

Numerical Investigation of
Ammonia-fueled Planar SOFC Stack
- Internal and External Cooling Effects

Tan Wee Choon

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Department of Aeronautics and Astronautics
Graduate School of Engineering
Kyoto University

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Chapter 1

Introduction

1.1 Background

A fuel cell is a device that harvests electrical energy from the supplied fuel through electrochemical reactions. The working principle of a fuel cell is to separate the transports of electrons and ions using an electrolyte layer. This electrolyte layer only allows ions transport from an electrode to another electrode through it. Meanwhile, the electrons are transported through an external circuit to complete the electrochemical reaction. A suitable catalyst is required for the electrochemical reaction to generate electrons or ions in a fuel cell. Among the various types of fuel cells, solid oxide fuel cell (SOFC) is one of the most outstanding types of the fuel cell. Both electrolyte and electrodes in SOFCs consist of ceramic materials to withstand high operating temperatures. There are three major types of SOFCs based on operating temperatures: (i) low-temperature SOFCs (723 – 873 K) [1–3], (ii) intermediate-temperature SOFCs (873 – 1073 K) [4–8], and (iii) high-temperature SOFCs (1073 – 1273 K) [9,10].

High operating temperature is preferable for SOFCs due to its low resistance to achieve high cell performance. Nonetheless, high operating temperatures result in high thermal stress among the SOFC components owing to the difference in the thermal expansion coefficients among the cell components [11]. Besides, long start-up time is required for a high-temperature SOFC, which can be a drawback during the selection of an energy converter [12]. Furthermore, expensive

materials (such as LaCrO_3 -based oxide) are used for separators of high-temperature SOFCs. This results in performance degradation due to the migration of Cr from the separator to the reaction sites of an electrode [13]. Therefore, cooling of SOFC stack is required to reduce the cell temperature. The cell temperature can be reduced by low fuel utilization, low air utilization, consideration of heat loss at walls of a cell/stack, or fuel that undergoes endothermic reaction. Firstly, high fuel utilization is an optimum operating condition for SOFCs to harvest electrical energy from the limited chemical energy in the supplied fuel. Therefore, it is not advisable to operate SOFCs with low fuel utilization. Secondly, low air utilization requires high energy consumption from the air blower to deliver a high flow rate of air to the cell, and it reduces overall system efficiency. As a result, SOFCs are encouraged to operate at high air utilization except for an SOFC with an adiabatic wall. Thirdly, heat loss at the walls of an SOFC cell can heat-up the supplied reactants or self-sustain an external component that undergo endothermic reaction. However, careful design of heat loss is required as failure can result in a significant non-uniformity of the cell temperature distribution and high local thermal stress in the cell. Lastly, fuel like direct ammonia or direct methane can undergo endothermic reaction within the anode with the aid of a suitable catalyst. The high endothermic heat can significantly reduce local cell temperature and trigger non-uniformity of current density and cell temperature in the cell. The cell can be stacked together to form a stack to provide the required electrical output. In such a case, the difficulty of thermal management within an SOFC stack is increased as the total heat released from the stack is multiplied.

Both ammonia and methane fuels can be supplied directly or indirectly to SOFCs depending on the operating temperature and its anode materials. Higher endothermic heat is generated from methane reforming reaction than ammonia decomposition reaction. The influence of endothermic

heat on SOFCs can be reduced under indirect fuel. An external decomposer (ammonia fuel) or a reformer (methane fuel) can be introduced to the SOFC system. The required heat to sustain its operation can be supplied from an afterburner or the SOFC. Afterburner combusts the remaining fuel from the outlet of SOFC; the generated heat can be useful to support the operation of decomposer/reformer. Alternatively, the high-grade heat from SOFC generated from the electrochemical reaction can be used to sustain the operation of decomposer/reformer through radiation heat. This radiation heat depends on the exposed surfaces and the temperature difference between decomposer/reformer and the wall of SOFC. From the perspective of thermal management, the endothermic heat is encouraged to be located close to the heat source to minimize the heat loss to the surrounding. Therefore, direct ammonia fuel with a mild endothermic heat can be tactically supplied to SOFCs for stack cooling purpose. Although there have been studies conducted with the direct methane [14–17] and indirect methane [18–20] fuel, only a few were conducted on ammonia fuel [21–24]. None of them design the ammonia fueled cell/stack in view of thermal management.

The flow configuration of an SOFC is similar to a heat exchanger [25]. Two different fluids (reactants) are supplied to an SOFC cell through fuel and air channels. The air within the air channels effectively removes the heat in an SOFC due to the high flow rate of air. A higher fuel flow rate can also be supplied to a cell. However, the performance of the cell is depressed under low fuel utilization. Co-, counter-, and cross-flow configurations of the air flow relative to the fuel flow are among the conventional flow configurations for a planar SOFC cell or stack. All these flow configurations have pros and cons. A counter-flow with a high average cell temperature is capable of maximizing the performance of a cell but has the major drawback of non-uniformity cell temperature distribution [17]. A cross-flow is preferred by SOFC manufacturers owing to the

simplicity of the manifold design [26]. However, local fuel depletion at high fuel utilization is more likely to occur under a cross-flow configuration than the other flow configurations [27]. A co-flow tends to have homogeneous distributions of current density [28] and cell temperature [29]. Therefore, the selection of the flow configuration can affect their performance. There is still the possibility of constructing new flow configurations in a stack assembly. The alternation for both fuel- and air-flows within the ribs of each cell was proposed by Fardadi et al. [30] to overcome the high peak temperature and large temperature gradient in the cross-flow. However, such design requires an extremely complex manifold design due to a large number of ribs per cell.

Strategic design of a cell can minimize poor cell performance of SOFCs at low cell temperature. Although increasing the active area in a single cell is a simple but effective approach to achieve a higher current output, the maximum active area tends to be limited by available manufacturing technologies. However, within the same active area, we still have design options for different cell aspect ratio. Geometry aspect ratio is defined as the ratio of the streamwise length to the spanwise width. Currently, most studies have been conducted with the aspect ratio of unity on both laboratory cells [31–35] and commercial cells [36,37]. Although there have been studies conducted with other aspect ratio cells [38–40], none of them have proposed guidelines to design SOFC in view of the geometry aspect ratio.

In principle, all the previously mentioned cooling methods for SOFC stack: pre-decomposition rate of ammonia fuel, flow configuration, and aspect ratio can be individually investigated by three-dimensional (3D) numerical models; however, it is not realistic due to high computation cost. Therefore, there are extensive works where the 3D models are simplified into a quasi-two-dimensional (quasi-2D) or quasi-3D model by employing zero-dimensional [41,42] analytical and one-dimensional [43,44] approaches for the mass transport in the electrodes. Iwai

et al. [45] proposed a quasi-3D numerical model to analyze an intermediate temperature SOFCs with direct internal methane reforming. The temperature gradient in a cell along its thickness direction was neglected. The electrochemical reaction is limited at the electrode-electrolyte interface. Lai et al. [29] developed a quasi-2D numerical model, which analyzes a planar SOFC stack consisting of 96 cells. However, this model is limited to co- and counter-flow configurations as it ignores the distribution perpendicular to the flow direction. Park and Min [46] proposed a quasi-3D non-isothermal dynamic model to analyze a proton exchange membrane fuel cell. All the models mentioned above can significantly reduce computation cost and can perform a stack level analysis. The strategy to reduce computation cost is conducted on the smallest dimension or least important dimension within a calculation domain. In this study, a quasi-3D numerical model is developed by tactically neglecting the changes in the thickness of each component. However, the change of charge-transfer current within an electrode is determined by an analytical approach based on its real microstructure properties as proposed by Onaka et al. [47].

The microstructure of electrodes is crucial to obtain reliable numerical results. There are three groups of microstructure properties: electronic, ionic, and gas phases. Each of these phases is responsible for the corresponding electrons, ions, or gas species transport. Volume fraction, tortuosity factor, the average diameter of the pore, connectivity of phases, and triple-phase or double-phase boundary density are among the important microstructure properties that influence the performance of a cell. This information can be obtained by the microstructure reconstruction after utilizing either focused ion beam scanning electron microscopy (FIB-SEM) [48–50] or nano-computed tomography (nano-CT) [51,52]. Brus et al. [53] implemented the real microstructure from a cell as well as artificially modified microstructure in numerical analysis and compared the results with the experimental results. The significant discrepancy with the experiment was found

for the artificially modified microstructure, which indicates the importance of implementation of real microstructure properties into numerical analysis.

The main objective of this numerical study is summarized into three parts: (i) evaluation of external cooling of radiation heat loss under indirect ammonia fuel, (ii) improvement of internal cooling through air flow configuration, and (iii) enhancement of the thermal management within an SOFC stack through pre-decomposition rate of ammonia fuel.

1.2 Outline of the thesis

Chapter 2 presents the detail of a numerical model that includes all the governing equations, electrochemical model, and gas diffusion models used in this study. The performance evaluation techniques of a cell or stack are explained. Besides, a statistical approach for the analysis of distribution in a cell or stack is also proposed.

Chapter 3 presents the verification and validation of the developed numerical model based on Chapter 2. The detail of the microstructure obtained from the literature is presented. The validity of the developed model with the implementation of real microstructure information is investigated through the comparison with experimental results of a six-cell stack fueled by diluted hydrogen.

Chapter 4 presents the effect of aspect ratio for an SOFC fueled with fully decomposed ammonia or also known as indirect ammonia fuel using the developed numerical model. The external cooling effect through radiation heat at sidewalls of SOFC short stack to sustain the external ammonia decomposer is taken into consideration. The influence of aspect ratio under various thermal boundary conditions, operation temperature, fuel utilization, and flow configuration of co- and counter-flow are discussed.

Chapter 5 presents the investigation of factors influencing the performance of an SOFC fueled with direct ammonia using the developed numerical model. A comparison between Fick's model and dusty-gas model for the transportation of gas species in an anode is conducted with the grid independence analysis for the newly introduced anode mesh for the implementation of the dusty-gas model. A parametric study is conducted towards the ammonia decomposition reaction rate to quantify the influence of each identified factor. The influence of internal cooling through endothermic heat, which is generated from ammonia decomposition reaction, is evaluated towards the cell performance. The effect of cell aspect ratio and flow configuration are evaluated again under direct ammonia fuel and discussed statistically.

Chapter 6 presents the comparison between direct and indirect ammonia fuel for an eight-cell stack. The conventional flow configurations of co-, counter-, and cross-flow with two newly introduced the alternation of the air flows in every other cell of a stack by either parallel (streamwise) or perpendicular (spanwise) direction to the fuel flow are discussed on its distributions of current density, cell temperature, and molar fraction of hydrogen. The performance of the stack under the influence of flow configuration, supplied fuel, and fuel utilization is compared under thermal adiabatic walls.

Chapter 7 summarizes all the major finding in this study. Recommendations for future work are also offered.

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Chapter 2

Numerical model

2.1 Introduction

The operation of SOFCs is complex involving the transport of mass, species, heat, ions, and electrons, the reaction kinetics, as well as the electrochemical and chemical reactions. Numerical analysis has the full capability to study the influence of each factor that contributes to the above complexities in order to achieve the highest performance of SOFCs. There are several numerical models found in the literature such as zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D), quasi-2D, three-dimensional (3D) and quasi-3D models that can be applied for a planar-type SOFC.

0D model is the simplest among the above-mentioned models. Both the model size and the distribution of fundamental parameters are neglected, only the changes between inlet and outlet are considered for the mass or energy conservation in 0D model [1–3]. Meanwhile, the 1D model can be performed either along the streamwise length of the reactants flow direction to focus on gas flow and heat transfer [4,5] (performed for tubular SOFCs), or along the thickness direction of a cell to focus on its electrochemistry and mass/charge transfer [6]. As a result, it is limited to either electrode mechanistic model or unit cell model. For general macroscopic modeling, the 2D model ignores one of the three dimensions, which has a minor influence on performance [7,8]. This 2D model can be reduced to the quasi-2D model when the physics in both considered dimension are

weakly coupled [9,10]. This uses low computation resources and maintains good calculation accuracy. A full multidimensional transport phenomenon can be solved by the 3D model [11,12]. This 3D model has no limitation when computation cost is not a consideration. However, this becomes an issue in the research and development phase of a product when cost is considered. 3D model can be reduced to the quasi-3D model by applying 0-dimensional transportation of masses and charges by the Fick's model (FM) [13] and charge-transfer current profile in the electrodes [14]. This reduction is due to the fact that the thickness of a cell is the shortest dimension in the computational domain of a cell/stack. Furthermore, a small variation of temperature is found along the thickness direction.

SOFCS have advantages of fuel flexibility against other types of fuel cell. It can be fueled with hydrogen (H_2), carbon monoxide (CO), methane (CH_4) and ammonia (NH_3) due to high operating temperatures and CO tolerance in the cell. Although H_2 and CO can be directly supplied to the reaction site and undergo electrochemical reaction, both CH_4 and NH_3 require additional reaction before it can be converted to either H_2 or CO. This additional reaction can be either internally or externally performed. In the case of an internal reaction, both CH_4 and NH_3 are converted to fuel in the anode with the aid of a suitable catalyst. CH_4 or NH_3 transported along with other gas species in the gas mixture must be considered in the anode. The FM used in the quasi-3D model [15] has the limitation of handling the significant change of concentration in the mixture due to methane reforming or ammonia decomposition reaction.

In this chapter, the detail of the numerical model is presented. Firstly, a brief of the quasi-3D model for a cell/stack is explained. Secondly, the governing equations and the electrochemical model used to solve the complex phenomenon in a cell/stack is presented. Thirdly, the implementation of the dusty-gas model in the developed quasi-3D model is proposed. Next, the

mathematical model for ammonia decomposition namely the ammonia decomposition rate, enthalpy change due to a decomposition reaction, and the thermal radiation from cell/stack to sustain external decomposer is described. Finally, a method to evaluate the performance of a cell/stack is suggested.

2.2 Quasi-three-dimensional model

A cell unit as shown in Fig. 2.1(a) consists of top and bottom separators, fuel and air channels, and a cell or also known as a positive-electrolyte-negative assembly (PEN), as shown in Fig. 2.1(b). Both the separators and PEN are dense solid layers. On the other hand, both fuel and air channels are filled with metal foam current collectors. Therefore, the fuel and air channel layers in Fig. 2.1(b) consist of both solid and fluid phase layers. This cell unit can be stacked-up to form a stack to deliver higher power density accordingly to the power requirement. A unique feature of the cell unit is the design of the fuel and air channels, with a single rib rather than multiple ribs. The cell unit includes an electrical insulator with a length of 4.5 mm at both the inlet and outlet of the PEN.

The quasi-3D numerical model consists of governing equations described in section 2.3, coupled with the electrochemical reaction in the cell illustrated in section 2.4. The masses of gas species generated or consumed, and the heat released from the electrochemical reaction are reflected by the source terms in the governing equations. All physical properties of the fluids depended on the mass fraction and local temperature of chemical species.

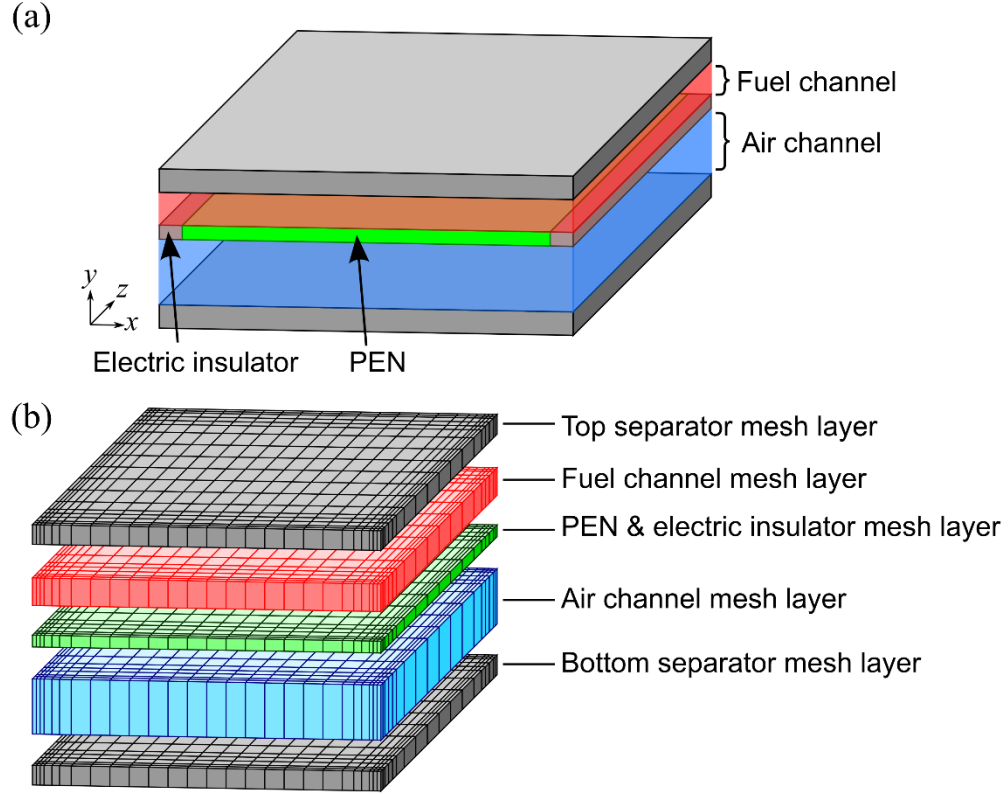


Fig. 2.1. (a) Schematic view of cell unit. (b) Mesh layers for the quasi-3D model.

For the analysis of cell aspect ratio, the cells are named after the dimensions of the effective area in the streamwise (x-) and spanwise (z-) directions as shown in Fig. 2.2. For example, cell X25Z192 has an effective size of 25 mm $\times$ 192 mm with an aspect ratio of 0.130. The cell used in the experiment has the same dimension as cell X80Z60.

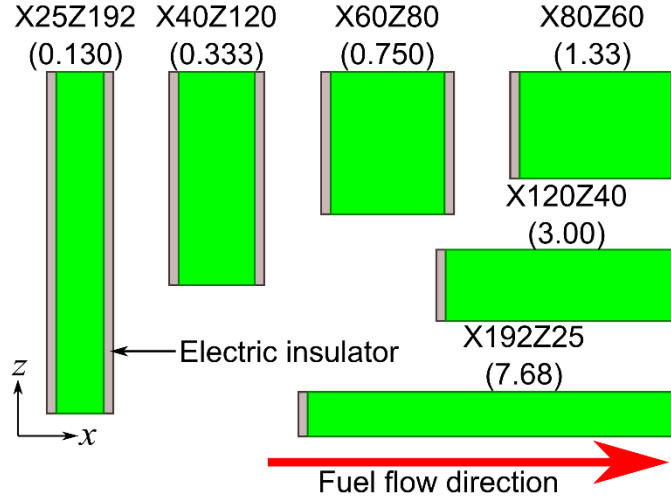


Fig. 2.2. Cells with various aspect ratios (shown in bracket).

2.3 Governing equations

The numerical analysis is based on conservation equations of the mass, momentum, species, and energy.

Mass conservation for gases:

$$\frac{\partial(\rho u)}{\partial x} + \frac{\partial(\rho w)}{\partial z} = \sum S_{Y_i} \quad (2.1)$$

Momentum conservation for gases:

$$\begin{aligned} & \left[\frac{\partial}{\partial x} \left(\frac{\rho u u}{\varepsilon} \right) + \frac{\partial}{\partial z} \left(\frac{\rho w u}{\varepsilon} \right) \right] \\ &= -\varepsilon \frac{\partial P}{\partial x} + \frac{\partial}{\partial x} \left(\mu \frac{\partial u}{\partial x} \right) + \frac{\partial}{\partial z} \left(\mu \frac{\partial u}{\partial z} \right) + \frac{1}{3} \frac{\partial}{\partial x} \left(\mu \frac{\partial u}{\partial x} \right) - \frac{2}{3} \frac{\partial}{\partial x} \left(\mu \frac{\partial w}{\partial z} \right) \\ &+ \frac{\partial}{\partial z} \left(\mu \frac{\partial w}{\partial x} \right) - \varepsilon \frac{\mu}{K} u - \varepsilon \frac{\rho f}{\sqrt{K}} |U| u \end{aligned} \quad (2.2)$$

$$\begin{aligned}
& \left[\frac{\partial}{\partial x} \left(\frac{\rho u w}{\varepsilon} \right) + \frac{\partial}{\partial z} \left(\frac{\rho w w}{\varepsilon} \right) \right] \\
& = -\varepsilon \frac{\partial P}{\partial z} + \frac{\partial}{\partial x} \left(\mu \frac{\partial w}{\partial x} \right) + \frac{\partial}{\partial z} \left(\mu \frac{\partial w}{\partial z} \right) + \frac{1}{3} \frac{\partial}{\partial z} \left(\mu \frac{\partial w}{\partial z} \right) - \frac{2}{3} \frac{\partial}{\partial z} \left(\mu \frac{\partial u}{\partial x} \right) \\
& + \frac{\partial}{\partial x} \left(\mu \frac{\partial u}{\partial z} \right) - \varepsilon \frac{\mu}{K} w - \varepsilon \frac{\rho f}{\sqrt{K}} |U| w
\end{aligned} \tag{2.3}$$

Energy conservation:

(fluid phase in both the fuel and air channels filled with metal foam)

$$\frac{\partial(\rho C_p u T_f)}{\partial x} + \frac{\partial(\rho C_p w T_f)}{\partial z} = \frac{\partial}{\partial x} \left(\lambda_f^{\text{eff}} \frac{\partial T_f}{\partial x} \right) + \frac{\partial}{\partial z} \left(\lambda_f^{\text{eff}} \frac{\partial T_f}{\partial z} \right) + h_{\text{sf}} a_{\text{sf}} (T_s - T_f) \tag{2.4}$$

(solid phase in both the fuel and air channels filled with metal foam)

$$0 = \frac{\partial}{\partial x} \left(\lambda_s^{\text{eff}} \frac{\partial T_s}{\partial x} \right) + \frac{\partial}{\partial z} \left(\lambda_s^{\text{eff}} \frac{\partial T_s}{\partial z} \right) + h_{\text{sf}} a_{\text{sf}} (T_f - T_s) \tag{2.5}$$

(solid phases in the separator and the cell)

$$0 = \frac{\partial}{\partial x} \left(\lambda_s \frac{\partial T_s}{\partial x} \right) + \frac{\partial}{\partial z} \left(\lambda_s \frac{\partial T_s}{\partial z} \right) + Q \tag{2.6}$$

Species conservation:

$$\frac{\partial}{\partial x} (\rho u Y_i) + \frac{\partial}{\partial z} (\rho w Y_i) = \frac{\partial}{\partial x} \left(\rho D_{i,m}^{\text{eff}} \frac{\partial Y_i}{\partial x} \right) + \frac{\partial}{\partial z} \left(\rho D_{i,m}^{\text{eff}} \frac{\partial Y_i}{\partial z} \right) + S_{Y_i} \tag{2.7}$$

$$\nabla \cdot N_i = S_{x_i} \tag{2.8}$$

Charge conservation

$$\frac{\partial}{\partial x} \left(\sigma_s^{\text{eff}} \frac{\partial \phi}{\partial x} \right) + \frac{\partial}{\partial y} \left(\sigma_s^{\text{eff}} \frac{\partial \phi}{\partial y} \right) + \frac{\partial}{\partial z} \left(\sigma_s^{\text{eff}} \frac{\partial \phi}{\partial z} \right) = S_\phi \tag{2.9}$$

In both the mass and species conservation equations, S_{Y_i} and S_{x_i} represent the mass and molar of gas species i consumed or generated by the electrochemical process, Y_i is the mass fraction of species i in the gas mixture, and ε is the porosity of the porous medium. The conservation

equations of mass, momentum, and species in the fuel and air channels are solved. The porosity and diameter of the pore for the porous metal foam d_p are taken as 0.9 and 2.0×10^{-4} m [14]. The permeability K , inertial coefficient f , and surface area a_{sf} of the porous metal foam are defined as follows [16]:

$$K = \frac{\varepsilon^2 d_p^2}{36\chi(\chi - 1)}, \quad (2.10)$$

$$\chi = \frac{4\varepsilon d_p^2}{\pi(d_p^2 - d_f^2)}, \quad (2.11)$$

$$f = 0.0095g^{-8} \sqrt{\frac{\varepsilon}{3(\chi - 1)}} \left[1.18 \sqrt{\frac{(1 - \varepsilon)1}{3\pi}} \frac{1}{g} \right], \quad (2.12)$$

$$g = 1 - \exp\left(-\frac{1 - \varepsilon}{0.04}\right), \quad (2.13)$$

$$d_f = 1.18d_p \sqrt{\frac{(1 - \varepsilon)1}{3\pi}} \frac{1}{g}, \quad (2.14)$$

$$a_{sf} = \frac{3\pi d_f}{d_p^2}. \quad (2.15)$$

where χ , G , and d_f are the tortuosity, shape function, and diameter of the porous matrix, respectively. d_f and d_p are the average diameters of the metal fibers and pores of the open-cell structure representation of the porous metal foam, respectively.

Equations (2.4) and (2.5) are the energy conservation equations used for the fluid phase and solid phase, respectively, in the fuel and gas channels filled with the metal foam. The subscripts s and f indicate the solid phase and fluid phase, respectively. Equation (2.6) is used for the solid phases in the separator and cell. Q in Eq. (2.6) is the heat source or heat sink, associated with the

exothermic heat from the electrochemical reaction or endothermic heat from the direct ammonia decomposition in a cell, respectively. The effective thermal conductivity λ^{eff} , the effective thermal conductivity of the fluid phase λ_f^{eff} , and the effective thermal conductivity of the porous metal foam, λ_s^{eff} , are defined as follows [17].

$$\lambda^{\text{eff}} = \frac{\sqrt{3}}{2} \left\{ \frac{r \left(\frac{b}{L}\right)}{\lambda_f - \left[1 + \left(\frac{b}{L}\right)\right] \frac{(\lambda_s - \lambda_f)}{3}} + \frac{(1-r) \left(\frac{b}{L}\right)}{\lambda_f - \frac{2}{3} \left(\frac{b}{L}\right) (\lambda_s - \lambda_f)} + \frac{\frac{\sqrt{3}}{2} - \left(\frac{b}{L}\right)}{\lambda_f - \frac{4r}{3\sqrt{3}} \left(\frac{b}{L}\right) (\lambda_s - \lambda_f)} \right\}^{-1}, \quad (2.16)$$

$$\lambda_f^{\text{eff}} = \frac{\sqrt{3}}{2} \lambda_f \left\{ \frac{r \left(\frac{b}{L}\right)}{1 - \frac{1}{3} \left[1 + \left(\frac{b}{L}\right)\right]} + \frac{(1-r) \left(\frac{b}{L}\right)}{1 - \frac{2}{3} \left(\frac{b}{L}\right)} + \frac{\frac{\sqrt{3}}{2} - \left(\frac{b}{L}\right)}{1 - \frac{4r}{3\sqrt{3}} \left(\frac{b}{L}\right)} \right\}^{-1}, \quad (2.17)$$

$$\lambda_s^{\text{eff}} = \frac{\sqrt{3}}{2} \lambda_s \left\{ \frac{r \left(\frac{b}{L}\right)}{\frac{1}{3} \left[1 + \left(\frac{b}{L}\right)\right]} + \frac{(1-r) \left(\frac{b}{L}\right)}{\frac{2}{3} \left(\frac{b}{L}\right)} + \frac{\frac{\sqrt{3}}{2} - \left(\frac{b}{L}\right)}{\frac{4r}{3\sqrt{3}} \left(\frac{b}{L}\right)} \right\}^{-1}, \quad (2.18)$$

$$\frac{b}{L} = \frac{-r + \sqrt{r^2 + 4(1-\varepsilon) \frac{\sqrt{3}}{2} \left\{ \left[2 - r \left(1 + \frac{4}{\sqrt{3}}\right)\right] / 3 \right\}}}{\frac{2}{3} \left[2 - r \left(1 + \frac{4}{\sqrt{3}}\right)\right]}. \quad (2.19)$$

r is given as 0.09 [17]. The thermal conductivity of the fluid phase λ_f in the multi-component gas mixture can be expressed based on the dimensionless number ψ_{ij} by Lindsay and Bromley [18].

$$\lambda_f = \sum_i \left(\frac{x_i \lambda_i}{\sum_j x_j \psi_{ij}} \right), \quad (2.20)$$

$$\psi_{ij} = \frac{1}{4} \left\{ 1 + \left[\frac{\mu_i}{\mu_j} \left(\frac{M_j}{M_i} \right)^{3/4} \frac{T + \theta_i}{T + \theta_j} \right]^{1/2} \right\}^2 \left[\frac{T + \theta_{ij}}{T + \theta_i} \right], \quad (2.21)$$

$$\theta_i = 1.5 T_{b,i}, \quad (2.22)$$

$$\theta_{ij} = \sqrt{\theta_i \theta_j}. \quad (2.23)$$

The thermal conductivity λ_i and viscosity coefficient of species μ_i are individually expressed by a polynomial equation that function to its temperature based on its physical properties [19]. $T_{b,i}$ is the boiling temperature of species i . On the other hand, the thermal conductivity of the solid phase is given in Table 2.1.

Table 2.1. Thermal conductivity

Component	λ_s (W m ⁻¹ K ⁻¹)
anode	11.0
electrolyte	2.70
cathode	0.880
separator	22.0
metal foam in channels	22.0

The average thermal conductivity of cell is given based on the thickness of each layer in a cell as follows.

$$\lambda_{s,PEN} = \frac{h_{PEN}}{\frac{h_{ano}}{\lambda_{s,ano}} + \frac{h_{ele}}{\lambda_{s,ele}} + \frac{h_{cat}}{\lambda_{s,cat}}} \quad (2.24)$$

The effective gas diffusion coefficient of species i in the gas mixture $D_{i,m}^{eff}$ in Eq. (2.7), is modeled by multiplying ε to $D_{i,m}$ [20]. The conservation equation of species as given in Eq. (2.8) is only applicable to the case where the dusty-gas model (DGM) is used. σ_s^{eff} and S_ϕ in Eq. (2.9) respectively represent the effective electronic conductivity and the source term corresponding to the current in the y -axis of the equivalent circuit model, which is discussed in section 2.4. The pressure fields in the fuel and air channels are solved by the semi-implicit method for pressure-linked equations (SIMPLE) algorithm [21]. The governing equations are discretized by the finite volume method. An in-house code is developed and used for the calculations.

2.4 Electrochemical model

The equivalent circuit model from [13] is modified as shown in Fig. 2.3 in this analysis, where the local cell terminal voltage is expressed as follows:

$$V_{cell} = E - (\eta_{act,ano} + \eta_{ohm,ano} + \eta_{conc,ano}) - \eta_{ohm,ele} - (\eta_{act,cat} + \eta_{ohm,cat} + \eta_{conc,cat}). \quad (2.25)$$

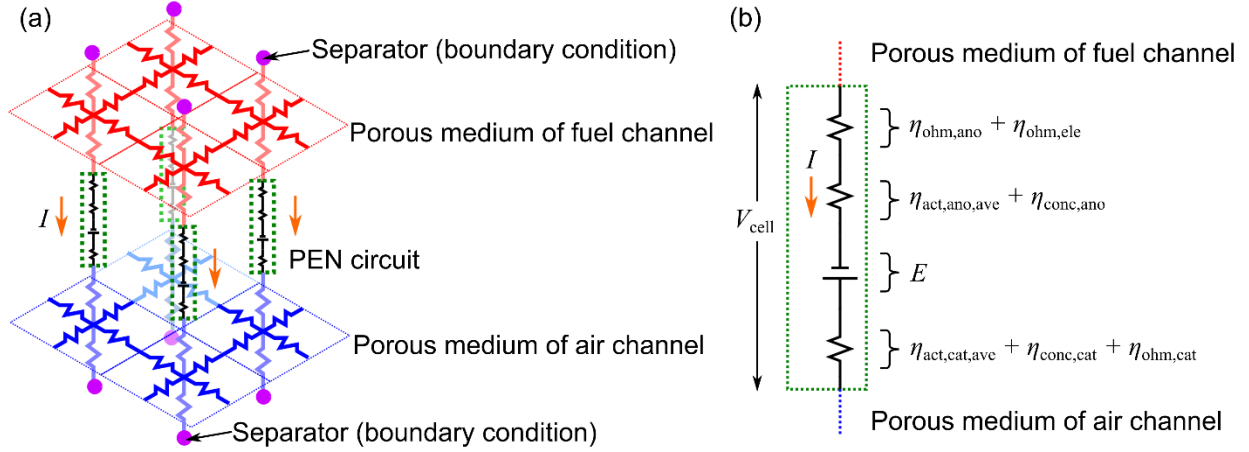


Fig. 2.3. Schematic view of (a) equivalent circuit model, and (b) equivalent circuit of PEN.

For a typical SOFC operation, the electrochemical reaction involves the reduction of oxygen at the cathode and the oxidation of hydrogen at the anode. The electromotive force (EMF) for this $\text{H}_2\text{-O}_2$ reaction can be given by the Nernst equation as follows:

$$E = -\frac{\Delta G^0}{2F} - \frac{RT_s}{2F} \ln \left[\frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2} (p_{\text{O}_2}/101325)^{0.5}} \right]. \quad (2.26)$$

The activation overpotential is determined from a Butler–Volmer-like equation. The PEN is treated as a dense solid layer within the quasi-3D model. A semi-analytical model is applied to the y -axis (the cell thickness direction) so that the electrode microstructures obtained from focused ion beam scanning electron microscope (FIB-SEM) tomography could be implemented to represent the porous electrodes. The charge-transfer current density within a control volume i_{ct} [22] is given by Eqs. (2.27) and (2.28) for the nickel/yttria-stabilized zirconia (Ni/YSZ) anode and lanthanum strontium cobalt ferrite (LSCF) cathode, respectively.

$$i_{\text{ct,ano}} = l_{\text{TPB}} i_{0,\text{ano}} \left[\exp\left(\frac{2F\eta_{\text{act,ano}}}{RT_s}\right) - \exp\left(-\frac{F\eta_{\text{act,ano}}}{RT_s}\right) \right] \quad (2.27)$$

$$i_{\text{ct,cat}} = A_{\text{DPB}} i_{0,\text{cat}} \left[\exp\left(\frac{1.2F\eta_{\text{act,cat}}}{RT_s}\right) - \exp\left(-\frac{F\eta_{\text{act,cat}}}{RT_s}\right) \right] \quad (2.28)$$

The exchange current per unit reaction site $i_{0,\text{ano}}$ for the Ni/YSZ anode in Eq. (2.29) is obtained from Kanno et al. [23], based on the empirical equation proposed by Bieberle et al. [24]. On the other hand, $i_{0,\text{cat}}$ for the cathode in Eq. (2.30) introduced by Matsuzaki et al. [25] from the experimental work of Esquirol et al. [26].

$$i_{0,\text{ano}} = 0.0013 p_{\text{H}_2,\text{TPB}}^{0.11} p_{\text{H}_2\text{O},\text{TPB}}^{0.67} \exp(-84900/RT_s) \quad (2.29)$$

$$i_{0,\text{cat}} = 1.47 \times 10^6 p_{\text{O}_2,\text{DPB}}^{0.2} \exp(-85859/RT_s) \quad (2.30)$$

Expressing η_{act} as a function of the other parameters in Eqs. (2.27) and (2.28) is a critical task. This study adopted the hyperbolic sine function to approximate Eq. (2.27) so that $\eta_{\text{act,ano}}$ can be written in the explicit form, whereas the first order of the Taylor series is used to approximate $\eta_{\text{act,cat}}$ as in [14]. The charge-transfer coefficients for both the forward and backward reactions in Eqs. (2.27) and (2.28) are assumed to be the same and replaced by α_0 . As a result, the local activation overpotential is expressed as follows [14]:

$$\eta_{\text{act,ano,local}} = \frac{RT_s}{\alpha_0 F} \sinh^{-1} \left(\frac{i_{\text{ct,ano}}}{2i_{0,\text{ano}}} \right), \quad (2.31)$$

$$\eta_{\text{act,cat,local}} = \frac{11}{5} \cdot \frac{i_{0,\text{cat}} F}{RT_s}. \quad (2.32)$$

Generally, oxide ions are transferred through the ionic phase, whose transfer has a higher resistance than that of electrons in the electronic phase. Consequently, the electrochemical reaction tends to be localized near the electrode-electrolyte interface and gradually decreases in intensity towards the outer surface of the electrode. The decay function is used to approximate the distribution of the charge-transfer current density as shown in Fig. 2.4 [22]:

$$i_{ct} = C \cdot \exp(-\lambda y), \quad (0 \leq y \leq h, \lambda \gg 0) \quad (2.33)$$

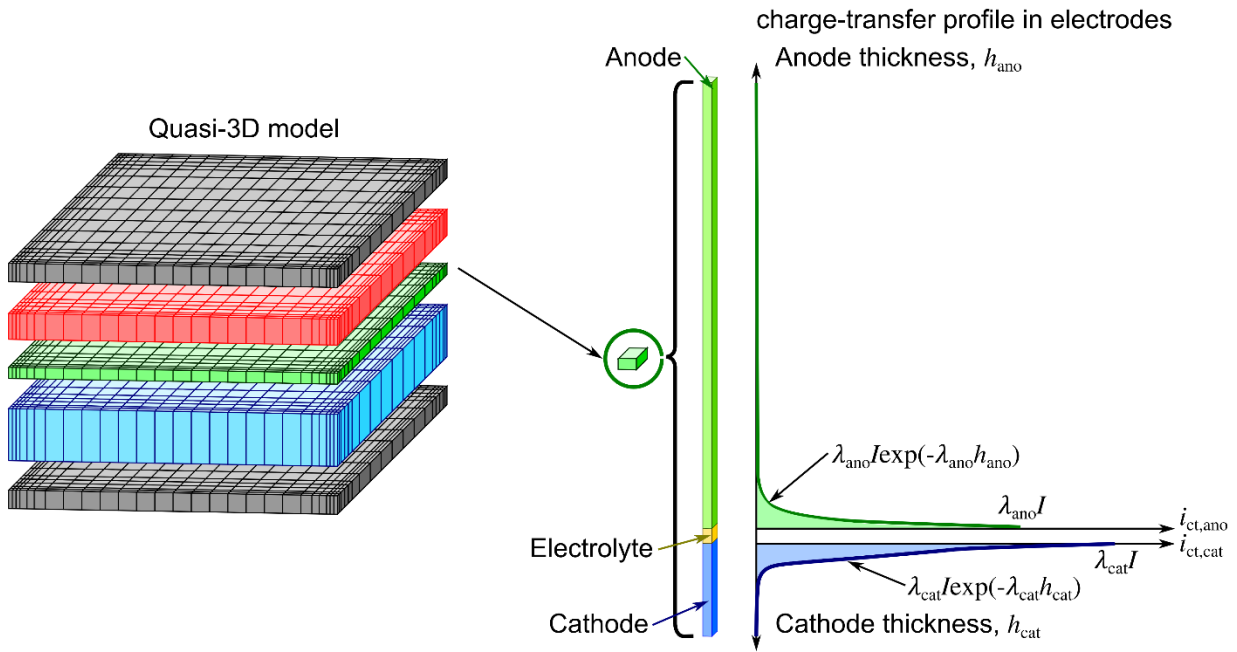


Fig. 2.4. Implementation of charge-transfer profile in quasi-3D model.

where λ is the attenuation factor, further discussion of λ can be found in section 2.6. The charge-transfer current density model should comply with the following two conditions: (i) the charge-transfer current density must be sufficiently small at the outer surface of the electrode, and (ii) the sum of the products for the local charge-transfer current density and the thickness of the finite

volume along the electrode thickness must be identical to the area-specific current density. The coefficient C can be given as λI using the area-specific current density to comply with the above two conditions. The relationship between the average voltage loss across an electrode thickness of h and the local voltage loss is as follows:

$$\eta_{\text{ave}} = \frac{\int_0^h \eta_{\text{local}} i_{\text{ct}} dy}{\int_0^h i_{\text{ct}} dy}. \quad (2.34)$$

The average activation overpotential across the electrode thickness is expressed as [14]

$$\eta_{\text{act,ano,ave}} = \frac{RT_s}{\alpha_0 F} \sinh^{-1} \left(\frac{\lambda_{\text{ano}} I}{2i_{0,\text{ano}}} \right) - \frac{2i_{0,\text{ano}} RT_s}{\lambda_{\text{ano}} I \alpha_0 F} \sqrt{\left(\frac{\lambda_{\text{ano}} I}{2i_{0,\text{ano}}} \right)^2 + 1} + \frac{2i_{0,\text{ano}} RT_s}{\lambda_{\text{ano}} I \alpha_0 F}, \quad (2.35)$$

$$\eta_{\text{act,cat,ave}} = \frac{22}{5} \cdot \frac{\lambda_{\text{cat}} I F}{RT_s}. \quad (2.36)$$

It is common for a quasi-3D to assume electrochemical reaction occurs at the electrode-electrolyte interface due to the limitation of the single mesh for the thickness of a cell. In the current study, the electrochemical reaction is locally extended towards the surface of electrodes by the charge-transfer profiles in both anode and cathode. This approach in the quasi-3D model is the first unique feature of the model.

The local ohmic losses for the electronic phase and the ionic phase at a distance of y from the electrode-electrolyte interface is expressed as follows:

$$\phi_{\text{el}}(h) - \phi_{\text{el}}(y) = \int_y^h i_{\text{el}}/\sigma_{\text{el}}^{\text{eff}} dy, \quad (2.37)$$

$$\phi_{\text{io}}(y) - \phi_{\text{io}}(0) = \int_0^y i_{\text{io}}/\sigma_{\text{io}}^{\text{eff}} dy, \quad (2.38)$$

where the subscripts el and io indicate the electronic and ionic phases, respectively. The electronic phase conductivity is generally a few orders higher than the ionic phase conductivity, and therefore the ohmic loss associated with the electronic conduction is neglected in this study. As a result, the average ohmic loss for the anode, cathode, and electrolyte are as per Eq. (2.34):

$$\eta_{\text{ohm,ano}} = I/2\lambda_{\text{ano}}\sigma_{\text{io}}^{\text{eff}}, \quad (2.39)$$

$$\eta_{\text{ohm,cat}} = I/2\lambda_{\text{cat}}\sigma_{\text{io}}^{\text{eff}}, \quad (2.40)$$

$$\eta_{\text{ohm,ele}} = Ih_{\text{ele}}/\sigma_{\text{io}}. \quad (2.41)$$

The electronic and ionic phase conductivities model for the anode and the electrolyte was proposed by Bessette et al. [27], while the electronic and ionic phase conductivity model for the cathode was proposed by Matsuzaki et al. [25]. The conductivities in the cell are given as follows:

Conductivity in anode [27]:

$$\sigma_{\text{el,ano}}^{\text{eff}} = \frac{\varepsilon_{\text{el}}}{\tau_{\text{el}}} \frac{1}{[2.98 \times 10^{-5} \exp(-1392/T_s)]} \quad (2.42)$$

$$\sigma_{\text{io,ano}}^{\text{eff}} = \frac{\varepsilon_{\text{io}}}{\tau_{\text{io}}} \frac{1}{[2.94 \times 10^{-5} \exp(10350/T_s)]} \quad (2.43)$$

Conductivity in electrolyte [27]:

$$\sigma_{\text{io,ele}} = \frac{1}{[2.94 \times 10^{-5} \exp(10350/T_s)]} \quad (2.44)$$

Conductivity in cathode [25]:

$$\sigma_{\text{el,cat}}^{\text{eff}} = \frac{\varepsilon_{\text{el}}}{\tau_{\text{el}}} \sigma_{\text{cat,ele}} \quad (2.45)$$

$$\sigma_{\text{io,cat}}^{\text{eff}} = -\frac{\varepsilon_{\text{io}}}{\tau_{\text{io}}} \cdot \frac{8F^2 \tilde{D}}{RT_s V_m} \cdot \frac{\partial \delta}{\partial \ln p_{\text{O}_2}} \quad (2.46)$$

V_m is the molar volume in the cathode and has a value of $35.5 \times 10^{-6} \text{ m}^3/\text{mol}$. The oxygen nonstoichiometry δ and the oxygen partial pressure p_{O_2} (in a unit of bar) are fitted by Matsuzaki et al. [25] from the experimental data of Bouwmeester et al. [28], and is given as follows:

$$\frac{\partial \delta}{\partial \ln p_{\text{O}_2}} = -3.36260 \times 10^{-5} \cdot T_s + 2.59403 \times 10^{-2} . \quad (2.47)$$

Both the chemical diffusion coefficient of oxide ion $\tilde{D}$, and the electronic conductivity $\sigma_{\text{el,cat}}$ are given as follows:

Electronic conductivity [25]:

$$\log_{10} \sigma_{\text{el,cat}} = -0.0080(\log_{10} p_{\text{O}_2})^2 - 0.0024 \cdot \log_{10} p_{\text{O}_2} + 4.8447 \quad (923.15 \text{ K}) \quad (2.48)$$

$$\log_{10} \sigma_{\text{el,cat}} = -0.0095(\log_{10} p_{\text{O}_2})^2 - 0.0011 \cdot \log_{10} p_{\text{O}_2} + 4.8152 \quad (973.15 \text{ K}) \quad (2.49)$$

$$\log_{10} \sigma_{\text{el,cat}} = -0.0222(\log_{10} p_{\text{O}_2})^2 - 0.0169 \cdot \log_{10} p_{\text{O}_2} + 4.8056 \quad (1023.15 \text{ K}) \quad (2.50)$$

$$\log_{10} \sigma_{\text{el,cat}} = -0.0237(\log_{10} p_{\text{O}_2})^2 - 0.0034 \cdot \log_{10} p_{\text{O}_2} + 4.8126 \quad (1073.15 \text{ K}) \quad (2.51)$$

Chemical diffusion coefficient of oxide ion [25]:

$$\log_{10} \tilde{D} = -0.1252(\log_{10} p_{O_2})^2 - 0.2051 \cdot \log_{10} p_{O_2} - 9.9554 \quad (923.15 \text{ K}) \quad (2.52)$$

$$\log_{10} \tilde{D} = -0.1882(\log_{10} p_{O_2})^2 - 0.2491 \cdot \log_{10} p_{O_2} - 9.7676 \quad (973.15 \text{ K}) \quad (2.53)$$

$$\log_{10} \tilde{D} = -0.1884(\log_{10} p_{O_2})^2 - 0.3243 \cdot \log_{10} p_{O_2} - 9.4969 \quad (1023.15 \text{ K}) \quad (2.54)$$

$$\log_{10} \tilde{D} = -0.1765(\log_{10} p_{O_2})^2 - 0.2724 \cdot \log_{10} p_{O_2} - 9.2256 \quad (1073.15 \text{ K}) \quad (2.55)$$

Both the electronic conductivity and the chemical diffusion coefficient of oxide ion are interpolated or extrapolated against the local cell temperature to obtain the corresponding conductivity in the cathode.

Both LSCF and gadolinia-doped ceria (GDC) are mixed ionic-electronic conducting (MIEC) materials. However, GDC is only capable of showing such MIEC characteristic under the reduction process. Since both LSCF and GDC can transport ions, there are still research gaps in understanding the phenomenon in the composite LSCF/GDC cathode. Kim et al. [29] and Leng et al. [30] studied the different ratio of LSCF:GDC in the composite LSCF/GDC cathode. Both studies agreed with the additional GDC ratio in the composite LSCF/GDC increases performance. Kim et al. [29] also found that further expansion of 80 vol% of GDC leads to the low connectivity of LSCF and further results in the weakest performance among the samples. The proposed ionic and electronic conductivities in the LSCF/GDC composite cathode is shown in Fig. 2.5.

It is noteworthy that the electrochemical reaction still occurs at the interface of the LSCF and pore phases in this study. Thus, the oxygen ions are transported to the electrolyte layer along the path with the lowest ohmic resistance. Here, the transportation of the oxygen ions is assumed to only occur within the GDC as the ionic conductivity of GDC is higher than that of LSCF. The oxygen ions are believed to travel from the reaction site of the LSCF-pore interface to the nearest

GDC phase. Afterward, the oxygen ions continue along their path in the GDC phase before reaching the yttria-stabilized zirconia (YSZ) electrolyte. Neglecting the ionic conductivity resistance within the LSCF phase simplifies the concept. In short, the first term on the right-hand side from left to right of Eq. (2.46) is the effective coefficient of the ionic conductivity, which is referred to the microstructure of the GDC phase in the LSCF/GDC composite cathode. This definition of the ionic and electronic path in LSCF/GDC cathode is the second unique features of this model.

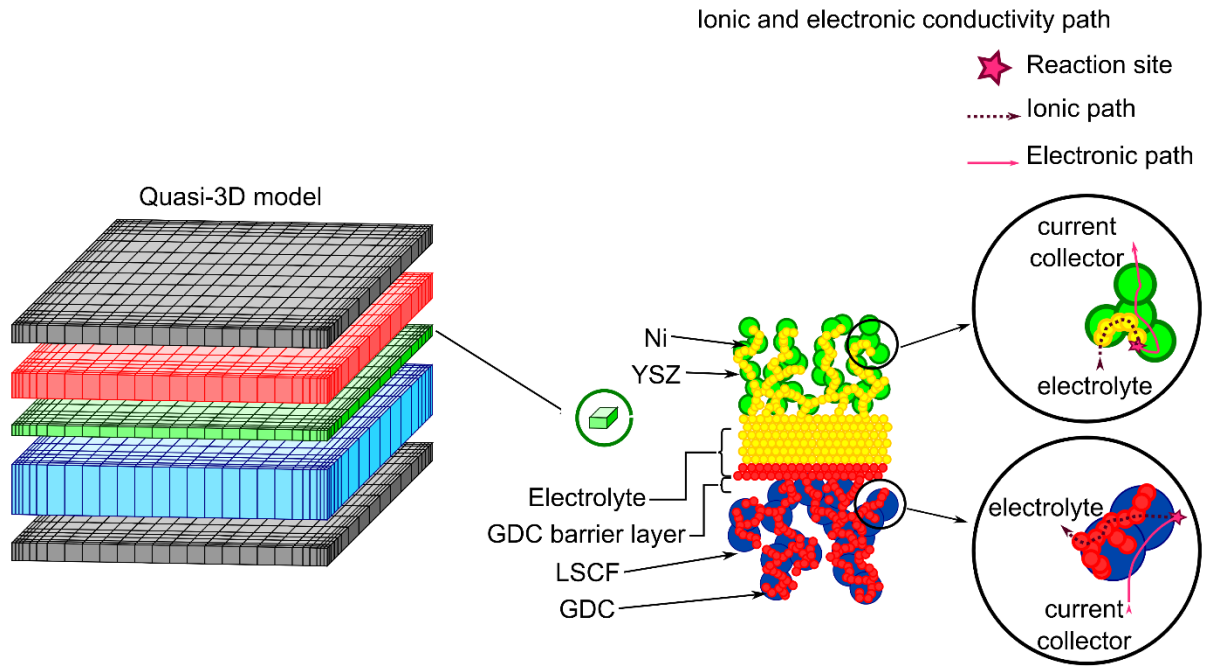


Fig. 2.5. Ionic and electronic conductivity path.

The conductivities in the cell are increased with the increment of cell temperature as previously discussed. This is not fully satisfied by a cell which consists of LSCF/GDC cathode, GDC barrier, and YSZ electrolyte. The diffusion of Zr and Sr during high temperature contributes to the formation of low ionic conductivity SrZrO_3 . This SrZrO_3 can be avoided by a dense layer of

GDC barrier layer using pulsed laser deposition [31]. However, this pulsed laser deposition is not feasible for a scale-up process such as screen printing technique in the SOFC industry [32]. Therefore, Zr diffusion along the porous GDC barrier layer is detected even just after the sintering process of GDC and results in the formation of small SrZrO_3 particles at LSCF-GDC interface after the sintering process of LSCF [33]. Polarization in the cell results in a change in the oxygen potential distribution and affects the cation diffusion of Sr and Zr [33,34]. De Vero et al. [34] observed the transverse growth of SrZrO_3 from the LSCF-GDC interface under cathodic polarization operated at 1073 K for 300 hrs. This growth of SrZrO_3 did not result in any performance degradation as compared to the lateral growth under open circuit voltage condition at 1073 K. Wang et al. [33] observed the similar transverse growth of SrZrO_3 at LSCF-GDC interface, and not reaching GDC-YSZ interface after cathodic polarization at 1173 K for 400 hrs. However, the transverse growth of SrZrO_3 reached GDC-YSZ interface, and lateral growth was also found along the interface after cathodic polarization at 1273 K for 400 hrs [33]. The ohmic resistances between GDC and YSZ increased with operating temperatures: -0.6%/1025 hrs at 873 K [35], 4.5%/1012 hrs at 1023 K [35], 17%/1031 hrs at 1173 K [35], and 26%/1000 hrs at 1223 K [36]. In short, the formation of SrZrO_3 cannot be avoided for the incompletely dense GDC barrier layer, and high-operating temperatures accelerate the diffusion of Zr and Sr for the growth of SrZrO_3 . Furthermore, only the lateral growth of SrZrO_3 along the GDC-YSZ interface results in a drop of performance. The formation of SrZrO_3 results in a change of microstructure that unable to be handled by the current numerical model.

The average effective electronic conductivity of a cell can be given similar to its average thermal conductivity as follows.

$$\sigma_{s,PEN}^{eff} = \frac{h_{PEN}}{\frac{h_{ano}}{\sigma_{ano}^{eff}} + \frac{h_{ele}}{\sigma_{ele}^{eff}} + \frac{h_{cat}}{\sigma_{cat}^{eff}}} \quad (2.56)$$

The effective electronic conductivity in the porous metal foam can be expressed similarly to its effective thermal conductivity in the solid phase as follows.

$$\sigma_s^{eff} = \frac{\sqrt{3}}{2} \sigma_s \left\{ \frac{r \left(\frac{b}{L} \right)}{\frac{1}{3} \left[1 + \left(\frac{b}{L} \right) \right]} + \frac{(1-r) \left(\frac{b}{L} \right)}{\frac{2}{3} \left(\frac{b}{L} \right)} + \frac{\frac{\sqrt{3}}{2} - \left(\frac{b}{L} \right)}{\frac{4r}{3\sqrt{3}} \left(\frac{b}{L} \right)} \right\}^{-1} \quad (2.57)$$

The electronic conductivity σ_s for both porous metal foam and separator has the value of 1×10^7 S m⁻¹.

The concentration overpotential depends on the partial pressures of the reactants and products at triple-phase boundaries (TPBs) or double-phase boundaries (DPBs) and in bulk. The concentration overpotential for the electrodes is defined as:

$$\eta_{conc,ano} = \frac{RT_s}{2F} \ln \left(\frac{p_{H_2} p_{H_2O,TPB}}{p_{H_2,TPB} p_{H_2O}} \right), \quad (2.58)$$

$$\eta_{conc,cat} = \frac{RT_s}{4F} \ln \left(\frac{p_{O_2}}{p_{O_2,DPB}} \right). \quad (2.59)$$

Since most of the electrochemical reaction takes place within a thin layer near the electrolyte interface, the overall electrochemical reaction is assumed to occur only at the electrolyte surface.

The assumption for the active layer used to determine the concentration overpotential is different from that in the method used to determine the activation overpotential and ohmic loss.

For the gas diffusion resistance, a simple model based on crude assumptions is employed in this study. The partial pressures at the reaction sites are used to calculate both the exchange current density and the concentration overpotential at both electrodes, given by the FM as follows [37]:

$$p_{\text{H}_2, \text{TPB}} = p_{\text{H}_2} - \frac{RT_s h_{\text{ano}} I}{2FD_{\text{H}_2}^{\text{eff}}}, \quad (2.60)$$

$$p_{\text{H}_2\text{O}, \text{TPB}} = p_{\text{H}_2\text{O}} + \frac{RT_s h_{\text{ano}} I}{2FD_{\text{H}_2\text{O}}^{\text{eff}}}, \quad (2.61)$$

$$p_{\text{O}_2, \text{DPB}} = P - (P - p_{\text{O}_2}) \exp\left(\frac{RT_s h_{\text{cat}} I}{4FD_{\text{O}_2}^{\text{eff}} P}\right). \quad (2.62)$$

The effective gas diffusion coefficient is related to both the gas diffusion coefficient in the mixture and the Knudsen diffusion coefficient as follows [38]:

$$D_i^{\text{eff}} = \frac{\varepsilon}{\tau} \left(\frac{1 - \alpha_{i,m} x_i}{D_{i,m}} + \frac{1}{D_{K,i}} \right)^{-1}, \quad (2.63)$$

$$\alpha_{i,m} = 1 - \left(\frac{M_i}{\bar{M}} \right)^{1/2}, \quad (2.64)$$

$$D_{K,i} = \frac{2}{3} \left(\frac{8RT_s}{\pi M_i} \right)^{1/2} \bar{r}. \quad (2.65)$$

where x_i is the mole fraction and τ is the pore tortuosity factor of the porous electrode.

2.5 Implementation of the dusty-gas model

Dusty-gas model (DGM) applies the dust concept, where gas species with larger and heavier molecules are less mobile in the mixture system. If there is a pressure gradient in the gas mixture, an external force must be applied to these large and heavy molecules to remain static. The DGM can be expressed as follows:

$$\frac{N_i}{D_{K,i}^{\text{eff}}} + \sum_{i \neq j} \frac{x_j N_i - x_i N_j}{D_{ij}^{\text{eff}}} = -\frac{P}{RT_s} \nabla x_i - \frac{x_i}{RT_s} \left(1 + \frac{KP}{\mu D_{K,i}^{\text{eff}}} \right) \nabla P, \quad (2.66)$$

$$D_{K,i}^{\text{eff}} = \frac{\tau}{\varepsilon} D_{K,i}, \quad (2.67)$$

where K and D_{ij} are the permeability constant for the gas phase in the porous medium and binary diffusion coefficients [39] which can be expressed by

$$K = \frac{\varepsilon^3 d_p^2}{72\tau(1-\varepsilon)^2}, \quad (2.68)$$

$$D_{ij} = \frac{0.01013 T_s^{1.75} \left(\frac{1}{10^3 M_i} + \frac{1}{10^3 M_j} \right)^{0.5}}{P \left[(\sum v_i)^{1/3} + (\sum v_j)^{1/3} \right]^2}. \quad (2.69)$$

The summation of all species in the gas mixture leads to the unity molar fraction and the pressure gradient as follows:

$$\nabla P = - \frac{\sum \frac{N_i}{D_{K,i}^{\text{eff}}}}{\frac{1}{RT_s} + \frac{K}{\mu} \sum X_i D_{K,i}^{\text{eff}}}. \quad (2.70)$$

d_p is the average diameter of the pore phase. The pressure across the thick electrode is not constant, Eq. (2.66) is written as a function of the molar densities as follows [40]:

$$\frac{N_i}{D_{K,i}^{\text{eff}}} + \frac{RT_s}{P} \sum_{j \neq i} \left(\frac{X_j N_i - X_i N_j}{D_{i,j}^{\text{eff}}} \right) = -\nabla X_i - \frac{X_i}{D_{K,i}^{\text{eff}}} \frac{K}{\mu} \nabla P, \quad (2.71)$$

$$X_i = \frac{x_i P}{RT_s} = \frac{p_i}{RT_s}. \quad (2.72)$$

Equation (2.71) can be rewritten as the total flux of species i function to molar densities as follows [41]:

$$N_i = -\Gamma_i^{\text{DGM}} \nabla X_i + v_i^{p,\text{DGM}} X_i + v_i^{N,\text{DGM}} X_i, \quad (2.73)$$

$$\Gamma_i^{\text{DGM}} = \frac{1}{\left[\frac{RT_s}{P} \sum_{j \neq i} \left(\frac{X_j}{D_{i,j}^{\text{eff}}} \right) + \frac{1}{D_{K,i}^{\text{eff}}} \right]}, \quad (2.74)$$

$$v_i^{p,\text{DGM}} = - \frac{\frac{K \nabla P}{D_{K,i}^{\text{eff}} \mu}}{\left[\frac{RT_s}{P} \sum_{j \neq i} \left(\frac{X_j}{D_{i,j}^{\text{eff}}} \right) + \frac{1}{D_{K,i}^{\text{eff}}} \right]} = -\Gamma_i^{\text{DGM}} \frac{1}{D_{K,i}^{\text{eff}}} \left(\frac{K \nabla P}{\mu} \right), \quad (2.75)$$

$$v_i^{N,\text{DGM}} = \frac{\frac{RT_s}{P} \sum_{j \neq i} \left(\frac{N_j}{D_{i,j}^{\text{eff}}} \right)}{\left[\frac{RT_s}{P} \sum_{j \neq i} \left(\frac{X_j}{D_{i,j}^{\text{eff}}} \right) + \frac{1}{D_{K,i}^{\text{eff}}} \right]} = \Gamma_i^{\text{DGM}} \frac{RT_s}{P} \sum_{j \neq i} \left(\frac{N_j}{D_{i,j}^{\text{eff}}} \right). \quad (2.76)$$

The total flux of species i in the porous medium is affected by three contributors as per Eq. (2.73). These are, from left to right: flux due to global molecular diffusion through a porous medium of the species i in the mixture Γ_i^{DGM} , flux due to the flow of species i caused by the pressure gradient or also known as Darcy's velocity $v_i^{p\text{DGM}}$, and flux due to the flow of species i induced by the flow of other species $v_i^{N\text{DGM}}$. The species conservation in the electrode as given in Eq. (2.8) can be rewritten as follows:

$$\nabla \cdot N_i = \nabla \cdot (-\Gamma_i^{\text{DGM}} \nabla X_i) + \nabla \cdot (v_i^{p\text{DGM}} X_i) + \nabla \cdot (v_i^{N\text{DGM}} X_i) = S_{x_i}. \quad (2.77)$$

Equation (2.77) can be solved implicitly using a finite volume method together with other governing equations simultaneously. Furthermore, the number of species that can be considered is unlimited, which is suitable for the consideration of ammonia decomposition or methane reforming reaction in the SOFC.

The developed quasi-3D numerical model applied a single layer of the mesh to absorb the whole information including charge-transfer current density and gas species transportation within a cell. Therefore, the species conservation expressed by Eq. (2.77) cannot be realized in the developed quasi-3D model. A 3D grid system is known as anode mesh as shown in Fig. 2.6, is introduced to the developed quasi-3D numerical model. The anode mesh has 16 layers of the mesh including two layers of a coupled boundary at each of the surface of anode and interface of the electrolyte. On the other hand, the thickness of the cathode for an anode-supported cell is relatively thinner than the anode. So, the gas species transportation in the cathode is substantially less critical. The FM is still reasonable to apply in the thin cathode to reduce computation cost. Although the

3D grid system can also be implemented in both electrodes, it is limited to the thick anode in this study.

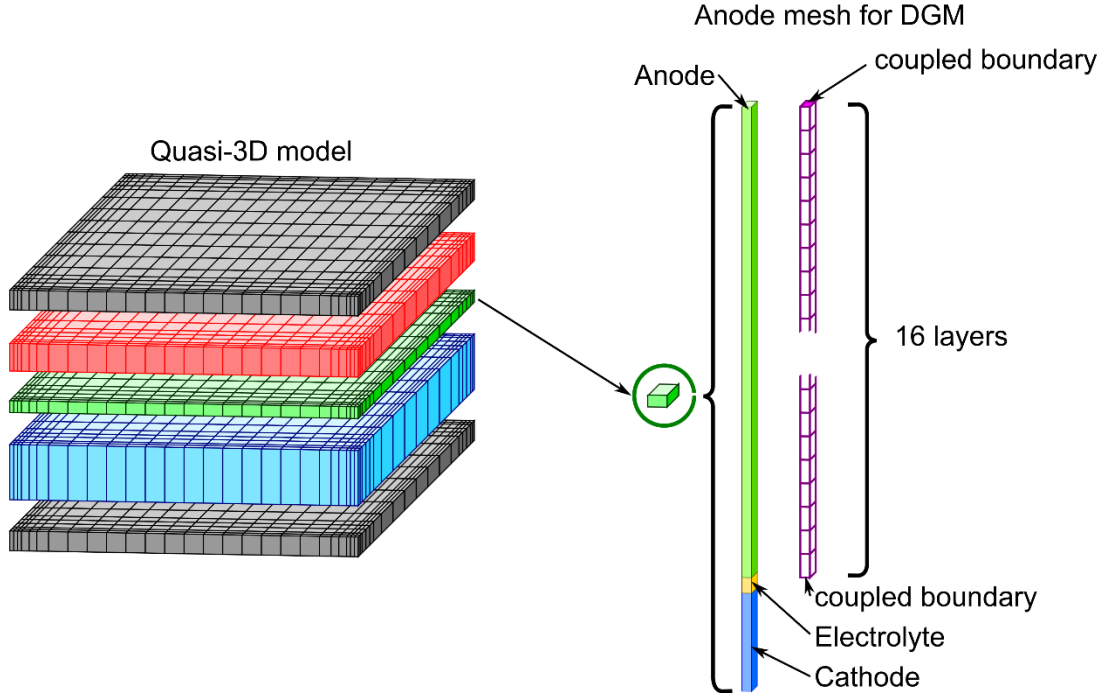


Fig. 2.6. Anode mesh for DGM in quasi-3D model.

The molar flux component due to the pressure gradient in Eq. (2.70) corresponds to Darcy's velocity, which strongly depends on the velocity component v normal to the anode surface. However, v is unavailable in the developed quasi-3D model. Therefore, conservation of mass is introduced locally along the anode thickness as shown in Fig. 2.7 to overcome this limitation.

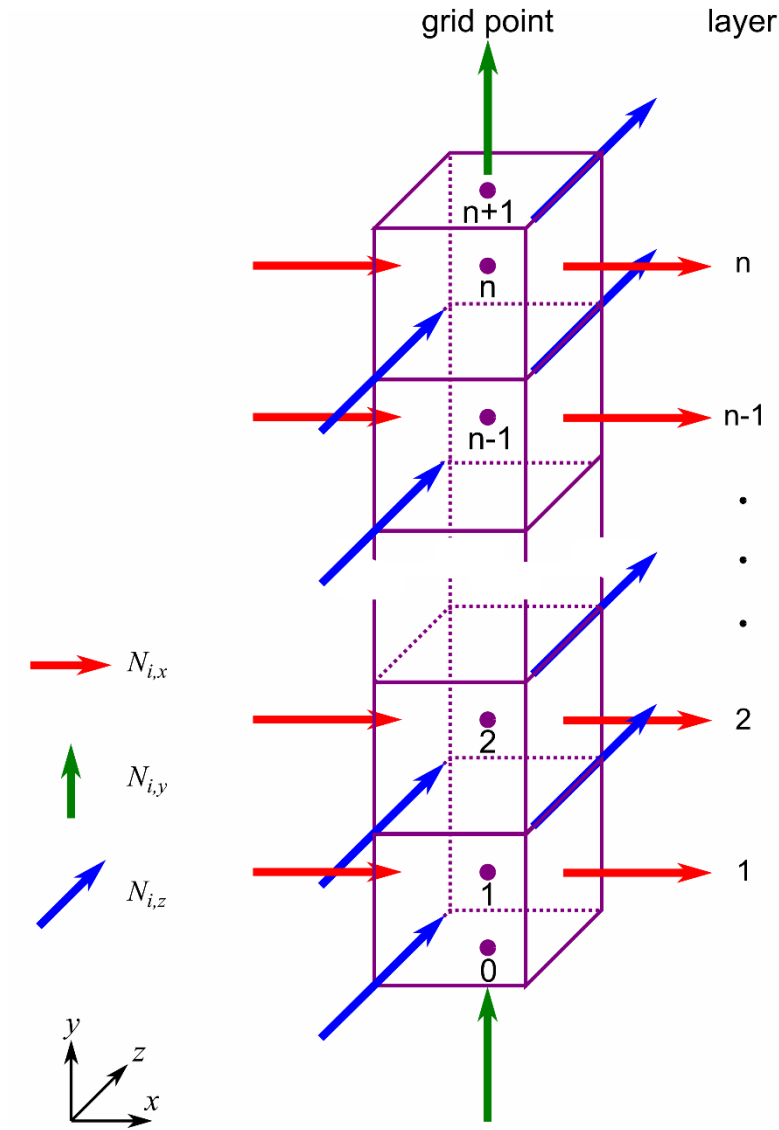


Fig. 2.7. Local conservation of mass in anode mesh

The mass flowrate components of species can be determined by multiplying the molar flux N_i of each component in the x -, y - and z -axis with its molecular weight W_i as well as the area of the considered mesh normal to the fluxes A_{yz} , A_{xz} , and A_{xy} , respectively. Hence, the molar flux $N_{i,y}$ at the anode surface (layer n) is computed with the total mass flowrate in the x - and z -axis, mass

flowrate at the anode-electrolyte interface (layer 1) due to electrochemical reaction, and the total mass source/sink term due to the chemical reaction within each considered volume V as follows:

$$\begin{aligned}
& (N_{i,y}A_{xz}W_i)_{n,\text{out}} \\
&= \sum_{l=1}^n \left[(N_{i,x}A_{yz}W_i)_{l,\text{in}} - (N_{i,x}A_{yz}W_i)_{l,\text{out}} \right] \\
&+ \sum_{l=1}^n \left[(N_{i,z}A_{xy}W_i)_{l,\text{in}} - (N_{i,z}A_{xy}W_i)_{l,\text{out}} \right] + (N_{i,y}A_{xz}W_i)_{1,\text{in}} \\
&+ \sum_{l=1}^n (S_{x_i}VW_i)_l.
\end{aligned} \tag{2.78}$$

The subscript l is referred to the number of layer of anode mesh from the anode-electrolyte interface. Equation (2.78) is applied to determine the mass and molar densities fluxes of gas species across the anode surface without providing the bulk flow of species. The mass fluxes flowrate at anode surface are feedbacked to the fuel channel as source/sink term S_{Y_i} in Eqs. (2.1) and (2.7). Meanwhile, molar densities fluxes at anode surface are used as one of the boundary conditions for Eq. (2.78). The mass flowrate at the anode surface is crucial for the molar density fluxes as one of the boundary conditions in anode mesh. The species molar sink or source term S_{x_i} in Eq. (2.78), within the local volume of element V is defined according to the reaction occurring in the anode.

The multi-component DGM is commonly introduced to the 2D or 3D model, but it has a significant drawback of high computation cost. The DGM can be coupled with a quasi-3D model using a semi-analytical approach [42,43]. However, a further modification of the analytical equations is required when other gas species are considered or involving other reactions such as methane reforming or ammonia decomposition. A simple approach solving the DGM as a molar

flux using the finite volume method is suggested in this study. The DGM is implemented in a quasi-3D model with the aid of anode mesh and solved together with other governing equations. This implementation of the DGM is the third unique of this numerical model.

2.6 Attenuation factor in charge-transfer current profile

The attenuation factor λ in Eq. (2.33) must be sufficiently large to satisfy the first condition used in the charge-transfer current density model. Since the concentration overpotential is assumed with the electrochemical reaction occurs at the electrode-electrolyte interface, it does not affect the total overpotential across the electrode thickness. Therefore, the concentration overpotential is not considered when determining the attenuation factor. On the other hand, the charge-transfer current density model of Miyawaki et al. [22] allows a simple yet realistic representation of the electrochemical reaction in a composite electrode such as Ni/YSZ and a mixed ion-electron conductor electrode. The transport of ions and electrons occurs under minimum total resistance, where $\partial\eta/\partial\lambda = 0$ must be satisfied. The attenuation factor is shown as follows [14]:

$$\lambda_{\text{ano}} = \frac{2i_{0,\text{ano}}}{I} \sqrt{\left(1 + \frac{\alpha_0 F I^2}{4i_{0,\text{ano}} R T_s \sigma_{\text{io}}^{\text{eff}}}\right)^2 - 1}, \quad (2.79)$$

$$\lambda_{\text{cat}} = \sqrt{\frac{22}{5} \cdot \frac{i_{0,\text{cat}} F}{R T_s \sigma_{\text{io}}^{\text{eff}}}}. \quad (2.80)$$

Figure 2.8 shows the effect of attenuation factor and current density towards charge-transfer current. The values of 0 and 1 at the normalized thickness of y/h refer to the locations of the

electrode-electrolyte interface and electrode surface, respectively. The high value of the attenuation factor is attributed to the high electrochemical reaction near the electrode-electrolyte interface in Fig. 2.8(a). Therefore, the low ohmic loss can be predicted by the high attenuation factor based on the ohmic loss discussed in the previous section. On the other hand, Fig. 2.8(b) shows that the electrochemical reaction is extended to the surface of an electrode when the current density is increased under the same attenuation factor.

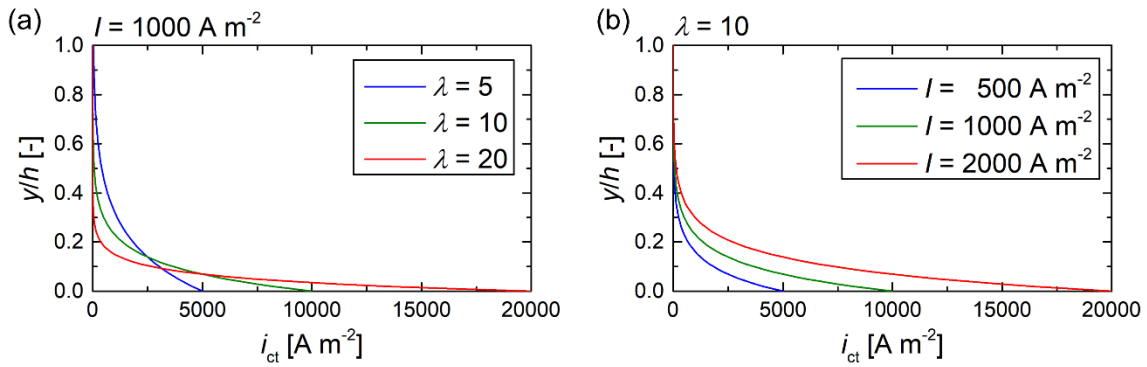


Fig 2.8. Charge-transfer current with (a) effect of the attenuation factor, (b) effect of current density.

2.7 Ammonia decomposition

Ammonia can be converted to hydrogen by decomposition reaction as given in Eq. (2.81). The corresponding enthalpy change for the formation of ammonia during ammonia decomposition for temperatures between 600 and 1200 K is given in Eq. (2.81) by Ni [44]. Ammonia decomposition reaction can be performed in an anode of SOFCs with a suitable catalyst or externally in an ammonia decomposer. Then, the temperature can be expressed either by the local cell temperature or the ammonia decomposer temperature accordingly to the application.



$$\Delta H_{f,\text{NH}_3} = 40265.095 + 24.23214T_s - 0.00946T_s^2, \quad (600\text{K} \leq T_s \leq 1200\text{K}) \quad (2.82)$$

The nickel (Ni) phase in the anode is an effective catalyst for ammonia decomposition at high temperatures. The ammonia decomposition rate R_{dec} by the Ni catalyst in the porous Ni/YSZ anode is given as follows [45]:

$$R_{\text{dec}} = S_{\text{Ni-pore}} R_{\text{dec}}^{\text{Ni-pore}}, \quad (2.83)$$

$$R_{\text{dec}}^{\text{Ni-pore}} = 98.4 \exp\left(-\frac{1.20 \times 10^5}{RT_s}\right) (p_{\text{NH}_3})^{0.69} (p_{\text{H}_2} + 750)^{-0.39}. \quad (2.84)$$

$S_{\text{Ni-pore}}$ is the Ni-pore interface area density. The decomposition rate is directly proportional to both the partial pressure of ammonia p_{NH_3} and cell temperature, and inverse proportional to the partial pressure of hydrogen p_{H_2} . A pressure gradient exists across the porous anode due to the Knudsen effect which is explained from the DGM by Eq. (2.70). Therefore, the decomposition rate is not constant across the anode thickness. Equation (2.84) is unsuitable for a common quasi-3D SOFC model, which treats the whole thickness of the cell as a single mesh as shown in Fig. 2.1(b). The pressure gradient can be used to determine the partial pressure of species with the aid of the anode mesh as shown in Fig. 2.4. Then, the decomposition rate can be used to determine the local decomposition rate of ammonia. The average decomposition rate across anode thickness is used

to calculate the amount of thermal absorbed during the decomposition reaction. The temperature in Eq. (2.82) is expressed as the local cell temperature for the direct ammonia decomposition.

On the other hand, external ammonia decomposer is used for indirect ammonia decomposition. An additional heat source is required to sustain the decomposition reaction. The temperature in Eq. (2.82) is the decomposer operation temperature for the indirect ammonia decomposition. In this study, the heat supply to the external ammonia decomposer came from the thermal radiation of the SOFC stack as shown in Fig. 2.9.

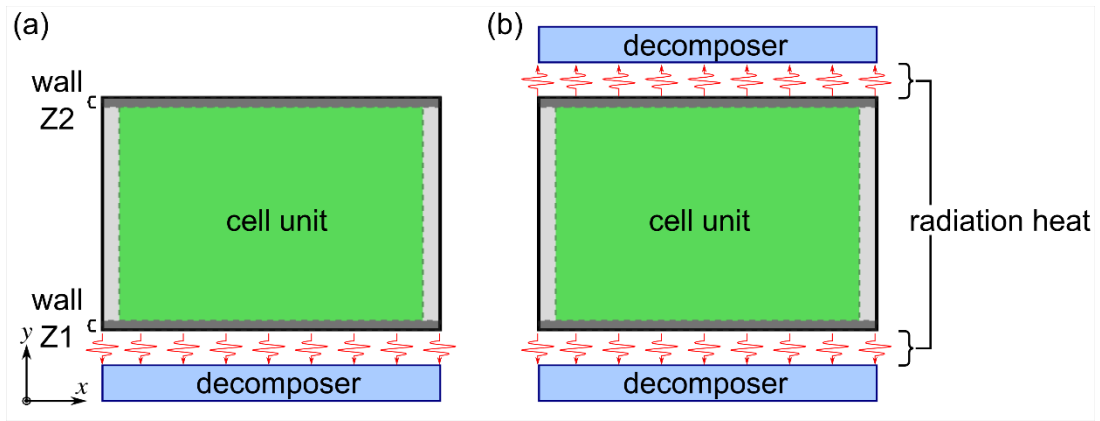


Fig 2.9. Radiation heat from cell unit to sustain operation of external ammonia decomposer at
(a) wall Z1, (b) both walls Z1 and Z2

A sidewall with a thickness of 5 mm is considered next to the cell unit (as given in Fig. 2.1(a)) at dimensionless Z' of 0 and 1.00. This sidewall has the same thermal conductivity as the separator. The heat from the stack is transferred through radiation at the sidewall of the stack to self-sustain the operation of the decomposer at a temperature of T_{dec} . The decomposer and the outer wall of the stack are assumed to be black bodies. The net thermal radiation from the short stack to one of the external decomposers is given as follows:

$$Q_{\text{rad}} = \sigma_{\text{SB}} F' A_{\text{wall}} (T_{\text{wall}}^4 - T_{\text{dec}}^4), \quad (2.85)$$

where Q_{rad} is the radiation heat, σ_{SB} is the Stefan-Boltzmann constant, and A is the surface area subjected to the thermal radiation. F' is the shape factor from the sidewall of the short stack to the surface of the decomposer as shown in Fig. 2.10, which is given as follows:

$$F' = \oint_{A_{\text{dec}}} \frac{\cos^2 \varphi}{\pi l^2} dA_{\text{dec}}, \quad (2.86)$$

$$F' = \frac{x_0}{2\pi\sqrt{x_0^2 + h^2}} \left(\tan^{-1} \frac{y_0}{\sqrt{x_0^2 + h^2}} + \tan^{-1} \frac{y_1}{\sqrt{x_0^2 + h^2}} \right) \\ + \frac{y_0}{2\pi\sqrt{y_0^2 + h^2}} \left(\tan^{-1} \frac{x_0}{\sqrt{y_0^2 + h^2}} + \tan^{-1} \frac{x_1}{\sqrt{y_0^2 + h^2}} \right) \\ + \frac{x_1}{2\pi\sqrt{x_1^2 + h^2}} \left(\tan^{-1} \frac{y_0}{\sqrt{x_1^2 + h^2}} + \tan^{-1} \frac{y_1}{\sqrt{x_1^2 + h^2}} \right) \\ + \frac{y_1}{2\pi\sqrt{y_1^2 + h^2}} \left(\tan^{-1} \frac{x_0}{\sqrt{y_1^2 + h^2}} + \tan^{-1} \frac{x_1}{\sqrt{y_1^2 + h^2}} \right). \quad (2.87)$$

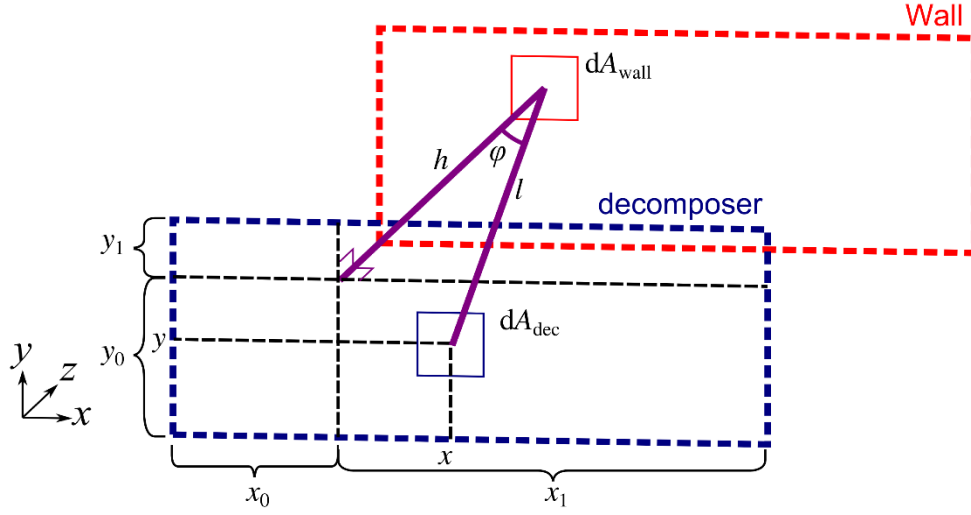


Fig 2.10. Schematic diagram to determine shape factor for radiation heat at wall Z1

2.8 Heat source and sink terms

The heat source or heat sink Q in energy conservation Eq. (2.6), is explained in this section. The heat source and sink components in an SOFC cell can be divided into two major components, which are heated due to reactions, and heated due to polarization in a cell. For the direct and indirect ammonia decomposition operated SOFC cell/stack, these involved hydrogen-oxygen electrochemical reaction, and ammonia decomposition reaction (under direct ammonia). The reversible heat due to hydrogen-oxygen electrochemical and ammonia decomposition reactions is given as follows:

$$Q_{TDS} = -I_{\text{local}} A_{\text{local}} \left(\frac{\Delta H_{f, \text{H}_2\text{O}}}{2F} + E \right), \quad (2.88)$$

$$Q_{\text{dec}} = -h_{\text{ano}} R_{\text{dec,ave}} \Delta H_{f, \text{NH}_3}. \quad (2.89)$$

$R_{\text{dec,ave}}$ is the average value of the ammonia decomposition rate along the anode thickness. The enthalpy changes for the steam formed during the electrochemical reaction occur between 800 K and 1400 K is shown in Table 2.2. A quadratic curve is fitted to the evolution of enthalpy for the steam formation as shown in Fig. 2.11.

Table 2.2. Change of enthalpy for steam formation [46]

Temperature (K)	$\Delta H_{\text{f,H}_2\text{O}}$ (kJ/mol)
800	-246.432
850	-246.812
900	-247.173
950	-247.518
1000	-247.846
1100	-248.448
1200	-248.986
1300	-249.462
1400	-249.882

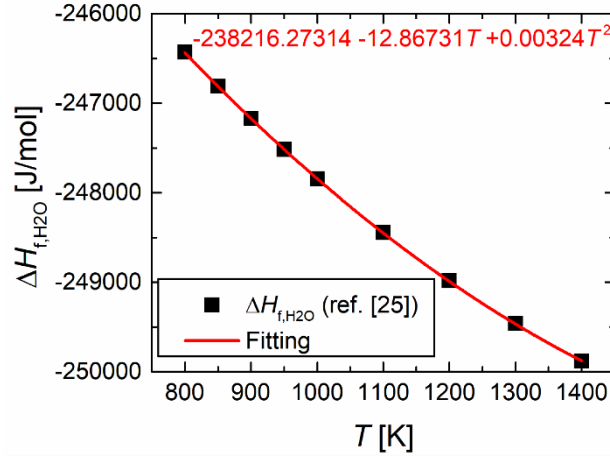


Fig 2.11. Change of enthalpy for a steam formation

There are three polarizations discussed previously: activation, ohmic and concentration. Navasa [47] studied the heat source and sink terms for an SOFC cell involving both water-gas shift and methane steam reforming reactions. The relative contribution by concentration polarizations was reported below 1%. However, concentration polarization is only subjected to the gas species transport in the electrodes. Hence, the concept of ohmic heat is irrelevant to concentration polarization. In short, the heat components due to the polarization are given as follows:

$$Q_{\text{act}} = I_{\text{local}} A_{\text{local}} \eta_{\text{act}}, \quad (2.90)$$

$$Q_{\text{ohm}} = I_{\text{local}} A_{\text{local}} \eta_{\text{ohm}}. \quad (2.91)$$

2.9 Cell/stack performance evaluation

The real efficiency of a cell/stack is expressed as [48]:

$$\varepsilon_{\text{real}} = \varepsilon_{\text{thermo}} \times \varepsilon_{\text{voltage}} \times \varepsilon_{\text{fuel}} = \frac{\Delta \hat{g}}{\Delta \hat{h}} \times \frac{V_{\text{cell}}}{E} \times \frac{(I_{\text{ave}} A_{\text{PEN}})/2F}{\dot{N}_{\text{H}_2, \text{in}}}. \quad (2.92)$$

where the three terms from left to right are the thermodynamic efficiency $\varepsilon_{\text{thermo}}$, voltage efficiency $\varepsilon_{\text{voltage}}$ and fuel utilization $\varepsilon_{\text{fuel}}$. First, the thermodynamic efficiency is defined as the ratio of the change in the molar Gibbs free energy to the change in the molar enthalpy in the electrochemical reaction at the inlet of the cell. The thermodynamic efficiency at the inlet is the same under the same inlet temperature of the supplied fuel and air. Next, the voltage efficiency is defined as the ratio of the terminal voltage of the cell V_{cell} to its EMF. In this study, the EMF is evaluated by averaging the local EMF in the entire cell using the local current density as a weight factor. Finally, fuel utilization is the ratio of the fuel consumed by the cell to generate an electric current to the total supply of fuel. $\dot{N}$ is the molar flowrate of gas species while A is the active area of the cell. In this study, the real performance of each cell in a stack is evaluated using the voltage efficiency under constant fuel utilization and constant thermodynamic efficiency. Then, the real performance of an N -cell stack is evaluated from the average cell efficiency of the cells as follows:

$$\varepsilon_{\text{voltage, stack}} = \left(\sum_{i=1}^N \varepsilon_{\text{voltage}, i} \right) / N. \quad (2.93)$$

Area-specific resistances (ASRs) in a stack is calculated by a weighted-average method by using the local current density as the weighted-factor. ASR for the activation resistance, ionic conduction resistance, and species diffusion resistance is given as follows:

$$ASR_{ave} = \frac{1}{I_{ave}} \cdot \frac{\sum(\eta_{local} I_{local} A_{local})}{\sum(I_{local} A_{local})}, \quad (2.94)$$

where η_{local} is the considered local voltage losses component in a cell. A_{local} and I_{local} are the local areas of PEN and the current density generated within the considered areas of PEN, respectively.

2.10 Statistical analysis of a distribution

The performance of a cell/stack is closely related with its distributions of current density and cell temperature as explained in sections 2.4 and 2.9. Extremely high local current density is caused by the occurrence of relatively high voltage losses at the nearby area in the cell. Low voltage losses are encouraged to increase the voltage efficiency of the cell. The high local current density is promoted in high local consumption of the supplied fuel, which will raise the risk of local fuel depletion at the downstream. On the other hand, high cell temperature is preferable for high cell performance. Extremely high local cell temperature raises the risk of thermal stress due to the different thermal expansion of the components in a cell. Both extremely high local current density and cell temperature also accelerate performance degradation. Therefore, a uniform distribution of both current density and cell temperature is preferable to extend the lifespan of a cell/stack.

The distributions of current density and cell temperature must be discussed regarding their dispersion within a cell/stack. A narrow-spread characteristic is referred to the local values being relatively close to its mean value, and vice-versa. Therefore, the dispersion analysis provides an overview of the distribution. Although the contour plot approach visualizes a distribution, it faces difficulty to discuss a distribution quantitatively. The statistical approach allows such discussion and allows an easier comparison among several distributions.

The meshes in quasi-3D model are unevenly meshed as shown in Fig. 2.1(b). Therefore, the numerical results cannot be directly statistically analyzed. Data resampling process is required to obtain the same representing cell area of each data. The random Renka–Cline algorithm [49] is used to resample the dataset.

The distribution of a resampled dataset is then represented by box chart with histogram as shown in Fig. 2.12. The left-hand side is the histogram of a dataset. This histogram illustrates how the values are spread within the data range. The main part of the box chart (the box) has three horizontal lines that indicate the lower, middle (median), and upper quartiles of the data. The square within the box indicates the mean value of the data. The standard deviation of the dataset is represented by the whiskers located at the top and bottom of the box. The minus signs at the top and bottom of the box indicate the maximum and minimum values of the dataset, respectively. The range of the dataset is given by the difference between these two values. The distribution of the dataset is categorized as negatively skewed when the distance from the median to the lower quartile is larger than that from the median to the upper quartile. On the other hand, the dataset is categorized as positively skewed when the distance from the median to the upper quartile is larger than that from the median to the lower quartile. The height of the box is equal to the interquartile range of the dataset, which indicates the range of the middle half of the dataset. A shorter box indicates that the sample data has a narrower distribution for the middle half of the dataset, which is a measurement of the dispersion of an observed dataset.

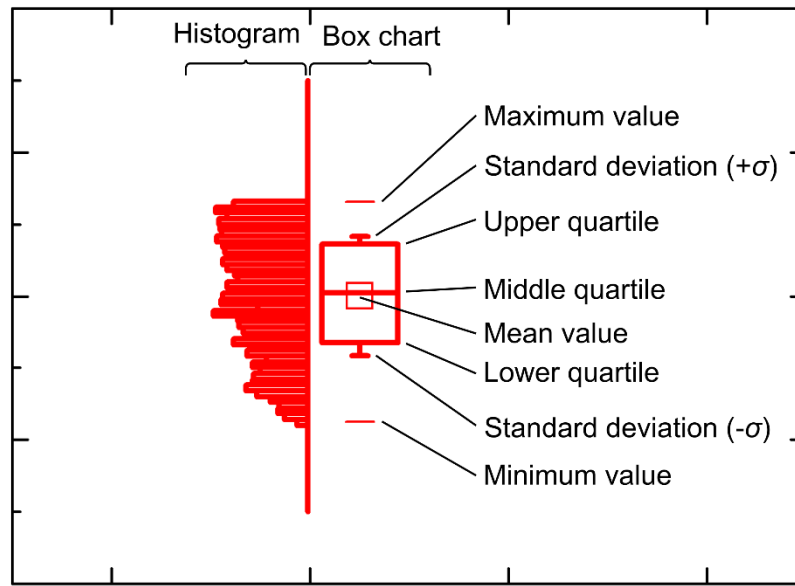


Fig 2.12. An example of a box chart with histogram plot.

2.11 Conclusion for numerical model

A quasi-3D numerical model used in this study is developed. Each of the separators, channels, and cells are treated as a single mesh layer. The conservation equations of mass, momentum, species, and energy (in term of fluid phase) are applied in the fuel and air channels mesh layers, while the energy conservation equation (in term of solid phase) implemented in all mesh layers. The cell mesh layer is treated as a dense solid layer and coupled with the electrochemical model using parallel circuit model. The real microstructure information (in the later chapter) is applied to the electrochemical model. The electrochemical reaction is no longer limited to the electrode-electrolyte interface, but it is extended from the interface by using the charge-transfer current profile. This electrochemical reaction allows a closer representation of both activation and ohmic resistance in a cell. The Fick's model is applied for the mass transportation of gas species in the

electrodes for a cell/stack fueled with hydrogen. On the other hand, a 3D mass transportation model using the dusty-gas model (DGM) is developed to analyze ammonia decomposition reaction in the anode. Additionally, new anode mesh is introduced in the anode for the implementation of the DGM.

In short, the developed quasi-3D numerical model has several unique features. First, the electrochemical reaction is extended from the electrode-electrolyte interface. A common quasi-3D mathematical model assumes the electrochemical reaction occurs at the interface due to the limitation of the single mesh to represent the thickness of the cell. Second, a precise definition of ionic conductivity in the LSCF/GDC composite cathode. Here, the electrochemical reaction in LSCF/GDC cathode still occurs at the interface of LSCF-pore and electrons is conducted in LSCF phase. The oxygen ions are assumed to be transported in the high conductivity phase of GDC. Therefore, the effective coefficient is referred to as the microstructure of GDC. Third, a multi-component DGM model is introduced in the quasi-3D model and solved using the finite volume method. A local mass conservation approach is used to overcome the unavailable velocity component that parallels with the cell thickness direction in the quasi-3D model. The verification and validation of the developed numerical model are discussed in the next chapter.

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Chapter 3

Verification and validation of numerical model

3.1 Introduction

Verification and validation are essential assessments of accuracy for a numerical model. Verification of a model means the truth has been demonstrated, which implies its reliability as a basis for decision-making [1]. Such verification can be performed by comparing a numerical solution with an analysis to demonstrate that both are matching over a range of operational conditions. Verification of the model can be divided into two classifications: code verification and calculation verification [2]. Code verification is to ensure the implementation of numerical algorithms used in the code. On the other hand, calculation verification is to quantify the error of a numerical model by demonstration of convergence under consideration. Validation of a model denotes legitimacy, typically regarding contracts, arguments, and methods [1]. A standard method of validation involves a comparison of the results from an in-situ experiment with the results from the numerical model. Although verification and validation are unable to prove that a model is correct and accurate in a real-world application, instead both processes can provide evidence that the developed model has a certain level of accuracy within the model application range.

Most of the model developers performed a model validation process by comparing the results obtained from the developed model with either experimental results or available results from literature. Shi et al. [3] considered the complex interdependency among the conduction of ions and

electrons, transport of multi-components species, electrochemical reaction, and microstructure in a cell with multi-dimensional numerical analysis for a multiple layers SOFC cell. The electrochemical reaction was extended from the electrode-electrolyte interface. The model was included with the contact resistance between electrodes and electrolyte as well as the leak overpotential. A few parameters were tuned to best fit the experimental data, such as the leak overpotential, pre-exponential factors for anodic and cathodic electrochemical kinetic expressions, and tortuosities for anode and cathode. Furthermore, the model was calibrated using polarization curves from experiments and validated with the cell component polarizations. Similarly, Jeon [4] also included the contact resistances in his 2D numerical model. The validation of the developed model was conducted by comparing with the experimental work of Jung et al. [5]. The calculation convergence was judged by the relative tolerance criteria of 1×10^{-6} . Besides, grid sensitivity analysis was also performed. The simulation result with contact resistances reduced the error at higher current density operation.

Brus et al. [6] investigated the relation between microstructure and performance of stack using a 2D numerical model. FIB-SEM was used to provide microstructure information of cell for numerical analysis, the first study that used the actual microstructures of anode and cathode from the same cell. The model was compared with an 18-cell stack and showed the importance of introducing real microstructure information in the numerical model. The convergence criteria were set to be 1×10^{-5} . The optimal grid resolution of 8000×300 was chosen based on the grid sensitivity study.

Bertei et al. [7] proposed a quasi-2D numerical model with a detail microstructure numerical model for planar SOFC. The electrochemistry and transport phenomena in the cell were locally described in 2D using mass conservation equation and global electro-kinetics, coupled with a 1D

representation of transportation of gas species in electrodes. The packing algorithm of overlapping spherical particles was used for the parametric study on the effect of the microstructure of electrode. The uniform temperature was assumed throughout the cell due to the small size of the stack investigated. A good agreement between the simulation results and experimental results was achieved without fitting any parameter. However, the verification of the model was not provided.

Raj et al. [8] proposed a 3D numerical analysis to study the influence of the critical operating parameters: temperature, stoichiometry, and degree of humidification on the performance of planar SOFC incorporating the influence of parasitic loads. The parasitic loads such as pumping power of compressors to supply reactants in channels, heating power for heaters to heat the reactants, humidification power required for humidifying reactants, and power required to pump coolant liquid were considered. The developed model was validated with the available literature. The convergence criterion was taken to be 1×10^{-3} , and grid independence was performed.

There are also some models developed without providing necessary results for the validation of the developed model. Andersson et al. [9] studied the electrochemical reactions in electrodes using a fully coupled computational fluid dynamic (CFD) model by COMSOL Multiphysics. The developed 2D model considered the conservation equations of heat, mass, momentum and charge transport as well as kinetics considering the internal reforming and electrochemical reactions. They reported that 90 % of the electrochemical reactions occurred within $2.4 \mu\text{m}$ in the composite lanthanum strontium manganite/yttria-stabilized zirconia (LSM/YSZ) cathode and $6.2 \mu\text{m}$ in the Ni/YSZ composite anode away from the electrode-electrolyte interface in the standard cases used in their study. The distribution of ionic current density was reported along the cell thickness direction. It was found that both the anode and cathode had the same maximum value of ionic current density at the interface and the values were exponential decay towards the surface of the

electrode. The tolerance of the developed model was 1×10^{-3} , and the grid independence was achieved at 716000 meshes.

In this chapter, a quasi-3D numerical model is developed based on the discussion in Chapter 2. The developed quasi-3D numerical model is coupled with an electrochemical model to analyze SOFC cell/stack. The developed quasi-3D numerical model is unique. Firstly, the electrochemical reaction is extended towards the surface for the determination of activation overpotential and ohmic loss in electrodes using charge-transfer current profile. Secondly, a precise definition of the ionic conductivity is made for the composite LSCF/GDC cathode. Lastly, the multidimensional molar fluxes in the anode are solved using the multi-component DGM with the aid of anode mesh. The uniqueness of a model can be meaningless without proper verification and validation processes. Therefore, the experimental setup for a six-cell short stack is discussed in this chapter. The material microstructure in a cell, which is useful in the numerical model is presented. Besides, the verification and validation of the developed model is discussed. The discussion is focused on the comparison between numerical analysis in single-cell and six-cell stack.

3.2 Experiment

The power generation experiment was conducted using an SOFC modular stack test bench designed and produced by SOLIDpower S.p.A. A short stack consisting of six cells with a standard power output of 100 W from SOLIDpower S.p.A. was tested as shown in Fig. 3.1. The SOFC analyzed in this study is an anode-supported cell consisting of a Ni/YSZ cermet anode, a dense YSZ electrolyte, a GDC barrier layer, an LSCF/GDC cathode functional layer, and a LSCF cathode current collector. The cell had an effective area of $80 \text{ mm} \times 60 \text{ mm}$ with thicknesses of 240, 8, 4,

and 50 μm for the anode, electrolyte, GDC barrier layer, and cathode layer, respectively. The supplied fuel was hydrogen diluted with nitrogen. Direct ammonia could not be supplied owing to a limitation in the system regarding the inlet gas composition. In the present configuration, the gas composition cannot exceed 70% of the hydrogen content in the fuel to prevent any excessive increase in temperature in the afterburner. Nevertheless, the supplied fuel enabled the model to be verified because the same fuel is used in the numerical analysis during model verification. The electric furnace operated at a temperature of 973, 1023, or 1073 K. Hydrogen and nitrogen were supplied to the six-cell stack at flow rates of 1.8 and 1.2 L min^{-1} , respectively. At the same time, air was supplied at a flow rate of 18.0 L min^{-1} . Details of the short-stack experiment can be found elsewhere [10,11].

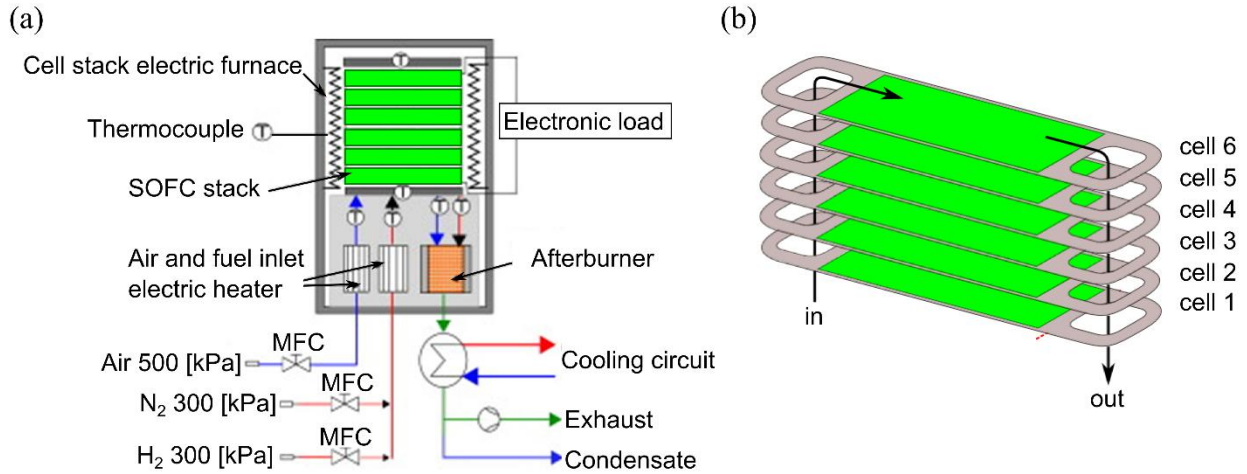


Fig 3.1. (a) Schematic of experimental setup. (b) The arrangement of the six-cell stack

3.3 Microstructure of SOFC

The 100 W short stack underwent an aging experiment, as reported in [12], and it was not possible to obtain the cell microstructure from the short stack during the aging experiment. The anode microstructure of the cell was obtained from a new supplementary cell, also from SOLIDpower S.p.A., together with that of the short stack. This supplementary cell was reduced and considered to be identical to the cells in the short stack. It was also assumed that the cells in the short stack did not undergo any microstructure changes after the initial power generation experiment. The supplementary cell was then impregnated using epoxy resin under vacuum conditions before being cut and polished for FIB-SEM tomography. The 3D microstructure was reconstructed using AVIZO software based on a series of 2D microstructure images obtained from FIB-SEM tomography. Details of the anode microstructure quantification procedure can be found in [12]. The anode reconstruction of 100 W stack is shown in Fig. 3.2(a) with the red, green and yellow representing the phases of the pore, Ni, and YSZ, respectively.

The cathode microstructure of the cell was obtained from the 300 W stack [6], which was also from SOLIDpower S.p.A. The cathode consisted of a GDC barrier layer, an LSCF/GDC functional layer, and a LSCF current collector layer. The thin GDC barrier layer prevents any reaction between the LSCF and the YSZ electrolyte while allowing the movement of ions. Note that the GDC barrier layer is not fully dense. Therefore, the diffusion of Zr and Sr can be easily diffused through the GDC barrier layer at high-operating temperature as discussed in section 2.4. On the other hand, the LSCF current collector layer is responsible for the transport of gas species and electrons. The volume fraction and tortuosity factor of the pore phase in the LSCF/GDC functional layer were like those in the LSCF current collector layer. Besides, because the electron

conductivity is generally a few orders higher than the ionic conductivity, the electronic conductivity resistance is generally ignored in the numerical analysis by researchers. Hereafter, the cathode is referred to as the LSCF/GDC functional layer. The cell reconstruction of 300 W stack is shown in Fig. 3.2(b) with the red, green, yellow, and blue representing the phases of GDC, Ni, YSZ, and LSCF, respectively. The microstructure information used in this study is summarized in Table 3.1.

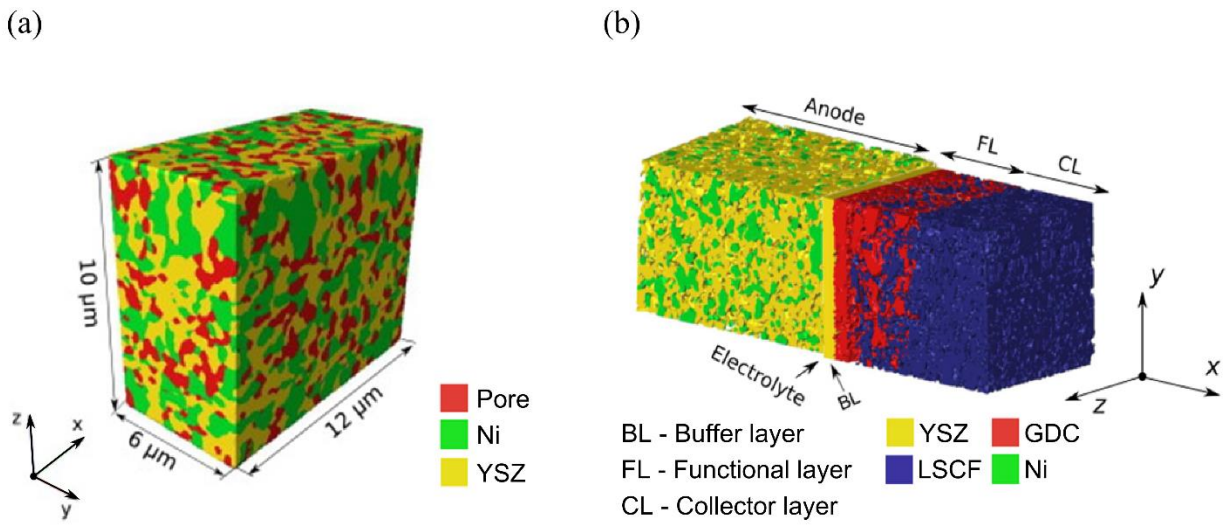


Fig 3.2. Microstructure reconstruction for (a) anode in 100 W stack [12], and (b) cell in 300 W stack [6].

Table 3.1. Microstructure information

Parameters	Anode [10]	Cathode [6]
Average radius of pore phase [μm]	0.566	1.01
Volume fraction of pore phase [-]	0.251	0.410
Volume fraction of ionic phase [-]		
YSZ (Anode), GDC/LSCF (Cathode)	0.383	0.260 / 0.330
Tortuosity factor of pore phase [-]	20.1	2.24
Tortuosity factor of ionic phase [-]		
YSZ (Anode), GDC/LSCF (Cathode)	2.44	20.3 / 4.29
Volumetric density of TPB line [m/m^3]	4.97×10^{12}	-
Volumetric density of DPB area [m^2/m^3]	-	6.67×10^6
Ni-pore interface area density [m^2/m^3]	9.80×10^5	-

3.4 Calculation and boundary conditions

The numerical results of a six-cell short stack with the FM is compared with the experimental data for verification. The partial pressure of species at the reaction site is described in section 2.4. The thermal boundary condition is given in Fig. 3.3, while the detail of the boundary condition is given in Table 3.2. The electric potential at the top separator of the highest position cell unit and the bottom separator of the lowest position cell unit of a stack is fixed at the value of 0.1 V and 0.1 V higher than the overall terminal voltage of the stack, respectively. The entirely isothermal boundaries are applied during the verification of the model using the six-cell short stack, with the aim of reproducing the conditions of the short-stack experiment in an electric furnace. The fluid

phase temperature at the inlet is the same as the operating temperature, while no temperature gradient is applied to the solid phase at the inlet of the channels. Both the fluid and solid phase temperatures within the channels have no gradient at the outlet.

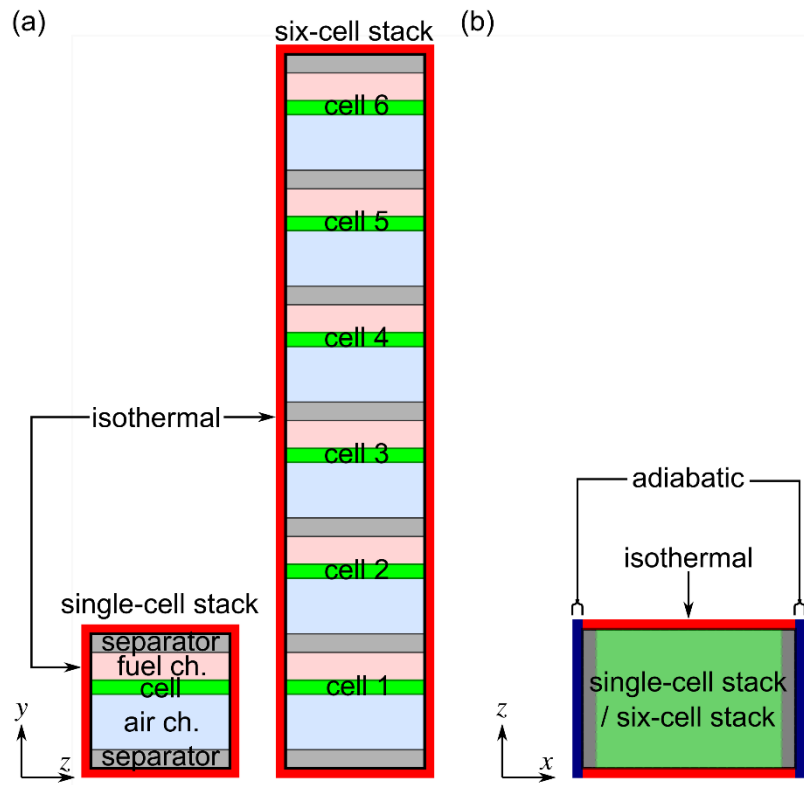


Fig 3.3. The thermal boundary for single-cell and six-cell stack in (a) side view, and (b) plan view.

Table 3.2. Boundary conditions

Quasi-3D:	Inlet	Outlet	Wall	Separators
u	$u = u_{\text{in}}$	$\frac{\partial u}{\partial x} = 0$	$u = 0$	-
w	$w = 0$	$\frac{\partial w}{\partial x} = 0$	$w = 0$	-
Y_i	$Y_i = Y_{i, \text{in}}$	$\frac{\partial Y_i}{\partial x} = 0$	$\frac{\partial Y_i}{\partial z} = 0$	-
ϕ	$\frac{\partial \phi}{\partial x} = 0$	$\frac{\partial \phi}{\partial x} = 0$	$\frac{\partial \phi}{\partial z} = 0$	-
T_f	$T_f = T_{\text{in}}$	$\frac{\partial T_f}{\partial x} = 0$	$\frac{\partial T_f}{\partial z} = 0$	-
T_s	$\frac{\partial T_s}{\partial x} = 0$	$\frac{\partial T_s}{\partial x} = 0$	$T_s = T_{\text{in}}$	$T_s = T_{\text{in}}$

Volumetric flow rates of 0.5 and 3.0 L/min/cell in the standard state with mole fraction ratios of 0.600: 0.020: 0.380 for H₂: H₂O: N₂ and 0.210: 0.790 for O₂: N₂ are applied to the fuel and air channels, respectively. The total pressure of both the fuel and air at the outlet is fixed at atmospheric pressure. The numerical analysis is conducted under galvanostatic-control with the increment of the current density of 500 A m⁻² and retaining the terminal voltage above 0.7 V same as the experimental data. The mass and molar of species source term in both the mass and species conservation equations given in section 2.3 is shown in Table 3.3.

Table 3.3. Sink and source term for mass and molar of species

	O ₂	N ₂	H ₂	H ₂ O
Equation (2.1):-				
Mass generation between channel and electrode using the FM [kg m ⁻³ s ⁻¹]	$-\frac{I}{4F}M_{O_2}$	-	$-\frac{I}{2F}M_{H_2}$	$\frac{I}{2F}M_{H_2O}$

3.5 Results and discussion

The comparison of the results from numerical analysis to the experimental results is conducted to validate the developed quasi-3D numerical model. The calculation verification is performed under the convergence criteria of 5×10^{-3} . The mesh size of $1 \times 1 \text{ cm}^2$ with finer meshes near the edges is applied to the entire quasi-3D numerical model.

The performance obtained from the numerical analysis using the FM in both anode and cathode is compared with the experimental results under single-cell and six-cell stack approaches in Fig. 3.4(a). The experimental results shown in the Fig. 3.4(a) is the average performance of all six units of cell X80Z60 in the short stack. Both single-cell and six-cell stack analysis using the developed quasi-3D numerical model are in line with the experimental data at 973, 1023, and 1073 K. Both single-cell and six-cell approaches show closer performance with the experimental result at low operating temperature. Although the single-cell approach is more in line than the six-cell approach, the latter approach is selected for further discussion in the study. The single-cell approach shows lower performance than experimental results at higher current density with the operation temperature of 973 K. Even though the electrochemical model used in this study considers all the well-known resistances in the equivalent circuit. There are still some minor resistances such as contact resistance, resistance in other components and electronic conductive

resistance that are existed during experiment but these resistances are not considered in the numerical model.

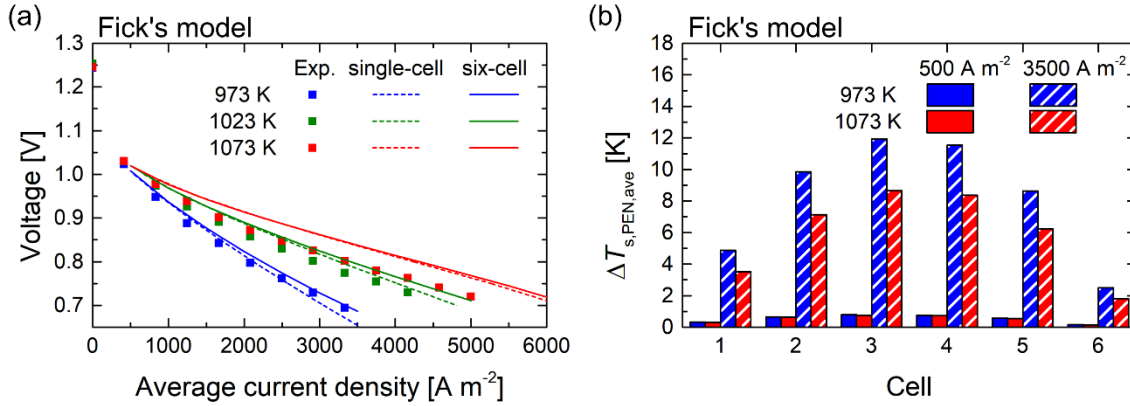


Fig. 3.4. (a) Comparison of numerical analysis obtained in single-cell and six-cell with experimental results. (b) Average cell temperature in the six-cell stack.

Furthermore, the actual experiment was conducted using a stack that consists of six units of X80Z60 cells. The cells in a stack has a deviation of average cell temperature even when the stack operated under isothermal boundary conditions. The difference in average cell temperature for each cell in a six-cell stack as compared to the average cell temperature for single-cell is given in Fig. 3.4(b). The blue and red colored-area indicates the operation temperature of 973 and 1073 K, respectively. On the other hand, the plain and hatch areas indicate the operation average current density of 500 and 3500 $A m^{-2}$, respectively. The cell temperature deviation depends on both the operation temperature and average current density. Small temperature deviation in a stack is found at either low current density or high operating temperature. Such observation is also found in Fig. 3.4(a) where the small different in performance between single-cell and six-cell approaches at either low current density or high operating temperature. Besides, the average cell temperature in

the single-cell approach is lower than the average cell temperature in any cell of the six-cell approach. This further causes high resistance with low performance for the single-cell approach.

In short, a full stack numerical analysis should be utilized for numerical analysis if the additional computation cost is affordable. A single-cell approach to represent a multiple-cell stack has difficulty to capture the cell temperature deviation in a stack, which has great influence on the overall performance of a stack.

3.5 Conclusion for verification and validation of numerical model

A method of numerically analyzing the developed quasi-3D numerical model of solid oxide fuel cell using actual electrode microstructure information was developed. A comparison was done for the numerical results under single-cell and six-cell stack to the experimental results. The developed model can qualitatively capture the trends observed in the experiment without any fitting parameters. A full stack numerical analysis should be considered if the additional computation cost is affordable. A single-cell approach to represent a multiple-cell stack has difficulty in capturing the cell temperature deviation in a stack, which has considerable influence on overall performance of a stack.

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Chapter 4

Indirect ammonia fueled cell

4.1 Introduction

Recently, ammonia has been identified as a potential fuel for SOFCs owing to its high gravimetric and volumetric energy density, ease of storage and transportation, and carbon-free nature. Additionally, leakage of ammonia can be easily detected even at concentrations of under 1 ppm [1]. Ammonia must undergo decomposition to convert it into hydrogen as the fuel for SOFCs. The decomposition of ammonia is an endothermic process, which helps to reduce local anode temperature under direct ammonia supply. It also increases the overall system efficiency by reducing energy consumption to supply the excess air in the air channel [2]. Meng et al. [3] reported that a high flow rate or low temperature of ammonia could result in poor cell performance in case of direct ammonia fuel. A higher flow rate of ammonia supplied to SOFCs leads to greater overall endothermic heating, while a lower temperature leads to lower operating temperature. Both factors increase voltage losses and decrease the cell performance. Ammonia can also be supplied through an external decomposer. The decomposer requires a heat source to sustain the endothermic reaction. This heat can be supplied from the stack, afterburner, heat exchanger or their combination.

An electrochemical reaction occurs in the active area in a cell. Increasing the active area is a simple and effective to achieve higher current output. Although the maximum active area tends to be limited by the available technologies, there are still design options with different cell aspect

ratios within the same active area. The aspect ratio is defined as the ratio of the streamwise length to the spanwise width. Most studies have been conducted with an aspect ratio of exactly unity for both laboratory cells [4–8] and commercial cells [9,10]. Other studies have been conducted with other aspect ratios [11–13], none of the previous works proposed guidelines for the aspect ratio in view of the heat balance, thermal leakage, and operating conditions. All these factors are considered important, especially for SOFCs that are fed by indirect ammonia fuel.

This chapter aims to study the cooling effect of caused by the radiation heat loss from SOFC sidewalls to sustain the external ammonia decomposer for indirect ammonia fuel, and air flow configuration within SOFC cell using the developed numerical model. The numerical analysis considered cells with aspect ratios from 0.130 to 7.68 with a constant active area of 4800 mm^2 under constant mass flow rates of reactants. Actual microstructure information of electrodes from a 3D microstructural analysis is used in the numerical simulation. A parametric study is performed using the model under the same fuel utilization to study the performance of cells with various aspect ratios regarding their voltage efficiency. The effects of the operational temperature, fuel utilization, air flow configuration, and thermal radiation from the SOFC to sustain the ammonia decomposer located next to the SOFC are also discussed.

4.2 Calculation and boundary conditions

A parametric study of indirect ammonia fuel is conducted using a single-cell unit with an ammonia decomposer. 2% humidified ammonia is supplied to the decomposer, assumed to be fully decomposed into hydrogen and nitrogen. The cell unit consists of various aspect ratios ranging from 0.130 to 7.68 as shown in Fig. 4.1. Constant mass flow rates of 2.44×10^{-6} and 2.43×10^{-5}

$\text{kg}\cdot\text{s}^{-1}$ and mole fraction ratios of 0.735: 0.0200: 0.245 for H_2 : H_2O : N_2 and 0.210: 0.790 for O_2 : N_2 are supplied to the fuel and air channels, respectively. Constant mass flow rates ensure that the same amounts of reactants are supplied to the calculation domain. A parametric study is conducted with thermal boundary conditions of TB1, TB2, and TB3 as shown in Figs. 4.2(a) to 4.2(c), respectively. The adiabatic sidewalls with isothermal separators are applied under TB1 to analyze the effects of the cell aspect ratio at various operating temperatures. TB2 and TB3 are used to examine the self-sustaining operation of a single-cell unit fueled with indirect ammonia. The ammonia decomposer is located 5 mm apart from the single-cell unit under both TB2 and TB3. Co- and counter-flow configurations are configured for the indirect ammonia fuel. The boundary conditions are given in Table 4.1.

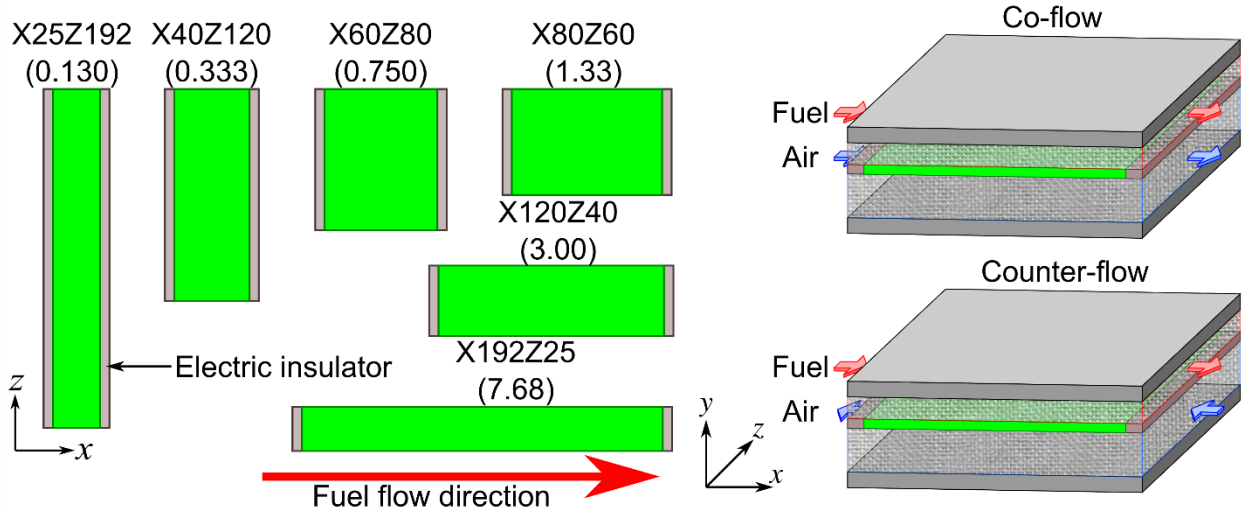


Fig. 4.1. Aspect ratios of cell and flow configurations.

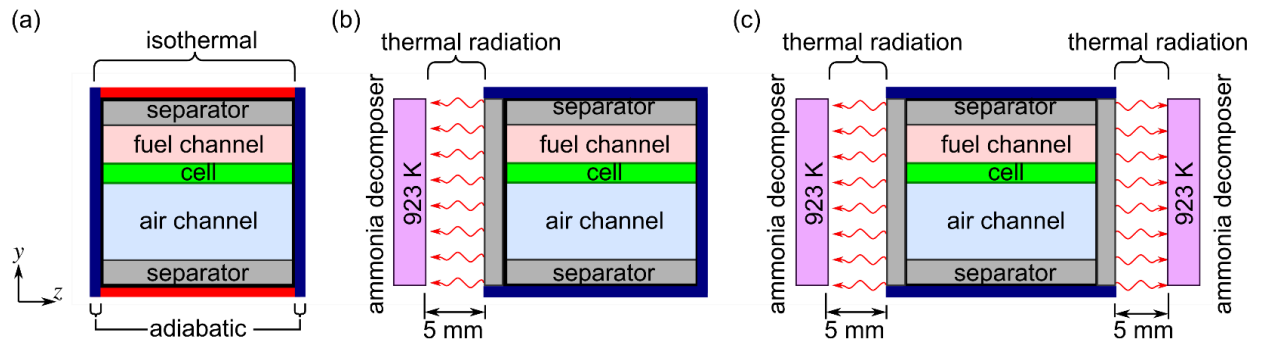


Fig. 4.2. Thermal boundary conditions: (a) TB1 - isothermal separator with adiabatic walls, (b) TB2 - adiabatic separators with thermal radiation at sidewall Z1, and (c) TB3 – similar to TB2 with thermal radiation on both sidewalls Z1 and Z2. (Not to scale)

Table 4.1. Boundary conditions.

Thermal boundary		Inlet	Outlet	Wall		Separators
				Z1	Z2	
u	all*	$u = u_{in}$	$\frac{\partial u}{\partial x} = 0$	$u = 0$	$u = 0$	-
w	all*	$w = 0$	$\frac{\partial w}{\partial x} = 0$	$w = 0$	$w = 0$	-
Y_i	all*	$Y_i = Y_{i, in}$	$\frac{\partial Y_i}{\partial x} = 0$	$\frac{\partial Y_i}{\partial z} = 0$	$\frac{\partial Y_i}{\partial z} = 0$	-
ϕ	all*	$\frac{\partial \phi}{\partial x} = 0$	$\frac{\partial \phi}{\partial x} = 0$	$\frac{\partial \phi}{\partial z} = 0$	$\frac{\partial \phi}{\partial z} = 0$	-
T_f	all*	$T_f = T_{in}$	$\frac{\partial T_f}{\partial x} = 0$	$\frac{\partial T_f}{\partial z} = 0$	$\frac{\partial T_f}{\partial z} = 0$	-
T_s	TB1	$\frac{\partial T_s}{\partial x} = 0$	$\frac{\partial T_s}{\partial x} = 0$	$\frac{\partial T_s}{\partial z} = 0$	$\frac{\partial T_s}{\partial z} = 0$	$T_s = T_{in}$
	TB2	$\frac{\partial T_s}{\partial x} = 0$	$\frac{\partial T_s}{\partial x} = 0$	Q_{rad}	$\frac{\partial T_s}{\partial z} = 0$	$\frac{\partial T_s}{\partial y} = 0$
	TB3	$\frac{\partial T_s}{\partial x} = 0$	$\frac{\partial T_s}{\partial x} = 0$	Q_{rad}	Q_{rad}	$\frac{\partial T_s}{\partial y} = 0$

* all thermal boundaries includes TB1, TB2, and TB3

4.3 Results and discussion

The results for the parametric study using the developed quasi-3D numerical model is discussed here. First, the effect of temperature without taking account of the heat supplied from the cell unit to sustain the operation of external ammonia decomposer is evaluated under TB1. Second, the effect of cell aspect ratio is evaluated in the event of radiation heat loss at either wall

Z1 (TB2) or combination of walls Z1 and Z2 (TB3). This heat is supplied to sustain ammonia decomposition reaction in the external decomposer located 5 mm apart from the cell unit. Third, the effect of flow configurations (co- and counter-flow) related to various aspect ratios is determined. Lastly, the sustainability of the external ammonia decomposer with the supply of radiation heat from cell unit corresponds to various aspect ratios is assessed.

4.3.1 Effect of temperature

A series of calculations are performed under a galvanostatic condition with the thermal condition of TB1 and the boundary conditions in Table 4.1 to discuss the effects of the cell aspect ratio. Figure 4.3 shows the terminal voltage, voltage losses, EMF, and voltage efficiency in the cells for fuel utilization of 0.2 to 0.8 with increments of 0.2 at the operating temperatures of 973, 1023, and 1073 K. The voltage losses and terminal voltage are represented by the hatched and plain areas, respectively. The sum of the voltage losses and the terminal voltage corresponds to the EMF of the cells.

Figure 4.3 shows that all cells have a high terminal voltage at low fuel utilization and the low terminal voltage at high fuel utilization, similar to the I - V characteristics shown in Fig. 3.4. The decrease in the terminal voltage at high fuel utilization is much larger than the decrease in EMF, especially at 973 K. As a result, low voltage efficiency is expected at high fuel utilization. It is also observed that the operating at high temperature allows the cell to achieve high voltage efficiency for all values of fuel utilization. A significant decrease in the voltage losses from both the activation overpotential in Eqs. (2.35) and (2.36) and the ohmic loss in Eqs. (2.39) – (2.41) is expected during operations at a higher temperature. Although the EMF also decreased with

increasing temperature, the decrease is significantly smaller than the decrease in the voltage losses. The cell with the highest aspect ratio (X192Z25) has the highest EMF and highest terminal voltage. In contrast, the cell with the lowest aspect ratio (X25Z192) with the lowest EMF and terminal voltage exhibits the lowest voltage losses. At low fuel utilization, the cell with the lowest aspect ratio shows the highest voltage efficiency at all operational temperatures. At high fuel utilization, the cell with the highest aspect ratio has a higher voltage efficiency than the cell with the lowest aspect ratio. As a result, both the highest- and lowest-aspect-ratio cells have the potential to achieve higher voltage efficiency than a cell with an aspect ratio close to unity. Overall, the differences in cell performances are small if the cell temperatures are kept almost uniform as observed in Fig. 4.3.

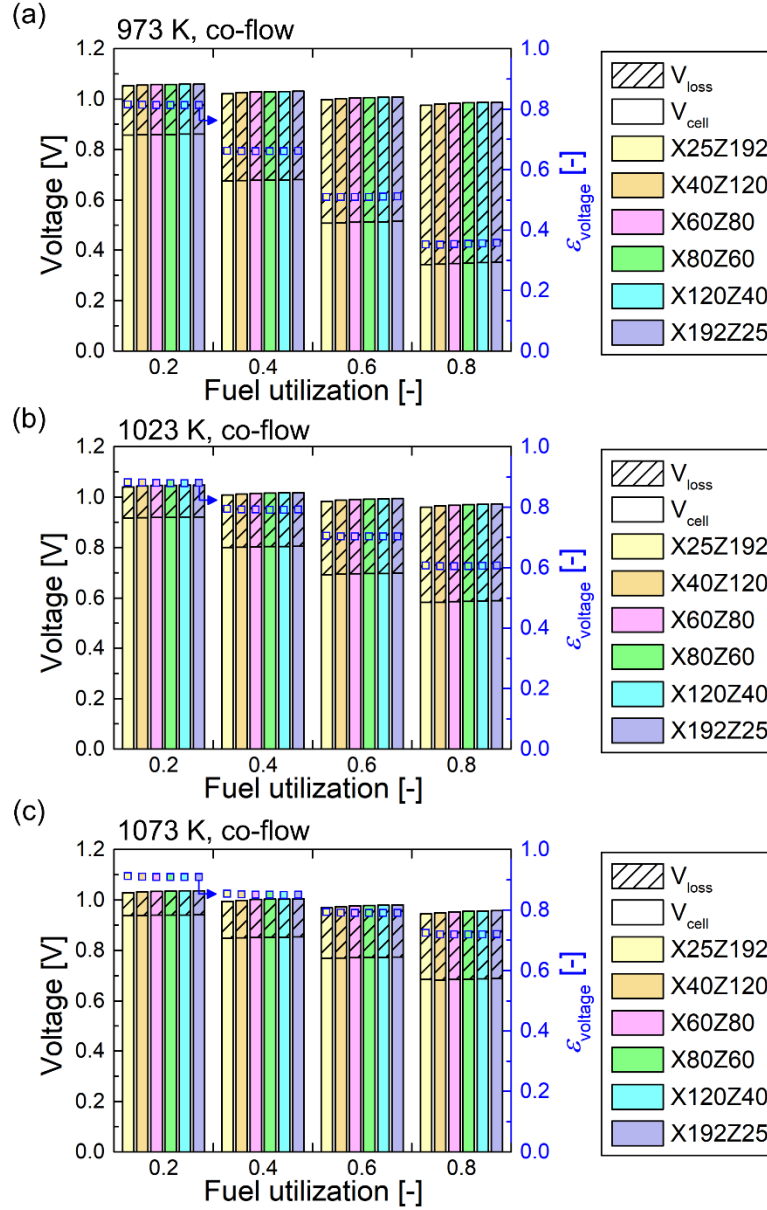


Fig. 4.3. Performance of the cells under TB1 in terms of $\epsilon_{\text{voltage}}$, V_{cell} , and V_{loss} at (a) 973 K, (b) 1023 K, and (c) 1073 K.

Figure 4.4(a) shows the average EMF of the cells, current density distribution, and the pressure losses in the fuel and air channels operating at 1073 K with a fuel utilization of 0.8. The cell with the highest aspect ratio (X192Z25) has the highest-pressure losses among the cells. As a result, high pressure at the inlet of both the air and fuel channels must be supplied to provide the

same mass flow rate to the cells. The high total pressure increases the partial pressure of the species, resulting in a high average EMF as given by Eq. (2.26). The high-pressure loss across the channels in a cell with a high aspect ratio in Fig 4.4(a) reduces the overall performance of SOFC systems because additional energy is required for the compressor/blower to deliver the reactants to the stack or cell. Figs. 4.4(b), 4.4(c), and 4.4(d) show the distributions of the partial pressures for the species of hydrogen, steam, and oxygen, respectively, at the channels and the interface between the electrode and electrolyte. It can be observed that a cell with a high aspect ratio not only has a high inlet pressure but also has high partial pressures of the reactant species (hydrogen and oxygen) but a low partial pressure of the produced species (steam). The high partial pressure of oxygen at the reaction site of the cathode increases the exchange current per reaction site in Eq. (2.30). On the other hand, the effect of the high partial pressure of hydrogen in a cell with a high aspect ratio is balanced by the effect of the low partial pressure of steam in the anode from Eq. (2.29). The high partial pressure of oxygen also increases ionic conductivity in the cathode and electrolyte, as suggested by Bessette et al. [14] and Matsuzaki et al. [15]. Figure 4.4(e) shows the current density plotted against the normalized streamwise coordinate X' at a normalized Z' of 0.50 for all the cells. The cell with the lowest aspect ratio (X25Z192) has the lowest current density in the upstream region. As a result, this cell must deliver a much higher current density in the downstream region. As the aspect ratio increases to unity, an increase in the current density in the upstream with a decrease in the downstream can be observed along the streamwise direction. A further increase in the aspect ratio beyond unity results in the opposite observation with a slight decrease in the upstream and a slight increase in the downstream.

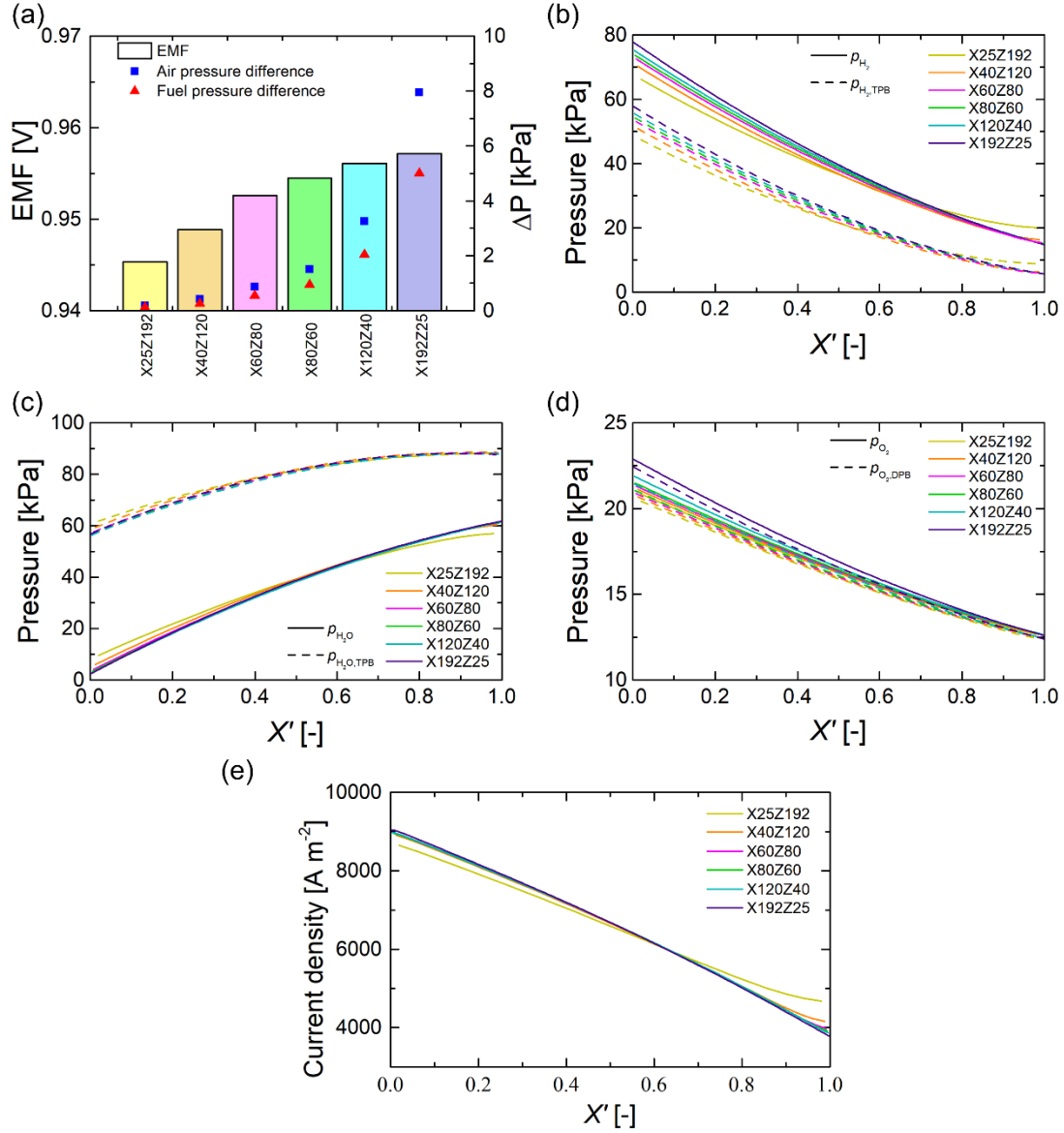


Fig. 4.4. Characteristics of the cells under TB1 with $\varepsilon_{\text{fuel}}$ of 0.8 at 1073 K.

(a) EMF and pressure loss in the channels, (b) hydrogen partial pressure distribution, (c) steam partial pressure distribution, (d) oxygen partial pressure distribution, and (e) current density distribution.

4.3.2 Effect of cell aspect ratio

The thermal boundary conditions are changed and subjected to heat loss by radiation under TB2 or TB3, with the fuel remaining as fully decomposed ammonia. The ammonia is decomposed in the ammonia decomposers, located next to the SOFC. The thermal radiation from the SOFC sustains the operation of the ammonia decomposer. Both the fuel and air are supplied at 923 K to avoid extremely high temperature at the downstream of the cell that would exceed the realistic operational temperature of the cathode. The analysis under TB2 and TB3 studies the effect of the cell aspect ratio on the thermal radiation emitted to sustain the operation of the ammonia decomposer. Figs. 4.5(a) and 4.5(b) show the performance of the cells under conditions TB2 and TB3, respectively. It can be observed that the aspect ratio plays a more important role in determining the performance of the cells under conditions of TB2 and TB3 than for cells operating in a controlled-temperature furnace such as under condition TB1 (Fig. 4.3). A low EMF is seen in a cell with a low aspect ratio, due to the low-pressure difference between the inlet and outlet in both channels. This is also observed under TB1. The lowest voltage losses with the highest voltage efficiency are found in cell X60Z80 with an aspect ratio close to unity. A high average temperature of PEN can be observed from these cells, as shown in Figs. 4.6(a) and 4.6(b), under conditions TB2 and TB3, respectively. A cell with a high aspect ratio has a large area exposed to thermal radiation, which leads to a low PEN temperature and high voltage losses. Nevertheless, the effect of thermal radiation is not significant for the cells with aspect ratios less than unity, which has a low average PEN temperature even with a small area exposed to thermal radiation.

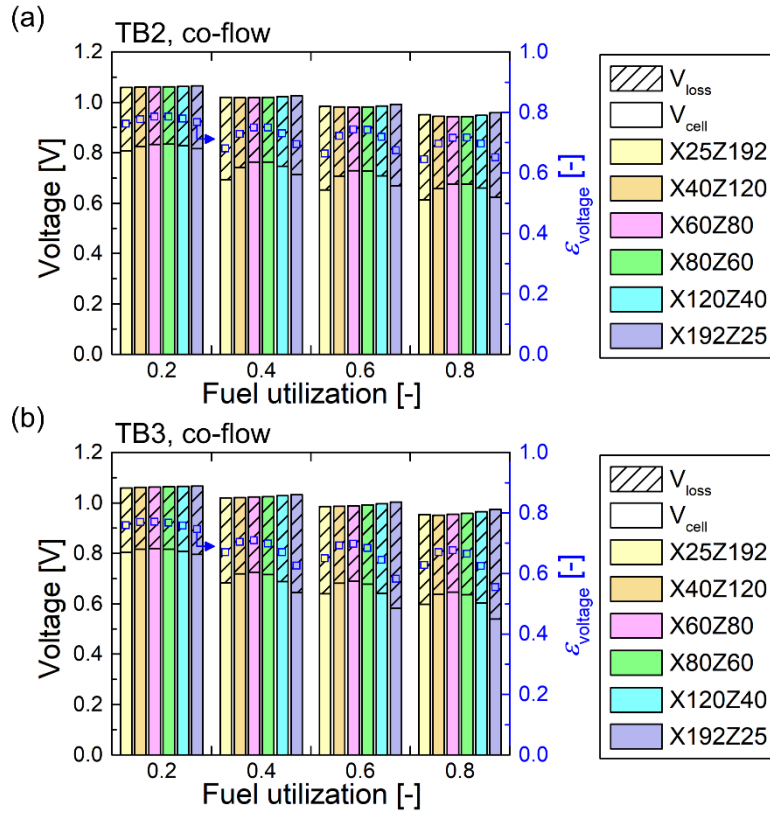


Fig. 4.5. Performance of the cells in terms of $\epsilon_{voltage}$, V_{cell} , and V_{loss} under thermal boundary conditions of (a) TB2, and (b) TB3

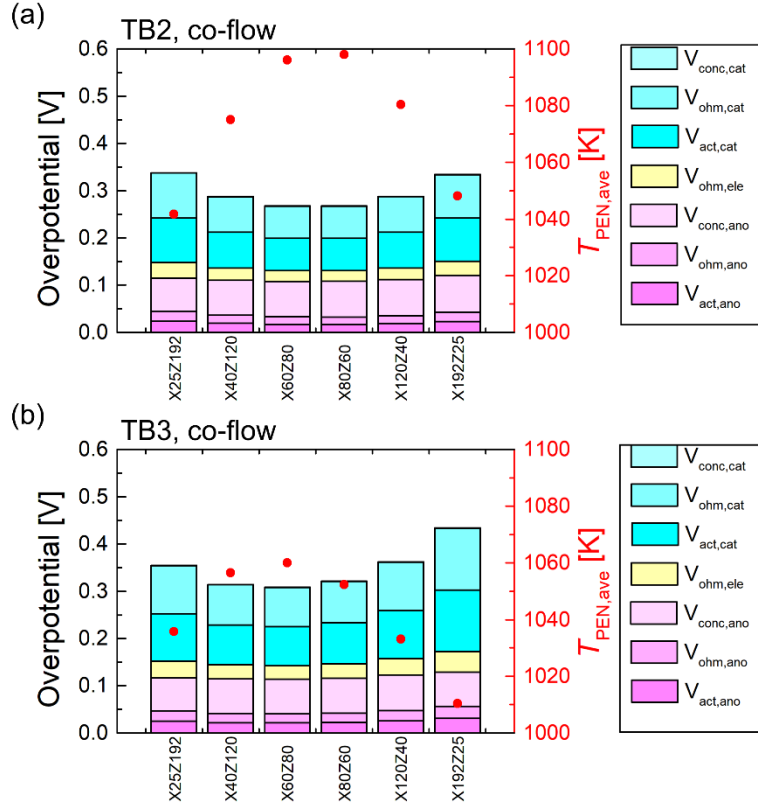


Fig. 4.6. Average V_{loss} under thermal boundary conditions of (a) TB2, and (b) TB3.

The heat generated in the cells is related to both the electrochemical reaction and the distribution of voltage losses. The lower average PEN temperature observed with an aspect ratio less than unity is due to the local distribution of the current density as shown in Fig. 4.7. Figure 4.7 shows the local current density distribution for a fuel utilization of 0.8. The red and blue arrows indicate the flow direction of fuel and air, respectively. Cell X25Z192 has a relatively uniform distribution of the current density in the active area compared to the cells with higher aspect ratios. This reduces the average PEN temperature compared to a large deviation of the current density, resulting in a large temperature gradient. The exothermic heat from the electrochemical reaction is partially transferred to the fuel channel and the nearby active area. Consequently, the active area downstream of the fuel flow has a higher local operating temperature than the upstream. The high

local operating temperature further promotes electrochemical reaction owing to the low voltage losses. A mild decrease in the PEN temperature is expected for a relatively uniform current density distribution.

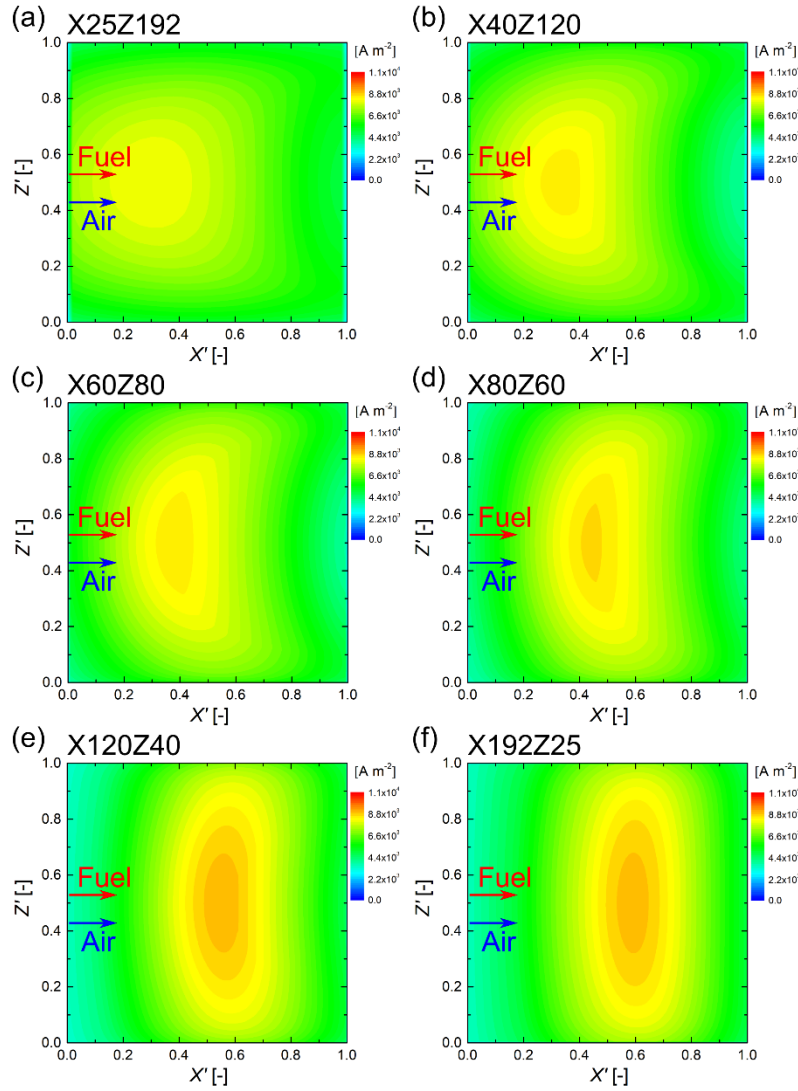


Fig. 4.7. Distribution of current density under TB3 for cells (a) X25Z192, (b) X40Z120, (c) X60Z80, (d) X80Z60, (e) X120Z40, and (f) X192Z25 under operation with $\varepsilon_{\text{fuel}} = 0.80$.

4.3.3 Effect of flow configuration

The co-flow configuration is changed to counter-flow configuration to investigate the effect of different flow configurations under indirect ammonia fuel. The cross-flow configuration is not considered due to the radiation heat from the SOFC short stack is affected by the manifold attached to the inlet and outlet of channels. Moreover, only TB3 is considered under the counter-flow configuration.

The performance of the cell with various aspect ratios is analyzed pertaining the distributions of current density and cell temperature within the effective area. In preparation for the statistical analysis, the distributions of local current density and cell temperature are resampled on the basis of a uniform grid system in the xz -plane. The temperature distribution within the electrical insulators is not considered for this process. Each mesh covers an area of $1\text{ mm} \times 1\text{ mm}$ of the cell. The random Renka–Cline algorithm [16] is used to resample the dataset.

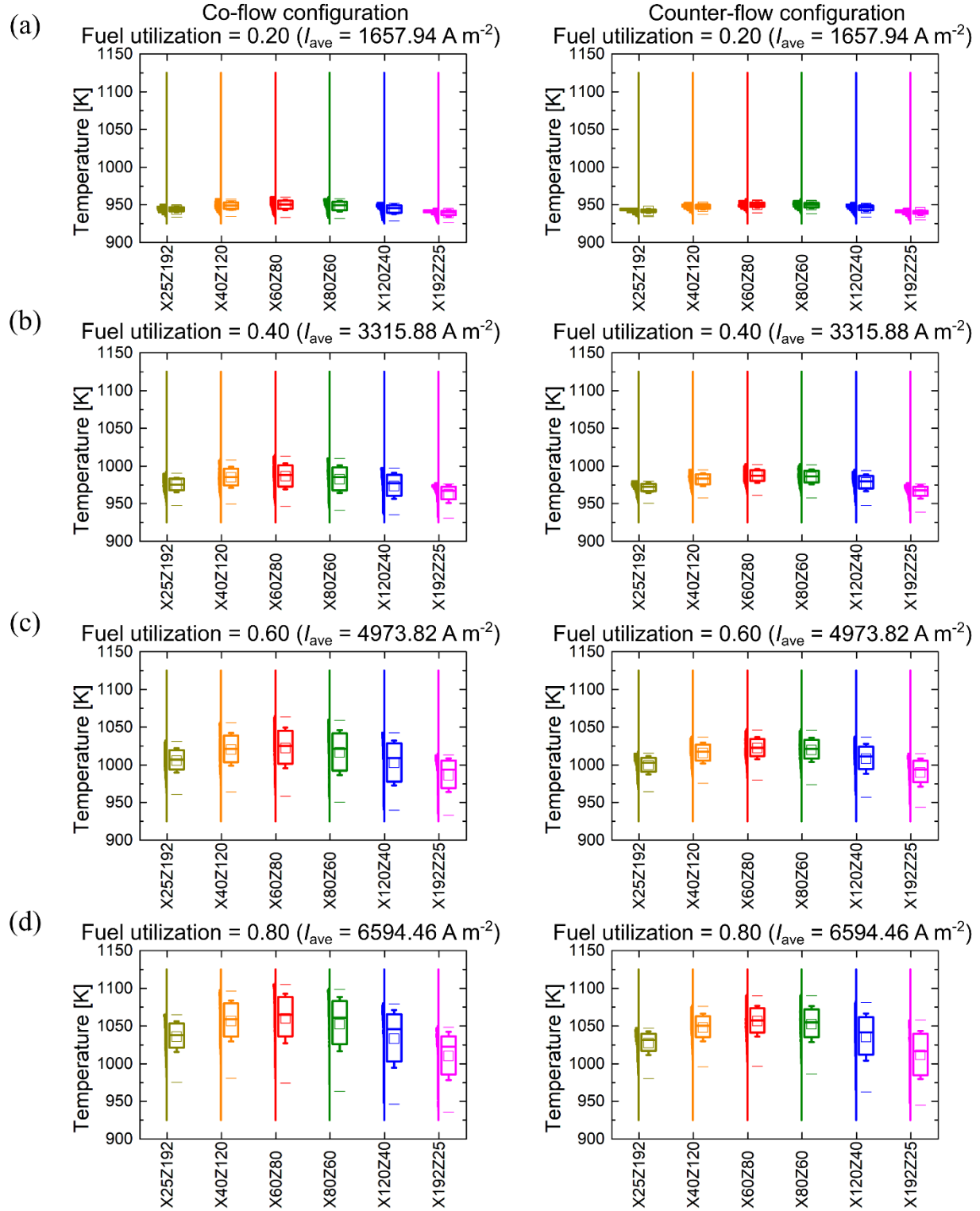


Fig. 4.8. Comparison of the cell temperature distributions between co- and counter-flow at fuel utilization of (a) 0.20, (b) 0.40, (c) 0.60, and (d) 0.80.

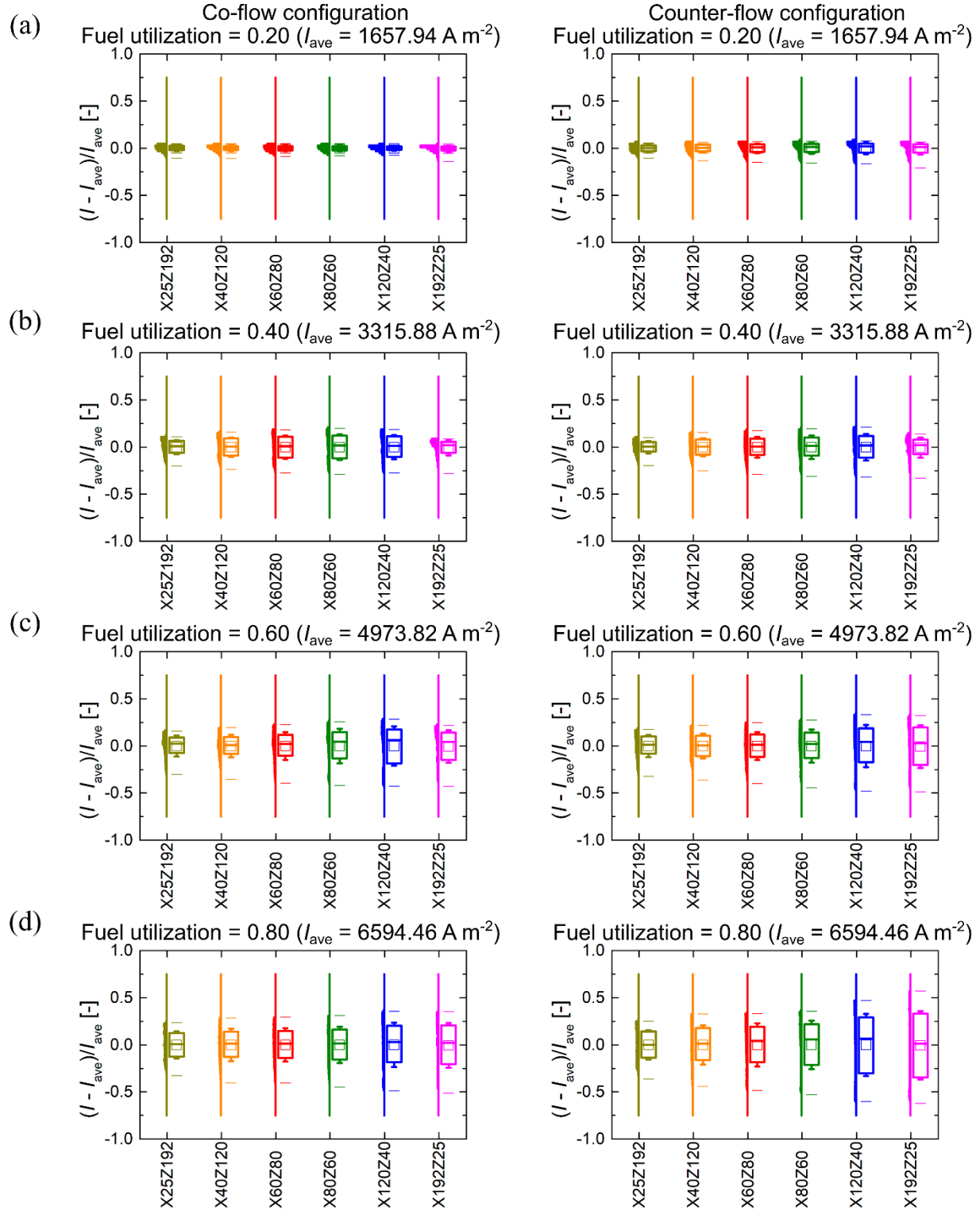


Fig. 4.9. Comparison of the current density distributions between co- and counter-flow at fuel utilization of (a) 0.20, (b) 0.40, (c) 0.60, and (d) 0.80.

Figures 4.8 and 4.9 show box charts with histograms of the distributions of cell temperature and current density, respectively, for various aspect ratio cells under both co- and counter-flow configurations. It is found that the counter-flow configuration has a narrow-spread in the overall range of cell temperature, except X192Z25 in Fig. 4.8. The low-temperature fuel partially absorbs the heat which is carried by air at the air downstream. Similarly, the heat that is carried by fuel is partially absorbed by the air at the fuel downstream. This results in an air-to-fuel and vice versa of heat circulation. The heat circulation is more prominent in the cells with an aspect ratio greater than unity with a long path for the circulation to take place. Therefore, high aspect ratio cells are found to have higher average cell temperature under the counter-flow than under co-flow configuration. The higher flow rate of air than fuel results in a low cell temperature (near to the air inlet temperature). These factors raise the overall cell resistances near the fuel downstream.

Figure 4.8 shows that the counter-flow configuration has a wide-spread in the overall range of current density. The circulation of heat in the counter-flow raises the cell temperature especially at the upstream of fuel, which significantly reduces activation and ohmic resistances. This area is also close to the fuel inlet, where the fuel concentration is high. On the other hand, the counter-flow cells face a much lower concentration of fuel at its downstream due to the high electrochemical activity at the upstream. This results in high local concentration resistance. Hence, the counter-flow cells have a higher local current density at fuel upstream than the co-flow cells.

Figures 4.10 shows the comparison between the performance of the cell under co-flow and counter-flow, respectively. The blue-edge square and red-edge round symbols indicate the voltage efficiency of various aspect ratio cells under co-flow and counter-flow, respectively. It is found that cell with an aspect ratio greater than unity tends to have high performance under counter-flow configuration. However, cell X60Z80 with an aspect ratio less than unity has higher voltage

efficiency at fuel utilization of 0.60 and 0.80. The difference in voltage efficiency between co- and counter-flow is magnified with high fuel utilization. The influence of thermal radiation at both sidewalls towards various aspect ratios remains the same as discussed in the section 4.3.2.

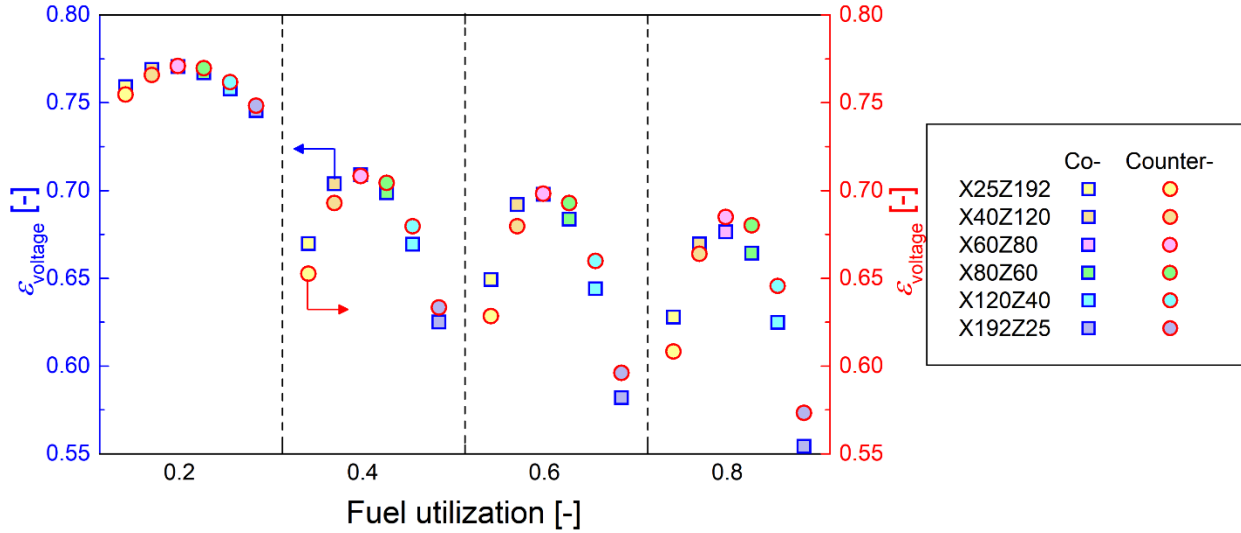


Fig. 4.10. Performance of the cells in terms of $\varepsilon_{\text{voltage}}$, V_{cell} , and V_{loss} under
(a) co-flow, and (b) counter-flow

4.3.4 Sustainability of external ammonia decomposer

The fuels used under conditions TB2 and TB3 come from the decomposition of ammonia from the external decomposer located 5 mm from the short stack as shown in Figs. 4.2(c) and 4.2(d), respectively. The heat required for the decomposer is supplied by the thermal radiation from the short stack. The ammonia decomposition reaction cannot be completed when the heat from the short stack is less than the endothermic reaction heat of ammonia decomposition given in Eq. (2.89). Figure 4.11 shows the heat required by the ammonia decomposition and the thermal

radiation from the SOFC under conditions TB2 and TB3 with both co- and counter-flow configurations. The plain and hatched bars indicate the thermal radiation at the SOFC sidewall at a normalized Z' of 0 and 1.0, respectively.

Figures 4.11(a) and 4.11(b) indicate the thermal radiation released from the SOFC short stack, which is operated under co-flow configuration and the heat required by the external ammonia decomposer. Only cells X120Z40 (at a fuel utilization of 0.8) and X192Z25 (at fuel utilization of 0.6 and 0.8) provide sufficient heat under TB2. These cells also provide sufficient thermal radiation for the ammonia decomposers under TB3 with the same fuel utilization. Additionally, the cell with the low aspect ratio of 0.750 (X60Z80) thermally sustains the ammonia decomposers and also has the highest voltage efficiency of 0.67 at fuel utilization of 0.8 taking into account thermal radiation at both sidewalls.

Conversely, the supply and demand of thermal radiation under counter-flow configuration is shown in Fig. 4.11(c) and 4.11(d). Almost the same results are observed for the cells under counter-flow configuration as in the co-flow. The high cell temperature (in high aspect ratio cells) under counter-flow configuration raises the radiation heat at the sidewalls. Hence, cell X60Z80 shows the capability of self-sustaining the external ammonia decomposers at fuel utilization of 0.6 under TB3.

An afterburner can provide additional heat to the ammonia decomposer to sustain operations of the cells especially with an aspect ratio less than unity. Cells with an aspect ratio greater than unity can rely on the heat circulation effect and radiation heat at the sidewalls to operate at higher fuel utilization.

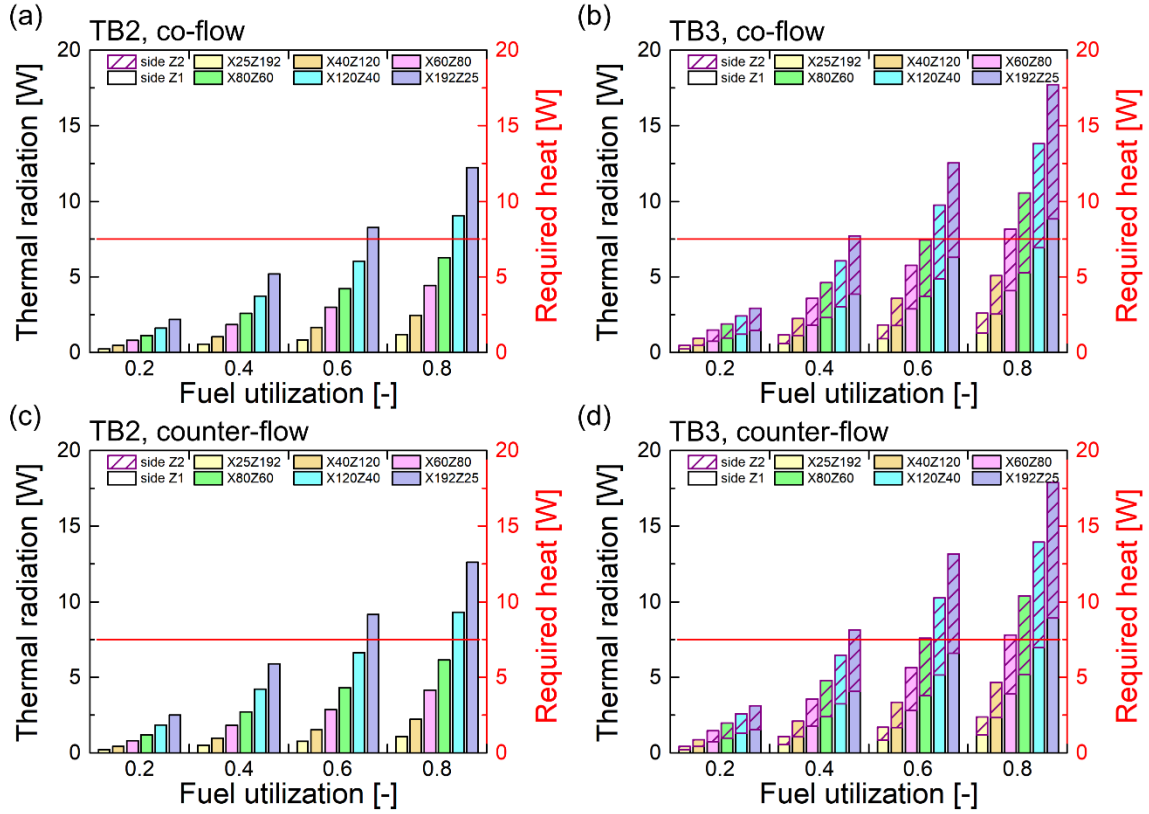


Fig. 4.11. Thermal radiation from SOFC and heat required by the external ammonia decomposer under conditions (a) TB2 (co-flow), (b) TB3 (co-flow), (c) TB2 (counter-flow) and (d) TB3 (counter-flow).

4.4 Conclusion for indirect ammonia fueled cell

This work aims to understand the effect of the external cooling subjected to radiation heat loss from sidewalls of SOFC short stack, which is fueled with fully decomposed ammonia. A parametric study was conducted to analyze cells with aspect ratios from 0.130 to 7.68 with a thermal boundary condition like a cell unit in an electrical furnace. The shortest and widest cell with the lowest aspect ratio was found to have the highest voltage efficiency at low fuel utilization.

However, the longest and narrowest cell with the highest aspect ratio had the highest voltage efficiency at high fuel utilization.

The effect of the aspect ratio on thermal radiation emitted from the cell was also investigated with the assumption that the supplied fuel used fully decomposed ammonia from an external ammonia decomposer located next to a short stack. The highest cell efficiency was found for the cells with aspect ratios close to unity. These cells had a higher average cell temperature, which reduced activation overpotential and ohmic loss. Cells with aspect ratio higher than unity had low average cell temperature. This low average temperature was caused by thermal radiation from the sidewalls. On the other hand, the highly uniform distribution of the local current density for the short and wide cells resulted in low average cell temperatures. Consequently, high voltage losses with low voltage efficiency are expected.

The longest and narrowest cell with the highest aspect ratios exhibited the best results in the case of a self-sustained ammonia-feed decomposer operated with the radiation heat from the short stack. A large thermal radiation area with high-fuel-utilization allows the possibility of an SOFC short stack fueled with decomposed ammonia from a self-sustained decomposer. On the other hand, the cell with the low aspect ratio of 0.750 (X60Z80) was not only capable of thermally sustaining the ammonia decomposers but also had the highest voltage efficiency of 0.67 at a fuel utilization of 0.80 taking into account thermal radiation at both sidewalls.

The results of this study indicate that aspect ratio of the active area influences the external cooling effect under radiation heat loss. A balance between cooling effect and cell efficiency is required to ensure the sustainability of an ammonia decomposer and achieve reasonable performance of short stack.

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Chapter 5

Direct ammonia fueled cell

5.1 Introduction

The indirect ammonia fuel can be realized with the aid of an external ammonia decomposer as reported in Chapter 4. However, the complexity of the SOFCs system is increased with the introduction of external ammonia decomposer to the system [1]. At the same time, this external ammonia decomposer increases cost [2] (similar to external methane reformer) of an SOFCs system. The thermal energy required to sustain the external ammonia decomposer can be supplied from the SOFC cell/stack. Therefore, the external ammonia decomposer should be located close to the SOFC cell/stack, which minimizes the heat loss to the environment and to promote the higher efficiency of the SOFCs system. The exothermic heats generated by the electrochemical reaction and voltage losses are located within a cell. On the other hand, ammonia decomposition reaction can occur with the aid of a suitable catalyst. Nickel is a suitable catalyst for this ammonia decomposition reaction [3], and available in most of the anode in commercial cells. As a result, high system efficiency can be achieved under direct ammonia fuel, where the ammonia decomposition reaction is located close to the exothermic heat sources.

Extreme cooling of SOFC stack that subjected to a high flow rate or low temperature of direct ammonia fuel can result in poor performance [4]. The flow rate of fuel is a pre-determined factor based on the required electrical output. The flow rate of ammonia can be equally divided

among SOFC cells in a stack. The high inlet temperature of reactants can be achieved through pre-heating the reactants before being channeled to a cell/stack. Ammonia decomposition reaction with the aid of nickel as catalyst relies on other parameters such as the concentration of gas species (hydrogen and ammonia) and nickel-pore interfacial area [5]. The nickel-pore interfacial area is one of the microstructure properties, which depends on its manufacturing process and the initial size of nickel-based powder used to produce an anode. The concentration of gas species relies on the pressure loss in the fuel channel and the molar fraction of gas species in the supplied mixture, which vary accordingly to the cell aspect ratio, local electrochemical activity, and amount of pre-decomposed ammonia within the supplied fuel.

This chapter aims to study the factors that influence the internal cooling of SOFC short stack due to ammonia decomposition reaction rate, pre-decomposed ratio of ammonia fuel, and air flow. First, a comparison between the FM and the DGM for the transportation of gas species in the anode, with an analysis on the effect of the number of layers for anode mesh for the implementation of the DGM. Second, a parametric study is conducted on the ammonia decomposition reaction rate to quantify the influence of each identified factor. Third, a numerical analysis is conducted on the same geometry used in the stack experiment reported in Chapter 3 to study the influence of direct ammonia fuel in terms of the generated endothermic heat, voltage losses, and cell performance. Forth, the study is extended to various ratios of pre-decomposed ammonia supplied to a cell. The analysis also considers cells with various aspect ratios to investigate the influence of pressure loss in channels. Lastly, the effects of flow configurations, especially under co- and counter-flow towards ammonia decomposition reaction are discussed for the various aspect ratio cells.

5.2 Calculation and boundary conditions

The numerical results of a six-cell short stack with the FM and the DGM implemented in the anode are compared with the experimental data for verification. The DGM is given accordingly to the gas species conservation in Eq. (2.77). The detail of the calculation condition and boundary condition for verification purpose is the same as section 3.4 with additional boundary condition for anode mesh in Table 5.1. The mass and molar of species source term in both the mass and species conservation equations given in section 2.3 is shown in Table 5.2.

The analysis of direct ammonia fuel is conducted with the inlet temperature of 973 K. A constant mass flow rate of $2.43 \times 10^{-5} \text{ kg}\cdot\text{s}^{-1}$ and mole fraction ratio of 0.210: 0.790 for O_2 : N_2 are supplied to the air channel. Constant mass flow rates of fuel are varied depending on the pre-decomposed ammonia ratio supplied to a cell to ensure similar amounts of fuel. The mass flow rates and mole fraction ratios of fuel are given in Table 5.3. The boundary conditions of TB4 as shown in Fig. 5.1 is given in Table 5.4.

Table 5.1. Boundary condition for anode mesh.

Anode mesh:	Anode surface	Electrolyte interface	Walls	
P	$P = P_{\text{channel}}$	$\frac{\partial P}{\partial y} = 0$	$\frac{\partial P}{\partial x} = 0$	$\frac{\partial P}{\partial z} = 0$
x_i	$x_i = x_{i,\text{channel}}$	$\frac{\partial x_i}{\partial y} = 0, i \neq \text{H}_2, \text{H}_2\text{O}$ $N_i = 0, i \neq \text{H}_2, \text{H}_2\text{O}$	$\frac{\partial x_i}{\partial x} = 0$	$\frac{\partial x_i}{\partial z} = 0$
N_i	Equation (2.78)	$N_{\text{H}_2} = -I/2F$ $N_{\text{H}_2\text{O}} = I/2F$	$N_{i,x} = 0$	$N_{i,z} = 0$

Table 5.2. Sink and source term for mass and molar of species

	O ₂	N ₂	H ₂	H ₂ O
Equation (2.1):-				
Mass generation between channel and anode using the DGM [kg m ⁻³ s ⁻¹]	-	$N_{\text{N}_2} M_{\text{N}_2}$	$N_{\text{H}_2} M_{\text{H}_2}$	$N_{\text{H}_2\text{O}} M_{\text{H}_2\text{O}}$
Equation (2.8):-				
Molar generation during electrochemical reaction [mol m ⁻³ s ⁻¹]	-	-	$-\frac{I}{2F}$	$\frac{I}{2F}$

Table 5.3. Mass flow rates and molar fraction ratios for direct ammonia decomposition.

Case	Pre-decompose ammonia ratio	Molar fraction ratio	Mass flow rate
	[%]	[H ₂ : H ₂ O: N ₂ : NH ₃]	[kg s ⁻¹]
Pre100	100	0.735 : 0.020 : 0.245 : 0	1.294×10^{-6}
Pre80	80	0.585 : 0.020 : 0.195 : 0.200	1.285×10^{-6}
Pre60	60	0.435 : 0.020 : 0.145 : 0.400	1.279×10^{-6}
Pre40	40	0.285 : 0.020 : 0.095 : 0.600	1.274×10^{-6}
Pre20	20	0.135 : 0.020 : 0.045 : 0.800	1.270×10^{-6}
Pre0	0	0.030 : 0.020 : 0.010 : 0.940	1.268×10^{-6}

Table 5.4. Boundary conditions of TB4.

	Inlet	Outlet	Wall		Separators
			Z1	Z2	
u	$u = u_{\text{in}}$	$\frac{\partial u}{\partial x} = 0$	$u = 0$	$u = 0$	-
w	$w = 0$	$\frac{\partial w}{\partial x} = 0$	$w = 0$	$w = 0$	-
Y_i	$Y_i = Y_{i, \text{in}}$	$\frac{\partial Y_i}{\partial x} = 0$	$\frac{\partial Y_i}{\partial z} = 0$	$\frac{\partial Y_i}{\partial z} = 0$	-
ϕ	$\frac{\partial \phi}{\partial x} = 0$	$\frac{\partial \phi}{\partial x} = 0$	$\frac{\partial \phi}{\partial z} = 0$	$\frac{\partial \phi}{\partial z} = 0$	-
T_f	$T_f = T_{\text{in}}$	$\frac{\partial T_f}{\partial x} = 0$	$\frac{\partial T_f}{\partial z} = 0$	$\frac{\partial T_f}{\partial z} = 0$	-
T_s	$\frac{\partial T_s}{\partial x} = 0$	$\frac{\partial T_s}{\partial x} = 0$	$\frac{\partial T_s}{\partial z} = 0$	$\frac{\partial T_s}{\partial z} = 0$	$\frac{\partial T_s}{\partial y} = 0$

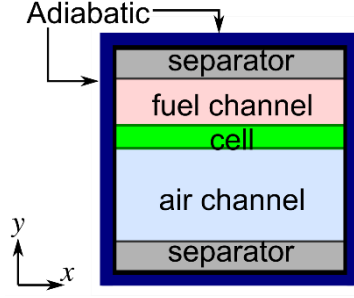


Fig. 5.1. The thermal boundary of TB4 with fully adiabatic walls.

5.3 Verification and validation of species transport in anode using the DGM

The calculation verification is performed under the convergence criteria of 5×10^{-3} , and the grid independence is performed in the anode mesh for the implementation of the DGM. The detail of the discussion follows

5.3.1 Effect of mesh layers for anode mesh

Anode mesh is introduced for the implementation of the DGM for the transport of gas species in the anode. The FM is kept unchanged in the cathode. The molar fluxes of gas species as expressed in Eq. (2.77) is solved by the finite volume method simultaneously with other fluxes in the quasi-3D grid system. It is essential to conduct the grid independence for this anode mesh. The anode mesh of 2 layers to 30 layers with two layers increment, are used for the grid independence analysis. The total anode mesh layers include two grid points located at the anode surface and anode-electrolyte interface as boundary grids. All the mesh layers have an equal thickness in y -axis. The size of the anode mesh in the xz -plane is the same as the meshes used in the quasi-3D model. Both direct and indirect ammonia fuels are considered in this grid independence analysis.

The calculation condition of indirect ammonia fuel is the same as the experimental condition. On the other hand, the mole fraction ratios of 0.030: 0.020: 0.010: 0.940 for H_2 : H_2O : N_2 : NH_3 is applied to the fuel channel for direct ammonia fuel. The numerical analysis is conducted under galvanostatic-control of 3500 A m^{-2} with the inlet temperature of 973 K.

Figure 5.2 shows the results of the grid independence analysis under both direct and indirect ammonia fuels. The transportation of gas species directly influences the resistance of gas transportation in electrodes as given in Eqs. (2.58) and (2.59). Hence, the analysis in term of the ASR for concentration resistance in the anode is provided in Fig. 5.2(a). It is found that under indirect ammonia fuel, the changes of concentration resistance is found below $1 \times 10^{-5} \Omega \text{ cm}^2$ beyond 12 layers of anode mesh. On the other hand, the concentration resistance reaches a peak value with eight layers of anode mesh then followed by a decrease under direct ammonia fuel. The changes of concentration resistance are found below $1 \times 10^{-5} \Omega \text{ cm}^2$ beyond ten layers of the anode mesh.

Besides, the transportation of gas species in anode also has a direct influence on the exchange current per unit reaction site as expressed by Kanno et al. [6] in Eq. (2.29). The attenuation factor for the charge-transfer current profile in the anode also functions against the exchange current per unit reaction site. Although the attenuation factor is derived based on the minimum total resistance in an electrode without considering the concentration overpotential (in section 2.6), it functions against exchange current per unit reaction site, which is influenced by the concentration resistance in an electrode. Figure 5.2(b) shows the grid independence analysis by considering the total ASR in a cell. The similar patterns as shown in Fig. 5.2(a) is also found for the total ASR in both direct and indirect ammonia decomposition fuel.

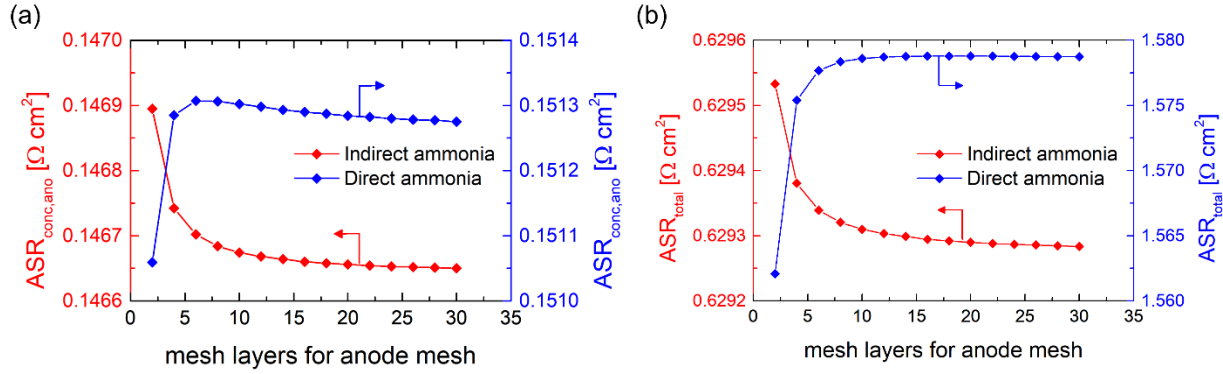


Fig 5.2. Grid independence analysis for anode mesh by considering

(a) ASR of concentration resistance in the anode, and (b) total ASR in a cell.

Overall, the grid independence depends on the supplied fuel. Fewer mesh layers are required for direct ammonia fuel. A total of 16 mesh layers for the anode mesh is proposed by considering the balance between computation cost and performance. On the other hand, an approximate 1 to 2 μm thickness per mesh in an electrode is recommended for the 2D, or full 3D numerical analysis, which results in a minimum of 120 mesh layers being required for the same thickness of anode in an anode-supported cell. Consequently, the 3D anode meshes not only solve the multi-dimensional molar fluxes but also significantly reduces computation cost.

5.3.2 Fick's model and dusty-gas model

The comparison between the FM and the DGM for the transportation of gas species in the anode is conducted in a six-cell stack. The entire mesh layers in the anode mesh are 16 layers for the implementation of the DGM based on the discussion in section 5.3.1. The transportation of gas species in the cathode is unchanged by the FM. Figure 5.3(a) shows the comparison for the two-gas diffusion models in the anode layer for a six-cell stack. Both gas diffusion models have the

similar results especially at the operating temperature of 973 K or low average current density operation. The simulation results with the gas diffusion model in the anode, either the FM or the DGM, tend to show slightly higher performance than the experiment results, especially at 1073 K.

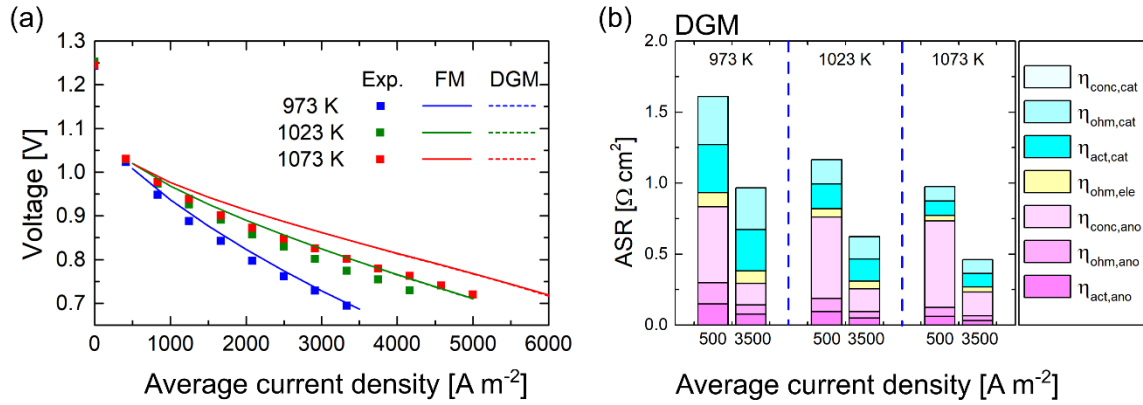


Fig. 5.3. (a) Comparison of the FM and the DGM with experimental results under the six-cell stack. (b) ASR in the six-cell stack under the DGM.

The short stack has a slightly higher average performance when the operating temperature is increased from 1023 to 1073 K. The comparison of the ASR at average current densities of 500 and 3500 A m^{-2} in Fig. 5.3(b) suggests that at 973 K the cell has high voltage losses on the cathode side. At such a low operation temperature, the cathode has low ionic conductivity. As a result, ohmic loss and attenuation factor of the cathode are increased. The increase in the attenuation factor indicates that the charge-transfer current density in the cathode is more concentrated near the cathode-electrolyte interface. Consequently, the average activation overpotential also increases as it is directly proportional to its attenuation factor and inversely proportional to the cell temperature accordingly to Eq. (2.36). The increase in the charge-transfer current density in the

cathode near the electrolyte interface due to the increase in the activation overpotential in line with the study by Kulikovsky [7].

Both the FM and the DGM can be alternatively selected for the analysis of hydrogen fuel or indirect ammonia fuel. The FM can be considered for transporting gas species in the anode under hydrogen or indirect ammonia fueled cell/stack to reduce the computation cost.

5.3.3 Direct ammonia fuel

The ammonia decomposition reaction can take place in porous anode with the aid of Ni catalyst. The ammonia decomposition rate proposed by Kishimoto et al. [5] in Eqs. (2.81) and (2.82) depends on the cell temperature and partial pressure of gas species (ammonia and hydrogen). Although cell temperature is assumed to be constant along the cell thickness direction, the pressure gradient still occurs due to the sum of molar flux in a thick porous electrode as expressed in Eq. (2.70). Therefore, the ammonia decomposition rate varies along cell thickness direction.

This study employs a quasi-3D model with the 3D DGM model in anode mesh to analyze direct ammonia fuel. A validation step is required to ensure that the technique can represent the actual scenario. The results of direct ammonia fuel obtained from the developed numerical model with the DGM are compared with the results obtained from a 2D numerical model by Kishimoto et al. [8] in Fig. 5.4. This 2D numerical analysis was conducted resolving the gas transport in the streamwise and cell thickness directions in the electrodes and fuel/air channels. The calculation conditions for the validation are given in Table 5.5. The boundary conditions are the same as Table 3.2 except for the fluid and solid phase temperatures. No heat flux at the inlet, outlet and walls are considered for this validation. Note that the exchange current density used for this validation

purpose is replaced with the model proposed by Boer [9]. Also, the quasi-3D numerical analysis in this section is conducted without the electric insulators located at the upstream and downstream of the cell to apply the same calculation condition that was used by Kishimoto et al. [8]. A slight difference between the quasi-3D numerical analysis and the 2D numerical analysis is the porous metal foam assumed in the fuel and air channels in the quasi-3D calculations, whereas the channels in 2D numerical analysis consist of void volume.

Table 5.5. Calculation condition [8].

Parameters	
Inlet gas temperature [K]	973
Flow velocity of fuel [m s^{-1}]	0.250
Flow velocity of air [m s^{-1}]	1.50
Molar ratio of fuel (H_2 : H_2O : N_2 : NH_3)	0.030 : 0.010 : 0.020 : 0.940
Molar ratio of fuel (O_2 : N_2)	0.210 : 0.790

Figure 5.4(a) shows the comparison between the quasi-3D numerical model with the DGM and 2D numerical model in terms of the current-voltage curve. Although the characteristic of the current-voltage curves is different between these two models, the quasi-3D model with the DGM can reasonably reproduce the performance of the direct ammonia fueled cell. On the other hand, the distribution of the molar fraction of gas species in the fuel channel at a terminal voltage of 0.75 V shown in Fig. 5.4(b) agrees with the 2D numerical results by Kishimoto et al. [8]. The distribution of ammonia decomposition rate in the anode is shown in Fig. 5.4(c). It indicates that

the ammonia decomposition reaction actively occurs in the entire thickness of the anode near the upstream edge of the anode but the reaction rate is significantly decreased towards the downstream.

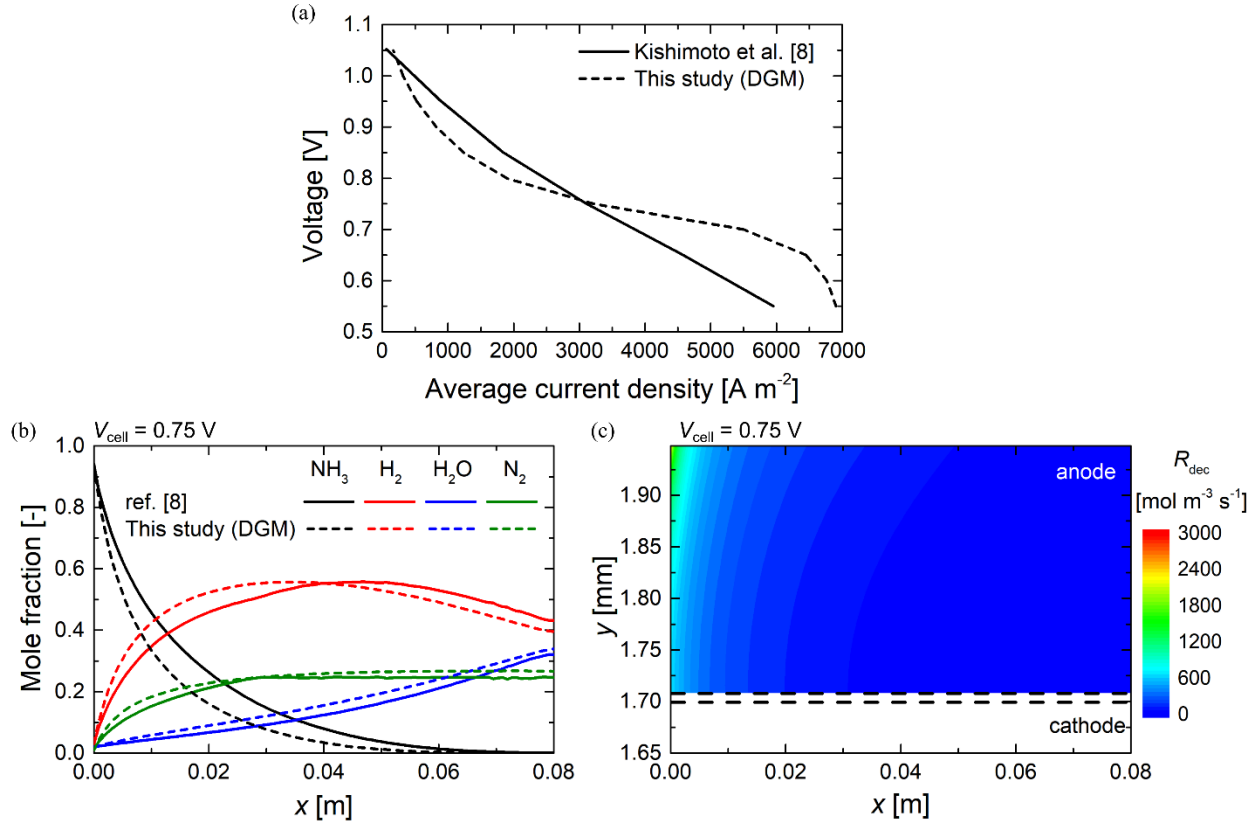


Fig. 5.4. Comparison between numerical results with the DGM and literature in terms of (a) current-voltage characteristics, (b) distribution of molar fraction in the fuel channel, and (c) NH_3 decomposition reaction rate in the anode.

In principle, the FM is not applicable to the gas transport in porous electrodes when a significant concentration change occurs due to chemical reactions. However, such a situation can be numerically avoided if the chemical reaction is assumed to occur only near the anode surface; the thickness of the reaction area can be called the “active thickness”. If the active thickness is substantially thin compared with the entire anode thickness, the FM can be used below the active

reaction area. A similar situation can be assumed for an electrochemical reaction with a relatively thin active thickness in the vicinity of the anode-electrolyte interface. The electrochemical reaction in a Ni/YSZ anode is estimated with an active thickness of 4.22 μm [10]. Because of the active thickness of the ammonia decomposition reaction $h_{\text{dec,ave}}$ is not available in open literature, it is estimated in this study as the equivalent thickness from the anode surface that decomposed the same total amount of ammonia within the anode in the DGM as follows,

$$h_{\text{dec,ave}} = \sum (R_{\text{dec,DGM}} V_{\text{local}}) / \sum (R_{\text{dec,FM}} A_{\text{local}}). \quad (5.1)$$

$R_{\text{dec,DGM}}$ and $R_{\text{dec,FM}}$ are the ammonia decomposition rate under the DGM and FM, respectively. Note that the ammonia decomposition rate under the FM is calculated on the basis of the concentration of gas species at the anode surface. V_{local} and A_{local} are the local volume of the anode mesh and surface area of the cell, respectively. The $h_{\text{dec,ave}}$ for the FM is iteratively calculated by Eq. (5.1) under a terminal voltage of 0.75 V so that desirable amount of ammonia decomposition is achieved. This $h_{\text{dec,ave}}$ is then applied for all terminal voltages under the analysis with the FM.

Figure 5.5 shows the comparison between the numerical results of the quasi-3D simulation with the FM employing $h_{\text{dec,ave}}$ and the results obtained from a 2D numerical model. It is found that the current-voltage curve in Fig. 5.5(a) from the FM are also apart from the 2D numerical analysis. Figure 5.5(b) shows the distribution of the molar fractions of gas species, in the fuel channel. It clearly shows that the differences between the two calculations in Fig. 5.5(b) are larger than those shown in Fig. 5.4(b). The average active thickness of the ammonia decomposition reaction in the quasi-3D simulation with the FM is estimated at 0.075 mm, which is approximately

31 % of the total anode thickness. It indicates that the assumption of the surface reaction is not realistic. The distribution of the local decomposition rate is shown in Fig. 5.5(c). A significant difference can be observed when the figure is compared with Fig. 5.4(c).

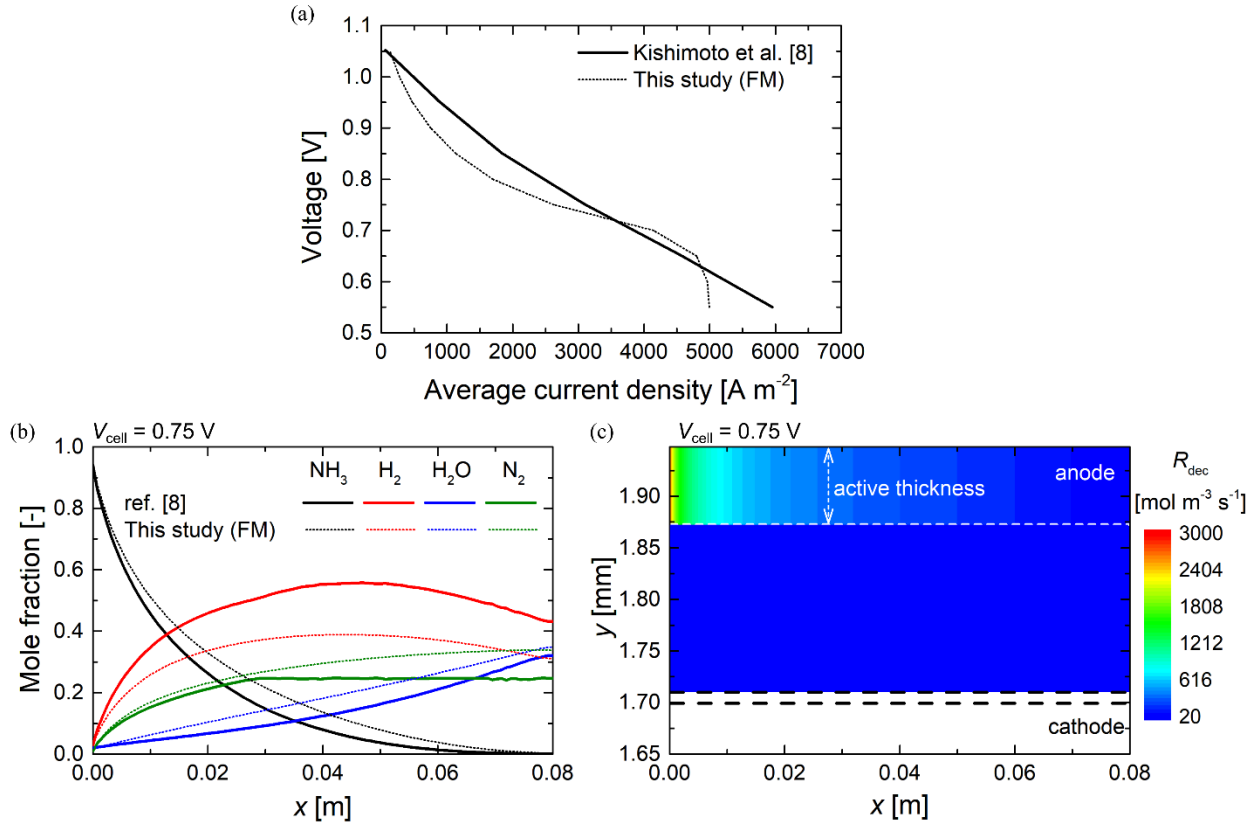


Fig. 5.5. Comparison between numerical results with the FM and literature in terms of (a) current-voltage characteristics, (b) distribution of molar fraction in the fuel channel, and (c) NH_3 decomposition reaction rate in the anode.

Noticeable differences between the DGM and the FM in the distribution of gas concentration in the fuel channel and the ammonia decomposition rate in the anode are found under direct ammonia fuel. The quasi-3D model with the DGM successfully captures the realistic non-uniform decomposition rate of ammonia in the anode. In conclusion, the implementation of the multi-

component DGM improves the capability of the quasi-3D model, making it possible to analyze gas species transport in the anode with chemical reactions such as ammonia decomposition, which cannot be achieved using the FM. Furthermore, the 16 layers of anode mesh are sufficient to provide reliable results.

5.4 Results and discussion

The factor affecting the ammonia decomposition rate is studied using an analytical approach. Then, the influence of the direct ammonia fuel is analyzed for cell X80Z60, which has the same geometry as in the stack experiment discussed in Chapter 3. Next, the influence of the ratio of pre-decomposed ammonia fuel is analyzed for the same cell. The influence of the aspect ratios ranging from 0.130 to 7.68 as well as the influence of the flow configuration are also analyzed.

5.4.1 Factors affecting ammonia decomposition rate

Direct ammonia fuel can be supplied to SOFCs with the aid of nickel as a catalyst in the porous anode. Kishimoto et al. [5] proposed the ammonia decomposition rate per nickel-pore interfacial area as in Eq. (2.83). From this equation, ammonia decomposition rate is directly proportional to both the partial pressure of ammonia p_{NH_3} as well as the cell temperature, and inversely proportional to the partial pressure of hydrogen p_{H_2} as described in Eq. (2.84). The partial pressure of gas species depends on the molar fraction of gas species and the local pressure P . Hence, the effect of the molar fraction of gas species, local pressure, and cell temperature toward ammonia decomposition are individually assessed.

The local pressure is varied accordingly to the location within the cell. The pressure at the outlet of the channel is fixed at atmospheric pressure, and the highest pressure is found at the inlet of the channel. The developed quasi-3D numerical model does not consider pressure gradient along the height of channel (y -axis). Therefore, the pressure at the anode surface is the same as the bulk pressure in the channel. The cell is an anode support cell, which consists of a thick layer of the anode. As a result, the pressure gradient that exists in the anode cannot be neglected. The anode-electrolyte interface has a higher pressure than the anode surface for a mixture of H_2 , H_2O , N_2 , and NH_3 . This is due to two factors; the relatively high molecular weight of steam to other gas species, as well as steam being transported out from the TPB. Figure 5.6 shows the influence of local pressure on the ammonia decomposition rate per unit surface density. The ammonia decomposition rate is linearly proportional to the local pressure P . Besides, the increment rate of ammonia decomposition for direct ammonia fuel is higher than any pre-decomposed ammonia fuel. This is because direct ammonia fuel has the highest partial pressure of ammonia with the lowest partial pressure of hydrogen. High ammonia decomposition rate near the fuel inlet region is also expected in high aspect ratio cells with a high-pressure loss in the fuel channel as shown in Fig. 4.4(a).

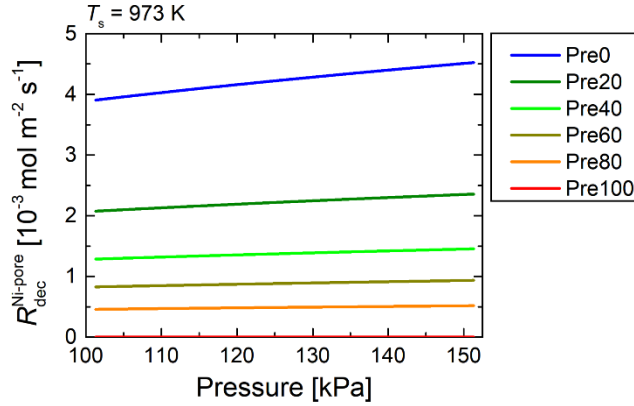


Fig. 5.6. Influence of pressure toward ammonia decomposition.

The effect molar fraction ratio of gas species especially hydrogen and ammonia are examined. The fuel is supplied with other gas species such as nitrogen and steam. Although the pre-decomposition of ammonia results in an increase in the nitrogen molar fraction, both the molar fractions of steam and nitrogen are fixed at 0.020 and 0.010, respectively. The balance of 97 % molar fractions consisted of hydrogen and ammonia with atmospheric pressure and cell temperature of 973 K. Figure 5.7 shows the influence of molar fractions of hydrogen and ammonia on the ammonia decomposition rate. It shows that the ammonia decomposition rate is approximately linear for the ammonia molar fraction below 0.6. Ammonia molar fraction beyond 0.6 results in a rapid increase in ammonia decomposition rate. Consequently, high ammonia decomposition rate at the upstream of fuel flow is based on the combination of the highest fuel pressure and the highest molar fraction of ammonia relative to other location in a cell. The ammonia decomposition rate is also expected to decrease rapidly towards midstream of fuel flow before a steady decline of decomposition rate due to the depletion of ammonia.

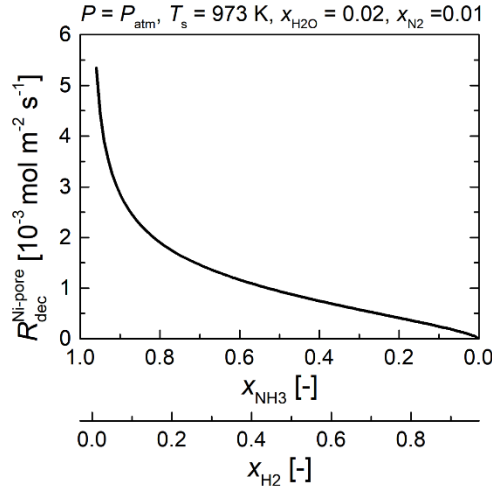


Fig. 5.7. Influence of molar fraction of hydrogen and ammonia toward ammonia decomposition.

The cell temperature where ammonia decomposition takes place is then studied. The highest ammonia decomposition rate occurs at the upstream of fuel flow and decreases towards its downstream. The cell temperature at the upstream has a reading close to the inlet temperature of the fuel channel. Low cell temperature is predicted near to the normalized length of $X' = 0$ due to the high ammonia decomposition rate. The cell temperature along the fuel streamwise direction is then expected to raise when the local generated exothermic heat is greater than the local endothermic heat. Figure 5.8 shows the influence of cell temperature on the ammonia decomposition rate. It is found that ammonia decomposes faster at higher temperatures. This implies that low ammonia decomposition rate is predicted after its significant high endothermic heat at the upstream.

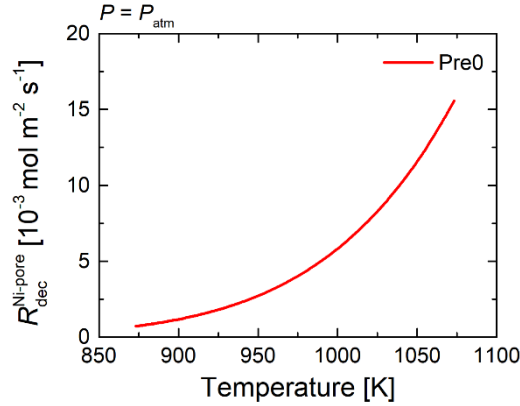


Fig. 5.8. Influence of cell temperature toward ammonia decomposition.

In short, the total pressure, molar fraction of species, and cell temperature play important roles in influencing the ammonia decomposition rate. Here, some hypotheses of the direct ammonia decomposition can be drawn. First, high ammonia decomposition rate can be observed at the normalized length of $X' = 0$ due to the high inlet pressure and the high molar fraction of ammonia. Second, the ammonia decomposition rate experiences a sharp decrease before the midstream region due to high decomposition rate. Third, the decomposition reaction extends its downstream, especially for a cell with high aspect ratio. High endothermic heat at the upstream is expected from the fast ammonia decomposition rate in a high aspect ratio cell. This further results in low cell temperature and molar fraction of ammonia before its midstream and prolongs the decomposition reaction.

5.4.2 Influence of direct ammonia fuel

The direct ammonia fuel can be supplied to the cell unit with the aid of nickel as a catalyst for ammonia decomposition reaction. The endothermic reaction of the ammonia decomposition

requires further attention as it reduces the cell temperature, which results in an increment of both activation and ohmic resistances of a cell. Figure 5.9 shows the exothermic and endothermic heat components generated in cell X80Z60 for both direct and indirect ammonia fuel under co-flow configuration. The external ammonia decomposer for indirect ammonia fuel is assumed to gain the required heat from an afterburner. It is found that the total exothermic heat generated under the direct ammonia fuel is higher than indirect ammonia fuel. The generated endothermic heat reduces the cell temperature and raises ohmic heat because of the increment of both activation and ohmic resistances in a cell. It is also found that the direct ammonia fueled cell is unable to self-sustain its operations at low fuel utilization of 0.2 as shown in Fig. 5.9(b). The overall exothermic heats are lower than the endothermic heat, which means that additional heat is required to sustain its operation. The exothermic heat components are directly proportional to the fuel utilization. On the other hand, the endothermic heat is not influenced by the fuel utilization. High ammonia decomposition reaction is expected near the upstream of fuel flow and rapidly decreased toward the midstream based on the discussion in the section 5.3.1. Although both ammonia decomposition rate and enthalpy change of ammonia for the endothermic heat in Eq. (2.89) are functioned against cell temperature; ammonia decomposition reaction actively occurs at its upstream. Hence, the ammonia decomposition reaction rate is strongly influenced by the inlet temperature and not influenced by the average cell temperature that is correlated to the fuel utilization.

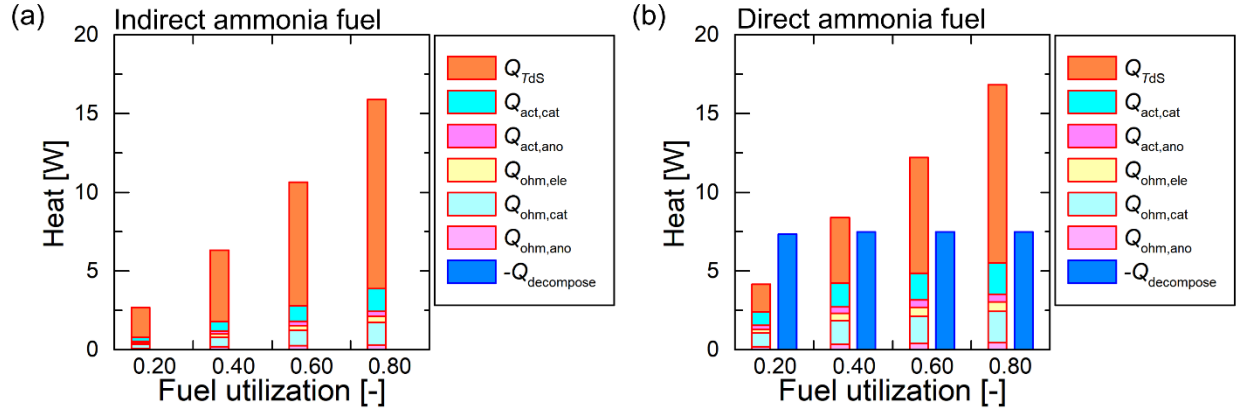


Fig. 5.9. Comparison of heat components for
(a) indirect ammonia fuel, and (b) direct ammonia fuel.

Figure 5.10 shows the voltage loss components in a cell fueled by direct and indirect ammonia fuel. The voltage losses in the anode, electrolyte, and cathode are represented by the green-, dark yellow-, and blue-lines, respectively. On the other hand, the voltage loss components of activation overpotentials, ohmic losses, and concentration overpotentials are shown by the solid-, dash-, and dot-lines with square-, circle-, and triangle-symbols, respectively. A significant increment of the anodic concentration overpotential, cathodic activation overpotential, and cathodic ohmic loss are found for the indirect ammonia fueled cell in Fig. 5.10(a). Although the anodic concentration overpotential for the direct ammonia fueled cell in Fig. 5.10(b) also has the same trend, both the cathodic activation overpotential and cathodic ohmic loss decreased with the increase in fuel utilization. The increased temperature is expected from the increment of fuel utilization, and it significantly reduces the ASRs for direct ammonia fueled cell. The extremely high cathodic activation overpotential and cathodic ohmic loss at the lowest fuel utilization in the direct ammonia fueled cell is in line with the previous observation in Fig. 5.9.

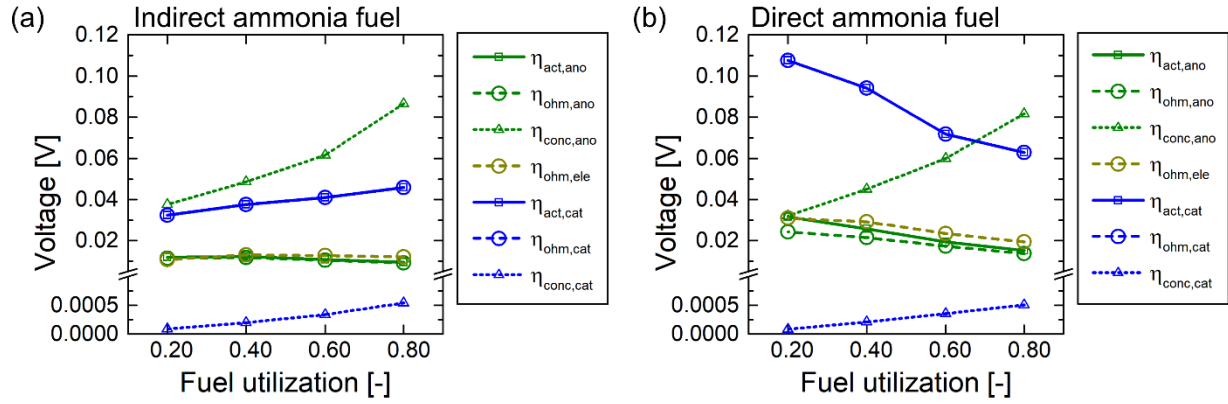


Fig. 5.10. Comparison of voltage loss components within

(a) indirect ammonia fueled cell, and (b) direct ammonia fueled cell.

The indirect ammonia fuel previously discussed is decomposed by an external ammonia decomposer, with the required heat coming from an afterburner. Here, the heat that is required to decompose the direct ammonia is discussed. An additional operating condition of the indirect ammonia fuel for cell X80Z60 is considered under TB3 as shown in Fig. 4.2. The inlet temperature and the operational temperature of external ammonia decomposer are also raised to 923 K. Figure 5.11 shows the comparison of performance between the direct and indirect ammonia fuel for fuel utilization of 0.2 to 0.8 with increments of 0.2. Regardless of the type of fuel, the EMF is low at a high fuel utilization. It is observed that the EMF of the direct ammonia fuel is the highest among the cases at low fuel utilization. On the other hand, the indirect ammonia fuel under TB3 is the highest for its EMF among the cases at high fuel utilization of 0.60 and 0.80. This is due to the low cell temperature caused by thermal radiation loss at the sidewalls as per Eq. (2.26). The high EMF does not provide an advantage for both operation conditions, high voltage losses are found and further result in low voltage efficiencies. The heat that provided for the external ammonia decomposer under TB4 is not taken into consideration as mentioned earlier. The direct ammonia

fuel performs better than the indirect ammonia fuel under TB3 at the highest fuel utilization. The indirect ammonia fueled cell under TB3 is capable of self-sustaining the external ammonia decomposer at fuel utilization of 0.80. Nevertheless, the direct ammonia fueled cell can be operated at fuel utility greater than 0.20. The changes in voltage losses for the direct ammonia fueled cell in Fig. 5.10(b) results in the maximum voltage efficiency at fuel utilization of 0.60 as observed in Fig 5.11.

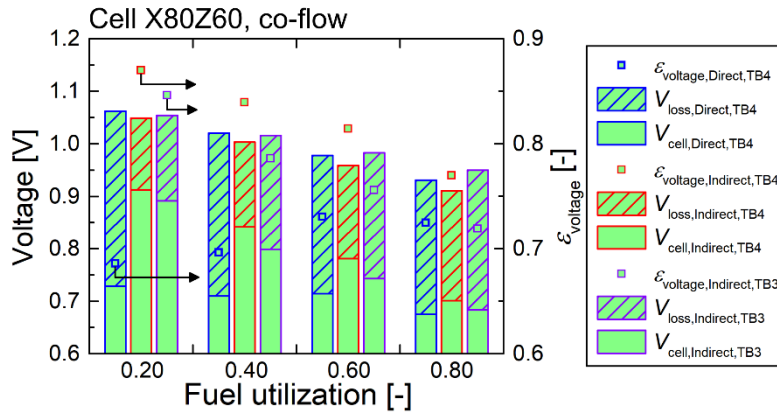


Fig. 5.11. Comparison of $\epsilon_{\text{voltage}}$, V_{cell} , and V_{loss} among direct and indirect ammonia fueled cell.

Overall, direct ammonia fueled cell has low performance due to low cell temperature caused by direct ammonia decomposition reaction. Significant low cell performance is found in the cell fueled by direct ammonia under low fuel utilization, which is opposite to the trend observed in a cell fueled by indirect ammonia fuel. Ammonia decomposition rate is not influenced by fuel utilization as previously discussed. Therefore, direct ammonia fueled cell has a high risk of failure to self-sustain its operations at low fuel utilization. The high cathodic activation and cathodic ohmic resistances require close attention, especially at low fuel utilization. The direct ammonia

fueled cell performs better than indirect ammonia fueled cell when considered together with the heat supplied to the decomposer.

5.4.3 Effect of the ratio of pre-decomposed ammonia

The direct ammonia fueled cell has a major disadvantage, especially at low fuel utilization. A portion of the fuel can be pre-decomposed in an external ammonia decomposer before being supplied to the SOFC. Here, the afterburner is again assumed to supply the required heat for external decomposer to maintain the fully thermal insulated wall for the SOFC. The pre-decomposed ammonia ratio is given in Table 5.4 for cell X80Z60 under co-flow configuration for fuel utilization of 0.20 to 0.80 with 0.20 increment.

The endothermic heat is not influenced by the fuel utilization as observed in Fig.5.9. The discussion of the heat components for the effect of the ratio of pre-decomposed ammonia focuses on the 0.2 fuel utilization. Figure 5.12 shows the comparison among the pre-decomposed ammonia ratios in terms of both the exothermic and endothermic heat components generated within cell X80Z60 for the 0.20 fuel utilization. It is found that the endothermic heat gradually increased with the amount of supplied ammonia (from left-side to right-side). The Pre80 case is capable of self-sustaining its operations. The strategy to use different pre-decomposed ammonia ratios does not efficiently help its operations at low fuel utilization.

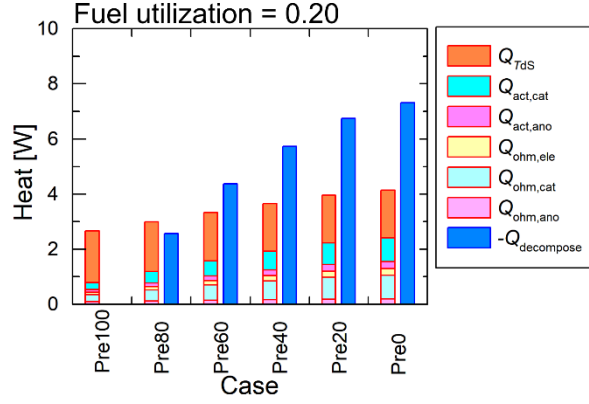


Fig. 5.12. Comparison of heat components among pre-decomposed ammonia ratios.

The performance of cell X80Z60 is analyzed statistically regarding the distributions of current density and cell temperature under fuel utilization of 0.2 to 0.8 with 0.2 increments. The temperature distribution within the electrical insulators is not considered for this process. The new grid system has 80 and 60 meshes in the x- and z-axis, respectively; one mesh covering an area of $1 \text{ mm} \times 1 \text{ mm}$ on the cell. The random Renka–Cline algorithm [11] is used to resample the dataset.

Figure 5.13 shows box charts with histograms of the distributions of current density for cell X80Z60 under the co-flow configuration. In general, the local current density within a cell should be kept close to the average current density to avoid extremely high local cell temperature and high local performance degradation in long-term operations. The narrow-spread in the overall range of current density distribution varies depending on the operation conditions. Pre100 has the narrowest-spread in the overall range of current density at fuel utilization of 0.20 and 0.40, while Pre80 and Pre0 have the narrowest-spread in the overall range of current density at fuel utilization of 0.60 and 0.80, respectively. Pre100 is second to Pre80 at 0.60 fuel utilization. Overall, the current density does not shift more than 60% of the required average current density.

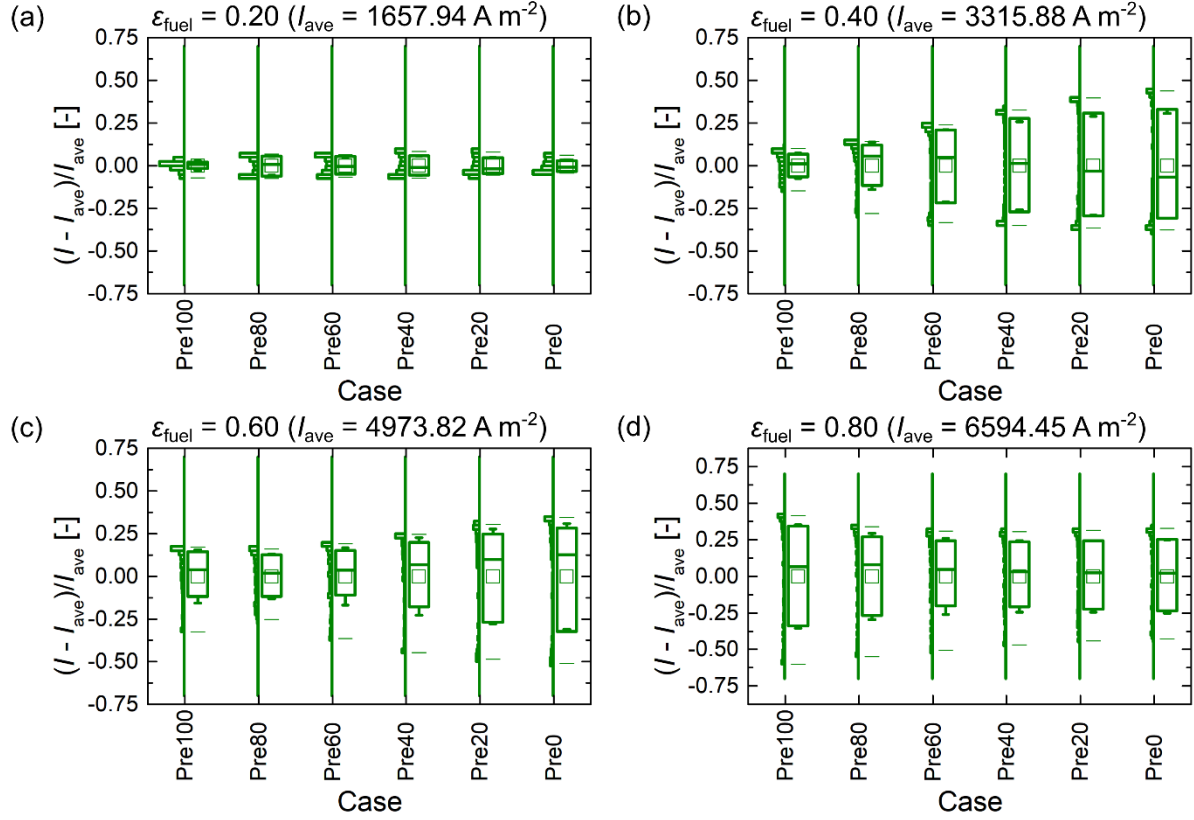


Fig. 5.13. Current density distributions at fuel utilization of (a) 0.20, (b) 0.40, (c) 0.60, and (d) 0.80.

Figure 5.14 shows box charts with histograms of the distributions of cell temperature for cell X80Z60 under co-flow configuration. Like the current density distribution, a narrow-spread characteristic in the overall range for the cell temperature distribution is preferred. This helps to reduce the risk of thermal cracking within a cell due to a large temperature gradient. High cell temperature has both the pros and cons for a cell. High cell performance can benefit from high cell temperature. On the other hand, this high cell temperature can increase the risk of thermal stress as well as accelerate the growth of SrZrO_3 [12–15] as discussed in section 2.4. The wide-spread in the overall range characteristic of the cell temperature distribution is observed for high fuel utilization. It is also found that a similar overall range with difference less than 25 K is found under

the same operating conditions. The highest mean cell temperature is found for the Pre100 due to the absence of endothermic reaction in the cell. The mean cell temperature gradually decreased with the increment of the supplied pre-decomposed ammonia. Close attention is required for the highly pre-decomposed and indirect ammonia fueled cell to avoid the formation of SrZrO_3 at high fuel utilization due to the high cell temperature.

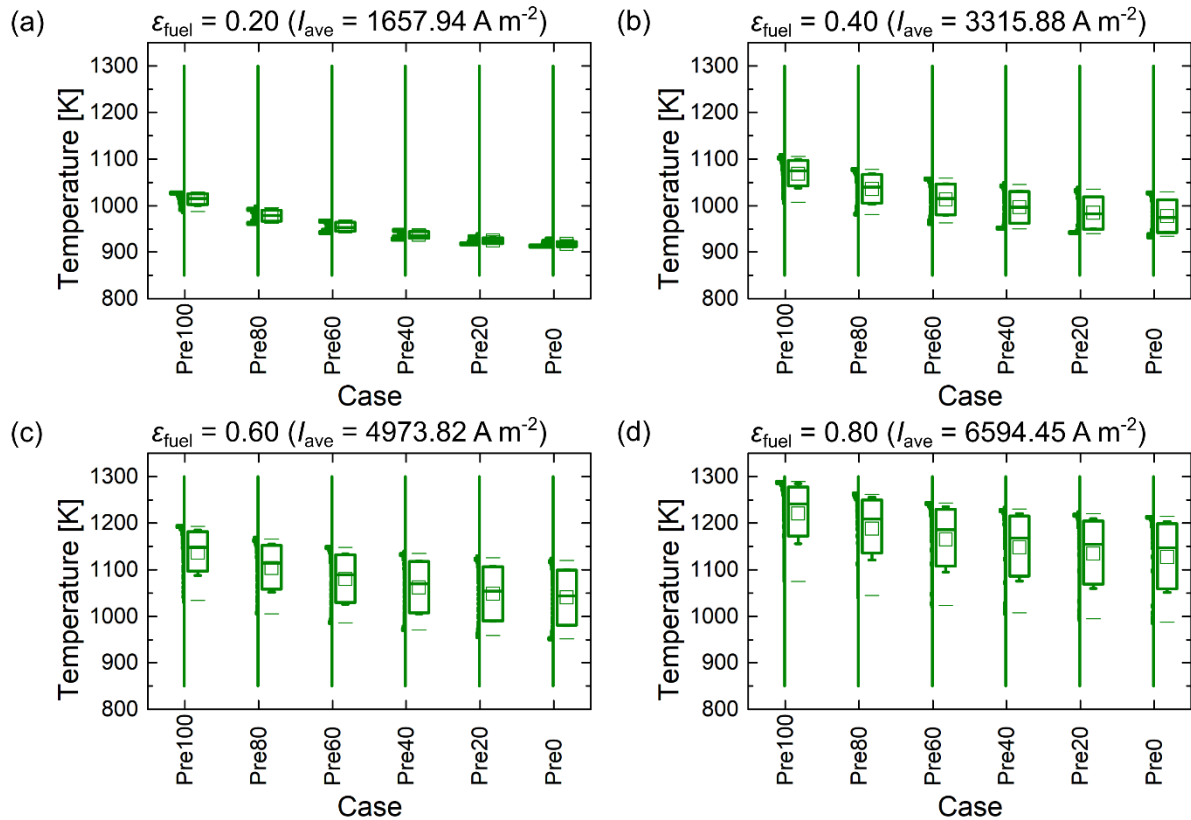


Fig. 5.14. Cell temperature distributions at fuel utilization of (a) 0.20, (b) 0.40, (c) 0.60, and (d) 0.80.

The performance of cell X80Z60 under various supplies of pre-decomposed ammonia is shown in Fig. 5.15. The Pre100 or the indirect ammonia fueled cell shows the highest voltage efficiency at the lowest fuel utilization. On the other hand, the highest voltage efficiency is shifted

toward high fuel utilization with the decrease in pre-decomposed ammonia. This is due to the significant drop in the voltage efficiency at the lowest fuel utilization, as explained in section 5.3.2.

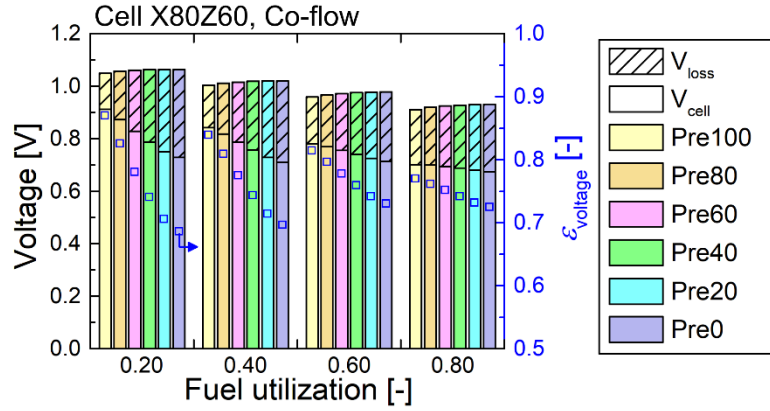


Fig. 5.15. Performance of the cells in terms of $\epsilon_{voltage}$, V_{cell} , and V_{loss} under co-flow.

The strategy to use different pre-decomposed ammonia ratio does not efficiently overcome the self-sustaining issue at low fuel utilization. The indirect ammonia fuel still has the highest cell performance. The highest voltage efficiency shifts from low to high fuel utilization of 0.60 with the decrease of the pre-decomposed ratio of ammonia.

5.4.4 Effect of cell aspect ratio

The effect of cell aspect ratio from 0.130 to 7.68 as shown in Fig. 4.1 is studied under a fully adiabatic thermal boundary conditions. The highly pre-decomposed ammonia fueled cell is capable of self-sustaining operations at low fuel utilization as previously discussed in section 5.3.3. Only direct and indirect ammonia fuel are considered for the effect of cell aspect ratio under the co-flow configuration.

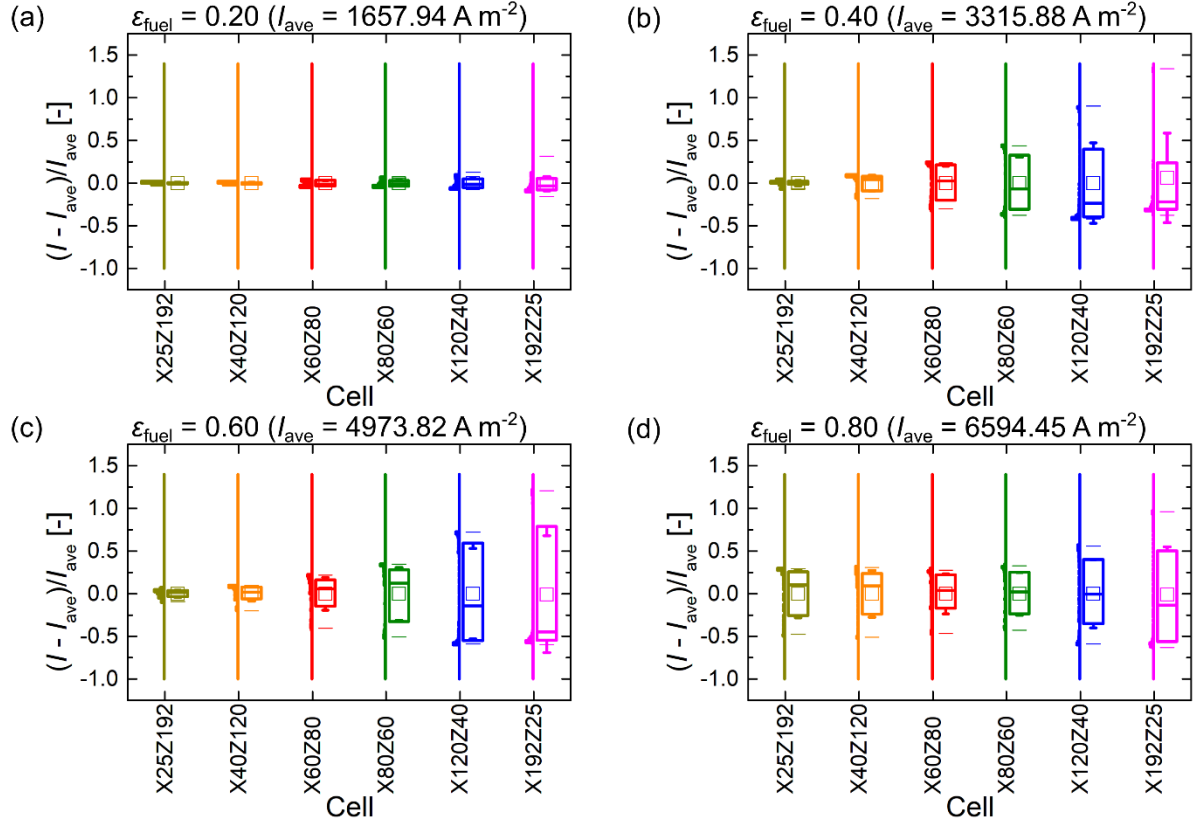


Fig. 5.16. Current density distributions of direct ammonia fuel at fuel utilization of (a) 0.20, (b) 0.40, (c) 0.60, and (d) 0.80.

The performances of the various aspect ratio cells are statistically analyzed regarding the distribution of current density and cell temperature, the same as the procedure discussed in section 5.3.3. Figure 5.16 shows box charts with histograms of the distribution of current density for the ammonia fueled cells with various aspect ratios under the co-flow configuration. It is found that high aspect ratio cell tends to withdraw the local current density twice as much as the required average current density. These areas can suffer significant performance degradation in the long-term. The wide-spread distribution is found in the overall range of the current density in high aspect ratio cell. The narrowest-spread is observed in the lowest aspect ratio cell from fuel utilization 0.20 to 0.60. At the highest fuel utilization, cell X60Z80 (0.750 aspect ratio) shows the

narrowest-spread, and it is followed by cell X80Z60 (1.33 aspect ratio). Hence, it can be concluded that cells with low aspect ratios tend to show a uniform distribution of the current density.

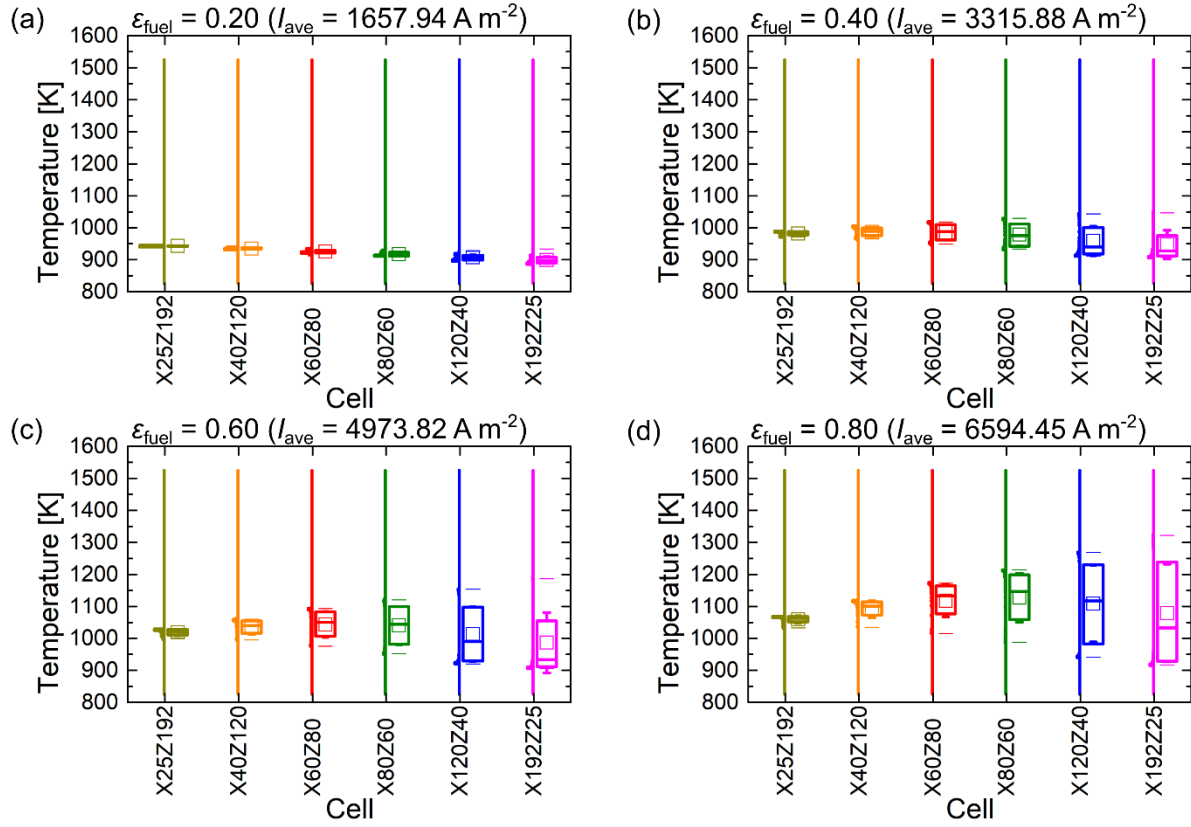


Fig. 5.17. Cell temperature distributions of direct ammonia fuel at fuel utilization of (a) 0.20, (b) 0.40, (c) 0.60, and (d) 0.80.

Figure 5.17 shows the box charts with histograms of the distribution of cell temperature for the direct ammonia fueled cells with various aspect ratios under co-flow configuration. The low aspect ratio cells tend to have a narrow-spread in the overall range for the cell temperature distribution. The wide dispersion of the cell temperature is found at high fuel utilization. Although a narrow-spread in cell temperature distribution is preferred to reduce the risk of thermal cracking, reasonably high cell temperature is still needed to achieve high cell performance. At the lowest

fuel utilization, the lowest aspect ratio cell of X25Z192 has the highest mean cell temperature. The cell with the highest mean cell temperature shifts to high aspect ratio cells with the increment of fuel utilization. On the other hand, cell X80Z60 has the highest mean cell temperature at the highest fuel utilization. It is also found that the cell with an aspect ratio greater than unity faces a high risk of SrZrO_3 growth due to the high maximum cell temperature.

Figure 5.18 shows the performance of various cell aspect ratios from 0.130 to 7.68 under both direct and indirect ammonia fuel. Direct ammonia fueled cell with an aspect ratio close to unity has the highest voltage efficiency. For example, cell X60Z80 (0.750 aspect ratio) at fuel utilization of 0.40 and 0.60, and cell X80Z60 (1.33 aspect ratio) at fuel utilization of 0.80. These observations are closely related to the observation in Fig. 5.16. None of the ammonia fueled cells can self-sustain their operations at the lowest fuel utilization of 0.20 under direct ammonia fuel based on the heat component analysis (Fig. 5.19), which will be discussed later. In general, all the cells fueled with direct ammonia have low voltage efficiency. All cells except X60Z80 and X80Z60 have a significant drop in voltage efficiency when supplied with direct ammonia fuel at the highest fuel utilization, which is explained by their cell temperature distribution. The low aspect ratio cell fueled by direct ammonia fuel has a uniform distribution of cell temperature. The mild endothermic heat at the upstream mildly decreases its cell temperature. On the other hand, high aspect ratio cells have much higher endothermic heat compared to low aspect ratio cells due to high inlet pressure.

A decrease in voltage efficiency is related to the endothermic heat that decreased the cell temperature in a cell when fueled by direct ammonia fuel. The decrease is less significant for a cell with an aspect ratio close to unity than others at the highest fuel utilization. It is also found that the cell with the highest aspect ratio experiences a significant drop in voltage efficiency under

co-flow configuration. The high ammonia decomposition rate at the upstream is expected due to a high-pressure loss in the channels for high aspect ratio cells. This results in a much lower cell temperature between the upstream and midstream of the fuel flow.

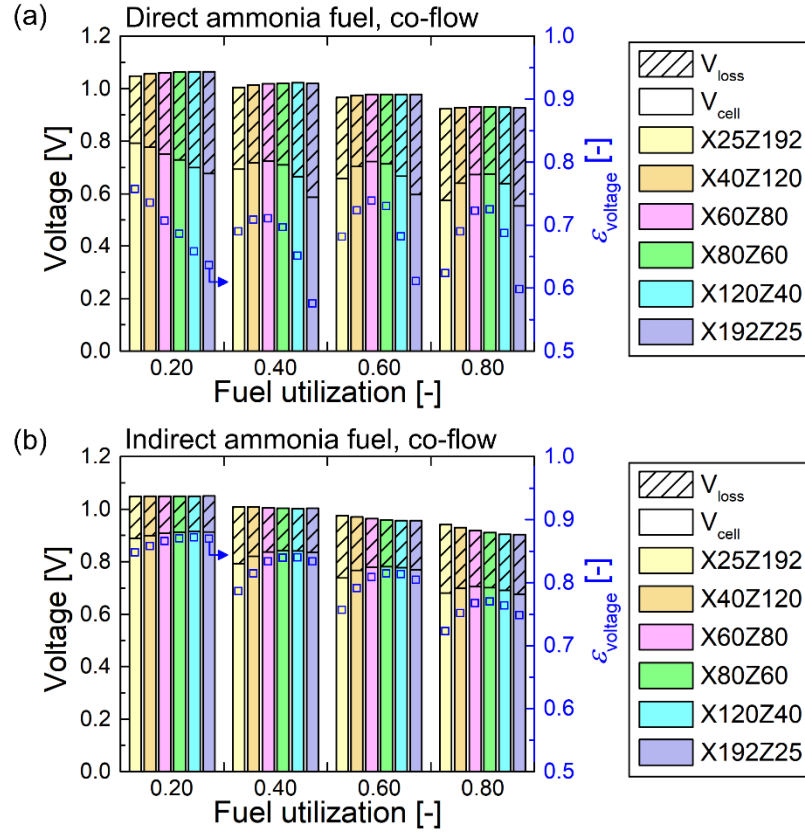


Fig. 5.18. Performance of the cells in terms of $\epsilon_{\text{voltage}}$, V_{cell} , and V_{loss} under co-flow for

(a) direct ammonia fuel, and (b) indirect ammonia fuel.

5.4.5 Effect of flow configuration

The flow direction of the air is changed from co-flow to counter-flow relative to the fuel flow as shown in Fig. 4.1 to study its effect on direct ammonia fuel. The counter-flow configuration

allows circulation of heat between the supplied fuel and air. This helps to raise the cell temperature and improve the voltage efficiency of a cell as observed in Chapter 4.

Figure 5.19 shows the comparison between the exothermic and endothermic heat components of various aspect ratios ranging from 0.130 to 7.68 supplied with direct ammonia fuel at low fuel utilization of 0.20 and 0.40. The results from these configurations are shown in the left-side and the right-side columns, respectively. It is similar to the previous discussion where the ammonia decomposition reaction is not influenced by fuel utilization. Similar values of the endothermic heat are observed between the configurations. The circulation of heat between the fuel and air increases cell temperature, which reduces ohmic heats caused by activation and ohmic resistances. Hence, low ohmic heats are observed under the counter-flow configuration. Its effect is prominent under high aspect ratio cell as the influence of the heat circulation between fuel and air is enhanced by the long flow path. The decrease in ohmic heats in the cells with an aspect ratio greater than unity results in its failure to self-sustain its operations when the endothermic heat is greater than the overall exothermic heat in the cell at 0.40 fuel utilization. Overall, close attention should be paid to direct ammonia fuel with the cell aspect ratio greater than unity at low fuel utilization.

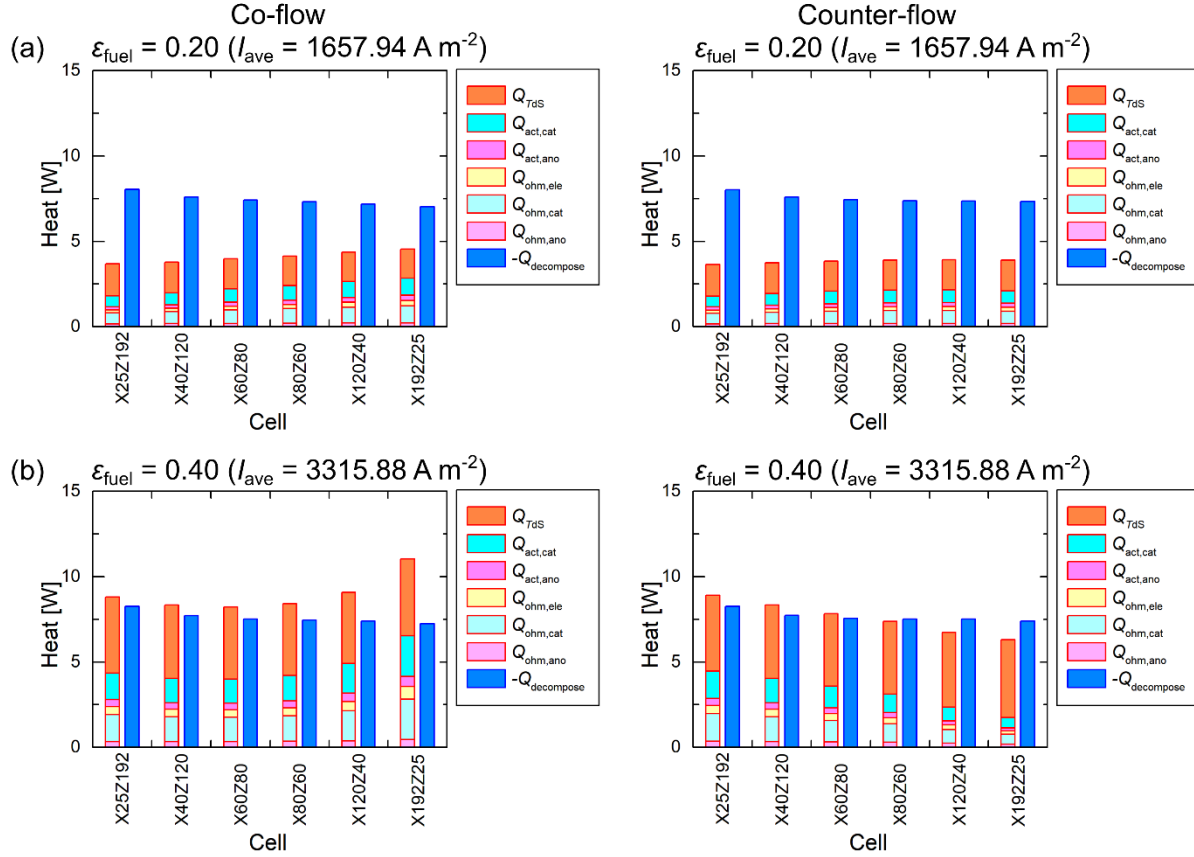


Fig. 5.19. Comparison of heat components under direct ammonia fuel among various aspect ratios at fuel utilization of (a) 0.20, and (b) 0.40.

A comparison is done on the distributions of current density and cell temperature at the highest fuel utilization of 0.80 between flow configurations. Both Figs. 5.20 and 5.21 show the box charts with histograms of the distributions of current density and cell temperature, respectively with various aspect ratios between the co- and counter-flow configurations. Figure 5.20 shows that counter-flow configuration helps to narrow the overall dispersion of current density distribution, especially in cells with high aspect ratios. The narrow-spread in the interquartile range for the highest aspect ratio cell is prominent. This helps to improve the performance of a high aspect ratio cell from suffering high voltage losses caused by the high local current density. Similarly, the

counter-flow configuration also helps enhance the narrow-spread in the overall range of the cell temperature as shown in Fig. 5.21. Almost all cells under counter-flow configuration have narrow-spreads in both the interquartile and overall ranges of the cell temperature owing to the heat circulation effect. The highest aspect ratio cell of X192Z25 shows a narrower-spread in the interquartile range and wider-spread in the overall range under counter-flow compared to co-flow. Both cells X120Z40 and X192Z25 have local cell temperatures beyond 1273 K. This temperature accelerates the lateral growth of SrZrO_3 along the GDC-YSZ interface [12–15]. Mean cell temperature can provide an overview of the performance of the cell. All cells except X25Z192 have high cell temperature distribution, reflected by the mean cell temperature under the counter-flow configuration.

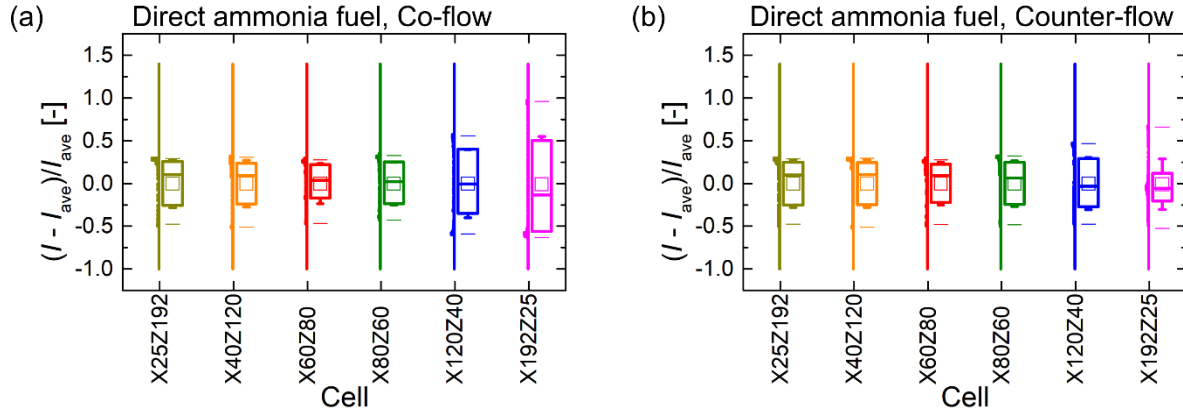


Fig. 5.20. Current density distributions of direct ammonia fuel at 0.80 fuel utilization under

(a) co-flow, and (b) counter-flow.

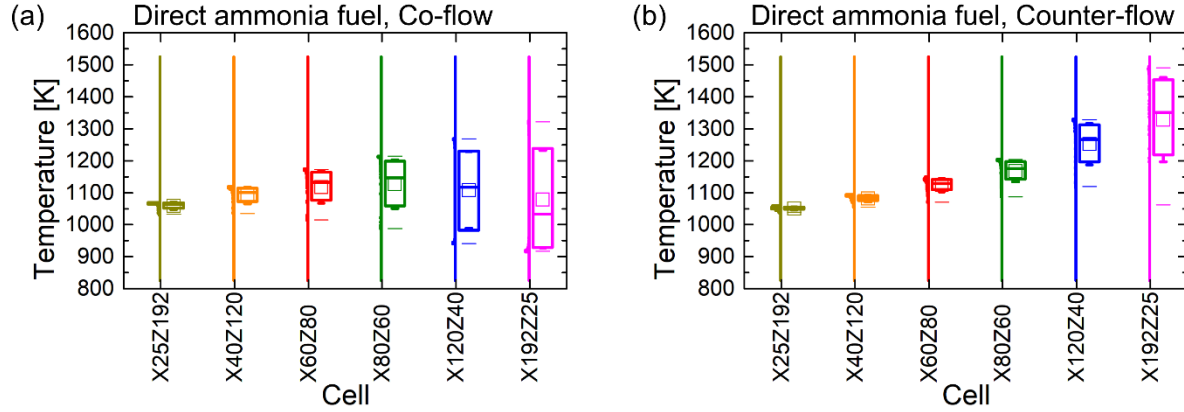


Fig. 5.21. Cell temperature distributions of direct ammonia fuel at 0.80 fuel utilization under (a) co-flow, and (b) counter-flow.

Figure 5.22 shows the performance of direct ammonia fueled cell with various aspect ratios at fuel utilization of 0.80 under both co- and counter-flow configurations. The cell X192Z25 has the highest voltage efficiency under counter-flow configuration. Besides, it is found that the cells perform very well under the counter-flow, except for cell X25Z192. This is due to the high cell temperature distribution as discussed in Fig. 5.21. The high cell temperatures reduce the voltage losses through activation and ohmic resistances, as well as improves the voltage efficiency of a cell. However, cell X120Z40 and X192Z25 suffer significant ohmic losses due to the lateral growth of the low ionic conductivity phase of SrZrO_3 . The numerical model is unable to handle the change of microstructure due to the growth of SrZrO_3 . Therefore, the increased ohmic loss is not reflected in Fig. 5.22.

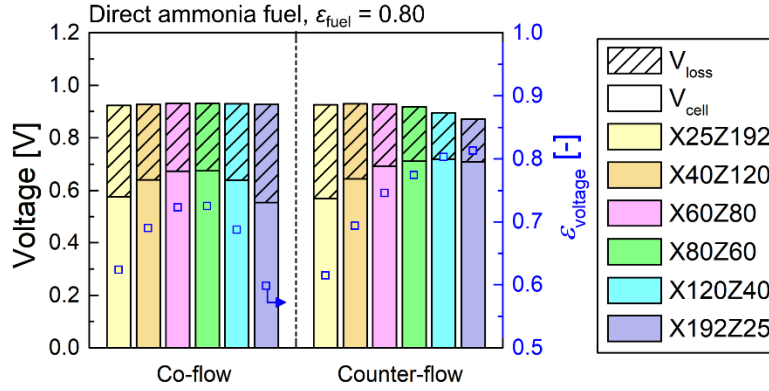


Fig. 5.22. Performance of the cells in terms of $\epsilon_{\text{voltage}}$, V_{cell} , and V_{loss} at 0.80 fuel utilization.

The performance of various aspect ratio cells except cell X25Z192 is improved under the counter-flow configuration. The circulation of heat between fuel and air increases the cell temperature. The heat circulation is more prominent under high aspect ratio cell than low aspect ratios. As a result, the performance of the cell with the high aspect ratio is improved under the counter-flow configuration. However, a cell with high cell performance has unfavorable maximum cell temperature that can accelerate the lateral growth of SrZrO_3 along the GDC/YSZ interface.

5.4 Conclusion for direct ammonia fueled cell

Additional 3D grid system in the anode known as anode mesh were introduced for the implementation of the multi-component dusty-gas model (DGM) for the transportation of gas species in the anode. This is used to handle the operation when the limitation of the Fick's model (FM) is reached with a significant change of concentration in the gas mixture. Grid independence analysis was conducted on the anode mesh and found to be strongly dependent on the reaction. A total of 16 mesh layers were used to handle both direct and indirect ammonia fuel. Both the FM

and the DGM was compared for the transport of gas species in the anode of a six-cell stack using the developed quasi-3D model. Both gas transport models can provide reliable results. The FM is recommended for the hydrogen or indirect ammonia fuel to reduce the computation cost, whereas the DGM is recommended to overcome the limitation of the FM when a significant change of concentration in the gas mixture occurs. The numerical results under direct ammonia fuel between the developed quasi-3D model with aid of anode mesh and present literature results was compared. The results were in line with the literature.

This work aims to understand the factors that influence ammonia decomposition rate, the influence of direct ammonia, the effect of supplied pre-decomposed ammonia, the effect of cell aspect ratio, and the effect of flow configurations between co- and counter-flow of a planar SOFC. First, an analytical approach was used to analyze factors affecting ammonia decomposition. Second, the influence of direct ammonia fuel was studied based on the developed quasi-3D numerical model of SOFC with the aid of additional anode mesh in the cell. Then, the strategy of supplying different pre-decomposed ammonia fuel was analyzed for the same cell. Next, the effect of the aspect ratios ranging from 0.130 to 7.68 under the direct ammonia fuel was studied. Finally, the influence of co- and counter-flow configurations on the cell with the various aspect ratio under direct ammonia fuel was explored.

Ammonia decomposition rate depends on the concentration of gas species, especially hydrogen and ammonia, cell temperature, and the available nickel-pore interfacial area. High ammonia decomposition rate can be achieved by either a high concentration of ammonia, low concentration of hydrogen, high inlet temperature, high nickel-pore interfacial area, or combination of them. High ammonia decomposition rate is observed in the upstream of fuel flow especially in the high aspect ratio cell due to the high-pressure loss in channels.

Direct ammonia fueled cell has low cell performance due to the endothermic heat from the ammonia decomposition reaction. Close attention should be given to direct ammonia fueled cell at low fuel utilization. The higher endothermic heat than exothermic heat at low fuel utilization results in high cathodic activation and cathodic ohmic resistances. Such problems under low fuel utilization are difficult to overcome using partial pre-decomposed ammonia. An extremely high amount of pre-decomposed ammonia ratio is required to sustain operations at low fuel utilization.

The influence of gas species concentration on direct ammonia fuel was further studied in cells with various aspect ratios ranging from 0.130 to 7.68 under co-flow configuration. The cells with aspect ratios close to unity have higher resistance against the decrease in voltage efficiency when supplied with direct ammonia fuel. A significant decrease in voltage efficiency affects the highest aspect ratio cell. The high-pressure loss in the channel enhances the ammonia decomposition rate and results in much lower cell temperature at the upstream. This low cell temperature can be improved by the circulation of heat between fuel and air under the counter-flow strategy. The effect is more prominent under high aspect ratio cell than low aspect ratios. However, close attention should be paid to its maximum cell temperature.

Ammonia is an alternative option to replace hydrogen as a fuel for SOFC. The mild endothermic heat from direct ammonia fuel can enhance stack cooling. The local extremely low cell temperature can be avoid through the control of the ammonia decomposition rate and ratio of pre-decomposed ammonia. Both the geometry aspect ratio of cell and air flow influence the ammonia decomposition reaction rate through the concentration of species and cell temperature near fuel upstream.

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Chapter 6

Direct and indirect ammonia fueled stack

6.1 Introduction

The single repeating units as shown in Fig. 2.1(a) can be stacked together to form an SOFC stack to provide the required electrical output. In this case, the difficulty of thermal management of an SOFC stack is increased as the total heat released from the stack is multiplied. High-operating temperatures are preferable for SOFCs to reduce ohmic losses and activation overpotentials to achieve higher cell efficiency. Conversely, high-operating temperatures cause high stress in SOFC components owing to the difference in the thermal expansion coefficients among the cell components. Moreover, the high-operating temperature is the main factor that accelerates the diffusion of Sr and Zr for the formation of low ions conductivity SrZrO_3 [1–4]. The decomposition of ammonia is an endothermic process, which helps to improve stack cooling under direct ammonia fuel.

The air channel of an SOFC is responsible not only for supplying oxygen to the cell but also for removing excess heat generated from electrochemical reactions. Co-, counter-, and cross-flow configurations of the air flow relative to the fuel flow are among the conventional flow configurations for a planar SOFC or an SOFC stack. There have been extensive studies on the effect of these flow configurations at the cell level. These SOFC cells were supplied with either humidified hydrogen [5–7] or internally reformed methane [8–10]. All these flow configurations

have advantages and disadvantages. A counter-flow with a high average cell temperature can maximize the performance of a cell but has the major drawback of an inhomogeneous temperature distribution [8]. Nakajo et al. [11] reported that a counter-flow could extend the lifespan of a cell operated with a partially reformed methane fuel compared with a co-flow. A cross-flow is preferred by SOFC manufacturers owing to the simplicity of the manifold design [12]. However, local fuel depletion during operation at high fuel utilization is more likely to occur under cross-flow configuration than other configurations [6]. Fardadi et al. [13] reported that cross-flow has the highest peak temperature and the largest temperature gradient, which can lead to high thermal fatigue and short lifespan of cell/stack as compared to co- and counter-flow. A co-flow tends to have homogeneous distributions of current density [14] and cell temperature [15]. Therefore, the selection of the flow configuration for an SOFC cell and stack affects not only their performance but also their durability. There is still the possibility of constructing new flow configurations in a stack assembly. Alternating both fuel- and air-flows within the ribs of each cell was proposed by Fardadi et al. [13] to overcome the high peak temperature and large temperature gradient in cross-flow. However, such design requires an extremely complex manifold design due to many ribs per cell. Such complexity can be reduced by alternating the air flows in every other cell of a stack by either parallel (streamwise) or perpendicular (spanwise) direction to the fuel flow.

All the computational works related to fully three-dimensional (3D) models by previous researchers had the common difficulty of being expensive in analyzing cross-flow configuration [16–18]. Therefore, works have been limited to the cell level. Some researchers have reduced the computation cost. Yuan [19] developed a two-dimensional (2D) numerical model in the streamwise and spanwise directions of flows to solve electrochemical reaction, mass balance, and energy balance equations. The conservation of energy in interconnects was derived by considering

the heat exchange between interconnects and working fluids as well as interconnects and neighboring cells. He et al. [20] implemented Monte Carlo simulation of a 2D spatially-smoothed non-isothermal model in a 3D planar SOFC stack to allow fast computation. The model claimed to have the capability of solving a stack consisting of hundreds of cells without incurring high computation cost. However, this 2D spatially-smoothed non-isothermal model is limited to co- and counter-flow configurations. Lai et al. [15] proposed a quasi-two-dimensional model capable of analyzing an SOFC stack with up to 96 cells, although the model is limited to co- and counter-flows. The model was validated to Recknagle et al. [6] and was capable of reproducing the effect of flow configuration (co- or counter-flow) under single-cell operation. However, no further work on the effect of flow configuration has been conducted for stack operations. As a new approach to overcoming the difficulty associated with stack-level simulations, a quasi-3D model with actual microstructure information of the electrodes is developed, and it is successfully reproduced experiments conducted using a six-cell stack. The quasi-3D model can analyze flows not only in the streamwise direction but also in the spanwise direction of a cell/stack, making it applicable for a wide variety of flow configurations as well as conventional co-, counter-, and cross-flow configurations. Additionally, the developed quasi-3D numerical model with the aid of the anode mesh allows the implementation of the DGM to analyze ammonia decomposition reaction within an anode.

As an important application of the model, the present work aims to study the effects of stack cooling with various air flow configuration in an eight-cell SOFC stack under both direct and indirect ammonia fuel. Flow configurations with alternating air flow in parallel and perpendicular to the fuel flows are considered in addition to conventional co-, counter-, and cross-flow configurations. In this study, the distributions of both the current density and cell temperature are

discussed statistically regarding the overall dispersion and its interquartile range. This approach aims to provide both qualitative and quantitative measurements for distributions. Moreover, the performance of stack subjected to the stack cooling from air flow is evaluated.

6.2 Calculation and boundary conditions

This study is conducted on an eight-cell stack. Each cell unit, consisting of top and bottom separators, fuel, and air channels, and a positive-electrolyte-negative assembly (PEN), is modeled as shown in Fig. 6.1. The PEN is treated as a dense solid layer. Both the fuel and air channels are filled with metal foam as a current collector. Figures 6.1(a) to (c) correspond to the conventional co-, counter-, and cross-flow configurations, while Figs. 6.1(d) and (e) show the cases with alternating air flow in the parallel (streamwise) and perpendicular (spanwise) directions to the fuel flow, respectively. Each cell has an aspect ratio of unity, an active area of 4900 mm^2 , and the thicknesses of 0.240, 0.008, and 0.050 mm for the Ni/YSZ cermet anode, YSZ electrolyte, and LSCF-GDC cathode, respectively. The thicknesses of the other components within a single repeating unit are 0.500, 1.40, and 0.700 mm for the separator, air channel, and fuel channel, respectively. The microstructure information is given in Table 3.1, quantified by Brus et al. [21,22] from a cell manufactured by SOLIDpower S.p.A.

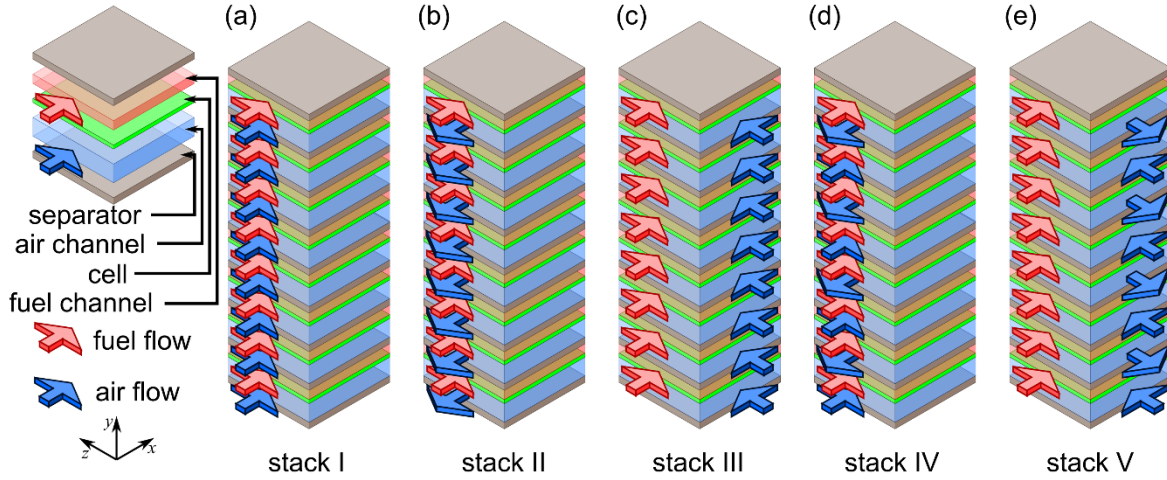


Fig. 6.1. Flow configurations in an eight-cell stack. (a) co-flow, (b) counter-flow, (c) cross-flow, (d) alternate air flow in the parallel direction to the fuel flow, and (e) alternate air flow in the perpendicular direction to the fuel flow.

Galvanostatic control is applied to the stacks with average current densities of 1500, 3000, 4500, and 6000 A m⁻², equivalent to fuel utilization of 0.193, 0.386, 0.579, and 0.772, and air utilization of 0.0308, 0.0615, 0.0923, and 0.123, respectively. The total pressure at the outlets of both channels is fixed at atmospheric pressure. The stack is assumed to be thermally insulated by applying an adiabatic condition at the stack surfaces. The boundary conditions are given in Table 6.1. The potential electrical difference between the top and bottom separators is the terminal voltage of the stack and is iteratively tuned to achieve a pre-determined average current density.

Both direct and indirect ammonia fuel are supplied with the same amount of fuel. The volumetric flow rates of 0.200 and 0.392 L/min/cell in the standard state with mole fraction ratios (H₂: H₂O: N₂: NH₃) of 0.030: 0.020: 0.010: 0.940 and 0.735: 0.020: 0.245: 0 are supplied to the fuel channel under direct and indirect ammonia fuel, respectively. The same volumetric flow rate of 4.2 L/min/cell in the standard state with mole fraction ratios of O₂: N₂ = 0.210: 0.790 is supplied

to the air channel. Both air and fuel are supplied to the stack at the same temperature and depends on the analysis conducted through the inlet.

Table 6.1. Boundary conditions.

Quasi-3D:	Inlet	Outlet	Wall	Separators
u	$u = u_{\text{in}}$	$\frac{\partial u}{\partial x} = 0$	$u = 0$	-
w	$w = 0$	$\frac{\partial w}{\partial x} = 0$	$w = 0$	-
Y_i	$Y_i = Y_{i, \text{in}}$	$\frac{\partial Y_i}{\partial x} = 0$	$\frac{\partial Y_i}{\partial z} = 0$	-
ϕ	$\frac{\partial \phi}{\partial x} = 0$	$\frac{\partial \phi}{\partial x} = 0$	$\frac{\partial \phi}{\partial z} = 0$	-
T_f	$T_f = T_{\text{in}}$	$\frac{\partial T_f}{\partial x} = 0$	$\frac{\partial T_f}{\partial z} = 0$	-
T_s	$\frac{\partial T_s}{\partial x} = 0$	$\frac{\partial T_s}{\partial x} = 0$	$\frac{\partial T_s}{\partial z} = 0$	$\frac{\partial T_s}{\partial y} = 0$
Anode mesh:	Anode surface	Electrolyte interface	Walls	
P	$P = P_{\text{channel}}$	$\frac{\partial P}{\partial y} = 0$	$\frac{\partial P}{\partial x} = 0$	$\frac{\partial P}{\partial z} = 0$
x_i	$x_i = x_{i, \text{channel}}$	$\frac{\partial x_i}{\partial y} = 0, i \neq \text{H}_2, \text{H}_2\text{O}$ $N_i = 0, i \neq \text{H}_2, \text{H}_2\text{O}$	$\frac{\partial x_i}{\partial x} = 0$	$\frac{\partial x_i}{\partial z} = 0$
N_i	Equation (2.78)	$N_{\text{H}_2} = -I/2F$ $N_{\text{H}_2\text{O}} = I/2F$	$N_{i,x} = 0$	$N_{i,z} = 0$

The FM is applied for the transportation of gas species in an anode when the stack is fueled by the indirect ammonia fuel to reduce computation cost. Therefore, a total of $103 \times 35 \times 103$ meshes are used in the model for an eight-cell stack. DGM is applied for the transportation of gas species in an anode for the analysis of direct ammonia fuel to handle the change of concentration in a mixture due to ammonia decomposition reaction. A total of 16 layers of anode mesh for each cell are used based on the discussion in Chapter 5.

6.3 Results and discussion

The eight-cell stacks are named stacks I to V according to their air-flow configurations as shown in Fig. 6.1. The performance of the stacks is analyzed in terms of average voltage efficiency and distributions of the current density, cell temperature, and hydrogen mole fraction in the fuel. Galvanostatic control is applied to the stacks with fuel utilization of 0.193, 0.386, 0.579, and 0.772.

6.3.1 Indirect ammonia fuel

The performance of indirect ammonia fuel stack is first analyzed with inlet temperature of 923 K. Figure 6.2 shows the distributions of the current density (1st column), cell temperature (2nd column), and hydrogen mole fraction (3rd column) in the 4th cell from the bottom of the eight-cell stack fueled with indirect ammonia fuel at fuel utilization of 0.772. Red and blue arrows, respectively show the corresponding fuel- and air-flow directions for the 4th cell. The dashed blue arrows represent the air-flow direction for the neighboring cells (3rd and 5th cells). It is found that stack III at this fuel utilization does not exhibit perfect convergence according to its current density

distribution in the 4th cell. The fuel is nearly depleted near the normalized coordinate of (1.0, 1.0). This is the reason why the fuel utilization of 0.772 is set as the highest in this study. The maximum local current density in the 4th cell in stacks I to V is 8707 A m⁻² ($X' = 0.69$), 10143 A m⁻² ($X' = 0.11$), 11826 A m⁻² ($X' = 0.20$, $Z' = 0.99$), 7694 A m⁻² ($X' = 0.33$), and 8157 A m⁻² ($X' = 0.29$, $Z' = 0.53$), respectively. The alternate flow configurations of stacks IV and V not only shift the location of the maximum current density towards the midstream of the air flow but also lowered the maximum current density within the cell. A lower maximum current density within the cells under galvanostatic operation indicates a more homogenous distribution of the current density with a low deviation from the average current density of 6000 A m⁻².

The maximum cell temperature in the 4th cell in the alternate flow configurations shifted to the midstream of the air flow compared to the conventional flow configurations. The maximum cell temperature in the 4th cell in stacks I to V is 1092 K ($X' = 1.0$), 1075 K ($X' = 0.16$), 1105 K ($X' = 0.40$, $Z' = 1.0$), 1140 K ($X' = 0.56$), and 1116 K ($X' = 0.64$, $Z' = 0.51$), respectively. Because the stack surface is thermally insulated in this study, the heat generated in the stack is removed by fuel- and air-flows. The cooling effect of fuel flow is weaker than that of air-flow owing to the small flow rate and low heat capacity; the stack is mainly cooled by air flow. In stacks I and III, the temperature of the air flow in an arbitrary cell in the stack increases as it flows downstream while accumulating the generated heat. The distributions of the local temperature in Fig. 6.2 follows the same trend. In stack II, the air flow is cooled by the fuel flow near the exit of the air channel, which is the inlet of the fuel channel, resulting in the cell temperature distribution being at a maximum at approximately $X' = 0.16$. This means that some of the heat energy accumulated in the air flow is circulated back to the stack by the fuel flow. In stacks IV and V, the circulation of heat energy is more prominent because it also occurs between the air flows. The heat energy

stored in the air-flow of an arbitrary cell is transferred to the air-flows of the neighboring cells flowing in the opposite direction. The air-to-air circulation of heat energy enhances the symmetry of the temperature distribution and shifts the high-temperature region to the cell center as shown in Fig. 6.2.

Another important difference between the conventional configurations (stacks I – III) and the alternate flow configurations is the existence of a low-temperature region. In Fig. 6.2, a thick blue region is observed near the air inlet region in stacks I to III, while it is not observed in stacks IV and V. In stacks IV and V, the main coolant (air) is divided into two streams and supplied to the stacks from two different directions. The cooling effect of one side is naturally reduced, which prevents the formation of low-temperature regions.

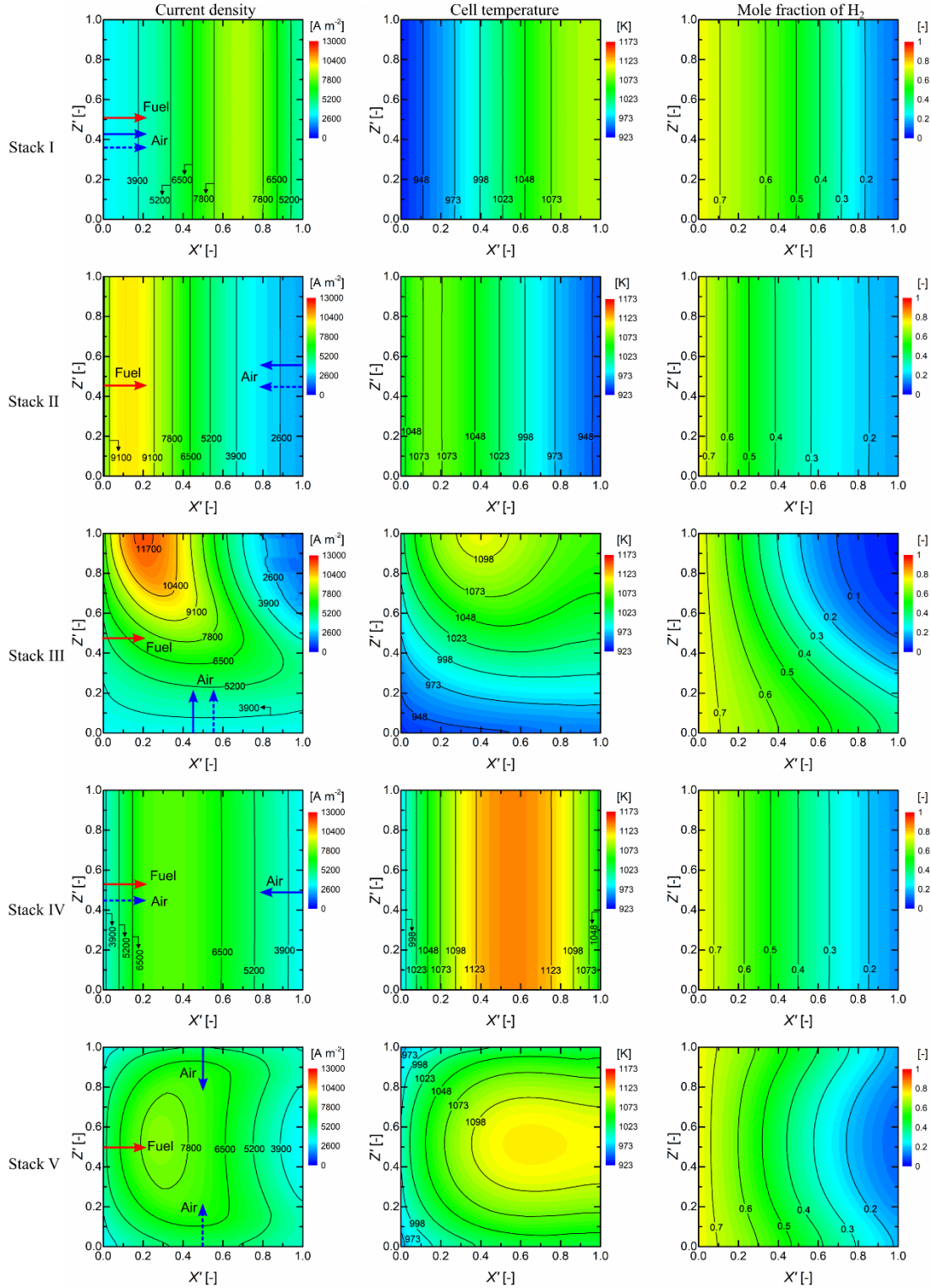


Fig. 6.2. Distributions of current density, cell temperature, and hydrogen mole fraction for the 4th cell of the stacks at a fuel utilization of 0.772.

Fuel depletion is a serious problem during high-fuel-utilization operation of an SOFC cell and stack and should be avoided. Fuel depletion not only results in a significant increase in the concentration overpotential but also triggers nickel oxidation in the anode and increases the risk of cracking at the thin electrolyte [23]. The distribution of the hydrogen mole fraction helps to identify the risk of fuel depletion at the downstream of the fuel channel. The right column in Fig. 6.2 shows the distribution of hydrogen mole fraction within the 4th cell of the stacks. Stacks I, II, and IV have the lowest hydrogen concentrations of 0.114, 0.169, and 0.151, respectively, at the outlet of the fuel channel ($X' = 1.0$), while stack V has values of 0.101 at (1.0, 0.53). The lowest hydrogen concentration observed at the outlet of the fuel channel in stack III is close to zero. On the other hand, stack V with an alternating air flow in the perpendicular direction to the fuel flow has a minimum hydrogen concentration of more than 0.1, which indicates that stack V does not exhibit fuel depletion. Overall, an alternating air flow in the perpendicular direction to the fuel flow, as in stack V, helps to reduce the risk of fuel depletion as compared to stack III, which allows the cell or stack to operate at high fuel utilization.

The distribution of the current density and cell temperature in stacks I to V is statistically analyzed. In preparation for the statistical analysis, the local current density distribution is resampled on a uniform grid system in the xz -plane because each data used in the statistical analysis must have the same weighting or represent the same area on a cell. The new grid system has 70 meshes in each direction; one mesh covers an area of $1 \text{ mm} \times 1 \text{ mm}$ on the cell. The random Renka–Cline algorithm [24] is used to resample the dataset. Figure 6.3 shows the box charts with histograms of the current density distribution for all the eight cells, i.e., the entire stack. Figure 6.3 (a) shows that the nonuniformity of the current density in stack II is the largest among the five stacks at an average current density of 1500 A m^{-2} . Nevertheless, the highest and the lowest values

remain within 20% of the average value, showing that nonuniformity of the local current density is not a significant problem under at low average current density. The dispersion increases with the average current density, showing that the nonuniformity becomes a severe problem when the average current density is high.

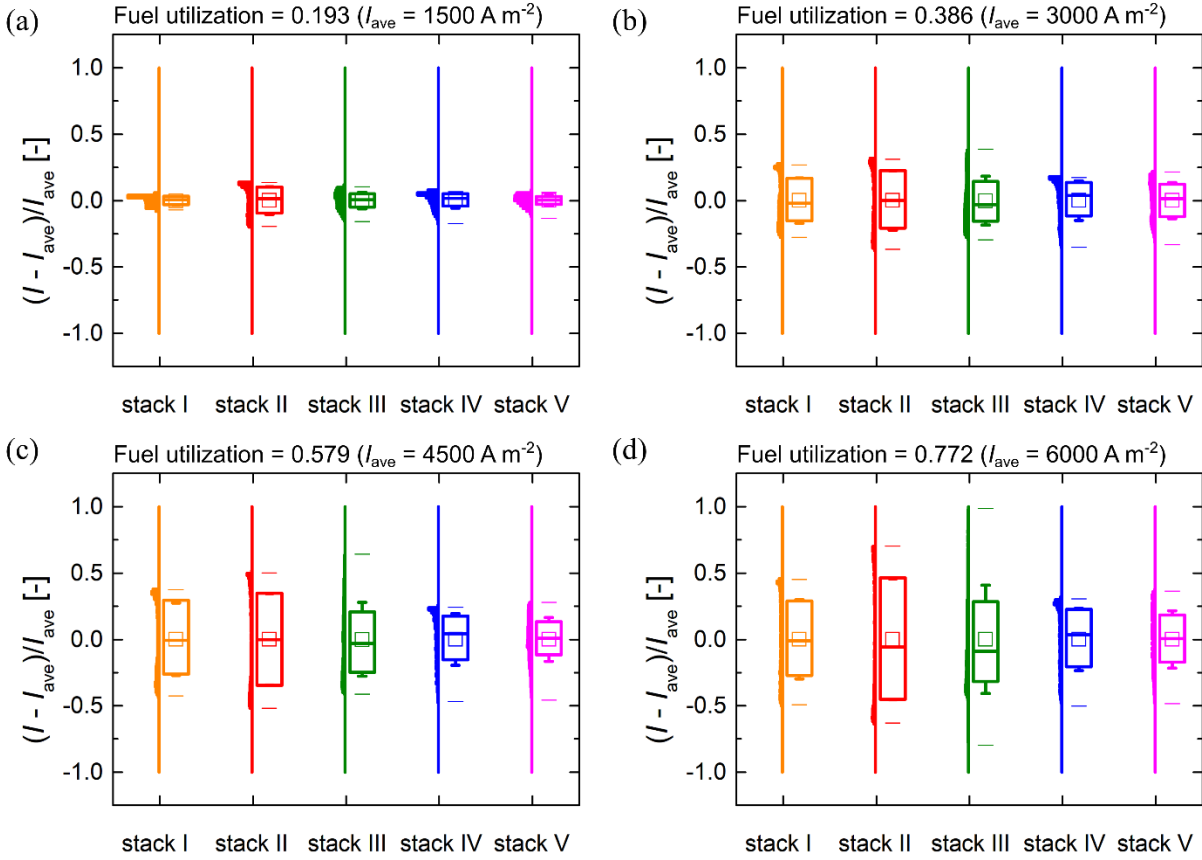


Fig. 6.3. Current density distributions for entire stack at fuel utilization of (a) 0.193, (b) 0.386, (c) 0.579, and (d) 0.772.

The mean values of the current density in all the stacks are the same for the same value of fuel utilization as shown in Fig. 6.3. In contrast, the median of the current density varies depending

on the current density distribution. At the highest fuel utilization of 0.772, the median value in stack V is close to the mean. This indicates that stack V has a reasonably symmetrical distribution of the current density without significant skewness. On the other hand, the current distributions in stacks I, II, and III are positively skewed, while that in stack IV is negatively skewed. This means that a larger area of the cells in stacks I, II, and III operates below the target average current density of 6000 A m^{-2} , while stack IV operates above the average current density. Stack V has the narrowest-spread in the interquartile range among the stacks, followed by stack IV. The results imply that alternate air-flow configurations help to reduce the spread of the current density distribution at high current densities.

The distributions of the current density in each cell in all the stacks are shown in Fig. 6.4 for fuel utilization of 0.722. The leftmost figure is the box chart with histograms of the current density distribution in the entire stack. This is followed by the box charts with histograms from the first cell located at the bottom of the stack to the eighth cell located at the top of the stack. The histograms and box charts show that all eight cells in each stack have similar current density distributions. However, slight differences are observed between the 1st and 8th cells in the stacks with conventional flow configurations. This is caused by the asymmetry of the stacks in the y -direction; the outermost passage of the 1st cell is for air flow, while the opposite side is for fuel flow. The difference caused by this asymmetry is found to be smaller in the stacks with alternate flow configurations. Figure 6.4 also shows that when the stack surfaces are assumed to be adiabatic, the distributions in each cell are similar.

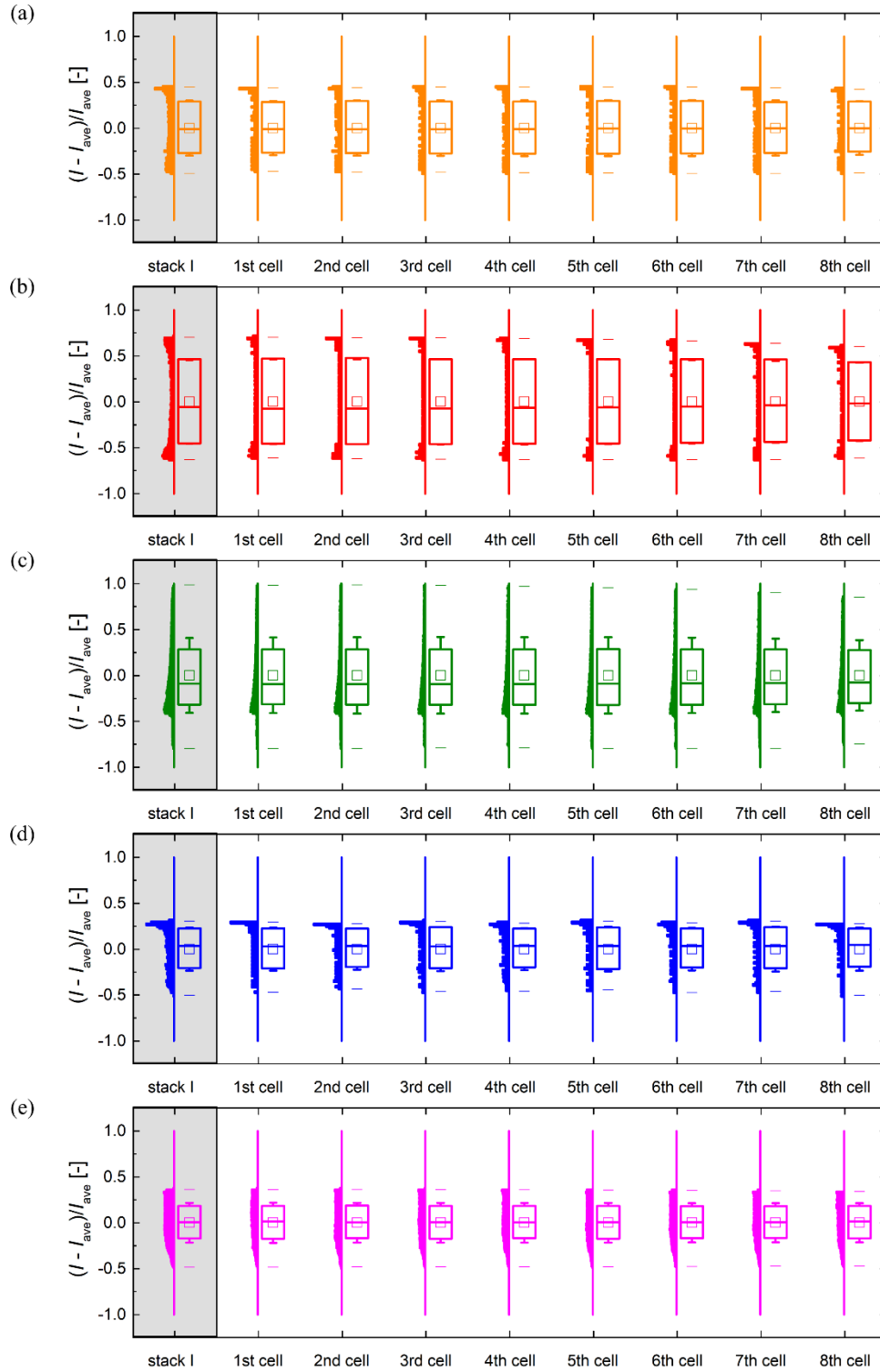


Fig. 6.4. Current density distributions at fuel utilization of 0.772 (6000 A m⁻²) for (a) stack I, (b) stack II, (c) stack III, (d) stack IV, and (e) stack V.

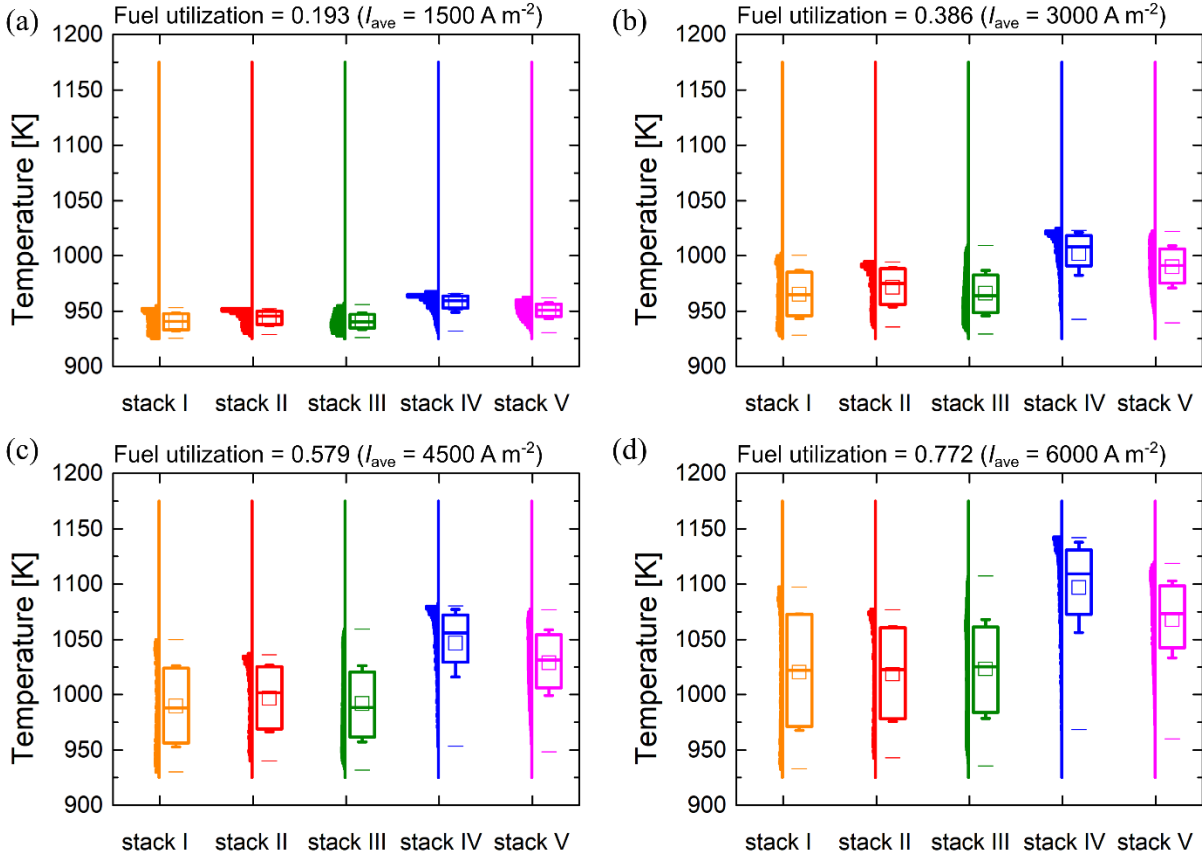


Fig. 6.5. Cell temperature distributions for entire stack at fuel utilization of (a) 0.193, (b) 0.386, (c) 0.579, and (d) 0.772.

Figure 6.5 shows the box charts with histograms of the cell temperature distribution in the stacks. Regardless of the fuel utilization, stack IV shows the highest average cell temperature, followed by stack V. This is a result of the heat circulation previously discussed. At low fuel utilization, although the average cell temperature of the stacks is different, the temperature difference from the average is within 50 K in all the stacks. As fuel utilization increases, the range of the local temperature becomes wider. In stacks I to III with the conventional flow configurations, the histogram of the local temperature has a relatively uniform distribution, while the histogram

of the local temperature in stacks IV and V are biased to the high-temperature side. This is also expressed by the negative skew characteristic of the cell temperature in stacks IV and V at high fuel utilization as observed in Fig. 6.5. This indicates the existence of a small area in the stack that operates at a considerably lower temperature than the mean temperature of the stack. However, the lowest cell temperatures in both stacks IV and V are still higher than the lowest cell temperature in the other stacks with the conventional flow configurations.

Here, the interquartile range is used as a measure of the dispersion of the cell temperature. The alternate air-flow configurations always have a smaller interquartile range than the conventional flow configurations, i.e., stacks IV and V have a narrow-spread in the middle half of the dataset for the cell temperature. This narrow-spread of the cell temperature indicates the relatively uniform cell temperature distribution. High and uniform cell temperature distribution is a preferable condition for SOFCs.

Figure 6.6 shows box charts with histograms of the temperature distribution in the entire stacks and those in each cell at fuel utilization of 0.772. The cells located at high positions tend to have high temperatures, and the temperature difference between neighboring cells is about 0.6 – 3.9 K. The shapes of the distributions in both the histograms and the box charts are similar for all the cells. Both Figs 6.4 and 6.6 indicate that a single-cell simulation with an adiabatic boundary condition gives a reasonable prediction for well-insulated stacks. This is not the case for heat leakage from the stack surface [25].

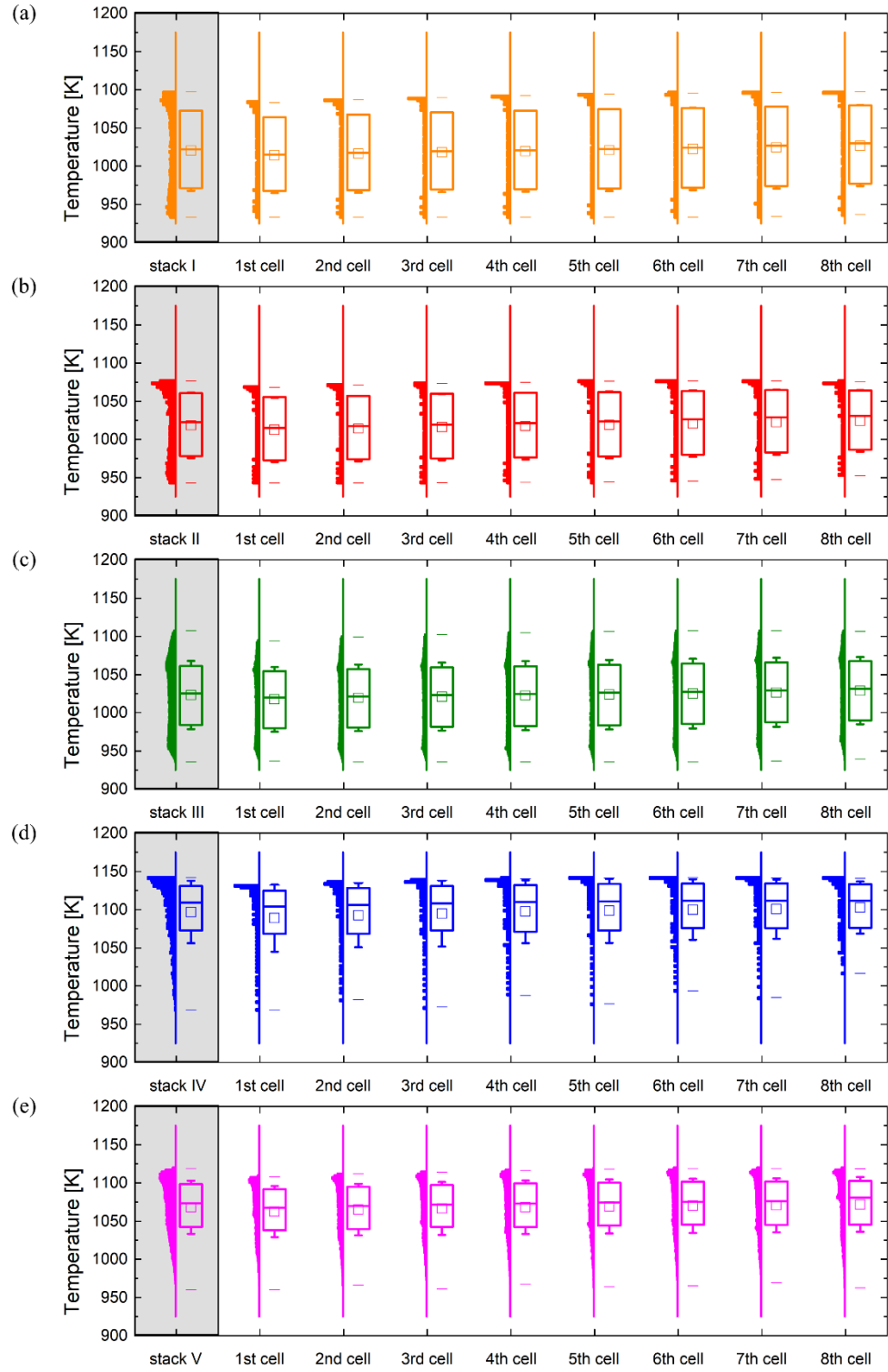


Fig. 6.6. Cell temperature distributions at fuel utilization of 0.772 (6000 A m^{-2}) for (a) stack I, (b) stack II, (c) stack III, (d) stack IV, and (e) stack V.

The statistical approach with the aid of box charts and histograms enable both qualitative and quantitative measurement of the dispersion, in contrast to the contour plot approach for the current density and cell temperature. Both the range and the interquartile range of the dataset are measures that cannot be obtained from the contour plot approach. Additionally, the interquartile range is relevant to the discussion of cell temperature.

It is possible to compare the performance of the stacks in terms of voltage efficiency under galvanostatic operation with a constant fuel/air inlet temperature at the inlets of the channels. The average voltage efficiency of a stack is defined as the mean value of the voltage efficiencies of all the cells within the stack by Eq. (2.93). Figure 6.7(a) shows the EMFs, voltage losses, and terminal voltages of the cells within indirect ammonia fueled stacks under galvanostatic operation. Figure 6.7 (b) shows average voltage efficiency, average cell temperature, ohmic resistance in the electrolyte, and ohmic loss in the electrolyte for the stacks. Regardless of fuel utilization, stack IV shows the highest voltage efficiency with the highest average cell temperature and the lowest dispersion of current density among the stacks. On the other hand, stack I at lower fuel utilization of 0.193, 0.386, and 0.579 has the lowest voltage efficiency owing to its lowest average cell temperatures. Stack II still has the highest performance among the conventional flow configurations under stack-level operation as observed in single-cell operation.

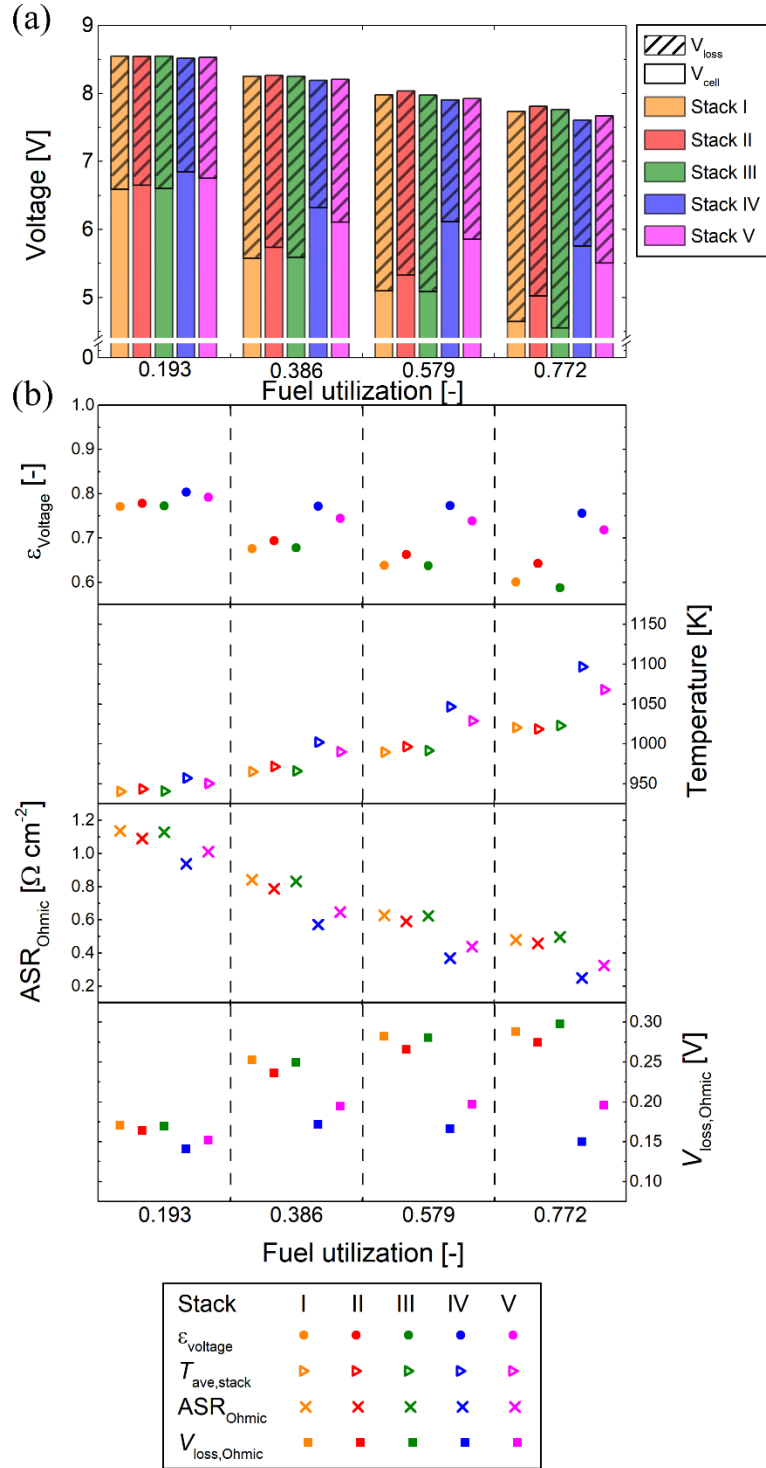


Fig. 6.7. Comparison of (a) terminal voltage, voltage loss, and EMF, (b) average voltage efficiency, average cell temperature, electrolyte ohmic resistance, and electrolyte ohmic loss.

The stacks with the alternate air-flow configurations have the advantage of maintaining high voltage efficiency even at high fuel utilization, which is due to the decrease in the ohmic loss as shown in Fig. 6.7(b). In general, the ohmic loss is proportional to the current density or fuel utilization of the stack. However, electrolyte ohmic loss in the alternate air-flow configurations decreases as the fuel utilization increases after fuel utilization of 0.386 and 0.579 in stacks IV and V, respectively. The ohmic loss in the electrolyte is strongly affected by (i) distribution of current density and (ii) local ionic conductivity. The stacks with the alternate air-flow configurations have a lower dispersion of the current density distribution than those with the conventional air-flow configurations, as observed in Fig. 6.3, which helps reduce ohmic loss. On the other hand, the ionic conductivity of the electrolyte is a function of the cell temperature [26]. The confined heat in the stacks with the alternate air-flow configurations increases the average cell temperature of these stacks, which increases ionic conductivity followed by a decrease in ohmic loss in the electrolyte. Both the negatively skewed characteristics and the small interquartile range for the cell temperature in stacks IV and V observed in Fig. 6.5 are closely related to the low dispersion of the local current density distribution. Hence, a reduction in the ohmic loss is observed at high fuel utilization. In short, high voltage efficiency in the alternate air-flow configurations at the highest fuel utilization is ensured by the low dispersion of the current density distribution and the increase in cell temperature.

Comparing stacks IV and V, stack IV has 3.8% higher voltage efficiency than stack V at fuel utilization of 0.772 as shown in Fig. 6.7(b). This is due to the distribution of the cell temperature in the stacks. The combination of the highly negatively skewed distribution of the cell temperature and the high average cell temperature in stack IV indicate a wide active area at high temperatures due to the circulation of heat energy between the air flows as discussed previously. A high cell

temperature reduces the voltage loss and increases the voltage efficiency of the stack. The average cell temperature of stack IV is 1097 K, compared with 1068 K for stack V at fuel utilization of 0.772. This may be too high for an intermediate-temperature SOFCs. The average temperature can be lowered by increasing the air-flow rate; however, a high mass flow rate of the supplied air can reduce the overall efficiency of the system.

6.3.2 Direct ammonia fuel

The inlet temperature of 923 K resulted in the local fuel depletion in stack III. Moreover, the low inlet temperature results in a low ammonia decomposition rate for direct ammonia fuel as discussed in Chapter 5. Hence, the inlet temperature for both the direct and indirect ammonia fuel in this section is increased to 973 K, which is 50 K higher than the previous section.

Figures 6.8 and 6.9 show the distributions of the current density (1st column), cell temperature (2nd column), and hydrogen mole fraction (3rd column) in the 4th cell from the bottom of the eight-cell stack at fuel utilization of 0.772 under direct and indirect ammonia fuel with inlet temperature of 973 K, respectively. Regardless of the flow configuration, the direct ammonia fuel has higher maximum local current density than indirect ammonia fuel. Besides, the locations of these local current density peaks in the 4th cell shifted toward downstream of the fuel flow. This is due to high ammonia decomposition rate at the anode near upstream of fuel flow. This endothermic reaction decreased the local cell temperature, which increased both activation and ohmic resistances. Low current density is withdrawn from this high resistance area. Therefore, high current density needs to be withdrawn from the low resistance area to achieve the required average current density.

The surface of SOFC stack is thermally insulated in this study. Hence, the heat generated in the stack is removed by fuel and air flows. The cooling effect of fuel-flow is weaker than that of air-flow owing to the small flow rate and low heat capacity; the stack is mainly cooled by air-flow. Additional cooling can only take place under direct ammonia fuel due to the endothermic decomposition reaction. In stacks IV and V, the circulation of heat energy is substantial because it also occurs between the air flows as discussed in section 6.4.1. However, the area near fuel inlet is less influenced by the heat circulation under direct ammonia fuel.

The distribution of the mole fraction of hydrogen shows that none of the stacks undergo fuel depletion when the inlet temperature is increased to 973 K. The increment of 50 K for the inlet temperature solved the local fuel depletion issue for stack III under indirect ammonia fuel as discussed in section 6.4.1. A lower concentration of hydrogen is found at the outlet of the fuel channel under direct ammonia fuel regardless of the flow configuration. This means stack under direct ammonia fuel has low resistance against fuel depletion. Therefore, additional attention should be given to high fuel utilization.

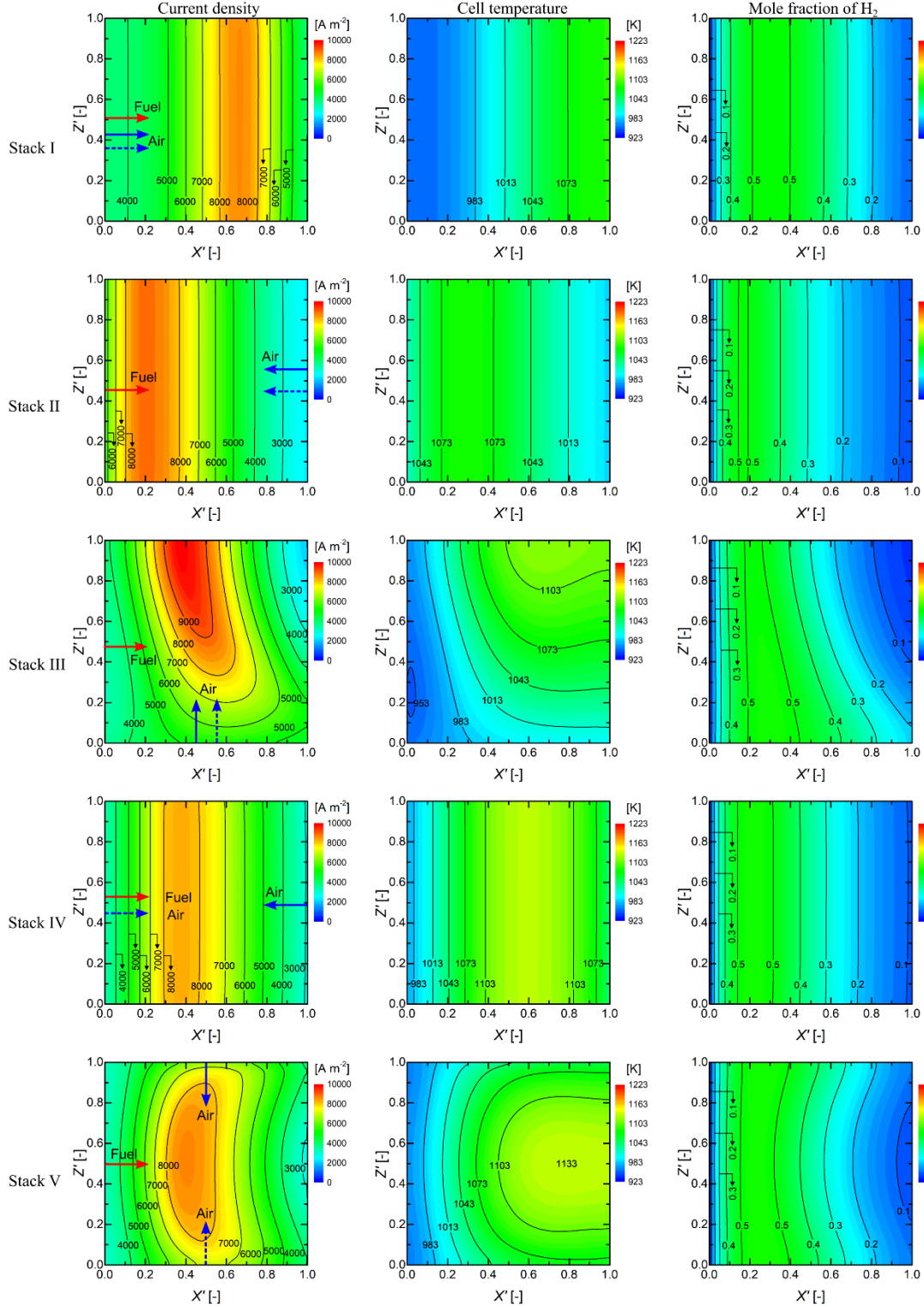


Fig. 6.8. Distributions of current density, cell temperature, and hydrogen mole fraction for the 4th cell of the direct ammonia fueled stacks at a fuel utilization of 0.772.

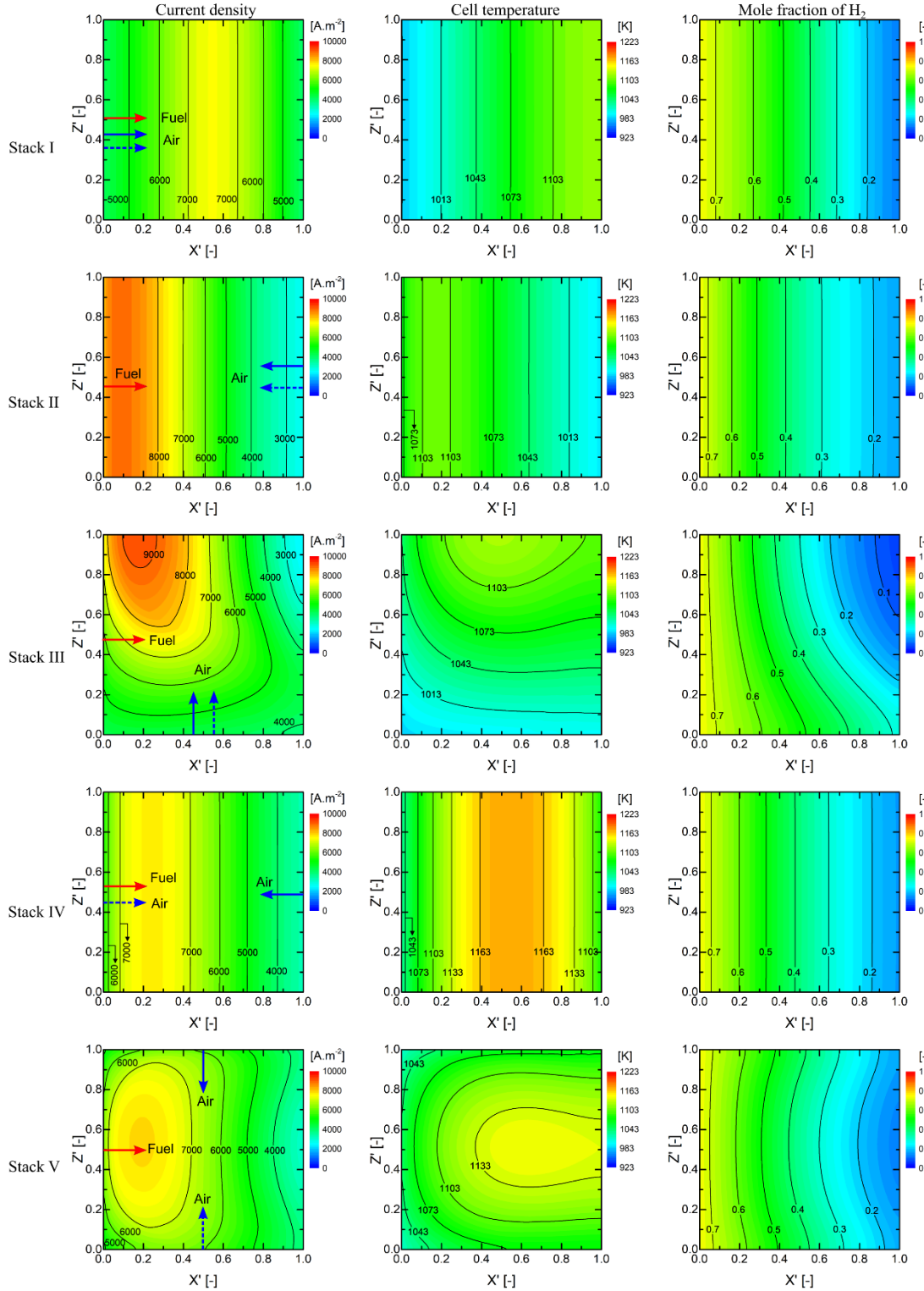


Fig. 6.9. Distributions of current density, cell temperature, and hydrogen mole fraction for the 4th cell of the indirect ammonia fueled stacks at a fuel utilization of 0.772.

The distribution of the current density and cell temperature in stacks I to V is statistically analyzed for both direct and indirect ammonia fuel. Figure 6.10 shows the box charts with histograms of the current density distribution for all stacks. The distributions under the direct and indirect ammonia fuel are given in the left-side and right-side column, respectively. For most of the operational conditions, stacks are both widely-spread in the overall range and the interquartile range of the current density distribution under direct ammonia fuel. This is shown in the 4th cell in Figs. 6.8 and 6.9. The narrow-spread in the overall range of the current density for the indirect ammonia fueled stacks can reduce performance degradation in long-term operations. Stack II has a wide-spread in the overall range at fuel utilization of 0.386 and 0.579, while stacks I and II have a wide-spread in the interquartile range at fuel utilization of 0.193 under indirect ammonia fuel.

The distribution of the cell temperature is given in Fig. 6.11 under direct and indirect ammonia fuel. Direct ammonia fuel generally has low cell temperature as per the previous observation in Fig. 6.10 with a wide-spread distribution of the current density. The discussion in the previous section suggested that the interquartile range of cell temperature provides a better measure of the dispersion of the dataset than the overall range. The direct ammonia fuel stacks except stack II, have a wide-spread in the interquartile range of the cell temperature at high fuel utilization of 0.579 and 0.772. Although the narrow-spread is preferred to reduce the risk of thermal cracking of the cell, the low cell temperature distribution of the direct ammonia fuel reduces the thermal stress between components of the cell. This will counterbalance the effect of wide-spread cell temperature to the risk of thermal cracking.

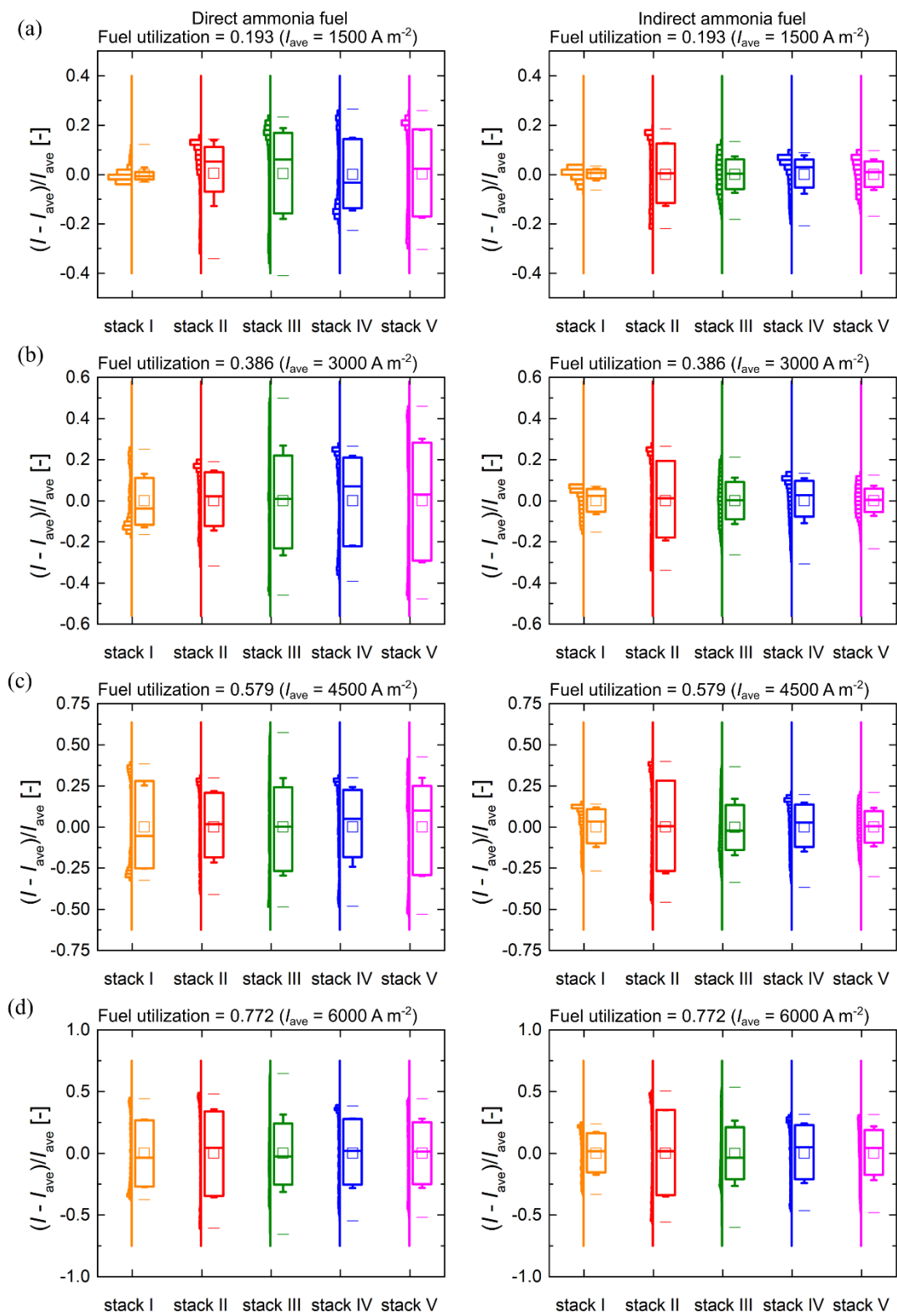


Fig. 6.10. Current density distribution for entire stack at fuel utilization of (a) 0.193, (b) 0.386, (c) 0.579, and (d) 0.772.

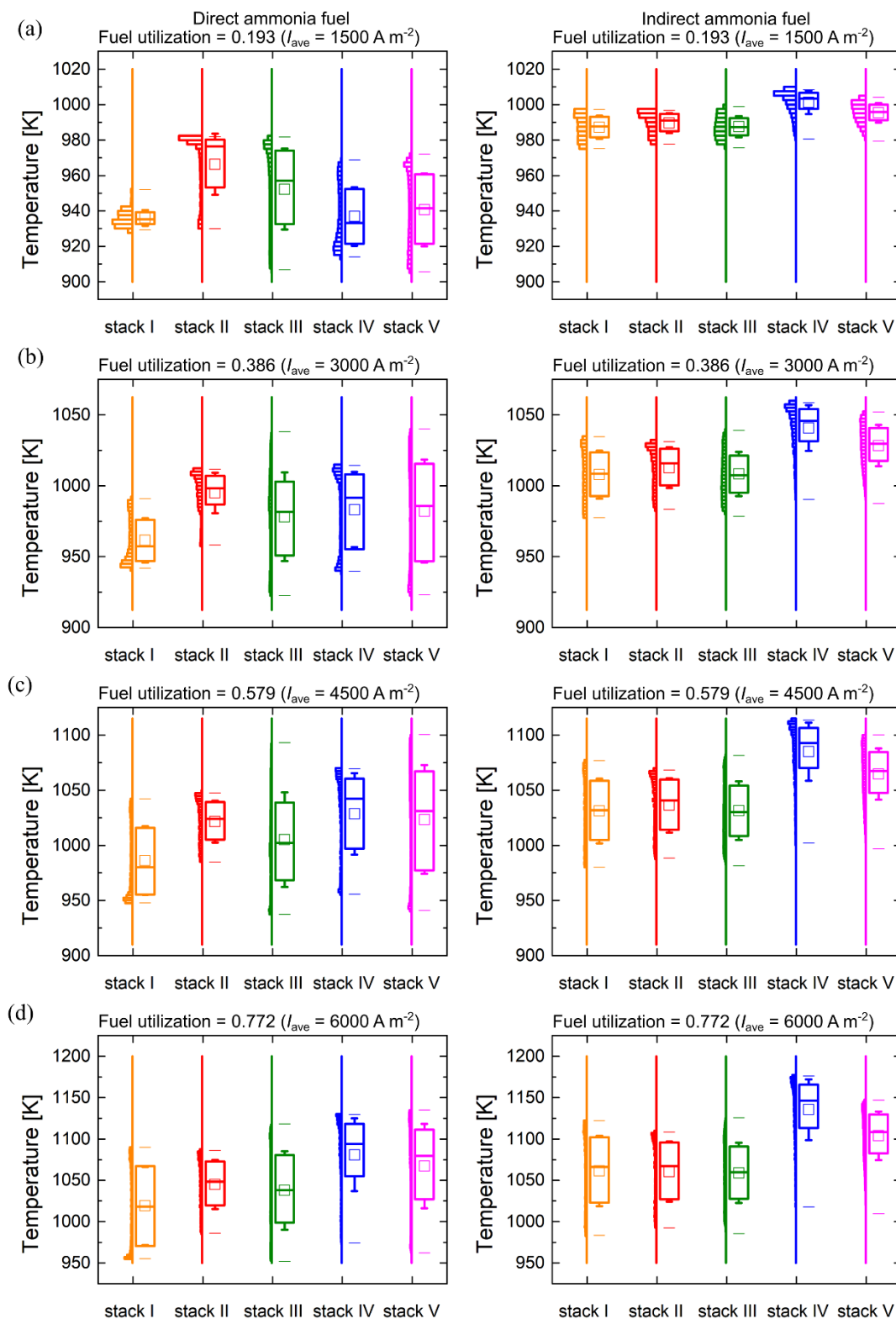


Fig. 6.11. Cell temperature distribution for entire stack at fuel utilization of (a) 0.193, (b) 0.386, (c) 0.579, and (d) 0.772.

Although the indirect ammonia fueled stacks has advantages based on the narrow-spread in the interquartile range of the cell temperature, the high cell temperature within stacks IV and V is a major issue for the long-term operation of an LSCF/GDC cathode with YSZ electrolyte. The high-operating temperature accelerates the diffusion of Zr and Sr for the lateral growth of SrZrO_3 along GDC-YSZ interface as discussed in section 2.4. The direct ammonia fueled stack, especially both the stacks IV and V at high fuel utilization can be balanced between performance (correlated with its cell temperature distribution) and degradation of performance in the long-term run.

The temperature distribution for the direct ammonia fuel in Fig. 6.11 does not provide a full explanation of the thermal energy stored in the stacks. The direct ammonia fuel involves endothermic decomposition. Therefore, it is important to consider the total exothermic and endothermic heats generated within a stack. Figure 6.12 shows the exothermic heat generated from the electrochemical reaction and the voltage losses as well as the endothermic heat generated from the ammonia decomposition reaction. At low fuel utilization of 0.193 and 0.386, all stacks except stack I (at fuel utilization of 0.386) are not self-sustaining as the overall endothermic heat is higher than exothermic heat. Although endothermic heat does not occur in the indirect ammonia fuel, some heat energy is still required to operate the external ammonia decomposer.

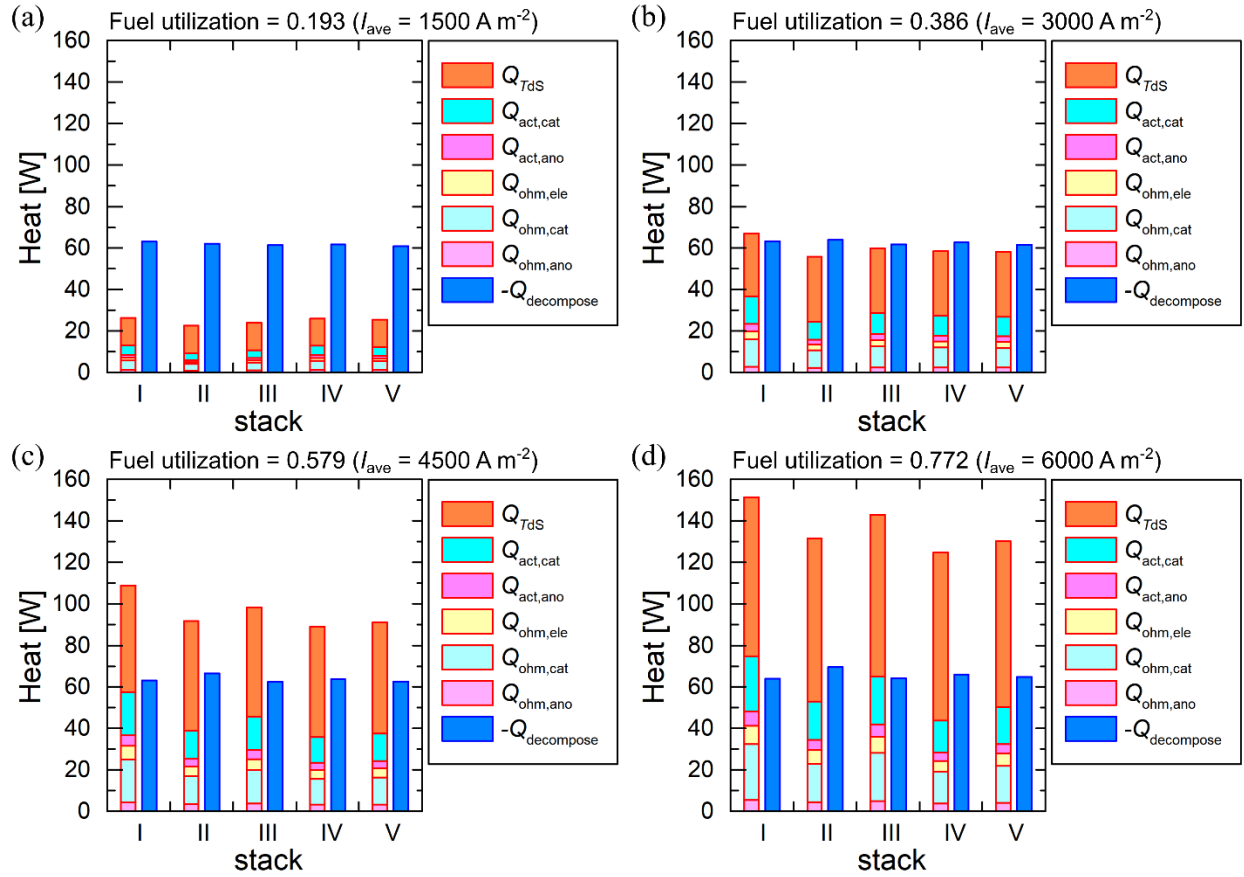


Fig. 6.12. Heat source components for entire stack fueled with direct ammonia at fuel utilization of (a) 0.193, (b) 0.386, (c) 0.579, and (d) 0.772.

The average voltage efficiency of a stack is defined as the mean value of the voltage efficiency of all the cells within the stack. Figure 6.13 shows the average voltage efficiency for the stacks under both direct and indirect ammonia fuel. Although stack II has the highest average voltage efficiency at low fuel utilization of 0.193 and 0.386 under direct ammonia fuel, the results in Fig. 6.12 suggest that stack II is not self-sustaining. Therefore, the discussion of the average voltage efficiency under direct ammonia fuel is limited to high fuel utilization of 0.579 and 0.772. Stack IV has the highest voltage efficiency stack, followed by stack V. This is due to the circulation of heat energy between the air flows for the alternate air-flow stacks. The heat energy stored in the

air flow of an arbitrary cell is transferred to the air flows of the neighboring cells flowing in the opposite direction. As a result, stacks IV and V have high cell temperature distribution as shown in Fig. 6.11, and results in low ohmic resistance in the electrolyte, with a similar explanation as per Fig. 6.7. The alternative air-flow configurations perform better than the conventional flow configuration of co-, counter-, and cross-flow for both direct and indirect ammonia fuel. However, attention must be paid to the maximum cell temperature within stacks IV and V as previously explained.

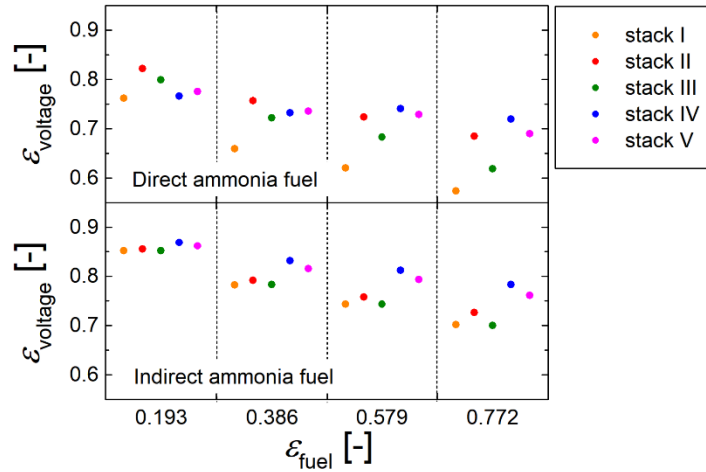


Fig. 6.13. Comparison of average voltage efficiency for direct and indirect ammonia fueled stacks.

Stack II performs well above other conventional stacks. The counter-flow configuration reduced the influence of endothermic heat caused by the ammonia decomposition at the upstream of fuel flow as shown in Fig. 6.8. As a result, high cell temperature promotes low ohmic resistance in the electrolyte, and a low activation resistance in the electrodes is expected.

The stacks perform better under indirect ammonia fuel than direct ammonia fuel, in line with a single-cell level. The high cell temperature distribution within the indirect ammonia fueled stack reduces both activation and ohmic resistances. Meanwhile, the direct ammonia fuel stacks can reduce the cell temperature and slow down the formation of SrZrO_3 along the GDC-YSZ interface. Furthermore, the endothermic heat within the direct ammonia fuel can reduce ancillary energy consumption for the air flow as reported by Cinti et al. [27]. This can help to increase the efficiency of the SOFC system.

6.5 Conclusion for direct and indirect ammonia fueled stack

The effects of the stack cooling by air flow configuration approach within an eight-cell SOFC stack fueled by either direct or indirect ammonia fuel were numerically investigated. The stacks with alternate flow configurations had either alternating co- and counter- flow cell units or cross-flow cell units with opposite air-flow directions between the layers. These effects were analyzed at fuel utilization of 0.193, 0.386, 0.579, and 0.772. The dusty-gas model and the Fick's model were separately used for the transport of gas species in the anode under the direct and indirect ammonia fuel, respectively.

A counter-flow stack has higher voltage efficiency than co- and cross-flow stacks at the same fuel utilization regardless of the fuel. The statistical analysis revealed that the counter-flow stack, especially those fueled by the indirect ammonia has the highest dispersion in terms of the interquartile range of the current density distribution. This dispersion increases with average current density, showing that nonuniformity becomes a severe problem when the average current density is high.

Local fuel depletion was found in the cross-flow stack fueled by indirect ammonia at 0.772 fuel utilization (inlet temperature of 923 K). The increment of inlet temperature helps to reduce the local fuel depletion. Low concentration of hydrogen at the outlet of fuel channel was found under direct ammonia fuel regardless of flow configuration. Therefore, extra attention should be given to a stack fueled with direct ammonia fuel at high fuel utilization. Appropriate selection of the air-flow configuration within stacks allows operation at a high fuel utilization without local fuel depletion.

Alternating the air-flow direction within a stack results in air-to-air circulation of the heat energy, which enhances the symmetry of the temperature distribution and shifts the high-temperature region to the cell center. Moreover, the air is divided into two streams and supplied to the stack from two different directions under alternating air flow, which helps to prevent the formation of a low-temperature region. This results in low dispersion and high cell temperature, which enhances the ionic conductivity in a cell. Therefore, high voltage efficiency was observed for the alternate air-flow configurations regardless of the type supplied fuel. The wide active area that operates at high temperatures within the alternate air flows in the parallel direction contribute to higher voltage efficiency than the alternate air flows in the perpendicular direction to the fuel flow.

The indirect ammonia fuel with a narrow-spread of the current density and the cell temperature is subject to less performance degradation beneficial for long-term use which also entails higher performance. The endothermic heat from direct ammonia fuel improve stack cooling to reduce cell temperature. This helps to reduce the thermal stress between components of a cell and also slows down the formation of SrZrO_3 along the GDC-YSZ interface.

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Chapter 7

Conclusion

7.1 The overall conclusion of the study

This study developed a quasi-3D numerical model. The conservation equations of mass, momentum, species, charge, and energy (in term of fluid phase) were applied in the fuel and air channels mesh layers, while the energy conservation equation (in term of solid phase) was implemented in all mesh layers. The cell mesh layer was treated as a dense solid layer and coupled with a parallel circuit electrochemical model. Real microstructure information was applied to the model. Electrochemical reaction was extended from the electrode-electrolyte interface by using a local charge-transfer current profile. This reaction allows a close representation of both activation and ohmic resistance in a cell. The ionic conductivity in the LSCF/GDC composite cathode was defined based on the microstructure properties of GDC. The Fick's model (FM) was applied for mass transportation of gas species in the electrodes for a cell/stack fueled with indirect ammonia fuel. The dusty-gas model (DGM) was used to analyze direct ammonia fuel with the aid of a newly introduced anode mesh.

The numerical model with real microstructure implementation qualitatively captured the trends observed in the experiment without any fitting parameters. A full stack numerical analysis should be considered if the additional computation cost is affordable. A single-cell approach to

represent a multiple-cell stack has difficulty in capturing the cell temperature deviation in a stack, which influences overall stack performance.

The effect of cooling effect under cell aspect ratio and flow configuration (limited to co- and counter-flow) were numerically investigated for indirect ammonia fuel. The ammonia fuel was assumed to be fully pre-decomposed before being supplied to an SOFC cell. The cell performance was increased with the increase in operating temperatures due to the reduction of activation and ohmic resistances in the cell. Aspect ratios ranging from 0.130 to 7.68 were analyzed. The shortest and widest cell with the lowest aspect ratio was found to have the highest voltage efficiency at a low fuel utilization. However, the longest and narrowest cell with the highest aspect ratio had the highest voltage efficiency at high fuel utilization. The external cooling by radiation heat loss at SOFC sidewalls was evaluated with the effect of aspect ratio. The highest cell performance was found for cells with aspect ratios close to unity. These cells had high average cell temperatures, which reduced activation and ohmic resistances. It was found that cells with aspect ratios greater than unity tend to perform better under counter-flow configuration. However, the 0.750 aspect ratio cell was found to have high voltage efficiency at fuel utilization of 0.60 and 0.80. High aspect ratio cells did not have high cell efficiency, but capable of providing sufficient heat to sustain external ammonia decomposer. Hence, a balance between cooling effect and cell efficiency is required to ensure the sustainability of an ammonia decomposer and achieve reasonable performance of short stack.

Both the FM and the DGM were compared for the transportation of gas species in the anode of a six-cell stack using the developed quasi-3D model under both hydrogen and direct ammonia fuels. Both models provided reliable results. The FM is recommended for the hydrogen or indirect ammonia fuel to reduce computation cost. The DGM is recommended to overcome the limitation

of the FM when a significant change of concentration in the mixture occurs. Furthermore, the numerical analysis of the DGM used was in line with the literature results under direct ammonia fuel. The factors that influence internal cooling of SOFC cell under direct ammonia fuel were analyzed with the aid of anode mesh. Attention was paid to ammonia decomposition rate, ratio of pre-decomposed fuel, and air flow configurations (limited to co- and counter-flow). High ammonia decomposition rate can be achieved by either a high concentration of ammonia, low concentration of hydrogen, high inlet temperature, high nickel-pore interfacial area, or combination of them. Direct ammonia fueled cell has low cell performance due to low cell temperature caused by high endothermic heat. The direct ammonia fueled cell must avoid operating at low fuel utilization. An extremely high amount of pre-decomposed ammonia is required to sustain operations at low fuel utilization. The cell with an aspect ratio close to unity has high resistance against the decrease in voltage efficiency when it is supplied with direct ammonia fuel than indirect ammonia fuel under co-flow configuration. On the other hand, high aspect ratio cell has high cell performance under counter-flow configuration owing to the circulation of heat between fuel and air. However, close attention should be paid to its maximum cell temperature.

The cooling effects of the air flow configuration for an eight-cell SOFC stack fueled by either direct or indirect ammonia fuel were numerically investigated. The conventional flow configurations of co-, counter-, and cross-flow, as well as alternating the air-flow in every other cell of a stack by either parallel (streamwise) or perpendicular (spanwise) direction to the fuel flow were analyzed in term of the stack performance, the distribution of the current density, and the distribution of cell temperature. A counter-flow stack has higher voltage efficiency than co- and cross-flow stacks at same fuel utilization regardless of supplied fuel. However, the counter-flow stack, especially those fueled by indirect ammonia has the highest dispersion in terms of the

interquartile range of the current density distribution. Local fuel depletion was found in the cross-flow stack fueled by indirect ammonia at high fuel utilization. The increment of inlet temperature helped to reduce local fuel depletion. A lower concentration of hydrogen at the outlet of fuel channel was found under direct ammonia fuel than indirect ammonia fuel. The air-to-air circulation of heat energy within the alternating air flow stack results in a low dispersion and high cell temperature distribution with a low dispersion of the current density, increasing ionic conductivity. High voltage efficiency was achieved by alternating the air-flow configurations regardless of the type of supplied fuel. High stack performance was found under indirect ammonia fuel. The low cell temperature distribution due to internal cooling effect from direct ammonia fuel helps to reduce the thermal stress between components of a cell and slow down the formation of SrZrO_3 along the GDC-YSZ interface.

7.2 Recommendations for future study

Series of thermal management analysis were conducted using cell/stack fueled with either direct or indirect ammonia fuel in this study. Other components such as heat exchanger, afterburner, and ammonia decomposer within an SOFC system can be further analyzed in the future to provide an understanding of overall thermal management in an SOFC system. The current work assumed that sufficient heat is delivered by the afterburner or SOFC stack to the external ammonia decomposer. However, the heat delivered is strongly related to the change in enthalpy of fuel, which functions against its inlet temperature as well as the efficiency of the component. This should improve the overall efficiency of an SOFC system which needs further research. For example, the direct ammonia fueled cell/stack can operate with a lower flow rate of supplied air

than indirect ammonia fueled cell/stack. This can reduce the power consumption of the air blower. The low flow rate of air can reduce the heat required to heat-up to the required temperature before being supplied to SOFC cell.

In this study, the reduction of oxygen is assumed to occur at the double-phase boundary of LSCF-pore. The ions are transported to the nearest GDC and continue its path in the GDC within the LSCF/GDC cathode to reach the YSZ electrolyte. This is due to the higher ionic conductivity of GDC than that of LSCF. The electrons only travel in the LSCF to reach the current collector. Both LSCF and GDC show mixed ionic and electronic conductivity characteristics in the reduction environment. Experimental work is suggested to verify this assumption since GDC has a low effective ratio of volume fraction to tortuosity factor.

Abbreviations

ASR	area-specific resistance
CFD	computational fluid dynamic
CH ₄	methane
CO	carbon monoxide
Cr	chromium
CT	computed tomography
DGM	dusty-gas model
DPB	double-phase boundary
EMF	electromotive force
FIB-SEM	focused ion beam scanning electron microscope
FM	Fick's model
GDC	gadolinium-doped ceria
H ₂	hydrogen
H ₂ O	steam
LaCrO ₃	lanthanum chromium oxide
LSCF	lanthanum strontium cobalt ferrite
LSM	lanthanum strontium manganite
MFC	mass flow controller
MIEC	mixed ionic-electronic conducting
NH ₃	ammonia
Ni	nickel
N ₂	nitrogen

O ₂	oxygen
PEN	positive-electrolyte-negative assembly
SIMPLE	semi-implicit method for pressure-linked equations
SOFC	solid oxide fuel cell
Sr	strontium
SrZrO ₃	strontium zirconia oxide
TB	thermal boundary
TPB	triple-phase boundary
YSZ	yttria-stabilized zirconia
Zr	zirconia
1D	one-dimensional
2D	two-dimensional
3D	three-dimensional

Nomenclature

A	area	(m ²)
A_{DPB}	volumetric density of DPB area	(m ² ·m ⁻³)
A_{PEN}	active area of cell	(m ²)
A_{yz}, A_{xz}, A_{xy}	surface area of meshed grid	(m ²)
a_{sf}	surface area of porous materials	(m ²)
b	half-thickness of bump in porous metal foam	(m)
C_p	heat capacity	(J·kg ⁻¹ ·K ⁻¹)
D_i	diffusion coefficient of gas species	(m ² ·s ⁻¹)

D_{ij}	binary diffusion coefficient	$(\text{m}^2 \cdot \text{s}^{-1})$
$D_{i,m}$	molecular diffusion coefficient of multicomponent gas	$(\text{m}^2 \cdot \text{s}^{-1})$
D_K	Knudsen diffusion coefficient	$(\text{m}^2 \cdot \text{s}^{-1})$
$\tilde{D}$	chemical diffusion coefficient of oxide ion	$(-)$
d_f	average diameter of metal fibers in porous metal foam	(m)
d_p	average diameter of pore phase in porous metal foam	(m)
E	electromotive force	(V)
F	Faraday constant	$(\text{C} \cdot \text{mol}^{-1})$
F'	shape factor	$(-)$
f	inertia coefficient	$(-)$
G	Gibbs free energy change for reaction	(J)
g	geometric function for porous metal foam	$(-)$
$\hat{g}$	molar Gibbs free energy change for reaction	$(\text{J} \cdot \text{mol}^{-1})$
H	enthalpy	$(\text{J} \cdot \text{mol}^{-1})$
H_f	formation enthalpy	$(\text{J} \cdot \text{mol}^{-1})$
h	thickness	(m)
h_{sf}	porous interfacial heat transfer coefficient	$(\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1})$
$\hat{h}$	molar enthalpy change (based on higher heating value) for reaction	$(\text{J} \cdot \text{mol}^{-1})$
I	current density	$(\text{A} \cdot \text{m}^{-2})$
i_{ct}	charge-transfer current density	$(\text{A} \cdot \text{m}^{-2})$
i_{el}	electronic current density	$(\text{A} \cdot \text{m}^{-2})$
i_{io}	ionic current density	$(\text{A} \cdot \text{m}^{-2})$
i_0	exchange current density	$(\text{A} \cdot \text{m}^{-2})$

K	permeability	(m ²)
L	half-length of fiber in porous metal foam	(m)
l_{TPB}	volumetric density of TPB length	(m·m ⁻³)
M_i	molecular mass of gas species	(kg·mol ⁻¹)
$\bar{M}$	average molecular mass of gas mixture	(kg·mol ⁻¹)
N_i	molar flux of gas species	(mol·m ⁻² ·s ⁻¹)
$\dot{N}_i$	molar flow rate of gas species	(mol·s ⁻¹)
P	total pressure	(Pa)
p_i	partial pressure of species i	(Pa)
Q	heat generation term	(W·m ⁻³)
Q_{rad}	thermal radiation	(W)
R	ideal gas constant	(J·mol ⁻¹ ·K ⁻¹)
R_{dec}	ammonia decomposition rate	(mol m ⁻³ ·s ⁻¹)
r	area ratio in porous metal foam	(-)
$\bar{r}$	average radius of pore phase	(m)
S	entropy	(J·mol ⁻¹)
$S_{\text{Ni-pore}}$	Ni-pore interface area density	(m ² m ⁻³)
S_{x_i}	species transport source term for gas species i	(mol·m ⁻³ ·s ⁻¹)
S_{Y_i}	mass transport source term for gas species i	(kg·m ⁻³ ·s ⁻¹)
S_{ϕ}	charge transport source term	(V·m ⁻³)
T	temperature	(K)
U	velocity	(m·s ⁻¹)
u	x-velocity component	(m·s ⁻¹)

V	volume of meshed grids	(m ³)
V_{cell}	cell terminal voltage	(V)
V_{loss}	total overpotential of cell	(V)
V_{m}	molar volume in the cathode	(m ³ mol ⁻¹)
v_i	diffusion volume of gas species	(m ³ kg ⁻¹ mol ⁻¹)
$v_i^{N^{\text{DGM}}}$	velocity of gas species caused by flow of other species	(m s ⁻¹)
$v_i^{p^{\text{DGM}}}$	velocity of gas species caused by pressure gradient	(m s ⁻¹)
w	z-velocity component	(m·s ⁻¹)
x_i	molar fraction of gas species	(-)
X_i	molar density of gas species	(mol m ⁻³)
X'	normalized x-coordinate in streamwise direction in active area	
Y_i	mass fraction of gas species	(-)
Z'	normalized z-coordinate in spanwise direction in active area	

Greek symbols

Γ_i^{DGM}	global molecular diffusion through a porous medium of gas species	(m ² s ⁻¹)
Θ_i	Sutherland constant of gas species	(K)
Θ_{ij}	binary Sutherland constant	(K)
α_i	parameter defined in Eq. (2.64)	(-)
α_0	symmetric coefficient in Butler–Volmer-like equation	(-)
δ	oxygen nonstoichiometry	(-)
ε	porosity	(-)
$\varepsilon_{\text{fuel}}$	fuel utility factor of cell	(-)

$\varepsilon_{\text{real}}$	real performance of cell	(-)
$\varepsilon_{\text{thermo}}$	thermodynamic efficiency of cell	(-)
$\varepsilon_{\text{voltage}}$	voltage efficiency of cell	(-)
η	voltage loss	(V)
λ	thermal conductivity	(W·m ⁻¹ ·K ⁻¹)
$\lambda_{\text{ano}}, \lambda_{\text{cat}}$	attenuation factor for anode and cathode	(-)
μ	viscosity	(Pa·s)
ρ	density	(kg·m ⁻³)
σ	conductivity	(S·m ⁻¹)
σ_{SB}	Stefan-Boltzmann constant	(kg·s ⁻³ ·K ⁻⁴)
τ	tortuosity factor	(-)
χ	tortuosity of porous metal foam	(-)
Ψ	Lindsay and Bromley's dimensionless number	(-)
ϕ	electric potential	(V)

Superscripts

eff	effective
0	standard state

Subscripts

act	activation overpotential
ano	anode
ave	average value

b	boiling point
cat	cathode
conc	concentration overpotential
dec	decomposer
el	electronic phase
ele	electrolyte
f	fluid phase
in	value at inlet
io	ionic phase
local	local value
m	gas mixture
ohm	ohmic loss
s	solid phase
sf	solid-fluid interface
wall	sidewall of stack