

Influence of H₂S Impurities at Operation of MSC Cells

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The energetic utilization of biomass as a sustainable primary energy source for power generation is attaining more and more widespread attention. The use of gasified biomass in combination with solid oxide fuel cells (SOFC) promises highly efficient systems for decentralized energy generation. Additionally to the main constituents of the product gas of the gasification process also contaminants such as particulates, tar, H₂S and others appear in the product gas which may have detrimental effects on SOFC performance and durability and should therefore be removed or reduced before entering the SOFC. These contaminants and their interaction particularly with the anode need to be studied and the tolerance levels of the contaminants must be determined. This paper reports results of experimental investigations which were performed with metal supported SOFC cells (MSC) when exposed with H₂S in the concentration range of 4 to 10 ppm over a period of some hundred hours.

INTRODUCTION

The energetic utilization of biomass as a sustainable primary energy source for power generation is attaining more and more attention. Instead of a gas engine also a SOFC system could be connected with a biomass gasifier promising high electrical efficiency and low NO_x emission. Solid oxide fuel cells (SOFC) are very flexible with respect to the fuel to be used including hydrocarbons of different types and sources that must be converted into a mixture of H₂ and CO via external or internal reforming. But the product gas from the gasification process of biomass also contains contaminants such as particulates, tar, H₂S and others as traces which may have detrimental effects on the SOFC performance and durability and should therefore be reduced or removed in a cleaning process before entering the SOFC. It is expected that tar and particulates as well as H₂S and alkali compounds can be cleaned to a level of a few ppm with viable cleaning technologies. In particular, sulfur compounds which are converted readily to H₂S in a hydrogen rich environment at SOFC operating temperature can cause poisoning of fuel electrodes, mainly of the SOFC anode, and thus give rise to enhanced degradation of electrochemical performance. The interactions of the anode materials and the contaminants need to be studied and the tolerance level of the contaminants must be determined. Some studies and investigations on the impact of sulfur compounds on the performance of tubular as well as planar electrolyte and anode supported SOFCs were already reported [1 – 6]. In this paper results of experimental investigations with metal supported cells (MSC) which were fabricated according to the DLR spray concept [7] and exposed with H₂S containing fuel gas is presented.

EXPERIMENTAL

DLR has developed a concept of a planar metal supported SOFC (MSC) based on advanced plasma deposition processes which has been described in detail previously [8]. For the study of VPS cells under exposure of H₂S containing fuel gas small plasma sprayed cells of circular shape with an active area of 12.5 cm² were electrochemically characterized. Cells with an anode consisting of NiO and YSZ (50 μm), a YSZ electrolyte (40 μm) and a LSM cathode (40 μm) were prepared by VPS. During activation of the cell the NiO of the anode was reduced by hydrogen to Ni forming anodes with a porosity of 25 – 30 vol. %. As substrate a porous knitted wire structure (1mm thickness) consisting of CroFer22APU (Rhodius, Germany) was used. For first preliminary short-term experiments a mixture of H₂/N₂ with a content of 5 ppm H₂S was prepared by Air Liquide, Germany. For longer test runs the composition of H₂ with 4 ppm and 10 ppm H₂S, respectively, was mixed in the test rig by the gas supply unit from bottles of pure H₂ and a H₂/H₂S mixture with a content of 100 ppm H₂S. The electric load during the test run was 200 mA/cm² and the operating temperature was 800°C. The cell voltage was monitored during the whole test run and after some characteristic durations also I–V characteristics measurements were performed additionally.

RESULTS AND DISCUSSION

SHORT-TERM RUNS WITH H₂/N₂ FUEL AND H₂S

In order to get first information on the influence of sulfur impurities in the fuel gas on the electrochemical behaviour of MSC cells 4 cells were studied under exposure of H₂/N₂ and 5 ppm H₂S as fuel gas which had been pre-mixed in a bottle by monitoring the cell voltage and the power density under a load of 200 mA/cm². Fig. 1 reveals that immediately after the addition of 5 ppm H₂S to the fuel gas the power density at a load of 200 mA/cm² decreased by approximately 10 – 15 % with all 4 cells and then remained nearly constant for the period of H₂S exposure of about 8 hours. This is in accordance with previously reported experiments [1, 2, 3, 5]. It is supposed that the performance degradation of the anode occurs mainly through the selective adsorption of H₂S on active sites near or on triple phase boundaries. After switching back to operation with H₂/N₂ as fuel gas without H₂S addition the power densities increased again achieving even slightly better performance values than observed before H₂S exposure. In the test run depicted in Fig. 1 the power density decreased from 132 mW/cm² to 113 mW/cm² (- 14.4 %) during operation with H₂/N₂ + H₂S as fuel gas. After switching off the H₂S addition and operating again with H₂/N₂ as fuel gas the power density at a load of 200 mA/cm² increased again to 138 mW/cm². The change in power density of the three other cells was in the same range and amounted to 13.8 %, 12.3 % and 10.6 %, respectively.

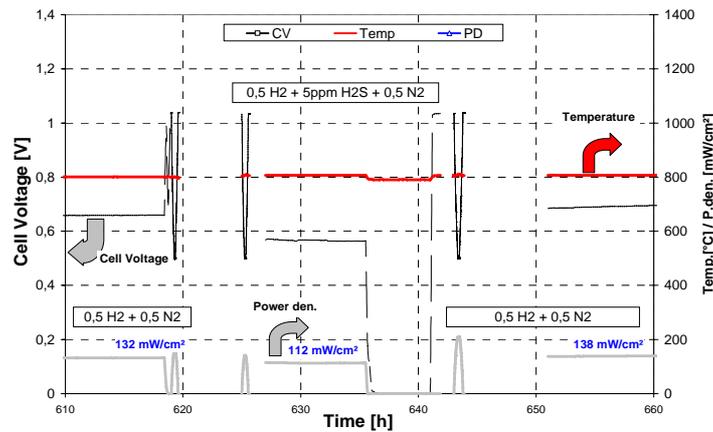


Fig. 1 Cell voltage, power density and temperature as a function of time of a MSC cell operated with H₂/N₂ + 5 ppm H₂S.

Impedance spectra can provide additional information about changes of electrical resistances of the cell during operation. They revealed that the addition of H₂S leads only to a little change of the ohmic resistance whereas the total resistance increases significantly indicating a considerable increase of the polarization resistance. It is concluded that H₂S is adsorbed on active sites of Ni in the anode and partly blocking them. The H₂S concentration of 5 ppm applied and the short-term operation of some hours apparently leads to a reversible behavior when operating again with H₂/N₂ as fuel gas.

LONGER TERM OPERATION UNDER EXPOSURE WITH H₂S IN THE FUEL GAS

The influence of sulfur impurities in the fuel gas on the performance of cells for a longer period of approximately 300 hours was investigated with further test runs of 2 DLR standard cells and varying the sulphur content in the fuel gas. After the activation by using H₂ and air as the operating gases both cells proved similar power densities of 222 mW/cm² and 232 mW/cm² at a voltage of

0.7 V and 800°C. After operation of 250 hours two different concentrations of H₂S of 4 ppm and 10 ppm, respectively, were added to the fuel gas. As already observed with previous investigations the exposure of H₂S on the cells' anode causes an abrupt decrease of the power densities of the cells. The monitored cell voltages and power densities of both cells operated at a load of 200 mA/cm² and 800°C as a function of time is shown in Fig. 2 (H₂ + 4 ppm H₂S) and Fig. 3 (H₂ + 10 ppm H₂S).

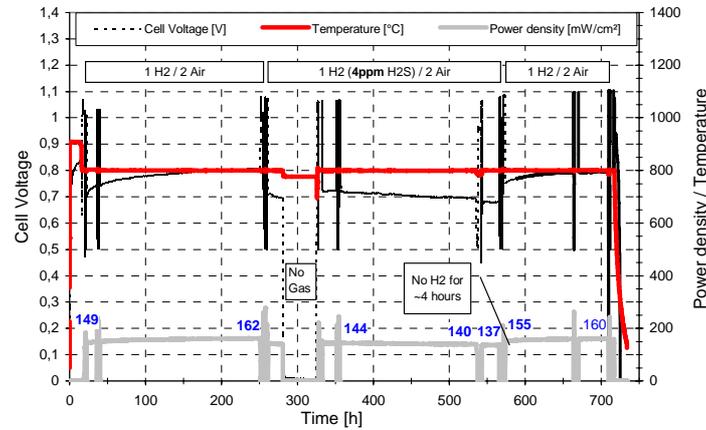


Fig. 2 Cell voltage and power density of a MSC cell operated with H₂ and air at a load of 200 mA/cm² and 800°C as a function of time when exposed with 4 ppm H₂S.

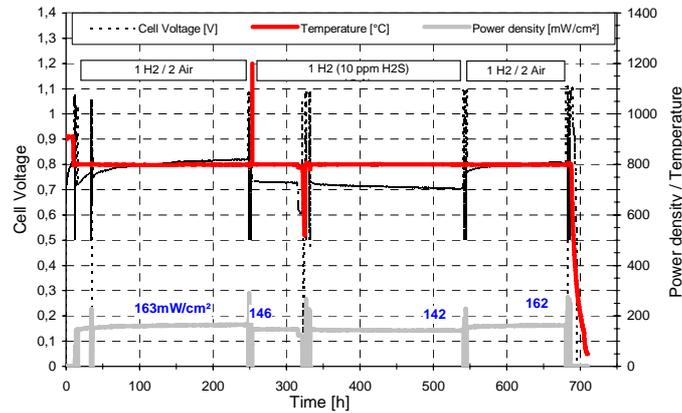


Fig. 3 Cell voltage and power density of a MSC cell operated with H₂ and air at a load of 200 mA/cm² and 800°C as a function of time when exposed with 10 ppm H₂S.

During the activation phase of approximately 250 hours the power densities increased continuously due to the activation of the electrodes until a constant power density of 162 mW/cm² and 163 mW/cm², respectively, was reached at a load of 200 mA/cm². By adding H₂S to the fuel gas after 250 hours of operation the power densities decreased immediately to 144 mW/cm² (H₂ + 4 ppm H₂S) and 146 mW/cm² (H₂ + 10 ppm H₂S), respectively, corresponding to a loss of power density of 11 % and 10.5 %, respectively. A dependence of the decrease of power density on

the H₂S concentration could not be observed. During the exposure of the cells with H₂S for the next 300 hours the power densities decreased slightly from 149 mW/cm² to 137 mW/cm² (H₂ + 4 ppm H₂S) and from 146 mW/cm² to 142 mW/cm² (H₂ + 10 ppm H₂S). The open circuit voltage which is an indication for the gas tightness of the cells remained stable during the whole test period between 1067 mV and 1080 mV (H₂ + 4 ppm H₂S) and between 1082 mV and 1092 mV (H₂ + 10 ppm H₂S) proving gas tight cells without any leakage for the whole test run. After certain intervals which can be noticed in the diagrams (Figs. 2 and 3) I-V curves were measured over a wide range. The power densities determined in this way at a voltage of 0.7 V showed a significantly higher loss in power density for both H₂S concentrations in the range of 27 – 28 % immediately after H₂S exposure and a further decrease during the period of H₂S exposure of another 17 %. This degradation behavior of both cells indicates enhanced degradation under the influence of H₂S exposure and operation at high current density. After termination of the addition of H₂S to the fuel gas both cells were operated for 150 more hours with H₂ and air. As can be seen in the figures the cells recovered and the power densities measured before the H₂S addition were reached again. Also the I-V characteristics reflect this reversible cell behavior. It is concluded that within the range of H₂S concentration considered between 4 and 10 ppm only adsorption of H₂S on anode sites occurs but no chemical reaction between sulfur and nickel takes place as it has been detected at higher H₂S concentration levels.

CONCLUSION

The influence of sulfur impurities which might be present in the product gas of a biomass gasifier after a cleaning process was investigated experimentally by exposing MSC cells with fuel gas containing H₂S in the concentration range of 4 to 10 ppm. Under these conditions an abrupt decrease of the chemical performance of the cells by approximately 10 – 14 % when operated at a load of 200 mA/cm² and by up to more than 25 % at high current densities was observed immediately after H₂S exposure. After stopping the H₂S addition and operation with pure H₂ as fuel gas the cells totally recovered proving a completely reversible behavior of the cells. This behavior can be explained by an adsorption of sulfur on the active nickel centers of the anode and partly blocking these sites. At a concentration of 4 – 10 ppm H₂S a dependence of the loss of performance on the H₂S concentration could not be found.

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