Modelling of Ammonia-Fed Solid Oxide Fuel Cells in COMSOL

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Abstract: Recently ammonia has been proposed as a potential fuel for solid oxide fuel cells (SOFCs). It is widely produced and distributed globally and stores hydrogen naturally in its bonds. Ammonia can be decomposed thermally within the nickel based anode typically used in SOFCs. Very few models of ammonia-fed SOFCs have been reported, all of which focus on high temperature operation (800 – 1000 °C) and are based on the Tamaru model of ammonia decomposition. This paper presents a 2D model of an intermediate temperature ammonia-fed SOFC (400 – 700 °C) based on the Temkin-Pyzhev model of ammonia decomposition. Phenomenological equations are implemented in COMSOL using the Navier-Stokes / Darcy's Law, Heat Transfer in Porous Media, Fick's Law, and Current Conduction modules. The Dusty Gas Model is used to model species transport in porous media, however since COMSOL does not have a dedicated module for that, a modification of Fick's Law is used.

Keywords: fuel cells, dusty gas model, ammonia, Temkin-Pyzhev model.

1. Introduction

Recently ammonia has been proposed as a potential fuel for high temperature fuel cells. It stores hydrogen in its bonds, and possesses many advantages over hydrogen gas. Its worldwide distribution network makes it easier to store and transport. The temperature of solid oxide fuel cells (SOFCs) enables thermal decomposition of ammonia within the nickel anode. Ammonia is also carbon free.

To date very few models of ammonia-fed fuel cells have been reported. Most of them are electrochemical or thermodynamic 0D models. Only two models are based on computational fluid dynamics (CFD) [1,2]. All of the existing models are applicable for high temperature operation (800 – 1000 °C) and as a result employ the Tamaru model of ammonia decomposition [3]. However there are many advantages of operating SOFCs at intermediate temperatures (400 – 700 °C). Experimental research has

shown that the decomposition kinetics are different at these lower temperatures, and as a result the Temkin-Pyzhev model of ammonia decomposition is more appropriate [3]. The essential difference is that the Tamaru model is first order with respect to ammonia and does not account for the inhibition effect of hydrogen on the rate of ammonia decomposition. The Temkin-Pyzhev model uses a rate equation that depends on both ammonia and hydrogen partial pressures.

This paper presents a 2D steady state CFD model of an ammonia-fed SOFC based on the Temkin-Pyzhev model of ammonia decomposition. This model is implemented and solved in COMSOL MultiPhysics 4.3.

2. Model Development

The governing partial differential equations used in this paper account for bulk fluid flow (Navier-Stokes equations with Darcy's Law, Eqn. 1), heat transfer in porous media (Eqn. 2), chemical species transport (Dusty Gas Model, Eqn. 3,4), charge conservation (Eqn. 5), and fuel cell electrochemical equations (Butler-Volmer equation, Eqn. 6,7). These equations are listed below.

$$\rho u \cdot \nabla u = \nabla p + \nabla \left(\mu \nabla u \right) + \frac{\mu}{\beta} u \tag{1}$$

$$\nabla \cdot \left(\rho c_p u T \right) = \nabla \left(k \nabla T \right) + S_T \tag{2}$$

$$\frac{N_i}{D_{i,k}^{eff}} + \sum_{j \neq i} \frac{x_j N_i - x_i N_j}{D_{i,j}^{eff}} = -\frac{\nabla \left(x_i P \right)}{RT} \tag{3}$$
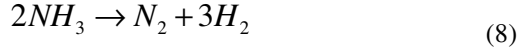
$$\nabla \cdot N_i = S_i \tag{4}$$

$$\nabla \cdot \left(\sigma_e \nabla \varphi_e \right) = 0 \tag{5}$$

$$j = 2 j_{0,a}^{ref} \frac{c_{H_2}}{c_{H_2}^{ref}} \frac{c_{H_2O}^{ref}}{c_{H_2O}} \sinh \left(\frac{F \eta_{act,a}}{RT} \right) \tag{6}$$
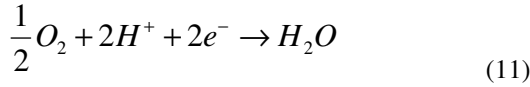
$$j = 2 j_{0,c}^{ref} \left(\frac{c_{O_2}}{c_{O_2}^{ref}} \right)^{1/2} \sinh \left(\frac{F \eta_{act,c}}{RT} \right) \tag{7}$$

The 2D geometry is specifically for a planar type SOFC, however the model can easily be applied to a tubular geometry. The computational domain is shown in Figure 1. Pure ammonia is supplied to the anode while air enters the cathode. In this model, ammonia decomposes into hydrogen and nitrogen in the anode porous domain according to the Temkin-Pyzhev model [4].

$$2NH_3 \rightarrow N_2 + 3H_2 \qquad (8)$$

$$r_{NH_3} = \left(6x10^7\right)\exp\left(-\frac{95600}{RT}\right)\left(\frac{p_{NH_3}^2}{p_{H_2}^3}\right)^{0.209} \qquad (9)$$

The produced hydrogen then reacts electrochemically at the anode / electrolyte interface. Note that intermediate temperature SOFCs require proton conducting electrolytes, and are denoted SOFC-H.

$$H_2 \rightarrow 2H^+ + 2e^- \qquad (10)$$

$$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \qquad (11)$$

$$S_{H_2} = -j\frac{M_{H_2}}{2F} \qquad (12)$$

$$S_{O_2} = -j\frac{M_{O_2}}{4F} \qquad (13)$$

$$S_{H_2O} = +j\frac{M_{H_2O}}{2F} \qquad (14)$$

The heat generation source terms are interfacial as well as domain. The electrochemical reactions are reckoned at the electrode / electrolyte interfaces, therefore reaction heat sources are interfacial. Ohmic heating is dominant in the electrolyte domain. Ammonia decomposition occurs in the anode domain, and is endothermic, therefore this represents a heat sink in the anode domain.

$$S_{T,decomp} = -r_{NH_3}\Delta H_R \qquad (15)$$

$$S_{T,fuelcell} = j\left(\eta - \frac{T\Delta S}{2F}\right) \qquad (16)$$

The dusty gas model is considered the most accurate model for chemical species transport in porous media [5]. It accounts for Knudsen diffusion, and it has been shown this cannot be neglected in fuel cell applications [5]. Unfortunately, the dusty gas model is not presently available in COMSOL 4.3. However, Kong et al [6] have shown that the following manipulation of Fick's law with modified diffusivities very accurately depicts the dusty gas model for a wide range of geometrical and operating conditions used in fuel cells. This modified Fick's law is used in the present model.

$$N_i = -D_i^{corr}\nabla c_i - c_i\frac{k_i^{corr}\nabla p}{\mu} \qquad (17)$$

$$\frac{1}{D_i^{corr}} = \frac{1}{D_{ik}^{eff}} + \left(\sum_{j \neq i}\frac{x_j}{D_{ij}^{eff}}\right)\cdot\left(1 + \frac{x_i\sqrt{M_i}}{\sum_{j \neq i}x_j\sqrt{M_j}}\right) \qquad (18)$$

$$k_i^{corr} = k + \frac{\mu}{p}D_i^{corr} \qquad (19)$$

The model, with a mesh containing 18,500 rectangular elements, is solved on a 2 GB, 2 GHz Intel CPU platform using the MUMPS direct stationary non-linear solver. Convergence is achieved by first solving an uncoupled problem, and then gradually introducing coupling parameters in subsequent solves.

3. Results and Discussion

All of the results shown in this section are based on an operating cell potential of 0.7 V (~ 5000 A/m²) which represents the optimal power point on the iV curve, and inlet temperature of 500 °C (773 K) of supply gases. Figure 2 shows the ammonia mole fraction at the anode (which is the same as the partial pressure in atmospheres). It enters the anode channel at 1 atm. Within the anode domain, it decomposes into hydrogen and nitrogen and as a result its concentration decreases both in the direction of bulk flow and also in the direction anode-to-electrolyte. Because of the relatively low temperature of operation, the ammonia decomposition rate is low and the ammonia is not well utilized (lowest mole fraction is 0.83).

Figure 3 shows the corresponding plot for hydrogen mole fraction. The inlet gas has no hydrogen (zero mole fraction). But the hydrogen concentration increases as it is produced in the anode. If there were no electrochemical reactions

occurring at the anode/electrolyte interface, the maximum hydrogen mole fraction would have been higher. At 0.7 V, the maximum mole fraction is 0.0864. Better ammonia to hydrogen conversion is expected at higher temperatures. However, at the intermediate temperatures, this conversion can be improved by recycling the anode exhaust. Also the hydrogen partial pressures can be improved by pressurizing the ammonia.

Figure 4 shows the steady state temperature. Cathode and anode gases enter at 773 K. For these conditions, the changes in temperature are not large. It decreases to a minimum value of 770.3 K and increases to a maximum of 774.2 K. Temperature sink is due to the endothermic ammonia decomposition reaction. The temperature rise is due to heat produced by the fuel cell reactions and ohmic heating. As a result, there is an initial sink at the anode entrance region, followed by a gradual rise in temperature. In high temperature SOFCs, this temperature sink is much more pronounced. In other works, temperature sinks of 30 – 70 K have been reported [1,2], which pose deleterious material problems. The results shown in this work suggest that problems of thermal shock can be significantly reduced by operating ammonia-fed SOFCs at intermediate temperatures.

4. Conclusions

This paper presented a 2D CFD model of an ammonia-fed SOFC implemented and solved in COMSOL 4.3. This model was based on the Temkin-Pyzhev model of ammonia decomposition. In addition, it utilized a modified version of Fick's law to simulate the dusty gas model of chemical species transport in porous media. Convergence was achieved by gradually introducing coupling parameters.

The results showed that the rate of ammonia decomposition is lower for intermediate temperature SOFCs than for high temperature SOFCs. As a result, ammonia to hydrogen conversion is low (17%). This will result in lower current densities. One possible solution is to pressurize the ammonia being supplied to the SOFC, and recycling the anode outlet.

As a result of the low ammonia decomposition rate, the temperature sink or cold spot in the anode is not as severe as with high temperature ammonia-fed SOFCs. The

temperature only drops by about 3 K compared with 30-70 K for high temperature SOFCs. This means that material problems associated with thermal shock for high temperature ammonia-fed SOFCs are alleviated by intermediate temperature operation.

COMSOL aids in the model development by providing rigorous solvers for coupled problems. They also offer a wide range of modules which are sufficient for most applications. However, there is no module that contains equations for the dusty gas model. The dusty gas model resembles the Stefan-Maxwell equations, however, it may not be feasible or possible to sufficiently modify the Stefan-Maxwell model to simulate the dusty gas model. Instead in this paper, Fick's law is modified to simulate the dusty gas model. This modification has been shown to be very accurate for SOFC applications. However, in the future, COMSOL should consider introducing a dusty gas model in the chemical species module.

5. References

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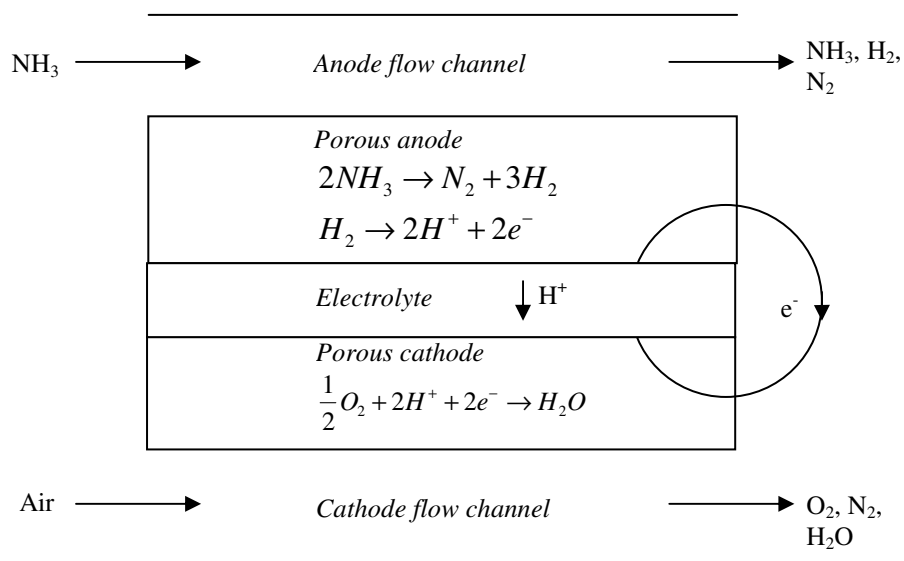
Figures

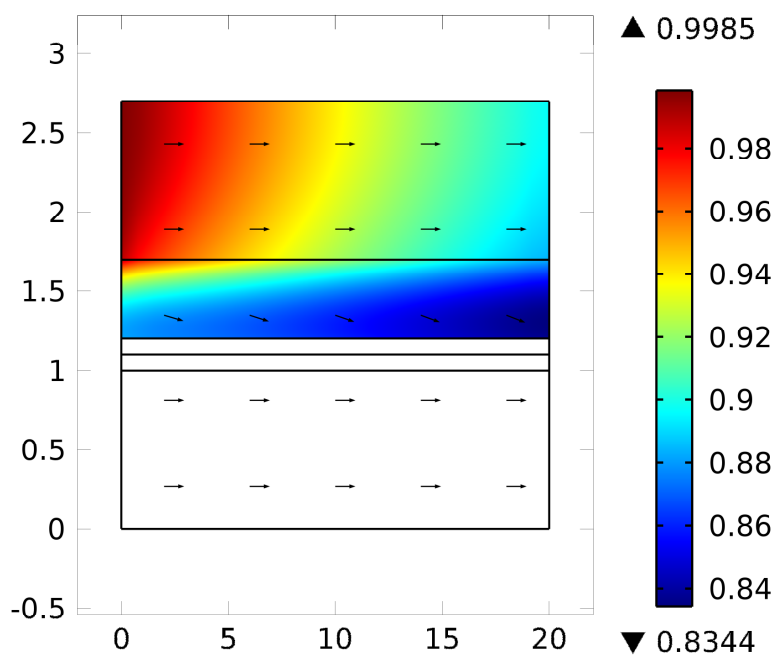Figure 1. Schematic and Computational Domains.
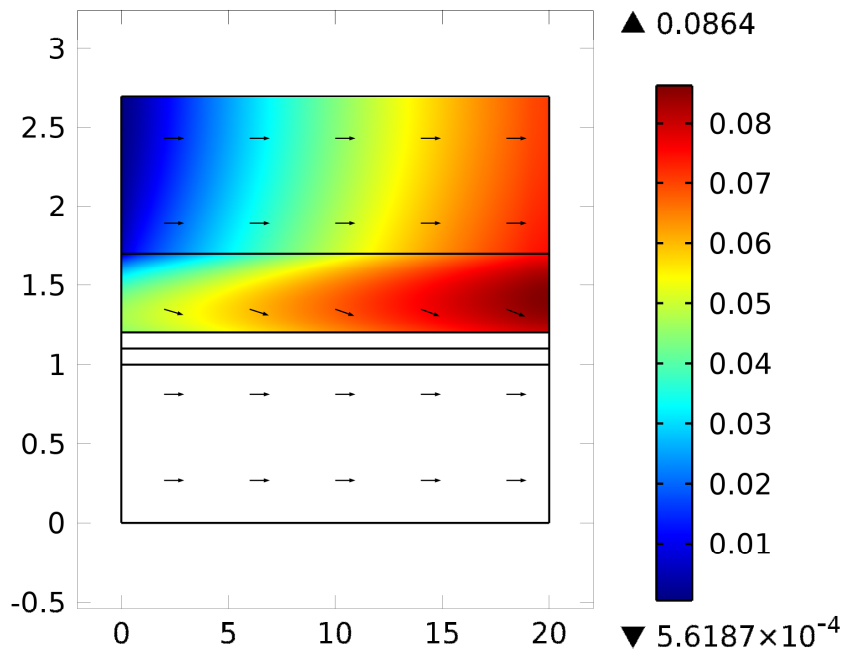

Figure 2. Ammonia mole fraction (0.7 V, 5000 A/m²).
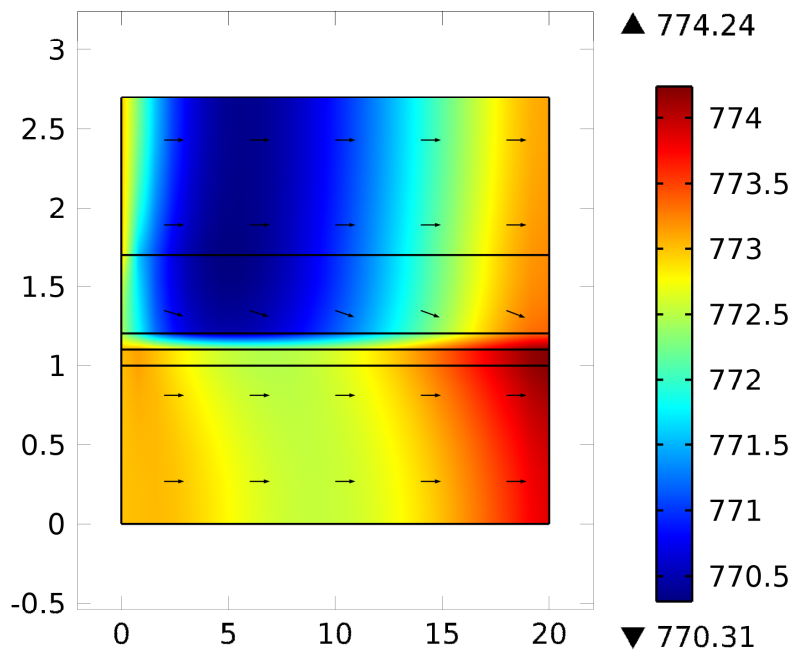
Figure 3. Hydrogen mole fraction (0.7 V, 5000 A/m²).

Figure 4. Temperature (K)