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# Modeling of the mixed potential in hydrogen peroxide-based fuel cells

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## ABSTRACT

A one-dimensional mathematical model is developed for the study of the mixed potential associated with the hydrogen peroxide oxidation reaction (HPOR) at the cathode of hydrogen peroxide-based fuel cells. The complicated physicochemical processes, including mass transport, charge transport, and three simultaneous electrochemical reactions (the hydrogen peroxide reduction, hydrogen peroxide oxidation, and oxygen reduction reactions) are considered. The model is experimentally validated and shows good agreement with the literature experimental data. The model is then applied to the study of the mixed potential by varying the current density. It is found that the largest potential loss due to the HPOR occurs under the open-circuit condition (OCC), and the potential loss decreases with the superficial current density. In addition, the numerical results suggest that under the OCC, an increase in the concentrations of hydrogen peroxide and  $H^+$  ions leads to a decrease in the potential loss, but an increase in the hydrogen peroxide decomposition rate and the oxygen evolution rate.

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## Introduction

Being energy efficient and environmentally benign, fuel cells are emerging as alternative energy-conversion devices for portable, mobile and stationary power applications [1–3]. Generally, fuel cells require oxygen as the electron acceptor (oxidant) typically from the ambient air [4,5]. Their application, however, in air-free environments such as outer space and underwater leads to the requirement of an additional oxygen tank in the system, much lowering the energy density of the fuel cell system [6,7]. As an alternative oxidizer, hydrogen peroxide ( $H_2O_2$ ) have recently received ever-increasing attention, primarily because of its several unique

characteristics as opposed to the gaseous oxygen [8–11]: 1) fuel cells that use hydrogen peroxide can operate with the absence of oxygen environment, such as outer space and underwater conditions [8]; 2) the use of hydrogen peroxide as an oxidant can substantially increase the theoretical voltage of fuel cells and thus improve cell performance [9]; 3) the use of hydrogen peroxide offers the low activation loss of the reduction reaction due to two-electron transfer [10]; and 4) fuel cell systems that use hydrogen peroxide avoid water flooding problem due to its intrinsically liquid phase [11]. For these reasons, efforts have been devoted to the development of the fuel cells that use hydrogen peroxide as the oxidant [12–20]. Raman et al. [21] proposed a direct borohydride fuel cell (DBFC) employing hydrogen peroxide as the oxidant with

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a higher theoretical voltage of 3.02 V as opposed to the voltage of 1.64 V by using oxygen. Their experimental results showed that the fuel cell yielded an open-circuit voltage (OCV) of  $\sim 1.90$  V and a peak power density of  $350 \text{ mW cm}^{-2}$  at  $70^\circ\text{C}$ . Recently, An et al. [22] developed a hybrid direct ethanol fuel cell (DEFC) using hydrogen peroxide as the oxidant with a higher theoretical voltage of 2.52 V as compared to the voltage of 1.14 V with oxygen. The experimental results showed that such a fuel cell yielded an OCV of  $\sim 1.60$  V and a peak power density of  $360 \text{ mW cm}^{-2}$  at  $60^\circ\text{C}$  [23]. Among previous investigations, however, it should be noted that the potential of the hydrogen peroxide reduction reaction (HPRR) under the open-circuit condition (OCC) is roughly ranging from 0.8 V to 0.9 V (vs. SHE), which is much lower than the theoretical voltage of 1.78 V [21,22]. The previous investigation also showed that the large potential loss was attributed to the hydrogen peroxide oxidation reaction occurring at the cathode of the hydrogen peroxide-based fuel cells [24]. Generally, the presence of an oxidation reaction on the cathode results in a so-called mixed potential by spontaneously combining the reduction reaction. In a fuel cell system, the formation of the mixed potential not only lowers the cell voltage, but also decreases the utilization efficiency of hydrogen peroxide [25]. For this reason, it is essential to understand the formation mechanism of the mixed potential at the cathode of hydrogen peroxide-based fuel cells. As the present fuel cell system involves the complicated physicochemical processes, including mass transport, charge (ionic and electronic) transport, and three simultaneous electrochemical reactions, it is difficult to shed light on the formation mechanism of the mixed potential through experimental investigations. On the other hand, the mathematical modeling, as a powerful and economical tool, may play an important role in quantifying the complicated physicochemical processes. To our best knowledge, there is no attempt to mathematically investigate the mixed potential at the cathode of hydrogen peroxide-based fuel cells. In this work, we develop a half-cell mathematical model for hydrogen peroxide-based fuel cells by considering the complicated physicochemical processes, including mass/charge transport and electrochemical reactions. With this model, the study of the mixed potential under both the close-circuit condition (CCC) and OCC is studied and discussed.

## Formulation

We consider a half cell, as shown in Fig. 1, which consists of a flow field (FF), a diffusion layer (DL) and a catalyst layer (CL). The fuel-electrolyte-mixed solution (hydrogen peroxide and sulfuric acid) flowing into the FF is transported through the DL to the CL, where hydrogen peroxide reacts with protons and electrons to form water according to [24]:



In the meantime, the hydrogen peroxide oxidation reaction (HPOR) can take place at such a high potential to form oxygen, protons and electrons according to [26]:

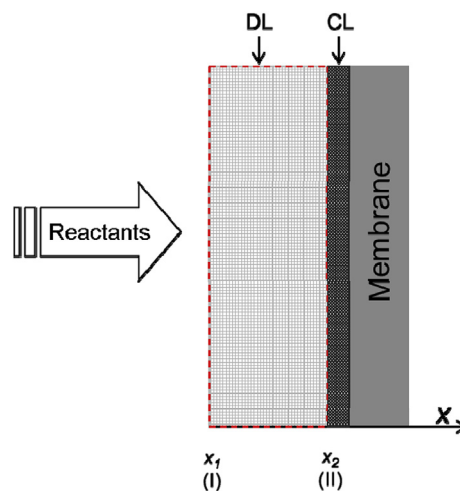
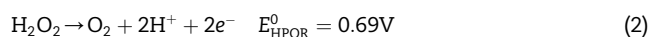
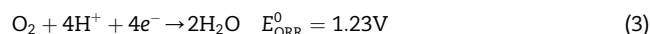


Fig. 1 – The schematic of a half cell considered in the present work.

In addition, since oxygen is produced (see Eq. (2)), the oxygen reduction reaction (ORR) is probable to occur according to [27]:



Among the three electrochemical reactions, one is the oxidation reaction (electron donor), whereas the other two are the reduction reaction (electron acceptor). Therefore, two oxidation–reduction reactions can be spontaneously established at the cathode of hydrogen peroxide-based fuel cells, apparently forming a mixed potential and thereby resulting in a potential loss. It is clear from the above description that the half cell considered in this work actually involves rather complex mass/charge transport processes coupled with the three simultaneous electrochemical reactions. To make the complicated process tractable, we develop a one-dimensional model ( $x$  axis: through-plane direction) with the following simplifications and assumptions:

- (1) The fuel cell is assumed to operate under steady-state and isothermal conditions.
- (2) The mass/charge transport through the DL is assumed to be a diffusion-predominated process and the convection effect due to bulk flow is ignored.
- (3) The CL is treated as an interface since it is much thinner than the DL.
- (4) The generated oxygen will remain in the aqueous solution.

## Mass transport

The mass conservation is expressed as:

$$\nabla N_i = 0 \quad (4)$$

where  $i$  represents hydrogen peroxide, proton, oxygen, and the species flux ( $N_i$ ) is related to the concentration gradient based on the Fick's law [28]:

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