Direct ethanol fuel cells using an anion exchange membrane

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ABSTRACT

Direct ethanol fuel cells (DEFCs) with a PtRu anode and a Pt cathode were prepared using an anion exchange membrane (AEM) as an electrolyte instead of a cation exchange membrane (CEM), as in conventional polymer electrolyte fuel cells. The maximum power density of DEFCs significantly increased from 6 mW cm^{-2} to 58 mW cm^{-2} at room temperature and atmospheric pressure when the electrolyte membrane was changed from CEM to AEM. The anode and cathode polarization curves showed a decrease in the anode potential and an increase in the cathode potential for AEM-type DEFCs compared to CEM-type. This suggests that AEM-type DEFCs have superior catalytic activity toward both ethanol oxidation and oxygen reduction in alkaline medium than in acidic medium. The product species from the exhausted liquid from DEFCs operated at a constant current density were identified by enzymatic analysis. The main product was confirmed to be acetic acid in AEM-type, while both acetaldehyde and acetic acid were detected in 1:1 ratio in CEM-type. The anodic reaction of AEM-type DEFCs can be estimated to be the oxidation of ethanol to acetic acid via a four-electron process under these experimental conditions.

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1. Introduction

Direct oxidation fuel cells (DOFCs), in which the organic fuel is directly fed into the anode without any previous chemical modification, have attracted considerable attention as power sources in mobile phones, portable PCs, etc. as alternatives to rechargeable batteries [1,2]. Methanol has been considered to be one of the best fuels, and direct methanol fuel cells (DMFCs) have been developed for practical use. They offer several advantages, including high energy density for fuel storage, theoretically complete oxidation to CO_2, and low cost [3,4]. However, several unsolved problems still remain in the practical use of DMFCs, such as the need for Pt-based catalysts due to the large overvoltage toward the electrooxidation of methanol [4], large methanol crossover through the polymer membrane [5], and the toxicity of methanol and by-product species, i.e., formaldehyde and formic acid.

We recently reported the rapid evaluation of the electrooxidation of fuel compounds to identify alternatives to methanol for use in DOFCs [6] and the possible use of environmentally and biologically friendly L-ascorbic acid, well known as vitamin C [7–9]. Direct L-ascorbic acid fuel cells (DAAFCs), in which an aqueous solution of L-ascorbic acid is directly supplied to the anode, offered several advantages compared to DMFCs, although the maximum power density was only about one-third of that for DMFCs. The

electrochemical oxidation of L-ascorbic acid proceeded on a carbon electrode to produce dehydroascorbic acid via a two-electron process, the same as in its metabolic conversion. Therefore, DAAFCs do not require a precious metal anode and both the fuel and product are non-toxic. In addition, the crossover of L-ascorbic acid in DAAFCs through a typical proton exchange membrane, Nafion 117, was not as serious (about 100-fold less) as that of methanol in DMFCs.

Ethanol is also interesting as an alternative fuel. The energy density of ethanol (8030 Wh kg^{-1}) is greater than that of methanol (6100 Wh kg^{-1}) if complete oxidation to CO_2 is attained [1,10]. Ethanol and its oxidation by-products, i.e., acetaldehyde and acetic acid, are less toxic than methanol and its by-products. Ethanol is a major renewable biofuel that is obtained by the fermentation of biomass. The use of so-called bio-ethanol for vehicle engines has been commercialized to reduce carbon dioxide emissions.

However, direct ethanol fuel cells (DEFCs) still show poor performance compared to DMFCs due to the large overpotential for the electrochemical oxidation of ethanol at low temperature [11,12]. Fig. 1 shows cell voltage and power density plots versus the current density of typical direct fuel cells with a PtRu anode, a Pt cathode, and a Nafion 117 electrolyte membrane using 1.0 M aqueous solutions of methanol and ethanol as fuels. The maximum power density of the DEFC was only about 1/7 of that of the DMFC at room temperature, although the open circuit voltage was higher due to the small crossover of ethanol compared to that of methanol. The main reason for this is that ethanol has slower kinetics of oxidation on platinum-based catalysts at low
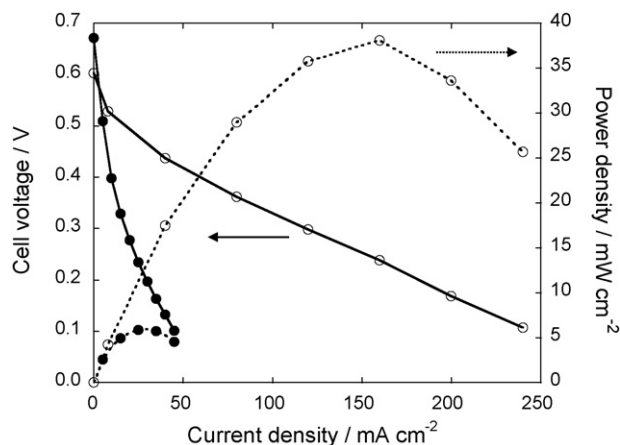
Fig. 1. Cell voltage versus current density plots of direct fuel cells using 1.0 M methanol (○) and ethanol (●) aqueous solution (4 ml min^{-1}) as fuels at room temperature and atmospheric pressure. Membrane: Nafion 117, anode: 3 mg cm^{-2} PtRu black, cathode: 3 mg cm^{-2} Pt black, and cathode gas: humidified O$_2$ (100 ml min^{-1}).

temperature compared to methanol. In addition to the large over-voltage toward ethanol oxidation, cleavage of a C—C bond for total oxidation to CO$_2$ is also a major problem [13,14]. Partial oxidation to acetaldehyde or acetic acid lowers the energy density of ethanol.

To overcome those problems, effort has been made to develop novel catalysts with high activity toward ethanol oxidation. Binary PtRu and PtSn and the corresponding ternary PtRu-based and PtSn-based catalysts have been extensively investigated [13–20]. The addition of metals such as Ru or Sn to Pt catalysts can reduce the poisoning effect of CO and enhance catalytic activity by a bi-functional mechanism, although the impact on the CO$_2$ yield is now under discussion [13,14,16–19]. Various studies have been carried out to optimize the composition and the method for preparing the catalysts. However, DEFCs still show poor performance.

Another approach is the use of a higher catalytic activity in alkaline than acidic medium. Several DOFCs which use an anion exchange membrane (AEM) as a polymer electrolyte membrane have already been reported. Direct fuel cells which use methanol [21–24], ethanol [24], ethylene glycol [23–25], and hydrazine [26] are typical examples. These previous studies showed much better kinetics for fuel oxidation in alkaline medium than in acidic medium. In addition, Pt-free fuel cells have been successfully demonstrated by replacing the conventional acidic membrane with an AEM [26].

The AEM-type DEFCs prepared as described here showed improved performance that was comparable to that of conventional DMFCs. An AEM was used as an electrolyte membrane in DEFCs instead of a conventional proton exchange membrane, i.e., a cation exchange membrane (CEM), to realize high catalytic activity toward both ethanol oxidation and oxygen reduction under alkaline conditions. The performance of DEFCs with various anolytes was evaluated and compared with those of conventional DEFCs using a CEM as an electrolyte. Quantitative analyses of the product species during the operation of DEFCs were carried out to determine the stoichiometry of DEFCs.

2. Experimental

2.1. Materials

Unsupported Pt and PtRu black catalysts (Johnson-Matthey, specific surface area is typically 20 m^2 g^{-1}), were used as electrocat-

alysts to prepare membrane electrode assemblies (MEAs) in DEFCs. An AEM (ion exchange capacity: 1.7 mequiv. g^{-1}, thickness: 27 μm, quaternary ammonium form) and anion exchange resin solution (2.0 mequiv. g^{-1}), both provided by Tokuyama Corporation, were used to prepare AEM-type fuel cells. Nafion 117 membrane (ion exchange capacity: 0.91 mequiv. g^{-1}, sulfonic acid form, DuPont) was used as a CEM after pretreatment with 3% H$_2$O$_2$ and 1 M H$_2$SO$_4$ at 80 °C. Nafion solution (5 wt.% solution in a lower aliphatic alcohol and water, Aldrich) was used as an ionomer to prepare CEM-type fuel cells. All other chemicals were analytical grade and used as received.

2.2. Electrochemical measurements in electrolyte solution

The electrochemical oxidation of ethanol on a Pt disk (3 mm diameter) electrode after it was polished to a mirror finish with 0.05 μm alumina powder was examined by the rotating disk electrode technique. Cyclic voltammetry (CV) was conducted in a conventional three-electrode arrangement with a Pt disk as a working electrode, a reversible hydrogen electrode (RHE) for reference, and a Pt spiral counter electrode under an Ar atmosphere at 25 °C. An electrochemical analyzer with a rotating disk electrode setup (ALS, model 660A and RDE-2) was used and the working electrode was rotated at 2500 rpm during all measurements. CV was also conducted on PtRu-modified glassy carbon (GC) electrodes prepared by the method described by Schmidt et al. [27]. Briefly, GC disk electrodes (3 mm diameter) were polished to a mirror finish with 0.05 μm alumina powder. Three microliters of aqueous suspensions containing ultrasonically dispersed PtRu black (4 mg ml^{-1}) were dropped onto the GC substrate. After the water evaporated, the GC electrode was coated with a 0.1 μm-layer of Nafion or anion exchange resin for measurement in acid and alkaline electrolyte, respectively, and then dried at 150 °C for 1 h.

2.3. Preparation and evaluation of DEFCs

PtRu and Pt black used as anode and cathode catalysts, respectively, were suspended in anion exchange solution and the obtained slurry was spread on a PTFE sheet. The catalyst layers (catalysts 3.0 mg cm^{-2}, anion exchange resin 5 wt.%) were prepared after drying in a vacuum at 80 °C for 1 h. MEAs were prepared by decal transfer [28] of the electrode layers onto both sides of an AEM. CEM-type fuel cells were prepared using Nafion 117 membrane and Nafion solution instead of AEM and anion exchange solution, respectively, by the same method as for AEM-type fuel cells.

MEAs were sandwiched between two carbon-cloths (E-TEK) used as gas-diffusion media. DEFC performance was evaluated using a single cell with a geometric electrode area of 2 cm^2 at room temperature and at atmospheric pressure. 1.0 M ethanol with or without alkaline solution was delivered to the anode at 4 ml min^{-1}, while humidified oxygen was supplied to the cathode (100 ml min^{-1}). The current–voltage behaviors were measured galvanostatically and the internal resistance of the cell was determined by the current interruption method with a programmable electronic load (Scribner 890CL). The individual electrode potentials were detected versus a RHE connected to the periphery of the anode side by a 0.5 M KOH or 0.5 M H$_2$SO$_4$ electrolyte junction for AEM- or CEM-type fuel cells, as shown previously [29].
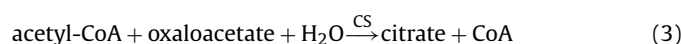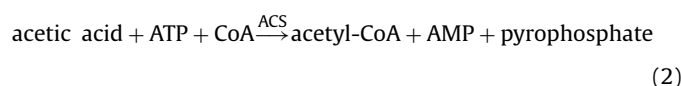
2.4. Product analysis of DEFCs

The exhausted liquid from the anode outlet in DEFCs was adjusted to pH 7–9 with sulfuric acid, if necessary, and then analyzed by an enzymatic method [30,31]. The concentrations of acetaldehyde and acetic acid in the exhausted liquid were deter-

mined during the steady-state operation of DEFCs at a constant current density. Acetaldehyde and acetic acid were quantitatively assayed by using sets of reagents marketed by R-Biopharm AG as F-kit. The principle of the enzymatic analysis is briefly as follows.

Acetaldehyde is quantitatively oxidized to acetic acid by nicotinamide-adenine dinucleotide (NAD) in the presence of aldehyde dehydrogenase (Al-DH) (Eq. (1)) [30]. The amount of NADH produced is stoichiometric with regard to the amount of acetaldehyde. NADH is determined by means of its light absorbance at 340 nm:

$$\text{acetaldehyde} + \text{NAD}^+ + \text{H}_2\text{O} \xrightarrow{\text{Al-DH}} \text{acetic acid} + \text{NADH} + \text{H}^+ \qquad (1)$$
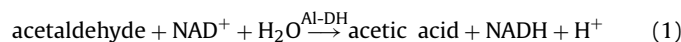
Acetic acid (acetate) is converted to acetyl-CoA in the presence of the enzyme acetyl-CoA synthetase (ACS), adenosine-5′-triphosphate (ATP) and coenzyme A (CoA). Acetyl-CoA reacts with oxaloacetate to citrate in the presence of citrate synthase (CS) (Eq. (3)) [31]. Oxaloacetate required for reaction (3) is formed from L-malate and NAD in the presence of L-malate dehydrogenase (L-MDH) (Eq. (4)). In this reaction, NAD is reduced to NADH. The determination is based on the formation of NADH measured by the increase in light absorbance at 340 nm:

$$\text{acetic acid} + \text{ATP} + \text{CoA} \xrightarrow{\text{ACS}} \text{acetyl-CoA} + \text{AMP} + \text{pyrophosphate}$$
$$(2)$$

$$\text{acetyl-CoA} + \text{oxaloacetate} + \text{H}_2\text{O} \xrightarrow{\text{CS}} \text{citrate} + \text{CoA} \qquad (3)$$

$$\text{L-malate} + \text{NAD}^+ \xrightarrow{\text{L-MDH}} \text{oxaloacetate} + \text{NADH} + \text{H}^+ \qquad (4)$$

3. Results and discussion

3.1. Electrochemical oxidation of ethanol in electrolyte solution

The electrochemical oxidation of ethanol was investigated in both acidic and alkaline media. Fig. 2 compares CVs for a Pt electrode obtained in 0.1 M ethanol + 0.1 M H$_2$SO$_4$ and 0.1 M ethanol + 0.1 M KOH. Two obvious peaks were observed at around 0.85 V and 1.1 V in the positive sweep in acidic medium, which correspond to oxidation to CO$_2$ and acetaldehyde, respectively [16]. The relatively large peak current at around 0.63 V in the negative sweep indicates that adsorbed species on the electrode surface
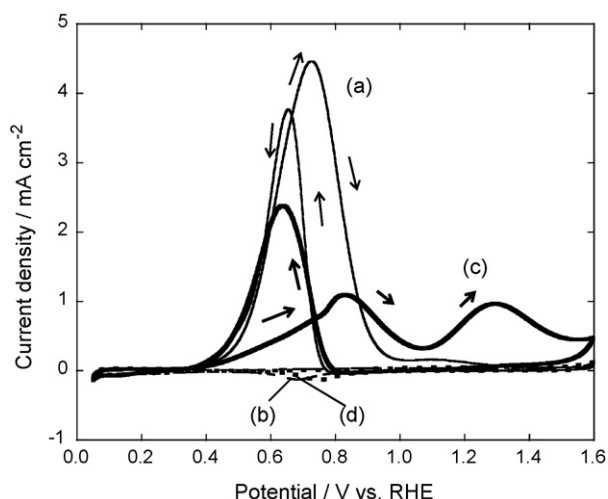
Fig. 2. Cyclic voltammograms of Pt electrode in 0.1 M ethanol + 0.1 M KOH (a), 0.1 M KOH (b), 0.1 M ethanol + 0.1 M H$_2$SO$_4$ (c), and 0.1 M H$_2$SO$_4$ (d) obtained by the rotating disk electrode technique. Sweep rate: 20 mV s^{-1}, temperature: 25 °C, and rotation rate: 2500 rpm.
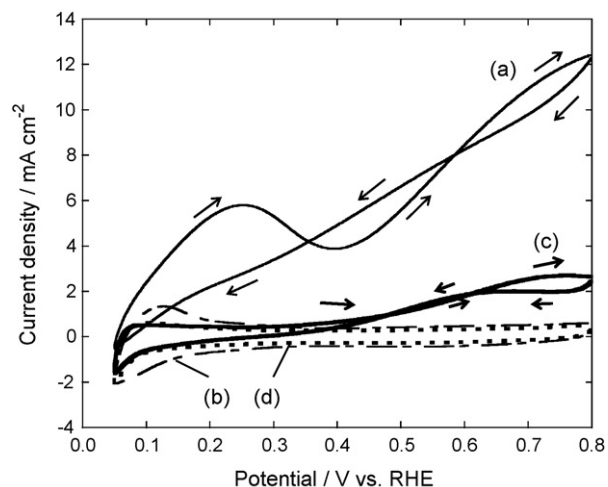
Fig. 3. Cyclic voltammograms of PtRu black electrode in 0.1 M ethanol + 0.1 M KOH (a), 0.1 M KOH (b), 0.1 M ethanol + 0.1 M H$_2$SO$_4$ (c), and 0.1 M H$_2$SO$_4$ (d) obtained by the rotating disk electrode technique. Sweep rate: 20 mV s^{-1}, temperature: 25 °C, and rotation rate: 2500 rpm.

were oxidized during the negative sweep. In contrast, there is only one peak at around 0.73 V with no second peak in alkaline medium, although a peak was observed at around 0.66 V in the negative sweep. The peak in the positive-going scan was shifted negatively and the current density increased about fivefold in alkaline medium compared with those in acid medium. These findings are consistent with the results reported previously [32]. The enhanced activity in alkaline medium can be explained by the lack of specifically adsorbing ions in alkaline solutions, and the higher coverage of adsorbed OH at low potential, which is required for ethanol oxidation [33]. These behaviors suggest that the catalytic activity for ethanol oxidation is greater in alkaline medium than in acid medium and suggests that the overpotential for ethanol oxidation is decreased and gives better performance in DEFCs in alkaline medium. This prompted us to study DEFCs with AEM as an electrolyte membrane.

CVs in acid and alkaline electrolyte were also compared with regard to a PtRu electrode, which is often used as an anode catalyst in direct fuel cells (Fig. 3). The oxidation current starts to increase at around 0.05 V and reaches 12 mA cm^{-2} at 0.8 V in alkaline electrolyte, whereas oxidation starts at around 0.3 V and the current density remained small (2.4 mA cm^{-2}) at 0.8 V in acid electrolyte. The advantage of ethanol oxidation in alkaline compared to acid media was confirmed throughout the anodic potential region of DEFCs (below 0.6 V vs. RHE).

3.2. I–V performance of DEFCs with various anolytes

DEFCs using AEM were first operated by supplying aqueous solution of 1.0 M ethanol as fuel. However, the performance of the DEFC was very poor, as shown in Fig. 4 (○). The current density reached only 8 mA cm^{-2}, although the open circuit voltage showed a certain value (0.74 V). This is due to the insufficient OH$^-$ conductivity of the AEM used in the present study. Fig. 4 also shows I–V curves of AEM-type DEFCs supplied with alkaline aqueous solutions of ethanol. The co-supply of KOH solution with ethanol improved the I–V performance. The open circuit voltage and maximum current density reached 1.17 V and 100 mA cm^{-2} with 0.1 M KOH, 0.83 V and 350 mA cm^{-2} with 0.5 M KOH, and 0.84 V and 400 mA cm^{-2} with 1.0 M KOH, respectively. The OCV with 0.1 M KOH was relatively higher than those with 0.5 M and 1.0 M KOH, due to the higher cathode potential resulting from the
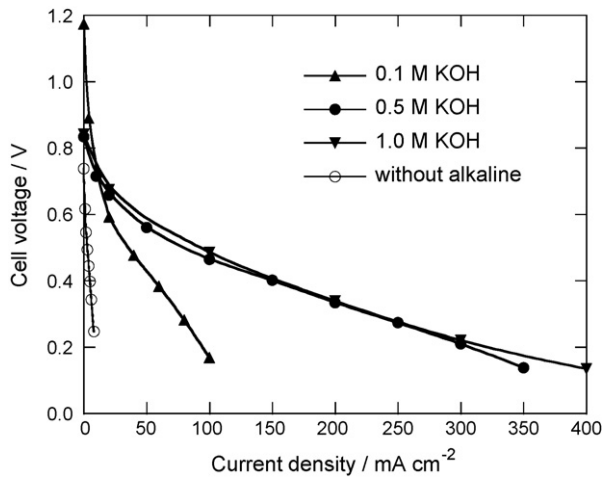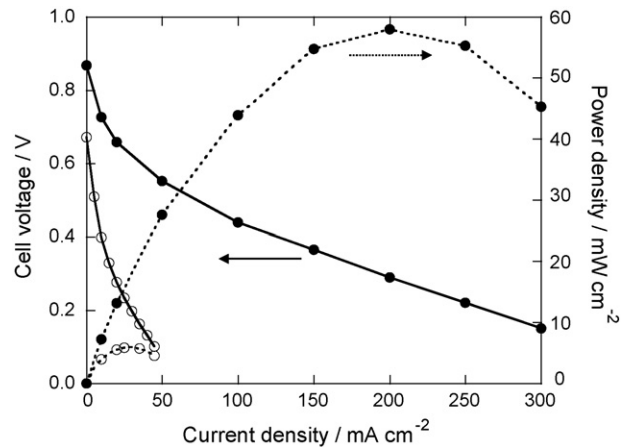
Fig. 4. Cell voltage versus current density plots of DEFCs using 1.0 M ethanol with 0.1 M KOH (▲), 0.5 M KOH (●), and 1.0 M KOH (▼), and without alkaline solution (○) (4 ml min^{-1}) at room temperature and atmospheric pressure. Membrane: AEM, anode: 3 mg cm^{-2} PtRu black, cathode: 3 mg cm^{-2} Pt black, and cathode gas: humidified O$_2$ (100 ml min^{-1}).

smaller ethanol crossover compared with 0.5 M and 1.0 M KOH. A KOH concentration of 0.5–1.0 M was appropriate for the function of anolyte to increase the I–V performance of DEFCs, although the open circuit voltage was smaller than that with 0.1 M. In principle, DEFCs using an aqueous solution of ethanol without alkaline solution as fuel can be operated, if AEM and an ionomer solution with sufficient OH$^-$ conductivity are developed. Previous studies have adopted a similar strategy, in which fuel dissolved in alkaline solution is fed to the anode to ensure the hydroxyl ion conductivity of the AEM [21,23,25,26]. Based on our observations, subsequent experiments were carried out by supplying 0.5 M KOH with ethanol fuel to maintain sufficient ionic conductivity.

3.3. Comparison of DEFCs using AEM and CEM as electrolyte membranes

The performance of DEFCs using AEM and CEM were compared. The cell voltage and power density versus current density of AEM- and CEM-type DEFCs are plotted in Fig. 5. The advantage of the AEM-type is obvious when the anode and cathode catalysts, their loading amount, and operating conditions are the same. The open circuit voltage and maximum power density were 0.87 V and 58 mW cm^{-2} for AEM, and 0.67 V and 6 mW cm^{-2} for CEM, respectively. The maximum power density in AEM-type is almost 10-fold greater than that in CEM-type. The performance of AEM-type DEFCs was even better than that of typical DMFCs using CEM (Nafion 117) and a PtRu anode catalyst, which shows a maximum power density of 38 mW cm^{-2} (Fig. 1). This suggests that DEFCs using AEM are potential power sources for portable electronic devices.
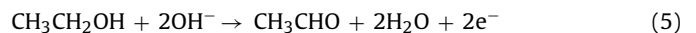
Anode and cathode polarization were also compared between AEM and CEM (Fig. 6). The cathode potential was increased about 200 mV with AEM compared to CEM, whereas the anode potential decreased 80–300 mV depending on the current density. The advantage of the AEM-type DEFCs is based on the reduction of both anode and cathode overvoltage with the use of AEM as an alternative to CEM [33]. The cathode potential may also be influenced by ethanol crossover. However, the ethanol crossover was slightly larger in AEM-type than in CEM-type and gives only small impact on the cathode potential.
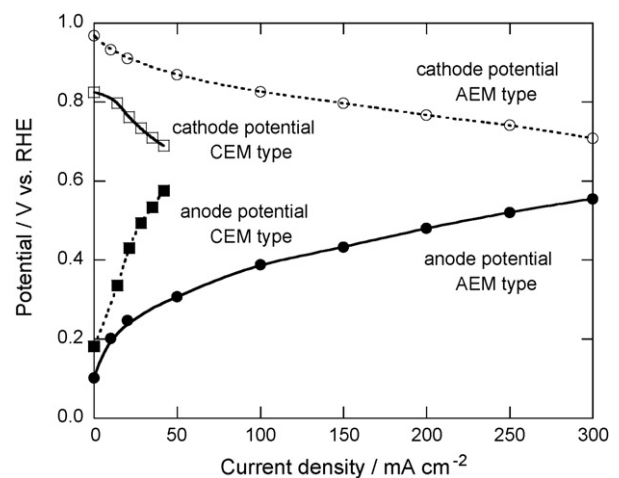

Fig. 5. Cell voltage and power density versus current density plots of DEFCs using an AEM and 1.0 M ethanol + 0.5 M KOH solution (●) or a CEM and 1.0 M ethanol aqueous solution (○) (4 ml min^{-1}), as an electrolyte membrane and a fuel, respectively, at room temperature and atmospheric pressure. Anode: 3 mg cm^{-2} PtRu black, cathode: 3 mg cm^{-2} Pt black, and cathode gas: humidified O$_2$ (100 ml min^{-1}).

3.4. Product analysis of DEFCs

The product species in exhausted liquid from the anode side during the operation of DEFCs were quantitatively analyzed to better understand the principle of the operation of DEFCs. The formation of acetaldehyde or acetic acid as oxidation products from ethanol was expected during the operation of AEM-type DEFCs, as described by Eqs. (5) and (6), respectively:

$$CH_3CH_2OH + 2OH^- \rightarrow CH_3CHO + 2H_2O + 2e^- \qquad (5)$$

$$CH_3CH_2OH + 4OH^- \rightarrow CH_3COOH + 3H_2O + 4e^- \qquad (6)$$

AEM-type DEFCs were operated at a constant current density of 30 mA cm^{-2} and 200 mA cm^{-2} and the contents of acetaldehyde and acetic acid were determined by enzymatic methods. For comparison, a product assay was also carried out for CEM-type DEFCs operated at a constant current density of 25 mA cm^{-2}. DEFCs used for the product analyses were the same as those for which performance is shown in Fig. 5. The yields of acetaldehyde and acetic acid

Fig. 6. Anode and cathode polarization curves of DEFCs using an AEM and 1.0 M ethanol + 0.5 M KOH solution (●, ○) or a CEM and 1.0 M ethanol aqueous solution (■, □) (4 ml min^{-1}), as an electrolyte membrane and a fuel, respectively, at room temperature and atmospheric pressure. Anode: 3 mg cm^{-2} PtRu black, cathode: 3 mg cm^{-2} Pt black, and cathode gas: humidified O$_2$ (100 ml min^{-1}).

Table 1
Products and their yields during the operation of DEFCs.

Membrane	Current density	Anode potential	CH$_3$CHO (yield)	CH$_3$COOH (yield)
AEM	30 mA cm^{-2}	0.28 V	0.066 mM (1.4 ± 2%)	2.15 mM (92 ± 9%)
AEM	200 mA cm^{-2}	0.48 V	0.226 mM (0.7 ± 1%)	14.32 mM (92 ± 9%)
CEM	25 mA cm^{-2}	0.48 V	1.98 mM (51 ± 5%)	1.03 mM (53 ± 5%)

were calculated from their concentration, flow rate (4 ml min^{-1}), the electric charge, Faraday constant, and the number of electrons related to the corresponding oxidation reaction (two for acetaldehyde and four for acetic acid, as described in Eqs. (5) and (6), respectively).

The results of the product analyses and operating conditions are summarized in Table 1. AEM-type DEFCs operated at both 30 mA cm^{-2} and 200 mA cm^{-2} produced more than 90% acetic acid and trace amounts of acetaldehyde, despite the difference in anode potential (0.28 V and 0.48 V, respectively). In contrast, in CEM-type DEFCs operated at 25 mA cm^{-2}, both acetaldehyde and acetic acid were detected in a ratio of about 1:1 at the anode potential of 0.48 V. The results of a previous study, in which ethanol oxidation was investigated using alkaline MEAs with a Pt anode by differential electrochemical mass spectrometry, suggest that the current efficiency of CO$_2$ formation was around 55% at 0.8 V versus RHE and 60 °C, whereas it was only 2% for acidic MEAs under the same conditions [34]. On the other hand, our experiment shows that only slight CO$_2$ formation is possible, since the sum of acetaldehyde and acetic acid formation reaches almost 93%. The difference between these results is due to the difference in the experimental conditions. The present study used more moderate conditions than the previous study, i.e., below 0.5 V versus RHE at room temperature. If the same experiments were carried out at higher temperature and higher anodic potential, the contribution of CO$_2$ formation is expected to be higher. The possible formation of CO$_2$ during the operation of the AEM-type DEFCs may form carbonate in alkaline medium and decrease the ionic conductivity of AEM. However, the decrease in the cell performance was not observed, since the co-supply of KOH solution with ethanol replaces the carbonate with OH$^-$ in AEM.

The results listed in Table 1 suggest that four electrons can be obtained from 1 mol of ethanol in AEM-type fuel cells, whereas about three electrons can be obtained in CEM-type fuel cells, as evaluated from the equal contribution of two- and four-electron processes. AEM-type DEFCs can convert 1.3 times more electric energy from ethanol fuel than with a CEM. This advantage should contribute to the development of power sources with higher energy density. From these product assays, the anodic reaction of AEM-type DEFCs can be estimated to be a four-electron oxidation of ethanol to acetic acid, as described by Eq. (6). The total reaction of the DEFCs can be explained by Eq. (8) in combination with the cathode reaction in Eq. (7). The theoretical voltage of the fuel cell can be calculated to be 1.172 V from the redox potentials of −0.769 V and 0.403 V for Eqs. (6) and (7), respectively, under standard conditions:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{7}$$

$$CH_3CH_2OH + O_2 \rightarrow CH_3COOH + H_2O \tag{8}$$
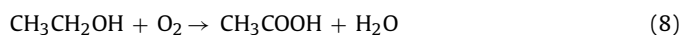
4. Conclusions

The electrochemical oxidation of ethanol was enhanced in alkaline medium compared with acid medium. DEFCs were prepared using an AEM, PtRu, and Pt catalysts as electrolyte membrane, anode, and cathode, respectively. The fundamental characteristics of the DEFCs were investigated in terms of cell performance and product analyses, and compared with those of conventional CEM-type DEFCs. The AEM-type DEFCs still needed the co-supply of alkaline solution, e.g., 0.5 M KOH aqueous solution, with fuel to compensate for insufficient OH$^-$ conductivity in an AEM. The maximum power density of AEM-type DEFCs was about 10-fold greater than that of CEM-type DEFCs. The catalytic activity for both ethanol oxidation in the anode and oxygen reduction in the cathode was enhanced in AEM-type DEFCs compared with CEM-type DEFCs. The product analysis suggested that the anodic reaction of AEM-type DEFCs is four-electron oxidation from ethanol to acetic acid at room temperature.

References

[1] U.B. Demirci, J. Power Sources 169 (2007) 239.
[2] W. Qian, D.P. Wilkinson, J. Shen, H. Wang, J. Zhang, J. Power Sources 154 (2006) 202.
[3] S.K. Kamarudin, W.R.W. Daud, S.L. Ho, U.A. Hasran, J. Power Sources 163 (2007) 743.
[4] H. Liu, C. Song, L. Zhang, J. Zhang, H. Wang, D.P. Wilkinson, J. Power Sources 155 (2006) 95.
[5] A. Heinzel, V.M. Barragán, J. Power Sources 84 (1999) 70.
[6] N. Fujiwara, Z. Siroma, T. Ioroi, K. Yasuda, J. Power Sources 164 (2007) 457.
[7] N. Fujiwara, K. Yasuda, T. Ioroi, Z. Siroma, Y. Miyazaki, T. Kobayashi, Electrochem. Solid-State Lett. 6 (2003) A257.
[8] N. Fujiwara, S. Yamazaki, Z. Siroma, T. Ioroi, K. Yasuda, Electrochem. Commun. 8 (2006) 720.
[9] N. Fujiwara, S. Yamazaki, Z. Siroma, T. Ioroi, K. Yasuda, J. Power Sources 167 (2007) 32.
[10] C. Lamy, A. Lima, V. LeRhun, F. Delime, C. Coutanceau, J.-M. Léger, J. Power Sources 105 (2002) 283.
[11] S. Song, P. Tsiakaras, Appl. Catal. B: Environ. 63 (2006) 187.
[12] A.S. Aricò, P. Cretì, P.L. Antonucci, V. Antonucci, Electrochem. Solid-State Lett. 1 (1998) 66.
[13] S. Rousseau, C. Coutanceau, C. Lamy, J.-M. Léger, J. Power Sources 158 (2006) 18.
[14] Q. Wang, G.Q. Sun, L. Cao, L.H. Jiang, G.X. Wang, S.L. Wang, S.H. Yang, Q. Xin, J. Power Sources 177 (2008) 142.
[15] E. Antolini, J. Power Sources 170 (2007) 1.
[16] N. Fujiwara, K.A. Friedrich, U. Stimming, J. Electroanal. Chem. 472 (1999) 120.
[17] A. Ghumman, C. Vink, O. Yepez, P.G. Pickup, J. Power Sources 177 (2008) 71.
[18] F. Vigier, C. Coutanceau, F. Hahn, E.M. Belgsir, C. Lamy, J. Electroanal. Chem. 563 (2004) 81.
[19] R. Alcala, J.W. Shabaker, G.W. Huber, M.A. Sanchez-Castillo, J.A. Dumesic, J. Phys. Chem. B 109 (2005) 2074.
[20] Z.B. Wang, G.P. Yin, Y.G. Lin, J. Power Sources 170 (2007) 242.
[21] E.H. Yu, K. Scott, J. Power Sources 137 (2004) 248.
[22] K. Scott, E. Yu, G. Vlachogiannopoulos, M. Shivare, N. Duteanu, J. Power Sources 175 (2008) 452.
[23] C. Coutanceau, L. Demarconnay, C. Lamy, J.-M. Léger, J. Power Sources 156 (2006) 14.
[24] J.R. Varcoe, R.C.T. Slade, E. Lam How Yee, S.D. Poynton, D.J. Driscoll, J. Power Sources 173 (2007) 194.
[25] K. Matsuoka, Y. Iriyama, T. Abe, M. Matsuoka, Z. Ogumi, J. Power Sources 150 (2005) 27.
[26] K. Asazawa, K. Yamada, H. Tanaka, A. Oka, M. Taniguchi, T. Kobayashi, Angew. Chem. Int. Ed. 46 (2007) 8024.

[27] T.J. Schmidt, H.A. Gasteiger, G.D. Stäb, P.M. Urban, D.M. Kolb, R.J. Behm, J. Electrochem. Soc. 145 (1998) 2354.
[28] M.S. Wilson, S. Gottesfeld, J. Appl. Electrochem. 22 (1992) 1.
[29] M. Mizuhata, K. Yasuda, K. Oguro, H. Takenaka, Denki Kagaku 64 (1996) 692.
[30] H.-O. Beutler, in: H.U. Bergmeyer, J. Bergmeyer, M. Graßl (Eds.), Methods of Enzymatic Analysis, vol. VI, 3rd edn., Verlag Chemie, Weinheim, Deerfield Beach/Florida/Basel, 1984, pp. 606–613.
[31] H.-O. Beutler, in: H.U. Bergmeyer, J. Bergmeyer, M. Graßl (Eds.), Methods of Enzymatic Analysis, vol. VI, 3rd edn., Verlag Chemie, Weinheim, Deerfield Beach/Florida/Basel, 1984, pp. 639–645.
[32] S. Chen, M. Schell, J. Electroanal. Chem. 478 (1999) 108.
[33] J.S. Spendelow, A. Wieckowski, Phys. Chem. Chem. Phys. 9 (2007) 2654.
[34] V. Rao, Hariyanto, U. Cremers, C. Stimming, Fuel Cells 7 (2007) 417.