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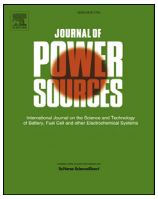

A two-dimensional modeling of solid oxide fuel cell button cells with detailed electrochemistry mechanism

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HIGHLIGHTS

- A 2D SOFC button cell model with detailed electrochemistry mechanism was developed.
- Oxygen ion transportation from cathode to anode TPBs was explicitly modeled.
- Anodic electrochemical reactions occur within ~20 μm from the electrolyte interface.
- Ni catalyst surface is covered mainly by adsorbed hydrogen atoms.
- Fuel tube diameter should not be smaller than that of cathode for best performance.

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ABSTRACT

A two-dimensional model of nickel/yttria-stabilized zirconia (Ni/YSZ) solid oxide fuel cell (SOFC) was developed for a button cell system. The model integrates the detailed catalytic, electrochemical elementary reactions with ionic/electronic conduction and multiple gas transport processes in SOFC. The model is validated using published experimental data for H_2–H_2O fuel gas under different cell sizes and operating conditions. The distributions of gas/surface phase species concentration and current density were predicted and the effects of operating temperature, fuel gas composition and fuel channel tube design on the cell performance were studied. The results show that the electrochemical reaction processes occurs mainly within a 20 μm distance from the anode/electrolyte interface and that the Ni catalyst surface is covered mainly by H(s). For the chamber channel design, the calculations show that the tube chamber should have a diameter no smaller than the cathode electrode to obtain the best SOFC performance.

1. Introduction

Solid oxide fuel cell (SOFC) produces electricity directly from electrochemical oxidation of the fuel gas, such as H_2, CH_4 and CO. As a promising energy conversion device, the development and better design of SOFC have attracted considerable attention. A typical SOFC consists of two porous ceramic electrodes: anode and cathode, separated by a dense electrolyte layer. During the operation of the SOFC, the fuel gas mixture and air are supplied to the anode and cathode surface, respectively. At the cathode side, oxygen ion (O^{2-}) is produced and then transported through the electrolyte to the anode. At the anode, the fuel gas mixture diffuses through the porous anode where it is oxidized by O^{2-} at the gas/ceramic/catalyst triple phase boundaries (TPBs).

In fact, the physicochemical processes occurring in SOFC are very complex. They involve highly coupled catalytic and electrochemical reactions and transport processes within the cell, such as fuel gas diffusion in both chambers and porous electrode, fuel gas catalytic reactions, electrochemical reactions at the TPBs, O^{2-} migration in solid-state anodes and electrolyte. Understanding the detailed physicochemical mechanisms of these integrated processes is a key step towards improving SOFC electrochemical performance. Since direct measurement of the electrochemical reactions at solid/gas interface in porous electrodes is very challenging, many efforts have been devoted to develop an accurate model to understand the complex electrochemical reaction processes in SOFC [1–5]. In a common computational study of SOFC, a

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set of conservation equations are used to describe the heat transfer, fuel gas transport, ion and electron migration processes. These processes are then coupled together with the global electrochemical reactions through Butler–Volmer equation [6–12]. Accordingly, these SOFC models mainly focus on the macro scale processes in SOFC. Although these model predictions agree well with the experiments under different operating conditions, there is still a lack of insights on the concentrations of surface species considering detailed electrochemistry mechanism in SOFC.

To overcome the limitations of the modeling methods mentioned above, many researchers have tried to develop more sophisticated SOFC models, in which the microscale elementary surface reactions and charge-transfer reactions at the TPBs were employed and integrated with fuel gas transport processes [13–21]. Among these SOFC mechanistic modeling studies that couple heterogeneous elementary reactions, electrochemical reactions, electrode microstructure and mass and charge transport, most of them are 1D model. For example, Zhu et al. [14] and Li et al. [15] developed a 1D SOFC model considering detailed reaction mechanism to study the distribution of gas-phase species, surface adsorbates, electric potentials within pore spaces electrode. Effects of microstructure, thickness and temperature on the cell performance in SOFC were also investigated with such 1D model [17]. These 1D models, however, have intrinsic drawbacks. For example, they are not capable of modeling the fuel/air flow at the channels. Moreover, they fail to predict the radial property variations of SOFC. Until now, there are only a few 2D SOFC models with detailed heterogeneous catalysis and electrochemical reactions reported in the open literature [18–20]. For example, Janardhanan et al. [18] developed a 2D SOFC model with a detailed heterogeneous reaction mechanism for water-gas shift reactions on Ni catalysts. In that study, they investigated the steam content effect on the resulting overpotential losses and surface coverages of various species at the TPBs. Xie et al. [19] also developed a 2D model for a button cell test system. By integrating detailed electrochemical elementary reactions for H_2/H_2O system with multiple transport processes, they studied the distribution of surface adsorbed species, e.g. O(s), OH(s) and H_2O(s), at the anode/electrolyte interface at different fuel compositions and cell voltage.

In the present study, a 2D SOFC model with detailed catalytically and electrochemical reaction mechanism was developed. The gas transport in the chambers and porous electrode and the electrical processes were coupled together in the model. The fuel gas used in the present study is an H_2-H_2O mixture. Different from previous 2D SOFC modeling studies, in addition to the complex interactions between fuel/gas compositions, adsorbed surface species and operating temperature, we also studied the flow rate effect and fuel gas chamber design on SOFC performance. Moreover, the effect of operating temperature on the distribution of O^{2-}_{YSZ} was also reported in the present study. It represents a more comprehensive SOFC modeling study compared to earlier models. Such a 2D model provides a better understanding of the behaviors in a fuel cell and could facilitate the SOFC design.

2. Model development and governing equations

2.1. Geometry and assumptions

Fig. 1 is the schematic illustration of a typical button cell test stand. An anode-supported Ni-YSZ button cell is fixed on one end of a large ceramic tube. The fuel gas is supplied to the anode electrode via a small ceramic tube. The cathode electrode is exposed to the ambient air. The temperature is controlled by a test furnace. Due to the axial symmetry, 2D model was developed based on this the button cell test system. The main model assumptions are as follows: *i*) all gases are assumed to be ideal gases and the cell temperature is uniformly distributed; *ii*) heterogeneous elementary reactions occur on the Ni surface in anode; *iii*) electrochemical reactions are assumed to take place at TPB and in only one step, see Section 2.3.

2.2. Heterogeneous chemistry

When H_2-H_2O mixture is fueled to the SOFC anode compartment, H_2 oxidization reaction occurs. There is no significant heterogeneous chemistry proceeding in the cathode and electrolyte [18]. In this work, Ni-YSZ is considered to be the anode cermet as Ni is an effective catalyst for H_2 oxidization surface elementary reactions. After hydrogen diffuses into the porous anode, it dissociates into two H atoms on Ni, referred as H(s) hereafter. The H(s) atoms can react with the O(s) atom transferred from YSZ at the Ni/YSZ interface to form OH(s) and H_2O(s) surface species. Similar to H_2, H_2O can also adsorb on Ni surface and then dissociate into H(s) and OH(s). All these reactions are reversible. A detailed H_2/H_2O surface reaction mechanism on Ni is listed in Table 1.

For all the surface reactions and desorption reactions, the rate constants of these reactions are expressed in the following general modified Arrhenius form [18] (Eq. (1)):

$$k_m = A_m T^{\beta_m} exp\left(-\frac{E_m}{RT}\right) \prod_{k=1}^{K_s} \theta_i^{\mu_{km}} exp\left(-\frac{\varepsilon_{km}\theta_i}{RT}\right) \tag{1}$$

where k_m is the rate constant for the mth reaction, A_m is pre-exponential factor, β_m is symmetry factor, E_m is activation energy, μ_{km} and ε_{km} the parameters modeling the coverage dependency of rate constant and θ_i is the surface coverage of ith species. The rate of production s_i of the *i*th specie is then given by

$$s_i = \sum_m v_{i,m}\left(k_{f,m}\prod_{R_{f,m}} c_i^{v_i'} - k_{r,m}\prod_{R_{r,m}} c_i^{v_i''}\right) \tag{2}$$

where v_i' and v_i'' are the stoichiometric coefficients of products and reactants in reaction m, respectively. $v_{i,m}$ is their difference, c_i is surface concentration. For surface chemistry, the reaction rate is usually expressed as a function of the surface coverage θ_i, which is defined as [22]:

$$\theta_i = \frac{c_i}{\Gamma} \tag{3}$$

where Γ is the area-specific density of Ni ($mol \cdot m^{-2}$).

2.3. Electrochemistry

In addition to the heterogeneous chemistry, electrochemical reactions obviously play a critical role in the SOFC electrodes. At the cathode side, the oxygen gas ($O_{2,gas}$) catches e^- and is converted into oxygen ion (O^{2-}_{YSZ}) on the surface of YSZ ionic conductor, according to Eq. (4):

$$\frac{1}{2}O_{2,gas} + 2e^- + (YSZ) \rightarrow O^{2-}_{YSZ} \tag{4}$$

The O^{2-}_{YSZ} ion is then conducted toward the anode through the oxygen vacancies $V^{\cdot\cdot}_{YSZ}$ in YSZ electrolyte:

$$O^{2-}_{YSZ} + V^{\cdot\cdot}_{YSZ} \leftrightarrow O^{X}_{YSZ} + (YSZ)$$