Electrochemistry Modeling of Proton Exchange Membrane (PEM) Water Electrolysis for Hydrogen Production

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ABSTRACT:
An electrochemistry model was developed to analyse the J-V characteristics of a Proton Exchange Membrane (PEM) water electrolyser for hydrogen production. The Butler-Volmer equation and water transport characteristics through electrolyte membrane were employed to simulate the electrode activation overpotential and membrane ohmic overpotential, respectively. The modeling results are found to agree reasonably well with experimental data published in the literature. The parametric simulations show that the ohmic overpotential is relatively small with typical water content in the membrane. Compared with the cathode overpotential, the anode overpotential is more significant and constitutes the major source of voltage loss. The high anode overpotential is due to the relatively slow oxidation kinetics, which is related to anode material property and microstructure. This model can be integrated with a photovoltaic or wind turbine model to predict the performance of sustainable hydrogen production systems and optimise their designs.

KEYWORDS: Proton exchange membrane; Water electrolysis; Hydrogen Production; Electrochemistry model

1. Introduction
Hydrogen will play an important role as an energy carrier for sustainable development in the future [1-3]. Hydrogen can be used in fuel cells to generate electricity efficiently, with water as the only byproduct [4,5]. Besides, hydrogen is the lightest element and any leakage of hydrogen gas can disperse quickly, thus hydrogen is as safe as other commonly used fuels [4]. However, hydrogen is not an energy source, but an energy carrier. Hydrogen must be produced from other sources with energy input. Presently, hydrogen can be economically produced from hydrocarbon reforming, which is neither renewable nor clean from the life cycle point of view [6-8]. Powered by solar energy, hydrogen can be produced from water, via photocatalysis, thermochemical cycles, and water electrolysis [9,10]. These methods offer renewable and clean production of hydrogen fuel and, therefore, have attracted increasing research interests in recent years. So far, the efficiencies of photocatalysis and thermochemical cycles are still too low to be economically competitive. Water electrolysis is hence the most promising technology for large-scale hydrogen production [10]. Compared with traditional alkaline electrolysis, in which corrosive potassium hydroxide (KOH) solution is used as the electrolyte, proton exchange membrane (PEM) electrolysis have more advantages, such as ecological cleanness, high degree of gases purity, and easy maintenance [11]. As the cost of hydrogen production by PEM electrolysis can be further reduced due to continuous technology development, research on PEM electrolysis has been very active in recent years. Investigations on PEM electrolysis for hydrogen production are focused on demonstration of PEM electrolysis for hydrogen production [12], development of new catalysts [11,13], and development of new proton exchange membrane electrolytes [14]. Unfortunately, theoretical modeling works are relatively scarce.

In this paper, an electrochemistry model was developed to simulate the J-V characteristics of PEM electrolysis for hydrogen production. Model validation was conducted by comparing the modeling results with experimental data from the literature. Parametric analyses were performed to study individual overpotentials contributing to the overall voltage loss. Effects of membrane thickness and anode exchange current density on cell potential were also analyzed.

2. Modeling
The fundamental mechanisms of PEM electrolysis are illustrated in Fig. 1. A potential higher than that required for water splitting is applied to the electrodes to initiate electrochemical reactions. Water is fed
to the anode, where water molecules lose electrons and decompose into oxygen gas and hydrogen ions. The produced oxygen gas together with un-reacted water is collected at the anode flow channel. The hydrogen ions produced together with water molecules are transported through the proton exchange membrane to the cathode, where they receive electrons to reduce to hydrogen gas. The net reaction for PEM electrolytic hydrogen production is

\[
\text{H}_2\text{O} \rightarrow \text{H}_2 + 0.5\text{O}_2
\]  

(1)

![Diagram showing working mechanisms of PEM electrolysis for hydrogen production](image)

Figure 1. Working mechanisms of PEM electrolysis for hydrogen production

The required voltage for PEM electrolysis can be expressed as

\[
V = E + \eta_{\text{ohmic}} + \eta_{\text{act,a}} + \eta_{\text{act,c}}
\]  

(2)

where \( E \) is the equilibrium voltage; \( \eta_{\text{ohmic}} \) is the ohmic overpotential across the proton exchange membrane, \( \eta_{\text{act,a}} \) and \( \eta_{\text{act,c}} \) are activation overpotentials at anode and cathode, respectively. The concentration overpotential is neglected because the gas transport limitations in thin electrodes are insignificant for PEM electrolysis under normal operation conditions [15].

2.1. Equilibrium voltage

The equilibrium voltage for PEM electrolysis can be empirically expressed as [16],

\[
E = 1.23 - 0.9 \times 10^{-3} (T - 298) + 2.3 \frac{RT}{4F} \log \left( \frac{P_{\text{H}_2}^2 P_{\text{O}_2}}{} \right)
\]  

(3)

where \( R \) is the universal gas constant (8.3145Jmol\(^{-1}\)K\(^{-1}\)); \( F \) is the Faraday constant (9.6485x10\(^4\)Cmol\(^{-1}\)); \( T \) is the absolute temperature; \( P_{\text{H}_2} \) and \( P_{\text{O}_2} \) are the partial pressures of hydrogen and oxygen, respectively.

2.2. Ohmic overpotential across proton exchange membrane

Ohmic overpotential across the proton exchange membrane is caused by the resistance of the membrane to the hydrogen ions transporting through it. The ionic resistance of the membrane is related to the degree of humidification and thickness of the membrane as well as the membrane temperature. The local ionic conductivity \( \sigma(x) \) of the membrane has been empirically determined as [17]

\[
\sigma(x) = \left[ 0.5139 \lambda(x) - 0.326 \right] \exp \left[ 1268 \left( \frac{1}{303} - \frac{1}{T} \right) \right]
\]  

(4)

where \( x \) is the location in the membrane measured from the cathode-membrane interface; \( \lambda(x) \) is the water content at location \( x \) in the membrane, which can be expressed linearly in terms of water content at the membrane-electrode interfaces [17],

\[
\lambda(x) = \frac{\lambda_a - \lambda_c}{L} \cdot x + \lambda_c
\]  

(5)

where \( L \) is the membrane thickness, \( \lambda_a \) and \( \lambda_c \) are the water contents at the anode-membrane and the cathode-membrane interface, respectively. The overall ohmic resistance can thus be determined as
The ohmic overpotential can be expressed in terms of ohm's law as follows,
\[ \eta_{\text{ohmic}} = J R_{\text{PEM}} \]  

where \( J \) is the current density.

### 2.3. Activation overpotentials at the electrodes

The activation overpotential is a measure of the activity of the electrodes. It represents the overpotential required for electrochemical reaction. The electrode activation overpotential can be expressed by Butler-Volmer equation,

\[
J = J_{0,i} \left[ \exp \left( \frac{\alpha zF \eta_{\text{act},i}}{RT} \right) - \exp \left( \frac{(1-\alpha)zF \eta_{\text{act},i}}{RT} \right) \right], \ i = a, c
\]

where \( J_{0,i} \) is the exchange current density and subscripts \( a \) and \( c \) represent anode and cathode, respectively; \( \alpha \) is the symmetrical factor; and \( z \) is the number of electrons involved per reaction. For water electrolysis, \( \alpha \) and \( z \) are found to be 0.5 and 2, respectively [18]. The activation overpotential of an electrode can be explicitly expressed as

\[
\eta_{\text{act},i} = \frac{RT}{F} \sinh^{-1} \left( \frac{J}{2J_{0,i}} \right) = \frac{RT}{F} \ln \left[ \frac{J}{2J_{0,i}} + \sqrt{\left( \frac{J}{2J_{0,i}} \right)^2 + 1} \right], \ i = a, c
\]

Exchange current density is an important parameter in calculating the activation overpotential. It represents the electrode’s readiness to proceed with the electrochemical reaction. High exchange current density means high reactivity of the electrode. The exchange current density for PEM electrolysis can be expressed as [19]

\[
J_{0,i} = J_i^{\text{ref}} \exp \left( - \frac{E_{\text{act},i}}{RT} \right), \ i = a, c
\]

where \( J_i^{\text{ref}} \) is the pre-exponential factor; and \( E_{\text{act},i} \) is the activation energy for anode and cathode, respectively. Substituting Eqs. (3), (7), and (9) into Eq. (2) yields the \( J-V \) characteristics of PEM electrolysis for hydrogen production.

### 3. Model validation

The model was used to simulate experiments published in the literature and a comparison between the modeling results and the experimental data was conducted for model validation. The electrolyte used in the experiments [20,21] was Nafion, a perfluorosulfonic (PFSA) polymer widely used as electrolyte in fuel cells/electrolysers. The thicknesses of electrolytes tested in references [20] and [21] were 50 \( \mu \text{m} \) and 178 \( \mu \text{m} \), respectively. Platinum was used as the electrode catalyst. At 353 K, the values of exchange current density for anode and cathode are 1.0x10\(^{-5}\) A/m\(^2\) and 10 A/m\(^2\), respectively [22,23]. Adopting these values in Eq. (10), the pre-exponential factors were determined. In both studies, electrolytic hydrogen production was conducted at one atmospheric pressure. The typical values of other parameters used in the modeling study are summarized in Table 1.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P_{\text{O}_2} ) (atm)</td>
<td>1.0</td>
<td>[20,21]</td>
</tr>
<tr>
<td>( P_{\text{H}_2} ) (atm)</td>
<td>1.0</td>
<td>[20,21]</td>
</tr>
<tr>
<td>( E_{\text{act},a} ) (KJ/mol)</td>
<td>76</td>
<td>[19]</td>
</tr>
<tr>
<td>( E_{\text{act},c} ) (KJ/mol)</td>
<td>18</td>
<td>[19]</td>
</tr>
<tr>
<td>( \lambda_a )</td>
<td>14</td>
<td>[17]</td>
</tr>
<tr>
<td>( \lambda_c )</td>
<td>10</td>
<td>[17]</td>
</tr>
</tbody>
</table>
The simulated J-V characteristics of PEM electrolysis were compared with experimental data from [20] as shown in Fig. 2a. The modeling results agreed very well with experimental data, indicating the capability of the present model. It was found that the cell potential increased rapidly when \( J < 200 \text{ A/m}^2 \). As \( J \) exceeded 200 \( \text{A/m}^2 \), the cell potential increased steadily with \( J \).

Figure 2b presents the comparison between the modeling results and experimental data from [21] for operating temperature ranging from 298 K to 353 K and \( J = 5000 \text{ A/m}^2 \). The cell potential was found to decrease with increasing temperature. At a higher operating temperature, the electrochemical reaction is faster, thus the exchange current density is higher, leading to a lower activation overpotential. In addition, the electrolyte ionic conductivity increases with temperature, leading to a lower ohmic overpotential. The combined effects of temperature increase result in considerable decrease in cell potential.

In Figures 2a and 2b, as the comparison between the modeling results and experimental data shows a good agreement, the electrochemistry model developed in this study has been validated.

4. Results and discussion

In order to better understand the working mechanisms, individual overpotentials were studied in more detail by theoretical modeling analysis. The input parameters used were consistent with reference [20]. As shown in Fig. 3, the ohmic overpotential was very small and increased steadily with current density. It was because the membrane ionic conductivity was high at typical humidity (\( \lambda \approx 14 \)) and operating temperature (353 K). Though larger than ohmic overpotential, the cathode activation overpotential was much smaller than the anode activation overpotential, as the reduction in kinetics at the cathode Pt surface was fast. The anode activation overpotential increased abruptly at \( J < 200 \text{ A/m}^2 \), and then increased steadily with \( J \). These detailed modeling results explained the J-V variation presented in Figure 2a as the anode activation overpotential dominates the overall voltage loss.
In practice, the thickness of the electrolyte membrane of a PEM electrolyser could range from 50 $\mu$m to 200 $\mu$m. The membrane thickness effect on electrolyser $J$-$V$ characteristics was modeled. As shown in Fig. 4, membrane thickness had insignificant effect on the cell potential for $J < 2000$ A/m$^2$. For large $J$, the effect became more apparent; the cell potential was found to increase with membrane thickness. During normal operation, membrane ionic resistance was very low, thus the variation in membrane thickness did not affect the ohmic overpotential much.

![Figure 4. Membrane thickness effect on $J$-$V$ characteristics of PEM electrolyser](image)

Figure 4. Membrane thickness effect on $J$-$V$ characteristics of PEM electrolyser

Figure 5 shows the effect of anode exchange current density on $J$-$V$ characteristics of PEM electrolyser. The cell potential decreased with increasing anode exchange current density, leading to a higher energy conversion efficiency. Similarly, increasing cathode exchange current density could also reduce cell potential. As Pt cathode shows the fastest reduction kinetics, the effect of cathode exchange current density is not presented here.

![Figure 5. Effect of anode exchange current density on $J$-$V$ characteristics of PEM electrolyser](image)

Figure 5. Effect of anode exchange current density on $J$-$V$ characteristics of PEM electrolyser

It can be seen from the above analyses that it is of paramount importance to develop new anode catalyst to reduce anode activation overpotential. The exchange current density is a measure of the reaction kinetics of electrode. Therefore, exchange current density not only depends on the operating temperature, but also highly depends on the material properties, i.e. electronic interaction of the catalyst with reactant species, microstructure of catalyst layer, porosity, pore size, grain boundary length, and specific area. Recent studies have shown that using PtIr as an anode catalyst could increase exchange current density to $1.0 \times 10^{-3}$ A/m$^2$ or above [20,24-26]. In the study by Thampan et al. [19], exchange current density was expressed proportional to roughness factor of catalyst layer, indicating the importance of microstructure effect. In order to obtain higher exchange current density, more efforts should be given to develop new catalyst as well as to optimize the electrode structural parameters.
5. Conclusion

The J-V characteristics of PEM electrolysis for hydrogen production were analyzed by means of an electrochemistry model. Activation overpotential and ohmic overpotential were considered in the model. Model validation was conducted by comparing modeling results with experimental data from the literature.

Simulation results showed that the cell potential of PEM electrolysis increased abruptly at low J and increased steadily for higher J. It was also found that increasing operating temperature could significantly decrease cell potential due to the enhanced exchange current density and membrane ionic conductivity. Modeling analyses showed that anode activation overpotential was the major source of voltage loss due to slow anode oxidation reaction kinetics. For comparison, cathode activation overpotential was small as the cathode reduction reaction kinetics were very fast. Working with normal membrane water content, the electrolyte ohmic overpotential was the lowest overpotential.

In a renewable-hydrogen system, PV arrays or wind turbines are connected with electrolyser s to supply electricity for hydrogen production. The electrochemistry model developed in this paper can be integrated with PV/wind turbine electrical models for a complete study on hydrogen production system performance.

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References: