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COMMUNICATION

A high-performance ethanol-hydrogen peroxide fuel cell

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In conventional ethanol-hydrogen peroxide fuel cells, the cathode potential is created by the reduction reaction of hydrogen peroxide. In this work, we propose to create the cathode potential by introducing a redox couple to the cathode while using hydrogen peroxide to chemically charge the redox ions. The idea not only completely eliminates the mixed-potential issue associated with the direct reduction of hydrogen peroxide, but also enables faster cathodic electrochemical kinetics with no catalysts. Experimentally, it is demonstrated that the ethanol-hydrogen peroxide fuel cell with a redox couple of V(IV)/V(V) yields a peak power density of 450 mW cm^{-2} at 60°C , which is 87.5% higher than that of the conventional cell with direct reduction of hydrogen peroxide.

The use of hydrogen peroxide in fuel cells has recently received increasing attention, primarily due to its several unique characteristics when compared with the use of gaseous oxygen [1, 2]. Fuel cells that use hydrogen peroxide can operate with the absence of an oxygen environment, such as outer space or underwater conditions [3]. Additionally, the use of hydrogen peroxide as the oxidant can substantially increase the theoretical voltage of fuel cells and thus improve cell performance [4]. For these reasons, much effort has been devoted to the development of hydrogen peroxide-based fuel cells [5-13]. However, there are three issues associated with the direct reduction of hydrogen peroxide in fuel cells. First, the actual cathode potential (0.8 V - 0.9 V vs. SHE) is much lower than the theoretical one (1.78 V vs. SHE), which is mainly attributed to the mixed potential resulting from the simultaneous hydrogen peroxide oxidation reaction (HPOR) on the cathode [14]. Second, the HPOR releases gaseous oxygen, leading to a two-phase mass transport in the cathode [15, 16]. Third, the direct reduction of hydrogen peroxide in fuel cells has to use metal catalysts, such as platinum, palladium, gold [17-20]. In this work, we propose to create the cathode potential by introducing a redox couple to the cathode while to use hydrogen peroxide to chemically charge to redox ions. The redox cathode not only completely eliminates the mixed-potential problem associated with the direct reduction of

hydrogen peroxide, but also enables a faster cathodic electrochemical kinetics even with no noble metal catalysts.

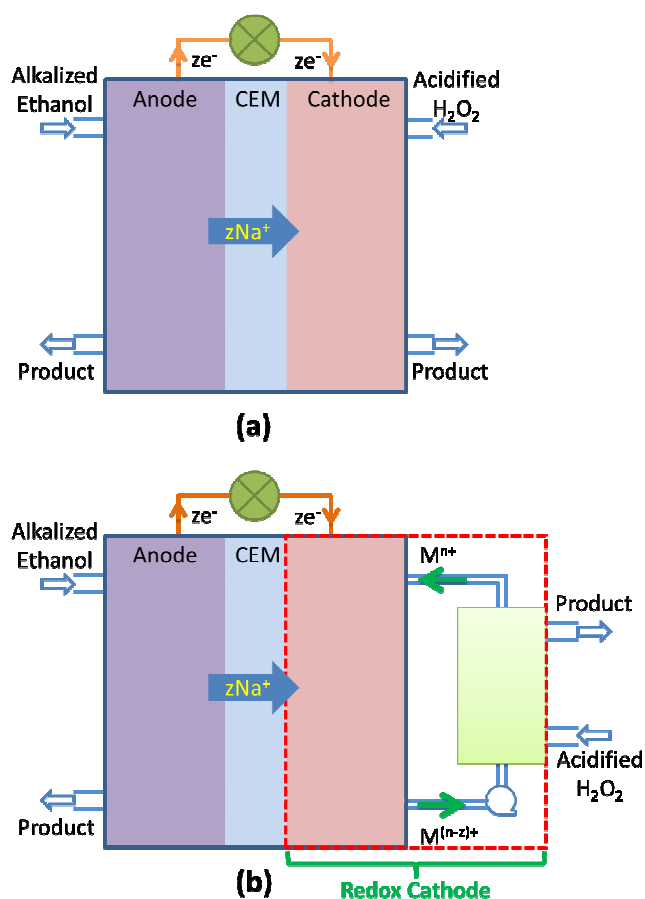


Figure 1 Schematic of the conventional (a) and present (b) ethanol-hydrogen peroxide fuel cells.

As shown below, the use of the redox cathode (V(IV)/V(V) as the redox couple) in a ethanol-hydrogen peroxide fuel cell results in an open-circuit voltage (OCV) of 2.07 V and a peak power density of 450 mW cm⁻² at 60°C as opposed to 1.60 V and 240 mW cm⁻² achieved by using the conventional one.

Fig. 1 illustrates the working principles of the conventional and redox cathodes. First, let us focus our attention to the conventional cathode (Fig. 1a), where hydrogen peroxide directly reacts with protons and electrons to form water according to [14]:



During this process, the HPOR can take place at such a high potential to form oxygen, protons and electrons according to [14]:

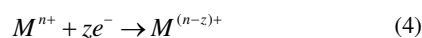


In addition, since oxygen is produced (see Eq. 2), the oxygen reduction reaction (ORR) is probable to occur according to [14]:

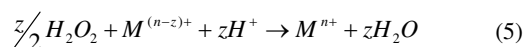


Among the three electrochemical reactions, one is an oxidation reaction (electron donor), whereas the other two are reduction reactions (electron acceptor). Therefore, two oxidation-reduction reactions can be spontaneously established on the conventional cathode, forming a mixed potential and thereby resulting in a potential loss [14].

We now look at the working principle of the redox cathode, as shown in Fig. 1b. It can be seen that there are two compartments for the redox cathode, i.e.: the left one for electrochemical discharge and the right one for chemical charge. In the left compartment, the high-valence redox ions (Mⁿ⁺) are reduced (electrochemically discharged) by accepting electrons to form the low-valence redox ions (M^{(n-z)+}) according to:



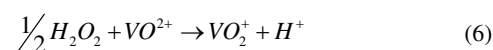
The discharging product, M^{(n-z)+} ions, is pumped out of the left compartment and then fed into the right one, where the low-valence redox ions (M^{(n-z)+}) are oxidized (chemically charged) by reacting with hydrogen peroxide to regenerate the high-valence redox ions (Mⁿ⁺):



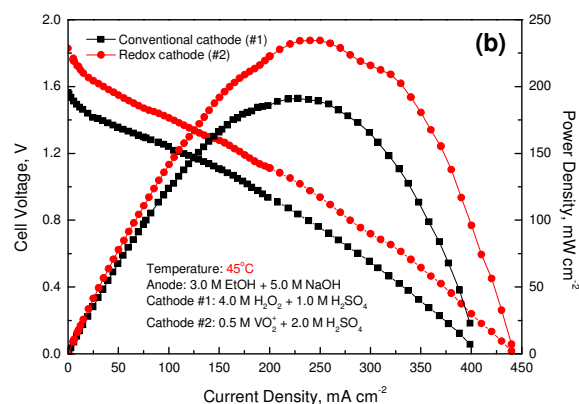
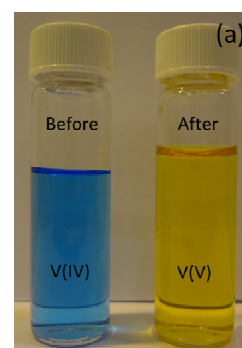
The charging product, Mⁿ⁺ ions, is continuously fed into the left compartment for the electrochemical discharge. The overall reaction on the redox cathode is the same as Eq. (1).

Three fuel cells were prepared in this work, each of which consists of a membrane electrode assembly (MEA) sandwiched by an anode and a cathode flow fields. The MEA, with an active area of 1.0 cm × 1.0 cm, was comprised of a pre-treated Nafion 117 membrane between an anode electrode and a cathode electrode [21]. The anode electrode is the same for three cells, which was made by brushing the catalyst ink (1.0 mg cm⁻² PdNi/C and 5 wt. % Nafion) onto a piece of nickel foam [22]. The conventional cathode (Cathode #1) 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. The redox cathode is composed of an electrochemical compartment and a chemical compartment. The electrochemical compartment is simply made of a piece of carbon paper (Toray 120: Cathode #2) or three pieces of carbon paper (SGL AA10: Cathode #3). The chemical compartment is a glass tank, where hydrogen peroxide is fed to chemically regenerate the redox ions. In this work, the alkalized ethanol is used as the fuel; while, the catholyte is the acidized hydrogen peroxide [23]. In addition, V(IV)/V(V) is used as the redox couple. It should be noted that many redox couples could be an alternative to V(IV)/V(V), such as Fe²⁺/Fe³⁺, Br₂/Br⁻ and Cl₂/Cl⁻ [24-26]. Fig. 2a shows the colors of the aqueous solution containing vanadium ions before and after feeding hydrogen peroxide. It can be seen that prior to the chemical charge process, the color of the aqueous solution containing 0.1 M V(IV) ions is blue; while, after feeding hydrogen peroxide, the aqueous solution turns yellow immediately (within few seconds), indicating that the V(IV) ions are chemically oxidized to V(V) ions [27]. The V(IV) ions are chemically charged by reacting with hydrogen peroxide according to:



This chemical charge process can be finished in the bulk solution at room temperature, which does not involve any catalysts for the vanadium-ion conversion [28]. It should be noted that oxygen could also chemically oxidize the V(IV) ions to the V(V) ions [29, 30]. However, the chemical charge by using oxygen needs the catalysts to speed up the chemical reaction, negating the present fuel cell system [31].



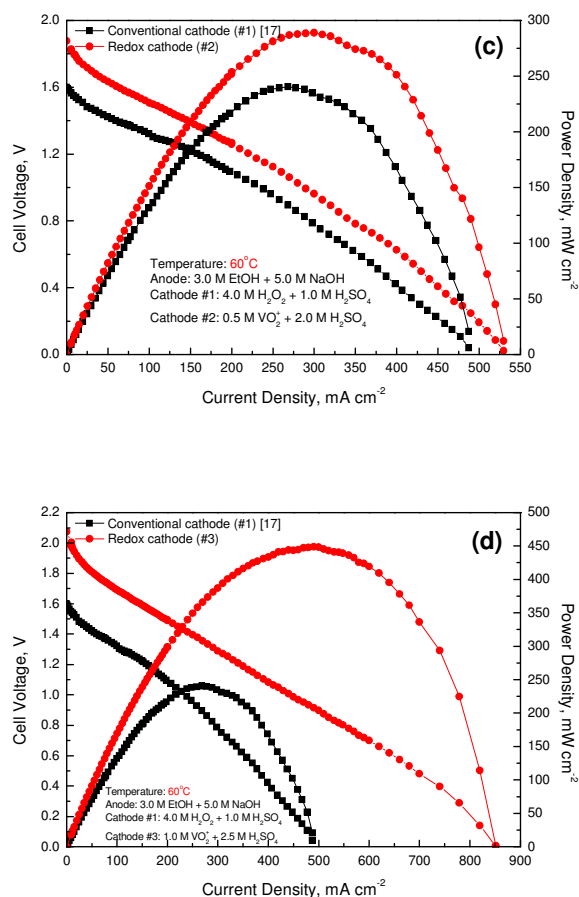


Figure 2 Performance evaluations of the present fuel cell system. (a) The vanadium ions before and after charge; (b) the cell performance at 45°C; (c) the cell performance at 60°C; (d) the optimal performance at 60°C.

Fig. 2b shows the polarization and power density curves of two types of ethanol-hydrogen peroxide fuel cell at 45°C. During this process, the V(V) ions are electrochemically discharged by accepting electrons according to:



It is seen that the OCV and the peak power density of the conventional fuel cell are 1.56 V and 190 mW cm⁻² at 45°C, respectively; while, the redox one results in an OCV of 1.83 V and a peak power density of 235 mW cm⁻² at the same temperature. As such, the peak power density of this redox fuel cell is 23.7% higher than that of the conventional one. The improved performance can be mainly attributed to the avoidance of the mixed-potential phenomenon and the faster electrochemical kinetics of the reduction reaction of the redox ions ($i_{0,V(V)}=200 \text{ A m}^{-2}$ [32] vs. $i_{0,H_2O_2}=10 \text{ A m}^{-2}$ [14]). In addition to the improvement in performance, the redox cathode does not include any catalysts for the electrochemical and chemical reactions, significantly lowering the system cost. It is interesting to notice that the theoretical voltage of the conventional ethanol-hydrogen peroxide fuel cell (2.52 V) is much larger than that of the present fuel cell (1.74 V); however, the actual OCV (1.56 V) of the conventional fuel cell is lower than that of the present one

(1.83 V). As discussed earlier, the lower OCV of the conventional fuel cell results from the mixed-potential phenomenon as a result of the HPOR [14]. The theoretical voltage (1.74 V) here refers to the potential difference at standard state, which is with solutes at an effective concentration of 1.0 M. Based on Nernst equation:

$$E_{V(V)/V(V)} = E_{V(V)/V(V)}^0 + \frac{RT}{F} \ln \frac{c_{V(V)} c_{H^+}^2}{c_{V(IV)}} \quad (7)$$

the larger actual OCV (1.83 V) is mainly attributed to the high sulfuric acid concentration (2.0 M) in vanadium aqueous solution.

Fig. 2c shows the polarization and power density curves of two types of ethanol-hydrogen peroxide fuel cell at 60°C. It is seen that the OCV increases from 1.83 V to 1.88 V and the peak power density increases from 235 mW cm⁻² to 290 mW cm⁻² when the operating temperature is increased from 45°C to 60°C. The previous investigation [17] showed that the conventional fuel cell results in an OCV of 1.60 V and a peak power density of 240 mW cm⁻² at the same temperature. As such, the peak power density of this redox fuel cell is 20.8% higher than that of the conventional one. The increased performance as a result of increasing the operating temperature is attributed to the enhanced electrochemical kinetics of the oxidation and reduction reactions, the improved membrane conductivity, and the increased reactant delivery and product removal rates, respectively [33, 34]. In addition, we further optimized the structural and operating parameters and demonstrated that the present fuel cell results in an OCV of 2.07 V and a peak power density of 450 mW cm⁻² at 60°C. Thus, the peak power density of the present fuel cell is 87.5% higher than that of the conventional one with direct reduction of hydrogen peroxide (240 mW cm⁻²), as shown in Fig. 2d.

Conclusions

In this work, we propose to create the cathode potential of ethanol-hydrogen peroxide fuel cell by introducing a redox couple to the cathode while using hydrogen peroxide to chemically charge the redox ions. The introduction of the redox couple to the cathode brings the following striking features. First, the absence of hydrogen peroxide in the reduction reaction eliminates the mixed-potential issue. Second, the presence of the redox couple in the reduction reaction significantly improves the electrochemical kinetics, thereby resulting in a high-performance fuel cell (450 mW cm⁻² at 60°C). Lastly, the use of the catalyst-free carbon materials for the reduction reaction makes this fuel cell system more cost-effective.

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Notes and references

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