IMPACT OF BIOSYNGAS AND ITS COMPONENTS ON SOFC ANODES

P. V. Aravind1, J. P. Ouweltjes2, E. de Heer1, N. Woudstra1, G. Rietveld2
1Section Energy Technology, TU Delft
Mekelweg 2, NL-2628 CD Delft, The Netherlands
2Energy Research Center of the Netherlands
NL-1755 ZG Petten, The Netherlands

ABSTRACT

Biosyngas was investigated as a potential fuel for solid oxide fuel cells. C-H-O ternary diagrams were employed to evaluate the thermodynamics of carbon deposition with selected gas compositions. Impedance measurements were carried out with Ni/GDC and SDC anodes. Gas compositions representing biosyngas were used in the experiments. Both anodes gave reasonable performance with biosyngas compositions when compared to humidified hydrogen. Impact of the H2S in the gas stream on the performance of Ni/GDC anodes was presented. No impact was observed up to 9 ppm H2S.

INTRODUCTION

Biomass is widely considered a sustainable primary energy source suitable for power generation. For decentralized energy production, biomass gasification offers great advantages over other conversion technologies. Especially when solid oxide fuel cells (SOFCs) are used for electricity production, highly efficient systems are possible. Hence the use of biosyngas in SOFCs is getting widespread attention (1-7).

Biomass gasification is partial oxidation of solid fuel and can be carried out with different gasifying agents like air, oxygen, and steam. Air is the most common gasification agent and generates gas containing significant amounts of nitrogen. Table I gives a brief comparison of biosyngas generated with different gasification agents (8-10). Biosyngas also contains other contaminants like tar and particulates. A typical contaminant level in an air blown fluidized bed gasifier after two cyclones is given in Table II (11,12).

Table I. Comparison of biosyngas generated with different gasification agents.

| Gasifying agent | Representative gas composition (vol) | HHV (approx) MJ/Nm³ |
|-----------------|------------------------------------|---------------------|
| Air             | 20% H₂, 20% CO, 12% CO₂, 2% CH₄, 2.5% H₂O and the rest N₂ | 4-6 |
| Oxygen          | 32% H₂, 48% CO, 15% CO₂, 2% CH₄ and 3% N₂ | 10-15 |
| Steam           | 38% CO, 35% H₂, 12% CO₂, 10% CH₄ and 5% other hydrocarbons | 12-18. |
Table II. Typical contaminant presence in an air blown fluidized bed gasifier.

| Contaminant    | Concentration |
|----------------|---------------|
| Tar            | 5-20 g/Nm³    |
| Particulates   | 5-30 g/Nm³    |
| H₂S            | 50-200 ppm    |
| Alkali metals  | 1 ppm –wt     |
| NH₃            | 4000 ppm      |
| Halides        | Few ppm       |

These contaminants will need to be cleaned before the gas is fed to SOFCs. There are different cleaning methods being considered for removal of these contaminants from the gas. It is expected that tars and particulates can be cleaned to a few ppm level (9,13), acid gases and alkali compounds can be cleaned to sub-ppm level (14,15), and H₂S can be cleaned to around 1 ppm (5) with viable technologies. NH₃ is known as a fuel (16,17) for SOFCs, and H₂S affects performance when it is about 1 ppm or more (18). These numbers are suggested for SOFCs with Ni/YSZ anodes. No hard data are available for tolerance levels for other contaminants and for other SOFC anodes.

Because the fuel interacts with the anode inside a SOFC, interactions between the anode materials and the contaminants need to be studied. There are many choices emerging for anode materials. Different anode materials will have different kinds of interactions with the contaminants and hence their tolerance levels for these contaminants may vary considerably.

Of the main components of the gas, hydrogen, carbon monoxide, and methane are fuels for SOFCs. N₂ is expected to be inert but may cause diffusion problems. H₂O and CO₂ will help the shift reaction, and CH₄ will be reformed inside the cell. Fuels containing carbon can cause carbon deposition in certain circumstances. Weber et al. (19) have reported that Ni/YSZ anodes can run with gas mixture of H₂, CO and CH₄. Complete CO feeding causes carbon deposition and may degrade the cell. Methane caused no problem under load but did cause carbon deposition at open circuit condition, probably because of the lack of oxygen ions available at the anode under open circuit. Zhu et al. studied the performance of salt oxide composite anodes with biosyngas at intermediate temperatures and measured the current voltage characteristics (6). They indicate reasonable performance of the cell except when there is a presence of more than 20% nitrogen. Baron et al. studied intermediate temperature SOFCs with Ni/GDC anodes for operation with biosyngas. They report higher anodic impedance when CO replaced hydrogen in the fuel stream (7).

**EXPERIMENTS**

Nickel is widely considered as an attractive material for SOFC anodes because it is a good electronic conductor and catalytically active for electrochemical oxidation of hydrogen. To increase the mechanical properties, nickel is mixed with an ion conducting material, most commonly YSZ. Doped ceria, like GDC or SDC, is a mixed conductor. It offers increased surface area for electrochemical reactions unlike the ionic conductors,
which limit the reactions to fuel/electrode/electrolyte boundaries. They are also expected to give better performance with fuels containing hydrocarbons (20). For this reason, two anodes based on doped ceria were selected for the experiments. The first anode consisted of nickel mixed with GDC, the second consisted of pure SDC with gold for current collection.

The prepared Ni/GDC anodes consisted of the following three layers: an adherence layer of $\text{Gd}_{0.4}\text{Ce}_{0.6}\text{O}_{1.8} + 2 \text{ mol}\% \text{ Co}$ adjacent to the electrolyte, a functional layer of NiO/$\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$ 65/35 wt%, and finally a contact layer of NiO. The anodes were 22 mm in diameter and 35 microns thick. They were printed to 130-140 micron thick 3YSZ electrolytes with 25 mm diameter and sintered at 1200°C. SDC anodes were prepared with a Sm$_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$ layer on a similar electrolyte and were sintered at 1100°C. The SDC layer is 10 microns thick. To improve the electronic conductivity, a gold layer was applied and sintered at 600°C.

The samples were supported on ceramic supports in a single gas chamber through which the fuel gas was passed. A gas mixing station was fabricated with provisions for mixing hydrogen, carbon monoxide, carbon dioxide, nitrogen, methane, and various contaminants. The gas was humidified in a temperature-controlled two chamber humidifier. Figure 1 shows the experimental setup.

![Figure 1. The experimental setup.](image)

Hydrogen was diluted with $\text{N}_2$, $\text{CO}$, and $\text{CO}_2$ by mixing them in various percentages. Experiments were carried out at four temperatures: 1023 K, 1073 K, 1123 K, and 1173 K. The fuel was humidified at 30°C. $\text{CO}_2$ was added to the gas mix after humidification. Experiments were also carried out with three different biosyngas compositions. To study the impact of $\text{H}_2\text{S}$ on anode performance, $\text{H}_2\text{S}$ was added to a $\text{H}_2$ gas stream after humidification. Contaminant concentrations up to 9 ppm were employed. Tests with $\text{H}_2\text{S}$ are reported only for Ni/GDC anodes.

Impedance measurements were performed with a Solartron frequency response analyzer 1255 in combination with a Solartron electrochemical interface 1287. The samples were measured at zero bias with a frequency sweep between 0.1 Hz and 100 KHz, using a four-probe configuration.
RESULTS

Ternary C-H-O Diagrams

Carbonaceous fuels can cause carbon deposition at SOFC operating temperatures, as discussed. C-H-O ternary diagrams describing parameters and conditions relevant for fuel cell operation are useful to understand the thermodynamics of carbon deposition behavior (21). Even though chemical reaction kinetics, in addition to thermodynamics, can play a role in carbon deposition, thermodynamic equilibrium studies give the first-hand indication about the possibility of carbon deposition with the given fuel. Nitrogen, because it is a diluting species, can be ignored in certain conditions and it is assumed that it is the case in the conditions presented here. Figure 2 shows the carbon deposition limit lines, the carbon-rich side of which corresponds to the carbon deposition region at each temperature. From the figure we can observe that carbon formation is not present at biosyngas compositions employed in the present experiments and temperatures at which experiments were carried out.

Figure 2. C-H-O equilibrium with representative biosyngas compositions: • = 40% H₂, 40% CO, 20% CO₂; ▲ = 20% H₂, 20% CO, 10% CO₂, 50% N₂, ■ = 50% H₂, 40% CO, 10% CO₂ (all mixtures humidified at 30°C).

Dilution of Hydrogen with Nitrogen

The experiments were started with pure hydrogen. The gas was diluted in steps by adding 15% nitrogen at each step until it reached a composition of 40% H₂ and 60% N₂. Impedance measurements were taken at each step. Figure 3 shows the impedance spectra observed at 1173K and 1123K adjusted for the series resistance. The impedance decreased with temperature. Dilution with nitrogen increased the impedance for both the anodes. This could probably be due to diffusion limitations (7). A detailed analysis of the spectra is not attempted here and will be presented later.
Figure 3. Variation of anodic impedance with various H2/N2 mixtures at different temperatures, Ni/GDC anodes (above), SDC anodes (below).

Dilution with CO and CO2

CO and CO2 are increased by steps of 15% from 0% to 45% and the obtained spectra at 1123K are shown in Figure 4.

Figure 4. Variation anodic impedance with various H2/CO and H2/CO2 mixtures at 1123 K for Ni/GDC anodes and SDC anodes.

Contrary to experiments with CO and N2, addition of CO2 has shown to decrease the anodic impedance with the LF semicircle becoming smaller. It seems impossible to
explain this based on diffusion. However, chemical equilibrium calculations in the above mentioned experimental conditions show the possibility of a significant amount of H₂O generated because of a shift reaction (H₂ + CO₂ → H₂O + CO). This has been confirmed with detection of CO in the gas coming at the exit of the reactor when the fuel gas used was a humidified mixture of H₂ and CO₂. Increased presence of H₂O could be playing a role in bringing down the impedance, but a more detailed analysis of the results is required to get a better understanding.

**Experiments with Simulated Biosyngas**

Experiments were carried out with three different biosyngas compositions. A nitrogen-rich gas with composition comparable to gas from air gasification, a hydrogen-rich gas representing pre-reformed syngas from steam gasification, and a third composition representing syngas from oxygen gasification in which H₂ and CO are present in equal amounts are used, and the results are presented in Figure 5. Methane was ignored except for steam gasification because its presence is considerably lower when compared to H₂, CO, CO₂ and N₂. It was again observed that the mixtures containing CO₂ gave rise to lower impedance. No significant carbon deposition is observed during the experiments.

**Figure 5. Impedance with different biosyngas compositions at 1173 K and 1023 K for Ni/GDC anodes (above), SDC anodes (below).**
Experiments with H$_2$S

H$_2$S is considered to be one of the contaminants that can cause problems for SOFC operation. It is also present in biosyngas. Studies until now indicate that fuel must be cleaned to sub-ppm H$_2$S levels before it can be fed to the Ni/YSZ anode. Only zinc-based sorbents working at 673-823 K are said to be effective in cleaning H$_2$S to 1 ppm levels at elevated temperatures. But their temperature operation range of 673 to 823 K is considerably lower than the operation temperatures of SOFCs and biomass gasifiers. Hence they limit the options of configuring optimal systems with gasifiers and SOFCs.

The limitation with Ni/YSZ anodes could be the small active anode surface for catalytic electrochemical oxidation of the fuels. At concentrations around few ppm H$_2$S, it is said that the possible performance degradation of the anode occurs mainly because of selective adsorption of H$_2$S on active sites near or on triple phase boundaries.

Ni/GDC anodes were fed with H$_2$ humidified at 30°C to which H$_2$S was added at concentrations of 3, 6, and 9 ppm for 90 minutes each in every experiment. Impedance spectra were taken every 15 minutes. Results are shown in Figure 6.

![Figure 6. Impact of H$_2$S on Ni/GDC anode at 1123 K and 1023 K.](image)

No significant impact from sulfur was observed on the anodes. This could be due to the fact that even when a nickel surface is covered with H$_2$S, a large surface area of doped ceria is still catalytically active. Even when contaminated with adsorption of the surface, nickel can probably continue to act as a good current collector. In fact, such a possibility was suggested in early studies (22). At higher H$_2$S levels there could be chemical reactions between sulfur and nickel depending upon the fuel conditions, and there could be other influences contributing to performance degradation. This must be studied in detail.

But if the observation that Ni/GDC anodes can work safely with few ppm H$_2$S present is true at higher current densities, that offers the possibility of employing a few gas cleaning sorbents other than the conventional zinc-based ones. Sorbents that could work at higher temperatures could significantly increase the flexibility in design of gasifier SOFC systems.
DISCUSSION AND CONCLUSIONS

To study SOFC anode performance with biosyngas as fuel, impedance measurements were taken on Ni/GDC and SDC anodes. In the case of \( \text{N}_2 \) and \( \text{CO} \), the diameter of the LF semicircle, which might represent the diffusion process, appeared to be increasing with increasing dilution. But with the addition of \( \text{CO}_2 \) to the fuel gas, the total impedance and LF circle diameter appeared to have come down. This could probably be explained on the basis of formation of \( \text{H}_2\text{O} \) to reach equilibrium composition for the gas mixture at the given conditions and subsequent lowering of the impedance. This has yet to be confirmed. C-H-O ternary diagrams have shown that the biosyngas compositions used are in a thermodynamically safe region. This has been confirmed with the experiments on both the anodes tested. \( \text{H}_2\text{S} \) up to 9 ppm has shown no impact on the anodic impedance of Ni/GDC anodes. This is probably because doped ceria is not affected by \( \text{H}_2\text{S} \). Nickel, which has a higher chance of being affected, still plays the role of an electronic conductor.

Ongoing activities related to the present work include theoretical as well as experimental studies on the impact of different contaminants on anodes, design of a suitable gas cleaning system, testing of the fuel cells connected to a real gasifier, and system studies to conceive concepts of high-efficiency systems with gasifiers and fuel cells.

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