A Parameter Sensitivity Study of Solid Oxide Fuel Cells Based on One-dimensional Model

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Abstract. Solid oxide fuel cells (SOFCs) are promising and efficient energy conversion devices. The modeling method was widely used to study characteristics of SOFCs due to limitation of experiments. Values of material properties such as porosity, tortuosity and pore radius are required information in modeling. Current modeling works usually employ material properties used in the literature, which are not exactly measured and the values vary in wide ranges. However, inappropriate selection of material properties can result in incorrect modeling results of SOFCs. In this study, a one-dimensional model of SOFCs was established to analyze the effects of different material parameters on the modeling results. A parameter sensitivity analysis was also conducted to determine the most influential parameters on the polarization curve. The results provide a reference for selection values of SOFC material parameters. This work can also be used as a guideline to fit the experimental polarization curve in numerical simulations by adjusting appropriate material parameters.

1. Introduction
Solid oxide fuel cells (SOFCs) directly convert chemical energy of fuels into electrical energy through electrochemical reactions [1]. Electrical performances of SOFCs are determined by activation polarization, concentration polarization and Ohmic polarization. All polarizations are largely affected by material parameters of SOFCs such as porosity, tortuosity, and pore radius of electrodes and so on [2]. However, it is extremely complicated to experimentally measure the values of all material parameters. Therefore, current modeling works of SOFCs usually employ values used in the literature which vary in wide ranges [3].

Celik et al. [4] coupled fluid flow, species concentration, and electric field to develop a model of SOFC. The effects of exchange current density, effective diffusion coefficient, limiting current and other physical parameters were studied. A new semi-empirical model was established to calculate the potential difference between the electrode and electrolyte interface. Vural et al. [5] proposed a mathematic model for SOFC concentration polarization. The dust gas model (DGM), Binary Friction model (BFM), and Stefan-Maxwell model (SMM) were used to calculate the multi-component diffusion in SOFCs. Besides pore size, current density, and reactant concentration, the results show that tortuosity also has important effect on concentration polarization calculation. Diego [6] established a sensitivity analysis model for high temperature proton-exchange membrane fuel cells. The effects of different parameters on fuel cell performance were quantitatively analyzed. Corigliano and Fragiacomo [7] developed a SOFC model for different types of fuels. The model can evaluate the voltage and power density of fuel cells operating at different conditions by varying initial parameters.
However, current work in the literature did not specifically study influences of SOFC material parameters on the polarization curve. Different parts of the curve are dominated by activation polarization, Ohmic polarization and concentration polarization, respectively, which are sensitive to different material parameters. The present study established a one-dimensional (1D) mathematic model of SOFCs for estimation influences of material properties on the electrical performance. The model was validated by experimental data. Sensitivity analyses were also conducted for different properties, which provided a reference for selection of SOFC material parameters in modeling work.

2. 1D SOFC model

Equations for the proposed 1D SOFC model are shown in Table 1. The output voltage of a single cell is calculated by Eq. (1), in which Open circuit voltage (OCV) is the output voltage when the cell is disconnected. The electrochemical reaction needs to be driven by the voltage difference in the equilibrium state, which is called activation polarization. The anode and the cathode have different activation polarization voltage $\eta_{\text{act, anode}}$ and $\eta_{\text{act, cathode}}$. Activation polarization is calculated by the B-V equation in Eq. (3) [8]. The exchange current density $i_0$ [9-11] has the greatest influence on the activation polarization voltage, which can be calculated by simplified Eq. (4).

Concentration polarization occurs when reactants are rapidly consumed on the electrodes to form a concentration gradient. The concentration of reactants on the catalyst surface depends on the current density. The higher the current density, the lower the surface concentration. When the consumption rate is equal to the diffusion rate, the surface concentration reaches zero. The current density at this time is called the limiting current density $i_L$. The concentration polarization is calculated by Eqs. (5-9).

Resistance loss is due to the resistance to transport of ions and electrons as shown in Eqs. (10) and (11). Eqs. (12-15) are empirical formulas for electrical conductivities of the electrodes and electrolyte. Figure 1 shows validation of the 1D model by experimental data reported in Ref. [12]. A good agreement is achieved between the calculated results and experimental data.

Table 1. Equations for the 1D SOFC model [8-12]

| Equation | Description |
| --- | --- |
| $E_{\text{out}} = OCV - E_{\text{act}} - E_{\text{ohm}} - E_{\text{con}}$ | Output voltage |
| $E_{\text{act}} = \eta_{\text{act, anode}} + \eta_{\text{act, cathode}}$ | Activation polarization |
| $i = i_0 \exp\left(\frac{\beta n_i F \eta_{\text{act}}}{RT}\right) - \exp\left[-\frac{(1-\beta) n_i F \eta_{\text{act}}}{RT}\right]$ | (3) |
| $i_0 = \frac{RT}{n_i F} A \exp\left(-\frac{E_a}{RT}\right)$ | (4) |
| $E_{\text{con}} = E_{\text{con,a}} + E_{\text{con,c}}$ | Concentration polarization |
| $E_{\text{con}} = \frac{RT}{n_i F} \ln\left(\frac{i_L}{i_L - i}\right)$ | (6) |
| $c_n = 0 = \frac{i_L M_i}{n_i F} \left(\frac{1}{D_i} + \frac{\delta_j}{D_j}\right)$ | (7) |
| $D_{i,k} = \frac{2}{3} \sqrt{\frac{8RT}{\pi M_i}}$ | (9) |
| $E_{\text{ohm}} = I \times R$ | Ohmic polarization |
| $R = \delta/\sigma$ | (11) |
| $\sigma_{\text{eff}} = \frac{1 - \varepsilon}{\tau} \sigma \times V_{\text{eff}}$ | (12) |
| $\sigma_{\text{ele,a}} = \frac{4.2 \times 10^7 \exp\left(-\frac{1200}{T}\right)}{T}$ | (13) |
| $\sigma_{\text{ele,c}} = \frac{9.5 \times 10^7 \exp\left(-\frac{1150}{T}\right)}{T}$ | (14) |
| $\sigma_{\text{ion}} = \frac{3.34 \times 10^7 \exp\left(-\frac{10300}{T}\right)}{T}$ | (15) |
3. Results and discussion
Table 2 summarized commonly used values for material parameters of SOFC in the literature. Generally, each parameter has a range because various values of one parameter can be found in different references.

Figure 2 shows polarization curves obtained by varying the anode and cathode exchange current density pre-coefficients $A_{ia}$ and $A_{ic}$. Eq. (4) indicates that the exchange current density pre-coefficient $A_i$ mainly affects the activation polarization. The calculated results based on the 1D model shown in Figure 2 also confirm that the activation polarization is mostly influenced by varying $A_i$. In contrast, the Ohmic polarization dominated part of the curve is almost parallel at different exchange current density pre-coefficients.

Figure 2(a) shows that the earlier the activation polarization appears as the smaller $A_{ia}$ is used, because greater activation polarization voltage consumed is corresponding to smaller $A_{ia}$. When $A_{ia}$ is $1.67 \times 10^8$ A/m², the activation polarization voltage loss is about 0.6 V. However, only 0.3 V voltage loss is obtained when $A_{ia}$ is $1 \times 10^{11}$ A/m². The influence of cathode exchange current density pre-coefficient $A_{ic}$ is shown in Figure 2(b). Similar results of the polarization curves are observed by varying $A_{ic}$. It can be concluded that increasing both $A_{ia}$ and $A_{ic}$ can reduce the loss of activation polarization and improve cell performance. And $A_{ia}$ and $A_{ic}$ are related to the conductivity of the electrode and the pressure of fuels.

Table 2. Values of SOFC material parameters reported in the literature [5,13-17]

| Parameter                              | Value                      |
|----------------------------------------|----------------------------|
| Anode diffusion layer pore radius, [m] | $r_{ad}$ $5 \times 10^{-7}$~$7.5 \times 10^{-5}$ |
| Anode diffusion layer porosity         | $\varepsilon_{ad}$ 0.3~0.6 |
| Anode diffusion layer tortuosity       | $\tau_{ad}$ 2~10           |
| Anode functional layer pore radius, [m]| $r_{af}$ $5 \times 10^{-7}$~$2 \times 10^{-6}$ |
| Anode functional layer porosity        | $\varepsilon_{af}$ 0.2~0.5 |
| Anode functional layer tortuosity      | $\tau_{af}$ 3~13.3         |
| Anode exchange current density pre-coefficient, [A/m²] | $A_{ia}$ $1.67 \times 10^8$~$6.54 \times 10^{11}$ |
| Cathode diffusion layer pore radius, [m]| $r_{cd}$ $5 \times 10^{-7}$~$5 \times 10^{-5}$ |
| Cathode diffusion layer porosity       | $\varepsilon_{cd}$ 0.3~0.5 |
| Cathode diffusion layer tortuosity     | $\tau_{cd}$ 2~10           |
| Cathode functional layer pore radius, [m]| $r_{cf}$ $2 \times 10^{-7}$~$2 \times 10^{-6}$ |
| Cathode functional layer porosity      | $\varepsilon_{cf}$ 0.27~0.5 |
| Cathode functional layer tortuosity    | $\tau_{cf}$ 2~10           |
| Cathode exchange current density pre-coefficient, [A/m²] | $A_{ic}$ $5.19 \times 10^8$~$2.7 \times 10^{13}$ |
Figure 2. Polarization curves obtained when varying the different pre-exponential factor for reaction rate constant. (a) $A_{ia}$; (b) $A_{ic}$.

Figure 3 demonstrates variation of polarization curves corresponding to different porosities of anode and cathode functional layers. The porosity affects calculation of the limiting current $i_l$ through the diffusion coefficient $D$, thereby influencing the concentration polarization. The porosity also affects calculation of the electrode material conductivity which is related to the Ohmic polarization.

Eq. (6) indicates that the minimum limiting current density determines the position of the voltage drop when concentration polarization becomes significant. Figure 3 shows that the limiting current density of the cathode is smaller than that of the anode, so the position of the voltage drop in concentration polarization is basically determined by the cathode limiting current density. The change of anode porosity has negligible effect on the output voltage. However, the variation of cathode porosity leads to significant difference of the polarization curves. The greater the cathode porosity, the greater the current density at which the polarization curve suddenly drops. Moreover, the porosities of electrodes have negligible influences on the polarization curves before reaching the limit currents. The results can be verified by Ref [6].

Figure 3. Polarization curves obtained when varying the porosity. (a) $\varepsilon_{af}$; (b) $\varepsilon_{cf}$.

The tortuosity $\tau$ of anode and cathode functional layers also affects the calculation of limiting current $i_l$ through the diffusion coefficient $D$. Moreover, the tortuosity influences the conductivity of the electrodes. The polarization curves obtained when varying the tortuosity of electrodes are shown in Figure 4.
Similar to porosity, the position of the voltage drop in concentration polarization is basically determined by the cathode limiting current density. The change of anode tortuosity has negligible effect on the output voltage. The results show that the concentration polarization is mainly determined by the cathode limiting current density. Therefore, the sensitivity of the cathode tortuosity is greater than that of the anode, which is consistent with the analysis of porosity.

Figure 5 demonstrates variation of polarization curves corresponding to different pore radius of the anode and cathode functional layers. The pore radius of electrodes affects calculation of the limiting current $i_L$ through the diffusion coefficient $D$, thereby influencing the concentration polarization. The pore radius affects the diffusion of fuels in the porous electrode. The larger the pore radius, the greater the limiting current density is. The change of anode pore radius has negligible effect on the output voltage. However, the variation of cathode pore radius leads to significant difference of the polarization curves. The results show that the concentration polarization is mainly determined by the cathode limiting current density.

Many factors affect the performance of SOFC, but the influence degree of different parameters are not the same. A sensitivity study was employed as shown in Eq. (16) to compare influences of different parameters.

$$S_{p,x} = \left. \frac{O_x - O_0}{x - x_0} \right|_{x=x_0}$$  \hspace{1cm} (16)

The sensitivity model is originally used in Ref [6]. Sensitivity analysis results of different material parameters are illustrated in Figure 6.
Figure 6. Sensitivity of different material parameters

The results show that the exchange current density pre-coefficient $A_i$ has the greatest influence on the polarization curve. The most influential factors in the concentration polarization are the porosity, tortuosity and pore radius of the cathode. Concentration polarization mainly depends on the smaller limiting current density of the cathode and anode. Because the cathode limiting current density is less than that of the anode, the anode change has negligible influence on the fuel cell performance.

4. Conclusion

In this study, a one-dimensional model of SOFCs was developed to analyze the effects of different material parameters on polarization curves. The results show that the influence of exchange current density pre-coefficient is the greatest. The results further show that it mainly affects the activation polarization dominant part of the polarization curve. Parameters such as porosity, tortuosity, and pore radius mainly affect the concentration polarization dominant part. The cathode-related material parameters have greater impact on the overall polarization curve than that of anode. Different parts of the calculated polarization curve can be adjusted by varying different material parameters, which is of great significance to the verification of model simulation with experimental data.

Nomenclature

$E_{out}$ Output voltage, [V] 
$OCV$ Open circuit voltage, [V] 
$E_{act}$ Activation polarization voltage, [V] 
$E_{con}$ Concentration polarization voltage, [V] 
$E_{ohm}$ Ohmic polarization voltage, [V] 
$i$ Current density, [A/m$^2$] 
$i_0$ Exchange current density, [A/m$^2$] 
$\beta$ Transfer coefficient 
$n_e$ Number of electrons transferred per reaction 
$F$ Faraday constant [C/mol] 
$\eta_{act,c}^{act}$ Anode/cathode activation polarization voltage, [V] 
$R$ Ideal gas constant, [J/(mol·K)] 
$T$ Temperature, [K] 
$A_i$ pre-exponential factor, [A/cm$^2$] 

$i_c$ Limit current density, [A/m$^2$] 
$c_0$ Concentration of fuel gas in the channel, [mol/m$^3$] 
$M_i$ Molar mass, [kg/mol] 
$h$ Convective heat transfer coefficient 
$\delta_{fd}$ Function/diffusion layer thickness, [m] 
$D_{fd}$ Function/diffusion layer diffusivity coefficient 
$\tau$ Tortuosity 
$\varepsilon$ Porosity 
$D_{k}$ Knudsen diffusion coefficient 
$D_{ij}$ Binary diffusion coefficient 
$r_e$ Pore radius of porous electrode, [m] 
$\sigma_{eff}$ Effective conductivity, [S/m] 
$V_{eff}$ Effective volume fraction
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