Reduced cell and stack modeling of planar solid oxide fuel cells

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REDUCED CELL AND STACK MODELING OF PLANAR SOLID OXIDE FUEL CELLS

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Table of Contents

Acknowledgements	i
Table of Contents	iii
Abstract.....	ix
List of Figures.....	xiv
List of Tables.....	xxi
Nomenclature	xxiii
Chapter 1 Introduction	1
1.1. Background of solid oxide fuel cell (SOFC)	5
1.2. Motivation and objectives.....	11
1.3. Thesis outline	13
Chapter 2 Literature Review	16
2.1. Cell design	16
2.1.1. Geometrical structure.....	17
2.1.1.1. Planar SOFC (P-SOFC)	17
2.1.1.2. Tubular SOFC (T-SOFC)	19
2.1.1.3. Remarks	21
2.1.2. Support structure	22
2.1.3. Operating temperature	25
2.1.4. Flow configuration.....	26
2.1.5. Fuel reforming	28
2.2. Mathematical models for P-SOFC.....	30
2.2.1. Polarizations.....	31
2.2.1.1. Reversible potential	33

2.2.1.2.	Activation polarization.....	34
2.2.1.3.	Ohmic polarization.....	38
2.2.1.4.	Concentration polarization	39
2.2.1.5.	Leak polarization.....	40
2.2.2.	Transport phenomena in electrodes.....	41
2.2.2.1.	Volume averaging for porous media	42
2.2.2.2.	Mass transfer	43
2.2.2.3.	Momentum transfer	47
2.2.2.4.	Energy transfer	49
2.2.2.5.	Reaction zone	51
2.2.3.	Spatial dimension	52
2.2.3.1.	Zero-dimensional model	52
2.2.3.2.	One-dimensional model	53
2.2.3.3.	Two-dimensional model.....	54
2.2.3.4.	Three-dimensional model.....	55
2.2.3.5.	Remarks.....	56
2.2.4.	Time dependence.....	56
2.2.5.	Thermo-mechanical modeling	58
2.2.6.	P-SOFC stack models	59
2.2.7.	Model simplification	60
2.2.8.	Sensitivity analysis.....	61
2.3.	Numerical methods for SOFC.....	63
2.4.	Summary	65
Chapter 3	Full 3D P-SOFC Model.....	71
3.1.	Introduction.....	71

3.2.	Assumptions.....	71
3.3.	Modeling domains	72
3.4.	Mathematical model.....	73
3.4.1.	Governing equations	74
3.4.1.1.	Conservation of mass	74
3.4.1.2.	Conservation of momentum.....	74
3.4.1.3.	Conservation of species	75
3.4.1.4.	Conservation of charge	76
3.4.1.5.	Conservation of energy	76
3.4.2.	Constitutive relations and boundary conditions.....	77
3.5.	Numerical implementation.....	83
3.6.	Validation	85
3.7.	Numerical convergence test	90
3.8.	Summary	93
Chapter 4	Development of a Reduced Model: Asymptotic Spatially-Smoothed Isothermal (ASSI) Cell Model.....	94
4.1.	Introduction.....	94
4.2.	Spatial smoothing with novel correlation factors	95
4.2.1.	Momentum and mass transport in flow field	98
4.2.2.	Mass and charge transport in backing layer.....	100
4.3.	Asymptotic reduction.....	105
4.3.1.	Nondimensionalization	105
4.3.2.	Reference and scale factors.....	108
4.3.2.1.	Reference factors	109
4.3.2.2.	Scale factors for velocity and pressure drop	109

4.3.2.3.	Scale factors for diffusivity and correlation.....	112
4.3.2.4.	Scale factors for potential and current density	113
4.3.3.	Asymptotic spatially-smoothed formulation.....	114
4.4.	Numerical implementation.....	115
4.5.	Verification.....	117
4.6.	Computational cost analysis.....	123
4.7.	Summary	125
Chapter 5	Development of Advanced Spatially-Smoothed Isothermal Cell Models	
		127
5.1.	Introduction.....	127
5.2.	Mathematical model.....	128
5.2.1.	Governing equations and boundary conditions.....	128
5.2.2.	Novel variation factors to capture the variability of dependent variables underneath flow channels.....	131
5.3.	Numerical implementation.....	134
5.4.	Verification.....	135
5.5.	Summary	141
Chapter 6	Monte Carlo Simulation of Advanced ASSI Cell Model: Sensitivity Analysis of Cell Performance	143
6.1.	Introduction.....	143
6.2.	Advanced ASSI model	143
6.3.	Monte Carlo simulation.....	147
6.4.	Numerical implementation.....	149
6.5.	Statistical results and sensitivity analysis	151
6.6.	Summary	161

Chapter 7	Development of Reduced Models: Asymptotic Spatially-Smoothed Thermal (ASST) Cell and Stack Models.....	163
7.1.	Introduction.....	163
7.2.	Cell and stack modeling.....	164
7.3.	Spatially smoothed energy equation	166
7.3.1.	Local thermal equilibrium.....	166
7.3.2.	Local thermal non-equilibrium	170
7.4.	Asymptotic reduction.....	172
7.4.1.	Local thermal equilibrium.....	173
7.4.2.	Local thermal non-equilibrium	176
7.5.	Numerical implementation.....	180
7.6.	Verification.....	181
7.6.1.	Cell performance.....	181
7.6.2.	Stack performance	184
7.6.2.1.	Stack without perturbation between cells	184
7.6.2.2.	Stack with perturbation between cells	187
7.7.	Summary	190
Chapter 8	Conclusions and Future Work.....	192
8.1.	Conclusions from the present work	192
8.2.	Recommendations for future work	197
Appendix A	Scaling Analysis for Current Collector	200
Appendix B	Scaling Analysis for Flow Field.....	201
Appendix C	Scaling Analysis for Backing Layer.....	204
Appendix D	Scaling Analysis for Reaction Zone Layer	207
Appendix E	Scaling Analysis for Electrolyte	211

References212

Publications Arising from This Thesis236

Abstract

A solid oxide fuel cell (SOFC) is an electrochemical energy conversion device operating at high temperatures from 500 to 1000 °C fueled by hydrogen or hydrocarbon, and is developed for environmentally friendly and sustainable energy production. The cell performance typically involves complicated multiphysical behaviours, such as transport phenomena and electrochemical performance. To understand the characteristics and mechanism of the SOFC, mathematical modeling is an efficient approach, compared with repetitive and costly experimental techniques. In general, however, three-dimensional (3D) modeling of SOFCs is computationally expensive, especially for stacks, due to the highly coupled and nonlinear nature of the mathematical formulation as well as a large number of functional domains in the cell. Although there are simplified P-SOFC models from 3D to 2D, the assumptions on dimensionality tend to lower the fidelity of model prediction.

In this thesis, novel reduced models are developed for the planar SOFC (P-SOFC) and stack equipped with parallel plain flow channels to significantly reduce computational cost with desired numerical accuracy, while capturing both the average properties and the variability of the dependent variables in the 3D model. The model reduction is performed based on a full 3D cell model that is validated with experimental measurements from the literature, where the 3D model consists of a set of governing equations for the conservation of mass, momentum, species, charge and energy, and provides a detailed description of the transport phenomena and electrochemical

performance of a P-SOFC.

The first achievement of the present work is the development of novel correlation factors to spatially smooth the flow fields of parallel plain channels and solid ribs based on the 3D single-cell model under isothermal conditions. The factors are derived based on the full set of governing equations over a cell cross section, such that they can handle not only variations in diffusion pathways due to ribs but also the coupling effects between governing equations. They are specified for the cathode and anode separately. The complexity of the mathematical model is reduced via spatial smoothing and asymptotic analysis without sacrificing the leading-order physics. The numerical computation is sped up further via a space-marching algorithm. As a result of spatial smoothing with the developed correlation factors, the isothermal 3D single-cell model is reduced to a two-dimensional (2D) counterpart with effective physical parameters, which is solved with respect to directions along the cell length (streamwise direction, $\mathbf{e}_x$) and through the cell thickness (normal direction, $\mathbf{e}_z$). When performing spatial smoothing for model reduction, there is no loss in physical information except that the local pointwise information is replaced with spanwise averaged counterparts. The 2D spatially-smoothed counterpart is then asymptotically reduced to a set of parabolic partial differential equations (PDEs) and ordinary ones (ODEs) with a space marching algorithm. This reduced model, called the 2D asymptotic spatially-smoothed isothermal (ASSI) P-SOFC model, is finally verified with the 3D counterpart in terms of global and local cell properties. Good agreement is achieved for the verification in view of the relative errors between the solutions from the 3D and reduced models. The fidelity of model prediction is guaranteed by the formulated correlation factors and effective parameters. Moreover, the computing time and memory requirement are reduced by three and two orders of magnitude, respectively, in comparison with the original 3D

model.

The second achievement is the development of novel variation factors for spatial smoothing to capture the variability of dependent variables in the spanwise direction (e_y) along the cell width, although the spanwise direction is reduced for the 3D model in this study. The resulting 2D spatially-smoothed model is verified in terms of mass fractions, allowing for the study of depletion of reactants underneath the ribs. The spanwise variability of mass fractions is quantified in terms of their standard deviations along the cell width. The variation factors are obtained by normalizing the standard deviations with respect to the concentration drop across the electrode, such that they only vary with geometrical parameters and are applicable at different current densities. The resulting variation factors are expressed in the form of polynomial expressions in terms of dimensionless geometrical parameters for the cathode and anode, respectively. Good agreement between the 3D and 2D models verifies that the developed variation factors can capture the variability of mass fractions underneath ribs in the original 3D model for various cell designs with parallel flow channels. Furthermore, the present method for the development of the variations factors of mass fractions can be extended to the other dependent variables in the 3D domain.

In terms of sensitivity analysis of isothermal single-cell performance, apart from the development of the above correlation and variation factors for spatial smoothing, Monte Carlo simulation (MCS) is conducted for an advanced 2D ASSI P-SOFC model, in which the previously achieved 2D ASSI model for the leading-order average predictions is coupled with the variation factors for the spanwise variability of mass fractions, in order to statistically assess the effects of stochastic material properties, operating conditions, and geometrical parameters on cell behaviours. The advanced 2D ASST model is computationally cost-efficient and takes about 1 second for each run and thus

allows MCS with a sample size on the order of magnitude of 10^3 . Sensitivity analysis of cell performance to the stochastic modeling parameters is conducted in two scenarios: only one parameter varying at a time, and all parameters varying together. The former investigates the influence of a single modeling parameter on the variation of cell performance, while the latter studies the impact of a combination of varying parameters. The analysis is elaborated in terms of the average current density, the average value of oxygen mass fractions and their spanwise variation underneath the ribs. According to the contribution of each parameter to the variation of the cell performance, the modeling parameters are ranked for each scenario and then two distinct rankings are obtained, which is not captured by conventional parametric studies.

The last achievement is the development of 2D spatially-smoothed non-isothermal single-cell and stack models as well as their asymptotic counterparts that are called the asymptotic spatially-smoothed thermal (ASST) cell and stack models, in which the spatially smoothed energy equations are in particular developed subject to both the local thermal equilibrium (LTE) and non-equilibrium (LTNE) conditions in the volume-averaged flow field. The variation in the pathways of conductive heat transfer between the flow field and adjacent layers is captured by functional correlation factors that are derived based on a Laplace equation. The selection of the reduced models under either the LTE or LTNE condition for use depends on the temperature difference between the working fluid in channels and the interconnect of the original 3D model. Verifying the reduced models with the 3D counterparts, it is found that the accuracy of the LTE model decreases when the temperature difference in the 3D flow field increases. When the temperature difference is more than 10 K, the LTNE model is preferable for high accuracy. Moreover, good agreements are obtained for single-cell modeling, and for stack modeling with negligible perturbations of dependent variables between cells. If the

perturbations are not negligible, the relative error between the 2D ASST and 3D stack models increases significantly.

List of Figures

Fig. 1.1 Schematic of a planar SOFC.....	8
Fig. 2.1 (a) Planar SOFC stack and (b) cell components [28].	18
Fig. 2.2 Tubular SOFC stack (bottom) [34] and detailed schematic (up) [35].	20
Fig. 2.3 Self-supporting structure of the SOFC: (a) YSZ electrolyte-supported cells, (b) Ni/YSZ cermet anode-supported cells with thin YSZ electrolyte [43].....	22
Fig. 2.4 Schematic of flow configurations: (a) co-flow, (b) counter-flow, and (c) cross-flow.....	27
Fig. 2.5 Schematic of the polarization curve for the SOFC.	32
Fig. 2.6 Graphs showing polarization curves of typical fuel cells: (a) a low-temperature fuel cell operating at 70 °C; (b) a SOFC operating at 800 °C [101].....	41
Fig. 2.7 Bottoming SOFC/GT hybrid system with variable speed GT and supplemental oxidizer fuel [59].....	53
Fig. 2.8 Schematic of co- or counter-flow planar SOFC: (a) 3D view, (b) 2D cross-sectional view.	55
Fig. 2.9 Anode-supported SOFC stack built by Forschungszentrum Jülich in 2004 [164].	59
Fig. 3.1 Schematic of (a) a SOFC stack with parallel plain channels, (b) a 3D unit cell, (c) a repeating unit with a pair of channels, and (d) a 3D button cell and its 1D computed domain.....	73
Fig. 3.2 Locations of boundary conditions for the 3D P-SOFC model.....	82
Fig. 3.3 Polarization curves by experiment (symbols) and simulation (lines) at different temperature conditions: 700 °C (●) for a training set, 800 (■) and 600 °C (▲)	

for test sets.	90
Fig. 3.4 Relation between the estimated error and iteration numbers for the simulation of the 3D full non-isothermal model with relative convergence errors ϵ of (a) 1×10^{-3} and (b) 1×10^{-6} , when solving from 1.0 to 0.3 V with an interval of 0.1 V.	91
Fig. 3.5 Comparison of numerical results associated with relative convergence errors of 1×10^{-3} (color lines) and 1×10^{-6} (x), in terms of the solutions at the intersection line of the backing/reaction zone interface and the outer vertical wall of the cell at voltages of 1.0 to 0.3 V decreasing with an interval of 0.1 V: (a) temperature; (b) oxygen mass fraction; (c) the velocity component in the normal direction.	92
Fig. 4.1 Schematic of (a) a SOFC with parallel plain channels, (b) a 3D repeating unit with a pair of channels, (c) 3D and (d) 2D single-cell models with volume-averaged flow fields, (e) an asymptotically reduced model with PDEs ($\rightarrow$) and ODEs ($\bullet$) in the flow field, and ODEs in the remainder of the cell.	96
Fig. 4.2 Schematic of (a) a flow field of parallel plain channels separated by ribs and (b) its volume-averaged counterpart, the pathways of mass (solid arrows) and charge transport (dashed arrows) in a SOFC cross section (c) without and (d) with a volume-averaged flow field.	98
Fig. 4.3 The correlations for the (a) cathode and (b) anode correction factors $\zeta(\mathcal{H}, \mathcal{W})$: training sets for calibration ($\bullet$) and test sets for verification ($\blacklozenge$).	104
Fig. 4.4 Polarization curves by 3D models with a $\mathcal{W}_c$ of 0.4 ($\blacktriangledown$) and 0.7 ($\blacksquare$), and $\mathcal{W}_a = 0.4$ at (a) $\mathcal{H}_c = 0.1$ and $\mathcal{H}_a = 0.5$, and (b) $\mathcal{H}_c = 0.5$ and $\mathcal{H}_a = 0.1$, by 2D volume-averaged counterparts with (-) and without (--) correlation factors, and by 2D ASSI models for the $\mathcal{W}_c$ of 0.4 (+) and 0.7 ($\times$).	119

- Fig. 4.5** Distribution of (a) oxygen and (b) hydrogen at the backing/reaction zone interface in the original geometry with channels and ribs (separated by the dashed line), and (c, d) the volume-averaged counterpart, with $\mathcal{H}_c = 0.125$, $\mathcal{H}_a = 0.375$, $\mathcal{W} = 0.55$ at 0.2 V. 120
- Fig. 4.6** (a) Average mass fraction of oxygen and hydrogen, and (b) average current density at the backing/reaction zone interface on cathode (-) and anode (--) at 0.8 (▼), 0.5 (■), 0.2 V (▲), by 3D (symbols), 2D spatially-smoothed (lines), and 2D ASSI (×) models with $\mathcal{H}_c = 0.125$, $\mathcal{H}_a = 0.375$, $\mathcal{W} = 0.55$. Filled symbols stand for cathode variables and unfilled for anode. Error bars represent standard deviation. 121
- Fig. 4.7** Average cathode (■) and anode (◆) gauge pressure, mass fraction of oxygen (▼) and hydrogen (▲) in a 3D flow field with $\mathcal{H}_c = 0.125$, $\mathcal{H}_a = 0.375$, $\mathcal{W} = 0.55$ at 0.2 V. The volume-averaged pressure (--) and mass fraction (-) by the 2D spatially-smoothed model. The pressure (+) and mass fraction (×) by the 2D ASSI model. 123
- Fig. 5.1** Schematics of (a) a repeating unit of a SOFC with one pair of fuel and air channels enclosed by ribs, and the pathways of the mass (solid arrow) and charge (dashed arrow) transport in a cross section (b) without and (c) with a volume-averaged flow field. 129
- Fig. 5.2** The correlations for (a) the correlation factor ζ and (b) the variation factor $\tilde{\sigma}$ on the cathode side: training sets for calibration (●) and test sets for verification (◆). 130
- Fig. 5.3** Average mass fractions of (a, c, e) oxygen and (b, d, f) hydrogen at the backing/reaction zone interface at (a, b) 0.8, (c, d) 0.5, and (e, f) 0.2 V: 3D

model with $\mathcal{H}_c = 0.125$, $\mathcal{H}_a = 0.375$, $\mathcal{W} = 0.55$ (■); 2D spatially-smoothed counterpart (—). Standard deviations for 3D (▼) and 2D spatially-smoothed (—) solutions.	137
Fig. 5.4 Average mass fractions and standard deviations at the backing/reaction zone interface with cathode backing layers of different thicknesses: (a) $\mathcal{H}_c = 0.5$ and (b) $\mathcal{H}_c = 0.05$, with $\mathcal{H}_a = 0.375$, $\mathcal{W} = 0.55$. 3D results for ω (filled) and σ (unfilled) at 0.8 (▲), 0.6 (■), 0.4 V (▼). 2D results for ω (solid lines) and σ (dash lines).....	139
Fig. 5.5 Average mass fractions and standard deviations at the backing/reaction zone interface with anode backing layers of different thicknesses: (a) $\mathcal{H}_a = 0.5$ and (b) $\mathcal{H}_a = 0.05$, with $\mathcal{H}_c = 0.375$, $\mathcal{W} = 0.4$. 3D results for ω (filled) and σ (unfilled) at 0.8 (▲), 0.6 (■), 0.4 V (▼). 2D results for ω (solid lines) and σ (dash lines).	140
Fig. 6.1 Schematic of an asymptotic spatially-smoothed domain with PDEs (→) and ODEs (●) in the flow field, and ODEs in the remainder of the cell.	144
Fig. 6.2 Empirical cumulative distribution function (CDF) of average current densities at 0.5 V with different sample sizes (N) for Monte Carlo simulation. Kolmogorov-Smirnov test statistics of samples based on a case of $N = 5000$ at $\alpha = 5\%$	152
Fig. 6.3 Probability distribution of average current densities at 0.5 V by varying one parameter at a time: (a-g) cathode material properties; (h, i) operating conditions. Fitted normal distribution (—).....	153
Fig. 6.4 Probability distributions of average current densities at 0.5 V by varying one geometrical parameter at a time. Fitted normal distribution (—).....	154

Fig. 6.5 Coefficients of variation c_v of the average current density at 0.5 V with respect to stochastic input parameters varied one at a time: (a) operating conditions; (b) geometrical parameters; (c) material properties.	155
Fig. 6.6 Probability distributions of average current densities at 0.5 V by varying all modeling parameters.	156
Fig. 6.7 Scatter plots of the average current density at 0.5 V against input parameters: (a, c, e, g) varying one parameter at a time; (b, d, f, h) varying all parameters together. The dash-dot line (— · —) refers to the mean value.	157
Fig. 6.8 Correlation coefficients ρ_s of stochastic input parameters and dependent variables at 0.5 V. Stochastic parameters: (a) operating conditions; (b) geometrical parameters; (c) material properties. Dependent variables: average current density (■); average value (■) and spanwise variation (■) of oxygen mass fractions at the backing/reaction zone interface at $x = 0.09$ m. All stochastic parameters are varied together. The ranking numbers of the varying parameters are labeled for each dependent variable in view of the magnitude of ρ_s	159
Fig. 7.1 Schematic of the pathways of heat transfer by solid (→) and gas (- →) phases through the flow field and its adjacent layers (a) without and (b) with spatial smoothing. (c) 2D spatially-smoothed stack model of n repeating units (denoted as j) and (d) its asymptotic counterpart with PDEs (→) and ODEs (●) in the flow field, and ODEs in other cell layers.	167
Fig. 7.2 Correlation for the correction factor $\zeta(\mathcal{H}, \mathcal{W})$ derived from a Laplace equation: training sets for calibration (●), and test sets for verification (◆).	169
Fig. 7.3 Temperature distribution at 0.5 V at the backing/reaction zone interface on the	

- (a, c) cathode and (b, d) anode with $\mathcal{H}_c = 0.125$, $\mathcal{H}_a = 0.375$, and $\mathcal{W} = 0.55$: (a, b) 3D model with plain channels and ribs (separated by the dashed line); (c, d) 2D spatially-smoothed model. 182
- Fig. 7.4** Average (a) temperature and (b) oxygen mass fraction at the cathode backing/reaction zone interface: 3D model with $\mathcal{H}_c = 0.125$, $\mathcal{H}_a = 0.375$, and $\mathcal{W} = 0.55$ at 0.8 (▼), 0.6 (■), and 0.4 V (▲); 2D spatially-smoothed model with (solid lines) and without (dashed lines) correlations for heat transfer; 2D ASST model (×). Error bars represent standard deviations. 183
- Fig. 7.5** Average cross-sectional temperatures in the cathode rib (under the current collector) (■) and channel (▼) by the 3D model with $\mathcal{H}_c = 0.125$, $\mathcal{H}_a = 0.375$, and $\mathcal{W} = 0.55$ at 0.4 V. Predictions by the spatially smoothed model with correlations for heat transfer: T in LTE (—); T_s (— —) and T_g (— ·) in LTNE. 185
- Fig. 7.6** Average temperature and oxygen mass fraction at the backing/reaction zone interface: 3D model with $\mathcal{H}_c = 0.125$, $\mathcal{H}_a = 0.375$, and $\mathcal{W} = 0.55$ at 0.8 (▼), 0.6 (■), and 0.4 V (▲); 2D spatially-smoothed model with (solid lines) and without (dashed lines) correlations for heat transfer by (a, b) LTE and (c, d) LTNE approaches; 2D ASST model (×). Error bars represent standard deviations. 186
- Fig. 7.7** Polarization curves for a 3-cell stack with $\mathcal{H}_c = 0.1$, $\mathcal{H}_a = 0.5$, and $\mathcal{W} = 0.4$: 3D (▼), 2D spatially-smoothed (—), and 2D asymptotic spatially-smoothed (×) non-isothermal models. 188
- Fig. 7.8** Average (a) temperature, (b) current density, and (c) oxygen mass fraction at the backing/reaction zone interface for a 3-cell stack with $\mathcal{H}_c = 0.1$, $\mathcal{H}_a = 0.5$, and $\mathcal{W} = 0.4$ at $V_{\text{stack}} = 1.2$ V: 3D (filled) and 2D ASST (unfilled) models for cell 1

(▼), 2 (■), and 3 (▲); 2D spatially-smoothed models for cell 1 (–), 2 (– –),
 and 3(– ·)..... 189

List of Tables

Table 1.1	World energy demand in cities [2].	2
Table 1.2	Operational characteristics and technological status of various fuel cells....	4
Table 1.3	Advantages and disadvantages of the SOFC technology [10, 11].	5
Table 2.1	Classification of solid oxide fuel cells [27].	17
Table 2.2	Comparison between planar and tubular SOFC [4, 5].	21
Table 2.3	Comparison of SOFCs in terms of support structure and operating temperature.....	25
Table 2.4	Computational methods for the SOFC in different length scales [75].....	64
Table 2.5	Planar SOFC models in literature.	67
Table 3.1	Constitutive relations of the 3D P-SOFC model [47, 88, 96, 106, 122, 186-189].	78
Table 3.2	Modeling parameters of the 3D P-SOFC model.	87
Table 3.3	Fluid and thermal properties of species, valid in the range of 273-1473 K [195].	88
Table 4.1	Cell geometry and the coefficients of correlation factors.	97
Table 4.2	Governing equations and boundary conditions of the ASSI P-SOFC model.	115
Table 4.3	Additional constitutive relations of the P-SOFC model.	122
Table 4.4	Computational cost of modeling.	125
Table 5.1	Coefficients of correlation and variation factors.....	131
Table 6.1	Formulation of the advanced ASSI P-SOFC model.....	146
Table 6.2	Nominal values of stochastic parameters for the MCS of the advanced ASSI	

P-SOFC model.	148
Table 7.1 Geometry and operating conditions of 3D non-isothermal cell and stack models.	165
Table 7.2 Coefficients of correlation factors for the ASST P-SOFC model.	170
Table 7.3 Governing equations and boundary conditions of the ASST P-SOFC model.	178

Nomenclature

a_{ij}, c_{ij}	constants for functional polynomials
A	area (m^2)
$\mathcal{A}$	actual reactive surface area per unit volume of the reaction zone (m^{-1})
$\mathcal{A}$	specific surface area of porous media for heat exchange (m^{-1})
$\langle \mathbf{B} \rangle$	superficial volume average of quantity $\mathbf{B}$
c_F	form-drag constant
c_i	molar concentration of species i (mol m^{-3})
c_p	specific heat capacity ($\text{J kg}^{-1} \text{K}^{-1}$)
c_v	coefficient of variation
d	characteristic pore diameter (m)
d_{par}	average particle diameter of porous media (m)
D_h	hydraulic diameter (m)
$\mathcal{D}_{ij}$	combined diffusivity of species i and j involving both ordinary and Knudsen diffusion ($\text{m}^2 \text{s}^{-1}$)
D_{ij}	ordinary binary diffusivity of species i and j ($\text{m}^2 \text{s}^{-1}$)
D_{ij}^0	binary diffusivity of species i and j at the reference temperature and 1 atm ($\text{m}^2 \text{s}^{-1}$)
$D_{\text{Kn},i}$	Knudsen diffusivity of species i ($\text{m}^2 \text{s}^{-1}$)
$\mathcal{D}_{ij}$	the ij component of the multicomponent Fick diffusivity matrix ($\text{m}^2 \text{s}^{-1}$)
$\mathcal{D}_{ij}$	the ij component of the multicomponent Fick diffusivity tensor ($\text{m}^2 \text{s}^{-1}$)
$\mathbf{e}_x, \mathbf{e}_y, \mathbf{e}_z$	coordinate vector
E^{act}	activation energy for electrochemical reactions (J mol^{-1})
E^{rev}	reversible potential (V)
E^{ocv}	open circuit voltage (V)
E^0	reversible potential at standard conditions (V)
F	Faraday's constant (A s mol^{-1})

h_j	thickness of a layer j (m)
h_{ks}	statistic indicating the result of the Kolmogorov-Smirnov test
$\hat{h}$	convective heat transfer coefficient ($\text{W m}^{-2} \text{K}^{-1}$)
$\mathcal{H}$	dimensionless height
$\mathbf{i}, i$	current density (A m^{-2})
i_0	exchange current density (A m^{-2})
$\mathbf{I}$	unit matrix
j	repeating unit in a stack
J	volumetric current density (A m^{-3})
k	thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)
K	equilibrium constant of electrochemical reactions
L	cell length (m)
M_i	molecular mass of species i (kg mol^{-1})
m, n	numbers of terms in polynomials
n	number of cells in a stack
n_{fc}	number of flow channels in a flow field
n_i	molar number of species i (mol)
$\mathbf{n}$	unit normal vector pointing out of the domain
$\mathbf{n}_i$	total mass flux of species i ($\text{kg m}^{-2} \text{s}^{-1}$)
Nu	Nusselt number
p	pressure (Pa)
p_{ks}	statistic of the Kolmogorov-Smirnov test
Pr	Prandtl number
$\mathbf{q}$	heat flux (W m^{-2})
R	gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
$\mathcal{R}$	electric resistance (Ω)
$\Re$	asymmetry factor
Re	Reynolds number
r	average pore radius (m)
S	wetted perimeter of a rectangular duct (m)
S_i	mass source term of species i ($\text{kg m}^{-3} \text{s}^{-1}$)

S_{mass}	mass source term ($\text{kg m}^{-3} \text{s}^{-1}$)
S_{pot}	electric source term (A m^{-3})
S_{temp}	heat source (W m^{-3})
$\mathbf{t}$	unit tangential vector to the boundary
T	temperature (K)
$\mathbf{v}, u, v, w, U$	velocities (m s^{-1})
V_{cell}	cell voltage (V)
w	width (m)
$\mathcal{W}$	dimensionless width
x, y, z	coordinate (m)
x_i	mole fraction of species i
X_i	input parameter
X_i', Y_i'	ranked data (X_i, Y_i) in a sample
Y_i	dependent variable
$z_{\alpha/2}$	upper $100(1-\alpha/2)^{\text{th}}$ percentile of the standard normal distribution at a confidence level of α
$ $	at a certain height in the cell

Greek symbols

$\alpha_{1,2}$	charge transfer coefficient
β	pre-exponential factor of exchange current density (A m^{-2})
ΔG^0	Standard Gibbs free energy change (J mol^{-1})
Δp	gauge pressure (Pa)
Δs	molar entropy change ($\text{J mol}^{-1} \text{K}^{-1}$)
Φ	place holder for dependent variables
γ	reaction order of the electrochemical reaction
ε	porosity
ϵ	relative convergence error for the nonlinear solver in COMSOL
μ	mean of a population
η	polarization (V)

μ_i	dynamic viscosity of species i ($\text{kg m}^{-1} \text{s}^{-1}$)
μ_{mix}	dynamic viscosity of gas mixture ($\text{kg m}^{-1} \text{s}^{-1}$)
κ	permeability (m^2)
Ω	placeholder for dependent variables
ρ	density (kg m^{-3})
σ	standard deviation
σ_{elc}	electrical conductivity ($\Omega^{-1} \text{m}^{-1}$)
σ_{ion}	ionic conductivity ($\Omega^{-1} \text{m}^{-1}$)
$\tilde{\sigma}_i$	normalized standard deviation or variation factor of species i
ϕ	potential (V)
Φ	volume fraction of the electron conducting particles in electrodes
τ	tortuosity
ω	mass fraction
ζ	stoichiometry
ξ, ζ	correlation factors for the pathways of transport processes

Subscripts

α, β, i, j	index for the species: $\text{O}_2, \text{N}_2, \text{H}_2, \text{H}_2\text{O}$
a, c	anode, cathode
avg	average
bl	backing layer
el	electrolyte
elc	electronic
cc	current collector
crit	critical number
fc	flow channel
ff	flow field
g	gas phase
H_2	hydrogen
H_2O	water
ic	interconnect
ion	ionic

j	functional layer j
Kn	Knudsen diffusion
mass	mass source term
max	maximum
mix	gas mixture
mom	source term for the momentum conservation
N ₂	nitrogen
O ₂	oxygen
pot	potential, or source term for the electric conservation
rib	rib
rl	reaction zone layer
s	solid phase
/	interface between layers
⊥	surface perpendicular to the streamwise direction

Superscripts

act	activation polarization
con	concentration polarization
eff	effective
(ff)	flow field
(fc)	flow channel
g-s	heat exchange between the gas and solid phases
(ic)	interconnect
in	inlet
leak	leak polarization
ohm	ohmic polarization
oper	operating condition
out	outlet
ref	reference
†	transpose of a tensor
0	standard condition

Chapter 1

Introduction

Sustainable energy development for a growing population is a critical issue in the 21st century. The energy report of European Environment Agency (EEA) in 2008 showed that the global energy requirement would be 55 % higher in 2030 than that in 2005, if governments around the world continued with current policies [1]. About 84 % of the increase in primary energy demand would come from fossil fuels [1]. This increase in energy demand was also presented by International Energy Agency (IEA) in 2008 [2], as shown in Table 1.1. Excessive use of fossil fuels must pose a number of environmental impacts such as oil supply insecurity, air pollution, greenhouse gas emissions, and adverse influences on ecosystems during energy production processes. Increasing energy demand, diminishing natural resources, and growing environmental concerns invoke the continuous development of new energy conversion technologies to fulfill the sustainable development strategy and environmental friendliness while meeting the anticipated annual growth in energy demand shown in Table 1.1.

One of the promising new energy technologies is fuel cell [3, 4], which directly converts the free energy of chemical reactants to electrical energy and heat without combustion. It is widely accepted that the fuel cell was invented by Sir William Robert Grove, who convincingly demonstrated the principle of fuel cell in 1839 [3]. Nowadays, the fuel cell has grown up into a big family of many members operating at specific temperatures. The most common ones are proton exchange membrane fuel cell

(PEMFC), phosphoric-acid fuel cell (PAFC), alkaline fuel cell (AFC), molten-carbonate fuel cell (MCFC), and solid oxide fuel cell (SOFC) [5], as introduced in Table 1.2. Generally, a number of cells are stacked together in electric-series to generate desired output voltage and power ranging from microwatt for micro-electromechanical systems to megawatt for power plants. Applications of the fuel cell have spread to four major areas: portable electric products (e.g., laptop, digital camera, hand phone, and PDA), residential electricity, transport facilities (e.g., car and bus), and small/big power stations [6]. As an innovative source of energy, the fuel cell technology has gained a good reputation for high efficiency, environmental friendliness, and compatibility with renewable energy sources [3-5]. Many governments (U.S, European Union, China, Japan, etc.) and companies have invested plenty of human power and capital on the fuel cell technology for many years [7, 8].

Table 1.1 World energy demand in cities [2].

	2006		2015		2030		2006-2030*
	Mtoe	Cities as a % of world	Mtoe	Cities as a % of world	Mtoe	Cities as a % of world	
Coal	2330	76%	3145	78%	3964	81%	2.2%
Oil	2519	63%	2873	63%	3394	66%	1.2%
Gas	1984	82%	2418	83%	3176	87%	2.0%
Nuclear	551	76%	630	77%	726	81%	1.2%
Hydro	195	75%	245	76%	330	79%	2.2%
Biomass and waste	280	24%	358	26%	520	31%	2.6%
Other renewable	48	72%	115	73%	264	75%	7.4%
Total	7908	67%	9785	69%	12374	73%	1.9%
Electricity	1019	76%	1367	77%	1912	79%	2.7%

* Average annual growth rate.

In the fuel cell family, the high-temperature fuel cell, namely the SOFC, has attracted much interest in its potential applications to stationary power station, mobile power, auxiliary power for vehicles, and specialty applications [9]. As shown in Table

1.3, the SOFC technology provides advantages over other types of fuel cells, such as fuel variety, relatively high sulphur resistance, and high electrical efficiency [10, 11]. Nevertheless, the SOFC technology is still away from commercialization due to some critical issues like long start-up transient time, thermal stresses and expansion mismatches, and sealing problems between cells in a SOFC stack. In order to investigate the characteristics and mechanism of the SOFC, mathematical modeling is a widely applied approach in comparison with repetitive and costly experimental approaches.

The rest part of this chapter introduces the background of SOFC modeling in Section 1.1, states the research motivation and objectives in Section 1.2, and provides the outline of this thesis in Section 1.3.

Table 1.2 Operational characteristics and technological status of various fuel cells.

Properties	PEMFC	AFC	PAFC	MCFC	SOFC	Ref
Operating temperature	50 – 100 °C	60 – 220 °C	160 – 200 °C	600 – 700 °C	500 – 1000 °C	[3, 5, 9, 12, 13]
Prime cell components	Carbon-based	Carbon-based	Graphite-based	Stainless-based	Ceramic	[10, 12]
Electrolyte	Hydrated polymeric ion exchange membranes	Mobilized or immobilized potassium hydroxide (KOH) in asbestos matrix	Immobilized liquid phosphoric acid (H ₃ PO ₄) in SiC	Immobilized liquid molten carbonate in LiAlO ₂	Perovskites (ceramics)	[10, 12]
Electrodes	Carbon	Transition metals	Carbon	Nickel and nickel oxide	Perovskite and perovskite/metal cermet	[10, 12]
Catalyst	Platinum	Platinum	Platinum	Electrode material	Electrode material	[10, 12]
Interconnect	Carbon or metal	Metal	Graphite	Stainless steel or nickel	Nickel ceramic or steel	[10, 12]
Fuel	H ₂ , methanol	H ₂	H ₂	H ₂ , CH ₄	H ₂ , CH ₄ , CO, other hydrocarbons	[9]
Charge carrier	H ⁺	OH ⁻	H ⁺	CO ₃ ²⁻	O ²⁻	[9, 10]
External reforming for hydrocarbon fuels	Yes	Yes	Yes	No, for some fuels	No, for some fuels and cell designs	[10, 12]
External shift conversion of CO to H ₂	Yes, plus purification to remove trace CO	Yes, plus purification to remove CO and CO ₂	Yes	No	No	[10, 12]
Produce water management	Evaporative	Evaporative	Evaporative	Gaseous product	Gaseous product	[10]
Product heat management	Process gas + liquid cooling medium	Process gas + electrolyte circulation	Process gas + liquid cooling medium or steam generation	Internal reforming + process gas	Internal reforming + process gas	[10]
System output	<1 kW – 250 kW	10 kW – 100 kW	50 kW – 1 MW	<1 kW – 1 MW	<1 kW – 3 MW	[3, 12]
Electrical efficiency	53-58% (transport), 35% (stationary)	60%	32 – 38%	45 – 47%	50 – 60%	[14, 15]
Energy efficiency	40 – 50%	40 – 70%	70%	60%	70%	[12]
Lifetime projected (hours)	> 40,000	> 10,000	> 40,000	> 40,000	> 40,000	[5]
Capital cost projected (U.S.\$/kW)	> 200	> 200	3000	1000	1500	[5]
Applications	1. Backup power 2. Portable power 3. Small distributed generator 4. Transportation 5. Specialty vehicles	1. Military 2. Space	Distributed generator	1. Electric utility 2. Large distributed generator	1. Auxiliary power 2. Electric utility 3. Large distributed generator	[3]

Table 1.3 Advantages and disadvantages of the SOFC technology [10, 11].

Advantages	Disadvantages
<ul style="list-style-type: none"> • The high operating temperature allows SOFCs to reform fuel internally, which enables the use of a variety of fuels and reduces the cost associated with adding a reformer to the system. • SOFCs are not poisoned by carbon monoxide (CO), which can even be used as fuel. • The high operating temperature also allows the use of most of the waste heat of SOFC for cogeneration or in bottoming cycles. • SOFC is the most sulphur-resistant type of fuel cell. It can tolerate more sulphur than other cell types by several orders of magnitude. • The solid electrolyte alleviates any corrosion problem in the cell, allows precise engineering of the three-phase boundary, and avoids electrolyte movement or flooding in the electrodes. • The kinetics of the cell is relatively fast, and CO is a directly useable fuel as it is in the MCFC. Unlike MCFC, there is no requirement for CO₂ at the cathode of the SOFC. • The materials used in SOFC are modest in cost, because there is no need of precious metal catalyst such as Pt in PEMFC. • Planar SOFC unit cells with thin electrolyte are demonstrated to be cable of power densities close to those achieved with PEMFC. • The efficiency of a SOFC system can reach 55-60%. Analysis indicates that a higher electrical efficiency up to 70% is possible in a SOFC/gas turbine hybrid system. 	<ul style="list-style-type: none"> • SOFC needs a long start-up transient time to reach the high operating temperature. This may be acceptable for utility application, but unacceptable for transportation or small portable application. • Thermal stresses and expansion mismatches among materials weaken the durability and increase the maintenance cost of SOFC. • Corrosion of metal stack components such as interconnects in some designs is a challenge. • Sealing between cells is difficult in the flat plate configurations. Fabrication and assembly methods employed in the construction of cell stacks significantly raise the manufacturing cost.

1.1. Background of solid oxide fuel cell (SOFC)

The SOFC is typically fabricated at temperatures between 1200 and 1300 °C and operates at temperatures ranging from 500 to 1000 °C. It produces electricity and heat directly from gaseous hydrogen or hydrocarbon fuels, such as natural gas, via electrochemical reactions with ambient air as an oxidant. The first SOFC was proposed by Schottky using the Nernst mass as the solid electrolyte, and then it was constructed

by Baur and Preis in 1937 . The core components of a SOFC are two porous electrodes (*i.e.*, anode and cathode) separated by a thin and dense ion-conducting ceramic electrolyte layer, as shown in Fig. 1.1. The gastight electrolyte is conventionally made of yttria (Y_2O_3)-stabilized zirconia (ZrO_2) (YSZ), in which yttrium is used within a range of 3-10 mol% to stabilize the zirconia lattice [16]. Conventionally, the YSZ can be named according to the contained amount of yttria, such as 3YSZ, 8YSZ, and 10YSZ refer to the YSZ with 3, 8, and 10 mol% of yttria, respectively. YSZ provides high ionic conductivity but negligible electric conductivity at temperatures above 700 °C. The solid electrolyte enables the SOFC to be free from many of the management issues in other types of fuel cells, such as electrode flooding, electrolyte migration, and catalyst wetting [5]. The cathode is commonly composed of strontium (Sr)-doped lanthanum manganite (LaMnO_2) (LSM) due to its high electronic conductivity, high catalytic activity at high temperatures (800-1000 °C), and good compatibility with the YSZ electrolyte. For SOFCs at intermediate temperatures (600-800 °C), ionically conducting second phase such as YSZ or gadolinia-doped ceria (GDC) are added to LSM so as to improve the cathode performance (*e.g.*, reducing the electrode polarization resistance) [13, 14]. The anode consists of a ceramic-metal composite (cermet), typically nickel/yttria stabilized zirconia (Ni/YSZ). The pore size of the electrode ranges from about 80 nm to 3 μm . Depending on which component is the thickest, the SOFC can be fabricated into three self-supporting configurations, called the electrolyte-, anode-, and cathode-supported SOFC.

The fundamental working principle of a SOFC is shown schematically in Fig. 1.1. During operation, oxygen diffuses from the air flow channel into the porous cathode through pores and moves towards to the cathode/electrolyte interface. It is subsequently ionized by combining with electrons in the electrochemical reaction sites called the triple

phase boundaries (TPB) near the electrode/electrolyte interface. Then, the oxide ions are driven by the chemical potential difference between the two sides of the electrolyte to cross the electrolyte. The half-cell reaction for the reduction of O_2 at the cathode is

After reaching the anode TPB, the oxygen ions react with the hydrogen (H_2) that diffuses from the fuel flow channel to produce gaseous water (H_2O) and free electrons ($2e^-$). The half-cell reaction for the oxidation of H_2 at the anode is

The produced H_2O diffuses back to the fuel flow channel through the pores in the anode. The electrons travel through the electrically conducting solid phase of the anode to the current collector, and finally back to the cathode via an external circuit to perform useful work. The overall cell reaction in a SOFC is

The fuel composition affects the anode electrochemical reaction process which in turn dominates the anode performance. For example, the presence of steam in the fuel flow of humid hydrogen may accelerate the adsorption/desorption of hydrogen [17]. It is also reported that anodic overpotential is relatively independent of H_2 concentration under dry condition and can be significantly reduced in the presence of steam [17, 18].

Fig. 1.1 Schematic of a planar SOFC.

Furthermore, the high operating temperature allows the SOFC to be fueled by hydrocarbon such as methane (CH_4), thereby eliminating the demand for pure H_2 that is not directly available from the nature. At a high operating temperature, the methane is converted to H_2 and carbon monoxide (CO) via an endothermic steam reforming reaction,

associated with a shifting reaction

The reforming process can take place within or out of the cell, such that the cell is designed correspondingly to an internal or external type.

The SOFC performance is studied both experimentally and computationally in literature; the latter, in particular, can provide detailed insights into the inherent limiting mechanisms, transport phenomena, structural integrity, and electrochemistry on a local level throughout the SOFC. One of the first calculations of SOFC performance was conducted by Vayenas and Hegedus in 1985 [19]. Since that time, the study on the SOFC has been carried out continuously. Referring to the previous studies in literature, the

performance of SOFCs significantly depends on the cell design with respect to the geometrical structure, support structure, operating temperature, flow configuration, and reforming type. The cell performance such as transport phenomena and electrochemical properties are described mathematically by modeling and predicted numerically by simulation.

For SOFC modeling, detailed three-dimensional (3D) multiphysics models are computationally expensive in general, due to not only the highly coupled and nonlinear nature of the mathematical formulation but also a large number of functional domains, especially for stacks. Two common assumptions to reduce the mathematical and computational complexity of SOFC modeling are discerned in literature. First, the geometry is simplified from 3D to two- (2D) [6-9], one- (1D) [6-8], or zero-dimensional (0D) [20] counterparts. Second, the reaction zones comprising the TPB for the electrochemical reactions (*i.e.*, Eqs. (1.1) to (1.3)) to take place are modeled as a boundary or interface condition, rather than a spatial domain, when predicting the global cell performance [7-13] or the local distribution of mass fraction, current density, and/or temperature [21, 22]. These assumptions are likely to lower the fidelity of model prediction for two reasons. Firstly, the flow fields of P-SOFC are generally 3D entities that consist of both plain channels and solid ribs. The ribs affect the diffusion pathways of gaseous working fluid, electronic charges, and heat between the flow field and the electrode. An improper design for the geometry of ribs and electrodes may cause the depletion of reactants to take place in the porous electrode underneath the ribs at high current densities. These effects of ribs are not captured by existing 2D P-SOFC models. This makes it difficult to achieve agreement between model predictions and experimental results at high current densities [23]. Secondly, dependent variables actually undergo spatial changes in the reaction zones that are spread out some distance

(10 - 50 μm) into the electrode from the electrode/electrolyte interface [24, 25].

The performance of SOFC depends on extrinsic operating conditions and intrinsic material properties and component geometries. The effects of these factors on the global power output and local multiphysical mechanisms within the cell are generally studied via sensitivity analysis. The analysis is typically conducted by modeling with a few different values for every investigated modeling parameter and varying one parameter at a time [6, 12-16]. The existing parametric studies generally aim at optimal values for the design parameters of SOFCs. However, optimal nominal solutions are not enough for a cell design to go into mass production, since the actual cell properties can deviate from the designed nominal value in high volume manufacturing processes. The influence of a combination of varying design parameters on the cell performance should be taken into account as well. In addition, it is difficult to perform deterministic analysis with just a few testing cases for a typically large population in manufacturing. Therefore, a method is required to not only find the input parameter showing the largest impact on results but also reveal what could possibly happen among a large population. Monte Carlo simulation (MCS) is one of such methods. The MCS can provide insight on understanding the impact of each input factor on the variability of the output dependent variable, based on generating a large number of random samples for input factor.

Among the research works on SOFC modeling, single-cell models are generally the first consideration for researchers to embark on a new product design and conduct modeling, while stack modeling is necessary for the scale-up system design and often involves parametric studies. A single SOFC only produces a voltage of 0.7-0.5V [24], such that a large amount of single cells must be stacked up to achieve a necessary high output voltage. The majority of computational studies focus on a SOFC single cell [7, 12-15], an anode [26, 27], or a cathode [28, 29], whereas relatively fewer can be found

for stacks [20, 30] or the overall system [23-25]. The latter two in particular are challenging to solve with detailed mechanistic models, because of the highly coupled and non-linear nature of the underlying mathematical formulation and the large number of functional domains in each and every cell in a SOFC stack.

1.2. Motivation and objectives

In view of the highly coupled and non-linear nature of detailed 3D multiphysics single-cell and stack models for the SOFC, reductions of the model formulation and/or geometry that do not sacrifice the leading-order physics can alleviate the computational cost and complexity of cell and stack modeling. When reducing the 3D domain to a lower dimension, not only the average predictions but also the variability of dependent variables in the neglected direction should be captured. The resulting fast and efficient models allows statistical sensitivity analysis of the cell or stack performance with respect to a single and a group of stochastic modeling parameters without a prohibitive computational cost.

In this context, the objectives of this research and the corresponding scopes are elaborated as follows.

1. Development of an asymptotic spatially-smoothed isothermal (ASSI) P-SOFC model with novel correlation factors for spatial smoothing. A fast and accurate reduced isothermal single-cell model is developed via spatial smoothing and asymptotic analysis, based on a 3D P-SOFC model that is developed in this study and validated with experimental measurements from the literature. For spatial smoothing over the flow field of parallel plain channels surrounded by solid ribs, novel correlation factors are developed to handle not only variations in diffusion pathways due to ribs but also coupling effects between governing equations. The

spatial smoothing and asymptotic reduction are conducted to reduce the complexity of modeling without sacrificing the leading-order physics in the original 3D model.

2. Development of novel variation factors for spatial smoothing to capture the variability of dependent variables under flow fields. Novel variation factors for spatial smoothing are developed to capture the variability of dependent variables along the cell width in the spanwise direction of the 3D P-SOFC model, while the spanwise direction is reduced for the 3D model. This results in an advanced 2D spatially-smoothed model to capture not only the average values of dependent variables but also their variations along the cell width, which allow for the study of depletion of reactants underneath the ribs. The validity and variability of spatial smoothing are investigated and demonstrated on various designs of the P-SOFC with parallel channels.
3. Sensitivity analysis of cell performance with respect to a single and a group of stochastic modeling parameters via Monte Carlo simulation of an advanced ASSI P-SOFC model. Monte Carlo simulation of an advanced ASSI P-SOFC model is performed to statistically assess the sensitivity of the variation of cell behaviours to a single and a group of stochastic modeling parameters, respectively. The advanced ASSI model is obtained by coupling the developed variation factors with the ASSI model. According to the contribution of each parameter to the variation of the cell performance, the varying parameters are ranked in order to identify the principle ones for cell design.
4. Development of spatially smoothed non-isothermal cell and stack models and their asymptotic counterparts for the P-SOFC. Reduced non-isothermal P-SOFC cell and stack models are developed via spatial smoothing and asymptotic reduction.

Particularly, the energy equations of the original 3D model are spatially smoothed under both local thermal equilibrium (LTE) and non-equilibrium (LTNE) conditions. The selection of either the LTE or LTNE reduced model for use depends on the temperature difference between the working fluid and interconnect in the 3D flow field. Correlation factors are developed to capture the variation in the pathways of conductive heat transfer between the flow field and adjacent layers. The LTE and LTNE spatially-smoothed models are reduced further via asymptotic analysis, resulting in asymptotic spatially-smoothed thermal (ASST) models under either the LTE or LTNE condition. The full and reduced cell models are then taken as the repeating unit for stack modeling. The reduced cell and stack models are verified with their 3D counterparts. For stack modeling, the influence of perturbations between cells on the reduced stack model is investigated.

1.3. Thesis outline

This thesis consists of eight chapters and five appendices, detailed as follows.

Chapter 1 introduces the background of the SOFC, states the motivation to develop reduced cell and stack models for the planar SOFC, and elaborates the objectives of the present research work, followed by the outline of this thesis.

Chapter 2 reviews the published research works on SOFC modeling in the literature, regarding cell design, mathematical modeling with a focus on the planar SOFC, and common numerical methods, respectively.

Chapter 3 develops a 3D non-isothermal P-SOFC model equipped with parallel plain channels surrounded by solid ribs, and validates the mathematical model with experimental measurements from the literature. This 3D P-SOFC model will be used as the benchmark model for the development of reduced models in Chapters 4, 5, and 7.

Chapter 4 develops novel correlation factors for spatial smoothing to capture the variations in diffusion pathways due to ribs and the coupling effects between governing equations. With the novel correlation factors, the 3D P-SOFC model developed in Chapter 3 is reduced via spatial smoothing and asymptotic analysis under an isothermal condition for significant reduction of computational cost with desired numerical accuracy, resulting in a 2D asymptotic spatially-smoothed isothermal (ASSI) model. The 2D isothermal model is verified with the 3D counterpart to prove the retained leading-order physics and the computational gains.

Chapter 5 develops novel variation factors for spatial smoothing to capture the variability of dependent variables – here, mass fractions – underneath ribs along the cell width, which leads to an advanced 2D spatially-smoothed isothermal P-SOFC model. The validity of the advanced spatially-smoothed isothermal model is investigated for various cell designs with parallel flow channels.

Chapter 6 analyses the effects of a single and a combination of stochastic modeling parameters on the variation of cell performance. Monte Carlo simulation of an advanced 2D ASSI P-SOFC model is conducted for sensitivity analysis in terms of global and average local cell behaviours as well as the variability of local mass fractions. The advanced 2D ASSI model is obtained by coupling the ASSI model developed in Chapter 4 with the variation factors developed in Chapter 5.

Chapter 7 develops 2D spatially-smoothed non-isothermal P-SOFC cell and stack models as well as their asymptotic counterparts which are called the asymptotic spatially-smoothed thermal (ASST) cell and stack models. The energy equations are spatially smoothed subject to the local thermal equilibrium (LTE) and non-equilibrium (LTNE) conditions in the volume-averaged flow field. Correlation factors are developed to account for the variation in the pathways of heat transfer due to ribs. The reduced

non-isothermal cell and stack models are verified with their 3D counterparts. Perturbations of dependent variables between cells are investigated for reduced stack modeling.

Chapter 8 draws conclusions from the present research work and recommends possible future work.

Apart from the above chapters, Appendices A-E are provided to elaborate the scaling analysis for the developed 2D spatially-smoothed model under the LTE condition, regarding the governing equations describing the conservations of mass, momentum, species, energy, and charge in each cell component.

Chapter 2

Literature Review

The performance of the SOFC is studied both experimentally and numerically in the literature. Compared with repetitive and costly experimental techniques, numerical simulation is an efficient approach to investigate the transport phenomena, electrochemistry, structural integrity, and limiting mechanisms of the SOFC. For a better understanding of the state of the art of SOFC modeling and the cell characteristics, this chapter presents a review on the existing SOFC models and concentrates on the models for the planar SOFC (P-SOFC). Section 2.1 introduces the modeling for different cell designs that are classified according to cell geometry, support structure, operating temperature, flow configuration, and fuel reforming. Section 2.2 focuses on the mathematical models for the P-SOFC. Section 2.3 reviews common numerical methods for SOFC modeling.

2.1. Cell design

In view of the cell design, the SOFC can be classified based on different criteria including cell geometry, support structure, operating temperature, working flow configuration, and reforming type, as shown in Table 2.1 [31]. This section reviews the research work on these types of SOFCs.

Table 2.1 Classification of solid oxide fuel cells [31].

Classification criteria	Categories
Cell geometry	Planar SOFC (flat-planar and radial-planar design) Tubular SOFC (tubular and micro-tubular design)
Support structure	Electrolyte-supported Anode-supported Cathode-supported
Operating temperature	Low temperature SOFC (LT-SOFC) (500-600 °C) Intermediate temperature SOFC (IT-SOFC) (650-800 °C) High temperature SOFC (HT-SOFC) (800-1000 °C)
Flow configuration	Co-flow Counter-flow Cross-flow
Reforming type	External reforming SOFC (ER-SOFC) Direct internal reforming SOFC (DIR-SOFC) Indirect internal reforming (IIR-SOFC)

2.1.1. Geometrical structure

In the SOFC, both the electrodes and electrolyte are solid. This is different from the other types of fuel cells like PEMFC, PAFC, and MCFC, in which the electrolyte is in liquid phase [10]. The solid structure allows the SOFC to be made into rich geometrical configurations. The most common two configurations are the planar and the tubular design [31].

2.1.1.1. Planar SOFC (P-SOFC)

In a P-SOFC single cell, a thin ionically conducting electrolyte is between a porous anode and cathode, which in turn are sandwiched between flow channels [15, 17, 24, 25]. For large-scale electricity generation, cells are electrically connected in series in a stack by situating a metallic or ceramic interconnect between each cell [32], as shown in Fig. 2.1. The interconnect functions as a current collector to collect the induced current and as a housing for the flow channels of the air/fuel supplied via manifolds. Wen *et al.* [32] established a two-cell stack and a 10-cell stack with cell size of 40×40 mm² (Fig.

2.1b) for material research. A SOFC manufacturer, NexTech Materials, routinely fabricates cells with areas of 500 to 700 cm² and demonstrates the manufacture of cells with an area of 1200 cm², which are currently the world's largest planar P-SOFC [33].

Fig. 2.1 (a) Planar SOFC stack and (b) cell components [32].

Many research works were conducted to study the factors that affect the performance of the P-SOFC. For instance, Achenbach *et al.* [34] investigated on the effect of temperature changes on output voltage response with a 3D model for the planar SOFC stack. Cheng *et al.* [35] conducted a parametric study of the temperature and composition effects on the transport phenomenon in the P-SOFC from micro to macro aspects. The planar geometry has good features from the electrical point of view. Short current paths within the P-SOFC result in low internal electrical resistances and consequently high power density, which is much better than that of the tubular design [3, 8]. The highest power density of the P-SOFC was reported to be 0.48 W cm⁻² for small cells when operating on air and hydrogen, and 0.9 W cm⁻² when operating on pure

oxygen and hydrogen [5]. The main drawback of this design is that it is built from brittle ceramic components with rather high thermal expansion coefficients [3]. At a high operating temperature of about 1000 °C, the intrinsic lack of thermal expansion compliance results in cracking of the solid structure, with consequent cross-over of reactants and loss of performance. Yakabe *et al.* [36] and Lin *et al.* [37] analysed the distribution of thermal stresses within the P-SOFC.

2.1.1.2. *Tubular SOFC (T-SOFC)*

Compared with all the other types of fuel cells that are based on the planar structure, the tubular structure is exclusive for the SOFC, and the cell is fed along the axial coordinate. The T-SOFC is usually in larger size than P-SOFC and can reach almost 1 m in length [38], as shown in Fig. 2.2. The electrolyte is the middle tube, and either the anode or the cathode tube is located on the inner side of the electrolyte tube [39]. According to Li [5], in earlier developed cells, the anode was used on the inner side; however, more recent cells have the cathode on the inner side and the anode on the outside because of easy stacking consideration. Meanwhile, a relatively thick support tube on the inner side is often employed to support the thin cell-composite layers. A detailed three dimensional tubular model was proposed by Bessette *et al.* [40], in which rigorously derived electrochemical and thermal factors were considered along the axial, radial, and circumferential coordinates.

In general, the current in the T-SOFC is assumed to flow within the electrode and the electrolyte in planes perpendicular to cell axis [40]. The T-SOFC has high cell resistance due to its long current paths [5]. In order to avoid an increase of the length of the current paths over a certain value, the cell diameter must be kept as small as about 2 cm, which is one of the reasons for the high manufacturing cost [5]. The disadvantages of low volumetric power density and long current in the T-SOFC can be outweighed by

the advantage of a simple sealing arrangement and desire structure design outweighs [10]. The cylindrical shape of the T-SOFC can be made easily with better resistance against the thermal stress damage to the composite structure [4, 5]. Thus, the T-SOFC is less mechanically constrained to expansion and contraction.

Fig. 2.2 Tubular SOFC stack (bottom) [38] and detailed schematic (up) [39].

Lazzareo *et al.* [41] presented a zero-dimensional model of the T-SOFC and discussed the choice of the independent variables and the setting of the operating parameters at design and off-design conditions. Qi *et al.* [42] found that the fuel flow, inlet pressure, and temperature had significant effects on the dynamic performance of for the T-SOFC with direct internal reforming. In particular, the air inlet temperature on the cathode side had the most significant influence on the solid-phase temperature and cell performance, while the effect of flow velocity was not significant in comparison with the inlet pressures and temperature. Stiller *et al.* [43] compared two 2D steady-state models for SOFC fed by methane in planar and tubular geometries, respectively, and found that

both systems could reach an electric efficiency above 65%.

2.1.1.3. Remarks

The cell geometry should be design properly in order to maximize system efficiency and reduce the risk of components damage. The pros and cons of the two main designs of SOFCs are summarized in Table 2.2. Compared with the P-SOFC, the T-SOFC is much easier to seal air from the fuel and does not suffer from severe thermal expansion mismatch. However, the power density of the tubular design is smaller than that of the planar design. The P-SOFC has received much attention recently due to its compactness, simplicity in manufacturing, and higher specific power density, although the development of the planar type started much later than that of T-SOFC.

Table 2.2 Comparison between planar and tubular SOFC [4, 5].

Geometry	Advantages	Disadvantages
Planar	Low fabrication cost; Ease in flow arrangement; High power density.	High-temperature gas-tight sealing; High assembly effort and cost; Stricter requirement on thermal expansion match.
Tubular	Ease of manufacturing; No need for gas-tight cell sealing; Less thermal cracking due to thermal expansion mismatch (durable).	Edge current collection; Low-power density; High materials cost.

Apart from the planar and tubular SOFCs, there are also other types of geometrical configurations under development, and most of them are the derivatives of the planar and tubular designs. For instance, the integrated planar SOFC (IP-SOFC) is substantially a cross between tubular and planar geometries [44], which seeks to borrow thermal compliance qualities from the T-SOFC as well as low cost component fabrication and short current paths from the P-SOFC. Another highly promising design, called the modified planar SOFC (MPC or MPSOFC) [45], shares the advantages of both the

planar and tubular cells, in which a wave-like structure replaces the traditional flat configuration of the planar cell.

2.1.2. Support structure

The SOFC is fabricated into a variety of self-supporting configurations, by modifying the thickness of the solid electrode and electrolyte for a purpose of structure supporting. All the SOFCs are either electrolyte-supported or electrode-supported depending on the thickness of fuel cell components [31, 46-48], as demonstrated in Fig. 2.3.

Fig. 2.3 Self-supporting structure of the SOFC: (a) YSZ electrolyte-supported cells, (b) Ni/YSZ cermet anode-supported cells with thin YSZ electrolyte [47].

In the electrolyte-supported SOFC [49], the anode and cathode are thin (50 μm), and the electrolyte is the thickest component (> 100 μm) and thus works as the support structure. A thick electrolyte means large ohmic losses and thus is only suitable for high operating temperatures around 1000 °C, which guarantee low electrolyte resistivity such as 0.2 Ω m [50]. In contrast, the electrode-supported design with a thick anode or cathode (300-1500 μm) as the support substrate is more suitable to operate at low or intermediate temperatures [21, 50-52]. A thin electrolyte implies a small ohmic contribution to the total potential loss in the electrode-supported SOFC. In order to

improve cell performance, new electrolyte materials like gadolinia-doped ceria (CGO) are under development to replace the conventional yttria-stabilized zirconia (YSZ) [53, 54]. However, the YSZ-electrolyte SOFC still shows higher power density than the CGO-electrolyte SOFC at a temperatures greater than 750 °C [53].

In the anode-supported SOFC, an YSZ layer of typically 10-20 µm in thickness is deposited on a relatively thick Ni-YSZ anode [21, 50, 55, 56]. The cermet materials based on Ni-YSZ are the most common anodes in the SOFC in view of their high electrochemical activity for H₂ oxidation reaction and long-term stability. Chan *et al.* [20] found that the performance of the anode-supported SOFC was superior to that of the electrolyte-supported or cathode-supported cells with the same materials, electrode kinetics, and operational constraints. They also revealed that the cathode-supported SOFC could not surpass the anode-supported one for high cell performance, even under elevated pressure conditions at the cathode compartment to compensate for the serious cathode concentration polarization loss. Chan *et al.* [20] and Pramuanjaroenkij *et al.* [53] showed that the anode-supported design had a wider operating current density range and hence higher power density than the cathode-supported and electrolyte-supported designs.

In the cathode-supported SOFC, a layer of YSZ that is 30-40 µm thick is deposited on a porous Sr-doped LaMnO₃ (LSM) layer of a thickness about 2 mm [21, 57, 58]. The reason for using LSM as the cathode is that LSM remains a metallic conductor in O₂ atmosphere. Nevertheless, Huang *et al.* [59] proved that this traditional cathode material was the poorest cathode material in view of its high electrode resistance in comparison to other perovskites. Comparing different cathode materials experimentally, they found that the electrode resistance increased in the order SrCo_{0.8}Fe_{0.2}O_{3-δ} (SCF) < La_{0.8}Sr_{0.2}Co_{0.8}Ni_{0.2}O_{3-δ} (LSCN) < La_{0.6}Sr_{0.4}CoO_{3-δ} (LSCo) < La_{0.7}Sr_{0.3}Fe_{0.8}Ni_{0.2}O_{3-δ}

(LSFN) < $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ (LSM). Ackmann *et al.* [21] was the first to simulate a cathode-supported P-SOFC in 2D. They investigated both the anode- and cathode-supported P-SOFCs fed by methane, and analysed the distributions of temperature and species concentration.

The thicknesses of cell components affect the drop in the cell voltage strongly. A thick electrolyte usually means high ohmic polarization, while a thick electrode associates with large concentration polarization. According to a thickness sensitivity analysis by Chan *et al.* [20], when all three cell components were originally of the same thickness, the cell voltage was most sensitive to the change of electrolyte thickness, then the change of cathode thickness, and finally the change of anode thickness. The strength of thickness sensitivity could be reduced by reducing the thickness of all three components with an improved operating current density range. Many of the recent efforts in fuel cell technology development are devoted to reduce the thickness of critical cell components in order to obtain higher and more stable performance at a lower cost [4]. The recent trend of development for the P-SOFC is to apply the electrolyte-supported concept for the high-temperature SOFC [49] and electrode support for low- and the intermediate-temperature SOFC [21, 50, 55-58], as shown in Table 2.3. In view of the large concentration polarization inherently associated with a thickness electrode, the electrode structure in an electrode-supported SOFC needs to be optimized to minimize both activation and concentration polarizations. In contrast, the electrolyte-supported structure possesses small concentration polarization, but large ohmic polarization [20].

Table 2.3 Comparison of SOFCs in terms of support structure and operating temperature.

	High temperature SOFC (~ 1000 °C)	Low and intermediate temperature SOFC (700-800 °C or lower)	
Cell structure	Electrolyte-supported	Anode-supported	Cathode-supported
Cathode	50 μm	50 μm	300-1500 μm
Electrolyte	> 100 μm	< 20 μm	$\leq$ 50 μm
Anode	50 μm	300-1500 μm	50 μm
Sample models	[49]	[21, 50, 55, 56]	[21, 57, 58]
Main drawbacks	Large ohmic polarization	Large concentration polarization	

2.1.3. Operating temperature

Apart from the solid electrolyte, the high operating temperature is another attractive feature of the SOFC for three reasons [5]. First, this high operating temperature allows the internal reforming of hydrocarbon to generate hydrogen within the cells, so that the SOFC can utilize hydrocarbon like methane as fuel [55, 60]. This mitigates the reliance on pure hydrogen, which is not directly available from nature. Second, the oxide-ion conductivity of the electrolyte and the rate of reaction kinetics are satisfactorily high at a high temperature. Thus, the need of expensive catalysts is eliminated [61]. Thirdly, the heat in the high-temperature exiting gas is recycled in a hybrid system for a high efficiency [62, 63]. All these advantages make it possible to apply the SOFC technology to large-scale stationary power generation.

This high temperature also places rigorous requirements on the ceramic materials and thus affects the cost of fabrication greatly [61]. The conventional high-temperature SOFC (HT-SOFC) (800-1000 °C) generally suffers from thermal stresses and mismatch between thermal expansion coefficients of components [37]. Both can weaken the cell structure stability badly, such that an extra routine maintenance on system operation is required. The current trend of the development of the SOFC is to decrease the operating temperature. Intermediate-temperature (IT) (650-800 °C) [51, 52] and low-temperature

(LT) (500-650 °C) [64] SOFCs are under development, in which cheaper materials can be used for electrode, electrolyte, interconnect, and manifold components. A low operating temperature not only widens the selection of materials for of cell components but also significantly reduces the risk of thermal shock and interface reactivity between different cell components, so that the cell stability and reliability are increased [65]. However, the LT-SOFC faces a challenge to increase the ionic conductivity of the electrolyte while reducing the operating temperature. Yuan *et al.* [64] claimed that when lowering the operating temperature, the cell performance was also lowered due to a higher ohmic loss in electrolyte and slower electrochemical kinetics in the cathode. Apart from being affected by the operating temperature, the performance of the LT-SOFC is influenced by various microstructure properties of the electrode, such as the particle size and TPB length [66].

2.1.4. Flow configuration

For the planar SOFC, there are three kinds of flow configurations for air and fuel feeding, called the co-, counter-, and cross-flow configuration [31, 67], as shown schematically in Fig. 2.4. The cross-flow configuration is only modeled in 3D [19, 68], while the co- and counter-flow configurations are modeled in 3D or 2D [23, 55, 68, 69].

Fig. 2.4 Schematic of flow configurations: (a) co-flow, (b) counter-flow, and (c) cross-flow.

Cheng *et al.* [35] presented the temperature distribution in a P-SOFC single cell with all the three flow configurations. They found that the co-flow design provided the most uniform temperature distribution for the YSZ electrolyte and generated a hot area near the outlet portion of the flow channels. The counter-flow design had a uniform temperature gradient with a large temperature difference from the inlet to the outlet. The cross-flow design had the most non-uniform temperature distribution, and the hot spot was at the corner. The uniform current density and temperature distribution in the co-flow configuration was also reported by Wang *et al.* [70].

Hu *et al.* [71] also proved the uniform current density distribution in the co-flow design and the non-uniform temperature and current density distributions in the cross-flow configuration. The current in the counter-flow configuration decreased from the fuel inlet to the outlet, which was different from that in the co-flow configuration [71]. They concluded that a more uniform temperature distribution was possible in the counter-flow configuration than in the co-flow case, if proper operating conditions were

selected.

Furthermore, the superiority of the co-flow configuration was proved not only at the single-cell level but also at the stack level [34]. According to the research work of Achenbach [34] observed the most uniform current density distribution in a co-flow stack, and the largest temperature gradients in the solid structure occur in the cross-flow stack. Recknagle *et al.* [72] stated that the co-flow stack design had the most uniform temperature distribution and the smallest thermal gradients, which meant that the co-flow configuration offered thermo-structural advantages over the counter- and cross-flow design for a cell stack.

Therefore, the co-flow design is currently the best of the three flow configurations, although the cross-flow design is popular for the P-SOFC stack design.

2.1.5. Fuel reforming

One essential advantage of the SOFC over the other types of fuel cells is that it can be fueled by not only pure hydrogen but also the mixture of methane and carbon monoxide [4]. When fed with a gas mixture, the SOFC converts a hydrocarbon primary fuel such as CH_4 into a hydrogen-rich gas for the subsequent electrochemical reaction on the anode. This is achieved via the methane steam reforming reaction described by Eq. (1.4), typically associated with the water-gas shift reaction by Eq. (1.5).

Among the earliest studies on the methane steam reforming reaction, Achenbach and Riensche [73] determined the kinetics of the reforming reaction experimentally. They proposed an equation in the Arrhenius form for the reforming kinetics, in which the activation energy was derived from the slope of the Arrhenius equation. After that, many studies on the reforming kinetics emerged. Paradis *et al.* [74] compared the internal reforming kinetics described by three different reaction rate equations either in the Arrhenius form or in the Langmuir–Hinshelwood form. In addition, the water-gas

shift reaction can be considered to be either in kinetic state [56, 75, 76] or in equilibrium [34, 51, 52, 74, 77-80].

The reforming procedure can be performed either externally or internally for the SOFC. The external reforming SOFC (ER-SOFC) requires an external catalytic steam reformer or partial oxidation reactor to process the fuel indirectly [81]. In contrast, the internal reforming SOFC (IR-SOFC) eliminates the requirement for a separate fuel reformer and significantly reduce the requirement for cell cooling that is usually done by flowing excess air through the cathode [55, 74]. Furthermore, the IR-SOFC is subdivided into two types: direct internal reforming (DIR-SOFC) [52, 77] and indirect internal reforming (IIR-SOFC) [82, 83].

In the DIR-SOFC, the hydrocarbon fuel is fed directly into the cell and the reforming reaction occurs simultaneously with the electrochemical reaction at the anode [52, 75, 77]. The concentration of the reformed H_2 depends on the conversion rate of methane which may be affected by cell structure. Lehener *et al.* [75] found that among the experimentally determined structure parameters of a cermet, the ratio of porosity, ε , to tortuosity, τ , affected the methane conversion most significantly, followed by the mean value of pore radii. Compared with the ER-SOFC, the IR-SOFC encounters two main issues including the formation of large temperature gradients along the cell and deposition of carbon on conventional anode catalysts [55, 84]. Nikooyeh *et al.* [55] analysed these two issues with a 3D DIR-SOFC model. The large temperature gradients resulted from the relative rates of the endothermic methane steam reforming reaction and exothermic electrochemical reaction at different locations in the PEN structure. In their opinion, these large temperature gradients could be reduced by recycling an amount of the anode exhaust gases, which would change the composition of the feed. The increasing concentration of H_2 enhanced the exothermic electrochemical reaction and

thus reduced the temperature drop at the inlet. Meanwhile, the increasing concentrations of H_2 , H_2O , and CO_2 might also decrease the amount of carbon deposition.

In the IIR-SOFC, the endothermic reforming reaction takes place at a reformer, which is separate from but in close thermal contact with the anode side, where exothermic electrochemical reaction occurs [85]. When developing the IIR-SOFC, the mismatch between the rates of endothermic and exothermic reactions should be avoided; otherwise, a significant local temperature drop near the entrance of the internal reformer may occur and cause thermally induced stresses and even mechanical failure [86]. In order to manage thermal stresses, it is essential to study the temperature distribution as well as the generation and consumption of heat within the cell. Based on a steady-state IIR-T-SOFC, Aguiar *et al.* [82] presented a detailed description of the spatial distributions of temperature, electromotive force, and concentration of participating chemical species, and analysed their relationship to the cell performance. Their analysis indicated that increasing the operating pressure was an effective way to reduce both the local cooling caused by the reforming reactions and the overall temperature increment across the cell. Zhang *et al.* [87] analysed the characteristic of thermal energy generation in the IIR-T-SOFC. The exothermic electrochemical reaction contributed 82.7% in the total heat generation, while the left 17.3% was possessed by ohmic heat. About 47.3% of the generated heat in the cell was absorbed by the reforming reaction. The air flow took away 36.6% the generated heat, and the remainder 16% was taken away by the fuel flow.

2.2. Mathematical models for P-SOFC

The first significant solid electrolyte fuel cell models were presented almost thirty years ago. In 1983, De Benedetti and Vayenas [88] developed a mathematical model for the solid electrolyte cell as an electrochemical reactor in order to describe the cell

performance under steady-state conditions [89]. Two years later, Vayenas *et al.* [19] developed a model with a cross-flow monolithic structure. After that, the works on SOFC modeling emerged increasingly in the literature. Nowadays, the modeling development of the SOFC has covered all the cell designs [31, 79, 90, 91]. A general target of fuel cell modeling is to calculate the cell polarization curve under various operating and design conditions, because the relationship between cell voltage and current density drawn from the cell constitutes the primary measure of a fuel cell performance [5]. Then three irreversible voltage losses, called the activation, ohmic, and concentration polarization, can be determined based on the conservation equations for the transport of total mass, each species, momentum, and energy. According to objectives of studies, multi-dimensional SOFC models are developed in 3D, 2D, 1D, or 0D with certain simplifications and assumptions for transient or steady-state problems. Moreover, mathematical modeling is an efficient approach for parametric studies, compared with repetitive and costly experimental techniques

This section reviews the research works on the P-SOFC modeling regarding the polarizations, transport phenomena in electrodes, spatial dimension, time dependence, thermo-mechanical behaviours, stack performance, model simplification, and sensitivity analysis.

2.2.1. Polarizations

A typical polarization curve for the fuel cell mainly consists of three regions for the activation, ohmic, and concentration polarizations [9], as shown schematically in Fig. 2.5. The first region represents the activation voltage drop called the activation polarization, η^{act} , due to the slowness of the chemical reactions taking place at electrode surfaces. Depending on the operating temperature and pressure as well as

electrode structure, this region is more or less wide. The second region represents the resistive losses called the ohmic polarization, η^{ohm} , due to the internal resistance to the transport of elections and ions in the solid structure of the cell. The last region represents the mass transport losses called the concentration polarization, η^{con} , resulting from the change in concentration of reactants as the reactants are consumed. In addition, there is another voltage drop called the leakage polarization, η^{leak} , that makes the actual measured open circuit voltage, E^{OCV} , often fall slightly below the reversible potential, E^{rev} [9, 92]. The real output voltage of the cell, V_{cell} , is then obtained by subtracting all the polarizations from the reversible potential, given by [5, 9, 10, 92]:

$$V_{cell} = E^{rev} - \eta^{act} - \eta^{ohm} - \eta^{con} - \eta^{leak}. \quad (2.1)$$

The reversible potential and the four kinds of polarizations on the right-hand side of Eq. (2.1) are explained in details below.

Fig. 2.5 Schematic of the polarization curve for the SOFC.

2.2.1.1. Reversible potential

The reversible potential, E^{rev} , is usually determined by the Nernst equation for an electrochemical reaction with n electrons transferred at a temperature of T [5, 9, 10],

$$E^{rev} = E^0 + \frac{RT}{nF} \ln \left(\frac{\left(\frac{p_{H_2}}{p^0} \right) \left(\frac{p_{O_2}}{p^0} \right)^{0.5}}{\left(\frac{p_{H_2O}}{p^0} \right)} \right), \quad (2.2)$$

in which F is the Faraday's constant. The reversible potential at standard conditions, E^0 , is 1.18 V for the SOFC fueled by hydrogen [10], according to $E^0 = -\Delta G^0 / (nF)$, in which ΔG^0 is the standard Gibbs free energy change. Then,

As shown in Eq. (2.2), the reversible Nernst potential depends on the partial pressure of the reactant and product species. The partial pressure of species is defined in different ways in the existing SOFC models. For example, Chan *et al.* [20] used the inlet partial pressure of species to calculate the reversible Nernst potential in a 0D model, given by

$$E^{rev} = \frac{RT}{2F} \ln K - \frac{RT}{2nF} \ln \left(\frac{(p_{H_2O}^{in})^2 p^0}{p_{H_2}^{in} p_{O_2}^{in}} \right), \quad (2.3)$$

where K is the equilibrium constant from the JANAF table, the number of transfer elections $n = 2$, and p^{in} is the inlet pressure in Pa. The inlet partial pressure is applicable, because the cell was treated as a black box and only the performance of the entire cell was in interest.

Instead of using the inlet pressure, Yuan *et al.* [64] expressed E^{rev} in terms of the partial pressure of species in the bulk flow in the channel:

$$E^{rev} = E^0 + \frac{RT}{nF} \ln \left(\frac{p_{H_2,fc} p_{O_2,fc}^{0.5}}{p_{H_2O,fc}} \right), \quad (2.4)$$

where $E^0 = 1.2723 - 2.7645 \times 10^4 T$, $n = 2$, and $p_{i,fc}$ is pressure in bar for species i in the flow channel. The reaction sites were considered to be uniformly distributed in the electrode, which means that the electrochemical half-cell reaction takes place through the entire electrode rather than only at the electrode/electrolyte interface. On the other hand, if the reactions are assumed to occur merely at the electrode/electrolyte interface, the local partial pressures at this interface are used instead [55, 93]. Eq. (2.4) was also employed by Ni *et al.* [94] with $E^0 = 1.253 - 2.4516 \times 10^4 T$.

In addition, Lazzareo *et al.* [41] evaluated the Nernst potential as an intermediate value between those at both cell inlet and outlet, given by

$$E^{\text{rev},\text{in}} = -\frac{\Delta G^0}{2F} + \frac{RT^{\text{in}}}{2F} \ln \left(\frac{p_{\text{H}_2}^{\text{in}} (p_{\text{O}_2}^{\text{in}})^{0.5}}{p_{\text{H}_2\text{O}}^{\text{in}}} \right), \quad (2.5)$$

$$E^{\text{rev},\text{out}} = -\frac{\Delta G^0}{2F} + \frac{RT^{\text{out}}}{2F} \ln \left(\frac{p_{\text{H}_2}^{\text{out}} (p_{\text{O}_2}^{\text{out}})^{0.5}}{p_{\text{H}_2\text{O}}^{\text{out}}} \right), \quad (2.6)$$

$$E^{\text{rev}} = k_v \frac{E^{\text{rev},\text{in}} + E^{\text{rev},\text{out}}}{2}. \quad (2.7)$$

The tuning constant, k_v , in Eq. (2.7) was between 0.97 and 1.02 to increase the accuracy of experimental data prediction.

2.2.1.2. Activation polarization

The activation polarization derives from the activation barrier that the energy of reactants must exceed to trigger the electrochemical reactions [9]. The activation loss at the anode or cathode is evaluated according to the Butler-Volmer equation in terms of the asymmetry factor, $\mathfrak{R}$, which is usually between 0.4 and 0.6 experimentally [95],

$$i = i_0 \left[\exp \left(\frac{\mathfrak{R}nF}{RT} \eta^{\text{act}} \right) - \exp \left(-\frac{(1-\mathfrak{R})nF}{RT} \eta^{\text{act}} \right) \right], \quad (2.8)$$

or in terms of the transfer coefficient α as

$$i = i_0 \left[\exp\left(\frac{\alpha_a F}{RT} \eta^{\text{act}}\right) - \exp\left(-\frac{\alpha_c F}{RT} \eta^{\text{act}}\right) \right], \quad (2.9)$$

where α_a and α_c are the anodic and cathodic apparent transfer coefficient respectively, usually between 0.2 and 2 [96]. Both β and α are related to how an applied potential favors one direction over the other in the half-cell reactions by Eqs. (1.1) and (1.2). The exchange current density, i_0 , represents the rate of exchange between the reactant and product states at equilibrium. Eqs. (2.8) and (2.9) assume a single rate determining step.

The exchange current density can be expressed in different equivalent forms. It is mainly affected by four factors including reactant concentration, activation barrier, temperature, and the number of possible reaction sites [9]. Moreover, some adjustable parameters may be involved in the expression of the exchange current density to fit the experimental data [97]. For example, the anodic exchange current density used by Shi *et al.* [97, 98] is

$$i_{0,a} = \frac{\mathcal{B}_a RT}{3F} \left(\frac{c_{\text{H}_2}}{c_{\text{H}_2}^{\text{ref}}} \right) \exp\left(-\frac{E_a^{\text{act}}}{RT}\right) (p_{\text{H}_2\text{O},a})^{0.133}, \quad (2.10)$$

where $c_{\text{H}_2}^{\text{ref}}$ is the hydrogen concentration in the reference case, and $p_{\text{H}_2\text{O},a}$ is the water vapor partial pressure at the anode. For the anode support layer, an activation energy $E_a^{\text{act}} = 1.2 \times 10^5 \text{ J mol}^{-1}$ and an adjustable parameter $\mathcal{B}_a = 6.17 \times 10^{11} \Omega^{-1} \text{ m}^{-2}$ were specified. For the anode active layer, $E_a^{\text{act}} = 1.2 \times 10^5 \text{ J mol}^{-1}$ and $\mathcal{B}_a = 6.8 \times 10^{12} \Omega^{-1} \text{ m}^{-2}$, which were tuned to fit the experimental data [97]. The cathodic exchange current density corresponding to both cathode support and active layers is determined by [99]

$$i_{0,c} = \frac{\mathcal{B}_c RT}{4F} \exp\left(-\frac{E_c^{\text{act}}}{RT}\right) (p_{\text{O}_2,c})^{0.25}, \quad (2.11)$$

where $i_{0,c}$ is the cathodic exchange current density, $p_{O_{2,c}}$ is the oxygen partial pressure at the cathode, $E_c^{\text{act}} = 1.3 \times 10^5 \text{ J mol}^{-1}$ and $\mathcal{B}_c = 5.8 \times 10^{10} \Omega^{-1} \text{ m}^{-2}$ which are adjustable [97].

VanderSteen *et al.* [100] introduced the effects of gaseous species partial pressure, temperature, reaction order, and activation energy on the exchange current density,

$$i_{0,c} = i_{0,c}^{\text{ref}} \left(\frac{p_{O_2}}{p_{O_2}^0} \right)^\gamma \exp \left[\frac{-E_c^{\text{act}}}{R} \left(\frac{1}{T} - \frac{1}{T^0} \right) \right], \quad (2.12)$$

$$i_{0,a} = i_{0,a}^{\text{ref}} \left(\frac{p_{H_2}}{p_{H_2}^0} \right)^{\gamma_1} \left(\frac{p_{H_2O}}{p_{H_2O}^0} \right)^{\gamma_2} \exp \left[\frac{-E_a^{\text{act}}}{R} \left(\frac{1}{T} - \frac{1}{T^0} \right) \right], \quad (2.13)$$

where $i_{0,c}^{\text{ref}}$ and $i_{0,a}^{\text{ref}}$ are the reference exchange current densities, γ and $\gamma_1 + \gamma_2$ are the reaction order, T^0 is the reference temperature, and E^{act} is the activation energy. According to electrochemical kinetics, the reference exchange current density, the transfer coefficients, and the reaction order depend on the rate determining step(s) of the electrochemical reaction and the electrode microstructure [101].

The exchange current density is also affected by pore radius and porosity, which determine the TPB length in the electrode as reported by Meng *et al.* [102]:

$$\begin{aligned} i_{0,a} &= \beta_a \frac{1-\varepsilon}{r} \exp \left(-\frac{E_a^{\text{act}}}{RT} \right), \\ i_{0,c} &= \beta_c \frac{1-\varepsilon}{r} \exp \left(-\frac{E_c^{\text{act}}}{RT} \right), \end{aligned} \quad (2.14)$$

where $E_a^{\text{act}} = 1.0 \times 10^5 \text{ J mol}^{-1}$ and $E_c^{\text{act}} = 1.2 \times 10^5 \text{ J mol}^{-1}$ are the activation energy of anode and cathode respectively, ε is the porosity of electrode, r is the pore radius, β_a and β_c are the coefficients for exchange current density of the anode and cathode respectively. Increasing electrode porosity or pore size decrease the concentration polarization and

increase the activation polarization of CH₄ fed SOFC [102]. At low current densities, low porosity and small pore size are desirable to reduce the electrode total polarizations, as concentration polarization is insignificant compared with activation polarization. At high current densities, the total polarizations can be minimized by optimizing the porosity and pore size.

The form of the Butler-Volmer equation for each half-cell reaction also depends on the assumption on where the reaction takes place. When the reaction is assumed to occur at the interface between the electrode and the electrolyte, the Butler-Volmer equation is expressed as a current density in A m⁻² in terms of roughness factor a of the electrode, reference exchange current density i_0^{ref} , reference and local reactant mole concentration c_R^{ref} and c_R , and reaction order γ ,

$$i = ai_0^{\text{ref}} \left(\frac{c_R}{c_R^{\text{ref}}} \right)^{\gamma_{\text{a/c}}} \left[\exp\left(\frac{\mathfrak{R}nF}{RT} \eta^{\text{act}} \right) - \exp\left(-\frac{(1-\mathfrak{R})nF}{RT} \eta^{\text{act}} \right) \right]. \quad (2.15)$$

When the reaction takes place over a layer of finite volume, the Butler-Volmer equation is expressed as a volumetric current density in A m⁻³ involving the specific reactive surface area of electrode $\mathcal{A}$ [56-60]

$$J = \mathcal{A}i_0^{\text{ref}} \left(\frac{c_R}{c_R^{\text{ref}}} \right)^{\gamma_{\text{a/c}}} \left[\exp\left(\frac{\mathfrak{R}nF}{RT} \eta^{\text{act}} \right) - \exp\left(-\frac{(1-\mathfrak{R})nF}{RT} \eta^{\text{act}} \right) \right]. \quad (2.16)$$

Furthermore, the Butler-Volmer equation can be simplified depending on the desired accuracy and the expected activation polarization [15, 46, 47, 50, 51]. For a SOFC at 1073 K, under high activation polarization with $|\eta^{\text{act}}| > 0.2516$, Eq. (2.16) can be simplified to the Tafel equation,

$$J_c = -\mathcal{A}i_{0,\text{O}_2}^{\text{ref}} \left(\frac{c_{\text{O}_2}}{c_{\text{O}_2}^{\text{ref}}} \right)^{\gamma_{\text{O}_2}} \exp\left(-\frac{\mathfrak{R}nF}{RT} \eta_c^{\text{act}} \right), \quad (2.17)$$

for the cathode side with an error of 5%. Under low activation polarization with

$|\eta^{\text{act}}| < 0.1006$, a linear current-potential relation is applicable, such that Eq. (2.16)

becomes

$$J_a = A_{i_{0,H_2}}^{\text{ref}} \left(\frac{c_{H_2}}{c_{H_2}^{\text{ref}}} \right)^{\gamma_{H_2}} \frac{\Re n F}{RT} \eta_a^{\text{act}}, \quad (2.18)$$

for the anode side.

2.2.1.3. Ohmic polarization

Electricity in the SOFC is transported through the conducting solid porous backing layer by the flow of electrons, through the solid dense electrolyte by the flow of ions, and through the reaction zone layer of a finite volume by the flow of both electrons and ions. Therefore, the ohmic polarization in the cell arises due to electrical resistance in the cell components including [5, 9]:

- 1) Resistance to the flow of ions in the electrolyte (ionic resistance);
- 2) Resistance to the electrons and ions in the reaction zone layer (ionic and electronic resistance);
- 3) Resistance to the flow of electrons through the electrode-backing layer (or gas diffusion layer) (electronic resistance); and
- 4) Resistance to the flow of electrons through interconnects (electronic resistance).

The resistance to the electron or ion transport is described by the Ohm's law [9, 92],

$$\eta^{\text{ohm}} = I\mathcal{R} = (JA)\mathcal{R}, \quad (2.19)$$

where I is the current density, J is the volumetric current density, and A is the cross-sectional area of the conducting cell component normal to the conducting path, $\mathcal{R}$ is the electronic/ionic resistance in a cell component. The total cell ohmic loss, η^{ohm} , is the sum of electronic and/or ionic ohmic loss in anode/cathode interconnect, backing and reaction zone layers as well as the electrolyte, expressed as

$$\eta^{\text{ohm}} = \eta_{\text{ic,c}}^{\text{ohm}} + \eta_{\text{bl,c}}^{\text{ohm}} + \eta_{\text{rl,c}}^{\text{ohm}} + \eta_{\text{el}}^{\text{ohm}} + \eta_{\text{rl,a}}^{\text{ohm}} + \eta_{\text{bl,a}}^{\text{ohm}} + \eta_{\text{ic,a}}^{\text{ohm}}. \quad (2.20)$$

The ohmic polarization at the electrolyte usually dominates the total ohmic loss in fuel cell, because the electrolyte resistance is usually larger than the electrode resistance [9, 20].

2.2.1.4. Concentration polarization

Concentration polarization is the voltage loss that is caused by non-uniform distributions of reactants, which result from processes hindering the transport of mass. In SOFC, these processes are the convective mass transfer of gaseous species from the flow channel to the porous electrode, and the slow diffusion of reactants and products through the porous electrodes. The chemical reactions are hindered due to the lack of reactants which transports slowly to reach the reaction sites. This is usually the case that the electrochemical reaction is too fast corresponding to a high current density. Wang *et al.* [70] suggested that the total concentration potential of the cell could be decreased by decreasing the thickness or increasing the porosity of the anode.

The concentration polarization is determined by

$$\eta^{\text{con}} = -\frac{RT}{nF} \ln \left(1 - \frac{i}{i_L} \right), \quad (2.21)$$

where i_L is the limiting current density, which is the maximum current density produced by the cell. At the limiting current density, the rate of reactants consumed is equal to the amount of reactants supplied, such that no extra reactants would accumulate at the reaction sites. η^{con} can also be formulated in the Nernst form in terms of species concentration as follows [103]

$$\eta_a^{\text{con}} = \frac{RT}{2F} \left(\ln \frac{c_{\text{H}_2}^{\text{channel}}}{c_{\text{H}_2}^{\text{TPB}}} - \ln \frac{c_{\text{H}_2\text{O}}^{\text{channel}}}{c_{\text{H}_2\text{O}}^{\text{TPB}}} \right), \quad (2.22)$$

$$\eta_c^{\text{con}} = \frac{RT}{4F} \left(\ln \frac{c_{\text{O}_2}^{\text{channel}}}{c_{\text{O}_2}^{\text{TPB}}} \right). \quad (2.23)$$

Furthermore, the concentration polarizations can even be formulated in more complicated ways to show the dependence of η^{con} on diffusivities, electrode thickness, and mole fraction of species together, based on how the mass transport is modeled using the Fick's model, the Stefan-Maxwell model, or the Dusty-gas model [104]. All these three diffusion models are introduced in Section 2.5.2.

2.2.1.5. Leak polarization

The maximum cell voltage is measured experimentally when there is no electric current drawn from the cell, thereby obtaining the open circuit, E^{OCV} . This open circuit cell voltage is always slightly less than the thermodynamic reversible cell potential, E^{rev} [92], as shown schematically in Fig. 2.5. The difference between E^{OCV} and E^{rev} is called leak polarization, η^{leak} , which may result from residual electronic conduction in the electrolyte, gases crossing over the electrolyte via micro cracks and fissures, and/or a leak current that is wasted by unwanted side reactions or non-electrochemical reactions at the electrodes [9, 92, 105]. To the best of my knowledge, there is no mathematical formula to evaluate the leak polarization involving all the causes above. The η^{leak} can be specified as a modeling parameter and its value is tuned to fit the numerically predicted polarization curve with experimental data [97, 98]. Typically, the leak polarization is considerable for low-temperature fuel cells such as PEMFCs, but less markedly for high-temperature fuel cells such as SOFCs, as demonstrated in Fig. 2.6 [105]. For example, it was estimated that $\eta_{\text{leak}} \sim 0.2 \text{ V}$ with respect to $E^{\text{rev}} \sim 1.2 \text{ V}$ for a PEMFC (i.e., $\eta_{\text{leak}}/E^{\text{rev}} \sim 17\%$) [105], and $\eta_{\text{leak}} \sim 0.03 \text{ V}$ to $E^{\text{rev}} \sim 1.1 \text{ V}$ for a SOFC (i.e., $\eta_{\text{leak}}/E^{\text{rev}} \sim 3\%$) [97].

Fig. 2.6 Graphs showing polarization curves of typical fuel cells: (a) a low-temperature fuel cell operating at 70 °C; (b) a SOFC operating at 800 °C [105].

2.2.2. Transport phenomena in electrodes

Before determining the various voltage and heat losses in the SOFC, it is essential to understand the transport of mass, momentum, and energy within the cell components, especially in the porous electrodes [106]. The electrode can be subdivided into a backing (or gas diffusion) layer and a reaction zone layer, which are made of the same material but function differently [92]. The difference between them is that the half-cell electrochemical reactions by Eqs. (1.1) and (1.2) take place at the reaction sites (namely, the triple phase boundaries (TPB)) in the reaction zone layer, but not in the backing layer.

Both ions and electrons transfer in the reaction zone layer, while only electrons transfer in the backing layer.

2.2.2.1. Volume averaging for porous media

In the porous electrode of the SOFC, gas and solid phases coexist. A detailed description of every pore is not practical. In order to obtain the governing equations of the mass, momentum, and energy transport in porous media, a common approach, called the volume-averaging method [107], is implemented by taking an average of the governing equations originally describing the fluid in free flow fields over a representative elementary volume, whose length scale is considerably smaller than that of the macroscopic flow domain, but large enough to incorporate sufficient solid and void elements for an accurate average description [5, 107, 108].

It is worth mentioning a difference between an average taken over the whole representative elementary volume V , and that taken over a volume element $V^{(g)}$ consisting of pores filled by gaseous fluid. Let $\mathbf{B}$ be a quantity, either scalar, vector, or tensor, associated with the gas phase. Let $\langle \mathbf{B} \rangle$ represent the superficial volume average of $\mathbf{B}$:

$$\langle \mathbf{B} \rangle = \frac{1}{V} \int_{V^{(g)}} \mathbf{B} dV. \quad (2.24)$$

Let $\langle \mathbf{B} \rangle^{(g)}$ be the intrinsic volume average of $\mathbf{B}$ in the gas phase,

$$\langle \mathbf{B} \rangle^{(g)} = \frac{1}{V^{(g)}} \int_{V^{(g)}} \mathbf{B} dV. \quad (2.25)$$

The relation between the superficial and intrinsic volume average is

$$\langle \mathbf{B} \rangle = \varepsilon \langle \mathbf{B} \rangle^{(g)}, \quad (2.26)$$

in which ε is the porosity defined as the ratio of the pore space $V^{(g)}$ to the overall space

V including both pores and solid, given by

$$\varepsilon = V^{(g)}/V. \quad (2.27)$$

The value of porosity can vary from zero for pure solid regions to unity for free fluid flow. The cell performance is strongly dependent on porosity as well as detailed porous microstructure distributions of electrodes [109].

Generally, the superficial average velocity is the preferred quantity for the macroscopic or volume averaged velocity field, while the intrinsic average concentration and pressure are preferred in the representation of governing equations for porous media [107]. For simplicity, all angle brackets and superscript (g) are ignored in the following context.

2.2.2.2. Mass transfer

The mass transfer of gaseous working fluid in the electrode is typically governed by the continuity equation [110],

$$\nabla \cdot (\rho \mathbf{v}) = S_{\text{mass}}, \quad (2.28)$$

where ρ is the density of the gaseous mixture, and $\mathbf{v}$ is the superficial velocity for the porous electrode. The mass source/sink term, S_{mass} , due to the electrochemical reactions at the reaction sites is calculated by the Faraday's law [96],

$$S_{\text{mass}} = -\sum_i \frac{s_i M_i |J|}{nF}, \quad (2.29)$$

where s_i is the stoichiometric coefficient, and n is the number of electrons consumed or produced by the cathode or anode half-cell reaction. Taking the reactions defined by Eqs. (1.1) and (1.2) for instance, S_{mass} is zero for the backing layer, but $M_{\text{O}_2} J_c / 4F$ for the cathode reaction zone layer and $-M_{\text{H}_2} J_a / 2F + M_{\text{H}_2\text{O}} J_a / 2F$ for the anode

reaction zone layer in terms of the cathodic, J_c , and anodic volumetric current density, J_a . Here, J_c is inherently negative and J_a is positive.

The working fluid actually consists of various gaseous species. In theory, no molecule can go through the dense electrolyte from one electrode side to the other in the SOFC [61]. The mass transport of uncharged species involves both convection and diffusion in the electrode and is dominated by the latter [66]. Among these species, oxygen molecules are much larger in size than hydrogen molecules. Therefore, the transport of molecular oxygen to the electrode surface is much more difficult, and hence much slower, than the transport of the molecular hydrogen at the anode. The transport of gaseous species can be represented in terms of either the mass flux [53, 100, 111],

$$\nabla \cdot (\rho \omega_i \mathbf{v} + \mathbf{j}_i) = S_i, \quad (2.30)$$

$$S_i = \begin{cases} +\frac{M_{\text{O}_2} J_c}{4F} & (\text{O}_2, \text{cathode rl}) \\ +\frac{M_{\text{H}_2\text{O}} J_a}{2F} & (\text{H}_2\text{O}, \text{anode rl}) \\ -\frac{M_{\text{H}_2} J_a}{2F} & (\text{H}_2, \text{anode rl}) \\ 0 & (\text{bl}) \end{cases}, \quad (2.31)$$

or the molar flux

$$\nabla \cdot (c_i \mathbf{v} + \mathbf{J}_i) = S_i, \quad (2.32)$$

$$S_i = \begin{cases} +\frac{J_c}{4F} & (\text{O}_2, \text{cathode rl}) \\ +\frac{J_a}{2F} & (\text{H}_2\text{O}, \text{anode rl}) \\ -\frac{J_a}{2F} & (\text{H}_2, \text{anode rl}) \\ 0 & (\text{bl}) \end{cases}. \quad (2.33)$$

The first term on the left-hand side of Eqs. (2.30) and (2.32) corresponds to convection, and the second one stands for diffusion. In the literature, three diffusion models are

available to describe the mass transfer of each species in porous media, called the Fick's model, the Stefan-Maxwell model, and the Dusty-Gas model [100].

The Fick's model (FM) is the simplest diffusion model [91, 100, 110-112], in which the mass diffusive flux of species i is defined as

$$\mathbf{j}_i = -\rho D_{ij} \nabla \omega_i, \quad (2.34)$$

and the molar diffusive flux of species i is

$$\mathbf{J}_i = -D_{ij} \nabla c_i = -c D_{ij} \nabla x_i, \quad (2.35)$$

where ω_i is the mass fraction, x_i is the mole fraction, c_i is the molar concentration of species i , c is the total molar concentration of the gas mixture, and D_{ij} is the binary diffusivity for a binary mixture of component i and j . The mass fraction formalism for chemical species concentration is better than the mole fraction, molar concentration or species partial pressure, in respect of the fact that reactions occur in a gas phase which is able to modify its local density due to variations in composition and temperature [113]. The FM is only used for dilute or binary systems, but not applicable when a large number of gaseous species is present [53].

The Stefan-Maxwell model (SMM) is a general alternative to calculate the diffusion in a multi-component system [100, 110]. The Stefan-Maxwell equations determining the diffusion flux for a multi-component system of n species are [9, 100, 104, 110, 114]

$$-c \nabla x_i = \sum_{j=1, i \neq j}^n \frac{1}{D_{ij}} (x_j \mathbf{N}_i - x_i \mathbf{N}_j), \quad (2.36)$$

where c is the concentration of the mixture, D_{ij} is the ordinary or binary diffusion coefficient of species i in j , x_i is the mole fraction of species i , and $\mathbf{N}_i$ is the diffusion flux of species i .

The Dusty-Gas model (DGM) or extended Stefan-Maxwell model combines the Stefan-Maxwell model with the Knudsen diffusion for small pore sizes [115]. Knudsen diffusion takes the frequent collisions between gaseous molecules and the solid porous material into account. In contrast, this molecule-wall collision effect is neglected in the FM and the SMM. A diffusion model accounting for both the ordinary and Knudsen diffusion are expressed as [91, 100, 104, 114]

$$-c\nabla x_i = \sum_{j=1, i \neq j}^n \frac{1}{D_{ij}} (x_j \mathbf{N}_i - x_i \mathbf{N}_j) + \frac{\mathbf{N}_i}{D_{\text{Kn},i}}, \quad (2.37)$$

where D_{ij} is the ordinary or binary diffusion coefficient and $D_{\text{Kn},i}$ is the Knudsen diffusion coefficient of species i . Mathematically, the two terms on the right-hand side of Eq. (2.37) can be combined to get modified Stefan-Maxwell equations for the multi-component diffusion in the porous electrodes,

$$-c\nabla x_i = \sum_{j=1, i \neq j}^n \frac{1}{\mathcal{D}_{ij}} (x_j \mathbf{N}_i - x_i \mathbf{N}_j), \quad (2.38)$$

where $\mathcal{D}_{ij}$ is the combined diffusion coefficient defined as [79, 100]

$$\mathcal{D}_{ij} = \frac{D_{ij} D_{\text{Kn},i}}{D_{ij} + D_{\text{Kn},i}}. \quad (2.39)$$

Because both electrodes are porous, in order to account for the effect of the porous matrix on the diffusive transport, the intrinsic diffusion coefficient $\mathcal{D}_{ij}$ is corrected with some geometric factors like porosity and tortuosity as follows [100]

$$D_{ij}^{\text{eff}} = \frac{\varepsilon}{\tau} \mathcal{D}_{ij}. \quad (2.40)$$

Alternatively, the Bruggeman correction is also widely used in the estimation of the effective diffusivity in a porous medium [100],

$$D_{ij}^{\text{eff}} = \varepsilon^{1.5} \mathcal{D}_{ij}, \quad (2.41)$$

where the exponent of 1.5 is an empirical constant. At high temperatures, Eq. (2.40) for the effective diffusivity is more accurate than Eq. (2.41) [9]. Consequently, the modified Stefan-Maxwell Eq. (2.38) becomes [110]

$$-c\nabla x_i = \sum_{j=1, i \neq j}^n \frac{1}{D_{ij}^{eff}} (x_j \mathbf{N}_i - x_i \mathbf{N}_j). \quad (2.42)$$

The diffusion process is characterized by the Knudsen number $Kn = \lambda/d$, where λ is the mean free path length in the gas, and d is a characteristic pore diameter [116]. When $Kn < 0.01$, bulk diffusion is dominant [116]. When $Kn > 1$, Knudsen diffusion is dominant, and interparticle collisions are less frequent than collisions with the pore wall, such that the continuum theory is invalid for the diffusive mass transfer to occur through sub-micron size pores with a large Knudsen number [116]. When $0.01 < Kn < 1$, which is the typical situation in the SOFC electrode, both bulk diffusion and Knudsen diffusion are comparable, and thus should be considered together. The dusty-gas model (DGM) was developed to represent multicomponent transport in this situation [116].

All these three models are applicable to predict the concentration polarization inside the electrode. Cayan *et al.* [117] compared the distribution of the species mole fraction inside the porous anode between two models with the SMM and the FM, respectively. Both two models accounted for the Knudsen diffusion. These two models agreed well at low current densities, whereas an obvious difference appeared as the current increased. Yakabe *et al.* [51] and Lehnert *et al.* [75] developed mass transport models similar to the dusty-gas model considering the water-gas shift reaction. Suwanwarangkul *et al.* [104] employed all the three models to simulate two binary systems (H_2 – H_2O and CO – CO_2) and a ternary system (H_2 – H_2O – Ar) without considering the shift reaction.

2.2.2.3. Momentum transfer

The momentum transfer in the electrode of the SOFC can be described by the Darcy's

law [5, 106], which is commonly applied with an assumption of a steady-state incompressible flow [35, 69, 80],

$$\nabla p = -\frac{\mu_{\text{mix}}}{\kappa} \mathbf{v}, \quad (2.43)$$

where p is the intrinsic pressure, $\mathbf{v}$ is the superficial velocity, μ_{mix} is the dynamic viscosity of the gas mixture, and κ is the permeability of porous media.

However, the Darcy equation cannot model a no-slip condition at a wall nor the resulting boundary layers, which means that it can only describe the flow within the porous structure well away from the walls and is problematic to define interfacial conditions at the interface between two domains [118]. Haberman and Yong [115] provided an estimation on the thickness the boundary layers formed over a solid surface and at the electrode/channel interface. They suggested to modify the Darcy's law by adding a so-called "Brinkman" term [119-121], such that another well-know equation, Brinkman equation, was obtained to allow their calculation at boundaries. The Brinkman equation for steady incompressible flow was developed by Brinkman in 1949 with an additional viscous term in the momentum balance [122, 123]:

$$\nabla p = -\frac{\mu_{\text{mix}}}{\kappa} \mathbf{v} + \nabla \cdot \left[\frac{\mu_{\text{mix}}}{\varepsilon} \left(\left(\nabla \mathbf{v} + (\nabla \mathbf{v})^\dagger \right) \right) \right]. \quad (2.44)$$

Although the Darcy's law was also used to describe the weakly-compressible flow in some models [69, 124], many other models involved a non-zero rate of expansion, $\nabla \cdot \mathbf{v}$, in Eq. (2.44) to govern the steady weakly-compressible flow, such that the Brinkman equation became [80, 125]

$$\frac{\mu_{\text{mix}}}{\kappa} \mathbf{v} + \frac{1}{\varepsilon^2} \nabla \cdot (\rho \mathbf{v}) \mathbf{v} = -\nabla p + \nabla \cdot \left[\frac{\mu_{\text{mix}}}{\varepsilon} \left(\left(\nabla \mathbf{v} + (\nabla \mathbf{v})^\dagger \right) - \frac{2}{3} (\nabla \cdot \mathbf{v}) \mathbf{I} \right) \right]. \quad (2.45)$$

The second term on the left-hand side of Eq. (2.45) is derived from the convective term in Navier-Stokes equation, when applying the volume-averaging method to the electrode.

For the transfer of gaseous species in porous electrodes, diffusion is dominant over convection [66, 79]. For the left-hand side of Eq. (2.45), in view of the order of magnitude, the second term is much smaller than the first term and thus can be dropped from the equation. Then, Eq. (2.45) becomes [126]

$$\frac{\mu_{\text{mix}}}{\kappa} \mathbf{v} = -\nabla p + \nabla \cdot \left[\frac{\mu_{\text{mix}}}{\varepsilon} \left((\nabla \mathbf{v} + (\nabla \mathbf{v})^\dagger) - \frac{2}{3} (\nabla \cdot \mathbf{v}) \mathbf{I} \right) \right], \quad (2.46)$$

Moreover, the Darcy's law was modified with a form-drag constant, c_F , to get the Forchheimer's equation in some other models [64, 125, 127],

$$\nabla p = -\frac{\mu_{\text{mix}}}{\kappa} \mathbf{v} - c_F \frac{\rho}{\sqrt{\kappa}} |\mathbf{v}| \mathbf{v}. \quad (2.47)$$

2.2.2.4. Energy transfer

Although an isothermal state is often imposed on SOFC mathematical models [26, 28, 51, 97, 102, 128, 129], the temperature may not distribute uniformly throughout the cell or stack [130]. Detailed non-isothermal numerical models began to emerge in the early 1990s, such as [131, 132]. In fact, the temperature distribution is related to the electrochemical kinetics of the cell: heat can be generated by the electrochemical reactions within the reaction zones and the current passing through the cell, and be consumed by the endothermic internal reforming reactions at the anode side [5]. Large temperature gradients can cause undesired large thermal-mechanical stresses and thermal expansion mismatches, since the cell generally consists of ceramic components with different thermal expansion coefficients [23]. This may thus result in the thermal-mechanical degradation and/or structure failure of a SOFC. Moreover, the material properties of the cell are strong functions of temperature, and reaction rates are temperature-dependent as well [100]. Therefore, accurate prediction of the heat transfer and temperature distribution is essential for designing and optimizing a SOFC single cell

and stack.

In the electrode of the SOFC, the heat transfer in the solid structures occurs mainly through conduction, while convective heat transfer dominates in the gas channels and pores. Based on volume-averaging for porous media, the heat transfer in the porous electrodes of the SOFC is generally modeled in two ways: local thermal equilibrium (LTE) and local thermal non-equilibrium (LTNE) [79]. LTE prescribes the same temperature, T , for the gas and solid phases associated with effective transport parameters. The heat flux is given by [53, 69, 100, 115, 126, 133, 134]

$$\mathbf{q} = -\nabla \cdot (k^{\text{eff}} \nabla T) + \rho c_{p, \text{mix}} \mathbf{v} \cdot \nabla T, \quad (2.48)$$

in which $c_{p, \text{mix}}$ is the specific heat of the gas mixture. The effective thermal conductivity $k^{\text{eff}} = \varepsilon k_{\text{mix}} + (1 - \varepsilon) k_s$ depending on the porosity of the electrode, ε , and thermal conductivities of the gas mixture and solid structure, k_{mix} and k_s . In contrast, LTNE predicts the temperatures of the solid and gas phases, T_s and T_g , separately. The heat flux is specified as [135, 136]

$$\mathbf{q}_s = -\nabla \cdot (k_s^{\text{eff}} \nabla T_s), \quad (2.49)$$

for the solid electrode, and

$$\mathbf{q}_g = -\nabla \cdot (k_g^{\text{eff}} \nabla T_g) + \rho c_{p, \text{mix}} \mathbf{v} \cdot \nabla T_g, \quad (2.50)$$

for the gas mixture. Here, the effective thermal conductivity $k_s^{\text{eff}} = (1 - \varepsilon) k_s$ for the solid phase and $k_g^{\text{eff}} = \varepsilon k_{\text{mix}}$ for the gas phase.

The LTE approach is applied when the difference between the temperatures of the fluid and the solid structure are small; otherwise, the LTNE approach is adopted. According to the results provided by Zheng *et al.* [137], the temperature difference between the solid and gas phases in the porous electrode remained on the order of 10^{-3} K

under a wide range of operating conditions and structural parameters for H₂-fueled SOFCs, and 1 K for NH₃-fueled SOFCs at high operating temperatures such as 1200 K. The temperature difference is negligible in view of its order of magnitude. Therefore, it is safe to apply LTE to the electrode for the SOFC fueled by hydrogen or hydrocarbon.

In consideration of the high operating temperature of SOFC, thermal radiation was studied by some researchers for an accurate heat balance, [138, 139]. Nevertheless, radiation is generally neglected in the SOFC model, especial in the cell model [31, 70, 90, 92, 100].

2.2.2.5. Reaction zone

For SOFC modeling, the reaction zones comprising the triple-phase boundaries for the electrochemical reactions to take place are generally modeled as a boundary or interface condition, rather than a spatial domain, when predicting the global cell performance [36, 51, 53, 55, 70, 72, 140] or the local distribution of mass fraction, current density, and/or temperature [21, 22]. Correspondingly, the source terms for the conservation of mass, species, energy, and charge appear as the boundary conditions at the electrode/electrolyte interface. In fact, however, dependent variables undergo spatial changes in the reaction zones that are spread out some distance (10-50 μm) into the electrode from the electrode/electrolyte interface [24, 25, 50, 141].

Kim *et al.* [50] and Zhu and Kee [142] discussed the existence of the reaction zone layers, but still modeled them as boundary conditions rather than individual domains of finite volumes. Chung *et al.* assumed the TPB to distribute over the entire electrode of their model, because the thicknesses of the electrodes investigated were small and less than 50 μm [103]. Hussain *et al.* published a series of papers to predict the performance of the anode [114, 128] and the whole planar SOFC [25, 143, 144], in which the reaction zone was modeled as a separate layer of a finite volume adjacent to the backing layer.

They also compared the approaches to model the anode reaction zone as a boundary condition and as a discrete volume [128]. Verda and Spakovsky [80] developed a continuous model for the electrochemistry, which allows one to examine different TPB geometries, instead of utilizing an equivalent resistive circuit approach or a homogeneous distribution of TPB.

2.2.3. Spatial dimension

A practical problem of SOFC can be solved by 3D, 2D, 1D, or 0D modeling [31, 91, 92]. A 2D grid in the plane of the cell can be used to model the P-SOFC with co- or counter-flow configurations [23, 53]. A third coordinate is at times considered to take into account concentration and temperature gradients along the perpendicular direction for the cross-flow configuration [35, 72]. T-SOFC can be modeled in one, two, or three dimensions in a cylindrical coordinate system associated with the axial, radial, and tangential coordinate [40, 145, 146].

2.2.3.1. Zero-dimensional model

The simplest approach for SOFC modeling is to consider system as a black box, resulting in a 0D model. Based on principles of thermodynamics and electrochemistry, the fuel cell is modeled into a group of algebra equations to solve for the cell output such as cell voltage, power output, and cell efficiency based on predefined operating conditions such as inlet gas composition, inlet temperature, fuel and air utilization ratio [92]. Therefore, the 0D models are fit to evaluate the performance of the whole cell or stack, rather than the local multiphysical phenomena inside the cell or stack. For example, Chan *et al.* [20] fully described the cell voltage and all three types of polarization in a 0D model, and conducted a sensitivity test to investigate the effect of the thickness of respective cell components on the drop in cell voltage. Akkaya *et al.*

presented a 1D dynamic DIR-P-SOFC model based on mass and energy balances as well as electrochemical principles to predict some SOFC variables and their variation with time, including cell temperature, gas molar fractions, cell voltage, and current density along the cell length. 1D modeling is applicable for the co-flow and counter-flow configurations, but not for the cross-flow design [92].

2.2.3.3. Two-dimensional model

For 2D modeling, the cell is represented by a 2D cross-sectional domain, and the changes of physics in the third dimension are ignored. The most reasonable and representative sectional view for a co- or counter-flow P-SOFC is shown in Fig. 2.8. The figure presents the interconnects, flow channels, and the positive electrode/electrolyte/negative electrode (PEN) structure in a single cell. Based on the schematic structure in Fig. 2.8b, Jin and Xue [129] developed a transient 2D isothermal model, which could be operated in both SOFC mode and SOEC (solid oxide electrolyzer cell) mode to investigate complicated multi-physics processes during the transient process of mode switching. Verda and Spakovsky [80] applied their CFD model to an anode-supported P-SOFC in 2D. Mahcene *et al.* [22] constructed a 2D P-SOFC single-cell model with co-flow pattern in Fortran language to investigate the distribution of the chemical species, temperature, current density, and power density. Their analysis was based on the fundamental conservation laws of momentum, energy, and species. In addition, when all the components are modeled in 2D, convective and radiative heat transfer become boundary conditions for the conservation of energy in gas channels and solid structures [130].

Fig. 2.8 Schematic of co- or counter-flow planar SOFC: (a) 3D view, (b) 2D cross-sectional view.

2.2.3.4. Three-dimensional model

Compared with 2D, 1D, and 0D modeling, 3D modeling can provide more detailed information of the SOFC behaviours [92]. Pasaogullari and Wang [155] proposed a 3D model to describe the electrochemical kinetics, multi-dimensional gas dynamics, and multi-component transport of species in the SOFC. Recknagle *et al.* [72] presented a 3D model for P-SOFC stacks to investigate the effect of the flow configuration on fuel utilization and the distribution of species mass fraction, temperature, and current density. All the three types of flow configurations, namely the co-, counter, and cross-flow configuration, can be modeled in 3D. The effects of the three flow configurations were compared and analysed not only at the single-cell level [67, 93] but also at the stack level [34, 72]. Yakabe *et al.* [36] analysed the distributions of chemical species concentrations, temperature, electric potential, and current density in two 3D single-cell models with co-flow and counter-flow configurations respectively. The effects of cell size, operating voltage, and thermal conductivities of the cell components on the simulation results were also investigated in their 3D models. Wang *et al.* [70] used two

3D P-SOFC single-cell models, with air and fuel channels in co-flow and counter-flow respectively, to predict the temperature distribution, molar concentration of gaseous species, current density, and over potential based on the fundamental conservation laws of mass, momentum, energy, and electrical charge.

2.2.3.5. Remarks

Detailed 3D fuel cell models are usually very computationally expensive due to the highly coupled and nonlinear nature of their mathematical formulation as well as a large number of functional domains in the cell. In order to simplify the mathematical and computational complexity, the cell geometry is usually assumed to be 2D [21, 23, 53, 64], 1D [140, 153, 154], or 0D [20] instead of 3D. However, these assumptions are likely to lower the fidelity of model predictions. The flow fields of P-SOFCs in general are 3D entities comprising not only plain channels but also solid ribs. The ribs can affect the diffusion pathways of gaseous working fluid and electronic charges between the flow field and the backing layer [92]. An improper design for the geometry of ribs and electrodes may even cause the depletion of reactants to take place in the porous electrode at spanwise locations away from the channels at high current densities. These effects of ribs are generally not taken into account in existing 2D P-SOFC models, especially when modeling with respect to the streamwise and normal directions. This makes it difficult to achieve agreement between model predictions and experimental results [23].

2.2.4. Time dependence

The modeling of SOFC can be assumed to be under a steady-state or transient condition according to the research requirement [92]. When developing a model from the beginning or assessing the average cell working performance for applications like stationary power plants, the steady-state condition is selected for simplicity. So far, much

effort has been paid to the cell structure and performance optimization at steady state [21, 28, 35, 36, 51, 53, 55, 64, 67, 70, 72, 97, 102, 124, 128, 147, 155, 156]. Pisani and Murgia [157] developed a steady-state model to investigate the Stefan-Maxwell-Knudesn diffusion, micro-diffusion to the reaction sites, reaction kinetics, internal reforming reaction, shift reaction equilibrium, and thermal sources evaluation. Verda and Spakovsky [80] proposed a detailed steady-state CFD model for an anode-supported P-SOFC, which accounted for mass, thermal, and charge transport as well as electrochemistry and the chemistry of internal fuel reforming.

Many researchers have started to pay attention to transient SOFC modeling [34, 139, 153, 158, 159]. The transient performance of the SOFC is important for the control of the SOFC power system, especially at the switching stage [5]. When the SOFC is heated from ambient temperature to operating temperature (600-1000 °C) during startup and cooled down to room temperature during shutdown, damaging thermal gradients within the cell components tend to occur [160]. Achenbach [34] examined the transient cell voltage performance, which relied on temperature changes and perturbations in current density. Padullés *et al.* [158] were among the first researchers to consider species dynamics in SOFC modeling. Sedghisigarchi and Feliachi [159] investigated both heat transfer dynamics and species dynamics. Hall *et al.* [161] developed a model to simulate the transient electrochemical and thermal behaviours of the T-SOFC, without taking the dynamics of chemical species into account. Petruzzi *et al.* [162] developed a transient SOFC model for the heat-up and start-up simulation, which was used to evaluate the time for the cell stack to reach the operating temperature from an initial temperature distribution and the largest temperature gradients.

Comparisons between the steady-state and dynamic models were conducted in some research works. Chaisantikulwat *et al.* [69] analysed the performance of both

steady-state and dynamic 3D P-SOFC models. Iora *et al.* [140] evaluated the impact of neglecting the variation of the gas stream properties on the predictions of both steady-state and dynamic 1D models of an anode-supported IT-DIR-P-SOFC. They found that an assumption of constant flow properties was less appropriate at high current density. Hofmann and Panopoulos [163] presented a detailed flexible mathematical model of the P-SOFC, which allowed for the numerical prediction of the steady-state performance such as the voltage-current density relation, and of the dynamic behaviour like the electrochemical impedance spectroscopy.

2.2.5. Thermo-mechanical modeling

For the P-SOFC, internal stresses in cell components are one of the critical problems to be addressed [36, 37, 61]. Mechanical stress leads to the mechanical breakdown of the cell components and can be classified into two types, called the residual thermal stress and thermal stress [61]. The former generally takes place during the fabrication process, while the latter is typically caused by a non-uniform temperature distribution in the cell or stack. A large amount of internal stress can be induced by the irregular deformation of cell components due to non-homogeneous temperature distribution within the cell or stack [164]. The thin electrolyte and electrode layers usually tend to delaminate or crack when undergoing excessive thermal shock, temperature gradients, and thermal cycling during startup or shut down processes.

The thermal stresses are relevant to the material properties and operating conditions. Chiang *et al.* [165] evaluated the thermal stresses of an anode-supported SOFC single cell under different operating conditions. They recommended that when the thermal expansion coefficient of the interconnect was close to that of the PEN, thermal stresses would effectively decrease, and the change of temperature on the PEN surface should be controlled within 50 °C for the concern of structure integrity. Yakabe *et al.* [36]

expressed the internal stresses as a function of cell size, operating voltage, and the thermal conductivities of cell components and suggested the operating conditions to reduce internal stresses. Compared with the single-cell design, the stack design confronts a more critical thermal stress problem, which can be attributed to the non-uniform temperature distribution [37, 166, 167]. Thermal stress and expansion mismatch in each repeat element may accumulate and cause the structure failure of the entire stack.

2.2.6. P-SOFC stack models

Most research works mentioned above are about the development of single cells, which can only provide small power output. For power generation on a large scale, tens or hundreds of SOFC unit cells are usually combined into high-performance cell stacks to increase the working voltage up to a necessary high value [3, 92]. In 2004, Forschungszentrum Jülich [168] built a stack of 60 anode-supported SOFCs as shown in Fig. 2.9, which provided 13.3 kW with hydrogen as fuel and 11.9 kW with methane. This cell stack was the largest P-SOFC stack in the world at that time.

Fig. 2.9 Anode-supported SOFC stack built by Forschungszentrum Jülich in 2004 [168].

In a stack, fuel and air are typically introduced via manifolds with the co-, counter-, or cross-flow configuration [3]. Generally, the main concerns in stack design are pressure gradients and the uniformity of the distributions of species, temperature, and current density [34, 72]. Aiming at reducing spatial variations in temperature and current density at the fuel source, Ayman *et al.* [169] proposed a novel stack design by

introducing a mechanism of distributed fuel feed, in which the heat generation profile was directly influenced. Kulikovsky [170] derived an approximate analytical expression for a rapid estimate on the temperature gradient along the air channel in a P-SOFC stack under real operating conditions.

Some models assume that all the cells within the stack are identical, such that a unit cell is simulated to represent the distribution of dependent variables for the entire stack [70, 92, 171]. On the other hand, the variations in performance among cells were investigated by some other authors such as Burt *et al.* [172]. The perturbations between cells may result from asymmetry properties in the cells, such as different inlet conditions from channel to channel in the unit cell and/or from cell to cell in the stack [172]. Although some authors used 3D models to predict the stack performance, they are confined to component level modeling, because detailed stack modeling in 3D is typically computational expensive [92].

2.2.7. Model simplification

Numerical simulation for fuel cell at the stack level usually accompanies with rigorous computational requirements. In order to address this issue, Roos *et al.* [124] applied the volume-averaging theory to omit the transverse direction in the flow field and thus reduced a 3D flow field of channels and ribs to a 2D counterpart. However, they did not formulate the effective parameters for the flow field counterpart or analyse the loss of information due to dimensional reduction. In contrast, Ly *et al.* [173] provided a quantifiable loss of information for spatial smoothing based on volume averaging over a flow field comprising parallel channels separated by ribs for a proton exchange membrane fuel cell (PEMFC). The spatially smoothed model was then reduced further from 3D to 2D when all the channels are under the same inlet conditions. Their reduced model was coupled with effective transport properties and correlations to account for the

variation in the pathways of charges and species in the backing layer due to ribs. However, they derived the correlations by solving a general Laplace equation over the cross section of the flow field and its adjacent backing layer in the spanwise and normal directions, such that the resulting correlations could not handle the coupling effect between the governing equations for transport processes.

Ly *et al.* [174] applied the method of asymptotic reduction to a PEMFC with porous flow fields. Based on a scaling analysis, the terms that did not affect the leading order of solutions were dropped from the governing equations, thereby reducing the model to an asymptotic counterpart with a space-marching numerical algorithm. This approach significantly reduced computational requirements in terms of memory usage and execution time, while preserving geometrical resolution. About 8-15 minutes and 8.5 GB RAM are required to solve a 10-cell stack model with the full set of equations of PEMFC, but only 14-18 seconds and 0.6 GB RAM for the reduced set.

For the SOFC, Billingham *et al.* [111] adopted the method of asymptotic expansions to construct solutions to a steady-state isothermal model for the combustion of methane in a loaded unit P-SOFC, such that the model was reduced from 3D to 2D. Only electrochemical flux and conservation of mass were taken into account, which means the model could not fully present the multiphysical phenomena such as the distribution of pressure, temperature, and mass fraction in the cell. Lately, Kulikovsky [175] developed a simple model of heat transport in a stack element consisting of the fragment of interconnect with the single linear air channel, and constructed asymptotic solutions to the problem.

2.2.8. Sensitivity analysis

The performance of SOFCs depends on operating conditions, material properties, and component geometries [92]. Sensitivity analysis is usually conducted to study the effect

of these factors on the global and local cell performance. The analysis is typically performed via mathematical modeling with a few different values for every investigated modeling parameter and varying one parameter at a time [20, 130, 176-179]. The existing parametric studies generally aim at optimal values for the design parameters of SOFCs. However, optimal nominal solutions are not enough for a cell design to go into mass production. The actual cell properties can deviate from the designed nominal value in high volume manufacturing processes. The influence of the variability of a combination of design parameters on the cell performance needs to be taken into account. Moreover, with just a few cases, it is difficult to perform deterministic analysis for a typically large population in manufacturing. Therefore, a method is required to not only find the input parameter showing the largest impact on results but also reveal what could possibly happen among a large population. Monte Carlo simulation (MCS) is one of such methods, based on generating a large number of random samples.

The MCS can provide insight on understanding the impact of each input factor on the variability of the output dependent variable. Cornu and Wuillemin [180] performed the MCS of a computational fluid dynamics model to assess the impact of random geometric distortions on the fuel flow distribution in the anode channels of an SOFC. Their fluid dynamic model only solved for the fuel flow distribution in the channels under isothermal conditions without electrochemical reactions. The MCS is much more computationally expensive when solving a detailed electrochemical mechanistic model in 3D, in view of the highly coupled and nonlinear nature of the mathematical formulation and the large number of functional domains in the model as well as the large amount of runs. Pan *et al.* [181] conducted a MCS of a reduced SOFC model to analyse the sensitivity of output variables to operating conditions. Their MCS is based on a 1D reduced model that was developed by Lai *et al.* [182]. For the model reduction by Lai *et*

al., the changes of physics along the width and through the thickness for each domain in the cell were assumed to be negligible. These assumptions were made according to simulation results predicted at a moderate cell voltage of 0.7 V [72]. However, these assumptions may become invalid at lower cell voltages or higher current densities. At high current densities, a large amount of reactants are consumed, resulting in large gradients in the distribution of dependent variables through the cell thickness and along the width [23, 183]. The depletion of species may even occur in the electrode at spanwise positions away from the channel due to the existence of the solid ribs that affect the pathways of transport processes. The impact of ribs should be taken into account when reducing the dimensionality of 3D SOFC models; otherwise, the fidelity of prediction will be weakened [8, 10, 11].

2.3. Numerical methods for SOFC

The existing SOFC models range from molecular/atomic level on half cell [28, 156, 184, 185] to single fuel cell level [21, 30, 35, 93, 142], stack-level [30, 34], and finally to system level [152, 186, 187]. Micro-scale or nano-scale studies aim at the development of better electrodes through mathematical analysis considering detailed transport phenomena. Single-cell models (scale in 10^{-2} m) are often the first consideration for fuel cell manufacturers embarking on a new product design [92]. The results obtained from the single-cell models subsequently serve as the basis for stack-level and eventually for system-level simulations. Table 2.4 lists common computational methods applied according to the length scale of the model. For the macro-scale modeling, in particular, numerical solution methods like finite difference method (FDM), finite volume method (FVM), or finite element method (FEM) are proper approaches to discretize the governing equations.

Table 2.4 Computational methods for the SOFC in different length scales [79].

Microscale ($\sim 10^{-9}$ m)	Meso-scale ($\sim 10^{-6}$ m)	Macro-scale ($> 10^{-5}$ m)
Density functional theory (DFT)	Monte Carlo (MC)	Finite element method (FEM)
Quantum chemistry (QC)	Brownian dynamics (BD)	Finite volume method (FVM)
Lattice-Boltzman method (LBM)	Dissipative particle dynamics	Finite difference method (FDM)
Molecular dynamics (MD)	(DPD)	
Mechanistic models (MM)		

The main advantage of the FEM over the finite volume procedures is its wide use in many engineering disciplines. This makes it perfectly suitable for the solution of multidisciplinary problems, which is crucial in fuel cell. Chaisantikulwat *et al.* [69] implemented a 3D model in the FEM-based COMSOL (2005) to solve the coupled transport and electrochemical equations. Moreover, a combination of the thermo-fluid and structural models allows the thermo-mechanical modeling for fuel cells [36]. The FEM was also used by some researchers to solve meso-scale problems, although it was developed for phenomena occurring in the macro-scale. Huang *et al.* [188] used the COMSOL Multiphysics to investigate the multiphysics processes in the SOFC cathode-electrolyte interfaces at meso-scale. They took the detailed distribution and geometry of the ionic conducting phase, the electronic conducting phase, and the pores into account. Furthermore, some researchers applied both FVM and FEM for their works. Yakabe *et al.* [36] employed the FVM in the simulation of fluid flow phenomena including heat transfer, mass transfer, and chemical reactions in Star-CD, and the FEM for thermal stress analysis in a 3D unit P-SOFC model by the commercial code ABAQUS.

With the advancement of computer science and numerical techniques, it becomes possible to solve the equations for sophisticated geometrical design. Nevertheless, another problem in the development of numerical models is the validation of the simulation results against experimental data, due to the lack of such data in the available

literature. The validation of existing detailed cell and stack models usually involve tuning parameters [50, 69, 79, 97, 98, 126, 129, 189], which are not available from the published experimental results.

2.4. Summary

This chapter has reviewed the SOFC models in the literature, especially the models for the planar SOFC (P-SOFC), which is typically equipped with parallel plain channels surrounded by solid ribs. The transport phenomena and electrochemical characteristics of the SOFC can be affected by the geometrical and support structure, operating conditions, flow configurations, and fuel reforming mechanism. Table 2.5 illustrates and depicts some of the existing P-SOFC models. According to the results of the present literature survey, four conclusions on the modeling of the P-SOFC are highlighted and presented below.

First, more mathematical models are developed in 2D than in 3D in recently years to predict the cell performance. Detailed 3D mechanistic SOFC models are challenging to solve numerically, because of not only the highly coupled and non-linear nature of the underlying mathematical formulation but also the large number of functional domains, especially for stacks. In order to reduce the mathematical and computational complexity of modeling, the following two assumptions are generally imposed on the P-SOFC models.

- The geometry is assumed to be in low dimensionality instead of 3D. This assumption is likely to lower the fidelity of model predictions, because the influence of ribs on the pathways of transport processes is not taken into account. Spatial smoothing based on volume-averaging the flow field is a possible approach to handle the variation in the pathways for the fuel cells with parallel channels and

slender sandwiched structure like the P-SOFC and the PEMFC. Nevertheless, existing spatially-smoothed models were only developed for single cells under isothermal conditions, and did not account for the coupling effects between the governing equations for transport phenomena.

- The reaction zones comprising the triple-phase boundaries for the electrochemical reactions to take place are modeled as a boundary or interface condition rather than a spatial domain, when predicting the global cell performance or the local distribution of mass fraction, current density, and/or temperature. However, dependent variables actually undergo spatial changes in the reaction zones that are spread out some distance (10-50 μm) into the electrode from the electrode/electrolyte interface.

Second, the existing 2D P-SOFC models are typically developed with respect to the cell length in the streamwise direction and the thickness in the normal direction, and neglect the physics along the cell width in the spanwise direction, in which dependent variables may undergo leading-order changes at high current densities. The information about the spanwise variability of dependent variables is necessary for cell design in order to avoid undesired cell performance such as depletion of reactants underneath the ribs.

Third, parametric studies on cell performance are generally performed by varying a single modeling parameter with a few testing cases. In order to adopt statistical measures to analyse the sensitivity of cell performance to varying parameters, efficient and accurate reduced models are needed for the simulation with a large population of testing cases without a prohibitive computational cost.

Last, the majority of computational studies in the open literature focus on a single cell or cell components, whereas relatively fewer are found for stacks, although there is a

trend to raise the study from the cell to stack level. When seeking for a detailed description of the transport phenomena and electrochemical characteristics in the stack, 3D stack models are computationally expensive to solve.

Table 2.5 Planar SOFC models in literature.

Year of publication		1994	2000	2000	2001	2001	2001	2003	2003
References		[34]	[51]	[93]	[20]	[36]	[156]	[21]	[72]
Dimensionality	0D				✓				
	1D						✓		
	2D			✓				✓	
	3D	✓	✓	✓		✓			✓
Level of modeling	Half-cell						✓		
	Single Cell	✓	✓	✓	✓	✓		✓	
	Stack								✓
	Combined system								
Fuel components	Humid H ₂				✓				
	Gas mixture (methane)	✓	✓	✓		✓		✓	✓
Flow configuration	Co-flow	✓		✓		✓			✓
	Counter-flow	✓	✓	✓		✓			✓
	Cross-flow	✓		✓					✓
Reforming type	External					✓			
	DIR	✓	✓	✓		✓		✓	✓
	IIR								
Dependence of time	Steady-state		✓			✓	✓	✓	✓
	Transient	✓							
Conservation equation	Mass	✓	✓	✓		✓	✓	✓	✓
	Momentum		✓			✓			✓
	Energy	✓		✓		✓		✓	✓
	Charge			✓			✓		✓
Radiation	With	✓							
Thermo-mechanical	With					✓			
Reaction zone	Mathematical surface	✓	✓		✓	✓		✓	✓
	Layer of finite volume								
	TPB length*						✓		
Numerical method	FDM								
	FVM		✓			✓		✓	✓
	FEM					✓			
Validation with	Experiment		✓				✓		
	Other models								

*TPB length: the reaction sites are uniformly distributed in the anode and cathode electrode.

Table 2.5 (Continued)

Year of publication		2003	2003	2004	2005	2005	2005	2005	2007
References		[124]	[155]	[28]	[35]	[67]	[128]	[140]	[55]
Dimensionality	0D								
	1D			✓				✓	
	2D	✓				✓	✓		
	3D	✓	✓		✓				✓
Level of modeling	Half-cell			✓			✓		
	Single Cell	✓	✓		✓	✓		✓	✓
	Stack	✓							✓
	Combined system								
Fuel components	Humid H ₂		✓		✓				
	Gas mixture (methane)					✓	✓	✓	✓
Flow configuration	Co-flow		✓		✓	✓		✓	✓
	Counter-flow				✓	✓			
	Cross-flow		✓		✓	✓			
Reforming type	External								
	DIR	✓				✓	✓	✓	✓
	IIR								
Dependence of time	Steady-state	✓	✓	✓	✓	✓	✓	✓	✓
	Transient							✓	
Conservation equation	Mass	✓	✓	✓	✓		✓	✓	✓
	Momentum	✓	✓		✓			✓	
	Energy	✓	✓		✓			✓	✓
	Charge	✓	✓	✓	✓		✓		✓
Radiation	With								
Thermo-mechanical	With								
Reaction zone	Mathematical surface				✓		✓	✓	✓
	Layer of finite volume		✓				✓		
	TPB length*			✓					
Numerical method	FDM							✓	
	FVM		✓			✓	✓		
	FEM	✓			✓				✓
Validation with	Experiment		✓	✓					
	Other models					✓			

*TPB length: the reaction sites are uniformly distributed in the anode and cathode electrode.

Table 2.5 (Continued)

Year of publication		2007	2007	2007	2008	2008	2008	2009	2009
References		[70]	[97]	[153]	[53]	[69]	[147]	[64]	[102]
Dimensionality	0D						✓		
	1D			✓					✓
	2D		✓		✓			✓	
	3D	✓				✓			
Level of modeling	Half-cell								
	Single Cell	✓		✓	✓	✓		✓	✓
	Stack								
	Combined system						✓		
Fuel components	Humid H ₂	✓	✓		✓	✓		✓	
	Gas mixture (methane)						✓		✓
Flow configuration	Co-flow	✓			✓			✓	
	Counter-flow	✓				✓			
	Cross-flow								
Reforming type	External								
	DIR								✓
	IIR								
Dependence of time	Steady-state	✓	✓		✓	✓	✓	✓	✓
	Transient			✓		✓			
Conservation equation	Mass	✓	✓	✓	✓	✓		✓	
	Momentum	✓		✓	✓	✓		✓	
	Energy	✓		✓	✓	✓		✓	
	Charge	✓	✓		✓	✓		✓	
Radiation	With								
Thermo-mechanical	With								
Reaction zone	Mathematical surface	✓			✓	✓			✓
	Layer of finite volume								
	TPB length*		✓					✓	
Numerical method	FDM								
	FVM	✓			✓				✓
	FEM		✓			✓			
Validation with	Experiment		✓			✓			
	Other models			✓					✓

*TPB length: the reaction sites are uniformly distributed in the anode and cathode electrode.

Table 2.5 (Continued)

Year of publication		2009	2010	2011					
References		[154]	[129]	[22]					
Dimensionality	0D								
	1D	✓							
	2D		✓	✓					
	3D								
Level of modeling	Half-cell								
	Single Cell	✓	✓	✓					
	Stack								
	Combined system								
Fuel components	Humid H ₂		✓	✓					
	Gas mixture (methane)	✓							
Flow configuration	Co-flow	✓	✓	✓					
	Counter-flow								
	Cross-flow								
Reforming type	External								
	DIR	✓							
	IIR								
Dependence of time	Steady-state	✓		✓					
	Transient	✓							
Conservation equation	Mass	✓	✓	✓					
	Momentum		✓	✓					
	Energy	✓		✓					
	Charge	✓	✓						
Radiation	With								
Thermo-mechanical	With								
Reaction zone	Mathematical surface			✓					
	Layer of finite volume								
	TPB length*		✓						
Numerical method	FDM	✓							
	FVM			✓					
	FEM		✓						
Validation with	Experiment		✓						
	Other models	✓							

*TPB length: the reaction sites are uniformly distributed in the anode and cathode electrode.

Chapter 3

Full 3D P-SOFC Model

3.1. Introduction

This chapter presents the development of a full 3D non-isothermal P-SOFC model that describes the transport phenomena and electrochemical kinetics in the cell, under several assumptions as specified in Section 3.2. The computed domain of this 3D model is introduced in Section 3.3. Section 3.4 presents the governing equations for the transport of mass, momentum, species, charge, and energy, as well as the coupled constitutive relations and boundary conditions of the present 3D model, which is solved numerically as depicted in Section 3.5. Section 3.6 elaborates the validation of the present mathematical model with experimental data from the literature. Finally, Section 3.7 presents a numerical convergence test for the full 3D non-isothermal model.

3.2. Assumptions

The following assumptions are made for modeling and applied globally in the present work, unless otherwise stated:

- 1) The cell operates at steady state;
- 2) The flow channels on the same electrode are under the same inlet conditions;
- 3) The working fluid is in single phase, *i.e.*, gas phase;
- 4) All gas mixtures are considered as weakly compressible and laminar ideal gas;

- 5) The reaction zones are numerically treated as functional domains, in which the electrochemical reaction takes place;
- 6) The half-cell electrochemical reaction on each electrode is a two-electron process;
- 7) The leak polarization is negligible;
- 8) The porous electrodes are isotropic and macro-homogeneous, and the electrolyte is impermeable to mass transport;
- 9) The adsorption of gaseous species in the electrode is not considered for modeling;
- 10) The heat transfer within the porous electrodes is in local thermal equilibrium; and
- 11) Radiation effects are negligible.

3.3. Modeling domains

A P-SOFC single cell is the unit block of a stack that may be comprised of tens or hundreds of cells, as shown in Fig. 3.1a. Each single cell typically consists of two flow fields of parallel plain channels separated by ribs, two porous backing layers, two reaction zone layers, and a solid electrolyte. Fig. 3.1b illustrates the typical configuration of a P-SOFC, showing the streamwise direction (x), spanwise direction (y), and normal direction (z). The single-cell performance is represented by a repeating unit enclosed by the dashed line in Fig. 3.1b, provided that the channels on the same electrode are under the same inlet conditions. Moreover, because of the symmetric geometry of the repeating unit, half of the unit structure is taken into account as the computational domain associated with symmetry boundary conditions at the central cross section A-A, as shown in Fig. 3.1c.

Fig. 3.1 Schematic of (a) a SOFC stack with parallel plain channels, (b) a 3D unit cell, (c) a repeating unit with a pair of channels, and (d) a 3D button cell and its 1D computed domain.

3.4. Mathematical model

In order to predict the electrochemical kinetics and transport phenomena in the repeating unit shown in Fig. 3.1c, steady-state conservation equations for mass, weakly-compressible momentum, species, charge, and energy are solved for seven dependent variables: the velocity of working fluid, $\mathbf{v}$, the pressure, p , the mass fractions of oxygen and hydrogen, ω_{O_2} and ω_{H_2} , the electronic and ionic potentials, ϕ_{elc} and ϕ_{ion} , and temperature, T .

3.4.1. Governing equations

3.4.1.1. Conservation of mass

The mass transfer of the gaseous working fluid takes place in the flow channels (fc), backing layers (bl), and reaction zone layers (rl). As such, the continuity equation for a weakly compressible flow is specified by

$$\nabla \cdot (\rho \mathbf{v}) = S_{\text{mass}}, \quad (3.1)$$

$$S_{\text{mass}} = \begin{cases} +\frac{M_{\text{O}_2} J_c}{4F} & (\text{cathode rl}) \\ -\frac{M_{\text{H}_2} J_a}{2F} + \frac{M_{\text{H}_2\text{O}} J_a}{2F} & (\text{anode rl}) \\ 0 & (\text{fc, bl}) \end{cases}, \quad (3.2)$$

where ρ is the density, $\mathbf{v}$ is the velocity, M_i is the molecular weight of species i , F is the Faraday's constant, J_a and J_c are the volumetric current densities for the anode and cathode reaction zone layer and are defined by the Butler-Volmer equations in Table 3.1.

3.4.1.2. Conservation of momentum

The transport of momentum is described in the plain flow channels and porous backing and reaction zone layers. For the plain channels, the Navier-Stokes equation for the weakly-compressible flow is used as

$$\nabla \cdot \left[\mu_{\text{mix}} \left(\left(\nabla \mathbf{v} + (\nabla \mathbf{v})^\dagger \right) - \frac{2}{3} (\nabla \cdot \mathbf{v}) \mathbf{I} \right) \right] = \rho (\mathbf{v} \cdot \nabla) \mathbf{v} + \nabla \cdot (p \mathbf{I}), \quad (3.3)$$

where p is the pressure, μ_{mix} is the dynamic viscosity of the gas mixture, $\mathbf{I}$ is the identity tensor, and † denotes the transpose of a tensor.

For the porous backing and reaction zone layers, the Brinkman equation is applied [9, 10, 12, 13]:

$$\nabla \cdot \left[\mu_{\text{mix}} \left((\nabla \mathbf{v} + (\nabla \mathbf{v})^{\dagger}) - \frac{2}{3} (\nabla \cdot \mathbf{v}) \mathbf{I} \right) \right] = \frac{\varepsilon \mu_{\text{mix}}}{\kappa} \mathbf{v} + \varepsilon \nabla \cdot (p \mathbf{I}), \quad (3.4)$$

where $\mathbf{v}$ is the superficial velocity, p is the intrinsic pressure, ε is the porosity, and κ denotes the permeability.

3.4.1.3. Conservation of species

The distribution of species is solved for in the air and fuel plain channels as well as the porous backing and reaction zone layers. For the mass balance of each species in the fuel and air, the conservation equation is specified as

$$\nabla \cdot \mathbf{n}_i = S_i, \quad (3.5)$$

$$S_i = \begin{cases} +\frac{M_{\text{O}_2} J_c}{4F} & (\text{O}_2, \text{cathode rl}) \\ -\frac{M_{\text{H}_2} J_a}{2F} & (\text{H}_2, \text{anode rl}) \\ 0 & (\text{fc, bl}) \end{cases}, \quad (3.6)$$

in which the mass fluxes of species are defined as [110, 126]

$$\mathbf{n}_i = \rho \omega_i \mathbf{v} - \rho \omega_i \sum_{j=1}^n (\mathcal{D}_{ij}^{\text{eff}} \nabla x_j). \quad (3.7)$$

Here, $\mathcal{D}_{ij}^{\text{eff}}$ is the intrinsic effective multicomponent Fick diffusivity for the gas mixture in the porous media, and it becomes $\mathcal{D}_{ij}$ for the plain channels. The relations between the multicomponent Fick diffusivity $\mathcal{D}_{ij}$ and the combined diffusivity $\mathcal{D}_{ij}$, which involves both the original binary diffusivity D and the Knudsen diffusivity $D_{\text{Kn},i}$, are presented in Table 3.1.

3.4.1.4. Conservation of charge

The equation for the transfer of ions is solved in the reaction zone layers and electrolyte, while the transfer of elections is considered in the interconnect, backing layer, and reaction zone layer. The conservation of charge is governed by

$$\nabla \cdot \mathbf{i}_{\text{elc}} = -S_{\text{pot}}, \quad (3.8)$$

$$\nabla \cdot \mathbf{i}_{\text{ion}} = S_{\text{pot}}, \quad (3.9)$$

$$S_{\text{pot}} = \begin{cases} J_{\text{c}} & (\text{cathode rl}) \\ J_{\text{a}} & (\text{anode rl}) \\ 0 & (\text{ic, bl, el}) \end{cases}. \quad (3.10)$$

The local current density, $\mathbf{i}$, is carried by elections or ions and defined as

$$\mathbf{i}_{\text{elc}} = -\sigma_{\text{elc}}^{\text{eff}} \nabla \phi_{\text{elc}}, \quad (3.11)$$

$$\mathbf{i}_{\text{ion}} = -\sigma_{\text{ion}}^{\text{eff}} \nabla \phi_{\text{ion}}, \quad (3.12)$$

where ϕ_{elc} and ϕ_{ion} are the potentials of the electronic and ionic phases, $\sigma_{\text{elc}}^{\text{eff}}$ and $\sigma_{\text{ion}}^{\text{eff}}$ are the effective electronic and ionic conductivities defined in Table 3.1.

In addition, the current is purely conducted by electrons in the backing layers and purely conducted by ions in the electrolyte, but conducted by both elections and ions in the reaction zone layers in which electronic and ionic charge migration processes coexist [25]. As such, the resulting current density in the cell is described as

$$\mathbf{i} = \begin{cases} \mathbf{i}_{\text{elc}} & (\text{ic, bl}) \\ \mathbf{i}_{\text{ion}} & (\text{el}) \\ \mathbf{i}_{\text{elc}} + \mathbf{i}_{\text{ion}} & (\text{rl}) \end{cases}. \quad (3.13)$$

3.4.1.5. Conservation of energy

The energy transport in the SOFC can be modeled either in a local thermal equilibrium (LTE) or local thermal non-equilibrium (LTNE) approach [79]. LTE prescribes the same temperature for the gas and solid phases in the electrode associated with effective

transport parameters based on volume-averaging for porous media [53, 69, 100, 115, 126, 133, 134], whereas LTNE predicts the temperatures of the solid and gas phases within the porous media separately, namely T_s and T_g [135, 136]. Zheng *et al.* [137] proved that the difference between the solid and gas phases in the porous electrode is insignificant for SOFC and it is safe to apply LTE for SOFC modeling. Therefore, the LTE approach is employed for the full 3D model of the SOFC.

The temperature distribution in the cell is obtained by solving a convection-conduction equation for T :

$$-\nabla \cdot (k^{\text{eff}} \nabla T) + \rho c_{p, \text{mix}} \mathbf{v} \cdot \nabla T = S_{\text{temp}}, \quad (3.14)$$

$$S_{\text{temp}} = \begin{cases} J \left(\eta^{\text{act}} + T \frac{\partial E^{\text{rev}}}{\partial T} \right) + \sigma_{\text{elc}}^{\text{eff}} (\nabla \phi_{\text{elc}})^2 + \sigma_{\text{ion}}^{\text{eff}} (\nabla \phi_{\text{ion}})^2 & \text{(rl)} \\ \sigma_{\text{elc}}^{\text{eff}} (\nabla \phi_{\text{elc}})^2 & \text{(ic, bl)}, \\ \sigma_{\text{ion}}^{\text{eff}} (\nabla \phi_{\text{ion}})^2 & \text{(el)} \\ 0 & \text{(fc)} \end{cases} \quad (3.15)$$

in which the thermal convection term, $\rho c_{p, \text{mix}} \mathbf{v} \cdot \nabla T$, is dropped from the energy equation for the solid current collector and electrolyte. Eq. (3.15) describes the heat source in each cell component. The first two terms in the reaction zone layer in Eq. (3.15) are the irreversible heat and reversible entropic heat generated by the electrochemical reaction, while the last two terms represent ohmic heating due to the electronic and ionic current, respectively.

3.4.2. Constitutive relations and boundary conditions

Constitutive relations embodying the correlation between dependent variables and the dependence of physical parameters on the variables are necessary for modeling, as summarized in Table 3.1.

Table 3.1 Constitutive relations of the 3D P-SOFC model [51, 92, 100, 110, 126, 190-193].

$\rho = pM/RT$	$A_{\text{rl/bl}} = L(w_{\text{rib}} + w_{\text{fc}})/2$
$M = \sum_{i=1} x_i M_i = 1/\sum_i (\omega_i/M_i)$	$J = Ai_0 \left[\exp\left(\frac{\alpha_1 F}{RT} \eta^{\text{act}}\right) - \exp\left(-\frac{\alpha_2 F}{RT} \eta^{\text{act}}\right) \right]$
$\omega_i = \rho_i/\rho = c_i M_i/\rho$	$A = (1-\varepsilon)/(1-0.3) A^{\text{ref}}$
$\omega_{\text{H}_2\text{O}} = 1 - \omega_{\text{H}_2}$	$i_{0,\text{a}} = \beta_{\text{a}} (p_{\text{H}_2}/p^0)^{\gamma_1} (p_{\text{H}_2\text{O}}/p^0)^{\gamma_2} \exp(-E_{\text{a}}^{\text{act}}/(RT))$
$\omega_{\text{N}_2} = 1 - \omega_{\text{O}_2}$	$i_{0,\text{c}} = \beta_{\text{c}} (p_{\text{O}_2}/p^0)^{\gamma} \exp(-E_{\text{c}}^{\text{act}}/(RT))$
$x_{\text{N}_2} = 1 - x_{\text{O}_2}$	$\eta^{\text{act}} = \phi_{\text{elc}} - \phi_{\text{ion}} - E^{\text{rev}}$
$x_{\text{H}_2\text{O}} = 1 - x_{\text{H}_2}$	$E_{\text{a}}^{\text{rev}} = RT/(2F) \ln(p_{\text{H}_2\text{O}}/p_{\text{H}_2})$
$x_i = (\omega_i/M_i) / \left(\sum_j \omega_j/M_j \right)$	$E_{\text{c}}^{\text{rev}} = E^0 + \Delta s/(2F)(T-T^0) - RT/(4F) \ln(p^0/p_{\text{O}_2})$
$c = \begin{cases} c_{\text{H}_2} + c_{\text{H}_2\text{O}} & \text{anode} \\ c_{\text{O}_2} + c_{\text{N}_2} & \text{cathode} \end{cases}$	$\sigma_{\text{elc,a}} = \frac{9.5 \times 10^7}{T} \exp\left(-\frac{1150}{T}\right)$
$c_i = x_i c = \omega_i \rho / M_i$	$\sigma_{\text{elc,c}} = \frac{4.2 \times 10^7}{T} \exp\left(-\frac{1200}{T}\right)$
$\mu_{\text{mix}} = \sum_i \omega_i \mu_i$	$\sigma_{\text{ion}} = 3.4 \times 10^4 \exp\left(-\frac{10350}{T}\right)$
$D_{ij} = D_{ij}^0 (T^0, p^0) (T/T^0)^{1.5} (p^0/p)$	$\sigma_{\text{elc}}^{\text{eff}} = \begin{cases} \sigma_{\text{elc}} \Phi(1-\varepsilon)/\tau & \text{(rl)} \\ \sigma_{\text{elc}} (1-\varepsilon)/\tau & \text{(bl)} \\ \sigma_{\text{elc,ic}} & \text{(ic)} \end{cases}$
$D_{\text{Kn},i} = (2/3) \bar{r} \sqrt{8RT/(\pi M_i)}$	$\sigma_{\text{ion}}^{\text{eff}} = \begin{cases} \sigma_{\text{ion}} (1-\Phi)(1-\varepsilon)/\tau & \text{(rl)} \\ \sigma_{\text{ion}} & \text{(el)} \end{cases}$
$\mathcal{D}_{ij} = D_{ij} D_{\text{Kn},i} / (D_{ij} + D_{\text{Kn},i})$	$c_{\text{p,mix}} = \sum_i \omega_i c_{\text{p},i}$
$D_{ij}^{\text{eff}} = \begin{cases} \varepsilon^{1.5} \mathcal{D}_{ij} & \text{(bl, rl)} \\ D_{ij} & \text{(fc)} \end{cases}$	$k_{\text{mix}} = \sum_i \omega_i k_i$
$\mathcal{D}_{\alpha-\alpha}^{\text{eff}} = \omega_{\beta}^2 / (x_{\alpha} x_{\beta}) D_{\alpha-\beta}^{\text{eff}}$	$k^{\text{eff}} = \varepsilon k_{\text{mix}} + (1-\varepsilon) k_{\text{s}}$
$\mathcal{D}_{\alpha-\beta}^{\text{eff}} = \mathcal{D}_{\beta-\alpha}^{\text{eff}} = -(\omega_{\alpha} \omega_{\beta}) / (x_{\alpha} x_{\beta}) D_{\alpha-\beta}^{\text{eff}}$	
$\mathcal{D}_{\beta-\beta}^{\text{eff}} = \omega_{\alpha}^2 / (x_{\alpha} x_{\beta}) D_{\alpha-\beta}^{\text{eff}}$	
$i_{\text{avg}} = \pm \frac{1}{A_{\text{rl/bl}}} \iiint_V J dx dy dz \quad \text{or} \quad \iiint_V i_{\text{bl},z} dx dy dz / V \quad (3\text{D})$	

Additionally, a set of boundary conditions are specified to complete the full 3D

model. Fig. 3.2 shows the locations where boundary conditions are required for the 3D model. The boundary conditions B1 to B14 in Fig. 3.2 are specified as follows:

Boundary condition 1 (B1)

At the cathode channel inlet, an average streamwise velocity, constant air composition, and a constant temperature are specified for the air inflow:

$$u = U_c^{\text{in}}, \quad v = w = 0, \quad \omega_{\text{O}_2} = \omega_{\text{O}_2}^{\text{in}}, \quad T = T_c^{\text{in}}. \quad (3.16)$$

Boundary condition 2 (B2)

At the anode channel inlet, an average streamwise velocity, constant fuel composition, and a constant temperature are specified for the fuel inflow:

$$u = U_a^{\text{in}}, \quad v = w = 0, \quad \omega_{\text{H}_2} = \omega_{\text{H}_2}^{\text{in}}, \quad T = T_a^{\text{in}}. \quad (3.17)$$

Boundary condition 3 (B3)

At the cathode and anode channel outlets, a constant reference pressure is specified, and the mass and heat transfers are purely convective:

$$p_c^{\text{out}} = p_a^{\text{out}} = p^{\text{ref}}, \quad \frac{\partial \omega_i}{\partial x} = \frac{\partial T}{\partial x} = 0. \quad (3.18)$$

Boundary condition 4 (B4)

At the top surface of the cathode interconnect, a potential of the cell voltage and a constant operating temperature are specified:

$$\phi_{\text{elc,c}} = V_{\text{cell}}, \quad T = T^{\text{oper}}. \quad (3.19)$$

Boundary condition 5 (B5)

At the bottom surface of the anode interconnect, the electric potential is zero and an operating temperature is specified:

$$\phi_{\text{elc,a}} = 0, \quad T = T^{\text{oper}}. \quad (3.20)$$

Boundary condition 6 (B6)

At the interconnect/channel interfaces on the cathode and anode, a no-slip boundary

condition is implemented to the momentum conservation, and the species mass fluxes normal to the channel walls are zero:

$$\mathbf{v} = 0, \quad \mathbf{n} \cdot \nabla \omega_i = 0. \quad (3.21)$$

Boundary condition 7 (B7)

At the outer vertical walls of interconnects, electrical and thermal insulation is specified:

$$\mathbf{n} \cdot \nabla \phi_{\text{elc}} = \mathbf{n} \cdot \nabla T = 0. \quad (3.22)$$

Boundary condition 8 (B8)

At the vertical walls of porous backing and reaction zone layers, a slip boundary condition is applied for the momentum conservation, and the fluxes of species mass, charge, and heat normal to the walls are zero due to insulation:

$$\mathbf{n} \cdot \mathbf{v} = 0, \quad \mathbf{n} \cdot \nabla \omega_i = \mathbf{n} \cdot \nabla \phi_{\text{elc/ion}} = \mathbf{n} \cdot \nabla T = 0. \quad (3.23)$$

Boundary condition 9 (B9)

At the vertical walls of the electrolyte, the fluxes of charge and heat normal to the walls are zero due to electrical and thermal insulation:

$$\mathbf{n} \cdot \nabla \phi_{\text{ion}} = \mathbf{n} \cdot \nabla T = 0. \quad (3.24)$$

Boundary condition 10 (B10)

At the channel/backing interface, the charge flux normal to the interface is zero due to electrical insulation:

$$\frac{\partial \phi_{\text{elc}}}{\partial z} = 0. \quad (3.25)$$

Boundary condition 11 (B11)

At the rib/backing interface, a slip boundary condition is employed for the momentum conservation, the velocity and the mass flux normal to the interface are zero:

$$w = 0, \quad \frac{\partial \omega_i}{\partial z} = 0. \quad (3.26)$$

Boundary condition 12 (B12)

At the backing/reaction zone interface, electrical insulation is specified:

$$\frac{\partial \phi_{\text{ion}}}{\partial z} = 0. \quad (3.27)$$

Boundary condition 13 (B13)

At the reaction zone/electrolyte interface, a slip boundary condition is used for the momentum conservation, the species mass flux is zero, and electrical insulation is applied:

$$w = 0, \quad \frac{\partial \omega_i}{\partial z} = \frac{\partial \phi_{\text{elc}}}{\partial z} = 0. \quad (3.28)$$

Boundary condition 14 (B14)

At the symmetry plane, the velocity and the fluxes of species mass, charge, and heat normal to the plane are all zero:

$$v = 0, \quad \frac{\partial \omega_i}{\partial y} = \frac{\partial \phi_{\text{elc/ion}}}{\partial y} = \frac{\partial T}{\partial y} = 0. \quad (3.29)$$

Fig. 3.2 Locations of boundary conditions for the 3D P-SOFC model.

For the P-SOFC considered here, flow velocities are specified as the inlet boundary conditions for the air and fuel flow, as given by Eqs (3.16) and (3.17). Correspondingly, a potentiostatic boundary condition which means a constant cell voltage is predefined at the top surface of the cell, as specified by Eq. (3.19). A fuel cell can also be operated at a certain stoichiometry for the air/fuel flow, $\varsigma_{c,a}$, which is the ratio of the amount of reactant supplied to the number of reactant required by the electrochemical reaction in the reaction zone layer to generate the overall average current density, i_{avg} . With the stoichiometries for the inlet conditions, the corresponding inlet velocities in Eqs. (3.16) and (3.17) can be determined by

$$U_{c,a}^{in} = \frac{i_{avg} L (w_{fc} + w_{rib})}{2 F h_{fc} w_{fc} c_{O_2, H_2}^{in}} \varsigma_{c,a}, \quad (3.30)$$

where the inlet molar concentration of oxygen/hydrogen $c_{O_2, H_2}^{in} = p^{in} x_{O_2, H_2}^{in} / RT_{c,a}^{in}$. The

average current density i_{avg} in Eq. (3.30) can be predefined as a constant at the top surface of the cell, which means a galvanostatic boundary condition, instead of the potentiostatic condition in Eq. (3.19). More information about the interchange between potentiostatic and galvanostatic boundary conditions for fuel cell modeling can be found in Ref. [194].

3.5. Numerical implementation

A commercial finite-element solver COMSOL Multiphysics 3.5a is used to numerically solve the present 3D P-SOFC model. The linear direct solver PARDISO is employed for 3D modeling. Quadratic Lagrange elements and a relative convergence error ϵ of 10^{-3} are implemented for all variables after ensuring mesh-independent solutions. According to the solver algorithm of COMSOL Multiphysics [195, 196], the convergence criterion employed for the present full model is

$$\left(\frac{1}{N} \sum_{i=1}^N |E_i|^2 \right)^{1/2} < \epsilon, \quad (3.31)$$

where E_i is the estimated error in the latest approximation to the i th component of the true solution vector, N is the number of degrees of freedom. The validity of the $\epsilon=1 \times 10^{-3}$ will be justified in Section 3.7 via a numerical convergence test which illustrates that decreasing the ϵ to values lower than 1×10^{-3} (e.g., 1×10^{-6}) does not cause distinguishable changes in simulation results.

Further, a number of relational operators are introduced to facilitate convergence. The volumetric current density, J , is multiplied with the factor ($\omega_{\text{O}_2, \text{H}_2} > 0$) to ensure that the source terms become zero when the oxidant or fuel is used up. The computed mass fraction is confined within $[0, 1]$ by

$$\omega_{\text{O}_2, \text{H}_2} \left(\omega_{\text{O}_2, \text{H}_2} > 0 \right) \left(\omega_{\text{O}_2, \text{H}_2} < 1 \right) + \left(\omega_{\text{O}_2, \text{H}_2} \geq 1 \right), \quad (3.32)$$

which results in $x_{\text{O}_2, \text{H}_2} \in [0, 1]$ according to the constitutive relation between $\omega_{\text{O}_2, \text{H}_2}$ and $x_{\text{O}_2, \text{H}_2}$ in Table 3.1. However, from the numerical point of view, $x_{\text{O}_2, \text{H}_2}$ cannot be zero, since it appears in the logarithms for the expression of the reversible electric potential E^{rev} . In order to avoid singularity of logarithms when solving for E^{rev} numerically, a small value of 10^{-6} is assigned to the expression of $x_{\text{O}_2, \text{H}_2}$ via

$$10^{-6} \left(\omega_{\text{O}_2, \text{H}_2} \leq 0 \right) + x_{\text{O}_2, \text{H}_2} \left(\omega_{\text{O}_2, \text{H}_2} > 0 \right) \left(\omega_{\text{O}_2, \text{H}_2} \leq 1 \right) + \left(\omega_{\text{O}_2, \text{H}_2} > 1 \right), \quad (3.33)$$

which guarantees $x_{\text{O}_2, \text{H}_2} \in [10^{-6}, 1]$.

The inlet gauge pressure Δp for the 3D model is specified by making the average inflow velocity equal to a predefined inlet velocity via an algebraic relation

$$\frac{1}{A_{\perp}^{(\text{fc})}} \iint_{A_{\perp}^{(\text{fc})}} u dy dz = U^{\text{in}}. \quad (3.34)$$

When plotting the polarization curves predicted by the 3D model, the average current density is obtained by,

$$i_{\text{avg}} = \iiint_V i_{\text{bl}, z} dx dy dz / V \quad \text{or} \quad \pm \frac{1}{A_{\text{rl/bl}}} \iiint_V |J| dx dy dz \quad (3\text{D}), \quad (3.35)$$

which takes the volumetric average of the local current density over the backing layer. It can also be obtained by dividing the integral of the absolute value of the volumetric current density (either $-J_c$ or $+J_a$) over the reaction zone layer by the area of the backing/reaction zone interface $A_{\text{rl/bl}}$.

The regular geometry of the P-SOFC allows a straightforward application of the structured mesh with quadrilateral elements in COMSOL. Special attention should be drawn to the meshing of the 3D models. For the 3D geometries, the supplied oxygen may deplete in the cathode porous layers in locations away from the channel at low cell

voltages (or high current densities closed to the limiting value), whence a dens mesh is needed in these critical locations. As such, the mesh density is gradually increased along the spanwise edges from the symmetric cross-section A-A in Fig. 3.1c to the vertical walls of porous layers so as to facilitate the convergence of 3D models.

Post-processing of the model predictions are conducted in MATLAB R2010a.

3.6. Validation

The mathematical model needs to be validated with experiment in order to guarantee that it describes the performance of a real fuel cell. In the SOFC literature, the experiments of the P-SOFC are usually conducted based on a button cell (Fig. 3.1d) for research and development of new materials and characterization thereof, rather than a planar cell with parallel flow channels (Fig. 3.1a) that is better suited for applications. Due to the lack of the experiments based on the planar cell configuration, researchers have to validate their P-SOFC models with button cells [69, 129, 130].

The present full P-SOFC model is calibrated and validated with the measurements of the button cell presented by Zhao and Virkar [197] in the literature. The cell is fed by air and 3% humid hydrogen, and tested at 600, 700, and 800 °C at 1 atm. Here it is assumed that the pressure and species distribution in the radial direction from the centre of the jet impinging on the porous backing is uniform and that the resistance to transport is negligible through the thin boundary layers in the flow field. One can thus reduce the computed button cell to a 1D domain, as depicted in Fig. 3.1d. For boundary conditions, a constant potential of the cell voltage and the operating temperature are imposed to the top surface of the cell for the cathode, and a zero potential and the operating temperature to the bottom surface for the anode. The other boundary conditions are referred to Eqs. (3.23), (3.24), (3.27), and (3.28). The layer thicknesses are set according to the

experiment setup of Zhao and Virkar [197], which are 5×10^{-5} m for the cathode backing layer, 8×10^{-6} m for the electrolyte, 1×10^{-3} m for the anode backing layer as well as 2×10^{-5} m for both the cathode and anode reaction zone layers. The other physical parameters for modeling are referred to Table 3.2, including physical constants, operating conditions, and material properties. The temperature-dependent fluid and thermal properties of the gaseous species are presented in Table 3.3.

Table 3.2 Modeling parameters of the 3D P-SOFC model.

Parameter	Value [Units]	Reference
Physical constants		
$D_{\text{H}_2\text{-H}_2\text{O}}^0$	$9.15 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$	[126]
$D_{\text{O}_2\text{-N}_2}^0$	$2.2 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$	[126]
E^0	1.18 V	[10]
$E_{\text{a,c}}^{\text{act}}$	$(1.2, 1.15) \times 10^5 \text{ J mol}^{-1}$	adapted
F	96485 C mol^{-1}	-
$M_{\text{H}_2}, M_{\text{H}_2\text{O}}, M_{\text{N}_2}, M_{\text{O}_2}$	$(2, 18, 28, 32) \times 10^{-3} \text{ kg mol}^{-1}$	-
R	$8.314 \text{ J mol}^{-1} \text{ K}^{-1}$	-
$T_{\text{H}_2\text{-H}_2\text{O}}^0, T_{\text{N}_2\text{-O}_2}^0$	307.1, 307.5 K	[126]
$\alpha_{1,\text{a}}, \alpha_{2,\text{a}}$	2, 1	[190]
$\alpha_{1,\text{c}}, \alpha_{2,\text{c}}$	1.4, 0.6	[190]
Δs	$-44.43 \text{ J mol}^{-1} \text{ K}^{-1}$	[9]
$\gamma_1, \gamma_2, \gamma$	1, -0.5, 0.25	[190]
Operating conditions		
$p_{\text{atm}}, p^0, p^{\text{ref}}$	$1.01 \times 10^5 \text{ Pa}$	[126]
$T^{\text{in}}, T^{\text{oper}}$	973.15 K	-
$U_{\text{a,c}}^{\text{in}}$	1 m s^{-1}	-
$\nu_{\text{H}_2}^{\text{in}}$	97%	-
$\nu_{\text{O}_2}^{\text{in}}$	21%	-
Planar cell geometry		
h_{cc}	$5 \times 10^{-4} \text{ m}$	-
$h_{\text{fc,a}}, h_{\text{fc,c}}$	$2 \times 10^{-3} \text{ m}$	-
$h_{\text{bl,a}}, h_{\text{bl,c}}$	$(5.625, 1.875) \times 10^{-4} \text{ m}$	-
$h_{\text{rl,a}}, h_{\text{rl,c}}$	$2 \times 10^{-5} \text{ m}$	-
h_{el}	$5 \times 10^{-5} \text{ m}$	-
L	$9 \times 10^{-2} \text{ m}$	-
$w_{\text{fc}} + w_{\text{rib}}$	$3 \times 10^{-3} \text{ m}$	-
Material properties		
$k_{\text{bl}}, k_{\text{rl}}, k_{\text{ic}}, k_{\text{el}}$	3, 3, 3.5, $2 \text{ W m}^{-1} \text{ K}^{-1}$	[193]
$\beta_{\text{a}}, \beta_{\text{c}}$	$(5.7, 700) \times 10^7 \text{ A m}^{-2}$	[190]
r	$5 \times 10^{-7} \text{ m}$	[26]
$\mathcal{A}^{\text{ref}}$	$4.51 \times 10^5 \text{ m}^{-1}$	[25, 128, 198]
Φ	0.5	[25]
$\kappa_{\text{a}}, \kappa_{\text{c}}$	$(1, 1) \times 10^{-12} \text{ m}^2$	[70]
$\varepsilon_{\text{bl,c}}, \varepsilon_{\text{bl,a}}, \varepsilon_{\text{rl,c}}, \varepsilon_{\text{rl,a}}$	0.45, 0.48, 0.26, 0.23	[197]
$\sigma_{\text{elc,ic}}$	$4 \times 10^6 \Omega^{-1} \text{ m}^{-1}$	[69]
$\tau_{\text{a,c}}$	2.75	[25]

Table 3.3 Fluid and thermal properties of species, valid in the range of 273-1473 K [199].

<i>Dynamic viscosity</i>								
	a_0	a_1	a_2	a_3	a_4	a_5	a_6	μ (973.15K)
H ₂	15.553	299.78	-244.34	249.41	-167.51	62.966	-9.9892	202.0091
H ₂ O	-6.7541	244.93	419.5	-522.38	348.12	-126.96	19.591	365.4964
N ₂	1.2719	771.45	-809.2	832.47	-553.93	206.15	-32.43	408.4639
O ₂	-1.6918	889.75	-892.79	905.98	-598.36	221.64	-34.754	480.907
$\mu(10^{-7} \text{ kg m}^{-1} \text{ s}^{-1}) = \sum_{i=0}^6 a_i \tau^i$, where $\tau = T(\text{K})/1000$.								
<i>Isobaric specific heat capacity</i>								
	b_0	b_1	b_2	b_3	b_4	b_5	b_6	c_p (973.15K)
H ₂	10.579	28.018	-75.275	99.645	-68.075	23.4515	-3.2363	15.056
H ₂ O	2.0763	-2.2892	8.1117	-12.06	10.0856	-4.4116	0.7786	2.2723
N ₂	1.0367	0.1750	-1.3586	3.7561	-4.0557	1.9841	-0.3696	1.1624
O ₂	1.089	-1.8117	6.365	-9.3866	7.2413	-2.8694	0.4618	1.0854
$c_p (\text{kJ kg}^{-1} \text{ K}^{-1}) = \sum_{i=0}^6 b_i \tau^i$, where $\tau = T(\text{K})/1000$.								
<i>Thermal conductivity</i>								
	c_0	c_1	c_2	c_3	c_4	c_5	c_6	k (973.15K)
H ₂	1.504	62.892	-47.19	47.763	-31.939	11.972	-1.8954	0.4223
H ₂ O	2.0103	-7.9139	35.922	-41.39	35.993	-18.974	4.1531	0.0943
N ₂	-0.3216	14.8	-25.473	38.837	-32.133	13.493	-2.2741	0.0678
O ₂	-0.1857	11.118	-7.3734	6.713	-4.1797	1.4910	-0.2278	0.072
$k(\text{W m}^{-1} \text{ K}^{-1}) = 0.01 \sum_{i=0}^6 c_i \tau^i$, where $\tau = T(\text{K})/1000$.								

Firstly, the model is calibrated with respect to a set of experimental data for the polarization curve at 700 °C [197]. Here, two parameters – the activation energies for the anode E_a^{act} and cathode E_c^{act} – are adapted to fit the predicted polarization curve to the experimental measurements. The accuracy of curve fitting is estimated by a global error defined as [200]

$$\varepsilon_{\text{gle}} = \frac{1}{|V_{\text{cell}}^e|_{\text{max}}} \sqrt{\frac{1}{n_p} \sum_{i=1}^{n_p} (V_{\text{cell},i}^e - V_{\text{cell},i}^n)^2}, \quad (3.36)$$

in which n_p presents the number of measured points, V_{cell}^e and V_{cell}^n are the experimentally measured cell voltage and the numerically predicted value at the same

current density. The calibration is stopped when the global error at 700 °C became 2%. Subsequently, the calibrated model is validated with the measurements at 600 and 800 °C as shown in Fig. 3.3, and good agreement is achieved in view of the resulting global error of 3% and 7% respectively. The experimental open circuit voltage, which is the cell voltage at the zero current density, is always less than its theoretical counterpart. This voltage difference may be caused by the residual electronic conduction in the electrolyte, gases crossing over the electrolyte via micro cracks and fissures, and/or a leak current that is wasted by unwanted side reactions or non-electrochemical reactions at the electrodes in the practical experiment [97, 105]. Moreover, the global error of model validation increases with the operating temperature. At 800 °C in Fig. 3.3, the voltages experimentally measured drop below the predicted values over the entire polarization curve. This may be because the gas crossing, current leakage, and/or unwanted side reactions become more intense as the high operating increases. If one attempts to have better curve fitting, the global voltage drop can be offset by introducing a constant potential loss, namely the leak polarization η^{leak} depicted in Section 2.2.1.5, to the cell model. The value of η^{leak} can be determined by parameter adaption during curve fitting [97, 98].

For 3D non-isothermal P-SOFC modeling in the present work, the validated model is applied to the 3D planar geometry shown in Fig. 3.1c, in which the flow field of parallel plain channels separated by ribs allows the model to be spatially smoothed, based on the assumption that the electrokinetics remains the same for a change in the flow field.

Fig. 3.3 Polarization curves by experiment (symbols) and simulation (lines) at different temperature conditions: 700 °C (●) for a training set, 800 (■) and 600 °C (▲) for test sets.

3.7. Numerical convergence test

Based on the 3D non-isothermal P-SOFC model shown schematically in Fig. 3.1c, a numerical convergence test is presented here to justify that a relative convergence error of 10^{-3} is valid to guarantee sufficient numerical accuracy for all variables. The widths of the channel and rib in the cell are 1.65×10^{-3} and 1.35×10^{-3} m, respectively. All the other modeling parameters are referred to Tables 3.2 and 3.3.

Fig. 3.4 compares the numerical convergence of the present 3D full model in two cases with relative convergence errors ϵ of 1×10^{-3} and 1×10^{-6} . The model is solved over a range of cell voltages from 1 to 0.3 V with an interval of 0.1 V. Starting from 1 V, the estimated error (*i.e.*, the left-hand side of Eq. (3.31)) decreases from a value in an order of magnitude of 10^4 as the iteration number increases. The nonlinear-solver iterations stop when the estimated error is smaller than the $\epsilon = 1 \times 10^{-3}$ for Fig. 3.4a and

the $\epsilon=1\times10^{-6}$ for Fig. 3.4b. Then, the software proceeds to solve the model at 0.9 V. The solutions obtained previously at 1 V are employed automatically as the initial guesses for the simulation at 0.9 V, such that fewer iterations are required to achieve an estimate error smaller than the predefined ϵ . The software subsequently moves on to solve the model at the next voltage, until it finishes all the target eight runs. As shown in Fig. 3.4a, the first run at 1 V takes about 50 iterations, whereas only 2 iterations are needed for each of the subsequent seven runs. The case with $\epsilon=1\times10^{-3}$ (Fig. 3.4a) requires fewer iterations than the case with 1×10^{-6} (Fig. 3.4b), which means a lower computational cost.

Fig. 3.4 Relation between the estimated error and iteration numbers for the simulation of the 3D full non-isothermal model with relative convergence errors ϵ of (a) 1×10^{-3} and (b) 1×10^{-6} , when solving from 1.0 to 0.3 V with an interval of 0.1 V.

Comparing the model predictions from the two cases with $\epsilon=1\times10^{-3}$ and 1×10^{-6} ,

the simulation results are the same in view of the eight obtained significant figures of the solution. Fig. 3.5 illustrates the good agreement between the two cases in terms of the distributions of the temperature, T (Fig. 3.5a), the oxygen mass fraction, ω_{O_2} (Fig. 3.5b), and the velocity component in the normal direction (e_z), w (Fig. 3.5c), along the intersection line of the backing/reaction zone interface and the outer vertical wall of the cell. Therefore, the relative convergence error ϵ of 10^{-3} is valid to ensure sufficient numerical accuracy for all the variables.

Fig. 3.5 Comparison of numerical results associated with relative convergence errors of 1×10^{-3} (color lines) and 1×10^{-6} (x), in terms of the solutions at the intersection line of the backing/reaction zone interface and the outer vertical wall of the cell at voltages of 1.0 to 0.3 V decreasing with an interval of 0.1 V: (a) temperature; (b) oxygen mass fraction; (c) the velocity component in the normal direction.

3.8. Summary

This chapter presents the governing equations for the change of mass, momentum, species, charge, and energy, as well as the constitutive relations and boundary conditions of a full 3D non-isothermal P-SOFC model, in which the reaction zones are resolved spatially. The implementation of the reaction zone as an individual functional layer aims to describe the transport phenomena and electrochemical characteristics as precisely as possible, in view of the fact that the reaction zone layer is actually spread out into the electrode for some distance from the electrolyte/electrode interfaces.

The development of the present SOFC model does not aim at surpassing all the existing models in literature. Instead, this full single-cell model is expected to be able to describe the cell performance in desired accuracy, which has been proved by model validation. The predicted polarization curves are validated with the experimental measurements from the literature at operating temperatures of 800, 700, and 600 °C, and the corresponding global error does not exceed 7, 2, and 3%, respectively. Based on the assumption that the electrokinetics remains the same for a change in the flow field, the validated model is applicable for a 3D planar geometry. This 3D P-SOFC model will be employed as the benchmark model for the development of reduced models in Chapters 4, 5, and 7.

Chapter 4

Development of a Reduced Model:

Asymptotic Spatially-Smoothed Isothermal (ASSI) Cell Model

4.1. Introduction

This chapter presents the development of a reduced P-SOFC model via both spatial smoothing with novel correlation factors and asymptotic reduction, based on the 3D P-SOFC model introduced in Chapter 3 under an isothermal condition, in order to get significant reduction of computational cost with desired numerical accuracy. Section 4.2 depicts the spatial smoothing of the isothermal governing equations for the mass, momentum, and charge transports. Novel correlation factors for the spatial smoothing over flow fields with parallel plain channels are developed to handle not only variations in the pathways of transport processes but also coupling effects between the governing equations. Subsequently, Section 4.3 elaborates the asymptotic reduction of the spatially smoothed model, followed by an introduction to numerical implementation in Section 4.4. Section 4.5 verifies the resulting spatially smoothed model and its asymptotic counterpart, called the asymptotic spatially-smoothed isothermal (ASSI) model, with the 3D counterpart in terms of global and local cell behaviours. The difference between the predictions of the 3D and reduced models is quantified. At last, a computational cost

analysis is conducted in Section 4.6 to investigate the computational gains.

4.2. Spatial smoothing with novel correlation factors

A P-SOFC comprising two flow fields with parallel plain channels separated by ribs, two porous backing layers, two reaction zone layers, and a solid electrolyte is considered in this chapter, as shown in Fig. 4.1a. The air and fuel are supplied in a co-flow configuration. Generally, the repeating unit enclosed by the dashed line in Fig. 4.1a is used for the simulation of single-cell performances. Moreover, because of the symmetric geometry of the repeating unit, half of the unit structure is taken into account as the computational domain associated with symmetry boundary conditions at the central cross section A-A, as shown in Fig. 4.1b.

The 3D P-SOFC single-cell model presented in Chapter 3 is used to predict the electrochemical kinetics and transport phenomena in the domain in Fig. 4.1b under an isothermal condition. Isothermal steady-state conservation equations for weakly-compressible momentum, charge, and species are solved for six dependent variables: the mass fractions of oxygen for the cathode and hydrogen for the anode, ω_{O_2} and ω_{H_2} , the velocity, $\mathbf{v}$, the pressure, p , as well as the electronic and ionic potentials, ϕ_{elc} and ϕ_{ion} . The charge transport in the interconnect is not solved here, because only the effects of ribs on the diffusion pathways from the flow field to the backing layer are taken into account in this chapter. If one wants to consider the variation in pathways from the flow field to not only the backing layer but also the upper part of the interconnect, the charge transport in interconnect should be accounted for, as presented in next chapter. The governing equations of the full isothermal model here (before being spatially smoothed or asymptotically reduced) are specified by Eqs. (3.1) to (3.12). The boundary conditions for the 3D model without solving the charge

transport in the ribs are referred to Eqs. (3.16) to (3.29), except that Eqs. (3.19) and (3.20) are implemented at the interface of the ribs and the backing layer. The geometrical parameters of the model are shown in Table 4.1. The other modeling parameters can be found in Table 3.2.

Fig. 4.1 Schematic of (a) a SOFC with parallel plain channels, (b) a 3D repeating unit with a pair of channels, (c) 3D and (d) 2D single-cell models with volume-averaged flow fields, (e) an asymptotically reduced model with PDEs ($\rightarrow$) and ODEs ($\bullet$) in the flow field, and ODEs in the remainder of the cell.

Table 4.1 Cell geometry and the coefficients of correlation factors.

Parameter	Value
<i>Cell geometry</i>	
$h_{fc,a}, h_{fc,c}$	2×10^{-3} m-
$h_{rl,a}, h_{rl,c}$	2×10^{-5} m
h_{el}	5×10^{-5} m-
L	9×10^{-2} m
n_{fc}	20
$w_{fc} + w_{rib}$	3×10^{-3} m
$\mathcal{H}$	0.1 – 0.5
$\mathcal{W}$	0.4 -0.7
<i>Coefficients for the polynomials of correlation factors</i>	
$a_{00}, a_{01}, a_{02}, a_{03}, a_{04},$	0.5242, -1.945, 0.5577, 0.4294, 1.673,
$a_{10}, a_{11}, a_{12}, a_{13},$	-5.086, 18.51, 5.198, -12.81,
$a_{20}, a_{21}, a_{22},$	17.15, -54.54, 13.43,
$a_{30}, a_{31},$	-12.32, 36.47,
a_{40}	-2.031
$b_{00}, b_{01}, b_{02}, b_{03}, b_{04}, b_{05},$	-0.3358, 3.887, -10.41, 3.3703, 8.26, -3.842,
$b_{10}, b_{11}, b_{12}, b_{13}, b_{14},$	-0.9629, -23.65, 99.58, -69.27, -0.4384,
$b_{20}, b_{21}, b_{22}, b_{23},$	31.04, -19.77, -153.2, 97.22,
$b_{30}, b_{31}, b_{32},$	-84.72, 168.3, 11.82,
b_{40}, b_{41}	61.3, -121.4.

According to the methodology of spatial smoothing over a flow field of plain channels separated by solid ribs [173], the flow channels are considered as the pores and ribs as the solid matrix of porous media respectively, such that the flow field in Fig. 4.2a is volume-averaged and becomes equivalent to a porous counterpart in Fig. 4.2b. Correspondingly, the governing equations for the momentum and mass transport in the flow field should be modified, such that the transport information in the original plain flow channels is captured by the volume-averaged counterpart. Moreover, the variance in the pathways of the mass and charge transport in the adjacent porous backing due to ribs needs to be taken into account as well.

Fig. 4.2 Schematic of (a) a flow field of parallel plain channels separated by ribs and (b) its volume-averaged counterpart, the pathways of mass (solid arrows) and charge transport (dashed arrows) in a SOFC cross section (c) without and (d) with a volume-averaged flow field.

4.2.1. Momentum and mass transport in flow field

Instead of the Navier-Stokes equation (3.3) of the full model, for the original plain flow channels (Fig. 4.2a), Darcy's law is applied to govern the momentum transport for the porous flow field counterpart (Fig. 4.2b),

$$\nabla \langle p \rangle_{\text{ff}} = - \frac{\mu_{\text{mix}}}{\kappa_{\text{ff}}(w_{\text{fc}}, h_{\text{fc}}, w_{\text{rib}}, \text{directions})} \langle \mathbf{v} \rangle, \quad (4.1)$$

associated with the dynamic viscosity of a gas mixture μ_{mix} and an effective permeability tensor $\kappa_{\text{ff}}(w_{\text{fc}}, h_{\text{fc}}, w_{\text{rib}}, \text{directions})$, in order to solve for the intrinsic local pressure $\langle p \rangle_{\text{ff}}$ and the superficial velocity $\langle \mathbf{v} \rangle$, which are the counterparts of the

pressure drop and velocity inside the channels of the original 3D model. Considering the flow velocity in the original flow field as an intrinsic velocity $\langle \mathbf{v} \rangle_{\text{ff}}$ for porous media, the superficial velocity $\langle \mathbf{v} \rangle$ is related to its intrinsic counterpart $\langle \mathbf{v} \rangle_{\text{ff}}$ via $\langle \mathbf{v} \rangle = \varepsilon_{\text{ff}} \langle \mathbf{v} \rangle_{\text{ff}}$ [125]. The effective porosity $\varepsilon_{\text{ff}} = n_{\text{fc}} w_{\text{fc}} / w$ is the ratio of the volumes of n_{fc} flow channels (of width w_{fc}) to the volume of the entire flow field (of width $w = (n_{\text{fc}} w_{\text{fc}} + (n_{\text{fc}} + 1) w_{\text{rib}})$ and excluding the solid part of current collectors above the flow channels), as shown in Fig. 4.2a. Moreover, the superficial inlet velocity for the spatially smoothed flow field is given by $\langle U^{\text{in}} \rangle = \varepsilon_{\text{ff}} U^{\text{in}}$. The average inlet velocity of the original plain flow channel, U^{in} , is obtained by averaging the inlet velocity over the inlet surface. The permeability tensor, $\boldsymbol{\kappa}_{\text{ff}}(w_{\text{fc}}, h_{\text{fc}}, w_{\text{rib}}, \text{directions})$ is defined as [173]

$$\boldsymbol{\kappa}_{\text{ff}}(w_{\text{fc}}, h_{\text{fc}}, w_{\text{rib}}, \text{directions}) = \frac{D_h^2 \varepsilon_{\text{ff}}}{32} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \quad (4.2)$$

where the hydraulic diameter $D_h = 4A_{\perp}^{(\text{fc})} / S_{\perp}^{(\text{fc})}$ is related to the wetted perimeter $S_{\perp}^{(\text{fc})} = 2(h_{\text{fc}} + w_{\text{fc}})$ for the cross section (in the yz -plane) of a rectangular plain flow channel with a cross-sectional area $A_{\perp}^{(\text{fc})} = h_{\text{fc}} w_{\text{fc}}$ (perpendicular to the streamwise direction). The 3×3 matrix in Eq. (4.2) means the permeability component is of the value of $D_h^2 \varepsilon_{\text{ff}} / 32$ in the streamwise ($\mathbf{e}_x$) and normal ($\mathbf{e}_z$) directions, and zero in all the other directions. It is postulated $\boldsymbol{\kappa}_{\text{ff},xx} = \boldsymbol{\kappa}_{\text{ff},zz}$ here to get a simple form for the permeability tensor. The permeability component, $\boldsymbol{\kappa}_{\text{ff},yy}$, in the spanwise direction ($\mathbf{e}_y$) is zero, because the channels are not connected in this direction. The off-diagonal permeability components are set to zero, because the parallel flow channels are aligned just in the

streamwise direction.

In order to modify the mass transport in the flow field, Ly *et al.* [173] introduced the following tensorial binary diffusivity

$$\mathbf{D}_{ij,\text{ff}}^{\text{eff}} = \varepsilon_{\text{ff}} D_{ij,\text{fc}} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (4.3)$$

to Fick's law for species i in a binary mixture of component i and j . In the present work, Eq. (4.3) is extended to the modified Stefan-Maxwell equation for a mixture of more than two components, such that the mass flux for the spatially smoothed flow field becomes

$$\mathbf{n}_{i,\text{ff}} = \rho \omega_i \langle \mathbf{v} \rangle - \rho \omega_i \sum_{j=1}^n \left(\mathcal{D}_{ij,\text{ff}}^{\text{eff}} \nabla x_j \right), \quad (4.4)$$

associated with

$$\mathcal{D}_{ij,\text{ff}}^{\text{eff}} \nabla x_j = \varepsilon_{\text{ff}} \mathcal{D}_{ij,\text{fc}} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \nabla x_j, \quad (4.5)$$

in which $\mathcal{D}_{ij,\text{fc}}$ is the multicomponent Fick diffusivity for the original plain flow channels, and $\mathcal{D}_{ij,\text{ff}}^{\text{eff}}$ the corresponding intrinsic effective diffusion tensor for the volume-averaged flow field. The relations between the multicomponent Fick diffusivities ($\mathcal{D}$) and the binary diffusivities (D) are presented in Table 3.1. For brevity, the superficial velocity $\langle \mathbf{v} \rangle$ for the spatially smoothed flow field is denoted as $\mathbf{v}$ henceforth, since the velocities in the other cell components are also superficial quantities.

4.2.2. Mass and charge transport in backing layer

The existence of solid ribs between parallel channels affects not only the mass and

momentum transport in the flow field, but also the pathways of the mass and charge transport in the adjacent porous backing layer. Thus, when spatially smoothing the flow field, a correction factor $\zeta(h_{bl}, w_{fc}, w_{rib}, \text{material property})$ is necessary to modify every second-order term of the mass and charge transport equations in the full model for the backing layer, so as to capture the change in the pathways from the flow field to the backing layer due to ribs. For simplicity, the discussion here is limited to isotropic transport properties, such that the correction factor ζ is independent of material properties of the backing layer, and hence it becomes $\zeta(h_{bl}, w_{fc}, w_{rib})$.

The schematics of pathways over the cross section of a single cell without spatial smoothing are shown in Fig. 4.2c, and with spatial smoothing in Fig. 4.2d. The blue and green solid arrows represent the pathways of the gaseous oxygen in the cathode and hydrogen in the anode, respectively, diffusing from the channels to the reaction zone layers where electrochemical reactions occur. The black dashed arrows represent the pathways of negative charges (*i.e.*, electrons in backing layers, oxygen ions in the electrolyte, and both in reaction zone layers). Instead of solving a generic Laplace equation [173], the correction factors, ζ_c and ζ_a , are determined by solving all the coupled governing equations together for a cross section in the normal and spanwise directions through all the original 3D solid layers (Fig. 4.2c) and the spatially smoothed counterpart (Fig. 4.2d), such that they can handle the coupling effect between governing equations. The correlation factors are introduced into the mass fluxes of O_2 and H_2 for the porous backing layer adjacent to the spatially smoothed flow field (Fig. 4.2d) as

$$\mathbf{n}_i = \rho\omega_i\mathbf{v} - \rho\omega_i \sum_{j=1}^n \left(\zeta \mathcal{D}_{ij}^{\text{eff}} \nabla x_j \right), \quad (4.6)$$

based on the modified Stefan-Maxwell equation [110] for the original backing layer adjacent to the plain flow channels and ribs (Fig. 4.2c). Moreover, the flux of charges is

modified as

$$\mathbf{i}_{\text{bl}} = -(1 - \zeta) \sigma_{\text{elc}}^{\text{eff}} \nabla \phi_{\text{elc}}, \quad (4.7)$$

since the pathways of the charge transport in the backings are different from that of the mass transport as shown in Fig. 4.2c.

The boundary conditions of the cross-section model remain the same as that of the full model, except for the flow channel/backing interface where now the inlet mass fractions and the reference pressure are prescribed. The latter holds well for any cross section along the channel since the pressure change Δp in a P-SOFC is typically much less than the reference pressure p_{atm} in $p = p_{\text{atm}} + \Delta p$; the former, however, can cause some errors since the mass fractions vary along the channel due to the electrochemical reactions. In order to ensure that the variations do not influence the correlations unduly, three cases with varying mass fractions at the flow channel/porous backing interface ($\omega_{\text{O}_2, \text{H}_2}^{\text{in}}$ to $\omega_{\text{O}_2, \text{H}_2}^{\text{in}}/2$ and $\omega_{\text{O}_2, \text{H}_2}^{\text{in}}/10$) are simulated. The resulting changes in the correlation factors did not exceed 5% for ζ_{c} and 7% for ζ_{a} . This error is reasonable and acceptable to provide significant reduction in computational cost and model complexity with reserved model fidelity.

Finally, the flow channel width, w_{fc} , and the backing layer thickness, h_{bl} , are varied while keeping the total width, $w_{\text{fc}} + w_{\text{rib}}$, constant. The obtained discrete values of $\zeta(h_{\text{bl}}, w_{\text{fc}}, w_{\text{rib}})$ are then employed as a training set to construct polynomials for the correction factors, $\zeta_{\text{a,c}}$, via surface fitting as shown in Fig. 4.3. The polynomial is expressed as

$$\zeta_{\text{a}} = \sum_{i=0}^n \sum_{j=0}^{m-i} a_{ij} \mathcal{H}_{\text{a}}^i \mathcal{W}^j \quad (4.8)$$

for the anode, and

$$\zeta_c = \sum_{i=0}^n \sum_{j=0}^{m-i} b_{ij} \mathcal{H}_c^i \mathcal{W}^j \quad (4.9)$$

for the cathode. Here, $\mathcal{W} = w_{fc} / (w_{fc} + w_{rib})$ and $\mathcal{H} = (2h_{bl}) / (w_{fc} + w_{rib})$ with $0.4 \leq \mathcal{W} \leq 0.7$ and $0.1 \leq \mathcal{H} \leq 0.5$. The range of $\mathcal{W}$ and $\mathcal{H}$ is chosen with respect to the cell design. The numbers of terms in the polynomials, n and m , are selected to obtain a sufficiently high accuracy for the surface fitting. Comparing the predicted and actual values of ζ in the training set, the sum of squared errors (SSE) decreases from 2×10^{-3} with $n = m = 3$ for both sides to 1×10^{-4} with $n = m = 4$ for the anode, and 2×10^{-5} with $n = 4, m = 5$ for the cathode. A SSE smaller than 1×10^{-3} is considered desirable for this study, such that $n = m = 4$ is selected for Eq. (4.8) and $n = 4, m = 5$ for Eq. (4.9). The corresponding coefficients of the polynomials, a_{ij} and b_{ij} , are presented in Table 4.1. The resulting polynomials for $\zeta_{a,c}$ obtained from the training set are then verified with four test sets with good agreement, as shown in Fig. 4.3. Comparing the correlation factors, $\zeta_{a,c}$, predicted by Eqs. (4.8) and (4.9) with their actual values over $0.4 \leq \mathcal{W} \leq 0.7$ and $0.1 \leq \mathcal{H} \leq 0.5$, the relative errors do not exceed 6% for the ζ_a by Eq. (4.8) and 3% for the ζ_c by Eq. (4.9), which are considered acceptable here. The accuracy can be improved further by adjusting the order of the polynomial and/or narrowing the ranges of $\mathcal{W}$ and $\mathcal{H}$ when calibrating Eqs. (4.8) and (4.9). Furthermore, the variance in the pathways of electrons in the backings due to ribs is negligible over the demonstrated range of $\mathcal{W}$ and $\mathcal{H}$, in view of the maximum relative error of about 1% between the resulting discrete values of ζ with and without modifying the charge flux to Eq. (4.7). In addition, since the correlation factors are derived based on the full model over the cross section of the cell, the resulting polynomials of correlation factors are valid over a certain range of $\mathcal{W}$ and $\mathcal{H}$ under a set of predefined operating conditions. When the cell

geometry is out of the investigated range or the operating conditions change, recalibration of the correlation factors will be needed.

After the spatial smoothing of the flow field with parallel plain flow channels, the non-linear Navier-Stokes equation in the full model is replaced by the linear Darcy's law, which is much easier to be solved numerically. Effective transport properties and correlation factors are introduced in order to account for the physics pertaining to the spanwise direction, such that the 3D spatially smoothed model can capture the volume-averaged behaviour of the original full model. Furthermore, the 3D spatially smoothed geometry shown in Fig. 4.1c can be reduced to a 2D counterpart in Fig. 4.1d, provided that the inlet conditions are the same for each cathode (anode) channel. This is because the average behaviour of the transport processes in the spatially smoothed domain does not vary in the spanwise direction in this case. In contrast, if the inlet conditions vary from one channel to another because of the design of the interconnect, one would need to solve the 3D spatially smoothed domain.

Fig. 4.3 The correlations for the (a) cathode and (b) anode correction factors $\zeta(\mathcal{H}, \mathcal{W})$: training sets for calibration (●) and test sets for verification (◆).

4.3. Asymptotic reduction

The 2D spatially-smoothed counterpart is further reduced via the method of asymptotic model reduction [201]. A scaling analysis of the spatially smoothed governing equations is conducted below, and the terms in the orders of magnitude much smaller than the leading order are dropped from the equations.

4.3.1. Nondimensionalization

The first step of the scaling analysis is to nondimensionalize the governing equations and boundary conditions. The following nondimensional quantities are defined globally:

$$\begin{aligned}\tilde{x} &= \frac{x}{L}, \quad \tilde{z} = \frac{z}{h}, \quad \tilde{\ell} = \frac{h}{L}, \quad \tilde{u} = \frac{u}{[u]}, \quad \tilde{w} = \frac{w}{[w]}, \quad \tilde{\rho} = \frac{\rho}{[\rho]}, \quad \tilde{D}_{ij} = \frac{D_{ij}}{[D_{ij}]}, \quad \tilde{\mathcal{D}}_{ij}^{\text{eff}} = \frac{\mathcal{D}_{ij}^{\text{eff}}}{[\mathcal{D}_{ij}^{\text{eff}}]}, \\ \tilde{M} &= \frac{M}{[M]}, \quad \tilde{p} = \frac{p - p^{\text{ref}}}{[p]}, \quad \tilde{p}' = \frac{p' - p'^{\text{ref}}}{[p']}, \quad \tilde{\phi}_{\text{elc}} = \frac{\phi_{\text{elc}} - \phi_{\text{elc}}^{\text{ref}}}{[\phi_{\text{elc}}]}, \quad \tilde{\phi}_{\text{ion}} = \frac{\phi_{\text{ion}}}{[\phi_{\text{ion}}]}, \quad \tilde{\mathbf{i}} = \frac{\mathbf{i}}{[\mathbf{i}]}, \\ \tilde{J} &= \frac{J}{[J]},\end{aligned}$$

where $[\dots]$ is a pending scale factor assigned to an originally dimensional parameter or dependent variable. Reference factors, namely p^{ref} and ϕ^{ref} , are defined for independent and dependent variables that are not referenced to zero in the initial and boundary conditions. The above factors are specific for each cell layer. To differentiate them, a subscript ($j = \text{ff}, \text{bl}, \text{rl}, \text{el}$) is introduced to indicate the functional layers including the spatially smoothed flow channel (ff), backing layer (bl), reaction zone layer (rl), and electrolyte (el), while a and c stand for the anode and cathode respectively. For brevity, a modified pressure for the backing and reaction zone layers is defined:

$$p' = p + \frac{1}{3} \frac{\mu_{\text{mix}}}{\varepsilon} \nabla \cdot \mathbf{v} \quad (4.10)$$

Substitute the above scale and reference factors into the dimensional governing

equations (4.1), (4.4) and (4.6) as well as (3.1) to (3.12), resulting in the following dimensionless governing equations:

$$\ell[u] \frac{\partial}{\partial \tilde{x}} (\tilde{\rho} \tilde{u}) + [w] \frac{\partial}{\partial \tilde{z}} (\tilde{\rho} \tilde{w}) = \begin{cases} \frac{[M_c][J]h_{rl}}{4F[\rho]} \tilde{M}_{O_2} \tilde{J}_c & \text{(cathode rl)} \\ \frac{[M_a][J]h_{rl}}{2F[\rho]} (\tilde{M}_{H_2O} - \tilde{M}_{H_2}) \tilde{J}_a & \text{(anode rl)} \\ 0 & \text{(ff, bl)} \end{cases} \quad (4.11)$$

for the mass transfer, and

$$\begin{cases} \frac{\mu_{mix}}{\kappa_{ff}} \tilde{u} = -\frac{[p]}{L[u]} \frac{\partial \tilde{p}}{\partial \tilde{x}} \\ \frac{\mu_{mix}}{\kappa_{ff}} \tilde{w} = -\frac{[p]}{h[w]} \frac{\partial \tilde{p}}{\partial \tilde{z}} \end{cases} \quad \text{(ff)} \quad (4.12)$$

$$\begin{cases} \frac{\mu_{mix}}{\kappa} \tilde{u} = -\frac{[p']}{L[u]} \frac{\partial \tilde{p}'}{\partial \tilde{x}} - \frac{\mu_{mix}}{\varepsilon h^2} \left(\ell^2 \frac{\partial^2}{\partial \tilde{x}^2} + \frac{\partial^2}{\partial \tilde{z}^2} \right) \tilde{u} \\ \frac{\mu_{mix}}{\kappa} \tilde{w} = -\frac{[p']}{h[w]} \frac{\partial \tilde{p}'}{\partial \tilde{z}} - \frac{\mu_{mix}}{\varepsilon h^2} \left(\ell^2 \frac{\partial^2}{\partial \tilde{x}^2} + \frac{\partial^2}{\partial \tilde{z}^2} \right) \tilde{w} \end{cases} \quad \text{(bl, rl)} \quad (4.13)$$

for the momentum transfer, and

$$\begin{aligned} & \ell[u] \frac{\partial}{\partial \tilde{x}} (\tilde{\rho} \tilde{u} \omega_i) + [w] \frac{\partial}{\partial \tilde{z}} (\tilde{\rho} \tilde{w} \omega_i) - \frac{\ell^2}{h} \frac{\partial}{\partial \tilde{x}} \left(\tilde{\rho} \omega_i \sum_{j=1}^n \left([\mathcal{D}_{ij}^{eff}] \varepsilon_{ff} \tilde{\mathcal{D}}_{ij} \frac{\partial \tilde{x}_j}{\partial \tilde{x}} \right) \right) \\ & - \frac{1}{h} \frac{\partial}{\partial \tilde{z}} \left(\tilde{\rho} \omega_i \sum_{j=1}^n \left([\mathcal{D}_{ij}^{eff}] \varepsilon_{ff} \tilde{\mathcal{D}}_{ij} \frac{\partial \tilde{x}_j}{\partial \tilde{z}} \right) \right) = 0 \end{aligned} \quad \text{(ff)} \quad (4.14)$$

$$\begin{aligned} & \ell[u] \frac{\partial}{\partial \tilde{x}} (\tilde{\rho} \tilde{u} \omega_i) + [w] \frac{\partial}{\partial \tilde{z}} (\tilde{\rho} \tilde{w} \omega_i) - \frac{\ell^2}{h} \frac{\partial}{\partial \tilde{x}} \left(\tilde{\rho} \omega_i \sum_{j=1}^n \left([\mathcal{D}_{ij}^{eff}] \zeta \tilde{\mathcal{D}}_{ij}^{eff} \frac{\partial \tilde{x}_j}{\partial \tilde{x}} \right) \right) \\ & - \frac{1}{h} \frac{\partial}{\partial \tilde{z}} \left(\tilde{\rho} \omega_i \sum_{j=1}^n \left([\mathcal{D}_{ij}^{eff}] \zeta \tilde{\mathcal{D}}_{ij}^{eff} \frac{\partial \tilde{x}_j}{\partial \tilde{z}} \right) \right) = 0 \end{aligned} \quad \text{(bl)} \quad (4.15)$$

$$\begin{aligned}
& \ell[u] \frac{\partial}{\partial \tilde{x}} (\tilde{\rho} \tilde{u} \omega_i) + [w] \frac{\partial}{\partial \tilde{z}} (\tilde{\rho} \tilde{w} \omega_i) - \frac{\ell^2}{h} \frac{\partial}{\partial \tilde{x}} \left(\tilde{\rho} \omega_i \sum_{j=1}^n \left([\mathcal{D}_{ij}^{\text{eff}}] \tilde{\mathcal{D}}_{ij}^{\text{eff}} \frac{\partial \tilde{x}_j}{\partial \tilde{x}} \right) \right) \\
& - \frac{1}{h} \frac{\partial}{\partial \tilde{z}} \left(\tilde{\rho} \omega_i \sum_{j=1}^n \left([\mathcal{D}_{ij}^{\text{eff}}] \tilde{\mathcal{D}}_{ij}^{\text{eff}} \frac{\partial \tilde{x}_j}{\partial \tilde{z}} \right) \right) = \begin{cases} \frac{h}{[\rho_c]} \frac{[M_c][J]}{4F} \tilde{M}_{\text{O}_2} \tilde{J}_c & (\text{O}_2, \text{cathode rl}) \\ -\frac{h}{[\rho_a]} \frac{[M_a][J]}{2F} \tilde{M}_{\text{H}_2} \tilde{J}_a & (\text{H}_2, \text{anode rl}) \end{cases}
\end{aligned} \tag{4.16}$$

for the species mass transfer, and

$$\ell^2 \frac{\partial^2 \tilde{\phi}_{\text{elc}}}{\partial \tilde{x}^2} + \frac{\partial^2 \tilde{\phi}_{\text{elc}}}{\partial \tilde{z}^2} = \begin{cases} \frac{[J]}{[\phi_{\text{elc}}]} \frac{h^2}{\sigma_{\text{elc}}^{\text{eff}}} \tilde{J}_c & (\text{cathode rl}) \\ \frac{[J]}{[\phi_{\text{elc}}]} \frac{h^2}{\sigma_{\text{elc}}^{\text{eff}}} \tilde{J}_a & (\text{anode rl}) \\ 0 & (\text{bl, ff, cc}) \end{cases} \tag{4.17}$$

$$\ell^2 \frac{\partial^2 \tilde{\phi}_{\text{ion}}}{\partial \tilde{x}^2} + \frac{\partial^2 \tilde{\phi}_{\text{ion}}}{\partial \tilde{z}^2} = \begin{cases} -\frac{[J]}{[\phi_{\text{ion}}]} \frac{h^2}{\sigma_{\text{ion}}^{\text{eff}}} \tilde{J}_c & (\text{cathode rl}) \\ -\frac{[J]}{[\phi_{\text{ion}}]} \frac{h^2}{\sigma_{\text{ion}}^{\text{eff}}} \tilde{J}_a & (\text{anode rl}) \\ 0 & (\text{el}) \end{cases} \tag{4.18}$$

for the charge transfer.

The corresponding dimensionless boundary conditions are as follows:

1) At the cathode flow field inlet

$$\tilde{u} = \frac{\varepsilon_{\text{ff}} U_c^{\text{in}}}{[u_{\text{ff,c}}]}, \quad \tilde{w} = 0, \quad \omega_{\text{O}_2} = \omega_{\text{O}_2}^{\text{in}}, \quad \frac{\partial \tilde{\phi}_{\text{elc}}}{\partial \tilde{x}} = 0; \tag{4.19}$$

2) At the anode flow field inlet

$$\tilde{u} = \frac{\varepsilon_{\text{ff}} U_a^{\text{in}}}{[u_{\text{ff,a}}]}, \quad \tilde{w} = 0, \quad \omega_{\text{H}_2} = \omega_{\text{H}_2}^{\text{in}}, \quad \frac{\partial \tilde{\phi}_{\text{elc}}}{\partial \tilde{x}} = 0; \tag{4.20}$$

3) At the flow field outlets

$$\tilde{p}_a^{\text{out}} = \tilde{p}_c^{\text{out}} = \frac{p^{\text{out}} - p^{\text{ref}}}{[p]}, \quad \frac{\partial \omega_i}{\partial \tilde{x}} = \frac{\partial \tilde{\phi}_{\text{elc}}}{\partial \tilde{x}} = 0; \tag{4.21}$$

4) At the cell top surface

$$\tilde{\phi}_{\text{elc},c} = \frac{V_{\text{cell}} - \phi_{\text{elc},c}^{\text{ref}}}{[\phi_{\text{elc},c}]}; \quad (4.22)$$

5) At the cell bottom surface

$$\tilde{\phi}_{\text{elc},a} = \frac{0 - \phi_{\text{elc},a}^{\text{ref}}}{[\phi_{\text{elc},a}]}; \quad (4.23)$$

6) At the vertical walls of current collectors

$$\frac{\partial \tilde{\phi}_{\text{elc}}}{\partial \tilde{x}} = 0; \quad (4.24)$$

7) At the vertical walls of backing layers

$$\tilde{u} = 0, \quad \frac{\partial \omega_i}{\partial \tilde{x}} = \frac{\partial \tilde{\phi}_{\text{elc}}}{\partial \tilde{x}} = 0; \quad (4.25)$$

8) At the vertical walls of reaction zone layers

$$\tilde{u} = 0, \quad \frac{\partial \omega_i}{\partial \tilde{x}} = \frac{\partial \tilde{\phi}_{\text{elc/ion}}}{\partial \tilde{x}} = 0; \quad (4.26)$$

9) At the vertical walls of the electrolyte

$$\frac{\partial \tilde{\phi}_{\text{ion}}}{\partial \tilde{x}} = 0; \quad (4.27)$$

10) At current collector/flow field interface

$$\tilde{w} = 0, \quad \frac{\partial \omega_i}{\partial \tilde{z}} = 0; \quad (4.28)$$

11) At the backing /reaction zone interface

$$\frac{\partial \tilde{\phi}_{\text{ion}}}{\partial \tilde{z}} = 0; \quad (4.29)$$

12) At the reaction zone /electrolyte interface

$$\tilde{w} = 0, \quad \frac{\partial \omega_i}{\partial \tilde{z}} = \frac{\partial \tilde{\phi}_{\text{elc}}}{\partial \tilde{z}} = 0. \quad (4.30)$$

4.3.2. Reference and scale factors

The next step is to determine the unknown reference factors including p^{ref} and $\phi_{\text{elc}}^{\text{ref}}$,

and the unknown scaling factors including $[u]$, $[w]$, $[p]$, $[p']$, $[\phi_{\text{elc}}]$, $[\phi_{\text{ion}}]$, $[\rho]$,

$[\mathbf{i}]$, $[J]$, $[M]$, $[D_{ij}]$, and $[\mathcal{D}_{ij}^{\text{eff}}]$. These factors are specified to ensure that the dimensionless dependent variables and their derivatives are bounded to $\mathcal{O}(1)$, such that the importance of each dimensionless term in the non-dimensionalized governing equations can be determined according to the magnitude of its dimensionless coefficient group.

4.3.2.1. Reference factors

Referring to Eq. (4.21), the reference pressure factor p^{ref} for both the pressure p and modified pressure p' is equal to the outlet pressure of the air and fuel channels,

$$p^{\text{ref}} = p^{\text{out}} = p_{\text{atm}}, \quad (4.31)$$

such that the pressure drop becomes zero at the outlet. Similarly, the electronic potential reference factor ϕ^{ref} is

$$\phi_{\text{elc,c}}^{\text{ref}} = V_{\text{cell}} \quad (4.32)$$

for the cathode by Eq. (4.22), and

$$\phi_{\text{elc,a}}^{\text{ref}} = 0 \quad (4.33)$$

for the anode by Eq. (4.23).

4.3.2.2. Scale factors for velocity and pressure drop

The scale factor of the streamwise velocity for the flow field is obtained by setting the dimensionless inlet velocity to one for the inlet boundary conditions by Eqs. (4.19) and (4.20). Thus, we have

$$[u_{\text{ff}}] \sim \varepsilon_{\text{ff}} U^{\text{in}} \sim 10^{-1} \text{ m s}^{-1}, \quad (4.34)$$

for the anode and cathode, in which $\varepsilon_{\text{ff}} = n w_{\text{fc}} / (n w_{\text{fc}} + (n+1) w_{\text{rib}})$ as introduced in Section 4.2.1, and $\varepsilon_{\text{ff}} \sim 10^{-1}$. According to the x -component of Eq. (4.12), the scale

factor for the streamwise pressure drop in the flow field, $[p_{ff}]$, is determined by

$$[p_{ff}] \sim \frac{\mu_{\text{mix}} L [u_{ff}]}{\kappa_{ff}} \sim 10 \text{ Pa.} \quad (4.35)$$

Here, $\kappa_{ff} \sim 10^{-8} \text{ m}^2$ given by Eq. (4.2). The typical values of μ_{mix} and L is $10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}$ and 10^{-1} m , respectively. If the streamwise pressure drop in the flow field is considered as the driving force for flow at the flow field/backing layer interface, the scale factor of the modified pressure for the backing layer, $[p'_{bl}]$, is estimated as

$$\frac{[p'_{bl}]}{L} \sim \frac{[p_{ff}]}{L} \sim \frac{\mu_{\text{mix}} [u_{ff}]}{\kappa_{bl}}, \quad (4.36)$$

such that $[p'_{bl}] \sim [p_{ff}]$. It is approximated that $[p'_{rl}] \sim [p'_{bl}]$ as the pressure is continuous across the backing/reaction zone interface. Substituting Eq. (4.35) into Eq. (4.36) results in

$$[u_{bl}] \sim \frac{\kappa_{bl}}{\kappa_{ff}} [u_{ff}]. \quad (4.37)$$

For the SOFC investigated here, a typical value of 10^{-12} m^2 [70] is used for the permeability, κ_{bl} , thereby $[u_{bl}] \sim 10^{-5} \text{ m s}^{-1}$ by Eq. (4.37). The same scale factor is applied to the streamwise velocity in the reaction zone layer, because they are continuous across the backing/reaction zone interface. Thus, we have

$$[u_{bl}] \sim [u_{rl}], \quad (4.38)$$

On the other hand, for the scale factor of the normal velocity, we start from $[w]$ for the reaction zone layer. In fuel cell, the normal flow in porous layers is mainly caused by the electrochemical reactions in reaction zone layers. Hence, we balance the normal inertia term with the mass source due to reaction in Eq. (4.11) to get

$$[w_{rl}] \sim \frac{[M][J]h_{rl}}{F[\rho]} \sim 10^{-3} \text{ m s}^{-1}. \quad (4.39)$$

The scale factor for the molecular weight of gas mixture, $[M]$, is estimated via the constitutive relation, $M = \sum_{i=1}^3 x_i M_i$, with the inlet flow composition, resulting in $[M_a] \sim 10^{-3} \text{ kg mol}^{-1}$ and $[M_c] \sim 10^{-2} \text{ kg mol}^{-1}$. The magnitude of the volumetric current density is related to the output current density of the cell as $[J] \sim [i]/h_{\text{rl}}$ given by Eq. (4.52) which is introduced in Section 4.3.2.4. Typically, $[J] \sim 10^8 \text{ A m}^{-3}$ at current densities of around 10^3 A m^{-2} . The scale factor for the density of the working fluid is estimated by the density of the inlet flow, because the air and fuel flows are generally considered as incompressible or weakly compressible. Then, the typical values of $[\rho]$ is $10^{-1} \text{ kg m}^{-3}$ and $10^{-2} \text{ kg m}^{-3}$ for the air and fuel flow, respectively, which is given by $[\rho] \sim p^{\text{in}}[M]/RT^{\text{in}}$.

In the backing layer, there is no electrochemical reaction. The normal velocity scale of the backing layer is the same as that of the reaction zone layer, since the normal velocity is continuous at the interfaces between adjacent porous layers. Therefore, we have

$$[w_{\text{bl}}] \sim [w_{\text{rl}}]. \quad (4.40)$$

In the volume-averaged flow field, the normal velocity is bounded between the velocity at the flow field/backing layer interface and zero at the top wall of the flow field. As such, $[w_{\text{ff}}]$ is estimated by $[w_{\text{bl}}]$, *i.e.*,

$$[w_{\text{ff}}] \sim [w_{\text{bl}}]. \quad (4.41)$$

It is shown that $[u_{\text{bl}}] \sim [u_{\text{rl}}] \sim 10^{-5} \text{ m s}^{-1}$ and $[w_{\text{bl}}] \sim [w_{\text{rl}}] \sim 10^{-3} \text{ m s}^{-1}$. Meanwhile, the backing and reaction zone layers of SOFCs are typically slender, such that $\ell \ll O(1)$. These imply

$$[w] \gg \ell[u] \quad (4.42)$$

for the backing and reaction zone layers in Eqs. (4.11), (4.15), and (4.16), such that the streamwise inertia and diffusion terms in the backing layer and the reaction zone layer are neglected without scarifying the leading-order physics. In short, mass is mainly transported across the shortest distance that is in the normal direction from the reaction zone layer to the flow field, and the streamwise mass transport in the backing and reaction zone layers is safely neglected.

4.3.2.3. Scale factors for diffusivity and correlation

The scale factor for the effective multicomponent Fick diffusivity $[\mathcal{D}_{ij}^{\text{eff}}]$ is determined via the constitutive relation between $[\mathcal{D}_{ij}^{\text{eff}}]$ and the effective binary diffusivity $[D_{\alpha-\beta}^{\text{eff}}]$ presented in Table 3.1. Considering x_i and ω_i are in the same order of magnitude, we get $[\mathcal{D}_{ij}^{\text{eff}}] \sim [D_{ij}^{\text{eff}}]$. The scale factor for the effective binary diffusivity is

$$[D_{ij}^{\text{eff}}] = \begin{cases} [D_{ij}] & (\text{ff}) \\ \varepsilon^{1.5} [\mathcal{D}_{ij}] & (\text{bl, rl}) \end{cases} \quad (4.43)$$

where $[D_{ij}]$ is the scalar of the original binary diffusivity and $[\mathcal{D}_{ij}]$ for the combined diffusivity involving both the binary and Knudsen diffusivity. The magnitude of $[D_{ij}]$ is set according to the value of D_{ij} for the inlet flow, i.e., $[D_{ij}] \sim D_{ij}^{\text{in}}$. Meanwhile, $[\mathcal{D}_{ij}]$ is determined by the formulation of $\mathcal{D}_{ij}$ presented in Table 3.1, such that

$$[\mathcal{D}_{ij}] \sim [D_{ij}][D_{\text{Kn},i}]/([D_{ij}] + [D_{\text{Kn},i}]) \quad (4.44)$$

in which $[D_{\text{Kn},i}] \sim 2r(8RT/\pi M_i)^{1/2}/3$. As a result, the effective multicomponent Fick diffusivity, $[\mathcal{D}_{ij}^{\text{eff}}]$, is about $10^{-4} \text{ m}^2 \text{ s}^{-1}$ for the anode and $10^{-5} \text{ m}^2 \text{ s}^{-1}$ for the cathode.

In addition, the correlation factor in Eq. (4.15) for spatial smoothing is a number between zero and one, such that

$$\zeta \sim 10^{-1}. \quad (4.45)$$

4.3.2.4. Scale factors for potential and current density

For the scale factors for the potential, $[\phi_{\text{elc}}]$ and $[\phi_{\text{ion}}]$, and current density, $[\mathbf{i}]$, we are just interested in the scale factors for the reaction zone layer, while the counterparts of these factors for the other layers do not affect the significance of the dimensionless coefficient groups in the dimensionless governing equations (4.17) and (4.18).

For the reaction zone layer, $[\phi_{\text{elc}}]$ and $[\phi_{\text{ion}}]$ are obtained by balancing the normal diffusion term with the electric source term in Eqs. (4.17) and (4.18), resulting in

$$[\phi_{\text{elc, rl}}] \sim \frac{h_{\text{rl}}^2}{\sigma_{\text{elc}}^{\text{eff}}} [J], \quad (4.46)$$

$$[\phi_{\text{ion, rl}}] \sim -\frac{h_{\text{rl}}^2}{\sigma_{\text{ion}}^{\text{eff}}} [J] \quad (4.47)$$

in which h_{rl} is the thickness of the reaction zone layer.

The electronic and ionic charge fluxes are

$$\mathbf{i}_{\text{elc}} = -\sigma_{\text{elc}}^{\text{eff}} \nabla \phi_{\text{elc}}, \quad (4.48)$$

$$\mathbf{i}_{\text{ion}} = -\sigma_{\text{ion}}^{\text{eff}} \nabla \phi_{\text{ion}}. \quad (4.49)$$

The current is drawn throughout the cell in the normal direction during operation. As such, the current density scale factor $[\mathbf{i}]$ is determined by

$$[\mathbf{i}_{\text{elc}}] \tilde{\mathbf{i}}_{\text{elc}} \sim -\sigma_{\text{elc}}^{\text{eff}} \frac{[\phi_{\text{elc}}]}{h} \frac{\partial \tilde{\phi}_{\text{elc}}}{\partial \tilde{z}}, \quad (4.50)$$

$$[\mathbf{i}_{\text{ion}}] \tilde{\mathbf{i}}_{\text{ion}} \sim -\sigma_{\text{ion}}^{\text{eff}} \frac{[\phi_{\text{ion}}]}{h} \frac{\partial \tilde{\phi}_{\text{ion}}}{\partial \tilde{z}}. \quad (4.51)$$

Then we get

$$[\mathbf{i}_{\text{elc}}] \sim \frac{\sigma_{\text{elc}}^{\text{eff}}}{h_{\text{rl}}} [\phi_{\text{elc, rl}}] \sim [J] h_{\text{rl}}, \quad (4.52)$$

$$[\mathbf{i}_{\text{ion}}] \sim -\frac{\sigma_{\text{ion}}^{\text{eff}}}{h_{\text{rl}}} [\phi_{\text{ion, rl}}] \sim -[J] h_{\text{rl}}. \quad (4.53)$$

Based on the reference and scale factors obtained above, the dimensionless governing equations (4.11) to (4.18) are asymptotically reduced by dropping the terms associated with coefficient groups in orders of magnitude smaller than $O(10^{-3})$ from the equations, as demonstrated in Appendices A to E.

4.3.3. Asymptotic spatially-smoothed formulation

As a result of the asymptotic reduction, the original 2D spatially-smoothed model consisting of steady-state elliptic PDEs (4.1), (4.4) and (4.6) as well as (3.1) to (3.12) become an asymptotic 2D model of ODEs and parabolic PDEs in the porous flow fields and ODEs in the rest of the cell. Moreover, some of the boundary conditions by Eqs. (4.19) to (4.30) become redundant for the reduced model. For the parabolic PDEs in the flow field, only the boundary conditions at the inlet are necessary. The downstream outlet conditions are not needed any more since the PDEs become parabolic now. The ODEs only require boundary conditions at the internal, upper, and lower boundaries of the cell. The inlet, outlet, and vertical wall conditions become redundant for the ODEs and thus are removed. The governing equations and boundary conditions of the asymptotically spatially-smoothed isothermal (ASSI) model are presented in Table 4.2. The dimensional form the ASSI model is used for numerical implementation to solve for the dependent variables. The obtained 2D ASSI model is computationally treated as a 1D domain in the normal direction ($\mathbf{e}_z$) with space marching in the streamwise direction ($\mathbf{e}_x$), as schematically shown in Fig. 4.1e. The space-marching algorithm is applied to handle the variation of dependent variables in the streamwise direction.

Table 4.2 Governing equations and boundary conditions of the ASSI P-SOFC model.

Domain	Governing equations
Flow field	$\frac{\partial}{\partial x}(\rho u) + \frac{\partial}{\partial z}(\rho w) = 0, \quad \frac{\partial p}{\partial x} = -\frac{\mu_{\text{mix}}}{\kappa_{\text{ff}}} u, \quad \frac{\partial p}{\partial z} = 0,$ $\frac{\partial}{\partial x}(\rho u \omega_i) + \frac{\partial}{\partial z}(\rho w \omega_i) = \frac{\partial}{\partial z} \left(\rho \omega_i \sum_{j=1}^n \left(\varepsilon_{\text{ff}} \mathcal{D}_{ij} \frac{\partial x_j}{\partial z} \right) \right);$
Backing layer	$\frac{\partial}{\partial z}(\rho w) = 0, \quad \frac{\partial p}{\partial z} = -\frac{\mu_{\text{mix}}}{\kappa} w,$ $\frac{\partial}{\partial z}(\rho w \omega_i) = \frac{\partial}{\partial z} \left(\rho \omega_i \sum_{j=1}^n \left(\zeta \mathcal{D}_{ij}^{\text{eff}} \frac{\partial x_j}{\partial z} \right) \right), \quad \frac{\partial}{\partial z} \left(-\sigma_{\text{elc}}^{\text{eff}} \frac{\partial \phi_{\text{elc}}}{\partial z} \right) = 0,$
Reaction zone layer	$\frac{\partial}{\partial z}(\rho w) = \begin{cases} \frac{M_{\text{O}_2} J_c}{4F} & (\text{cathode rl}) \\ \frac{M_{\text{H}_2\text{O}} J_a}{2F} - \frac{M_{\text{H}_2} J_a}{2F} & (\text{anode rl}) \end{cases}, \quad \frac{\partial p}{\partial z} = -\frac{\mu_{\text{mix}}}{\kappa} w,$ $\frac{\partial}{\partial z}(\rho w \omega_i) - \frac{\partial}{\partial z} \left(\rho \omega_i \sum_{j=1}^n \left(\mathcal{D}_{ij}^{\text{eff}} \frac{\partial x_j}{\partial z} \right) \right) = \begin{cases} +\frac{M_{\text{O}_2} J_c}{4F} & (\text{O}_2, \text{cathode rl}) \\ -\frac{M_{\text{H}_2} J_a}{2F} & (\text{H}_2, \text{anode rl}) \end{cases},$ $\frac{\partial}{\partial z} \left(-\sigma_{\text{elc}}^{\text{eff}} \frac{\partial \phi_{\text{elc}}}{\partial z} \right) = -J, \quad \frac{\partial}{\partial z} \left(-\sigma_{\text{ion}}^{\text{eff}} \frac{\partial \phi_{\text{ion}}}{\partial z} \right) = J;$
Electrolyte	$\frac{\partial}{\partial z} \left(-\sigma_{\text{ion}}^{\text{eff}} \frac{\partial \phi_{\text{ion}}}{\partial z} \right) = 0.$
Location	Boundary conditions
Inlets	$u = \varepsilon_{\text{ff}} U_{\text{c,a}}^{\text{in}}, \quad w = 0, \quad \omega_{\text{O}_2} = \omega_{\text{O}_2}^{\text{in}}, \quad \omega_{\text{H}_2} = \omega_{\text{H}_2}^{\text{in}};$
Top and bottom	$u = w = 0, \quad \partial \omega_i / \partial z = 0;$
flow field/backing	$\phi_{\text{elc,c}} = V_{\text{cell}}, \quad \phi_{\text{elc,a}} = 0;$
Backing/reaction zone	$\partial \phi_{\text{ion}} / \partial z = 0;$
Reaction zone/electrolyte	$w = 0, \quad \partial \omega_i / \partial z = \partial \phi_{\text{elc}} / \partial z = 0.$

4.4. Numerical implementation

The 3D P-SOFC model, the 2D cross-section model for the discrete values of correlation factors, the 2D spatially-smoothed model, and the ASSI model are solved in COMSOL.

The linear direct solver PARDISO are employed for the 3D, 2D cross-section, and 2D spatially-smoothed models, while a transient solver with the backward differentiation

formula method for the ASSI model to march in space (treating x as a time like variable).

The details of the solver algorithms of COMSOL can be found in Refs. [195, 196].

When plotting the polarization curves, the average current density of the 2D model is calculated by

$$i_{\text{avg}} = \iint_A i_{\text{bl},z} dx dz / A \quad \text{or} \quad \pm \frac{1}{L} \iint_A J dx dz, \quad (4.54)$$

in which the area of the interface between the backing and reaction zone layers

$A_{\text{bl/bl}} = L(w_{\text{rib}} + w_{\text{fc}})/2$. For the 3D model, the average current density is obtained by Eq. (3.35). More details about the implementation of the 3D model can be found in Section 3.5.

When determining the correlation factors, the discrete value of $\zeta(\mathcal{H}, \mathcal{W})$ for the cathode or anode is set as a dependent variable described by the following algebraic relation at the backing/reaction zone interface,

$$\underbrace{\int_0^{(w_{\text{fc}} + w_{\text{rib}})/2} \omega_{\text{O}_2/\text{H}_2} \Big|_{\text{bl/rl}} dy}_{\text{real geometry (Fig. 4.2c)}} - \underbrace{\int_0^{(w_{\text{fc}} + w_{\text{rib}})/2} \omega_{\text{O}_2/\text{H}_2} \Big|_{\text{bl/rl}} dy}_{\text{volume-averaged geometry (Fig. 4.2d)}} = 0, \quad (4.55)$$

which coupled the computational domains in the cross section of the real geometry (Fig. 4.2c) and the domains of the porous counterpart (Fig. 4.2d).

When implementing the ASSI model in COMSOL, the stream function Ψ is applied to the flow field [201],

$$u = \frac{1}{\rho} \frac{\partial \Psi}{\partial z}, \quad w = -\frac{1}{\rho} \frac{\partial \Psi}{\partial x}, \quad (4.56)$$

such that the continuity equation for the flow field is automatically satisfied. This reduces the number of dependent variables, and only p and Ψ are needed to solve for, instead of the previous p , u , and w . The boundary conditions at the inlets for the momentum equation becomes

$$\Psi = U_{a,c}^{\text{in}} \rho_{a,c}^{\text{in}} z. \quad (4.57)$$

At the current collector/flow field interface, the boundary condition for the momentum equation becomes

$$\Psi|_{\text{cc/ff}} = U_{\text{a,c}}^{\text{in}} \rho_{\text{a,c}}^{\text{in}} z. \quad (4.58)$$

Calibration and validation of the developed polynomials of the correlation factors, and post-processing of the model predictions are performed in MATLAB R2010a. In addition, it should be noted that the present full and reduced models can be solved with other numerical methods and is thus not limited to finite-elements alone.

4.5. Verification

As analysed previously, the original 3D flow field is volume-averaged to a porous counterpart, in which the momentum transport is described by Darcy's law associated with effective properties and a correlation for the variations in the pathways of diffusive transport in the backing layer due to ribs. The 3D spatially smoothed model is then further reduced to 2D and finally to a set of parabolic PDEs and ODEs associated with space marching, namely the ASSI model. In this section, the feasibility of the reduced models in capturing the behaviour of their 3D counterpart is verified in terms of the global polarization curve and the local distributions of species mass fraction, current density, and pressure. At last, a comparison in the computational cost in terms of memory requirement and solution time between the 3D, 2D, and ASSI models is provided.

First of all, the global cell performance is verified by comparing the polarization curves predicted by the original and reduced models for different channel widths and backing layer thicknesses. The results predicted by the 2D model with correlation factors agree well with the results by the 3D counterpart, as illustrated in Fig. 4.4. The maximum relative error generally occurs at the limiting current densities. For narrow

flow channels with a small $\mathcal{W}$ such as 0.4 in Fig. 4.4a, the maximum relative error is 4% at 0.3V for $\mathcal{H}_c = 0.1$ and $\mathcal{H}_a = 0.5$, and it increases to 10% if the correction factors are not involved in the 2D counterpart model. This illustrates the necessity of the correlation factors for modeling to correct the pathways of diffusion in the backing layers, especially for models with narrow flow channels of small $\mathcal{W}$. On the other hand, when $\mathcal{W}$ increases, the difference between the 2D models with and without the correlation factors becomes smaller, such as a maximum relative error of 0.5% with and 2% without the factors at 0.3V in Fig. 4.4a. A similar situation is observed in Fig. 4.4b as well. The possible reason is that the narrow ribs corresponding to large $\mathcal{W}$ cause little variation in the pathways of diffusion from the flow field to the backing layer. In contrast, the variance in pathways becomes significant for the cells with wide ribs, and hence it has to be addressed by the correlation factors when applying spatial smoothing. Furthermore, the two correlation factors ζ_c and ζ_a can work separately when varying the channel width and backing layer thickness of the cathode and/or anode, as illustrated in Fig. 4.4a and 4.4b. In addition, the polarization curves by the ASSI model with the correlation factors, also agree well with its 3D counterpart, with relative errors that do not exceed 3% for narrow channels and 0.8% for wide channels.

Fig. 4.4 Polarization curves by 3D models with a $\mathcal{W}_c$ of 0.4 ($\blacktriangledown$) and 0.7 ($\blacksquare$), and $\mathcal{W}_a = 0.4$ at (a) $\mathcal{H}_c = 0.1$ and $\mathcal{H}_a = 0.5$, and (b) $\mathcal{H}_c = 0.5$ and $\mathcal{H}_a = 0.1$, by 2D volume-averaged counterparts with (-) and without (--) correlation factors, and by 2D ASSI models for the $\mathcal{W}_c$ of 0.4 (+) and 0.7 ($\times$).

Secondly, in order to further investigate how well the correlation factors can correct the pathways of diffusion and enable the model to predict the cell performance, the 2D spatially-smoothed model is verified in terms of the local values of key dependent variables at the backing/reaction zone interface, which is in the xy -plane in Fig. 4.1. Fig. 4.5 shows the local distribution of oxygen and hydrogen at this interface, predicted by the (a, b) 3D model and (c, d) 2D counterpart, for $\mathcal{H}_c = 0.125$, $\mathcal{H}_a = 0.375$, and $\mathcal{W} = 0.55$ at 0.2V. The distributions of variables in Fig. 4.5c and 4.5d are obtained by extruding the solutions at the 1D backing/reaction zone interface of the 2D counterpart model to the spanwise direction ($\mathbf{e}_y$). Comparing the distribution of oxygen in Fig. 4.5a with Fig. 4.5c, the mass fractions predicted by the two models descend along the streamwise direction

in a similar way, and so do the mass fractions of hydrogen in Fig. 4.5b and 4.5d. There is variation in pointwise details predicted by two models, since the equations of the 2D reduced model just describe the average behaviour of its 3D counterpart. The loss of information due to spatial smoothing can be indicated by the relative error between the local dependent variables predicted by the reduced models and the average solutions by the 3D counterpart, as discussed below.

Fig. 4.5 Distribution of (a) oxygen and (b) hydrogen at the backing/reaction zone interface in the original geometry with channels and ribs (separated by the dashed line), and (c, d) the volume-averaged counterpart, with $\mathcal{H}_c = 0.125$, $\mathcal{H}_a = 0.375$, $\mathcal{W} = 0.55$ at 0.2 V.

Next, we proceed to verify the reduced models in terms of local dependent variables. The local mass fractions and current density predicted by the 2D spatially-smoothed and ASSI models along the streamwise direction at the backing/reaction zone interface agree well with the averaged solutions of the original 3D model, as illustrated in Fig. 4.6. Comparing the results of the 3D and 2D models, the maximum relative error is around 10% for the mass fraction of oxygen and 4% for hydrogen, 1% and 2% for the anode and

cathode local current densities respectively at a low cell voltage of 0.2V corresponding to a high average current density. For the ASSI model, the maximum relative error of 12% in ω_{H_2} and of 5.6% in ω_{O_2} at the flow outlets may be attributed to the fact that the present correlation factors are achieved based on $\omega_{\text{O}_2, \text{H}_2}^{\text{in}}$ as the boundary condition at the flow field/backing interface for the 2D cross section model, as discussed in Section 4.2.2. In Fig. 4.6b, the profiles for the anode and cathode local current densities overlap with each other, due to the conservation of normal current throughout the cell. The relative errors in local current densities predicted by the reduced models do not exceed 2%.

Fig. 4.6 (a) Average mass fraction of oxygen and hydrogen, and (b) average current density at the backing/reaction zone interface on cathode (-) and anode (-) at 0.8 (▼), 0.5 (■), 0.2 V (▲), by 3D (symbols), 2D spatially-smoothed (lines), and 2D ASSI (×) models with $\mathcal{H}_c = 0.125$, $\mathcal{H}_a = 0.375$, $\mathcal{W} = 0.55$. Filled symbols stand for cathode variables and unfilled for anode. Error bars represent standard deviation.

In addition, the error bars in Fig. 4.6 represent the standard deviation $\sigma(x)$ that

reflects the spread of the dependent variables due to ribs for the 3D model and is formulated in Table 4.3. For the distribution of oxygen, the large standard deviation at 0.2V indicates that the local mass fraction of oxygen badly deviate from the average spanwise value that is the counterpart of the spatial smoothed solutions by the 2D model. This is consistent with the variation in the pointwise details between Fig. 4.5a and 4.5c for oxygen. Similarly, the small variation between the mass fraction of hydrogen by the 3D (Fig. 4.5b) and 2D (Fig. 4.5d) models correlates to the small standard deviation for hydrogen in Fig. 4.6a.

Table 4.3 Additional constitutive relations of the P-SOFC model.

$\bar{\Omega}(x) = \frac{2}{w_{fc} + w_{rib}} \int_0^{(w_{fc} + w_{rib})/2} \Omega(x, y, z _{bl/rl}) dy$
$\sigma(x) = \left(\frac{2}{w_{fc} + w_{rib}} \int_0^{(w_{fc} + w_{rib})/2} \left(\Omega(x, y, z _{bl/rl}) - \bar{\Omega}(x) \right)^2 dy \right)^{1/2}$
$\bar{\Omega}(x)_{ic} = \frac{1}{A_{\perp}^{(ic)}} \iint_{A_{\perp}^{(ic)}} \Omega(x, y, z)_{ic} dy dz \quad (3D)$
$\bar{\Omega}(x)_{fc} = \frac{1}{A_{\perp}^{(fc)}} \iint_{A_{\perp}^{(fc)}} \Omega(x, y, z)_{fc} dy dz \quad (3D)$
$\bar{\Omega}(x)_{ff} = \frac{1}{h_{fc}} \int_0^{h_{fc}} \Omega(x, z)_{fc} dz \quad (2D)$

Fourthly, in order to investigate the computational accuracy of the predicted dependent variables in the flow field, the averaged pressure and mass fractions of oxygen and hydrogen in the flow fields of the 3D model and its 2D and ASSI counterparts are compared. The formulae of these average quantities, denoted as $\bar{\Omega}(x)_{ff}$, are presented in Table 4.3. As illustrated in Fig. 4.7, the maximum relative error is 0.6% for the mass fraction of oxygen and 3% for hydrogen predicted by the 2D counterpart, and 2.2% in ω_{O_2} and 11% in ω_{H_2} by the ASSI model. The maximum

relative error in gauge pressure does not exceed 14% for both two reduced models, and this relative error becomes negligible in terms of absolute pressure. Similar good agreement in the predicted solutions by the original and reduced models is achieved for a range of cell voltages from small to large values (not shown here).

Fig. 4.7 Average cathode (■) and anode (◆) gauge pressure, mass fraction of oxygen (▼) and hydrogen (▲) in a 3D flow field with $\mathcal{H}_c = 0.125$, $\mathcal{H}_a = 0.375$, $\mathcal{W} = 0.55$ at 0.2 V. The volume-averaged pressure (--) and mass fraction (-) by the 2D spatially-smoothed model. The pressure (+) and mass fraction (×) by the 2D ASSI model.

4.6. Computational cost analysis

Finally, a comparison in memory requirement and computing time is carried out in order to verify the reduction in the computational cost and the efficiency of the reduced models. Generally, the highly nonlinear nature of a 3D SOFC model requires a high computational cost for numerical solutions. This is more apparent when solving a stack model that may consist of tens or hundreds of single cells. In the present work, based on a single-cell mesh (case (i)), the mesh density for edges along the normal direction ($\mathbf{e}_z$) in each domain is multiplied by 10 and 50 times to represent a stack of 10 (case (ii)) and

50 (case (iii)) cells. The degree of freedom (DOF) is used to approximately embody the number and order of mesh elements, coupled with the number of unknowns to be solved for. As shown in Table 4.4, for the single-cell mesh, the spatial smoothing methodology ensures a reduction in solution time from more than 10 minutes by 3D modeling to less than 5 seconds by 2D modeling when solving at a single value of cell voltage (cases (i)). Moreover, the DOF increases by one or two orders of magnitude when the modeling arises from the single-cell to stack level. The high DOF on the order of $O(10^6)$ of the 3D stack models makes the 64G-RAM workstation run out of memory when solving with a direct solver in COMSOL Multiphysics 3.5a. One may need to switch to an iterative solver to address the issue of computational cost for cases (ii) and case (iii). However, the solutions of these two cases are not pursued any further, since the 2D reduced stack models can be solved properly with a relatively small amount of memory with the direct solver. Furthermore, the solution time for the 2D model is 2 orders of magnitude lower than that for the original 3D model, when solving the single-cell model over a range of cell voltage from 1.1 to 0.2V (case (iv)). Based on the 2D spatially-smoothed model for stack modeling, the computational cost is further reduced via asymptotic reduction, such as one order of magnitude lower in solution time. All in all, the reduced models are less computationally expensive than the original 3D model with respect to DOF, convergence time, and memory requirement.

Table 4.4 Computational cost of modeling.

		3D	2D	2D ASSI
Case (i) (1-cell mesh)	DOF	2.5×10^5	1.7×10^4	1.7×10^2
	Time (s) for 0.8, 0.5, 0.2 V	$(5, 6.2, 7.8) \times 10^2$	4.6, 4.6, 4.2	1.9, 1.9, 2.1
	Memory (GB)	6.7	0.28	0.14
Case (ii) (10-cell mesh)	DOF	2.3×10^6	1.5×10^5	1.4×10^3
	Time (s) for 0.8, 0.5, 0.2 V	-	43, 38, 38	3.2, 3.3, 3.5
	Memory (GB)	-	1.14	0.17
Case (iii) (50-cell mesh)	DOF	1.2×10^7	7.7×10^5	6.9×10^3
	Time (s) for 0.8, 0.5, 0.2 V	-	$(2.3, 2, 2) \times 10^2$	7.4, 7.6, 7.8
	Memory (GB)	-	5	0.19
Case (iv) (1-cell mesh)	DOF	2.5×10^5	1.7×10^4	1.7×10^2
	Time (s) from 1.1 – 0.2 V	3.8×10^3	16	20
	Memory (GB)	7.2	0.3	0.17

4.7. Summary

This chapter elaborates the reduction of a 3D isothermal P-SOFC model by spatial smoothing with developed correlation factors followed by asymptotic reduction, resulting in a 2D asymptotic spatially-smoothed isothermal (ASSI) model that is essentially a set of parabolic PDEs and ODEs with a space marching algorithm. In view of the quantified loss of information due to model reduction, good agreement between the ASSI and full 3D models is obtained in view of the global polarization curve and the average local properties at the backing/reaction zone interfaces and in the flow fields.

Particularly, the developed correlation factors for spatial smoothing can account for the coupling effects between governing equations, apart from the variation in diffusion pathways due to ribs, because they are derived based on the full set of governing equations over a cross section through all the solid layers, instead of solving a Laplace equation [173]. They are functions of general geometrical parameters of the electrode (*i.e.*, the anode or cathode channel width and backing layer thickness) and thus can work for the anode and electrode separately. Moreover, the correlation factors are especially essential for models with narrow flow channels. After removing the correlation factors

from modeling, the maximum relative error increases from 4% to 10% for the polarization curve predicted by the 2D spatially-smoothed model with narrow channels. In contrast, this error changes from 0.5% to 2% for the model with wide channels.

Compared with the existing 2D P-SOFC models, the fidelity of model predictions is reserved by the developed correlation factors and effective transport properties that embody the influence of ribs on transport processes and the information pertaining to the neglected third dimension (*i.e.*, the spanwise direction along the cell width here). When performing spatial smoothing for model reduction, there is no loss in physical information except that the local pointwise information is replaced with spanwise averaged counterparts. Moreover, the obtained 2D ASSI model can be solved in a 1D domain with a space marching algorithm, such that the numerical computation is sped up further. The solution time and memory requirements are reduced by more than two orders of magnitude.

Furthermore, apart from the co-flow configuration, the presented method of spatial smoothing can also be applied to the counter- and cross-flow configurations for 3D P-SOFCs. The counter-flow configuration allows further model reduction from 3D to 2D via the asymptotic analysis. With the research results based on a flow field of straight channels, spatial smoothing for more complicated flow fields such as a serpentine design becomes possible as well.

Chapter 5

Development of Advanced

Spatially-Smoothed Isothermal Cell Models

5.1. Introduction

In this chapter, novel variation factors are developed for spatial smoothing to capture the variability of dependent variables – here, mass fractions – underneath ribs along the cell width in the spanwise direction, such that an advanced 2D spatially-smoothed isothermal model is obtained. Section 5.2 depicts the 3D isothermal P-SOFC model and its 2D spatially-smoothed counterpart investigated in this chapter, and also presents the development of the novel variation factors accounting for the spanwise variations of local mass fractions. Section 5.3 describes the numerical implementation of the 3D and 2D models. Based on the simulation results, Section 5.4 verifies the advanced 2D spatially-smoothed model with its 3D counterpart in terms of the average and variation of local mass fractions as well as global current output. The validity of the advanced spatially-smoothed isothermal model is investigated for various cell designs with parallel flow channels.

5.2. Mathematical model

5.2.1. Governing equations and boundary conditions

The 3D P-SOFC considered here comprises a pair of air and fuel flow channels (fc), two interconnects (ic), two porous backing layers (bl), two reaction zone layers (rl), and a solid electrolyte (el), as shown in Fig. 5.1a. Considering the symmetry of the planar cell structure, only half of the repeating unit is resolved with symmetry boundary conditions at the cross section A-A. The cell is fed by air for the cathode and by humid hydrogen for the anode in a co-flow configuration. Eqs. (3.1) to (3.10) are applied to describe the cell performance under an isothermal condition. The boundary conditions are referred to Eqs. (3.16) and (3.29). The geometrical and physical parameters as well as operating conditions can be found in Table 3.2.

The 3D model is spatially smoothed over the flow field considering plain channels as the pores and ribs as the solid matrix of a porous medium. The spatially-smoothed governing equations for the species and momentum transport are the same as those introduced previously in Section 4.2. The effective permeability, κ_{ff} , porosity, ε_{ff} , and diffusivity, $\mathcal{D}_{ij,ff}^{eff}$, introduced in Section 4.2.1 are applied to the momentum and mass transports in the flow field, so as to capture the average mechanics in the neglected spanwise direction ($\mathbf{e}_y$ in Fig. 5.1). In view of the variation of the pathways of the mass transport due to ribs as shown in Fig. 5.1b, correlation factors, $\zeta_{H_2}(\mathcal{H}, \mathcal{W})$ and $\zeta_{O_2}(\mathcal{H}, \mathcal{W})$, are needed to account for this variation. Fig. 5.1c shows the pathways of species and charge transports in a cross section with spatial smoothing.

Fig. 5.1 Schematics of (a) a repeating unit of a SOFC with one pair of fuel and air channels enclosed by ribs, and the pathways of the mass (solid arrow) and charge (dashed arrow) transport in a cross section (b) without and (c) with a volume-averaged flow field.

Based on the methodology introduced in Section 4.2.2, the discrete values of ζ_{H_2} and ζ_{O_2} are generated over $0.4 \leq \mathcal{W} \leq 0.9$ and $0.05 \leq \mathcal{H} \leq 0.55$. The dimensionless width and thickness, $\mathcal{W}$ and $\mathcal{H}$, are specified as $w_{\text{fc}}/(w_{\text{fc}} + w_{\text{rib}})$ and $(2h_{\text{bl}})/(w_{\text{fc}} + w_{\text{rib}})$, respectively. ζ_{H_2} and ζ_{O_2} are expressed as functional polynomials in the same form as Eqs. (4.8) and (4.9), and are calibrated and validated as illustrated in Fig. 5.2a with ζ_{O_2} . The resulting coefficients of the polynomials for the anode and cathode, a_{ij} and b_{ij} , are presented in Table 5.1. For the charge transport in the

spatially smoothed flow field, the effective electronic conductivity, $\sigma_{\text{elc,ff}}^{\text{eff}}$, is obtained by multiplying the conductivity of the interconnect, $\sigma_{\text{elc,ic}}$, with a factor, $1 - \varepsilon_{\text{ff}}$ [173]. No correlation factor is specified for the charge transport, because it is shown in Section 4.2.2 that the influence of ribs on the ohmic drop in the porous backings is negligible.

Fig. 5.2 The correlations for (a) the correlation factor ζ and (b) the variation factor $\tilde{\sigma}$ on the cathode side: training sets for calibration (●) and test sets for verification (◆).

Furthermore, assuming that the inlet conditions are the same for all the channels for the cathode and anode respectively, the 3D spatially smoothed geometry is reduced to a 2D counterpart in the streamwise and normal directions to capture the volume-averaged

values of the 3D solutions.

Table 5.1 Coefficients of correlation and variation factors.

<i>Correlation factors</i>	
$a_{00}, a_{01}, a_{02}, a_{03}, a_{04},$	1.562, -9.656, 21.28, -23.34, 11.52,
$a_{10}, a_{11}, a_{12}, a_{13},$	-5.411, 21.52, -2.177, -8.687,
$a_{20}, a_{21}, a_{22},$	16.32, -53.42, 15.99,
$a_{30}, a_{31},$	-11.22, 33.12,
$a_{40},$	-1.721.
$b_{00}, b_{01}, b_{02}, b_{03}, b_{04}, b_{05},$	-9.505, 91.83, -347.2, 641.8, -588.9, 216.9,
$b_{10}, b_{11}, b_{12}, b_{13}, b_{14},$	0.7869, -23.65, 94.46, -67.97, 2.189,
$b_{20}, b_{21}, b_{22}, b_{23},$	17.45, -2.769, -149, 88.92,
$b_{30}, b_{31}, b_{32},$	-52.1, 124.1, 23.48,
b_{40}, b_{41}	36.73, -96.48.
<i>Variation factors</i>	
$c_{00}, c_{01}, c_{02}, c_{03}, c_{04}, c_{05},$	5.716, -51.54, 197.3, -354.5, 322.8, -121.8,
$c_{10}, c_{11}, c_{12}, c_{13}, c_{14},$	1.075, 29.87, -117.9, 48.94, 23.13,
$c_{20}, c_{21}, c_{22}, c_{23},$	-41.01, 9.69, 254.5, -135,
$c_{30}, c_{31}, c_{32},$	125.3, -240.8, -51.93,
c_{40}, c_{41}	-96.94, 197.1.
$d_{00}, d_{01}, d_{02}, d_{03}, d_{04}, d_{05},$	2.804, -23.92, 92.48, -156.5, 139.2, -55.15,
$d_{10}, d_{11}, d_{12}, d_{13}, d_{14},$	2.93, 27.38, -118.3, 39.26, 33.11,
$d_{20}, d_{21}, d_{22}, d_{23},$	-51.71, 21.49, 280.4, -151.1,
$d_{30}, d_{31}, d_{32},$	152.9, -292.6, -54.14,
d_{40}, d_{41}	-119.1, 239.

5.2.2. Novel variation factors to capture the variability of dependent variables underneath flow channels

In addition to the prediction of the volume-averaged values of 3D solutions, novel variation factors for the 2D spatially-smoothed model are developed to account for the spanwise variability of local mass fractions in the 3D model. This section elaborates the development of the variation factors in details below.

First, the spanwise variability of mass fractions in the 3D model is quantified in terms of the standard deviations of mass fractions along the cell width. The standard

deviations are determined based on a separate two-dimensional cross-sectional model ($\mathbf{e}_y$ - and $\mathbf{e}_z$ - plane) and a spatially smoothed counterpart ($\mathbf{e}_z$ -direction) that is solved for not only the correlation factors, ζ_{H_2} and ζ_{O_2} as in Section 4.2.2 but also for the spatial deviations. In the cross-section geometry in Fig. 5.1b, the standard deviation of the mass fraction of species i at the backing/reaction zone interface, $\sigma_i|_{\text{bl/rl}}$, is evaluated by taking the square root of the average of the squared differences of the pointwise mass fractions, $\omega_i|_{\text{bl/rl}}$, from their average value, $\bar{\omega}_i|_{\text{bl/rl}}$:

$$\sigma_i|_{\text{bl/rl}} = \left(\frac{2}{w_{\text{fc}} + w_{\text{rib}}} \int_0^{(w_{\text{fc}} + w_{\text{rib}})/2} \left(\omega_i|_{\text{bl/rl}} - \bar{\omega}_i|_{\text{bl/rl}} \right)^2 dy \right)^{1/2}, \quad (5.1)$$

in which

$$\bar{\omega}_i|_{\text{bl/rl}} = \frac{2}{w_{\text{fc}} + w_{\text{rib}}} \int_0^{(w_{\text{fc}} + w_{\text{rib}})/2} \omega_i|_{\text{bl/rl}} dy. \quad (5.2)$$

Here, i refers to O_2 for the cathode and H_2 for the anode.

The resulting value of $\sigma_i|_{\text{bl/rl}}$ from Eq. (5.1) depends on not only the cell geometry but also the distribution of mass fractions – the latter varies with the current density. In particular, at high current densities, there is a significant concentration drop in the porous backings. To account for this effect, $\sigma_i|_{\text{bl/rl}}$ in Eq. (5.1) is normalized by dividing it with the change of the mass fraction across the backing layer in the cross-section model:

$$\tilde{\sigma}_i = \frac{\sigma_i|_{\text{bl/rl}}}{\Delta\omega_i}, \quad (5.3)$$

resulting in the variation factor for species i , $\tilde{\sigma}_i$. The change of the mass fraction, $\Delta\omega_i$, is the difference between the average mass fractions at the flow channel/backing and backing/reaction zone interfaces:

$$\Delta\omega_i = \frac{2}{w_{fc}} \int_0^{w_{fc}/2} \omega_i|_{fc/bl} dy - \frac{2}{w_{fc} + w_{rib}} \int_0^{(w_{fc}+w_{rib})/2} \omega_i|_{bl/rl} dy. \quad (5.4)$$

Here, we have focused on the interface between the porous backing and the reaction zone layer, because that is the interface close to which the electrochemical reactions occur in a fuel cell. If another region/layer is of interest, one could derive similar standard deviations and variation factors.

Like the correlation factors ζ developed in Chapter 4, the discrete values of $\tilde{\sigma}_i$ are employed as a training set to construct polynomials of the variation factors via surface fitting with $0.4 \leq \mathcal{W} \leq 0.7$ and $0.1 \leq \mathcal{H} \leq 0.5$. The resulting polynomials are

$$\tilde{\sigma}_{H_2}(\mathcal{H}, \mathcal{W}) = \sum_{i=0}^4 \sum_{j=0}^{5-i} c_{ij} \mathcal{H}^i \mathcal{W}^j \quad (5.5)$$

associated with a sum of squared errors (SSE) of 5×10^{-4} for the anode, and

$$\tilde{\sigma}_{O_2}(\mathcal{H}, \mathcal{W}) = \sum_{i=0}^4 \sum_{j=0}^{5-i} d_{ij} \mathcal{H}^i \mathcal{W}^j \quad (5.6)$$

with a SSE of 2×10^{-4} for the cathode. The polynomials of $\tilde{\sigma}_{H_2}$ and $\tilde{\sigma}_{O_2}$ obtained from the training set are then verified with eight test sets, respectively, and good agreement is achieved as illustrated by the result for the cathode in Fig. 5.2b. A similar result is obtained for the anode side. The coefficients, c_{ij} and d_{ij} , of Eqs. (5.5) and (5.6) are summarized in Table 5.1. Comparing the dimensionless variation factors $\tilde{\sigma}$ predicted by Eqs. (5.5) and (5.6) with their actual values over the investigated range of $\mathcal{W}$ and $\mathcal{H}$, the relative errors do not exceed 10% for $\tilde{\sigma}_{H_2}$ by Eq. (5.5) and 8% for $\tilde{\sigma}_{O_2}$ by Eq. (5.6), which are considered acceptable here. The accuracy can be improved further by adjusting the order of the polynomial and/or narrowing the ranges of $\mathcal{W}$ and $\mathcal{H}$ when calibrating Eqs. (5.5) and (5.6).

With the normalized standard deviation or variation factor, $\tilde{\sigma}_i$, specified by Eqs.

(5.3) to (5.6), the dimensional form of the standard deviation of mass fractions in the volume-averaged geometry (Fig. 5.1c), σ_i , is obtained by multiplying $\tilde{\sigma}_i$ by the difference between the spanwise average of local mass fractions at the flow field/backing layer interface and the average at the backing/reaction zone interface:

$$\sigma_i = \tilde{\sigma}_i \delta\omega_i, \quad (5.7)$$

in which the change of mass fractions $\delta\omega_i$ is given by

$$\delta\omega_i = \overline{\omega_i} \Big|_{\text{ff/bl}} - \overline{\omega_i} \Big|_{\text{bl/rl}}. \quad (5.8)$$

For the 2D spatially-smoothed model, the average mass fractions, $\overline{\omega_i} \Big|_{\text{ff/bl}}$ and $\overline{\omega_i} \Big|_{\text{bl/rl}}$, are the pointwise values on the flow field/backing layer interface and the backing/reaction zone interface, respectively. For the 3D spatially-smoothed model, they would be determined by applying Eq. (5.2) to the corresponding interface. The resulting standard deviations by Eq. (5.7) indicate how the local mass fractions in the original 3D domain deviate from their spanwise volume-averaged values that are captured by the spatially smoothed model.

5.3. Numerical implementation

The commercial finite-element solver COMSOL Multiphysics 3.5a is employed to solve the 3D, 2D cross-section coupled with 1D model, and 2D spatially-smoothed models on a 64G-RAM workstation. In short, the linear direct solver PARDISO is used; and quadratic Lagrange basis functions and a relative convergence error of 10^{-3} are employed for all variables. The regular geometry of the P-SOFC allows a straightforward application of the structured mesh with quadrilateral elements. Post-processing of the model predictions and calibration and validation of the developed polynomials of the correlation and variation factors are conducted in MATLAB R2010a. Apart from

finite-element method, the spatially smoothed model can be solved with other numerical methods as well.

5.4. Verification

In this section, the present advanced spatially-smoothed model is verified to be able to capture not only the volume-averaged values of the mass fractions of oxygen and hydrogen but also their spanwise variation underneath the ribs in the original 3D model. After that, the validity of spatial smoothing is investigated in terms of the average and spanwise variations of local mass fractions as well as the global current output in different cell designs.

First, the mass fractions of oxygen and hydrogen at the backing/reaction zone interfaces from the 2D spatially-smoothed model is compared with that from the original 3D model, as shown in Fig. 5.3. Two key findings are obtained. First, good agreement is obtained for not only the average mass fractions along the streamwise direction but also their variation in the spanwise direction. For the volume-averaged mass fractions, the relative errors do not exceed 4% at all the three voltages for the hydrogen mass fraction, and 3% at 0.8 and 0.5 V and 14% at 0.2V for oxygen. For the spanwise variation of local mass fractions that is quantified in terms of the standard deviation σ , the relative errors do not exceed 10% for the oxygen and hydrogen mass fractions. The good agreement justifies the feasibility of the variation factors given by Eqs. (5.5) and (5.6) to capture the spanwise variability of mass fractions in the original 3D domain at different current densities. The spanwise variability at a certain streamwise position in the 3D domain reflects the spread of the mass fractions along the cell width. It increases as the cell voltage decreases as shown in Fig. 5.3. This is because more oxidants and fuels are consumed at lower voltages (or higher current densities) resulting in larger gradients of

the mass fraction across the porous backings and underneath the ribs. The second finding is the depletion of oxygen tends to occur in not only the streamwise but also the spanwise direction at low cell voltages such as 0.2 V, *e.g.*, at $x = 0.09$ m, $\omega_{\text{O}_2} \approx 0.05 \pm 0.03$.

Next, the verified variation factors $\tilde{\sigma}_{\text{H}_2, \text{O}_2}$ (*i.e.*, the normalized standard deviations) are applied to investigate the variability of mass fractions underneath the ribs for different cell geometries. The geometrical features of the electrode are reflected by the correlation factor $\zeta(\mathcal{H}, \mathcal{W})$, which is formulated in terms of the dimensionless backing layer thickness and channel width. A thin backing layer and/or a narrow flow channel results in a small ζ . On the other hand, for the ζ and $\tilde{\sigma}$ that fall outside of the region of validity of the polynomials, their values are determined by interpolation on the fitted surface shown in Fig. 5.2.

Fig. 5.3 Average mass fractions of (a, c, e) oxygen and (b, d, f) hydrogen at the backing/reaction zone interface at (a, b) 0.8, (c, d) 0.5, and (e, f) 0.2 V: 3D model with $\mathcal{H}_c = 0.125$, $\mathcal{H}_a = 0.375$, $\mathcal{W} = 0.55$ (■); 2D spatially-smoothed counterpart (—). Standard deviations for 3D (▼) and 2D spatially-smoothed (—) solutions.

Fig. 5.4 compares the 3D and 2D solutions for cell designs with different cathode thicknesses. The relative errors for the oxygen mass fractions do not exceed 4% with a thick cathode backing layer ($\zeta_{O_2} = 0.7$ in Fig. 5.4a) and 5% with a thin backing layer ($\zeta_{O_2} = 0.072$ in Fig. 5.4b). In comparison with the cell having a thick backing layer in

Fig. 5.4a, the design with a thin backing layer in Fig. 5.4b undergoes larger standard deviations that are more comparable with the average value of mass fractions, such as $\sigma_{\text{O}_2} = 0.047$ with respect to $\omega_{\text{O}_2} = 0.09$ at $x = 0.09$ m at 0.4 V. Such a large variation of the mass fraction can be attributed to the large consumption of reactants at high current densities as well as the thin porous backing layer that hinders the gas diffusion in the spanwise direction. Especially, when the thickness of the cathode backing layer is reduced, it becomes more difficult for the air flow to diffuse along the cell width towards the locations under the ribs. Consequently, the variation in the distribution of oxygen mass fractions along the cell width increases, such that the standard deviation representing the variation increases accordingly. A large standard deviation associated with a small spanwise average mass fraction implies a high probability for the depletion of reactants to occur within the porous electrode at positions in the spanwise direction away from the channels. In such a case, the cell design needs to be modified so as to avoid the depletion. The large variation of the mass fraction in Fig. 5.4b is captured by the developed variation factor with a maximum relative error less than 5%. On the anode side in both Fig. 5.4a and 5.4b, the relative errors between the 3D and 2D results do not exceed 3% for the spanwise average of hydrogen mass fraction ω_{H_2} and 13% for the standard deviation σ_{H_2} . Moreover, the obtained σ_{H_2} is smaller than the spanwise average by nearly two orders of magnitude.

Fig. 5.4 Average mass fractions and standard deviations at the backing/reaction zone interface with cathode backing layers of different thicknesses: (a) $\mathcal{H}_c = 0.5$ and (b) $\mathcal{H}_c = 0.05$, with $\mathcal{H}_a = 0.375$, $\mathcal{W} = 0.55$. 3D results for ω (filled) and σ (unfilled) at 0.8 ($\blacktriangle$), 0.6 ($\blacksquare$), 0.4 V ($\blacktriangledown$). 2D results for ω (solid lines) and σ (dash lines).

Fig. 5.5 presents the results for cells different in the thickness of the anode backing layer. With a thick anode backing layer ($\zeta_{H_2} = 0.58$) in Fig. 5.5a, the standard deviation σ_{H_2} is less than 3% of the spanwise average mass fraction even at high current densities. In contrast, with a thin porous backing layer ($\zeta_{H_2} = 0.037$) in Fig. 5.5b, the value of σ_{H_2} increases to around 10% of the spanwise average at 0.8V and 20% at 0.4V. The relative errors between the 3D and 2D solutions do not exceed 3% for the hydrogen mass fraction ω_{H_2} and 15% for the standard deviation σ_{H_2} at all the three voltages in both Fig. 5.5a and 5.5b.

Fig. 5.5 Average mass fractions and standard deviations at the backing/reaction zone interface with anode backing layers of different thicknesses: (a) $\mathcal{H}_a = 0.5$ and (b) $\mathcal{H}_a = 0.05$, with $\mathcal{H}_c = 0.375$, $W = 0.4$. 3D results for ω (filled) and σ (unfilled) at 0.8 (▲), 0.6 (■), 0.4 V (▼). 2D results for ω (solid lines) and σ (dash lines).

At last, the validity of spatial smoothing for various cell designs is further investigated in terms of the average current density. The thickness of the cathode or anode backing layer is varied, while the thickness of the other electrode is fixed. Comparing the average current densities predicted by the 3D and 2D models, the relative errors do not exceed 2% for the cell with a varying cathode backing thickness and 0.4% with a varying anode backing thickness. Therefore, the spatially smoothed model coupled with the auxiliary correlation factors is robust to predict the charge transport in SOFCs, even if the cell geometry has a thin backing layer such as a thickness of $\mathcal{H} =$

0.05.

5.5. Summary

In this chapter, in addition to predicting the average behaviour of a 3D P-SOFC by spatial smoothing, novel variation factors have been developed to capture the variability of species mass fractions with respect to their average value in the spanwise direction, resulting in the advanced 2D spatially-smoothed isothermal model. The resulting variation factors are expressed as functional polynomial in terms of dimensionless geometrical parameters and applicable at different current densities.

From the point of view of cell design, not only the average value but also the variability of mass fractions underneath the ribs is necessary in order to avoid depletion of oxidants or fuels that typically takes place at higher current densities. It is found that spatial smoothing is valid to capture the above information in the 3D geometry for various cell designs with parallel flow channels. Good agreement with relative errors less than 15% is obtained when comparing the results of the 2D reduced model and the 3D counterpart.

The present approach to develop the variation factors can be extended from mass fractions to the other dependent variables of the P-SOFC model. It is believed that the spatially smoothed model with auxiliary polynomials accounting for the variability of dependent variables and the variation in the pathways of transport processes can serve as a useful tool for the design and investigation of SOFCs and stacks. Typically, a large spanwise variation and a small average value of the mass fractions predicted by the model imply that the designed cell/stack probably undergoes depletion of species underneath ribs along the cell width, especially at positions away from the channel and/or towards the outlet, which can give rise to uneven current density distributions.

Then, modification on the design of cell geometry, materials, and/or operation conditions will be required.

Chapter 6

Monte Carlo Simulation of Advanced ASSI

Cell Model: Sensitivity Analysis of Cell

Performance

6.1. Introduction

In this chapter, Monte Carlo simulation (MCS) of an advanced 2D asymptotic spatially-smoothed isothermal (ASSI) cell model for the P-SOFC is conducted to analyse the effects of a single and a combination of stochastic modeling parameters on the variation of cell performance. Section 6.2 introduces the advanced 2D ASSI model that is obtained by coupling the 2D ASSI single-cell model developed in Chapter 4 with the variation factors developed in Chapter 5. The MCS is elucidated in Section 6.3, followed by a description of numerical implementation in Section 6.4. Section 6.5 presents the statistical results of the MCS and analyses the sensitivity of the global cell output and the average and spanwise variations of local dependent variables with respect to the varying parameters.

6.2. Advanced ASSI model

The 3D P-SOFC single cell introduced in Chapter 3 is considered in this chapter under an isothermal condition. The cell structure is repetitive and symmetric, so that the cell

performance is represented by a repeating unit that consists of two interconnects, a pair of air and fuel channels, two porous backing layers, two reaction zone layers, and a solid electrolyte, as shown in Fig. 3.1c. Moreover, only half of the repeating unit is taken into account for modeling associated with symmetry boundary conditions at the cross section A-A. The fuel and air are supplied in a co-flow configuration. Steady-state conservation equations for weakly-compressible momentum, mass, species, and charge are solved for dependent variables including the flow velocity, $\mathbf{v}$, pressure, p ; the mass fraction of oxygen, ω_{O_2} , for the cathode and hydrogen, ω_{H_2} , for the anode; as well as the electronic, ϕ_{elc} , and ionic, ϕ_{ion} , potentials.

Fig. 6.1 Schematic of an asymptotic spatially-smoothed domain with PDEs ($\rightarrow$) and ODEs ($\bullet$) in the flow field, and ODEs in the remainder of the cell.

The leading-order behaviour in the 3D domain is described by a reduced model that consists of parabolic PDEs and ODEs for the flow field and ODEs for the rest of the cell with a space marching algorithm in the streamwise direction, as shown schematically in Fig. 6.1. Table 6.1 shows the governing equations and boundary conditions of this

reduced model. The charge transport in the interconnect is governed by an ODE in the normal direction as a result of spatial smoothing and asymptotic reduction [173, 174]. The asymptotic spatially-smoothed equations for the momentum, mass, and charge transports in the flow field, electrode, and electrolyte are developed in Chapter 4. All the constitutive relations for modeling can be found in Table 3.1.

The correlation factors, ζ_{H_2} and ζ_{O_2} , given by Eqs. (4.8) and (4.9) are applied here to account for the influence of ribs on the pathway of mass transport from the flow field to adjacent layers and for the coupling effects between equations. Moreover, the spanwise variation of local mass fractions in the 3D model is captured by the variation factors, $\tilde{\sigma}_{\text{H}_2}$ and $\tilde{\sigma}_{\text{O}_2}$, specified by Eqs. (5.5) and (5.6). The coefficients of the polynomials for ζ_{H_2} and ζ_{O_2} , a_{ij} and b_{ij} , as well as the coefficient for $\tilde{\sigma}_{\text{H}_2}$ and $\tilde{\sigma}_{\text{O}_2}$, c_{ij} and d_{ij} , are referred to Table 5.1. The variation factor is then multiplied with the drop of mass fraction across the backing layer to get the dimensional spanwise variation of mass fractions at a certain streamwise position, σ_{H_2} or σ_{O_2} , as described by Eqs. (5.7) and (5.8). For the 2D asymptotic spatially-smoothed domain considered here (Fig. 6.1), this entails

$$\sigma_i = \tilde{\sigma}_i \left(\omega_i|_{\text{ff/bl}} - \omega_i|_{\text{bl/el}} \right), \quad (6.1)$$

in which i refers to H_2 for the anode and O_2 for the cathode.

Table 6.1 Formulation of the advanced ASSI P-SOFC model.

Domain	Governing equations
Interconnect	$\frac{\partial}{\partial z} \left(-\sigma_{\text{elc, ic}} \frac{\partial \phi_{\text{elc}}}{\partial z} \right) = 0;$
Flow field	$\frac{\partial}{\partial x} (\rho u) + \frac{\partial}{\partial z} (\rho w) = 0, \quad \frac{\partial p}{\partial x} = -\frac{\mu_{\text{mix}}}{\kappa_{\text{ff}}} u, \quad \frac{\partial p}{\partial z} = 0,$ $\frac{\partial}{\partial x} (\rho u \omega_i) + \frac{\partial}{\partial z} (\rho w \omega_i) = \frac{\partial}{\partial z} \left(\rho \omega_i \sum_{j=1}^n \left(\varepsilon_{\text{ff}} \mathcal{D}_{ij} \frac{\partial x_j}{\partial z} \right) \right),$
Backing layer	$\frac{\partial}{\partial z} \left(-(1 - \varepsilon_{\text{ff}}) \sigma_{\text{elc, ic}} \frac{\partial \phi_{\text{elc}}}{\partial z} \right) = 0;$ $\frac{\partial}{\partial z} (\rho w) = 0, \quad \frac{\partial p}{\partial z} = -\frac{\mu_{\text{mix}}}{\kappa} w,$ $\frac{\partial}{\partial z} (\rho w \omega_i) = \frac{\partial}{\partial z} \left(\rho \omega_i \sum_{j=1}^n \left(\zeta \mathcal{D}_{ij}^{\text{eff}} \frac{\partial x_j}{\partial z} \right) \right),$ $\frac{\partial}{\partial z} \left(-\sigma_{\text{elc}}^{\text{eff}} \frac{\partial \phi_{\text{elc}}}{\partial z} \right) = 0;$
Reaction zone layer	$\frac{\partial}{\partial z} (\rho w) = \begin{cases} \frac{M_{\text{O}_2} J_{\text{c}}}{4F} & (\text{cathode rl}) \\ \frac{M_{\text{H}_2\text{O}} J_{\text{a}}}{2F} - \frac{M_{\text{H}_2} J_{\text{a}}}{2F} & (\text{anode rl}) \end{cases}, \quad \frac{\partial p}{\partial z} = -\frac{\mu_{\text{mix}}}{\kappa} w,$ $\frac{\partial}{\partial z} (\rho w \omega_i) - \frac{\partial}{\partial z} \left(\rho \omega_i \sum_{j=1}^n \left(\mathcal{D}_{ij}^{\text{eff}} \frac{\partial x_j}{\partial z} \right) \right) = \begin{cases} +\frac{M_{\text{O}_2} J_{\text{c}}}{4F} & (\text{O}_2, \text{cathode rl}) \\ -\frac{M_{\text{H}_2} J_{\text{a}}}{2F} & (\text{H}_2, \text{anode rl}) \end{cases},$ $\frac{\partial}{\partial z} \left(-\sigma_{\text{elc}}^{\text{eff}} \frac{\partial \phi_{\text{elc}}}{\partial z} \right) = -J, \quad \frac{\partial}{\partial z} \left(-\sigma_{\text{ion}}^{\text{eff}} \frac{\partial \phi_{\text{ion}}}{\partial z} \right) = J;$
Electrolyte	$\frac{\partial}{\partial z} \left(-\sigma_{\text{ion}}^{\text{eff}} \frac{\partial \phi_{\text{ion}}}{\partial z} \right) = 0.$
Location	Boundary conditions
Inlets	$u = \varepsilon_{\text{ff}} U_{\text{c, a}}^{\text{in}}, \quad w = 0, \quad \omega_{\text{O}_2} = \omega_{\text{O}_2}^{\text{in}}, \quad \omega_{\text{H}_2} = \omega_{\text{H}_2}^{\text{in}};$
Top surface	$\phi_{\text{elc, c}} = V_{\text{cell}};$
Bottom surface	$\phi_{\text{elc, a}} = 0;$
Current collector/flow field	$u = w = 0, \quad \partial \omega_i / \partial z = 0;$
Backing/reaction zone	$\partial \phi_{\text{ion}} / \partial z = 0;$
Reaction zone/electrolyte	$w = 0, \quad \partial \omega_i / \partial z = \partial \phi_{\text{elc}} / \partial z = 0.$

6.3. Monte Carlo simulation

For the MCS of the advanced 2D ASSI P-SOFC model, stochastic input parameters are generated first. The modeling parameters that are varied include the operating temperature, T , the inlet velocities of the air and fuel flow, u_c^{in} and u_a^{in} , the cell length and the thicknesses of layers, L and h_j ($j = \text{cc, ff, bl, rl, el}$), as well as material properties of the anode and cathode (including the activation energy, E^{act} , and pre-exponential factor for electrochemical reactions, β , specific area, A , permeability, κ , tortuosity, τ , porosity of the backing layer, ε_{bl} , and average pore radius, r). Each stochastic parameter is sampled in a normal distribution with a predefined population mean, μ , and a standard deviation, σ . The mean for each parameter is the nominal value displayed in Table 6.2, and the standard deviation is assumed to be 10% of the mean (*i.e.*, $\sigma/\mu = 0.1$), such that the stochastic parameters distribute in the ranges of their typical values [20, 94, 102, 144, 176, 177]. In addition, the cell voltage V_{cell} for the SOFC investigated in this chapter is 0.5 V, the widths of the channel and the rib, w_{fc} and w_{rib} , are 1.2×10^{-3} m and 1.8×10^{-3} m, respectively. All the other modeling parameters can be found in Table 3.2.

Table 6.2 Nominal values of stochastic parameters for the MCS of the advanced ASSI P-SOFC model.

<i>Operating conditions</i>		<i>Material properties</i>	
T	700 °C	$\mathcal{A}_{a, c}$	$4.51 \times 10^5 \text{ m}^{-1}$
$U_{a,c}^{\text{in}}$	1 m s ⁻¹	$E_a^{\text{act}}, E_c^{\text{act}}$	$(1.2, 1.15) \times 10^5 \text{ J mol}^{-1}$
<i>Cell geometry</i>		β_a, β_c	$(5.7, 700) \times 10^7 \text{ A m}^{-2}$
h_{cc}	$5 \times 10^{-4} \text{ m}$	$r_{a, c}$	$5 \times 10^{-7} \text{ m}$
$h_{ic,a}, h_{ic,c}$	$2 \times 10^{-3} \text{ m}$	$\varepsilon_{bl,a}, \varepsilon_{bl,c}$	0.48, 0.45
$h_{bl,a}, h_{bl,c}$	$(7.5, 1.5) \times 10^{-4} \text{ m}$	$\kappa_{a, c}$	$1 \times 10^{-12} \text{ m}^2$
$h_{rl,a}, h_{rl,c}$	$2 \times 10^{-5} \text{ m}$	$\tau_{a, c}$	2.75
h_{el}	$5 \times 10^{-5} \text{ m}$		
L	$9 \times 10^{-2} \text{ m}$		

In a statistical point of view, it is essential to ensure that the sample size of every set of random parameters is large enough to guarantee the predefined normal distribution. Based on the central limit theorem and the confidence bounds estimate for a normal distribution, the critical sample size, N_{crit} , is determined by [202, 203]

$$N_{\text{crit}} = \left(\frac{z_{\alpha/2} \frac{\sigma}{Er} \mu}{\mu} \right)^2, \quad (6.2)$$

in which $z_{\alpha/2}$ is the upper $100(1-\alpha/2)^{\text{th}}$ percentile of the standard normal distribution at a confidence level of α , and Er is the relative error between the sample and population means. Based on the resulting critical sample size, a sample-size independence test is conducted to guarantee a reliable sample size for stable results. For this purpose, a hypothesis test called the two-sample Kolmogorov-Smirnov test (K-S test) is performed [204]. If the significance level, α , is smaller than the degree of rarity of the result, p -value, the difference between two investigated samples in different sizes would be negligible resulting in a statistic, h_{ks} , of zero for the K-S test [205]. In this work, the values of α and p_{ks} are provided based on a two-tailed test.

When predicting the cell performance, the varied modeling parameters, X_i , are employed in two ways: one at a time and simultaneously in each run of the MCS. The former results in the same sample mean, $\bar{Y}$, but different standard deviations,

$$\sigma_{Y_i} = \left(\frac{1}{N} \sum_{i=1}^N (Y_i - \bar{Y})^2 \right)^{1/2}, \quad (6.3)$$

in the probability distributions of the investigated dependent variable, Y_i , such that the effect of each input parameter X_i on the dependent variable Y_i is quantified by the coefficient of variation,

$$c_v = \frac{\sigma_{Y_i}}{\bar{Y}}, \quad (6.4)$$

for ease of comparison. The latter allows one to observe the variation of the significance of input parameters for the cell performance when the parameters are varied simultaneously as opposed to individually. The correlation between the modeling parameter and the dependent variable is quantified by the Spearman's rank correlation coefficient [206].

$$\rho_s = \frac{\sum (X'_i - \bar{X}') (Y'_i - \bar{Y}')}{\sqrt{\sum (X'_i - \bar{X}')^2} \sqrt{\sum (Y'_i - \bar{Y}')^2}}, \quad (6.5)$$

in which X'_i and Y'_i are the ranks of paired data (X_i , Y_i) in a sample. The resulting coefficient is a number between ± 1 and describes the monotonic relationship between pairs of quantitative variables. The value of the coefficient indicates the strength of the relationship, while a positive (negative) sign indicates an increasing (decreasing) relationship.

6.4. Numerical implementation

The asymptotic spatially-smoothed P-SOFC model is implemented in the commercial

finite-element solver COMSOL Multiphysics 3.5a. The model is solved in a 1D domain in the normal direction and space-marched along the streamwise direction. The stream function given by Eqs. (4.56) to (4.58) is introduced to the flow field in order to reduce the number of variables. A transient solver with the backward differentiation formula (BDF) method is used to march in space by treating x as a time-like variable. Quadratic Lagrange basis functions and a relative convergence error of 10^{-3} are employed for all dependent variables.

For the MCS, the automated generation of the cell model with stochastic modeling parameters is carried out in MATLAB R2010a by using the bidirectional interface between COMSOL Multiphysics and MATLAB, so as to avoid the time-consuming manual regeneration of the computational domain with varying geometrical parameters in COMSOL. The FEM structure of the cell model in COMSOL is saved as a MATLAB code that contains all the information about the model ranging from the geometry to solver properties. In the MATLAB environment, the code reads the input modeling parameters specified by the user, builds the cell geometry, constructs the numerical mesh, defines the mathematical model, solves the cell models, and finally performs postprocessing as instructed by the user. A loop structure is employed for the regeneration and solving of the model to perform all the runs of the MCS. Each run takes only about 1 second on a computer with 12 CPUs of 3.2GHz. This allows parametric studies with stochastic parameters in a large sample size of 10^3 with a computational cost that is not prohibitive. Apart from the finite-element method, the asymptotic spatially-smoothed model can be solved with other numerical methods as well.

6.5. Statistical results and sensitivity analysis

This section presents the results of the MCS of the asymptotic spatially-smoothed model and discusses the sensitivity of the cell performance to the varying input modeling parameters. The investigated cell behaviours include the average current density, i_{avg} , oxygen mass fraction, ω_{O_2} , and the spanwise variation of the oxygen mass fraction, σ_{O_2} , to elucidate the sensitivity analysis. The present method can be directly applied to other dependent variable.

First of all, the critical sample size for each input parameter, N_{crit} , is 700 given by Eq. (6.2). In Eq. (6.2), the ratio of the population mean μ and standard deviation σ is assumed to be 10% to represent the variability of each parameter, such that the stochastic parameters are within their typical ranges [20, 94, 102, 144, 176, 177]. The relative error, Er , is set to 1%, which implies good agreement between the sample and population means. An upper 99.5th percentile $z_{0.005}$ at a confidence level of $\alpha = 0.01$ is applied here, which means a cumulative probability of 99.5% for the difference between the sample and population means not to exceed $Er = 1\%$. The corresponding value of $z_{0.005}$ is 2.576 according a z-score table [205]. For a sample-size independence test, the two-sample K-S test is conducted at a significance level $\alpha = 0.05$. Fig. 6.2 illustrates the test results with the cathode activation energy, E_c^{act} . The empirical cumulative distribution functions (CDFs) of three tested samples with $N = 500$, 1000, and 2000, are compared with the CDF with $N = 5000$. The statistic p_{ks} is larger than the significance level $\alpha = 0.05$ for all the three testing cases, which means the difference between the distributions of the tested sample and the sample with $N = 5000$ is insignificant at the 5% significance level. Meanwhile, the sample size

should not be smaller than the calculated critical value N_{crit} of 700. Therefore, the sample size, $N = 1000$, is adopted for the MCS.

Fig. 6.2 Empirical cumulative distribution function (CDF) of average current densities at 0.5 V with different sample sizes (N) for Monte Carlo simulation. Kolmogorov-Smirnov test statistics of samples based on a case of $N = 5000$ at $\alpha = 5\%$.

For the first scenario of the sensitivity analysis, the stochastic parameters are varied individually. Figs. 6.3 and 6.4 show the probability distribution of the average current density with respect to the material properties and operating conditions of the cathode (similar results are obtained for the anode), and geometrical parameters of the entire cell when varying one parameter for each run of the MCS. With the same resulting sample mean for the average current density i_{avg} in all the histograms, the sensitivity of i_{avg} to each input parameter is evaluated by the coefficient of variation c_v defined by Eq. (6.4) that reflects the deviation of the resulting discrete values of i_{avg} from the mean. The coefficient c_v is used as an indicator to rank the significance of the influence of the input parameters on the average current output, as shown in Fig. 6.5. The operating

temperature, T , the cathode and anode activation energy, E_c^{act} and E_a^{act} , are the first three important factors, followed by the electrolyte thickness, h_{el} , and the cell length, L . The ranking for the sensitivity to the thicknesses of the electrolyte, cathode, and anode in Fig. 6.5b is consistent with the results provided by Chan *et al.* [20]. A thick electrolyte causes large ohmic polarization due to high electrolyte resistivity. It is found that the average current density is not sensitive to the change in the thickness of the current collector in Fig. 6.5b and the electrode permeability in Fig. 6.5c.

Fig. 6.3 Probability distribution of average current densities at 0.5 V by varying one parameter at a time: (a-g) cathode material properties; (h, i) operating conditions. Fitted normal distribution (-).

Fig. 6.4 Probability distributions of average current densities at 0.5 V by varying one geometrical parameter at a time. Fitted normal distribution (-).

Fig. 6.5 Coefficients of variation c_v of the average current density at 0.5 V with respect to stochastic input parameters varied one at a time: (a) operating conditions; (b) geometrical parameters; (c) material properties.

After the sensitivity analysis with stochastic parameters varied individually, all the investigated modeling parameters are now varied together in each run in order to investigate the variation in the significance of their influence on the cell performance. The resulting average current density has a bimodal distribution as shown in Fig. 6.6, although the stochastic parameters are assigned to distribute normally. This reflects the high non-linearity of the relationship between the average current density, i_{avg} , and the parameters varied together. Fig. 6.7 illustrates the relationship between the i_{avg} and the stochastic parameters to compare the scenarios with parameters varied one at a time (Fig. 6.7(a, c, e, g)) and all together (Fig. 6.7(b, d, f, h)). For the first scenario where only one input parameter is varied, the varying parameters that have a negative monotonic

relationship with the average current density include the thicknesses of the electrolyte and the anode backing layer, h_{el} and, $h_{bl,a}$ the cell length, L , the activation energy, E^{act} , and the tortuosity, τ . All the other parameters have a positive relationship. Some of them are illustrated in Fig. 6.7(a, c, e, g). The findings of these monotonic relationships were secured from simple parametric studies as well [20, 94, 102, 130, 144, 176-179]. Compared with the case just varying one parameter at a time, there is no obvious monotonic relationship between the varied parameters (except the operating temperature) and the current density, as illustrated in Fig. 6.7(b, d, f, h). The obvious positive monotonic relationship in Fig. 6.7h reflects the strong influence of temperature on cell performance which surpasses the effects from other varying parameters and thus dominates the variation in cell performance.

Fig. 6.6 Probability distributions of average current densities at 0.5 V by varying all modeling parameters.

Fig. 6.7 Scatter plots of the average current density at 0.5 V against input parameters: (a, c, e, g) varying one parameter at a time; (b, d, f, h) varying all parameters together. The dash-dot line (—·) refers to the mean value.

As illustrated in Fig. 6.7(b, d, f), it is difficult to observe the strength of the influence of a varying parameter on cell performance, when a group of input parameters are varied together. Therefore, the correlation between every input parameter and the cell output is assessed with the Spearman's rank correlation coefficient, ρ_s , which is calculated by Eq. (6.5) and then used as an indicator to compare the significance of input parameters for the cell performance. According to the magnitude (*i.e.*, absolute value) of

resulting correlation coefficients for the average current density, i_{avg} , the inputs parameters are ranked in Fig. 6.8, where the ranking numbers of the stochastic parameters are labeled for each dependent variable. The obtained ranking of the stochastic modeling parameters is different from that in Fig. 6.5. For examples, the cathode inlet velocity, u_c^{in} , becomes the fourth most significant factor for the i_{avg} under the effects of the parameters varied simultaneously in Fig. 6.8, whereas its individual effect on the i_{avg} is the fourteenth among the 26 investigated input parameters referring to Fig. 6.5. In Fig. 6.8b, the flow channel thickness, $h_{\text{fc,c}}$, ranks above all the other geometric parameters in view of its highest ρ_s of 0.09. The u_c^{in} and $h_{\text{fc,c}}$ affect the amount of oxygen provided to the cell. For practical operation, sufficient oxygen should be supplied to the cell, especially for the cell with a thin cathode backing layer and/or operating at a high temperature; otherwise, a large gradient of the mass fraction across the cathode backing layer will occur resulting in a decrease in the current density. In Fig. 6.8c, the permeability of the cathode backing layer, κ_c , (with $\rho_s = -0.06$) becomes the third most significant material property for the i_{avg} , although its individual influence ranks the last among the investigated material properties as shown in Fig. 6.5c. A large κ_c may facilitate the penetration of species in the cathode backing layer to have a large Darcy's velocity. Apart from T , E_c^{act} , and E_a^{act} , the average current density is most sensitive to the $h_{\text{fc,c}}$, h_{el} , and κ_c in the considered situation. Because of the simultaneous impacts of different input parameters, the variation of the cell performance due to the change in a parameter may be compensated or reinforced by the change in another one. For instance, a decrease in the current output due to an increase in the electrolyte thickness can be compensated by an increase in the operating temperature,

since the electric conductivity of the electrolyte increases with temperature. An increase in the exchange current density, i_0 , due to an increase in the pre-exponential factor, β , can be reinforced by a decrease in the activation energy, E^{act} . The operating temperature, T , the porosity, ε , and the tortuosity, τ can simultaneously affect the electrode electric conductivity which in turn influences the current distribution in the cell.

Fig. 6.8 Correlation coefficients ρ_s of stochastic input parameters and dependent variables at 0.5 V. Stochastic parameters: (a) operating conditions; (b) geometrical parameters; (c) material properties. Dependent variables: average current density (■); average value (■) and spanwise variation (■) of oxygen mass fractions at the backing/reaction zone interface at $x = 0.09$ m. All stochastic parameters are varied together. The ranking numbers of the varying parameters are labeled for each dependent variable in view of the magnitude of ρ_s .

Furthermore, the sensitivity analysis is extended from the global performance to local dependent variables. Apart from the average current density, Fig. 6.8 also presents

the correlation coefficients for the local oxygen mass fractions ω_{O_2} and their spanwise variations σ_{O_2} (given by Eq. (6.1)) at the backing/reaction zone interface at $x = 0.09$ m. At high current densities, a small spanwise average of the local oxygen mass fraction ω_{O_2} associated with a large spanwise variation σ_{O_2} implies a high probability for the depletion of reactants to occur within the porous electrode underneath the ribs near the outlet. For the mass fraction of oxygen, the most significant factors are the operating temperature T and cathode and anode activation energy $E_{\text{c,a}}^{\text{act}}$, followed by the cell length L and flow channel thicknesses, $h_{\text{fc,a}}$ and $h_{\text{fc,c}}$. The anode and cathode channel thicknesses, $h_{\text{fc,a}}$ and $h_{\text{fc,c}}$, have opposite effects on the distribution of oxygen mass fractions. An increase in the former causes more oxygen consumed, whereas an increase in the latter increases the amount of oxygen supplied. Compared with the average current density and oxygen mass fraction, the spanwise variation of mass fraction σ_{O_2} is more sensitive to the operating conditions and cell structure than to the parameters describing the mechanism of electrochemical reactions, such as E^{act} . The most significant factors are the operating temperature T , the porosity ε_{c} , backing layer thickness $h_{\text{bl,c}}$, and channel thickness $h_{\text{fc,c}}$ of the cathode, followed by the cell length L , cathode inlet velocity u_{c}^{in} , and activation energy $E_{\text{c}}^{\text{act}}$. Such information is necessary for the fabrication of a SOFC in order to avoid undue depletion related to the design of the cell geometry, materials, and operating conditions. In addition, the present MCS also allows the analysis of dependent variables at other local positions in the cell (not shown here).

6.6. Summary

In this chapter, a Monte Carlo simulation of a computationally cost-efficient P-SOFC model, namely the advanced asymptotic spatially-smoothed isothermal P-SOFC (ASSI) model developed in Chapters 4 and 5, is presented and applied to analyse the correlation between the global and local cell behaviours with the variations of operating conditions, cell geometry, and material properties. The average current density and the volume-averaged value and spanwise variation of local oxygen mass fractions are considered here to elucidate a sensitivity analysis with respect to stochastic modeling parameters. Based on the reduced single-cell model that consumes 1 second to solve, it takes less than 20 minutes for the present MCS with a sample size of 1000 for each stochastic parameter.

Different from traditional parametric studies, the present sensitivity analysis is performed not only by varying one modeling parameter at a time but also varying all the parameters simultaneously. The latter investigates the effect of a combination of varying parameters on the cell performance. It is found that the rankings of the varying parameters based on their contribution on the variation of cell performance are different in these two scenarios, which is not captured in existing parametric studies. According to the rankings of the investigated 26 stochastic modeling parameters, the average current density is most sensitive to the operating temperature, T , the cathode and anode activation energy, E_c^{act} and E_a^{act} , the electrolyte thickness, h_{el} , and the cell length, L , in the first scenario, but has the cathode inlet velocity and channel thickness, u_c^{in} and $h_{\text{fc,c}}$, as the fourth and fifth significant factor in the second scenario. Additionally, when all the parameters are varied together, the top 5 most influential parameters are T , the cathode and anode activation energy, $E_{\text{c,a}}^{\text{act}}$, followed by L and the anode channel

thickness, $h_{fc,a}$, for the oxygen mass fraction; and T , the porosity, ε_c , the cathode backing layer thickness, $h_{bl,c}$, followed by $h_{fc,c}$ and L for the spanwise variation of oxygen mass fractions.

The present Monte Carlo simulation can work as a tool to analyze how the cell properties deviating from the nominal design values affect the cell performance, and finally to determine the input parameters for optimal operation for high volume manufacturing processes. With respect to a set of different means μ and coefficients of variation c_v for one or a combination of input parameters, design charts can be constructed to show the relation of the mean or variation of the cell performance with the mean or variation of the input parameters and/or the dependent variables (*e.g.*, average current and power densities). The design charts will allow one to address the optimal input parameters in terms of their μ and c_v that lead to desired cell output, such as the maximum achievable mean or the minimum variation of the average power density. Furthermore, the present stochastic modeling can be extended from the single-cell to stack level to investigate the sensitivity of stack performance such as global average stack current and power densities as well as perturbations of local variables between cells to stochastic design parameters. The advanced ASSI single-cell model with one-second solution time allows computationally cost-efficient stochastic modeling of a large stack of hundreds of cells, which can be built up with automated code generation.

Chapter 7

Development of Reduced Models:

Asymptotic Spatially-Smoothed Thermal (ASST) Cell and Stack Models

7.1. Introduction

In order to develop a reduced non-isothermal model that can capture the leading-order change of temperature in the P-SOFC, this chapter develops spatially-smoothed non-isothermal P-SOFC cell and stack models as well as their asymptotic counterparts which are called the asymptotic spatially-smoothed thermal (ASST) models, based on the 3D non-isothermal cell model developed in Chapter 3. In particular, the energy equations are spatially smoothed subject to the local thermal equilibrium (LTE) and non-equilibrium (LTNE) conditions in the volume-averaged flow field. Correlation factors are developed to capture the variation in the pathways of heat transfer. Section 7.2 describes the full 3D cell and stack models considered in this chapter. Sections 7.3 and 7.4 elaborate the spatial smoothing and the asymptotic analysis of the energy equations, respectively. Section 7.5 describes the numerical implementation of the full and reduced models. In Section 7.6, the resulting spatially-smoothed non-isothermal cell and stack models as well as the ASST models are verified with their 3D counterparts. The influence of perturbations between cells on the accuracy of the reduced stack

models is investigated as well.

7.2. Cell and stack modeling

The fuel cell considered here is an anode-supported P-SOFC fed by air for the cathode and by humid hydrogen for the anode in a co-flow configuration. The cell comprises two interconnects (ic), a pair of air and fuel channels (fc), two porous backing layers (bl), two reaction zone layers (rl), and a solid electrolyte (el), as shown in Fig. 3.1c. The performance of the unit P-SOFC is described by the full 3D non-isothermal model introduced in Chapter 3. Steady-state conservation equations (3.1) to (3.15) for weakly-compressible momentum, mass, species, charge, and energy are solved for dependent variables including the flow velocity, $\mathbf{v}$, pressure, p ; the mass fraction of oxygen, ω_{O_2} for the cathode and hydrogen, ω_{H_2} , for the anode; the electronic, ϕ_{elc} , and ionic, ϕ_{ion} , potentials; as well as the temperature, T . The boundary conditions are described by Eqs. (3.16) to (3.29).

Apart from the single cell, the performance of the P-SOFC stack is considered as well. For stack modeling, the single-cell model described by Eqs. (3.1) to (3.29) is taken as the repeating unit that is assumed to locate in the middle of a large 3D stack. All the cells in the stack are assumed to be under the same inlet conditions. The perturbations of dependent variables between cells in the stack are assumed to be negligible, such that the stack performance can be represented by the repeating unit associated with adiabatic conditions on the top and bottom surfaces of the cell [70, 92, 171], instead of constant temperatures for Eqs. (3.19) and (3.20). An inlet velocity of 10 m s^{-1} is assigned to the air flow so as to supply sufficient oxygen and avoid depletion at high current densities. Subsequently, we also investigate the validity of the reduced stack models when the perturbations between cells are taken into account, based on a 3-cell stack model with

different air inlet conditions for the cells. Table 7.1 shows the geometrical parameters and operating conditions for the single-cell and stack modeling. All the other modeling parameters can be found in Tables 3.2 and 3.3.

Table 7.1 Geometry and operating conditions of 3D non-isothermal cell and stack models.

	Case (a) Single cell	Case (b) Unit cell in the middle of a stack	Case (c) 3-cell stack
<i>Geometry</i>			
L	9×10^{-2} m	5×10^{-2} m	2×10^{-2} m
h_{cc}	5×10^{-4} m	5×10^{-4} m	5×10^{-4} m
$h_{fc,a}, h_{fc,c}$	2×10^{-3} m	2×10^{-3} m	2×10^{-3} m
$h_{bl,a}, h_{bl,c}$	$(5.625, 1.875) \times 10^{-4}$ m	$(5.625, 1.875) \times 10^{-4}$ m	$(7.5, 1.5) \times 10^{-4}$ m
$h_{rl,a}, h_{rl,c}$	2×10^{-5} m	2×10^{-5} m	2×10^{-5} m
h_{el}	5×10^{-5} m	5×10^{-5} m	5×10^{-5} m
n_{fc}	20	20	20
w_{fc}	1.65×10^{-3} m	1.65×10^{-3} m	1.2×10^{-3} m
w_{rib}	1.35×10^{-3} m	1.35×10^{-3} m	1.8×10^{-3} m
<i>Operating conditions</i>			
U_c^{in}	1 m s^{-1}	10 m s^{-1}	$1, 1.5, 2 \text{ m s}^{-1}$
U_a^{in}	1 m s^{-1}	1 m s^{-1}	1 m s^{-1}
T^{in}, T^{oper}	973.15 K	973.15 K	973.15 K
$\nu_{H_2}^{in}$	97%	97%,	97%
$\nu_{O_2}^{in}$	21%	21%	21%
P_{atm}, P^{ref}	1.01×10^5 Pa	1.01×10^5 Pa	1.01×10^5 Pa

For model reduction, the investigated 3D non-isothermal single-cell model is spatially smoothed and asymptotically reduced. The analysis of spatial smoothing and asymptotic reduction for the mass, momentum, and charge transports is introduced in Chapter 4. The asymptotic spatially-smoothed equations for the mass, momentum, and charge transports can be found in Table 6.1. The spatial smoothing of the energy equations (3.14) and (3.15) in the full 3D model is introduced below, followed by the asymptotic reduction. The resulting reduced cell model is then employed as the element of the stacks for stack modeling.

7.3. Spatially smoothed energy equation

According to the analysis of spatial smoothing in Chapter 4, the flow field comprising of parallel plain channels and solid ribs in the original 3D model becomes a porous counterpart after being spatially smoothed. In this porous flow field, the ribs and the gaseous working fluid in channels are considered as the solid and gas phases in a porous medium, respectively. Although the porous electrode of SOFCs is generally under the local thermal equilibrium (LTE) condition [137], the flow field may undergo a significant temperature difference between the ribs and fluid depending on the inlet conditions [69, 207]. Therefore, both the LTE and local thermal non-equilibrium (LTNE) conditions are considered here for the spatial smoothing of the energy equation. The selection of either the LTE or LTNE model for use depends on the temperature difference between the gas mixture and solid ribs in the flow field.

7.3.1. Local thermal equilibrium

In the original 3D flow field (Fig. 7.1a), heat is transferred by conduction within both the solid ribs and gaseous fluid and by convection within the gas. When spatially smoothing the flow field in LTE, an effective thermal conductivity is specified as

$$k_{\text{ff}}^{\text{eff}} = \varepsilon_{\text{ff}} k_{\text{mix}} + (1 - \varepsilon_{\text{ff}}) k_{\text{ic}} \quad (7.1)$$

to capture the conduction in the solid and gas phases. Here, the effective porosity of the spatially smoothed flow field, ε_{ff} , is the ratio of the volumes of n flow channels (of width w_{fc}) to the volume of the entire flow field (of width $w = (n_{\text{fc}} w_{\text{fc}} + (n_{\text{fc}} + 1) w_{\text{rib}})$) and excluding the solid part of current collectors above the flow channels), *i.e.*, $\varepsilon_{\text{ff}} = n_{\text{fc}} w_{\text{fc}} / w$. Then, the energy equation for the spatially smoothed flow field (Fig. 7.1b) is obtained:

$$-\nabla \cdot (k_{\text{ff}}^{\text{eff}} \nabla T) + \rho c_{\text{p, mix}} \mathbf{v} \cdot \nabla T = \sigma_{\text{elc, ic}} (\nabla \phi_{\text{elc}})^2. \quad (7.2)$$

Fig. 7.1 Schematic of the pathways of heat transfer by solid ($\rightarrow$) and gas ($\dashrightarrow$) phases through the flow field and its adjacent layers (a) without and (b) with spatial smoothing. (c) 2D spatially-smoothed stack model of n repeating units (denoted as j) and (d) its asymptotic counterpart with PDEs ($\rightarrow$) and ODEs ($\bullet$) in the flow field, and ODEs in other cell layers.

In the layers adjacent to the flow field, heat is transferred by conduction in the solid phase and convection in the gas phase for the porous backing layer, and by conduction

for the current collector (*i.e.*, solid upper part of the interconnect). The pathways of heat transfer between the adjacent layers and the flow field are affected by the existence of the ribs, as shown schematically in Fig. 7.1a. In order to account for the variation in the pathways of heat conduction due to the ribs, correlation factors are needed to modify the energy equation for the backing layer and current collector in the spatially smoothed model. Comparing Fig. 7.1a with Fig. 5.1b, the conductive heat transfer has the same pathway of transport as the charge transfer. As such, we derived a correlation factor for the heat transport based on a generic Laplace equation in the approach introduced by Ly *et al.* [173] for the charge transport. For this purpose, correlation factors, $\zeta(\mathcal{H}, \mathcal{W})$ and $\xi(\mathcal{H}, \mathcal{W})$, are determined by solving a Laplace equation correlated to its volume-averaged counterpart over the cross section of a representative backing layer and a flow field in the spanwise ($\mathbf{e}_y$) and transverse ($\mathbf{e}_z$) directions. The obtained discrete values of $\zeta(\mathcal{H}, \mathcal{W})$ are employed as a training set to construct a functional polynomial via surface fitting as shown in Fig. 7.2, where the sum of squared errors for surface fitting decreases from 2×10^{-2} with the numbers of terms in polynomials $n = m = 3$ to 3×10^{-4} with $n = 4, m = 5$. The obtained polynomials of correlation factors are

$$\zeta(\mathcal{H}, \mathcal{W}) = \sum_{i=0}^4 \sum_{j=0}^{5-i} p_{ij} \mathcal{H}^i \mathcal{W}^j \quad (7.3)$$

for the species transport, and

$$\xi(\mathcal{H}, \mathcal{W}) = \sum_{i=0}^4 \sum_{j=0}^{5-i} p_{ij} \mathcal{H}^i (1 - \mathcal{W})^j \quad (7.4)$$

for the charge and heat transports. The coefficients of the polynomials, p_{ij} , are shown in Table 7.2. The resulting polynomial for $\zeta(\mathcal{H}, \mathcal{W})$ obtained from the training set is then verified with test sets, and good agreement is achieved as shown in Fig. 7.2. The relative errors between the predictions by Eq. (7.3) and the actual values of the correlation factors, ζ , do not exceed 5% over the investigated range $0.4 \leq \mathcal{W} \leq 0.7$ and

$0.05 \leq \mathcal{H} \leq 0.55$. As such, the order of the polynomial, Eq. (7.3), is sufficiently high. In addition, the accuracy can be improved further by adjusting the order of the polynomial and/or narrowing the ranges of $\mathcal{W}$ and $\mathcal{H}$ when calibrating Eq. (7.3). Eq. (7.4) is specified based on Eq. (7.3), such that it shares the same set of polynomial coefficients as Eq. (7.3). Moreover, the derivation based on the Laplace equation reduces the number of correlation factors, because the charge transfer and the conductive heat transfer can share the same factor ξ . Introduce Eq. (7.4) to the conductive heat fluxes in Eq. (3.14) for the current collector and backing layer and obtain

$$\mathbf{q} = -\xi k_{\text{cc, bl}}^{\text{eff}} \nabla T, \quad (7.5)$$

where $k_{\text{cc}}^{\text{eff}} = k_{\text{ic}}$ and $k_{\text{bl}}^{\text{eff}} = \varepsilon k_{\text{mix}} + (1 - \varepsilon) k_{\text{bl}}$.

Fig. 7.2 Correlation for the correction factor $\xi(\mathcal{H}, \mathcal{W})$ derived from a Laplace equation: training sets for calibration ($\bullet$), and test sets for verification ($\blacklozenge$).

Table 7.2 Coefficients of correlation factors for the ASST P-SOFC model.

$p_{00}, p_{01}, p_{02}, p_{03}, p_{04}, p_{05},$	1.251, -11.72, 45.32, -86.34, 76.22, -24.37,
$p_{10}, p_{11}, p_{12}, p_{13}, p_{14},$	1.222, -19.87, 39.04, 25.75, -30.69,
$p_{20}, p_{21}, p_{22}, p_{23},$	12.68, 68.79, -210.4, 50.55,
$p_{30}, p_{31}, p_{32},$	-74.6, 59.82, 140.6,
p_{40}, p_{41}	80.57, -142.9.

7.3.2. Local thermal non-equilibrium

For the spatially smoothed model in LTNE, a thermal convection-conduction equation is solved for the gas phase temperature, T_g , and a thermal conduction equation for the solid phase temperature, T_s . And hence, the original energy equations (3.14) and (3.15) are replaced by

$$-\nabla \cdot (k_g^{\text{eff}} \nabla T_g) + \rho c_{p, \text{mix}} \mathbf{v} \cdot \nabla T_g = 0 \quad (\text{fc, bl, rl}), \quad (7.6)$$

$$-\nabla \cdot (k_s^{\text{eff}} \nabla T_s) = S_{\text{temp}}, \quad (7.7)$$

$$S_{\text{temp}} = \begin{cases} J \left(\eta + T_s \frac{\partial E^{\text{rev}}}{\partial T_s} \right) + \sigma_{\text{elc}}^{\text{eff}} (\nabla \phi_{\text{elc}})^2 + \sigma_{\text{ion}}^{\text{eff}} (\nabla \phi_{\text{ion}})^2 & (\text{rl}) \\ \sigma_{\text{elc}}^{\text{eff}} (\nabla \phi_{\text{elc}})^2 & (\text{ic, bl}), \\ \sigma_{\text{ion}}^{\text{eff}} (\nabla \phi_{\text{ion}})^2 & (\text{el}) \end{cases} \quad (7.8)$$

which is modified further below to get the spatially smoothed domain in LTNE.

For the spatially smoothed flow field, effective thermal conductivities are specified as

$$k_{g, \text{ff}}^{\text{eff}} = \varepsilon_{\text{ff}} k_{\text{mix}}, \quad (7.9)$$

$$k_{s, \text{ff}}^{\text{eff}} = (1 - \varepsilon_{\text{ff}}) k_{\text{ic}}, \quad (7.10)$$

for the gas mixture and solid ribs, respectively. In view of the heat exchange between the gas and solid phases in porous media [135], additional heat source terms,

$\pm \mathcal{H}_{\text{ff}}^{\text{g-s}} \mathcal{A}_{\text{ff}}^{\text{g-s}} (T_g - T_s)$, are introduced to Eq. (7.8) for the flow field with a positive sign for

the solid phase and negative for the fluid. Then, the LTNE energy equations for the spatially smoothed flow field are obtained:

$$-\nabla \cdot (k_{g,ff}^{\text{eff}} \nabla T_g) + \rho c_{p,mix} \mathbf{v} \cdot \nabla T_g = -\hat{h}_{ff}^{g-s} \mathcal{A}_{ff}^{g-s} (T_g - T_s), \quad (7.11)$$

$$-\nabla \cdot (k_{s,ff}^{\text{eff}} \nabla T_s) = \sigma_{\text{elc,ic}} (\nabla \phi_{\text{elc}})^2 + \hat{h}_{ff}^{g-s} \mathcal{A}_{ff}^{g-s} (T_g - T_s), \quad (7.12)$$

for the gas and solid phases, respectively. The heat transfer coefficient, $\hat{h}_{ff}^{g-s}$, is defined as [110]

$$\hat{h}_{ff}^{g-s} = \text{Nu } k_{\text{mix}} / D_h, \quad (7.13)$$

in which k_{mix} is the thermal conductivity of the gas mixture. The hydraulic diameter $D_h = 4A_{\perp}^{(\text{fc})} / S_{\perp}^{(\text{fc})}$ is related to the wetted perimeter $S_{\perp}^{(\text{fc})} = 2(h_{\text{fc}} + w_{\text{fc}})$ for the cross section (in the yz -plane) of a rectangular plain flow channel with a cross-sectional area $A_{\perp}^{(\text{fc})} = h_{\text{fc}} w_{\text{fc}}$ (perpendicular to the streamwise direction). The specific area for heat exchange, $\mathcal{A}_{ff}^{g-s}$, is specified as

$$\mathcal{A}_{ff}^{g-s} = 4\varepsilon_{ff} / D_h. \quad (7.14)$$

The Nusselt number for a rectangular channel, Nu , is estimated as [110]

$$\text{Nu} \sim 1.86 (\text{Re Pr } D_h / L)^{1/3}, \quad (7.15)$$

based on the fluid properties of the inflow depicted by the Reynolds number, $\text{Re} = \rho U^{\text{in}} D_h / \mu_{\text{mix}}$, and Prandtl number, $\text{Pr} = c_{p,mix} \mu_{\text{mix}} / k_{\text{mix}}$.

In order to account for the heat exchange between the gas and solid phases in the backing and reaction zone layers, an heat source term, $\pm \hat{h}_{bl,rl}^{g-s} \mathcal{A}_{bl,rl}^{g-s} (T_g - T_s)$, is added to Eq. (7.8) with a positive sign for the solid phase and negative for the fluid in these two porous layers. The formulae of the heat transfer coefficient, $\hat{h}_{bl,rl}^{g-s}$, and specific area, $\mathcal{A}_{bl,rl}^{g-s}$, are approximated by [135]:

$$\hat{h}_{\text{bl,rl}}^{\text{g-s}} \sim \frac{2k_{\text{mix}}}{d_{\text{par}}}, \quad (7.16)$$

$$\mathcal{A}_{\text{bl,rl}}^{\text{g-s}} = \frac{2\varepsilon}{r}, \quad (7.17)$$

which are correlated via the average particle diameter of porous media, $d_{\text{par}} = 6(1-\varepsilon)/\mathcal{A}_{\text{bl,rl}}^{\text{g-s}}$.

Furthermore, the influence of ribs on the pathways of conductive heat transfer is also considered for the LTNE model. As shown in Fig. 7.1a, the pathways of the heat delivered by the gas mixture and the solid structure are different. The conductive heat fluxes in Eqs. (7.6) and (7.7) are modified to

$$\mathbf{q}_{\text{g, bl}} = -\zeta k_{\text{mix}}^{\text{eff}} \nabla T_{\text{g}}, \quad (7.18)$$

for the gas mixture in the backing layer, and

$$\mathbf{q}_{\text{s, bl, cc}} = -\xi k_{\text{bl, cc}}^{\text{eff}} \nabla T_{\text{s}}, \quad (7.19)$$

for the solid structure of the backing layer and the current collector. Here,

$$k_{\text{bl}}^{\text{eff}} = \varepsilon k_{\text{mix}} + (1-\varepsilon)k_{\text{bl}} \quad \text{and} \quad k_{\text{cc}}^{\text{eff}} = k_{\text{ic}}.$$

As introduced at the end of Section 4.2, the 3D spatially smoothed geometry (Fig. 4.1c) can be reduced to a 2D counterpart, provided that the inlet conditions are the same for all the channels on the same electrode. The average behaviour of the transport processes in the spatially smoothed domain does not vary in the spanwise direction, such that the spanwise coordinate (e_y) is removed, resulting in a 2D computational domain for the single cell in the streamwise (e_x) and normal (e_z) direction that is a repeating unit in a stack as shown in Fig. 7.1c.

7.4. Asymptotic reduction

In Section 4.3, the 2D spatially-smoothed equations for the change of mass, species,

momentum, and charge are reduced from elliptic PDEs to parabolic PDEs and ODEs for the spatially smoothed flow fields and ODEs for the rest of the cell. This section depicts the scaling analysis for the asymptotic reduction of the LTE and LTNE energy equations in the 2D spatially-smoothed non-isothermal model.

7.4.1. Local thermal equilibrium

First, the 2D LTE spatially-smoothed energy equations are nondimensionalized with the following scale factors,

$$\tilde{T} = \frac{T - T^{\text{ref}}}{[T]}, \tilde{k}^{\text{eff}} = \frac{k^{\text{eff}}}{[k^{\text{eff}}]}, \tilde{c}_{p,\text{mix}} = \frac{c_{p,\text{mix}}}{[c_{p,\text{mix}}]},$$

resulting in the dimensionless counterparts below:

$$-\frac{\xi[k^{\text{eff}}][T]}{h_{\text{cc}}^2} \left[\ell_{\text{cc}}^2 \frac{\partial}{\partial \tilde{x}} \left(\tilde{k}^{\text{eff}} \frac{\partial \tilde{T}}{\partial \tilde{x}} \right) + \frac{\partial}{\partial \tilde{z}} \left(\tilde{k}^{\text{eff}} \frac{\partial \tilde{T}}{\partial \tilde{z}} \right) \right] = S_{\text{temp, cc}} \quad (\text{cc}), \quad (7.20)$$

$$\begin{aligned} & -\frac{[k^{\text{eff}}][T]}{h_{\text{ff}}^2} \left[\ell_{\text{ff}}^2 \frac{\partial}{\partial \tilde{x}} \left(\tilde{k}^{\text{eff}} \frac{\partial \tilde{T}}{\partial \tilde{x}} \right) + \frac{\partial}{\partial \tilde{z}} \left(\tilde{k}^{\text{eff}} \frac{\partial \tilde{T}}{\partial \tilde{z}} \right) \right] \\ & + \frac{[\rho][c_{p,\text{mix}}][T][w_{\text{ff}}]}{h_{\text{ff}}} \tilde{\rho} \tilde{c}_{p,\text{mix}} \left(\frac{\ell_{\text{ff}}[u_{\text{ff}}]}{[w_{\text{ff}}]} \tilde{u} \frac{\partial \tilde{T}}{\partial \tilde{x}} + \tilde{w} \frac{\partial \tilde{T}}{\partial \tilde{z}} \right) = S_{\text{temp, ff}} \end{aligned} \quad (\text{ff}), \quad (7.21)$$

$$\begin{aligned} & -\frac{\xi[k^{\text{eff}}][T]}{h_{\text{bl}}^2} \left[\ell_{\text{bl}}^2 \frac{\partial}{\partial \tilde{x}} \left(\tilde{k}^{\text{eff}} \frac{\partial \tilde{T}}{\partial \tilde{x}} \right) + \frac{\partial}{\partial \tilde{z}} \left(\tilde{k}^{\text{eff}} \frac{\partial \tilde{T}}{\partial \tilde{z}} \right) \right] \\ & + \frac{[\rho][c_{p,\text{mix}}][T][w_{\text{bl}}]}{h_{\text{bl}}} \tilde{\rho} \tilde{c}_{p,\text{mix}} \left(\frac{\ell_{\text{bl}}[u_{\text{bl}}]}{[w_{\text{bl}}]} \tilde{u} \frac{\partial \tilde{T}}{\partial \tilde{x}} + \tilde{w} \frac{\partial \tilde{T}}{\partial \tilde{z}} \right) = S_{\text{temp, bl}} \end{aligned} \quad (\text{bl}), \quad (7.22)$$

$$\begin{aligned} & -\frac{[k^{\text{eff}}][T]}{h_{\text{rl}}^2} \left[\ell_{\text{rl}}^2 \frac{\partial}{\partial \tilde{x}} \left(\tilde{k}^{\text{eff}} \frac{\partial \tilde{T}}{\partial \tilde{x}} \right) + \frac{\partial}{\partial \tilde{z}} \left(\tilde{k}^{\text{eff}} \frac{\partial \tilde{T}}{\partial \tilde{z}} \right) \right] \\ & + \frac{[\rho][c_{p,\text{mix}}][T][w_{\text{rl}}]}{h_{\text{rl}}} \tilde{\rho} \tilde{c}_{p,\text{mix}} \left(\frac{\ell_{\text{rl}}[u_{\text{rl}}]}{[w_{\text{rl}}]} \tilde{u} \frac{\partial \tilde{T}}{\partial \tilde{x}} + \tilde{w} \frac{\partial \tilde{T}}{\partial \tilde{z}} \right) = S_{\text{temp, rl}} \end{aligned} \quad (\text{rl}), \quad (7.23)$$

$$-\frac{[k^{\text{eff}}][T]}{h_{\text{el}}^2} \left[\ell_{\text{el}}^2 \frac{\partial}{\partial \tilde{x}} \left(\tilde{k}^{\text{eff}} \frac{\partial \tilde{T}}{\partial \tilde{x}} \right) + \frac{\partial}{\partial \tilde{z}} \left(\tilde{k}^{\text{eff}} \frac{\partial \tilde{T}}{\partial \tilde{z}} \right) \right] = S_{\text{temp, el}} \quad (\text{el}). \quad (7.24)$$

The corresponding dimensionless boundary conditions are:

- 1) At the cathode flow field inlet,

$$\tilde{T} = \frac{T_c^{\text{in}} - T^{\text{ref}}}{[T]}; \quad (7.25)$$

- 2) At the anode flow field inlet,

$$\tilde{T} = \frac{T_a^{\text{in}} - T^{\text{ref}}}{[T]}; \quad (7.26)$$

- 3) At the flow field outlets,

$$\frac{\partial \tilde{T}}{\partial \tilde{x}} = 0; \quad (7.27)$$

- 4) At the top surface of the cathode interconnect and the bottom surface of the anode interconnect,

$$\tilde{T} = \frac{T^{\text{oper}} - T^{\text{ref}}}{[T]}; \quad (7.28)$$

- 5) At the vertical walls of the interconnect, backing layers, reaction zone layers, and electrolyte,

$$\frac{\partial \tilde{T}}{\partial \tilde{x}} = 0. \quad (7.29)$$

The next step is to determine the unknown reference and scale factors including T^{ref} , $[c_{p,\text{mix}}]$, $[k^{\text{eff}}]$, and $[T]$. The scale factors for the density and velocities are introduced in Section 4.3.2.2. The reference factor for the temperature, T^{ref} , is determined by setting dimensionless group on the right-hand side of Eq. (7.25) or (7.26) equal to zero. Moreover, the air and fuel flows are assumed to have the same inlet temperature that is equal to the nominal operating temperature, T^{oper} . Therefore, we get

$$T^{\text{ref}} = T_c^{\text{in}} = T_a^{\text{in}} = T^{\text{oper}}. \quad (7.30)$$

The orders of magnitude of the specific heat of the gas mixture, $[c_{p,\text{mix}}]$, and the effective thermal conductivity, $[k^{\text{eff}}]$, are determined according to the constitutive relations in Table 3.1 and the typical values of the thermal properties of gas and cell

components as shown in Tables 3.2 and 3.3. As a result, we have $[c_{p,\text{mix}}] \sim 10^3 \text{ J kg}^{-1} \text{ K}^{-1}$ for the cathode and $10^4 \text{ J kg}^{-1} \text{ K}^{-1}$ for the anode, and $[k^{\text{eff}}] \sim 1 \text{ W m}^{-1} \text{ K}^{-1}$. For the SOFC, the order of magnitude of the change in temperature may vary from 10 to 10^2 K depending on the operating and cooling conditions [22, 69, 70, 208]. As such, the temperature difference scale factor, $[T]$, varies from $O(10)$ to $O(10^2)$ in K. In fact, $[T]$ does not affect the comparison of dominance between the convective and conductive terms in the dimensionless governing equations (7.20) to (7.24), because $[T]$ exists in the coefficient groups of both terms. In addition, the correlation factor for the spatial smoothing of the energy transport described by Eqs. (7.20) and (7.22) is a number between zero and one and thus

$$\xi \sim 10^{-1}. \quad (7.31)$$

Based on the reference and scale factors obtained above, the dimensionless 2D spatially-smoothed energy equations (7.20) to (7.24) are reduced asymptotically by dropping the terms with coefficient groups in orders of magnitude equal to and smaller than $O(10^{-3})$. The streamwise convective term for the flow field is retained considering the fact that the heat generated by ohmic heating and electrochemical reactions is removed from the cell mainly by the gas flow in the channel, especially when the cell is inside a large stack. The detailed procedures of the asymptotic reduction for the LTE energy equation in different cell components are presented in Appendices A to E.

The resulting asymptotic counterpart of the spatially smoothed energy equation in LTE consists of parabolic PDEs in the porous flow fields and ODEs in the rest of the cell. Regarding the boundary conditions, the ones at the inlet are necessary for the parabolic PDEs in the flow field. The ODEs only require boundary conditions at the upper and lower boundaries of the cell.

7.4.2. Local thermal non-equilibrium

For the spatially smoothed energy equation in LTNE, an order-of-magnitude counterpart is expressed as

$$\underbrace{\frac{[k_g^{\text{eff}}][T_g]}{L^2}}_{\text{streamwise conduction}} + \underbrace{\frac{[k_g^{\text{eff}}][T_g]}{h_j^2}}_{\text{normal conduction}} + \underbrace{\frac{[\rho][c_{p,\text{mix}}][u][T_g]}{L}}_{\text{streamwise convection}} + \underbrace{\frac{[\rho][c_{p,\text{mix}}][w][T_g]}{h_j}}_{\text{normal convection}} \quad (\text{ff, bl, rl}) \quad (7.32)$$

for the gas phase, and as

$$\underbrace{\frac{[k_s^{\text{eff}}][T_s]}{L^2}}_{\text{streamwise conduction}} + \underbrace{\frac{[k_s^{\text{eff}}][T_s]}{h_j^2}}_{\text{normal conduction}} \quad (\text{cc, ff, bl, rl, el}) \quad (7.33)$$

for the solid phase. Here, the scale factors for the density, $[\rho]$, and the heat capacity, $[c_{p,\text{mix}}]$, are the same as those for the LTE model, which are introduced in Section 7.4.1.

The scale factors for the velocity, $[u]$ and $[w]$, are referred to Eqs. (4.34) and (4.37) to (4.41) in Section 4.3.2.2. The orders of magnitude of the thermal conductivities of the solid cell components and gas mixtures are $[k_s^{\text{eff}}] \sim 1 \text{ W m}^{-1} \text{ K}^{-1}$ and $[k_g^{\text{eff}}] \sim 10^{-1} \text{ W m}^{-1} \text{ K}^{-1}$ according to the material and gas properties in Tables 3.2 and 3.3. The scale factors for the temperature, $[T_g]$ and $[T_s]$, are redundant as they do not affect the results of the scaling analysis here.

Eqs. (7.32) and (7.33) are simplified for each layer by neglecting the terms that are smaller than the dominant term by three orders or more. Comparing the conductive and convective terms in Eq. (7.32) regarding the energy transport by the gas mixture, the normal conduction and streamwise convection are retained for the flow field, whereas only the normal convection is retained for the backing and reaction zone layers. The streamwise convective term for the flow field is kept, because the heat generated by ohmic heating and electrochemical reactions is removed from the cell by the gas flow in

the channel. In Eq. (7.33), the normal conduction is kept for all the solid cell components, and the streamwise conduction is neglected.

Consequently, the spatially smoothed energy equation in LTNE is reduced to a set of a parabolic PDE solving for T_g in the porous flow fields and ODEs for T_g in the rest of the cell as well as ODEs for T_s throughout the solid structure of the cell. For the boundary conditions, the conditions at the inlet are necessary for the parabolic PDE in the flow field. The ODEs for T_s only require boundary conditions at the upper and lower boundaries of the cell. For the PDE solving for T_g , a heat flux of $-\hat{h}_{\text{ff}}^{\text{g-s}}(T_g - T_s)$ is specified at the current collector/flow field interface due to the heat exchange between the current collector and the gas mixture. Moreover, it is estimated that $T_g \approx T_s$ at the reaction zone/electrolyte interface, because Zheng *et al.* [137] showed that the temperature difference between the gas and solid phases in the electrode of SOFCs is on the order of 10^{-3} K.

As a result, a 2D asymptotic spatially-smoothed thermal (ASST) single-cell model accounting for both the LTE and LTNE conditions is obtained. Table 7.3 summarizes the governing equations for the conservation of mass, species, charge, and energy as well as the boundary conditions of this 2D ASST model in the dimensional form. The dimensional set of the ASST model is used for numerical implementation to solve for the dependent variables. This 2D reduced cell model is numerically solved over a 1D domain in the normal direction ($\mathbf{e}_z$) with space marching in the streamwise direction ($\mathbf{e}_x$) and is employed as the repeating unit of a reduced stack model, as schematically shown in Fig. 7.1d.

Table 7.3 Governing equations and boundary conditions of the ASST P-SOFC model.

Domain	Governing equations
Current collector	$\frac{\partial}{\partial z} \left(-\xi \sigma_{\text{elc,ic}} \frac{\partial \phi_{\text{elc}}}{\partial z} \right) = 0, \quad -\xi k_{\text{ic}} \frac{\partial^2 T}{\partial z^2} = \sigma_{\text{elc,ic}} \left(\frac{\partial \phi_{\text{elc}}}{\partial z} \right)^2 \quad (\text{LTE})$ $-\xi k_{\text{ic}} \frac{\partial^2 T_s}{\partial z^2} = \sigma_{\text{elc,ic}} \left(\frac{\partial \phi_{\text{elc}}}{\partial z} \right)^2 \quad (\text{LTNE})$
Flow field	$\frac{\partial}{\partial x} (\rho u) + \frac{\partial}{\partial z} (\rho w) = 0, \quad \frac{\partial p}{\partial x} = -\frac{\mu_{\text{mix}}}{\kappa_{\text{ff}}} u, \quad \frac{\partial p}{\partial z} = 0,$ $\frac{\partial}{\partial x} (\rho u \omega_i) + \frac{\partial}{\partial z} (\rho w \omega_i) = \frac{\partial}{\partial z} \left(\rho \omega_i \sum_{j=1}^n \left(\varepsilon_{\text{ff}} \mathcal{D}_{ij} \frac{\partial x_j}{\partial z} \right) \right),$ $\frac{\partial}{\partial z} \left(-(1 - \varepsilon_{\text{ff}}) \sigma_{\text{elc,ic}} \frac{\partial \phi_{\text{elc}}}{\partial z} \right) = 0,$ $-k_{\text{ff}}^{\text{eff}} \frac{\partial^2 T}{\partial z^2} + \rho c_{\text{p, mix}} u = \sigma_{\text{elc,ic}} \left(\frac{\partial \phi_{\text{elc}}}{\partial z} \right)^2 \quad (\text{LTE})$ $\begin{cases} -k_{\text{g, ff}}^{\text{eff}} \frac{\partial^2 T_{\text{g}}}{\partial z^2} + \rho c_{\text{p, mix}} u \frac{\partial T_{\text{g}}}{\partial x} = -\hat{h}_{\text{ff}}^{\text{g-s}} \mathcal{A}_{\text{ff}}^{\text{g-s}} (T_{\text{g}} - T_{\text{s}}) \\ -k_{\text{s, ff}}^{\text{eff}} \frac{\partial^2 T_{\text{s}}}{\partial z^2} = \sigma_{\text{elc,ic}} \left(\frac{\partial \phi_{\text{elc}}}{\partial z} \right)^2 + \hat{h}_{\text{ff}}^{\text{g-s}} \mathcal{A}_{\text{ff}}^{\text{g-s}} (T_{\text{g}} - T_{\text{s}}) \end{cases} \quad (\text{LTNE})$
Backing layer	$\frac{\partial}{\partial z} (\rho w) = 0, \quad \frac{\partial p}{\partial z} = -\frac{\mu_{\text{mix}}}{\kappa} w,$ $\frac{\partial}{\partial z} (\rho w \omega_i) = \frac{\partial}{\partial z} \left(\rho \omega_i \sum_{j=1}^n \left(\zeta \mathcal{D}_{ij}^{\text{eff}} \frac{\partial x_j}{\partial z} \right) \right), \quad \frac{\partial}{\partial z} \left(-\sigma_{\text{elc}}^{\text{eff}} \frac{\partial \phi_{\text{elc}}}{\partial z} \right) = 0,$ $-\xi k^{\text{eff}} \frac{\partial^2 T}{\partial z^2} = \sigma_{\text{elc}}^{\text{eff}} \left(\frac{\partial \phi_{\text{elc}}}{\partial z} \right)^2 \quad (\text{LTE})$ $\begin{cases} -\zeta k_{\text{g}}^{\text{eff}} \frac{\partial^2 T_{\text{g}}}{\partial z^2} = -\hat{h}_{\text{bl}}^{\text{g-s}} \mathcal{A}_{\text{bl}}^{\text{g-s}} (T_{\text{g}} - T_{\text{s}}) \\ -\xi k_{\text{s}}^{\text{eff}} \frac{\partial^2 T_{\text{s}}}{\partial z^2} = \sigma_{\text{elc}}^{\text{eff}} \left(\frac{\partial \phi_{\text{elc}}}{\partial z} \right)^2 + \hat{h}_{\text{bl}}^{\text{g-s}} \mathcal{A}_{\text{bl}}^{\text{g-s}} (T_{\text{g}} - T_{\text{s}}) \end{cases} \quad (\text{LTNE})$
Reaction zone layer	$\frac{\partial}{\partial z} (\rho w) = \begin{cases} \frac{M_{\text{O}_2} J_{\text{c}}}{4F} & (\text{cathode rl}) \\ \frac{M_{\text{H}_2\text{O}} J_{\text{a}}}{2F} - \frac{M_{\text{H}_2} J_{\text{a}}}{2F} & (\text{anode rl}) \end{cases}, \quad \frac{\partial p}{\partial z} = -\frac{\mu_{\text{mix}}}{\kappa} w,$ $\frac{\partial}{\partial z} (\rho w \omega_i) - \frac{\partial}{\partial z} \left(\rho \omega_i \sum_{j=1}^n \left(\mathcal{D}_{ij}^{\text{eff}} \frac{\partial x_j}{\partial z} \right) \right) = \begin{cases} +\frac{M_{\text{O}_2} J_{\text{c}}}{4F} & (\text{O}_2, \text{cathode rl}) \\ -\frac{M_{\text{H}_2} J_{\text{a}}}{2F} & (\text{H}_2, \text{anode rl}) \end{cases},$ $\frac{\partial}{\partial z} \left(-\sigma_{\text{elc}}^{\text{eff}} \frac{\partial \phi_{\text{elc}}}{\partial z} \right) = -J, \quad \frac{\partial}{\partial z} \left(-\sigma_{\text{ion}}^{\text{eff}} \frac{\partial \phi_{\text{ion}}}{\partial z} \right) = J,$

$$-k^{\text{eff}} \frac{\partial^2 T}{\partial z^2} = J \left(\eta^{\text{act}} + T \frac{\partial E_{\text{rev}}}{\partial T} \right) + \sigma_{\text{elc}}^{\text{eff}} \left(\frac{\partial \phi_{\text{elc}}}{\partial z} \right)^2 + \sigma_{\text{ion}}^{\text{eff}} \left(\frac{\partial \phi_{\text{ion}}}{\partial z} \right)^2 \quad (\text{LTE})$$

$$\begin{cases} -k_g^{\text{eff}} \frac{\partial^2 T_g}{\partial z^2} = -\hat{h}_{\text{rl}}^{\text{g-s}} \mathcal{A}_{\text{rl}}^{\text{g-s}} (T_g - T_s) \\ -k_s^{\text{eff}} \frac{\partial^2 T_s}{\partial z^2} = J \left(\eta + T_s \frac{\partial E_{\text{rev}}}{\partial T_s} \right) + \sigma_{\text{elc}}^{\text{eff}} \left(\frac{\partial \phi_{\text{elc}}}{\partial z} \right)^2 + \sigma_{\text{ion}}^{\text{eff}} \left(\frac{\partial \phi_{\text{ion}}}{\partial z} \right)^2 + \hat{h}_{\text{rl}}^{\text{g-s}} \mathcal{A}_{\text{rl}}^{\text{g-s}} (T_g - T_s) \end{cases} \quad (\text{LTNE}) ;$$

Electrolyte

$$\frac{\partial}{\partial z} \left(-\sigma_{\text{ion}} \frac{\partial \phi_{\text{ion}}}{\partial z} \right) = 0, \quad -k_{\text{el}} \frac{\partial^2 T}{\partial z^2} = \sigma_{\text{ion}} \left(\frac{\partial \phi_{\text{ion}}}{\partial z} \right)^2 \quad (\text{LTE})$$

$$-k_{\text{el}} \frac{\partial^2 T_s}{\partial z^2} = \sigma_{\text{ion}} \left(\frac{\partial \phi_{\text{ion}}}{\partial z} \right)^2 \quad (\text{LTNE})$$

Location	Boundary conditions
Inlets	$u = \varepsilon_{\text{ff}} U_{\text{a,c}}^{\text{in}}, \quad w = 0, \quad \omega_{\text{O}_2} = \omega_{\text{O}_2}^{\text{in}}, \quad \omega_{\text{H}_2} = \omega_{\text{H}_2}^{\text{in}}, \quad T = T^{\text{in}} \quad (\text{LTE}),$ $T_g = T^{\text{in}} \quad (\text{LTNE});$
Top and bottom	$\phi_{\text{elc,c}} = V_{\text{cell}}, \quad \phi_{\text{elc,a}} = 0, \quad T = T^{\text{oper}} \quad (\text{LTE}), \quad T_s = T^{\text{oper}} \quad (\text{LTNE});$
Current collector/flow field	$u = w = 0, \quad \partial \omega_i / \partial z = 0, \quad -k_g^{\text{eff}} \partial T_g / \partial z = -\hat{h}_{\text{ff}}^{\text{g-s}} (T_g - T_s) \quad (\text{LTNE});$
Backing/reaction zone	$\partial \phi_{\text{ion}} / \partial z = 0;$
Reaction zone/electrolyte	$w = 0, \quad \partial \omega_i / \partial z = \partial \phi_{\text{elc}} / \partial z = 0, \quad T_g = T_s \quad (\text{LTNE}).$

7.5. Numerical implementation

The present full and reduced cell and stack models are solved with the commercial finite-element solver COMSOL Multiphysics 3.5a on a 64G-RAM workstation. The linear direct solver PARDISO is chosen for the 3D, 2D cross-sectional, and 2D spatially-smoothed models, and a transient solver with the backward differentiation formula (BDF) method is used for the 2D ASST model to march in space by treating x as a time-like variable. Quadratic Lagrange basis functions and a relative convergence error of 10^{-3} are employed for all variables. Relational operators are used to avoid the appearance of non-physical quantities (see Section 4.4 for more details). The stream function given by Eqs. (4.56) to (4.58) is introduced to the flow field in order to reduce the number of variables.

When implementing the stack models, the Array function in COMSOL is employed for the 3D and 2D spatially-smoothed models. This function required us to specify the height of the unit cell and the number of cells as the displacement and array size in a certain direction, and then it automatically generated an array of cells that have the same geometry, meshing, and subdomain setting. Subsequently, only a few minor modifications are performed including changing the potential at the top of the stack from V_{cell} to V_{stack} and adjusting the initial guesses of electric potential for the conservation of charges (*i.e.*, electrons and ions) in each cell according to the cell level. This allows a quick implementation without tedious programming for 3D and 2D stack modeling. However, COMSOL does not provide the Array function for a 1D domain. As such, the 1D domain of the small 2D ASST stack model considered here is created manually in COMSOL. If the stack is in a large size such as 100 cells, it requires programming using the bidirectional interface between COMSOL Multiphysics and MATLAB with a loop for the automate generation of the stack.

In addition, the post-processing of all the model predictions and the calibration and validation of the polynomial of correlation factors are all conducted in MATLAB R2010a.

7.6. Verification

According to the analysis in Sections 4.2, 4.3, 7.2, and 7.3, the original 3D non-isothermal single-cell model presented in Chapter 3 is spatially smoothed to a 2D counterpart and further asymptotically reduced to a set of parabolic PDEs and ODEs associated with space marching, namely the ASST model subject to both the LTE and LTNE conditions. In this section, the spatially smoothed thermal model and its asymptotic counterpart are verified with their 3D counterparts at both the cell and stack levels. The verification is conducted in three cases: (a) a single-cell model; (b) a stack model without considering perturbations of dependent variables between cells; (c) a stack model consisting of 3 cells considering perturbations between cells.

7.6.1. Cell performance

First, the reduced single-cell model is verified with the original 3D counterpart (*i.e.*, Case (a)). According to the prediction of the 3D model, the relative errors between the temperatures of the gas mixture and the interconnect are on the order of $O(10^{-3})$. Thus, the developed LTE reduced model is applied here. The verification is performed in terms of the local dependent variables at the backing/reaction zone interface (in the xy -plane in Fig. 3.1c), which is the region of the SOFC that is most sensitive to the influence of the variations in the variables. Fig. 7.3a and 7.3b show the temperature at the backing/reaction zone interface for the cathode and anode side in the 3D model in Case (a). The spanwise averages of the 3D solutions in Fig. 7.3a and 7.3b are similar to the

results shown in Fig. 7.3c and 7.3d, which are obtained by extruding the solutions at the 1D backing/reaction zone interface of the 2D spatially-smoothed geometry to the spanwise direction ($\mathbf{e}_y$).

Fig. 7.3 Temperature distribution at 0.5 V at the backing/reaction zone interface on the (a, c) cathode and (b, d) anode with $\mathcal{H}_c = 0.125$, $\mathcal{H}_a = 0.375$, and $\mathcal{W} = 0.55$: (a, b) 3D model with plain channels and ribs (separated by the dashed line); (c, d) 2D spatially-smoothed model.

Fig. 7.4a compares the spanwise average value of temperature at the backing/reaction zone interface predicted by the 3D model (defined as $\bar{\Omega}(x)$ in Table 4.3) with the predictions by the reduced models. The maximum relative error between the 3D model and the 2D spatially-smoothed counterpart with the correlation factor ξ for heat transfer is about 0.1%. The 2D spatially-smoothed model without ξ always underestimates the temperature, because the effective thermal conductivities of the backing layer and the current collector are overestimated. Moreover, the 2D spatially-smoothed model with correlations agrees well with its asymptotic counterpart

(i.e., the ASST model) with relative errors less than 0.01%. Fig. 7.4 also presents a comparison of the oxygen mass fractions from the full and reduced models. The relative errors do not exceed 3% for the 2D spatially-smoothed model with ξ and 2% for the ASST model, as shown in Fig. 7.4b. The standard deviations in Fig. 7.4, which are formulated as $\sigma(x)$ in Table 4.3, reflect the spread of the dependent variables along the width of the cell due to the ribs for the 3D model. At low voltages such as 0.6 and 0.4 V, the large standard deviations indicate that the variables tend to deviate from the spanwise average value that is the counterpart of the solution by the reduced models.

Fig. 7.4 Average (a) temperature and (b) oxygen mass fraction at the cathode backing/reaction zone interface: 3D model with $\mathcal{H}_c = 0.125$, $\mathcal{H}_a = 0.375$, and $\mathcal{W} = 0.55$ at 0.8 ($\blacktriangledown$), 0.6 ($\blacksquare$), and 0.4 V ($\blacktriangle$); 2D spatially-smoothed model with (solid lines) and

without (dashed lines) correlations for heat transfer; 2D ASST model ($\times$). Error bars represent standard deviations.

7.6.2. Stack performance

After the verification for single-cell modeling (Case (a)), we proceed by raising the verification from the cell to stack level in two cases: a stack with a large variation in temperature neglecting perturbations of dependent variables between cells (Case (b)) and a 3-cell stack considering perturbations between cells (Case (c)).

7.6.2.1. Stack without perturbation between cells

For the case (b), the 3D stack performance is represented by a repeating unit in the center of the stack based on the full single-cell model specified by Eqs. (3.1) to (3.15) with adiabatic conditions at the top and bottom of the domain instead of original constant temperatures. According to the prediction of the 3D model, the maximum temperature difference between the gas flow in the channel and the interconnect is about 50 K for the air flow and 5 K for the fuel flow. The large temperature difference between the air and rib at high current densities can be attributed to the cooling effect invoked by the air flow [10]. The high-speed air flow has an inlet temperature of the nominal operating value (*i.e.*, 973.15 K) that is much smaller than the stack temperature, which is up to 1080 K in the present case. Fig. 7.5 presents the average cross-sectional temperatures of the air flow and the rib (under the current collector) and compares the 3D model with both the LTE and LNTE spatially smoothed counterparts. The LTE spatially-smoothed model cannot accurately capture the temperatures in the flow field, because the spatially smoothed flow field investigated here is actually not in LTE. In contrast, the LTNE model agrees well with the 3D solutions with a maximum relative error of 0.8% for T_g and 1% for T_s .

Fig. 7.5 Average cross-sectional temperatures in the cathode rib (under the current collector) (■) and channel (▼) by the 3D model with $\mathcal{H}_c = 0.125$, $\mathcal{H}_a = 0.375$, and $\mathcal{W} = 0.55$ at 0.4 V. Predictions by the spatially smoothed model with correlations for heat transfer: T in LTE (—); T_s (---) and T_g (-·-) in LTNE.

Next, we verify the reduced models with the 3D counterpart in terms of the local temperature and oxygen mass fraction at the backing/reaction zone interface, as shown in Fig. 7.6. The LTE spatially-smoothed model and its asymptotic counterpart underestimate the results at high current densities. The maximum relative error is 2.3% in T and 17% in ω_{O_2} for the former, and 3% and 20% for the latter, as shown in Fig. 7.6a and 7.6b. Compared with the LTE models, the LTNE reduced models provides more accurate predictions. In Fig. 7.6c and 7.6d, the relative errors do not exceed 0.8% for the temperature of the flow, T_g , and 8% for ω_{O_2} by the LTNE spatially smoothed model, and 1.4% and 13% by the asymptotic counterpart. Similar results are also obtained for the temperature of the solid phase, T_s , which is almost equal to T_g in the porous electrode. Moreover, the accuracy of the LTE and LTNE spatially smoothed models is considerably

affected by the correlation factors accounting for the variation in the pathway of heat transfer in the backing and current collector (*i.e.*, ξ for T in LTE, ζ for T_g and ξ for T_s in LTNE). For instance, without the correlations factors, the maximum relative error increases from 0.8% to 1.3% in T_g (Fig. 7.6c) and from 8% to 12% in ω_{O_2} (Fig. 7.6d) for the LTNE spatially smoothed model.

Fig. 7.6 Average temperature and oxygen mass fraction at the backing/reaction zone interface: 3D model with $\mathcal{H}_c = 0.125$, $\mathcal{H}_a = 0.375$, and $\mathcal{W} = 0.55$ at 0.8 ($\blacktriangledown$), 0.6 ($\blacksquare$), and 0.4 V ($\blacktriangle$); 2D spatially-smoothed model with (solid lines) and without (dashed lines) correlations for heat transfer by (a, b) LTE and (c, d) LTNE approaches; 2D ASST model ($\times$). Error bars represent standard deviations.

In addition, as shown in Fig. 7.6, the relative errors between the results from the 2D

spatially-smoothed and 3D models increase as the cell voltage decreases. At lower cell voltages (or high current densities), more reactants are consumed and more heat is generated, resulting in large variations in the distribution of local dependent variables, such as species mass fractions and temperature, in the 3D model. The local dependent variables along the cell width (*i.e.*, in the spanwise direction, $\mathbf{e}_y$) deviate more from their spanwise averages that are the counterparts of the solutions by the 2D reduced model.

7.6.2.2. *Stack with perturbation between cells*

After verifying the reduced non-isothermal stack models without considering the perturbations between cells in the stack, we now proceed to investigate how well the reduced models agree with the 3D counterpart when the influence of the perturbations are taken into account (Case (c)). A 3D 3-cell stack model with a constant temperature at the top and bottom is investigated here. For this small stack, in order to get significant perturbations between cells, different air inlet velocities for the three cells as specified in Table 7.1. In view of the 3D results, the maximum temperature difference between the flow and the interconnect is about 10 K at the outlet of the air channel of cell 3. This implies the volume-averaged flow field in the spatially smoothed model can be considered to be in LTE. Therefore, the developed LTE spatially smoothed model and its asymptotic counterpart are employed here. Compared with the 3D model, the maximum relative error in the polarization curve is 2% for the 2D LTE model and 2.3% for the 2D asymptotic LTE spatially smoothed model, as can be referred in Fig. 7.7.

Fig. 7.7 Polarization curves for a 3-cell stack with $\mathcal{H}_c = 0.1$, $\mathcal{H}_a = 0.5$, and $\mathcal{W} = 0.4$: 3D (▼), 2D spatially-smoothed (—), and 2D asymptotic spatially-smoothed (×) non-isothermal models.

Fig. 7.8 compares the distributions of local temperature, current density, and oxygen mass fraction at the interface between the backing and reaction zone layer in each cell. The comparison is conducted at $V_{\text{stack}} = 1.2$ V which means 0.4 V for each cell. Such a small voltage corresponds to large spatial variations in the dependent variables. For the 2D LTE spatially smoothed model, the maximum relative error is 0.1% in cell 1, 0.4% in cell 2, and 0.3% in cell 3 for the temperature distribution (Fig. 7.8a), and 2.5, 3.3, and 3% for the current density distribution (Fig. 7.8b). For the ASST model, the relative errors increase up to 0.6, 1, and 0.5% for the temperature. Moreover, the current density varies due to redistribution between cells in the 3D and 2D spatially-smoothed model, whereas the ASST model predicts the same current density for all the cells. The increasing relative errors can be attributed to the inherent errors in the ASST model involved by

neglecting the streamwise second-order diffusive terms in the equation for the conservation of energy and electronic charge. In contrast, similar relative errors for the oxygen mass fraction are obtained by the spatially smoothed model and its asymptotic counterpart, as shown in Fig. 7.8c. The reason is that the transport of mass, species, momentum, and ionic charge are limited to every cell of the stack, whereas the transport of energy and electronic charge take place throughout the stack. These findings suggest that if the perturbations between cells are significant at the leading order for stack modeling, one may choose the 2D spatially-smoothed model or include the streamwise second-order terms in the ASST counterpart.

Fig. 7.8 Average (a) temperature, (b) current density, and (c) oxygen mass fraction at the backing/reaction zone interface for a 3-cell stack with $\mathcal{H}_c = 0.1$, $\mathcal{H}_a = 0.5$, and $\mathcal{W} = 0.4$ at $V_{\text{stack}} = 1.2$ V: 3D (filled) and 2D ASST (unfilled) models for cell 1 ($\blacktriangledown$), 2 ($\blacksquare$), and 3 ($\blacktriangle$); 2D spatially-smoothed models for cell 1 (—), 2 (— —), and 3 (— ·).

7.7. Summary

This chapter presents the reduction of 3D non-isothermal P-SOFC cell and stack models to 2D spatially-smoothed counterparts with developed effective parameters and correlation factors, and finally to parabolic PDEs and ODEs with the space marching algorithm, namely the ASST models. In particular, spatially smoothed energy equations are developed subject to both the local thermal equilibrium (LTE) and non-equilibrium (LTNE) conditions in the volume-averaged flow field. The variation in the pathways of conductive heat transfer between the flow field and adjacent layers is captured by the developed correlation factors.

The reduced models are verified with the 3D counterparts. Good agreement is obtained for the single-cell model and the stack model with negligible perturbations of dependent variables between cells. When the perturbations in the stack are not negligible, the relative error between the 2D ASST and 3D stack models increases significantly. In this case, the present ASST stack model can be improved by adding the streamwise second-order diffusive terms to the equations for the energy and electronic charge transports, so as to capture the redistribution of temperature and current density between cells. In addition, the selection of either the LTE or LTNE reduced model for use depends on the temperature difference between the working fluid and the interconnect in the flow field of the 3D model. When the temperature difference increases, the accuracy of the 2D LTE reduced model decreases. If the temperature difference is more than 10 K, the LTNE model is preferable for high accuracy.

Furthermore, the reduction of non-isothermal modeling is expected to be more significant for P-SOFCs fed by hydrocarbon, which involves a more complex multi-component gas mixture and additional chemical reactions resulting in an increase in the complexity and number of governing PDEs and dependent variables for 3D

modeling. Moreover, the idea of spatial smoothing for non-isothermal modeling can be extended to the thermo-mechanical analysis for P-SOFCs and stacks by developing correlations to capture the deformation of cell components in a certain direction in the 3D model. The reduced non-isothermal stack model also allows the statistical sensitivity analysis of the stack performance with respect to material properties, operating conditions, and cell geometry in a large sample size (*i.e.*, the number of varying parameters, and/or the amount of cells in a stack) at a computational cost that is not prohibitive.

Chapter 8

Conclusions and Future Work

This chapter summarizes the achievements of the research work presented in this thesis and provides recommendations for future work.

8.1. Conclusions from the present work

The present research work is devoted to the development of reliable reduced cell and stack models for the planar solid oxide fuel cell (P-SOFC) with parallel plain channels, based on a full 3D P-SOFC model that is developed, validated with experimental results from the literature, and solved in a finite-element solver called COMSOL Multiphysics. This 3D cell model provides a detailed description of the transport phenomena and electrochemical behaviours in the P-SOFC, and is employed as the building block for 3D stack modeling. Based on this full 3D model solved with respect to the streamwise direction along the cell length (x), the spanwise direction along the cell width (y), and the normal direction through the cell thickness (z), spatial smoothing and asymptotic analysis are adopted for model reduction. Consequently, the following four main achievements are obtained.

The first achievement of this research work is the development of a 2D asymptotic spatially-smoothed isothermal (ASSI) P-SOFC model with novel correlation factors for spatial smoothing to capture the leading-order average of dependent variables in the original 3D cell model, as presented in Chapter 4. The developed correlation factors

handle not only the variations in diffusion pathways due to ribs but also the coupling effect between governing equations, and are specified for the anode and electrode separately. The mathematical complexity of single-cell modeling for the SOFC is reduced via spatial smoothing and asymptotic analysis. When performing spatial smoothing for model reduction, there is no loss in physical information except that the local pointwise information is replaced with spanwise averaged counterparts. The numerical computation of the 2D ASSI model is sped up further by solving with a space marching algorithm. Comparing the 2D reduced and 3D full models, good agreement is obtained in view of the relative errors for their predictions of the global polarization curve and the spanwise average of local dependent variables. The computation time and memory requirements are reduced by more than two orders of magnitude. In comparison with the existing 2D P-SOFC models, the present 2D reduced model with respect to the streamwise (x) and normal (z) directions accounts for the influence of ribs on transport processes and the information pertaining to the neglected third dimension (*i.e.*, the spanwise direction (y) along the cell width), which are embodied by the developed correlation factors and effective transport properties. Based on the achieved results for the P-SOFCs with a flow field of straight channels, spatial smoothing for more complicated flow fields such as a serpentine design becomes possible. Moreover, apart from the co-flow configuration, the presented method of spatial smoothing can also be applied to the counter- and cross-flow configurations for 3D P-SOFCs. The former allows further model reduction from 3D to 2D via the asymptotic analysis.

The second achievement is the development of novel variation factors for spatial smoothing to capture the variability of local dependent variables in the spanwise direction along the cell width underneath flow fields, as presented in Chapter 5. The variation factors compliment the developed 2D spatially-smoothed model, such that the

spatially-smoothed model can predict not only the local average but also the spanwise variability of the dependent variables along the cell width in the 3D model. The variation factors vary with geometrical parameters and are applicable at different current densities. The validity of the developed validation factors has been verified in view of the variability of mass fractions along the cell width under the ribs, which provides information on depletion of oxidants from a design point of view. Good agreement is obtained between the 3D and 2D results for various planar geometries with parallel plain channels. In addition, the present method to derive the variation factors can be extended from mass fractions to the other dependent variables of the P-SOFC model. It is believed that the developed spatially-smoothed model with auxiliary polynomials accounting for the spanwise variability of dependent variables (via the variation factors) and the variation in the pathways of transport processes (via the correlation factors) can serve as a useful tool for the design and investigation of P-SOFCs and stacks. A computationally cost-efficient stack model can be built up with the present reduced cell model as a building block via automate code generation. Typically, a resulting large spanwise variation and a small spanwise average of species mass fractions in a cell/stack imply that the designed cell/stack probably undergoes depletion of species underneath ribs along the cell width and thus uneven current density distributions, such that modification on the cell/stack design is required.

Based on the achieved 2D ASSI P-SOFC single-cell model for the leading-order average and the variation factors for the spanwise variability of dependent variables, the third achievement of the present research work is sensitivity analysis of cell performance to stochastic modeling parameters via a Monte Carlo simulation (MCS) of the 2D reduced model, as presented in Chapter 6. Different from traditional parametric studies, the present sensitivity analysis is performed not only by varying one modeling parameter

at a time but also varying all the parameters simultaneously. With respect to the stochastic material properties, operating conditions, and geometrical parameters in a sample size on the order of $O(10^3)$, the sensitivity of the global and local cell behaviours is assessed statistically in terms of average current density, the average value of oxygen mass fractions and their spanwise variability underneath the ribs. The fast and efficient 2D reduced model takes 1 second to solve for each run of the present MCS, such that it takes less than 20 minutes for stochastic modeling with a sample size of 1000 for each varying parameter. The investigated 26 varying parameters are ranked according to their individual contribution to the variation of the cell performance. It is found that the rankings of the parameters are different when they vary separately and when they vary together, which is not captured by existing parametric studies. As a result, the average current density is most sensitive to the operating temperature, T , the cathode and anode activation energy, E_c^{act} and E_a^{act} , the electrolyte thickness, h_{el} , and the cell length, L , in the first scenario, but has the cathode inlet velocity and channel thickness, u_c^{in} and $h_{\text{fc,c}}$, as the fourth and fifth significant factor in the second scenario. Additionally, when all the parameters are varied together, the top 5 most influential parameters are T , the cathode and anode activation energy, $E_{\text{c,a}}^{\text{act}}$, followed by L and the anode channel thickness, $h_{\text{fc,a}}$, for the oxygen mass fraction; and T , the porosity, ε_c , the cathode backing layer thickness, $h_{\text{bl,c}}$, followed by $h_{\text{fc,c}}$ and L for the spanwise variation of oxygen mass fractions. The present Monte Carlo simulation predicts how the design parameters deviating from the nominal values affect the cell performance for high volume manufacturing processes, and can work as a tool to determine the input parameters for optimal operation. With respect to a set of different means μ and coefficients of variation c_v for one or a combination of input parameters, design charts

can be constructed to show the relation of the mean or variation of the cell performance with the mean or variation of the input parameters and/or the dependent variables (*e.g.*, average current and power densities). The design charts will then allow one to address the optimal input parameters in terms of their μ and c_v that lead to desired cell output, such as the maximum achievable mean or the minimum variation of the average power density. Furthermore, the present stochastic modeling can be extended from the single-cell to stack level to investigate the sensitivity of stack performance (*e.g.*, global average stack current and power densities and perturbations of local variables between cells) to stochastic design parameters at a computational cost that is not prohibitive.

The last achievement is the development of 2D spatially smoothed non-isothermal single-cell and stack models and their asymptotic counterparts for the P-SOFC, in which the energy equations of the 3D model are spatially smoothed and asymptotically reduced subject to both the local thermal equilibrium (LTE) and non-equilibrium (LTNE) conditions in the flow field, as presented in Chapter 7. The variation in the pathways of conductive heat transfer between the flow field and adjacent layers is captured by correlation factors derived based a generic Laplace equation. The original 3D model of elliptic PDEs is finally reduced to a parabolic PDEs and ODEs for the flow fields and ODEs for the rest of the cell with the space marching algorithm, called the 2D asymptotic spatially-smoothed thermal (ASST) model. The 3D full and 2D reduced cell models are then taken as the repeating unit for stack modeling. The verification of the 2D reduced models with the 3D counterparts shows good agreement for single-cell modeling and stack modeling with negligible perturbations of dependent variables between cells. When the perturbations in the stack are not negligible, the present 2D ASST stack model needs to be improved by including the streamwise second-order diffusive terms for the energy and electronic charge transport, in order to capture the

redistribution of temperature and current density between cells. The accuracy of the LTE model decreases with the increasing temperature difference between the interconnect and the working fluid in the original 3D model. If the temperature difference is more than 10 K, the LTNE model is preferable for high accuracy. Furthermore, the reduction of non-isothermal modeling is expected to be more significant for P-SOFCs and stacks fed by hydrocarbon, which involves a more complex multi-component gas mixture and additional chemical reactions resulting in an increase in the complexity and number of governing PDEs and dependent variables for 3D cell/stack modeling. The reduced non-isothermal stack model also allows the statistical sensitivity analysis of the stack performance with respect to material properties, operating conditions, and cell geometry in a large sample size (*i.e.*, the number of varying parameters, and/or the amount of cells in a stack) at a low computational cost. Moreover, the idea of spatial smoothing for non-isothermal modeling can be extended to the thermo-mechanical analysis for the P-SOFC and stack by developing correlations to capture the deformation of cell components in a certain direction in the 3D model.

8.2. Recommendations for future work

Based on the research results presented in this thesis, some potential areas for future work related to SOFC modeling are recommended below.

1. *Improvement for the present 3D non-isothermal P-SOFC benchmark model.* For 3D non-isothermal stack modeling, heat loss in the form of convection and radiation to surroundings will be taken into account. The heat loss will be considered not only in the normal ($\mathbf{e}_z$) direction, but also in the streamwise ($\mathbf{e}_x$) and spanwise ($\mathbf{e}_y$) directions. Moreover, the adsorption of gaseous species in the electrode will be considered for each cell of a stack model, where an anode reaction mechanism involving several

sequential steps [17, 18, 209] will be employed. The adsorption of gases and/or intermediate species can be described by the Langmuir-type isotherm [209].

2. *Reduced thermo-mechanical modeling.* Thermal stress is one of the most critical issues for the SOFC, because it can cause the breakdown of the cell or even the entire stack. The thermal stresses typically result from large temperature gradients within the cell or stack, and depend on material properties and operating conditions. The present reduced non-isothermal models can facilitate the thermo-mechanical analysis for the P-SOFC and stack. When spatially smoothing the thermo-mechanical model for dimensionality reduction, new correlation factors are needed to capture the deformation of cell components in a certain direction in the 3D model due to thermal stresses. Based on a fast and efficient reduced thermo-mechanical model, the sensitivity of the thermal stress to the design parameters, such as mechanical properties, can be investigated for a large population via the Monte Carlo simulation.
3. *Monte Carlo simulation of reduced P-SOFC stack models.* The achieved reduced stack models allow an extension of the present Monte Carlo simulation from the cell to stack level. The sensitivity analysis of the stack performance to design parameters can be investigated with a large sample size (*i.e.*, number of varying parameters, cells, and/or stacks) at an acceptable computational cost. If the perturbations between cells are negligible, the present 2D asymptotic spatially-smoothed thermal (ASST) stack model can be employed directly for the statistical sensitivity analysis. Otherwise, the 2D ASST model needs to be improved first to capture the redistribution of temperature and current density in the stack by including streamwise diffusion terms in the equations for heat and charge transfers.

4. *Spatial smoothing for counter- and cross-flow configurations.* Apart from the co-flow configuration considered for the present full and reduced models, there are the other two types of flow configurations for the P-SOFC, namely the counter- and cross-flow configuration. For the counter-flow design, the present method of spatial smoothing can be applied directly. The 3D counter-low P-SOFC model can be reduced to a 3D spatially-smoothed model, or a 2D counterpart provided that all the channels on the same side are under the same inlet conditions. In contrast, the cross-flow design may not allow the further dimensionality reduction from 3D to 2D. Based on the results of research works for the P-SOFCs with a flow field of straight channels, spatial smoothing for cells with a more complicated flow field like a serpentine design becomes possible as well.

5. *Reduced tubular SOFC (T-SOFC) modeling.* The tubular SOFC is the most well developed type of the SOFC. It is believed that reduced modeling, especially at the stack level, can facilitate the investigation of the performance of T-SOFCs. Compared with the other kinds of fuel cells, which are based on the planar structure, the tubular design is exclusive for the SOFC. Different from the flow field of parallel channels surrounded by ribs in planar cells, the flow field in the T-SOFC consists of an annular tube and a spherical closed end. Reducing a 3D T-SOFC model may require spatial smoothing and asymptotic analysis in a cylindrical system along the tube and in a spherical coordinate system at the end of the tube.

Appendix A

Scaling Analysis for Current Collector

Equation of charge conservation

$$10^{-4} \cancel{\ell_{cc}^2} \frac{\partial^2 \tilde{\phi}_{\text{elc}}}{\partial \tilde{x}^2} + \frac{\partial^2 \tilde{\phi}_{\text{elc}}}{\partial \tilde{z}^2} = 0 \quad (4.17)$$

$$\frac{\partial^2 \tilde{\phi}_{\text{elc}}}{\partial \tilde{z}^2} = 0 \quad (\text{A-1})$$

Equation of energy conservation

$$-\frac{\xi [k^{\text{eff}}] [T]}{h_{cc}^2} \left[\ell_{cc}^2 \frac{\partial}{\partial \tilde{x}} \left(\tilde{k}^{\text{eff}} \frac{\partial \tilde{T}}{\partial \tilde{x}} \right) + \frac{\partial}{\partial \tilde{z}} \left(\tilde{k}^{\text{eff}} \frac{\partial \tilde{T}}{\partial \tilde{z}} \right) \right] = S_{\text{temp, cc}} \quad (7.20)$$

$$-\frac{\xi_{10^{-1}} [k^{\text{eff}}]_1 [T]_{10 \sim 10^2}}{h_{cc10^{-8}}^2} \left[10^{-4} \cancel{\ell_{cc}^2} \frac{\partial}{\partial \tilde{x}} \left(\tilde{k}^{\text{eff}} \frac{\partial \tilde{T}}{\partial \tilde{x}} \right) + \frac{\partial}{\partial \tilde{z}} \left(\tilde{k}^{\text{eff}} \frac{\partial \tilde{T}}{\partial \tilde{z}} \right) \right] = S_{\text{temp, cc}} \quad (\text{A-2})$$

Appendix B

Scaling Analysis for Flow Field

Equation of mass conservation

$$\ell_{\text{ff}} [u_{\text{ff}}] \frac{\partial}{\partial \tilde{x}} (\tilde{\rho} \tilde{u}) + [w_{\text{ff}}] \frac{\partial}{\partial \tilde{z}} (\tilde{\rho} \tilde{w}) = 0 \quad (4.11)$$

$$\underbrace{\frac{10^{-2} \ell_{\text{ff}} [u_{\text{ff}}]^{10^{-1}}}{10^{-3} [w_{\text{ff}}]}}_1 \frac{\partial}{\partial \tilde{x}} (\tilde{\rho} \tilde{u}) + \frac{\partial}{\partial \tilde{z}} (\tilde{\rho} \tilde{w}) = 0 \quad (\text{B-1})$$

$$\frac{\partial}{\partial \tilde{x}} (\tilde{\rho} \tilde{u}) + \frac{\partial}{\partial \tilde{z}} (\tilde{\rho} \tilde{w}) = 0 \quad (\text{B-2})$$

Equation of momentum conservation

$$\begin{cases} \frac{\mu_{\text{mix}}}{\kappa_{\text{ff}}} \tilde{u} = - \frac{[p_{\text{ff}}]}{L[u_{\text{ff}}]} \frac{\partial \tilde{p}}{\partial \tilde{x}} \\ \frac{\mu_{\text{mix}}}{\kappa_{\text{ff}}} \tilde{w} = - \frac{[p_{\text{ff}}]}{h_{\text{ff}}[w_{\text{ff}}]} \frac{\partial \tilde{p}}{\partial \tilde{z}} \end{cases} \quad (4.12)$$

$$\begin{cases} \tilde{u} = - \frac{10^{-8} \kappa_{\text{ff}}^{10} [p_{\text{ff}}]}{\underbrace{10^{-5} \mu_{\text{mix}} 10^{-1} L[u_{\text{ff}}]^{10^{-1}}}_1} \frac{\partial \tilde{p}}{\partial \tilde{x}} \\ \tilde{w} = - \frac{10^{-8} \kappa_{\text{ff}}^{10} [p_{\text{ff}}]}{\underbrace{10^{-5} \mu_{\text{mix}} 10^{-3} h_{\text{ff}}[w_{\text{ff}}]^{10^{-3}}}_{10^4}} \frac{\partial \tilde{p}}{\partial \tilde{z}} \end{cases} \quad (\text{B-3})$$

$$\begin{cases} \tilde{u} = - \frac{\partial \tilde{p}}{\partial \tilde{x}} \\ \frac{\partial \tilde{p}}{\partial \tilde{z}} = 0 \end{cases} \quad (\text{B-4})$$

Equation of species conservation

$$\begin{aligned} & \ell_{\text{ff}} [u_{\text{ff}}] \frac{\partial}{\partial \tilde{x}} (\tilde{\rho} \tilde{u} \omega_i) + [w_{\text{ff}}] \frac{\partial}{\partial \tilde{z}} (\tilde{\rho} \tilde{w} \omega_i) - \frac{\ell_{\text{ff}}^2}{h_{\text{ff}}} \frac{\partial}{\partial \tilde{x}} \left(\tilde{\rho} \omega_i \sum_{j=1}^n \left([\mathcal{D}_{ij}^{\text{eff}}] \varepsilon_{\text{ff}} \tilde{\mathcal{D}}_{ij} \frac{\partial x_j}{\partial \tilde{x}} \right) \right) \\ & - \frac{1}{h_{\text{ff}}} \frac{\partial}{\partial \tilde{z}} \left(\tilde{\rho} \omega_i \sum_{j=1}^n \left([\mathcal{D}_{ij}^{\text{eff}}] \varepsilon_{\text{ff}} \tilde{\mathcal{D}}_{ij} \frac{\partial x_j}{\partial \tilde{z}} \right) \right) = 0 \end{aligned} \quad (4.14)$$

$$\begin{aligned} & \underbrace{\frac{10^{-2} \ell_{\text{ff}} [u_{\text{ff}}] 10^{-1}}{[w_{\text{ff}}] 10^{-3}}}_{1} \frac{\partial}{\partial \tilde{x}} (\tilde{\rho} \tilde{u} \omega_i) + \frac{\partial}{\partial \tilde{z}} (\tilde{\rho} \tilde{w} \omega_i) - \\ & - \underbrace{\frac{10^{-4} [\mathcal{D}_{ij}^{\text{eff}}] \varepsilon_{\text{ff}} 10^{-1}}{10^{-3} [w_{\text{ff}}] h_{\text{ff}} 10^{-3}}}_{10} \left[10^{-4} \cancel{\ell_{\text{ff}}} \frac{\partial}{\partial \tilde{x}} \left(\tilde{\rho} \omega_i \sum_{j=1}^n \left(\tilde{\mathcal{D}}_{ij} \frac{\partial x_j}{\partial \tilde{x}} \right) \right) + \frac{\partial}{\partial \tilde{z}} \left(\tilde{\rho} \omega_i \sum_{j=1}^n \left(\tilde{\mathcal{D}}_{ij} \frac{\partial x_j}{\partial \tilde{z}} \right) \right) \right] = 0 \end{aligned} \quad (B-5)$$

$$\frac{\ell_{\text{ff}} [u_{\text{ff}}]}{[w_{\text{ff}}]} \frac{\partial}{\partial \tilde{x}} (\tilde{\rho} \tilde{u} \omega_i) + \frac{\partial}{\partial \tilde{z}} (\tilde{\rho} \tilde{w} \omega_i) - \frac{[\mathcal{D}_{ij}^{\text{eff}}] \varepsilon_{\text{ff}}}{[w_{\text{ff}}] h_{\text{ff}}} \frac{\partial}{\partial \tilde{z}} \left(\tilde{\rho} \omega_i \sum_{j=1}^n \left(\tilde{\mathcal{D}}_{ij} \frac{\partial x_j}{\partial \tilde{z}} \right) \right) = 0 \quad (B-6)$$

Equation of charge conservation

$$\ell_{\text{ff}}^2 \frac{\partial^2 \tilde{\phi}_{\text{elc}}}{\partial \tilde{x}^2} + \frac{\partial^2 \tilde{\phi}_{\text{elc}}}{\partial \tilde{z}^2} = 0 \quad (4.17)$$

$$\cancel{10^{-4} \ell_{\text{ff}}^2} \frac{\partial^2 \tilde{\phi}_{\text{elc}}}{\partial \tilde{x}^2} + \frac{\partial^2 \tilde{\phi}_{\text{elc}}}{\partial \tilde{z}^2} = 0 \quad (B-7)$$

$$\frac{\partial^2 \tilde{\phi}_{\text{elc}}}{\partial \tilde{z}^2} = 0 \quad (B-8)$$

Equation of energy conservation

$$\begin{aligned} & - \frac{[k^{\text{eff}}] [T]}{h_{\text{ff}}^2} \left[\ell_{\text{ff}}^2 \frac{\partial}{\partial \tilde{x}} \left(\tilde{k}^{\text{eff}} \frac{\partial \tilde{T}}{\partial \tilde{x}} \right) + \frac{\partial}{\partial \tilde{z}} \left(\tilde{k}^{\text{eff}} \frac{\partial \tilde{T}}{\partial \tilde{z}} \right) \right] \\ & + \frac{[\rho] [c_{\text{p, mix}}] [T] [w_{\text{ff}}]}{h_{\text{ff}}} \tilde{\rho} \tilde{c}_{\text{p, mix}} \left(\frac{\ell_{\text{ff}} [u_{\text{ff}}]}{[w_{\text{ff}}]} \tilde{u} \frac{\partial \tilde{T}}{\partial \tilde{x}} + \tilde{w} \frac{\partial \tilde{T}}{\partial \tilde{z}} \right) = S_{\text{temp, ff}} \end{aligned} \quad (7.21)$$

$$\begin{aligned}
 & - \cancel{10^{-4}} \ell_{\text{ff}}^2 \frac{\partial}{\partial \tilde{x}} \left(\tilde{k}^{\text{eff}} \frac{\partial \tilde{T}}{\partial \tilde{x}} \right) - \frac{\partial}{\partial \tilde{z}} \left(\tilde{k}^{\text{eff}} \frac{\partial \tilde{T}}{\partial \tilde{z}} \right) \\
 & + \underbrace{\frac{10^{-3} h_{\text{ff}} ([\rho] [c_{\text{p, mix}}])^{10^2} [w_{\text{ff}}]^{10^{-3}}}{1 [k^{\text{eff}}]}}_{10^{-4}} \tilde{\rho} \tilde{c}_{\text{p, mix}} \left(\underbrace{\frac{10^{-2} \ell_{\text{ff}} [u_{\text{ff}}]^{10^{-1}}}{10^{-3} [w_{\text{ff}}]}}_1 \tilde{u} \frac{\partial \tilde{T}}{\partial \tilde{x}} + \cancel{\tilde{w} \frac{\partial \tilde{T}}{\partial \tilde{z}}} \right) = \frac{h_{\text{ff}}^2}{[k^{\text{eff}}] [T]} S_{\text{temp, ff}}
 \end{aligned}
 \tag{B-9}$$

$$- \frac{\partial}{\partial \tilde{z}} \left(\tilde{k}^{\text{eff}} \frac{\partial \tilde{T}}{\partial \tilde{z}} \right) + \frac{h_{\text{ff}}^2 [\rho] [c_{\text{p, mix}}] [u_{\text{ff}}]}{[k^{\text{eff}}] L} \tilde{\rho} \tilde{c}_{\text{p, mix}} \tilde{u} \frac{\partial \tilde{T}}{\partial \tilde{x}} = \frac{h_{\text{ff}}^2}{[k^{\text{eff}}] [T]} S_{\text{temp, ff}} \tag{B-10}$$

Appendix C

Scaling Analysis for Backing Layer

Equation of mass conservation

$$\ell_{\text{bl}} [u_{\text{bl}}] \frac{\partial}{\partial \tilde{x}} (\tilde{\rho} \tilde{u}) + [w_{\text{bl}}] \frac{\partial}{\partial \tilde{z}} (\tilde{\rho} \tilde{w}) = 0 \quad (4.11)$$

$$\underbrace{\frac{10^{-3} \ell_{\text{bl}} [u_{\text{bl}}] 10^{-5}}{10^{-3} [w_{\text{bl}}]}}_{10^{-5}} \frac{\partial}{\partial \tilde{x}} (\tilde{\rho} \tilde{u}) + \frac{\partial}{\partial \tilde{z}} (\tilde{\rho} \tilde{w}) = 0 \quad (\text{C-1})$$

$$\frac{\partial}{\partial \tilde{z}} (\tilde{\rho} \tilde{w}) = 0 \quad (\text{C-2})$$

Equation of momentum conservation

$$\frac{\mu_{\text{mix}}}{\kappa} \tilde{w} = - \frac{[p'_{\text{bl}}]}{h_{\text{bl}} [w_{\text{bl}}]} \frac{\partial \tilde{p}'}{\partial \tilde{z}} - \frac{\mu_{\text{mix}}}{\varepsilon h_{\text{bl}}^2} \left(\ell_{\text{bl}}^2 \frac{\partial^2}{\partial \tilde{x}^2} + \frac{\partial^2}{\partial \tilde{z}^2} \right) \tilde{w} \quad (4.13)$$

$$\frac{h_{\text{bl}}}{\kappa} \frac{\mu_{\text{mix}} [w_{\text{bl}}]}{[p'_{\text{bl}}]} \tilde{w} = - \frac{\partial \tilde{p}'}{\partial \tilde{z}} - \frac{1}{\varepsilon h_{\text{bl}}} \frac{\mu_{\text{mix}} [w_{\text{bl}}]}{[p'_{\text{bl}}]} \left(\ell_{\text{bl}}^2 \frac{\partial^2}{\partial \tilde{x}^2} + \frac{\partial^2}{\partial \tilde{z}^2} \right) \tilde{w} \quad (\text{C-3})$$

$$\underbrace{\frac{h_{\text{bl}} 10^{-4} 10^{-5} \mu_{\text{mix}} [w_{\text{bl}}] 10^{-3}}{\kappa 10^{-12} 10 [p'_{\text{bl}}]}}_{10^{-1}} \tilde{w} = - \frac{\partial \tilde{p}'}{\partial \tilde{z}} - \underbrace{\frac{1}{10^{-1} \varepsilon h_{\text{bl}} 10^{-4}} \frac{10^{-5} \mu_{\text{mix}} [w_{\text{bl}}] 10^{-5}}{10 [p'_{\text{bl}}]}}_{10^{-4}} \left(10^{-6} \ell_{\text{bl}}^2 \frac{\partial^2}{\partial \tilde{x}^2} + \frac{\partial^2}{\partial \tilde{z}^2} \right) \tilde{w} \quad (\text{C-4})$$

$$\tilde{w} = - \frac{\partial \tilde{p}'}{\partial \tilde{z}} \quad (\text{C-5})$$

Equation of species conservation

$$\begin{aligned} & \ell_{\text{bl}} [u_{\text{bl}}] \frac{\partial}{\partial \tilde{x}} (\tilde{\rho} \tilde{u} \omega_i) + [w_{\text{bl}}] \frac{\partial}{\partial \tilde{z}} (\tilde{\rho} \tilde{w} \omega_i) - \frac{\ell_{\text{bl}}^2}{h_{\text{bl}}} \frac{\partial}{\partial \tilde{x}} \left(\tilde{\rho} \omega_i \sum_{j=1}^n \left([\mathcal{D}_{ij}^{\text{eff}}] \zeta \tilde{\mathcal{D}}_{ij}^{\text{eff}} \frac{\partial \tilde{x}_j}{\partial \tilde{x}} \right) \right) \\ & - \frac{1}{h_{\text{bl}}} \frac{\partial}{\partial \tilde{z}} \left(\tilde{\rho} \omega_i \sum_{j=1}^n \left([\mathcal{D}_{ij}^{\text{eff}}] \zeta \tilde{\mathcal{D}}_{ij}^{\text{eff}} \frac{\partial \tilde{x}_j}{\partial \tilde{z}} \right) \right) = 0 \end{aligned} \quad (4.15)$$

$$\begin{aligned} & \underbrace{\frac{10^{-3} \ell_{\text{bl}} [u_{\text{bl}}] 10^{-5}}{[w_{\text{bl}}] 10^{-3}}}_{10^{-5}} \frac{\partial}{\partial \tilde{x}} (\tilde{\rho} \tilde{u} \omega_i) + \frac{\partial}{\partial \tilde{z}} (\tilde{\rho} \tilde{w} \omega_i) - \\ & \underbrace{\frac{10^{-5} [\mathcal{D}_{ij}^{\text{eff}}] \zeta 10^{-1}}{10^{-3} [w_{\text{bl}}] h_{\text{bl}} 10^{-4}}}_{10} \left[\cancel{10^{-6} \ell_{\text{bl}}^2} \frac{\partial}{\partial \tilde{x}} \left(\tilde{\rho} \omega_i \sum_{j=1}^n \left(\tilde{\mathcal{D}}_{ij}^{\text{eff}} \frac{\partial \tilde{x}_j}{\partial \tilde{x}} \right) \right) + \frac{\partial}{\partial \tilde{z}} \left(\tilde{\rho} \omega_i \sum_{j=1}^n \left(\tilde{\mathcal{D}}_{ij}^{\text{eff}} \frac{\partial \tilde{x}_j}{\partial \tilde{z}} \right) \right) \right] = 0 \end{aligned} \quad (C-6)$$

$$\frac{\partial}{\partial \tilde{z}} (\tilde{\rho} \tilde{w} \omega_i) - \frac{[\mathcal{D}_{ij}^{\text{eff}}] \zeta}{[w_{\text{bl}}] h_{\text{bl}}} \frac{\partial}{\partial \tilde{z}} \left(\tilde{\rho} \omega_i \sum_{j=1}^n \left(\tilde{\mathcal{D}}_{ij}^{\text{eff}} \frac{\partial \tilde{x}_j}{\partial \tilde{z}} \right) \right) = 0 \quad (C-7)$$

Equation of charge conservation

$$\ell_{\text{bl}}^2 \frac{\partial^2 \tilde{\phi}_{\text{elc}}}{\partial \tilde{x}^2} + \frac{\partial^2 \tilde{\phi}_{\text{elc}}}{\partial \tilde{z}^2} = 0 \quad (4.17)$$

$$\cancel{10^{-6} \ell_{\text{bl}}^2} \frac{\partial^2 \tilde{\phi}_{\text{elc}}}{\partial \tilde{x}^2} + \frac{\partial^2 \tilde{\phi}_{\text{elc}}}{\partial \tilde{z}^2} = 0 \quad (C-8)$$

$$\frac{\partial^2 \tilde{\phi}_{\text{elc}}}{\partial \tilde{z}^2} = 0 \quad (C-9)$$

Equation of energy conservation

$$\begin{aligned} & - \frac{\xi [k^{\text{eff}}] [T]}{h_{\text{bl}}^2} \left[\ell_{\text{bl}}^2 \frac{\partial}{\partial \tilde{x}} \left(\tilde{k}^{\text{eff}} \frac{\partial \tilde{T}}{\partial \tilde{x}} \right) + \frac{\partial}{\partial \tilde{z}} \left(\tilde{k}^{\text{eff}} \frac{\partial \tilde{T}}{\partial \tilde{z}} \right) \right] \\ & + \frac{[\rho] [c_{\text{p, mix}}] [T] [w_{\text{bl}}]}{h_{\text{bl}}} \tilde{\rho} \tilde{c}_{\text{p, mix}} \left(\frac{\ell_{\text{bl}} [u_{\text{bl}}]}{[w_{\text{bl}}]} \tilde{u} \frac{\partial \tilde{T}}{\partial \tilde{x}} + \tilde{w} \frac{\partial \tilde{T}}{\partial \tilde{z}} \right) = S_{\text{temp, bl}} \end{aligned} \quad (7.22)$$

$$\begin{aligned}
 & - \cancel{10^{-6}} \ell_{\text{bl}}^2 \frac{\partial}{\partial \tilde{x}} \left(\tilde{k}^{\text{eff}} \frac{\partial \tilde{T}}{\partial \tilde{x}} \right) - \frac{\partial}{\partial \tilde{z}} \left(\tilde{k}^{\text{eff}} \frac{\partial \tilde{T}}{\partial \tilde{z}} \right) \\
 & + \underbrace{\frac{\cancel{10^{-4}} h_{\text{bl}} ([\rho] [c_{\text{p, mix}}]) \cancel{10^2} [\cancel{w_{\text{bl}}}]^{10^{-3}}}{\cancel{1} [k^{\text{eff}}] \cancel{\xi}_{10^{-1}}}}_{10^{-4}} \tilde{\rho} \tilde{c}_{\text{p, mix}} \left(\underbrace{\frac{\cancel{10^{-3}} \ell_{\text{bl}} [\cancel{u_{\text{bl}}}]^{10^{-3}}}{\cancel{10^{-3}} [\cancel{w_{\text{bl}}}]}}_{10^{-5}} \tilde{u} \frac{\partial \tilde{T}}{\partial \tilde{x}} + \tilde{w} \frac{\partial \tilde{T}}{\partial \tilde{z}} \right) = \frac{h_{\text{bl}}^2}{\xi [k^{\text{eff}}] [T]} S_{\text{temp, bl}}
 \end{aligned} \tag{C-10}$$

$$- \frac{\partial}{\partial \tilde{z}} \left(\tilde{k}^{\text{eff}} \frac{\partial \tilde{T}}{\partial \tilde{z}} \right) = \frac{h_{\text{bl}}^2}{\xi [k^{\text{eff}}] [T]} S_{\text{temp, bl}} \tag{C-11}$$

Appendix D

Scaling Analysis for Reaction Zone Layer

Equation of mass conservation

$$\ell_{\text{rl}} [u_{\text{rl}}] \frac{\partial}{\partial \tilde{x}} (\tilde{\rho} \tilde{u}) + [w_{\text{rl}}] \frac{\partial}{\partial \tilde{z}} (\tilde{\rho} \tilde{w}) = \begin{cases} \frac{h_{\text{rl}} [M_{\text{c}}] [J]}{4 [\rho_{\text{c}}] F} \tilde{M}_{\text{O}_2} \tilde{J}_{\text{c}} \\ \frac{h_{\text{rl}} [M_{\text{a}}] [J]}{2 [\rho_{\text{a}}] F} (\tilde{M}_{\text{H}_2\text{O}} - \tilde{M}_{\text{H}_2}) \tilde{J}_{\text{a}} \end{cases} \quad (4.11)$$

$$\underbrace{\frac{10^{-4} \ell_{\text{rl}} [u_{\text{rl}}] 10^{-5}}{10^{-3} [w_{\text{rl}}]} \frac{\partial}{\partial \tilde{x}} (\tilde{\rho} \tilde{u}) + \frac{\partial}{\partial \tilde{z}} (\tilde{\rho} \tilde{w})}_{10^{-6}} = \begin{cases} \underbrace{\frac{10^{-5} h_{\text{rl}} [J]^{10^8}}{4 [w_{\text{rl}}]^{10^{-3}} F^{10^5}} \left(\frac{[M_{\text{c}}]}{[\rho_{\text{c}}]} \right)^{10^{-1}}}_{1} \tilde{M}_{\text{O}_2} \tilde{J}_{\text{c}} \\ \underbrace{\frac{10^{-5} h_{\text{rl}} [J]^{10^8}}{2 [w_{\text{rl}}]^{10^{-3}} F^{10^5}} \left(\frac{[M_{\text{a}}]}{[\rho_{\text{a}}]} \right)^{10^{-1}}}_{1} (\tilde{M}_{\text{H}_2\text{O}} - \tilde{M}_{\text{H}_2}) \tilde{J}_{\text{a}} \end{cases} \quad (D-1)$$

$$\frac{\partial}{\partial \tilde{z}} (\tilde{\rho} \tilde{w}) = \begin{cases} \tilde{M}_{\text{O}_2} \tilde{J}_{\text{c}} \\ (\tilde{M}_{\text{H}_2\text{O}} - \tilde{M}_{\text{H}_2}) \tilde{J}_{\text{a}} \end{cases} \quad (D-2)$$

Equation of momentum conservation

$$\frac{\mu_{\text{mix}}}{\kappa} \tilde{w} = - \frac{[P_{\text{rl}}']}{h_{\text{rl}} [w_{\text{rl}}]} \frac{\partial \tilde{p}'}{\partial \tilde{z}} - \frac{\mu_{\text{mix}}}{\varepsilon h_{\text{rl}}^2} \left(\ell_{\text{rl}}^2 \frac{\partial^2}{\partial \tilde{x}^2} + \frac{\partial^2}{\partial \tilde{z}^2} \right) \tilde{w} \quad (4.13)$$

$$\underbrace{\frac{10^{-5} h_{\text{rl}}^{10^{-5}} \mu_{\text{mix}} [w_{\text{rl}}]^{10^{-3}}}{10^{-12} \kappa} \tilde{w}}_{10^{-2}} = - \frac{\partial \tilde{p}'}{\partial \tilde{z}} - \underbrace{\frac{1}{10^{-1} \varepsilon h_{\text{rl}}^{10^{-5}} \frac{\mu_{\text{mix}} [w_{\text{rl}}]^{10^{-3}}}{10 [P_{\text{rl}}']}}}_{10^{-3}} \left(10^{-8} \ell_{\text{rl}}^2 \frac{\partial^2}{\partial \tilde{x}^2} + \frac{\partial^2}{\partial \tilde{z}^2} \right) \tilde{w} \quad (D-3)$$

$$\tilde{w} = -\frac{\partial \tilde{p}'}{\partial \tilde{z}} \quad (D-4)$$

Equation of species conservation

$$\begin{aligned} & \ell_{\text{rl}} [u_{\text{rl}}] \frac{\partial}{\partial \tilde{x}} (\tilde{\rho} \tilde{u} \omega_i) + [w_{\text{rl}}] \frac{\partial}{\partial \tilde{z}} (\tilde{\rho} \tilde{w} \omega_i) - \frac{\ell_{\text{rl}}^2}{h_{\text{rl}}} \frac{\partial}{\partial \tilde{x}} \left(\tilde{\rho} \omega_i \sum_{j=1}^n \left([\mathcal{D}_{ij}^{\text{eff}}] \tilde{\mathcal{D}}_{ij}^{\text{eff}} \frac{\partial x_j}{\partial \tilde{x}} \right) \right) \\ & - \frac{1}{h_{\text{rl}}} \frac{\partial}{\partial \tilde{z}} \left(\tilde{\rho} \omega_i \sum_{j=1}^n \left([\mathcal{D}_{ij}^{\text{eff}}] \tilde{\mathcal{D}}_{ij}^{\text{eff}} \frac{\partial x_j}{\partial \tilde{z}} \right) \right) = \begin{cases} \frac{h_{\text{rl}}}{[\rho_c]} \frac{[M_c][J]}{4F} \tilde{M}_{\text{O}_2} \tilde{J}_c \\ -\frac{h_{\text{rl}}}{[\rho_a]} \frac{[M_a][J]}{2F} \tilde{M}_{\text{H}_2} \tilde{J}_a \end{cases} \quad (4.16) \end{aligned}$$

$$\begin{aligned} & \underbrace{\frac{10^{-4} \ell_{\text{rl}} [u_{\text{rl}}] 10^{-5}}{10^{-3} [w_{\text{rl}}]} \frac{\partial}{\partial \tilde{x}} (\tilde{\rho} \tilde{u} \omega_i) + \frac{\partial}{\partial \tilde{z}} (\tilde{\rho} \tilde{w} \omega_i)}_{10^{-6}} \\ & - \underbrace{\frac{[\mathcal{D}_{ij}^{\text{eff}}] 10^{-5}}{10^{-3} [w_{\text{rl}}] h_{\text{rl}} 10^{-5}}}_{10^3} \left[\underbrace{10^{-8} \ell_{\text{rl}}^2}_{10^{-8}} \frac{\partial}{\partial \tilde{x}} \left(\tilde{\rho} \omega_i \sum_{j=1}^n \left(\tilde{\mathcal{D}}_{ij}^{\text{eff}} \frac{\partial x_j}{\partial \tilde{x}} \right) \right) + \frac{\partial}{\partial \tilde{z}} \left(\tilde{\rho} \omega_i \sum_{j=1}^n \left(\tilde{\mathcal{D}}_{ij}^{\text{eff}} \frac{\partial x_j}{\partial \tilde{z}} \right) \right) \right] \\ & = \begin{cases} \underbrace{\frac{h_{\text{rl}} 10^{-5}}{10^{-1} [\rho_c] [w_{\text{rl}}] 10^{-3}} \frac{10^{-2} [M_c][J] 10^8}{4F 10^5} \tilde{M}_{\text{O}_2} \tilde{J}_c}_1 \\ - \underbrace{\frac{h_{\text{rl}} 10^{-5}}{10^{-2} [\rho_a] [w_{\text{rl}}] 10^{-3}} \frac{10^{-3} [M_a][J] 10^8}{2F 10^5} \tilde{M}_{\text{H}_2} \tilde{J}_a}_1 \end{cases} \quad (D-5) \end{aligned}$$

$$\frac{\partial}{\partial \tilde{z}} (\tilde{\rho} \tilde{w} \omega_i) - \frac{[\mathcal{D}_{ij}^{\text{eff}}]}{[w_{\text{rl}}] h_{\text{rl}}} \frac{\partial}{\partial \tilde{z}} \left(\tilde{\rho} \omega_i \sum_{j=1}^n \left(\tilde{\mathcal{D}}_{ij}^{\text{eff}} \frac{\partial x_j}{\partial \tilde{z}} \right) \right) = \begin{cases} \frac{h_{\text{rl}}}{[\rho_c] [w_{\text{rl}}]} \frac{[M_c][J]}{4F} \tilde{M}_{\text{O}_2} \tilde{J}_c \\ - \frac{h_{\text{rl}}}{[\rho_a] [w_{\text{rl}}]} \frac{[M_a][J]}{2F} \tilde{M}_{\text{H}_2} \tilde{J}_a \end{cases} \quad (D-6)$$

Equation of charge conservation

For the electronic charge transfer:

$$\ell_{\text{rl}}^2 \frac{\partial^2 \tilde{\phi}_{\text{elc}}}{\partial \tilde{x}^2} + \frac{\partial^2 \tilde{\phi}_{\text{elc}}}{\partial \tilde{z}^2} = \begin{cases} \frac{[J]}{[\phi_{\text{elc,rl}}]} \frac{h_{\text{rl}}^2}{\sigma_{\text{elc}}^{\text{eff}}} \tilde{J}_c \\ \frac{[J]}{[\phi_{\text{elc,rl}}]} \frac{h_{\text{rl}}^2}{\sigma_{\text{elc}}^{\text{eff}}} \tilde{J}_a \end{cases} \quad (4.17)$$

$$\cancel{10^{-8}} \ell_{\text{rl}}^2 \frac{\partial^2 \tilde{\phi}_{\text{elc}}}{\partial \tilde{x}^2} + \frac{\partial^2 \tilde{\phi}_{\text{elc}}}{\partial \tilde{z}^2} = \begin{cases} \underbrace{\frac{10^8 [J]}{10^{-5} [\phi_{\text{elc,rl}}]} \frac{h_{\text{rl}}^{210^{-10}}}{\sigma_{\text{elc}}^{\text{eff}} 10^3}}_1 \tilde{J}_{\text{c}} \\ \underbrace{\frac{10^8 [J]}{10^{-5} [\phi_{\text{elc,rl}}]} \frac{h_{\text{rl}}^{210^{-10}}}{\sigma_{\text{elc}}^{\text{eff}} 10^3}}_1 \tilde{J}_{\text{a}} \end{cases} \quad (\text{D-7})$$

$$\frac{\partial^2 \tilde{\phi}_{\text{elc}}}{\partial \tilde{z}^2} = \begin{cases} \tilde{J}_{\text{c}} \\ \tilde{J}_{\text{a}} \end{cases} \quad (\text{D-8})$$

For the ionic charge transfer:

$$\ell_{\text{rl}}^2 \frac{\partial^2 \tilde{\phi}_{\text{ion}}}{\partial \tilde{x}^2} + \frac{\partial^2 \tilde{\phi}_{\text{ion}}}{\partial \tilde{z}^2} = \begin{cases} -\frac{[J]}{[\phi_{\text{ion,rl}}]} \frac{h_{\text{rl}}^2}{\sigma_{\text{ion,rl}}^{\text{eff}}} \tilde{J}_{\text{c}} \\ -\frac{[J]}{[\phi_{\text{ion,rl}}]} \frac{h_{\text{rl}}^2}{\sigma_{\text{ion,rl}}^{\text{eff}}} \tilde{J}_{\text{a}} \end{cases} \quad (4.18)$$

$$\cancel{10^{-8}} \ell_{\text{rl}}^2 \frac{\partial^2 \tilde{\phi}_{\text{ion}}}{\partial \tilde{x}^2} + \frac{\partial^2 \tilde{\phi}_{\text{ion}}}{\partial \tilde{z}^2} = \begin{cases} -\underbrace{\frac{10^8 [J]}{10^{-1} [\phi_{\text{ion,rl}}]} \frac{h_{\text{rl}}^{210^{-10}}}{\sigma_{\text{ion,rl}}^{\text{eff}} 10^{-1}}}_1 \tilde{J}_{\text{c}} \\ -\underbrace{\frac{10^8 [J]}{10^{-1} [\phi_{\text{ion,rl}}]} \frac{h_{\text{rl}}^{210^{-10}}}{\sigma_{\text{ion,rl}}^{\text{eff}} 10^{-1}}}_1 \tilde{J}_{\text{a}} \end{cases} \quad (\text{D-9})$$

$$\frac{\partial^2 \tilde{\phi}_{\text{ion}}}{\partial \tilde{z}^2} = \begin{cases} -\tilde{J}_{\text{c}} \\ -\tilde{J}_{\text{a}} \end{cases} \quad (\text{D-10})$$

Equation of energy conservation

$$\begin{aligned} & -\frac{[k^{\text{eff}}][T]}{h_{\text{rl}}^2} \left[\ell_{\text{rl}}^2 \frac{\partial}{\partial \tilde{x}} \left(\tilde{k}^{\text{eff}} \frac{\partial \tilde{T}}{\partial \tilde{x}} \right) + \frac{\partial}{\partial \tilde{z}} \left(\tilde{k}^{\text{eff}} \frac{\partial \tilde{T}}{\partial \tilde{z}} \right) \right] \\ & + \frac{[\rho][c_{\text{p,mix}}][T][w_{\text{rl}}]}{h_{\text{rl}}} \tilde{\rho} \tilde{c}_{\text{p,mix}} \left(\frac{\ell_{\text{rl}} [u_{\text{rl}}]}{[w_{\text{rl}}]} \tilde{u} \frac{\partial \tilde{T}}{\partial \tilde{x}} + \tilde{w} \frac{\partial \tilde{T}}{\partial \tilde{z}} \right) = S_{\text{temp,rl}} \end{aligned} \quad (7.23)$$

$$\begin{aligned}
 & - \cancel{10^{-8} \ell_{\text{rl}}^2} \frac{\partial}{\partial \tilde{x}} \left(\tilde{k}^{\text{eff}} \frac{\partial \tilde{T}}{\partial \tilde{x}} \right) - \frac{\partial}{\partial \tilde{z}} \left(\tilde{k}^{\text{eff}} \frac{\partial \tilde{T}}{\partial \tilde{z}} \right) \\
 & + \underbrace{\frac{10^{-5} h_{\text{rl}} ([\rho] [c_{\text{p, mix}}])^{10^2} [w_{\text{rl}}]^{10^{-3}}}{1 [k^{\text{eff}}]}}_{10^{-6}} \tilde{\rho} \tilde{c}_{\text{p, mix}} \left(\underbrace{\frac{10^{-4} \ell_{\text{rl}} [u_{\text{rl}}]^{10^{-3}}}{10^{-3} [w_{\text{rl}}]}}_{10^{-6}} \tilde{u} \frac{\partial \tilde{T}}{\partial \tilde{x}} + \tilde{w} \frac{\partial \tilde{T}}{\partial \tilde{z}} \right) = \frac{h_{\text{rl}}^2}{[k^{\text{eff}}] [T]} S_{\text{temp, rl}}
 \end{aligned} \tag{D-11}$$

$$- \frac{\partial}{\partial \tilde{z}} \left(\tilde{k}^{\text{eff}} \frac{\partial \tilde{T}}{\partial \tilde{z}} \right) = \frac{h_{\text{rl}}^2}{[k^{\text{eff}}] [T]} S_{\text{temp, rl}} \tag{D-12}$$

Appendix E

Scaling Analysis for Electrolyte

Equation of charge conservation

$$\ell_{\text{el}}^2 \frac{\partial^2 \tilde{\phi}_{\text{ion}}}{\partial \tilde{x}^2} + \frac{\partial^2 \tilde{\phi}_{\text{ion}}}{\partial \tilde{z}^2} = 0 \quad (4.18)$$

$$\cancel{10^{-8} \ell_{\text{el}}^2} \frac{\partial^2 \tilde{\phi}_{\text{ion}}}{\partial \tilde{x}^2} + \frac{\partial^2 \tilde{\phi}_{\text{ion}}}{\partial \tilde{z}^2} = 0 \quad (\text{E-1})$$

$$\frac{\partial^2 \tilde{\phi}_{\text{ion}}}{\partial \tilde{z}^2} = 0 \quad (\text{E-2})$$

$$-\frac{\sigma_{\text{ion}} [V_{\text{cell}}]}{L^2} \nabla^2 (\tilde{\phi}_{\text{ion}}) = 0 \quad (\text{E-3})$$

Equation of energy conservation

$$-\frac{[k^{\text{eff}}][T]}{h_{\text{el}}^2} \left[\ell_{\text{el}}^2 \frac{\partial}{\partial \tilde{x}} \left(\tilde{k}^{\text{eff}} \frac{\partial \tilde{T}}{\partial \tilde{x}} \right) + \frac{\partial}{\partial \tilde{z}} \left(\tilde{k}^{\text{eff}} \frac{\partial \tilde{T}}{\partial \tilde{z}} \right) \right] = S_{\text{temp, el}} \quad (7.24)$$

$$-\cancel{10^{-8} \ell_{\text{el}}^2} \frac{\partial}{\partial \tilde{x}} \left(\tilde{k}^{\text{eff}} \frac{\partial \tilde{T}}{\partial \tilde{x}} \right) - \frac{\partial}{\partial \tilde{z}} \left(\tilde{k}^{\text{eff}} \frac{\partial \tilde{T}}{\partial \tilde{z}} \right) = \frac{h_{\text{el}}^2}{[k^{\text{eff}}][T]} S_{\text{temp, el}} \quad (\text{E-4})$$

$$-\frac{\partial}{\partial \tilde{z}} \left(\tilde{k}^{\text{eff}} \frac{\partial \tilde{T}}{\partial \tilde{z}} \right) = \frac{h_{\text{el}}^2}{[k^{\text{eff}}][T]} S_{\text{temp, el}} \quad (\text{E-5})$$

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Publications Arising from This Thesis

Journal Papers

1. **He Z**, Li H, Birgersson E. *Reduced model for the planar solid oxide fuel cell*. Computers & Chemical Engineering, 52(2013) 155-167.
2. **He Z**, Birgersson E, Li H. *Spatially smoothed fuel cell models: variability of dependent variables underneath flow fields*. International Journal of Hydrogen Energy, 39(2014) 4566-4575.
3. **He Z**, Li H, Birgersson E. *Correlating variability of modeling parameters with cell performance: Monte Carlo simulation of a 3D planar solid oxide fuel cell model*. Fuel Cells (submitted).
4. **He Z**, Birgersson E, Li H. *Reduced non-isothermal model for the planar solid oxide fuel cell and stack*. Energy (accepted).

Conference Papers

1. **He Z**, Li H, Birgersson E. *Validated reduction and accelerated numerical computation of a model for the transport phenomena in a solid oxide fuel cell*. International Conference on Materials for Advanced Technologies (ICMAT). Singapore 2011.