METHANE REFORMING ON Ni/ZIRCONIA SOFC ANODES

Rolf Ødegård\textsuperscript{a),} Einar Johnsen\textsuperscript{a) and Håvard Karoliussen\textsuperscript{b)}

\textsuperscript{a)Statoil Research Centre}
Postuttak
N-7005 Trondheim
Norway

\textsuperscript{b)Norwegian Institute of Technology}
Department of Electrochemistry
N-7034 Trondheim
Norway

ABSTRACT

Methane steam reforming on Ni-YSZ anodes (60 vol-% Ni) was studied with $P_{\text{H}_2O}/P_{\text{CH}_4}$ between 1.5 and 2.5 at temperatures between 1173 K and 1273 K. The following expression for the rate of methane reforming was found:

$$r_{\text{CH}_4} = k' \exp \left( \frac{-\Delta H_{\text{act}}}{R T} \right) (P_{\text{CH}_4})^{1.29},$$

where $r_{\text{CH}_4}$ is given in moles of $\text{CH}_4/h \cdot \text{g} N_1$, $k'$ is typically $6300 \text{ mol/(h \cdot g} N_1 \cdot \text{atm}^{1.29})$ and the activation energy, $\Delta H_{\text{act}}$, is 58 $\text{kJ/mole CH}_4$. No significant dependence between the reforming rate and $P_{\text{H}_2O}$ could be found. The amount of $\text{H}_2$ formed corresponded to a current density of approximately 10 $\text{A/cm}^2$ at the inlet (under the assumption that all $\text{H}_2$ formed by the reforming reaction takes part in the electrochemical reaction with $\text{O}_2^\cdot$).

INTRODUCTION

In SOFC natural gas is oxidized, whereas electricity, $\text{CO}_2$ and $\text{H}_2\text{O}$ are produced. This is made possible by an electrochemical reaction including $\text{H}_2$ and $\text{O}_2^\cdot$ as reactants and $\text{H}_2\text{O}$ as the chemical product. The electrochemical reaction between $\text{H}_2$ and $\text{O}_2^\cdot$ takes place at the anode in the SOFC. As anode a mixture of NiO and $\text{ZrO}_2$ is used. NiO is reduced to Ni before methane is let into the cell. Ni serves three objectives: electrocatalytical active component, electronic current collector (anode) and catalyst for reforming of methane (natural gas).

It is generally considered that natural gas (or pure $\text{CH}_4$) is not electrochemically oxidized at the anode in question. Therefore; natural gas has to be reformed to $\text{H}_2$ and CO to make the electrochemical reaction possible. The reforming reaction is catalyzed by one of the components (Ni) which is used as anode (YSZ/Ni composite) in the SOFC. The reforming reactions for natural gas and methane are given in equations 1 and 2. Equation 2 is the same as equation 1 for $n=1$.

$$\text{C}_n\text{H}_{2n+2} + n\text{H}_2\text{O} \rightarrow n\text{CO} + (2n+1)\text{H}_2$$  \[1\]
\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \tag{2}
\]

The water-gas shift reaction is at equilibrium at these temperatures (1173 K - 1273 K):

\[
\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \tag{3}
\]

The electrochemical reaction gives the electric current:

\[
\text{H}_2 + \text{O}^{-} \rightarrow \text{H}_2\text{O} + 2\text{e}^{-} \tag{4}
\]

When \( \text{H}_2 \) is consumed in the electrochemical reaction, equation 3 is shifted to the right, and \( \text{CO} \) is consumed. Whether \( \text{CO} \) also is directly consumed in an electrochemical reaction like \( \text{H}_2 \) is (eq. 4), is therefore not of very great practical importance.

As complete reforming as possible is of vital interest to achieve a good utilization of the energy in the system. At the same time reforming is an endothermic reaction cooling the surroundings and the gases involved. This results in several technical problems. Studies of reforming is therefore of great interest. By a study of reforming of methane and natural gas a mathematical expression of reforming rate dependent on partial pressures and temperature can be found. This expression can be used in modelling of the reactions, the gas flows, the temperature and the current distributions in fuel cells. Knowledge of all these parameters is a necessity to make the right choice of materials and design of dimensions for bigger entities than single cells.

**EXPERIMENTAL**

**Apparatus**

The experimental setup is depicted in Figure 1. The quartz reactor extended outside the furnace in both ends. The fuel gas, consisting of \( \text{CH}_4, \text{N}_2 \), and \( \text{H}_2\text{O} \), was introduced into the reactor outside the furnace (mixed at approximately 373 K). The exhaust gas was lead through a cold zone (approx. 280 K) where the excess (unreacted) water condensed. The almost water free exhaust gas was analyzed by a GC (HP 5890 with TCD, Poraplot Q and Molsieve 5A coloumns in series).

Two electrolyte plates with anodes were positioned in channels very much like the channels in fuel cells, see Figures 2 and 3. The thermocouple was placed 1.5 cm in front of the electrolyte plates (with anodes).

**Anodes**

The Ni-cermet (60 vol-% Ni after reduction) was prepared by carefully mixing and milling \( \text{NiO} \) and \( \text{ZrO}_2 \) (8 mol-% \( \text{Y}_2\text{O}_3 \)). After preiring, remilling and mixing the resulting powder with organic solvents, the electrode suspension was spray painted on
YSZ (8 mol-% Y₂O₃) electrolyte plates (thickness 200 µm). The same slurry was used for preparing all of the anodes. After drying and firing in air at 1520 K, the thickness of the two anodes used in these experiments was 39 and 44 µm, respectively. Even though the same slurry was used to make the two anodes, different spraying time resulted in quite different densities of the anode layers; 1.29 g/cm³ and 1.93 g/cm³, respectively. Table 1 gives information about the anodes used in the present investigations.

### Table 1. Anodes used in the reforming experiments.

| Anode no. | Anode area (cm²) | Height of unreduced anode (µm) | Weight of Ni (mg) | Comments       |
|-----------|------------------|-------------------------------|------------------|----------------|
| 1         | 15.95            | 39                            | 80.3             | "Less dense"   |
| 2         | 15.95            | 44                            | 135.3            | "More dense"   |

### Parameters

Temperature, water-to-carbon ratio and \( p_{CH_4} \) were varied in the experiments.

### RESULTS AND DISCUSSION

#### Amount of \( H_2 \) formed

With the highest \( CH_4 \) flow rate used in the present investigation (50 Nm³/min), the amount of \( H_2 \) created corresponded to a current density over the total channel length of 1.52 A/cm² and 1.70 A/cm² for the less dense and the more dense anodes, respectively. These current densities were calculated under the assumption that all \( H_2 \) formed by the reforming reaction would be consumed electrochemically by \( O_2^- \). Under the same assumption, current density at the channel inlet will be about 10 A/cm².

#### Reforming rate as function of \( p_{CH_4} \)

Figure 4 shows the reforming rate (given in mole \( CH_4 \) converted pr. h pr. g\( Ni \)) as a function of the inlet \( CH_4 \) partial pressure. The two anodes depict linear functions which can be expressed as in equations 5 and 6 for the less and the more dense anode, respectively.

\[
r_{CH_4} = 4.8p_{CH_4,inlet} \quad [5]
\]
\[
r_{CH_4} = 3.2p_{CH_4,inlet} \quad [6]
\]

The factor in equation [6] is smaller than the corresponding factor in equation [5], apparently due to less access to each Ni atom in the more dense anode.

The \( CH_4 \) partial pressures used in Figure 4 and equations 5 and 6 are not experienced by the anodes except for the very first Ni clusters in the inlet. Methane is reformed and the partial pressure falls sharply along the anode. Equations 5 and 6 are
therefore not applicable for using in modelling and for comparing with results from other
experiments. However, the volume along the anode can be treated as an integral plug
flow reactor with $n$ steps, each with a volume equal to the total volume divided by $n$.
(Calculations showed that the reactor volume must at least be divided into 20 steps to
generate reasonable results.) The inlet gas composition into one volume is equal to the
composition exhausting the previous volume. Within each volume there is a conversion
of the inlet gas according to the assumed reaction rate model: $r_{\text{CH}_4} = k(p_{\text{CH}_4})^\alpha$. The water
shift reaction is assumed to be in equilibrium. The boundary conditions are the inlet
and the outlet gas composition from the reactor. The gas composition is calculated for
each step along the reactor. The $k$ that gives a good match between calculated and
experimental outlet gas composition is chosen for the chosen value of the exponent $\alpha$. A
curve where $k$ is plotted as a function of $\alpha$ is made for each total gas flow. Where the
differences between the curves are at a minimum the $k$ and $\alpha$ for this anode can be
found. The value of $\alpha$ is dependent on the reaction mechanism and not on the anode
itself. The value of $k$ will be an inherent parameter of the anode. For the less dense
anode Figure 5 shows that at 1273 K $\alpha$ is approximately 1.20, and the $k$ value is about
20 mol/(h*gNi*atm$^{1.20}$). Another experiment with the same anode gave a $k$ value of 27
mol/(h*gNi*atm$^{1.20}$). Corresponding calculations for the more dense anode gave an $\alpha$ value
slightly above 1.15. Calculations of $k$ are made for values of $\alpha$ in steps of 0.05. In
Figure 6 the relative mean standard deviation of the $k$ values are plotted as a function of
$\alpha$. This figure shows that the exponent $\alpha$ probably has a value between 1.15 and 1.20.
The value 1.20 is chosen for $\alpha$ in the present work. (A less detailed modelling gave
$\alpha=1.25$ as presented earlier.) For $\alpha$ equal to 1.20 the $k$ value for the more dense anode
is about 23 mol/(h*gNi*atm$^{1.20}$). This shows that the $k$ values for the two anodes are
about the same. This stands in contrast to the results given in equations [5] and [6]
which shows that there is a distinct difference in the methane consumption pr. gNi. The
uncertainty in the experiments is indicated by this fact. One problem was the high
conversion of methane (between 85 % and 96 %) which makes the modelling of $k$ very
sensitive to minor differences in the gas composition. Another potential problem is the
amount of gas which does not "see" the anode. If this amount is different from
experiment to experiment, the uncertainty is additionally increased.

Figure 7 shows the calculated partial pressure of CH$_4$ through the channel at
1273 K. The channel length is divided into 100 steps.

Reforming rate as a function of $p_{\text{H}_2\text{O}}$
Within the employed water-to-methane ratio in the feed gas no significant
dependence between the reforming rate and $p_{\text{H}_2\text{O}}$ could be found.
Reforming rate as a function of temperature - activation energy

The activation energy, $\Delta H_{\text{act}}$, for the reforming reaction can be calculated from equation 7.

$$\ln \frac{r_{\text{CH}_4,2}}{r_{\text{CH}_4,1}} = \frac{\Delta H_{\text{act}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

[7]

As mentioned above at least 20 steps are needed to get reliable values for $r_{\text{CH}_4}$. This number of steps is therefore also needed for calculations of activation energies. In Figure 8 the $\Delta H_{\text{act}}$ for the less dense anode is given as a function of the number of steps. The activation energy is assumed to be constant in the temperature region from 1173 K to 1273 K. The calculated value for $\Delta H_{\text{act}}$ is close to 58 kJ/mole CH$_4$ which is low compared to recently published values (75 and 98 kJ/mole)$^{1,2}$. The $k$ value calculated in the paragraph above is a function of the activation energy;

$$k = k' \exp \left( \frac{-\Delta H_{\text{act}}}{RT} \right)$$

[8]

where $\Delta H_{\text{act}} = 57840$ J/mole CH$_4$. The value $k'$ is calculated to be 6339 (mol/(h*g$_{\text{Ni}}$*atm$^{1,20}$)). The reforming rate equation for the less dense anode can hence be expressed as:

$$r_{\text{CH}_4} = 6339 \exp \left( \frac{-57840}{RT} \right) (P_{\text{CH}_4})^{1.20}$$

[9]

For the more dense anode experiments were performed at one temperature only.

Comparison with literature data

For comparison the $r_{\text{CH}_4}$ is also calculated on the basis of expressions given in other publications. The temperature is chosen to be 1233 K because one of the references$^4$ has given a rate expression for this temperature and no information on the activation energy. In the calculations $P_{\text{CH}_4}$ is chosen to be 0.25 atm.

| Reference                  | Reforming rate (mol/h*g$_{\text{Ni}}$) | Comments                      |
|----------------------------|----------------------------------------|--------------------------------|
| Present work               | 4.3                                    |                                |
| Ødegård$^3$                | 4.9                                    | Same exp. results as present work |
| Lee et al.$^2$             | 0.103                                  | $P_{\text{H}_2}$=0.5, cermet called N4Z4 |
| Parsons and Randall$^4$    | 10.6                                   | Assumption: 50 % porosity      |
| Achenbach et al.$^1$       | 14.8                                   | 1.4$^*$ (Randall and Parsons)  |

Table 2. Reforming rate at $P_{\text{CH}_4}$=0.25 and 1233 K calculated from literature sources and present work.
The rate found in the present work has the same order of magnitude as those found earlier, apart from that calculated from the work of Lee et al.\(^2\).

**CONCLUSIONS**

Under SOFC conditions (1273 K, 1.1 bar) two anodes were tested with respect to their ability to reform methane with steam. The following expression for the reforming rate of methane; \( r_{\text{CH}_4} = k(p_{\text{CH}_4})^{1.28} \) was found, where \( r_{\text{CH}_4} \) is given in mol/(h*atm). The \( k \) value is approximately 23 mol/(h*atm*atm). The value for \( k \) was approximately the same whether there were more or less Ni packed in the same volume or at the same area. A reforming rate given pr. cm\(^2\) anode is higher when more Ni/area is applied in the anode. The value \( k \) is a function of the activation energy; \( k = k' \exp\left(-\frac{\Delta H_{\text{act}}}{RT}\right) \). In the temperature region 1173 K - 1273 K the activation energy for steam reforming of methane was found to be 58 kJ/mole. This is 59-77 % of values reported elsewhere\(^1\). The reforming rate is in the same order of magnitude as those values given by Parsons and Randall\(^4\) and by Achenbach et al.\(^1\).

No significant dependence between the reforming rate and \( p_{\text{H}_2\text{O}} \) could be found.

To get reliable values for reforming rates and activation energies the anode has to be divided into at least 20 steps in the calculations.

**REFERENCES**

1. E. Achenbach, Ch. Rechenauer, and E. Riensche, Proc. SOFC, Materials Process Eng. and Electrochem., 5th IEA Workshop, Jülich, Germany, March 2-4 1993, 279-285
2. A.L. Lee, R.F. Zabransky, and W.J. Huber, Industrial & Engineering Chemistry Research, 29 (5), 766-773 (1990)
3. R. Ødegård, Proc. of the First European Solid Oxide Fuel Cell Forum, Lucerne, Switzerland, October 3-7 1994
4. J. Parsons and S. Randall, SOFC Micromodelling, IEA SOFC Task report, Berne, Switzerland, May 1992
Figure 1. The experimental setup for the steam reforming

Figure 2. Support with the ceramic plates positioned in the quartz reactor.
Figure 3. The support for the electrolyte plates (made of ZrO$_2$ doped with 8 % Y$_2$O$_3$)

Figure 4. The reforming rate at 1273 K as a function of the inlet methane partial pressure for the two different anodes. For experimental conditions, see text.
Figure 5. Fitting of the equation $r_{CH_4} = k(P_{CH_4})^\alpha$ to experimental data for the less dense anode. 100 steps are used in the calculations. Water/C=2.4. Temperature is 1273 K.

Figure 6. Relative mean standard deviation of $k$ as a function of the exponent value $\alpha$. The values are based on the results given in Figure 6.
Variation in partial pressure of CH$_4$ at different positions in the cell

Figure 7. Calculated variations in partial pressure of CH$_4$ along the anode at 1273 K for the less dense anode. Total anode length was 55 mm.

Activation energy as a function of number of unit cell steps

Figure 8. Calculated activation energy for the methane reforming reaction at 1273 K (the less dense anode) as a function of the number of step which the plug flow reactor is divided into.

Examples of calculated activation energies:

| Steps | J/moles |
|-------|---------|
| 1     | 12907   |
| 2     | 23244   |
| 10    | 52590   |
| 100   | 57839   |