**Lattice Boltzmann Modeling of Carbon Deposition in Porous Anode of a Solid Oxide
Fuel Cell with Internal Reforming**

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Abstract:

A pore scale Lattice Boltzmann (LB) model is developed for multi-component mass transport and carbon deposition in the porous anode of a solid oxide fuel cell (SOFC) fed with methane. In this model, the reforming and electrochemical reactions are discretely coupled via local molar fluxes of reactive gas species at catalytically active sites and triple phase boundaries (TPBs). By considering the heterogeneity of anode microstructure, the present pore scale LB model is capable of quantitatively predicting the local distributions of both the position and the amount of deposited carbon in the irregular porous anode. Using this model, the characteristics of carbon deposition in the anode are investigated. It is found that the heterogeneity of anode microstructure has significant influence on mass transport and carbon deposition. Increasing the pre-reforming extent of methane and decreasing the operating temperature are beneficial for the suppression of carbon deposition, whereas they will cause a relatively inferior cell performance. The LB model and results presented in this study are beneficial to mechanism investigation of carbon deposition. Furthermore, they are also helpful for studying the correlations between anode microstructure and carbon deposition and then bridging the manufacture of SOFC electrodes and their performance, which is useful to propose effective suggestions for avoiding performance degradation of SOFC induced by carbon deposition.

Keywords: Solid oxide fuel cell; Anode microstructure; Lattice Boltzmann method; Pore scale; Mass transport; Carbon deposition

1. Introduction

Solid oxide fuel cells (SOFCs) are considered as one of the most promising power generation technologies due to their high generating efficiency and low pollutant emissions[1]. Low temperature fuel cells such as proton exchange membrane fuel cells are usually fed with hydrogen, but there are still big challenges in the production, storage and transportation of hydrogen[2]. In contrast, high operating temperature ($550\sim 1000^{\circ}\text{C}$)[3] facilitating the cleavage of chemical bounds to release chemical energy confers SOFCs an attractive advantage, i.e., remarkable fuel flexibility[4]. Most of hydrocarbon fuels (even solid carbon) can be used as fuels of SOFCs, such as natural gas, biogas and gasified coal[5-8]. Therefore, SOFCs offer great prospects for more efficient and cleaner utilization of fossil fuels. However, there are also some critical technical barriers in utilization of these hydrocarbon fuels, and one of them is the carbon deposition in SOFC anodes[9].

Ni-based cermet such as nickel/yttria stabilized zirconia (Ni/YSZ) and nickel/scandia stabilized zirconia (Ni/ScSZ) is widely used as the anode material for SOFCs owing to its excellent electronic conductivity and electrocatalytic activity for H_2 and CO oxidation reactions[10]. Nevertheless, when hydrocarbon fuels are fed into Ni-based anodes, carbon deposition may occur since Ni also catalyzes some carbon formation reactions of hydrocarbon fuels. The deposited carbon covers the surface of Ni particles, which may deactivate the catalyst[1]. Besides, the deposited carbon blocks pores of the anode resulting in deterioration of mass transport, and it even induces irreversible damages to anode geometrical structures[11]. As a consequence, carbon deposition may cause a significant degradation of cell performance. Therefore, a thorough understanding of carbon deposition in

porous anodes is crucial for the development of SOFCs fed with hydrocarbon fuels.

Current researches on carbon deposition of SOFCs are mainly focused on optimizing anode materials[6,12-22] and operating conditions[5,7,8,11,23-29]. Modifying/altering the catalyst of the Ni-based anode and adopting other anode materials such as perovskite are widely employed to develop more robust anodes immune to carbon deposition. These researches are mostly focused on the design and manufacture of new anodes and the attenuation characteristics of relevant macroscopic output parameters to characterize their resistance to carbon deposition[6,12-22]. However, the formation of carbon deposition is seldom investigated. Carbon deposition can also be suppressed by proper selection of operating parameters, such as fuel types[5,7,8], molar ratio of steam to carbon[23,24], average current density[25,26], operating temperature[27,28], molar ratio of hydrogen to methane[29] and fuel utilization[11]. However, these parameters are interactional and the existing concluded adjusting strategies are sometimes inconsistent. Therefore, a thorough understanding of the formation of carbon deposition is necessary for developing more robust anodes and selecting more proper operating parameters to mitigate carbon deposition in SOFC anodes.

Compared to experimental approaches, numerical approaches are more effective to reveal the underlying mechanisms of carbon deposition in both qualitative and quantitative terms. C–H–O ternary equilibrium diagram and carbon formation activity [27,30-32] are often employed to investigate carbon deposition qualitatively, but they can only predict the possibility of carbon deposition. Since the deposited carbon is the product of the reforming reaction which is complexly coupled with the mass transport and electrochemical reaction in

the anode and the reforming reaction is a heterogeneous catalytic chemical reaction, the elementary reaction kinetic model is usually adopted to investigate carbon deposition quantitatively[33-35]. This model has superiority in revealing reforming reaction mechanisms, but it is cumbersome and time-consuming to implement. Comparatively, the macroscopic reaction kinetic model is more effective[11,24,28,36]. Yang et al. [28] adopted macroscopic reaction kinetic model to analyze the methane reforming process in the anode and found that a smaller Ni particle is more likely to cause carbon deposition. Wang et al. [24,36] also employed macroscopic reaction kinetic model to study the carbon deposition in a planar SOFC anode and concluded that the variation of porosity resulted from deposited carbon which blocks pores of porous anodes had indispensable effect on cell performance. However, aforementioned numerical studies are based on the assumption that anode microstructure is homogenous and hence describe related physical quantities using volume-averaged methods. The heterogeneity of anode microstructure plays a crucial role in the transport of reactive gas species in the pore phase of anodes and in the distribution of catalytically active sites (Ni particles), thus has a great influence on both the amount and the position of carbon deposition. Therefore, the heterogeneity of anode microstructure needs to be taken into consideration in order to confirm both the amount and the position of carbon deposition quantitatively, thus a pore scale research is indispensable.

In this paper, a pore scale model is developed to predict the mass transport, reforming and electrochemical reactions in an SOFC anode, which is based on the coupling of a five-component Lattice Boltzmann (LB) model for reactive gas transport, a macroscopic reaction kinetic model for the reforming process and the Faraday's Law for the

electrochemical reaction. Using this model, the characteristics of carbon deposition in the anode is investigated with considering the heterogeneity of anode microstructure. The local molar fraction distributions of gas species in the irregular pores, as well as the amount and the position of the discrete deposited carbon at catalytically active sites are obtained. Furthermore, the influences of anode microstructure, average current density, pre-reforming extent of methane and operating temperature on mass transport and carbon deposition are discussed.

2. Mathematical model

2.1. General description

Fig. 1(a) illustrates PEN (positive electrode|electrolyte|negative electrode) structure of an anode-supported button SOFC. Since this paper is mainly focused on characteristics of mass transport and carbon deposition in the anode, the anode microstructure from a button SOFC anode was experimentally obtained using scanning electron microscope (SEM) as shown in Fig. 1(b). The anode is a porous cermet composed of the electronic conductor and ionic conductor. By binarization processing, the binary image of this anode microstructure is obtained (Fig. 1(c)) to get better contrast between solid and pore phases, which is the geometric input condition of latter pore scale simulations.

Based on the binary image in Fig. 1(c), the computational domain and boundary conditions in this paper are depicted in Fig. 2. The anode/electrolyte interface is assumed as the three phase boundary (TPB) for electrochemical reaction for simplicity, which is commonly adopted in relevant literatures[37-40]. The solid obstacles are assumed to be

catalytically active, on which reforming reactions take place and carbon deposition may occur. Notably, the carbon deposition may alter the geometrical structure of the porous anode. However, the effects of the deposited carbon on anode microstructure and on mass transport and reactions are not considered because the present study focuses on the formation of deposited carbon. The mass transport, electrochemical reaction and reforming reaction are discretely coupled by the local flux of each species at TPBs and catalytically active sites via Neumann boundary condition.

The total concentration and molar fraction of each species are specified at fuel channel/anode interface ($x = 0$) and the molar flux of each species is specified at anode/electrolyte interface ($x = L$) based on the current generated by the cell. Since the thickness of the anode is much shorter than the length of the cell and this paper primarily focuses on the transport phenomena along the x direction, periodic boundary condition is employed at the top and bottom boundaries of the computational domain and a reasonable height H is adopted in order to provide a realistic representation of the porous anode.

2.2. *Mass transport model*

McCracken et al.[41] established a LB model for binary mixtures with different molecular weights, which needs N sets of grid for streaming of N species and is proved that the maximum ratio of molecular weights is limited to be below 9 due to the numerical diffusion. In this paper, we extend the LB model for binary mixtures developed in Ref.[41] to five-component mixtures. Particularly, we adopt the finite-difference method to deal with the streaming process instead of the interpolation scheme employed in Ref.[41], thus only one set

of grid is needed for N species and the numerical diffusion resulted from the interpolation scheme can be avoided. Therefore, the present model offers the potential to simulate multi-component fluid flows with the maximum ratio of molecular weights larger than 9.

The Boltzmann equation for five-species flow based on two-fluid theory is described as follows (take species 1 for example):

$$\frac{\partial f^1}{\partial t} + \boldsymbol{\xi} \cdot \frac{\partial f^1}{\partial \mathbf{r}} + \mathbf{a}^1 \cdot \frac{\partial f^1}{\partial \boldsymbol{\xi}} = J^{11} + J^{12} + J^{13} + J^{14} + J^{15} \quad (1)$$

where f is the particle density distribution function. Superscript numbers from 1 to 5 represent H_2 , H_2O , CH_4 , CO and CO_2 , respectively. $\boldsymbol{\xi}$ is the velocity and $\mathbf{a}$ is the acceleration. J^{11} represents the effect of collisions between particles of H_2 and the cross-collision terms from J^{12} to J^{15} represent the effect of collisions between particles of H_2 and other species.

By discretizing Eq.(1), the following equation is obtained:

$$\frac{\partial f_\alpha^1}{\partial t} + \mathbf{e}_\alpha^1 \cdot \nabla f_\alpha^1 = J_\alpha^{11} + J_\alpha^{12} + J_\alpha^{13} + J_\alpha^{14} + J_\alpha^{15} + F_\alpha^1 \quad (2)$$

where α is the velocity direction. The self-collision term J_α^{11} , cross-collision term J_α^{12} (the other cross-collision terms can be obtained following the expression of J_α^{12}), equilibrium distribution function $f_\alpha^{1(0)}$ and forcing term F_α^1 (existing only when the external force occurs) are given by following equations:

$$J_\alpha^{11} = -\frac{1}{\tau^1} \left[f_\alpha^1 - f_\alpha^{1(0)} \right] \quad (3)$$

$$J_\alpha^{12} = -\frac{1}{\tau_D} \frac{\rho^2}{\rho} \frac{f_\alpha^{1(eq)}}{R_1 T} (\mathbf{e}_\alpha^1 - \mathbf{u}) \cdot (\mathbf{u}^1 - \mathbf{u}^2) \quad (4)$$

$$f_\alpha^{1(0)} = \left[1 + \frac{1}{R_1 T} (\mathbf{e}_\alpha^1 - \mathbf{u}) \cdot (\mathbf{u}^1 - \mathbf{u}) \right] f_\alpha^{1(eq)} \quad (5)$$

$$f_{\alpha}^{1(eq)} = \rho^1 \omega_{\alpha} \left[1 + \frac{\mathbf{e}_{\alpha}^1 \cdot \mathbf{u}}{R_1 T} + \frac{(\mathbf{e}_{\alpha}^1 \cdot \mathbf{u})^2}{2(R_1 T)^2} - \frac{u^2}{2R_1 T} \right] \quad (6)$$

$$F_{\alpha}^1 = \rho^1 \omega_{\alpha} \frac{\mathbf{e}_{\alpha}^1 \cdot \mathbf{a}^1}{R_1 T} \quad (7)$$

Here, τ^1 is the self-collision relaxation time controlling the kinematic viscosity and τ^{12} is the cross-collision relaxation time determining the inter-species diffusivities. For the D2Q9 model, $\mathbf{e}_{\alpha}$ and ω_{α} are given by

$$\mathbf{e}_{\alpha}^1 = \begin{cases} (0, 0), & (e_{\alpha}^1)^2 = 0 \\ c^1 (\cos[(\alpha-1)\pi/2], \sin[(\alpha-1)\pi/2]), & (e_{\alpha}^1)^2 = (c^1)^2 \\ \sqrt{2}c^1 (\cos[(2\alpha-1)\pi/4], \sin[(2\alpha-1)\pi/4]), & (e_{\alpha}^1)^2 = 2(c^1)^2 \end{cases} \quad (8)$$

$$c^1 = \frac{\delta_x}{\delta_t}, \quad c^2 = \sqrt{\frac{M^1}{M^2}}c^1, \quad c^3 = \sqrt{\frac{M^1}{M^3}}c^1, \quad c^4 = \sqrt{\frac{M^1}{M^4}}c^1, \quad c^5 = \sqrt{\frac{M^1}{M^5}}c^1 \quad (9)$$

$$\omega_{\alpha} = \begin{cases} 4/9, & (e_{\alpha}^1)^2 = 0 \\ 1/9, & (e_{\alpha}^1)^2 = (c^1)^2 \\ 1/36, & (e_{\alpha}^1)^2 = 2(c^1)^2 \end{cases} \quad (10)$$

The density and velocity for each species are moments of distribution functions (take species 1 for example):

$$\rho^1 = \sum_{\alpha} f_{\alpha}^1 = \sum_{\alpha} f_{\alpha}^{1(0)} \quad (11)$$

$$\rho^1 \mathbf{u}^1 = \sum_{\alpha} f_{\alpha}^1 \mathbf{e}_{\alpha}^1 = \sum_{\alpha} f_{\alpha}^{1(0)} \mathbf{e}_{\alpha}^1 \quad (12)$$

The density and velocity of the mixture are defined as

$$\rho = \rho^1 + \rho^2 + \rho^3 + \rho^4 + \rho^5 \quad (13)$$

$$\rho \mathbf{u} = \rho^1 \mathbf{u}^1 + \rho^2 \mathbf{u}^2 + \rho^3 \mathbf{u}^3 + \rho^4 \mathbf{u}^4 + \rho^5 \mathbf{u}^5 \quad (14)$$

Dividing Eq.(2) into collision step and streaming step, and then discretizing them by an

explicit first-order Euler scheme and a second-order Lax-Wendroff scheme on one set of grid, respectively, the following equations are obtained:

$$\text{Collision: } f_{\alpha}^{1+} = f_{\alpha}^1 + \delta_t J_{\alpha}^{11} + \delta_t J_{\alpha}^{12} + \delta_t J_{\alpha}^{13} + \delta_t J_{\alpha}^{14} + \delta_t J_{\alpha}^{15} + \delta_t F_{\alpha}^1 \quad (15)$$

$$\begin{aligned} \text{Streaming: } f_{\alpha}^1(\mathbf{x}, t + \delta_t) &= f_{\alpha}^{1+}(\mathbf{x}, t) - \delta_t (\mathbf{e}_{\alpha}^1 \cdot \nabla) f_{\alpha}^{1+}(\mathbf{x}, t) \\ &+ \frac{1}{2} \delta_t^2 (\mathbf{e}_{\alpha}^1 \cdot \nabla)^2 f_{\alpha}^{1+}(\mathbf{x}, t) + o(\delta_t^3) \end{aligned} \quad (16)$$

where superscript + represents variables after collision.

By means of Chapman-Enskog analysis, the viscosity of each species (take species 1 as an example) and diffusivity between different species (take species 1 and 2 as an example) are obtained:

$$\nu^1 = \left(\tau^1 - \frac{1}{2} \right) \delta_t c_{1,s}^2 \quad (17)$$

$$D_{12} = \frac{p\rho}{n^2 M^1 M^2} \left(\tau_D - \frac{1}{2} \right) \delta_t \quad (18)$$

2.3. LB model for multi-component flow in porous media

The pore scale LB model is employed to simulate the five-component flow in porous media, in which the characterization of the porous media is critical. SEM images of the cross-sections of SOFC anodes are obtained experimentally (Fig. 1b) and the grayscale value of each pixel in the SEM images is further obtained. Then, a threshold of grayscale is selected to distinguish the pore phase and solid phase. A binary image (Fig. 1(c)) according to the SEM image (Fig. 1(b)) is obtained, in which the black region represents the solid phase (the mixture of electronic and ionic conductors) and the white region represents the pore phase. Another important factor of pore scale model is to describe the irregular inner interface. We

employ the non-equilibrium extrapolation scheme[42] for the Neumann boundary condition at the interface of solid phase and pore phase.

2.4. Internal reforming reaction model

The chemical reactions included in the internal reforming kinetics of the anode fed with methane are shown in Table 1[23,24]. C_s represents the deposited carbon. Then, the reaction rate of each chemical reaction can be obtained.

(1) Methane steam reforming reaction

$$R_r = k_{fr} p_{CH_4} p_{H_2O} - k_{br} p_{H_2}^3 p_{CO} \quad (19)$$

where R_r is the reaction rate of methane steam reforming reaction, and k_{fr} and k_{br} are relevant forward and backward reaction rate constants. The equilibrium constant and k_{fr} are defined as[43]

$$K_{pr} = \frac{k_{fr}}{k_{br}} = 1.0267 \times 10^{10} \times \exp(-0.2513\theta^4 + 0.3665\theta^3 + 0.5810\theta^2 - 27.134\theta + 3.2770) \quad (20)$$

$$\theta = \frac{1000}{T} - 1 \quad (21)$$

$$k_{fr} = 2395 \exp\left(-\frac{231266}{RT}\right) \quad (22)$$

(2) CO water-gas shift reaction

$$R_s = k_{fs} p_{CO} p_{H_2O} - k_{bs} p_{CO_2} p_{H_2} \quad (23)$$

where R_s is the reaction rate of CO water-gas shift reaction, and k_{fs} and k_{bs} are relevant forward and backward reaction rate constants. The equilibrium constant and k_{fs} are defined as[43]

$$K_{ps} = \frac{k_{fs}}{k_{bs}} = \exp(-0.2935\theta^3 + 0.635\theta^2 + 4.1788\theta + 0.3169) \quad (24)$$

$$k_{fs} = 0.0171 \exp\left(-\frac{103191}{RT}\right) \quad (25)$$

(3) Methane cracked reaction[44]

$$R_C = \frac{1}{3600M_C} \frac{k_{fc} (p_{CH_4} - p_{H_2}^2 / K_{pc})}{(1 + k_{H_2} \sqrt{p_{H_2}})^2} \quad (26)$$

where R_C is the reaction rate of methane cracked reaction, k_{fc} is the forward reaction rate constant, M_C is the molecular weight of carbon, K_{pc} is the equilibrium constant of methane cracked reaction, and k_{H_2} is the adsorption constant of H_2 .

$$k_{fc} = \exp\left(20.492 - \frac{104200}{RT}\right) \quad (27)$$

$$K_{pc} = 5.088 \times 10^5 \exp\left(20.492 - \frac{104200}{RT}\right) \quad (28)$$

$$k_{H_2} = \exp\left(\frac{163200}{RT} - 22.426\right) \quad (29)$$

(4) Boudouard reaction

$$R_B = \frac{1}{3600M_C} \frac{k_{fB} k_{CO} \left(p_{CO} - \frac{p_{CO_2}}{K_{pB} p_{CO}}\right)}{\left(1 + k_{CO} p_{CO} + \frac{p_{CO_2}}{k_{CO_2} k_{CO} p_{CO}}\right)^2} \quad (30)$$

where R_B is the reaction rate of Boudouard reaction, k_{fB} and K_{pB} are relevant forward reaction rate constant and equilibrium constant, and k_{CO} and k_{CO_2} are adsorption constants of CO and CO_2 .

$$k_{fB} = 26732820 \exp\left(-\frac{108379}{RT}\right) \quad (31)$$

$$K_{\text{pB}} = \exp\left(-\frac{160.6}{R}\right) \exp\left(\frac{133100}{RT}\right) \quad (32)$$

$$k_{\text{CO}} = 1.0245 \times 10^{-6} \exp\left(-\frac{108379}{RT}\right) \quad (33)$$

$$k_{\text{CO}_2} = 30190322 \exp\left(-\frac{89805}{RT}\right) \quad (34)$$

At discrete catalytically active sites (surfaces of obstacles within the anode), the local flux of each species generated by reforming reaction is given in Table 2.

2.5. Electrochemical model

At discrete TPBs ($x = L$), the following electrochemical reaction occurs:

Therefore, the molar flux at discrete TPBs can be calculated by Faraday's law:

$$J_{\text{H}_2}^{\text{Far}} = -J_{\text{H}_2\text{O}}^{\text{Far}} = \frac{i}{2F} \quad (36)$$

3. Results and discussion

The lattice unit is employed in the present LB model and dimensionless parameters are adopted to convert lattice unit and physical unit optionally. Involved dimensionless parameters governing the mass transport and reactions in the porous anode include porosity ε and dimensionless reaction flux J^* .

$$J^* = \frac{J_{\text{H}_2}^{\text{Far}} L}{cD_{13}} \Big|_{\text{LB}} = \frac{J_{\text{H}_2}^{\text{Far}} L}{cD_{13}} \Big|_{\text{phy}} \quad (37)$$

Accordingly, the local flux of each species caused by the reforming reaction at catalytically active sites is obtained by the following conversion relationship:

$$J^{\text{ref}}(\mathbf{X}, \mathbf{Z})|_{\text{LB}} = J^{\text{ref}}(\mathbf{X}, \mathbf{Z})|_{\text{phy}} \left(\frac{J_{\text{H}_2}^{\text{Far}}|_{\text{LB}}}{J_{\text{H}_2}^{\text{Far}}|_{\text{phy}}} \right) \quad (38)$$

3.1. Model validation

3.1.1. LB model for five-component flow

The Stefan-Maxwell equation, which is qualified for m -component continuum transport, is employed to validate the five-component LB model developed in this study. The computational domain is a representative of SOFC anode (as shown in Fig. 2, $x = 0-L$, $z = 0-H$) without considering the porous media. The relevant input parameters are (in lattice units): $y_{\text{H}_2, \text{bulk}} = 0.5$, $y_{\text{H}_2\text{O}, \text{bulk}} = 0.1$, $y_{\text{CH}_4, \text{bulk}} = 0.2$, $y_{\text{CO}, \text{bulk}} = 0.1$, $y_{\text{CO}_2, \text{bulk}} = 0.1$, $J_{\text{H}_2, \text{A/E}} = 0.0862$, $J_{\text{H}_2\text{O}, \text{A/E}} = -0.0646$, $J_{\text{CH}_4, \text{A/E}} = 0.0215$, $J_{\text{CO}, \text{A/E}} = 0.0108$, $J_{\text{CO}_2, \text{A/E}} = -0.0539$, $c_T = 20$, $L = 20$, $D_{\text{H}_2-\text{H}_2\text{O}} = 0.76577$, $D_{\text{H}_2-\text{CH}_4} = 0.61992$, $D_{\text{H}_2-\text{CO}} = 0.64194$, $D_{\text{H}_2-\text{CO}_2} = 0.55312$, $D_{\text{H}_2\text{O}-\text{CH}_4} = 0.23242$, $D_{\text{H}_2\text{O}-\text{CO}} = 0.22162$, $D_{\text{H}_2\text{O}-\text{CO}_2} = 0.17242$, $D_{\text{CH}_4-\text{CO}} = 0.19595$, $D_{\text{CH}_4-\text{CO}_2} = 0.15961$ and $D_{\text{CO}-\text{CO}_2} = 0.14074$. As shown in Fig. 3, the average molar fraction distributions along the primary transport direction obtained by the present LB model are overlapped with that from Stefan-Maxwell Model for all the five species, which assures the accuracy and reliability of the five-component LB model developed in this study.

3.1.2. Inner boundary treatment

The reforming reaction takes place at catalytically active sites (the irregular inner boundary). Therefore, the reliability of the treatment of Neumann boundary condition at inner boundary is of significant importance. For simplicity, we employ the two-component mass transport around a square cylinder to validate the inner boundary treatment. The square

cylinder with a height of $20H/3$ and a length of $L/3$ is in the center of the computation domain with a height of H and a length of L . H_2 and H_2O with constant molar fluxes is consumed and generated perpendicular to the square cylinder surface, respectively, and the four corners is impermeable. The molar fractions of H_2 and H_2O are 0.9 and 0.1 at inlet of the entire computational domain. The outlet boundary is impermeable. Periodic boundary is employed at $Z = 0$ and $Z = H$. In this simulation, J^* is fixed at 0.25.

Fig. 4(a) presents the molar fraction distribution of H_2 . When $X^* < 1/3$, the molar fraction of H_2 decreases along the primary transport direction as it is consumed at the square cylinder surface. When $1/3 < X^* < 2/3$, in the region closer to the square cylinder surface, smaller molar fraction of H_2 is observed and the contour is gradually parallel to the square cylinder surface, which indicate that H_2 is consumed at the square cylinder surface. When $X^* > 2/3$, the molar fraction of H_2 increases gradually due to the impermeable boundary condition at outlet. The contour of the molar fraction of H_2 is perpendicular to the four corners indicating that H_2 is not consumed, which is accordant with the impermeable boundary condition used at comers.

Fig. 4(b) presents the average molar fraction of H_2 along the primary transport direction at $Z^* = 8/15$ (the upper surface of the square cylinder) from the present model, in which the results obtained from Laplace equation and Chiu et al.[45] are also given for comparison. The good agreement assures the accuracy of the inner boundary treatment in this paper. It should be noted that Chiu et al.[45] employed the multi-component LB model developed by McCracken et al.[25], in which the maximum ratio of molecular weights is limited to be blow 9, and the investigation of carbon deposition in the anode is not involved in their research.

3.2. Parametric analysis

3.2.1. Standard case

The anode microstructure employed in the parametric analysis is reconstituted by three-dimensional particle element method[46] and a cross-section of the reconstituted microstructure is selected as the geometrical input condition of the standard case. Other input parameters are given in Table 3. Unless stated otherwise, the following parametric analyses are all based on the standard case. In the standard case, the mesh size is 102×106 . All self-collision relaxation times are set to 1 ($\tau_1 = \tau_2 = \tau_3 = \tau_4 = \tau_5 = 1$) and cross-collision relaxation times are obtained via Eq. (18). The corresponding input parameters in lattice units are: $L = 102$, $c_T = 2.4$, $D_{H_2-CH_4} = 0.1117$ and $J_{H_2,TPB} = 4.352 \times 10^{-6}$. Therefore, $J^* = 1.7 \times 10^{-3}$.

Fig. 5(a)–Fig. 5(e) are molar fraction distributions of all the five gas species. Fig. 5(f) shows the mean, maximum and minimum values of molar fraction of each gas species along the primary transport direction. It is calculated that $R_r > 0$, $R_s < 0$ and $R_C > 0$ at inlet, and $R_r > 0$, $R_s > 0$ and $R_C < 0$ at outlet. Moreover, the reaction rate of each reaction at inlet is much faster than that at outlet. CH_4 is nearly consumed completely when $0 < X^* < 0.2$, which causes a sharp decrease of y_{CH_4} . In downstream region, the inverse methane cracked reaction results in a slight rise of y_{CH_4} . The production of H_2 from methane steam reforming reaction and methane cracked reaction is much larger than its consumption from CO water-gas shift reaction in upstream region, which results in a great increase of y_{H_2} in regions where CH_4 reacts fiercely. In downstream region, the production of H_2 from methane steam reforming reaction and CO water-gas shift reaction is slightly larger than its consumption from methane cracked reaction and electrochemical reaction, thus the increasing tendency of y_{H_2} slows

down gradually. Regarding H_2O , in upstream region, its consumption from methane steam reforming reaction is much larger than its production from CO water-gas shift reaction, which results in the decreasing tendency of $y_{\text{H}_2\text{O}}$. In downstream region, the consumption of H_2O from methane steam reforming reaction and CO water-gas shift reaction is larger than its production from electrochemical reaction, which leads to a further decrease of $y_{\text{H}_2\text{O}}$. Since the reaction rate of Boudouard reaction is smaller than that of other reactions, y_{CO} is mainly determined by methane steam reforming reaction and CO water-gas shift reaction. CO is generated in upstream region but in downstream region its production is larger than its consumption, which causes the increase of y_{CO} . The changing tendencies of the above species result in that y_{CO_2} firstly increases, and then decreases.

It is clearly shown in Fig. 5(c) that CH_4 is almost consumed completely when $0 < X^* < 0.2$, which is the reason of that carbon deposition mainly appears in this area as shown in Fig. 6(a). In Fig. 6(b), it is observed that the average amount of carbon deposition along the primary transport direction does not change monotonously because the amount of catalytically active sites in the cross-section perpendicular to X^* is not constant along the primary transport direction. The catalytically active sites in cross-section reaches the maximum at $X^* \approx 0.05$ (Fig. 6(b)), which causes the largest average amount of carbon deposition. It is also observed that carbon deposition mainly occurs in the region adjacent to fuel channel/anode interface and is closely related to the profile of the anode microstructure.

3.2.2. *Effect of anode microstructure*

In order to investigate the effect of anode microstructure on mass transport and carbon deposition, two different anode microstructures with the same porosity of $\varepsilon = 43\%$, tortuosity

factor of $\tau^2 = 3.734$ and TPB length of $l_{\text{TPB}} = 1.1 \times 10^{-3}$ m are adopted: one is the microstructure of the standard case reconstituted by three-dimensional particle element method represented as microstructure A and the other is from literature[47] represented as microstructure B. Other input parameters are $y_{\text{H}_2, \text{bulk}} = 0.2$, $y_{\text{H}_2\text{O}, \text{bulk}} = 0.45$, $y_{\text{CH}_4, \text{bulk}} = 0.25$, $y_{\text{CO}, \text{bulk}} = 0.07$, $y_{\text{CO}_2, \text{bulk}} = 0.03$, $i_{\text{av}} = 20000 \text{ A} \cdot \text{m}^{-2}$, $L = 1.2 \times 10^{-3}$ m and $T = 1223$ K. Therefore, $J^* = 0.022$.

The effects of anode microstructure on mass transport and carbon deposition in the anode are illustrated in Fig. 7 and Fig. 8. As shown in Fig. 7, when $0.4 < X^* < 0.8$ and $0.2 < Z^* < 0.8$, there are much more catalytically active sites in microstructure B compared with microstructure A, which causes a larger reactive flux of each species. Therefore, the differences in mean, maximum and minimum of molar fraction of H_2 , H_2O , CO and CO_2 between microstructure A and microstructure B become remarkable in this area (Fig. 8), except for CH_4 which is nearly consumed completely when $0 < X^* < 0.2$. Moreover, the maximum molar fraction of H_2 (Fig. 7(a)) and the minimum molar fraction of H_2O (Fig. 7(b)) also appear in this area.

Fig. 8(f) presents the average amount of carbon deposition along the primary transport direction in different anode microstructures. Since CH_4 is almost consumed completely at $0 < X^* < 0.2$, the amount of carbon deposition is around 0 when $X^* > 0.2$ in both microstructures. The changing tendencies of the average amount of carbon deposition in two microstructures are quite different at $0 < X^* < 0.2$, because the position and the amount of catalytically active sites in two microstructures are different.

Though both the boundary condition and the statistical parameters including porosity,

tortuosity factor and TPB length are the same, the characteristics of mass transport and carbon deposition in different microstructures can be quite different. Therefore, the numerical method assuming that the porous media is homogeneous is not qualified to accurately describe the mass transport, electrochemical and reforming reactions in porous electrodes with heterogeneous microstructures. Performance degradation caused by carbon deposition is one of the pressing technology barriers of SOFCs fed with hydrocarbon fuels. Since both distribution and amount of carbon deposition are closely related to the molar fraction distributions of gas species and the anode microstructure, it is of great significance to investigate the carbon deposition in the porous anode at pore scale.

3.2.3. *Effect of average current density*

Fig. 9(a)–(f) are curves reflecting the effect of average current density on mass transport and carbon deposition along the primary transport direction. H_2 is consumed and H_2O is generated by the electrochemical reaction at TPB ($X^* = 1.0$). Meanwhile, in the anode adjacent to TPB, methane steam reforming reaction and CO water-gas shift reaction generate H_2 and consume H_2O , while methane cracked reaction consumes H_2 slightly. These processes reflect the coupling among mass transport, electrochemical and reforming reactions. As average current density increases, the consumption of H_2 and production of H_2O increase, thus molar fraction of H_2 decreases and molar fraction of H_2O increases. As a consequence, methane steam reforming reaction, CO water-gas shift reaction and methane cracked reaction occur forwardly. Hence, average molar fraction of CH_4 decreases and average molar fraction of CO_2 rises at TPB. The leading role of CO water-gas shift reaction is the main reason why average molar fraction of CO decreases at TPB.

As methane cracked reaction reacts much faster than Boudouard reaction, carbon deposition is mainly govern by methane cracked reaction. It is clearly shown in Fig. 9(c) that molar fraction of CH_4 has no significant change after $X^* = 0.2$ and the average current density has insignificant effect on it. Therefore, the amount of carbon deposition is around 0 after $X^* = 0.2$ and it changes little as average current density increases.

In summary, average current density only affects the molar fraction of each species at $X^* > 0.2$, but carbon deposition mainly occurs at $X^* < 0.2$. Thus, average current density has insignificant influence on carbon deposition in the anode.

3.2.4. *Effect of pre-reforming extent of methane*

CH_4 is often mixed with steam and partially pre-reformed in the pre-reformer before entering the anode of SOFC. We assume that only methane steam reforming reaction and CO water-gas shift reaction occur in the pre-reformer, steam-to-carbon ratio is 2.0 and pre-reforming temperature is 1073K. Fuel compositions under different pre-reforming extent of methane are listed in Table 4. As the pre-reforming extent increases, molar fractions of H_2 and CO increase, molar fractions of H_2O and CH_4 decrease, and molar fraction of CO_2 firstly increases and then decreases slightly.

Fig. 10 presents the influences of pre-reforming extent on average molar fraction of each species and average amount of carbon deposition. As the pre-reforming extent increases, average molar fraction of each species maintains the same tendency, but their changes along X direction are much more smoothly. Meanwhile, a larger pre-reforming extent means a smaller amount of CH_4 at fuel channel/anode interface, thus carbon deposition decreases. Fig. 10 also indicates that the larger the pre-reforming extent is, the smaller its influence on mass

transport, electrochemical and reforming reactions in anode is.

It is concluded that a larger pre-reforming extent of methane has the potential of preventing carbon deposition. However, it is summarized in Ref.[48] that with increasing the pre-reforming extent of methane, the generating efficiency decreases and the cell is more likely to exceed the maximum temperature of safe operation(1050°C). Therefore, the selection of pre-reforming extent of methane should balance the carbon deposition and the cell performance.

3.2.5. Effect of operating temperature

Fig. 11 presents the effect of operating temperature on mass transport and carbon deposition. When the operating temperature increases, average molar fractions of H_2 and CO go up, while average molar fractions of H_2O and CH_4 fall down. The average molar fraction of CO_2 does not change monotonously. Meanwhile, a larger operating temperature leads to a larger forward reaction rate of methane crack reaction. Therefore, the average amount of carbon deposition continuously decreases with the reduction of operating temperature and it reaches 0 when the operating temperature decreases to 873K as illustrated in Fig. 11(f). Hence, carbon deposition is more likely to generate in anode with higher temperature. Accordingly, the operating temperature should be as low as possible to suppress carbon deposition. However, it is noteworthy that lower operating temperature induces worse cell performance as well.

4. Conclusion

A pore scale Lattice Boltzmann (LB) model capable of considering the heterogeneity of

anode microstructure is developed to predict the multi-component mass transport and carbon deposition in SOFC anodes. The present model is qualified to confirm the catalytically active sites (Ni) for the reforming reaction and hence to quantitatively demonstrate the local distributions of both the positions and the amount of the deposited carbon.

Using the present model, the characteristics of carbon deposition are investigated by discussing the effects of anode microstructure, average current density, pre-reforming extent of methane and operating temperature. Main results are as follows: (1) For different porous anodes with the same statistical parameters including porosity, tortuosity factor and TPB length, the characteristics of carbon deposition can be quite different even under the same boundary condition, which indicates the dramatic effects of the heterogeneity of porous electrodes on cell performance; (2) average current density has insignificant effect on carbon deposition; (3) higher pre-reforming extent of methane is beneficial for inhibiting carbon deposition and (4) the carbon deposition can be effectively suppressed by lowering the operating temperature. Nevertheless, the strategies beneficial for the suppression of carbon deposition are usually accompanied by a relatively inferior cell performance. Therefore, the adjustment of related operating parameters should balance the carbon deposition characteristics and cell performance.

Performance degradation induced by carbon deposition is one of the pressing barriers affecting the cell durability. The present pore scale model is beneficial to further study on underlying mechanism of carbon deposition and its effects on cell performance. Additionally, the present model can correlate the anode microstructure and carbon deposition, which offers great prospects for building a bridge between the manufacture of anodes and their durability.

Therefore, the present study is helpful for the design and optimization of efficient and durable SOFCs.

Nomenclature

c	Total molar concentration, mol m ⁻³
D_{ij}	Diffusion coefficient between species i and species j, m ² 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
<i>Superscript</i>	
*	Non-dimensional

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Table 1 Internal reforming reactions in the anode of SOFC fed with methane[23,24]

Reactions	Equations	NO.
Methane steam reforming reaction	$\text{CH}_4 + \text{H}_2\text{O} \longleftrightarrow \text{CO} + 3\text{H}_2$	(39)
CO water-gas shift reaction	$\text{CO} + \text{H}_2\text{O} \longleftrightarrow \text{CO}_2 + \text{H}_2$	(40)
Methane cracked reaction	$\text{CH}_4 \longleftrightarrow \text{C}_s + 2\text{H}_2$	(41)
Boudouard reaction	$2\text{CO} \longleftrightarrow \text{C}_s + \text{CO}_2$	(42)

Table 2 Local flux of each species at discrete catalytically active sites

Species	Local flux	NO.
H ₂	$R_{\text{H}_2} = 3R_{\text{r}} + R_{\text{s}} + 2R_{\text{c}}$	(43)
H ₂ O	$R_{\text{H}_2\text{O}} = -R_{\text{r}} - R_{\text{s}}$	(44)
CH ₄	$R_{\text{CH}_4} = -R_{\text{r}} - R_{\text{c}}$	(45)
CO	$R_{\text{CO}} = R_{\text{r}} - R_{\text{s}} - 2R_{\text{b}}$	(46)
CO ₂	$R_{\text{CO}_2} = R_{\text{s}} + R_{\text{b}}$	(47)
C _s	$R_{\text{C}_s} = R_{\text{c}} + R_{\text{b}}$	(48)

Table 3 Input parameters of standard case

Parameter	Value
Operating temperature / K	1073
Operating pressure / Pa	101325
Average current density / $\text{A}\cdot\text{m}^{-2}$	3000
Anode thickness / m	750×10^{-6}
Porosity	0.43
Total concentration / $\text{mol}\cdot\text{m}^{-3}$	11.358
Molar flux at TPB / $\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$	1.5546×10^{-2}
Diffusivity / $10^{-4}\cdot\text{m}^2\cdot\text{s}^{-1}$	$\text{H}_2\text{--H}_2\text{O}$: 7.6577, $\text{H}_2\text{--CH}_4$: 6.1992,
	$\text{H}_2\text{--CO}$: 6.4194, $\text{H}_2\text{--CO}_2$: 5.5312,
	$\text{H}_2\text{O--CH}_4$: 2.3242, $\text{H}_2\text{O--CO}$: 2.2162,
	$\text{H}_2\text{O--CO}_2$: 1.7242, $\text{CH}_4\text{--CO}$: 1.9595,
	$\text{CH}_4\text{--CO}_2$: 1.5961, CO--CO_2 : 1.4074
Fuel composition	30.0% H_2 , 42.2% H_2O , 19.4% CH_4 , 3.3% CO , 5.0% CO_2

Table 4 Fuel compositions under different pre-reforming extent of methane

Pre-reforming extent	Fuel composition
0.1	12.0% H ₂ , 56.8% H ₂ O, 28.1% CH ₄ , 0.5% CO, 2.6% CO ₂
0.3	30.0% H ₂ , 42.2% H ₂ O, 19.4% CH ₄ , 3.3% CO, 5.0% CO ₂
0.5	43.1% H ₂ , 31.9% H ₂ O, 12.5% CH ₄ , 6.9% CO, 5.6% CO ₂
0.7	53.0% H ₂ , 24.3% H ₂ O, 6.8% CH ₄ , 10.6% CO, 5.3% CO ₂