CHAPTER 4 MATHEMATICAL MODEL

To model direct methanol fuel cell (DMFC), mass transport and electrochemical kinetics are considered. In this Chapter, the model domains consisting of six parts: anode porous region, cathode porous region, membrane, boundary condition, electrochemical kinetics, and cell current and cell voltage is described.

The assumptions of this model are:

1. An ideal gas mixture
2. Isothermal cells
3. The methanol that crossover the membrane is completely reacted at the cathode catalyst layer.
4. Water content and ionic conductivity of the membrane are constant since DMFC is fully dominated by liquid phase.

4.1 Model of Direct Methanol Fuel Cell

A single DMFC comprises an anode diffusion layer (ADL), an anode catalyst layer (ACL), a membrane (MEM), a cathode catalyst layer (CCL), and a cathode diffusion layer (CDL). The schematic model of a single DMFC is shown in Figure 4.1.

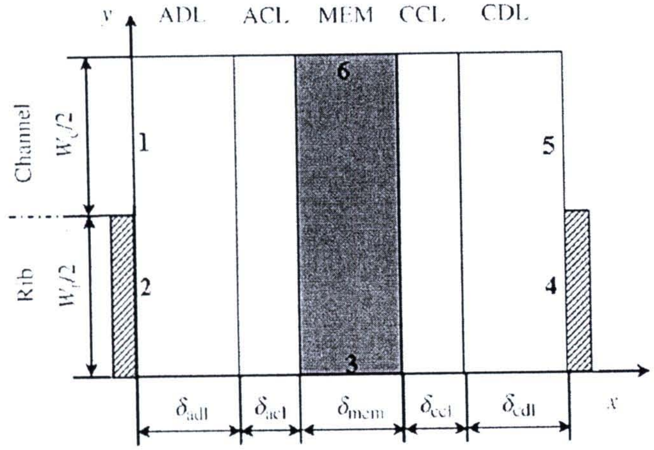

Figure 4.1 Schematic of the model domain

4.1.1 Electrochemical Kinetics

On the DMFC anode using the platinum-ruthenium catalysts, the electrochemical oxidation of methanol is described by the mechanism of a simplified two-step reaction. The first step is the electrochemical adsorption of methanol to the platinum catalyst which strongly forms adsorbed carbon monoxide with four protons and four electrons. Noticing this step is irreversible.

$$CH_3OH + Pt \rightarrow CH_3OH_{ads} \xrightarrow{R_1} CO_{ads} + 4H^+ + 4e^- \tag{4.1}$$

In the second step, the reaction relates to two consecutive reactions:

(a) Electrochemical adsorption of water to the ruthenium catalyst to form OH_{ads} with a proton and an electron. This reversible reaction is assumed in quasi-equilibrium.

(b) The formation of carbon dioxide with proton and electron by the reaction of formed OH_{ads} and CO_{ads}. This irreversible reaction is assumed to be the rate-determining step.

The combination of these two consecutive reactions is described by:

$$CO_{ads}+H_2O \xrightarrow{\text{Ru}, R_2} CO_2 + 2H^+ + 2e^- + Pt \tag{4.2}$$

These both electrochemical reaction steps are irreversible, so the form of Tafel kinetics is used to formulate the rate expressions. The adsorption and desorption of species affect the surface of the platinum catalyst thereby the rate expressions contain a term which considers the influence of the surface coverage of this catalyst with adsorbed CO and the rate expression is governed as follow.

$$R_1 = k_{a1}\frac{C_{MeOH}}{C_{MeOH}^{ref}}(1-\theta_{CO})\exp\left(\frac{\alpha_{a1}F}{RT}\eta_a\right) \tag{4.3}$$

$$R_2 = k_{a2}\theta_{CO}\exp\left(\frac{\alpha_{a2}F}{RT}\eta_a\right) \tag{4.4}$$

where θ_{CO} represents the surface coverage of platinum catalyst with adsorbed CO species. Next equation gives the overall balance of CO:

$$\Gamma\frac{d\theta_{CO}}{dt} = R_1 - R_2 \tag{4.5}$$

To consider the current generated in both reaction steps, the kinetics of the anodic reductive reaction can be expressed by

$$j_a = (4FA_s)k_{a1}\frac{C_{MeOH}}{C_{MeOH}^{ref}}(1-\theta_{CO})\exp\left(\frac{\alpha_{a1}F}{RT}\eta_a\right) + (2FA_s)k_{a2}\theta_{CO}\exp\left(\frac{\alpha_{a2}F}{RT}\eta_a\right) \tag{4.6}$$

with A_s denoting the specific surface area of active reaction sites.

On the DMFC cathode, the kinetics of oxygen reduction reaction (ORR) can be described by first-order Tafel expression

$$j_c = A_s j_{0,O_2}^{ref}\left(\frac{C_{O_2}/k_{H,O_2}}{C_{O_2}^{ref}}\right)\exp\left(\frac{\alpha_c F}{RT}\eta_c\right) \tag{4.7}$$

where C_{O_2} represents oxygen concentration in the gas pores. The term k_{H,O_2} denotes the Henry factor to capture the effect of dissolving process. The overpotential η_c in

Equation 4.7 represents the absolute difference between the real potential and the thermodynamic-equilibrium potential of ORR which are also referenced to a SHE.

Furthermore, the crossover of methanol results the parasitic reaction in the CCL. The methanol crossover is immediately consumed in the cathode since the parasitic reaction is very fast. Notice that this parasitic reaction ultimately results in the cathode mixed overpotential.

4.1.2 Cell Current Density and Cell Voltage

Under dynamic operations, the charging/discharging process of the DLC may occur, accompanying the dynamic variation in the electrode potential. If true, part of the current will be used to charge the DLC or released from the DLC. Consequently, the dynamic cell current density satisfies

$$C_{ACL}\frac{d\eta_a}{dt} = I_{cell} - \frac{\iint_{ACL} j_a dxdy}{(W_c + W_r)/2} \tag{4.8}$$

Where, C_{ACL} is the DLC of the anode electrode. The first term on RHS of the equation 4.8 denote the current required for charging or releasing of the DLC in dynamic operations.

Methanol that permeates across the membrane to cathode is the influence of current loss called 'parasitic' current. The parasitic current is the current that cannot be used to do work. It is assumed that cell and parasitic current are consumed by the ORR. Moreover, the DLC in the cathode electrode is considered.

$$C_{CCL}\frac{d\eta_c}{dt} = I_{cell} + I_{para} - \frac{\iint_{CCL} j_c dxdy}{(W_c + W_r)/2} \tag{4.9}$$

with I_{para} denoting the 'parasitic' current density, which can be determined by:

$$I_{para} = \frac{6F\int_0^{(W_c+W_r)/2} N_M|_{MEM/CCL}dx}{(W_c + W_r)/2} \tag{4.10}$$

In summary, for a given dynamic cell current density, the dynamic anode overpotential can be determined from Equation 4.8, while the dynamic cathode overpotential can be obtained from Equation 4.9. Finally, the dynamic cell voltage can be obtained from

$$V_{Cell} = V_0 - \eta_a - \eta_c - I_{Cell}\left(R_{Contact} + \frac{\delta_{mem}}{\kappa}\right) \tag{4.11}$$

where V_0, $R_{Contact}$ and κ denote the thermodynamic equilibrium voltage of a DMFC, the contact resistance and the proton conductivity of the membrane, respectively.

4.1.3 Anode Porous Region

In the anode porous region, there are the anode diffusion and catalyst layers. The variables for this region are liquid methanol concentration ($C_{M,l}$), methanol vapor concentration ($C_{M,g}$), liquid saturation ($s_{l,a}$) and liquid pressure (p_l). The equation of each variable is given by

$$C_{M,l}: \quad \frac{\partial}{\partial t}\left(\varepsilon s_{l,a} C_{M,l}\right) = -\nabla \cdot \mathbf{N}_{M,l} + \dot{R}_{M,l} \tag{4.12}$$

$$C_{M,g}: \quad \frac{\partial}{\partial t}\left[\varepsilon(1 - s_{l,a}) C_{M,g}\right] = -\nabla \cdot \mathbf{N}_{M,g} + \dot{R}_{M,g} \tag{4.13}$$

$$C_{WV,g}: \quad \frac{\partial}{\partial t}\left[\varepsilon(1 - s_{l,a}) C_{WV,g}\right] = -\nabla \cdot \mathbf{N}_{WV,g} + \dot{R}_{WV,g} \tag{4.14}$$

$$s_{l,a}: \quad \frac{\partial}{\partial t}\left[\rho_g \varepsilon (1 - s_{l,a})\right] = \nabla \cdot \left[\rho_g K \frac{k_{rg}}{\mu_g}\left(\frac{dp_c}{ds} \nabla s_{l,a} + \nabla p_l\right)\right] + \dot{m}_{g,a} \tag{4.15}$$

$$p_{l,a}: \quad \frac{\partial}{\partial t}\left(\rho_l \varepsilon s_{l,a}\right) = \nabla \cdot \left(\rho_l K \frac{k_{rl}}{\mu_l} \nabla p_l\right) + \dot{m}_{l,a} \tag{4.16}$$

To calculate the overall flux of methanol for liquid and vapor phases, transport mechanism of methanol including the molecular diffusion, macroscopic convection and electro-osmotic drag are taken into account as presented by Equations 4.17 and 4.18, respectively.

$$\mathbf{N}_{M,l} = \begin{cases} C_{M,l}\vec{\mathbf{u}}_l - D_{M,l}^{eff} \nabla \cdot C_{M,l} & ADL \\ C_{M,l}\vec{\mathbf{u}}_l - D_{M,l}^{eff} \nabla \cdot C_{M,l} + n_{d,w} x_m \dfrac{\mathrm{i}_+}{F} & ACL \end{cases} \tag{4.17}$$

and

$$\mathbf{N}_{M,g} = C_{M,g}\vec{\mathbf{u}}_g - D_{M,g}^{eff} \nabla \cdot C_{M,g} \tag{4.18}$$

The evaporation and condensation of methanol affected mass conservation are considered. The interfacial transfer rate between gas and liquid phases is given by:

$$\tilde{R}_m = A_{lg} h_{lg} \varepsilon (1 - s) \frac{(p_{MV}^{sat} - p_{MV})}{RT} \tag{4.19}$$

where p_{MV}^{sat} denotes the saturation pressure of methanol vapor.

4.1.4 Cathode Porous Region

In the cathode porous region, there are the cathode diffusion and catalyst layers. The variables for this region are oxygen concentration ($C_{O_2,g}$), water vapor concentration ($C_{WV,c}$), liquid saturation ($s_{l,c}$) and gas pressure ($p_{g,c}$). The equation of each variable is given by

$$C_{O_2,g}: \frac{\partial}{\partial t}\left[\varepsilon(1-s_{l,c})C_{O_2,g}\right] = -\nabla\cdot\mathbf{N}_{O_2,g} + \dot{R}_{O_2,g} \tag{4.20}$$

$$C_{WV,g}: \frac{\partial}{\partial t}\left[\varepsilon(1-s_{l,c})C_{WV,g}\right] = -\nabla\cdot\mathbf{N}_{WV,g} + \dot{R}_{WV,g} \tag{4.21}$$

$$s_{l,c}: \quad \frac{\partial}{\partial t}(\rho_l\varepsilon s_{l,c}) = \nabla\cdot\left[\rho_l K\frac{k_{rl}}{\mu_l}\left(-\frac{dp_c}{ds}\nabla s_{l,c} + \nabla p_{g,c}\right)\right] + \dot{m}_{l,c} \tag{4.22}$$

$$p_{g,c}: \quad \frac{\partial}{\partial t}\left[\rho_g\varepsilon(1-s_{l,c})\right] = \nabla\cdot\left(\rho_g K\frac{k_{rg}}{\mu_g}\nabla p_{g,c}\right) + \dot{m}_{g,c} \tag{4.23}$$

Where, $\mathbf{N}_{O_2,g}$ and $\mathbf{N}_{WV,g}$ are the transport fluxes of gas oxygen and water vapor in the cathode porous region, respectively. These variables can be obtained from

$$\mathbf{N}_{i,g} = C_{i,g}\vec{\mathbf{u}}_g - D_{i,g}^{eff}\nabla\cdot C_{i,g} \qquad \mathrm{i} = \mathrm{O_2,\ WV} \tag{4.24}$$

The evaporation and condensation of water affected to mass conservation are considered. The interfacial transfer rate between gas and liquid phases is given by

$$\tilde{R}_w = \begin{cases} k_e\dfrac{\varepsilon s\rho_l}{M_{H_2O}}\left(y_{WV}p_g - p_{WV}^{sat}\right) & y_{WV}p_g < p_{WV}^{sat} \\ k_c\dfrac{\varepsilon(1-s)y_{WV}}{RT}\left(y_{WV}p_g - p_{WV}^{sat}\right) & y_{WV}p_g < p_{WV}^{sat} \end{cases} \tag{4.25}$$

Where, p_{WV}^{sat} and y_{WV} are the saturation pressure of water vapor and mole fraction of water vapor in the cathode gas phase, respectively.

4.1.5 Membrane

In the anode and cathode region, the mass transport of gas and liquid phase are considered. But in the membrane, only liquid phase is considered, since the membrane is normally treated as a gas insulator.

$$\frac{\partial}{\partial t}(\varepsilon_{mem}C_{MeOH}) = -\nabla\cdot\mathbf{N}_M \tag{4.26}$$

Where, $\mathbf{N}_M$ is the vector flux of methanol in the membrane. Typically, transport of methanol through the membrane relates to molecular diffusion and electro-osmotic drag. Thus, the flux of methanol in the membrane is given by:

$$\mathbf{N}_M = -D_{M,N}^{eff}\cdot\nabla C_{MeOH} + n_{d,M}\frac{\mathrm{I}}{F} \tag{4.27}$$

However, some constitutive correlations and definitions are required to make the above equation to be closed. The correlations, definitions and the source terms are described in the next topic.

4.1.6 Constitutive Relations

These correlations and definitions are capillary pressure, relative permeability for both gas and liquid phase, effective diffusion coefficients for each species and the source terms.

Capillary pressure

In the diffusion layer, the liquid-gas transport is the relationship between the capillary and the liquid saturation. The capillary pressure is the difference between the pressures of any two phases at the interface. The capillary pressure can be expressed by:

$$p_c = p_g - p_l = \sigma cos\theta_c \left(\frac{\varepsilon}{K}\right)^{0.5} J(s) \tag{4.28}$$

$$J(s) = \begin{cases} 1.417(1-s) - 2.120(1-s)^2 + 1.263(1-s)^3 & 0^o < \theta_c \leq 90^o \\ 1.417s - 2.120s^2 + 1.263s^3 & 90^o < \theta_c < 180^o \end{cases} \tag{4.29}$$

Relative permeabilities

$$k_{rl} = s^3 \qquad Liquid \tag{4.30}$$

$$k_{rg} = (1-s)^3 \qquad Gas \tag{4.31}$$

Effective diffusion coefficients of species

From the Bruggmann correction, the effective diffusivity of two-phase system as shown below was apply from Equation 2.14.

$$D_{i,g}^{eff} = D_{i,g}\varepsilon^{1.5}(1-s)^{1.5} \qquad i:\, O_2, WV, MV \tag{4.32}$$

$$D_M^{eff} = \begin{cases} D_{M,l}\varepsilon^{1.5}s^{1.5} & ADL \\ \dfrac{(\varepsilon + \varepsilon_N)}{\left[\varepsilon/\left(D_{M,l}\varepsilon^{1.5}s^{1.5}\right) + \varepsilon_N/\left(D_{M,N}{\varepsilon_N}^{1.5}\right)\right]} & ACL \\ D_{M,N}\varepsilon^{1.5} & MEM \end{cases} \tag{4.33}$$

General generation rate of mass in liquid phase

$$\dot{m}_{l,a} = \begin{cases} M_{H_2O}\tilde{R}_W - M_M\tilde{R}_W & ADL \\ -\left(M_{H_2O} + M_M\right)\dfrac{j_a}{6F} + M_{H_2O}\tilde{R}_W - M_M\tilde{R}_W & ACL \end{cases} \tag{4.34}$$

$$\dot{m}_{l,c} = \begin{cases} M_{H_2O}\tilde{R}_W & CDL \\ M_{H_2O}\left(\dfrac{j_c}{2F} - \dfrac{I_p}{6F\delta_{CCL}}\right) + M_{H_2O}\tilde{R}_W & CCL \end{cases} \tag{4.35}$$

General generation rate of mass in gas phase

$$\dot{m}_{g,a} = \begin{cases} -M_{H_2O}\tilde{R}_W + M_M\tilde{R}_W & ADL \\ M_{CO_2}\dfrac{j_c}{6F} - M_{H_2O}\tilde{R}_W + M_M\tilde{R}_W & ACL \end{cases} \tag{4.36}$$

$$\dot{m}_{g,c} = \begin{cases} -M_{H_2O}\tilde{R}_W & CDL \\ -M_{O_2}\dfrac{j_c}{4F} + M_{CO_2}\dfrac{I_p}{6F\delta_{CCL}} - M_{H_2O}\tilde{R}_W & CCL \end{cases} \tag{4.37}$$

Mole generation rate of species

$$\dot{R}_{O_2} = \begin{cases} 0 \\ -\dfrac{j_c}{4F} \end{cases}, \quad \dot{R}_{WV,c} = \begin{cases} \tilde{R}_W & CDL \\ \tilde{R}_W & CCL \end{cases} \tag{4.38}$$

$$\dot{R}_{M,l} = \begin{cases} -\tilde{R}_M \\ -\dfrac{j_a}{6F} - \tilde{R}_M \end{cases}, \quad \dot{R}_{MV,a} = \begin{cases} \tilde{R}_M \\ \tilde{R}_M \end{cases}, \quad \dot{R}_{WV,g} = \begin{cases} -\tilde{R}_W & ADL \\ -\tilde{R}_W & ACL \end{cases} \tag{4.39}$$

4.1.7 Boundary Conditions

The system of DMFC is divided to six boundaries as referred in Figure 4.1.

Boundary 1: This boundary is the inlet of the anode region. The inlet conditions which are the concentration of liquid methanol, the concentrations of methanol vapor, liquid-phase pressure and liquid saturation are specified as constant.

$$C_{M,l} = C_M^{in}, C_{MV} = C_{MV}^{in}, s = 1, p_l = p_l^{in} \tag{4.40}$$

Boundary 2: All fluxes in the *x* direction are zero, since this boundary is an impermeable wall between anode diffusion layer and rib collector.

$$\frac{\partial C_M}{\partial x} = 0, \frac{\partial C_{MV}}{\partial x} = 0, \frac{\partial s}{\partial x} = 0, \frac{\partial p_l}{\partial x} = 0 \tag{4.41}$$

Boundaries 3 and 6: These two boundaries are the middle point of rib width and the middle point of channel width, so the boundaries are symmetrical. Consequently, the gradients of all variables in *y* direction are set to zero.

$$\frac{\partial \emptyset}{\partial y} = 0 \quad \emptyset : C_{M,l}, C_{MV}, s, p_l, C_{O_2}, C_{WV}, p_g \tag{4.42}$$

Boundary 4: This boundary is similar to Boundary 2. This boundary is an impermeable wall between cathode diffusion layer and rib collector. Thus, all mass fluxes across this boundary are zero.

$$\frac{\partial C_{O_2}}{\partial x} = 0, \frac{\partial C_{WV}}{\partial x} = 0, \frac{\partial s}{\partial x} = 0, \frac{\partial p_g}{\partial x} = 0 \tag{4.43}$$

Boundary 5: This boundary is the inlet of oxygen supply and outlet of water removal which is treated as constant similar to Boundary 1:

$$C_{O_2} = C_{O_2}^{in}, C_{WV} = C_{WV}^{in}, s = 0, p_g = p_g^{in} \tag{4.44}$$

All others boundaries at the interfaces between layers are based on continuity equation and mass conservation of the entire cell.