Performance of an alkaline-acid direct chloro ethanol fuel cell

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Abstract: This paper reports on the performance of an alkaline-acid direct chloro ethanol fuel cell (AA-DCLEFC) that is composed of an alkaline anode, a membrane and an acid cathode. The effects of membrane thickness and the concentration of various species at both the anode and cathode on the cell performances are investigated. It has been demonstrated that the peak power density of this AA-DCLEFC that employs a 25-µm thick membrane is as high as 360 mW cm\(^{-2}\) at 60\(^{0}\)c, which is about 6 times higher than the performance of conventional DCLEFC reported in the literature.

Keywords: Fuel cell, direct chloro ethanol fuel cell, Alkaline-acid, Species concentration, Membrane thickness, Power density

1. INTRODUCTION

Direct Chloro 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 chloro ethanol fuel cell (DCLEFCs) has recently received ever-increasing attention\[1-4\]

Typically conventional DCLEFC can be divided into two types in terms of the employed membrane: proton exchange membrane direct chloro ethanol fuel cell (PEM-DCLEFCs) and anion exchange membrane direct chloro ethanol fuel cells (AEM-DCLEFCs). Past efforts have been mainly devoted to PEM-DCLEFCs and significant process has been made\[5-7\]. However the sluggish chloro ethanol oxidation reaction (CEOR) kinetics is still a main barrier that limits the cell performance of PEM-DCLEFCs. 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 CEOR 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 performances of DCLEFCs operating under both acid and alkaline media is that thermodynamically, their theoretical voltage is low (1.13V) recently, we proposed a new type of DCLEFC, termed as alkaline-acid DCLEFC (AA-DCLEFC) shown in fig1. This is composed of an alkaline anode, a membrane and an acid cathode [14]. The anolyte is an aqueous solution of chloro ethanol and sodium hydroxide, while the catholyte is an aqueous solution of
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hydrogen peroxide and sulfuric acid. In addition a cation exchange Membrane (CEM) is employed to conduct sodium ions. On the anode, chloro ethanol reacts with OH\textsuperscript{-} provided by NaOH according to \cite{1, 15}

\begin{equation}
\text{CH}_2\text{Cl}\text{CH}_2\text{OH}+5\text{NaOH} \rightarrow \text{CH}_2\text{ClCOONa} +4\text{Na}^+ +4\text{e}^- +4\text{H}_2\text{O} \tag{1}
\end{equation}

The produced electrons pass through an external electrical load and arrive at the cathode. In the mean time, Na\textsuperscript{+} 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\textsuperscript{+} provided by H\textsubscript{2}SO\textsubscript{4} and electrons to produce water according to:

\begin{equation}
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} \tag{2}
\end{equation}

Hence Na\textsubscript{2}SO\textsubscript{4} will be produced by combining Na\textsuperscript{+} and SO\textsubscript{4}\textsuperscript{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.:

\begin{equation}
\text{CH}_2\text{Cl}\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}_2\text{ClCOONa}+2\text{Na}_2\text{SO}_4+8\text{H}_2\text{O} \tag{3}
\end{equation}

We tested the above described AA-DCLEFC and demonstrated that the peak power density was as high as 230mW cm\textsuperscript{-2} at 60\textdegree c, as can be evidenced from fig.2 \cite{14}. The high performance of this type of DCLEFC can be attributed to the following reasons: 1) the fuel cell has a high theoretical voltage (2.94V) rendered by the alkaline anode and acid cathode \cite{14}, 2) it has a low over potential of HPRR \cite{16-22}, and 3) it renders fast kinetics of the EOR at a lower potential (E\textsubscript{a}= 0.79V) \cite{9, 12, 14}.
2. EXPERIMENTAL

2.1 FUEL-CELL SET UP 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 chloro 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 (\(\text{H}_2\text{SO}_4\)) 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 a thermocouple located at the anode current collector, and two electrical heating rods were installed in the cell fixture to control the operating temperature. The internal resistance of the cell was measured by the built in function of the Arbin BT2000. Anode polarization data for these fuel cells were obtained employing an Hg/HgO (MMO) reference electrode.

2.2 MEMBRANE ELECTRODE ASSEMBLY

Four membrane electrode assemblies (MEAs) with different thickness CEMs were prepared in this work. The CEM used in this work were the Nafion series membrane, N211 (25 µm), N212 (50µm), N115(125µm) and N117(175µm) which were treated as the cation conductor .The procedure of treating the Nafion membrane included \([23,24]:1\) immersing them in 10 wt.% NaOH solution ; 2) heating them to 80\(^{\circ}\)C for 1h; and 3) 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\(\times\)1.0 cm. The anode electrode was formed by the following steps: i) a catalyst ink was prepared by mixing a homemade PdNi/C with a loading of 1.0 mg cm\(^{-2}\) chloro 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 (Horsens crop. Japan) that served as the backing layer.
3. RESULT AND DISCUSSION

3.1 EFFECT OF NaOH CONCENTRATION

The effect of NaOH concentration 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 transfers of species to the anode \cite{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 chloro 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 result in an optimal NaOH concentration (5.0) that give the best cell performance for a fixed ethanol concentration (3.0), which is an agreement with the result of our previous work in an AEM-DCLEFC\cite{12}.

![Graph showing the effect of NaOH concentration on cell performance.](image)

**Fig. 6** – Effect of NaOH concentrations on cell performance.

3.2 EFFECT OF CHLORO ETHANOL CONCENTRATION

We also investigate the effect of chloro ethanol concentration 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 chloro ethanol concentration, but at high current densities the cell voltage first increased with the chloro ethanol concentration and then decreased. In general, for a given anode catalyst, the anode potential depend upon the local concentration of both chloro ethanol and hydroxyl ions in the anode CL. A change in either chloro ethanol or hydroxyl ions concentration will lead to a change in the other\cite{10-12}. At low current density region, the solutions with 1.0 M and 3.0 M chloro ethanol cause the relatively poor kinetics as a result of insufficient chloro ethanol.
concentration in the anode CL. Hence increasing the chloro ethanol concentration to 5.0M can maintain the concentration of both chloro ethanol and hydroxyl ions at an appropriate level and thus yield the highest cell voltage. However the appropriate concentrations of both chloro 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 5.0M there is optimal chloro ethanol concentration of 3.0M, yielding the best cell performance.

3.3 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 the 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 potential, 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 result presented in fig.7 suggests that the predominant factor affecting the cell performance of this AA-DCLEFC varied with current density. Under the OCV and low current density condition. Fig.7 indicates that the mixed potential problem associated with the thinner membrane (25µm) is more serious. At the moderate and high current densities, however the effect of the internal resistance becomes predominant; thus the use of the thinner membrane yielded higher cell performance.
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![Graph](image)

**Fig. 7** – Effect of membrane thickness on cell performance.

![Graph](image)

**Fig. 8** – Effect of membrane thickness on the open-circuit voltage and internal resistance.

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.

### 3.4 EFFECT OF HYDROGEN PEROXIDE CONCENTRATION

Fig.3a show the polarization curves with different hydrogen peroxide concentration ranging from 1.0M to 6.0M when the sulfuric acid concentration was fixed at 1.0M and the anode solution was composed of 3.1M chloro ethanol and 5.0 NaOH. It can be seen that in the low current density region (below 100mA cm$^{-2}$) the cell voltage decreased with an increase in hydrogen peroxide concentration, but at higher current densities the cell voltage increased with the hydrogen peroxide concentration and then decreased. The 4.0M 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 H$_2$O$_2$ can react with chloro ethanol and thus form the mixed potential at the anode, which increase the anode potential, thus decreasing the voltage. Increasing the hydrogen
peroxide concentration at the cathode can cause a higher rate of H₂O₂ crossover, leading to an increase in the mixed potential at the anode, thereby increasing the anode potential, as evidenced by the measured anode potential shown in fig.3b. As a result, the cell voltage decreased with the hydrogen peroxide concentration at low densities. At high current densities, the underlying mechanism leading to the performance behavior is more complex. When the hydrogen peroxide concentration is increased from concentration is increased from 1.0M to 4.0M although the anode potential slightly increases with the hydrogen peroxide concentration as a result of the H₂O₂ 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 H₂O₂ crossover but also improve the cell performance. Therefore the cell voltage improved with increasing the hydrogen peroxide concentration from 1.0M to 4.0M.

When the hydrogen peroxide concentration was further increased to 6.0M the cathode potential does not change much as hydrogen peroxide concentration in the cathode catalyst layer (CL) is sufficient to ensure the H₂O₂ transport. On the other hand, the high hydrogen peroxide concentration causes potential and thus decreasing the cell performance as shown in the fig.3b. Therefore the cell voltage was degraded when the hydrogen peroxide concentration was increased to 6.0M, resulting in an optimal hydrogen peroxide concentration that can yield the highest performance at high current densities.
3.5 EFFECT OF SULFURIC ACID CONCENTRATION

The polarization curve for different sulfuric acid concentration ranging from 0.5M to 2.0M at a fixed hydrogen peroxide concentration of 4.0M 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 a mechanism leading to the behavior, the respective anode and cathode potential were also measured, respectively, and shown in fig.4b. It can be seen that the anode potential remained almost the same for the different sulfuric acid concentration but the cathode potential slightly increased with 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 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.

![Polarization curve](image)

![Potential vs. Current Density](image)

Fig. 4 – Effect of H₂SO₄ concentrations on cell performance. (a) Polarization curves. (b) Anode and cathode potentials.

4. CONCLUDING REMARKS
In this work, we investigated the effect of membrane thickness and the concentration of various species, including hydrogen peroxide, sulfuric acid, chloro ethanol and sodium hydroxide, on the performance of the alkaline acid direct chloro ethanol fuel cell. We have shown that hydrogen peroxide concentration, chloro ethanol concentration, NaOH concentration, and membrane thickness, have significant influence on the cell performance. In particular, we demonstrated that the peak power density of the AA-DCLEFC with a thinner membrane (25µm) was as high as 360mWcm$^{-2}$, 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 term 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.

References

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