

암모니아 공급 고체산화물 연료전지의 1D 반응 모델

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1D Kinetics Model of NH₃-Fed Solid Oxide Fuel Cell

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Abstract >> Cracking ammonia inside solid oxide fuel cell (SOFC) stack is a compact and simple way. To prevent sharp temperature fluctuation and increase cell efficiency, the decomposition reaction should be spread on whole cell area. This leading to a question that, how does anode thickness affect the conversion rate of ammonia and the cell voltage? Since the OD model of SOFC is useful for system level simulation, how accurate is it to use equilibrium solver for internal ammonia cracking reaction? The 1D model of ammonia fed SOFC was used to simulate the diffusion and reaction of ammonia inside the anode electrode, then the partial pressure of hydrogen and steam at triple phase boundary was used for cell voltage calculation. The result shows that, the ammonia conversion rate increases and reaches saturated value as anode thickness increase, and the saturated thickness is bigger for lower operating temperature. The similar cell voltage between 1D and OD models can be reached with NH₃ conversion rate above 90%. The OD model and 1D model of SOFC showed similar conversion rate at temperature over 750°C.

Key words : Kinetic model(반응 모델), SOFC(고체산화물 연료전지), OD model (0차원 모델), 1D model (1차원 모델), Ammonia conversion(암모니아 전환)

1. Introduction

To mitigate climate change, the world energy is

transformed into renewable energy, such as solar power and wind power¹⁾. The renewable energy can be transported directly to the customers or through a

form of hydrogen or its carriers²). The hydrogen carriers are getting attention because hydrogen has low volumetric energy density and difficult to be stored. For example, liquid hydrogen has volumetric energy density of 8.49 MJ/l, but required to be kept at a very low temperature of -253°C.

There are several types of hydrogen carriers with different development level. For high volumetric energy density, using metal hydrides could be a promising approach. However, so far, they are suffering from low gravimetric energy density, since metals are normally heavy^{3,4}). For relatively high volumetric and high gravimetric energy density, ammonia is a good option. Ammonia has energy density of 12.7 MJ/l, and 18.7 MJ/kg, and it can be stored stably in liquid state at 11 bar and 25°C⁵).

Ammonia can be made from H₂ and N₂ using renewable energy with very little carbon footprint. Firstly, hydrogen is produced by electrolysis using electricity from solar farm or wind farm. And nitrogen can be extracted from air by liquefaction using renewable energy. Ammonia has been being produced using Haber-Bosch process since earlier than 100 years ago. However, scientists are still working on finding new ways with lower required pressure and temperature⁶).

Though ammonia was first mass produced more than 100 years ago, they have been mostly for agricultural applications⁷). To be a good energy carrier, ammonia should be used effectively to generate electricity. So far fuel cells system showed the highest electrical efficiency among hydrogen-fueled power generation technologies. Ammonia needs to decompose to produce H₂ and then be fed to fuel cells. The decomposition process is an endothermic reaction, so the overall system efficiency can be improved if heat generated from fuel cells is used. Owing to high operating temperature, solid oxide fuel

cell can provide high temperature for internal cracking of ammonia fuel.

To analyze whole fuel cell system, a 0D model of fuel cell stack is normally used⁸). The 0D model is very quick to compute and quite accurate when there is only electrochemical reaction occurs inside fuel cell. However, when there is direct internal decomposition of NH₃ occurs, the simple 0D model might lose its accuracy. In that case 1D model will be more reliable, which considers NH₃ decomposition reaction takes place inside the anode electrode. Nonetheless, the computation cost of 1D model is not acceptable for system modeling.

So far, the 0D model approach typically considers all decomposition or reforming reactions finished inside the fuel channel, and the fuel composition at triple phase boundary will be estimated using multi-components diffusion models. The 1D model approach, in other hand, considers the decomposition reaction happens only in anode electrode. The anode is discretized along its thickness direction and the material composition in whole anode field are estimated using iteration calculation method. In this paper, the results of 0D and 1D models are compared, and then the applicable condition where 0D model and 1D model show similar output will be suggested.

2. Mathematic model of solid oxide fuel cell (SOFC)

2.1 Assumptions

For modeling of SOFC, the following assumptions were used:

- The temperature of SOFC cell is uniformly distributed.
- The material composition of fuel and air channel are uniform.

- The Ohmic loss on interconnector and electrodes are negligible.
- SOFC is modeled in steady state.
- In 0D model, the equilibrium reaction occurs inside the fuel channel
- In 1D model, the cracking reaction occurs inside the fuel electrode

2.2. Electrochemical model

The SOFC cell voltage was modeled considering three types of voltage loss: Ohmic loss, activation loss, and concentration loss, as following:

$$U = U_{rev} - U_{act} - U_{ohm} - U_{con}$$

where Nernst voltage was calculated:

$$U_{rev} = \frac{\Delta G}{2F} + \frac{RT}{2F} \ln \frac{y_{H_2} \sqrt{y_{O_2}}}{p y_{H_2O}} \quad (1)$$

where:

ΔG : Gibbs free energy change of electrochemical reaction at temperature T

R : Universal gas constant

F : Faraday constant

y_i : molar fraction of the substance i

p : pressure of anode channel

Activation loss was calculated based on molar fraction of substance at the triple phase boundary and current density:

$$U_{act} = \text{sign}(j) \frac{2RT}{nF} \sinh^{-1} \left(\frac{|j|}{2j_0} \right) \quad (2)$$

Where j_0 is exchange current density:

$$j_{o,air} = \gamma_a y_{O_2tpb}^{0.25} e^{-E_{O_2}/RT} \quad (3)$$

$$j_{o,fuel} = \gamma_f y_{H_2tpb} y_{H_2Otpb} e^{-E_{H_2}/RT} \quad (4)$$

where γ_a and γ_f are fitting parameters. E_{O_2} and E_{H_2} are activation energy of cathode and anode electrodes, respectively.

Ohmic loss is calculated depending on the thickness of electrolyte, current density, and temperature of SOFC:

$$U_{ohm} = \frac{j d_e}{\sigma_0} e^{\frac{80,000}{RT}} \quad (5)$$

Concentration loss will become significant at high current density, due to the slow diffusion speed compared to reaction rate.

$$U_{con} = \frac{RT}{4F} \ln \frac{y_{O_2tpb}}{y_{O_2}} + \frac{RT}{2F} \ln \frac{y_{H_2tpb} y_{H_2O}}{y_{H_2} y_{H_2Otpb}} \quad (6)$$

where:

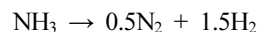
y_{O_2tpb} : molar fraction of O_2 at triple phase boundary

y_{H_2tpb} : molar fraction of H_2 at triple phase boundary

From here, the 0D and 1D model will have different method of calculating molar fractions at triple phase boundary (TPB).

2.3. 0D model

The ammonia decomposition reaction was assumed an equilibrium process that takes place at the fuel channel, as shown in Fig. 1:



The reaction constant was used as following⁹⁾:

$$k = 10^{-\left(2.6899 + \frac{2001.6}{T} + 1.848863 T^2 \times 10^{-7} - 2.691122 \log_{10}(T) - 5.519265 T \times 10^{-5}\right)} \quad (7)$$

Set the reacted rate of ammonia is a_{NH_3} (mol/s) and total inlet molar flow is n. Based on current density and dimension of the SOFC stack, the reaction rate of H₂ (a_{H_2}) can be estimated.

$$a_{H_2} = \frac{NAJ}{2F} \quad (8)$$

$$k = \frac{\left(\frac{0.5a_{NH_3}}{n + a_{NH_3}}\right)^{0.5} \left(\frac{1.5a_{NH_3} - a_{H_2}}{n + a_{NH_3}}\right)^{1.5}}{\frac{ny_{NH_3} - a_{NH_3}}{n + a_{NH_3}}} \quad (9)$$

With given molar flow rate and composition of inlet fuel, the equation (1) can be solved for X_{NH_3} . And then the equilibrium composition of fuel channel can be calculated.

The molar fraction of all substances at TPB was

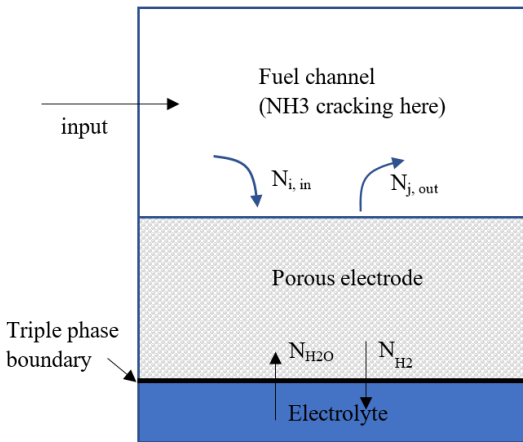


Fig. 1. Decomposition reaction location in 0D model explanation

calculated using dusty gas diffusion model.

$$y_{O_2tpb} = 1 + (y_{O_2} - 1) \exp\left[\frac{RTjd_a}{4F \cdot 10^5 PD_{effO_2}}\right] \quad (10)$$

$$y_{H_2tpb} = y_{H_2} - \frac{RT}{2F} \frac{jd_c}{PD_{effH_2}} \quad (11)$$

$$D_{effH_2} = \frac{\zeta}{\epsilon} \left(\frac{1}{D_{i,k}} + \frac{1}{D_i}\right)^{-1} \quad (12)$$

$$D_{i,k} = \frac{2}{3} r_{particle} \sqrt{\frac{8000RT}{\pi M_i}} \quad (13)$$

$$D_i = \frac{1 - y_i}{\sum_{k=1, k \neq i}^m \frac{y_k}{D_{i,k}}} \quad (14)$$

where:

d (m) : electrode thickness

M_i (g/mol) : molar weight of substance i

i, j : H₂, H₂O

m : number of substances

k : substance index

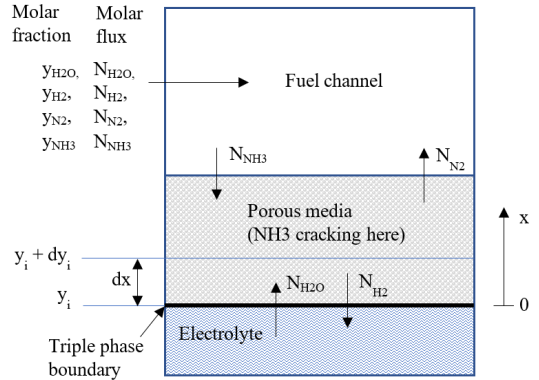


Fig. 2. 1D model explanation

2.4. 1D model

The anode electrode was assumed consist of n layers, each layer has thickness of $dx=da/n$ (da =anode electrode thickness), as shown in Fig. 2. The molar flux of each substance N_i [$\text{mol}/(\text{m}^2\text{s})$] was calculated following Dusty gas model:

$$\frac{N_i}{D_{i,k}^{eff}} + \sum_{j=1, j \neq i}^m \frac{y_j N_i - y_i N_j}{D_{ij}^{eff}} \quad (15)$$

$$= -\frac{1}{RT} \left[\frac{P dy_i}{dx} + \frac{y_i dP}{dx} \left(1 + \frac{B_0 P}{D_{i,k}^{eff} \mu} \right) \right]$$

$$\frac{dP}{dx} = \frac{\sum_{i=1}^m \left(\frac{N_i}{D_{i,k}^{eff}} \right)}{\frac{1}{RT} + \frac{B_0 P}{RT \mu} \sum_{i=1}^m \left(\frac{y_i}{D_{i,k}^{eff}} \right)} \quad (16)$$

where P and k are pressure and the layer number. Therefore, $dy_{i,k}=y_{i,k}-y_{i,k-1}$ and $dP_k=P_k-P_{k-1}$. B_0 is permability of porous electrode¹⁰, μ is viscosity of the mixture. D_{eff} is effective diffusion coefficient.

There are m unknowns (y_i) and m equations (15) for each layer. The molar flux N_i is calculated from N_{i-1} , which originated from boundary condition:

$$N_i = N_{i-1} + dN_i$$

The dN_i was calculated from reaction rate r of NH_3 in the porous electrode:

$$r = A \exp\left(-\frac{E}{RT}\right) P_{\text{NH}_3} \quad (17)$$

where E and P_{NH_3} are activation energy and partial pressure of NH_3 . A is pre-exponential term, which is fitting coefficient. Accordingly, we have:

$$dN_{\text{NH}_3} = -r dx, \quad dN_{\text{H}_2} = 1.5 r dx, \quad dN_{\text{N}_2} = 0.5 r dx$$

And boundary condition at triple phase boundary ($x=0$) is:

$$N_{\text{NH}_3} = 0, \quad N_{\text{H}_2} = -J/2F, \quad N_{\text{N}_2} = 0$$

The molar fraction of all substance at whole anode electrode was calculated subsequently from triple phase boundary to the surface of the electrode and then backward from the surface to the triple phase boundary until all result values are close enough. The calculation flow is shown in Fig. 3. Firstly, the molar fraction of all substances was initialized at surface of electrode. Using forward calculation, the composition, molar flux, and pressure at each discretized layer were calculated one by one until the values at TPB were reached. And then by using the calculated condition at TPB and electrochemical reaction at the TPB, the molar fluxes were updated. And then the backward calculation was used to calculate the new composition at surface of the electrode. The new cal-

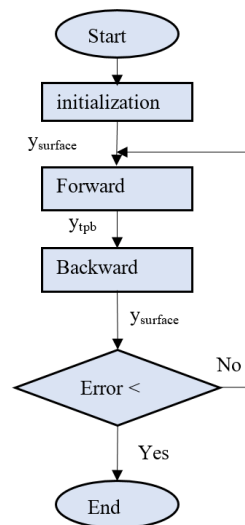


Fig. 3. Calculation flow in 1D model

culated values will be compared to the old ones. If the error is below requirement the loop was stopped.

Table 1. SOFC cell information and fitted parameters

Parameters	Unit	Value	
Electrode thickness	m	1.25e-5	
Interconnect thickness	m	2.00e-4	
γ_f	-	6.79e+11	
γ_a	-	7.44e+7	
$\sigma_{electrolyte}$	-	2.01e+8	
E_{H_2}	J/mol	1.4e+5	
E_{O_2}	J/mol	99,178.57	
Fuel electrode	Porosity	-	0.3
	Tortuosity	-	6
	Particle radius	m	5.00e-7
	Charge transfer coefficient	-	0.5
	Thickness	m	3.15e-4
	Channel height	m	1.02e-3
Air electrode	Porosity	-	0.3
	Tortuosity	-	6
	Particle radius	m	5.00e-7
	Charge transfer coefficient	-	0.5
	Thickness	m	1.75e-5
	Channel height	m	1.02e-3

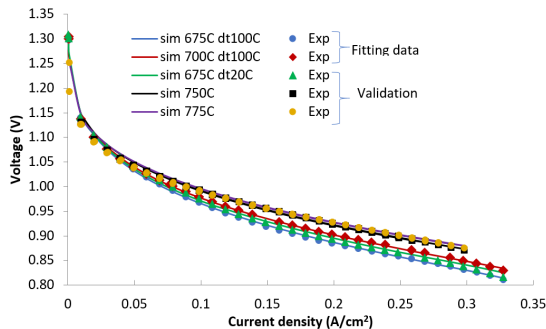


Fig. 4. Validation of 0D model with experimental data

3. Results and discussion

3.1 Model validation

Electrochemical and 0D model was validated with experimental data of N_2/H_2 fed SOFC¹¹⁾. Information of SOFC cell and fitted parameters are listed in Table 1. The experimental data at 675°C and 700°C were used for fitting model parameters. The data on the other temperature were used for validation. As shown in Fig. 4, the 0D model well agrees with experimental data.

The electrochemistry model was validated with experiment without cracking reaction. The purpose of the current study is comparing the conversion rate and composition at TPB between 0D and 1D model. So conversion rate in experiment is enough to validate 1D kinetics model. 1D model was validated by comparing simulated conversion rate of NH_3 with that in experiment of reference¹²⁾, as shown in Fig. 5. The simulated result showed error max error of 2.7% compared to experiment.

Fitted parameters are as following: $A=8e11$; $E=2.5e5$. Fuel composition along anode electrode thickness in case of no current and current density of 3,000 A/m^2 are illustrated in Figs. 6, 7. The forward calculation results well match with backward calculation results. As current density equal 0, all molar flux become

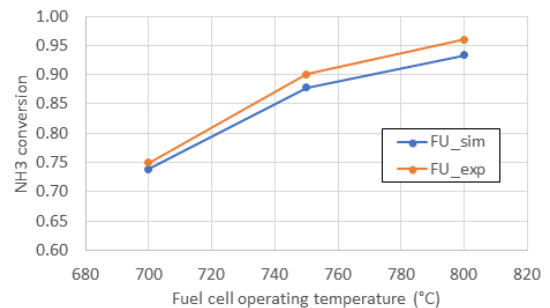


Fig. 5. NH_3 conversion rate at different operating temperature

zero at the TPB. The positive molar flux means the substances go from surface of anode to the TPB. Because NH_3 cracking reaction induces generation of molar flow, the pressure near TPB is higher than at the surface of anode.

3.2. Effect of electrode thickness on NH_3 conversion rate

NH_3 conversion rate decreased at higher current density. This might be attributed to the increasing of

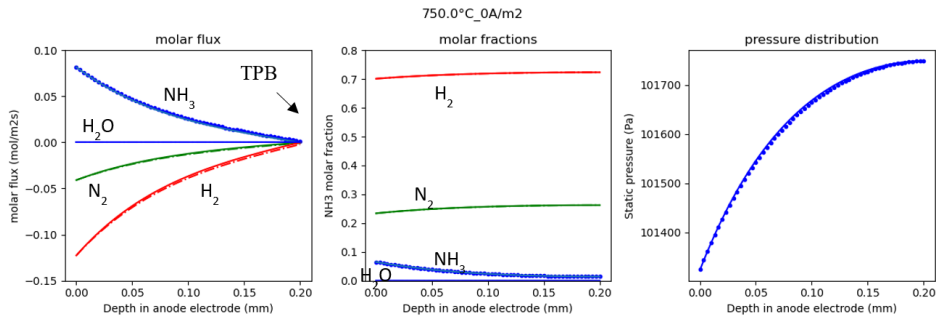


Fig. 6. Molar flux, molar fraction, and pressure in anode electrode at 0 current density (dotted lines are forward calculation result, solid lines are backward calculation results).

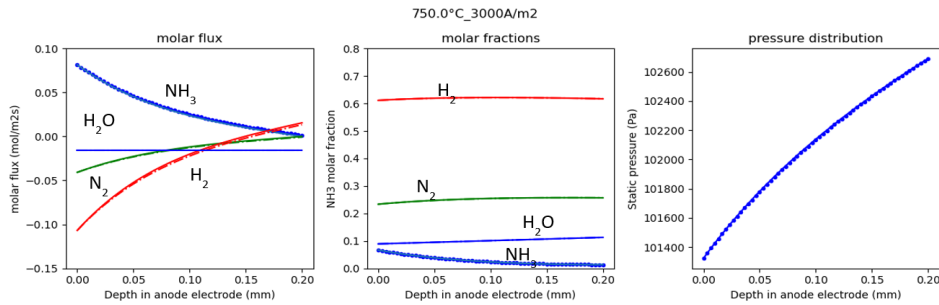


Fig. 7. Molar flux, molar fraction, and pressure in anode electrode at 3000 A/m^2 (dotted lines are forward calculation result, solid lines are backward calculation results).

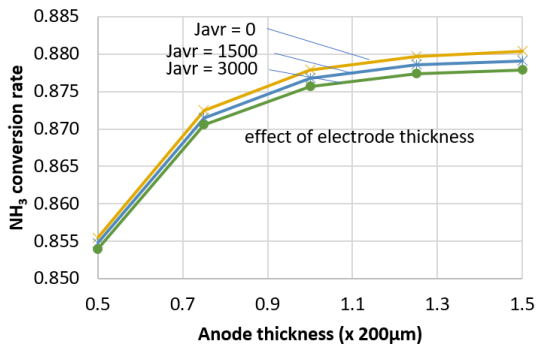


Fig. 8. NH_3 conversion rate as function of anode thickness and operating temperature

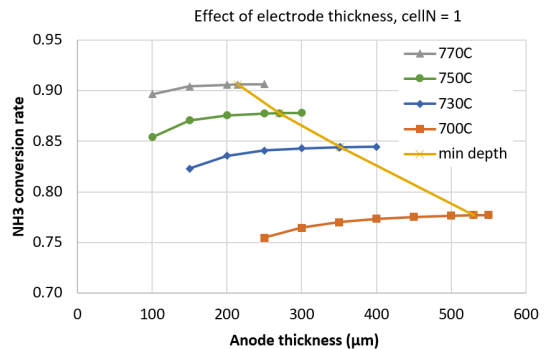


Fig. 9. NH_3 conversion rate as function of anode thickness and operating temperature

diffusion flow of water at high current density. Though hydrogen was consumed faster at high current density, the effect on NH_3 diffusion flow is smaller than that of water. As shown in Fig. 8, at anode thickness of $200\ \mu\text{m}$, NH_3 conversion rate slightly decreased from 0.8779 to 0.8757 as current density increased from 0 to $3,000\ \text{A}/\text{m}^2$. Fig. 8 also indicates that, the NH_3 conversion rate slowly increase at thicker anode electrode. This could be attributed to the slow diffusion flux of NH_3 at thicker anode electrode.

An investigation of NH_3 conversion rate at different operating temperature showed that, the saturated thickness (where the NH_3 conversion rate increase

less than $1\%/50\ \mu\text{m}$) increased with decreasing operating temperature, as shown in Fig. 9. Here, min depth line is for connecting the saturated thickness points. This means, at lower temperature, we need thicker anode electrode to significantly decompose NH_3 . The min depth line connects the saturated points.

3.3. Comparison between 0D model and 1D model

Calculation results from 0D and 1D models were compared in molar fraction output and stack voltage at different cell number. Cell voltage at operating temperature from 730°C and above showed error less than 1% between 0D and 1D model. Though the molar fraction of H_2 at anode off-gas showed 6.7% difference. Moreover, at 730°C , 1 cell, the NH_3 conversion rate was only 85%, as shown in Fig. 10. This might be caused by dominant effect of water molar fraction in the Nernst Voltage. At more cell number, the molar fraction of H_2 in 0D and 1D models showed closer values as shown in Fig. 11.

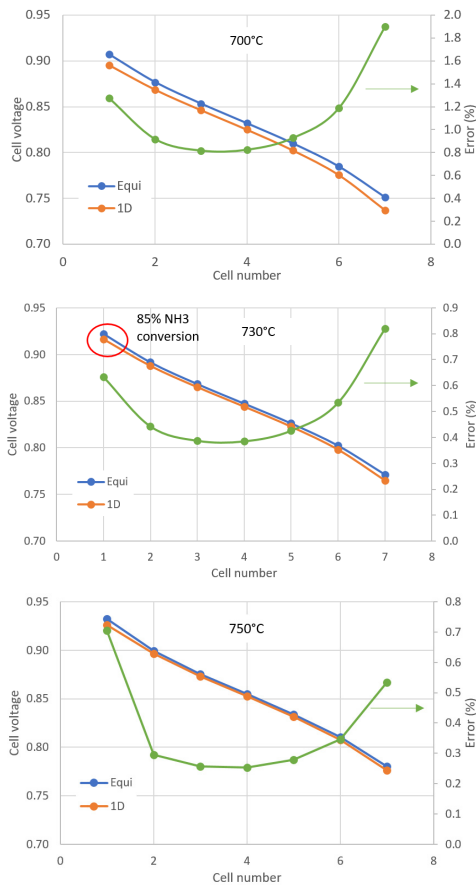


Fig. 10. Cell voltage of equilibrium (0D) model and 1D model at difference temperature

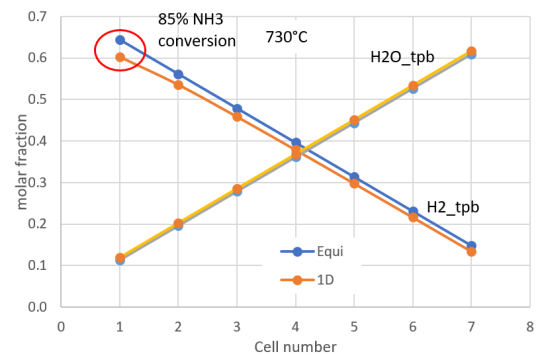


Fig. 11. Molar fraction of H_2 and H_2O at anode off-gas as function of cell number at 730°C .

4. Conclusion

SOFC stack model using 0D and 1D approaches were investigated. The 0D model used equilibrium reaction assumption to find fuel composition at the channel and then applied Dusty gas model to find composition of all substances at triple phase boundary. The 1D model used reaction kinetic of NH_3 cracking at porous anode electrode. We found that:

- The NH_3 decomposition rate quickly get saturated as anode thickness increases. As operating temperature increase, the effective thickness decreases.
- The similar cell voltage doesn't mean the composition of output flows are similar.
- As conversion of NH_3 is higher than 90%, 0D and 1D model results in similar cell voltage (error below 1%).
- At cell temperature of 750°C and above, the conversion rate of NH_3 and cell voltage are similar for both 0D and 1D kinetics model. So, it is acceptable to consider equilibrium reaction occur only in the channel.
- At temperature lower than 750°C , it is necessary to simulate the NH_3 fed SOFC using 1D kinetic model due to large different in molar fraction of anode off-gas flow.

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