

Hydrogen production by methanol–water solution electrolysis

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Abstract

The production of hydrogen by methanol–water solution electrolysis was investigated. Hydrogen and carbon dioxide were contained in the cathode exhaust gas and the hydrogen concentration was 95.5–97.2 mol%. The hydrogen flow rate in the cathode exhaust gas increased in proportion to the current density and almost agreed with the theoretical hydrogen-production rate. The voltage and electrical energy needed to produce hydrogen were less than that for water electrolysis. The electrical energy needed in methanol–water solution electrolysis was less than 60% of that required in water electrolysis. Permeation of methanol, water and carbon dioxide from the anode to the cathode of the electrolytic cell occurred with hydrogen production. The permeation rate of methanol became greater than that of water as the current density increased. When the current density was constant, the permeation rate of water did not depend on the methanol concentration in the methanol–water solution supplied to the anode, and that of methanol increased while that of carbon dioxide decreased as the methanol concentration increased.

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1. Introduction

Direct methanol fuel cells (DMFCs) [1–3], direct formic acid fuel cells (DFFCs) [4–6] and polymer electrolyte fuel cells (PEFCs) using a micro fuel processor for hydrogen production [7] are viewed as viable candidates to replace batteries in portable power applications. However, the power generation performances of DMFCs and DFFCs are lower than that of PEFCs [8]. On the other hand, in a PEFC, the micro fuel processor must be kept at a temperature of more than 250 °C to produce hydrogen [9] and is hard to start up in a short time. This is a serious problem because frequent start-up and shutdown are necessary for portable power applications.

Therefore, we investigated hydrogen production by methanol–water solution electrolysis using an electrolytic cell instead of that by methanol steam reforming using a micro fuel processor for application to small PEFCs that show high performance for portable power applications. Hydrogen pro-

duction by methanol–water solution electrolysis is suitable for portable power applications because methanol–water solution electrolysis can start up and shut down in a moment and can produce hydrogen at a low temperature. In methanol–water solution electrolysis, hydrogen is produced by applying DC voltage to the electrolytic cell. The construction of the electrolytic cell is the same as that of the DFMC. The electrolytic cell can be used as a reformer to produce hydrogen, and PEFCs can generate electrical energy using this hydrogen as their fuel. If the voltage in the methanol–water solution electrolysis can be sufficiently decreased compared with that in PEFCs, hydrogen can be produced using some of the electrical energy generated by the PEFCs. High-energy-density and high-performance power sources for portable power applications can be constructed by combining an electrolytic cell for hydrogen production with a PEFC. Except for the patent by Narayanan et al. [10] on hydrogen production by electrolysis of aqueous organic solutions not much work has been reported in the literature.

In this paper, we report the results obtained on hydrogen production by methanol–water solution electrolysis using an electrolytic cell. We report the characteristics of methanol–water solution electrolysis, the hydrogen-production characteristics and the permeation characteristics of methanol, water and carbon

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dioxide and confirm the effectiveness of producing hydrogen by methanol–water solution electrolysis.

2. Methanol–water solution electrolysis and water electrolysis

Fig. 1 shows schematic diagrams of water electrolysis and methanol–water solution electrolysis. The electrolytic cell is composed of an anode and a cathode with a membrane electrolyte between them. Precious metal—such as platinum acts as an electrode catalyst in the anode and cathode. In water electrolysis, water supplied to the anode of the electrolytic cell is electrolyzed using a DC power supply. At the anode, water reacts to produce oxygen, protons and electrons according to the anode reaction expressed by Eq. (1).



The oxygen produced by the anode reaction is exhausted outside the anode. The protons produced by the anode reaction move to the cathode of the electrolytic cell through the membrane electrolyte and the electrons produced by the anode reaction move to the cathode through the external circuit containing the DC power supply. At the cathode, protons supplied from the anode react with electrons supplied from the anode. The cathode reaction is expressed by Eq. (2).



The water electrolysis reaction is expressed by Eq. (3), which combines the anode and cathode reactions expressed by Eqs. (1) and (2), respectively.



In methanol–water solution electrolysis, the methanol–water solution supplied to the anode of the electrolytic cell is electrolyzed using a DC power supply. At the anode, methanol reacts with water to produce carbon dioxide, protons and electrons according to the anode reaction expressed by Eq. (4).

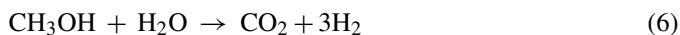


The carbon dioxide produced by the anode reaction is exhausted outside the anode. The protons produced by the anode

reaction move to the cathode of the electrolytic cell through the membrane electrolyte and the electrons produced by the anode reaction move to the cathode through the external circuit containing the DC power supply. At the cathode, protons supplied from the anode react with electrons supplied from the anode. The cathode reaction is expressed by Eq. (5).



The methanol–water-solution electrolysis reaction is expressed by Eq. (6), which combines the anode and cathode reactions expressed by Eqs. (4) and (5), respectively.



The theoretical voltages in water electrolysis and in methanol–water solution electrolysis are 1.23 and 0.03 V, respectively. The voltage in methanol–water solution electrolysis is much lower than that in water electrolysis. Therefore, the electrical energy needed to produce hydrogen by methanol–water solution electrolysis is less than that needed for water electrolysis. In methanol–water solution electrolysis, carbon dioxide can be effectively collected because its concentration in the anode exhaust gas is high.

3. Experimental

A schematic diagram of the experimental apparatus is shown in Fig. 2. Methanol–water solution was supplied to the anode of the electrolytic cell from the liquid tank at a flow rate of $5 \text{ cm}^3 \text{ min}^{-1}$. In the electrolysis of the methanol–water solution, argon was supplied to the cathode of the electrolytic cell at the flow rate of $50 \text{ cm}^3 \text{ min}^{-1}$ to carry the produced hydrogen away from the cathode immediately and stabilize the voltage. The methanol–water solution was prepared by diluting methanol having a purity of 99.9% (Kanto Kagaku Co.) with distilled water. In water electrolysis, distilled water was used.

The electrolysis was conducted by applying a constant current to the electrolytic cell using a DC power supply. The current was measured with a digital ammeter and controlled with the DC power supply. The voltage was measured with a digital voltmeter. The temperature of the electrolytic cell was measured using a platinum resistance thermometer placed near the

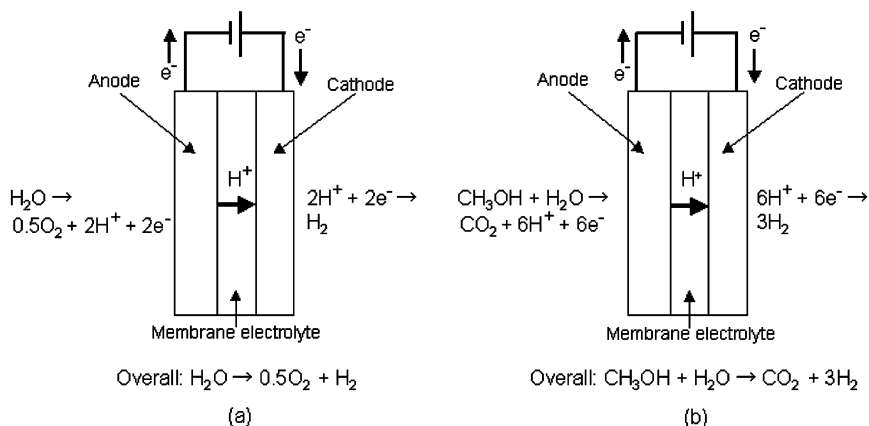


Fig. 1. Schematic diagrams of (a) water electrolysis and (b) methanol–water solution electrolysis.

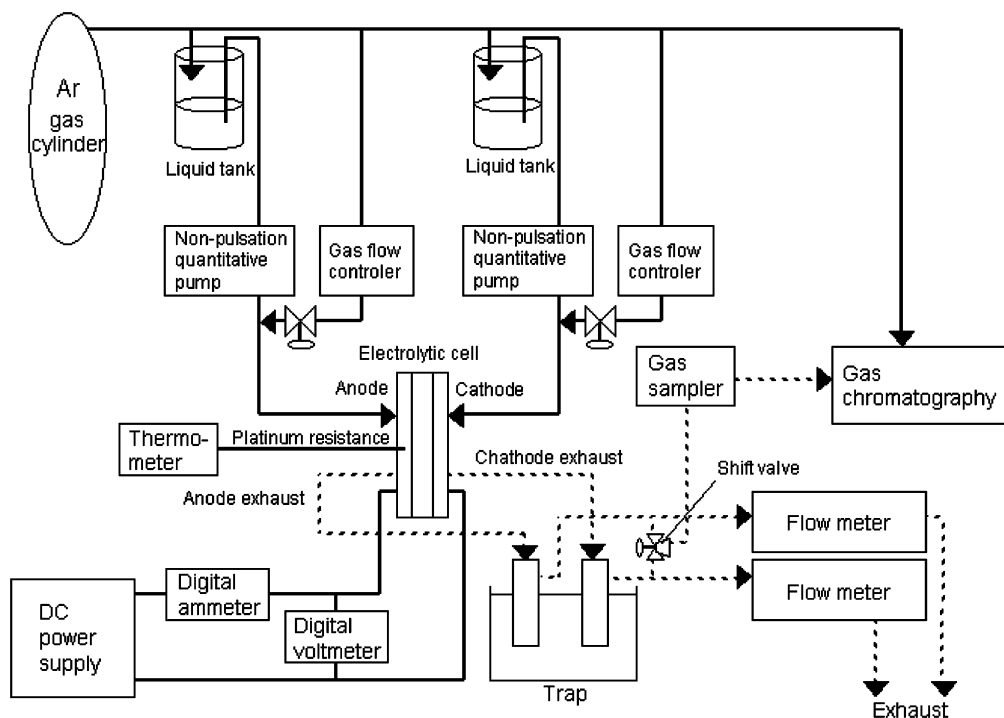


Fig. 2. Schematic diagram of experimental apparatus.

anode surface. The methanol–water solution and water were supplied to the anode of the electrolytic cell. The flow rates were controlled using the non-pulsation quantitative pump. A Nafion 117 membrane was used as the membrane electrolyte of the electrolytic cell. It was placed between the anode and cathode. Platinum catalyst was used as the anode and cathode catalyst. The shapes of the anode and cathode were circular. Their diameter and effective electrode surface area were 5.4 cm and 23 cm², respectively. The cathode exhaust gas was analyzed by gas chromatography. The cathode-exhaust liquid was collected in a trap cooled by dry ice and water solution and analyzed by gas chromatography. The flow rate of the cathode-exhaust gas was measured using a soap-membrane flow meter after the cathode-exhaust liquid was collected in the trap.

4. Results and discussion

4.1. Dependence of voltage and temperature on time in methanol–water solution electrolysis

The dependence of voltage on time in the methanol–water solution electrolysis is shown in Fig. 3. The methanol concentration of the methanol–water solution was 17 mol dm⁻³ and the current density was set to 0.087, 0.17, 0.26, 0.35 and 0.39 A cm⁻². When the current density was less than 0.35 A cm⁻², the voltage reached the steady state and was almost constant after 60 min from the beginning of electrolysis.

At a current density of 0.39 A cm⁻², the voltage increased as time passed. A rapid increase in voltage occurred after 40 min of elapsed time and it exceeded 2.26 V, which correspond to the voltage in water electrolysis at a current density of 0.43 A cm⁻². The reason might be that as the applied current could not be

sustained with only the oxidation of methanol, the voltage drifted to higher value at which oxygen evolution could also take place.

The dependence of temperature on time in methanol–water solution electrolysis is shown in Fig. 4. The methanol concentration in the methanol–water solution and current density settings were as given above. All of the experimental data described below were measured after 60 min from the beginning of the electrolysis when the voltage and temperature were steady.

4.2. Rapid increase in voltage in methanol–water solution electrolysis

Fig. 5 shows the dependence of the current density at which the voltage rapidly increased with methanol concentration in the methanol–water solution supplied to the anode in the electrolytic

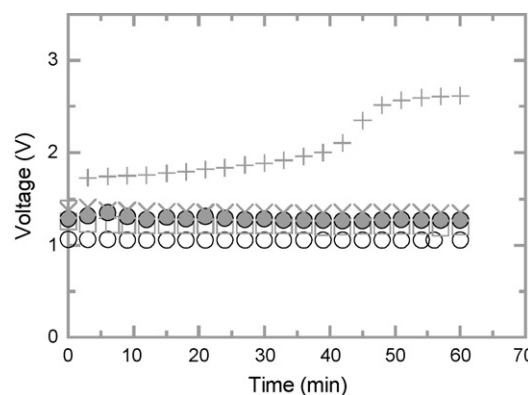


Fig. 3. Dependence of voltage on time in methanol–water solution electrolysis as a function of current density. The methanol concentration was 17 mol dm⁻³. The current density was (○) 0.087 A cm⁻², (□) 0.17 A cm⁻², (●) 0.26 A cm⁻², (×) 0.35 A cm⁻² and (+) 0.39 A cm⁻².

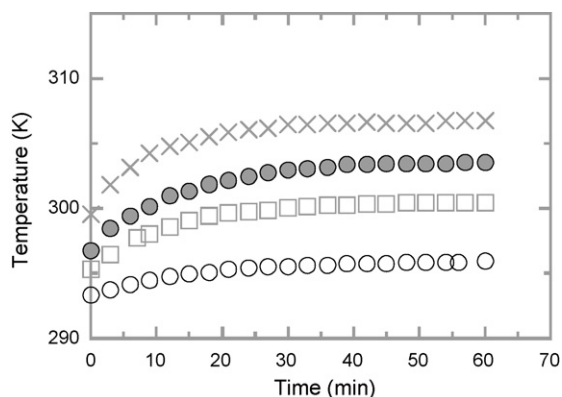


Fig. 4. Dependence of temperature on time in methanol–water solution electrolysis as a function of current density. The methanol concentration was 17 mol dm^{-3} . The current density was (○) 0.087 A cm^{-2} , (□) 0.17 A cm^{-2} , (●) 0.26 A cm^{-2} and (×) 0.35 A cm^{-2} .

cell in the methanol–water solution electrolysis. At this point, a limiting current density is defined as the current density at which the voltage rapidly increased and exceeded 2.0 V for a particular concentration of methanol. The methanol concentration was changed from 1 to 18 mol dm^{-3} in steps of 1 mol dm^{-3} and the current density was changed from 0.043 A cm^{-2} to the maximum current density of 0.39 A cm^{-2} in steps of 0.043 A cm^{-2} at each methanol concentration. The limiting current density value changes with methanol concentration. However, the limiting current density attained a maximum value of 0.39 A cm^{-2} at the methanol concentration of 17 mol dm^{-3} , where the molar ratio of water to methanol was 1.0 . With further increase in methanol concentration increased to 18 mol dm^{-3} , the current density dropped to 0.17 A cm^{-2} . These results indicate that the rapid voltage increase in the methanol–water solution electrolysis is closely related to the methanol concentration.

The experiments on methanol–water electrolysis described below were performed at a current density of less than 0.35 A cm^{-2} to avoid the rapid increase in voltage.

4.3. Electrolytic voltage

Fig. 6 shows the dependence of voltage on current density in the methanol–water solution electrolysis and the water

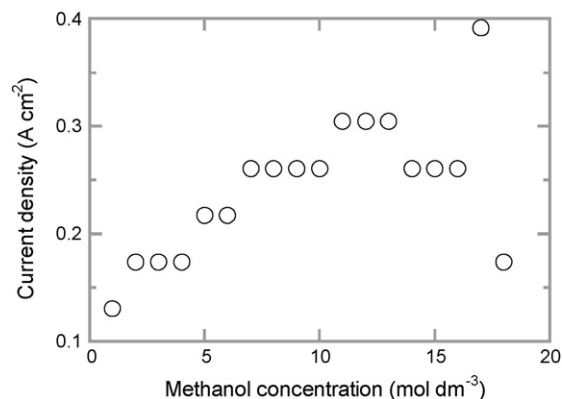


Fig. 5. Dependence of current density at which voltage rapidly increased with methanol concentration in methanol–water solution electrolysis.

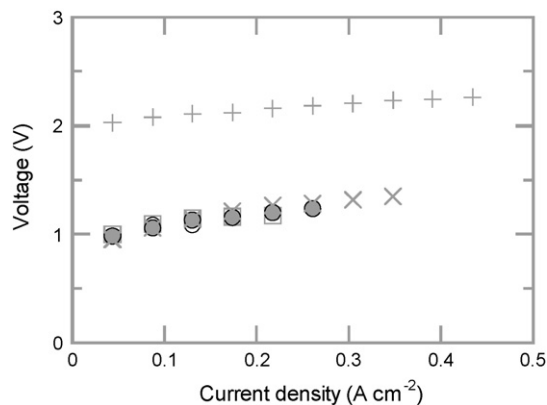


Fig. 6. Dependence of voltage on current density in methanol–water solution electrolysis and water electrolysis. The methanol concentration was (○) 3 mol dm^{-3} , (□) 7 mol dm^{-3} , (●) 11 mol dm^{-3} and (×) 17 mol dm^{-3} . The component was (+) water.

electrolysis. In the methanol–water solution electrolysis, the current density was changed from 0.043 A cm^{-2} to the maximum current density of 0.35 A cm^{-2} in steps of 0.043 A cm^{-2} until the voltage rapidly increased. All of the data shown in Fig. 6 was measured before the rapid voltage increase occurred. In the water electrolysis, the current density was changed from 0.043 to 0.43 A cm^{-2} in steps of 0.043 A cm^{-2} . In the methanol–water solution electrolysis, the methanol concentration of the methanol–water solution supplied to the anode of the electrolytic cell was changed from 1 to 18 mol dm^{-3} in steps of 1 mol dm^{-3} . In Fig. 6, the dependence of voltage on current density at methanol concentrations of 3 , 7 , 11 and 17 mol dm^{-3} is shown as typical results. In the methanol–water solution electrolysis, the voltage did not depend on the methanol concentration and depended only on the current density. The voltage in the methanol–water solution electrolysis increased in proportion to the current density like that in the water electrolysis. The voltage in the methanol–water solution electrolysis increased from 0.951 to 1.34 V when the current density increased from 0.043 to 0.35 A cm^{-2} . On the other hand, the voltage in the water electrolysis increased from 2.03 to 2.26 V when the current density increased from 0.043 to 0.43 A cm^{-2} . We assume that these voltage increases were caused by the increase in overvoltage.

4.4. Hydrogen production

Fig. 7 shows the dependence of the composition of the cathode exhaust gas in the electrolytic cell on current density in the methanol–water solution electrolysis. The methanol concentration of the methanol–water solution supplied to the anode of the electrolytic cell was 17 mol dm^{-3} and the current density was changed from 0.043 to 0.35 A cm^{-2} in steps of 0.043 A cm^{-2} . The cathode exhaust gas contained hydrogen and carbon dioxide. The hydrogen concentration was 95.5 – $97.2 \text{ mol}\%$ and the carbon dioxide concentration was 2.8 – $4.5 \text{ mol}\%$. The hydrogen in the cathode exhaust gas was produced at the cathode according to the cathode reaction expressed by Eq. (5). The carbon dioxide in the cathode exhaust gas was due to permeation of carbon dioxide produced at the anode according to the anode

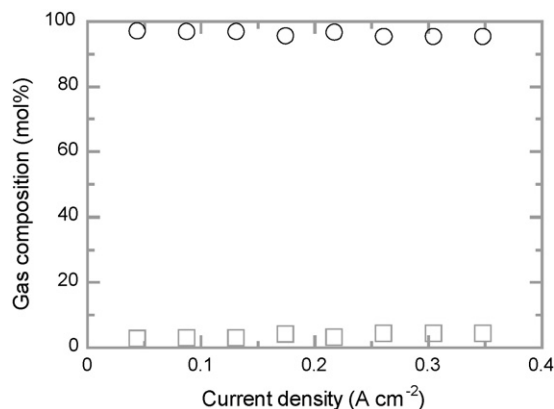


Fig. 7. Dependence of composition of cathode exhaust gas in the electrolytic cell on current density in methanol–water solution electrolysis. The methanol concentration was 17 mol dm^{-3} . The gas components were (○) hydrogen and (□) carbon dioxide.

reaction expressed by Eq. (4). In methanol–water solution electrolysis, the oxidation of methanol that has permeated from the anode does not occur in the cathode and carbon dioxide does not produce there because oxygen is not supplied to the cathode. It is well known that the permeation of carbon dioxide occurs in DMFCs [11]. We conclude that the permeation of carbon dioxide also occurred in the methanol–water solution electrolysis similar to that in DMFCs. The cathode exhaust gas can be directly supplied to the anode of a PEFC and used for its power generation because the hydrogen concentration of the cathode exhaust gas is high and because carbon monoxide, which is harmful to platinum-containing catalyst in the anode, is not contained in the gas.

Fig. 8 shows the dependence of the composition of the cathode exhaust gas in the electrolytic cell on the methanol concentration of the methanol–water solution supplied to the anode of the cell in the methanol–water solution electrolysis. The methanol concentration was changed from 1 to 17 mol dm^{-3} in steps of 1 mol dm^{-3} and the current density was 0.087 A cm^{-2} . The hydrogen concentration of the cathode exhaust gas increased from 91.1 to $96.3 \text{ mol}\%$ and the carbon dioxide concentration of the cathode exhaust gas decreased from 8.9 to $3.7 \text{ mol}\%$ when

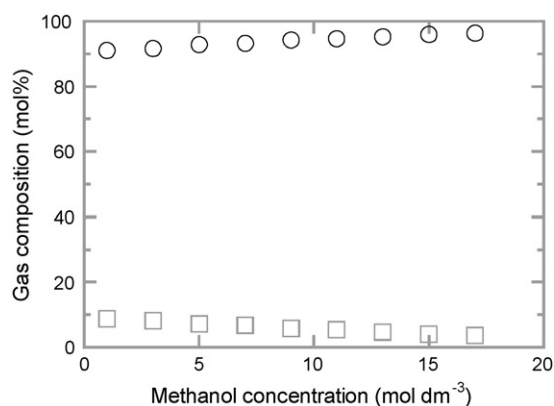


Fig. 8. Dependence of composition of cathode exhaust gas in the electrolytic cell on methanol concentration in methanol–water solution electrolysis. The current density was 0.087 A cm^{-2} . The gas components were (○) hydrogen and (□) carbon dioxide.

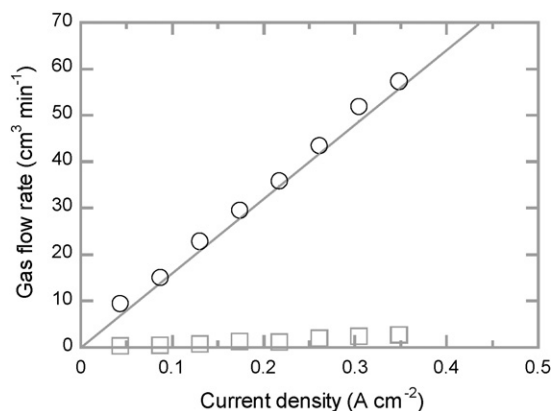


Fig. 9. Dependence of flow rate of each component in the cathode exhaust gas in the electrolytic cell on current density in methanol–water solution electrolysis. The solid line in the figure means the theoretical hydrogen-production rate. The methanol concentration was 17 mol dm^{-3} . The gas components were (○) hydrogen and (□) carbon dioxide.

the methanol concentration increased from 1 to 17 mol dm^{-3} . This indicates that the carbon dioxide permeation rate decreased as the methanol concentration increased.

Fig. 9 shows the dependence of flow rate of each component of the cathode exhaust gas in the electrolytic cell on current density in the methanol–water solution electrolysis. The flow rate of each component was calculated using the flow rate of the cathode exhaust gas measured by a soap-membrane flow meter and the composition of the cathode exhaust gas was measured by gas chromatography. In Fig. 9, the theoretical hydrogen-production rate at each current density is shown as a straight line. The theoretical hydrogen-production rate was calculated supposing that all of the current was used for hydrogen production. The methanol concentration of the methanol–water solution supplied to the anode of the electrolytic cell was 17 mol dm^{-3} and the current density was changed from 0.043 to 0.35 A cm^{-2} in steps of 0.043 A cm^{-2} . The hydrogen flow rate in the cathode exhaust gas increased in proportion to the current density and almost agreed with the theoretical hydrogen-production rate. This shows that hydrogen was produced effectively. The flow rate of carbon dioxide in the cathode exhaust gas was less than that of hydrogen in the cathode exhaust gas and slightly increased as the current density increased. This indicates that the quantity of carbon dioxide produced by the anode reaction expressed by Eq. (4) and permeated from the anode to the cathode increased as the current density increased.

4.5. Permeation of methanol, water and carbon dioxide

Fig. 10 shows the dependence of the permeation rates of methanol and water from the anode to the cathode of the electrolytic cell on current density in the methanol–water solution electrolysis. The methanol concentration of the methanol–water solution supplied to the anode was 17 mol dm^{-3} and the current density was changed from 0.043 to 0.35 A cm^{-2} in steps of 0.043 A cm^{-2} . The cathode exhaust liquid was composed of water and methanol regardless of the current density. This indicates that the water and methanol in the methanol–water

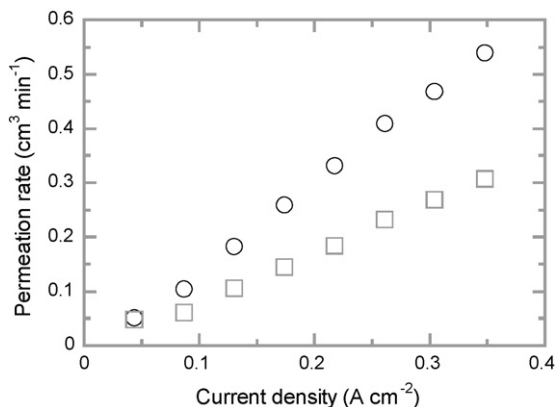


Fig. 10. Dependence of permeation rates of methanol and water from the anode to the cathode on current density in methanol–water solution electrolysis. The methanol concentration was 17 mol dm^{-3} . The components were (○) methanol and (□) water.

solution supplied to the anode permeated from the anode to the cathode through the membrane electrolyte. It is well known that methanol permeation, which is called methanol crossover, occurs in DMFCs [11,12]. We conclude that methanol permeation also occurs in methanol–water solution electrolysis the same as in DMFCs. The permeation rates were calculated using the measured liquid collection rate and the composition of the cathode exhaust liquid. Both of the permeation rates increased in proportion to the current density. This result indicates that the methanol and water moved from the anode to the cathode with protons through the membrane electrolyte and that the permeation of the methanol–water solution occurred in the methanol–water solution electrolysis. The permeation rate of methanol was nearly equal to that of water at a current density of 0.043 A cm^{-2} and became greater than that of water as the current density increased. The difference between the permeation rate of methanol and that of water became greater in proportion to the current density. These results indicate that the quantity of methanol that moves with protons through the membrane electrolyte becomes more than that of the water that moves with protons through the membrane electrolyte as the current density increases.

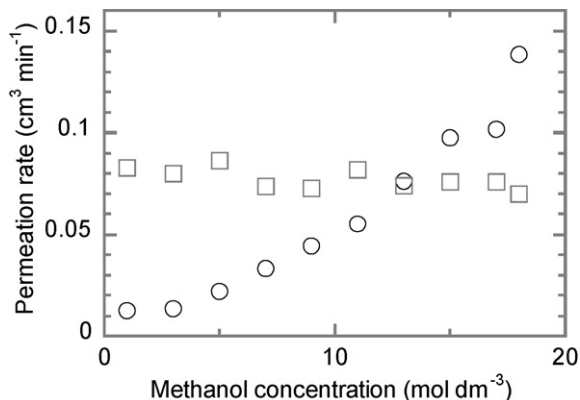


Fig. 11. Dependence of permeation rates of methanol and water from the anode to the cathode on methanol concentration in methanol–water solution electrolysis. The current density was 0.087 A cm^{-2} . The permeation components were (○) methanol and (□) water.

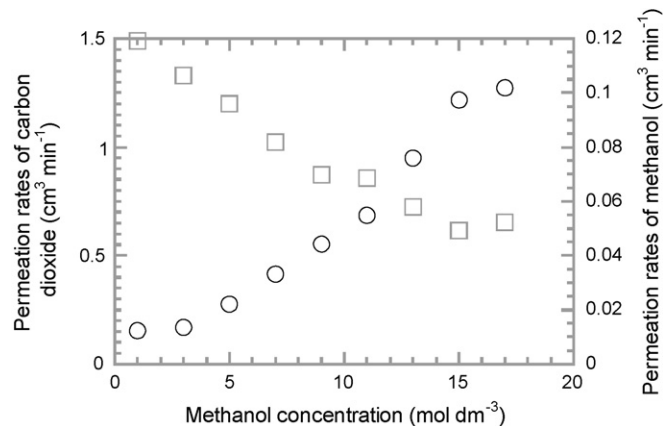


Fig. 12. Dependence of permeation rates of carbon dioxide and methanol from the anode to the cathode on methanol concentration in methanol–water solution electrolysis. The current density was 0.087 A cm^{-2} . The permeation components were (□) carbon dioxide and (○) methanol.

Fig. 11 shows the dependence of the permeation rates of methanol and water from the anode to the cathode of the electrolytic cell on the methanol concentration of the methanol–water solution supplied to the anode in the methanol–water solution electrolysis. The methanol concentration was changed from 1 to 18 mol dm^{-3} and the current density was 0.087 A cm^{-2} . The permeation rate of methanol increased as the methanol concentration was increased. The permeation rate of water did not depend on the methanol concentration and was almost constant. These results indicate that the quantity of the methanol that moves with protons through the membrane electrolyte increases as the methanol concentration increases and that the quantity of the water that moves with protons does not depend on the methanol concentration.

Fig. 12 shows the dependence of the permeation rates of carbon dioxide and methanol from the anode to the cathode of the electrolytic cell on the methanol concentration of the methanol–water solution supplied to the anode in the methanol–water solution electrolysis. The methanol concentration was changed from 1 to 18 mol dm^{-3} and the current density was 0.087 A cm^{-2} . The permeation rate of carbon dioxide was calculated using the measured flow rate and composition of the cathode exhaust gas. The permeation rate of carbon dioxide decreased as the methanol concentration was increased. In contrast, the permeation rate of methanol increased as the methanol concentration was increased. These results indicate that the permeation rates of carbon dioxide and methanol are correlated and that the permeation of carbon dioxide is suppressed as that of methanol is promoted.

Fig. 13 shows the dependence of the methanol concentration of the methanol–water solution permeated from the anode to the cathode of the electrolytic cell on that supplied to the anode in the methanol–water solution electrolysis. The methanol concentration of the permeated solution was obtained by analyzing the cathode exhaust liquid collected in the trap by gas chromatography. The methanol concentration of the supplied methanol–water solution was changed from 1 to 18 mol dm^{-3} and the current density was 0.087 A cm^{-2} . The straight line in

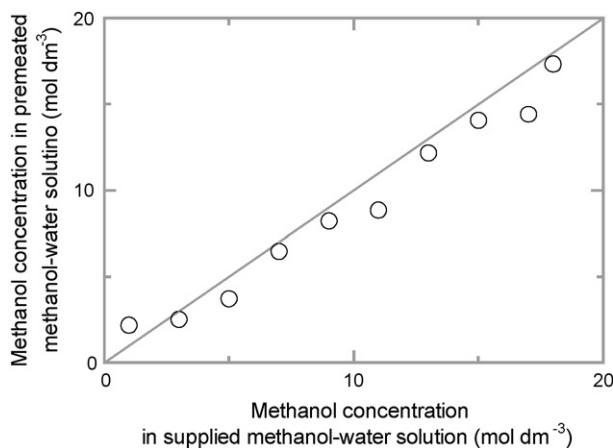


Fig. 13. Dependence of methanol concentration of methanol–water solution permeated from the anode to the cathode on that supplied to the anode in methanol–water solution electrolysis. The straight line shows that methanol concentration in the permeated methanol–water solution was equal to that in the supplied methanol–water solution. The current density was 0.087 A cm^{-2} .

Fig. 13 shows that the methanol concentration of the permeated methanol–water solution was equal to that of the supplied methanol–water solution. The methanol concentration of the permeated methanol–water solution was nearly equal to that of the supplied methanol–water solution. Therefore, we conclude that the methanol–water solution that permeated from the anode to the cathode through the membrane electrolyte can be directly recycled to the anode and can be reused for the methanol–water solution electrolysis without regulating its methanol concentration and mixing it with a fresh methanol–water solution.

Fig. 14 shows the dependence of the methanol concentration of the methanol–water solution permeated from the anode to the cathode of the electrolytic cell on current density in the methanol–water solution electrolysis. The methanol concentration of the methanol–water solution supplied to the anode was 17 mol dm^{-3} and is shown as a straight line in Fig. 14. The current density was changed from 0.043 to 0.35 A cm^{-2} in steps of 0.043 A cm^{-2} . The methanol concentration of the permeated solution was nearly equal to that of the supplied solution except

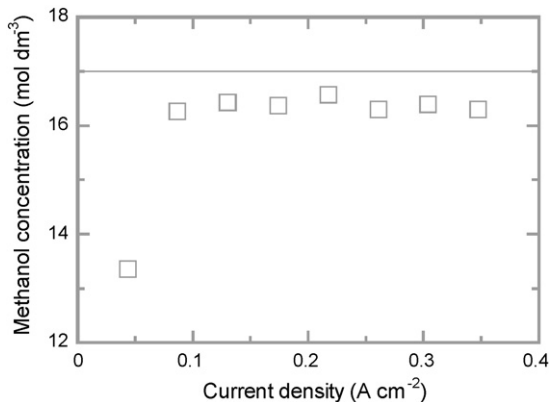


Fig. 14. Dependence of methanol concentration of methanol–water solution permeated from the anode to the cathode on current density in methanol–water solution electrolysis. The line is methanol concentration of the methanol–water solution supplied to the anode.

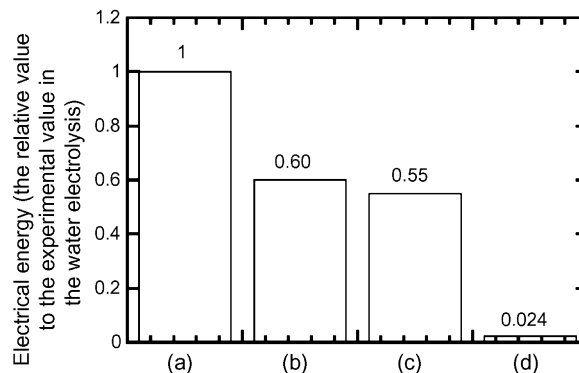


Fig. 15. Comparison of electrical energy needed to produce hydrogen in methanol–water solution electrolysis and in water electrolysis. Values are: (a) experimental value in water electrolysis, (b) experimental value in methanol–water solution electrolysis, (c) theoretical value in water electrolysis and (d) theoretical value in methanol–water solution electrolysis. The methanol concentration was 17 mol dm^{-3} . The current density was 0.35 A cm^{-2} .

at the current density of 0.043 A cm^{-2} , where the methanol concentration of the permeated solution was much less than that of the supplied methanol solution. The reason for this is not yet clear.

4.6. Electrical energy needed for hydrogen production by methanol–water solution electrolysis and by water electrolysis

Fig. 15 compares the electrical energy needed to produce hydrogen in the methanol–water solution electrolysis and in the water electrolysis. The experimental values were measured at the current density of 0.35 A cm^{-2} in both cases. The experimental value in the methanol–water solution electrolysis was measured at the methanol concentration of 17 mol dm^{-3} . In Fig. 15, each electrical energy value is shown relative to the experimental value in the water electrolysis. Fig. 15 also shows the theoretical values for comparison. They were calculated using the theoretical voltages of 1.23 V for the water electrolysis reaction and 0.03 V for the methanol–water solution electrolysis reaction. The experimental value in the methanol–water solution electrolysis was 60% of the experimental value in the water electrolysis. The theoretical value in the water electrolysis was 55% of the experimental value. These results indicate that the experimental value for methanol–water solution electrolysis is nearly equal to the theoretical value for water electrolysis. Therefore, we conclude that the electrical energy needed to produce hydrogen in the methanol–water solution electrolysis is much less than that in the water electrolysis and that hydrogen is effectively produced. The theoretical value in the methanol–water solution electrolysis is only 1.5% of the experimental value in the water electrolysis. This indicates that the electrical energy needed to produce hydrogen in the methanol–water solution electrolysis can be decreased even more.

5. Conclusions

We investigated the production of hydrogen by methanol–water solution electrolysis. In the methanol–water

solution electrolysis, hydrogen and carbon dioxide were contained in the cathode exhaust gas and the hydrogen concentration was 95.5–97.2 mol%. The hydrogen flow rate in the cathode exhaust gas increased in proportion to the current density and almost agreed with the theoretical hydrogen-production rate. The electrical energy needed to produce hydrogen in the methanol–water solution electrolysis was much less than that in the water electrolysis and 60% of that in the water electrolysis. The permeation of methanol, water and carbon dioxide from the anode to the cathode of the electrolytic cell occurred in production of hydrogen by methanol–water solution electrolysis. The permeation rate of methanol became larger than that of water as the current density increased. The difference between the permeation rates of methanol and water increased in proportion to the current density. The permeation rate of water did not depend on the methanol concentration of the methanol–water solution supplied to the anode when the current density was constant. Under the same condition, the permeation rate of methanol increased and that of carbon dioxide decreased as the methanol concentration of the methanol–water solution supplied to the anode increased. The methanol concentration of the methanol–water solution permeated from the anode to the cathode was nearly equal to that supplied to the anode.

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