MODELLING OF THE METHANE CONVERSION
ON A Ni/CGO-ANODE

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ABSTRACT

A one-dimensional model was developed which describes the conversion of methane on a planar Ni/CGO-anode. The model includes the reforming and the shift reactions. The simulation results were compared to gas concentrations measured at the inlet, the center and the outlet of the anode gas compartment by gas chromatography. The anode was operated at T = 800°C and T = 950°C, volumetric feed rates of V_ON = 115 to 420 ml/min and steam-to-carbon ratios of 2 and 3, respectively. The results of the simulation agree well with the measured values.

INTRODUCTION

An important property of the SOFC is its capability to reform methane at the anode ("internal reforming") which is due to its high operating temperature (800-950°C). In the reforming process, hydrocarbons (in this case methane) are converted with steam to a H₂- and CO-rich gas according to equation [1]. Parallel to this reaction, the watergas-shift reaction has to be considered as well (equation [2]).

\[
\begin{align*}
\text{CH}_4 + \text{H}_2\text{O} & \rightarrow \text{CO} + 3\text{H}_2 & \Delta_{\text{R}} H^0 = +206 \text{ kJ/mol} \ [1] \\
\text{CO} + \text{H}_2\text{O} & \rightleftharpoons \text{H}_2 + \text{CO}_2 & \Delta_{\text{R}} H^0 = -41 \text{ kJ/mol} \ [2]
\end{align*}
\]

The SOFC anode typically is a Ni/YSZ cermet with high catalytic activity but also with the tendency to crack methane, resulting in carbon deposition and deactivation of the anode. Alternatives are ceria based materials. These materials have the ability to suppress carbon deposition on electrodes in methane-rich atmospheres (1, 2).

The aim of this work was to investigate the progress of the methane conversion in the reforming reaction along a planar Ni/CGO anode. For this purpose a one-dimensional mathematical model of the steam-reforming and the watergas-shift reaction in an anode gas channel was developed yielding local gas composition in the channel as a function of the (x)-coordinate in flow direction at open circuit condition. The results of simulation for the methane conversion were compared to measured values that were obtained by gas analysis at the inlet, the center and the outlet of the anode gas compartment (for results obtained in further measurements see also (3)).
MODELLING

The model includes the reforming reaction and the shift reaction. To our knowledge, there is no kinetic expression for the reforming reaction on a Ni/CGO anode in the open literature yet. Clarke et al. describe a kinetic expression for a Ni/ceria cermet which is first order in methane, but the values of the kinetic parameters are not available (4).

Nakagawa et al. used a kinetic expression of the Langmuir-Hinshelwood type for a Ni/YSZ/CeO₂ anode (50:37.8:12.2 vol%) (5). The Langmuir-Hinshelwood expression used assumes the adsorption of steam and methane to be the rate-limiting steps, Nakagawa et al. however, obtained a positive activation energy for the steam adsorption. Other processes that the model does not account for therefore have to be involved.

In our model we use a kinetic expression of the type

\[ r_{\text{ref}} = kp_{\text{CH}_4}^n p_{\text{H}_2\text{O}}^m \]  

with

\[ k = k_0 \exp \left( \frac{-E_A}{RT} \right) \]

\( r_{\text{ref}} \) is the reaction rate which is related to the external anode surface, \( p_i \) is the partial pressure of component \( i \), \( k_0 \) a constant and \( E_A \) the activation energy of the reforming reaction. \( R \) denotes the universal gas constant and \( T \) temperature.

Table I shows the values for the parameters \( k_0, E_A, n \) and \( m \) which were determined by fitting the modeled results to the values obtained in the measurements using a least-squares program.

| \( k_0 \) (mol/(s·m²·Pa₁·¹⁹)) | \( E_A \) (kJ/mol) | \( n \) | \( m \) |
|-------------------|-------------------|------|------|
| \( 4.05 \times 10^{-5} \) | 26.3 | 1.19 | 0 |

The shift reaction is, at the observed temperatures (800°C-950°C), very fast so that it is assumed to be at equilibrium (4, 6).

Steady state and ideal gas behavior are assumed. Diffusive gas transport in the anode gas channel over the width of the channel is neglected because the channel is very narrow (1.5 mm). To determine if mass transfer from the gas channel to the external surface of the anode can be neglected, the dimensionless number \( Da_{\text{II}}^* \) is defined. \( Da_{\text{II}}^* \) is similar to the Damköhler-number of the second type, but is formed with the mass transfer rate instead of the diffusion rate.

\[ Da_{\text{II}}^* = \frac{\text{maximum reaction rate}}{\frac{k}{h} \cdot p_{\text{CH}_4}^{1.19}} \]

\[ = \frac{\text{maximum mass transfer rate}}{\frac{\beta_i}{h} \cdot p_{\text{CH}_4}} \]
In Equation 5, $\beta_i$ denotes the mass transfer coefficient for the mass transfer from the gas channel to the anode surface (7). The $D_{ar}{*}$ number is highest at the anode entrance since there the reaction rate is highest. The maximum value at the anode inlet is $< 0.1$ at open circuit condition; mass transfer from the gas channel to the anode surface therefore is fast compared to the reaction and will consequentially not be considered in this model (homogeneous model).

The influence of axial dispersion can be estimated by the Bodenstein number $Bo$, which is defined as the ratio of convective transport to diffusive transport (8):

$$Bo = \frac{v \cdot l}{D_{ax}}$$

with the flow velocity $v$, the axial dispersion coefficient $D_{ax}$ (8) and the channel length $l$. The Bodenstein number is in the range of $10$ – $60$ for the lowest flow velocity and in the range of $44$ – $230$ for the highest flow velocity, depending on the components considered. These values indicate that at least in some cases, axial dispersion should not be neglected; however, as the flow velocity increases through the reaction along the channel, the $Bo$ number will increase. For the sake of simplicity, axial dispersion is therefore neglected in this analysis.

Since the experimental data are obtained from a cell which is kept in an oven at high temperature, temperature gradients that might occur by the heat consumption of the reforming reaction are flattened by radiation from the surface of the oven walls. Therefore the temperature is considered to be uniform in the cell and energy balances are not included in this version of the model. Atmospheric pressure is assumed to prevail constantly throughout the gas channel.

These assumptions reduce the number of unknown variables to 6:

- The flow velocity $v$ in $x$-direction which changes because of the increase in mole flow by reaction [1]
- The partial pressures of the components in the gas channel $p_i$ with $i = \text{CH}_4, \text{H}_2\text{O}, \text{CO}, \text{H}_2$ and $\text{CO}_2$

All these variables are a function of the coordinate $x$ in flow direction.

With the above mentioned assumptions we get the balance for each species $i$: [7]-[11]

$$0 = -\frac{d(p_i v)}{R T d x} \cdot \frac{h}{h}$$

For methane, the source term consists of the area-specific conversion rate of the reforming reaction (eq. [3]), which has to be divided by the height of the anode gas channel $h$ ($1.5 \text{ mm}$) to become volume specific. For the other components, the conversion in the shift reaction can be accounted for by assuming thermodynamic equilibrium (see also (9)).
\[ K_s = \frac{P_{\text{CO}_2} \cdot P_{\text{H}_2}}{P_{\text{CO}} \cdot P_{\text{H}_2\text{O}}} \]  

To determine the partial pressure of the components in equilibrium, we first calculate the conversion due to the reforming reaction only. Further we define:

\[ N_\phi_i = N_{\phi_i} + \Delta N_{\phi_i} \]  

with \( N_{\phi_i} \) denoting the mole flow of component \( i \) after the reforming reaction divided by the cross sectional area of the channel. \( N_{\phi_i} \) is calculated by using the expression

\[ N_{\phi_i} = \frac{v \cdot P_i}{R \cdot T} \]

after solving the discretized equations [7]-[11] for \( P_i \) at \( x \). \( \Delta N_{\phi_s} \) is the area specific conversion rate of the shift reaction. With equations 12 and 13 we obtain

\[ \frac{P_{\text{CO}_2} \cdot P_{\text{H}_2}}{P_{\text{CO}} \cdot P_{\text{H}_2\text{O}}} = \frac{(N_{\phi_i}^{\text{CO}_2} + \Delta N_{\phi_s})(N_{\phi_i}^{\text{H}_2} + \Delta N_{\phi_s})}{(N_{\phi_i}^{\text{CO}} - \Delta N_{\phi_s})(N_{\phi_i}^{\text{H}_2\text{O}} - \Delta N_{\phi_s})} = K_s \]

Which can be rearranged to give

\[ \Delta N_{\phi_s} = A \pm \sqrt{A^2 - B} \]

where

\[ A = \frac{K_s (N_{\phi_i}^{\text{CO}} + N_{\phi_i}^{\text{H}_2\text{O}}) + N_{\phi_i}^{\text{CO}_2} + N_{\phi_i}^{\text{H}_2}}{2(K_s - 1)} \]

and

\[ B = \frac{K_s N_{\phi_i}^{\text{CO}} N_{\phi_i}^{\text{H}_2\text{O}} - N_{\phi_i}^{\text{CO}_2} N_{\phi_i}^{\text{H}_2}}{(K_s - 1)} \]

The sign before the square root has to be chosen so that

\[ \Delta N_{\phi_s} > 0 \quad \text{if} \quad \frac{P_{\text{CO}_2} \cdot P_{\text{H}_2}}{P_{\text{CO}} \cdot P_{\text{H}_2\text{O}}} < K_s \quad \text{after the reforming reaction} \]
In this case CO and H₂O are converted to H₂ and CO₂ in the shift reaction. The reaction proceeds backward for

\[ \Delta^N \phi_s < 0 \quad \text{if} \quad \frac{P_{CO_2} \cdot P_{H_2}}{P_{CO} \cdot P_{H_2O}} > K_s \text{ after the reforming reaction} \quad [20] \]

After obtaining \( \Delta^N \phi_s \), the partial pressures of H₂O, H₂, CO and CO₂ after both reforming reaction and shift equilibrium can be calculated using equation [13] and the ideal gas law. The last condition that has to be fulfilled is Dalton’s law:

\[ p = \sum_i p_i \quad [21] \]

This system of equations was implemented in Matlab®, where equations [7-11] were discretized and solved by the Euler method.

**EXPERIMENTAL**

Electrolyte supported single cells based on a 10Sc1CeSZ (10 mol% Sc₂O₃ / 1 mol% CeO₂ doped ZrO₂) electrolyte substrate (50 x 50 mm², 150 µm thickness) with a screen printed strontium doped lanthanum manganite (LSM: La₀.₇₅Sr₀.₂₅MnO₃) cathode and a cermet anode with 10.5 cm² electrode area (3.0 x 3.5 cm² working electrode) were used. The Ni/CGO anode (10 mol% Gd₂O₃ doped CeO₂ from Rhodia) was prepared by co-sintering in air at 1300°C. Details regarding the preparation procedure are given by Roesch et al. (10).

The cells were integrated in a ceramic housing. An Al₂O₃ frame was used for sealing. The cells were operated with internal reforming of methane at varying steam-to-carbon ratios (S/C = 2...3) and temperatures (800°C and 950°C) at open circuit voltage. The volumetric feed rate was varied from \( \phi_N = 115 \) to 420 ml/min, \( \phi_N \) refers to standard conditions) resulting in flow velocities at the cell entrance from \( v^0 = 0.31 \) to 1.15 m/s at 800°C and 0.36 to 1.31 m/s at 950°C, respectively.

Air was used as oxidant at the cathode. All flows were adjusted by mass flow controllers. The water was injected directly into the hot gas flow. Its flow was adjusted by a liquid mass flow controller. Weber et al. give a detailed description of the experimental setup (11). For analysing the internal reforming process of the fuel passing the anode, gas extraction ports were incorporated in the Al₂O₃-housing. The local gas composition can be analysed at the gas in- and outlet of the anode as well as at the center of the cell (12). A Varian Micro-Gas Chromatograph CP-2003 with a PoraplotQ- and a Molsieve5A-column was used for analysing the gas compositions. A small amount of argon was used as internal standard to allow the calculation of the molar flows from the measured gas compositions. The methane conversion was then calculated according to equation [22]:

\[ X_{CH_4} = \frac{N_{\phi_{CH_4,in}} - N_{\phi_{CH_4,out}}}{N_{\phi_{CH_4,in}}} \quad [22] \]

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RESULTS AND DISCUSSION

The results of the simulation were compared to the measured values. As shown in (3), there is no dependence of the methane conversion on the S/C ratio at 950°C. The equilibrium value of 100% methane conversion is reached already in the middle of the cell.

The dependence of the methane conversion on the initial flow velocity is shown in Figure 1 for a temperature of 950°C and a S/C ratio of 3. An increase in gas flow leads to a decrease in residence time so that the equilibrium value is reached at a later point. The maximum deviation of the measured results from the simulation curve is less than 4%.

![Figure 1. CH₄-conversion at T = 950°C and S/C = 3. Comparison of the simulation results with measured values for different initial flow velocities v°.](image)

Because plotting over the channel length gives only two data points (see Figure 1), the residence time according to [23] and with the local mean flow velocity \( \bar{v}(x) \) (which is averaged over \( x \)) is introduced as a new variable.

\[
\tau = \frac{x}{\bar{v}(x)} \quad [23]
\]

A correct model should also fit a plot of the methane conversion against residence time.

The highest deviation of the measured values from the simulation curve in Figure 2 is less than 6% so that there is again a good accordance between measured and simulated values.

At 800°C the methane conversion is independent of the S/C ratio, as at 950°C (Figure 3), but the decline in methane conversion with increasing initial flow velocity is more distinct at 800°C than at 950°C (Figure 4 as compared to Figure 1).
Figure 2. $\text{CH}_4$-conversion at $T = 950^\circ\text{C}$ and $S/C = 3$ as a function of local residence time $\tau$. Comparison of simulation results with measured values.

In Figure 5 the methane conversion at $800^\circ\text{C}$ and at $950^\circ\text{C}$ is plotted against the Damköhler number $D_{\text{ai}}$ (8). In this case, $D_{\text{ai}}$ is given by

$$D_{\text{ai}} = \frac{k_0 \exp \left( \frac{-E_A}{RT} \right) \cdot p_{\text{CH}_4,0}^{0.19} \cdot \tau \cdot R \cdot T}{h}$$  \hspace{1cm} [23]$$

$p_{\text{CH}_4,0}$ denotes the partial pressure of methane at the reactor inlet. The influence of temperature is excluded in this diagram because an increase in the conversion rate caused by an increase in temperature leads to a decrease in residence time at the same conversion. The plot in Figure 5 shows as well a good correlation between simulated and measured values so that the model is validated for the two investigated temperatures of $800^\circ\text{C}$ and $950^\circ\text{C}$.

These results suggest that the kinetic expression employed in this model seems to be appropriate to describe the rate of the methane reforming reaction on a Ni/CGO anode under the conditions investigated. The reaction order is 1.19 with respect to methane and 0 with respect to steam. For steam, Achenbach and Riensche also found the order 0 for a Ni/YSZ anode, but an order of 1 for methane (13).

The apparent activation energy of 26 kJ/mol for our Ni/CGO anode is much lower than the one obtained by Achenbach and Riensche for the Ni/YSZ cermet (82 kJ/mol). One reason for this higher activation energy is a higher catalytic activity of the Ni/CGO anode compared to a Ni/YSZ anode (3). Another reason could be the limitation of the reaction rate by diffusion in the porous anode, which would lead to an apparent activation energy of only half of the intrinsic activation energy. The influence of pore diffusion can be estimated by the Weisz-Prater criterion (14) with an effective pore diffusion coefficient $D_{\text{eff}}$ and the thickness of the anode $d$.  

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If this condition is fulfilled, pore diffusion can be neglected (14). In our case we obtain values between 0.047 and 0.250 at 800°C and values between 0.053 and 0.258 at 950°C for the quotient, depending on the components considered. So pore diffusion cannot be totally neglected in every case investigated and the intrinsic activation energy has to be between 26 kJ/mol and 52 kJ/mol. The exact value has to be determined in further investigations.

Nevertheless, using an apparent activation energy of 26 kJ/mol, the simulation results are in good accordance with the measured values and the accuracy of the model is sufficient to describe the methane conversion on a Ni/CGO anode under the conditions investigated.

Figure 3. \( CH_4 \)-conversion at \( T = 800°C \) and \( v^0 = 0.31 \) m/s. Comparison of the simulation results with measured values for different S/C ratios.
SUMMARY AND CONCLUSIONS

A one-dimensional model was developed which describes the conversion of methane on a Ni/CGO-anode at open circuit condition. The model includes a kinetic description of the reforming reaction and supposes equilibrium for the shift reaction. The simulation results were compared to results from measurements that were determined at the inlet, the center and the outlet of the anode gas compartment by gas chromatography. The measurements
were conducted at $T = 800^\circ C$ and $T = 950^\circ C$, volumetric feed rates of $V_{\text{in}} = 115$ to 420 ml/min and steam-to-carbon ratios of 2 and 3.

The results from measurements do not show a dependence of the methane conversion on the steam-to-carbon-ratio so that the reaction order in steam is equal to zero. At both investigated temperatures the methane conversion reaches the equilibrium value of nearly 100% at the lowest volumetric feed rate. An increase in the volumetric feed rate leads to a decrease in methane conversion. This decrease is more distinct at 800°C than at 950°C. While it is unclear whether pore diffusion and axial dispersion influence the obtained results, the results of the simulation fit well to the measured values. The employed kinetics thus seems to be appropriate to describe the progress of the methane conversion on a Ni/CGO anode under the conditions investigated.

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