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Alexander Michaelis (Hrsg.)

Sena Kavurucu Schubert

**Effects of hydrogen sulfide in fuel gas
on SOFC stack performance with nickel
containing anodes**

Fraunhofer-Institut für
Keramische Technologien und Systeme IKTS

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Prof. Alexander Michaelis

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Fakultät Maschinenwesen
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Effects of hydrogen sulfide in fuel gas on SOFC stack performance with nickel containing anodes

Dissertation

zur Erlangung des Akademischen Grades
Doktoringenieur
(Dr.-Ing.)

vorgelegt von

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Abbreviations

10CGO	10 mol % Gd_2O_3 doped CeO_2
3YSZ10Sc1CeSZ	50 wt % 3 mol % Y_2O_3 doped ZrO_2 , 50 wt % 10 mol % Sc_2O_3 and 1 mol % CeO_2 doped ZrO_2
3YSZ	3 mol % Y_2O_3 doped ZrO_2
8YSZ	8 mol % Y_2O_3 doped ZrO_2
AFC	Alkaline fuel cell
ASC	Anode supported cell
BSE	Backscattered electrons
BET	Brunauer-Emmett-Teller method for calculating specific surface area
Cermet	Ceramic-metal composite
CFY	CrFe5 alloy from Plansee SE
CHP	Combined heat and power
C_xH_y	Hydrocarbons
DFT	Density functional theory
DRT	Distribution function of relaxation times
EDX	Energy-dispersive X-ray spectroscopy
EIS	Electrochemical impedance spectroscopy
ESC	Electrolyte supported cell
FESEM	Field emission scanning electron microscope
GDC	Gadolinium doped ceria
IKTS	Institute for ceramic technologies and systems
LEED	Low energy electron diffraction
LDC	$\text{La}_{0.4}\text{Ce}_{0.6}\text{O}_{1.8}$
LNG	Liquefied neutral gas
LPG	Liquefied petroleum gas
LSGM	$\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{3-\delta}$
LSM	$\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3+\delta}$
LSV	$\text{La}_{1-x}\text{Sr}_x\text{VO}_{3+\delta}$
MCFC	Molten carbonate fuel cell
MEA	Membrane electrode assembly
MFC	Mass flow controller

MFM	Mass flow meter
MIEC	Mixed ionic-electronic conductivity
MSC	Metal supported cell
NG	Natural gas
OCV	Open circuit voltage
PAFC	Phosphoric acid fuel cell
PEMFC	Polymer electrolyte membrane fuel cell
PLC	Programmable logic controller
REM	Raster electron microscopy
SE	Secondary electrons
SOFC	Solid oxide fuel cell
SRN	Straight run naphtha
SSZ	Sc ₂ O ₃ doped ZrO ₂
SYT	Sr _{0.88} Y _{0.08} TiO _{3-δ}
TEC	Thermal expansion coefficient
TGA	Thermogravimetric analysis
THT	Tetrahydrothiophene
TOF-SIMS	Time-of-flight secondary ion mass spectrometry
TPB	Triple phase boundary
XAS	X-ray absorption spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

Symbols

Latin

Symbol	Unit	Name
A	cm ²	surface area
c	mol/l	concentration
D	m ² /s	diffusion coefficient
f	Hz	frequency
F_U	1	fuel utilization
G	J	Gibbs free energy
H	J	enthalpy
j	A/cm ²	current density
i	1	imaginary unit (impedance)
I	A	current
I_F	A	maximum current available from electrochemical conversion
k	1/s	rate constant parameter (1. order)
l	m	length
m	g	weight
M	g/mol	standard atomic weight
n	mol	number of moles participating in a reaction
$\dot{n}$	mol/s	molar flow rate
O_O^x	mol/m ³	oxygen ion concentration in solid oxide
p	Pa	pressure
P	W	power
Q	As	charge
R	Ω	ohmic resistance
R_{Area}	Ωcm ²	area specific resistance
S	J/(molK)	entropy
t	s, h, min	time
T	°C , K	temperature
U	V	cell potential
V	m ³	volume
V_O''	mol/m ³	oxygen vacancy concentration in solid oxide
z	1	number of electrons transferred in a reaction
Z	Ω	total electrical impedance
Z'	Ω	real part of the impedance

Z''	Ω	imaginary part of the impedance
-------	----------	---------------------------------

Greek

Symbol	Unit	Name
α_{TEC}	1/K	thermal expansion coefficient
β	1	charge transfer coefficient
δ	m	thickness of diffusion layer
ε	1	efficiency
η	V	polarization
θ	1	fractional coverage of nickel surface
μ_i	J/mol	chemical potential
σ_i	S/cm	oxygen ionic conductivity
ϕ	°	phase shift
ω	1/s	angular frequency

Indices

Symbol	Name
*	adsorbed intermediate
Ω	ohmic
0 (subscript)	initial
0 (superscript)	standard conditions
act	activation
ad	adsorption
A	area
An	anode
B	bulk
C	capacitance
Cat	cathode
con	contaminated
conc	concentration
ch	chemical
e^-	electrons
el	electrical
El	electrolyte
f	formation
g	gas
imag	imaginary

I	limiting
L	inductance
lin	linear
Ni	nickel
O	oxygen
OC	open circuit
Ph1	phase 1
p	isobar
r	reaction
R	resistor
real	real
reg	regeneration
S	surface
sat	saturation
therm	thermodynamic
tot	total

Constants

Symbol	Unit	Name
F	96485 As/mol	Faraday constant
R	8.314 J/(molK)	Universal gas constant

1 INTRODUCTION

1.1 Motivation

The world's continually increasing demand for energy combined with concern for climate change motivates us to develop innovative methods to achieve more efficient energy conversion with low emissions. Increasing the efficiency of systems consuming conventional fossil fuels as well as developing energy systems using renewable sources are some of the efforts to reach this goal.

Fuel cells can be one of the solutions to reach higher efficiencies since the operating limits imposed by the second law of thermodynamics are much less severe than for conventional energy conversion systems [Mit10].

Solid oxide fuel cells can be used for many applications such as stand-alone auxiliary power units or due to their high operating temperatures (between 600 °C and 1000 °C) they can also be coupled with gas turbines or modified to form combined heat and power (CHP) systems. The electrical efficiency of conventional power systems reaches 30 – 35 % [Ono06] whereas SOFC electrical efficiencies of up to 60 % have already been demonstrated [Lov09]. The total efficiency of an SOFC-CHP can even reach 80 % [Ono06] since the produced heat can also be utilized for heating purposes.

Due to their high operating temperature, wide varieties of fuels such as hydrogen, carbon monoxide, hydrocarbons, alcohols as well as synthesis gases from natural gas, biogas and petroleum can be used to fuel SOFC. The possibility of using such a wide range of fuels unfortunately introduces the risk of unwanted impurities, which can affect the function of the SOFC and the efficiency of an SOFC system. One of the known impurities is sulfur and fuels such as natural gas or biogas nearly always contain small amounts of sulfur. Sulfur is a well known catalyst poison and may also poison the electrodes of fuel cells.

The following work deals with the effect of sulfur containing fuel gas on the SOFC stack performance under various conditions; as well as regeneration processes and their underlying mechanisms.

1.2 Objectives

SOFC is an electrochemical conversion device and the heart of this device, the electrochemically active part, is called a MEA (Membrane Electrode Assembly). MEA is composed of an electrolyte and two electrodes: anode and cathode. At high temperatures (600 °C – 1000 °C) the electrolyte becomes conductive for oxygen ions. In the cathode, oxygen is reduced into oxygen ions. The oxygen ions are transferred through the electrolyte and electrochemically oxidize the fuel in the anode. During this reaction, electrons are released. Electrons flow through an

external circuit to the cathode to reduce the oxygen into oxygen ions and the cycle repeats.

When there is sulfur in the fuel, the electrochemical oxidation process in the anode cannot be fully completed since sulfur blocks the electrochemically active sites. The amount of released electrons decreases, and accordingly the electrical power and the efficiency of SOFC decreases.

Every anode material reacts differently to sulfur. The most commonly used anodes contain nickel and are responsive to sulfur in the fuel. In this work, the sulfur poisoning of Ni/8YSZ anodes and Ni/10CGO anodes was investigated.

Although SOFCs and particularly sulfur poisoning mechanisms have been investigated for some years, the understanding of especially the reasons of irreversible poisoning remains limited.

The following questions should be answered with this work:

- How does sulfur affect the performance of an SOFC stack?
- How can a sulfur poisoned stack be regenerated?
- What are the effects of conditions such as sulfur concentration, fuel composition, contamination duration and SOFC current density on poisoning?
- What are the differences of SOFCs with Ni/8YSZ and Ni/10CGO anodes with respect to sulfur poisoning?
- What are the mechanisms behind sulfur poisoning and regeneration?

The answers to these questions may help to develop sulfur resistant SOFCs and SOFC system operating strategies with respect to poisoning.

To fulfill these objectives SOFC stacks were investigated systematically. Single cell SOFC stacks as well as an SOFC stack test bench were constructed for this purpose. A minimized model of an SOFC stack (rather than the MEA alone) was investigated in order to maintain as much similarity as possible to real-world conditions. Thermodynamic calculations and in-situ and ex-situ analysis techniques were applied to understand the underlying mechanisms.

2 FUEL CELL FUNDAMENTALS

2.1 Types of fuel cells

A fuel cell is an electrochemical device that converts chemical energy in fuels directly into electrical energy by combining a gaseous fuel and an oxidizing gas electrochemically through an ion conducting electrolyte [FCH04]. Fuel cells differ from conventional electrochemical batteries which convert stored chemical energy to electrical energy whereas fuel cells can be operated with continually supplied gaseous fuel and an oxidation medium. Theoretically there is no limiting endurance. Compared with conventional combustion devices, fuel cells are capable of achieving higher efficiencies since they do not operate on thermal cycles. The limiting Carnot efficiency is therefore irrelevant. Fuel cells operate at constant temperature and pressure, for this reason maximal useful work is equal to free enthalpy.

A fuel cell with three components; anode, electrolyte and cathode; is the electrochemically active part of a fuel cell system. There are five common fuel cell types which differ in materials, operating temperatures and the electrochemical reactions. Fuel cells are classified by the applied electrolyte. In Table 2.1, the types of the fuel cells and some of their features are listed in order of increasing operating temperature.

Table 2.1 Comparison of fuel cells [Dre93]. (PEMFC: Polymer Electrolyte Membrane Fuel Cell, AFC: Alkaline Fuel Cell, PAFC: Phosphoric Acid Fuel Cell, MCFC: Molten Carbonate Fuel Cell, SOFC: Solid Oxide Fuel Cell)

Fuel Cell	Common Electrolyte / Ion conducting	Operating Temperature	Fuel	Applications
PEMFC	Polymeric Ion Exchange Membrane / H^+	50 – 100 °C	H_2	Backup power Portable power Small-distributed generation Transportation Speciality vehicles
AFC	Aqueous solution of potassium hydroxide soaked in a matrix (KOH) / OH^-	90 – 100 °C	H_2	Military Space
PAFC	Liquid phosphoric acid soaked in a matrix (H_3PO_4) / H^+	150 – 200 °C	H_2	Distributed generation
MCFC	Liquid solution of lithium, sodium, and/or potassium carbonates, soaked in a matrix (Li_2CO_3 , K_2CO_3 , Na_2CO_3) / CO_3^{2-}	600 – 700 °C	CO , H_2	Electric utility Large distributed generation
SOFC	Yttria stabilised zirconia (YSZ) / O^{2-}	600 °C – 1000 °C	H_2 , CO , C_xH_y	Auxiliary power Electric utility Large distributed-generation

2.2 Thermodynamics of SOFCs

In solid oxide fuel cells, the nonporous oxygen ion conducting electrolyte separates the air (oxygen) in the cathode from the fuel gas rich in hydrogen (H_2) and carbon monoxide (CO) in the anode and prevents a direct oxidation reaction. The oxygen ions diffuse through the electrolyte due to the chemical potential difference between both sides of the electrolyte and then react with hydrogen and carbon monoxide.

The following electrochemical reactions take place with hydrogen and carbon monoxide fuel in the anode:



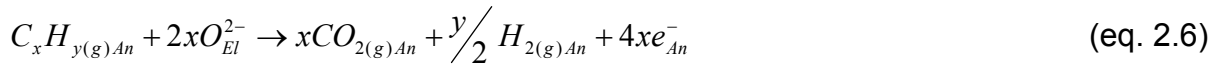
and in the cathode:



with overall reactions:



When hydrocarbons are present in the fuel, they may be reformed in the anode to H_2 and CO or may directly react with diffused O^{2-} ions with the following reaction:



Whether this reaction takes place or not depends on the operating conditions such as temperature, gas composition and catalyst type [Fra09].

When oxygen ions diffuse from the cathode to the anode due to the difference in the partial pressures, an electrical field will be induced in open circuit conditions since the electrolyte is electrically an isolator (Figure 2.1). This electrical field compensates the diffusion of oxygen ions from the cathode to the anode. The open circuit voltage (OCV) of a cell is the potential difference where no oxygen ion transport occurs.

If fuel cell is considered to be a closed system, this potential difference can be determined by the Gibbs free energy. In case of an SOFC, Gibbs free energy equals to the electrical work to move a charge (Q) through an electrical potential difference. The moving charges here are the electrons and it is convenient to use moles of electrons. For z moles of electrons the charge (Q) can be written as:

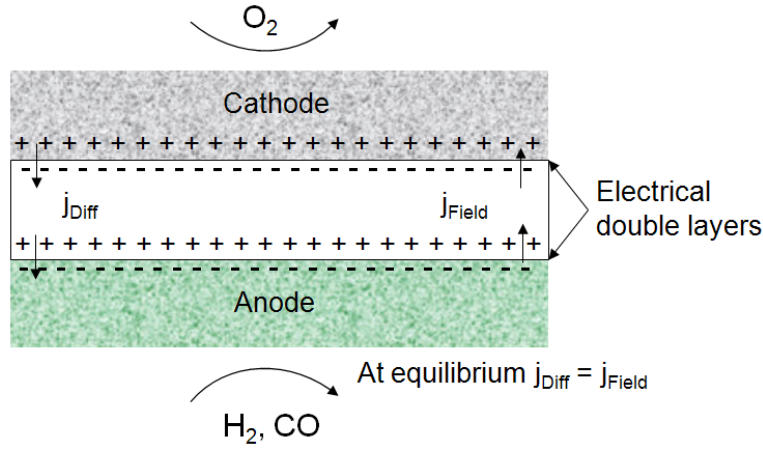


Figure 2.1 Development of electrical double layers (modified from [Tif00]).

$$Q = -z \cdot F \quad (\text{eq. 2.7})$$

where F is the Faraday constant (96485 C/mol).

If the Gibbs free energy is defined as:

$$\Delta G^0 = -z \cdot F \cdot U^0 \quad (\text{eq. 2.8})$$

then

$$U^0 = -\frac{\Delta G^0}{z \cdot F} \quad (\text{eq. 2.9})$$

where ΔG^0 is the standard Gibbs free energy change and U^0 is the standard reversible cell potential at standard conditions of $T = 293.15$ K and $P = 101.325$ kPa. This statement represents the highest possible electrical work output by any fuel cell device.

The Gibbs free energy of the cell depends on the equilibrium constant of the reaction due to the change of the partial pressures of the reaction components from standard pressure:

$$\Delta G = \Delta G^0 + R \cdot T \cdot \ln K_p \quad (\text{eq. 2.10})$$

where R is the gas constant, T is the temperature and K_p is the equilibrium constant for the overall reaction with hydrogen fuel:

$$K_p = \frac{p_{H_2O}}{p_{H_2} \cdot p_{O_2}^{1/2}} \quad (\text{eq. 2.11})$$

Thus the thermodynamic cell voltage is calculated with the equation:

$$U_{therm} = -\frac{\Delta G^0 + R \cdot T \cdot \ln K_p}{z \cdot F} = U^0 - \frac{R \cdot T}{z \cdot F} \ln K_p \quad (\text{eq. 2.12})$$

The cell voltage for the reaction (eq. 2.3) is then calculated through Nernst equation:

$$U_{therm} = U^0 - \frac{R \cdot T}{2 \cdot F} \ln \left(\frac{P_{H_2O}}{P_{H_2} \cdot P_{O_2}^{1/2}} \right) \quad (\text{eq. 2.13})$$

Similarly if CO is used as the fuel, the cell potential can be calculated as follows:

$$U_{therm} = U^0 - \frac{R \cdot T}{2 \cdot F} \ln \left(\frac{P_{CO_2}}{P_{CO} \cdot P_{O_2}^{1/2}} \right) \quad (\text{eq. 2.14})$$

2.3 Fuel cell efficiency

A fuel cell converts chemical energy directly into electrical energy. In the ideal case, the change in Gibbs free energy (ΔG) is available as useful electrical energy at the given operating temperature. The ideal efficiency is then the thermodynamic efficiency (ε_{therm}). The efficiency of a fuel cell is however always less than the theoretical thermodynamic efficiency owing to irreversible kinetic effects in the fuel cell. In this case, the voltage efficiency ($\varepsilon_{voltage}$) should be taken into account. For both of these efficiencies, it is considered that the fuel is completely converted. In reality, the fuel utilization is always less than hundred percent which is referred as current efficiency (ε_{fuel}).

The total cell efficiency is the multiplication of these factors and formulated by the following expression:

$$\varepsilon_{tot} = \varepsilon_{therm} \cdot \varepsilon_{voltage} \cdot \varepsilon_{fuel} \quad (\text{eq. 2.15})$$

In reality, the efficiency of the fuel cell system is affected by further components such as the reformer, cooling, gas supply unit, etc. For this reason, the total electrical efficiency ($\varepsilon_{el,real}$) of a fuel cell system is defined as the ratio of the electrical power output to the chemical energy input per unit of time:

$$\varepsilon_{el,real} = \frac{P_{el,real}}{P_{ch}} \quad (\text{eq. 2.16})$$

The following parts give detailed information on thermodynamic (ε_{therm}), voltage ($\varepsilon_{voltage}$), current (ε_{fuel}) and total electrical efficiencies (ε_{el}).

2.3.1 Thermodynamic efficiency

In SOFCs the free enthalpy change of the cell reaction ΔG may be totally converted to electrical energy. The thermodynamic efficiency (ε_{therm}) is then the highest efficiency to achieve:

$$\varepsilon_{therm} = \frac{\Delta G}{\Delta H} = \frac{\Delta H - T \cdot \Delta S}{\Delta H} \quad (\text{eq. 2.17})$$

where ΔH is the enthalpy change of the reaction, T is the temperature and ΔS is the change in entropy.

With this formula the maximum thermodynamic efficiencies for H_2 , CO and CH_4 fuels are calculated (Figure 2.2). According to calculations using H_2 fuel increases the efficiency when compared with CO fuel whereas both decrease with increasing temperature. The highest thermodynamic efficiency was observed with methane fuel (about 100 %) for the given temperature region.

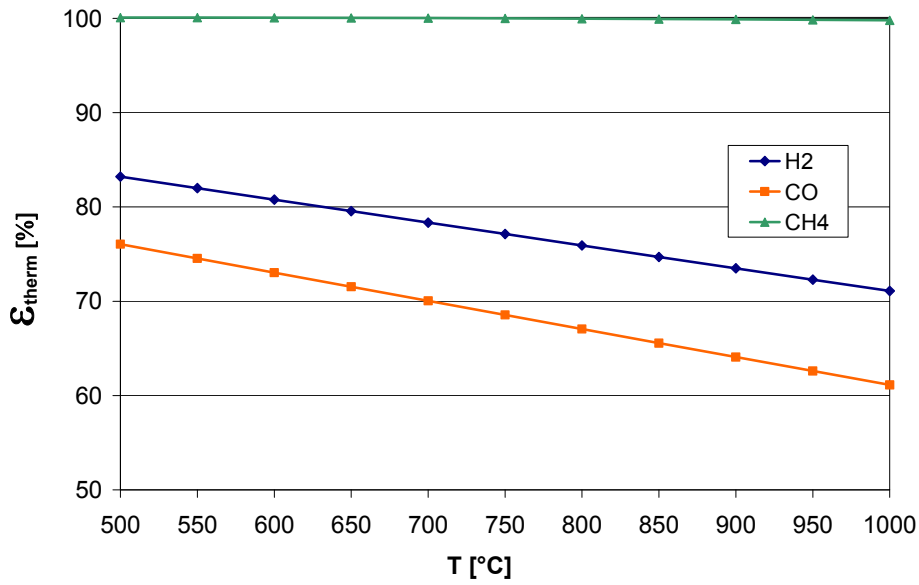
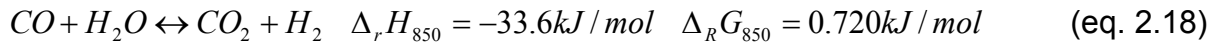


Figure 2.2 Calculated thermodynamic efficiencies with thermodynamic data from Barin [Bar93].

It should be considered that the water-gas shift reaction also takes place at SOFC operating temperatures besides the electrochemical oxidation of CO in the anode:



CO causes higher anodic concentration polarization and slower electrochemical oxidation at the anode when compared with H_2 [Jia03].

2.3.2 Voltage efficiency

The voltage efficiency ($\varepsilon_{voltage}$) of the fuel cell can be expressed as the ratio of the operating cell voltage to the thermodynamic cell voltage.

$$\varepsilon_{voltage} = \frac{U_{real}}{U_{therm}} \quad (\text{eq. 2.19})$$

Voltage efficiency of the fuel cell incorporates the losses due to irreversible kinetic effects in the fuel cell.

In open circuit conditions the cell voltage can deviate from the theoretical cell voltage where the difference is called overvoltage. The main reason for overvoltage is the insufficient catalytic activity of the electrodes. Other reasons are the possible electrical conductivity of the electrolyte and gas leakages. The ratio of the overvoltage to the overall losses in solid oxide fuel cells is relatively small in a solid oxide fuel cell [Tif00].

When the fuel cell starts to supply electrical current to an external load the cell voltage decreases because of irreversibilities owing to internal resistances.

$$U_{real} = f(\eta_{\Omega}, \eta_{act}, \eta_{conc})$$

The difference between the maximum reversible cell voltage and the operating cell voltage is called polarization loss (η) and depends on the current density and factors such as temperature, pressure, gas flow rate and cell material [Boe98]. The total polarization loss of a cell consists of three types of polarizations:

- Ohmic polarization (η_{Ω}) (losses due to electronic and ionic conduction)
- Activation polarization (η_{act}) (losses due to electrochemical reaction)
- Concentration polarization (η_{conc}) (losses due to mass transport)

and is defined as:

$$\eta = \eta_{\Omega} + \eta_{act} + \eta_{conc} \quad (\text{eq. 2.20})$$

The *ohmic polarization* (η_{Ω}) is the straightforward resistance to the flow of ions through the electrolyte as well as to the flow of electrons through the electrodes and the various contacting materials [FCS01]. Ohmic loss (η_{Ω}) is linear and is proportional to the current density and obeys Ohm's law:

$$\eta_{\Omega} = I \cdot R_{tot} \quad (\text{eq. 2.21})$$

where I is the current and R_{tot} is the total ohmic cell resistance. The total ohmic cell resistance includes electronic, ionic and contact resistances [FCH04]:

$$R_{tot} = R_{electronic} + R_{ionic} + R_{contact}$$

Ohmic losses are minimized by producing electrolytes as thin as possible and applying high conductivity materials [O'Ha06].

Activation polarization (η_{act}), also called charge transfer polarization, is the energy required to reduce the energy barrier of a rate-determining step for an electrochemical reaction (activation energy) in the electrodes that is due to the transfer of charges between the electronic and ionic conductors.

Activation polarization is expressed by the Butler-Volmer equation [Bel68]:

$$j = j_0 \left(\exp \left(\beta \cdot \frac{z \cdot F \cdot \eta_{act}}{R \cdot T} \right) - \exp \left(-(1 - \beta) \cdot \frac{z \cdot F \cdot \eta_{act}}{R \cdot T} \right) \right) \quad (\text{eq. 2.22})$$

where β is the charge transfer coefficient, j_0 the exchange current density, η_{act} is the activation polarization and F the Faraday constant. Solving this equation for η_{act} yields:

$$\eta_{act} = -\frac{R \cdot T}{\beta \cdot z \cdot F} \cdot \ln j_0 + \frac{R \cdot T}{\beta \cdot z \cdot F} \cdot \ln j \quad (\text{eq. 2.23})$$

This loss is dependent on the reactions, the electrocatalyst material and microstructure, reactant activities and weakly on current density [FCH04]. It manifests itself at the lower current density region as shown in Figure 2.3.

Concentration polarization (η_{conc}), also known as mass transfer polarization, results from the change in the concentration of the reactants at the surface of the electrodes as the fuel is used. This phenomenon is also called as gas transport loss since there the reactants have not been transported – or the products not released fast enough in the electrodes. The concentration polarization is given by the equation:

$$\eta_{conc} = \frac{R \cdot T}{z \cdot F} \cdot \ln \frac{C_0}{C_B} \quad (\text{eq. 2.24})$$

where C_0 is the initial concentration of the reacting species and C_B their concentrations on the electrode surface. The concentration polarization occurs when current density is very high so that the products can not be transported fast enough and reactant concentration is not high enough for electrochemical reactions. It is also dependent on the reactant activity and electrode flow structure and temperature.

Figure 2.3 shows the plot of a typical voltage – current density curve showing all three types of losses.

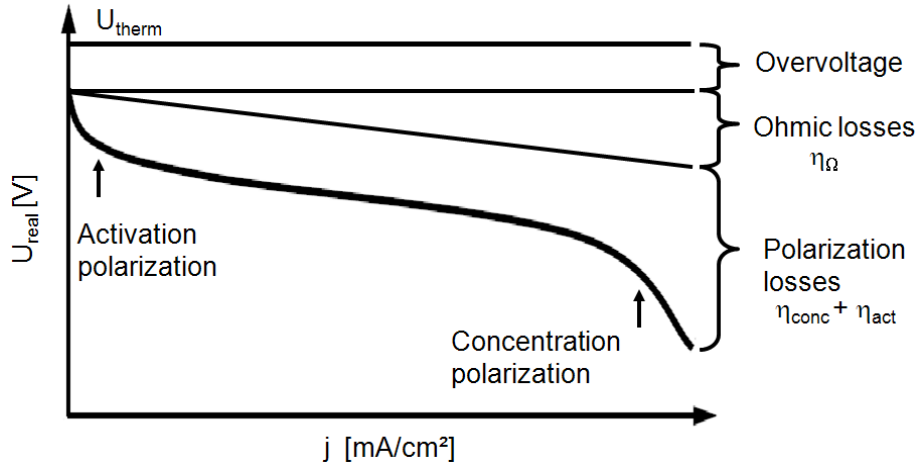


Figure 2.3 A typical voltage-current curve of an SOFC with ohmic and polarization losses.

2.3.3 Current efficiency (Fuel utilization)

When an electrical load is applied to an SOFC, not all fuel is converted to products. Some of the fuel may undergo side reactions which don't produce electrical power or simply flow through the fuel cell which results in a decrease of the cell efficiency. This ratio is called current efficiency (ε_{fuel}) or commonly referred to as fuel utilization (F_U). The current efficiency is defined as:

$$\varepsilon_{fuel} = \frac{I}{I_F} \quad (\text{eq. 2.25})$$

where I is current and I_F is the maximum current available from electrochemical conversion of the complete fuel according to Faraday's law. Stated by Faraday, the electrical current is the result of the number of flowing electrons (charge carriers) per unit of time and is directly proportional to the converted amount of fuel in mole ($\Delta \dot{n}$). For a 100 % fuel utility with H_2 and CO as fuel, the current is then:

$$I_F = 2 \cdot F \cdot \Delta \dot{n}_{H_2} + 2 \cdot F \cdot \Delta \dot{n}_{CO} \quad (\text{eq. 2.26})$$

2.3.4 Total electrical efficiency

The total electrical efficiency of a fuel cell system defines the electrical power output in relation to the energy consumed as in eq. 2.16. The electrical power output (P_{el}) is:

$$P_{el} = I \cdot U \quad (\text{eq. 2.27})$$

and the chemical power input:

$$P_{chem} = \dot{n}_{fuel} \cdot \Delta H_{LHV} \quad (\text{eq. 2.28})$$

where $\dot{n}_{fuel}$ is the molar flow rate and ΔH_{LHV} is the lower heating value of the fuel. The total electrical efficiency is then:

$$\varepsilon_{tot} = \frac{I \cdot U}{\dot{n}_{fuel} \cdot \Delta H_{LHV}} \quad (\text{eq. 2.29})$$

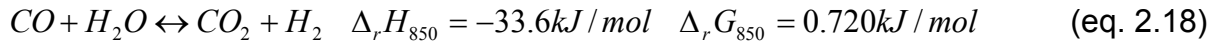
2.4 Gas phase reactions in an SOFC

Due to high temperatures and the presence of a catalyst (nickel) several reactions may take place in SOFC anodes when carbon monoxide and hydrocarbons are also present. The chemical reactions in the anode occur in three regions:

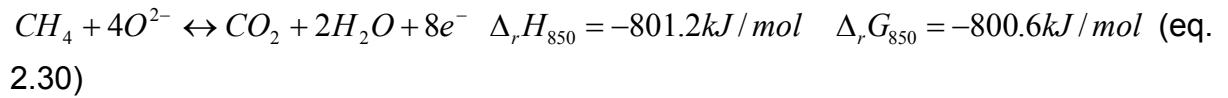
- in the anode channel (gas phase),
- on the surface (heterogeneous catalysis), and
- at the three phase boundaries (electrochemical reactions).

The reactions and their enthalpy and entropy values for 850°C at which the SOFC operates throughout this work are given below.

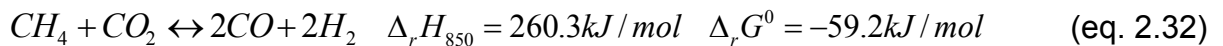
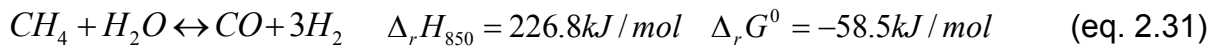
Besides the electrochemical oxidation of carbon monoxide in the anode, CO may take part in the water-gas shift reaction:



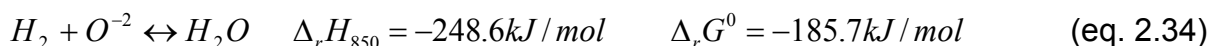
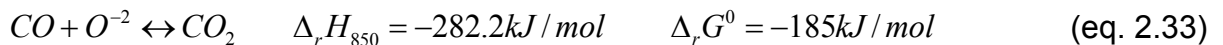
Hydrocarbons may be directly oxidized in the anode as well as internally reformed in the anode. If methane is taken into consideration, there are different options with which reactions it is utilized in SOFCs [Fra09]. It may be directly oxidized in the anode as follows:



Methane may also be internally reformed:

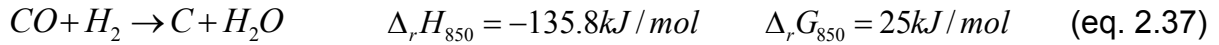
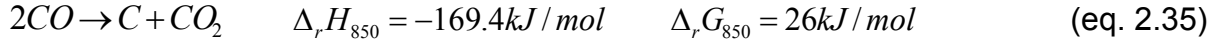


The products of methane reforming, hydrogen and carbon monoxide may then electrochemically oxidize in the anode.



Both of the paths release the same amount of energy.

The catalytic properties of anode is highly important however it should be noted that the activities shouldn't be extended to the promotion of unwanted side reactions such as the Boudouard reaction or hydrocarbon pyrolysis followed by carbon formation as shown in the reactions below:



A fuel gas composition shifts towards thermodynamic equilibrium at high temperatures and with the presence of a catalyst (nickel). In this work, the equilibrium compositions are calculated with the *Equilib* program of *FactSage 6.1* software which uses the Gibbs free energy minimization approach.

The equilibrium composition of a multi component system is reached when the Gibbs free energy of a system is minimized. The Gibbs free energy for a mixture is defined as:

$$dG = V \cdot dp - S \cdot dT + \sum_{i=1} \mu_i \cdot dn_i \quad (\text{eq. 2.38})$$

where μ_i is the chemical potential and n_i the number of moles. The equilibrium in a gas with a constant T and p is defined with the minimum Gibbs energy where dp and dT is 0 with the condition $dG = 0$. Therefore:

$$dG = 0 = \sum_{i=1} \mu_i \cdot dn_i \quad (\text{eq. 2.39})$$

The chemical potential of the each component is:

$$\mu_i = \mu_i^0 + R \cdot T \cdot \ln \frac{p_i}{p_0} \quad (\text{eq. 2.40})$$

where μ_i^0 is the molar Gibbs function of ideal gas i at standard pressure p^0 . Therefore

$$\sum_i \mu_i \cdot dn_i = \sum_i \mu_i^0 \cdot n_i + \sum_i R \cdot T \cdot \ln \left(\frac{p_i}{p_0} \right)^{n_i} = 0 \quad (\text{eq. 2.41})$$

$$\Delta G^0 = \sum_i \mu_i^0 \cdot n_i = - \sum_i R \cdot T \cdot \ln \left(\frac{p_i}{p_0} \right)^{n_i} \quad (\text{eq. 2.42})$$

where ΔG^0 is the standard molar free reaction enthalpy.

$$\Delta G^0 = -R \cdot T \cdot \ln \prod_i \left(\frac{p_i}{p_0} \right)^{n_i} \quad (\text{eq. 2.43})$$

The thermodynamic equilibrium is reached when $\ln \prod_i \left(\frac{p_i}{p_0} \right)^{n_i}$ is equal to the equilibrium constant [Fra09].

2.5 Design and functional layers of an SOFC

The basic electrochemical unit of an SOFC is composed of three layers; a gas tight ionically conductive electrolyte covered on one side by an anode and on the other side by a cathode. The abbreviation MEA (Membrane Electrolyte Assembly) is also used to describe this unit and will be used throughout this thesis. There are several requirements for a MEA: it should hinder the polarizations within the MEA as explained in the previous section; and supply mechanical and chemical stability. The thickness of the electrolyte (ohmic overpotential), the electrode/electrolyte interface (activation overpotential), the thickness, porosity and tortuosity of the anode and cathode (concentration overpotential) are important factors for polarization resistances.

The requirements for a MEA are:

- thermal and chemical stability at high temperatures
- chemical stability at applied gas atmospheres
- minimal reactivity and interdiffusion among different cell components
- matched thermal expansion coefficients
- sufficient ionic and electronic conductivities of the anode and cathode
- sufficient ionic conductivity of the electrolyte
- sufficient porosity of the anode and cathode
- sufficient mechanical stability
- low cost and availability of the chemicals

2.5.1 MEA design

The MEA geometry can vary between a planar design and a tubular design. The planar design is the most applied geometry for SOFCs due to its' higher power density, short current path, higher efficiency, simpler processing methods (e.g. tape

casting, screen printing) and lower cost [Fer09]. There are three main up to date planar design MEA types which are classified according to their mechanical support layer: Electrolyte Supported Cell (ESC), Anode Supported Cell (ASC) and Metal Supported Cell (MSC) (Figure 2.4).

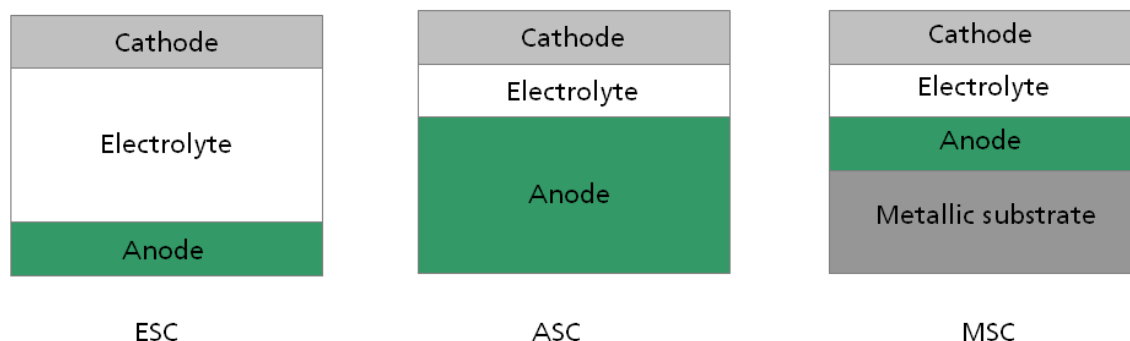


Figure 2.4 Schematic illustration of planar SOFC designs.

The support layer of the ESC design is the electrolyte which is with 100 – 200 μm far thicker than the anode and the cathode layer. The thickness of the electrolyte requires high working temperatures in order to have sufficient oxygen ion conductivity. One of the disadvantages is the increase of the ohmic resistance as the electrolyte thickness increases and the decrease of the mechanical stability as the electrolyte thickness decreases. In the ASC design, the support layer is the porous anode with a thickness of $\sim 300 \mu\text{m}$. The current density of the ASC cell is higher than the ESC cell; however the redox stability of the nickel containing anode is the main disadvantage for this design. A metallic substrate supports the MEA in the MSC design. The substrate provides a high mechanical stability however the diffusion of Fe, Cr and Ni to the anode/substrate boundary layer is the main concern of this design. Even though the use of metallic substrate is economical when compared with ceramic supports, the surface coating of the metallic substrate to avoid the unwanted diffusions increases the costs to similar levels [Mos09].

The tubular design was particularly designed for large, high-power stacks of 100 kW or greater [Fer09] and in recent years has also been used as microtubular cells. The most widely commercialized tubular design is cathode layer supported (e.g. Siemens Westinghouse). However in recent years, anode supported or electrolyte supported tubular cells are also in development for the low scale tubular stacks. The low volumetric power density, long current paths and relatively high production costs (e.g. electrophoretic deposition, extrusion) are some drawbacks of the tubular design. There are studies on the increase of the performance of tubular SOFCs by improving the design (Figure 2.5).

Throughout this work the types of MEAs used were the electrolyte supported (ESC) planar cells.

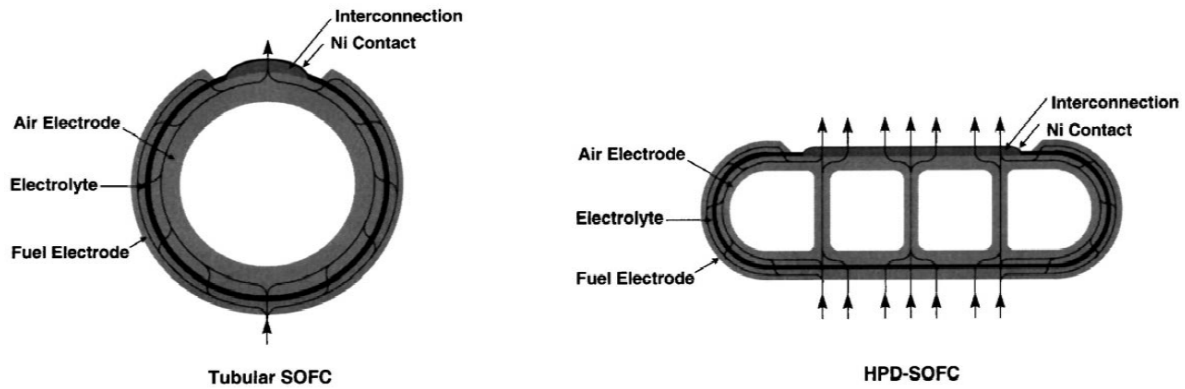


Figure 2.5 Comparison of the current paths in two different tubular SOFC designs [Sin03].

2.5.2 Electrolyte

The electrolyte separates the two gas atmospheres located at the electrodes and thus hinders the spontaneous oxidation reaction of the fuel gas. In order to prevent a short-circuit it also has to have low electronic conductivity. To ensure the electrochemical oxidation reaction, the electrolyte has to provide high oxygen ion mobility between the two electrodes which is provided by thermally activated hopping of oxygen ions from one crystal lattice to its neighbouring site. Furthermore, the electrolyte has to mechanically support the cell in electrolyte supported cells (ESC) and is typically 100 – 300 μm thick [Min95]. For ASC and MSC cells, about 10 μm thickness of the electrolyte is sufficient.

Yttria-stabilised zirconia (Y_2O_3 stabilised ZrO_2 , YSZ) is the most commonly used electrolyte material for SOFCs [Fer06]. Zirconium oxide in its pure form has low ionic conductivity and therefore is not a good electrolyte. It exists in three different structures [Bad92]:

- monoclinic structure at room temperature (m- ZrO_2),
- tetragonal phase at $T \geq 1170^\circ\text{C}$ (t- ZrO_2) and
- cubic fluorite phase at $T \geq 2370^\circ\text{C}$ (c- ZrO_2)

These phase transformations are reversible by cooling the temperature but the transition from c- $\text{ZrO}_2 \rightarrow$ t- ZrO_2 occurs at lower temperatures (950 – 1000 $^\circ\text{C}$) [Fer09]. The volume changes during phase transformations which may cause mechanical stress during thermal cycles. The monoclinic structure has low ionic conductivity and is mainly an electronic conductor. By doping the ZrO_2 with an aliovalent oxide, the high temperature tetragonal and cubic phases stabilize at lower temperatures. The oxygen vacancies increase and thus the ionic conductivity increases. The generation of oxygen vacancies by doping ZrO_2 with Y_2O_3 due to electroneutrality condition can be written in Kröger-Vink notation as follows:



The oxygen vacancy (V''_O) is considered to be transportable and therefore the reason for oxygen ion conduction in stabilized zirconia. The ionic conductivity depends on the used cations (e.g. Y^{3+} , Ca^{2+} , Sc^{3+}) and their concentrations [Mos09]. 8 mol % Y_2O_3 in ZrO_2 is a composition known as having the highest conductivity amongst YSZs and also is supposed to be the minimum amount of yttria required to stabilize the cubic zirconia as is cooled to room temperature [Fer09].

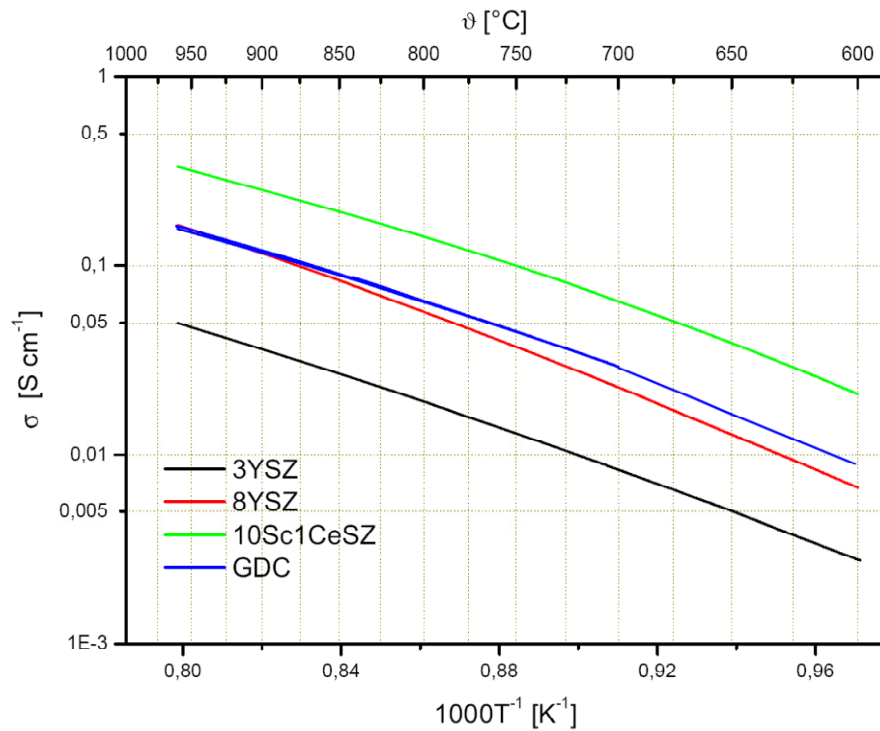


Figure 2.6 Comparison of ionic conductivities of different electrolyte materials between 600 °C – 960 °C [Mos09].

In addition to the conductivities, the mechanical stabilities, thermal expansion coefficients, elastic constants of the electrolytes for ESCs are also of importance. In the following table (Table 2.1) these characteristics are compared for 3YSZ, 8YSZ, CGO and 10Sc1CeSZ type electrolytes.

Table 2.1 Comparison of bending strengths and ionic conductivities of electrolytes (3YSZ: $(Y_2O_3)_{0.03}(ZrO_2)_{0.97}$, 8YSZ: $(Y_2O_3)_{0.08}(ZrO_2)_{0.92}$, 10Sc1CeSZ: $(Sc_2O_3)_{0.1}(CeO_2)_{0.01}(ZrO_2)_{0.89}$) *(from room temperature to 1000 °C) [Mos09], [Yak08].

Properties	3YSZ	8YSZ	CGO	10Sc1CeSZ
Mechanical strength [MPa]	> 1000	> 265	120 - 169	> 250
Elastic constant [GPa]	207	180	200	-
Thermal expansion coefficient [$10^{-6} K^{-1}$]*	11.5	10.5	12.96	-
Ionic conductivity [@850 °C, S/cm]	0.03	0.08	-	0.19

In this thesis the 3YSZ and 10Sc1CeSZ electrolyte supported SOFCs are used.

2.5.3 Cathode

In SOFCs the cathode is the electrode where pure oxygen or oxygen in air is reduced through the following reaction [Adl04]:



The cathode should therefore have high electrocatalytic activity for this reaction. Furthermore it should provide the following features:

- Compatible thermal expansion coefficient with other materials
- Minimal chemical interaction with the electrolyte and interconnect materials during fabrication and operation
- Chemical, phase, microstructural and dimensional stability at high temperatures in oxidizing atmosphere
- High electronic conductivity
- Sufficient porosity for gas transport
- High adhesion to the electrolyte surface and to the current collector
- High long-term stability
- Ease of fabrication and low cost of production

There are several state of the art materials for SOFC cathodes. The perovskites (ABO_3) and noble metals are candidates which have the above listed properties. Due to the high cost of the noble metals, perovskites are in use as cathode materials. The most popular cathode material is Sr-doped LaMnO_3 (LSM). Through the substitution of La^{3+} with Sr^{2+} it is possible to increase the conductivity of the material (Figure 2.7).

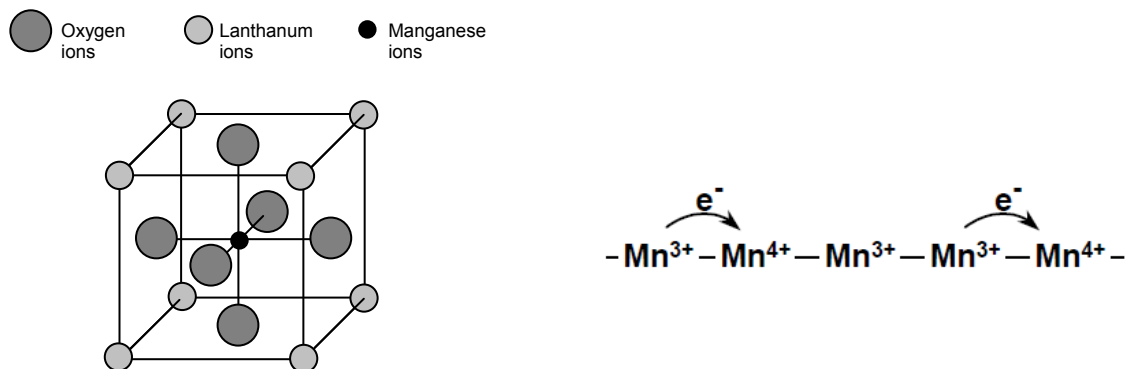


Figure 2.7 A perovskite structure e.g. LaMnO_3 and schematic illustration of small polaron hopping through Mn^{3+} and Mn^{4+} ions [Tif00].

LaMnO_3 has an orthorhombic structure at room temperature and shows an orthorhombic/rhombohedral crystallographic transformation at 600 °C [Tif00]. Due to this transformation some Mn^{3+} ions oxidize to Mn^{4+} ions. The transition temperature is dependent on the Mn^{4+} content and the stoichiometry. When the La sites are doped with lower valence cations (e.g. Sr^{2+}) the Mn^{4+} concentration in LaMnO_3 increases which affects the transformation temperature and the charge carrier mobility.

Since a perovskite is a metal oxide, oxygen ions can also move between the lattices. However the oxygen ion mobility of LaMnO_3 is far less than its electron mobility. The low oxygen ionic conductivity of LSM is considered to be the main factor in the high polarization losses of LSM cathode for the O_2 reduction at reduced SOFC operating temperatures [Fer09] as well the low oxygen surface exchange coefficient and low oxygen diffusion coefficients [Kuz99]. For this reason LaMnO_3 is usually mixed with YSZ. In that case the oxygen reduction takes place between LSM/YSZ/air triple phase boundaries. In the table below, the important factors; oxygen diffusion coefficient, oxygen surface coefficient and oxygen ionic conductivity of LSM based oxides are given.

Table 2.2 Diffusion coefficient of oxygen (D_o), oxygen surface exchange coefficient (K) and oxygen ionic conductivity (σ_i) of LaMnO_3 based oxides at 900 °C measured with SIMS technique [Fer09].

Composition	D_o [cm^2s^{-1}]	K [cms^{-1}]	σ_i [Scm^{-1}]
$\text{La}_{0.65}\text{Sr}_{0.35}\text{MnO}_3$	$4 \cdot 10^{-14}$	$5 \cdot 10^{-8}$	-
$\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$	$3 \cdot 10^{-12}$	$9 \cdot 10^{-8}$	-
$\text{La}_{0.95}\text{Sr}_{0.05}\text{MnO}_3$	$2.44 \cdot 10^{-13}$	-	$1 \cdot 10 \cdot 10^{-7}$
$\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$	$1.27 \cdot 10^{-12}$	-	$5.93 \cdot 10^{-7}$
YSZ wt % LSM	$6 \cdot 10^{-9}$	$1 \cdot 10^{-7}$	$3 \cdot 10^{-3}$

A mixed ionic electronic conductivity (MIEC) of a cathode is desirable since the oxygen reduction reaction takes places then not only in triple phase boundaries but over the whole cathode. The disadvantages of a mixed ionic-electronic conductive perovskite are the very high thermal expansion coefficients up to $18 \cdot 10^{-6} \text{ K}^{-1}$ and the low durability as well as reactions with the substrate [Mos09].

2.5.4 Anode

The main function of the anode is to promote the electrochemical oxidation of the fuel gases. The anode is also the layer of the MEA where the electrons are released. The requirements for an anode material include:

- high catalytic activity for the oxidation of the fuel gases

- high electronic conductivity under operating parameters
- good chemical and physical stability under high operating temperatures and a fuel gas environment
- good chemical stability during redox and thermal cycles
- high thermal expansion compatibility with the other cell components
- optimal porosity for sufficient gas transport and mechanical strength
- ease of fabrication and low cost
- tolerance to contaminants in the fuel gas

Several materials were studied as SOFC anode materials such as the noble metals ruthenium, rhodium, palladium, silver, platinum and gold; and the transition metals manganese, iron, cobalt, nickel and copper in the early stages of SOFC development [Gau04]. Platinum is a good catalyst however high vapour pressure of oxides at 900 °C – 1000 °C hinders the use in SOFC anodes. Gold shows no catalytic activity and poor adhesion to oxides [Gau04]. Ruthenium has a high melting point (2310 °C) and therefore low grain growth during operation and high catalytic activity for steam reforming and shows negligible carbon deposition; however evaporation of ruthenium oxide above 1200 °C is a problematic issue [Jia04]. Besides these factors the high costs of noble materials is a barrier to their use as anode materials. Among the transition metals nickel is a typical material used in solid oxide fuel cells. Nickel is cheap and has been shown as having the highest catalytic activity among different anode materials in a systematic study [Set92]. It has high chemical stability and good chemical compatibility with other SOFC components [Bie01] and low cost. Among these advantages, nickel also has some drawbacks. It expands more than 30 % in an oxidizing atmosphere which can cause delamination of the anode after redox cycles. Under high partial pressure of water $\text{Ni}(\text{OH})_2$ species can be formed which cause long term instability [Bie00]. Finally nickel has a high sensitivity towards sulfur and carbon containing gases in terms of deactivation resulting in performance loss and degradation of the anode. Pure nickel has a tendency towards grain growth at elevated temperatures and has a thermal expansion coefficient of $18 \cdot 10^{-6} \text{ K}^{-1}$ which is much higher than SOFC electrolytes (e.g. $10.8 \cdot 10^{-6} \text{ K}^{-1}$ and $10.1 \cdot 10^{-6} \text{ K}^{-1}$ for 3 and 8 mol % YSZ respectively [Yas00]).

Nickel is usually combined with a ceramic material. The use of yttria stabilised zirconia (YSZ) with nickel as an SOFC anode by Spacil in 1970s showed promising results and since then has been the most widely used SOFC anode material [Spa70]. The YSZ phase in the anode provides the oxygen ion conductivity and the nickel phase provides the electronic conductivity (Figure 2.8). Mixing YSZ with nickel lowers the thermal expansion coefficient and reduces nickel agglomeration in the anode.

Overall reaction in the anode is:



A simplified illustration of this reaction is shown in the following figure.

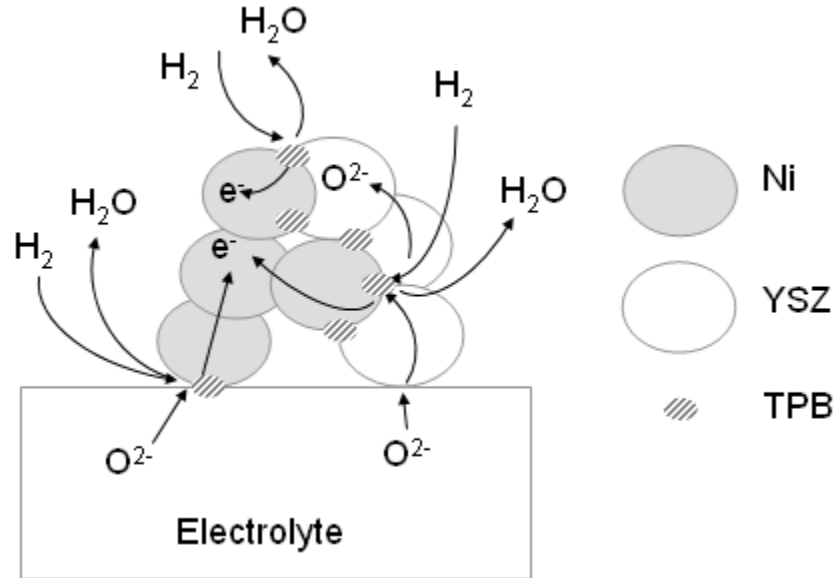
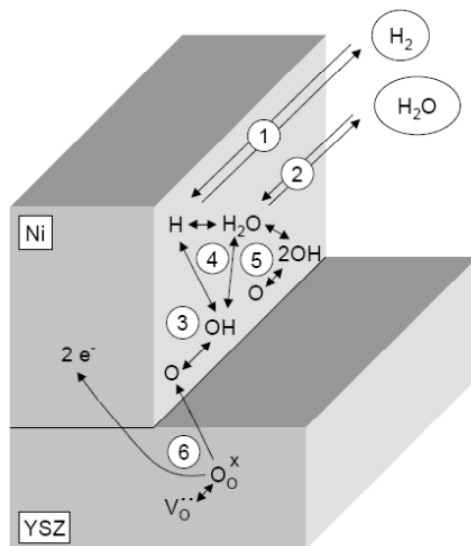
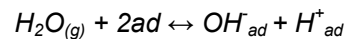
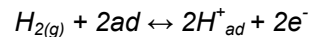


Figure 2.8 A simplified illustration of electrochemical hydrogen oxidation reaction at triple phase boundaries (TPB) of a Ni/YSZ anode. At TPBs the electrochemical oxidation of hydrogen occurs.

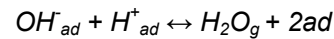
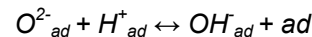
There are several models for the kinetics for the adsorption, surface and interface reactions in the anode. Bieberle [Bie00] predicted the model below for the kinetics of SOFC anodes.



Adsorption/ Desorption (1,2)



Surface reactions (3, 4, 5)



Interface reaction (6)

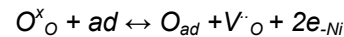


Figure 2.9 Electrochemical model for the Ni, H₂-H₂O/YSZ system under SOFC operating conditions [Bie00].

According to Bieberle, the electrochemical reactions take place only on the Ni surface and TPB; however it is also assumed that on the YSZ surface it is possible

for the formation of hydroxyl and chemisorption of water. It is generally accepted that H_2 adsorbs dissociatively on Ni. The charge transfer reaction is assumed to take place in one step [Bie00].

From this point of view, the morphology, particle size and distribution of nickel, YSZ and gas phases in the anode have crucial importance for the electrical conductivity of the anode.

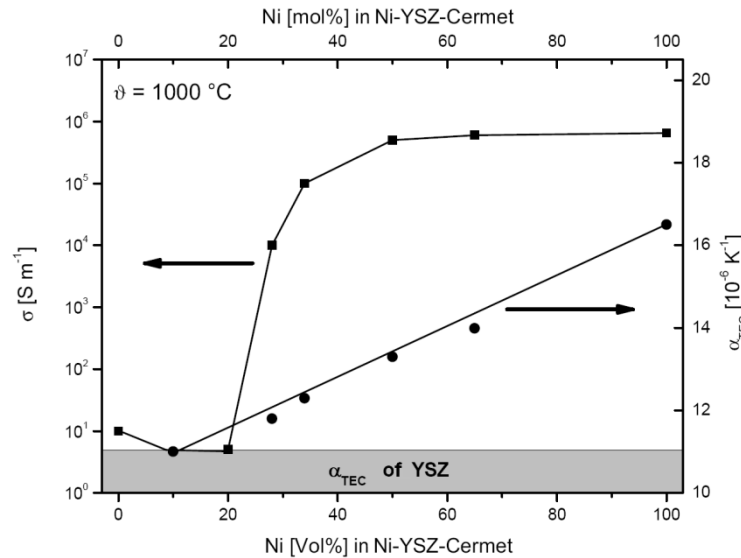


Figure 2.10 Effect of nickel ratio in Ni/YSZ to electronic conductivity and thermal expansion coefficient [Mos09].

In Figure 2.10, the effect of anode composition on electrical conductivity and thermal expansion coefficient of an anode is shown. The electrical conductivity of the anode increases significantly at 30 vol % nickel in the anode as shown in the figure as predicted by the percolation theory. According to this theory of Pratihari [Pra99] the sudden increase of the electronic conductivity at ≥ 30 vol % nickel in the anode (percolation threshold) is due to the percolation through interconnected nickel chains in the YSZ matrix. The percolation threshold for the nickel phase decreases as the particle size of NiO starting material reduces and the particle size of YSZ powder increases. When the particle sizes are similar, the percolation threshold is not dependent on the particle sizes [Fer09]. Similarly, the electrical conductivity of the anode increases as the NiO particle size is reduced when other parameters are kept constant [Yu07]. Using fine NiO and YSZ led to anodes with high electrical conductivity according to Yu et al. [Yu07]. The effects of starting materials on electrical conductivity are shown in Figure 2.11.

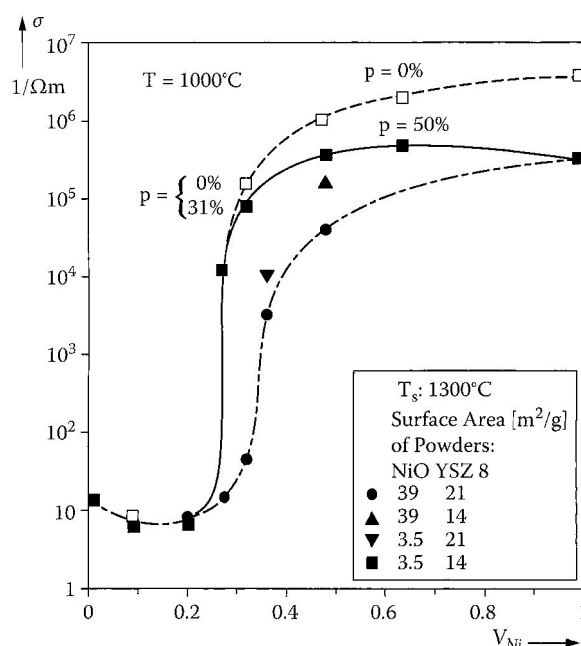


Figure 2.11 Electrical conductivity versus Ni volume fraction for Ni/YSZ cermets fabricated using different starting materials [Tif90].

Besides Ni/YSZ anodes, new materials are continually investigated with regard to higher performance and resistivity to several fuel gases and contaminants. In recent years doped ceria mixed with nickel or copper has been introduced. Doped ceria features mixed ionic electronic conductivity (MIEC) at low oxygen partial pressures and high catalytic activity. The MIEC can be enhanced by doping ceria with gadolinium. Doped ceria is more stable for the carbon deposition however shows higher volume changes during redox cycles. The better sulfur resistance of Ni/10CGO anodes has been shown in recent years; the underlying mechanisms are investigated in this work. Copper (in addition to nickel) is used owing to its inertness to carbon formation and its low price whereas the loss of catalytic activity is compensated by ceria [Joe04]. However the relatively low melting temperature of copper (1083 °C) reduces its' compatibility with many high temperature fabrication techniques. Besides nickel and copper, cobalt has high electronic conductivity and electrochemical activity as well as high sulfur tolerance, it also inhibits carbon deposition. However the high cost of cobalt limits its application. To support internal reforming reactions in the anode, nickel can be partially replaced by iron which has high electronic conductivity and less catalytic activity. However, the stability of iron depends on the oxygen partial pressure [Onu97]. In addition to metals, investigations have also been done with mixed ionic electronic conducting oxides, titanate based oxides, and lanthanum chromite type oxides [Jia04]. More detailed information on alternative anode materials with respect to sulfur poisoning is given in Chapter 3.

3 STATE OF THE ART

3.1 SOFC stack degradation mechanisms

Commercialization of SOFC technology depends on the reliability of the technology and the amortizability of the costs. The issue of degradation is the key to success for commercialization of fuel cell technologies since the commercialization can be achieved only with SOFC systems with high lifetimes. An SOFC system is profitable only with > 40000 hours of operation with an electrical power degradation rate of < 10 % compared with its initial power [Stü02]. An SOFC stack should not only be durable under stable operating conditions but also under reduction/oxidation and thermocycles. There are several mechanisms which affect the durability and degradation rates of an SOFC. The SOFC cell power can degrade due to deterioration of cell components under operating parameters and/or due to the interactions between the components. In the following table, the most important mechanisms for electrolyte, cathode and anode degradation are listed.

Table 3.1 The reasons of SOFC electrolyte, cathode and anode degradation. The references are indicated in brackets.

Electrolyte [Ste09]	Cathode [Haw09], [Yok08]	Anode [Haw09], [Yok08], [Ste09]
Cracking through mechanical impacts	Poisoning with gaseous chromium species evaporated from interconnects	Agglomeration of nickel particles: loss of conductivity, loss of catalytically active surface and TPBs, change in the porosity
Ageing due to conglomeration of contaminants on grain boundaries, separation of YSZ between Ytria-rich cubic and Ytria-poor tetragonal phases and the change in the grain boundary resistance. It should be noted that this ageing does not occur when $T > 900\text{ }^{\circ}\text{C}$	Enrichment of Sr component at the cathode/electrolyte and cathode/current collector interfaces	Loss of nickel-nickel contact
	Reaction of the cathode with electrolyte or interconnect to form insulating phases	Transfer of gas phase nickel from the anode
	Delamination from electrolyte	Nickel oxidation
	Low chemical valence stability of transition metal oxides	Delamination from electrolyte
	Decomposition and spallation of the cathode	Sulfur poisoning and poisoning by other impurities
		Carbon deposition

Among the reasons listed above, SOFC power can degrade due to factors external to the MEA such as growth of a poorly conductive oxide layer between the metallic interconnect plates and the electrodes, or lack of contact between one or more interconnect bars and the electrode; caused, for example, by cell bending prior to stack assembly [Kes07]. Some of the mechanisms listed above are consequences of thermal or redox cycling.

In the following chapter, the main subject of this thesis, the effects of sulfur contamination on the anode, are introduced in detail.

3.2 Degradation due to sulfur poisoning

Sulfur and its bondings are known to exist in almost every fossil and biogenic fuel and are known as a severe poison for most metal catalysts. Total sulfur concentrations can reach up to 23 ppm with 4 ppm H₂S in Group 2 types of gases (methane rich gases) and 50 ppm in Group 3 types of gases (liquefied gas)¹, 10 ppm in gasoline and diesel² and 700 ppm H₂S in biogas³. Sulfur traces in fuels have been shown to cause serious degradation in the performance of nickel-based anodes of SOFCs where nickels' catalytic and electrochemical activities are severely degraded in the presence of sulfur. The state of the art industrial sulfur removal technology is hydrodesulfurization which is not an attractive option for SOFC systems because of requiring high pressure (25 – 60 bar), elevated temperatures (300 – 400°C), hydrogen and wastewater disposal [deW06], [Onk96]. The dry desulfurization is an alternative method to hydrodesulfurization [Ric08]. However, desulfurization units add complexity and extra cost to SOFC systems. It is known that even 0.05 ppm H₂S has an effect on the performance of SOFC, dependent on the operating conditions [Mat00]. Additionally a desulphurization unit breakdown may also affect the performance of the system. For this reason, it is of a great importance to understand the mechanisms behind the sulphur poisoning.

In the table below, sulfur containing compounds in various fuels are listed.

Table 3.2 Sulfur containing compounds. R' is an alkyl or phenyl substituent. Modified from [Vie03]. (*THT values regulated for some European countries are given in the Appendix.)

Compound	Structure	Fuels containing
Hydrogen sulfide	H ₂ S	Natural gas (NG), liquefied natural gas (LNG), liquefied petroleum gas (LPG)
Carbonyl sulfide	COS	NG, LPG
Mercaptans	R-SH	Associated natural gas, small quantities in LNG, LPG, gasoline, diesel
Sulfides	R-S-R'	Straight run naphtha (SRN)
Tetrahydrothiophene (THT)*		Added as a commercial odorant to NG, LNG, LPG
Thiophenes		Gasoline, SRN
Benzothiophenes		Gasoline, diesel
Dibenzothiophenes		Gasoline, diesel

¹ Technische Regel, Arbeitsblatt G 260, Gasbeschaffenheit, DVGW Regelwerk, 2008.

² Verordnung über die Beschaffenheit und die Auszeichnung der Qualitäten von Kraftstoffen – 10.BImSchV, 2004.

³ Technische Regel, Arbeitsblatt G 262, Nutzung von Gasen aus regenerativen Quellen in der öffentlichen Gasversorgung, DVGW Regelwerk, 2004.

In this work, the poisoning of SOFC anodes by hydrogen sulfide (H_2S) is investigated since sulfur compounds thermodynamically react to form H_2S under hydrogen rich atmospheres at SOFC operating conditions.

In the next section, the following aspects of the state of the art information will be summarized:

- Fundamentals of catalyst deactivation mechanisms: general information, chemisorption steps of sulfur on metals, adsorption of H_2S on nickel
- Sulfur poisoning of SOFC anodes: Sulfur poisoning of Ni/YSZ anodes, sulfur poisoning of Ni/CGO anodes and finally sulfur tolerant anode materials

3.2.1 Fundamentals of catalyst deactivation mechanisms due to sulfur poisoning

Sulfur poisoning of catalysts has been extensively studied since the 1950s in industrial laboratories with the aim of being able to predict catalyst life and behaviour. Topics remaining under study include: modelling deactivation processes, designing stable catalysts and optimizing processes to prevent or slow catalyst deactivation [Bar01].

Although catalyst deactivation is a complex phenomenon, six major mechanisms are known to decrease catalytic activity. Following Bartholomew [Bar01], the mechanisms are:

- Poisoning (chemical)
- Fouling (mechanical)
- Thermal degradation (thermal)
- Vapour compound formation accompanied by transport (chemical)
- Vapour-solid and/or solid-solid reactions (chemical)
- Attrition / crushing (mechanical)

Deactivation of catalysts by sulfur is classified as a type of poisoning. By poisoning, it is meant that a chemical compound, usually an impurity, reacts with the catalyst and does not release from it. Therefore, it blocks the active sites of the catalyst, or chemically alters the catalyst. The catalyst can be poisoned temporarily (reversible) or permanently (irreversible). In the former situation, the poison is not too strongly adsorbed on the catalyst and can be desorbed when simply removed from the feed or if the catalyst is cleaned by oxidation or steaming. In the latter situation, the poison is strongly adsorbed on the catalyst and the catalyst structure is greatly changed by adsorption; it is not possible to regenerate the catalyst by removing the poison from the feed.

The interaction of sulfur with metals depends on the electron pairs available for bonding and the degree of shielding of the sulfur by ion ligands [Max51]. For this reason the order of decreasing toxicity for poisoning is $\text{H}_2\text{S} > \text{SO}_2 > \text{SO}_4^{2-}$ [Bar01].

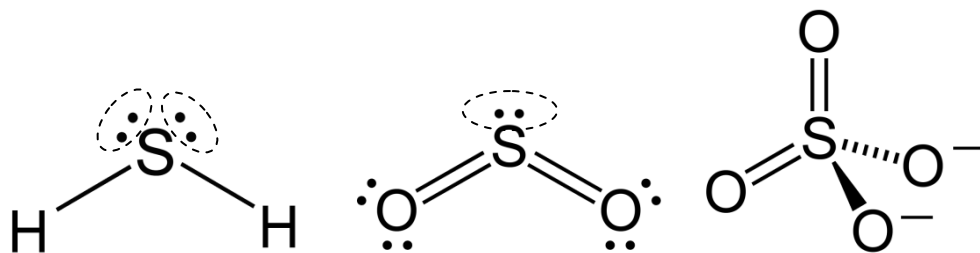


Figure 3.1 The Lewis Structures of the molecules H_2S , SO_2 and SO_4^{2-} .

Sulfur in H_2S has unshared electron pairs which can lead to very strong chemisorption on a metal surface. Under reducing conditions the adsorption on a surface is typically dissociative, leaving a reduced sulfur atom strongly bonded to the surface [Bar87]. LEED (Low Energy Electron Diffraction) studies demonstrated that at high temperatures and above certain coverage, islands of well-ordered structures are formed. At lower temperatures the chemisorption of H_2S results in occupation of sites of high coordination [Ros81].

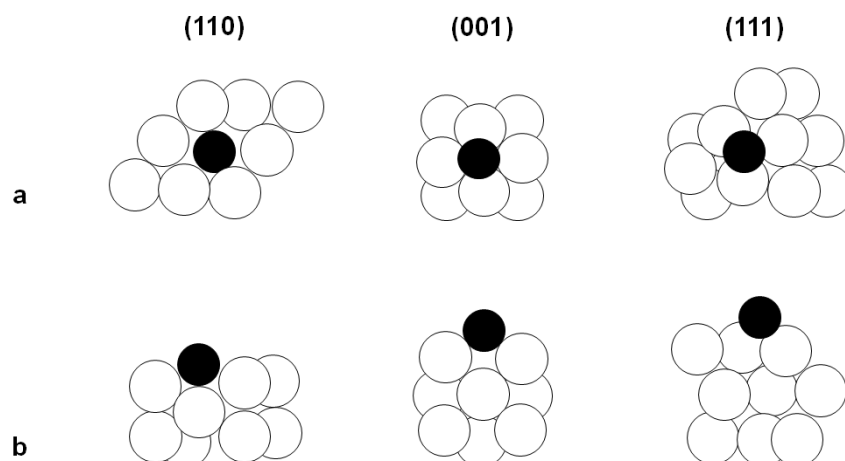


Figure 3.2 Location of adsorbed atomic sulfur on the (110), (100) and (111) planes of nickel determined from LEED intensity measurements. a) View from top, b) Side view [Bar82].

Based on the length of the bonding, Marcus et al [Mar75] came to the conclusion that the bonding should be covalent in nature. Sulfur adsorbs on Ni(100) monocrystal in forms of $\text{P}(2 \times 2)$ structure when the number of sulfur atoms and nickel atoms per cm^2 have a ratio of $\text{S}/\text{Ni} = 0.25$ (max. one sulfur atom for each nickel atom). When the number of sulfur atoms increases ($\text{S}/\text{Ni} = 0.25 - 0.5$) they form $\text{C}(2 \times 2)$ coverage structure where one sulfur atom bonds to two nickel atoms [Bar82].

Since the electronegativity of sulfur (2.58) is less than that of oxygen (3.44), metal sulfides tend to be more covalent than metal oxides. Since metal sulfides are non-ionic, they are often nonstoichiometric rather than stoichiometric compounds.

The number of sulfur atoms required for the saturation of a nickel surface which builds a monolayer for different nickel planes was studied by Oudar [Oud80]. They had analyzed the adsorption isotherms of the saturation of several nickel planes with sulfur and found reproducible values of maximum number of the sulfur atoms per square centimetre nickel surface (Table 3.3). The number of sulfur atoms for saturation for different planes was relatively similar to each other with $\pm 10\%$ difference.

Table 3.3 Maximum number of the sulfur atoms per square centimetre nickel surface* ($\times 10^{14}/\text{cm}^2$) and sulfur concentration at saturation** (ngS/cm^2) under given experimental parameters. The given numbers differ from each other about 10 %. The values give an average saturation concentration of $44 \text{ ngS}/\text{cm}^2$ [Oud80].

	Planes					$p(\text{H}_2\text{S})/p(\text{H}_2)$	T [°C]
Material	(111)	(100)	(110)	(210)	Poly-crystalline		
*($\times 10^{14}/\text{cm}^2$)	8.84	8.09	8.37	7.9	8.37	$10^{-4} - 2 \cdot 10^{-3}$	700 – 900
**(ngS/cm^2)	47	43	44.5	42	44.5	$10^{-4} - 2 \cdot 10^{-3}$	700 – 900

3.2.1.1 Chemisorption steps of sulfur on metals

The steps of the chemisorption of a poison (sulfur) on a metallic surface are known as follows [Bar01]:

- A strongly adsorbed atom of sulfur physically blocks at least one three- or four-fold adsorption/reaction site (projecting into three dimensions) and three or four topside sites on the metal surface.
- With help of its strong chemical bond, it electronically modifies its nearest neighbour metal atoms and possibly its next nearest neighbour atoms, thereby modifying their abilities to adsorb and/or dissociate reactant molecules. It is to point out that these effects do not extend beyond about 5 atomic units.
- The restructuring of the surface which possibly causes dramatic changes in catalytic properties, especially for reactions sensitive to surface structure.
- As a fourth effect, the adsorbed poison blocks access of adsorbed reactants to each other and prevents or slows the surface diffusion of adsorbed reactants.

Under suitable thermodynamical parameters, the formation of nickel sulfides is the next step. In Figure 3.3, it is shown that the formation of nickel sulfide is thermodynamically favourable at high $p(\text{H}_2\text{S})/p(\text{H}_2)$ ratios.

Nickel sulfide formation is thermodynamically unfavourable under usual SOFC operating conditions where the temperature is approximately 850°C and the H_2S concentration is in the lower ppm range. For this reason the poisoning observed with

H₂S addition to the cell is expected to be related to the sulfur adsorption on the surface of the nickel.

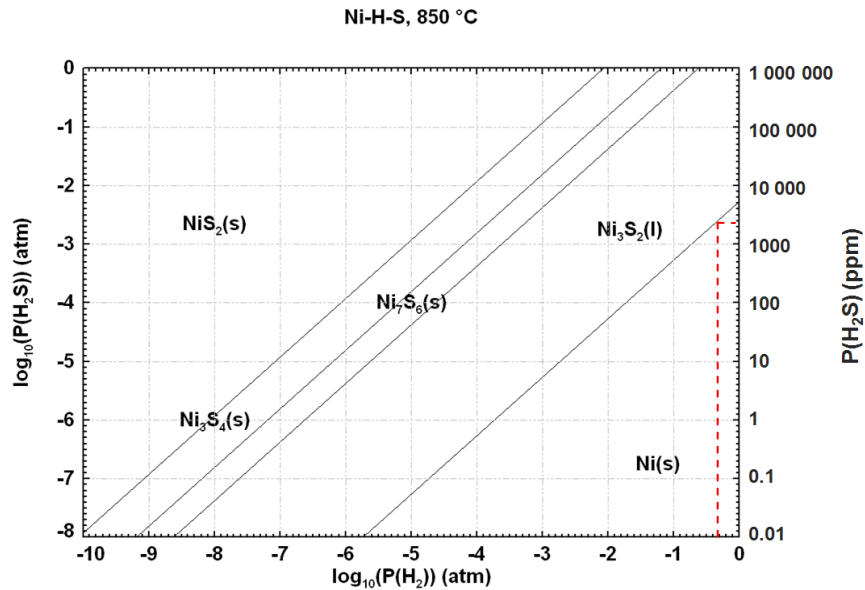


Figure 3.3 Thermodynamical calculation of $\log_{10}(P(H_2))$ versus $\log_{10}(P(H_2S))$ for the nickel-sulfide system at 850 °C by FactSage. The limit of H₂S concentration for nickel sulfide formation with 50 volume percent hydrogen in the fuel gas is approximately 2500 ppm H₂S.

3.2.1.2 Adsorption of hydrogen sulfide on nickel

Studies on the kinetics of H₂S adsorption state that the adsorption of H₂S on metals is quite rapid and that the high sticking probability suggests that no barrier to adsorption and dissociation exists until saturation is approached [Bar82]. Temperature is known as a significant effect on the adsorption kinetics where low temperatures are favourable for the adsorption. With the help of Density Functional Theory (DFT) Alfonso demonstrated that the binding of H₂S and its S-containing dissociated species is stronger on the transition metals [Alf08]. According to Choi et al.'s [Cho06] computer simulations there are two reaction pathways for the adsorption process: the molecular and dissociative adsorption process of gaseous H₂S on metallic surfaces.

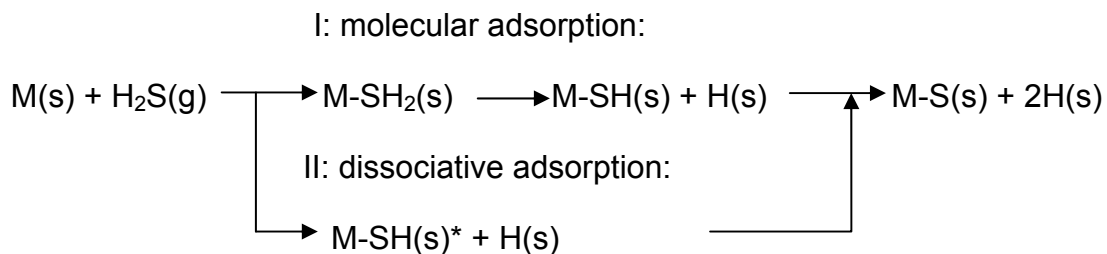


Figure 3.4 Adsorptions schematics of H₂S on metallic anode surfaces [Cho06].

Here, the dissociative adsorption was found to be the dominant reaction with adsorption energy of -1.75 eV when compared to the molecular adsorption with

adsorption energy of 0.48 eV. The adsorption process takes place at H_2S/H_2 ratios far lower than the ratios for sulfide formation [Ros68].

The adsorption isotherms at various temperatures under H_2 and H_2S gas mixture were experimentally studied to determine the energy of adsorption by some researchers. With the help of Van't Hoff Equation one can calculate the energy of adsorption through slope of (p_{H_2S}/p_{H_2}) versus $1/T$:

$$\frac{d \ln \frac{p_{H_2S}}{p_{H_2}}}{d \frac{1}{T}} = \frac{\Delta H^0}{R} \quad (\text{eq. 3.1})$$

McCarthy and Wise [McC80] and Oliphant [Oli78] have determined the heat of adsorption for Ni/Al_2O_3 in a range of $(\Delta H_{ad}: -150 \text{ kJ/mol})$ that decreases slowly at high temperatures which is energetically more favourable than the heat of formation of bulk sulfide $(\Delta H_f: -75 \text{ kJ/mol})$ on various forms of nickel [Ros75]. Attempts to correlate the data with Langmuir-Type isotherm were not successful because of departures from the Langmuir model due to the strong interaction between adsorbed atoms, high surface mobility and the dependency on the surface coverage [Ros75]. Rostrup-Nielsen proposed the following Temkin like isotherm [Ros81] to correlate data obtained from these works:

$$\frac{p_{H_2S}}{p_{H_2}} = \exp(\Delta H^0 \cdot (1 - \alpha \cdot \theta) / R \cdot T - \Delta S^0 / R) \quad (\text{eq. 3.2})$$

where α is constant and θ is the fractional coverage of nickel surface. As in Temkin theory, this model predicts a linear increase in the enthalpy with increase of the coverage but entropy is independent from coverage. Rostrup-Nielsen used this equation to correlate the data and obtained the following figure.

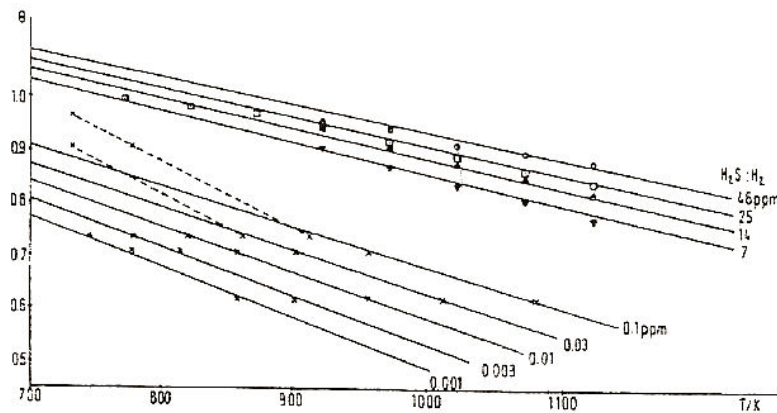


Figure 3.5 Isobars for H_2S chemisorption on Ni catalysts [Ros81].

Figure 3.5 shows the straight isobars in the θ versus T plot. The deviations at low temperatures were explained by Rostrup-Nielsen [Ros81] as adsorption on the

support. The plotted lines corresponded to the constants ΔH^0 : 289 kJ/mol, ΔS^0 : -19 kJ/molK and α : 0.69 which formed the equation [Ros81]:

$$\theta = 1.45 - 9.53 \cdot 10^{-5} \cdot T + 4.17 \cdot 10^{-5} \cdot T \cdot \ln \frac{P_{H_2S}}{P_{H_2}} \quad (\text{eq. 3.3})$$

This expression is not valid for θ close to zero and close to 1. It was shown with this equation that even with very low H_2S concentrations the coverage of the nickel surface with sulfur will be high (Figure 3.6).

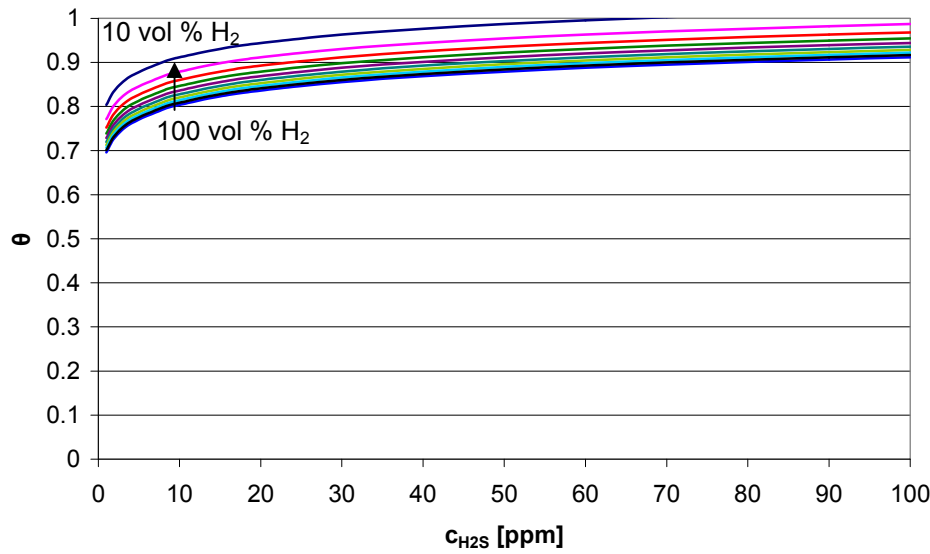


Figure 3.6 Nickel surface coverage dependent on sulfur concentration at 850 °C with hydrogen concentrations from 10 vol % to 100 vol % calculated with equation 3.3.

Since the adsorption of sulfur on oxides is negligible at low H_2S concentrations [Bar82] this value represents a good approach for the sulfur adsorption on Ni/YSZ and Ni/CGO cermets. It was shown that CeO_2 does not react with H_2S when H_2S concentration is below 450 ppm at 800°C. At higher concentrations Ce_2O_2S may form [He05]. On the other hand doped ceria with oxygen ion vacancy is not an effective sulfur adsorbent as ceria oxide (CeO_2) [Tom06]. The oxidic structure of CGO prevents sulfur adsorption at low H_2S concentrations.

3.2.2 Sulfur poisoning of SOFC anodes

Over the past decade the effects of the sulfur content of the fuel on SOFC anodes have been studied by numerous groups. Studies have been focused mainly on the effect of H_2S concentration in fuel on nickel based anodes or developing alternative anode materials with high sulfur resistance. H_2S was chosen as a sulfur containing component due to its high stability among other sulfur containing compounds under SOFC operating conditions [Sas06]. Most of the studies were done with H_2/H_2O or CH_4 fuel gas mixtures and Ni/YSZ anodes. Degradation rates of the electrical power

due to sulfur poisoning from the studies differentiate from each other due to differences in anode material, structure, experimental procedures and different comparison criteria such as chemical stability, electrochemical stability, operation times, etc.

Some typical observations generalized from these studies are as follows:

- Immediate voltage drop as H_2S is added to the fuel. In some cases the voltage is stable after an initial degradation, in some cases a second phase of degradation follows.
- When H_2S addition is switched off, the voltage either increases slowly to initial value or does not increase.
- Degradation rate increases as temperature decreases.
- Degradation rate increases as H_2S concentration increases.
- Degradation rate decreases as oxygen ion diffusion from cathode increases.

Even though the tendencies are known, the mechanisms for sulfur poisoning of nickel based anodes are still not completely understood. Irreversible damage caused by sulfur could not be inferred since no sulfur traces or morphological changes were found with post-mortem analyses.

It is assumed that sulfur adsorbs easily at low temperatures on the anode. Thermodynamical calculations show that the formation of nickel sulfide with several ppm of H_2S at high temperatures is not favourable [Sas06]. In order to analyze the contaminated anodes, FESEM, EDX, XRD, XPS or Raman Spectroscopy have been typically used. The following sections summarize the results of the previous studies on sulfur poisoning of SOFC anodes.

3.2.2.1 Sulfur poisoning of Ni/YSZ anodes

The studies had been mainly focused on the sulfur poisoning of Ni/YSZ anodes in recent years due to their common usage as an SOFC anode. Table 3.5 summarizes some of the studies on this topic. The following section presents a detailed view on sulfur poisoning of Ni/YSZ anodes.

Feduska and Isenberg [Fed83] were the first scientists to report on the sulfur poisoning behaviour of Ni/YSZ anode at 1000 °C in a seven-cell stack. They reported an immediate power decrease of 5 % as 50 ppm H_2S was added to 5 vol % H_2 / 10 vol % CO / 85 vol % CO_2 fuel (Figure 3.7). The cell power was then stable. Upon removal of H_2S from the fuel feed, the cell voltage recovered totally. They claimed that the H_2S concentration limit for reversible degradation would be at concentrations below the necessary concentration for sulfide formation.

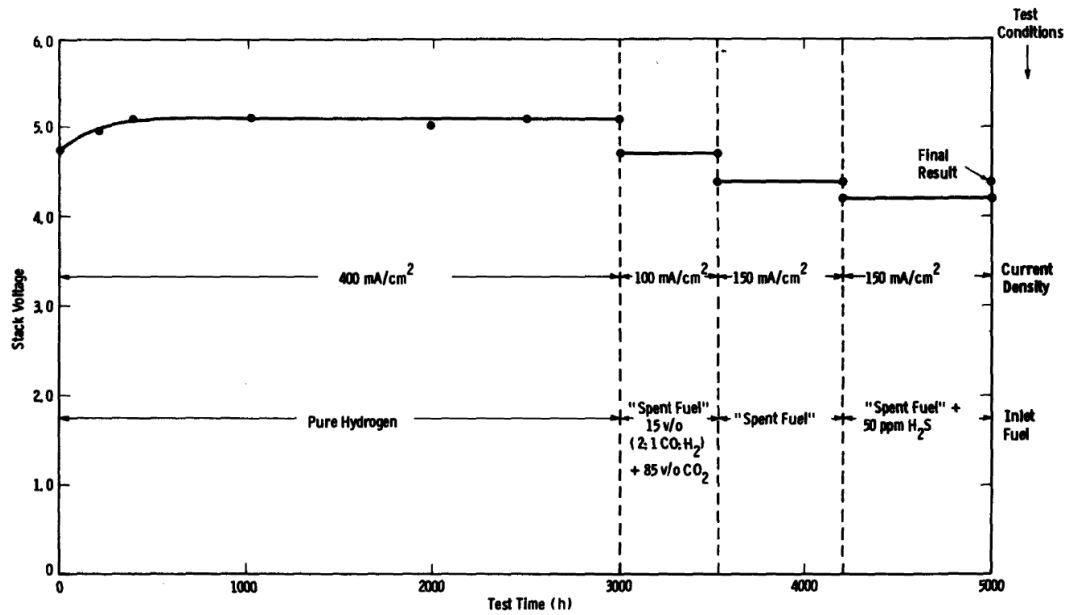


Figure 3.7 Effect of 50 ppm H_2S addition to fuel on stack voltage under constant current [Fed83].

Singhal et al. [Sin86] studied the effect of 10 ppm H_2S in the fuel stream on a Ni/YSZ anode at 900 °C and 1000 °C. At a current density of 250 mA/cm² at 1000 °C the cell voltage decreased rapidly from 0.61 V to 0.54 V (dP/P₀: 11.5 %). The cell voltage continued to decrease in 80 hours from 0.54 V to 0.52 V with 15 % total power degradation. As H_2S was removed from the cell, the voltage recovered to 0.61 V in about 80 hours (Figure 3.8). The same group also studied on the effect of H_2S as a function of concentration (2 ppm, 10 ppm), temperature (900 °C, 1000 °C) and current density (160 mA/cm², 250 mA/cm²). In general they observed that the poisoning was more severe with decreasing temperature, increasing H_2S concentration and increasing current density.

Dees et al. [Dee89] introduced 105 ppm H_2S to 97 vol % H_2 and 3 vol % H_2O fuel at 1000 °C. They observed a ~ 67 % increase in polarization resistance of the Ni/YSZ anode in the impedance frequency range ~ 1 – 1000 Hz. During post-mortem analyzes they observed a darkened YSZ electrolyte and related that to sulfur incorporation or oxygen depletion of the electrolyte. They claimed that the sulfur incorporated into the electrolyte could be the reason why sulfur effects were irreversible. However, they are the only group who observed a darkened YSZ electrolyte throughout further studies.

Geyer et al. [Gey97] observed a 33 % increase in the anode polarization resistance of a symmetrical cell at 950 °C by adding 5 ppm H_2S to 97 vol % H_2 and 3 vol % H_2O fuel at frequencies ~ 1000 Hz. They believed that at this frequency range the charge transfer reaction and the ionic resistance in the cermet is shown and not the mass transfer process which was believed to take place at lower frequency ranges and not affected by H_2S .

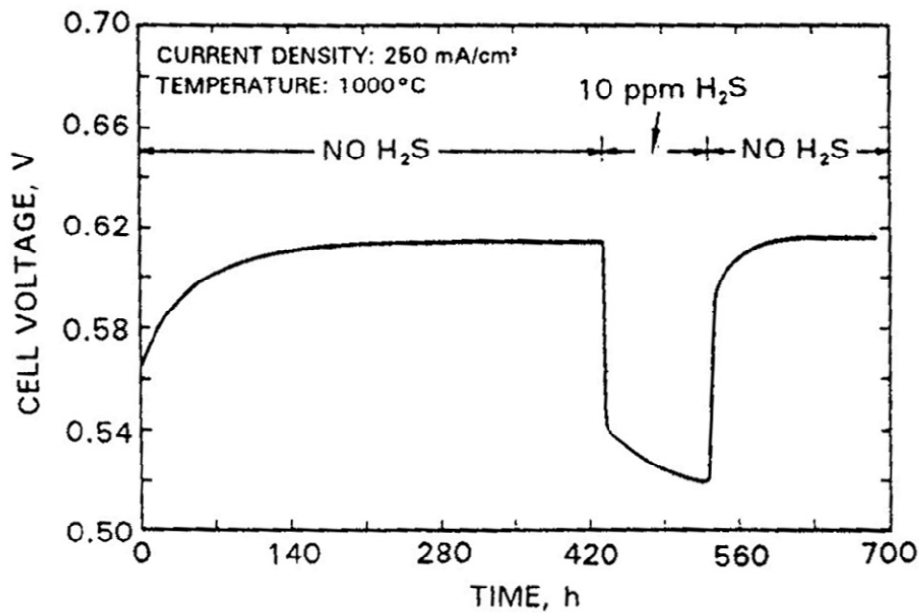


Figure 3.8 Effect of 10 ppm H₂S addition to the cell voltage with Ni/YSZ anode at 1000 °C with 250 mA/cm² current density [Sin86].

Primdahl and Mogensen [Pri99] contaminated Ni and Ni/YSZ cermet anodes with 35 ppm H₂S at 850 °C and 1000 °C under 0 and 100 mA/cm². They observed a 60 % increase in anode polarization resistance irrespective to the temperature, current density and anode structure. The increase in resistance was totally reversible. Due to the indifference of the results with Ni and Ni/YSZ anodes, the authors claimed that nickel surface is either the location of rate limiting reaction sites or it provides a species to the rate-limiting reaction and adsorbed H₂S may block one or more types of adsorption sites on nickel.

Matzusaki et al. [Mat00] investigated the time-constant of sulfur saturation and removal, and the dependence of the poisoning effect on the operating temperature, the sulfur concentration and the equilibrium partial pressure of S₂ produced in fuels containing H₂S on Ni/YSZ anodes (84 % Ni / 16 % YSZ) with 79 vol % H₂ / 21 vol % H₂O fuel (Figure 3.9). They reported that the polarization impedance and the direct current overvoltage of the Ni/YSZ electrode increased when the H₂S concentration exceeded 0.05, 0.5 and 2 ppm at 750 °C, 900 °C and 1000 °C respectively. The recovery time within removing the sulfur source was found as 360, 90 and 4 ks at 750 °C, 900 °C and 1000 °C, respectively. Saturation time was concluded to be almost independent from the concentration. The degree of sulfur poisoning was found to depend not on the equilibrium partial pressure of S₂ but on the total sulfur content in the fuel. The poisoning was recoverable when H₂S was removed from the fuel.

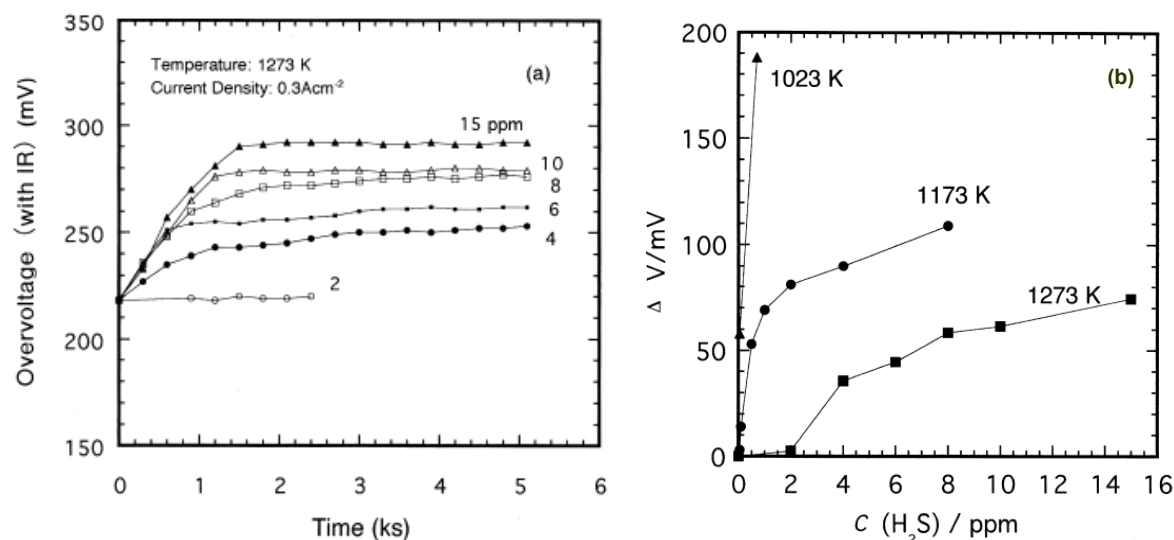


Figure 3.9 a) The overvoltage of the electrode as a function of time at a current density of 0.3 A/cm² after addition of H₂S b) The difference between the steady-state overvoltage in the fuel with H₂S and the initial overvoltage in H₂S free fuel as a function of C(H₂S) at the current density of 0.3 mA/cm² [Mat00].

Sasaki et. al. [Sas06] analyzed the influence of H₂S on the power of SOFC cells by measuring cell voltage at constant current density as a function of H₂S concentration (1, 2, 3, 5, 10, 20 ppm H₂S), operating temperature and gas composition. They compared Ni/YSZ anodes and Ni/SSZ anodes (80 weight % Ni for both types) in various H₂ / CO / H₂O fuel mixtures. At 1000 °C, they contaminated the Ni/YSZ anode with H₂S at 200 mA/cm² and found that the voltage drop was saturated above 5 ppm H₂S. Even with low ppm H₂S concentrations (1 ppm) they observed two stages of cell voltage degradation; an initial cell voltage drop within a short time to a metastable cell voltage, followed by a gradual but larger cell drop. At 900 °C and 1000 °C the cell voltage was recovered after removing 5 ppm H₂S from the H₂ fuel stream, however not at 850 °C. Adding of 5 ppm H₂S to the fuel with CO vol % > 90 at 1000 °C caused a total breakdown of the cell. They also showed that the sulfur tolerance of the cell was improved by substituting the electrolyte component with SSZ (Sc₂O₃ + CeO₂ + ZrO₂) in the anodes. After these experiments, the cells were analyzed with FESEM and EDX. The authors didn't find any traces of sulfur in the anode but instead found nickel oxide, even though the cells were cooled down under a nitrogen atmosphere. They came to the conclusion that with a constant oxygen ion flow through electrolyte to the anode (200 mA/cm² in the study), "the poisoned Ni electrode catalysts were no longer active for electrode reactions, i.e., oxygen ions supplied to the anode side may be used to oxidize Ni particles themselves rather than to oxidize fuel gases". In Figure 3.10 the sulfur poisoning mechanisms proposed from the authors are shown.

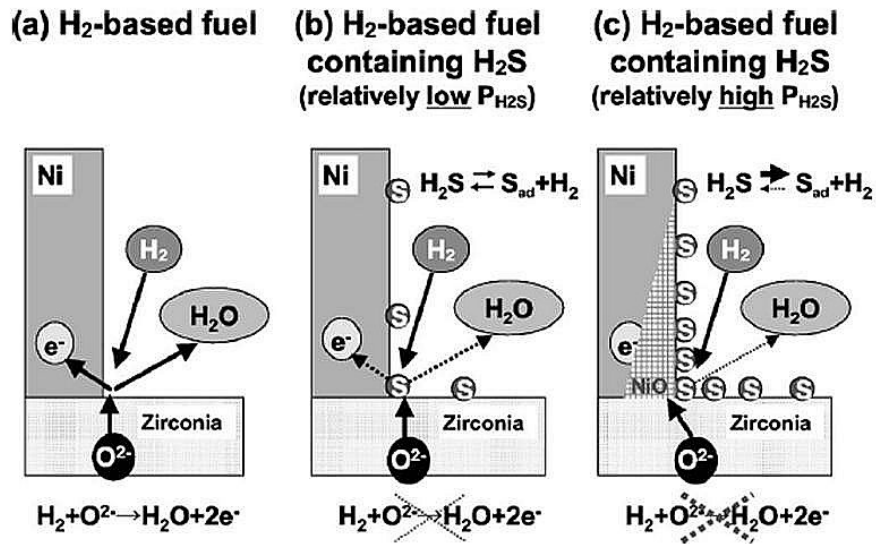


Figure 3.10 Sulfur poisoning mechanisms proposed by Sasaki et al.: a) H_2 -based fuel containing no H_2S (no poisoning), b) H_2 -based fuel with relatively low $P_{\text{H}_2\text{S}}$, in which chemisorption of sulfur leads to a decrease in electrochemical reaction sites and thus an increase in anodic polarization and cell voltage drop, and c) H_2 -based fuel with relatively high $P_{\text{H}_2\text{S}}$, in which further chemisorption of sulfur leads to an oxidation of Ni anodes and thus an increasingly larger anodic polarization and cell voltage drop (for a given current density) [Sas06].

Cheng et al. [Che07] investigated the sulfur poisoning behaviour of Ni/YSZ anodes in SOFCs under both potentiostatic and galvanostatic conditions. They reported that while the observed relative drop in cell power output caused by sulfur poisoning (up to 10 ppm) decreases as the cell voltage was lowered potentiostatically (thus more current passing through the cell), it increased as more current had been drawn from the cell galvanostatically (thus leading to lower terminal voltage). The studies were validated using impedance analysis and the results suggested that the relative increase in cell internal resistance caused by sulfur poisoning is smaller when more current is drawn from the cell under either potentiostatic or galvanostatic conditions. They suggested that the adsorbed sulfur could be oxidized electrochemically by oxygen ions at triple phase boundaries.

Lussier et al. [Lus08] studied the effect of higher H_2S concentrations on the performance of Ni/YSZ (and additionally Ni/10CGO) anodes. They exposed the anodes to H_2S with concentrations between 100 ppm and 1500 ppm H_2S in 43.5 vol % H_2 / 56.5 vol % N_2 fuel at 750 °C. They observed degradation of the cell performance as well as total disruption of the contacting nickel foam after the experimental series as shown in Figure 3.11.

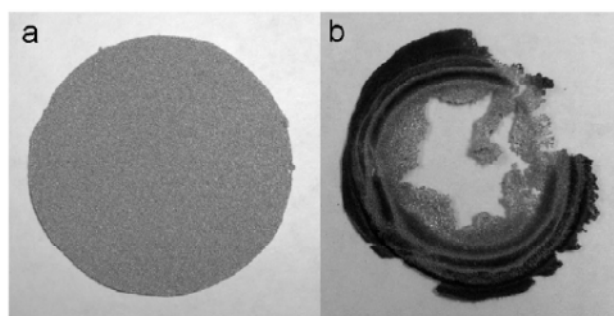


Figure 3.11 Nickel contacting foam a) before and b) after H₂S exposure [Lus08].

Lussier et al. analyzed the anodes after the experiments with XPS, XAS, and XRD. They didn't find sulfur in any form (such as pure sulfur or nickel sulfide) however they did observe nickel depletion by using XPS. They claimed that the nickel depletion must be the main cause of permanent cell performance degradation at the H₂S exposure concentrations in the 200 - 500 ppm range which is also strongly affected by operating parameters.

Li et al. [Li09] evaluated the effect of the composition of a simulated coal-derived gas on the behaviour of H₂S poisoning; with 10 ppm and 12.5 ppm H₂S at 800 °C. They observed that increasing the H₂ content from 27 % to 53 % had no influence on the H₂S poisoning. With removal of H₂S, the cell voltage recovered completely when the cell was fuelled with H₂/N₂ mixture. Adding the mixture of CO, CO₂, and H₂O to fuel increased the H₂S poisoning effect. The authors also claimed that increasing the CO₂ and H₂O content may be helpful for performance recovery.

Another study of Li et al. [Li10] investigated the effect of high H₂S concentration. Ni/YSZ anode supported SOFCs at 750 °C and 800 °C under various current densities were tested with 2000 ppm H₂S in H₂ fuel. They observed immediate and severe cell power drop upon the injection of H₂S and recovery with removal of H₂S.

Table 3.4 The dependence of degradation and recovery values on temperature and current density [Li10]. *The recovery values were calculated after 800 h and 1400 h for the experiments at 800 °C and 750 °C, respectively.

Temperature [°C]	Current density [A/cm ²]	Degradation [%]	Recovery* [%]
800	0.25	21	93
	0.40	19	97
	0.60	17	98
750	0.25	27	88
	0.40	19	94

Sulfur was detected in the anode-active zone with EDX during post mortem analysis and was therefore concluded to the cause of the immediate cell voltage drop after injecting H₂S. The sulfur or sulfide in the anode-active layer could not be completely

removed at lower current densities and operating temperatures, resulting in irrecoverable degradation.

Rasmussen and Hagen [Ras09], studied the effect of 2 - 100 ppm H_2S in 4 vol % H_2O / 96 vol % H_2 fuel in 24 hour intervals on the cell voltage at 850 °C. The cell voltage degradation of about 14 % and saturation coverage was reached approximately with 40 ppm H_2S . The cell voltage regenerated to the initial value after removing H_2S . They concluded that the poisoning effect of S was primarily due to chemisorption and thus blocking of Ni particles and not a significant change in the microstructure of the anode or a formation of an insulating layer.

3.2.2.2 Sulfur tolerant anode materials

Due to the high sensitivity of Ni/YSZ based anodes towards sulfur, several studies have been conducted to develop sulfur resistant anode materials. The sulfur tolerant anode materials must be electronically and ionically conductive, chemically and thermally stable, compatible with other SOFC components and catalytically active for electrochemical oxidation and fuel processing reactions such as water-gas shift and reforming. summarizes some of the studies on this topic.

Since undoped or doped ceria based oxides are widely applied in sulfur removal processes (owing to their high coking resistance in the catalytic processes, good performance and relatively low costs), they were commonly applied as sulfur resistant components in anode cermets [Gon07].

An alternative approach was to utilize perovskite structures which can support the oxide-ion vacancies to give good oxide-ion conduction and to have a mixed-valent cation from the 4d or 5d block that provides good electronic conduction, while exhibiting high sulfur tolerance.

Metal sulfides and thiospinels with good conductivities were chosen for the preliminary experiments as hydrogen sulfide tolerant anodes because of their activity towards H_2S oxidation and stability. However, their low performance and catalytic activity issues are the main factors why they have not found a place in conventional systems.

The following section summarizes some of the results of these studies with ceria based anodes, thiospinels, metal sulfide materials and perovskites.

3.2.2.2.1 Ceria based anodes

The initial efforts were to analyze the resistance of ceria based anodes to H_2S in SOFCs.

Kirk et al. [Kir93] tested ceria based oxygen ion conducting electrolyte $\text{Pt/Ce}_{0.81}\text{M}_{0.19}\text{O}_{2-\sigma}$ (M: Y or Sm) for H_2S -SOFCs and achieved 3.2 mW/cm² at a potential of 0.393 V with pure H_2S at 750 °C and 5.5 mW/cm² at 0.248 V with

20 vol % H_2S in nitrogen at 690 °C for yttrium-doped and samaria-doped ceria respectively (the electrolyte thickness was 1.4 mm and 0.64 mm for the former and for the latter, respectively). Peterson et al. [Pet98] reported that the performance of a cell having the configuration $\text{H}_2\text{S}/\text{Pt}/(\text{CeO}_2)_{0.8}(\text{SmO}_{1.5})/\text{Pt}$, air at 600 °C - 800 °C using pure H_2 and 1 – 25 % H_2S in N_2 as fuels. They analyzed the product gas and claimed that the complete oxidation of H_2S to SO_2 and H_2O appeared to be the favoured reactions. However, the maximum power reached was about 3.3 mW/cm² with 55 mA/cm².

He et al. [He05] (from the same group) investigated the sulfur tolerance of SOFCs with Cu-CeO₂-YSZ anodes at 800 °C and reported that operating SOFCs with hydrogen containing H_2S levels up to 450 ppm had no effect on the anode performance. They reported a cell performance of ~ 300 mW/cm² under constant voltage of 0.65 V for 300 h in 90 vol % H_2 / 10 vol % H_2O with 50 - 450 ppm H_2S (Figure 3.12).

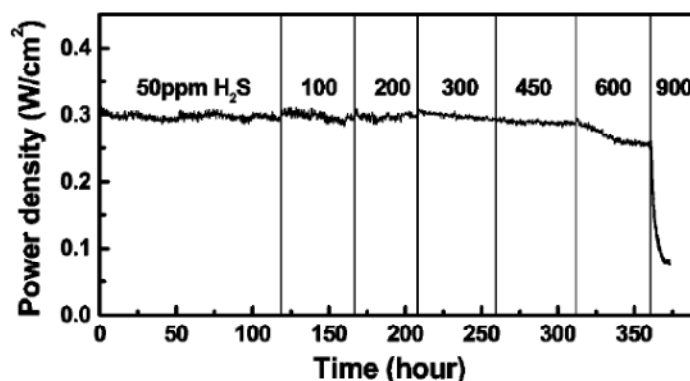


Figure 3.12 Performance of an SOFC as a function of time with (90 vol % H_2 , 10 vol % H_2O with various H_2S concentrations) ($T = 800$ °C, $U = 0.65$ V) [He05].

At higher H_2S concentrations, 13 % power deactivation with 600 ppm H_2S and 73 % with 900 ppm H_2S was observed. They claimed that CeO_2 does not react with H_2S to form $\text{Ce}_2\text{O}_2\text{S}$ at H_2S concentrations below 450 ppm.

Kim et al. [Kim01] investigated the use of copper ceria anodes in SOFCs operated with hydrocarbons containing H_2S . They used copper to eliminate carbon formation whilst maintaining the high electronic conductivity necessary for good anode performance. Since Cu-YSZ anodes are not active for the oxidation of hydrocarbons, they added ceria to the anode [Kim01]. The resistance of a Cu-ceria-YSZ cermet did not increase as the fuel was switched from hydrogen to 50 mol% n-decane containing 5000 ppm H_2S at 700 °C. However, as they tested the performance of the whole cell, they recognised a dramatic drop in the current density (while the cell voltage was maintained at 0.5 V) by switching the fuel from 5 mol% n-decane (0 ppm H_2S) to 50 mol % n-decane (5000 ppm H_2S). The current density could not be recovered by simply switching to sulfur-free fuel, they had to introduce steam (50 mol % in N_2) to regain the initial performance. They conducted a test with lower n-decane and H_2S concentrations and reported a stable performance of the cell with 5 mol% n-

decane containing 100 ppm H_2S (Figure 3.13). They claimed that with 5000 ppm S no copper sulfide (CuS_2) formation is favourable but the formation of $\text{Ce}_2\text{O}_2\text{S}$. With decreasing sulfur concentration to 100 ppm, $\text{Ce}_2\text{O}_2\text{S}$ formation is also not favourable. Since the role of the copper is providing only the electronic conductivity, surface sulfur adsorption on copper would not affect the anode performance.

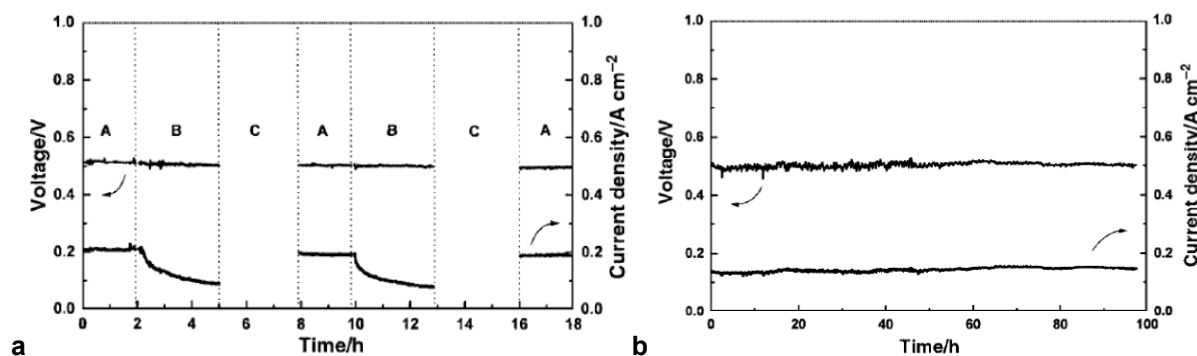


Figure 3.13 Effect of H_2S addition to the performance of the cell with Cu-Ce-YSZ anode as a function of time. a) Single cell performance at 700 °C, holding the cell potential at 0.5V. The feed to the anode was (A) 50 mol% n-decane in N_2 , (B) 50 mol % n-decane in N_2 having 5000 ppm S, (C) 50 mol % H_2O in N_2 . b) Single cell performance at 700 °C with 5 mol % n-decane containing 100 ppm S [Kim01].

The high resistivity of copper anodes to sulfur makes them attractive for use in systems. However the low melting point of copper and its oxides (when compared with nickel) make them more difficult to manufacture. For example, the electrolyte component requires pre-sintering with pore formers prior to Cu impregnation [Gor00].

Tremblay et al. [Tre06] studied the effect of 200 – 240 ppm H_2S on the electrical power of Ni/CGO/YSZ/LSM cells at 850 °C. They reported cell power degradation of 10 - 12.5 % with addition of H_2S to 34.8 vol % H_2 , 35.7 vol % N_2 , 40 vol % CO , which reached a stable level. However, after removing H_2S from the fuel, the cell did not fully regenerate. They analyzed the cells operated with 200 ppm H_2S for 650 hours with EDX. A sulfur peak was observed where the Ni, Ce and Gd presence was essentially same when compared to spectra of the cell operated without H_2S addition. Using XPS, they determined that there was a 5 – 7 % loss in the nickel content of the anode and a 1 – 2 % gain in sulfur on the anode surface while Ce and Gd remained unchanged. They claimed that the possible formation of sulfur compounds such as NiS and/or CeS_2 may be the reason for the irreversible degradation of the cell with 200 ppm H_2S .

It should be noted that the usage of nickel with ceria oxide and nickel with doped ceria may differ from each other since ceria oxide is an effective sulfur adsorbent.

3.2.2.2.2 Thiospinel – metal sulfide

The first studies in this area were conducted by groups who worked on the feasibility of electrochemically oxidising H_2S in order to gain electricity through the following overall reaction:



One of the first studies was conducted by Pujare et al [Puj87] where he utilized almost pure H_2S (99.5 vol %). The anode of the SOFC was a thiospinel $CuFe_2S_4/8YSZ$ that was prepared in situ at the anode from an oxide spinel via the following general reaction:



However, they reached a current of 4.5 mA/cm² with an 0.7 V cell potential, which was very low for practical applications. Due to the results, the same group also worked on various spinels such as $NiFe_2SO_4$, WS_2 , $CuCo_2S_4$ [Puj89]. Rapid anode kinetics was found for the anodic reaction with a trend for the exchange currents $NiFe_2S_4 > WS_2 > CuCoS_4 > CuFeS_4 \cong NiCo_2S_4 > CuNi_2S_4$. The power densities were found to be lower than 5mW/cm² between 800 °C and 900 °C.

Yates et al. [Yat99] studied $CoS_{1.035}$, WS_2 and $Li_2S/CoS_{1.035}$ anode materials with a YSZ electrode operated with 25 vol % H_2S content. The peak power density was 20 mW/cm² at 800 °C. However the stability was low due to phase change from CoS_2 to $CoS_{1.035}$. The peak power densities were 16 mW/cm² at 820 °C and 90 mW/cm² at 820 °C for WS_2 and $Li_2S/CoS_{1.035}$, respectively. Though the cells did not run more than 24 hours according to stability problems.

Wei et al. [Wei04] reported on H_2S -SOFCs where the anode material comprises a mixture of Mo-Ni-S with up to 10 % Ag as an electronic conductor and YSZ as an ionic conductor as the anode with an optimum composition of 90 wt % Mo-Ni-S, 5 wt % Ag, 5 wt % YSZ. At 850 °C over 200 mW/cm² had been produced with pure H_2S as feed.

Liu et al [Liu04] investigated composite metal sulfides for electrochemical oxidation of hydrogen in SOFCs. They found that MoS_2 and composite catalysts were found to be more active than Pt. In contrast, composite catalysts (M-Mo-S) derived from a mixture of sulfides of Mo and other transition metals (Fe, Co, Ni) were shown to be stable and effective for electrochemical conversion of H_2S in SOFCs up to 850 °C.

The group of Chuang worked on utilizing metals other than nickel in anodes and increasing the sulfur resistance or even using them as H_2S -SOFCs [Che08]. Liu et al. [Liu01] tested a cell having the configuration $H_2S, Pt/(ZrO_2)_{0.92}(Y_2O_3)_{0.08}/Pt$, air at 750 – 800 °C using pure and 5 vol % H_2S in N_2 fuel. The highest current density achieved was 15.4 mW/cm² with 5 vol % H_2S in N_2 . The Pt anode was degraded significantly by the addition of pure H_2S . The authors claimed that the degradation of the cell was due to the formation of PtS and therefore platinum is not a promising material to use in sulfur resistant anodes.

He et al. [He02] interposed a thin layer of TiO_2 between the platinum and YSZ to stabilize the membrane structure and performance. The performance was stabilized however a power of only 2 mW/cm^2 could be gained from the cell.

In 2003, Liu et al. [Liu03] published an article on anode catalysts comprising MoS_2 and composite Fe-Mo-, Co-Mo- and Ni-Mo-sulfides at temperatures up to 850°C . All composite metal sulfides were shown to be stable up to 850°C however MoS_2 sublimed above 450°C . The highest power density (110 mW/cm^2) was observed for a Co-Mo sulfide/Ag composite anode using 100 % H_2S . Wei et al. [Wei04] reached 220 mW/cm^2 power with anode consisted of 90 wt % Mo-Ni-S with 5 wt % Ag and 5 wt % YSZ at 850°C . However, no long term stability was demonstrated.

3.2.2.2.3 Perovskite based materials

Studies of Huang et al. [Hua06] showed long-term stable double perovskite $\text{Sr}_2\text{Mg}_{1-x}\text{Mn}_x\text{MoO}_{6-\delta}$ anodes in presence of 50 ppm H_2S in H_2 at 800°C , without formation of sulfur species (Figure 3.14).

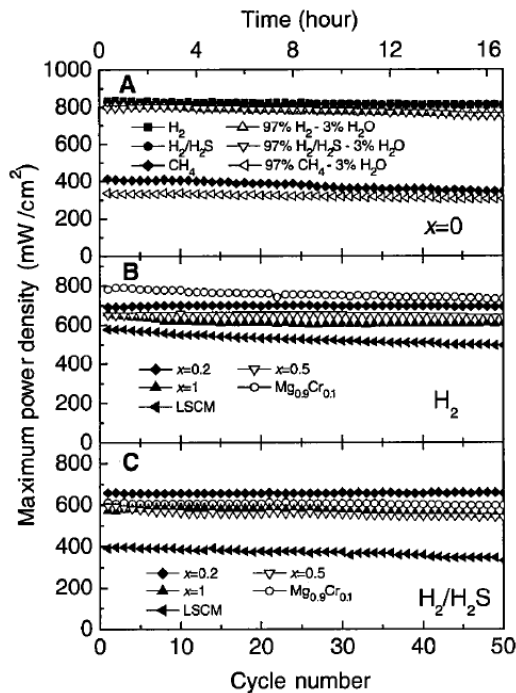


Figure 3.14 The maximum power density at 800°C versus cycle number and testing time for the single fuel cells with various $\text{Sr}_2\text{MgMnMoO}$ anodes. A) $\text{Sr}_2\text{MgMnMoO}$ obtained in dry and wet H_2 , $\text{H}_2/\text{H}_2\text{S}$ and CH_4 B) Other anodes in dry H_2 C) Other anodes in dry $\text{H}_2/\text{H}_2\text{S}$. The data for $(\text{La}_{0.75}\text{Sr}_{0.25})_{0.9}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ (LSMC) and $\text{Sr}_2\text{Mg}_{0.9}\text{Cr}_{0.1}\text{MoO}_{6-\delta}$ anodes are shown for comparison[Hua06].

Mukundan et al. [Muk04] tested SOFCs using YSZ electrolytes, LSM cathodes and $\text{La}_{12-x}\text{Sr}_x\text{BO}_3/\text{YSZ}$ anodes where B was Mn, Cr, and Ti at 1000°C in a $\text{H}_2/\text{H}_2\text{O}$ fuel. The $\text{La}_{0.4}\text{Sr}_{0.6}\text{TiO}_3/\text{YSZ}$ ~50/50 wt% anode showed no degradation (200 mW/cm^2) but a power increase (175 mW/cm^2 without H_2S) in the presence of 5000 ppm of H_2S in a hydrogen fuel.

Marina et al. [Mar04]'s studies with $\text{La}_{0.4}\text{Sr}_{0.6}\text{TiO}_3 / \text{Ce}_{0.5}\text{La}_{0.5}\text{O}_{1.75}$ anodes however did not show the same behaviour. They reported that when 1000 ppm H_2S was added to the fuel the cell current dropped about 60 % and 30 % for the cell voltage 0.7 V and 0.3 V at 850°C , respectively. By introducing 280 ppm H_2S to the fuel,

current density decreased from 450 mA/cm² to 400 mA/cm². The degradation of the cell was reported to be reversible.

Aguilar et al. [Agu04a], [Agu04b] developed $\text{La}_x\text{Sr}_{1-x}\text{VO}_{3-\delta}$ (LSV) anodes for SOFCs operating on H_2S containing fuels. They reached a maximum power density of 90 mW/cm² at 220 mA/cm² with 5 vol % H_2S / 95 vol % N_2 at 1000 °C with $\text{La}_{0.7}\text{Sr}_{0.3}\text{VO}_3$ /YSZ/LSM-YSZ cells. The power density increased to 135 mW/cm² at 280 mA/cm² when the fuel was switched to 5 vol % H_2S / 95 vol % H_2 and the performance was stable for 48 hours. They claimed that the formation of a conductive vanadium sulfide phase increased the conductivity of the anode instead of the insulating $\text{Sr}_3\text{V}_2\text{O}_8$ compound which was expected to be formed in the anode at low oxygen partial pressures.

Wang et al [Wan01] studied the stabilities and conductivities of sulfides and lithiated sulfides derived from $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Cr}_{0.2}\text{O}_3$, $\text{LaCr}_{0.9}\text{Ti}_{0.1}\text{O}_3$, $\text{Y}_{0.9}\text{Ca}_{0.1}\text{FeO}_3$ and $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$ by exposing them to H_2 with 4 vol % H_2S at 900 °C. These materials showed low conductivities and high reactivities with H_2S and therefore concluded to be not promising for use in SOFCs (Figure 3.15).

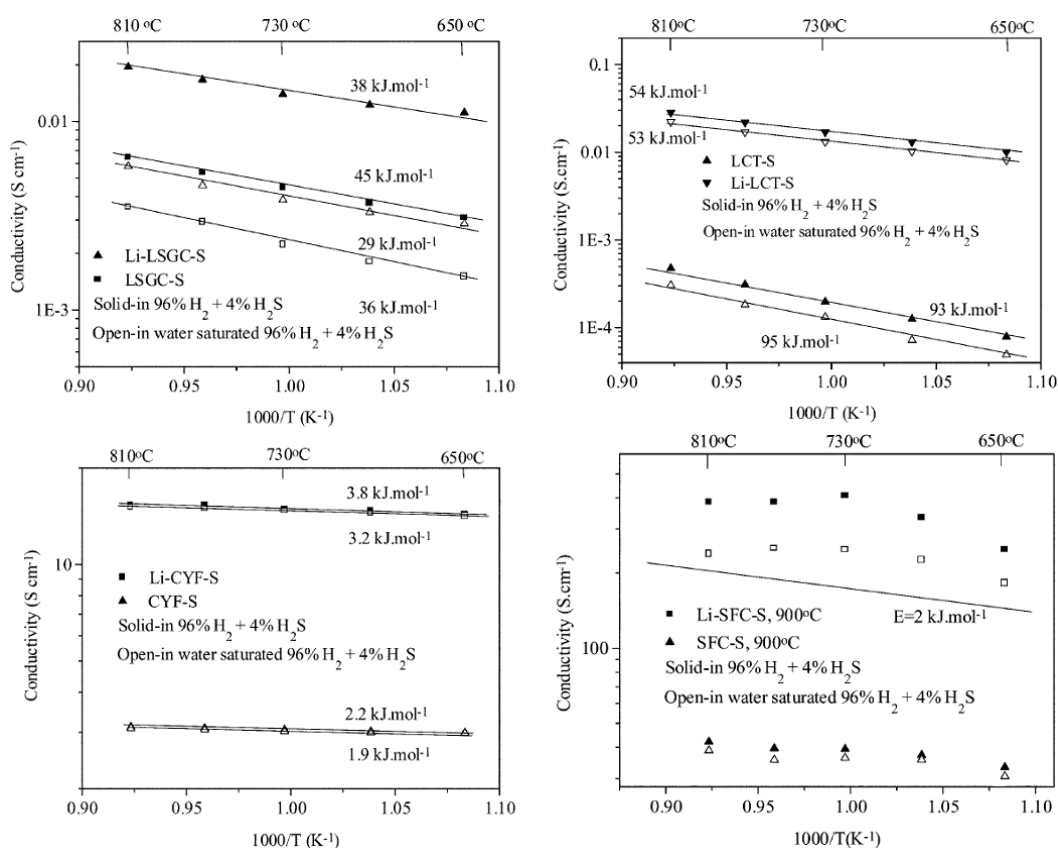


Figure 3.15 Arrhenius plots of conductivities as measured in dry or humidified gas mixtures (96 % H_2 , 4 % H_2S) of pellets sintered at 900 °C for 2 h. The abbreviations refer to sulfides of $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Cr}_{0.2}\text{O}_3$ (LSGC-S), $\text{LaCr}_{0.9}\text{Ti}_{0.1}\text{O}_3$ (LCT-S), $\text{Y}_{0.9}\text{Ca}_{0.1}\text{FeO}_3$ (CYF-S) and $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$ (SFC-S) and their lithiated forms which were mixed with $(\text{Li}_{0.62}\text{K}_{0.38})_2\text{CO}_3$ during preparation [Wan01].

Lu et al. [Lu09] tested $\text{Sr}_{0.88}\text{Y}_{0.08}\text{TiO}_{3-\delta}$ (SYT)/ $\text{La}_{0.4}\text{Ce}_{0.6}\text{O}_{1.8}$ (LDC) composite impregnated with Pd for the $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{3-\delta}$ (LSGM) supported cells with 50 ppm H_2S in H_2 . SrTiO_3 was selected for its high electrical conductivity and sulfur tolerance. In order to increase the catalytic activity of SrTiO_3 towards hydrogen oxidation, it should be improved by doping with high-level of Mn or Mn and Ga. LDC was component selected as a mixed ionic electronic conductor with sulfur tolerance in the fuel. They reported a maximum power density of 1006 mW/cm^2 at 850°C and no power degradation with 50 ppm H_2S addition. However, a slight degradation of the cell voltage can be observed in the following diagram.

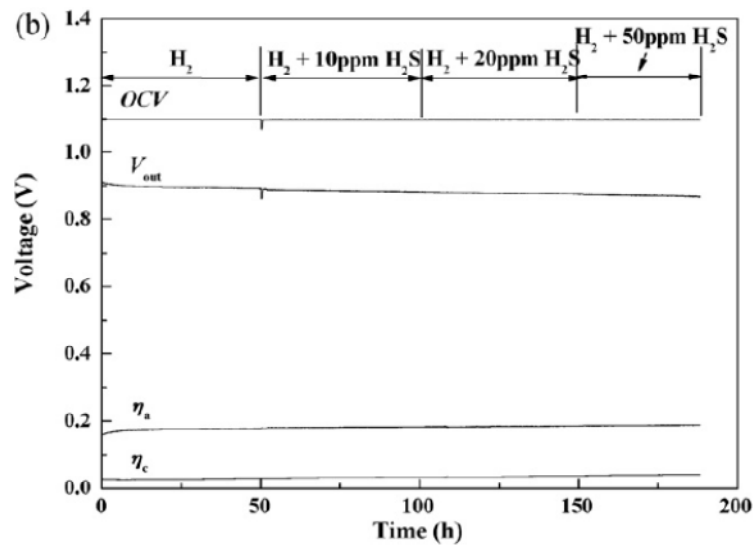


Figure 3.16 The change in OCV, output voltage, anodic and cathodic overpotential of single cells at 800°C with Pd-impregnated SYT/LTC anode in H_2 and $\text{H}_2/\text{H}_2\text{S}$ fuels under a fixed current density of 417 mA/cm^2 (V_{out} , output voltage, η_a anodic overpotential, η_c cathodic overpotential).

Table 3.5 Summary of some of the studies with respect to H₂S poisoning of Ni/YSZ anodes.

Author	Publication Year	Sample	H ₂ S concentration [ppm]	Temperature [°C]	Fuel [vol %]	Result
Feduska [Fed83]	1983	7-cell stack	50	1000	5 H ₂ / 10 CO / 85 CO ₂	5% immediate power decrease with 50 ppm H ₂ S followed by a stable power for 800 hours. H ₂ S concentration limit for reversible degradation was claimed to be at concentrations below the necessary concentration for sulfide formation.
Singhal [Sin86]	1986	Button cells	10	1000	H ₂ / H ₂ O / N ₂	11.5 % immediate power decrease with 15 % total power degradation. Total regeneration as H ₂ S is removed from the fuel after 80 hours of contamination. The poisoning was more severe with decreasing temperature, increasing H ₂ S concentration and increasing current density.
Dees [Dee89]	1989	Symmetrical button cells	105	1000	97 H ₂ / 3 H ₂ O	67 % polarization resistance increase in the impedance frequency range 1 - 1000 Hz. (Duration of the poisoning was not mentioned.) The sulfur incorporated into the electrolyte could be the reason why sulfur effects were irreversible. (This phenomenon was not observed by any other studies).
Geyer [Gey97]	1997	Symmetrical button cells	5	950	97 H ₂ / 3 H ₂ O	33 % polarization resistance increase at frequencies about 1000 Hz where the charge transfer reaction and the ionic resistance in the cermet occurs. The mass transfer process which was believed to take place at lower frequency ranges was claimed not to be affected by H ₂ S. (Duration of the poisoning was not mentioned.)
Primdahl [Pri99]	1999	Symmetrical button cells	35	850, 1000	97 H ₂ / 3 H ₂ O	60 % polarization resistance increase irrespective to the temperature, current density and anode structure. The increase in resistance was totally reversible. Adsorbed H ₂ S may block one type or two or more types of adsorption sites on nickel. (Duration of the poisoning was not mentioned.)
Matsuzaki [Mat00]	2000	Button cells	0.05, 0.5, 2	750, 900, 1000	79 H ₂ / 21 H ₂ O	Polarization impedance and direct current overvoltage of the Ni/YSZ electrode increased when cH ₂ S exceeded 0.05, 0.5 and 2 ppm at 750°C, 900°C and 1000°C, respectively. Recovery time after sulfur removal was found to be 360, 90 and 4 ks at 750 °C, 900 °C and 1000 °C, respectively. Saturation time had been reported as almost independent from cH ₂ S and was found to be 12, 9 and 4 ks at 750 °C, 900 °C and 1000 °C. Degree of sulfur poisoning was found to not depend on the equilibrium partial pressure of S ₂ but on the total sulfur in the fuel. The poisoning was recoverable when with H ₂ S removal.

Author	Publication Year	Sample	H ₂ S concentration [ppm]	Temperature [°C]	Fuel [vol %]	Result
Xia [Xia05]	2005	Button cells	10	800	H ₂ / H ₂ O / N ₂	10 ppm H ₂ S for 18 hours caused a cell voltage drop of 19.5% and 56.4% when the current density was 130 and 400 mA/cm ² , respectively, at 800 °C. The authors explained this result with high local current density at sites not blocked with sulfur which may enhance the sulfur species adsorption process or induces the formation of a thin layer of Ni ₃ S ₂ . An alternative explanation was that the higher overpotential could result in nickel oxide formation and may contribute to anode deactivation.
Rostrup-Nielsen [Ros06]	2006	10-cell stack	2, 5, 10, 50	700, 800	11.5 H ₂ / 10.5 CO / 12.5 CO ₂ / 1.5 CH ₄ / 63.2 N ₂	10 % voltage decrease with the addition of 50 ppm H ₂ S at 700 – 720 °C. When extra H ₂ was submitted to the fuel an almost complete recovery of the voltage loss was achieved. Sulfur blocked the sites for methane conversion. The reforming activity decreased with sulfur coverage to the 3 rd power. (Duration of the poisoning was not mentioned.)
Sasaki [Sas06]	2006	Button cells	1, 2, 3, 5, 10, 20	1000	various H ₂ / CO / H ₂ O / N ₂	The voltage drop was saturated above 5 ppm H ₂ S. Two stage cell voltage degradations were observed. At 900°C and 1000°C the cell voltage was recovered after removing 5 ppm H ₂ S from H ₂ fuel stream within a few hours (exact duration not mentioned), however not at 850°C. Sulfur tolerance of the cell was improved by substituting the electrolyte component with SSZ (Sc ₂ O ₃ -doped ZrO ₂). The oxygen ions supplied to the anode side were claimed to have oxidized Ni particles rather than the fuel gases.
Cheng [Che07]	2007	Button cells	0 - 10	800	50 H ₂ / 1.5 H ₂ O / 48.5 N ₂	The relative increase in cell internal resistance caused by sulfur poisoning was smaller when more current was drawn from the cell under either potentiostatic or galvanostatic conditions. The adsorbed sulfur could be oxidized electrochemically by oxygen ions at triple phase boundaries.
Zha [Zha07]	2007	Button cells	2, 50	800	50 H ₂ / 1.5 H ₂ O / 48.5 N ₂	16.67 % and 12.7 % cell power degradation with 50 ppm and 2 ppm H ₂ S, respectively. The performance of Ni-YSZ anode in an SOFC drops dramatically in minutes upon exposure to H ₂ S containing fuel, followed by a gradual but steady degradation over days.
Lussier [Lus08]	2008	Button cells	100, 1500	750	43.5 H ₂ / 56.5 N ₂	Degradation of the cell performance and total disruption of the contacting nickel foam. Nickel depletion was claimed to be the main cause of permanent cell performance degradation with cH ₂ S in the 200-500 ppm range. No sulfur was detectable with XPS, XAS or XRD.

Author	Publication Year	Sample	H ₂ S concentration [ppm]	Temperature [°C]	Fuel [vol %]	Result
Rasmussen [Ras09]	2009	1-cell stack	2 - 100	850	4 H ₂ O / 96 H ₂	14 % cell voltage degradation and saturation coverage with 40 ppm H ₂ S addition. The cell voltage regenerated to the initial value after removing H ₂ S. They concluded that the poisoning effect of S was primarily due to chemisorption and thus blocking of Ni-particles and not a significant change of the microstructure of the anode or a formation of an insulating layer.
Li [Li10]	2010	Button cells	2000	750, 800	100 H ₂	The degradation rate increased from 17 to 21 % with a decrease in current density from 0.60 to 0.25 A/cm ² or an increase in voltage from 0.63 to 0.86 V. The authors explained that as after removing the H ₂ S from the fuel, more water will be produced at the anode when the cell is operated at a higher current density load, which could help to recover the cell performance. Degradations were irrecoverable.

Table 3.6 Summary of some of the studies with respect to H₂S poisoning of anodes other than Ni/YSZ.

Author	Publication Year	Anode	H ₂ S concentration [ppm]	Temperature [°C]	Fuel [vol %]	Result
Kim [Kim01]	2001	Button cells with Cu/CeO ₂ /YSZ anode	5000	700	5 - 50 mol % n-decane in N ₂	55 % drop of the current density (from 0.2 A/cm ² to 0.09 A/cm ²) with constant voltage at 0.5 V by addition of 5000 ppm H ₂ S to 50 mol % n-decane. The current density could not be recovered by switching to sulfur-free fuel, steam had to be introduced (50 mol % H ₂ O in N ₂) to regain the initial performance. Stable performance of the cell with 5 mol% n-decane containing 100 ppm H ₂ S. With 5000 ppm H ₂ S no copper sulfide (CuS ₂) formation is favourable but the formation of Ce ₂ O ₂ S. With 100 ppm H ₂ S, Ce ₂ O ₂ S formation is also not favourable. It is assumed that since the role of the copper is providing only the electronic conductivity, surface sulfur adsorption on copper would not affect the anode performance.
He [He05]	2005	Button cells with Cu/CeO ₂ /YSZ anode	50 - 900	800	90 H ₂ / 10 H ₂ O	13 % and 73 % power deactivation was observed with 600 ppm and 900 ppm H ₂ S, respectively. With 50 - 450 ppm H ₂ S power was 300 mW/cm ² under a constant voltage of 0.65 V for 300 h. The deactivation at high H ₂ S concentrations was due to the reaction of CeO ₂ with H ₂ S to form Ce ₂ O ₂ S.
Tremblay [Tre06]	2006	Button cells with Ni/GDC anode	200 - 240	850	34.8 H ₂ / 35.7 N ₂ / 40 CO	6 - 8% initial power loss with the addition of 200 - 240 ppm H ₂ S, with the total power degradation rising eventually to 10 - 12.5%. The cell power was constant for the next 500 hours when operation was discontinued. The XPS analysis comparison between poisoned and unpoisoned anode showed loss of Ni composition and gain of S. Ce and Gd remained unchanged suggesting Ni-S interactions was the reason for degradation.
Lohsoontorn [Loh08]	2008	Button cells with Ni/GDC anode	1, 3	560, 600	9.7 - 97 H ₂ / 3 H ₂ O / balance N ₂	Polarization resistance increased from approximately 4 to 15 ohmcm ² , from 2.5 to 6.5 ohmcm ² and from 2 to 4 ohmcm ² with 1 ppm H ₂ S exposure to fuels with 9.7 %, 48.5 % and 97 % H ₂ respectively. Performance degradation worsens when pH ₂ S increases and pH ₂ and temperature decrease. The anode performance loss at low pH ₂ is dominated by the interaction of sulfur with nickel rather than ceria. As pH ₂ increases recovery increases, too.

Author	Publication Year	Anode	H ₂ S concentration [ppm]	Temperature [°C]	Fuel [vol %]	Result
Grigicak [Gri08]	2008	Button cells with Co/YSZ anode	300 - 10000	800	H ₂ and CH ₄	Cell performance was stable for concentrations of H ₂ S > 10000 ppm. Below 10000 ppm, activity decreased as a function of H ₂ S partial pressure. The loss in performance may be a result of decreased H ₂ production and/or a change in cobalt sulfide stoichiometry to another sulfide species. At low sulfur partial pressures Co _{1-x} S may convert to Co, Co ₄ S ₃ or Co ₉ S ₈ . The performance suggests metal-sulfides are viable anode materials for carbon and sulfur resistant SOFC systems.
Yun [Yun11]	2011	Button cells with Ni/YSZ with 20 % Ce and with 50 % Sm _{0.2} Ce _{0.8} O _{2.8}	100	600	H ₂	Cell performance decreased by 43% (0.28 W/cm ² to 0.16 W/cm ²) with 100 ppm H ₂ S with the unmodified anode; by 30% (0.34 W/cm ² to 0.24 W/cm ²) in the ceria-modified anode; and by 14% (0.45 W/cm ² to 0.39 W/cm ²) in the SDC-modified anode. A porous SDC layer on the Ni/YSZ anode pore wall was claimed to act as a sulfur sorbent as well as providing additional TPB areas. Otherwise, ceria mainly acted as a sulfur sorbent at high concentrations of H ₂ S (> 60 ppm).
Xu [Xu10]	2010	Button cells with Ni/YSZ with and without CeO ₂ coating on top the anode layer	20	850	32 CH ₄ / 48 H ₂ O / 20 CO ₂ (ISR) and 30 CH ₄ / 20 H ₂ O / 20 O ₂ / 30 air (IASR)	Irreversible degradation of cell voltage to 0 V with 20 ppm H ₂ S for ISR without CeO ₂ coating. With CeO ₂ coating the cell voltage also dropped to 0 V however could be recovered to 89 % after removing H ₂ S. With IASR, the uncoated cell voltage dropped from 0.660 V to 0 V, with removal of H ₂ S the cell voltage recovered to 0.642 V (99.2 % of initial value). The covered cell degraded to 80.6 % of its initial value and recovered to 95.6 % with IASR. The Ni-CeO ₂ coating barrier can increase H ₂ S tolerance with lower degradation rate and high recoverability.

4 EXPERIMENTAL PROCEDURES

During this work, the effects of sulfur on SOFC stack performance were studied. In order to study these effects, an operating fuel cell, and a method of introducing sulfur is required. SOFC stack and a test bench were designed for this purpose. The following chapter presents the experimental apparatus and experimental procedures. Additionally, the SOFC anodes were examined with post-mortem-analysis techniques after experiments in order to determine any changes in the morphology of anode caused by sulfur. These techniques are presented in Chapter 4.2.3. In order to study the sulfur intake of Ni/8YSZ material independent from the stack conditions and electrochemical reactions, in-situ-thermal analysis was applied at SOFC operating temperatures. The details of this analysis technique are explained in Chapter 4.2.4.

4.1 Experimental apparatus

Planar single cell SOFC stacks were used for the experiments. A detailed description of the SOFC MEAs, single cell stacks and test benches is presented in the following sections.

4.1.1 SOFC membrane electrode assemblies (MEA)

SOFCs used in this work were electrolyte supported cells (ESC) with dimensions of 50 x 50 mm with an active area of 40 x 40 mm. Fuel cells from two different suppliers (Fraunhofer IKTS and H.C. Starck GmbH) were used.

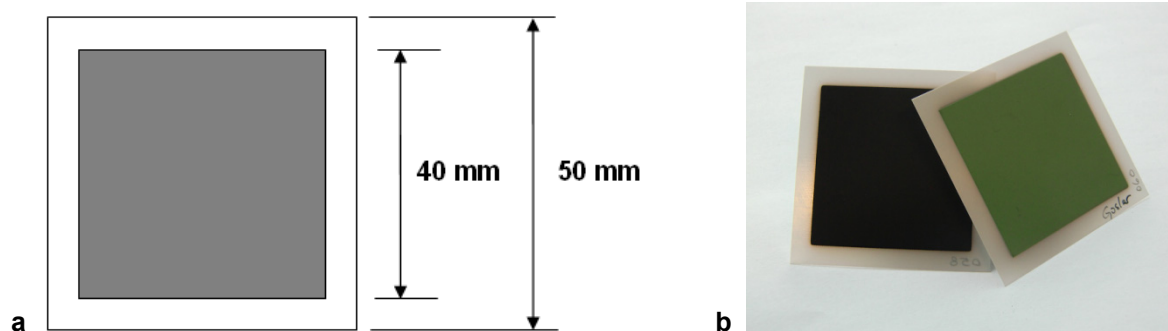


Figure 4.1 a) The schematics of a MEA b) The SOFC MEAs with anode (green) and cathode (black) layers on the electrolyte.

Both suppliers used similar production methods. The electrolytes were fabricated by tape casting; and the anode and cathode layers were applied using screen printing. The compositions and thicknesses of both types of the MEAs are shown in Table 4.1.

Electrolytes from Fraunhofer IKTS were composed of 3YSZ (3 mol % Y_2O_3 doped ZrO_2) or 3YSZ10Sc1CeSZ (50 wt % 3 mol % Y_2O_3 doped ZrO_2 , 50 wt % 10 mol %

Sc₂O₃ and 1 mol % CeO₂ doped ZrO₂). Electrolytes from HC Starck were composed of 3YSZ. Anodes in both of the MEAs are made of three sub layers:

- Anode adhesion layer between the electrolyte and the anode active layer; for a better adhesion between the anode and the electrolyte.
- Anode active layer composed of a porous electrolyte material optimised for electrochemical reactions. The layers are mixtures of nickel and 8YSZ (8 mol % Y₂O₃ doped ZrO₂) or 10CGO (10 mol % Gd₂O₃ doped CeO₂) for IKTS cells and HC Starck cells respectively.
- Anode contacting layer composed of a high percentage of nickel for improved contact to the stack contact layer (Ni Mesh) in the stack.

The cathode layer is composed of two sub layers; an adhesion layer and an active layer. The adhesion layer is composed of a porous electrolyte material and a cathode material (for better adhesion of the cathode to the electrolyte). The electrochemically active layer is composed of LSM for both MEA types.

Table 4.1 The properties of the MEAs that were used in the work [Bal09], [Hcs10].

Type	Anode	Electrolyte	Cathode
Type I H.C.Starck (ESC2)	NiO/10CGO layers (30 - 50 µm)	3YSZ (80 – 110 µm)	La _{1-x} Sr _x MnO ₃ /8YSZ - La _{1-x} Sr _x MnO ₃ double layer (30 – 50 µm)
Type II Fraunhofer IKTS	NiO/8YSZ layers (30 - 50 µm)	3YSZ (150 – 200 µm)	La _{1-x} Sr _x MnO ₃ /SZ - La _{1-x} Sr _x MnO ₃ double layer (30 – 50 µm)
Type III Fraunhofer IKTS	NiO/8YSZ layers (30 - 50 µm)	3YSZ10Sc1 CeSZ (150 – 200 µm)	La _{1-x} Sr _x MnO ₃ /SZ - La _{1-x} Sr _x MnO ₃ double layer (30 – 50 µm)

4.1.2 SOFC stack module

The SOFC stack module was designed to have similar conditions as commercial stacks by using Fe-Cr based ferritic stainless steel bipolar plates, nickel and silver contacting elements and glass sealings. To be able to measure reliable current and potential for accurate characterization was also of importance. The main stack components of the single cell stacks used in this work are as follows:

- Bipolar plates
- Glass sealings
- Contacting elements
- MEA

MEAs were placed between chromium-iron alloy bipolar plates (70 x 70 x 6 mm) (manufactured by Plansee SE) and were sealed with glass sealings. Bipolar plates provide mechanical stability to the stack; they have the function of electrical conduction and transfer and homogeneously distribute gases to anode and cathode through rills. The cathode side of the bipolar plates was covered with a mixture of cobalt, manganese and iron paste (applied using roll coating) to minimise or prevent chromium poisoning the cathode. The anode side of the bipolar plates was covered with a 10 μm thick coat of nickel (applied using galvanisation) for improved electrical contact. Contacting elements (between the bipolar plates and the MEA) were nickel mesh and silver stretch metal for the anode and cathode respectively. 0.17 mm or 1 mm thick platinum wires were connected to bipolar plates (using spot welding) for voltage monitoring and current drawing, respectively.

Both the anode and cathode gases were supplied and exhausted from the base of the stack. The flow configuration in the stacks was cross-flow.

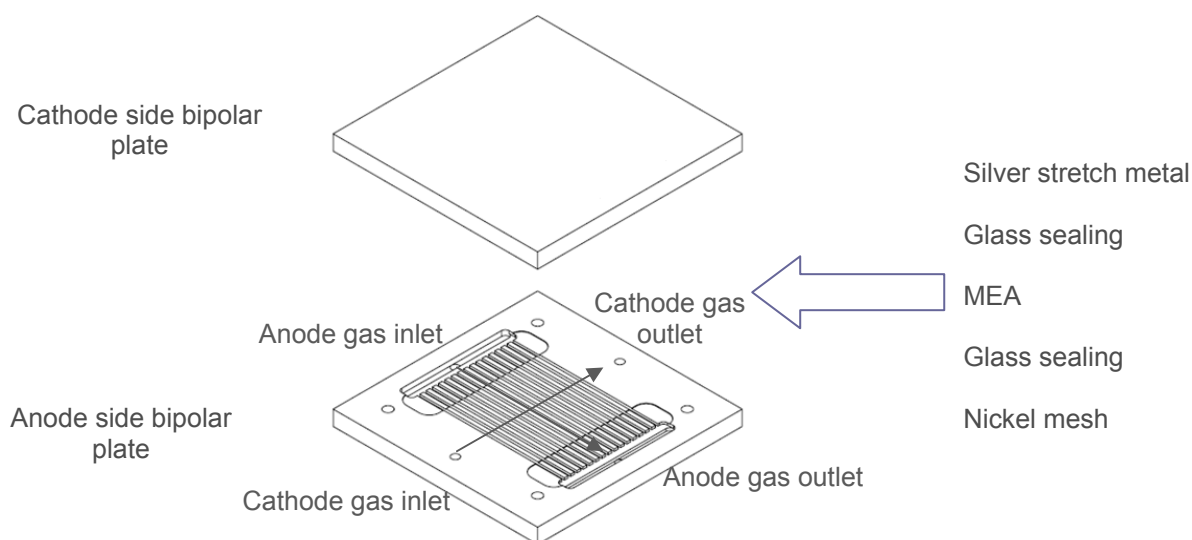
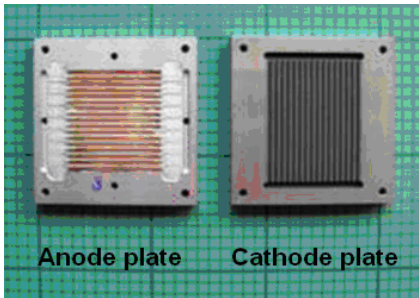
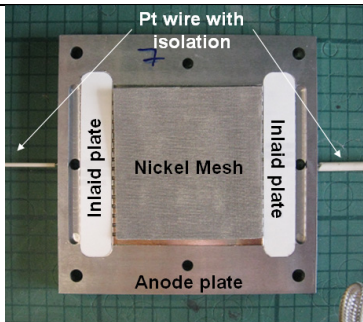
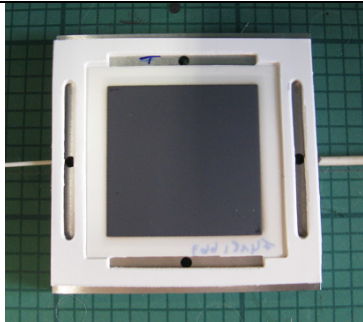
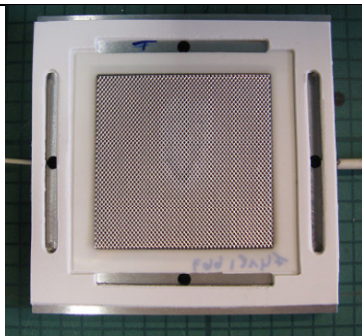
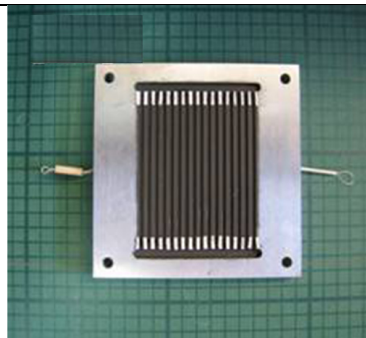
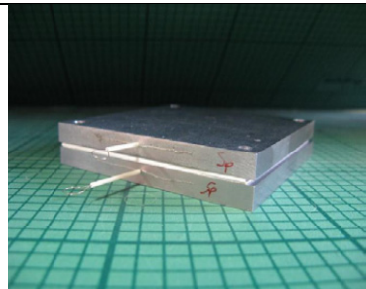


Figure 4.2 Schematics of bipolar plates. Between the plates, contacting and sealing elements and MEAs are placed. Both anode and cathode gases are delivered from anode side bipolar plate.

The stages of the stack assembling and the functions of the materials are presented in Table 4.2.

Table 4.2 Stack assembling stages.

Visualization	Components / Materials	Function
Cathode and anode side bipolar plates		
1 	Bipolar plates: Chromium based alloys (CrFe5 alloy) by Plansee AG	• Mechanical stability of the SOFC • Conducting the electrical current and voltage • Gas distribution through inlet, outlets and gas channels
	Anode plate: plated with 10µm nickel with galvanization technique	For a better contacting of bipolar plate and anode contacting
	Cathode plate: covered with a Co, Mn, Fe – Mix paste by roll coating technique	Protection of MEA towards chromium contamination
Installations on the anode side bipolar plate		
2 	Nickel mesh	Electrical contacting of anode to the bipolar plate
	3YSZ inlaid plates	Gas distribution in the stack
	Platinum wires connected by point welding	Voltage recording / Impedance Analysis
3 	Glass tapes with BaO-Al ₂ O ₃ -SiO ₂ system (rolled, stamped)	• Sealing of the stack against leakages • Electrical isolation between the bipolar plates
	Terpineol (C ₁₀ H ₁₈ O)	Fixing the glass sealing to the bipolar plates at room temperature
	Membrane Electrode Assembly (MEA)	SOFC for electrochemical reactions
4 	Silver mesh placed on the cathode side	Contacting the cathode of the MEA to bipolar plate

Installations on the cathode side bipolar plate			
5		Glass sealings	Gas distribution
		Platinum wires connected with point welding	Electrical contacting
Assembling the stack			
6		Platin wires contacted to anode and cathode bipolar plates by point welding	Voltage recording / Impedance analysis

4.1.3 SOFC test bench

An SOFC stack test bench was constructed to provide an operating environment for the SOFC stacks. The test bench was required to allow the SOFC stack to operate normally whilst also allowing accurate electrochemical measurements such as impedance analysis. The fuel, temperature and electrical load profiles are the input values and the voltage-current and impedance values are the output values of the test bench as shown in Figure 4.3.

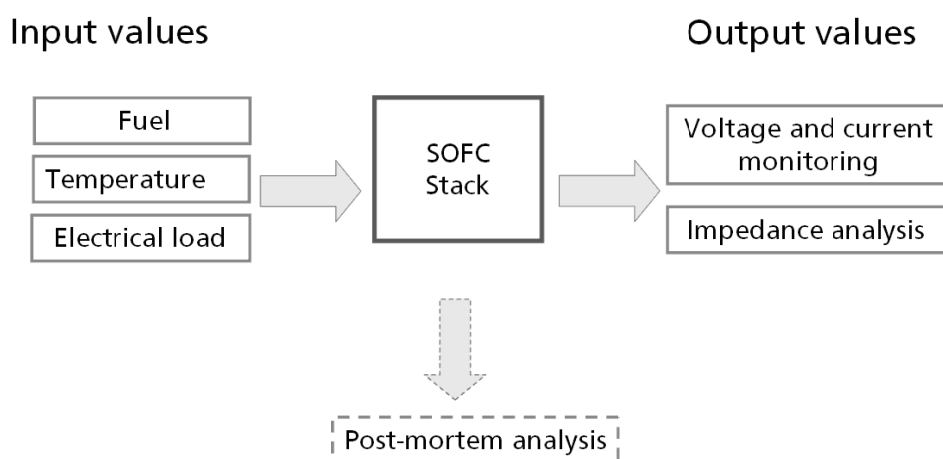


Figure 4.3 Basic functions of the SOFC test bench.

The test bench should be able to supply a variety of different fuel gas compositions and air to the stack. The precise temperature regulation of the stack also has a crucial importance since any deviation of the temperature regulation can cause e.g. false temperature for glass sealing which may cause a leakage in the stack or wrong power outputs. The test bench has the following components in order to obtain the experimental conditions:

- Gas supply unit
- Furnace and stack integration module
- Control and monitoring module
- Module for electrochemical measurements
- Sensors
- Safety related modules

In the following figure the SOFC test bench with its components is shown. Sensors and safety related modules are distributed through whole test bench.



Figure 4.4 SOFC test bench.

4.1.3.1 Gas supply unit

The gas supply components of the test bench are presented in the process flow sheet in Figure 4.5. The gases H_2 , CO , CO_2 , CH_4 , H_2O , N_2 and H_2S/N_2 can be supplied to the anode and air to the cathode side of the stack.

The gas flow rates are controlled using Bronkhorst Mass Flow Controllers (MFC) with an error of 0.8 percent full scale. The gases (except H_2S) were mixed together and flushed through a deionized water evaporator (Controlled Evaporator Mixer from Bronkhorst) to moisturize the fuel. The water dosage is controlled with Bronkhorst Mass Flow Meter (MFM) with an error of 1 percent full scale. The moisturized gas mixture is then mixed with H_2S/N_2 in the fuel pipe before being introduced to the anode. H_2S has separate piping due to its solubility in water which make the solution

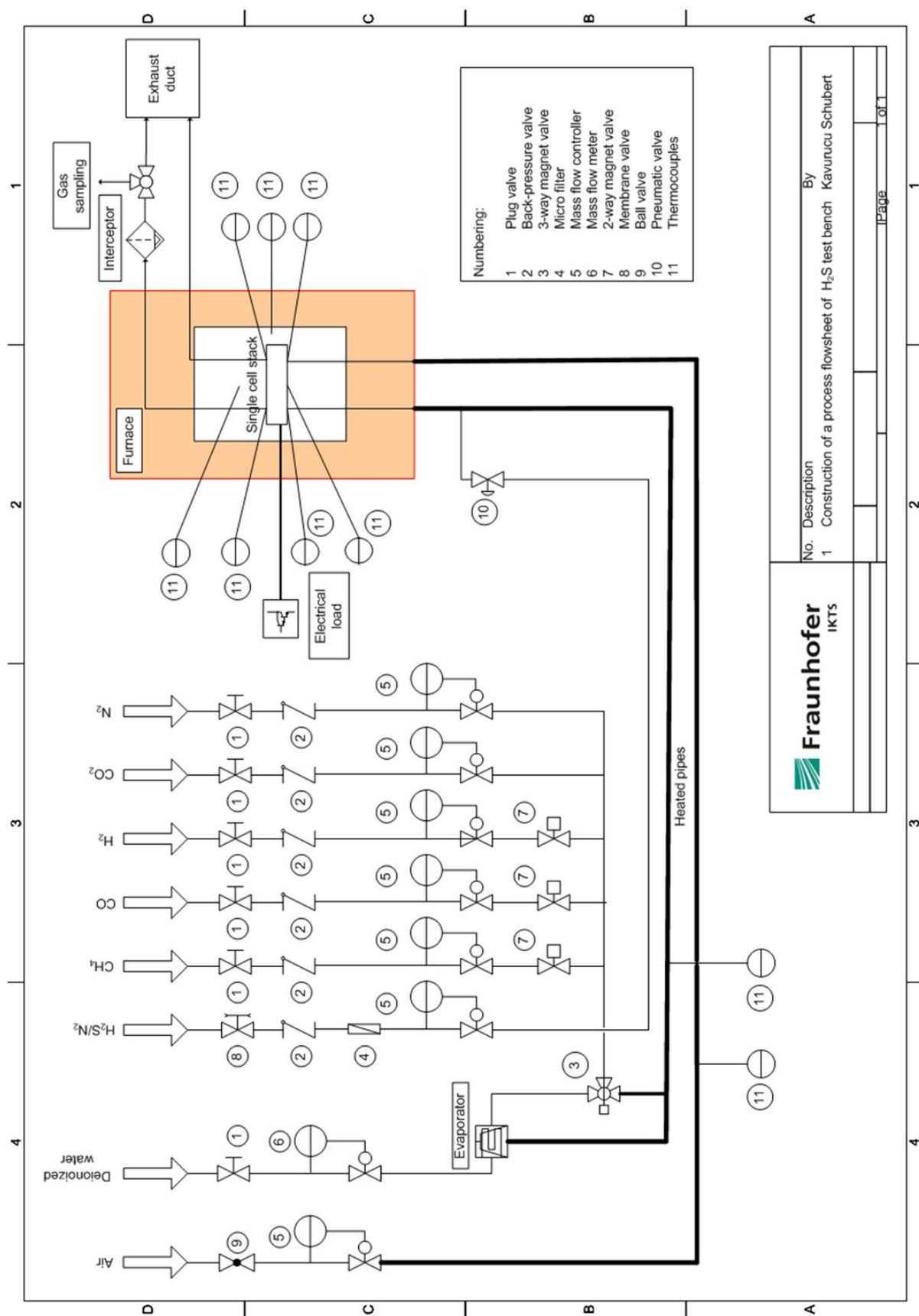


Figure 4.5 The process flow sheet of the test bench.

weakly acidic. The pipings with liquid phases are all heated with heating cables. The exhaust gas from the anode is first condensed in a condenser and then sent to the exhaust gas pipe where the cathode exhaust gas is directly sent to the exhaust gas pipe. Inconel® is used for the piping due to its temperature resistance.

4.1.3.2 Furnace and stack integration module

The SOFC single cell stack is placed in a top head furnace (Type: Efco 135) which was modified for this purpose. The furnace has a power of 1.2 kW and can heat the stack up to 1100 °C. The stack temperature can be regulated to the desired temperature using closed-loop control (thermocouples and a regulator for the furnace power). The single cell SOFC stack is placed on an adapter plate that is manufactured for this purpose. A simplified schematic of the furnace and stack integration module is shown in Figure 4.6.

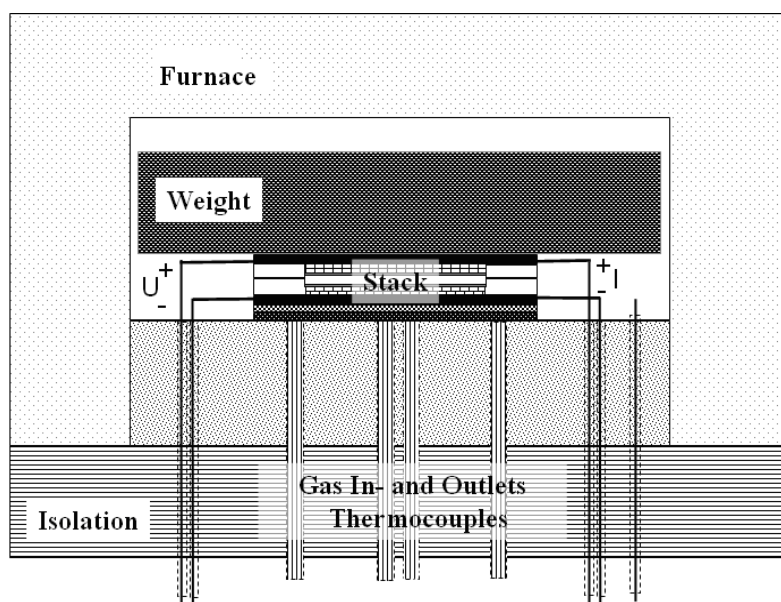


Figure 4.6 Schematic of the furnace and stack integration module with stack.

A CrFe5 alloy (CFY by Plansee AG) adapter plate is placed on top of isolation material in the furnace. The plate is connected to gas inlet and outlet piping with brazing technique. Between stack and the adapter plate nickel rings are used for the electrical contacting and mica seals (cogebi Hi-Temp 710 – with 500 µm thickness) are used in order to avoid gas leakages. The bottom side and the top side of the stack were anode and cathode, respectively. The anode and cathode voltages are contacted with 0.17 mm platin wires which were covered with Al₂O₃ isolation. The current was contacted via 1mm platin wires on either sides or Inconel® plate on the cathode side. The stack is loaded with 6800 g weight for glass sealing and contacting in the stack. All of the materials used in the hot zone in the furnace are made of temperature resistant materials.

4.1.3.3 Module for electrochemical measurements

In this work, Siemens (UOP Power Supply D2408) as power supply unit was used. The impedance analyzers from Zahner-Elektrik GmbH and from FuelCon AG were used for the impedance measurements. A detailed discussion on electrochemical measurements is given in Chapter 4.2.2.

4.1.3.4 Control module

The units in the test bench are controlled with programmable logic controller (PLC) from National Instruments. Real-time software is running in this controller which is responsible for the data acquisition and control of the test bench. Through an Ethernet adapter, PLC communicates with the computer. In this computer, the data from the experiments are then saved in a data bank and logged as text data. In a host application the status of the test bench can be monitored and controlled. VAC NT/32 Software from Intega GmbH as well is used as software. Figure 4.7 shows the data flow of the test bench.

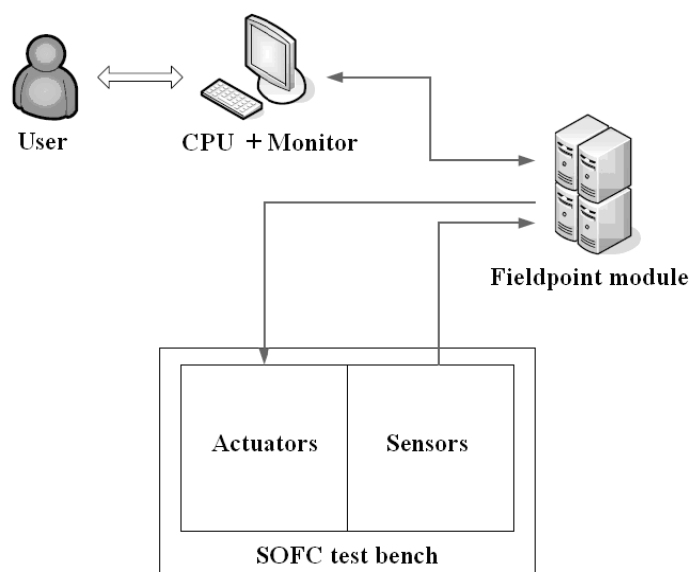


Figure 4.7 Schematic of the data flow in the test bench.

VAC NT/32 is an operating system which shows set values and measured values of the experiment. The software screen of the test bench is divided into three parts: Program setting (Programmeinstellung), Control (Steuerung) and values over time (Zeitverläufe). VAC NT/32 makes it possible for the user to program the steps of the experiment beforehand (auto programming) or during the experiments where one can set the parameters such as temperature, volume flows, current, etc.

4.1.3.5 Sensors

Temperatures in different positions in the oven are monitored with mantle thermocouples (T.M.H. Type K and Type N, 375 °C – 1000 °C, ± 1.5 °C) with a

diameter of 1 mm in order to define the stack temperature, temperature differences in various places and to avoid cold areas where condensation may be a problem. The exhaust gas from the anode can be analyzed with gas chromatography with the help of a valve which is located on the anode exhaust gas piping.

4.1.3.6 Safety related modules

Toxic and explosive gases (H_2 , CO , C_xH_y) are monitored permanently with gas sensors placed in test bench. When the concentrations exceed maximum occupational exposure limits, a laboratory or test bench alarm will be initiated and the test bench program changes to safety mode.

4.2 Experimental procedures

4.2.1 Bringing SOFC stack to experimental conditions

The experimental procedures include some standard procedures which were repeated in every experiment. These procedures are critical to determine if the apparatus and stack meets the minimum quality to begin the experiment. These include the following phases:

1. Preparations: Installation of the stack to the test bench, software programming
2. Glass sealing: Heating the stack with defined heating rates and gas compositions
3. Reduction of the anode: Applying hydrogen to the anode gradually for reduction
4. Activation of the cell: Cell voltage increase with applying current load
5. Experiment: Characterization of the cell under experimental conditions
6. End of the experiment: Cooling down the cell to room temperature, demounting, post-mortem-analysis.

After the stack is placed in the test bench, a standard glass sealing procedure is applied to the stack with the help of auto programming of the software. The sealing procedure includes the stepwise heating of the stack glass sealing procedures under different parameters. First, the oven will be heated up to 500 °C with 2 °C/min with flushing the SOFC cathode with 30 l/h dry air. The stack will be held at 500 °C for two hours for debinding glass from binder. Afterwards, it will be heated up to 930 °C, to the sealing temperature where from 700 °C the anode will be flushed with nitrogen. At 930 °C, the stack will be held for five hours for the sealing where glass melt and form a gastight layer. Following nickel oxide in the anode will be reduced with hydrogen to metallic nickel in gradually (Figure 4.8).

The complete reduction of nickel oxide to nickel occurs first just before the experiments since during the production of SOFC anodes, sintering will be carried

out in air due to production costs. This is a necessary process due to increase of catalytic activity and electrical conductivity with the reduction of nickel (Figure 4.9).

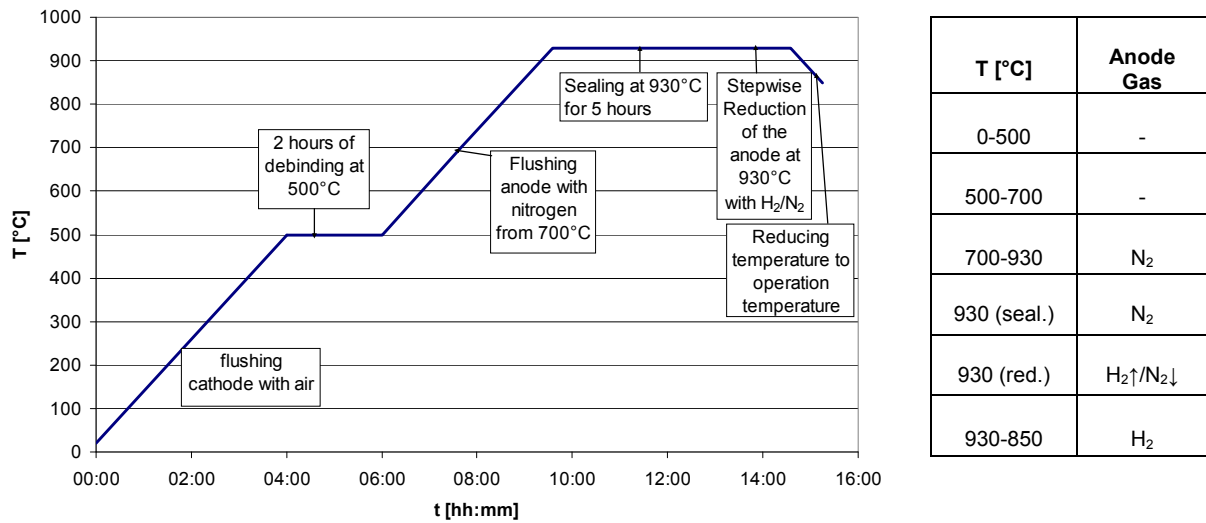


Figure 4.8 Glass sealing temperature profiles of the single cell SOFC stacks. The standard heating and cooling rates are 2 °C/min. The anode gases during different phases are given in table. Cathode gas is air throughout the procedure.

During the reduction process at 930 °C the nitrogen flow to the anode will be reduced and hydrogen flow will be increased. Since this reduction is exothermal, it will be done stepwise. The gradual reduction, compared with a step change, avoids creating a severe temperature change and hinders the damage of the anode microstructure by a sudden reduction. At the end of the reduction phase with 100 vol % H₂ as anode gas, the cell voltage reaches to open circuit voltage (OCV) > 1.15 V. Any gas leakages in the cell can be recognized at this step with lower OCV values. If the OCV of the stack is within the specification, the temperature can be decreased to standard operating temperature of 850 °C and the desired gas composition will be introduced.

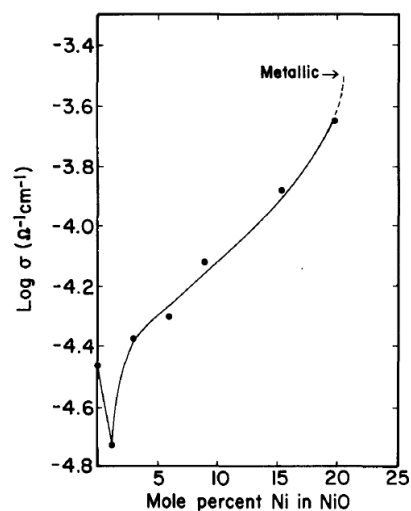


Figure 4.9 Logarithm of conductivity as a function of mole percent nickel in nickel oxide at 1000 K [Tar83].

The anode and cathode gas flows were set as 40 l/h for both sides throughout this work. Low fuel utilization during the study (F_U : max. 30 %) was chosen in order to maximize the performance of the stack by reducing the concentration overpotentials to maximize the effects of the gas composition.

When the cell reaches a constant OCV under experimental parameters, current is applied to the cell with 0.5 A/min steps until the cell voltage decreases to 0.7 V. If the current is applied abruptly, there is a danger of cell damage due to rapid changes of the cell temperature because of exothermic reactions. The cell voltage should not decrease below 0.65 V which can result in oxidation of the nickel in the anode.

During the first period of the stack operation, the cell voltage increases slowly and is then constant. This period is called the activation period and is normally not longer than 120 hours under constant electrical load.

The activation process is associated with increase of the electrocatalytic properties of the electrodes (changes in the oxygen bond-breaking activity and/or oxygen surface diffusion on the cathode [Koc06]) and better contacting of anode and cathode, reduction of remained nickel oxide in the anode as well as temperature increase due to exothermal reactions with electrical load. When the voltage reaches to a constant value, the experimental procedures can begin.

4.2.2 In-situ characterization of the stacks

In this work, the performance of the test articles (SOFCs) are characterized with three electrochemical measurement methods. These include voltage-current characteristic curves, electrochemical impedance spectroscopy, and voltage-current relationship over time.

The voltage-current curve allows the total resistance of the entire fuel cell stack to be calculated; the electrochemical behaviour of the electrode/electrolyte interfaces, the conductivity of electrolyte and the electrical contacts as well as providing insights into the effect of the gas supply.

Electrochemical impedance analyzer is used in order to distinguish these various resistances. Voltage-current relationship over time gives the information of the voltage and current changes under experimental parameters.

4.2.2.1 Voltage-current curves

Voltage-current characteristics curves are used as a method to characterize fuel cells frequently. During each series of experiments throughout this work, voltage-current characteristic curves have been taken before and after each experimental phase. By voltage-current curves, the dependence of the cell voltage - between OCV and the critical cell voltage (0.65 V) - with respect to current density is given. The

curves present the performance of the fuel cell dependent of the parameters such as temperature, gas composition and applied electrical load. It is a tool to define e.g. overall resistance, long term stability and degradation. The cell voltage decreases by increasing the current density due to the ohmic and polarization losses as explained in Chapter 2.

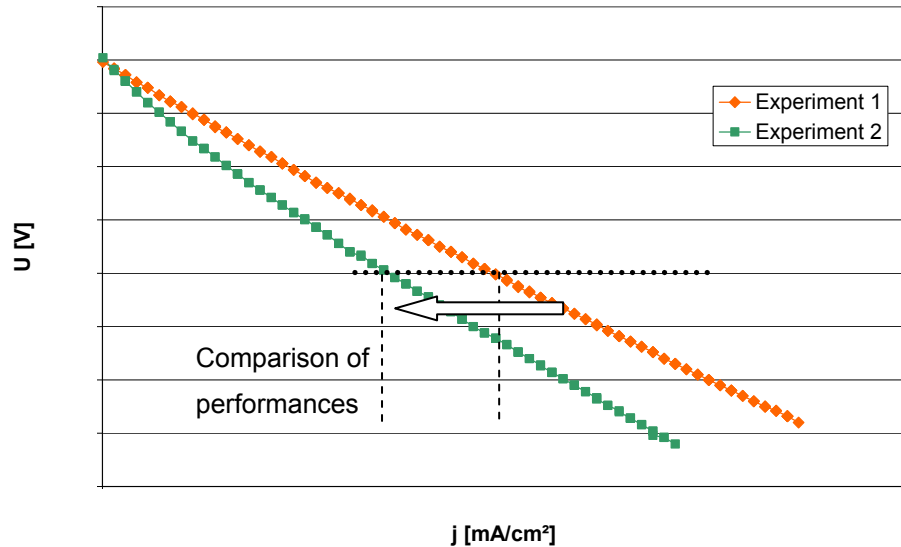


Figure 4.10 Comparison of voltage current density curves of SOFC during two different experimental parameters; shift of the curve to left shows the degradation of the stack power.

The voltage-current curve may give the information of area specific resistance of an SOFC stack that is the sum of all resistances (activation, ohmic, concentration). Therefore it is an important tool to show the performance of SOFC stacks in various systems under various parameters.

To produce a voltage-current curve, the cell current is increased gradually in 0.5 A/min until the voltage decreases to 0.65 V. As a reference value, the current density will be read at 0.7 V. In this work, the electrical loads from Zentro-Elektrik (Type ELA) and power supply unit Siemens (UOP Power Supply D2408) were used in the test benches.

Voltage-current relationship over time during an experiment may show the differences on the SOFC performance over time. During the experiments, current drawn from the cell was usually kept constant and voltage changes and current were recorded.

For detailed information on resistances of the single components impedance spectroscopy is used.

4.2.2.2 Impedance spectroscopy

Impedance measurements were applied systematically during this work to electrochemically characterize the polarizations of SOFC. Measurements were

carried out in the frequency range 0.01 Hz to 100 kHz using two different systems; Zahner (Model Zennium) and FuelCon (Model TrueData-EIS). The electrochemical impedance is normally measured by applying a potential to an electrochemical cell and measuring current through the cell (potentiostatic mode) or vice versa (galvanostatic mode).

The stacks were contacted to the impedance analyzers in four-electrode modus as follows.

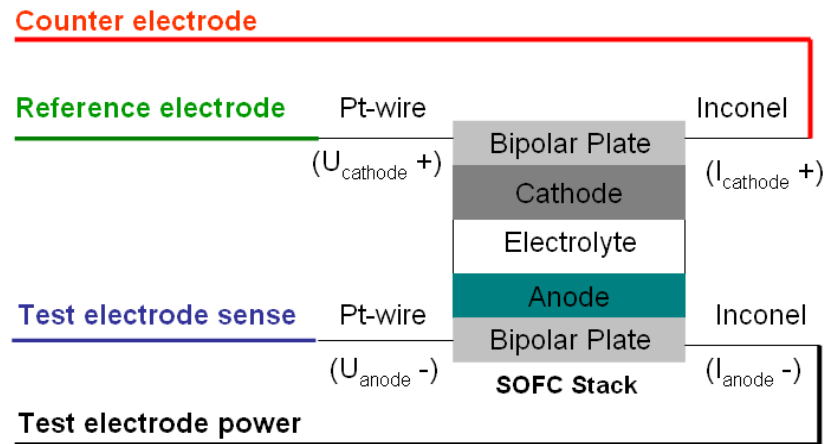


Figure 4.11 Connections of the single cell SOFC stack to impedance analyzer.

In this work, the analyses were performed using potentiostatic mode, where a small voltage (10 mV) was applied. The results of the analysis were plotted in Nyquist-Diagrams where real and imaginary parts of the impedances are plotted in x-axis and y-axis respectively. The Nyquist diagram gives a better overview of the frequency dependent processes of the total reaction when compared to Bode diagram where the impedance is plotted with log frequency on the x-axis and both the absolute value of the impedance $|Z|$ and phase shift angle on the y-axis.

The resistive and capacitive/inductive components of impedance of a fuel cell must be determined in order to plot Nyquist diagrams. In a linear system, the current response to a sinusoidal potential will be a sinusoid at the same frequency but shifted in phase (Figure 4.12).

The small voltage applied in a sinusoidal form as a function of time is defined as follows:

$$U(t) = U_0 \cdot \cos(\omega t) \quad (\text{eq. 4.1})$$

where U_0 is the amplitude of the signal and ω is the angular frequency. The angular frequency is related to the frequency as:

$$\omega = 2 \cdot \pi \cdot f \quad (\text{eq. 4.2})$$

The current response is then also sinusoidal and has a phase shift by an angle ϕ :

$$I(t) = I_0 \cdot \cos(\omega \cdot t + \phi) \quad (\text{eq. 4.3})$$

where I_0 is the current amplitude.

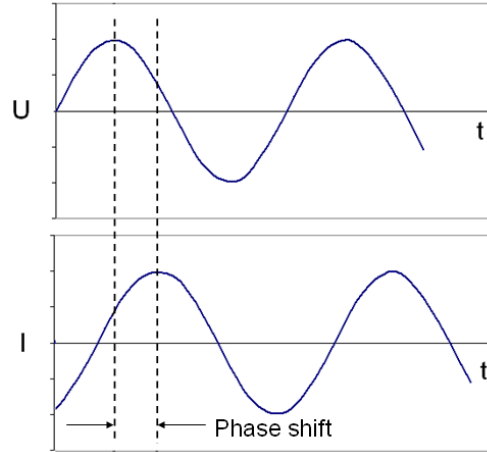


Figure 4.12 Sinusoidal current response in a linear system.

The impedance of the system, analogous to Ohm's Law, can be expressed as:

$$Z = \frac{U(t)}{I(t)} = \frac{U_0 \cdot \cos(\omega \cdot t)}{I_0 \cdot \cos(\omega \cdot t + \phi)} \quad (\text{eq. 4.4})$$

$$\text{with } |Z| = \frac{U_0}{I_0} \quad (\text{eq. 4.5})$$

$$\text{and } Z = |Z| \cdot \frac{\cos(\omega \cdot t)}{\cos(\omega \cdot t + \phi)} \quad (\text{eq. 4.6})$$

Using the Euler's equation:

$$\exp(i \cdot \phi) = \cos \phi + i \cdot \sin \phi \quad (\text{eq. 4.7})$$

where i is the imaginary unit, it is possible to express the impedance as a complex function. The potential is described as:

$$U(t) = U_0 \cdot \exp(i \cdot \omega \cdot t) \quad (\text{eq. 4.8})$$

The current response can be written as:

$$I(t) = I_0 \cdot \exp(i \cdot \omega \cdot t - i \cdot \phi) \quad (\text{eq. 4.9})$$

The impedance can then be expressed as a complex number with a real and imaginary part:

$$Z = \frac{U}{I} = |Z| \cdot \exp(j \cdot \phi) = |Z| \cdot (\cos \phi + i \cdot \sin \phi) = Z' + Z'' \cdot i \quad (\text{eq. 4.10})$$

where:

$$\phi = \tan^{-1} \cdot \left(\frac{Z''}{Z'} \right) \quad (\text{eq. 4.11})$$

$$\text{and } |Z| = \left[(Z')^2 + (Z'')^2 \right]^{\frac{1}{2}} \quad (\text{eq. 4.12})$$

Impedance is a complex quantity and it is only real when ϕ is zero and thus $Z(\omega) = Z'(\omega)$ for purely resistive behaviour. In this case the impedance is frequency independent.

In order to understand the SOFC impedance spectra, it is necessary to understand impedance expressions for some basic electrical circuits.

The impedance of a resistor Z_R is simply the resistance R where $Z(\omega) = Z'(\omega)$ shown with a single plot in the Nyquist plot, whereas a capacitance (Z_C) is shown as a straight line in the imaginary axis.

$$Z_C = \frac{1}{i \cdot \omega \cdot C} \quad (\text{eq. 4.13})$$

Here C represents the capacitance in Farad (F).

The total impedance of a resistance and capacitance in series is:

$$Z_{R-C} = Z_R + Z_C = R + \frac{1}{i \cdot \omega \cdot C} \quad (\text{eq. 4.14})$$

while total impedance of resistance and capacitance in parallel is:

$$\frac{1}{Z_{RC}} = \frac{1}{Z_R} + \frac{1}{Z_C} = \frac{1}{R} + i \cdot \omega \cdot C \quad (\text{eq. 4.15})$$

where Z_{RC} is then:

$$Z_{RC} = \frac{R}{1 + R^2 \cdot \omega^2 \cdot C^2} - \frac{R^2 \cdot \omega \cdot C}{1 + R^2 \cdot \omega^2 \cdot C^2} i \quad (\text{eq. 4.16})$$

Z_{RC} has a semicircle shape on the Nyquist diagram. At low frequencies the current flows through the resistor, at higher frequencies the current is short circuited by a capacitor.

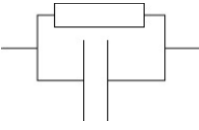
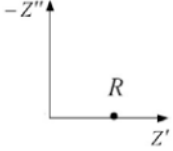
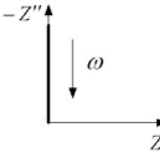
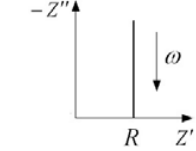
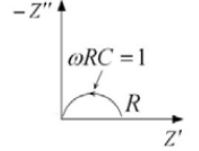
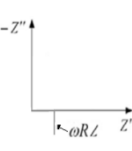
The inductance (Z_L) of a system can be also described similar to resistance and capacitance as:

$$Z_L = i \cdot \omega \cdot L \quad (\text{eq. 4.17})$$

where L is the inductance in Henrys (H).

It is possible to draw the Nyquist Diagram of a system by plotting the real part on x-axis and the imaginary part on y-axis. In Table 4.3, the circuit elements, their formula and Nyquist plots are summarized.

Table 4.3 The basic circuit elements, their formulas and Nyquist plots [Fan07].

Circuit elements				
				
Formula				
R	$Z_C = \frac{1}{i\omega C}$	$Z_{R-C} = Z_R + Z_C = R + \frac{1}{i\omega C}$	$Z_{RC} = \frac{R}{1 + R^2\omega^2 C^2} - \frac{R^2\omega C}{1 + R^2\omega^2 C^2} j$	$Z_L = i\omega L$
Corresponding Nyquist plots				
				

The equivalent circuit of a solid oxide fuel cell can be described as a combination of inductors, capacitors and resistors. Mosch [Mos09] presented an equivalent circuit for the processes that take place in an SOFC.

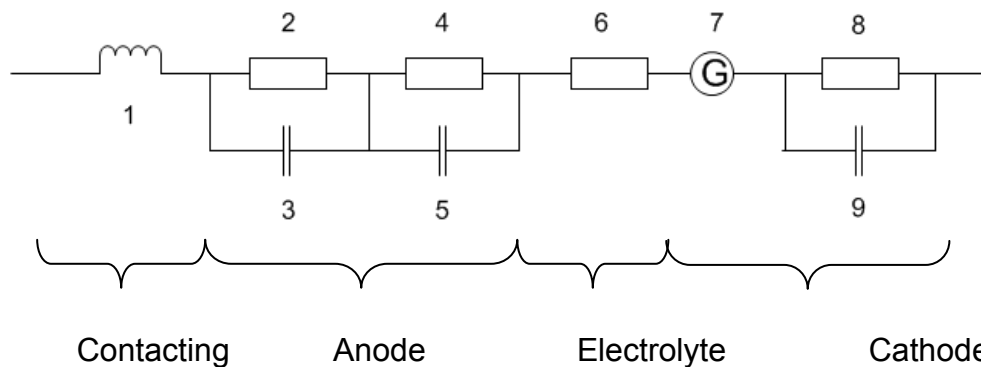


Figure 4.13 Equivalent circuit of a MEA [Mos09].

Basically, the circuit consists of one inductor for the contacting of the cell (1), three charge capacitance elements (3, 5, 9) and four resistance elements (2, 4, 6, 8). 2, 4 and 8 represent the charge transfer resistances in anode and cathode respectively. 3, 5 and 9 represent the charge double layer capacitors between anode and electrolyte and cathode and the electrolyte respectively. Elements 2 and 3 represent the processes at the triple phase boundaries in the anode where hydrogen dissociates to hydrogen ions as well as the reaction with the oxygen ions to produce water. The 4th and 5th elements represent the dissociation and absorption processes in the anode. Element 6 represents resistance due to the ionic conductivity of the electrolyte which follows the Ohm's law. 8th and 9th elements represent the adsorption and diffusion processes of the oxygen in the cathode. We observe here a third element which can not be explained by resistivity, conductivity or inductivity. The 7th element called Gerisher element (Z_G) that represents a process where a chemical-electrochemical-chemical reaction takes place (e.g. diffusion processes and chemical reactions) and used also for the solid state reactions taking place in SOFCs. The Gerisher element is defined as:

$$Z_G = \frac{Z_0}{\sqrt{k + j \cdot \omega}} \quad (\text{eq. 4.18})$$

where k is the rate constant parameter [Mos09].

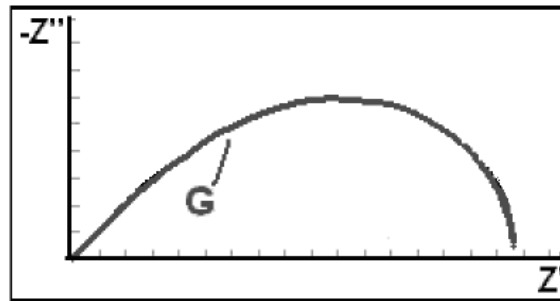


Figure 4.14 Effect of Gerisher element on a semicircle on a Nyquist Plot. (Modified from [Con09]).

The suitability of Gerisher element for description of electrochemical processes in the cathode was explained by Kuznecov et al. [Kuz03]. With the impedance data, one may not be able to define the exact equivalent circuit elements with the impedance data due to the complexity of SOFC system. Leonide [Leo08] and Sonn [Sonn08] studied the impedance data of Ni/8YSZ/8YSZ/La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} at different temperatures and with various gas compositions. They analyzed the data by calculating the distribution function of relaxation times (DRT) for each parameter. Figure 4.15 shows the impedance data of anode supported cell at OCV with Ni/8YSZ anode at 717 °C in H₂ (9.4 vol % H₂O) with air at the cathode side and corresponding semicircles analyzed with DRT method.

According to the figure, the high frequency region of Nyquist plot represents the gas diffusion in the anode coupled with charge transfer reactions whereas low frequencies represents the O^{2-} diffusivity and surface exchange kinetics in the cathode as well as mass transfer resistance in the anode. This explanation may help us to understand the effect of the H_2S contamination on impedance data.

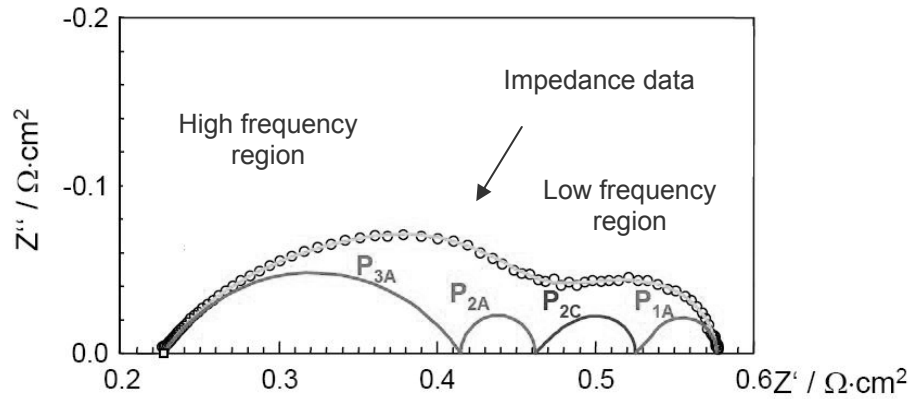


Figure 4.15 Nyquist plot of the impedance data in and corresponding semicircles of various processes. (P_{1A} : mass transfer resistance in the anode, P_{2A} , P_{3A} : gas diffusion coupled with charge transfer reaction and ionic transport (at anode functional layer), P_{1C} : gas diffusion (cathode – not shown due to low values), P_{2C} : oxygen surface exchange kinetics and O^{2-} diffusivity in the cathode) (Modified from [Web09])

4.2.3 Post-Mortem-Analysis techniques

After the stacks have cooled down to room temperature the SOFCs are analyzed with the methods described below. The aims of these analyses were to determine any changes in the morphology of anode caused by sulfur contamination and qualify and quantify sulfur if any exists in sample.

4.2.3.1 Field Emission Scanning Electron Microscopy (FESEM)

FESEM reveals information on the morphology of SOFC with very high resolution images of the surfaces, revealing details as small as 1 nm (which is 3 to 6 times finer than scanning electron microscope). To obtain an electron microscopic image, the surface sample is swept in a raster pattern with a focused beam of electrons. In standard electron microscopes, the electrons are generated either by heating a tungsten filament by current to about 2800 °C or sometimes produced by a crystal with lanthanumhexaboride (LaB_6) mounted on a tungsten filament. In FESEM, an electric field is applied, where an extremely thin and sharp tungsten filament functions as a cathode in front of two anodes and the voltage in between is in the order of 0.5 to 30 kV. The electron beam produced by field emission source is about 1000 times smaller than a standard scanning electron microscope, for this reason the quality of the images are better [Jan10]. Schematic of a FESEM is shown in Figure 4.16.

When a sample surface is bombarded with energetic beam of electrons, most incident electrons interact with specimen atoms and are scattered. The scattering can be either inelastic or elastic. In elastic scattering the electron path changes but the kinetic energy and the velocity remain constant due to the difference between the mass of electron and atomic nuclei. In inelastic scattering, energy of the electron is lost through interacting with the orbital electrons of atoms in the sample. The interactions produce a number of signals from different interaction volumes as shown in Figure 4.17.

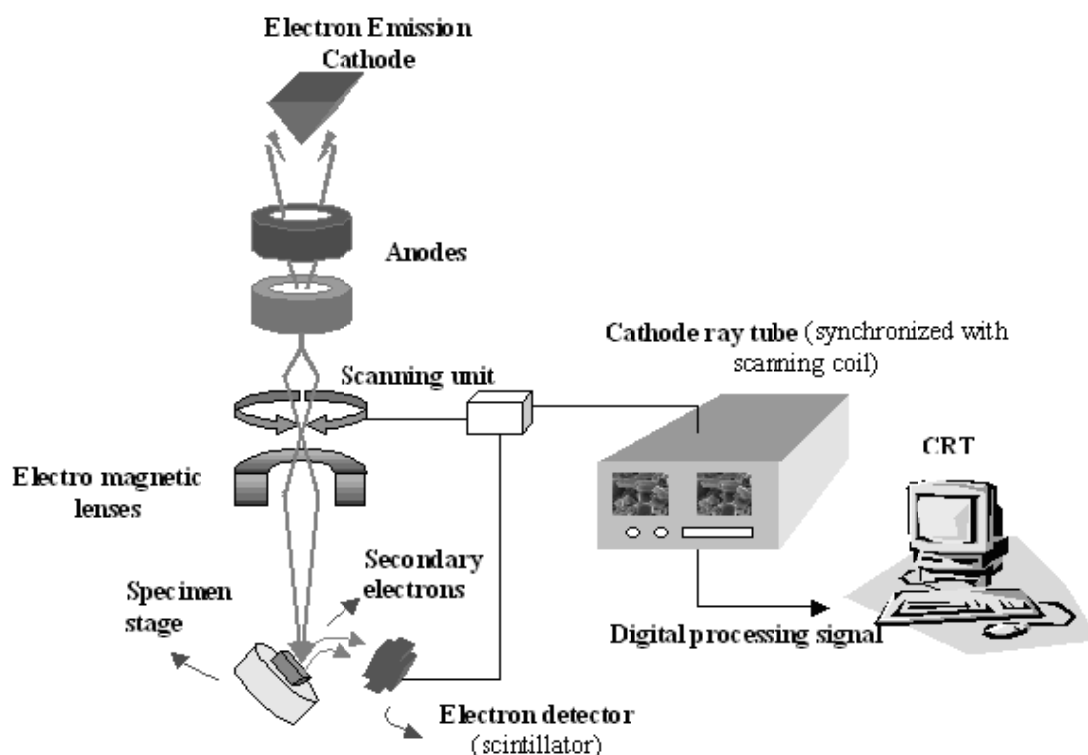


Figure 4.16 Schematic of a FESEM [Nmt10].

The secondary electrons (SE) (electrons triggered from the sample) or backscattered electrons (BSE) of the primary electron beam are detected by the detectors in a FESEM. The number of the backscattered electrons is proportional to the mean atomic number of the sample; larger atoms have higher probability of producing an elastic collision due to their larger cross-sectional area. Due to this feature, BSE images are very helpful to analyze the phase or composition differences of the sample. BSE detectors are either scintillator or semiconductor types. The detected SE images give information about the topography of the sample. The secondary electrons are detected by an Everhart-Thornley detector which is a type of scintillator-photomultiplier system [Goo01]. In this work, the Field Emission Scanning Electron Microscope of the company Zeiss (Model LEO DSM 982) is used.

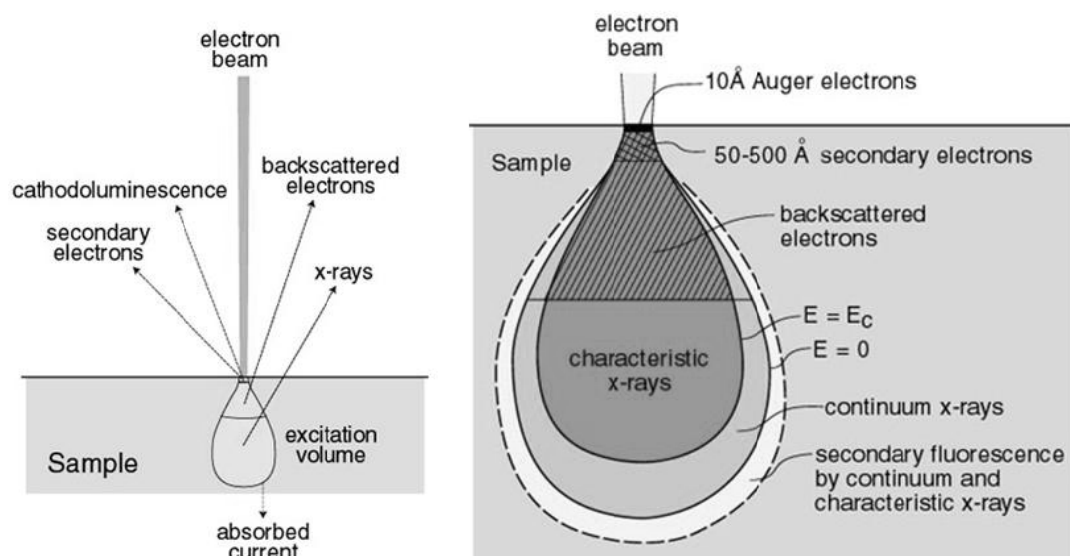


Figure 4.17 Simple schematics of the scattering interactions and detail of the interaction volumes in the sample for various interactions. (E : energy of an electron, E_c : x-ray requiring energy) [Wit08].

4.2.3.2 Energy Dispersive X-Ray Spectroscopy (EDX)

Besides back scattered or secondary electrons, characteristics x-rays will also be emitted from a sample (Figure 4.17). When a sample is bombarded with an electron beam, electrons from the inner shells of the atoms will be scattered and the new empty places of the shells will be filled with other electrons with different energy levels. Characteristic x-rays will be emitted with this electron transfer. Since each element has unique atomic structure, it is possible to identify the elements of the sample with this method. The EDX detectors are usually also installed in SEM and therefore is possible to characterize the elements of the SEM samples. The FESEM of Zeiss (Model LEO DSM 982) has also this feature and is used during this work. EDX spectroscopy is a useful method to characterize the samples however its high detection limit made it inadequate to analyze the traces in very low concentrations (Figure 4.18). Therefore TOF-SIMS method was used to analyze the sulfur traces in the anode.

4.2.3.3 Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS)

TOF-SIMS method was used to analyze the sulfur traces in the anode since EDX detection limit was not low enough to detect sulfur. By TOF-SIMS, the sample surface is bombarded with pulsed primary ion beams. The ion beam desorbs and ionizes species (secondary ions) from the sample. The secondary ions are accelerated then into a mass spectrometer and their masses are analyzed by measuring their time-of-flight from the surface to the detector.

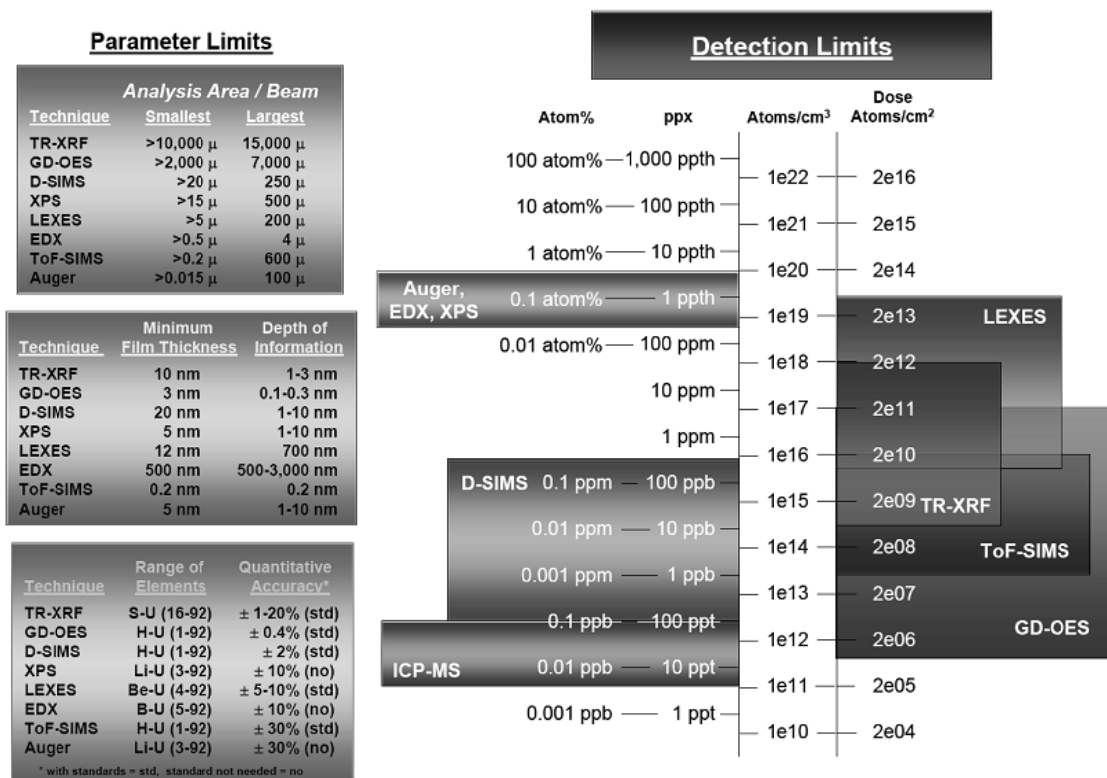


Figure 4.18 Comparison of the parameter and detection limits of some characterization methods [xps07].

Three different operation modes are possible:

- mass spectroscopy mode to determine the elemental and molecular species on the surface,
- surface imaging to visualize the distribution of individual species on the surface,
- depth profiling to determine the distribution of different chemical species as a function of depth from the surface [Phi10].

The depth profiling method was used in this work to analyze sulfur in anode surfaces. Examples of images for the methods are given in Figure 4.19. The TOF-SIMS used in this work "TOF-SIMS.5-100P" was the product of the company ION-TOF GmbH and is located in Institute of Solid State Physics RAS in Chernogolovka / Russia.

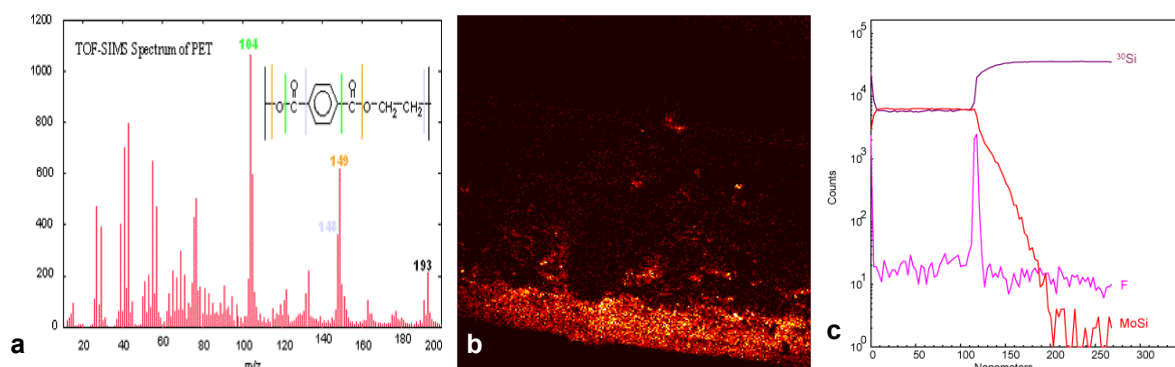


Figure 4.19 Examples of three operation modes of TOF-SIMS a) mass spectroscopy mode; spectrum of poly-ethylene-teraphthalate (PET) b) surface imaging mode, Fe^+ image of steel from the razor blade c) depth profiling mode, sputter depth profile of a thin MoSi_2 film on silicon [Phi10].

4.2.4 In-Situ Thermogravimetric Analysis (TGA)

In addition to post mortem analyses of the anodes, additionally, sulfur intake of NiO and 8YSZ powders at operation temperature of SOFC (850 °C) are thermogravimetrically analyzed with simultaneous thermal analyzer from Netzsch (Model STA 449 C Jupiter) (Figure 4.20). With thermogravimetric analysis (TGA) it is possible to measure any change in weight of the sample as a function of temperature or time, caused by the interaction of the sample with its surrounding atmosphere, in our case with sulfur under isothermal conditions.

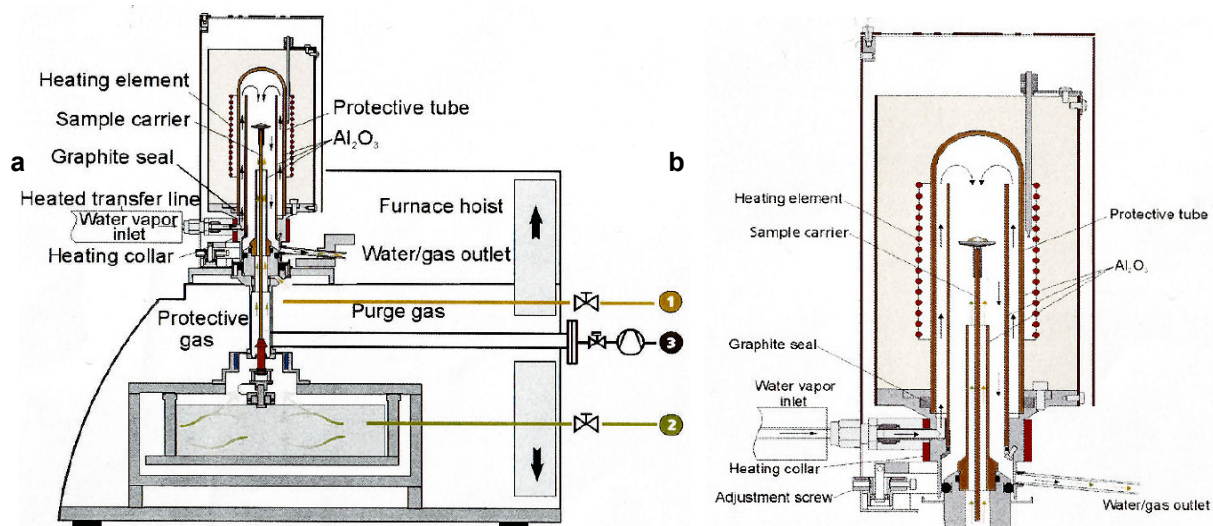


Figure 4.20 a) Schematic of the thermoanalyzer b) Oven schematics detail from a).

The samples are mounted on the sample carrier in a special high-temperature furnace with an almost nonexistent temperature gradient in the sample chamber. The effect of H_2S addition to $\text{H}_2/\text{H}_2\text{O}/\text{N}_2$ gas mixture to the weight of the sample had been analyzed with an electromagnetically compensated balance system with a resolution of 0.1 μg with $\pm 2 \mu\text{g}$ inaccuracy. It should be noted that the samples were not electrochemically active during measurements. Details on TGA experimental procedure and the results are explained in Chapter 5.

5 RESULTS AND DISCUSSION

In this chapter, the results of experiments on the effects of sulfur (H_2S) containing fuel gas on the performance of a single cell SOFC stack under various operating parameters are presented; and the mechanisms behind the effects are discussed.

The chapter is divided into three parts. In chapter 5.1 the H_2S contamination behaviour of stacks with Ni/8YSZ anodes is presented; and in chapter 5.2 the behaviour with Ni/10CGO anodes is presented. In chapter 5.3 the results and underlying mechanisms are discussed.

5.1 Effect of H_2S containing fuel on the performance of a SOFC with a Ni/8YSZ anode

The sulfur effects on stack performance are studied by several experiments. First, the effect of a single contamination is examined then, multiple contaminations. These studies are followed by experiments to study the effects of H_2S concentration, current density and H_2O concentration. Hydrogensulfide (H_2S) was selected as a sulfur contaminant owing to its high stability under SOFC operating conditions as explained in Chapter 3.2.2.

5.1.1 Effect of single contamination

This experiment examines the change in stack performance after contaminating the anode gas with 2 ppm H_2S . A single cell stack with MEA Type III was brought to experimental conditions using standard heating up procedures (Chapter 4.2.1). The anode was flushed with standard gas mixture (43.8 vol % H_2 / 6.2 vol % H_2O / 50 vol % N_2) with 40 NI/h volume flow throughout the experiment. The cathode of the cell was supplied with 40 NI/h air. As the stack reached a constant voltage, voltage-current characteristics curve and impedance measurements were performed. The fuel utilization of the cell was calculated as 24.3 % after 350 hours of operation under 319 mA/cm² with 0.743 V. For the experiment, 2 ppm H_2S was added to the anode gas for fifteen hours. The voltage history is shown in Figure 5.1 and 5.2.

In the first 15 minutes of contamination the cell voltage fell from 0.743 V to 0.656 V ($dU/U_0 = 11.70\%$). This voltage decrease was followed by a slow drop from 0.656 V to 0.642 V ($dU/U_0 = 13.51\%$) over the next twelve hours. Voltage – current characteristic curves and impedance analysis were performed before removing the H_2S from the anode gas. Upon removal of H_2S , the cell voltage first had a quick rebound then recovered gradually. The recovery was not complete and the cell voltage stabilized at 98.9 % of its initial value (0.735 V) after 85 hours. Figure 5.2 shows the cell voltage, current density and H_2S as a function of time for both before, during and after poisoning with H_2S . The points where impedance analysis was conducted are marked as 1, 2 and 3.

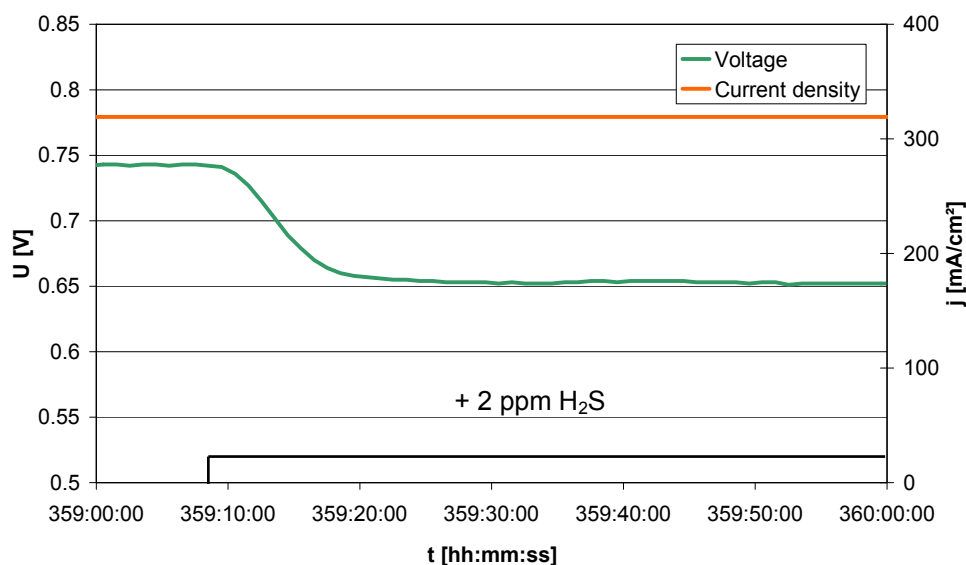


Figure 5.1 The cell voltage development with 2 ppm H₂S addition to fuel gas.

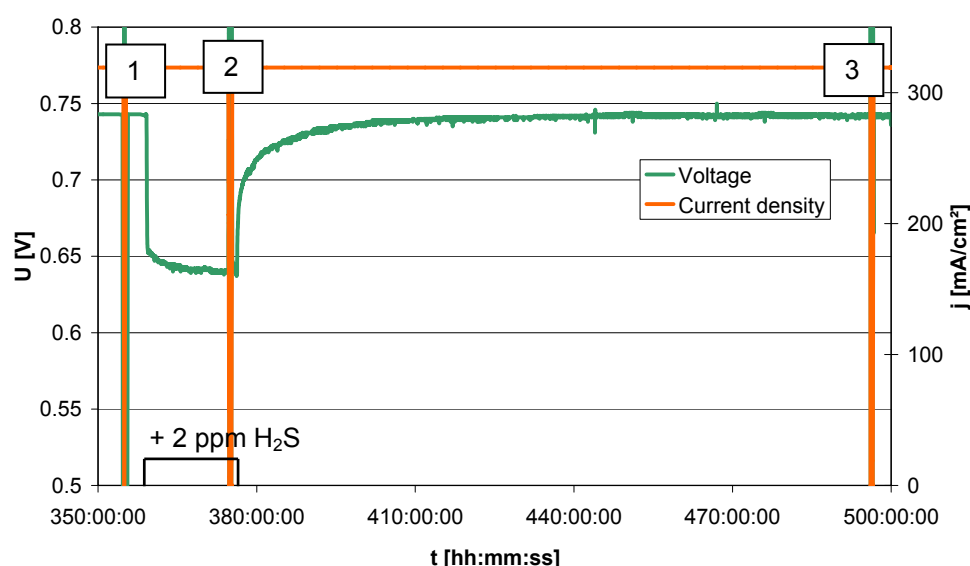


Figure 5.2 The effect of 2 ppm H₂S addition on single cell stack voltage. The impedance analysis points are marked as 1, 2 and 3 in figure.

Impedance spectra of the stack were recorded under open-circuit conditions before, during and after 140 hours of H₂S contamination between the frequencies 0.1 Hz and 50 000 Hz. The Nyquist diagrams are shown in Figure 5.3. Two arcs seemed to be overlapped in the impedance plots. The addition of H₂S had no effect on the ohmic resistance of the stack (50 000 Hz) which remained at ~ 400 mΩcm². In the lower frequency range, the addition of H₂S increased both real and imaginary impedances of the first arc to a large extent whereas the second arc remained same. After the regeneration of the stack the impedances decreased almost to initial values however not completely which is consistent with the cell voltage records. The increase of the impedances at low frequencies can be attributed to the increase of resistances in the anode (see Fig. 4.14, elements 2 and 4) due to hindered hydrogen

adsorption on nickel surface coupled with charge transfer reactions with H_2S addition. Contrary to initial impedance spectra strong shift of characteristic peak frequency for first arc towards lower frequencies happened in the presence of H_2S . This phenomenon takes place due to slowing down of anodic reactions in presence of sulfur on nickel surface.

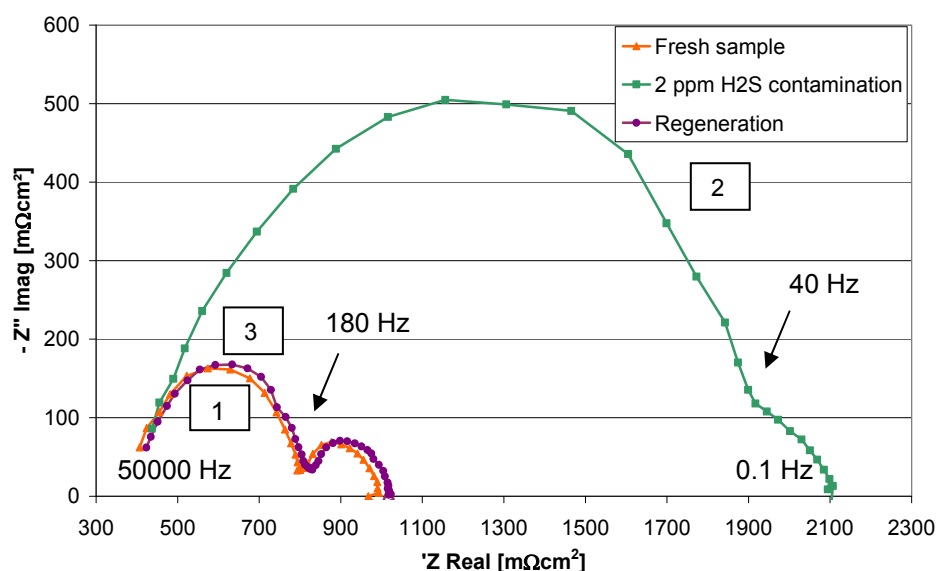


Figure 5.3 Impedance spectra measured under open-circuit conditions before, during and after H_2S contamination.

According to voltage-time diagram (Figure 5.4), the sulfur poisoning of MEA with Ni/8YSZ anode consisted of two phases.

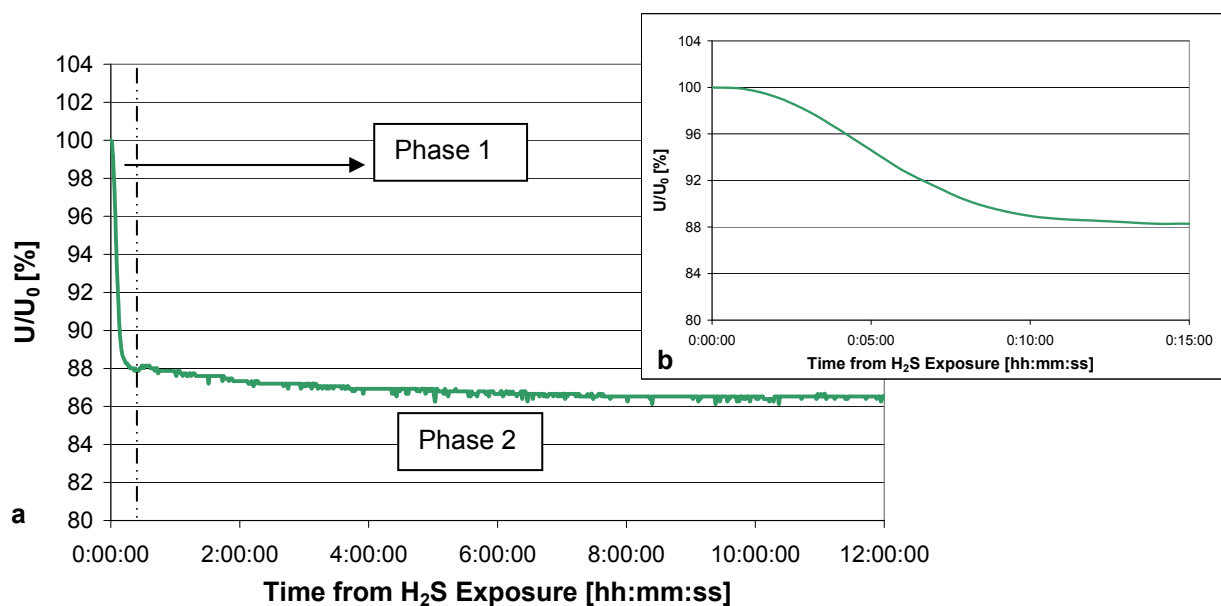


Figure 5.4 a) Voltage decrease as a function of time after 2 ppm H_2S exposure. b) Phase I (Detail from a)).

In the first poisoning phase an immediate voltage drop was observed. The cell voltage decreased to 88 % of its initial value in 15 minutes. In the second poisoning

phase the cell voltage decreased gradually from 88 % to 86.5 % of initial cell voltage in approximately 12 hours. In Figure 5.4 the two phases are shown where the percentage of the voltage to the initial voltage is plotted as a function of H_2S exposure time.

Upon removal of H_2S from the fuel, the cell voltage recovered gradually. The recovery rate shows decreasing behaviour over time as shown in Figure 5.5.

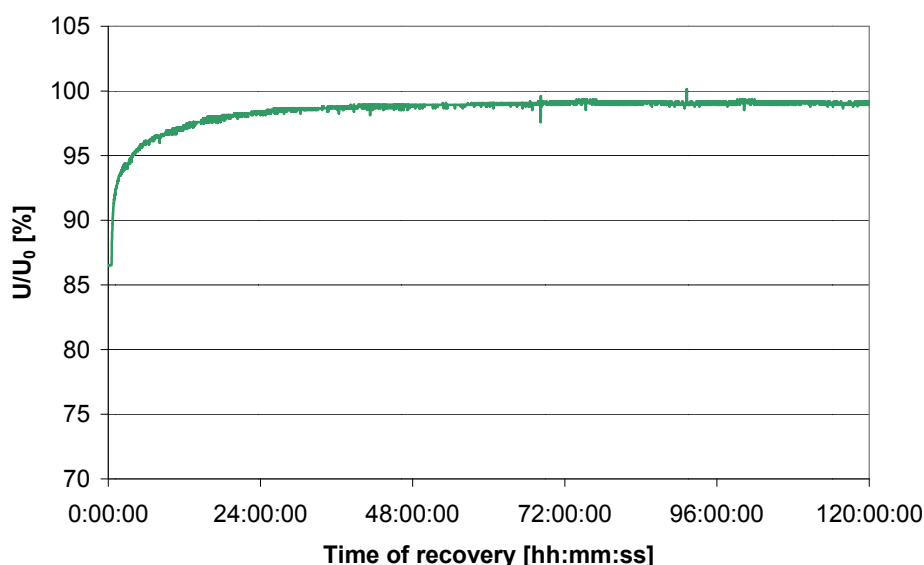


Figure 5.5 Percentage of cell voltage compared to initial cell voltage during recovery.

As shown in Figure 5.5, the cell voltage increased from 86.5 % to 98.4 % of the initial value within first 24 hours. During the following 96 hours the cell voltage increased from 98.4 % to 98.9 % of its initial value and then stabilized. The cell voltage did not recover completely to its' pre- H_2S value.

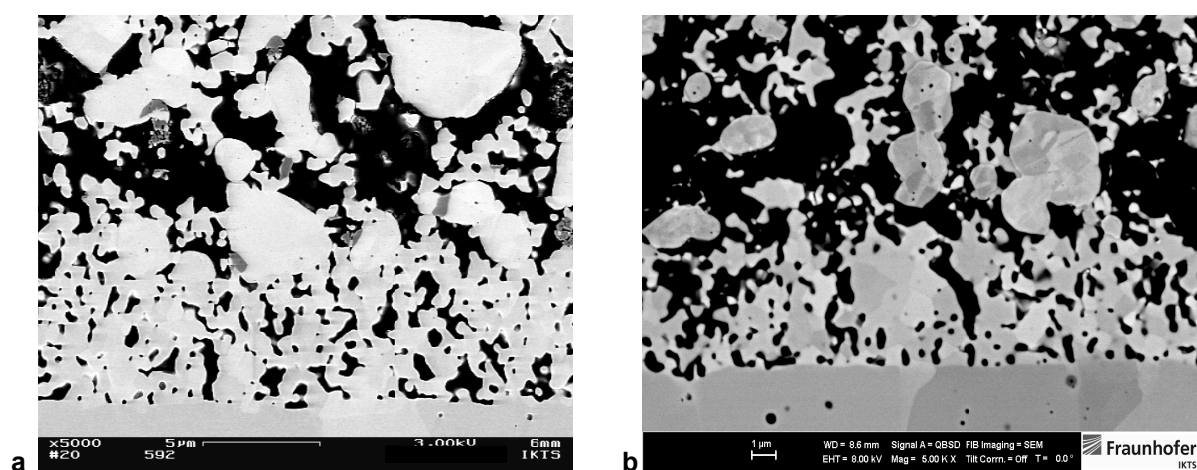


Figure 5.6 FESEM Images of cross-sections of anodes a) without H_2S contamination (335 operation hours with 50 vol % H_2 , 50 vol % N_2 at 850°C) b) contaminated with 2 ppm H_2S at 850°C under current.

The anode of the cell was analyzed with FESEM and EDX (after the stack had cooled down to room temperature under exposure to forming gas). The FESEM image of the anode was compared to a FESEM image of another anode which had operated under similar parameters but without H_2S contamination. The microstructures of the Ni/8YSZ cermet appear to be similar (Figure 5.6).

The EDX spectra of the anode cross section shows no peaks corresponding to sulfur while the peaks corresponding to Ni/8YSZ are observable as shown in Figure 5.7.

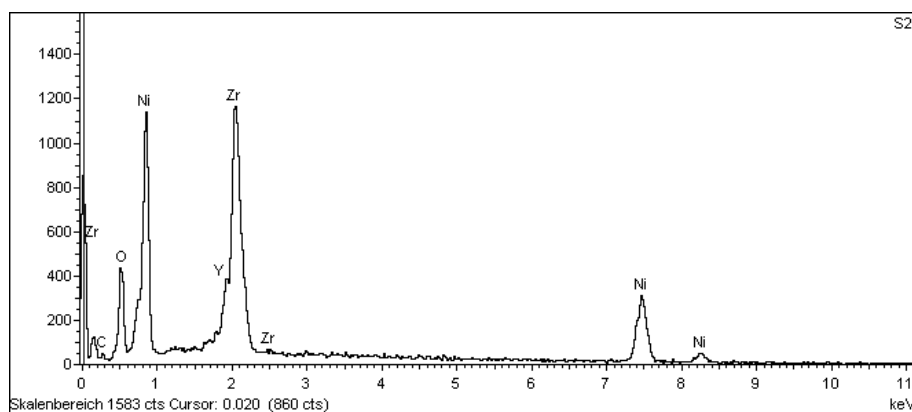


Figure 5.7 EDX Spectrum of anode cross section of Figure 5.6 b.

With FESEM and EDX analyses no morphological changes could be observed which clarifies the irreversible degradation of the cell performance.

5.1.2 Effect of H_2S contamination cycles

In this experiment, the effect of multiple cycles of contamination was examined. Similarly to the experiment described in section 5.1.1, the contamination was 2 ppm H_2S in the anode gas, and other experimental parameters remained the same. The SOFC stack was exposed to five cycles of contamination and regeneration. Figure 5.8 shows the cell voltage profile.

Constant current density of 319 mA/cm^2 had been drawn from the stack. Cell voltage degradation behaviours as in previous experiment were observed with each H_2S contamination. The initial cell voltage was recorded as 0.756 V. 2 ppm H_2S contamination period with 15 hours and the following 105 hours of regeneration period was applied five times one after another with 120 hours of total poisoning cycle time. Figure 5.8 shows the cell voltage, current density and H_2S addition as a function of time.

Experimental results clearly show that the performance degrades with each contamination cycle. In Figure 5.9, the cell voltage from each cycle is presented as a percentage of the initial voltage.

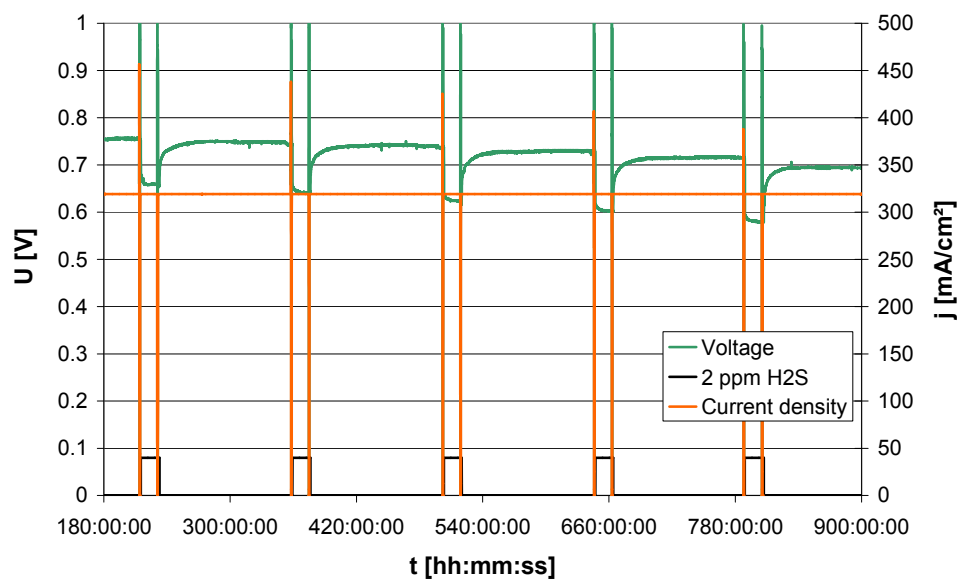


Figure 5.8 Cell voltage degradation by multiple contamination cycles with 2 ppm H_2S containing anode fuel gas.

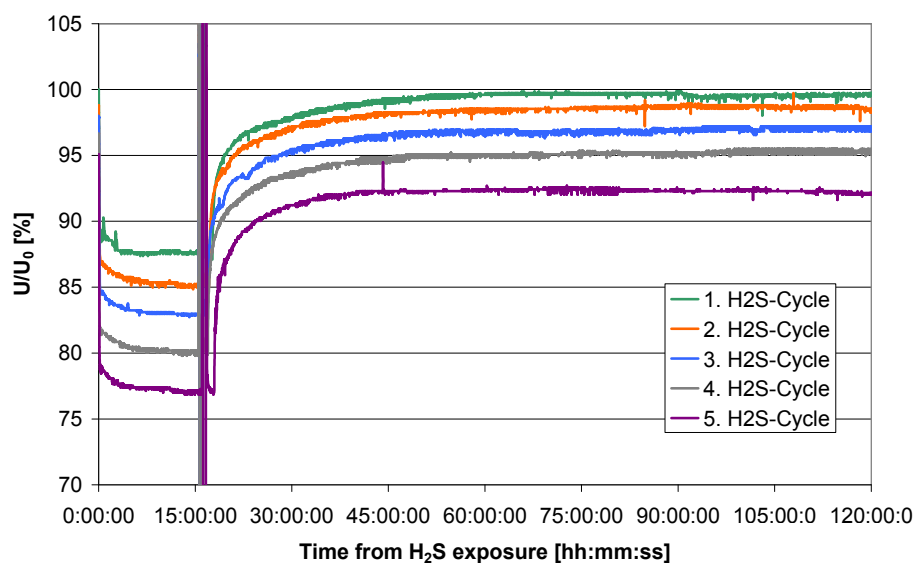


Figure 5.9 Decrease of the cell voltage with each H_2S contamination cycle. At 0th hour H_2S is added to the fuel, at ~16th hour H_2S was switched off. (The disruptions of cell voltages at 15th hour were caused by impedance analysis.)

As can be seen in Figure 5.9, the cell voltage responds to H_2S addition to anode gas each time with two phase degradation behaviour followed by long time regeneration behaviour. With each contamination cycle, the poisoned cell voltage as well as regenerated cell voltage decreases to a lower value. The poisoning and regeneration durations were nevertheless remained same. In Figure 5.10, the relation between cell resistance at 15th contamination hour and at 105th regeneration hour is given.

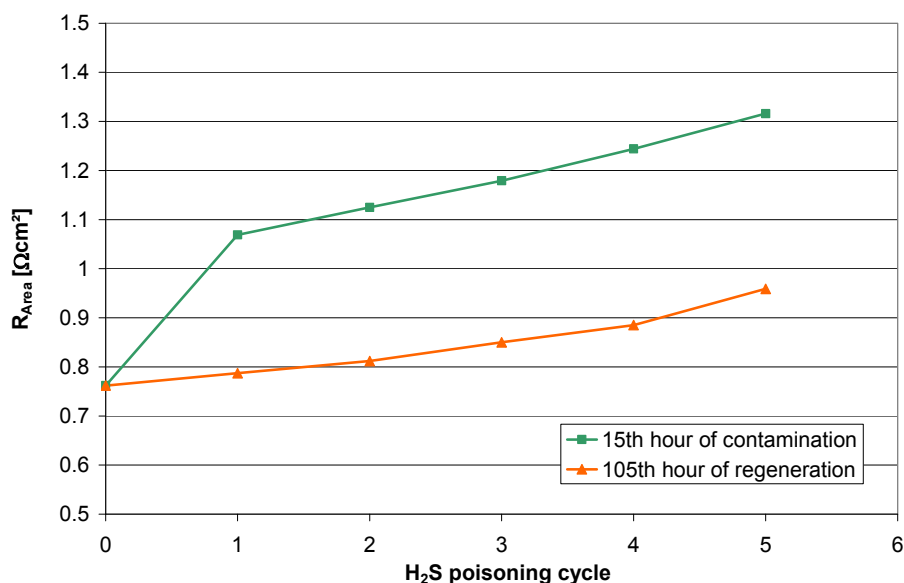


Figure 5.10 Cell resistances and their ratios to initial resistance at 15th (contamination) and 105th (regeneration) hours by each H₂S contamination cycle.

Figure 5.10 shows that the cell resistance increases linearly with each poisoning cycle. This is expected since the initial cell voltage for each of the cycle is shifted to a lower value due to incomplete regeneration. The relation between the voltage of the poisoned and regenerated cell to the initial voltage is given in Figure 5.11. According to the figure, the contamination increases and regeneration decreases with each H₂S poisoning cycle.

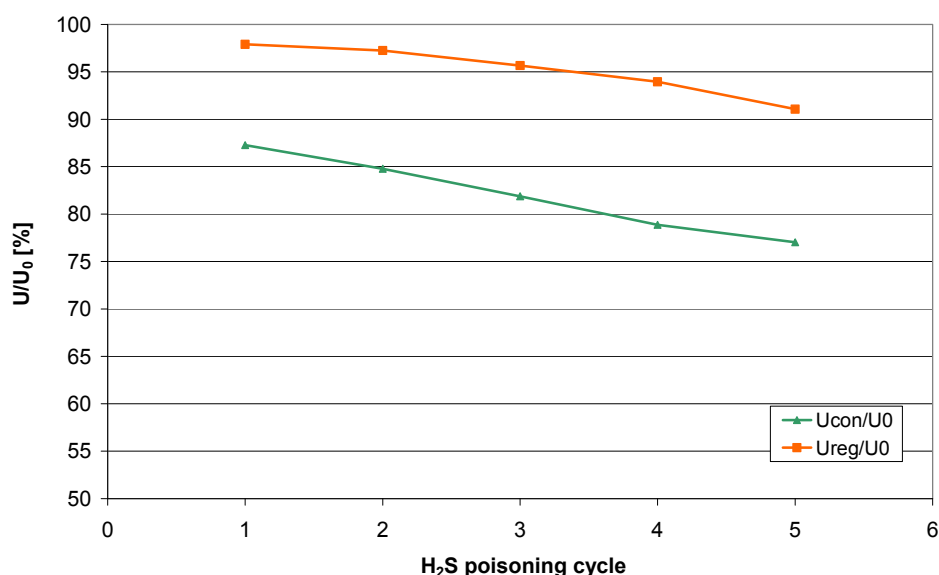


Figure 5.11 The ratio of the contamination and regeneration cell voltage to the initial cell voltage (U₀).

The impedance spectra recorded before, during and after each contamination cycle show that the impedance increases with each cycle (Figure 5.12). According to the Nyquist plots the total internal resistance of the cell increases each time as H₂S is

added to the fuel. The arcs at the low frequency region remained the same whereas the shape of the arcs at the high frequency region was enlarged to a large extent similar to Figure 5.3. Even after regeneration, the resistances increase with each cycle each time even after regeneration phases, and did not regain their initial value. The ohmic resistances remained relatively constant throughout the experiment with only a slight increase (from 361 to 423 $\text{m}\Omega\text{cm}^2$) at 50 000 Hz.

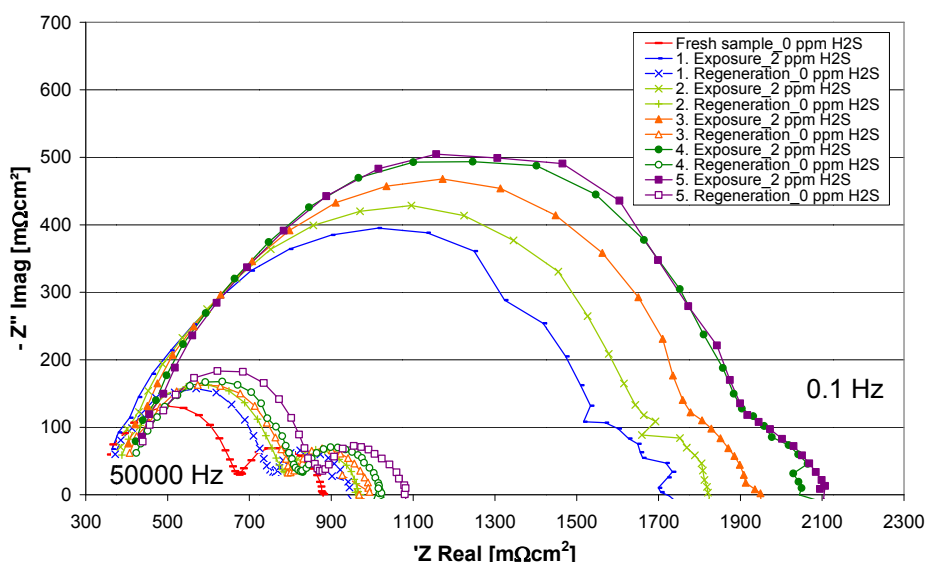


Figure 5.12 Impedance spectra of the cell during contamination cycles at 850 °C.

Similar to the previous experiment, the stack was cooled down to room temperature with forming gas in order to analyze the cermet anode with FESEM and EDX. No sulfur traces on the anode could be determined with FESEM image and EDX spectrum even though the cell resistance increased from 0.762 to 0.959 Ωcm^2 during the whole experiment.

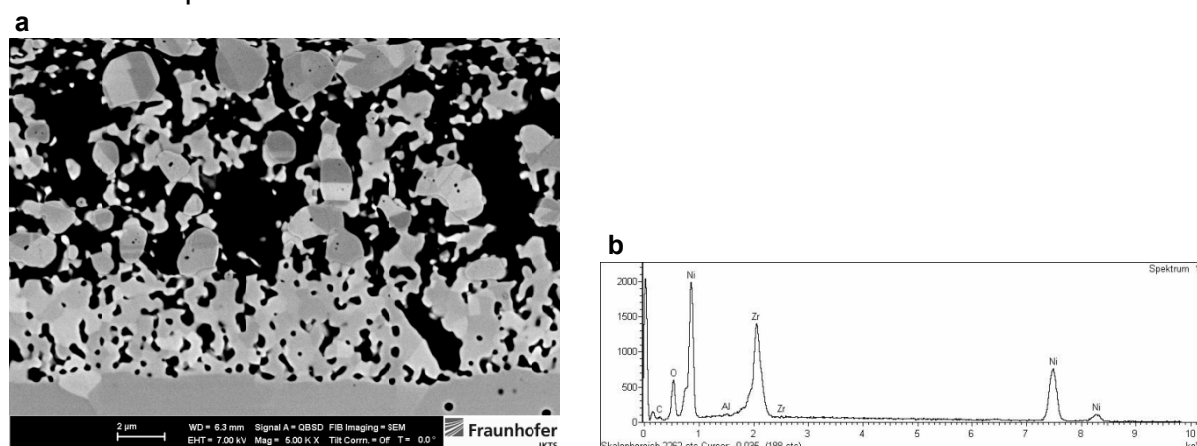


Figure 5.13 a) FESEM Image and b) EDX spectrum of cross-section of the anode contaminated with 2 ppm H_2S five times for 15 hours at 850 °C under current.

The results suggest that either there is no sulfur in the anode or detection limits of EDX and FESEM are not enough to detect small amount of traces of sulfur.

As no traces of H_2S could be found with FESEM and EDX, the Raman spectroscopy method was applied (due to its higher sensitivity to low concentrations). The anodes with and without sulfur contamination were compared with Raman microscope (Renishaw 3000, excitation 514nm Ar Laser static 520 cm^{-1} , amplification 50 x, Laser power 100 % (app. 3,5 mW), 10 x 60 s) (Figure 5.14).

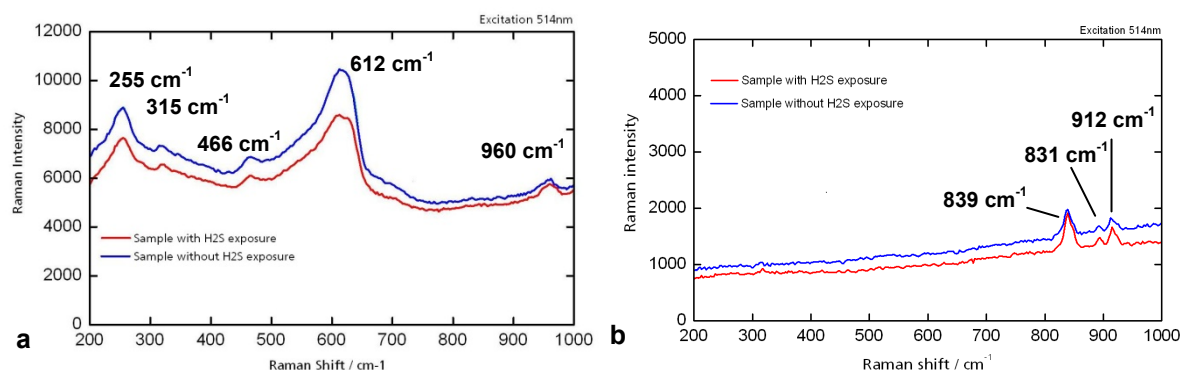


Figure 5.14 Raman Spectra taken from a) YSZ region and b) Nickel region of the anodes with and without H_2S exposure at an excitation wavelength of 514 nm.

No difference was observed in the spectra of poisoned and not poisoned samples. The irreversible decrease of the cell performance could not be clarified with this method for the applied experimental conditions.

5.1.3 Effect of H_2S concentration

The H_2S concentration, particularly the $\text{pH}_2\text{S}/\text{pH}_2$ ratio, may have an influence on the poisoning rate (Chapter 3.2.1.2). In the following experiment, the H_2S concentration effect is studied with 1 ppm, 2 ppm, 4 ppm, 8 ppm, 16 ppm, 32 ppm and 50 ppm H_2S added to fuel gas (43.8 vol % H_2 / 6.2 vol % H_2O / 50 vol % N_2) one after another each for thirty minutes. The stack with Type II MEA had been run under a constant current density of 200 mA/cm^2 and fuel utility of 17.7 %. H_2S addition took place as the cell had a constant voltage of 0.753 V. After 30 minutes of 50 ppm H_2S addition, H_2S is removed from the fuel (Figure 5.15).

A common decrease in cell voltage was detected for all of the concentrations just after increasing H_2S concentration in the fuel. Cell voltage drop was decreased as the H_2S concentration was increased. However, even with 1 ppm H_2S , an 11 % power degradation was observed. In Figure 5.16 the effect of H_2S concentration on cell resistance under constant current density is shown.

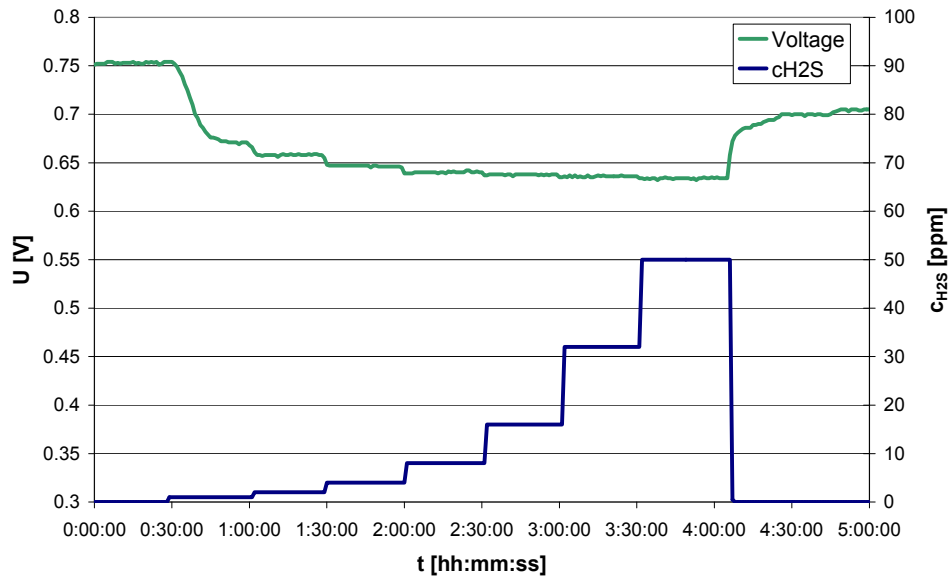


Figure 5.15 Voltage and H₂S concentration versus time diagram.

The highest increase in resistance increase (from 1.269 to 1.684 Ωcm^2) was observed as 1 ppm H₂S was added to the fuel. As the level of H₂S contamination was increased to 2, 4, 8, 16, 32 and 50 ppm H₂S) the effect of each step became smaller. This behaviour correlates well with Temkin type isotherm as explained in Chapter 3.2.1.2. Both values are compared in Figure 5.17.

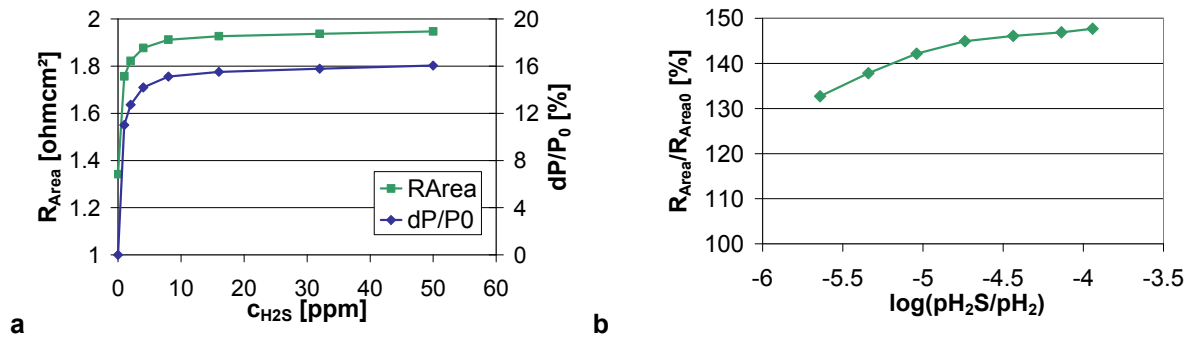


Figure 5.16 Increase of the cell resistance and power decrease with increasing H₂S concentration.

Even with 1 ppm H₂S in the fuel, the surface coverage of nickel will be as high as 75 %. With 50 ppm H₂S nickel surface coverage is calculated as high as 95 %. As H₂S was removed, the cell voltage increased to 96.6 % of its initial voltage in 96 hours and was stable. It has been observed that the cell voltage drop decreased with increasing H₂S concentration and was almost saturated above 10 ppm H₂S.

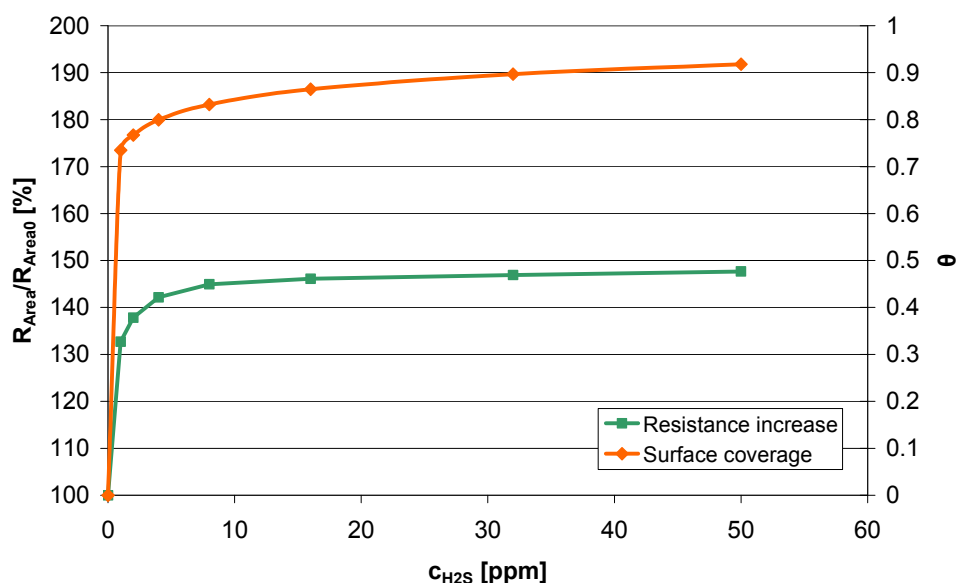


Figure 5.17 Effect of H_2S concentration on cell resistance increase and calculated surface coverage using equation 3.3.

5.1.4 Effect of current density

In this experiment, the effect of current density on degradation was examined. The experiment described in Section 5.1.1 was repeated with Type III MEA, but without drawing current from the stack during contamination phases. The stack's initial open circuit voltage (OCV) was 0.999 V. Impedance analysis was performed as in the previous experiment. Figure 5.18 presents the changes of the impedances during contamination cycles with 2 ppm H_2S at 850 °C under open cell voltage (OCV) and under constant cell current (319 mA/cm²) during the previous experiment (Section 5.1.1).

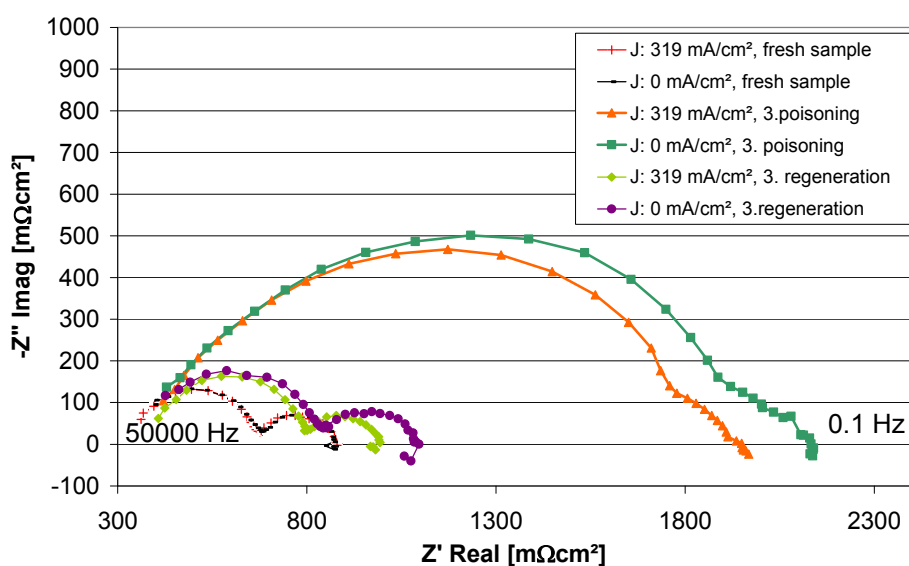


Figure 5.18 Comparison of Nyquist plots of the stacks during 2 ppm H_2S contamination cycle under 319 mA/cm² and under OCV.

From five poisoning cycles, the impedances of third poisoning cycle (poisoning and regeneration) have been chosen to compare. Before contamination, the impedance values of both the fresh samples were similar. By the third poisoning cycle the impedances increased for both of the stacks for a large extent while stack without current drawing shows higher degradation. As the stacks were regenerated, impedances of the stack running under OCV were higher than the impedances of the stack running with current. The incomplete regeneration was observed for both of the stacks whereas the stack run under current showed better resistance to sulfur poisoning. Together with impedance analysis, the voltage-current characteristics were measured to calculate the stack power of the stack run without current during the H_2S poisoning cycles. In Figure 5.19 the power degradations both for contamination and regeneration values are compared.

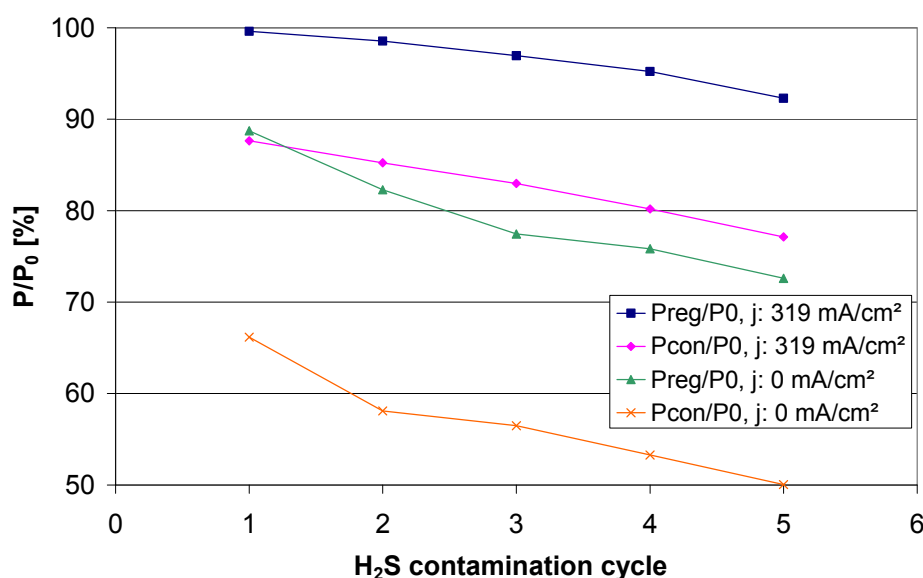


Figure 5.19 Comparison of the power degradation of stacks with 2 ppm H_2S during five poisoning cycles. The cells were operated at OCV (0 mA/cm^2) and 319 mA/cm^2 . The stack power of the stack run without current is calculated from voltage – current characteristics.

The poisoning with H_2S becomes noticeable by each contamination cycle. The cell runs at OCV shows higher degradation rates which agrees well with the impedance results.

5.1.5 Effect of H_2O concentration

The positive effect of current density on H_2S resistance reveals the question of whether this effect depends on the partial pressure of water. Therefore, the effect of H_2O concentration was studied by adding 2 ppm H_2S to two fuel types with different concentrations of water. Hydrogen concentrations were kept constant in order to have equal $\text{pH}_2\text{S}/\text{pH}_2$ values. The compositions were balanced with nitrogen. The fuel compositions for the stacks were set as “Inlet” concentrations as shown in Table 5.1. The outlet water concentrations differ from inlet concentrations due to the

applied current of 3.2 A (current density of 200 mA/cm²) and are calculated using Faraday's law.

Table 5.1 Inlet and outlet fuel compositions. (j : 200 mA/cm², F_U : 15.2 %)

Fuel		p_{H_2O}/p_{H_2}	H_2		H_2O		N_2	
			[Vol %]	$\log p_{H_2}$	[Vol %]	$\log p_{H_2O}$	[Vol %]	$\log p_{N_2}$
1	Inlet	0.14	43.8	-0.36	6.2	-1.2	50	-0.3
	Outlet	0.35	37.1	-0.43	12.9	-0.89	50	-0.3
2	Inlet	0.57	43.8	-0.36	24.8	-0.6	31.4	-0.5
	Outlet	0.85	37.1	-0.43	31.5	-0.5	31.4	-0.5

The experiments were performed at 850°C with a Type II MEA. After the cell voltages were stable, 2 ppm H₂S was added to each fuel for thirty minutes. H₂S was then removed from the fuel. Cell voltage with respect to time was recorded. In Figure 5.20, the cell voltage degradations as a percentage of the initial value are compared for both types of fuel.

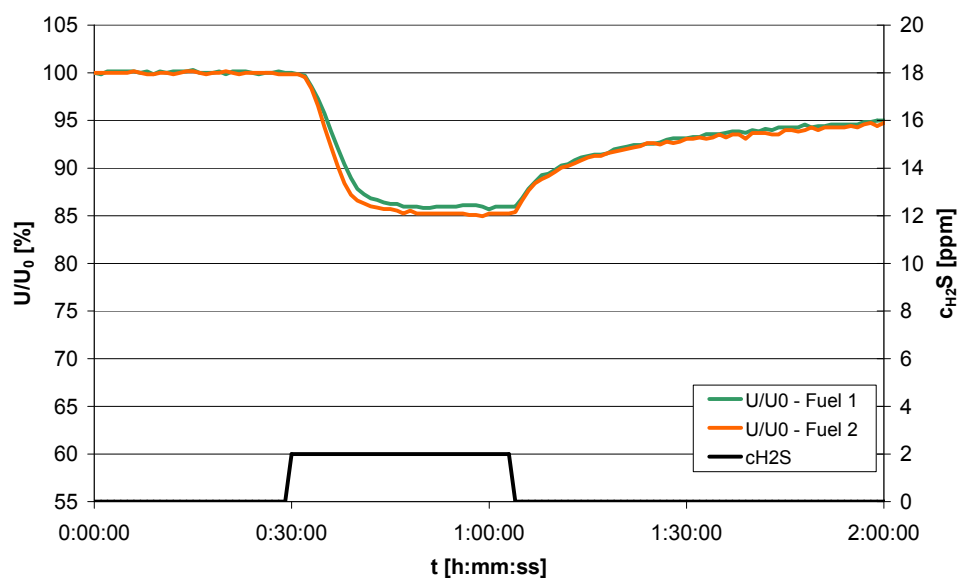


Figure 5.20 Comparison of cell voltage decrease due to poisoning with 2 ppm H₂S.

As shown in Figure 5.20, the concentration of H₂O in the fuel does not affect the cell voltage. Additionally, the stack power and the voltages with two fuel types are compared as shown in Table 5.2. The power degradations due to sulfur poisoning were similar to each other with and without more water content in the fuel.

Table 5.2 Effect of 2 ppm H₂S on the degradation of stack power with Fuel 1 and Fuel 2. (The indices 0, H₂S, and reg represent initial value, value with H₂S addition and value after regeneration, respectively.)

Fuel	J [mA/cm ²]	U ₀ [V]	U _{H₂S} [V]	P _{H₂S} /P ₀ [%]	U _{reg} [V]	P _{reg} /P ₀ [%]
1	200	0.699	0.601	86.1	0.690	98.8
2	200	0.664	0.566	85.2	0.654	98.5

The impedance spectra were recorded before H₂S poisoning and after 24 hours of regeneration for both of the stacks. The Nyquist plots are shown in Figure 5.21. According to the diagram, the ohmic resistances have similar values ($\sim 700 \text{ m}\Omega/\text{cm}^2$) whereas for higher water concentrations the impedance is lower due to absence of conversion impedance, which is present in case of fuels with low H₂O content. The water vapour enhances the oxygen surface exchange rate both on the metal and YSZ surfaces of Ni/YSZ anodes. This phenomenon was observed also by some previous studies [Sak03], [Sak06]. However, the addition of H₂S to fuel causes similar increase of the impedance for both fuel types which shows that pH₂O in fuel has no influence on poisoning.

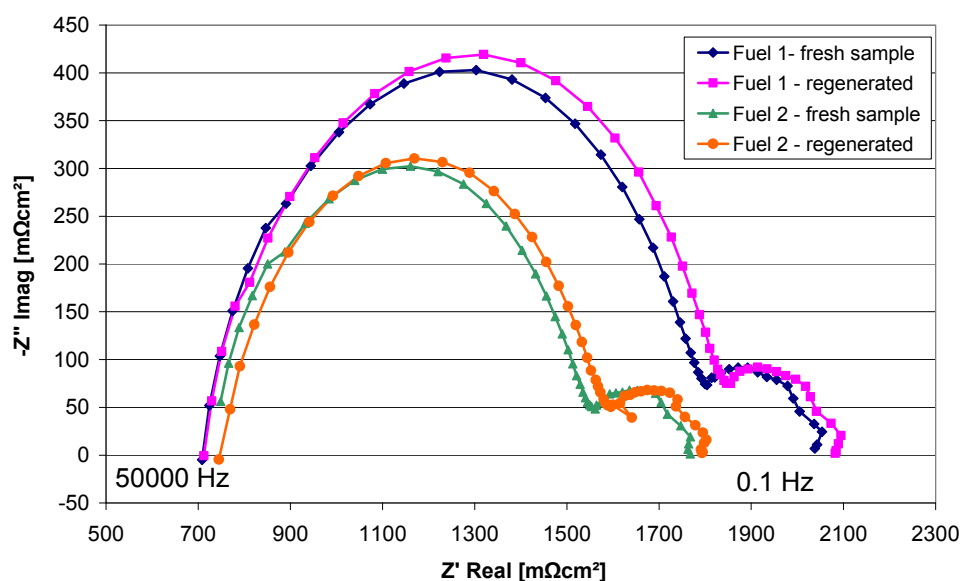


Figure 5.21 Comparison of Nyquist plots of the stacks before poisoning and after 24 hours of regeneration.

5.2 Effect of H₂S containing fuel on the performance of a SOFC with a Ni/10CGO anode

The sulfur poisoning of cells with Ni/10CGO anodes was investigated by performing similar experiments to those previously conducted with Ni/8YSZ anodes. Experiments were performed under the same conditions for the two anode types. The fuel composition for the stacks consisted of 43.8 vol % H₂, 6.2 vol % H₂O and 50 vol % N₂.

5.2.1 Effect of single contamination

In Figure 5.22, the cell voltage response to 2 ppm H_2S is compared for Ni/10CGO und Ni/8YSZ anodes. Stack current was kept constant 225 mA/cm^2 (for the cells with Ni/8YSZ initial current density of 319 mA/cm^2 has been achieved). The initial cell voltages at given conditions were 0.743 V and 0.71 V for Ni/8YSZ and Ni/10CGO anode respectively.

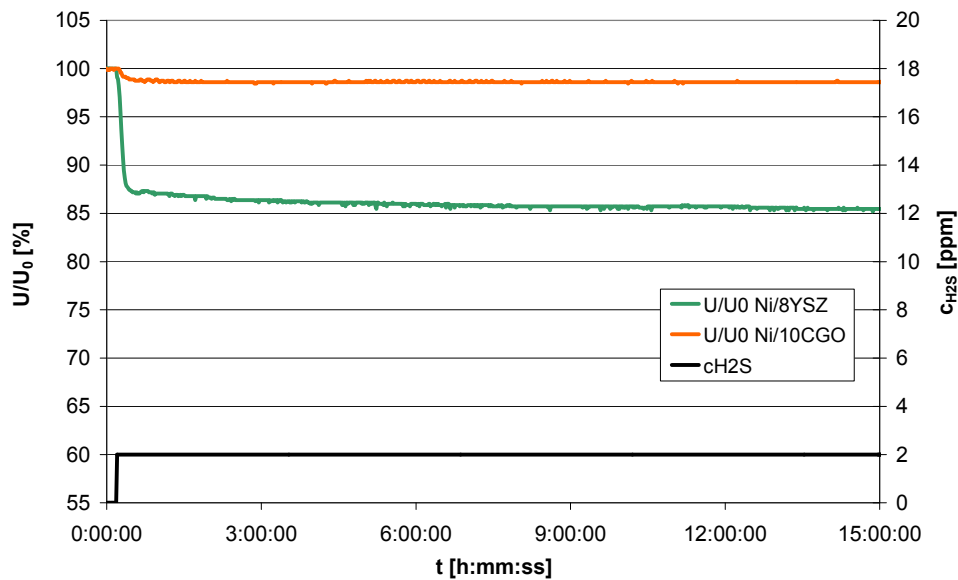


Figure 5.22: Comparison of the voltage decrease due to H_2S poisoning for stacks with Ni/8YSZ and Ni/10CGO anodes.

As shown in Figure 5.22, there is an immediate voltage drop for both of the cells with 2 ppm H_2S addition to the fuel. Nevertheless the voltage degradation for the cell with Ni/8YSZ anode is much higher (13.6 %) than for Ni/10CGO anode (1.3 %). Both stacks were operated for 15 hours with 2 ppm H_2S (similarly to previous experiments, see Chapter 5.1.2). The H_2S was then removed from the fuel. The voltage regeneration behaviour of the stacks are compared in Figure 5.23.

An immediate increase of the cell voltage for both of the stacks was observed after removing H_2S . After ninety hours of operation, the cell voltages reached constant values of 98.9 % (0.735 V) and 100 % (0.710 V) for the stacks with Ni/8YSZ and Ni/10CGO anodes, respectively. These results show that the stack with Ni/10CGO cell recovered its cell voltage completely; while the stack with Ni/8YSZ anode regained only 98.9 % of its initial power.

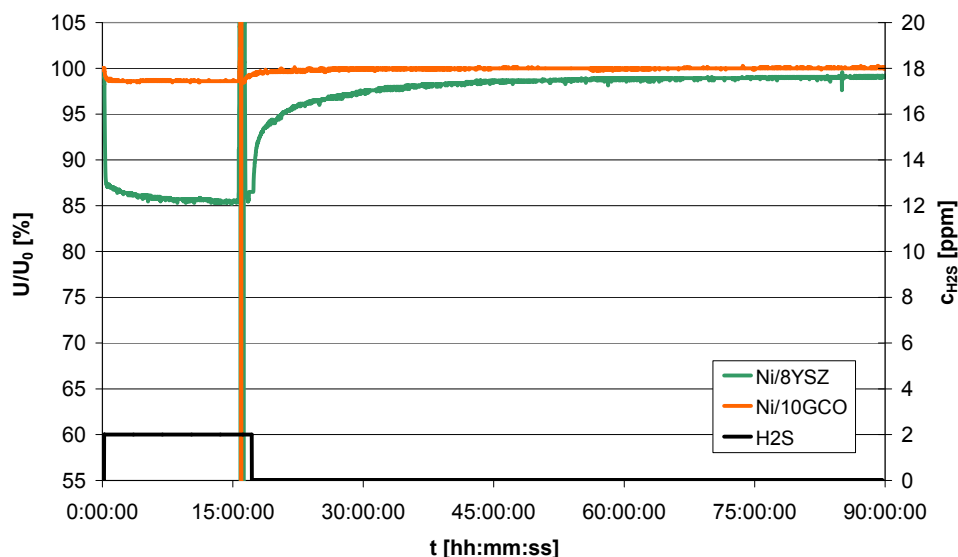


Figure 5.23 Comparison of the contamination and regeneration behaviours of the stacks with Ni/8YSZ anode and Ni/10CGO anode.

The following table gives an overview of the experimental results with both of the anode types.

Table 5.3 Effect of 2 ppm H₂S contamination on the degradation of stack power with Ni/8YSZ and Ni/10CGO anodes. (The indices 0, H₂S, and reg represent initial value, value with H₂S addition and value after regeneration, respectively.)

Anode Type	J [mA/cm ²]	U ₀ [V]	U _{H₂S} [V]	P _{H₂S} /P ₀ [%]	U _{reg} [V]	P _{reg} /P ₀ [%]
Ni/8YSZ	319	0.743	0.642	86.4	0.735	98.9
Ni/10CGO	225	0.710	0.701	98.7	0.710	100

FESEM and EDX analysis of the Ni/10CGO anode shows no change in the microstructure. The analysis results can not be published in this thesis due to a confidentiality agreement with H.C. Starck GmbH.

5.2.2 Effect of H₂S contamination cycles

The effect of multiple cycles of H₂S contamination on stack power was examined by exposing the Ni/10CGO anode to 2 ppm H₂S containing anode gas five times with regeneration times in between. Figure 5.8 shows the change of the cell voltage as a function of the H₂S contamination cycles. A constant current density of 225 mA/cm² was drawn from the stack. The fuel consisted of 43.8 Vol % H₂, 6.2 vol % H₂O and 50 vol % N₂. Cell voltage degradation behaviour was recorded with each H₂S contamination. The initial cell voltage was 0.71 V. The duration of the contamination period was 15 hours and the duration of the regeneration period was ~ 50 hours. The poisoning / regeneration cycle was applied five times resulting in 65 hours of cumulative poisoning time. Figure 5.24 shows the cell voltage and H₂S concentration

in fuel as a function of time. No significant cell voltage drops were observed during the experiments.

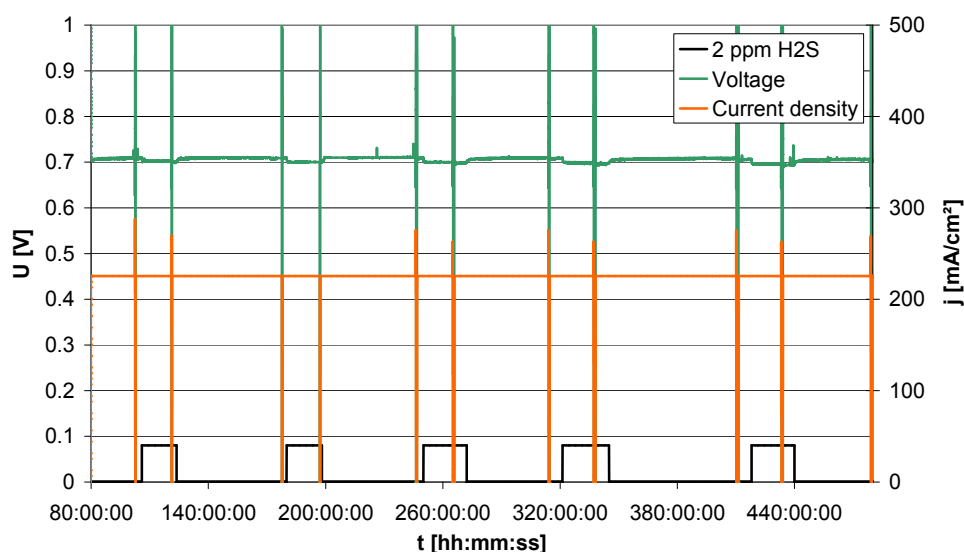


Figure 5.24 Voltage and H_2S values as a function of time during H_2S poisoning cycles.

In Table 5.4 stack voltage changes are presented as a function of the H_2S contamination cycles. U_0 represents the initial cell voltage. $U_{\text{H}_2\text{S}}$ represents the cell voltages with 2 ppm H_2S contamination and U_r the cell voltages after regeneration for each cycle.

Table 5.4 Effect of the H_2S contamination cycles on stack voltage with j : 225 mA/cm^2 . (The indices 0, H_2S , and reg represent initial value, value with H_2S addition and value after regeneration, respectively.)

H_2S Cycle	U_0 [V]	$U_{\text{H}_2\text{S}}$ [V]	$U_{\text{H}_2\text{S}}/U_0$ [%]	U_{reg} [V]	U_{reg}/U_0 [%]
1.	0.710	0.701	98.7	0.710	100
2.	0.710	0.700	98.6	0.710	100
3.	0.710	0.699	98.5	0.710	100
4.	0.710	0.696	98.0	0.709	99.9
5.	0.710	0.693	97.6	0.707	99.6

In Figure 5.25, the effect of multiple cycles on the degradation of stack power is given. The values are obtained from Table 5.4. $dP_{\text{H}_2\text{S}}/P_0$ represents the ratio of power (with H_2S contamination) to initial power; dP_{reg}/P_0 represents the ratio of power (after regeneration) to the initial power. Even though regeneration rates at the beginning of the experiment are 100 % (even after third contamination cycle), the cell power could not regenerate itself completely after more than four cycles. The degradation rate of power after the fifth cycle (480 hours of operation) was 0.4 %.

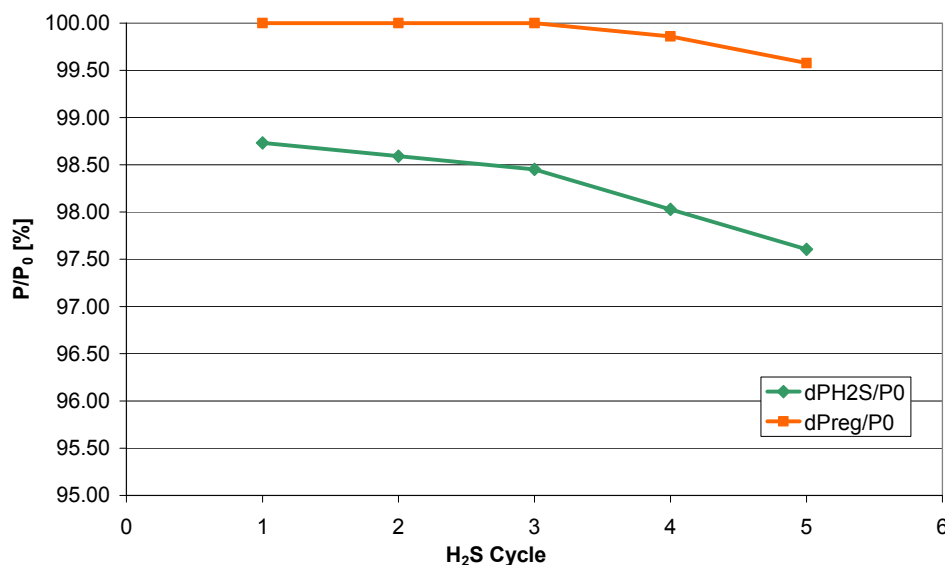


Figure 5.25 Effect of 2 ppm H₂S contamination and regeneration cycles on the total power of the stack with Ni/10CGO anodes.

Impedances of the stack between 50.000 Hz and 0.01 Hz were analyzed for each contamination cycle before each contamination and after each regeneration period (Figure 5.26).

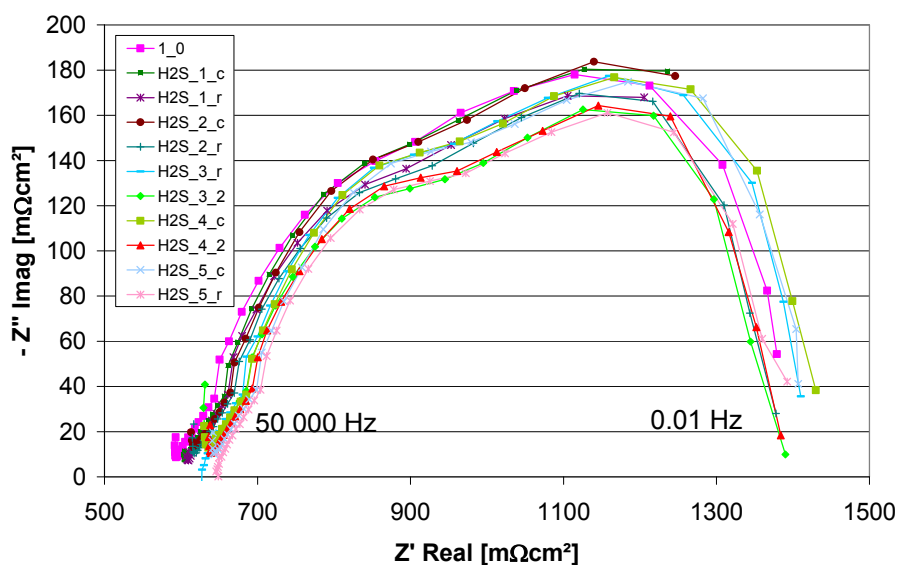


Figure 5.26 Impedance spectra of the stack during H₂S contamination cycles. The abbreviation 1_0 represents the initial impedance. In H₂S_x x represents the number of contamination cycle. H₂S_x_c and H₂S_x_r represent impedances during the contamination and after regeneration respectively.

According to the impedance spectra no polarization resistances but ohmic resistances increased from 594 mΩcm² to 653 mΩcm² ($dZ/Z_0 = 1.1\%$) in 480 hours of operation with five H₂S contamination cycles. The results indicate that not the H₂S contamination cycles, but the degradation of contact resistance causes the reduction

of stack power. Thus the Ni/10CGO anode seems to be stable towards H_2S contamination.

5.2.3 Effect of H_2S concentration

The influence of sulfur concentration in the fuel on power output was investigated by contaminating the fuel with 1, 2, 4, 8 and 10 ppm of H_2S . Standard fuel gas (43.8 vol % H_2 , 6.2 vol % H_2O , 50 vol % N_2) was used as the fuel. Current density during the experiment was 260 mA/cm^2 . Figure 5.27 shows the stack voltage and H_2S concentration change versus time for a stack with a Ni/10CGO anode.

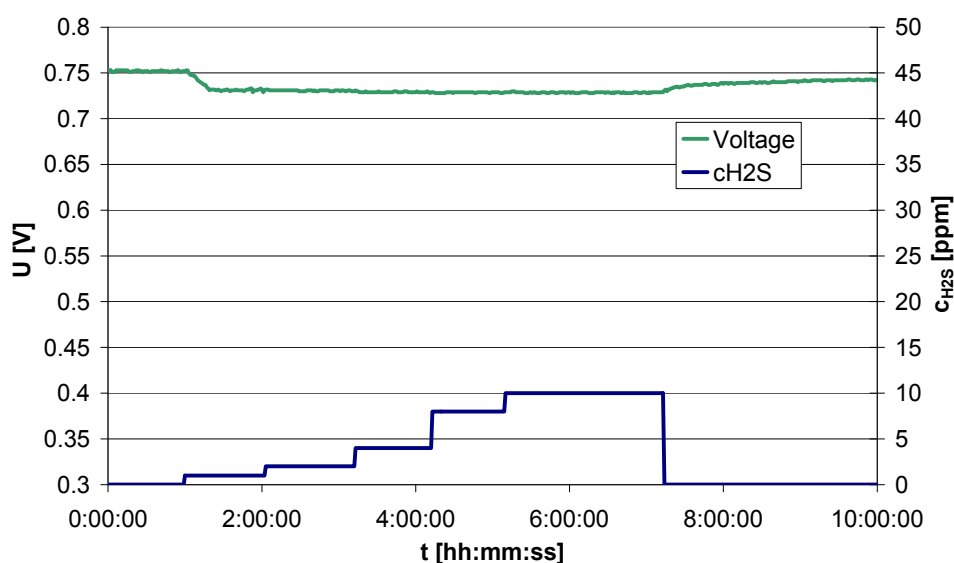


Figure 5.27 Cell voltage and hydrogen sulfide concentration diagram as a function of time

With addition of 1 ppm H_2S to the fuel, the stack voltage decreased immediately from 0.752 V to 0.741 V ($P/P_0 = 98.5\%$). Increasing the H_2S concentration from 1 ppm to 2, 4, 8 and 10 ppm did not change the stack voltage significantly. During two hours of contamination with 10 ppm H_2S , the cell voltage was stable. As the H_2S addition to fuel gas was stopped, the cell voltage increased and reached its initial value in 25 hours. The results of the experiments done with Ni/8YSZ and with Ni/10CGO anodes are compared in Figure 5.28. The cell with Ni/10CGO anode shows much better resistance with respect to poisoning with various H_2S concentration than Ni/8YSZ anode.

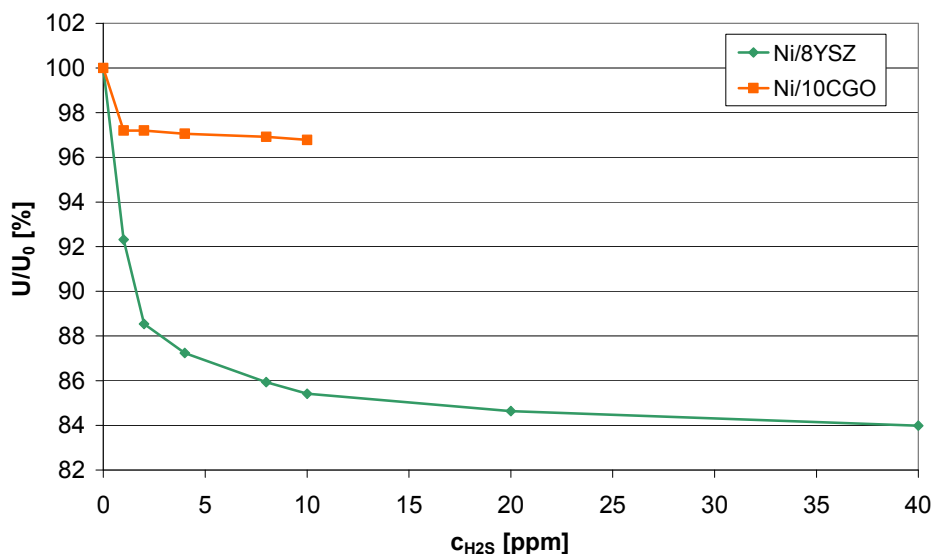


Figure 5.28 Comparison of H_2S concentration dependence on the cell voltage (percentual change of initial value) for the cells with Ni/8YSZ and Ni/10CGO anodes.

5.2.4 Effect of current density

The effect of current density on H_2S contamination was studied by applying multiple H_2S contamination cycles without current drawing throughout the experiment. The stack generated an initial OCV of 1 V. Impedance analysis was performed as in previous experiments, before and after each poisoning cycle. The Nyquist plots of third 2 ppm H_2S poisoning cycle (poisoning and regeneration) were chosen to compare the degradation behaviour of the stack under current (Chapter 5.2.2) and without current at 850°C. Figure 5.29 presents the changes of the impedances during contamination cycles.

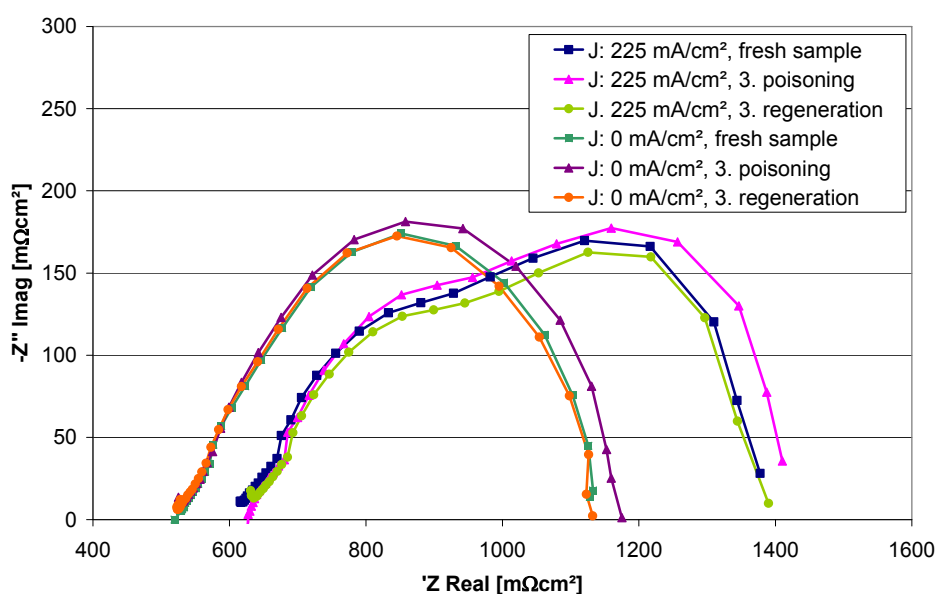


Figure 5.29 Nyquist plots of the impedances of the stacks run with and without current during 2 ppm H_2S poisoning.

Figure 5.29 shows that (unlike with Ni/8YSZ anodes) current density has no effect on the poisoning behaviour of the Ni/10CGO anodes. The increase of the impedance with addition of H_2S is similar for both of the stacks. The deviation of the ohmic losses (resistance at 50 kHz) is the result of differences in contacting resistance due to component tolerances scattering by stack manufacturing. The difference of the shapes of the Nyquist plots can be the result of the gas concentration differences due to fuel utilization with current.

5.2.5 Effect of H_2S with pre-mixed natural gas reformat

The effect of H_2S concentration on stack power when operated with pre-mixed natural gas reformat fuel (27 vol % H_2 , 11 vol % CO , 6.2 vol % H_2O , 2.8 vol % CO_2 , 0.8 vol % CH_4 , 51 vol % N_2) was analyzed by measuring the cell voltage and the impedance spectra under constant current load. The cells were tested with various H_2S concentrations at 850 °C. Dry air was fed to the cathode. The current density during the experiment was 280 mA/cm². After the cell reached a constant cell voltage at 0.735 V, the fuel was contaminated with 8, 10 and 15 ppm H_2S for 24 hours each. After a regeneration period of approximately 100 hours, contamination with 15, 20 and 30 ppm H_2S for 24 hours was used. An additional exposure of 30 ppm H_2S was followed for 160 hours.

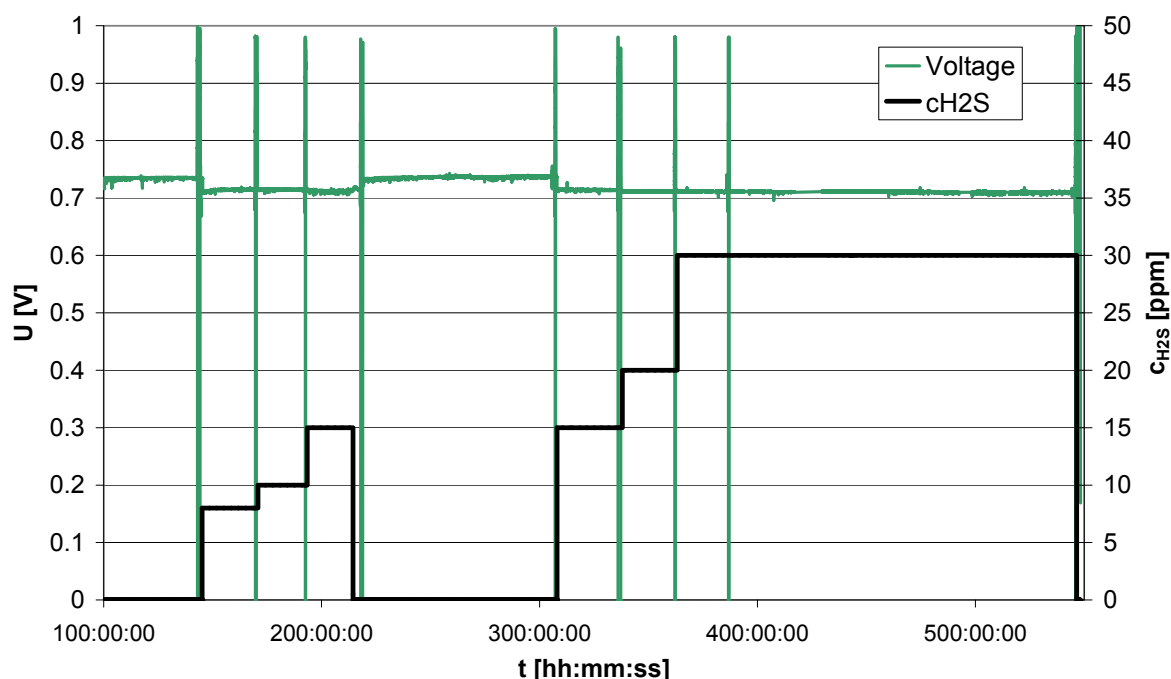


Figure 5.30 Voltage and H_2S values with pre-mixed natural gas reformat fuel as a function of time during H_2S poisoning.

The sulfur resistance of the Ni/10CGO anode with pre-mixed natural gas reformat fuel was tested and essentially no negative effect of the gas composition was observed up to 30 ppm H_2S . The results were consistent with the results of the experiments performed with $\text{H}_2/\text{H}_2\text{O}/\text{N}_2$ fuel. The cell operated with constant power

density for 160 hours with 30 ppm H₂S in fuel. In the following table, the cell voltages, power densities and degradation rates with different H₂S concentrations are shown.

Table 5.5 Stack performance during addition of H₂S to fuel.

H ₂ S [ppm]	J [mA/cm ²]	U [V]	P [mW/cm ²]	P _{H₂S} /P ₀ [%]
0	280	0.734	205.5	100
8	280	0.714	199.9	97.3
10	280	0.714	199.9	97.3
15	280	0.713	199.6	97.1
0	280	0.734	205.5	100
15	280	0.714	199.9	97.3
20	280	0.712	199.4	97.0
30	280	0.711	199.1	96.9

The impedance spectra of the stack running with different fuel compositions with/without H₂S addition are compared in Figure 5.30. The comparison shows that the addition of H₂S had no significant effect on stack power either with standard or reformat fuel of which the pH₂S/pH₂ ratios have similar values.

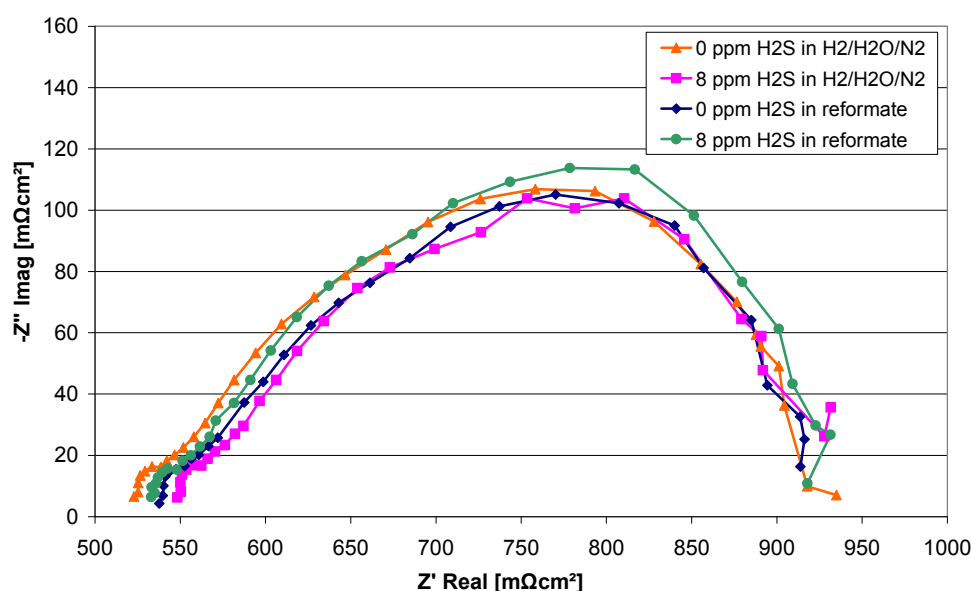


Figure 5.31 Impedance spectra of the stacks operated with standard and reformat fuel with and without 8 ppm H₂S poisoning.

This experiment showed that the effect of H₂S on the stack power with Ni/10CGO anodes is independent of fuel composition (under the given experimental conditions).

5.2.6 Effect of H₂O concentration

The effect of H₂O concentration was studied by adding 2 ppm H₂S to pre-mixed reformat with different water concentrations. Hydrogen concentrations were kept constant in order to have equal $p_{\text{H}_2\text{S}}/p_{\text{H}_2}$ values. The compositions were balanced with nitrogen. 345 mA/cm² current density were applied throughout the experiment. The fuel compositions were set as shown in Table 5.6.

Table 5.6 Fuel compositions and $p_{\text{H}_2\text{O}}/p_{\text{H}_2}$ value during experiments.

Fuel	H ₂ [vol %]	H ₂ O [vol %]	N ₂ [vol %]	CO [vol %]	CO ₂ [vol %]	CH ₄ [vol %]	$p_{\text{H}_2\text{O}}/p_{\text{H}_2}$
1	27	6.2	51	11	2.8	2	0.23
2	27	12.4	44.8	11	2.8	2	0.46
3	27	24.8	26.2	11	2.8	2	0.92

After the stack had indicated a stable voltage, 2 ppm H₂S was added to fuels for 30 minutes. After removal of H₂S, 24 hours of regeneration time was applied. Before and after the H₂S addition, impedance spectra of the stack were recorded.

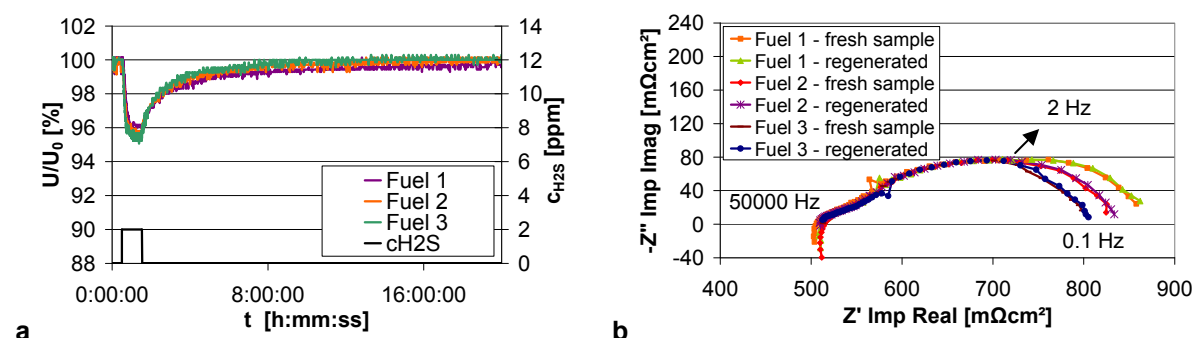


Figure 5.32 Effect of 2 ppm H₂S on the cell voltage (a) and impedances (b) running on pre-mixed reformat with varying water concentrations.

As shown in Figure 5.32, neither voltage degradation and regeneration rates nor impedance responses due to H₂S addition were affected by changing the water concentration. The change of the impedances at low frequency arc region (2 - 0.1 Hz) should be attributed to conversion impedance appearing in the spectra at low water concentrations in fuel.

5.2.7 Effect of H₂S contamination duration on regeneration duration

The effect of contamination duration on regeneration duration of SOFC stacks with Ni/10CGO anodes was examined by contaminating pre-mixed natural gas reformat (27 vol % H₂, 11 vol % CO, 2 vol % CH₄, 6.2 vol % H₂O, 2.8 vol % CO₂, 51 vol % N₂) with 2 ppm H₂S for 4, 10, 30 and 60 minutes. The regeneration duration is defined as the time required for the cell to recover to 99 % of the initial cell voltage (t_{99}). The current density during the experiment was 345 mA/cm². Figure 5.33 shows the

voltage degradation and the hydrogen sulfide concentration as a function of time for various contamination durations.

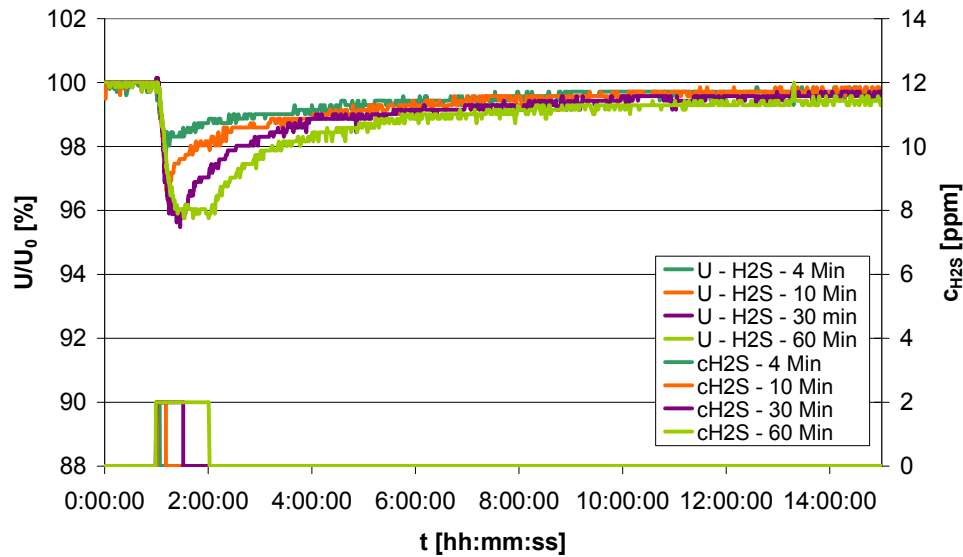


Figure 5.33 The ratio of stack voltage to initial stack voltage as well as H₂S-concentration change during experiment as a function of time.

The regeneration duration increases with increasing contamination duration. In the following diagrams (Figure 5.34 a and b) voltage degradation and regeneration duration as a function of contamination duration are shown.

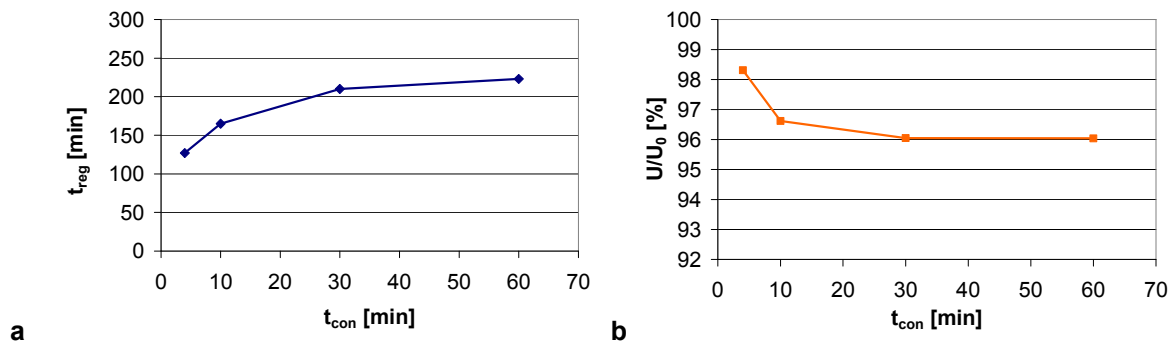


Figure 5.34 a) Regeneration duration and b) voltage degradation as a function of contamination duration with addition of 2 ppm H₂S.

According to results sulfur desorption takes longer than sulfur adsorption. Recovery time increases non-linearly by increasing contamination duration and reaches saturation for contamination periods ≥ 30 min. It can be assumed that in 30 minutes the whole electrochemically active area of the cell (16 cm²) is uniformly contaminated with sulfur.

5.3 Discussion and summary

The influence of hydrogen sulfide on the performance of SOFC stacks was investigated by analysing the electrochemical performance of stacks with impedance

spectroscopy and voltage-time characteristics at 850 °C. The following results were obtained:

Ni/8YSZ anodes:

- An abrupt cell voltage decrease to ≤ 89 % of the initial cell voltage takes place within a few minutes of adding $c_{\text{H}_2\text{S}} \geq 1$ ppm to the fuel (Phase I).
- Phase I is followed by a slower degradation of the stack voltage over several hours (Phase II), after which the voltage then stabilizes.
- Voltage recovery takes place up to 98 % of the initial value, after removing 2 ppm H_2S and 96.5 % after removing 50 ppm H_2S from the fuel.
- The voltage drop is almost saturated with 10 ppm H_2S . At higher H_2S concentrations a further increase in H_2S contamination doesn't significantly affect the cell power.
- Current reduces the sulfur poisoning of the cells.
- No effect of $p_{\text{H}_2\text{S}}/p_{\text{H}_2\text{O}}$ on H_2S contamination or recovery of anode was observed.
- No sulfur traces could be found either with FESEM, EDX or Raman spectroscopy during post-mortem-analysis.

Ni/10CGO anodes:

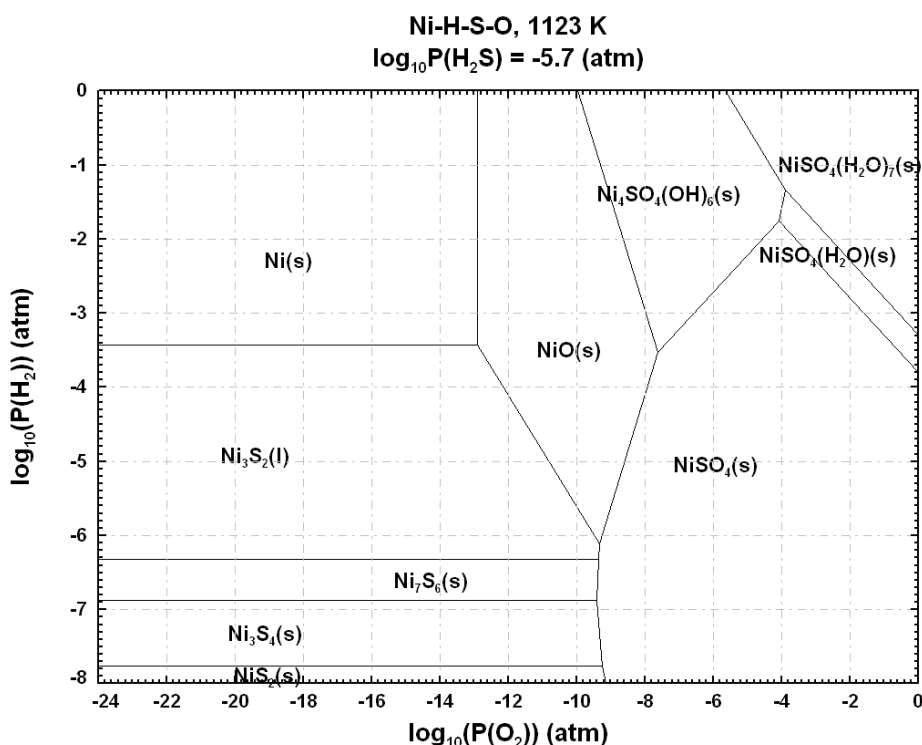
- An abrupt cell voltage decrease to 98.7 % of the initial cell voltage takes place within a few minutes of adding $c_{\text{H}_2\text{S}} \geq 1$ ppm to the fuel (Phase I).
- No further voltage degradation occurs (compared with Ni/8YSZ anodes).
- Recovery time increases non-linearly with increasing contamination duration and reaches saturation for contamination periods ≥ 30 min.
- Complete voltage recovery occurs after removing H_2S contamination in levels up to 15 ppm H_2S . Higher concentrations were not tested with respect to recovery.
- The voltage drop is almost saturated with 1 ppm H_2S . At higher H_2S concentrations a further increase in H_2S contamination doesn't significantly affect the cell power.
- No effect of current on the sulfur poisoning resistivity of the cells was observed.

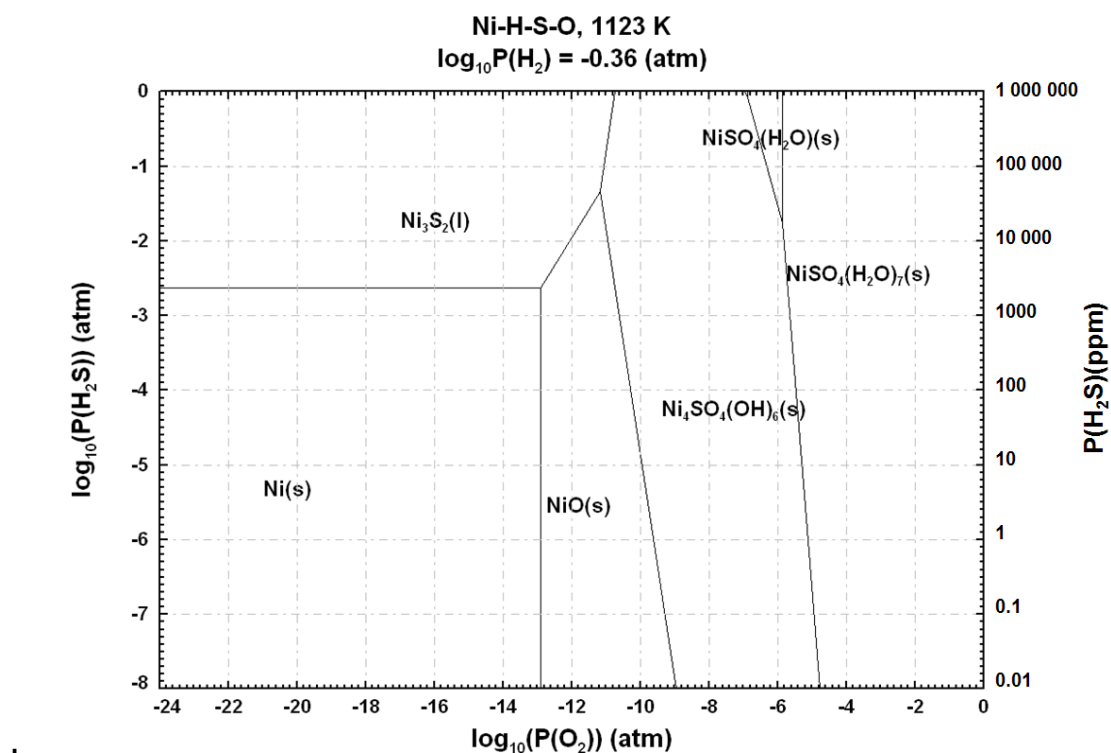
- No effect of $\text{pH}_2\text{S}/\text{pH}_2\text{O}$ on H_2S contamination or recovery of anode was observed.
- The performances of stacks fuelled with pre-mixed reformat gas or $\text{H}_2/\text{H}_2\text{O}$ fuel don't differ with respect to H_2S poisoning.
- No sulfur traces were found either with FESEM, EDX or Raman spectroscopy during post-mortem-analysis.

5.3.1 Thermodynamic calculations

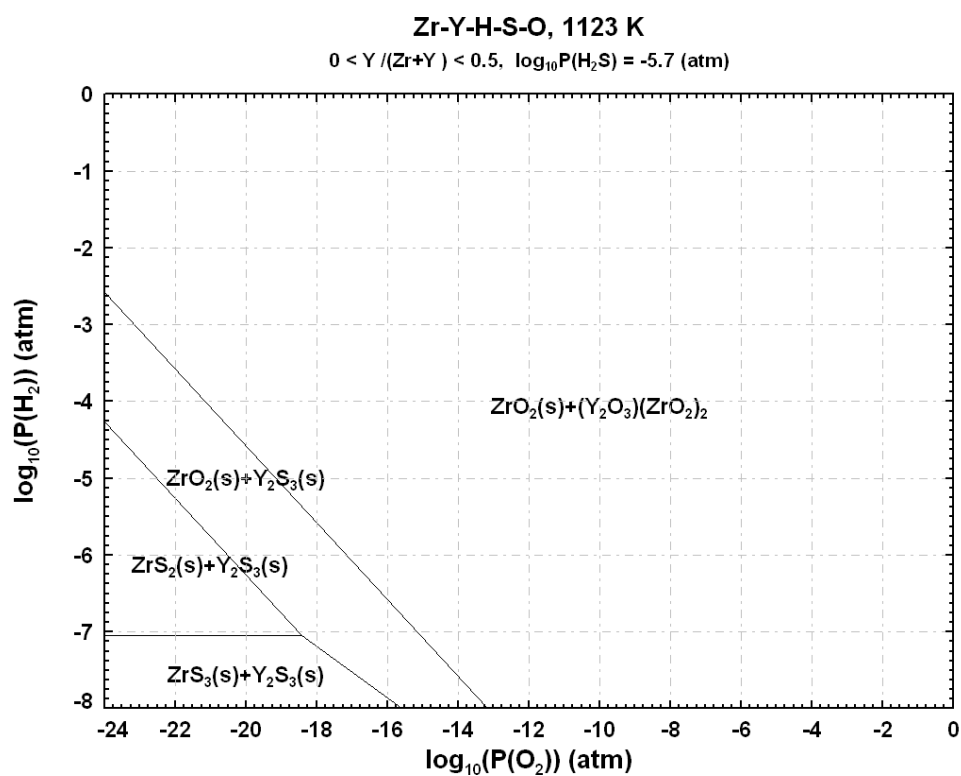
As soon as H_2S was introduced to the fuel, the cell voltage decreased without any induction time for both cell types (Ni/8YSZ and Ni/10CGO anodes). The impedance analyzes showed simultaneously an increase in the polarization resistance of the cell. Thermodynamic calculations were conducted with the aim of identifying whether sulfide formation was favourable under the experimental conditions.

Phase equilibrium calculations for experimental parameters were performed using FactSage©. The Ni-O-H-S, Y-Zr-O-H-S and Ce-Gd-O-H-S equilibrium diagrams calculated for constant pH_2S (2 ppm H_2S) and pH_2 (43.8 vol %) at 850°C are shown in Figure 5.35. The $\log_{10}(\text{pO}_2)$ values were approximately -18 and $\log_{10}(\text{pH}_2)$ approximately -0.4 as given in Table 5.7.

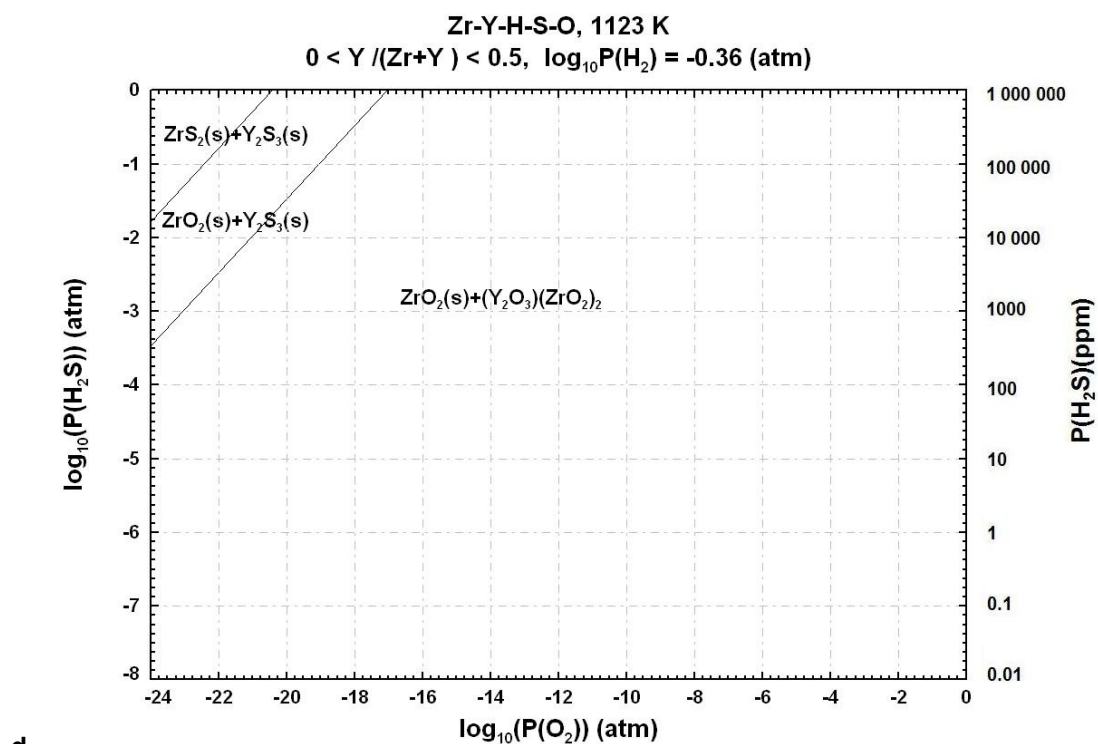




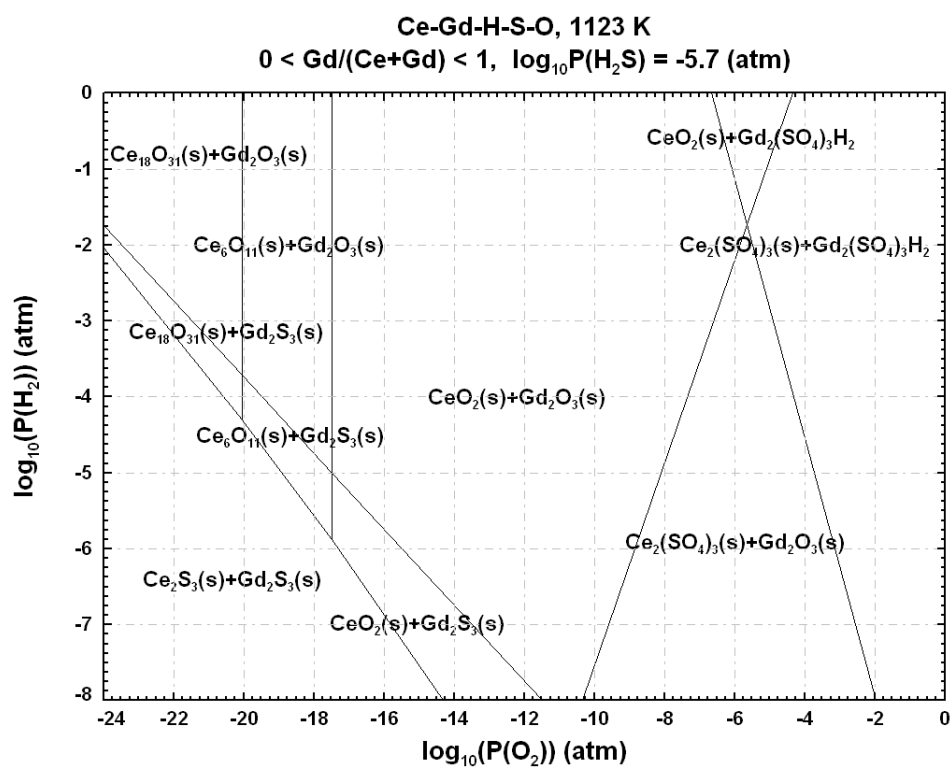
b



c



d



e

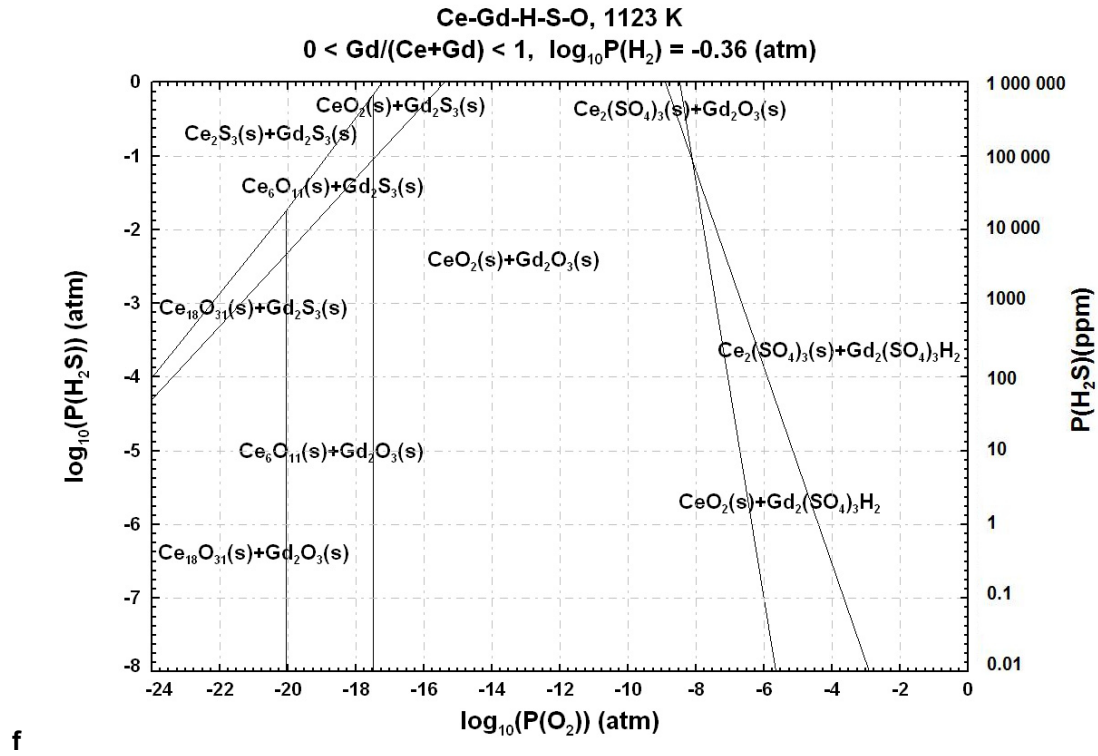


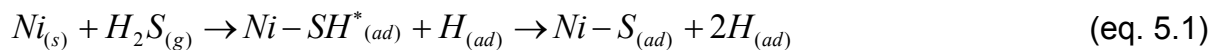
Figure 5.35 Phase equilibrium of the a) Ni-S-O-H system at 1123 K calculated for 2 ppm H_2S b) constant H_2 with various H_2S concentrations c) Phase equilibrium of the Y-Zr-S-O-H system at 1123 K calculated for 2 ppm H_2S d) constant H_2 with various H_2S concentrations. e) Phase equilibrium of the Ce-Gd-S-O-H system at 1123 K calculated for 2 ppm H_2S f) constant H_2 with various H_2S concentrations. The indicated areas show the area that match with experimental parameters.

The logarithmic values of the partial pressures of H_2 , H_2O and O_2 are as given in Table 5.7. Based upon the equilibrium calculations it was found that formation of any sulfides was not thermodynamically possible up to ~ 2500 ppm H_2S .

Table 5.7 The $\log_{10}(P(\text{O}_2))$ and $\log_{10}(P(\text{H}_2))$ and $\log_{10}(P(\text{H}_2\text{O}))$ values by inlet and outlet of stack with 2 ppm H_2S (a fuel mixture of 43.8 vol % H_2 / 6.2 vol % H_2O / 50 vol % N_2 was used as the input, with 25 % fuel utility - providing 33 vol % H_2 and 17 vol % H_2O as output values).

$\text{Log}_{10}(P(\text{H}_2\text{S})) = -5.7$			
	$\text{Log}_{10}(P(\text{H}_2))$	$\text{Log}_{10}(P(\text{H}_2\text{O}))$	$\text{Log}_{10}(P(\text{O}_2))$
Inlet	-0.36	-1.21	-18.97
Outlet	-0.48	-0.77	-17.86

Thermodynamic calculations as well as post mortem analysis of the anodes eliminate the possibility of sulfide formation. The power degradation of the SOFC stack due to H_2S addition to fuel gas can therefore be attributed to the dissociative H_2S adsorption on nickel as follows:



Adsorption of sulfur on oxides has been shown to be negligible [Bar82]. Therefore adsorption on YSZ or CGO is excluded as a possible poisoning mechanism for nickel containing anodes.

5.3.2 Phases of the sulfur poisoning of Ni/8YSZ anodes

During contamination experiments, it was observed that the addition of H₂S caused an initial rapid decrease in the cell voltage (Phase I) followed by a slow decrease (Phase II) occurring over the following hundred hours.

Phase I

The stack performance degradation during Phase I is concluded to be due to the dissociative adsorption of sulfur on active sites (nickel) in the anode.

When a sulfur atom contacts a nickel surface, it immediately adsorbs on the nickel and blocks the adsorption of hydrogen or carbon monoxide and therefore decreases the activity of the anode. The sticking probability of sulfur on nickel is known to be as high as unity [Bla83]. H₂S has a high adsorption energy on nickel. The reaction is exothermic and is more favourable than hydrogen adsorption [Bar82]. The polarization resistance then increases and therefore the performance of the cell decreases.

For the Phase I, one should consider the area specific resistance (R_{Area}) of the cell which is affected by H₂S addition:

$$R_{Area} = R \cdot A = \frac{U_{OC} - U}{I} \cdot A \quad (\text{eq. 5.2})$$

where R is the resistance and A is the active surface of the cell (here the anode surface).

A parallel relationship between the area specific resistances of the contaminated surface ($R_{Areacon}$) to the uncontaminated surface (R_{Area0}) of the anode can be considered. The total area surface resistance is then:

$$\frac{1}{R_{Area}} = \frac{1}{R_{Area0}} + \frac{1}{R_{Areacon}} \quad (\text{eq. 5.3})$$

As H₂S gas is added to fuel, it first contacts the nearest anode surface (fuel inlet) and rapidly adsorbs on the nickel surface. A simplified schematics of an anode surface with Δx as the contaminated length is presented in Figure 5.36. The thickness of the anode in this simplified model is not taken into consideration.

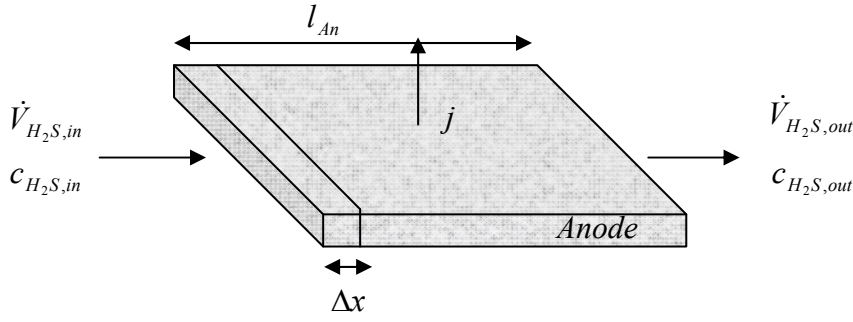


Figure 5.36 Progress of sulfur contamination of the anode beginning from the fuel inlet to the fuel outlet. Δx represents the length of the contaminated surface.

The relationship of whole area specific resistance to the contaminated and uncontaminated area specific resistances is dependent on the length of contaminated area; and can be expressed in terms of cell potential as follows:

$$R_{Area} = \frac{A_{An}}{I} \cdot \frac{1}{l_{An}} \cdot \int_0^l (U(x) - U_{OC}) dx \quad (\text{eq. 5.4})$$

If we assume that Δx is known, it is possible to calculate the area specific resistance [Her08]:

$$\frac{1}{R_{Area}} = \frac{1}{R_{Area0} \cdot \frac{l_{An}}{l_{An} - \Delta x}} + \frac{1}{R_{Areacon} \cdot \frac{l_{An}}{\Delta x}} \quad (\text{eq. 5.5})$$

If we consider that there is a direct relationship with contaminated length and contamination time, the dependence of the time (t_{PhI}) during Phase I is:

$$\Delta x = \frac{l_{An}}{t_{PhI}} \cdot \Delta t \quad (\text{eq. 5.6})$$

The area specific resistance is then:

$$R_{Area} = \frac{R_{Area0} \cdot R_{Areacon}}{R_{Areacon} \cdot \left(1 - \frac{\Delta t}{t_{PhI}}\right) + R_{Area0} \cdot \frac{\Delta t}{t_{PhI}}} \quad (\text{eq. 5.7})$$

As an example, an R_{Area} of a cell was calculated as 0.926 ohmcm² before H₂S contamination (Figure 5.4). After 2 ppm H₂S was added to the cell, the cell voltage decreased in 10 minutes and the R_{Area} was calculated as 1.274 ohmcm². Figure 5.37 shows the observed and calculated R_{Area} values for this example. The real R_{Area} values differ at the beginning and at the end of the Phase I whereas in between the linear behaviour can be observed (Figure 5.37).

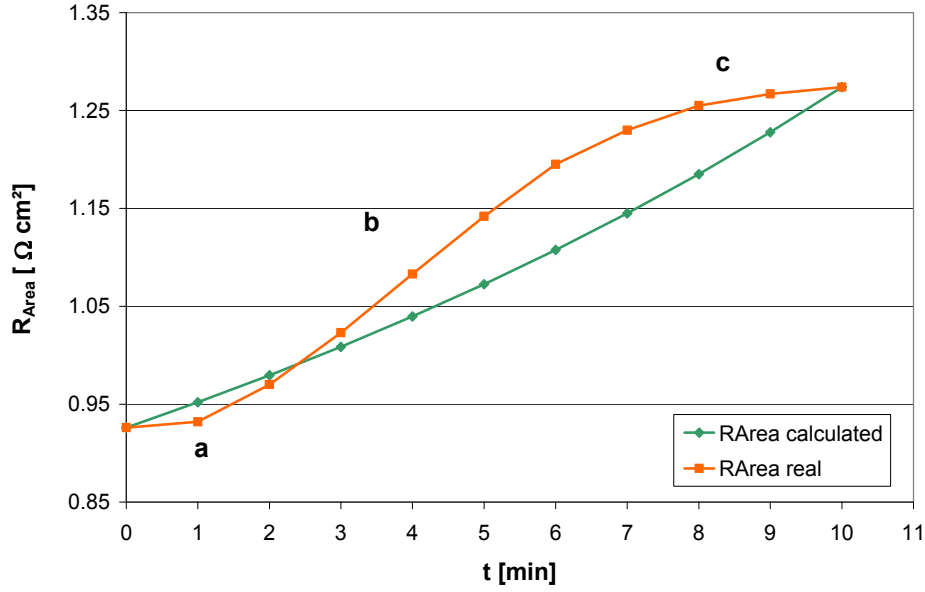


Figure 5.37 The comparison of real and calculated R_{Area} values of the cell from Figure 5.4.

The calculated R_{Area} has an almost linear behaviour whereas the real R_{Area} increase begins with a delay (a), and flattens (c) at the end of the Phase I. The time in between however obeys the linear behaviour.

The delay of the resistance increase (a) can be explained by considering the time required to flash the anode compartment with H_2S . As the concentration reaches 2 ppm H_2S at the inlet of the anode, R_{Area} increases linearly with the time (b). The flattening effect (c) at the end of the contamination phase is caused by the decreasing rate of sulfur adsorption; due to the decreasing probability of each sulfur atom finding a vacant adsorption site on the nickel surface (with increasing coverage of the nickel surface with sulfur).

If it is considered that adsorption on the nickel surface takes place only during Phase I (b), the nickel surface area can be calculated. With the total fuel volume flow ($\dot{V}_{tot}$) 40 ± 0.2 l/h under ideal gas conditions ($V = 22.414$ l/mol) the molar flow rate of H_2S ($\dot{n}_{H_2S}$) is $3.57 \pm 0.04 \cdot 10^{-6}$ mol/h.

If the sulfur saturation concentration for nickel surface is 44 ± 2 ngS / $cm^2 Ni_{SA}$ (Table 3.3), the molar sulfur saturation concentration (c_{sat}) is calculated as:

$$c_{sat} = 1.37 \pm 0.07 \cdot 10^{-9} \text{ mol} / \text{cm}^2 Ni_{SA}$$

If it is assumed that H_2S is homogeneously distributed on the nickel surface and every sulfur atom that hits the surface adsorbs on nickel, one can calculate the nickel surface area as:

$$A_{Ni} = \frac{\dot{n}_{H_2S} \cdot t_{lin}}{c_{sat}} \quad (\text{eq. 5.8})$$

where A_{Ni} is nickel surface area and t_{lin} is the duration of the linear R_{Area} increase. Under experimental conditions, A_{Ni} of the anode has been calculated as $0.03 \pm 0.03 \text{ m}^2$. This area is accessible for H_2S molecules whereas very small micropores are not counted. Equation 5.8 shows the indirect proportion between H_2S molar flow and t_{lin} .

An experiment was performed to confirm the relationship between H_2S concentration and t_{lin} . A stack with an Ni/8YSZ anode was brought to experimental conditions using the standard procedures as described in Chapter 4.2.1. The cell was first contaminated with 4 ppm H_2S for one hour and then regenerated by removing the H_2S in order to have the same “contaminated” condition for all of the contamination cycles. 1 ppm, 2 ppm and 4 ppm H_2S were added to the fuel and the following voltage drops as a function of time were observed.

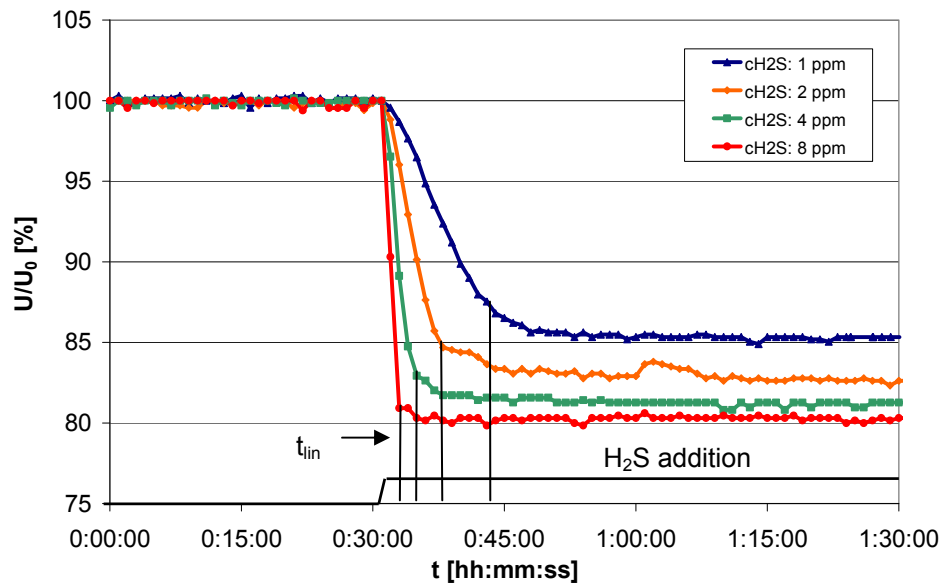


Figure 5.38 Voltage drop as a function of time and H_2S concentration. (Cell Type II, fuel: 43.8/6.2/50 vol % $\text{H}_2/\text{H}_2\text{O}/\text{N}_2$, T: 850 °C, current density: 318 mA/cm^2).

The diagram above shows the data recorded between 30 minutes before and 60 minutes after H_2S addition. t_{lin} for 1 ppm, 2 ppm and 4 ppm H_2S contamination were recorded as 13 minutes, 6 minutes, 3 minutes and 1,5 minutes, respectively in consistence with equation 5.6.

Figure 5.39 shows an indirect relation between t_{lin} and H_2S concentration. The linear dependence between t_{lin}^{-1} and H_2S concentration confirms the proposed mechanism of anode poisoning.

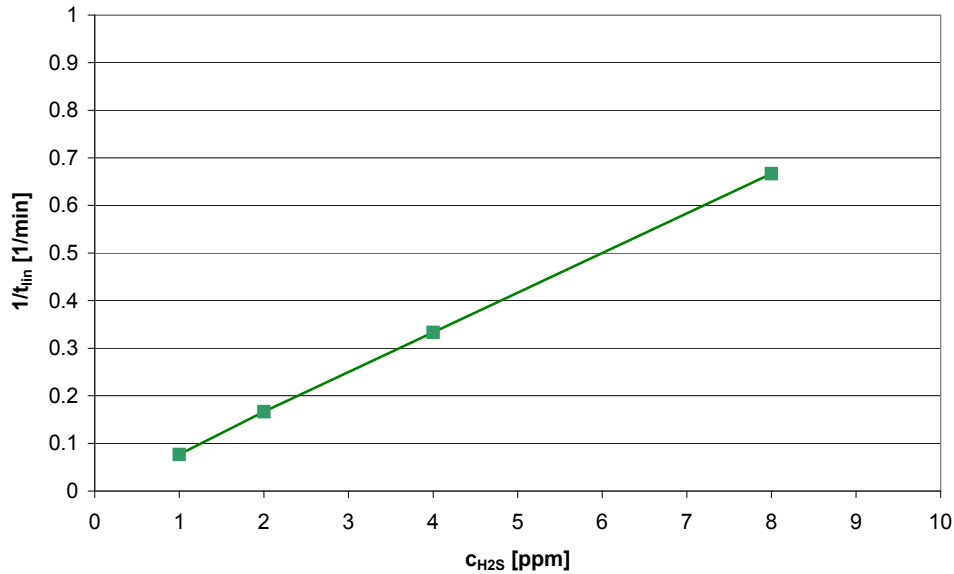


Figure 5.39 The linear relation between $1/t_{lin}$ and H_2S concentration.

Phase II

During the second degradation phase (Phase II), a lower cell voltage decrease was observed ($\sim 1\%$) for a relatively long period of time. This can be attributed to the surface mechanisms which are slower than adsorption of sulfur. A possible reason may be the surface restructuring of nickel (after the adsorption of sulfur reaches equilibrium) by continuing addition of H_2S . This effect has been reported on multiple occasions in studies on the poisoning mechanisms of catalysts. Oliphant et al. [Oli78] found nickel surface reconstruction with addition of 25 - 30 ppm H_2S in H_2 . Edmonds et al. [Edm71] observed a change in the crystal surface structure by sulfur adsorbed at near saturation coverage as well as Bartholomew [Bar82]. Oudar [Oud80] claimed that reconstruction takes place in favour of the highest symmetry with the number of adsorbed sulfur atoms. The reconstruction process is expected to be much slower than the surface adsorption process and therefore may cause much slower degradation of the fuel cell performance by changing the exposed crystal planes to less active ones [Wan07]. The restructuring of nickel and formation of more stable Ni-S structures on the surface increases the bonding enthalpy of sulfur and therefore hinders the desorption (increases the desorption time).

Regeneration

Chemisorption is reversible (if no additional reactions takes place) and thermodynamically the adsorption reaction will be reversed after the removal of H_2S during regeneration:



The driving force of this reaction is very small and decreases with decreasing sulfur coverage. The stack voltage recovery as a function of time showed that sulfur

desorption is much slower than sulfur adsorption (Figure 5.5). In SOFC conditions, the thermal desorption temperature $> 1500\text{ K}$ [Bla83] as an option can be neglected since this temperature is much higher than SOFC operating temperatures. Simply removing H_2S was insufficient to regenerate the anode. This result is consistent with the results of previous nickel catalyst regeneration studies [Bar82]. Regeneration in reducing atmospheres may result in a slow regeneration because the rate of diffusion-controlled desorption is decreasing exponentially with time. The exponential decay is even true without diffusion restriction where the gas leaves any reactor saturated with H_2S [Ros81].

Another approach for examining regeneration was to study the effect of $p\text{H}_2\text{O}/p\text{H}_2$. The experiments mentioned in 5.1.5 and in 5.2.6 were tested without any effect of water concentration on poisoning or regeneration behaviour of the stacks with Ni/8YSZ and Ni/10CGO anodes with $p\text{H}_2\text{O}/p\text{H}_2$ values between 0.14 – 0.92. This result is consistent with the results of studies done with nickel catalysts [Ros71]. In his studies, Rostrup-Nielsen observed no improvement in the regeneration of nickel containing reforming catalysts when the $p\text{H}_2\text{O}/p\text{H}_2$ was slightly increased at 700°C to values of 2 – 3. Only at $p\text{H}_2\text{O}/p\text{H}_2$ above 200 – 250 was a significant change in the degree of regeneration of the catalyst observed.

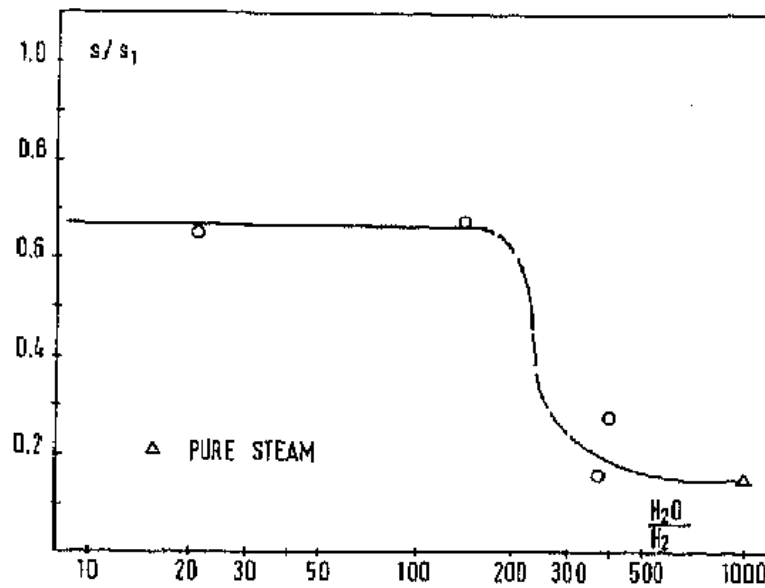


Figure 5.40 Influence of $p\text{H}_2\text{O}/p\text{H}_2$ on regeneration process at 700°C (Catalyst: 10 wt % Ni on magnesium spinel). (s/s_1 = ratio of sulfur content before regeneration to after regeneration) [Ros71].

The increased removal of sulfur was achieved at $p\text{H}_2\text{O}/p\text{H}_2$ ratios which are close to the equilibrium constant for the oxidation of the catalyst.



With sulfur present, this equation will take the form:



and



which are the possible reactions for desorption.

However, due to nickel oxide formation, this approach is not beneficial for sulfur contaminated SOFC nickel based anodes. Any regeneration approach with high oxygen partial pressures in the fuel (as with catalyst studies [Hol72]) can not be applied to SOFCs due to nickel oxidation.

Increasing the oxygen concentration in the anode through increasing the oxygen flux from the cathode was shown to be a successful approach to decrease the effects of sulfur on the performance of the stack. The passage of oxygen ions transferred through the electrolyte to the electrochemically active sites in the anode showed a positive effect in terms of resistance against sulfur poisoning (Chapters 5.1.4). It can be assumed that oxygen ions may directly react at triple phase boundaries with sulfur under SOFC conditions:



It should be noted that the formed $SO_{2(g)}$ will be converted to H_2S under anode fuel conditions and therefore be a transient component with $pSO_2/pH_2S = 7 \cdot 10^{-9}$.



The important conclusion made from the experiments with Ni/YSZ anodes is that the poisoning takes place through nickel surface contamination and can be significantly reduced in the presence of oxygen.

5.3.3 Sulfur poisoning of Ni/10CGO anodes

Compared with the anodes containing Ni/8YSZ, Ni/10CGO anodes showed much better resistance to sulfur poisoning. The cell voltage of a stack with Ni/10CGO anode decreased down to 97 % of its initial value when 2 ppm H_2S was added to the fuel at 850 °C. Further increases of H_2S concentration didn't cause further degradation for Ni/10CGO anodes, which is contrary to Ni/8YSZ anodes (voltage drop increased up to 84 % with 40 ppm H_2S). After the removal of the sulfur, the cell voltage regenerated to its initial value with Ni/10CGO anodes meanwhile with Ni/8YSZ anodes a power loss of 2 % was observed. To explain this behavior the properties of CGO and YSZ as well as the mechanisms of anodic reaction in Ni/YSZ and Ni/CGO have to be compared.

CGO (when compared to YSZ) has a superior feature of being a mixed ionic electronic conductor at low pO_2 . Ceramics based on CeO_2 show activity for electrochemical oxidation in SOFCs in reducing environments at $T > 500\text{ }^\circ\text{C}$ due to the reduction of Ce^{4+} to Ce^{3+} [Sun07], [DeC09]. The ability of CGO to transport electrons as well as oxygen ions extends the triple phase boundaries to a large extent. The following proposed Kröger-Vink notation shows the charge-transfer via oxide / hopping at the ceria / YSZ two-phase boundary [DeC09]:



In the following figure, the conductivities of 8YSZ and 20CGO from the studies of Lübke [Lüb99] and Kawada [Kaw92] are compared.

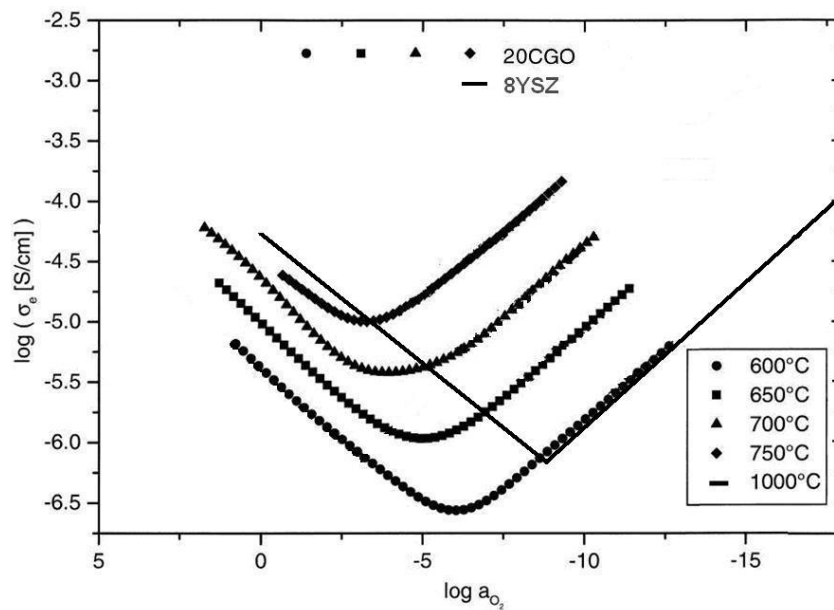


Figure 5.41 Electronic conductivity of 8YSZ at 1000 °C and of 20CGO ($Ce_{0.8}Gd_{0.2}O_{1.9-x}$) at 600 °C, 650 °C, 700 °C and 750 °C as a function of oxygen activity (a_{O_2} : pO_2 in atm). Modified from Lübke [Lüb99] and Kawada [Kaw92].

The diagram shows the dependency of electrical conductivity on temperature and the partial pressure of oxygen. In the oxygen partial pressure region relevant for SOFC (approximately at $\log a_{O_2} < -18$) the electronic conductivity increases with increasing temperature and decreasing pO_2 . The electrical conductivity of 20CGO then can be estimated as much higher than the electrical conductivity of 8YSZ under the same conditions.

In

Table 5.8, both the ionic and electronic conductivities of 8YSZ and 10CGO at 850°C at constant pressure of pO_2 : 5.5×10^{-21} atm (97 vol % H_2 , 3 vol % H_2O) are compared. The comparison shows that 10CGO has much higher electronic conductivity than 8YSZ, too. It should be noted that the electronic conductivity of doped ceria is not sufficient to take care of the current collection in an SOFC stack [Mog04], [Gil07].

Table 5.8 Approximate conductivities of ceramics at 850°C [Pri02].

Ceramic	$\sigma_{O^{2-}}$ [S/cm]	σ_{e^-} [S/cm]
8YSZ	0.07	1×10^{-5}
10CGO	0.06	2

The electrochemical mechanisms occurring at Ni/CGO interfaces has not been investigated in the same depth as those occurring at Ni/YSZ interfaces. An interesting approach to defining the anode electrochemical reactions at metal/oxide interfaces was applied by the group of H. Yokokawa. There, the mechanisms were studied with isotope labeling/secondary ion mass spectrometry (SIMS) with respect to oxygen surface reactivity and catalytic activity with patterned anodes. It was found that the proton (H^+) solubility of yttria doped ceria (YDC) is two orders of magnitude higher than YSZ. However, the proton conductivity was not identified; probably due to low magnitudes compared to oxide ion conductivity [Yok04]. The high proton solubility is found to enhance the interface reaction (increase of H^+ and OH^- in YDC). The solubility of water as hydrogen was found to be about 10^{-4} mol per mole doped CeO_2 whereas 10^{-6} mol per mole YSZ at 1073 K [Hor06]. Due to this property of CeO_2 containing anodes, the effective anodic reaction area around TPB changes dramatically.

Based on these observations, the mechanisms shown in Figure 5.42 are proposed for the possible reaction process for H_2 oxidation around H_2/H_2O /metal/oxide interfaces with and without the presence of H_2S .

As shown in Figure 5.42, in the absence of H_2S in the gas phase for Ni/YSZ anodes (Figure 5.42 a), the dissociative adsorption of H_2 and H_2O takes place on the nickel surface. It is assumed that the adsorption of hydrogen on the YSZ surface is very small and therefore can be neglected [Wag68]. It should also be noted that water indirectly helps to enhance the surface exchange rate of oxygen on the surface of YSZ [Sak03]. The charge transfer reaction is assumed to take place in one step on the Ni-YSZ interface. When H_2S is added to the gas (Figure 5.42 b), H_2S immediately dissociatively adsorbs on the nickel surface. Since H_2S adsorption is more favourable, hydrogen adsorption on nickel as well as the charge transfer reaction is hindered mechanically.



This effect increases as pH_2S/pH_2 increases and explains the observed rapid increase of voltage drop up to 10 ppm H_2S in Ni/YSZ anodes in the experiments. Between concentrations $10 \text{ ppm} < c_{H_2S} \leq 50 \text{ ppm}$, this effect is not strong since the nickel surface coverage increases in this region only slightly. The effect of pH_2O is found to be insignificant. Oxygen ion flux (current density) from the electrolyte is

found to have a positive effect on sulfur resistance where oxygen reacts with sulfur at TPB and forms an unstable intermediary $\text{SO}_{2(g)}$ which reacts with H_2 to form H_2S . Therefore the intermediate SO_2 species can not be directly measured in our experiments to confirm this regeneration/protection mechanism induced by oxygen flux through the cell.

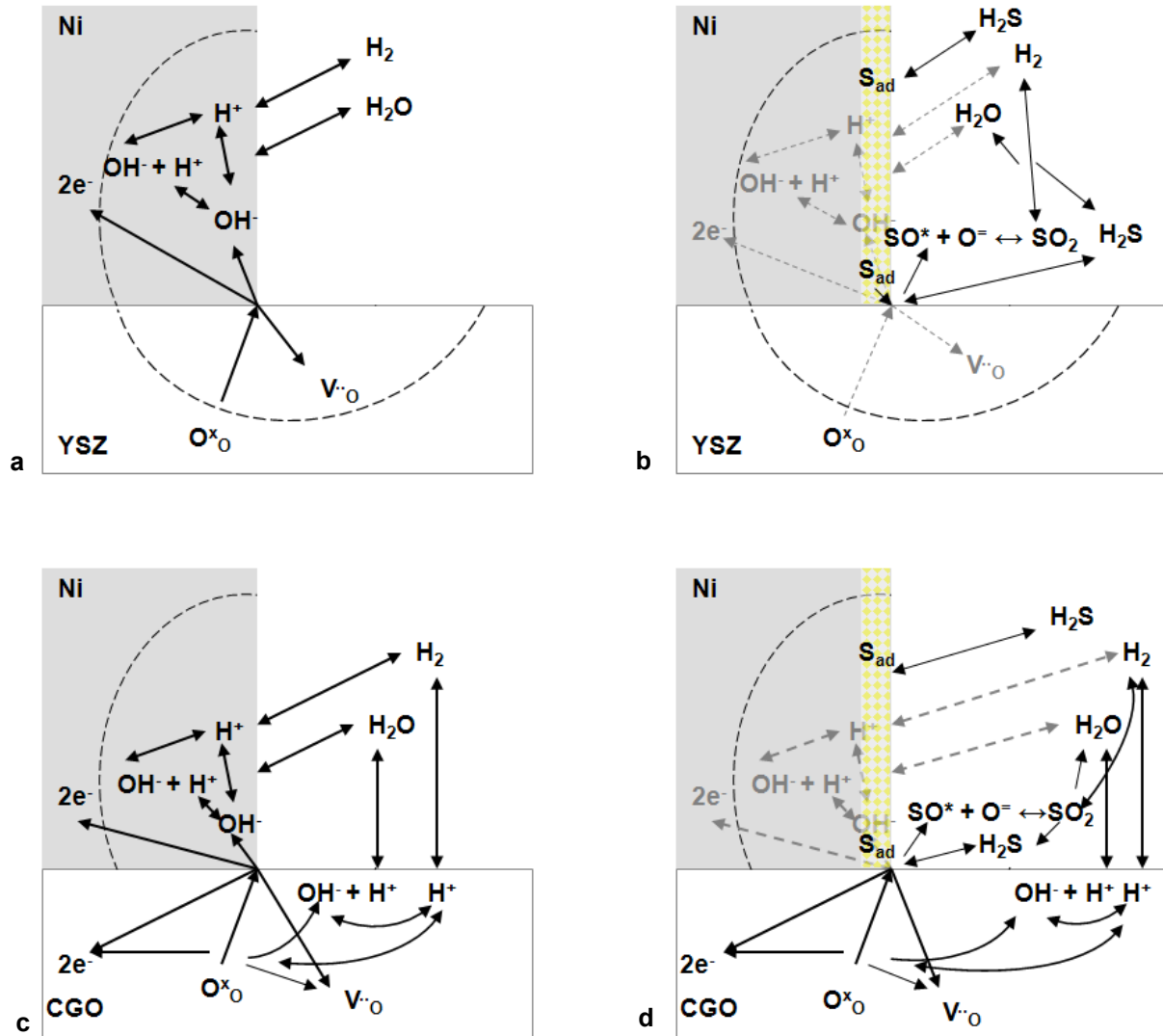


Figure 5.42 Proposed electrochemical processes in the anode around a) $\text{H}_2\text{-H}_2\text{O}/\text{Ni}/\text{YSZ}$ interface without H_2S , b) with H_2S and possible electrochemical processes for H_2 oxidation around c) $\text{H}_2\text{-H}_2\text{O}/\text{Ni}/\text{CGO}$ interface without H_2S , d) with H_2S .

In case of Ni/CGO anodes (Figure 5.42 c and d), the reactions on the nickel surface are similar whereas H_2 and H_2O adsorption and electronic conductivity can take place also on CGO. Furthermore, the results show that the electrochemical reaction takes place mostly on the CGO surface. This explains also the low voltage drop by sulfur addition to the fuel which blocks only nickel surfaces and has only a small effect on CGO due to its oxidic nature.



CGO works as an oxygen storage material which provides protection against sulfur deposition.



Nickel in the investigated Ni/CGO anode has almost the function of a current collector.

Due to these properties of CGO, Ni/CGO anodes have far more resistance to sulfur poisoning when compared with Ni/YSZ. The current density effect with Ni/8YSZ anodes was more obvious than with Ni/CGO most probably due to the compensation of blocked nickel reaction sites with CGO sites.

5.3.4 Detection of sulfur traces in the anode

During all of the experiments, with Ni/8YSZ anodes the cell voltage did not recover 100 % but regained about 98 % of its initial value after removal of H₂S. With repeated contamination cycles, cell voltage decreased further each time (Figure 5.10). The contaminated anodes were analyzed with a scanning electron microscope, energy dispersive x-ray and raman spectroscopy; but no sulfur traces were found in the anode, no morphological changes were observed. Microstructural changes are therefore excluded as a reason of incomplete regeneration.

Reasons for the irreversible degradation of the anodes have been discussed by some groups. Cheng et al. observed the anodes in-situ and ex-situ with REM, EDX and Raman during and after exposure to H₂S containing fuel (50 ppm H₂S in 1.5 vol % H₂O, 48.5 vol % N₂ and 50 vol % H₂ at 800 °C for 48 h) [Che07]. For the ex-situ analysis, they cooled the stacks down to room temperature using the same fuel gas composition. According to his ex-situ observations, nickel morphology changes and nickel sulfide forms whereas no changes were observed for YSZ. Their in-situ analyzes with Raman and REM shows no sulfide formations or morphology changes at 800 °C under the given fuel but at lower temperatures below 500 °C for fuels with 100 ppm H₂S. This is consistent with the theory that there is no nickel sulfide formation at high temperatures in low ppm H₂S region. The observed nickel sulfide during ex-situ analysis was formed at low temperature regions during cooling.

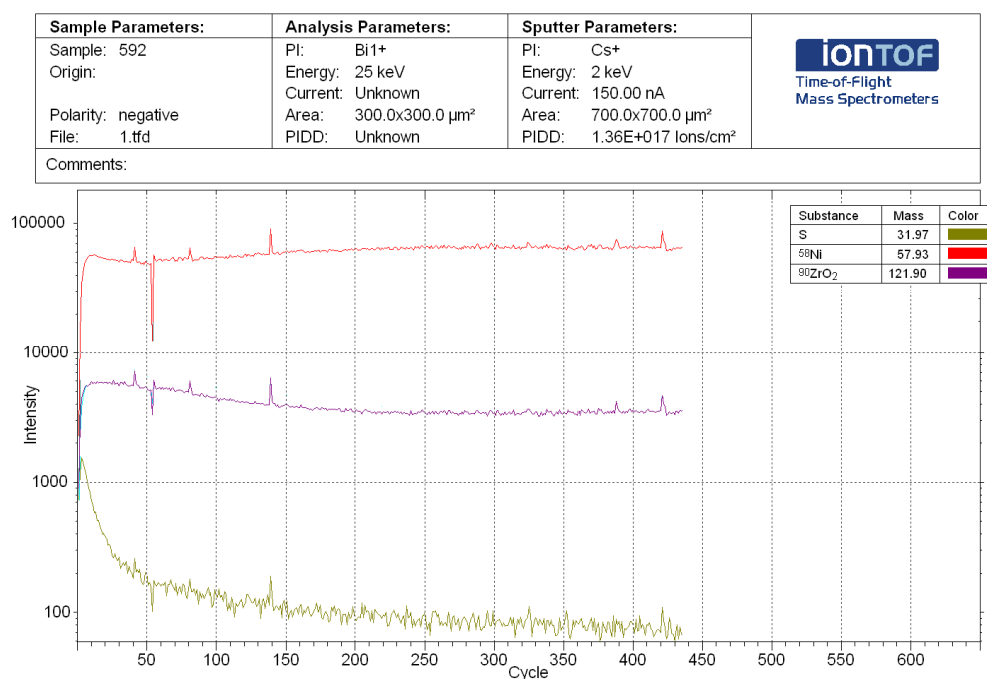
Sasaki et al. [Sas06] claimed on the basis of EDX analyses of anodes (exposed to 5 ppm H₂S in 100 % H₂ at 800 °C) that irreversible degradation may be the result of nickel oxidation. According to the thesis poisoned nickel electrode catalysts were no longer active for electrode reactions with a constant oxygen ion flow through the electrolyte to the anode, which means that oxygen ions supplied to the anode side may be used to oxidize nickel particles themselves rather than to oxidize fuel gases (Figure 3.10).

Time-of-flight Secondary Ion Mass Spectrometry (TOF-SIMS) Analysis

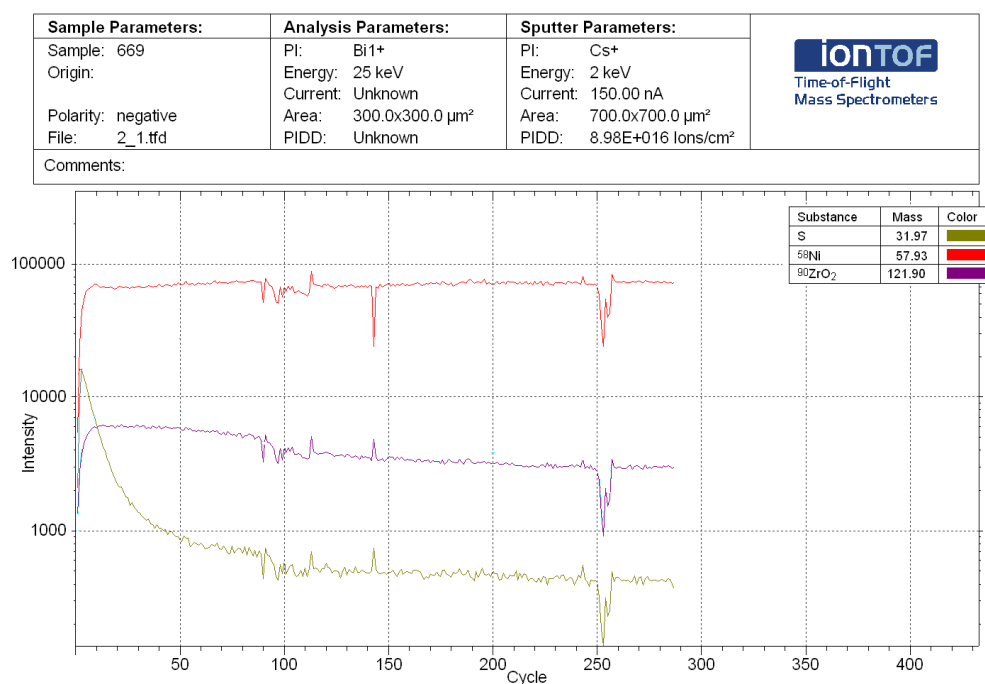
Due to the apparent incapability of EDX and Raman method to detect sulfur, it was decided to analyse samples with TOF-SIMS with higher sensitivity to low sulfur concentrations. Three samples were chosen to analyse with TOF-SIMS method:

- a reference sample (a) MEA operated with 50 % H₂, 50 % H₂O without H₂S at 850 °C for 335 hours. The stack was cooled down to room temperature with forming gas (5 % H₂, 95 % N₂).
- sample (b) MEA operated with 43.8 vol % H₂, 6.2 vol % H₂O, 50 vol % N₂ at 850 °C for 1000 hours (5 x 15 hours of 2 ppm H₂S contamination followed by 80 hours of regeneration (without H₂S) for each cycle). The stack was cooled down to room temperature with forming gas (5 vol % H₂, 95 vol % N₂).
- sample (c) MEA operated with 43.8 vol % H₂, 6.2 vol % H₂O, 50 vol % N₂ at 850 °C for 500 hours, last 15 hours with 50 ppm H₂S. No regeneration was followed. The stack was cooled down to room temperature with forming gas (5 vol % H₂, 95 vol % N₂).

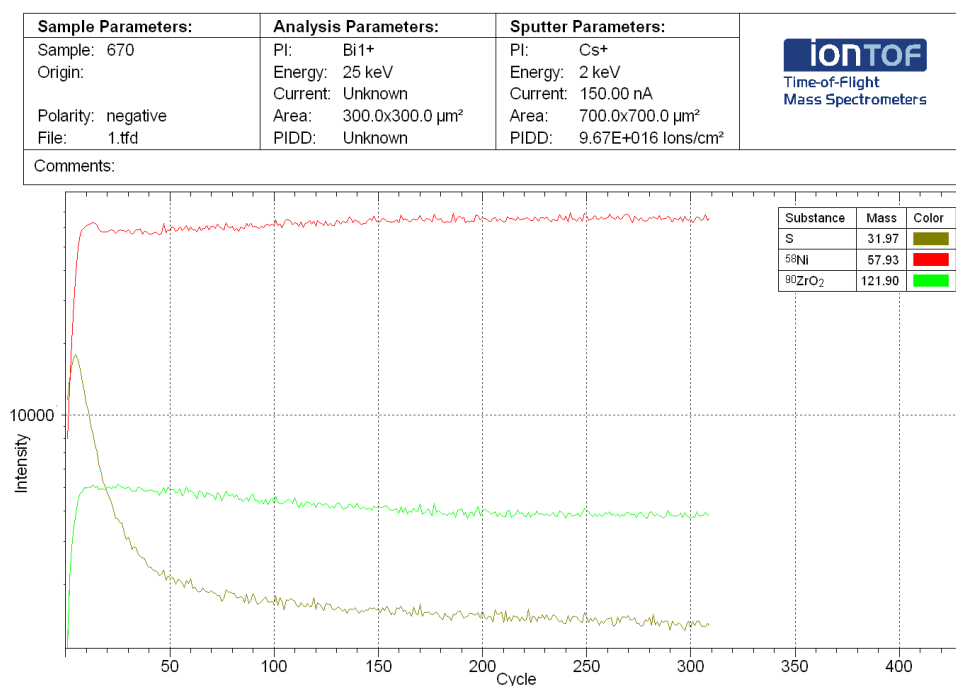
The samples were analysed with the depth profiling method to determine the distribution of sulfur as a function of depth from the anode surface. An area of 300 x 300 µm² was bombarded with a primary ion dose density of 1.36.10¹⁷. The results are shown in Figure 5.43.



a



b



c

Figure 5.43 Depth profile of a) reference sample and contaminated samples b) with regeneration and c) without regeneration. (Each cycle represents 2.67 nm depth from surface. The total analysis depth for samples are for a) 1.15 μm , b) 0.77 μm and 0.63 μm .

While nickel and ZrO₂ signal intensities are approximately the same for all of the samples, sulfur signal intensities differ from each other. The first 50 cycles of the bombardement show decreasing sulfur intensities for all of the samples. Therefore this region is omitted from the analysis. The intensities from all samples over the following cycles are stable. The result are summarized in Table 5.9.

Table 5.9 The approximate depth profile intensities of nickel, ZrO₂ and sulfur in the samples as shown in Figure 5.43.

Elements / Molecules	Intensity		
	Sample a	Sample b	Sample c
Ni	70000	70000	60000
ZrO ₂	4000	4000	4000
S	90	500	1500

According to the diagrams, samples b and c have approximately 50 and 150 times more sulfur content in the anode than sample a. This is consistent with the fact that sample a had not been contaminated with H₂S. The sample contaminated with the highest concentration of sulfur (50 ppm) showed the highest sulfur intensity among the investigated samples. Even though 80 hours of regeneration of sample b, it is shown that a sulfur amount is left in the anode. The sulfur traces found in the anode show that desorption of sulfur from the anode surface is not complete and may therefore still block the adsorption sites in the anode. The remaining traces of sulfur block the active sites in the anode and therefore total power recovery of the stack performance is not possible.

Thermogravimetric analysis (TGA)

The irreversible sulfur poisoning of anodes were examined with thermogravimetric analysis (TGA). For this purpose, the Ni, 8YSZ and Ni/8YSZ powder samples were prepared. The BET analyses of NiO powder and 8YSZ powder resulted in values of 1.21 m²/g and 13 – 19 m²/g surface area, respectively.

The samples were first heated up to 930 °C at 5 °C/min with 100 % N₂. At 930°C they were reduced using 10 vol % H₂ / 90 vol % N₂ gas mixture for 60 minutes. The samples were then cooled down to 850 °C and flushed with the same gas mixture for an additional 30 minutes. The samples were then flushed with a fuel gas mixture of 39.3 vol % H₂ / 44.6 vol % N₂ / 16.1 vol % H₂O ($\dot{V}$ = 5.6 l/h) for 60 minutes. Due to the limits of the evaporator of the system, the gas composition could not be regulated exactly to replicate the standard fuel gas (44.8 vol % H₂ / 50 vol % N₂ / 6.2 vol % H₂O). 90 ppm H₂S was then added to the gas mixture for 120 minutes. In the following diagrams, the mass change in percent as a function of time is presented from the beginning of the addition of the fuel gas mixture.

For the reference experiment, 200 mg 8YSZ powder was used as a sample. The weights of the Y₂O₃ and ZrO₂ in the sample were known and specified as in Table 5.10.

Table 5.10 The sample specifications for thermogravimetric analysis. ($M_{Y_2O_3}$: 225.81 g/mol, M_{ZrO_2} : 123.218 g/mol)

Species	Weight [g]	Weight [%]	Mol	Mol [%]
Total sample (8YSZ)	200	100	1.524	100
Y_2O_3	26.48	13.42	0.119	7.798
ZrO_2	173.16	86.58	1.405	92.202

Figure 5.44 shows the change in mass percent as a function of time. The sample was flushed with $H_2/H_2O/N_2$ gas mixture for the first 60 minutes. A slight decrease in the sample weight can be observed most probably due to water adsorption – desorption from the sample at the beginning. The sample weight was in the region of sample-to-noise ratio as 90 ppm H_2S was added to the gas. It can be accepted that there was no interaction between 8YSZ and H_2S as claimed in Chapter 5.3.

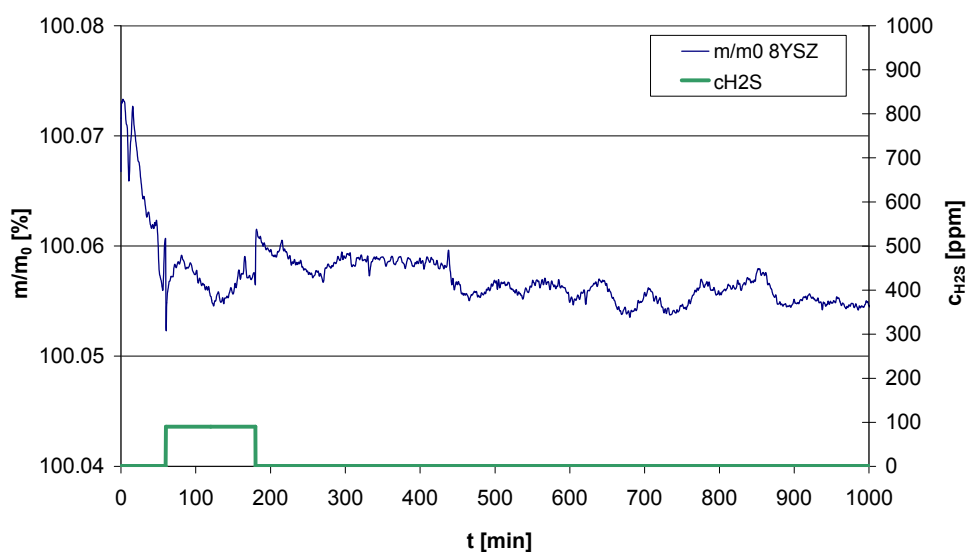


Figure 5.44 Effect of 90 ppm H_2S addition to gas mixture (39.3 vol % H_2 / 44.6 vol % N_2 / 16.1 vol % H_2O) on the mass change of 200 mg 8YSZ powder sample at 850°C as a function of time.

The same experiment was repeated for NiO powder. Figure 5.45 shows the change of mass in percent as a function of time. In contrast to the behaviour of the 8YSZ sample, the weight change is becoming obvious for NiO powder.

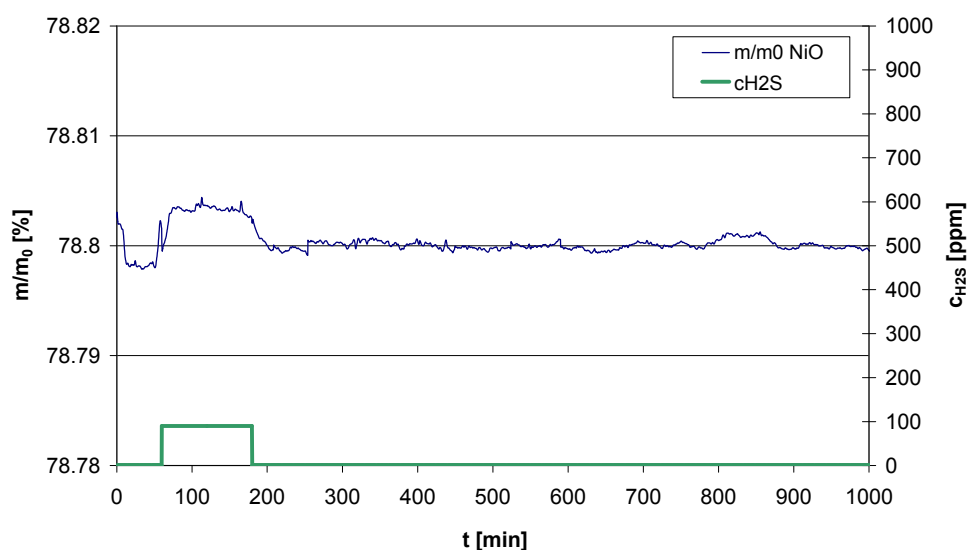


Figure 5.45 Effect of 90 ppm H_2S addition to gas mixture on the mass change of NiO powder sample as a function of time.

At the beginning of the experiment the weight decreases to approximately 78.8 % of its initial value due to the reduction of NiO powder to Ni. Assuming that the sample was composed of 100 % NiO the following table with the precise values shows that the oxidation was almost complete.

Table 5.11 The sample specifications for thermogravimetric analysis. (M_{NiO} : 74.69 g/mol, M_{Ni} : 58.69 g/mol, M_{O} : 15.99 g/mol)

	Before oxidation (m_0) (calculated)		After oxidation (m_1) (observed)	
Species	Weight [mg]	Mol	Weight [mg]	Mol
NiO (sample)	461.256	$6.175 \cdot 10^{-3}$	363.459	-
Ni	362.454	$6.175 \cdot 10^{-3}$	362.453	$6.175 \cdot 10^{-3}$
O	98.802	$6.175 \cdot 10^{-3}$	1.006	$0.062 \cdot 10^{-3}$

The addition of 90 ppm H_2S for 120 minutes increased the weight of the sample to 78.803 % ($m_1 + 0.0267$ mg). After the H_2S addition was stopped, the weight of the sample decreased to 78.799 % ($m_1 + 0.0069$ mg) of its initial value. The difference in the sample weight indicates that desorption of sulfur from nickel surface was not complete.

A similar material to that found in Ni/8YSZ anodes; 1127 mg NiO/8YSZ powder (63 % NiO, 37 % 8YSZ by weight) was used for a third experiment. After the weight of the sample was stable with the gas composition 39.3 vol % H_2 / 44.6 vol % N_2 / 16.1 vol % H_2O at 850 °C, 90 ppm H_2S was added to the fuel. For this experiment, the sample was flushed with the given gas composition for 17 hours to assure a

stable point. 90 ppm H_2S was added to the sample for 9 hours. The weight change before, during and after H_2S addition is shown below.

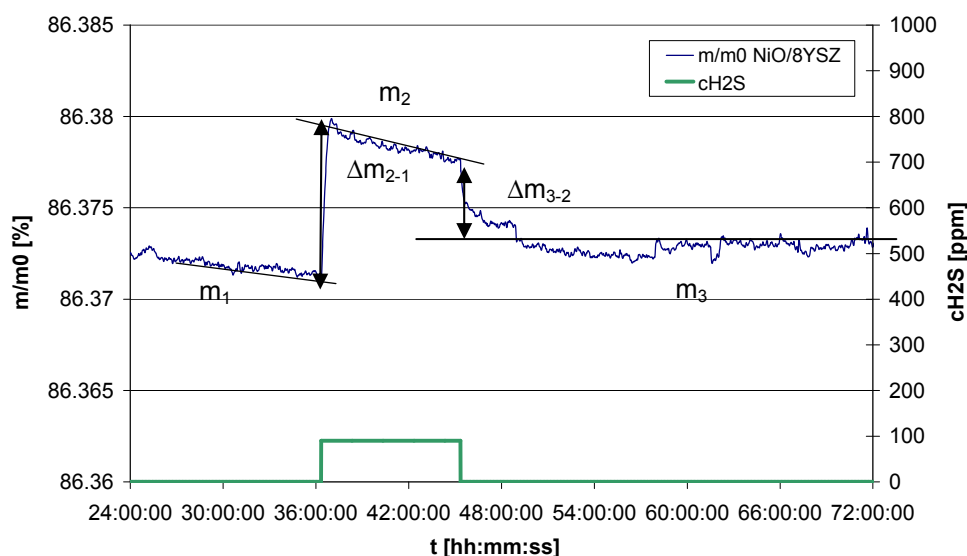


Figure 5.46 Relative mass change of the NiO/8YSZ powder before, during and after 90 ppm H_2S addition to the gas.

As shown in Figure 5.46, the weight of the sample before the H_2S addition corresponds not to 100 % (m_0) but to 86.371 % (m_1) due to the complete reduction of NiO to nickel at 950 °C with hydrogen. With the addition of 90 ppm H_2S , the sample weight increased ($\Delta m_{2-1} = 0.008$ %) due to sulfur chemisorption on the nickel. As H_2S was removed from the gas after 9 hours, the weight of the sample reduced to 86.372 % with a difference of 0.00111 % compared with the weight before H_2S exposure. The weight, weight changes and calculated molar values throughout the experiment with NiO/8YSZ powder are given in Table 5.12

It is known that the average sulfur saturation concentration for polycrystalline nickel surface is 44 ng S/cm² (Table 3.3). In order to compare the results with this value, the nickel surface area in the TGA sample should be known. To measure this, same experimental procedures were applied to pure NiO powder without H_2S exposure in TGA Analyzer followed with BET surface area analysis. The surface value of nickel was found as 0.3865 ± 0.0441 m²/g.

The calculated nickel surface area in the anode powder during H_2S experiment is 0.215 m². If it is accepted that the sulfur saturation concentration is 44 ng S/cm², the amount of sulfur required for total coverage of this area is 0.0957 mg. If it is assumed that the increased weight (Δm_{3-2}) of the anode powder is the result of the chemisorption of sulfur on nickel, sulfur amount is found as 0.0903 mg. In this case, the calculated and observed values have surprisingly similar values.

Table 5.12 The weight, weight changes and calculated molar values throughout the experiment with NiO/8YSZ powder.

Species	Before reduction (m_0)			After reduction ($m_1 = 0.8637125 m_0$)		
	Weight [mg]	Mol	%	Weight [mg]	Mol	%
Ni (NiO)	710	$9.505 \cdot 10^{-3}$	63	556.412	$9.479 \cdot 10^{-3}$	57.161
8YSZ	417	-	37	417	-	42.839
S	0	0	0	0	0	0
Total	1127.01	-	100	973.412	-	100
	After H ₂ S addition ($m_2 = 0.8637926 m_0$)			After H ₂ S removal ($m_3 = 0.8637236 m_0$)		
	mg	mol	%	mg	mol	%
Ni (NiO)	556.412	$9.479 \cdot 10^{-3}$	57.155	556.413	$9.479 \cdot 10^{-3}$	57.160
8YSZ	417	-	42.835	417	-	42.838
S	0.0903	$2.815 \cdot 10^{-6}$	0.0092	0.0125	$3.901 \cdot 10^{-7}$	0.0013
Total	973.502	-	100	973.425	-	100

Similar to the results of TOF-SIMS analysis, even though the regeneration process (removal of H₂S from gas) follows the contamination process, there is still a difference between the initial (m_1) and regenerated (m_3) mass of the sample ($\Delta m_{3-1} = 0.0011$ % which corresponds to 0.013 mg S). This result shows that sulfur doesn't desorb totally when H₂S is removed from the gas under experimental parameters.

Using TGA experiments, it has been shown that there is no interaction between 8YSZ and H₂S at 850°C under the given experimental conditions. The adsorption of sulfur on nickel as well the incomplete desorption from nickel is demonstrated. The results are consistent with the values observed by Oudar (Table 3.3). Thermogravimetric analysis was found to be a promising method and can help to understand the effect of temperature and/or various gas compositions on various anode materials with respect to sulfur poisoning.

6 Summary and Outlook

The effect of sulfur on single cell SOFCs with Ni/8YSZ and Ni/10CGO anodes with 4 x 4 cm active areas was studied. Thermodynamic calculations, electrochemical measurements and microstructural analysis were performed in order to clarify the underlying mechanisms of sulfur poisoning and regeneration.

H₂S was chosen as a sulfur containing contaminant due to its stability under SOFC operating conditions. Investigations were focussed on H₂S concentrations in the range 1 ppm H₂S to 50 ppm H₂S, at the operating temperature of 850 °C. Higher concentrations were not considered, owing to the probable application of desulfurization units in SOFC systems, which can decrease sulfur concentrations to $c_{\text{H}_2\text{S}} < 1$ ppm.

Thermodynamic calculations showed that the formation of sulfides in the anode under SOFC operating conditions is first possible at $c_{\text{H}_2\text{S}} > 2500$ ppm (at 850 °C with 50 vol % H₂) and therefore can not explain the SOFC power degradation. Instead, dissociative adsorption of H₂S thereby the chemisorption of sulfur on nickel is the mechanism behind SOFC power degradation.

It is found that there are differences between the reaction of Ni/YSZ and Ni/10CGO anodes to sulfur contamination. Ni/8YSZ containing anodes showed much higher sensitivity to sulfur than Ni/10CGO anodes.

With Ni/8YSZ anodes, the addition of H₂S to the fuel caused a rapid loss of power in the first few minutes (Phase I) followed by slower rates of degradation in the following hours (Phase II). Even adding 1 ppm of H₂S to the fuel caused an 11 % decrease in the power within 30 minutes.

Using electrochemical impedance spectroscopy, it was shown that adding H₂S to the fuel causes a strong increase in the impedances at low frequencies, owing to hindered hydrogen adsorption on the nickel surface coupled with charge transfer reactions with H₂S.

In the equation below, hindered H₂ adsorption on the nickel surface due to surface coverage with sulfur is shown:



For this type of anode the electrochemical oxidation of hydrogen takes place on the nickel surface (whereas the YSZ is electrochemically almost inert). When sulfur blocks the electrochemical and catalytically active nickel surface, the electrochemical reactions on the triple phase boundaries will be hindered.

The rapid voltage drop (Phase I) takes place due to the immediate chemisorption of sulfur on nickel sites in the anode progressing from the fuel inlet to the fuel outlet. The slower degradation phase (Phase II) is caused by the subsequent adsorption of sulfur to nickel in deeper positions in the anode and restructuring of the nickel surface.

Increasing the H₂S concentration up to 10 ppm caused the degradation rate to increase noticeably. Between c_{H₂S}: 10 – 50 ppm, the degradation rates were almost the same, but with a slight increase. It was also shown that the higher the H₂S concentration, the faster the degradation will be. This observation was in good agreement with the calculated thermodynamical nickel surface coverage values (Figure 5.17).

The stacks were regenerated by removing the H₂S from the fuel. The stack voltages increased in the first 24 hours to ~ 97 % of their initial value however the stacks needed approximately one hundred hours to achieve a stable voltage. Even so, regeneration was not complete and only 98.9 % of the initial power could be reached.

H₂S contamination cycle behaviour was also studied by adding 2 ppm H₂S to the fuel for fifteen hours followed by one hundred hours of regeneration, then repeating the cycle five times. It was observed that with each contamination cycle, the stack power degraded. At the end of the fifth contamination, the stack had lost almost 23 % of its' initial power. The regeneration phase could only increase the stack power to a maximum of 91 % of its' initial power. These results show that the more often the anode is subjected to H₂S poisoning, the greater the loss in the electrical power.

The effect of current density was investigated by contaminating stacks with 2 ppm of H₂S at the open circuit voltage. The results were compared with the stacks operated with current. It was found that the oxygen ion flux from the electrolyte has a positive effect on the resistivity of the anode to sulfur.

Nevertheless, another experiment examining the effect of increasing the concentration of water up to ~ 30 % showed that water concentration has no effect on the resistivity of the stack. The higher oxygen ion flux causes a better sulfur resistivity at the fuel inlet side. To explain this behaviour, the following mechanisms are proposed to occur at the triple phase boundary:



It should be reminded that the formed SO_{2(g)} will be converted to H₂S under anode fuel conditions and therefore be a transient component with pSO₂/pH₂S= 7.10⁻⁹.



Throughout the experiments the anodes were analyzed with FESEM, EDX and Raman spectroscopy. No sulfur traces or microstructural changes were observed. To date, mechanisms able to describe the irreversible degradation of Ni/8YSZ could not be found in the literature. Two new methods, TOF-SIMS and thermogravimetric analysis, were applied in order to prove that sulfur remains in the anode even after regeneration. The TOF-SIMS method was able to detect traces of sulfur in the anode samples during post-mortem analysis of the anode. Thermogravimetric analysis of the anode powders showed that the sulfur had incompletely desorbed from the nickel. Therefore, it can be concluded that the reason for irreversible degradation of Ni/8YSZ anodes is the incomplete desorption of sulfur from the nickel.

Ni/10CGO anodes showed enhanced resistance to sulfur poisoning when compared with Ni/8YSZ anodes.

Adding 2 ppm of H_2S to the fuel caused a rapid but smaller electrical power drop of 1.3 % compared to the 13.6 % power drop with Ni/8YSZ anodes. The stack voltage was constant afterwards. The second phase of poisoning was not observed for Ni/10CGO anodes. Complete recovery could be achieved with the removal of H_2S from the fuel. Increases in the impedance at high or low frequencies were not observed for Ni/10CGO anodes.

Furthermore, H_2S contamination cycles did not affect the sulfur tolerance of the stacks. In contrast to the stacks with Ni/8YSZ anodes, after the 5th contamination cycle the stack power had 98.7 % and 99.6 % of the initial value during contamination and after regeneration, respectively. Impedance measurements showed that the degradation was due to an increase in the ohmic resistance of the stack on which the addition of H_2S has no effect.

The better performance of Ni/10CGO towards sulfur poisoning can be explained by the mixed ionic electronic conductivity of the anode, as well as the catalytic activity of CGO towards H_2 and H_2O adsorption. Almost whole hydrogen oxidation in investigated anodes took place on CGO surface with sulfur presence. Detailed mechanisms of the electrochemical reactions on CGO surface despite H_2S poisoning are described in Chapter 5.3.3 – Figure 5.42.

Unlike in Ni/8YSZ anodes, when the nickel surface of a Ni/10CGO anode is blocked, the anode can continue to its electrochemical reactions due to the presence of CGO.



The electrochemical impedance analysis also supports the theory that the charge transfer reactions in the anode are not hindered.

Neither water concentration nor current density was found to have had an effect on the poisoning of Ni/10CGO anodes. Once contaminated, an increase in the H₂S concentration didn't significantly affect the performance of Ni/10CGO cells. The addition of 30 ppm of H₂S to pre-mixed reformat gas decreased the performance to approximately 97 %.

CGO works as an oxygen storage material which provides the anode protection against sulfur deposition:



In the Ni/10CGO anode, nickel functions almost exclusively as a current collector. Due to the properties of CGO, Ni/CGO anodes are superior to Ni/YSZ anodes in terms of sulfur poisoning.

With this work, a deep insight into the mechanism of sulfur interaction with anode materials under various operating conditions has been gained. With respect to sulfur poisoning, the advantage of using mixed ionic electronic conductive materials in the anode has been shown. New methods to screen the sulfur content of the anode were demonstrated.

According to the results, Ni/CGO anodes may be especially suited to applications using liquid fuels, such as auxiliary power units, owing to the complexity of desulfurizing liquid fuels.

Further investigations should be made to define the long term effects of sulfur contamination on SOFC performance. The interactions between sulfur, anode internal reforming activity and carbon formation from hydrocarbons in the fuel are important topics which are appropriate for systematic study.

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8 APPENDIX

	France	United Kingdom	Germany	Belgium	The Netherlands	Italy	Spain	Denmark
Regulations	gas distributed: odour level 2 for gas < 1 % in air	gas transported: odour level 2 for gas < 1 % in air	gas distributed: odour level 2 for gas < 1 % in air	gas distributed: odour level 2 for gas < 1 % in air	gas distributed: odour level 2 for gas < 1 % in air	gas distributed: odour level 2 for gas < 1 % in air	gas distributed: odour level 2 for gas < 1 % in air	gas distributed: odour level 2 for gas < 1 % in air
Location of odour addition	at distribution points for gas transportation	centralised at distribution points for gas transportation	localised at points of distribution for public supply	localised at points of distribution for public supply	-	localised at points of distribution for public supply	gas terminals and complimented at points of distribution for	localised at points of distribution for public supply
Products	THT	Odorant BE	THT	THT	THT	THT	THT	THT
Nominal amount of odour (mg/m³ gas)	25 (equivalent THT)	16 (odorant BE)	15	20	18	> 32	15 + 10	10 - 15
Permitted limits (mg/m³ gas)	15 - 40	9 - 60	8 - 30	17 - 34	10 - 36	> 32 (level not exceeding odour level 3)	8 - 30	7.5 - ?

Figure A.1 Odour addition to natural gas across Europe [Rol04].

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Solid oxide fuel cells (SOFC) can use wide varieties of fuels such as hydrogen, carbon monoxide, hydrocarbons, alcohols as well as synthesis gases from natural gas, biogas and petroleum. Using such a wide range of fuels introduces the risk of unwanted impurities, which can affect the function of the SOFC. One of the known impurities is sulfur which is a well known catalyst poison. This work deals with the effect of hydrogen sulfide (H_2S) containing fuel gas on SOFC stack performance with nickel containing anode under various conditions as well as regeneration processes and their underlying mechanisms.

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