

Characterisation of Sulphur Poisoning of Anodes in Single-Cell SOFC Stacks Using Impedance Spectroscopy

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Abstract

The effect of H₂S on single cell stack power using simulated syngas and hydrogen/steam mixture as a fuel is investigated using impedance spectroscopy. The different concentrations of H₂S (2-50 ppm) were added to the pre-mixed reformat containing H₂, CO, CO₂, H₂O, CH₄ and N₂ during cell operation. Electrolyte supported cells are tested at operation temperature of 850°C. The effect of different concentrations of H₂S and steam on sulphur tolerance of cells is investigated. The impedance measurements are carried out to identify the processes which take place in the anode. The reversibility of sulphur poisoning is investigated and the observed regeneration processes are discussed. X-ray diffractometer (XRD) was used to characterize the microstructural changes that occurred after H₂S poisoning.

Introduction

Solid Oxide Fuel Cells (SOFC) are known as the most flexible type of fuel cell in regard to fuel type. The wide variation of fuels such as hydrogen, carbon monoxide, hydrocarbons, alcohols and synthesis gases from e.g. natural gas, biogas and petroleum make them attractive energy sources for the future. However direct usage of different fuels may also cause degradation of the cell power due to contaminant content. Major contaminants which are known to poison the SOFC anodes are sulphur compounds e.g. added to the natural gas as odorant for safety reasons or naturally existing in e.g. biogas. Previous studies from Sasaki et al. indicate that the hydrogen sulphide (H₂S) among sulphur compounds is the most stable compound at operating temperature of SOFC that causes power degradation [1]. Many studies also show the degradation of the cell power when the cell is exposed to H₂S. These studies indicate that the sulphur poisoning increases as the H₂S concentration increases and the temperature decreases [2]. However there are only few studies about H₂S poisoning with synthesis gas composition in a stack which would be the case in the practical use.

By means of Electrochemical Impedance Spectroscopy (EIS) it is possible to separate the degradation mechanisms of an SOFC, such as, degradation due to sulphur poisoning. Due to its unique advantage to ensure clean separation of the process kinetics of different steps, the EIS technique is widely used for the investigation of a large scale of electrochemical objects.

Experimental

The experimental setup for testing SOFC stack with H₂S is illustrated in Figure 1. The test bench includes a furnace, electrical load, mass flow controllers, evaporator and an automation system. The screen printed SOFC Membrane-Electrode Assemblies (MEAs) with 3YSZ (3 mol% Y₂O₃ – 97 mol% ZrO₂) electrolyte, Nickel Oxide/Gadolinia-doped Ceria (NiO/CGO) anodes and LSM perovskite cathodes supplied from HC Starck were used for experiments.

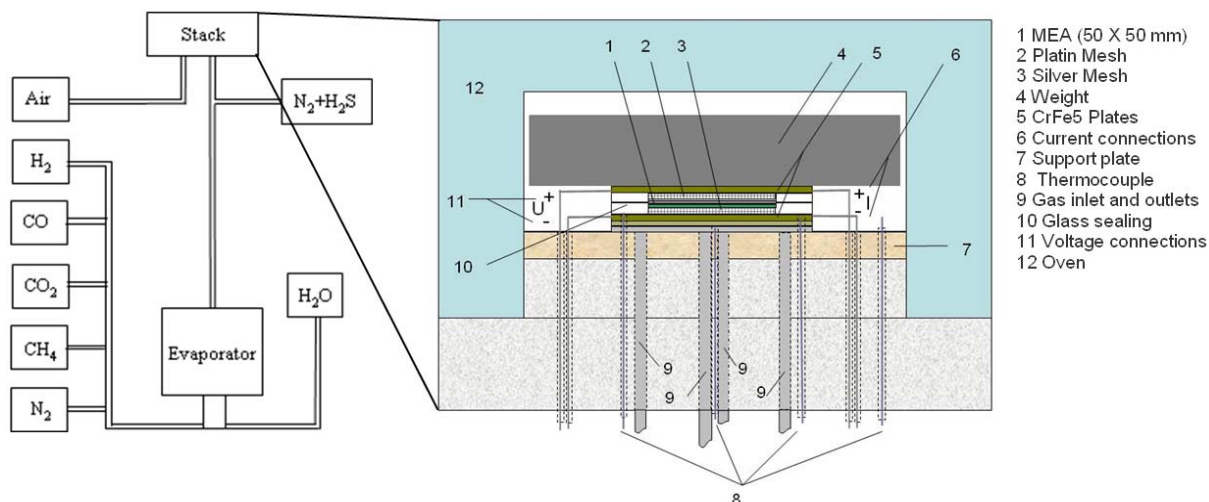


Figure 1 Experimental set-up for the investigation on single cell stacks.

The cells were placed in chromium-iron alloy bipolar plates which were sealed with glass sealings. The contacting elements were nickel and silver meshes for anode and cathode respectively. The bipolar plates and the cell have the dimensions 80 x 80 mm and 50 x 50 mm (40 x 40 mm active area) respectively. Both the anode and cathode gases are delivered from the bottom of the stack. The flow configuration in the cell is cross-flow.

The measurement procedures started with heating, glass sealing and the reduction of the cell. The cell is then exposed to the gas mixture containing H₂, CO, CH₄, H₂O and CO₂ and waited to have a constant power density. The different H₂S concentrations were then added to the gas mixture and the cell run with this concentration at least for 24 hours. The electrochemical impedance analysis of the cells was conducted in between with TrueData-EIS from FuelCon AG within a frequency range 0.1 Hz – 10000 Hz.

Results and Discussion

The effect of the H₂S impurity on the stack power is analysed by measuring the cell voltage and the impedance spectra under constant current load. The cells were tested at 1123 K with the supplied pre-mixed reformat gas composition (27 vol% H₂, 11 vol% CO, 6.2 vol% H₂O, 2.8 vol% CO₂, 0.8 vol% CH₄, 51 vol% N₂) and H₂ based fuel (H₂, H₂O and N₂) with varying steam content and H₂S contamination. Dry air was fed to the cathode.

Figure 2 shows the voltage - current characteristics of the stack over the experimental run with synthetic gas composition (27 vol% H₂, 11 vol% CO, 6.2 vol% H₂O, 2.8 vol% CO₂, 2 vol% CH₄, 51 vol% N₂) with different H₂S concentrations. The test was performed under constant current density (275 mA/cm²) at 1123K. The sharp changes of voltage and current indicate the time points for the impedance measurements. At the beginning of the experiment, there was an increase of the cell voltage from 0.706 V to 0.734 V because of

the activation of the electrodes and decrease of contact resistances. After 144 hours of activation time, the cell is exposed to 8 ppm H₂S (Fig. 2).

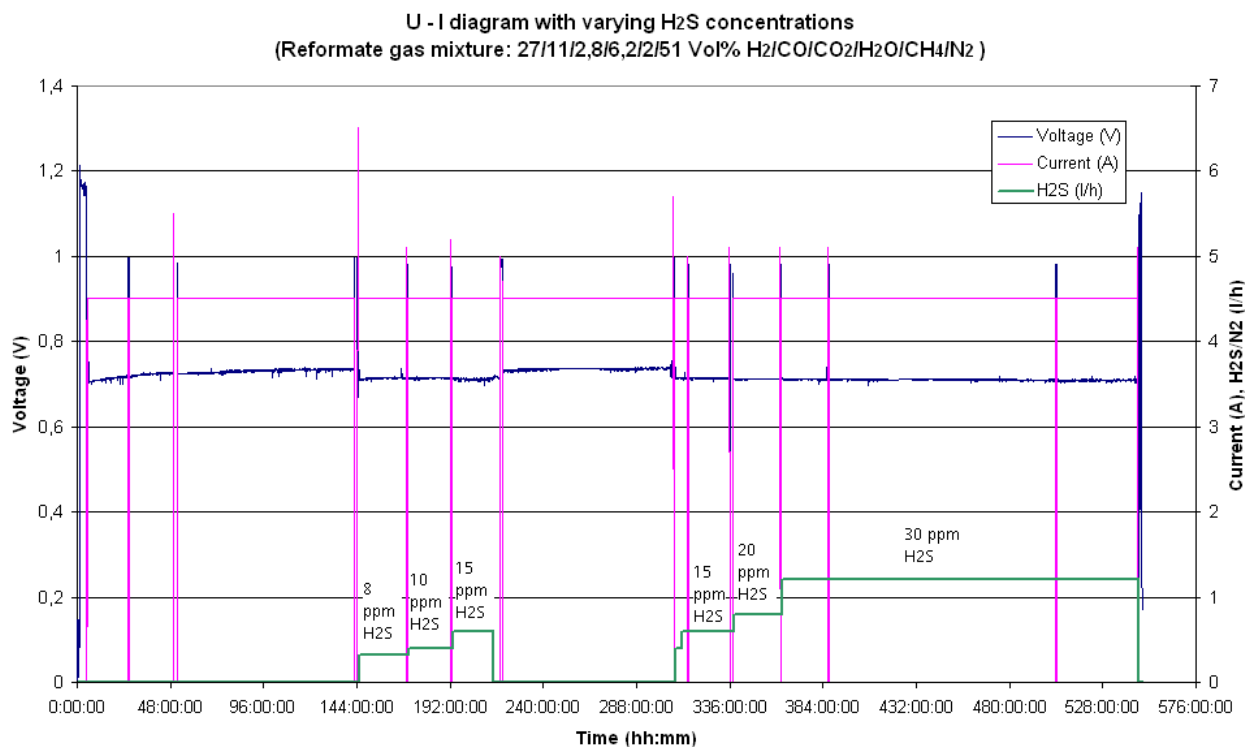


Figure 2 Cell voltage and current as a function of time at 850°C with reformat gas composition.

By addition of 8 ppm H₂S, the voltage of the cell dropped immediately from 0.734 V to 0.714 V within a short time period, followed by a stable cell voltage under this poisoning condition. With the following 10 ppm H₂S addition, no additional voltage drop of the cell was observed. 15 ppm H₂S addition caused a very small amount of cell voltage drop from 0.715 V to 0.713 V. The cell voltage remained stable for 24 hours. The H₂S concentration is then set to 0 ppm in order to see if any recovery takes place. The recovery kinetics was slower than the poisoning kinetics. The cell voltage arrived to its initial level in approximately 4 hours. The addition of 15 and 20 ppm H₂S to the cell afterwards decreased the cell voltage to 0.714 V. The increase of the H₂S concentration from 20 ppm to 30 ppm caused a voltage decrease from 0.714 V to 0.712 V (Fig 3). There was no cell voltage change till the end of the experiment. This behaviour of the cell can be explained by the chemisorption processes in the anode.

Sulphur is known to be one of the most toxic materials for catalysts such as nickel [4]. Firstly, an adsorbed sulphur atom blocks at least three of four metal atom surfaces physically (in three dimensional space). By its strong chemical bond, it electronically modifies its nearest neighbour atoms and their capability to adsorb and/or dissociate reactant molecules. The surface structure would be changed by strongly adsorbed poison. By the changed surface structure the surface diffusion of adsorbed reactants would be prevented or slowed down [4].

Detail - U-I diagram with varying H₂S concentrations

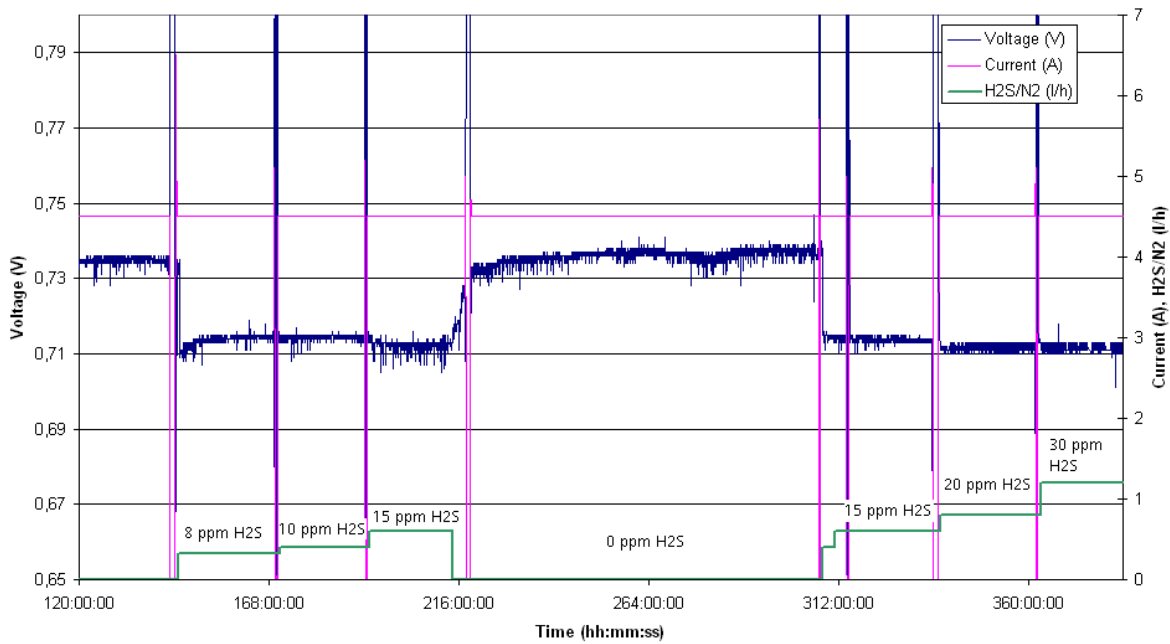


Figure 3 Details from Figure 2.

The distribution of sulphur on the catalyst is complex due to significant gradients of temperature and hydrogen partial pressure in the fuel cell. However, if we consider that sulphur attacks the nickel atom at constant temperature and H₂S/H₂ ratio one can calculate the sulphur coverage on nickel. At high temperatures H₂S is chemisorbed dissociatively on the nickel surface:



The sulphur coverage on the nickel surface (θ) at equilibrium for reaction (1) depends on the H₂S/H₂ ratio and temperature. Rostrup-Nielsen and co-workers found the parameters for sulphur on nickel by correlation of data to a Temkin like adsorption isotherm [3]:

$$\theta = 1.45 - 9.53 \times 10^{-5} T + 4.17 \times 10^{-5} T \ln(p_{\text{H}_2\text{S}}/p_{\text{H}_2}) \quad (2)$$

The sulphur coverage on nickel surface by 1 to 50 ppm H₂S is calculated using formula (2) with H₂ volume percentages from 10 to 100. The result is given in Figure 4.

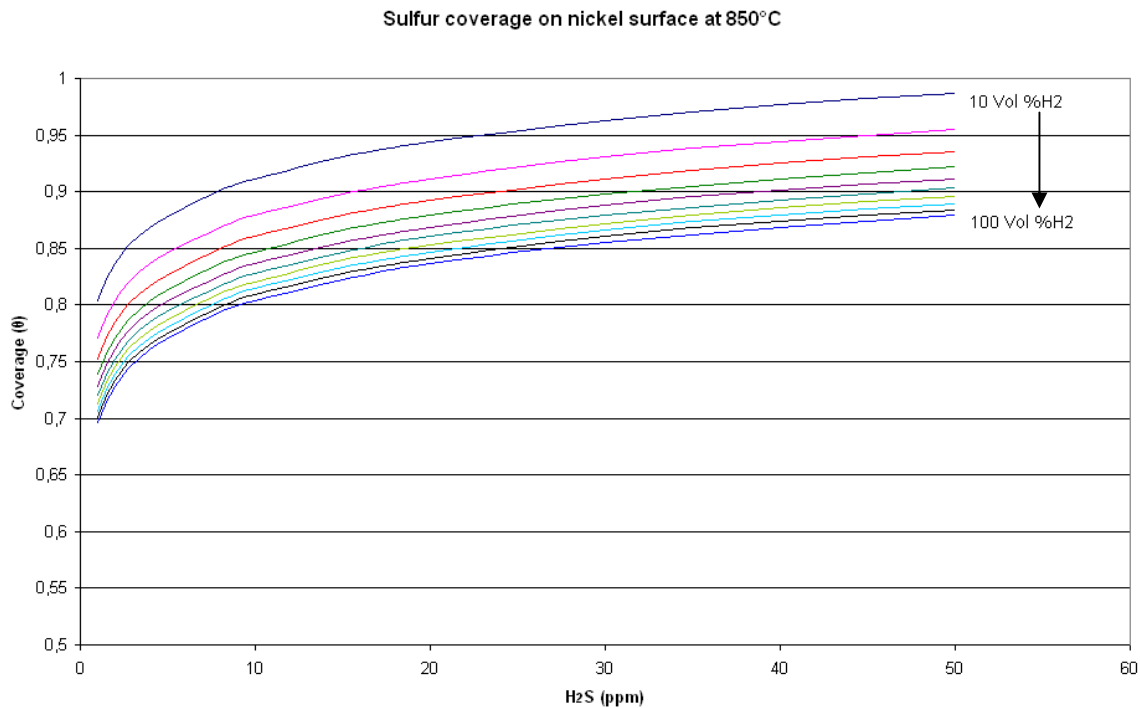


Figure 4 The calculated sulphur coverage on nickel at 850°C for gases with different hydrogen content.

The curves in Figure 4 show that the sulphur coverage reaches saturation already above 70 % even if the concentration of H₂S is very low. This tells us why the voltage drop reaches its highest value when the cell is exposed from 0 ppm H₂S to 8 ppm H₂S. In this figure we also see that the coverage decreases as the hydrogen concentration in the fuel gas increases. The expression (2) is not valid for θ close to zero and close to one. It is known that above $H_2S/H_2 = 100 - 1000 \times 10^{-6}$ the bulk formation of Ni₃S₂ takes place that causes irreversible cell voltage drop and destruction of the anode [3]. Below these concentrations it is possible to remove sulfur from the catalyst by decreasing the sulphur content since the chemisorption of H₂S on nickel is reversible. For this reason, it was possible to regenerate the cell voltage during the experiment by decreasing the H₂S concentration from 15 ppm to 0 ppm (Figure 3).

After the end of the experiment, the cell which was exposed to different H₂S concentrations was cooled down to room temperature with a rate of 2 K/min with forming gas (5 vol% H₂, 95 vol% N₂). The XRD analysis of the anode is done afterwards in order to see if there is any nickel sulphide formation in the cell (Fig 5).

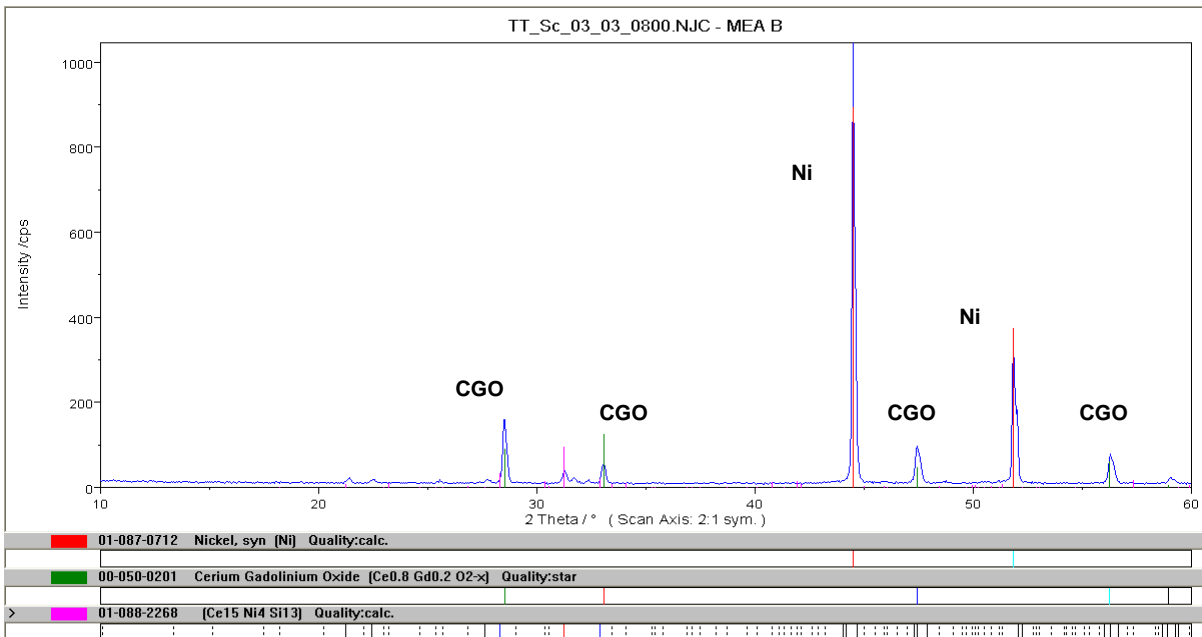


Figure 5 The XRD Pattern of the anode after exposure to H₂S at 850°C. No nickel sulphide peaks are observed.

The XRD pattern of the anode which was exposed to the synthetic fuel mixture (27 vol% H₂, 11 vol% CO, 6.2 vol% H₂O, 2.8 vol% CO₂, 2 vol% CH₄, 51 vol% N₂) with varying H₂S concentrations at 850°C for 550 hours is shown in Figure 5. The XRD pattern shows that there are no nickel sulphide phase formations in the anode.

The impedance measurements were recorded at each H₂S concentration level. The Nyquist diagrams from the measurements are shown in Figure 6. Below 1 Hz, the quality of the impedance response was low as can be seen in Figure 6.

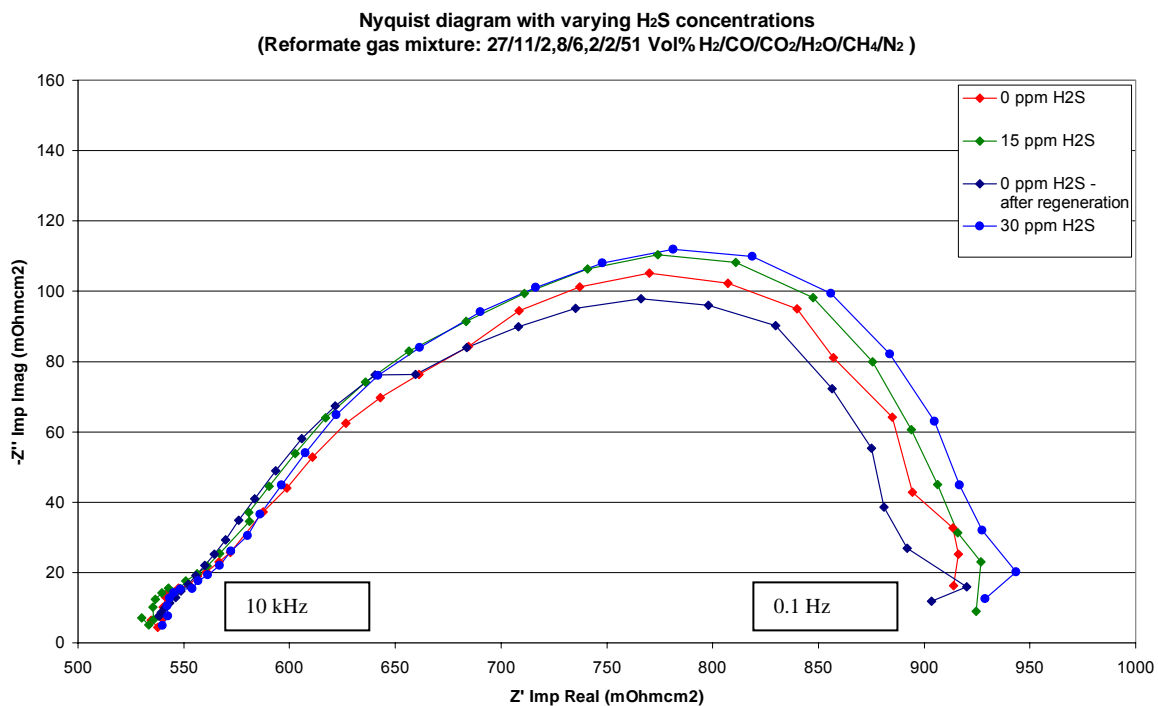


Figure 6 Impedance spectra of the cell exposed to reformate gas composition with varying H₂S concentrations.

Two arcs seemed to be overlapped in the impedance plots. As shown in the figure, the addition of H₂S did not change the impedances at higher frequencies. Almost all ohmic (high frequency) resistances of the samples remain between 545 – 555 mΩcm². In the lower frequency range, the differences are more obvious. It is found that the impedance curve at that frequency shifted to right with H₂S addition. The EIS spectra after regeneration of the cell without H₂S had the lowest impedances at lower frequencies. But no significant difference appeared in the shape of the curves. These results indicate the very low deactivation of the cell due to the processes in the anode. The effect of higher H₂S concentrations (40 ppm H₂S and 50 ppm) is also tested with the same gas composition (27 vol% H₂, 11 vol% CO, 6.2 vol% H₂O, 2.8 vol% CO₂, 0.8 vol% CH₄, 51 vol% N₂) at the operation temperature of 850°C with another stack. Similar behaviour of the cells was observed (Fig 7).

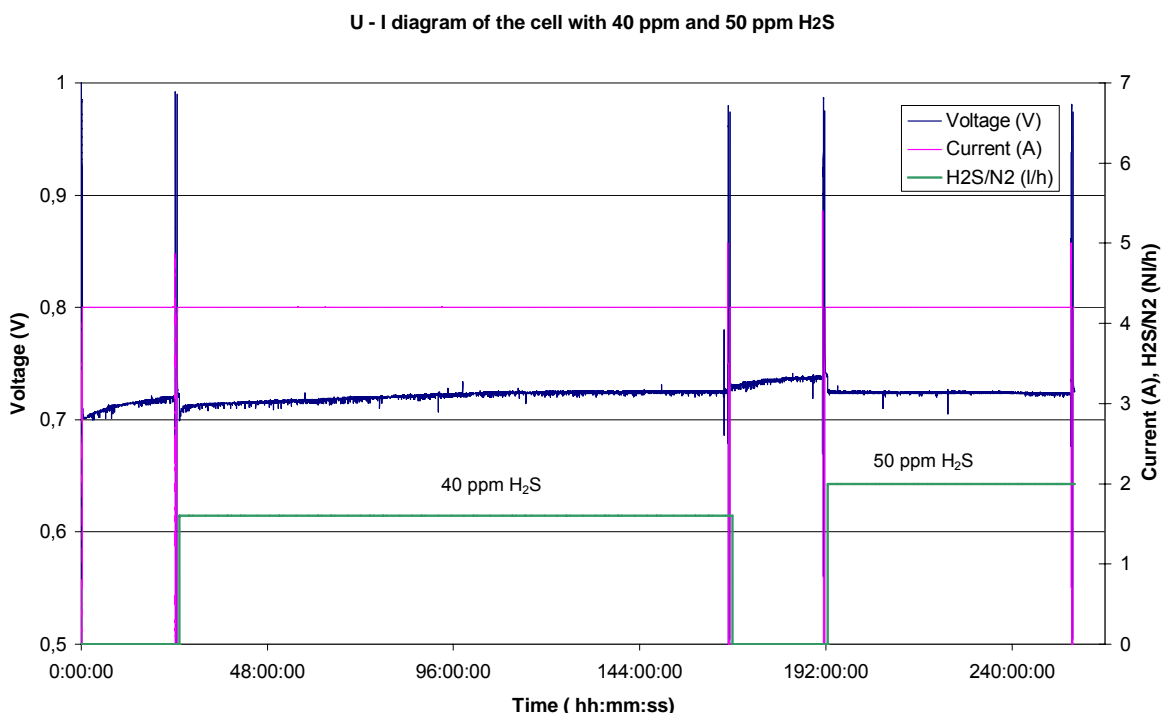


Figure 7 Voltage current diagram of the cell as a function of time with reformate gas composition and 40 ppm and 50 ppm H₂S at 850 °C.

The effect of higher H₂S concentrations on cell voltage is given in Figure 7. The experiment was done with a constant current density of 260 mA/cm². The test continued for 250 hours. Till about 100th hour, there was a cell voltage increase because of the activation of the electrodes and decrease of contact resistances as explained before. Similar to lower H₂S concentration tests, there was an immediate voltage drop from 0.72 V to 0.711 V by adding 40 ppm H₂S. Upon removing H₂S from the fuel gas, the cell voltage started to recover. With the addition of 50 ppm, the cell voltage decreased again and was stable for 60 hours.

Further tests are done with H₂, H₂O and N₂ gas mixture in order to find the behaviour of the poisoning without carbon containing gases. Figure 8 shows the voltage current diagram of another cell run with 45/5/50 vol % H₂/H₂O/N₂ respectively. The experiment is performed under constant current density of 320 mA/cm² at 1123K. H₂S is exposed to the cell with concentrations from 2 ppm to 50 ppm stepwise.

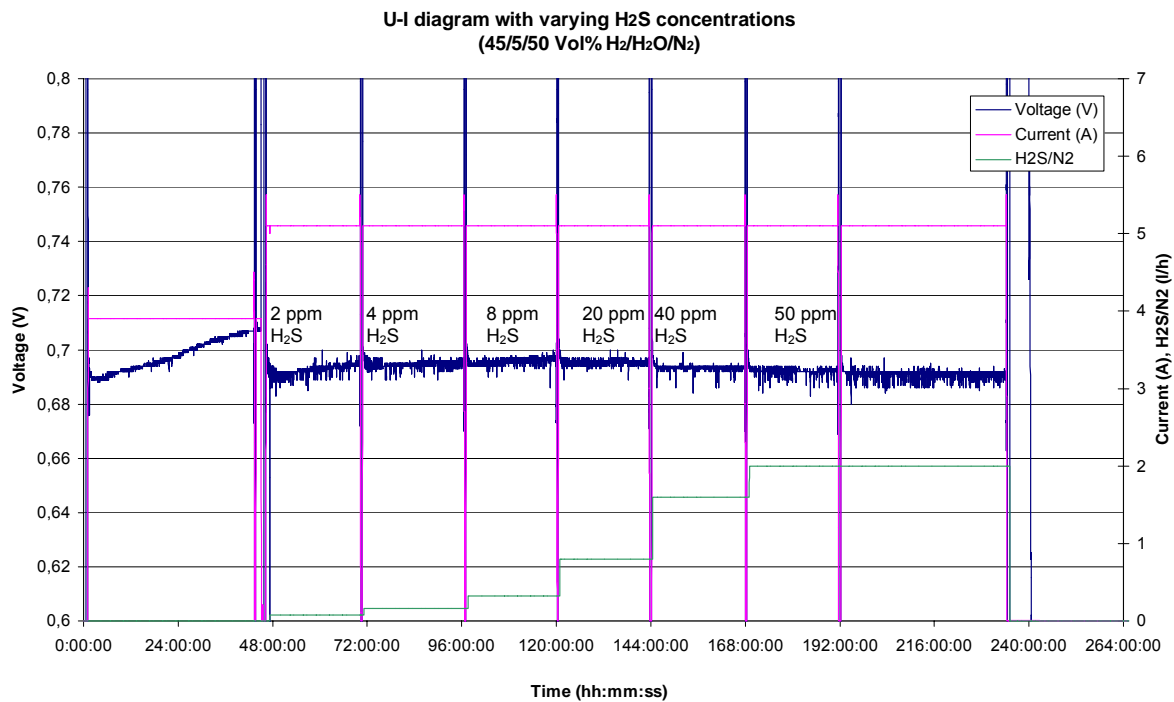


Figure 8 Cell voltage and current as a function of time at 850 °C with given gas composition and various H₂S concentrations.

The overall cell voltage degradation rate calculated for 190 hours (without the cell activation time) is 1.2 %. It could be seen that the voltage slightly increases till 144. hour even with addition of 20 ppm H₂S. This was caused by the activation of the cell. After this point, with the addition of 40 ppm H₂S there was a voltage drop from 0.695 V to 0.693 V and with the addition of 50 ppm H₂S from 0.693 V to 0.692 V. The cell had a stable voltage and no additional degradation is observed till the end of the experiment. The stack is then cooled down with the forming gas to the room temperature with 2K/min. An XRD analysis of the cell is done.

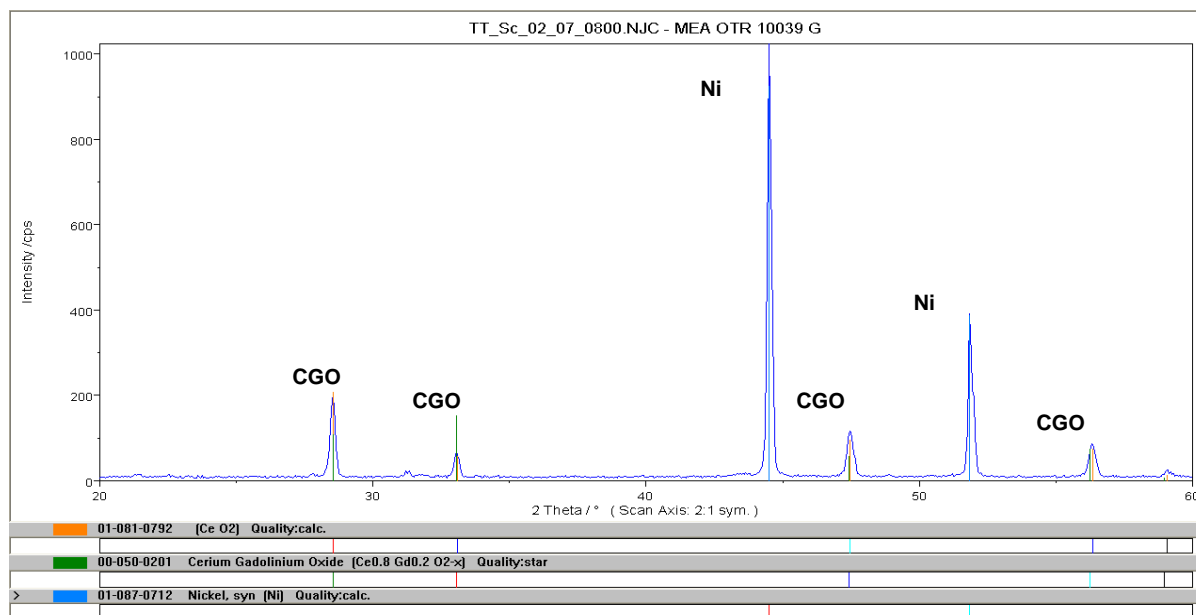


Figure 9 The XRD pattern of the anode after exposure to H₂S at 850°C. No nickel sulphide peaks are observed.

Figure 9 shows the XRD pattern taken from the sample after it was exposed to the fuel mixture H₂/45 vol%, H₂O/5 vol%, N₂/50 vol% with varying H₂S concentrations at 850 °C for 240 hours. The XRD pattern of the anode shows that there are no nickel sulphide phase formations in the anode.

The analysis verifies that under given experimental conditions the H₂S adsorption on the anode surface was reversible. Although no regeneration occurred after H₂S exposing, the cell could regenerate itself during cooling down with the forming gas.

The analysis of the cell with the electrochemical impedance spectroscopy shows very similar Nyquist plots for each H₂S concentration added to the fuel gas (Fig 10).

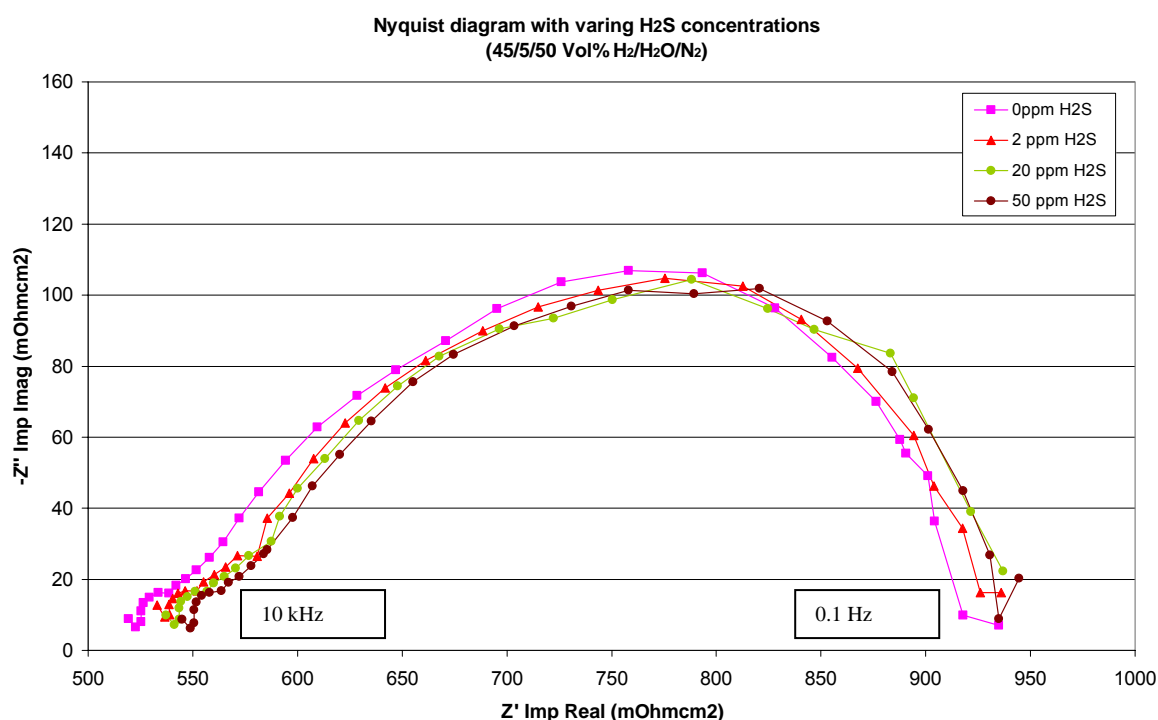


Figure 10 Impedance spectra of the cell exposed to H₂/H₂O/N₂ gas mixture with varying H₂S concentrations.

The ohmic resistances of the samples remain between 545 – 560 mOhmcm². The ohmic resistance in fuel with 0 ppm H₂S has the lowest value when compared to the other Nyquist plots which shows that there is a slight worsening of the contacting. However at lower frequency ranges, no difference could be seen between the other samples. According to the Nyquist plots, there was no deactivation of the cell even during 50 ppm H₂S addition.

In order to find out the effect of the partial pressure of oxygen on H₂S poisoning, the water amount of the fuel gas is increased to 10 vol%. It is known that the reaction of the nickel with sulphur is favourable as the temperature and hydrogen partial pressure decrease. It is also predicted that the reaction of the ceria with sulphur becomes favourable as partial pressure of oxygen decreases and temperature increases [5].

The experiment is done with a new stack with fuel gas composition H₂/40 vol%, H₂O/10 vol%, N₂/50 vol% with varying H₂S concentrations at 850°C for 300 hours with regeneration step.

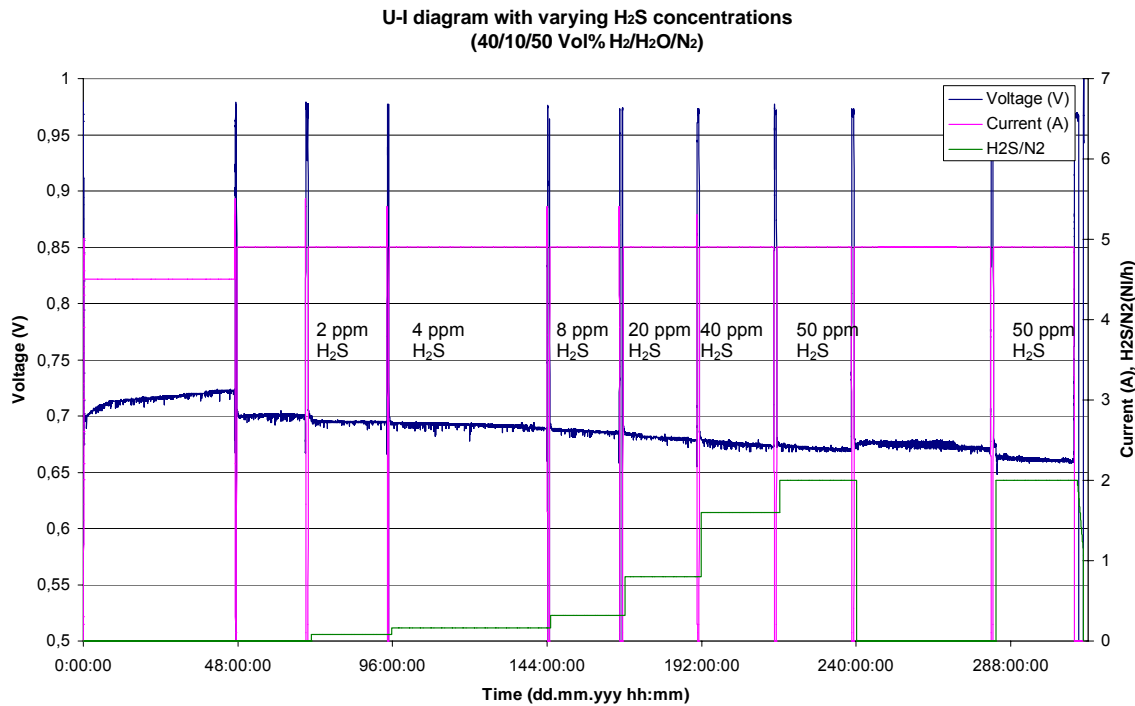


Figure 11 Voltage current diagram of the cell as a function of time.

The voltage-current diagram of the cell with 0.3 mA/cm² current density with the given concentrations is shown in Figure 11. The cell ran for 70 hours without H₂S addition in order to have a complete activation of the cell and a constant voltage. A degradation of the cell voltage from 0.7 V to 0.694 V after addition of 2 ppm H₂S is observed. No additional degradation of the cell is observed within the next 24 hours. As the given H₂S concentration has been increased, the cell power began to degrade. After returning to initial conditions at 240 hour, the cell voltage increased from 0.671 V to 0.676 V. However, the cell voltage decreased continuously even no H₂S addition to the fuel gas took place.

At the end of the experiment, the cell is cooled down to the room temperature with forming gas with 2K/min. The XRD analysis of the anode is done in order to see if there is any nickel sulphide formation in the cell (Fig 12).

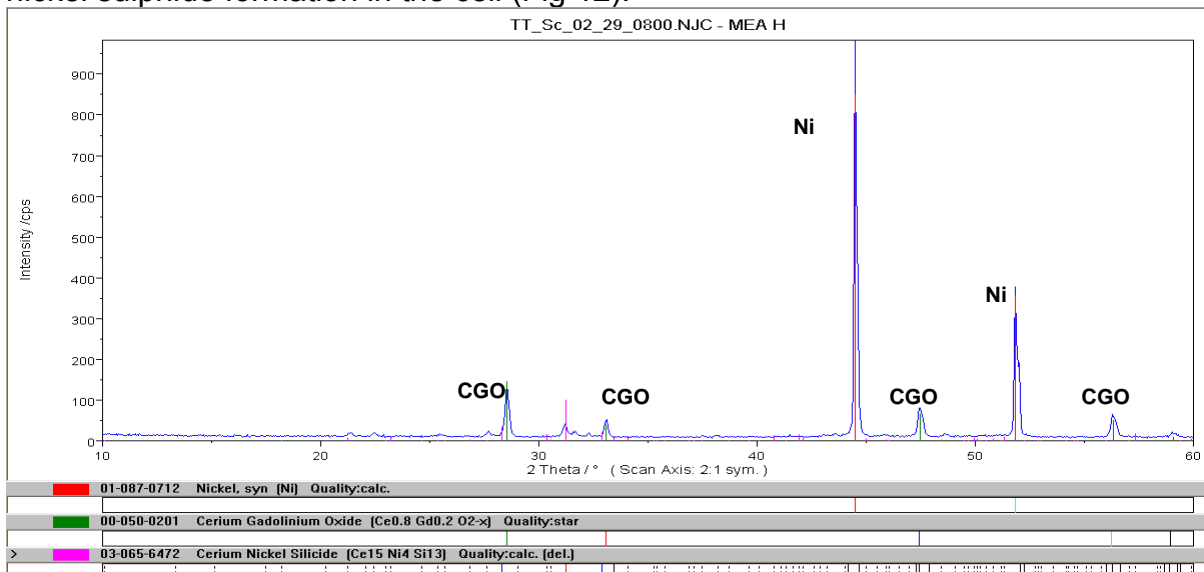


Figure 12 The XRD pattern of the anode after exposure to H₂S at 850°C. No nickel sulphide peaks are observed.

The analysis of the impedances of the cell with varying H₂S concentrations indicates similarities with the previous studies (Fig 13).

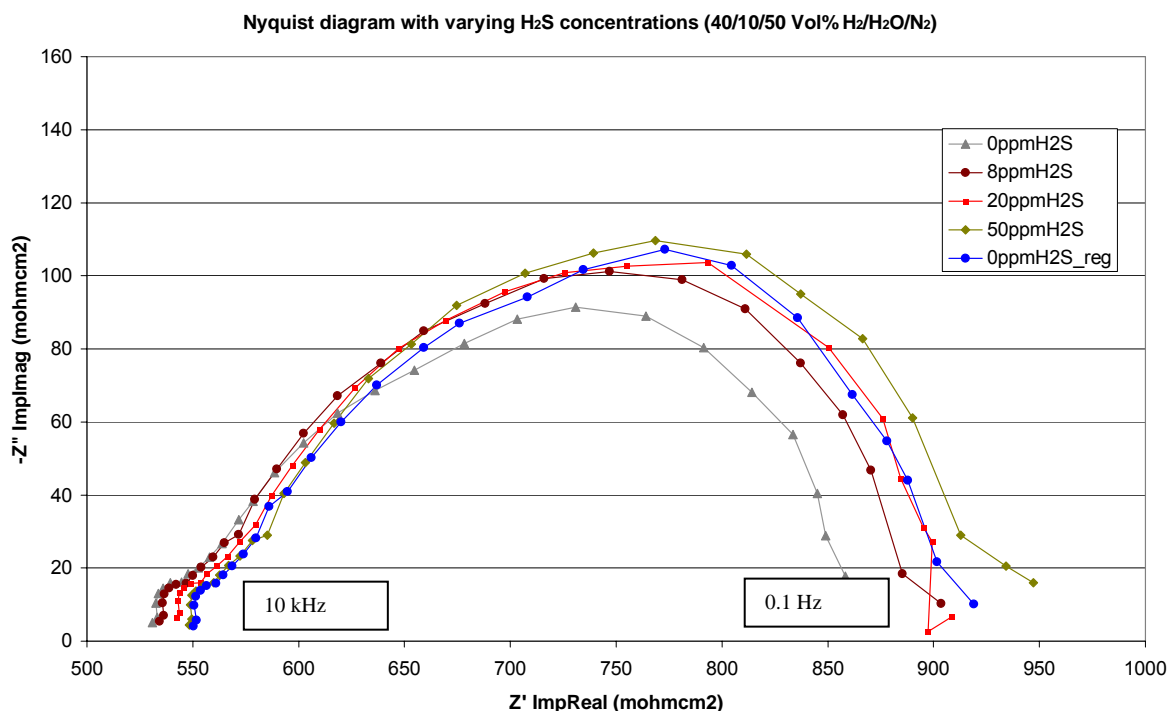


Figure 13 Impedance spectra for the cell running at 850°C with 0 to 50 ppm H₂S.

As shown in Figure 13, at high frequencies, there were no differences between the impedances during the experiment. The ohmic resistances of the samples remain constant between 550 – 560 mOhmcm². However, the impedance behaviour shows the increase of the overall resistance of the cell while the ohmic resistance remains constant at each concentration level. This indicates that the cell degradation is only caused by deactivation of the electrode processes, but the influence of the anode and the cathode can not be separated. Post-examination of the stack revealed evidence of leakages which caused the oxidation of the anode. For this reason it is not clear whether degradation of the cell was caused by H₂S or other factors.

Conclusion

It was found that the contamination of the cell with up to 50 ppm hydrogen sulphide causes no continuous voltage degradation in the cell with reformat gas composition and with 45/5/50 Vol % H₂/H₂O/N₂ respectively at 850 °C. The cell voltages decreased rapidly after the H₂S additions followed by a stable cell voltage under this poisoning conditions. By withdrawing the hydrogen sulphide from the gas composition a slower voltage recovery followed. The effect of the sulphur poisoning was mostly observed by the initial H₂S addition even though the H₂S concentration was low since the coverage of the anode surface by sulphur atoms reaches to high values even at lower H₂S concentrations. Work will now focused on the effect of oxygen partial pressure on the sulphur poisoning of the cell and the effect of higher H₂S concentrations. More experiments are needed to be done in order to have reproducible results and understanding the poisoning mechanism.

References

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