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Alkaline direct alcohol fuel cells using an anion exchange membrane

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Abstract

Alkaline direct alcohol fuel cells using an OH-form anion exchange membrane and polyhydric alcohols were studied. A high open circuit voltage of ca. 800 mV was obtained for a cell using Pt–Ru/C (anode) and Pt/C (cathode) at 323 K, which was about 100–200 mV higher than that for a DMFC using Nafion®. The maximum power densities were in the order of ethylene glycol > glycerol > methanol > erythritol > xylitol. Silver catalysts were used as a cathode catalyst to fabricate alkaline fuel cells, since silver catalyst is almost inactive in the oxidation of polyhydric alcohols. Alkaline direct ethylene glycol fuel cells using silver as a cathode catalyst gave excellent performance because higher concentrations of fuel could be supplied to the anode.

Keywords: Direct alcohol fuel cells; Polyhydric alcohol; Anion exchange membrane; Alkaline fuel cells; Silver catalyst

1. Introduction

The direct alcohol fuel cell (DAFC) has attracted considerable attention as an energy source for transport and other portable applications. DAFCs are compact compared to polymer electrolyte fuel cells that use hydrogen and are particularly suitable as power sources for portable electric devices, such as cellular phones, notebook computers, etc. Liquid fuels, such as methanol [1–3], ethanol [4,5], ethylene glycol [6,7], etc., which have a higher volumetric energy density and better energy efficiency, are more easily stored and transported than gaseous fuels.

Direct methanol fuel cells (DMFCs) that use perfluorinated cation exchange membranes such as Nafion® and precious metal catalysts have been extensively studied and are promising candidates for use in portable power sources [8]. However, the development of DMFCs has been hampered due to several serious problems: (i) slow electrode-kinetics, (ii) CO poisoning of Pt catalyst at lower temperature, (iii) methanol crossover and (iv) high costs of the membrane, catalyst, separator and so on. In addition, the high volatility and toxicity of methanol may cause serious problems when portable electronic devices with DMFCs as power sources are commercialized, though such problems are currently underestimated.

It is well known that the electrode-kinetics of oxygen reduction are enhanced in an alkaline medium [9]. One of the advantages of alkaline direct fuel cells is the use of non-precious metals, such as silver catalysts [10] and perovskite-type oxides [11]. These catalysts are not only inexpensive, they are also tolerant to methanol crossover, and are very active for the reduction of oxygen to OH^- in alkaline solution, but are almost inactive for alcohol oxidation.

A problem with alkaline fuel cells is the progressive carbonation of the solution due to CO_2 from air or the oxidation product of the fuel:

$$2OH^- + CO_2 \rightarrow CO_3{}^{2-} + H_2O.$$

Carbon dioxide reduces the pH of the alkaline solution, leading to a decrease in reactivity for the electro-oxidation of methanol. We systematically studied the electro-oxidation of polyhydric alcohols in alkaline solutions using a platinum electrode. As a result, ethylene glycol showed the highest re-

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activity among the alcohols examined in KOH and K_2CO_3 solutions and, therefore, ethylene glycol may be able to overcome the above carbonation problem. In addition, ethylene glycol is much less toxic and volatile than methanol. Therefore, ethylene glycol was examined preliminarily in a simple model fuel cell under alkaline conditions [12].

Recently, we reported preliminary results with direct alcohol fuel cells using hydrocarbon-type anion exchange membrane and platinum catalysts [13]. Hydrocarbon-type anion exchange membranes are known to be less expensive than perfluorinated cation exchange membranes. Although hydrocarbon-type membranes are not as chemically stable as perfluorinated membranes, an alcohol penetrating into an anion exchange membrane is expected to protect the membrane from attack by active substances such as peroxide.

In the present study, alkaline direct alcohol fuel cells were fabricated for the first time by using anion exchange membrane, polyhydric alcohols and silver catalyst. In addition, the performance and polarization behaviors of the anode and cathode are discussed.

2. Experimental

2.1. Preparation of an OH-form anion exchange membrane

Ammonium-type anion exchange membrane (AHA) was supplied by Tokuyama Co., Japan in Cl form. The AHA membrane is composed of tetraalkyl ammonium groups as fixed cation groups bonded to a polyolefin backbone chain with a thickness of 240 μm. The Cl-form membrane was changed to an OH-form as follows.

The Cl-form membranes were rinsed several times with ultra-pure water, and then immersed in 300 ml of 1 mol dm^{-3} KOH aqueous solution at 313 K for 2 h to exchange Cl^- with OH^-. The resultant membranes were washed again with ultra-pure water and immersed in ultra-pure water at 313 K for 2 h and 298 K for 24 h. The conductivity of this membrane was ca. 14 mS cm^{-1} [13].

2.2. Fabrication of direct alkaline fuel cells

Fig. 1 shows a schematic representation of a direct alkaline fuel cell that uses an anion exchange membrane. The cell consists of a membrane, anode, cathode and a dynamic hydrogen electrode (DHE). An OH-form anion exchange membrane was used as the electrolyte. Pt/C (E-TEK, loaded with 1 mg cm^{-2} Pt with gas diffusion layer) or Ag/C (E-TEK, E-TEK, loaded with 1 mg cm^{-2} Ag with gas diffusion layer) was used as a cathode and Pt–Ru/C (E-TEK, loaded with 4 mg cm^{-2} of Pt–Ru) was used as an anode. The geometric surface area of electrode was 5 cm^2. Quarternalized poly(4-vinylpyridine) (Koei Chemical Co., M.W. ca. 102,000) 4-VP was used as electrolyte in electrode-layer. The DHE was prepared by pressing two platinized platinum plates (ca. 2 mm × 20 mm) on both sides of the membrane. The resultant DHE showed almost the same potential as the RHE. Unless otherwise noted, all potentials are referenced to the DHE.

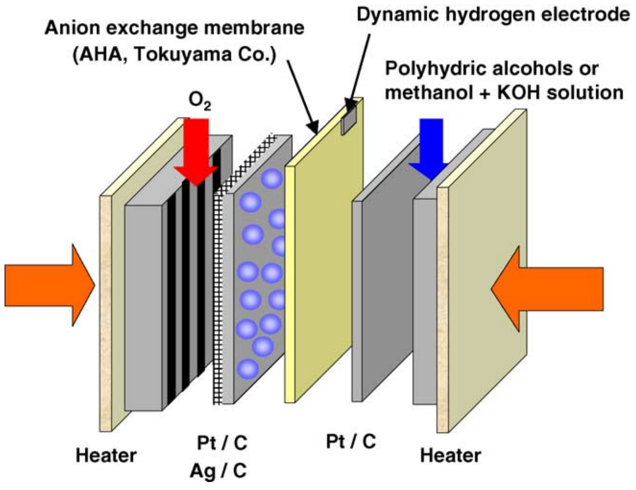

Fig. 1. Schematic representation of a direct alkaline fuel cell using an anion exchange membrane.

2.3. Single-cell tests

The polyhydric alcohols examined in the present study were ethylene glycol (Aldrich, 99.9%), glycerol (Wako Pure Chemicals, 99.9%), *meso*-erythritol (Nacalai Tesque, 98%) and xylitol (Nacalai Tesque, 98%). Methanol (Wako Pure Chemicals) was used for comparison. Methanol and the four polyhydric alcohols were dissolved at 1 mol dm^{-3} in 1 mol dm^{-3} KOH aqueous solution and supplied to the anode at 50 mL min^{-1}. Humid oxygen (99.9999%, Teisan) was used as a cathode gas at a flow rate of 50 mL min^{-1}. All reactions were performed at an operating temperature of 323 K.

3. Results and discussion

Fig. 2 shows current density–cell voltage curves of fuel cells fed with 1 M polyhydric alcohols and methanol at 323 K.

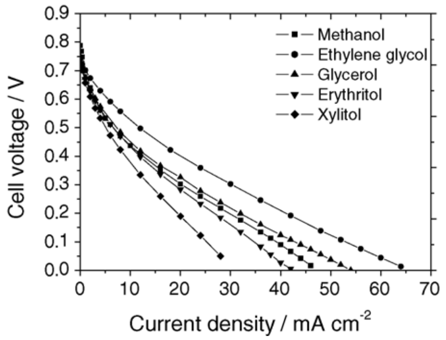

Fig. 2. Cell voltage curves for alkaline direct alcohol fuel cells using polyhydric alcohols. Anode: Pt–Ru/C; cathode: Pt/C; temperature: 323 K. Methanol (■), ethylene glycol (●), glycerol (▲), erythritol (▼), xylitol (♦).

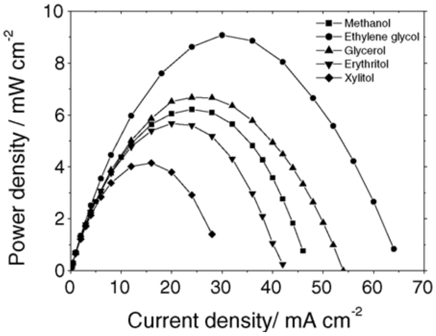

Fig. 3. Power density curves calculated from the data shown in Fig. 2. Anode: Pt–Ru/C; cathode: Pt/C; temperature: 323 K. Methanol (■), ethylene glycol (●), glycerol (▲), erythritol (▼), xylitol (♦).

The anode and cathode catalysts were Pt–Ru/C and Pt/C, respectively. The open circuit voltages of the cells using methanol and polyhydric alcohols were almost identical at about 800 mV. These values were about 100–200 mV higher than that of a DMFC with Nafion® at 303–363 K [14]. It has been reported that the open circuit potential of oxygen reduction in alkaline media was more positive than that in acidic media [9]. Furthermore, CO poisoning of the Pt catalyst in alkaline solution was less significant than that in acidic solution [15], and the open circuit potential in alkaline solution was more negative. Accordingly, higher open circuit voltages for direct alcohol fuel cells using an anion exchange membrane were achieved in the present study.

Fig. 3 shows the power density curves calculated from the data shown in Fig. 2. The maximum power densities were in the order of ethylene glycol > glycerol > methanol > erythritol > xylitol. The direct ethylene glycol fuel cell showed the highest power density of 9.5 mW cm^{-2}. Peled et al. reported direct ethylene glycol fuel cells using a nanoporous proton-conducting membrane (NP-PCM) at 353–403 K; the cell using methanol showed a higher power density than that using ethylene glycol [16,17].

The alkaline direct ethylene glycol fuel cells in this study showed higher cell performance than the alkaline direct methanol fuel cell. In our previous study, we studied the electro-oxidation of methanol and polyhydric alcohols in acid and alkaline solutions. Although methanol showed higher reactivity than ethylene glycol in acid solutions, ethylene glycol gave much higher reactivity than methanol in alkaline solutions [12,18]. Therefore, these results in the present study were in good agreement with those in our previous study.

Figs. 4 and 5 show the polarization curves of the anode and cathode in alkaline direct alcohol fuel cells at 323 K, respectively. The open circuit potential of a direct ethylene glycol fuel cell was ca. 200 mV (versus DHE) for the anode and ca. 800 mV (versus DHE) for the cathode. At both the anode and cathode, the open circuit potentials of a direct alcohol fuel cell using an anion exchange membrane showed higher performance than those of a DMFC using Nafion®. This is ascribed to the higher reactivity of polyhydric alcohol and oxygen in alkaline media. The difference between the anode and cathode potentials in the present study is somewhat difficult to explain. The potentials depended on the kinds of alcohols. This potential dependency was observed on both the anode and cathode sides. The differences in the anode potential were ascribed to the reactivity of the fuels in alkaline media. Potential changes at the cathode seemed to involve two important factors. One was the crossover rate of fuels from the anode to cathode, which is closely related to the molecular weight, interaction between the membrane and fuel, current density and so on. The other was the reactivity of the permeated fuel at the cathode. As mentioned above, methanol and the polyhydric alcohols showed different electro-chemical activities. Thus, the cathode potential was influenced by these two factors.

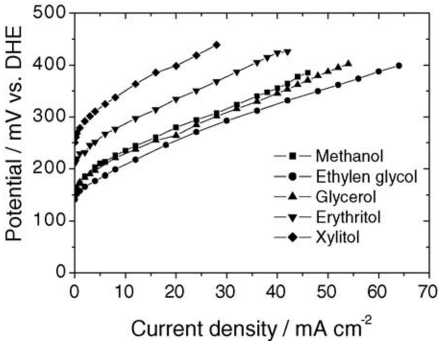

Fig. 4. Polarization curves of anode for alkaline direct alcohol fuel cells using polyhydric alcohols. Anode: Pt–Ru/C; cathode: Pt/C; temperature: 323 K. Methanol (■), ethylene glycol (●), glycerol (▲), erythritol (▼), xylitol (♦).

Fig. 6 shows the performance of alkaline direct ethylene glycol fuel cells using Ag/C as a cathode catalyst and 1–5 M ethylene glycol as a fuel. The open circuit voltage of a cell with a silver catalyst was ca. 650 mV, which was ca. 150 mV lower than that of a cell with a platinum catalyst under the same conditions, as shown in Fig. 2. However, the performance of alkaline direct ethylene glycol fuel cells using Ag/C was improved by increasing the concentration of ethylene glycol. The performance of a cell with 3 or 5 M ethylene glycol solution was comparable to that of a cell using Pt/C

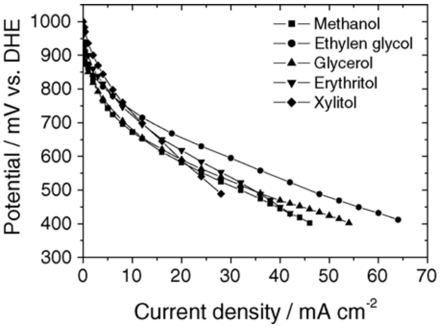

Fig. 5. Polarization curves of cathode for alkaline direct alcohol fuel cells using polyhydric alcohols. Anode: Pt–Ru/C; cathode: Pt/C; temperature: 323 K. Methanol (■), ethylene glycol (●), glycerol (▲), erythritol (▼), xylitol (♦).

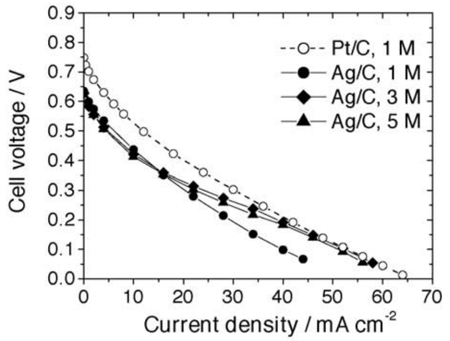

Fig. 6. Cell voltage curves for alkaline alcohol direct fuel cells using 1–5 M ethylene glycol. Concentration of ethylene glycol: 1 M (○, ●), 3 M (◆) and 5 M (▲). Anode: Pt–Ru/C; cathode: Ag/C (closed symbol) or Pt/C (open symbol); temperature: 323 K.

catalyst in the large current density region (>40 mA cm^2). The maximum power densities were 8.1 and 7.4 mW cm^{-2} at 3 and 5 M ethylene glycol, respectively. Considerable work has been done on methanol crossover for DMFCs, which use 1 M methanol solution, since concentrated methanol significantly increased methanol crossover, resulting in higher methanol flux and electro-osmotic drag [19–21]. The performance of alkaline direct ethylene glycol fuel cells with a platinum catalyst was decreased by the use of concentrated ethylene glycol, since oxygen reduction and ethylene glycol oxidation take place on a Pt catalyst, which impairs cathode performance. Silver catalyst shows good catalytic activity for oxygen reduction with predominant direct four-electron charge transfer in alkaline solution [9]. In addition, the electro-chemical oxidation of ethylene glycol was very slow on a silver catalyst. Therefore, silver catalyst showed high performance even in concentrated ethylene glycol.

Fig. 7 shows the anode and cathode potential curves for an alkaline direct ethylene glycol fuel cell using a silver catalyst and 1–5 M ethylene glycol at 323 K. The performance of the anode was improved by increasing the ethylene glycol concentration and showed an anode polarization of 315 mV versus DHE at a load current density of 40 mV cm^{-2} with 5 M ethylene glycol. The performance of the cathode was almost identical even at a higher concentration of ethylene glycol. We confirmed that silver was an excellent catalyst for selective oxygen reduction in the presence of permeated ethylene glycol.

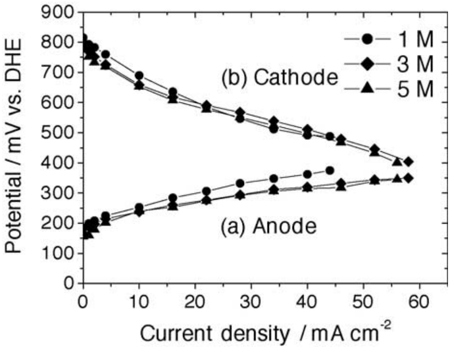

Fig. 7. Polarization curves of anode (a) and cathode (b) for alkaline direct alcohol fuel cells using 1–5 M ethylene glycol at 323 K. Concentration of ethylene glycol: 1 M (○, ●), 3 M (◆) and 5 M (▲). Anode Pt–Ru/C; cathode Ag/C.

The power density of an alkaline direct alcohol fuel cell was lower than that of a DMFC using Nafion®, since the polarization at the cathode was about twice as large as that at the anode of an alkaline direct alcohol fuel cell. The further development of alkaline direct alcohol fuel cells will require a chemically stable triple phase boundary at the cathode side, for example by introducing anion exchange solution, similar to Nafion® solution used in acid-type DMFC.

4. Conclusions

Alkaline direct alcohol fuel cells using an anion exchange membrane were demonstrated at 323 K, and showed a high open circuit voltage of ca. 800 mV. Ethylene glycol showed the highest power density (9.8 mW cm^{-2}) among the alcohols examined.

In addition, alkaline direct alcohol fuel cells using silver as a cathode catalyst showed good performance comparable to that using platinum catalyst with 3–5 M ethylene glycol.

Acknowledgement

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