Effects of membrane electrode assembly properties on two-phase transport and performance in proton exchange membrane electrolyzer cells

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Abstract

A mathematical model is developed to simulate the two-phase transport behaviors and the performance in a proton exchange membrane electrolyzer cell (PEMEC). The parameter effects of the liquid/gas diffusion layer (LGDL), including contact angle, porosity, and pore size, on the capillary flow and liquid water distribution are comprehensively studied. In addition, the effects of the LGDL pore size and membrane humidity on the performance and efficiency of PEMEC are also investigated. The results indicate that LGDL properties have significant impacts on its capillary pressure and liquid water distribution, which consequently affects the two-phase transport and performance in the PEMEC. Increasing the porosity and/or pore size or decreasing the contact angle can enhance the liquid water saturation along the LGDL thickness direction, and consequently improve the performance and efficiency of PEMEC. The variation of PEM humidity contributes to a portion of the cell ohmic loss as well.

Keywords: Proton exchange membrane electrolyzer cell, liquid/gas diffusion layer properties, capillary pressure, two-phase transport, performance modeling

1 Introduction

Water electrolysis technology using a proton exchange membrane (PEM) can be used to produce pure hydrogen, which is considered one of the most promising clean energy carriers. Compared with other electrolysis technologies, such as alkaline and solid oxide electrolyzer cells, the PEM electrolyzer cell (PEMEC) has a lot of advantages [1, 2], including a faster response time to variable electrical input, higher purity hydrogen production, and higher pressure operation condition [3, 4]. As shown in Figure 1, the PEMEC, which has a similar structure to PEM fuel cells (PEMFCs), is mainly composed of two bipolar plates with flow channels, two liquid/gas diffusion layers (LGDLs), and catalyst layers (CLs) that are separated by a PEM. Recently, many efforts [5-10] have been made to study two-phase flow and transport behaviors in fuel cells, which will be useful for PEMEC issues. In theory, water can be split into hydrogen and oxygen by operating a PEMFC in reverse direction, but there are some differences between a fuel cell and electrolyzer cell. During the PEMEC operation, a thermal, electrical, and humid condition at the anode side can create a highly oxidative environment, which will corrode the electrode and lead to poor interfacial contact, electron conduction, and mass transport. Therefore, porous electrodes based on carbon paper or other carbon materials, which are widely used in PEMFCs, are not suitable for the anode side of a PEMEC [11]. Currently, titanium mesh and felt have been used as electrode materials for the anode of a PEMEC due to their highly corrosion resistances, excellent electrical conductivity and microstructural properties [12, 13]. To optimize and improve the cell performance, it is important to obtain a deep understanding of the effects of LGDL properties and operating parameters on the two-phase transport behaviors and cell performance.

In the past decade, studies [13-18] associated with two-phase transport phenomena and performance evaluation in a PEMEC mostly focused on experimental analysis. For instance, Hoeh et al. [17] used synchrotron X-ray radiography to investigate the evolution phenomenon of oxygen and hydrogen on an operating PEMEC. Ito et al. [15, 19, 20] experimentally investigated the effects of porous electrode structure including porosity and pore diameter on the performance of PEMECs and analyzed the two-phase flow phenomena at the anode flow channel. Their works revealed that pore diameter and porosity might affect the electrolysis performance and the liquid water transport was

restricted by the oxygen bubbles with different patterns, which are produced from different pores in the flow channel. Selamet et al. [21] used neutron radiography and optical imaging technology simultaneously to observe the two-phase transport characteristics in a PEMEC. The results indicated that the operating temperature, current density, and water flow rate had a significant influence on the gas/liquid two-phase distribution at both the anode and cathode. Mo et al. [13] also reported the two-phase flow phenomena in the flow channel of a PEMEC and a high-speed and micro-scale visualization device was first used to observe and investigate the two-phase transport behaviors with different operating conditions. For the mathematical modeling of PEMECs, previous models [22-24] mostly paid attention to the cell electrochemical performance analysis. Few models have been developed to deal with two-phase transport issues of PEMECs. Marangio et al. [25] developed several relationships to determine the oxygen and hydrogen concentration, which was used to estimate the diffusion overpotential of a high pressure PEMEC. In their model, water flow from the anode to cathode was evaluated simply based on the Faraday' law, Darcy' law, Fick' law of diffusion, and mass conservation. Grigoriev et al. [16] proposed a model to examine the transport behaviors of gas and liquid phase in a hydrophilic porous electrode of a high pressure PEMEC. Two-phase governing equations were derived from general mass and momentum conservation and the liquid saturation was calculated by the relationship of capillary pressure and Leverett function. Although some effects have been taken in the PEMEC two-phase modeling, these previous two-phase models for PEMECs mostly focus on the primary estimation of the content of liquid and gas phase, while few mention the effects of different parameters on the cell performance. Therefore, a comprehensive model combining two-phase transport and performance analysis is highly needed. In addition, the ohmic losses also contribute a large portion of the cell potential, but previous studies usually neglected interface and CL effects and paid few attentions to the interfacial resistances and CL resistances, so a detailed equivalent resistance model for a PEMEC is needed to calculate these effects as well.

In this study, a two-phase transport model is developed to investigate the liquid water distribution inside the LGDL, and an electrochemical performance model coupled with an equivalent resistance model is employed to calculate the effects of different physical

parameters on the cell performance and efficiency. The effects of LGDL properties including contact angle, porosity, and pore size on the two-phase transport dynamics are investigated. The liquid saturation distribution inside the LGDL is presented. Furthermore, the effects of two-phase transport on the performance and efficiency of a PEMEC is examined. Results provide better understandings for two-phase flow in a PEMEC and theoretical supports for future experimental studies.

2 Model development

The fundamental schematic of two-phase flow in a PEMEC is shown in Figure 1. At the anode side, the liquid water from flow channel passes through the LGDL and reaches the CL where the electrochemical reaction occurs; on the other hand, the oxygen produced by the reaction needs to get out of the anode, which results in the two-phase transport phenomenon inside the LGDL. The reaction at the anode and cathode by a single PEMEC can be expressed as below [3]:

LGDL properties are essential to ensure highly efficient transport of liquid water and oxygen. To understand the effects of LGDL properties and operating parameters on the two-phase flow and cell performance, a full performance model coupling two-phase transport effect and equivalent resistance model is developed in this section. First, the gas/liquid two-phase transport equations can be derived from mass and momentum conservations, which will be separated into gas phase and liquid phase equations, as listed in the following [16, 26-28].

Gas phase transport in the LGDL is considered at first. A steady state conservation equation of oxygen transport can be expressed as:

$$\nabla \cdot \left(-\frac{Kk_{O_2}}{\mu_{O_2}/\rho_{O_2}} \nabla p_{O_2} \right) = N_{O_2} \quad (3)$$

In a similar way, a steady state conservation equation of liquid water transport in the LGDL can be written as:

$$\nabla \cdot \left(-\frac{Kk_{H_2O}}{\mu_{H_2O}/\rho_{H_2O}} \nabla p_{H_2O} \right) = N_{H_2O} \quad (4)$$

where K is the absolute permeability of a LGDL, k is the relative permeability for gas or liquid phase, μ is the fluid dynamic viscosity, ρ is the fluid density, p is the fluid pressure, and N is the fluid flux due to electrochemical reaction.

According to the Kozeny-Carman equation, which is a relation of the fluid pressure drop through a porous media for laminar flow, the absolute permeability can be expressed as [29]:

$$K = \frac{d^2}{180} \frac{\varepsilon^3}{(1-\varepsilon)^2} \quad (5)$$

Here, d and ε are the pore diameter and porosity of a LGDL respectively.

Relative permeability [30]:

$$k_{O_2} = (1 - s)^3 \quad (6)$$

$$k_{H_2O} = s^3 \quad (7)$$

The liquid saturation, s , which is defined as the ratio of liquid water volume to total pore volume of a porous media, is an important parameter for two-phase flow and can be used to quantify the water distribution inside a LGDL. Since the liquid water flows across the LGDL is mainly controlled by the capillary pressure that is related to the liquid saturation, the relationship of capillary pressure and Leverett's function is used to calculate the liquid saturation distribution, as shown in the following [31, 32]:

$$p_c = \sigma \cos \theta \left(\frac{\varepsilon}{K} \right)^{1/2} J(s) \quad (8)$$

Where σ is the surface tension and θ is the LGDL contact angle. The Leverett's function $J(s)$ of a hydrophilic and hydrophobic LGDL takes the following form [31]:

$$J(s) = \begin{cases} 1.417(1 - s) - 2.120(1 - s)^2 + 1.263(1 - s)^3, & 0 < \theta < 90^\circ \\ 1.417s - 2.120s^2 + 1.263s^3, & 90^\circ < \theta < 180^\circ \end{cases} \quad (9)$$

For a hydrophilic LGDL, the non-wetting phase is oxygen and the wetting phase is liquid water. Therefore, the capillary pressure can be expressed as [26]:

$$p_c = p_{\text{non-wetting}} - p_{\text{wetting}} = p_{O_2} - p_{H_2O} \quad (10)$$

By applying equations (5) and (9) to equations (8), one can obtain the relationship of capillary pressure, pore size and liquid saturation. Then, substituting equations (6-8) and (10) into equations (3-4), the gas/liquid two-phase transport equations inside a hydrophilic LGDL along the x-direction can be rewritten in the following form:

$$\left\{ \begin{array}{l} 3(1-s)^2 \frac{ds}{dx} \frac{dp_{O_2}}{dx} - (1-s)^3 \frac{d^2 p_{O_2}}{dx^2} = 180 \frac{N_{O_2} \mu_{O_2} (1-\varepsilon)^2}{\rho_{O_2} d^2 \varepsilon^3} \\ \frac{13.4(1-\varepsilon)}{d\varepsilon} \sigma c \cos \theta \left[\begin{array}{l} (-2.898s^2 + 13.252s^3 - 18.945s^4) \left(\frac{ds}{dx} \right)^2 + \\ (-0.966s^3 + 3.338s^4 - 3.789s^5) \frac{d^2 s}{dx^2} \end{array} \right] \\ -3s^2 \frac{ds}{dx} \frac{dp_{O_2}}{dx} - s^3 \frac{d^2 p_{O_2}}{dx^2} = 180 \frac{N_{H_2O} \mu_{H_2O} (1-\varepsilon)^2}{\rho_{H_2O} d^2 \varepsilon^3} \end{array} \right. \quad (11)$$

In order to solve Equation (11), three boundary conditions are needed, as shown in Figure 2. (a) The liquid water and oxygen flux due to the electrochemical reaction can be calculated by $N_{H_2O} = \frac{iM_{H_2O}}{2F}$, $N_{O_2} = \frac{iM_{O_2}}{4F}$. (b) The interfacial saturation between the flow channel and LGDL is mainly related to current density, which is set to be $\frac{1.0}{1.0+a_0 i}$ [33]. Here, a_0 is a coefficient that can be adjusted to better fit experimental data, which is suggested to be 0.1 in the present model. (c) The interfacial gas pressure between the flow channel and LGDL is set to cell operating pressure.

Next, an electrochemical performance model is developed to investigate the effects of two-phase flow parameters on the cell performance and efficiency. The total potential of a single PEMEC should consist of four parts, including open circuit voltage, activation over-potential, diffusion over-potential, and ohmic loss. The relationship can be expressed as [25]:

$$V_{cell} = V_{ocv} + V_{act} + V_{diff} + V_{ohmic} \quad (12)$$

The open circuit voltage (OCV) can be calculated as [34]:

$$V_{ocv} = V_0 + \frac{RT}{2F} \ln \left(\frac{\alpha_{H_2} \alpha_{O_2}^{0.5}}{\alpha_{H_2O}} \right) \quad (13)$$

$$V_0 = 1.229 - 0.9 \times 10^{-3} (T - 298) \quad (14)$$

Here V_0 is the reversible voltage that is mainly dependent on the operating temperature, R is the gas constant, T is the operating temperature, F is the Faraday constant, and α_i is the activity of species. Table 1 shows the effects of different temperatures on the OCV and the OCV decreases with temperature increasing.

The activation over-potential due to the electrochemical reaction in the CL and the diffusion over-potential can be calculated by [25]:

$$V_{act} = \frac{RT_{an}}{\alpha_{an} F} \ln \left(\frac{i}{2si_{0,an}} + \sqrt{1 + \left(\frac{i}{2si_{0,an}} \right)^2} \right) + \frac{RT_{cat}}{\alpha_{cat} F} \ln \left(\frac{i}{2si_{0,cat}} + \sqrt{1 + \left(\frac{i}{2si_{0,cat}} \right)^2} \right) \quad (15)$$

$$V_{diff} = \frac{RT_{an}}{n_{an}F} \ln \left(\frac{C_{O_2,m}}{C_{O_2,m0}} \right) + \frac{RT_{cat}}{n_{cat}F} \ln \left(\frac{C_{H_2,m}}{C_{H_2,m0}} \right) \quad (16)$$

The ohmic losses contribute a large portion of the total potential. Most of previous models used some simple empirical formulas to estimate the ohmic losses in an electrolyzer cell and fuel cell, while few include full equivalent resistances of a PEMEC. In this study, an equivalent resistance model is introduced to calculate the cell ohmic loss, as shown in Figure 3. The total ohmic loss can be expressed as [35, 36]:

$$V_{ohm} = (R_{plate} + R_{LGDL} + R_{CL} + R_{PEM} + R_{interface})iA \quad (17)$$

3 Results and discussion

3.1 Comparison of modeling and experimental data

Table 2 lists the geometrical, operating, and physical parameters for two-phase transport and cell performance modeling. The present model is numerically solved by a self-written computational program, which is developed and performed in a Fortran 90 compiler. Specifically, the computational program is used to solve the two-phase transport equations (11) and performance equation (12) under various conditions. After computing, the results including capillary pressure distribution, liquid saturation distribution, and polarization and efficiency curve can be directly obtained. To validate the present model, the newest experimental data reported in the open literatures are chosen to be compared with the present modeling results. The first experimental case was performed in our previous study [12]. The operating temperature is 80°C and the operating pressure is 1 atm at both the anode and cathode. Titanium felt with a thickness of 350 μm, a porosity of 0.78, and a contact angle of 70° is used as anode LGDL material. Carbon paper with a thickness of 275 μm and a porosity of 0.7 is used as cathode LGDL material. The PEM thickness is 125 μm. Other modeling parameters can be found in Table 2. In the model, the exchange current densities and membrane humidification degrees are input parameters, allowing the modeling results to better fit to the experimental data. The exchange current densities for the anode and cathode are 0.5×10⁻⁶ A/cm² (anode) and 0.1 A/cm² (cathode), respectively. The membrane humidification degree is set to be 30. Furthermore, the numerical results is found to be almost identical with adjusting the grid number to around 200 along the LGDL thickness direction, which

ensures that the numerical results from the present model are dependent on the used grid number. As shown in Figure 4a, the modeling results have a good agreement with experimental data. For instance, at a current density of 2.0 A/cm^2 , the cell voltage from modeling and experiment is respectively 1.91 V and 1.898 V. Another experimental polarization curve of PEMECs was reported by Debe et al [37], which represents the real performance of a current commercial electrolyzer cell. In their experiment, the cell is operated at a temperature of 80°C . There are different pressure values at the anode and cathode, an anode pressure of 1 atm and a cathode pressure of 13.6 atm, respectively. The membrane humidification degree is set to be 25 during the modeling. Some studies [1] reported that a high-pressure operation condition is beneficial to hydrogen production and storage. As shown in Figure 4b, it can be seen that the modeling curve also shows a good agreement to the experimental data, which thus validates the present model. The parameters in Figure 4b case, as shown in Table 2, will be used as the basic modeling parameters to calculate the effects in the following.

3.2 Capillary pressure inside a LGDL

In a PEMEC, since the LGDL pore diameter is at the micron level, the capillary pressure, which is defined as the pressure difference between the non-wetting phase and wetting phase, is the main driven force for liquid water transport inside the LGDL. The effects of capillary pressure on the cell performance can vary with LGDL properties. To obtain a more detailed understanding of gas/liquid two-phase transport through the LGDL of a PEMEC, it is critical to analyze and quantify the capillary flow in porous LGDLs with different physical parameters. There are generally several factors that affect the capillary pressure distribution in a LGDL and consequently affect the two-phase transport dynamics, including material wetting characteristics and micro-structure. In the present model, to examine the relationship between the capillary pressure and LGDL properties, the effects of contact angle, pore size, and liquid saturation on the capillary pressure are presented, as shown in Figure 5 and Figure 6.

In Figure 5, to determine the LGDL morphological mechanism that can result in the variation of the capillary pressure, it is necessary to investigate the effects of pore diameter distribution. It can be seen that as the pore diameter increases from 10 to $40 \mu\text{m}$, the capillary pressure has a sharp decrease. However, when the pore diameter becomes

larger values such as an increase from 80 to 100 μm pore diameter, the change in capillary pressure is very slight. For example, at a contact angle of 30° , the capillary pressure is 22.7 kPa with 20 μm pore, 5.7 kPa with 80 μm pore, and 4.5 kPa with 100 μm pore. This phenomenon indicates that the capillary pressure is sensitive to a porous LGDL with a pore size of $< 80 \mu\text{m}$. In addition, it is also found that the material wetting characteristics for LGDL have a significant impact on the capillary pressure distribution. As shown in Figure 5, as the contact angle increases from 30° to 80° , the capillary pressure decreases, which means that a smaller contact angle leads to a larger capillary pressure that can drive water across the LGDL more easily.

Moreover, in a porous media, the capillary pressure is strongly correlated to liquid water saturation. As shown in Figure 6, the relationship of capillary pressure and liquid saturation in hydrophilic LGDLs is presented, with five different contact angles, 30° , 50° , 60° , 70° , and 80° . As expected, the liquid saturations have a strong impact on the capillary pressure, especially at a small contact angle. For instance, when the contact angle is equal to 30° that indicates the LGDL is highly hydrophilic, a relatively sharp change in the capillary pressure is observed as the liquid saturation ranges from 0 to 1.0. And the capillary pressure will reach the minimum value when the liquid saturation is equal to 1.0, which means no gas phase in a LGDL. As the liquid saturation increases from 0.25 to 0.75, the capillary pressure will decrease from 15.5 kPa to 9.3 kPa. For a higher contact angle, the predicted curve changes for the relationship of the capillary pressure and liquid saturation will become relatively gentle. For example, at a contact angle of 80° , the capillary pressure only decrease by 1.24 kPa as the liquid saturation increases from 0.25 to 0.75. Furthermore, for a fixed liquid saturation of 0.5, as the contact angle ranges from 30° to 80° , the predicted capillary pressure will decrease by around 10.4 kPa, which also indicates the contact angle has a significant effect on the capillary pressure distribution, which influences the two-phase transport behaviors inside a LGDL.

3.3 Liquid saturation distribution

Since the liquid water is fed into the anode side of a PEMEC, in which the water is split into oxygen, protons, and electrons, the present model will focus on the two-phase transport behaviors taking place at the anode LGDL. An important parameter that can be

used to quantify the water distribution inside a LGDL is the liquid saturation, which is defined as the ratio of liquid water volume to total pore volume of a porous media. According to equations (15) and (16) for performance modeling, it can be found that increasing the liquid saturation can improve the cell performance and efficiency. As the liquid saturation increases, there will be more liquid water near the reaction areas, which can make the electrochemical reaction easier and consequently decrease the activation and diffusion over-potentials. Therefore, it is important to accurately predict the liquid water saturation distribution inside membrane electrode assemblies under various conditions. To understand the effects of different parameters on the liquid saturation, the variations of liquid saturation with different contact angles, porosities, and pore sizes along the LGDL thickness direction are investigated.

Figure 7 shows the liquid water saturation profile along the LGDL thickness direction under three different contact angles, 50° , 70° , and 80° , at a current density of 2.0 A/cm^2 . There is a significant change in the liquid saturation through the LGDL while the contact angle is equal to 80° , but at a contact angle of 50° , the variation of the liquid saturation along the LGDL thickness direction is not very obvious. It can be predicted that if the contact angle continually becomes small, the modeling liquid saturation will almost keep identical along the LGDL thickness direction. At a LGDL thickness of $x=100 \text{ }\mu\text{m}$, the liquid saturation is 0.82 for a contact angle of 50° while the liquid saturation is 0.77 for a contact angle of 80° . The liquid saturation reaches the minimum value that is equal to around 0.62 for a contact angle of 80° at the interface between the LGDL and CL ($x=200 \text{ }\mu\text{m}$).

The porosity is considered as one of the most important structural parameters for a LGDL and has a great influence on the two-phase transport behaviors of a PEMEC. The porosity of a LGDL may vary with cell compression pressure and operating conditions. In the present modeling, in order to investigate the effects of pore sizes on the two-phase transport dynamics, the porosity is assumed to be fixed during PEMEC operation. According to the modeling equations in the section 2, the porosity directly contributes to capillary pressure, permeability, diffusion over-potential and ohmic loss, which will consequently affect the liquid water distribution and cell potential. Figure 8 shows the variations of the liquid saturation along the LGDL thickness direction with different

porosities at a current density of 2.0 A/cm^2 . As shown in Figure 8, x-coordinate is the LGDL thickness direction and y-coordinate is the liquid water saturation. It can be seen that the liquid saturation along the LGDL thickness direction decreases with the porosity decreasing. At the interface between the LGDL and CL, the liquid saturation decreases from 0.83 to 0.63 as the porosity decreases from 0.75 to 0.35. It is also found that at a larger porosity, the liquid saturation in the LGDL will become almost identical along the LGDL thickness direction. This is because large porosity will improve liquid water transport in the LGDL pore. For example, when the porosity is 0.75, the liquid saturation only decrease by around 0.01 as the LGDL thickness ranges from 0 to $200 \text{ }\mu\text{m}$. The modeling results indicate that a LGDL with larger porosity will have better liquid water transport dynamics. Here, it should be noted that larger porosity will lead to larger electrical resistance for LGDL, which will contribute more to cell ohmic loss and worse the cell performance, so a balance between two-phase transport and ohmic loss is of vital importance to cell performance.

Pore size of a LGDL is also an important parameter for two-phase transport in a PEMEC, because the pore size affects the cell ohmic loss and reaction dynamics based on the previous experimental observation [13]. So far, few papers have paid special attentions to the modeling of pore size effects in a PEMEC. In this present modeling, the relationship of permeability and pore diameter is introduced to examine the effect of pore size on the two-phase transport. As shown in Figure 9, the effects of four different pore diameters including $35 \text{ }\mu\text{m}$, $55 \text{ }\mu\text{m}$, $75 \text{ }\mu\text{m}$, and $95 \text{ }\mu\text{m}$ on the liquid saturation is investigated at a current density of 2.0 A/cm^2 . The modeling results show that as the pore size increases, the liquid saturation increases significantly, which means the liquid water transport may benefit from a large pore. For instance, at the interface between LGDL and CL ($x=200 \text{ }\mu\text{m}$), it can be calculated that the liquid saturation is respectively 0.63, 0.75, 0.78, 0.79. In addition, it can be noticed that when the pore diameter becomes larger, the variation of liquid saturation along the LGDL thickness direction will become less significant, which means the LGDL is filled with more liquid water. This phenomenon indicated that the variation of two-phase transport dynamics should be more sensitive to a LGDL with a smaller pore size.

3.4 Performance and efficiency

In this section, to understand the variation of cell performance and efficiency under different parameters, the polarization curve, which is the most common way of describing the performance of a PEMEC, is plotted to find out how two-phase transport affects the cell performance. As mentioned in the model development section, the total potential should consist of four parts, including OCV, activation over-potential, diffusion over-potential, and ohmic loss. Here, activation and diffusion over-potentials are related to the liquid water saturation and transport.

In this study, the relationship of the pore diameter and permeability have been incorporated into the two-phase transport equations to model the effects of LGDL pore size, and four cases with different pore diameters, including 35 μm , 55 μm , 75 μm , and 95 μm , are examined. In Figure 10, x-coordinate is the operating current density ranging from 0 to 2.0 A/cm^2 , y-coordinate presents both total cell voltage and efficiency. It can be seen that at a relative low current density, there is very small change in the cell voltage and efficiency within the pore size range from 35 to 95 μm . Under the same porosity, pore size changes impact the ohmic loss very little, and their effects on the activation and diffusion over-potentials are closely related to the current density and the associated liquid water distribution, according to Equations (5) and (8). A very small over potential change occurs at small current density ranges. For example, at an anode porosity of 0.35 and a current density of 0.5 A/cm^2 , the cell voltage changes only by 0.003 V as the pore diameter increases from 35 to 95 μm . While at a high current density, it can be found that the cell voltage reduces more significantly with pore size increases. Particularly, as the current density increases to more than 2.0 A/cm^2 , an interesting phenomenon can be captured: there is a sudden change in cell voltage and efficiency, which is different from a single-phase model. This phenomenon can be attributed to the fact that liquid water at the reaction interface is completely consumed by the electrochemical reaction due to a large current density. Furthermore, it can be concluded that the limiting current density contributing to a sudden change in cell voltage and efficiency is dependent on the LGDL properties. For example, the limiting current density is respectively equal to 2.205 A/cm^2 for 35 μm , 2.703 A/cm^2 for 55 μm , 3.088 A/cm^2 for 75 μm , and 3.41 A/cm^2 for 95 μm .

The other case is about the effects of PEM humidification, which directly contributes to the cell ohmic loss, as defined in the following relation [35]:

$$\sigma_{PEM} = (0.005139\lambda - 0.00326)\exp\left[1268.0\left(\frac{1}{303} - \frac{1}{T}\right)\right] \quad (18)$$

Here, σ_{PEM} is the PEM conductivity that is inversely proportional to the ohmic resistance of PEM, T is the cell operating temperature, and λ is the humidification degree defined as the water content in a PEM, which can change in a large range due to different operating conditions. Some papers suggest λ should be in the range from 14 to 25 [25, 34]. Since huge liquid water is fed into the anode side of a PEMEC, the values including 10, 20, and 30 are used to investigate the effects of humidification degree on the cell performance and efficiency, as shown in Figure 11. As expected, with the humidification degree increasing, the cell voltage decreases and the cell efficiency enhances. This is because that large humidification degree leads to a large PEM conductivity according to equation (18). It can be calculated that the PEM resistance can decrease by around 34.1% as the humidification degree increases from 20 to 30.

4 Conclusions

In this study, a PEMEC model for two-phase transport and electrochemical performance is developed and validated. Particularly, the relationships of pore size effect and equivalent resistance are incorporated into two-phase transport equations and performance model. This comprehensive model is then carried out to investigate the effects of LGDL properties and PEM properties including contact angle, porosity, pore size, and humidity on the two-phase transport dynamics and cell performance. Analysis results reveal that the capillary pressure, which controls the liquid water transport in the LGDL, is affected by the LGDL wetting characteristics, micro-structure and liquid water distribution. In addition, contact angle, porosity, and pore size have a significant influence on the liquid saturation. Increasing the porosity and pore size while decreasing the contact angle can enhance the liquid water saturation along the LGDL thickness direction. Further, the polarization curves shows large pore can improve the performance and efficiency of a PEMEC, especially at a high current density. Large humidification degree can lead to a good conductivity for PEM and relatively small ohmic resistance. For two-phase transport, there will be a sudden change in cell voltage and efficiency as the current density increases and different pore sizes can result in different limiting current density values.

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List of symbols

A	Reaction area, cm^2
a_0	Empirical coefficient
$C_{H_2,m}$	Hydrogen concentration at the interface of electrode and PEM, mol/cm^3
$C_{i,m0}$	Reference concentration, mol/cm^3
$C_{O_2,m}$	Oxygen concentration at the interface of electrode and PEM, mol/cm^3
i	Current density, A/cm^2 , or fluid species, cell component
i_0	Exchange current density, A/cm^2
K	Permeability
k_r	Relative permeability
M	Molar mass, g/mol
N	Fluid mass flux, mol/s
p	Pressure, atm
R_i	Component resistance, Ω
R	Gas constant, $\text{J}/\text{mol K}$
s	Liquid saturation
s_0	Interfacial liquid saturation
t	Time, s
T	Temperature, K
V	Voltage or overpotential, V
V_0	Reversible voltage, V
x	Distance along the LGDL thickness direction, μm
Greek	
n	Charge transfer coefficient, atm
α_i	Activity of species
ε	Porosity
θ	Contact angle, degree ($^\circ$)
μ	Fluid dynamic viscosity, $\text{N s}/\text{m}^2$
ρ	Fluid density, kg/m^3
σ	Surface tension, N/m

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Temperature ($^{\circ}\text{C}$)	V_{ocv} (V)
20	1.233
25	1.229
30	1.224
50	1.206
80	1.179
90	1.170

Table 1

Description, symbol	Value, unit
MEA active area	5.0 cm ²
Flow channel thickness	0.5 mm
Operating pressure, P	Anode: 1 atm, cathode: 13.6atm
Operating temperature, T	80 ⁰ C
LGDL thickness	200 μ m
LGDL porosity	Anode: 0.35, cathode: 0.7
CL thickness	10 μ m
CL porosity	0.2
Titanium resistivity	5.0 $\times 10^{-3}$ Ω cm
Carbon paper resistivity	80.0 $\times 10^{-3}$ Ω cm
Graphite resistivity	5.0 $\times 10^{-3}$ Ω cm
Anode CL resistivity (catalyst: Ir _x Ru _{1-x} O ₂)	0.05 Ω cm [38]
Cathode CL resistivity (catalyst: Pt/C)	1.4 $\times 10^{-3}$ Ω cm [39]
Contact angle in the LGDL, θ	80 ⁰
Faraday constant, F	96487.0 C/mol
Water molar mass, M_{H_2O}	18 g/mol
Oxygen molar mass, M_{O_2}	32 g/mol
Liquid water dynamic viscosity, μ_{H_2O}	3.55 $\times 10^{-4}$ N s/m ²
Liquid water density, ρ_{H_2O}	1000 kg/m ³
Oxygen dynamic viscosity, μ_{O_2}	2.34 $\times 10^{-5}$ N s/m ²
Oxygen density, ρ_{O_2}	1.0 kg/m ³
Surface tension, σ	0.0625 N/m
Empirical coefficient, a_0	0.1

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Figure 1

Figure 2

Figure 3

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