CHAPTER IV
MODEL DEVELOPMENT

As mentioned previously, to test the performance of a PSOFC operating with various compositions of synthesis gas, a one-cell stack PSOFC is fabricated. The objective of this chapter is to develop a mathematical model for a PSOFC using syngas to simulate cell performance. The model geometry and parameters are based on the one-cell stack, as discussed in the experiment.

4.1 Modeling Approach

In SOFC operation, electrochemical reactions, chemical reactions, electrical conduction, ionic conduction and heat transfer all take place at the same time and are tightly coupled. Therefore, to develop a reliable and predictive SOFC model, all effective heat, mass, species, charge and momentum transport equations, as well as accurate electrochemical and chemical reaction rates, are required. All the required model components to approach a mechanistic modeling and the expected output from such a model are summarized in Fig. 4.1.
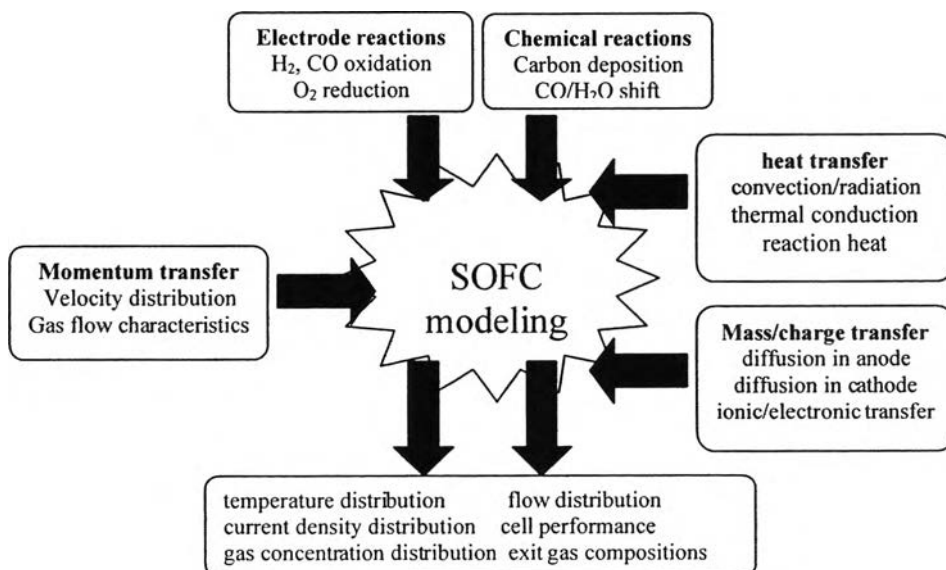

Figure 4.1 Mechanistic modeling approach.

4.2 Mathematical Model

4.2.1 Model Geometry and Assumptions

A schematic of a half PSOFC, including one-cell stack plates, as carried out in the experiment, is shown in Fig. 4.2(a). It is composed of several repeating units. For simplicity, only a single unit in the one-cell stack is considered in the model. It is illustrated in Fig. 4.2(b). Within the single unit, fuel and air simultaneously flow over the anode and cathode. Moreover, to reduce the calculation, the model considers only two dimensions along the flow channel (x and z directions). The model geometry, therefore, consists of fuel and air channels, anode, electrolyte, and cathode, as shown in Fig. 4.3.
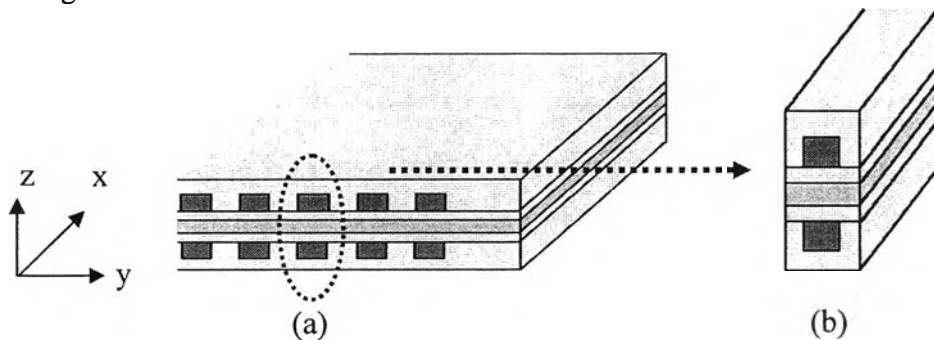

Figure 4.2 (a) Half PSOFC including one-cell stacks plates and (b) single unit.
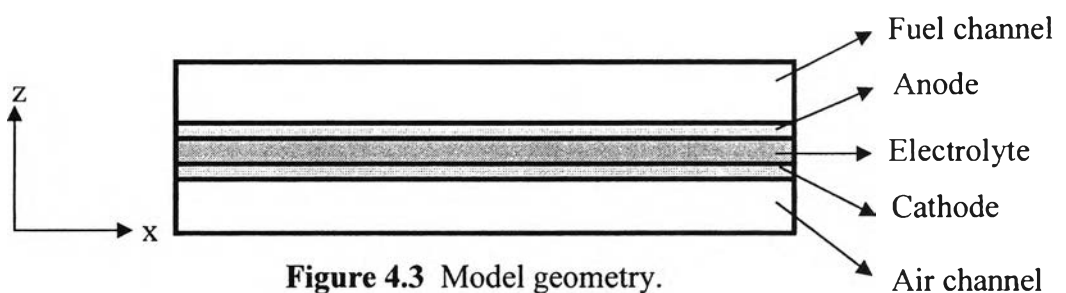

Figure 4.3 Model geometry.

The assumptions used in this model development are as follows:

- The model is considered to be at the steady state.

- The transports through the anode and cathode are neglected because of their ultra thin thickness. It is expected that all transport phenomena in these two layers are uniform. Therefore, the anode and cathode are neglected by considering as the electrolyte boundary.

- Since the anode and cathode are neglected, the active triple-phase boundary layers are also neglected. Therefore, the electrochemical reactions take place only at the fuel channel/electrolyte and air channel/electrolyte interfaces.

- Since the anode is neglected, the WGS reaction takes place at the fuel channel/electrolyte interface.

- It is assumed that the velocities of fuel and air in the flow direction (x direction) are constant; consequently, the momentum transportation equation is neglected. This is valid because the flow channel is quite short (4 cm); hence the velocity does not change drastically.

- The surface of the plates along the flow path is considered to be adiabatic. Therefore, the heat generated in the cell is not transported through the surrounding atmosphere.

- The heat radiation between the cell and the plate is neglected.

- Syngas used in this model consists of H_2, CO, CO_2, H_2O and N_2

Based on these assumptions, then, the model geometry, (i.e. only the fuel channel, air channel and electrolyte), including electrochemical, chemical reactions and flow configuration is shown in Fig. 4.4.

$H_2 + O^{2-} \rightarrow H_2O + 2e^-$
$CO + O^{2-} \rightarrow CO_2 + 2e^-$ $\qquad\qquad\qquad\qquad\qquad$ $CO + H_2O \leftrightarrow CO_2 + H_2$

H_2, CO, CO_2, N_2, H_2O $\qquad\qquad$ Fuel channel $\qquad\qquad$ H_2O, CO, CO_2, N_2, H_2

Electrolyte

Air (Co flow) $\qquad$ Air channel

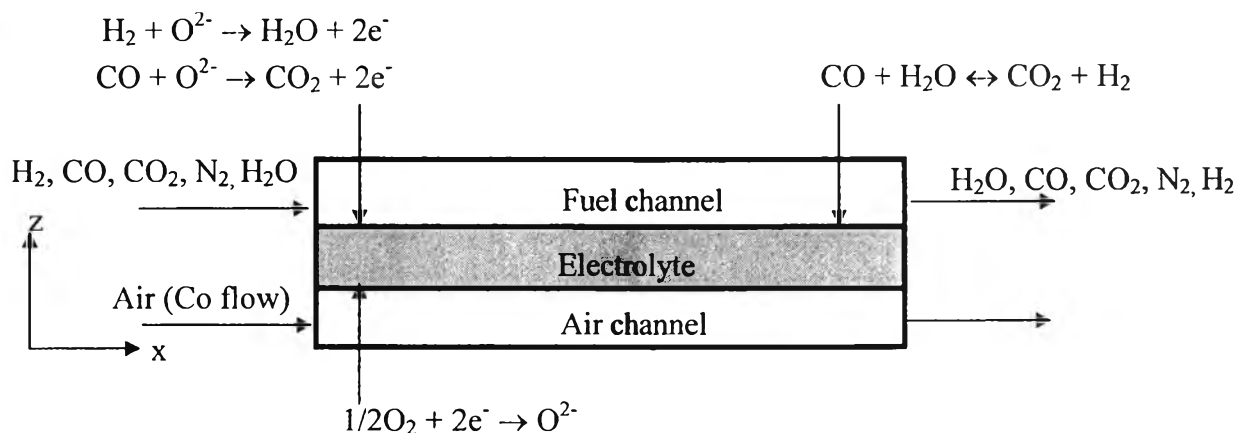$1/2O_2 + 2e^- \rightarrow O^{2-}$

Figure 4.4 Model geometry including electrochemical, chemical reactions and flow configurations.

4.2.2 Flow Channel

Considering that the working fluid in the gas channels of an SOFC is a reacting mixture of gases, the mass conservation can be described by the following generalized steady state transport equation (Bird *et al.*, 2002):

$$\nabla \cdot (\rho \vec{u} y_i) = \nabla \cdot \vec{m}_i + w_i \quad , \tag{4-1}$$

where i denotes the generic ith species, w_i is the rate of production or consumption of the species, y_i is the mass fraction of the ith species, ρ is the density of gas, $\vec{u}$ is the gas velocity, and $\vec{m}_i$ is the mass diffusion flux which can be obtained from Equation. 4-2,

$$\vec{m}_i = (\rho D_{i-m} \nabla y_i) \quad , \tag{4-2}$$

where D_{i-m} is the multicomponent diffusion coefficient of the ith species in the gaseous mixture which can be determined using the weighted average of binary diffusion coefficient (D_{ij}). D_{ij} is the binary diffusion coefficient of ith species with respect to jth species. The D_{i-m} is given by (Bird *et al.*, 2002):

$$D_{i-m} = \frac{\sum_{j=1, i \neq j}^{n} y_j D_{ij}}{\sum_{j=1}^{n} y_j} \quad . \tag{4-3}$$

D_{ij} can be determined as (Bird *et al.*, 2002)

$$D_{ij} = 0.001858 \sqrt{T^3 (\frac{1}{M_i} + \frac{1}{M_j})} \frac{1}{\rho \sigma_{ij}^2 \Omega_{Dij}} \quad , \tag{4-4}$$

where T is the temperature, M_i and M_j are the molecular weights of the ith and jth species, respectively, σ_{ij} is the characteristic length, and Ω_{Dij} is the collision integral. Ω_{Dij} is given by (Yakabe et al., 2000)

$$\Omega_{Dij} = \frac{A}{T_N^B} + \frac{C}{\exp(DT_N)} + \frac{E}{\exp(FT_N)} + \frac{G}{\exp(HT_N)} , \qquad (4\text{-}5)$$

where the constants A to H are A = 1.06036, B = 0.15610, C= 0.19300, D = 0.47635, E = 1.03587, F = 1.52996, G = 1.76474, H = 3.89411 and T_N is defined as

$$T_N = \frac{kT}{\varepsilon_{ij}} , \qquad (4\text{-}6)$$

where k is the Boltzmann constant and ε_{ij} is the characteristic Lennard-Jones energy. From the usually employed simple rules, σ_{ij} and ε_{ij} are given by the following:

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \qquad (4\text{-}7)$$

and

$$\varepsilon_{ij} = \left(\varepsilon_i \varepsilon_j \right)^{1/2} \qquad (4\text{-}8)$$

where σ_i and σ_j are the diameters of the molecular collision of ith and jth, respectively. The parameters used for the calculation of D_{i-m} in the model are listed in Appendix A.

The temperature profile inside the cell can be obtained through the energy equation. In this model, only conduction and convection mechanisms are considered for heat transport which heat conduction mainly occurs in solid components because

of their greater conductivities, while heat convection is the heat transport due to bulk transport. Therefore, its direction is the same as the flow direction. The generalized energy steady state transport equation inside the flow channel is as follows (Bove *et al.*, 2005):

$$\nabla \cdot (\rho c_p T \vec{u}) = \nabla \cdot \vec{Q} + S_q,$$ (4-9)

where S_q is the heat consumption or production due to electrochemical and chemical reactions, c_p is the heat capacity, and $\vec{Q}$ is the heat flux only from conduction. According to Fourier's law, $\vec{Q}$ is determined as

$$\vec{Q} = -\lambda \nabla T,$$ (4-10)

where λ is the thermal conductivity coefficient.

4.2.2.1 Fuel Channel

In the fuel channel, H_2 and CO oxidation (Equations 2-1 and 2-2) takes place at the fuel channel/electrolyte interface. The rate expression for H_2 oxidation used in this work is given by (Nagata *et al.*, 2001)

$$J_{H_2} = J_{0,H_2} \left\{ \exp\left(\frac{2F\eta_{H_2}}{RT}\right) - \exp\left(\frac{-F\eta_{H_2}}{RT}\right) \right\},$$ (4-11)

where J_{0,H_2} and η_{H_2} are the exchange current density and activation over-potential (V) for H_2 oxidation, respectively. J_{0,H_2} is expressed as

$$J_{0,H_2} = \frac{\sigma_0 RT}{(2+\alpha)F},$$ (4-12)

where α is the apparent transfer coefficient and σ_0 is the interface conductivity $\left(\Omega^{-1}m^{-2}\right)$ and expressed as

$$\sigma_0 = \beta \exp\left(\frac{-\Delta G_{act}}{RT}\right) P_{O_2,H_2}^{\gamma}, \tag{4-13}$$

where β is a constant, γ is the reaction order, ΔG_{act} is the activation energy and P_{O_2,H_2} is the oxygen partial pressure which is given as

$$P_{O_2,H_2} = \left(\frac{P_{H_2O,B}}{K_{eq,H_2} P_{H_2,B}}\right)^2, \tag{4-14}$$

Where $P_{H_2O,B}$ and $P_{H_2,B}$ are the partial pressure of water and hydrogen at electrolyte/fuel channel interface, respectively. K_{eq,H_2} is the equilibrium constant of oxidation of hydrogen. The coefficients for rate expression of hydrogen oxidation are given in Table 3. η_{H_2} is defined as

$$\eta_{H_2} = \phi_{an} - \phi_e - E_{H_2}^o, \tag{4-15}$$

where ϕ_{an} and ϕ_e represent the anode and electrolyte potentials at the fuel channel/electrolyte interface, respectively. $E_{H_2}^o$ is the reversible potential for H_2 oxidation;

$$E_{H_2}^o = \left(\frac{RT}{2F}\right) \ln\left(\frac{P_{H_2O}}{K_{eq,H_2} P_{H_2}}\right). \tag{4-16}$$

Table 4.1 Coefficients for rate expression of H_2 oxidation and O_2 reduction.

Reaction	α	β	γ	ΔG_{act} (kJ/mol)
H_2 oxidation	1	$10^{7.79}$	0.133	120
O_2 reduction	2	$10^{6.02}$	0.5	130

It is believed that the rate of CO oxidation is 2-3 times less than H_2 oxidation, while the interface conductivity is the same as H_2 oxidation (Suwanwarangkul *et al.*, 2006). Based on this statement, the rate of CO oxidation is assumed to be 2.5 times less than H_2 oxidation. Therefore, the rate expression of CO oxidation is as follows:

$$J_{CO} = 0.4 J_{0,CO} \left\{ \exp\left(\frac{2F\eta_{CO}}{RT} \right) - \exp\left(\frac{-F\eta_{CO}}{RT} \right) \right\}, \tag{4-17}$$

where $J_{0,CO}$ is given as

$$J_{0,CO} = \frac{\beta \exp\left(\frac{-\Delta G_{act}}{RT} \right) P_{O_2,CO}^{\gamma}}{(2+\alpha)F}, \tag{4-18}$$

where $P_{O_2,CO}$ is the partial pressure of oxygen and is given as

$$P_{O_2,CO} = \left(\frac{P_{CO_2,B}}{K_{eq,CO} P_{CO,B}} \right), \tag{4-19}$$

where $P_{CO_2,B}$ and $P_{CO,B}$ are the partial pressure of carbon dioxide and carbon monoxide at electrolyte/fuel channel interface, respectively. $K_{eq,CO}$ is the equilibrium constant of carbon monoxide oxidation. The coefficients for rate expression of carbon monoxide oxidation are the same as H_2 oxidation. η_{CO} is defined as

$$\eta_{CO} = \phi_{an} - \phi_e - E_{CO}^o \,, \tag{4-20}$$

where E_{CO}^o is the reversible potential of CO oxidation, as given by

$$E_{CO}^o = \left(\frac{RT}{2F}\right)\ln\left(\frac{P_{CO_2,B}}{K_{eq,CO}P_{CO,B}}\right). \tag{4-21}$$

Due to its high operating temperature, nickel on the anode surface can act as a catalyst for the WGS reaction (Equation 2-4) when syngas is used as fuel. The rate expression of the WGS reaction is given by (Habermann $et\ al.$, 2004)

$$R_{WGS} = k_{WGS}\left(P_{H_2O,B}P_{CO,B} - \frac{P_{H_2,B}P_{CO_2,B}}{K_{eq,WGS}}\right), \tag{4-22}$$

where k_{WGS} is the rate constant and $K_{eq,WGS}$ is the equilibrium constant for the WGS reaction. From the experimental data, the k_{WGS} and $K_{eq,WGS}$ are given as

$$k_{WGS} = 1.71\times10^8 \times \exp\left(-\frac{103191}{RT}\right) \tag{4-23}$$

and

$$K_{WGS} = \exp\left(-0.2935Z^3 + 0.6351Z^2 + 4.1788Z + 0.3169\right), \tag{4-24}$$

where $Z = \dfrac{1000}{T} - 1.$

Since electrochemical and chemical reactions take place at the fuel channel/electrolyte interface, heat generated from these reactions is incorporated into the energy transportation equation as a boundary condition. For the heat generated from

the electrochemical reactions $(Q_{electrochem})$, the heat generated from H_2 and CO oxidations, and electrical power production is considered. $(Q_{electrochem})$ is expressed as

$$Q_{electrochem} = \left(-\frac{J_{H_2}\Delta H_{H_2}}{2F}\right) + \left(-\frac{J_{CO}\Delta H_{CO}}{2F}\right) - \left(J_{H_2} + J_{CO}\right)V_{cell},$$ (4-25)

where ΔH_{H_2} and ΔH_{CO} are the enthalpies of the H_2 and CO oxidations, respectively. For the chemical reaction, only heat generated from the WGS reaction along the fuel channel/electrolyte interface is considered. Hence, heat due to chemical reaction $(Q_{chemical})$ is given by

$$Q_{chemical} = R_{WGS}\Delta H_{WGS},$$ (4-26)

where R_{WGS} and ΔH_{WGS} are the rate and the enthalpy of the WGS reaction, respectively.

4.2.2.2 Air Channel

In the air channel, oxygen reduction takes place at the air channel/electrolyte interface. The rate of O_2 reduction is determined by the rate of O_2 adsorption as the rate-determining step and is given by (Suwanwarangkul et al, 2006 and Nagata et al., 2001)

$$J_{O_2} = J_{0,O_2}\left\{\exp\left(\frac{2F\eta_{O_2}}{RT}\right) - \exp\left(\frac{-F\eta_{O_2}}{RT}\right)\right\},$$ (4-27)

where J_{0,O_2} is the exchange current density of oxygen reduction and given as

$$J_{0,O_2} = \frac{\beta\exp\left(\frac{-\Delta G_{act}}{RT}\right)P_{O_2}^{\gamma}}{(2+\alpha)F},$$ (4-28)

where P_{O_2} is the partial pressure of oxygen at the electrolyte/air channel interface and coefficients for reduction of oxygen are given as Table 3. η_{O_2} is the activation over-potential for O_2 reduction defined as

$$\eta_{O_2} = \phi_{cat} - \phi_e - E^o_{O_2},$$ (4-29)

where ϕ_{cat} and ϕ_e represent the cathode and electrolyte potentials, respectively. $E^o_{O_2}$ is the reversible potential for O_2 reduction:

$$E^o_{O_2} = \left(\frac{RT}{4F}\right)\ln P_{O_2}.$$ (4-30)

4.2.3 Electrolyte

In electrolyte, only oxygen ion (O^{2-}) flow through, thus requiring only the equations needed for modeling the electrical problem and temperature distribution. Considering that the electrolyte is very thin and is usually made of very high conductive materials, the ohmic resistance is usually ignored; consequently, heat generation can be ignored. The generalized steady state charge transportation equation is given by (Bove et al., 2005)

$$\nabla \cdot \vec{J} = \nabla \cdot \left(-\sigma \nabla \phi\right) = 0,$$ (4-31)

where σ and ϕ are ionic conductivity and cell potential, respectively.

In the electrolyte, heat is transported by conduction only and heat generation due to ohmic resistance can be ignored, as mentioned earlier. Therefore, Equation 4-9 can be reduced to

$$\nabla \vec{Q} = 0$$ (4-32)