Analysis of equilibrium and kinetic models of internal reforming on solid oxide fuel cell anodes: Effect on voltage, current and temperature distribution

Khaliq Ahmed a, *, 1, Karl Föger b, 1

a Curtin University, Kent Street, Bentley, WA 6102, Australia
b Xinnotec Pty. Ltd., Kew, Victoria 3101, Australia

HIGHLIGHTS

- Impact of fuel reforming chemistry on cell’s characteristic performance profiles.
- Importance of including reverse methanation in internal reforming reaction scheme.
- Simultaneous generation of current density and voltage profiles along cell length.

ARTICLE INFO

Article history:
Received 24 March 2016
Received in revised form
28 December 2016
Accepted 9 January 2017
Available online 17 January 2017

Keywords:
SOFC anode
Internal reforming
Reaction chemistry
Kinetics and equilibrium
1D model

ABSTRACT

The SOFC is well-established as a high-efficiency energy conversion technology with demonstrations of micro-CHP systems delivering 60% net electrical efficiency [1]. However, there are key challenges in the path to commercialization. Foremost among them is stack durability. Operating at high temperatures, the SOFC invariably suffers from thermally induced material degradation. This is compounded by thermal stresses within the SOFC stack which are generated from a number of interacting factors. Modelling is used as a tool for predicting undesirable temperature and current density gradients. For an internal reforming SOFC, fidelity of the model is strongly linked to the representation of the fuel reforming reactions, which dictate species concentrations and net heat release. It is critical for simulation of these profiles that the set of reaction rate expressions applicable for the particular anode catalyst are chosen in the model. A relatively wide spectrum of kinetic correlations has been reported in the literature. This work presents a comparative analysis of the internal distribution of temperature, current, voltage and compositions on a SOFC anode, using various combinations of reaction kinetics and equilibrium expressions for the reactions. The results highlight the significance of the fuel reforming chemistry and kinetics in the prediction of cell performance.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

High efficiency SOFC [1-2] are almost invariably of the direct internal reforming type with conversion of methane on the anode via steam reforming. Other modes of operation viz., indirect internal reforming, external reforming, partial oxidation and auto-thermal reforming lead to significant lowering of the electrical efficiency through additional cooling requirement and/or fuel dilution.

At the heart of internal reforming on the SOFC anode is the steam reforming of methane; other accompanying reactions like the water-gas shift reaction play a much smaller role. Carbon forming reactions will play a significant detrimental role when operating under low steam-to-carbon ratios, but can largely be avoided by use of high steam-to-carbon ratios or by the use of additives in the anode composition, which prevent or minimize the risk of carbon formation [2-4]. Although steam reforming is a mature technology with a significant body of knowledge and understanding [3-6] acquired over decades of industrial practice in the petrochemical industry complemented by some rigorous and well-defined research by the industry, academia and research
organizations, experience with internal reforming on SOFC anodes of various geometry under the influence of variable current density and temperature is still limited and not well understood. Several groups have reported detailed investigations [7–13] of the kinetics of internal reforming in various platforms — from pelletized catalysts to anode substrates. Significant differences exist in the reaction orders and activation energies reported. These differences would obviously lead to differences in predicted concentration, voltage, temperature and current density profiles within the fuel cell anode. The profiles resulting from operation will depend to a large extent on the actual reaction rates prevailing on the anode with accompanying heat and mass transfer limitations.

A number of modelling studies focusing on the internal reforming aspects have been reported in the literature [14–31]. Sanchez et al. [21] studied the effect of different reforming kinetics and thermodynamic equilibrium on temperature, concentration and reaction rate profiles using a 1-D heterogeneous model. They observed that the main difference in these profiles occurred in the first half of the cell near the anode inlet section. These differences lead to a 20% difference in electrical performance and a 30 °C difference in temperature. As the differences were negligible in the second half of the anodic chamber, as long as all the methane was converted, it would suffice to use a 0-D model based on thermodynamic equilibrium for a lumped-volume based system simulation. They considered their “mixed” model to be the most accurate, where the “mixed” model was based on application of the limiting local reforming rate, kinetic or equilibrium. It is not clear how the authors came to this conclusion. While it is extremely cumbersome, if not impractical, to measure dimensional profiles of temperature, concentration and current density, a multidimensional model can be validated by comparing the outlet temperature, concentration, current and voltage with experimental values for a range of conditions of flow rate, current, fuel utilisation, temperature and voltage. Kang et al. [18] presented a 1D model of a planar internal reforming SOFC neglecting solid phase heat-transfer and gas-phase diffusion and compared this with a 1-D model where no such simplifications were applied. In their reduced model, voltage was calculated from average current density saving computational complexity and time. Compared to the detailed 1-D model, the accuracy of the reduced 1-D model for predictions of outlet gas flow rates, mole fractions, temperature and cell voltage were acceptable except under extreme operating conditions. Nikooyeh et al. [24] studied the potential for carbon deposition using a heterogeneous 3-D model of anode-supported planar SOFC with internal reforming of methane. Areas most susceptible for thermal stress and carbon formation were identified from temperature distribution through the PEN (positive electrode/electrolyte/negative electrode) and profiles of gas composition through the gas channels. They also showed that with 60% recycling of the anode exhaust gas, both temperature gradients and the risk of carbon formation are reduced while maintaining high current density. With a detailed heterogeneous 1-D model, Aguilar et al. [28] showed that SOFC operation under counter-flow of fuel and air leads to steep temperature gradients and uneven current density distribution. Ni et al. [29] employed a 1-D pseudo-homogeneous model to simulate distributions of mole fraction, pressure and reaction rates inside porous electrodes. The model was validated by comparing I-V characteristics with literature [26]. Haberman and Young [31] applied a 3-D heterogeneous model to highlight the importance of the reforming kinetics and thermal boundary conditions on the flow field within the porous structure. Although there were not compared with any experimental data it demonstrates the effect of temperature on local reforming rates which impacts concentration and velocity distributions inside the porous structure and in the fuel supply channel.

In this paper we report a comparative investigation of the profiles for concentration, temperature, Nernst voltage, operating voltage and current density resulting from using equilibrium, kinetic and a combination of equilibrium and kinetic models for the internal reforming reactions. For modelling internal steam reforming on SOFC anodes, it is customary to consider the following two reactions:

Methane Steam Reforming (MSR):

$$\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2 \quad \Delta H_{298} = 206.1 \text{ kJ/mole} \quad (1)$$

Water-Gas Shift (WGS):

$$\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2 \quad \Delta H_{298} = -41.15 \text{ kJ/mole} \quad (2)$$

However, while studying the intrinsic steam reforming of methane, Xu and Froment [32] concluded that it is unlikely that CO2 would be formed exclusively out of CO and therefore reaction schemes with a parallel contribution to CO2 formation are required. In this work we have included an option to include this third reaction, which is the reverse methanation reaction:

Reverse Methanation (RMTN):

$$\text{CH}_4 + 2\text{H}_2\text{O} = \text{CO}_2 + 4\text{H}_2 \quad \Delta H_{298} = 165 \text{ kJ/mole} \quad (3)$$

Two kinetic expressions for the internal methane steam reaction (1) and one kinetic expression for the water-gas shift reaction were chosen from literature. In addition, the thermodynamic equilibrium of the Methanation reaction was also considered. Various combinations of the kinetics and thermodynamic equilibrium of methane steam-reforming and water-gas shift and the reverse methanation reaction were considered in a simple 1-D pseudo-homogeneous model of the anode reaction chamber and anode. Interaction between flow in the porous medium and in the adjacent fuel supply channel is ignored. Although a pseudo-homogeneous model does not adequately represent the fluid or solid phase of the reactor/catalyst, the effect of the different kinetic and equilibrium models is clearly demonstrated by the 1-D pseudo-homogeneous model. The models in this work, based on various combinations of kinetically controlled or purely thermodynamically limited rate expressions for the reforming reactions involved demonstrate how current density, temperature and voltage profiles along the cell length can be affected by fuel reforming chemistry. In a similar but less extensive work, Paradis et al. [33] studied the effect of the type of the kinetic model, power-law or Langmuir-Hinshelwood, applied to the steam reforming reaction along with equilibrium of the water-gas shift reaction, on the reaction rate. They simulated temperature and mole fraction distribution under the conditions reported in the literature they used for the reforming rates. The steam reforming reaction rates were fast and differed only slightly across three models, two of which were Arrhenius type and one Langmuir-Hinshelwood. They found that the active surface area to volume ratio had a greater effect on the initial temperature drop due to the endothermic reforming reaction than on the overall temperature distribution. They attributed these differences to large differences in pre-exponential factor and activation energy values. They concluded that this suggests that the anode structure and catalytic composition can significantly affect the reforming reaction rate so that microscale modelling would be required for a better understanding of the relationship between these parameters and reaction rates. Unlike in this work, they did not study the effect of different reforming kinetics on current density, voltage or fuel utilisation profiles. Andersson et al. [34] reviewed the global reaction kinetics, surface reaction kinetics and kinetic pathways for the steam reforming reaction. They also carried out a thermodynamic analysis of the catalytic materials.
They attributed the differences in predictions by detailed models and global models to the variable structures in metal particle surfaces and the differences in the assumptions of reaction pathways and rate-limiting steps and the fact that reaction orders vary significantly in the global models.

The novel feature of the mathematical model developed in this work is the ability to generate voltage as well as current density profiles. In a real system as the stack/cell degrades, current is continually increased to compensate for the voltage loss due to degradation, in order to maintain the power output, at a high level of fuel utilisation, to maintain high electrical efficiency, until it reaches a point where the power output and/or the efficiency can longer be maintained due to significant degradation. It is important to realize that at any point in time, even though a single value of cell voltage is measured, a profile of voltage invariably exists along the cell length. In the same way that a current density profile exists, even with a constant current, due to variation in the availability of hydrogen and in temperature, a cell voltage profile also exists firstly, due to a variation in Nernst voltage along the cell length as a result of the composition change along the cell length and secondly due to variation in cell electrical losses along the cell length. In this work we have integrated all such variations within the solver due to variation in cell electrical losses along the cell length. In this manner in the open literature, particularly with respect to reforming chemistry.

2. Model development

2.1. Chemistry of reactions

For fossil-fuel based SOFC systems, the fuel of choice is natural gas with its abundant reserve and a reticulated supply infrastructure. The natural gas mixed with steam at the desired steam-to-carbon ratio is fed to a pre-reformer for converting natural gas to a gas mixture containing methane, hydrogen, carbon dioxide, carbon monoxide and steam. The relative amounts of the principal components methane and hydrogen depend on the steam/carbon (S/C) ratio, temperature and pressure of the pre-reformer. It suffices to assume the pre-reformer reactions are at thermodynamic equilibrium and can be represented by the following overall reactions, along with the water-gas shift reaction (2):

$$\text{C}_2\text{H}_6 + \text{H}_2\text{O} = \text{CH}_4 + 2\text{H}_2 + \text{CO} \quad \Delta H_{298} = -140.2 \text{ kJ/mole}$$  \hspace{1cm} (4)

$$\text{C}_3\text{H}_8 + 2\text{H}_2\text{O} = \text{CH}_4 + 4\text{H}_2 + 2\text{CO} \quad \Delta H_{298} = -289.8 \text{ kJ/mole}$$  \hspace{1cm} (5)

$$\text{C}_4\text{H}_{10} + 3\text{H}_2\text{O} = \text{CH}_4 + 6\text{H}_2 + 3\text{CO} \quad \Delta H_{298} = -442.5 \text{ kJ/mole}$$  \hspace{1cm} (6)

$$\text{C}_3\text{H}_{12} + 4\text{H}_2\text{O} = \text{CH}_4 + 8\text{H}_2 + 4\text{CO} \quad \Delta H_{298} = -593.2 \text{ kJ/mole}$$  \hspace{1cm} (7)

Similar reactions can be written for any higher hydrocarbons, if present.

The reactions occurring on the internal reforming SOFC anode are (1), (2) and potentially reaction (3). Additionally, for the fuel cell reaction, the hydrogen oxidation reaction chemistry is included:

$$\text{H}_2 + 1/2\text{O}_2 = \text{H}_2\text{O} \quad \Delta H_{298} = -241.8 \text{ kJ/mole}$$  \hspace{1cm} (8)

The electrochemical oxidation of CO is assumed to be negligible and the usual assumption that CO consumption is via the WGS reaction only, is made. Because the stoichiometry of CO conversion is the same for both routes, this assumption has no effect on mass balance.

The rates of consumption of reactants and formation of products are then calculated from the following equations:

$$r_{\text{CH}_4} = -r_{\text{MSR}} - r_{\text{RMTN}}$$  \hspace{1cm} (9)

$$r_{\text{H}_2\text{O}} = -r_{\text{MSR}} - r_{\text{WGS}} - 2r_{\text{RMTN}} + r_{\text{FC}}$$  \hspace{1cm} (10)

$$r_{\text{CO}} = r_{\text{MSR}} - r_{\text{WGS}}$$  \hspace{1cm} (11)

$$r_{\text{CO}_2} = r_{\text{WGS}} + r_{\text{RMTN}}$$  \hspace{1cm} (12)

$$r_{\text{H}_2} = 3r_{\text{MSR}} + r_{\text{WGS}} + 4r_{\text{RMTN}} - r_{\text{FC}}$$  \hspace{1cm} (13)

Where $r_{\text{FC}}$ is the rate of consumption of hydrogen by reaction (8) and is calculated by applying Faraday's Law.

$$r_{\text{FC}} = \frac{I}{N F}$$  \hspace{1cm} (14)

When the reverse methanation reaction is not included, $r_{\text{RMTN}}$ is set to zero. For the thermodynamic equilibrium models, the rates of reactions (1), (2) and (3) are calculated from

$$r_{\text{MSR}} = k_f (\text{MSR}) \left( \frac{p_{\text{CH}_4}p_{\text{H}_2}O - p_{\text{CO}p_{\text{H}_2}}^3}{K_{eq\text{MSR}}} \right)$$  \hspace{1cm} (15)

$$r_{\text{WGS}} = k_f (\text{WGS}) \left( \frac{p_{\text{CO}p_{\text{H}_2}O} - p_{\text{CO}p_{\text{H}_2}}^4}{K_{eq\text{WGS}}} \right)$$  \hspace{1cm} (16)

$$r_{\text{RMTN}} = k_f (\text{RMTN}) \left( \frac{p_{\text{CH}_4}p_{\text{H}_2}O - p_{\text{CO}p_{\text{H}_2}}^3}{K_{eq\text{RMTN}}} \right)$$  \hspace{1cm} (17)

with arbitrarily high values given to $k_f (\text{MSR})$, $k_f (\text{WGS})$ and $k_f (\text{RMTN})$.

The equilibrium constants were calculated from the following temperature dependent equations obtained from fitting data generated using the chemical reaction and equilibrium software HSC Chemistry from Outokumpu [35].

$$K_{eq\text{MSR}} = 1.001643E13 \exp (-26716.56E04 \left(1/T\right))$$  \hspace{1cm} (18)

$$K_{eq\text{WGS}} = 9.100463E19 \left(1/T\right)^6 - 5.893048E17 \left(1/T\right)^5$$

$$+ 1.625659E15 \left(1/T\right)^4 - 2.409942E12 \left(1/T\right)^3$$

$$+ 2.016418E09 \left(1/T\right)^2 - 8.992573E05 \left(1/T\right)$$

$$+ 1.668321E02$$  \hspace{1cm} (19)

$$K_{eq\text{RMTN}} = 1.712971E11 \exp (-22302.18 \times 1\left(1/T\right))$$  \hspace{1cm} (20)

The kinetics of methane steam reforming is given by the following expression:

$$r_{\text{MSR}} = k_o \exp \left( -E_a/RT \right) \left( \frac{p_{\text{CH}_4}}{p_{\text{H}_2}O} \right)^{\alpha} \left( \frac{p_{\text{H}_2}O}{p_{\text{CH}_4}} \right)^{\beta}$$  \hspace{1cm} (21)

Two different kinetics were considered, one reported by Ahmed and Föger [9] and the other reported by Achenbach and Riensche [13]. The values of the constants in Eq. (17), reported by Ahmed and Föger are $k_0 = 8542 \text{ mol/m}^2\text{bar}^{1/2}/\text{s}$, $\alpha = 0.85$, $\beta = 0.35$ and $E_a = 95 \text{ kJ/mol}$ while Achenbach and Riensche reported $k_0 = 4274 \text{ mol/m}^2\text{bar}/\text{s}$, $\alpha = 1$, $\beta = 0$ and $E_a = 82 \text{ kJ/mol}$.

Only one kinetic case for the reverse WGS reaction was
considered as reported by Tingey [36].

\[
\begin{align*}
    r_{\text{RWGS}} &= 7.6E04 \exp(-39.2/RT)P_{H_2}^{0.333}P_{CO_2}^{1.2E13} \exp(-78/RT)P_{H_2}^{0.5}P_{CO_2}^{1.2E13} \\
    \text{With these thermodynamic and kinetic reaction rates eight different models were considered as shown in Table 1. For models VI, VII and VIII, the usual assumption is made that CO}2 \text{ formation occurs via WGS only and the rate of the reverse methanation reaction, }r_{\text{RMTN}} \text{ is set to zero in these models. A kinetic rate expression for the reverse methanation reaction is not considered in any of the models.}
\end{align*}
\]

2.2. Continuity equations

The continuity equation for mass balance of each species is written as:

\[
\frac{dF_i}{dz} = -r_i
\]  

where, \(i = \text{CH}_4, \text{H}_2\text{O, CO, CO}_2, \text{H}_2\).

The continuity equation for energy balance is:

\[
\frac{dT}{dz} = \frac{\Sigma(-r_j)(\Delta H_j) - P_E}{F_1C_p}
\]  

where, \(j = \text{MSR, WGS, RMTN and H}_2 \text{ oxidation and PE is the electrical power output of the cell. The heats of reactions were calculated from the following temperature dependent equations obtained from fitting data generated using the chemical reaction and equilibrium software HSC Chemistry from Outokumpu [35].}

\[
\begin{align*}
    \Delta H_{\text{MSR}} &= -0.00002113138 \ T^2 + 0.04151301 \ T + 206.2635 \\
    \Delta H_{\text{WGS}} &= 0.01071393 \ T - 42.47663 \\
    \Delta H_{\text{MTN}} &= -0.00002299941 \ T^2 + 0.05362858 \ T + 163.4044 \\
    \Delta H_{\text{H}_2-\text{OXIDATON}} &= 0.000003410207 \ T^2 - 0.01143889 \ T - 241.3694
\end{align*}
\]

Heat is generated in the electrodes in several ways. Firstly, there is ohmic heat generated due to resistance to current flow. In addition, there is heat generation due to the activation losses and resistance to mass transport. These two together constitute the lowering of the reversible equilibrium potential corresponding to \(\Delta G\). Finally, there is heat generated due to entropy loss; the term \(T\Delta S\) in equation (29) cannot be utilized as electrical energy and results in heat generation.

\[
\Delta H = \Delta G + T\Delta S
\]  

Reaction heat effect can be endothermic or exothermic. Steam reforming and the reverse methanation reactions are endothermic while the water-gas shift reaction is exothermic. The numerator in the right hand side of equation (24) can also be written as:

\[
\Sigma(-r_j)(\Delta H_j) + T\Delta S (i/nF) + i^2R_0 + \eta
\]  

where \(R_0\) is cell ohmic resistance, \(\eta\) is the sum of activation and concentration losses, and \(j\) stands for MSR, WGS and RMTN and does not include the H2 oxidation reaction heat, as it is already accounted for by the terms in the expression above. It is assumed that the heat released from chemical reactions and electrical and entropy losses are absorbed by the cell.

The sets of equation (23) written for each species together with equation (24) are solved by the fourth-order Runge-Kutta routine to calculate local distributions of reaction rates, concentrations and temperature along the length of the anode.

2.3. Nernst voltage

The equilibrium potential at any location is calculated from the Nernst equation (26) using local concentrations computed as described in section 2.2.

\[
E = \frac{-\Delta G_0}{nF} + \frac{RT}{nF} \ln \left( \frac{P_{H_2}P_{O_2}^{1/2}}{P_{H_2}O} \right)
\]  

The change in Gibbs Free Energy is a function of temperature and can be described by the following equation obtained by fitting data generated using the chemical reaction and equilibrium software HSC Chemistry from Outokumpu [35].

\[
\Delta G_0 = 54.1659T - 246712.9
\]  

Eq. (32) has previously been shown to be adequate for calculating equilibrium potentials of gas mixtures containing \(\text{CH}_4, \text{CO}, \text{H}_2, \text{CO}_2\) and \(\text{H}_2\text{O} [37,38].

2.4. Overpotential and ohmic losses

The equation used for calculating the overpotential was:

\[
\eta = (1/a)j^xU_f^y \exp(E_b/RT)
\]  

where \(j\) is the current density and \(U_f\) is the fuel utilisation. The values of the constants \(a = 4.43, x = 0.77, y = -0.15\) and \(E_b = 10560\) were determined by regression analysis of experimental measurement of cell overpotential at various current densities and fuel utilisation at the three temperatures 750, 800 and 850 °C by the galvanostatic current-interruption (G.C.I.) technique [39].

<table>
<thead>
<tr>
<th>Models for Internal Reforming Reactions occurring on a SOFC anode.</th>
<th>Methane steam reforming</th>
<th>Water gas shift</th>
<th>Reverse methanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model I</td>
<td>Equilibrium</td>
<td>Equilibrium</td>
<td>Equilibrium</td>
</tr>
<tr>
<td>Model II</td>
<td>Kinetics (Ahmed)</td>
<td>Equilibrium</td>
<td>Equilibrium</td>
</tr>
<tr>
<td>Model III</td>
<td>Kinetics (Achenbach)</td>
<td>Equilibrium</td>
<td>Equilibrium</td>
</tr>
<tr>
<td>Model IV</td>
<td>Kinetics (Ahmed)</td>
<td>Equilibrium</td>
<td>Equilibrium</td>
</tr>
<tr>
<td>Model V</td>
<td>Kinetics (Tingey)</td>
<td>Equilibrium</td>
<td>Equilibrium</td>
</tr>
<tr>
<td>Model VI</td>
<td>Equilibrium</td>
<td>Equilibrium</td>
<td>Not included</td>
</tr>
<tr>
<td>Model VII</td>
<td>Kinetics (Ahmed)</td>
<td>Equilibrium</td>
<td>Not included</td>
</tr>
<tr>
<td>Model VIII</td>
<td>Kinetics (Achenbach)</td>
<td>Equilibrium</td>
<td>Not included</td>
</tr>
</tbody>
</table>
measurements showed that cell overpotential generally decreases with increase in the level of fuel utilisation, whereas the cell ohmic resistance is independent of fuel utilisation as expected [37].

The ohmic resistance is calculated by the equation of the type [38]:

$$\text{R}_O = (t_e / A) \exp \left( B / T \right)$$

where $t_e$ is the electrolyte thickness and $A = 21428$ and $B = 7776$ are constants, with their values determined empirically [37]. The variables $U_f$, $R_f$, and $R_R$ at any location are calculated by linking these expressions with the solutions for equations (23) and (24).

3. Results and discussion

Different rate models lead to differences in various aspects of the performance of the SOFC anode. The key features are shown in Table 2. Significant differences in maximum current density and minimum current density can be seen between Models I to VI on the one hand and models VII and VIII on the other. Models VII and VIII also result in significantly lower Nernst Voltage resulting in lower cell voltage and correspondingly lower efficiency. While there is not a significant difference in the average temperature in the various models, Models I and VI have the highest $dT$ and Models VII and VIII have the lowest. This is due to not accounting for the reverse methanation reaction in Models VII and VIII. Although, model VI also does not account for the reverse methanation explicitly, it implicitly accounts for RMTN, as will be explained later with discussion of hydrogen profiles in Fig. 2; this is the reason why Model VI's predictions are nearly identical to Model I's predictions in Table 2.

An advantageous feature of Models VII and VIII is a more uniform current density as evidenced by the difference between maximum and minimum current densities in Table 2. Current density at a given location depends on temperature and $H_2$ availability, with total current determined by fuel utilisation target. Current density profiles are further discussed under Fig. 4.

The difference in predicted temperatures at any location is small, as shown in Fig. 1, because the difference in heat of reaction after accounting for the different extents of reaction for kinetically controlled and equilibrium limited schemes is small. Temperature at a given location is determined by the net effect of heat absorbed by the reforming reactions and the heat released by the water-gas shift reaction and from the electrical resistances and entropy loss of the fuel cell reaction. Of the three models not accounting for RMTN, models VII and VIII have the lowest temperatures in the bulk of the anode, commencing at 10% entry length, due to the fact that these models have the highest endothermic heat demand. Even though model VI also does not explicitly account for RMTN, equilibrium of MSR and WGS together accounts for the equilibrium of all three reactions for all practical purposes. This is because RMTN is not an independent reaction from a stoichiometric viewpoint. Differences between accounting for RMTN and not accounting for it, is seen only when either the MSR or the WGS or both are kinetically controlled.

In Fig. 2 a significant difference exits between models VII and VIII on the one side and the remaining models on the other, in the first 30% of the active area. Models VI, VII and VIII do not account for the RMTN reaction, but in contrast with models VII & VIII, model VI allows MSR and WGS to reach equilibrium, whereas in models VII and VIII, MSR is kinetically controlled. This suggests that under equilibrium conditions, inclusion of the RMTN makes little difference to the amount of $H_2$ produced compared to the equilibrium case where it is not accounted for i.e. model VI. There is a small difference in the first 15% of the cell, but thereafter these two models overlap, largely on account of the equilibrium of WGS and suggest that the equilibrium of the two reactions are mostly sufficient to capture the equilibrium conditions for the case when all three reactions are considered to be in equilibrium. Under these conditions, it matters little if the thermodynamics of the reverse methanation reaction is included or not. This is not unexpected as the reverse methanation reaction, which is a parallel steam reforming reaction along with MSR, is also a stoichiometric addition of the reactions MSR and WGS. For mass and heat balance purposes under thermodynamic equilibrium conditions, it is not an independent reaction. Any difference in results between models I and VI could be due to the accuracies of the expressions for equilibrium constants between MSR and RMTN. However, when MSR is kinetically controlled, there can be a substantial additional conversion of methane when RMTN is included. This explains the lower $H_2$ peak and average values in Models VII and VIII and the nearly similar profiles for models I and VI.

Fig. 3 shows that Models I and VI predict that most of the methane (>99%) is converted in the first 20% of the length. According to Models II, III, IV and V this occurs in the first 30–40% of the cell. Models VII and VIII without RMTN results in requiring 60% and 100% of the length respectively. The profiles for $H_2$ in Fig. 2 are not in agreement with the profiles for methane in Fig. 3. This is not surprising as $H_2$ is produced by WGS in addition to being produced by MSR and RMTN. As the fuel cell reaction proceeds, the equilibrium of the WGS reaction is shifted further to the right producing more hydrogen, while the level of conversion of methane may still remain the same due to kinetic limitations.

The current density profiles in Fig. 4 are consistent with the $H_2$ mole fraction profiles and reflect the assumption in the model that

<table>
<thead>
<tr>
<th>CH₄ conversion, %</th>
<th>Ave Nernst voltage, V</th>
<th>Ave hydrogen mole fraction</th>
<th>Ave cell voltage, V</th>
<th>Ave temperature, K</th>
<th>Max $dT$, °C</th>
<th>Max current density, mA/cm²</th>
<th>Min current density, mA/cm²</th>
<th>Efficiency, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model I 100</td>
<td>0.969</td>
<td>0.395</td>
<td>0.787</td>
<td>987.5</td>
<td>45</td>
<td>534</td>
<td>151</td>
<td>56.6</td>
</tr>
<tr>
<td>Model II 100</td>
<td>0.968</td>
<td>0.385</td>
<td>0.782</td>
<td>985.9</td>
<td>44</td>
<td>510</td>
<td>155</td>
<td>56.2</td>
</tr>
<tr>
<td>Model III 100</td>
<td>0.967</td>
<td>0.381</td>
<td>0.781</td>
<td>985.5</td>
<td>43</td>
<td>503</td>
<td>157</td>
<td>56.1</td>
</tr>
<tr>
<td>Model IV 100</td>
<td>0.968</td>
<td>0.386</td>
<td>0.781</td>
<td>984.7</td>
<td>41</td>
<td>540</td>
<td>112</td>
<td>56.1</td>
</tr>
<tr>
<td>Model V 100</td>
<td>0.971</td>
<td>0.396</td>
<td>0.783</td>
<td>984.3</td>
<td>40</td>
<td>516</td>
<td>130</td>
<td>56.3</td>
</tr>
<tr>
<td>Model VI 100</td>
<td>0.969</td>
<td>0.392</td>
<td>0.786</td>
<td>987.2</td>
<td>45</td>
<td>530</td>
<td>152</td>
<td>56.5</td>
</tr>
<tr>
<td>Model VII 99.95</td>
<td>0.957</td>
<td>0.328</td>
<td>0.764</td>
<td>981.9</td>
<td>38</td>
<td>473</td>
<td>174</td>
<td>54.9</td>
</tr>
<tr>
<td>Model VIII 96.86</td>
<td>0.952</td>
<td>0.306</td>
<td>0.761</td>
<td>982.7</td>
<td>37</td>
<td>478</td>
<td>174</td>
<td>54.7</td>
</tr>
</tbody>
</table>
the electrochemical process occurs by hydrogen oxidation alone and CO consumption is according to WGS equilibrium or kinetics. Less Hydrogen is available for the fuel cell reaction when RMTN is not included, which results in lower current density values. Generally speaking the H₂O mole fraction profiles in Fig. 5 are consistent with H₂ profiles, but there is a wider spread in the cluster of graphs representing kinetically controlled models, i.e. Models II to V. This is because water consumption will vary according to the extents of MSR and WGS when they are kinetically controlled. However, this effect is small as 3–4 times more H₂ is generated than water is consumed by MSR and WGS.

The impact of the different rate models on the Nernst Voltage during cell operation is shown in Fig. 6. These voltages reflect the equilibrium voltage at any axial position as the fuel is progressively depleted owing to the fuel cell reaction. The Nernst voltage profiles essentially mimic H₂ and H₂O concentration profiles according to Equation (26). In the first 5–30%, depending on the reforming kinetics, of the cell length, Nernst voltage increases, as this section is dominated by additional production of H₂ from the progress of the steam reforming reaction. The remaining section is dominated by consumption of hydrogen, with the steam reforming reaction rate slowing down as it approaches thermodynamic equilibrium or its kinetic limit, as per the chosen model.

Fig. 7 shows the cell voltage profile which results as a consequence of the Nernst Voltage, temperature and the current applied. Some smoothening of the profile occurs due to the fact that current

Fig. 1. Temperature along axial length.

Fig. 2. H₂ concentration along axial length.
densities are lower where Nernst Voltage is lower. Models VII and VIII give the flattest voltage profiles as they have more uniform current densities. This flattening however, comes at the expense of a 3% loss in output voltage of the cell. It is important to realize here, there are at least four components in cell voltage loss along the length of the cell, compared to the Nernst Voltage (Open-circuit voltage) at inlet of the cell. The first drop is the Nernst voltage loss that results due to consumption of fuel, in this case H2. This is purely due to change in chemical composition i.e. dilution of fuel that occurs due to consumption of H2 and generation of H2O. This becomes more and more significant as the fuel is increasingly utilized along the cell length. The remaining three components are the classical drops:

1. Activation loss
2. Concentration loss
3. Ohmic loss

A comparison of Figs. 6 and 7, show that the drop in Nernst Voltage is more drastic along the length of the cell than the drop in cell voltage. This is consistent with the negative value of exponent y in equation (33). The model developed in this work calculates voltage at each step of the computation, along the cell length by taking into account all four components mentioned above.

Fig. 8 shows the consequences of the different rate models on fuel utilisation profiles. The equilibrium models I and VI result in 70% of the fuel utilized in <15% of the length. This would have a
significant effect on cell degradation as cell degradation is presumably higher at higher utilisation levels. In contrast, models VII and VIII predict lower degradation. These four models together predict two extreme behaviours which are most likely far from reality. In general the profiles for fuel utilisation mimic the CH₄ profiles. This is easily explained as follows. None of the models in this work allow for the direct electrochemical oxidation of methane since such a reaction is not proven to be occurring on the widely-used Ni-based SOFC anode. The only route for the fuel to be utilized in this work is via the conversion of CH₄ to H₂ followed by the electrochemical oxidation of H₂. Accordingly, in regions where methane conversion is low due to kinetic limitations, H₂ supply is limited and consequently fuel utilisation is low.

Overall, the differences in composition, temperature, current density and voltage profiles can all be grouped according to three different approaches for modelling of internal reforming on SOFC anodes.

1) Assumption of thermodynamic equilibrium for MSR and WGS.
2) Use of kinetic rates for MSR along with kinetic or thermodynamic equilibrium rates for WGS.
3) Not accounting for the reverse methanation reaction.

The steepest profiles are obtained with the thermodynamic equilibrium approach. When the reverse methanation reaction is not included and a kinetic scheme is used for MSR in conjunction
with a thermodynamic equilibrium or kinetic rate for WGS, profiles with lowest steepness are predicted. This indicates that the widely used approach of using a kinetic expression for MSR, along with thermodynamic equilibrium limited WGS, but not accounting for the reverse methanation reaction may be fraught with error. While the full thermodynamic approach is likely to overpredict rates and consequently the steepness of profiles, primarily due to the endothermic MSR reaction, models accounting for the reverse methanation along with approach 2 mentioned above are more likely to result in profiles which are close to reality. Approach 3 most likely results in underprediction, when MSR and WGS are not in equilibrium.

4. Conclusions

This work has demonstrated how different rates of each of the individual reactions — steam reforming of methane, water-gas shift and methanation — involved in the internal reforming of methane can affect current density, temperature and cell voltage profiles due to different composition and temperature profiles resulting from differences in kinetics. A fast kinetic rate does not necessarily lead to the most desirable current density and temperature profiles from a cell degradation viewpoint. More uniform current density and temperature profiles can be attained using anodes with somewhat reduced kinetic rates, albeit with a small sacrifice in efficiency. This work highlights the importance of including the reverse
methanation reaction when the methane steam reforming reaction is modelled using a kinetic rate expression. Models using thermodynamic approach for MSR and WGS with or without RMTN will result in over-predicting composition, temperature, current density and voltage profiles. Models using kinetic expressions for MSR and either kinetic or equilibrium rates for WGS, but not accounting for RMTN result in some degree of under-prediction of these characteristic variables of cell performance. Based on Xu and Froment's [32] contention and the results of this work, the most reliable predictions can be made by accounting for RMTN in a reaction scheme that includes the MSR kinetics and allows for kinetic or equilibrium rates for WGS. Inclusion of RMTN in the reactions scheme for internal reforming on SOFC anode is therefore crucial in developing robust models for predicting and controlling the performance of internal reforming type SOFC systems.

Interestingly, the kinetic rate expression for WGS used in some of the models does not appear to have a significant effect on the results suggesting that the WGS reaction is close to thermodynamic equilibrium as is widely assumed. This could be largely due to the fact that the reaction equilibrium is shifted to the right as more and more H2 are consumed by the fuel cell reaction.

The effect of the kinetics of the reactions involved in internal reforming of methane on resistance as a function of temperature and voltage profiles during steady state operation or its impact on cell degradation from the standpoint of hot-spot location, cell thermal gradient and high current density points. In particular, the reaction kinetics will have significant influence on temperature profile changes within the cell during power modulation and during start-up and shut-down due to the fact that temperature, space velocity and accompanying heat and mass transport processes will have different effects depending on the kinetics at play which will be further compounded by additional mass transport effects resulting from differences in concentration profiles due to differences in kinetics. The magnitude of the effect of not accounting for RMTN will depend on the temperature.

Therefore, there is little value in developing detailed models for simulating the performance of real systems, for mapping thermomechanical stresses in stacks or for developing control algorithms based on such models if the model is constructed from kinetics of internal reforming sourced from the literature and does not apply to anodes in real systems, commercial or prototype, to which these models are intended to be applied.

Acknowledgement

Part of this work was carried out at Ceramic Fuel Cells Ltd in Melbourne, Australia, where the authors were engaged in research and development of the SOFC technology.

Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>a constant in the empirical correlation for overpotential losses</td>
</tr>
<tr>
<td>A</td>
<td>a constant in the expression of electrolyte resistance as a function of temperature</td>
</tr>
<tr>
<td>B</td>
<td>coefficient of temperature in the expression of electrolyte resistance as a function of temperature</td>
</tr>
<tr>
<td>$C_p$</td>
<td>Heat capacity, kJ/mole K</td>
</tr>
<tr>
<td>$\Delta f_i$</td>
<td>Change in molar flow, mole/h</td>
</tr>
<tr>
<td>$dz$</td>
<td>differential axial distance, m</td>
</tr>
<tr>
<td>$dT$</td>
<td>differential temperature, K</td>
</tr>
<tr>
<td>$E$</td>
<td>Equilibrium potential, volts</td>
</tr>
<tr>
<td>$E_a$</td>
<td>Activation Energy, kJ/mole</td>
</tr>
<tr>
<td>$E_0$</td>
<td>coefficient of temperature in the expression of overpotential losses as a function of temperature, kJ/mole</td>
</tr>
<tr>
<td>F</td>
<td>Faraday Constant</td>
</tr>
<tr>
<td>$F_T$</td>
<td>Total molar flow, mole/h</td>
</tr>
<tr>
<td>$\Delta G_0$</td>
<td>Entropy change, kJ/K</td>
</tr>
<tr>
<td>$\Delta H_i$</td>
<td>Reaction Enthalpy, kJ/mole</td>
</tr>
<tr>
<td>I</td>
<td>Current, A</td>
</tr>
<tr>
<td>j</td>
<td>Current density, mA/cm²</td>
</tr>
<tr>
<td>$K_{eqMSR}$</td>
<td>Equilibrium constant for methane steam reforming reaction (MSR)</td>
</tr>
<tr>
<td>$K_{eqWGS}$</td>
<td>Equilibrium constant for water-gas shift reaction (WGS)</td>
</tr>
<tr>
<td>$K_{eqMTN}$</td>
<td>Equilibrium constant for reverse methanation reaction (MTN)</td>
</tr>
<tr>
<td>$k_f(MSR)$</td>
<td>Forward rate constant in MSR</td>
</tr>
<tr>
<td>$k_f(WGS)$</td>
<td>Forward rate constant in WGS</td>
</tr>
<tr>
<td>$k_f(MTN)$</td>
<td>Forward rate constant in MTN</td>
</tr>
<tr>
<td>$k_o$</td>
<td>Arrhenius constant in power law rate equation</td>
</tr>
<tr>
<td>$p_{CH_4}$</td>
<td>partial pressure of CH₄</td>
</tr>
<tr>
<td>$p_{CO}$</td>
<td>partial pressure of CO</td>
</tr>
<tr>
<td>$p_{CO_2}$</td>
<td>partial pressure of CO₂</td>
</tr>
<tr>
<td>$P_E$</td>
<td>Electrical Power</td>
</tr>
<tr>
<td>$p_{H_2}$</td>
<td>partial pressure of H₂</td>
</tr>
<tr>
<td>$p_{H_2O}$</td>
<td>partial pressure of H₂O</td>
</tr>
<tr>
<td>$p_{O_2}$</td>
<td>partial pressure of O₂</td>
</tr>
<tr>
<td>$R$</td>
<td>Universal Gas Constant</td>
</tr>
<tr>
<td>$r_{CH_4}$</td>
<td>rate of consumption of CH₄, mole/h</td>
</tr>
<tr>
<td>$r_{CO}$</td>
<td>rate of consumption of CO, mole/h</td>
</tr>
<tr>
<td>$r_{CO_2}$</td>
<td>rate of consumption of CO₂, mole/h</td>
</tr>
<tr>
<td>$r_{FC}$</td>
<td>rate of consumption of hydrogen by the fuel cell reaction, mole/h</td>
</tr>
<tr>
<td>$r_{H_2}$</td>
<td>rate of consumption of H₂, mole/h</td>
</tr>
<tr>
<td>$r_{H_2O}$</td>
<td>rate of consumption of H₂O, mole/h</td>
</tr>
<tr>
<td>$r_i$</td>
<td>rate of consumption of species i, where i = CH₄, H₂O, CO, CO₂, H₂, mole/h</td>
</tr>
<tr>
<td>$r_{MSR}$</td>
<td>rate of methane steam reforming reaction, mole/h</td>
</tr>
<tr>
<td>$r_{MTN}$</td>
<td>rate of reverse methanation reaction, mole/h</td>
</tr>
<tr>
<td>$r_{WGS}$</td>
<td>rate of water-gas shift reaction, mole/h</td>
</tr>
<tr>
<td>$R_Ω$</td>
<td>ohmic resistance, ohm</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature, K</td>
</tr>
<tr>
<td>$t_e$</td>
<td>thickness of electrolyte, m</td>
</tr>
<tr>
<td>$U_f$</td>
<td>fuel utilisation, %</td>
</tr>
<tr>
<td>$x$</td>
<td>exponent of current density in the empirical correlation for overpotential losses</td>
</tr>
<tr>
<td>$y$</td>
<td>exponent of fuel utilisation in the empirical correlation for overpotential losses</td>
</tr>
</tbody>
</table>

Greek letters

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>reaction order in methane</td>
</tr>
<tr>
<td>$\beta$</td>
<td>reaction order in steam</td>
</tr>
<tr>
<td>$\eta$</td>
<td>cell overpotential losses, volts</td>
</tr>
</tbody>
</table>

Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSR</td>
<td>Methane steam reforming</td>
</tr>
<tr>
<td>WGS</td>
<td>Water-gas shift</td>
</tr>
<tr>
<td>RMTN</td>
<td>Reverse methanation</td>
</tr>
<tr>
<td>SOFC</td>
<td>Solid oxide fuel cell</td>
</tr>
<tr>
<td>CHP</td>
<td>Combined Heat and Power</td>
</tr>
</tbody>
</table>

References


