The Performance Improvement of a Thick Electrode Solid Oxide Fuel Cell

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Abstract

Solid oxide fuel cells (SOFCs) are becoming one of the main competitors among environmental friendly energy sources for the future due to low emission rates, high electrical generating efficiency and potential for low operating cost. This work presents systematic approach to develop and validate the microscopic scale models of a single cell SOFC supplied with humidified hydrogen. The model considers the common thick-anode supported SOFC in which the electrode microstructure is packed by spherical shaped ionic and electronic conducting particles. The evolution of performance versus electrode geometries is studied. The investigation confirms the strong effects of microstructure geometry to improve the SOFC performance, especially the increasing of the electrochemical active surface area. The largest active surface area of electrode is achieved when the size and solid volumetric fraction of ion and electron conducting particles are equal and then, the optimal thicknesses of the electrodes are also investigated. Finally, the accuracy of the model was validated by comparing with published experimental data.

1. Introduction

SOFCs are highly efficient energy conversion devices that transform chemical energy to electrical energy and heat directly from fuels through electrochemical reactions at electrodes. Operating at high temperature (673 K - 1273 K), SOFCs eliminate the need for noble catalyst and, thus, is more cost-effective. In addition, high temperature enables direct reforming of hydrocarbons in SOFC, resulting in more flexible fuel choices. Furthermore, the high temperature waste heat can be effectively recovered for...
### Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
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<tbody>
<tr>
<td>$A_v$</td>
<td>Active surface area per unit volume ( [m^2 \cdot m^{-3} \text{ or } m^{-1}] )</td>
</tr>
<tr>
<td>$D_{ij}$</td>
<td>Binary diffusion coefficient ( [m^2 \cdot s^{-1}] )</td>
</tr>
<tr>
<td>$D_{i,k}$</td>
<td>Knudsen diffusion coefficient of the species ( i ) ( [m^2 \cdot s^{-1}] )</td>
</tr>
<tr>
<td>$D_{ij}^{\text{eff}}$</td>
<td>Effective binary diffusion coefficient ( [m^2 \cdot s^{-1}] )</td>
</tr>
<tr>
<td>$J_e$</td>
<td>Electronic current density ( [A \cdot m^2] )</td>
</tr>
<tr>
<td>$J_i$</td>
<td>Ionic current density ( [A \cdot m^2] )</td>
</tr>
<tr>
<td>$J_{H_2}^{\text{ref}}$</td>
<td>Reference exchange current density for ( H_2 ) oxidation ( [A \cdot m^2] )</td>
</tr>
<tr>
<td>$J_{O_2}^{\text{ref}}$</td>
<td>Reference exchange current density for ( O_2 ) reduction ( [A \cdot m^2] )</td>
</tr>
<tr>
<td>$n_{el}$</td>
<td>Number fraction of electron conducting particle in the electrode</td>
</tr>
<tr>
<td>$n_{io}$</td>
<td>Number fraction of ion conducting particle in the electrode</td>
</tr>
<tr>
<td>$n_t$</td>
<td>Total number of particles in the electrode per unit volume ( [m^{-3}] )</td>
</tr>
<tr>
<td>$N_i$</td>
<td>Molar flux of species ( i ) ( [mol \cdot m^{-2} \cdot s^{-1}] )</td>
</tr>
<tr>
<td>$p_{el}$</td>
<td>Probability of percolation of electron conducting particles in the electrode</td>
</tr>
<tr>
<td>$p_{io}$</td>
<td>Probability of percolation of ion conducting particles in the electrode</td>
</tr>
<tr>
<td>$r_{el}$</td>
<td>Radius of electron conducting particles in the electrode ( [m] )</td>
</tr>
<tr>
<td>$r_{io}$</td>
<td>Radius of ion conducting particles in the electrode ( [m] )</td>
</tr>
<tr>
<td>$R_a$</td>
<td>Volumetric current density produced due to hydrogen oxidation ( [A \cdot m^3] )</td>
</tr>
<tr>
<td>$R_i$</td>
<td>Reaction rate ( [mol \cdot m^{-3} \cdot s^{-1}] )</td>
</tr>
<tr>
<td>$t_{an}$</td>
<td>Anode thickness ( [m] )</td>
</tr>
<tr>
<td>$t_{cat}$</td>
<td>Cathode thickness ( [m] )</td>
</tr>
<tr>
<td>$t_{elec}$</td>
<td>Electrolyte thickness ( [m] )</td>
</tr>
<tr>
<td>$y_i$</td>
<td>Molar fraction of species ( i ) ( [mol \cdot mol^{-1}] )</td>
</tr>
<tr>
<td>$Z$</td>
<td>Total average particle coordination number in electrode which equal to 6</td>
</tr>
<tr>
<td>$Z_{el}$</td>
<td>Coordination number of electronic conducting particles in the electrode</td>
</tr>
<tr>
<td>$Z_{el-el}$</td>
<td>Coordination number of electronic to electronic conducting particles</td>
</tr>
<tr>
<td>$Z_{io}$</td>
<td>Coordination number of ionic conducting particles in the electrode</td>
</tr>
<tr>
<td>$Z_{io-io}$</td>
<td>Coordination number of ionic to ionic conducting particles</td>
</tr>
<tr>
<td>$\gamma_{H_2}$</td>
<td>Reaction order for hydrogen oxidation reaction</td>
</tr>
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</table>
power generation by driving an integrated gas turbine to enhance the overall energy efficiency. Mathematical modeling is an essential aspect of SOFC technology development process. Influence of the electrode structures on the electrochemical reaction at the three phase boundary (TPB) has recently been included in microscopic modeling. Numerous microscopic-models of SOFCs exist in the literatures, varying in used assumptions. Literature reviews showed that the electrode microscopic model of SOFCs can roughly be divided into pore model [1], random resistor network model [2–4] and random packing sphere model [5]. At the present, random packing sphere model is the most appropriate and really useful for modeling, the electrode is assumed to be random of the packing spheres. The application this model on the microscopic SOFCs modeling is shown below.

Costamagna et al. [5] has developed a microscopic model of SOFC with random packing sphere electrode model. The model is used for the evaluation of the performance of an electrode formed by a mixture of electronic and ionic conductor with spherical particle shape. The results of the model show that the effects of morphology, i.e., the volumetric composition of the electrode and the dimensions of the particles, strongly influence the electrode resistance. However, in this model, the complex gas transport phenomena in the electrode were ignored, despite their importance. Chen et al. [6] applied the electrode microscopic model with random packing sphere theory to develop a mechanistic model for oxygen reduction at YSZ/LSM interface. A complete microscopic model for YSZ/LSM composite cathode considering all forms of overpotentials was developed and established the interrelationship among the transport phenomena, electrochemical processes and the microstructure of the composite cathode. Deseure et al. [7] developed a microscopic model for a composite cathode similar to Chen et al. [6]. Simulation was conducted to predict the optimal design parameters, i.e., cathode thickness, particle size. Hussain et al. [8] applied the electrode microscopic model with random packing sphere theory to consider on an anode-supported planar SOFC with thin layer reaction zone in the vicinity of electrolyte. Their results have shown that the better cell performance is obtained when the volume fraction of electronic conducting particles is approximately equal to that of ionic conducting particles in reaction zone. Ni et al. [9] applied the electrode microscopic model with random packing sphere theory to develop a mathematical model for modeling the performance of SOFC with functionally graded electrodes. The model considered all forms of overpotentials and was able to capture the coupled electrochemical reactions and mass transport involved in the SOFC operation. Micro-structural grading could significantly
enhance the gas transport but had negligible effects on the ohmic and activation overpotentials, especially for thick electrodes. Hussain et al. [10] applied the electrode microscopic model with random packing sphere theory with thin layer reaction zone in the vicinity of electrolyte. The model takes into account the transport of multi-component mixture in an electrode together with electrochemical reaction.

In the present study, a microscopic model of the SOFC porous electrode, formed by mixture of electronic and ionic conductor is developed. The mathematical model is based on the assumption that the electrodes were composed of spherical-shaped particles with the random packing sphere model [5] and takes into account electronic, ionic, and gas transport together with the electrochemical reaction. This works was extended from our previous works [11-14] that were developed the micro-scale mathematical model of a planar anode - supported SOFC by maximizing the SOFC performance with the minimization of the SOFC overpotential losses. But in this works are considered in the forms of the electrode reactive surface area with the intention to maximize the SOFC performance by optimally design the microstructure of SOFC electrodes. The effect of various key operating and design conditions on the performance of an anode-supported SOFC is investigated.

2. Modeling and governing equations

2.1. The cell geometry

An illustration of physical domain of a SOFC is shown in Fig. 1. Part (a) shows a structure of a cell with multiple flow channels, part (b) shows cross-sectional representation of a composite anode and part (c) shows cross – sectional representation of a composite cathode. The electrolyte was made of Yttria – Stabilized Zirconia (YSZ).
In part (b) of Fig. 1, the light gray spherical particles represent the ionic conducting particles that in this case are YSZ (Yttria-Stabilized Zirconia) and the dark gray represent the electronic conducting particles that in this case is Nickel (Ni). The parameter $N_i$ represents the rate of mass transport (or denotes as the molar flux of each species, mol m$^{-2}$ s$^{-1}$) for both of reactant ($H_2$) flowing from the flow channel to the reaction sites of the anode and product ($H_2O$) removed from the reaction sites to the flow channel. In this study, the concentration of each specie $y_i$ varies only in the vertical direction or in the $x-$direction. The parameter $x_a$ represents the anode distance, where $x_a = 0$ refers to the position at the anode outermost surface and $x_a = t_{an}$ refers to the position at the interface between anode and electrolyte. In the similar way, the light gray spherical particles in part (c) of Fig. 1 represent the ionic conducting particles that in this case are YSZ (Yttria-Stabilized Zirconia), while the dark gray represent the electronic conducting particles that in this case is LSM (Strontium-doped Lanthanum Manganite). The parameter $x_c$ represents the cathode distance, where $x_c = 0$ refers to the position at cathode outermost surface and $x_c = t_{cat}$ refers to the position at the interface between cathode and electrolyte. As the electrochemical reaction is governed by the complex transport phenomena in the electrode, it is necessary to make the assumptions to simplify the model calculation.

2.2. The Model Assumptions

The cell is assumed to operate under steady state and to assume that the parameters vary only in the vertical direction. The fuel is the humidified with $H_2$ 0.95 mole fraction and $H_2O$ 0.05 mole fraction and the oxidant is air. The reactant gas mixtures are approximated as ideal gases. Temperature and total pressure are constant and uniform throughout the entire electrode. The total pressure gradient inside the electrode is assumed to be negligible. The mass transfer process inside the porous electrode is by means of diffusion [15-18]. For SOFC, Suwanwarangkul et al. [16] was concluded that the dusty-gas model (DGM) is the most appropriate to simulate gas transport phenomena inside the SOFC electrode. The solid phases of ionic and electronic conducting particles inside the electrodes are considered to be homogeneous. These parameters are the porosity ($\varepsilon$), the tortuosity ($\tau$) and the reactive surface area for electrochemical reaction within electrodes ($A_V$) can be described below as:

In the unit cell, based on the binary random packing of sphere proposed by Bouvard and Lange [19] and Costamagna et al. [5], each particle has co-ordination number equal to 6. The arrangements of particles in a unit cell are divided into two configurations. The first configuration is that in the unit cell with the centre particle is the ionic conducting particle and the others six attached particles are the electronic conducting particles. Another configuration is in the opposite of the first one. The porosity of each configuration is shown as.
The porosity averaging over some possible arrangement of the particle inside the unit cell is:

\[
e = \frac{\varepsilon_1 + \varepsilon_2}{2}
\]

The second major property that mainly affects the transport phenomena within a porous electrode is the tortuosity. The tortuosity in porous media can also be determined by experiments of Comiti and Renaud [20].

\[
\tau = 1 + 0.41(\ln(1/e))
\]

The most important characteristic of porous electrodes is the active surface area for electrochemical reaction \(A_v, \text{m}^2\text{m}^{-3}\). The parameter \(A_v\) can be calculated with the method based on the particle coordination number in binary random packing of spheres proposed by Costamagna et al. [5], given as

\[
A_v = \pi \sin^2 \theta r_e^2 n_\text{el} n_\text{io} Z Z_\text{el} Z_\text{io} p_\text{el} p_\text{io} \frac{Z}{Z}
\]

All above-mentioned parameters required to calculate \(A_v\) [5] related to each other as shown here:

\[
n_\text{el} = \frac{\phi}{[\phi + ((1-\phi)/(r_\text{el} / r_\text{d})^3)]}
\quad \text{and} \quad
n_\text{io} = 1 - n_\text{el}
\]

\[
Z_\text{el} = 3 - \frac{Z-3}{[n_\text{el} + (1-n_\text{el})(r_\text{el} / r_\text{d})^2]^2}
\quad \text{and} \quad
Z_\text{io} = 3 + \frac{(Z-3)(r_\text{el} / r_\text{d})^2}{[n_\text{el} + (1-n_\text{el})(r_\text{el} / r_\text{d})^2]^2}
\]

\[
p_\text{el} = \left[1 - (4Z_\text{el} - 3)^2\right]^{0.4}
\quad \text{and} \quad
p_\text{io} = \left[1 - (4Z_\text{io} - 3)^2\right]^{0.4}
\]

\[
Z_{\text{el},\text{el}} = \frac{n_\text{el} Z_\text{el}^2}{Z}
\quad \text{and} \quad
Z_{\text{io},\text{io}} = \frac{n_\text{io} Z_\text{io}^2}{Z}
\]

\[
n_1 = \frac{1 - e}{(4/3)\pi r_e^3 [n_\text{el} + (1-n_\text{el})(r_\text{el} / r_\text{d})^3]}
\]

Equation (10) can be expressed in a term of tortuosity relation instead of porosity by,

\[
n_t = \frac{1}{e^{(\tau-1)/0.41}} \left[ (4/3)\pi r_e^3 [n_\text{el} + (1-n_\text{el})(r_\text{el} / r_\text{d})^3] \right]^2
\]
$\theta$ is the contact angle between electron and ion conducting particle, $r_{el}$ is the radius of the electron conducting particles, $n_i$ is the total number of particles per unit volume, $n_{el}$ and $n_{io}$ are the number of electron and ion conducting particles, $Z_{el}$ and $Z_{io}$ are the coordination number of electron and ion conducting particles. $Z$ is the total average particle coordination number in the electrode which is equal to 6 [5]. The $p_{el}$ and $p_{io}$ are the probabilities for an electron and an ion conducting particles that belong to the connecting ends of the electrode, respectively. $\varphi$ is a volumetric fraction of the electron conducting particle in an electrode, $Z_{el}$ represents the average coordination number between electronic particles and $Z_{io}$ represents the average coordination number between ionic particles [5]. For the microscopic scale modeling in this work, the model took into account of mass transport, electrode electrochemical reactions and charge transport. The modeling details of anode, cathode and electrolyte are described as follows.

2.3. Anode Side Modeling Equations

The configuration of a SOFC anode can be simply modeled as shown of Fig.1 (b). Charge balance in the electronic and ionic conducting particles can be written as

$$\nabla \cdot J_{e,a} = R_a \quad \text{or} \quad \nabla \cdot J_{i,a} = -R_a$$

(12)

$$\nabla \cdot J_{i,a} = -R_a \quad \text{or} \quad \nabla \cdot J_{i,a} = -A_v J_{n,a}$$

(13)

According to Butler -Volmer equation [7, 8], the volumetric current density produced in the anode $R_a$ (A m$^{-3}$) and the transfer current density $J_{n,a}$ (A m$^{-2}$) can be determined from :

$$R_a = A_{J_{n,a}} \left\{ \left( \frac{c_{H_2}}{c_{H_2,ref}} \right)^{\eta_{n,a}} \left\{ \frac{\alpha z F \eta_{a}}{RT} \right\} - \left\{ \frac{(1-\alpha) z F \eta_{a}}{RT} \right\} \right\}$$

(14)

$$J_{n,a} = J_{0,a} \left\{ \frac{P_{H_2}}{P_{H_2,ref}} \exp \left( \frac{\alpha z F \eta_{a}}{RT} \right) - \frac{P_{H_2,ref}}{P_{H_2,ref}} \exp \left( \frac{(1-\alpha) z F \eta_{a}}{RT} \right) \right\}$$

(15)

where $J_{e,a}$ and $J_{i,a}$ are the current density (Am$^{-2}$) in the electronic and ionic conducting particles. $J_{0,ref}$ is the reference exchange current densities at the reference concentration (c$_{ref}$). $J_{0}^{ref}$ is the reference exchange current density of the electrode. $P_{H_2,ref}$ and $P_{H_2,ref}$ are respectively the partial pressures of H$_2$O within the porous anode and at the anode surface. Similarly, $P_{H_2}$ and $P_{H_2}$ are the partial pressures of H$_2$ within the porous anode and at the anode surface. The parameter $\alpha$ is the charge transfer coefficient which is 0.5 [21], $z$ is the number of charges involved in a reaction. The overpotential at the anode $\eta_a$ [5, 22] is

$$\eta_a = (\phi_{e,a}^{0} - \phi_{i,a}^{0}) - (\phi_{e,a} - \phi_{i,a})$$

(16)

where $\phi_{i,a}$ and $\phi_{e,a}$ denote the ionic and electronic potentials. The superscript 0 represents the equilibrium state. The electronic and ionic potentials can be obtained from applying Ohm’s law as Eq. (17).

$$\nabla \cdot \phi_{e,a} = \rho_{e,a}^{eff} J_{e,a} \quad \text{and} \quad \nabla \cdot \phi_{i,a} = \rho_{i,a}^{eff} J_{i,a}$$

(17)
where \( \rho_{\text{eff}} \) is the effective resistivity (\( \Omega \cdot \text{m} \)) and \( J \) is the current density. The subscripts \( \text{i} \) and \( \text{e} \) represent ionic and electronic conductors, respectively. \( \rho_{\text{eff}} \) can be determined by Eq. (18) [8].

\[
\rho_{\text{eff}, \text{e}, \alpha} = \left(1 - \phi\right) \rho_{\text{e}, \alpha} \quad \text{and} \quad \rho_{\text{eff}, \text{i}, \alpha} = \left(1 - \phi\right) \left(1 - \sigma_{\text{i}, \alpha}\right) \rho_{\text{i}, \alpha}
\]  

(18)

where \( \sigma_{\text{e}} \) is the conductivity of electronic conductor. \( \sigma_{\text{i}} \) is the ionic conductivity.

The first and second derivatives of \( \eta_{\alpha} \) are,

\[
\frac{d\eta_{\alpha}}{dx} = \rho_{\text{eff}, \alpha} J_{\text{i}, \alpha} - \rho_{\text{eff}, \alpha} J_{\text{e}, \alpha} \quad \text{and} \quad \frac{d^2\eta_{\alpha}}{dx^2} = \rho_{\text{eff}, \alpha} \frac{dJ_{\text{i}, \alpha}}{dx} - \rho_{\text{eff}, \alpha} \frac{dJ_{\text{e}, \alpha}}{dx} = A_{\alpha} J_{\text{n}, \alpha} \left(\rho_{\text{eff}, \alpha} + \rho_{\text{e}, \alpha}\right)
\]  

(19)

\[
\frac{d^2\eta_{\alpha}}{dx^2} = \frac{p_{\text{H}_2}}{p_{\text{H}_2,0}} \exp\left(\frac{\alpha Z F \eta_{\alpha}}{R T}\right) - \frac{p_{\text{H}_2}}{p_{\text{H}_2,0}} \exp\left(-\frac{(1 - \alpha) Z F \eta_{\alpha}}{R T}\right)
\]  

(20)

The term \( A_{\alpha} \) relates to the electrode porosity (\( \varepsilon \)), the electrode tortuosity (\( \tau \)), the particle radius (\( r_{\text{io}} \), \( r_{\text{a}} \)) and a volume fraction of the electron conducting particle in an electrode (\( \phi \)). At the anode surface, \( J_{\text{i}, \alpha} = 0 \) and \( J_{\text{e}, \alpha} = J_{\text{total}} \). At the electrolyte interface, \( J_{\text{i}, \alpha} = J_{\text{total}} \) and \( J_{\text{e}, \alpha} = 0 \). The two boundary conditions for above second order differential Eq. (20) can be written as,

\[
\eta_{\alpha} \bigg|_{x = x_a = 0} = 0 \quad \text{and} \quad \frac{d\eta_{\alpha}}{dx} \bigg|_{x = x_a = t_{\text{an}}} = \rho_{\text{eff}, \alpha} J_{\text{total}}
\]  

(21)

The positions of \( x = x_a = 0 \) and \( x = x_a = t_{\text{an}} \) are shown in part (b) of Fig. 1.

The electrochemical reactions due to mass transport occur in SOFC electrode, mass transport through porous medium can be determined using concepts described in Ref. [14, 15]. In the steady state, the mass transport equation can be written as

\[
\nabla \cdot \mathbf{N}_i = R_i
\]  

(22)

where \( \mathbf{N}_i \) represent the rate of mass transport (or denotes as the molar flux of each species, mol m\(^{-2}\) s\(^{-1}\)) into porous media. \( R_i \) is the rate of reaction inside the porous medium (mol m\(^{-3}\) s\(^{-1}\)). The rates of reaction for \( \text{H}_2\text{O} \) and \( \text{H}_2 \) can be expressed as \( R_{\text{H}_2} = (-\alpha J_{\text{n}, \alpha})/(2F) \) and \( R_{\text{H}_2\text{O}} = (\alpha J_{\text{n}, \alpha})/(2F) \).

The rate of mass transport, \( \mathbf{N}_i \), generally depends on the operating conditions and the microstructure of material. The DGM, was used to develop the expressions for \( \mathbf{N}_i \) in this modeling. The mass flux of hydrogen can be determined by the Dusty Gas Model (DGM) as [14],

\[
\mathbf{N}_{\text{H}_2} = \frac{p}{RT} \left( \frac{1 - \alpha y_{\text{H}_2}}{D_{\text{H}_2, \alpha, \text{H}_2}} + \frac{1}{D_{\text{H}_2, k, \text{H}_2}} \right) \frac{dy_{\text{H}_2}}{dx}
\]  

(23)
where \( \alpha = 1 - \sqrt{M_{H_2}/M_{H_2O}} \). The parameters \( M_{H_2} \) and \( M_{H_2O} \) are the molecular weight of \( H_2 \) and \( H_2O \), respectively. The \( D_{H_2,k}^{eff} \) and \( D_{H_2O-H_2}^{eff} \) are the effective Knudsen diffusion coefficient of \( H_2 \) and the effective binary diffusion coefficient of \( H_2-H_2O \) [16] respectively.

By substituting Eq. (23) into Eq. (22), the governing equation of \( H_2 \) concentration becomes

\[
\frac{d^2 y_{H_2}}{dx^2} + \frac{\alpha}{D_{H_2O-H_2}^{eff}} \left( \frac{1}{D_{H_2,k}^{eff}} + \frac{1 - \alpha y_{H_2}}{D_{H_2O-H_2}^{eff}} \right) \left( \frac{dy_{H_2}}{dx} \right)^2 - \frac{A_n J_{n,a} RT}{2FP} \left( \frac{1}{D_{H_2,k}^{eff}} + \frac{1 - \alpha y_{H_2}}{D_{H_2O-H_2}^{eff}} \right) = 0
\]

Equation (24) is in the form of an ordinary differential equation, which can be solved by involving the following initial conditions. In Eqs. (25) and (26), \( \text{Dalton’s law of an ideal gas, } y_{H_2} = P_{H_2}/P_{H_2}^0 \) and the initial conditions are following as:

\[
IC.1: y_{H_2} \bigg|_{x=0} = y_{H_2, \text{bulk}}
\]

\[
IC.2: \frac{dy_{H_2}}{dx} \bigg|_{x=0} = -\frac{RT J_{n,\text{total}}}{2FP} \left( \frac{1 - \alpha y_{H_2, \text{bulk}}}{D_{H_2O-H_2}^{eff}} + \frac{1}{D_{H_2,k}^{eff}} \right)
\]

the mole fraction of \( H_2O \) can be obtained as:

\[
y_{H_2O} = 1 - y_{H_2}
\]

In the above mentioned equations, the gas molar fraction, gas diffusion coefficients, current density, reaction rate, and the overpotential are dependent of depth in the vertical direction (x). Due to the complicated phenomena involved, an iterative scheme is used to solve the non-linear equations. The iterative computation is successful if a convergence is obtained. Therefore, the differential equation was solved numerically in MATLAB [23]. After obtaining the distributions of species concentration, current densities, and overpotentials, the overall electrode overpotential can be determined [5].

\[
\eta_{e,n} = (\phi_{e,n}^0 - \phi_{t,n}^0) - (\phi_{e,n(x=0)}^0 - \phi_{t,n(x=t_m)}^0)
\]

2.4. Cathode Side Modeling Equations

Similar to the anode, the coupled electrochemical reactions and transport behaviors at the cathode can be determined from

\[
\frac{d^2 \eta_{e}}{dx^2} = \rho_{e,c} \frac{dJ_{e,c}}{dx} - \rho_{e,c} \frac{dJ_{e,c}}{dx} = A_n J_{n,e} (\rho_{e,c} + \rho_{e,c})
\]
\[
\frac{d^2 \eta}{dx^2} = A_e J_{0,c}^\text{ref} (\rho_{e,c}^{\text{eff}} + \rho_{e,c}^{\text{eff}}) \left\{ \frac{P_{O_2}}{p_0^{\text{eff}}} \exp \left( \frac{\alpha Z F \eta}{RT} \right) - \exp \left( -\frac{(1 - \alpha) Z F \eta}{RT} \right) \right\} \tag{30}
\]

\[
\nabla \cdot J_{e,c} = -A_i J_{n,c} = -A_i J_{0,c}^\text{ref} \left\{ \frac{P_{O_2}}{p_0^{\text{eff}}} \exp \left( \frac{\alpha Z F \eta}{RT} \right) - \exp \left( -\frac{(1 - \alpha) Z F \eta}{RT} \right) \right\} \tag{31}
\]

Similar to the anode, the boundary conditions for Eqs. (30) and (31) are

\[
x = 0; J_{e,c} = J_{\text{total}} \quad \text{and} \quad \frac{d \eta}{dx} = -\rho_{e,c}^{\text{eff}} J_{\text{total}} \quad \text{and} \quad x = t_{\text{cat}}; J_{i,c} = J_{\text{total}} \quad \text{and} \quad \frac{d \eta}{dx} = \rho_{i,c}^{\text{eff}} J_{\text{total}} \tag{32}
\]

The positions of \( x = x_c = 0 \) and \( x = x_c = t_{\text{cat}} \) are shown in part (c) of Fig. 1.

Because the flux of nitrogen does not participate in the electrochemical reaction on the cathode side, only the oxygen becomes part of the electrochemical reaction at the cathode. The transport of \( O_2 \) can be described by the self-diffusion mechanism \[24, 14\],

\[
\frac{d P_{O_2}}{dx} = -\frac{RT J_{e,c}^{\text{eff}}}{4FD_{O_2}^\text{eff}P_{C}} (P_C - (D_{O_2,k}^{\text{eff}} / (D_{O_2,k}^{\text{eff}} + D_{O_2-N_2}^{\text{eff}})) - P_{O_2}) \tag{33}
\]

where \( P_{O_2} \) is the partial pressure of oxygen at the cathode reaction sites. The boundary condition for the transporting \( O_2 \) in Eq. (33) is \( P_{O_2} = P_{O_2}^0 \) at \( x = 0 \). The cathode overpotential then can be expressed as Eq. (34) \[5\],

\[
\eta_{c} = (\phi_{i,c}^0 - \phi_{e,c}^0) - (\phi_{i,c}(x = t_{\text{cat}}) - \phi_{e,c}(x = 0)) \tag{34}
\]

2.5. The Electrolyte Modeling Equations

Once the molecular oxygen has been converted to oxygen ions it must migrate through the electrolyte to the fuel side of the cell. As with the other materials, it must be chemically, thermally, and structurally stable across a wide temperature range. It is typically made from Yttria - Stabilized Zirconia (YSZ). The overpotential of the dense electrolyte can be determined by Ohm’s law,

\[
\eta_{\text{elec}} = J_{\text{total}} R_{\text{elec}} t_{\text{elec}} \tag{35}
\]

where \( R_{\text{elec}} \) and \( t_{\text{elec}} \) are the resistivity (\( \Omega \)m) and thickness (m) of the electrolyte, respectively.

3. Model validation

For validating this model, we compare results to available experimental data from Rogers et al. \[25\] and from Hussain et al. \[8\] by using parameters in Table 1.
The measured current density and cell voltage data were compared with this theoretical simulation results as plotted in Fig. 2. A good agreement between present simulation results, former simulation results and experimental data was found. The comparison results confirm the validity of this present SOFC model algorithm. The R²-value, an indicator between 0 and 1 which can reveal how closely the predicted values correspond to the experimental data, is obtained for the present model as 0.989. However, some parameters that recommended by Hussain et al [8] are used in place of unavailable parameters in Roger et al’s work. The value of these latter parameters are consistent with other studies [5 -7, 9, 21-22, 24, 26-29].

Table 1. Parameters used for model validation [25]

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating temperature, T (K)</td>
<td>1073</td>
</tr>
<tr>
<td>Total pressure, P (atm)</td>
<td>1</td>
</tr>
<tr>
<td>Fuel composition, xH₂, xH₂O</td>
<td>0.95, 0.05</td>
</tr>
<tr>
<td>Air composition, xO₂, xN₂</td>
<td>0.21, 0.79</td>
</tr>
<tr>
<td>Conductivity of electronic conductor of anode, σe,a (Sm⁻¹)</td>
<td>71428.57</td>
</tr>
<tr>
<td>Conductivity of electronic conductor of cathode, σe,c (Sm⁻¹)</td>
<td>5376.34</td>
</tr>
<tr>
<td>Conductivity of ionic conductor of anode, σi,a (Sm⁻¹)</td>
<td>0.64</td>
</tr>
<tr>
<td>Conductivity of ionic conductor of cathode, σi,c (Sm⁻¹)</td>
<td>0.64</td>
</tr>
<tr>
<td>Electrolyte conductivity, κ_elec (S/m)</td>
<td>0.64</td>
</tr>
<tr>
<td>Anode electrode layer thickness, t_a (µm)</td>
<td>1000.0</td>
</tr>
<tr>
<td>Cathode electrode layer thickness, t_c (µm)</td>
<td>50.0</td>
</tr>
<tr>
<td>Electrolyte thickness, t_e (µm)</td>
<td>10.0</td>
</tr>
<tr>
<td>Porosity of anode and cathode, ε</td>
<td>0.375</td>
</tr>
<tr>
<td>Tortuosity of anode and cathode, τ</td>
<td>2.75</td>
</tr>
<tr>
<td>Pore radius of anode and cathode, r_p (µm)</td>
<td>0.75</td>
</tr>
<tr>
<td>Contact angle between e and O⁺ conducting particles, θ (°) [8]</td>
<td>15</td>
</tr>
<tr>
<td>Radius of electronic conducting particle, r_e (µm) [8]</td>
<td>0.1</td>
</tr>
<tr>
<td>Radius of ionic conducting particle, r_i (µm) [8]</td>
<td>0.1</td>
</tr>
<tr>
<td>Volume fraction of electronic conducting particle, φ [8]</td>
<td>0.5</td>
</tr>
<tr>
<td>Volume fraction of ionic conducting particle, 1-φ [8]</td>
<td>0.5</td>
</tr>
<tr>
<td>Reference H₂ concentration, cH₂(req) (mol m⁻³) [8]</td>
<td>10.78</td>
</tr>
<tr>
<td>Reference O₂ concentration, cO₂(req) (mol m⁻³) [8]</td>
<td>2.38</td>
</tr>
<tr>
<td>Reference exchange current density for H₂ oxidation, J₁H₂(req) (A m⁻²) [8]</td>
<td>1320</td>
</tr>
<tr>
<td>Reference exchange current density for O₂ reduction, J₁O₂(req) (A m⁻²) [8]</td>
<td>400</td>
</tr>
<tr>
<td>Reaction order for H₂ oxidation, γ₁H₂ [8]</td>
<td>0.5</td>
</tr>
<tr>
<td>Reaction order for O₂ reduction, γ₁O₂ [8]</td>
<td>0.5</td>
</tr>
</tbody>
</table>
4. Results and discussion

The developed SOFC model can be used to investigate the effect of electrode microstructure parameters on cell performance. The dimension of cell components and standard parameters used in calculations listed in Table 2.

Table 2. Standard parameters used in model calculation

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating temperature, T (K)</td>
<td>1073</td>
</tr>
<tr>
<td>Operating pressure, P (atm)</td>
<td>1</td>
</tr>
<tr>
<td>H₂ and H₂O in fuel mixture inlet mole fraction</td>
<td>0.95, 0.05</td>
</tr>
<tr>
<td>O₂ and N₂ in air inlet mole fraction</td>
<td>0.21, 0.79</td>
</tr>
<tr>
<td>Anode thickness, t_a (µm.)</td>
<td>2000</td>
</tr>
<tr>
<td>Anode tortuosity, τ_a</td>
<td>(Eq. (4))</td>
</tr>
<tr>
<td>Porosity of anode, ε_a</td>
<td>(Eq. (3))</td>
</tr>
<tr>
<td>Anode pore radius, r_p (µm.)</td>
<td>0.5</td>
</tr>
<tr>
<td>Cathode thickness, t_c (µm.)</td>
<td>60</td>
</tr>
<tr>
<td>Cathode tortuosity, τ_c</td>
<td>(Eq. (4))</td>
</tr>
<tr>
<td>Porosity of cathode, ε_c</td>
<td>(Eq. (4))</td>
</tr>
<tr>
<td>Cathode pore radius, r_c (µm.)</td>
<td>0.5</td>
</tr>
<tr>
<td>Electrolyte thickness, t_lect (µm.)</td>
<td>60</td>
</tr>
<tr>
<td>Contact angle between e⁻ and O²⁻ conducting particles, θ (°)</td>
<td>15</td>
</tr>
<tr>
<td>Radius of electronic conducting particle, r_el(µm.)</td>
<td>0.1</td>
</tr>
<tr>
<td>Radius of ionic conducting particle, r_i(µm)</td>
<td>0.1</td>
</tr>
<tr>
<td>Reference exchange current density for H₂ oxidation, J_{0,e,x} (A m⁻²)</td>
<td>1320</td>
</tr>
<tr>
<td>Reference exchange current density for O₂ reduction, J_{0,o,c} (A m⁻²)</td>
<td>400</td>
</tr>
<tr>
<td>Total average particle coordination number in electrode, Z</td>
<td>6</td>
</tr>
<tr>
<td>Charge transfer coefficient, α</td>
<td>0.5</td>
</tr>
<tr>
<td>Conductivity of electronic conductor of anode, σ_{e,a} (Sm⁻¹)</td>
<td>2e6</td>
</tr>
<tr>
<td>Conductivity of electronic conductor of cathode, σ_{e,c} (Sm⁻¹)</td>
<td>1e4</td>
</tr>
<tr>
<td>Conductivity of ionic conductor of anode, σ_{i,a} (Sm⁻¹)</td>
<td>3.44e4*(exp(-10300/T))</td>
</tr>
<tr>
<td>Conductivity of ionic conductor of cathode, σ_{i,c} (Sm⁻¹)</td>
<td>3.44e4*(exp(-10300/T))</td>
</tr>
<tr>
<td>Faraday constant, F (C mol⁻¹)</td>
<td>96485</td>
</tr>
</tbody>
</table>
The porosity versus the particle size ratio is plotted in Fig. 3 and for modeling purpose, the tortuosity was obtained by the experiments on flow through beds packed with sphere that are arranged as a binary random packing of spheres with an average number of contact equal to 6 [19]. The experiment was done by Comiti and Renaud [20], and proposes a relation for calculating the tortuosity which is given in Eq. (4). The tortuosity model being expressed as a function of porosity confirms the dominant effect of the particles radius ratios \( r_{io}/r_{el} \) on characteristics of electrode microscopic structure, as shown in Fig. 4. The electrode tortuosity increases when increasing of the particle radius ratio. The relation between the electrode porosity and tortuosity of electrode packed with spherical shaped particles at various \( r_{io}/r_{el} \) is shown in Fig. 5. The electrode tortuosity decreases when increasing the electrode porosity. The electrode tortuosity and porosity relate to the electrical conductivity and diffusion coefficient of reactant species, which strongly affects on electrochemical reaction of SOFC. Figure 6 shows the relation between the volumetric fraction of the electron conducting particle \( \phi \) and the dimensionless electrochemical active surface area of the porous electrodes. The result shows that the highest active surface area for electrochemical reaction of the electrode occurs at \( r_{io}/r_{el} \) equal to unity and \( \phi \) is equal to 0.5, so hence providing the best performance.
Figure 7 shows the effect of the electrode tortuosity (τ) on the electrochemical active surface area (A_V) at the different size ratio between \( r_{io}/r_{el} \) and \( \phi \) of 0.5. The optimal tortuosity (\( \tau_{opt} \)) giving the maximum electrochemical active surface area seems to change according to the particle size ratio (\( r_{io}/r_{el} \)). However, a peak of A_V appears in a tortuosity range of 1.3 to 1.5. Figure 8 shows the effect of electrode porosity (\( \varepsilon \)) on the electrochemical active surface area at the different size ratio \( r_{io}/r_{el} \) and at the optimum \( \phi \) of 0.5. Similar to Fig. 7, the optimum porosity giving the peak value of A_V varies accordingly to the given particle size ratio. The maximum A_V is in the porosity range of 0.3 to 0.7. Figure 9 shows the contour plot of A_V corresponding to \( \varepsilon \) and \( \tau \). The peak A_V is in the tortuosity range of 1.35 to 1.45 and the porosity range of 0.35 to 0.50 as in Fig 9. Meng et al. [9] indicated that the SOFC spherical particle electrodes have the normal radii range between 0.012 and 5.0 \( \mu \)m and the achievable porosity range between 0.3 and 0.7. For the electrode porosity less than 0.3, the extent of overlap between spherical particles increases with decreasing porosity, causing the active surface area (A_V) to decrease considerably [6, 9]. In the opposite way, increasing the porosity then increases the void fraction and decreases the solid fraction of the porous electrode resulting in the reduction of the active surface area available for the electrochemical reaction. Moreover, the effective ionic and electron conductivities of the porous electrode decrease with the increase of porosity, which results in the increase of ohmic overpotential. Although the concentration overpotential decreases with the increase of porosity due to the increase mass transport rates, the cell performance decreases due to increase of ohmic overpotential with porosity. Kenney and Karan [30] have indicated that the achievable porosity for the high SOFC performance is in the range of 0.3 to 0.5.
This study the microstructure geometric relation are established and used to optimize the electrode performance by including the effect of electrode microstructure on the SOFC overpotentials. Because the anode is much thicker than the cathode; thus the overall overpotential depends on the anode geometry. The effect of the solid volumetric fraction of the electron conducting particle (φ) of the electrodes on the anode overpotentials (n_a) at various r_o/r_e is shown in Fig. 10. Figure 10 shows that cell overpotential decreases when φ in the reaction zone layers is increased from 0.4 to 0.5, and decreases as becomes greater than 0.5. The increase and decrease in cell overpotential with φ demonstrate the fact that the largest active area is achieved when the dimensions and volumetric fractions of the ion conducting and electron conducting particles are equal [5]. From Fig. 10., it can be seen that the minimum overpotential occurs the particle size ratio r_o/r_e in the range of 1 to 1.25. Figure 11 shows the combined effect of anode thickness and particle sizes on the anode overpotential. The optimal electrode thickness is evaluated at the typical operating current density of 10,000 Am^2. The electrode porosity (ε) is 0.4 and φ is 0.5. The particle size ratio r_o/r_e is equal to unity and also the standard parameters used in this calculation were provided in Table 2. The anode thickness could lead to the optimum performance or minimum anode overpotential.

Fig. 6. The corresponding dimensionless active surface area (A_A) according to the solid volume fraction of electron conducting particle (φ) when r_o is in different sizes of r_e

Fig. 7. The effect of tortuosity (τ) due to the particle size ratio (r_o/r_e) that takes into account the contrast of porosity on the electrochemical active surface area when φ = 0.5
In Fig. 11 for the particle radii of 0.5, 0.4, 0.3, 0.2, 0.1, 0.05 and 0.025 μm., the anode overpotential reaches the minimum at the anode thickness of roughly 900, 800, 750, 700, 600, 650 and 675 μm, respectively. The value of overall overpotential reaches its minimum when the particle radius is 0.1 μm and the optimum anode thickness is 600 μm. The anode performance deteriorates when the anode becomes very thin. This is mainly caused by insufficient reaction sites of the thin anode for the electrochemical reactions. Normally, with the decrease of particle size, the performance of the composite anode can be improved due to the increase of the active three phase boundary length per unit volume. However, too small particle size creates tiny pore size in the composite anode and results in high concentration overpotential. The overall performance of the composite anode is determined by the combined effects of the increased active sites and the retarded hydrogen transport. There exists a minimum overpotential at a certain particle radius. When the particle radius is smaller than necessary, the gas diffusion process dominates the anode performance. Otherwise, the active site areas are the dominant factor.

Figure 12 shows the combined effect of cathode thickness and particle size on the cathode overpotential. In Fig. 12, it can be seen that for particle radii of 0.5, 0.4, 0.3, 0.2, 0.1, 0.05 and 0.025 μm., the cathode overpotential reaches the minimum at cathode thickness of roughly 35, 31.1, 29.2, 27.2, 23.3, 25.3 and 26.3 μm, respectively, which suggests that the larger the particle size used, the thicker the cathode should be to achieve minimum cathode overpotential. In Fig. 12, the value of overall overpotential reaches its minimum when the particle radius is 0.1 μm and the optimum cathode thickness is 23.3 μm. The performance of the composite cathode is determined by the combined effects of the active site areas and the retarded oxygen transport [5]. There exists a minimum overpotential at a certain particle radius.
Fig. 9. The electrochemical active surface area ($A_v$) in corresponding to porosity ($\varepsilon$) and tortuosity ($\tau$)

Fig. 10. The effect of the particle radius ratio ($r_\text{io}/r_\text{el}$) on the anode overpotential at various volumetric fraction of the electron conducting particle ($\phi$)

Fig. 11. Effect of anode thickness on the anode overpotentials as a function of particle size at $\phi = 0.5$
5. Conclusion

A micro scale model of solid oxide fuel cell (SOFC) has been developed. The model considers the common thick-anode supported SOFC in which the electrode microstructure is packed by spherical shaped ionic and electronic conducting particles. The predicted cell performance is validated with the experimental data found in the literature. The investigation confirms the strong effects of microstructure geometry to improve the SOFC performance, especially the increasing of the electrochemical active surface area. The largest active surface area is achieved when the size and solid volumetric fraction of ion and electron conducting particles are equal; the optimal thicknesses of electrodes are also investigated. For both anode and cathode, the optimal particle radius ratio $r_{io}/r_{el}$ of 1.0 leads to the optimal corresponding porosity ($\varepsilon$) and tortuosity ($\tau$). A particle size of 0.1 μm packed in a cell operating at 1.0 atm and 1073 K leads the minimal anode overpotential of 0.059 volt at the anode thickness of 600 μm and the minimal cathode overpotential of 0.05 volt at the cathode thickness of 23.3 μm.

References


