Performance Evaluation of Low-Temperature Solid Oxide Fuel Cells with SDC–Based Electrolyte

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A mathematical model has been known to be an important tool for designing and improving chemical processes. The aim of this work is to develop an electrochemical model of low-temperature solid oxide fuel cell (SOFC) with SDC–based electrolyte. To analyze the ohmic, activation and concentration overpotentials occurring within the fuel cell, the structural and operational parameters and mass transport of gases in porous electrodes are taken account into the electrochemical model. The predicted current density-voltage curves at operating temperatures of 500 and 600 °C are in good agreement with the experimental data. The validated model of the low temperature SOFC is used to assess the SOFC performance. The effects of anode thickness and operating temperatures of SOFC with SDC-based electrolyte are investigated. The results demonstrate that an increase in the anode thickness results in a significant increase in the anode concentration overpotential, whereas the activation overpotentials increase with increasing anode thickness at high current densities. In addition, the increase of operating temperature reduces the activation and ohmic overpotentials.

1. Introduction

Solid oxide fuel cell (SOFC) is regarded as an efficient device for power generation. SOFCs offer many advantages, such as a high electrochemical reaction rate, the flexibility of using various fuel types, and the prospect for combined heat and power systems (Chatrattanawet et al., 2014). The current state-of-the-art SOFC material is yttria-stabilized zirconia (YSZ) for electrolyte, Ni-yttria-stabilized zirconia (YSZ) for anode, and lanthanum strontium manganate/yttria-stabilized zirconia (LSM/YSZ) for cathode. To achieve high performance of the electrolyte, the SOFC is needed to operate at high temperatures (800-1,000 °C). However, the high temperature operation increases the thermal expansion of ceramic and metal components and thermal gradient (Kariya et al., 2016). These factors shorten cell lifetimes and lead to high maintenance costs. Another key problem of SOFC is slow start-up and shut-down cycles. Alternatively, a decrease in the operating temperature of SOFC can reduce the start-up and shut-down times and the thermal stress on the SOFC stack. Thus, the development of low-temperature SOFCs is an interesting research topic. A novel samaria-doped ceria (SDC) is a promising electrolyte for low-temperature SOFCs because it has higher oxygen-ion conductivity than YSZ. Moreover, the SDC is less likely to interact with cathode materials (Sugihara et al., 2014). Because the oxidation and reduction reactions occurring at the electrode/electrolyte interfaces are slow and inefficient at low temperature, new materials for the electrode have been proposed. Wang et al. (2004) reported that the activity of Ni anode can be improved by adding the SDC particles to Ni, which results in the increase of the three-phase boundary area and maintaining the suitable porosity. Moreover, $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF), which is an excellent current conductor having high ionic and electronic conductive, is proper for the cathode material at low temperatures (Lee et al., 2009).

To insight inter-physics occurring inside the cell and determine the optimal condition of cell, a mathematical model of SOFC is an essential tool for the development of low-temperature SOFC. The major voltage losses, i.e., ohmic, activation, and concentration overpotentials can be evaluated via the electrochemical model. Aguiar et al. (2004) investigated the electrochemical performance of anode-supported intermediate temperature SOFC. The simulation results indicated that the major losses within the cell are the cathode activation and ohmic overpotentials at 800 °C and 1 atm. Effect of the different cell support structures, i.e., electrode (anode and cathode) and electrolyte supports were analyzed based on the electrochemical model by Patcharavorachot et al. (2008). Their results showed that the electrolyte-supported SOFC with YSZ-based electrolyte is the lowest of the cell performance because of its high activation and ohmic overpotentials, while the anode-supported SOFC exhibits the higher performance than others.

The determination of optimal operating conditions and structure of the SOFC based on YSZ by performing the analysis of the electrical characteristics has been studied in a number of research groups. However, there have been a few studies focusing on the SOFC with SDC-based electrolyte. Therefore, a detailed electrochemical model of the SOFC with SDC-based electrolyte is proposed in this work. The electrical characteristics of the SOFC with SDC-based electrolyte are analyzed. The influences of the anode, cathode, and electrolyte thicknesses and the operating temperature on the cell performance and the potential losses are investigated.

2. SOFC Model

In simulation of a low-temperature SOFC, SDC electrolyte, Ni/SDC composite anode, and LSCF/SDC composite cathode are considered as materials for the present model. The structural component of SOFC-based SDC electrolyte at lower temperature is shown in Figure 1.
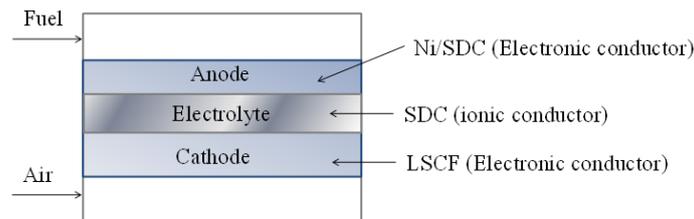

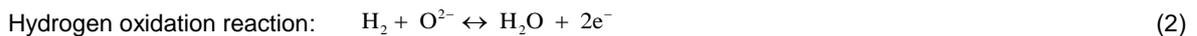Figure 1: Schematic diagram of the low-temperature SOFC

2.1 Model assumptions
To simulate SOFC behaviour, the following assumptions used for the development of SOFC model are:
(1) The reactant gases are considered as an ideal gas;
(2) Pressure drops in the SOFC are negligible;
(3) The operation of SOFC is assumed to be isothermal condition; and
(4) The model is considered as a lumped control volume.

2.2 Electrochemical model
SOFC can produce the electricity from the electrochemical reactions between hydrogen and oxygen. Humidified hydrogen is fed to the fuel channel while air is fed to the air channel. Oxygen is reduced into oxygen ions at cathode/electrolyte interface. Oxygen ions pass through the electrolyte and react with hydrogen at the anode/electrolyte interface. The electrons from the hydrogen oxidation reaction flow to an external circuit. The electrochemical reactions in SOFC are concluded as follows:

Oxygen reduction reaction: $\quad 1/2O_2 + 2e^- \leftrightarrow O^{2-}$ (1)

Hydrogen oxidation reaction: $\quad H_2 + O^{2-} \leftrightarrow H_2O + 2e^-$ (2)

Overall cell reaction: $\quad H_2 + 1/2O_2 \leftrightarrow H_2O$ (3)

The reversible cell voltage (E^{OCV}) is a maximum voltage of the cell at open-circuit condition expressed by the Nernst equation:

$$E^{\text{OCV}} = E^0 - \frac{RT}{2F}\ln\left(\frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}P_{\text{O}_2}^{0.5}}\right) \tag{4}$$

The reversible cell voltage is reduced due to the occurrence of voltage losses within the cell at closed circuit. The dominant voltage losses are ohmic overpotentials (η_{ohmic}), activation overpotentials (η_{act}), and concentration overpotentials (η_{conc}). The operative cell voltage of SOFC is expressed by Eq.(5):

$$V = E^{\text{OCV}} - (\eta_{\text{act}} + \eta_{\text{ohm}} + \eta_{\text{conc}}) \tag{5}$$

where η is the voltage overpotentials within the internal cell.

Ohmic overpotentials are related to resistance along the ionic flow in the electrolyte and the electron flow though the electrode and current collectors. These overpotentials can be calculated by Ohm's law, normally expressed as:

$$\eta_{\text{ohm}} = jR_{\text{ohm}} \tag{6}$$

where R_{ohm} is the internal electrical resistance, which is a function of the conductivity and thickness of the individual layers.

Activation overpotentials occur from the sluggishness of the electrochemical reaction at the electrode/electrolyte interfaces. Thus, the activation overpotentials are the energy required to exchange load between ions. The Butler–Volmer equation is used to describe the activation overpotentials, which can be written as:

$$j = j_{0,\text{anode}}\left[\frac{p_{\text{H}_2,\text{TPB}}}{p_{\text{H}_2,\text{f}}}\exp\left(\frac{\alpha nF}{RT}\eta_{\text{act,anode}}\right) - \frac{p_{\text{H}_2\text{O,TPB}}}{p_{\text{H}_2\text{O,f}}}\exp\left(-\frac{(1-\alpha)nF}{RT}\eta_{\text{act,anode}}\right)\right] \tag{7}$$

$$j = j_{0,\text{cathode}}\left[\exp\left(\frac{\alpha nF}{RT}\eta_{\text{act,cathode}}\right) - \exp\left(-\frac{(1-\alpha)nF}{RT}\eta_{\text{act,cathode}}\right)\right] \tag{8}$$

wherewhich is regularly 0 is the transfer coefficient α .5; n is the number of electrons exchanged in reaction step; and $j_{0,\text{anode}}$ and $j_{0,\text{cathode}}$ are the exchange current density pre-exponential factors of the anode and cathode, respectively. The exchange current densities are calculated from the Arrhenius law.

$$j_{0,\text{anode}} = \frac{RT}{nF}k_{\text{anode}}\exp\left(-\frac{E_{\text{anode}}}{RT}\right) \tag{9}$$

$$j_{0,\text{cathode}} = \frac{RT}{nF}k_{\text{cathode}}\exp\left(-\frac{E_{\text{cathode}}}{RT}\right) \tag{10}$$

where k_{anode} and k_{cathode} are the pre-exponential factors of the exchange current densities of anode and cathode, and E_{anode} and E_{cathode} are the activation energies of the anode and cathode exchange current densities, respectively (Saebea et al., 2013).

Concentration overpotentials are related to decrease in the concentration of substance during the reaction at the electrode surface, which is the resistance to mass transport and results in the voltage loss. Concentration overpotentials are calculated as follows:

$$\eta_{\text{conc}} = \frac{RT}{2F}\ln\left(\frac{p_{\text{H}_2\text{O,TPB}}\,p_{\text{H}_2,\text{f}}}{p_{\text{H}_2\text{O,f}}\,p_{\text{H}_2,\text{TPB}}}\right) + \frac{RT}{4F}\ln\left(\frac{p_{\text{O}_2,\text{a}}}{p_{\text{O}_2,\text{TPB}}}\right) \tag{11}$$

where $p_{i,\text{TPB}}$ is the partial pressures of H_2, H_2O and O_2 at the electrode/ electrolyte interfaces and can be expressed by a gas transport model in porous electrode, as shown in Eq.(12).

$$J_{i,\text{electrode}}^{\text{TPB}} = -D_{i,\text{eff}}\nabla C_i + C_i v \tag{12}$$

where $D_{\text{eff,electrode}}$ is an average effective diffusivity, given in Eq.(13).

$$\frac{1}{D_{i,\text{eff}}} = \frac{\tau}{\varepsilon}\left(\frac{1}{D_{i,k(\text{eff})}} + \frac{1}{D_{i\text{-}j}}\right) \tag{13}$$

3. Validation of model

The SOFC with SDC-based electrolyte is simulated from the mathematical equations in previous section. The proposed model of SOFC forms in the nonlinear algebraic equations, which is solved by using MATLAB. The parameters of the kinetic and material properties are concluded in Table 1. To ensure the reliability of the simulated model, the results from the model prediction are verified with the experimental data of Cui et al. (2010). The value of the parameters for the model validation is listed in Table 2. The comparisons of the I-V curves from the model prediction and the experiment at operating temperature of 500 and 600 °C are shown in Figure 2. It can be seen that the results of model prediction are in good agreement with the experimental data.
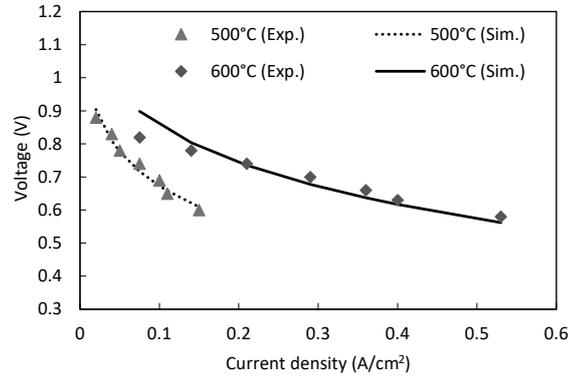

Figure 2: Comparison between the simulated data and the experimental results of Cui et al. (2010)

Table 1: Values of the kinetic and material property parameters for the SOFC

Parameters	Value	Ref.
Cathode electronic conductivity (S m^{-1})	$\dfrac{3.927\times10^6}{T}\exp\left(\dfrac{-1.74\times10^3}{T}\right)$	Lai et al., 2009
Cathode ionic conductivity (S m^{-1})	$1.39\times10^9\exp\left(\dfrac{-1.32}{8.6173\times10^{-5}T}\right)$	Cui et al., 2010
Anode conductivity (S m^{-1})	$3.27\times10^6 - 1065T$	Yuan et al., 2009
Activation energy of anode (J mol^{-1})	63,000	Yun et al., 2012
Activation energy of cathode (J mol^{-1})	120,000	Lui et al., 2004
Porosity	30%	Cui et al., 2010

Table 2   Input parameters for the model validation

Parameters	Value	Parameters	Value
Air composition	21 % O_2, 79 % N_2	Fuel composition	97 % H_2, 3 %H_2O
Operating pressure (bar)	1	Electrolyte thickness (µm)	20
Anode thickness (µm)	350	Cathode thickness (µm)	20

4. Results and discussion

In the study of performance of SOFC with SDC-based electrolyte, the structure of SOFC used for the investigation is an anode-supported SOFC. The operating parameters for the SOFC under nominal conditions are shown in Table 3.

4.1 Effect of anode thickness
The impact of the anode thickness on the cell performance is analyzed in this section. The anode thickness varies from 150 to 450 µm while the cathode and electrolyte thicknesses are fixed at 20 µm. The cell voltage

and power density as a function of the current density are shown in Figure 3(a). The results demonstrate that the cell performance decreases when the anode thickness increases, especially at a high current density. The main cause of the decrease of cell performance is an increase of the anode concentration overpotential with a thicker anode as a shown in Figure 3(b). This is because the increase of anode thickness results in the longer diffusion path for gases from the gas channel to the three-phase boundary. For the activation overpotentials, the increase of anode thickness has significant effect on the activation overpotentials at a high current density. It is noted that a lower gas concentration at three-phase boundary for the oxidation reaction with a higher anode thickness. Although the higher anode thickness is directly related to the increase of resistance from ohmic overpotentials, these overpotentials slightly increases due to high conductivity of Ni-SDC material.

Table 3: Values of the operating parameters for the SOFC under nominal conditions.

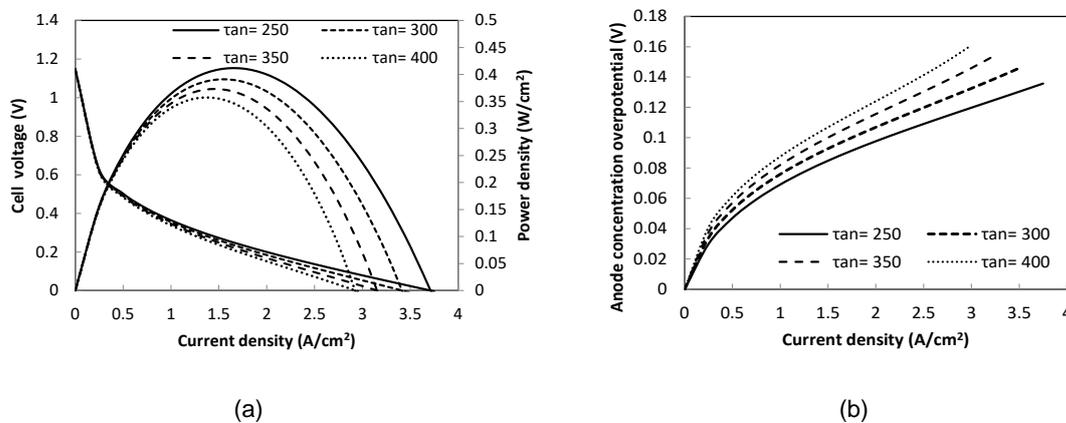| Parameters	Value	Parameters	Value
Temperature (ºC)	550	Fuel composition	97% H_2, 3%H_2O
Operating pressure (bar)	1	Electrolyte thickness (µm)	20
Anode thickness (µm)	350	Cathode thickness (µm)	20

(a)   (b)

Figure 3: Effect of anode thickness on (a) cell voltage and power density and (b) anode concentration overpotential

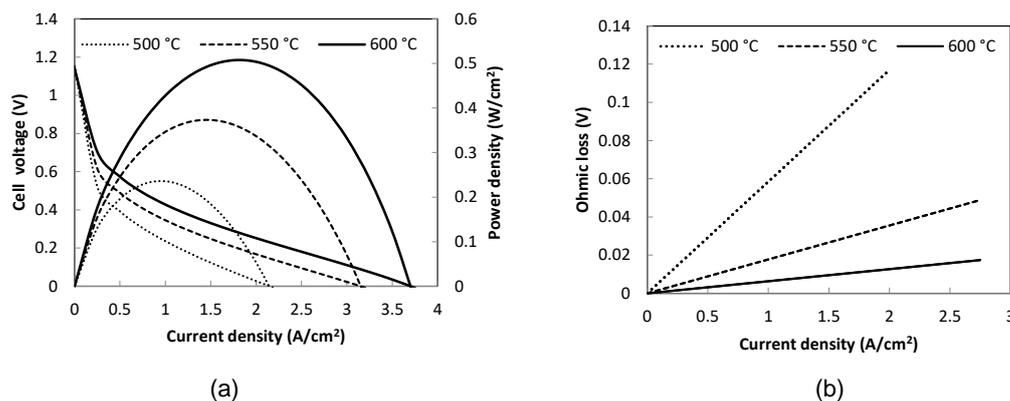## 4.2 Effect of temperature

(a)   (b)

Figure 4: Effect of operating temperature on (a) cell voltage and power density and (b) ohimic losses.

The characteristic curves of cell voltage and power density as a function of the current density at 500, 550 and 600 ºC is illustrated in Figure 4(a). The decrease of operating temperature has an adverse effect on the cell performance. The maximum power density is about 0.236 W/cm^2 for 500 ºC, 0.373 W/cm^2 for 550 ºC and 0.507 W/cm^2 for 600 ºC. The cell voltage directly relate to the power density. Figure 4(b) shows that the cell voltage decreases with decreasing the operating temperature. The decrement of the operating temperature increases the internal voltage losses, especially ohmic overpotentials. This can be explained that the ionic conductivity of electrolyte is lower when decreasing the cell temperature. Furthermore, the activation

overpotentials are also higher at low operating temperature, resulting from the lower rate of the electrode reaction with a lower temperature. When considering the effect of operating temperature on the concentration overpotentials, it decreases when reducing the cell temperature. However, the decrement of concentration overpotentials has less influence on the cell performance, compared with the increment of activation and ohmic overpotentials.

5. Conclusions

An electrochemical model of SOFC with SDC–based electrolyte has been presented. To ensure an accuracy of predicted results, the model of SOFC with SDC–based electrolyte has been verified by comparison between the simulated and experiment data. A good agreement has been observed between simulation and experimental data. The cell performance of anode-supported SOFC with SDC–based electrolyte has been analyzed for different anode thicknesses and the operating temperatures. It has been shown that the thicker anode leads to increase of cathode concentration overpotentials and the decrease of the cell performance. A decrease in thickness of anode can improve the cell performance. The operating temperature is also main factor on the cell temperature. The power density reduces when the operating temperature is decreased. The decrease of operating temperature results in ohmic and activation overpotentials enhanced, while the concentration overpotentials slightly decrease.

Acknowledgements

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