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Operating Microtubular SOFCs With Hydrogen Chloride and Hydrogen Sulfide Containing Fuels and Synthetic Wood Gas

Solid oxide fuel cells are known to be able to handle a large variety of different fuels. Because of the greenhouse effect the use of carbon dioxide neutral gases or liquids are of special interest. In this context wood-gas has a big potential to be an alternative fuel for solid oxide fuel cells (SOFCs). The gas is generated by a fluidized bed steam gasifier and consists of various components such as 25 Vol % carbon monoxide, 20 Vol % carbon dioxide, 10 Vol % methane, 2.5 Vol % ethylene, 0.5 Vol % propylene, 2 Vol % nitrogen, and the rest hydrogen (values in dry state). The water concentration of the original pyrolysis gas is about 35 Vol %. Besides these main ingredients there are of course many impurities like dust, tars, ammonia, hydrogen sulphide, and hydrogen chloride present in the product gas. Especially the last two ones may lead to degeneration of the fuel cell anode and must therefore be almost totally removed before feeding the gas into the cell. In order to reduce energy losses, hot gas cleaning systems are favored. This, however, limits the possibility to reduce the impurity concentrations to very low levels. Therefore the aim of this work is to define the maximum acceptable output concentrations for the hydrogen chloride adsorber also in combination with hydrogen sulphide, since for a micro-tubular SOFC there are as yet hardly any data available. In order to determine the influence of the hydrogen chloride on the performance of the fuel cell, different concentrations of this impurity were fed to the cell. Here, also the flow rate was changed while the electrochemical output was determined. In addition it was analyzed if there were any effects when changing from pure hydrogen to the HCl containing fuel. This was investigated at 1123 K and 1173 K, which are the preferred working temperatures for our cells. Cooling down as well as heating up procedures were tested with cells between 1173 K and 573 K. In a second series of experiments, combinations of hydrogen chloride and hydrogen sulphide of variable concentrations were tested. As before, changing between pure hydrogen and the acid containing fuel at above given temperatures was analyzed by determining the cell performance. In parallel to the above experiments, synthetic wood gas was used for operating the microtubular fuel cell while monitoring the electrochemical output with time. [DOI: 10.1115/1.2205361]

Keywords: SOFC, hydrogen chloride, hydrogen sulfide, wood gas, fuel cell

Introduction

Because of the rise in prices of the conventional fuels like petrol on the one side and the increase of the green house effect on the other side, renewable energy resources become more and more important. Hydrogen is said to be a possible solution for these problems. However the lack of a good hydrogen supply system and problems with the storage of the gas affects the need of looking for alternatives.

One of the main advantages of the solid oxide fuel cells (SOFCs) is the possibility to use hydrocarbon rich fuels instead of

pure hydrogen [1–3]. This provides the possibility of reducing the green house effect by the use of renewable primary products as fuels. In this context wood gas promises to be a cheap and carbon dioxide neutral option.

There are different ways how wood gas can be produced, for example it can be made by gasification with air, oxygen, or steam [4,5]. Today in many cases the generation of electricity with such gases is then performed using gas engines. The replacement of these by SOFCs offers the potential to achieve substantially higher efficiency and may therefore be a very interesting combination of two environmentally friendly technologies. But in order to achieve this goal it is extremely necessary to reduce all energy losses to a minimum, e.g., in order to minimize thermal losses, hot gas cleaning systems are favored which in some cases are very difficult. Also hydrogen chloride and hydrogen sulfide can be re-

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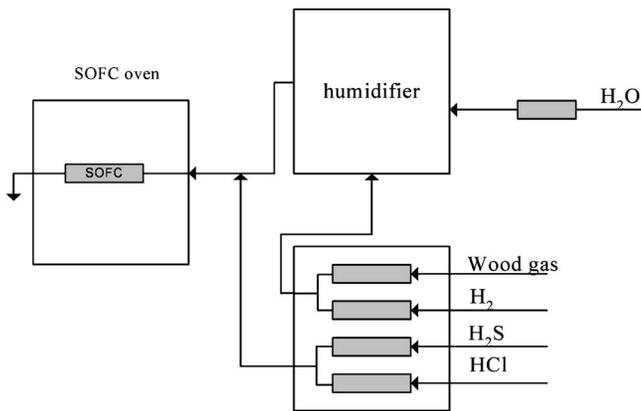


Fig. 1 Experimental setup

moved by adsorption which may decrease the power performance and cell life [6,7]. Here unfortunately the minimum concentration one can achieve is limited by the temperature, which means that the gas has to be cooled down to get very low levels of the harmful substances. So here a compromise has to be made between the maximum poison concentration which is allowed by the SOFC and the minimum energy loss which is possible. Therefore an exact determination of the maximum allowed concentrations of the impurities is very important for an optimized design of such a combination of SOFC technology and a wood gas plant.

Materials

The solid oxide fuel cells were made by the company Adelan. The microtubular cells were electrolyte based (YSZ), the anodes were made of Nickel/YSZ (inside), and the cathode of LSM/YSZ (outside). The surface areas of the cathode were about 2 cm², the electrolyte tubes had got a length of 55 mm, an outer diameter of 2.7 mm, and a wall thickness of about 200 μm.

High purity gases were purchased from Air Liquide Austria (Linz) and were delivered with a certificate. The tested gases were synthetic wood gas (C₃H₆ 0.488 Vol %; C₂H₄ 1.99 Vol %; N₂ 2.01 Vol %; CH₄ 10 Vol %; CO₂ 19.89 Vol %, CO 25.02 Vol %, balance gas hydrogen); HCl-mixture (47.4 ppm hydrogen chloride in hydrogen); H₂S mixture (10.4 ppm hydrogen sulfide in nitrogen), and hydrogen with quality 5.0.

Controlling the gas flows was done by computer-operated flow controllers (Vögtling AG, Aesch, Switzerland). The humidifier was a Bronkhorts HI-Tech (CEM—liquid delivery system with vapor control, W-102A-222-P) purchased from hl-trading, Salzburg, Austria. The temperature of the cell was controlled by an oven from Nabertherm (Type L4, Lilienthal, Germany).

The power was controlled using the electronic load ECL 150 from ElectroChem. Inc., Woburn, Massachusetts.

Experiment

For these experiments a test stand was built with the following main components: gas mixing and humidification part, oven with temperature controlled cell, and the electronic load (Fig. 1). In all experiments with hydrogen chloride and hydrogen sulfide perfluoroalkoxy-Teflon (PFA) tubes were used to prevent adsorption and reaction of these gases. Only the direct supply and exhaust tubes in the oven were made of high grade steel. All tubings following the humidifier were kept at 393 K.

The current connection for the anode was made using a nickel cage, the cathode connection from silver wires. Sealing was done with a ceramic cement.

The working temperatures of the cell were 1123 K and 1173 K, respectively, the heating and cooling rates for the temperature cycles were 10 K/min, the maximum temperature was 1173 K,

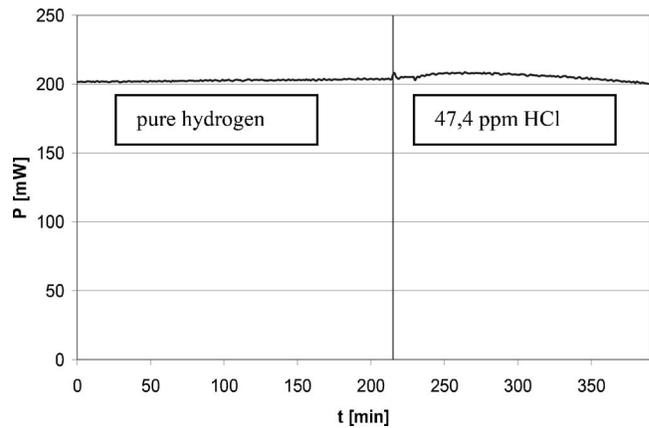


Fig. 2 Typical performance of the SOFC with 100 ml_N/min 47.4 ppm HCl in dry hydrogen at 1173 K

and the minimum temperature was 573 K. Every tested cell was first operated with pure hydrogen as reference before feeding any other gas. The test gas supply was changed without interruption during the operation.

The different concentrations of hydrogen chloride and hydrogen sulfide were made by mixing the HCl and H₂S gas mixtures with pure and dry hydrogen. This was done using the calibrated flow controllers.

The cells were operated with the maximum power densities which normally caused a working voltage of 0.5 V.

Results

Experiments with Hydrogen Chloride. In these experiments the fuel cells operated in the presence of different concentrations of hydrogen chloride in dry hydrogen. Increasing the concentration to 47.4 ppm HCl with a total flow of 100 ml_N/min at 1173 K did not result in any considerable difference compared to pure hydrogen as fuel (Fig. 2).

Following this the influence of different flows with 47.4 ppm hydrogen chloride was tested. Reducing the flow from 100 ml_N/min to 75 ml_N/min resulted in a decrease of the power by about 2.5%. Here, a flow reduction to 50 ml_N/min reduced the cell performance by 5.5% compared to the higher flux. A further decrease of the flow to 25 ml_N/min generated a power loss of 9.5% and to 10 ml_N/min a power loss of 17.5% compared to 100 ml_N/min. These results are closely comparable to the experiments performed with pure hydrogen.

In a next experiment, alternating operation with the acid containing fuel and pure hydrogen with a total flow of 50 ml_N/min at

Table 1 Influence of the alternating operation with HCl containing fuel and dry hydrogen with a total flow of 50 ml_N/min. After every change of the fuel, the cell was operated under constant conditions for 30 min. The operating voltage was 0.5 V.

Test condition						
Temperature (K)	Concentration (ppm HCl)	P_B [mW] test begin	P_E [mW] test end	ΔP_{cum} [mW]	ΔP_{cum} [%]	
1123	47.4	188	181	7	3.7	
1123	0	175	174	14	7.4	
1123	47.4	165	165	23	12.2	
1123	0	162	164	24	12.7	
1173	47.4	212	212	0	0	
1173	0	212	211	1	0.47	
1173	47.4	211	208	4	1.88	
1173	0	208	207	5	2.3	

Table 2 Influence of hydrogen chloride on cooling down and heating up procedures of the cell. The different performances during startup are due to the use of different cells.

Test conditions					
Concentration (ppm HCl)	Cycle	P_B [mW] test begin	P_E [mW] test end	ΔP_{cum} (mW)	ΔP_{cum} (%)
4.74	1. cycle	110	107	3	2.7
4.74	2. cycle	110	100	10	9
4.74	Following performance for 120 min	110	110	0	0
47.4	1. cycle	130	128	2	1.5
47.4	2. cycle	130	130	0	0
47.4	Following performance for 120 min	130	130	0	0

1123 K and 1173 K was tested. The different results are listed in Table 1. One can see that at the lower temperature extremely notable power losses were detectable. But at the higher working temperature the differences in the performance of the cell was much smaller. After every change of the fuel the cell was driven under constant conditions for **30 min**.

In order to analyze if the start and shut down procedures with hydrogen chloride containing fuel have any effect on the cell performance (which would make it necessary to operate the cell in this stage with pure hydrogen), SOFCs were heated up and cooled down between 573 K and 1173 K. This was done under load in the presence of different concentrations of hydrogen chloride. The results are listed in Table 2. There was nearly no influence of the impurity on the cell performance.

Experiments with HCl and H₂S Containing Fuels. At the beginning of these experiments a cell was driven with 50 ml_N/min dry hydrogen for about 23 h at 1123 K. The power output of the cell was 304 mW. After adding 5 ppm hydrogen chloride to the fuel (total flow 50 ml_N/min) the SOFC was operated for two hours under these conditions. Very similar to the above analysis there was no change in the performance. Then the fuel was modified by adding 5 ppm HCl and 0.2 ppm H₂S in hydrogen. Over a period of about 62 h the power output of the cell decreased from 304 mW to 243 mW. After this time the cell passed through an alternating operation with pure hydrogen and

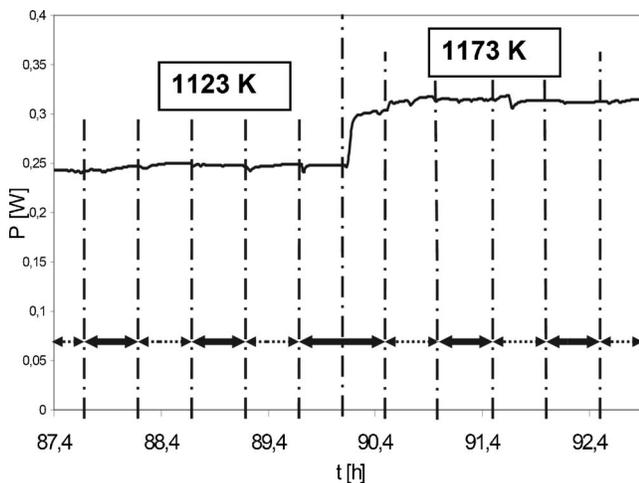


Fig. 3 Alternating operation with pure and dry hydrogen and 0.2 ppm H₂S/5 ppm HCl in dry hydrogen

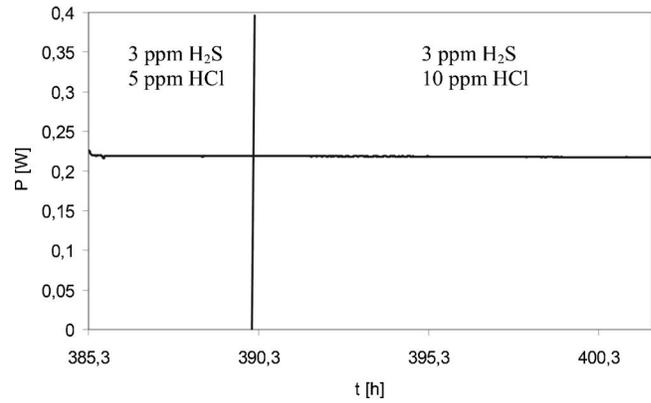


Fig. 4 SOFC performance at 1173 K in the presence of 3 ppm hydrogen sulfide and 5/10 ppm hydrogen chloride in dry hydrogen

the acids containing fuels at 1123 K and 1173 K. As one can see, the fast changes of test conditions did not really affect the cell performance (Fig. 3).

After these experiments at 1173 K the cell was operated with the contaminated hydrogen for about 60 h. In this period the power decreased once more from 310 mW to 300 mW in a few hours but then remained stable at this value.

Similar to the HCl experiments heating up and cooling down experiments between 573 K and 1173 K with about 10 K/min were tested. But in contrast to the HCl results in this case after two cycles the cell performance deteriorated to 254 mW.

The influence of the impurities concentrations was tested with a total flow of 50 ml/min. After feeding 5 ppm HCl and 0.2 ppm H₂S for about 90 h at 1173 K the cell still had a power output of 254 mW. Increasing the hydrogen sulfide concentration to 0.5 ppm resulted in 253 mW after 30 h. After changing the conditions for 51 h to 0.2 ppm H₂S and 10 ppm HCl, the SOFC delivered 250 mW. Reducing the hydrogen chloride concentration to 5 ppm and increasing the hydrogen sulfide content to 1 ppm for 63 h resulted in a power output of 235 mW. Changing the HCl contamination to 10 ppm for 32 h did not nearly have any effect. The same was observed when the sulfide amount was increased to two parts per million. The power dropped to 224 mW after minutes and remained stable at this value for 20 h but after increasing the HCl concentration to 10 ppm no change of the power was detected for a period of 4 h. Raising the concentration of hydrogen sulfide to 3 ppm combined with 5 ppm (for 4 h) and 10 ppm HCl (for 13 h) just had only a very small influence on the power. The cell delivered in both cases 223 mW (Fig. 4). The cell power results obtained for the different concentrations of hydrogen sulfide and hydrogen chloride are given in Table 3.

Table 3 Cell power results obtained for different concentrations of impurities

Temperature (K)	Impurities (ppm)		P_E (mW)	ΔP (mW)	ΔP (%)
	H ₂ S	HCl			
1173	0.2	5	254	0	0
1173	0.5	5	253	1	0.4
1173	0.2	10	250	4	1.6
1173	1	5	235	19	7.5
1173	1	10	233	21	8.3
1173	2	5	224	30	11.8
1173	2	10	224	30	11.8
1173	3	5	223	31	12.2
1173	3	10	223	31	12.2

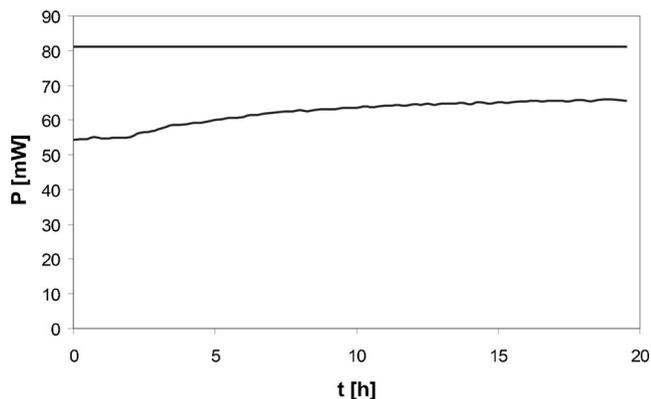


Fig. 5 Cell performance of a cell operated with synthetic wood gas

Operating the SOFC with Synthetic Wood Gas. The results for operating the fuel cells with synthetic wood gas humidified with 35 Vol % water were partly contradictory. In some experiments it was possible to operate the cell for about 20 h at 1123 K and 1173 K (compare Fig. 5), but in other experiments the cell power decreased very fast and stabilized at a only very low level after a few hours. Post-mortem analysis showed in such cases that carbon deposits were visible at the anode. This did not happen in the successful experiments. In Fig. 5 the result of such a successful run at 1123 K is shown. Using 100 ml_N/min of pure hydrogen with a water content of 3 Vol % the cell delivered a power of about 81 mW. After cooling down in hydrogen and heating up again (20 K/min) using the synthetic wood gas (including 35 Vol % water), the cell had a power output of 54 mW at 1123 K which increased within a few hours to 65 mW.

Discussion and Summary

The experiments performed in the presence of hydrogen chloride in otherwise pure hydrogen showed that a stable operation of a SOFC is possible with nearly 50 ppm HCl at least for the investigated time period. Because of that we foresee no major problems concerning HCl if a hot gas cleaning of wood gas is applied.

Combinations of hydrogen sulfide and hydrogen chloride showed that changing the HCl concentration nearly had no affect on the performance, but increasing the H₂S amount in the fuel resulted in some detectable decrease in the power output. However, with all investigated concentration in the as-yet observed periods of time, an operation of the SOFC was possible even when the performance was not as high as with pure hydrogen.

The experiments on operating the fuel cells with synthetic wood gas did as yet not really give clear results. In some experiments it was possible to drive the fuel cell with the gas mixture

but in others the cell performance decreased very fast to a low level. Until now it is not very clear why there had been such differences. It was found that the cells tested showed varied considerably when operated with pure hydrogen. This fact could be responsible for the varying results with wood gas. Here more experiments will be necessary with more reproducible fuel cells.

Outlook

In further experiments the combination of synthetic wood gas with different impurities like tars, hydrogen sulfide, hydrogen chloride, and mercaptans will be tested. They will then lead to operating the SOFC with real wood gas purified in a hot gas cleaning system directly at an operating power plant.

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Nomenclature

SOFC	=	solid oxide fuel cell
HCl	=	hydrogen chloride
H ₂ S	=	hydrogen sulfide
LSM	=	lanthanum strontium manganite
YSZ	=	yttria-stabilized zirconia

References

- [1] McIntosh, S., and Gorte, R. J., 2004, "Direct Hydrocarbon Solid Oxide Fuel Cells," *Chem. Rev. (Washington, D.C.)*, **104**, pp. 4845–4865.
- [2] Kendall, K., Finnerty, C. M., Saunders, G., and Chung, J. T., 2002, "Effects of Dilution on Methane Entering an SOFC Anode," *J. Power Sources*, **106**, pp. 323–327.
- [3] Saunders, G. J., and Kendall, K., 2002, "Reactions of Hydrocarbons in Small Tubular SOFCs," *J. Power Sources*, **106**, 258–263.
- [4] Sridhar, G., Paul, P. J., and Mukunda, H. S., 2001, "Biomass Derived Producer Gas as a Reciprocating Engine Fuel — An Experimental Analysis," *Biomass Bioenergy*, **21**, pp. 61–72.
- [5] Bridgwater, A. V., 1995, "The Technical and Economic Feasibility of Biomass Gasification for Power Generation," *Fuel*, **74**(5), pp. 631–653.
- [6] Cunningham, R. H., Fowles, M., Ormerod, R. M., and Staniforth, J., 2004, "Sulphur Poisoning of the Active Materials used in SOFCs," *Rolls-Royce plc 2004, F/01/00222/REP, URN 04/559*.
- [7] Matsuzaki, Y., and Yasuda, I., 2000, "The Poisoning Effect of Sulfur-Containing Impurity Gas on a SOFC Anode: Part I. Dependence on Temperature, Time, and Impurity Concentration," *Solid State Ionics*, **132**, pp. 261–269.