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New Methodology of Studying H₂S Poisoning Effects on SOFC's Fueled by Carbon Containing Fuels like Biogas

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Solid oxide fuel cells are an option to convert carbon containing fuels like natural gas or biogas into electricity with high efficiency. Natural gas consists mainly of CH₄ and is based on fossil fuels nowadays but can be based on renewable sources in the future. Biogas is a renewable source and consists of 40%-70% CH₄ and 30%-60% CO₂. One advantage of the SOFC is that direct internal reforming of these fuels is possible. Impurities like sulfur components, which are present in both fuels, can have negative effects on the internal reforming of the fuel in the SOFC and the electrochemical reaction. These effects have been widely investigated. The current study presents a new, time efficient approach to investigate sulfur poisoning. It is possible to predict the effect of H₂S expressed as the well-known voltage drop occurring due to sulfur exposure via the evaluation of iV-curves taken with and without sulfur.

Introduction

Electricity production is moving towards using entirely renewable energy sources. Due to the fluctuating nature of these sources, technologies are needed that produce electricity and heat with high efficiency using stable sources, which are independent on solar and wind. Such sources can be carbon containing fuels like for example natural gas and biogas. Natural gas consists mainly of CH₄ and is based on fossil fuels at the moment. But it might be obtained based on renewable sources in the future, for example through electrolysis using electricity from wind or solar (e-gas). Biogas consists mainly of: 40%-70% CH₄ and 30%-60% CO₂ and is derived from biomass (1), which is a renewable source. The electricity production from biomass was 62500 GWh in the European Union in 2016, which was an increase by around 2% from 2015 to 2016 (2). According to H. Chum et al. (3) the energy produced from biomass could lie between 100 and 300 EJ by 2050 worldwide.

In commercial biogas power plants biogas is burned off with rather low electric efficient combustion engines. For some biogas compositions, for example from landfill sources, the heating value is even too low to be compatible with combustion engines. Due to their fuel flexibility, solid oxide fuel cells (SOFC) are able to convert this fuel with low heating value into electricity with efficiencies over 50%.

In order to avoid the thermodynamically preferred carbon formation, methane needs to be converted to H₂ and CO using a reforming agent like steam, CO₂ or O₂. State-of-

the-art SOFC anodes contain nickel, which catalysis this reaction at the typical operating temperatures of 700 - 850 °C. The following reforming reactions, which normally occur, where considered in this study (4):

Dry reforming:

Steam reforming:

Water-gas shift reaction:

The dry reforming (eq.: [1]), which occurs with CO₂ is especially interesting for biogas, as it already contains significant amounts of this reforming agent.

All these catalytic reactions can be affected by impurities in the natural gas and biogas. Among various species, sulfur compounds have attracted special attention because they are known poisons (table 8.5 in ref. (5)). In addition to the catalytic reactions (reforming, water gas shift) of natural gas and biogas, sulfur has a poisoning effect on the electrochemical reaction in a SOFC (6) (7) (8) (9) (10). The poisoning effect of sulfur is believed to occur via chemisorption (eq.: [4]) of sulfur (S) at the nickel surface of the SOFC anode, thus blocking active sites for the reforming and the electrochemical reactions (11) (12).

Sulfur poisoning studies in SOFCs are typically carried out by starting the SOFC operation in a certain fuel composition followed by addition of H₂S with different concentrations over different time periods until a steady state cell voltage is reached, often followed by a removal of H₂S from the fuel to observe the recovery. The general observations include an initial drop of the cell voltage after introducing sulfur in the feed of the fuel stream (6) (11). This immediate loss of performance is reversible to a certain degree and the magnitude is a function of operating parameters such as temperature, fuel composition and applied current density. When comparing hydrogen and hydrocarbon fuels, the poisoning effect is larger for the latter, i.e. the reforming process is more sensitive to sulfur poisoning than the electrochemical reaction (6) (10) (13) (14). With increasing sulfur amount the reforming reaction is more and more poisoned and the voltage drop increased. These effects behave in an approximately exponential way and are reversible under conditions of a short term (24 h) exposure to sulfur and H₂S concentrations in the ppm range below ca. 50 in methane containing fuel and below ca. 100 ppm in hydrogen fuel (8) (14) (15).

Such an approach is very time consuming and has to be repeated for all potential operating conditions such as current density, temperature and fuel composition. It also bears the risk of gradual degradation of the cell and might require several tests of fresh cells necessary to obtain the correct correlation of p(H₂S) to cell voltage drop. The current study is aimed at investigating the effects of sulfur on the SOFC performance using a new approach. Based on results obtained following conventional studies, the

sulfur poisoning effect is evaluated in terms of iV-curves – a standard SOFC characterization tool, while varying the fuel composition. The target parameter for correlation is the well-known cell voltage drop.

Experimental

Cell and Test Setup

An anode supported planar Ni-ScYSZ/ScYSZ/LSCF:CGO cell with a CGO barrier layer was used. The cell had a total size of 5x5 cm² with an active area of 16 cm². The cell was placed in an alumina test house, sandwiched between gas distribution plates (see figure 1). A nickel plate (anode side) and gold stripes (cathode side) were used for current collection. Platinum voltage probes were connected. On the anode side a Ni-mesh was placed between the nickel plate and the anode side of the cell to ensure the gas supply and a good contact. The Ni-mesh was framed by a gold sealing. The equivalent mesh on the cathode side was a gold-mesh without a sealing. Further details about the test set up are given in reference (16).

Figure 1. Sketch of the cell test house.

Test Procedure

Start-Up Procedure. The cell was heated to 850 °C fueled with argon to the anode side and air to the cathode side. After 850 °C was reached, argon was changed to 9% H₂ in N₂ for 2h to reduce the nickel oxide to nickel in the anode. Afterwards, the anode gas was changed to pure hydrogen and a standard electrochemical characterization of the performance of the cell ('fingerprint') was done at open circuit voltage (OCV), at 750 °C, 800 °C, and 850 °C. The 'fingerprint' contained iV-curves and electrochemical impedance spectra (EIS) in hydrogen with up to 20% humidification. This procedure was repeated after the sulfur poisoning studies.

Sulfur Poisoning Tests. Four different anode gas compositions were used (see table 1). The first two tests differed in the degree of humidification of hydrogen and total flow rate, whereas the last two cases included methane and pre-mixed biogas (60% CH₄, 40% CO₂) in the feed. To avoid carbon deposition, a biogas to steam ratio of 0.6 was chosen based

on thermodynamic calculations. The cathode gas supply was fixed to 140 l/h air during all tests. The experimental procedure is shown in figure 2. Three to four different sulfur concentrations were applied from a bottle containing 200 ppm H₂S in H₂. The sulfur was added to the fuel stream by substituting the corresponding H₂ flow by the 200 ppm H₂S in H₂ until a steady state of the OCV was reached (between 5 and 12 h). For each sulfur concentration, an EIS was recorded initially, followed by iV-curves. The data were analyzed with programs written in Python and for the impedance data the software RAVDAV (17) was used.

Figure 2. Experimental procedure of the short term sulfur poisoning tests at 850 °C (for gas composition see table 1).

TABLE I. Gas composition, total flow and applied sulfur concentration of the short term poisoning tests.

Test	Gas Composition	Total Flow [l/h]	H ₂ S Amount [ppm]
a) H ₂ -test (high flow)	82 vol% H ₂ , 18 vol% H ₂ O	24	0, 2, 10, 20
b) H ₂ -test	47 vol% H ₂ , 53 vol% H ₂ O	10	0, 2, 10, 20, 90
c) CH ₄ -test	29 vol% CH ₄ , 13 vol% H ₂ , 58 vol% H ₂ O	10	0, 2, 10, 20
d) Biogas-test	50 vol% biogas (60 vol% CH ₄ , 40 vol% CO ₂), 10 vol% H ₂ , 40 vol% H ₂ O	10	0, 2, 10, 20

For validation of the iV analysis approach, a long-term test was done with pre-mixed biogas at a current density of 0.5 A/cm². After ca. 25 h, a sulfur concentration of 2 ppm was applied for the next ca. 220 h. Then the H₂S supply was removed from the fuel stream. EIS measurements were done every 12 h under current.

Results and Discussion

Sulfur Poisoning iV-Curves

In figure 3 iV-curves are shown as a function of sulfur concentration. In the tests shown in figure 3a) and b) hydrogen and steam were used as fuel. At OCV, this gas composition (hydrogen/steam) is not affected by the presence of sulfur, because no catalytic reactions occur. This results therefore in the same OCV at all sulfur concentrations, as expected. In tests shown in figure 3c) and d), methane containing fuel

was used. In the presence of steam and CO₂, methane reforming reaction (reactions 1-3) occur at OCV, which are purely catalytic reactions as long as no current is applied. Sulfur is affecting these catalytic reactions and therefore the gas composition in the SOFC anode. This is reflected in a change of the OCV (according to the Nernst relation). Specifically, the OCV decreased as the sulfur concentration was increased. This illustrates a smaller methane conversion and thus a smaller share of H₂ and CO in the fuel as compared to the sulfur free, not poisoned case.

Evaluating the iv-trends, the slope increased and the maximum current density decreased with increasing sulfur concentration in all four tests, also the ones with hydrogen/steam and no methane. This proves that the electrochemical reactions are poisoned by sulfur.

Evaluating the tests with hydrogen, the slopes of the iV-curves increase most when adding 2 ppm H₂S (circle and cross curves in figure 3a), while they do not change as significantly when the H₂S concentration was increased further (figure 3a), i.e. the poisoning effect is levelling off. This indicates that the largest poisoning effect occurs already at smaller H₂S concentrations. This trend is in line with the results of conventional poisoning tests in hydrogen, even though they were performed with cells of different anode and cathode compositions and at constant current density (6).

Figure 3. Linear interpolated iV-curves with various sulfur concentrations (0ppm-90ppm) fueled with a) H₂, (high flow), b) H₂ (low flow), c) CH₄ and d) pre-mixed biogas at 850 °C and 140 l/h air on the cathode side. Further specifications are given in table 1.

In tests shown in figure 3b)-d), with the same anode flow rates of 10 l/h also significant diffusion losses were observed at high current densities. When comparing the test in figure 3a) conducted with an anode flow rate of 24 l/h and figure 3b) with only hydrogen/steam fuel, this observation is related to the hydrogen content. The small share of hydrogen initially present in the fuel in test figure 3b) and the lower anode fuel flow rate leads to a faster fuel starvation already in the absence of H_2S . In tests figure 3c) and d) the starvation is in addition related to the poisoning of the reforming reaction, which leads to smaller in-situ formed hydrogen with increasing degree of poisoning.

The obtained results of the iV-curves were further evaluated in terms of the more common approach of estimating the immediate voltage drops (ΔU) and ASR increase as consequence of the addition of sulfur. This was achieved by subtracting iV-curves under H_2S from the one without H_2S in the fuel. The results are shown in figure 4 as a function of the current density. The data were taken from the measured iV-curves (see figure 3) after linear interpolation as a first approximation.

Using hydrogen/steam fuel in the regime where no fuel starvation occurs (linear range in figure 3a, b), the resulting cell voltage drop (delta voltage) are superimposed, i.e. the poisoning effect is the same (line a) and b) in fig. 4). These results indicate that the total flow rate in the range between 24 l/h (test a)) and 10 l/h (test b)) has no influence on the degree of H_2S poisoning because the ratio of $p(\text{H}_2\text{S})$ and $p(\text{H}_2)$ is the determining parameter and not the flow rate. As soon as the regime of fuel starvation is reached, the poisoning effect becomes more significant, not only affecting the anode reaction but also diffusion.

The voltage drops of test c) and d) increased with increasing current density, which points to a critical effect of fuel starvation with progressing poisoning of the reforming reaction caused by the low flow rate of hydrogen and CO. The voltage drop increased more in test d) than in test c). The reason for this could be the lower hydrogen amount (10% vs. 13%, respectively) and the larger share of CO_2 in the initial fuel stream of test d). For the tests with CH_4 and biogas (test c) and d)), two poisoning regimes can be distinguished as function of current density, one at low current density (more flat slope) and one at high current density (steep slope). The poisoning regime at lower current densities (more flat slope) is observed in the H_2 fuel as well (test a) and b)).

These two regions become even more apparent when calculating the increase of ASR due to H_2S addition (18). In figure 5 the immediate ASR value increases as a function of the current density are shown using the results obtained in this study. The curves were derived by taking the gradient of the immediate voltage drop curves shown in figure 4 and applying a Savitzky-Golay filter for smoothing the data.

There has been a discussion of the effect of current on the sulfur poisoning, with arguments in favor of current (12) (19) (20) (21) (22) (23) (24) and against an effect (25) (26). Interestingly, when looking at the region where the iV-curves are linear (compare to figure 3c) and d)), there is basically no change of the immediate ASR increase as function of current density. In figure 5 the curves a) and b) show no change of the ASR up to current density of ca. 0.5 A/cm^2 and curve c) up to ca 0.2 A/cm^2 . On the other hand, the ASR values increase steeply at higher current density (see figure 5). Hagen et al. (18) found that current has no effect on the increase of ASR due to H_2S poisoning in the low-

current region, where the poisoning effect is mainly due to poisoning of the anode polarization. However, at higher current density, where fuel starvation due to the poisoning of the reforming reaction occurs more severely, there is an increase of ASR with increasing current density. The results in this study, which were obtained through a different approach, completely support these findings.

Figure 4. Immediate voltage drops for 2 ppm H₂S in relation to 0 ppm H₂S as a function of the current density in fuels a) to d). The curves were derived from the interpolated iV-curves shown in figure 3.

Figure 5. Area specific resistance (ASR) increase for 2 ppm H₂S in relation to 0 ppm H₂S as a function of the current density in fuels a) to d). Curves were derived by taking the gradient of the immediate voltage drop curves shown in figure 4. Furthermore a Savitzky-Golay filter was applied for smoothing the data.

Comparative Test to Validate the H₂S iV-Curve Approach

The current study suggests that it is possible to determine cell voltage drops and increase of ASR due to H₂S poisoning by analyzing iV-curves (figure 4, 5), which is significantly faster than the conventional approach that measures under steady state conditions – as long as reversible changes occur.

In order to validate the results and compare to values obtained with the traditional poisoning tests, a test with pre-mixed biogas as fuel was carried out with a constant current density of 0.5 A/cm². Figure 6 shows the cell voltage and the serial resistance (R_s) and polarization resistance (R_p) which were determined from EIS spectra over time. In the absence of sulfur, the cell voltage was 871 mV and thus close to the expected value of 868 mV from the iV-curve (see figure 3d)). After addition of 2ppm H₂S the cell voltage dropped (for values see table 2) by 61.9 mV. This value is very close to the one calculated from the iV-curves; the relative error is only 2.2% (see table 2, figure 4). This confirms the validity of the cell voltage drop values obtained with the faster iV-curve approach.

Figure 6. Steady state test with pre-mixed biogas at 0.5 A/cm², 850 °C. Cell voltage (circle, left-axis) and serial resistance R_s (cross, right-axis), polarization resistance R_p (square, right-axis) before and after addition of 2 ppm H₂S.

TABLE II. Expected (see fig. 4) and measured (after 61 hours of test, figure 6) cell voltage drop after addition of 2 ppm H₂S to pre-mixed biogas fuel at 850 °C and 0.5 A/cm².

Expected Voltage Drop [mV]	Measured Voltage Drop [mV]	Relative Error [%]
60.9	61.9	2.2

The R_p and R_s values for the EIS recorded over time as presented in figure 6 show that R_p is increasing (and decreasing) when H₂S is added (or removed) from the fuel, while R_s remains constant. This is a clear indication of a reversible poisoning effect. In figure 7, selected EIS spectra are shown. They confirm that the serial resistance remained constant. The R_p increased and two main contributions to this increase can be clearly identified (see figure 7 bottom). There is an increase of impedance at lower (4 Hz, diffusion) and higher (800 Hz, anode reaction) frequencies. The result confirms the expectations from the iV-curves in figure 3d), where a current density of 0.5 A/cm² is

located in a regime where the anode reaction is poisoned and also fuel starvation (increased diffusion impedance) due to the degree of poisoning starts to occur.

Figure 7. Nyquist (top) and differences (bottom) plot (bode plot) of the pre-mixed biogas before and after addition of 2 ppm H_2S sulfur in pre-mixed biogas, 850 °C, 0.5 A/cm².

Conclusion

A new approach of testing SOFC in regard to sulfur poisoning was introduced. This approach is significantly less time consuming as compared to the traditional steady state approach of starting SOFC operation, adding of a certain H_2S concentration, observing a steady state response, removing the H_2S and awaiting recovery, followed by the H_2S addition of the next concentration and later on other variations of operating parameters such as current density. In this study it was demonstrated that a fast approach is to compare iV-curves recorded at a certain H_2S concentration in the fuel with sulfur free conditions. The comparison of the iV-curves with and without sulfur allows for the calculation of the well-known voltage drop due to H_2S poisoning. The values are in the same range as obtained by the traditional steady state approach.

The magnitudes of the voltage drops were seen to change with current density. In addition to a general increase of the voltage drop with increasing current density, also the differentiation between two major poisoning regimes, one at low and one at higher current densities was possible. These regimes are related to the poisoning of the anode reaction and the increase of fuel starvation, respectively.

Apart from evaluating the cell voltage drop as parameter for the degree of H₂S poisoning, also the increase of ASR was evaluated based on the iV-curves. It was shown that the ASR increase due to H₂S poisoning is independent on the current density as long as there is no severe fuel starvation. In the operating regime of severe fuel starvation, the ASR increase grows with increasing current density.

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