Composition and evaluation of single-layer electrode proton exchange membrane fuel cells for mass transfer analysis

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Abstract
Single-layer electrodes (SLEs) were used to replace conventional multi-layer electrodes for proton exchange membrane fuel cells (PEMFCs), and their performance in the analysis of mass transfer in an electrode was evaluated. The cell comprises a polymer electrolyte membrane, catalyst layers, and separators with a microchannel. The removal of conventional microporous and gas diffusion layers has the potential to enhance the through-plane mass transfer efficiency. The biggest challenge is the degradation of in-plane diffusivity of gas and water under ribs. Finding optimum microchannel and SLE structure by evaluating the cell performance under a rib and channel, respectively, is necessary. In this study, two types of cells were developed to obtain a fundamental understanding of gas and water transport in SLE-PEMFCs using microfabrication techniques. One cell had its cathode active area under a microchannel, and the other had it under a rib. A silicon wafer was used as a separator. A microchannel was fabricated on a silicon substrate. A current-collecting layer was coated on the substrate by Au sputtering. The reaction area was determined by the anode electrode, which was buried in the microchannel. The width of both the microchannel and rib was 100 μm. Performance evaluation was conducted using the cells, and the performance was compared under the cathode channel and rib. Results indicated that the overpotential under the rib was much larger than that under the channel. To achieve high performance as an overall cell, a large channel area is preferable. Therefore, performance evaluation was conducted under channels with widths of 50–400 μm. The channel performance over the range of widths studied (50–100 μm) was consistent, although the performance was low for widths above 100 μm. This could be because of the electrical conductivity and delamination of the electrode.

Key words: Proton exchange membrane fuel cells, Transport phenomena, Single layer electrodes, Catalyst layers, Microchannel, Microfabrication

1. Introduction
Proton exchange membrane fuel cells (PEMFCs) have been developed for dispersed power systems and fuel cell vehicles. Satisfying the dual requirements of high performance and low cost is one of the most important challenges faced in the fabrication of PEMFCs. A new approach for the fabrication of PEMFCs is suggested in this study. Single-layer electrodes (SLEs) were used instead of the conventional multi-layer electrodes. The cell comprises a polymer electrolyte membrane (PEM), catalyst layers, and separators with a microchannel. Conventional PEMFCs contain gas diffusion layers (GDLs) and microporous layers (MPLs) on both the anode and cathode catalyst layers. They contain multi-layer electrodes to improve gas supply from a mini channel and drainage of generated water to the channel. Therefore, transport phenomena in the MPL/GDL have been studied in detail over the last two decades (Cindrella et al., 2009). Channel/rib-segmented performance evaluations have been conducted using the conventional multi-layer electrodes for the fundamental understanding of the transport phenomena in the electrode under the channel and rib, independently (Higier and Liu, 2009, Wang and Liu, 2008). However, placing the MPL/GDLs leads to degradation of
through-plane oxygen and water diffusivity. Furthermore, delamination of the MPL from a catalyst layer might occur during the fuel cell operation (Tsushima and Hirai, 2015). Removing MPL/GDLs and exposing the catalyst layers to a flow field has the potential to enhance the mass transfer efficiency.

There are several reports on substrate-less diffusion layers, which consist of only MPL without GDL (Park et al., 2014, 2015). They show that decreasing the thickness of MPL results in improvement in the cell performance. In principle, removing the MPL can result in the further improvement of through-plane gas and water transport. The biggest challenge is the degradation of in-plane diffusivity of gas and water under the ribs. Therefore, downsizing the flow channel from the conventional mini channel to the microchannel is necessary. The microchannel has been used for micro fuel cells fabricated using MEMS techniques (Kobayashi et al., 2014). Ito et al. demonstrated that decreasing the microchannel pitch from 500 μm to 100 μm contributes to performance improvement of the micro fuel cell without MPL/GDL (Ito et al., 2009). However, a fundamental understanding of mass transfer in the microchannel and electrode is not enough. Total design of the microchannel and electrode structure based on mass transfer is required to develop novel PEMFCs with higher performance.

The key technology is the fabrication of the catalyst layers. Typical catalyst layers consist of platinum-supported carbon (Pt/C), an ionomer, and pores. They have nanoscale and microscale porous structures and their components are responsible for the transport of electrons, protons, reactant gases, and the water generated. Catalyst layers are electrodes and are thus indispensable components in PEMFCs. Several methods of fabricating catalyst layers are in common use (Bender et al., 2003, Ihm et al., 2004, Wilson and Gottesfeld, 1992). The fundamental process involve blending the materials to produce a slurry called catalyst ink, which is then applied to form a thin layer followed by drying to evaporate the solvents, leaving a porous structure. The fabrication techniques are mainly categorized based on the coating methods, such as doctor blading, spray coating, and ink-jet printing (Saha et al., 2011). The coating is applied in two ways: direct coating on a PEM or a combination of coating on a substrate and decal transferring to the PEM. The decal transfer method is often used to prevent solvents from swelling into the PEM. The structure of the catalyst layers has received widespread attention in recent years because it is recognized that the structure strongly affects cell performance (Shin et al., 2002, Xie et al., 2004, Xie et al., 2010). The relationship between the fabrication process, resultant porous structure, and cell performance has been investigated (Suzuki et al., 2011, 2013, Suzuki et al., 2015).

For the total design of the microchannel and electrode structure based on mass transfer, fundamental understanding of the effect of mass transfer on the cell performance under the microchannel and rib is required and can be acquired by using structurally controlled electrodes fabricated by a specific process. The objective of this paper is to establish a method to evaluate cell performance of SLE-PEMFC under the microchannel and rib, independently, and to clarify the performance under the channel and rib. Test SLE-PEMFCs for mass transfer analysis were developed, and performance evaluation of the cells was conducted in this study.

2. Experimental

In this study, two types of the cells were fabricated for the fundamental understanding of oxygen and water transport in the SLE-PEMFCs. Schematic of the cell is shown in Fig. 1 (a). Both anode and cathode separators have one or two straight microchannels. The anode channel faces the cathode channel in a channel evaluation cell (C/C cell, Fig. 1 (b)) and faces cathode rib in a rib evaluation cell (R/C cell, Fig. 1 (c)). The separator was made of silicon and the microchannel and current-collecting Au layer on it were formed by utilizing wet-etching and sputtering, respectively. The channel length was 4 mm and the channel width was variable between 50 and 400 μm. The thickness of the anode and cathode separators is 100 and 525 μm, respectively. The anode microchannel penetrated through the separator to bury the catalyst layer. On the other hand, through-holes which connect to the cathode microchannel were formed for gas supply in the cathode separator. Schematic of the fabrication process is shown in Fig. 2. To bond the two separators at a precisely determined position, a mask aligner and an in-house fabricated glass mask with a microscale (the minimum gap is 5 μm) were used. Catalyst ink, which consists of platinum-supported carbon (50 wt.% Pt, TEC10E50E, Tanaka Kikinzoku Kogyo), Nafion ionomer solution (20 wt.% Nafion, DE2020, Wako Pure Chemical Industries), water, and n-propanol (NPA), was prepared. The blending ratio is shown in Table 1. The cathode catalyst layer was formed following the conventional doctor-blading method (Suzuki et al., 2011). The thickness of the layer was 7 μm and the Pt loading was 0.2 mg/cm². The cathode catalyst layer was decaled on the polymer electrolyte membrane (Nafion212, DuPont) by hot-pressing in advance to incorporate in the cell. The anode catalyst layer was formed by means of tapping the catalyst ink.
into the microchannel, placed on a hot plate at 140°C, using a thin needle. The active area was determined after the cell bonding.

Cross-section of the cell was obtained by polishing the cell, which was buried into the resin, to observe the positioning accuracy. The cross-section was observed using an optical microscope (BX-51, Olympus). Performance evaluation was conducted using the test cells, which were set in an in-house fabricated jig to supply reactant gas. 30 cm$^3$/min of humidified hydrogen and 40 cm$^3$/min of humidified oxygen or air were supplied to the anode and cathode, respectively. The cell temperature was maintained at 60°C.

Fig. 1 (a) Schematic of the SLE-PEMFC test cell. The cross-section and mass transfer of (b) the C/C cell and (c) the R/C cell.

Fig. 2 The fabrication process of cathode and anode separators with a microchannel and a current-collecting layer.
Table 1 Catalyst ink recipe.

|                         | Anode | Cathode |
|-------------------------|-------|---------|
| Ionomer to carbon ratio | 1.0   |         |
| Solvent (Water to NPA)  | 1.25  |         |
| Non-volatile ratio      | 0.1, 0.2 | 0.1     |

3. Results and discussion
3.1 Cell fabrication

A cross-sectional microscopic image of the bonded anode and cathode separators is shown in Fig. 3 (a). The two separators were bonded with a double-sided adhesive tape (50 μm thick). Therefore, there is about 50 μm gap between the two separators where the cathode catalyst coated membrane is inserted. The length of the flow channel is 4 mm. The microchannel must face the counter rib or channel through the overall flow field. Therefore, the cross-section of the cell was obtained at three points along the flow direction, which are the upper, middle, and lower streams of the channel, as shown in Fig. 3 (b)–(d). The positioning accuracy is less than 10 μm for a 100 μm-width microchannel and rib.

Fig. 3 (a) Cross-sectional view of the R/C cell. (b) Upper, (c) middle, and (d) lower stream of the flow channel in the R/C cell.

Anode catalyst layer was formed by tapping catalyst ink into the anode microchannel. Two types of the catalyst ink with varying non-volatile (NV) ratio, which is weight of solid in the ink to the overall weight, were prepared. Catalyst layer formed in the microchannel is presented in Fig. 4. The dark part shows catalyst layer. The 0.1 NV ratio ink generated particle agglomerations and large voids as shown in Fig. 4 (a) and (b). The bottom of the channel or a PEM can be observed in the magnified image, Fig. 4 (b), although enough catalyst ink to form the catalyst layer was put into the microchannel. On the other hand, the 0.2 NV ratio ink deposited on the bottom of the microchannel and formed a relatively uniform catalyst layer as shown in Fig. 4 (c) and (d). This could be because of the particle mobility in the catalyst ink. 0.1 NV ratio ink is slurry and viscosity is relatively low. Solid particles contained in the ink aggregate following evaporation and volume decrease, while 0.2 NV is almost gel-like and it is difficult for the solid particles to move during the drying process.
The anode catalyst layer deposited on a PEM was observed under a microscope. PEM and Si separator were placed on a glass plate, attaching the separator to the glass plate using a bonding tape. Catalyst ink of 0.2 NV was filled in the same manner. The catalyst layer formed was observed under the microscope through the glass plate as shown in Fig. 5. The catalyst layer was accurately formed in the microchannel without the spread of the layer under the rib. Therefore, the reaction area of the cell performance was defined as the anode microchannel area.

**3.2 Performance evaluation**

Performance evaluation was conducted using the two cell types shown in Fig. 6 (a). The R/C cell shows a lower performance than the C/C cell under conditions of oxygen and air flow. This could result from the increase...
in oxygen diffusion loss in the R/C cell, even under oxygen flow. Oxygen gain ($\Delta V$) of the cells is shown in Fig. 6 (b). $\Delta V$ is calculated as

$$\Delta V = V_{O2} - V_{Air}$$

(1)

Where $V_{O2}$ and $V_{Air}$ are the cell voltages measured under the application of hydrogen/oxygen and hydrogen/air, respectively. This result indicates that the R/C cell has large oxygen gain, implying that oxygen transport is the rate determining process in the R/C cell. The rib width is 100 $\mu$m, while the thickness of the electrode is about 10 $\mu$m. This implies that the in-plane gas diffusion distance is much longer than through-plane distance. A lower aspect ratio is required for better performance with a low overpotential. The design of the flow field including a microchannel and a porous electrode is another approach. Improving gas diffusivity in the porous structure under the rib is important. On the other hand, the channel evaluation showed a unique performance, which does not contain concentration overpotential even under air flow condition. Decreasing the ohmic loss is necessary to achieve a higher current density in the cell.

![Polarization curve and oxygen gain](image)

**Fig. 6 (a) Polarization curves and (b) oxygen gain of C/C and R/C cells with 100 $\mu$m-width channel.**

Widening the microchannel is another approach to improve the performance as an overall cell. Performance evaluation as a function of the current of the C/C cell, while varying microchannel width from 50 to 400 $\mu$m, was carried out for acquiring a fundamental understanding of the effect of the channel width and the results are presented in Fig. 7 (a). The voltage as a function of current, which corresponds to the output power, of the 100 $\mu$m-wide cell is the highest and that of the 50 $\mu$m-wide cell is the lowest. Reaction area of the cell increases with an increase in the channel width because the reaction area is determined by the anode channel width. However, the maximum power decreases as channel width increases to more than 100 $\mu$m. The polarization curve indicated by current density is presented in Fig. 7 (b). The performances of cells with 50 and 100 $\mu$m wide channels are almost the same, although the performance degraded as the width of the channel is increased to more than 100 $\mu$m. The reaction area was determined by the anode channel width. However, cathode catalyst layer exists under both the microchannel and rib. If protons effectively diffuse in the membrane under the rib, the cathode reaction would occur not only under the channel, but also under the rib. The effect of the rib would be same for all channel-widths. If the cathode reaction under the rib contributes effectively, the polarization curve normalized by the anode channel width, as the reaction area, would vary according to the channel width. The contribution is relatively large in the smaller channel cell. Therefore, the similar performance of 50 and 100 $\mu$m channels indicates that the cathode reaction occurs mainly under the microchannel and the contribution from the reaction under the rib is negligible. The performance degradation in the cell over 100 $\mu$m-channel width should be discussed. The important effect to be considered is the increase of ohmic loss because of electron transport as discussed below.

The difference in overpotential as a function of channel width was evaluated and is shown in Fig. 8. The increase of overpotential in the 100, 200, and 400 $\mu$m-wide cells, obtained by subtracting their polarization curves from the polarization curve of the 50 $\mu$m-wide cell, is defined as $\Delta \eta_{ohm}$. Simple estimation of the difference of the ohmic overpotential was performed as follows:
\[ \Delta \eta_{\text{chem}} = iA \Delta R \]  
\[ \Delta R = \frac{1}{\sigma A_x} \times \frac{l - l_{\text{ref}}}{2} \]

where, \( i \) is current density, \( A \) is the reaction area, \( \Delta R \) is the difference in resistance, \( \sigma \) is electrical conductivity, \( A_x \) is cross-sectional area of the electrode along the flow direction, \( l \) is channel width, and \( l_{\text{ref}} \) is channel width of the reference cell (50 \( \mu \)m). \( \sigma \) is determined as 2 S/cm, which is an experimentally determined value (Siroma et al., 2010). This estimation implies that all cathode reactions occur at the centerline of the channel, although there is reaction distribution in the electrodes of real cells. Therefore, this estimation gives the maximum value of the overpotential, which should be taken as the ohmic loss because of the increase in electron transport distance. The estimation is indicated by lines in Fig. 8. Channel width under 100 \( \mu \)m does not significantly affect the increase of overpotential. The experimental result indicated by plots in the same figure is lower than the estimated maximum value. Channel width over 100 \( \mu \)m can significantly affect the overpotential. The widening microchannel results not only increases the electron transfer distance, but also increases the electron flux. Electrodes under the large channel undergo a larger electrochemical reaction even at the same current density because electrochemical reaction area increases, while the cross-sectional area, where electron passes through, is constant. The through-plane electron flux increases and results in the increase of the overpotential. Actually, the experimental result shows a significant increase in the overpotential, which is based on the performance evaluation shown in Fig. 7 (b). However, the increase is larger than the estimated maximum value. Therefore, the experimental result not only contains the effect of the increase of electron transfer distance, but also contains other factors such as plugging of the channel by the membrane and delamination of the anode electrode. The channel plugging would occur by membrane swelling (Bauer et al., 2005). The electrode delamination in the anode would occur during the cycle of the membrane swelling and shrinking because the anode electrode is attached to the PEM by tapping and did not undergo hot-pressing. The adhesion force of the anode electrode might be weaker than that of the cathode electrode, which was decal-transferred using the conventional hot-pressing method. To determine these effects, performance evaluation of 45%RH was conducted after the evaluation of 90%RH. If channel plugging by the membrane swelling is dominant, the performance degradation would be recovered by the performance evaluation under a relatively low humidity condition. Otherwise, the electrode delamination would be enhanced and the performance degradation would increase. The experimental results are presented in Fig. 9. The performance degradation was enhanced by the humidity cycling. Therefore, the electrode delamination is the most prominent cause contributing to performance degradation. To decrease this effect, application of a low swelling membrane and improving the anode electrode fabrication method should be considered. Anyway, performance evaluation of cells, which have a channel width of less than 100 \( \mu \)m, was successfully demonstrated in this study.

![Fig. 7 Polarization curves as a function of (a) current and (b) current density of the C/C cell at varying channel width from 50 to 400 \( \mu \)m.](image-url)
Conclusions

A new concept for the fabrication of PEMFCs using single-layer electrodes (SLEs) instead of the conventional multi-layer electrodes is suggested and a test cell for mass transfer analysis was developed. The test cell can evaluate the performance under the microchannel and rib, and can use a catalyst layer fabricated by any processes as it was made. Two types of evaluation cells, which are intended for mass transfer analysis under the microchannel and rib, respectively, were fabricated using MEMS fabrication techniques. The anode channel faces the cathode channel or rib with an accuracy of 10 μm. The reaction area was determined as the anode channel area by forming an anode catalyst layer in the microchannel.

Performance evaluation was conducted using the cells at the highly humidified condition, 90%RH. The performance under the channel showed a unique performance, which does not contain concentration overpotential. The performance under the rib showed drastic degradation even in a narrow rib of 100 μm. The oxygen gain under the rib is much higher than that under the channel, suggesting oxygen transport under the rib is the most important factor that enhances the cell performance. Humidity condition strongly affect the cell performance under the channel and rib. Especially in the dry condition, the membrane under the channel might be degraded because of dehydration, and the membrane under the rib may show more wet condition and higher performance. Further discussion of the relationship between water management and cell performance under the channel and rib is required.

Performance evaluation of the channel evaluation cell containing channels of width ranging from 50 to 400 μm was conducted for the fundamental understanding of the effect of the channel width on cell composition and performance. Channels of 50 and 100 μm width showed a similar performance in terms of current density, which implies that the through-plane electron transfer resistance is negligible. In addition, reaction area is accurately determined by the anode
channel and reaction under the rib is negligible. Delamination of the anode electrode by dry-wet cycling might occur and performance degradation was observed in channels wider than 100 μm. To decrease this effect, use of a low swelling membrane and improvement in the fabrication method of the anode electrode should be considered. The membrane swelling may have relation with degradation of the cell. Further study about the durability is needed and some approaches to improve it such as applying a low swelling membrane, a functional gasket, and/or novel stack design may be required.

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