

PORE-SCALE MODELING OF OXYGEN TRANSPORT IN THE AIR-BREATHING CATHODE OF MEMBRANELESS MICROFLUIDIC FUEL CELLS

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ABSTRACT

The performance of membraneless microfluidic fuel cells can be predominated by the air-breathing cathode, making it essential to understand the effect of nano- and micro-structures on the oxygen transport and reaction. For the first time, pore-scale Lattice Boltzmann Method (LBM) models have been developed to simulate the oxygen transport in air-breathing cathode based on reconstructed structures. The underneath electrolyte microchannel is also considered. A modified LBM model is used to handle the numerical instability caused by large diffusivity ratio (10^4) between the gaseous and dissolved oxygen. The oxygen is found to penetrate into the microchannel. The distribution of oxygen and reaction rate suggest the nano- and micro-structures can affect the oxygen transport and electrochemical reaction.

Keywords: Microfluidic fuel cell, Air-breathing cathode, Pore-scale modeling, Lattice Boltzmann method, Mass transport

1. INTRODUCTION

Air-breathing membraneless microfluidic fuel cells (AMMFC) exploit the co-laminar interface of fuel-electrolyte flow to replace the ion-exchange membrane, have been regarded as promising micro power sources.

The Air-breathing cathode is in direct contact with the flowing aqueous electrolyte in the underneath electrolyte channel (CH), instead of the solid ion-exchange membrane, suggesting the oxygen transport can be different from conventional membrane-based micro fuel cells. Due to the recent progress in fuel transport and anode reaction kinetics, the cell performance can be predominated by the air-breathing

cathode at high current density, making it essential to understand the oxygen transport and reaction.

The air-breathing cathode consists of porous nano-structured catalyst layer (CL) and micro-structured gas diffusion layer (GDL). However, previous reports were mainly based on macroscopic continuum models which considered the CL and GDL as homogeneous porous media with isotropic transport properties, failed to capture the oxygen transport and electrochemical reaction characteristics within the nano- and micro-structures.

In this study, for the first time, pore-scale Lattice Boltzmann Method (LBM) models have been developed for the air-breathing cathode in couple with an underneath electrolyte microchannel. The nano- and micro-structures of porous CL and GDL were reconstructed, and the inner oxygen transport and reaction are investigated. Particularly, a modified MRT-LBM was used to handle the numerical instability caused by large diffusivity ratio (10^4) between gaseous and dissolved oxygen.

2. METHDOLOGY

2.1 Computational domain

Two LBM models were developed to investigate the mass transport and reaction in the porous CL and GDL regions, respectively. And the underneath electrolyte channel (CH) was also considered. Fig. 1 shows the computational domain. The models are based on the following assumptions: (1) The system is isothermal and at steady state at room temperature. (2) The oxygen and water vapor are ideal gas with constant properties. (3) The CL is submerged in the aqueous electrolyte. (4) Only diffusion is considered in the porous CL and GDL. (5) The

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electrolyte flow is unidirectional and fully-developed. (6) The aqueous electrolyte couldn't enter the hydrophobic GDL. (7) The electrolyte is deoxidized, which means the concentration of dissolved oxygen is zero at the electrolyte inlet.

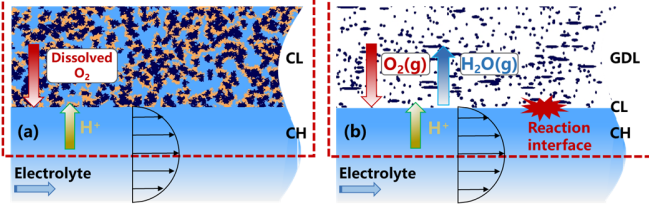


Fig. 1 Computational domain for the (a) CL-CH, and (b) GDL-CL-CH models.

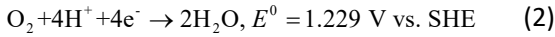
2.2 Theoretical model

(1) CL-CH model

The electrolyte flow in the microchannel:

$$\begin{cases} \nabla \cdot \mathbf{u} = 0 \\ \partial_t \mathbf{u} + \nabla \mathbf{u} \mathbf{u} = -\nabla P + \nu \nabla^2 \mathbf{u} \end{cases} \quad (1)$$

The oxygen reduction reaction (ORR) takes place on the carbon/Pt surface:



The oxygen diffusion in the pores:

$$D_{\text{O}_2,p} \nabla^2 C_{\text{O}_2,p} = 0 \quad (3)$$

The oxygen diffusion in the ionomer:

$$D_{\text{O}_2,e} \nabla^2 C_{\text{O}_2,e} = 0 \quad (4)$$

The oxygen dissolution at the pore-ionomer interface:

$$C_{\text{O}_2,e} = C_{\text{O}_2,p} \frac{RT}{H} \quad (5)$$

$$H = 1.01325 / 10 \times \exp(-666 / T + 14.1) \quad (6)$$

The convection-diffusion transport of oxygen in the electrolyte channel:

$$\mathbf{u} \nabla C_{\text{O}_2,w} - D_{\text{O}_2,w} \nabla^2 C_{\text{O}_2,w} = 0 \quad (7)$$

The ORR rate is determined by the Tafel equation:

$$j = j_{\text{ref}} \left(\frac{C_{\text{O}_2,e}}{C_{\text{O}_2,\text{ref}}} \right)^{\gamma_c} \exp\left(-\frac{\alpha F}{RT} \eta\right) \quad (8)$$

The mass source term S at the carbon/Pt surface is:

$$S = \frac{j}{nF} \quad (9)$$

(2) GDL-CL-CH model

As the CL is much thinner than the GDL, the CL was treated as a reaction interface here. The ORR only produced water vapor, which wouldn't condense in the GDL when its concentration was below saturation.

Water vapor diffusion in the pores:

$$D_{\text{vp},p} \nabla^2 C_{\text{vp},p} = 0 \quad (10)$$

2.3 Lattice Boltzmann method (LBM) framework

(1) CL-CH model

The transport of dissolved oxygen in the CL and CH can be governed by the simple D2Q5 BGK-LBM model. The evolution equation of density distribution function is:

$$g_{i,\sigma}(\mathbf{x} + \mathbf{e}_i \delta_t, t + \delta_t) - g_{i,\sigma}(\mathbf{x}, t) = -\frac{1}{\tau_\sigma} (g_{i,\sigma}(\mathbf{x}, t) - g_{i,\sigma}^{\text{eq}}(\mathbf{x}, t)) + J_{i,\sigma} \delta_t S_\sigma \quad (11)$$

The equilibrium distribution function is:

$$g_{i,\sigma}^{\text{eq}} = C_\sigma \left(J_i + K_i \frac{\mathbf{e}_i \cdot \mathbf{u}}{c_s^2} \right) \quad (12)$$

$$J_i = \begin{cases} J_0 & i = 0 \\ (1 - J_0)/4 & i = 1, 2, 3, 4 \end{cases} \quad (13)$$

where subscript σ denotes the σ th component. The diffusivity is given by:

$$D_\sigma = \delta_t c_s^2 C_\sigma (1 - J_0) (\tau_\sigma - 1/2) \quad (14)$$

(2) GDL-CL-CH model

Gaseous oxygen was considered in the GDL, while dissolved oxygen in the CL and CH. Since the diffusivity ratio of gaseous and dissolved oxygen is about 4 orders of magnitude, numerical instability and divergence occurred in the simple BGK-LBM and normal MRT-LBM models. The BGK-LBM model works in a limited range of diffusivities, a small diffusivity ratio may lead to numerical instability. Although J_0 can be adjusted to increase the relaxation time τ , J_0 must be very close to 1 in order to make τ slightly larger than 0.5, which would also lead to divergence. In addition, the normal MRT-LBM requires the relaxation rate between (0, 2), also failed to handle this large diffusivity ratio. Therefore, the modified D2Q9 MRT-LBM model proposed by Meng^[1] was adopted, where an adjustable Parameter B was added to modify the diffusivity.

The evolution equation of the concentration distribution function for convection-diffusion equation is:

$$g(\mathbf{x} + \mathbf{c}_i \delta_t, t + \delta_t) - g(\mathbf{x}, t) = -(\mathbf{M}^{-1} \mathbf{S} \mathbf{M})_{ij} [g(\mathbf{x}, t) - g^{\text{eq}}(\mathbf{x}, t)] + \delta_t \bar{R}_i \quad (15)$$

The equilibrium distribution function is:

$$g_i^{\text{eq}} = \omega_i C \left[1 + \frac{c_i \cdot \mathbf{u}}{c_s^2} + \frac{(c_i \cdot \mathbf{u})^2}{2c_s^4} - \frac{u^2}{2c_s^2} \right] + \omega_i B \delta_i (c_i \cdot \nabla C) \quad (16)$$

Similarly, the evolution equation in moment space is:

$$g(\mathbf{x} + \mathbf{c}_i \delta_t, t + \delta_t) - g(\mathbf{x}, t) = -\mathbf{M}^{-1} \mathbf{S} \left[\hat{g}(\mathbf{x}, t) - \hat{g}^{\text{eq}}(\mathbf{x}, t) \right] + \mathbf{M}^{-1} \left[\delta_t \hat{R} + \frac{\delta_t^2}{2} \partial_i \hat{R} \right] \quad (17)$$

The diffusivity is written as:

$$D_{xx} = c_8^2 (1/\lambda_3' - 1/2 - B) \delta_i, \quad D_{yy} = c_8^2 (1/\lambda_5' - 1/2 - B) \delta_i \quad (18)$$

2.4 Boundary conditions & parameters

The boundary conditions and geometric parameters for both models are shown in Fig. 2. The given concentration condition was achieved by the non-

equilibrium extrapolation method. Non-slip boundary was obtained by using the bounce-back boundary condition. The surface reaction was treated as Zhou et al^[2]. The parameters are listed in Table 1.

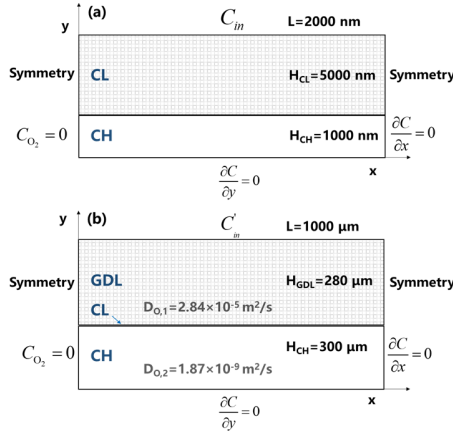


Fig. 2 Boundary conditions and geometric parameters for the (a) CL-CH and (b) GDL-CL-CH models.

Table 1 Parameters used in the LBM models.

Parameter	Value
Universal gas constant, R	$8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
Faraday's constant, F	96485 C mol^{-1}
Reference oxygen concentration, $C_{O,ref}$	8.6 mM
Oxygen mole fraction, X_{O_2}	0.21
Oxygen diffusivity in ionomer, $D_{O_2,e}$	$10^{-10} \times (0.1543(T-273) - 1.65) \text{ m}^2 \text{ s}^{-1}$
Water vapor diffusivity, D_{vp}	$3.55 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$
Cathode transfer coefficient, α	1.0
ORR reaction order, γ_c	1
Reference exchange current density j_{ref}	$0.04222 \times \exp \left[\frac{73200}{R} \times \left(\frac{1}{353} - \frac{1}{T} \right) \right]$

2.5 Porous media reconstruction

The 3D structure of CL and GDL were reconstructed using the QSGS method^[3] at 10 nm/pixel resolution, and the stochastic method as Schladitz^[4] at 1 μm/pixel resolution, respectively, as shown in Fig. 3. Vertical-sections were used in the computational domains.

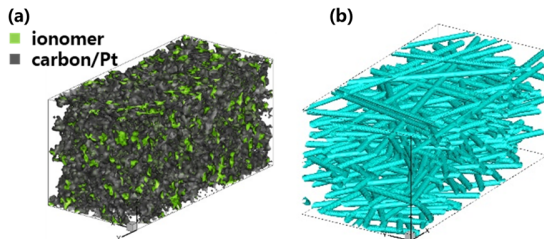


Fig. 3 Reconstructed CL and GDL.

3. RESULTS AND DISCUSSION

3.1 Model validation

Both models were validated by the convection-diffusion problem^[5]:

$$\mathbf{u} \nabla C - D \nabla^2 C = KC \quad (19)$$

where K is the reaction rate.

Here only shows the validation for the modified D2Q9 MRT-LBM model. Fig. 4 shows that the LBM results agreed well with the analytical solution with different Parameter B , indicating that the developed model can properly predict the flow and mass transport. In addition, it also confirms that the Parameter B would not affect the model accuracy.

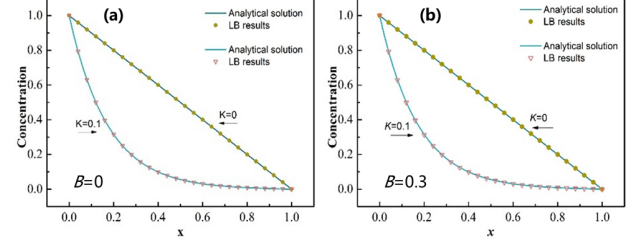


Fig. 4 Comparison of the LBM results and analytical solution with different reaction rates and adjustable parameter B .

3.2 Mass transport in the CL (CL-CH model)

Fig. 5a shows the concentration distribution of dissolved oxygen in the CL and electrolyte channel.

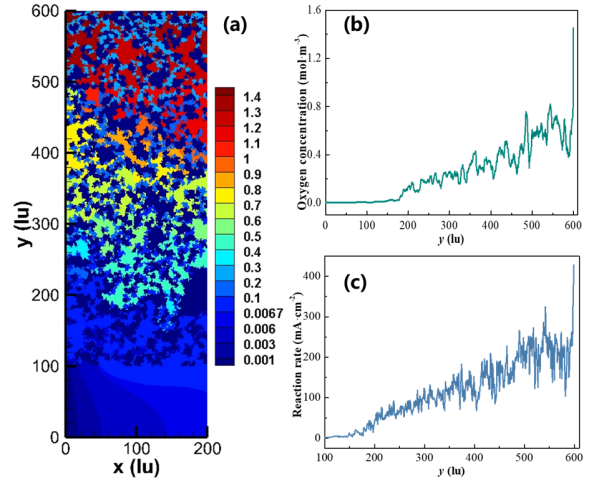


Fig. 5 (a, b) Oxygen concentration distribution, (c) averaged reaction rate along y direction at the porosity of 0.4.

As shown in Fig. 5a, the oxygen concentration gradually decreases from the CL top to the electrolyte channel because of the ORR consumption. The oxygen distribution is highly non-uniform as affected by the CL nano-structure. Interestingly, it's noted that ionomer hinders the oxygen transfer as indicated by the ionomer dots (with low concentration), mainly due to the oxygen diffusivity is much lower in the ionomer as compared to the pores. Together with the fact that the proton conduction is higher in aqueous electrolyte than the ionomer, the ionomer is found to add extra transfer resistance, and its content should be low. Moreover, the dissolved oxygen can penetrate into the electrolyte channel. However, since the concentration of dissolved

oxygen is low, and the cell is typically operated at high Peclet number (>2000), it's unlikely to induce oxidant crossover. To be quantitative, Fig. 5b suggests that oxygen concentration drops in the CL, and diminishes to nearly zero in the electrolyte channel. As a result, the averaged reaction rate shows similar trend in Fig. 5c, in good accordance with the oxygen distribution.

3.3 Mass transport in the air-breathing cathode (GDL-CL-CH model)

For the GDL-CL-CH model, neither the simple BGK-LBM nor normal MRT-LBM models can handle the large diffusivity ratio (10^4) between gaseous and dissolved oxygen. The modified MRT-LBM model successfully overcame the numerical challenges. Fig. 6 depicts the distribution of oxygen and water vapor concentration. As consumed by the ORR in the CL, the oxygen concentration gradually decreases along the -y direction, as shown in Fig. 6a. The water vapor transfers in the counter direction (see Fig. 6b). Both the oxygen and vapor concentration are affected by the GDL microstructure. The oxygen can penetrate into the electrolyte channel. And it's interesting to note that the flowing electrolyte can affect the oxygen and water vapor distribution. The oxygen concentration in the GDL is lower near inlet, because the local oxygen transfer to the channel is enhanced by the deoxidized electrolyte. By contract, the local oxygen concentration in the GDL at downstream is higher, inducing higher local electrochemical reaction rate and higher local vapor concentration (see Fig. 6b).

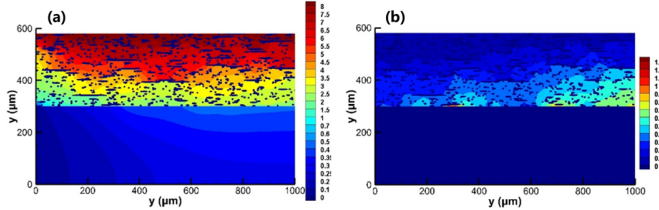


Fig. 6 Distribution of the (a) oxygen and (b) water vapor at the porosity of 0.76 and overpotential of 0.48 V.

To be quantitative, the averaged oxygen and water vapor concentration along y direction are shown in Fig. 7a. The counter transfer of oxygen and water vapor induces inversed concentration distribution. An oxygen concentration jump at the GDL/CH interface ($y=300 \mu\text{m}$) is observed, caused by the dissolution of gaseous oxygen into the electrolyte. As the local oxygen concentration is lower near the electrolyte inlet, the local reaction rate is also lower there, but rapidly increases and reaches plateau at downstream (see Fig. 7b), suggesting the air-breathing cathode can be affected by the entrance effect from flowing electrolyte, but the influence is limited.

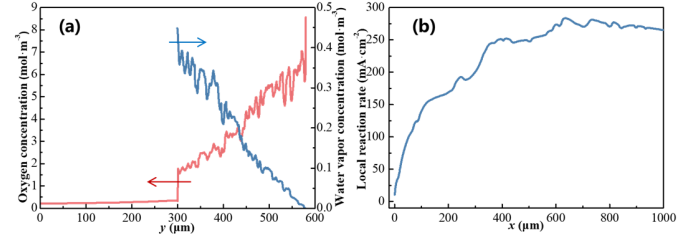


Fig. 7 (a) Averaged oxygen and water vapor concentration along y direction, and (b) local reaction rate distribution along x direction at $\varepsilon=0.76$.

4. CONCLUSIONS

Two sets of LBM models were developed to investigate the oxygen transport and electrochemical reaction in the air-breathing cathode with an underneath electrolyte channel for AMFCs. A modified MRT-LBM model was used and successfully handled the large diffusivity ratio (10^4) between gaseous and dissolved oxygen. The oxygen was found to penetrate into the electrolyte channel. The distribution of oxygen and reaction rate suggested that the CL and GDL structures played a significant role in oxygen transport. The porous structure induced non-uniform distribution of local reaction rate.

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