Investigation of Current Density Effect on Water Vapor Concentration Profile along PEMFC Channels by TDLAS*

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Abstract

In this article, we applied tunable diode laser absorption spectroscopy (TDLAS) technique to measure variation of water vapor concentration in gas flow channels in an operating polymer electrolyte membrane fuel cell (PEMFC). TDLAS measurement offered an optical remote sensing to detect slight change of water vapor concentration, showing that electrochemical reaction in an operating PEMFC is not uniformly observed. We performed TDLAS measurement in gas flow channels in the anode and the cathode with variation of cell current density. We observed increase of water vapor concentration due to electrochemical reaction along the cathode channel as well as along the anode channel from the inlet, suggesting that generated water was exhausted through the both channels. It was also shown that less electrochemical reaction was observed in the upstream of the channel presumably due to less hydration of the membrane because of dry gas supply.

Key words: Polymer Electrolyte Membrane Fuel Cell, Tunable Diode Laser Absorption Spectroscopy, Mass Transfer, Electrochemical Reaction

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are expected to be future power sources for vehicles and on-site power generation applications due to their relatively low operating temperature and swift startup/shutdown. For successful implementation of PEMFCs, water management is essential to keep membrane hydration under fuel cell operation without ‘flooding’ and ‘plugging’ (1)(2). To improve water management, fundamental understandings on mass transport processes involved in PEMFCs, not only in the membrane but also in the gas flow channel, are highly necessary.

In the cathode of PEMFCs, supplied protons (H+) are consumed by electrochemical reaction with oxygen (O2) and water vapor concentration increases. Consequently, oxygen and water vapor concentration change along the cathode channel. Additionally, water is transported between the cathode and anode by electro-osmosis, back-diffusion and pressure driven permeation. This possibly results in intensive variation of water vapor concentration along the anode channel as well.

In our previous study(3), we introduced Tunable Diode Laser Absorption Spectroscopy (TDLAS)(4)(5) techniques in order to demonstrate optical remote sensing of water vapor and oxygen concentration in PEMFC channel as a diagnostic tool for understanding on mass transport processes involved in PEMFC. It was shown that absorption coefficient measured
by TDLAS could be readily converted into actual water vapor concentration as well as oxygen concentration with a calibration equation that was experimentally obtained and that was also in good agreement with theoretical prediction. TDLAS technique could offer its unique advantage on flexibility of the measuring point along the PEMFC channels. One-dimensional investigation along the gas flow channel in PEMFCs has been reported because of its simple geometry which is advantageous for comparison with numerical analysis.\(^6\)\(^7\)\(^8\)\(^9\)\(^10\)\(^11\) Segmented cell was widely used for investigation of local current density.\(^8\) However, segmentation of the electrodes of the fuel cell needs extra treatment on the cell. Although the measurement of distribution of water vapor concentration in the cathode channel using the humidity sensor have been reported, the measurement of distribution of water vapor concentration in both cathode and anode channel is necessary in order to investigate the local water transport between anode and cathode channel. In our experiment, the water vapor concentration in not only the cathode channel but also the anode channel was measured and the water transport between anode and cathode channel was observed. The measurement at about every 15cm along the cathode and the anode channel using gas chromatograph have been also reported. However, the measurement at shorter interval is essential for the deeper investigation. In our experiment, the measurement was done at every 1cm along the cathode and the anode channel. Additionally, it has been reported to measure the water vapor partial pressure in the channel using the TDLAS system.\(^11\) However, space resolution was not enough to measure the distribution of water vapor concentration because average water vapor pressure of 7cm along the channel was measured in their experiment. In our experiment, the space resolution of the TDLAS system is set to 1mm to improve the measurement of distribution of water vapor concentration in the channel.

In this study, we focused our attentions on variation of water vapor concentration along the gas flow channels in the anode and the cathode side, because it reflects local electrochemical reaction, i.e. local current density, and it can be monitored by TDLAS technique. We performed experiments with variation of cell current density to investigate variation of water vapor concentration profiles along the anode and the cathode gas channels.

2. Experimental

In this experiment, we used a custom single-channel fuel cell with transparent endplates to allow optical access. The cell had a channel length of 100mm. The width and the depth of the channel are 3mm and 5mm. The transparent end plate was glass with an antireflection coating of 1392nm for water vapor tests. The thickness of the coating was chosen to match the wavelength used for TDLAS measurements. The membrane electrode assembly consisted of two 200-µm-thick carbon papers, the length and width of which are 60mm and 10mm, coated with 1.0mg/cm² of Pt catalyst (Electrochem Inc.). These were hot-pressed to a polymer electrolyte membrane (Du Pont, Nafion115) for 25 minutes at 393K with a pressure of 30N/cm².

Figure 1 shows a schematic of experimental setup. Dry O₂ and H₂ were supplied at a fixed flow rate of 12 mL/min. In this experiment, it is focused on figuring out relationship between membrane hydration relating to the ohmic overpotential and the local current density based on measurement of water vapor concentration in the channel. Due to this, oxygen gas was used as oxidant in order to remove an effect of the concentration overpotential. Temperature of the cell was controlled at 333K and cell current was controlled by an electric load (1280C, solartron analytical). In this experiment, we varied cell current densities at 0.05, 0.10 and 0.15 A/cm². The utilization rate of supplied oxygen was 31.2%, 20.8%, and 10.4%, respectively. We worked on measurement of distribution of
local current densities along the channel under the condition that water vapor concentration changes significantly along the channel as the first step of our study. These low current densities were chosen in order to change water vapor concentration significantly along the channel because the water vapor concentration reaches the amount of saturated water vapor at forefront part of the channel and is stayed almost constant at the end of the channel under high current density.

Figure 2 shows measurement principle of the TDLAS measurement system, which was introduced in our previous study\(^3\). The time and space resolution is set to 0.1 second and 1.0mm, respectively. A sensor head projects a laser beam through a glass cover into the fuel cell channel. The back of the fuel cell channel scatters some of the laser light back into the sensor head, the scattered light is collected onto a photo detector. The photo detector converts the received light into an electrical signal and supplies the signal to the control module. The control module analyzes the detector signal using the technique called Wavelength Modulation Spectroscopy (WMS)\(^{12,13}\), which is the most commonly used technique in order to reduce noise and remove baseline off-sets. In this technique, the input
laser light wavelength is scanned continuously across the target absorption line at a constant frequency, and the detected signal is demodulated by a lock-in amplifier at a harmonic frequency of the input laser light modulation. In this experiment, the wavelength of the diode laser is scanned across 1392nm for water vapor measurement. For the precise measurement of water vapor concentration in the channel, the 5 mm depth of the channel is sufficient to measure with the WMS technique. Additionally, it is thought that this TDLAS system can measure water vapor concentration in the channel of 1mm depth with 0.1% accuracy based on theoretical estimation. The output value of the sensor for water vapor concentration updated 10 times per second. The water vapor concentration, ppm, is obtained by divided the output value by optical path lengths because the unit of the output value is ppm*m. Variation of water vapor concentration in the sample gas can be readily obtained by monitoring variation of absorption coefficient in the channel, although water vapor concentration showed non-linear relationship with absorption coefficient of water vapor observed by TDLAS at a wavelength of 1392nm. A calibration equation and more detail can be found in our previous study(3).

3. Results and Discussion

![Figure 3](image3.png)

Figure 3. Averaged and converted measurement values in the cathode channel at a load of 0.05 A/cm²

![Figure 4](image4.png)

Figure 4. Averaged and converted measurement values in the anode channel at a load of 0.05 A/cm²
Figure 3 and 4 show the time-averaged water vapor concentrations in the cathode and the anode channel measured by the H\textsubscript{2}O-TDLAS at numerous locations, respectively. Current density of the cell was 0.05A/cm\textsuperscript{2}. These results are obtained by time averaging and converting the measured water vapor concentration during 2 minutes at each measurement position into amount of water vapor. We can see similar amount of water vapor observed both at the cathode and at the anode. This means generated water was exhausted to both sides of the gas channel from the membrane electrode assembly (MEA). This suggests that membrane hydration exceeds in its equilibrium state determined by relative humidity in the gas channel due to electrochemical reaction in the cathode and its back diffusion to the anode.

Figure 5 shows total amount of water vapor in the cell obtained by averaging the results shown in Figure 3 and 4. The theoretical line is the predicted amount of water vapor assuming that the electrochemical reaction is occurring uniformly along the length of the flow channel and that all generated water is exhausted to the cathode or anode gas flow channel as vapor. It can be seen that the increase rate of the amount of water vapor was smaller than the predicted in beginning of the channel and was larger than the predicted in middle and end of the channel. It is thought that the increase rate of amount of water vapor, which is generated by electrochemical reaction, is almost proportional to amount of power generation. In fact, the beginning of the channel suffers lower performance since the inlet gases are not humidified and membrane in this region is dry. In contrast to the beginning of the channel, the middle and the end of the channel show higher performance because membrane in these regions is hydrated by increase of the amount of water vapor in the channel. Besides of these, the measurement results approach the theoretical line near the end of the channel.

Figure 6 and 7 show the time-averaged amount of water vapor in the cathode and the anode channel at a load of 0.10 A/cm\textsuperscript{2}. Figure 8 show total amount of water vapor in the cell. The same trend as observed in the case of 0.05 A/cm\textsuperscript{2} was observed on amount of water vapor in the cell. Inlet of the channel shows less water vapor concentration than a theoretical line due to less water generation while more intensive reaction was observed in the middle and end of the channel.

Figure 9 and 10 show variation of water concentration profiles along the gas channel in the cathode and the anode, respectively, at the loads of 0.15A/cm\textsuperscript{2}. Figure 11 shows total amount of water vapor in the cell at the loads of 0.15A/cm\textsuperscript{2}. It can be shown that the same trend on water vapor concentration profiles at the cathode and the anode as observed in 0.05

![Figure 5](image-url)
and 0.10 A/cm², in which less electrochemical reaction was occurring in the inlet of the channel. However, it should be noted that the experimental plots in Fig.11 was not observed to approach to the theoretical line at the end of the channel. A gap between the experimental value and the theoretical value is observed at the end of the channel in Fig.11.

To clarify the reason, we visualized water droplet in the channel at current density of 0.15A/cm². Fig.12 shows a visualized result in the cathode channel. The area framed by blue line indicates the cathode channel and framed by red line indicates the droplet on the end of the cathode channel. This indicates that water vapor concentration at the end of channel exceeds in saturated vapor concentration and thus condensation of water vapor was occurring. This can be confirmed in TDLAS measurement in the cathode (Fig.9) and the anode (Fig.10). Figure 9 and 10 shows relationship between the measurement results in the cathode and the anode channel and amount of saturated water vapor, respectively. Red lines show amount of saturated water vapor which can be calculated under the cell temperature at 60 ºC. Amount of water vapor measured in the cathode channel reaches to the amount of saturated water vapor at the end of the channel. This causes condensation of water vapor in the end of channel in the cathode. The theoretical line in Fig.11 is predicted amount of

![Figure 6](image)

Figure 6. Averaged and converted measurement values in the cathode channel at a load of 0.10 A/cm²

![Figure 7](image)

Figure 7. Averaged and converted measurement values in the anode channel at a load of 0.10 A/cm²
water vapor as assuming that all generated water is exhausted to the cathode or the anode channel as vapor. Under this operating condition, as observed in Fig.9 and Fig.12, there are some condensed water droplets in the cathode gas channel, although the TDLAS system can only measure water vapor concentration. Therefore, the experimental results are different from the theoretical line.

Water droplet in the anode channel was not observed in our experiment because amount of water vapor in the anode channel did not reach to the amount of saturated water vapor along the anode channel. In addition to this, amount of water vapor in the anode channel increases at the end of the channel. This indicates that electrochemical reaction is occurring at the end of the channel even though condensed liquid water droplet was observed in the cathode at the end of channel. This shows no ‘flooding’ and ‘plugging’ was observed in this experimental condition because of low current density and oxygen supply.

![Graph](image)

Figure 8. Total amount of exhausted water vapor to the channels at a load of 0.10 A/cm²

![Graph](image)

Figure 9. Amount of water vapor in the cathode channel at the loads of 0.15A/cm²
Figure 10. Amount of water vapor in the anode channel at the loads of 0.15 A/cm²

Figure 11. Total amount of exhausted water vapor to the channels at a load of 0.15 A/cm²

Figure 12. Generation of water droplet at the load of 0.15 A/cm²
Conclusions

Water vapor concentration profile and its variation with cell current density was measured by TDLAS technique. We performed TDLAS measurement in the cathode and the anode. It was shown that less water vapor concentration than a theoretical line due to less water generation was observed in the beginning of the channel while more intensive reaction was observed in the middle and end of the channel due to membrane hydration.

At cell current density of 0.15A/cm², water vapor concentration at the cathode exceeded in saturated water vapor concentration and thus condensation of water droplet was observed in both TDLAS and visualization results. TDLAS technique successfully shows its performance to monitor variation of localized electrochemical reaction.

References