The co-flow planar anode-supported solid oxide fuel cell micro-scale model

Penyarat Saisirirat*

Department of Mechanical Engineering Technology, College of Industrial Technology, King Mongkut's University of Technology North Bangkok, 1518, PrachaRat 1 Road, Wongsawang, Bangsue , Bangkok, 10800, Thailand

Abstract:
Solid Oxide Fuel Cells (SOFCs) are of great interest due to their high energy efficiency, low emission level, and multiple fuel utilization. In this study, a mathematical model of a co-flow planar anode-supported SOFC has been developed. The model simultaneously solves mass transport equations coupled with electrochemical reaction, as well as transportation of electrons and ions through the respective spherical shaped electron and ion conducting particles inside the electrodes. The influence of electrode microstructure on cell performance was investigated. The investigation confirmed the strong effects of microstructure geometry, especially the electrochemical active surface area (A_v), on the SOFC performance. The largest A_v is achieved when the size and solid volumetric fraction of ion and electron conducting particles are equal. The model was validated with existing experimental results from the available literature.

Keywords: *Electrochemical reaction; Microstructure; Solid Oxide Fuel Cell (SOFC); Spherical – shaped particles*

**Corresponding author. Tel.: +66-555-2000 ext 6353, Fax: +66-587-3981*
E-mail address: penyaratc@kmutnb.ac.th, penyarat@gmail.com

1. Introduction

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 micro-scale modeling. Numerous micro-scale models of SOFCs exist in the literatures, varying in used assumptions. Literature reviews showed that the electrode micro-scale model of SOFCs can roughly be divided into pore model (Tanner et al., 1997), random resistor network model (Sunde, 1995; Sunde, 1996(a); Sunde, 1996(b)) and random packing sphere model (Costamagna et al., 1998). The application of the random packing sphere model is shown as Costamagna et al. (Costamagna et al., 1998) has developed a micro-scale model of SOFC with random packing sphere electrode. 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 strongly influence the electrode resistance. However, in this model, the complex gas transport phenomena in the electrode were ignored. Hussain et al. (Hussain et al., 2006) applied the electrode micro-scale 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 increase of either porosity or tortuosity of electrodes leads to worse cell performance, while 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. (Meng et al., 2007) applied the electrode micro-scale model with random packing sphere theory to develop a mathematical model for modeling the performance of SOFC with functionally graded electrodes. In the present study, a micro-model of the SOFC porous electrode, formed by mixture of electronic and ionic conductor is developed. The model is based on the assumption that the electrodes were composed of spherical-shaped particles with the random packing sphere model and takes into account electronic, ionic, and gas transport together with the electrochemical reaction. This works was extended from our previous works (Chinda et al., 2011) and the work is considered in the forms of the electrode reactive surface area with the intention to maximize the SOFC performance.

2. Modeling and governing equations

An illustration of physical domain of a SOFC is shown in Fig. 1 The most important characteristic of porous electrodes is the active surface area for electrochemical reaction (A_v, m^2m^{-3}), given as Costamagna et al. (1998).

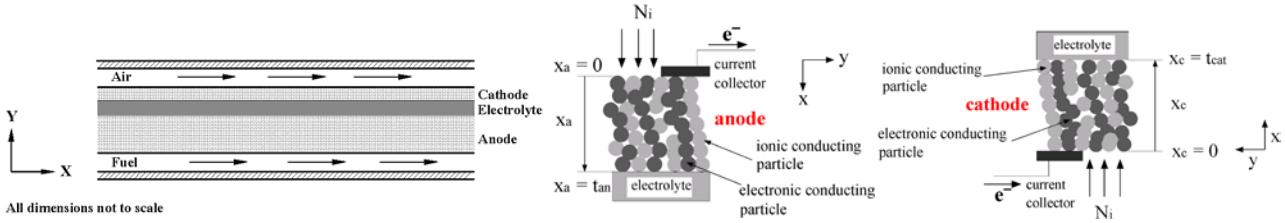
$$A_v = \pi \sin^2\theta r_{el}^2 n_t n_{el} n_{io} \left(Z_{el} Z_{io}/Z\right) p_{el} p_{io}, \quad n_{el} = \varphi/[\varphi+((1-\varphi)/(r_{io}/r_{el})^3)], \quad n_{io} = 1-n_{el} \tag{1}$$

$$Z_{el} = 3+\left(Z-3/[n_{el}+(1-n_{el})(r_{io}/r_{el})^2]\right), \quad Z_{io}=3+\left((Z-3)(r_{io}/r_{el})^2/[n_{el}+(1-n_{el})(r_{io}/r_{el})^2]\right) \tag{2}$$

$$p_{el} = \left[1-\left(4-Z_{el-el}\right)^{2.5}\right]^{0.4}, \quad p_{io} = \left[1-\left(4-Z_{io-io}\right)^{2.5}\right]^{0.4}, \quad Z_{el-el} = n_{el} Z_{el}^2/Z, \quad Z_{io-io} = n_{io} Z_{io}^2/Z \tag{3}$$

$$n_t = (1-\varepsilon)/(4/3)\pi r_{el}^3 [n_{el}+(1-n_{el})(r_{io}/r_{el})^3] \tag{4}$$

θ is the contact angle between electron and ion conducting particle, r_{el} is the radius of the electron conducting particles, n_t 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 (Costamagna et al., 1998). 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. φ is a volumetric fraction of the electron conducing particle in an electrode, Z_{el-el} and Z_{io-io} represent the average coordination number between electronic and ionic particles (Costamagna et al., 1998).



(a) (b) (c)

Fig. 1 (a) Co-flow planar anode-supported SOFC (b) Anode cross section (c) Cathode cross section.

Anode side modeling equations

From the derivation that is given the second derivative of the overpotential at the anode η_a is,

$$\frac{d^2\eta_a}{dx^2} = A_v J_{0,a}^{ref} (\rho_{i,a}^{eff} + \rho_{e,a}^{eff}) \left\{\left(P_{H_2}/P_{H_2}^0\right) exp\left((\alpha z F \eta_a)/(RT)\right) - \left(P_{H_2O}/P_{H_2O}^0\right) exp\left(-((1-\alpha) Z F \eta_a/(RT))\right)\right\} \tag{5}$$

At the anode surface, $J_{i,a} = 0$ and $J_{e,a} = J_{total}$. At the electrolyte interface, $J_{i,a} = J_{total}$ and $J_{e,a} = 0$. The two boundary conditions for above second order differential Eq. (5) can be written as,

$$x = x_a = 0, \left.\frac{d\eta_a}{dx}\right|_{x=0} = -\rho_{e,a}^{eff} J_{total} \quad \text{and} \quad x = x_a = t_{an}, \left.\frac{d\eta_a}{dx}\right|_{x=t_{an}} = \rho_{i,a}^{eff} J_{total} \tag{6}$$

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

Cathode side modeling equations

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

$$\frac{d^2\eta_c}{dx^2} = A_v J_{0,c}^{ref} (\rho_{i,c}^{eff} + \rho_{e,c}^{eff}) \left\{\left(P_{O_2}/P_{O_2}^0\right) exp\left((\alpha z F \eta_c)/(RT)\right) - exp\left(-((1-\alpha) Z F \eta_c/RT)\right)\right\} \tag{7}$$

Similar to the anode, the boundary conditions for Eq. (7) is

$$x = 0 ; J_{e,c} = J_{total} \text{ and } \frac{d\eta_c}{dx} = -\rho_{e,c}^{eff} J_{total} \quad \text{and} \quad x = t_{cat} ; J_{i,c} = J_{total} \text{ and } \frac{d\eta_c}{dx} = \rho_{i,c}^{eff} J_{total} \tag{8}$$

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

The electrolyte modeling equations

The overpotential of the dense electrolyte can be determined by Ohm's law,

$$\eta_{elec} = J_{total} R_{elec} t_{elec} \tag{9}$$

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

3. Model validation

For validating this model, that compare results to available experimental data from Rogers et al. (Rogers et al., 2003) and from Hussain et al. (Hussain et al., 2006). In Rogers et al.'s experiments, the anode, the cathode and the electrolyte were made of Nickel-doped Yttria-Stabilized Zirconia (Ni/YSZ), Strontium-doped Lanthanum Manganite (LSM or $La_{0.8}Sr_{0.2}MnO_3$) and Yttria-Stabilized Zirconia (YSZ), with the thickness about 1 mm., 50 μm. and 10 μm., respectively. Experiments were done at a pressure of 1 atm, temperature of 1073 K, H_2 molar fraction of 95% (5% H_2O) and O_2 is from air. A good agreement between present simulation results, former simulation results and experimental data was found in Fig 2.

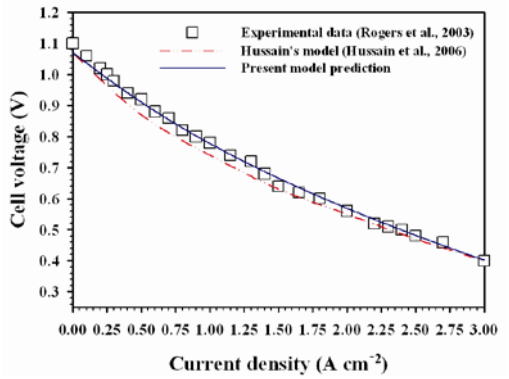


Fig. 2 The comparison between a model prediction and experimental results of Rogers et al. (2003)

4. Results and discussion

The developed model can be used to investigate the design parameters, especially the geometry of electrode microstructure on the performance of a co-flow planar anode-supported SOFC. The results of the model calculation are shown in Fig. 3 about the relation between the volumetric fraction of the electron conducting particle (φ) and the dimensionless electrochemical active surface area of the porous electrodes. The result shows that the highest active surface area for electrochemical reaction of electrode occurs at r_{io}/r_{el} equal to unity and φ is equal to 0.5.

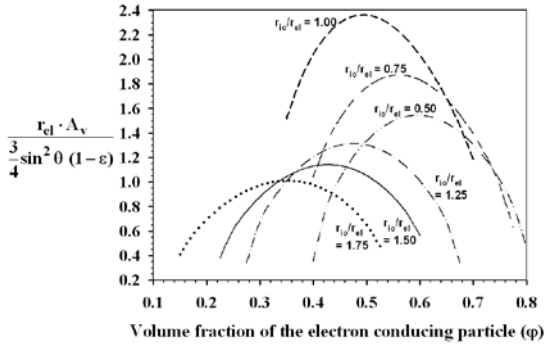
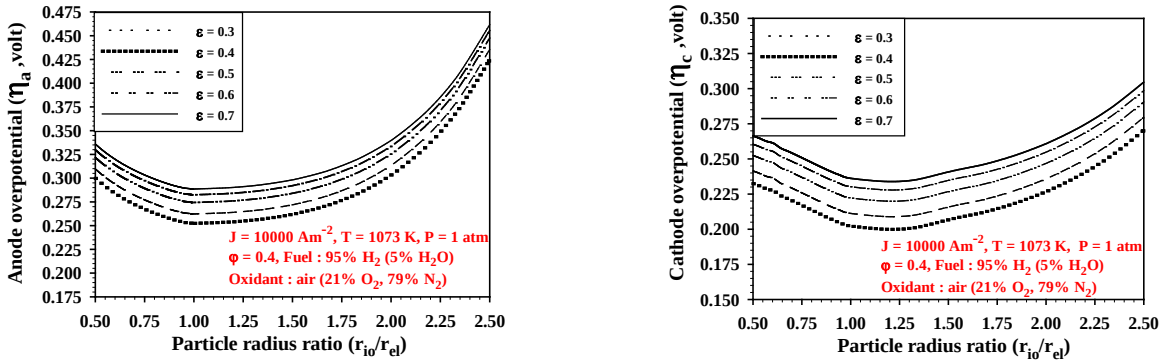


Fig. 3 The corresponding dimensionless active surface area ($\tilde{A}_v$) according to the solid volume fraction of electron conducting particle (φ) when r_{io} is in different sizes of r_{el}.

For both anode and cathode results in Fig. 4, the minimum overpotentials were found at the particle size ratio between the ionic and electronic conducting particles (r_{io}/r_{el}) of about 1 to 1.25. The results agree well with the results reported by Costamagna et al.'s work (Costamagna et al., 1998). Consider again in Fig 4, it can be seen that for both figures the minimum overpotential is found at the porosity equal to 0.4. Reducing porosity that means having more solid particles available to facilitate the transport of electronic and ionic charges can increase the cell performance. In addition, decreased porosity can also increase the active surface area for electrochemical reaction. However, decreasing porosity lowers the space available for gas transport. This work is aimed to find the optimal value of porosity. Because the anode in an anode-supported SOFC is much thicker than the

cathode; thus the overall overpotential depends on the anode geometry.



(a) (b)

Fig. 4 The effect of the particle radius ratio (r_{io}/r_{el}) on the (a) anode overpotential and (b) cathode overpotential both are at various porosity (ε)

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. A good agreement is obtained between the predicted values and the measured data. The evolution of performance versus electrode geometries is studied. The investigation confirms the strong effects of microstructure geometry to improve SOFC performance, especially the increasing of the electrochemical active surface area. The largest active surface area for electrochemical reaction of electrode is achieved when size and solid volumetric fraction of ion and electron conducting particles are equal and then an optimal porosity is recommended at 0.4.

6. References

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