



HAL
open science

The Effect of H₂S on the Performance of SOFCs using Methane Containing Fuel

Jens F.B. Rasmussen, Anke Hagen

► **To cite this version:**

Jens F.B. Rasmussen, Anke Hagen. The Effect of H₂S on the Performance of SOFCs using Methane Containing Fuel. Fuel Cells, 2010, 10 (6), pp.1135. 10.1002/fuce.201000012 . hal-00576976

HAL Id: hal-00576976

<https://hal.science/hal-00576976>

Submitted on 16 Mar 2011

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



The Effect of H₂S on the Performance of SOFCs using Methane Containing Fuel

Journal:	<i>Fuel Cells</i>
Manuscript ID:	face.201000012.R1
Wiley - Manuscript type:	Original Research Paper
Date Submitted by the Author:	07-Jul-2010
Complete List of Authors:	Rasmussen, Jens Hagen, Anke; Risø National Laboratory DTU, Fuel Cells and Solid State Chemistry Division
Keywords:	SOFC, hydrogen , sulfide, Methane , Reforming, poisoning



view

The Effect of H₂S on the Performance of SOFCs using Methane Containing Fuel

J. F. B. Rasmussen¹, A. Hagen^{1,*}

¹Risø DTU, Fuel Cells and Solid State Chemistry Division, Frederiksborgevej 399, 4000 Roskilde, Denmark

[*] Corresponding author: anke@risoe.dtu.dk, phone: +45 4677 5884, fax: +45 4677 5858

Abstract

In recent years the interest for using biogas derived from biomass as fuel in solid oxide fuel cells (SOFCs) has increased. To maximize the biogas to electrical energy output it is important to study the effects of the main biogas components (CH₄ and CO₂), minor ones and traces (e.g. H₂S) on performance and durability of the SOFC. Single anode-supported SOFCs with Ni-YSZ anodes, YSZ electrolytes and LSM-YSZ cathodes have been tested with a CH₄-H₂O-H₂ fuel mixture at OCV and 1 Acm⁻² current load (850°C). The cell performance was monitored with electric measurements and impedance spectroscopy. At OCV 2-24 ppm H₂S were added to the fuel in 24 h intervals. The reforming activity of the Ni-containing anode decreased rapidly when H₂S was added to the fuel. This ultimately resulted in a lower production of fuel (H₂ and CO) from CH₄. Applying 1 Acm⁻² current load, a maximum concentration of 7 ppm H₂S was acceptable for a 24 h period.

Keywords

hydrogen sulfide, methane reforming, poisoning, SOFC.

1 Introduction

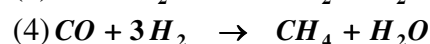
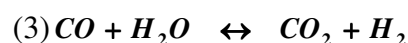
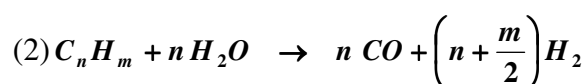
Technological solid oxide fuel cells (SOFCs) have been demonstrated to operate very well when running on H₂, synthesis gas or CH₄-containing fuels for long operation times (e.g., [1]). It has thus become interesting to study the applicability of alternative fuel sources, like biogas derived from biomass. Biogas produced by anaerobic digestion of biomass mainly consists of CH₄ and CO₂, but also small amounts of impurities, such as for example H₂S (>30 ppm), halogens, and siloxanes. At the high operational temperature of SOFCs (700-900°C) and the presence of Ni-catalyst electrodes, the main components CH₄, CO₂ and H₂O are converted to H₂ and CO (Reaction (1)).



As both H₂ and CO are fuels to the SOFC the use of biogas in SOFCs seems very attractive. However, the effect of the fuel on performance and durability has to be studied; specifically the main constituents methane vs. hydrogen and impurities such as H₂S.

CH₄-containing fuels in Ni-YSZ anode based SOFCs have been investigated using oxygen-species O₂, H₂O and/or CO₂, to convert CH₄ with the Ni in the anode acting as catalyst [2-8]. A critical issue in these studies has been the conversion of CH₄ on the anode's Ni particles without producing coke, as coke lowers the performance of an SOFC. The coke formation can be controlled by different factors, for example the operational temperature and the O:C ratio. A large part of the studies has thus included varying the operational temperature and the O:C ratio to find out how these parameters affect SOFC performance. Typically, increasing the oxygen-species concentration decreases the coke formation, but leads to a decrease in the SOFC efficiency as the oxygen-species dilute the fuel. Furthermore, the Ni particles risk being oxidised at high oxygen-species concentrations in the fuel [9]. It is thus necessary to optimize the fuel component concentrations and the operational temperature to optimize the SOFC performance.

Special attention has been given to the steam reforming of methane, in particular due to the close relations between the typical nickel containing steam reforming catalyst and the nickel containing SOFC anode. In the steam reforming of CH₄, three main reactions occur, i.e. the steam reforming reaction (Reaction (2)), the water gas shift reaction (Reaction (3)) and the methanation reaction (Reaction (4)):



Having a steam to carbon ratio of 2 at typical SOFC operational temperature (~800°C) is considered to prevent coke formation [10].

Impurities like H₂S in the fuel are critical. From catalysis it is also known that sulphur poisons the reforming activity of Ni-based catalysts and the underlying mechanism is fairly well understood [11]. The natural gas (methane) is usually desulphurized prior to the reforming process in order to prevent the reforming catalyst from being poisoned. Also in the SOFC, H₂S naturally affects the reforming, as a nickel containing anode is used, and the electrochemical activity as well [10].

Several research groups have experimentally studied the effect of having S-compounds in an H₂-containing fuel on the performance and the durability of an SOFC [12-14], but also the effect of S-compounds in CH₄-containing fuels [15, 16] has been studied. It was shown that H₂S had a significant effect on the reforming activity, which in this way also affected the power output of the SOFCs. It has to be noted that the studies were performed in fuel with very low methane concentrations ([15]: catalytic partial oxidation (CPO) gas with 1.5 vol% CH₄, [16]: natural gas reformate) and that the direct use of biogas poses a larger challenge due to the high concentrations. It was also concluded that the Ni-sites active for reforming were different from the sites active for the electrochemical reaction [15]. Summarizing, when using biogas as fuel in an SOFC, two effects of H₂S have to be considered: Poisoning of the reforming and of electrochemical activity and the interplay between these.

In a former study [13], the effect of H₂S on the electrochemical activity (performance) of a SOFC using an H₂-H₂O gas mixture was evaluated. In the current study CH₄ was included in the fuel and thus the aspect of poisoning of reforming activity introduced. Varying concentrations of H₂S were added at intervals. Electrical measurements and impedance spectroscopy were used to monitor the effect of S-poisoning on the cell voltage and the internal resistance of the SOFCs. Mass spectrometry was used to monitor the steam reforming activity of CH₄ as a function of the H₂S concentration. This gave the possibility to study the effect of H₂S on both the electrochemistry and the reforming activity.

2 Experimental

2.1 Cells and Initial Electrochemical Characterization

The used planar SOFCs were produced at the pre-pilot facility located *Risø DTU* and had a Ni/Yttria-Stabilized-Zirconia (Ni/YSZ) anode support and an active Ni/YSZ anode, a YSZ electrolyte, and a Lanthanum-Strontium-Manganate (LSM)/YSZ cathode [17]. The active area was 4 x 4 cm² (total area of 5 x 5 cm²). In the testing setup the cells were placed between Ni containing anode and LSM containing cathode gas distribution layers, and secondly, between current collector foils, i.e. a Ni foil on the anode side and an Au foil on the cathode side. The setup was sealed using glass/ceramic-composite bars. A more detailed description of the setup can be found in [18].

The tests were started by sealing and reducing the cells at 1000 °C followed by an initial electrochemical characterisation (fingerprint) at 850, 800 and 750 °C to verify that the cell performances were as expected. The fingerprint measurements comprised of iV-curves and impedance spectra in 96% H₂ + 4% H₂O and 80% H₂ + 20% H₂O fuel composition. In the impedance measurements an oscillating current of approximately 60 mA was applied over the frequency range 0.08 Hz to 82 kHz with a *Solartron* impedance analyser.

2.2 Cell Testing

In Figure 1 the setup for single cell testing in different fuels is illustrated. The fuel gases (H₂, CH₄ and O₂) were supplied through mass flow controllers. Firstly, the H₂ and O₂ ($p_{\text{H}_2} > p_{\text{O}_2}$) were mixed, this way forming an H₂/H₂O gas mixture. Additionally, the H₂ could be moisturized in a water bottle (~ 4% H₂O) before mixing with O₂. H₂S from a pressurised H₂S/H₂-bottle containing 218 ppm H₂S was mixed with the CH₄. The thus obtained two mixtures were combined and led into the cell test house. The total fuel flow at the cell inlet was kept constant at 10 lh⁻¹. Air was used on the cathode side (140 lh⁻¹).

Two different test series were carried out. The aim of the first test series was to measure the effect of H₂S on the reforming activity in the anode. An SOFC was run at OCV with a quadrupole mass spectrometer (QMS) attached to the fuel inlet and outlet tubes. This way the changes in gas composition as a function of the H₂S concentration were monitored. In this test series the H₂S was added in steps for periods of 25-75 h (illustrated in A on the right-hand side of Figure 1).

The second series of tests involved measuring the effect of H₂S on the performance of the SOFCs. Three SOFCs were run under current load. Illustration B on the right-hand side of Figure 1 shows how H₂S was added with increasing concentrations for 24 h intervals.

Figure 1

The test setup included temperature, current and voltage probes. Furthermore, pO_2 probes were placed in the fuel inlet and outlet tubes to measure the oxygen partial pressure by measuring voltages (pO_{2-in} voltage and pO_{2-out} voltage, respectively). The pO_2 probes were made of single ended zirconia based tubes, and were supplied with a constant flow of air on the inside. Two Pt wires (one on the inside and one on the outside of the tube) measure the potential difference across the tube wall. By using the Nernst equation the partial pressure of oxygen on the outside (the fuel inlet or outlet) was calculated. A third Pt/Rh wire was welded together with the inside Pt wire, and was used to measure the inlet and outlet fuel temperature. The SOFC performance was evaluated by measuring the cell voltage, the in-plane voltage in anode and cathode (Figure 1) as well as by impedance spectroscopy (see also [13]).

2.3 Mass Spectrometry

An OmniStar™ GSD 301 01 quadrupole mass spectrometer (QMS) from Pfeiffer Vacuum was used. It was equipped with an approximately 1 m long stainless steel capillary ($\phi 0.12$ mm). The capillary was heated by a heating tape and was connected to the cell house fuel tubes via a ~30 cm long stainless steel tube with $\phi 5$ mm. Both transfer lines between the cell testing setup and the QMS were heated (> 100 °C).

3 Results and Discussion

3.1 Steam Reforming Activity of the Ni-YSZ Anode

The first test series was carried out to study the effect of H_2S on the catalytic activity of the Ni/YSZ-anode in an SOFC for the steam reforming. The measurements were carried out at 850°C with a fuel composition of 13% H_2 , 29% CH_4 and 58% H_2O . The total fuel flow was 10 $l\ h^{-1}$. The measured OCV under these S-free conditions was 984 mV, the pO_{2-in} voltage 850 mV and the pO_{2-out} voltage 980 mV. These three voltage values can be directly translated to fuel compositions and were used to evaluate the tightness of the testing setup and the reforming activity.

The theoretical cell voltage (Emf) for the SOFC for the present gas mixture was calculated to be ~995 mV. We consider an SOFC to have a gas tight electrolyte and to be sealed sufficiently gas tight from the surroundings if the voltage values do not differ from the Emf by more than approximately 10-15 mV. This demand was fulfilled with the obtained pO_{2-out} of 980 mV. We can thus conclude the setup to be sufficiently tight and the influence of leaking gases on the fuel composition and thus mass spectrometry analysis to be negligible.

The OCV and pO_{2-out} values of 984 and 980 mV, respectively, correspond to the equilibrium gas mixture, when steam reforming has occurred (Emf : 995 mV). The pO_{2-in} at the fuel inlet was smaller, which means that the hydrogen concentration in the fuel before entering the SOFC was lower than under the equilibrium conditions, i.e. the reforming reaction had not taken place before the fuel had contacted the SOFC anode. This finding was expected as it is known that reforming does not proceed spontaneously but needs a catalyst. The cell voltage (OCV) and the pO_{2-out} on the other hand were the same and corresponded to the equilibrium gas composition of the reformed fuel. Therefore, reforming happened quite fast after the first contact of the methane containing fuel with the SOFC anode (in absence of H_2S).

To monitor the effect of H_2S on the steam reforming activity in the anode, the H_2S was added in steps of increasing concentration from 2 ppm to 24 ppm. After adding the H_2S to the fuel, the cell voltage initially dropped fast and then an almost constant cell voltage about 25-75 h after adding the H_2S was reached. At each of these constant periods iV-curves were measured. The cell voltage development is shown in Figure 2. The measured cell voltages at each step were: 984 mV (0 ppm), 949 mV (2 ppm), 921 mV (4 ppm), 910 mV (7 ppm), 902 mV (9 ppm), 885 mV (20 ppm) and 882 mV (24 ppm) (see also Figure 2). As the H_2S was turned off, the cell voltage returned to a similar level as before adding the H_2S .

Figure 2

As the fuel composition was only changed to a small extent (ppm amounts of H_2S were added), this drop of the cell voltage cannot be related to the H_2S concentrations in the fuel but indicates a significantly changed fuel composition regarding the other components, i.e. the steam reforming reaction was affected and the fuel composition gradually changed towards the initial fuel inlet composition (850 mV, pO_{2-in}) when increasing the H_2S concentrations. The drop in OCV was thus a direct effect of S chemisorbed on the active sites for the methane reforming.

Simultaneously to the voltage measurements under addition of H₂S, also the gas composition was measured at the fuel outlet using mass spectrometry. In steam reforming, the main reactions (2)-(4) proceed, i.e. an increased amount of CO and CO₂ in the fuel can be directly related to the converted CH₄.

At the times of constant cell voltage during addition of H₂S, the fuel gas composition was analysed using the QMS. In Figure 3 the relative ratios of the measured CO, CO₂ and CO+CO₂ intensities (reaction products, see Equation (2)-(3)) to the CH₄ intensity (reactant, see Equation (1)) are shown. To avoid having to correct for small pressure differences (and thus differences in absolute intensities) between the single QMS measurements, only ratios of the intensities have been considered. The ratios between product/reactant decreased first rapidly when between 0 ppm and 4 ppm H₂S were added. At 4 ppm the ratios had dropped by ~90%. This indicated that the steam reforming of CH₄ was strongly affected even at a low H₂S concentration. With further increasing the H₂S concentration, this ratio decreased slower.

Figure 3

Based on the measured cell voltage values under H₂S, the fuel gas composition in the cell was calculated using a program developed in house. In Figure 4 the thus calculated CH₄ conversion is plotted as a function of the H₂S concentration. Even low concentrations of H₂S in the fuel (2-4 ppm) have a large effect on the steam reforming activity of the SOFC anode, thereby confirming the observed inhibition of reforming as measured by the QMS (see Figure 3). At 24 ppm H₂S less than 15% of the CH₄ in the fuel is converted.

Rostrup-Nielsen [19] published a relation between the coverage of S on a Ni catalyst, θ_s , the temperature T in Kelvin and the ratio between the partial pressures of H₂S and H₂, $Y = p_{H_2S}/p_{H_2}$ (equation (5))

$$(5) \theta_s = 1.45 - 9.53 \cdot 10^{-5} \cdot T + 4.17 \cdot 10^{-5} \cdot T \cdot \ln(Y)$$

When applying the p_{H_2S} and p_{H_2} values used in our CH₄ tests, θ_s becomes 0.86 at 850°C and 4 ppm H₂S (see insert in Figure 4). Having covered the active sites to such a large extent, the observed rapid poisoning of the CH₄ reforming seems quite reasonable.

Figure 4

3.2 SOFC Performance

The first test series discussed above was aimed at studying the effect of H₂S at OCV and reflected thus purely catalytic activity and poisoning. However, current might have a significant effect. Among others Koh et al. [20] found that less coke was formed on an SOFC under current load compared to an SOFC at OCV. It was speculated that the coke was being reacted off the Ni particles at the three-phase-boundaries (TPB) by O²⁻-ions. O²⁻-ions have also been suggested to facilitate desorption of S species from the TPB [14, 15, 21]. The degree of poisoning of the CH₄ conversion might be moderated when the SOFC is in use, i.e. under current load.

Three SOFCs were tested under current load (1 Acm⁻²) in CH₄-containing fuel and were exposed to H₂S for 24 h intervals in order to study the effect of H₂S on the steam reforming activity and electrochemistry. In all three tests a steam to carbon ratio of ~2:1 was used to prevent coke formation on the Ni particles. The tests were run at a temperature of 850°C. In test 1, a smaller CH₄ concentration was used than in test 2 and 3, in order to study the importance of CH₄ concentration. The fuel compositions, the fuel utilization (FU) and the initial area specific resistance values corrected for FU (ASR_{cor}) [18] of the cells in test 1-3 (denoted CH_4 tests) are shown in Table 1.

Table 1

The cell voltage developments are shown in Figure 5. After turning on the current load, the SOFCs were run in the CH₄/H₂/H₂O fuel for 300-500 h before adding the first portion of H₂S. During this period each of the cells degraded (50-60 mV per 1000 h). Addition of H₂S to the fuel resulted in an initial voltage drop, followed by a nearly constant cell voltage degradation. After turning off the H₂S the cell voltage regenerated to a level consistent with the overall degradation observed in the absence of H₂S. The insert in Figure 5 shows these effects after adding the 4 ppm H₂S to the fuel in test 1 as example. In test 2 and 3, the current load was interrupted for ~100 h due to work on the lab facilities. These interruptions (indicated by horizontal arrows) did not affect the overall cell voltage development.

The cell voltage development had thus much similar characteristics as in the poisoning tests in H₂ fuel [13]. The first voltage drop was ascribed a fast adsorption of S on the Ni surface, blocking the active sites for hydrogen

adsorption and oxidation [13, 14]. The reason for the following voltage degradation is not completely clear at the moment.

During regeneration from 2 ppm (second time) in test 1, the cell voltage did not return entirely to the overall voltage development, but instead started to decrease progressively. The test was stopped, when a critical cell voltage was reached. When adding 9 ppm H₂S in test 3 the cell voltage dropped rapidly below 450 mV, which resulted in an automatic turn off of current (cell voltage set to OCV by the system, see vertical arrow in Figure 5). After stopping the H₂S addition and turning on the current load again, the cell voltage regenerated to a level consistent with the overall development. Adding 7 ppm H₂S also resulted in a rapid, large voltage drop below 450 mV, which again triggered the system to turn off the current (OCV). Afterwards, it was not possible to apply the same current load (1 Acm⁻²) and the test was stopped.

Therefore the maximum H₂S amount, which can be allowed in the CH₄-containing fuels during a 24 h time period under the present conditions, is around/below 7 to 9 ppm. Taking the CH₄ conversion determined at OCV as a guideline (see section above and Figure 4) only 20-30% of the CH₄ was converted at these H₂S concentrations. As a consequence, the fuel gas in the cell should contain less CO and H₂ and more methane.

During the three tests the *p*O₂-in voltage and -out voltage were monitored in order to gather information about the gas compositions entering into and leaving the SOFC. They were both constant except for *p*O₂-out in the cases when 4 ppm and 7 ppm H₂S were added in test 1, and when 4 ppm and 9 ppm H₂S were added in test 3.

In test 1 the *p*O₂-out voltage dropped by 15 mV ± 5 mV when 4 ppm was added and by 32 mV ± 5 mV when 7 ppm was added. In test 3 the *p*O₂-out voltage dropped by 18 mV ± 2 mV when 4 ppm H₂S was added. It was not possible to determine how much the *p*O₂-out voltage dropped at 9 ppm as the current was stopped almost immediately. The *p*O₂-in voltage remained constant in all three tests as expected, because the fuel gas flows and thus the gas compositions entering the cells were kept constant. The drop of the *p*O₂-out voltage at the large H₂S concentrations is thus a result of the lower concentrations of H₂ and CO in the fuel outlet gas due to a smaller CH₄ conversion, a direct consequence of the decreased reforming activity of the anode.

Figure 5

A lower production of these fuels would also affect the fuel utilization, which might reach values critical for the SOFC anode. The fuel utilization in these cases of strong poisoning was therefore calculated using the gas compositions determined during H₂S poisoning tests at OCV (see Figure 6).

Indeed, adding 7 ppm and 9 ppm H₂S in test 3 resulted in a *FU* >90%, i.e. all of the initially added H₂ and a small amount of H₂ + CO from the remaining steam reforming reaction of CH₄ were converted in the electrochemical reaction. Operating the cells at these large *FUs* resulted in very low concentrations of H₂ and CO as measured near the outlet part of the cells, which can result in oxidation of the Ni particles (Ni particles become oxidised by O²⁻-ions from the cathode). This explains the rapid voltage drop below 450 mV in test 3, when 9 ppm H₂S were added. A larger amount of H₂ in the initial fuel can counteract such over-critical *FUs*. A gradual poisoning of the CH₄ reforming and thus smaller supply of H₂ and CO has then a less severe effect (see test 1).

Figure 6

During poisoning tests in H₂ fuel, a clear correlation between the initial cell voltage drop and the H₂S concentration was found [13]. This parameter was also analysed for the CH₄ tests in this study. In Table 2 the initial voltage drops (ΔV_{ini}) for the cells in the CH₄ tests and for an SOFC with the same test parameters, but running on fuel consisting of only H₂ and H₂O (referred to as *H₂ test* [13]), are listed as a function of the H₂S concentration. At low H₂S concentration (2 ppm H₂S) the initial voltage drops were approximately the same for the cells in the CH₄ tests 1 and 2 (present study) as for the H₂ test [13]. At higher H₂S concentrations the cells in the CH₄ tests started to experience a larger initial voltage drop than in the H₂ test.

After the initial voltage drop the SOFCs degraded (more than the overall cell voltage degradation). In Table 2 the degradation rates (τ_{deg}) are listed as a function of the H₂S concentration.

Table 2

Analysing the degradation rates under H₂S exposure, the CH₄ tests show much larger rates at comparable H₂S concentrations (Table 2). These results suggest that the effects of S-poisoning on SOFCs fuelled with CH₄-containing gases are much more severe. From investigations of steam reforming catalysts it was concluded that steam reforming primarily happens at the defect sites (steps), which are also the preferred adsorption sites for S [22]. The electrochemical oxidation of H₂ is less site-sensitive. The S-poisoning effects are thus more significant for the tests with CH₄-containing fuels, because of the sensitive steam reforming reaction.

After stopping the H₂S addition, the cell voltage regenerated slowly (Figure 5). The poisoning reflected by the drop of cell voltage occurred within ~24 h, while the whole recovery occurred over ~200 h in both the CH₄ tests and in the H₂ test [13]. The entire poisoning was thus faster than the entire recovery (see Figure 5). A way to quantify the poisoning and recovery rates is to determine the times for 50% change, i.e. 50% initial voltage drop compared to 50% voltage recovery.

In Figure 7 the rates of the initial poisoning rates (50% voltage drop) and initial recovery rates (50% voltage increase) in the CH₄ tests (top figure) and in the H₂ test [13] (bottom figure) are plotted. In the CH₄ tests the initial poisoning and initial recovery rates were almost the same over the used concentration range, while there was a difference in the H₂ test; the initial poisoning rate was larger than the initial recovery rate (see Figure 7). This difference increased with H₂S concentration (10 times larger at 100 ppm H₂S).

Figure 7

Comparing the CH₄ tests and the H₂ test, the initial poisoning rates were almost the same in these, while the initial recovery rate for the test in H₂ was much smaller. This result points to different recovery mechanisms depending on the fuel. Assuming the recovery to be due to desorption of S-species from the Ni particles in the SOFC anode, this process can be in general facilitated by an increase of temperature, a decrease of the pressure or by addition of a displacement agent. The faster recovery in the CH₄ tests could thus be explained by the presence of a higher H₂O concentration in the fuel in the CH₄ tests, H₂O acting as an efficient displacement agent.

Impedance spectroscopy was used to obtain more detailed information about the effect of H₂S on the cells internal resistances. This was done by measuring the impedance of the SOFCs before, during and after each H₂S cycle. To determine the most relevant times for recording impedance spectra the anode in-plane voltages were followed and impedance spectra were taken at the times of constant levels [13]. In test 1 it was not possible to achieve acceptable resolution on the low frequency part of the spectra (< ~10 Hz), due to small cell voltage oscillations. However, the development of the high frequency arc showed similar development during the poisoning cycles for all the CH₄ tests. The case of 2 ppm H₂S addition in test 2 is shown in Figure 8 as an example. The Nyquist plots show that the total internal resistance of the cell increased as H₂S was added to the fuel until the cell was at steady state (the constant level in the in-plane voltage indicates steady state: Δ in the insert). But it returned nearly to the initial level when the H₂S addition was stopped. The serial resistance increased minimally during the interval (< 0.02 Ωcm^2), which was consistent with the overall degradation of the cell voltage. As the cell voltages degraded in the CH₄ tests even before the first H₂S addition, this increase in series resistance is assigned to the overall voltage degradation. The reason for the overall cell voltage degradation might be related to coke formation on the Ni particles, even though a steam to carbon ratio of 2 was applied.

Mainly the polarization resistance changed under addition of H₂S. From Figure 8 it can be concluded that the polarization resistance increase was reversible and that mainly the high frequency arc increased. These results thus coincide with those obtained during H₂S poisoning in H₂-fuel, although at much smaller H₂S-concentrations [13].

Figure 8

4 Conclusions

It was studied, how H₂S affects the reforming and electrochemical activity of a Ni/YSZ anode in a technological SOFC by adding H₂S to a CH₄-containing fuel. It was found that H₂S had a larger effect on the reforming activity than on the electrochemical activity. At 4 ppm H₂S addition, more than 60% of the reforming activity was eliminated at OCV, which meant that the production of fuel (H₂ and CO) was diminished significantly. When operating an SOFC under current load a maximum H₂S concentration just below 7-9 ppm was acceptable during a 24 h period. At these H₂S concentrations the production of CO and H₂ fuel from steam reforming was

suppressed to a large extent. If not additional hydrogen is added to the fuel, a critical fuel utilization and thus oxidation of the Ni particles leading to a severe degradation of the cell voltage might occur.

The poisoning of the electrochemical activity proceeded similarly in methane and hydrogen fuel. The recovery of the cell voltage after stopping the H₂S exposure was accelerated in the methane/steam containing fuel. Probably, steam facilitates efficient desorption of S from Ni-sites.

Acknowledgement

We acknowledge the project "Effektiv konvertering af vedvarende energi vha. fastoxid-celler" under Det Strategiske Forskningsråds Programkomite for Energi og miljø, sagsnr. 2058-03-0014 for sponsoring this work.

List of Symbols

ASR	Area specific resistance
CPO	Catalytic partial oxidation
ΔV	Voltage drop
EMF	electro motive force
FU	Fuel utilization
iV	Current voltage curves
LSM	Lanthanum strontium manganite
OCV	Open circuit voltage
pO_2	Partial pressure of oxygen
θ	Coverage
QMS	Quadrupole mass spectrometer
SOFC	Solid Oxide Fuel Cell
τ_{deg}	Cell voltage degradation rate
TPB	Three-phase boundary
YSZ	Yttria stabilized zirconia

References

- [1] A. Hagen, R. Barfod, P.V. Hendriksen, Y.-L. Liu, S. Ramousse, *J. Electrochem. Soc.* **2006**, 153(6), A1165.
- [2] J. Staniforth, R. M. Ormerod, *Catalysis Letters* **2002**, 81, 19-23.
- [3] G. Goula, V. Kioussis, L. Nalbandian, I. V. Yentekakis, *Solid State Ionics* **2006**, 177, 2119-2123.
- [4] Y. Matsuzaki, Y. Baba, T. Sakurai, *Solid State Ionics* **2004**, 174, 81-86.
- [5] C. M. Finnerty, R. M. Ormerod, *Journal of Power Sources* **2000**, 86, 390-394.
- [6] T. Horita, K. Yamaji, T. Kato, H. Kishimoto, Y. Xiong, N. Sakai, M. E. Brito, H. Yokokawa, *Journal of Power Sources* **2005**, 145, 133-138.
- [7] Y. Lin, Z. Zhan, J. Liu, S. A. Barnett, *Solid State Ionics* **2005**, 176, 1827-1835.
- [8] K. Sasaki, K. Watanabe, K. Shiosaki, K. Susuki, Y. Teraoka, *Journal of Electroceramics* **2004**, 13, 669-675.
- [9] J.-H. Wang, M. Liu, *Journal of Power Sources* **2008**, 176, 23-30.
- [10] M. Mogensen, K. Kammer, *Annu. Rev. Mater. Res.* **2003**, 33, 321-331.
- [11] J.R. Rostrup-Nielsen, J. Sehested, J.K. Nørskov, *Adv. Catal.* **2002**, 47, 65.
- [12] K. Sasaki, K. Susuki, A. Iyoshi, M. Uchimura, N. Imamura, H. Kusaba, Y. Teraoka, H. Fuchino, K. Tsujimoto, Y. Uchida and N. Jingo, *Journal of Electrochemical Society* **2006**, 153 (11), A2023-A2029.
- [13] J. F. B. Rasmussen, A. Hagen, *Journal of Power Sources* **2009**, 191, 534.
- [14] S. Zha, Z. Cheng, M. Liu, *Journal of the Electrochemical Society* **2007**, 154, B201-B206.
- [15] J. R. Rostrup-Nielsen, J. B. Hansen, S. Helveg, N. Christiansen, A.-K. Jannasch, *Appl. Phys., A* **2006**, 85, 427-430.
- [16] M. Noponen, M. Halinen, J. Kiviaho, J. Saarinen, *Journal of Fuel Cell Science and Technology* **2006**, 3, 438-444.
- [17] S. Ramousse, M. Menon, K. Brodersen, J. Knudsen, U. Rahbek, P. H. Larsen, *ECS Transactions* **2007**, 7 (1), 317-327.
- [18] M. Mogensen, P. V. Hendriksen, in "High Temperature Solid Oxide Fuel Cells. Fundamentals, Design and Applications", Elsevier Ltd, **2003**.
- [19] J. R. Rostrup-Nielsen, *Catalytic Steam Reforming*, Springer-Verlag, Berlin, **1984**.
- [20] J.-H. Koh, Y.-S. Yoo, J.-W. Park, H. C. Lim, *Solid State Ionics* **2002**, 149, 157-166.
- [21] Z. Cheng, S. Zha, M. Liu, *Journal of Power Sources* **2007**, 172, 688-693.
- [22] H. S. Bengaard, J. K. Nørskov, J. Sehested, B. S. Clausen, L. P. Nielsen, A. M. Molenbroek, J. R. Rostrup-Nielsen, *Journal of Catalysis* **2002**, 209, 365-384.

Tables

Table 1: Fuel compositions, FU and ASR_{cor} values for the three CH_4 tests.

Test	H ₂ (%)	CH ₄ (%)	H ₂ O (%)	H ₂ S (ppm)	FU (%)	ASR_{cor}^* (Ωcm^2)
1	46	17	37	2, 4, 7, 2	60	0.19
2	13	29	58	2	57	0.22
3	13	29	58	4, 9, 7	58	0.19

* Obtained during initial fingerprint, see section 2.1

Table 2: The initial voltage drop (ΔV_{ini}) and Degradation rate (τ_{deg}) of the H₂ test [13] and the three CH₄ tests (Test 1, 2 and 3). $T = 850^\circ\text{C}$; 1 Acm^{-2} .

H ₂ S conc. (ppm)	H ₂ test		CH ₄ tests					
	[13]		Test 1		Test 2		Test 3	
	ΔV_{ini}	τ_{deg}	ΔV_{ini}	τ_{deg}	ΔV_{ini}	τ_{deg}	ΔV_{ini}	τ_{deg}
2	75	0.1	79	0.7	73	1.1		
4	83	0.2	82	1.3			93	2.8
7	87	0.2	107	1.2				
9	96	0.3						
18	98	0.3						
42	100	0.5						
100	108	0.7						

ΔV_{ini} : Initial voltage drop (mV)

τ_{deg} : Linear degradation rate (mVh^{-1})

Figure Captions

Figure 1: Left: The test setup. Right: H₂S was added in two different ways, i.e. in steps of increasing concentrations with the cell at OCV (A) and in intervals with the cell under current load (B).

Figure 2: The cell voltage development. H₂S was added in concentration steps of 2 ppm, 4 ppm, 7 ppm, 9 ppm, 20 ppm and 24 ppm. $T = 850^\circ\text{C}$; OCV, CH₄/H₂/H₂O fuel. Insert: OCV at different H₂S concentrations (see also values in the text).

Figure 3: The CO/CH₄, CO₂/CH₄ and (CO+CO₂)/CH₄ ratios measured at fuel outlet by QMS as function of H₂S concentration in the fuel. $T = 850^\circ\text{C}$; OCV, CH₄/H₂/H₂O fuel.

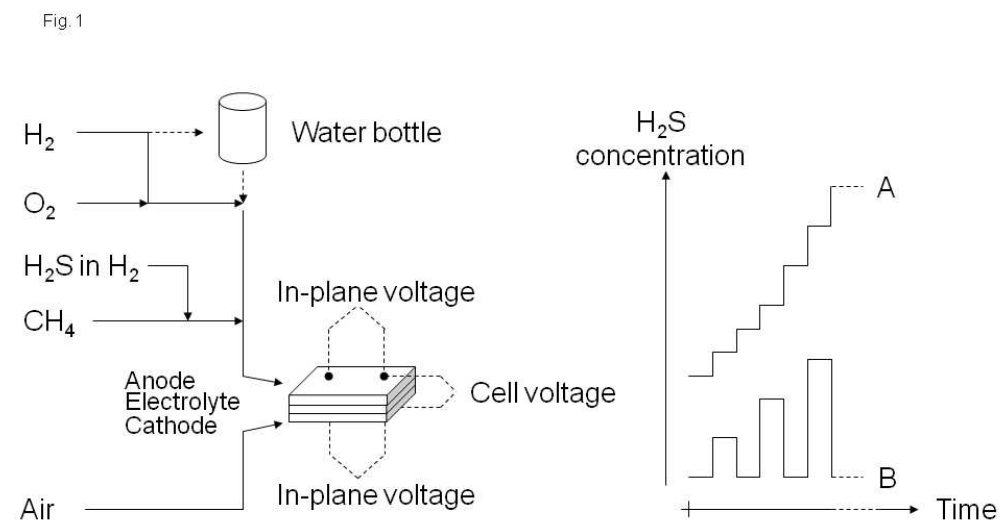
Figure 4: The calculated CH₄ conversion, based on the measured OCV. $T = 850^\circ\text{C}$; OCV, insert: S-coverage as calculated according to [19].

Figure 5: The cell voltage developments. Black: test 1, green: test 2, and blue: test 3. The letters a, b, c and d indicate where the varying concentrations of H₂S were added to the fuel. The horizontal arrows show the periods under OCV due to maintenance work in the lab. The insert illustrates the initial voltage drop and the degradation rate under 4 ppm H₂S addition in test 1. $T = 850^\circ\text{C}$; 1 Acm^{-2} , CH₄/H₂/H₂O fuel (compositions see Table 1).

Figure 6: The calculated FU for the cells in test 1 and 3. $T = 850^\circ\text{C}$; 1 Acm^{-2} .

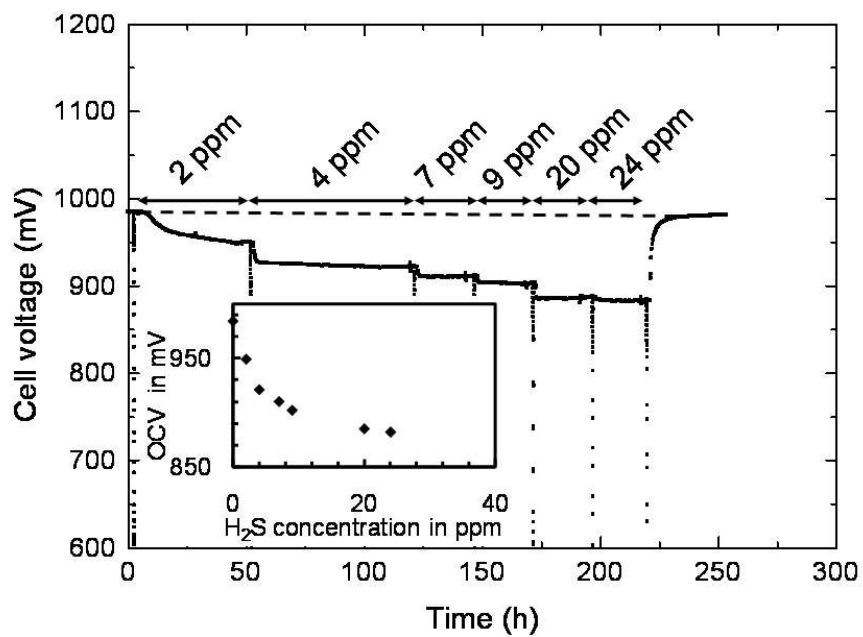
Figure 7: The initial poisoning rates (50% voltage drop) compared to the initial recovery rates (50% voltage increase) as function of H₂S concentration. Top: CH₄ tests; Bottom: H₂ test [13]. $T = 850^\circ\text{C}$; 1 Acm^{-2} .

Figure 8: The internal resistance development (impedance spectra), when 2 ppm H₂S was added in test 2. $T = 850^\circ\text{C}$; 1 Acm^{-2} .



Left: The test setup. Right: H₂S was added in two different ways, i.e. in steps of increasing concentrations with the cell at OCV (A) and in intervals with the cell under current load (B).
254x190mm (96 x 96 DPI)

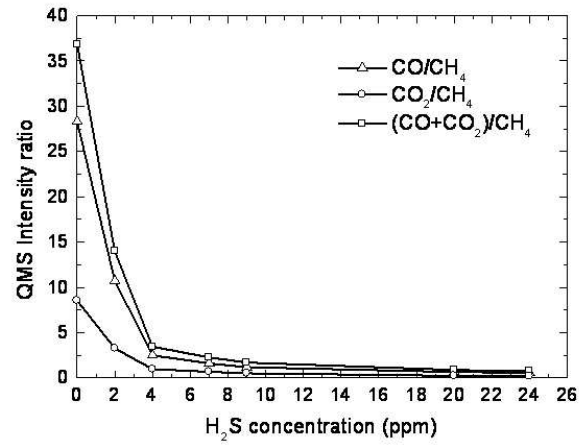
Fig. 2



The cell voltage development. H₂S was added in concentration steps of 2 ppm, 4 ppm, 7 ppm, 9 ppm, 20 ppm and 24 ppm. T = 850 °C; OCV, CH₄/H₂/H₂O fuel. Insert: OCV at different H₂S concentrations (see also values in the text).

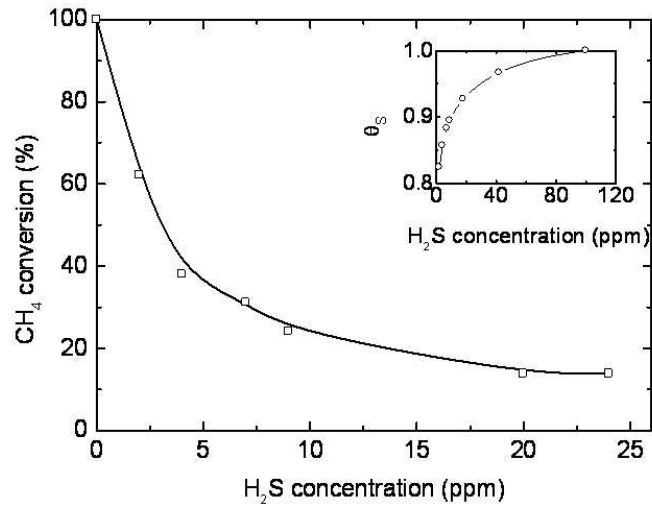
254x190mm (96 x 96 DPI)

Fig. 3



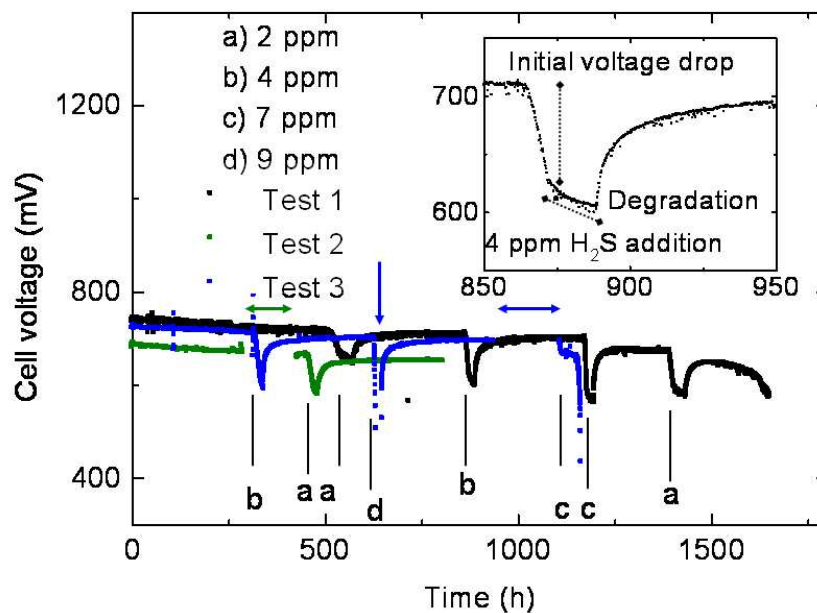
The CO/CH₄, CO₂/CH₄ and (CO+CO₂)/CH₄ ratios measured at fuel outlet by QMS as function of H₂S concentration in the fuel. T = 850 °C; OCV, CH₄/H₂/H₂O fuel.
254x190mm (96 x 96 DPI)

Fig. 4



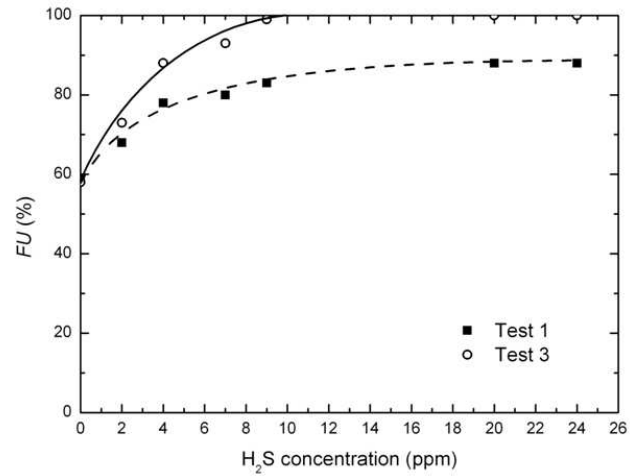
The calculated CH₄ conversion, based on the measured OCV. T = 850 °C; OCV, insert: S-coverage as calculated according to [19].
254x190mm (96 x 96 DPI)

Fig. 5



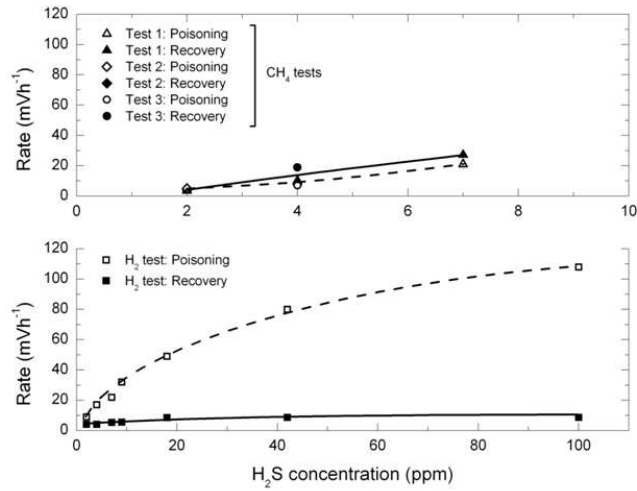
The cell voltage developments. Black: test 1, green: test 2, and blue: test 3. The letters a, b, c and d indicate where the varying concentrations of H₂S were added to the fuel. The horizontal arrows show the periods under OCV due to maintenance work in the lab. The insert illustrates the initial voltage drop and the degradation rate under 4 ppm H₂S addition in test 1. T = 850 °C; 1 Acm⁻², CH₄/H₂/H₂O fuel (compositions see Table 1).
254x190mm (96 x 96 DPI)

Fig.



The calculated FU for the cells in test 1 and 3. $T = 850\text{ }^{\circ}\text{C}$; 1 Acm^{-2} .
254x190mm (96 x 96 DPI)

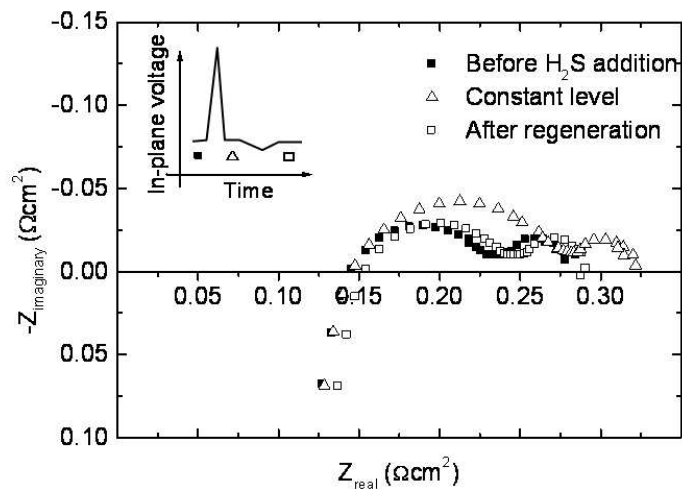
Fig. 7



The initial poisoning rates (50% voltage drop) compared to the initial recovery rates (50% voltage increase) as function of H₂S concentration. Top: CH₄ tests; Bottom: H₂ test [13]. T = 850 °C; 1 Acm⁻².

254x190mm (96 x 96 DPI)

Fig. 8



The internal resistance development (impedance spectra), when 2 ppm H₂S was added in test 2. T = 850 °C; 1 Acm⁻².
254x190mm (96 x 96 DPI)