Efficient Hydrogen Production from Aqueous Methanol in a Proton Exchange Membrane Electrolyzer with Porous Metal Flow Fields

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ABSTRACT: This paper reports the electrolysis of aqueous methanol for hydrogen production in a proton exchange membrane electrolyzer with a novel porous flow field made of sintered spherical metal powder. Results show that the use of porous flow field has a significant improvement in hydrogen production performance compared to a conventional groove flow field. This could be attributed to an increase in effective electrode area by using the porous material which enables the flow field to supply reactant evenly to the electrode and removes products smoothly. Influences of the operating conditions such as methanol concentration and cell temperature on hydrogen production are also discussed.

KEY WORDS: EV and HV systems, Hydrogen production, Fuel cell, Electrolysis, Methanol, Porous flow field, PEM [A3]

1. Introduction

It is crucial to produce hydrogen efficiently for establishing the sustainable society with hydrogen energy. Among many methods to produce hydrogen, water electrolysis with proton exchange membrane (PEM) is the most convenient way to produce hydrogen quickly with a high purity in a small scale application at low temperatures. Besides the water, alcohols can also be electrolyzed to generate hydrogen and have a very important advantage of lower theoretical voltage for electrolysis than water. While the water electrolysis requires 1.23V, aqueous methanol electrolysis needs just 0.02V theoretically to start producing hydrogen. The following reactions describe the principle of aqueous methanol electrolysis shown in Fig. 1:

Anode: \( \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \) (1)
Cathode: \( 6\text{H}^+ + 6\text{e}^- \rightarrow 3\text{H}_2 \) (2)
Overall: \( \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO}_2 \) (3)

The very low theoretical voltage for aqueous methanol electrolysis presents a significant improvement in hydrogen production performance compared to water electrolysis and may lead to lower cost for hydrogen production even when the cost of methanol is included. Since the hydrogen purity is quite high and carbon monoxide is found to be absent, the hydrogen produced from PEM methanol electrolysis can be readily used for PEM fuel cells.

Recently, there were some reports showing that porous flow fields increase the performance of direct methanol fuel cell (DMFC). Especially a porous flow field (PFF) made of sintered spherical metal powder (SMP) exhibits three times higher output compared with a conventional groove flow field (GFF). The significant improved cell performance is attributed to the improved reactant supply and product removal by the porous structure and to the increase in effective electrode area by the flow field having no ribs. Meanwhile, the setup for an aqueous methanol electrolyzer cell can be quite similar to that for DMFC. Due to this similar structure, the sintered spherical metal powder porous flow field can also be effective in a PEM methanol electrolyzer cell. In addition to the low voltage for methanol, the utilization of the PFF made of SMP could be useful to produce hydrogen efficiently.

This current paper studies the electrolysis of aqueous methanol for efficient hydrogen production in a PEM electrolyzer cell employing the PFF made of SMP.

2. Experimental

The experiments used a single cell with an assembly of a proton exchange membrane (Nafion117) and electrodes. Setup of the tested hydrogen production cell is schematically shown in Fig. 2. The electrolysis was conducted by applying electric current from a DC power supply to the electrolyzer at a constant voltage.
mode to generate hydrogen at the cathode. Temperatures of the cell and aqueous methanol were controlled during experiments by putting them into a constant temperature vessel (As one DOV-450P). Methanol-water mixtures were fed into the anode by using a peristaltic pump, the cell temperature was measured with a thermocouple. Kikusui AC impedance meter (KFM2030) was used to measure the cell impedance with a frequency range from 3000 to 0.1Hz.

Specifications of the tested membrane electrode assembly (MEA) are shown in Table 1. Carbon paper with 0.28mm thickness was used as gas diffusion layer (GDL) on both sides of the MEA. A Nafion 117 polymer membrane was sandwiched between the electrodes. The reaction area of the electrode is 25cm². The catalyst loading on the anode was 1.0mg/cm² (Pt-Ru), while that on cathode was 1.0mg/cm² (Pt). The catalysts were with carbon support. Percentages of Pt-Ru and Pt to carbon powder were 50wt%. The use of Pt-Ru catalyst on the anode is to improve the problem of poisoning by carbon monoxide (CO). As known in DMFC operation, during the methanol oxidation reaction, CO is formed and strongly adsorbs onto the Pt catalyst. This results in reducing the catalyst utilization and thus the cell performance; hence, it is important to remove CO for recovering the catalytic activity of Pt/C catalyst. The addition of Ru to the catalyst tends to improve this problem since Ru acts as promoting sites to oxidize water as shown in the following reactions (6). The OH from the oxidized water molecule oxidizes CO to produce carbon dioxide (CO₂). This would ensure the durability of catalyst during the aqueous methanol electrolysis process.

\[
\begin{align*}
\text{CH}_3\text{OH} & \rightarrow \text{CO} + 4\text{H}^+ + 4\text{e}^- \quad (4) \\
\text{H}_2\text{O} & \rightarrow \text{H}^+ + \text{OH}^- \quad (5) \\
\text{OH}^- + \text{CO} & \rightarrow \text{CO}_2 + \text{H}^+ + \text{e}^- \quad (6)
\end{align*}
\]

Table 2 shows the specifications of the tested PFF. The current research tested a separator with the PFF made of sintered spherical metal powder shown in Fig. 3(a). The metal powder is made of a corrosion resisting type stainless steel (JIS SUS316L; Fe-19Cr-12Ni-2Mo) by an inert gas atomization method. It has a porosity of around 48% and a grain size distribution of 350-500μm. The surface image of the porous medium which was obtained with a laser scanning microscope (Keyence VK-9700) is shown in Fig. 4. For comparison, solid stainless steel separator with a groove (straight–channel) type flow field shown in Fig. 3(b) was also used. Both separators are made of the same material as the metal powder and have the same depth of 2mm. The flow field volume for the groove type is 2.9cc and is almost same as that for the porous type.

### Table 1 Specification of MEA

| Polymer membrane | Nafion117 (175μm) |
|------------------|-------------------|
| Reaction area    | 25 cm² (5 x 5 cm) |
| Anode catalyst   | Pt-Ru 1.0 mg/cm²  |
| Cathode catalyst | Pt 1.0 mg/cm²     |

### Table 2 Specification of the tested PFF made of sintered spherical metal powder

| Composition               | Fe-19Cr-12Ni-2Mo (JIS SUS316L) |
|---------------------------|---------------------------------|
| Grain diameter            | 350-500μm                       |
| Pore ratio                | 48%                             |

3. Results and Discussion

3.1. Comparison of water and aqueous methanol in PEM electrolyzer cell

Fig. 5 shows the results of experiments comparing the hydrogen production performances with water and aqueous methanol in PEM electrolyzer cell. The conventional groove type
flow field was used in this comparison. Aqueous methanol with 4M concentration or water was fed to the anode at the flow rate of 10cc/min during the electrolysis process. Temperatures of the cell were set at 298K, and the applied voltage was varied from 0 to 2V. The onset voltage to generate hydrogen for aqueous methanol electrolysis is around 0.45V, while that for water is about 1.4V. Compared with water electrolysis, the aqueous methanol electrolysis requires much lower voltage to produce the same amount of hydrogen, since the same current density corresponds to the same amount of hydrogen production for both water and methanol cases. For instance, for achieving a current density of 0.1A/cm², water electrolysis requires approximately a voltage of 1.95V, while aqueous methanol electrolysis needs only 0.76V to generate the same amount of hydrogen. This lower electrolysis voltage with methanol could be mainly explained by the lower Gibbs free energy of methanol compared to water in Redox reactions (i.e. oxidation-reduction reactions).

The lower voltage leads to the lower electric energy consumption as shown in Fig. 6. The electric energy consumption with aqueous methanol electrolysis is much lower than that with water electrolysis, and the difference is larger at higher current densities. This suggests that the use of methanol-water mixture would be especially attractive to produce hydrogen economically in the case of high electricity cost and low price of methanol.

3.2. Comparison of porous flow field and groove flow field

(a) Hydrogen production performance

The hydrogen production performance comparison of porous and groove flow fields in PEM methanol electrolyzer cell is discussed in this section. Fig. 7 shows the results when varying the applied voltage from 0 to 0.9V. Porous flow fields or groove flow fields were placed on both sides of the cell. Aqueous methanol with 4M concentration was fed to the anode at the flow rate of 10cc/min. Temperatures of the cell and aqueous methanol were set at 298K. From the results, the PFF exhibits higher current density than the GFF at the same applied voltage, and the difference increases with increasing the applied voltage. Since the current density is theoretically proportional to the rate of hydrogen production, this indicates that the hydrogen production performance with the PFF is higher than that with the GFF in PEM methanol electrolyzer cell.

(b) Energy conversion efficiency

Fig. 8 shows the electric energy consumption and energy conversion efficiency for the results in Fig. 7. The energy conversion efficiency in the figure was calculated with the higher heating value (HHV) of produced hydrogen, electric energy consumption, and the HHV of the consumed methanol as follows:

$$\eta = \frac{(\text{HHV}_\text{H}_2)}{\text{Electric Energy} + \text{HHV}_\text{CH}_3\text{OH}}$$  \hspace{1cm} (7)

The rates of hydrogen production and methanol consumption for Eq. (7) were estimated by the Reaction (3) with the measured current densities in Fig. 7.

The figure shows that the electric energy consumption with the PFF is lower than that with the GFF for achieving the same current density. This means the PFF is more efficient to produce hydrogen, because the theoretical methanol consumption is same for both PFF and GFF cases at the same current density and the current density corresponds to the hydrogen production rate. The energy conversion efficiency of PEM electrolyzer cell tends to decrease with increasing the current density (i.e. hydrogen production rate). However, the case with PFF can ease this deterioration in energy conversion efficiency and can maintain higher efficiency than the conventional GFF. The difference between the two cases increases with the hydrogen production rate.

Fig.5 Hydrogen production performance comparison of water and aqueous methanol in PEM electrolyzer cell by employing GFF

Fig.6 Electric energy consumption comparison of water and aqueous methanol in PEM electrolyzer cell

Fig.7 Hydrogen production performance comparison of GFF and PFF with 4M aqueous methanol concentration
supposedly caused by a lower interfacial contact resistance between the PFF and MEA since the difference between the two setups is just the separators. The PFF made of sintered spherical metal powder with rough surface of grains would contact three-dimensionally to the relatively soft surface of carbon paper and achieves lower contact resistance than the case with groove flow field which is commonly used by many researchers. This can be a reason for the improved hydrogen production with the PFF.

Beside the lower cell resistance, the reaction resistance which includes activation resistance and diffusion resistance is also decreased significantly with the PFF. The smaller arc in Fig. 9 would show this reduced reaction resistance since the arc diameter corresponds to reaction resistance. The low frequency range of the Cole-Cole plot represents the diffusion resistance, and the high frequency range represents the activation resistance. The arc with the frequency range below 1Hz which is in right hand side in Fig. 9 is largely decreased by using the PFF. This indicates that the reduced reaction resistance with the PFF is mainly with the diffusion resistance. Compared to the conventional GFF, the PFF has no ribs which may act as an obstacle to the reactant supply to and product removal from electrode, resulting in the increased effective electrode area. The PFF can supply reactant evenly to and remove CO2 smoothly from the anode and the diffusion polarization can be reduced significantly. This would improve the hydrogen production performance especially at higher current densities. The results of impedance analyses suggest that the lower cell resistance and reaction resistance are the reasons for the improved hydrogen production with the PFF.

3.3. Influence of operating conditions on aqueous methanol electrolysis with the sintered spherical metal powder porous flow fields

Previous sections have shown that the combination of PFF made of SMP and aqueous methanol is very advantageous for efficient hydrogen production in PEM electrolyzer cell. This section further studies the influence of operating conditions such as methanol concentration and cell temperature on the hydrogen production.

(a) Methanol concentration

Fig. 10 shows the results of experiments with varying the methanol concentration from 2 to 6M. The applied voltage was varied from 0 to 0.8V, while the anode feed rate and cell temperature were set at the same conditions as the experiments shown in Fig. 7. The higher methanol concentration brings higher current density, especially at higher applied voltage conditions. The reason for the improved performance of hydrogen production may be related to the change in surface tension of methanol-water solutions shown in Table 3. The surface tensions of 2, 4, and 6M were estimated based on the experimental data and correlation reported by Vazquez et al.(7) Due to the lower surface tension of methanol compared to water, higher concentration solution has lower surface tension and higher wettability level. The higher wettability may allow more aqueous methanol reactant diffuse through GDL to anode catalyst layer and result in higher rate of hydrogen production.
Table 3 Surface tension of water, methanol and aqueous methanol

|                  | Surface tension (mN/m) @ 298K |
|------------------|--------------------------------|
| Water            | 72                             |
| Methanol         | 22.51                          |
| Aqueous methanol (2M) | 60.75                         |
| Aqueous methanol (4M) | 52.91                         |
| Aqueous methanol (6M) | 47.06                         |

Fig. 10 Influence of aqueous methanol concentration on hydrogen production performance of PEM electrolyzer cell with the PFF

(b) Cell temperature

This section attempts to show the influence of cell temperature on the hydrogen production in aqueous methanol electrolysis with the PFF. Fig. 11 shows the experimental results of hydrogen production at cell temperature of 298, 323, and 348K. Methanol solution with 4M concentration was fed to the anode with the feed rate of 10cc/min. The current density is found to increase with increasing cell temperature at the same applied voltage. In other words, it is possible to operate the PEM methanol electrolyzer at lower cell voltages when increasing temperature. For instance, at the same current density of 0.2A/cm², the cell voltages of PEM methanol electrolyzer are 0.81, 0.73, and 0.63V at cell temperature of 298, 323, and 348K, respectively. The lower voltage at the same hydrogen production rate leads to the lower electric energy consumption.

Fig. 12 shows the electric energy consumption and energy conversion efficiency for the results in Fig. 11. Since the higher cell temperature requires lower voltage at the same hydrogen production rate (i.e. same current density), this reduces the electric energy consumption significantly. Based on Eq. (7), at the same rate of hydrogen production, the energy conversion efficiency is improved when the electric energy consumption is reduced. For achieving the same current density of 0.2A/cm², the electric energy consumptions are 19.8, 17.8, and 15.4kWh to produce 1kg of hydrogen at cell temperature of 298, 323, and 348K, respectively. This corresponds to the energy conversion efficiency of 71.8, 74.7, and 78.6%. The above results indicate that the temperature is an important factor for efficient hydrogen production in PEM methanol electrolyzer cell.

Fig. 13 Influence of cell temperature on AC impedance spectra
Fig. 13 shows the measured AC impedance for the experiments in Fig. 11 at the current density of 0.15A/cm². The cell resistance decreases significantly with the increase in cell temperature. Cell resistances are 16.5, 13.5, and 10mΩ at cell temperature of 298, 323, and 348K, respectively. It is known that the water uptake (i.e. the number of water molecules per sulfonic acid site) increases with temperature, resulting in higher water content inside the membrane(9). In addition, even with the same value of water uptake, the ion conductivity of Nafion membrane increases with temperature(9)(10). The increase in water content and ion conductivity results in lower ionic resistance of membrane, thus the cell resistance is reduced at higher cell temperatures. Regarding the reaction resistance, the Cole-Cole plot shows a large reduction when increasing cell temperature. While the arc diameter of the plot corresponds to the reaction resistance including activation and diffusion resistances, the arc diameter is largely reduced by increasing cell temperature. This reduction in reaction resistance would be mainly caused by the enhanced activity of the catalytic reaction at higher cell temperatures. In addition, the surface tension of aqueous methanol decreases at higher temperature(7). The lower surface tension may allow more aqueous methanol diffuse through the anode GDL to the catalyst, thus reducing the diffusion resistance. The reductions in ionic resistance of membrane and reaction resistance would be the reason for the largely improved hydrogen production performance at higher cell temperatures.

4. Conclusion

This study newly proposes the combination of aqueous methanol and porous metal flow field in PEM electrolyzer cell for producing hydrogen efficiently. Results derived from the studies can be summarized as follows:

(1) By using methanol-water mixture in PEM electrolyzer, hydrogen can be produced at much lower voltage compared to the use of water, and hydrogen production performance is improved.

(2) By employing the PFF made of sintered spherical stainless steel powder, the hydrogen production performance and energy conversion efficiency of PEM methanol electrolyzer cell are improved significantly compared to operation with the conventional straight groove type flow field. The combination of PFF and methanol-water mixture is advantageous to produce hydrogen efficiently in PEM electrolyzer cell.

(3) The measured AC impedance data indicate that the lower cell resistance and reaction resistance are the reasons for the higher hydrogen production performance with the PFF. The lower cell resistance can be explained by the lower interfacial contact resistance with PFF, while the lower reaction resistance is attributed to the increased effective electrode area by using the PFF which can supply reactant evenly to and remove CO₂ smoothly from the anode.

(4) Hydrogen production performance of the cell tends to be improved with increases in methanol concentration and cell temperature. Especially, the temperature has a large influence on cell performance and is an important factor for producing hydrogen efficiently.

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