Parameter study of transient carbon deposition effect on the performance of a planar solid oxide fuel cell ☆

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HIGHLIGHTS

- An unsteady 2D model was used to study carbon deposition process in planar SOFC.
- The biggest change of performance occurs in inlet domain of anode support layer.
- The low operating voltage is helpful to inhibit carbon deposition.
- The high H_2 molar fraction, pressure and temperature increase carbon deposition.

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ABSTRACT

Carbon deposition has a serious effect on the performance of solid oxide fuel cells (SOFCs). An unsteady-state 2D model based on COMSOL software is used to study the carbon deposition process in a planar SOFC. The carbon deposition, catalyst activity, reaction rate and temperature fields are obtained to analyse the mechanism of carbon deposition in the SOFC at different operating time. The effects of the operating voltage, inlet H_2 molar fraction, operating pressure and operating temperature on the performance of the SOFC are investigated in detail. It is found that the biggest variation of the performances caused by carbon deposition occurs in the inlet domain of the anode support layer. The increase of operating voltage, inlet H_2 molar fraction, operating pressure and temperature accelerates the carbon deposition process. The predicted results could deepen our understanding of carbon deposition and its transient quantitative effects on the catalyst, structure and cell performance.

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1. Introduction

Solid oxide fuel cells (SOFCs) have received considerable attention due to their advantages, such as high energy conversion rate, low pollution and good poison resistance. Besides, a wide range of fuels including various hydrocarbon fuels can be utilized. Considerable research efforts have focused on improving the conversion efficiency of SOFCs by exploring new materials for electrode, electrolyte, interconnector, catalyst and sealing. The widely recognized material for intermediate temperature SOFC cathode is Lanthanum Strontium Manganite and Yttria Stabilized Zirconia (LSM/YSZ) [1]. Nickel/Yttria Stabilized Zirconia (Ni/YSZ) is usually used for the anode and different composition of stainless steel is applied to the interconnector [2,3]. However, in order to achieve a high efficiency, the SOFCs should operate at a high temperature. Siengchum et al. [4] found that the operation of a solid oxide fuel cell with coconut carbon at 1023 K could produce a maximum current density of 0.27 (A cm^{-2}). The average current density contributed by carbon monoxide in the direct internal reforming solid oxide fuel cells at 1123 K was 10 times greater than that at 923 K [5]. Increasing the inlet temperature from 973 K to 1173 K could considerably increase the electric output of SOFC fed with CO_2 and CH_4 mixture [6]. The SOFCs at such a high temperature can achieve a high efficient power conversion, fast internal reforming reactions and a high quality by-product heat for the cogeneration or the bottom cycle [7]. However, the high temperature causes the SOFCs to lose functions partially or totally [8]. In the hydrocarbon-fed SOFC, the coke formation at the surface of catalyst Ni is more serious, which reduces the anode porosity and catalyst activity, and may have a negative effect on the diffusion coefficients, the effective charge conductivity and the thermal conductivity as well.

Nomenclature

a	catalyst activity (%)
c	molar concentration of carbon (mol m^{-3})
D_{ij}	binary diffusion coefficient (m^2 s^{-1})
J	kinetically controlled local current density (A m^{-3})
k_a	catalyst activity attenuation constant
M	molecular weight (kg mol^{-1})
p	pressure (Pa)
q	power density, W cm^{-2}
r_C	carbon deposition rate (mol m^{-3} s^{-1})
R_r	methane steam reforming reaction rate (mol m^{-3} s^{-1})
R_s	CO water–gas shift reforming reaction rate (mol m^{-3} s^{-1})
R_C	methane cracked reaction rate (mol m^{-3} s^{-1})
R_B	Boudouard reaction rate (mol m^{-3} s^{-1})
T	temperature (K)
t	time (s)
u	velocity vector (m s^{-1})
V	voltage (V)

Greek symbols

ε	porosity
κ	permeability (m^2)
ρ	density (kg m^{-3})
σ	electrical/ionic conductivity (S m^{-1})

Subscripts

an	anode
C	methane cracked reaction; carbon
cell	fuel cell
el	electron
io	ion

Superscripts

eff	effective

During the last decades, many researchers have paid much attention on the carbon deposition in SOFCs. Chen et al. [9] conducted an experiment to study the carbon deposition in the nickel/yttrium-stabilized zirconia (Ni/YSZ) anode-supported SOFCs. The results indicated that the operating temperature had a great influence on the carbon deposition and the microstructure damage was close to the anode surface. To effectively suppress the carbon deposition, alkaline earth oxides were added to the anodic materials [10]. Millichamp et al. [11] applied a novel bulk acoustic wave (BAW) microgravimetric sensor to investigate the coking of SOFC anodes, and the induction period of several hours was identified. Li et al. [12] experimentally studied the carbon deposition characteristics of CO/CO_2 based fuel on nickel cermet anodes of SOFC. It was found that the anodic carbon deposition increased with the increase of the discharging time, operation temperature and mole fraction of CO in the anode gas. The carbon deposition characteristics produced by the CO and CH_4 were different. The carbon deposition behaviours of SOFC with Cu–CeO$_2$–ScSZ (Scandia Stabilized Zirconia) anodes that exposed to the ethanol fuels for 300 h were examined by Ye et al. [13]. It indicated that the increased water, copper content and current load could prevent the carbon deposition, while the increased nickel and cobalt in the anode promoted the carbon deposition. Maher et al. [14] adopted the ex situ and in situ Raman spectroscopy combined with computational simulations to study the carbon deposition process on the SOFC Ni-based anodes that exposed to the carbon monoxide. The results showed that the carbon formed preferentially in the location where gas access was restricted, thus significantly affecting the current densities elsewhere. Wang et al. [15] found that the most favourable region of carbon formation was in the front of the porous anode sample, especially on the surface of the sample's front part. The kinetic model along with the catalyst deactivation model was more suitable for the qualitative and quantitative description of the carbon formation process than the previous models [16]. The above researches indicated that the operating temperature, fuel composition, operating voltage, operating pressure has a significant effect on the amount and location of carbon deposition in the anode of SOFC.

In our previous work [17], an unsteady two-dimensional planar SOFC model that considered the carbon deposition was established in the COMSOL software. The focus was paid on the mathematic model and numerical method. The effect of anode porosity, catalyst activity and inlet H_2O/CH_4 on the carbon deposition was also analysed. It was found by many researchers that the operating parameters, such as operating voltage, inlet H_2 molar fraction, operating pressure and operating temperature had an obvious influence on the electrical performance of SOFC. However, the electrochemical reaction rate changes as well if the time-dependent carbon deposition is considered, which may affect the relationship between operating parameters and electrical performance. Thus, this paper quantitatively examines the effects of operating parameters on the performance of SOFC under the transient carbon deposition condition. The special attention is paid on discerning the mechanism of carbon deposition in the planar SOFC from the distributions of carbon deposition, catalyst activity, reaction rate and temperature fields.

2. Physical models and computational method

2.1. Physical model and assumptions

As shown in Fig. 1, the physical model of SOFC is composed of fuel channel, anode support layer, anode reaction layer, electrolyte layer, cathode reaction layer, cathode support layer and air channel. The values of geometrical parameters are summarized in Table 1. The materials of anode and cathode are Ni/YSZ and LSM/YSZ respectively, which are homogeneous porous media. The electrochemical reactions are assumed to be occurred only in the electrode reaction layers. The operating voltage of fuel cell is kept as a constant. The methane steam reforming reaction, CO water–gas shift reforming reaction, methane cracking reaction and Boudouard reaction occur in the porous media anode supporting and reaction layers.

The fuel gases in the anode gas channel consist of CH_4, H_2, H_2O, CO and CO_2, while the air in the cathode gas channel comprises O_2 and N_2. All the gases are considered as ideal gases. During the analysis, the inlet velocity in the two gas channels is assumed to be 4 (m s^{-1}) so that it can be regarded as a laminar flow. The operating temperature and pressure are assumed as 1073 K and 1 atm. The values of baseline operating parameters are summarized in Table 2. The geometrical and operating parameters are taken from the Refs. [18–20].

2.2. Mathematical model and computational method

For the analysis of carbon deposition in SOFC, the mathematical model consists of chemical kinetic equations, unsteady-state Navier-Stokes equations, unsteady-state mass transfer equations,