Electrochemical performance modeling of a proton exchange membrane electrolyzer cell for hydrogen energy

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Abstract

This paper presents a comprehensive computational model for the proton exchange membrane (PEM) electrolyzer cells, which have attracted more attention for renewable energy storage and hydrogen production. A new ohmic loss model of a PEM electrolyzer cell has been developed and the influence of different operating conditions and physical design parameters on its performance has been investigated, including operating temperature, pressure, exchange current density, electrode thickness, membrane thickness and interfacial resistance. The interfacial resistance between the membrane and electrode has been found to play an important part for electrolyzer performance and an overpotential is increased significantly with the interfacial resistance. At a current density of 1.5 A/cm^2 , the performance loss due to the interfacial resistance between the membrane and electrode comprises 31.8% of the total ohmic loss. Thickness changes in either electrode or membrane also have significant impacts on the electrolyzer performance mainly due to their contributions to the diffusion overpotential and ohmic loss. Increasing the operating temperature will result in lower electrolyzer overpotential, while increasing the operating pressure will lead to higher electrolyzer overpotential, which is mainly controlled by the open circuit voltage. Results obtained from the present model will provide a comprehensive understanding of design parameter effects and consequently improve the design/performance in a PEM electrolyzer cell.

Keywords: PEM electrolyzer cell; Performance loss; Modeling; Ohmic loss; Hydrogen production; Interfacial resistance

1 Introduction

A electrolyzer cell taking advantage of a proton exchange membrane (PEM) has attracted more attention for renewable energy storage and pure hydrogen/oxygen production due to their higher energy efficiency/density, faster charging/discharging, and a more compact design [1, 2]. Compared with conventional hydrogen production processes including fossil fuel reforming and alkaline water electrolysis, PEM electrolyzer cells offer a more environmentally friendly approach as well as high hydrogen purity. PEM fuel cells are well known as clean and sustainable energy devices. PEM electrolyzer cells have similar working components to a PEM fuel cell, but operate in the reverse direction. There is an abundance of papers detailing PEM fuel cell modeling [3-7] and direct methanol fuel cell modeling [8, 9], which will be useful for PEM electrolyzer cell issues. Many physical parameters, including the operating conditions, electrode and membrane characteristics, significantly affect PEM electrolyzer cell system performance and durability. In order to optimize and design a PEM electrolyzer cell system properly, a full performance analysis and modeling of PEM electrolyzer cells is necessary.

In the past years, some experimental studies [10-16] have been conducted to investigate PEM electrolyzer cell performance under different conditions, but there are only a few papers regarding PEM electrolyzer cell modeling.

Choi et al. [17] introduced a simple mathematical model of solid polymer electrolyte water electrolysis. In the model, the cell voltage was calculated by the sum of open circuit voltage, electrode overpotential, ohmic overpotential due to the membrane and interfacial resistances. Gorgun [18] introduced the first dynamic model of PEM electrolyzer cells. This model included water transport phenomenon through the membrane due to electro-osmotic drag and diffusion.

Lebbal et al. [19] conducted a dynamical model including a steady state electrical model and a dynamic thermal model to monitor the PEM electrolysis safety and efficiency. In the model, the total relationship of voltage and current density was expressed as four parts: open circuit voltage, activation overpotential, diffusion overpotential and ohmic overpotential. The diffusion overpotential was related to the values of current due to the effects of gas and water transport and the ohmic loss was given by an empirical relation.

Grigoriev et al. [20, 21] developed mathematical models in order to evaluate the electrochemical performance of atmosphere and high pressure (up to 130 bars) PEM electrolyzer cells. To evaluate and optimize electrolyzer efficiency and performance, different operating conditions including pressure, temperature, current density, membrane thickness are discussed.

Marangio et al. [22] also conducted a detailed theoretical model to analyze characteristics of a high pressure PEM electrolyzer cell. In their model, the Gibbs free energy was used to calculate the open circuit voltage under non-standard temperature and pressure conditions. Water flow inside the electrolysis cell included several parts: water inlet and outlet flow in the anode and cathode, water transport due to concentration difference, water transport due to the electro-osmotic drag, water transport due to pressure difference across the membrane, and water consumed by the electro-chemical reaction. The ohmic resistance was calculated by the sum of electrodes, plates, and membrane resistance. A series of modeling polarization curves of PEM electrolyzer cells was obtained and then compared with the experimental results.

Based on the above reviews, since existing models did not fully consider the effects of various operating conditions and design parameters on the cell performance, a comprehensive model for better correlating the effects of both design parameters and operating conditions with PEM electrolyzer cell performance is strongly desired. In this paper, the authors focus on a full mathematical model and electrochemical performance analysis of PEM electrolyzer cells. A new model with different electrode materials and interface equivalent resistance has been developed. Different operating conditions and physical parameters effects, including operating temperature and pressure, exchange current density, electrode thickness, membrane thickness and interfacial resistance, which may affect and even reduce the electrolysis cell performance, have been investigated. These numerical results help obtain a deeper understanding of PEM electrolyzer cells and improve cell performance.

2 Mathematical models

A geometric schematic of PEM electrolyzer cells used for the modeling calculations is shown in Figure 1. Water enters through the flow channel at the anode and then diffuses across the porous gas diffusion layer (GDL). In the catalyst layer (CL) reaction site, water is dissociated into electrons, protons, and oxygen. The protons migrate through PEM and combine with electrons to generate hydrogen at the cathode. In this process, different operating conditions and physical parameters may significantly influence the performance.

The performance of PEM electrolyzer cells can be expressed by the voltage and current density relationship formula. The present model assumes that: (a) the CL is infinitely thin and the electrochemical reaction only occurs at the interface of GDL and PEM; (b) gases transferred inside the electrode and channel are ideal gases; (c) the porous electrode means GDL and CL together and its physical parameters refer to those of GDL. The potential of a single PEM electrolyzer cell is composed by the open circuit voltage, activation overpotential, diffusion overpotential, and ohmic loss overpotential. The total relationship formula is:

$$V = V_{ocv} + V_{act} + V_{diff} + V_{ohm} \quad V = V_{ocv} + V_{act} + V_{diff} + V_{ohm} \quad (1)$$

Where V_{ocv} is the open circuit voltage as well as the theoretical minimum voltage for PEM electrolyzer cells when neglecting other overpotential, V_{act} is the overpotential due to the electrochemical reaction, V_{diff} is the diffusion overpotential caused by the mass transport in the electrolyzers, and V_{ohm} is the ohmic overpotential caused by the electrolysis resistances. Each of these overpotential models will be determined in the following sections.

2.1 Open circuit voltage

The open circuit voltage (OCV) is also called reversible voltage. For PEM electrolyzer cells, OCV can be calculated from the Nernst equation [23]

$$V_{ocv} = V_0 + \frac{RT}{zF} \ln \left(\frac{\alpha_{H_2} \alpha_{O_2}^{0.5}}{\alpha_{H_2O}} \right) \quad (2)$$

Here V_0 is the reversible voltage with standard pressure, which can be calculated by the following relation [24]

$$V_0 = 1.229 - 0.9 \times 10^{-3}(T - 298.0) \quad (3)$$

R is the gas constant, T is the electrolyzer operating temperature, z is the mole number of electrons transferred during the electrolysis reaction, F is the Faraday constant, α_i is the activity of species i , $\alpha_i = P_i / P_0$ for ideal gas (P_i is the partial pressure of species i and P_0 is equal to standard atmosphere pressure) and $\alpha_i = 1.0$ for liquid water.

2.2 Activation overpotential

The activation overpotential is a potential loss from the electrolysis electrochemical reaction, which can be significantly affected by physical and chemical parameters, such as operating temperature, catalyst property, active reaction site, and electrode morphology. Since some effects are very difficult to model, the activation overpotential in the present model will be typically derived from the Butler-Volmer equation [24], which is the fundamental electrochemical relationship describing how current depends on the voltage in the electrode.

$$V_{act} = V_{act,a} + V_{act,c}$$

(4)

$$V_{act,a} = \frac{RT_a}{\alpha_a F} \sinh^{-1}\left(\frac{j}{2j_{0,a}}\right) = \frac{RT_a}{\alpha_a F} \ln \left(\frac{j}{2j_{0,a}} + \sqrt{1 + \left(\frac{j}{2j_{0,a}}\right)^2} \right)$$

(5)

$$V_{act,c} = \frac{RT_c}{\alpha_c F} \sinh^{-1}\left(\frac{j}{2j_{0,c}}\right) = \frac{RT_c}{\alpha_c F} \ln \left(\frac{j}{2j_{0,c}} + \sqrt{1 + \left(\frac{j}{2j_{0,c}}\right)^2} \right)$$

(6)

Where $V_{act,a}$ and $V_{act,c}$ are the anode and cathode voltage respectively, T_a and T_c indicate the anode and cathode operating temperature respectively, which are equal to electrolyzer operating temperature in the present model, and α_a and α_c are the charge transfer coefficient at the anode and cathode. $\alpha_a = 2.0$ and $\alpha_c = 0.5$ are typically values for PEM electrolyzer cells [22, 23]. j is the current density on the electrodes. $j_{0,a}$ and $j_{0,c}$ are the exchange current density on the anode and cathode electrode, which also vary greatly according to different papers and play an important role in PEM electrolyzer cell modeling. Exchange current density values for several different PEM electrolyzer cell models are shown in Table 1.

2.3 Diffusion overpotential

The diffusion overpotential is produced due to the mass transport inside of the porous electrodes of PEM electrolyzer cells. During the electrochemical reaction of PEM electrolyzer cells, because liquid water must be transported to the reaction layer and gas needs to be removed

from the reaction site, mass transport losses play an important role in PEM electrolyzer cell performance. Figure 2 shows the schematic of mass flow transport in a single PEM electrolyzer cell. Water flow consists of five parts: inlet and outlet flow on the anode (1: $n_{H_2O,a}$), flow due to electrochemical reaction (2: $n_{H_2O, reaction}$), flow due to the concentration difference and electro-osmotic drag across the membrane (3: $n_{H_2O, ce}$), flow due to the pressure difference across the membrane only from the cathode to anode (4: $n_{H_2O, pressure}$), and outlet flow on the cathode (5: $n_{H_2O,c}$). $n_{H_2O, reaction}$ and $n_{H_2O, ce}$ can be calculated by Faraday's law and $n_{H_2O, pressure}$ can be calculated by Darcy's law. Each item can be expressed as the following:

$$n_{H_2O, reaction} = \frac{j}{2F} \quad (7)$$

$$n_{H_2O, ce} = \frac{D_w (C_{H_2O, m, c} - C_{H_2O, m, a})}{\delta_m} + \frac{n_d j}{F} \quad (8)$$

$$n_{H_2O, pressure} = \frac{K_{darcy} A}{\mu_{H_2O}} \nabla p \frac{\rho_{H_2O}}{M_{m, H_2O}} \quad (9)$$

Where D_w is the diffusion coefficient of water inside the membrane, $C_{H_2O, m, a}$ and $C_{H_2O, m, c}$ are the anode and cathode water concentrations at the interface of electrode and membrane respectively, n_d is the coefficient due to the electro-osmotic drag, K_{darcy} is the water permeability coefficient inside the membrane, A is the reaction area, ∇p is the pressure gradient throughout the PEM, ρ_{H_2O} is the water density, μ_{H_2O} is the water dynamic viscosity and M_{m, H_2O} is the water molar mass.

According to Faraday's law, oxygen produced at the anode and hydrogen produced at the cathode can be calculated as the following:

$$n_{O_2} = \frac{j}{4F} \quad (10)$$

$$n_{H_2} = \frac{j}{2F}$$

(11)

Once each species flow in the electrode is determined, the oxygen and hydrogen concentration at the electrode and membrane interface can be calculated by the following relationship:

$$C_{O_2,m} = \frac{P_a \frac{n_{O_2}}{n_{O_2} + n_{H_2O,a}}}{RT_a} + \frac{\delta_{e,a}}{D_{eff,a}} n_{O_2}$$

(12)

$$C_{H_2,m} = \frac{P_c \frac{n_{H_2}}{n_{H_2} + n_{H_2O,c}}}{RT_c} + \frac{\delta_{e,c}}{D_{eff,c}} n_{H_2}$$

(13)

Where P_a and P_c are the operating pressure at the anode and cathode, $\delta_{e,a}$ and $\delta_{e,c}$ are the anode and cathode electrode thickness, and D_{eff} is the diffusion coefficient in the porous electrode.

The diffusion coefficient in the porous electrode is related to the porosity. The diffusion coefficient of a two substance mixture can be calculated by [25]

$$D_{eff,1-2} = D_{1-2} \epsilon \left(\frac{\epsilon - \epsilon_p}{1 - \epsilon_p} \right)^\alpha$$

(14)

$$D_{1-2} = a \left(\frac{T}{\sqrt{T_{c1} T_{c2}}} \right)^b (p_{c1} p_{c2})^{1/3} (T_{c1} T_{c2})^{5/12} \left(\frac{1}{M_{m1}} + \frac{1}{M_{m2}} \right)^{0.5} / P$$

(15)

Where D_{1-2} is the mixture diffusion coefficient, $\alpha = 0.785$, $\epsilon_p = 0.11$ [26], $a = 3.64 \times 10^{-4}$, and $b = 2.334$ [22] are the empirical coefficients or values, P_{cr} (H_2O : 218.3, O_2 : 49.7, H_2 : 12.8), T_{cr} (H_2O : 647.3, O_2 : 154.4, H_2 : 33.3), and M_m (

H_2O : 18, O_2 : 32, H_2 : 2) are respectively the critical pressure (atm), critical temperature (K) and substance molar mass.

Lastly, the diffusion overpotential at the anode and cathode can be calculated using the Nernst equation [22]

$$V_{diff} = V_{diff,a} + V_{diff,c} = \frac{RT_a}{4F} \ln \left(\frac{C_{O_2,m}}{C_{O_2,m0}} \right) + \frac{RT_c}{2F} \ln \left(\frac{C_{H_2,m}}{C_{H_2,m0}} \right) \quad (16)$$

Where $C_{O_2,m0}$ and $C_{H_2,m0}$ are the oxygen and hydrogen concentrations under a reference operating condition.

2.4 Ohmic overpotential

The bipolar plate resistance, electrode resistance, membrane resistance, and interfacial resistance between different layers are the main cause of the ohmic overpotential. The relationship can be expressed as the following:

$$V_{ohm} = V_{ohm,a} + V_{ohm,c} + V_{ohm,m} = (R_{p,a} + R_{e,a} + R_{in,a}) jA + (R_{p,c} + R_{e,c} + R_{in,c}) jA + R_m jA \quad (17)$$

Where R_m is the resistance due to the membrane, A is the reaction area, R_p is the resistance due to the plates, R_e is the resistance due to the porous electrodes, and R_{in} is the resistance due to the interface between the electrode and membrane. Figure 3 shows the equivalent resistance of a simplified PEM electrolyzer cell model for the ohmic overpotential calculation (corresponding to Figure 1). Some of these resistances can be calculated using the relationship of the material resistivity and others are based on empirical values and formulas. These resistances all can be used for the anode and cathode.

The resistance due to the plates:

$$R_{p1} = \rho_p \frac{L_{ab}}{A} \quad (18)$$

The resistance due to the plates and gas channel:

$$R_{p2} = \rho_p \frac{L_{bc}}{0.5L_{ik}L}$$

(19)

The resistance due to the porous electrodes and gas channel (parallel to gas channel):

$$R_{e1} = \rho_e \frac{0.25L_{kl}}{\delta_e L(1 - \varepsilon)}$$

(20)

The resistance due to the porous electrodes:

$$R_{e2} = \rho_e \frac{\delta_e}{0.5L_{ik}L(1 - \varepsilon)}$$

(21)

The resistance due to the porous electrodes and gas channel (perpendicular to gas channel):

$$R_{e3} = \rho_e \frac{\delta_e}{L_{kl}L(1 - \varepsilon)}$$

(22)

Where ρ_p and ρ_e are the electrode material resistivity, L is the Membrane-Electrode-Assembly (MEA) length and L_{ik} is the distance between point i and point k, as shown in Figure 1.

The resistance due to the interface between the electrode and membrane is initially assumed to be $2R_{e2}$ [27] that is found to be able to better fit the experimental data.

The membrane resistance loss can be calculated as [17]

$$V_{ohm,m} = \delta_m \frac{j}{\sigma_m}$$

(23)

Where δ_m is the membrane thickness and σ_m is the membrane conductivity. The membrane conductivity can be determined by an empirical relationship [28]

$$\sigma_m = (0.005139\lambda - 0.00326) \exp \left[1268 \left(\frac{1}{303} - \frac{1}{T} \right) \right]$$

(24)

Where λ is the membrane humidification degree, and the value is suggested from current papers to be in the range of 14-25. Since a large amount of liquid water is provided to the anode during operation, the membrane of PEM electrolyzer cells is considered to be fully humidified. In the present model, the membrane humidification degree is assumed to 22 for better model validation.

3 Results and discussion

3.1 Model validation

A comprehensive mathematical model for electrochemical performance analysis has been developed above. In particular, a new ohmic loss model with electrode porosity and interfacial resistance are integrated for the first time. In order to effectively analyze the performance of PEM electrolyzer cells, the present model is firstly computed and validated with recent experimental data [29]. In this validation case, the corresponding operating temperature value was 80°C and the PEM thickness was 178 microns. The values of the exchange current density and membrane humidification are used to adjust and optimize the present model so that the model data could better fit the experimental data. Figure 4 presents the comparison of the present model and experimental data of PEM electrolyzer cell polarization curve under the same pressure, temperature and membrane thickness. The numerical results obtained from the present model show good agreement with the experimental data.

The above model is then used to calculate and analyze the overall performance of PEM electrolyzer cells under different operating conditions with various physical parameters. The relevant initial parameters used in the present modeling of PEM electrolyzer cells are presented in Table 2. The numerical results including exchange current density effects, temperature effects, pressure effects, electrode thickness effects, membrane thickness effects and interfacial resistance effects are shown and discussed in the following sections.

3.2 Effects of exchange current density

The exchange current density is closely associated to the catalyst materials, operating temperature and other physical parameters at the anode and cathode that are difficult to quantify. According to existing data listed in Table 1, the value varies over several magnitudes of order and many studies used an exchange current density that can better fit their respective model to existing experimental data. Therefore, it is important to determine the values for the present

model. Based on the model validation as discussed in the above section, the exchange current density at the anode and cathode for the model is respectively 2.0×10^{-6} and 1.0×10^{-1} A/cm². Figure 5 shows the effects of the anode exchange current density on the whole polarization curve and three different values of exchange current density, namely, 10^{-6} , 10^{-8} and 10^{-10} A/cm², are examined. It is found that when exchange current density becomes small, the total voltage increases significantly, which means the electrolyzer performance decreases. Using these exchange current density values, the overall overpotentials of electrolyzer at 1.5A/cm² are 1.84V (10^{-6} A/cm²), 1.91V (10^{-8} A/cm²) and 1.98V (10^{-10} A/cm²), respectively. Similar results are obtained at the cathode. As shown in Figure 6, decreasing the exchange current density from 10^{-1} to 10^{-5} A/cm² can result in larger differences of the voltage than those at the anode. At a current density of 1.0A/cm², the voltage difference between two cases with exchange current densities of 10^{-1} and 10^{-5} A/cm² is up to 0.56V. Results indicate that exchange current density at both the anode and cathode has a great effect on the final performance of PEM electrolyzer. Optimization of the CL can improve electrolyzer performance since the exchange current density is dependent on catalyst properties [23].

3.3 Effects of temperature and pressure

In the present model, open circuit voltage, activation overpotential, hydrogen, oxygen and water concentration in the electrode, diffusion coefficient, and membrane conductivity are closely related to the operating temperature. In terms of the theoretical analysis (Eq. 5 and Eq. 6), when increasing the operating temperature, only the activation overpotential increases whereas other voltage values decrease. The effect of different operating temperatures on the performance of PEM electrolyzer cells is illustrated in Figure 7. The results confirm that increasing the operating temperature from 40 to 80°C could result in voltage decrease and consequently improve the performance of PEM electrolyzer cells. Voltage difference among different temperatures will become large with increasing current density. At a current density of 0.5 A/cm², the voltage difference between 40 and 80°C is 0.02 V, while at a current density of 2.0 A/cm², the voltage difference amounts to 0.08 V. Similar conclusions have been confirmed with recent experimental results [14].

Figure 8 displays the effects of different cathode pressures on the performance of PEM electrolyzer cells. It can be seen that a higher operating pressure at the cathode lead to a higher

voltage. The voltage at 1.5 A/cm^2 is 1.75 V for a pressure of 1 atm and 1.8 V for a pressure of 5 atm. There are two explanations for such result. First, a high operating pressure would directly result in an increase in the open circuit voltage. At the same time, based on the present diffusion model, an increasing species partial pressure may prevent water diffusion inside the electrode and membrane, which consequently increases diffusion loss. Marangio et al. [22] also reported that an increasing pressure could lead to an electrolyzer voltage increase since a high operating pressure could reduce the movement of hydrogen ions across the membrane and make the electrochemical reaction more difficult. According to the above analysis, it seems that PEM electrolyzer cell performance would worsen due to a high operating pressure; however, for a real PEM electrolyzer cell, a high-pressure operation condition makes better performance improvement with an increase of operating temperatures and is beneficial to hydrogen production and storage. Specifically, at a pressure of 1 atm, an increase from low temperature to high temperature can cause a slight voltage decrease; however, at high pressure conditions, an increase from low temperature to high temperature would result in a more significant voltage decrease. In addition, hydrogen subsequent compression of PEM electrolyzer cells at atmospheric conditions requires high pump power, but a high-pressure electrolyzer can help improve this process [12].

3.4 Effects of electrode and membrane thickness

In a practical PEM electrolyzer cell, the thickness of the electrode may range from 25 to 600 microns and can affect mass transport process and ohmic loss. The new model combined with two different types of electrode materials is developed to calculate the effect of various electrode thicknesses on the electrolyzer performance. As shown in Figure 9 and Figure 10, the effects of the electrode thickness on the polarization curve of a single PEM electrolyzer cell are examined. In Figure 9, the electrode materials of anode and cathode used in the present model are titanium and carbon paper, respectively. Their average porosity for titanium and carbon paper electrode is assumed to be 0.3. Other calculation conditions can be found in Table 2. From the results, the performance of PEM electrolyzer cells becomes worse with an increase in electrode thickness, as shown in Figure 9. This is because a thicker electrode leads to both higher diffusion and ohmic losses. In Figure 10, Titanium is used in both the anode and cathode. It can be found that the differences between Figure 9 and Figure 10 are very small and the corresponding polarization curves are almost identical. As shown in Figure 10, at a current density of 0.5 A/cm^2 , it can be

calculated that the voltage difference between 25 and 600 microns electrode is about 0.02V, but when the current density increases to 2.0 A/cm^2 , the voltage difference between 25 and 600 microns electrode is up to 0.08V. For an electrode of 200 microns and a current density of 1.5 A/cm^2 , the ohmic loss due to the electrode and plate resistances comprises 4.6% of the total ohmic loss of an electrolyzer.

The PEM plays a key role in a PEM electrolyzer cell system. Some important factors affecting the membrane performance are the membrane conductivity, permeability, humidification degree, thickness, and operating temperature. In the present model, the ohmic loss is directly related with the membrane conductivity and membrane thickness and the diffusion overpotential is also affected by the membrane thickness. The effects of different membrane thicknesses on the whole performance of PEM electrolyzer cells are shown in Figure 11. Increasing the membrane thickness from 50 to 200 microns would result in a significant increase in overpotential. The trends are found to be well consistent with recent experimental data [1]. This result is due to the fact that a thicker membrane would lead to higher ohmic resistance and diffusion loss. For a membrane of 178 microns and a current density of 1.5 A/cm^2 , the loss due to membrane resistance will comprise 63.6% of the total ohmic loss of an electrolyzer. As shown in Equation (23), when increasing the membrane thickness δ_m , the membrane resistance loss $V_{mem,m}$ would increase. In addition, it also can be seen from Equation (8), the molar water flow $n_{H_2O,oe}$ due to the concentration difference and electro osmotic drag across the membrane would decrease with an increasing of the membrane thickness δ_m . Based on the above analysis, the balancing of membrane thickness is an important factor to improve the electrolyzer cell performance.

3.5 Effects of interfacial resistance

For interfacial loss between various components, the present model coupled a new ohmic loss model, which can be affected by electrode porosity and interfacial resistance. As shown in Figure 3, this model has a new capability to examine the effects of interfacial resistance on the electrolyzer performance. In a PEM electrolyzer cell, the interfacial resistances mainly include the interface between a membrane and electrode (ME) and the interface between an electrode and plate (EP), which could be caused by various material properties, assembly methods and

mechanical conditions. They are difficult to be calculated using a specific relationship. Pivovar et al. [27] presented an experimental method to quantify interfacial resistance between a membrane and electrode for different membranes in PEM fuel cells. In their work, interfacial resistance values ranged from 8 to 57 $\text{m}\Omega \text{ cm}^2$.

In this study, in order to address the effects of the interfacial resistance on the whole performance of the PEM electrolyzer cell, an adjustable resistance is employed to quantify the interfacial resistance of membrane and electrode in both the anode and cathode, as shown in Figure 3. The total interfacial resistance value in the present model is initially assumed to be equal to $2R_{e2}$. The resistance value is equal to 12.8 $\text{m}\Omega \text{ cm}^2$ when the electrode resistivities are set to be 5.0 $\text{m}\Omega \text{ cm}$ at both the anode and cathode side, respectively. Figure 12 shows the effects of various interfacial resistance values between membrane and electrode (R_{ME}) on the performance of electrolyzer. The interfacial resistance varies from R_{e2} to $4R_{e2}$ and the electrolyzer voltage significantly increases as the interfacial resistance increases. At a current density of 2.0 A/cm^2 , increasing the interfacial resistance from R_{e2} to $4R_{e2}$ can lead to a voltage increase of around 0.07V and the differences will increase with current density. It is expected to have a more significant effect when considering a practical electrolyzer, because the interface issues not only affect the ohmic loss but also the diffusion overpotential due to the electro-osmotic drag and diffusion coefficient. Results clearly indicate that the interfacial resistance plays an important role in electrolyzer performance and improvement of the overall performance can be obtained under a low interfacial resistance.

In addition, to further address the effects of other interfaces on the electrolyzer performance, various interfacial resistances between the electrode and plate (R_{EP}) are also discussed here, as shown in Figure 13. According to the numerical results, when increasing the interfacial resistance from 0 to $4R_{e2}$, the voltage values change slightly and the three polarization curves are almost identical. Results indicate that the interfacial resistance between the electrode and plate has little impact on the overall performance of electrolyzer while the interface resistance between the membrane and electrode is a significant part for electrolyzer performance.

In summary, based on the above analysis, the total ohmic loss is composed of three different types of losses due to the component resistances of an electrolyzer, which will significantly affect the electrolyzer performance. Figure 14 clearly illustrate the effects of various component resistances, including electrode and plate resistance, membrane resistance and interfacial

resistance, on the electrolyzer performance. At a current density of 1.5 A/cm^2 , it can be calculated that the total ohmic loss comprises 33% of an electrolyzer overpotential ($V_{act} + V_{diff} + V_{ohm}$) and the interface loss due to interfacial resistance between the membrane and electrode comprises 31.8% of the total ohmic loss. It is well known that increasing a resistance value of each component will lead to a proportionate increase in corresponding overpotential. Further, as shown in Figure 15, when the resistance values of each component doubled, it can be found that the overpotential due to membrane resistance will get a maximum change at a same current density. For instance, at a current density of 2.0 A/cm^2 , the maximum voltage difference due to membrane resistance is 0.09V, but the minimum one due to electrode and plate resistances is less than 0.01V. These numerical results demonstrate that decreasing these resistances through optimizing interface and membrane materials could significantly improve the electrolyzer performance.

4 Conclusions

A comprehensive computational model has been developed to calculate the effect of various operating conditions and design parameters on the performance of PEM electrolyzer cells. The ohmic resistance model at a given electrode porosity, which is correlated to the interfacial resistances is introduced for the first time, and the interfacial resistance between the membrane and electrode is found to play an important part for electrolyzer performance. In addition, the performance of PEM electrolyzer cells is greatly dependent on the exchange current density, temperature, pressure, and electrode and membrane properties. Increasing the operating temperature will improve the performance of PEM electrolyzer cells. The operating pressure also has considerable effects on PEM electrolyzer cell performance. The overpotential increases with the operating pressure increasing due to the high open circuit voltage under high pressure. PEM electrolyzer cell performance improves with the decrease of electrode thickness and membrane thickness due to low diffusion overpotential and ohmic loss. These modeling results can help obtain better understanding of PEM electrolyzer cells and improve electrolysis system performance.

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List of symbols

V	Overpotential or voltage, V
V_0	Reversible voltage, V
T	Operating temperature, K
z	Mole number of electrons
P_i	Partial pressure of species, atm
P_0	Standard atmosphere pressure, atm
j	Current density, A/cm ²
j_0	Exchange current density, A/cm ²
n_{H_2O}	Molar water flow, mol/s
D_w	Water diffusion coefficient inside the membrane, cm ² /s
C	Concentration, mol/cm ³
$C_{H_2O,m}$	Water concentrations at the interface of electrode and membrane, mol/cm ³
n_d	Electro-osmotic drag coefficient
K_{darcy}	Water permeability coefficient inside the membrane, cm ²
P	Operating pressure, atm
D	Diffusion coefficient, m ² /s
P_{cr}	Critical pressure, atm
T_{cr}	Critical temperature, K
M_m	Molar mass, g/mol
R	Resistance, ohm
A	Reaction area, cm ²
L	Membrane-Electrode-Assemble length
ρ_{H_2O}	Water density, 1.0 g/cm ³
μ_{H_2O}	Water dynamic viscosity, 3.5×10^{-7} N S/cm ²

Greek

α_i	Activity of species
α	Charge transfer coefficient
δ_e	Electrode thickness, cm
ρ	Material resistivity, ohm cm
δ_m	Membrane thickness
σ_m	Membrane conductivity
λ	Membrane humidification degree

Superscripts and subscripts

ocv	Open circuit voltage
act	Activation
$diff$	Diffusion
ohm	Ohmic
i	Species index
a	Anode
c	Cathode
H_2O	Water
ce	Concentration difference and electro-osmotic drag
H_2	Hydrogen
O_2	Oxygen
e	Electrode
m	Membrane
cr	Critical
p	Plates
in	Interface
ME	Interface between membrane and electrode
EP	Interface between electrode and plate

Constants

R	Gas constant, 8.314 J/mol K
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F Faraday constant, 96485.0 C/mol

M_{m,H_2O} Water molar mass, 18 g/mol

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Table 1: Exchange current density for several different PEM electrolyzer cell models

Table 2: Initial calculation parameters for a PEM electrolyzer cell

$j_{0,a} \text{ (A/cm}^2 \text{)}$	$j_{0,c} \text{ (A/cm}^2 \text{)}$	Anode and cathode catalyst	References
1.0×10^{-12}	1.0×10^{-3}	Pt-Ir anode Pt cathode	[17]
1.65×10^{-8}	9.0×10^{-2}	Pt-Ir anode Pt cathode	[30]
1.0×10^{-7}	1.0×10^{-3}	Pt-Ir anode Pt cathode	[22]

Table 1

Description, unit	Value
Faraday constant, F (C/mol)	96485.0
Gas constant, R (J/mol K)	8.314
The cell operating temperature, T (K)	353.15
The cell operating pressure, P (atm)	1 (anode), 13.6 (cathode)
The maximum current density, (A/cm ²)	2.0
Exchange current density, (A/cm ²)	2.0e-6 (anode), 1.0e-1 (cathode)
The electrode thickness, (microns)	200
The electrode porosity	0.3
The membrane thickness, (microns)	178
Titanium resistivity, (ohm cm)	5.0e-3 [20]
Carbon paper resistivity, (ohm cm)	80.0e-3 [31]
Transfer coefficient	2.0 (anode), 0.5 (cathode)
Water dynamic viscosity (N s/cm ²)	3.55e-8
Water density, (g/cm ³)	1.0
L _{ab} , (mm)	2.0
L _{bc} , (mm)	1.0
L _{ki} , (mm)	1.0
L, (cm)	$\sqrt{5}$
MEA area, (cm ²)	5

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