ABSTRACT

During the last decade several papers have been published concerning the use of SOFC as a reactor for the co-generation of chemicals as well as heat and power. One of the interesting applications of the SOFC technology is the partial oxidation of hydrocarbons, like the conversion of methane to syngas. This paper demonstrates the possibility to use SOFC technology for the partial oxidation of methane to syngas, resulting in a conversion of 85-95 % and selectivity to syngas of 97-98 % at an operating temperature of 850°C. Stable performance under syngas producing conditions has been shown over an operating period of 1200 hours.

INTRODUCTION

Solid Oxide Fuel Cells (SOFC) are one of the most promising fuel cell systems for (1) distributed cogeneration (several 100 kWe to several Mwe) with the option of SOFC being a topping cycle in a combined system with a gas turbine and (2) micro combined heat and power (1-10 kWe). During the last decade several papers [1-6] have also been published concerning the use of SOFC’s as reactors for the co-generation of chemicals as well heat and power. One of the interesting applications of the SOFC technology for the production of chemicals is the partial oxidation of methane to syngas. Syngas, a mixture of hydrogen and carbon monoxide with preferably a \( \frac{H_2}{CO} \) ratio of 2, is an important starting gaseous mixture for the production of liquid fuels for transport applications, environment friendly fuel additives and chemicals, like methanol and ammoniac. The conventional processes for syngas production are: Partial Oxidation (POX), Steam/Methane Reforming (SMR) and Autothermal Reforming (ATR), which is a combination of SMR and POX. The POX and ATR processes are economically attractive when pure oxygen is being used instead of air. However, the present production of oxygen by cryogenic processes forms an important part of the cost of syngas production (25-45%) [7]. It has been proposed that the cryogenic oxygen production unit can be replaced by high temperature oxygen ionic conducting membranes, capable of separating oxygen from air and feeding it directly into the reaction zone for the conversion of methane into syngas. The lower partial oxygen pressure in the reaction zone creates the driving force for oxygen transport within the ionic conducting membranes. Two types of membranes are interesting for this process, namely 1/ Solid Electrolyte Oxygen Separators (SEOS), requiring an electric potential over the membrane for transport of oxygen ions, being identical to SOFC and 2/ Mixed Electrolyte Oxygen Separators (MEOS), requiring a
partial oxygen pressure difference along the membrane (See Figure 1). Both types of membranes are under development at ECN. The MEOS is interesting on the basis of the possibility of large oxygen fluxes (10 ml O₂/cm²·min at 940°C) [8] and conversion efficiencies higher than 98%.

This paper deals with the use of SOFC for the production of syngas. The expected advantages of this system are the following:

• Cogeneration of syngas, heat and power
• Controllability of the syngas production by the possibility of oxygen flux regulation

Despite these advantages it is clear that more knowledge is required on the costs and operational properties of such a system in order to determine the most appropriate applications and market entries for this technology. These issues are being addressed by ECN in several studies. Within this paper the technical feasibility for the production of syngas by SOFC is being demonstrated by single cell experiments.

CHOICE OF ANODE MATERIAL

Nickel-zirconia cermets have been widely used as fuel electrode materials for SOFC. In the literature it is very often suggested that Ni-containing anode materials can not be used for the oxidation of dry methane due to the fact that nickel is a catalyst for cracking of methane resulting in carbon deposition. Therefore, a lot of research has been done on oxide materials as alternative anode material instead of Ni-based anode materials. However, it has been shown that the application of oxides as alternative anode material is limited due to the following reasons:

• A good contact between current collector and anode material is required, which can be a problem when using oxide materials as anode material.
• The electronic conductivity in conventional Ni/zirconia cermets is very high and difficult to obtain with mixed conducting oxide materials.
• Instability of the oxides under the wide range of partial oxygen pressures present under anode conditions.
• The reactivity between oxide material and electrolyte.

The use of Ni-based anode materials is preferred due to some very important advantages:

• Nickel on a ceramic carrier has very good internal reforming properties
• Nickel containing anode materials can be combined very well with a nickel current collector
• Ni/cermet anodes have very well defined electrochemical properties.

On basis of these arguments Ni-containing anodes were used within this study. In addition it was reported [9] and confirmed in our laboratory that carbon deposition in a Ni-containing anode could be prevented by using a doped ceria support for the nickel, which is capable of removing the deposited carbon by its mixed conducting behaviour. In this report Ni/ Gd-doped ceria cermets have been used as anode material.
EXPERIMENTAL

Cell Manufacturing

A screen print paste of NiO/Gd-doped ceria mixture has been prepared with a Ni-content of 40 vol% Ni after reduction. This paste has been screen printed on a 130 μm thick zirconia (8YSZ) electrolyte with dimensions of 10*10 cm². The cathode material consists of a standard LSM-YSZ/LSM double layer. Both electrodes are sintered at 1200°C for one hour. These cells have been used for partial oxidation experiments on methane.

Partial oxidation of methane

The partial oxidation experiments were performed in alumina cell housings with noble metal current collectors at an operating temperature between 700 and 900°C with air at the cathode and dry methane at the anode. The inlet and outlet gas composition of the anode could be analysed by means of gas chromatography. The gas analysis will be discussed in terms of conversion and selectivity of the partial oxidation reaction, defined as:

Methane conversion in %:  \((1 - \frac{\text{CH}_4(\text{out})}{\text{CH}_4(\text{in})})\) \times 100\%

Selectivity towards syngas in %:  \((\frac{\text{CO}(\text{out})}{\text{CO}(\text{out}) + \text{CO}_2(\text{out})})\) \times 100\%

The resulting data for the methane conversion and selectivity for syngas were obtained as a function of the following parameters:

a/ Operating temperature varying between 700 and 900°C
b/ Methane flow at constant methane-flow/current ratio (resulting in CH₄/O₂ = 2) at 850°C
c/ Current at 850°C
d/ Endurance behaviour at 850°C

The results of these experiments are discussed in the following chapter.

RESULTS

Conversion of Methane to Syngas as a Function of Temperature

These tests have been performed at an operating temperature varying between 750 to 900°C with a dry CH₄ flow and a constant methane flow/current ratio, resulting in a CH₄/O₂ ratio of 2. The current density was chosen in such a manner that the cell potential is 700 mV. This means that the current density is increasing with increasing temperature. The resulting conversion and selectivity data are shown in Figure 2 and Table I. The conversion and selectivity are decreasing with decreasing temperature, as expected on basis of the thermodynamic equilibrium for which data are also included in Figure 2.
Comparing the thermodynamic and measured data in Figure 2, it can be seen that the measured methane conversion is lower than the thermodynamic equilibrium. However, with increasing temperature the current density and methane flow are also increasing which has its influence on the conversion value, resulting in an increasing deviation from the thermodynamic value with increasing temperature.

Table I. Conversion of methane and selectivity towards syngas in % as a function of temperature at a constant methane flow/current ratio. The current density is chosen in such a manner that the cell potential is approximately 700 mV.

| Temperature in °C | Methane flow in ml/min | Current density in mA/cm² | Conversion of methane in % | Selectivity in % |
|-------------------|------------------------|----------------------------|---------------------------|-----------------|
| 750               | 77                     | 123                        | 80.7                      | 90.0            |
| 750               | 77                     | 123                        | 80.5                      | 90.2            |
| 800               | 154                    | 250                        | 82.9                      | 94.5            |
| 850               | 202                    | 320                        | 84.4                      | 96.4            |
| 850               | 202                    | 320                        | 84.2                      | 96.6            |
| 850               | 202                    | 320                        | 85.1                      | 96.8            |
| 900               | 310                    | 490                        | 86.5                      | 98.2            |

Syngas Production as Function of the Methane Flow at Constant Methane/Current Ratio

These tests were performed at an operating temperature of 850°C under similar conditions as described in the previous chapter. The resulting conversion of methane and selectivity to syngas as a function of the methane flow is shown in Figure 3. Increasing methane flow results in decreasing conversion but the selectivity remains constant.

With decreasing methane flow, the conversion of methane approaches the expected theoretical thermodynamic values of 96%. This demonstrates that with increasing flow one or several reaction rates in the gas mixture are insufficient in order to reach equilibrium. These reactions may be steam reforming and/or water gas shift reactions. It is very likely that the steam reforming reaction is not fast enough because if this reaction reaches the equilibrium conditions the theoretical conversion should have been approached. In that case the conversion can be improved by using steam reforming catalysts.

Figure 4 shows the I-V characteristics associating with this experiment. This figure shows that a current density of 0.8 A/cm² can be reached with a corresponding methane flow of 500 ml/min, resulting in a conversion of 83% and a selectivity of 95.4%. The yield of syngas can be further improved by lowering the impedance of the cell, i.e. by improving the electrodes or diminishing the electrolyte thickness.
**Endurance Behaviour under Syngas Forming Conditions**

An endurance test under syngas forming conditions has been performed at an operating temperature of 850°C with a constant methane flow of 202 ml/min and with a current density of 320 mA/cm², resulting in a CH₄/O₂ ratio of 2. The conversion and selectivity were constant during a period of more than 1000 hours at values of 86-87% and 97-98% respectively, as shown in Figure 5. This is also an indication that the anode is resistant to carbon deposition.

**CONCLUSIONS**

The conclusions of the study on the use of SOFC technology for the co-generation of syngas can be summarised as follows:

- The partial oxidation of methane to syngas is possible using SOFC technology.
- The selectivity of the conversion of methane to syngas amounts 97-98 % at 850°C.
- The conversion of methane to syngas diminishes with increasing methane flow. It is likely that the conversion can be improved by the application of steam reforming catalysts.
- The yield of syngas depends upon the impedance of the cell. The impedance can be further diminished by improvement of electrode performance and/or thinner electrolyte foils.
- The methane conversion has been shown to be stable over a period of 1200 hours.
- It seems possible to use Ni/Ceria cerments as anode material without performance degradation due to carbon deposition.

**FUTURE INVESTIGATIONS**

The study on the use of the SOFC technology for the co-generation of power/heat and syngas will be continued in three areas:

- Study on application possibilities for production of syngas by SOFC technology ranging from large to small scale industrial or energy related applications.
- Study on further improvement of the ceramic membranes: Improvement of yield of syngas and further study on endurance behaviour of present anode materials under syngas conditions.
- Study on scale up of technology

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Figure 1. Schematic drawing of a MEOS membrane (top figure) and a SEOS membrane (bottom figure).
Figure 2. The theoretical and measured fractional values for the conversion of methane and selectivity to syngas as function of the operating temperature at constant CH₄/O₂ ratio of 2.

Figure 3. Conversion and selectivity of methane to syngas in percentage as function of the methane flow at 850°C.
Figure 4. Cell voltage, open cell voltage (OCV) and methane flow in ml/min as function of the current density in mA/cm$^2$.

Figure 5. The endurance behaviour of the cell in terms of conversion, selectivity and cell voltage as function of time at 850°C, 320 mA/cm$^2$ and 202 ml/min CH$_4$. 

1184 Electrochemical Society Proceedings Volume 99-19