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Alkaline direct alcohol fuel cells using an anion exchange membrane

Koji Matsuoka [a], Yasutoshi Iriyama [a], Takeshi Abe [a], Masao Matsuoka [b], Zempachi Ogumi [a,*]

[a] *Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan*
[b] *Faculty of Science and Engineering, Ritsumeikan University, Kusatsu, Shiga 525-8577, Japan*

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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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[*] Corresponding author. Tel.: +81 75 383 2487; fax: +81 75 383 2488.
E-mail address: ogumi@scl.kyoto-u.ac.jp (Z. Ogumi).

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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.

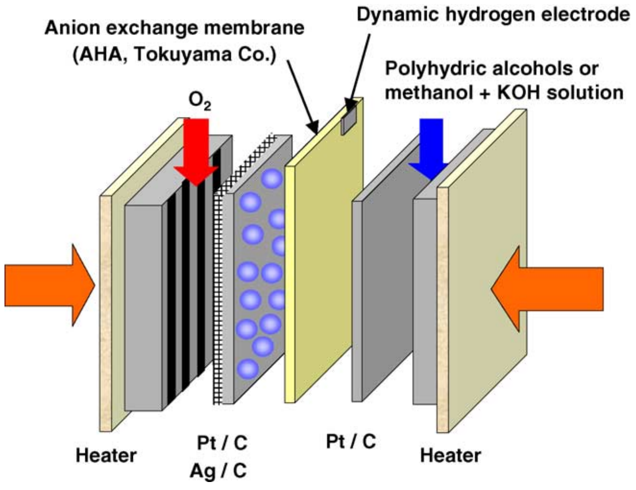

Fig. 1. Schematic representation of a direct alkaline fuel cell using an anion exchange membrane.

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.

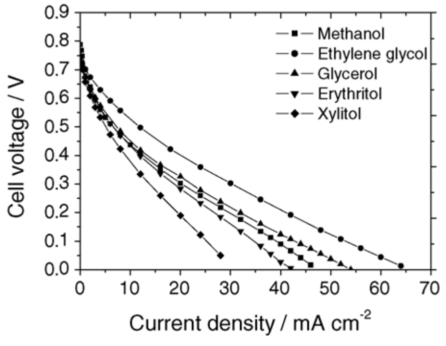

Fig. 2. Cell voltage curves for alkaline direct alcohol fuel cells using polyhydric alcohols. Anode: Pt–Ru/C; cathode: Pt/C; temperature: 323 K. Methanol (■), ethylene glycol (●), glycerol (▲), erythritol (▼), xylitol (♦).