Short communication

Fuel cells using dimethyl ether

Jung-Han Yoo [a], Hoo-Gon Choi [b], Chan-Hwa Chung [a], Sung Min Cho [a],*

[a] *Department of Chemical Engineering, Sungkyunkwan University, Suwon 440-746, Republic of Korea*
[b] *Department of Systems Management Engineering, Sungkyunkwan University, Suwon 440-746, Republic of Korea*

Abstract

The performance of fuel cells using dimethyl ether (DME) fuel is presented in this study at a relatively low temperature of 80 °C. DME is known to be less electrochemically active to Pt catalysts, compared with typical fuels for fuel cells such as hydrogen and methanol, especially at low temperatures. In order to compensate the poor performance of fuel cells using the less active DME fuel, the DME and methanol fuels are mixed and supplied to the fuel cells simultaneously. The methanol fuel is delivered to the fuel cells by the high vapor pressure of DME without a liquid pump. In this study, we investigated the effect of anode catalysts and the effect of mixing fuels of DME, water, and methanol on the performance of the fuel cell. For preparing a fuel mixture with DME, the solubility of DME in water and methanol solution has been also investigated.
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1. Introduction

Recently, fuel cells for portable applications have been investigated extensively with a target to replace the lithium batteries. Direct methanol fuel cell (DMFC) has been a fuel-cell type of choice for the application since it can be operated at a low temperature and is relatively safer than polymer electrolyte membrane fuel cell (PEMFC) using hydrogen [1–3]. Methanol is a cheap liquid fuel and is more efficiently oxidized than other fuels except hydrogen. However, the use of methanol as a fuel presents several problems. Methanol is not only toxic and highly flammable but also prone to pass through the polymer electrolyte membrane causing the reduction of the fuel-cell performance. Due to this reason, alternative fuels have been sought consistently even though DMFC has been investigated intensively for commercialization.

A number of alternative fuels have been studied for portable applications [4]. Among them, a few new fuels have attracted attentions, which are dimethyl ether (DME) [5–7], formic acid (FA) [8], and alcohols [9]. DME that is a fuel of choice for this study has a molecular structure similar to that of methanol and

has been in mass-production stage in recent years. In addition, since it is a virtually non-toxic and easy to liquefy at a room temperature, DME is expected to be a new alternative fuel for direct fuel cells. For a fuel cell using DME fuel, it is expected that energy loss due to fuel crossover could be greatly reduced since the molecular weight of DME is larger and its solubility in water is much lower than those of methanol. In addition, since DME can be stored as a liquid and delivered to fuel cells as a gas, it is possible for the fuel cell to be operated without a liquid pump which could make the portable fuel-cell system bigger and complicated.

Even though DME fuel has the aforementioned advantages over methanol, DME also has a critical shortcoming that DME is much less electrochemically active than methanol especially at low temperatures. In order to obtain high performance of a fuel cell using DME fuel even with the low electrochemical activity of DME, one way is to add more electrochemically active methanol into DME fuel while having the advantage of using DME fuel that the fuel cell can be operated without a liquid pump. For this purpose, in this study we investigated the effect of anode catalysts and the effect of mixing fuels of DME, water, and methanol on the performance of DMFC. For preparing a fuel mixture with DME, the solubility of DME in water and methanol solution has been also investigated.

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* Corresponding author. Tel.: +82 31 290 7251; fax: +82 31 290 7272.
  E-mail address: sungmcho@skku.edu (S.M. Cho).

2. Experimental

A 3 cm × 3 cm MEAs used in this study were prepared in the following procedure. The diffusion backing layers for anode and cathode were a Teflon-treated (20 wt.%) carbon paper (Toray 090, E-Tek) of 0.29 mm thickness. A thin diffusion layer was formed on top of the backing layer by spreading Vulcan XC-72 (85 wt.%) with PTFE (15 wt.%) for both anode and cathode. After the diffusion layers were sintered at a temperature of 360 °C for 15 min, the catalyst layer was then formed with anode catalysts and Nafion (1 mg cm^{-2}) for anode and with Pt (4 mg cm^{-2}) and Nafion (1 mg cm^{-2}) for cathode. The anode catalysts used in this study were Pt–Ru (4 mg cm^{-2}), Pt (4 mg cm^{-2}), or Pt/Pd (2 mg cm^{-2} each). The prepared electrodes were placed both sides of a pretreated Nafion 115 membrane and the assembly was hot-pressed at 85 kg cm^{-2} for 3 min at 135 °C.

The fabricated MEA was sandwiched by two graphite flow-field plates and finally the assembly was held together with two plastic insulation sheets and two aluminum backing plates using a set of retaining bolts positioned around the periphery of the cell. We used an interdigitated flow field for anode side and a serpentine flow field for cathode.

Pure DME cylinder (outlet pressure of 4.5 bar) was connected with the water (or 3 M methanol solution) container so that DME vapor was bubbled into water to form DME solution. At equilibrium, DME vapor in the fuel container should reach 4.5 bar and an equilibrium amount of DME at the vapor pressure should dissolve into water (or methanol–water). From an outlet port installed at the bottom of the container, DME–water (or DME–methanol–water) solution was delivered to the anode of fuel cell by the vapor pressure exerted on the solution. For the cathode, air was supplied at a flow rate of 500 ml min^{-1}.

3. Results and discussion

3.1. DME solubility in pure water and methanol–water solution

The solubility of DME was investigated by measuring the vapor pressure of a fuel container at a room temperature of 20 °C. For the experiment, a fixed amount of pure water (200 ml) was filled in a stainless steel fuel container at first and subsequently pure DME was poured into the container excessively in order to obtain supersaturated DME solution. Then, the vapor pressure and pure weight of the fuel in the container was measured. Initially, the vapor pressure of DME in the container was measured to be 4.7 bar, which should be the same as the vapor pressure of pure DME since DME was loaded excessively. After opening up a valve installed on top of the fuel container to let an amount of DME vapor out of the container for a short moment, the weight of the fuel left in the container was measured again to check the amount of DME vapor leaked. Thereafter, we left the fuel container standing still for a while until the phase equilibrium reached by checking the pressure gauge settled, and then measured the stabilized vapor pressure. We repeated the same procedure a number of times by recording the vapor pressure
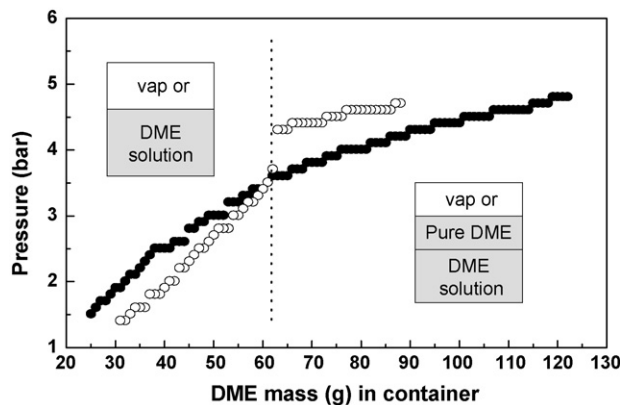

Fig. 1. Solubility of DME in water (open circle) and methanol–water (solid circle). The pressure has been measured repeatedly by leaking small amount of pure DME vapor out of the container and weighing the total weight to get the DME mass left in the container. All the data were obtained at the temperature of 20 °C.

and weight of the fuel in the container. Since we loaded the fuel container excessively with DME initially, it was expected that an amount of pure DME should have been condensed in the container. As can be seen in Fig. 1, the pressure of the container decreased little from 4.7 to 4.4 bar even though DME vapor was repeatedly taken out of the fuel container from initial 90 g DME to final 62 g DME. In this region, it was considered that DME liquid continuously vaporized and repeatedly taken out of the container while the pressure of the container kept almost constant. Until the pure DME liquid above the saturated DME solution completely disappeared, the concentration of DME in DME–water solution should have been close to the saturated solubility of DME in water at the saturated vapor pressure and a temperature of 20 °C. The pressure of the container decreased discontinuously at the saturation point and below the point the pressure continued to decrease linearly. It can be explained by the Raoult's law that the equilibrium solubility of DME in water decreases linearly as the vapor pressure of DME decreases. As depicted in Fig. 1, until the DME mass in the container is reduced to 62 g by letting DME vapor leak out of the container from the initial mass of 90 g, the condensed DME liquid is present in the container. With further removal of DME vapor, we could obtain the equilibrium solubility of DME in water at a certain DME vapor pressure. The saturation of DME in water was found to occur at 62 g DME dissolution in 200 g water at the experimental temperature of 20 °C, which corresponded to 31% solubility. The solubility of 31% means that 1 mol of DME is dissolved in 5.6 mol of water. The stoichiometric ratio of DME:water for the complete electro-oxidation of DME is 1:3 and it corresponds to the solubility of 46%.

On the other hand, in a case of dissolving DME in 3 M methanol solution instead of pure water, the similar behavior was observed in a sense that the same saturation point was found at 31% solubility. It is an expected result because the majority of the 3 M methanol solution should be water. Beyond the saturation point, however, there was not an abrupt change in the pressure of the container. We presume that the 3 M methanol
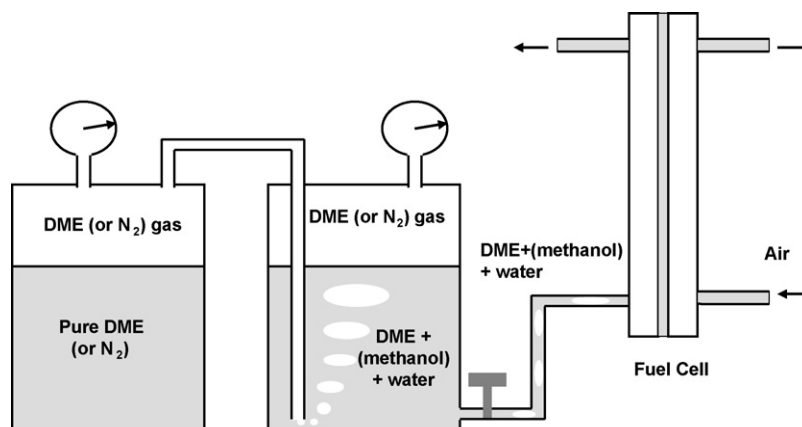
Fig. 2. Schematic diagram of the experimental apparatus.

solution shows higher solubility of DME even beyond the saturation point due to methanol.
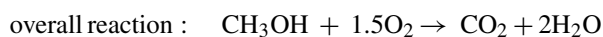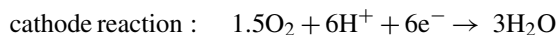
3.2. Delivery of a mixed fuel to a fuel cell

For a fuel cell using DME fuel, the usual practice to run the fuel cell has been to supply the vaporized water separately for the electro-oxidation of DME fuel at anode. Since DME is in a gas state at normal operating conditions for a fuel cell, the water vapor is usually supplied by a bulky humidifier as an electro-oxidant of DME for facilitating the mixing of DME and water fuels. In this study, however, we used a mixed liquid-phase fuel of DME–water or DME–methanol–water in order to simplify the fuel delivery. In order to deliver a mixed fuel to a fuel cell, a mixed liquid fuel with a fixed vapor pressure was delivered directly to a fuel cell. A vapor pressure in the fuel container was fixed by connecting the container to a pure DME or nitrogen cylinder and adjusting the cylinder pressure. Since DME is in a gas state in room temperature, DME is supposed to vaporize readily from a mixed liquid fuel as soon as the fuel exits the container. The mixed fuel exists as a two-phase state when transporting and flowing through a fuel cell. The schematic diagram for the delivery of mixed fuel to a fuel cell is shown in Fig. 2. For facilitating the contact between liquid-phase water and vapor-phase DME around anode catalysts, we have used an interdigitated flow field of which the inlet channel is disconnected with the outlet channel.
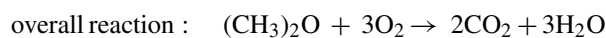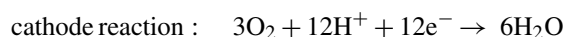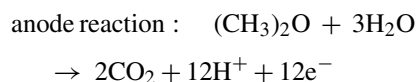
3.3. Effect of anode catalysts

Methanol and DME undergo the following anode oxidation and cathode reduction reactions:

- Methanol (DMFC):

anode reaction : $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$

cathode reaction : $1.5O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$

overall reaction : $CH_3OH + 1.5O_2 \rightarrow CO_2 + 2H_2O$

- DME (DME fuel cell):

anode reaction : $(CH_3)_2O + 3H_2O$
$\rightarrow 2CO_2 + 12H^+ + 12e^-$

cathode reaction : $3O_2 + 12H^+ + 12e^- \rightarrow 6H_2O$

overall reaction : $(CH_3)_2O + 3O_2 \rightarrow 2CO_2 + 3H_2O$

For the DMFC, typical anode and cathode catalysts are Pt–Ru and Pt, respectively. The biggest difference between methanol and DME is the amount of water required for the complete oxidation of the fuels at anode. Typical open-circuit voltage (OCV) for DMFC using the anode Pt–Ru and cathode Pt catalysts ranges from 0.6 to 0.7 V, while that for DME fuel cell ranges from 0.8 to 0.9 V using the same catalysts. It has been known that the electrochemical oxidation rate of DME is slower than that of methanol for Pt–Ru catalysts.

It is a well known fact that the Pt–Ru catalyst is the best anode catalyst for the DMFC. For the fuel cells using DME, however, the proper anode catalyst has not yet been studied thoroughly [5–7]. In order to get the maximum performance out of using the mixed fuel of DME–methanol–water, the anode catalyst should be good for both methanol and DME. We have tested Pt black, Pt–Ru alloy, and Pt/Pd mixed catalysts using the DME–water fuel. The tested results are shown in Fig. 3. Since Pd black catalyst showed no electrochemical activity on the DME electro-oxidation, here we tested with a mixed catalyst (50 wt.%) of Pt black and Pd black. As can be seen in the figure, the Pt–Ru catalyst showed the best performance on the DME electro-oxidation such as the case on the methanol electro-oxidation. On the other hand, the power density obtained using Pt black catalyst was found to be only 1/3 of that using Pt–Ru catalyst. As mentioned previously, since Pd catalyst was almost inactive to DME electro-oxidation at the temperature, it was natural that the mixed catalyst of Pt and Pd black showed only a half power density in comparison with the same amount of Pt black catalyst. Therefore, in order to obtain the maximum power density when using a mixed fuel of DME–methanol–water, it can be concluded that the Pt–Ru anode catalyst is the best for the purpose.
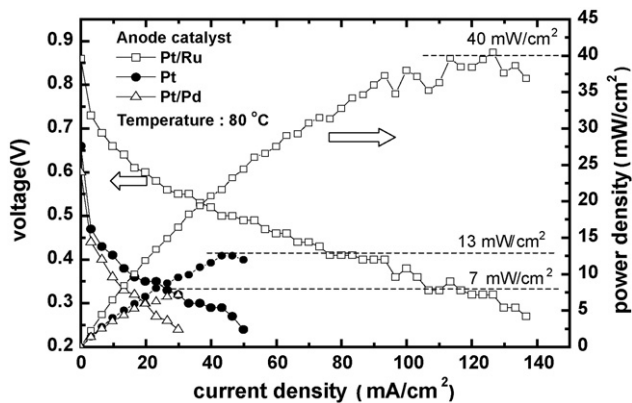
Fig. 3. Effect of anode catalysts on the performance of the fuel cell using the DME–water fuel delivered by DME vapor pressure at 4.5 bar. At cathode, air flow rate was 500 ml min^{-1}.
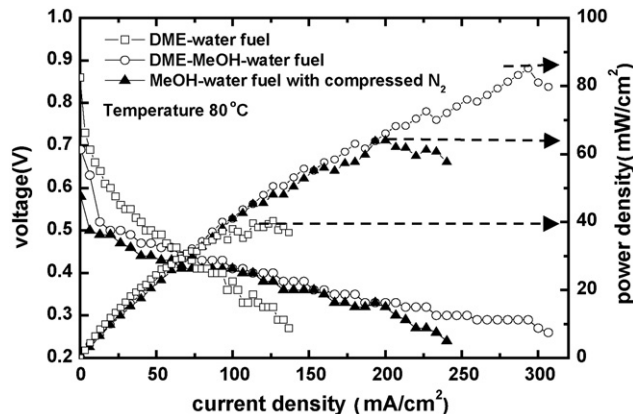

Fig. 4. Effect of methanol mixed with DME–water on the performance of the fuel cell using DME vapor pressure at 4.5 bar. At cathode, air flow rate was 500 ml min^{-1}.

3.4. Effect of methanol mixed with DME fuel

As mentioned earlier, using a fuel of DME–water mixture with Pt–Ru anode catalyst, the performance of the fuel cell was obtained to be slightly above 40 mW cm^{-2} at a temperature of 80 °C. It was expected that the addition of methanol to the DME–water mixture should have enhanced the performance due to the higher electrochemical activity of methanol over DME. As expected, in the case of using a mixed fuel of DME–methanol–water, the power density was measured to be about 85 mW cm^{-2} at the same temperature. The DME–methanol–water fuel was formed by mixing pure DME gas and 2 M methanol solution as shown in Fig. 2. If we assume that DME is dissolved in 2 M methanol solution with the maximum solubility of 31% at a pressure of 4.5 bar as given in Fig. 1, the DME–methanol–water mixed fuel could have the DME concentration of 7 M. It is presumed that the increase in power density could be responsible for the electro-oxidation of methanol added in the mixed fuel. In all experiments we fixed the total flow rate of 1 ml min^{-1} into the fuel cell. Even though we know that the power density increase should come from the methanol mixed with DME–water fuel, we do not know how much portion is responsible for the DME and methanol purely out of the power density of 85 mW cm^{-2}. In order to clarify the pure contribution of DME, we applied compressed nitrogen (4.5 bar) instead of DME to deliver the mixed fuel of methanol–water to the fuel cell. As shown in Fig. 4, the power density was found to be about 65 mW cm^{-2}, which was about 24% less than that obtained using DME–methanol–water fuel. So, we finally conclude that this 24% should be responsible for DME in the mixed fuel of DME–methanol–water. It should be also mentioned from the figure that the open circuit voltage (OCV) of DME–water fuel was the highest compared with the other fuels of methanol–water or DME–methanol–water. Even though the DME fuel shows the higher OCV than methanol, a problem using DME as a fuel for fuel cells is that the gaseous DME is not easily mixed with the water at a relatively low temperature of 80 °C and as the result DME is hard to deliver to the anode catalysts. In order to enhance the performance of DME-

fueled fuel cells, it should be useful to find a way of mixing DME and water to deliver easily to the catalysts, otherwise the fuel cells should be operated at higher temperatures above 100 °C. Another method to enhance the DME-fueled fuel cells at a relatively low temperature is using a mixed fuel as discussed in this study. The DME and methanol oxidizes competitively on the Pt–Ru anode catalysts with water. This method can be extended to other mixed fuels such as formic acid and methanol, formic acid and DME, etc. for the purpose of enhancing the performance of fuel cells at low temperatures.

4. Conclusions

The performance of fuel cells using DME fuel was investigated at a relatively low temperature of 80 °C in this study. In order to compensate the low electrochemical activity of DME, we added more electrochemically active methanol to DME for the anode fuel. For preparing a fuel mixture with DME, the solubility of DME in water and methanol solution has been investigated. We used the Pt–Ru black anode catalyst for the fuel cell and obtained about 85 mW cm^{-2} power density using DME–methanol–water fuel at a temperature of 80 °C. The 76% out of the power density was found to be responsible for methanol and the rest for DME.

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