Experimental and numerical analysis of transport phenomena in an internal indirect fuel reforming type Solid Oxide Fuel Cells using Ni/SDC as a catalyst

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Abstract. This paper presents experimental and numerical studies on the fuel reforming process on an Ni/SDC catalyst. To optimize the reforming reactors, detailed data about the entire reforming process is required. In the present paper kinetics of methane/steam reforming on the Ni/SDC catalyst was experimentally investigated. Measurements including different thermal boundary conditions, the fuel flow rate and the steam-to-methane ratios were performed. The reforming rate equation derived from experimental data was implemented in into numerical model which was numerically solved in order to discuss this process in details.

1. Introduction
The high working temperature of a Solid Oxide Fuel Cells makes hydrocarbons the most suitable fuel in achieving high efficiency from natural resources. The methane/steam reforming process is a conventional one for producing hydrogen [1, 2, 3, 4]. For hydrocarbon-based fuel, three types of fuel conversion can be considered in reforming reactions: an external reforming system, an indirect internal reforming system and a direct internal reforming system. High-temperature SOFC eliminates the need for an expensive external reforming system. The possibility of using internal reforming is one of the characteristics of high temperature fuel cells, SOFC. Methane/steam reforming using different catalyst materials has been studied in the past. Experiments have been carried out by Achenbach and Riensche [5] to determine the kinetics of the methane/steam reforming process at Ni/YSZ anode materials of a solid oxide fuel cell. Their reforming kinetics model [5] has been adopted to numerical analysis of a planar solid fuel cell stack [6] and to tubular solid oxide fuel cell with accompanying indirect internal fuel reforming [7]. Alternative model of methane reforming reaction rate was proposed by Odegard et. al. [8]. This model [8] was used in numerical analysis of characteristics tubular SOFC with internal reformer systems by different research groups [9, 10, 11]. Typical process over Ni/YSZ catalyst is preformed around 850 °C with a steam-to-carbon ratio between 2 and 5 to prevent carbon deposition. Carbon formation is one of the major problem during methane/steam reforming. It was found that samarium-doped ceria (SDC) is an effective catalyst material for the suppression of carbon deposition. This allows the utilization of methane-rich fuels with a low...
steam-to carbon ratio. Additionally, ceria oxide based materials exhibit catalytic properties for
a number of reactions, including water-gas shift and steam reforming [3, 12]. Therefore Ni/SDC
catalyst fulfills the requirements as a catalyst material for reforming process, where protecting
the catalyst from carbon formation is a key consideration.

The present paper describes a three-dimensional numerical model of heat and mass transfer
process in the module of an internal indirect reforming type SOFC using Ni/SDC as catalyst.
To describe kinetics of methane/steam reforming the experiment has been conducted. The gas
mixture composition and flow rate were measured at the outlet of the reformer to establish the
methane/steam reforming rate and kinetics of the reforming reaction. Experimentally obtained
data was used in the numerical model. Model takes account velocities field, convective heat
transfer, mass transfer of chemical species and chemical reaction associated with methane/steam
reforming.

2. Numerical Analysis
The geometry of the internal indirect reformer to be considered is shown schematically in Figure
1. The supplied fuel to the system is the methane (CH4). The gaseous fluids are assumed to
be Newtonian and the flow of fuel inside the fuel reformer is assumed to be laminar [13, 14],
steady and occurring in one direction. The temperature of in-flow fuel is taken to be instantly
approaching the temperature of the reformer.

2.1. Heat transfer model inside the reformer
The microstructure of porous media is not to be considered directly in the present model
therefore for the pours area, the governing equations derived by the volume-averaging method
are applied [15]. In the adopted method physical values are locally averaged for a representative
elementary volume [16, 17]. The heat transfer process inside the reformer porous media is
described by continuity, momentum, energy and mass transfer equations. Consequently the
following transport equations of the averaged physical values for laminar flows apply:

\[ \nabla (\rho_0 U) = 0 \]  \hspace{1cm} (1)

\[ \frac{\rho_0}{\varepsilon_0} (U \nabla U) = -\nabla P + \frac{\mu}{\varepsilon_0} \nabla^2 U - \frac{\mu}{K_p} U - \frac{(\rho_0 f)}{\sqrt{K_p}} | U | \]  \hspace{1cm} (2)
\[ \rho_0 C_p (U \nabla T) = \nabla (\lambda_{\text{eff}} \nabla T) + Q \quad (3) \]

\[ U \rho_0 \nabla Y_j = \nabla (\rho_0 D_{j,\text{eff}} \nabla Y_j) + S_j \quad (4) \]

The physical values in the above equations represent the local phase average of the gas control volume. In the above equations \( U \) is the gas phase average local velocity, \( T \) is the local average temperature both over gas and solid phase. The \( \epsilon_0 = 0.9 \) and \( K = 1.0 \times 10^{-7} \text{ m}^2 \) are the porosity and permeability of the porous medium, respectively. The \( f = 0.0088 \) is the inertia coefficient which depends on the Reynolds number and the microstructure of the porous medium [17]. \( \lambda_{\text{eff}} = \epsilon_0 \lambda_f + (1 - \epsilon_0) \lambda_s \text{ W m}^{-1} \text{ K}^{-1} \) is the effective thermal conductivity, where \( \lambda_f \) represents fluid thermal conductivity and \( \lambda_s = 10.0 \text{ W m}^{-1} \text{K}^{-1} \) is solid phase thermal conductivity [11]. \( D_{j,\text{eff}} \text{ m}^2 \text{s}^{-1} \) is the effective mass diffusivity of species \( j \). \( Y_j \) is the mass fraction of chemical species \( j \) and \( D_j \) is the mass diffusivity of species \( j \) in the multi-component mixture of gases respectively [18, 19].

2.2. Mathematical model of reforming process

The methane/steam reforming process is widely known as a conventional process for producing hydrogen [1, 2]. In the reforming process of methane with steam, the dominant reactions are the following two [10]

fuel reforming reaction:

\[ \text{CH}_4 + \text{H}_2\text{O} = 3\text{H}_2 + \text{CO} \quad (5) \]

shift reaction

\[ \text{CO} + \text{H}_2\text{O} = \text{H}_2 + \text{CO}_2 \quad (6) \]

The steam reforming reaction described by equation (5) is a slow and therefore a rate equation is needed. The water-gas shift reaction described by equation (6) is a fast and can be assumed to be in equilibrium at the reforming temperature [10]. The reaction rates of the two above reactions (equations (5) and (6)) \( R_{\text{st}} \) and \( R_{\text{sh}} \) are locally calculated as follows:

\[ R_{\text{st}} = w_{\text{cat}} A_{\text{st}} p_{\text{CH}_4}^a p_{\text{H}_2\text{O}}^a \quad (7) \]

\[ R_{\text{sh}} = K_{\text{sh}}^+ p_{\text{CO}} p_{\text{H}_2\text{O}} + K_{\text{sh}}^- p_{\text{H}_2} p_{\text{CO}_2} \quad (8) \]

Equation (7) is based on experimental data, where, \( w_{\text{cat}} \), is catalysis weight in a control volume of reformer \( \text{g m}^{-3} \), \( T \) K is temperature of fuel conversion, \( R = 8.314472 \text{ J mol}^{-1} \text{ K}^{-1} \) is universal gas constant, \( E \text{ J mol}^{-1} \) is the activation energy of the fuel reforming reaction [5], \( A_{\text{st}} \) is the pre-exponential factor (case dependent) [5], \( p_{\text{CH}_4} \) is the partial pressure of methane Pa and \( p_{\text{H}_2\text{O}} \) is the partial pressure of steam Pa. The rate constants of forward and backward water-gas shift reactions and the value of \( R_{\text{sh}} \) is determined by method described by Lehnert at el [20]. The water shift reaction given by equation (8) reaches equilibrium rapidly and therefore \( \text{CO}_2, \text{H}_2, \text{CO} \) and \( \text{H}_2\text{O} \) have to satisfy the equilibrium equation:

\[ K_{\text{sh}} = \frac{K_{\text{sh}}^+}{K_{\text{sh}}^-} = \exp \left( -\frac{\Delta G_{\text{sh}}^0}{RT} \right) \quad (9) \]

where \( G_{\text{sh}} \) is the change of standard Gibbs free energy of shift reaction. This equilibrium constant given by Eq. (9) is introduced into equation (8) to calculate the rate of the shift reaction.
The mass production or consumption rate of each chemical species by the fuel reforming reaction (Eq. (5)) and shift reaction (Eq. (6)) is also calculated as follows:

\begin{align*}
S_{\text{H}_2} &= 3R_{\text{st}}M_{\text{H}_2} + R_{\text{sh}}M_{\text{H}_2} \\
S_{\text{CO}} &= R_{\text{st}}M_{\text{CO}} - R_{\text{sh}}M_{\text{CO}} \\
S_{\text{CO}_2} &= R_{\text{sh}}M_{\text{CO}_2} \\
S_{\text{CH}_4} &= -R_{\text{st}}M_{\text{CH}_4} \\
S_{\text{H}_2O} &= -R_{\text{st}}M_{\text{H}_2O} - R_{\text{sh}}M_{\text{H}_2O}
\end{align*}

The value of mole production or consumption rate for each chemical species is introduced into the species mass transfer equation (Eq. (4)) as a part its source term. The thermodynamic heat generation rate by the reforming reactions (Eqs. (5) and (6)) are calculated base on the reaction rates, as follows:

\begin{align*}
Q_{\text{st}} &= -\Delta H_{\text{st}}R_{\text{st}} \\
Q_{\text{sh}} &= -\Delta H_{\text{sh}}R_{\text{sh}}
\end{align*}

where $\Delta H_{\text{st}}$ and $\Delta H_{\text{sh}}$ are the enthalpy change accompanied with each reaction. The heat conduction and convection equations were solved numerically by finite volume and Stone methods [21, 22].

3. Experimental investigation

3.1. Experimental setup

A schematic view of the experimental setup is shown in figure 2. A stainless steel reformer was located in an electrical furnace, which can be heated up to 1000 °C. High purity methane was the fuel used in the experiment. It was supplied to the reformer via a flow controller and evaporator, which was also used as a pre-heater. Water was fed to the system with a pump. The gas composition after the reforming process was analyzed by gas chromatography prior to which the steam had been separated by cooling down the gas mixture to 2 °C. The reforming reaction tube was filled by nickel supported on samaria-doped ceria provided by AGC SEIMI CHEMICAL CO [23] (see table 1). To control the thermal condition of the experiment, four thermocouples were placed in the experimental set-up as shown in figure 2 (marked as T). To derive correct kinetics data, the reaction has to occur in a whole volume of catalyst. This can be accomplished by keeping the reforming conversion rate low. To achieve a low level of methane conversion, the fuel was additionally mixed with nitrogen. Nitrogen does not directly influence the reforming reaction but the partial pressure of the components changed, which decreases both the reaction rate and methane conversion rate. All measurements presented in this paper have been performed at atmospheric pressure. Geometrical properties of the reactor has been summarized in table 2.

| Type  | Ni contain | Particle size | Active area | Mass |
|-------|------------|---------------|-------------|------|
| Ni/SDC | 60vol%     | 0.96 µm       | 4.4 m²/g    | 1.5 g |
3.2. Experimental procedure

It follows from the stoichiometry of the steam/methane reforming reaction (Eq. (5)) that the reaction rate expression can be approximated using equation (7) [24]. By following Vannice [24] the non-equilibrium reaction rate can be described as a ratio between the change in the flow rate of methane and the change in the amount of catalyst:

$$ R_{st} = -\frac{dF_{CH_4}}{dW_{cat}} \quad (17) $$

Combining equations (7) and (17) leads to mathematical formula describing reaction constant [24], [25]:

$$ k = \frac{F_{CH_4}^{in}}{w_{cat}} \int_{0}^{xcr_{out}} (1 + SC + NC + 2xcr)^{a+b} \ P^{a+b} (1 - xcr)^{b} \ (SC - xcr - ycr)^{b} \quad (18) $$

By following Itoh et al. [26] the methane conversion rate $xcr$ is determined by the outlet quantity and can be calculated as:

$$ xcr = \frac{(m_{CO} + m_{CO_2})}{(m_{CH_4} + m_{CO} + m_{CO_2})} \quad (19) $$

The shift reaction occurs very quickly and therefore the conversion rate of shift reaction $ycr$ can be estimated from the equilibrium equation (Eq. (9)).

Because the reaction constant (equation (18)) does not depend on the steam-to-carbon ratio $SC$ and the nitrogen-to-carbon ratio $NC$ ratio, $a$ and $b$ can be found [8], [25]. The real values
of $a$ and $b$ are those that result in the smallest $k$ derivation for different $SC$ and $NC$ ratios.  
Equation (18) was solved numerically for various values of $a$ and $b$ and for the different $SC$ and $NC$ ratios. The smallest reaction constant deviation was found to be 0.98 and -0.25 for $a$ and $b$, respectively.

The effect of the temperature on the reaction was studied by increasing the temperature from 600 °C to 750 °C. Based on experimentally obtained data, the reaction constant was calculated using equation (18). A straight line was fitted to calculated reaction constant as a result of approximation. The equation for the straight line for this experiment takes a form of Arrhenius (figure 4) equation and can be described

$$\ln k = \ln A - \left(\frac{E}{R}\right) \left(\frac{1}{T}\right)$$

Where $T$ K is the temperature of fuel conversion, $R = 8.314472$ J mol$^{-1}$ K$^{-1}$ the universal gas constant, $A=40$ mol g$^{-1}$ s$^{-1}$ bar$^{a+b}$ is called the pre-exponential factor and corresponds to the intercept of line at $1/T=0$ and $E=106451$ J mol$^{-1}$, which is obtained from the slope of the line, is the activation energy of the steam reforming reaction. Derived activation energy and pre-exponential factor was implemented into equation (7).

![Figure 3.](image1.png)

**Figure 3.** Figure caption for first of two sided figures.

![Figure 4.](image2.png)

**Figure 4.** Figure caption for second of two sided figures.

More details of the experimental apparatus, the process of measuring and used methodology are given in reference [25].

4. Results

In the numerical model presented in this section, gas composition at the outlet of the reformer can be predicted based on the inlet conditions. Examples of numerical results and their comparison with the experimental data are shown in figures 5. In the present results, the effect of the temperature on the steam reforming reaction was studied by increasing reaction temperature from 650°C to 750°C. The data shows the outlet dry gas composition to be a function of reaction temperature. Predictably, the outlet molar fraction of methane decreases with increasing reaction temperature and the opposite behavior can be observed for the molar fraction of hydrogen. As observed in figures 5, the amount of carbon monoxide increases as the reaction temperature increases. This observation is significant because in contrast to the low-temperature fuel cell, the carbon monoxide does no poison the high temperature solid oxide fuel cell anode but can be electrochemically converted as a fuel [5].
Figures 6, 7 and 8 show the results of numerical computations for Ni/SDC catalyst calculated for the different reformer wall temperatures, which was varied from 900 [K] to 1200 [K]. The volumetric average change of molar fraction of gas components in the longitudinal direction of the fuel reformer are illustrated by figure 6, which shows that the methane conversion process is strongly affected by the reaction temperature, which in turn results in an increasing mole fraction of hydrogen with increasing reaction temperature. The mole fraction of methane and steam both decrease with the reaction temperature as an effect of the increasing conversion rate. This figure also shows that carbon dioxide increases slightly with the reaction temperature while...
the carbon monoxide remains steady and at a low level. The carbon monoxide produced by the steam reforming is almost completely consumed in the water gas shift reaction. Optimization of the process to achieve full conversion of the carbon monoxide to hydrogen by the water gas shift reaction can be accomplished by changing the reaction temperature. This is possible for those reaction temperatures which are favourable for the forward water gas shift reaction [27].

5. Conclusions
The paper has presented experimental and numerical studies on fuel reforming process on Ni/SDC catalyst. The gas mixture composition and the flow rate of were measured at the outlet of the reformer to establish the methane reforming rate and kinetics of the reforming reaction. The reforming rate equation derived from experimental data was used in the mathematical model to predict gas composition at the outlet of the reformer. Three dimensional calculation has been conducted. Temperature and methane distribution in longitudinal direction of fuel reformer has been presented. The obtained results indicate how import combined, numerical and experimental studies are in process of designing SOFC reformers. It was show that applying such combine approach leads to the successful prediction of outlet gas composition.

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