Simultaneous visualization of oxygen partial pressure, current density, and water droplets in serpentine fuel cell during power generation for understanding reaction distributions

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Highlights

- Oxygen partial pressure, current density, and water droplets were visualized.
- PEFC performances were studied by visualizing the reaction distributions.
- Influence of liquid/gaseous water was elucidated in a running PEFC.

Abstract

Understanding the reaction distributions inside a polymer electrolyte fuel cell (PEFC) is essential for the higher performance and durability. We have developed a new see-through cell and visualized the distributions of oxygen partial pressure and current density inside a running PEFC at the temperature of 40 °C and 80 °C and the relative humidity of 53%. The oxygen utilization was changed from 0% to 80% by changing the current density. At higher oxygen utilizations, the current density was higher and therefore the water generation. Generated water droplets in the flow channel were also visualized, allowing for the simultaneous visualization of the distribution of the oxygen partial pressure, current density, and water droplets. By combining the observations of all three parameters, the reactions inside a membrane-electrode assembly were discussed.

1. Introduction

Polymer electrolyte membrane fuel cells (PEFCs) are intensively studied to be used for vehicles, residences, and portable devices with their cleanliness and high efficiency. There are, however, still issues to be overcome for the wider commercialization; higher
performance, durability, and lower costs. The distribution of reactions inside a fuel cell during the cell operation is known to be inhomogeneous, which may lead to lowering the cell performance and/or enhancing the degradation of membrane electrode assemblies (MEAs) [1–3]. Therefore, further understanding the PEFC system by elucidating the distributions of chemical (O2, H2, H2O, CO2, H2O2, etc.) and physical (temperature, current density, gas flux, pressure, etc.) parameters inside a PEFC during the power generation is essentially important. In order to achieve these demands for the cell diagnosis, various in situ measurement techniques, including visualizations, have been proposed.

Among in-situ visualizations inside a PEFC, much interest has been taken in liquid water formed in the MEA and the gas flow channels by using direct optical observation [4–9], X-ray imaging [10–13], neutron imaging [14–21], and magnetic resonance imaging [22–24], because of the importance of the water management that much affects the reaction distributions in PEFCs [25,26]. The distribution of current density at the MEA has also been actively studied for optimizing the operating conditions and designing MEAs and cells by using segmented current collectors [27–38] or by magnetotomography based on the measurement of the magnetic flux surrounding the fuel cell caused by the current inside [39–42]. Cleghorn et al. studied the effect of humidification and flow rate of reactant gases using the segmented gas diffusion backing and current collector with hydrogen gas flow channel at the anode [27]. Büchi et al. investigated the effect of gas humidification and gas stoichiometry on the current density distribution [35], and Reshefenko et al. reported the effects of different gas humidification in terms of the overpotentials [37]. In spite of various studies, the cause of the inhomogeneity inside PEFCs has not been fully elucidated only by detecting the current distributions; other physical/chemical parameters were needed to be understood.

In our group, the visualization of the oxygen partial pressure at the cathode has been studied using oxygen-sensitive dyes both on the upper gas-flow channels and the gas diffusion layers (GDLs) [8,43–48]. The concentration of CO2 has been visualized as well during the startup/shutdown cycles [44]. Under a high humidity, the formation of water droplets during the power generation has been also observed on different GDLs [9]. Besides the visualizations of individual parameters, the combination of multiple parameters gives rich and precise information. We have visualized liquid water in flow-channels and the oxygen partial pressure on GDLs simultaneously to elucidate the influence of water plugging on the oxygen partial pressure; essential differences were observed in the serpentine [8] and straight [47] flow channels.

In this study, the visualization of the oxygen partial pressure and the current density was simultaneously carried out using a newly developed single cell. At higher oxygen utilization (U02), the current density was higher and water droplets were additionally observed. The combination of chemical/physical parameters was helpful in understanding the materials transport derived by the reaction distributions inside a cell.

2. Experimental

2.1. Preparation of an MEA

Commercial Pt catalyst supported on carbon black (46 wt%-Pt, Tanaka Kikinzoku Kogyo K.K.) was mixed with pure water, ethanol, and 5 wt-% Nafton® ionomers (ion exchange capacity = 0.9 meq g⁻¹, DE521, E. I. Du Pont Nemours & Company, Inc.) by using a planetary ball mill for 30 min to form a catalyst paste with an ionomer/carbon ratio of 0.7. The catalyst paste was spray-coated on the microporous-layer side of the gas diffusion layers (GDLs, SIGRACET® 25BCCH, SGL Carbon Group Co., Ltd.) by a pulse-swirl-spray apparatus (Nordson) to prepare the gas diffusion electrodes (GDEs), and then dried at 60 °C for 12 h in an electric oven. The Nafton® membrane (NRE211, E. I. Du Pont Nemours & Company, Inc.) and two GDEs were hot-pressed at 140 °C and 1.0 MPa for 3 min to form a membrane-electrode assembly (MEA). The geometric area of the MEA was 29.2 cm², and the Pt loading was 0.50 mg cm⁻² on both the anode and the cathode.

As an oxygen sensor, a luminescent porphyrin dye film ([Tetraphenylporphyrin]platinum (PThPP) – poly(1-trimethylsilyl-1-propanyl) (PTMP) 5wt%) was used to visualize p(O2) [49,50]. Those values The dye was spray-coated uniformly with a thickness of 2 μm on the GDL surface at the cathode [43,47,48]. The luminescent life time of PtThPP is 120 μs, and the oxygen permeability coefficient of PTMP is 13,000 cm²(STP) cm⁻¹ s⁻¹ cmHg⁻¹ [51]. Therefore, the time resolution of the dye film for the oxygen detection is approximately 1 ms.

2.2. Visualization system for p(O2), current density, and liquid water

Fig. 1(a) schematically shows the new see-through PEFC. In order to look through the cell, a cathode plate with a single serpentine flow channel (channel length = 143.5 mm, rib width = 1 mm, channel width = 1 mm, channel depth = 1 mm), identical to that of the Japan Automobile Research Institute (JARI) standard cell, was made of a transparent acrylic resin (Fig. 1(b)) [43]. For this single cell, nine segmented current collectors were equipped with both at the cathode (Fig. 1(b)) and the anode (Fig. 1(c)), and the current density was measured at each collector [31,32,34]. Between the metal ribs plated with gold (14 mm in length, 1 mm in width), the ribs made of acrylic resin (3 mm in length, 1 mm in width) were transparent (Fig. 1(b)). The current collection was only possible by the metal ribs. The potentials of the current collectors were controlled to be the same by the external circuit. Thermocouples were inserted inside the outmost aluminum plate and the acrylic endplate at the cathode, and a platinum resistance thermometer inside the graphite channel plate at the anode (Fig. 1(a)). The cell temperature was controlled by rubber heaters both at the cathode and the anode to be the same. The cell performance of the see-through PEFC with dye coating was nearly identical to that of the Japan Automobile Research Institute (JARI) standard cell as shown in Fig. 2 at current densities lower than 800 ma cm⁻². In this study, the highest current density at a collector was 570 ma cm⁻², so the influence of the cell structure should be small on the distribution of current density.

During the cell operation in a dark room, the excitation light from a 407-nm laser was diffused, spread, and distributed uniformly onto the cell. The emission from the dye on the MEA was filtered (>600 nm) and captured with a CCD camera (500 × 500 pixels, 1 pixel = approximately 120 × 120 μm, Hamamatsu Photonics K.K.) [9]. The cell was operated at temperatures of 40 and 80 °C with a relative humidity of 53% RH. Gas flow rate both at the anode and at the cathode was set at 300 ml min⁻¹ during the operations. The stoichiometry data on the cathode and the anode are shown in Table 1. To obtain calibration curves before the cell operation, Stern–Volmer plots were acquired by supplying gas mixtures with various oxygen concentrations (0–25%) at the operating temperatures and humidity under ambient pressure [8,43,45–48]. Time required to obtain one image for the calibration was 100–3000 ms depending on the emission intensity. At each condition, the exposure time was set 60 s, when the emission images accumulated and averaged. The emission images were then converted to the p(O2) images by using the Stern–Volmer plots. The p(O2) and the current density were measured at U02 from 0% to 80% and at the average current density from 0 to 500 ma cm⁻².
With this visualization of \( p(O_2) \), liquid water was able to be detected as previously reported because of the light scattering by water inside cells [8,47,52]. The simultaneous visualization of \( p(O_2) \) and water droplets were conducted also in this study, together with the current density.

3. Results and discussion

3.1. Simultaneous visualization of \( p(O_2) \) and current density at a higher temperature

Fig. 3 shows the distributions of \( p(O_2) \) (Fig. 3(a), (b-1)–(e-1)) and the current density (Fig. 3(b-2)–(e-2)) simultaneously obtained with increasing \( U_{O_2} \) from 0 to 78% at the cell temperature of 80 °C and the relative humidity of 53%. The air was supplied from the upper right to the lower left. The colors of the images correspond to \( p(O_2) \) and the current density (see color bars on the right). Wires for current collecting are computationally masked by three black stripes seen running vertically on the \( p(O_2) \) images. \( p(O_2) \) in Fig. 3(a), (b-1)–(e-1) are seen to decrease from the inlet to the outlet, but not always monotonically along the flow channel because of the side flow through the GDL [2,54,55]. This tendency will be later discussed using a \( p(O_2) \) curve along the channel length. The image inside the blue square in Fig. 3(e-1) is enlarged as Fig. 3(e-1'). Under the ribs made of transparent acrylic resin, \( p(O_2) \) were observed lower due to the lower gas diffusivity under the ribs than under the neighboring flow channels as shown in white rectangles of Fig. 3(e-1'). In the purple rectangle on the left side of Fig. 3(e-1'), \( p(O_2) \) is very high on the GDL below, where the air was supplied by the cross flow through the GDL, due to the side flow around the GDL below, where the air was supplied by the cross flow through the GDL, due to the side flow through the GDL and/or a slight gap between gasket and GDL (Fig. 1(a)). This high \( p(O_2) \) at the rim was commonly observed. At \( U_{O_2} = 20, 30 \) and 50%, the current densities were relatively uniform throughout the cell (Fig. 3(b-2)–(d-2)). On the other hand, at \( U_{O_2} = 78\% \) (Fig. 3(e-1')), the current densities near the inlet became higher than that near the outlet. This change in current density could be explained by the liquid water formation in the catalyst layer near the outlet, which hindered the gas transport and lowered the oxygen consumption for the oxygen reduction reaction (ORR). Another reason for the smaller current density near the outlet at higher \( U_{O_2} \) or higher current density, with constant gas flow rate as used in the experiment, is the smaller stoichiometry (Table 1), and therefore the oxygen concentration and the current density. Both effects should play roles.

![Fig. 1. Schematic drawings of the new see-through PEFC (a), photographic view of the cathode side with a transparent acrylic plate (b), and photographic view of the anode side with nine current collectors (c).](image)

**Table 1**

<table>
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<th>( U_{O_2} ), %</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
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<tr>
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<td>8</td>
<td>13</td>
<td>17</td>
<td>21</td>
<td>25</td>
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<td>34</td>
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<tr>
<td>( O_2 ) Stoichiometry</td>
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<td>5.0</td>
<td>3.3</td>
<td>2.5</td>
<td>2.0</td>
<td>1.7</td>
<td>1.4</td>
<td>1.3</td>
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<tr>
<td>( H_2 ) Stoichiometry</td>
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<td>11.9</td>
<td>7.9</td>
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![Fig. 2. Cell potential (IR free) vs. current density.](image)
In order to understand the influence of liquid water clearly, the cell temperature was lowered from 80°C to 40°C. Fig. 4 shows the distribution of $p(O_2)$ (Fig. 4(b-1)–(g-1)) and current density (Fig. 4(b-2)–(g-2)) simultaneously obtained with increasing $U_{O_2}$ at the cell temperature of 40°C and the humidity of 53% RH. Fig. 4(d-1) and (d-2) were obtained 25 min after the $U_{O_2}$ was set at 30% (Fig. 4(c-1) and (c-2)), and Fig. 4(d-1) and (d-2) after 50 min. Fig. 4(b-1') and (c-1') are the images obtained by expanding the regions in blue rectangles in Fig. 4(b-1) and (c-1), respectively.

3.2. Simultaneous visualization of $p(O_2)$, current density, and water droplets at a lower temperature

In order to understand the influence of liquid water clearly, the cell temperature was lowered from 80°C to 40°C. Fig. 4 shows the distribution of $p(O_2)$ (Fig. 4(b-1)–(g-1)) and current density (Fig. 4(b-2)–(g-2)) simultaneously obtained with increasing $U_{O_2}$ at the cell temperature of 40°C and the humidity of 53% RH. Fig. 4(d-1) and (d-2) were obtained 25 min after the $U_{O_2}$ was set at 30% (Fig. 4(c-1) and (c-2)), and Fig. 4(d-1) and (d-2) after 50 min. Fig. 4(b-1') and (c-1') are the images obtained by expanding the regions in blue rectangles in Fig. 4(b-1) and (c-1), respectively.
When the cell was operated at $U_{o2} = 20\%$ (Fig. 4(b-1) and (b-1’)), round blue dots, $0.2–0.5$ mm in diameter, appeared on the upper flow channel near the ribs near the outlet. These blue dots are of water droplets observed by the scattering of light [8,47,53]. The water droplets were also directly observed with eyes. The current densities near the outlet in Fig. 4(b-2) were about 10% higher than the average value because of the positive effect of the humidification of membrane by the generated liquid water near the outlet, which increased the proton transport [34,56]. At $U_{o2} = 30\%$ (Fig. 4(c-1)), the number of water droplets increased near the outlet as shown in white circles of Fig. 4(c-1’). After 50 min (Fig. 4(d-1)), water droplets increased up to the middle of the flow channel. Near the outlet, the water droplets were accumulated to become much larger and they occasionally plugged the flow channel [8,47]. Accordingly, the distributions of the current density at $U_{o2} = 30\%$ at 0 min (Fig. 4(c-2)) and after 30 min (Fig. 4(d-2)) became more uniform than that at $U_{o2} = 20\%$, because the current density near the outlet was slightly lowered by the water formed at the catalyst layer. After 50 min (Fig. 4(e-2)), the current densities became higher near the inlet (ca. $+15\%$) and lower near the outlet (ca. $-15\%$). The difference of current density between at the inlet and the outlet became the largest at $U_{o2} = 50\%$ (Fig. 4(f-2)), because of the heavier flooding. Surprisingly, the difference in current density became smaller at the $U_{o2} = 80\%$ (Fig. 4(g-2)) in spite of the larger water formation by the higher power generation. A smoother distribution of $p(O_2)$ was seen in Fig. 4(g-1) than in Fig. 4(f-1). Interestingly, at $U_{o2} = 80\%$, the number of water droplets became smaller (Fig. 4(g-1)).

The cell temperature was measured at the anode separator made of carbon at different $U_{o2}$ from 0 to 80% in Fig. 5, while the automatic temperature controller was set at 80 and 40 °C. With the temperature control at 80 °C, the measured, actual cell temperature was constant at 80 °C. However, when the temperature control was set at 40 °C, the actual cell temperature began to be higher at the $U_{o2} = 30\%$. The cell temperature kept rising up to 54 °C at $U_{o2} = 80\%$ (Fig. 5). Because the temperature became higher by the higher power generation, the saturated vapor pressure became higher from 7.4 kPa at 40 °C to 15.0 kPa at 54 °C. Therefore, the amount of liquid water causing flooding became smaller even at a high $U_{o2}$ of 80% (Fig. 4(g-1)), and the difference in current density between inlet and outlet also became smaller (Fig. 4(g-2)).

### 3.3. $p(O_2)$ and current density along flow channel

In order to examine the visualization results in more detail, $p(O_2)$ and current density at 40 °C (blue lines) and 80 °C (red lines) are plotted along the flow channel from the inlet (0 mm) to the outlet (1430 mm) as shown in Fig. 6(a)–(g). For the current density, the current density at the outlet was significantly lower than that at the inlet, and the current density became more uniform along the flow channel as the power generation increased. The difference in current density between the inlet and the outlet became the largest at $U_{o2} = 50\%$, because of the heavier flooding. A smoother distribution of $p(O_2)$ was seen in Fig. 6(e) than in Fig. 6(d). Interestingly, at $U_{o2} = 80\%$, the number of water droplets became smaller (Fig. 6(f)).
densities, those of three sets of three collectors, (1, 2, 3), (4, 5, 6), (7, 8, 9) in Fig. 3, were averaged to represent the current densities at the central positions of collectors 2, 5, and 7, respectively. At Uo2 = 0% at the open-circuit voltage (Fig. 6(a)), the average p(O2) value at 40 °C of ca. 21 kPa was larger by ca. 4 kPa than at 80 °C, because of the difference in water vapor partial pressure. p(O2) both at 40 and 80 °C in Fig. 6(a) decreased gradually from the inlet to the outlet by approximately 1 kPa due to the total pressure loss along the flow channel, as reported previously [43,47,48,56]. In Fig. 6(b), the slopes of the curves apparently became larger than those in Fig. 6(a) by the consumption of oxygen along the channel. p(O2) at 80 °C decreased from the inlet to the outlet. As discussed in 3.1, the p(O2) decrease is not always monotonic because of the side flow through the GDL; increases in p(O2) at L = 350 and 500 mm are seen, for example. At 40 °C, the light scattering by water droplets formed on the upper flow channel (Fig. 4(b-1) and (b-1')) was seen from L = 1100 mm to the outlet, 1430 mm in the p(O2) curve. Current densities at 80 °C were relatively constant, whereas that at 40 °C was higher near the outlet than near the inlet probably due to the higher proton conductivity in the membrane near the outlet brought by an adequate amount of water generated. When the UO2 was changed to 30% (Fig. 6(c)), p(O2) at 80 °C gradually decreased, whereas a current density increased and the current density constant, along the channel length as was the case at UO2 = 30%. On the other hand at 40 °C, the light scattering by water droplets were observed from L = 800 nm to the outlet. At the inlet, p(O2) jumped up to 26 kPa, because of the increase in total pressure by the increase in the water partial pressure. Many periodic, sharp spikes were seen at 40 °C in both the upper and the lower direction on the curve as indicated by red arrows in Fig. 6(c). They are located at the turns of the serpentine channel as previously reported [38,43], showing the sudden change in p(O2) at turns. These periodic peaks are commonly seen at high current density [43]. Besides peaks at turns, the fluctuation of p(O2) near the inlet became larger. This increase in fluctuation could be explained assuming that p(O2) was measured not only on the GDL surface but also at a depth of several μm from GDL surface because the PtTPPP was coated on the GDL with micro pores; the oxygen closer to the catalyst layer was consumed more than that on the GDL surface when the UO2 increased, then the fluctuation increased [48]. In the p(O2) curve at 40 °C obtained 25 min after UO2 was set at 30% (Fig. 6(d)), the influence of water droplets became small between L = 800 and 1000 mm, because the water droplets on the upper flow channel at this area was swept downwards (Fig. 4(d-1)) by the air. The generated water became much accumulated in the latter half of the cell at 40 °C after 50 min at UO2 = 30% (Figs. 4(e-1) and 6(e)). The power generation in the area near the outlet was understood to be profoundly decreased by the flooding of the catalyst layer as seen in Fig. 6(e). The visualization image is a combination of the emission reflecting p(O2) and the light scattering by liquid water. The latter makes the quantification of p(O2) difficult. However, p(O2) at location with no liquid water can be obtained by examining the intensity at each pixel on the images. We carried out this operation and quantified p(O2) at L = 500, 1000, and 1430 mm to be 14, 7, and 6 kPa. Those values are in consistent with UO2 = 30%. At UO2 = 50%, p(O2) gradually decreased and the current density was relatively constant at 80 °C. At 40 °C, p(O2) of 26 kPa at the inlet rapidly decreased to 10 kPa at L = 500 mm and slowly decreased to 5 kPa at the outlet (Fig. 4(f-1) and 6(f)) by carefully checking the areas with no water droplets. The current density near the inlet was decreased by 40% near the outlet with the generation of liquid water at the catalyst layer lowering the gas diffusivity (Fig. 6(f)), reflected by the much smaller oxygen consumption as described above. In Fig. 6(g), p(O2) at 80 °C during the power generation at UO2 = 78% decreased rather sharply near the inlet of the gas flow channel around 500 mm, and the current density near the inlet was higher by 10% than that near the outlet; a larger amount of liquid water was accumulated at the catalyst layer, and the ratio of the oxygen consumption by the ORR was slightly lowered near the outlet. The fluctuation in p(O2) became the largest on curves for 40 °C at the largest UO2. At 40 °C, p(O2) decreased smoothly at UO2 = 80% compared with the results in Fig. 6(d)-(f) at UO2 = 50%, because of the temperature increase as discussed in 3.1. At the outlet, p(O2) at 40 °C was examined using Fig. 4(g-1) and obtained to be 2 kPa, which corresponds to UO2 = 80%.

4. Conclusions

A new see-through cell was developed and used for the visualization of the distributions of p(O2), current density, and liquid water droplets inside a running PEFC at 40 and 80 °C and 53%RH. At 80 °C, because of the high saturated-water vapor pressure, liquid water was not observed and the influence of the generated water was small. At 40 °C, water droplets were clearly observed especially near the outlet, where the current density was relatively low. At UO2 = 80%, the increase in cell temperature was detected, and the influence of liquid water was mitigated in spite of the larger formation of liquid water.

This new visualization system is expected to be used for the cell and MEA design of PEFCs, as well as the development of new materials and new operational protocols.

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