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Published in Electrochemical Society Proceedings Volume 2005-07, p1459-1467

IMPACT OF BIOSYNGAS AND ITS COMPONENTS ON SOFC ANODES

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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 were presented. No impact was observed up to 9 ppm H₂S.

INTRODUCTION

Biomass is widely considered as 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 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 the solid fuel and can be carried out with different gasifying agents like air, oxygen and steam. Gasifiers with air as gasification agent are most common and they generate gas containing significant amounts of nitrogen. Table I gives a brief comparison between biosyngas generated with different gasification agents [8,9,10]. 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 between biosyngas generated with different gasification agents

Gasifying agent	Representative gas composition (Vol)	HHV (Approx) MJ/Nm ³
Air	20% H ₂ , 20% CO, 12% CO ₂ , 2.0% CH ₄ , 2.5 % H ₂ O and the rest N ₂	4-6
Oxygen	32% H ₂ , 48% CO, 15% CO ₂ , 2% CH ₄ and 3% N ₂	10-15
Steam	38% CO, 35% H ₂ , 12% CO ₂ , 10% CH ₄ and 5% other hydrocarbons	12-18.

Table II. Typical contaminant presence in an air blown fluidized bed gasifier

Contaminant	Concentration
Tar	5-20 g/Nm ³
Particulates	5-30 g/Nm ³
H ₂ S	50-200 ppm
Alkali metals	1 ppm -wt
NH ₃	4000 ppm
Halides	Few ppm

These contaminants will have 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 SOFC and H₂S affects performance when it is around 1 ppm or more [18]. These numbers are suggested for SOFCs with Ni/YSZ anodes. No hard data is available for tolerance levels for other contaminants and for other SOFC anodes.

Since the fuel interacts with the anode inside SOFC, interactions between the anode materials and the contaminants have to be studied. There are many choices emerging for anode materials. Different anode materials will have different kinds of interactions with these 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 SOFC. N₂ is expected to be inert but may cause diffusion problems. H₂O and CO₂ will help the shift reaction, and CH₄ will get reformed inside the cell. Fuels containing carbon can cause carbon deposition in certain circumstances. Weber *et al.* have reported [19] 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 had caused carbon deposition at open circuit condition. This is probably because of the lack of oxygen ions available at anode under Open Circuit. Zhu *et al.* has studied the performance of salt oxide composite anodes with biosyngas at intermediate temperatures and has measured the current voltage characteristics [6]. They have indicated reasonable performance of the cell except when there is a presence of more than 20% nitrogen. Baron *et al.* have studied intermediate temperature SOFCs with Ni/GDC anodes for operation with biosyngas. They have reported higher anodic impedance when CO replaced hydrogen in the fuel stream [7].

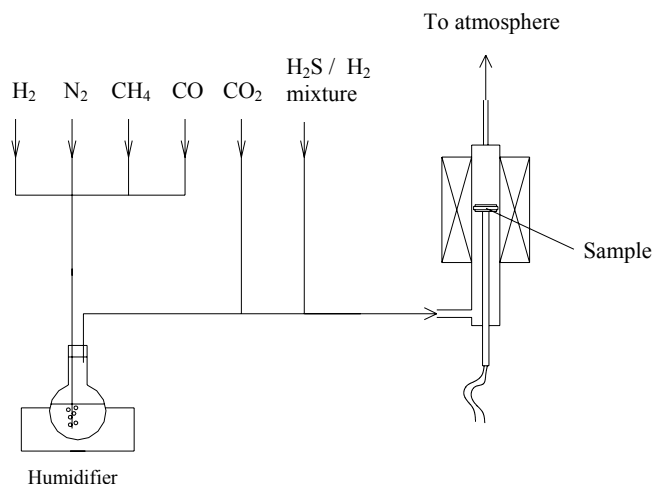
EXPERIMENTS

Nickel is widely considered as an attractive material for SOFC anodes, since it is a good electronic conductor and catalytically active for the electrochemical oxidation of hydrogen. In order 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 anode consisted of pure SDC, with gold used for current collection.

The prepared Ni/GDC anodes consisted of the following three layers: an adherence layer of Gd_{0.4}Ce_{0.6}O_{1.8} + 2 mol% Co adjacent to electrolyte, a functional layer of NiO / Gd_{0.1}Ce_{0.9}O_{1.95} 65/35 weight percent, and finally a contact layer of NiO. The anodes were 22 mm in diameter and 35 micron in thickness and were printed to 130-140 micron thick 3YSZ electrolytes with 25 mm diameter and sintered at 1200°C. SDC anodes were prepared with Sm_{0.1}Ce_{0.9}O_{1.95} layer on similar electrolyte and were sintered at 1100 °C. SDC layer is 10 micron 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. Fig.1 shows the experimental setup.

Figure 1. The experimental setup



Hydrogen was diluted with N_2 , CO and CO_2 by mixing them in various percentages. Experiments were carried out at four different temperatures: 1023K, 1073K, 1123K, and 1173K. The fuel was humidified at 30°C. 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 H_2S on anode performance, H_2S was added to a H_2 gas stream after humidification. Contaminant concentrations up to 9 ppm were employed. Tests with H_2S 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 0.1Hz 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 before. C-H-O ternary diagrams describing parameters and conditions relevant for fuel cell operation are useful to understand the thermodynamics of carbon deposition behaviour [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 being 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.

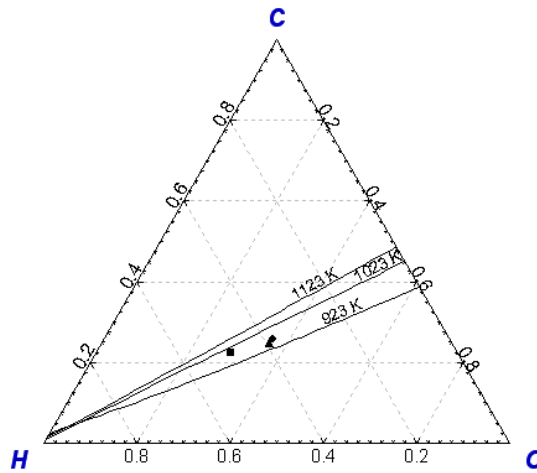


Figure 2. C-H-O equilibrium with representative biosyngas compositions-. ● 40% H₂, 40% CO, 20% CO₂, ▲ 20% H₂, 20% CO, 10% CO₂, 50% N₂, ■ 50% H₂, 40% CO, 10% CO₂ (all mixtures humidified at 30 °C).

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 till it reached a composition of 40% H₂ and 60% N₂. Impedance measurements were taken at each step. Fig 3 shows the impedance spectra observed at 1173 K and 1123 K adjusted for the series resistance. The impedance decreased with temperature. Dilution with nitrogen increased the impedance for both the anodes. This could probably because of diffusion limitations [7]. A detailed analysis of the spectra is not attempted here and will be presented later.

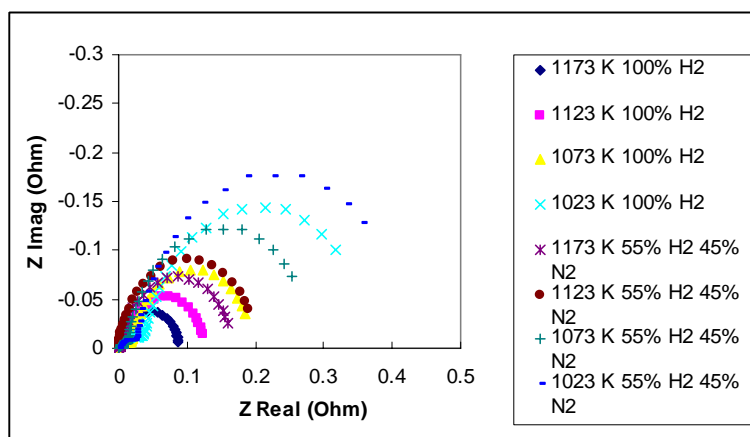
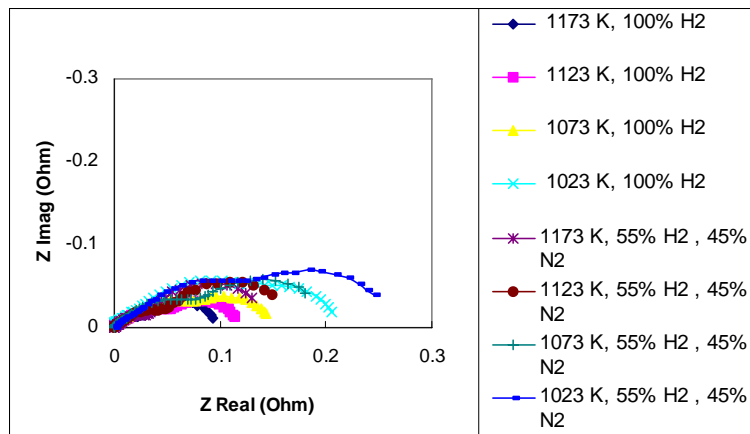


Figure 3. Variation of anodic impedance with various H₂/N₂ mixtures at different temperatures Ni/GDC anodes (above), SDC anodes (below)

Dilution with CO and CO₂

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

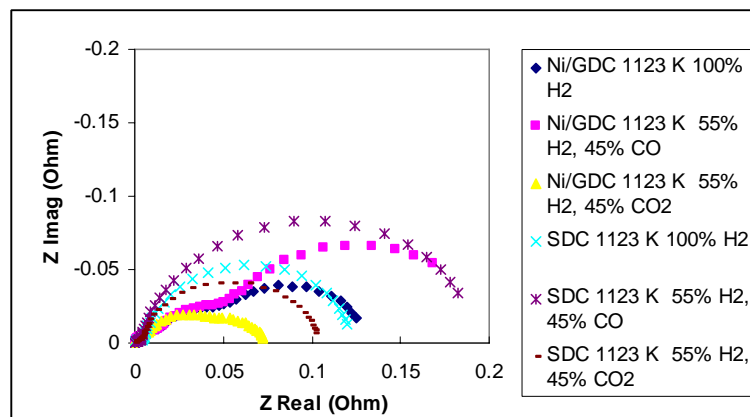
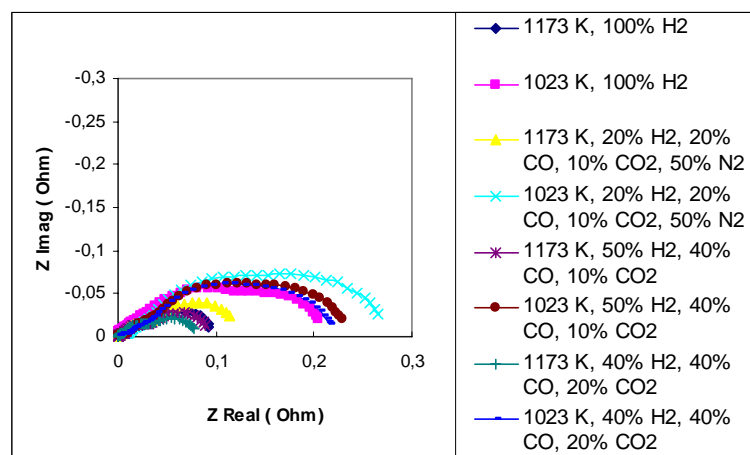


Figure 4. Variation of anodic impedance with various H₂/CO/CO₂ mixtures at 1123 K for Ni/GDC anodes and SDC anodes

Contrary to experiments with CO and N₂, addition of CO₂ has shown to decrease the anodic impedance with LF semicircle becoming smaller. It seems this is not possible to be explained based on diffusion. However chemical equilibrium calculations in the above mentioned experimental conditions show the possibility of significant amount of H₂O generated because of shift reaction ($H_2 + CO_2 \rightarrow H_2O + CO$). 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, 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 fig 5. Methane was ignored except for steam gasification, as 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.



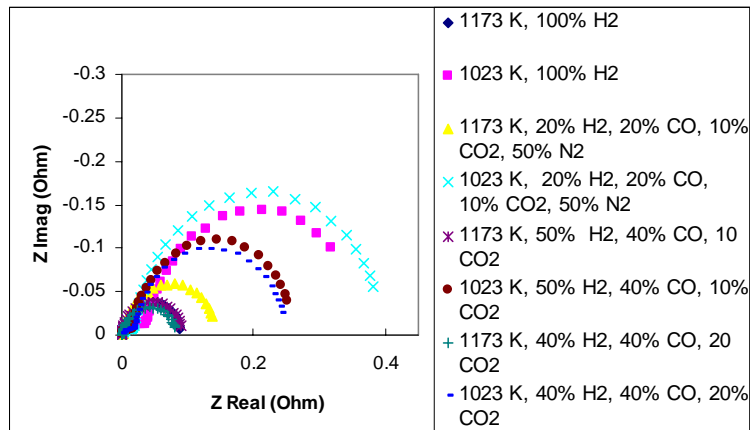


Figure 5. Impedance with different biosyngas compositions at 1173 K and 1023 K for Ni/GDC anodes (above), SDC anodes (below)

Experiments with H₂S

H₂S is widely considered as one of the contaminants that can cause problems for SOFC operation. They are also present in biosyngas. Studies till now indicate that fuel has to be cleaned to sub ppm H₂S levels before it can be fed to the Ni/YSZ anode. Only zinc based sorbents working around 673-823 K are said to be effective in cleaning H₂S to 1 ppm level at elevated temperature. But their temperature operation range of 673 –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 H₂S, it is said that the possible performance degradation of the anode occurs mainly because of selective adsorption of H₂S on active sites near or on triple phase boundaries.

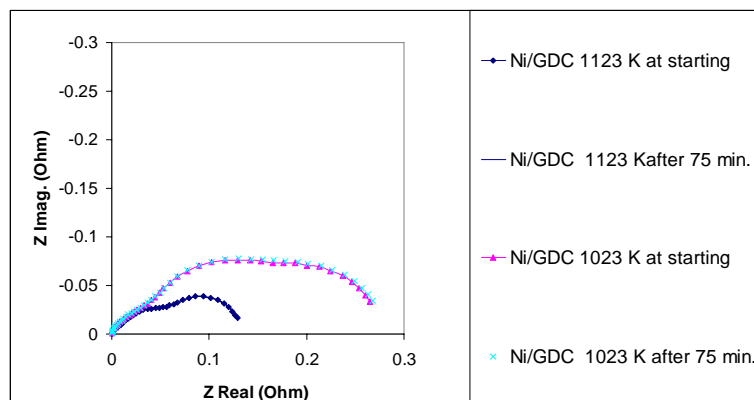


Figure 6. Impact of H₂S on Ni/GDC anode at 1123 K and 1023 K

Ni/GDC anodes were fed with H₂ humidified at 30° C to which H₂S was added at concentrations of 3 ppm, 6 ppm and 9 ppm for 90 minutes each in every experiment. Impedance spectra were taken at every 15 minutes. Results are shown in fig. 6.

No significant impact of sulfur was observed on the anodes. This could be due to the fact that even when nickel surface is covered with H₂S, 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 has been suggested in early studies [22]. At higher H₂S 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 has to be studied in detail.

But if the observation that Ni/GDC anodes can work safely with few ppm H₂S 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. Such sorbents which could work at higher temperatures can 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 carried out on Ni/GDC and SDC anodes. In case of N₂ and CO, diameter of the LF semicircle, which might be representing the diffusion process, appeared as increasing with increasing dilution. But with the addition of CO₂ 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 H₂O so as to reach equilibrium composition for the gas mixture at the given conditions and subsequent lowering of the impedance. This is yet to be confirmed. C-H-O ternary diagrams have shown that biosyngas compositions used are in thermodynamically safe region. This has been confirmed with the experiments on both the anodes tested. H₂S 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 H₂S. Nickel, which has a higher chance of getting affected, still playing 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.

ACKNOWLEDGEMENT

Authors wish to thank Ir. O Unal, Drs. J. Andries and Prof. H. Spliethoff of TU Delft for their advice and help. Authors also wish to thank J. Bakker of ECN for helping in carrying out the impedance measurements.

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