. The beams were irradiated onto the oxygen-sensitive dye film coated at the apex of the probes. The excitation light and the 650 nm emission were separated by a dichroic mirror, and the emission was detected by a CCD camera with a filter for the reflective excitation light placed in front of the camera. The probes were positioned as described in Section 2.3.

3. Experimental

3.1 Cell preparation

Figure 3 shows X-ray CT images of the GDLs without (SIG-RASET® 28BA, SGL Carbon Group Co., Ltd.) and with (28BC) an MPL measured at the beamline BL46XU of Spring-8, Japan. At the anode side, 28BC was always used, whereas at the cathode side, either 28BA or 28BC was employed. Cavities of tens of micrometers are seen in the assembly of carbon fibers. The thickness of the MPL was approximately 100 μm. The X-ray energy was 12.39 keV with a specific resolution of 0.37 μm voxel. The GDLs (20 mm × 20 mm) were processed to have through holes (100 μm in diameter created by laser ablation) for inserting the optical probes (Section 2.4). To prepare the catalyst coated mem-

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Fig. 1 (a) : Schematic representation of p(O2) measurement inside GDL. (b) : Interference between lights from probe tip and surface of CL, Fourier-transformed to determine distance (49 μm in this case).

Fig. 2 (a) : Cell designed for operando p(O2) measurement. (b) : Positions of holes at GDL for p(O2) measurement. Triangles under central rib, squares under flow channels.

Fig. 3 X-ray CT images of 28BA (without MPL) (a), and cross-sectional images of 28BA (b) and 28BC (with MPL) (c).
was used. The gases flew parallel and in the same direction at the cathode and the anode. Prior to the electrode assembly, 140 holes at the anode, hot-pressed at 140 °C and 2.5 kN for 3 minutes to form a membrane-electrode assembly (MEA).

3.2 \( p(O_2) \) measurement

For the power generation, a test bench (As-510-340PE, NF Corp.) was used. The gases flew parallel and in the same direction at the cathode and the anode. Prior to the \( p(O_2) \) monitoring, the current density was held at 1 A cm\(^{-2}\) for 3 hours and 0.2 A cm\(^{-2}\) for 12 hours at the gas flow rates of \( H_2/O_2 = 400/200 \) mL min\(^{-1}\) at 40 °C and 100% RH for the cell conditioning. Then, the gases were switched to \( H_2/N_2 = 100/100 \) mL min\(^{-1}\), and the cell voltage was cycled 40 times at 20 mV s\(^{-1}\) between 0.075 and 1.0 V for measuring the electrochemical surface area. Subsequently, the temperature and RH were changed to 60 °C and 60%, respectively. The optical probes were inserted and positioned at the same distance from the CL. For obtaining a calibration curve, mixed gasses with \( N_2 \) and Air at different concentrations were supplied to both the anode and the cathode first at 250 mL min\(^{-1}\) for 10 min. During the acquisition of the emission, the flow rate was reduced to 100 mL min\(^{-1}\) to minimize the pressure loss. At each gas-mixture rate, the emission was measured at each probe three times by a CCD camera to be averaged. The emission intensity of the oxygen sensitive dye was deteriorated by the laser irradiation rather linearly at approximately 0.03% s\(^{-1}\). To obtain \( p(O_2) \) using this dye film, the deterioration coefficient was taken into account after obtaining the emission data. A calibration curve of a probe is shown in Fig. 4 as an example.

For the power generation, the gas-flow rates were set at \( H_2/\text{Air} = 400/200 \) mL min\(^{-1}\) and the current density at 0.2 A cm\(^{-2}\). The current density was kept for 20 min and stepped to 0.6 A cm\(^{-2}\). During power generation, the differential pressure was continuously monitored (DT-8890, CEM, Shenzhen Everbest Machinery Industry Co., Ltd.) between the inlet and outlet.

4. Results

4.1 Period and amplitude of voltage oscillation

The power generation was carried out with a cell (Fig. 2) using a GDL without an MPL (28BA) at the cathode side at 60 °C, 60% RH, 0.6 A cm\(^{-2}\), and \( H_2/\text{Air} = 400/200 \) mL min\(^{-1}\). Figures 5(a) and (b) show the cell voltage and the differential pressure between the inlet and the outlet at the cathode, respectively. The results with/without probes were identical. Under these conditions, the voltage oscillation was clearly observed, whereas the differential pressure was lower than the detection limit (<0.01 kPa). In the previous report \(^\text{15,17}\), a fluctuation of the cell voltage was accompanied by the differential pressure at the cathode by water plugging \(^\text{15,17}\), which cannot explain this oscillation. The period of the cell voltage was approximately 1.5 s and the amplitude (\( \Delta V \)) 20 mV. Figures 6(a1) and (a2) show the period and amplitude, respec-

![Fig. 4](image-url) Calibration curve for oxygen using oxygen sensitive dye (PtTFPP).

![Fig. 5](image-url) Cell voltage (black filled circles) (a) and differential pressure (DP, red open circles) (b) between cathode inlet and outlet of cell with 28BA (without MPL).

![Fig. 6](image-url) Period (a1) and \( \Delta V \) (a2) of oscillation vs. air flow rate at cathode. \( H_2/\text{Air} = 400/100, 200, \) and 300 mL min\(^{-1}\). Current density = 0.6 A cm\(^{-2}\) (oxygen utilization = 19.9%). Period (b1) and \( \Delta V \) (b2) vs. current density. \( H_2/\text{Air} = 400/200 \) mL min\(^{-1}\), \( T = 60 \) °C and RH = 60% for all measurements. 28BA without MPL was used.
tively, with respect to the air flow rate at 60 °C, 60% RH, and 0.6 A cm⁻². Both the period and the amplitude decreased as the air flow rate increased. Figures 6(b1) and (b2) show the period and amplitude, respectively, with respect to the current density at 60 °C, 60% RH, and the air flow rate of 200 mL min⁻¹. The period continuously decreased from 4.7 to 3.6 s at 0.6 A cm⁻² as the current density increased from 0.3 to 0.6 A cm⁻² (Fig. 6(b1)). The amplitude monotonously increased with the increase in current density (Fig. 6(b2)). To investigate the voltage oscillations in a different cell, a single-serpentine cell (Japan Automobile Research Institute, JARI cell [34]) was used with a GDL without an MPL (28BA) at the cathode side. As shown in Fig. 7, the oscillations were also observed in a JARI cell with periods rather irregular.

4.2 \( p(O_2) \) measurement in GDLs at different distances from catalyst layer

Figure 8 shows \( p(O_2) \) inside the GDL without an MPL (28BA) (a) and that with an MPL (28BC) (b), respectively, obtained at different lateral/vertical probe positions (Fig. 2(d)) at the cathode side at 0.6 A cm⁻² and \( H_2/\text{Air} = 400/200 \text{ mL min}^{-1} \). The oxygen utilization was 19.9%. The measurement points near the inlet are shown in blue, at the center, and near the outlet in red, and the measurement points under the flow channels and the ribs are shown by squares and triangles, respectively. The distances between the probe apex and the CL was changed from 100 to 50, 10, and 5 μm, closer to the CL surface. \( p(O_2) \) was measured three times at each location and the averaged value was plotted with bars showing the highest and the lowest values that comes from the oscillation. In 28BA (Fig. 8(a)), \( p(O_2) \) near the inlet under the flow channel (blue squares, 5.0 μm from the edge of the catalyst area) was nearly constant, 18.6 kPa, regardless of the depth. \( p(O_2) \) near the outlet under the flow channel (red squares, 15.0 μm from the edge of the catalyst area) was also nearly constant, 17.0 kPa. The decrease in \( p(O_2) \) was 18.6 – 17.0 = 1.6 kPa between the two holes (5.0 and 15.0 mm from the edge of the catalyst area). Since the oxygen utilization was 19.9%, the decrease in \( p(O_2) \) is calculated as 1.8 kPa assuming the linear consumption of oxygen along the flow channel. Therefore, the consumption of oxygen was nearly at a fixed rate along the flow channel [19]. Near the inlet under the rib (blue triangles), \( p(O_2) \) decreased from 11.5 to 11.2 kPa as the probe approached to the CL surface (100 to 5 μm). At the center under the rib (green triangles), \( p(O_2) \) decreased largely from 11.3 to 9.6 kPa as the probe approached to the CL. Near the outlet under the rib (red triangles), \( p(O_2) \) slightly decreased from 13.4 to 13.1 kPa as the probe approached to the CL. Surprisingly, \( p(O_2) \) near the outlet under the rib was much higher than that near the inlet, and \( p(O_2) \) at the center was the lowest.

In the case of 28BC, \( p(O_2) \) near the inlet under the flow channel (blue squares) were 19.6, 18.7, 17.4, 16.8, and 15.5 kPa at 100, 50, 25, 10, 5 μm from the CL, respectively. \( p(O_2) \) clearly decreased as the probe approached to the CL. \( p(O_2) \) near the outlet under the flow channel (red squares) decreased from 17.5 to 12.7 kPa as the probe approached to the CL. \( p(O_2) \) near the inlet under the rib (blue triangles) slightly decreased from 14.9 to 13.9 kPa, and \( p(O_2) \) near the outlet under the rib (red triangles) decreased from 10.2 to 6.6 kPa.

4.3 Cell voltage and \( p(O_2) \) inside GDLs without/with MPL at cathode side

Subsequently, the cell voltage and \( p(O_2) \) were continuously measured for 20 s at 60 °C, 60% RH, and \( H_2/\text{Air} = 400/200 \text{ mL} \), before and after the change in current density. The apices of the probes were set at 10 μm from the CL. Figure 9 (a) shows the cell voltage and \( p(O_2) \) with 28BA (without MPL). The cell voltages are shown by black circles. The \( p(O_2) \) values under the flow channels and under the ribs are shown by squares and triangles, respectively, whereas those near the inlet, at the center, and

![Fig. 7](https://example.com/image7)

**Fig. 7** Cell voltage oscillated in JARI cell at different \( U_{\text{oc}}, H_2/\text{Air} = 40/20 \text{ mL min}^{-1} \). Linear velocities of \( H_2/\text{Air} = 0.66/0.33 \text{ m s}^{-1} \), the same as those with 10–straight channel cell. \( T = 60 \degree \text{C}, \text{RH} = 60\% \).

![Fig. 8](https://example.com/image8)

**Fig. 8** \( p(O_2) \) at 0.6 A cm⁻² at different locations with different distances from CL with 28BA (without MPL) (a) and 28BC (with MPL) (b) at cathode side. \( p(O_2) \) near inlet, at center, and near outlet are shown in blue, green, and red, respectively. \( p(O_2) \) under flow channels and ribs are shown by squares and triangles, respectively. See Fig. 2(b) for locations.
near the outlet are shown in blue, green, and red, respectively. The current density was abruptly changed from 0.2 to 0.6 A cm$^{-2}$ during the measurements (at perpendicular dashed lines). At 0.2 A cm$^{-2}$, the cell voltage was approximately 730 mV with the oscillation amplitude of 2 mV and the period of 2.0 s. When the current density was increased to 0.6 A cm$^{-2}$, the cell voltage suddenly decreased to 534 mV. At the same time, the voltage oscillation became larger with the oscillation amplitude of 16 mV and the period of 2.5 s. The cell voltage gradually increased with the oscillation with the same amplitude and the period. At the increase in current density, $p(O_2)$ abruptly decreased. Under the flow channel near the inlet (blue square), $p(O_2)$ changed from 18.3 to 17.3 kPa and gradually increased up to 19 kPa at 15 s. Under the flow channel near the outlet (red square), $p(O_2)$ changed from 18.5 to 16.2 kPa and gradually increased to approximately 17 kPa at 15 s. The average amplitude of $p(O_2)$ under the flow channel and the rib near the outlet were 3.0 kPa. Under the rib near the inlet, $p(O_2)$ decrease from 16.3 to 11.7 kPa and gradually decreased after changing the current density to 0.6 A cm$^{-2}$. The average amplitude of $p(O_2)$ was 0.1 kPa at 0.6 A cm$^{-2}$. Under the rib at the center, $p(O_2)$ changed from 15.2 to 10.5 kPa. These values were lower than those near the inlet under the rib both at 0.2 and 0.6 A cm$^{-2}$. Under the rib near the outlet, the amplitude of $p(O_2)$ was 1.3 kPa at 0.2 A cm$^{-2}$. When the current density was changed from 0.2 to 0.6 A cm$^{-2}$, $p(O_2)$ under the rib near the outlet was significantly decreased from 16.9 to 11.9 kPa, and the amplitude became larger from 1.3 to 2.7 kPa. The amplitude became larger from the inlet to the outlet along the flow channel length. Also, the voltage oscillation became larger from 2 to 20 mV after the current-density increase. The oscillations of the cell voltage and $p(O_2)$ all synchronized.

The cell voltage and $p(O_2)$ with 28BC (with MPL) are shown in Fig. 9(b). After increasing the current density, the voltage and $p(O_2)$ abruptly decreased. The cell voltage decreased from 740 to 569 mV, $p(O_2)$ near the inlet under the flow channel and rib, and that near the outlet under flow channel and rib decreased from 18.3 to 16.4 kPa, from 15.6 to 13.4 kPa, from 17.4 to 14.8 kPa, and from 11.0 to 7.1 kPa, respectively. Subsequently, $p(O_2)$ under the flow channels gradually increased and $p(O_2)$ under the ribs slowly decreased. The voltage and the $p(O_2)$ did not oscillate. The cell voltage became approximately 0.59 V at 0.6 A cm$^{-2}$. In comparison to the GDL without an MPL (28BA), the overvoltage became smaller by 0.02 V. The oscillation of $p(O_2)$ was not observed under any condition with the GDL and an MPL.

5. Discussions

5.1 Increase in $p(O_2)$ near outlet under rib

Interestingly, under the rib, $p(O_2)$ was higher near the outlet (red triangles) than those near the inlet (blue triangles) and at the middle (red triangles) as shown in Figs. 8(a) and 9(a), whereas $p(O_2)$ under the flow channels gradually decreased along the flow channel length by the oxygen consumption. $p(O_2)$ under the rib was naturally lower than that under the flow channel, because the oxygen diffusion from the flow channel beneath the rib was lowered by the existence of the rib itself. It should be noted that the amount of oxygen is generally determined by the oxygen supply from the flow channel and the consumption at the CL. The oxygen utilization was only 19.9% even at 0.6 A cm$^{-2}$, and $p(O_2)$ in the flow channel accordingly decreased from the inlet to the outlet under this operating condition. Under the rib, $p(O_2)$ decreased from the inlet to the center and increased near the outlet along the channel length (Figs. 8(a) and 9(a)). This might be indicating that the oxygen consumption at the CL under the rib near the outlet was very small, probably because of the accumulation of liquid water in the CL. The model is illustrated in Fig. 10. For understanding the oscillation phenomena, the existence of liquid water must be taken into account.

5.2 Mechanism of synchronized oscillation of cell voltage and $p(O_2)$

As shown in Fig. 9(a), the cell voltage oscillated clearly and distinctly in a cell with 28BA (without MPL) at the cathode side, and $p(O_2)$ synchronized with voltage under the flow channel and under the rib. However, the differential pressure was lower than the detection limit, which means that the excess water did not exist in the flow channels. Therefore the amplitudes of the oscillations of both voltage and $p(O_2)$ became larger at 0.6 A cm$^{-2}$. 

Fig. 9 Cell voltage and $p(O_2)$ at different measurement points using 28BA (without MPL) (a) and 28BC (with MPL) (b) at cathode side. Cell voltages are shown by black circles, $p(O_2)$ near inlet, at center, and near outlet are shown in blue, green, and red, respectively. $p(O_2)$ under flow channels and ribs are shown by squares and triangles, respectively. Optical probe was located at 10 μm from CL surface. Current density was changed from 0.2 to 0.6 A cm$^{-2}$ (oxygen utilization from 6.6 to 19.9%, respectively) at 2 s in graphs. $T = 60 \, ^\circ\text{C}$ and RH = 60%. Hz/Air = 400/200 mL min$^{-1}$. 

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than at 0.2 A cm⁻². The amplitude of the \( p(O_2) \) oscillation became larger from the inlet to the outlet. As discussed in the previous section, the accumulation of water in the CL could be the key to understand those oscillations. The mechanism of the oscillation of the cell voltage and \( p(O_2) \) in a PEFC with a GDL without an MPL at the cathode side is depicted in Fig. 11(a). The generated water increased and accumulated in the CL especially near the outlet, and the air permeation was lowered. To keep a constant current density, the overvoltage became larger and the heat was generated. Subsequently, the liquid water in the CL was removed as water vapor from the CL to the GDL. The temperature at the CL was then lowered by the heat of evaporation. By repeating this cycle, the voltage oscillation could continue. When liquid water turned into vapor, \( p(O_2) \) in the GDL should naturally decrease. The large influence of water and oxygen at the CL under rib near outlet at cathode side.

A schematic model of the water evacuation from the CL when using a GDL with an MPL at the cathode side is shown in Fig. 11 (b). Liquid water was constantly removed from the CL by the capillary phenomenon through the MPL with the pore size of nanometers and the thickness of 100 \( \mu \)m (Fig. 3(c)), so the voltage oscillation was not observed. Most of liquid water removed from the CL is expected to take forms of nano droplets and spontaneously vaporized at the MPL/GDL interface, where the nano water droplets were exposed to the gas flow at 60% RH. The overvoltage was also kept low compared to that with the GDL without an MPL without excess water at the CL.

### 5.3 Oscillations under different conditions

When the excess water accumulates in the cathode CL, the oxygen reduction reaction (ORR) is inhibited, and the ORR proceeds where water does not accumulate. The period and amplitude of the voltage oscillation depended on the balance between the amount of water and heat both generated by the power generation. Figures 6(a1) and (a2) show the dependency of the period and amplitude of the oscillating voltage on the air flow rate. Both the period and the amplitude decreased with increasing the air flow rate. This can be explained by an easier removal of the accumulated water at a high air flow rate. At high flow rates, the region of accumulated water might be limited only near the gas outlet. In contrast, under low flows, the amount of accumulated water is expected to be larger, and the accumulation region expand to the upper part of the MEA. Especially under the ribs, water accumulation was more likely to occur, because the gas diffusion was limited by the existence of ribs. In this way, the period of the voltage oscillation at high flow rates was shortened, because the amount of water, as well as the accumulated region, was smaller than that at low flow rates. In addition, the amplitude of the voltage oscillation at high flow rates decreased due to the smaller concentration overvoltage because of the decrease in the accumulation of water.

As seen in Figs. 6(b1) and (b2), the period and amplitude depended on the current density. As explained in Fig. 6(a2), the concentration overvoltage increased probably due to the increase in generated water in the CL. Therefore, the generated heat also increased with the increase in overvoltage with the current density increase. The accumulated water was rapidly removed by the generated heat, thus the period was shortened. The voltage oscillation amplitude increased with current density. As explained in Fig. 6(a2), the ORR should be inhibited more as the water accumulation regions increased in the CL at high current densities, where the concentration overvoltage increased and the amplitude of cell voltage oscillation became larger.

In these ways, the cathode air flow rate and current density were understood to influence the period and amplitude of the voltage oscillation.

### 6. Conclusions

The optical probes coated with an oxygen-sensitive dye were inserted directly into PEFCs to elucidate the mechanism of the oscillation of the cell voltage during power generation accompanied by an oscillation of \( p(O_2) \) inside the GDL without an MPL at the cathode side at the constant-current mode. The negligible pressure difference between the inlet and the outlet of the cathode during the voltage oscillation eliminated the possibility of the plugging by liquid water. As the air flow rate increased, both the period and the amplitude decreased. As the current density increased, the period continuously decreased, whereas the amplitude monotonously increased. \( p(O_2) \) was found to synchronize with the voltage oscillation. In particular, the amplitude of the oscillation of the \( p(O_2) \) was the largest under the rib and
near the outlet. The oscillation was proposed to be caused by the repeated evaporation and accumulation of liquid water in the CL. The oscillation was not observed when the GDL with an MPL was used at the cathode side because of a smooth removal of water from the CL improved by the capillary phenomenon in an MPL.

The oscillation phenomena is likely to be more pronounced in the future operation of PEFCs at high current densities. The mechanisms proposed in this paper could be applied to the water management in the CL and the GDL, as well as for optimizing the PEFC operation.

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