DIFFUSION AND METHANE REFORMING REACTIONS IN SOFC-ANODE SUBSTRATES

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ABSTRACT

Experiments were performed by evaluation of the gas concentration changes after variation of the anode thickness at constant temperature. With a steam/methane ratio of 3:1, the depth of the reaction zone is approximately 300 - 400 μm at 900°C for the standard composition of the SOFC anode cermet structure. Gas diffusion within SOFC anode substrates limits the overall reforming reaction. On basis of experimentally determined effective binary diffusion coefficients the values of the volume reaction constants of the steam reforming reaction, which takes place inside the SOFC cermet anode prior to the electrochemical anodic oxidation of the natural gas, were estimated. The activation energy of the reforming reaction was determined to 230 kJ/mol.

INTRODUCTION

Solid oxide fuel cells (SOFC) operate at temperatures between 800 °C and 1000°C using hydrogen as the fuel and atmospheric oxygen as the oxidant. The most interesting fuel for SOFC systems is natural gas consisting mainly of methane. It was shown, however, that the direct electrochemical oxidation of methane causes practical difficulties even at the high temperature level involved (1). For this reason, a methane steam reforming reaction according to the overall reaction scheme

$$\text{CH}_4 + 2\text{H}_2\text{O} \leftrightarrow 4\text{H}_2 + \text{CO}_2 \quad [1]$$

is used as the source of hydrogen, which can be oxidized electrochemically according to the reaction

$$\text{H}_2 + \text{O}^2- \leftrightarrow \text{H}_2\text{O} + 2\text{e}^- \quad [2]$$

In order to achieve a high energetic efficiency of the fuel cell, internal reforming of the methane is necessary, which takes place directly within the anode. Due to the great difference between the reaction rates of endothermic methane reforming reaction [1] and exothermic electrochemical hydrogen oxidation [2], cooling effects arise with resulting...
intolerable temperature gradients inside the anode structure in this case. There is only a small amount of kinetic reforming data available obtained from Ni cermet material (2,3,4). Up to now, only surface phenomena have been investigated (2,3,5). In order to control the course of reforming, detailed knowledge of the space reaction rates is necessary, which are still unknown at present. This study deals with the relationship of gas diffusion and reforming reaction in thick anode substrates.

EXPERIMENTAL DETAILS

Both the experimental details and full description of the catalytic experiments are given elsewhere (5). The anode material is a Ni/YSZ cermet formed originally from a sintered heterogeneous mixture of NiO and ZrO₂(8%Y₂O₃) powder particles. The NiO-containing cermet anodes were prepared as described in Ref. (6) and the NiO was gradually reduced in situ to metallic Ni in a gas stream consisting of 5% H₂ and 95% N₂ at 600°C. The resulting anode samples with the thickness between 0.36 and 1.90 mm were investigated. The temperature in the centre of the anode surface was taken for temperature evaluation. The dry gas mixture was continuously analysed for CH₄, CO, CO₂ and H₂. The mean pore radius of the used cermet material is much larger than the mean free-path length of the gas molecules. Therefore, it can be assumed that Knudsen diffusion does not occur. Bulk diffusion has to be considered in the cermet.

In order to characterise the effective gas diffusion within the porous cermet materials diffusion experiments have been carried out with a standard diffusion cell (Fig. 1). The upper and lower gas chambers were flooded with different gases (N₂ or Ar in the upper part; He or H₂ in the bottom part) and the total molar flux was measured during the diffusion process. Assuming the mean transport pore model the ratio of porosity and tortuosity ϕ can be estimated (7).

RESULTS AND DISCUSSION

In case of the used cermet materials ϕ, the ratio porosity to tortuosity values to 0.12. In Table 1 the effective binary diffusion coefficients (Deff) in the cermet determined from binary gas diffusion coefficients (D) and this measured value of ϕ:

\[ D_{\text{eff}} = D \cdot \varphi \]  \[ \text{[3]} \]

are given. Additionally, ϕ values of 0.06, 0.18 and 0.25 were chosen. The corresponding effective binary diffusion coefficients used later in the model calculations are summarised in Table 1. All data are related to atmospheric pressure and 800 °C. It appears that the higher the value of ϕ the higher are the diffusion coefficients. The gas transport is faster in cermet materials with higher porosity and/or lower tortuosity.
Tab. 1: Binary diffusion coefficients and effective binary diffusion coefficients in the
cermet material given for different values of $\varphi$

|                | $D \cdot 10^8 / \text{m}^2\text{s}^{-1}$ | $D_{\text{eff}} \cdot 10^8 / \text{m}^2\text{s}^{-1}$ ($\varphi = 0.06$) | $D_{\text{eff}} \cdot 10^8 / \text{m}^2\text{s}^{-1}$ ($\varphi = 0.12$) | $D_{\text{eff}} \cdot 10^8 / \text{m}^2\text{s}^{-1}$ ($\varphi = 0.18$) | $D_{\text{eff}} \cdot 10^8 / \text{m}^2\text{s}^{-1}$ ($\varphi = 0.25$) |
|----------------|------------------------------------------|------------------------------------------------|------------------------------------------------|------------------------------------------------|------------------------------------------------|
| $\text{H}_2/\text{H}_2\text{O}$ | 8.26                                     | 0.49                                           | 0.99                                           | 1.49                                           | 2.06                                           |
| $\text{H}_2/\text{CO}$       | 6.98                                     | 0.42                                           | 0.84                                           | 1.26                                           | 1.75                                           |
| $\text{H}_2/\text{CO}_2$     | 5.99                                     | 0.36                                           | 0.72                                           | 1.08                                           | 1.49                                           |
| $\text{H}_2/\text{CH}_4$     | 5.47                                     | 0.39                                           | 0.78                                           | 1.16                                           | 1.62                                           |
| $\text{H}_2\text{O}/\text{CO}$ | 2.43                                     | 0.15                                           | 0.29                                           | 0.44                                           | 0.61                                           |
| $\text{H}_2\text{O}/\text{CO}_2$ | 1.98                                     | 0.12                                           | 0.24                                           | 0.36                                           | 0.49                                           |
| $\text{H}_2\text{O}/\text{CH}_4$ | 2.52                                     | 0.15                                           | 0.30                                           | 0.45                                           | 0.63                                           |
| $\text{CO}/\text{CO}_2$     | 1.52                                     | 0.09                                           | 0.18                                           | 0.27                                           | 0.38                                           |
| $\text{CO}/\text{CH}_4$     | 2.03                                     | 0.12                                           | 0.24                                           | 0.37                                           | 0.51                                           |
| $\text{CO}_2/\text{CH}_4$   | 1.69                                     | 0.10                                           | 0.20                                           | 0.30                                           | 0.42                                           |

Tab. 2: Results of methane steam reforming on Ni cermet anode materials with different
thickness' (CH$_4$ area load: 2.78 Ncm$^3$ cm$^{-2}$ s$^{-1}$ H$_2$O/CH$_4$ mol ratio: 3, pressure: 1.5 bar)

| Experimental Conditions | Composition of dry product gas (vol.%) | Temp. (°C) | CH$_4$ velocity (Ncm$^3$ s$^{-1}$) | H$_2$ | CO | CH$_4$ | CO$_2$ |
|------------------------|--------------------------------------|------------|-----------------------------------|------|----|-------|-------|
| Anode thickness 0.36 mm|                                      | 888.5      | 9.166                             | 19.0 | 1.98 | 75.4  | 3.63  |
|                        |                                      | 853.9      | 9.166                             | 11.8 | 1.38 | 84.8  | 2.03  |
| Anode thickness 0.66 mm|                                      | 884.7      | 9.588                             | 33.1 | 3.7  | 57.5  | 5.2   |
|                        |                                      | 851.5      | 9.588                             | 26.2 | 2.5  | 66.7  | 4.4   |
|                        |                                      | 802.3      | 9.588                             | 17.8 | 1.5  | 78.9  | 3.3   |
| Anode thickness 1.35 mm|                                      | 892.1      | 10.800                            | 32.1 | 3.86 | 58.4  | 5.34  |
|                        |                                      | 848.8      | 10.800                            | 25.8 | 2.67 | 67.0  | 4.50  |
|                        |                                      | 798.5      | 10.800                            | 16.2 | 1.47 | 80.2  | 2.98  |
| Anode thickness 1.90 mm|                                      | 893.5      | 8.366                             | 34.8 | 3.32 | 53.9  | 5.94  |
|                        |                                      | 847.6      | 8.366                             | 26.9 | 2.82 | 65.0  | 4.47  |
|                        |                                      | 802.3      | 8.366                             | 18.6 | 1.88 | 75.9  | 3.06  |
It can be seen from the catalytic data given in Table 2 that a change in the methane conversion rate takes place up to the double sided anode thickness of 0.66 mm. In the thickness range from 0.66 to 1.9 mm no further significant difference in methane conversion was observed.

The following theoretical analysis of the experimental data was carried out. The methane steam reforming reaction [2] is actually a two-stage process taking place according to the scheme

\[
CH_4 + H_2O \rightleftharpoons 3H_2 + CO
\]

\[
CO + H_2O \rightleftharpoons CO_2 + H_2
\]

The first reaction is the reforming reaction characterised by the reforming constants \(k_r\) and \(k_r^-\), and the subsequent reaction is the shift reaction characterised by the constants \(k_s\) and \(k_s^-\). Both reactions produce the actual electrochemically active gases, \(H_2\) and \(CO\), which cause the oxidation products \(H_2O\) and \(CO_2\) to be formed in the anodic reactions. Both reactions can take place at the outer surface of the cermet and inside the anode structure of the fuel cell. This anode consists of a Ni/ZrO\(_2\) cermet, which has catalytic properties for the chemical reactions and for the subsequent electrochemical reactions. The flow scheme of the reforming reaction in the SOFC anode can be described as follows: The reforming gas flows through the gas channel from left to right in the direction of the \(x\)-coordinate (Fig. 2). The coordinate \(x = 0\) is assigned to the gas inlet point. The gas outlet is at the coordinate \(x = L_i\) with a gas composition which can be determined by gas analysis (5). The bottom boundary of the gas channel receives the coordinate \(y = 0\). In order to describe the volume processes in a simple manner, it is assumed that the \(z\)-direction has homogeneous properties. This assumption does not restrict the basic considerations of the method. The involved reactions proceed in the anode cermet which is then defined in the \(x\)-\(y\) region between \(0 \leq x \leq L_i\); \(0 \leq y \leq L_2\). In the gas channel, a laminar flow takes place along the coordinate \(y = 0\) in the \(x\)-direction. Due to diffusion and convection, the introduced gases \(CH_4\) and \(H_2O\) migrate in the \(y\)-direction where they are consumed by reactions [4]. The chemical sinks \(R_r\) and \(R_s\) [mol cm\(^{-3}\) s\(^{-1}\)] are postulated as the reactions

\[
R_r = -\frac{1}{RT} \frac{dP_{CH4}}{dt} = k_{r,+} P_{CH4} P_{H2O} - k_{r,-} P_{CO} P_{H2}^3
\]

\[
R_s = -\frac{1}{RT} \frac{dP_{CO}}{dt} = k_{s,+} P_{CO} P_{H2O} - k_{s,-} P_{CO2} P_{H2}
\]
Due to the high rate of the shift reaction (8), only one of the two constants have been calculated, whereas the other was determined from the product of \( k_c \) and the thermodynamic equilibrium constant. In our approach the electrochemical reactions have not been taken into consideration. The equation system [5] with the material balance with their boundary conditions were calculated by the Finite Integration Technique (control-volume approach) (9) to describe the process flow in the SOFC cermet structure.

The values for the individual reaction rate constants were obtained by comparing the calculated and the analytically determined concentration values in the gas inlet and outlet channels by means of the usual vector-gradient method with the least squares approximation as a criterion. The allowed relative differences between the experimental and calculated concentrations were as high as 10% for CO and CO\(_2\) and less than 1% for H\(_2\), CH\(_4\) and H\(_2\)O. The rate constants were determined for the different values of the effective diffusion coefficients. In Fig. 3a the change of reforming rate constants with \( \varphi \) and in Fig. 3b the one of reforming activation energy with \( \varphi \) are given. It appears that the choice of \( \varphi \) has a strong influence on the results. With \( \varphi \) values higher than the one determined experimentally (0.12) the rate constant and activation energy become independent of \( \varphi \). The resulting activation energy is in the range of 230 kJ mol\(^{-1}\). The calculated concentration profiles of the individual CH\(_4\), H\(_2\), CO and CO\(_2\) gases in the gas channel and in the SOFC anode cermet are shown in Fig. 4 and Fig. 5 for 802 °C, a thickness of 1900 \( \mu \)m and a \( \varphi \) value of 0.12. Due to experimental difficulties, the accuracy of the experiments is not completely satisfactory and must be improved. For this reason, the above values of the reaction constants must be considered preliminary and further experiments have to be carried out.

**CONCLUSIONS**

The calculated activation energy of the methane steam reforming is approximately 2 - 3 times higher than usually reported in literature (2, 5). This difference may arise from the influence of internal mass transport effects. The presented rate constants correspond to the surface reaction. In the model the diffusion of gases within the porous cermet was taken into consideration. The correctness of the reaction parameters depend strongly on the used values of the effective binary diffusion coefficients.
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Fig. 1: Diffusion cell according to Valus and Schneider

![Diagram of a diffusion cell](image)

Fig. 2: Scheme of steam reforming reaction in anode space

![Diagram of steam reforming reaction](image)

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Fig. 3a: Rate constant of steam reforming ($k_{\text{r,}\text{a}}$) in dependence of the ratio of porosity to tortuosity

$$k_{\text{r,}\text{a}} \text{ mol cm}^{-3} \text{bar}^{-2} \text{s}^{-1}$$

Fig. 3b: Energy of activation of steam reforming ($E_{\text{a},(k_{\text{r,}\text{a}})}$) in dependence of the ratio of porosity to tortuosity

$$E_{\text{a},(k_{\text{r,}\text{a}})} \text{ kJ mol}^{-1}$$
Fig. 5: Concentration profile of the gases CH₄, CO, H₂, H₂O and CO₂ in the anode cermet
Fig. 4: Concentration profile of the gases CH₄, CO, H₂, H₂O and CO₂ in the gas channels.