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.

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 (H₂O₂) 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
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 mW cm\(^{-2}\) at 70 °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 mW cm\(^{-2}\) at 60 °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]:

\[
\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O} \quad \varepsilon_{\text{HPRR}} = 1.78\text{V} \tag{1}
\]

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]:

\[
\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \quad \varepsilon_{\text{HPOR}} = 0.69\text{V} \tag{2}
\]

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

\[
\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \quad \varepsilon_{\text{ORR}} = 1.23\text{V} \tag{3}
\]

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:

\[
\nabla N_i = 0 \quad \tag{4}
\]

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]:
Kond step, i.e.: the oxygen evolution reaction \[31\]. As such, the Pt(OH)\(_2\)-form surface can also adsorb oxygen generated by the hydrogen peroxide oxidation\[30\]. In this work, however, we modeled the electro-oxidation of hydrogen peroxide in acid media. Generally, the activity of carbon in acid media is much lower than that in alkaline media. The electrochemical activity of the carbon for the hydrogen peroxide oxidation in this work should be much lower than that of platinum. Hence, we ignored the electrochemical activity of the carbon toward the oxidation of hydrogen peroxide in this work.

In the present model, the electro-oxidation of hydrogen peroxide is considered as a multistep reaction and its kinetics is based on the following reaction mechanism\[31–35\]:

\[
\text{H}_2\text{O}_2 + \text{Pt(OH)}_2 \rightarrow \text{Pt(OH)}_2 \cdot \text{H}_2\text{O}_2
\]  

\[7\]

\[
\text{Pt(OH)}_2 \cdot \text{H}_2\text{O}_2 \rightarrow \text{Pt} + 2\text{H}_2\text{O} + \text{O}_2
\]  

\[8\]

\[
\text{Pt} + 2\text{H}_2\text{O} \rightarrow \text{Pt(OH)}_2 \cdot 2\text{H}^+ + 2\text{e}^-
\]  

\[9\]

Here, the rate-determining step is proposed to be the second step, i.e.: the oxygen evolution reaction \[31\]. As such, the pure Pt sites produced (Eq. (8)) are immediately oxidized (Eq. (9)) so that the active surface exists in the form of Pt(OH)\(_2\) [31]. Besides the surface adsorbed by hydrogen peroxide, the Pt(OH)\(_2\)-form surface can also adsorb oxygen generated by the HPOR [31]:

\[
\text{O}_2 + \text{Pt(OH)}_2 \rightarrow \text{Pt(OH)}_2 \cdot \text{O}_2
\]  

\[10\]

In addition, the active surface occupied by hydrogen peroxide can further adsorb protons according to [31]:

\[
\text{Pt(OH)}_2 \cdot \text{H}_2\text{O}_2 + \text{H}^+ \rightarrow \text{Pt(OH)}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}^+
\]  

\[11\]

From the equilibrium reactions (7), (10) and (11), we can obtain the following expressions [31]:

\[
\frac{K_1}{k_1} = \frac{\theta_{\text{Pt(OH)}_2 \cdot \text{O}_2} \cdot C_{\text{Pt(OH)}_2 \cdot \text{O}_2}}{\theta_{\text{Pt(OH)}_2} \cdot C_{\text{Pt(OH)}_2}}
\]  

\[12\]

where \(C\) stands for the species concentration, and the effective diffusivity of species, \(D_{\text{eff}}\), is given by Ref. [28]:

\[
D_{\text{eff}} = \varepsilon^2 D
\]  

\[6\]

where \(\varepsilon\) and \(D\) represent the DL porosity and the free-space diffusivity of each species, respectively.

**Electrochemical kinetics**

As discussed earlier, there are three simultaneous electrochemical reactions in the half cell considered in this work, i.e.: HPRR, HPOR, and ORR. It should be noted that as the CL is commonly composed of carbon supported catalyst and ionomer, the carbon corrosion reaction might thermodynamically occur at potentials lower than 0.9 V. However, the corrosion is believed to be slow at low operating temperatures (<100°C) [29]. For this reason, we ignored the carbon corrosion reaction in this work. It should be also noted that in alkaline media, carbon is electrochemically active for the hydrogen peroxide oxidation [30]. In this work, however, we modeled the mixed-potential at the cathode of hydrogen peroxide-based fuel cells, in which all the reactions take place in acid media. Generally, the activity of carbon in acid media is much lower than that in alkaline media. The electrochemical activity of the carbon for the hydrogen peroxide oxidation in this work should be much lower than that of platinum. Hence, we ignored the electrochemical activity of the carbon toward the oxidation of hydrogen peroxide in this work.

Using the Nernst equation, the anodic current density resulting from the HPOR can be expressed as:

\[
j_{\text{HPOR}} = n_{\text{HPOR}} F k_2 \exp\left(\frac{\alpha_{\text{HPOR}} F}{RT} \eta_{\text{HPOR}}\right) \theta_{\text{Pt(OH)}_2 \cdot \text{H}_2\text{O}_2}
\]  

\[20\]

where \(k\), \(\alpha\), and \(\eta\) represent rate constant, transfer coefficient, and overpotential, respectively.

The cathodic current density resulting from the HPRR can be expressed by a Tafel-form kinetics as:

\[
j_{\text{HPRR}} = i_{0,\text{HPRR}} \left(\frac{C_{\text{Pt(OH)}_2 \cdot \text{H}_2\text{O}_2}}{C_{\text{Pt(OH)}_2}}\right)^{\gamma_{\text{HPRR}}} \exp\left(\frac{\alpha_{\text{HPRR}} F}{RT} \eta_{\text{HPRR}}\right)
\]  

\[21\]

\[
\gamma_{\text{HPRR}} = \begin{cases} 0 & C_{\text{Pt(OH)}_2 \cdot \text{H}_2\text{O}_2} > C_{\text{ref}} \\ 1 & C_{\text{Pt(OH)}_2 \cdot \text{H}_2\text{O}_2} \leq C_{\text{ref}} \end{cases}
\]  

\[22\]

and

\[
\gamma_{\text{HPOR}} = \begin{cases} 0 & C_{\text{Pt(OH)}_2} > C_{\text{ref}} \\ 1 & C_{\text{Pt(OH)}_2} \leq C_{\text{ref}} \end{cases}
\]  

\[23\]

where \(C_{\text{Pt(OH)}_2}\) is the species concentration in the CL and \(C_{\text{ref}}\) is the species reference concentration. The reaction order \(\gamma\) is related to the species concentration and is assumed to be zero-order when its concentration is higher than a reference value. Otherwise, a first-order reaction is specified.

With respect to the cathodic current density resulting from the ORR, a Tafel-form kinetics is employed:

\[
j_{\text{ORR}} = i_{0,\text{ORR}} \left(\frac{C_{\text{Pt(OH)}_2 \cdot \text{H}_2\text{O}_2}^{\gamma_{\text{ORR}}}}{C_{\text{Pt(OH)}_2}^{\gamma_{\text{ORR}}}}\right) \exp\left(\frac{\alpha_{\text{ORR}} F}{RT} \eta_{\text{ORR}}\right)
\]  

\[24\]
The superficial current density is equal to zero, i.e.: \( j_{\text{OCC}} = \begin{cases} 0 & \text{if } C_{\text{O}} > C_{\text{ref}} \\ 1 & \text{if } C_{\text{O}} < C_{\text{ref}} \end{cases} \) (25)

and

\( j_{\text{OCC}}^\text{H} = \begin{cases} 0 & \text{if } C_{\text{H}} > C_{\text{ref}}^\text{H} \\ 1 & \text{if } C_{\text{H}} < C_{\text{ref}}^\text{H} \end{cases} \) (26)

Therefore, the superficial current density can be determined by the three respective current densities. Under the OCC, the superficial current density is equal to zero, i.e.:

\[
0 = j_{\text{HPRR}} + j_{\text{ORR}} - j_{\text{HPOR}}
\]

(27)

where \( E_{\text{mixed}}^0 \) stands for the mixed potential under the OCC. Under the CCC, the superficial current density, \( i \), is expressed as:

\[
i = j_{\text{HPRR}} + j_{\text{ORR}} - j_{\text{HPOR}}
\]

(28)

Boundary conditions

At interface (1) \( (x=x_1) \), the species concentration is equal to the inlet concentration, i.e.:

\[
C_i = C_i^\text{inlet}
\]

(29)

where \( i \) represents \( \text{H}_2\text{O}_2, \text{H}^+, \) or \( \text{O}_2 \).

At interface (2) \( (x=x_0) \), the species flux is related to the three respective current densities according to the Faraday's law:

\[
N_{\text{H}_2\text{O}_2} = \frac{s_{\text{HPRR}} j_{\text{HPRR}} F}{n_{\text{HPRR}} F} + \frac{s_{\text{HPOR}} j_{\text{HPOR}} F}{n_{\text{HPOR}} F}
\]

(30)

and

\[
N_{\text{H}^+} = \frac{s_{\text{HPRR}} j_{\text{HPRR}} F}{n_{\text{HPRR}} F} + \frac{s_{\text{ORR}} j_{\text{ORR}} F}{n_{\text{ORR}} F} - \frac{s_{\text{HPOR}} j_{\text{HPOR}} F}{n_{\text{HPOR}} F}
\]

(31)

\[
N_{\text{O}_2} = \frac{s_{\text{OH}^+} j_{\text{OH}^+} F}{n_{\text{OH}^+} F} - \frac{s_{\text{ORR}} j_{\text{ORR}} F}{n_{\text{ORR}} F}
\]

(32)

where \( j \) represents the respective current density; \( s \) is the stoichiometric coefficient; \( n \) is the number of transferred electrons.

The physicochemical, operating, structural, and mass/charge transport parameters are listed in Tables 1–4, respectively. All potentials/mixed potentials are referred to standard

### Table 2 – Operating parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating temperature</td>
<td>( T )</td>
<td>333.15</td>
<td>K</td>
<td></td>
</tr>
<tr>
<td>Inlet concentration (( \text{O}_2 ))</td>
<td>( C_{\text{O}_2}^{\text{inlet}} )</td>
<td>0</td>
<td>mol m(^{-3})</td>
<td>Assumed</td>
</tr>
<tr>
<td>Reference concentration (( \text{H}_2\text{O}_2 ))</td>
<td>( C_{\text{H}_2\text{O}_2}^{\text{ref}} )</td>
<td>4000</td>
<td>mol m(^{-3})</td>
<td>[22]</td>
</tr>
<tr>
<td>Reference concentration (( \text{H}^+ ))</td>
<td>( C_{\text{H}^+}^{\text{ref}} )</td>
<td>2000</td>
<td>mol m(^{-3})</td>
<td>[22]</td>
</tr>
<tr>
<td>Reference concentration (( \text{O}_2 ))</td>
<td>( C_{\text{O}_2}^{\text{ref}} )</td>
<td>36.573</td>
<td>mol m(^{-3})</td>
<td>[28]</td>
</tr>
</tbody>
</table>
hydrogen electrode (SHE) in this work. The equations described above are numerically solved by Matlab.

Results and discussion

Model validation

The numerical results of the mixed potential and the experimental data are compared in Fig. 2. The experimental data were collected when the cell was operated at 60 °C with a fuel-electrolyte-mixed solution (4.0 M hydrogen peroxide + 1.0 M sulfuric acid) at the cathode [22]. It is seen that the predicted mixed potentials are in good agreement with the experimental data. In the following, we present the numerical results on the study of the mixed potential under both the CCC and OCC.

Mixed potential under the CCC

As discussed earlier, there are three simultaneous electrochemical reactions occurring at the cathode of hydrogen peroxide-based fuel cells, including the HPRR, HPOR and ORR. Among those reactions, the cathodic current density is generated by the HPRR and ORR, while the anodic current density is produced by the HPOR. The combination of the cathodic and anodic current densities results in a superficial current density (net current density). The red line in Fig. 3a represents the numerical results incorporating the HPOR. As a comparison, the predicted cathode potentials without considering the HPOR (i.e.: only the HPRR taking place) are also shown in Fig. 3a. It can be seen that the largest potential loss due to the HPOR occurs under the OCC, and the potential loss decreases with increasing the superficial current density, as shown in Fig. 3b. This result suggests that it is essential to incorporate the HPOR in developing the mathematical model for the cathode of hydrogen peroxide-based fuel cells, particularly at zero/low superficial current densities.

Fig. 4 presents the respective current density for the three electrochemical reactions, where the horizontal axis denotes the superficial current density and the vertical axis stands for the respective current density. It is interesting to note that the cathodic current density produced by the ORR is almost equal to zero, indicating that the cathodic current density is mainly attributed to the HPRR. This is because the kinetics of the HPRR is much faster than that of the ORR resulting from the two-electron transfer process in the HPRR as opposed to the four-electron transfer process in the ORR [11]. It can be seen from Fig. 4 that the cathodic current density generated by the HPRR increases with the superficial current density, which can be explained by the fact that the decrease in the mixed potential as a result of increasing the superficial current density causes an increase in the overpotential of the HPRR ($E_{\text{HPRR}}^0 - E_{\text{mixed}}^0$), thereby increasing the cathodic current density. In addition, it can be seen from Fig. 4 that with the superficial current density, the anodic current density resulting from the HPOR gradually decreases. This is because the decrease in the mixed potential as a result of increasing the superficial current density causes a decrease in the overpotential of the HPOR ($E_{\text{mixed}}^0 - E_{\text{HPOR}}^0$), thereby lowering the anodic current density. More importantly, it is found from Fig. 4 that when the superficial current density is larger than 2000 A m$^{-2}$ (or the cathode potential is lower than ~0.75 V), the anodic current density resulting from the HPOR becomes zero, apparently meaning that the HPOR does not take place. The disappearance of the HPOR at the cathode avoids the presence of the mixed potential and potential loss. This result suggests that when the cathode potential is lower than a certain value (around $E_{\text{HPOR}}^0$), the overpotential of HPOR ($E_{\text{mixed}}^0 - E_{\text{HPOR}}^0$) is not large enough to drive the HPOR. Therefore, the mixed potential appears only at zero/low current densities or in the high-potential region, where the HPOR takes place.

Fig. 5 shows the species concentration in the CL at various superficial current densities. It is seen that with the superficial current density, the hydrogen peroxide concentration in the CL first increases and then decreases, resulting in the presence of a peak concentration of hydrogen peroxide in the whole superficial current density region. As discussed earlier, the anodic current density generated by the HPOR decreases with the superficial current density, resulting in a decrease in the $H_2O_2$ decomposition rate, as shown in Fig. 4. On the other hand, the $H_2O_2$ consumption rate by the HPRR gradually increases with the superficial current density evident from the results in Fig. 4. Therefore, the decreased decomposition rate (by the HPOR) and the increased consumption rate (by the HPRR) results in the presence of a peak hydrogen peroxide
concentration in the whole superficial current density region. Also, it can be seen from Fig. 5 that the oxygen concentration in the CL decreases with the superficial current density. As the oxygen evolution rate is proportional to the anodic current density, the decreased anodic current density with the superficial current density results in a decrease in the oxygen concentration in the CL.

**Mixed potential under the OCC**

Fig. 6 shows the effect of the reactant concentration (hydrogen peroxide and $H^+$ ions) on the mixed potential ($E_{\text{mixed}}^{0}$) and potential loss ($E_{\text{HPRR}}^{0} - E_{\text{mixed}}^{0}$) due to the HPOR under the OCC. It can be seen that increasing the reactant concentration leads to an increase in the mixed potential and a decrease in the potential loss. The predicted trends are consistent with the experimental data in the open literature [36]. The reasons for this phenomenon are explained as follows. Under the OCC, as the superficial current density is equal to zero, the cathodic current density (resulting from the HPRR and ORR) is equal to the anodic current density (resulting from the HPOR). An increase in the hydrogen peroxide concentration can enhance the mass transport of hydrogen peroxide from the FF to the CL, yielding a higher concentration in the CL and accelerating the HPRR. Thus, the increased reaction rate of the HPRR brings an increase in the cathodic current density, as shown in Fig. 7a. On the other hand, as a result of the insignificant effect of the hydrogen peroxide concentration on the surface coverage fraction of hydrogen peroxide evident from the results in Fig. 8, the reaction rate of the HPOR should be almost the same at various hydrogen peroxide concentrations, apparently meaning that the anodic current density is almost unchanged with the hydrogen peroxide concentration. Therefore, it seems that the cathodic current density should be larger than the anodic current density. To maintain the net-zero superficial current density, a positive shift in the mixed potential not only can limit the increment rate of the cathodic current density by lowering the overpotential of the HPRR ($E_{\text{HPRR}}^{0} - E_{\text{ORR}}^{0} = E_{\text{mixed}}^{0}$), as shown in Fig. 7a, but also can exponentially increase the anodic current density through enlarging the overpotential of the HPOR ($E_{\text{HPOR}}^{0} - E_{\text{mixed}}^{0}$), as shown in Fig. 7b. Therefore, increasing the hydrogen peroxide concentration increases the mixed potential, thereby decreasing the potential loss.

Similarly, an increase in the $H^+$ concentration can accelerate the HPRR and ORR as a result of the enhanced charge transport of $H^+$ ions, but slow the HPOR as a result of the decreased surface coverage fraction of hydrogen peroxide evident from the results in Fig. 8. For this reason, it seems that the cathodic current density generated by two reduction reactions (HPRR and ORR) should be larger than the anodic current density created by the oxidation reaction (HPOR). To maintain the net-zero superficial current density under the OCC, however, a positive shift in the mixed potential not only can limit the increment rate of the cathodic current density through decreasing the overpotentials ($E_{\text{HPRR}}^{0}/E_{\text{ORR}}^{0} - E_{\text{mixed}}^{0}$), as shown in Fig. 7a, but also can exponentially increase the anodic current density through enlarging the overpotential of the HPOR ($E_{\text{mixed}}^{0} - E_{\text{HPOR}}^{0}$), as shown in Fig. 7b. Hence, increasing the $H^+$ concentration increases the mixed potential, thereby decreasing the potential loss.

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**Fig. 3** – The comparison between results with and without considering the HPOR (a) The potential/mixed potential; (b) the potential loss. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

**Fig. 4** – The respective current density for the three electrochemical reactions.
Fig. 9 shows the effect of the reactant concentration on the species concentration in the CL. It can be seen that with increasing the hydrogen peroxide concentration, both hydrogen peroxide and oxygen concentrations in the CL are increased, whereas with increasing the $\text{H}^+$ concentration, the hydrogen peroxide concentration in the CL is decreased, but the oxygen concentration in the CL is increased. The reasons for this phenomenon are explained as follows. An increase in the hydrogen peroxide concentration will enhance the mass transport of hydrogen peroxide, increasing the concentration of hydrogen peroxide in the CL, as shown in Fig. 9a. On the other hand, a higher hydrogen peroxide concentration results in a larger anodic current density (i.e.: oxygen evolution rate) (see Fig. 6e).
Fig. 7b), and thus a higher concentration of oxygen in the CL, as shown in Fig. 9b. As discussed earlier, increasing the H$^+$ concentration also causes the increase in both the anodic and cathodic current densities, as shown in Fig. 7a–c. The increased anodic current density means an increase in the hydrogen peroxide decomposition rate and thus a decrease in the concentration of hydrogen peroxide in the CL. On the other hand, the increased decomposition rate of hydrogen peroxide means an increase in the oxygen evolution rate, thereby resulting in an increase in the concentration of oxygen in the CL.

Concluding remarks

In this work, we have developed a one-dimensional mathematical model to investigate the mixed potential associated with the HPOR occurring at the cathode of hydrogen peroxide-based fuel cells. This model is applicable to hydrogen peroxide-based fuel cells. The present model incorporates the complicated physicochemical processes, such as mass transport, charge transport, and electrochemical reactions including simultaneous hydrogen peroxide reduction, hydrogen peroxide oxidation, and oxygen reduction reactions. The results of this model not only are in good agreement with the literature experimental data, but also show that the largest potential loss due to the HPOR occurs under the open-circuit condition, and the potential loss decreases with the superficial current density. The numerical results also suggest that the mixed potential appears only at zero/low superficial current densities or in the high-potential region, where the HPOR takes place. In addition, the investigation under the open-circuit condition shows that increasing 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 oxygen evolution rate. To operate a H$_2$O$_2$-based fuel cell, our modeling results indicate that the hydrogen peroxide decomposition rate can be lowered by regulating the operation parameters.

Acknowledgments

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References


**Glossary**

C: Concentration, mol m$^{-3}$

D: Diffusivity, m$^2$ s$^{-1}$

E: Potential, V

F: Faraday’s constant, A s mol$^{-1}$

i: Current density, A m$^{-2}$

i$\text{p}$: Exchange current density, A m$^{-2}$

j: Respective current density, A m$^{-2}$

k: Rate constant, mol m$^{-2}$ s$^{-1}$

K: Constant, m$^2$ mol$^{-1}$

l: Thickness, m

n: Number

N: Species flux, mol m$^{-2}$ s$^{-1}$
R: Universal gas constant, J mol$^{-1}$ K$^{-1}$
s: Stoichiometric coefficient
T: Operating temperature, K
x: Coordinate

Greek

α: Transfer coefficient
ζ: Porosity
γ: Reaction order
η: Overpotential, V
θ: Surface coverage fraction

Superscripts

0: Standard
CL: Catalyst layer
eff: Effective

Subscripts

DL: Diffusion layer
H$^+$: Proton
H$_2$O$_2$: Hydrogen peroxide
inlet: Inlet
O$_2$: Oxygen
ref: Reference

HPOR: Hydrogen peroxide oxidation reaction
HPRR: Hydrogen peroxide reduction reaction
i: Species
O$_2$: Oxygen
ORR: Oxygen reduction reaction