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APPENDIX A

COMSOL Multiphysics Programming

This appendix presents the steps for using *COMSOL Multiphysics*^{TM} version 3.5 which can solve partial differential equations by finite element method. Moreover, it has a powerful GUI (Graphic User Interface) that is easy to use and takes little programming time when compared with other computing programs. There are mainly seven steps in setting up the model as shown in the following steps;

1. Create mathematical model.
2. Create model geometry.
3. Define constants and expressions.
4. Set governing equations, boundary and initial conditions.
5. Create a finite element mesh for model geometry.
6. Set solver properties.
7. Post-processing, user get results and can plot parameters.

A.1 Creating mathematical model

After program installation, double-click the *COMSOL Multiphysics* icon in the desktop to open the program. The Model Navigator window will be appeared. Then, start building a model by selecting the main COMSOL Multiphysics application.

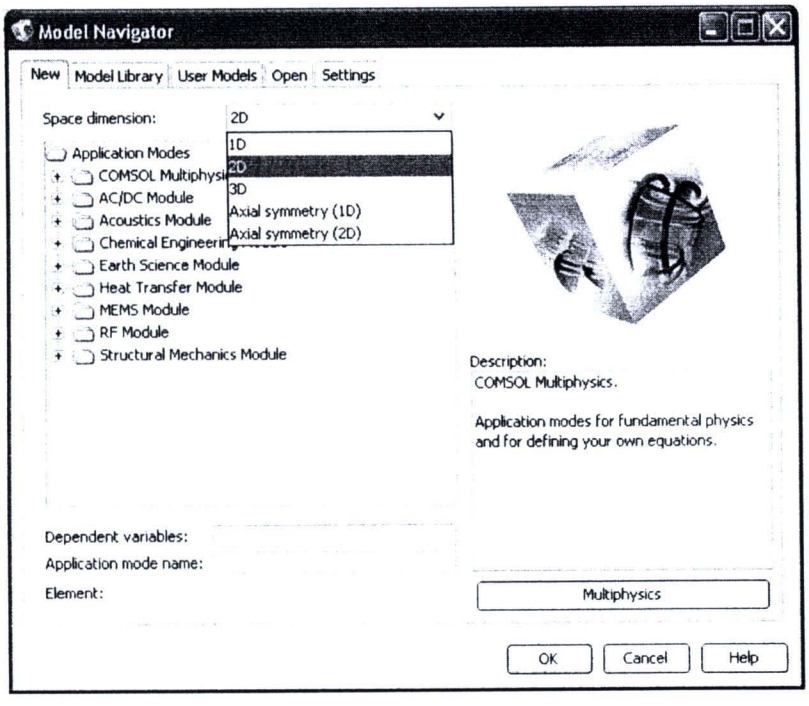

Figure A.1 Space dimension list in Model Navigator

1. Select **2D** from the **Space dimension** list which is always the first step.
2. Click the **Multiphysics** button
3. From the **Application Modes** tree, select **COMSOL Multiphysics>PDE Modes>PDE, General Form>Time-dependent analysis**
4. Type *Co2* in the **Dependent variables** edit field and *O2_cathode* in the Application mode name edit field. **Click Add**.

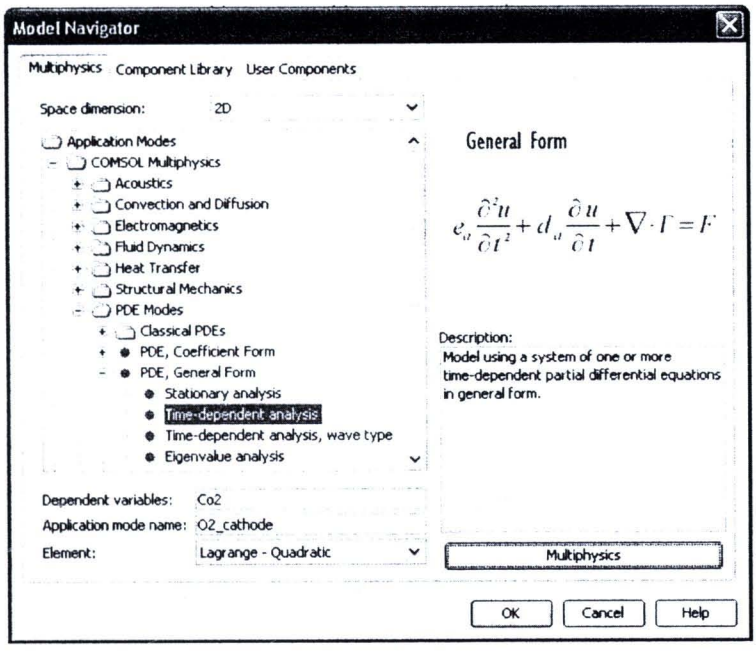

Figure A.2 PDE, General Form

5. Repeat the previous step to add other models, click **OK**

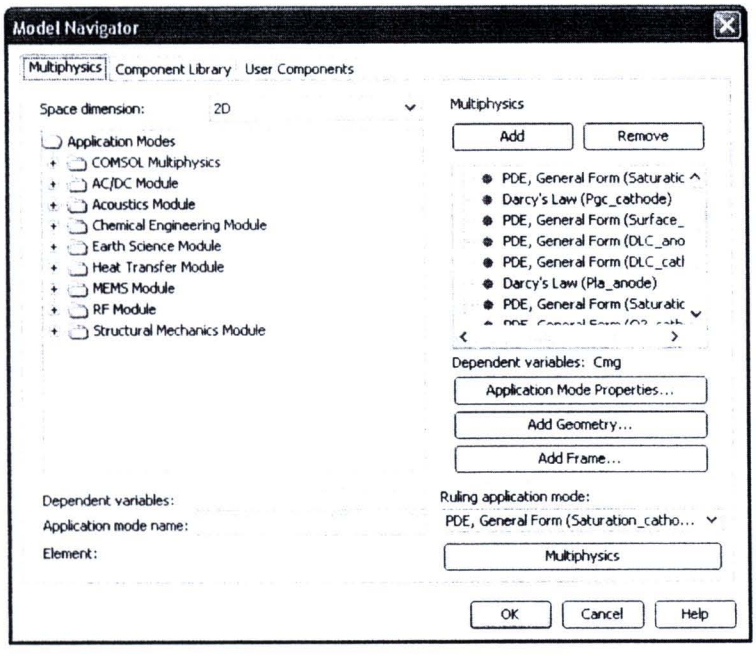

Figure A.3 Multiphysics window

A.2 Creating model geometry

The geometry of fuel cell consists of five domains which are 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 2D geometry is created using the Draw menu.

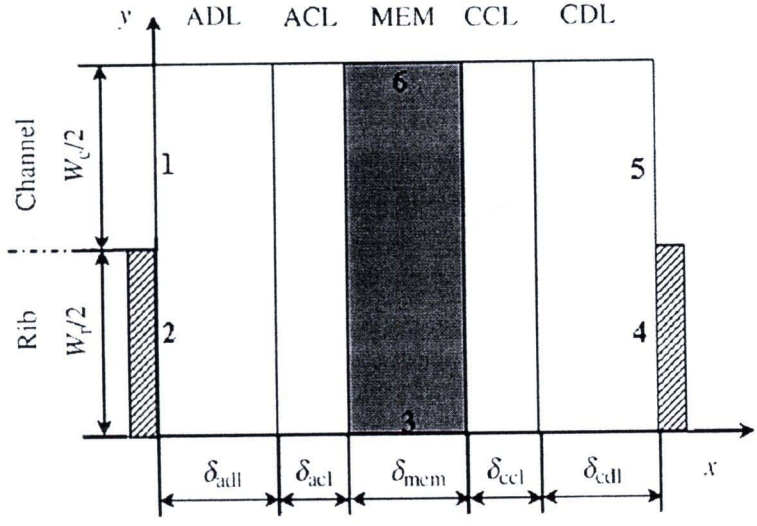

Figure A.4 Schematic of the model domain.

1. Shift-click the **Rectangle/Square** button on the Draw toolbar. Create the rectangle R1 by entering the properties in the Rectangle 1 column below; when done, click **OK**.

Table A.1 The properties of the Rectangle

Object Dimensions	Rectangle						
	1	2	3	4	5	6	7
Width	2.35e-4	2.35-4	6.5e-5	1.75e-4	6.5e-5	2.35e-4	2.35e-4
Height	5.0e-4	5.0e-4	1.0e-3	1.0e-3	1.0e-3	5.0e-4	5.0e-4
Position base	Corner	Corner	Corner	Corner	Corner	Corner	Corner
Position x	0	0	2.35e-4	3.0e-4	4.75e-4	5.4e-4	5.4e-4
Position y	0	5.0e-4	0	0	0	0	5.0e-4

2. Repeat the previous step six times using the properties listed in the remaining six columns to create the rectangles R2, R3, R4, R5, R6 and R7.
3. Select the rectangle R1 and R2 (Press Ctrl to make multiple selections)
4. Click the **Create Composite Object** button on the Draw toolbar. Clear the **Keep interior boundaries** check box, then click **OK**.
5. Select the rectangle R6 and R7. Repeat the previous step for these objects.

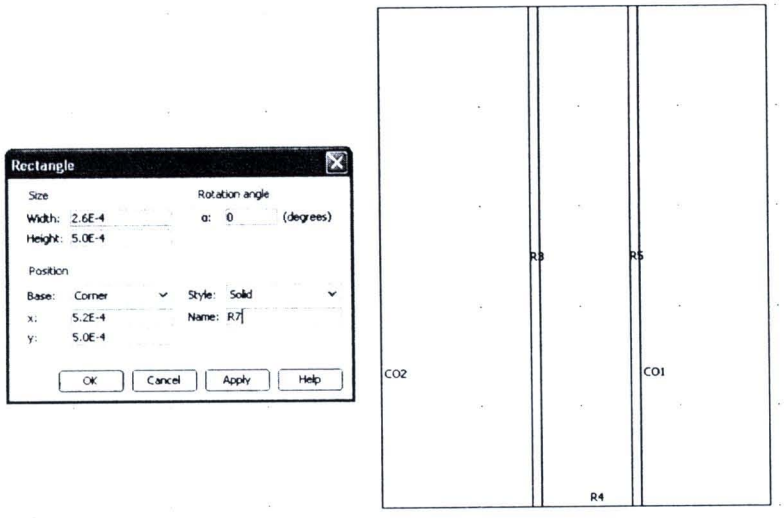

Figure A.5 Retangle window in Specify Objects

A.3 Defining Constants and Expressions

This step is how to define constant value and expression used in the model. The Option menu is used to define the constants and expressions.

1. Defining constants

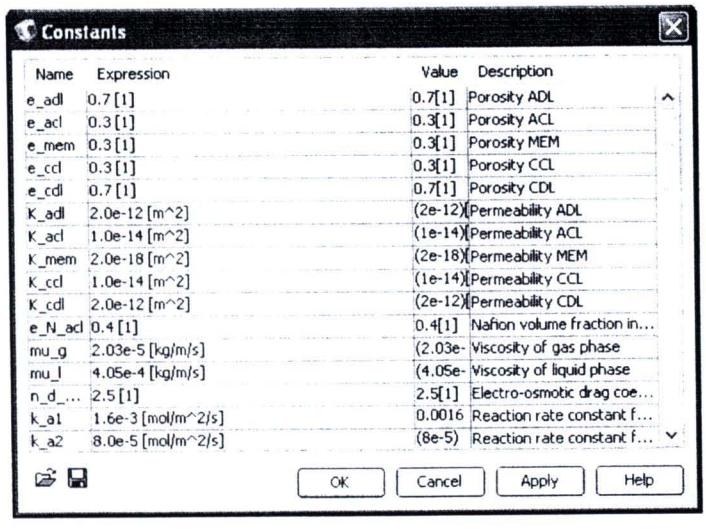

Figure A.6 Defining the constants

2. Defining scalar expressions

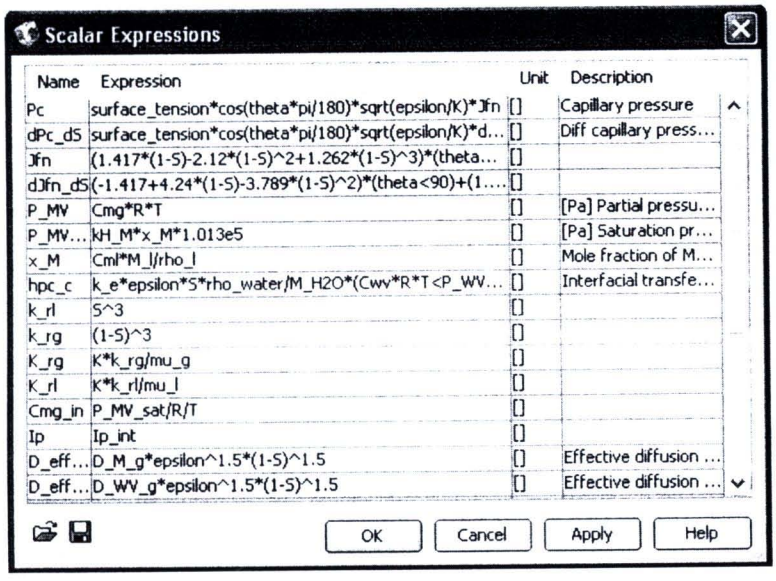

Figure A.7 Defining the scalar expressions

3. Defining subdomain expressions

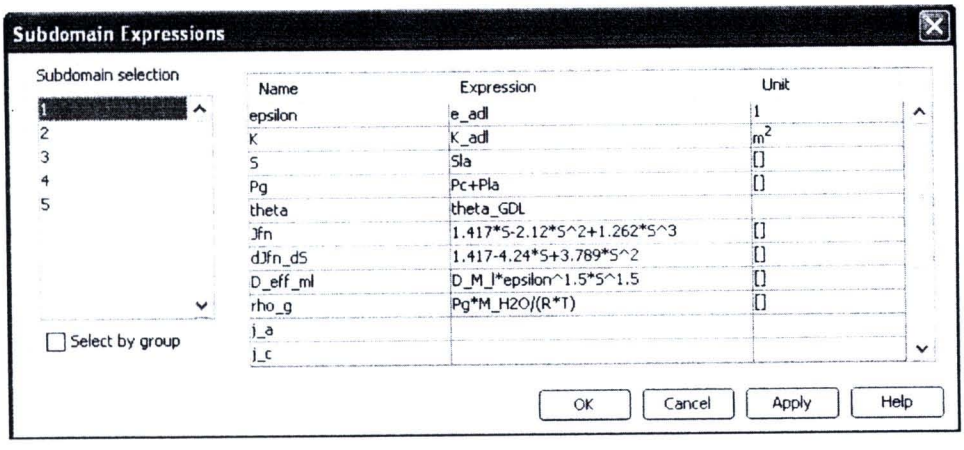

Figure A.8 Defining the subdomain expressions

4. Defining subdomain integration variables

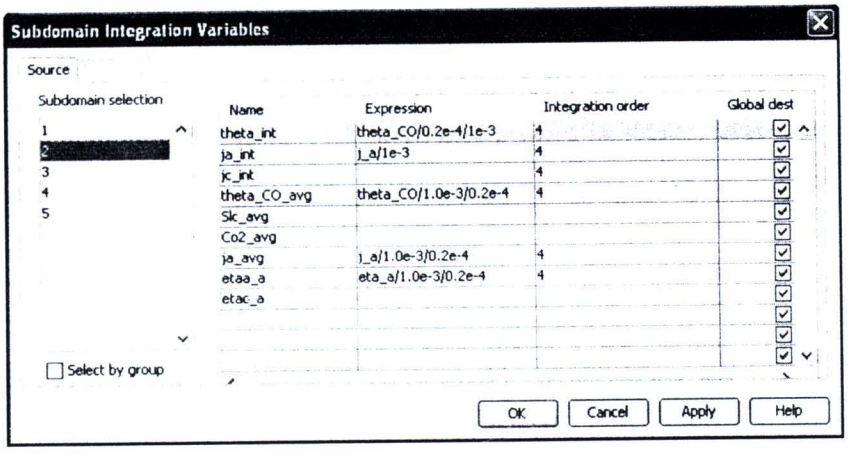

Figure A.9 Defining the subdomain integration variables

5. Defining boundary integration variables

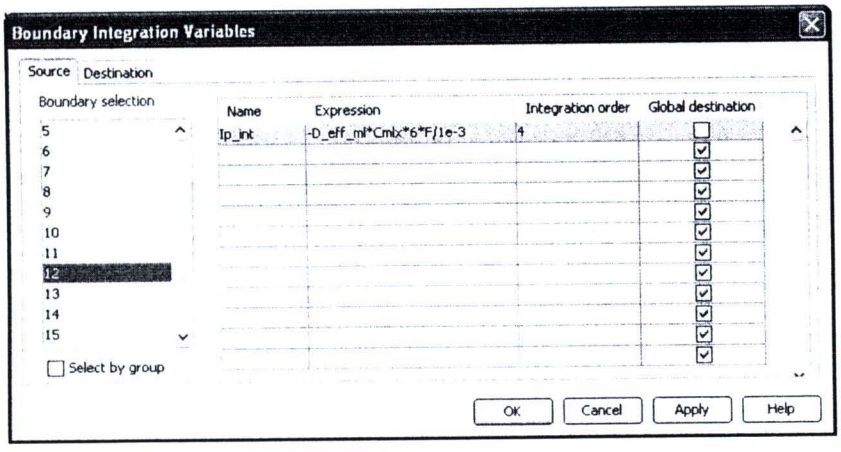

Figure A.10 Defining the boundary integration variables

A.4 Setting Governing Equations, Boundary and Initial Conditions

Physics setting consists of subdomain, boundary condition, and initial condition setting. In this part, species balance of oxygen is explained.

1. From the **Multiphysics** menu, select **PDE, General Form (O2_cathode)**.
2. From the **Physics** menu, select **Subdomain Setting**.
3. Select Subdomains 4 and 5, then type the value or expression in each edit field.
4. Select Subdomains 1, 2 and 3. Deactivate the application mode by clearing the **Active in this domain** check box.
5. Choose **Init** tab and fill the initial condition in $\mathbf{c(t_0)}$ edit field.
6. Click **OK** to confirm all settings and close the dialog box.

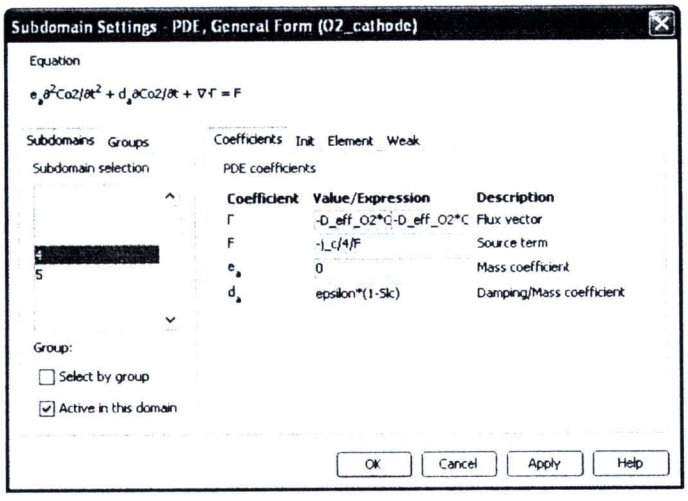

Figure A.11 Subdomain settings for species balance of oxygen

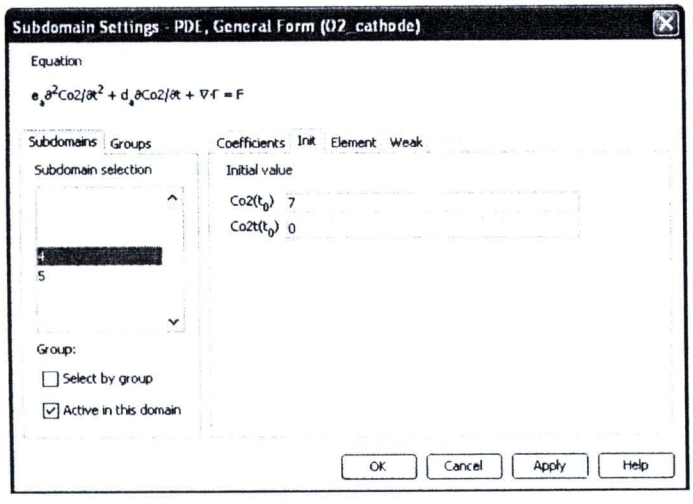

Figure A.12 Initial condition for species balance of oxygen

7. Set the boundary conditions by opening **Boundary Settings** on **Physics** menu.
8. For boundary 20, select Dirichlet boundary condition and fill the Coefficient Value/Expression.
9. For boundary other boundaries, Neumann boundary condition and fill the Coefficient Value/Expression.
10. Repeat the previous step to set the other equations.

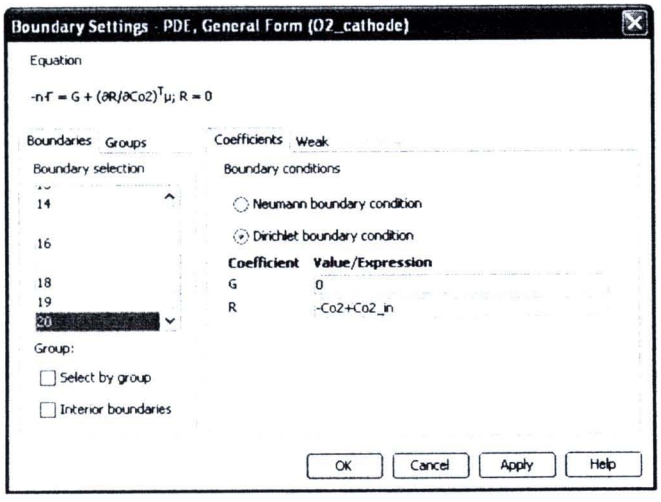

Figure A.13 Boundary settings for water diffusion process

A.5 Generating mesh

1. Click **Mesh** menu and select **Free Mesh Parameters**.
2. Choose **Subdomain** tab. Select Subdomain 2 and 4. Set the **Maximum element size** to 2e-5
3. Choose **Boundary** tab. Select Boundary 3 and 20. Set the **Maximum element size** to 1e-5
4. Click **Remesh** button and Click **OK** button to confirm the change

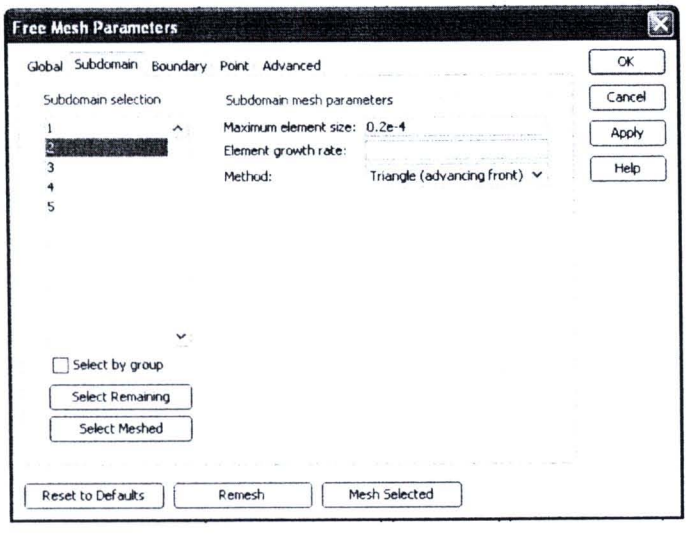

Figure A.14 Setting the maximum element size for subdomain 2 and 4

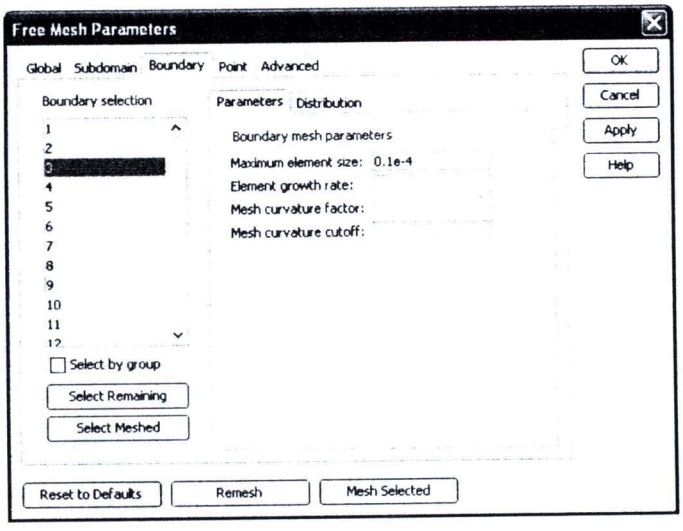

Figure A.15 Setting the maximum element size for boundary 3 and 20

A.6 Setting solver properties

1. Click **Solver Parameters** on **Solve** menu to open dialog box.
2. Enter **Time stepping** in DMFC operating process.
3. Use the default solver, the direct (UMFPACK) linear solver system, in this simulation as shown in Figure A.16.
4. Click **OK** to confirm all settings.
5. Click **Solve Problem** to start computing equation.

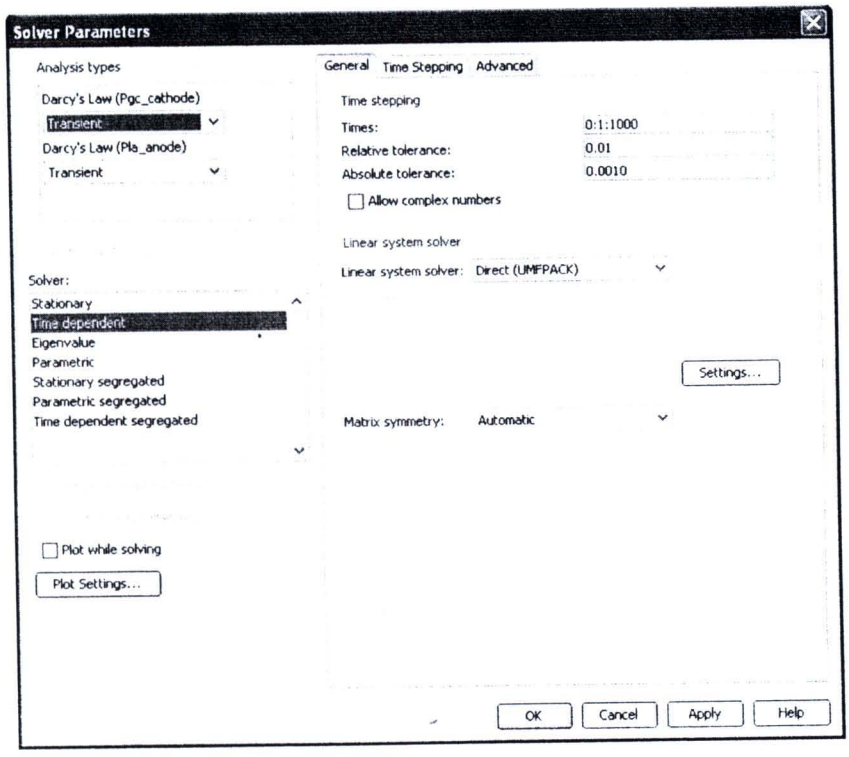

Figure A.16 Solver Parameters window

A.7 Post processing

Results or defined variables can be widely plotted using **Post processing** menu. For example, the cell voltage of DMFC can be plotted against time as shown in Figure A.17.

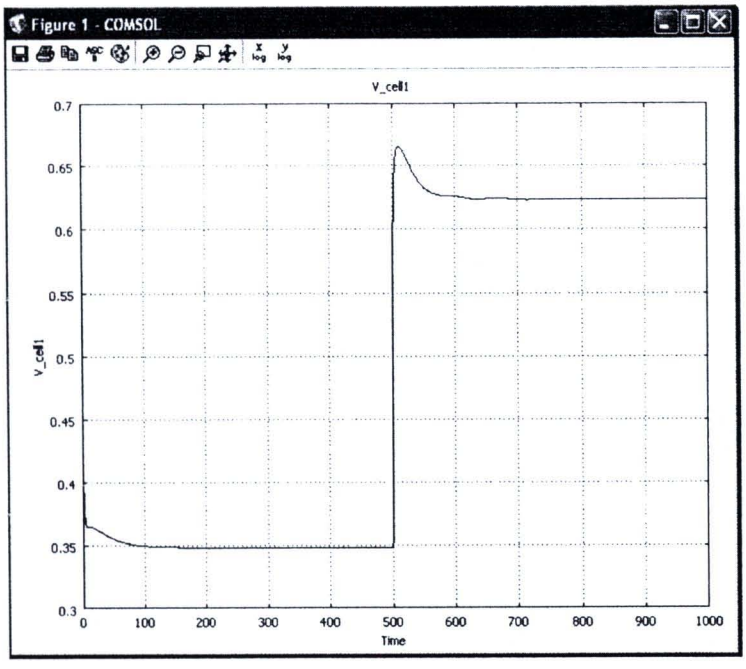

Figure A.17 Post processing

APPENDIX B

Constants and Expressions

The governing equations which described in chapter 4 for the cell geometric dimensions and operating parameters listed in Table B.1 subjected to the boundary conditions and the physicochemical properties listed in Table B.2.

Table B.1 Cell geometric dimensions and operating parameters

Parameters	Symbols	Value	Unit
Anode diffusion layer thickness	δ_{adl}	2.35×10^{-4}	m
Anode catalyst layer thickness	δ_{acl}	0.65×10^{-4}	m
Membrane thickness	δ_{mem}	1.75×10^{-4}	m
Cathode diffusion layer thickness	δ_{cdl}	2.35×10^{-4}	m
Cathode catalyst layer thickness	δ_{ccl}	0.65×10^{-4}	m
Channel width	W_c	1.0×10^{-3}	m
Rib width	W_r	1.0×10^{-3}	m
Operation temperature	T	363.15	K
Anode inlet pressure	p_l^{in}	1.013×10^{-5}	Pa
Cathode inlet pressure	p_g^{in}	1.013×10^{-5}	Pa
Inlet methanol concentration	C_M^{in}	1000	mol m^{-3}
Inlet methanol vapor concentration	C_{MV}^{in}	C_{MV}^{sat}	mol m^{-3}
Inlet oxygen concentration	$C_{O_2}^{in}$	9.25	mol m^{-3}
Inlet water vapor concentration at anode	$C_{WV,a}^{in}$	$C_{WV,a}^{sat}$	mol m^{-3}
Inlet water vapor concentration at cathode	$C_{WV,c}^{in}$	0	mol m^{-3}
Inlet liquid saturation at anode	s_a^{in}	1	-
Inlet liquid saturation at cathode	s_c^{in}	0	-

Table B.2 Physicochemical properties

Parameters	Symbols	Value	Unit
Porosity			
ADL	ε_{adl}	0.7	-
ACL	ε_{acl}	0.3	-
MEM	ε_{mem}	0.3	-
CCL	ε_{cdl}	0.3	-
CDL	ε_{ccl}	0.7	-
Permeability			
ADL	K_{adl}	2.0×10^{-12}	m^2
ACL	K_{acl}	1.0×10^{-14}	m^2
MEM	K_{mem}	2.0×10^{-18}	m^2
CCL	K_{cdl}	1.0×10^{-14}	m^2
CDL	K_{ccl}	2.0×10^{-12}	m^2
Nafion volume fraction in ACL	$\varepsilon_{N,acl}$	0.4	-

Table B.2 Physicochemical properties (Cont'd)

Parameters	Symbols	Value	Unit
Diffusivities			
MeOH in water	$D_{M,l}$	$10^{-5.4163-999.778/T}$	$m^2\ s^{-1}$
MeOH in Nafion	$D_{M,N}$	$4.9\times10^{-10}e^{[2436(1/333-1/T)]}$	$m^2\ s^{-1}$
MeOH vapor	$D_{M,g}$	$-6.954\times10^{-6}+4.5986\times10^{-8}T + 9.4979\times10^{-11}T^2$	$m^2\ s^{-1}$
O_2 in gas	$D_{O2,g}$	$1.775\times10^{-5}\left(\frac{T}{273.15}\right)^{1.823}$	$m^2\ s^{-1}$
water vapor in gas	$D_{WV,g}$	$2.56\times10^{-5}\left(\frac{T}{307.15}\right)^{2.334}$	$m^2\ s^{-1}$
Viscosity of gas phase	μ_g	2.03×10^{-5}	$kg\ m^{-1}\ s^{-1}$
Viscosity of liquid phase	μ_l	4.05×10^{-4}	$kg\ m^{-1}\ s^{-1}$
Electro-osmotic drag coefficients of			
water	n_{d,H_2O}	2.5	-
methanol	$n_{d,M}$	$n_{d,H_2O}x_M$	-
Reaction rate constant for			
anode reaction step 1	k_{a1}	1.7×10^{-5}	$mol\ m^{-2}\ s^{-1}$
anode reaction step 2	k_{a2}	9.0×10^{-5}	$mol\ m^{-2}\ s^{-1}$
Condensation rate constant for water	k_c	5.0×10^{-5}	$mol\ atm^{-1}\ s^{-1}\ cm^{-3}$
Evaporation rate constant for water	k_e	5.0×10^{-3}	$atm^{-1}\ s^{-1}$
Henry law constant for oxygen	k_{H,O_2}	$e^{(-666/T+14.1)}/R/T$	-
Henry law constant for MeOH	$k_{H,M}$	$0.096e^{0.04511(T-273)}$	atm
Double layer capacitance of ACL	C_{ACL}	1827	$C\ m^{-2}$
Double layer capacitance of CCL	C_{CCL}	907	$C\ m^{-2}$
Surface concentration of Pt catalyst	Γ_{Pt}	0.11	$mol\ m^{-2}$
Interfacial transfer rate constant for MeOH	h_{lg}	0.001	$m^2\ s^{-1}$
Specific interfacial area between liquid and gas	A_{lg}	10^5	m^{-1}
Specific surface area of anode catalyst	A_s	5000	m^{-1}
Proton conductivity in membrane	κ	$7.3e^{[1268(1/298-1/T)]}$	$\Omega^{-1}\ m^{-1}$
The saturation pressure of water vapor	$\log_{10} p_{WV}^{sat}$	$-2.1794+0.02953(T-273)-9.1837\times10^{-5}(T-273)^2+1.4454\times10^{-7}(T-273)^3$	atm
The saturation pressure of MeOH vapor	p_{MV}^{sat}	$k_{H,M}x_{M,l}$	atm
Thermodynamics voltage	V_0	1.21	V

Table B.2 Physicochemical properties (Cont'd)

Parameters	Symbols	Value	Unit
Transfer coefficient of			
anode reaction step 1	α_{a1}	0.5	-
anode reaction step 2	α_{a2}	0.5	-
Transfer coefficient of cathode	α_c	1	-
Cathode exchange current density	$A_{s,c}j^{ref}_{0,O_2}$	20	A m^{-3}
Anode reference concentration	C^{ref}_M	1000	mol m^{-3}
Cathode reference concentration	$C^{ref}_{O_2}$	0.52	mol m^{-3}
Ohmic contact resistance	$R_{contact}$	3.0×10^{-5}	A m^{-3}
Gas constant	R	8.314	J mol^{-1} K^{-1}
Faraday constant	F	96500	C mol^{-1}
Surface tension	σ	$-1.78\times10^{-4}T+0.1247$	N m^{-1}
Contact angle GDL	θ_{GDL}	50	Degree
Contact angle CTL	θ_{CTL}	120	Degree
Molecular weight of			
water	M_{H2O}	0.018	kg mol^{-1}
MeOH	M_M	0.032	kg mol^{-1}
carbondioxide	M_{CO2}	0.044	kg mol^{-1}
oxygen	M_{O2}	0.032	kg mol^{-1}

CURRICULUM VITAE

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King Mongkut's University of Technology Thonburi
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