Modeling of transport phenomena in proton-exchange-membrane fuel cell

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2010

Xu, J. (2010). Modeling of transport phenomena in proton-exchange-membrane fuel cell.
Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/42282>

<https://doi.org/10.32657/10356/42282>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**MODELING OF TRANSPORT PHENOMENA IN
PROTON-EXCHANGE-MEMBRANE FUEL CELL**

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IN

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SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING

2010

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IN
PROTON-EXCHANGE-MEMBRANE FUEL CELL**

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A thesis submitted to the Nanyang Technological University
in fulfillment of the requirement for the degree of
Doctor of Philosophy

2010

Acknowledgement

First and foremost, I would like to thank my supervisor Prof. Chan Siew Hwa for creating this research project, providing valuable guidance, advice, patience, constant encouragement and devotion in all respects to make this thesis happen.

I would express my gratitude and appreciation to As./P Birgersson, Karl Erik (NUS, Singapore) for providing me the opportunity to use the facilities in NUS and sharing with the invaluable original views on the simulation.

I would like to express my thanks to A/P Ho Hiang Kwee for his consistent support and encouragement and patience whenever I encountered the problem and providing invaluable help not only on the project but also the life.

I would also like to express my cordially thanks to all the members of fuel cell group. Dr. Xia Zetao and Dr. Chen Xiaojun for their constructive suggestions on modeling; Dr. Liu zengcai and Dr. Han and Dr. Tian Zhiqun for their kind guidance on the experiments; Dr. Wang Wei, Dr. Zheng Yongda and Dr. Zhang Lan, Mrs. Lia Maisarah Umar for their support; Technician Agnes, Roger and Lawrence for their helps on the materials and equipment's procurement; my good friend, Dr. Wang zhiying for her support and encouragement.

Finally, last but not least, I thank very much my mom Shen yaqin for her unconditional love and encouragement, constant support all her life and dedicated this to her though she passed away . I also thank my Dad, Mr. Xu Bingrong, for his continuous stimulating and encouragement, my husband, Dr. Yu weibo, for his strongest support and inspiration. This thesis is also dedicated to my lovely son Zhe Yuan (3 yrs old) who is my sunshine and spicy up my life a lot.

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Summary

Fuel cells are electrochemical devices whose performance is closely related to the transport of reactants (oxygen and hydrogen) and products (water). These transport processes are coupled with electrochemistry and further complicated by phase change, porous media (gas diffusion electrodes) and a complex microstructure. Several relatively simple yet representative models have been presented to better understand the fundamental of transport phenomena in PEMFC and to investigate the impact of various operating and design parameters on the performance to guide the optimal design of a fuel cell. These covered almost all major transport phenomena, including water and proton transport; electrochemical reaction; transport of electrons; heat generation within the cell; multi-component mass transport in the gas flow channels.

A simple 1D model is presented and validated using in-house experimental data on a laboratory-scale single cell with 2-pass serpentine flow field. Results showed that the measured polarization curves generally agree well with the predicted results in the lower and medium current densities but significant discrepancy exist in the high current densities. Predicting the cell performance at high current density is a tough and challenging task. Simple 1D model is not able to provide the necessary insights on the spatial and temporal variation of the performance-related parameters in the cell, posing limit on the predictable range. A multi-dimensional model is, therefore, required for studying the complex interaction among these parameters and is also useful for one to use it to guide the design of a fuel cell.

A 2D single-phase model for mass, momentum, species, charge, and energy transport coupled with a phenomenological membrane model and agglomerate model in the cathode catalyst layer for a PEMFC has been derived, discussed and validated with in-

house experimental data obtained from a single cell with porous flow field. Two GDL cases (single layer GDL and CFGDL) have been used to calibrate and validate the models. Close agreement between predicted results and experimental data was obtained for the two cases in the entire current density range.

In order to study the impact of these variations on stack performance, an extended mathematical model comprising two single cells and a coolant plate is considered. Several parameters are perturbed for one of the cells while the other is operating at base case conditions, an extension to larger stack units is also discussed.

A simple extension model to account for two-phase flow has been derived, implemented and the associated key parameters (E^* , ΔE , s^*) are discussed to study ‘curve-back’ phenomena that appeared in the polarization curve. Partial and full flooding have been simulated, which include localized liquid water accumulation and uniform liquid water accumulation.

A series of parametric studies have been conducted to identify the parameters (e.g. operating, geometric, intrinsic and extrinsic) that are sensitive or insensitive to the fuel cell performance. All the models have showed their predictive capabilities and various level of accuracy when validated with the experiment results and they are useful to guide the design of a fuel cell.

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Nomenclature

Symbol	Description	Units
A	Area	m^2
a	Water activity	-
a	Contact area of catalyst and membrane, per unit volume	m^2/m^3
C_i	Molar concentration of species i in the membrane phase	mol/m^3
C_p	Specific heat	$\text{J}/(\text{mol K})$
D	Diffusion coefficient	m^2/s
D_{ij}	Binary diffusion coefficient of the gas pair, i - j	m^2/s
e	Electronic charge	$1.6022 \times 10^{-19} \text{ C}$
E	Open circuit potential	V
e_x, e_y, e_z	Coordinate vectors	-
F	Faraday constant	96487 C/mol
G	Gibbs free energy	J/mol
g	Acceleration vector due to Gravity	m^2/s
H	Enthalpy	J/mol
h	Height	m
H_i	Henry's law constant for species i	$\text{atm}/(\text{m}^2 \text{ mol})$
i	Superficial current density in the membrane phase	A/m^2
I	Superficial operating current density	A/m^2
i_0	Exchange current density	A/m^2
i_{solid}	Superficial current density in the solid matrix	A/m^2
j	Volumetric Current Density	A/m^3
J_i	Superficial flux of species i in the gas phase	$\text{mol}/\text{m}^2/\text{s}$

Symbol	Description	Units
k	Thermal Conductivity	$\text{W}/(\text{m K})$
K_ϕ	Electrokinetic permeability	m^2
K_P	Hydraulic permeability	m^2
$K_{P,s}$	Hydraulic permeability for superficial velocity	m^2
l	Length	m
M	Molar mass	kg / mol
n	Amount of electrons transferred	-
P	Pressure	Pa
Q	Volumetric Flow rate	m^3/s
r	Area-specific resistance	Ω/ m^2
R	Universal Gas Constant	$8.314 \text{ J}/(\text{mol K})$
RH	Relative Humidity	%
z	Stoichiometric coefficient	-
s	Saturation	-
S	Source term	-
S	Entropy	$\text{J}/(\text{mol K})$
T	Temperature	K
U	Velocity	m/s
u	Velocity in x-direction	m/s
V	Membrane-pore-water velocity	m/s
v	Velocity in y-direction	m/s
V_s	Superficial water velocity	m/s
x,y,z	Coordinate	m
x_i	Gas phase mole fraction of species i	-

z	Distance	m
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Greek letter

Symbol	Description	Units
α	Transfer coefficient	-
γ	Concentration coefficient	-
δ	Thickness of the film	m
ε	Volume fraction/porosity	-
ζ	Stoichiometric flow ratio	-
η	Overpotential	V
$\bar{\eta}$	Efficiency	-
I	Second-order Identity Tensor	N/A
κ	Hydraulic Permeability	m ²
λ	Water Content	-
ρ	Density	kg/m ³
σ	Electrical conductivity	s/m
φ	Potential	V
ω_j	The mass fraction of species j	-

Abbreviations

Symbol	Description
PEM	Proton exchange membrane
1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
GDL	Gas diffusion layer
AFF	Anode flow field
AGDL	Anode gas diffusion layer
ACL	Anode catalyst layer
CCL	Cathode catalyst layer
CGDL	Cathode gas diffusion layer
CFF	Cathode flow field
M	Membrane
CFGDL	Carbon-filled GDL

Subscripts and superscripts

Symbol	Description
o	Inlet to flow field/ standard condition
a	Anode side of the cell
c	Cathode side of the cell
cl	Catalyst layer
cool	Cooling
d	Gas diffuser layer
dry	Dry membrane
eff	Effective factor
g	Gas phase
H or H ₂	Hydrogen
H ⁺	Proton
i	Mixture component
in	Inlet
L	Position at the CGC/CGD
m	Membrane
N ₂	Nitrogen
O ₂	Oxygen
ocv	Open Circuit Voltage
out	Outlet
ref	Reference condition
rev	Reversible
s	All layers except membrane

Symbol	Description
sat	Saturation
solid	Solid matrix
T	Transpose of second-order Tensor
th	Thermal
w	Water
ad	Anode diffusion layer
ac	Anode catalyst layer
cd	Cathode diffusion layer
cc	Cathode catalyst layer
m	Membrane

Other notations

Symbol	Description	Units
c_F	Form-drag constant	-
c_p	Specific heat capacity at constant temperature	J/(mol·K)
E_a	Activation energy	J/mol
E_{rev}	Reversible potential	V
j_o^{ref}	Volumetric exchange current density	A/m ³
M_m	Equivalent weight of dry membrane	Kg/mol
n_d	Electroosmotic drag coefficient	-
κ_d	Dilatational viscosity	Pa·s

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World total population is expected to increase to 7.94 - 8.33 billion in 2030, in which 4.72 - 5 billion will live in urban areas---an increase of 48.6 - 57.8 % from today. Economic development and population growth in many emerging markets are causing the global demand for energy to increase rapidly. The progressive drying out of resources (fossil, oil and gas) and the global warming and increasing local carbon dioxide emitting intrigue the whole world to rethink its energy strategies completely. Figure 1.1 shows the global demand of energy primary and local CO₂ Emission. Predicted results show the global demand of energy, the renewable energy and CO₂ emissions will rise by over 50 %, 100 % and 100 % from 1990 to 2030.

Figure 1.1 Predicted energy demand and CO₂ emission. (Source: IEA 2007)

Renewable energy sources (solar electric, wind, geothermal, biomass, and small hydro) can be used to produce electricity with fewer environmental impacts. The renewable energy

system resources (such as solar PV and wind turbines) are often available in remote areas and the power produced is delivered through high-tension transmission lines to large metropolitan centres. Large scale renewable energy system deployment in urban areas is not possible while small scale deployment will not give any encouraging investment return.

However, hydrogen preferably generated from renewable energy sources situated in the remote area can be supplied to households via existing gas piping network. It can be used for cooking and can produce heat and power by fuel cell combined heat and power (CHP) generation systems. Figure 1.2 shows the inexorable rise of hydrogen and fuel cell efficiency versus heat engines. Hydrogen is a versatile energy carrier that can be used to power nearly every end-use energy need. Fuel cells generally have higher efficiency than the traditional energy conversion systems (heat engines or turbines) and can be alternative to these existing energy systems on:

- Stationary fuel cells can be used for backup power, power for remote areas, distributed power generation, and cogeneration (in which excess heat released during electricity generation is used for other applications).
- Fuel cells can power almost every mobile device from hand-held devices to portable generators. They can be considered as battery replacement especially devices with high energy demand.
- Fuel cells can also power our transportation, including vehicles, trucks, buses, and marine vessels, as well as provide auxiliary power to traditional transportation technologies.

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Figure 1.2 Fuel cell advantages: (a) the inexorable rise of hydrogen; (b) fuel cell efficiency vs. heat engines.

The polymer electrolyte membrane (PEM) fuel cell is under consideration by vehicle manufacturers around the world as an alternative to the internal combustion engine, which illustrates the maturity of science and technology in fuel cells. As shown in Figure 1.3, fuel cell can offer a wide range of power rating requirements from micro to milli-watt applications such as micro-electromechanical systems (MEMS), to sub-wattage mobile phone, to 1 - 5 kilowatts portable generators, to more than 50 kilowatts automobiles and to megawatt power plant.

Figure 1.3 Fuel cell power range equipments.

1.1 Operation principle of a PEM fuel cell (PEMFC)

A schematic diagram of a PEMFC is shown in Figure 1.4. Theoretically, PEMFC can produce electricity endlessly provided that there are continuous supplies of oxygen or air on the cathode side and hydrogen gas at the anode side. The anode and the cathode are separated by a proton-conducting polymer membrane.

Hydrogen is oxidized at the anode side and following the mechanism:

At the cathode side oxygen is reduced to water in the presence of protons and electrons on platinum catalyst surface:

The overall reaction in a PEMFC can be written as:

Figure 1.4 Schematic diagram of a PEMFC.

Reaction (Eq. 1-1) is endothermic ($\Delta H(298\text{ K}, 1\text{ atm}) = 2829.0\text{ kJ/mol}$) while reaction (Eq. 1-2) is exothermic ($\Delta H(298\text{ K}, 1\text{ atm}) = -3114.8\text{ kJ/mol}$) (Lampinen and Fomino, 1993) causing an overall heat generation. Overall reaction for reaction (Eq. 1-3) is exothermic ($\Delta H(298\text{ K}, 1\text{ atm}) = -285.8\text{ kJ/mol}$), the ideal standard potential of an H_2/O_2 fuel cell is 1.23 V when the product water is in liquid form. However the actual cell potential is always lower as shown in Figure 1.5.

Figure 1.5 Typical polarization curve of a PEMFC.

The losses that occur in a fuel cell during operation can be summarized as follows:

- **Fuel crossover and internal currents:** occur even when the outer circuit is disconnected. It can be represented by the loss in open circuit voltage (OCV). The highly diffusive hydrogen can crossover the membrane and combine with the oxygen

at the cathode side. This loss can be reduced by increasing the thickness of the electrolyte and developing on electrode fabrication.

- **Activation losses:** are caused by the sluggish reactions taking place at the surface of the electrodes. A proportion of the voltage generated is lost in driving the chemical reaction that transfers the electrons to or from the electrodes. It can be represented by activation overpotential. In a PEM fuel cell this loss occurs mainly at the cathode side, since exchange current density i_0 of the anodic reaction is several orders of magnitude higher than the cathodic reaction. Activation overpotential η_{act} is usually represented by Butler-Volmer Equation (Bard and Faulkner, 1980) .

$$i = i_0 \left[\exp\left(\frac{\alpha_a F}{RT} \eta_{act}\right) - \exp\left(-\frac{\alpha_c F}{RT} \eta_{act}\right) \right] \quad (\text{Eq. 1-4})$$

where i_0 is the apparent exchange current density, α_a and α_c are the anodic and cathodic apparent transfer coefficients, respectively; F is Faraday's constant, and R is the universal gas constant.

- **Ohmic losses:** the result of the electrolyte resistance and are sometimes due to the electrical resistance in the electrodes. It can be represented by ohmic overpotential as (Eq. 1-5) where r is the total internal resistance. The largest part of resistance losses in PEMFC is from the membrane when hydrated improperly. Minimization of resistance loss requires thinner membrane and effective water management but at the risk of possible fuel crossover the membrane.

$$\eta_{ohm} = i r \quad (\text{Eq. 1-5})$$

- **Mass transport or concentration losses** result from the change in concentration of the reactants at the surface of the electrodes as the reactants are being consumed (Lampinen and Fomino, 1993). At a sufficiently high current density, the rate of

reactants consumption would become equal to the amount of reactants than can be supplied to the reaction site by diffusion, and this is denoted as the limiting current density (i_l). It is called concentration overpotential and can be expressed as (Larminie and Dicks, 2000):

$$\eta_{\text{conc}} = \frac{RT}{2F} \ln\left(1 - \frac{i}{i_l}\right) \quad (\text{Eq. 1-6})$$

where i_l is the limiting current density.

1.2 PEMFC components

1.2.1 Polymer electrolyte membrane (PEM)

The functionality of the fuel cell is dependent on the unique properties of the membrane. The desired characteristics of PEMs are high protonic conductivity, good electronic insulation, good separation of fuel in the anode side from oxygen in the cathode side, high chemical and thermal stability, and low production cost (Eikerling and Kornyshev, 2001).

In general, proton-conducting polymers are usually based on polymer electrolytes, which have negatively charged groups attached to the polymer backbone. Figure 1.6 shows the chemical structure of Nafion[®] (from Dupont) and Dow membranes (Dow Chemical Co.).

Figure 1.6 Chemical Structures of Nafion (a) and Dow membranes (b).

Nafion[®] is a perfluorosulfonic acid (PFSA) polymer, a perfluorosulfonic acid/polytetrafluoroethylene (PTFE) copolymer in the acid (H^+) form. When the membrane is fully hydrated, the negatively charged SO_3^- groups serve as fixed charge sites that attract positive hydrogen ions (Figure 1.7). It is believed that the protons jump from one negative site to another while moving along the membrane pore (Verbrugge and Hill, 1990)..

Figure 1.7 Hydrated PEM.

In order to reduce the cost and improve electrochemical properties, the development of new proton-conducting polymer electrolytes is necessary for extensive applications. Proton-conducting polymer electrolytes based on hydrocarbon polymers or inorganic polymers are one of the most promising materials for the development of new PEMFCs (Rikukawa and Sanui 2000; Jannasch 2003)

1.2.2 Catalyst layer (CL)

The gas diffusion electrode (GDE) in a PEMFC is a key component that affects the performance and cost of the fuel cell due to its noble metal Pt content. Improvement in the properties of electrode is the most practical way to increase fuel cell performance and decrease the cost of fuel cell. Typically, a GDE in a PEMFC comprises a catalyst layer (CL) and a gas diffusion layer (GDL).

Catalyst layers play a critical role in determining the performance of the membrane electrode assembly (MEA). The catalyst layer must provide high activities for the electrochemical oxidation of fuels at the anode and reduction of oxygen at the cathode

As shown graphically in Figure 1.8 (Barbir, 2005), the reactions take place at the three-phase boundary of ionomer, solid, and void phases (Figure 1.8 (a)). However, this boundary has an infinitesimally small area (essentially it is a line not an area) that would result in infinitely large current densities. In practice, because some gas may permeate through the polymer, the reaction zone is larger than a single three-phase boundary line. The reaction zone may be enlarged by either "roughening" the surface of the membrane or by incorporating ionomer in the catalyst layer (as shown in Figure 1.8 (b)). In an extreme case, the entire catalyst surface may be covered by a thin ionomer layer (Figure 1.8 (c)), except for some allowance for electrical contacts. Obviously, the ratios between the catalyst area covered by ionomer to

catalyst area opened to void to catalyst area contacting other catalyst particles or electrically conductive support must be optimized in order to provide the optimal performance. The key to improving the PEM fuel cell performance is not in increasing the Pt loading, but rather in increasing Pt utilization in the catalyst layer.

Figure 1.8 Graphical representation of the reaction sites.

1.2.3 Gas diffusion layer (GDL)

Gas diffusion layer has to permit homogenous transfer of reactants to and water away from the electrodes, as well as to offer appropriate electric conductivity, heat conduction and mechanical properties, thus, it needs to meet the following requirements such as: (Barbir, 2005):

- *Porous*: It must be sufficiently porous to allow flow of both reactant gases and product water. Depending on the design of the flow field, diffusion in both through plane and in-plane is important.
- *Pore size*: Because the catalyst layer is made of discrete small particles, the pores of the gas diffusion layer facing the catalyst layer must not be too big.
- *Electrically and thermally conductive*: Interfacial or contact resistance is typically more important than bulk conductivity.

- *Structure*: It must be sufficiently rigid to support the "flimsy" MEA. However, it must have some flexibility to maintain good electrical contacts.

Highly porous carbon cloth or carbon paper can meet above requirements and always be treated with hydrophobic resin, usually Teflon[®] to make gas diffusion layers which is also called as "wet-proof" process. The hydrophobic feature is desired for gas diffusion as water cannot stay and block the pores. In addition, they provide an interface where ionization and transfer electrons take place through the solid matrix. GDEs are characterized mainly by their thickness (between 100 μm and 300 μm) and porosity (0.2 - 0.8). The hot-pressed assembly of the membrane and the gas-diffusion layer including the catalyst is called the membrane-electrode-assembly (MEA).

Micro-Porous layer (MPL) now is commonly used to improve the fuel cell performance. Micro-porous layer is fabricated in between gas diffusion layer and catalyst layer with carbon black powder and some hydrophobic agent (PTFE), which provides proper surface pore size and hydrophobicity to avoid flooding and to enhance intimate electronic contact at its interface with the catalyst layer.

MPL thickness is primarily controlled by the applied carbon loading. It is generally accepted that a thin MPL improves gas transport and facilitates the removal of water, but it has high electronic resistance and does not give a non-permeable support for coating with the catalyst layer, while a thick MPL hampers gas accessibility because of the lengthened path through the MPL and also has poor gas diffusivity. Hence, an intermediate carbon loading may be beneficial.

1.2.4 Bipolar plate

The bipolar plate electrically connects adjacent cells and typically also distributes fuel and oxidant to the anode and cathode. This means that it is subjected to oxidizing conditions on one side and reducing conditions on the other. An optimized bipolar plate has to fulfill a number of materials and construction requirements (Vielstich, *et al.*, 2003; Brett and Brandon, 2005; Brett and Brandon, 2007):

- Good electrical conductivity ($\geq 10^3$ S/m);
- Good thermal conductivity ($\geq 2 \times 10^3$ W/m/K);
- Gas tightness;
- Corrosion resistance in acid with oxygen, heat and humidity;
- Minimal volume and weight;
- Inexpensive material and processing costs.

Historically, machined graphite had been chosen as a good compromise between all of these requirements, but alternatives are emerging, metals such as stainless steel, aluminum, or composite materials (Mehta and Cooper, 2003).

The usual geometries used for flow fields are parallel, serpentine, combination of parallel and serpentine, net flow etc. which is showed at Figure 1.9. The main requirement for an effective flow field is that it ensures a homogenous concentration profile for reactants throughout the active cell area.

Figure 1.9 Schematic of the flow distributors: (a) Single serpentine channels (b) Three passes serpentine channels (c) parallel channels (d) net flow

1.3 Objectives of the thesis

At the moment, PEM fuel cell technology is maturing towards commercialization, but challenges include cost reductions, reliability and system integration *etc.* Cost reductions are vital to make fuel cells comparable to other remain conversion systems formation. The reliability of fuel cells must be high enough so as to extend the life span of the fuel cells similar to or better than the existing energy systems. Finally, the system integration must be capable of gaining the public's interest by showing real examples of fuel cells in use and the results of such implementation. To achieve high performance, one has to consider uniform

reactant flow, water and thermal management, catalyst layer transport properties and utilization rate, *etc.* While prototyping and experiment are excellent tools, they are expensive to implement and subject to practical limitations. However, these experiments have limitation in revealing the detail of the transport phenomena occurring inside the fuel cell. This is where modeling can be a great complement to experimental techniques. Computer modeling is more cost effective, and easier to implement when design changes are made. There has been tremendous interest in PEMFC modeling to gain insight in water management, platinum utilization as well as other simultaneous transport and electrochemical processes and numerical models continue to gain increasingly more acceptance.

The objectives of this dissertation are:

- Investigation of the fuel cell phenomenology and transport mechanisms which pave the way for relatively simple yet representative models to predict the performance or to guide the optimal design of a fuel cell.
- Investigation of parameters (operating, geometric, intrinsic and extrinsic) that are sensitive /insensitive to the fuel cell performance, but may have implication on life span of the fuel cell through thorough parametric studies based on the model developed.

1.4 Scopes of the thesis

The Scopes of the thesis comprises of two parts: experiments and simulations.

For the experiments:

- PEMFC with serpentine 2-pass flow field is fabricated and investigated.
- PEMFC with porous flow field channel is fabricated and investigated. Two different gas diffusion layer (single layer GDL and carbon-filled GDL) are conducted.
- A 200W-PEMFC stack for Electrical bicycle was fabricated and investigated.

For the simulations:

-
- Developed a 1D model based on Bernardi and Verbrugge and Springer model.
 - A series of parametric studies on operating and geometric parameters (temperature, pressure, membrane thickness, porosity, *etc.*) has been conducted and validated with in-house experiment of single PEMFC with serpentine 2-pass flow field.
 - Developed a 2D, single phase, non-isothermal PEMFC model with porous flow field in COMSOL. Steady-state conservations of mass, momentum, species, energy, and charge are solved simultaneously with a phenomenological model for the membrane and an agglomerate model for the cathode catalyst layer. This model is validated with in-house experiment of single PEMFC with porous flow field.
 - A series of parametric studies (temperature, pressure, air flow rate, GDL thickness, permeability of flow field and GDL, size of agglomerate nuclei, platinum loading etc) has been conducted.
 - Developed a two cell stack model and perturbation studies (air flow rate, platinum loading, thermal conductivity, porosity, cathode inlet temperature) for the stack have been conducted.
 - Developed a simple 2D pseudo 2-phase single cell model and an original “curve back” phenomena had been investigated. Uniform liquid water accumulation and localized liquid water accumulation have been discussed. Three critical parameters (E^* , ΔE and s^*) have been introduced and a series of parametrical studies on these three parameters has been conducted.

All the models have been fully or partially validated with in-house experiments. Reasonable agreements had been achieved, which showed the predictive capability of the models developed.

Chapter 2 Literature review

2.1 Introduction

Although the fuel cell has received much attention in recent years, the underlying principles and concepts are still under heavy investigations. Using a mathematical model to simulate the fuel cell, for example, the transport phenomenon is a powerful tool to understand the fundamental physical and chemical processes of a fuel cell. Thus, reliable mathematical models are essential for fuel cell design, operation and optimization. In the early 1990s most models were exclusively one-dimensional in nature. From the late 1990s onward, the models extended to multi-dimensional and became more elaborate. Much effort has been expended upon development of numerical models with increasingly less restrictive assumptions and more physical complexities. Current development in PEMFC modeling is in the direction of applying computational fluid dynamics (CFD) to solve the complete set of transport equations governing mass, momentum, species, energy, and charge conservation. Several CFD software distributors, such as COMSOL (previous FEMLAB), FLUENT, STAR-CD and CFD Research (now ESI Group), etc., have developed fuel cell modules that can be used in conjunction with the original CFD codes. Researchers have used modeling to explore fuel cell, ranging from elucidating new fundamentals to characterizing fuel cell system performance.

Modeling work applied within a PEMFC can in general be represented by the solution of conservation equations for mass, momentum, energy, species, and current transport. Figure 2.1 shows the 3D structure of PEMFC unit cell. According to the number of directions considered, modeling work can be categorized as 0D; 1D (z); 2D(x-z or y-z); 2-2D(x-z and y-z); 3D models (x-y-z).

Figure 2.1 The 3D structure of a PEMFC unit cell.

As a PEMFC operating temperature is around $60\text{ }^\circ\text{C}$ - $120\text{ }^\circ\text{C}$, water can exist in liquid and gas states, therefore derived single-phase and two-phase models under individual dimensional as necessary. Figure 2.2 shows the challenges that may encounter during the modeling.

Figure 2.2 The challenge of a PEMFC unit cell modeling.

Modeling equations that deal specifically with phenomena in a fuel cell can be summarized

as (Barbir, 2005):

- Darcy's equation for fluid flow in porous media,
- Fick's Law for diffusion,
- Stefan-Maxwell equation for multi-species diffusion,
- Fourier's Law for heat conduction,
- Faraday's Law for relationship between electrical current and consumption of reactants in an electrochemical reaction,
- Butler-Volmer equation for relationship between electrical current and potential,
- Ohm's Law for electrical current conduction.

Also, empirical equations, particularly those describing water behavior in the polymer membrane and related phenomena, are often used in modeling, in the absence of equations that describe the actual physical phenomena.

Any model is as good as the assumptions that it is built upon. It is important to understand the assumptions made in order to understand the model's limitations and to accurately interpret its results. Common assumptions used in fuel cell modeling are:

- Ideal gas properties,
- Ideal gas mixtures,
- Incompressible flow,
- Laminar flow,
- Isotropic and homogeneous membrane and electrode structures,
- Negligible ohmic potential drop in solid phase components,
- Mass and energy transport through porous structures of porosity ε which is modeled in macro-perspective by using the volume-averaged conservation equations.

2.2 Literature survey of PEMFC modeling

2.2.1 One-dimensional Models

Bernardi and Verbrugge (widely known as BV model) (Bernardi, 1990; Bernardi and Verbrugge, 1991, 1992) and Springer *et al.* (1991, 1993) pioneered the PEMFC simulations. Their often cited models were essentially one-dimensional. Their models provided a fundamental framework to build complete multi-dimensional, multi-physics models. They were valid for fully hydrated membranes but were unable to predict flooding in the cathode backing layer due to water production. Based on BV model and Springer model, similar one dimensional models have been developed by Weisbrod *et al.* (1996) and Eikerling *et al.* (1998-2006).*etc.*

Weisbrod *et al.* (1996) incorporated the membrane water model of Springer *et al.* and explored the possibility of the water flux in the electrode backing layer. Eikerling *et al.* (1998-2006) viewed the catalyst layer as only an interface with negligible thickness.

Most recently, researchers conducted a one-dimensional modeling by including the phase change of water. Gurau *et al.* (2000) took into account the liquid water in the gas diffuser and catalyst layers by means of effective porosities that describe the porous media when the pores are partially filled with liquid water in thermodynamic and hydrodynamic equilibrium. Lin *et al.* (2004) used a thin film-agglomerate approach to model the catalyst layer. The effect of water flooding in the gas diffusion layer and catalyst layer of the cathode on the overall cell performance was investigated. The results showed that liquid water accumulation within the backing and catalyst layers of a cathode had a significant impact on the cell performance, which was in good agreement with the experimental observations.

Währ *et al.* (1998) have developed a one-dimensional model allowing for the simulation of the transient effects such as the change of electrical load or gas flow rate and humidification.

Ziegler *et al.* (2005) presented a model that contains a dynamic and two-phase description of the PEMFC and a membrane model that accounts for Schroeder's paradox-a hysteresis effect was found in the measured time-dependent current-voltage relation. The limiting current density was time dependent. For the first time, the results of a dynamic and two-phase model on a time scale of minutes were shown and compared with measurement data. The modeling results showed that this hysteresis was caused by an increase in the mass-transport limitation on the cathode side, due to the time-dependent accumulation of water on the cathode side. In recent years, Weber and Newman (2003; 2004), Shan and Choe (2005), Fimrite *et al.* (2005a; 2005b) also conducted similar studies.

To better understand the transport phenomena within the specific region, many researchers have focused the study on the catalyst layer, membrane, gas channel region individually.

Currently, catalyst models can be classified into different groups based on the way they deal with the catalyst structure. Macroscopic models consider the catalyst as a continuous medium, and consequently they are not able to identify the effects of the discrete distribution of the agglomerates, whereas microscopic models deal with the local geometry of the catalyst layer. Chan and Tun (2001) presented two simple macroscopic catalyst layer models---the pseudo-homogeneous model (where the catalyst is treated as a homogeneous phase with oxygen diffuses through the porous media) and the agglomerate model (where the catalyst is assumed to form agglomerates of certain ordered geometry. The oxygen diffused from the pores to the agglomerates and its concentration in the pores was assumed to be constant. The former was solved analytically whereas the latter was solved numerically to parameterize factors affecting the performance of the fuel cell with simple approach without going into detailed catalyst layer modeling. Broka and Ekdunge (1997) showed the influence of a geometry through a comparison of a pseudo-homogeneous model and an agglomerate model of the catalyst layer. In the pseudo-homogeneous approach, the oxygen concentration gradient

varies with the local current density in the active layer, whereas in the agglomerate model, the oxygen diffuses from the gas pores into the agglomerate, which implies a constant oxygen concentration. In the latter model, the effect of oxygen diffusion limitation was characterized by an effectiveness factor in which the characteristics of the agglomerate were taken into account. On the basis of their simulations and a structural study of the catalyst layer, they reached the conclusion that the agglomerate model gives a better representation of the catalyst layer. In particular, they claimed that the thickness of the Nafion film surrounding the carbon-platinum agglomerates was a crucial parameter in calculating the limiting current due to mass transport limitations. Similar conclusions can also be found in Gloaguen *et al.* (1998) and Xu *et al.* (1999).

You and Liu (2000-2002) presented a two-phase, pseudo-homogeneous model of the cathode catalyst layer of a PEMFC derived from a basic mass-current balance. The model was derived from a basic mass-current balance by the control volume approach. Their model considered the kinetics of the electrochemical reaction along with oxygen diffusion through the pores and proton transport within the membrane phase. A relaxation method was used to solve the two-point boundary problem. The effects of different parameters on the catalyst layer were studied in detail, which would help in the optimization design of cathode catalyst layer in PEMFCs. Most current models used a macroscopic approach, *i.e.* consider the catalyst layer as a whole.

Bultel *et al* (1998a; 1998b; 2005) presented a more in-depth study of the effects of the geometric arrangement within the catalyst layer at the particle level. This microscopic approach provided information on the effect of competition between neighboring particles and the ionic ohmic drop limitation. However, this study was restricted to the case of a highly porous layer where ohmic drop limitations are stronger than diffusion limitations. One of the

conclusions made by the authors was that the discrete distribution of the catalyst particles resulted in a local limitation effect that must be added to the ohmic drop effect.

Verbrugge and Hill (1990,1992) first studied the transient ion and solvent transport phenomena within an ion-exchange membrane. Nernst-Planck equation was employed to describe the ion transport by diffusion, migration, and convection. Solvent transport driven by pressure and electric-potential gradients was described by an equation of motion.

With recent popularity in the usage of reformed fuels to power the PEMFC, research groups such as Springer *et al.* (1996, 2001); Wang *et al.*(2001); Chan *et al.*(2003); Zhou and Liu (2004) had also constructed models to take into account the anode kinetics of the PEMFC. Springer *et al.* refined parameters for an anode kinetic model previously developed model and coupled it with the effects of hydrogen dilution and high fuel utilization. Chan *et al.* (2003) developed a mathematical model marrying the work of Bernardi and Verbrugge and Springer *et al.*'s model. Two cases of study were carried out in their work. First, the water self-sufficiency of fuel cell operation was conducted under different current density, temperature, pressure differential across the membrane-electrode-assembly (MEA), hydraulic permeability and electro-kinetic permeability. Comparison of superficial water velocities in the MEA under the effect of different current density with those from Bernardi and Verbrugge was conducted. Second, the effect of CO poisoning of fuel cell was presented in terms of cell polarization.

2.2.2 Two-dimensional Models

Two-dimensional (2D) models are developed to improve the earlier 1D models. As mentioned in the introduction, refer to Figure 2.1, there are two kinds of 2D model (x-z or y-z direction). One is the model investigated on the x-z direction ("along the channel" model). This kind of

model focuses on analyzing changes of properties along the channel due to reduced concentrations of reactant gases pressure drop, and increased concentrations of water. The domain may include only one side (typically cathode), or both sides if the effects of co- or counter-flow of hydrogen on the other side are of interest. The other is the model investigated on y-z direction ("above the channel" model). It is similar to the 1-D, but it extends into two dimensions to include the effect of the "ribs" and "lands" between the channels. Because the electrode portion covered by the ribs is not directly exposed to the channels, it suffers from a slow reactant gas mass transfer. The ribs can be regarded as barriers to the mass transfer. However, they are necessary for electric current conduction. A complete understanding of the mass transport phenomena within the gas diffusion layer, under the influence of current collector will facilitate a proper PEM fuel cell design.

Fuller and Newman (1993) were the first to publish a quasi two-dimensional model of the MEA, which was based on the concentration solution theory for the membrane and accounts for the thermal effects. They solved the transport equations across the cell at given stations along the channel and then integrated them along the MEA direction.

Nguyen and White (1993) and later Yi and Nguyen(1998), effectively demonstrated the important roles of water and heat management in maintaining high performance of PEMFCs.

Nguyen and White (1993) presented a steady-state, heat and mass-transfer model of a PEMFC. This model solved the transport equations of liquid water through the membrane by electro-osmotic drag and diffusion as well as the phase-change of water, but the MEA was greatly simplified by assuming "ultra-thin" gas-diffusion electrodes. The volume of the liquid phase in the anode side was assumed to be negligible. The temperature was considered constant in the solid materials and heat transfer by conduction in the gas phase was neglected. This model was used to investigate the effect of different humidification schemes on the fuel cell performance.

Yi *et al.* (1998) presented an along-the-channel model to evaluate the effects of various design and operating parameters on the performance of a PEMFC, modeled the pressure gradient also temperature distribution in the solid phase along the flow channel, and heat removal by natural convection and co-flow and counter-flow heat exchangers. The mass transport was in 2D while the heat transport was only in 1D. They concluded that the performance of a PEM fuel cell could be improved by anode humidification and positive differential pressure between the cathode and anode to increase the back transport rate of water across the membrane. Effective heat removal was necessary to prevent excessive temperature which could lead to local membrane dehydration. Yi and Nguyen (1999) extended the above model and formulated a two-dimensional model to explore hydrodynamics and multi-component transport in the air cathode of PEMFC with an interdigitated flow field. The model was used to evaluate the effectiveness of various humidification designs, higher cathode gas pressure, and heat removal schemes for PEM fuel cells. They strengthened that the counter-flow heat exchanger was more effective.

Ge and Yi (2003) also described the effect of different modes of flow (co-flow and counter-flow). They predicted that dry reactant gases could be well internally humidified and high performance can be achieved when PEMFC was operated in the counter-flow mode without external humidification. They also showed that counter-flow mode would not give any advantages if the reactant gases were high humidified or saturated. West and Fuller (1996) studied the effects of rib sizing and the GDL thickness on the current and water distributions within a PEM fuel cell. They found that dimensions of the ribs only slightly altered the cathode potential for a given current density, but had a significant influence on water management. Concentrated solution theory with variable transport properties was used to solve for the electrical potential and local water content.

Janssen (2001) introduced non-isothermal, two-phase model to describe the water transport in PEMFC. Concentrated solution theory was used to describe the transport of water in the membrane, and water vapor and liquid water in the electrodes. The incorporation of the liquid water transport into the model turned out to be essential for explaining recent experimental results on the effective drag coefficient and its dependence on operating conditions as well as on variations of the components that constitute the membrane electrode assembly, especially when the cell was operated with saturated gases.

Yan *et al.* (2004) focused on investigating the anode gas flow channel cross-section and GDL porosity effects. They found that an increase in either the GDL porosity, channel width fraction, or the number of channels could lead to better cell performance. Sun *et al.* (2005) investigated the influence of gas diffusion layer (GDL) property and flow-field geometry on the local reaction rate in the PEMFC cathode catalyst layer. The simulation results indicated that moderate GDL compression would not significantly influence the cathode performance for single-phase flow conditions. Moreover, channel-to-channel bypass flow under the land was predicted to have a positive impact on the cathode performance.

Siegel *et al.* (2004) presented a model that includes the transport of liquid water. Electrochemical kinetics was modeled with standard rate equations adapted to an agglomerate catalyst layer structure. The model predicted a net amount of water transport across the membrane of between 0.16 and 0.34 mole of water per mole of protons transported from the anode to the cathode. This accounted for 20 – 40 % of the total amount of water accumulation at the cathode, which was a combination of water produced electrochemically and water transported by electro-osmotic drag. When operating at high inlet humidity, any water accumulating at the cathode would remain in the liquid phase and filled the porous regions of the catalyst layer and the GDL. The fraction of pores filled with liquid water was highest within the catalyst layer near the inlet to the cell.

Jeng *et al.* (2004) took the current collector ribs into account, they concluded that the existence of ribs caused the GDL to be used only partly in the mass transfer process. The GDL effectiveness decreases with the cell current density and increases with the width of the gas flow channels. The PEM fuel cell performance decreases with an increase in GDL thickness if the GDL porosity was low. However, when a high-porosity GDL was used, the optimal thickness became an indicator determining the maximal PEM fuel cell performance. Hum *et al.* (2004) focused on the phenomena occurring in the catalyst layers. Results showed that the cathode catalyst layer exhibited more pronounced changes in potential, reaction rate, and current density generation than the anode catalyst layer counterparts due to the large cathode activation overpotential and the relatively low diffusion coefficient of oxygen. It was shown that the catalyst layers were two-dimensional in nature, particularly in areas of low reactant concentrations. The two-dimensional distribution of the reactant concentration, current density distribution, and overpotential was determined, which suggested that multi-dimensional simulation was necessary to understand the transport and reaction processes occurring in a PEM fuel cell.

To account for 2D effects, the methods of computational fluid dynamics (CFD) have recently been successfully applied to fuel cell modeling. Guvelioglu and Stenger (2005) used FEMLAB to investigate the complex water balance in the membrane. They concluded that smaller width channels and bipolar plate shoulders were required for high current density operations. The relative humidity of anode gas stream was found to be more critical for fuel cell performance than that in the cathode gas. Birgersson and Vynnycky (2006) used CFX to study four different flow-patterns: interdigitated, co-flow, counter-flow channels and foam. A quantitative comparison of the results showed that the interdigitated channels could sustain the highest current densities, followed in descending order by the foam, the counter-flow, and the co-flow channels. The foam yielded the most uniform

current density distribution at higher currents but care should be taken on its permeability to avoid unreasonably high-pressure drops.

Gurau *et al.* (1999; 2000) considered the gas phase and the liquid phase in separate computational domains, which meant that the interaction between both phases was not considered. Singh *et al.* (1999) indicated that the cathode potential loss associated with the slow O₂ reaction rate was dominant at all practical current densities. The simulations also showed that two-dimensionality had a significant effect on water management. In particular, the anode and cathode water fluxes were found to vary considerably along the oxidant and fuel flow channels and two new transitional water transport regimes. The influences of flow configuration and electrode porosity on predicted cell performance were also discussed.

Mench *et al.* (2003) and Meng H. and Wang C. Y. (2003, 2005a) used Fluent to study two-phase flow and liquid water transport on the multi-phase mixture model. Although they could handle liquid water transport and two-phase formation successfully, they predict liquid water saturation only up to 6.3% as flooding effects were neglected. The same problem was encountered in Liu and Zhou (2003)'s work. Meng H. (2007) mentioned two-phase PEM fuel cell modes accounting for the liquid water transport using either the multiphase mixture model or traditional two-fluid model. A common weakness remained in its inability to predict significant liquid saturation values in the porous gas diffusion layer and catalyst layer and consequently the flooding effects in PEMFCs. He brought up the mixed-domain concept to effectively determine the key parameters of condensation and evaporation rate coefficients. Numerical simulations showed that liquid water was mainly produced in the GDL in two regions; one was near to the current-collecting land owing to the low temperature and another was further into the GDL but still away from the catalyst layer. Thus the micro-porous layer at inlet region of the cell would effectively prevent liquid

water from entering the catalyst layer and to prevent severe liquid flooding in this region in the PEMFC design.

2.2.3 Three-dimensional models

As shown previously, two-dimensional models can be used to characterize fuel cell performance “along the channel” (x-z direction) or “above the channel” (y-z direction). In the y-z direction, the model focuses on the MEA or includes the effect of gas transport in the porous diffusion layer and gas channel. In the y-z direction, several channels can be considered in order to investigate the effects such as gas mixing between the channels occurring in the diffusion layer. A three-dimensional model can be used to consider all the aforementioned phenomena, but computational limitations often limit the model's fidelity. The equations used are the same as those in 1D and 2D models, but all the differential equations are applied in all three directions. Consequently, the boundary condition must be applied for all three dimensions.

Dutta *et al.* (Dutta, Shimpalee et al. 2000; Dutta, Shimpalee et al. 2001), first put the CFD code (FLUENT) to solve the three-dimensional models on serpentine flow field design. Later (Kumar and Reddy 2003) also used FLUENT to consider metal foam as the flow-field of the bipolar/end plates instead of the conventionally used rectangular channels. Results showed a significant effect of permeability of the metal foam on the performance of the fuel cell. The developed model offered fuel cell developers a scope for improvement on the bipolar/end plates in the fuel cell, by switching over to the metal foam flow-field concept.

Quan *et.al* (Quan, Zhou et al. 2005) also used FLUENT to simulate one U-shaped micro-channel to provide invaluable information for fuel cell flow field design and optimization. Results showed that the bend area of a serpentine flow channel had significant effects on the

flow field, which in turn affected the air-water flow and water liquid distribution inside the channel or along the interior channel surfaces. The simulation results also indicated that water flooding could occur in the "after-bend" section of a micro-channel.

Noponen *et al.* (2002, 2004a, 2004b) used the commercial software package FEMLAB (Comsol, Inc.) in the fuel cell modeling. Current densities near the edges of the computation domain and water migrating from anode to cathode showed higher current densities near the centerline. This effect could only be observed by including the width of the flow channel and gas diffusion layer in the model.

Kulikovskiy *et al.* (2003, 2005) developed a steady-state, isothermal, quasi-3D single-phase model of water transport in MEA. The model took into account nonlinear diffusion of liquid water in the membrane. It was shown that nonlinearity leads to the formation of closely located dry and wet regions in the membrane. The model qualitatively reproduced measured membrane resistance and the mean profile of water content across the membrane. Weng *et al.* (2005) predicted species concentration, current density distributions as well as cell performance with parallel straight, serpentine and interdigitated flow patterns. The simulation results revealed that serpentine and interdigitated flow patterns showed strong convection and high mass transfer. However, they also had larger pressure loss. Non-uniform distributions of concentration and current density appeared at high temperature, high current density, and low humidity operation.

Berning *et al.* (2002) developed a comprehensive non-isothermal single-phase model. The three-dimensional nature of the transport was particularly pronounced under the collector plates land area and had a major impact on the current distribution and predicted limiting current density. Berning and Djilali, (2003a) presented a parametric study. The study quantified the impact of operating and geometric parameters on performance. Berning and Djilali (2003b) modeled the transport of liquid water inside the gas-diffusion layers using

viscous forces and capillary pressure terms. The physics of phase change was accounted for by prescribing local evaporation as a function of the under-saturation and liquid water concentration. Berning *et al.* (2004) presented a model with serpentine flow field channels. The simulation results revealed current distribution patterns that were significantly different from those obtained in the studies assuming constant surface overpotential. Whereas the predicted distributions at high load showed current density maxima under the gas channel area, low load simulations exhibited local current maxima under the collector plate land areas.

Lee *et al.* (2003) introduced the non-isothermal and two-phase factors to predict the local current density and membrane conductivity inside a PEMFC with a serpentine flow path which could present the water balance data as well as estimate the water flux across the membrane.

Natarajan and Van Nguyen (2003) presented a pseudo-three-dimensional, two-phase, transient model to obtain qualitative insights into the distribution of liquid water in the diffusion layer and its effect on the distribution of the gas phase reactant species. They concluded that the liquid water transport mechanism is the slowest and most dominant in influencing the performance of the cathode. The current density distribution along the channel was strongly dependent on the oxygen concentration profile along the channel. The oxygen profile was influenced by consumption due to the electrochemical reaction and dilution due to water evaporation. The relative contribution of these two phenomena was greatly influenced by operating conditions like stoichiometric flow rate, inlet stream humidity and operating temperature.

Meng & Wang (2005) studied the current distribution and cell performance under two different boundary conditions, constant cell voltage and constant current density. They concluded that an identical polarization curve results with two different boundary conditions

while the current density profiles in the along-channel direction differ significantly, it is much flatter for the constant boundary condition. Increasing the electronic conductivity of the bipolar plate diminished the difference.

Similar and further approaches could also be found in recent works from Wang *et al* Group (2002-2009) and Liu *et al* group (2004-2005) and Djilali's group (2004-2009).

2.3 Summary and outlook

Overall, it can be said that up to around 1998, most of the fuel cell models were one-dimensional, focusing on the electrochemistry and mass transport inside the MEA. 1D model provides a good preliminary foundation for PEM fuel cell modeling. These 1D models are based on the fundamental transport properties where the potential losses incurred by the activation overpotential of the anode and cathode reactions; they cannot model the depletion of the reactants and the accumulation of products in the flow direction. In order to account for 2D and 3D effects, the methods of the computational fluid dynamics (CFD) have recently been successfully applied to fuel cell modeling but none of them can cover all the phenomena. For the energy conservation, very few of them really consider the temperature distribution in-depth. There are still rooms for improvements in developing each dimensional model. Recently most multi-dimensional models have energy equations included, but they cannot fully represent the local temperature distribution. *i.e.* isothermal is assumed in the current parametric studies.

Currently, two major themes arise in modeling of fuel cells (Barbir, 2005):

- The user needs to select the appropriate model that balances model capabilities, robustness, and accuracy.
- Model accuracy is strongly dependent on its validity. The fuel cell model must be chosen such that it properly represents the problem being modeled, and it must be

validated comprehensively in order to bring out its true predictive power.

Chapter 3 Experiments

In order to effectively validate the simulation results well. A series of experiments have been designed and fabricated and some physico-chemical characterizations have been conducted.

3.1 Development of a single PEMFC

The membrane electrode assembly (MEA) is the heart of proton exchange membrane fuel cells (PEMFCs), and determines both fuel cell performance and durability. The MEA component materials, structure, and fabrication technologies play important roles in performance improvement and optimization. For example, the catalyst layers, where the electrochemical reactions take place, are the most important of the several components in PEMFCs. The electrodes in PEMFCs, including both cathode and anode, are multi-component and gas porous matrices, also called gas diffusion electrodes (GDEs). A GDE is generally composed of a reaction layer (the CL) and an accessorial layer (the GDL). An ideal MEA would allow all active catalyst sites in the catalyst layer to be accessible to the reactant (H_2 or O_2), protons and electrons, and would facilitate the effective removal of produced water from the CL and GDL.

3.1.1 Preparation of gas diffusion layer

The GDL, adjacent to the catalyst layer and the flow field, plays an important role in PEMFC performance (Chapter 1). Here three types of GDLs have been fabricated.

- *PEMFC with 2-pass serpentine flow field*

GDL was prepared by a scraping method. Wet-proofed carbon paper (30% wet-proofed, Toray, TGPB-090, Japan) was used as substrate. The ink was prepared by intimately mixing

and sonicating the carbon powder (Vulcan XC-72, Cabot Corporation, US), PTFE (PTFE 30, 60 wt% PTFE, Dupont Corporation, US), distilled water and 2-propanol. Carbon powder loading was about 2 mg/cm^2 , PTFE content was 20 wt%. The sonicating time was around 30 - 60 mins under ambient temperature. After applying the ink, the electrode substrate was dried in the air for 30 mins and then sintered in the oven at 350°C for 0.5 hr.

- ***PEMFC with net flow field***

Two types of GDL have been designed and fabricated: Single layer GDL and Carbon-filled GDL (CFGDL).

Commercial available carbon papers, TGP-H-030 carbon paper (Toray carbon papers), was used as electrode backing material. Prior to the preparation of gas diffusion layer (GDL), the carbon papers must be hydrophobic-treated with polytetrafluoroethylene (PTFE) to strengthen the structure of the carbon paper and increase the hydrophobicity of the carbon paper. The PTFE emulsion (60 wt.%, Aldrich) was first diluted with deionized water (the mass ratio of 60 % PTFE to deionized water is 1:10) to form a diluted PTFE emulsion to reduce the dead pores in carbon paper when treated. The carbon paper was then repeatedly impregnated with the diluted PTFE emulsion followed by drying at 120°C until the weight of carbon paper was increased by 40 %; it was further heated at 240°C for 0.5 hr to remove the dispersant containing the PTFE and finally sintered at 340°C for 0.5 hr. The wet-proofed carbon paper can be directly used as single-layer GDL.

A mixture of carbon powder and PTFE polymer is used to fabricate carbon-filled gas diffusion layer (CFGDL). Vulcan XC-72 carbon powder (Cabot Co.) was used as the electrically conductive filler and PTFE (60 wt. %, Aldrich) was used as the binder. A paste composed of carbon powder and PTFE was prepared by dispersing Vulcan XC-72 carbon powder into anhydrous ethanol (the mass ratio of carbon powder to ethanol is 1:20) in an

ultrasonic tank with a frequency of 25 kHz followed by adding PTFE emulsion into the dispersion drop by drop under gently stirring. Afterwards, the paste was pressed into the PTFE treated carbon paper to form the CFGDL by brushing and the thickness of the composite structure was maintained the same as that of the carbon paper. These composite structures were finally dried and sintered at 340 °C for 1 hr for making the catalyst layer.

3.1.2 Preparation of catalyst layer

A homogeneous ink was prepared by mixing (20 % Pt/C or 40 % Pt/C catalyst, Electrochem), 20 wt% PTFE, distilled water and 2-propanol. The ink was sonicated for 30 - 60 mins under ambient temperature. The Pt loading was controlled at around 0.4 - 0.5 mg/cm². The catalyst layer supported on the gas diffusion layer was dried in the air for 30 mins and then sintered in the oven at 350 °C for 0.5 hr.

3.1.3 Electrode treatment

In order to achieve high performance, Nafion solution (5 % Nafion 1100 EW solution, Dupont) was brushed onto the catalyst layer to extend the three-phase reaction zone. Nafion amount was 0.6 - 1.6 mg/cm². The Nafion-impregnated electrode was placed in a vacuum oven at 80 °C for 1 hr after drying in the air for 30 mins.

Both the anode and cathode were prepared under the same procedures and with the same content.

3.1.4 Membrane pre-treatment

Nafion[®] 112 and 1135 (Dupont, 51 μm , 87 μm , respectively) were immersed in the boiling 5 % H_2O_2 solution at 80 °C for 1 hr to remove the organic impurities and followed by washing with hot distilled water for 2 - 3 times. Then it was immersed into 80 °C, 1 M sulfuric acid for 1 hr to remove the metallic impurities, this was followed by hot distilled water washing for 2 - 3 times and finally the membrane was placed in the distilled water prior to use.

3.1.5 Fabrication of membrane electrode assembly (MEA)

The MEA, which is composed of anode, membrane, and cathode, is a key unit in PEM fuel cells. The MEA is normally prepared by sandwiching a membrane between an anode and cathode under hot pressing. The hot-pressing process (also called MEA bonding) is a simple way to assemble the anode, cathode, and proton exchange membrane together, and ensures interfacial contact between the electrode and the membrane. The bonding conditions of the hot-pressing process, such as the bonding temperature, pressure, and time, play an important role in obtaining high-performance MEAs.

The MEA was fabricated following the procedures below:

- 1) Set the plates in the hot press at the softening temperature of the membrane which is at about 130 - 140 °C.
- 2) Place the MEA (which is still sandwiched between two stainless steel plates) in the press and compress it with 4 - 6 kgf/cm^2 for 90 - 120s
- 3) Too much pressure, too much time, or too much heat may push the catalyst layers completely through the membrane causing an electrical short.

3.1.6 Single-cell fixture

Two kinds of single-cell fixture have been fabricated: a) PEMFC with 2-pass serpentine flow field (Figure 3.1); and b) PEMFC with porous flow field (Figure 3.2). The experimental results with fixture a) is compared with the modeling results in Chapter 4 and the experiment results with fixture b) is compared with modeling results in Chapter 5.

a) PEMFC with serpentine 2-channel flow field.

Figure 3.1 Single PEMFC components (1, 9 Fixture; 2, 8 Graphite Plate; 3, 7: Gasket; 4, 6: electrode with catalyst; 5: Membrane).

A single cell with electrode areas of 10 cm^2 was used for testing. The schematic diagram of the single cell was shown in Figure 3.1. Sealing gasket (silicon rubber plate, 0.6 mm in thickness) which matches a pair of electrode (anode and cathode) in thickness was used for all cell fixture.

b) PEMFC with net flow field

A single cell with porous flow field is shown in Figure 3.2. this single cell was composed with stainless steel end plates (current collector), stainless steel meshes (net flow field) MEA and sealing gasket (silicon rubber plate, 0.6 mm in thickness) which matches a pair of electrode (anode and cathode) in thickness.

Figure 3.2 Schematic of a Single PEM fuel cell:(1, 6) Anode & cathode endplates; (2) hole for measuring temperature; (4) gaskets; (5) MEA; and (1, 3) end plate and flow fields.

3.2 Development of PEMFC stack

The stack assembling fixture was designed and then employed to assemble a fuel cell stack with 40 cells, as illustrated in Figure 3.3.

Figure 3.3 Fuel cell stack.

Figure 3.4 shows the comparison of OCV and voltage uniformity under stack OCV (38.5 V) and operating stack voltage (26 V). One can see that, roughly, the voltage is evenly distributed except for cell no. 20, 21 and 30, which deviate from the voltage of other cells. It was found during the experiments that the zone where these cells are located accumulated more heat, resulting in an increase of the local temperature. It was suspected that the inner temperature of these cells may reach as high as 60 °C, causing deterioration of overall stack performance. Based on our experience and supported by theoretical studies, the working temperature of the fuel cell stack without external gas humidification is around 40 – 50 °C depending on the design of the membrane-electrode-assembly (MEA) of the fuel cells. The whole stack performance and life span of stack decreases. The experiments showed that the importance of investigating the perturbation of each cell performance. This introduces the modeling studies conducted in Chapter 7.

Figure 3.4 Comparison of OCV and Voltage uniformity for a PEMFC Stack OCV (38.5 V) and Stack Voltage (26 V).

3.3 Cell pretreatments

Pretreatment of cells is necessary before they can be used to generate electricity. The procedure is listed below:

1) *Test the MEA for electrical shorts*

The resistance between electrodes should be at least $500 \Omega/\text{cm}^2$, if not, the membrane (or cell) has an electrical short.

2) *Test the MEA for holes and leakage*

Gas cross-over between electrodes may be due to leaks through the gasket of the test cell or through the holes in the membrane. Connect the gas supply tubing and flow gas through one side but not through the other. Check for the gas-cross over by pressurizing one side and watching for gas leaking out the other side.

3) *Test Cell leakage*

Nitrogen was fed to the cell to test the leakage after fabricated the cell fixture. Soap liquid was used in the leak test and bubble would come out if nitrogen happened to escape from a particular (usually joint) spot. The gas flow was adjusted to the operating flow rate to assure that the cell would work well in a particular experiment.

4) *Hydrate the membrane*

This step was fulfilled by purging the cell with humidified nitrogen for several minutes. Normally, we used two different flow rates; started with high flow rate to clear the path and remove the air while low flow rate to hydrate the membrane.

5) *Cell pretreatment/Cell activation*

Heating up the cell until it reaches its desired operating temperature. Operate the cell at low potential (0.3 V, 0.6 V) for several hours. The importance of this step was to assure electrochemical and transport activity within the cell had reached a steady-state.

6) *Test for the open circuit potential*

Check the open circuit voltage and make sure that it is about 0.96 V for air and 1V for O₂ at 1 atm. A low open circuit potential indicates shorting or gas cross-over.

3.4 PEM fuel cell testing systems

3.4.1 Half-cell testing system

A platinum electrode and a saturated calomel electrode (SCE) were used as counter and reference electrodes respectively for all electrochemical measurements. The working electrode (1 cm² in geometric area of gas diffusion electrode) was inserted into a holder, which exposed the membrane side to 1 M H₂SO₄ solution and its backside to flowing oxygen or nitrogen for polarization and cyclic voltammetric measurements, respectively. (Figure 3.5).

Figure 3.5 Half-cell testing system (1, Counter electrode (CE), 2, Reference electrode (SCE), 3, Electrolyte: 1M H₂SO₄, 4, Carbon paper, 5, Membrane).

3.4.2 Single fuel cell testing system (Autolab)

The single cell test system is shown in Figure 3.6. Due to the fast kinetic of hydrogen oxidation reaction, the anode was used as the reference and counter electrode. Gas flow rate was measured by the mass flow meter and controlled by a mass flow controller (MFM, Bronkhorst). Gas humidification was controlled by a humidifier and a condenser was used to collect the water in the exit gas. AUTOLAB PGSTAT 30 Potentiostat and Frequency Response Analyser was used as the electrical-load and testing instruments.

Figure 3.6 Fuel cell testing systems.

3.4.3 PEMFC stack testing system

Figure 3.7 shows a typical fuel cell testing system. Figure 3.8 shows in-house fuel cell stack testing system, which includes electronic load, gas handling unit, thermal control system, and humidifier.

The operation of a fuel cell stack requires multiple supporting systems. Besides the fuel cell/stack, which is a heart of the system, other units such as compressor, fuel storage, humidifier, cooling system, power conditioning, instrumentation and control are all needed. Therefore, both the fuel cell stack and the supporting components will affect the system performance, efficiency, total cost and system durability. The balance of plant including stack and system components plays an important role in the fuel cell development.

Figure 3.7 Typical PEMFC test system configuration.

Figure 3.8 Photo of fuel cell stack testing system.

3.5 Electrochemical techniques

3.5.1 Steady state polarization curve

Open circuit potential was obtained under no current passage for at least 5 mins. Scanning rate was 5 mV/s from open circuit potential to -0.241 V *vs.* SCE (half-cell) or 0 V *vs.* SHE (single cell).

3.5.2 Cyclic voltammetry (CV)

The cyclic voltammetric technique is used to estimate the electrochemically active surface areas (*ESA*) of Pt/C catalyst in the gas diffusion electrode of fuel cell. Figure 3.9 shows a typical CV with a description of various peaks in the curve, which can be described as three fundamental processes: (1) double layer charging, (2) hydrogen evolution at ~ 0 V and oxygen evolution ~ 1.5 V and (3) adsorption/desorption of H atoms $\sim 0.05 - 0.3$ V and the formation (> 0.8 V) and reduction of Pt oxides ($0.6 - 1.2$ V). The sweep rate in the measurements was 50 mV/s with a potential range of $0 \sim 1.5$ V.

Conventionally, CV was used to ascertain the electrochemically active surface areas of Pt electrodes. CV profiles were recorded at different scan rates between (-0.30 V *vs.* SCE) and oxygen evolution (1.5 V *vs.* SCE). All measurements were conducted after purging with Nitrogen condition.

Figure 3.9 Cyclic voltammogram of a fuel cell electrode (a) schematic curve (b) experimental curve.

3.5.3 AC impedance

In general, single PEMFC impedance curve and corresponding equivalent circuit are shown in Figure 3.10. The elements of an equivalent circuit model represent the various processes involved in the transport of mass and charge. R1 was treated as electrolyte resistance; R2 was

treated as the electrical material impedance that includes electrode geometry, surface irregularities, grain dispersion and electrode properties. R_3 was regarded as the charge transfer resistance and was dependent on the cathode overpotential. In-house experiments were within the frequency range of 0.005 Hz – 1 MHz.

Figure 3.10 Generic Schematic impedance and its equivalent circuit.

Impedance spectra over the frequency range of 0.005 Hz – 1 MHz are shown in Figure 3.11. Diffusion control at low frequencies is represented by a straight line close to 45° . The detailed analysis of the kinetic mechanism of the catalysts involves many factors which is beyond the scope of this study. Our focus is on measurement of the cell resistance so as to compensate the IR drop in polarization measurements. Therefore, the high frequency impedance can be used as representative of the total cell resistance, the value of $0.35 \, \Omega$ for 20% Pt/C catalyst, $0.4 \, \text{mg/cm}^2$ Pt loading was obtained.

Figure 3.11 Impedance with various potential vs. SCE (20 °C).

3.5.4 Morphological characterization (SEM)

Scanning Electron Microscope (Leica S360) was used. Vacuum was controlled within the range $10^{-3} \sim 10^{-5}$ Torr. Acceleration voltage was 10 ~ 20 KV. SEM provided the real images of surface structure and cross-section structure of the carbon paper and GDLs to obtain the information of the surface roughness and thickness of the samples.

Figure 3.12 (a) and (b) are the carbon paper under untreated and wet proofed condition respectively. From these micrographs, one can easily observe that after wet-proofing, the

formation of a film of hydrophobic polymer blocking the pores near the surface and give a larger average pore size.

(a) not-wet proofed

(b) 30% wet-proofed

Figure 3.12 SEM picture of E-tek carbon paper

(a)

(b)

Figure 3.13 SEM micrographs of the cross-section images of the investigated GDLs: (a) single-layer GDL, (b) carbon-filled GDL.

Figure 3.13 shows SEM micrographs of cross-section of the Single layer GDL and Carbon-filled GDL. The thickness of TGP-H-030 carbon paper is about 0.11 mm. The carbon-filled GDL achieves the same thickness as single layer GDL. Obviously, after applying the carbon powder and PTFE, there are smaller pore sizes available for passage of gas. It is well known that water is transported through the bigger pores while gas molecules are transported through the smaller pores (Pasaogullari and Wang, 2005). The carbon/PTFE conducting filler was uniformly disposed in the structure of the carbon paper. Thus, the conductivity of the carbon filled GDL would increase and be less anisotropic both in the in-plane and through-plane directions.

Figure 3.14 SEM micrographs of the top-view images of the investigated GDLs: (a) single-layer GDL, and (b) carbon-filled GDL.

Figure 3.14 shows the SEM micrographs of the top-view images of single layer GDL and carbon-filled GDL. Obviously, without carbon powder the GDL (Figure 3.14(a)) would have the poor support for Pt/C catalyst particles when the catalyst was directly deposited on its surface. The open structure of the carbon paper would cause the Pt/C catalyst particles and nafion particle to drop inside the carbon paper, losing the active catalyst sites. The open space on the surface could also increase the contact resistance between the electrode and the membrane when using carbon paper as GDL. The carbon-filled GDL is fabricated by coating a thin layer of carbon and PTFE mixture (micros porous layer, MPL) on single-layer GDL. It shows much smoother surface in comparison to single layer GDL and provide the better cell performance. A gradient in porosity will benefit the removal rate of liquid water and also enhance the transport of oxygen through the cathode GDL. MPL will enhance liquid-water removal and reduces the liquid saturation in the catalyst layer. (Pasaogullari and Wang, 2005; Sinha and Wang, 2006; Pasaogullari and Wang, 2007; Shaffer and Wang, 2009) MPL will enhance the transport of oxygen as well, the larger the porosity gradient is, the easier the gas diffuses. Hence CFGDL will improve the cell performance

3.5.5 Mercury intrusion porosimetry

Pore size and distribution of the GDL were measured by a Mercury intrusion porosimetry (Autopore III 9420, Micromeritics Inc.). Mercury is a non-wetting liquid to most solid, but it can intrude the pores under pressure. The pore volume is the volume of the intruded liquid, and the pore size is related to pressure, which is expressed by the Washburn equation (Diamond, 2000):

$$d = -\frac{4\sigma \cos \theta}{P} \quad (\text{Eq. 3-1})$$

where d is the pore diameter, P is the applied pressure, σ the surface tension of mercury and θ the contact angle between the mercury and the sample. The volume of mercury penetrating the pores is measured directly as a function of applied pressure. The measured intrusion volume and pressure were used to calculate pore size, pore volume and pore volume distribution. The surface tension and contact angles of mercury used in the calculations were 480 dynes/cm and 140, respectively.

3.5.6 Pore size distribution analysis

The porosity of GDL is a very important parameter for the design of gas diffusion electrode, since it significantly affect the reactants/product transport in the electrode. There is also a need to characterize this pore structure to provide the parameter of porosity for transport models. Figure 3.15 shows the cumulative pore volume (referred as to local porosity) and pore volume distribution in the gas diffusion layers (GDLs) with the two different types of structure obtained from mercury intrusion measurements.

Figure 3.15 The cumulative pore volume (referred as to local porosity) and pore volume distribution in the gas diffusion layers (GDLs) with (a) single-layer GDL, and (b) carbon-filled GDL (CFGDL).

For single-layer GDL, the first peak (1st down arrow) of pore volume distribution is located at an pore size of about 85 μm , that is comparable to the size of PTFE particles (100 μm), while the second peak (2nd down arrow) with a broad distribution has an average pore size of 40.3 μm (Figure 3.15(a)). For the carbon-filled structure of GDL, the first peak of pore volume distribution with a very broad distribution (0.47 – 2.7 μm) has average pore size of about 2.3 μm , while the second peak has an average pore size of about 30 μm . It is believed that the first peaks of pore volume distribution correspond to a space within the carbon / PTFE agglomerates and the second peaks correspond to a space from the open space and coarse cracks on the surfaces, which is supported by the evidence of the SEM image shown in Figure 3.14. For the purpose of comparison, a boundary of 10 μm is chosen to separate the primary (< 10 μm) and secondary (> 10 μm) pores for the carbon paper. A summary of the porosity measurement is shown in Table 3.1. Obviously, CFGDL has smaller average pore diameter.

Table 3.1 Pore characters of single-layer GDL and carbon-filled GDL.

	Total Porosity (%)	Average pore diameter (μm)	Average pore diameter (μm)		local porosity (%)	
			Primary pore	Secondary pore	Primary pore	Secondary pore
Single-layer	77	35.8	4.3	40.3	9.5	67.5
Carbon filled	67	4.7	2.3	30	61	6

Chapter 4 1D PEMFC Model

4.1 Model introduction

Since the early 1990's there has been growing interests in modeling PEMFC. Earlier classic models by Bernadi and Verbrugge (1990-1992) and Springer *et al.* (1991-1993) are fundamental studies toward the understanding of PEMFCs. These two groups developed a one-dimensional, isothermal model for MEA. Bernadi and Verbrugge studied the net water flux through the membrane and Springer *et al.* included variable membrane hydration in their model. In order to better understand the fundamental transport phenomena, a combination of BV model and Springer model have been conducted. Figure 4.1 shows the domains of a fuel cell under study.

Figure 4.1 Domains of a PEMFC (not drawn to scale)

(AFF---Anode Flow Field; AGDL--- Anode Gas Diffusion layer; ACL---Anode Catalyst Layer; M---Membrane; CCL---Cathode Catalyst Layer; CGDL---Cathode Gas Diffusion Layer; CFF---Cathode Flow Field) .

The following assumptions were made:

- The cell system is one-dimensional in z (as shown in Figure 4.1);
- isothermal and steady state conditions;
- The total gas pressure in the gas diffusion layers is assumed constant and equal to the gas pressure of the adjacent gas channel;
- Cell temperature control is efficient so that the gases approaching the cell reach the cell temperature immediately;
- The gases are ideal and well mixed in the gas channel and saturated with water vapor;
- Water is in vapor phase and there is no water phase change in all domains (single phase system);
- The membrane is fully hydrated at all times so that the protonic conductivity is constant at a given temperature and no diffusive terms have to be considered for the liquid water flux;
- Gas pores and liquid water pores are separated in the gas diffusion layer. *i.e.* No interaction between the gases and the liquid water exists;
- Catalyst layer is represented by the macro-homogeneous approach. (Verbrugge and Hill, 1990);
- All pores in the active catalyst layers are assumed to be filled with membrane phase; hence there is no gaseous phase within the catalyst layers;
- Electro-neutrality prevails inside the membrane. The proton concentration in the ionomer is assumed to be constant and equal to the concentration of the fixed sulfonic acid groups.

The 1D model derived from the following four basic, phenomenological equations:

- Nernst-Planck equation for species transport.
- Modified form of Schlögl's velocity equation for liquid water movement.
- Butler-Volmer equation for charge/current transfer in the catalyst layers.
- Stefan-Maxwell equation for multi-component diffusion and convection.

4.2 Governing and constitutive equations

4.2.1 Anode gas diffusion layer (AGDL)

1) Mass conservation

For the diffusion of a multi-component gas mixture through a porous medium, the Stefan-Maxwell equation is used. Since the total gas pressures in the gas diffusers are assumed to be constant and equal to that of the adjacent gas chamber, the total gas pressure of AGDL is simply equal to the pressure applied. The generic Stefan-Maxwell equation is given as:

$$\frac{dx_{H_2}}{dz} = \frac{RT}{P} \frac{x_{H_2} J_{w,g}^{ad} - x_w J_{H_2}^{ad}}{D_{H_2-w}^{eff,ad}} \quad (\text{Eq. 4-1})$$

As the gas-phase hydrogen flux is related to the current, thus

$$J_{H_2}^{ad} = - \frac{I}{2F} \quad (\text{Eq. 4-2})$$

In the gas pores (wet-proofed pores) of the gas diffusion layer, It is assumed that the water vapor is equilibrated with the liquid water in the liquid pores. That is to say

$$x_w = x_w^{sat,ad} \quad (\text{Eq. 4-3})$$

Solving this binary gas system, one can obtain:

$$J_{w,g}^{ad} = \frac{I}{2F} \frac{x_w^{sat,ad}}{1 - x_w^{sat,ad}} \quad (\text{Eq. 4-4})$$

2) Momentum conservation

In the porous gas diffusion layer, the momentum conservation can be expressed by the generalized Darcy's Law. The superficial velocity of liquid water (v_s) is related to the hydraulic pressure gradient as follows.

$$v_s^{ad} = -\frac{K_{p,s}^{ad}}{m} \frac{dP}{dz} \quad (\text{Eq. 4-5})$$

3) Potential in the matrix (Ohm's Law)

Ohm's law relates the apparent electrical current to the voltage potential in the matrix phase. The superficial current density in the solid electronically conductive phase can be expressed as:

$$i_{\text{solid}} = -s_{\text{eff}}^{\text{ac}} \frac{dj_{\text{solid}}}{dz} \quad (\text{Eq. 4-6})$$

Operating current density can be considered as the combination of the current in the solid carbon-catalyst matrix and the current in the membrane phase, *i.e.*

$$I = i + i_{\text{solid}} \quad (\text{Eq. 4-7})$$

As there is no membrane phase in this domain: $I=i_{\text{solid}}$

4.2.2 Anode catalyst layer (ACC)

1) Mass conservation

Mass balance is based on the standard porous-electrode theory:

$$\frac{dJ_i}{dz} = -\frac{s_i}{nF} \frac{di}{dz} \quad (\text{Eq. 4-8})$$

$$\text{Hence in this domain: } \frac{dJ_{H_2}}{dz} = -\frac{s_{H_2}}{nF} \frac{di}{dz} \quad (\text{Eq. 4-9})$$

While the anode side the reaction is assumed to involve one-electron electrochemical step

$$(s_{H_2} = \frac{1}{2}; n=1):$$

The Nernst-Planck equation was used for the species transport. The flux, J_i of species i in the membrane pore fluid can be generally expressed as a sum of the three terms, diffusion, migration and convection.

$$J_i = -D_i \frac{dc_i}{dz} - c_i u_i \frac{d\phi}{dz} + c_i v \quad (\text{Eq. 4-11})$$

$$\text{while } u_i = \frac{FD_i z_i}{RT}, \quad i = F \sum_i z_i J_i$$

For the membrane of PEMFC, the only mobile ions in the membrane pore fluid are hydrogen ions (H^+). Since the diffusion was assumed to be non-existent in a wet membrane, the transport equation in the membrane domain can be written as:

$$\kappa \frac{d\phi}{dz} = -i + Fv c_{H^+} \quad (\text{Eq. 4-12})$$

Where κ is the membrane ion conductivity and can be expressed as:

$$\kappa = \frac{F^2}{RT} D_{H^+} c_{H^+} \quad (\text{Eq. 4-13})$$

In the catalyst layer, the conductivity becomes:

$$\kappa^{\text{eff}} \frac{d\phi}{dz} = -i + Fv c_{H^+} \quad (\text{Eq. 4-14})$$

Where $\kappa^{\text{eff}} = \varepsilon_m^{\text{ac}} \kappa$;

If one considers only H_2 in this domain,

$$J_{H_2} = -D_{H_2} \frac{dc_{H_2}}{dz} - c_{H_2} u_{H_2} \frac{d\varphi}{dz} + c_{H_2} v \quad (\text{Eq. 4-15})$$

As hydrogen is not charged, the second item for migration in above can be omitted, then:

$$J_{H_2} = -D_{H_2} \frac{dc_{H_2}}{dz} + c_{H_2} v \quad (\text{Eq. 4-16})$$

As no water produced in this domain $\frac{dv}{dz} = 0$, Combining with (Eq. 4-9), it gives:

$$D_{H_2}^{\text{eff, ac}} \frac{d^2 c_{H_2}}{dz^2} = v \varepsilon_m^{\text{ac}} \frac{dc_{H_2}}{dz} + \frac{di}{dz} \left(\frac{s_{H_2}^{\text{ac}}}{n_{\text{ac}} F} \right) \quad (\text{Eq. 4-17})$$

2) Momentum conservation

In the porous media of the catalyst layer, the momentum conservation was expressed by a modified Schlögl equation:

$$v = \frac{K_{\varphi}^{\text{eff}}}{\mu} z_m c_m F \frac{d\varphi}{dz} - \frac{K_p^{\text{eff}}}{\mu} \frac{dp}{dz} \quad (\text{Eq. 4-18})$$

where $K_{\varphi}^{\text{eff}} = \varepsilon_m^{\text{ac}} K_{\varphi}$; $K_p^{\text{eff}} = \varepsilon_m^{\text{ac}} K_p$

3) Electrokinetic Equation (Butler-Volmer equation)

The kinetics of the electrochemical reaction is expressed by the Butler-Volmer Equation.

$$\frac{di}{dz} = a i_0^{\text{ac}} \left\{ \exp \left[\frac{a_a^{\text{ac}} n F}{RT} (\varphi_{\text{solid}} - \varphi) \right] - \exp \left[\frac{a_c^{\text{ac}} n F}{RT} (\varphi - \varphi_{\text{solid}}) \right] \right\} \quad (\text{Eq. 4-19})$$

where a ($\text{m}^2 \cdot \text{m}^{-3}$ or m^{-1}) is the specific interfacial area /the effective catalyst surface area per unit volume of the catalyst layer. α_a and α_c are the anodic and cathodic transfer

coefficient; φ_{solid} and φ are the potentials in the carbon-catalyst and membrane phases, respectively. The difference between φ_{solid} and φ is called the activation overpotential.

The exchange current density i_0^{ac} is the function of the dissolved H_2 and the membrane proton concentration, i.e.

$$ai_0^{ac} = ai_0^{\text{ref,ad}} \left(\frac{c_{\text{H}_2}}{c_{\text{H}_2}^{\text{ref}}} \right)^{\gamma_{\text{H}_2}} \left(\frac{c_{\text{H}^+}}{c_{\text{H}^+}^{\text{ref}}} \right)^{\gamma_{\text{H}^+}} \quad (\text{Eq. 4-20})$$

In which c_{H_2} in AGD/ACC is

$$c_{\text{H}_2} \Big|_{\text{AGD/ACC}} = c_{\text{H}_2}^{\text{sat}} = \frac{(1 - x_w^{\text{sat,ad}}) \cdot P^{\text{ad}}}{H_{\text{H}_2}} \quad (\text{Eq. 4-21})$$

Where H_{H_2} is a Henry law's constant

4) Current conservation

Operating current density can be considered as the combination of the current in the solid carbon-catalyst matrix and the current in the membrane phase:

$$I = i + i_{\text{solid}} \quad (\text{Eq. 4-22})$$

While the movement of electrons in the solid portion of the catalyst is governed by Ohm's

$$\text{Law as. } i_{\text{solid}} = -\sigma^{\text{eff,ac}} \frac{d\varphi_{\text{solid}}}{dz} \quad (\text{Eq. 4-23})$$

4.2.3 Membrane (M)

1) Mass conservation

The Nernst-Planck equation was used for the proton, hydrogen and oxygen transport.

Similar to (Eq. 4-12) for the proton in the membrane

$$\kappa \frac{d\varphi}{dz} = -i + Fvc_{\text{H}^+} \quad (\text{Eq. 4-24})$$

Where κ is the membrane ion conductivity, expressed as:

$$\kappa = \frac{F^2}{RT} D_{H^+} c_{H^+} \quad (\text{Eq. 4-25})$$

If one consider H_2 in this domain, hydrogen is not charged and hence the 2nd term in the Nernst-Planck equation for migration can be neglected, i.e.

$$J_{H_2} = -D_{H_2} \frac{dc_{H_2}}{dz} + c_{H_2} v \quad (\text{Eq. 4-26})$$

As no liquid water produced in this domain $\frac{dv}{dz} = 0$ and under the steady state,

$$\frac{dJ_{H_2}}{dz} = 0 \quad \text{Thus:}$$

$$D_{H_2} \frac{d^2 c_{H_2}}{dz^2} = v \frac{dc_{H_2}}{dz} \quad (\text{Eq. 4-27})$$

Similar deduction can be applied to oxygen transport:

$$D_{O_2} \frac{d^2 c_{O_2}}{dz^2} = v \frac{dc_{O_2}}{dz} \quad (\text{Eq. 4-28})$$

2) Momentum conservation

In the porous media of the catalyst layer, the momentum conservation was expressed by a modified Schlögl equation:

$$v = \frac{K_\phi}{\mu} z_m c_m F \frac{d\phi}{dz} - \frac{K_p}{\mu} \frac{dp}{dz} \quad (\text{Eq. 4-29})$$

3) Current conservation

While no movement of electrons in the membrane $i_{\text{solid}} = 0$, then

$$I = i + i_{\text{solid}} = i \quad (\text{Eq. 4-30})$$

4.2.4 Cathode catalyst layer (CCL)

1) Mass conservation

(Eq. 4-14) is applied to the proton transport with effective membrane conductivity.

$$\kappa^{\text{eff}} \frac{d\phi}{dz} = -i + Fv c_{\text{H}^+} \quad (\text{Eq. 4-31})$$

Where $\kappa^{\text{eff}} = \varepsilon_m^{\text{cc}} \kappa$;

By assuming that no hydrogen crossover and only liquid water and O_2 exist in this domain;

$$J_{\text{O}_2} = -D_{\text{O}_2} \frac{dc_{\text{O}_2}}{dz} - c_{\text{O}_2} u_{\text{O}_2} \frac{d\phi}{dz} + c_{\text{O}_2} v \quad (\text{Eq. 4-32})$$

Since oxygen is not charged, the second item for migration in above equation can be omitted, then:

$$J_{\text{O}_2} = -D_{\text{O}_2} \frac{dc_{\text{O}_2}}{dz} + c_{\text{O}_2} v \quad (\text{Eq. 4-33})$$

As the cathode side of the reaction is four-electron electrochemical step

From (Eq. 4-8), one will get $\frac{dJ_{\text{O}_2}}{dz} = -\frac{s_{\text{O}_2}}{nF} \frac{di}{dz}$ (where $s_{\text{O}_2} = -1$; $n = 4$), since only liquid

water is produced in this domain, $\rho \frac{dv_s}{dz} = -\frac{s_w}{nF} \frac{di}{dz}$, thus:

$$D_{\text{O}_2}^{\text{eff,cc}} \frac{d^2 c_{\text{O}_2}}{dz^2} = v \varepsilon_m^{\text{cc}} \frac{dc_{\text{O}_2}}{dz} + \frac{di}{dz} \left(\frac{s_{\text{O}_2}^{\text{cc}}}{n^{\text{cc}} F} - \frac{s_w^{\text{cc}}}{n^{\text{cc}} F} \frac{c_{\text{O}_2}}{\rho} \right) \quad (\text{Eq. 4-35})$$

2) Momentum conservation

In the porous catalyst layer, the momentum conservation was expressed by a modified Schlögl equation

$$v = \frac{K_{\phi}^{\text{eff}}}{\mu} z_m c_m F \frac{d\phi}{dz} - \frac{K_p^{\text{eff}}}{\mu} \frac{dp}{dz} \quad (\text{Eq. 4-36})$$

where $K_{\phi}^{\text{eff}} = \varepsilon_m^{\text{cc}} K_{\phi}$; $K_p^{\text{eff}} = \varepsilon_m^{\text{cc}} K_p$

3) Electro-kinetic Equation (Butler-Volmer equation)

The kinetics of the electrochemical reaction is expressed by the Butler-Volmer equation as follows.

$$\frac{di}{dz} = ai_0^{\text{cc}} \left\{ \exp \left[\frac{a_a^{\text{cc}} nF}{RT} (\phi_{\text{solid}} - \phi) \right] - \exp \left[\frac{a_c^{\text{cc}} nF}{RT} (\phi - \phi_{\text{solid}}) \right] \right\} \quad (\text{Eq. 4-37})$$

The exchange current density i_0^{cc} is a function of the dissolved O_2 and the membrane proton concentration:

$$ai_0^{\text{cc}} = ai_0^{\text{ref, cc}} \left(\frac{C_{\text{O}_2}}{C_{\text{O}_2}^{\text{ref}}} \right)^{\gamma_{\text{O}_2}} \left(\frac{C_{\text{H}^+}}{C_{\text{H}^+}^{\text{ref}}} \right)^{\gamma_{\text{H}^+}} \quad (\text{Eq. 4-38})$$

4) Current conservation

$$\text{As previous explanation: } I = i + i_{\text{solid}} \quad (\text{Eq. 4-39})$$

While the movement of electrons in the solid portion of the catalyst is governed by Ohm's Law.

$$i_{\text{solid}} = -\sigma^{\text{eff, cc}} \frac{d\phi_{\text{solid}}}{dz} \quad (\text{Eq. 4-40})$$

4.2.5 Cathode gas diffusion layer (CGDL)

1) Mass conservation

Taking the starting point from CCL/CGD interface, the Stefan-Maxwell equation for O_2 can be written as:

$$\frac{p^{ad}}{RT} \frac{dx_{N_2}}{dz} = \frac{x_{N_2} J_{O_2,g}}{D_{N_2-O_2}^{eff,cd}} + \frac{x_{N_2} J_{w,g}^{cd}}{D_{w-N_2}^{eff,cd}} \quad (\text{Eq. 4-41})$$

The gas phase oxygen flux is related to the current by

$$J_{O_2,g} = \frac{I}{4F} \quad (\text{Eq. 4-42})$$

$$\text{Then: } \frac{p^{cd}}{RT} \frac{D_{w-N_2}^{eff,cd}}{x_{N_2}} \frac{dx_{N_2}}{dz} = \frac{I}{4F} r_{N_2} + J_{w,g}^{cd} \quad (\text{Eq. 4-43})$$

$$\text{where, } \frac{D_{w-N_2}^{eff,cd}}{D_{N_2-O_2}^{eff,cd}} = r_{N_2} \quad (\text{Eq. 4-44})$$

As the water vapor is assumed to be in equilibrium with liquid water in the gas pores,

$$\text{therefore, } x_w^{cd} = x_w^{\text{sat+}}, \frac{dx_w}{dz} = 0 \quad (\text{Eq. 4-45})$$

$$\text{Where } N_2 \text{ is considered as inert: } J_{N_2,g} = 0 \quad (\text{Eq. 4-46})$$

Stefan-Maxwell equation is expressed as:

$$\frac{x_w J_{O_2,g} - J_{w,g}^{cd} x_{O_2}}{D_{w-O_2}^{eff,cd}} - \frac{x_{N_2} J_{w,g}^{cd}}{D_{w-N_2}^{eff,cd}} = 0 \quad (\text{Eq. 4-47})$$

$$\text{Together with } 1 = x_{O_2} + x_{N_2} + x_w^{\text{sat+}},$$

$$J_{w,g}^{cd} = -\frac{I}{4F} x_w^{\text{sat,cd}} \left[1 - x_w^{\text{sat,cd}} - x_{N_2} + \frac{x_{N_2}}{r_w} \right]^{-1} \quad (\text{Eq. 4-48})$$

$$\text{Where } \frac{D_{w-N_2}^{eff,cd}}{D_{w-O_2}^{eff,cd}} = r_w \quad (\text{Eq. 4-49})$$

Denoted $z = L$ at the cathode gas diffuser/gas chamber interface (CGD/CGC), x_{N_2} in terms of ζ_+ , the stoichiometric flow ratio is given as:

$$x_{N_2} = x_{N_2}^L = \left(1 - x_w^{\text{sat,c}} \right) \frac{\zeta_+}{\zeta_+ - 1} \frac{x_{N_2}^o}{x_{O_2}^o} / \left(1 + \frac{\zeta_+}{\zeta_+ - 1} \frac{x_{N_2}^o}{x_{O_2}^o} \right) \quad (\text{Eq. 4-50})$$

A water material balance results in:

$$\rho \frac{dv_s^{cd}}{dz} = -\frac{dJ_{w,g}^{cd}}{dz} \quad (\text{Eq. 4-51})$$

2) Momentum conservation

Similar to the anode diffusion layer, the superficial velocity of liquid water is related to

the hydraulic pressure gradient as follows.

$$v_s^{cd} = -\frac{K_{p,s}^{cd}}{\mu} \frac{dp}{dz} \quad (\text{Eq. 4-52})$$

3) Potential in the matrix (Ohm's Law)

Ohm's law relates the apparent electrical current to the voltage potential in the matrix phase. The superficial current density in the solid electronically conductive phase can be expressed as:

$$i_{solid} = -\sigma_{eff}^{cc} \frac{d\varphi_{solid}}{dz} \quad (\text{Eq. 4-53})$$

Operating current density can be considered as the combination of the current in the solid carbon-catalyst matrix and the current in the membrane phase:

$$I = i + i_{solid} \quad (\text{Eq. 4-54})$$

$$\text{As there is no membrane phase in this domain: } I = i_{solid} \quad (\text{Eq. 4-55})$$

4.3 Boundary conditions

The following provides the boundary conditions that apply for the coupled differential equations of the seven variables in the 1D model. It is assumed that the continuity holds in the every interface, thus the continuity equations of current density, water flux, hydrogen flux and oxygen flux can be written. Table 4.1 shows the boundary conditions for each domain.

Table 4.1 Model boundary condition at each interface

variables	AGD/ACL	ACL/M	M/CCL	CCL/CGD
i	$i = 0$	$i = I$	$i = I$	$i = 0$
φ		$\varphi = 0$		
φ_{solid}	$\sigma^{eff,ad} \frac{d\varphi_{solid}}{dz} \Big _{ad}$ $= \sigma^{eff,ac} \frac{d\varphi_{solid}}{dz} \Big _{ac}$		$\frac{d\varphi_{solid}}{dz} = 0$	$\sigma^{eff,cc} \frac{d\varphi_{solid}}{dz} \Big _{cc}$ $= \sigma^{eff,cd} \frac{d\varphi_{solid}}{dz} \Big _{cd}$
P	$P=P^a$			
c_{O_2}		$c_{O_2} = 0$	$D_{O_2} \frac{dc_{O_2}}{dz} \Big _m$ $= D_{O_2}^{cc,eff} \frac{dc_{O_2}}{dz} \Big _{cc}$	$c_{O_2} = c_{O_2}^{sat}$ $= \left(1 - x_w^{sat+} - x_{N_2}\right) \frac{p^{cd}}{K_{O_2}}$
c_{H_2}	$c_{H_2} = c_{H_2}^{sat}$ $= \frac{(1 - x_w^{sat,ad}) \cdot P^{ad}}{K_{H_2}}$	$D_{H_2}^{ac} \frac{dc_{H_2}}{dz} \Big _{ac}$ $= D_{H_2} \frac{dc_{H_2}}{dz} \Big _m$	$c_{H_2} = 0$	
v_s	$\rho v_s \Big _{ac} = \rho v_s^{ad} + J_{w,g}^{ad}$ $J_{w,g}^{ad} = \frac{I}{2F} \frac{x_w^{sat,ad}}{1 - x_w^{sat,ad}}$	$v_s \Big _{ac} = v_s \Big _m$	$v_s \Big _{cc} = v_s \Big _m$	$\rho v_s \Big _{cc} = \rho v_s^{cd} + J_{w,g}^{cd}$ $J_{w,g}^{cd} = -\frac{I}{4F} x_w^{sat,cd} \times$ $\left[1 - x_w^{sat,cd} - x_{N_2} + \frac{x_{N_2}}{r_w}\right]^{-1}$

4.4 Model parameters

Table 4.2 gives the basic physical and operational parameters of the fuel cell model. The simulation parameters were adopted from Bernardi and Verbrugge (1991,1992) and

Springer *et al.* (1991,1992) and validated with the experimental data from Ticianelli *et al.* (1988). This case is considered as the base-case condition.

A new base case (Nafion 1135, 353K, H₂/Air pressure :1/1 atm) is also studied to validate with in-house experiments. All the parametric studies are based on this new base condition and a series of experiments have been conducted accordingly.

Table 4.2. Physical and operational parameters for base-case conditions

l_m	2.3×10^{-4} m	P_c	3 atm
$l_{cd}; l_{ad}$	2.6×10^{-4} m	P_a	3 atm
$l_{cc}; l_{ac};$	1×10^{-5} m	RH	100 %
T_{cell}	353 K		
ζ_+	3	ζ_-	3

For all the tables, the values in Bold indicate the parameters remain constant in the course of study. The values in Italic will vary with temperature or other parameters.

Table 4.3 Nafion 117 membrane properties

D_{H^+}	<i>0.45 m²/s</i>	K_{O_2}	2.01×10^{11} atm / (m³ /mol)
C_f	1.2×10^3 mol /m³	K_{H_2}	4.5×10^{10} atm/ (m³ /mol)
Z_f	-1	μ	<i>3.6399×10^{-4} kg/(m·s)</i>
K_ϕ	7.18×10^{-12} m²	P_w^{sat}	<i>0.4669 atm</i>
K_p	1.8×10^{-10} m²	κ	<i>17.12 S/m</i>
ε_w^m	0.28	d	55×10^{-10} m
D_{O_2}	<i>1.2187×10^{-2} m²/s</i>	D_{H_2}	<i>2.5796×10^{-2} m²/s</i>

Some electrode values from Bernardi and Verbrugge listed in Table 4.4.

Table 4.4 Electrode properties at base case condition

$\sigma_{eff}^{cd}, \sigma_{eff}^{ad}$	0.53 mho cm ⁻¹	ε_m^c	0.4
ε_g^d	0.4	$K_{P,S}$	4.73 ×10 ⁻¹¹ m ²
Cathode		Anode	
n	4	n	1
S_w	2	S_w	0
S_{O_2}	-1	S_{O_2}	0
S_{H_2}	0	S_{H_2}	0.5
S_{H^+}	-4	S_{H^+}	-1
ai_o^{ref}	0.1 A/ m ³	ai_o^{ref}	1.4 ×10 ¹¹ A/m ³
a_c	2	a_c	0.5
a_a	2	a_a	0.5
$C_{H^+}^{ref}$	1200 mol /m ³	$C_{H^+}^{ref}$	1200 mol /m ³
$C_{O_2}^{ref}$	3.39 mol /m ³	$C_{O_2}^{ref}$	N.A.
$C_{H_2}^{ref}$	N.A.	$C_{H_2}^{ref}$	56.4 mol/ m ³
γ_{O_2}	0.5	γ_{O_2}	N.A.
γ_{H_2}	N.A.	γ_{H_2}	0.25
γ_{H^+}	0.5	γ_{H^+}	2
$PD_{O_2-N_2}$	2.821 ×10 ⁻⁵ atm m ² /s	$PD_{O_2-N_2}$	N.A.
PD_{w-N_2}	3.874 ×10 ⁻⁵ atm m ² /s	PD_{w-N_2}	N.A.
PD_{w-O_2}	3.701 ×10 ⁻⁵ atm m ² /s	PD_{w-O_2}	N.A.
PD_{w-H_2}	N.A.	PD_{w-H_2}	1.8891 ×10 ⁻⁴ atm m ² /s

4.5 Computational procedure

The 1D model equations comprise of the following seven variables: c_{O_2} , c_{H_2} , x_{N_2} , ϕ_{solid} , ϕ , i and v . The program is capable of determining the values of these variables at various interfaces of the fuel cell model by solving the system of coupled differential equations with different inputs of the operating current density I . The simplified equations were used to estimate the water velocity at anode side then followed by the flow diagram of the solution procedure (Figure 4.2).

Figure 4.2 flow diagram of the solution procedure.

The whole program code was developed in the Visual Basic language under Microsoft Excel interface. The algorithm employs the modified Euler predictor-corrector approach while utilizing secant and interval-halving methods to determine the six unknowns of the model, as a function of the operating current density, I . Simulation code was performed in an Excel environment, cell formulae can be used and model parameters can be adjusted easily, in addition to convenience in graph plotting and data presentation. An extensive database of fuel cell performance curves under various operating conditions can be easily generated.

Convergence 1:

$$c_{H_2}|_{\alpha} = 0 \quad (\text{Eq. 4-56})$$

where α is a point within the anode catalyst layer

Convergence 2

$$\frac{D_{H_2, \text{eff}}^{\text{ac}}}{\nu} \left[1 - \exp\left(\frac{\nu l_m}{D_{H_2}}\right) \right] \frac{dc_{H_2}}{dz} \Big|_{\text{ACL/M}} = c_{H_2} \Big|_{\text{ACL/M}} \quad (\text{Eq. 4-57})$$

Convergence 3

$$c_{O_2}|_{\alpha} = 0 \quad (\text{Eq. 4-58})$$

where α is a point within the cathode catalyst layer.

Convergence 4

$$\frac{D_{H_2, \text{eff}}^{\text{cc}}}{\nu} \left[1 - \exp\left(\frac{\nu l_m}{D_{H_2}}\right) \right] \frac{dc_{O_2}}{dz} \Big|_{\text{CCL/M}} = c_{O_2} \Big|_{\text{CCL/M}} \quad (\text{Eq. 4-59})$$

Convergence 5

$$\Delta p_{\text{AGD}} + \Delta p_{\text{ACL}} + \Delta p_{\text{M}} + \Delta p_{\text{CCL}} + \Delta p_{\text{CGD}} = p_c - p_a \quad (\text{Eq. 4-60})$$

In the simulation, the membrane pore water velocity approximation by combining (Eq.4-23) and (Eq.4-28):

$$v = \left[\frac{k_{\phi} c_m FI}{\mu \kappa} - \frac{k_p}{\mu} \frac{dp}{dz} \right] / \left(1 + \frac{k_{\phi} c_m^2 F^2}{\mu \kappa} \right) \quad (\text{Eq. 4-61})$$

By assuming the cathode and anode catalyst layers as interfaces, the pressure at the boundary of membrane region can be considered as

$$\frac{dp}{dz} = \frac{P_{\text{CGD/CCL}} - P_{\text{AGD/ACL}}}{l_m} \quad (\text{Eq. 4-62})$$

A water balance at the interface between the cathode and membrane will give the superficial water velocity in the gas diffusion cathode as

$$P_{\text{CGL/CCL}} = p_+ + l_{\text{cd}} \cdot \frac{\mu \cdot v_{\text{cd}}}{K_{\text{p,s}}^{\text{cd}}} \quad (\text{Eq. 4-63})$$

$$P_{\text{AGL/ACL}} = p_- + l_{\text{ad}} \cdot \frac{\mu \cdot v_{\text{ad}}}{K_{\text{p,s}}^{\text{ad}}} \quad (\text{Eq. 4-64})$$

Water balance at AGL/M and M/CGL, then:

$$V_s^{\text{ad}} = \varepsilon_w^{\text{m}} v - \frac{J_{\text{w,g}}^{\text{ad}}}{\rho} \quad (\text{Eq. 4-65})$$

$$V_s^{\text{cd}} = \varepsilon_w^{\text{m}} v - \frac{J_{\text{w,g}}^{\text{cd}}}{\rho} + \frac{I}{\rho \cdot 2F} \quad (\text{Eq. 4-66})$$

$$l_{\text{ad}} = l_{\text{cd}} = l_d \quad (\text{Eq. 4-67})$$

Thus, the approximated initial membrane pore water velocity is obtained:

$$v = \left(\frac{k_{\phi} c_f FI}{\kappa \mu} - \frac{(p_+ - p_-) k_p}{\mu l_m} + \frac{k_p l_d}{l_m \rho k_{\text{p,s}}^{\text{d}}} (-J_{\text{w}}^{\text{ad}} + J_{\text{w}}^{\text{cd}} + \frac{I}{2F}) \right) / \left(1 + \frac{F^2 c_{\phi}^2 k_{\phi}}{\kappa \mu} + \frac{2 k_p \varepsilon_w^{\text{m}} l_d}{l_m k_{\text{p,s}}^{\text{d}}} \right) \quad (\text{Eq. 4-68})$$

4.6 Base case results and discussions

4.6.1 Polarization curve

Figure 4.3 shows the components of the overall cell polarization for the base case model results. The dash line is the ideal open-circuit voltage (OCV), one can see that at low current density (less than 0.1 A/cm^2), the activation overpotential of the oxygen reduction reaction (cathode) is almost entirely responsible for the potential losses of the cell. The ohmic potential losses due to the membrane and electrodes become more significant while cathode activation overpotential keeps at a relatively constant value for the current densities greater than 0.2 A/cm^2 . The anode activation overpotential makes only a minor contribution to the fuel cell overpotential, even at the high operating current densities.

Figure 4.3 Simulation results of fuel cell potential losses on base case.

Figure 4.4 Predicted and measured polarization and power density curves (H_2/Air : 3/3 atm, 353K. Nafion 117).

Figure 4.4 compares the results of the model at the base case conditions with the experimental results obtained from Ticinanelli *et al.*(1988).A close agreement between the modelling results and experiments was obtained. It matches with the results published by Bernadi and Verbrugge.(1992).

Figure 4.5 shows the predicted results with in-house experimental data under the ambient pressure.It can be seen that the predicted results and experiment results have achieved a good agreement in low and medium current density but depart under high current density ($> 0.6 \text{ A/cm}^2$), with predicted results shown significantly higher than the experiment value. Similar to the polarization curve, the predicted power density curve shows a good agreement with the experimental curve in the load region below the mass transport

limitation. At high load condition, the predicted values are higher than the experimental values as expected. These discrepancies are mainly caused by one phase in nature of the model, *i.e.* the effect of reduced oxygen transport due to water flooding at the cathode at high current density is not accounted for. Note that the condition is under ambient temperature for both anode and cathode side, which, is a benign condition for water flooding.

Figure 4.5 Comparison of polarization curves and power density curves between the simulation and experiment (base case: H₂/Air: 1/1atm, 353K, Nafion 1135).

4.6.2 Transport of reactants

Due to the extremely slow exchange of current density in oxygen reduction reaction (ORR) compared to the hydrogen oxidation reaction (HOR), the ORR becomes the critical factor affecting the performance. The cathode operating conditions usually determine the limiting current density when the fuel cell is run on humidified air. This is

because an increase in current density would correspond to an increase in oxygen consumption. The concentration of oxygen at the catalyst layer is balanced by the oxygen that is being consumed and the amount of oxygen that diffuses towards the catalyst layer, driven by the concentration gradient.

Figure 4.6 Predicted concentration of dissolved gases in the membrane phase throughout the fuel cell (base case operating condition, not drawn to scale).

Figure 4.6 shows the concentration profiles of the dissolved gases throughout the cell for various current densities under the base-case conditions. It was found that when the current density is higher than 0.01 A/cm^2 , the dissolved hydrogen and oxygen is depleted before getting into the membrane. Then the reactant gas utilization can be thought as 100 % (all half-cell reaction reacted completely, no reactant gas crossover the catalyst layer).

Even at extremely low current density of 0.002 A/cm^2 , over 90% efficiency can be obtained.

The same phenomena leading to high oxidation and reduction efficiencies are also responsible for low utilization of catalyst during fuel cell operation. Catalyst is modeled uniformly distributed throughout the catalyst layer, thus, when the oxygen concentration within a portion of the catalyst layer is very low, then the electrochemical reaction cannot occur efficiently and the catalyst in that portion is not utilized. Many researchers have focused their work on identifying methods of catalyst loading that maximize catalyst utilization. (Taylor, Anderson et al. 1992; Fischer and Wendt 1996; Wendt, Brenscheidt et al. 1996; Fischer, Jindra et al. 1998; Antoine, Bultel et al. 2000; Haug, White et al. 2002)

4.6.3 Water transport

Figure 4.7 shows the hydraulic pressure profile, while Figure 4.8 corresponds to the water velocity profile throughout the whole region. The slopes of pressure profiles in the anode and cathode diffusion layer show the direction of water flow in these regions. *i.e.* the negative slope signifies liquid water flowing in the direction from left to right. The jump at the AGL/ACL indicates the water-vapor adsorption. The water vapor flux is absorbed forming liquid water when it contacts with the membrane phase. High temperature and low pressure will favor the water uptake. The sharp rise in velocity occurring from M/CCL to CCL/CGDL primarily reflects the production of water by oxygen reduction reaction.

Figure 4.7 Predicted effect of hydraulic pressure on the fuel cell under two current densities.

At low current density of 0.1 A/cm^2 , the liquid water flow throughout the cell is from the cathode to the anode side since the electro-kinetic flow of water is smaller relative to the pressure driven flow of water in the membrane. Even though some water is produced within the cathode catalyst layer and absorbed by the gas phase at the CCL/CGDL interface, water must be supplied at the outer face of the cathode as evidenced by negative value of velocity in the cathode diffusion layer.

Figure 4.8 Predicted superficial water velocity along the fuel cell under three current densities.

4.6.4 Membrane parameters influence

Figure 4.9 and Figure 4.10 show the effect of electro-kinetic permeability and hydraulic permeability on the membrane water-transport ratio. Results show that, within the range of the assigned values of these permeabilities, there is a slightly change in the polarization which is within 3 % difference. These parameters do influence the inner transport phenomena; they alter the membrane water transport ratio which is defined as the number of water molecules dragged across the membrane per proton. This value can be calculated from;

$$\frac{J_{w,g}^m}{J_{H^+}} = \varepsilon_w^m \cdot F \cdot \frac{\rho v}{I} \quad (\text{Eq. 4-69})$$

Figure 4.9 membrane water-transport ratio H_2O/H^+ with various electrokinetic permeability ($3.59 \times 10^{-12} m^2$; $7.18 \times 10^{-12} m^2$ and $1.43 \times 10^{-11} m^2$).

Figure 4.10 Membrane water-transport ratio H_2O/H^+ with various hydraulic permeability ($1.8 \times 10^{-9} m^2$; $1.8 \times 10^{-10} m^2$ and $1.8 \times 10^{-11} m^2$).

It is noted that this ratio increases with the increasing of the current density, which indicates that under high current density, more transportation of proton from the anode side to the cathode side occurs. When the ratio is negative as it occurs within the low current density, this indicates that the water is moving in the opposite direction of proton, which flows from the anode side to the cathode side of membrane under normal conditions.

4.7 Parametric studies

A parametric study was conducted to (i) identify the critical parameters for fuel cell performance, and (ii) determine the sensitivity of the model to various parameters and hence identify which of these needs to be specified more accurately. In order to do so, only one parameter was changed from the base case conditions at a time. Care had to be taken on how other modeling parameters depend on the parameter that was changed, such as the temperature influences all other transport parameters inside the fuel cell, ranging from the diffusivities of the species to the speed of the electrochemical reactions, and these had to be taken into account. The fuel cell performance at various operating conditions is compared using the polarization curves, power curves, and assessment of water drag coefficient. The parameters investigated include the operating temperature and pressure, stoichiometric flow ratio, the porosity of the GDL and the thickness of the membrane. The base case under this study is Nafion 1135, operating at 353K with H₂/Air under ambient atmosphere.

4.7.1 Effect of temperature

The temperature basically affects all aspects of transport phenomena inside the fuel cell,

Predominantly:

- *The composition of the incoming gas streams:* Assuming that the inlet gases are fully humidified, the partial pressure of water vapor entering the cell is depended on the temperature only. Thus, the molar fraction of water vapor is a function of the total inlet pressure and temperature, and so the molar fraction of the incoming hydrogen and oxygen depend on the temperature and pressure as well.
- *The exchange current density i_0 :* The exchange current density of an electrochemical reaction depends strongly on the temperature.
- *The membrane conductivity:* A higher temperature leads also to a higher diffusivity of the proton in the electrolyte membrane, thereby reducing the membrane resistance.
- *The gas-pair diffusivities (D_{ij}):* An increase in temperature leads to an increase in the gas-pair diffusivities.

In order to determine the inlet gas composition as a function of temperature, the following relationship between the temperature and the saturation pressure of water has been used (Springer, Zawodzinski et al. 1991):

$$\log_{10}^{Pat} = -2.1794 + 0.02953 \times (T - 273.15) - 9.1837 \times 10^{-5} \times (T - 273.15)^2 + 1.4454 \times 10^{-7} \cdot (T - 273.15)^3 \quad (\text{Eq. 4-70})$$

Where T is the temperature in K. The molar fraction of water vapour in the incoming gas stream is simply the ratio of the saturation pressure to the total pressure as it is fully humidified.

$$x_w^{\text{in}} = \frac{P_w^{\text{sat}}}{P^{\text{in}}} \quad (\text{Eq. 4-71})$$

Since the ratio of nitrogen and oxygen in dry air is known to be 79:21, the inlet oxygen fraction can be found by:

$$x_{O_2}^{\text{in}} = \frac{1 - x_w^{\text{in}}}{1 + \frac{79}{21}} \quad (\text{Eq. 4-72})$$

The molar nitrogen fraction can be determined from:

$$x_{N_2}^{\text{in}} + x_w^{\text{in}} + x_{O_2}^{\text{in}} = 1 \quad (\text{Eq. 4-73})$$

The resulting inlet gas composition for different pressures is shown in Figure 4.11. One can see that higher temperature or lower pressure will induce higher water vapor fraction and lower oxygen concentration.

Figure 4.11 Molar inlet fraction of oxygen and water vapour as a function of temperature at three different Pressures.

Figure 4.12 shows the comparison of the predicted and experiment results under different temperatures. When operating temperature is above 60 °C , the predicted results exhibit good qualitative agreement with the experimental data under low and medium current densities. Noted that our base case is under 1 atm for both anode and cathode side which easily causes water vapor condensation, which deviates from our one-phase assumption. Thus substantial discrepancy between the predicted and experiment results for the operating temperature at 50 °C and 25 °C.

Figure 4.12 Predicted and experiment polarization curves under different temperatures.

4.7.2 Effect of pressure

Similar to the temperature, the operating pressure enhances numerous transport properties in a PEMFC. It is noted that the following parameters' value will vary with the change of the operating pressure:

- The inlet gas compositions.
- The exchange current density i_0 .
- The gas-pair diffusivities D_{ij} in the Stefan-Maxwell equations.

Figure 4.13 shows the predicted and measured polarization under different fuel/Air pressures. The modelling and experiment result obtain a good agreement. It can be seen that the performance improves with the increasing pressure of the cathode side. As higher oxygen fraction at the cathode inlet under higher pressure, the experiment result shows that the maximum current density increases. The polarization curves of the experiment reveal a significant change in the initial drop-off with the pressure changes. This can be attributed to the change in the equilibrium potential that goes along with a decrease in the reactant pressure (Nernst equation).

Figure 4.13 Predicted and experiment polarization curves under different fuel/Air pressures.

4.7.3 Effect of stoichiometric flow ratio (ζ)

An increase in the stoichiometric flow ratio simply means an increase in velocity of the incoming gas with all other parameters remaining at the same value. From Figure 4.14, one can conclude that while the stoichiometric flow ratio is increased from $\zeta = 1.5$ to $\zeta = 2.0$, there is a little improvement in the performance. However, from $\zeta = 2.0$ to $\zeta = 3.0$ and then $\zeta = 4.0$ the influence is extremely small. Since there is a price to pay for an increase in the stoichiometric flow ratio, there must be an optimum, where the gain in the cell performance just outnumbers the additional costs of a more powerful blower. In practical ζ can be chosen as 3.0.

It is realized that the effect of the stoichiometric flow ratio on the water management cannot be assessed with the current 1D simple phase model. As the amount of the

incoming air determines how much water vapour that can be carried away from the cell.

Two-phase model is necessary to provide a more realistic result.

Figure 4.14 Predicted polarization curves under different stoichiometric air flow ratios.

4.7.4 Effect of gas diffusion layer (GDL) porosity

The porosity of the gas diffusion layers can affect the performance of the fuel cell in two ways. First the electrode porosity affects the mass transport of reactant gases from the channel towards the catalyst layers, with higher volume porosity providing less resistance to mass transport. The volume porosity also affects the gas diffusion coefficients through the Bruggemann correction and here we incorporate its effect to the hydraulic permeability in the simulation. Second, the electrode porosity has a negative effect on electron conduction, since the solid matrix of the gas diffusion layer provides the pathways for electron transport, the higher volume porosity increases resistance to electron transport in the gas diffusion layers.

Verbrugge and Hill (1990) outline a method in order to obtain a theoretical value for the permeability, based on the assumption that a GDL structure can be adequately represented by an array of capillary pores with a uniform cross section. To account for void content, the Kozeny-Carman equation was developed to provide a description of fluid flow. In this case the permeability can be described by Bear and Bachmat (1991):

$$K_{p,s} = \frac{\varepsilon^3}{K_0 S_0^2 (1-\varepsilon)^2} \quad (\text{Eq. 4-74})$$

Where $k_{p,s}$ is the hydraulic permeability, K_0 is the Kozeny Constant which is often assumed to be 5, S_0 a shape factor, and ε is the media porosity. The shape factor is found from

$$S_0 = \frac{\text{surface area of solid phase}}{\text{volume of solid phase}} \quad (\text{Eq. 4-75})$$

For an array of pores with circular cross section (Verbrugge and Hill, 1990):

$$S_0 = \frac{4\varepsilon}{d(1-\varepsilon)} \quad (\text{Eq. 4-76})$$

Where d is the pore-width. Combining above two equations yields a simple expression for the permeability:

$$K_{p,s} = \frac{\varepsilon^3}{5\left(\frac{4\varepsilon}{d(1-\varepsilon)}\right) \cdot (1-\varepsilon)^2} = \frac{d^2}{80} \varepsilon \quad (\text{Eq. 4-77})$$

Hence, assuming that the diameter of the pores remains constant the hydraulic permeability of the GDL is a linear function of the gas-phase porosity. Using this relationship the values in Table 4.5 have been obtained by scaling the value for the permeability for the base case of $\varepsilon = 0.4$ linearly with the porosity.

Table 4.5 Hydraulic permeabilities used for different GDL porosities

ε	0.1	0.2	0.3	0.4	0.5	0.6
$K_{p,s}(\text{m}^2)$	1.19×10^{-11}	2.39×10^{-11}	3.55×10^{-11}	4.73×10^{-11}	5.91×10^{-11}	7.1×10^{-11}

Though these changes were made to the permeability, the study showed that they do not affect the results in any way. This confirms that diffusion is the dominating transport mechanism that drives the reactant gases towards the catalyst layer.

The simulation results of the effects of electrode porosity on fuel cell performance are shown in Figure 4.15 for four different electrode porosities of 0.1, 0.2, 0.4, and 0.5. It is evident from the result that the fuel cell performs better at higher electrode porosity. When the porosity is above 0.2, there is virtually no transport impedance, but if the porosity is reduced to 0.1, a sharp drop in the cell potential can be seen when the current density is over 0.6 A/cm² due to the oxygen transport limitation.

Figure 4.15 Predicted polarization curves under various GDL porosities.

4.7.5 Effect of membrane thickness

Figure 4.16 shows the predicted result of polarization curve and power density curve using Nafion 112, Nafion1135 and Nafion117. It is obvious that better performance can be achieved with decreased membrane thickness. Thinner membrane thickness enhances the ability in driving the protons travel through the membrane thus fasten the electrochemical reaction process and increase the performance accordingly.

Figure 4.16 Predicted polarization curves with various Nafion membrane thicknesses.

4.8 Summary

This single-phase model is capable of predicting the distribution of the reactant gases, as well as the fuel cell performance under various operating conditions. Our modified one-dimensional steady-state isothermal model can well describe the major transport phenomena in the PEMFC. As macroscopic transport in the porous diffusion layer has the

same general form as the equations describing the microscopic transport in the gas channel, this enables us to use the same numerical algorithm to solve these equations and to consider the whole domain as a simple entity and thus the model is easy to compute and simple to implement.

A parametric study revealed the effect of various operating and geometrical parameters on the fuel cell performance. Possible qualitative comparisons were made between experimental results from the literature and those conducted in house with the model prediction. Good overall agreement was obtained under low and medium current density. Discrepancy at high current density was likely occurring due to water vapor condensation which is not considered in present study. A good agreement between experiment studies and simulation results on parametric studies shows the accuracy of the model.

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5.1 Model introduction

The 1D model presented in Chapter 4 showed that the predicted polarization curves generally agree well with the measured data in the lower and medium current densities range but significant discrepancy exists for high current densities. Predicting the cell performance at high current densities is a more challenging task as transport phenomena have become increasingly more important and complicated. The 1D model does not capture spatial (stream-wise (e_x) or span-wise direction (e_z) as discussed in Chapter 2) and temporal variations of the performance-related parameters in the cell, posing limits on the predictable range. A multi-dimensional model is, therefore, required for studying the complex interactions among these parameters. The latter is useful for deriving design guidelines and optimizing the fuel cell. Generally, a three-dimensional model is required to solve for the transport phenomena, but the computational cost can easily become excessive. For example, for the case of a non-stoichiometric three-dimensional model with a coarse mesh and a tolerance level of 10^{-3} , it takes hours and even days for a set of coupled partial differential equations (conservation of mass, species, momentum, energy, and charge; two-phase flow; transient conditions) to converge on a high performance single PC and the simulation requires a significant amount of memory. To cut down on the computational cost, both in terms of time and memory requirements, it is convenient to work with reduced mathematical models that can solve and predict the local behaviour of a single cell at a reasonable cost, whilst maintaining all the essential physic. For this purpose a series of experiments were carried out (Chapter 3) with a PEMFC equipped with a porous flow field on both the cathode and anode side (Figure 5.1(a)). The porous nature of the flow field allows a reduction in dimensionality since changes in dependent variables in the span-wise direction (e_z) are negligible due to slip conditions and no flux would be invoked at the left and right walls of the channel (Figure 5.1(b)). The cell can be

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treated as thermally insulated at these walls. A schematic of the two-dimensional geometry can be found in Figure 5.1(c). These model reductions allow for fast and cheap simulations as compared to fully three-dimensional computations. The geometry that one needs to resolve can thus be reduced to the stream-wise direction (e_x) and normal direction (e_y) in the cell, as illustrated in Figure 5.1(c).

Since the experimental PEMFC (base case) was operating at 60 °C and 1.5 bar, a gas-phase model is assumed sufficient to capture the behaviour of the cell, that is, liquid water in the cell will not impact the cell performance significantly. This is a common approximation as it removes the complexities and uncertainties of two-phase flow, which has yet to be described accurately. In the coming sections, the governing and constitutive equations will first be introduced. Then, the basic parameters are summarized and validation with the experimental cell will be carried out.

Figure 5.1 Schematic of a PEMFC with agglomerate nucleus.

5.2 Model assumptions

A typical PEMFC, be it a single cell or a stack, is three-dimensional, transient, and multi-phase (liquid, gas, solid), and involves transport of momentum, mass, charge, species

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(humidified air on the cathode side and humidified hydrogen on the anode side), and energy. These phenomena have to be considered in the various functional layers of the PEMFC, which further adds to the overall complexity of a mathematical model; thus, in order to obtain self-explanatory models, one needs to introduce a series of approximations and assumptions. For this model, the most important ones are as follows:

- Steady-state
- Compressible, ideal gases;
- Gas-phase only; that is, liquid water is not considered;
- Isotropic material properties for the porous regions (flow field, gas diffusion layer, catalyst layer, membrane);
- Thermal equilibrium between phases;
- No cross-over of hydrogen and oxygen through the membrane;
- Agglomerate model for the electrochemical reactions in the cathode catalyst layer, and Tafel equation is applied to the anode.

5.3 Governing and constitutive equations

To accurately describe the transport phenomena occurring in the fuel cell, one needs to solve for the continuity, momentum, conservation of species, energy and charge equations together with their respective constitutive equations. In this section, a single-phase model that takes into account conservation of momentum, mass, species, energy and charge coupled with a phenomenological membrane model and agglomerate model for the cathode catalyst layer is presented.

5.3.1 Conservation of momentum and mass

Weakly compressible flow is considered here with the continuity equation given by

$$\nabla \cdot (\rho \mathbf{v}) = S_m ,$$

$$\text{with } S_m = \begin{cases} \frac{M_{O_2} J_c}{4F} - \frac{M_{H_2O} J_c}{2F} & (\text{cathode CL}) \\ -\frac{M_{H_2} J_a}{2F} & (\text{anode CL}) \\ 0 & (\text{elsewhere}) \end{cases} \quad (\text{Eq. 5-1})$$

where ρ is the density, $\mathbf{v}$ is the velocity, M is the molecular weight, F is Faraday's constant, and J is the volumetric current density in the catalyst layers, where the electrochemical reactions take place (Note: $J_a > 0$, $J_c < 0$). The equation related to exchange current density of the cathode catalyst layer will be illustrated in detail in the section for the agglomerate model. For the anode, a simplified Butler-Volmer equation is used as the overpotentials are typically much smaller than those of the cathode side, and so do not warrant a more sophisticated agglomerate model. This assumption is justified *a posteriori* by comparison of model predictions with the experimental counterparts.

For fluid flow in a flow field comprising channels (for example, serpentine or parallel flow channels), the incompressible Navier-Stokes equation is usually solved for, which can be written as

$$\rho \mathbf{v} \cdot \nabla \mathbf{v} = \nabla \cdot \{-p\mathbf{I} + \mu[\nabla \mathbf{v} + (\nabla \mathbf{v})^T]\} + \rho \mathbf{g} \quad (\text{Eq. 5-2})$$

where p is the pressure, μ is the dynamic viscosity, $\mathbf{I}$ is the second-order identity tensor, T denotes the transpose of a second-order tensor, and $\mathbf{g}$ is the acceleration due to gravity.

In a porous flow field, on the other hand, the global momentum transport of the fluid is impeded due to the pore walls. In most applications, a detailed description of every pore is not practical and, hence, a common approach is to homogenize the porous and fluid media into a single medium. It is well known that Darcy's law is applicable to a control volume which is small compared to the typical macroscopic dimensions but large enough to contain a sufficient amount of pores and solid-matrix elements to give an accurate average description. Thus Darcy's law is commonly used:

$$\nabla p = -\frac{\mu}{\kappa} \mathbf{v} \quad (\text{Eq. 5-3})$$

where κ is the hydraulic permeability of the porous medium.

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A porous medium is characterized by the porosity ε , which is defined as the fraction of pore space as compared to the overall space (including both pores and solid). Thus, the value of porosity can vary from zero for pure solid regions to unity for free fluid flow. In general, for porous media with lower porosity (i.e. $\varepsilon < 0.6$), Darcy's law is applicable since the global transport of momentum by shear stresses in the fluid can be considered negligible. However, for a porous medium with large porosity (i.e. $\varepsilon > 0.6$), the momentum transport within the fluid due to shear stresses can become important^[1]. To account for flow through high-porosity porous media, a Brinkman extension and/or inclusion of inertia terms (e.g. a Forchheimer term) are usually employed. The Brinkman equation is an extension of Darcy's law with an added viscous term in the momentum balance, such that

$$\left(\frac{\mu}{\kappa}\right) \mathbf{v} = \nabla \cdot \left[-p\mathbf{I} + \left(\frac{1}{\varepsilon}\right) \{\mu[\nabla\mathbf{v} + (\nabla\mathbf{v})^T]\} \right] + \rho\mathbf{g} \quad (\text{Eq. 5-4})$$

The Forchheimer term with a form-drag constant, c_F , can be written as:

$$\nabla p = -\frac{\mu}{\kappa} \mathbf{v} - c_F \kappa^{-1/2} \rho |\mathbf{v}| \mathbf{v} \quad (\text{Eq. 5-5})$$

5.3.2 Conservation of species

For the mass balance of species, a gas phase comprising a ternary mixture of oxygen, water and nitrogen on the cathode side and hydrogen and water on the anode side are considered. The conservation of species can be written as follows:

$$\nabla \cdot \mathbf{N}_i = S_i,$$

$$\text{With } S_i = \begin{cases} \frac{J_c}{4F} \text{ (for O}_2\text{)} & \text{(cathode CL)} \\ -\frac{J_c}{2F} \text{ (for H}_2\text{O)} & \text{(cathode CL)} \\ -\frac{J_a}{2F} \text{ (for H}_2\text{)} & \text{(anode CL)} \\ 0 & \text{(elsewhere)} \end{cases} \quad (\text{Eq. 5-6})$$

where the flux $\mathbf{N}_i$ as

$$\mathbf{N}_i = c_i \mathbf{v} - D_i^{eff} \nabla c_i \quad (\text{Eq. 5-7})$$

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The flux of water in the membrane due to electro-osmotic drag and diffusion is expressed with the phenomenological model of Springer *et al.*(1991) in terms of the membrane water content, λ ,

$$\mathbf{N}_{H_2O,m} = \begin{cases} \frac{n_d \mathbf{i}_m}{F} - \frac{\rho_{dry}}{M_m} D_{H_2O,m} \nabla \lambda & \text{(membrane)} \\ c_{H_2O} \mathbf{v} - D_{H_2O}^{eff} \nabla c_{H_2O} & \text{(elsewhere)} \end{cases} \quad (\text{Eq. 5-8})$$

where n_d is the electro-osmotic drag coefficient, $\mathbf{i}_m$ is the current density, $D_{H_2O,m}$ is the diffusivity of water in membrane, ρ_{dry} and M_m are the density and equivalent weight of dry membrane, respectively.

5.3.3 Conservation of charges

Conservation of charge is taken into account for both protons and electrons. Conservation of protons is considered for the catalyst layers and membrane and is described as:

$$\nabla \cdot \mathbf{i}_m = S_{\phi_m}$$

$$\text{with } S_{\phi_m} = \begin{cases} J_a & \text{(anode CL)} \\ J_c & \text{(cathode CL)} \\ 0 & \text{(membrane)} \end{cases} \quad (\text{Eq. 5-9})$$

$$\text{where } \mathbf{i}_m = -\sigma_m \nabla \phi_m \quad (\text{Eq. 5-10})$$

The conservation of electron equation is used for all layers except the membrane

$$\nabla \cdot \mathbf{i}_s = S_{\phi_s}$$

$$\text{with } S_{\phi_s} = \begin{cases} -J_a & \text{(anode CL)} \\ -J_c & \text{(cathode CL)} \\ 0 & \text{(elsewhere)} \end{cases} \quad (\text{Eq. 5-11})$$

$$\text{where } \mathbf{i}_s = -\sigma_s \nabla \phi_s \quad (\text{Eq. 5-12})$$

Here, ϕ_m and ϕ_s are the potential of the ionic phase and electronic phase, respectively, σ_m and σ_s are the electrical conductivity of protons and electrons, respectively, and $\mathbf{i}_m$ and $\mathbf{i}_s$ are the current density carried by protons and electrons, respectively.

5.3.4 Conservation of energy

Conservation of energy is given by

$$\rho c_p \mathbf{v} \cdot \nabla T - \nabla \cdot (k^{eff} \nabla T) = S_T \quad (\text{Eq. 5-13})$$

with

$$S_T = \begin{cases} J_{a,c} \left(\eta_{a,c} + T \frac{\partial E_{rev}}{\partial T} \right) + \sigma_m (\nabla \phi_m)^2 + \sigma_s (\nabla \phi_s)^2 & (CLs) \\ \sigma_m (\nabla \phi_m)^2 & (membrane) \\ \sigma_s (\nabla \phi_s)^2 & (elsewhere) \end{cases} \quad (\text{Eq. 5-14})$$

where c_p is the heat capacity at constant pressure, T is the temperature, k^{eff} is the effective thermal conductivity, η is the overpotential and E_{rev} is the reversible potential.

S_T in the CL are irreversible heat and reversible entropic heat generated by the electrochemical reaction, whereas S_T in the other domains describe ohmic heating caused by proton and electron transport.

5.3.5 Constitutive equations

The density of the gaseous mixture can be calculated with the ideal gas law as:

$$\rho = \frac{pM}{RT} \quad (\text{Eq. 5-15})$$

where M denotes the mixture molecular weight as a function of the molar fraction x_i of species i , and is given by:

$$M = \sum_i M_i x_i \text{ with } x_i = \frac{c_i}{c}, \text{ and } \sum x_i = 1. \quad (\text{Eq. 5-16})$$

Concentrations can be calculated from molar fraction using the ideal gas law

$$c_i = x_i \frac{p}{RT} \quad (\text{Eq. 5-17})$$

The mass diffusion coefficient for each species is dependent on the local temperature and pressure, and is given by

$$D_i = D_i^0 (T^0, p^0) \left(\frac{T}{T^0} \right)^{1.5} \left(\frac{p^0}{p} \right) \quad (\text{Eq. 5-18})$$

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In the porous medium, a Bruggemann correction accounts for the retarded diffusivities of the species due to tortuosity. The effective diffusivity is expressed as

$$D_i^{eff} = \varepsilon^{1.5} D_i \quad (\text{Eq. 5-19})$$

where ε is the porosity, which is assigned different values in the flow fields, gas diffusion layer, catalyst layer and membrane, *i.e.* $\varepsilon = \varepsilon_{ff}, \varepsilon_{gdl}, \varepsilon_{cl}, \varepsilon_m$.

The two important parameters in the flux of water transport in the membrane are the electro-osmotic drag coefficient, n_d , and the diffusivity of water, $D_{H_2O,m}$. They are both expressed in terms of water content, λ :

$$n_d = \frac{2.5\lambda}{22} \quad (\text{Eq. 5-20})$$

$$D_{H_2O,m} = \begin{cases} 3.1 \times 10^{-7} \lambda [\exp(0.28\lambda) - 1] \exp\left(-\frac{2436}{T}\right) & (\lambda \leq 3) \\ 4.17 \times 10^{-8} \lambda [1 + 161 \exp(-\lambda)] \exp\left(-\frac{2436}{T}\right) & (\lambda > 3) \end{cases} \quad (\text{Eq. 5-21})$$

where the water content λ can be expressed in terms of activity, a , as

$$\lambda = \begin{cases} 0.043 + 17.81a - 39.85a^2 + 36.0a^3 & (a \leq 1) \\ 14 + 1.4(a - 1) & (1 < a \leq 3) \\ 16.8 & (a > 3) \end{cases} \quad (\text{Eq. 5-22})$$

with

$$a = \frac{c_{H_2O} RT}{p^{sat}} \quad (\text{Eq. 5-23})$$

The correlation for the proton conductivity in the conservation of charge equation is also given as a function of water content λ

$$\sigma_m = (0.5193\lambda - 0.326) \exp\left[1268 \left(\frac{1}{303.15} - \frac{1}{T}\right)\right] \quad (\text{Eq. 5-24})$$

The limitation of above equation is that the proton conductivity would be negative when the water content, λ , is smaller than 0.627. However, Fimrite *et al.* (2005) have shown that the water content, λ , in the membrane should not be smaller than 1.5. The anhydrous form of the membrane, which corresponds to $\lambda = 0$, is not common, since complete removal of water requires raising the temperature to a point where decomposition of the membrane begins to occur. One and a half water molecules per sulfonate group are

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approximately the minimum value of water content retained in membrane. Thus, the value of water content, λ , is set to 1.5 whenever the predicted value of λ is lower than 1.5. Furthermore, it is widely assumed that the water content, λ , is a constant 16.8 for all $a > 3$.

The volumetric current density, $J_{a,c}$, for the catalyst layers is given by the linear form of the Butler-Volmer equation at the anode, and by a Tafel equation (will later be modified to an agglomerate model) at the cathode as follows

$$J_a = j_{o,a}^{ref} \left(\frac{c_{H_2}}{c_{H_2}^{ref}} \right)^{0.5} \left(\frac{\alpha_a + \alpha_c}{RT} F \eta_a \right) \quad (\text{Eq. 5-25})$$

$$J_c = -j_{o,c}^{ref} \exp \left[-\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T^{ref}} \right) \right] \left(\frac{c_{O_2}}{c_{O_2}^{ref}} \right) \exp \left(-\frac{\alpha_c}{RT} F \eta_c \right) \quad (\text{Eq. 5-26})$$

where j_o^{ref} and α are the volumetric exchange current density and transfer coefficient, E_a is the activation energy, T^{ref} , $c_{H_2}^{ref}$ and $c_{O_2}^{ref}$ are the reference temperature and concentration of hydrogen and oxygen, respectively. The overpotential, $\eta_{a,c}$, is defined as

$$\eta_{a,c} = \phi_s - \phi_m - E_{rev} \quad (\text{Eq. 5-27})$$

The reversible potential, E_{rev} , is equal to zero at the anode side, and is a function of temperature at the cathode side

$$E_{rev} = E_{rev}^0 - 0.9 \times 10^{-3} \times (T - 298.15) \quad (\text{Eq. 5-28})$$

with E_{rev}^0 denoting the reversible potential at the standard conditions.

To compute the thermal conductivity in the conservation of heat equations, one must first determine the mixture viscosity, μ_{mix} , as follows:

$$\mu_{mix} = \sum_{\beta} \frac{x_{\beta} \mu_{\beta}}{\sum_{\alpha} x_{\alpha} \Phi_{\alpha\beta}} \text{ with } \alpha, \beta = H_2, O_2, H_2O, N_2 \quad (\text{Eq. 5-29})$$

where x_{α} are the mole fractions of species α , and

$$\Phi_{\alpha\beta} = \frac{1}{\sqrt{8}} \left(1 + \frac{M_{\alpha}}{M_{\beta}} \right)^{-\frac{1}{2}} \left[1 + \left(\frac{\mu_{\alpha}}{\mu_{\beta}} \right)^{\frac{1}{2}} \left(\frac{M_{\beta}}{M_{\alpha}} \right)^{\frac{1}{4}} \right]^2 \quad (\text{Eq. 5-30})$$

The thermal conductivity of the mixture, k_{mix} , is determined by

$$k_{mix} = \sum_{\beta} \frac{x_{\beta} k_{\beta}}{1.065 \sum_{\alpha} x_{\alpha} \Phi_{\alpha\beta}} \quad (\text{Eq. 5-31})$$

The effective thermal conductivity for the different layers in the fuel cell can be calculated as

$$k^{eff} = \varepsilon k_{mix} + (1 - \varepsilon) k_s \quad (\text{Eq. 5-32})$$

where $k_s = k_{ff}, k_{gd}, k_{cl}, k_m$ are thermal conductivities of the solid flow channel, gas diffusion layers, catalyst layers and membrane, respectively.

The specific heat capacity of the mixture at constant pressure, c_p , is expressed as

$$c_{p,mix} = (x_{H_2} c_{p,H_2} + x_{O_2} c_{p,O_2} + x_{H_2O} c_{p,H_2O} + x_{N_2} c_{p,N_2}) / M \quad (\text{Eq. 5-33})$$

where $c_{p,H_2}, c_{p,O_2}, c_{p,H_2O}, c_{p,N_2}$ (J/mol/K) are the specific heat capacities of hydrogen, oxygen, water and nitrogen, respectively

5.4 Parameters and operating conditions

The PEMFC model outlined above is described by a set of partial differential equations and is implemented into COMSOL Multiphysics[®], commercial computational software. This software can solve the coupled physico-chemical phenomena simultaneously based on the finite-element method. The size of each domain is summarized in Table 5.1.

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Table 5.1 Geometry parameters

The length of the single PEM fuel cell	1.5×10^{-2} m
The height of cathode current collector	1.0×10^{-2} m
The height of cathode net type flow channel	6.0×10^{-4} m
The height of cathode gas diffusion layer	1.1×10^{-4} m
The height of cathode catalyst layer	2×10^{-5} m
The height of membrane	5.1×10^{-5} m
The height of anode catalyst layer	2×10^{-5} m
The height of anode gas diffusion layer	1.1×10^{-4} m
The height of anode net type flow channel	6.0×10^{-4} m
The height of anode current collector	1.0×10^{-2} m

Operating conditions of the base case, as well as the physical parameters are shown in Table 5.2 and Table 5.3, respectively.

Table 5.2 Base-case operating conditions

T_a^{in}	65 °C	T_c^{in}	55 °C
T^{cool}	60 °C		
RH_a	100 %	RH_c	100 %
p_a^{in}	1.5 bar	p_c^{in}	1.5 bar
Q_a^{out}	12×10^{-6} m ³ /min	Q_c^{out}	60×10^{-6} m ³ / min

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Table 5.3 Base-case physical parameters

κ_f	$1 \times 10^{-8} \text{ m}^2$	α_a	1
κ_m	$1 \times 10^{-16} \text{ m}^2$	$c_{O_2}^{ref}$	40.88
ε_f	0.635	$c_{H_2}^{ref}$	40.88
$\varepsilon_c, \varepsilon_m$	0.296232	c_F	0.55
μ	$1.9 \times 10^{-5} \text{ Pa} \cdot \text{s}$	$D_{O_2}^0$	$3.2348 \times 10^{-5} \text{ m}^2/\text{s}$
σ_f	10^5 S/m	$D_{H_2O}^0$	$7.35 \times 10^{-5} \text{ m}^2/\text{s}$
σ_g, σ_c	530 S/m	$D_{H_2}^0$	$1.1028 \times 10^{-5} \text{ m}^2/\text{s}$
σ_m	5 S/m	E_{rev}^0	1.23 V
σ_{cc}	$1.37 \times 10^6 \text{ S/m}$	k_{cc}	16.3 W/m/K
F	96487 C/mol	k_f	13.3 W/m/K
R	8.314 J/mol/K	k_g, k_c	1.5 W/m/K
E_a	73269 J/mol	k_m	0.1 W/m/K
M_{H_2}	$2 \times 10^{-3} \text{ kg/mol}$	k_{H_2}	0.2028 W/m/K
M_{O_2}	$32 \times 10^{-3} \text{ kg/mol}$	k_{O_2}	0.0288 W/m/K
M_{H_2O}	$18 \times 10^{-3} \text{ kg/mol}$	k_{H_2O}	0.0216 W/m/K
M_{N_2}	$28 \times 10^{-3} \text{ kg/mol}$	k_{N_2}	0.0282 W/m/K
p^{ref}	1.5 bar	μ_{H_2}	$9.656 \times 10^{-5} \text{ Pa} \cdot \text{s}$
ρ_{dry}	2000 kg/m^3	μ_{O_2}	$22.618 \times 10^{-5} \text{ Pa} \cdot \text{s}$
M_m	1.1 kg/mol	μ_{H_2O}	$10.979 \times 10^{-5} \text{ Pa} \cdot \text{s}$
$j_{0,a}^{ref}$	10^9 A/m	μ_{N_2}	$19.386 \times 10^{-5} \text{ Pa} \cdot \text{s}$

5.5 Boundary conditions

The pressure, gas temperature and composition at the anode inlet (Figure 5.1) are specified as:

$$p = p_a^{in}, T = T_a^{in}, c_{H_2} = c_{H_2}^{in}, c_{H_2O} = c_{H_2O,a}^{in}, \frac{\partial \phi_s}{\partial x} = 0 \quad (\text{Eq. 5-34})$$

At the cathode inlet, the pressure, normal velocity, the gas temperature and composition are specified as:

$$p = p_c^{in}, T = T_c^{in}, c_{O_2} = c_{O_2}^{in}, c_{H_2O} = c_{H_2O,c}^{in}, \frac{\partial \phi_s}{\partial x} = 0 \quad (\text{Eq. 5-35})$$

At the outlets, the velocities based on the flow rates (Q^{out}) at their respective outlets, and the stream-wise gradients of the species, charge and temperature are set to zero, which is corresponding to fully developed flow conditions:

$$u_a = u_a^{out} = \frac{Q_a^{out}}{h_f \times w}, u_c = u_c^{out} = \frac{Q_c^{out}}{h_f \times w}, \frac{\partial c_i}{\partial x} = 0, \frac{\partial T}{\partial x} = 0, \frac{\partial \phi_s}{\partial x} = 0 \quad (\text{Eq. 5-36})$$

No normal flow as well as no species, charge and heat fluxes is specified at the vertical walls of the gas diffusion layers and catalyst layers:

$$u = 0 \quad \frac{\partial c_i}{\partial x} = \frac{\partial T}{\partial x} = \frac{\partial \phi_s}{\partial x} = 0 \quad (\text{Eq. 5-37})$$

No normal flow as well as no component fluxes is specified at the lowest wall, the temperature and zero potential is set as:

$$T = T^{cool} \quad \phi_s = 0 \text{ (Ground)} \quad (\text{Eq. 5-38})$$

At the top-most wall, no normal flow, no component fluxes, the temperature and potential are specified as:

$$v = 0, \frac{\partial c_i}{\partial x} = 0 \quad T = T^{cool} \quad \phi_s = E_{cell} \quad (\text{Eq. 5-39})$$

At the interface of current collector and porous flow field:

$$v = 0; \frac{\partial c_i}{\partial y} = 0 \quad (\text{Eq. 5-40})$$

At the gas diffusion layer/catalyst layer interface :

$$\frac{\partial \phi_m}{\partial y} = 0 \quad (\text{Eq. 5-41})$$

At the interface of the membrane and catalyst layer:

$$\frac{\partial C_{O_2}}{\partial y} = 0; \frac{\partial C_{H_2}}{\partial y} = 0. \quad (\text{Eq. 5-42})$$

5.6 Agglomerate model

Generally, most of the validations of mathematical models for the PEMFC in literature have been carried out by comparing the polarization curve obtained from numerical simulations with the one obtained from experiments in the low and medium current density region. As such, most authors do not validate their mathematical models and numerical simulations with the full limiting current density (in fact, similar to what was done in Chapter 4). An agglomerate model is thus necessary to predict the limiting current regime (Chapter 3). It is well known that the mass-transport limitation of a fuel cell depends not only on the inlet concentration of oxygen but also on the resistance of oxygen transportation from the inlet to the catalyst layer. Furthermore, one has to take into account the resistance of the oxygen transport from the bulk of the catalyst layer to the active catalyst sites. An agglomerate model can well represent the latter even for the mass-transport limiting region. The agglomerate model in this study is based on the assumption of a spherical shape of particles covered by a thin polymer film. Later, for the simulation of two-phase flow, a thin film of liquid water is considered since it increases the resistance of oxygen transportation as shown in Figure 5.1(c). In this context, the Tafel equation needs to be modified according to the corresponding resistances. Following the work of Rao *et al.*(2007), A modified Tafel equation is applied

$$J_c = -j_c^{ref} (1 - \varepsilon_c) \left(1 - \frac{\varepsilon_{pol}}{\varepsilon_{agg}}\right) \left(\frac{c_{O_2}}{c_{O_2}^{ref}}\right) \exp\left(-\frac{\alpha_c F}{RT} \eta_c\right) \frac{RT}{H_{O_2, pol}} Corr_1 \frac{1}{1 + Corr_2 + Corr_3} Corr_2 \quad (\text{Eq. 5-43})$$

where $H_{O_2, pol}$ is Henry's constant for air-ionomer interface; $Corr_1, Corr_2, Corr_3$ are the correction factors due to resistances of agglomerate itself, the ionomer and water films,

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respectively; the reference exchange current density is further modified to account for changes in the local temperature

$$j_c^{ref} = j_{o,c}^{ref} \exp \left(-\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right) \quad (\text{Eq. 5-44})$$

where ε_c , ε_{pol} , ε_{agg} are porosities of the catalyst layer, the polymer and the agglomerate, respectively, and are defined as:

$$\varepsilon_c = \frac{V_{void}}{V_T} = 1 - \varepsilon_{agg} \quad (\text{Eq. 5-45})$$

$$\varepsilon_{agg} = \frac{V_{agg}}{V_T}; \quad (\text{Eq. 5-46})$$

$$\varepsilon_{pol} = \frac{V_{pol}}{V_T} \quad (\text{Eq. 5-47})$$

in which

$$V_{agg} = V_{pt/c} + V_{pol}; \quad (\text{Eq. 5-48})$$

$$V_{void} = V_{gas} + V_w; \quad (\text{Eq. 5-49})$$

$$V_T = V_{agg} + V_{void} = V_{Pt/C} + V_{Pol} + V_{gas} + V_w; \quad (\text{Eq. 5-50})$$

According to the definition of the Platinum loading, m_{Pt} , the carbon loading and weight fraction of polymer are expressed as

$$m_c = \frac{m_{Pt}}{\%Pt} - m_{Pt} \quad (\text{Eq. 5-51})$$

$$pol = \frac{m_{pol}}{m_{Pt} + m_c + m_{pol}} \quad (\text{Eq. 5-52})$$

which provide the following relationships for the volume fraction of polymer and Pt/C

$$\varepsilon_{pol} = \frac{pol}{1-pol} \frac{1}{\rho_{pol}} \frac{m_{Pt}}{h_{cl}\%Pt} \quad (\text{Eq. 5-53})$$

$$\varepsilon_{Pt/c} = \frac{V_{Pt/c}}{V_T} = \left(\frac{1}{\rho_{Pt}} + \frac{1-\%Pt}{\%Pt\rho_c} \right) \frac{m_{Pt}}{h_{cl}} \quad (\text{Eq. 5-54})$$

and

$$\varepsilon_{agg} = \varepsilon_{pol} + \varepsilon_{Pt/c} \quad (\text{Eq. 5-55})$$

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where %Pt, ρ_{Pt} , ρ_c , ρ_{pol} are the percentage by mass of platinum in the catalyst in volume, the density of Platinum, carbon and polymer, respectively. Once m_{Pt} , %Pt, m_{pol} (or pol) are known, it is possible to compute the porosity of the catalyst layer, ε_c .

The correction factor $Corr_1$ is defined as the effectiveness of the mass transfer of oxygen through the spherical agglomerate nucleus, and is given as

$$Corr_1 = \frac{3}{\phi_L^2} [\phi_L \coth(\phi) - 1] \quad (\text{Eq. 5-56})$$

Here, the Thiele modulus is

$$\phi_L = r_{agg} \sqrt{\frac{K_c}{D_{O_2,agg}^{eff}}} \quad (\text{Eq. 5-57})$$

where r_{agg} is the radius of an agglomerate, and K_c is given by

$$K_c = \frac{j_c^{ref} (1 - \frac{\varepsilon_{pol}}{\varepsilon_{agg}}) \exp(-\frac{\alpha_c F}{RT} \eta_c)}{n F c_{O_2}^{ref}} \quad (\text{Eq. 5-58})$$

and the effective diffusivity of oxygen in the ionomer phase inside the agglomerate, $D_{O_2,agg}^{eff}$, is related to the diffusivity of oxygen in polymer film, $D_{O_2,mem}$, through the

Bruggeman correlation

$$D_{O_2,agg}^{eff} = D_{O_2,mem} \left(\frac{\varepsilon_{pol}}{\varepsilon_{agg}} \right)^{1.5} \quad (\text{Eq. 5-59})$$

The correction factor, $Corr_2$, accounts for the resistance due to the polymer film

$$Corr_2 = \frac{\delta_{pol}}{D_{O_2,mem}} \frac{Corr_1}{A_{pol}} k_c \quad (\text{Eq. 5-60})$$

where A_{pol} denotes the surface area of the agglomerate per unit volume of the catalyst layer

$$A_{pol} = 4n_{agg}\pi(r_{agg} + \delta_{pol})^2 \quad (\text{Eq. 5-61})$$

with n_{agg} is the number of agglomerate per unit volume

$$n_{agg} = \frac{3\varepsilon_{agg}}{4\pi(r_{agg} + \delta_{pol})^3} \quad (\text{Eq. 5-62})$$

The thickness of the polymer film can be calculated from the following expression

$$\delta_{pol} = \sqrt[3]{\varepsilon_{agg}^3 \left(1 + \frac{\varepsilon_{pol}}{\varepsilon_{Pt/c}}\right)} - \varepsilon_{agg} \quad (\text{Eq. 5-63})$$

Finally, the correction factor, $Corr_3$, due to liquid water film is given by

$$Corr_3 = \frac{\delta_w}{D_{O_2,w}} \frac{Corr_1}{A_w} Kc \frac{H_{O_2,w}}{H_{O_2,pol}} \quad (\text{Eq. 5-64})$$

Here, $H_{O_2,w}$ and $H_{O_2,pol}$ are Henry's constant for the air-water and air-polymer interfaces; $D_{O_2,w}$ is the diffusivity of oxygen in liquid water. A_w is the surface area of agglomerate including water per unit volume, and δ_w is the water thickness:

$$A_w = 4n_{agg}\pi(r_{agg} + \delta_{pol} + \delta_w)^2 \quad (\text{Eq. 5-65})$$

$$\delta_w = \sqrt[3]{(r_{agg} + \delta_{pol}) \left(1 + \frac{\varepsilon_w}{\varepsilon_{agg}}\right)} - (r_{agg} + \delta_{pol}) \quad (\text{Eq. 5-66})$$

Note that the volume fraction of water is expressed as the saturation, s , times the porosity of the catalyst layer

$$\varepsilon_w = \frac{V_w}{V_T} = s\varepsilon_{cl} \quad (\text{Eq. 5-67})$$

For the first one-phase model, the thin film of liquid water is neglected, thus $s=0$ which in turn implies $\varepsilon_w = 0$ and $Corr_3 = 0$, and only $Corr_1$ and $Corr_2$ are included. The effect of $Corr_3$ is studied further in Chapter 8.

5.7 Numerical methodology

The governing equations presented in the previous section form a set of PDEs consisting of nine unknowns; namely, $\phi_m, \phi_s, u, v, p, c_{O_2}, c_{H_2}, c_{H_2O}$ and T . A couple of governing and constitutive equations have been solved numerically by comsol[®].

Since the geometry is regular, it allows for a straightforward application of quadrilateral elements (structured mesh as opposed to an unstructured mesh of, for example, triangular elements). A total of 50 elements in the streamwise direction and 10 elements in the normal direction were implemented for each domain, leading to 500 elements per domain.

Here, thinner domains (particularly the catalyst layers) therefore have a larger number of

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elements per unit area to account for rapid changes, while the larger domains have a fewer number of elements per unit area. In all, this results in 4000 elements for the PEMFC model, which was found to be sufficient to ensure mesh-independent solutions. To incorporate the current collectors, two extra domains are added adjacent to each of the flow channels at the top and bottom of the PEMFC model. Since the only physics that these domains pertain to the electron potential and temperature, they are resolved with few elements: 50 elements in their streamwise direction (e_x) and 5 elements in the normal direction (e_y). In total, the whole PEMFC model with the current collectors has 4500 elements. Figure 5.2 shows the mesh of PEMFC model with current collectors.

Figure 5.2 Mesh of PEMFC model with current collector.

The correctness/quality of a CFD solution is dependent upon the level of discretization. In order to obtain a correct solution, the domain needs to be discretised adequately according to the flow conditions and the geometrical conditions. This can be considered as a mesh validation study. The basic idea is to refine the mesh until you have a solution that no longer changes with increasing mesh density (within the required accuracy!). Therefore half mesh and double mesh and four times meshes on each side compared with Figure 5.2 have been done to analysis the mesh independent solutions Figure 5.3 showed the polarization curves under the different meshes. It can be seen that the polarization curves

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are really close but the mesh qualities are quite different: for the half mesh, the mesh quality is only 0.0333 while for the base case mesh, the mesh quality is 0.1333. As suggested by COMSOL software, the mesh quality above 0.1 is recommended. In order to gain the accuracy and save the computational cost, in this study, base case mesh was used.

Figure 5.3 Polarization curves with various mesh size

All sub-domain settings except for the conservation of protons and electrons are resolved with linear (first order) Lagrange elements in the 'Element' tab under each of the physics sub-domain settings to reduce the number of freedoms to solve for and thus leading to faster computational time (while still giving mesh-independent solutions). For the conservation of protons and electrons, second order Lagrange elements are found to give a better prediction for the overall solution and the choice of mesh density. Figure 5.4 showed the comparison under the linear (first order) Lagrange element and second order Lagrange elements with the experiment data. It is obviously that the second order Lagrange elements are found to give a better prediction for overall solution.

Figure 5.4 Predicted polarization curves with linear and second order Lagrange elements validated with measured polarization curve.

Recent advances in central processing units (CPU) and random access memory (RAM), especially in terms of amount of cores available and amount of RAM, are also likely to provide savings in the time required to reach a converged solution, as well as allow for larger problems to be solved numerically. In light of this, a study was carried out to see how well our mathematical model in COMSOL scales with the amount of cores. For this purpose, a 64 GB RAM workstation with eight cores (Intel CPU@3.2GHz) was employed. Figure 5.5 shows the normalized solver time (all times divided by the time to reach a converged solution with one core) to reach a converged solution with an increasing amount of cores. the time drops by around 10 % from one to two cores, followed by a slower drop from three to eight cores by around another 10 %. The increase in time for eight cores as opposed to seven can be explained by the fact the operating system was

running on the eight cores. In this case, two cores would be sufficient as additional cores do not provide a significant improvement.

Figure 5.5 Normalized solver time for varying number of processors.

5.8 Calibration of electrochemical parameters

Most of the parameters in the mathematical model have been determined by the experimental data conducted in-house (Chapter 3) or from the work of others, as summarized in Table 5.1 to 5.3. A few parameters, however, cannot easily be determined; this is especially the case for the electrochemical parameters for the cathode, which depend on how the catalyst layer was fabricated. In this context, the anode oxidation is fast in comparison with the cathode reduction, and standard values can be used. For the cathode, a point at a low current density (around 0.3 A/cm^2) and another at a higher current density (around 1 A/cm^2) were chosen to determine the reference exchange current density (j_0) and the cathode transfer coefficient (a_c). After parameter adaptation of these two parameters (agglomerate radius (r_{agg}) was set to 10^{-7} m), the entire polarization curve was predicted (discussed in more detail in the following sections). Finally, the agglomerate radius was calibrated to capture the mass-transfer limiting region.

5.9 Validation with a PEMFC equipped with a single-layer GDL

As outlined in Chapter 3, two kinds of cells with two different GDLs were characterized experimentally: a conventional single-layer GDL and a carbon-filled GDL. These experiments and the measured polarization curves form the basis for the validation carried out here.

The conventional carbon-paper-based single-layer GDL will simply be referred to as single-layer GDL in the following discussion. Physical parameters as the permeability and porosity for this particular GDL were determined experimentally (see Chapter 3, $\kappa_g = 6.1 \times 10^{-11} \text{ m}^2$, $\varepsilon_g = 0.77$). With regard to the catalyst layer, no direct measurements were carried out to determine its permeability as it is very thin ($h_c=20\mu\text{m}$), and its permeability was set to be equal to that of the GDL ($\kappa_{cat} = 6.1 \times 10^{-11} \text{ m}^2$).

5.9.1 Polarization curves

A comparison of the single-layer GDL polarization and power density curve from experiments and model predictions is shown in Figure 5.6, and its corresponding polarization curve with iR correction is shown in Figure 5.7.

Figure 5.6 Polarization and power density curve of a PEMFC with a single-layer GDL.

Figure 5.7 Polarization curve w/o iR correction of a PEMFC with a single-layer GDL.

From Figure 5.6 it can be seen that the simulation results are in good agreement with the experimental results within the whole current density range, even close to and at the limiting current density. One can therefore conclude that this PEMFC model is an accurate 2D model for predicting PEMFC performance (within model assumptions) and at a relatively low computational cost (A 64-bit system, 64GB RAM@3.2G processor with 200 s for one entire polarization curve). Furthermore, and this is usually not explored when validation is carried out, the model predictions agree well with the iR -corrected counterpart, as illustrated in Figure 5.7. The model can thus capture the total internal resistance over the fuel cell.

5.9.2 Oxygen distribution

Figure 5.8 shows the oxygen concentration at the cathode side (cathode catalyst layer (CCL); cathode gas diffusion layer (CGDL); and cathode flow field (CFF)) for various cell potentials ($E_{cell}=0.9, 0.6, 0.3, 0$ V). Here, several features are apparent: First, as in the

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experimental setup, the flow rate at the outlet is fixed (60 ml/min), which for this cell (see Figure 5.8 (a)-(d)) is sufficient for all operating potentials as there is still oxygen available at the outlet. In other words, the cell is operating at a stoichiometry higher than one. The overall oxygen concentration, however, drops from the inlet to the outlet due to the consumption of oxygen in the catalyst layer. At a higher potential (0.9 V), the oxygen concentration everywhere is around 10 mol/m^3 and evenly distributed as only little oxygen is consumed. At a potential of 0.6 V, which is a typical operating voltage for a single cell^[2], the oxygen concentration ranges from around 10 mol/m^3 (inlet) to 7 mol/m^3 (outlet). At lower potentials, which are 0.3 and 0 V, the oxygen concentration at the outlet has dropped to around 4 and 3.5 mol/m^3 , respectively. This behaviour is as expected; however, it is interesting to note that the limiting current density (see Figure 5.4) is not due to the depletion of oxygen in the stream-wise (e_x) or normal direction (e_y), since there is still oxygen available throughout the cathode catalyst layer, which can be seen from Figure 5.6(c) and (d). Instead, it is the mass transport resistance in the agglomerates themselves that give rise to the limiting current density in this case. Without the agglomerate model, the limiting current would have been delayed until oxygen is depleted in the catalyst layer.

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Figure 5.8 Oxygen concentration (mol/m^3) at the cathode (CCL, CGDL, CFF) at the cell potentials: (a) 0.9 V; (b) 0.6V; (c) 0.3V; (d) 0 V

5.9.3 Hydrogen distribution

Figure 5.9 shows the hydrogen concentration at the anode side (anode catalyst layer (ACL); anode gas diffusion layer (AGDL); and anode flow field (AFF)) for different cell potentials ($E_{cell}=0.9, 0.6, 0.3, 0$ V). Similar to the cathode side, the outlet flow rate is prescribed. For the anode, the flow rate is set at 12 ml/min at the outlet, which provides the cell with a high concentration of hydrogen (around four times higher than the oxygen concentration at the cathode), as can be inferred from Figure 5.7. The hydrogen setting is sufficient for all operating potentials. Compared with Figure 5.6, the overall hydrogen concentration distribution has similar trend to the oxygen concentration, but the former is more evenly distributed than the oxygen concentration.

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Figure 5.9 Hydrogen concentration (mol/m^3) at the anode (ACL, AGDL, AFF) at the cell potentials: (a) 0.9 V; (b) 0.6V; (c) 0.3V; (d) 0 V

5.9.4 Water vapour distribution

Figure 5.10 shows the water vapour concentration along the whole fuel cell for different cell potentials. At a high cell potential (0.9 V), one can see that higher water vapour concentration is at the anode side. This can be explained by higher inlet humidification temperature than the operating temperature and there is not too much water vapour produced by the electrochemical reaction. For the lower potentials (0.6, 0.3, and 0 V), the water vapour concentration at the cathode is higher due to the water produced in the electrochemical reaction; hence, there is an increase in water vapour along the flow field towards the outlet. As expected, the lowest potential (0 V) gives rise to the largest increase in water concentration.

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Figure 5.10 Water vapour concentration (mol/m^3) for the fuel cell (from top to bottom: CFF, CGDL, CCL, M, ACL, AGDL, and AFF) at the cell potentials: (a) 0.9 V; (b) 0.6 V; (c) 0.3 V; (d) 0 V

5.9.5 Temperature distribution

Figure 5.11 shows the temperature distribution with respect to the coolant temperature (that is, $\Delta T = T(x, y) - T^{\text{cool}}$) throughout the fuel cell at varying cell potentials. The heat is generated due to the reaction occurring in the PEMFC, while the outer boundaries are being cooled to a certain temperature to maintain the operating temperature. Here, several features are apparent: At high potentials (0.9 and 0.6 V), the temperature is much more evenly distributed than that at the low potentials (0.3 and 0 V). It is clear that the main source of the heat is at the cathode catalyst layer, where the highest temperature difference appears due to the sluggish electrochemical reaction at the cathode (significantly higher overpotential than the anode). Thus, in practise, the cathode inlet temperature can be set to a slightly lower temperature as compared to the anode side in order to mitigate the overall heat management (at least near the entrance of the cell). A higher temperature can be set on the anode side to allow for a higher water content, which can help in keeping the membrane well humidified throughout the cell, especially at high potentials when there is less water produced at the cathode. For these two main purposes, the in-house experiment was designed and operated with a cathode and anode inlet temperature that were 5 °C lower and higher than the coolant operating temperature, respectively. Figure 5.12 shows the polarization curve of two cases (a) inlet temperature of the cathode and anode are the same as coolant temperature, (b) a cathode and anode inlet temperature that were 5 °C lower and higher than the coolant operating temperature, respectively. (base case). It is obviously that base case has better cell performance than the same temperature one.

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Figure 5.11 Temperature difference distribution, $\Delta T = T(x, y) - T^{\text{cool}}$, along the fuel cell (CFF, CGDL, CCL, M, ACL, AGDL, AFF from up to down) at the cell potentials: (a) 0.9 V; (b) 0.6 V; (c) 0.3 V; (d) 0 V.

Figure 5.12 Polarization curves with different inlet temperature.

5.9.6 Pressure distribution

The pressure drop in a fuel cell is important, as it is directly coupled to the parasitic load of the compressor or fan generating the airflow on the cathode side. For the anode side, the pressure drop does not have the same impact (in terms of parasitic load) if the hydrogen is provided by stored hydrogen at high pressures. For a porous-type flow field, the permeability, length, dynamic viscosity and overall velocity are the determining factors for the overall pressure drop. In this case, highly permeable porous flow fields are considered (permeability, $\kappa = 10^{-8} \text{ m}^2$) for which the gauge pressure drop is around 10 Pa, as can be inferred from Figure 5.13. The low pressure drop is also due to the short flow path of the cell ($L = 1.5 \times 10^{-2} \text{ m}$). Furthermore, the gauge pressure is negative as the fixed flow velocity is set at the outlet (experiments run with a fan in 'suction'-mode), which implies that the pressure in the cell is slightly below that of the ambient.

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Figure 5.13 Gauge pressure distribution along the flow field at the cell potentials:

(a) 0.9 V; (b) 0.6V; (c) 0.3 V; (d) 0 V.

5.9.7 Local current density distribution

The overall performance of a fuel cell is important, which is typically measured with global polarization curves (see Figure 5.6 and Figure 5.7). In addition, the local current density distribution is of importance to ensure an even utilization of the Pt throughout the cell. For the PEMFC equipped with a single layer GDL, the local current density distribution predicted by the model is depicted in Figure 5.14 for varying cell potentials. For high potentials ($E_{cell} > 0.5$ V), the current is drawn evenly from every part of the catalyst layer in the stream-wise direction, while the current density distribution becomes more uneven for lower cell potentials ($E_{cell} < 0.4$ V) region. This is more obviously and seriously when close to the entrance of the cell.

Figure 5.14 Local current density (averaged over the height in the cathode catalyst layer) along the fuel cell length for different cell potentials ($E_{cell} = 0.9; 0.8; 0.7; 0.6; 0.5; 0.4; 0.3; 0.2; 0.1; 0$ V).

5.10 Validation with a PEMFC equipped with a carbon-filled GDL

Besides the PEMFC equipped with a single-layer GDL, the mathematical model was also

adapted to the carbon-filled gas diffusion layer (CFGDL) and subsequently validated. Due to the micro-porous layer, the overall performance is higher than that of the single layer GDL. Physical parameters, that is the permeability, $\kappa_g = 3.4 \times 10^{-13} \text{ m}^2$, and porosity, $\varepsilon_g = 0.67$, were determined with suitable experiments (Chapter 3). It is further assumed that the permeability of the catalyst layer is the same as the permeability of the GDL ($\kappa_{cat} = 3.4 \times 10^{-13} \text{ m}^2$).

5.10.1 Polarization curves

A comparison of the carbon-filled GDL polarisation curve and corresponding power density curve for both the experiments and the model predications are shown in Figure 5.13. The PEMFC with the CFGDL exhibits an overall better performance than that with a single layer GDL, even though it has a lower porosity. CFGDL has a micro-porous layer (MPL) between catalyst layer and the GDL.

Figure 5.15 Polarization and power density curve for the PEMFC with the CFGDL.

Several reasons for this performance improvement can be postulated: First, it is likely that micro-water droplets formed in the CFGDL structure of the electrode can be quickly

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removed by the MPL, as stated on Chapter 2. Second, the MPL might provide a better electrical and thermal contact between the catalyst layer and the GDL by providing a 'smoother', more continuous interface. Third, the most notable impact of the MPL is its ability to sustain higher currents, which are likely to originate from locally improved mass transfer and so an extension of the limiting current density (compare Figure 5.15 with Figure 5.6). The cell with CFGDL reaches the limiting current density of around 1.6 A/cm², whilst the cell with single-layer GDL reaches the limiting current density of around 1.4 A/cm².

Figure 5.16 Polarization curve w/o iR correction for the PEMFC with the CFGDL.

Figure 5.16 Polarization curve w/o iR correction for the PEMFC with the CFGDL. From Figure 5.15, it can be seen that the simulation results are in good agreement with the experimental results for both the iR corrected and full polarization curves. Based on the ease of calibration (few parameters) and good agreement for the validation, one can conclude that this PEMFC model is an accurate 2D model for predicting PEMFC operations, if the fuel cell is operated at conditions where two-phase flow does not become limiting factor.

Similar to the GDL with the single-layer, the cell with the CFGDL has an even current density generation at high potentials and becomes more uneven at lower potentials as can be inferred from Figure 5.17.

Figure 5.17 Local current density along the fuel cell length for different cell potentials(E_{cell} = 0.9; 0.8; 0.7; 0.6; 0.5; 0.4; 0.3; 0.2; 0.1; 0 V).

5.10.2 Distributions

Similar to the GDL with the single-layer, the oxygen distribution, hydrogen distribution, water vapor distribution, temperature distribution and pressure distribution can be found in Appendix B, the similar trend with more evenly distributed was obtained.

5.11 Rational of agglomerate model

As mentioned earlier, most of the mathematical models in literature are validated at lower and medium current densities, as there is often a lack of experimental data for the limiting current density. In fact, running a cell at these conditions might be detrimental to the life span of the cell. Another reason is that it is generally more difficult to capture changes at the limiting current density, which is why this region is sometimes left out from validation. The in-house experiments and the calibrated agglomerate model provide the

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framework for accurate calibration and validation of key important parameter (the agglomerate radius, r_{agg}), as illustrated in Figure 5.17, which can be seen to greatly affect the predicted limiting current density for the operating conditions in this study. Clearly, without the experimental polarization curves up until the limiting regime, it would not be possible to set a valid radius as the polarization curves are insensitive to changes in the agglomerate radius at low to medium current densities ($< 0.9 \text{ A/cm}^2$). Here, different agglomerate nuclei radii will shift the onset of the limiting current density regime forwards or backwards. This, in turn, suggests that mass transport inside the agglomerates become a dominate effect, and that the agglomerate radius needs to be properly calibrated with experiments. Thus, for model predictions, the choice of agglomerate radius would be critical.

Figure 5.18 Measured polarization curve(■) vs. predicted polarization curve (-) for different agglomerate nuclei radii ($r_{agg}=5.2, 5.4, 5.6, 5.8, 6 \times 10^{-7} \text{ m}$) with the single-layer GDL.

5.12 Summary

A 2D single-phase model for mass, momentum, species, charge, and energy transport coupled with a phenomenological membrane model and agglomerate model in the cathode catalyst layer for a PEMFC has been derived and discussed. Two GDL cases (single layer GDL and CFGDL) have been used to calibrate and validate the models. Close agreement between predicted results and experimental data was obtained for the two cases in the entire current density range.

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The processes in the fuel cells are complicated because of the tight coupling between electrochemical and transport processes in the various functional layers of the cell. For a model of the fuel cell, this translates to a large number of phenomena that have to be solved, *i.e.*, electrochemical kinetics, fluid flow, charge transfer, mass transfer, heat transfer and species transfer. In addition, there are a large number of empirical or experimental parameters involved. To validate such a complex model, comparison with experimental data is necessary. Generally, validation of fuel cell models is carried out by comparing experimentally measured polarization curves (V–I curve) with model predictions. The choice of the V–I curve for the validation reflects the importance of the V–I curve, *i.e.*, it gives the overall cell performance. However, the V–I curve, while easy to measure experimentally as compared to trying to determine the local current density distribution, only represents an average value of all the physical phenomena inside the cell. This is the reason why various models in literature can be parameter adapted and made to fit experimental V–I curves. Often, as found through a careful review of the existing literature, several models have been adapted to the same experimental polarization curves, resulting in a good fit but with widely varying parameters. Clearly, there is a need to establish how sensitive the V–I curves are to perturbations in the parameters for the geometry, operating conditions, and materials.

In order to find out what parameters could cause the most significant effects on the V–I curve and whether it is sufficient to compare modelling results only with the V–I curve, a comprehensive study of the following operating conditions has been carried out:

- *Temperature*: affects, for example, the membrane conductivity and electrochemical reactions;
- *Pressure*: affects the cell performance as the concentration is increased;
- *Air flow rate*: helps remove product water and keep oxygen concentration high.

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Furthermore, the following material properties and geometries have been studied and will be discussed further later in this Chapter:

- *Thickness of the GDL*: affects the resistance to mass transfer to and from the catalyst layers;
- *Permeability of the flow field and GDL*: controls the flow pattern through the cell;
- *Size of agglomerates* in the cathode catalyst layer: has a direct impact on the cell performance, for example, in terms of the three-phase interfacial area;
- *Pt loading*: affects the electrochemical reactions in the catalyst layers.

All the simulation based on the base case in Chapter 5 (Single layer GDL). If not specified, parametric studies are at the cathode side.

6.1 Operating temperature

The temperature inside a fuel cell is generally not uniform, as it varies from inlet to outlet, from cathode to anode. It is therefore not clear where the temperature measurements should be carried out. In general, the cell temperature is approximated by the following temperatures ^[1]:

- *Surface temperature*, which is measured at an external wall of the cell;
- *Temperature of air leaving the cell*;
- *Temperature of coolant exiting the cell*.

In this study, the temperature of coolant leaving the cell is taken as the operating temperature. Furthermore, the anode and cathode inlet temperatures are 5 °C higher and lower than the operating cell temperature, respectively (as discussed in Chapter 5.8.5). Here, the effect of the cell operating temperature on the cell performance with porous flow fields is studied. The simulations were carried out at different cell temperatures ranging from 30 °C to 80 °C, with an increment of 10 °C.

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Figure 6.1 Fuel Cell performance under different operating temperatures (T=30 ,40 ,50 ,60 ,70 ,80 °C).

Figure 6.1 shows t

that the PEMFC cell performance improves when the cell temperature increases from 30 °C to 70 °C, followed by a slight decrease in performance at 80 °C. Furthermore, the effect of the cell temperature is more significant in the high current density region (around 1 A/cm²) where performance is increased with temperature increases; this is mainly due to the increase of membrane conductivity (Eq. 5-24) and increased rate of reaction in the electrochemical reactions reflected by increased exchange current density (Eq. 5-43). A high limiting current density is observed at high temperature.

The operating temperature of a PEMFC cannot be too low, as it may cause water vapour in the cell to condense, forming liquid water to such a degree that it hinders transport of reactants and products to and from the catalyst layers. In severe cases, it may even cause flooding in the cell with a sharp decrease in performance (this will be discussed in detail in Chapter 8).

As shown in (Eq. 5-24), the membrane conductivity is strongly related to the water content and temperature. In general, the proton conductivity of the membrane increases

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linearly with water content and exponentially with increasing temperature. The membrane conductivity (for the interface of M/ACL) at the cell potentials 0.6 V and 0.3 V for different temperatures is depicted in Figure 6.2 (a) and (b). Obviously, membrane conductivity is increased and membrane conductivity is higher at 0.6 V than 0.3 V for the temperature range from 30 °C to 80 °C.

Figure 6.2 Conductivity along the fuel cell length at cell potentials (a) 0.6 V and (b) 0.3 V for various temperatures at the interface M/ACL ($T=30, 40, 50, 60, 70, 80$ °C).

Figure 6.3 shows the average liquid water content at cathode side under different temperatures. It is clear that the average liquid water content increases with the increase of temperature and this helps to explain the increment of membrane conductivity as well.

Figure 6.3 Average liquid water saturation at cathode side under different operating temperature.

6.1 Operating pressure

As mentioned in Chapter 5.8.6, a fuel cell can operate either at ambient pressure or elevated pressures. The latter is typically the case when the fuel cell is fed with reactant gases from a pressurized tank with a discharge pressure control able by a backpressure regulator placed at the outlet. This pressure regulator keeps the desired, preset pressure at the fuel cell outlet. Very often, in laboratory settings, the inlet pressure is not recorded such that the pressure drop of the system is unknown. The inlet pressure is always higher than the outlet pressure because of inevitable pressure drop in the flow fields inside the fuel cell. Knowing the pressure drop is important, as the fan or the blower must be capable of delivering the required flow rate; the latter depends, in turn, on the pressure drop within the system (Barbir, 2005).

Here, same pressure conditions are applied to both the anode and cathode inlet whilst the flow rates (velocities) are still same at the cathode and anode outlet (Chapter 3 and Chapter 5).

Figure 6.4 PEMFC performance at different operating pressures ($P=1, 1.5, 2, 3$ bar).

Figure 6.4 shows the PEMFC performance for operating pressures ranging from 1 to 3 bars. It can be noted that at higher pressures, there is an increase in limiting current density, which is due to the increase of the inlet gas concentration (as the pressure is increased), the exchange current density i_0 and the gas-pair diffusivities D_{ij} in the Stefan-Maxwell equations. Clearly, an increase in pressure is mirrored by an increase in cell performance and an improvement in the limiting current density. However, increasing the pressure in the cell brings forth the cost of the parasitic load to power the fan/blower.

6.2 Air flow rate

In order to maintain high cell performance and to avoid reactant depletion, the inlet flow rate (inlet velocity) is critical. If flow rate is too low, fuel cell performance will drop due to reactants depletion; if flow rate is too high, it will lead to underutilization of the reactants and higher parasitic load. At the cathode, for example, oxygen is consumed in

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the cell, and its concentration in the cell depends mainly on the flow rate: the higher the flow rate, the higher the concentration throughout the cell. Further, a high velocity helps remove the product water from the cell and keep the oxygen concentration high in order to ensure good operating conditions for the cell. The specific outlet velocity is used in the in-house experiments to avoid the reactant depletion and ensure the high fuel utilization. As mentioned in Chapter 5, the outlet flow rates (velocity) are set at 12 ml/min (0.03 m/s) and 60 ml/min (0.17 m/s) for hydrogen and air, respectively, which are regarded as base case conditions. In this parametric study, the outlet velocity of hydrogen is fixed.

Figure 6.5 shows the PEMFC performance for increasing outlet air flow rate (velocity). Generally, the cell performance increases with a higher flow rate through the cell (from $0.5 U_0$ to $2 U_0$). An interesting finding is obtained when comparing the cases of $U^{\text{out}} = 4 U_0$; $U^{\text{out}} = 6 U_0$; $U^{\text{out}} = 12 U_0$ with $U^{\text{out}} = 2 U_0$. Increasing the flow rate does not show the corresponding improved cell performance.

Figure 6.5 PEMFC performance for increasing outlet air flow rate (velocity).

This can be explained by referring to Figure 6.6. It is clear that higher flow rate will give rise to higher oxygen concentration which also helps to remove product water from the cell. However, excessive high flow rate leads to more water taking away by the flow

causing lower humidity in cathode than necessary and hence reduce the cell performance.

Thus there is a balance between oxygen content and retain water content to achieve an optimal performance.

Figure 6.6 Average water and oxygen concentration at cathode side for increasing outlet air flow rate (velocity) (a) average water concentration; (b) average oxygen concentration.

6.3 GDL thickness

The GDL, adjacent to the catalyst layer and flow field, plays an important role in PEMFC performance and serves several functions:

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- *Transportation of reactant:* a well designed GDL should be able to provide good reactant pathways from the flow field channels to the catalyst layer and uniformly distribute the reactants onto the whole reaction surface;
- *Transportation of liquid water:* a well designed GDL offers pathways for liquid water removal from the catalyst layer to the flow field channels;
- *Conduction of electrons:* a well designed GDL allows charge transfer from the bipolar plate to the catalyst layer or vice versa;
- *Mechanical support:* a well designed GDL should be able to support the catalyst layers and the proton exchange membrane against pressure from the gases and the assembly forces;
- *Heat conduction:* a well designed GDL should be able to effectively remove the produced heat from the catalyst layer.

Toray TGP-H is a carbon-carbon composite paper, which has been used for the PEMFC for many years and it has a proven durability. Its high mechanical strength, conductivity and gas permeability make it suitable for use as a GDL in fuel cell application. Commercially, they offer four different standard sizes: TGP-H-030, TGP-H-060, TGP-H-090 and TGP-H-120 with the thickness of 0.11, 0.19, 0.28, and 0.37 mm, respectively. TGP-H-030 is used for the base case study (Chapter 5). To simulate the impact of GDL thickness on the cell performance, above four different standard-size GDLs were applied to both the cathode and the anode for investigating mass transport phenomena through the GDL, in particular, its effect on cell performance.

Figure 6.7 shows the PEMFC performance with various types of GDLs for the following outlet velocities: (a) $2 u_0$; (b) u_0 ; (c) $0.5 u_0$; and (d) $0.005 u_0$. At the highest velocity, the general trend shows that the cell performance is increased with decreasing GDL thickness. However, as the velocity decreases, the polarization curves move closer to each other until a reverse behaviour is observed for the lowest velocity, *i.e.*, case (d). This would be

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a similar phenomenon as discussed in section 6.3, the competing effects between the oxygen content and water content at cathode side. Figure 6.8 shows the average water and oxygen content at cathode side for case (c) and case (d). In case (c), the oxygen content increases slightly and water content decreases with increase of the GDL thickness; while in case (d), the oxygen content increases slightly and water content increases with increase of the GDL thickness.

Figure 6.7 Fuel cell performance with various types of GDL under outlet velocity: (a) $2 u_0$; (b) u_0 ; (c) $0.5 u_0$; (d) $0.005 u_0$.

Figure 6.8 Water and oxygen content at whole cathode side for outlet air flow rate (velocity): (a) $0.5 U_0$; (b) $0.005 U_0$.

6.4 Agglomerate nuclei

The important challenges in PEMFC research arise in the catalyst layers (CLs) because they are complex and heterogeneous. The catalyst layers (CLs) need to be designed so as to generate high rates of the desired reactions and minimize the amount of catalyst necessary for reaching the required levels of power output. To meet this goal, the following requirements need to be considered:

- Large three-phase interface in the CL
- Efficient transport of protons
- Easy transport of reactant and product gases and removal of condensed water
- Continuous electronic current passage between the reaction sites and the current collector.

Usually, the CL is prepared using a catalyst ink, which includes catalyst, carbon powder, binder and solvent; sometimes, other additives are added to improve the dispersion of the components and stabilize the catalyst ink. Traditionally, the CL is applied to the GDL by various methods: spraying, painting, rolling and screen-printing, and so forth. As outlined in Chapter 3.1.2, a PTFE ionomer can be added as a binder to form a hydrophobic CL using the spraying method. While preparing the catalyst layer, its structure and function evolve over a wide range of scales from microscopic at the supported catalyst nanoparticles to the operation in a fuel cell at the macroscopic device level. The modelling of the structure and operation of the CLs is therefore a multi-scale problem. The challenges for theory and modelling of catalyst layer operation are markedly reduced if the main structural effects occur at well-separated scales; viz. at catalyst nano-particle level ($r_{Pt} \sim 2$ nm), at the agglomerate level of carbon/Pt ($r_{agg} \sim 100$ nm), and at the macroscopic device level ($L_{cl} \sim 10$ μ m) of an operating fuel cell, at which CLs can be considered as an effective homogeneous media. Separate approaches in theory and

modelling can thus be considered at these different scales as illustrated in Figure 6.9 (Zhang jiujun, 2008).

Figure 6.9 Illustration of structure and phenomena at multiple scales that control the performance of catalyst layer in PEMFC. Left: Pt nanoparticle on carbonaceous substrate (~ 3 nm); middle: phase-segregation and agglomerate formation at mesoscale (~ 50 nm); right: the catalyst layer as a complex composite medium at macroscopic scale (~ 10 μ m). (Zhang jiujun, 2008).

The basic function of a CL is to provide the sites for electrochemical reactions. The main processes occurring in a CL include mass transport of the reactants, interfacial reactions of the reactants at the electrochemically active sites, proton transport in the electrolyte phase, and electron conduction in the electronic phase. The impact of varying agglomerate nuclei radii in the cathode CLs is shown in Figure 6.10. The typical agglomerate radius depends on the manufacturing process of the CL including the influence of temperatures, pressures and method used. As can be inferred from Figure 6.9, a decrease in agglomerate radius can significantly improve the cell performance, as diffusion limitations inside the agglomerates are reduced and more agglomerates can be found per unit volume (due to smaller size) as compared to larger-sized nuclei. In this case, a nuclei radius of 2×10^{-7} m gives 3.5 times better performance than the corresponding case with 1×10^{-6} m (where agglomerate nuclei radius is 5 times larger). It

is therefore of importance to seek the effective manufacturing methods to reduce the agglomerate radius in the CL to ensure close to optimal cell performance.

Figure 6.10 PEMFC performance for different agglomerate nuclei radii.

6.5 Platinum loading

The catalyst layer is the region where electrochemical reaction takes place. The big challenges in PEMFC research arise from catalyst layers because their structures are quite complicated and heterogeneous. The first-generation CLs using PTFE-bonded Pt black electrocatalysts displayed high performance but at a prohibitively high cost of platinum loading up to 4 mg/cm^2 . One of the most significant improvements has been made by fabricating a CL with dispersed Pt/C and by painting solubilised ionomers to reduce the Pt loading to 0.4 mg/cm^2 . With thin-film method, the Pt loading was further lower down to a level of $0.1\text{--}0.3 \text{ mg/cm}^2$. The important properties of a catalyst layer, such as electronic/photonic conductivity, porosity, active reaction area, as well as catalytic activity, are mainly determined by the fabrication method and the properties of the components. As mentioned previously, several manufacturing techniques such as blading, painting, printing, spraying, rolling and screening have been developed. It is

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known that the actual Pt loading may vary during the manufacturing. For spray painting, the velocity of the nozzle will determine the local Pt loading; bias or variations could lead to unevenness. This suggests that if one knows the typical operating condition, it should be possible to optimize the Pt load to minimizing the overall Pt load without the trade-off of the cell performance.

One can imagine several scenarios for the Pt load in a fuel cell, some of which describe case of intentionally different uniform loading amount (case a), some of which describe cases of uneven Pt loading due to bias or variations in the manufacturing process (cases d, e and f; outlined below); others, which seek to deliberately vary the Pt loading to reduce the overall amount in the cell whilst ensuring a good cell performance (cases b and case c; outlined below). In this study the following cases are considered:

- (a) Uniform Pt loading along the cell (typical model scenario);
- (b) In-plane positive gradient Pt loading: Linearly increasing Pt loading with the minimum load at the inlet and the maximum at the outlet;
- (c) In-plane negative gradient Pt loading: Same as (b) but a decreasing load from inlet to outlet, with the maximum Pt loading at the inlet and the minimum at the outlet;
- (d) Sinusoidal variation in Pt load (one cycle);
- (e) Sinusoidal variation in Pt load (three cycles);
- (f) Locally lower Pt loading.

These cases are highlighted in Figure 6.11, where the cases (b) to (f) are with the same average Pt loading of 0.4 mg/cm^2 .

Figure 6.11 Various Pt loading cases

6.5.1 Constant Pt loading (case a)

Figure 6.12 shows the polarization curves with different uniform Pt loading. It is obviously that the cell performance increases with increasing the overall Pt loading. It can be explained by the larger three-phase interface in the CL and more efficient transport of protons. The cell performance leads to substantial improvements (more than 6 times) from 0.1 mg/cm^2 (0.25 times the base Pt load, 0.25 mPt) to 0.4 mg/cm^2 (base case, mPt) while from 0.4 mg/cm^2 (base case, mPt) to 0.6 mg/cm^2 (1.5 times the base Pt load, 1.5 mPt) shows moderate improvements.

Figure 6.12 PEMFC performance with different Pt loading (case a).

Figure 6.13 shows the local current density distribution for Pt loading (0.5 mg/cm^2) at cell potentials: $E_{\text{cell}}=0.8, 0.6, 0.4, 0.2, 0 \text{ V}$. Similar trend is obtained for other uniform loading as well. It is obviously that the local current density distribution is uneven for cell potential ($E_{\text{cell}} < 0.4 \text{ V}$), which is not due to the Pt loading, but due to the amount of reactants available and hydration level of the membrane. The results for the case (a) suggested that it might be of advantageous to tailor the Pt loading to ensure more even current density distributions.

Figure 6.13 Local current density along PEMFC at different cell potentials: ($E_{\text{cell}}=0.8, 0.6, 0.4, 0.2, 0 \text{ V}$).

6.5.2 Linear variation (cases b and case c)

1) *In-plane positive gradient Pt loading (case b)*: Linearly increasing Pt loading with the minimum load at the inlet and the maximum at the outlet;

A non-uniform electrode is introduced. Two different gradients have been considered: case b1 and case b2, which has the Pt load of 0.35 mg/cm^2 , 0.3 mg/cm^2 at the inlets and 0.45 mg/cm^2 , 0.5 mg/cm^2 at the outlets, respectively. Figure 6.14 shows the polarization curves of the case b1 and case b2 compared with the base case. It turns out that both cases give marginal improved cell performance close to the limiting current density (cell potential around or below 0.4 V);

Figure 6.14 Comparison of PEMFC performance with in-plane positive gradient loading (case b1 and case b2) with that of base case.

Figure 6.15 (a)-(c) shows the local current density along PEMFC at different cell potentials: $E_{cell}=0.8, 0.6, 0.4, 0.2, 0 \text{ V}$ for case b1, case b2 and base case, respectively. A much more even local current density distribution is obtained for the case b1 and case b2. Though case b2 did not show any difference in the cell performance with the compared to case b1, the more uniform current density distribution was obtained. In these electrodes, the electro-catalyst concentration increases along the direction parallel to electrode

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substrate, it is expected that the effect of increased catalyst loading in the direction of gas flow could balance the effect of diminishing reactants in the gas stream. In this way, the reaction rate and current density distribution could be substantially uniform across the electrode surface and may increase the utilization of Pt and the cell performance. Overall, It can be seen that with the same catalyst loading (0.4 mg/cm^2), the in-plane positive gradient electrode displays better performance than the non-gradient electrode does, particularly in the high current density range. There would be an optimal gradient existing for the uniform distribution and better cell performance. The disadvantage is that the fabrication of a non-uniform electrode is much more complicated than that of a uniform electrode.

Figure 6.15 Local current density along PEMFC at different cell potentials ($E_{\text{cell}} = 0.8, 0.6, 0.4, 0.2, 0$ V): (a) case b1; (b) case b2 (c) base case.

2) *In-plane negative gradient Pt loading (case c):* Linearly decreasing Pt loading with the maximum load at the inlet and the minimum load at the outlets.

Two different negative gradients have been considered: case c1 and case c2, which has the Pt load of 0.45 mg/cm², 0.5 mg/cm² at the inlets and 0.35 mg/cm², 0.3 mg/cm² at the outlets, respectively. Figure 6.16 shows the polarization curves of the case c1 and case c2 compared with base case. It turns out that both cases give marginal lower cell performance close to the limiting current density (cell potential around or below 0.4 V).

Figure 6.16 Comparison of PEMFC performance with in-plane negative gradient Pt loading (case c1 and case c2 and base case) with that of base case.

Figure 6.17 (a)-(b) shows the local current density along PEMFC at different cell potentials: E_{cell} = 0.8, 0.6, 0.4, 0.2, 0 V for case c1, case c2, respectively. A much more uneven local current density distribution is obtained for the case c1 and case c2 compared with the base case (Figure 6.15 (c)), the worst current density distribution was obtained for case c2. All these results are expected. In these electrodes, the electro-catalyst concentration decreased along the direction parallel to electrode substrate, it is expected that the effect of decreased catalyst loading in the direction of gas flow could enhance the severity of the diminishing reactants in the gas stream effect. In this way, the reaction rate

and current density distribution could be substantially uneven across the electrode surface and thus decrease the cell performance.

Figure 6.17 Local current density along PEMFC at different cell potentials (E_{cell} = 0.8, 0.6, 0.4, 0.2, 0 V): (a) case c1 (b) case c2.

6.5.3 Sinusoidal variation in Pt loading (cases d and case e)

For the variations in the Pt load that may rise during applying the catalyst ink on the electrodes, two cases of sinusoidal variations (case d and case e) are studied, although the overall Pt load is same as that of the base case. Figure 6.18 shows the PEMFC performance with sinusoidal variation in Pt loading (cases d and case e). It is clear that a sinusoidal variation in Pt loading decreases the cell performance. Figure 6.19 (a) and (b)

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show the local current density along PEMFC at different cell potentials. It is clear from Figure 6.18 that a sinusoidal distribution affects the current density distribution in a negative way, with high valleys and deep troughs. For the sinusoidal case with a higher frequency (case e, three cycles), a higher valley and deeper trough is obtained. The local current density almost reaches 3 A/cm^2 and then quickly drops to around 0.5 A/cm^2 ; a behaviour that could be detrimental and contribute to aging effect on the electrodes.

Figure 6.18 Comparison of PEMFC performance with sinusoidal variation in Pt loading (case d and case e) with that of base case.

Figure 6.19 Local current density along PEMFC at different cell potentials: (E_{cell} = 0.8, 0.6, 0.4, 0.2, 0 V) (a) case d (b) case e.

6.5.4 Local deviation in Pt loading (case f)

Finally, the case of a local drop in Pt loading is studied, the results of which are shown in Figure 6.20 and Figure 6.21. case f1 and case f2 with Pt loading ranging from 0.35 mg/cm² to 0.45 mg/cm² and 0.3 mg/cm² to 0.5 mg/cm², respectively. Again, similar to the sinusoidal variations, the local current density is sensitive to perturbations in the Pt load. case f1 shows the similar performance as the base case while case f2 shows the negative effects on the cell performance. Both cases f1 and f2 show the uneven current density distributions and case f2 shows the worst distribution along the PEMFC ranging from 3

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A/cm^2 to 0.8 A/cm^2 , a behaviour that could be detrimental and cause aging to the electrodes

Figure 6.20 Comparison of PEMFC performance with different local deviation in Pt loading (case f1 and case f2) with that of base case.

Figure 6.21 Local current density along PEMFC at different cell potentials: $E_{\text{cell}} = 0.8, 0.6, 0.4, 0.2, 0$ V (a) case f1; (b) case f2.

6.6 Summary

PEMFC performance is affected by many parameters. A comprehensive parametric study on operating conditions (temperature, pressure, air flow rate) and some material properties, geometries and manufacturing properties (thickness of the GDL, size of agglomerate nuclei and various Pt loading) has been conducted.

Generally, cell performance increases with the increase of temperature as well as the pressure and air flow rate. Decrease the thickness of the GDL will shorten the distance of reactants pass through and improve the mass transport of the reactants. Decrease the size of agglomerates shows significant improvement on the cell performance. A series of Pt

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loading on the electrode performance has also been investigated. For the uniform Pt loading, cell performance increases with the increase of Pt loading. For the non-uniform Pt loading, different loading distribution cases have been investigated, but only the in-plane positive gradient loading has positive effect on the cell performance and yield more uniform current density distribution.

Chapter 7 Two-cell stack model

In practice, a single PEM fuel cell will not be able to provide sufficient power for electrical devices requiring high power input. One will have to combine several single cells into a stack to achieve the desired power output. The design of such a fuel cell stack requires careful consideration of several factors such as power requirement of the application; overall voltage required, space availability, weight and desired stack efficiency. However, some of these requirements may conflict with one another. One example of this can be found in automotive applications, where space is limited and weight has to be kept at a minimum. This, in turn, restricts the power output of the fuel cell stack and hence a compromise between power and size/weight has to be considered. The PEMFC stacks can comprise of a couple to hundreds of single cells. The behaviour of the stack is expected to be quite different from a single cell as the neighbouring cells will affect one another. Ideally, each cell should operate at the same operating condition to ensure a high performance and prolonged life span of the fuel cell stack.

According to Barbir (2005), the key aspects of a fuel cell stack design include:

- Uniform distribution of reactants to each cell;
- Uniform distribution of reactants inside each cell;
- Maintenance of required temperature in each cell;
- Minimum resistive losses (for example, choice of materials, configuration, and uniform contact pressure);
- No leakage of reactant gases;
- Mechanical sturdiness (for example, internal pressure including thermal expansion; external clamping forces during handling and operation including shocks and vibrations).

In order to improve fuel cell system performance, one needs to address three issues that are vital to the PEMFC performance:

- *Gas management:* Fuel cell performance is sensitive to the flow rate of the reactants. It is therefore absolutely necessary that each cell in a stack receives approximately the same amount of reactant gas. Uneven flow distribution would result in uneven performance between the cells. In addition, to avoid depletion of reactants and to ensure that enough hydrogen and oxygen reach the active layer to generate current, especially at high current densities, uniformly distributed fuel and oxidant is a prerequisite for generating uniform current distribution.
- *Thermal management:* To maintain the desired temperature inside the cells, the heat generated as a by-product of the electrochemical reactions must be taken away from the cell and from the stack effectively. An effective heat removal system is therefore necessary to keep the fuel cell/stack at a uniform operating temperature. It is well known that fuel cells are usually about 30 – 60 % electrically efficient at a typical operating power density; hence, energy which is not converted into electrical power is dissipated as heat. For a stack, to achieve high stack performance, each unit cell should be running at identical operating conditions. Hence, either an active or a passive cooling system should be applied. Active cooling usually either involves coolant channels embedded in the bipolar plate or as separate layers, where coolant liquid is pumped through to remove the heat, or external fans are used to improve the air flow over the fuel cell/stack. For passive cooling, natural convection is the only way that heat can be removed from fuel cell/stack. However, this mode of cooling is only sufficient for small portable fuel cells with power less than 100 W. passive cooling can be improved by edge-cooling, which means that if the bipolar plate of the fuel cell stack is made narrow enough, the heat generated can be removed from the sides of bipolar plate by adding fins and/or selecting high thermal conductivity material.

- *Water management:* Since the PEMFC operates at temperatures below 100 °C, water vapour can condense easily and form a liquid phase inside the fuel cell. Hence, to prevent flooding of the various cell components while keeping the membrane sufficiently hydrated for ionic conduction, a proper water management should be applied together with thermal management. Several methods have been employed in order to mitigate water flooding in the cathode of PEMFC such as proper flow field design, anode water purging, operating condition control, *etc.*

Very often, there is a need to optimize the stack efficiency and size, these are two conflicting requirements for a given power output and a given polarization curve. Typical fuel cell polarization curves are shown in Figure 7.1. Most of published fuel cell stack polarization curve fall within these two lines.(Barbir,2005)

Figure 7.1 (a) Typical PEMFC polarization curve and (b) stack efficiency (based on LHV) vs power output for different selected nominal cell potentials (solid line are for the higher power and dashed lines are for the lower power polarization curve in (a)). .

The nominal operating point (cell voltage and corresponding current density) is the operating point at nominal power output, and it may be selected anywhere from the polarization curve. Selection of this point has a profound effect on the stack size and efficiency. Lower selected cell voltage at nominal power would result in higher power density and consequently a smaller stack size for any given power output. A stack with

nominal cell voltage of 0.7 V would require about 40 % larger active area than a stack operated at 0.6 V/cell. Selection of 0.8 V/cell at nominal power would result in more than twice the size of a stack operated at 0.7 V/cell. However, higher cell voltage means better efficiency and consequently lowers fuel consumption. Currently, most fuel cell manufacturers/developers use between 0.6 V and 0.7 V at nominal power. Thus, in this simulation studies, predicted results for 0.6 V are highlighted.

As mentioned earlier, the operation of proton exchange membrane fuel cell (PEMFC) stacks requires careful thermal and water management for optimal performance. To study the impact of these design parameters and to extend the previous work on a single cell, a stack comprising two single cells separated by a cooling plate is considered (Figure 7.2). This unit is the smallest stack one can construct which facilitates fundamental studies on how the overall stack behaves when one of its constituent cells has different properties or experienced different operating condition. The flow fields in the single cells and the cooling plates are of porous nature (similar to the single-cell study earlier, both experimental and theoretical), which allows for a reduction of dimensionality from three to two (Chapter 5). The cooling plate has the same thickness as that of the bipolar plate.

Figure 7.2 Schematic of a basic two-cell stack.

As outlined above, various management issues are important for optimal operation of a PEMFC. However, for a stack, perturbations between cells in the stack can arise due to variations in manufacturing, external gas manifold design, non-uniform distribution of contact pressure across the stack, non-uniform cooling, and so forth. Such perturbations can be studied with the two-cell stack model derived here. In order to limit the number of

parameters, the following cases are studied (conditions for cell 1 are kept constant throughout):

- *Close to identical conditions* for both cells in the stack (base case), which represents ideal operating conditions of the stack;
- *Perturbed air flow rate* in the cathode flow field (cell 2), which could be due to an external manifold or a higher/lower flow resistance in a cell;
- *Perturbed Pt loading* in the cathode CL (cell 2), which could be due to the manufacturing process of the CL;
- *Perturbed thermal conductivity* in the cathode GDL (cell 2), which could be due to the manufacturing process of GDL and assembly of the stack;
- *Perturbed porosity* in the cathode GDL and CL (cell 2), which could be due to variations in clamping pressure or the manufacturing process;
- *Perturbed inlet temperature* at the cathode (cell 2), which could be due to the operating condition and inefficient thermal management.

7.1 Model introduction

The two-cell stack model presented here is based on the 2D single-cell model (Chapter 5): two single cells are connected via a cooling plate, as illustrated schematically in Figure 7.2. The stack model therefore inherits the model assumptions from the single-cell model. Note that the two-cell stack represents the smallest unit that can be called a stack, and that the presented models can easily be extended to encompass more cells. A stack comprising around or more than ten cells could be implemented at a reasonable computational cost as the 2D mathematical representation can capture the behaviour of the 3D PEMFC equipped with porous flow fields (Chapter 5). The governing equations are the same as those for the single cell, except for the addition of conservation of energy in the coolant flow field, which is given by

$$\rho^{(l)} C_p^{(l)} u^{(l)} \nabla T = \nabla \cdot (k^{eff} \nabla T) + \sigma_s (\nabla \phi_s)^2 \quad (\text{Eq. 7-1})$$

where $u^{(l)}$ is the set velocity of the coolant.

7.2 Base case parameters and operating conditions

Normally, PEMFC stacks are working in a temperature range of 20 °C up to 80 °C. The best working-temperature is between 50 °C up to 60 °C. Keep the consistency with previous single-cell model, the same base case temperature and pressure are used here. The geometry parameters are shown in Table 7.1. It is clear that the length of the PEMFC stacks changed to 0.01 m and one add on height of cooling plate of 0.01 m while other parameters are used the same as that of single-cell study.

Table 7.1 Geometry parameters

The length of the PEM fuel cell stack	1.0×10^{-2} m
The height of cathode current collector	1.0×10^{-2} m
The height of cooling plate	1.0×10^{-2} m
The height of cathode net type flow channel	6.0×10^{-4} m
The height of cathode gas diffusion layer	1.1×10^{-4} m
The height of cathode catalyst layer	2×10^{-5} m
The height of membrane	5.1×10^{-5} m
The height of anode catalyst layer	2×10^{-5} m
The height of anode gas diffusion layer	1.1×10^{-4} m
The height of anode net type flow channel	6.0×10^{-4} m
The height of anode current collector	1.0×10^{-4} m

The corresponding base case operating conditions and some material parameters of the base case are shown in Table 7.2, whereas other physical parameters are just the same as

those for the single cell (Table 5.3). The results will be discussed in terms of a normalized cell potential, which is defined as (number of cells equal to two in this case):

$$E^{cell} = E^{stack}/2 \quad (\text{Eq. 7-2})$$

Table 7.2 Base-case operating conditions and physical parameters

T_a^{in}	60 °C	T_c^{in}	60 °C
T^{cool}	60 °C	u^{in}	1 m/s
RH_a	100 %	RH_c	100 %
p_a^{in}	1.5 bar	p_c^{in}	1.5 bar
$u^{(l)}$	0.5 m/s	k^{eff}	0.65 W/(m · K)
$\rho^{(l)}$	1000 kg/m ³	$C_p^{(l)}$	4.18 kJ/(kg · K)

7.3 Boundary conditions

Most boundary conditions for each single cell are identical to those presented earlier (Chapter 5), except some modifications and some add-on:

Velocity condition at anode and cathode inlets:

$$u = u^{in} \quad (\text{Eq. 7-3})$$

Pressure condition at the anode and cathode outlets:

$$p = p^{ref} \quad (\text{Eq. 7-4})$$

At the top-most wall of cell 2, potential is specified as:

$$\phi_s = E_{stack} \quad (\text{Eq. 7-5})$$

One add-on boundary condition is introduced for the coolant flow:

$$T = T^{cool} \text{ (inlet), } \frac{\partial T}{\partial x} = 0 \text{ (outlet)} \quad (\text{Eq. 7-6})$$

7.4 Base case performance

The base case corresponds to running the stack at close to identical conditions of cell 1 and cell 2. The normalized polarization and power density curves for the stack are shown in Figure 7.3.

Figure 7.3 Normalized polarization and power density curves for the stack.

A comparison of the polarization of this stack with one single-cell counterpart is shown in Figure 7.4. It is obviously that the single cell and two-cell stack have achieved the same performance. It enhances the necessities of the identical single cell fabrication and working conditions to achieve predictable and preferable stack performance.

Figure 7.4 Polarization curves with single cell and two-cell stack.

The local current densities for both cells in the stack are depicted in Figure 7.5 (lines are overlapping), and is again similar to the one-cell counterpart.

Figure 7.5 Local current density under different normalized cell potentials ($E_{cell} = 0, 0.3, 0.6, 0.7, 0.8$ V).

The temperature distribution along the two cell stack at normalized cell potential (0.6 V) is shown in Figure 7.6, while the difference in actual operating temperature between interface of membrane and catalyst layers for the two cells in the stack is highlighted in Figure 7.7. The reason for the difference in temperature between the two cells can be found in the distance between the cathode (where most of the heat is generated) and the coolant flow field: the upper cell (cell 2) has a longer distance to the coolant plate as compared to the lower cell (cell 1). However, the cathode of cell 2 is closer to the cooled end-plate as compared to cell 1. Hence, the temperature is slightly lower for cell 1, since the coolant temperature increases along the stack (from inlet to outlet shown in Figure 7.6), whereas it is fixed for the upper and lower endplates.

Figure 7.6 Temperature distribution along the two-cell stack at normalized potential 0.6V.

Figure 7.7 Temperature distribution on CCL/M and ACL/M for both cells at normalized potential 0.6V.

7.5 Perturbation studies for the stack

7.5.1 Air flow rate

As mentioned in Chapter 6, fuel cell performance is sensitive to the flow rate of the reactants, it is absolutely necessary that each cell in a stack receives approximately the

same amount of reactant gases to achieve better performance. Uneven flow distribution would result in uneven performance between the cells. It is well known that the external manifold design of a stack, especially for a large stack, can give rise to an uneven flow rate distribution between the manifold (which is discussed in Chapter 3, U and Z-type manifold) and each individual cell. This is emulated by varying the flow rate for cell 2 whilst it is fixed for cell 1. The results of which can be found in Figure 7.8. Two features are apparent: First, when the flow rate (velocity) is lower than that of cell 1, the overall stack performance drops, as cell 2 has become the limiting factor. That is to say, while cell 1 could sustain a higher current density, the conditions for cell 2 are such that it effectively limits the overall performance. Second, when the flow rate is higher for cell 2, the performance is close to that of the base case, since cell 1 now has become limiting factor. In other words, cell 2 could effectively sustain a high current density, where cell 1 cannot.

Figure 7.8 Normalized polarization curves for different air flow rates for cell 2 (base case conditions for cell 1).

7.5.2 Platinum loading

Earlier in Chapter 6, it was shown that the Pt loading has some impacts on cell

performance. This is also the case for the stack, as can be inferred from Figure 7.9. Here, cell 2 has become the limiting factor with an overall lower stack performance when the Pt loading is lowered beyond that of cell 1. The opposite occurs when the Pt loading is increased beyond that of cell 1, as the overall stack performance is constant even though cell 2 could, theoretically, sustain a higher current.

Figure 7.9 Normalized polarization curves for varying Pt loading for cell 2 (base case conditions for cell 1).

7.5.3 Thermal conductivity

Material properties can vary between cells in the stack due to natural fluctuations or bias in the manufacturing process. Furthermore, assembly of the stack may affect the properties as well, since clamping pressure and so forth may vary. Unlike the previous two cases (flow rate and Pt loading), perturbations of the thermal conductivity of one cell does not alter the overall stack performance significantly, as can be seen from Figure 7.10; this, in turn, implies that temperature variations between the cells, as shown in Figure 7.11, does not affect the overall cell performance as long as the temperature difference is a few degrees C.

Figure 7.10 Normalized polarization curves for varying thermal conductivities of cell 2 (base case conditions for cell 1).

Furthermore, as expected, the temperature in cell 2 is higher when the thermal conductivity is lower than that of cell 1, and vice versa when the thermal conductivity is higher.

Figure 7.11 Temperature distribution at a cross-section of the PEMFC (at normalized 0.6 V; $x = L/2$).

7.5.4 Porosity

Another material property that is sensitive to the assembly of the stack is the porosity, as a cell that sees a higher clamping pressure could be compressed to a higher degree, with a lower porosity as a result. Figure 7.12 shows the simulation results see, it indicate that a lower porosity does, indeed, give rise to an overall lower stack performance, whereas a higher porosity does not alter the overall performance (base case: $\varepsilon = 0.77$). Similar to previous parameters studies, while porosities of GDL in cell 2 is lower than that of the cell 1, cell 2 becomes the limiting factor; while porosities of GDL in cell 2 is higher than that of the cell 1, cell 1 is the limiting cell.

Figure 7.12 Normalized polarization curves for varying porosities in cell 2 (base case conditions for cell 1).

7.5.5 Cathode inlet temperature

To maintain the desired temperature inside the cells, the heat generated as a by-product of the electrochemical reactions must be taken away from the cells and from the stack. Insufficient thermal management may cause the variation of the temperature in each cell.

The temperature difference is normally from a few degree C to 20 °C . Figure 7.13 shows the normalized polarization curves for varying cathode inlet temperature in cell 2, indicated that stack performance does not alter while a temperature variation within 10 °C, but a significant drop on cell performance can be seen when temperature difference achieves 20 °C or higher.

Figure 7.14 shows the temperature distribution for varying cathode inlet temperature in cell 2 (base case conditions for cell 1). In this studying, three cases are under consideration: (a) $T_0 + 20\text{ °C}$; (b) $T_0 + 10\text{ °C}$; (c) T_0 . For case (b) and (c), relatively uniform temperature was obtained since the temperature on the top and lowest wall are the same as the cooling temperature and water coolant can effectively remove the heat. For case (a), since the temperature variation is around 20 °C, the water coolant cannot effectively remove the heat to achieve the identical temperature distribution. If one checks the temperature distribution at the cathode side of cell 2 and cell 1, it can be seen that cell 2 shows a significant different temperature range from the inlet to outlet and an overall higher temperature than cell 1 causing the negative effect on the cell performance.

Figure 7.13 Normalized polarization curves for varying cathode inlet temperature in cell 2 (base case conditions for cell 1).

Figure 7.14 Temperature distribution for varying cathode inlet temperature in cell 2 (base case conditions for cell 1): (a) $T_0+20^\circ\text{C}$; (b) $T_0+10^\circ\text{C}$; (c) T_0 .

7.6 Perturbation studies for base case at ambient temperature and pressure.

Currently, a lot of PEMFC stack are operating at normal temperature and ambient pressure. Thus a series of perturbation studies for this base case (30 °C, 1 atm) has been conducted correspondingly and similar trend was obtained. All the results are presented in Appendix C.

7.7 Discussion and conclusions

In this Chapter, a stack model based on two cells has been presented and analyzed. Such a two-cell stack represents the smallest stack and can be extended to encompass more cells. A stack is more susceptible to variations than a single cell, as the overall design has to ensure close to identical operating conditions for each cell in the stack. For the base case where the two cells are run with the same material and operating conditions, it is demonstrated that the two cells are not experiencing exactly the identical conditions, as one cell is slightly warmer than the other, due to the coolant flow field and end plate placement. However, if more cells were considered, one can deduce that the cells in the middle region of the stack would be more similar performance as each constituent cell would have a coolant plate on top and bottom.

It was also shown that perturbations in inlet air flow rate, Pt loading and porosity can have a significant impact on the overall stack performance, as one cell becomes the limiting cell while the other cell could sustain a higher current. This has implications for the manufacturing of the various functional layers of the single cell, as well as the assembly of single cells into a stack. In other words, one could employ the model to study how variations in the manufacturing of the stack affect the overall performance. This model could thus provide good tolerance boundaries for the fabrication.

With regard to the thermal conductivity and its variation between cells, it was found that there were some effect on the temperature distributions on the two cells, whereas the cell

performance did not suffer much, indicating that as long as temperature variations are not too higher (within 10 °C) between the cells, the overall stack performance is not adversely affected.

Similarly, the variation of cathode inlet temperature shows that the cell performance did not suffer much within 10 °C difference but a significantly drop in performance was demonstrated when the temperature difference is 20 °C or higher. The temperature distribution pattern for the two cell stack shows the uneven temperature distribution on two cells.

Chapter 8 Simple two-phase model on 'curve-back' phenomena in cell polarization

8.1 Model introduction

In the previous Chapters, various one-phase models have been derived and validated. These models only consider the gas phase in the cell and so do not capture any two-phase phenomena. This is a valid approach as long as two-phase transport does not become significant in comparison with the gas-phase transport. Typically, two-phase transport is captured mathematically by introducing two-phase flow equations and the relevant closure relations and material parameters. The latter two, however, are usually associated with a range of assumptions and simplifications, as it is difficult to measure some of these properties *in-situ* or *ex-situ* for the various functional layers of the cell; for example, in terms of the Leverett function, the capillary pressure function, the wetting angles, and assumption of mist flow in the flow fields, and so forth. In other words, the additional unknowns that are introduced into such a two-phase framework do not necessarily ensure valid model predictions on a local level as parameter adaptation and validation are usually carried out with respect to overall polarization curves.

Figure 8.1 A typical 'curve-back' behaviour in a polarization curve.

Chapter 8 Simple two-phase model on 'curve-back' phenomena in cell polarization

Experimentally, significant two-phase flow can be observed for flooding conditions, when the cell performance drops rapidly due to excessive liquid water accumulation. One scenario that can be observed for certain conditions is the 'curve-back' phenomena of the polarization curve, for which the cell performance drops and then recovers to some degree, as shown schematically in Figure 8.1 .

This 'curve-back' behaviour was studied by Siroma *et al.* (2006) who explained it as transient phenomena of 'buffering of oxygen' on the cathode side, and by Liu *et al.* (2006) who showed how transient two-phase flow simulations can give rise to a curve-back (Chapter 3). In this Chapter, a simple extension to include two-phase phenomena into the one-phase 2D model is derived, after which 'curve-back' and liquid water accumulation is studied under steady-state condition. In short, the simple model has the advantage of (i) having less parameters than a full two-phase model, (ii) being able to, as shown in the parametric study, provide an insight into the effects of liquid water in the cell, and (iii) allowing for easy implementation in any one-phase model for the cell without the significant changes to the model formulation that a full two-phase formulation would require.

Two main scenarios are considered as shown in Figure 8.2:

- Liquid water accumulation occurs uniformly in the cathode catalyst layer under the steady-state condition;
- Liquid water accumulation is localized in the cathode catalyst layer under the steady-state condition.

Figure 8.2 Two main scenarios: (a) uniform liquid water accumulation (b) localized liquid water accumulation.

8.2 A simple model for liquid water accumulation in the cathode catalyst layer

The accumulation of liquid water is the major cause of the oxygen mass transport limitation in a PEM fuel cell. Water is generated in the cathode as a by-product by the Oxygen Reduction reaction (ORR). Since oxygen gas has much smaller diffusion coefficient compared to hydrogen, its transfer rate is limited, yielding a low concentration at the reaction sites. Water presence at the cathode requires a careful removal method to balance the water content there, which may be achieved at the designed operation condition but not quite easy to achieve over the wide range of conditions of a fuel cell may encounter during the load varying situation. Therefore, the cathode is susceptible to water flooding, which often occurs in real cells. Water flooding significantly reduces the rate of oxygen mass transfer, and lowers the oxygen concentration available for the reduction reaction, causing severe concentration polarization. It is well known that if the water removal rate does not keep up with the generation rate (at the cathode in particular), excessive water will accumulate, causing flooding and thus hindering the transport of oxygen by blocking the pores in the porous CCL and GDL, covering up active sites in the

Chapter 8 Simple two-phase model on 'curve-back' phenomena in cell polarization

CCL and plugging the gas transport channels in the flow field. In addition, flooding within the CCL, GDL and/or gas flow fields can result in a non-uniform distribution of reactants over the active catalyst area and cause very poor performance. Flooding will make the cell performance unpredictable, unreliable and unrepeatable under nominally identical operating conditions.

In order to avoid the ambiguities and uncertainties that are inevitable with a full two-phase formulation for the governing equations, a simple model is proposed here in order to study the 'curve-back' phenomena and the impact of liquid water. The model comprises a smoothed Heaviside function for the liquid saturation in the cathode catalyst layer is implemented with the parameters E^* , s^* , and ΔE (Figure 8.3), which one can easily add on to the one-phase model formulation (Chapter 5) and with a corresponding modification on:

$$J_c = -(1-s) j_c^{ref} (1-\varepsilon_c) \left(1 - \frac{\varepsilon_{pol}}{\varepsilon_{agg}}\right) \left(\frac{c_{O_2}}{c_{O_2}^{ref}}\right) \exp\left(-\frac{\alpha_c F}{RT} \eta_c\right) \frac{RT}{H_{O_2, pol}} \\ \times Corr_1 \frac{1}{1+Corr_2+Corr_3} Corr_2 \quad (Eq. 8-1)$$

As shown in Figure 8.3, based on the different parameters setting for a smoothed Heaviside function for the liquid saturation, the value of the parameters E^* , s^* , and ΔE can be adjusted judiciously and applied to the parametric studies.

Here, E^* is chosen as the midpoint between the maximum and minimum in current density of the polarization curve, as illustrated in Figure 8.3; s^* is correlated with the extent of the performance drop and the amount of liquid water present in the cathode catalyst layer; ΔE is coupled to the loss in potential between the maximum and minimum current density. If no curve-back is observed experimentally, but the cell is operating under two-phase conditions, one needs to adapt the three parameters with some numerical scheme (for example, least squares).

Figure 8.3 the schematic relationship of E^* , ΔE and s^* .

These parameters are then adapted to the observed polarization curve. Note that this approach only requires three parameters that can be estimated visually from experimental polarization curves, and so do not require sophisticated techniques and equipment. Despite its simplicity, the model allows for studies of the impact of liquid water on both the local as well as global cell performance. These parameters are necessary as one needs to prescribe the onset of liquid water accumulation and estimate the final liquid water saturation level, conditions that would be predicted by a full two-phase model.

8.3 Base case

In order to analyse the curve back phenomena in detail and well present the liquid phase occurrence, $E^* = 0.4$ V, $\Delta E = 0.1$ V, $s^* = 50$ % was set for the base case and a uniform liquid water accumulation was assumed. Figure 8.4 shows the simulation result. Obviously, there are turning points in the polarization curve as well as in the power density curve.

Figure 8.4 Polarization and power density curves for base case.

Figure 8.5(a)-(c) shows the local current distribution for the base case at different cell potentials. Referred back to Figure 5.12 (base case for the single cell in Chapter 5), higher local current distribution at each point along the PEMFC is always achieved at lower potential (higher current density) region. However, Figure 8.5 shows a different trend of local current density distribution around the turning point. Results in Figure 8.5 (a) ($E_{cell} > 0.45$ V) and Figure 8.5 (c) ($E_{cell} < 0.35$ V) show the similar trend as that in Figure 5.12 (lower potential, higher local current density); however, Figure 8.5 (b) shows an opposite trend (0.35 V $< E_{cell} < 0.45$ V), *i.e.* lower current density distribution is obtained at lower cell potential. Obviously, this opposite local current distribution around 0.35 V $< E_{cell} < 0.45$ V has negative effect on the cell performance and causes the totally average current density much lower than that of Figure 5.12. It is clearly known that this 'curve back' phenomena also happens within this region while cell potential roughly between $E^* - \Delta E/2$ (0.35 V) and $E^* + \Delta E/2$ (0.45 V). It will help us to better understand the experimental phenomena on turning point (E^*) and the amplitude of the curve back area ($E^* - \Delta E/2$ to $E^* + \Delta E/2$ *i.e.* ΔE) and the curvature of 'curve back' (s^*).

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Figure 8.5 Local current density distribution along PEMFC length at different cell potentials: (a) $E_{cell} > 0.45$ V; (b) 0.35 V $< E_{cell} < 0.45$ V; (c) $E_{cell} < 0.35$ V.

8.4 Parametric studies (uniform water accumulation)

The impacts of the three parameters on the cell performance (in terms of polarization curves) for the simple two-phase model are studied here.

8.4.1 Curve-back point (E^*)

The parameter, E^* , is determined from the mid-point in the cell potential between the maximum and minimum value in current density of the polarization curve, as can be seen from Figure 8.6 .

Figure 8.6 Polarization curves for varying E^* ($E^* = 0.3, 0.4, 0.5, 0.6$ V).

Several features are apparent; foremost is that all polarization curves for different E^* converge into one curve after the minimum value in current density of the 'curve back' region has been passed, irrespective of the onset of the curve-back, which is governed by E^* . This can be explained by the fact that the Heaviside function converges to the same s^* value. Furthermore, the maximum and minimum values (the amplitude of the 'curve back') of each polarization curve occur close to $E^* + \Delta E/2$ and $E^* - \Delta E/2$. These extreme values also drop in magnitude the sooner (that is, the higher the potential) the onset of

liquid condensation occurs.

8.4.2 Curve-back amplitude (ΔE)

The transition period from a liquid water saturation of zero to s^* is given by the magnitude of ΔE around E^* as demonstrated earlier in Figure 8.3 for the Heaviside function.

Figure 8.7 Polarization curves for varying ΔE ($\Delta E = 0.1, 0.2, 0.3, 0.4$ V).

Again, it is clear that all curves converge as the potential approaches zero for varying ΔE with the same s^* . As ΔE increases in the Heaviside function for the uniform water accumulation, the region where the onset of the curve-back occurs becomes wider whereas the maximum and minimum values lie fairly close in one region.

8.4.3 Flooding degree (s^*)

So far, the various polarization curves are all converged onto one line as the potential approaches zero, and one expects that this will not happen once s^* is varied. This is

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indeed the case, as can be inferred from Figure 8.8, which illustrates the polarization curves for no liquid water accumulation to 100 % liquid water (fully flooded), in the cathode catalyst layer.

Figure 8.8 Polarization curves for varying s^* ($s^* = 0\%$, 10% , 50% , 100%).

In the limiting case of no liquid water formed, the model reduces to a one-phase model, where the rapid drop as the potential goes towards zero originates primarily from mass transfer resistances in the agglomerates themselves. In the other limit, *i.e.*, a complete flooding, the cell performance drops down to zero as little to no oxygen can reach the active sites in the cathode catalyst layer due to the low oxygen diffusion coefficient in the liquid water. In between these two limiting cases, the drop in potential becomes steeper with the degree of liquid water accumulation increases. Furthermore, the limiting current density drops significantly as well, indicating that not only the resistance in the agglomerates to mass transfer but also the liquid phase cause the onset of the mass-transfer limiting region.

8.5 Parametric studies on localized liquid water accumulation

The distribution of water in PEMFC must be carefully managed to optimize the

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performance, durability and functionality of the system. It is well known that the proton conductivity of PEM decreases when membrane hydration is reduced, flooding at the cathode inhibits mass transport, and it can lead to failure of materials. Generally one can expect the highest degree of water accumulation occurs when the removal of the continuously created water from ORR in the cathode is not effective and localized liquid water accumulation exists.

As fabrication of single cell (human skills --- applying unevenly of catalyst ink in the electrodes) and fixture of the single cell (clamping pressure) may affect the properties, there could be some bias at the structure of the catalyst layer and introduce some localized hot spot. The localized liquid water accumulation is investigated and preset the localized liquid water accumulation cover region is 0.001m (from $s^* = 0$ to $s^* = 1$). Three cases of different localized liquid water accumulation positions are studied: (a) $\frac{1}{4}$ L; (b) $\frac{1}{2}$ L; (c) $\frac{3}{4}$ L. Figure 8.9 shows the results of these three cases with the comparison of the uniform liquid water saturation with no localized liquid water accumulation position case, *i.e.* $s^* = 1/15 = 6.7\%$ (assumed the liquid water amount of the localized liquid water accumulation is just the same as that of uniform liquid water accumulation). It is clear that the liquid water accumulation has negative effect on the cell performance compared with no liquid water saturation one and the localized liquid water accumulation showed worse effect than the one with uniform liquid water accumulation. Figure 8.10 shows the local current density distribution for all the cases at $E_{cell} = 0.3$ V. It is clearly known that the current was drawn to 0 for the localized point ("hot" spot) and relatively lower current at area nearby and was drawn similar value with that of no saturation at the area far away from the localized point. The position of the localized point does not alter the cell performance too much as shown in Figure 8.9 and Figure 8.10.

Figure 8.9 Polarization curves for varying locations of the localized liquid water accumulation ($x = 1/4 L, 1/2 L, 3/4 L$) with no liquid saturation and uniform liquid saturation of $s^* = 6.7\%$.

Figure 8.10 Local current density distribution for different localized liquid water accumulation at $E_{cell} = 0.3$ V.

8.6 Discussion and conclusions

In this Chapter, a simple extension to account for two-phase flow in a PEMFC for the overall cell performance has been derived, implemented and the associated key parameters (E^* , ΔE , s^*) are discussed. The model can easily be added on to a one-phase

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model in order to predict some two-phase characteristics without having to re-derive the mathematical formulation and numerical code. In summary, the model is based on a Heaviside function of the liquid water saturation as a function of the cell potential, with three parameters, E^* , ΔE , s^* that require some form of observation of a curve-back in the polarization curve (for example, from experiments), or parameter adaptation in the case of a cell operating at two-phase conditions but without a noticeable curve-back. The first parameter, E^* , governs the onset of the curve-back; the second parameter, ΔE , determines the width of the curve-back from the maximum to the minimum current density; and the third, s^* , gives the final liquid water saturation.

Localized liquid water accumulation and uniform liquid water accumulation have been investigated. It is clearly known that the localized liquid water accumulation will draw the current to 0 at the “hot” spot and relatively very low current at the area nearby and thus severely decrease the cell performance. Uniform liquid water accumulation will decrease the local current density all the region along the PEMFC. Localized liquid water accumulation shows worse cell performance than that of the uniform liquid water accumulation on the same amount of liquid water accumulation.

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In this study, a series of model have been conducted and fully or partially validated with in-house experiment results. Meanwhile, a series of parametric studies have been done to evaluate the sensitive /insensitive factor to the fuel cell performance of different types of parameters (operating, geometric, intrinsic and extrinsic). All the models show their capabilities and accuracy to validate the experiment results and to guide the design of fuel cell.

9.1 Conclusions

Based on the developed models and validation with corresponding experiments, A series of conclusion can be drawn:

- (a) 1D modified steady-state isothermal model can well describe the major transport phenomena in the PEMFC. This single-phase model is capable of predicting the distribution of the reactant gases, as well as the fuel cell performance under various operating conditions. As macroscopic transport in the porous diffusion layer has the same general form as the equations describing the microscopic transport in the gas channel, this enables us to use the same numerical algorithm to solve these equations and to consider the whole domain as a simple entity and thus the model is easy to compute and simple to implement.
- (b) A parametric study revealed the effect of various operating and geometrical parameters on the fuel cell performance. Possible qualitative comparisons were made between experimental results from the literature and those conducted in house with the model prediction. Good overall agreement was obtained under low and medium current density. Discrepancy at high current density was likely occurring due to water vapor condensation which is not considered in present study. A good agreement

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- between experiment studies and simulation results on parametric studies shows the accuracy of the model.
- (c) A 2D single-phase model for mass, momentum, species, charge, and energy transport coupled with a phenomenological membrane model and agglomerate model in the cathode catalyst layer for a PEMFC has been derived and discussed. Two GDL cases (single layer GDL and CFGDL) have been used to calibrate and validate the models. Close agreement between predicted results and experimental data was obtained for the two cases in the entire current density range.
- (d) A comprehensive parametric study on operating conditions (temperature, pressure, air flow rate) and some material properties, geometries and manufacturing properties (thickness of the GDL, size of agglomerate nuclei and various Pt loading) has been conducted. Generally, cell performance increases with the increase of temperature as well as the pressure and air flow rate. Decrease the thickness of the GDL will shorten the distance of reactants pass through and improve the mass transport of the reactants. Decrease the size of agglomerates shows significant improvement on the cell performance. A series of Pt loading on the electrode performance has also been investigated. For the uniform Pt loading, cell performance increases with the increase of Pt loading. For the non-uniform Pt loading, different loading distribution cases have been investigated, but only the in-plane positive gradient loading has positive effect on the cell performance and yield more uniform current density distribution.
- (e) A two-cell stack model based on two cells has been presented and analyzed. Such a two-cell stack represents the smallest stack and can be extended to encompass more cells. A stack is more susceptible to variations than a single cell, as the overall design has to ensure close to identical operating conditions for each cell in the stack.
- (f) A series of perturbation parameters has been conducted. It was shown that perturbations in inlet air flow rate, Pt loading and porosity can have a significant

- impact on the overall stack performance, as one cell becomes the limiting cell while the other cell could sustain a higher current. This has implications for the manufacturing of the various functional layers of the single cell, as well as the assembly of single cells into a stack. In other words, one could employ the model to study how variations in the manufacturing of the stack affect the overall performance. This model could thus provide good tolerance boundaries for the fabrication.
- (g) A simple extension to account for two-phase flow in a PEMFC for the overall cell performance has been derived, implemented and the associated key parameters (E^* , ΔE , s^*) are discussed. The first parameter, E^* , governs the onset of the curve-back; the second parameter, ΔE , determines the width of the curve-back from the maximum to the minimum current density; and the third, s^* , gives the final liquid water saturation.
- (h) Localized liquid water accumulation and uniform liquid water accumulation have been investigated. It is clearly known that the localized liquid water accumulation will draw the current to 0 at the “hot” spot and relatively very low current at the area nearby and thus severely decrease the cell performance. Uniform liquid water accumulation will decrease the local current density all the region along the PEMFC. Localized liquid water accumulation shows worse cell performance than that of the uniform liquid water accumulation on the same amount of liquid water accumulation.

9.2 Recommendations

Currently, several relatively simple yet representative models have been presented to better understand the fundamental of transport phenomena in PEMFC and to predict and explore most of the electrochemical and transport phenomena occurring within the PEMFC. These models show insight on various parameters impact and guiding the optimal design of a fuel cell. A series of experiments are conducted to give the platform

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to validate the accuracy and capability of the model. A number of improvements and suggestions are listed below:

For the experimental part:

- Conduct more simulation related experiments (such as measure pressure drop, amount of water at the anode and cathode exits, pressure drop vs. different flow velocities effect, *etc.*) and so forth, in order to validate the models in terms of more than just the standard polarization curves;
- Improve on the segment fuel cell experiments to understand the local current density distribution better and tailor the experiments to reproduce the curve-back phenomena.

For the simulation part:

- add two-phase transport for the model in the whole cell to further compare the simple two-phase model with a more detailed counterpart;
- for the stack model, one could carry out experiments with a stack, using the stack model for manifold design;
- Implement water saturation to study the effects of liquid water on the cell performance as well as improving model accuracy.
- System-level simulation encompassing various equipments, such as compressors, to study the effect of on-board equipment power consumption on the overall useful cell power generation. This could establish limits of operating conditions the cell can self-sustain its power generation capabilities;

List of Publications

Journal paper

1. Han, M., Xu, J. H., Chan, S. H., & Jiang, S. P. (2008). Characterization of gas diffusion layers for PEMFC. *Electrochimica Acta*, 53(16), 5361-5367.
2. “Perturbation Analysis of a Proton Exchange Membrane Fuel Cell Stack”, in preparation .
3. “A Parametric Study of Pt loading in a Proton Exchange Membrane Fuel Cell”, in preparation.
4. “A Simple Two-Phase Model with “curve-back” for a Proton Exchange Membrane Fuel Cell”, in preparation.

Conference paper

1. " Environmentally friendly electrical bicycle powered by a fuel cell stack" , S.H.Chan, Xu J.H., Ram B. *The 6th International Conference on Materials Processing for Properties and Performance*, Beijing, China (2007).

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Appendix A: Properties of Nafion PFSA Membrane

Properties of Nafion® PFSA Membrane

A. Thickness and Basis Weight Properties¹

Membrane Type	Typical Thickness (micrometer)	Basis Weight (g/m ²)
NR-211	25.4	50
NR-212	50.8	100

B. Physical Properties

Property ²	Typical Values				Test Method
	NR-211		NR-212		
	MD	TD	MD	TD	
Physical Properties					
- measured at 50% RH, 23 °C					
Tensile Strength, max., MPa	23	28	32	32	ASTM D 882
Non-Std Modulus, MPa	288	281	266	251	ASTM D 882
Elongation to Break, %	252	311	343	352	ASTM D 882

C. Other Properties

Property	NR-211	NR-212	Test Method
Specific Gravity ¹	1.97	1.97	DuPont
Available Acid Capacity ³ meq/g	0.92 min.	0.92 min.	DuPont NAE305
Total Acid Capacity ⁴ meq/g	0.95 to 1.01	0.95 to 1.01	DuPont NAE305
Hydrogen Crossover ⁵ , (ml/min·cm ²)	< 0.020	< 0.010	DuPont

D. Hydrolytic Properties

Property	Typical Value	Test Method
Hydrolytic Properties		
Water content, % water ⁶	5.0 ± 3.0%	ASTM D 570
Water uptake, % water ⁷	50.0 ± 5.0%	ASTM D 570
Linear expansion, % increase ⁸		
from 50% RH, 23 °C to water soaked, 23 °C	10	ASTM D 758
from 50% RH, 23 °C to water soaked, 100 °C	15	ASTM D 758

¹ Measurements taken with membrane conditioned to 23 °C, 50% RH.

² Where specified, MD - machine direction, TD - transverse direction. Condition state of membrane given.

³ A base titration procedure measures the equivalents of sulfonic acid in the polymer, and used the measurements to calculate the available acid capacity of the membrane (acid form).

⁴ A base titration procedure measures the equivalents of sulfonic acid in the polymer, and used the measurements to calculate the total acid capacity or equivalent weight of the membrane (acid form).

⁵ Hydrogen crossover measured at 22 °C, 100% RH and 50-psi delta pressure. This is not a routine test.

⁶ Water content of membrane conditioned to 23 °C and 50% RH (dry weight basis).

⁷ Water uptake from dry membrane to conditioned in water at 100 °C for 1 hour (dry weight basis).

⁸ Average of MD and TD. MD expansion is similar to TD expansion for NR membranes.

Appendix A Properties of Nafion PFSA Membrane

Properties of Nafion® PFSA Membrane

A. Thickness and Basis Weight Properties¹

Membrane Type	Typical Thickness (microns)	Basis Weight (g/m ²)
NE-1135	89	190
N-115	127	250
N-117	183	360
NE-1110	254	500

B. Physical and Other Properties²

Property	Typical Value	Test Method
Physical Properties		
Tensile Modulus, MPa (kpsi)		
50% RH, 23 °C	249 (36)	ASTM D 882
water soaked, 23 °C	114 (16)	ASTM D 882
water soaked, 100 °C	64 (9.4)	ASTM D 882
Tensile Strength, maximum, MPa (kpsi)		
50% RH, 23 °C	43 (6.2) in MD, 32 (4.6) in TD	ASTM D 882
water soaked, 23 °C	34 (4.9) in MD, 26 (3.8) in TD	ASTM D 882
water soaked, 100 °C	25 (3.6) in MD, 24 (3.5) in TD	ASTM D 882
Elongation at Break, %		
50% RH, 23 °C	225 in MD, 310 in TD	ASTM D 882
water soaked, 23 °C	200 in MD, 275 in TD	ASTM D 882
water soaked, 100 °C	180 in MD, 240 in TD	ASTM D 882
Tear Resistance - Initial, g/mm		
50% RH, 23 °C	6000 in MD, TD	ASTM D 1004
water soaked, 23 °C	3500 in MD, TD	ASTM D 1004
water soaked, 100 °C	3000 in MD, TD	ASTM D 1004
Tear Resistance ³ - Propagating, g/mm		
50% RH, 23 °C	>100 in MD, >150 in TD	ASTM D 1922
water soaked, 23 °C	92 in MD, 104 in TD	ASTM D 1922
water soaked, 100 °C	74 in MD, 85 in TD	ASTM D 1922
Specific Gravity	1.98	—
Other Properties		
Conductivity, S/cm	0.10 min	see footnote ⁴
Available Acid Capacity, meq/g	0.90 min	see footnote ⁵
Total Acid Capacity, meq/g	0.95 to 1.01	see footnote ⁵

¹ Measurements taken with membrane conditioned to 23 °C, 50% relative humidity (RH).² Physical Properties measured for N-115. Where specified, MD - machine direction, TD - transverse direction. Conditioning state of membrane given. Measurements taken at 23 °C, 50% RH.³ Tear resistance (g/mm) of dry membrane increases with thickness. Values given measured using 50 micron membrane.⁴ Conductivity measurement as described by Zawodzinski, et al, *J. Phys. Chem.*, 95 (15), 6040 (1991). Membrane conditioned in 100 °C water for 1 hour. Measurement cell submerged in 25 °C D.I. water during experiment. Membrane impedance (real) taken at zero imaginary impedance.⁵ A base titration procedure measures the equivalents of sulfonic acid in the polymer, and uses the measurement to calculate the acid capacity or equivalent weight of the membrane.

Appendix B Distributions of a Single PEMFC with CFGDL

- Oxygen distribution

Figure B.1 Oxygen concentration (mol/m³) at cathode (CCL, CGDL, CFF) under different cell potentials ($E_{cell} = 0.9, 0.6, 0.3, 0$ V).

Appendix B Distributions of a Single PEMFC with CFGDL

- Hydrogen concentration under different cell potential

Figure B.2 Hydrogen concentration (mol/m³) at Anode (ACL, AGDL, AFF) under different cell potentials ($E_{cell} = 0.9, 0.6, 0.3, 0$ V).

Appendix B Distributions of a Single PEMFC with CFGDL

- Water vapour concentration under different cell potential

Figure B.3 Water vapour concentration (mol/m^3) at fuel Cell (CFF, CGDL, CCL, M, ACL, AGDL, AFF from up to down) under different cell potentials ($E_{cell} = 0.9, 0.6, 0.3, 0$ V).

Appendix B Distributions of a Single PEMFC with CFGDL

- Temperature distribution

Figure B.4. Temperature difference ($T - T_0$) distribution along the fuel cell (CFF, CGDL, CL, M, ACL, AGDL, AFF from up to down) under different cell potentials ($E_{cell} = 0.9, 0.6, 0.3, 0$ V).

Appendix B Distributions of a Single PEMFC with CFGDL

• Pressure distribution

Figure B.5 Pressure drop along the flow field under different cell potentials ($E_{cell} = 0.9, 0.6, 0.3, 0$ V).

Appendix C Perturbation Studies for Base Case at Ambient Temperature and Pressure (30 °C, 1 bar)

1. Base case performance

Figure C.1 Normalized polarization and power density curves for the stack.

2. Perturbation studies for the stack

1) Air flow rate

Figure C.2 Normalized polarization curves for different air flow rates for cell 2 (base case conditions for cell 1).

Appendix C Perturbation studies for base case at ambient temperature and pressure

2) Platinum loading

Figure C.3 Normalized polarization curves for varying Pt loading for cell 2 (base case conditions for cell 1).

3) Thermal conductivity

Figure C.4 Normalized polarization curves for varying thermal conductivities of cell 2 (base case conditions for cell 1).

Appendix C Perturbation studies for base case at ambient temperature and pressure

Figure C.5 Temperature distribution at a cross-section of the PEMFC (at normalized 0.6 V; $x = L/2$).

4) Porosity

Figure C.6 Normalized polarization curves for varying porosities in cell 2 (base case conditions for cell 1).

Appendix C Perturbation studies for base case at ambient temperature and pressure

5) Cathode inlet temperature

Figure B.7 Normalized polarization curves for varying cathode inlet temperature in cell 2 (base case conditions for cell 1).