Short communication

Effect of pressure for direct fuel cells using DME-based fuels

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Abstract

The performance of direct fuel cells using dimethyl ether(DME)-based fuels is presented at a relatively low temperature of $80\,°C$. DME is supplied to the fuel cells either by gas phase or aqueous phase for the operation of direct fuel cells. In order to keep DME in liquid phase during operation, fuel cells were operated at higher pressure up to 5 bar. For further increase of the power density from direct DME fuel cells, DME was mixed with methanol solution and fed into the fuel cells by the vapor pressure of DME itself without a liquid pump. In this study, we have obtained the highest power density of $210\,mW\,cm^{-2}$ at a temperature of $80\,°C$ when the fuel cell is operated with the mixed fuel with 2 M methanol solution under 4 bar.
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Keywords: Dimethyl ether (DME); Direct methanol fuel cell (DMFC); Fuel cell

1. Introduction

Even though direct methanol fuel cells (DMFCs) have attracted much attention lately, some disadvantages of DMFCs have not yet been resolved. The disadvantages are such as methanol crossover to cathode, necessity of liquid pumps for feeding methanol, slow oxidation kinetics, toxicity and flammability of methanol [1]. As an alternative fuel to overcome some of the disadvantages, dimethyl ether (DME) has been studied recently [1–6]. DME is the simplest ether (CH_3OCH_3) existing as gas phase at ambient temperature, but it can be liquefied easily at a moderately elevated pressure (b.p.; $-25.1\,°C$, vapor pressure; 5 bar at $20\,°C$). Since a mole of DME can produce 12 electrons by the complete oxidation while 1 mol methanol can produce 6 electrons, the fuel cells using DME can result in more efficient fuel management. Moreover, DME has an important advantage on utilizing directly the technologies of storage and transportation of butane or propane, since the vapor pressure of DME is in the middle of both [2,3].

In the previous study [5], we have showed the maximum performance of direct DME fuel cells to be $40\,mW\,cm^{-2}$ at $80\,°C$ when the fuel cell is operated in atmospheric pressure. We also showed in the other study [6] the performance of direct fuel cells using a mixed fuel of DME with 2 M methanol solution to be $85\,mW\,cm^{-2}$ at the same temperature and pressure. The operation of the fuel cells at atmospheric pressure inevitably involves gas-phase DME and liquid-phase water because of the high vapor pressure of DME and low vapor pressure of water at the operating temperature. The phase separation of DME and water fuels should result in the reduction of power output from the fuel cells due to the reduced encounters of the reactant molecules in separated phases.

In the present study, the operation of direct fuel cells using DME-based fuels is presented at elevated pressure to keep DME more in the same phase with water and subsequently to facilitate the reaction kinetics of DME and water.

2. Experimentals

Membrane electrode assembly (MEA) of a size $3\,cm \times 3\,cm$ has been prepared as follows. As a backing layer, a teflonized carbon paper (Toray 090, E-Tek) has been utilized for managing moisture at electrodes. In order for a diffusion layer, we first prepare a slurry by the ultrasonic pulverization of a mixture of Vulcan (XC-72) and PTFE (PTFE 30 emulsion) with a ratio of 85:15. The slurry has been coated on the carbon paper by the

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knife-blade method with 4 mg cm^{-2}. For catalysts, the commercial catalysts of Pt/Ru black (Johnson Matthey) and Pt black (E-Tek) have been used for the oxidation and reduction electrodes, respectively. The catalyst slurry has been prepared by mixing the catalyst (4 mg cm^{-2}), Nafion solution (1 mg cm^{-2}) and alcohol solvent. The catalyst has been loaded on the diffusion layer with 5 mg cm^{-2}. Both electrodes were hot pressed with Nafion 117 membrane at the temperature and pressure of 135 °C and 85 kg cm^{-2} for 3 min, respectively.

All the experiments were performed at a temperature of 80 °C. For the experiments of gas-feeding fuel cells, DME gas was supplied to water bubbler maintained at a temperature of 90 °C to moisturize the DME gas. For the liquid-feeding experiments, DME gas was forced to dissolve in water or 2 M methanol solution by pressuring the fuel reservoir at 5 bar and the liquid phase was withdrawn from the bottom of fuel reservoir to feed fuel cell at the flow rate of 1.2 ml min^{-1}. In order to pressurize fuel cells, a pressure regulator was installed at its fuel outlet.

3. Results and discussion

In this experiment, the performance of DMEFC was tested by varying the feeding method of DME fuel. All the experiments were carried out at a temperature of 80 °C. DME fuel can be fed into the fuel cell as either gas phase or dissolved phase in water. In order to supply DME in gas phase, the water vapor should be accompanied as an oxidant of DME. For the experiment, the feeding line was heated to 90 °C in order to prevent water vapor from condensation, while the fuel cell was maintained at 80 °C. In order to feed DME fuel in aqueous solution phase, a saturated DME aqueous solution was prepared at the pressure and temperature of 5 bar and 20 °C, respectively. At the condition the solubility of DME in water was found to be 36 wt.%, which corresponds to the mole ratio of 1:4.5 (DME:water) [6]. The saturated DME solution was supplied at a flow rate of 1.2 ml min^{-1} into the fuel cell, of which the pressure was maintained at atmospheric pressure. In both cases of gas and solution feeding DMEFC operations, the flow rate of oxygen gas at the reduction electrode was set to 300 ml min^{-1}.

Fig. 1 shows the performance of DMEFC for the gas and solution feedings. In case of feeding DME in gas phase, the maximum power density was found to be about 7 mW cm^{-2}. Meanwhile, a solution-fed DMEFC exhibited the maximum power density of about 38 mW cm^{-2}. The water content is known to play a crucial role for the electro-oxidation of DME [2–4]. When DME gas is fed into the fuel cell with water vapor by bubbling in hot water at 90 °C, the amount of water supplied should be insufficient for complete oxidation of DME. Since the vapor pressure of water at the temperature is 70 kPa, the mole ratio of DME and water should be 1:2.2 when the gases are supplied to the fuel cell maintained at atmospheric pressure. In that the complete electro-oxidation of a mole DME requires 3 mol of water, the lack of water molecules around DME may lead to decrease the kinetics of DME electro-oxidation and may be responsible of the low power density of the fuel cell. When DME is fed into the fuel cell in aqueous solution phase, however, the maximum power density increases significantly as
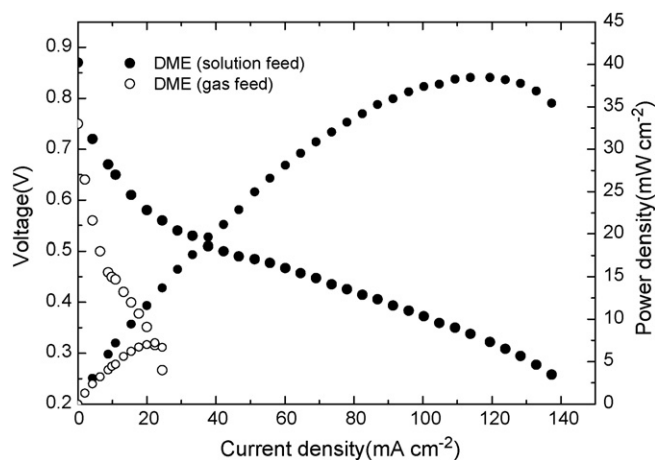

Fig. 1. Cell voltage and power density vs. current density curves for the direct fuel cells operated with moisturized DME gas and DME aqueous solution. The fuel cells were maintained at atmospheric pressure.

shown in Fig. 1 since the amount of water is sufficient for the electro-oxidation of DME.

Even though the DME-dissolved aqueous solution has been fed directly into the fuel cell at the flow rate of 1.2 ml min^{-1}, the dissolved DME should have vaporized readily as soon as the solution comes out of the solution reservoir (5 bar) since the outlet of fuel cell is open to atmospheric pressure. Therefore, the fuel should exist in the feeding line and the fuel cell with two phases which are DME gas, water vapor and liquid water. In this case, it could be difficult for the fuel to be mixed efficiently and thus the efficiency of the electro-oxidation of DME should be low. In order to keep DME more in aqueous phase, it is desired to operate the fuel cell at higher pressure. Thus, we have changed the operating pressure of the DMEFC and showed the performance in Fig. 2. For the experiment, a pressure regulator was installed at the outlet to control the pressure inside the fuel cell. At higher pressure over 1 bar, we expect the facilitation of DME electro-oxidation due to the reduction of phase separation in the fuel mixture (DME and water). When a solution-fed DMEFC was operated at 2 bar, the performance of the fuel cell
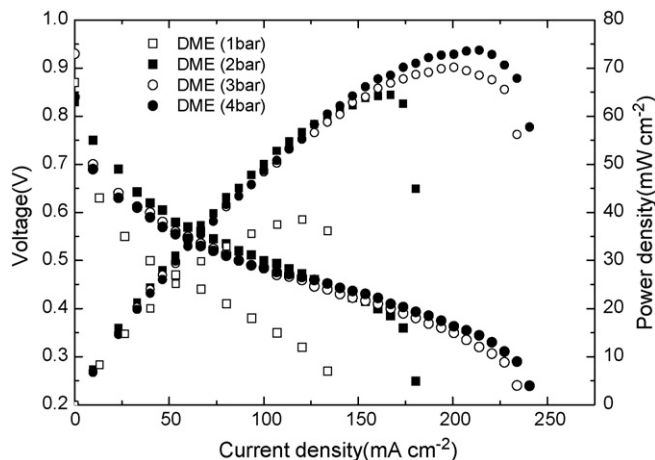

Fig. 2. Effect of pressure in the cells on cell voltage and power density vs. current density curves.

showed the maximum power density of 65 mW cm^{-2}. At the higher operating pressure of 3 and 4 bar, the maximum power efficiencies have increased to 70 and 75 mW cm^{-2}, respectively. The performance enhanced noticeably with the increase of operating pressure from 1 to 2 bar, while the enhancement was not so significant at the higher operating pressure of 3 and 4 bar. The similar experiment has been reported in the literature [4], where the maximum power density was around 30 mW cm^{-2} at an operating condition of 3 bar and 90 °C. We consider that much higher power density obtained in our experiment even at a lower temperature could be due to the different type of flow-field used in the fuel cell. As reported in an earlier study [5], we have used an optimized flow-field to facilitate the mixing of DME gas and liquid water in this experiment.

We have studied a mixed fuel of DME and methanol solution for maximizing the power density out of the same fuel cell. For preparing the mixed fuel solution, we saturated DME gas into 2 M methanol solution at 5 bar and 20 °C and we delivered the mixed solution into the fuel cell at a flow rate of 1.2 ml min^{-1}. The delivery of mixed fuel solution was done by the vapor pressure of DME in the fuel reservoir (5 bar) without a liquid pump. As shown in Fig. 3, the maximum power density was found to be 180 mW cm^{-2} when the mixed fuel of DME and 2 M methanol solution was used. The drastic increase in the power density should be caused by the methanol added. In order to find out the contribution of each methanol or DME out of the resultant power density, we have performed the same experiment using a fuel of 2 M methanol solution delivered by inert nitrogen gas at the same fuel reservoir pressure of 5 bar. By this way we could exclude the contribution of DME to the total power density. The maximum power density was measured to be 160 mW cm^{-2} in the experiment, which was 20 mW cm^{-2} in the power density less than that of the mixed fuel case. This difference could be considered responsible for the DME gas. Even though the effect of DME in the fuel was found insignificant at low current density, the difference in power density caused by DME added in methanol solution got bigger at higher current density.
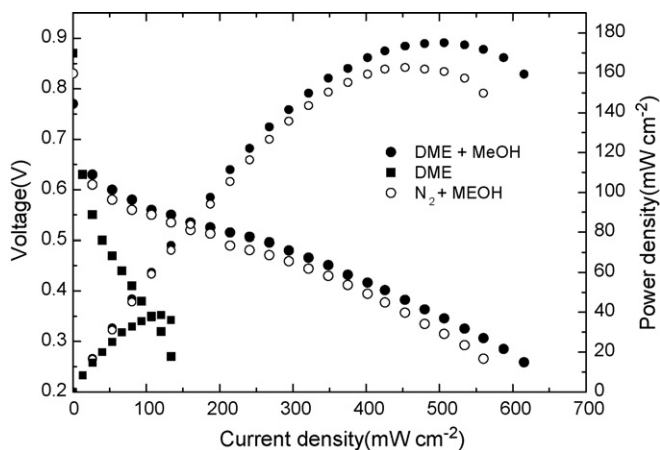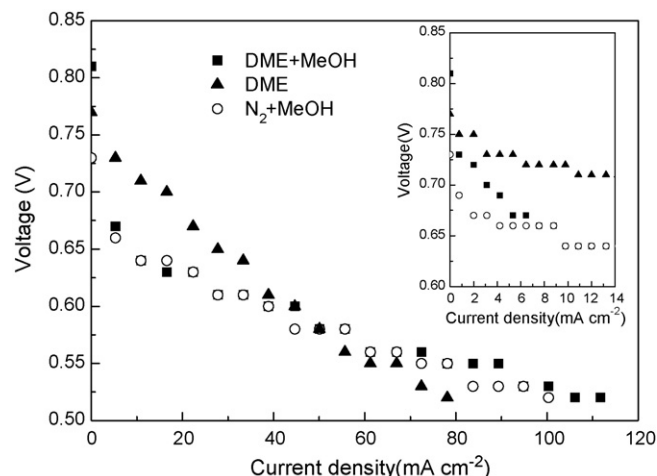

Fig. 4. Cell voltage and power density vs. current density curves for the direct fuel cells operated with the mixed fuel (DME and methanol) and single fuels (methanol with compressed N$_2$, DME) at low current density regions.

In Fig. 4, we show the polarization curves especially at low current density for pure DME, methanol solution driven by compressed N$_2$ and the mixed fuel solution. At the low current density less than 40 mA cm^{-2}, the cell voltage in case using the DME solution only was found higher than that using methanol solution only at the same current density. Meanwhile, the cell voltage in case using the DME solution only drops faster than that using methanol solution only. The polarization curve obtained using mixed fuel solution showed almost the same result as the case using methanol solution only. This result means that DME can provide higher electromotive force (EMF) than methanol thermodynamically but DME cannot contribute to the polarization curve in case with methanol since the electro-oxidation rate of DME is much slower than that of methanol kinetically. We show the enlarged polarization curves in the inset at lower current density. In the region of the current density from 0 to 6 mA cm^{-2}, the polarization curve obtained using the mixed fuel started to deviate from that obtained using pure DME fuel and ended up with that obtained using methanol

Fig. 3. Cell voltage and power density vs. current density curves for the direct fuel cells operated with the mixed fuel (DME and methanol) and single fuels (methanol with compressed N$_2$, DME).
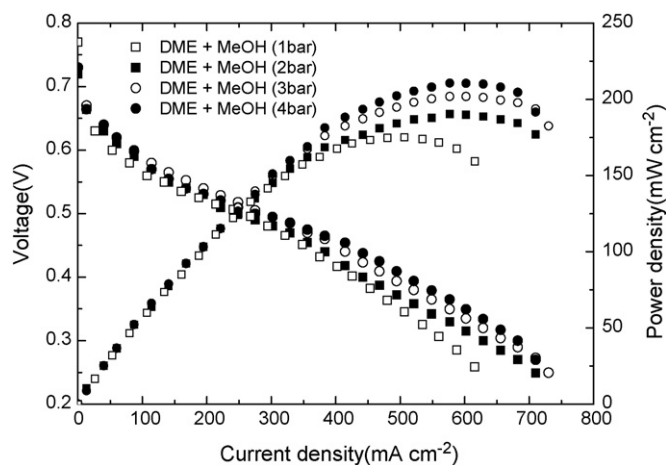

Fig. 5. Cell voltage and power density vs. current density curves for the direct fuel cells operated with the mixed fuel of DME and methanol solution at elevated pressure.

solution driven by compressed N_2. From this observation, we could conclude that the rate of electro-oxidation of DME should have been slowed when DME existed with methanol in the fuel mixture.

When we have operated the DMEFC with elevated operating pressures, the maximum power density was found to increase as the operating pressure increased as shown in Fig. 5. At an operating pressure of 4 bar the maximum power density was measured to be over 200 mW cm^{-2} at 80 °C. For this experiment, a flow rate of oxygen gas was set excess to be 500 ml min^{-1} at a pressure of 2 bar for the cathode.

4. Conclusions

The performance of direct DME fuel cells turned out to be enhanced significantly by pressuring the fuel cells. Pressuring the DME fuel helps the fuel to exist in condensed phase so as to facilitate the mixing of DME and water fuels. When a mixed fuel of DME and methanol solution was used, the resulting power density was found to be higher than that for the case when only the methanol solution was used. Effect of pressuring the fuel cells was found to be the same as the case for direct DME fuel cells. The best performance was obtained to be 210 mW cm^{-2} at 80 °C when the fuel cells were operated with the mixed fuel under 4 bar. We think that there is a clear advantage of using the mixed fuel because it does not only provide higher power density than the single fuel case but also there is no need to use a fuel pump for the operation.

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