DEVELOPMENT OF REDUCED MODELS FOR PROTON EXCHANGE MEMBRANE FUEL CELLS

LY CAM HUNG

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Preface

The thesis presents the development of reduced models for Proton Exchange Membrane Fuel Cell which is in parts based on the following journal as well as conference papers:

Journal papers


Conference papers


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Summary

In recent years, there have been significant advances in the development of mathematical and computational models that describe local physical phenomena - conservation of mass, momentum, species, heat, and charge transports - in the proton exchange membrane fuel cell (PEMFC). These models are by their very nature highly non-linear, coupled, multi-dimensional, and computationally expensive to solve for. As such, applying these models to PEMFC stacks, comprising tens or even hundreds of single cells, will come at a hefty computational cost, both in terms of memory usage and time consumption. It is therefore of interest to derive modified or reduced mathematical models that can solve for and predict the local behavior of each cell in a PEMFC stacks at sufficiently low cost, whilst maintaining all the essential physics.

To achieve such a reduction, we employ various methods: volume averaging, porous medium approach, scaling analysis, and asymptotic reduction that aids in systematic reduction of a PEMFC mathematical model. The volume averaging method with the porous medium approach allows us to reduce the model from three to two dimensions; the scaling analysis provides quick and cheap prediction of the fuel cell behavior, as well as good initial guesses for detailed numerical models; and the asymptotic reduction enable us to parabolize the governing equations, which is originally elliptic. All these assist in obtaining a reduced set of equations, which is referred to as a reduced model in this thesis.

Based on the above methodology, the result is twofold: first, we reduced the geometry of a three-dimensional (3D) model which is normally equipped by a traditional parallel channels to a two-dimensional (2D) model with porous flow field; The essential transport phenomena, such as that under the rib of the parallel channel – which can only be described by a 3D model – is captured by the comparatively lower cost 2D model; the solutions from the 2D model were verified against the 3D counterpart to ensure the accuracy of the former. Second, we developed the reduced models (both single- and multi-phase) for single cell in which the computational cost in terms of (i) time to reach convergence, (ii) degrees of freedom, as well as (iii) RAM usage decreased by 2-3 order of magnitude comparing to the 2D model; the results are verified numerically and validated experimentally, for which good agreements are obtained; these low-cost models build the foundation for extension to PEMFC stack modeling.

Finally, with the reduced single-cell model (single phase) as the base model, we are able to develop an automated model generator to handle a PEMFC stack comprising up to 400 cells, which requires reasonable amount of time (less than 15 minutes) and memory (around 2.3GB) to solve. This approach opens up the possibility for wide-ranging parameter studies and optimization of stacks at low computational cost, without having to manually redraw the computational domain and implement the equations at each iteration.
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<td>(a)</td>
<td>water activity</td>
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<td>(a^{(l)})</td>
<td>surface area of the agglomerate including water per unit volume, (m^{-1})</td>
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<tr>
<td>(a^{(p)})</td>
<td>surface area of the agglomerates per unit volume of catalyst layer, (m^{-1})</td>
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<td>(\epsilon_1, \epsilon_2, \epsilon_3, \epsilon_4)</td>
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<td>(c_T)</td>
<td>form-drag constant</td>
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<td>(c_i^{(g)})</td>
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<td>(D_i^{(c)})</td>
<td>capillary diffusion, (m^2 s^{-1})</td>
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List of Symbols

\( k_c \) dimensionless rate constant

\( k_{\text{cond}}, k_{\text{vap}} \) condensation and evaporation rate constants, kg \( \text{m}^{-3} \text{s}^{-1} \)

\( f_1 \) constant, V T\(^{-1} \)

\( L \) length of the channel, m

\( L^{(C)}, L^{(P)}, L^{(Pt)} \) carbon, polymer, and platinum loading, kg \( \text{m}^{-2} \)

\( m \) mobility of the liquid phase

\( \dot{m}_{\text{H}_2\text{O}} \) interphase mass transfer of water, kg \( \text{m}^{-3} \text{s}^{-1} \)

\( M^{(g)} \) mean molecular mass of the gas phase, kg \( \text{mol}^{-1} \)

\( M_i \) molecular mass of species \( i \), kg \( \text{mol}^{-1} \)

\( M^{(m)} \) equivalent weight of the dry membrane, kg \( \text{mol}^{-1} \)

\( n^{(\text{agg})} \) number of agglomerates per unit volume, m\(^{-3} \)

\( n_d \) electroosmotic drag coefficient

\( n_i \) mass flux of species \( i \), mol \( \text{m}^{-2} \text{s}^{-1} \)

\( N_i \) molar flux of species \( i \), mol \( \text{m}^{-2} \text{s}^{-1} \)

\( p^{(c)} \) capillary pressure, Pa

\( p^{(g)} \) pressure, Pa

\( p^{\text{sat}}_{\text{H}_2\text{O}} \) saturation pressure of water, Pa

\( R \) gas constant, J \( \text{mol}^{-1} \text{K}^{-1} \)

\( r^{(\text{agg})} \) radius of agglomerate, m

\( s \) saturation

\( S, \mathcal{S} \) source term

\( \mathcal{S} \) switch for interphase mass transfer

\( \Xi_0, \Xi_1, \Xi_2 \) constants, K

\( T \) temperature, K

\( v, u, v, U \) velocities, m \( \text{s}^{-1} \)

\( V \) volume, \( \text{m}^3 \)

\( x^{(g)}_i \) molar fraction of species \( i \)

\( x, y, z \) coordinate, m

\( w \) the width, m

Greek

\( \alpha \) transfer coefficient

\( \beta^{(m)} \) modification factor

\( \gamma \) volume fraction

\( \delta \) thickness of the film, m

\( \varepsilon \) porosity

\( \eta \) overpotential, V

\( \theta \) wetting angle

\( \kappa \) permeability, m\(^2 \)

\( \lambda \) water content

\( \mu \) dynamic viscosity, kg \( \text{m}^{-1} \text{s}^{-1} \)

\( \xi_1, \xi_2, \xi_3 \) correction factors for agglomerate model

\( \xi \) stoichiometry

\( \rho \) density, kg \( \text{m}^{-3} \)
List of Symbols

$\sigma$ surface tension, N m$^{-1}$
$\sigma^{(m)}$ protonic conductivity, S m$^{-1}$
$\sigma^{(s)}$ electric conductivity, S m$^{-1}$
$\phi$ potential, V
$\Phi$ Thiele modulus
$\Phi_{\alpha\beta}$ dimensionless quantities
$\psi$ stream function
$\omega^{(p)}$ mass fraction of polymer loading
$\omega^{(Pt)}$ mass fraction of platinum loading on carbon

Superscripts

(agg) agglomerate
(c) capillary
(C) carbon
cool cooling
(g) gas phase
in inlet
(l) liquid phase
(m) membrane
(p) polymer
(Pt) platinum
(PtC) platinum and carbon
ref reference
(s) solid phase
sat saturation

Subscripts

0 standard conditions
$\alpha, \beta$ index for the species: H$_2$, H$_2$O, N$_2$, O$_2$
(a, c) anode, cathode
(avg) average
(cc) current collector
cl catalyst layer
eff effective
(ff) flow channel
gdl gas diffusion layer
H$_2$ hydrogen
H$_2$O water
(i) species i
(j) functional layer j
mass mass
mix mixture
mom momentum
N$_2$ nitrogen
O$_2$ oxygen
pot potential
rel relative
temp temperature
tot total
void void

**Miscellaneous symbols**

[ ] scale
Chapter 1

Introduction

The fuel cell is an electrochemical system that converts the chemical energy stored in a fuel — normally containing hydrogen, e.g. H\textsubscript{2}, CH\textsubscript{4}, etc. — into electrical energy. The way a fuel cell operate is similar to that of a battery; however, while the latter contains a certain among of reactants which can be consumed in a limited period of time, the former can produce electricity continuously as long as a fuel is supplied. A typical cell consists of three principal parts - an anode (negative electrode), an electrolyte and a cathode (positive electrode). In addition, there is a catalyst layer, placed between the electrode and the electrolyte, where the electrochemical reaction are taken part in. A schematic of a fuel cell is illustrated in Figure 1.1. On the anode side, fuel is fed and consumed at the anode catalyst layer to generate the electrons (\(\bar{e}\)). The electrons travel through the external circuit to the cathode catalyst layer and react with the oxidant, e.g. pure oxygen or air, which is supplied from the cathode side. In this way, electricity is generated and the common by-products are heat and water.
1. Introduction

Figure 1.1: A schematic of a fuel cell

1.1 Advantages and Disadvantages of Fuel Cells

One of the key advantages of fuel cells is that this technology converts chemical energy directly to electricity, providing highly efficient energy generation as compared to the combustion engine which is normally limited by Carnot efficiency. Furthermore, since no moving part in the fuel cell, it operates quietly. The drawback of fuel cell is its producing cost—quite high as compared to battery or combustion engine. Furthermore, power density is also one of the main problems that this new technology is being faced now.

1.2 Types of Fuel Cells

There are six types of fuel cells that are currently in commercial use, differentiated according to the type of electrolyte:

1. Proton Exchange Membrane Fuel Cell (PEMFC),

2. Direct Methanol Fuel Cell (DMFC),

3. Alkaline Fuel Cell (AFC),
4. Phosphoric Acid Fuel Cell (PAFC),

5. Molten Carbonate Fuel Cell (MCFC),


The characteristics of fuel cell electrolyte indicate the operating condition, charge carrier, efficiency and its primary applications. All of these are summarized in Table 1.1; furthermore, the electrode reactions are also presented in Table 1.2.

The PEMFC uses a polymer membrane as electrolyte with platinum catalyst, operating at low temperature (e.g. 60 - 80°C) makes it become a prime candidate for automotive, portable, as well as stationary applications. Furthermore, it presents most of advantages of a fuel cell such as high efficiency, quiet, and no emission; hence, no environmental issue is faced with this type of fuel cell.

Similar to the PEMFC, DMFC also uses a polymer membrane as electrolyte with platinum catalyst. The fuel is methanol instead of hydrogen. However, its efficient is not as high as the PEMFC. One of the reasons is that the kinetic of electrochemical reaction of methanol are complicated which requires several steps, and some of which are slow. Another reason is the fuel crossover; this is also the main issue of DMFC which many researchers are trying to come over. Low operating temperature is a key advantage of the DMFC; is is useful for applications which require fast start-ups and frequent shutdowns. DMFC is also used in small applications like mobile phones and laptops where efficiency isn’t a critical issue. Like the PEMFC, the high cost of manufacturing is one of the major disadvantages of the DMFC. Other disadvantages include the requirement for good water management within the cell, low working temperatures which would require large radiators and a low tolerance for CO (generated via the water-gas shift).

The AFC operates at a low temperature of 80°C. It can use any alkaline as electrolyte but potassium hydroxide (KOH) is normally used as it is the most conducting. This type
<table>
<thead>
<tr>
<th>Type</th>
<th>Operating Temperature (°C)</th>
<th>Electrolyte</th>
<th>Catalyst</th>
<th>Components</th>
<th>Cell Components</th>
<th>Cell Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEMFC</td>
<td>70-80</td>
<td>Polymer membrane</td>
<td>Pt</td>
<td>H₂, CO</td>
<td>50-60</td>
<td>Automotive and stationary power</td>
</tr>
<tr>
<td>DMFC</td>
<td>70-80</td>
<td>Polymer membrane</td>
<td>Pt</td>
<td>H₂</td>
<td>50-60</td>
<td>Portable devices</td>
</tr>
<tr>
<td>AFC</td>
<td>60-65</td>
<td>Alkaline KOH</td>
<td>Ni</td>
<td>H₂</td>
<td>50-65</td>
<td>Space vehicles</td>
</tr>
<tr>
<td>PAFC</td>
<td>60-90</td>
<td>Phosphoric acid</td>
<td>Ni</td>
<td>H₂</td>
<td>30-50% KOH</td>
<td>Medium to large scale CHP systems</td>
</tr>
<tr>
<td>SOFC</td>
<td>800-1000</td>
<td>Yttrium-stabilized Zircon dioxide melts (ZrO₂/Y₂O₃)</td>
<td>Pt</td>
<td>H₂</td>
<td>55-65</td>
<td>Medium to large scale CHP systems</td>
</tr>
<tr>
<td>MCFC</td>
<td>450-750</td>
<td>Molten carbonate melts (Li₂CO₃/Na₂CO₃)</td>
<td>Ni</td>
<td>Ni</td>
<td>60-65</td>
<td>Medium to large scale CHP systems</td>
</tr>
<tr>
<td>SOFC</td>
<td>800-1000</td>
<td>Yttrium-stabilized Zircon dioxide melts (ZrO₂/Y₂O₃)</td>
<td>Pt</td>
<td>H₂</td>
<td>55-65</td>
<td>Medium to large scale CHP systems</td>
</tr>
</tbody>
</table>

Table 1.1: Description of fuel cell types. [1, 2]
of fuel cell can reach efficiencies of 80% when used as a water heating device. The AFC also uses a variety of non-precious metal catalysts. However, the AFC must be fuelled by pure hydrogen as it is extremely susceptible to carbon dioxide poisoning. Large amounts of catalyst must be used as well because of its low operating temperature. It was used by NASA to provide electricity and water to astronauts for space missions.

The PAFC operates at a temperature of 160-220°C and is the oldest type of fuel cell. It uses liquid phosphoric acid as an electrolyte and can tolerate low amounts of contaminants (1-2% CO and 5ppm of sulfur) in the fuel stream. This tolerance would reduce the requirement for pure hydrogen from the steam reformer feeding the cell. It can be fuelled by waste methane, propane and natural gas. The liquid electrolyte has to be contained between porous graphite carbon coated with Teflon to keep liquid in, but allow gases to reach the reaction sites. The efficiency can be improved if the amount of heat generated can be harnessed for use in the steam reformer. PAFCs are good for stationary power generation.

The MCFC operates at a temperature of 600°C and above and uses a molten carbonate salt mixture suspended in a porous ceramic matrix of beta-alumina solid electrolyte. It is fuelled by hydrogen but the high temperature allows it to take natural gas directly without the prior need for reforming. The cell is tolerant towards carbon impurities

---

<table>
<thead>
<tr>
<th>Type</th>
<th>Anode reaction</th>
<th>Charge carriers</th>
<th>Cathode reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEMFC</td>
<td>$\text{H}_2 \rightarrow 2\text{H}^++2e^-$</td>
<td>$\text{H}^+$</td>
<td>$1/2\text{O}_2+2\text{H}^++2e^- \rightarrow \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>DMFC</td>
<td>$\text{CH}_3\text{OH}+\text{H}_2\text{O} \rightarrow 6\text{H}^++\text{CO}_2+6e^-$</td>
<td>$\text{H}^+$</td>
<td>$6\text{H}^++6e^-+3/2\text{O}_2 \rightarrow 3\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>AFC</td>
<td>$\text{H}_2+2\text{OH}^- \rightarrow 2\text{H}_2\text{O}+2e^-$</td>
<td>$\text{OH}^-$</td>
<td>$1/2\text{O}_2+\text{H}_2\text{O}+2e^- \rightarrow 2\text{OH}^-$</td>
</tr>
<tr>
<td>PAFC</td>
<td>$\text{H}_2 \rightarrow 2\text{H}^++2e^-$</td>
<td>$\text{H}^+$</td>
<td>$1/2\text{O}_2+2\text{H}^++2e^- \rightarrow \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>MCFC</td>
<td>$\text{H}_2+\text{CO}_3^{2-} \rightarrow \text{H}_2\text{O}+\text{CO}_2+2e^-$</td>
<td>$\text{CO}_3^{2-}$</td>
<td>$1/2\text{O}_2+\text{CO}_2+2e^- \rightarrow \text{CO}_3^{2-}$</td>
</tr>
<tr>
<td>SOFC</td>
<td>$\text{H}_2+\text{O}^- \rightarrow \text{H}_2\text{O}+2e^-$</td>
<td>$\text{O}^-$</td>
<td>$1/2\text{O}_2+2e^- \rightarrow \text{O}^-$</td>
</tr>
</tbody>
</table>

Table 1.2: Electrode reactions for the different types of fuel cells [1]
but is easily poisoned by sulfur. Due to the high operating temperature, there is good oxygen kinetics which enhances the performance of the cell and the heat produced can be easily utilized for heating. However, the high operating temperature makes start-up slow and unresponsive.

The SOFC operates at 800-1000°C. Although this is the highest operating temperature among fuel cells, it is not the most reactive type. This is mainly due to the low conductivity of its electrolyte, which is made of a ceramic called yttrium-stabilized zirconium. Advances in research has increased the SOFC’s chemical to electrical efficiency to 50% and because of its high operating temperature, it requires no expensive catalysts, humidification or fuel treatment, significantly reducing the cost of SOFCs. It can use light hydrocarbons as fuel. However, the main drawback to this type of fuel cell is that it must be contained in casings made from expensive ceramics which must have similar expansion rates. The high operating temperature also limits its usefulness to large power plants and industrial applications.

1.3 Fuel cell commercialization

There are several factors that restrict widespread commercialization of fuel cells in the world today. One of the major challenges in developing of the fuel cell technology is the high costs which involves the manufacturing the system, operating the system, as well as the materials in building a fuel cell. Since a PEMFC normally operate at low temperatures, a catalyst is required to speed up the electrochemical reaction to generate high power density. This catalyst is normally platinum, which averages around $1,600 USD/ounce. This leads to the cost of powering a system with a fuel cell typically around $5000 per kilowatt, whereas the market price of producing electricity is around $1000 - $1500 per kilowatt. Fortunately, effort is being made in this area. In May 2010, Toyota’s managing director for advanced autos, Yoshihiko Masuda, announced that the
company would be ready to sell retail models of its hydrogen cars at a price of $50,000 in 2015[4] by cutting production costs by 90% of its early estimated $1 million a car. According to Masuda, the company will lower cost by reducing platinum use by a third and developing cheaper methods to manufacture the thin film and hydrogen fuel tanks.

Since the PEMFC uses air or pure oxygen as fuel, we need to build a system of hydrogen refuelling stations around the world. The production, transportation and storage of hydrogen are also key challenges. Hydrogen is the lightest element, containing the highest energy per unit weight, but lowest volumetric power density as compared to combustion engine and battery [2]. Many energy companies currently do not possess the necessary equipment and infrastructure to deal with hydrogen on a large scale. In Europe, the Scandinavian Hydrogen Highway Partnership (SHHP) has been formed by three hydrogen companies in Norway, Denmark and Sweden to tackle this problem[5]. It hopes to bring hydrogen and hydrogen vehicles closer to commercialization. For this purpose, they has built a network of 45 hydrogen stations and to operate a fleet of at least 100 buses, 500 cars and 500 specialty vehicles by 2015. By doing so, consumers within this region would not be restricted by the lack of refuelling stations and would thus be encouraged to switch to hydrogen vehicles.

The fuel cell has proven itself to be an efficient and viable source of clean energy which can potentially replace fossil fuels. However, the leap from stationary power generation to mobile applications is hindered by obstacles which many countries in the world are unprepared to handle. In short, fuel cell technology is still not sufficiently developed to compare with batteries and combustion engines. This new technology is currently at the state of pre-commercialization and many more innovations are required for it to gain acceptance; both experiments as well as mathematical modeling are required. Most researches were carried out experimentally to develop new material, e.g. gas diffusion layer, catalyst layer and membrane, for improvement of fuel cell performance and
reducing material cost; whereas mathematical modeling helps to optimize design and operating condition. Mathematical modeling of the fuel cell aids in our understanding of the series of intrinsically coupled physicochemical processes, which include mass and species transfer, momentum transfer, heat transfer, charge transfer and multiple electrochemical reactions. These processes are taking place simultaneously during fuel cell operation and are difficult to quantify experimentally. A good understanding of the transport phenomena is necessary and mathematical modeling can aid in elucidating and understanding the complex physical phenomena as well as limitations in the fuel cell. Mathematical modeling can further save time and money as numerical experiments can be carried out at a significantly lower cost as compared to practical experiments.

The research work described in this thesis is focused on the PEMFC; hence, a brief description of the PEMFC will be given in the next section.

1.4 Objectives

Mathematical modeling that seeks to resolve the essential phenomena that occur within a PEMFC stack at the local level is highly challenging, as it needs to consider coupled transport phenomena – mass, momentum, species, energy, and charge transfer in several or all of the length scales, varying from \( O(1 \text{ nm}) \) to \( O(1 \text{ m}) \) in a typical PEMFC stack. Currently, the development of mathematical models and simulation tools is at the stage where one can model single fuel cells \([6, 8]\) or just simple stacks of fuel cells, i.e. less than 6-cell stacks \([9, 11]\). Some reduced PEMFC stack models have been developed \([12, 22]\) which can, in principle, model a stack of any size, but oversimplify the inherent physics and geometry. The main objective of this project is therefore to derive reduced mathematical models for single cells at a reasonable cost, while preserving the essential physics. These will then be extended to encompass stacks comprising of tens or even hundreds of cells. For this purpose, the main tools are volume averaging, scale-analysis,
and asymptotic reduction. As shown in Fig. 1.2, the following steps will be carried out:

1. Implement a 3D single-phase mathematical model for later verification of the reduced models. This model will also provide a benchmark for comparison of the efficiency of the reduced models;

2. Apply the volume averaging method together with the porous medium approach to reduce the 3D model in step (1) to a 2D counterpart with a porous flow field that still retains the essential features of the three-dimensional flow field;

3. Apply a scaling analysis to achieve fast prediction of the cell performance without solving the full set of PDEs;

4. With the aid of step (3), the 2D model in step (2) will be parabolized to a ‘space-marching model’, or named as a reduced model in this thesis;

5. Extend the reduced single cell models to PEMFC stacks comprising hundreds of cells;

6. Extend the work to include multi-phase transport.

Note that, most of the steps (3) and (4) will be first carried out for the half-cell and then extended to the full cell. The reduced model can be then used for many application studies such as:

- Optimizing operating conditions and design parameters.
- Thermal and water management (PEMFC).
- Integrating a cell or a stack with other systems such as pump, compressor.
- Design control systems.
- Minimize the stack size whereas maximize the power output.
- Reduce time-to-market.
1.5 Structure of the thesis

The thesis consists of eleven chapters. A brief introduction to the fuel cells in general and the proton exchange membrane fuel cell as a particular case studied in this thesis are given in Chapters 1 and 2; followed by a literature review in Chapter 3. In Chapter 4, we aim to summarize all relevant equations, e.g. the governing equations of single- and multi-phase models, constitutive relations and agglomerate model; all base-case parameters which will be employed in subsequent chapters are also tabulated in this
chapter. The main work of this thesis is presented in subsequent chapters. Each chapter
starts with its own introduction summarizing the research background, the literature,
and the gap; then, a mathematical formulation for the specific case study is provided
with a section on numerics, results and discussion generally involving the calibration,
validation, verification, and computational cost; and the final section is the conclusion.

In summary, in Chapter 5, a novel way to reduce the dimensionality, i.e. from a
three-dimensional model equipped a traditional parallel channels to two-dimensional
model with porous flow field, of a PEMFC model is presented. Chapter 6 and 7 include
the half-cell models to show how we deal with the scale analysis and develop the fast
and efficient mathematical models for the cathode of a PEMFC. This is as a first step
toward the single-cell model reduction shown in Chapter 8. As a result, a fast and
memory-efficient reduced model for a single PEMFC is derived to form a numerical
building block for stack modelling presented in Chapter 9; the procedure of simulating
the stack model is automated to avoid the time-consuming task of manually creating
the stack, as well as to remove the possibility of human error during the setup phase.

In Chapter 10, we present a reduced multiphase, multicomponent, and non-isothermal
model of a PEMFC as well as thermally-decoupled reduced and full models. The model
can then be employed for wide-ranging parameter and design studies, for multi-objective
optimization, and as a building block for stack models. Finally, Chapter 11 contains an
overall summary of results and recommendations for future work.
Chapter 2

Proton Exchange Membrane Fuel Cell

A single-cell of the PEMFC consists of two flow channels adjacent to the gas diffusion layer, with the two catalyst layers and the membrane in the middle of the cell as illustrated in Figure 2.1 and 2.2. Each component holds a significant role in the performance of the fuel cell. For example, the flow channels are used for distribution of the reactants to the respective part of the cell, transfer of current, as well as to facilitate the removal of excess heat and water. Good design of the flow field not only improves the performance of the cell but also reduces the size and weight of the cell; the latter is important for stacks, which can comprise up to tens or even hundreds of cells. The gas diffusion layers allow access for reactant gases from the flow channel to the catalyst layers, and also provide a medium for the liquid water to be removed from the catalyst layers to the flow channel. Additionally, the gas diffusion layers also provide electron transport and heat conduction. The catalyst layers are the place where electrochemical reactions occur. The catalyst layers together with the membrane are also known as the 'heart of the fuel cell', and play a significant role in completing the electrochemical reactions. The membrane allows for transport of the protons that are produced by the reaction in the catalyst layer at the anode to the cathode catalyst layer, and at the same time separates the reactants at both half-cells from direct reaction. Finally, a bipolar plate,
which sometimes includes cooling channels, is added to both sides. In a PEMFC stack, the bipolar plate acts as a separator between the single cells. Further, for a stack, one usually also adds an endplate and current collector to each side (not shown in Figure 2.1).

![A schematic of a PEMFC single cell and a stack](image)

Figure 2.1: A schematic of a PEMFC single cell and a stack

The dominating electrochemical reactions in the fuel cell are straightforward and are illustrated in Figure 2. On the anode side, hydrogen is fed and consumed at the anode catalyst layer to produce protons ($H^+$) and electrons ($\bar{e}$)

$$2H_2 \rightarrow 4H^+ + 4\bar{e}. \quad (2.1)$$
Figure 2.2: Fuel cell mechanism

The produced protons transport through the membrane and the electrons travel through the external circuit where both concurrently meet at the cathode catalyst layer to react with the oxygen and results in the production of water

\[ O_2 + 4H^+ + 4\bar{e} \rightarrow 2H_2O. \] (2.2)

We will in the remainder of this section give a short outline of the main transport phenomena occurring in the flow field, as diffusion layer, catalyst layer, and the membrane, and finish with a definition of cell performance.

2.1 Flow field

The transport of reactant gases within the flow channel depends strongly on the geometrical configuration of the gas flow field. The main function of the flow channel is to provide as uniform a distribution of the reactants gases as possible over the surface of the cell. At present, there are no final optimized designs and a variety of different flow field designs are in use. As shown in Figure 2.3, some of the basic designs of the flow channel are the parallel straight, serpentine, multiple serpentine flow channels (i.e. mix of parallel straight and serpentine) and porous flow field.
As reviewed by Li and Sabir [23], the parallel straight flow channel flow field (Figure 2.3a) is regarded as a simple design compared to the serpentine (Figure 2.3b) and multiple serpentine (Figure 2.3c). Its flow distribution, however, is not uniform since the gas will not flow through the channels with the same speed. Above and beyond that, the non-uniform distribution can become severe, especially when water droplets are formed and result in local flooding. On the other hand, serpentine flow channels provide a more uniform flow distribution and hence, minimize the possibility of local flooding. However, to achieve a sufficiently high flow rate, a higher pressure drop is required to drive the flow for the serpentine design due to its winding length. The combination of the parallel straight and serpentine flow channels, i.e. the multiple serpentine flow channels, gives better performance since it does not require too large a pressure drop. Beside this, the
multiple serpentine design provides a more homogeneous flow distribution due to its capability to avoid stagnant area formation caused by water accumulation. In addition to these three designs, more complicated configurations such as the integrated flow field, interdigitated flow field (consisting of dead-ended flow channels) and flow channel from the metal sheets are also presented in Li’s review [23].

In modeling the above channels, the Navier-Stokes equations as well as conventional heat and mass transfer governing equations can be applied to describe the effects of the transport phenomena within the flow fields on the performance of the fuel cell.

For a more uniform flow of reactant gases, albeit at the cost of a higher pressure drop, a porous flow field can be employed. In modeling the porous flow field, the Brinkman’s or Forchheimer’s equations [24] will be applied instead of the Navier-Stokes equations. In addition, the charge transfer balance should also be considered to account for the charge transfer in the porous flow channel.

2.2 Gas diffusion layer

The gas diffusion layer is primarily a porous medium and flow in the gas diffusion layer may be single-phase or two-phase depending on the operating conditions, e.g. temperature, relative humidity, and contact angles. In modeling the transport phenomena in the gas diffusion layer, Darcy’s law should be applied and correspondingly, the diffusive flux needs to be corrected to account for the effect of porosity of the gas diffusion layer. Based on the Bruggemann correction, the effective diffusivity can be expressed as

$$D_i^{\text{eff}} = \varepsilon^{3/2} D_i,$$  \hspace{1cm} (2.3)

where $\varepsilon$ is porosity and $D_i$ is the diffusion coefficient of species $i$.

The validity of the expression given in equation (2.3) breaks down if one considers
two phase flow. Two phase flow usually occurs in the cathode during low temperature operation coupled with high humidification levels of the inlet flow as well as high current density (i.e. high water production rate at the cathode side). The water vapor thus becomes saturated, resulting in condensation. The amount of liquid present in the gas diffusion layer, i.e. liquid saturation, is defined as

$$s = \frac{\text{volume of liquid in the pore}}{\text{total volume of the pores}}.$$  \hspace{1cm} (2.4)

Consequently, the effective porosity accounting for two-phase flow should be revised as

$$\varepsilon_{\text{eff}} = (1 - s) \varepsilon.$$  \hspace{1cm} (2.5)

One of the main issues arising from two-phase flow in the cathode gas diffusion layer is that if the rate of water removal is lower than the rate of water generation, excess water will accumulate and, consequently, result in flooding. This accumulation of liquid water can block the pores within the gas diffusion layer and thus lead to an increased resistance to mass transport.

The operation of the fuel cell also results in heat generation in the gas diffusion layer due to electron transport, which is commonly known as ohmic heating.

### 2.3 Catalyst layer

The electro-chemical reactions take place in the catalyst layers. We can see from equations (2.1) and (2.2) that for one mole of hydrogen consumed, two moles of electrons will travel through the external circuit to the cathode side and react with half a mole of oxygen to produce one mole of water. Therefore, for every mole of oxygen fed, we need four electrons produced from the anode catalyst layer to complete the reaction. These
reaction rates will be invoked in the source (or sink) terms of the continuity equation as well as the species conservation equations. Note that, in the catalyst layer, the reaction rate should be based on unit volume. Hence, the volumetric current density, $J$ (A/m$^3$), should be used instead of current density. And the volumetric current density relates to the current density via the conservation of charge and is as follows

$$\nabla \cdot \mathbf{i} = J,$$  \hspace{1cm} (2.6)

here, the current density can also be defined as the charge conductivity, $\sigma$, time the gradient of potential, $\phi$

$$\mathbf{i} = -\sigma \nabla \phi.$$  \hspace{1cm} (2.7)

To evaluate the performance of the fuel cell, the Tafel equation, which is an approximation of the Butler-Volmer equation, is established to obtain the relationship of the volumetric current density, species concentration ($c_i$), temperature ($T$), and overpotential ($\eta$)  

$$J_a = -j_{a, a}^{\text{ref}} \left(c_{H_2}^{\text{ref}} \right)^{1/2} \left( \frac{\alpha_n + \alpha_c \cdot F \cdot \eta_a}{RT} \right),$$  \hspace{1cm} (2.8)

$$J_c = -j_{a,c}^{\text{ref}} \exp \left[ - \frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right] \left( \frac{c_{O_2}^{\text{ref}}}{c_{H_2}^{\text{ref}}} \right) \exp \left( - \frac{\alpha_c \cdot F \cdot \eta_c}{RT} \right),$$  \hspace{1cm} (2.9)

where $j_{a,c}^{\text{ref}}$ and $\alpha$ are volumetric exchange current density and transfer coefficient, $E_a$ is the activation energy, $T_{\text{ref}}$ and $c_{i}^{\text{ref}}$ are the reference temperature and reference concentration respectively.

Other than the aforementioned influence the electrochemical reactions have on the mass transfer, these half-cell reactions play a significant role in the heat conservation since heat can be generated by reaction as well as charge transfer [26]. The former depends on the irreversible heat of the electrochemical reaction and reversible entropic
heat, whereas the latter is known as ohmic heating caused by electron and proton transport. It is also worth to note that to properly describe the fuel cell, one must also take into account the porous effect of the diffusivity, the thermal conductivity, as well as electron and proton conductivities of the catalyst layer.

2.4 Membrane

The function of the membrane is to efficiently separate the anode and cathode electrodes and to facilitate the conduction of protons. Thus, the membrane serves as the electrolyte and completes the electrical circuit in the fuel cell. Transport in the membrane is governed by species transfer of water as well as protons and the mechanisms of water transport in the membrane are known as electro-osmotic drag and back diffusion.

Electro-osmotic drag refers to the water transport from the anodic side to the cathodic side due to water ‘dragging’ the hydrated protons that are transferred from the anode catalyst layer. To account for this effect in modeling, Springer et al. [27] had introduced the drag coefficient, \( n_d \), describing the flux of water transport due to electro-osmotic drag and is defined as

\[
N_{\text{H}_2\text{O,drag}} = n_d \frac{i}{F}.
\]  

(2.10)

The expression of \( n_d \) is given in equation (2.11) and is correlated based on Springer et al.’s evaluation on their experiment data

\[
n_d = \frac{2.5\lambda}{22},
\]

(2.11)

where \( \lambda \) is the water content, which is defined as the ratio of the number of water molecules to the number of sulfonic sites in Nafion membrane and can be computed as
a function of water activity \( a \), that is

\[
\lambda = \begin{cases} 
0.043 + 17.81a - 39.85a^2 + 36.0a^3, & a \leq 1 \\
14 + 1.4(a - 1), & 1 < a \leq 3
\end{cases}.
\] (2.12)

Water back diffusion occurs when the water produced at the cathode permeates to the anodic side due to a concentration driving force. Based on Fick’s law, the flux of water due to back diffusion can be expressed in terms of the water content and is as follows

\[
N_{H_2O,\text{diff}} = -\frac{\rho_{\text{dry}}}{M_m} D_{H_2O,m} \nabla \lambda,
\] (2.13)

where \( \rho_{\text{dry}} \) and \( M_m \) are the density and equivalent weight of the dry membrane respectively. \( D_{H_2O,m} \) refers to the diffusion coefficient of water in the membrane and are defined by many correlated expressions in the open literature \[27\ 31\]. Nonetheless, Motupally’s correlation gives good agreement with experiments and is used by many authors for its simplicity and this expression is given by

\[
D_{H_2O,m} (m^2/s) = \begin{cases} 
3.1 \times 10^{-7} \lambda \left[ e^{0.28 \lambda} - 1 \right] e^{-\frac{2436}{T}} & \text{for } \lambda \leq 3 \\
4.17 \times 10^{-8} \lambda \left[ 1 + 161e^{-\lambda} \right] e^{-\frac{2436}{T}} & \text{for } 3 < \lambda
\end{cases}.
\] (2.14)

One of the important aspects that the membrane of the fuel cell must provide is to efficiently conducts protons. For this reason, in modeling the fuel cell, one must consider the phenomena of proton transport through the membrane. Accordingly, Springer et al. \[27\] developed an useful correlation that relates proton conductivity as a function of water content.

\[
\sigma_m \left( \text{S/m} \right) = (0.5193\lambda - 0.326) \exp \left( 1268 \left( \frac{1}{303.15} - \frac{1}{T} \right) \right),
\] (2.15)
2.5 Cell performance

Fuel cell performance is generally evaluated by plotting the polarization curve i.e. plot of cell voltage versus the current density and a typical expression of the cell voltage is defined as

\[ E_{\text{cell}} = E_{\text{rev}} - |\eta_a| - |\eta_c| - \sum (iR_m) - \sum (iR_s), \]  

(2.16)

where \( E_{\text{rev}} \) is the reversible cell potential and can be obtained from the following expression

\[ E_{\text{rev}} = E_{\text{rev}}^0 - 0.9 \times 10^{-3} (T - 298.15), \]  

(2.17)

with \( E_{\text{rev}}^0 \) denoting the reversible potential at standard conditions.

Note that the overpotential at the anode side is positive whereas the overpotential at the cathode side is negative. And, the last two terms in the equation (2.16) represent the ohmic losses in the membrane as well as other solid parts of the fuel cell.
Chapter 3

Literature review

The transport phenomena in a PEMFC are challenging to model owing to the coupled hydrodynamics, mass, species, heat, charge transport as well as phase transfer. In addition, these processes take place throughout the various layers of the fuel cell, i.e. membrane, catalyst layer, gas diffusion layer, flow field, and current collector. Typical fuel cell models are generally on a micro-scale and/or macro-scale level or on the system level, depending on the nature and objectives of the modeling. Here, micro-scale modeling refers to the study of transport phenomena at the smallest scales, e.g. in the pores of the gas diffusion layer or membrane. One of the purposes of micro-scale modeling is to understand the membrane structure and physical properties, e.g. how the pore size and porosity influence the transport coefficients such as membrane conductivity, permeability, water absorption and ion exchange capacity [32]. Besides this, micro-scale modeling also allows one to understand how the protons are transferred in an individual pore [33]. These micro-scale models are useful and suitable for predicting the performance of the membrane, particularly if one is interested in designing new membranes.

Macro-scale modeling, on the other hand, considers the various layers, e.g. gas diffusion layer, catalyst layer, or membrane as a homogeneous medium characterized by its porosity, permeability and conductivity, and as such does not resolve the small scales
explicitly. Macro-scale modeling allows one to investigate the transport phenomena within a single cell or a stack and to carry out studies on for example design, impact of material properties, thermal and water management, and various optimizations.

System-level modeling refers to models that aim to capture the overall behavior of a fuel cell system, which includes not only the fuel cell itself but all the auxiliary equipment like pumps, fans, compressors, controllers etc.

The main focus of this thesis is mathematical modeling of the PEMFC on the macro-scale, focus of this review will be mainly based on previously published macro-scale models for a single fuel cell and stacks. Although, there are numerous models published on PEMFC, the fundamental approach has remained the same over the years and can be traced back to several pioneering papers.

As mentioned, numerous mathematical models on the PEMFC are presented in the literature, and we choose to classify them according to their dimensionality, that is one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) models. Fig. 3.1 illustrates a typical fuel cell configuration, showing the streamwise direction (x), normal direction (y), and spanwise direction (z). We will in the following refer to the coordinates of this figure to discuss various mathematical models that have been developed through the years.

### 3.1 One-dimensional models

The 1D model takes into consideration the cross section of the fuel cell, i.e. the y-direction as shown in Fig. 3.1 Some of the early and classical 1D models are the work of Springer et al. [27], Bernardi and Verbrugge [34, 35], Gurau et al. [36] and Rowe and Li [37]. They described various regions within the fuel cells emphasizing on different aspects affecting the performance of the cell.

Springer et al. [27] developed a 1D, isothermal, steady-state model in which the water
3.1. One-dimensional models

Figure 3.1: Schematic of a fuel cell equipped with flow channels and its coordinate system.

transport in the membrane is simulated based on their experiments and observations. The authors highlight the important role of water content in the membrane. The flux of water, the electro-osmotic drag coefficient, diffusion coefficient, and proton conductivity were correlated based on the water content. The model shows that the electro-osmotic drag coefficient representing the net steady state water flux per proton is $0.2 \text{H}_2\text{O}/\text{H}^+$ at $80^\circ\text{C}$ under most operating condition. This value is smaller than the one obtained for fully hydrated membrane, i.e. $2.5 \text{H}_2\text{O}/\text{H}^+$. Owing to its simplicity and accurate prediction under certain conditions, this model had been widely referenced by many authors in multi-dimensional modeling.

Bernardi and Verbrugge have developed a 1D model under steady-state condition with the assumption of constant temperature and fully hydrated membrane. The domain includes the membrane, cathode catalyst layer and gas diffusion layer [34], and was later extended to include the anode catalyst layer [35]. In contrast to Springer’s model, Bernardi build the model based on Schlögl’s equation which describe the velocity of liquid water in the pore of the membrane as a function of the hydraulic pressure and the potential gradients. The model is used to study the transport limitation of reactants in the catalyst layer, the water management within the fuel cell as well as the effect of
membrane thickness on the cell potential. These models agreed well with experiments for current densities up to 1 A/cm$^2$.

Gurau’s 1D model [36] is the same as Bernardi’s first model [34], but they included the cathode flow channel. In their model, the authors assumed the oxygen reduction reaction (cathode) as an irreversible, first order reaction. With this, a simple form of Thiele modulus can be applied and then the equations can be solved analytically.

Rowe and Li [37] presented a complete 1D model consisting of all layers from the anode channel to the cathode channel. The thermal management is considered and discussed in this model by solving the energy conservation equation in which the phase transfer of vapor water to liquid water is included. The results of the model show that under most operating conditions, the temperature reach a maximum at the catalyst layer due to the exothermic reaction. The temperature gradient within the cell is found to be small (around 1 K).

Even though the aforementioned 1D models present most or all of the physics and chemistry in the normal direction, the changes of various properties along the flow channel cannot be captured. Nevertheless, these 1D models provide a good foundation for the subsequent development of multi-dimensional models.

### 3.2 Two-dimensional models

2D models are more comprehensive compared to 1D models as they are able to grasp the effects of reactants consumption and product generation along the channel direction. 2D models can be divided into two categories, namely, ‘across-the-channel’, i.e. in the $yz$-plane, and ‘along-the-channel’, i.e. in the $xy$-plane (see Fig. 3.2).

In the 2D ‘across-the-channel’ models, the changes of the dependent variables along the channel (i.e. pressure, velocity, concentration, and temperature gradients) are assumed to be small and negligible. As such, these models are strictly only applicable for
fuel cells operating at high stoichiometry, i.e. the reactants fed at the inlet are much higher than that consumed at the catalyst layers, or other conditions when changes in the streamwise direction can be neglected. To capture these changes, the 2D ‘along-the-channel’ models had been developed. The subsequent sections will discuss the ‘across-the-channel’ models, followed by ‘along-the-channel’ models.

Figure 3.2: Schematic of 2D (a) ‘across the channel’ and (b) ‘along-the-channel’ models
3.2.1 ‘Across-the-channel’ models

The 2D ‘across-the-channel’ models, presented by Natarajan and Nguyen [38], Lin and Nguyen [39], Birgersson et al. [40], Hwang et al. [41], Acosta et al. [42], etc., consider the membrane-electrode-assembly (MEA) and gas diffusion layer but not the flow channels. The work of Natarajan and Nguyen [38] is one of the earliest 2D models developed solely for the cathode gas diffusion layer of a PEMFC. In their model, the species conservation equation which includes phase transfer was solved under transient condition. The results obtained allow the authors to study the effect of various operating conditions (temperature, relative humidity) as well as design parameters (gas diffusion layer thickness and porosity, channel and shoulder size, and channel to shoulder ratio) on the performance of the fuel cell. Subsequently, Lin and Nguyen [39] extended Natarajan’s model to the cathode catalyst layer and membrane under isothermal, isobaric and steady-state conditions. A more recent model is the work of Birgersson et al. [40] where the authors develop a two-phase, non-isothermal model for both the anode and cathode gas diffusion layers as well as the membrane under steady state condition. The catalyst layers are considered to be very thin and reduced to boundary conditions. Heat and charge transfers are solved for the whole fuel cell domain, but conservation of mass and momentum of the liquid and gas phases are solved only in the cathode gas diffusion layer. Scale analysis had been applied so that the transport mechanisms within the cell can be discussed in terms of dimensionless numbers and their magnitudes.

Wu et al. [43] implemented a transient model accounting for the whole domain of a fuel cell including the flow channels in which species, energy, electrons and protons conservation equations are solved along with appropriate boundary conditions. However, Wu et al. only considered single phase transport for which water is assumed to be super-saturated since its relative humidity exceeds 100%. In this model, the authors optimized
the membrane thickness requirements by investigating different types of membranes, i.e. Nafion 112, Nafion 115, Nafion 117. This model took one hour to converge on a 64-bit Linux system with dual core processor at 2.8 GHz and 4 GB memory and is solved by COMSOL Multiphysics software.

### 3.2.2 ‘Along-the-channel’ models

As mentioned previously, in contrast to the ‘across-the-channel’ models, the variations of dependent properties along the channel are taken into account in this type of models. There are a number of publications on ‘along-the-channel’ models and a selected few will be presented in the following section.

One of the earliest ‘along-the-channel’ models is the work of Fuller and Newman \[31\] who examined the water and thermal management in the PEMFC. They assumed that the transport occurs only in the $y$-direction due to the fact that the ratio of the channel length to the width of the cell, i.e. $x/y$, is large. Consequently, the transport equations are solved only in the $y$-direction at a given value of $x$ and integrated down the membrane electrode assembly in the $x$-direction. In so doing, they also assumed that the gas outside the diffusion layers is of uniform composition in the $y$-direction i.e. the direction across the cell. The thermal equations are solved by applying the first law of thermodynamics and assumed that the temperature is only a function of the $y$-direction. However, they did not solve for water condensation. Their results show that thermal and water managements are intrinsically coupled and thermal considerations must be included in the analysis of water management. They had also presented that the rate of heat removal is critical in achieving optimum operation of the fuel cells.

Nguyen and White \[30\] also consider a water and heat management model for the PEMFC and established algebraic expressions for concentration along the flow channel with their constitutive equations. They solved the problem iteratively by using the
fourth-order Runge-Kutta method and the Newton-Raphson method. The model accounts for water condensation and evaporation in the flow channel as well as the water transport across the membrane. However, the water concentration profile across the membrane is assumed to be linear to reduce the complexity of this model. Besides, they also assumed that the pressure along the flow channel is constant to avoid solving the momentum conservation equations. Their results showed that ohmic loss in the membrane can account for a large fraction of the voltage loss in the cell, which is due to the poor water management within the cell.

Gurau’s model [44] accounts for the conservation of mass, momentum, species, energy, and charge. All equations were converted to non-dimensional forms and the domain was divided into three sub-domains which are coupled via the catalyst layers. A numerical program using the SIMPLE algorithm was developed to solve the transport equations iteratively by first setting the cell potential and then computing the current density. They solved momentum equations together with the species concentration and electrochemical equations, and their results compared very well with experimental results from the literature.

Um et al. [45] also developed an ‘along-the-channel’ model for transient conditions under isothermal operation conditions. In contrast to Gurau’s model, Um et al. treated the whole cell of the model as a single domain and employed a finite-volume-based computational fluid dynamic approach. The main advantage of considering the problem as a single domain is that a single set of governing equations can be solved with no internal boundary conditions required. Their model is also validated against published experimental data and is in good agreement. Subsequently, the model is used to understand the hydrogen dilution effects in the anode feed.

A more recent model is the work of Liu et al. [46] who developed a 2D partial flooding model. For the first time, pore size distribution of the gas diffusion layer is
taken into consideration to explain the water management within the fuel cell. The focus of this paper is the flooding in the gas diffusion layer. Their model predicts that the partial flooding within the fuel cell will reduce the active reaction area. Additionally, they investigated pore size distribution and pore diameter effects on the performance of the cell and realized that smaller pore sizes lead to improve performance i.e. higher current density. Nonetheless, the model only gives reasonable correspondence with that of experiments.

### 3.3 Three-dimensional models

The 3D models are basically similar to the 2D counterparts with the third dimension added. Numerous papers had been published accounting for three-dimensionality of the PEMFC under different conditions such as isothermal or non-isothermal operations and single-phase or two-phases. Some consider only a single channel for their computational domain [25, 26, 47-51] whereas other researchers modeled a full 3D domain with different geometrical configuration of the gas flow field such as the aforementioned serpentine [29, 52-54] and multiple serpentine flow channels [55].

Berning et al. [47], developed a 3D non-isothermal model for straight parallel flow channels, and used the Schlögl equation for liquid water transport through the membrane. The model is used to study the distribution of reactant concentrations, current density and temperature within the cell. Besides this, liquid water flux and potential distribution inside the membrane were addressed as well. However, Berning et al. did not take into account the relationship between liquid water and water vapor such as condensation/evaporation in their model despite the existence of liquid water. The converging time takes about 50hrs with $2 \times 10^4$ iterations for high current density operation (e.g. $1.4 \times 10^4 \text{ A} \text{ m}^{-2}$) on a PC with a 450MHz Pentium II. The model is then used for a parametric study [56], where the effect of temperature, pressure, stoichiometry,
porosity and thickness of gas diffusion layer, as well as the geometry of the flow channel on the performance of the fuel cell were analyzed. Their results also suggest that the 3D nature of the transport is particularly pronounced and cannot be neglected under the collector plates land area and significantly affect the current distribution and the predicted limiting current density.

In contrast to Berning et al., who apply the Schlögl equation for liquid water transport through the membrane, most of the published 3D models use Springer’s phenomenological membrane correlation instead. One of these is the work of Um and Wang [48], who developed a model based on a single straight flow channel under isothermal condition with the assumption of single-phase flow. Wang and Wang [49] extended Um’s model to consider the transient processes occurring in the fuel cell. A full 3D model of a 50cm$^2$ fuel cell with serpentine flow channels is presented by Ju and Wang [52]. In their work, a single-domain approach is utilized in order to make a single set of governing equation valid for all layers within the PEMFC. The validation of Ju and Wang’s model shows good agreement with their own experiments. Their model with 1.3 millions grid points takes around 10-15h to converge on a single PC (2GHz). A similar model to that of Ju and Wang is presented by Meng and Wang [53].

Meng and Wang later extended their work to a non-isothermal model for a single flow channel [50]. The model is used to study the thermal effects on the fuel cell performance under different design and operating conditions. Similarly, Ju et al. also derived a non-isothermal model for a single flow channel [25] which contains $1.4 \times 10^5$ computational cells and requires roughly 3-4h to obtain a converged solution and then extended their model which was described in the previous paragraph (see [52]) to a full 3D non-isothermal model [29]. The model is now more computationally expensive and contains up to 2.3 millions computational cells, and they used a 10-PC parallel computer to solve it. Wang and Wang [55] also presented a 3D model with multiple serpentine
flow channels. Their model contains 23.5 millions cells and takes 20h on a 32 processor PC cluster (each PC is 2.8GHz Intel Pentium 4 CPU and 1.0GB of RAM) to converge.

The aforementioned 3D models so far only account for single-phase flow. Wang and Wang [26] extended their work to a two-phase model invoking the water phase transport due to condensation/evaporation where the amount of liquid water is represented by liquid saturation. The model is used to completely investigate the thermal and water management within the cell and contours of the temperature, liquid saturation, and local current distributions are presented in the paper. It is worth to note that in order to reduce computational cost, Wang and Wang [26] consider a single flow channel and also neglect mass source/sink terms in the continuity equation. Luo et al. [51] did not invoke the assumption of negligible mass source/sink term, but they assumed that liquid water exist in the flow channel as tiny water droplets which travel in the same velocity as the gas phase. A single flow channel with 3D geometry is considered in Luo et al’s work, which takes around 10h to converge on a single PC (2.8GHz) with around $1.1 \times 10^5$ unit cells.

There are more similar 3D models as those mentioned above in the open literature. The models presented in this section provide an overview of 3D modeling. For more information about the single cell modeling, one can reference to the reviews of Cheddie and Munroe [6] or Liu et al. [7]. In the following section, a brief review on the modeling techniques for fuel cell stacks is presented.

### 3.4 Fuel cell stack models

A single fuel cell usually produces a voltage less than 1V. Therefore, several unit cells are connected in series in order to achieve a higher voltage output for practical applications. The experimental model for a stack is easy to build [57, 59] with various arrangements of single cell in a stack such as the back-to-back or the side-to-side configurations [57] (see
Fig. 3.3. However, the modeling of a stack is difficult to be done without appropriate simplifications. Hence, very few papers present the numerical models of a stack of PEMFC due to the computational cost. The few research groups working on modeling of fuel cell stacks include Karimi et al. [60], Liu et al. [9], Shan et al. [10], Chang et al. [14], to name but a few.

Liu et al. [9] presented an air cooled mini fuel cell stack consisting of six cells in which the active area was 8 cm². For simplicity, the authors considered the flow field to be a porous media with a porosity of 0.67 according to the geometry of the flow channel which took 2/3 of the total volume. With this simplification, the number of grid points can be reduced by at least four times. For stack performance at low current density (i.e. lower than 0.1 A/cm²), the model gives good prediction. However, the model failed to predict accurately as the current density increases, particularly at the
limiting current density. Furthermore, the model ignored the source/sink terms in the continuity equation, the presence of liquid water as well as heat transfer within the cell. Despite the above assumptions and simplifications, the model requires around 30h to converge with 2500 iterations on a personal computer (Intel Pentium IV 2.4 GHz and 1GB RAM).

Shan et al. [10] developed an improved transient 2D model for PEM fuel cell stack comprising of two single cells taking into account temperature effects. They conducted simulations to analyze start-up behavior and stack’s performance. Similar to Liu’s model, the authors do not consider water phase transfer and assume that no liquid water is generated. Their model provides considerable insights to the dynamic temperature distribution in both the through-plane direction and along the channel direction of the fuel cell stack. The effect of the various source terms for the current density and the dynamic oxygen concentration distribution is also provided by their model.

Chang et al. [14] presented a comprehensive model of a PEMFC stack in which the dimensionality is reduced from 3D to an ‘across the channel’ model, where the model is solved for each location x and connected to 1D models for the flow channel. The ‘across-the-channel’ model is further reduced by taking the average over the spanwise direction (z-direction in Fig. 3.1). The advantages of this model are that both temperature and water transport including liquid water are considered which gave understanding of the influencing factors affecting these physical processes. The model shows good agreement with experiments in terms of global behavior, overall water crossover, and also current density under various operating conditions. However, the model did not consider the liquid water transport in channels and electrodes, thermal end cell effects and flow sharing effects between cells from shared gas headers.
3.5 Summary

This literature review discussed the published research efforts on modeling of transport phenomena in the proton exchange membrane fuel cell in terms of dimensionality, simplifications and computational cost. As such, the literature review sets the framework where we work for developing reduced mathematical models, that seek to cut down on the computational cost by several orders of magnitude whilst not sacrificing any of the essential physics and geometrical resolution. For review on other aspects of the fuel cell, one can look at the review of Cheddie and Munroe [6] who compared the various approaches of modeling, Cheng et al. [61] for contamination impacts, poisoning mechanisms as well as contamination mitigation of the fuel cell, Li et al. [62] who discussed water flooding issues within the cell, Bruijin et al. [63] and Schmittinger et al. [64] on the durability and degradation issues of the PEMFC. In the subsequent Chapters, we will also provide comprehensive reviews on specific topics discussed within each Chapter. The next Section gives a summary of the proposed objectives and research direction.
Chapter 4

Mathematical formulations

In this chapter, we will present a general governing equations including both single-phase as well as multi-phase formulations. Since the equations are formulated in generalized vector notation, they can easily applied for 1-, 2-, or 3-dimensional models. Furthermore, the base-case parameters are also given in a tabular form so that it is easily to trace back in subsequent chapters. Note that, we include numbers in this table to refer the chapters where the parameters are applied to.

4.1 Governing Equations

Refer to the Figure 2.1, we consider a model for a slender three-dimensional single fuel cell consisting of several functional layers – flow field (ff), gas diffusion layer (gdl), catalyst layer (cl), and membrane (m). Note that the bipolar plate includes the flow field and the current collector (cc). At the stack level, additional coolant flow field (cff) layers might be added to the overall stack for the thermal management.

4.1.1 Single-Phase Model

We will present the mathematical formulation of the 3D PEMFC model equipped with porous flow fields. The conservation of mass, momentum, species, energy and charge in
the PEMFC can be expressed as

\[ \nabla \cdot (\rho^{(g)} \mathbf{v}^{(g)}) = S_{\text{mass}}^{(g)}, \text{ (ff, gdl, cl, m)} \]  

(4.1)

\[ \nabla p^{(g)} = -\frac{\mu^{(g)}}{\kappa} \mathbf{v}^{(g)} + S_{\text{mom}}^{(g)}, \text{ (ff, gdl, cl, m)} \]  

(4.2)

\[ \nabla \cdot N_i^{(g)} = S_1^{(g)}, \text{ (ff, gdl, cl, m)} \]  

(4.3)

\[ \nabla \cdot i^{(m)} = S_{\text{pot}}, \text{ (cl, m)} \]  

(4.4)

\[ \nabla \cdot i^{(s)} = -S_{\text{pot}}, \text{ (cc, ff, gdl, cl)} \]  

(4.5)

\[ \rho^{(g)} c_p^{(g)} \mathbf{v}^{(g)} \cdot \nabla T = \nabla \cdot (k_{\text{eff}} \nabla T) + S_{\text{temp}}, \text{ (cc, ff, gdl, cl, m)}. \]  

(4.6)

The molar fluxes of species and current densities are defined as

\[ N_i^{(g)} = c_i^{(g)} \mathbf{v}^{(g)} - D_i^{(g)} \nabla c_i^{(g)}, \text{ (i = O}_2, \text{ H}_2 - \text{ff, gdl, cl)} \]  

(4.7)

\[ N_{\text{H}_2\text{O}}^{(g)} = \begin{cases} 
\frac{n_{\text{H}_2\text{O}}^{(m)}}{M_{\text{H}_2\text{O}}} - \frac{\rho^{(m)}}{M_{\text{H}_2\text{O}}} D_{\text{H}_2\text{O},\text{eff}}^{(m)} \nabla \lambda^{(m)} \text{ (m)} \\
\frac{c_{\text{H}_2\text{O}}^{(g)}}{M_{\text{H}_2\text{O}}} \mathbf{v}^{(g)} - D_{\text{H}_2\text{O},\text{eff}}^{(g)} \nabla c_{\text{H}_2\text{O}}^{(g)} \text{ (ff, gdl, cl)} 
\end{cases} \]  

(4.8)

\[ i^{(m)} = -\sigma_{\text{eff}}^{(m)} \nabla \phi^{(m)}, \text{ (cl, m)} \]  

(4.9)

\[ i^{(s)} = -\sigma_{\text{eff}}^{(s)} \nabla \phi^{(s)}, \text{ (cc, ff, gdl, cl)}. \]  

(4.10)

The source terms in Eqs. 4.1-4.6 are given by

\[ S_{\text{mass}}^{(g)} = \begin{cases} 
\frac{M_{\text{O}_2} J_e}{4F} - \frac{M_{\text{H}_2\text{O}} J_e}{2F} \text{ (cathode cl)} \\
-\frac{M_{\text{H}_2} J_n}{2F} \text{ (anode cl)} \\
0 \text{ (elsewhere)} 
\end{cases}, \quad S_i^{(g)} = \begin{cases} 
\frac{J_e}{4F} \text{ (O}_2\text{, cathode cl)} \\
-\frac{J_e}{2F} \text{ (H}_2\text{O, cathode cl)} \\
-\frac{J_n}{2F} \text{ (H}_2\text{, anode cl)} \\
0 \text{ (elsewhere)} 
\end{cases} \]  

(4.11)


\[ S_{\text{pot}} = \begin{cases} 
J_c \text{ (cathode cl)} \\
J_a \text{ (anode cl)} \\
0 \text{ (elsewhere)} 
\end{cases}, \quad S_{\text{mom}}^{(g)} = \begin{cases} 
-\frac{c_p^{(g)}}{\sqrt{\kappa}} |v^{(g)}| v^{(g)} \text{ (ff)} \\
0 \text{ (elsewhere)} 
\end{cases}, \quad (4.12) \\
\]

\[ S_{\text{temp}} = \begin{cases} 
J_{a,c} (\eta_{a,c} + T \frac{\partial E_{\text{rev}}}{\partial T}) + \sigma_{\text{eff}}^{(m)} \left( \nabla \phi^{(m)} \right)^2 + \sigma_{\text{eff}}^{(s)} \left( \nabla \phi^{(s)} \right)^2 \text{ (cl)} \\
\sigma_{\text{eff}}^{(m)} \left( \nabla \phi^{(m)} \right)^2 \text{ (m)} \quad (4.13) \\
\sigma_{\text{eff}}^{(s)} \left( \nabla \phi^{(s)} \right)^2 \text{ (elsewhere)} 
\end{cases} \\
\]

In the above equations, \( \rho^{(g)} \) is the density, \( v^{(g)} \) is the velocity, \( p^{(g)} \) is the pressure, \( \mu^{(g)} \) is the dynamic viscosity, \( \kappa \) is the hydraulic permeability of the porous medium, \( c_p^{(g)} \) is the specific heat capacity, \( T \) is the temperature, and \( k_{\text{eff}} \) is the effective thermal conductivity. We point out that, in general, the hydraulic permeability is an anisotropic tensor; however, Vynnycky et al. \[65\] have shown that, for the gas diffusion layer, it is only the through-plane component that contributes as a leading-order effect, and hence for simplicity we assume here that the gas diffusion layer’s permeability tensor is isotropic and has the value obtained from through-plane measurements. As for the flow field, its properties are experimentally much more poorly characterized, so we assume simply that its permeability tensor is isotropic also. Furthermore, the gas velocities within it are high enough to require the inclusion of inertia effects; we do this by incorporating a Forchheimer term \[24\], \( S_{\text{mom}}^{(g)} \), into Darcy’s law in Eq. \[4.2\]. We solve for a ternary mixture of water (H\(_2\)O), nitrogen (N\(_2\)) and oxygen (O\(_2\)) at the cathode side, and H\(_2\)O, N\(_2\) and hydrogen (H\(_2\)) at the anode side, with \( c_i^{(g)} \) denoting the concentration of species \( i \), and \( D_{i,\text{eff}}^{(g)} \) denoting the effective diffusivity. The flux of water in the membrane due
to electroosmotic drag and diffusion is expressed using a phenomenological model \cite{27} in terms of the membrane water content, $\lambda$. Here, $n_d$ is electroosmotic drag coefficient, $i^{(m)}$ is the current density carried by protons, $F$ is Faraday’s constant, $D_{H_2O,eff}^{(m)}$ is the diffusivity of water in the membrane, $\rho^{(m)}$ and $M^{(m)}$ are the density and equivalent weight of the dry membrane, respectively. In Eqs. \[4.4\] and \[4.5\], $\phi^{(m)}$ represents the potential of the ionic phase and $\phi^{(s)}$ the solid phase, and $\sigma_{eff}^{(m)}$ and $\sigma_{eff}^{(s)}$ are the electrical conductivities of proton and electron transport, respectively. Note that, $J_a, c$ ($J_a > 0$, $J_c < 0$) are the volumetric current density, $c_F$ is the form-drag constant, $\eta_{a,c}$ ($\eta_a > 0$, $\eta_c < 0$) are the overpotential, and $E_{rev}$ is the reversible potential.

\section*{4.1.2 Multi-phase Model}

We consider multiphase, multicomponent fluid flow in all functional layers of a PEMFC in which the conservation of mass (liquid and gas), momentum, species in gas phase (cathode: $O_2$, $H_2O$, and $N_2$; anode: $H_2$, and $H_2O$), water in membrane, energy and charge are given as

\begin{align}
\nabla \cdot (\rho^{(g)} \mathbf{v}^{(g)}) &= S_{mass}^{(g)}, \ (ff, gdl, cl) \\
\nabla \cdot (\rho^{(l)} \mathbf{v}^{(l)}) &= S_{mass}^{(l)}, \ (ff, gdl, cl) \\
\nabla p^{(g)} &= -\frac{\mu^{(g)}}{\kappa_{rel}^{(g)}} \mathbf{v}^{(g)} + S_{mom}^{(g)}, \ (ff, gdl, cl) \\
\nabla \cdot n_i^{(g)} &= S_i^{(g)}, \ (ff, gdl, cl) \\
\nabla \cdot n_{H_2O}^{(m)} &= S_{H_2O}^{(m)} , \ (cl, m) \\
\nabla \cdot i^{(m)} &= S_{pot}, \ (cl, m) \\
\nabla \cdot i^{(s)} &= -S_{pot}, \ (cc, ff, gdl, cl) \\
\n\nabla \cdot q &= S_{temp}, \ (cc, m)
\end{align}
\[
\left( \rho^{(l)} v^{(l)} + \rho^{(g)} v^{(g)} \right) \cdot \nabla T + \nabla \cdot q = S_{\text{temp}}, \quad (ff, \text{ gdl, cl}). \tag{4.22}
\]

In these equations, the superscripts represent the phases, i.e. ‘g, l, m, s’ for the gas, liquid, membrane, and solid phases respectively; \( \kappa_{\text{rel}} \) is the relative permeability, \( n_i \) is the mass flux of the species \( i \), \( \mathbf{i} \) is current density, and \( q \) is the heat flux. Other notations are defined similar to the ones of single-phase formulation.

It should be noticed that the momentum equations, i.e. Eq. 4.16, is applied for the model equipped with porous flow fields. In case of the parallel-channel flow fields machined in the bipolar plate, the Navier-stokes equations will be employed for the flow fields, coupled with the Brinkman equations for the gas diffusion layers and catalyst layers,

\[
\nabla p^{(g)} = \begin{cases} 
- \nabla \cdot \left( \rho^{(g)} \mathbf{v}^{(g)} \mathbf{v}^{(g)} \right) + \nabla \cdot \mathbf{\tau}, & \text{(ff)} \\
- \frac{1}{\varepsilon^2} \nabla \cdot \left( \rho^{(g)} \mathbf{v}^{(g)} \mathbf{v}^{(g)} \right) + \frac{1}{\varepsilon} \nabla \cdot \mathbf{\tau} - \frac{\mu^{(g)}}{\kappa^{(g)}} \mathbf{v}^{(g)}, & \text{(gdl, cl)}
\end{cases} \tag{4.23}
\]

where \( \mathbf{\tau} \) is the viscous stress tensor defined by

\[
\mathbf{\tau} = \mu^{(g)} \left[ \nabla \mathbf{v}^{(g)} + \left( \nabla \mathbf{v}^{(g)} \right)^T \right] - \frac{2}{3} \mu^{(g)} \left( \nabla \cdot \mathbf{v}^{(g)} \right) \mathbf{I}, \tag{4.24}
\]

and \( \mathbf{I} \) is a unit tensor.

The mass fluxes for oxygen in the cathode side, water (in gas and membrane phases), current densities, and liquid velocity in the above equations are defined as

\[
n^{(g)}_i = \rho^{(g)} \omega_i^{(g)} \mathbf{v}^{(g)} - \rho^{(g)} D_i^{(g)} \nabla \omega_i^{(g)}, \quad (ff, \text{ gdl, cl}) \tag{4.25}
\]

\[
n^{(m)}_{\text{H}_2\text{O}} = M_{\text{H}_2\text{O}} \left( \frac{n_i^{(m)}}{F} - \frac{\rho^{(m)}}{M^{(m)}_{\text{H}_2\text{O}}} D^{(m)}_{\text{H}_2\text{O} \text{eff}} \nabla \chi \right), \quad (\text{cl, m}) \tag{4.26}
\]
\( i^{(m)} = -\sigma_{\text{eff}}^{(m)} \nabla \phi^{(m)}, \) (cl, m) \hfill (4.27)

\( i^{(s)} = -\sigma_{\text{eff}}^{(s)} \nabla \phi^{(s)}, \) (cc, ff, gdl, cl). \hfill (4.28)

\[
\mathbf{v}^{(l)} = \frac{k_{rel}^{(l)}(g)}{\mu^{(l)}} \mathbf{v}^{(g)} - \frac{k_{rel}^{(l)}}{\mu^{(l)}} S_{\text{mom}}^{(g)} + \frac{k_{rel}^{(l)} dp^{(c)}}{ds} \nabla s, \) (ff, gdl, cl) \hfill (4.29)

\( q = -k_{\text{eff}} \nabla T, \) (everywhere) \hfill (4.30)

where \( \omega_i \) is the mass fraction of the species \( i \), \( M_{\text{H}_2\text{O}} \) is the molecular mass of water.

The source terms in Eq. 4.14-4.22 are given by

\[
S_{\text{mass}}^{(g)} = \begin{cases} 
\dot{m}_{\text{H}_2\text{O}}^{(1=g)} - \dot{m}_{\text{H}_2\text{O}}^{(g=p)} S^{(g=p)} + \frac{M_{\text{O}_2} J_c}{4F} - \frac{M_{\text{H}_2\text{O}} J_c}{2F} S^{(l=g)} & \text{(cathode cl)} \\
\dot{m}_{\text{H}_2\text{O}}^{(1=g)} - \dot{m}_{\text{H}_2\text{O}}^{(g=p)} S^{(g=p)} - \frac{M_{\text{H}_2\text{O}} J_a}{2F} & \text{(anode cl)} \\
\dot{m}_{\text{H}_2\text{O}}^{(1=g)} & \text{(elsewhere)}
\end{cases}
\hfill (4.31)

\[
S_{\text{mass}}^{(l)} = \begin{cases} 
-\dot{m}_{\text{H}_2\text{O}}^{(1=g)} - \dot{m}_{\text{H}_2\text{O}}^{(g=p)} (1 - S^{(g=p)}) - \frac{M_{\text{H}_2\text{O}} J_c}{2F} (1 - S^{(l=g)}) & \text{(cathode cl)} \\
-\dot{m}_{\text{H}_2\text{O}}^{(1=g)} - \dot{m}_{\text{H}_2\text{O}}^{(g=p)} (1 - S^{(g=p)}) & \text{(anode cl)} \\
-\dot{m}_{\text{H}_2\text{O}}^{(1=g)} & \text{(elsewhere)}
\end{cases}
\hfill (4.32)

\[
S_i^{(g)} = \begin{cases} 
\dot{m}_{\text{H}_2\text{O}}^{(1=g)} - \dot{m}_{\text{H}_2\text{O}}^{(g=p)} S^{(g=p)} + \frac{M_{\text{O}_2} J_c}{4F} & \text{(O}_2, \text{ cathode cl)} \\
\dot{m}_{\text{H}_2\text{O}}^{(1=g)} - \dot{m}_{\text{H}_2\text{O}}^{(g=p)} S^{(g=p)} - \frac{M_{\text{H}_2\text{O}} J_c}{2F} S^{(l=g)} & \text{(H}_2\text{O, cathode cl)} \\
\dot{m}_{\text{H}_2\text{O}}^{(1=g)} - \dot{m}_{\text{H}_2\text{O}}^{(g=p)} S^{(g=p)} & \text{(H}_2\text{O, anode cl)} \\
\dot{m}_{\text{H}_2\text{O}}^{(1=g)} & \text{(H}_2\text{O, elsewhere)} \\
0 & \text{(elsewhere)}
\end{cases}
\hfill (4.33)
4.2 Constitutive Relations

The density of the multicomponent gas mixture is given by the ideal gas law,

\[ \rho^{(g)} = \frac{p^{(g)} M^{(g)}}{RT}, \]  

(4.37)

where \( M \) denotes the mixture molecular weight as a function of the molar fraction \( x_i \), and is given by
\[ M^{(g)} = M_{O_2} x_{O_2}^{(g)} + M_{H_2} x_{H_2}^{(g)} + M_{H_2O} x_{H_2O}^{(g)} + M_{N_2} x_{N_2}^{(g)}; \quad (4.38) \]

also,
\[ x_i^{(g)} = \frac{c_i^{(g)}}{c_{O_2}^{(g)} + c_{H_2}^{(g)} + c_{H_2O}^{(g)} + c_{N_2}^{(g)}}, \quad (4.39) \]

Note that Eq. 4.38 and 4.39 are compact representations for \( M^{(g)} \) and \( x_i^{(g)} \) for both anode and cathode sides of the cell, since \( c_{O_2}^{(g)} \equiv 0 \) on the anode side and \( c_{H_2}^{(g)} \equiv 0 \) on the cathode side. We also can express the molecular weight as a function of the mass fraction
\[ M^{(g)} = \left( \omega_{O_2}^{(g)}/M_{O_2} + \omega_{H_2}^{(g)}/M_{H_2} + \omega_{H_2O}^{(g)}/M_{H_2O} + \omega_{N_2}^{(g)}/M_{N_2} \right)^{-1} \quad (4.40) \]

and the relation between the mass fraction and the molar fraction is given as
\[ x_i^{(g)} = \omega_i^{(g)} M^{(g)}/M_i. \]

The relative humidity (%) which determines the water content at the inlets is defined as
\[ h = \frac{p^{(g)} x_{H_2O}^{(g)}}{p_{H_2O}^{\text{sat}}} \times 100, \quad (4.41) \]

where \( p_{H_2O}^{\text{sat}} \) is the saturation pressure of water and given as [27]
\[ p_{H_2O}^{\text{sat}} \text{(Pa)} = 101325 \times 10^{\epsilon_1 + \epsilon_2 (T - T_0) + \epsilon_3 (T - T_0)^2 + \epsilon_4 (T - T_0)^3}. \quad (4.42) \]

By retaining the ratio \( x_{O_2}^{(g)}/x_{N_2}^{(g)} = 21/79 \), the molar fraction of oxygen at the inlet can be determined from
\[ x_{O_2}^{\text{in}} = \frac{1 - x_{H_2O}^{\text{in}}}{1 + 79/21}. \quad (4.43) \]

The volumetric current density, \( J_{a,c} \), for the catalyst layers is given by linearizing
the Butler–Volmer equation at the anode side and a Tafel equation which will be later modified by an agglomerate model (see next section) at the cathode side, as follows:  

\[ J_a = j_{a,0}^\text{ref} (1 - s) \left( \frac{c_{\text{H}_2}^{\text{g}}}{c_{\text{H}_2}^{\text{ref}}} \right)^{1/2} \left( \frac{\alpha_a + \alpha_c}{RT} - F\eta_a \right), \]  

(4.44)

\[ J_c = -j_{c,0}^\text{ref} (1 - s) \exp \left[ -\frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{\bar{T}_1} \right) \right] \left( \frac{c_{\text{O}_2}^{\text{g}}}{c_{\text{O}_2}^{\text{ref}}} \right) \exp \left( -\frac{\alpha_c}{RT} F\eta_c \right). \]  

(4.45)

In Eq. (4.44) and (4.45), \( j_{0}^\text{ref} \) and \( \alpha \) are volumetric exchange current density and transfer coefficient, which will be adapted to experimental polarization curves, \( s \) is liquid saturation, \( E_a \) is the activation energy, and \( \bar{T}_1 \), \( c_{\text{H}_2}^{\text{ref}} \) and \( c_{\text{O}_2}^{\text{ref}} \) are the reference temperature, concentration of hydrogen and oxygen, respectively. Note that \( s = 0 \) for single phase.

Here, the overpotentials, \( \eta_{a,c} \) are defined as

\[ \eta_{a,c} = \phi^{(s)} - \phi^{(m)} - E_{\text{rev}}, \]  

(4.46)

where the reversible potential, \( E_{\text{rev}} \), is equal to zero on the anode side, and is a function of temperature at the cathode side, that is

\[ E_{\text{rev}} = E_{\text{rev,0}} + \xi_1 (T - \bar{T}_2), \]  

(4.47)

with \( E_{\text{rev,0}} \) denoting the reversible potential at standard conditions, and \( \xi_1 \) and \( \bar{T}_2 \) are constants given in Table 4.2.

The mass diffusion coefficient for each species \( i \) depends on the local temperature and pressure, and is given by

\[ D_i^{(g)} = D_i^{(g)} (T_0, p_0) \left( \frac{T}{T_0} \right)^{3/2} \left( \frac{p_0}{p^{(g)}} \right). \]  

(4.48)
In the porous layers, the Bruggeman correction gives us the effective diffusivity as

\[ D^{(g)}_{i,\text{eff}} = \varepsilon^{3/2} D^{(g)}_i, \quad (4.49) \]

where \( \varepsilon \) is the porosity, which is assigned different values in the flow fields, gas diffusion layer, catalyst layer and membrane, i.e. \( \varepsilon = \varepsilon_{\text{fl}}, \varepsilon_{\text{gdl}}, \varepsilon_{\text{cl}}, \varepsilon_{\text{m}} \).

Two important parameters for describing the flux of water transport in the membrane are the electroosmotic drag coefficient, \( n_d \), and water diffusivity, \( D^{(m)}_{\text{H}_2\text{O,eff}} \), which is modified by a factor \( \beta^{(m)} \) \([25]\); both are expressed in terms of water content, \( \lambda \), according to \([28]\)

\[ n_d = \frac{2.5\lambda}{22}, \quad (4.50) \]

\[ D^{(m)}_{\text{H}_2\text{O,eff}} \left( \text{m}^2\text{s}^{-1} \right) = \beta^{(m)} \begin{cases} 
3.1 \times 10^{-7}\lambda \left[ \exp \left( 0.28\lambda \right) - 1 \right] \exp \left( -\frac{0.2436}{T} \right) & \text{for } \lambda \leq 3 \\
4.17 \times 10^{-8}\lambda \left[ 1 + 161 \exp \left( -\lambda \right) \right] \exp \left( -\frac{0.2436}{T} \right) & \text{for } 3 < \lambda 
\end{cases} \quad (4.51) \]

where the water content itself can be expressed in terms of the activity, \( a \), as

\[ \lambda = \begin{cases} 
0.043 + 17.81a - 39.85a^2 + 36.0a^3 & \text{for } a \leq 1 \\
14 + 1.4 \left( a - 1 \right) & \text{for } 1 < a \leq 3
\end{cases} \quad (4.52) \]

with

\[ a = \frac{c^{(g)}_{\text{H}_2\text{O}}RT}{P_{\text{H}_2\text{O}}} \quad (4.53) \]

Note that, in the multi-phase model, by solving directly the conservation of water in membrane phase, e.g. Eq. \([4.18]\) we are able to obtain the water content which is used to
calculate the water activity, $a$. In the literature, Springer’s correlation is widely used to express the water content as a function of water activity [27], hence, we need to invert this correlation to have the water activity expressed as a function of water content

$$a = \begin{cases} a_0 + a_1 f(\lambda)^{1/3} + a_2 f(\lambda)^{-1/3}, & \text{for } \lambda \leq 14 \\ 1 + (\lambda - 14)/1.4, & \text{for } \lambda \geq 14 \end{cases} \quad (4.54)$$

with $f(\lambda) = f_1 + f_2 \lambda + f_3 (f_4 + f_5 \lambda + f_6 \lambda^2)^{1/2} \quad (4.55)$

Furthermore, the inverse relation has been extended by providing an additional function so that it is continuous up to its second derivative at $\lambda = 14$; this enhances the convergence in solving the code. The modified inverse relation can be expressed as

$$a = \begin{cases} a_0 + a_1 f(\lambda)^{1/3} + a_2 f(\lambda)^{-1/3}, & \text{for } \lambda \leq 13 \\ b_0 + b_1 \lambda + b_2 \lambda^2 + b_3 \lambda^3, & \text{for } 13 < \lambda < 15 \\ 1 + (\lambda - 14)/1.4, & \text{for } \lambda \geq 15 \end{cases} \quad (4.56)$$

where $a_0, a_1, a_2, b_0, b_1, b_2, b_3, f_1, f_2, f_3, f_4, f_5,$ and $f_6$ are constants. All expressions are depicted in Fig. 4.1 comparing to the expression presented by Seigel et al. [66], the inverse relation presents exactly the Springer’s correlation.

The correlation for the proton conductivity in the conservation of charge equation is also given as a function of water content [27] with the modification factor $\beta^{(m)}$ [25] in the form

$$\sigma_{\text{eff}}^{(m)} \left( \text{S m}^{-1} \right) = \beta^{(m)} (0.5193\lambda - 0.326) \exp \left[ 1268 \left( \frac{1}{303.15} - \frac{1}{T} \right) \right]. \quad (4.57)$$
When using Eq. \(4.57\) we have to take care when the water content in the membrane is low, as the proton conductivity becomes negative when \(\lambda\) is less than 0.627. Based on arguments by Fimrite et al. \(67\), who have shown that the water content in the membrane typically should not be smaller than roughly 1.5, and the fact that 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, we will modify Eq. \(4.52\) as follows: approximately one and a half water molecules per sulfonate head are considered to remain in the membrane as a minimum value of water content, so that we set the value of \(\lambda\) equal to 1.5 in Eqs. \(4.51\) and \(4.57\) if the predicted value of \(\lambda\) from Eq. \(4.52\) is lower than 1.5. Furthermore, we also assume that the water content, \(\lambda\), takes the value 16.8 if \(a > 3\).
4.2. Constitutive Relations

In order to compute the thermal conductivity for the conservation of energy, we first determine the mixture viscosity, \( \mu^{(g)}_{\text{mix}} \), as \([68]\)

\[
\mu^{(g)}_{\text{mix}} = \sum_{\beta} \frac{x^{(g)}_{\beta} \mu^{(g)}_{\beta}}{\sum_{\alpha} x^{(g)}_{\alpha} \Phi_{\alpha\beta}} \quad \text{with } \alpha, \beta = \text{H}_2, \text{O}_2, \text{H}_2\text{O}, \text{N}_2,
\]

where \( x_{\alpha} \) are the mole fractions of species \( \alpha \), and

\[
\Phi_{\alpha\beta} = \frac{1}{\sqrt{8}} \left( 1 + \frac{M_{\alpha}}{M_{\beta}} \right)^{-\frac{1}{4}} \left[ 1 + \left( \frac{\mu^{(g)}_{\alpha}}{\mu^{(g)}_{\beta}} \right) \frac{1}{2} \left( \frac{M_{\beta}}{M_{\alpha}} \right)^{\frac{1}{4}} \right]^2.
\]

The thermal conductivity of the mixture, \( k^{(g)}_{\text{mix}} \), is given by

\[
k^{(g)}_{\text{mix}} = \sum_{\beta} \frac{x^{(g)}_{\beta} k^{(g)}_{\beta}}{1.065 \sum_{\alpha} x^{(g)}_{\alpha} \Phi_{\alpha\beta}}.
\]

The effective thermal conductivity for the different layers in the fuel cell can be estimated from

\[
k_{\text{eff}} = \varepsilon (1 - s) k^{(g)}_{\text{mix}} + \varepsilon s k^{(l)} + (1 - \varepsilon) k^{(s)},
\]

where \( k^{(s)} = k_{\text{fl}}, k_{\text{gd}}, k_{\text{cl}}, k_{\text{m}} \) are the thermal conductivities of the solid phase of the flow channel, gas diffusion layer, catalyst layer and membrane, respectively.

The mixture specific heat capacity, \( c^{(g)}_p \), is written as

\[
c^{(g)}_p (\text{J kg}^{-1}\text{K}^{-1}) = \frac{1}{M^{(g)}} \left( x^{(g)}_{\text{H}_2} C^{(g)}_{\text{p,H}_2} + x^{(g)}_{\text{O}_2} C^{(g)}_{\text{p,O}_2} + x^{(g)}_{\text{H}_2\text{O}} C^{(g)}_{\text{p,H}_2\text{O}} + x^{(g)}_{\text{N}_2} C^{(g)}_{\text{p,N}_2} \right),
\]

where \( C^{(g)}_{\text{p,H}_2}, C^{(g)}_{\text{p,O}_2}, C^{(g)}_{\text{p,H}_2\text{O}}, C^{(g)}_{\text{p,N}_2} (\text{J mol}^{-1}\text{K}^{-1}) \) are the specific heat capacities of hydrogen, oxygen, water and nitrogen, respectively, and can be expressed \([30]\) as

\[
C^{(g)}_{\text{p,H}_2} = 28.84 + 7.65 \times 10^{-5} (T - \bar{T}_s) - 3.29 \times 10^{-6} (T - \bar{T}_s)^2 + 8.70 \times 10^{-10} (T - \bar{T}_s)^3,
\]
\[ C_{p,O_2}^{(g)} = 29.10 + 1.16 \times 10^{-3} (T - \Theta_0) - 6.08 \times 10^{-6} (T - \Theta_0)^2 + 1.31 \times 10^{-9} (T - \Theta_0)^3, \]
\[ C_{p,H_2O}^{(g)} = 33.46 + 6.88 \times 10^{-3} (T - \Theta_0) + 7.60 \times 10^{-6} (T - \Theta_0)^2 - 3.59 \times 10^{-9} (T - \Theta_0)^3, \]
\[ C_{p,N_2}^{(g)} = 29.00 + 2.20 \times 10^{-3} (T - \Theta_0) + 5.72 \times 10^{-6} (T - \Theta_0)^2 - 2.87 \times 10^{-9} (T - \Theta_0)^3. \]

When the multi-phase model is employed, additional relations are required such as the relative permeability in gas and liquid phases, liquid dynamic viscosity, Leverett functions and the mass fraction of Nitrogen and Hydrogen:

\[ \kappa_{rel}^{(g)} = \begin{cases} 
    (1 - s) \text{ (ff)} \\
    (1 - s)^3 \text{ (gdl, cl)}
\end{cases} \quad (4.63) \]

\[ \mu^{(l)} = 0.6612(T - 229)^{-1.562} \quad (4.65) \]

\[ \mu^{(l)} = \begin{cases} 
    1.417(1 - s) - 2.12(1 - s)^2 + 1.263(1 - s)^3, \theta < 90^0 \\
    1.417s - 2.12s^2 + 1.263s^3, \theta > 90^0
\end{cases} \quad (4.66) \]

\[ \omega_{N_2}^{(g)} = 1 - \omega_{O_2}^{(g)} - \omega_{H_2O}^{(g)} \quad (4.67) \]

\[ \omega_{H_2}^{(g)} = 1 - \omega_{H_2O}^{(g)} \quad (4.68) \]

### 4.3 Agglomerate Model

We consider an agglomerate model for the electrochemistry at the cathode side and retain a simple Butler-Volmer-type expression for the anode catalyst layer, as the oxygen reduction reaction (ORR) is more sluggish than the hydrogen oxidation reaction (HOR), which typically manifests itself in \(|\eta_c| \gg \eta_a\). The agglomerate model introduces addi-
4.3. Agglomerate Model

Agglomerate model of mass transfer resistances in the cathode catalyst layer via mass transport inside spherical agglomerates [69–73] and the polymer and liquid water films [74–77] which are assumed to cover the agglomerates. We formulate the agglomerate model based on the expression given by Jaouen et al. [73] with a modification for the resistance of a water film similar to the work of Rao et al. [77] as

\[
J_c = -J_{c}^{\text{ref}} (1 - s) (1 - \gamma_{cl})(1 - \frac{\gamma^{(p)}}{\gamma^{(agg)}}) \frac{c^{(g)}_{O_2}}{c^{\text{ref}}_{O_2}} \exp \left( -\frac{\alpha_c F}{RT} \eta_c \right) \frac{RT}{H_{O_2}^{(p)}} \frac{1}{1 + \xi_1 + \xi_2 + \xi_3},
\]

(4.69)

where \(H_{O_2}^{(p)}\) is Henry’s constant for the air-ionomer interface; \(\xi_1, \xi_2, \) and \(\xi_3\) are the correction factors due to resistances of the agglomerate itself, the ionomer and water films, respectively. Note that \(s = 0\) for single phase. The temperature dependency of the reference volumetric exchange current density, \(J_{c}^{\text{ref}}\), can be captured with an Arrhenius-type relation [69],[72]

\[
J_{c}^{\text{ref}} = J_{c,0}^{\text{ref}} \exp \left[ -\frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T_1} \right) \right].
\]

(4.70)

In Eq. 4.69 \(\gamma_{cl}, \gamma^{(p)}, \) and \(\gamma^{(agg)}\) are the porosities of the catalyst layer, volume fraction of polymer and agglomerates, respectively, and are defined as

\[
\gamma_{cl} = \frac{V_{\text{void}}}{V_{tot}} = 1 - \gamma^{(agg)},
\]

(4.71)

\[
\gamma^{(agg)} = \frac{V^{(agg)}}{V_{tot}}, \quad \gamma_{pol} = \frac{V^{(p)}}{V_{tot}},
\]

(4.72)

with

\[
V^{(agg)} = V^{(PtC)} + V^{(p)}, \quad V_{\text{void}} = V^{(g)} + V^{(l)},
\]

(4.73)

\[
V_{tot} = V^{(agg)} + V_{\text{void}} = V^{(PtC)} + V^{(p)} + V^{(g)} + V^{(l)}.
\]

(4.74)

According to the definition of the platinum loading, \(m_{Pt}\), we have the definition of
carbon loading and weight fraction of polymer as

\[ \mathcal{L}(C) = \frac{\mathcal{L}(Pt)}{\omega(Pt)} - \mathcal{L}(Pt), \quad (4.75) \]

\[ \omega(p) = \frac{\mathcal{L}(p)}{\mathcal{L}(Pt) + \mathcal{L}(C) + \mathcal{L}(p)}, \quad (4.76) \]

providing the relationships for the volume fraction of polymer and Pt/C as \[72, 78\]

\[ \gamma(p) = \frac{\omega(p)}{1 - \omega(p) \frac{1}{\rho(m) h_{cl} \omega(Pt)}}, \quad (4.77) \]

\[ \gamma(PtC) = \frac{V(PtC)}{V_{tot}} = \left[ \frac{1}{\rho(Pt)} + \frac{1 - \omega(Pt)}{\omega(Pt) \rho(C)} \right] \frac{\mathcal{L}(Pt)}{h_{cl}}, \quad (4.78) \]

and with

\[ \gamma(agg) = \gamma(p) + \gamma(PtC), \quad (4.79) \]

here, \( h_{cl} \) is the thickness of catalyst layer, \( \omega(Pt) \) is the percentage by mass ratio of platinum and carbon black, \( \rho(Pt), \rho(C) \), and \( \rho(m) \) are the densities of platinum, carbon and polymer, respectively. By prescribing \( \mathcal{L}(Pt), \omega(Pt), \mathcal{L}(p) \), we are able to compute the porosity of the catalyst layer, \( \gamma_{cl} \).

The correction factor, \( \xi_1 \), is defined as the effectiveness of the mass transfer of oxygen through the spherical agglomerate nucleus, and is given as \[68\]

\[ \xi_1 = \frac{3}{\Phi^2} [\Phi \coth(\Phi) - 1]; \quad (4.80) \]

here, the Thiele modulus, \( \Phi \), is given by

\[ \Phi = r^{(agg)} \sqrt{\frac{k_c}{D_{O_2,eff}}}, \quad (4.81) \]

where \( r^{(agg)} \) is the radius of an agglomerate, and \( k_c \) is given by
\[ k_c = \frac{j_c^{\text{ref}} (1 - \gamma^{(p)}) \exp \left( -\frac{\alpha_c F}{RT} \eta_c \right)}{4F c_0^{\text{ref}}}. \] (4.82)

The effective diffusion coefficient of oxygen in ionomer inside the agglomerate, \( D_{O_2,\text{eff}}^{(\text{agg})} \), is related to the diffusion coefficient of oxygen in the polymer film, \( D_{O_2}^{(p)} \), through the Bruggeman correlation \[69 \, 73\] as

\[ D_{O_2,\text{eff}}^{(\text{agg})} = D_{O_2}^{(p)} \left( \frac{\gamma^{(p)}}{\gamma^{(\text{agg})}} \right)^{1.5}. \] (4.83)

The correction factor, \( \xi_2 \), representing the resistance due to the polymer film is given as \[77\]

\[ \xi_2 = \frac{\delta^{(p)}}{D_{O_2}^{(p)}} \left( \frac{\xi_1}{a^{(p)}} \right) k_c, \] (4.84)

where \( a^{(p)} \) denotes the agglomerate surface area per unit volume of the catalyst layer, and is defined by

\[ a^{(p)} = 4\pi n^{(\text{agg})} (r^{(\text{agg})} + \delta^{(p)})^2, \] (4.85)

where \( n^{(\text{agg})} \) is the number of agglomerates per unit volume and is given by

\[ n^{(\text{agg})} = \frac{3\gamma^{(\text{agg})}}{4\pi \left( r^{(\text{agg})} + \delta^{(p)} \right)^3}. \] (4.86)

In Eqs. \[4.84\] and \[4.86\] the thickness of the polymer film, \( \delta^{(p)} \), can be estimated from the expression

\[ \delta^{(p)} = \sqrt[3]{(r^{(\text{agg})})^3 \left( 1 + \frac{\gamma^{(p)}}{\gamma^{(\text{PtC})}} \right)} - r^{(\text{agg})}. \] (4.87)

Finally, the correction factor, \( \xi_3 \), due to liquid water film is given by

\[ \xi_3 = \frac{\delta^{(l)}}{D_{O_2}^{(l)}} \frac{\xi_1}{a^{(l)}} \frac{H_{O_2}^{(l)}}{H_{O_2}^{(p)}} k_c. \] (4.88)
where $H_{O_2}^{(l)}$ and $H_{O_2}^{(p)}$ are Henry’s constants for the air-water and air-polymer interfaces, $D_{O_2}^{(l)}$ is the diffusion coefficient of oxygen in liquid water; $a^{(l)}$ is the surface area of the agglomerate including water per unit volume and $\delta^{(l)}$ is the thickness of the water layer, defined respectively by

$$a^{(l)} = 4\pi n^{(agg)}(r^{(agg)} + \delta^{(p)} + \delta^{(l)})^2,$$

$$\delta^{(l)} = \sqrt[3]{(r^{(agg)} + \delta^{(p)})^3(1 + \frac{s^{(l)}}{\gamma^{(agg)}}) - (r^{(agg)} + \delta^{(p)})}.$$ (4.89) (4.90)

The volume fraction of water is expressed in terms of the liquid saturation, $s$, as

$$\gamma^{(l)} = \frac{V^{(l)}}{V_{tot}} = s\gamma_{cl}.$$ (4.91)

For our one-phase model, we set $s = 0$, which in turn implies that $\delta^{(l)} = 0$ and $\xi_3 = 0$, so that we only consider the factors $\xi_1$ and $\xi_2$.

### 4.4 Base-case parameters

For the purpose of calibration, verification and validation of the mathematical models, three different experimental PEMFCs equipped with a porous flow field were used: (a) a segmented cell,[79] (b) a cell with a single-layer gas diffusion layer,[80] and (c) a cell with a carbon-filled gas diffusion layer.[80] However, when a half-cell models was developed in Chapters[6] and[7] only the first case was involed.
### 4.4. Base-case parameters

<table>
<thead>
<tr>
<th>Case (a)</th>
<th>Case (b)</th>
<th>Case (c)</th>
</tr>
</thead>
</table>

#### Physical parameters

<table>
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<th>Case (b)</th>
<th>Case (c)</th>
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</thead>
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<td>$3.4 \times 10^{-13}$ m$^2$</td>
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<td>0.635</td>
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<td>$\varepsilon_{gdl}$</td>
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<td>0.77</td>
<td>0.67</td>
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<td>491 S m$^{-1}$</td>
<td>600 S m$^{-1}$</td>
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<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>$\gamma_{(Pt)}$</td>
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<td>$0.4 \times 10^{-2}$ kg m$^{-2}$</td>
<td>$0.4 \times 10^{-2}$ kg m$^{-2}$</td>
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#### Geometry

<table>
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<td>$6 \times 10^{-4}$ m</td>
<td>$6 \times 10^{-4}$ m</td>
</tr>
<tr>
<td>$h_{ff}$</td>
<td>$5 \times 10^{-4}$ m</td>
<td>$6 \times 10^{-4}$ m</td>
<td>$6 \times 10^{-4}$ m</td>
</tr>
<tr>
<td>$h_{gdl}$</td>
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<td>$1.1 \times 10^{-4}$ m</td>
<td>$1.1 \times 10^{-4}$ m</td>
</tr>
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<td>$h_{cl}$</td>
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<td>$2 \times 10^{-5}$ m</td>
<td>$2 \times 10^{-5}$ m</td>
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<tr>
<td>$h_{m}$</td>
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<td>$5.1 \times 10^{-5}$ m</td>
<td>$5.1 \times 10^{-5}$ m</td>
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<tr>
<td>$L$</td>
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<td>0.015 m</td>
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#### Operating conditions

<table>
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<td>95%, 95%</td>
<td>100%, 100%</td>
<td>100%, 100%</td>
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<td>$T_{a,c}$</td>
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<td>338 K, 328 K</td>
<td>338 K, 328 K</td>
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<tr>
<td>$s_{in}$</td>
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<td>0</td>
<td>0</td>
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<tr>
<td>$p_{ref}$</td>
<td>101325 Pa</td>
<td>$1.5 \times 10^5$ Pa</td>
<td>$1.5 \times 10^5$ Pa</td>
</tr>
<tr>
<td>$\xi_{a,c}$</td>
<td>3.35, 2.3</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$U_{a,c}$</td>
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<td>0.03, 0.16 m s$^{-1}$</td>
<td>0.03, 0.16 m s$^{-1}$</td>
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<td>0.1 V</td>
<td>0.1 V</td>
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Table 4.1: Base-case parameters
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<th>Units</th>
<th>Reference</th>
<th>Chapters</th>
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<td>$c_{\text{ref}}^{\text{ref}}$</td>
<td>40.88, $p_0/\hat{H}_\text{O}_2^{(p)}$</td>
<td>mol m$^{-3}$</td>
<td>[29] [77]</td>
<td>5.6,7,8,9,10</td>
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<tr>
<td>$c_p^{(l)}$</td>
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<tr>
<td>$D_{\text{H}_2\text{O}}^{(g)}$</td>
<td>11.03 $\times$ 10$^{-5}$</td>
<td>m$^2$ s$^{-1}$</td>
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<td>5.6,7,8,9,10</td>
</tr>
<tr>
<td>$D_{\text{H}_2\text{O}}^{(g)}$</td>
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<td>m$^2$ s$^{-1}$</td>
<td>[29]</td>
<td>5.6,7,8,9,10</td>
</tr>
<tr>
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<td>m$^2$ s$^{-1}$</td>
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<tr>
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<td>m$^2$ s$^{-1}$</td>
<td>[78]</td>
<td>5.10</td>
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<tr>
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<td>m$^2$ s$^{-1}$</td>
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<td>J mol$^{-1}$</td>
<td>[82]</td>
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<tr>
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<td>V</td>
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<td>A s mol$^{-1}$</td>
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<td>$H_{\text{O}_2}^{(l)}$</td>
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<td>Pa m$^3$ mol$^{-1}$</td>
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<tr>
<td>$H_{\text{O}_2}^{(p)}$</td>
<td>$p_0 \times$ 1.33 exp($-666/T$)</td>
<td>Pa m$^3$ mol$^{-1}$</td>
<td>[77]</td>
<td>5.8,9,10</td>
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<tr>
<td>$H_{\text{vap}}$</td>
<td>2.3 $\times$ 10$^6$</td>
<td>J kg$^{-1}$</td>
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<td>5.10</td>
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<tr>
<td>$j_{\text{ref}}$</td>
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<td>A m$^{-3}$</td>
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<tr>
<td>$k_{cc}$, $k_{cl}$, $k_{gf}$</td>
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<td>W m$^{-1}$ K$^{-1}$</td>
<td>[83] [10] [81]</td>
<td>5.8,9,10</td>
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<td>[81] [79]</td>
<td>5.8,9,10</td>
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<tr>
<td>$k_{\text{H}<em>2}^{(g)}$, $k</em>{\text{H}_2\text{O}}^{(g)}$</td>
<td>(20.28, 2.16) $\times$ 10$^{-2}$</td>
<td>W m$^{-1}$ K$^{-1}$</td>
<td>[81]</td>
<td>5.8,9,10</td>
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<tr>
<td>$k_{\text{N}<em>2}^{(g)}$, $k</em>{\text{O}<em>2}^{(g)}$, $k</em>{\text{l}}^{(l)}$</td>
<td>(2.82, 2.89, 65.8) $\times$ 10$^{-2}$</td>
<td>W m$^{-1}$ K$^{-1}$</td>
<td>[81]</td>
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<tr>
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<td>kg m$^{-3}$ s$^{-1}$</td>
<td>-</td>
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<td>$\gamma^{(p)}$</td>
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<td>$M_{\text{H}<em>2}$, $M</em>{\text{H}_2\text{O}}$</td>
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<td>(28, 32) $\times$ 10$^{-3}$</td>
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<tr>
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<td>Pa</td>
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<tr>
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<td>1.9 $\times$ 10$^{-5}$</td>
<td>kg m$^{-1}$ s$^{-1}$</td>
<td>[79]</td>
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<tr>
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<td>[81]</td>
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<td>kg m$^{-1}$ s$^{-1}$</td>
<td>[81]</td>
<td>5.8,9,10</td>
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</table>
### 4.4. Base-case parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
<th>Reference</th>
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<tbody>
<tr>
<td>$\rho(C)$, $\rho(m)$</td>
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<td>[77], [29]</td>
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<td>K$^{-2}$, K$^{-3}$</td>
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<td>V K$^{-1}$</td>
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<td>K</td>
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</tbody>
</table>

Table 4.2: Additional base-case parameters (for all cases).
Chapter 5

Geometrical Reduction of 
Three-Dimensional Flow Channels into 
Two-Dimensional Porous Counterparts 
in Fuel Cells

A novel way to reduce the dimensionality, i.e., from three to two dimensions, of a proton exchange membrane fuel cell (PEMFC) model is presented. As a first step of the reduction, a traditional parallel channels which is commonly equipped in a three-dimensional (3D) PEMFC model is simulated by a two-dimensional (2D) porous flow field. A correction factor is added to the latter to capture the transport occurring the gas diffusion layer and current collector, which are affected by the ribs of the parallel channels in the 3D model. The solution obtained from the 2D model is verified with the 3D counterpart; good agreement is achieved at both the global and local levels. Finally, an extension of the reduction to the other type of flow field, e.g., serpentine, and multiple serpentine channels is discussed.
5.1 Introduction

The flow field normally machined in a bipolar plate as shown in Fig. 5.1, plays an important role in the fuel cell system with various functions – distributing fuel and oxidant, removing heat and byproducts from electrochemical reaction, conducting electrons from cell to cell, providing mechanical support for each cell, and separating individual cells in the stack. Taking more than 80% of weight in the stack [23], good design of flow field is vital in development of fuel cell technology.

Figure 5.1: A schematic of [(a) and (b)] the various functional layers in a PEMFC single cell equipped with parallel channels, [(c) and (d)] three- and two-dimensional models with porous flow field, and (e) a space-marching model.
5.1. Introduction

The most common configuration of the flow fields are parallel channels, serpentine channels, a combination of parallel and serpentine channels known as multiple serpentine channels, and porous flow field, as illustrated in Fig. 2.3. Furthermore, integrated and interdigitated flow fields have also been developed to suit the needs of flow field design. Based on these configurations, various designs have been presented in the open literature as summarized in a review published by Li and Sabir [23]. To enhance the aforementioned functions of the flow field, different material such as graphite, stainless steel or metallic materials have been explored in manufacturing of such various flow field designs [85–87].

Among various types of flow fields, the porous flow field has attracted interest due to its advantages comparing to the other traditional flow channels, e.g. parallel or serpentine channels [88, 89]. From the technological point of view, the porous flow field is able to provide uniform distribution of reactant and current throughout the active area which enhance the performance of a PEMFC [79, 90–94]. From the numerical point of view, a model equipped with porous flow field allows us to reduce its dimensionality from three to two dimensions due to slip and no flux of species and heat invoked at the side walls in the spanwise direction ($e_z$) of the cell, as shown in Fig. 5.1c. A 2D PEMFC model with a porous flow field in the streamwise ($e_x$) and normal ($e_y$) directions (see Fig. 5.1d) is able to describe the three-dimensional PEMFC behavior. This entails minimal computational effort since a full 3D model for a PEMFC may require a supercomputer, multi-processor system, and/or a multi-core parallel computing system to handle the computation. As presented in the literature [25, 29, 47, 51–53, 55, 95], solving a 3D model requires huge amount of random access memory (RAM) and is time consuming. Such a model may only be suitable for a single cell model. At the stack level, our proposed 2D model with porous flow field becomes advantageous since it can be further reduced to a space-marching model by properly applying a scaling analysis and simple
asymptotic to the governing equations [96] (as illustrated in Fig. 5.1e). As shown later in Chapter 9, a reduced stack model comprising up to 400 cells – using the reduced 2D model as a building block – can be solved within 15 minutes and only 2.3 GB of RAM is required on a single computer [97].

The question now is whether the 2D model with porous flow field can be used to describe the transport phenomena in a PEMFC equipped with channels, instead of applying the commonly formulated 3D model for a channel-type PEMFC of either parallel or serpentine flow fields. The answer is yes if we treat the 2D model properly with the aid of volume-averaging approach. Hence, the aim of this chapter is therefore to develop a 2D model with porous flow field which can capture the global as well as local transport phenomena occurring inside a 3D model equipped with parallel channels. In other words, we expect the solution provided by the 2D model to fit that of the 3D model.

In the next section, we will present the mathematical formulation of the 3D PEMFC model equipped with parallel-channels flow fields, followed by a set of governing equations for the 2D model with porous flow field. Then, the Numerics section is presented to provide essential information for solving these models. A correlation section is introduced to show how the 2D porous-type PEMFC model capture the transport phenomena of its 3D channel-type counterpart. A comparison of both local as well as global solutions obtained from these models is shown in the section of verification. Finally, we finish with a conclusion to discuss the extension of this concept to other types of flow channel such as serpentine and/or multiple serpentine channels.

5.2 Mathematical formulation

In this section, we provide the mathematical formulation for the 3D model with parallel channels and the 2D model with porous flow field together with their boundary condi-
5.2. Mathematical formulation

The models contain several functional layers, as illustrated in Fig. 5.1: current collector (cc), flow field (ff), gas diffusion layer (gdl), catalyst layer (cl), and membrane (m).

5.2.1 3D model

The computational domain for the 3D model is chosen as a single channel with symmetrical boundaries provided at both side walls to represent a full 3D model. The governing equations are given by Eq. 4.14 - 4.36. Note that the Navier-stokes equations will be employed to capture the momentum transport in the parallel-channel flow fields where as we use the Brinkman equation in the porous media, e.g. gas diffusion layer and catalyst layer.

**Boundary conditions** – The boundary conditions of the 3D case are identical to the 2D model counterpart; the latter is presented in the next section. Here, we write the additional boundary conditions required for the 3D case:

- At the left and right walls of the cell in the z-direction: symmetrical boundary conditions are applied

\[
v^{(g)} \cdot e_z = v^{(l)} \cdot e_z = 0, \quad \frac{\partial \omega_i^{(g)}}{\partial z} = \frac{\partial \phi^{(s)}}{\partial z} = \frac{\partial \phi^{(m)}}{\partial z} = \frac{\partial T}{\partial z} = 0, \quad n_{H_2O} \cdot e_z = 0. \quad (5.1)
\]

- At the current collector/channel interface:

\[
v^{(g)} = v^{(l)} = 0, \quad \frac{\partial \omega_i^{(g)}}{\partial y} = \frac{\partial \phi^{(s)}}{\partial y} = 0. \quad (5.2)
\]

- At the channel/rib interface:

\[
v^{(g)} = v^{(l)} = 0, \quad \frac{\partial \omega_i^{(g)}}{\partial z} = \frac{\partial \phi^{(s)}}{\partial z} = 0. \quad (5.3)
\]
• At the gas diffusion layer/rib interface:

\[ \mathbf{v}^{(g)} \cdot \mathbf{e}_y = \mathbf{v}^{(l)} \cdot \mathbf{e}_y = 0, \quad \frac{\partial \omega^{(g)}}{\partial y} = 0. \quad (5.4) \]

5.2.2 Geometrically reduced 2D Model

The governing equations for the 2D model equipped with the porous flow field are exactly the same as the one presented in the 3D model except for the momentum equations. Here, we employ the Darcy law for the momentum transport in porous media instead of the Brinkman equations, that is

\[ \nabla p^{(g)} = -\frac{\mu^{(g)}}{\kappa^{(g)}_{rel}} \mathbf{v}^{(g)} \text{, (ff, gdl, cl)} \quad (5.5) \]

Boundary conditions – The boundary/interface conditions are as follows

• At the cathode inlet:

\[ p^{(g)}_c = p^{\text{in}}_c, \quad \omega^{(g)}_O, \quad \omega^{(g)}_O, \quad \omega^{(g)}_H_2O, x, \quad \frac{\partial \phi^{(s)}}{\partial x} = 0, \quad T = T^{\text{in}}_c, \quad s^{\text{in}} = 0. \quad (5.6) \]

• At the anode inlet:

\[ p^{(g)}_a = p^{\text{in}}_a, \quad \omega^{(g)}_H_2O = \omega^{\text{in}}_H_2O, a, \quad \frac{\partial \phi^{(s)}}{\partial x} = 0, \quad T = T^{\text{in}}_a, \quad s^{\text{in}} = 0. \quad (5.7) \]

• At the outlet:

\[ p^{(g)} = p^{\text{ref}}, \quad \frac{\partial \omega^{(g)}}{\partial x} = \frac{\partial \phi^{(s)}}{\partial x} = \frac{\partial T}{\partial x} = \frac{\partial s}{\partial x} = 0. \quad (5.8) \]

• At the vertical walls:

\[ \mathbf{v}^{(g)} \cdot \mathbf{e}_x = \mathbf{v}^{(l)} \cdot \mathbf{e}_x = 0, \quad \frac{\partial \omega^{(g)}}{\partial x} = \frac{\partial \phi^{(s)}}{\partial x} = \frac{\partial \phi^{(m)}}{\partial x} = \frac{\partial T}{\partial x} = 0, \quad \mathbf{n}^{(m)}_H_2O \cdot \mathbf{e}_x = 0. \quad (5.9) \]
At the upper wall:

$$\phi^{(s)} = E_{\text{cell}}, \quad T = T^{\text{cool}}. \quad (5.10)$$

At the current collector/flow field interface:

$$v^{(g)} \cdot e_y = v^{(l)} \cdot e_y = 0, \quad \frac{\partial \omega_i^{(g)}}{\partial y} = 0. \quad (5.11)$$

At the gas diffusion layer/catalyst layer interface:

$$\frac{\partial \phi^{(m)}}{\partial y} = 0, \quad n_{\text{H}_2\text{O}}^{(m)} \cdot e_y = 0. \quad (5.12)$$

At the catalyst layer/membrane interface:

$$v^{(g)} \cdot e_x = v^{(l)} \cdot e_x = 0, \quad \frac{\partial \omega_i^{(g)}}{\partial y} = \frac{\partial \phi^{(s)}}{\partial y} = 0. \quad (5.13)$$

At the lower wall:

$$\phi^{(s)} = 0, \quad T = T^{\text{cool}}. \quad (5.14)$$

The constitutive relations and a detailed agglomerate model for the cathode active layer are given in Chapter 4.

5.3 Numerics

Both the 3D model with parallel channels and the 2D model with porous flow field were implemented in the commercial finite element solver COMSOL Multiphysics 3.5a. With Quadratic Lagrange elements employed for all variables. The geometrical and operating parameters are bases on case (b) given in Table 4.1, other parameters can be found in Table 4.2. In solving the 3D model, a segregated solver was chosen with a
relative convergence tolerance of $10^{-3}$ for all variables; this value was low enough for our purposes. Less memory usage was required as one employed the segregated solver by which the variables were divided into smaller groups instead of solving all at once; four groups were selected – group 1 ($\phi^{(m)}$, $\phi^{(s)}$), group 2 ($\mathbf{v}^{(g)}$, $p^{(g)}$), group 3 ($\omega_{O_2}^{(g)}$), and group 4 ($\omega_{H_2O}^{(g)}$, $s$, $\lambda$, $T$) – to ensure a convergence obtained. Since the equations are highly coupled together, some of variables have to be put in the same group, e.g. group 4, to secure a converged solution. For the 2D model, a direct solver Pardiso was applied with a relative convergence tolerance of $10^{-6}$ to achieve sufficient accuracy of the solutions for comparison with the 3D counterparts. The solutions obtained from the models were tested for mesh independence. All computations were carried out on a workstation with two quad-core processors 3.2 GHz and a total of 64 GB RAM.

5.4 Correlation

The section consists of two parts. The first part describes how to simulate a parallel channels by using a volume-averaging approach with effective transport properties. The second part shows how to modify the physical transport in gas diffusion layer and current collector of the 2D model which take into account the effect of the rib of the parallel channels in the 3D model.

5.4.1 Correlation for transport properties of the flow fields

*Porosity* – The porosity of the porous flow field in the 2D model, $\varepsilon_f$, is defined as the ratio of the volume occupied by the plain channel to the total volume of the flow field in the 3D model. In this particular case, it can be simply computed based on the ratio, $\mathcal{R}$, of the width of the channel, $w_f$, to the total width of the domain, $w_T$, as shown in Fig. 5.2

$$\varepsilon_f = \mathcal{R} = \frac{w_f}{w_T}$$  \hspace{1cm} (5.15)
5.4. Correlation

Permeability – We obtain the numerical permeability for the porous flow field in the 2D model by setting up a 3D test case in which we vary the pressure drop and measure the corresponding velocities along the channel. Note that the Navier-Stokes equation is solved for the 3D model with straight parallel channel whereas we employ the Darcy’s law for the porous flow field from which the numerical permeability is computed. As the width ratio, $\mathcal{R}$, changes, the value of numerical permeability will be varied accordingly. As shown in Fig. 5.3, the numerical permeability of the porous flow field increases with the width ratio. For the sake of brevity, we only derive the correlation in a range of width ratio from 0.3-0.6 \cite{99, 100}; however one could easily extend the correlation for a wider range of width ratio to suit their needs. The correlation of numerical permeability is given as

$$\kappa_{\text{eff}} = 10^{-8} \left( -0.435 + 2.80 \mathcal{R} \right), \quad 0.3 \leq \mathcal{R} \leq 0.6$$  \hspace{1cm} (5.16)
Diffusive coefficient — We consider the diffusive transport in the parallel channels and the homogeneous porous flow field taken the forms as

\[
\nabla (-D \nabla \Psi) = 0, \quad \text{(parallel channels)} \tag{5.17}
\]

\[
\nabla (-D_{\text{eff}} \nabla \Psi) = 0, \quad \text{(porous flow field)} \tag{5.18}
\]

where \(D\) and \(D_{\text{eff}}\) are diffusive coefficient and effectively diffusive coefficient which are, in this context, identical to the diffusivity of the species, thermal and electric conductivities in conservation of species, energy and charge, respectively. We will show how to obtain analytically the relationship between these two diffusive coefficient.

When modeling the porous flow field, it is not important to capture exactly the local
distribution in the parallel channels; the most interesting issue is that the flux at the
outlet of the porous flow field must be equal to the one at the outlet of the parallel
channels with the same provided inlet properties. For this purpose, we set the fluxes as

\[ n_{\text{out}}^{\text{para}} = n_{\text{out}}^{\text{poro}} \quad (5.19) \]

where \( n_{\text{out}}^{\text{para}} \) and \( n_{\text{out}}^{\text{poro}} \) are the average fluxes at the outlet of the parallel channels and
porous flow field, respectively, which are defined as

\[ n_{\text{out}}^{\text{para}} = \frac{1}{A} \int_0^{A_{\text{out}}^{\text{para}}} (-D \nabla \Psi) \cdot \mathbf{n} dA, \quad \text{(parallel channels)} \quad (5.20) \]
\[ n_{\text{out}}^{\text{poro}} = \frac{1}{A} \int_0^{A_{\text{out}}^{\text{poro}}} (-D_{\text{eff}} \nabla \Psi) \cdot \mathbf{n} dA, \quad \text{(porous flow field)} \quad (5.21) \]

in which \( \mathbf{n} \) is the normal vector, \( A \) is the total cross-section area, \( A_{\text{out}}^{\text{para}} \) and \( A_{\text{out}}^{\text{poro}} \) are
the cross-section area occupied by the plain channels and porous flow field respectively.
It is clearly that \( A_{\text{out}}^{\text{poro}} = A \), and the porosity of the homogeneous porous flow field \( \varepsilon_{\text{eff}} \)
can be related as

\[ \varepsilon_{\text{eff}} = \frac{A_{\text{out}}^{\text{para}}}{A}. \quad (5.22) \]

Combining the Eq. 5.20-5.22 we are able to derive the expression of effective diffusive
coefficient as

\[ D_{\text{eff}} = \varepsilon_{\text{eff}} D \quad (5.23) \]

Applying the above expression for the diffusivity, thermal and electric conductivities
with a notice that electron transport occurs in the solid part whereas heat can be
conducted through both solid and fluid. The expressions are given as

\[ D^{(g)}_{1,\text{eff}} = \varepsilon_{\text{eff}} D^{(g)}_1 \quad (5.24) \]
\[ \sigma_{\text{eff}}^{(s)} = (1 - \varepsilon_{\text{ff}}) \sigma_{\text{ff}}^{(s)} \quad (5.25) \]
\[ k_{\text{eff}} = \varepsilon_{\text{ff}} (1 - s) k_{\text{mix}}^{(g)} + \varepsilon_{\text{ff}} s k^{(l)} + (1 - \varepsilon_{\text{ff}}) k^{(s)} \quad (5.26) \]

At this state, with the resulted correlations, we can replace the parallel channels by a porous flow field. As a result, the porous flow fields quipped in a PEMFC model allows us to simplify the 3D model to a 2D model due to the nature of porous media which provides slip and no-flux conditions at the side walls; this is illustrated in Fig. 5.1 and 5.11. However, we note that the channels also affect the transport occurring in gas diffusion layers and current collectors which we intend to capture in the next section.

### 5.4.2 Correlation for parameters of the gas diffusion layers and current collectors

With a porous flow field, the transports of species, momentum, heat and electron are straightforward in the \( y \)-direction from the flow field to the catalyst layer. However, with a parallel channel, it is clearly that the rib of the channel will change the pathway of species, momentum, heat and electron transportations in the gas diffusion layers as well as in the current collectors. Consequently, it is necessary to introduce a correction factor for the diffusive coefficient such as permeability, diffusivity, heat and charge conductivities in the porous-type model so that it can capture the transport due to rib effects.

To determine the correction factor, we consider a general case with the variable \( \Psi \) that applies for all diffusive processes; the conservation equation for the 3D model with parallel channels is identical to Eq. 5.18 whereas the equation for the 2D model with porous flow field is given as

\[ \nabla (-\zeta D_{\text{eff}} \nabla \Psi) = 0, \quad (\text{gdl, cc}) \quad (5.27) \]
where \( \zeta \) is the correction factor. The procedure is similar to the one we use in obtaining the effective diffusive coefficient – providing the same inlet value of \( \Psi \) at flow field/gas diffusion layer interface, and then trying to get the same average flux at gas diffusion layer/catalyst layer interface – but we need to compute the correction factor numerically in this case. Furthermore, the correction factor is strongly depended on the width ratio; in other words, as the width ratio become larger, species and momentum transport is enhanced but such a geometry results in poor heat and charge transports, and vice versa. We therefore need to establish a correlation to describe the relation of correction factor with the ratio of channel width. For this purpose, the above general equations are implemented for a simple domain, e.g. the gas diffusion layer in Fig. 5.2 to compute automatically the values of the correction factor as the values of the width ratio vary. Fig. 5.4 shows the relation between the width ratio and correction factor, from which the correlation of \( \zeta \) expressed as a function of the width ratio \( R \) is given as

\[
\zeta = 0.160 - 0.052R + 1.287R^2, \quad 0.3 \leq R \leq 0.6
\]  

\[(5.28)\]

### 5.5 Verification

It is time to address the question we have raised previously in the introduction whether the 2D model with porous flow field can be replaced the 3D model with parallel channels in describing the transport phenomena in a PEMFC. To answer this question, we first secure the global verification by comparing the polarization curves obtained from both 2D and 3D models. As shown in Fig. 5.5, good agreement is achieved with maximum relative error of 2\%, comparing to 10\% error if no modification – porous medium approach and correction factor – is provided.

Further verifications are conducted by considering the local solutions – current den-
sity, mass fraction of oxygen and water, liquid saturation and temperature. For the 2D model, the local values are collected at the cathode gas diffusion layer/catalyst layer interface whereas the average values at a specified $x$-locations are computed at the same interface for the 3D model; here, we secure the local verification in a wide range of operating condition by presenting the results at three different cell voltages, e.g. $E_{\text{cell}} = 0.8, 0.5, 0.2$ V. As shown in Figs. 5.6a-5.6c, good agreements were achieved for local current density, mass fraction of oxygen and water in gas phase with maximum errors of around 5%. However, we lose the accuracy for the cases of temperature and liquid saturation – around 35% and 70% errors, respectively. As illustrated in Fig. 5.6d, the temperature predicted by the 2D model is higher than the 3D counterpart; that means the correction factor applied for the conservation of energy is too high. The reason is that heat is conducted through both fluid and solid phases in which the fluid will move to the plain channel whereas the heat conducted by solid will transfer to the
rib; this is in contrast to the cases of electron and species transports which are just transferred to either the plain channel or the rib – the general case where we obtain the correction factor. Since the temperature is overestimated, the liquid saturation computed from the 2D model is definitely lower than the one in 3D model as inferred in Fig. 5.6e.
Figure 5.6: The contribution of (a) local current density, [(b) and (c)] mass fraction of oxygen and water, (d) temperature and (e) liquid saturation from the 3D model at the cell voltage of (♦) 0.8V, (□) 0.5V, (▲) 0.2V and (—) corresponding 2D model.
5.6 Conclusions

A 3D PEMFC model equipped with parallel channels was reduced to a 2D model with porous flow field. We obtained the numerical permeability and effectively diffusive coefficients for a porous flow field; such a flow field can be used to replace the parallel channels in modeling the 3D model. The effect of the rib to the transport in gas diffusion layer and current collector was captured by introducing a correction factor. The verifications showed that good agreements were achieved at both global and local levels except for the temperature and liquid saturation distribution, which may require a thermal non-equilibrium model – two-equation model for the conservation of energy – is employed \cite{101}. In that case, we will be able to provide the correction factors separately for heat transfer in fluid and solid phases.

So far, the correction factor is correlated as a function of the width ratio. To enhance the feasibility of this modeling framework, it is necessary to generalize the correlation of the correction factor by taking into account the thickness and width of both the gas diffusion layer and current collector. Furthermore, the concept of porous medium approach can be extended to encompass other types of flow fields, e.g. serpentine or multiple serpentine channels.

As illustrated in Fig. 5.1 once the 3D model with parallel channels is reduced to the 2D model with porous flow field, it can be further reduced to a space-marching model by which we are able to reduce significantly the computational cost in building a stack of tens or even hundreds of single cells.
Chapter 6

Scaling Analysis and a Simple Correlation for the Cathode of a PEMFC

Scaling analysis of a two-dimensional (2D) steady-state, isothermal single-phase model for the cathode of a Proton Exchange Membrane Fuel Cell (PEMFC) had been carried out in order to, firstly, secure the typical scales for all variables a priori to numerical computation and secondly, to obtain a simple correlation accounting for quick and cheap prediction of the overall performance of the cathode as well as the whole cell. The cathode was chosen for the analysis, as it is the limiting half-cell of the PEMFC under most operating conditions. One of the key scales is that for current density, which is used to obtain a correlation for the overall cathode performance (in terms of iR-corrected polarization curve). A comparison of the scaling results with the experimental polarization curve (iR-corrected) as well as the full set of equations (solved numerically) reveals that the correlations give a good fit at current densities up to \(1.4 \times 10^4\) A m\(^{-2}\). Finally, we illustrate that we are able to predict the performance of the entire PEMFC in term of the polarization curve by incorporating the ohmic losses in the membrane.
and anode.

### 6.1 Introduction

Mathematical modeling of the fuel cell aids in our understanding of the series of intrinsically coupled physicochemical processes, which include mass and species transfer, momentum transfer, heat transfer, charge transfer and multiple electrochemical reactions. These processes are taking place simultaneously during fuel cell operation and are generally difficult to quantify experimentally. There is a large amount of models for the polymer electrolyte membrane fuel cell (PEMFC) that are one-, two- or three-dimensional, which take into account multiphase and non-isothermal conditions [6, 7]. These models are developed to study the water flooding issue [62], durability and degradation [63, 64], and fuel cell contamination [61]. However, these models are generally complex and not suitable for modelling of stacks that can comprise tens or even hundreds of single cells. Overall, modeling of the highly coupled non-linear transport phenomena is a challenge in light of the dimensionality and computational cost involved.

In our previous work [40], we have studied the relevant dimensionless numbers and scales to investigate the mechanisms for mass, momentum, species, heat and charge transfer. Here, a scaling analysis of a 2D steady-state, isothermal single-phase model for the cathode of a PEMFC is carried out in order to, firstly, secure the typical scales for all variables \textit{a priori} to numerical computation and, secondly, to obtain a simple correlation accounting for the overall performance of the cathode as well as the whole cell. These scales can be employed for (i) quick and cheap prediction of the fuel cell behavior, (ii) incorporation into system models as a PEMFC subset model, and (iii) providing good initial guesses for detailed numerical models. The cathode was chosen for the analysis, as it is the limiting half-cell of the PEMFC under most operating conditions.
## 6.2 Mathematical formulation

We consider a slender three-dimensional geometry consisting of a porous flow field (ff) adjacent to the gas diffusion layer (gdl) and the catalyst layer (cl) in the cathode of a PEMFC. The cathode was chosen as the starting point for the analysis since it is the limiting half-cell of the PEMFC in most operating conditions. The porous nature of the flow field and porous backing allows a reduction in dimensionality, since the changes in dependent variables in the spanwise direction are negligible due to slip conditions and no flux that can be invoked at the left and right walls of the channel. The geometry that we need to resolve can thus be reduced to the streamwise ($x$) and normal direction ($y$), as shown in Fig. 6.1.

![Figure 6.1: Schematic of the cathode side of a PEMFC.](image)

### 6.2.1 Governing equations

We solve for the continuity of mass, momentum, a ternary mixture of water ($\text{H}_2\text{O}$), nitrogen ($\text{N}_2$) and oxygen ($\text{O}_2$), and the conservation of charge in the solid phase given in Eq. 4.1, 4.2, 4.3, and 4.5. Note that, we have taken inertia into account in the mesh flow field by incorporating the Forchheimer term [24] into Darcy’s law in Eq. 4.2. The constitutive relations are given in Chapter 4.
6.2.2 Boundary conditions

Boundary conditions are prescribed at the inlet, outlet, upper wall, vertical walls, and membrane/catalyst layer interface:

- At the inlet \((x = 0 \text{ and } 0 \leq y \leq h_{\text{ff}})\) :
  \[ u^{(g)} = U^{\text{in}}, \quad c_{\text{O}_2}^{(g)} = c_{\text{in}}^{\text{O}_2}, \quad c_{\text{H}_2\text{O}}^{(g)} = c_{\text{in}}^{\text{H}_2\text{O}}, \quad \frac{\partial \phi^{(s)}}{\partial x} = 0. \]  \hspace{1cm} (6.1)

- At the outlet \((x = L \text{ and } 0 \leq y \leq h_{\text{ff}})\) :
  \[ p^{(g)} = p^{\text{ref}}, \quad \frac{\partial c_{\text{H}_2\text{O}}^{(g)}}{\partial x} = \frac{\partial \phi^{(s)}}{\partial x} = 0. \]  \hspace{1cm} (6.2)

- At the upper net wall \((y = h_{\text{ff}} \text{ and } 0 \leq x \leq L)\) :
  \[ v^{(g)} = 0, \quad \frac{\partial c_{\text{H}_2\text{O}}^{(g)}}{\partial y} = 0, \quad \phi^{(s)} = E_{\text{cathode}}. \]  \hspace{1cm} (6.3)

Note that, we reference the potential \(\phi^{(s)}\) to \(E_{\text{cathode}}\) instead of \(E_{\text{cell}}\) since only the cathode is considered. Hence, it is not suitable to use \(E_{\text{cell}}\) which includes the anode overpotential \(\eta_a\) and the ohmic loss in the membrane.

- At the vertical walls \((x = 0, L \text{ and } -(h_{\text{cl}} + h_{\text{gdl}}) \leq y \leq 0)\) :
  \[ u^{(g)} = 0, \quad \frac{\partial c_{\text{H}_2\text{O}}^{(g)}}{\partial x} = \frac{\partial \phi^{(s)}}{\partial x} = 0. \]  \hspace{1cm} (6.4)

- At the lowest boundary \((y = -(h_{\text{cl}} + h_{\text{gdl}}) \text{ and } 0 \leq x \leq L)\), we introduce the normal flow and flux due to water transport in the membrane, and no normal flux of
oxygen and temperature, as well as insulation of electric transfer

\[ \rho \mathbf{v} \cdot \mathbf{e}_y = \frac{i(s) \cdot \mathbf{e}_y}{4F} 4\alpha \text{H}_2\text{O}, \quad \text{N}_\text{H}_2\text{O} \cdot \mathbf{e}_y = \frac{i(s) \cdot \mathbf{e}_y}{4F} 4\alpha, \quad \text{N}_\text{O}_2 \cdot \mathbf{e}_y = 0, \quad \text{and} \quad \nabla \phi (s) \cdot \mathbf{e}_y = 0. \]

(6.5)

where \( \alpha = 0.25 \) is the amount of water molecules dragged with each proton through the membrane.[40]

### 6.3 Scaling analysis

In order to obtain the correlation for the overall cathode performance, we apply scaling analysis by non-dimensionalizing the governing equations and appropriate boundary conditions as well as the constitutive relations. The resulting scales can be used for quick and inexpensive prediction of the fuel cell behavior and provides good initial guesses for detailed numerical models.

#### 6.3.1 Nondimensional form

We introduce the following dimensionless variables

\[
\tilde{x} = \frac{x}{L}, \quad \tilde{y} = \frac{y}{h}, \quad \sigma = \frac{h}{L}, \quad \tilde{u} = \frac{u}{[u(s)]}, \quad \tilde{v} = \frac{v}{[v(g)]}, \quad \tilde{p} = \frac{p - p\text{ref}}{[p(g)]}, \quad \tilde{c}_i = \frac{c_i - c_i\text{ref}}{c_i\text{ref}}, \quad \tilde{N}_i = \frac{N_i}{[N_i]}, \quad \tilde{\phi} = \frac{\phi - \phi\text{ref}}{\phi\text{ref}}, \quad \tilde{J}_e = \frac{J_e}{[J_e]}, \quad \tilde{i} = \frac{i}{i(0)}, \quad \tilde{\rho} = \frac{\rho}{[\rho(g)]}, \quad \tilde{D}_i = \frac{D_i}{[D_i(g)]}.
\]

Here, [...] represents a typical scale. Note that the pressure gradient in the streamwise direction is scaled with the pressure drop in the \( x \) direction divided by the length scale \( L \). However, the normal pressure gradient does not necessary scale with this pressure drop divided by the normal length scale. Hence, we introduce different scales for pressure drop on the \( x \) and \( y \) directions as \( p_x^{(g)} \) and \( p_y^{(g)} \). Similarly for the concentrations,
we have $\left[ c_{i,x}^{(g)} \right]$ and $\left[ c_{i,y}^{(g)} \right]$ as concentration drop in the $x$- and $y$- directions, respectively. The above scales are different for various layers in the fuel cell and to differentiate them, we add subscripts to represent a specific layer, i.e. ‘ff’, ‘gdl’, ‘cl’ for flow field, gas diffusion layer and catalyst layer, respectively.

Introduce the above dimensionless variables into the describing equations and rearranging, we have

$$
\left[ u^{(g)} \right] \sigma \frac{\partial \left( \tilde{\rho}^{(g)} \tilde{u}^{(g)} \right)}{\partial \tilde{x}} + \left[ v^{(g)} \right] \frac{\partial \left( \tilde{\rho}^{(g)} \tilde{v}^{(g)} \right)}{\partial \tilde{y}} = \begin{cases}
- \frac{|J_c| h}{4F \rho^{(g)}} (2M_H_2O - M_O_2) \tilde{J}_c & \text{(cathode cl)} \\
0 & \text{(elsewhere)}
\end{cases}
$$

(6.6)

$$
\left[ \frac{p_x^{(g)}}{h_f} \right] \frac{\partial \tilde{p}^{(g)}}{\partial \tilde{x}} = - \frac{\mu^{(g)}}{\kappa} \left[ u^{(g)} \right] \tilde{u}^{(g)} - \frac{c_F \left[ \rho^{(g)} \right]}{\sqrt{\kappa}} \frac{\left[ u^{(g)} \right]^2}{\sqrt{\kappa}} \left( \tilde{u}^{(g)} \right)^2 + \frac{\left[ v^{(g)} \right]^2}{\left[ u^{(g)} \right]^2} \tilde{v}^{(g)} \tilde{\rho}^{(g)} \tilde{u}^{(g)}
$$

(6.7)

$$
\left[ \frac{p_y^{(g)}}{h_f} \right] \frac{\partial \tilde{p}^{(g)}}{\partial \tilde{y}} = - \frac{\mu^{(g)}}{\kappa} \left[ v^{(g)} \right] \tilde{v}^{(g)} - \frac{c_F \left[ \rho^{(g)} \right]}{\sqrt{\kappa}} \frac{\left[ v^{(g)} \right]^2}{\sqrt{\kappa}} \left( \tilde{v}^{(g)} \right)^2 + \frac{\left[ u^{(g)} \right]^2}{\left[ v^{(g)} \right]^2} \tilde{u}^{(g)} \tilde{\rho}^{(g)} \tilde{v}^{(g)}
$$

(6.8)

$$
\left[ u^{(g)} \right] \sigma \frac{\partial \left( \tilde{c}_{i,x}^{(g)} \tilde{u}^{(g)} \right)}{\partial \tilde{x}} + \left[ v^{(g)} \right] \frac{\partial \left( \tilde{c}_{i,x}^{(g)} \tilde{v}^{(g)} \right)}{\partial \tilde{y}} = \frac{\varepsilon^{3/2}}{h} \left[ \frac{D_i^{(g)}}{h} \right] \left[ \sigma^2 \frac{\partial}{\partial \tilde{x}} \left( \tilde{D}_i^{(g)} \frac{\partial \tilde{c}_{i,x}^{(g)}}{\partial \tilde{x}} \right) + \frac{\left[ c_{i,y}^{(g)} \right]}{c_{i,x}^{(g)}} \frac{\partial}{\partial \tilde{y}} \left( \tilde{D}_i^{(g)} \frac{\partial \tilde{c}_{i,x}^{(g)}}{\partial \tilde{y}} \right) \right] = \begin{cases}
- \frac{h}{c_{i,x}^{(g)}} \frac{|J_c|}{4F \rho^{(g)}} \tilde{J}_c & \text{(O}_2\text{ in cathode cl)} \\
- \frac{h}{c_{i,x}^{(g)}} \frac{|J_c|}{2F \rho^{(g)}} \tilde{J}_c & \text{(H}_2\text{O in cathode cl)} \\
0 & \text{(elsewhere)}
\end{cases}
$$

(6.9)

$$
- \sigma^2 \frac{\partial^2 \tilde{\phi}^{(s)}}{\partial \tilde{x}^2} - \frac{\partial^2 \tilde{\phi}^{(s)}}{\partial \tilde{y}^2} = - \frac{|J_c| h^2}{\sigma_{eff}^{(s)} \phi^{(s)}} \tilde{J}_c
$$

(6.10)
The dimensionless boundary conditions are now

\[ \tilde{u}(g) = \frac{U^{in}}{u(g)}, \quad \tilde{c}_i = \frac{c_i - c_1^{ref}}{c_i^{(g)}}, \quad \frac{\partial \tilde{c}_i}{\partial \tilde{x}} = 0 \quad \text{at} \quad \tilde{x} = 0, \quad 0 \leq \tilde{y} \leq 1, \quad (6.11) \]

\[ \tilde{p}(g) = 0, \quad \frac{\partial \tilde{c}_i}{\partial \tilde{x}} = \frac{\partial \tilde{\phi}^{(s)}}{\partial \tilde{x}} = 0 \quad \text{at} \quad \tilde{x} = 1, \quad 0 \leq \tilde{y} \leq 1, \quad (6.12) \]

\[ \tilde{v}(g) = 0, \quad \frac{\partial \tilde{c}_i}{\partial \tilde{y}} = \frac{\tilde{\phi}^{(s)}}{\tilde{\phi}(s)} = \frac{E_{\text{cathode}} - \phi^{ref}}{\tilde{\phi}(s)} \quad \text{at} \quad \tilde{y} = 1, \quad 0 \leq \tilde{x} \leq 1, \quad (6.13) \]

\[ \tilde{u}(g) = 0, \quad \frac{\partial \tilde{c}_i}{\partial \tilde{x}} = \frac{\partial \tilde{\phi}^{(s)}}{\partial \tilde{x}} = 0 \quad \text{at} \quad \tilde{x} = 0 \quad \text{and} \quad 1, \quad -\frac{h_{gdl} + h_{cl}}{h_{ff}} \leq \tilde{y} \leq 0, \quad (6.14) \]

At the lowest boundary, \( \tilde{y} = -\frac{h_{gdl} + h_{cl}}{h_{ff}} \) and \( 0 \leq \tilde{x} \leq 1 \), we have

\[ \tilde{v}(g) = \left[ \frac{\tilde{i}(s)}{\tilde{\rho}(g)} \right] \frac{M_{H_2O}}{[\rho(g)]} \frac{\alpha}{F} \frac{\tilde{\eta}(g)}{[\rho(g)]} \tilde{e}_y, \quad \tilde{N}_{H_2O} \cdot \tilde{e}_y = \left[ \frac{\tilde{i}(s)}{\tilde{\rho}(g)} \right] \frac{\alpha}{F} \frac{\tilde{\eta}(g)}{[\rho(g)]} \tilde{e}_y, \quad \tilde{N}_{O_2} \cdot \tilde{e}_y = 0, \quad \text{and} \quad \nabla \tilde{\phi}^{(s)} \cdot \tilde{e}_y = 0 \]

(6.15)

### 6.3.2 Determination of scales

At this stage, \([u(g)], [v(g)], [p(g)], [c_i^{(g)}], c_1^{ref}, [\tilde{\phi}(g)], [\tilde{\phi}(s)], [\tilde{\rho}(g)], \) \([\tilde{\phi}(s)], [\tilde{\rho}(g)], \) \([D_i^{(g)}], \) are unknown and will now be identified. These unknown will be determined to ensure that all dimensionless variables are bounded between zero and of order one.

Basically, the scales will be obtained by balancing two dominated terms in the equation. Here, we only present the scales which are necessary for securing the correlation of the fuel cell behavior.

**Velocity scales** - The \( x \)-velocity scale can be obtained from the inlet boundary condition, Eq. (6.11) By setting the dimensionless velocity equal to one, the scale of the velocity in the flow direction is as

\[ [u(g)]_H = U^{in}. \quad (6.16) \]
Next, considering the normal velocity, we know that the normal flow is caused by the reaction in the catalyst layer and normal flux at the lowest boundary. Hence, we balance the second term of the left hand side of Eq. \(6.6\) with the right hand side to get the first part of the scale for normal velocity accounting for flow due to reaction. The other part of this scale is obtained by balancing both sides of the lowest boundary condition, i.e. Eq. \(6.15\) and we have the following

\[
\left[ v^{(g)} \right] \sim \frac{\left[ i^{(s)} \right]}{4F \rho^{(g)}} \left[ 2(2\alpha + 1)M_{\text{H}_2\text{O}} - M_{\text{O}_2} \right], \tag{6.17}
\]

here, we have accounted for the fact that \(i^{(s)} = [J_c]h_{\text{cl}}\) as shown later in Eq. \(6.21\).

It should be noticed that the reaction is the dominant driving force for flow in the \(y\)-direction within the layers of the cathode, since no reaction occurs in the gas diffusion layer and flow field, the normal velocity scale obtained above is valid for these two layers due to the interfacial continuity.

Thus far, the scale for current density, \([i^{(s)}]\), remains unknown. However, the typical scale for current density is around \(10^4\text{A m}^{-2}\). Consequently, we estimate \([v^{(g)}]\) using Eq. \(6.17\) and deduce that the normal velocity scale is much larger than the aspect ratio multiply the streamwise velocity scale, we have the following criterion for the gas diffusion layer and catalyst layer that is

\[
[v^{(g)}] \gg \sigma [u^{(g)}]. \tag{6.18}
\]

With the satisfaction of criterion \(6.18\), we are able to neglect all the terms which are much smaller than order of one or in the order of \(\sigma^2\), the governing equations that are originally partial differential equations now become ordinary differential equations in the gas diffusion layer and catalyst layer. This indicates that all variables depend only in the \(y\)-direction in the gas diffusion layer and catalyst layer.
6.3. Scaling analysis

**Potential scales** - Considering the catalyst layer, the scale for potential can be derived by balancing the diffusion term with the source term in Eq. (6.10) as,

\[
\left[ \phi^{(s)} \right]_{cl} \sim \frac{[J_c] h_{cl}^2}{\sigma_{eff,cl}}.
\]

(6.19)

where \( h_{cl} \) is the thickness of catalyst layer. The scales for the potential within the flow field and gas diffusion layer can be obtained from the continuity of flux of charge at the flow field/gas diffusion layer and gas diffusion layer/catalyst layer interfaces respectively whereas the reference factors of potential can be obtained from the continuity of charge at the corresponding interface.

**Current density scale** - The dimensionless form of the local current density defined in Eq. (4.10) is as follows

\[
\bar{i}^{(s)} \left[ i^{(s)} \right] = -\sigma_{eff,cl} \frac{[\phi^{(s)}]}{h_{cl}} \frac{\partial \phi^{(s)}}{\partial \bar{y}}.
\]

(6.20)

Since terms on both sides of the above equation are equivalently important in physical sense, we hence balance both sides of the above equation and combining with Eq. (6.19) to obtain the scale for the local current density

\[
\left[ i^{(s)} \right] \sim \sigma_{eff,cl} \frac{[\phi^{(s)}]}{h_{cl}} = [J_c] h_{cl}
\]

(6.21)

**Scales for oxygen concentration** - Similar to potential, we balanced the normal diffusion term in Eq. (6.9) with the reaction term to obtain the scale for the concentration of oxygen in this active layer as

\[
\left[ c_{O_2,y}^{(g)} \right]_{cl} \sim \frac{[J_c] h_{cl}^2}{4F \varepsilon_{cl}^{3/2} D_{O_2}^{(g)}}.
\]

(6.22)
Note that the scales for the mass diffusion coefficients for each species are given as its value at the inlet condition, \[ D^{(g)}_1 = D^{(g)}_{1,0}. \]

To determine the scales for the concentration of oxygen in flow field and gas diffusion layer, we consider the gas diffusion layer/catalyst layer and flow field/gas diffusion layer interfaces. Due to the nature of the porous media, the mass transport in the normal direction is dominated by diffusion. Hence, the scale of the concentration flux can be obtained by non-dimensionalizing the flux of oxygen in Eq. (6.7) and balancing the left hand side with the diffusion term, and that is
\[
N^{(g)}_{\text{O}_2,y} = \frac{\varepsilon^{3/2} [D^{(g)}_{\text{O}_2}] [c^{(g)}_{\text{O}_2,y}]}{h}. \tag{6.23}
\]

The normal flux of concentration at the interfaces should be continuous and are given as
\[
N^{(g)}_{\text{O}_2,y}|_{\text{ff}} = N^{(g)}_{\text{O}_2,y}|_{\text{gdl}}, \quad \text{and} \quad N^{(g)}_{\text{O}_2,y}|_{\text{gdl}} = N^{(g)}_{\text{O}_2,y}|_{\text{cl}}. \tag{6.24}
\]

Based on these continuity conditions, we obtained the relationship of the scales for the normal flux of concentration of oxygen in the flow field and gas diffusion layer as the following
\[
\left[ c^{(g)}_{\text{O}_2,y} \right]_{\text{ff}} \sim \frac{[J_c] h_{\text{cl}} h_{\text{ff}}}{4F \varepsilon_{\text{ff}}^{3/2} [D^{(g)}_{\text{O}_2}]}, \quad \text{and} \quad \left[ c^{(g)}_{\text{O}_2,y} \right]_{\text{gdl}} \sim \frac{[J_c] h_{\text{cl}} h_{\text{gdl}}}{4F \varepsilon_{\text{gdl}}^{3/2} [D^{(g)}_{\text{O}_2}]}.
\tag{6.25}
\]

**Volumetric current density scale** - The inlet oxygen will be adsorbed into the flow field/gas diffusion layer interface and subsequently diffuse through the gas diffusion layer and into the active sites of the catalyst layer where electrochemical reaction takes place. The reference factor for the concentration of oxygen in the catalyst layer can be defined as the inlet concentration of oxygen subtract the drop of oxygen in the flow channel, gas diffusion layer and catalyst layer where it corresponds to the minimum concentration
6.3. Scaling analysis

value of oxygen. Specifically, this can be expressed mathematically as

$$c_{O_2, cl}^{ref} = c_{O_2}^{in} - \left[ c_{O_2,y}^{(g)} \right]_{fl} + \left[ c_{O_2,y}^{(g)} \right]_{gdl} + \left[ c_{O_2,y}^{(g)} \right]_{cl}. \quad (6.26)$$

Non-dimensionalizing the volumetric current density and incorporating the reference factor of concentration, we have the following dimensionless form of Eq. 4.45

$$J_c \left[ J_c \right] = -j_{c,0}^{ref} \exp \left[ -\frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{\bar{T}} \right) \right] \exp \left( -\frac{\alpha_c}{RT} F \eta_c \right) \times$$

$$\times \left[ c_{O_2, cl}^{(g)} \right]_{cl} + \left[ c_{O_2}^{in} - \left( \left[ c_{O_2,y}^{(g)} \right]_{fl} + \left[ c_{O_2,y}^{(g)} \right]_{gdl} + \left[ c_{O_2,y}^{(g)} \right]_{cl} \right) \right] \left( \frac{c_{O_2}^{in}}{c_{O_2, cl}^{ref}} \right). \quad (6.27)$$

The scale for volumetric current density can be extracted from the above equation and is given as

$$\left[ J_c \right] = j_{c,0}^{ref} \exp \left[ -\frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{\bar{T}} \right) \right] \exp \left( -\frac{\alpha_c}{RT} F \eta_c \right) \frac{c_{O_2}^{in}}{c_{O_2, cl}^{ref}} - \left( \left[ c_{O_2,y}^{(g)} \right]_{fl} + \left[ c_{O_2,y}^{(g)} \right]_{gdl} + \left[ c_{O_2,y}^{(g)} \right]_{cl} \right). \quad (6.28)$$

Substituting Eq. 6.25 into the above equation and rearranging, we have the following scale for the volumetric current density

$$\left[ J_c \right] = \frac{\Theta c_{O_2}^{in}}{1 + \Theta \frac{h_{el}}{4F \left[ c_{O_2, cl}^{ref} \right]_{fl}} \left( \frac{h_{fl}}{\varepsilon_{fl}} + \frac{h_{gdl}}{\varepsilon_{gdl}} \right)}, \quad (6.29)$$

where

$$\Theta = j_{c,0}^{ref} \exp \left[ -\frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{\bar{T}} \right) \right] \exp \left( -\frac{\alpha_c}{RT} F \eta_c \right) \frac{1}{c_{O_2, cl}^{ref}}. \quad \text{(6.28)}$$

The limiting volumetric current density can be obtained directly from Eq. 6.29. One knows that when the over-potential reaches negative infinity ($\eta_c \rightarrow -\infty$), the current

$$\left[ J_c \right] = \frac{\Theta c_{O_2}^{in}}{1 + \Theta \frac{h_{el}}{4F \left[ c_{O_2, cl}^{ref} \right]_{fl}} \left( \frac{h_{fl}}{\varepsilon_{fl}} + \frac{h_{gdl}}{\varepsilon_{gdl}} \right)}, \quad (6.29)$$

where

$$\Theta = j_{c,0}^{ref} \exp \left[ -\frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{\bar{T}} \right) \right] \exp \left( -\frac{\alpha_c}{RT} F \eta_c \right) \frac{1}{c_{O_2, cl}^{ref}}. \quad \text{(6.28)}$$

The limiting volumetric current density can be obtained directly from Eq. 6.29. One knows that when the over-potential reaches negative infinity ($\eta_c \rightarrow -\infty$), the current
density reaches its limiting value, hence, Eq. \[6.29\] reduces to the Eq. \[6.30\]

\[
[J_c]_{\text{limit}} = \lim_{n_c \to \infty} [J_c] = \frac{c_{\text{in}}^{\text{O}_2}}{4F D_{\text{O}_2}^{(g)} \left( \frac{h_{\text{eff}}}{3/2} + \frac{h_{\text{gdl}}}{5/2} \right)}.
\] \[6.30\]

Additionally, the limiting volumetric current density can also be determined when the oxygen from the net diffusing through the gas diffusion layer are consumed completely in the active layer, i.e. the concentration of oxygen at the gas diffusion layer/catalyst layer interface is equal to zero.

**Stoichiometry** - The definition of stoichiometry is given as the ratio between the total mass fluxes of oxygen supplied into the cathode to the oxygen consumed by the electrochemical reaction in the active layer. For our 2D model, we are able to extract the following relationship according to the definition of stoichiometry

\[
\xi_c^{\text{in}} U_c^{\text{in}} = \frac{\left[i(s)\right] L}{4F h_{\text{eff}}} \xi_c.
\] \[6.31\]

Performing a global mass balance for the oxygen component which mean the flux of oxygen at the inlet equal to the one at the outlet plus the one consumed by the reaction at the catalyst layer, yields the scale for flux of oxygen at the outlet and is given as

\[
c_{\text{O}_2}^{\text{out}} U_c^{\text{out}} = \frac{\left[i(s)\right] L}{4F h_{\text{eff}}} (\xi_c - 1).
\] \[6.32\]

Now, considering the overall mass balance for the net only, we have the following expression for the outlet velocity from which the scale for concentration of oxygen at the outlet is derived by combining with equation \[6.17\], \[6.31\] and \[6.32\]

\[
U_c^{\text{out}} = U_c^{\text{in}} + \frac{\left[v(g)\right] L}{h_{\text{eff}}}, \quad \text{and} \quad c_{\text{O}_2}^{\text{out}} = \frac{\xi_c - 1}{\frac{c_{\text{in}}^{\text{O}_2}}{c_{\text{O}_2}} + \frac{2(2a+1)M_{\text{H}_2O} - 2M_{\text{O}_2}}{\rho_{\text{eff}}}}.
\] \[6.33\]
From Eq. 6.33, one can see that when the stoichiometry becomes one corresponding to total mass fluxes of oxygen going into the cathode equals to that of the oxygen being consumed at the active layer, the concentration at the outlet will be zero. On the other hand, when the stoichiometry reaches infinity, the amount of oxygen consumed in active layer is negligible as compared to the inlet oxygen concentration and consequently, the concentration of oxygen at the outlet will be equal to that of the inlet.

### 6.4 Correlation for cathode performance

The correlation for the performance of cathode is based on Eq. 6.29 and can be improved for more accurate by introducing various means of the concentrations of oxygen. Since the concentration of oxygen is at its highest at the inlet and drops non-linearly along the channel, using inlet concentration as the reference factor for concentration of oxygen in Eq. 6.29 results in an over-estimate of the current density compared to the average current density value. For this reason, an average concentration of the inlet and outlet oxygen concentrations should be applied using various means such as arithmetic, geometric, harmonic, log means and are given as follows.

\[
c_{\text{Arith}}^{O_2} = \frac{c_{\text{in}}^{O_2} + c_{\text{out}}^{O_2}}{2}; c_{\text{Geom}}^{O_2} = \sqrt{c_{\text{in}}^{O_2}c_{\text{out}}^{O_2}}; c_{\text{Harm}}^{O_2} = \frac{2(c_{\text{in}}^{O_2}c_{\text{out}}^{O_2})}{c_{\text{in}}^{O_2} + c_{\text{out}}^{O_2}}; c_{\text{log}}^{O_2} = \frac{c_{\text{in}}^{O_2} - c_{\text{out}}^{O_2}}{\log\left(\frac{c_{\text{in}}^{O_2}}{c_{\text{out}}^{O_2}}\right)}
\]  

(6.34)

Introducing the means and the scale presented by Eq. 6.21 into Eq. 6.29 and 6.30, we have

\[
\left[ \dot{i}(s) \right] = \frac{\Theta h_{cl}c_{\text{mean}}^{O_2}}{1 + \Theta \frac{h_{cl}}{4F} \left[ \frac{h_{\text{eff}}}{e^{\mu_2}z_{\text{eff}}} + \frac{h_{\text{gdl}}}{e^{\mu_2}z_{\text{gdl}}} \right]}, \quad \text{and} \quad \left[ \dot{i}(s) \right]_{\text{limit}} = \frac{h_{cl}c_{\text{mean}}^{O_2}}{4F} \left[ \frac{h_{\text{eff}}}{e^{\mu_2}z_{\text{eff}}} + \frac{h_{\text{gdl}}}{e^{\mu_2}z_{\text{gdl}}} \right]
\]

(6.35)
6.5 Results and discussion

In this section, we first carry out the validation of the numerical solution (full set of equations), for which the base case geometrical and physical parameters, as well as operating conditions are based on the experiments by Noponen et al. [79] (see case \(a\) in Table 4.1); other parameters are given in Table 4.2. Here, we assume the electrical conductivity of membrane as constant, i.e. \(5 \text{ S m}^{-1}\). Furthermore, we have obtained the adapted parameters – the cathode reference exchange current density, \(j_{\text{c}, \text{ref}} = 5 \times 10^4 \text{ A m}^{-2}\), and cathode transfer coefficient, \(\alpha_c = 0.88\).

Finally, a simple correlation of the performance of the entire cell is given, which includes the anode as well as membrane. This extension requires that the anode and membrane are operated at conditions of sufficiently high stoichiometry and humidification, so that the anode does not adversely affect the overall cell performance.

6.5.1 Cathode performance and validation

The full set of governing equations are solved numerically for the case of 2D, isothermal and steady-state conditions with COMSOL Multiphysics [98]. Polarization curves based on the correlation from Eq. 6.35 and from the full set of equations were obtained for validation with experimental data. The results in Fig. 6.2 show that all polarization curves agree well with the experimental counterpart above around \(2 \times 10^3 \text{ A m}^{-2}\). The deviation at lower current densities most likely originate from the limitations of the Tafel law. Overall, the predictions from the scaling analysis give a good fit with the numerical results for the whole range. Furthermore, we have verified (not shown here) the correlation with the full set of equations at various stoichiometries.
6.5. Results and discussion

<table>
<thead>
<tr>
<th>Current density / A.m$^{-2}$</th>
<th>Voltage / V</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.84</td>
</tr>
<tr>
<td>5,000</td>
<td>0.74</td>
</tr>
<tr>
<td>10,000</td>
<td>0.76</td>
</tr>
<tr>
<td>15,000</td>
<td>0.78</td>
</tr>
</tbody>
</table>

Figure 6.2: Polarization curves at a stoichiometry of 2.3: (— — —) full set of equations, (· · ·) harmonic, (— —) geometric, (— — —) log, (— —) arithmetic means, and (■) experiments [79].

6.5.2 A correlation for the overall cell performance

Using the scaling analysis results, we are able to obtain a simple correlation for the performance of the entire cell based on the Eq. 2.16 and the expression is given as follows

$$E_{\text{cell}} = E_{\text{cathode}} - |\eta_a| - \bar{i}_{\text{avg}} \left( \frac{h_m}{\sigma_{\text{eff},m}} + \frac{2h_{\text{cl}}}{\sigma_{\text{eff},\text{cl}}} + \frac{2h_{\text{gdl}}}{\sigma_{\text{eff},\text{gdl}}} + \frac{2h_{\text{ff}}}{\sigma_{\text{eff},\text{ff}}} \right) \quad (6.36)$$

where $E_{\text{cathode}} = E_{\text{rev}} - |\eta_c|$. $h_m$, $h_{\text{cl}}$, $h_{\text{gdl}}$, $h_{\text{ff}}$ are the thickness of membrane, catalyst layer, gas diffusion layer and flow channel respectively, and $\sigma_{\text{eff},m}^{(m)}$, $\sigma_{\text{eff},\text{cl}}^{(s)}$, $\sigma_{\text{eff},\text{gdl}}^{(s)}$, $\sigma_{\text{eff},\text{ff}}^{(s)}$ are the corresponding electrical conductivities for different layers in the fuel cell. In most operating condition, the value of anode overpotential is very small and can be ignored. The polarization curve for the whole cell running at a cathode stoichiometry condition of...
2.3 is depicted in Fig. 6.3. Predictions based on the correlation using the aforementioned various means show good agreement up to a current density of $1.4 \times 10^4$ A m$^{-2}$.

![Polarization curves for experiments and model predictions at a stoichiometry of 2.3. Experimental polarization curves [79]: (▼) the measured potential of the cell, (■) the iR-corrected potential. Model predictions: (——) full set of equations, (····) harmonic, (-----) geometric, (---) log, (- - -) arithmetic means.](image)

6.6 Conclusions

A 2D, single-phase model, consisting of the continuity, momentum, species and charge conservation equations, have been implemented and scaling analysis was applied to extract the proper scales that allows us to quantify the transport mechanisms in the cathode side of the cell a priori to numerical computation. The governing equations are then solved numerically for the cathode side of a PEMFC under steady state condition,
and the obtained polarization curves are validated with experiments.

We have obtained a half-cell correlation based on the current density scale and various means of the inlet and outlet oxygen concentrations are investigated. All correlations agree well with the experimental polarization curve (iR-corrected) as well as the predicted polarization curves from the full set of equations (solved numerically). Finally, the performance of the whole cell can be predicted by incorporating the resistances of the membrane and anode without having to solve the full set of governing equations.

We will in the next Chapter show how the scaling analysis can help in reducing the governing equations from elliptic to parabolic partial differential equations.
Chapter 7

Development of Fast and Efficient Mathematical Models for the Cathode of a PEMFC

An isothermal one-phase model that takes into account conservation of momentum, mass, species and charge in the cathode of a proton exchange membrane fuel cell (PEMFC) is presented and analyzed. The original elliptic partial differential equations (PDEs) are reduced to a set of parabolic PDEs in the flow field (ff), coupled with a set of ordinary differential equations (ODEs) in the gas diffusion layer (gdl) and catalyst layer (cl) on the cathode side. The present cathode model is shown to capture the overall behavior of the PEMFC, including the membrane and anode, provided these are operated at sufficiently high stoichiometry and humidification levels. The computational cost in terms of (i) time to reach convergence as well as (ii) memory usage is reduced significantly by this approach. The original and reduced models are validated with experiments, both for the iR-corrected as well as the full polarization curves, and good agreement is achieved. The introduction of stoichiometry with a potentiostatic boundary condition requires iterations to obtain the inlet velocity, which causes the
computational time to increase. These iterations can be omitted by implementing a 'numerical current collector' with a galvanostatic boundary condition, which leads to speedier convergence rate for the full set of equations.

7.1 Introduction

In recent years, there have been significant advances in the development of mathematical and computational models that describe local physical phenomena in the PEMFC. These models are by their very nature generally highly non-linear, elliptic, coupled, multi-dimensional and computationally expensive to solve for (see e.g. 6, 7, 61–64). As such, applying these models to PEMFC stacks, comprising tens or even hundreds of single cells, will come at a hefty computational cost, both in terms of computational power and time. It is therefore of interest to derive modified or reduced mathematical models that can solve for and predict the local behavior of each cell in a PEMFC stacks at a reasonable cost, whilst maintaining all the essential physics. To achieve such a reduction, we exploit the slenderness of the typical PEMFC cell to obtain a model for the conservation of momentum, mass, species and charge whose mathematical nature, originally elliptic, is reduced to a set of parabolic PDEs in the flow field and a set of ODEs in the gas diffusion layer and catalyst layer of the cathode. We focus on the cathode – the limiting half-cell under most operating conditions – as a first step towards a fully reduced cell model that can be incorporated into a stack model. This model extends our previous work 102 to encompass the catalyst layer, as illustrated in Fig. 7.1.

The present cathode model is also able to predict the overall cell performance (polarization curve), provided that the membrane and anode are operated at sufficiently high stoichiometry and humidification levels.

The introduction of stoichiometry with a potentiostatic boundary condition requires
iterations to obtain the inlet velocity, which causes the computational time to increase. These iterations can be omitted by implementing a galvanostatic boundary condition at the current collector of the cathode. However, in doing so, one needs to be careful so as not to affect the current density distribution in the cell. We show here that this can be accomplished by the introduction of an additional layer, a 'numerical current collector', on top of the flow field or existing current collector, which results in faster convergence rate for the full set of equation.

7.2 Mathematical formulation

In this section, we present the reduced model with the reduced set of governing equations based on the simplifications obtained from the scaling analysis (see Chapter 6 and [103]) and our previous work [102]. The reduced governing equations comprise of a set of parabolic PDEs in the flow field coupled with a set of ODEs in the $y$-direction in the gas diffusion layer and catalyst layer, as illustrated schematically in Fig. 7.1. The computational domain consists of a flow field equipped with a mesh adjacent to the gas diffusion layer and the catalyst layer of the cathode.
7.2.1 Governing equations

We solve for the continuity of mass, momentum, a ternary mixture of water \((H_2O)\), nitrogen \((N_2)\) and oxygen \((O_2)\), and the conservation of charge in the solid phase given in Eq. 4.1, 4.2, 4.3, and 4.5. Note that, we have taken inertia into account in the mesh flow field by incorporating the Forchheimer term \([24]\) into Darcy’s law in Eq. 4.2. The constitutive relations are given in Chapter 4.

7.2.2 Governing equations for the reduced model

According to the scaling analysis shown in Chapter 6, we can introduce the following main simplifications (leading order approximations):

- Darcy’s equation can be used instead of the Forchheimer equation in the gas diffusion layer and catalyst layer;

- The governing equations reduce to a set of parabolic PDEs in the flow field;

- The governing equations reduces to a set of ODEs in the \(y\)-direction in the gas diffusion layer and catalyst layer;

- The equation for conservation of charge reduces to an ODE in the \(y\)-direction everywhere.

Based on these simplifications, the reduced governing equations for the porous flow field can be written as

\[
\frac{\partial}{\partial x} \left( \rho^{(g)} u^{(g)} \right) + \frac{\partial}{\partial y} \left( \rho^{(g)} v^{(g)} \right) = 0
\]  
\[
\frac{\partial p^{(g)}}{\partial x} = -\frac{\mu^{(g)}}{\kappa} u^{(g)} - \frac{\rho^{(g)} c_F}{\sqrt{\kappa}} \sqrt{(u^{(g)})^2 + (v^{(g)})^2} u^{(g)}
\]  
\[
\frac{\partial p^{(g)}}{\partial y} = 0
\]
\[
\frac{\partial}{\partial x} \left( c_i^{(g)} u^{(g)} \right) + \frac{\partial}{\partial y} \left( c_i^{(g)} v^{(g)} \right) - \varepsilon^{3/2} \frac{\partial}{\partial y} \left( D_i^{(g)} \frac{\partial c_i^{(g)}}{\partial y} \right) = 0 \tag{7.4}
\]

\[
\frac{\partial^2 \phi^{(s)}}{\partial y^2} = 0 \tag{7.5}
\]

For the gas diffusion layer and catalyst layer, we obtain

\[
\frac{\partial}{\partial y} \left( \rho^{(g)} u^{(g)} \right) = \begin{cases} 
\frac{M_{O_2} J_e}{4F} - \frac{M_{H_2O} J_e}{2F} & \text{(cathode cl)} \\
0 & \text{(cathode gdl)}
\end{cases}, \tag{7.6}
\]

\[
\frac{\partial p^{(g)}}{\partial y} = -\frac{\mu^{(g)}}{\kappa} v^{(g)}, \tag{7.7}
\]

\[
\frac{\partial}{\partial y} \left( c_i^{(g)} v^{(g)} \right) - \varepsilon^{3/2} \frac{\partial}{\partial y} \left( D_i^{(g)} \frac{\partial c_i^{(g)}}{\partial y} \right) = \begin{cases} 
\frac{J_e}{2F} & \text{(O}_2\text{ in cathode cl)} \\
-\frac{J_e}{2F} & \text{(H}_2\text{O in cathode cl)} \\
0 & \text{(cathode gdl)}
\end{cases}, \tag{7.8}
\]

\[
\frac{\partial}{\partial y} \left( -\sigma^{(s)} \phi^{(s)} \right) = \begin{cases} 
-J_e & \text{(cathode cl)} \\
0 & \text{(cathode gdl)}
\end{cases}. \tag{7.9}
\]

To further reduce the number of dependent variables, we introduce the stream function, \(\psi\), in the flow field, defined as

\[
u^{(g)} = \frac{1}{\rho^{(g)}} \frac{\partial \psi}{\partial y} \quad \text{and} \quad v^{(g)} = -\frac{1}{\rho^{(g)}} \frac{\partial \psi}{\partial x}. \tag{7.10}
\]

With the stream function, the continuity Eq. 7.1 in the flow field is automatically satisfied; hence, we only need two dependent variables (\(p^{(g)}\) and \(\psi\)) instead of three (\(p^{(g)}, u^{(g)}, v^{(g)}\)). Furthermore, we can implement the model numerically by considering the \(x\)-dependent variables as a timelike variable in order to reduce the dimensionality.
and employ fast space-marching algorithms with adaptive stepping in the streamwise direction ($x$-direction).

For the sake of brevity, we refer the boundary conditions for the full set of equations in Chapter 6 and present the boundary conditions for the reduced model as.

- At the inlet ($x = 0$, $0 \leq y \leq h_{ff}$), we specify the inlet velocity, pressure (for the reduced model), and concentrations

$$u^{(g)} = U^{\text{in}}, \quad p^{(g)} = p^{\text{ref}}, \quad c_{\text{in}}^{(g)} = c_{\text{O}_2}^{\text{in}}, \quad c_{\text{in}}^{(g)} = c_{\text{H}_2\text{O}}^{\text{in}},$$  \hspace{1cm} (7.11)

here, the boundary conditions of velocity can be rewritten in terms of the stream function as

$$\psi = U^{\text{in}} \rho^{\text{in}} y.$$  \hspace{1cm} (7.12)

In general, a fuel cell is operated at a certain stoichiometry. The stoichiometry, $\xi_c$, is defined as the ratio of the amount of reactant supplied to the amount of reactant required by the electrochemical reaction in the catalyst layers to generate the overall average current density, $i_{\text{avg}}$. With the introduction of stoichiometry, the cathode inlet velocities can be computed as

$$U^{\text{in}} = \frac{i_{\text{avg}} L}{4Fh_{ff}c_{\text{in}}^{\text{in}} \xi_c}.$$  \hspace{1cm} (7.13)

- At the upper net wall ($y = h_{ff}$, $0 \leq x \leq L$), we set no normal flow, no componental fluxes, and the cathode potential

$$v^{(g)} = 0, \quad \frac{\partial c^{(g)}}{\partial y} = 0, \quad \phi^{(s)} = E_{\text{cathode}},$$  \hspace{1cm} (7.14)

where the boundary condition of velocity can be written in terms of the stream
function as

$$\psi = u^{\text{in}} \rho^{\text{in}} h_{\text{eff}}$$  \hspace{1cm} (7.15)

- At the lowest boundary \((y = -(h_{\text{cl}} + h_{\text{gdl}}))\) and \(0 \leq x \leq L\), we have normal flux due to water transport in the membrane, no normal flux of oxygen, and no electric charge transfer

$$v_1^{(g)} = \frac{\alpha M_{\text{H}_2\text{O}}}{F \rho^{(g)}} \cdot i^{(s)} \cdot e_y, \quad N_{\text{H}_2\text{O}}^{(g)} \cdot e_y = \frac{\alpha}{F} i^{(s)} \cdot e_y, \quad N_{\text{O}_2}^{(g)} \cdot e_y = i^{(s)} \cdot e_y = 0$$  \hspace{1cm} (7.16)

### 7.2.3 Potentiostatic vs. galvanostatic boundary condition

The potentiostatic condition is used by many authors in the literature due to its straightforward implementation. However, once a stoichiometric flow condition is introduced, the use of the potentiostatic condition leads to an increase in computational time as we have to iterate until we find the correct inlet velocity that corresponds to the stoichiometry. If we apply a galvanostatic boundary condition, i.e. a stated average current density value to calculate the cell voltage, the inlet velocity can be directly determined without any iteration. The galvanostatic approach, however, requires careful implementation so as not to artificially disturb the local current density distribution in the cell. This is especially the case if the current density distribution at the flow field/current collector \((y = h_{\text{eff}})\) or at the current collector (not shown here) is uneven, and usually unknown \textit{a priori} to computations. To ensure that a prescribed current density (galvanostatic condition) gives the same solution as a prescribed potential (potentiostatic condition), we add a 'numerical current collector', as shown in Fig. 7.2.

If one considers the actual current collector of the cathode as well, one would introduce this 'numerical current collector' on top of the current collector instead of the flow
field as here. The boundary condition at \( y = h_{ff} + h_{ncc} \) can now be given as

\[
- \sigma_{eff}^{(s)} \frac{\partial \phi^{(s)}}{\partial y} = i_{avg}. \tag{7.17}
\]

Here, it is important that the thickness, \( h_{ncc} = 3 \times 10^{-4} \) m (assumed), and electrical conductivity, \( \sigma_{eff,ncc} = 10^{10} \) S m\(^{-1}\) (assumed), of this 'numerical current collector' are large enough so as not to influence the current density profile.

### 7.3 Results and discussion

In this section, the full set of governing equations (elliptic PDEs) presented in Section 7.2.1 is solved with Comsol Multiphysics [98], and validated with experimental results. Then, the reduced model outlined in Section 7.2.2 is implemented in COMSOL Multiphysics as well, and the predictions from the reduced model are verified with those from the full set of equations. Finally, the computational cost in terms of time and memory consumption are highlighted and discussed.
7.3. Results and discussion

7.3.1 Validation

The base case for the geometrical and physical parameters, as well as operating conditions are based on the experimental setup and operating conditions in Noponen’s paper [79], (see case (a) in Table 4.1); other parameters are given in Table 4.2.

![Polarization curves](image)

Figure 7.3: Polarization curves for experiments and model predictions at a stoichiometry of 2.3. Experimental polarization curves [79]: (▼) the measured potential of the cell, (■) the iR-corrected potential. Model predictions using (—) potentiostatic and (★) galvanostatic conditions.

First, the full set of governing equations are solved for with both potentiostatic and galvanostatic (added layer for the ’numerical current collector’) and the resulting cathode polarization curves (iR corrected polarization curve, anode overpotential neglected) are compared with experiments [79]. As can be inferred from Fig. 7.3 good agreement was obtained and both boundary conditions predict the same polarization curve. The deviation at low current densities ($\lesssim 2 \times 10^3$ A m$^{-2}$) is most likely due to the limitations
of the Tafel law, which is not valid at low current densities. We are further able to predict
the overall fuel cell performance by introducing scales (see [103] for details), as can be
inferred from the lower curve/symbols in Fig. 7.3.

7.3.2 Verification

The model based on the full set of equations is then solved parametrically for various
values of the stoichiometry. The obtained local current density in the streamwise direc-
tion (x-direction) for different stoichiometries at a cathode potential of \(E_{\text{cathode}} = 0.73\)
V are used to compare with the corresponding counterparts from the reduced govern-
ing equations, and the results can be found in Fig. 7.4. Good agreement between the
solution of the full set of equations and the reduced model is achieved.

Figure 7.4: Verification of the reduced model with the full set of equations at various
stoichiometries. The lines correspond to the predictions from the reduced model and
the symbols from the full set of equations: (♦) 1.5, (▼) 2.0, (★) 2.3, (▲) 3.0, (■) 5.0.
7.3.3 Computational cost

Next, we consider the computational cost in terms of time to reach a converged solution and the memory requirements for the full set of elliptic PDEs and the reduced model. The computational cost depends strongly on i) the mesh, ii) the initial guess of the variables, as well as iii) the tolerance that is set. The geometry of the domain is uniform, allowing us to use quadrilateral elements for the elliptic model with 25 elements in the $y$-direction and 150 elements in the $x$-direction. Note that we increase the number of elements in the $x$-direction at the inlet and outlet for a smoother converged solution.

For the reduced model, implemented as a 1D model for the $y$-direction and space-marching for the $x$-direction, 25 nodes are specified for the $y$-axis. The resolution in the $x$-direction is adaptively iterated for by stepping to maintain the specified tolerance, whilst minimizing the amount of steps required.

One way to reduce the computational time is to provide good initial guesses for the variables, which can be obtained from the scaling analysis that we have carried out in Chapter 6. Here, we focus on the initial guess of the velocity, since it varies strongly and is highly dependent on the stoichiometry. It can be determined from

$$U_{\text{in}} = \left[ \frac{\dot{i}^{(b)}}{i_{\text{in}}} \right] \frac{L}{4Fh_{\text{eff}}c_{\text{O}_2}} \xi_c. \quad (7.18)$$

For the case where the scales are not invoked, the inlet velocity is arbitrarily set to a 'standard' 1 ms$^{-1}$.

Finally, addressing the last point stated above, the time required also depends on the accuracy of the solution based on the tolerance we set. In solving the reduced model, we set the tolerance to $10^{-3}$, which is sufficiently low for our purpose. Table 7.1 shows the time required for solving the elliptic and the reduced model, both with and without stoichiometry at $E_{\text{cathode}} = 0.73$ V. Furthermore, we also record the random
access memory (RAM) usage that is required. When solving the elliptic model with 
potentiostatic condition, we require 1 GB RAM for the case with constant inlet velocity, 
and around 1.7 - 1.8 GB for the case with stoichiometry. For galvanostatic conditions, 
only 1 GB RAM is needed, irrespective of whether stoichiometry is invoked or not. For 
the reduced model, we require only 0.23 GB RAM.

The results show that without introducing stoichiometric flow conditions, a typical run (at a fixed voltage, e.g. $E_{\text{cathode}} = 0.73V$) takes around 3 seconds and 29 seconds for 
the reduced and elliptic models, respectively, to converge.

With stoichiometry, which requires iteration to obtain the inlet velocity when a po-
tentiostatic condition is used, the computational time is increased to 100-130 seconds 
(depending on the stoichiometry) and the memory required is almost doubled for the 
elliptic code. One can also see that the number of iterations required increases with the 
value of stoichiometry. It is clear that the inlet velocity is dependent on the stoichiom-
etry and hence, the increase in stoichiometry leads to higher inlet velocity values and, 
consequently, these higher values deviate significantly from the original initial guess of 
1 ms$^{-1}$. As such, it is difficult to achieve a converged solution when running at high 
stoichiometry values, in particular at stoichiometry conditions above 5 due to the large 
deviation from the initial guess. In contrast to the potentiostatic condition, by using the 
galvanostatic condition, the computational time is not adversely affected by introducing 
the stoichiometry and changing its value. We can see that the number of iterations 
remain at 4 since the inlet velocity can be computed directly from the average current 
density (see Eq. 7.18). In this way, we are able to more easily obtain the converged 
solution at high stoichiometries.

For the reduced model, the introduction of stoichiometry also leads to an increase 
in computational time (around 15-20 seconds). However, introduction of the initial 
values from the scaling analysis can achieve a reduction of computational time to less
Table 7.1: Time required for the various case in seconds. The numbers indicated in the brackets represent the iterations required by COMSOL Multiphysics.

<table>
<thead>
<tr>
<th>Stoichiometry</th>
<th>Elliptic Potentiostatic</th>
<th>Galvanostatic</th>
<th>Parabolic without scale</th>
<th>with scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>130 (5)</td>
<td>39 (6)</td>
<td>20 (6)</td>
<td>4 (1)</td>
</tr>
<tr>
<td>2.0</td>
<td>110 (6)</td>
<td>27 (4)</td>
<td>19 (6)</td>
<td>7 (2)</td>
</tr>
<tr>
<td>2.3</td>
<td>100 (6)</td>
<td>28 (4)</td>
<td>19 (6)</td>
<td>10 (3)</td>
</tr>
<tr>
<td>3.0</td>
<td>110 (7)</td>
<td>28 (4)</td>
<td>19 (6)</td>
<td>9 (3)</td>
</tr>
<tr>
<td>5.0</td>
<td>—</td>
<td>30 (4)</td>
<td>15 (5)</td>
<td>9 (3)</td>
</tr>
<tr>
<td>Constant $U^{in}$</td>
<td>29 (4)</td>
<td>28 (4)</td>
<td>3</td>
<td>—</td>
</tr>
</tbody>
</table>

7.4 Conclusions

The full set of governing equations (elliptic PDEs), consisting of the continuity, momentum, species and charge conservation equations have been implemented and solved successfully for the cathode of a PEMFC in which both potentiostatic and galvanostatic conditions are used. The reduced model is derived based on a scaling analysis. The local current density from the reduced model was verified and was found to be in good agreement with the elliptic counterpart. The results show that implementation of the elliptic model with a galvanostatic condition can help to avoid the increase of computational
cost when stoichiometry is invoked. Furthermore, both time and memory required for solving the reduced model with initial values obtained from the scales is reduced significantly compared to solving the elliptic model with a potentiostatic condition. The cathode model presented here was also shown to be able to predict the overall cell behavior, i.e. including membrane and anode, provided these are operated at sufficiently high stoichiometries and humidification.
Chapter 8

Validated Reduction and Accelerated Numerical Computation of a Model for the PEMFC

Amongst the severest drawbacks of many models for the proton exchange membrane fuel cell (PEMFC) are excessive memory requirements and computing time; consequently, using these for stack modeling is impractical. Whilst reduced models alleviate these difficulties to some extent, most of the available reduced models do not preserve geometrical resolution. In this chapter, we present a reduced model for a PEMFC that both reduces computational requirements and preserves geometrical resolution. The model is for a PEMFC equipped with porous flow fields and takes into account conservation of mass, momentum, species, energy and charge. The results of the reduced model are then verified against those of the full model, and validated against global polarization curves and local current density distributions for three different experimental fuel cells; good agreement is obtained. In computational terms, the solution of the reduced model is found to require between two to three orders of magnitude less random access memory (RAM) and execution time than that of the full model; furthermore, it scales well when
run on up to four processors. Finally, we discuss the suitability of our reduced model for extension to a PEMFC stack model comprising tens or hundreds of single cells.

8.1 Introduction

In the last decade, mathematical modeling and numerical simulations have come to play an important part in the research and development of the PEMFC. Their role as a complement to experimental design and materials research can be summarized as follows. Firstly, as shown in Fig. 8.1, because a PEMFC comprises several functional layers - current collector (cc), flow field (ff), gas diffusion layer (gdl), catalyst layer (cl), membrane (m) and coolant flow field (cfl) - which differ greatly in thickness and some of which are only tens of micrometers thick, it is difficult to make in situ experimental measurements of, for example, the local distributions of temperature, species concentrations and current densities; a mathematical model, on the other hand, that captures the essential details of fuel cell operation can provide insight and detailed information about the various physical phenomena that occur in the cell. Secondly, parametric studies can be carried out to investigate the effect of design parameters, material properties, and operating conditions; such studies would otherwise be time-consuming and expensive to carry out experimentally. Thirdly, a valid model could aid in troubleshooting malfunctioning cells. Fourthly, models can be employed in overall fuel cell system studies, optimization, and control schemes.

The last few years have seen the appearance of numerous models for the PEMFC [8, 62]. Generally speaking, a model that seeks to capture the vast array of macroscopic effects that are thought to occur in the cell has to be three-dimensional (3D), multi-componental, non-isothermal, multiphase and time-dependent, has to take into account the material properties of the various functional layers and has to resolve the inherent electrochemistry in the catalyst layers. In order to obtain tractable models, simplifica-
Figure 8.1: A schematic of (a-b) the various functional layers in a PEMFC single cell, and (c) a stack comprising three cells.

Tions are commonly invoked in order to reduce the number of spatial dimensions and the scope of the physical processes; the former usually involves model geometries that are one- or two-dimensional (2D) \([27, 34, 36, 40, 43, 45]\), and the latter can take the form of model assumptions, e.g. that the cell is isothermal \([38, 39, 45]\) or that there is no liquid water in the cell, i.e. the flow is gas-phase only \([43, 44]\).

Detailed PEMFC models normally consist of a large number of highly coupled non-linear partial differential equations (PDEs) that govern the conservation of mass, momentum, species, heat and charge transfer in the various layers, and usually result in a high computational cost. As such, applying these models to PEMFC stacks, comprising tens or even hundreds of single cells, has so far proved prohibitive: whilst recent increases in computational power have enabled the solution of physically more complex models, such models are not yet suitable for wide-ranging parameter studies or optimization, or for extension to stack level.
Consequently, there has been interest in deriving reduced mathematical models that can predict the local behavior in a single cell, and/or in each cell in a PEMFC stack, at a reasonable cost, whilst preserving the essential physics \[14, 104-110\]. However, whilst these models certainly require considerably less computational expense than the original full models, they lose geometrical resolution (in terms of variations in dependent variables for all three space coordinates) and hence cannot, in general, reproduce in a consistent way the results of full models.

In our earlier work \[102, 111-113\], we have adopted an approach which both preserves geometrical resolution and reduces computing time. The methodology uses asymptotic reduction, whereby the governing equations are nondimensionalised and systematically simplified \[114\]. Although the method was initially used for 2D models for just one side of the cell, the cathode for the PEMFC and the anode for direct methanol fuel cell (DMFC), it has most recently been applied to a 3D model for a whole PEMFC having straight channels and operating in co-flow \[65\]. The basis of the reduction is the slenderness of a typical PEMFC and the relatively impermeable nature of the gas diffusion layer, catalyst layer and membrane, compared to that of the flow field; thus, a model for the conservation of mass, momentum, species, energy and charge that consists initially of a system of elliptic PDEs is reduced to one consisting of a system of PDEs and ordinary differential equations (ODEs) in the flow fields and a set of ODEs in the current collector, gas diffusion layer, catalyst layer and membrane, as illustrated schematically in Fig. 8.2 by the computational molecule. As a result, a 2D or a 3D steady-state model can be reduced to a transient-like propagation problem by marching along the streamwise-direction \((e_x)\); that is to say, a 2D \((e_x, e_y)\) or a 3D \((e_x, e_y, e_z)\) steady-state model can be reformulated as a 1D \((e_y)\) or 2D \((e_y, e_z)\) problem, respectively, followed by integrating along the streamwise direction \((e_x)\), as we will see later. One constraint here is that the flow field should be sufficiently symmetric to allow for the reduction, e.g. of
porous mesh-type or consisting of parallel channels; models for other flow field patterns, such as serpentine flow channels, cannot be reduced in such a straightforward manner, unless one is willing to assume that the serpentine flow field can be solved for along the streamwise direction as a parallel channel flow and that corner effects are neglected [74]. Another constraint is that the cell is operating in co-flow mode; however, asymptotic reduction is certainly possible in a formal sense for cells operating in counterflow mode, although whether there will be a corresponding saving in computational cost remains unclear [65]. These model reductions allow for fast and computationally inexpensive simulations of single cells or stacks, opening up avenues for inclusion in system and optimization studies, where the computational overhead of the fuel cell model has to be kept at a minimum.

Figure 8.2: Schematic of a PEMFC and the computational molecule for the reduced model with a system of parabolic PDEs (\(
\frac{\partial P}{\partial t} = 0
\)) and ODEs (\(\frac{\partial y}{\partial t} = 0\)) in the flow field, and ODEs (\(\frac{\partial y}{\partial t} = 0\)) in the remainder of the cell, viz., cc, gdl, cl, and m. Boundaries are marked with Roman numerals. (N.B. \( h_{MEA} = 2 \times h_{cl} + h_m \))

The specific aim of this chapter is therefore to continue our development of asymptotically reduced cell models towards asymptotically reduced stack models. For this purpose, we will consider a PEMFC equipped with porous-type flow fields; such flow
fields have attracted interest from the technological point of view because of the uniformity in reactant distribution that they are able to provide [79, 90, 91, 115]. From the scientific point of view, such cells are an attractive focus of study because there is much less spatial variation in the spanwise direction than, say, for a parallel channel distributor; hence, a 2D model ought to be able to capture the behavior of a 3D cell and, consequently, a stack having cells with porous-type flow distributors represents the situation for which rigorous stack model validation should be possible for the least amount of computing time.

In the next section, we introduce the mathematical formulation, which is then followed by scaling arguments to support the model reductions. After a summary of the numerics necessary to solve the models, the results of the reduced model are verified against those of the full model and validated with experimental global polarization curves for three different fuel cells equipped with porous-type flow fields and a set of measured local current density distributions. The computational cost and efficiency is then discussed in terms of memory requirements, computational time and number of processors, and the effect of upscaling the mesh, in order to emulate the computational load necessary for a 10-cell or 100-cell stack, is indicated. Finally, we draw conclusions and highlight extensions of the present model in terms of two-phase flow and counterflow conditions.

8.2 Mathematical formulation

We consider a model for a slender three-dimensional PEMFC (see Fig. 8.1) equipped with a porous flow field on both the cathode and anode sides and operating in co-flow mode. The porous nature of the flow field and the other functional layers (gas diffusion layer, catalyst layer, membrane) and the solid nature of the current collector allow for a reduction from three \((x, y, z)\) to two dimensions \((x, y)\), since changes in the dependent
variables in the spanwise direction \((z)\) are negligible to a first approximation due to slip and zero species and heat flux conditions that can be invoked at the left and right walls of the cell, marked "A" in the 3D scheme of the geometry given in Fig. 8.1.

We assume further that a gas-phase model is sufficient to capture the behavior of the cell, which appears, at first sight, to limit the mathematical formulation to cases where there is no significant flooding or other liquid water effects. Although there already exist numerous two-phase models in the PEMFC literature [8, 62], there are several generic reasons for the continued use of gas-phase only models to describe PEMFC behavior:

- their value lies in that they describe a situation that one would prefer in the gas diffusion layer and flow distributors, were it not for the fact that it is simultaneously necessary to keep the membrane moist; in this context, they serve as a limiting case which modeling would assist in finding an optimal set of operating parameters for;

- unless a cell is operated at high relative humidities, there are likely to be large regions of the cell, particularly near inlets, which are under single-phase conditions; thus, a single-phase model is a necessary prerequisite for describing PEFC operation in many cases;

- a recent trend is a growing interest in operating PEMFCs (with modified functional layers that can withstand the higher temperatures) in the temperature range 120-200°C, for which single-phase models will be appropriate [116–118].

More specifically in the context of this work, we find that a one-phase model is able to reproduce experimental polarization curves obtained under ostensibly two-phase conditions if a model parameter associated with the catalytic layer is adapted appropriately; we will discuss the reasons for this later.
In short, the mathematical model comprises governing equations for the conservation of mass, momentum, species (cathode: O$_2$, H$_2$O, and N$_2$; anode: H$_2$, H$_2$O, and N$_2$), energy and charge, coupled with a phenomenological model for water transport in the membrane and a detailed agglomerate model for the cathode active layer; all of these are presented in Chapter 4. The geometrical and operating parameters for the three different PEMFC experimental data sets that we will use later for validation purposes can be found in Tables 4.1 and 4.2.

**Boundary conditions** - The boundary/interface conditions are as follows:

- At the cathode inlet (I):

  \[
  u_c^{(g)} = U_{in}^c, \quad c_{O_2}^{(g)} = c_{in}^{O_2}, \quad c_{H_2O}^{(g)} = c_{in}^{H_2O,c}, \quad \frac{\partial \phi^{(s)}}{\partial x} = 0, \quad T = T_{in}^c. \tag{8.1}
  \]

- At the anode inlet (II):

  \[
  u_a^{(g)} = U_{in}^a, \quad c_{H_2}^{(g)} = c_{in}^{H_2}, \quad c_{H_2O}^{(g)} = c_{in}^{H_2O,a}, \quad \frac{\partial \phi^{(s)}}{\partial x} = 0, \quad T = T_{in}^a. \tag{8.2}
  \]

In general, a fuel cell is operated at a certain stoichiometry. The stoichiometries, $\xi_{a,c}$, are defined as the ratio of the amount of reactant supplied to the number of reactant required by the electrochemical reaction in the catalyst layers to generate the overall average current density, $i_{avg}$, where

\[
  i_{avg} = \frac{1}{L} \int_0^L i(x') \, dx', \tag{8.3}
\]

and $i$ is the local current density. With the introduction of stoichiometries, the inlet velocities can be computed as:
we use this for the validation with the segmented cell results obtained by Noponen et al. [79] 

- At the outlet (III):

\[ p(g)^\oplus = p_{\text{ref}}^\oplus, \frac{\partial c_i^{(g)}}{\partial x} = \frac{\partial \phi^{(s)}}{\partial x} = \frac{\partial T}{\partial x} = 0. \quad (8.5) \]

For the validation with Han et al. [80], note that we prescribe an outlet velocity for both the anode and cathode coupled with inlet pressures, similar to how Han et al. carried out their measurements.

- At the vertical walls (IV):

\[ u(g)^\oplus = 0, \frac{\partial c_i^{(g)}}{\partial x} = \frac{\partial \phi^{(m)}}{\partial x} = \frac{\partial T}{\partial x} = 0. \quad (8.6) \]

- At the upper wall (V):

\[ \phi^{(s)} = E_{\text{cell}}, \quad T = T^{\text{cool}}. \quad (8.7) \]

- At the current collector/flow field interface (VI and XI):

\[ v(g)^\oplus = 0, \frac{\partial c_i^{(g)}}{\partial y} = 0. \quad (8.8) \]

- At the flow field/gas diffusion layer (VII):

\[ p(g)^\mid_{\text{VII}+} = p(g)^\mid_{\text{VII}_-}, \quad v(g)^\mid_{\text{VII}+} = v(g)^\mid_{\text{VII}_-}. \quad (8.9) \]
• At the gas diffusion layer/catalyst layer interface (VIII):

$$\frac{\partial \phi^{(m)}}{\partial y} = 0.$$  \hfill (8.10)

• At the catalyst layer/membrane interface (IX and X):

$$\frac{\partial c^{(g)}_{O_2}}{\partial y} = \frac{\partial c^{(g)}_{H_2}}{\partial y} = \frac{\partial \phi^{(s)}}{\partial y} = 0.$$  \hfill (8.11)

• At the lower wall (XII):

$$\phi^{(s)} = 0, \quad T = T^{\text{cool}}.$$  \hfill (8.12)

### 8.3 Analysis

#### 8.3.1 Scaling

We will employ scaling arguments to justify the model reductions, i.e. to show how it is possible to reduce a system of elliptic PDEs to a system of ODEs and parabolic PDEs in the flow fields and ODEs in the rest of the cell. For a more mathematically-oriented discussion based on non-dimensionalization, scaling analysis, and simple asymptotics to obtain leading order solutions, we refer to our earlier work [65, 102, 111, 112].

We start by exploiting the inherent slenderness of a typical fuel cell where the length of the cell, $L$, is typically significantly larger than the thickness, $h_j$, of each of the various functional layers ($j = cc, ff, gdl, cl, m$), i.e. $h_j/L \ll 1$. This allows the use of a narrow-gap approximation, in which the second-order diffusive terms in the $x$-direction are negligible at leading order, thus reducing all the elliptic PDEs to parabolic ones except for the conservation of charge, which takes the form of an ODE in the normal direction ($y$).

Two analogies to illustrate this procedure can be found in lubrication theory and for boundary-layer flow along a flat plate for the transport of mass, momentum, species and
energy, which results in the well-known boundary-layer approximation [119].

We proceed by observing the low permeability to flow in the gas diffusion layer, catalyst layer, and membrane, which would suggest that reactants and products would tend to flow the minimum distance through these layers to and from the flow fields. This being the case, it is possible to reduce the parabolic PDEs in these functional layers still further. In order to estimate the magnitude of the convective flow contribution to mass, species and energy transfer in these layers, we note that flow is usually driven by an external pump or fan and is therefore of a forced convective nature, with the velocity being determined by the operating conditions; here, the velocity is typically on the order of 1 ms\(^{-1}\) in the flow field [26, 77, 79]. In the gas diffusion layer adjacent to the flow fields, there will be a streamwise velocity induced via the interface by the stream in the flow fields, a convective flow originating from the consumption/production in the catalyst layer, and flow through the membrane between the anode and cathode. The magnitude of the first can be estimated by returning to Eq. 4.2 for the flow field; an order-of-magnitude estimate in the streamwise direction (\(x\)) gives

\[
\frac{\Delta p_{\text{ff}(g)}}{L} \sim \frac{\mu}{\kappa_{\text{ff}}} |u_{\text{ff}(g)}|, \tag{8.13}
\]

where \(\Delta p_{\text{ff}(g)}\) and \(|u_{\text{ff}(g)}| \approx U_{\text{in}}\) are the scales for the pressure drop and velocity in the streamwise direction, respectively. Here, we have scaled with respect to the Darcy term for the pressure drop, rather than the Forchheimer correction term, as they are of equal order of magnitude for the values of \(|u_{\text{ff}(g)}|\) we consider here; at elevated velocities (> 1 ms\(^{-1}\)) in the flow field, however, we would scale the streamwise pressure drop with the Forchheimer correction term. Now, if we take this pressure drop as the driving force for flow at the interface of the gas diffusion layer and the flow field, then Eq. 4.2 implies
\[
\frac{\Delta p_{\text{gdl}}^{(g)}}{L} \sim \frac{\Delta p_{\text{ff}}^{(g)}}{L} \sim \mu \frac{\kappa_{\text{gdl}}}{\kappa_{\text{ff}}} [u_{\text{gdl}}^{(g)}],
\]

(8.14)

where \(\Delta p_{\text{gdl}}^{(g)}\) is the scale for the pressure drop in the streamwise direction in the gas diffusion layer. Substituting the expression for \(\Delta p_{\text{ff}}^{(g)}\) in Eq. 8.13 into Eq. 8.14 yields

\[
[u_{\text{gdl}}^{(g)}] \sim \frac{\kappa_{\text{gdl}}}{\kappa_{\text{ff}}} [u_{\text{ff}}^{(g)}],
\]

which for a typical gas diffusion layer, for which \(\kappa_{\text{gdl}} \sim 10^{-12} \text{ m}^2\) [25, 120], and for the flow field in this case, for which \(\kappa_{\text{ff}} \sim 10^{-8} \text{ m}^2\) [9, 121–123], gives \([u_{\text{gdl}}^{(g)}] \sim 10^{-4} \times [u_{\text{ff}}^{(g)}]\), i.e. \([u_{\text{gdl}}^{(g)}] \ll [u_{\text{ff}}^{(g)}]\).

We proceed by turning our attention towards the consumption/production of species in the catalyst layers, for which the conservation of mass, Eq. 4.1, gives the following scales for the three terms

\[
\begin{align*}
[u_{\text{cl}}^{(g)}][\rho^{(g)}] \quad \frac{L}{\text{streamwise mass transport}} \quad [e_{\text{cl}}^{(g)}][\rho^{(g)}] \quad \frac{h_{\text{cl}}}{\text{normal mass transport}} \quad [M^{(g)}][J] \quad \frac{F}{\text{electrochemical reaction}}
\end{align*}
\]

Here, \([u_{\text{cl}}^{(g)}]\) and \([u_{\text{cl}}^{(g)}]\) are the velocity scales in the catalyst layer in the streamwise \((x)\) and normal direction \((y)\), respectively. \([J]\), \([\rho^{(g)}]\) and \([M^{(g)}]\) are the scales for the volumetric current density, the gas density and its molecular mass, respectively. Typical values for these are: \([\rho^{(g)}] \approx 1 \text{ kgm}^{-3}\); \([M^{(g)}] \sim 10^{-2} \text{ kgmol}^{-1}\); \([J] \sim 10^9 \text{ Am}^{-3}\) (at current densities of around \(10^4 \text{ Am}^{-2}\)); \(h_{\text{cl}} \approx 10^{-5} \text{ m}\); \(L \approx 10^{-1} \text{ m}\). If we were to balance the streamwise mass transport term with the electrochemical reaction term, we would obtain unrealistically high velocities and pressure drops in the catalyst layer and gas diffusion layer, as this would imply

\[
[u_{\text{cl}}^{(g)}] \sim \frac{[M^{(g)}][J]L}{\rho^{(g)}F} \approx 10 \text{ ms}^{-1};
\]
instead, balancing the normal mass transport term (\(y\)-direction) with the mass generated/consumed in the electrochemical reaction, provides the correct scaling as

\[
[v_{cl}] \sim \frac{[M^{(g)}] [J] h_{cl}}{F [\rho^{(g)}]} \approx 10^{-3} \text{ ms}^{-1},
\]

which is consistent with the velocity scale obtained by Birgersson et al. [40] For the convective contribution from the flow through the membrane, we would require considerable pressure differences between the anode and cathode due to the low permeability of a typical membrane, \((\kappa_m \sim 10^{-18} \text{ m}^2)\) [29, 34, 51], as can be estimated from an order-of-magnitude counterpart of the Darcy equation in the membrane. We can further set \([u^{(g)}_{gd}] \sim [u^{(g)}_{cl}]\) and \([v^{(g)}_{gd}] \sim [v^{(g)}_{cl}]\) as they are continuous across the interface between catalyst layer and the gas diffusion layer. For the normal velocity in the flow field, we can overestimate it by setting \([v^{(g)}_{ff}] \sim [v^{(g)}_{gd}]\), as it will be bounded between the velocity at the interface to the gas diffusion layer and zero at the upper wall. Clearly, mass is mainly transported in the normal direction from the catalyst layer to the flow fields (shortest distance), and we can safely ignore the streamwise mass transport in the gas diffusion layer and catalyst layer. The same argument can be applied for the membrane and the species transport equation.

For the conservation of energy, an order-of-magnitude counterpart of Eq. 4.6 without the streamwise heat conduction term can be expressed as

\[
\frac{[\rho^{(g)}] [c_p^{(g)}] \Delta T [u^{(g)}]}{L}, \quad \frac{[\rho^{(g)}] [c_p^{(g)}] \Delta T [v^{(g)}]}{h}, \quad \frac{k_{eff} \Delta T}{h^2}, + \text{ heat generation terms,}
\]

which shows that the dominating mechanism is heat conduction in the normal direction, since

\[
\frac{k_{eff} \Delta T}{h^2} \gg \frac{[\rho^{(g)}] [c_p^{(g)}] \Delta T [u^{(g)}]}{L}, \quad \frac{[\rho^{(g)}] [c_p^{(g)}] \Delta T [v^{(g)}]}{h},
\]
where $\Delta T$ is a temperature scale and $[c_p^{(g)}] \approx 10^3 \text{ J kg}^{-1}\text{K}^{-1}$ is a specific heat capacity scale. In other words, we only need to consider an ODE for conservation of energy in the normal direction throughout the cell. Note also that it is not necessary to know the order of magnitude of $\Delta T$ in order to establish that conduction dominates convection; however, experiments [124] and detailed analysis [65] indicate that it should be the order of a few K, and this is indeed what we find in our computations later.

### 8.3.2 Summary of reduced model equations

Based on these arguments, the reduced governing equations for the flow fields can be written as

\[
\frac{\partial}{\partial x} \left( \rho^{(g)} u^{(g)} \right) + \frac{\partial}{\partial y} \left( \rho^{(g)} v^{(g)} \right) = 0, \quad (8.15)
\]

\[
\frac{\partial p^{(g)}}{\partial x} = -\frac{\mu^{(g)}}{\kappa} u^{(g)} - \frac{\rho^{(g)} c_F}{\sqrt{\kappa}} \left( u^{(g)} \right)^2, \quad (8.16)
\]

\[
\frac{\partial p^{(g)}}{\partial y} = 0, \quad (8.17)
\]

\[
\frac{\partial}{\partial x} \left( c_i^{(g)} u^{(g)} \right) + \frac{\partial}{\partial y} \left( c_i^{(g)} v^{(g)} \right) = \frac{\partial}{\partial y} \left( D_{i,\text{eff}}^{(g)} \frac{\partial c_i^{(g)}}{\partial y} \right), \quad (8.18)
\]

\[
0 = \frac{\partial}{\partial y} \left( k_{\text{eff}} \frac{\partial T}{\partial y} \right) + S_{\text{temp}}, \quad (8.19)
\]

\[
\frac{\partial^2 \rho^{(g)}}{\partial y^2} = 0. \quad (8.20)
\]

For the current collector, gas diffusion layer, catalyst layer, and membrane, we solve

\[
\frac{\partial}{\partial y} \left( \rho^{(g)} u^{(g)} \right) = S_{\text{mass}}^{(g)}, \quad (\text{gdl, cl, m}) \quad (8.21)
\]

\[
\frac{\partial p^{(g)}}{\partial y} = -\frac{\mu^{(g)}}{\kappa} v^{(g)}, \quad (\text{gdl, cl, m}) \quad (8.22)
\]

\[
\frac{\partial}{\partial y} \left( c_i^{(g)} v^{(g)} \right) = \frac{\partial}{\partial y} \left( D_{i,\text{eff}}^{(g)} \frac{\partial c_i^{(g)}}{\partial y} \right) + S_i^{(g)}, \quad (\text{gdl, cl}) \quad (8.23)
\]

\[
\frac{\partial}{\partial y} \left( \frac{n_{q,m}^{(m)}}{F} \right) = \frac{\partial}{\partial y} \left( \rho^{(m)} M_{H_2O}^{(m)} D_{H_2O,\text{eff}}^{(m)} \frac{\partial \lambda}{\partial y} \right), \quad (m) \quad (8.24)
\]
8.3. Analysis

\[ 0 = \frac{\partial}{\partial y} \left( k_{\text{eff}} \frac{\partial T}{\partial y} \right) + S_{\text{temp}}, (\text{cc, gdl, cl, m}) \] (8.25)

\[ \frac{\partial}{\partial y} \left( -\sigma_{\text{eff}}^{(m)} \frac{\partial \phi^{(m)}}{\partial y} \right) = S_{\text{pot}}, (\text{cl, m}) \] (8.26)

\[ \sigma_{\text{eff}}^{(s)} \frac{\partial^2 \phi^{(s)}}{\partial y^2} = S_{\text{pot}}, (\text{cc, gdl, cl}) \] (8.27)

Note that the source term for the equations of conservation of energy, Eq. 8.19 and 8.25 now only contain derivatives in the normal direction \((y)\). To reduce the number of dependent variables further, we introduce the stream function, \(\psi\), in the flow fields, defined by

\[ u^{(g)} = \frac{1}{\rho^{(g)}} \frac{\partial \psi}{\partial y}, \quad v^{(g)} = -\frac{1}{\rho^{(g)}} \frac{\partial \psi}{\partial x}, \] (8.28)

so that the continuity equation, Eq. 8.15 is automatically satisfied; we thus only need consider the two dependent variables \((p^{(g)}\) and \(\psi\), instead of the previous three \((p^{(g)}, u^{(g)}, \text{and } v^{(g)})\). The boundary conditions for the momentum equation at the inlets (I and II), i.e. the first terms in Eq. 8.1 and 8.2, can be rewritten in terms of the stream function as

\[ \psi = U_{a,c}^{\text{in}} \rho_{a,c}^{\text{in}} y. \] (8.29)

Similarly, for the current collector/flow field interface (VI and XI), the boundary condition for the momentum equation, Eq. 8.8 becomes

\[ \psi|_{\text{VI, XI}} = U_{a,c}^{\text{in}} \rho_{a,c}^{\text{in}} \psi|_{\text{VI, XI}}. \] (8.30)

For the remaining boundary conditions, the ODEs only need conditions at the internal, upper and lower boundaries (from V to XII) of the cell, so that inlet (I, II), outlet (III) and vertical wall (IV) conditions for these can be removed. For the parabolic PDEs in the flow field, we only need to retain the boundary conditions at the inlet, as the downstream outlet conditions are no longer needed because the PDEs are parabolic.
Note also that, if we had considered a three-dimensional geometry, we would have had to solve for the conservation equations (elliptic PDEs) in the spanwise \((z)\) and normal \((y)\) directions only in the current collector, gas diffusion layer, catalyst layer, and membrane, which represents a reduction from three to two dimensions. In the flow field, we would have 3D parabolic PDEs for the conservation of mass, momentum, and species coupled with 2D elliptic PDEs for charge and energy conservation. Such a reduced model can be solved as a ‘2D’ model by employing a space-marching algorithm for the third dimension \((x)\); this has been done by Vynnycky et al. [65].

### 8.4 Numerics

A commercial finite-element solver, COMSOL 3.5a [98], was employed to solve both the full and reduced models (see Appendices A-D and the previous section, respectively). The former, comprising 2D steady-state elliptic PDEs, and the latter, which is treated computationally as a one-dimensional geometry in the \(y\)-direction coupled with space marching in the \(x\)-direction, are assigned the same number of elements (mesh points) in the \(y\)-direction. For the comparison later between the full set and reduced counterpart, we note that the number of steps for the space-marching solver varied from around 60 to 100 (higher for lower cell potentials), as compared to a fixed number of 50 elements in the \(x\)-direction for the full set. While one cannot directly equate the number of steps with the elements in the \(x\)-direction for the full set, it is fair to say that we are not trying to reduce the computational cost of the reduced model by solving for a geometry with overall lower numerical resolution. Quadratic Lagrange elements were implemented for all variables and the direct solvers UMFPACK and PARDISO were chosen as linear solvers with a relative convergence tolerance of \(10^{-3}\) for all variables; this value was low enough for our purposes. Furthermore, solutions from both models were tested for mesh independence. As the space-marching solver (in COMSOL Multiphysics, a transient
8.5 Calibration, verification, and validation

The complex and non-linear nature of the system of coupled equations (PDEs and ODEs) that are solved for in a typical PEMFC model, as well as the large number of material parameters in such a model (see Tables 4.1 and 4.2), mean that some form of model calibration, verification and validation is necessary [126]. For a fuel cell model, calibration is usually carried out in terms of quantitative adaption of electrochemical parameters by comparing model predictions with experimentally obtained global polarization curves; verification aims to ensure that no mistakes have been made whilst writing the numerical code; and validation seeks to ensure that the model is indeed predicting the performance of an actual PEMFC. These steps are especially important when model reductions have been carried out, in order to ensure that no leading order terms have been inadvertently discarded. For this purpose, we have chosen experimental results from studies on three
different PEMFCs, all of which employ a porous-type flow field: (a) Noponen et al. [79], who carried out a series of measurements on a segmented fuel cell; Han et al. [80], who carried out a characterization study with several different types of gas diffusion layers, from which we will compare with results for (b) a single-layer gas diffusion layer and (c) a carbon-filled gas diffusion layer.

Calibration for the segmented cell by Noponen et al. [79] was carried out by choosing two points on the experimental $iR$-corrected polarization curve at low and high current densities (around $0.2 \times 10^4$ and $10^4$ Am$^{-2}$, respectively), and then parameter-adapting the cathode reference exchange current density, $j_{c,0}^{\text{ref}}$, and cathode transfer coefficient, $\alpha_c$, to obtain a good fit for these two points. Furthermore, a modification factor ($\beta_m = 0.62$), similar to that used by Ju et al. [29], was introduced for the membrane, in order to adapt the expressions typically used for the membrane diffusion and protonic conductivity expressions of a Nafilm$^\text{TM}$ membrane, Eq. 4.51 and 4.57 respectively, to the Gore$^\text{TM}$ membrane which Noponen et al. [79] employed in their segmented cell. At this stage, a typical value for the agglomerate radius, $r^{(\text{agg})}$, of $10^{-7}$ m was assumed [73, 75, 77] (see Table 8.1). Validation for the polarization curve and its $iR$-corrected counterpart was then carried out by predicting the whole range of potentials and current densities, as shown in Fig. 8.3.

<table>
<thead>
<tr>
<th>Adapted Parameters</th>
<th>Case (a)</th>
<th>Case (b)</th>
<th>Case (c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>r$^{(\text{agg})}$</td>
<td>Segmented cell [79]</td>
<td>5.4 $\times 10^{-7}$ m (adapted)</td>
<td>4.55 $\times 10^{-7}$ m (adapted)</td>
</tr>
<tr>
<td>$j_{c,0}^{\text{ref}}$</td>
<td>$10^3$ A m$^{-3}$ (adapted)</td>
<td>3.5 $\times 10^5$ A m$^{-3}$ (adapted)</td>
<td>3 $\times 10^5$ A m$^{-3}$ (adapted)</td>
</tr>
<tr>
<td>$\alpha_c$</td>
<td>1.27 (adapted)</td>
<td>0.65 (adapted)</td>
<td>0.7 (adapted)</td>
</tr>
<tr>
<td>$\beta^{(m)}$</td>
<td>0.62 (adapted)</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 8.1: Adapted parameters for single-phase model
Figure 8.3: Experimental polarization curves [79]: (△) measured potential of the cell, (●) iR-corrected potential. Full (— —) and reduced (×) model predictions with increasing agglomerate nucleus radius $r_{agg}$: 0.8, 0.9, 1.0, 1.1, 1.2 ($\times 10^{-7}$) m.

Here, several features are apparent; foremost is the good agreement between model predictions and experiments up to around $1.3 \times 10^4$ Am$^{-2}$, after which there is no further experimental data. The absence of data points in the higher current density range ($>1.3 \times 10^4$ Am$^{-2}$) introduces an arbitrariness in the agglomerate model, since the agglomerate radius cannot be calibrated. At current densities up to around the last data point, the choice of agglomerate radius does not, in this case, have a leading order impact on the model predictions for reasonable values ($r_{agg} \approx 10^{-7}$ m$^2$). As we approach the mass-transport limited regime (in this case around $2 \times 10^4$ Am$^{-2}$), the theoretical polarization curves for a range of agglomerate radii start to deviate. This, in turn, suggests that mass transport inside the agglomerates become a leading order effect, and that the agglomerate radius needs to be properly calibrated with experiments. This has implications for model predictions even at lower average current densities (around
$10^4 \text{Am}^{-2}$), as the local current density can exceed the average current density, and so locally fall into the high current density region where the choice of agglomerate radius is critical.

In this particular case, we also have access to the local current densities measured with the segmented cell, as illustrated in Fig. 8.4, which compares these measurements with the results of the full and reduced models. Here, the comparison between the full and reduced models can be seen as the verification of the latter, with good agreement in model predictions between the two, except for a deviation at the inlet ($x \approx 0$ m) for current densities in excess of around $6 \times 10^3 \text{Am}^{-2}$. The deviation at the inlet originates from the nature of the narrow-gap approximation, which requires that $h_{\text{eff}}/L \ll 1$; as we approach the inlet, however, the length can no longer be taken as the overall length of the cell, but should be taken as the distance from the inlet, $x$, such that $h_{\text{eff}}/x \sim 1$, whence the narrow-gap approximation is no longer valid. The error, however, is small and confined to the inlet region for $x \sim O(h_{\text{eff}})$ and does not affect the model predictions of the reduced model as long as the overall length is larger than the height of the various functional layers. The deviation between model predictions and the experiments at the inlet and outlet at higher current densities are most likely due to the placement of the inlet and outlet holes for the experimental cell, which should have re-circulation zones of fluid (a three-dimensional effect), which is not captured by the two-dimensional representation we have employed here. Note also that this agreement between the results of the full and reduced models also illustrates concretely what is meant by asymptotic reduction: the reduced model is able to reproduce the results of the full model, whereas reduced models based on, for example, averaging along the cell would not necessarily be able to do this (as averaging does not satisfy the governing equations locally, only globally).

In order to study how the model behaves near to the limiting current density, cali-
8.5. Calibration, verification, and validation

Calibration was carried out with polarization curves for the two fuel cells studied by Han et al. [80], who measured up until the limiting region, as shown in Fig. 8.5. The calibration was carried out for two points on the polarization curve that were sufficiently far away from the limiting current density, in this case at low and high current densities (around $0.2 \times 10^4$ and $10^4$ Am$^{-2}$, respectively); this was done for a reasonable agglomerate radius, similar to that used for the calibration of the cell studied by Noponen et al. [79]. The entire range of the polarization curve was then predicted, and the agglomerate radius was fine-tuned via iteration until a close match between model predictions and experiments could be secured. It is interesting to note that the limiting current density in Fig. 8.5 mainly originates from mass-transport limitations in the agglomerates themselves, since there is still oxygen available throughout the cathode catalyst layer, as can be inferred from the data points.

Figure 8.4: Local current densities measured by Noponen et al. [79] (symbols) corresponding to the points A-J in Fig. 8.3, and full (—) and reduced (×) model predictions.
Figure 8.5: Polarization curves from experiments [80]: (■) case (b), (▲) case (c), and corresponding full (— —) and reduced (×) model predictions.

We would therefore not have been able to capture this region without the agglomerate model, as the onset of the limiting current would have been postponed until depletion of oxygen in the catalyst layer due to mass transport limitations in the gas diffusion layer and/or in the flow field. Furthermore, a deeper question is why the one-phase model we have employed here has been able to capture the behavior of cells operating in two-phase conditions near the limiting current density. From Fig. 8.3, it is clear that increasing the value of $r^{(ag)}$ will lead to lower current densities; using Fig. 8.2, it is evident that the presence of liquid water around each agglomerate will lead qualitatively to the same trend as increasing the value of $r^{(ag)}$, since the reactant’s pathway to the catalyst is more hindered. This appears to be why, heuristically at least, we are able to vary $r^{(ag)}$ in a one-phase model so as to obtain agreement against two-phase experimental data. However, the gas-phase model presented here should not be
employed at high current densities and conditions where two-phase transport are significant; instead, one would need to extend the model to encompass two-phase transport in the various functional layers to ensure valid predictions.

Before we proceed to consider the computational cost and efficiency of the reduced model, it is worthwhile to return to the scaling arguments that were in part based on the negligible convective transport in the streamwise direction in the gas diffusion layer, catalyst layer, and membrane. Of key importance are the velocities which can be determined from the solution to the full set of equations. For example, for cell (a) operating at an average current density of $10^4 \text{ Am}^{-2}$, we find $0.75 \lesssim |u_{\text{ff}}^{(g)}| \lesssim 1.9 \text{ ms}^{-1}$; $0 \lesssim |v_{\text{ff}}^{(g)}| \lesssim 10^{-3} \text{ ms}^{-1}$; $10^{-5} \text{ ms}^{-1} \lesssim |u_{\text{gdl}}^{(g)}| \lesssim 10^{-3} \text{ ms}^{-1}$; $10^{-4} \text{ ms}^{-1} \lesssim |v_{\text{gdl}}^{(g)}| \lesssim 10^{-3} \text{ ms}^{-1}$; $10^{-5} \text{ ms}^{-1} \lesssim |u_{\text{cl}}^{(g)}| \lesssim 10^{-4} \text{ ms}^{-1}$; $10^{-5} \text{ ms}^{-1} \lesssim |v_{\text{cl}}^{(g)}| \lesssim 10^{-3} \text{ ms}^{-1}$; $0 \lesssim \Delta T (= T - T_{\text{cool}}) \lesssim 4 \text{ K}$. These values support a posteriori the scaling arguments used earlier.

Figure 8.6: Oxygen concentration (mol m$^{-3}$) at the cathode for case (b) at the limiting current density ($E_{\text{cell}} = 0 \text{ V}$).
8.6 Computational cost and efficiency

Once the fidelity of the mathematical model has been established, the computational cost and scalability of the numerics become important issues, as they set constraints on the suitability of the model for wide-ranging parameter studies and/or for inclusion in optimization, control and system studies. All of these require that the model can be solved within a reasonable amount of time, as dictated by the application. Generally, the complexity of a typical 2D or 3D PEMFC model comes at a hefty computational cost, both in terms of memory requirements and solution time. Further, the computational cost is amplified many times over when one is seeking to capture the behavior of not only one single cell but of several, as is the case for a PEMFC stack which comprises tens or even hundreds of single cells, all of which might behave differently due to imperfections during manufacture, external manifold design, and external boundary conditions, such as heat transfer with the surroundings. Here, the computational cost of each single cell model has to be kept at a minimum to even be able to solve for the stack, which is what the reduced set of equations aims to accomplish. Even though we only consider (i) a single-cell model in this chapter, we will emulate two different stacks, comprising either (ii) ten or (iii) one hundred single cells and operating under the conditions used by Noponen et al. [79], by increasing the density of the computational mesh of the single-cell model to the corresponding number of nodes/elements that we would require to resolve a stack of cells; this will give an indication of how the full and reduced models scale computationally. The number of elements and their order, coupled with the number of unknowns to be solved for, can conveniently be summarized by their degrees of freedom (DoF) for the finite-element method we have employed, and are summarized in Table 8.2 for the full and reduced models. As expected, the DoF increases as we go from a single-cell to a stack comprising ten or a hundred cells, as does the computational
cost in terms of the solution time and memory requirements (in terms of random access memory [RAM]).

<table>
<thead>
<tr>
<th>Case (i)</th>
<th>DoF</th>
<th>Full set</th>
<th>Reduced set</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1-cell mesh)</td>
<td></td>
<td>6 × 10^4</td>
<td>6 × 10^2</td>
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<tr>
<td>Time (s) for 0.8, 0.5, 0.2 V</td>
<td>80, 90, 110</td>
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<td>Iterations for 0.8, 0.5, 0.2 V</td>
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<td>—</td>
<td></td>
</tr>
<tr>
<td>Memory (GB)</td>
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<td>Case (ii)</td>
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<td>6 × 10^3</td>
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<tr>
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<td>4.3, 5.0, 6.0</td>
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<td>Iterations for 0.8, 0.5, 0.2 V</td>
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</tr>
<tr>
<td>Memory (GB)</td>
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<td>Case (iii)</td>
<td>DoF</td>
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<td>32, 41, 43</td>
</tr>
<tr>
<td>Iterations for 0.8, 0.5, 0.2 V</td>
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<td>—</td>
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</tr>
<tr>
<td>Memory (GB)</td>
<td></td>
<td>—</td>
<td>0.45</td>
</tr>
</tbody>
</table>

Table 8.2: Computational cost for the full and reduced sets of governing equations.

As the cell potential is decreased, the mathematical set of equations becomes more non-linear and difficult to solve for, as is evident in the number of iterations needed to reach convergence at various cell voltages. For the full set of equations, the number of iterations remains the same for case (i) and (ii), whereas the amount of time and memory increases by a factor of $O(10)$, scaling approximately linearly with the increase in DoF from $6 \times 10^4$ to $6 \times 10^5$. For case (iii), it is no longer feasible to use a direct solver and one would need to switch to an iterative solver, requiring fine-tuning to solve the full set of equations, especially at lower cell voltages. We did not pursue a solution for this case any further, as the reduced set is superior in terms of DoF, convergence time and memory requirements. The DoF for the reduced set is two order of magnitude lower than the for the full model, and the convergence time is two to three orders of magnitude lower, with around 2-3 s being required for a single cell, and around 6 and
40 s for cases (ii) and (iii), respectively.

Convergence for the full set of equations at low cell potentials can be improved in some cases by starting the solution procedure at a high cell voltage (≈ 0.85 V), which is easier to solve for as the variations in dependent variables are significantly lower than at lower potentials (higher current densities). One can then proceed by using this solution as a starting guess in an iterative manner until the desired cell voltage is reached. This iterative solution procedure is not possible for the reduced model, which uses a space-marching algorithm in the streamwise direction (x). We have instead implemented a smoothed Heaviside function for the cell voltage with continuous first derivative for values of x that are small compared to the overall length of the cell, in order to improve convergence at high current densities. In short, the smoothed Heaviside function is set up so that the cell voltage, $E_{\text{cell}}$, equals 0.85 V at $x = 0$ m, but then drops to the desired cell voltage over a short distance, e.g. from $x = 0$ to $x = \delta x$ (in our case $\delta x = 10^{-7}$ m).

This provides the space-marching solver a smooth transition from the more linear case at a high cell voltage to the more non-linear one for lower cell voltages, which is mirrored in the size of the steps that the adaptive solver takes: around the transition point for the smoothed Heaviside function, the step is small enough to resolve the changes, after which it can take longer steps to resolve the rest of the cell; this provides a robust algorithm for any cell potential. One possible disadvantage of this approach might be thought to be that an error is introduced at the inlet until the actual cell voltage has been reached; however, this error is confined to a very short space interval ($0 \lesssim x \lesssim \delta x$), and does not have a leading order effect on the solution since $\delta x \ll L$.

Finally, we turn our attention towards the reduced model and its scalability with number of processors, as an increase of the latter could lead to substantial savings in time to reach convergence. This is indeed the case when the number of processors is increased, as can be inferred from Fig. 8.7. For the single cell and extended mesh that emulates ten
or one hundred cells, the reduction in computational time is around 65% (UMFPACK), 40% (UMFPACK), and 20% (PARDISO), respectively, for four processors, after which the gain levels off with the increase in the number of processors. Note that we switched to the linear solver PARDISO for the third case as it allowed for faster convergence times overall compared to UMFPACK.

![Graph showing normalized real solver time as a function of the number of processors for different meshes.](image)

Figure 8.7: Normalized real solver time (with respect to one processor) as a function of the number of processors for the reduced model with (●) a ‘1-cell mesh’ (case i), (▲) a ‘10-cell mesh’ (case ii), and (■) a ‘100-cell mesh’ (case iii) for the operating conditions given by Noponen et al. [79].

### 8.7 Conclusions

In this chapter, we have presented and validated, against three different sets of experimental data, a reduced model for a PEMFC equipped with porous flow fields and operating in co-flow mode. The reduced model is obtained by reducing the full set of equations (system of PDEs) to a set of PDEs and ODEs in the flow field and a set of ODEs in the remainder of the cell.

Significant for future model development is the fact that our modeling approach
both reduces computational requirements, in terms of memory usage and execution time, and preserves geometrical resolution; almost all other reduced models achieve the first of these goals, but fail in the second. Scale-up tests carried out on the reduced model indicated that it would be well-suited for detailed PEMFC stack modeling for cells comprising ten or even one hundred cells.

Furthermore, this modeling framework can also be used for other extensions, e.g. for a proper two-phase flow model, or for a cell operating in counterflow mode. For the first case, we would expect the reduced model to lead to similar computational savings, as compared to the full model, to the ones presented here; the computational saving for the case of counterflow is rather more indeterminate in terms of execution time, although the fact that the PDEs that are being solved are parabolic, rather than elliptic, ought to lead to a saving in memory usage that is on a par with that for co-flow.
Chapter 9

Asymptotically Reduced Model for a PEMFC Stack: Automated Model Generation and Verification

A proton exchange membrane fuel cell (PEMFC) stack can comprise a large number of cells and coolant plates; the former, in turn, contain further functional layers and groups. The large number of transport phenomena that occur at differing length scales throughout the stack pose a challenging problem for mathematical modeling. In this context, we present a ‘bottom-up’ approach to overcome the difficulties in mathematical modeling of a PEMFC stack; in short, a fast and memory-efficient reduced model for a single PEMFC derived earlier is coupled to a model for heat and charge transfer in a coolant plate to form a numerical building block, which can be replicated to form a virtual stack having the required number of cells. This procedure is automated to avoid the time-consuming task of manually creating the stack, as well as to remove the possibility of human error during the setup phase. The automated, reduced stack model is verified for a 10-cell stack with the full set of equations; good agreement is found when perturbations between cells are ‘small’. We then study the computational efficiency of
the reduced model for stacks comprising up to 400 cells: a typical run for a 10-cell and a 100-cell stack takes around 20 seconds and 3-4 minutes, and requires 0.6 and 1.2 GB of random access memory, respectively. Finally, extensions to include the effects of perturbed flow, additional physics, external manifolds and other types of flow fields are discussed.

\section{Introduction}

A proton exchange membrane fuel cell (PEMFC) stack can comprise in the range of two to several hundred single cells depending on the power and voltage requirements. Each cell in the stack further contains several functional layers, as illustrated in Fig. 9.1: separator plate (sp), flow field (ff), gas diffusion layer (gdl), catalyst layer (cl), and membrane (m); if the flow fields are machined in the bipolar plates, then the latter would replace the separator plates in the stack layout. In addition, depending on the type of thermal management – liquid water cooling, forced or natural air-convection cooling, or cooling via phase-change materials – additional coolant flow field (cff) layers might be added to the overall stack. Several of the functional layers are, in turn, porous in nature and thus comprise micro-sized pores and other functional structures; one example of this is the composite structure that can be found in the catalyst layers (see Fig. 9.1c).

Ideally, each individual cell in the stack should be exposed to identical or close to identical operating conditions to avoid non-uniformities between cells, which can result in decreased stack performance, reliability and/or durability. Typical non-uniformities between cells can arise in, for example, current and potential distributions between cells \cite{127,132}, in the flow distribution at the cell inlets due to external manifold design \cite{13,15,133,134}, in the temperature distribution \cite{135,136}, and uneven clamping pressure \cite{137,141}.

Mathematical modeling that seeks to resolve the essential phenomena that occur
9.1. Introduction

Figure 9.1: Schematic of a) a PEMFC stack, b) the various functional layers, and c) a typical agglomerate in the cathode catalyst layer.

within such a PEMFC stack on a local level is highly challenging, as it needs to consider coupled transport phenomena – mass, momentum, species, energy and charge transfer – in several or all of the length scales that can be found in a PEMFC stack: nano-sized pores in the membrane with a typical length scale of $O(1\, \text{nm})$; agglomerate structures in the catalyst layer that are typically $O(10^{-7}\, \text{m})$; functional layers that are around $O(10^{-5} - 10^{-3}\, \text{m})$ in thickness; every cell in the stack, where the typical height of the stack depends on the number of cells; and perhaps also the external manifolds and ambient of the stack with a typical length scale of $O(1\, \text{m})$. In view of the mathematical complexity due to the multiphysical phenomena that occur at different length scales in a PEMFC stack and the associated computational cost of solving the model numerically, it is therefore perhaps not surprising that most of the detailed, mechanistic modeling effort has so far focused on a single PEMFC, rather than an entire stack. Broadly speaking, the stack models that do exist take one of two approaches:

- full models which provide full geometrical resolution and resolve full partial differ-
ential equations (PDEs) [9–11], but are computationally time-consuming: consequently, the largest PEMFC stack that has been modelled using this approach is one consisting of just six cells;

• reduced PEMFC models [12–22] which can, in principle, model a stack of any size, but oversimplify the inherent physics and geometry; such reduced models can also be found, e.g., for direct methanol fuel cell stacks [142–145] and solid oxide fuel cell stacks [146–154].

Clearly, deriving a mechanistic model, which can predict all relevant field variables locally throughout the entire stack, is a challenging task. One possible strategy to overcome the hurdles – and the one we adopt here – is to employ a ‘bottom-up’ approach; that is to say, we first aim to develop a fast single-cell model that requires a minimum of random access memory (RAM), which we can then use as a building-block for a stack equipped with an arbitrary number of cells and coolant plates. Second, and equally important, is some form of automation of the numerical procedure when generating the geometry, mesh, and so forth for the entire stack, since the risk of introducing errors increases with the number of cells in the stack and the overall effort in manually setting up a stack model quickly becomes prohibitive. Such an approach would open up the possibility for wide-ranging parameter studies of stacks; the optimization of stacks in terms of, e.g. the number and placement of coolant plates, without having to manually redraw the computational domain at each iteration; and the study of how variations in component parameters, such as porosity, permeability and so forth, that can arise during manufacture or assembly of the stack, affect the overall stack performance.

We have in our previous work [65, 96] addressed the first point with asymptotically reduced, steady-state mathematical models for a single cell operating in co-flow conditions. In particular, this was found to significantly reduce the convergence time and
memory requirement by between two and three orders of magnitude for typical operating conditions, as compared to the original full model [96]; this was achieved through a reduction in dimensionality from three to two dimensions that is strictly valid for porous flow fields, followed by a scaling analysis and asymptotic reduction of the nature of the governing equations from elliptic PDEs to a set of leading-order parabolic PDEs and ordinary differential equations (ODEs), thus allowing for a fast, efficient space-marching algorithm. The model was then verified with the full set of equations (the original set of elliptic PDEs) and validated with three different sets of fuel cell experiments. Most importantly, we were able to show that our model simultaneously preserved geometrical resolution and reduced computing time. Here, we will employ the reduced single-cell model as a building block for a stack model that is, from the numerical point of view, fully automated and sufficiently cheap to solve. As a first approximation, we will further decouple the stack from the external gas/liquid manifolds by assuming the inlet velocity at the cathode, anode and coolant flow fields. The final stack model is then verified with the full set of equations for a smaller 10-cell stack, in terms of a global polarization curve, local temperature and potential distributions. One limitation of the proposed stack model is that we only consider the leading-order terms, i.e. neglect second order derivatives in the streamwise direction; the reduced stack model does therefore not capture redistribution of temperature and current density between cells (see e.g. [130, 132, 135, 136]) due to perturbations and non-uniformities between cells in the stack; this is shown for the case of a 10-cell stack with perturbed inlet velocities for the cathodes. After discussing the error that arises due to perturbations with the reduced stack model, we explore its scalability for stacks comprising up to 400 cells. We finish with conclusions and a discussion of extensions of the current model to capture redistribution between cells, to account for external manifolds, such as Z- and U-type flow designs [13, 134], and other types of internal flow fields, e.g. serpentine and parallel
9.2 Mathematical Formulation

We consider a PEMFC stack comprising $n$ cells and $n - 1$ liquid-coolant plates, as illustrated in Fig. 9.2. The building block is a single cell, equipped with a porous flow field, and one coolant plate, denoted by $j$, for which we employ our previously derived reduced cell model [96] and further introduce conservation of charge and energy for the coolant plates. The stack is decoupled from the external manifolds by assigning the inlet velocities for the cathode and anode flow fields of each cell and liquid coolant plates between cells, as we are mainly concerned with the stack itself and not the external manifolds or auxiliary equipment such as compressors and humidifiers.

In essence, the single-cell reduced model embodies the following major features:

- Porous flow fields for the cathode, anode and coolant plates, as illustrated in Fig. 9.2. The porous nature of the flow field allows a reduction in dimensionality from three to two dimensions due to the slip- and no-flux conditions that can be assigned at the side walls in the spanwise direction ($e_z$). From the technological point of view, porous flow fields are able to provide a high degree of uniformity in reactant distribution [79, 88–92, 115].

- Second-order diffusive terms in the streamwise direction ($e_x$) are negligible at leading order for the conservation of species, energy, and charge in each cell and coolant plate, which reduces the elliptic PDEs to parabolic counterparts.

- In the membrane, catalyst layer, and gas diffusion layer, transport is at leading-order in the normal direction ($e_y$), which further reduces the conservation equations from parabolic PDEs to ODEs.
In the flow fields and separator plates, transport of energy occurs at leading order through heat conduction in the normal direction, such that we only need to consider an ODE for conservation of energy; the same applies to conservation of charge.

The model assumes that two-phase transport is negligible in the cell.

The reduced model thus comprises parabolic PDEs for mass, momentum, and species and ODEs for energy and charge in the flow fields, and ODEs for all
conservation equations in the other layers, except for the coolant plates, in which
we consider a parabolic PDE for conservation of energy (see Fig. 9.2).

For the sake of brevity, we will in the following summarize the full set of governing
equations and reduced counterpart, and refer to Chapter 8 for more details.

9.2.1 Full set of governing equations

The conservation of mass, momentum, species, energy and charge in the PEMFC, are
presented in Chapter 4, i.e. Eq. 4.1–4.13.

For the coolant flow fields, we only need to consider conservation of energy and
charge, which can be written as

\[ \rho^{(1)} c_p^{(1)} U_{cool} e_x \cdot \nabla T = \nabla \cdot (k_{\text{eff}} \nabla T) + S_{\text{temp}}, \quad \text{(eff)} \quad (9.1) \]

\[ \nabla \cdot \left( -\sigma_{\text{eff}}^{(s)} \nabla \phi^{(s)} \right) = 0. \quad \text{(eff)} \quad (9.2) \]

In the above equations, \( T \) is the temperature, and \( k_{\text{eff}} \) is the effective thermal conductivity, \( \rho^{(1)} \)
and \( c_p^{(1)} \) are the density and the specific heat capacity of the liquid coolant (H\(_2\)O in this
case), \( U_{\text{cool}} \) is the average velocity of the flow through the porous coolant plates (N.B. for
passive flow in a channel comprising a porous medium with slip-conditions, a constant
velocity profile is obtained, which is given by \( U_{\text{cool}} \) in Eq. 9.1), and \( e_x \) is the streamwise
coordinate vector.

9.2.2 Reduced governing equations

We solve for the continuity of mass and momentum, given by

\[ \frac{\partial p^{(g)}}{\partial x} = -\frac{\mu^{(g)}}{\kappa \rho^{(g)}} \frac{\partial \psi}{\partial y} - \frac{c_F}{\sqrt{\kappa \rho^{(g)}}} \left( \frac{\partial \psi}{\partial y} \right)^2, \quad \text{(ff)} \quad (9.3) \]
9.2. Mathematical Formulation

\[ \frac{\partial p^{(g)}}{\partial y} = 0, \quad (ff) \]  
\[ \frac{\partial}{\partial y} \left( \rho^{(g)} v^{(g)} \right) = S_{\text{mass}}^{(g)}, \quad (gdl, cl, m) \]  
\[ \frac{\partial p^{(g)}}{\partial y} = -\frac{\mu^{(g)}}{\kappa} \tau^{(g)}, \quad (gdl, cl, m) \]

where \( v \) is the velocity in the \( y \)-direction. The streamfunctions, \( \psi \), are defined through

\[ u^{(g)} = \frac{1}{\rho^{(g)}} \frac{\partial \psi}{\partial y}, \quad v^{(g)} = -\frac{1}{\rho^{(g)}} \frac{\partial \psi}{\partial x}, \]

such that they satisfy conservation of mass in the flow fields; here, \( u^{(g)} \) is the velocity in the \( x \)-direction. Note that we solve for \( \psi \) and \( p^{(g)} \) in the flow fields, in lieu of \( u^{(g)} \), \( v^{(g)} \), and \( p^{(g)} \), whereas we solve for \( v^{(g)} \) and \( p^{(g)} \) in the gas diffusion layer, catalyst layers and membranes.

We further consider species transfer of a ternary mixture of water (\( H_2O \)), nitrogen (\( N_2 \)) and oxygen (\( O_2 \)) at the cathode side, and \( H_2O, N_2 \) and hydrogen (\( H_2 \)) at the anode side, for which the equations for the conservation of species can be expressed as

\[ \frac{\partial}{\partial x} \left( \frac{c_i^{(g)}}{\rho^{(g)}} \frac{\partial \psi}{\partial y} \right) + \frac{\partial N_1^{(g)}}{\partial y} = 0, \quad (ff) \]  
\[ \frac{\partial N_1^{(g)}}{\partial y} = S_1^{(g)}, \quad (gdl, cl, m) \]

with the molar flux of species \( i \) in the \( y \)-direction, \( N_i \), for \( H_2O \) in the entire cell defined as

\[ N_{H_2O}^{(g)} = \begin{cases} 
-\frac{c_{H_2O}^{(g)}}{\rho^{(g)}} \frac{\partial \psi}{\partial x} D_{H_2O,eff}^{(g)} \frac{\partial c_{H_2O}^{(g)}}{\partial y} \quad , \quad (ff) \\
\rho_{H_2O}^{(g)} v^{(g)} - D_{H_2O,eff}^{(g)} \frac{\partial c_{H_2O}^{(g)}}{\partial y} \quad , \quad (gdl, cl) \\
\frac{n_{H_2O}^{(m)}}{F} - \frac{D_{H_2O,eff}^{(m)}}{M_{H_2O}} \frac{\partial \lambda}{\partial y} \quad , \quad (m)
\end{cases} \]
and for \( \text{O}_2 \) in the cathode and \( \text{H}_2 \) in the anode as

\[
N_i^{(g)} = \begin{cases} 
-\frac{c_i^{(g)}}{\rho_i^{(g)}} \frac{\partial \psi}{\partial x} - D_{\text{eff}}^{(g)} \frac{\partial \phi_i^{(g)}}{\partial y}, & (\text{ff}) \\
-c_i^{(g)} T^{(g)} - D_{\text{eff}}^{(g)} \frac{\partial \phi_i^{(g)}}{\partial y}, & (\text{gdl, cl}) 
\end{cases} 
\]  
(9.11)

Conservation of energy and charge are accounted for by

\[
\frac{\partial q}{\partial y} = S_{\text{temp}}, \quad (\text{sp, ff, gdl, cl, m}) 
\]  
(9.12)

\[
\frac{\partial i^{(s)}}{\partial y} = -S_{\text{pot}}, \quad (\text{sp, ff, gdl, cl}) 
\]  
(9.13)

\[
\frac{\partial i^{(m)}}{\partial y} = S_{\text{pot}}, \quad (\text{cl, m}) 
\]  
(9.14)

with the normal heat flux, \( q \), electron flux, \( i_s \), and proton flux, \( i_m \), defined as

\[
i^{(s)} = -\sigma^{(s)} \frac{\partial \phi^{(s)}}{\partial y}, \quad i^{(m)} = -\sigma^{(m)} \frac{\partial \phi^{(m)}}{\partial y}, \quad q = -k_{\text{eff}} \frac{\partial T}{\partial y}. 
\]  
(9.15)

For the coolant flow fields, analogous to the reduction in the equation for the conservation of energy and charge in the single-cell model \[96\], the governing equations can be reduced to

\[
\rho^{(l)} c_p^{(l)} U_{\text{cool}} \frac{\partial T}{\partial x} + \frac{\partial q}{\partial y} = S_{\text{temp}}, \quad (\text{eff}) 
\]  
(9.16)

\[
\frac{\partial i^{(s)}}{\partial y} = 0. \quad (\text{eff}) 
\]  
(9.17)

### 9.2.3 Reduced boundary conditions

The boundary/interface conditions can be summarized as follows (see Fig. [9.2] for placement of roman numerals):
9.2. Mathematical Formulation

- At the cathode inlet (I):
  \[ \psi = U_{\text{c}}^\text{in} \rho_{\text{c}}^\text{in} y, \quad p = p^\text{ref}, \quad c_{\text{O}_2} = c_{\text{O}_2}^\text{in}, \quad c_{\text{H}_2\text{O}} = c_{\text{H}_2\text{O}}^\text{in}, \quad (9.18) \]

- At the anode inlet (II):
  \[ \psi = U_{\text{a}}^\text{in} \rho_{\text{a}}^\text{in} y, \quad p = p^\text{ref}, \quad c_{\text{H}_2} = c_{\text{H}_2}^\text{in}, \quad c_{\text{H}_2\text{O}} = c_{\text{H}_2\text{O}}^\text{in}, \quad (9.19) \]

- At the coolant flow field inlet (III):
  \[ T = T^{\text{cool}}. \quad (9.20) \]

- At the separator plate/flow field interface (IV and IX):
  \[ \psi|_{\text{IV,IX}} = U_{\text{a,c}}^\text{in} \rho_{\text{a,c}}^\text{in} y|_{\text{IV,IX}}, \quad \frac{\partial c_i^{(g)}}{\partial y} = 0. \quad (9.21) \]

- At the flow field/gas diffusion layer (V):
  \[ p^{(g)}|_{V_+} = p^{(g)}|_{V_-}, \quad v^{(g)}|_{V_+} = v^{(g)}|_{V_-}. \quad (9.22) \]

- At the gas diffusion layer/catalyst layer interface (VI):
  \[ \frac{\partial \phi^{(m)}}{\partial y} = 0. \quad (9.23) \]

- At the cathode catalyst layer/membrane interface (VII):
  \[ \frac{\partial c_{\text{O}_2}^{(g)}}{\partial y} = \frac{\partial \phi^{(s)}}{\partial y} = 0. \quad (9.24) \]

- At the anode catalyst layer/membrane interface (VIII):
  \[ \frac{\partial c_{\text{H}_2}^{(g)}}{\partial y} = \frac{\partial \phi^{(s)}}{\partial y} = 0. \quad (9.25) \]

- At the upper wall (X) of cell \( n \):
  \[ \phi^{(s)} = E_{\text{stack}}, \quad T = T^{\text{cool}}. \quad (9.26) \]
At the lower wall (XI) of cell 1:

\[
\phi^{(s)} = 0, \quad T = T^{\text{cool}}. \quad (9.27)
\]

Note that one could replace the boundary conditions at the two walls (X, XI) with Newton’s law of cooling to account for external heat transfer conditions or add additional current collectors for the stack.

The constitutive relations and a detailed agglomerate model for the cathode active layer are given in Chapter 4.

### 9.3 Numerics

We implement two stack models, both in the commercial finite-element solver COMSOL Multiphysics 3.5a [98]: one based on the reduced set of equations, via an automated procedure outlined in the next Section, and the other set manually based on the full set of elliptic PDEs [96] for a five- and ten-cell stack. The automated model generation was carried out in the commercial general programming environment Matlab 2008 [155] by exploiting the bidirectional interface between COMSOL Multiphysics and Matlab. For both models, quadratic Lagrange elements were employed for all dependent variables throughout the stack: viz., \( p^{(p)} \) (ff, gdl, cl, m), \( \psi \) (ff), \( \nu^{(p)} \) (gdl, cl, m), \( T \) (everywhere), \( \phi^{(s)} \) (eff, sp, ff, gdl, cl), \( \phi^{(m)} \) (cl, m), \( c_{\text{O}_2}^{(p)} \) (cathode: ff, gdl, cl), \( c_{\text{H}_2}^{(p)} \) (anode: ff, gdl, cl), and \( c_{\text{H}_2\text{O}}^{(p)} \) (ff, gdl, cl, m); note that \( c_{\text{H}_2\text{O}}^{(p)} \) is solved as dummy variable for \( \lambda \) in the membrane. The direct solvers, PARDISO for the full set of equations and UMFPACK for the reduced set of equations, were chosen as the respective linear solvers with a relative convergence tolerance of \( 10^{-3} \) for all variables, as they both gave better overall performance for the respective stack models that they were applied to. The reduced model is solved by resolving the \( y \)-direction as the computational domain and then...
marching along the $x$-direction with a space-marching algorithm (see [96] for a more detailed discussion); a total of 62 elements were used in the $y$-direction (full and reduced set) for each building block, and 60 elements in the $x$-direction for the full set, whereas the reduced set required around 200 steps in the $x$-direction (treating the $x$-direction as a time variable in COMSOL, for which the total amount of steps depends on the adaptive time-stepping). All computations were carried out on a workstation with two quad-core processors (3.2 GHz, with a total of eight processor cores) and 64 GB RAM. The wall-clock time and peak memory usage were estimated from Comsol’s graphical user interfaces and Matlab’s `tic` and `toc` commands, with all unnecessary processes stopped to secure reasonably accurate times. Mesh-independence tests were carried out prior to verification for both stack models. The base-case parameters are summarized in Table 4.1 (case b) and Table 4.2.

### 9.4 Automated Model Generation

We have so far presented a reduced stack model based on a building block comprising a single PEMFC and one coolant plate. The advantage of this building block, from the computational point of view, is its low memory requirement for each constituent cell and speed of convergence – around or more than two orders of magnitude faster and less memory intense than the corresponding full set of equations for a single cell, as shown in Chapter 8. The disadvantage, however, is the need for internal interface and boundary conditions due to the fact that not all dependent variables are solved everywhere, which adds to the numerical complexity once one seeks to implement a large stack model: e.g. a 10-cell stack contains around 100 domains with different sets of equations and constitutive relations, together with around 200 boundary and interface conditions. In this context, we note that we required around four to five hours to painstakingly implement the stack model based on the full set of equations without the automated model gener-
ation for verification purposes; implementing a stack with, e.g. 100 cells – amounting to around 1000 functional layers/domains and around 2000 interface/boundary conditions – would be prohibitive, to say the least. Nonetheless, once the automated procedure was in place for the reduced model, the various layers, equations and so forth could easily be implemented without any risk of human error during the setup stage. One could at this stage argue that a single-domain formulation for each cell and by extension the entire stack, in which all equations are solved everywhere in the computational domain, would be a better approach, as one would not require any internal boundary or interface conditions; however, while this would certainly reduce the complexity of the stack model, one would have to live with the significantly larger computational cost as every dependent variable is solved for throughout the computational domain – this becomes increasingly more restrictive as the number of cells in the stack increase.

Now, let us turn our attention to the automated procedure to generate the numerical reduced stack-model, which is based on a Matlab script that manipulates a COMSOL-associated structure, known as a FEM structure, that contains all the information about the entire model, ranging from the geometry to solver properties. This structure is of an aggregate data type, similar to a structure in, e.g., the high-level language C. In short, the automated code generator operates as follows (see Fig. 9.3 for the corresponding flowchart): (i) it reads in all operating and physical parameters as specified by the user; (ii) it builds the geometry comprising of a given number of cells ($n$ in Fig. 9.2) and their functional layers, as well as coolant flow fields; (iii) it constructs the numerical mesh; (iv) it defines all governing equations (PDEs and ODEs) for the various functional layers and their boundary/interface conditions; (v) it allocates the respective constitutive relations and phenomenological agglomerate and membrane models to the various layers; (vi) it solves the model; (vii) it carries out postprocessing as instructed by the user. Here, a loop structure is employed for (i) to (v) to loop through all the cells as the entire stack is
built virtually. One can easily write the Matlab script as a function, which can interface with other modules in Matlab, such as Simulink and the Optimization Toolbox, thus allowing for easy, automated manipulation of all variables, including, e.g., the number of cells and/or coolant plates, with a view towards optimization or overall system models.

Figure 9.3: Flowchart for the automated model generator.

On a final note as regards the automated model generation: The reduced stack model could also be implemented with, e.g., a Keller Box or a Modified Box method in a high-level language such as Fortran or C – we have previously demonstrated these two efficient numerical methods for both DMFC and a PEMFC half-cell
models. This approach would be different from the one outlined above for COMSOL and Matlab, as one would be constructing a large block-tridiagonal matrix based on \( n \) building blocks. This system could then be solved with a special-purpose algorithm that exploits the large number of zero entries in the overall matrix.

9.5 Calibration and Validation

The building block, denoted \( j \) in Fig. [9.2], is based on a PEMFC model that was calibrated and validated (without the coolant plate) against three fuel cell experiments in Chapter 8; good agreement was found throughout the range of the global polarization curves as well as for the local current density distribution for one of these, where the experimental cell was equipped with a segmented current collector. Given the validity of each building block, we loosely assume that stacking these does not affect the validity of the single-cell model nor the overall stack model, and note that while experimental evidence and validation for a corresponding stack would be ideal, the lack of such evidence has no bearing on the ‘bottom-up’ approach and automation that is at the heart of the concept presented here.

9.6 Verification without perturbations between cells

The automated, reduced stack model for \( n \) building blocks comprises a vast number of functional layers and associated dependent variables that are solved in the form of a set of parabolic PDEs and ODEs when \( n \gg 1 \). It is therefore vital that some form of verification with a corresponding stack model that is based on the full set of equations (elliptic PDEs), i.e., without any model reductions, is carried out to ensure that the reduced stack model captures the leading-order behavior. For this purpose, we start by assuming uniform inlet conditions for every cell in the stack, and compare the predicted
global polarization curve for a 10-cell stack from the models based on the full and reduced sets of equations, as shown in Fig. 9.4.

Figure 9.4: Polarization curves for uniform inlet conditions: (■) full and (—) reduced models; and for perturbed cathode inlet velocities: (▼) full and (—–) reduced models.

Overall, good agreement is found throughout the entire polarization curve with a slight deviation as we approach the limiting current density – the maximum relative error is less than 1% for the entire curve. We proceed by verifying the results for three field variables: the temperature and the potentials in the solid and ionic phases.

The first can be found in Fig. 9.5 and the latter two in Fig. 9.6, which depict these distributions at a cross-section in the middle of the stack at an overall stack potential, $E_{\text{stack}}$, of 1 V; a low stack potential was chosen as it corresponds to a high current density that is typical of large spatial variations in the dependent field variables. Here, several features are apparent; foremost is the good agreement between the results of the full and reduced models, which suggests that we are resolving all leading-order phenomena;
Asymptotically Reduced Model for a PEMFC Stack

Figure 9.5: Local temperature distribution at a cross-section \((x = L/2, 0 \leq y \leq h_{\text{stack}})\) of a 10-cell stack at \(E_{\text{stack}} = 1\ \text{V}\): full set of equations (●) and reduced counterpart (—).

the same applies to all dependent variables, although we omit this here for the sake of brevity. Furthermore, the temperature, for which the local maxima occur at each cathode catalyst-layer/membrane interface, and ionic and electronic potentials are more or less similar for each cell in the stack. The similarity originates from the fact that we have one liquid coolant plate between each cell with a sufficiently high coolant flow rate to ensure that each cell experiences close to the same operating conditions. The slight deviation in the temperature distribution in the first and final cell originate from the fact that these cells are adjacent to the edges of the stack, at which we have prescribed temperature \(T = T_{\text{cool}}\), and the fact that the cathode of the first cell is further away from its nearest exterior boundary than the cathode of the \(n^{\text{th}}\) cell is from its; this gives rise to a slightly lower temperature in the final cell than in the first.
Figure 9.6: Local potential distribution of the (●) solid and (■) ionic phases for the full set of equations and corresponding reduced counterpart (−) at a) a cross-section \(x = L/2, 0 \leq y \leq h_{\text{stack}}\) and b) a close-up of cell 5 at the same cross-section, for a 10-cell stack operating at \(E_{\text{stack}} = 1\) V. The position of the coolant flow fields is highlighted with (○○).
9.7 Verification with perturbations between cells

While the reduced model agrees well with the full set when every cell is operated at identical inlet conditions, we expect that this may not be the case when there are significant perturbations between cells since the leading-order stack model does not consider streamwise diffusive transport. In order to study how the reduced model fares, we introduce a leading-order perturbation in the inlet velocities at the cathodes for a 10-cell stack, given by

\[ U_{\text{in}}^{c_j} = U_{\text{in}}^c + j \Delta U, \]  

(9.28)

where \( j \) denotes the number of the cell in the stack (see Fig. 9.2); \( U_{\text{in}}^{c_j} \) is the velocity of cell \( j \) and \( \Delta U \) is the increment in inlet velocity from cell to cell. In this particular case, \( \Delta U \) is chosen such that the inlet velocity increases by a factor two between the first and the last cell, which is larger than the typical variation in inlet velocities between 5 and 25% that have been studied for U- and Z-shaped external manifolds of stacks comprising between 25 and 100 cells \[13, 15, 134\]. The maximum relative error between the reduced model and the full set is around 2% for the perturbed global polarization curve, as can be inferred from Fig. 9.4. The order of magnitude of the error is related to the inherent error in neglecting the streamwise diffusive terms for conservation of charge (electrons) and energy: namely, \( O(h_{\text{stack}}^2/L^2) \), where \( h_{\text{stack}} \) is the height of the stack; this ratio loosely represents the order of magnitude difference between the streamwise and normal diffusive terms in the elliptic governing equations (see. Refs. \[96, 102, 103\] for more details), and is for the 10-cell stack \( \sim 10^{-1} \).

Proceeding with the distributions of the local current density in Fig. 9.7 for the first, fifth and tenth cell in the stack at \( E_{\text{stack}} = 6 \text{ V} \) (corresponds roughly to around 0.6 V for each cell, which is a typical operating point for the PEMFC), we see that
the local current density varies due to redistribution between cells, whereas the reduced model predicts the same local current density for each x-location in the stack – here, the maximum relative error is around 4%, again on the order of $O(h_{\text{stack}}^2/L^2)$. Similarly, the relative error for the local temperature distribution is around 4% (see Fig. 9.8) and around 0.1% for the oxygen concentration. While the former is expected, the latter is significantly lower than that of the local current density and temperature; the reason can be found in the nature of the dependent field variables in the stack: transport of energy and charge (electrons) occur throughout the stack, whereas transport of momentum, charge (ions), species, and mass are limited to each cell of the stack. Thus, heuristically speaking, we expect the error in neglecting the streamwise second order diffusive terms for energy and charge of electrons to be on the order of $h_{\text{stack}}^2/L^2$, and for the remaining transport mechanisms to be on the order of $h_{\text{cell}}^2/L^2$, where $h_{\text{cell}}$ is the height of a unit cell in the stack, provided that the perturbations are not so large as to introduce larger errors through the source terms, Eq. 4.13 which couple the global current density with
the variables that are bound to a cell.

Figure 9.8: Local distributions for a 10-cell stack \( E_{\text{stack}} = 6 \) V along the \( x \)-axis at the interface between the cathode catalyst layer and the membrane (VII in Fig. 9.2) for the full set of equations for temperature in cell (■) 1, (▲) 5, and (▼) 10; concentration of oxygen in cell (♦) 1, (◆) 5, and (◇) 10; and the corresponding predictions of the reduced set in cell (--) 1, (----) 5, (-----) 10.

Decreasing the stack voltage to around 1 V, which roughly amounts to 0.1 V or less for each cell, increases the maximum relative errors for temperature, local current density and oxygen concentration to around 100%, 30%, and 1%, respectively (not shown here); i.e. all errors are – loosely speaking – of the order of \( O(h_{\text{stack}}^2/L^2) \), suggesting that the perturbation is now so large that even the field variables limited to each cell are affected. While the latter comparison at a stack voltage of 1 V is more of an academic interest since it does not make any practical sense to operate a fuel cell stack in the mass-transport limiting region, these findings suggest that one may want to include the streamwise second-order terms if perturbations are significant; however, this should be accomplished without solving for the full set of equations since the computational cost would then again become prohibitive if one seeks to include the essential physics at a
local level. For this purpose, we therefore suggest two possible extensions: The first would be to solve the reduced stack model and add the solution for the next order term in an asymptotic series expansion with the "small parameter" related to $h_{\text{stack}}^2/L^2$ and possibly an estimate of the perturbation. The second would be to split the dependent field variables into two sets of equations; i.e., to solve for conservation of energy and charge of electrons with the full set of elliptic governing equations and couple these in an iterative manner with the reduced model for conservation of momentum, mass, species and charge of ions. Both approaches should lead to substantial savings in computational cost.

9.8 Computational Cost and Efficiency

Generally, a numerical model should be robust and efficient with the exact constraints in terms of memory requirements and rate of convergence dictated by the application at hand. In our case, we expect the reduced stack model to provide significant advantages over simply solving the full set of equations; this is indeed the case, as can be inferred from Table 9.1.

<table>
<thead>
<tr>
<th></th>
<th>Full set</th>
<th>Reduced set</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>DoF</strong></td>
<td>$6 \times 10^4$</td>
<td>$6 \times 10^2$</td>
</tr>
<tr>
<td><strong>1-cell stack</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time (s) for 0.8, 0.5, 0.2 V</td>
<td>80, 90, 100</td>
<td>$(0.21)$ 2.1, 2.5, 2.8</td>
</tr>
<tr>
<td>Memory (GB)</td>
<td>1.3</td>
<td>0.22</td>
</tr>
<tr>
<td>DoF</td>
<td>$3.9 \times 10^5$</td>
<td>$3 \times 10^3$</td>
</tr>
<tr>
<td><strong>5-cell stack</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time (s) for 4, 2.5, 1 V</td>
<td>215, 435, 530</td>
<td>$(3.4)$ 7.5, 8.5, 9.5</td>
</tr>
<tr>
<td>Memory (GB)</td>
<td>4.5</td>
<td>0.5</td>
</tr>
<tr>
<td>DoF</td>
<td>$7.8 \times 10^5$</td>
<td>$6 \times 10^3$</td>
</tr>
<tr>
<td><strong>10-cell stack</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time (s) for 8, 5, 2 V</td>
<td>450, 660, 940</td>
<td>$(6)$ 14, 15, 18</td>
</tr>
<tr>
<td>Memory (GB)</td>
<td>8.5</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Table 9.1: Computational cost for the full and reduced sets; the numbers in the brackets indicate the time required to automatically generate the reduced numerical model prior to solving it.
Noteworthy are the reductions in degrees of freedom (DoF) and convergence time by around two orders of magnitude and the memory requirement, which grows slowly for the reduced set as compared to the full counterpart when the number of cells in the stack is increased from one to ten: for example, around 8-15 minutes and 8.5 GB RAM are required to solve a 10-cell stack model with the full set of equations, as opposed to around 14-18 seconds and 0.6 GB RAM for the automated reduced set. One could switch to an iterative solver for the full set, which would lower the memory usage after finetuning the solver; we did not pursue this further, as the automated, reduced model is superior in every aspect provided that perturbations are ‘small’, not the least in the time to set up the geometry, mesh and to implement the mathematical formulation, as illustrated in Fig. 9.9. Here, we see that the time to set up the model increases – in this case roughly quadratically – with the number of cells in the stack, whereas the time to solve the final reduced model increases roughly linearly; around 90 to 95% of the total time to automatically generate the model is spent on finalizing the FEM structure in COMSOL, which suggests that a Keller Box or Modified Box method – if properly implemented with an efficient construction of the block-tridiagonal matrix for the entire stack – could reduce the setup time significantly. Overall, the automated, reduced model can be generated within 0.3 seconds for a single cell and within six minutes for a 400-cell stack; once verified, this can be done without any potential human error or the painstaking task of manually setting up the problem, which took us around four to five hours for a 10-cell stack. Further, the convergence time is around 25% longer when modeling a stack in which every cell operates at \( 0.2 \text{V} \) instead of \( 0.8 \text{V} \), which can be explained by the increasingly more non-linear behavior of the model at lower voltages and higher current densities. On average, it takes around 2 seconds per cell in the stack if we divide the total convergence time by the number of cells studied here, which indicates that the overall solver time is consistent as more cells are added.
Figure 9.9: Computational cost in terms of the time required for (▲) setting up and solving the automated, reduced stack model in which each cell operates at (▼) ∼ 0.8 V, (■) ∼ 0.5 V, and (◆) ∼ 0.2 V for an increasing number of cells in the stack.

As regards memory issues when increasing the number of cells for the automated, reduced model (see Fig. 9.10), we find that the DoF increase linearly with $n$, which is to be expected since each building block is identical, and that the memory (RAM) usage increases rapidly for $n \lesssim 20$, but then grows more slowly for larger $n$. In general, the memory usage can be adjusted by the choice of solver, i.e. direct or iterative, although we note that a direct solver is typically preferable when it can be employed for the non-linear set of coupled PDEs and ODEs considered here.

9.9 Conclusions

We have presented a PEMFC stack model that is based on a ‘bottom-up’ approach: a computationally-efficient reduced single-cell model is combined with a model for heat and charge transfer in a coolant plate as a building block, allowing us to build a virtual PEMFC stack. To facilitate this, an automated script was implemented that carries out
Figure 9.10: Computational cost in terms of the (▲) memory and (■) degrees of freedom required for solving the automated, reduced stack model at an increasing number of cells.

every step – from drawing the geometry and meshing it, assigning governing equations and boundary conditions, to solving and postprocessing – in an efficient manner, thus removing the tedious task of manually setting up the stack geometry, as well as eliminating potential human error once the automated procedure is verified with the full set of equations.

The automated, reduced stack model captures all the essential physics (except for two-phase transport) and preserves geometrical resolution throughout the stack without sacrificing any salient features if perturbations are ‘small’ and, most importantly: It does so at a significantly reduced computational cost compared to solving the full set of equations. Although the model considers gas-phase flow only, the mathematical framework presented serves as the basis for incorporating a two-phase model for simultaneous liquid and gas flow. If perturbations are not negligible, the reduced stack model can be augmented with either an additional linear model that would solve the
next order expansion of an asymptotic series for the governing equations, or a ‘hybrid’
model that would solve conservation of energy and charge of electrons with the full set
of equations and the remaining transport equations with the reduced counterpart. We
note that these two extensions could allow, where the sample size (i.e. number of cells)
is sufficiently large, for statistical modeling of variations and perturbations in material
properties arising from stack manufacture and assembly, e.g. porosity, conductivities
and uneven flow resistance between flow fields of different cells, to name but a few.
Other possibilities include fully automated optimization studies for operating, design
and geometrical features of the stack, and overall system studies where the sub-model
for the PEMFC stack is not limited to empirical or semi-empirical correlations.

Furthermore, the concept can be extended to encompass other types of internal
flow fields (e.g., serpentine or parallel), by solving for a three-dimensional unit cell as
building block, or external manifolds for the anode, cathode and coolant plates (e.g., U-
or Z-shaped flow patterns [13, 134]); the latter could be accomplished either numerically
where one aims to resolve the three-dimensional nature of the manifolds themselves or
from mathematical approximations (see, e.g., [156]). One could also vary the building
block itself, e.g. in terms of coolant plate size and/or placement.
Chapter 10

Computationally Efficient Multi-Phase Models for a PEMFC: Asymptotic Reduction and Thermal Decoupling

Generally, multi-phase models for the proton exchange membrane fuel cell (PEMFC) that seek to capture the local transport phenomena are inherently non-linear with high computational overhead. We address the latter with a reduced multi-phase, multicomponent, and non-isothermal model that is inexpensive to compute without sacrificing geometrical resolution and the salient features of the PEMFC – this is accomplished by considering a PEMFC equipped with porous flow fields operating in co-flow coupled with scaling arguments and leading-order asymptotics. The reduced model is verified with the calibrated and validated full model for three different experimental fuel cells: good agreement is found. The reduced model is shown to scale well with increased mesh density and up to 5 processors; it also reduces memory requirements and computational time by around 2-3 orders of magnitude. In addition, thermal decoupling – by solving the set of equations isothermally first, followed by solving the energy equation in a post-processing step – is explored in an attempt to further reduce computational
cost. Finally, we discuss how other types of flow fields and transient conditions can be incorporated into the mathematical and numerical framework presented here.

10.1 Introduction

The operation of the low-temperature proton exchange membrane fuel cell (PEMFC) requires careful balancing of the water content throughout the various functional layers. To date, the transport mechanisms and state of water in these layers are not yet fully understood – mainly due to the small length scales that impede straightforward experimental measurements and visualization, as well as the inherent complexity in mathematical modeling and simulation of multi-phase flows. Various in-situ visualization techniques, such as nuclear magnetic resonance imaging, beam interrogation, and direct optical photography, have been employed to measure water distributions in a PEMFC; however, the first two methods only provide limited temporal resolution and the third can only provide details of the water transport in the flow channels and upper layers of the gas diffusion layer. Similarly, a number of mathematical models have been developed, ranging from multi-phase mixture models to multi-fluid and volume-of-fluid models, with the aim of resolving coupled liquid and gas flow in the flow fields and/or other functional layers. These models are generally highly non-linear and coupled and require more constitutive relations than single-phase counterparts: e.g., wetting angles, capillary pressures, and flow patterns. As a result, the computational cost is significantly higher, with more fine-tuning of numerical solvers required in order to ensure a fully converged solution compared to single-phase models – see Refs. for comprehensive reviews of single- and multi-phase models. There have been some attempts to lower the computational cost by deriving reduced multi-phase models; these, however, do not preserve geometrical resolution – i.e., they are not able to capture
variations in dependent variables in all three space dimensions.

In view of the computational cost of multi-phase models, the aim of this chapter is to present a fast, robust, and efficient multi-phase reduced steady-state model for the PEMFC that captures the global performance and the salient features of the local multi-phase transport phenomena whilst preserving geometrical resolution. The model can then be employed for wide-ranging parameter and design studies, for multi-objective optimization, and as a building block for stack models. To accomplish this, we exploit the methodology that allowed us to secure a reduced, leading-order one-phase PEMFC model\cite{96, 203} viz., a PEMFC equipped with porous flow fields, which allows us to reduce a three-dimensional cell to two-dimensional model since changes in the spanwise direction can be considered negligible due to no-flux and slip conditions (z-direction in Fig. 10.1); a systematic reduction of the mathematical formulation through leading-order asymptotics and scaling arguments; and a fast space-marching algorithm for the reduced model.

In short, our previous one-phase PEMFC model\cite{96, 203} is extended to include a multi-phase formulation and a more detailed transport of water in the membrane based on Siegel et al.’s work\cite{66}, after which the resulting mathematical multi-phase formulation is analyzed and reduced by scaling arguments and leading-order asymptotics from a set of elliptic partial differential equations (PDEs) to a set of parabolic PDEs and ordinary differential equations (ODEs). In addition, the commonly-used phenomenological membrane transport model by Springer et al.\cite{27} is inverted and a closed-form expression for it is obtained. In an effort to further reduce the computational cost, the transport equation for energy is decoupled based on scaling arguments\cite{65} and solved in a post-processing manner. The full set of equations is then calibrated and validated with polarization curves from three different experimental PEMFCs\cite{79, 80} the reduced formulation is verified against the full set of equations. Thermal decoupling is studied
and verified, after which the computational cost and efficiency is explored. Finally, conclusions are drawn and extensions within the mathematical and numerical framework to include other types of common flow fields and transient cell behavior are highlighted.

### 10.2 Mathematical formulation

Figure 10.1: Schematic of a PEMFC and the computational molecule for the reduced model with a system of parabolic PDEs (\(\rightarrow\)) and ODEs (\(\bullet\)) in the flow field, and ODEs (\(\bullet\)) in the remainder of the cell, viz., cc, gdl, cl, and m. Boundaries are marked with Roman numerals (N.B. \(h_{\text{MEA}} = 2 \times h_{\text{cl}} + h_{\text{m}}\)).

We consider multi-phase, multicomponent, and non-isothermal fluid flow in the functional layers – current collector (cc), flow field (ff), gas diffusion layer (gdl), catalyst layer (cl), and membrane (m) – of a PEMFC equipped with a porous flow field operating in coflow mode, as illustrated schematically in Fig. [10.1](#). The full set of governing equations comprising conservation of mass (liquid and gas), momentum, species in the gas phase (cathode: \(\text{O}_2\), \(\text{H}_2\text{O}\), and \(\text{N}_2\); anode: \(\text{H}_2\), and \(\text{H}_2\text{O}\)), water in the membrane[^66], energy and charges (electrons and protons), together with the constitutive relations, an
agglomerate model for the cathode catalyst layer, and a short discussion of the treatment of the relation for water activity in the membrane as a function of water content can be found in Chapter 3.

10.2. Boundary conditions

According to the roman numerals shown in Fig. 10.1, the boundary/interface conditions can be written as follows.

- At the cathode inlet (I):

\[
u(g) = U_{c}^{in}, \quad \omega_{O_2}^{(g)} = \omega_{O_2}^{in}, \quad \omega_{H_2O}^{(g)} = \omega_{H_2O,c}^{in}, \quad \frac{\partial \phi^{(s)}}{\partial x} = 0, \quad T = T_{c}^{in}, \quad s = s^{in}. \tag{10.1}\]

- At the anode inlet (II):

\[
u(g) = U_{a}^{in}, \quad \omega_{H_2}^{(g)} = \omega_{H_2}^{in}, \quad \omega_{H_2O}^{(g)} = \omega_{H_2O,a}^{in}, \quad \frac{\partial \phi^{(s)}}{\partial x} = 0, \quad T = T_{a}^{in}, \quad s = s^{in}. \tag{10.2}\]

In general, a PEMFC is operated at a specified stoichiometry. The stoichiometries, \(\xi_{a,c}\), are defined as the ratio of the amount of reactant supplied to the amount of reactant required by the electrochemical reaction in the catalyst layers to generate the overall average current density, \(i_{avg}\), where

\[i_{avg} = \frac{1}{L} \int_{0}^{L} i(x') \cdot e_y dx', \tag{10.3}\]

and \(i\) is the local current density which can be obtained either from \(i^{(m)}\) or \(i^{(s)}\). With the introduction of stoichiometries, the inlet velocities can be computed as:

\[U_{a}^{in} = \frac{i_{avg}LM_{H_2}}{2Fh_{ff}^{in}\omega_{H_2}^{in} r_{a}^{in} \xi_{a}}, \quad U_{c}^{in} = \frac{i_{avg}LM_{O_2}}{4Fh_{ff}^{in}\omega_{O_2}^{in} r_{c}^{in} \xi_{c}}. \tag{10.4}\]
we use this for the validation with the segmented cell results obtained by Noponen et al. [79]

- At the outlet (III):

\[
p^{(g)} = p^{\text{ref}}, \quad \frac{\partial \omega_i^{(g)}}{\partial x} = \frac{\partial \phi^{(s)}}{\partial x} = \frac{\partial T}{\partial x} = \frac{\partial s}{\partial x} = 0. \tag{10.5}\]

For the validation with experiments done by Han et al. [80], note that we prescribe an outlet velocity for both the anode and cathode coupled with inlet pressures, e.g. \(p^{(g)} = p^{\text{ref}}\) (at boundaries I and II) and \(u^{(g)} = U_{\text{out}}^{\text{a,c}}\) (at boundaries III). These conditions are similar to how Han et al. carried out their measurements.

- At the vertical walls (IV):

\[
u^{(g)} = u^{(l)} = 0, \quad \frac{\partial \omega_i^{(g)}}{\partial x} = \frac{\partial \phi^{(s)}}{\partial x} = \frac{\partial \phi^{(m)}}{\partial x} = \frac{\partial T}{\partial x} = 0, \quad \mathbf{n}^{(m)} \cdot \mathbf{e}_x = 0. \tag{10.6}\]

- At the upper wall (V):

\[
\phi^{(s)} = E_{\text{cell}}, \quad T = T^{\text{cool}}. \tag{10.7}\]

- At the current collector/flow field interface (VI and XI):

\[

\nu^{(g)} = v^{(l)} = 0, \quad \frac{\partial \omega_i^{(g)}}{\partial y} = 0. \tag{10.8}\]

- At the flow field/gas diffusion layer (VII):

\[
p^{(g)} |_{\text{VII}^+} = p^{(g)} |_{\text{VII}^-}, \quad v^{(g)} |_{\text{VII}^+} = v^{(g)} |_{\text{VII}^-}. \tag{10.9}\]

- At the gas diffusion layer/catalyst layer interface (VIII):
\[ \frac{\partial \phi^{(m)}}{\partial y} = 0, \quad n_{H_2O}^{(m)} \cdot e_y = 0. \]  (10.10)

- At the catalyst layer/membrane interface (IX and X):

\[ u^{(g)} = u^{(l)} = 0, \quad \frac{\partial u^{(g)}}{\partial y} = \frac{\partial \phi^{(s)}}{\partial y} = 0. \]  (10.11)

- At the lower wall (XII):

\[ \phi^{(s)} = 0, \quad T = T_{\text{cool}}. \]  (10.12)

10.2.2 Reduced model

To reduce the full set of equations of the multi-phase model, the methodology developed in our previous work\cite{96, 203} for a one-phase formulation is employed and extended to encompass the transport of liquid water. In essence, the reduced multi-phase model embodies the following main features:

1. \textit{Reduction in dimensionality}. As illustrated in Fig. [10.1] the porous nature of the flow field allows a reduction in dimensionality from three to two dimensions due to the slip- and no-flux conditions that can be assigned at the side walls in the spanwise direction (\(e_z\)).

2. \textit{Narrow-gap approximation}. The slenderness of a typical fuel cell, for which the thickness of a functional layer is much smaller than the overall length of the cell, \(h_j \ll L\), is exploited to remove second-order diffusive terms in the streamwise direction (\(e_x\)) at leading order for the conservation equations – thus reducing the elliptic PDEs to parabolic counterparts.

3. \textit{Reduction of PDEs to a set of PDEs and ODEs}. The transport equations – for charge, energy, species, momentum, and mass in the gas phase – in the membrane,
catalyst layers, and gas diffusion layers are at leading order in the normal direction ($e_y$), which further reduces these conservation equations from parabolic PDEs to ODEs. In addition, one can show that the same applies to the conservation of liquid mass, Eq. 4.15 by first estimating the scale of the normal mass flow of liquid per volume in the catalyst layer by balancing it with the electrochemical reaction; i.e.

$$
\frac{[v^{(l)}]_c \rho^{(l)}}{h_{cl}} \sim \frac{M_{\text{H}_2\text{O}}[J]}{F} \approx 10^2 \text{ kg m}^{-3} \text{ s}^{-1},
$$

(10.13)

where $[v^{(l)}]_c$ is the velocity scale in the normal ($e_y$) direction, $\rho^{(l)} \sim 10^3 \text{ kg m}^{-3}$ is the liquid density, $h_{cl} \sim 10^{-5} \text{ m}$ is the thickness of the catalyst layer, $M_{\text{H}_2\text{O}}$ is the molecular mass of water, $[J] \sim 10^9 \text{ A m}^{-3}$ (at current densities of around $10^4 \text{ A m}^{-2}$) is the volume current density, and $F$ is Faraday’s constant. If we extract $[v^{(l)}]_c$ from Eq. 10.13, we find that $[v^{(l)}]_c \sim 10^{-6} \text{ m s}^{-1}$, which is consistent with our earlier scaling analysis. If we over-estimate the velocity in the streamwise direction by scaling it with the induced velocity from the interface between the flow field and the gas diffusion layer (see Ref. 96 for details), i.e.

$$
[u^{(l)}]_c \sim \frac{\kappa_{\text{gdl}}}{\kappa_{\text{ff}}} [u^{(g)}]_f ,
$$

(10.14)

and further employ the relation between the liquid and gas phase velocities, Eq. 10.27 we arrive at

$$
[u^{(l)}]_c \sim [m] \frac{\kappa_{\text{gdl}}}{\kappa_{\text{ff}}} [u^{(g)}]_f.
$$

(10.15)

Here, $[u^{(l)}]_c$ and $[u^{(g)}]_f \sim 1 \text{ m s}^{-1}$ are the scales for the streamwise velocity ($e_x$) in the catalyst and flow field respectively, $\kappa_{\text{gdl}} \sim 10^{-12} \text{ m}^2$ and $\kappa_{\text{ff}} \sim 10^{-8} \text{ m}^2$ are the permeabilities of the gas diffusion layer and flow field respectively, and $[m] \sim 10^{-2}$ is the mobility of the liquid phase. The streamwise flow of liquid water per volume
thus becomes

\[
\frac{[u_{cl}^{(l)}][\rho^{(l)}]}{L} \sim \frac{[m] \kappa_{gdl} [\nu_{eff}^{(g)}] \rho^{(l)}}{\kappa L} \approx 10^{-2} \text{ kg m}^{-3} \text{ s}^{-1}, \tag{10.16}
\]

which is negligible in comparison to the mass flux per volume of liquid in the normal direction, i.e.

\[
\frac{[u_{cl}^{(l)}][\rho^{(l)}]}{L} \ll \frac{[v_{cl}^{(l)}][\rho^{(l)}]}{h_{cl}}. \tag{10.17}
\]

This shows that the transport equation for the liquid mass reduces to an ODE in the gas diffusion and catalyst layers. In addition, in the flow fields and current collectors, transport of heat and charge occur at leading order in the normal direction, such that we only need to consider ODEs for these equations.

**Reduced form of the governing equations** – For the flow fields, we solve

\[
\frac{\partial}{\partial x} \left( \rho^{(l)} u^{(l)} \right) + \frac{\partial}{\partial y} \left( \rho^{(l)} v^{(l)} \right) = S_{\text{mass}}^{(l)}, \tag{10.18}
\]

\[
\frac{\partial p^{(g)}}{\partial x} + \frac{\nu_{eff}^{(g)}}{\kappa_{rel} \kappa} u^{(g)} = - \frac{\rho^{(g)} c_F}{\kappa_{rel} \sqrt{\kappa}} \left( u^{(g)} \right)^2, \tag{10.19}
\]

\[
\frac{\partial p^{(g)}}{\partial y} = 0, \tag{10.20}
\]

\[
\frac{\partial}{\partial x} \left( \rho_i^{(g)} \omega_i^{(g)} u^{(g)} \right) + \frac{\partial}{\partial y} \left( \rho_i^{(g)} \omega_i^{(g)} v^{(g)} - \rho^{(g)} D_i^{(g)} \frac{\partial \omega_i^{(g)}}{\partial y} \right) = S_i^{(g)}, \tag{10.21}
\]

\[
\frac{\partial}{\partial y} \left( -k_{eff} \frac{\partial T}{\partial y} \right) = S_{\text{temp}}, \tag{10.22}
\]

\[
\frac{\partial}{\partial y} \left( -\sigma_{eff} \frac{\partial \phi^{(s)}}{\partial y} \right) = 0. \tag{10.23}
\]

In the flow fields, we are able to reduce the number of dependent variables by combining Eq. 4.14 and 4.15 as

\[
\frac{\partial}{\partial x} \left( \rho^{(g)} u^{(g)} + \rho^{(l)} u^{(l)} \right) + \frac{\partial}{\partial y} \left( \rho^{(g)} v^{(g)} + \rho^{(l)} v^{(l)} \right) = 0 \tag{10.24}
\]
since \( S_{\text{mass}}^{(g)} + S_{\text{mass}}^{(l)} = 0 \) in the flow fields; we then introduce the stream function, \( \psi \), which is defined by

\[
\rho^{(g)} u^{(g)} + \rho^{(l)} u^{(l)} = \frac{\partial \psi}{\partial y}, \tag{10.25}
\]

\[
\rho^{(g)} v^{(g)} + \rho^{(l)} v^{(l)} = -\frac{\partial \psi}{\partial x}, \tag{10.26}
\]

so that the combined continuity equation, Eq. [10.24], is automatically satisfied; we thus only need to solve for the two dependent variables, \( p^{(g)} \) and \( \psi \), instead of the original three variables, \( p^{(g)}, u^{(g)}, \) and \( v^{(g)} \).

We can now derive explicit expressions for both gas and liquid velocities in terms of the stream function. According to the scales obtained from our previous work,[96] the gas velocity scale in the \( y \)-direction is much smaller than the one in the \( x \)-direction for the flow field, i.e. \([v^{(g)}] \ll [u^{(g)}] \sim 1 \text{ m s}^{-1}\), and \( h_{\text{g}}/L \ll 1 \), whence the expression for the liquid velocity, Eq. [4.29] and [4.35], can be rewritten as

\[
u^{(l)} = m v^{(g)} + m_F u^{(g)} v^{(g)} - D^{(c)} \frac{\partial s}{\partial y}, \tag{10.28}\]

where

\[
m = \frac{\kappa^{(l)} \mu^{(g)}}{\kappa^{(g)} \mu^{(l)}} \quad m_F = \frac{c_F \rho^{(g)} \kappa^{(l)} \sqrt{\kappa}}{\rho^{(l)} \kappa^{(g)} \mu^{(l)}}, \quad D^{(c)} = -\frac{\kappa^{(l)} \mu^{(g)}}{\mu^{(l)}} \frac{d p^{(c)}}{d s}. \tag{10.29}\]

Substituting Eqs. [10.27] and [10.28] into Eqs. [10.25] and [10.26] yields

\[
u^{(g)} = \frac{-\left(\rho^{(g)} + \rho^{(l)} m\right) + \sqrt{\left(\rho^{(g)} + \rho^{(l)} m\right)^2 + 4 \rho^{(l)} m F \frac{\partial \psi}{\partial y}}}{2 \rho^{(l)} m_F \frac{\partial \psi}{\partial y}}, \tag{10.30}\]

\[
u^{(g)} = \frac{\rho^{(l)} D^{(c)} \frac{\partial s}{\partial y} - \frac{\partial \psi}{\partial x}}{\rho^{(g)} + \rho^{(l)} m + \rho^{(l)} m_F u^{(g)}}. \tag{10.31}\]
Note that Eq. [10.30] is obtained by solving the quadratic Eq. [10.25] and discarding the root that gives a negative $u^{(g)}$.

For the current collectors, gas diffusion layers, catalyst layers, and membrane, we have

\[ \frac{\partial}{\partial y} \left( \rho^{(g)} v^{(g)} \right) = S_{\text{mass}}^{(g)}, \quad (\text{gdl, cl}) \] (10.32)

\[ \frac{\partial}{\partial y} \left( \rho^{(l)} v^{(l)} \right) = S_{\text{mass}}^{(l)}, \quad (\text{gdl, cl}) \] (10.33)

\[ \frac{\partial p^{(g)}}{\partial y} + \frac{\mu^{(g)}}{\kappa^{(g)}} v^{(g)} = 0, \quad (\text{gdl, cl}) \] (10.34)

\[ \frac{\partial}{\partial y} \left( \rho^{(g)} \rho^{(g)} v^{(g)} - \rho^{(g)} D_{\text{eff}}^{(g)} \frac{\partial}{\partial y} \right) = S_{1}^{(g)}, \quad (\text{gdl, cl}) \] (10.35)

\[ \frac{\partial}{\partial y} \left( \frac{n_{d}^{(m)} M_{\text{H}_{2}\text{O}}}{F} - \frac{\rho^{(m)} M_{\text{H}_{2}\text{O}}}{M^{(m)}} D_{\text{H}_{2}\text{O,eff}}^{(m)} \frac{\partial}{\partial y} \right) = S_{\text{H}_{2}\text{O}}^{(m)}, \quad (\text{m}) \] (10.36)

\[ \frac{\partial}{\partial y} \left( -k_{\text{eff}} \frac{\partial T}{\partial y} \right) = S_{\text{temp}}, \quad (\text{cc, gdl, cl}) \] (10.37)

\[ \frac{\partial}{\partial y} \left( -\sigma_{\text{eff}}^{(m)} \frac{\partial \phi^{(m)}}{\partial y} \right) = S_{\text{pot}}, \quad (\text{cl, m}) \] (10.38)

\[ \frac{\partial}{\partial y} \left( -\sigma_{\text{eff}}^{(g)} \frac{\partial \phi^{(g)}}{\partial y} \right) = -S_{\text{pot}}, \quad (\text{cc, gdl, cl}) \] (10.39)

Reduced from of the boundary conditions – The reduced model only requires upstream (I, II) boundary conditions for the flow field and boundary conditions in the normal direction (V-XII) – the other boundary conditions (III, IV) need only be solved for the full set of equations. With the introduction of the stream function for the reduced model, we need to rephrase the associated boundary conditions as follows.

- At the inlet (I and II):

\[ \psi = \left( \left( \rho^{(g)} \right)_{\text{in}} + \rho^{(l)}_{\text{in}} m_{\text{in}} \right) U_{\text{a,c}}^{\text{in}} + \rho^{(l)}_{\text{in}} m_{\text{F}}^{\text{in}} \left( U_{\text{a,c}}^{\text{in}} \right)^{2} y|_{\text{L,H}}. \] (10.40)

- At the current collector/flow field interface (VI and XI):
\[ \psi|_{V_{I\text{III}}} = \left( \rho^{(g)\text{in}} + \rho^{(l)\text{in}} m^{\text{in}} \right) t_{a,c}^{\text{in}} + \rho^{(l)\text{in}} m_F^{\text{in}} \left( U_{a,c} \right)^2 \right) \psi|_{V_{I\text{III}}}. \] (10.41)

- At the flow field/gas diffusion layer interface (VII):

\[ p^{(g)}|_{VII+} = p^{(g)}|_{VII-}, \quad -\frac{\partial \psi}{\partial x} \bigg|_{VII+} = \rho v^{(g)}|_{VII-}. \] (10.42)

Note that \( m^{\text{in}} \) and \( m_F^{\text{in}} \) are computed from Eq. 10.29 based on the inlet liquid saturation, \( s^{\text{in}} \).

### 10.3 Numerics

Both the full and the reduced models were implemented and solved with the commercial finite-element solver COMSOL Multiphysics 3.5a. 10 dependent variables — \( u^{(g)}, v^{(g)}, p^{(g)}, \omega^{(g)}_{\text{O}_2}, \omega^{(g)}_{\text{H}_2\text{O}}, \lambda, s, T, \phi^{(s)} \) and \( \phi^{(m)} \) — were solved for the full set of equations (Eq. 4.14-4.22), whereas 9 variables — \( \psi, p^{(g)}, \omega^{(g)}_{\text{O}_2}, \omega^{(g)}_{\text{H}_2\text{O}}, \lambda, s, T, \phi^{(s)} \) and \( \phi^{(m)} \) — were involved in solving the reduced counterpart (Eq. 10.32-10.39). The geometrical and operating parameters can be found in Tables 4.1 and 4.2.

Similar to our previous work [96], the reduced model is treated computationally as a one-dimensional geometry in the \( y \)-direction coupled with space-marching in the \( x \)-direction, whereas the full set of equations were solved with an elliptic solver in both space dimensions at once. The difference in the numerical schemes does not allow for a strict comparison of computational cost since the space-marcher employs an adaptive stepper. Therefore, in order to ensure a comparison that does not favour the reduced model, we implemented 95 elements for both the full and reduced set in the \( y \)-direction whilst ensuring that the number of steps from the space-marching algorithm, 180-230, were always larger than the prescribed 60 elements in the \( x \)-direction for the full set;
quadratic Lagrange elements were employed for all dependent variables together with a direct linear solver (PARDISO). Furthermore, mesh independence tests were carried out before calibration, verification and validation for both the full and reduced models.

In order to ensure convergence, and so a more robust code, a non-zero constant, $D_0$, is added in the numerical implementation of the capillary diffusion coefficient, $D^{(c)}$, since the latter tends to zero as the region of solely one-phase flow is approached, i.e. where the liquid saturation is zero; see Refs. [185] and [112] for a more detailed discussion. In doing so, the value for $D_0$ has to be chosen carefully by balancing the accuracy of the solution with the robustness of the code; in our case, $D_0 = 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for the gas diffusion and catalyst layers and $D_0 = 10^{-6} \text{ m}^2 \text{ s}^{-1}$ for the porous flow fields were found to satisfy both requirements. In addition, the full set of equations are solved in a three-step procedure to ensure convergence for all conditions studied in this paper: first, we change the Neumann boundary conditions for the conservation of liquid mass at the upper (VI) and lower (XI) walls of the cell to Dirichlet conditions by setting the liquid saturation equal to zero, i.e., $s|_{VI, XI} = 0$; second, the modified model is solved and the solution stored; and third, the interim solution is applied as initial condition, the boundary conditions are changed back to the original Neumann no-flux conditions, and the model solved again.

All computations were carried out on a workstation with two quad-core processors (3.2 GHz) and a total of 64 GB random access memory (RAM). Eight processors were used for all calculations, except when the effect of the number of processors on computational time was studied. The real execution times (wall-clock time) and peak memory usage were estimated from the graphical user-interface of COMSOL.
10.4 Calibration, verification, and validation

The full set of equations is calibrated with global polarization curves for three different experimental PEMFCs equipped with a porous flow field: (a) a segmented cell,\(^{[79]}\) (b) a cell with a single-layer gas diffusion layer,\(^{[80]}\) and (c) a cell with a carbon-filled gas diffusion layer.\(^{[80]}\) Similar to our earlier one-phase model,\(^{[96]}\) we calibrate the cathode volumetric exchange current density, \(j_{c,0}^{\text{ref}}\), and the cathode transfer coefficient, \(\alpha_c\), for all three cells, as well as the modification factor for the Gore membrane, \(\beta^{(m)}\), for case (a) and the agglomerate radius, \(r^{(\text{agg})}\), for cases (b) and (c). All adapted parameters are given in Table 10.1.

<table>
<thead>
<tr>
<th>Adapted parameters</th>
<th>Case (a)</th>
<th>Case (b)</th>
<th>Case (c)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Segmented cell (^{[79]})</td>
<td>Single-layer gas diffusion layer (^{[80]})</td>
<td>Carbon-filled gas diffusion layer (^{[80]})</td>
</tr>
<tr>
<td>(r^{(\text{agg})})</td>
<td>(10^{-7}) m</td>
<td>(5.9 \times 10^{-7}) m (adapted)</td>
<td>(5.2 \times 10^{-7}) m (adapted)</td>
</tr>
<tr>
<td>(j_{c,0}^{\text{ref}})</td>
<td>(10^3) A m(^{-3}) (adapted)</td>
<td>(4.5 \times 10^3) A m(^{-3}) (adapted)</td>
<td>(8 \times 10^3) A m(^{-3}) (adapted)</td>
</tr>
<tr>
<td>(\alpha_c)</td>
<td>1.27 (adapted)</td>
<td>0.95 (adapted)</td>
<td>1 (adapted)</td>
</tr>
<tr>
<td>(\beta^{(m)})</td>
<td>0.8 (adapted)</td>
<td>1 (adapted)</td>
<td>1 (adapted)</td>
</tr>
</tbody>
</table>

Table 10.1: Adapted parameters for multi-phase model

Overall, good agreement – maximum relative error of around 3% – is obtained between experiments and the full and reduced set of equations, as can be inferred from Fig. 10.2; however, returning to Ref. \(^{[96]}\), we also note that the one-phase counterpart gave a slightly better agreement overall (maximum relative error of around 2%), which can be attributed to the multi-phase parameters, e.g. wetting angles and Leverett functions, that have not been calibrated – the latter requires additional experimental information that traditional polarization curves are not able to provide. Proceeding with local validation and verification for case (a) in Fig. 10.3, we find reasonable agreement between the multi-phase full and reduced set of equations, although the models do not capture
the maxima in the local current density that are evident in the experimental results for high current densities. These maxima can most likely be attributed to the humidity level in the membrane, which will depend on the local liquid saturation - the parameters of which have not been calibrated here - and the design of the experimental segmented cell; see Ref. [79, 96] for a brief discussion of the design.

![Polarization curves](https://via.placeholder.com/150)

**Figure 10.2:** Polarization curves: (▲) case (i), (▼) case (ii), (■) case (iii) from experiments [79, 80], and corresponding full (——) and reduced (×) model predictions.

We continue by verifying the reduced equations with the full set for the local temperature and liquid saturation profiles, as illustrated in Figs. 10.4 and 10.5 respectively: good agreement is found throughout the domain except close to the inlet for the temperature distribution; in this region, \( x \sim h_g \), whence the narrow-gap approximation is no longer valid. Nevertheless, the error associated with the inlet is sufficiently small that the reduced model can be employed with confidence for both global and local model
predictions; furthermore, we note that this error does not propagate downstream in the cell.

Figure 10.3: Polarization curves: (▲) case (i), (▼) case (ii), (▪) case (iii) from experiments [79, 80], and corresponding full (——) and reduced (×) model predictions.
Figure 10.4: Temperature distribution for case (ii) at the cell voltage of 0.1V: (a) full and (b) reduced models.
Figure 10.5: Liquid saturation for case (ii) at the cell voltage of 0.1V: (a) full and (b) reduced models.
10.5 Thermal Decoupling

So far, we have employed scaling arguments to reduce the full set of equations for a non-isothermal, multicomponent model of a PEMFC; and calibrated, validated and verified both the full and reduced models. The solution process for both of these models involves solving all of the coupled transport equations simultaneously; however, one can again resort to a scaling analysis and show that the multi-phase models, which solve for all the coupled transport equations simultaneously, can be reduced further by decoupling the energy equation from the other equations[65] – at least at cell voltages around or larger than the typical operating point of 0.6-0.7 V of a PEMFC. In essence, the scaling analysis can be initiated by scaling the dimensional temperature as $T = T_{\text{ref}}(T_{\text{e}} + 1)$, where $T_{\text{ref}} = T_{\text{cool}} \sim 300$ K, $T = \Delta T / T_{\text{ref}}$, and $T_{\text{e}}$ is the dimensionless temperature bounded between zero and one if the temperature change $\Delta T$ is chosen to reflect the overall temperature increase in the cell. Typically, $\Delta T \sim 10$ K for a PEMFC, whence $T \ll 1$, which in turn suggests that we should be able to “safely” set $T = T_{\text{ref}}$. Some caution is required since the temperature does appear in exponential terms, but this argument is sufficient for the present discussion. In other words, it should therefore be possible to decouple the equation for heat from the other equations by first solving the model isothermally with $T = T_{\text{ref}}$, after which one could solve the equation for heat separately as a postprocessing step to determine the temperature increase throughout the cell; this could be of use, for example, in order to identify the location of hotspots. This approach should lead to significant reductions in computational cost, since the dependent variable for temperature has to be solved throughout the cell in all functional layers: in our case, the thermal decoupling leads to a reduction in degrees of freedom of around 15-20%, as we shall see in the next Section.

To see in detail how successful thermal decoupling proves to be quantitatively, we
present first Fig. 10.6, which shows the temperature increase with and without thermal decoupling for a range of current densities.

![Figure 10.6: Polarization curves for the full non-isothermal model (--), the full (●) and reduced (×) thermal-decoupling models, and corresponding average increment in temperature in the cathode catalyst layer.](image)

Clearly, the global polarization curves predicted by the thermally decoupled models agree well with the non-decoupled counterpart for the entire range, especially for $E_{\text{cell}} \geq 0.6$ V, with a maximum relative error of around 6% when $E_{\text{cell}} \approx 0.45$ V, corresponding to a current density of $10^4$ A m$^{-2}$. Similarly, the average temperature increase for the cathode catalyst layer, which we define by

$$
\Delta T = \frac{1}{h_{cl}L} \left( \int_0^{h_{cl}} \int_0^L T_{cl} \, dx \, dy \right) - T_{\text{cool}},
$$

differs by a maximum relative error of around 20%. Note the reason for choosing Eq.
10.5. Thermal Decoupling

as a representative indicator: the cathode catalyst layer is typically the hottest region in the cell due to sluggish reaction kinetics by comparison with the anode catalyst layer, which manifests itself in a relatively higher reversible and irreversible heat generation. The error on the local level can be observed in Fig. 10.7 for the local temperature distribution at a cell potential of 0.1 V – the low potential was chosen because the heat generation is close to maximum when the cell potential approaches short-circuit conditions.

In summary: we have heuristically justified decoupling of the energy equation by scaling arguments, so that the remaining equations can first be solved in an isothermal setting, after which the temperature distribution is determined by solving the energy equation alone in a post-processing step where the other dependent variables are retained from the isothermal solution. This procedure accelerates the numerical scheme due to the reduced number of degrees of freedom – essentially one dependent variable less – as well as reduced nonlinearity, since the numerical solver does not have to consider thermal coupling; however, the computational speed-up has to be weighed against the error incurred, which is around 20% or less than for the global and local temperature distributions with the geometry and operating conditions considered here.
Figure 10.7: Temperature distribution for case (ii) at the cell voltage of 0.1V: (a) full and (b) reduced thermal-decoupling models.
10.6 Computational cost and efficiency

We have already hinted at a lowered computational cost for the reduced and thermally decoupled models; that this is indeed the case can be inferred from Table 10.2, which summarizes the degrees of freedom (DoF), memory requirements in gigabyte (GB), the time required to reach a converged solution, and postprocessing time for the energy equation of the thermally-decoupled models for three different cases: (i) a 1-cell mesh; (ii) a 10-cell mesh; and (iii) a 100-cell mesh, which is, however, only solved for the reduced model since the computational cost is prohibitive for the full set. These cases correspond to estimates of the computational cost and scalability of the models when solving a 1-cell PEMFC and a 10- and 100-cell PEMFC stack, where we have increased the overall single-cell mesh by a factor of 10 and 100 respectively to emulate the stacks. Here, several features are apparent. First and foremost is the reduction in the DoFs for the reduced model of around 2 orders of magnitude, as compared to the full set of equations, which leads to substantial savings in compute time and memory: around 2-3 orders of magnitude. Overall, the reduced model scales well as the mesh density increases, which makes it a good candidate for detailed stack models.[97]

Further, thermally decoupling the full set of equations leads to around 30-50% improvement in memory and convergence time, whereas the reduced model only displays a significant gain for the 100-cell mesh with a reduction in memory and time of around 10-20%.

Finally, we also study how the various multi-phase models scale with the number of processors (cores) in Fig. 10.8 from which it can be seen that the normalized real time drops by around 30% and 60% for the full set and reduced counterparts as the number of processors are increased from 1 to 5, after which the computational gain levels off.
Table 10.2: Computational cost in terms of DoF, memory, and time for case (b).

## 10.7 Conclusions

In this chapter, we have presented a reduced multiphase, multicomponent, and non-isothermal model of a PEMFC as well as thermally-decoupled reduced and full models. The reduced model – justified by scaling arguments – has been verified with a calibrated, validated full model with overall good agreement and shown to reduce the computational cost by 2-3 orders of magnitude; the thermally-decoupled models – heuristically justified by scaling arguments – incurred a larger error viz-a-viz the full model of around 20% at high current densities whilst reducing the computational cost in terms of memory.
10.7. Conclusions

requirements and computational time by around 30-50% and 10-20% for the thermally-decoupled full and reduced models. One therefore has to carefully weigh the error versus the reduction in computational cost when decoupling the equation of change for energy and solving it in a post-processing step.

The reduced model has been shown to scale well with both increasing number of processors (up until 5 processors) and with increased mesh density, which renders it suitable as a building block for detailed stack models that aim to resolve transport phenomena locally throughout the stack.

The model is based on porous flow fields, which might be considered limiting at first sight, because it should not be able to capture three-dimensional effects that occur in other types of flowfields, e.g., parallel or serpentine flow channels; however, we expect that one should be able to reduce repetitive flow-channel-based flow fields to a porous
counterpart by applying volume-averaging over the channels; such a porous counterpart could then, in turn, be reduced to the two-dimensional model presented here.

Finally, we note that whilst the models considered here are for steady-state conditions, we also expect that a similar methodology – scaling arguments and leading-order asymptotics – can be applied for transient conditions to secure reduced formulations that are efficient from the computational point of view; e.g., we envision a numerical solver that not only marches in the streamwise direction, such as presented here, but also marches in time.
Chapter 11

Conclusions and Future Work

The overall objective of this research study is to develop fast and efficient mathematical models of a proton exchange membrane fuel cell (PEMFC), which can resolve the essential transport phenomena at the local level as well as be able to extend to model a stack comprising hundreds of single cells – establishing a modeling framework on several length scales ranging from $O(1 \text{ nm})$ to $O(1 \text{ m})$. In view of this, volume averaging, scale-analysis, asymptotic reduction, and thermal decoupling were employed for attempts at model reduction. The achievements, limitations, as well as recommendation for future work were summarized as follows.

11.1 Summary of results

First of all, a three-dimensional (3D) PEMFC model equipped with parallel channels was successfully implemented in Comsol Multiphysics. The volume-averaging technique was employed to reduce the parallel channels to porous flow field with a numerical permeability and effectively diffusive coefficients obtained. Furthermore, a correction factor was introduced to the governing equations to capture the effect of the ribs on the transport in the gas diffusion layers and current collectors. All of these provide a major
step towards reduction of the 3D model with parallel channels to a two-dimensional (2D) model with porous flow field. The result is significant reduction in computational cost and time as compared to solving a 3D PEMFC model. In terms of accuracy, the verifications show good agreement at both the global and local levels except for the case of temperature and liquid saturation, which have to be further explored for better agreements.

Secondly, a scaling analysis was applied to the cathode of a PEMFC to secure typical scales for all variables from which we are able to predict the performance of the fuel cell without having to solve the full set of governing equations. The scales allow us to quantify the transport mechanisms in several domains in a PEMFC, thus, building a first step towards reduction of the model for the whole cell. This methodology is, however, suitable for a simple problem, and it becomes complicated as one invoke the whole cell comprising of a large number of highly coupled non-linear partial differential equations (PDEs).

Following on, a 2D single-phase PEMFC equipped with porous flow field was analyzed with asymptotic reduction to develop a space-marching model (reduced model). The reduced model was obtained by reducing the full set of equations (system of PDEs) to a set of PDEs and ODEs in the flow field and a set of ODEs in the remainder of the cell; this preserved the geometrical resolution. The computational cost in terms of random access memory and execution time required for solving the reduced model was between two to three orders of magnitude less than that of the full model. This modeling approach provides a feasible solution for stack modeling, accelerating wide-range parameters studies, and speeding up the optimization processes.

Next, the reduced single phase model was employed as a building-block for a stack equipped with an arbitrary number of cells and coolant plates. An automatic code generator was developed to facilitate the implementation of the stack model – from drawing
11.2. Recommendations for future work

the geometry and meshing it, assigning governing equations and boundary conditions, to solving and postprocessing. As a result, we were able to build and solve a stack consisting of 400 single cells within 15 minutes and 2.3GB of RAM required, without any effort and human errors made in implementation of the code. The low computational cost coupled with the level of resolution (in terms of transport phenomena that are solved locally throughout the stack) opens up avenues for wide-ranging parameter studies, fully automated optimization of stacks and detailed system models.

Finally, the single-phase reduced model was successfully extended to include liquid water transport in a multi-phase counterpart. The model has been validated against three different sets of experimental data with good agreement achieved. The thermal effect on operating condition has been analyzed and decoupled from the rest of governing equations.

11.2 Recommendations for future work

Based on the results obtained, some potential areas for further investigation related to PEMFC modeling are highlighted below.

1. Porous medium approach – The key advantage of the reduction method employed in this thesis is that the fuel cell equipped with a porous flow field allows a reduction from the three-dimensional model to two-dimensional counterpart. As a first step to generalize this methodology to other types of flow fields, we have applied the porous medium approach to reduce the three-dimensional parallel-channel flow field to a two-dimensional porous one. Practically, many other types of flow field have been developed, e.g. serpentine, parallel serpentine, integrated, interdigitated flow fields, etc.\cite{23}. The main purpose of the development of these designs is to enhance the mass transfer between the flow fields and gas diffusion.
layers. However, modeling these flow field in three-dimensional model results in a high computational cost; even for a single cell model, a multi-processor system and/or multi-core parallel computing system is required to handle the computation [53]. Hence, modeling a stack equipped such flow field may be prohibitive. The aforementioned methodology can be extended to reduce such channel-type flow field in three dimensions to porous-type flow field in two dimensions, providing an additional consideration of the corner effects in such channel-type flow field.

2. Multi-phase stack model – For the single-phase models, we have developed a stack consisting of arbitrary number of cells. The drawback of this model is that when the number of cells in the stack becomes large, e.g. more than 10 cells, with high perturbations of inlet conditions between cells, error in local solutions of charge and heat transport will occur, larger and larger as moving away from the central cell of the stack. To overcome this issue, a hybrid model – consisting of the conservation of energy and charge of electrons with the full set of equations and the remaining transport equations with the reduced counterpart – can be considered to capture the perturbations in a stack with large number of cells. The procedure can base on the two-phase single cell model developed in this thesis; a stack model can be developed with the aid of automated model generation.

3. Validation of liquid water – So far, we have provided a global validation based on the polarization curves of three experimental data. At the local level, we have validated the local current density local current densities measured with the segmented cell [79]. Although, in the multi-phase model, we have solved the liquid water in the flow fields, gas diffusion layers, and catalyst layers, no validation of the local liquid water have been carried out in this thesis. This requires additional experimental information so that the multi-phase parameters, e.g. wetting angles
and Leverett functions, can be calibrated. Then, the multi-phase model, which locally captures a liquid level of water, will be a useful aid in water management in fuel cell system.

4. **Optimization** – This is one of the main purposes that the research aims towards. With the aid of the automatic code generator, we are able to carry out optimizations. The operating conditions and design parameters can be the first target of the optimizing processes. Different optimization techniques such as direct search, genetic algorithm, simulated annealing and evolutionary strategy can be employed to identify the best possible operating conditions as well as design for PEMFC stack. This optimization process will play an essential role to bring the fuel cell technology to the energy market.
Bibliography


