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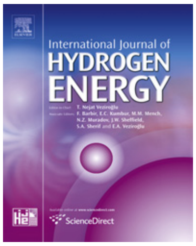

Performance of an alkaline-acid direct ethanol fuel cell

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ABSTRACT

This paper reports on the performance of an alkaline-acid direct ethanol fuel cell (AA-DEFC) that is composed of an alkaline anode, a membrane and an acid cathode. The effects of membrane thickness and the concentrations of various species at both the anode and cathode on the cell performance are investigated. It has been demonstrated that the peak power density of this AA-DEFC that employs a 25-μm thick membrane is as high as 360 mW cm^{-2} at 60 °C, which is about 6 times higher than the performance of conventional DEFCs reported in the literature.

1. Introduction

Ethanol is a sustainable, carbon-neutral transportation fuel source. It is an ideal fuel for direct oxidation fuel cells for portable and mobile applications, as it offers multiple advantages over hydrogen and methanol, including higher energy density and ease of transportation, storage and handling. Hence, direct ethanol fuel cells (DEFCs) have recently received ever-increasing attention [1–4].

Typically, conventional DEFCs can be divided into two types in terms of the employed membrane: proton exchange membrane direct ethanol fuel cells (PEM-DEFCs) and anion exchange membrane direct ethanol fuel cells (AEM-DEFCs). Past efforts have been mainly devoted to PEM-DEFCs and significant progress has been made [5–7]. However, the sluggish ethanol oxidation reaction (EOR) kinetics is still a main barrier that limits the cell performance of PEM-DEFCs. Moreover, this problem is rather difficult to be solved based on the acid electrolyte, even with the Pt-based catalysts. On the other hand, unlike in acid media, the kinetics of both the EOR and oxygen reduction reaction (ORR) in alkaline media become much faster than that in the acid medium. It has been recently demonstrated that when the acid electrolyte was changed to alkaline one, i.e. AEM, the cell performance could be substantially improved [8–13]. Although promising, the cell performance still needs to be substantially improved before the widespread commercialization. Another important parameter that limits the performance of DEFCs operating under both acid and alkaline media is that thermodynamically, their theoretical voltage is low (1.14 V).

Recently, we proposed a new type of DEFC, termed as alkaline-acid DEFC (AA-DEFC) shown in Fig. 1, which is composed of an alkaline anode, a membrane and an acid cathode [14]. The anolyte is an aqueous solution of ethanol

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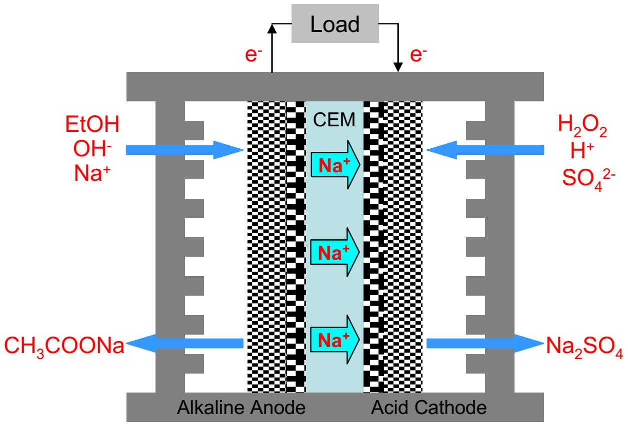

Fig. 1 – Schematic of the alkaline-acid direct ethanol fuel cell.

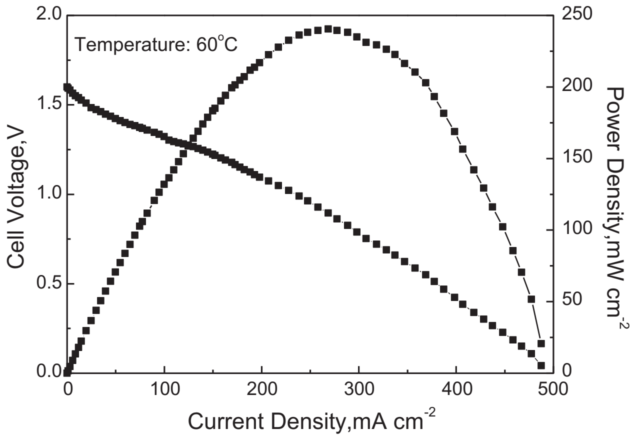

Fig. 2 – Polarization and power density curves of the alkaline-acid DEFC [14].

and sodium hydroxide, while the catholyte is an aqueous solution of hydrogen peroxide and sulfuric acid. In addition, a cation exchange membrane (CEM) is employed to conduct sodium ions. On the anode, ethanol reacts with OH^- provided by NaOH according to [1,15]:

$$CH_3CH_2OH + 5NaOH \rightarrow CH_3COONa + 4Na^+ + 4e^- + 4H_2O \quad (1)$$

The produced electrons pass through an external electrical load and arrive at the cathode. In the meantime, Na^+ ions as the charge carrier migrate from the anode to the cathode to close the internal circuit.

On the cathode, hydrogen peroxide reacts with H^+ provided by H_2SO_4 and electrons to produce water according to:

$$2H_2O_2 + 2H_2SO_4 + 4e^- \rightarrow 2SO_4^{2-} + 4H_2O \quad (2)$$

Hence, Na_2SO_4 will be produced by combining Na^+ and SO_4^{2-} in the cathode, which can be taken away by the cathode solution flow. The overall reaction is obtained by combining the EOR given by Eq. (1) and the hydrogen peroxide reduction reaction (HPRR) given by Eq. (2), i.e.:

$$CH_3CH_2OH + 5NaOH + 2H_2O_2 + 2H_2SO_4 \rightarrow CH_3COONa + 2Na_2SO_4 + 8H_2O \quad (3)$$

We tested the above-described AA-DEFC and demonstrated that the peak power density was as high as 240 mW cm^{-2} at 60 °C, as can be evidenced from Fig. 2 [14]. The high performance of this type of DEFC can be attributed to the following reasons: 1) the fuel cell has a high theoretical voltage (2.52 V) rendered by the alkaline anode and acid cathode [14], 2) it has a low overpotential of HPRR [16–22], and 3) it renders fast kinetics of the EOR at a lower potential ($E_a^o = 0.74$ V) [9,12,14].

The main objective of this work was to investigate the effect of membrane thickness on the performance of the AA-DEFC. In addition, we also investigated the effects of the concentrations of various species, including hydrogen peroxide, and sulfuric acid, ethanol, and sodium hydroxide, on the cell performance. We show that the AA-DEFC employing a thinner membrane (25 μm) can yield a peak power density as high as 360 mW cm^{-2} at 60 °C.

2. Experimental

2.1. *Membrane electrode assembly*

Four membrane electrode assemblies (MEAs), with different thickness CEMs, were prepared in this work. The CEMs used in this work were the Nafion series membrane, N211 (25 μm), N212 (50 μm), N115 (125 μm), and N117 (175 μm), which were treated as the cation conductors. The procedures of treating the Nafion membranes included [23,24]: i) immersing them in 10 wt.% NaOH solution; ii) heating them to 80 °C for 1 h; and iii) washing them by deionized (DI) water several times. The four CEM-MEAs had the same anode and cathode electrodes and the same active area of 1.0 cm × 1.0 cm. The anode electrode was formed by following the steps: i) a catalyst ink was prepared by mixing a homemade PdNi/C with a loading of 1.0 mg cm^{-2}, ethanol as the solvent and 5 wt.% Nafion as the binder [25]; ii) the anode catalyst ink was stirred continuously in an ultrasonic bath for 20 min such that it was well dispersed and iii) the anode catalyst ink was brushed onto a piece of nickel foam (Hohsen Corp., Japan) that served as the backing layer. Similarly, on the cathode, the catalyst ink was prepared by mixing 60 wt.% Pt/C (Johnson-Matthey) with a loading of 3.9 mg cm^{-2}, ethanol as the solvent, and 5 wt.% Nafion as the binder [14]. Subsequently, the cathode catalyst ink was brushed onto a piece of carbon cloth (ETEK, Type A) that served as the backing layer to form a cathode electrode.

2.2. *Fuel-cell setup and instrumentation*

Each MEA was fixed between an anode and a cathode flow field. The both flow fields were made of 316 L stainless steel plate, in which a single serpentine flow channel, 0.5 mm deep and 1.0 mm wide, was grooved by the wire-cut technique. An alkaline solution containing ethanol and NaOH was fed into the anode flow channel at a flow rate of 2.0 mL min^{-1} by a peristaltic pump, while an acid solution containing H_2O_2 and sulfuric acid (H_2SO_4) was fed into the cathode flow channel at a flow rate of 2.0 mL min^{-1} by another peristaltic pump. Additionally, the cell temperature was measured with