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
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 $\text{OH}^-$ provided by NaOH according to [1,15]:

$$
\text{CH}_3\text{CH}_2\text{OH} + 5\text{NaOH} \rightarrow \text{CH}_3\text{COONa} + 4\text{Na}^+ + 4\text{e}^- + 4\text{H}_2\text{O} \quad (1)
$$

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

On the cathode, hydrogen peroxide reacts with $\text{H}^+$ provided by $\text{H}_2\text{SO}_4$ and electrons to produce water according to:

$$
2\text{H}_2\text{O}_2 + 2\text{H}_2\text{SO}_4 + 4\text{e}^- \rightarrow 2\text{SO}_4^{2-} + 4\text{H}_2\text{O} \quad (2)
$$

Hence, $\text{Na}_2\text{SO}_4$ will be produced by combining $\text{Na}^+$ and $\text{SO}_4^{2-}$ 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.:

$$
\text{CH}_3\text{CH}_2\text{OH} + 5\text{NaOH} + 2\text{H}_2\text{O}_2 + 2\text{H}_2\text{SO}_4 \rightarrow \text{CH}_3\text{COONa} + 2\text{Na}_2\text{SO}_4 + 8\text{H}_2\text{O} \quad (3)
$$

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 ($E^*_{\text{a}} = 0.74$ 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.

![Fig. 1 – Schematic of the alkaline-acid direct ethanol fuel cell.](image1)

![Fig. 2 – Polarization and power density curves of the alkaline-acid DEFC [14].](image2)

### 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 $\text{H}_2\text{O}_2$ and sulfuric acid (H$_2$SO$_4$) 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
3. Results and discussion

3.1. Effect of hydrogen peroxide concentrations

Fig. 3a shows the polarization curves with different hydrogen peroxide concentrations ranging from 1.0 M to 6.0 M when the sulfuric acid concentration was fixed at 1.0 M and the anode solution was composed of 3.0 M ethanol and 5.0 M NaOH. It can be seen that in the low current density region (below 100 mA cm\(^{-2}\)), the cell voltage decreased with an increase in hydrogen peroxide concentration, but at high current densities the cell voltage first increased with the hydrogen peroxide concentration and then decreased. The 4.0-M hydrogen peroxide concentration exhibited the highest performance. At low current densities, the decrease in the cell voltage with the hydrogen peroxide concentration can be mainly attributed to \(\text{H}_2\text{O}_2\) crossover from the cathode to the anode as the Nafion membranes are also permeable to \(\text{H}_2\text{O}_2\) [26]. The permeated \(\text{H}_2\text{O}_2\) can react with ethanol and thus form the mixed potential at the anode, which increases the anode potential, thus decreasing the voltage. Increasing the hydrogen peroxide concentration at the cathode can cause a higher rate of \(\text{H}_2\text{O}_2\) crossover, leading to an increase in the mixed potential at the anode, thereby increasing the anode potential, as evidenced by the measured anode potentials shown in Fig. 3b. As a result, the cell voltage decreased with the hydrogen peroxide concentration at low current densities. At high current densities, the underlying mechanisms leading to the performance behavior is more complex. When the hydrogen peroxide concentration is increased from 1.0 M to 4.0 M, although the anode potential slightly increases with the hydrogen peroxide concentration as a result of the \(\text{H}_2\text{O}_2\) crossover, the mass transport at the cathode are also enhanced, reducing the concentration polarization loss. Moreover, the reduced polarization loss not only compensates the mixed potential in the anode resulting from the \(\text{H}_2\text{O}_2\) crossover but also improves the cell performance. Therefore, the cell voltage improved with increasing the hydrogen peroxide concentration from 1.0 M to 4.0 M. When the hydrogen peroxide concentration was further increased to 6.0 M, the cathode potential did not change much as hydrogen peroxide concentration in the cathode catalyst layer (CL) is sufficient to ensure the \(\text{H}_2\text{O}_2\) transport. On the other hand, the high hydrogen peroxide concentration causes rather serious \(\text{H}_2\text{O}_2\) crossover, leading to the increased anode potential and thus decreasing the cell performance, as shown in Fig. 3b. Therefore, the cell voltage was degraded when the hydrogen peroxide concentration was increased to 6.0 M, resulting in an optimal hydrogen peroxide concentration that can yield the highest performance at high current densities.

3.2. Effect of sulfuric acid concentrations

The polarization curves for different sulfuric acid concentrations ranging from 0.5 M to 2.0 M at a fixed hydrogen peroxide concentration of 4.0 M are presented in Fig. 4a, which shows that the cell performance slightly increased with the sulfuric acid concentration. Similarly, in order to gain insight into the mechanisms leading to the behavior, the respective anode and cathode potentials were also measured, respectively, and are shown in Fig. 4b. It can be seen that the anode potential remained almost the same for different sulfuric acid concentrations but the cathode potential slightly increased with the sulfuric acid concentration. As a result, it can be concluded that the improved cell performance with increasing the sulfuric acid concentration is mainly attributed to the increase in the cathode potential. This is because an increase in the sulfuric acid concentration leads to a higher \(\text{H}^+\) concentration, accelerating the hydrogen peroxide reduction reaction [18]. Therefore the kinetic loss resulting from the hydrogen peroxide reduction reaction can be reduced as the sulfuric...
acid concentration increases, so that the cathode potential and cell performance can be upgraded.

3.3. Effects of ethanol concentrations

We also investigated the effect of ethanol concentrations on the cell performance when the NaOH concentration was fixed at 5.0 M and the cathode solution was composed of 4.0 M hydrogen peroxide and 1.0 M sulfuric acid, as shown in Fig. 5. It can be seen that in the low current density region, the cell voltage increased with increasing the ethanol concentration, but at high current densities the cell voltage first increased with the ethanol concentration and then decreased. In general, for a given anode catalyst, the anode potential depends on the local concentrations of both ethanol and hydroxyl ions in the anode CL. A change in either ethanol or hydroxyl ions concentrations will lead to a change in the other [10–12]. At low current density region, the solutions with 1.0-M and 3.0-M ethanol cause the relatively poor kinetics as a result of insufficient ethanol concentrations in the anode CL. Hence, increasing the ethanol concentration to 5.0 M can maintain the concentrations of both ethanol and hydroxyl ions at an appropriate level and thus yield the highest cell voltage. However, the appropriate concentrations of both ethanol and hydroxyl ions in the anode CL are changed as a result of the increased consumption of reactants at high current densities. For a given NaOH concentration of 5.0 M, there is an optimal ethanol concentration of 3.0 M, yielding the best cell performance. The reason for this behavior is explained as follows. Too low ethanol concentration will result in the slow electrochemical kinetics and the high concentration loss, and thus the decrease in the cell performance; too high ethanol concentration will cause too low hydroxyl ion concentration at the active surfaces, leading to the difficulty in the adsorption of hydroxyl on the active site, hence the electrochemical kinetics is lowered and thus the cell performance is reduced.

3.4. Effect of NaOH concentrations

The effect of NaOH concentrations on the cell performance was also investigated, as shown in Fig. 6. It can be seen that there exists an optimal NaOH concentration of 5.0 M, yielding the best cell performance. The reason for this phenomenon is explained as follows. Generally, the alkalinity of the anode environment not only affects the electrochemical kinetics, but also the transfer of species to the anode [27,28]. Hence, increasing the NaOH concentration can enhance the kinetics of EOR. On the other hand, the solution with too high NaOH concentration (7.0 M) will lead to too low ethanol concentration in the anode CL, causing the high concentration loss and thus the decreased cell performance. Consequently, the competition between the favorable effect of the faster EOR and the adverse effect of the increased concentration loss results in an optimal NaOH concentration (5.0 M) that gives the best cell performance for a fixed ethanol concentration (3.0 M), which is in agreement with the result of our previous work in an AEM-DEFC [12].

3.5. Effect of membrane thickness

The effect of the membrane thickness on the cell performance was investigated and the results are shown in Fig. 7. It can be
seen when the cell discharged, the effect of the membrane thickness on cell performance can be divided into two distinct regions. In the low current density region (<200 mA cm\(^{-2}\)), the cell with a thicker membrane gave a better performance, whereas in the high current density region, the cell with a thinner membrane yielded a better performance. As shown in Fig. 8, the change in membrane thickness leads not only to a change in the rate of species crossover, but also to a change in the internal resistance of the cell. On one hand, due to the higher rate of species crossover, a thinner membrane tends to cause the larger mixed potentials, degrading the cell performance. On the other hand, the use of a thinner membrane will yield a smaller internal resistance, which tends to increase the cell performance. The results presented in Fig. 7 suggest that the predominant factor affecting the cell performance of this AA-DEFC varied with current density. Under the OCV and low current density conditions, Fig. 7 indicates that the mixed potential problem associated with the thinner membrane (25 \(\mu\)m) is more serious. At the moderate and higher current densities, however, the effect of the internal resistance becomes predominant; thus the use of the thinner membrane yielded a higher cell performance. It should be mentioned that the rate of species crossover decreases with increasing current density. This might also contribute to the improved performance with the use of the thinner membrane at higher current densities [29]. It should also be mentioned that there are four species in this system, resulting in the complicated species crossover phenomenon. The parallel work underway is focused on the amount of the species crossover and their effects on the cell performance.

4. Concluding remarks

In this work, we investigated the effects of membrane thickness and the concentrations of various species, including hydrogen peroxide, sulfuric acid, ethanol, and sodium hydroxide, on the performance of the alkaline-acid direct ethanol fuel cell. We have shown that hydrogen peroxide concentration, ethanol concentration, NaOH concentration, and membrane thickness, have significant influences on the cell performance. In particular, we demonstrated that the peak power density of the AA-DEFC with a thinner membrane (25 \(\mu\)m) was as high as 360 mW cm\(^{-2}\), which is about 6 times higher than the performance of conventional DEFCs reported in the literature. It should be mentioned that although this present fuel cell is promising in terms of the cell performance, some fundamental issues with respect to this present fuel cell, such as the hydrogen peroxide decomposition and species crossover, merit extensive future research.

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References


