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EFFECTS OF THE WETTABLITY OF THE POROUS TRANSPORT LAYER ON PEMEC CONSIDERING THE DETAILED CHANNEL TWO-PHASE FLOW

Lizhen Wu, Guobin Zhang, Zhijun Peng, Kui Jiao*

State Key Laboratory of Engines, Tianjin University, 135 Yaguan Rd, Tianjin, China, 300350
*Corresponding author: kjiao@tju.edu.cn; tel: +86-22-27404460; fax: +86-22-27383362

ABSTRACT

In this study, a novel method that integrates the detailed channel two-phase flow into the 3D (three-dimensional) model of PEMEC (proton exchange membrane electrolyzer cell) is proposed. We explored the effect of L/GDL (liquid/gas diffusion layer) wettability on the two-phase flow and performance of PEMEC. The results show that in the hydrophilic contact angle range, the more hydrophilic contact angle will deteriorate the performance and hinder the discharge of bubbles to the channel. The novel gradient type L/GDL will further promote the flow of water and gas due to the gradient effect of its wettability. In addition, adding MPL also can improve the two-phase management.

Keywords: PEMEC; 3D model; VOF method; Wettability.

1. INTRODUCTION

Due to its advantages of faster dynamic response and wide range of operating current density, etc. Proton exchange membrane electrolyzer cell (PEMEC) is now attaching strong attention in water electrolysis technology [1]. However, the management of the two-phase flow in the porous layer is particularly important. The blockage of bubbles will limit the supply of liquid water and cause excessive mass transfer losses [2], limiting its commercial application. Therefore, it is necessary to explore the mechanism of how its wettability affect the two-phase flow and performance of PEMEC, and take measures to solve it.

Although there were related studies exploring the effects of liquid/gas diffusion layer (L/GDL) wettability on PEMEC [3-4], the results were not very credible due to the oversimplified model. For example, Han et al. [3] ignored the oxygen jump phenomenon between adjacent porous layers by simplifying the interface between L/GDL and catalyst layer (CL) into reaction positions. Olesen et al. [4] also did not consider the realistic two-phase flow in the channel in 3D model. In addition, adding the MPL (microporous layer) has been proven to improve PEMEC performance [5-6], but its effects of wettability for the internal two-phase flow is still unknown. Thus, in this study, we apply the newly proposed method of integrating the detailed channel two-phase flow into the 3D model to explore the effects of L/GDL wettability and the addition of MPL on the improvement of two-phase flow and performance.

2. NUMERICAL METHOD

2.1 Computational domain

The computational domain of the 3D model in this study also includes the following parts: BP, channel, L/GDL, CL, PEM, which can be shown in Fig 1. The relative parameters of the parts can be found in [7]. Each part is divided into 10 layers of grids along the X and y directions, and 300 layers along the Z direction. The grid independence test has been completed.

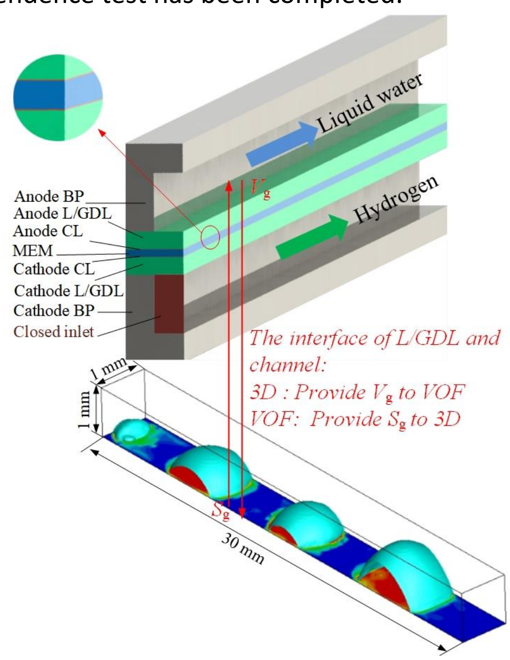

Fig 1 Computational domain and coupled method

2.2 Governing equations

The detailed two-phase flow in the channel is simulated by the VOF method, and the conservation equation is given in the Table 1, and the continuous surface force (CSF) model which is used for the inclusion of surface tension is as follows：

$$F_s = \sigma k \delta(\mathbf{r} - \mathbf{r}_{int})\vec{n} \tag{1}$$

$$k = -\nabla\cdot\vec{n} = -\nabla\cdot\left(\frac{\nabla\alpha}{|\nabla\alpha|}\right) \tag{2}$$

$$\vec{n} = \vec{n}_{\mathrm{w}}\cos\theta + \vec{t}_{\mathrm{w}}\sin\theta \tag{3}$$

where σ (N m^{-1}) is the surface tension coefficient, k the radius of curvature, $\delta(\mathbf{r} - \mathbf{r}_{int})$ the Dirac delta function, $\vec{n}$ the unit normal vector at the interface, $\vec{n}_{\mathrm{w}}$ and $\vec{t}_{\mathrm{w}}$ the unit vectors normal and tangential to the channel wall, respectively, and θ (°) the contact angle at channel walls.

This 3D model describes the electrochemical electrode kinetics and the two-phase fluids of entire PEMEC through some conservation equations. The new proposed method is shown in Fig 1, which can refer to [8] for details. The emerging velocity of oxygen simulated by the 3D model is provided to the VOF method at the interface of L/GDL and channel, and the oxygen saturation at the interface is simulated furtherly by VOF method. Since the transient calculation of VOF method, it is returned to the 3D model to update the emerging velocity of oxygen when the oxygen saturation value at the interface is almost unchanged. It requires several loops to reach a stable solution. The conservation equations are solved by software Fluent and UDF written by C code, which are summarized as follows:

Table 1: Governing equations.

Name	Conservation equations
	VOF method
Mass	$\frac{\partial\rho_{\mathrm{m}}}{\partial t} + \nabla\cdot(\rho_{\mathrm{m}}u_{\mathrm{m}}) = 0$
Momentum	$\frac{\partial(\rho_{\mathrm{m}}u_{\mathrm{m}})}{\partial t} + \nabla\cdot(\rho_{\mathrm{m}}u_{\mathrm{m}}u_{\mathrm{m}}) = -\nabla P + \nabla\cdot\left[\mu_{\mathrm{m}}\left(\nabla u_{\mathrm{m}} + \nabla u_{\mathrm{m}}^{T}\right)\right] + \rho_{\mathrm{m}}g + F_s$
Volume fractions of gas	$\frac{\partial s_{\mathrm{g}}}{\partial \mathrm{t}} + \nu\cdot\nabla s_{\mathrm{g}} = 0$
	3D model
Mass	$\frac{\partial}{\partial t}(\varepsilon s_{\mathrm{x}}\rho_{\mathrm{x}}) + \nabla\cdot(\rho_{\mathrm{x}}\vec{u}_{\mathrm{x}}) = S_{\mathrm{mx}}$
Momentum	$\frac{\partial}{\partial t}\left(\frac{\rho_{\mathrm{x}}\vec{u}_{\mathrm{x}}}{\varepsilon s_{\mathrm{x}}}\right) + \nabla\cdot\left(\frac{\rho_{\mathrm{x}}\vec{u}_{\mathrm{x}}\vec{u}_{\mathrm{x}}}{\varepsilon^2 s_{\mathrm{x}}^{2}}\right) = -\nabla P_{\mathrm{x}} + \mu_{\mathrm{x}}\nabla\cdot\left(\nabla\left(\frac{\vec{u}_{\mathrm{x}}}{\varepsilon s_{\mathrm{x}}}\right) + \nabla\left(\frac{\vec{u}_{\mathrm{x}}^{\mathrm{T}}}{\varepsilon s_{\mathrm{x}}}\right)\right) - \frac{2}{3}\mu_{\mathrm{x}}\nabla\left(\nabla\cdot\left(\frac{\vec{u}_{\mathrm{x}}}{\varepsilon s_{\mathrm{l}}}\right)\right) + S_{\mathrm{ux}}$
Gas species	$\frac{\partial}{\partial t}(\varepsilon s_{\mathrm{g}}\rho_{\mathrm{g}}Y_{\mathrm{i}}) + \nabla\cdot(\rho_{\mathrm{g}}\vec{u}_{\mathrm{g}}Y_{\mathrm{i}}) = \nabla\cdot(\rho_{\mathrm{g}}D_{\mathrm{i}}^{\mathrm{eff}}\nabla Y_{\mathrm{i}}) + S_{\mathrm{i}}$
Gas pressure	$\frac{\partial}{\partial t}(\rho_{\mathrm{O_2}}\varepsilon s_{\mathrm{O_2}}) + \nabla\cdot\left(\rho_{\mathrm{O_2}}\frac{Kk_{\mathrm{O_2}}}{\mu_{\mathrm{O_2}}}\nabla P_{\mathrm{O_2}}\right) = S_{\mathrm{P_{O_2}}}$
Liquid pressure	$\frac{\partial}{\partial t}(\rho_{\mathrm{l}}\varepsilon s_{\mathrm{l}}) + \nabla\cdot\left(\rho_{\mathrm{l}}\frac{Kk_{\mathrm{l}}}{\mu_{\mathrm{l}}}\nabla P_{\mathrm{l}}\right) = S_{\mathrm{l}}$
Electronic potential	$0 = \nabla\cdot(\kappa_{\mathrm{e}}^{\mathrm{eff}}\nabla\varphi_{\mathrm{e}}) + S_{\mathrm{e}}$
Ionic potential	$0 = \nabla\cdot(\kappa_{\mathrm{ion}}^{\mathrm{eff}}\nabla\varphi_{\mathrm{ion}}) + S_{\mathrm{ion}}$
Energy	$\frac{\partial}{\partial t}(\varepsilon s_{\mathrm{l}}\rho_{\mathrm{l}}C_{\mathrm{p,l}}T + \varepsilon s_{\mathrm{g}}\rho_{\mathrm{g}}C_{\mathrm{p,g}}T) + \nabla\cdot(\varepsilon s_{\mathrm{l}}\rho_{\mathrm{l}}C_{\mathrm{p,l}}u_{\mathrm{l}}T + \varepsilon s_{\mathrm{g}}\rho_{\mathrm{g}}C_{\mathrm{p,g}}u_{\mathrm{g}}T) = \nabla\cdot(k^{\mathrm{eff}}\nabla T) + S_{\mathrm{T}}$

The electro-chemical reaction rate J (A m^{-3}) in CL is defined by the modified Butler-Volmer (B-V) equations [6], as shown below:

$$J_{\mathrm{a}} = s_l^2 \cdot J_{0,\mathrm{a}}^{\mathrm{ref}} \left(\exp\left(\frac{\alpha_{\mathrm{a}} F}{RT} \eta_{\mathrm{act},a} \right) - \exp\left(-\frac{(1-\alpha_{\mathrm{a}})F}{RT} \eta_{\mathrm{act},a} \right) \right) \quad (4)$$

$$J_{\mathrm{c}} = J_{0,\mathrm{c}}^{\mathrm{ref}} \left(\exp\left(\frac{\alpha_{\mathrm{c}} F}{RT} \eta_{\mathrm{act},c} \right) - \exp\left(-\frac{(1-\alpha_{\mathrm{c}})F}{RT} \eta_{\mathrm{act},c} \right) \right) \quad (5)$$

$$J_{0,\mathrm{a}}^{\mathrm{ref}} = j_{0,\mathrm{a}} \exp\left(\frac{-E_{\mathrm{act,a}}}{R} \left(\frac{1}{T} - \frac{1}{T_{\mathrm{ref}}} \right) \right) \quad (6)$$

$$J_{0,\mathrm{c}}^{\mathrm{ref}} = j_{0,\mathrm{c}} \exp\left(\frac{-E_{\mathrm{act,c}}}{R} \left(\frac{1}{T} - \frac{1}{T_{\mathrm{ref}}} \right) \right) \quad (7)$$

Where sl is liquid saturation in anode CL, E_{act} (J) the activation energy in CL, η_{act} the overpotential in CL, α the transfer coefficient (0.5). The relevant boundary conditions are similar to those in the literature of PEM fuel cell [9].

3. RESULT & DISSCUTION

3.1 Model Validation

For the 3D multi-phase model adopted in this study, it has been validated with experimental data in terms of the polarization curve together with the ohmic loss [2], and two-phase flow state in channel [7, 10]. The simulation results are in good agreement with the experimental results. The qualitative difference is less than 1% and the bubble state is also very similar, as shown in Fig 2.

3.2 Effects of wettability on oxygen and performance

It can be known that hydrophilic pores help the transportation of liquid water and gas bubbles in PEMEC from the similar study, so this paper will focus on the hydrophilic LGDL [3]. As shown in Fig 1, the wettability of L/GDL does affect the performance of the PEMEC. The more hydrophilic L/GDL will deteriorate its performance. The reason is probably that too hydrophilic L/GDL can easily trap water and make it difficult to flow. And as the operating current increases, the faster oxygen production rate will aggravate this effect.

In Fig 4 (a), the channel two-phase distribution of the final loop obtained by the VOF method shows a discontinuous state closest to the actual situation. It can be seen that when the contact angle of L/GDL is 30°, bubbles tend to accumulate at the interface of L/GDL and channel under the same working current density (2.0 A cm^{-2}), which hinders the supply of water to CL. When the contact angle of L/GDL is 70°, dispersed bubbles appear in the channel and the oxygen saturation value at the interface is lower, which means that the more hydrophilic the contact angle at the interface is not suitable to be adopted.

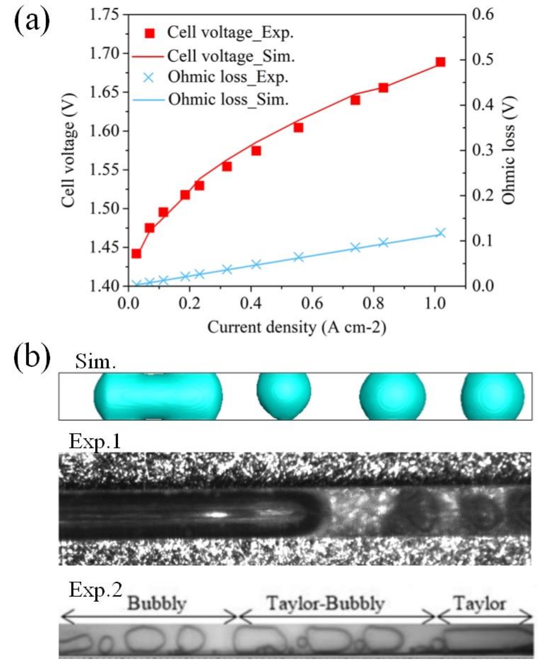

Fig 2 Comparsion between model and experiment: (a) polarization and ohmic loss [2] (b) two phase flow in channel [7, 10]

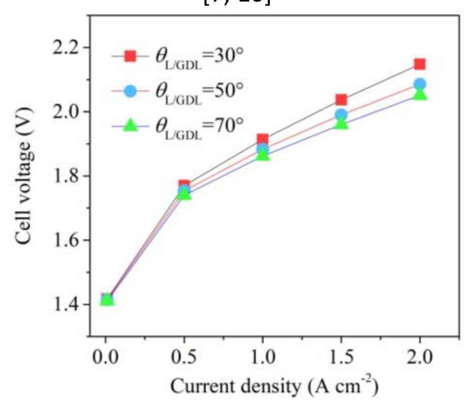

Fig 3 Effects of wettability on performance.

It can be seen from Fig 4(b) and (c) that the considering or ignoring the two-phase flow in channel results in the big difference of the oxygen saturation distribution in CL and cell voltage. The discrete local oxygen bubble distribution in channel will cause a similar distribution of oxygen saturation in the CL. Compared with ignoring oxygen in the channel, the performance difference of different wettability L/GDL is more obvious when considering oxygen in the channel. Increasing the L/GDL contact angle from the bottom to the top will not only reduce the oxygen saturation, but also improve the uneven distribution of its oxygen saturation while improving its performance, thereby extending its durability.

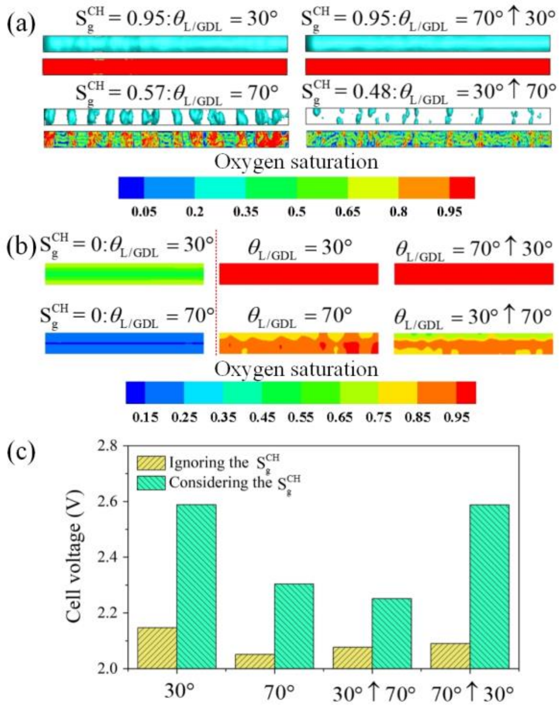

Fig 4 Effects of wettability on: (a) oxygen saturation in anode channel, (b) oxygen saturation in anode CL, (c) current density in anode CL.(2.0 A cm^{-2})

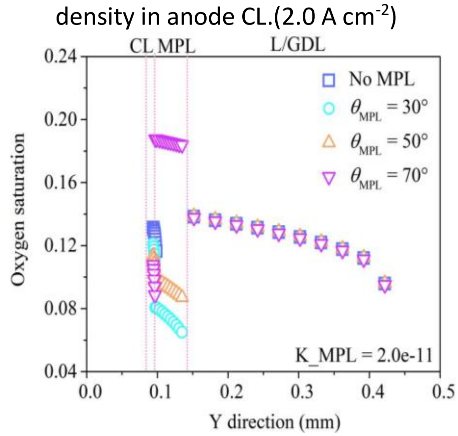

Fig 5 Effects of MPL on oxygen in porous layers.

3.3 Effects of MPL on oxygen and performance

The Fig 5 shows the obvious oxygen jumping phenomenon between different porous layers. Lettenmeier et al. [5] mentioned the improvement of the contact resistance of the interface between L/GDL and CL by MPL, but there are few studies about MPL on two-phase flow management. It can be found that the more hydrophilic MPL will also cause the accumulation of oxygen in the CL and the specific principle is the same as that of L/GDL，which can help guide the treatment of wettability in the future MPL design.

3.4 Conclusion

In this paper, a 3D model of PEMEC considering the detailed channel two-phase flow was developed. Then, the effects of L/GDL wettability and the addition of MPL on the improvement of two-phase flow and performance were carried out. The conclusions are as follows:

1) In terms of qualitative and quantitative model validation, the polarization curve, ohmic loss, and two-phase flow in channel were validated respectively.
2) When considering the detailed two-phase flow in channel and oxygen saturation jump phenomenon between the porous layer, the more hydrophilic contact angle should not be applied to L/GDL. The oxygen saturation distribution of CL is obviously affected by the two-phase flow in the channel. The increased contact angle from bottom to top will improve the two-phase flow and performance.
3) The addition of MPL will improve the two-phase management of CL, but the more hydrophilic the MPL will reduce the effect.

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