A bi-functional cathode structure for alkaline-acid direct ethanol fuel cells

L. An, T.S. Zhao*, J.B. Xu

Department of Mechanical Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong SAR, China

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Abstract

An issue associated with the use of hydrogen peroxide as the oxidant in the so-called alkaline-acid direct ethanol fuel cell (AA-DEFC) is the problem of H₂O₂ decomposition, which causes a significant decrease in the cathode potential. The present work addresses this issue by developing a bi-functional cathode structure that is composed of the nickel-chromium (Ni–Cr) foam (functioning as the diffusion layer) with a highly dispersed gold particles (functioning as the catalyst layer) deposited onto the skeleton of the foam. This integrated cathode structure allows not only a reduction in H₂O₂ decomposition, but also an enhancement in the species transport in the cathode of the AA-DEFC. The fuel cell performance characterization shows that the use of the bi-functional cathode structure in the AA-DEFC enables the peak power density to be increased to 200 mW cm⁻² from 135 mW cm⁻² resulting from the use of the conventional cathode.

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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]. DEFCs can be divided into two types in terms of the membrane employed: proton exchange membrane DEFCs (PEM-DEFCs) and anion exchange membrane DEFCs (AEM-DEFCs). In the past, efforts have been mainly made to the development of 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. Unlike in acid media, the EOR kinetics in alkaline media becomes 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]. However, a barrier that limits the performance of AEM-DEFCs is that state-of-the-art AEMs do not allow the fuel cell to operate at high temperatures (< 60 °C) [14]. 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. 1a, which is composed of an alkaline anode, a membrane and an acid

* Corresponding author. Tel.: +852 2358 8647.
E-mail address: metzhao@ust.hk (T.S. Zhao).
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cathode [15]. 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 OH⁻ provided by NaOH according to [16]:

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

The produced electrons pass through an external electrical load and arrive at the cathode. In the meantime, 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 H₂SO₄ 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, Na₂SO₄ will be produced by combining Na⁺ and 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.:

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

The theoretical voltage of the above described AA-DEFC is 2.52 V, which is much higher than that of the conventional DEFCs (1.14 V) [17]. It was demonstrated that the peak power density of the above described AA-DEFC with a 175-μm thick CEM was found to be as high as 240 mW cm⁻² at 60 °C, which is about 4 times higher than the performance of conventional DEFCs reported in the literature [15]. However, an issue with the use of the oxidant in the fuel cell is the problem of H₂O₂ decomposition, causing a drastic drop in the cathode potential as a result of the following. First, H₂O₂ decomposition to H₂O and O₂ results in both the HPRR and oxygen reduction reaction (ORR) simultaneously taking place at the cathode, but the potential associated with the ORR is much lower than that of the HPRR, leading to a drastic drop in the cathode potential [18]. Second, its decomposition will lower the H₂O₂ concentration in the cathode catalyst layer (CL), causing the large concentration loss. Third, the presence of gaseous O₂ in the cathode leads to an increase in the gas void fraction, lowering the effective active area [19]. In general, H₂O₂ can decompose into water and oxygen homogeneously and heterogeneously [20]. Homogeneous decomposition represents the spontaneous decomposition of H₂O₂ due to its intrinsic instability, and the rate of decomposition is dependent on the temperature and concentration of hydrogen peroxide, as well as the pH value, while the heterogeneous decomposition takes place on the surface of the catalysts, e.g.: Pt and Pd, and its decomposition rate depends on the specific catalyst [20]. Therefore, in order to alleviate H₂O₂ decomposition, on one hand, the operating temperature, H₂O₂ concentration, and pH value should be optimized, lowering the homogeneous decomposition rate [17,21]; on the other hand, the appropriate cathode catalysts need to be developed that can promote the direct electro-reduction of H₂O₂, eliminating the heterogeneous decomposition. Recently, Gu et al. used Pourbaix diagrams to guide an experimental testing, and found that gold is an effective catalyst, which can minimize gas evolution of hydrogen peroxide [22].

In addition, due to its liquid phase, hydrogen peroxide has much lower diffusivity \(D_{\text{H}_2\text{O}_2, \text{water}} = 1.37 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}\) [23] than the gaseous oxidant, i.e.: oxygen \(D_{\text{O}_2, \text{air}} = 1.775 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}\) [24], indicating that the mass transfer rate of hydrogen peroxide is much smaller than oxygen. For this reason, the mass transport resistance of liquid-phase H₂O₂ in the cathode electrode is much larger than the gaseous O₂. Conventionally, the electrode for O₂-based fuel cells is composed of a dense CL and a backing layer (BL), as shown in Fig. 1a, and typically their porosities are 30% and 73%, respectively. It should be mentioned that the porosity of the electrode is one of the key factors affecting the mass transport [25]. Hence, a highly porous electrode is needed for the AA-DEFC to lower the mass transport resistance. Also, the high-porosity electrode can facilitate the produced oxygen removal, thereby alleviating the side reaction (ORR). Based on the understanding of the above-mentioned hydrogen peroxide transportation and the conventional electrode structure, catalyst deposition on a porous substrate is an attractive approach to reduce the electrode polarization [26]. This approach not only can decrease the mass transport resistance due to its high porosity, but also can increase the active area as compared to the conventional method [22]. For this reason, a variety of electrocatalytic cathodes for the hydrogen peroxide reduction reaction have been investigated in recent years [21,27,28]. Cao et al. prepared an Au/Ni foam electrode with a three dimensional network structure by the spontaneous deposition for an alkaline direct NaBH₄–H₂O₂ fuel cell, exhibiting an open-circuit voltage of about 1.07 V and a peak power density of 75 mW cm⁻² at 40 °C [21]. Yang et al. proposed a nanostructured Ag catalyzed nickel cathode for an aluminum-hydrogen peroxide using an electrodeposition technique, yielding a maximum power density of 420 mW cm⁻² at 45 °C [27]. They also prepared a novel nanostructured Pd—Ag catalyzed porous cathode for the magnesium-hydrogen peroxide fuel cell, resulting in a maximum power density of 140 mW cm⁻² at 50 °C [28].

In this work, we report a bi-functional cathode structure using the impregnation-reduction method for an alkaline-acid direct ethanol fuel cell (AA-DEFC). This bi-functional structure is composed of a nickel-chromium (Ni–Cr) foam layer with a highly dispersed gold layer deposited onto the skeleton of the foam. The motivation of applying the bi-functional

![Fig. 1 – Schematic of the alkaline-acid direct ethanol fuel cell (AA-DEFC).](image-url)
structure to the cathode of the AA-DEFC is to increase the catalytic activity, lower the H₂O₂ decomposition rate, and lower the mass transport resistance. We demonstrated that the AA-DEFC with the bi-functional electrode can yield a much higher power density of 200 mW cm⁻² than that with the conventional one (135 mW cm⁻²).

2. Experimental

2.1. Preparation of the bi-functional electrode

A simple impregnation-reduction method described elsewhere [29,30] was used in the present work to prepare the bi-functional electrode. Au particles were deposited directly onto the surface of the Ni–Cr foam by chemical reduction of Au precursor salt using NaBH₄ as the reductant. The Ni–Cr foam supplied by the RECMAT International offers over 95% porosity and the estimated average pore diameter of 0.4 mm. To clean the substrate surface, the Ni–Cr foam was immersed in 0.5 M sulfuric acid for 20 min to remove the oxide layer at room temperature. After that, the Ni–Cr foam substrate was rinsed with deionized (DI) water to remove chemicals prior to further use.

The bi-functional electrode was prepared by following the steps: 1) the Ni–Cr foam substrate with the pre-treatment was immersed in 2.0 mM sodium citrate (Na₃C₆H₅O₇) aqueous solution with a 10-min magnetic stirring; 2) the precursor, 2.0 mM HAuCl₄ aqueous solution, was injected into the sodium citrate aqueous solution for a 10-min magnetic stirring. It should be mentioned that the molar ratio of Na₃C₆H₅O₇ to HAuCl₄ is equal to one in the aqueous solution; 3) the pre-prepared 5.0 mM NaBH₄ aqueous solution as the reductant was added into the Na₃C₆H₅O₇-HAuCl₄ mixed solution for a 24-h magnetic stirring; 4) the Ni–Cr foam substrate was taken out and dried at 70 °C for 3 h; 5) the substrate was weighed and then the Au loading was calculated (this procedure was repeated until the Au loading was enough); 6) the Au/Ni–Cr was rinsed in the DI water to remove the chemicals for 24 h and the accurate Au loading was weighed (1.2 mg cm⁻² in this work) after 3-h drying at 70 °C prior to further use.

2.2. Membrane electrode assembly

A membrane electrode assembly (MEA), with an active area of 1.0 cm × 1.0 cm, was comprised of a CEM between an anode electrode and a cathode electrode. The CEM was a Nafion 117 membrane, (175 μm thick), which was treated as a cation conductor. The procedures of treating the Nafion membrane included [31]: i) immersing it in 10 wt.% NaOH solution; ii) heating it to 80 °C for 1 h; and iii) washing it by the DI water several times. 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 solution as the binder; 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. In this work, a conventional cathode electrode was prepared for comparison by following the steps: i) the cathode catalyst ink was prepared by mixing a commercial 30 wt.% Au/C (Fuel Cell Store) with a loading of 1.2 mg cm⁻², ethanol as the solvent and 5 wt.% Nafion solution as the binder; ii) the cathode catalyst ink was stirred continuously in an ultrasonic bath for 20 min such that it was well dispersed and iii) the cathode catalyst ink was brushed onto a piece of carbon cloth (type A, ETEK) as the backing layer to form a cathode electrode.

2.3. Fuel-cell setup and instrumentation

As shown in Fig. 1, each MEA was fixed between an anode and a cathode flow field. Both flow fields were made of 316L stainless steel plate, in which a single serpentine flow channel, 1.0 mm wide and 0.5 mm deep, was grooved by the wire-cut technique. An alkaline solution containing 3.0 M ethanol and 5.0 M NaOH was fed into the anode flow channel by another peristaltic pump at a flow rate of 2.0 mL min⁻¹; while an acid solution containing 4.0 M H₂SO₄ and 1.0 M sulfuric acid (H₂SO₄) was fed into the cathode flow channel by another peristaltic pump at a flow rate of 2.0 mL min⁻¹ [17]. 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 fixtures to control the operating temperature. An Arbin BT2000 (Arbin Instrument Inc.) was employed to measure the polarization curves. Anode polarization data for this present fuel cell were obtained employing an Hg/HgO (MMO) reference electrode. Cathode polarization data were derived by subtracting anode polarization values from the respective cell polarization data. The internal resistance of the cell was measured by the built-in function of the Arbin BT2000. The morphologies of the Ni–Cr metal foam and bi-functional electrode were examined with a scanning electron microscope (JEOL-6700F). The X-ray diffraction (XRD) patterns were obtained with a Philips powder diffraction system (model PW 1830).

3. Results and discussion

3.1. Characterization of the bi-functional electrode

Fig. 2 shows the SEM images of the morphology and structure of the Ni–Cr foam. It can be seen that the Ni–Cr foam shows the highly porous structure, suggesting that the mass transport resistance is much lower than the conventional electrode. After deposition, it is seen from Fig. 3 that the skeleton of the Ni–Cr foam is coated by a uniform Au layer, which can be demonstrated by the composition analysis using XRD shown in Fig. 4. At the higher magnification, the coated layer has a 3-D structure and consists of fine particles, as shown in Fig. 3b.

3.2. Cell performance comparison

Fig. 5 compares the cell performance of the AA-DEFC with three different MEAs consisting of the same anode, the same CEM, but different cathode electrodes, i.e.: MEA-1: PdNi/C + CEM + the conventional cathode (Au/C brushed on the
carbon cloth), MEA-2: PdNi/C + CEM + the substrate (Ni–Cr foam without the Au catalyst), and MEA-3: PdNi/C + CEM + the bi-functional cathode (Au deposited on the Ni–Cr foam). It is seen from Fig. 5a that the cell with the bi-functional electrode can yield a peak power density of 200 mW cm$^{-2}$, which is 48% higher than that with the conventional one (135 mW cm$^{-2}$). Also, the cell with the bi-functional electrode yields a maximum current density of 525 mA cm$^{-2}$, which is 50% higher than the conventional design (350 mA cm$^{-2}$). The substantially increased performance is mainly attributed to the higher catalytic activity and the enhanced species transport in the cathode. It is worth mentioning that during the experiments, it was observed that in the cathode outlet that the H$_2$O$_2$ decomposition was indeed alleviated in the AA-DEFC with the Au-based electrode as compared to the AA-DEFC with the Pt-based electrode reported earlier [16].

3.2.1. Discussion of polarization curves

As shown in Fig. 5a, the AA-DEFC with the bi-functional electrode can yield the higher cell performance than that with the conventional one in the whole current density range. It can also be seen from Fig. 5b that the improved cell performance mainly results from the cathode contribution, i.e.: the bi-functional structure. The reasons for this behavior are explained as follows. Generally, in the low current density region, the overpotential is predominated by the activation polarization. Hence, it can be seen from Fig. 5c that the cathode overpotential with the bi-functional electrode is smaller than that with the conventional design, indicating that the activation loss of the bi-functional electrode is lower than the conventional one at the low current densities. This
fact shows that the catalytic activity toward HPRR of the bi-functional electrode is higher than the conventional one. At moderate current densities, although the bi-functional electrode has the higher internal resistance (IR) than the conventional one (Table 1), the overall cathode performance with the bi-functional electrode is higher than that with the conventional one, as evidenced by Fig. 5b. The higher IR with the bi-functional electrode is mainly attributed to the increased contact resistance between the porous electrode and the stainless steel current collector, due to that the bi-functional electrode has an extremely high porosity (over 95%), whereas the porosity of the carbon cloth is only 73% [32]. However, its higher catalytic activity and lower mass transport resistance due to the extremely high porosity not only can compensate the increased ohmic loss, but also can improve the cathode performance. Therefore, at moderate current densities, the cell with the bi-functional electrode can also yield the better performance. As for the high current density region, it can be seen from Fig. 5c that the conventional electrode has much higher overpotential as compared to the present one, where the main overpotential is the concentration loss. This behavior can be explained as follows. With regard to the conventional electrode, the low porosity and small pore size are formed in the dense CL, resulting in a low permeability resisting the mass transport of reactants [33]. On the other hand, as illustrated in Fig. 3, the bi-functional electrode made of the Ni–Cr foam has much higher porosity and larger open pores, resulting in a higher permeability that facilitates the species transport. In summary, the improved cell performance is mainly attributed to both the higher catalytic activity and the enhanced mass transfer in the cathode.

3.2.2. EIS analysis
As mentioned above, the improved performance of the AA-DEFC with the bi-functional electrode can be mainly attributed to the higher catalytic activity and the enhanced species transport in the cathode. In order to further prove this point, the electrochemical impedance spectra (EIS) for the AA-DEFC with the bi-functional and conventional electrodes were measured and the results are shown in Fig. 6. It is seen from this figure that the cell with the bi-functional electrode shows a larger impedance spectra than does the conventional one at the high frequency, whereas the bi-functional electrode

Table 1 – The open-circuit voltage and internal resistance with various cathode electrodes.

<table>
<thead>
<tr>
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<th>MEA-1</th>
<th>MEA-2</th>
<th>MEA-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCV (V)</td>
<td>1.469</td>
<td>1.376</td>
<td>1.465</td>
</tr>
<tr>
<td>IR (Ω)</td>
<td>0.676</td>
<td>1.250</td>
<td>0.938</td>
</tr>
</tbody>
</table>

Fig. 5 – Cell performance comparison among various cathode electrodes. (a) Polarization curves. (b) Anode and cathode potentials. (c) Anode and cathode overpotentials.

Fig. 6 – Nyquist plots of the AA-DEFC impedance spectra.
exhibits the smaller impedance spectra in the moderate and low frequency regions. The arc at high frequency is related to the internal cell resistance [34,35]. The increased contact resistance as a result of an extremely high porosity (over 95%) results in the increased internal cell resistance for the cell with the bi-functional electrode. Hence, the bi-functional electrode shows larger impedance spectra at the high frequency. At moderate and low frequencies, the arc is mainly attributed to the catalytic activity and mass transfer resistance. The smaller impedance spectra at the moderate and low frequencies for the cell with the bi-functional electrode imply that the activation loss and concentration loss are smaller than the conventional one, meaning that both the HPRR and species transport are enhanced with the bi-functional electrode. Therefore, the above EIS spectra confirmed that the improved performance with the bi-functional electrode is primarily attributed to the higher catalytic activity and the enhanced species transport in the cathode.

3.3. Effect of H$_2$O$_2$ concentrations

Fig. 7 shows the polarization curves with different hydrogen peroxide concentrations ranging from 2.0 M to 8.0 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 the cell voltage first increased with the hydrogen peroxide concentration and then decreased over the whole current density range; the 4.0-M hydrogen peroxide concentration exhibited the highest performance. The reason leading to this phenomenon is explained as follows. When the hydrogen peroxide concentration is increased from 2.0 M to 4.0 M, the cell voltage is increased. In general, increasing the H$_2$O$_2$ concentration can lower the anode performance as a result of the H$_2$O$_2$ crossover; in the meantime, the H$_2$O$_2$ transport at the cathode is also enhanced, thereby reducing the concentration polarization loss. Moreover, it can be seen from Fig. 7 that the reduced concentration loss not only compensates the mixed potential in the anode resulting from the H$_2$O$_2$ crossover but also improves the cell performance. Therefore, the cell voltage improved with increasing the hydrogen peroxide concentration from 2.0 M to 4.0 M. When the hydrogen peroxide concentration was further increased to 8.0 M, the cell voltage is decreased. This is because when the hydrogen peroxide concentration exceeds 4.0 M, it is sufficient to ensure the H$_2$O$_2$ transport in the cathode [17]. On the other hand, the high hydrogen peroxide concentration causes rather serious H$_2$O$_2$ crossover, leading to the large anode overpotential and thus decreasing the cell performance, as shown in Fig. 7. Therefore, the cell voltage was degraded when the hydrogen peroxide concentration was increased to 8.0 M, resulting in an optimal hydrogen peroxide concentration that can yield the highest performance.

4. Concluding remarks

In this work, we have developed a bi-functional cathode structure for the alkaline-acid direct ethanol fuel cell. The bi-functional structure is composed of the Ni–Cr foam with a uniform Au layer deposited onto its skeleton. The experimental results indicate that the use of the bi-functional electrode as the cathode of the AA-DEFC can significantly improve the cell performance as compared with the use of the conventional one. The AA-DEFC with the bi-functional electrode can yield a peak power density of 200 mW cm$^{-2}$, which is 48% higher than that with the conventional one (135 mW cm$^{-2}$). The improved performance with the bi-functional electrode can mainly be attributed to the facts: i) the bi-functional structure reduces H$_2$O$_2$ decomposition and fast removes the produced O$_2$; ii) the bi-functional structure has a well deposited Au layer onto the skeleton of the highly porous Ni–Cr foam, resulting in the higher catalytic activity and lower the species transport resistance.

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