Implementation of multi-component dusty-gas model for species transport in quasi-three-dimensional numerical analysis of solid oxide fuel cell. Part II: direct ammonia fuel

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Abstract. The Fick’s model is applied to analyze the species transport in the porous electrodes for an in-house developed quasi-three-dimensional numerical model of solid oxide fuel cell. It may not be reliable when significant concentration difference is formed in the gas mixture, owing to chemical reactions such as steam methane reforming and ammonia decomposition. In this study, the multi-component dusty-gas model is implemented to solve the conservation of species on a three-dimensional grid system in the anode layer involving direct ammonia decomposition. The results with the developed model are compared with the available two-dimensional numerical analysis. The obtained results show that the dusty-gas model can accurately predict the transport of gas species in the porous anode even when a chemical reaction occurs.

1. Introduction
Solid oxide fuel cell (SOFC) is one of the high-efficiency fuel cells that are operated at high temperatures. It can convert the chemical energy of fuel to electrical energy through electrochemical processes. The supplied fuel is not limited to hydrogen. Fuel like methane and ammonia also can be directly supplied to SOFC owing to its high operating temperature. Furthermore, nickel that found in the anode of SOFC is a suitable catalyst to produce hydrogen from the supplied fuel.

A quasi-3D numerical model was developed in the authors’ group to study the effect of cell aspect ratio on cell performance [1] and the effects of the air-flow configuration in a short stack [2]. However, the developed quasi-3D model was limited to hydrogen-fueled SOFCs owing to the simplicity of the implemented Fick’s model (FM) in the porous anode. In the case of direct supply of methane- or ammonia-based fuels, chemical reactions such as steam methane reforming and ammonia decomposition occur in the porous anode, which results in a significant change of concentration in the gas mixture and thus, limits the implementation of the simple FM. Hence, a more accurate transport model like the dusty-gas model (DGM) is required to predict multi-component gas transport in the porous anode involving chemical reactions. García-Camprubí and co-authors [3–5] adopted the suggestion by Pisani [6] and rewrote the DGM equation to express the total molar flux of each species in the gas mixture. Our recent work [7] had successfully validated the developed quasi-3D numerical model with the implementation of multi-component DGM to the anode with experimental results from a six-cell stack fueled with hydrogen.
In this short communication, we implement the same gas diffusion model based on the DGM to the anode in a quasi-3D numerical model to predict the species transport in the anode from an ammonia-fueled cell in reference [8].

2. Numerical modeling
The cell unit as shown in Figure 1 is considered in this study. Note that the 3D grid system of anode mesh for the anode in the PEN is solely used in the gas diffusion analysis in the anode.

![Figure 1. Schematic view of mesh layers in the y-direction for the quasi-3D model with an anode mesh.](image)

Details of the mesh and the quasi-3D numerical modeling have already been described in our previous reports [1,2,7], therefore only essential equations are summarized below. The numerical analysis was based on conservation equations of the mass, momentum, species, and energy. The species conservation within the anode mesh based on the multi-component DGM [5] can be expressed as follows:

\[ \nabla \cdot \mathbf{N}_i = S_{x_i}. \]  

The species molar source/sink term \( S_{x_i} \) in Equation (1), within each mesh volume \( V \) is associated with the chemical reaction in the anode. This study considers an SOFC single cell fueled with direct ammonia. \( S_{x_i} \) is associated with the ammonia decomposition reaction on the nickel-pore interfacial area in the anode, and the following reaction rate equation [9] is used in this study.

\[ \text{NH}_3 \rightarrow \frac{1}{2} \text{N}_2 + \frac{3}{2} \text{H}_2 \]  

\[ R_{\text{dec}} = S_{\text{Ni-pore}} R_{\text{dec}}^{\text{Ni-pore}} \]  

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

where \( S_{\text{Ni-pore}} \) is the volumetric density of the nickel-pore interfacial area.

2.1. Calculation conditions
The same boundary conditions that reported in part I [7] are considered. The source terms for molar of species in Equation (1) are given in Table 1. The mass generation between channel and anode was explained in our previous report [7], except for the species of ammonia is \( N_{\text{NH}_3} \).

| \( \text{O}_2 \) | \( \text{N}_2 \) | \( \text{H}_2 \) | \( \text{H}_2\text{O} \) | \( \text{NH}_3 \) |
|---|---|---|---|---|

Table 1. Source terms for molar of species.
Molar generation in the cell from the electrochemical reaction \([\text{mol m}^{-3} \text{s}^{-1}]\)

\[ \frac{I}{4F} \]

Molar generation in the anode from the ammonia decomposition reaction \([\text{mol m}^{-3} \text{s}^{-1}]\)

\[ - \frac{I}{2F} \quad \frac{1}{2} R_{\text{doc}} \quad \frac{3}{2} R_{\text{doc}} \quad - \quad - \]

3. Results and discussion

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 Figure 2. This 2D simulation was conducted resolving the gas transport in the streamwise and cell thickness directions in the electrodes and fuel/air channels. Note that the quasi-3D 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]. Also, there is a slight difference between the quasi-3D simulation and the 2D simulation in the fuel and air channels; they are filled with porous metal form in the quasi-3D simulation, whereas they are void volume in the 2D simulation. Figure 2(a) shows the comparison of the two models 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 Figure 2(b) agrees with the 2D numerical results by Kishimoto et al. [8]. Also, the distribution of the ammonia decomposition rate in the anode is shown in Figure 2(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.

![Figure 2](image-url)
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 is frequently 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 was estimated with an active thickness of 4.22 μm [10]. Because the active thickness of the ammonia decomposition reaction is not available in open literature, it is estimated in this study as the equivalent thickness from the anode surface that can decompose the same total amount of ammonia within the anode in the DGM as follows,

\[ h_{\text{dec, ave}} = \frac{\sum (R_{\text{dec,DGM}} V_{\text{local}})}{\sum (R_{\text{dec,FM}} A_{\text{local}})}. \] (5)

\( R_{\text{dec,DGM}} \) 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 using the concentration of gas species at the anode surface. \( V_{\text{local}} \) and \( A_{\text{local}} \) 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 Equation (5) 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 the other terminal voltages under the analysis with the FM.

**Figure 3.** 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) NH3 decomposition reaction rate in the anode.
Figure 3 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 characteristic of the current-voltage curve in Figure 3(a) from the FM are also apart from the 2D simulation. Figure 3(b) shows the distribution of the molar fractions of gas species in the fuel channel. It clearly shows that the differences between the two simulations in Figure 3(b) are larger than those shown in Figure 2(b). The average active thickness of the ammonia decomposition reaction in the quasi-3D simulation with the FM is estimated as 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 Figure 3(c). A significant difference can be observed when the figure is compared with Figure 2(c).

Noticeable differences between the DGM and FM model 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.

4. Conclusions

The numerical results with the DGM and FM were compared with the 2D numerical results from literature under direct ammonia fuel. An active thickness of ammonia decomposition reaction was pre-determined from the numerical analysis with the DGM at a terminal voltage of 0.75 V, and used for the analysis with the conventional FM. It was found that the FM was not able to accurately reproduce the distribution of gas concentrations in the anode. Also, the pre-determined average active thickness was approximately 31 % of the anode thickness, which is beyond the applicable range of the assumption of surface reaction. On the other hand, DGM successfully reproduces the similar distribution of gas concentration in the fuel channel and captures the realistic non-uniform decomposition rate of ammonia in the anode. This study proved that the implementation of the DGM can accurately predict the transport of species involving reactions in the anode that significantly changes the concentration in the mixture, whereas the implementation of the FM is not suitable for analyzing direct ammonia fuel.

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5. References

[1] Tan W C, Iwai H, Kishimoto M, Brus G, Szmyd J S and Yoshida H 2018 Numerical analysis on effect of aspect ratio of planar solid oxide fuel cell fueled with decomposed ammonia J. Power Sources 384 367–378.

[2] Tan W C, Iwai H, Kishimoto M and Yoshida H 2018 Quasi-three-dimensional numerical simulation of a solid oxide fuel cell short stack: Effects of flow configurations including air-flow alternation J. Power Sources 400 135–146.

[3] García-Camprubí M and Fueyo N 2010 Mass transfer in hydrogen-fed anode-supported SOFCs Int. J. Hydrogen Energy 35 11551–11560.

[4] García-Camprubí M, Izquierdo S and Fueyo N 2014 Challenges in the electrochemical modelling of solid oxide fuel and electrolyser cells Renew. Sustain. Energy Rev. 33 701–718.

[5] García-Camprubí M, Sánchez-Insa A and Fueyo N 2010 Multimodal mass transfer in solid-oxide fuel-cells Chem. Eng. Sci. 65 1668–1677.
[6] Pisani L 2008 Multi-component gas mixture diffusion through porous media: A 1D analytical solution *Int. J. Heat Mass Transf.* 51 650–660.

[7] Tan W C, Iwai H, Kishimoto M, and Yoshida H 2019 Implementation of multi-component dusty-gas model for species transport in quasi-three-dimensional numerical analysis of solid oxide fuel cell. Part I: hydrogen fuel *Proc. 6th Int. Conf. on Applications & Design in Mechanical Engineering* (Penang) (submitted).

[8] Kishimoto M, Kume T, Iwai H and Yoshida H 2017 Numerical analysis of ammonia-fueled planar solid oxide fuel cells *ECS Trans.* 78 2845–2853.

[9] Kishimoto M, Furukawa N, Kume T, Iwai H and Yoshida H 2017 Formulation of ammonia decomposition rate in Ni-YSZ anode of solid oxide fuel cells *Int. J. Hydrogen Energy* 42 2370–2380.

[10] Nagasawa T and Hanamura K 2017 Prediction of overpotential and effective thickness of Ni/YSZ anode for solid oxide fuel cell by improved species territory adsorption model *J. Power Sources* 353 115–122.