



Short communication

A novel direct ethanol fuel cell with high power density

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ARTICLE INFO

Article history:

Received 16 January 2011

Received in revised form 2 March 2011

Accepted 3 March 2011

Available online 31 March 2011

Keywords:

Fuel cell

Direct ethanol fuel cell

Hydrogen peroxide

Theoretical voltage

Power density

ABSTRACT

A new type of direct ethanol fuel cell (DEFC) that is composed of an alkaline anode and an acid cathode separated with a charger conducting membrane is developed. Theoretically it is shown that the voltage of this novel fuel cell is 2.52 V, while, experimentally it has been demonstrated that this fuel cell can yield an open-circuit voltage (OCV) of 1.60 V and a peak power density of 240 mW cm^{-2} at 60°C , which represent the highest performance of DEFCs that has so far been reported in the open literature.

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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.

Typically, conventional DEFCs can be divided into two types in terms of the employed membrane: proton exchange membrane DEFCs (PEM-DEFCs) and anion exchange membrane DEFCs (AEM-DEFCs). Past efforts have been mainly devoted to PEM-DEFCs and thus significant progress has been made [1–3]. Nevertheless, the sluggish kinetics of the ethanol oxidation reaction (EOR) 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 acid media. It has recently been demonstrated that when the acid electrolyte was changed to alkaline one, i.e. AEM, the cell performance could be substantially improved [4–7]. Li et al. [7] developed and tested an AEM-DEFC, yielding an OCV of 0.90 V and a maximum power density of 60 mW cm^{-2} at 40°C . Although promising,

the cell performance still needs to be substantially improved before the widespread commercialization. Presently, the main limitation to the cell performance in AEM-DEFCs is the physical and chemical properties of the AEM [8]. One of the problems with the AEM is that its ionic conductivity is about one order of magnitude lower than that of Nafion membranes. The other problem is that the AEM has a poor thermal stability, which limits the fuel cell operating temperature, and thus limiting the cell performance. In addition, another important parameter that limits the performance of conventional DEFCs operating under both acid and alkaline media is that thermodynamically, their theoretical voltage is low (1.14 V).

It has recently been demonstrated that the use of hydrogen peroxide (H_2O_2) as an alternative oxidant can substantially increase the fuel cell theoretical voltage, and thus improve performance. Another important advantage of the fuel cells that use hydrogen peroxide is that they can operate with the absence of oxygen environment, such as underwater and space conditions. In addition, hydrogen peroxide offers many other advantages compared with oxygen, such as the low activation loss of the reduction reaction due to two-electron transfer and no water flooding problem [9]. For these reasons, the fuel cells employing hydrogen peroxide as the oxidant have received increasing attention [10–15].

In this work, a new type of direct ethanol fuel cell that is composed of an alkaline anode and an acid cathode separated with a charger conducting membrane is proposed. As shown below, theoretically the voltage of this novel fuel cell is as high as 2.52 V. Experimentally this fuel cell can yield a peak power density of 240 mW cm^{-2} at 60°C .

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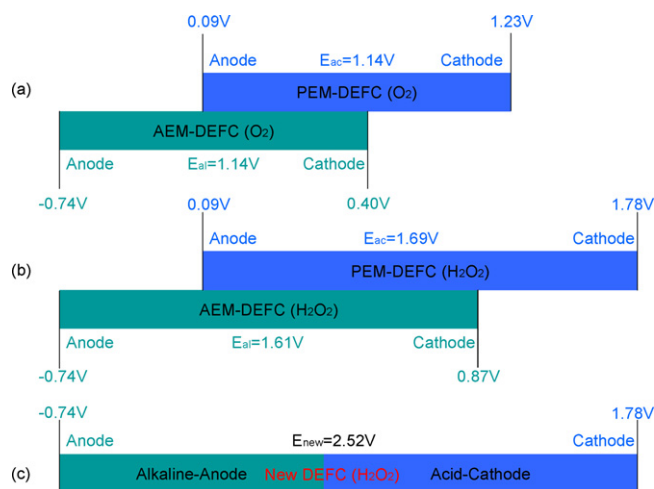


Fig. 1. Theoretical voltages of direct ethanol fuel cells.

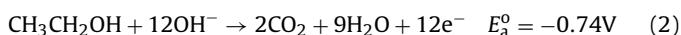
2. Theoretical voltage of this new type of DEFC

Fig. 1 compares the theoretical voltages of conventional PEM- and AEM-DEFCs, respectively, with oxygen and hydrogen peroxide oxidants with that of this new type of DEFC with hydrogen peroxide oxidant. First, let us focus our attention to Fig. 1a, where the upper portion shows the anode/cathode potentials and cell voltage of a conventional PEM-DEFC, while the lower portion shows the anode/cathode potentials and cell voltage of a conventional AEM-DEFC. Note that the both cells employ oxygen as oxidant. It is seen that both the PEM- and AEM-DEFC yield the same cell voltage, i.e.: 1.14 V, but the anode/cathode potentials of the AEM-DEFC are lower than those of the PEM-DEFC. The negative shift of anode/cathode potentials in alkaline media means that the AEM-DEFC enables faster kinetics on both the EOR and ORR.

We now look at how the respective anode/cathode potential and cell voltage for the both cells shown in Fig. 1a change when the oxidant is changed from oxygen to hydrogen peroxide. As seen from Fig. 1b, the anode potentials of both the PEM- and AEM-DEFC (H_2O_2) remain the same as those in Fig. 1a, whereas the cathode potentials of both the PEM- and AEM-DEFC (H_2O_2) are increased from 1.23 V to 1.78 V and from 0.40 V to 0.87 V, respectively. As a result, the respective cell voltages of both the PEM- and AEM-DEFC (H_2O_2) can be 1.69 V and 1.61 V. It is important to notice from Fig. 1a and b that the anode potential of the AEM-DEFC is lower than that of the PEM-DEFC, while the cathode potential of the PEM-DEFC is higher than that of the AEM-DEFC. This observation suggests that combining the lower anode potential of the alkaline cell and the higher cathode potential of the acid cell to form a new cell would result in a higher voltage and faster kinetics of the EOR. In line with this idea, an alkaline anode-membrane-acid cathode fuel cell with hydrogen peroxide as oxidant is formed and shown in Fig. 1c. To create the alkaline environment at the anode, sodium hydroxide (NaOH) is added to ethanol solution at the anode, so that hydroxyl ions are formed according to:



The ionized Na^+ as the charge carrier will migrate through a cation exchange membrane (CEM) to the cathode [16]. In the meantime, OH^- will react with ethanol according to:



It should be mentioned that the above reaction is based on the assumption that the final product is carbon dioxide. It has been proven that with existing electrocatalysts at low temperatures the

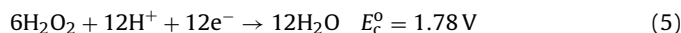
final product of the EOR is predominated by acetic acid in the alkaline DEFC system according to [17]:



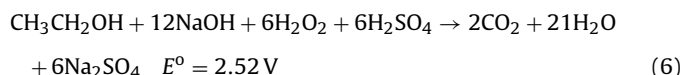
At the cathode side, the acid environment is achieved by adding sulfuric acid, so that protons are formed according to:



The ionized SO_4^{2-} will combine with Na^+ from the anode to form Na_2SO_4 at the cathode. On the other hand, H^+ will react with hydrogen peroxide and electrons to produce water, i.e.:



As a result, the overall reaction of this new cell can be obtained by combining the EOR given by (2) and the hydrogen peroxide reduction reaction given by (5), i.e.:



which results in a voltage of 2.52 V. This theoretical voltage shows a tremendous increase as compared with that of conventional DEFCs (1.14 V). Moreover, as the EOR in this cell takes place at a lower potential ($E_a^0 = -0.74\text{V}$), the kinetics in this type of fuel cell will be faster than conventional PEM-DEFCs. It is worth mentioning that the present DEFC with the alkaline anode-membrane-acid cathode setup is different from the so-called hybrid fuel cell systems reported elsewhere [18,19] in terms of the cell structure, the working principle, and the fuel used.

3. Fuel-cell setup

As shown in Fig. 2, the present fuel cell consists of a membrane electrode assembly (MEA) sandwiched between two flow fields. The MEA, with an active area of $1.0\text{cm} \times 1.0\text{cm}$, was comprised of a sodium conducting membrane between an anode electrode and a cathode electrode. It should be mentioned in this work a pre-treated Nafion 117 membrane was used as the Na^+ form CEM. The as-received Nafion 117 membrane was immersed in 10 wt.% NaOH solution and heated to 80°C for 1 h for Na^+ exchange and then washed by deionized (DI) water several times before assembled [16]. In the anode, the catalyst ink was prepared by mixing PdNi/C consisting of a homemade PdNi/C with a loading of 1.0mg cm^{-2} , ethanol as the solvent, and 5 wt.% Nafion solution as the binder [20]. Subsequently, the anode catalyst ink was brushed onto a piece of nickel foam (Hohsen Corp., Japan) that served as the backing

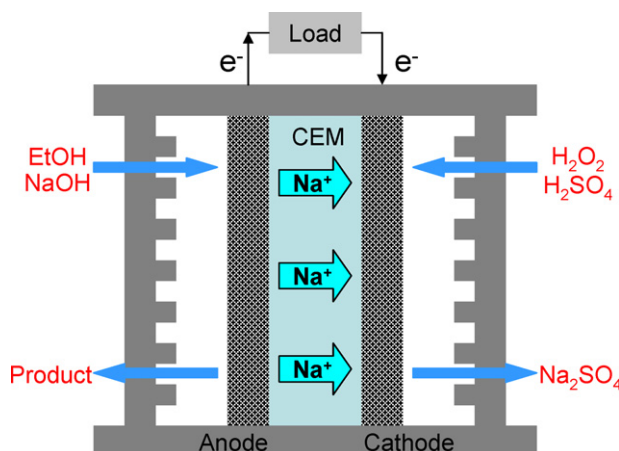


Fig. 2. Schematic of the alkaline anode-membrane-acid cathode DEFC.

layer to form an anode electrode. Similarly, the cathode catalyst ink was prepared by mixing 60 wt.% Pt/C (Johnson–Matthey) with a loading of 3.9 mg cm^{-2} , ethanol and 5 wt.% Nafion solution, and was brushed onto a piece of carbon cloth (ETEK, Type A) to form a cathode electrode.

4. Results and discussion

The polarization and power density curves of this new type of DEFC are shown in Fig. 3a. It is seen that the OCV and the peak power density of this DEFC were 1.60 V and 240 mW cm^{-2} , respectively. The OCV and the peak power density of this present fuel cell are about 2 and 4 times higher than those of conventional DEFCs, respectively [3,7]. The substantially better performance can be mainly attributed to: (1) its higher theoretical voltage (2.52 V) rendered by the alkaline medium at the anode and the acid medium at the cathode, (2) the lower cathode overpotential due to the two-electron transfer of the hydrogen peroxide reduction reaction, and (3) the faster kinetics of the EOR as a result of the lower anode potential.

Although the actual OCV in this new type of fuel cell is much higher than that of conventional DEFCs, it is still much lower than its theoretical value, as shown in Fig. 3b. There are two main reasons that cause the actual OCV to be lower than the theoretical value. First, part of hydrogen peroxide may be decomposed into oxygen on the Pt catalyst at the cathode, i.e.:

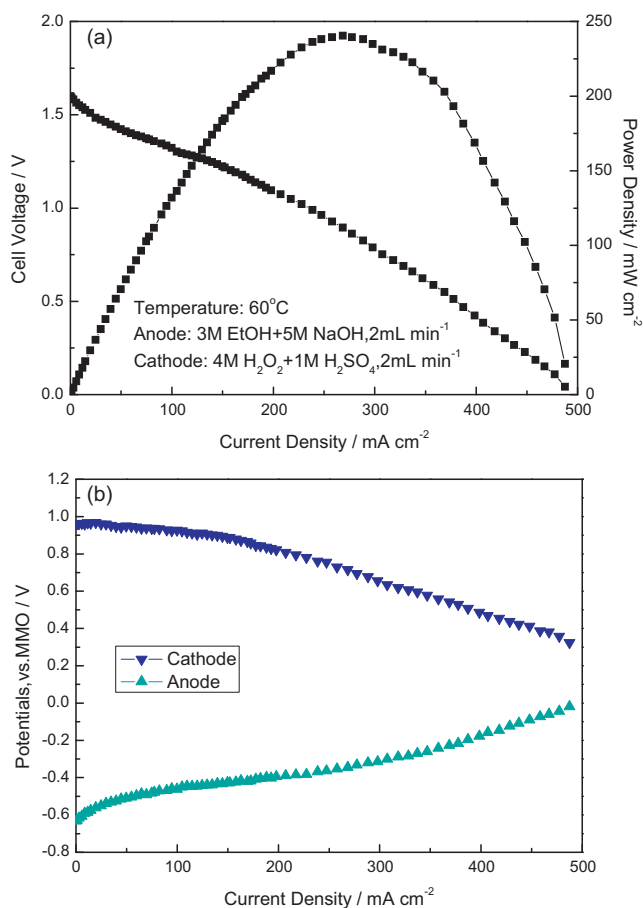
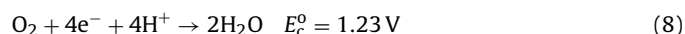


Fig. 3. The cell performance of the DEFC. (a) Polarization and power density curves. (b) Anode and cathode potentials.

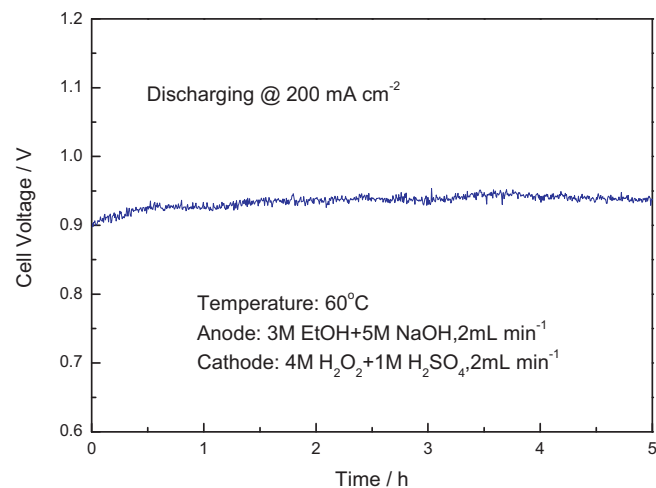


Fig. 4. Constant-current discharging behavior.

Since the cathode potential associated with the oxygen reduction reaction ($E_c^\circ = 1.23 \text{ V}$) is lower than that due to the hydrogen peroxide reduction reaction ($E_c^\circ = 1.78 \text{ V}$), the actual OCV will be lower than the theoretical value without taking account of hydrogen peroxide decomposition [10]. The second reason that leads to a lower actual OCV is that ethanol can permeate the membrane, leading to the mixed potential in the cathode side and thus lowering cathode potential, although the fuel crossover in the DEFCs is not as serious as in the DMFCs [21]. Therefore, the low OCV is mainly attributed to the large loss in the cathode potential caused by the hydrogen peroxide decomposition and ethanol crossover.

The cell discharging behavior at a constant current density (200 mA cm^{-2}) is investigated. As shown in Fig. 4, no degradation in the cell voltage was found during the 5-h continuous operation.

5. Concluding remarks

In this work, an alkaline anode-membrane-acid cathode direct ethanol fuel cell with hydrogen peroxide as oxidant is proposed and tested. Theoretically it is shown that the theoretical voltage of this novel fuel cell is as high as 2.52 V, while experimentally it has been demonstrated that this fuel cell can yield an OCV of 1.60 V and a peak power density of 240 mW cm^{-2} at 60°C. These results represent the highest performance of DEFCs that has so far been reported in the open literature. It should be pointed out that as the theoretical voltage of this system is as high as 2.52 V, there is still plenty of room for the cell performance to be further upgraded. A unique feature associated with the use of hydrogen peroxide as oxidant in this system is its high volumetric power density, making this power pack particularly suitable for space or underwater applications where oxygen is not readily available from air. On the other hand, it should be also mentioned that although the fuel cell system developed in this work shows substantially higher performance than conventional DEFCs, some fundamental issues in this new type of fuel cell, such as the hydrogen peroxide decomposition and ethanol crossover, merit extensive future research.

Acknowledgements

The work described in this paper was fully supported by a grant from the Research Grants Council of the Hong Kong Special Administrative Region, China (Project No. 623709).

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