



Short communication

Effect of conditioning method on direct methanol fuel cell performance

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ABSTRACT

We investigated the effect of the conditioning methods on improving the direct methanol fuel cell (DMFC) performance. The DMFC performance after the conditioning was measured using a newly developed single cell having an Ag/Ag₂SO₄ reference electrode, which is not influenced by methanol. As a result, we succeeded in developing an original two-step conditioning method in which the conditioning by fueling H₂ gas is conducted prior to a conventional DMFC conditioning. The anode and cathode characteristics after the two-step conditioning were measured with respect to a reference electrode. Based on the obtained *i*-*E* curves, the two-step conditioning is found to improve the methanol oxidation performance at the anode and also suppress the decline of the O₂ reduction performance at the cathode. The high DMFC performance based on the two-step conditioning is well explained by the anode and cathode characteristics.

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1. Introduction

In direct methanol fuel cells (DMFCs), methanol supplied to the anode is directly oxidized. This needs no reforming equipment, which leads to a small and compact size fuel cell system. Based on this feature, the DMFC is expected to be used as a power source for portable electronic devices. However, the practical applications of the DMFC are still not realized because of its low power generation performance. With regard to the reasons for the lower DMFC power generation, (i) a low methanol oxidation activity of an anode catalyst [1–3] and (ii) a decline in the O₂ reduction performance due to methanol crossover [4] have been stated. To tackle these problems, a number of studies on novel anode catalysts [5–7] and electrolyte membranes [8–10] have been carried out.

In the DMFCs, a conditioning operation of the membrane-electrode assembly (MEA) is generally conducted before the power generation [11–14]. The conditioning is considered to play an important role in achieving a high DMFC performance. However, the conditionings are carried out under various conditions [11–14] and also there are not many reports concerning the effect of the conditioning method on the DMFC power generation performance. Thus, we focused our attention on the conditioning methods in order to improve the DMFC power generation performance.

To investigate the effect of the conditioning method, it is important to independently assess the change in the anode and cathode characteristics. The anode characteristic or the cathode characteristic can be evaluated singly by the linear sweep voltammetry

technique [15–17]. However, in the DMFCs, the anode and cathode performances are gradually changed during the power generation due to CO poisoning [2,18] and the above-mentioned methanol crossover. Therefore, another method to simultaneously measure the anode and cathode characteristics of the single cell is needed.

Based on these concerns, we developed an original DMFC single cell having a reference electrode, which is not influenced by methanol. By using the single cell, the effect of the conditioning method on the DMFC performance has been evaluated. As a result, we succeeded in developing a new conditioning technique (denoted as two-step conditioning) where the conditioning by fueling H₂ gas is conducted prior to a conventional DMFC conditioning. Moreover, the anode and cathode polarization curves were measured in the single cell and the accuracy of the measurement was investigated, so that the anode and cathode performances could be discussed based on the experimental data.

2. Experimental

2.1. Preparation of MEA

The MEA (geometric electrode area: 5 cm²) used in this study was prepared as follows [19]. Nafion 117 (Dupont) was used as the polymer electrolyte membrane. The membrane (5 cm × 5 cm) was boiled in 0.5 mol dm⁻³ H₂SO₄ and then washed twice by boiling in pure water for 1 h each. Commercially available Pt/C (amount of deposited Pt: 45.9 wt.%, Tanaka Kikinokogyo) and Pt–Ru/C (amount of deposited Pt–Ru: 49.5 wt.%, Pt:Ru atomic ratio = 1:1, Tanaka Kikinokogyo) samples were used as the cathode and anode catalysts, respectively. The catalyst was ground using a ball mill with a 5 wt.% Nafion solution (Wako Pure Chemical Industries) diluted by a mixed

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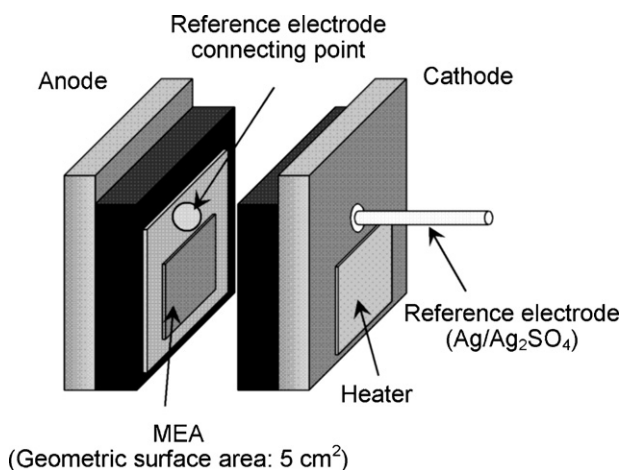


Fig. 1. A schematic illustration of a DMFC single cell containing a reference electrode.

solvent of methanol, 2-propanol, and Millipore water (1:1:1 weight ratio). The obtained slurry was spread on carbon paper (5 cm^2), so that the amount of Pt or Pt–Ru used could be 1.0 mg cm^{-2} . Subsequently, the Nafion 117 membrane was sandwiched between the two catalyst-coated carbon papers and then hot-pressed at 4.5 kN and 140°C for 10 min.

2.2. Conditioning method

Prior to the power generation, the prepared MEA was installed in a single cell having a reference electrode, as seen in Fig. 1. The following two conditioning techniques were examined. One is a conventional DMFC conditioning and the other is a two-step conditioning.

The conventional DMFC conditioning was carried out at a cell temperature of 60°C for 30 h; a 1 mol dm^{-3} methanol solution was supplied to the anode at the rate of 5 ml min^{-1} and humidified O_2 gas was fed to the cathode at 50 ml min^{-1} . The temperatures of the supplied methanol solution and the humidified O_2 gas were adjusted to 60°C . During the conditioning, the cell voltage was set at 0.21 V using a fuel cell analyzer system (AS-510-S4CV, NF Corporation).

For the two-step conditioning, a pre-conditioning by supplying H_2 gas to the anode and O_2 gas to the cathode was first carried out at a cell temperature of 80°C for 3 h. The humidified H_2 and O_2 gases were fed at 50 ml min^{-1} and 80°C . The cell voltage was controlled at 0.21 V using the fuel cell analyzer system. Subsequently, the conventional DMFC conditioning was conducted for 27 h under the same conditions as those for the above-mentioned conventional DMFC conditioning. Thus, the two-step conditioning was accomplished.

2.3. Measurements of DMFC performance and polarization curves of anode and cathode

After the conditionings, the DMFC power generation was conducted at a cell temperature of 60°C as follows. The current–cell voltage (i – V) and current–power (i – P) curves were measured by gradually increasing the current at the rate of 0.02 A . The current was controlled in a galvanostatic mode using the same fuel cell analyzer system for the conditionings. The current holding time per one step was 30 s. For this measurement, 1, 5, or 10 mol dm^{-3} methanol solution and humidified O_2 gas were supplied under the same conditions as those for the conventional DMFC conditioning.

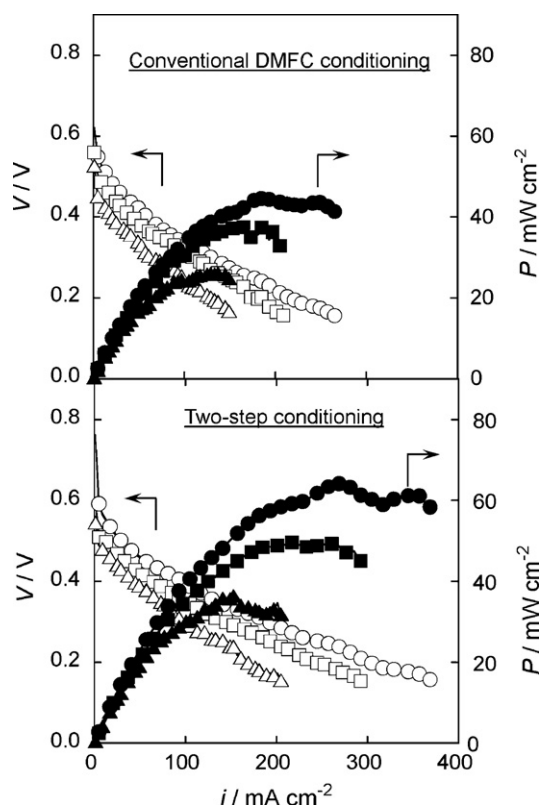


Fig. 2. i – V and i – P curves measured after conventional DMFC conditioning (upper) and two-step conditioning (lower) by supplying methanol solutions of 1 (circle), 5 (square), and 10 mol dm^{-3} (triangle) at 5 ml min^{-1} to the anode and humidified O_2 gas at 50 ml min^{-1} to the cathode. Cell temperature: 60°C .

Also, the current–electrode potential (i – E) curves were measured for the anode and cathode of the single cell having an $\text{Ag}/\text{Ag}_2\text{SO}_4$ reference electrode [19,20], which is not influenced by the methanol fuel. The reference electrode was installed from the cathode side of the single cell and brought into contact with the Nafion membrane [19], as shown in Fig. 1.

3. Results and discussion

3.1. DMFC performance after the conventional DMFC conditioning and the newly developed two-step conditioning

First, the cell performances after the conventional DMFC conditioning and the two-step conditioning were compared by the i – V and i – P curves measured during fueling 1, 5, or 10 mol dm^{-3} methanol solution to the anode. The upper graphs of Fig. 2 show the i – P and i – V curves after the conventional DMFC conditioning. From the i – V curves, the cell voltage is found to gradually decrease with the increasing current density [21]. The slope of the curves increases when the methanol concentration increases in the order of 1, 5, and 10 mol dm^{-3} . Moreover, the magnitude of the maximum power density observed in the i – P curves declines with the increase in the methanol concentration. These results indicate that the cell performance after the conventional DMFC conditioning is reduced by increasing the methanol concentration [21].

The i – V and i – P curves measured after the two-step conditioning are shown in the lower graphs of Fig. 2. When we evaluate the i – V curves, the cell voltage is found to gradually decrease with an increase in the current density, and the slope of the curve increases by increasing the methanol concentration. These phenomena are similar to those observed in the upper graphs of Fig. 2. However, when the i – V curves of the upper and lower graphs are compared,

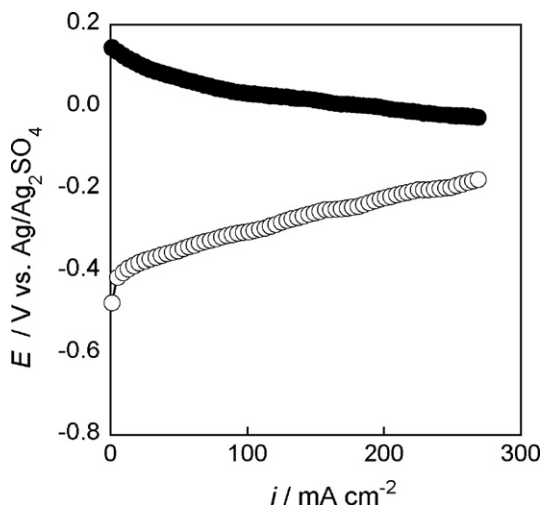


Fig. 3. i - E curves measured after conventional DMFC conditioning in the single cell having an $\text{Ag}/\text{Ag}_2\text{SO}_4$ reference electrode. 1 mol dm^{-3} methanol and humidified O_2 gas were supplied to the anode and cathode, respectively. Cell temperature: 60°C .

the change in the i - V slope after the two-step conditioning is found to be lower than that after the conventional DMFC conditioning. In addition, when we compare the i - P curves obtained for the same methanol concentration in Fig. 2, the magnitude of the maximum power densities obtained after the two-step conditioning is known to be obviously higher than those after the conventional DMFC conditioning. These results imply that the cell performance after the two-step conditioning is superior to that after the conventional DMFC conditioning, demonstrating that the two-step conditioning is effective for improving the DMFC power generation performance.

3.2. Accuracy of i - E curve measurement in the single cell

Based on the above result, the DMFC performance is found to be improved by the newly proposed two-step conditioning. To investigate the improved mechanism, the anode and cathode characteristics should be evaluated from the anode and cathode polarization curves, which will be measured using the $\text{Ag}/\text{Ag}_2\text{SO}_4$ reference electrode in the single cell.

First, the accuracy of the i - E curves measured from the single cell was estimated by comparing those to the i - V curves of the conventional DMFC conditioning. Fig. 3 shows the i - E curves obtained by supplying 1 mol dm^{-3} methanol to the anode and the humidified O_2 gas to the cathode. In the figure, the plots, which are symbolized by the black circles, corresponds to the O_2 reduction reaction at the cathode. From this curve, it is found that the O_2 reduction starts at around $0.15 \text{ V vs. Ag}/\text{Ag}_2\text{SO}_4$ and the electrode potential shifts to the negative direction with the increasing current density. Whereas, the plots expressed by the white circles is assigned to the methanol oxidation at the anode. This curve shows that the onset of the methanol oxidation is observed at ca. $-0.5 \text{ V vs. Ag}/\text{Ag}_2\text{SO}_4$ and the electrode potential shifts to the positive potential direction with the increasing current density.

The i - V curve, which represents the cell voltage to discuss the accuracy of the above i - E curves, was calculated by subtracting the cathode and anode potentials of the same current density. The obtained i - V curve is plotted as the white circles in Fig. 4. In the figure, the experimental i - V curve shown in Fig. 2 is also plotted by the black squares for comparison. When we compare the two, no difference is observed. Based on this result, the i - E curve measured using the single cell having the $\text{Ag}/\text{Ag}_2\text{SO}_4$ reference electrode was proved to be significantly accurate.

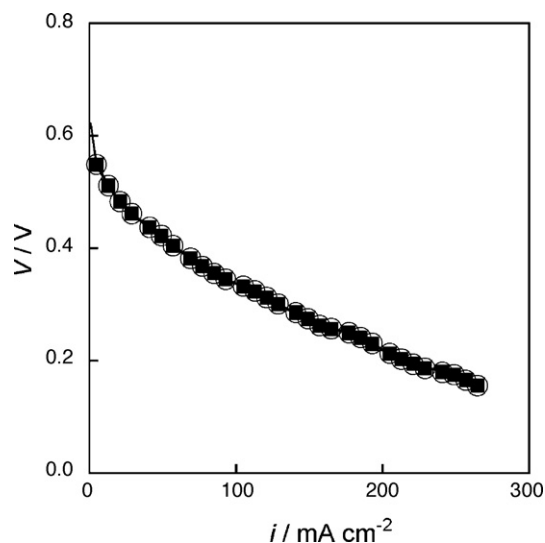


Fig. 4. Comparison of i - V plots between experimental (black square) and calculated data (white circle). Data are taken from Figs. 2 and 3.

3.3. i - E characteristics of DMFC electrodes based on the two types of conditioning

Next, the anode and cathode characteristics for the high DMFC performance improved by the two-step conditioning was investigated from the polarization curves measured using the single cell. Fig. 5 shows the anode and cathode polarization curves obtained after the conventional DMFC conditioning (upper) and the two-step conditioning (lower). In the upper and lower graphs of Fig. 5, the i - E curves observed at the anode (white symbols) is found to shift in the negative potential direction with the increasing methanol fuel concentration. This indicates that the increase in the methanol concentration leads to an improvement in the methanol oxidation activity at the anode, irrespective of the conditioning methods. However, for the same methanol concentration, the slope of the i - E curve versus the current density after the two-step conditioning is lower than that after the conventional DMFC conditioning. This result indicates that the two-step conditioning realizes a higher methanol oxidation performance at the anode.

As seen in the upper graph of Fig. 5, the i - E curves at the cathode for the conventional DMFC conditioning (black symbols) shift in the negative potential direction in the order of the 1, 5, and 10 mol dm^{-3} methanol concentrations. This result indicates that the O_2 reduction performance at the cathode declines with the increasing methanol concentration. One reason for the O_2 reduction declining can be considered as follows. The methanol permeability in a Nafion membrane is reported to increase with its increasing concentration [22,23]. Based on this result, it is assumed that when the high-concentration methanol solution is supplied to the anode, the extent of the methanol crossover increases. Therefore, since the O_2 reduction and methanol oxidation simultaneously occur at the cathode, the obtained electrode potential becomes a mixed-potential between the two reactions [24,25]. As a result, the cathode polarization curve shifts in the negative potential direction with the increasing methanol concentration. The above-mentioned decline in the O_2 reduction performance is explained by the methanol crossover.

In the case of the two-step conditioning, the negative shift of the i - E curve at the cathode is also observed. However, at the same methanol concentration and the same electrode potential, the magnitude of the obtained current density after the two-step conditioning is obviously greater than that after the conventional DMFC conditioning. This means that the two-step conditioning

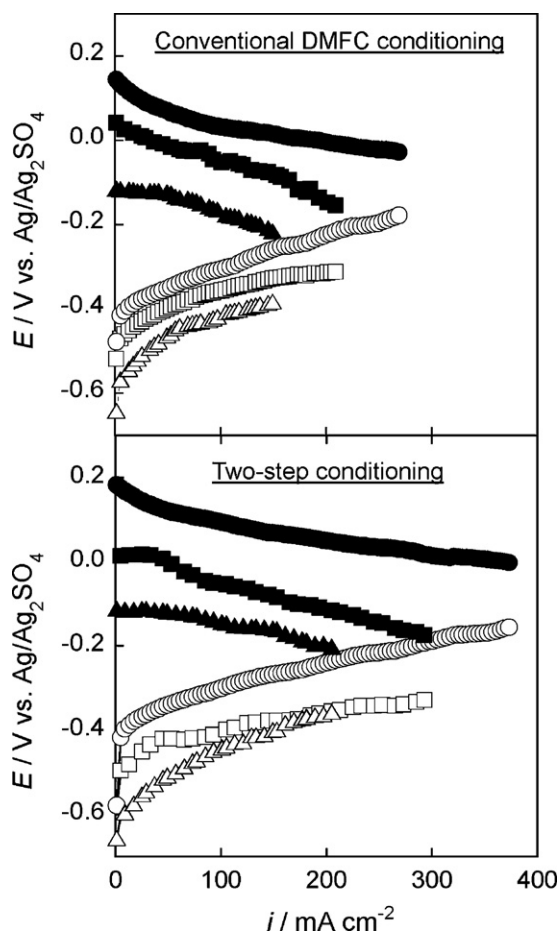


Fig. 5. i - E curves measured in the single cell having an $\text{Ag}/\text{Ag}_2\text{SO}_4$ reference electrode after conventional DMFC conditioning (upper) and two-step conditioning (lower) by supplying methanol solutions of 1 (circle), 5 (square), and 10 mol dm^{-3} (triangle) at 5 ml min^{-1} to the anode and humidified O_2 gas at 50 ml min^{-1} to the cathode. Cell temperature: 60°C .

affects the O_2 reduction performance so that it has not significantly declined by increasing the methanol concentration. In other words, the two-step conditioning could suppress the effect of the methanol crossover.

Consequently, the high DMFC performance induced by the two-step conditioning is attributed to the high performance of the methanol oxidation reaction at the anode and the suppression of the decline in the O_2 reduction reaction at the cathode. However, the extent of the improvement of the anode and cathode performances caused by the two-step conditioning is still uncertain. In the future, we plan to investigate the detailed mechanism of the activation.

4. Conclusions

In this study, we investigated the effect of the conditioning method on the DMFC performance using a newly developed single

cell having an $\text{Ag}/\text{Ag}_2\text{SO}_4$ reference electrode, which is not influenced by methanol. As a result, we succeeded in developing an original two-step conditioning method in which the conditioning by fueling H_2 gas is conducted prior to the conventional DMFC conditioning. The two-step conditioning is effective for improving the DMFC power generation performance. Also, the anode and cathode characteristics were evaluated from the i - E curves, which were measured with respect to the reference electrode. The obtained results demonstrate that the two-step conditioning increases the methanol oxidation performance at the anode and also suppresses the decline in the O_2 reduction performance at the cathode. Consequently, the high DMFC performance induced by the two-step conditioning is satisfactorily explained by the anode and cathode characteristics.

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