Practical and Reliable Methanol Concentration Sensor for Direct Methanol Fuel Cells

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ABSTRACT

An electrochemical methanol concentration sensor with practicality and reliability has been developed to apply for a direct methanol fuel cell (DMFC) system. The methanol concentration can be estimated simply by the original algorithm based on the Arrhenius law and diffusion limiting current, even though the complex oxidation current characteristics for the methanol concentration and temperature. The oxidation current of methanol shows linearity against the methanol concentration up to 10 wt% (15 mgPt cm⁻² at anode) with quick response. The sensor also has a high durability for 6500 h in the simulated DMFC operating temperature.

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Keywords : Direct Methanol Fuel Cell, Methanol Concentration Sensor, Methanol Concentration Correlation Algorithm, Durability

1. Introduction

Direct methanol fuel cells (DMFCs) are promising as a small-sized portable power source or emergency power source because of their simple system configuration, low cost, and easy fuel handling.^{1,2} The DMFCs require accurate control of methanol concentration as a fuel to maintain the efficiency of power generation. In addition, methanol crossover is an issue that needs to be resolved to improve the power generation efficiency of DMFCs.^{3,4} The methanol crossover is a phenomenon wherein methanol permeates the polymer electrolyte membrane and reaches the cathode through the anode, where it reacts directly with oxygen. Further, the methanol crossover causes a reduction in fuel utilization and cathode potential. To suppress the methanol crossover, the DMFC system efficiently utilizes methanol by controlling the methanol concentration to a low concentration within a range that can generate electricity before feeding it to the DMFC stack. Therefore, the methanol concentration measurement method is very important for controlling the methanol concentration in the system.

The first method of measuring methanol concentration uses the physical properties.^{5–9} For example, the means of density, sound waves, refractive index, or dielectric constant correlation with methanol concentration. The second measurement method uses electrochemical properties. The electrochemical method converts the methanol concentration into a readable electrical signal via the oxidation of methanol. The structure of the sensor is similar to that of a membrane-electrode assembly (MEA) in DMFCs. Akbari et al. and Zhao et al. reported that the electrochemical method has many advantages over the physical method: it can be constructed with a structure compatible with the DMFC manufacturing process, and it uses a simple electrical signal output, which makes it more economical and widely used in small DMFC systems.^{10,11} Elec-

trochemical sensors can be classified into fuel cell-based^{12,13} and oxidation current type.^{14–19} The fuel cell-based type sensor determines methanol concentration by measuring the open-circuit voltage or short-circuit current using a small DMFC cell. This sensor needs a continuous feed of oxidant to the cathode; hence, the structure of the cathode and the oxidant feeder needs to be considered. The oxidation current type sensor determines the methanol concentration based on the concentration dependence of the methanol diffusion limit current of the anode under a constant applied voltage. The oxidation current type sensor has attracted considerable attention because of its simple structure, low cost, and ease of miniaturization attributable to the fact that the sensor requires only immersion in a methanol solution as fuel for installation. However, the oxidation current type sensor has an issue of decreasing sensitivity caused by the saturation of the oxidation current at the high concentration side. The limiting current of methanol diffusion, where i_{Limit} is the limiting current, can be expressed as

$$i_{Limit} = nFA \frac{D_m}{\delta} C_m \quad (1)$$

where n , F , A , D_m , δ , and C_m denote the charge number, Faraday constant, electrode area, methanol diffusion constant, Nernst diffusion layer, and methanol concentration, respectively. Equation (1) shows that the limiting current increases linearly with methanol concentration; however, there is a limiting current caused by catalytic activity owing to the slow methanol oxidation reaction rate on the catalyst electrode. Accordingly, the oxidation current characteristics of the sensor exhibit the behavior shown in Fig. 1(a) because these two limiting currents cannot be exceeded. At lower concentrations, the oxidation current is dominated by the limiting current of Eq. (1), and it shows a linear trend with methanol concentration. At higher concentrations, the amount of methanol reaching the catalyst electrode increases and the relationship is (methanol diffusion rate) > (methanol oxidation reaction rate); therefore, the oxidation current changes depending on the limiting current caused by catalytic activity. Furthermore, the oxidation current characteristics have temperature dependence and interaction

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Figure 1. Conceptual diagram of oxidation current characteristics as a function of methanol concentration.

Figure 2. Fabricated methanol concentration sensor of (a) schematic diagram of sensing principle, (b) magnified view and (c) photograph of the device.

with concentration dependence, which pose a complex issue of correlation between methanol concentration and oxidation current. Concentration correlation algorithms have not been fully discussed; however, they have been reported by Barton et al.¹⁸

In addition, the use of oxidation current sensors is limited by the degradation of the catalyst during sensor operation. Geng et al. reported an alternating pulse electrochemical methanol concentration sensor¹⁹ to solve this issue. The evolution of hydrogen at the electrodes increases the number of reactant-catalyst-electrolyte sites and reduces the overpotential for both oxygen reduction and methanol oxidation.²⁰ Alternating the applied voltage allows hydrogen to be produced alternately at each electrode. This study reported on the self-cleaning of the electrode surface and the maintenance a catalyst active surface, as demonstrated by a 4 h stability test. However, the durability of the sensor for practical use has not been reported.

This study investigates a practical concentration sensor that can be implemented in a system. A simple concentration correlation algorithm to output the concentration of methanol from the measured temperature and oxidation current is derived, issues to apply this algorithm are solved, and the specification of the sensor is improved. In particular, the specification of the diffusion layer and catalyst loadings contributing to the diffusion limit current and limit current caused by catalytic activity are controlled to improve the linearity of the oxidation current characteristics.

2. Experimental

2.1 Operating principle of methanol concentration sensor

The operating principle for the methanol concentration sensor used in this study is based on that of the electrochemical oxidation of methanol on a typical anode. Figure 2(a) shows the operating principle of the methanol concentration sensor. The reactions for the sensor are as

the reactions shown in Eqs. (2) and (3) proceed at the anode and the cathode, respectively. The methanol concentration is calculated using the property that the current value of six electrons per methanol molecule depends on methanol concentration. The entire reaction is represented as Eq. (4) by eliminating the electrons and hydrogen ions in Eqs. (2) and (3). The reaction in Eq. (4) proceeds by applying a voltage between the methanol oxidation electrode and hydrogen generating electrode. This process allows applying a voltage to the MEA in the range of the water potential window (0 to 1.23 V based on the hydrogen redox potential). Thus, if no methanol is present, no oxidation current will be generated and the current of the oxygen reduction reaction in Eq. (5) at the cathode will not interfere with the methanol concentration measurement.

2.2 Construction of the methanol concentration sensor

The basic structure of the methanol concentration sensor is the same as that of a DMFC with a general polymer electrolyte membrane as shown in Fig. 2(b). The sensing component has catalyst electrodes (TEC10E70TPM, Tanaka) formed on both sides of a polymer electrolyte membrane (SM-PES: Sulfonated Methyl-Poly Ether Sulfone, Hitachi). A carbon paper is used as a diffusion layer (TGP-H-60, Toray) and placed on each of the catalyst electrodes to form a membrane-electrode assembly (MEA). Table 1 lists the specifications of the MEA. Two current collectors are fabricated from Au-coated Titanium. They have a circular window with an 8 mm diameter. A methanol solution is fed through the anode side window, and carbon dioxide gas is expelled. Further, hydrogen gas is expelled through the cathode side window. A gasket

Table 1. Specifications of the MEA for the sensor.

	Material	Dimensions	Thickness	Pt loading
Electrolyte membrane	SM-PES (HITACHI)	15 × 15 mm	0.05 mm	
Electrodes	TEC10E70TPM (TANAKA)	11 × 11 mm		2.0 mg cm ⁻²
Diffusion layer	TGP-H-60 (TORAY)	11 × 11 mm	0.19 mm

Figure 3. Schematic diagram of the experimental apparatus.

(PTFE) is installed around the MEA to prevent short-circuits between current collectors. Figure 2(c) shows a photograph of the fabricated sensor.

2.3 Operation of the sensor

In the DMFC system, the sensor is designed to detect methanol concentration in the fuel mixture tank. Therefore, the evaluation of the sensor in this study is performed under the simulated installation in the system. Figure 3 shows the experimental apparatus of this study. The tank that simulates the mixing tank for the DMFC system is connected to a feed pump (7038, Namiki) with fluorine tubes to circulate the methanol solution. The sensor is immersed in the tank and connected to an electronic loading device (1470, Solartoron).

The sensitivity of the sensor increases as the rate of change of oxidation current with respect to methanol concentration increases. Geng et al. reported both the limiting current for methanol oxidation and the corresponding potential increase with methanol concentration.¹⁹ This report suggests that the higher applied voltage increases the sensitivity of the sensor. Further, a high applied voltage is required to extend the sensing range of the methanol concentration. A previous study using Pt as a catalyst electrode reported that the linear current-concentration relationship may be extended to a high concentration if the cell potential is raised, based on results measuring methanol concentrations of up to 4 mol dm⁻³ at an applied voltage up to 1.1 V.¹⁸ In this study, the sensor applied voltage is set at 1.1 V, and the oxidation current is measured when a constant voltage is applied to the sensor. The methanol concentration is set in the range of 0 wt% to 10 wt%, and the methanol solution temperature is set in the range from 25 °C to 60 °C.

2.4 Methanol concentration correlation algorithm

The oxidation current characteristics of the sensor depend on the methanol concentration. In addition, they have temperature dependence. Assuming that the slope of the Arrhenius plot is constant regardless of the concentration,

$$\text{Log}_{10}(I_0) - \text{Log}_{10}(I) = \alpha \times \left(\frac{1000}{T_0} - \frac{1000}{T} \right) \quad (6)$$

where I , I_0 , α , T , and T_0 denote the oxidation current density, the current density after temperature correction, the slope of the Arrhenius plot, the measurement temperature, and the correction temperature (333 K), respectively. The extent to which the linearity between methanol concentration and oxidation current exists can be obtained as

$$C_m = \beta \times I_0 + \gamma \quad (7)$$

where C_m , β , and γ denote the methanol concentration, the coefficient of concentration, and a constant, respectively. The values of α , β , and γ are obtained by the following method.

α : Obtain the temperature dependent characteristics of the oxidation current at concentrations above three points. The obtained characteristics (Arrhenius plot, e.g., Fig. 9) are linearly approximated and the slope is averaged.

β and γ : Obtain the methanol concentration characteristics of the oxidation current at a methanol solution temperature of 60 °C (333 K). The obtained characteristics are fitted using Eq. (7).

3. Results and Discussion

3.1 Dependence on methanol concentration of the sensor

Figure 4(a) shows the oxidation current response of the sensor to changes in methanol concentration. The oxidation current response was evaluated at 50 °C with a stepwise change in concentration from 0 to 9 wt% by adding 40 wt% methanol solution. When the methanol solution was added, the sensor responded quickly and the oxidation current increased. This trend was evident in the relatively low concentration range from the start of the test to the vicinity of 4000 s, namely between 0 and about 5 wt% methanol concentration. However, above 5 wt%, the sensitivity of the sensor decreased as the methanol concentration increased. Figure 4(b) shows the result of converting the result of Fig. 4(a) as a dependence of oxidation current density on methanol concentration. The oxidation current density shows a linear relationship with methanol concentration at relatively low concentrations from 0 to 3 wt%, while it is nonlinear above 4 wt%. According to Fig. 1(a), this can be attributed to the oxidation current being linearity dependent on the limiting current caused by methanol diffusion in Eq. (1) up to 3 wt%; above 3 wt%, the oxidation current changes to depend on the limiting current caused by catalytic activity. From Eq. (1), the sensitivity of the diffusion rate can be controlled by D_m , δ , which is the specification of the diffusion layer, as shown in Fig. 1(b). By increasing D_m or reducing δ , the slope of the limiting current can be increased. On the contrary, by reducing D_m or increasing δ , the slope of the limiting current can be reduced.

Therefore, the specification of the diffusion layer was manipulated via simulations to improve the linearity of the oxidation current characteristic to shift the intersection of the two limiting currents to the higher concentration side. It was manipulated assuming a specification where D_m is reduced or δ is increased, and the former was replaced with an Omnipore membrane filter (JMWP04700, Millipore) with smaller pores than the conventional diffusion layer; the latter was replaced with multiple layers of the conventional diffusion layer, respectively. The results are shown in Fig. 5. The slope of the limiting current becomes smaller with reducing D_m or increasing δ , which confirms that the behavior follows Eq. (1) at relatively low concentrations. Therefore, it was verified that the linearity of the oxidation current characteristics can be improved by controlling the diffusion constant or the thickness of the diffusion layer as a countermeasure against nonlinearity at higher concentrations.

Figure 4. Oxidation current characteristics of sensor at 50 °C (a) sensor response to methanol concentration with a stepwise change in concentration from 0 to 9 wt% by adding 40 wt% methanol solution and (b) dependence of oxidation current density on methanol concentration.

Figure 5. Dependence of oxidation current density on methanol concentration at 25 °C by changing diffusion layer specification (a) effect of D_m in Eq. (1) using the diffusion layer (◇) and the filter (●) and (b) effect of δ in Eq. (1) using one (◇), 3 stacked (▲), and 6 stacked (■) diffusion layer.

3.2 Dependence on the temperature of the sensor

Figure 6 shows the oxidation current characteristics at methanol solution temperatures of 20, 40, and 50 °C. The oxidation current characteristics tend to change not only the current value but also the slope with temperature. The results can be qualitatively explained based on Fig. 1(a). The slope of the limiting current caused by methanol diffusion increases with temperature because D_m in Eq. (1) is proportional to temperature (① in Fig. 6). The limiting current caused by catalytic activity improves with increasing temperature because the catalytic activity increases with temperature (② in Fig. 6). These results can be attributed to the variations in the oxidation current characteristics under the influence of the temperature dependence of the respective limiting currents. The intersection of the two limiting currents shifts toward lower concentrations as the temperature increases, and this suggests that temperature is one of the factors affecting the linearity of the oxidation current characteristics.

Figure 7 shows an Arrhenius plot of oxidation current density for the methanol concentrations of 1, 3, 5, and 10 wt%. The oxidation current tends to increase as the temperature increases (as T^{-1} decreases). The slope of the oxidation current characteristics is linear at 1 wt% methanol concentration; however, the slope changes at methanol concentrations above 3 wt%. In addition, there is almost

Figure 6. Dependence of oxidation current density on methanol concentration for sensor at 50 (○), 40 (△), and 25 (◇) °C.

no difference in the oxidation current between the two current densities at 5 wt% and 10 wt% methanol concentrations as the temperature is increased. These phenomena were discussed using Fig. 6 to classify the oxidation current characteristics for each concentration condition using two limiting currents as the dominat-

Figure 7. Arrhenius plot of the oxidation current density for methanol concentrations of 1 wt%, 3 wt%, 5 wt%, and 10 wt%.

ing factor: the limiting current caused by methanol diffusion and the limiting current caused by catalytic activity. At 1 wt%, the dominant factor in the oxidation current characteristics is the diffusion limiting current. At 5 wt% and 10 wt%, the dominant factor is the limiting current caused by catalytic activity. Further, at 3 wt%, the oxidation current characteristics can be affected by each limiting current because it is located near the intersection of the two limiting currents. According to this classification, the Arrhenius plot in Fig. 7 shows that the slope of the oxidation current of 1 wt% is constant, thereby suggesting that diffusion energy is the main cause. The slope of the oxidation current at concentrations above 5 wt% varies with temperature, which suggests that there is another factor influencing the change in catalytic activation energy. Since this phenomenon occurs at relatively high oxidation current densities, the interruption of the methanol oxidation reaction caused by carbon dioxide retention in the electrode is a probable cause. Thus, as the generation reaction rate of carbon dioxide gas increases with an increase in oxidation current, carbon dioxide gas remains on the electrocatalyst because the generation reaction rate is higher than the emission rate of the carbon dioxide gas, which reduces the methanol oxidation reaction area.

In this study, we propose raising the limiting current caused by catalytic activity by increasing the amount of catalyst loading, as shown in Fig. 1(c). This proposal is expected to shift the intersection of each limiting current to the higher concentration side that will help reduce the effect of oxidation inhibition caused by the retention of carbon dioxide. Figure 8 shows the oxidation current characteristics of sensors with Pt loading of 2, 5, 10, and 15 mg cm⁻². The linearity of the oxidation current characteristic of 5 mg cm⁻² is not improved from the conventional specification of 2 mg cm⁻². The results could be attributed to the retention of carbon dioxide, and the possibility that this difference in catalyst amount was not significant. The characteristic of 10 mg cm⁻² improves linearity up to 6 wt%; further, the characteristic of 15 mg cm⁻² improves linearity up to 10 wt%. The slope of the oxidation current characteristic of 15 mg cm⁻² is smaller than the other conditions according to Eq. (1) because of the change in the methanol diffusivity of the electrode layer as the thickness of the electrode layer increases with Pt loading. Figure 9 shows the Arrhenius plots of the sensors with 10 mg cm⁻² and 15 mg cm⁻² of Pt loading; increasing the Pt loading improves the linearity to temperature.

3.3 Methanol concentration correlation algorithm

The proposed original algorithm was verified. The sensor with 15 mg cm⁻² of Pt loading was immersed in methanol solutions with methanol concentrations of 1 wt%, 2 wt%, 3 wt%, and 4 wt%, respectively. The oxidation current was measured by applying a

Figure 8. Dependence of oxidation current density on methanol concentration for sensors with 15 mg cm⁻² (▲), 10 mg cm⁻² (◆), 5 mg cm⁻² (●), and 2 mg cm⁻² (□) of Pt loading at 25 °C.

Figure 9. Arrhenius plot of the oxidation current density for the sensors (a) with 10 mg cm⁻² and (b) with 15 mg cm⁻² of Pt loading.

Figure 10. Temperature dependence of measured methanol concentration in 1, 2, 3, and 4 wt% methanol solutions by original algorithm.

voltage of 1.1 V while the temperature was varied from 25 °C to 60 °C using the heater shown in Fig. 3. The measured oxidation currents were calculated as methanol concentrations obtained using Eqs. (6) and (7). The validation result is shown in Fig. 10. A good agreement was obtained in comparison with the real concentration.

3.4 Durability evaluation

A 6500-h durability evaluation was conducted under the conditions of 60 °C in a methanol solution, 2.3 wt% methanol

Figure 11. Circuit configuration for alternating pulse methanol sensor.

Table 2. Switch combination for changing polarity.

Switch	A	B	C	D
Polarity 1	On	Off	Off	On
Polarity 2	Off	On	On	Off

concentration, and 1 V applied voltage with the polarity switched every 30 s. The applied voltage in the alternating pulse was achieved by a circuit configuration with four switches (A, B, C, and D) shown in Fig. 11. As listed in Table 2, the configuration was used to generate an alternating pulse by turning on the combination of either A and D or B and D. In this study, a MOS-FET semiconductor switch was used, and the switch was controlled using a micro-controller. The response to the change in concentration with prolonged operation was adjusted by adding methanol at any given time; the result is shown in Fig. 12. The decay rate of the current is about $0.02 \text{ mA cm}^{-2} \text{ h}^{-1}$ at 6500 h which is considerably smaller than the results (about $1.16 \text{ mA cm}^{-2} \text{ h}^{-1}$ at 4 h) reported in the literature.¹⁹ The low current decay rate can be attributed to the improvement of the electrode specifications described above. The improvement in the current decay rate was attributed to the relaxation of the current concentration per Pt specific surface area by increasing the catalyst amount. Further investigations are needed to verify the improvement.

4. Conclusions

A methanol concentration sensor with original algorithm was developed for application in DMFC systems. The methanol concentration is estimated from an Arrhenius law and diffusion limiting current, and long linearity to the methanol concentration up to 10 wt%. The responsive against the methanol is quite fast. The sensor can be operated under the temperatures from 25 °C to

Figure 12. Durability evaluation of the sensor for 6500 h at 60 °C, 2.3 wt% methanol concentration, and 1 V applied voltage with the polarity switched every 30 s.

60 °C for long periods (<6500 h) with low degradation ($0.02 \text{ mA cm}^{-2} \text{ h}^{-1}$), which is adequate for the application of DMFC systems. The methanol concentration sensor with original algorithm will contribute to the widespread use of DMFC in future.

References

1. C. Y. Chen, D. H. Liu, C. L. Huang, and C. L. Chang, *J. Power Sources*, **167**, 442 (2007).
2. A. Heinzl and V. M. Barragan, *J. Power Sources*, **84**, 70 (1999).
3. M. S. Lee, J. Sohn, J. Shim, and W. M. Lee, *Sens. Actuators, B*, **124**, 323 (2007).
4. C. H. Wan and C. H. Lin, *J. Power Sources*, **186**, 229 (2009).
5. J. Kondoh, S. Tabushi, Y. Matsui, and S. Shiokawa, *Sens. Actuators, B*, **129**, 575 (2008).
6. D. Sparks, K. Kawaguchi, M. Yasuda, D. Riley, V. Cruz, N. Tran, A. Chimbayo, and N. Najafi, *Sens. Actuators, A*, **145–146**, 9 (2008).
7. Q. Mao and U. Krewer, *Electrochim. Acta*, **68**, 60 (2012).
8. C. C. Sung, Y. L. Tseng, Y. F. Chiang, and C. Y. Chen, *Sens. Actuators, A*, **161**, 101 (2010).
9. S. Doerner, T. Schultz, T. Schneider, K. Sundmacher, and P. Hauptmann, *SENSORS, 2004 IEEE*, **2**, 639 (2004).
10. H. Zhao, J. Shen, J. Zhang, H. Wang, D. P. Wilkinson, and C. E. Gu, *J. Power Sources*, **159**, 626 (2006).
11. E. Akbari, Z. Buntat, A. Nikoukar, A. Kheirandish, M. Khaledian, and A. Afrozeh, *Renewable Sustainable Energy Rev.*, **60**, 1125 (2016).
12. T. Kumagai, T. Horiba, T. Kamo, S. Takeuchi, K. Iwamoto, K. Kitami, and K. Tamura, US Patent 4,810,597 (1989).
13. A. Kulikovskiy, *J. Electrochem. Soc.*, **152(6)**, A1121 (2005).
14. W. Sun, G. Sun, W. Yang, S. Yang, and Q. Xin, *J. Power Sources*, **162**, 1115 (2006).
15. S. R. Narayanan, T. I. Valdez, and W. Chun, *Electrochem. Solid-State Lett.*, **3**, 117 (2000).
16. Z. Qi, C. He, M. Hollett, A. Attia, and A. Kaufman, *Electrochem. Solid-State Lett.*, **6**, A88 (2003).
17. L. Yan, J. Liao, L. Feng, X. Zhao, L. Liang, W. Xing, and C. Liu, *J. Electroanal. Chem.*, **688**, 49 (2013).
18. S. A. C. Barton, B. L. Murach, T. F. Fuller, and A. C. West, *J. Electrochem. Soc.*, **145**, 3783 (1998).
19. J. Geng, X. Li, G. Sun, and B. Yi, *Sens. Actuators, B*, **147**, 612 (2010).
20. Q. Ye and T. S. Zhao, *Electrochem. Solid-State Lett.*, **8**, A211 (2005).