Numerical investigation of coupled mass transport and electrochemical reactions in porous SOFC anode microstructure

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Abstract: To investigate the coupled mass transport and electrochemical reactions in porous anode of solid oxide fuel cell (SOFC), a pore scale model employing the multi-component Lattice Boltzmann (LB) model for mass transport in the pore phase and a six-step reaction for electrochemical reactions at three phase boundaries is established. This model is superior in including the effects of heterogeneity of anode microstructure, making it qualified to quantitatively simulate local distributions of various physical fields without dependence on any statistical parameters. The characteristics of coupled interactions of mass transport and electrochemical reaction are analyzed visually by comparing H_2 molar fraction distributions within the pore phase of the anode. It is demonstrated that, for anodes with different heterogeneous microstructures but with same porosity and tortuosity factor, the mass transport and electrochemical reaction process can be quite different, even under the same boundary conditions. Meanwhile, based on the same anode microstructure, species molar fraction varies similarly along the primary transport direction, even though the operating conditions are quite different. Besides, the influences of fuel composition, activation overpotential and operating temperature are also discussed at pore scale by the present model.

Keywords: Solid oxide fuel cell; Heterogeneous anode microstructure; Electrochemical kinetics, Coupled interaction; Lattice Boltzmann method

1. Introduction

Electrodes of solid oxide fuel cells (SOFCs) play a crucial role in determining the main transport processes and reactions[1]. Therefore, as a technological barrier of the SOFC commercialization, the development of durable electrodes with high performance has attracted lots of attention[2,3]. To achieve this goal, a fully understanding of the transport and reactions in SOFC electrodes is indispensable[4,5]. Numerical simulation approach is considered as a convenient tool to efficiently predict the transport processes in SOFC electrodes. Note that the electrodes are usually porous microstructures with submicron-sized pores, the heterogeneity of which determines both the pathway of irregular pores and the positions of electrochemically active sites. Therefore, to accurately simulate the transport and reactions in electrodes, both the micro-scale effect and the heterogeneity of microstructure should be taken into consideration.

Most of previous numerical works on SOFC electrodes assume that the porous electrode is homogenous[6,7]. In such models, the effects of solid skeleton on the fluid flow in pores are introduced by an additional external force, and some macroscopic statistical parameters, such as porosity and tortuosity factor, are involved to characterize different geometries of porous electrodes. These parameters can be obtained by in-situ measurements or are treated as fitting parameters, which introduce indispensable errors[8]. More importantly, different microstructures with the same porosity or tortuosity factor are likely to have different hydraulic characteristics, thus macroscopic parameters might fail in describing the relevant phenomena at micro-scale[9]. To compensate the drawbacks resulted from the assumption that the porous electrode is homogeneous; the pore scale numerical method is involved to effectively describe the heterogeneity of electrode microstructure. On the other hand, to consider the micro-scale

effect, Lattice Boltzmann (LB) method is qualified because it is derived from kinetic theory[10]. In addition, due to the simple bounce-back rule for no-slip boundary condition, LB method is with great potential in simulating fluid flows in complex geometries, such as porous media. Consequently, increasing numerical investigations on SOFC electrode performance employ pore scale LB method[8,10-23].

Chiu et al.[11,14-16] employed multi-component LB model proposed by McCracken and Abraham[24] to study the mass transport and reactions in SOFC anode by simplifying the anode as pore/solid domain, without distinguishing the electronic phase and ionic phase within the solid phase. Even if such simplification of the anode microstructure is employed due to the limitation of experimental techniques, the numerical approach using LB model by Chiu et al. is still reasonable to predict the anode performance. However, the employed multi-component LB model is restricted to simulating mixtures with molecular weight ratio below 9[24]. Moreover, they used porosity to characterize different anode microstructures and studied the effects of porosity on mass transport and reactions based on six phenomenological anode microstructures with different porosity and tortuosity factor[11,14], which is similar to the traditional SOFC modeling works assuming that the electrode is homogeneous. Notably, although they adopted the pore scale model, they did not consider the effect of the heterogeneity of anode microstructure quantitatively. Shikazono et al.[13,17-19,21,22] developed a pore scale LB model for the transport and reactions in anode with distinguishing the electronic phase and ionic phase within the solid phase. Recently, they further considered the anode microstructure evolution[21] and the anode degradation during redox cycling[22]. However, the multi-component LB model used in their works is still dependent on macroscopic

statistical parameters including porosity and tortuosity factor. In summary, current pore scale LB modeling works of SOFC electrodes is limited by the drawbacks of the employed multi-component LB models, and the heterogeneity of electrode microstructure has not been investigated quantitatively.

In our recent work[3], a pore scale LB model has been developed to study the multi-component mass transport in the porous anode of an SOFC, which is independent on any macroscopic statistical parameters. This model is capable of simulating mixture flow with molecular weight ratio much larger than 9, which is the main limitation of previous models[24]; consequently, it can meet the fuel flexibility of SOFC. Then, another pore scale LB model is further established to study the carbon deposition characteristics in the anode, in which the three phase boundaries (TPBs) are assumed at anode/electrolyte interfaces for simplicity[5]. In the present work, to investigate the coupled mass transport and electrochemical reaction processes in the anode microstructure, a pore scale LB model is further developed by integrating the detailed six-step reaction kinetics for modeling the electrochemical reactions into mass transport model developed in Ref.[3]. The coupled interactions of the mass transport and electrochemical reactions are involved at TPBs, which are extended to the pore phase/solid phase interfaces within the anode instead of the anode/electrolyte interfaces in Refs.[3,5]. Besides, the effects of the heterogeneity of anode microstructure on the coupled mass transport and electrochemical reactions are investigated thoroughly and quantitatively. Finally, the effects of fuel composition, activation overpotential and operating temperature are analyzed in terms of local molar fraction distribution of each species in irregular pores, current density and mass transport-related losses.

2. Numerical approach

Fig. 1(a) depicts the mass transport and electrochemical reactions in a Ni/YSZ anode. Reactive gas (H_2) from the fuel channel diffuses through the pores and is oxidized by the oxygen ion (O^{2-}) travelling through the ionic conductors from the electrolyte; as a result, steam (H_2O) and electron (e^-) are formed. Then, H_2O diffuses to the fuel channel through the pores, and e^- travels through the electronic conductors to the current collector to meet the external electricity load. The electrochemical reaction can be expressed by:

which takes place at TPBs, i.e., the interfaces among electronic conductor phase (Ni), ionic conductor phase (YSZ) and pore phase. To assure the electrochemical reaction to occur, the above three phases must have continuous pathways to current collector, electrolyte and fuel channel, respectively.

2.1. Detailed electrochemical kinetics at TPBs

As shown in Fig. 1(b), the six-step electrochemical kinetics initially proposed by Bieberle et al.[25] is adopted in the present study, which employs more complete pathway and detailed reaction steps for describing the hydrogen oxidation process. The adsorption/desorption of $H_2^{(g)}$ and $H_2O^{(g)}$ (1) occur at Ni surfaces. All intermediates (2) taking part in surface reactions diffuse and propagate through a number of reaction pathways on Ni surfaces (3). An interstitial O^{2-} spills out of YSZ onto Ni surface near TPBs and releases two electrons (4). A vacancy occurs after the spillover and is refilled by ionic transport (5). The corresponding

Langmuir-Hinshelwood type surface reaction mechanisms at Ni surface are as follows.

Charge transfer reaction:

Surface reactions:

Adsorption/desorption reactions:

where $\text{O}_\text{O}^\text{x}$ is oxygen ion interstitial, $[\]_\text{Ni}$ is vacancy at Ni surface, i_Ni represents intermediate at Ni surface, V_O is oxygen ion vacancy and $k_{\pm n}$ is reaction rate constant.

According to the above six-step reaction mechanism, i.e., Reactions (2)–(7), the following rate equations are obtained:

$$\begin{cases} \frac{\partial \theta_\text{O}}{\partial t} = k_1\theta_\text{Ni} - k_{-1}\theta_\text{O} - k_2\theta_\text{O}\theta_\text{H} + k_{-2}\theta_\text{OH}\theta_\text{Ni} - k_3\theta_\text{O}\theta_\text{H}_2\text{O} + k_{-3}\theta_\text{OH}^2 \\ \frac{\partial \theta_\text{H}}{\partial t} = -k_2\theta_\text{O}\theta_\text{H} + k_{-2}\theta_\text{OH}\theta_\text{Ni} - k_4\theta_\text{OH}\theta_\text{H} + k_{-4}\theta_\text{H}_2\text{O}\theta_\text{Ni} + 2k_6\theta_\text{Ni}^2 - 2k_{-6}\theta_\text{H}^2 \\ \frac{\partial \theta_\text{OH}}{\partial t} = k_2\theta_\text{O}\theta_\text{H} - k_{-2}\theta_\text{OH}\theta_\text{Ni} + 2k_3\theta_\text{O}\theta_\text{H}_2\text{O} - 2k_{-3}\theta_\text{OH}^2 - k_4\theta_\text{OH}\theta_\text{H} + k_{-4}\theta_\text{H}_2\text{O}\theta_\text{Ni} \\ \frac{\partial \theta_\text{H}_2\text{O}}{\partial t} = -k_3\theta_\text{O}\theta_\text{H}_2\text{O} + k_{-3}\theta_\text{OH}^2 + k_4\theta_\text{OH}\theta_\text{H} - k_{-4}\theta_\text{H}_2\text{O}\theta_\text{Ni} + k_5\theta_\text{Ni} - k_{-5}\theta_\text{H}_2\text{O} \\ \theta_\text{O} + \theta_\text{H} + \theta_\text{OH} + \theta_\text{H}_2\text{O} + \theta_\text{Ni} = 1 \end{cases} \quad (8)$$

where θ_i is the surface coverage of species i calculated as the fraction of available surface sites covered by this surface species. The relevant reaction rate constants are listed in Table1. Since Reaction (6) and Reaction (7) involve $\text{H}_2^{(\text{g})}$ and $\text{H}_2\text{O}^{(\text{g})}$, k_5 and k_6 are dependent on partial

pressures. According to Reaction (2), $k_{\pm 1}$ is associated with oxygen vacancies and ion concentrations.

k_5 and k_6 are related to the gas adsorption process. Note that they are key factors to combine electrochemical kinetics with mass transport. Based on the gas kinetic theory, k_5 and k_6 can be calculated as:

$$k_5, k_6 = 2.6 \times 10^{24} \frac{p_i}{\sqrt{M_i T}} \frac{s_i^0}{N_0} \quad (9)$$

where p_i is the partial pressure of species i , M_i is the molecular weight, T is the temperature, s_i^0 is the initial sticking coefficient and N_0 is the total number of active sites.

According to charge balance, we have:

$$i = 2F \frac{N_0}{N_A} (k_1 \theta_{Ni} - k_{-1} \theta_O) \quad (10)$$

with

$$k_1 = k_1^0 \exp\left(\beta \frac{zF}{RT} \eta_{act}\right) \quad (11)$$

$$k_{-1} = k_{-1}^0 \exp\left(-(1-\beta) \frac{zF}{RT} \eta_{act}\right) \quad (12)$$

where i is the faradaic current density, N_A is Avogadro's number, $k_{\pm 1}^0$ is equilibrium reaction rate constant at $\eta_{act} = 0$ V, β is the charge transfer coefficient which is usually set as 0.5 and z is the number of electrons per hydrogen. Since the faradaic current density is zero at $\eta_{act} = 0$ V, the following equation can be obtained according to Eq.(10):

$$k_1^0 \theta_{Ni}^0 = k_{-1}^0 \theta_O^0 \quad (13)$$

where θ_i^0 represents the equilibrium coverage at $\eta_{act} = 0$ V. Since the equilibrium coverage is characteristic thermodynamic property of the electrochemical system, k_1^0/k_{-1}^0 is a fixed value

as well. $k_{\pm 1}^0$ can be expressed as follows[26]:

$$k_1^0 = \frac{N_A i_0}{2FN_0 \theta_{Ni}^0} \quad (14)$$

$$k_{-1}^0 = \frac{N_A i_0}{2FN_0 \theta_O^0} \quad (15)$$

where i_0 denotes the reference exchange current density. The charge transfer reaction can be neglected at $\eta_{act} = 0$ V, thus the equilibrium coverage can be obtained by solving Eq.(8) with setting $k_{\pm 1}^0$ as 0.

The cumulative current density is defined as a function of the position along the primary transport direction as:

$$i_{cu}(X) = \frac{1}{H} \int \int_{(s)} i(X, Z) ds \quad (16)$$

where H is the length of computational domain. Thus, the average current density of the whole computational domain is:

$$i_{av} = i_{cu}(0) \quad (17)$$

The present electrochemical kinetics described by the rate equations contains different processes with remarkably different time scales; as a result, the differential equations (8) are a stiff system of equations, which is solved by Treanor method in the present study.

2.2. Lattice Boltzmann model for mass transport in pore phase

Grew et al.[14] employed the LB model proposed by McCracken and Abraham[24] to describe the mass transport in pore phase, in which the interpolation scheme is adopted for the streaming. This model is limited to mixtures with molecular weight ratio below 9 owing to the numerical diffusion resulted from the interpolation scheme, which is pointed out by

McCracken and Abraham[24]. In the present paper, we employ the multi-component LB model proposed in our recent work[3] to study the mass transport in porous anode. In our LB model, we adopt the finite-difference scheme to describe the streaming and use the non-equilibrium extrapolation method[27] combined with the mass modified scheme[28] to deal with the outlet boundary. It is verified that our model can be used for multi-component fluids with larger molecular weight ratios and is with higher accuracy for the mass conservation between inflow and outflow. The influence of porous media is involved by the irregular inner boundary instead of additional force adopted in the traditional macroscopic numerical technology, thus it is independent on any structure statistical parameters of the porous media. To obtain the detailed geometry of the porous anode microstructure as the input condition of our pore scale model, we get the SEM image of the cross section of an SOFC anode. We only characterize the pore phase and solid phase of the SEM image without distinguishing the electronic phase and ionic phase within the solid phase, which is a common simplification in relevant publications[10,23]. The grayscale of each pixel within the SEM image is obtained and a threshold of grayscale is set to get the binary image from this SEM image. For the domain with the greyscale below the threshold, we set the greyscale to 0 (black) representing the solid phase (i.e., the mixture of electronic and ionic conductors); for the remaining, we set the greyscale to 255 (white) representing the pore phase. A two-dimensional array distinguishing the solid phase, pore phase and their interface (i.e., inner boundary) is defined, which is used as the geometrical input condition for the pore scale LB model.

The concentration overpotential associated with the mass transport is described as:

$$\eta_{con} = -\frac{RT}{2F} \ln \left(\frac{y_{H_2,A/E} y_{H_2O,bulk}}{y_{H_2,bulk} y_{H_2O,A/E}} \right) \quad (18)$$

where bulk and A/E denote fuel channel/anode interface and anode/electrolyte interface, respectively.

2.3. Lattice Boltzmann model for the coupled mass transport and electrochemical reaction

To couple the electrochemical kinetics into the multi-component LB model, TPBs need to be confirmed first. Since the present work can only distinguish the solid phase and pore phase, we do not consider the actual transport paths of electrons and ions and assume that all the inner boundaries (interfaces of pore phases and solid phases) are TPBs (i.e., electrochemically active sites), which is a common assumption in previous modeling works[23,29]. At each TPB in every iteration step, the unknown reaction rate constants k_5 , k_6 and $k_{\pm 1}$ are calculated according to local partial pressure and overpotential. Then, the surface coverage of each intermediate can be obtained by solving differential equations (8). Based on Eq.(10), we can get the faradaic current density at each TPB and the molar flux of H_2 and H_2O by Faraday's law as:

$$\mathbf{J}_{H_2} \cdot \mathbf{n} = -\mathbf{J}_{H_2O} \cdot \mathbf{n} = \frac{i}{2F} \quad (19)$$

where $\mathbf{n}$ is the unit normal vector. As the bridge between mass transport model and electrochemical model, the updated molar flux of each species at TPBs serves as the inner boundary of the flow in the pore phase and affects the mass transport process in the next iteration step. In the multi-component LB model, the implementation of Neumann boundary at the interface between the solid phase and pore phase is described in our previous work[3].

2.4. Boundary conditions

As illustrated in Fig. 1(a), the molar fraction of each species and the total concentration are specified at the fuel channel/anode interface. Since only oxygen ion can travel through the electrolyte, all the gas species is impermeable at the anode/electrolyte interface. Periodic boundaries are adopted at the top and bottom of the computational domain. Moreover, all the inner boundaries are assumed to be electrochemically active.

3. Results and discussion

3.1. Model validation

The multi-component LB model for mass transport in the pore phase has already been validated in our previous study[3,5], thus the present paper only examines the accuracy of the electrochemical model and the LB model for coupled mass transport and electrochemical reaction. Firstly, the species surface coverages under different activation overpotentials are employed to verify the implementation of the electrochemical kinetics. The verification parameters are: $T = 973$ K, $p = 101325$ Pa, $p_{H_2} = 2.5 \times 10^4$ Pa, $p_{H_2O} = 40$ Pa, $N_0 = 10^{19} \text{ m}^{-2}$, $i_0 = 420 \text{ A} \cdot \text{m}^{-2}$, $s_{H_2}^0 = 0.4$ and $s_{H_2O}^0 = 1.0$. As shown in Fig. 2, the forward reaction rate of charge transfer reaction increases as activation overpotential increases, resulting in the increase of O_{Ni} . Consequently, the production of OH_{Ni} from Reaction (3) and Reaction (4) increases. Meanwhile, Reaction (5) serves as the rate-limiting step of the whole system, since its reaction rate is very low. Thus, the consumption of OH_{Ni} is much smaller than its production, which leads to the increase of θ_{OH} as activation overpotential rises. As increasing number of active sites are covered by OH, both θ_H and θ_{Ni} fall down. When the overpotential is increased to 0.4 V,

almost all the active sites are covered by OH and the whole reaction system becomes saturated. It is indicated by Fig. 2 that the results from our model agree well with that given by Bessler[26], which assures the reliability and accuracy of both the electrochemical model and the implementation of Treanor method for solving the stiff differential equations.

To validate the LB model for coupled mass transport and electrochemical reaction in the porous anode, the microstructure of a subsection of XCT reconstruction for a real SOFC anode in Ref.[29] is employed. Other simulation parameters in Ref.[29] for validation include $\eta_{\text{act}} = 0.35 \text{ V}$ and $y_{\text{H}_2, \text{inlet}} = 0.15$. Because H_2 molar fraction changes slightly along the primary transport direction (i.e., x-axis) in such case, the normalized molar fraction of H_2 is employed as:

$$y_{\text{H}_2}^* (\text{X}, \text{Z}) = \frac{y_{\text{H}_2} (\text{X}, \text{Z}) - y_{\text{H}_2, \text{min}}}{y_{\text{H}_2, \text{inlet}} - y_{\text{H}_2, \text{min}}} \quad (20)$$

As shown in Fig. 3, $y_{\text{H}_2}^* (\text{X}, \text{Z})$ decreases gradually along the primary transport direction, because H_2 is consumed at TPBs due to the electrochemical reaction. Meanwhile, there are more electrochemically active sites distributed in the upper half of the microstructure than that in the bottom half, thus H_2 molar fraction decreases more sharply in the upper half. By comparing our results for the distribution of $y_{\text{H}_2}^* (\text{X}, \text{Z})$ with that by Chiu et al.[29], Fig. 3 provides the successful validation of the present LB model for coupled mass transport and electrochemical reaction.

3.2. Coupled interaction of mass transport and electrochemical reaction

3.2.1. Effect of anode microstructure

In this work, the anode microstructure (Fig. 4a) with the porosity of 43% is reconstituted

by three-dimensional particle element method[30] and its cross-section is obtained as the geometry basis of the standard case. Other simulation parameters under standard case are set as follows: $T = 1073$ K, $p = 101325$ Pa, $y_{\text{H}_2, \text{inlet}} = 97\%$, $y_{\text{H}_2\text{O}, \text{inlet}} = 3\%$, $\eta_{\text{act}} = 0.4$ V, $l_a = 750$ μm .

We adopt two different anode microstructures: one is the microstructure of the standard case represented as microstructure A (Fig. 4a) and the other is from Ref.[11] expressed as microstructure B (Fig. 4c). However, these two different anode microstructures are with the same porosity ($\varepsilon = 43\%$) and tortuosity factor ($\tau^2 = 3.734$), which are typical geometrical statistical values for real SOFC anodes. In this section, we aim at two purposes: (i) based on microstructure A, we simulate the mass transport as well as coupled mass transport and electrochemical reaction to study the coupled interaction of the two processes; (ii) we simulate the coupled mass transport and electrochemical reaction in microstructures A and B to reveal the effect of anode microstructure on the coupled interaction of the two processes. The following cases are involved:

CASE1: Microstructure A; mass transport (constant molar flux of H_2 and H_2O is applied at TPBs, the value of which is calculated by the average of all the local faradaic current densities in CASE2);

CASE2: Microstructure A; coupled mass transport and electrochemical reaction;

CASE3: Microstructure B; coupled mass transport and electrochemical reaction.

Fig. 4 displays the effect of anode microstructure on mass transport and electrochemical reaction. Because H_2 is consumed at TPBs, its molar fraction presents a decreasing tendency. In CASE2, in the upstream region, the local faradaic current density is smaller than its average value, thus the H_2 consumption is smaller than that in CASE1, which explains why H_2 molar

fraction in CASE2 is larger than that in CASE1 in this area. In the downstream region, H_2 continues to be consumed. However, its molar fraction in CASE2 is larger than that in CASE1 in the whole computational domain, which reflects the coupling of species field (i.e., mass transport) and local faradaic current density (i.e., electrochemical reaction). Meanwhile, it is clearly shown in Fig. 4(d) that the difference between the maximum and the minimum of H_2 molar fraction varies similarly along the primary transport direction in CASE1 and CASE2, since they are based on the same microstructure.

In Fig. 4, the solid obstacles in microstructure B distribute more densely in the region of $0.4 < X^* < 0.8$ and $0.2 < Z^* < 0.8$, resulting in more TPBs, thus larger amount of H_2 is consumed. Therefore, in the whole downstream region, H_2 molar fraction in microstructure B is smaller than that in microstructure A. Meanwhile, in microstructure B, the difference between the maximum and the minimum is relatively larger at $0.4 < X^* < 0.8$ and $0.2 < Z^* < 0.8$. However, in microstructure A, the solid obstacles distribute more uniformly; as a result, the difference of the maximum and the minimum is smaller than that in microstructure B. Fig. 4(e) depicts the changing tendency of the cumulative current density along the primary transport direction in CASE2 and CASE3. The fuel channel/anode interface ($X^* = 0$) is connected with the current collector, thus the cumulative current density at $X^* = 0$ can be considered as the average current density of the whole anode. Because the H_2 molar fraction is larger in CASE2, the cumulative current density is relatively smaller according to the electrochemical kinetics. Notably, the effect of the heterogeneity of anode microstructure is presented clearly in Fig. 4(b)–(e).

As depicted in Fig. 4, for two different microstructures with the same porosity and

tortuosity factor, remarkably different distributions of species molar fraction and current density can appear even under the same boundary conditions, which can result in different macroscopic anode performance including average molar fraction of each species and average current density along the primary transport direction. Notably, if the traditional numerical method based on the assumption of homogenous porous media is employed, the same macroscopic anode performance should be predicted for two anode microstructures with the same porosity and tortuosity factor under the same boundary condition. Therefore, the heterogeneity of anode microstructure is with indispensable effect on the coupled interaction between mass transport and electrochemical reaction. The traditional numerical technology assuming that the porous media is homogenous cannot predict the anode performance difference resulted from the microstructure heterogeneity, while the pore scale LB model developed in this study shows this ability.

3.2.2. *Effect of fuel composition*

The molar fraction of H_2 at the inlet is served as the parameter representing the fuel composition. Fig. 5(a) and (b) are curves reflecting the effect of H_2 molar fraction at the inlet on mass transport and electrochemical reaction, in terms of H_2 molar fraction along the primary transport direction, average current density and concentration overpotential. As presented in Fig. 5(a), under different inlet H_2 molar fractions, the maximum, minimum and average values of H_2 molar fraction along the primary transport direction present similar decreasing tendency. Meanwhile, the differences between $y_{H_2,out}$ and $y_{H_2,inlet}$ are all 0.017 when $y_{H_2,inlet} = 0.17, 0.57$ and 0.97. Furthermore, the difference between the maximum and the minimum of H_2 molar fraction changes similarly as well. The abovementioned phenomena can be traced back to the

fact that all these three cases are based on the same microstructure. As inlet H_2 molar fraction increases, concentration overpotential first decreases and then increases. Compared with Grew et al. who investigated the effects of fuel composition at $0.001 < y_{H_2, \text{inlet}} < 0.333$ and concluded that current density increases monotonically as $y_{H_2, \text{inlet}}$ increases[14], we investigate the effects of fuel composition at $0.17 < y_{H_2, \text{inlet}} < 0.97$, which covers the majority of possible inlet H_2 molar fractions of SOFC. We find that the average current density presents an increasing tendency at $0.17 < y_{H_2, \text{inlet}} < 0.37$ and a decreasing tendency at $0.37 < y_{H_2, \text{inlet}} < 0.97$. As expected, the changing trend of concentration overpotential is in accordance with the prediction from our previous study[3], which verifies the reliability of the present model further.

3.2.3. *Effect of activation overpotential*

Fig. 6 presents the effect of activation overpotential on mass transport and electrochemical reaction. As expected, the difference between the maximum and the minimum of H_2 molar fraction varies similarly along the primary transport direction, since they are based on the same anode microstructure. When the activation overpotential increases, k_1 increases and k_2 decreases according to Eq.(11) and Eq.(12), respectively; as a result, the local faradaic current density increases according to Eq.(10). Therefore, the cumulative current density shows an increasing trend. Meanwhile, a larger local faradaic current density means larger H_2 consumption, which is the reason for that H_2 molar fraction decreases as overpotential increases (Fig. 6(a)). Consequently, the concentration overpotential rises continuously according to Eq.(18). In the predictions given by Grew et al.[14], the change rate of H_2 molar

fraction between outlet and inlet is only 0.039% when $\eta_{\text{act}} = 0.5$ and $\varepsilon = 0.45$. Note that the computational error of the LB model employed by Grew et al. can reach 2% [31]. In contrast, it is clear from Fig. 6 that the change rate of H_2 molar fraction in our work is 2% when $\eta_{\text{act}} = 0.5$ and $\varepsilon = 0.43$, and the computational error is only 0.014% for our present LB model [3].

3.2.4. *Effect of operating temperature*

As displayed in Fig. 7(a), with increasing operating temperature, H_2 molar fraction decreases. Meanwhile, k_1 decreases and k_{-1} increases with increasing operating temperature, which leads to the decrease of local faradaic current density and cumulative current density (Fig. 7(b)). Accordingly, the increase of operating temperature and decrease of H_2 molar fraction cause the increase of concentration overpotential, which is consistent with the results given by Ref.[6] and can serve as a further validation of the present LB model for coupled mass transport and electrochemical reactions.

4. Conclusion

The irregular anode microstructure determines the pathway of pores and the positions of TPBs (i.e., electrochemically active sites), which are therefore key factors affecting the mass transport and electrochemical reaction processes in porous SOFC anode. In this paper, a six-step electrochemical kinetics is integrated with a pore scale multi-component LB model for the simulation of the coupled mass transport and electrochemical reaction processes in a porous SOFC anode. By this model, we thoroughly investigate the effects of the anode microstructure heterogeneity on the coupled interactions between the mass transport and electrochemical

reactions. It is numerically demonstrated that, different characteristics of coupled mass transport and electrochemical reactions can appear in two porous anodes with different microstructures but with same macroscopic statistical parameters. Notably, the effects of the heterogeneity of porous anode microstructure on anode performance are indispensable. Under the same anode microstructure, similar changing tendency of species molar fraction along the primary transport direction is observed for largely different inlet H_2 molar fractions and activation overpotentials, which further verifies the crucial role of microstructure heterogeneity. When the inlet H_2 molar fraction is relatively small, its increasing tendency has a positive effect on mass transport-related losses, whereas a negative effect is observed at relatively large values of the inlet H_2 molar fraction. However, its effect on current density is contrary. Larger activation overpotential is beneficial to the current density, but it is harmful to the mass transport-related losses. Besides, increasing operating temperature deteriorates both mass transport-related losses and current density. Notably, the present model has the capability to quantitatively simulate the mass transport and electrochemical reactions in porous anodes without dependence on any statistical parameters, once the heterogeneous anode microstructure is quantitatively characterized with distinguishing the pore phase, ionic phase and electronic phase.

Nomenclature

c	Total molar concentration, mol m^{-3}
D_{ij}	Diffusion coefficient between species i and species j , $\text{m}^2 \text{s}^{-1}$
e_α	Discrete velocity set

f	Density distribution function
F	Faraday constant, 96485 C mol ⁻¹
i	Current density, A m ⁻²
J	Molar flux, mol m ⁻² s ⁻¹
L	Thickness, m
M	Molecular weight, kg mol ⁻¹
p	Pressure, Pa
R	Gas constant, J mol ⁻¹ K ⁻¹
t	Time, s
T	Temperature, K
u	Velocity, m s ⁻¹
y_i	Molar fraction of species i

Greek symbols

ρ	Density, kg m ⁻³
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Subscripts

α	Discrete velocity direction
a	Anode
A/E	Interface between anode and electrolyte
Bulk	Gas channel
e	Electrolyte

Superscript

*	Non-dimensional
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List of Figurers

1. Fig. 1 (a) Schematic diagram of SOFC; computational domain and boundary conditions for mass transport and electrochemical reaction in anode presented in this work; (b) detailed electrochemical kinetics at TPBs in anode.
2. Fig. 2 Species surface coverages versus activation overpotential simulated by the present model (symbols) and by Bessler[26] (lines).
3. Fig. 3 The distribution of normalized molar fraction of H_2 simulated (a) by the present model and (b) by Chiu et al.[29].
4. Fig. 4 Effect of anode microstructure on mass transport and electrochemical reaction: distributions of H_2 molar fraction in (a) Case 1, (b) Case 2 and (c) Case3; (d) maximum (solid lines), average (symbols) and minimum (dash lines) of H_2 molar fraction along the primary transport direction; and (e) cumulative current density along the primary transport direction.
5. Fig. 5 Effect of fuel composition on mass transport and electrochemical reaction: (a) maximum (solid lines), average (symbols) and minimum (dash lines) of H_2 molar fraction along the primary transport direction; and (b) concentration overpotential and average current density under different inlet H_2 molar fractions.
6. Fig. 6 Effect of activation overpotential on mass transport and electrochemical reaction: (a) maximum (solid lines), average (symbols) and minimum (dash lines) of H_2 molar fraction along the primary transport direction; (b) cumulative current density; and (c) concentration overpotential versus activation overpotential.
7. Fig. 7 Effect of operating temperature on mass transport and electrochemical reaction: (a) average molar fraction of H_2 along the primary transport direction and concentration overpotential versus operating temperature; and (b) cumulative current density under different operating temperatures.

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List of Tables

1. Table 1 Electrochemical reaction rate constants refer to Reactions (2)–(7) from Ref.[26].

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	k_{+n} / s^{-1}	k_{-n} / s^{-1}
k_1	x	x
k_2	2.0×10^{11}	1.3×10^4
k_3	1.0×10^{12}	5.8×10^2
k_4	1.5×10^0	6.0×10^5
k_5	x	1.0×10^{11}
k_6	x	2.4×10^8

Effect of heterogeneity of anode microstructure on mass transport and electrochemical reaction

Case 1, 2 and 3 are under the same boundary condition; Microstructure A and B are with the same porosity and tortuosity factor

Case 1: Microstructure A

Constant molar flux at inner interface

Case 2: Microstructure A

Coupled mass transport and electrochemical reaction

Case 3: Microstructure B

Coupled mass transport and electrochemical reaction