Short communication

Cell performance of Pd–Sn catalyst in passive direct methanol alkaline fuel cell using anion exchange membrane

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ABSTRACT

Direct methanol alkaline fuel cell (DMAFC) using anion exchange membrane (AEM) was operated in passive condition. Cell with AEM exhibits a higher open circuit voltage (OCV) and superior cell performance than those in cell using Nafion. From the concentration dependences of methanol, KOH in fuel and ionomer in anode catalyst layer, it is found that the key factors are to improve the ionic conductivity at the anode and to form a favorable ion conductive path in catalyst layer in order to enhance the cell performance. In addition, by using home-made Pd–Sn/C catalyst as a cathode catalyst on DMAFC, the membrane electrode assembly (MEA) using Pd–Sn/C catalyst as cathode exhibits the higher performance than the usual commercially available Pt/C catalyst in high methanol concentration. Therefore, the Pd–Sn/C catalyst with high tolerance for methanol is expected as the promising oxygen reduction reaction (ORR) catalyst in DMAFC.

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1. Introduction

Direct methanol fuel cell (DMFC) has been attracting attention as a promising alternative energy converting source, because of high theoretical energy density and the advantages to use liquid fuel [1,2]. However, the currently available DMFC systems contain some technical problems. One of the problems is methanol crossover through membrane, which results in wasted fuel and low power densities and cost [3]. The other is that the electro-oxidation of methanol is inherently sluggish, which reduces performances and leads to the requirement for high loading of expensive catalysts [4]. Accordingly, many researches on the replacement of proton exchange membranes and electrocatalysts for DMFC have been performed to improve the performance of DMFC [5–7]. Besides, many researchers have proposed alternative approaches, such as the mixed-reactants solid polymer DMFC [8] and direct methanol alkaline fuel cell (DMAFC) using anion exchange membrane (AEM) [9–11] to improve the performance of DMFC.

DMAFC has potential advantages, compared to DMFC in acidic media. First, electrocatalytic reaction of methanol oxidation and oxygen reduction reaction (ORR) in alkaline media are more facile than in acidic media [12]. That allows to use low catalysts loadings and to select a wide range of catalysts, e.g. non-noble metals [13].

Second, it is possible to suppress the methanol crossover, because the conducting pathway of OH ions from the cathode to the anode through the membrane is opposite to the direction of the electro-osmotic drag. Reduced methanol crossover will allow the use of thinner membranes, improving fuel cell performances. In addition, water management can be easily performed in accordance with reduction of flooding at the cathode. However, carbon dioxide poisoning remains as a common issue to be solved in present research level, even though the alkaline fuel cell with AEM has the possibility that would enable a cell to run reducing the carbon dioxide poisoning, as there would be no free potassium cations to which the carbonate anions could be reacted. Nevertheless, DMAFC system can be expected to use in air by systematic approach such as an application of membrane with selectivity of CO_2 and the design of system for reducing the problems by carbon dioxide poisoning [14–17].

Many recent works on the development of AEMs for application in fuel cells were focused on the fabrication of membranes [10,18,19] and application of various fuels, such as ethylene glycol and sodium borohydride [11,20,21]. Yu and Scott reported feasibility study on development of DMAFC [9]. Slade and coworkers carried out a study on developing alkaline AEMs for applications in low temperature portable DMFCs [10]. Ogumi and coworkers reported DMFCs and direct ethylene glycol fuel cells using AEM. Their results present that the use of AEM in fuel cells can broaden the choice of the liquid fuels at the anode in direct alcohol fuel cells [11].

In this study, we present feasibility study on passive DMAFC applying AEM. We examined the effects of methanol concentration

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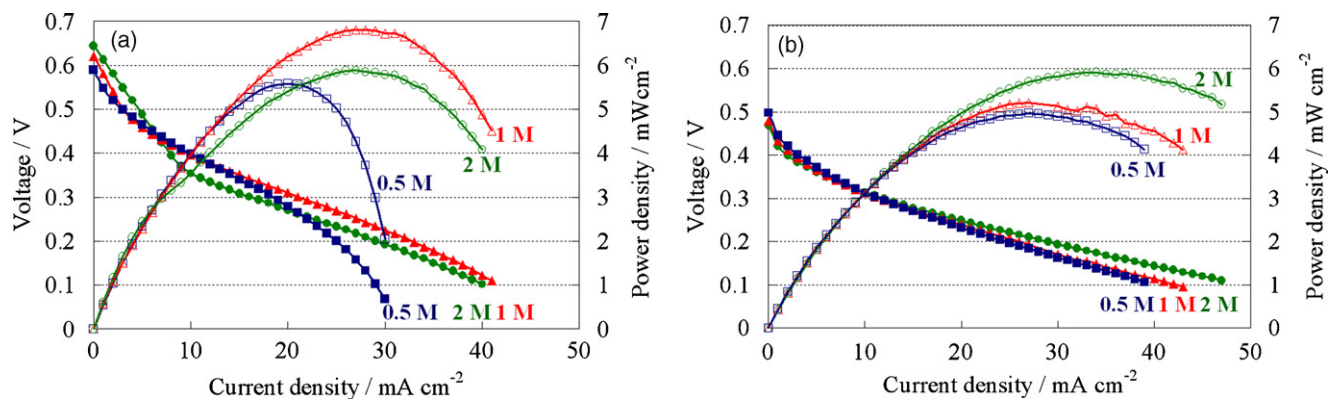
Fig. 1. Polarization curves of (a) MEA with anion exchange membrane (AEM) (anode: PtRu/C, 1.8 mg cm^{-2}, anionic ionomer: 28%; cathode: Pt/C, 2.0 mg cm^{-2}, anionic ionomer: 27%), and (b) MEA with Nafion (anode: PtRu/C, 1.8 mg cm^{-2}, Nafion: 23%; cathode: Pt/C, 2.0 mg cm^{-2}, Nafion: 33%) in the various concentration of MeOH (0.5 M (■ and □), 1 M (● and ○), and 2 M (▲ and △)) (in case of AEM, MeOH solution contains 1 M KOH).

and electrode structure in anode on performance of passive DMAFC. We evaluated the performance of MEA with Pd–Sn catalyst, which was reported to have a high electrocatalytic activity for ORR and a high tolerance for methanol in our previous study [22], in order to confirm the possibility for application of a non-Pt catalyst.

2. Experimental

2.1. Preparation of carbon-supported Pd–Sn catalyst (Pd–Sn/C)

Pd–Sn/C catalyst was prepared by applying ultrasonic irradiation method. 0.06 g of Vulcan XC-72R was added with constant stirring into an aqueous 10 vol.% ethanol solution and prepared by dissolving metal salts (0.0534 g of Pd(NH$_4$)$_2$Cl$_2$ and 0.032 g of SnCl$_2$) and 20 mM citric acid as a stabilizing agent. This mixture was irradiated by ultrasound. Ultrasonic irradiation was performed with a collimated 20 kHz beam from a ceramic transducer with a titanium amplifying horn (13 mmØ, Branson Sonofier 450D) directly immersed in the solution and operated with an input power of 42 W cm^{-2} for 2 h. The prepared Pd–Sn/C catalysts were washed with a large amount of H$_2$O and dried at 50 °C overnight.

2.2. Evaluation of methanol permeability of membrane

Two well-stirred reservoirs (20 ml) were separated by the membrane material (membrane cross-section area: 0.785 cm^2) under test. One reservoir was filled with methanol and the other with de-ionized water. Each membrane was soaked in a 20 vol.% methanol solution for 20 min at room temperature. Small aliquots (10 μl) of solution were withdrawn from reservoirs with de-ionized water in every 4 min. Each experiment was repeated three times to ensure reproducibility. Methanol concentration was determined by gas chromatography (GL science, GC323N) with FID detector.

2.3. Preparation of membrane electrode assembly (MEA)

MEAs were comprised of catalyst-coated electrode and an AEM (thickness: 28 μm, IEC: 1.9 mmol g^{-1}, Tokuyama Co.). Non-coated carbon paper (TGP-060T, Toray) and Teflon coated carbon paper (TGPH-060, Toray) were used as a gas diffusion electrode in anode and cathode, respectively. Carbon-supported PtRu catalysts (54.4 wt% on Ketjen black, Pt:Ru = 1:1, TKK Co.) for anode and carbon-supported Pt catalysts (47.2 wt% on Vulcan XC-72R, TKK Co.) for a cathode were used. In addition, Pd–Sn/C catalysts were used as a cathode catalyst to investigate the potentiality for application of a non-Pt catalyst. Each catalyst was suspended in mixture of 2-

ethoxyethanol and anion exchange ionomer (Tokuyama Co.), and then stirred to form homogeneous slurry. Catalysts were coated on carbon paper using a spray method. The catalyst loading at the anode and cathode were 2 mg$_{Pt}$ cm^{-2}. The MEAs for a unit cell test were prepared by hot-pressing (120 °C, 2 MPa for 10 min) the anode and cathode layers onto both sides of a pretreated AEM sample.

MEA with Nafion® 117 (Du-Pont) was also prepared for comparative purposes. To prepare the catalyst layer, the desired amounts of the catalysts and Nafion solution (5 wt%, Aldrich) were mixed. Then, electrodes were prepared by the same process as mentioned. The MEAs were prepared by hot-pressing (135 °C, 2 MPa for 10 min).

2.4. Evaluation of performance in passive DMFCs

The prepared MEA was sandwiched between two gold meshes as current collector. A methanol solution tank of 15 ml was built in the anode fixture. Methanol diffused into the anode catalyst layer from the tank through the anode current collectors, while oxygen transferred into the cathode catalyst layer from the surrounding air through the cathode current collectors by natural convection.

I–V curve measurements were performed with a galvanostat (Hokuto Denko, HA-501G). Each measurement was started after the methanol solution was poured in the cell for 30 min. The cell voltage was recorded after setting up the current for 3 min to stabilize the voltage. The passive DMFC operated at ambient temperature.

3. Results and discussion

3.1. Comparison of cell performance of AEM and Nafion using Pt/C cathode

A passive DMAFC with AEM catalyst was operated using PtRu/C catalyst and Pt/C catalyst as anode catalyst and cathode catalyst. Fig. 1(a) illustrates the voltage–current density and the power density–current density curves of passive DMFC with AEM. The voltage–current density and the power density–current density curves of cell using Nafion® 117 were shown in Fig. 1(b) for comparison. Open circuit voltages (OCVs) of cell with AEM exhibit a vicinity of 0.6 V and the OCVs of cell with Nafion are close to 0.5 V in various methanol concentration. The high OCV in cell with AEM is considered to represent low concentration at cathode due to low methanol permeability of AEM. Our experimental results for methanol permeability of each membrane confirmed that AEM has about 20% of methanol permeability in Nafion® 117 membrane, although the thickness of AEM is one-fifth, compared to Nafion® 117 membrane. In addition, the cell with AEM exhibits higher peak power density
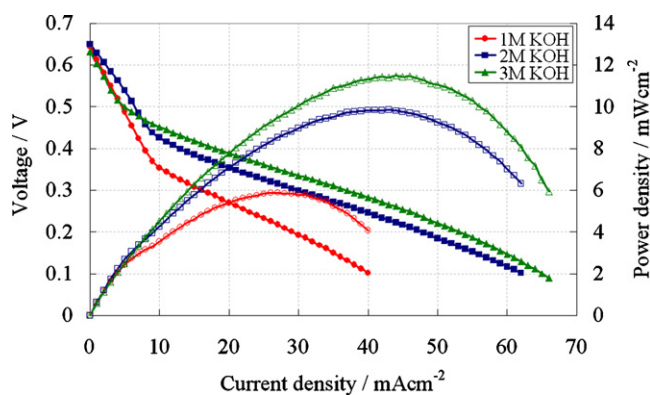
Fig. 2. Polarization curves of MEA with anion exchange membrane (AEM) in 2 M MeOH containing the various concentration of KOH (1 M (● and ○), 2 M (■ and □), and 3 M (▲ and △)). The measured MEA is the same MEA in Fig. 1(a).

Fig. 3. Polarization curves of cells with different fractions of ionomer (10 wt% (▲ and △), 20 wt% (● and ○), 30 wt% (■ and □), and 35 wt% (♦ and ◇)) in the anode catalyst layers in 1 M MeOH containing 1 M KOH (cathode is the same electrode in Fig. 1(a)).

than that of Nafion for all methanol concentration as shown in Fig. 1. In 1 M methanol concentration, the peak power density of AEM is 6.8 mW cm^{-2} while that of Nafion® 117 is 5.2 mW cm^{-2}. AEM and Nafion® 117 are the same the peak power density of 5.9 mW cm^{-2} in methanol concentration of 2 M. The high cell performance of AEM can be thought as a facile electrochemical reaction in alkaline media. These results imply the availability of DMAFC using AEM.

However, two MEAs exhibit different behavior of cell performance as methanol concentration increases. The peak power density of cell with Nafion® 117 increases, while peak power density of cell with AEM does not increase as methanol concentration increases from 1 M to 2 M. This result is thought to relate that the current density of AEM does not increase although methanol concentration increases. The current density at a cell voltage of 0.1 V of cell with Nafion® 117 increases from 42 mA cm^{-2} to 47 mA cm^{-2} as methanol concentration increases from 1 M to 2 M. On the other hand, the current density at a cell voltage of 0.1 V decreases from 41 mA cm^{-2} to 39 mA cm^{-2} in cell with AEM despite of increasing methanol concentration. The polarization curves of cell with AEM exhibit large slope in ohmic region and small decrease of slope according to increasing methanol concentration, compared to those of Nafion® 117. Scott et al. reported that contact resistances and ionic resistances in the electrocatalysts layers as well as anode and cathode polarization influenced shape of polarization curves and the cell performance [23]. Our results are considered that a low ionic conductivity affects the cell performance at the high concentration.

3.2. Effect of ion conductivity on cell performance

To investigate an effect of ion conductivity on cell performance, the cell with AEM was operated varying KOH concentration in anode fuel. Fig. 2 shows the polarization curves of cell in 2 M MeOH with various KOH concentrations. The current density at a cell voltage of 0.1 V increases from 39 mA cm^{-2} to 65 mA cm^{-2} as KOH concentration in 2 M MeOH solution increases from 1 M to 3 M. Moreover, the peak power density in 3 M KOH is about two times larger than that in 1 M KOH from 5.9 mW cm^{-2} to 11.5 mW cm^{-2}. The improved cell performance is considered as OH^{-} ion required for methanol oxidation reaction is sufficiently supplied by the addition of KOH into anode fuel and leads to improve cell performance. These results imply that it is necessary to enhance ionic conductivity at anode side to improve the cell performance.

MEAs with various ionomer contents in anode catalyst layer were prepared in order to examine the effect of the ion conductivity of catalyst layer. Fig. 3 shows that the polarization curves of each MEA with different fraction of ionomer were obtained in
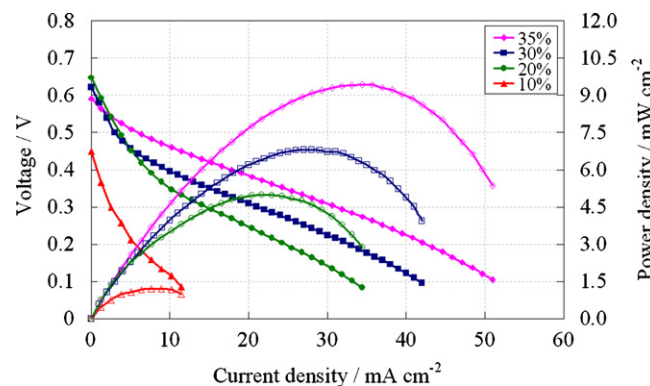
1 M MeOH containing 1 M KOH. The polarization curve of MEA with 10% of ionomer content shows that cell voltage quickly fall down as the current density increases. This behavior is considered that a sufficient ion conducting path is not formed because of small amount of ionomer. However, the peak power densities of cell are 1.2 mW cm^{-2}, 5.0 mW cm^{-2}, 6.8 mW cm^{-2}, and 9.4 mW cm^{-2} as ionomer content in anode catalyst layer increases 10%, 20%, 30%, and 35% of ionomer content, respectively. These results are considered that the charge transfer resistance decreases because a favorable ion conductive path is formed at higher ionomer content. The improvement of cell performance by increasing ionomer content in anode catalyst layer is similar to the results by increasing KOH concentration in fuel, as mentioned above. From these results, it found that it is important to improve the ionic conductivity at the anode and form a favorable ion conductive path in catalyst layer in order to enhance the cell performance in DMAFC system. However, ionomer might reduce the electric path way and limit the mass transport of the methanol by reducing pore volume in the catalyst layer, while ionomer enhances the ionic conductivity in the catalyst film. It can be thought that it is important to form an ionic conductive path with optimum ionomer content. Accordingly, we select a 35% of ionomer content as ionomer contents in anode catalyst layer for our further study.

3.3. Application of Pd–Sn/C catalyst to DMAFC

In order to examine potentiality of a non-Pt catalyst to DMAFC, *I–V* measurements were carried out using home-made Pd–Sn/C catalyst as a cathode catalyst. Pd–Sn catalyst prepared by sonochemical method was reported that it exhibited a high electrocatalytic activity for ORR and a high tolerance for methanol in our previous study [18]. Fig. 4 shows polarization curves of MEA using Pd–Sn/C catalyst as cathode catalyst were with various concentrations of MeOH. OCV of cell using Pd–Sn/C catalyst decreases, as methanol concentration increases. Scott et al. [23] reported that methanol crossover affected DMAFC performance, although the influence by methanol crossover was not severe compared to DMFC using Nafion. The decrease of OCV is considered as an effect of methanol crossover. This result implies that methanol crossover is not completely suppressed by using AEM and it is important to use catalyst with high tolerance for methanol, regardless of DMAFC system. However, MEA using Pd–Sn/C catalyst shows 5.5–5.8 mW cm^{-2} of peak power densities when the methanol concentration increases from 1 M to 3 M, while cell performance slightly decreased in 4 M MeOH. These results are considered that Pd–Sn/C catalysts have a high tolerance for methanol.
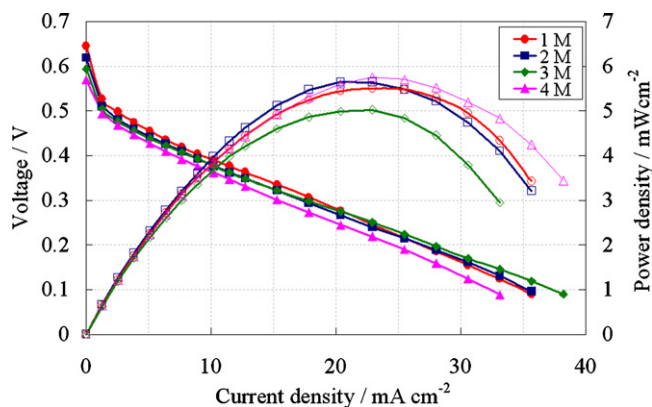
Fig. 4. Polarization curves of MEA using Pd–Sn/C catalyst as cathode catalyst in the various concentration of MeOH (1 M (■ and □), 2 M (● and ○), 3 M (▲ and △), 4 M (♦ and ◊)) containing 1 M KOH (anode: PtRu/C (53 wt%), 2.0 mg cm⁻², anionic ionomer: 34%; cathode: Pd–Sn/C (30 wt%) (Pd loading 18 wt%), 1.46 mg cm⁻², anionic ionomer: 30%).
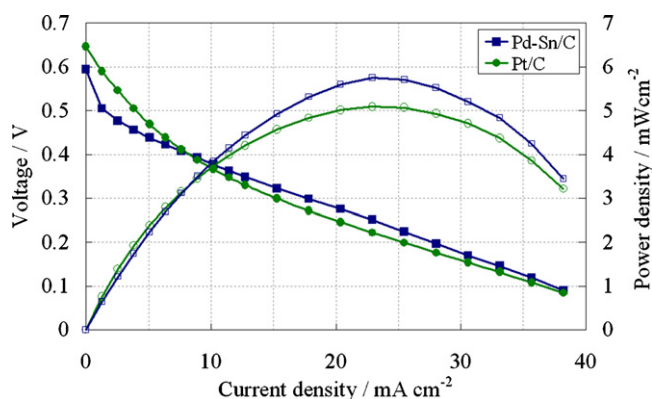

Fig. 5. Polarization curves for MEA using Pd–Sn/C (■ and □) and commercial Pt/C (● and ○) catalysts in 3 M MeOH in 1 M MeOH containing 1 M KOH (both of cells were used the same anode; PtRu/C, 2.0 mg cm⁻², anionic ionomer: 34%).

Fig. 5 shows cell performance using Pd–Sn/C and commercial Pt/C catalysts in 3 M MeOH. The maximum power densities of MEA using Pd–Sn/C catalyst and commercial Pt/C catalyst are 5.8 mW cm⁻² and 5.1 mW cm⁻² in 3 M MeOH, respectively. The max power density of Pd–Sn/C catalyst is greater than that of commercial Pt/C in 3 M MeOH, although cell performance of Pd–Sn/C are lower than those of commercial Pt/C catalyst at low methanol concentration of methanol (1 M and 2 M). Moreover, MEA using Pd–Sn/C catalyst exhibits a slight decrease of cell performance the highest peak power density in 4 M of methanol concentration, while cell using Pt/C catalyst exhibited a decrease of performance at methanol concentrations of 3 M and greater. This result indicates that MEA using Pd–Sn/C catalyst is a promising ORR catalyst in high methanol concentration because Pd–Sn/C catalyst has higher tolerance for methanol than that of Pt/C catalyst.

The catalyst layer using Pd–Sn/C is thicker about 30% than that using Pt/C, because Pd–Sn/C catalyst used in this study is less than 30 wt% of catalyst loading (Pd loading: 18 wt%) on carbon, compared to 47 wt% of catalyst loading for Pt/C catalyst. The electrode using our catalyst is not optimized. Thus, an improved cell performance can be expected by increasing metal loading on carbon and optimizing the electrode structure.

4. Conclusions

We successfully operated a passive DMAFC using AEM. The cell with AEM exhibits higher OCV and performance than those of Nafion. In this system, the ionic conductivity at the anode has a significant effect on the performance and the structure of the anode catalyst layer is supposed to have an important role on the formation of ion conductive path. In addition, we evaluated the performance of MEA with Pd–Sn catalyst as a cathode catalyst, which showed a high electrocatalytic activity for ORR and a high tolerance for methanol. MEA using Pd–Sn/C catalyst as cathode exhibits a higher performance than commercial Pt/C catalyst in high methanol concentration. It is found that DMAFC can be effectively operated at high methanol concentration by using catalyst with high tolerance for methanol. Based on these results, Pd–Sn/C catalysts are expected a promising as cathode catalyst in DMAFC system.

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