



Short communication

Influence of anion ionomer content and silver cathode catalyst on the performance of alkaline membrane electrode assemblies (MEAs) for direct methanol fuel cells (DMFCs)

Hideaki Bunazawa*, Yohtaro Yamazaki

Department of Innovative and Engineered Materials, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama, Kanagawa 226-8502, Japan

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ABSTRACT

Alkaline membrane electrode assemblies (MEAs) were fabricated by a dry spraying method in order to evaluate and improve their performance. *I*–*V* tests indicated that the performance of alkaline direct methanol fuel cells (DMFCs) deeply depends on the ionomer contents of MEAs. MEA with 45.4% mass ionomer content showed the highest performance when non-alkaline (MeOH (1 M)) and alkaline (MeOH (1 M), NaOH (0.5 M)) fuels were used. When alkaline fuel was used, the anode and cathode performances of MEAs were also measured. The ionomer content has been shown to contribute ohmic polarization of the anode and diffusion polarization of the cathode. Furthermore, the performance of MEA with an Ag cathode catalyst was characterized. The Ag cathode catalyst was demonstrated to be a promising alternative to a Pt cathode catalyst because of its tolerance for methanol crossover.

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1. Introduction

Direct methanol fuel cells (DMFCs) are now widely investigated for their use in portable devices such as mobile phones and laptops. This interest stems from the increase in the quantity of portable devices in recent years, and the need for higher amounts of energy. DMFCs directly convert the chemical energy of methanol and oxygen into electric energy, so they can generate energy efficiently even at low temperature. In addition, unlike hydrogen gas fuel in proton electrolyte fuel cells (PEFCs), liquid methanol fuel can be easily stored.

Since Nafion® was developed by Dupont, proton exchange membranes have been used as electrolytes in DMFCs. Proton exchange membranes have high ionic (H⁺) conductivity, so DMFCs using proton exchange membranes show high performance. Nevertheless, there are some problems induced by the acid atmosphere. One of the most serious problems is that of corrosion. Non-noble metals cannot be used as catalysts because they are corrosive in an acid atmosphere. Therefore, noble metals such as platinum have become necessary for use as electrode catalysts, making the price of DMFCs much higher. Moreover, there are also such prob-

lems as methanol crossover [1,2] and low electrode kinetics of the oxidation–reduction reaction, which negatively impact the performance of the cathode.

In order to solve the problems mentioned above, alkaline DMFCs that use anion exchange membranes [3–8] as electrolytes are investigated. Although the structure of membrane electrode assemblies (MEAs) is similar to DMFCs using proton exchange membranes, the conduction ion (OH[−]) is transferred in an anion exchange membrane from cathode to anode. As a result, the atmosphere of the catalyst layer is alkaline. It is very innovative that alkaline DMFCs are not related to corrosion problems. Therefore, non-noble metals such as Ag, Co, Ni and Fe [9,10] can be used as electrode catalysts, and it is expected that the cost of catalysts can be extremely reduced. In addition, the cathode overvoltage in an alkaline atmosphere is expected to be lower than that in an acid atmosphere because the kinetics of the electrode reaction are faster [11]. Nevertheless, there are not only superior properties but also some problems. The OH[−] conductivity and thermal stability of the anion exchange membrane are not enough to observe good performance. Above all, anion exchange membranes are superior to proton exchange membranes in terms of their properties, yet show low performance.

One of the reasons for the restricted performance of alkaline DMFCs is that there are no excellent anion ionomers. Almost all studies about alkaline DMFCs have used poly(tetrafluoroethene)

* Corresponding author. Tel.: +81 45 924 5429; fax: +81 45 924 5429.
 E-mail address: bunazawa.h.aa@m.titech.ac.jp (H. Bunazawa).

(PTFE) to stabilize the catalyst layer. PTFE does not contribute to OH^- transfer, so the performance of this type of alkaline DMFCs has been low. However, in this study, an anion ionomer that is suitable in liquid form is used. Although there are many reports about alkaline DMFCs, there is no report about the electrochemical property of MEAs with this type of ionomer. In this paper, therefore, MEAs with various amounts of anion ionomer were fabricated, and electrochemical tests were conducted to evaluate their properties.

In addition, for decreasing the cost of the catalyst, it is important to investigate more inexpensive catalysts than Pt. It is assumed that there may be many non-noble metal catalysts that have good redox activity for MeOH or O_2 in alkaline media. In this paper, Ag is investigated as an alternative to a Pt cathode catalyst. The price of 1 g Ag is nearly 100 times less expensive than that for the equivalent amount of Pt. The performance of MEA with an Ag cathode catalyst is measured to confirm the possibility of a non-noble metal catalyst.

2. Experimental

2.1. MEA fabrication method

Both the anode and cathode catalyst ink were prepared by means of following procedure [12–14]. Catalyst supported carbon, 1-propanol, distilled water (Millipore MilliQ 18 M Ω cm) and anion ionomer solution (A3-solution, Tokuyama) were placed in a bottle with a proper quantity of zirconia ball. The catalysts used were PtRu/C (30% mass Pt, 23.3% mass Ru, Vulcan-XC72, Tanaka-kikinokoku) for the anode, Pt/C (46.6% mass Pt, Vulcan-XC72, Tanaka-kikinokoku) for the cathode, and Ag/C (20% mass Ag, Vulcan-XC72, E-TEK) for the cathode. The catalyst ink is prepared as a result of stirring the mixture by ball mill.

Subsequently, the prepared ink was applied onto both anion exchange membranes (A-006, thickness: 28 μm , Tokuyama) and carbon papers (TGP-H-060, thickness: 190 μm , containing microporous layer, TORAY) by spray gun [15]. Prior to catalyst ink spraying, anion exchange membranes used for the electrolyte of the MEAs were dried by means of holding between two filter papers for 1 day. The carbon papers used for the diffusion layers of the MEAs were cut into square pieces of 5 cm^2 , which is set as the geometric electrode area of MEAs. The prepared anode ink was sprayed onto one side of the membranes and carbon papers. After drying at room temperature for 1 day, the prepared cathode ink was sprayed similarly onto the other side of the membranes and carbon papers.

Finally, the electrodes of the membranes and carbon papers were assembled by hot-pressings (10 kg cm^{-2} , 100 $^\circ\text{C}$, 90 s). Anion ionomers and anion exchange membranes are said to have lower thermal stability than Nafion, so the hot-press temperature is set lower.

2.2. Investigation of the effect of anion ionomer content on electrode properties

When MEAs are fabricated, the anion ionomer contents of MEAs (anion ionomer content = mass of anion ionomer / mass of anion ionomer + carbon particle) are very important for their performances. An ionomer is used for the OH^- transfer pass, but interferes with the fuel or oxidant supply. Therefore, the length of the three-phase boundary depends deeply on the ionomer content.

In order to evaluate the effect of anion ionomer content, four types of MEAs were fabricated. Each of their electrodes consisted of anode catalysts (Pt loading: 0.75 mg cm^{-2} ; Ru loading: 0.58 mg cm^{-2}), and a cathode catalyst (Pt loading: 1.40 mg cm^{-2}). The anion ionomer contents of MEAs were 30%, 39.2%, 45.4%, and 51.7% mass. The anion ionomer content of the anode and cathode is the same value for all MEAs.

Although there are a lot of reports about DMFCs using anion exchange membranes, most of these reports use alkaline fuel (MeOH aqueous solution with NaOH (or KOH)). It is true that additional NaOH is effective to increase the performance of alkaline DMFCs. Nevertheless, it is not recommended for the practical use because NaOH is strong base. Therefore, in this paper, non-alkaline fuel (1 M MeOH aqueous solution without NaOH) was used. The electrochemical properties were measured by periodically recording I - V curves (25 mV point^{-1} from OCV, 1 min point^{-1}). Prior to measurement, the distilled water and nitrogen were purged for 30 min at 80 $^\circ\text{C}$. Distilled water was supplied to the anode with a constant flow rate of 5.0 mL min^{-1} from the 1 L reservoir. Humidified nitrogen (100% RH) was supplied to the cathode with a constant flow rate of 100 mL min^{-1} . After that, 1 M MeOH aqueous solution was supplied to the anode with a constant flow rate of 5.0 mL min^{-1} from the 1 L reservoir. Humidified oxygen (100% RH) was supplied to the cathode with a constant flow rate of 100 mL min^{-1} . After keeping at OCV for 10 min, the I - V curve was measured.

In order to compare performance, the I - V curves were also measured when alkaline fuel (1 M MeOH aqueous solution with 0.5 M NaOH) was used. In this test, anode and cathode polarization curves were also measured. Fig. 1 is the schematic diagram of the measurement. Ag/AgCl (+0.199 V vs. SHE) is used as the reference electrode and is connected to the anode fuel pass.

2.3. Ag cathode test

In alkaline media, as written above, non-platinum catalysts can be used. The Ag cathode catalyst was one of the candidates for non-platinum catalyst. This catalyst is not strongly influenced by methanol crossover because Ag has low activity for methanol oxi-

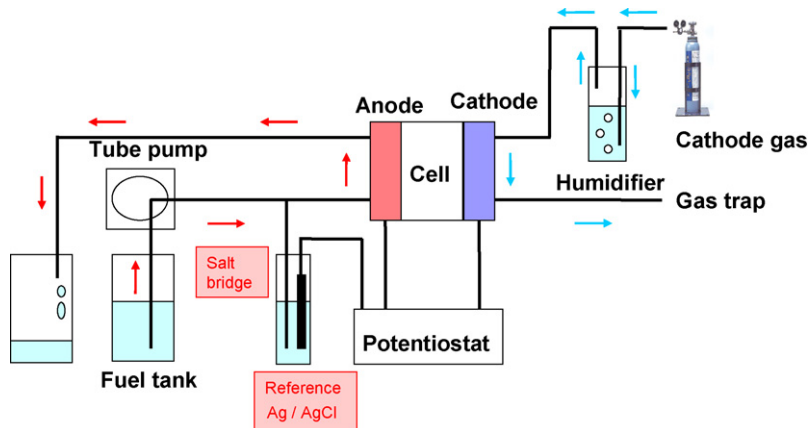


Fig. 1. Schematic diagram of electrochemical measurement.

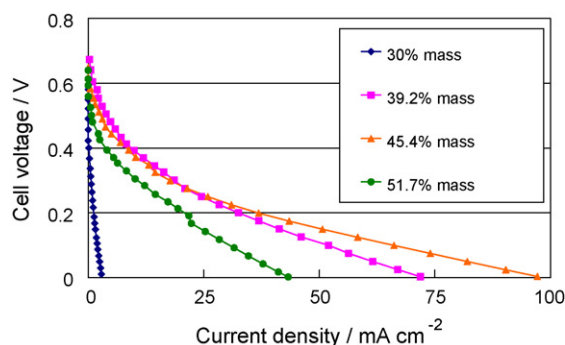


Fig. 2. I - V curves of MEAs at 80 °C with non-alkaline fuel. Anode catalyst: PtRu (Pt loading: 0.75 mg cm⁻²; Ru loading: 0.58 mg cm⁻²); cathode catalyst: Pt (Pt loading: 1.40 mg cm⁻²); anode fuel: MeOH (1 M) (fuel flow rate: 5.0 mL min⁻¹); cathode gas: O₂ (100% RH) (O₂ flow rate: 100 mL min⁻¹). I - V measurement conditions: single test, 25 mV min⁻¹ from OCV, 1 min point⁻¹.

dation; that is, the Ag cathode catalyst may have a tolerance to methanol crossover. Therefore, MEA with an Ag cathode catalyst was fabricated and evaluated. This consisted of anode catalysts (Pt loading: 0.75 mg cm⁻²; Ru loading: 0.58 mg cm⁻²), a cathode catalyst (Ag loading: 0.50 mg cm⁻²) and an anion ionomer (45.4% mass of electrode). The conditions of electrochemical measurement were the same as that in Section 2.2.

3. Results

3.1. Alkaline MEAs with PtRu anode and Pt cathode

Fig. 2 shows I - V curves of MEAs with non-alkaline fuel. It can be seen that the performance deeply depends on the ionomer content. The ionomer content of 45.4% mass was optimum. A maximum current density of 97.3 mA cm⁻² and a maximum power density of 7.57 mW cm⁻² were observed. These values are very high as alkaline DMFCs. Comparing to MEA with 45.4% mass ionomer, MEA with 39.2% mass ionomer showed higher OCV, but the I - V curve was sharp. This indicates that the OH⁻ transfer of this MEA was low because of the low ionomer content. On the other hand, MEAs with 51.7% and 56.3% mass showed higher activation polarization. It is expected that the ionomer content was at a surplus, and the reactant supply was impeded.

Fig. 3 shows the I - V curves of MEAs when alkaline fuel was used. As with non-alkaline fuel, the MEA with 45.4% mass ionomer mass was optimum. A maximum current density of 359 mA cm⁻² and a maximum power density of 58.9 mW cm⁻² were observed. How-

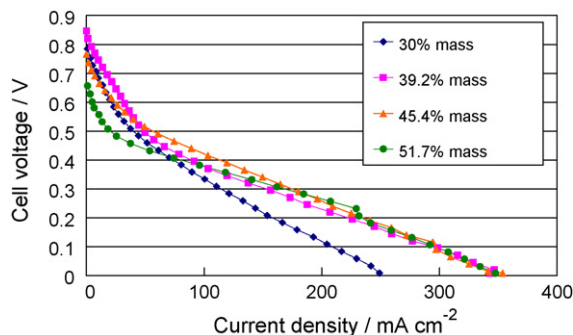


Fig. 3. I - V curves of MEAs at 80 °C with alkaline fuel. Anode catalyst: PtRu (Pt loading: 0.75 mg cm⁻²; Ru loading: 0.58 mg cm⁻²); cathode catalyst: Pt (Pt loading: 1.40 mg cm⁻²); anode fuel: MeOH (1 M) + NaOH (0.5 M) (fuel flow rate: 5.0 mL min⁻¹); cathode gas: O₂ (100% RH) (O₂ flow rate: 100 mL min⁻¹). I - V measurement conditions: single test, 25 mV min⁻¹ from OCV, 1 min point⁻¹.

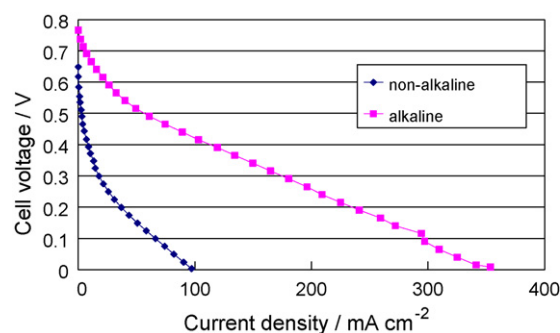


Fig. 4. I - V curves of MEAs at 80 °C with non-alkaline or alkaline fuel. Anode catalyst: PtRu (Pt loading: 0.75 mg cm⁻²; Ru loading: 0.58 mg cm⁻²); cathode catalyst: Pt (Pt loading: 1.40 mg cm⁻²); ionomer content: 45.4% mass, anode fuel: MeOH (1 M) with and without NaOH (0.5 M) (fuel flow rate: 5.0 mL min⁻¹); cathode gas: O₂ (100% RH) (O₂ flow rate: 100 mL min⁻¹). I - V measurement conditions: single test, 25 mV min⁻¹ from OCV, 1 min point⁻¹.

ever, the maximum current densities of MEAs were comparable to each other. This indicates that the OH⁻ conductivity of MEAs was extremely enhanced by the added NaOH.

The performance of MEA with 45.4% mass is optimum in both cases (non-alkaline fuel or alkaline fuel). Therefore, the performance is compared in Fig. 4. It is clear that the additional NaOH extremely enhanced the performance of alkaline DMFCs. NaOH may have a role in OH⁻ transfer, so further improvement of OH⁻ conductivity of the membranes and ionomers must be inevitable to use alkaline DMFCs practically.

In addition to I - V curves (Fig. 3), anode and cathode polarization curves were measured. Figs. 5 and 6 show the anode and cathode polarization curves of MEAs, respectively. In comparing these polarization curves, it can be seen that cathode polarization is nearly two times as high as anode polarization. The activation polarization of the cathode is especially high, so it is expected that the kinetics of oxygen reduction reaction are lower than that of methanol oxidation, even in alkaline media. Furthermore, the properties of anode and cathode polarization were quite different. In the case of the anode, it can be seen that the slopes of the polarization curves were influenced by the ionomer content. This indicates that the ionomer content influenced OH⁻ transfer in the anode compartment. On the other hand, the high current density ranges of the cathode polarization curves were influenced by the ionomer content. This indicates that the ionomer content influenced oxygen diffusion in the cathode compartment.

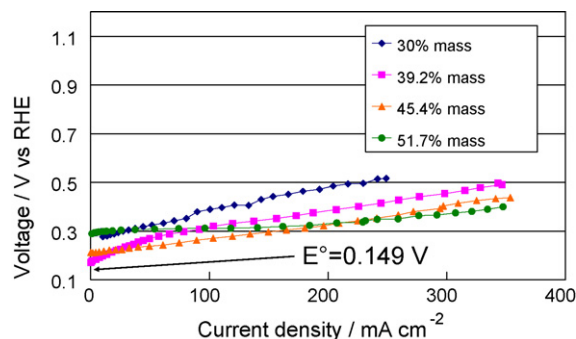


Fig. 5. Anode polarization curves of MEAs containing various amount of ionomer. Anode catalyst: PtRu (Pt loading: 0.75 mg cm⁻²; Ru loading: 0.58 mg cm⁻²); cathode catalyst: Pt (Pt loading: 1.40 mg cm⁻²); anode fuel: MeOH (1 M) + NaOH (0.5 M) (fuel flow rate: 5.0 mL min⁻¹); cathode gas: O₂ (100% RH) (O₂ flow rate: 100 mL min⁻¹). I - V measurement conditions: single test, 25 mV min⁻¹ from OCV, 1 min point⁻¹.

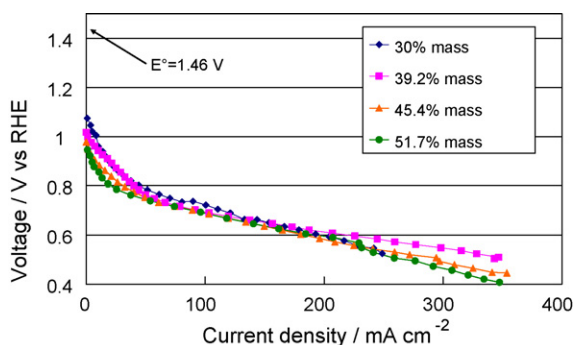


Fig. 6. Cathode polarization curves of MEAs containing various amount of ionomer. Anode catalyst: PtRu (Pt loading: 0.75 mg cm^{-2} ; Ru loading: 0.58 mg cm^{-2}); cathode catalyst: Pt (Pt loading: 1.40 mg cm^{-2}); anode fuel: MeOH (1 M) + NaOH (0.5 M) (fuel flow rate: 5.0 mL min^{-1}); cathode gas: O_2 (100% RH) (O_2 flow rate: 100 mL min^{-1}). *I*-*V* measurement conditions: single test, 25 mV min^{-1} from OCV, 1 min point^{-1} .

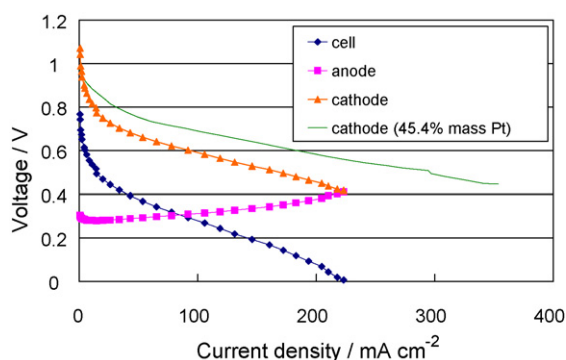


Fig. 7. Polarization curves of MEA using Ag cathode catalyst. Anode catalyst: PtRu (Pt loading: 0.75 mg cm^{-2} ; Ru loading: 0.58 mg cm^{-2}); cathode catalyst: Ag (Ag loading: 0.50 mg cm^{-2}); ionomer content: 45.4% mass for both of anode and cathode; anode fuel: MeOH (1 M) + NaOH (0.5 M) (fuel flow rate: 5.0 mL min^{-1}); cathode gas: O_2 (100% RH) (O_2 flow rate: 100 mL min^{-1}). *I*-*V* measurement conditions: single test, 25 mV min^{-1} from OCV, 1 min point^{-1} .

3.2. Ag cathode test

Fig. 7 shows the polarization curves of MEA using an Ag cathode catalyst. In order to evaluate the performance of the Ag cathode catalyst, the polarization curve of the Pt cathode catalyst with 45.4% mass (Fig. 6) is shown together. The performance of the MEA with Ag cathode catalyst was relatively high, but lower than the MEA with Pt cathode catalyst. A maximum current density of 223 mA cm^{-2} and a maximum power density of 28.4 mW cm^{-2} were observed. In the case of cathode polarization, the OCV of Ag was higher than that of Pt. It is expected that the influence of methanol crossover on Ag is lower than that of Pt. Nevertheless,

the activation polarization of Ag was very high. This is because the activity of Ag for oxygen reduction is lower than that of Pt. To sum up, an Ag cathode catalyst is a promising alternative to a Pt cathode due to the tolerance of methanol crossover, but there is still a need to enhance the activity.

4. Conclusion

In this study, an anion ionomer was used for fabricating alkaline MEAs. In order to investigate the effect of ionomer content on the performance of MEAs, *I*-*V* curves were measured. *I*-*V* tests revealed that the performance of alkaline DMFCs deeply depends on ionomer content, and the optimum ionomer content was observed to be 45.4% mass. MEA with 45.4% mass ionomer content showed relatively high performance even when non-alkaline fuel (MeOH (1 M)) was used. It also showed high performance when alkaline fuel (MeOH (1 M) + NaOH (0.5 M)) was used. The anion ionomer enhances the performance of alkaline DMFCs. However, in comparing tests with non-alkaline and alkaline fuel, it is clear that the additional NaOH extremely enhanced the performance, so the further improvement of OH^- conductivity of membranes and ionomers is inevitable for the practical use. In addition, the anode and cathode polarization of MEAs were measured. This test revealed that the ionomer content contributed to the ohmic polarization of the anode and the diffusion polarization of the cathode.

Furthermore, for the sake of reducing cost, MEA with an Ag cathode catalyst was investigated. Although the performance of MEA using an Ag cathode was not high enough, it showed low activity for methanol oxidation. Therefore, it is expected that the Ag cathode catalyst is a promising alternative to the Pt cathode catalyst.

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