Investigation on Start-up Purge Strategy for PEM Fuel Cell

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ABSTRACT

Proton exchange membrane fuel cells are promised to be the future choice for transportation power systems. Start-up procedure has significant impacts on fuel cell degradation. Most damages induced by start-up procedure relate to the hydrogen/air interface inside fuel cell. Studying on hydrogen/air interface is crucial for start-up degradation mitigation. It is difficult to monitor the internal distribution and transfer of hydrogen and oxygen by experiments. Therefore, this paper establishes a three-dimensional two-phase fuel cell model to simulate the gas concentration distribution in anode compartment, and proposes a start-up purging strategy by injecting hydrogen into the anode. The hydrogen/air interface removal process is simulated and visualized. Subsequently, the impacts of initial residual oxygen concentration and hydrogen flow rate on air removal in anode compartment are studied. It is proved that decrease initial oxygen concentration and increase hydrogen injection flow rate can significantly shorten the purge time. However, small flow rate of hydrogen injection is more economical for start-up purging when residual oxygen concentration is small. The results found in this paper can guide the experimental study of startup purging strategy, and enrich high-performing and long-lasting design application theory of fuel cell.

Keywords: Proton exchange membrane fuel cell; hydrogen/air interface; start-up purging strategy

1. INTRODUCTION

Proton exchange membrane fuel cell (PEMFC) has been deemed to be a promising candidate for the next generation power system [1]. Up to now, durability is one of the most critical issues affecting PEMFC commercialization [2]. Continuous start-stop cycles lead to corrosion of catalyst layer, which have significant effect on fuel cell's durability [3]. Most of the damages induced by start-up procedure come from the presence of hydrogen/air interface in anode compartment [4]. Reise et al. [5] first proposed the 'reverse-current decay mechanism' and found that hydrogen/air interface in anode compartment will result in the electrochemically active surface area loss and cell performance degradation.

Researchers have found that reducing the residence time of hydrogen/air interface in anode is vital for mitigating the start-up degradation [6]. Lamibrac et al. [7] found carbon corrosion was most serious in the section where air existed for the longest time. Moreover, the flow rate of hydrogen injection had a significant influence on the degradation. Brightman et al. [8], Dillet et al. [9] increased hydrogen flow rate during start-up to reduce the damage of hydrogen/air interface to the electrode. some researchers also purge nitrogen before fuel cell start-up to shorten the residence time of hydrogen/air interface or even avoid the formation of hydrogen/air interface in anode [10]. However, the preparation, storage and carrying of nitrogen became another thorny problem in the common use of fuel cell vehicles [11]. Based on the above studies, purging hydrogen before start-up is considered a promising method to remove the hydrogen/air interface before PEMFC is start-up, which does not require an additional gas storage device and can effectively mitigate the internal degradation [12].

In this paper, the hydrogen/air interface propagation process is visualized by simulation. The impacts of initial residual oxygen concentration and hydrogen injection flow rate on hydrogen/air interface removal in anode compartment are analyzed as well. Since experimental method is difficult to observe and measure the gas

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distribution and transmission inside fuel cell, a threedimensional two-phase PEMFC model is established to monitor the real-time residual oxygen concentration and oxygen removal rate in anode. The result of this paper provides a theoretical basis the experimental study of start-up purging strategy and can be the reference of the further study.

2. MODEL DEVELOPMENT

2.1 Model assumptions

On the premise that the main reactions of fuel cell are thoroughly described, the following hypotheses are put forward to simplify the fuel cell model establishment and calculation in this paper [13,14]:

(1) The reaction gas is ideal and incompressible

(2) The state of the gas in the flow channel is laminar flow(3) Reactant gas cannot pass through proton exchange membrane

2.2 Governing equations of fuel cell

The complex reactions inside the fuel cell involve basic fluid dynamics equations, electrochemical reaction equations, gas diffusion equations, and water transfer equations, etc.

(1) Conservation equations of mass, momentum, energy and composition

$$\frac{\partial(\eta\rho)}{\partial t} + \nabla(\eta\rho\vec{u}) = S_M \tag{1}$$

 $\frac{\partial(\eta\rho\vec{u})}{\partial t} + \nabla(\eta\rho\vec{u}\vec{u}) = -\eta\nabla P + \nabla \cdot (\eta\xi\nabla\vec{u}) + S_{\vec{u}}$ ⁽²⁾

$$\frac{\partial(\eta\rho C_P T)}{\partial t} + \nabla \cdot (\eta\rho C_P T \vec{u}) = \nabla \cdot (\lambda^{eff} \nabla T) + S_H$$
(3)

$$\frac{\partial(\eta c_i)}{\partial t} + \nabla \cdot (\eta \vec{u} c_i) = \nabla \cdot (D_i^{eff} \nabla c_i) + S_i$$
(4)

(2) Open circuit voltage control equation

$$E = \frac{-\Delta G_0}{2F} + \frac{RT}{2F} \ln\left(\frac{P_{H_2} P_{O_2}}{P_{H_{2O}}}\right)$$
(5)

(3) Consumption and production of substances in electrochemical reactions

$$W_{O_2} = \frac{I}{4F} \cdot M_{O_2} \qquad W_{H_2} = \frac{I}{2F} \cdot M_{H_2} \qquad W_{H_2O} = \frac{I}{2F} \cdot M_{H_2O}$$
(6)



Fig. 1. Three-dimensional geometry model of PEMFC with five-channel serpentine flow field

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Channel width	Channel height	Ridge width	Area of MEA
1.2mm	0.8 mm	0.8 mm	52mmx31.2mm
GDL height	Catalyst height	PEM height	Plate height
0.2mm	0.012mm	0.036mm	2mm

2.3 Geometry and mesh

The three-dimensional PEMFC model built in this paper is composed of cathode/anode current collector, cathode/anode flow channel, cathode/anode gas diffusion layer (GDL), cathode/anode catalyst layer (CL) and proton exchange membrane as is shown in Fig.1. According to the literature [14] The main geometric parameters of the model are shown in Table 1.

2.4 Material setting

In this paper, FLUENT is used to simulate the single fuel cell model in first-order discrete format. The model parameters used are all based on the real properties of the material and are set in combination with literature [14,15]. The specific parameter of the model is shown in Table 2.

2.5 Model validation

In order to verify the accuracy of the model, this paper selects the experimental data in the literature [14] with the same flow field form and size for comparison, and uses the experimental conditions to set the boundary conditions of simulation, as shown in Table 3. The polarization curve of both simulation model and experimental model are shown in Fig.2. When the current density is less than 0.8 A/cm², the simulation

Table 2. Farameters of the	mouel			
Plate	Density	Specific heat capacity	Thermal conductivity	Conductivity
	2719 kg⋅m ⁻³	871 J·kg ⁻¹ ·k ⁻¹	100W·m ⁻¹ ·k ⁻¹	500 Ω ^{_1} ⋅m ⁻¹
Gas diffusion layer	Density	Porosity	Conductivity	Viscous resistance
	2719 kg⋅m ⁻³	0.5	580 Ω ^{_1} ·m ⁻¹	3.33x10 ¹² m ⁻²
Catalyst layer	Porosity	Viscous resistance	Surface-volume ratio	
	0.3	3.33x10 ¹² m ⁻²	200000 m-1	
Electrode	H2 diffusion coefficient	O2 diffusion coefficient	H2O diffusion coefficient	Open circuit voltage
	9.15x10 ⁻⁵ m ² ·s ⁻¹	2.2x10 ⁻⁵ m ² ·s ⁻¹	2.56x10 ⁻⁵ m ² ⋅s ⁻¹	0.98V
Proton exchange membrane	Thermal conductivity	Proton conductivity		
	2W·m ⁻¹ ·k ⁻¹	1		

Table 2. Parameters of the model

model is consistent with the experimental results, but when the current density is greater than 0.8 A/cm², the simulation and experimental results are quite different. This is because this paper assumes that water exists only in gaseous form, and does not consider the harsh conditions of flooding under high current density. Since this paper mainly focused on the internal status in fuel cell during start-up. The involved current density is far less than 0.8A/cm², and flooding rarely occurs during start-up. Therefore, the model is reliable within this study.



Fig. 2. Comparisons of the experimental and simulation polarization curve of PEMFC model

Table 3. Boundary conditions

Pressure	Temperature	Anode humidity	
1.5 atm	343 k	100%	
Cathode humidity	Anode stoichiometry	Cathode stoichiometry	
100%	2.0	2.5	

3. RESULTS AND DISCUSSION

3.1 Visualization of hydrogen/air interface removal process during start-up purging

Injecting hydrogen can remove air from the anode compartment, which effectively mitigates carbon corrosion and performance degradation caused by hydrogen/air interface. This paper simulates the start-up purging process: Firstly, air is injected into both cathode and anode for 5s until air is uniformly distributed, to simulate the spread of air into the anode compartment from outside. Secondly, the anode gas is exchanged from air to hydrogen. To the cathode, air is continuously supplied to prevent the harm caused by differential pressure between membrane. Every 0.1s, gas distribution data on anode catalyst layer are obtained until air is completely replaced by hydrogen. The gas flow rates in both anode and cathode flow-channels are calculated according to the setting operating condition, and are updated in Fluent by UDF function.

The hydrogen/air interface removal process is as shown in Fig.3. The color from red to blue represents the oxygen concentration from high to low, namely, the red area is the 'oxygen zone' with higher oxygen content and the dark blue area is the 'hydrogen zone' where oxygen is basically cleared. The green and yellow banded areas is the 'transition zone', which is a mixture of oxygen and hydrogen. The boundary of 'hydrogen zone' is defined as hydrogen/air interface in later analysis.



Fig. 3. Hydrogen/air interface propagates on anode catalyst layer during purging process

It can be seen in Fig.3 that, hydrogen/air interface is not the cross-section of anode flow channel. Its shape is affected by gas diffusion and fuel cell structure. The injected hydrogen not only diffuses vertically but also laterally on the porous diffusion layer, resulting in its area on the catalyst layer much larger than the occupied channel area. Therefore, the area of hydrogen/air interface also has a dynamic process of increasing and decreasing as hydrogen diffuses. hydrogen/air interface forms at anode inlet at 0.2s. In 0.2s to 3.0s, the area of the hydrogen/air interface increases gradually with the continuous injection of hydrogen. In the following 3.0s to 5.0s, the area of the hydrogen/air interface decreases on account of the discharge of oxygen. At 6.0s, hydrogen/air interface disappears at the outlet when oxygen is completely replaced by hydrogen in anode.

3.2 Impact of initial residual oxygen concentration

When fuel cell is shut-down, air will enter into the anode compartment as a result of poor gas tightness. The more air entering anode compartment before fuel cell start-up, the higher the initial oxygen concentration in anode, which has impact on the purging process. 4 groups of different initial oxygen concentration are selected, which are 5.865 mol/m³, 7.057 mol/m³, 8.276 mol/m³, and 9.518 mol/m³, respectively. The hydrogen injection flow rate keeps constant. The other operating parameters are the same as in Table 3.

Fig.4 shows the relationship between time and residual oxygen concentration on anode catalyst layer

under different initial oxygen concentration, i.e., the process of hydrogen/air interface being discharged from anode. The four residual oxygen concentration curves the same changing trend. have The oxygen concentration on anode catalyst layer reduces fast at first and then slows down. The initial oxygen concentration has great influence on purging: the higher the initial oxygen concentration, the longer the necessary purge time, the larger the purge consumption. According to Fig.4, the necessary purge time is proportional to the initial oxygen concentration, which is 4.25s, 5.37s, 6.52s, 7.71s respectively. Since the same hydrogen injection flow rate is adopted in four groups, hydrogen consumption is proportional to the initial anode oxygen concentration as well as shown in Fig.5. Therefore, it is significant to enhance the gas tightness of fuel cell to keep oxygen concentration at a low value in anode compartment, which is conducive to the removal of hydrogen/air interface before fuel cell is start-up, and reduce purge consumption as well.



Fig. 4. Anode residual oxygen concentration declines in purging process-different initial oxygen concentration



Fig. 5. Necessary purge time and corresponding hydrogen consumption - different initial oxygen concentration

3.3 Impact of hydrogen purge flow rate

In this section, the impacts of hydrogen injection flow rate on purging efficiency are discussed. Hydrogen flow rate is changed by increasing gas stoichiometry. The base flow rate is the hydrogen flow rate required for fuel cell to operate at 100mA/cm²(the current density used for fuel cell start-up). 1.5, 2.0, 2.5, 3.0, 4.0, 5.0 times the base flow rate (the corresponding stoichiometry are: 3, 4, 5, 6, 8, 10, respectively) are selected and other operating parameters are the same as in Table 3.

Fig.6 gives the relationship between time and residual oxygen concentration on anode catalyst layer under different hydrogen flow rates. It can be seen that hydrogen injection flow rate has a significant effect on purging efficiency. With the increase of hydrogen flow rate, the necessary purge time is also significantly shorter, which are 7.31s, 5.37s, 4.25s, 3.53s, 2.66s, 2.14s, respectively. What's more, in the purging process, residual oxygen concentration reduces rapidly at first and then decreases. Take the group '5.0 times the base flow rate' as an example, it takes almost half of the total purge time to remove the last 1mol/m³ oxygen, as can be seen in Fig.6.

Fig.7 shows the relationship between time and anode oxygen removal rate under six different hydrogen injection flow rates. At the former stage of purging process, oxygen removal rate is large, but the oxygen removal rate decreases rapidly with the reduction of oxygen. The higher the hydrogen flow rate, the larger the initial oxygen removal rate, and the faster the removal rate declines.



Fig. 6. Anode residual oxygen concentration declines in purging process - different hydrogen flow rates



Fig. 7. The change of anode oxygen removal rate - different hydrogen flow rates

Combing Fig.6 and Fig.7, large flow rate of hydrogen injection will increase the removal rate of oxygen in the early stage, and remove most of the oxygen faster. However, when the residual oxygen concentration is small, such as 1mol/m³, even the large hydrogen flow

rate is used, the oxygen removal rate is still very low. Base on this result, small flow rate of hydrogen injection is considered more economical for the second half of the purging with low oxygen concentration. Since the page is limited, this part of the research will be included in future articles.

4. CONCLUSIONS

The main conclusions are as follows:

During purging process, the shape of hydrogen/air interface and its propagation velocity are affected by gas diffusion.

Decrease the initial oxygen concentration could proportionally reduce the necessary purge time and purge consumption.

large flow rate of hydrogen injection will increase the removal rate of oxygen in the early stage, and remove most of the oxygen faster. However, when the residual oxygen concentration is small, such as 1mol/m³, even the large hydrogen flow rate is used, the oxygen removal rate is still very low. Base on this result, small flow rate of hydrogen injection is considered more economical for the second half of the purging process with low oxygen concentration.

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