Methane steam reforming kinetics over Ni-YSZ anodematerials for Solid Oxide FuelCells

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Ph.D. Thesis
January 2011

DTU Chemical Engineering
Department of Chemical and Biochemical Engineering
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Technical University of Denmark
Topsoe Fuel Cell A/S
Riso-DTU
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Preface

This work is financed by the Technical University of Denmark, Topsoe Fuel Cell A/S, and the graduate school in Chemical Engineering: MP2T. All parties involved are greatly acknowledged for financial support, and for providing facilities.

Topsoe Fuel Cell A/S and Haldor Topsøe A/S, are also acknowledged for providing both catalyst material and stacks. A special thanks to Mikko Pihlatie from Risø-DTU for providing catalyst samples from his own thesis work.

I am grateful to my supervisors Peter Vang Hendriksen (Risø-DTU) Jens Ulrik Nielsen (Topsoe Fuel Cell A/S), Kim Dam-Johansen (DTU) and especially Jan-Dierk Grunwaldt (DTU) for their guidance and discussions.

I would like to thank the CHEC group at KT-DTU, the SOFC group at Risø-DTU, and employees at Topsoe Fuel Cell, for invaluable assistance in both practical and theoretical issues. In particular Anders Tiedje (DTU) for his technical assistance and Mads Finn Madsen (Topsoe Fuel Cell A/S) for his input and interest in the project. Jakob Birkedal Wagner (Center for Electron Nanoscopy DTU) is thanked for for his aid with electron microscopy measurements. Also a thank you to Jon Geest Jakobsen (DTU) for proofreading.

Finally, I would like to thank friends, family and colleagues for support, encouragement and understanding.
Dansk Resumé

Faststof oxid brændselsceller (SOFC) er en teknologi med stort potentiale. Dens høje effektivitet gør den til et relevant alternativ til eksisterende teknologier til at udnytte fossile brændstoffer, og dens fleksibilitet med hensyn til brændstof gør den uvurderlig i overgangen fra et energisystem baseret på fossile brændsler til et baseret på bæredygtige energikilder.

Den samlede effektivitet af et SOFC system med naturgas som brændsel kan blive væsentligt forbedret ved at lade en del af reformeringen finde sted inde i SOFC stakken. For at undgå kraftige temperaturgradienter som følge af den stærkt endotherme dampreformerings reaktion, er det nødvendigt, at graden af intern dampreforming bliver nøje kontrolleret. Formålet med denne afhandling er at gøre sådan en kontrol mulig ved at undersøge dampreformerskinetikken over SOFC anode materialet, Ni-YSZ.

Ni-YSZ’s katalytiske damp reformerings aktivitet blev testet både i et ”packed bed” forsøg for at bestemme kinetikken uden massetransport begrænsninger, og i en stak struktur for at bestemme den observerede kinetik under realistiske SOFC betingelser. De kinetiske udtryk fundet for henholdsvis ”packed bed” målingerne og stak målinger kan ses i Ligning 1 og 2.

\[
\frac{r}{P_{CH_4}} = \frac{110 \text{mole/gPa} \exp\left(\frac{-198\text{kJ/mole}}{RT}\right) P_{CO}}{1 + 1.7 \times 10^{-6} P_{a}^{-1} \exp\left(\frac{-26\text{kJ/mole}}{RT}\right) P_{CO}^2} \quad (1)
\]

\[
r = 2 \times 10^{4} \text{mole/sm}^2 P_{a} \exp\left(-166.1 \frac{1}{T} \frac{P_{CH_4}}{P_{CO}} \right) \quad (2)
\]

Desuden blev der lavet en simpel model, som præcist kan forudsige dampreformerings reaktionshastigheden i en stak, ud fra udtrykket fundet fra ”packed bed” målingerne.

Under forsøgene blev der observeret en langsom dynamisk effekt i katalysatorens opførsel, som ikke tidligere har været rapporteret. Efter opstart var der først en høj aktivitet, som langsamt blev reduceret med en faktor 5-10 over en periode på flere dage eller flere uger, afhængig af temperaturen. Det blev også fundet, at en længere tids kørsel med en H2O/H2 uden CH4 resulterede i en re-aktivering af katalysatorens aktivitet op til det oprindelige høje niveau. Det forsøges at redegøre for denne opførsel ved hjælp af karakterisering med SEM, TEM, XRD og EXAFS.
Abstract

Solid Oxide Fuel Cells (SOFC) is a technology with great potential. Its high efficiency makes it a relevant alternative to existing technologies for utilizing fossil fuels and its fuel versatility makes it invaluable in the transition from a fossil fuel based energy system to one based on renewable energy.

The overall efficiency of a fuel cell system operating on natural gas can be significantly improved by having part of the steam reforming take place inside the SOFC stack. In order to avoid large temperature gradients as a result of the highly endothermal steam reforming reaction, the amount of internal reforming has to be carefully controlled. The objective of this thesis is to make such a careful control possible by examining the rate of internal steam reforming in SOFCs.

The catalytic steam reforming activity of Ni-YSZ anode material was tested both in a packed bed reactor to determine intrinsic kinetics, and in a stack configuration to determine the rate observed under realistic SOFC conditions. The kinetic expressions obtained from respectively the packed bed measurements and the stack measurements are shown in Equations 3 and 4.

\[ r = \frac{110 \, \text{mole/m}^2 \text{Pa}}{\exp \left( -\frac{188 \text{kJ/mole}}{RT} \right) P_{CH4} \left( 1 - \frac{Q_{sr}}{K_{sr}} \right)^2 \left( 1 + 1.7 \times 10^{-6} P_{CO} \right)^{0.7}} \]  

\[ r = 2 \times 10^4 \, \text{mole/m}^2 \text{Pa} \exp \left( -\frac{166.1 \, \text{kJ/mole}}{RT} \right) P_{CH4}^{0.7} \] 

Furthermore, a simple model was derived, which can accurately predict the steam reforming rate in a stack from the rate expression obtained from the packed bed experiments.

During the experiments a previously unreported long term dynamic behavior of the catalyst was observed. After startup, the initial high reactivity was slowly reduced by a factor 5-10 over a period of several days or several weeks depending on operating temperature. It was also found that prolonged exposure to a H2O/H2 mixture without CH4 resulted in a reactivation of the catalytic activity up to the initial high level. It was attempted to account for this behavior through characterization with SEM, TEM, XRD and EXAFS.
Chapter 1

Introduction

During the last decades there has been an increasing awareness of global warming indicated by long term global temperature measurements [2]. Even though there is widespread consensus in the scientific world that global warming is man made [37], it is still uncertain if the world community can or will make the necessary changes to obtain sufficient decreases in the emissions of greenhouse gases. There is, however, also a much more tangible problem regarding fossil fuels, namely the fact that fossil fuel reserves are limited, and we are rapidly approaching that limit. Worldwide fossil fuel reserves have recently been estimated to last for another 35 years for oil, 37 years for gas, and 107 years for coal [67]. Furthermore, worldwide crude oil production is estimated to peak in 2014 [48], with following increase in prices, long before reserves run out. For these reasons it is vital to gradually build up the usage of renewable energy sources, such as solar, wind, water, and geothermal energy. Nuclear energy is also a viable alternative to fossil fuels, but is also dependent on a limited fuel source, so it will only be a postponement of the supply problem. Energy from biomass is one of the intensely studied research topics at the moment, but in a system without fossil fuels, biomass will probably be needed as a carbon source for products presently made from oil, such as plastics, paint and medicine. A common problem for most of these energy sources is that they have very limited flexibility in the production and because of this a renewable energy system will be dependent on a storage and conversion as well as production. Many different energy carriers have been suggested for this purpose, e.g. electricity, hydrogen, dimethylether, alcohols, ammonia, and synthetic diesel. In such a system, fuel cells would be a suitable technology for direct electrochemical energy conversion with high efficiencies for a wide variety of fuels.

The fuel cell principle was invented by William Robert Grove in 1838 and because it is not limited by the Carnot cycle, like heat engines, it has always been viewed as a technology with great potential because of the high theoretical maximum efficiency [22]. It has, however, proven difficult to utilize the great potential of fuel cell technology and progress in the field has for long periods been slow. In the beginning of the 1960’s the use of alkaline fuel cells in the Apollo project re-ignited the interest in fuel cells and since then it has been a subject of many research
campaigns. There are many types of fuel cells and they are normally divided into high temperature and low temperature cells. Among the low temperature fuel cells, Polymer Electrolyte Membrane (PEM) cells have received most attention recently, while Solid Oxide Fuel Cells (SOFC) are the most promising of the high temperature fuel cells. These two types of fuel cells are suited for different types of applications. PEM is best suited for small mobile applications, such as cell phones, mp3 players and laptops. SOFC are best suited for stationary applications such as central or distributed power power production where it is possible to utilize the high gas outlet temperature to recover waste heat either for district heating or further power production.

1.1 Motivation for this Thesis

One of the major challenges in the transition from fossil fuel to fuels produced from renewable energy is the question of what comes first, fuel supply infrastructure, or the applications that use the fuel. This transition can be eased by promoting SOFC systems that can operate on both natural gas, which is readily available now, and on fuels produced from renewable energy sources, if the possibility should arise later.

There are many different materials being used for SOFCs, but this thesis work will only consider cells with Lanthanum Strontium Manganese (LSM) cathode, YSZ electrolyte and Ni-YSZ anode. Since Ni is a highly active steam reforming catalysts, it is possible to incorporate the steam reforming inside the SOFC stack. The possible advantages of this is that the waste heat from the electrochemical reactions can be used to drive the highly endothermic steam reforming. This will also reduce the need for cooling of the cell, which is normally achieved through a high cathode gas flow. Furthermore, internal steam reforming can, if controlled properly, result in lower temperature, and concentration gradients by gradually removing heat and producing hydrogen through the cell.

The overall aim of this work is to increase the understanding of internal steam reforming in SOFC’s to a point where the theoretical knowledge can be used to optimize design and operation of SOFC systems.

A literature review of internal steam reforming in SOFCs has been published as a part of this thesis [43]. One of the important facts is that with present SOFC technology and operating temperatures, the steam reforming reaction is much faster than the electrochemical reactions. The result of this is that internal steam reforming causes rapid cooling at the anode inlet, resulting in large temperature gradients, reduced performance and even, in some cases, physical destruction of the cell due to mechanical stress caused by the large temperature gradient.

Another major conclusion was that a large amount of modeling has been published on the subject, but the model works are based on a very small number of experimental studies of the catalytic activity of Ni-YSZ with respect to steam reforming. The few experimental studies are in
great disagreement, with rates varying by an order of magnitude, different reaction mechanisms and values for the activation energy in the range 58–228 kJ/mol. Because of this, it was decided that the focus of this thesis should be to obtain a reliable rate expression for catalytic steam reforming over Ni-YSZ anode material. This was done both in a packed bed, to obtain the intrinsic kinetics and in a stack configuration to obtain the rate under realistic SOFC conditions. During the experimental work a number of previously unreported long-term dynamic effects were discovered, which can explain many of the disagreements in the rate expressions reported in literature, these are described in detail in Section 3.1.

1.2 Solid Oxide Fuel Cell Technology

The basic operating principle of a fuel cell is similar to that of a battery, i.e. it works by producing electricity directly from a fuel via electrochemical reactions. The big difference between batteries and fuel cells is that in a battery there is a limited amount of fuel and in a fuel cell, the fuel is supplied continuously as illustrated in Figure 1.1(a). Thus making it possible to run a fuel cell uninterrupted as long as it does not break down.

![Operating principle of an SOFC](image1.png)

(a) Operating principle of an SOFC [4].

![Fuel cell stack](image2.png)

(b) Fuel cell stack [1].

*Figure 1.1: Illustrations of the basic operating principle of an SOFC as well as the stacking of fuel cells.*

The dominant electrochemical reactions taking place in an SOFC is the oxidation of hydrogen via the two half-cell reactions shown in Reactions 1.1 and 1.2.

Anode \[ H_2 + O^{2-} \rightarrow H_2O + 2e^- \] (1.1)

Cathode \[ \frac{1}{2}O_2 + 2e^- \rightarrow O^{2-} \] (1.2)
When carbon species are present at the anode, Reaction 1.3 will also be taking place at the anode.

\[
\text{Anode} \quad CO + O^{2-} \rightarrow CO_2 + 2e^{-} \quad (1.3)
\]

The maximum voltage that these reactions can provide is 1.1 V, and this will decrease significantly with increasing current. A voltage of this size is not usable for any large scale application, so in order to increase the voltage, single cells are connected in series by stacking them as illustrated in Figure 1.1(b).

### 1.3 Steam Reforming

The conversion of hydrocarbons to CO, CO\(_2\) and H\(_2\) is known as steam reforming. The process is widely used in industry with the major uses being production of ammonia and methanol. It is also by far the largest source of hydrogen for various purposes [62]. In a SOFC system fueled with hydrocarbons, it is necessary to pre-reform the fuel to an extent where methane is the only remaining hydrocarbon, since higher hydrocarbons would cause carbon deposition in the SOFC stack. Because of this, only steam reforming of methane will be considered in this thesis.

The overall reaction for methane steam reforming is shown in Reaction 1.4 and this reaction is always accompanied by the water gas shift reaction as shown in Reaction 1.5. The steam reforming reaction is highly endothermic with a reaction enthalpy of 206 kJ/mol at 25 \(^\circ\)C and the water gas shift reaction is slightly exothermic with a reaction enthalpy of -41 kJ/mol at 25 \(^\circ\)C.

\[
\text{Steam reforming:} \quad CH_4 + H_2O \rightleftharpoons 3H_2 + CO \quad (1.4)
\]
\[
\text{Water gas shift:} \quad CO + H_2O \rightleftharpoons CO_2 + H_2 \quad (1.5)
\]

Many different metals are active steam reforming catalysts, but the most commonly used in industrial catalysts is nickel, because it is relatively cheap and has a high activity. Even though nickel is also the catalytic material in SOFC anodes, there are still large differences between traditional steam reforming catalysts and Ni-YSZ for SOFCs. The traditional catalyst typically uses alumina magnesium spinel as support material, and has a Ni content around 5\% and Ni Particle sizes around 5-10 nm. SOFC anodes use YSZ as support material, have a Ni content around 40 vol\% and the typical Ni particle size is \(\approx 1\mu m\). These differences mean that the research performed on traditional steam reforming catalysts, cannot necessarily by transferred directly to Ni-YSZ. Furthermore, there are still widespread disagreements on the kinetics of steam reforming on traditional catalysts, in spite of the extensive research in the field. A review paper on this subject has been published as a part of this thesis work, see Article I [43].
Chapter 2

Experimental Equipment and Methods

The focus of the experimental work has been to determine the reaction kinetics of the steam reforming reaction over Ni-YSZ anode material. In order to determine both the intrinsic kinetics and the kinetics under realistic conditions, both the intrinsic kinetics over crushed catalyst material in a packed bed reactor and the kinetics in an actual SOFC cell were investigated. The experimental equipment used to perform the measurements is described in this chapter, along with the standard procedures used during experiments.

2.1 Packed Bed Reactor Setups

Two different, but almost identical, fixed bed setups were used for determination of reaction kinetics, hereafter referred to as 137-4A and 137-5B. The quartz reactor used in these setups is illustrated in Figure 2.1, and a complete flowsheet of the setup can be seen in Appendix A.2. The quartz reactor has a diameter of 2.8 cm, the catalyst bed has a diameter of 1.8 cm and the typical bed height is around 2 cm. The catalyst bed is placed on a porous quartz frit where the holes have a diameter of 100-160 μm. In order to avoid particles getting stuck in the frit, a layer of around 0.5 cm quartz wool was placed between the frit and the bed. The distance from the thermocouple to the bottom of the bed is 2-2.5 cm. The bed has approximately 4g of particle material, primarily consisting of inert alumina, the amount of catalyst used is around 0.1g at high temperatures (700-800°C) and 0.4g at low temperatures (600-700°C). The catalyst materials were supplied by Topsoe Fuel Cell A/S and Risø DTU.

To ensure that the reacting gas has the desired temperature, the primary inlet gas enters at the bottom and flows through $1\frac{1}{2}$ times the oven height, in order to preheat it before it comes in contact with the catalyst. The secondary inlet is mixed with the primary inlet just above the catalyst bed, which means that the effect of CO and CO$_2$ on the reaction rate can be investigated.
Figure 2.1: Quartz reactor used for kinetic measurements on crushed catalysts [35].

at conditions where the water gas shift reaction is not at equilibrium. The inlets contains the following gases.

primary inlet: CH$_4$, H$_2$O, N$_2$ and CO$_2$

secondary inlet: H$_2$ and CO

CO and CO$_2$ are only added in the experiments that investigate the influence of these species. A small amount of hydrogen is added through the secondary inlet in all experiments, both to maintain a reducing environment and to avoid having a dead volume in the secondary inlet tube. The water is delivered by leading nitrogen through a heated bubble flask which is kept at 80°C, and variations in water partial pressure are achieved by varying the amount of nitrogen going through the bubble flask. In order to avoid unwanted condensation, the gas line was traced and kept above 100°C. The bubble flask must be manually refilled daily in order to keep the water flow steady. An extra heated water tank is added to the system in order to avoid a drop in temperature when refilling the bubble flask.
2.2 Cell and Stack Setup

The setup used for cell and stack testing is an "Evaluator C50" from FuelCon [3], which has undergone some modifications to fit the purpose of these experiments. The P&ID diagram for the setup can be seen in Appendix A.2. The setup consists of an oven with room for a 12x12cm SOFC stack. The maximum temperature is 1100°C or 1000°C for prolonged operation. Dry gas flows are controlled with mass flow controllers, and water is added by bubbling nitrogen through a bubble flask at 90°C. The gas line from the evaporator to the stack is traced to above 100°C in order to avoid condensation in the tubes. Most of the setup is controlled by a Programmable logic controller (PLC), but some modifications to the setup are controlled manually, primarily the mechanical pressure system and the nitrogen flow to the bubble flask. In order to protect the stack from carbon deposition and from being reoxidized, the system has been set up so that if hydrogen or steam flow is cut off or in case of a power outage, the gas flow to the anode is changed to 5% H₂ in N₂ automatically. The major modification to the setup is the mechanical pressure system for pressing the stack elements together to ensure a good connection between the cells and to keep the glass seals gas tight. An illustration of the mechanical pressure system is shown in figure 2.2. The system is centered around a solid steel plate called the center plate, which, on the test stand, is located right below the oven. The cylinder is connected to the bottom of the center plate, and when the cylinder is activated it will put pressure on the plate while pulling down on the pull rods. The pull rods are connected to the topmost pressure plate, which is pulled down towards the lower pressure plate, which is connected to the center plate. The major advantage of this pressurization system is that it will not stress the structure of the test stand since all forces in the system are applied to the center plate. The pressure plates are located inside the oven, with a gas distribution plate placed on the bottom pressure plate, and the gas inlet and outlet tubes are placed in the bottom and going out through the center plate. The fuel cell stack or stack element is placed between the gas distribution plate and the top pressure plate.

2.3 Auxiliary Equipment

Gas flows on all three setups were controlled with Mass Flow Controllers (MFC) of the type "LOW ΔP FLOW" and "EL-FLOW" from Bronkhorst HI-TEC. The MFCs had analogue control on the fixed bed setups and digital control through the PLC on the stack setup. All MFC’s flows were controlled with a Gilibrator 2 soap bubble flow meter from Gilian with a specified measuring range of 20-6000 ml/min. All temperature measurements were done with K-type thermo couples for the temperature range -40-850°C. Two IR-analyzers of the type NGA 2000 MLT Analyzer from Fisher-Rosemount were used interchangeably. The analyzers only measured CO and CO2 contents, but as seen in section 2.7
all contents relevant to steam reforming can be calculated from the measurement of these two components when inlet flows of all gases are known. The analyzers have a measurement error of 1% of the given measuring limit. Both fixed bed setups included a HygroFlex humidity sensor from ROTRONIC, but tests indicated that these did not give trustworthy measurements, so they were primarily used to indicate whether or not the water supply was stable. Instead a calibration curve was made for each evaporator, these can be seen in Appendix A.1

2.4 Reduction Procedure

The same reduction procedure was used as pre-treatment for both the packed bed experiments and the cell/stack experiments: First, the sample was heated to 860°C in N₂, the cell/stack heating was limited to 1 °C/min, while there was no restriction on the heating ramp in the packed bed setup. At 860°C the gas was changed to 20% H₂ in N₂ for at least 4 hours, after which the sample was cooled to the test temperature and measurements were started.
2.5 Test Conditions

In order to achieve a complete understanding of the steam reforming kinetics over Ni-YSZ anode material, two different types of experiments were conducted.

Packed bed experiments were performed with crushed anode material diluted in a bed of inert material. The purpose of these experiments was to determine the intrinsic kinetics of the catalyzed steam reforming under conditions where mass transport limitations are negligible.

Measurements of the kinetics over an SOFC cell were performed in order to investigate the observed kinetics for the catalyst in an SOFC structure and with realistic mass transport limitations. Because of the slow approach to steady state in the tests, as described in Section 3.1, there was not enough time to wait for steady state for all measurements. Instead, the majority of the rate determination measurements were made by waiting for steady state at the standard gas composition, and then rapidly going through all gas composition changes. This was done two times for each gas species in each measurement series, first starting with the lowest concentration and then increasing it. Second starting with the highest concentration and decreasing it.

2.5.1 Packed Bed Experiments

The packed bed experiments were designed to measure the intrinsic kinetics of the catalyst. A rule of thumb for such experiments is that the diameter of the bed should be at least 10 times the particle diameter \( d_p \) and the length of the bed should be at least 50 times the particle diameter. In these experiments particle sizes were \( d_p = 63-300 \, \mu m \), most often particles in the larger part of the range is used in order to minimize pressure drop over the bed. The bed diameter was \( d_b = 18 \, mm \) and the bed height was \( h_b = 17-21 \, mm \), giving:

\[
\frac{d_b}{d_p} > 60 \quad \& \quad \frac{h_b}{d_p} > 55
\]  

In principle, the bed height should also be 10 times the diameter, but that would require more sample, which in results the reactor pressure becoming higher than what is allowed by the quartz connections. So this compromise was used instead. The ranges of the total flow, temperature and pressure in the experiments were: \( F_{tot} = 1.4-2.2 \, Nl/min, T = 600-800^\circ C, P = 1.1-1.25 \, atm \).

In order to keep the degree of conversion low (below 15\%) the catalyst is diluted 10-40 times, depending on operating temperature.

The gases used in the experiments, on both setups, and their purities are shown in Table 2.1. The standard flow in the experiments was 2 Nl/min and Table 2.2 shows the standard gas composition as well as the range in which each gas is varied.

In order to ensure that only the activity of the catalyst is measured, a blind test was made where the reactor was loaded with quartz wool and the alumina powder used to dilute the catalyst material. The inert material was treated according to the standard procedure, including reduction procedure, and no activity was observed.
Table 2.1: Gases used during experiments.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>N3.5</td>
</tr>
<tr>
<td>CH₄</td>
<td>N5.5</td>
</tr>
<tr>
<td>H₂</td>
<td>N5</td>
</tr>
<tr>
<td>N₂</td>
<td>N5</td>
</tr>
<tr>
<td>CO</td>
<td>N3.7</td>
</tr>
<tr>
<td>CO₂</td>
<td>N4</td>
</tr>
<tr>
<td>4.50% CO, 19.0% CO₂, 9.51% O₂, balance N₂</td>
<td>±2% rel.</td>
</tr>
<tr>
<td>3940 ppm CO, 3750 ppm CO₂, 9.48% O₂, balance N₂</td>
<td>±2% rel.</td>
</tr>
<tr>
<td>10% H₂, balance N₂</td>
<td>unknown</td>
</tr>
<tr>
<td>5% H₂, balance N₂</td>
<td>±2% rel.</td>
</tr>
</tbody>
</table>

Table 2.2: Overview of the gas composition at standard conditions and the range each gas is varied in.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Standard</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kPa</td>
<td>kPa</td>
</tr>
<tr>
<td>CH₄</td>
<td>16</td>
<td>8-20</td>
</tr>
<tr>
<td>H₂O</td>
<td>33</td>
<td>24-39</td>
</tr>
<tr>
<td>H₂</td>
<td>8</td>
<td>8-24</td>
</tr>
<tr>
<td>CO</td>
<td>0</td>
<td>0-8</td>
</tr>
<tr>
<td>CO₂</td>
<td>0</td>
<td>0-8</td>
</tr>
</tbody>
</table>

Furthermore, a test was made on a classical industrial steam reforming catalyst, with alumina support material. This was done to test if the observed dynamic effects was caused by the setup or the catalyst material. The tests with the industrial steam reforming catalyst showed very little dynamic behavior, and stability was achieved within 10 minutes after any change in test conditions.

2.5.2 Stack/Cell Measurements

The first attempt of measuring the steam reforming kinetics was made on a 5-cell SOFC 12cmx12cm standard stack from Topsøe Fuel Cell A/S. It was found that the methane was completely converted, even at the highest flows that the setup could deliver.

Therefore, a special stack was made, also by Topsøe Fuel Cell A/S, with only a single crossflow cell. Half of the cell was cut away so that half of the cathode flow channels were removed, and the length of the anode flow channels were halfed, as illustrated in Figure 2.3. A cell, where three quarters of the cell was removed, was also used, in order to reduce the degree of conversion even
further. This means that the anode and cathode gasses are mixed at the outlet of the anode channels. Furthermore, four thermocouples were placed in the gas distribution plates close to the flow channels, in order to monitor the temperature gradient. One at each corner of the fuel inlet side and one at the corner with fuel outlet and air inlet, and finally one at the fuel outlet and halfway through the air channel. The cathode side was only fed with nitrogen, both in order to avoid mixing of air with the anode gas, and to avoid electrochemical reactions in the cell. It is desired to avoid the electrochemical reactions because it is easier to study the steam reforming reaction when no other reactions are taking place.

![Figure 2.3](image-url)  
*Figure 2.3: Illustration of the orientation of the halfcell with respect to flow directions.*

The majority of the rate measurements on this cell were performed at flows that are much higher than what is used during optimal operation of an SOFC, $F_{\text{tot}} \approx 2 \, \text{Nm} / \text{min}$. This was done in order to decrease the degree of conversion of methane. The pressure and temperature were, $T = 600-700^\circ\text{C}$, $P = 1.1-1.25\, \text{atm}$.

Table 2.3 shows the standard gas composition as well as the range each gas species is varied in.

*Table 2.3: Overview of the gas composition at standard conditions and the range each gas is varied in.*

<table>
<thead>
<tr>
<th>Gas</th>
<th>Standard range</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>12 12-30</td>
</tr>
<tr>
<td>H₂O</td>
<td>56 45-70</td>
</tr>
<tr>
<td>H₂</td>
<td>7 7-18</td>
</tr>
<tr>
<td>CO</td>
<td>0 0-6</td>
</tr>
<tr>
<td>CO₂</td>
<td>0 0-9</td>
</tr>
</tbody>
</table>
2.6 Mass Transfer Limitation

When measuring intrinsic catalytic activity, it is vital to avoid having mass transfer limitations in the measurement since this will give a lower activity than the true value for the catalyst. It is especially important to be aware of this when measuring steam reforming kinetics since this reaction is exceptionally fast at relevant conditions [40, 50, 70].

There are two types of mass transfer limitations, internal and external, and a control has been made on both of them to ensure that none of them has a significant influence on the observed kinetics. The tests were conducted at the highest temperature used, so they are valid for all measurements. If there is significant internal mass transfer limitation, then the center of the catalyst particles will not be used fully in the reaction, since the reactant concentration will be lower here than in the bulk of the gas. Therefore, a decrease in particle size will show higher activity since a larger part of the catalyst is used. Figure 2.4 shows the measured reaction rate at similar conditions for two different particle sizes. Sample 1 and 3 did not reach steady state, which means that values here are lower than what would have been measured at steady state. Sample 2 and 4 both reached steady state, and the measured rates are very close, showing that there is no mass transfer limitation for these measurements. It should however be noted that particles are not spherical, as shown by the SEM images in Section 3.2.1. This means that the term particle radius is somewhat simplified, since some of the particles will have only one side with a length corresponding to the particle radius.

![Figure 2.4: Measured reaction rate at two different particle sizes](image)

External mass transfer limitation occurs when diffusion through the gas film surrounding the catalyst particle results in a large concentration gradient. An increase in total flow rate will decrease the gas film thickness and, thereby, decrease the effect of external mass transfer. Figure
2.5 shows the rate constant at different flow rates, corresponding to a change in the Sherwood number from 3.6 to 4.4. It is seen that the measured rate constant is not significantly affected by changing the total flow rate, meaning that there is no significant external mass transfer limitation in the measurements.

Figure 2.5: Average value of the rate constant measured at different total inlet flows. All measurements were performed on the same sample at $T = 775^\circ C$ and for different methane concentrations.
2.7 Data Treatment

Since the available gas analyzers can only measure CO and CO$_2$ concentrations, it is necessary to calculate the remaining gas concentrations from a mass balance in order to determine the conversion and the reaction rate. The advantage of using this type of mass balance is that it is not necessary to assume that the water gas shift reaction is at equilibrium. In order to do this, a stoichiometric table is set up as shown below, including both the steam reforming reaction (Reaction 2.2) and the water gas shift reaction (Reaction 2.3).

\[
\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2 \quad (2.2)
\]
\[
\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \quad (2.3)
\]

Table 2.4: Stoichiometric table for the combined steam reforming (SR) and water gas shift (WGS) reactions

<table>
<thead>
<tr>
<th>Gas</th>
<th>$F_{in}$</th>
<th>SR</th>
<th>WGS</th>
<th>$F_{out}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>$F_{CH_4,0}$</td>
<td>-$F_{CH_4,0}X_1$</td>
<td>-</td>
<td>$F_{CH_4,0}(1-X_1)$</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>$F_{H_2O,0}$</td>
<td>-$F_{CH_4,0}X_1$</td>
<td>-($F_{CO,0}+F_{CH_4,0}X_1$)$X_2$</td>
<td>$F_{H_2O,0} - F_{CH_4,0}X_1 - (F_{CO,0}+F_{CH_4,0}X_1)X_2$</td>
</tr>
<tr>
<td>H$_2$</td>
<td>$F_{H_2,0}$</td>
<td>+3$F_{CH_4,0}X_1$</td>
<td>+($F_{CO,0}+F_{CH_4,0}X_1$)$X_2$</td>
<td>$F_{H_2,0} + 3F_{CH_4,0}X_1 + (F_{CO,0}+F_{CH_4,0}X_1)X_2$</td>
</tr>
<tr>
<td>CO</td>
<td>$F_{CO,0}$</td>
<td>+$F_{CH_4,0}X_1$</td>
<td>-($F_{CO,0}+F_{CH_4,0}X_1$)$X_2$</td>
<td>$F_{CO,0} + F_{CH_4,0}X_1 - (F_{CO,0}+F_{CH_4,0}X_1)X_2$</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>$F_{CO_2,0}$</td>
<td>-</td>
<td>+($F_{CO,0}+F_{CH_4,0}X_1$)$X_2$</td>
<td>$F_{CO_2,0} + (F_{CO,0}+F_{CH_4,0}X_1)X_2$</td>
</tr>
<tr>
<td></td>
<td>$F_{tot,0}$</td>
<td>+2$F_{CH_4,0}X_1$</td>
<td>-</td>
<td>$F_{tot,0} + 2F_{CH_4,0}X_1$</td>
</tr>
</tbody>
</table>

$X_1$ is the degree of conversion of the steam reforming reaction, with respect to CH$_4$, and $X_2$ is the degree of conversion of the water gas shift reaction with respect to CO. Change 1 and change 2 are the changes in molar flows of the different species in the steam reforming reaction and the water gas shift reaction respectively. From this stoichiometric table it is possible to find both $X_1$ and $X_2$ as described in the Algorithm shown in Figure 2.6. The partial pressures of the outlet gasses ($P_i$) can then be found as seen in Equation 2.4.

\[ P_i = \frac{F_i}{F_{tot}} \times P_{reac} \quad (2.4) \]

$F$ is the molar flow, $i$ denotes a specific gas, and $tot$ denotes the sum of all gasses. $P_{reac}$ is the measured reactor pressure. These partial pressures are used when determining the reaction rate’s dependence of the different gasses. The sum of CO and CO$_2$ in the outlet, $P_{prod}$, in Equation 2.5 can be used to calculate the degree of conversion of the steam reforming, $X_1$, and afterwards either $P_{CO}$ or $P_{CO_2}$ can be used to find $X_2$. This is done by the two small loops in Figure 2.6.

\[ P_{prod} = P_{CO} + P_{CO_2} \quad (2.5) \]
Unfortunately the partial pressures of CO and CO\textsubscript{2} are measured after the water in the gas has been removed, where the total molar flow is not independent of X\textsubscript{2}, see (Equation 2.6) and, furthermore, the total pressure at the analyzer is ambient pressure, which is lower than the reactor pressure.

\[ F_{\text{tot, anal}} = F_{\text{tot,0}} - F_{\text{H}_2\text{O,0}} + 3F_{\text{CH}_4,0}X_1 + (F_{\text{CO,0}} + F_{\text{CH}_4,0}X_1)X_2 \]  

(2.6)

\[ P_{i,\text{anal}} = \frac{F_{i,\text{anal}}}{F_{\text{tot,anal}}} \cdot P_{\text{atm}} \]  

(2.7)

This means that P\text{prod} is not only dependent on X\textsubscript{1} but also X\textsubscript{2} and therefore an additional loop is needed around the two small loops in the algorithm, in order to obtain consistent results. This algorithm has been implemented in matlab and the bisectional method was used for obtaining new values of X\textsubscript{1} and X\textsubscript{2} in the loops.

2.7.1 Experimental Uncertainty

Following is an evaluation of the uncertainties in the experimental setups. All uncertainties are given as a relative error.

**Gas analysis:** 1 % of range, evaluated for each experiment, normally between 1 and 4 %. The error on the gas analysis is the same on an entire measurement series, so it should have a very low impact on measured rate orders.

**Gas inlet flows:** 2%

**Water inlet flow:** 7% (does not influence the estimation of the reaction rate)

**Temperature:** 1% for the thermocouples. They are, however, not placed directly where the reaction takes place, so the measurement may also be influenced by temperature gradients.

**Catalyst weight:** 1%

**Anode area:** 2%

This results in a total estimated uncertainty on the reaction rate of 4-7 % in the packed bed setups, and 5-8 % for the stack setup.

In order to test the accuracy of the method used where only CO and CO\textsubscript{2} in the outlet are measured and the other gas concentrations are calculated from a mass balance, a gas sample was sent to Haldor Topsøe A/S for analysis of all species with a gas chromatograph (GC). The comparison between the gas concentrations measured on the GC and calculated from a mass balance is shown in Table 2.5. Furthermore, it is shown that the gas sample for the GC contained 0.2% O\textsubscript{2} indicating that 1% air has slipped in during sampling. In column 4 in the table this...
Figure 2.6: Algorithm for calculating outlet partial pressures, degree of conversion and reaction rate in both the packed bed and stack experiments.
has been subtracted and the concentrations normalized. The deviance given in the table is with respect to this adjusted value. The estimated uncertainty for the outlet gases in this experiment is 5% and the uncertainty of the GC measurements is 3%. The deviance between the found values is well within these estimated uncertainties. On this background, the calculated outlet values are used from here on, but it should be kept in mind that all outlet concentrations other than CO and CO\textsubscript{2} are calculated values.

Table 2.5: Test of the precision of outlet gas estimation from mass balance and IR gas analysis, by comparison with gas chromatograph measurement.

<table>
<thead>
<tr>
<th>Gas Species</th>
<th>Mass balance</th>
<th>GC measurement</th>
<th>GC measurement corrected for air</th>
<th>deviance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>vol %</td>
<td>vol %</td>
<td>vol %</td>
<td>%</td>
</tr>
<tr>
<td>CH\textsubscript{4}</td>
<td>4.89</td>
<td>4.73</td>
<td>4.78</td>
<td>2.32</td>
</tr>
<tr>
<td>H\textsubscript{2}</td>
<td>38.92</td>
<td>36.9</td>
<td>37.3</td>
<td>2.65</td>
</tr>
<tr>
<td>CO</td>
<td>6.83</td>
<td>6.67</td>
<td>6.74</td>
<td>1.34</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>3.81</td>
<td>3.74</td>
<td>3.78</td>
<td>0.79</td>
</tr>
<tr>
<td>N\textsubscript{2}</td>
<td>45.5</td>
<td>47.5</td>
<td>47.2</td>
<td>-3.74</td>
</tr>
<tr>
<td>O\textsubscript{2}</td>
<td>-</td>
<td>0.20</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Chapter 3

Experimental Results

In order to achieve a good understanding of the steam reforming kinetics in a SOFC with Ni-YSZ anode material, the reactivity of the catalyst is measured both in a packed bed and in stack configuration. Tests are conducted at temperatures between 600°C and 800°C and the inlet concentration of CH₄, H₂O, H₂, CO and CO₂ are varied in order to determine the dependency on each species. Below is listed the different samples that have been tested in the two setups:

**Packed bed**

**Model anode material:** A Ni-YSZ material similar to a real SOFC anode, this is the most thoroughly tested in this thesis. The model anode material was produced and by Mikko Pihlatie from Risøe-DTU for use in his thesis work [53–57].

**Industrial anode material:** A crushed Ni-YSZ anode from a cell supplied by Topsoe Fuel Cell. Preparation and exact composition are disclosed to open literature.

**New stack sample:** Ni-YSZ anode from a stack that has been subjected to a short term test, supplied by Topsoe Fuel Cell. Principally identical with the industrial anode material.

**Old stack sample:** Ni-YSZ anode material from a stack that has been subjected to a long term test, supplied by Topsoe Fuel Cell. Principally identical with the industrial anode material.

**Traditional steam reforming catalyst** A traditional Ni on alumina steam reforming catalyst, supplied by Haldor Topsøe.

**Stack Measurements**

Preparation and exact composition of all stacks is disclosed to open literature.

**5-cell stack** A typical small SOFC stack from Topsoe Fuel Cell.

**Half-cell stack** A single cell stack, with half the cell cut away, see 2.5.2.
Quarter-cell stack A single cell stack, with 3/4 of the cell cut away, similarly to the half-cell stack.

In the packed bed experiments the crushed catalyst is diluted in alumina in order to decrease the conversion while maintaining a bed size sufficiently large to ensure a uniform flow. Such a dilution is not possible for the stack measurements, so degree of conversion is instead decreased by reducing the cell area, i.e. using half-cell and quarter-cell stacks.

3.1 Dynamic Catalyst Behavior

During this project it was found that this catalyst has an exceptionally slow dynamic behavior. This may help explain the lack of consensus on the reaction rate of steam reforming over Ni-YSZ anode material found in the litterature [43].

At low methane concentrations an initial rapid activation of the catalyst was followed by a short deactivation period, as would be expected, see Figure 3.1. However, after a few hours of apparent steady state, the catalyst was slowly reactivated over a period of several days as shown in Figure 3.2.

![Figure 3.1: First 4 hours of Approach to steady state after startup over crushed anode material in the packed bed reactor at T = 750°C and low methane concentration (≈ 7.3 kPa).](image1.png)

![Figure 3.2: The same experiment as in Figure 3.1, on a longer time scale.](image2.png)

In his thesis, J.G. Jakobsen [32] reported a similar behavior for steam reforming over 5% Rhodium on a MgAlO₄ support although this occurred significantly faster and was seen at 500-600°C during a temperature cycle instead of stable operation.
Figure 3.3 shows two startups similar to that in Figures 3.1 and 3.2, but at high methane concentration. Here it is seen that there is a long deactivation period (just under a week at low temperature) and no subsequent reactivation was observed.

After a change in the inlet hydrogen concentration or temperature, a slow approach to steady state was observed. Figure 3.4 shows the effect of gas concentration changes on the outlet concentration of CO and CO2 on a packed bed setup. For all gases except hydrogen, a new steady state is achieved rapidly after a concentration change. After a change in temperature hydrogen concentration it takes several hours, or even days to achieve a new steady state, depending on temperature.

Similar tests were made with a traditional steam reforming catalyst and no long term dynamic
effect was observed. Figure 3.5 shows the outlet concentration of CO and CO$_2$ at the start up of a traditional steam reforming catalyst in a packed bed at low methane concentration (6.5 kPa) and low temperature ($\approx$640°C). First of all, this shows that the observed dynamic effects are an actual property of the catalyst, not an effect from the setup or experimental method. Secondly it means that the dynamic effect is either caused by the support material, Yttria stabilized Zirconia, or by the fact that the Ni particles are 2-3 orders of magnitude larger in SOFC anode material than in traditional steam reforming catalysts.

![Figure 3.5: Outlet concentration of CO and CO$_2$ from start up of an industrial steam reforming catalyst in a packed bed at $P_{\text{CH}_4}=6.5$ kPa and $T\approx640^\circ$C).](image)

Furthermore, during measurements on the half-cell stack it was found that a shut down of the setup reactivates the catalyst. Figure 3.6 shows the start up of a 1/2 cell stack. The deviation around 150 hours on the plot is a shutdown of the stack for approximately 2 weeks (the timeline is distorted for a better overview) after which the activity increases slightly. During the measurements on the stack, an alarm triggered an emergency shut down of the setup, meaning that the stack was cooled to 68°C in a gas flow consisting of 2% H$_2$, 46% N$_2$ and 52% H$_2$O. The stack was immediately reheated in 5% H$_2$ in N$_2$, whereafter the startup sequence shown in Figure 3.7 was measured with the same conditions as in Figure 3.6. This shows that cooling the stack in an water rich gas resulted in a complete reactivation of the catalytic properties of the anode material. Hydrogen was also present during the shutdown, so the cell was not subjected to oxidising environment. Later tests showed that a shutdown with no water in the gas did not reactivate the catalytic properties.

This reactivation was tested further in the packed bed experiments. It was found that a shutdown without water in the gas, did not reactivate the catalytic properties. Figure 3.8 shows a test to reactivate the catalytic properties at constant temperature by passing a water rich gas (including H$_2$) through the catalyst bed. It is seen that one hour exposure to a water rich gas did not have any effect, but 16 hours exposure resulted in more than a doubling of the catalytic activity. This
Figure 3.6: Startup curve for a half-cell stack at $T = 600^\circ C$, $P_{CH_4} = 20$ kPa, $P_{H_2O} = 59$ kPa, $P_{H_2} = 4$ kPa, $P_{N_2} = 36$ kPa.

behavior will be discussed further on the basis of the observations made in Section 3.2.

Figure 3.7: Startup of the same cell as in 3.6 under similar conditions, after a shutdown in a water rich environment.

Figure 3.8: A test of the reactivation of catalytic activity of Ni-YSZ in the packed bed reactor with crushed anode material. $T = 790^\circ C$, $P_{CH_4} = 15$ kPa, $P_{H_2O} = 30$ kPa, $P_{H_2} = 7$ kPa. The three plots show the sum of CO and CO$_2$ in the outlet for the catalyst after rate determination experiments, and after respectively 1 hour and 16 hours with no methane in a water rich environment.
3.2 Characterization of Ni-YSZ Model catalyst

The model Ni-YSZ catalyst material was provided by Risø-DTU as a part of the thesis work by Mikko Pihlatie [53–57]. It was produced like an industrial SOFC anode, and have similar Ni content, porosity, and particle sizes. The majority of the kinetic measurements was performed on the model Ni-YSZ catalyst, and the catalyst has been characterized using several techniques such as SEM, TEM, XRD, EXAFS, IET, TGA and Dilatometry [54–57]. The preparation of the model anode material is described in [56], where it is designated "Sample E". The results of some of these characterization techniques are not directly relevant to the work in this thesis and are therefore not included.

Before reduction of NiO to Ni the catalyst has a density = 4.2-4.4 g/cm³, porosity of 31-34% v/v and a NiO content of 51% w/w. After reduction, the density is 3.9-4 g/cm³, porosity is approximately 44-46% v/v and the Ni content is 42% w/w.

3.2.1 Scanning Electron Microscopy (SEM)

One of the reasons for the large changes in catalytic activity of the Ni-YSZ material was caused by sintering and other structural changes. In order to test this theory, three samples of the model Ni-YSZ catalyst were prepared for analysis with Scanning Electron Microscopy (SEM). The first sample was reduced. The second sample was reduced, and then run at standard gas conditions at 800°C until the activity was stable. The third sample was reduced, stabilized as the second sample and then subject to a gas consisting of N₂, H₂ and H₂O at 800°C for 16 hours in order to achieve the reactivation observed in section 3.1.

Figure 3.9 is an overview picture of the reduced and stabilized sample. It clearly shows that the rigidity of the sample results in non-spherical particles when crushed. It was later observed that reducing the sample made it significantly less rigid. The fibrous material is residue of the quartz wool used to separate the particles from the quartz frit in the reactor.

An example of a SEM image using backscattered electrons (BSE) is shown in Figure 3.10 corresponding to Figure 3.11(c) and 3.11(d). The images illustrate that it was difficult to distinguish between Ni and YSZ particles, especially since the topography of the sample also influences the gray levels in the SEM BSE image.

Figure 3.11 shows representative SEM pictures of all three samples at two degrees of magnification. Comparing the images of the only reduced sample, Figure 3.11(a) and 3.11(b) with the images of sample that has been reduced and run to steady state, Figure 3.11(c) and 3.11(d). It seems that some degree of sintering is taking place during the stabilization period, which was expected from the decrease in catalytic activity. More surprisingly, the images in Figure 3.11(e) and 3.11(f) indicate that particle size has actually decreased again by reactivation in H₂/H₂O after stability has been reached. Since it is not possible to distinguish between Ni and YSZ particles, it is however difficult to say anything conclusive from the SEM images. So it was decided to
Figure 3.9: Overview picture of the reduced and stabilized sample

Figure 3.10: BSE SEM pictures of of the model Ni-YSZ anode material after reduction and operation to steady state at 800°C under standard gas conditions corresponding to Figure 3.11(c) and 3.11(d).

perform Transmission Electron Microscopy (TEM) as well, since it can give a more detailed view of the catalyst and has the possibility of determining local compositions by Energy-dispersive X-ray spectroscopy (EDX).
Figure 3.11: SEM pictures using secondary electrons, of three samples of the model Ni-YSZ anode material which have been subjected to; a-b) reduction c-d) reduction and run to steady state at 800°C under standard gas conditions e-f) reduction, run to steady state at 800°C under standard gas conditions, run in H$_2$O/H$_2$ (no methane) for 16 hours.
3.2.2 Transmission Electron Microscopy (TEM)

Before examining the samples with Transmission Electron Microscopy (TEM), they were crushed even further in order to decrease the particles to a size where TEM can be used effectively. The same three samples that were examined with SEM were also examined with TEM. Furthermore, an unreduced sample of the model catalyst was examined.

(a) 1) 10.3% Ni, 89.7% Zr
(b) 2) 90.0% Ni, 5.2% Zr, 4.8% Al 3) 9.3% Ni, 4.5% Y, 86.2% Zr
(c) zoom on the NiO particle (2)
(d) zoom on the YSZ particle (3)

Figure 3.12: TEM images of an unreduced sample of the model anode material.

In addition to the images, dark field imaging was used to ease the observation of small crystals. Some of the particles were also tested with Energy-dispersive X-ray spectroscopy (EDX), in order to distinguish between Ni (or NiO) and YSZ particles. The areas where EDX was performed are marked on the TEM images with white numbered circles, and the measured compositions are
given in the figure text as % mole/mole. The sample holder is made of copper and carbon, so these
two materials are removed from the composition. Oxygen is also removed from the composition
because it is not quantified correctly by the EDX. In a few of the EDX measurements Al was also
observed, for example Figure 3.12(b), this is most likely a residue of the the quartz wool used to
separate the samples from the glass frit in the tubular reactor.

Normally, TEM images can be used to determine particle size distribution of the catalytically
active material, but for this catalyst there is a huge span in the size of the Ni particles, i.e. 2-3
orders of magnitude. This means that if a particle size distribution was to be measured with
TEM it would require huge amounts of data in order to achieve statistical precision.

TEM images taken on the unreduced sample are shown in Figure 3.12. Notice the structural
difference between the NiO particle in Figure 3.12(c) and the YSZ particle in Figure 3.12(d).
The YSZ particle seems to have clearly defined edges, whereas the surface of the NiO particle is
even more erratic.

Figure 3.13 shows images taken on the reduced model anode material. Both the dark field imaging
in Figure 3.13(c) and 3.13(d) as well as the zoom in Figure 3.13(b) show a cluster of particles
in the size 5-10 nm. Unfortunately EDX measurements could not be performed on such small
sample areas, but it is assumed that the nano particles are residue left behind when a Ni/NiO
particle is reduced in size during reduction. This has been described previously by King et al.
[38] and has very recently been shown with in-situ TEM by Jeangros et. al [34]. Such clusters of
nano particles were observed on several of the larger particles in the sample and they are most
likely the cause for the high initial reactivity of the catalyst.

The sample that has been run to stability under standard conditions has clear signs of sintering
compared to the only reduced sample. Both the dark field imaging in Figures 3.14(c) and 3.14(d)
and the image in Figure 3.14(b) show that there are still nm scale particles present. There are,
however, fewer of them and instead intermediate sized particles are observed. Furthermore, some
large Ni particles were observed in this sample, for example the 2 μm Ni particle in Figure 3.14(a)
(EDX measurement 7). Particles of this size were not observed in the only-reduced sample.

So after the initial reduction in activity of the model anode material, the Ni particle size spans
from 5 nm to 2 μm, i.e. almost 3 orders of magnitude. The images further indicate that it is no
longer only nm particles and μm particles, there are also Ni particles in all sizes in between.

Figure 3.15 shows representative TEM images of the last sample, which, after the initial deacti-
vation, has been subjected to a gas mixture of 7.6% H₂, 31.5% H₂O and balance N₂ at a total
pressure of 1.1 bar for 24 hours. This procedure has previously been seen to completely recover
the activity of the catalyst, see Section 3.1.

The TEM images for this sample indicate a reorganization of the catalyst structure, especially
the YSZ particles. An example of this is seen in Figure 3.15(a), where EDX measurement 8 shows
that the transparent material making up the overall structure of the particle is pure Zr, while
EDX measurement 11 apparently shows a 300 nm Ni particle almost completely covered by Zr.
(a) 10) 7.2% Y, 92.8% Zr 11) 6.61% Y, 93.4% Zr 12) 17.6% Ni, 5.5% Y 76.9% Zr 13) 34.1% Ni, 3.8% Y, 62.1% Zr.

(b) Zoom of particle 11 in Figure 3.13(a).

(c) dark field imaging of particle 11 in Figure 3.13(a).

(d) Dark field image of reduced Ni-YSZ particle.

Figure 3.13: TEM images of a reduced sample of the model anode material.

Since the images are only two dimensional it is, however, just as likely that the Ni particle lies on top of the YSZ material.

There were also observed large Ni particles (0.2-0.5 μm) that did not appear to be in close contact with Zr. Furthermore, they did not appear to be agglomerates of smaller crystals. No particles larger than 0.5 μm were observed, which can either be a coincidence or an indication that some degree of re-dispersion has taken place. Furthermore, a few clusters of 5-10 nm sized particles were observed as seen in Figure 3.15(b) and the dark field image in Figure 3.15(c), which could be residue from the re-dispersion of a large particle. This looks very similar to the clusters seen in
the freshly reduced sample in Figure 3.13, but they were not nearly as abundant in this sample. Possible mechanisms that could induce such a re-dispersion is discussed in section 3.2.4. Even though some particles with a size of a few nm were observed they not appear to be as abundant as in the only-reduced sample, so it is not likely that this is the sole explanation for the regained catalytic activity. There is, however, also observed what appears to be flat Ni particles, as seen in the dark field image in Figure 3.15(d). It is plausible that such a change in the shape of the Ni particles can result in an increased number of step sites, which has been reported to be highly active [28, 65].

Figure 3.14: TEM images of a sample of the model anode material that has been reduced and run to stability under standard gas conditions at 800°C.
Figure 3.15: TEM images of a sample of the model anode material that has been reduced and run to stability under standard gas conditions at 800°C, after which it was run for 24 hours in 7.6% H₂, 31.5% H₂O and balance N₂ at a total pressure of 1.1 bar to regain the catalytic activity.
3.2.3 X-Ray Diffraction

In light of the observations made during TEM measurements it was decided to test the same four samples with X-Ray Diffraction (XRD) hoping to find further evidence of restructuring of the YSZ support material. Furthermore, XRD measurements can give an average crystallite size, which can perhaps shed some further light on the suspected re-dispersion of the Ni particles. Figure 3.16 shows an XRD pattern for the just reduced sample. First of all no Ni reflections were observed in the unreduced sample, and no NiO peaks were observed in the reduced samples, indicating that no undesired reduction or oxidation have taken place.

![](image)

**Figure 3.16: XRD pattern on the just reduced sample**

The peak width observed in the XRD patterns can be influenced by a number of things. The major contributors are the crystallite size in the sample, and the instrument itself and if it is assumed that these two are the only contributions, then the peak width can be used to estimate the crystallite size. This was done by using the Scherrer formula, as seen in Equation 3.1.

$$\tau = \frac{K\lambda}{\beta \cos(\theta)}$$  

(3.1)

$\tau$ is the mean crystallite size, $K$ is the shape factor, which is set to 0.9, $\lambda$ is the x-ray wavelength, \( \theta \) is the Bragg angle, and $\beta$ is the line broadening at half the maximum intensity in radians minus the instrumental broadening as determined by calibration. There were large differences in the results depending on which peak was chosen, as seen in table 3.1, which shows the average crystallite size calculated from each of the four major peaks in a XRD diagram of Ni in the sample that has only been reduced. This is not surprising since this technique is only suitable for crystallite sizes up to 100 nm, which is further confirmed by the fact that the instrumental broadening corresponds to approximately two thirds of the Ni particle peak width. It should also be kept in mind that this method has a tendency to underestimate the crystallite size, since all unaccounted influences will result in a wider peak, and thereby a lowering of the estimated...
Table 3.1: Volume based average crystallite size determined from the different major Ni peaks of the just reduced sample

<table>
<thead>
<tr>
<th>peak No.</th>
<th>2θ</th>
<th>Crystallite size [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>44</td>
<td>166</td>
</tr>
<tr>
<td>2</td>
<td>51</td>
<td>149</td>
</tr>
<tr>
<td>3</td>
<td>76</td>
<td>243</td>
</tr>
<tr>
<td>4</td>
<td>93</td>
<td>273</td>
</tr>
<tr>
<td>avg</td>
<td></td>
<td>208</td>
</tr>
</tbody>
</table>

crystallite size.

These uncertainties resulted in large variations in the measured average Ni particle size, giving values between 200 nm and 300 nm for different measurements on the same sample. Because of these large deviations it was not possible to determine possible differences in the three reduced samples.

The average crystallite sizes found for YSZ in the different samples are very similar (≈ 50 nm), so they do not give any information on a possible change in the YSZ structure. The average YSZ particle sizes found from XRD are, however, much smaller than the YSZ particle sizes observed in the TEM images, this is probably because the large YSZ particles observed via TEM are agglomerates of smaller crystals.

3.2.4 Discussion

Apart from the characterization shown here, the samples have also been examined with X-ray Absorption Spectroscopy, as reported in article II [42]. It was found that the reduced sample is the one which is most defined and therefore gives the highest average particle size > 5 nm. The deactivated sample is found to have a slightly lower average particle size and the reactivated sample has a significantly smaller coordination number. This is partly in contradiction to TEM and XRD results. This may be due to a large fraction of small particles or a strong disorder including dissolved oxygen/carbon.

The different long term changes in the catalyst activity that has been reported here are highly unusual, but not completely unheard of. In his thesis J.G. Jakobsen [32] recently reported a deactivation followed by reactivation of a steam reforming catalyst consisting of 5% Rh on MgAl₂O₄. Although the observation was made during a temperature cycle instead of under stable conditions at low methane concentration as in this work (see Figure 3.2), J.G. Jakobsen suggests that the behavior might be caused by a mechanism where the support material covers the catalytically active material followed by the catalytic material re-emerging from the support. This theory is at first sight supported by the observation made in the TEM images in this work, were the YSZ support material apparently covers Ni particles up to several hundred nm in size.
At closer inspection the is however not conclusive, first of all, the observed Ni particle can just as well lie on top or below a thin layer of YSZ. Secondly there is the objection that J.G. Jakobsen suggest the YSZ coverage of Ni as an explanation for temporarily decreased activity, while the images showing the apparent coverage of Ni in this work was made on a sample with relatively high activity. Further investigations of this behavior is needed.

Regarding the slow de-activation of the catalyst when operating at higher methane concentration as shown in Figure 3.3, it is definitely connected with the sintering of nano Ni particles that are produced when the Ni/NiO particles shrink during reduction. Since the behavior of the reactivated sample closely resembles that of the freshly reduced sample, the obvious theory is that the treatment with H$_2$O/H$_2$ without methane, has re-oxidized the nickel, followed by a re-reduction, which would give rise to new Ni nano particles like for the initial reduction. This can, however, be dismissed since the H$_2$O/H$_2$ during the re-activation corresponds to a oxygen partial pressure of $10^{-13}$-$10^{-12}$ atm, depending on temperature, while the partial pressure needed for oxidation of Ni is in the range $10^{-4}$-$10^{-6}$ atm at the relevant temperatures. This is also confirmed by the XRD measurements, which showed no sign of NiO in the re-activated sample. Nano particles may, however, behave differently than expected from larger particles, and may have surface oxidation under conditions that do not cause bulk oxidation.

Ruckenstein and Hu [63] have also reported dispersion of Ni particles, and from experimental observations they found the following three step mechanism: "(1) extension of films from the crystallites, (2) coalescence of the films surrounding neighboring crystallites, and (3) further extension of the films."

There is a striking correspondence between the deactivation time observed for the catalytic steam reforming activity in this thesis and the initial degredation of the performance of an SOFC stack, i.e. a slow deactivation over 1-200 hours, depending on conditions [25]. It has recently been shown by A. Hauch et al. [25, 26] that this initial degradation of the cell performance is caused by some unidentified impurities settling on the triple phase boundaries. The triple phase boundary is not important to the catalytic steam reforming activity of the anode material, and therefore such impurities should not influence the steam reforming activity. The correspondence in deactivation time is, however, reason to consider possible common causes, which could be either changes in structure, impurities or a combination.

The observation made in TEM of the re-activated sample, that some YSZ particles had apparently undergone a drastic change in structure and absorbed or coated large Ni particles, is surprising but not completely new. It has been reported by Hauch et. al [24] that during a high current test on a solid oxide electrolysis cell, a dense layer of Ni and YSZ has formed at the electrolyte-hydrogen electrode interface. Where it appears as if the YSZ electrolyte has changed structure and absorbed the closest Ni particles completely, the conditions were very different from those used in the present thesis, but the structural change is also much more pronounced. It has also been reported recently that during the first few hundred hours of operation of an SOFC stack/cell,
a loss of Ni percolation is observed [53], which could theoretically also be caused by YSZ covering some of the Ni particles. It should here be emphasized that this is purely a theoretic possibility at the moment since no proof exists to confirm this phenomena.

There has not been found a satisfactory explanation for the long term change in catalytic activity after a change in the H$_2$ inlet flow (see Figure 3.4). It is suspected that the H$_2$ concentration effects one or more of the possible mechanisms described for explaining the other long term changes in catalytic activity.

Recently it has been shown by In-situ microscopy that step sites on the Ni catalyst particles are the most active nucleation sites for both carbon formation and steam reforming [28, 65]. This has also been backed up by density functional theory calculations [5, 11], which show that the step sites are approximately 100 times more active than terrace sites. This large difference in activity opens for another possible explanation for the slow approach to steady state after a change in temperature or hydrogen concentration, namely that the Ni particles change shape. This will change the Ni surface area but, more importantly, it could change the number of the highly active step sites. No observations were made that clearly support or contradict this theory. There was, however, observed a tendency that the stabilized sample had defined single crystal particles, while the two samples with higher activity, i.e. the freshly reduced and the sample reactivated in H$_2$/H$_2$O gas, showed less clearly defined structures with a higher degree of interaction between Ni and YSZ.

### 3.3 Packed Bed Measurements

#### 3.3.1 Model Anode Material

In this section the kinetic data measured on the model anode is presented and a power law expression as shown in equation 3.2 is used to aid in the description of the observed trends.

\[
r = kP_{CH_4}^{\alpha}P_{H_2O}^{\beta}P_{H_2}^{\gamma}P_{CO}^{\delta}P_{CO_2}^{\lambda}
\]  

(3.2)

The reaction orders, \(\alpha, \beta, \gamma, \delta\) and \(\lambda\) is found from measurements with varying partial pressures of the different species, all of which are shown in Appendix B.2. The rate for each measurement is determined under the assumption that the partial pressures are constant through the bed and is taken as the average if the inlet and the outlet partial pressure. This assumption can be used since the degree of conversion in the measurements is in the range 5-15\% mole/mole and is below 10\% mole/mole for the majority of the measurements. The method used to speed up the measurements, i.e. rapid consecutive changes in gas composition after the initial steady state has been reached, may result in inaccuracies. It is attempted to counteract this by first varying each gas by increasing the partial pressure and later with decreasing partial pressures, over the same interval. In some cases this results in plots similar to Figure 3.20(a) where the two sets of measurements are easily distinguished.

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Figure 3.17 shows the observed reaction rate as function of changes in the different gas species at 650°C and similar in Figure 3.18 at 700°C. The methane dependency has also been determined at other temperatures; these are all shown in Appendix B.1.

The most clearcut observations to be made is that methane has an apparent rate order of around 0.9 while the water partial pressure has no effect on the reaction rate. The observed orders are, however, not that unambiguous. All three species, H\(_2\), CO and CO\(_2\) apparently have some effect on the observed rate, which furthermore changes with temperature. For example the reaction order for CO is measured as -0.14 at 650°C and 0.10 at 700°C. This change with temperature may be caused by a change in which elementary reaction is rate determining or an increase in the species adsorbed on the catalyst at lower temperatures or a change in the approach to equilibrium. For the sake of the power law expression, the rate order is set as a mean of the observed rates, i.e. 0 for CO. In section 4.1 a more thorough discussion of such effects is made as a part of trying to obtain an accurate description of the reaction mechanism and a achieve a suitable kinetic expression.

The resulting power law expression is shown in Equation 3.3.

\[ r = kP_{CH_4}^{0.9}P_{H_2}^{-0.2}P_{CO_2}^{0.2} \quad (3.3) \]

Figure 3.19 shows an Arrhenius plot for the kinetic constant obtained with the power law expression, giving an activation energy of 185 kJ/mol and a pre-exponential factor of 139 mol/s g P\(_a^{0.9}\).

Because of the large range in the measured reaction rates a sum of squares is not suitable as a figure for the deviance between model and experimental data, since it would value the high temperature measurements much higher than the low temperature measurements. Instead, an average of the absolute value of the percentage deviation between the model and each data point is used as calculated from Equation 3.4.

\[ \text{deviation} = \left| \frac{\text{rate}_{\text{measured}} - \text{rate}_{\text{model}}}{\text{rate}_{\text{measured}}} \right| \times 100\% \quad (3.4) \]

The calculated deviation for the power law expression is 43.7%. The major deviations are in the measurements with variations in H\(_2\), CO and CO\(_2\), as expected, because the observed dependencies of these gases change with temperature.
Figure 3.17: Measured dependencies of the different gas species over the model Ni-YSZ catalyst at 650°C
Figure 3.18: Measured dependencies of the different gas species over the model Ni-YSZ catalyst at 700°C
Figure 3.19: Arrhenius plot for measured rate constants on the model anode material with respect to a power law expression. The reaction constant, $k$, has the unit $\frac{\text{mol}}{\text{g cat} \cdot \text{Pa}^{0.9}}$. 

$A = 139 \text{ mol/s g Pa}^{0.9}$

$E_a = 185 \text{ kJ/mol}$

\[ \ln(k) = \frac{-E_a}{R} \left( \frac{1}{T} \right) + \ln(A) \]
3.3.2 Industrial Anode

The sample designated as the industrial anode is an anode plate from the production facility at Topsoe Fuel Cell A/S. The sample has been crushed down to be used for these tubular reactor measurements. The rate order determination for the different gas species over the industrial anode is shown in Figure 3.20 at 650°C and in Figure 3.21 at 750°C. The methane rate order has also been determined at other temperatures, these are all shown in Appendix B.2.

The observed rate orders are very similar to those for the model anode material, and the values are shown in Equation 3.5. The largest difference is that the observed order for methane is here 0.8 where it was 0.9 for the model anode. Even though the mean of the observed order for H2, CO and CO2 are the same as for the model anode, the difference in the rates at the two temperatures is larger. This is most likely just an effect of the larger temperature difference between the two measurements. Furthermore, a slight dependency on water is observed at 750°C.

\[ r = k P_{CH_4}^{0.8} P_{H_2}^{-0.2} P_{CO_2}^{0.2} \]  

Figure 3.22 shows Arrhenius plots for the rate constants found for each measurement point for the obtained power law expression.

The activation energy is found to be 166 kJ/mol, with a pre-exponential factor of 23 mol/s g Pa0.8, and the average deviation between the kinetic expression and the experimental data is 41.4%.

The difference in measured activation energies is rather large considering that the two Ni-YSZ materials are very similar in both Ni content, structure and production method. The only intended difference between the two Ni-YSZ materials is that the YSZ particles in the model anode material are larger. This is yet another indication that the YSZ support material has a large influence on the reforming activity of Ni in SOFC anodes.
Figure 3.20: Measured dependencies of the different gas species over crushed industrial Ni-YSZ anode material at 650°C
Figure 3.21: Measured dependencies of the different gas species over crushed industrial Ni-YSZ anode material at 750°C
Figure 3.22: Arrhenius plot for measured rate constants on the industrial anode material for the power law expression. The reaction constant, $k$, has the unit $\frac{\text{mol}}{\text{s g \ Pa}}$. 

$A = 23.3 \text{ mol/s g Pa}$

$E_a = 166 \text{ kJ/mol}$
3.3.3 Stack Samples

The measurements in this section are made over two samples from cells that have been in operation in SOFC stacks, both samples are principally identical to the "Industrial anode material", but have been subjected to different treatments. The first sample is from a relatively new stack, and the second sample is from an older stack. After the stack tests were completed, a cell from each stack was taken as sample for the measurements presented here. Before the reforming rate measurements, the cathode has been removed from the cell with hydrochloric acid and the remaining anode and electrolyte were crushed.

The sample from the new stack has been subject to a short test program over a few days, first on hydrogen, and afterwards on methane. The stack has furthermore been through a current cycle with both hydrogen and methane as fuel. The operating temperature of the stack was approximately 740°C. Figure 3.23 shows the dependency of the different species, observed over the new stack anode material. The methane rate order has also been determined at other temperatures, these are all shown in Appendix B.3.

It is seen from Figure 3.23(d) that the dependency of CO is very high, i.e. 0.84. However, when it was attempted to fit a rate expression with this CO dependency to the measurements, it resulted in an activation energy close to zero. This happens because the amount of CO formed in the reactor increases with temperature, and it illustrates that the high dependency of CO is only seen in the measurements where CO is added to the inlet, it is not relevant for the other measurements. The same problem was encountered when trying to fit a Langmuir-Hinshelwood expression to the measurements, as is described in Section 4. On this basis, it is assumed that the observed CO dependency is the result of an unknown experimental error. The remaining measurements are fitted with the power law expression shown in Equation 3.6.

\[ r = k P_{\text{CH}_4}^{0.8} P_{H_2}^{0.2} \]

Figure 3.24 shows Arrhenius plots for the rate constants found for each measurement point for the obtained power law expression.

The activation energy is found to be 183 kJ/mol, with a pre-exponential factor of \(1.7 \cdot 10^{-3}\) mol/s g Pa\(^{0.6}\), and the average deviation between the kinetic expression and the experimental data is 14.3%.

The old stack sample is from a stack which has been subjected to a long-term test on simulated pre-reformed natural gas with O/C = 2 for a duration of 5500 hours with an operating temperature between 640°C and 820°C. Figure 3.25 shows the dependencies found for the old stack anode material. Methane rate order at other temperatures are found in Appendix B.3.

A relatively strong dependency is seen for both CO and CO\(_2\), and when trying to fit the measurements to a power law expression including these strong dependencies, problems similar to those described with the new stack material measurements were encountered. The CO and CO\(_2\)
Figure 3.23: Measured dependencies of the different gas species on the new stack sample at 700°C.
dependency on the old stack material are, however, described rather well by adding an approach to equilibrium term as described in Section 4. This clearly illustrates an inherent weakness in power law expressions namely that they are more descriptive than accurate. All measurements, including those with CO and CO$_2$ variations in the inlet, are fitted by a power law expression that only describes the CH$_4$ dependency as shown in Equation 3.7.

$$r = kP_{\text{CH}_4}^{0.8}$$

(3.7)

Figure 3.26 shows Arrhenius plots for the rate constants found for each measurement point with Equation 3.7.

The activation energy is found to be 164 kJ/mol, with a pre-exponential factor of 15.3 mol/s g Pa$^{0.8}$. and the average deviation between the kinetic expression and the experimental data is 16.1%. This relatively low overall error in spite of the poor fit to the measurements with CO and CO$_2$ variations is an effect of a very good fit to the rest of the data.
Figure 3.25: Measured dependencies of the different gas species on the old stack sample at 700°C.
Figure 3.26: Arrhenius plot for measured rate constants on old stack anode material for the power law expression. The reaction constant, $k$, has the unit $\text{mol} \cdot \text{g}^{-0.8} \cdot \text{Pa}^{1.8} \cdot \text{K}^{-0.5}$. 

\[ A = 15.3 \text{ mol/s g Pa}^{0.8} \]
\[ E_a = 164 \text{kJ/mol} \]
3.3.4 Temperature Dependence at Non-Steady State

There is a large span in the observed activation energies, 58-229 kJ/mol, reported for methane steam reforming in literature [43]. There are several possible reasons for these large differences, for example transport limitations, differences in catalyst structure, lack of an approach to equilibrium term, rate determining step changes with temperature or species covering the surface resulting in different observed kinetic expressions at different conditions.

![Arrhenius plots for the reaction measured on the model anode material without waiting for stability at each temperature.](image)

Figure 3.27: Arrhenius plots for the reaction measured on the model anode material without waiting for stability at each temperature.

There is, however, also the possibility that lacking knowledge of the long stabilization period observed in this thesis work (see Section 3.1) can have a large influence on the observed activation energy. In order to illuminate this, measurements were made with fast changes in temperature. A model anode sample was reduced, and then operated with standard gas conditions at 800°C.
until the activity has stabilized. After this, three series of temperature changes were made, with different holding time at each temperature before the activity measurement was taken. One with a 60 min waiting period, one with a 30 min waiting period and one where the reactor was cooled from 800°C to 650°C without pause. After each series, the temperature was kept at 800°C until stability had been reached again.

Figure 3.27 shows the Arrhenius plot for the three measurement series for the reaction constant with respect to the power law expression in Equation 3.3. The observed activation energy of the three measurement series are close to each other because the approach to steady state is so slow that the change in activity after an hour is not significant. In the measurement series with no holding time, seen in Figure 3.27(c), a change in the slope is observed around $1/T = 1.03$. This is most likely an effect of the temperature changes being so fast that the surface coverage of the different species does reach a new steady state at each temperature. More interesting is the fact that the observed activation energy, i.e. 71-76 kJ/mol in these fast measurement series is less than half of the 185 kJ/mole, which is obtained when waiting for stability at each temperature. It is likely that the activation energy found with fast temperature changes is the actual activation energy of the reaction, and the increased activation energy found when waiting for stability is caused by reversible structural changes in the catalyst. This theory should in future work be examined with in-situ TEM or other in-situ characterization techniques, since it is likely that the catalyst structure will also change during shutdown.

These two different activation energies for the reactivity, combined with the dynamic behavior described in section 3.1, may very well be the reason for the large variations in the activation energy values reported in literature. The measurements made here with fast temperature changes were made after steady state was achieved at 800°C. If the temperature changes are made while the approach to steady state is still taking place, then any value can be measured for the activation energy, depending on the procedure. The measured activation energy will in this case depend on whether temperature changes are performed by increasing or decreasing temperature, as well as how fast the temperature changes are made.

### 3.4 Stack Measurements

The rate of catalytic steam reforming of methane over an industrial SOFC anode is extremely high. This is because of the combined effect of high operating temperature, a highly active catalyst material, a high catalyst content and a low flow. Furthermore, the electrochemical reactions in an SOFC convert hydrogen to water, in other words it removes product from the steam reforming reaction and adds reactant. In order to avoid this, all measurements were performed without electrochemical reactions in the cell, by having no oxidant on the cathode side. The result of this is high degrees of conversion and large temperature gradients which makes it very challenging to obtain reliable measurements on the steam reforming rate over a real anode structure.
The high reaction rate and the structure of the anode, also means that the observed rate will be limited by mass transport effects. The purpose of these stack measurements is to measure the rate with realistic mass transport and by comparison with the results from the packed bed measurements the mass transport effect is evaluated in section 4.2.

It was first attempted to measure the steam reforming rate on a 5-cell stack, but complete conversion was observed. In order to decrease the degree of conversion, a stack with only one half cell was produced, see Section 2.5.2, and the stack was also operated at high total flow rate, ie. ≈ $2\frac{NL}{min\text{cell}}$ (normal operation ≈ $0.5\frac{NL}{min\text{cell}}$). The observed degrees of conversion were, however, still rather high (0.3-0.8), especially at high temperature, so in order to decrease conversion even further stacks with one quarter of a cell were also produced.

A further decrease in cell area would have been preferred, but removing part of the cell significantly reduced the durability of the cells, and several of the modified cells cracked under conditions that a normal stack could withstand. Furthermore, it was feared that removing more than 3/4 of the cell would result in a significant change in the flow pattern of the gas, with respect to a full cell.

### 3.4.1 Half Cell

During experiments on this stack there were several practical problems with things such as gas supply and faulty gas analyzers. The stack was destroyed because of an error in the shutdown procedure during a blackout. So the amount of data on this cell is very limited. All rate order determination measurements are shown in Appendix B.4. The measurements have large uncertainties from the high conversion in the measurements which is between 40 and 98%. This results in large deviations in the observed reaction orders, the order of water is found in the range -0.5 to 0.25 and the order of CO$_2$ is in the range 0 to 1.4.

Because of the high experimental uncertainty, the rate expression found from these measurements should only be considered as an estimation. First of all it is assumed that the reaction is first order in methane and independent of the other species, Equation 3.8.

$$r = kP_{CH_4}$$  \hspace{1cm} (3.8)

The Arrhenius plot for the rate constant is shown in Figure 3.28, where $E_A = 63$ kJ/mol and $A = 0.0059$ mol/s m$^2$ Pa. The activation energy observed in these measurements is much lower than those measured in the tubular reactor. It is important to keep in mind that the measurements are possibly unreliable because of the experimental difficulties. This is also illustrated by the fact that even though there are only measurements at three different temperatures, it is clear to see that the Arrhenius plot does not give a straight line. The dotted line in Figure 3.28 is the rate expression measured on the quarter cell stack (see Section 3.4.2). It is seen that there is a very good correspondence between the measurements on the two stacks, except at 600°C.

This clearly illustrates that the measurements at 600°C are invalid, which was already suspected
because these measurements were subject to massive complications.

\begin{equation}
A = 0.0059 \text{ mol/s m}^2 \text{ Pa}
\end{equation}

\begin{equation}
E_a = 63 \text{ kJ/mol}
\end{equation}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{arrhenius.png}
\caption{Arrhenius plot for a half cell stack. The reaction constant, \( k \), has the unit \( \frac{\text{mol}}{\text{sm}^2 \text{Pa}} \), where \( m^2 \) refers to the geometric anode area.}
\end{figure}

The average deviation between the measurements and the expression is 29%. This relatively low average deviation is an effect of the low amount of measurements. Furthermore, as is indicated by the plot in Figure 3.28, the high and low temperature results fit well with the kinetic expression while the measurements at the intermediate temperature has deviations of 60-95%.

### 3.4.2 Quarter Cell

The measurements made on the half cell stack showed that a further reduction in cell area would be advantageous in order to decrease the degree of conversion, especially at high temperatures. The other possibility of reducing the degree of conversion is to increase the total flow rate. The flow rate is, however, already 5-10 times higher than what would be used under normal operation of an SOFC stack. Figures 3.29 and 3.30 show the influence on the flow rate by varying the gas composition at respectively 650°C and 750°C.

The observed dependencies are very similar to those seen both for the half cell stack and the measurements made in the packed bed measurements. i.e. a reaction order a little lower than one for methane, and close to zero for the other species. Plots showing the measured dependency of methane at other temperatures can be seen in Appendix B.5. Figure 3.31 shows an Arrhenius plot for the quarter cell measurements, with the rate constant values obtained for an expression with a 0.7 order dependency on methane, and no dependency of the other species. This gives the rate expression seen in Equation 3.9.

\begin{equation}
r = 2 \cdot 10^4 \frac{\text{mole}}{\text{sm}^2 \text{Pa}} \exp\left(-\frac{166.1}{T} \frac{k}{\text{mol}} \frac{R}{T} \right) P_{CH_4}^{0.7}
\end{equation}

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Figure 3.29: Measured dependencies of the different gas species over the quarter cell stack at 650°C
Figure 3.30: Measured dependencies of the different gas species over the quarter cell stack at 750°C
The average deviation between the model and the measurement points is 20.6%. This is similar to the deviation for the expression found for the half-cell measurements, but because the number of measurements on the quarter cell is much higher, it has much better credibility.

In Section 4.2, the rate measurements on the quarter cell stack will be compared to rates predicted from the intrinsic kinetics measured in the tubular reactor combined with an estimate of the mass transport limitations in the stack.
Chapter 4

Kinetic Expressions

A great number of elementary reactions are known to take place during catalytic steam reforming of methane [13, 27]. It is, however, often estimated that the 9 elementary reactions shown below are sufficient to give a complete understanding of the mechanism [19, 32, 36].

1. $\text{CH}_4 + 2^* \rightarrow \text{CH}_3^* + H^*$
2. $\text{CH}_3^* + * \rightleftharpoons \text{CH}_2^* + H^*$
3. $\text{CH}_2^* + * \rightleftharpoons \text{CH}^* + \text{H}^*$
4. $\text{CH}^* + * \rightleftharpoons \text{C}^* + \text{H}^*$
5. $\text{H}_2\text{O} + 2^* \rightleftharpoons \text{HO}^* + \text{H}^*$
6. $\text{HO}^* + * \rightleftharpoons \text{O}^* + \text{H}^*$
7. $\text{C}^* + \text{O}^* \rightleftharpoons \text{CO}^{*+}$
8. $\text{CO}^* \rightleftharpoons \text{CO}^{*+}$
9. $2\text{H}^* \rightleftharpoons \text{H}_2 + 2^*$

It is generally agreed, that Reaction 1 is a rate limiting step, but both experimental studies and Density Functional Theory (DFT) calculations have shown Reaction 7 may also be rate limiting [10, 36]. Furthermore, the dissociation of water, Reaction 5, has also been proposed as a rate limiting step [47, 51].

Assuming that the surface is clean from adsorbents and that Reaction 7 is the rate limiting step, results in the kinetic expression shown in Equation 4.1, see Appendix C for derivation.

$$r = k \frac{P_{\text{CH}_4} P_{\text{H}_2\text{O}}}{P_{\text{H}_2}^2} \left(1 - \frac{Q_{sr}}{K_{sr}}\right) \theta_s^2$$

(4.1)
$K_{sr}$ is the equilibrium constant for the steam reforming reaction and $Q$ is defined as shown in Equation 4.2. The term $(1-Q/K)$ is referred to as the approach to equilibrium and when equilibrium is reached the rate becomes 0 because $Q = K$. $\theta_*$ is the fraction of free surface sites, which is equal to 1 according to the assumption of clean surface.

$$Q = \frac{P_{H_2}^3 P_{CO}}{P_{CH_4} P_{H_2O}}$$

(4.2)

There is no experimental observation showing a negative third order dependency on hydrogen, neither in literature or in this thesis, therefore Reaction 7 is not considered a rate limiting step in this thesis.

Assuming a clean catalyst surface and that Reaction 1 is the only rate limiting step, results in the following kinetic expression.

$$r = k_{CH_4} P_{CH_4} \left( 1 - \frac{Q_{sr}}{K_{sr}} \right)$$

(4.3)

If the dissociation of water is also assumed to be rate limiting, the resulting kinetic expression will also have a first order dependence on the partial pressure of water. Even though a few studies report such a dependence, most experimental studies of steam reforming kinetics, including the measurements in this thesis (see Chapter 3), do not observe any dependence of water partial pressure. In this work, Reaction 5 is therefore not considered a rate limiting step.

The assumption that the catalyst surface is completely clean and available for reaction is not always valid, meaning that the free surface area, $\theta_*$, is not equal to 1. Even though the temperatures used in this study are rather high, it is observed that the reaction rate has a low order dependency on both $H_2$, CO and $CO_2$, which could be an indication of some degree of surface coverage. Equation 4.4 shows the kinetic expression where CO and H are the most abundant species on the surface area (See Appendix C).

$$r = k_{CH_4} P_{CH_4} \left( 1 - \frac{Q_{sr}}{K_{sr}} \right) \frac{1}{\left( 1 + k_{CO} P_{CO} + k_{H_2} P_{H_2}^{1/2} \right)^2}$$

(4.4)

4.1 Intrinsic Kinetics

Kinetic expressions with clean surface and with either H, CO or H+CO as most abundant species, have been fitted to the reaction rates measured over the model anode. It was found, however that several different sets of parameter values could give similar fit to the experimental data, a summary of the different fits is given in Table 4.1. The deviation values given in the table is an average of the deviation between each measurement point and the corresponding model point, calculated from Equation 4.5.
\[
err = \sqrt{\left(\frac{r_{\text{measured}} - r_{\text{model}}}{r_{\text{measured}}} \times 100\%\right)^2};
\]

Looking at the power law and clean surface expressions in Table 4.1, it is immediately seen that the approach to equilibrium term accounts for a large part of the deviations in the power law expression. Apparently only the CO dependence is not completely described by the clean surface expression, i.e. a deviation of 58% compared to 16.9% and 19.6% for \(\text{H}_2\) and \(\text{CO}_2\) and 18.9% overall deviation. This indicates that CO covers a significant part of the catalyst surface and the tests of different kinetic expressions have been focused on this. \(\text{H}_2\), CO and \(\text{CO}_2\) were all observed to effect the reaction rate. Even though the approach to equilibrium term seems to account for the dependency on \(\text{H}_2\) and \(\text{CO}_2\), expressions with adsorption of both species have been tested, since the three species are connected through the water gas shift reaction. The expression with \(\text{CO}_2\) adsorption is not included in Table 4.1, but gave a fit very similar to that for the expression with \(\text{H}_2\) adsorption, i.e. no significant improvement compared to the clean surface expression. The different parameter fits found for the expression assuming CO as the most abundant surface species in table 4.1, exemplify an inherent weakness in micro kinetic models. Several different sets of parameter values were found that gave a good fit to the experimental data, illustrating that the large number of model parameters enables a fit, event though the assumptions may not be correct. In litterature, the activation energy of CO adsorption is reported to be around -100 kJ/mol [6, 7, 27]. The first set of parameters for the expression with CO adsorption is an attempt to find a fit with an adsorption energy in the reported range. It was not possible to obtain even a decent fit with such high values of \(E_{a,\text{CO}}\). The best fit was obtained with a small negative or positive activation energy. Even a fit with \(E_{a,\text{CO}} = 0\) (i.e. temperature independent) gave a good fit. It is, however, expected that the activation energy of adsorption of gases is negative, since adsorption is normally reported to decrease with increasing temperature. An expression with both CO and \(\text{H}_2\) adsorption is also tested, and with positive values of \(E_{a,\text{CO}}\) it was possible to achieve a slightly better fit than for only CO adsorption. Because positive values of activation energy for adsorption are unrealistic and because only a slight improvement was achieved by the addition of two extra model parameters, an expression with CO adsorption only is chosen as the best fit, see Equation 4.6.

\[
\begin{align*}
\begin{align*}
\frac{110 \text{mole}}{\text{gsPa}} &\times \exp\left(-\frac{198 \text{kJ/mole}}{RT}\right) \text{P}_{\text{CH}_4} \left(1 - \frac{Q_r}{K_r}\right) \\
(1 + 1.7 \times 10^{-6} \text{Pa}^{-1} \exp\left(-\frac{26 \text{kJ/mole}}{RT}\right) \text{P}_{\text{CO}})\end{align*}^2 
\end{align*}
\]

This expression was also determined fitted to the kinetic measurements for the industrial anode material, as shown in Equation 4.7, with an overall deviation from experimental data of 19%.

\[
\begin{align*}
\begin{align*}
\frac{100 \text{mole}}{\text{gsPa}} &\times \exp\left(-\frac{195 \text{kJ/mole}}{RT}\right) \text{P}_{\text{CH}_4} \left(1 - \frac{Q_r}{K_r}\right) \\
(1 + 4.6 \times 10^{-7} \text{Pa}^{-1} \exp\left(-\frac{32 \text{kJ/mole}}{RT}\right) \text{P}_{\text{CO}})\end{align*}^2 
\end{align*}
\]
Table 4.1: Summary of the different kinetic expressions fitted to the experimental data, the first six columns show the values of the pre-exponential factor and activation energy for respectively, methane dissociation, CO adsorption and H₂ dissociation. The last five columns show the average deviation between the kinetic expression and the experimental data for: All data points and data with varying H₂O content, H₂ content, CO content and CO₂ content, respectively.

<table>
<thead>
<tr>
<th>Species</th>
<th>Parameter values</th>
<th>Deviation</th>
<th>overall</th>
<th>H₂O</th>
<th>H₂</th>
<th>CO</th>
<th>CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A₀CH₄ mol/g s Pa</td>
<td>EaCH₄ kJ/mol</td>
<td>A₀CO Pa⁻¹</td>
<td>EaCO kJ/mol</td>
<td>A₀H₂ Pa⁻¹/²</td>
<td>EaH₂ kJ/mol</td>
<td>%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Power law</td>
<td>139</td>
<td>185</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>43.7</td>
</tr>
<tr>
<td>Clean surface</td>
<td>227</td>
<td>205</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>18.9</td>
</tr>
<tr>
<td>H</td>
<td>90</td>
<td>196</td>
<td>-</td>
<td>-</td>
<td>1.20E-06</td>
<td>-46</td>
<td>18.6</td>
</tr>
<tr>
<td>CO</td>
<td>100</td>
<td>150</td>
<td>4.70E-07</td>
<td>-100</td>
<td>-</td>
<td>-</td>
<td>67.2</td>
</tr>
<tr>
<td>CO</td>
<td>100</td>
<td>197</td>
<td>4.60E-07</td>
<td>-41</td>
<td>-</td>
<td>-</td>
<td>15</td>
</tr>
<tr>
<td>CO</td>
<td>110</td>
<td>198</td>
<td>1.70E-06</td>
<td>-26</td>
<td>-</td>
<td>-</td>
<td>14.7</td>
</tr>
<tr>
<td>CO</td>
<td>103</td>
<td>197</td>
<td>8.40E-05</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>14.6</td>
</tr>
<tr>
<td>CO</td>
<td>110</td>
<td>198</td>
<td>5.50E-04</td>
<td>18</td>
<td>-</td>
<td>-</td>
<td>14.4</td>
</tr>
<tr>
<td>H+CO</td>
<td>100</td>
<td>196</td>
<td>6.90E-08</td>
<td>-54</td>
<td>9.80E-06</td>
<td>-32</td>
<td>14.7</td>
</tr>
<tr>
<td>H+CO</td>
<td>100</td>
<td>194</td>
<td>1.80E-05</td>
<td>-10</td>
<td>3.70E-05</td>
<td>-37</td>
<td>14.3</td>
</tr>
<tr>
<td>H+CO</td>
<td>100</td>
<td>195</td>
<td>9.10E-05</td>
<td>0</td>
<td>1.70E-05</td>
<td>-34</td>
<td>13.9</td>
</tr>
<tr>
<td>H+CO</td>
<td>100</td>
<td>195</td>
<td>1.10E-03</td>
<td>19</td>
<td>7.50E-06</td>
<td>-40</td>
<td>13.5</td>
</tr>
<tr>
<td>H+CO</td>
<td>100</td>
<td>196</td>
<td>1.10E-02</td>
<td>36</td>
<td>6.00E-06</td>
<td>-45</td>
<td>13.3</td>
</tr>
</tbody>
</table>
The average deviation for the final expression over the industrial anode is 4 percentage points higher than that over the model anode. This increase is, however, located in the measurements with temperature and methane concentration changes, not from the changes in H₂, CO and CO₂ concentrations.

\[ y_{\text{CH}_4} = 40\%, \ y_{\text{H}_2\text{O}} = 60\% \]

\[ y_{\text{CH}_4} = 40\%, \ y_{\text{H}_2\text{O}} = 60\% \]

\[ y_{\text{CH}_4} = 10\%, \ y_{\text{H}_2\text{O}} = 35\%, \ y_{\text{H}_2} = 35\%, \ y_{\text{CO}} = 10\%, \ y_{\text{CO}_2} = 10\% \]

\[ \text{Temperature [}^\circ\text{C}] \]

\[ \text{Rate [mol/s m}^2_{\text{Ni}} \text{]} \]

\[ \text{Log(Rate)} \]

\[ x 10^{-3} \]

Figure 4.1: Comparison of obtained rate expressions with expressions from literature: Boder [14], King [38], and Wei [71].

Assuming an average Ni particle size of 250 nm and that all Ni particle are spherical and only have single point contact with other particles, the Ni surface area of the model anode and industrial anode material is estimated to be 0.16 \text{m}^2/\text{g}. From this estimate, a comparison is made of the expressions obtained in thesis with expressions found in literature, see Figure 4.1. A more thorough comparison of the literature expressions is given in [43]. The rate expression measured by Wei and Iglesia [71] is measured over a classical steam reforming catalyst, and is included as a reference. It is seen that the rates obtained in this thesis are in the same range as those reported in literature, but clearly in the high end of the range, especially at high temperatures.
Furthermore, it is seen that the rates measured for the industrial anode and the model anode are almost identical, and in one instance they are in fact completely overlapping. The packed bed measurements on samples from stacks that have been in use (see Section 3.3.3) have also been fitted with microkinetic expressions. The resulting expressions are shown in Equations 4.8 and 4.9, for the new and old stack, respectively.

\[
\begin{align*}
    r &= 7.1 \text{ mole g}^{-1} P_a \exp \left( \frac{-169 kJ/mole}{RT} \right) P_{CH_4} \left( 1 - \frac{Q_{sr}}{K_{sr}} \right) \\
    r &= 1.12 \text{ mole g}^{-1} P_a \exp \left( \frac{-159 kJ/mole}{RT} \right) P_{CH_4} \left( 1 - \frac{Q_{sr}}{K_{sr}} \right) \left( 1 + 1.1 \times 10^{-8} P_a^{-1} \exp \left( \frac{23 kJ/mole}{RT} \right) P_{CO} \right)^2
\end{align*}
\] (4.8) (4.9)

The measurements on the new stack anode material with variations in CO inlet concentration showed a strong influence of CO on the rate. It was not possible to obtain a good description of this behavior with any of the expressions described in this thesis without also getting a significantly worse fit to the other measurements on this catalyst sample. Because of this, the CO variation measurements are discarded, and as a result no CO dependency is present in the rate expression (Equation 4.8).

On the old stack sample a strong dependency of both CO and CO\(_2\) was observed. These are, however, described reasonably well with the expression in Equation 4.9, even though there is still a rather large deviation from the measurements with variations in CO\(_2\) inlet concentration, i.e. 33%.

Two very interesting observations can be made for the two anode samples that have been subject to stack operation with current production. The first is that they have similar activity with respect to steam reforming, meaning that the rate is not significantly changed after 5500 hours of operation. The second observation is that these two samples have significantly lower activation energy than the samples that have not been used for current production (Equations 4.6 and 4.7). This indicates that the catalytic activity of Ni-YSZ anode material changes significantly when first subjected to a current, but remains relatively constant over time afterwards.

### 4.2 Prediction of Stack Reforming Rate from Intrinsic Kinetics

The rates measured in the stack/cell setup experiments are highly dependent on the configuration of the stack. This means that the rate expression should only be used for modeling stacks with the exact same configuration. So in order to obtain a more general description of the steam reforming rate in a SOFC stack, it has been attempted to make a simple model that can describe the reforming rate in the stack from the intrinsic reaction rate measured in the tubular reactor experiments. The thought is to describe the cell via the design equation for a fixed bed reactor, as shown in Equation 4.10.
\[ \frac{dX_{CH_4}}{dW_{cat}} = \frac{r_{eff}}{N_{CH_4,in}} \]  

(4.10)

\(X_{CH_4}\) is the conversion of methane, \(W_{cat}\) is the catalyst weight, \(N_{CH_4,in}\) is the molar inlet flow of methane, and \(r_{eff}\) is the effective reaction rate described by Equation 4.11.

\[ r_{eff} = \eta \cdot r_{intrinsic} \]  

(4.11)

\(r_{intrinsic}\) is the rate calculated from the kinetic expression determined over the industrial anode, see Equation 4.7 and \(\eta\) is the efficiency factor, calculated from Equation 4.12. \(\eta\) describes how big a fraction of the available catalyst material that is being fully used, i.e. an efficiency factor = 1 corresponds to full usage of the catalyst [19].

\[ \eta = \frac{Tanh(\phi)}{\phi} \]  

(4.12)

\(\phi\) is the Thiele modulus, which is calculated from the expression for a first order reaction on a slab shaped catalyst:

\[ \phi = L \sqrt{\frac{k}{D}} \]

\(L\) is the anode thickness, \(k\) is the rate constant (s\(^{-1}\)), and \(D\) is the effective diffusion coefficient (m\(^2\)s\(^{-1}\)) of methane which is set to 10\(^{-5}\). This value has been estimated based on the experience gained during the model work described in Section 5 and was chosen to represent the diffusion at high temperatures, since this is where diffusion has the largest influence. The expression used here for determining \(\eta\) is valid for systems where pore diffusion is dominant, i.e. intermediate values of \(\phi\). At high and low values of \(\phi\) other estimations should be used. The differential equation is solved using ode45 on matlab, the full matlab code can be seen in Appendix D.

Figure 4.2 shows a comparison of the values obtained with the model described here, with the measurement points as well as the expression fitted to the measurements from the quarter cell stack, see Section 3.4.2. The temperature used in the model is the average of the measurements from the four thermocouples in the quarter cell stack.

Considering the simplicity of the model, it is surprisingly good at predicting the conversion in the stack, with an average deviation between model data and measurements of 44.6%. Keep in mind that the only inputs to the model is the gas composition, the efficiency factor calculated from the structure of the anode, the temperature, and the rate expression from the fixed bed measurements. This approach differs from the majority of the modeling work in literature on two points (1) The study is based on experiments in both a packed bed reactor and a stack, and the results are then compared via this model (2) The influence mass transport limitation through the anode is simplified by describing it with an efficiency factor. This approach is a textbook method in catalytic reaction engineering [23], but is normally not used in fuel cell modeling.
It is seen in Figure 4.2 that the model most often overestimates the degree of conversion, which indicates a systematic error in the measurements or model. Since the steam reforming rate has a high activation energy, it will be sensitive to relatively small variations in temperature, so this parameter is examined closer. As described in Sections 2.1 and 2.5.2, thermocouples are placed close to the catalyst in both setups. There is, however, a difference in the placement of the thermocouples in the two setups. In the fixed bed setup, the thermocouple is placed in the gas channel just after the reaction zone, meaning that an error in the measurement will most likely give a too low temperature. In the stack setup, the thermocouples are placed in the gas distribution plate, and since the stack has lower temperature than the oven chamber, due to cooling both from the gas flow and the steam reforming, any errors in the measurements are likely to overestimate the temperature. In order to see the effect of such a systematic error in the measured temperature, the model is compared to the stack data again, this time with the temperature in the model set 10°C lower than the measurement in the stack, corresponding to a 5°C systematic error in each setup. The result of this is shown in Figure 4.3.

It is seen that the correspondence between measured and predicted values has increased significantly, giving an average deviation of just 26.0%, similar to the error of the first order expression that was fitted directly to the quarter cell stack measurements, see Section 3.4.2.

Figure 4.4 shows a comparison of the measured conversion and the conversion predicted by the model, both at the measured temperature 4.4(a)-4.4(b) and with a 10°C lowered temperature 4.4(c)-4.4(d). With this representation of the deviation between model and measurements, it seems that the 10°C decrease in model temperature does not significantly prove the fit. The greatly improved average deviation for the model with decreased temperature is a bit misleading.
Figure 4.3: Comparison of the measured conversion for the quarter cell stack with both the expression fitted to the data and the results of the model.

since it is the result of an improved fit at the temperatures with many measurements at the expense of a worse fit at other temperatures.

It can also be seen in Figures 4.4(b) and 4.4(d) that the major deviations are at low conversion while higher conversions have a better fit. The points with the largest deviance between model and measurements in Figure 4.4(b) are for measurements with variations in methane concentration at 600°C (four points underestimated by the model) and 675°C (four points overestimated by model). These deviations do not seem to be systematic, and are therefore ascribed to experimental uncertainty.

In conclusion, it has been shown that the model presented here can be used to predict the steam reforming reforming rate over a SOFC anode with reasonable accuracy from an estimated efficiency factor and an intrinsic rate expression. Since the model is easily computed, it is feasible to include it in any type of SOFC model.
(a) Results with measured temperature.  
(b) Zoom at low conversion values from Figure 4.4(a).

(c) Results with temperature lowered by 10°.  
(d) Zoom at low conversion values from Figure 4.4(c).

Figure 4.4: Comparison of measured conversion and the conversion predicted by the model, at the measured temperature 4.4(a)-4.4(b) and with a 10° lowered temperature 4.4(c)-4.4(d)
Chapter 5

Modeling

5.0.1 Model Setup

The gPROMS model describes a fuel cell at steady state as a system of tank reactors, this is illustrated for a single cell crossflow SOFC in figure 5.1. It is assumed that the supplied gases are equally distributed to each channel and that there is no pressure drop in the channel. Since the material used to separate the gas channels is highly porous, it is also assumed that the total cell area is available for reactions and that the gas composition in the ribs between the gas channel is the same as the composition in the channels.

The anode consists of two layers, a 10-20 μm dense layer close to the electrolyte, designed to give good connection between Ni and YSZ, and a 300 μm layer with high porosity in order to ease gas diffusion. This layer is the structural backbone of the cell. These two layers are referred to as the active anode and the anode support.

![Figure 5.1: Illustration of dividing a crossflow cell into nodes [58].](image)

The ribs between the channels are porous and it is assumed that the entire cell area is available for reaction, and that the partial pressures inside the ribs are equal to those in the gas channels. The calculations start in the corner, where both fuel and oxidant enter and then gradually work its way towards the opposite corner. Co- and counter-flow cells are modeled in a similar way, but only for a single channel since all the channels in the cell will be almost identical.

The current density changes across the cell are taken into account by assigning an average current...
density ($i_{ave}$) for the cell and then setting up the constraint shown in eq. 5.1.

$$i_{ave}A_{tot} = \sum i_n A_n$$  \hspace{1cm} (5.1)

It is assumed that the cell voltage is the same for all cell units.

The outlet from each volume element is calculated from the standard equation for a continuously stirred tank reactor (CSTR), where the reaction rate is substituted with the flux through the electrode surface, $J_{i}^{surf}$, eq. 5.2.

$$V = \frac{F_{i0} - F_i}{J_{i}^{surf}}$$  \hspace{1cm} (5.2)

The current density for each cell is calculated from Equation 5.3.

$$U = U_{rev} - i \cdot R_{tot}$$  \hspace{1cm} (5.3)

$U_{rev}$ is the reversible cell voltage and $R_{tot}$ is the sum of the ohmic resistance, $R_{ohm}$, and two resistances used to describe the electrochemical reaction kinetics, $R_{cat}$ and $R_{ano}$.

$$R_{ohm} = k_{0,m} \cdot e^{\frac{E_{A,m}}{RT}}$$  \hspace{1cm} (5.4)

cathode:

$$\frac{1}{R_{cat}} = \frac{4F_a}{R_g T} k_{cat} \left( \frac{p_{O_2}}{p^0} \right)^{m_1} \exp \left( -\frac{E_{A,cat}}{R_g T} \right)$$  \hspace{1cm} (5.5)

anode:

$$\frac{1}{R_{ano}} = \frac{2F_a}{R_g T} k_{ano} \left( \frac{p_{H_2}}{p^0} \right)^{m_2} \exp \left( -\frac{E_{A,ano}}{R_g T} \right)$$  \hspace{1cm} (5.6)

The resistance expressions are based on the impedance data from Barfod et al. [8, 9]. $m_1$ and $m_2$ are both set to 0.25, and the activation energies used are: $E_{A,m} = 1$ eV, $E_{A,cat} = 1.6$ eV and $E_{A,ano} = 1.1$ eV.

The reversible cell voltage is calculated from the Nernst equation, using the gas concentrations at the electrode surface.

$$U_{rev} = -\frac{\Delta G}{2F_a} + \frac{R_g T}{2F_a} \ln \left[ \frac{P_{H_{2}O,ano} \cdot P_{O_{2},cat}^{1/2}}{P_{H_{2}O,cat}^{1/2}} \right]$$  \hspace{1cm} (5.7)

These concentrations are found by modeling the gas diffusion through the electrodes with the dusty gas model which is shown in Equation 5.8. It is assumed that there is no temperature gradient across the electrodes (perpendicular to the gas flow channels) and that the difference in total pressure does not influence the diffusion. The validity of these assumptions are evaluated in Appendix E.

$$\frac{J_i}{D_{j,k}^{eff}} + \sum_{j=1,j\neq i}^n \frac{X_j J_j - X_i J_i}{D_{j,j}^{eff}} = \frac{P}{R_g T} \frac{dX_i}{dz}$$  \hspace{1cm} (5.8)
z is the position in the electrode with \( z = 0 \) at the gas channel, \( D_{i,k}^{eff} \) is the effective Knudsen diffusion, and \( D_{ij}^{eff} \) is the effective binary diffusion coefficient (see Appendix G for further information). The effective diffusion coefficient \( (D_{i}^e) \) for each component is defined so that eq. 5.9 is true.

\[
J_i = -\frac{D_i^e}{R_g T} \frac{dP_i}{dz}
\]  

(5.9)

Which gives an effective diffusion coefficient \( (D_{i}^e) \) as shown in eq. 5.10.

\[
D_{i}^e = \left(\sum_j \frac{1}{D_{ij}^{eff}} \left( X_j - \frac{J_j}{J_i} X_i \right) + \frac{1}{D_{i,k}^{eff}}\right)^{-1}
\]  

(5.10)

For co- and counter-flow \( D_{i}^e \) is calculated for the average value of the gas concentrations across the electrode in each unit cell. For crossflow configuration a single value is used for the entire cell in order to reduce the number of equations.

When the cell is modeled without methane, the molar flux of hydrogen and water on the anode side and oxygen on the cathode side is found from Faraday’s law, describing the rate of the electrochemical reactions \( (r_{EC}) \) through the current density, as shown below.

\[
r_{EC} = \frac{i}{F_a} = 2J_{H_2} = -2J_{H_2O} = -4J_{O_2}
\]  

(5.11)

\( F_a \) is the Faraday constant.

When steam reforming is included in the model, the flux changes through the anode support as gas species are produced or consumed. The flux change is described by Equation 5.12 derived from a mass balance at steady state.

\[
\frac{dJ_i}{dz} = \sum r_i |z|
\]  

(5.12)

\( r_i \) is the reaction rate for the species as shown in Table 5.1. The reaction rate of the electrochemical reaction is used as boundary condition for Equation 5.12.

<table>
<thead>
<tr>
<th>( r_i ) term, ( \text{mol} )</th>
<th>CH4</th>
<th>CO</th>
<th>CO2</th>
<th>H2</th>
<th>H2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode Support</td>
<td>(-r_{SR})</td>
<td>(r_{SR} - r_{WGS})</td>
<td>(r_{WGS})</td>
<td>(3r_{SR} + r_{WGS})</td>
<td>(-r_{SR} - r_{WGS})</td>
</tr>
<tr>
<td>Active Anode</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>(1/2 - r_{EC})</td>
<td>(1/2r_{EC})</td>
</tr>
</tbody>
</table>

The steam reforming rate is found from the intrinsic reaction rate expression found in the packed bed experiments and the rate of the water gas shift reaction is found by assuming that it is at equilibrium in all points.

The temperature in a cell unit is calculated from an energy balance.
\[
In + \text{Produced} = \text{out} + \text{accumulated}
\]
\[
In = Q
\]
\[
\text{Produced} = \sum_{i=1}^{n} F_i H_i|_{in} - \sum_{i=1}^{n} F_i H_i|_{out}
\]
\[
\text{out} = P_{el}
\]
\[
\text{accumulated} = \frac{dE_{\text{sys}}}{dt} = 0
\]
\[
\frac{dE_{\text{sys}}}{dt} = 0 = Q - P_{el} + \sum_{i=1}^{n} F_i H_i|_{in} - \sum_{i=1}^{n} F_i H_i|_{out}
\]

(5.13)

Q is the heat supplied from the surroundings and P_{el} is the electrical power produced in the cell unit. This means that Q is heat transferred through the interconnect material as described by eq. 5.14.

\[
Q = \frac{Ak(T_{\text{sur}} - T)}{L}
\]

(5.14)

\(T_{\text{sur}}\) is the temperature of the surroundings, which can be either other cells in a stack, or the oven, depending on the system and the placement of the cell in question. The produced electrical power, P_{el}, is calculated as described by eq. 5.15.

\[
P_{el} = AiU
\]

(5.15)

By inserting eq. 5.14 and 5.15 into eq. 5.13, as well as inserting the temperature dependent expression for the enthalpy, eq. 5.16 is obtained.

\[
2\frac{Ak(T_{\text{sur}} - T_{\text{out}})}{L} - AiU + \sum_{i=1}^{n} F_i(\Delta H_{f,i} + C_p T)|_{in} - \sum_{i=1}^{n} F_i\Delta H_{f,i} + C_p T)|_{out} = 0
\]

(5.16)

The temperature at the gas inlet is assumed to be the temperature of the oven. This assumption is valid for a small lab test, as the one used for comparison here, but it will not be valid for an industrial size stack. The heat capacity of the gases is found from eq. 5.17.

\[
C_{p,i} = C_{1,i} + C_{2,i}T + C_{3,i}T^2
\]

(5.17)

The values of the constants for each species can be found in appendix F.

5.0.2 Performance and Results

The gPROMS model was developed over several stages, with each step including an additional effect. Only results from the two last versions of the model will be presented here, ie. with and without internal steam reforming. For further information on the model work, see [20, 41].
While adding internal steam reforming to the model another change was also made. Previously, it was assumed that the first unit cell in each flow direction had the same temperature as the oven temperature. This assumption was abandoned and replaced with a total energy over the cell. The effect of this change can be seen in Figure 5.2.

Figure 5.2: Comparison of predicted temperature profiles while respectively assuming that the temperature of first unit cell in each flow direction has the same temperature as the oven (gray curves) and calculating the temperature of the first unit cell from an overall energy balance (black curves) [20].

Since most of the cooling is caused by the air flow, the biggest change is seen for the countercurrent cell. In this configuration the air at the cathode outlet has been heated significantly from the inlet temperature, which is in direct conflict with this assumption.

The addition of internal steam reforming significantly increased the number of equations. In the model for coflow and counterflow where only a single channel was modelled, it was still possible to solve the equation system. For crossflow it is, however, necessary to model an entire cell so when reforming was included, the number of equations became too large for gPROMS to solve.

Figure 5.3 show the temperature and current profile for a crossflow cell without steam reforming. The sharp drop in temperature at the anode inlet is an effect of the assumption that was later removed as described in Figure 5.2.

Figure 5.4 show the modeled temperature and current profiles for coflow and counterflow cells at T = 750°C and different S/C ratios. It is seen that for counterflow, both ends of the channel are cooled by steam reforming at the anode inlet and the large air flow at the cathode inlet. For cocurrent flow it is seen that there is a rapid cooling at the anode inlet caused by steam reforming followed by heating from the electrochemical reactions through the rest of the cell.

The cell potential calculated for the two configurations is 0.498 for cocurrent flow and 0.546 for countercurrent flow, meaning that the countercurrent configuration has better efficiency at the same conditions. This also means that less waste heat is generated in the countercurrent configuration, as illustrated by in Figure 5.4 where the cathode outlet temperature is lower for
Figure 5.3: Temperature and current profile in a crossflow cell without internal steam reforming.

Figure 5.4: Temperature and current profiles in coflow and counterflow cells with internal steam reforming at \( T = 750^\circ C \) for different S/C ratios with an average current density set to 10,000 A/m\(^2\). Grey lines represent countercurrent flow and black lines represent cocurrent flow.
countercurrent than for cocurrent flow.

In conclusion, the model gives a good representation of the effects taking place in a SOFC with internal steam reforming but further refinement of the model is needed in order to give an accurate representation of a real cell. Severe problems have, however, been encountered during the final work on this model in gPROMS. The difficulties occur because of the way gPROMS handles differential and integral problems. When making a numerical differentiation with for example 10 sections, gPROMS takes all equations and variables in the differential problem and solves them separately in each section of the differentiation, i.e. 10 equations in 10 sections give a total of 100 variables and equations. When such a problem is expanded to 20 equations, 10 sections through the anode, 10 sections through the cathode, and 100 sections in each of the two flow directions (cross flow cell), the result is an equation system with 4 million variables and equations. gPROMS will attempt to solve this as if all equations and variables are completely independent. This also makes trouble-shooting exceedingly difficult, when an error message states that the system contains 4,000,001 independent variables and only 4,000,000 independent equations and then provides a list of all equations and variables.

Even though it was attempted to reduce the number of equations generated, the final system could only be solved with starting values very close to the result. Because of this, it is not recommended to use gPROMS for models involving differential or integral equations in multiple dimensions. The model presented here may still be viable to use for stack modeling, but it will need to be implemented in another program, which is better suited for computational heavy models. In literature, the issue of accuracy versus computational requirements is addressed by three different overall approaches, depending on the intended use of the model [43]:

**Micro Models (electrode models)** describe in great detail the catalytic, electrochemical and gas phase reactions in the porous electrodes, often taking into account mass and heat transfer effects as well as electrical conduction. This type of model will normally be 1-dimensional and describes the performance of a cell in a single point with known bulk concentrations, this can be used to determine key issues for material research and micro structural optimization. [27, 68, 69]

**Cell/stack Models** examine the changes in composition and temperature in the gas channels of an SOFC and they will often have a simplified description of the electrodes and electrolyte in order to avoid excessive computations. These models are 2- or 3-dimensional and can be used to evaluate concentration and temperature profiles in the cell/stack, and thereby identify trouble areas such as hotspots or areas with low S/C ratio. single cell models can to some extent incorporate a micro structure model [17, 27, 29, 33, 46, 49, 66]

**System Models** describe the performance of a complete stack, they are highly simplified and are normally focused on the interaction of the stack with the surroundings. These models are zero- or 1-dimensional and intended to be incorporated in flow sheets in order to
evaluate and optimize complete systems which includes an SOFC. [15, 16, 18, 21, 44, 52, 64]

Since SOFC technology is approaching maturity [31, 39, 60], a special emphasis should be placed on system models. A particularly strong approach for future work in obtaining a simple stack model for flow sheeting, would be to start from an extensive stack model, as the one presented in this section, and then gradually remove or simplify the different effects in the model, while evaluating the influence of each effect on the model results.
Chapter 6

Summary and Conclusion

During the experimental rate measurements, it was discovered that the Ni-YSZ catalyst showed a previously unreported dynamic behavior with respect to steam reforming activity. First of all, the anode material has very high catalytic activity but this activity is reduced with a factor 5-10 during the initial deactivation period which takes several days at high temperature (800°C) and up to two weeks at low temperature (600°C). It has recently been reported that Ni nano particles are produced during the reduction of NiO [34, 38]. Such nano particles are also observed in the TEM measurements in Section 3.2.2 and this explains the high initial activity of the catalyst. The subsequent deactivation is most likely caused by sintering of the nano particles, this is also supported by TEM, see Section 3.1.

After the initial deactivation, changes in temperature or hydrogen partial pressure resulted in an approach to steady state over several days. Such slow response indicates that structural changes are taking place and since the effect is completely reversible, it is suspected that it is caused by the individual Ni particles changing structure, i.e. the sphericity of the particles is changed. Such a change will affect the Ni surface area, but more importantly, it will affect the amount of the Ni step sites, which has been shown by in-situ spectroscopy to be the most active sites for steam reforming [28, 65]. Density functional theory calculations have further shown that these step sites are approximately 100 times more active than terrace sites [5], so it is plausible that this can effect the overall reaction rate. In a SOFC stack under normal operation, temperature, and especially hydrogen concentration will vary with position in the stack. Meaning that the micro structure of the anode material will not necessarily be the same throughout the stack.

It was also discovered that exposing the Ni-YSZ anode material to H$_2$O/H$_2$ for longer periods (16 hours) results in a reactivation of the catalyst up to the initial activity. Examination of a reactivated sample with TEM indicated that a redispersion of the Ni particles had taken place, i.e. a lowering of the average Ni particle size. A mechanism for such a redispersion has been reported by Ruckenstein and Hu [63] involving extension of films from the crystallites, followed by coalescence of the films.

It should be emphasized that the characterization of the samples did not unanimously show redispersion...
persion of Ni particles, and other possibilities should still be considered, for example poisoning of the active sites or other surface effects. The YSZ particles were also observed to change structure, but this was not investigated further.

A practical conclusion from these observations is that initial operation of a new stack should be done with a low methane content in order to avoid steep temperature gradients due to the high initial reforming rate. After deactivation has taken place, the methane content can be increased to the intended operating level. Furthermore, it is important to be aware of possible reactivation of catalyst activity after operation without methane, in this case a new deactivation with low methane content should be conducted, before normal operation is resumed.

Kinetic measurements were also made on anode samples from two stacks, which have been operated with current production, one for a few days and the other for 5500 hours. The results indicate that the catalytic activity of Ni-YSZ anode material changes significantly when first subjected to a current, but it remains relatively constant over time afterwards.

A model of a SOFC stack element with internal steam reforming was made, and implemented in gPROMS. It was found that gPROMS is not suited for this type of model because the number of generated equations become to large to handle. More work is needed on this model before it can be used for practical applications.

The catalytic steam reforming activity of Ni-YSZ anode material was measured both in a packed bed setup and in a stack configuration, with good repeatability in both setups. The packed bed measurements were designed to measure intrinsic, i.e. no mass transport limitations. Four different samples were tested in this setup, a model anode material, a fresh sample of an industrial anode, and two samples from stacks that have been in use. It was found that the observed rates were best described by a kinetic expression derived by assuming CH\textsubscript{4} dissociation as the rate determining step, and with CO being the most abundant species on the catalyst surface.

Equation 6.1 shows the rate expression found for the model anode material, and this expression is also valid for the fresh industrial anode, since the observed rates on these two catalysts were nearly identical.

\[
r = \frac{110 \text{ mole/gPa} \exp\left(-\frac{1986 \text{kJ/mol}}{RT}\right) P_{\text{CH}_4} \left(1 - \frac{Q_{\text{sr}}}{kT}\right)}{\left(1 + 1.7 \times 10^{-6} P a^{-1} \exp\left(-\frac{262 \text{kJ/mol}}{RT}\right) P_{\text{CO}}\right)^2}
\]  

(6.1)

Stack measurements were made on a half cell stack and a quarter cell stack, and the obtained rate expression is shown in 6.2.

\[
r = 2 \times 10^4 \frac{\text{mole}}{\text{sm}^2P_a} \exp\left(-\frac{166.3 \frac{kJ}{\text{mole}} R_g}{T}\right) P_{\text{CH}_4}^{0.7}
\]  

(6.2)

Finally a simple model was made to try and predict the activity in a stack from the intrinsic rate expression obtained in the packed bed measurements. The model describes the activity in the stack by the design equation for a fixed bed reactor and includes mass transport limitations.
via an estimation of the efficiency factor. The model had an surprisingly good fit to the stack measurements with an average deviation comparable to that of the rate expression that was fitted to the measurements, Equation 6.2. The combination of simplicity and good accuracy in predicted reaction rate makes this model ideal for use in stack models for flow sheeting.
Chapter 7

Outlook

There is still more work to be done before steam reforming over Ni-YSZ SOFC anode material is completely understood. The most important experimental work for future investigations is the observed reactivation of the catalyst when exposed to $\text{H}_2\text{O}/\text{H}_2$ without methane. Examinations in this thesis indicate that the reactivation was caused by a redispersion and/or restructuring of the Ni particles. An in-situ investigation of this effect would be very interesting, but is complicated by the long time-frame of the Ni particle changes. An increase in steam reforming rate with a factor of 5-10 can be critical to an SOFC stack, so it would also be highly useful to examine more thoroughly which conditions may cause a reactivation.

Another observation that could be examined more closely is the effect of $\text{H}_2$ content on the rate. In short term it does not influence the rate, but in long term it seems to have an effect, possibly by changing the sphericity of the Ni particles. Since hydrogen partial pressures change greatly across an SOFC, it would be interesting to investigate this further, especially, at high $\text{H}_2$ content, which has not been examined in this thesis.

Observations also indicated that the structure of the YSZ support material can be subject to change. Similar observations have been reported in literature, but the phenomena has not been subject to an actual investigation.

The results presented in this thesis are an excellent basis for deeper modeling. A highly detailed stack model was developed, but for future work it is recommended to split the effort into two separate directions: 1) A detailed model for a small part of a cell, either a small unit cell or at most a single gas flow channel. 2) A stack model using simplified descriptions of the cells. These simplified descriptions should preferably be made on the basis of knowledge gained both from experimental work and detailed modeling work. Especially a simple but reasonably accurate stack model for use in flow sheet calculation could be instrumental in the development of optimized design and operation of SOFC systems. The dual approach is, however, preferable since experience from detailed modeling will greatly aid in deciding which effects does not need to be included in a simple model.
Bibliography


Appendix A

Equipment

A.1 Evaporator tests

Three different water evaporators were used in this thesis. The evaporators on the stack setup, 137-1A, and on of the packed bed setups, 137-5B, were both principally a heated bubble flask. The evaporator on setup 137-1A was delivered as a part of the setup from FuelCon, the evaporator on setup 137-5B was built in-house. The performance of these two evaporators is shown in Figures A.1 and A.2

\[ y = -0.7776x^2 + 2.4207x \]
\[ R^2 = 0.9601 \]

![Figure A.1: Steam flow as a function of the nitrogen flow through the evaporator of the stack setup 137-1A.](image)

The evaporator on the second packed bed setup, 137-4A, was also built in-house. It consists of a Nafion tube (Perma Pure, MD Gas Dryer) with a outer diameter of 0.108 inches in a heated water bath. The Nafion tube is permeable by water gas, and the idea is that there should be no liquid water present inside the tube but the gas should be fully saturated by water. A schematic

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A drawing of this evaporator is shown in Figure A.3. This evaporator did not work well. The tube had to be replaced several times because of leaks, and, as a result of this, the performance was highly unreliable, often the water flow had large and rapid fluctuations. Even in the periods, where it worked relatively good, it was difficult to predict the amount of water delivered at a certain flow. Instead a HygroFlex humidity sensor from ROTRONIC was used to measure the water content in the inlet gas. Unfortunately, it was later discovered that this humidity sensor was not reliable.
Figure A.2: Steam flow as a function of the nitrogen flow through the evaporator of the packed bed setup 137-5B.

Figure A.3: A schematic drawing of the evaporator for the packed bed setup 137-4A.
A.2 Piping and Instrumentation Diagrams

Figure A.4: P&ID diagram for the packed bed setups [20].
Figure A.5: P&ID diagram for the stack setup.
Appendix B

Reaction Rate Order Measurements

B.1 Reaction Rate Orders in Methane for the Model Anode

![Graphs showing reaction rate orders in methane for different temperatures: (a) Measured CH$_4$ dependency at 600°C, (b) Measured CH$_4$ dependency at 625°C, (c) Measured CH$_4$ dependency at 650°C, (d) Measured CH$_4$ dependency at 675°C.]

Rate order = 0.779

Partial Pressure [kPa]: $P_{H_2O} = 30 \pm 0.11$ kPa, $P_{H_2} = 7.46 \pm 0.053$ kPa

Rate order = 0.839

Partial Pressure [kPa]: $P_{H_2O} = 29.9 \pm 0.13$ kPa, $P_{H_2} = 7.58 \pm 0.054$ kPa

Rate order = 0.906

Partial Pressure [kPa]: $P_{H_2O} = 29.8 \pm 0.27$ kPa, $P_{H_2} = 8.19 \pm 0.27$ kPa

Figure B.1: Measured CH$_4$ dependencies over the model anode material.
(a) Measured CH$_4$ dependency at 700°C.

(b) Measured CH$_4$ dependency at 725°C.

(c) Measured CH$_4$ dependency at 750°C.

(d) Measured CH$_4$ dependency at 775°C.

(e) Measured CH$_4$ dependency at 800°C.

**Figure B.2:** Measured CH$_4$ dependencies over the model anode material.
B.2 Reaction Rate Orders in Methane for the Industrial Anode

(a) Measured CH\textsubscript{4} dependency at 625°C.  
(b) Measured CH\textsubscript{4} dependency at 650°C.  
(c) Measured CH\textsubscript{4} dependency at 675°C.  
(d) Measured CH\textsubscript{4} dependency at 700°C.

Figure B.3: Measured CH\textsubscript{4} dependencies over the industrial anode material.
Figure B.4: Measured CH₄ dependencies over the industrial anode material.
B.3 Reaction Rate Orders in Methane for the Stack Samples

Figure B.5: Measured CH$_4$ dependencies over the old stack anode sample.
Figure B.6: Measured CH4 dependencies over the new stack anode sample.
B.4 Half Cell Stack

B.4.1 Gas Composition Changes at T = 600°C

Figure B.7: Measured dependencies over the half cell stack at 600°C.
B.4.2 Gas Composition Changes at $T = 700^\circ C$

(a) Measured $H_2$ = dependency at 700°C.

(b) Measured $H_2$ dependency at 700°C.

(c) Measured CO dependency at 700°C.

(d) Measured CO$_2$ dependency at 700°C.

Figure B.8: Measured dependencies over the half cell stack at 700°C.
B.4.3 Gas Composition Changes at $T = 800^\circ C$

(a) Measured $\text{CH}_4$ dependency at $800^\circ C$.

(b) Measured $\text{H}_2\text{O}$ dependency at $800^\circ C$.

(c) Measured CO dependency at $800^\circ C$.

(d) Measured $\text{CO}_2$ dependency at $800^\circ C$.

Figure B.9: Measured dependencies over the half cell stack at $800^\circ C$. 
B.5 Quarter Cell Stack

(a) Measured CH$_4$ dependency at 600°C.

(b) Measured CH$_4$ dependency at 625°C.

(c) Measured CH$_4$ dependency at 675°C.

(d) Measured CH$_4$ dependency at 725°C.

Figure B.10: Measured CH$_4$ dependencies over quarter cell stack.
Figure B.11: Measured CH₄ dependencies over quarter cell stack.
Appendix C

Derivation of Kinetic Expressions

The 9 elementary reactions used to describe the catalytic steam reforming of methane are shown below, where a * denotes an active site on the catalyst.

1. \( CH_4 + 2^* \rightarrow CH_3^* + H^* \)
2. \( CH_3^* + ^* \rightleftharpoons CH_2^* + H^* \)
3. \( CH_2^* + ^* \rightleftharpoons CH^* + H^* \)
4. \( CH^* + ^* \rightleftharpoons C^* + H^* \)
5. \( H_2O + 2^* \rightleftharpoons HO^* + H^* \)
6. \( HO^* + ^* \rightleftharpoons O^* + H^* \)
7. \( C^* + O^* \rightleftharpoons CO^* + ^* \)
8. \( CO^* \rightleftharpoons CO + ^* \)
9. \( 2H^* \rightleftharpoons H_2 + 2^* \)

The derivation of kinetic expressions all build on assuming which one or two of the above reactions are rate limiting, and then assuming that all other reactions are at quasi-equilibrium. The Equilibrium equations for each reaction is written as shown below, where \( \theta_i \) denotes the surface coverage of the species \( i \).

1. \( K_1 = \frac{\theta_C \theta_H}{\theta_{CH_4} \theta_H^*} \)
2. \( K_2 = \frac{\theta_C \theta_H}{\theta_{CH_3} \theta_H^*} \)
3. \( K_3 = \frac{\theta_C \theta_H}{\theta_{CH_2} \theta_H^*} \)
4. \( K_4 = \frac{\theta_C \theta_H}{\theta_{CH} \theta_H^*} \)
5. \( K_5 = \frac{\theta_{CH_4}\theta_H}{P_{H_2}^2} \)
6. \( K_6 = \frac{\theta_{C}\theta_{H_2}}{P} \)
7. \( K_7 = \frac{\theta_{CO}\theta_{H}}{P_{CO}} \)
8. \( K_8 = \frac{P_{CO}\theta_{H}}{P_{H_2}} \)
9. \( K_9 = \frac{P_{H_2}\theta_2}{\theta_{H_2}} \)

**Assumption: Reaction 1 is RDS**

The rate expression for Reaction 1 is:

\[
r = k_{1+} P_{CH_4} \theta_{CH_4}^2 - k_1 - \theta_{CH_4} \theta_H \tag{C.1}
\]

\( \theta_H \) is determined from equation 9

\[
\theta_H = \frac{1}{\sqrt{K_9 P_{H_2}}} P_{H_2}^{1/2} \theta_* \tag{C.2}
\]

\( \theta_{CH_4} \) is determined from equation 2, and is then rewritten by inserting expressions for the coverages of different species obtained from reactions 3-8, as shown below. Each new line is commented with what equations has been used to obtain it from the previous line.

\[
\theta_H = \frac{1}{K_2 \theta_{CH_4}} \theta_* \tag{eq.2}
\]

\[
\theta_H = \frac{1}{K_2 K_3 K_4 \theta_{H_2}} \theta_* \tag{eq.3 + 4}
\]

\[
\theta_H = \frac{1}{K_2 K_3 K_4 K_7 K_8 \theta_{H_2}} \theta_* \tag{eq.7}
\]

\[
\theta_H = \frac{1}{K_2 K_3 K_4 K_5 K_6 K_7 K_8 \theta_{H_2}} \theta_* \tag{eq.8}
\]

\[
\theta_H = \frac{1}{K_2 K_3 K_4 K_5 K_6 K_7 K_8 \theta_{H_2}} \theta_* \tag{eq.9}
\]

Inserting the expressions for \( \theta_{CH_4} \) and \( \theta_H \) into Equation C.1 gives the following:

\[
r = k_{1+} P_{CH_4} \theta_{CH_4}^2 - \frac{k_1 - \theta_{CH_4} \theta_H}{K_2 K_3 K_4 K_5 K_6 K_7 K_8 K_9 \theta_{H_2}^2} \tag{C.11}
\]
Which in turn can be re-written to:

\[ r = kP_{CH_4} \left( 1 - \frac{Q_{sr}}{K_{sr}} \right) \theta_2^* \quad (C.12) \]

Where all the equilibrium constants have been combined to give the equilibrium constant of the steam reforming reaction, the forward reaction rate for reaction 1 has been renamed as the rate constant for the entire reaction, and Q is defined as shown in C.13.

\[ Q = \frac{P_{H_2}^3 P_{CO}}{P_{CH_4} P_{H_2} O} \quad (C.13) \]

The number of free sites, \( \theta_2^* \), is then either assumed to be 1, i.e. clean surface, or is determined from the adsorption of the species assumed to be the most abundant on the surface, as shown later in this appendix.

**Assumption: Reaction 7 is RDS**

The rate expression for Reaction 7 is:

\[ r = k_7 \theta_C \theta_O - k_7^- \theta_{CO} \theta_2^* \quad (C.14) \]

\( \theta_C \) can be determined by combining equilibrium equations 1, 2, 3, 4 and 9:

\[ \theta_C = K_1 K_2 K_3 K_4 K_9 \frac{P_{CH_4}}{P_{H_2}} \theta_2^* \quad (C.15) \]

\( \theta_O \) can be determined by combining equilibrium equations 5, 6 and 9:

\[ \theta_O = K_5 K_6 K_9 \frac{P_{H_2} O}{P_{H_2}} \theta_2^* \quad (C.16) \]

\( \theta_{CO} \) can be determined from equilibrium equation 8:

\[ \theta_{CO} = \frac{1}{K_8} P_{CO} \theta_2^* \quad (C.17) \]

and now the reaction rate can be written as:

\[ r = k_7 \theta_C \theta_O - k_7^- \frac{1}{K_8} P_{CO} \theta_2^* \]

Which can be re-written to:

\[ r = kP_{CH_4} \frac{P_{H_2} O}{P_{H_2}^3} \left( 1 - \frac{Q_{sr}}{K_{sr}} \right) \theta_2^* \quad (C.19) \]

**Surface Coverage**

\[ 104 \]
If it is assumed that the catalyst surface is free from adsorbents, then $\theta_*$ in the rate expressions is set to 1. This assumption is more likely to be correct as the temperature increases.

If this assumption cannot be made, then an assumption must be made instead on which adsorbent is the most abundant species on the catalyst surface. As an example, H and CO are assumed to be the most abundant species giving the following expression for the number of free surface sites ($\theta_*$)

$$\theta_* = 1 - \theta_{CO} - \theta_H$$  \hfill (C.20)

Inserting Equilibrium equations 8 and 9 gives:

$$\theta_* = 1 - \frac{1}{K_8} P_{CO} \theta_* - \frac{1}{\sqrt{K_9}} P_{H_2}^{1/2} \theta_*$$  \hfill (C.21)

$$\theta_* = \frac{1}{1 + \frac{1}{K_8} P_{CO} + \frac{1}{\sqrt{K_9}} P_{H_2}^{1/2}}$$  \hfill (C.22)

Equation C.22 can then be inserted in the kinetic expression. Note that this is a typical Langmuir-Hinshelwood isotherm.
Appendix D

Matlab Code for Simple Stack Reforming Model Calculations

clear all
close all
clear all
clc

% loading the experimental data
M = dlmread('800C_CH4.txt');
M = [M ; dlmread('800C_CH4_Part1.txt')];
M = [M ; dlmread('775C_CH4.txt')];
M = [M ; dlmread('750C_CH4.txt')];
M = [M ; dlmread('725C_CH4.txt')];
M = [M ; dlmread('700C_CH4.txt')];
M = [M ; dlmread('675C_CH4.txt')];
M = [M ; dlmread('650C_CH4.txt')];
M = [M ; dlmread('625C_CH4.txt')];
M = [M ; dlmread('600C_CH4.txt')];
M = [M ; dlmread('650C_H2.txt')];
M = [M ; dlmread('650C_H2O.txt')];
M = [M ; dlmread('650C_CO2.txt')];
M = [M ; dlmread('750C_H2.txt')];
M = [M ; dlmread('750C_H2O.txt')];
M = [M ; dlmread('750C_CO.txt')];
M = [M ; dlmread('750C_CO2.txt')];
% dividing the loaded data into proper variables
for i = 1:6
    P_in(:,i) = M(:,i+8);
P_out(:,i) = M(:,i+14);
end

rate_measured = M(:,7);
k = M(:,8);
T_all = M(:,3:6);

% taking the average of the 4 T measurements for each measurements point
for i = 1:length(k)
    T(i,1) = mean(T_all(i,:));
end

Ftot = 2; % Nl/min

Rg = 8.314; % J/mol K
l = length(M(:,1));

X1 = M(:,1);
X2 = M(:,2);
N_in = P_in*1000*Ftot/(60*1000)/(Rg*298);

% input of size of the stack
anode_area = 9.6*2.4/10000; % m2
anode_volume = anode_area * 300 * 10^-6; % m3 half cell
anode_density = 0.52 * 7.7 * 10^6; % g/m3
anode_weight = anode_volume * anode_density; % g

% Calculating the conversion predicted by the model using ode45 and the
% differential system in the function diffsystem_rate
options = odeset('abstol', 1e-12, 'MaxStep', 1/10);
for i = 1:l
    Ptot(i) = sum(P_in(i,:))*1000;
    [W,X] = ode45(@(W,X)diffsys_rate(W, X,N_in(:,i),T(i),Ptot(i),X2(i)), [0 anode_weight], 0,op-
\( X_{\text{model}}(i) = X(\text{length}(X)); \)
\( \text{dev}(i) = \sqrt{((X1(i) - X_{\text{model}}(i))/X1(i)*100)^2}; \)
\end{tabular}

% calculating the average error
\( \text{avg\_err} = \text{mean(\text{dev})} \)

% plotting measured conversion and model conversion against temperature
figure(1)
hold on
plot(X, X_{\text{model}}, 'or')
plot(X, X1, 'x')
xlabel('T [^\circ\text{C]}', 'fontsize', 16)
ylabel('Conversion', 'fontsize', 16)
axis([540 775 0 0.8]);
legend('Model', 'Measured')
set(gca, 'fontsize', 16);
hold off

% plotting model conversion and measured conversion against each other
figure(2)
hold on
plot(X1, X_{\text{model}}, 'xk')
plot([0 1], [0 1], 'k')
axis([0 0.8 0 0.8]);
xlabel('Measured conversion', 'fontsize', 16)
ylabel('Model conversion', 'fontsize', 16)
set(gca, 'fontsize', 16);
hold off
% differential equations system

function dXdW = difsys_rate(W, X1,N_in,Temperature,Ptot,X2)  

N = [N_in(1).*(1-X1), 
N_in(2), 
N_in(3)-N_in(1).*X1.*(1+X2)-N_in(5).*X2, 
N_in(4)+N_in(1).*X1.*(3+X2)+N_in(5).*X2, 
N_in(5)+N_in(1).*X1.*(1-X2)-N_in(5).*X2, 
N_in(6)+N_in(1).*X1.*X2+N_in(5).*X2];  % molar flows at the anode outlet

P = N/sum(N)*Ptot;  
D = 10^-5;  % diffusion coefficient

% calculating the reaction rate at the given conditions using the function  
% func
rate = func(P,Temperature,[110 1.7*10^-6], [197000 -26000]);

k = rate/P(1)*8.314*(Temperature+273);  
thiele = 300* 10^-6*(k*6*(10^-6)-1/D)^*(1/2);  
eff = tanh(thiele)/thiele

% differential equations
dXdW(1,1) = N_in(1)*-1* eff* rate;  %mol/g s
function r = func(PartP,Temperature, par,Ea) % antager X2 konstant over hele reaktoren

% calculating the approach to equilibrium of the steam reforming reaction using the function
SReq
QK_SR = SReq(Temperature,PartP);

% calculating the rate
r = par(1) * exp(-Ea(1)/(Temperature+273.15)*8.314)) * PartP(1).* (1-QK_SR)/(1+par(2)* exp(-Ea(2)/(Temperature+273.15)*8.314)) * PartP(5))^-2;
% Approach to equilibrium of Steam reforming reaction (1-Q/K)

function QK = SReq(T,P) %T in oC, P in Pa
R = 8.314; %m^3·Pa·K^-1·mol^-1
a = [8.563 379.724 -1305.0038 1925.624 -1513.266 616.624 -102.4073]; % Cp parameters

% calculating enthalpy and entropi
H = 206.170 + a(1)*((T+273.15)./1000-a(1)*298.15/1000);
S = 214.61 + a(1)*log((T+273.15)./1000) - a(1)*log(298.15/1000);
for i=1:6
    H = H + a(i+1)*((T+273.15)./1000).^(i+1)/(i+1) - a(i+1)*(298.15/1000).^(i+1)/(i+1);
    S = S + a(i+1)*((T+273.15)./1000).^i/(i) - a(i+1)*(298.15/1000).^i/(i);
end

% calculating gibbs energy and the equilibrium constant
G = H*1000-(T+273.15).^S;
K = exp(-G./(R.*(T+273.15)));
P = P/10^5; % converting from Pa til bar

% calculating the approach to equilibrium
Q = P(5).*P(4).^3./(P(1).*P(3));
QK = Q/K;
Appendix E

Estimation of Effects Neglected in Model Work

E.1 Temperature

In order to determine whether it is necessary to include the temperature change over the anode support in the model, an order of magnitude calculation is performed. These calculations are performed as a worst case scenario, i.e. highest possible temperature difference over the anode, which means that the following simplifying conditions are used:

- Only methane and water are supplied from the fuel gas flow channel.
- All reactions take place at the boundary between electrolyte and anode.
- Heat transfer only takes place through the YSZ part of the anode support.
- current density = 3 A/cm², Voltage = 0.6 V

The flux of methane is calculated from Faraday’s law.

\[ J_{CH_4} = \frac{i}{4F} = \frac{3 A/cm^2}{4 \cdot 96485 C/mol} = 7.8 \cdot 10^{-2} \frac{mol}{m^2s} \]

The heat produced inside the cell, per second and per geometric anode area (Q/tA), is calculated as the difference between the enthalpy change and the produced electric power.

\[ r_l \frac{Q}{tA} = -\Delta H \cdot J_{CH_4} - i \cdot U \]
\[ = 560.5 \cdot 10^3 \frac{J}{mol} \cdot 7.8 \cdot 10^{-2} \frac{mol}{m^2s} - 3 \frac{A}{cm^2} \cdot 0.6 V \]
\[ = 25.7 \frac{J}{m^2s} \]
Finally the temperature difference over the anode support at steady state can be calculated as the driving force needed to transport the produced heat through YSZ.

\[ \Delta T = \frac{(1 - \epsilon) Q L}{t A k} = \frac{25.7 \cdot 10^3 J}{m^2 s} \cdot \frac{0.6 \cdot 300 \cdot 10^{-6} m}{4 J \text{ms}} = 3.2 \text{K} \]

3°K is such a low temperature difference that it is acceptable to neglect it. When it is furthermore kept in mind that these calculations are for a worst case scenario, it is found that it is valid to assume isothermal conditions across the cell, in the direction perpendicular to the gas flow channels.

E.2 Pressure

There are two causes for mass transport in gasses, concentration gradients causing diffusion, or a total pressure gradient causing a flow. The combined diffusion and reactions taking place in the electrodes can result in a pressure difference across the electrodes. This pressure difference will give a total flow which might result in a change in the partial pressures with respect to a system were diffusion is the only transport mechanism. An order of magnitude calculation of the potential pressure induced flow is calculated for the anode support at the pressure differences observed in the diffusion simulation. The calculations are performed by using the Hagen-Poiseuille equation, eq. E.1 [45].

\[ J = \frac{\epsilon r^2 \Delta P}{8 \eta \tau \Delta x} \quad (E.1) \]

\( \eta \) is the viscosity.

\[ J = \frac{0.4 \cdot (10^{-6} m)^2}{8 \cdot 10^{-5} \text{Pas} \cdot \frac{2000 \text{Pa}}{3 \cdot 300 \cdot 10^{-6} m}} = 11.1 \cdot 10^{-3} \text{m/s} = 0.12 \frac{\text{mol}}{m^2 s} \]

The last conversion is performed by using the ideal gas equation at \( P = 10^5 \text{ Pa} \) and \( T = 1073 \text{ K} \). The result from these calculations is a flux in the same order of magnitude as that caused by diffusion, which indicates that this effect should be included in the model. The actual pressure difference caused by diffusion will be notably lower than calculated here, since the flow caused by pressure difference will decrease the effect. In order to examine this more closely, eq. E.2 can be used. This has, however, not been done in this thesis.

\[ J_i = -\frac{D_{\text{eff}}}{R_k \bar{T}} \frac{d p_i}{d z} + \frac{p_i}{P_{\text{tot}}} \bigg|_{\text{electrolyte}} \frac{\epsilon r^2}{8 \eta \tau} \frac{d P_{\text{tot}}}{d z} \quad (E.2) \]

This is a combination of the Hagen-Poiseuille equation and the expression used for the gas diffusion. If this equation is used it is no longer a good assumption that the partial pressure profile across the electrode is a straight line. Since the efficient diffusion coefficient will also be changing across the electrode, it is not possible to use an analytic solution to the equation, so it will have to be solved by numerical differentiation.
Appendix F

Heat Capacity

Table F.1 lists the constants needed to calculate heat capacity from Equation F.1.

\[
C_{p,i} = C_{1,i} + C_{2,i}T + C_{3,i}T^2
\]  

\[\text{(F.1)}\]

<table>
<thead>
<tr>
<th>Gas</th>
<th>(C_1) J/molK</th>
<th>(C_2) J/molK(^2)</th>
<th>(C_3) J/molK(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)</td>
<td>30.12844245</td>
<td>-5.79294 \cdot 10^{-3}</td>
<td>6.04 \cdot 10^{-6}</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>14.77089659</td>
<td>-7.447162 \cdot 10^{-2}</td>
<td>-1.744 \cdot 10^{-5}</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>30.83658949</td>
<td>9.02285 \cdot 10^{-3}</td>
<td>1.21 \cdot 10^{-6}</td>
</tr>
<tr>
<td>CO</td>
<td>25.8874019</td>
<td>1.22692 \cdot 10^{-2}</td>
<td>-5.17 \cdot 10^{-6}</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>26.50982067</td>
<td>3.959087 \cdot 10^{-2}</td>
<td>-1.146 \cdot 10^{-5}</td>
</tr>
<tr>
<td>O(_2)</td>
<td>23.93966885</td>
<td>2.066157 \cdot 10^{-2}</td>
<td>-1.022 \cdot 10^{-5}</td>
</tr>
<tr>
<td>H(_2)</td>
<td>26.58183734</td>
<td>9.48178 \cdot 10^{-3}</td>
<td>-3.55 \cdot 10^{-6}</td>
</tr>
</tbody>
</table>

Table F.1: Constants for finding the heat capacity of gas species by eq. F.1 [61]
Appendix G

Binary Diffusion Coefficients

The Chapman-Enskog expression, eq. G.1, is used to determine binary diffusion coefficients ($D_{ij}$).

$$D_{ij} = 0.0018583 \sqrt{T^3 \left( \frac{1}{M_i} + \frac{1}{M_j} \right)} \frac{1}{P\sigma_{ij}^2 \Omega_{D_{ij}}}$$  \hspace{1cm} (G.1)

$M$ is the molar mass of the denoted species, $\Omega$ is the dimensionless collision integral, which is a function of the dimensionless temperature, $\kappa T/\epsilon_{ij}$. The parameters $\sigma$ and $\epsilon/\kappa$ can be found as tabulated values for each species, and the value for each pair of species can be estimated by eqs. G.2 and G.3. [12]

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}$$  \hspace{1cm} (G.2)

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$$  \hspace{1cm} (G.3)

The tabulated values of $\sigma$ and $\epsilon$ that are used in this project are shown in table G.1.

<table>
<thead>
<tr>
<th>Species</th>
<th>$\sigma$</th>
<th>$\epsilon/\kappa$</th>
<th>$M$ (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O2</td>
<td>3.433</td>
<td>113</td>
<td>31.999</td>
</tr>
<tr>
<td>N2</td>
<td>3.667</td>
<td>99.8</td>
<td>28.013</td>
</tr>
<tr>
<td>H2</td>
<td>2.915</td>
<td>38</td>
<td>2.016</td>
</tr>
<tr>
<td>H2O</td>
<td>2.641</td>
<td>809.1</td>
<td>18.016</td>
</tr>
<tr>
<td>CO</td>
<td>3.590</td>
<td>110</td>
<td>28.010</td>
</tr>
<tr>
<td>CO2</td>
<td>3.996</td>
<td>190</td>
<td>44.010</td>
</tr>
<tr>
<td>CH4</td>
<td>3.780</td>
<td>154</td>
<td>16.040</td>
</tr>
</tbody>
</table>
In the book "Transport Phenomena" by Bird et al. [12], $\Omega_{D_{ij}}$ is given in a table for different values of $\kappa T/\epsilon_{ij}$. This is not a practical method for programming, so in this project, the equation given by Reid. et al. [61] is used instead, see eq. G.4

$$\Omega_{D_{ij}} = \frac{A}{(T^*)^{B}} + \frac{C}{\exp(DT^*)} + \frac{E}{\exp(FT^*)} + \frac{G}{\exp(HT^*)}$$  \hspace{1cm} (G.4)

$T^* = \kappa T/\epsilon_{ij}$ is the dimensionless temperature and the constants A-H are given below

$$A = 1.06036 \quad B = 0.15610 \quad C = 0.19300$$
$$D = 0.47635 \quad E = 1.03587 \quad F = 1.52996$$
$$G = 1.76474 \quad H = 3.89411$$

The method described here should give the binary diffusion coefficients within 10%.

The Knudsen diffusion is calculated by eq. G.5.

$$D_{i,k} = \frac{8d_p}{3} \sqrt{\frac{R_g T}{2\pi M_i}}$$  \hspace{1cm} (G.5)

The effective diffusion coefficient is calculated from eq. G.6, which is used for calculating both the effective binary and Knudsen diffusion.

$$D_{eff_{ij}} = \frac{\epsilon}{\tau} D_{ij}$$  \hspace{1cm} (G.6)

$\epsilon$ is the porosity and $\tau$ is the tortuosity. The values used for these parameters as well as the pore diameter and thickness are given in table G.2. If values different from those shown here have been used in a simulation, then it will be specifically stated.

| Table G.2: The chosen standard values for $\epsilon$, $\tau$, $d_p$ and thickness. [8] / [59] |
|---------------------------------|----------|----------|----------|
| Anode support                  | 0.5      | 3        | 1        | 300      |
| Anode                           | 0.3      | 8        | 0.4      | 10       |
| Cathode                         | 0.35     | 3        | 0.15     | 15       |

The tortuosity value that is normally used for porous media is 3, but on the basis of work by Peter Vang Hendriksen a value of 8 is chosen for the anode [30].
Article I
Review

Internal steam reforming in solid oxide fuel cells: Status and opportunities of kinetic studies and their impact on modelling

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A B S T R A C T

Solid oxide fuel cells (SOFC) systems with internal steam reforming have the potential to become an economically competitive technology for cogeneration power plants, exploiting its significantly higher electrical efficiency compared to existing technologies. Optimal design and operation of such a system require SOFC models that include accurate description of the steam reforming rate. The objective of this article is to review the reported kinetic expressions for the steam reforming reaction. Extensive work has been performed on traditional catalysts for steam reforming. Because of differences in operating conditions, catalyst support material and structure it is critical to transfer this knowledge directly to internal reforming in SOFCs, which is discussed in further detail in this article. There are big differences in the reported kinetic expression for steam reforming over both industrial Ni catalysts and SOFC anode materials. Surprisingly, there is a good agreement between measured rates pr. geometric anode area at high operating temperatures, even for very different anodes. Detailed experimental data on the intrinsic steam reforming kinetics of Ni-YSZ are necessary for micro structure SOFC modeling, such expression are however lacking, but it may be viable to use measurements on industrial steam reforming catalysts instead. Nevertheless there is a further need for experimental studies on determining the exact steam reforming kinetics for SOFC anodes.

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1. Introduction

Solid oxide fuel cells (SOFC) systems have a strong potential to become economically competitive with existing technologies for power generation, such as gas turbines in co-generation plants [1–3]. The striking advantage of fuel cells is that they directly convert fuel electrochemically to electricity and thus the efficiency is not limited by the Carnot cycle. In addition, high efficiency can be achieved in small units, applicable for power production for refrigerated trucks, mobile homes and other small scale applications [4]. Small power generation units also allow alternative fuel sources such as gasified biomass or agricultural biogas, to be harnessed to a greater extent, without expensive transportation [5–7].

Among the different types of fuel cells, SOFCs have attracted strong attention [8–14] due to the higher outlet temperature (ease of waste heat utilization), its fuel flexibility, and its resistance to some of the poisons that affect other fuel cells [4]. The most straightforward fuel in a fuel cell is hydrogen at present mainly produced from hydrocarbons. For low temperature fuel cell systems this hydrocarbon to hydrogen conversion is typically achieved by external steam reforming. In contrast, for SOFC’s, internal steam reforming can also be applied, because the Ni containing SOFC anode support can act as a steam reforming catalyst and the operating temperature is suitable for methane conversion [15–17].

One of the advantages of internal steam reforming is that part of the heat generated in the cell by electrochemical reactions, and ohmic heating is directly used for the endothermic reforming reaction [3,18,19]. In consequence, less heat needs to be supplied for the pre-reformer and less cooling of the stack is needed. Both aspect decrease the operating costs of the system. Furthermore, the equipment costs are lower since a smaller pre-reformer is needed and finally more even temperature distributions in the SOFC, than with pure hydrogen can potentially be achieved, if proper control of the catalytic activity is achieved.

With the current SOFC technology, the internal steam reforming is much faster than the electrochemical reactions, which means that the temperature gradients are actually larger than for SOFC’s running on pure hydrogen. By gradually removing heat and producing hydrogen through the cell, the temperature and concentration gradients can be decreased which could significantly improve its performance [20]. This requires, however, detailed knowledge of the kinetics of the steam reforming reaction in order to tune the conditions and the anode structure or composition.

The kinetics of the steam reforming reaction of nickel-based catalysts have been studied widely in literature, especially in catalytic reactors, because of the industrial importance of this process [21]. However, the studies have often been performed at conditions or on materials that are far from those of SOFC anodes. Only a few suitable kinetic data sets on real SOFC anode materials are available in literature.

The aim of this article is to give a present status on the available information on the internal steam reforming reaction over fuel cell anode catalysts. Focus is first laid on the material aspect followed in the second part by how the steam reforming activity can be tuned and which conditions are preferred for internal steam reforming over Ni-based anodes. The key part of the review focuses on a comparison of steam reforming kinetics on catalytic materials and in SOFCs. Finally, its impact on the modeling of solid oxide fuel cells is briefly discussed.

2. The structure of an SOFC

An SOFC is a continuously fed electrochemical cell, where the electrodes and electrolyte are ceramic materials. The major electrochemical reaction which takes place in an SOFC is the oxidation of fuel. A large variety of materials are used in SOFCs and novel materials are presented regularly [22–34]. Typical SOFCs use anode supported cells with [4,22–27]:

- yttria stabilized zirconia (YSZ) electrolyte \( (\tau_{\text{cat}} \approx 10\,\mu\text{m}) \).
- Ni-YSZ anode \( (\tau_{\text{cat}} \approx 10\,\mu\text{m}) \) and support \( (\tau_{\text{cat}} = 300 – 1000\,\mu\text{m}) \).
- Strontium doped lanthanum manganate (LSM) cathode \( (\tau_{\text{cat}} = 50\,\mu\text{m}) \).

These thicknesses \( (T_{\text{el}}, \; T_{\text{an}}, \; T_{\text{sup}}, \; T_{\text{cat}}) \) are used as estimations later in this article. A cell is illustrated schematically in Fig. 1. Typical structural parameters for a Ni-YSZ SOFC anode support are: porosity \( \approx 40–50\% \), Ni content \( \approx 40 \,\text{vol.}\% \), \( d_{\text{Ni}} \approx 1 \,\mu\text{m} \) [4,22–27]. The anode support can be manufactured by first tape casting a slurry of NiO and YSZ powders. The active anode, electrolyte and cathode are then sprayed or screenprinted on the anode support. The active anode material normally has a composition similar to that of the support, but is denser. Finally, the NiO in the anode and anode support is reduced, which significantly increases the porosity [23,26,27,35]. Note, that the nickel particle size is much larger than in traditional steam reforming catalysts and the amount of nickel is significantly higher in order to ensure a high conductivity.

It is convenient to use Ni-YSZ as the structural backbone of the cell because it has desirable mechanical properties, low ohmic resistance and it allows preparation by cofiring of the entire cell, which decreases production costs [36].

3. Steam reforming catalyst

Steam reforming has been used for hydrogen production since 1930 and the process as well as the kinetics have been examined in numerous studies [21,37–43]. The most commonly used catalyst in this process is nickel on a support of \( \alpha-\text{Al}_{2}\text{O}_{3}, \; \text{MgO} \) or \( (\text{Mg,Al})\text{O}_{3} \) spinel. The nickel loading is around 25% w/w, with nickel particles that are preferably smaller than 10 nm.

\[
\begin{align*}
\text{CH}_4 + \text{H}_2\text{O} &\rightleftharpoons \text{CO} + 3\text{H}_2 \\
\text{CO} + \text{H}_2\text{O} &\rightleftharpoons \text{CO}_2 + \text{H}_2
\end{align*}
\]

(1) (2)

The steam reforming reaction (reac. 1) is highly endothermic \( (\Delta H_{\text{cat}} = 206 \,\text{kJ mol}^{-1}) \) whereas the water gas shift reaction (reac. 2) is slightly exothermic \( (\Delta H_{\text{cat}} = -41 \,\text{kJ mol}^{-1}) \), which means that energy must be supplied for the total reaction to proceed. A number of different existing reactor designs [42,44–46] allow for such
large energy supply. In the traditional industrial process the reaction takes place over catalyst particles in large number of vertical tubes. Heat is supplied by placing the tubes in a furnace, which is heated by combustion of natural gas \cite{21,42}. The operating conditions of a typical industrial steam reforming process are 700–1000°C with a pressure around 30 bar and a steam-to-carbon ratio (S/C) of 2.5–4 \cite{39,47}. Often more than one reactor will be used in series, with different conditions. The first reactor is designed for high reaction rate and the subsequent reactors to increase output by shifting the equilibrium.

The catalyst in an SOFC is different from the commercial catalyst, even though nickel is also the main catalytic component. As described in Section 2, Ni is mixed with YSZ. Both the Ni content and particle size are significantly higher than in industrial steam reforming catalysts, to ensure a high electrical conductivity. Furthermore, the geometry is also different (thin plate). Operating conditions are: \( T = 600–1000^\circ\text{C} \), S/C \( \approx 1.5 \) and P = 1–15 bar \cite{4}. High pressure is theoretically advantageous since it increases the cell voltage and improves electrode kinetics, but is non-trivial to realize in practice due to the brittle character of the cells and sealing used, which do not tolerate large pressure differences.

The energy for steam reforming is supplied by the waste heat from the electrochemical reactions and ohmic heating. The continuous consumption of hydrogen in a SOFC and the requirement of high fuel consumption lead to complete conversion of methane.

It would be highly advantageous if the extensive knowledge gained in the industrial steam reforming process could be transferred to internal steam reforming in SOFCs. Despite nickel is the catalyst in both processes, the above descriptions show that the support material, catalyst structure and pressure are not similar. This means that knowledge from the industrial steam reforming process does not necessarily apply directly to internal reforming in SOFCs.

One of the major issues for internal steam reforming at the temperatures used in SOFCs today is that the reforming reaction is much faster than the electrochemical reactions. This is mainly due to the high nickel content, which is required for electric conductivity, but also offers a high number of catalytic sites. Steam reforming consumes energy and the electrochemical reactions produce energy and since the steam reforming is fastest, the result is cooling at the fuel inlet and heating at the fuel outlet. This introduces large temperature gradients, resulting in thermal stress and reduced efficiency \cite{20}. The result is that in contrast to what is normally desired when investigating catalytic reactions, the goal for optimizing internal steam reforming is to lower the reaction rate of steam reforming, while maintaining high electric conductivity and high reactivity of the electrochemical reactions. The techniques used in industrial steam reforming for altering the reaction rate are also relevant for changing the reaction rate in SOFCs. However, the goals are opposite i.e. lowering the reaction rate. The major challenge for industrial steam reforming is to avoid a reduction in activity by minimizing sintering, sulfur poisoning and carbon formation \cite{38}. This is also relevant for internal steam reforming in SOFCs to achieve long-term performance.

3.1. Carbon poisoning

The deposition of elemental carbon on the catalyst is a major issue for both industrial steam reforming and SOFCs with internal reforming. The carbon may be formed by the methanation reactions shown below, and similar for higher hydrocarbons. It is especially important to be aware of carbon poisoning when using Ni-YSZ anodes, since these are vulnerable to carbon deposition \cite{48}.

\[
\begin{align*}
\text{CH}_4 &\rightarrow \text{C} + 2\text{H}_2 \quad (3) \\
2\text{CO} &\rightarrow \text{C} + \text{CO}_2 \quad (4)
\end{align*}
\]

Fig. 2 shows that carbon deposition should not occur for O/C > 1 at 900–1200°C (corresponding to S/C > 1 at the inlet) and at lower temperatures higher O/C ratios are needed. In a model study by Hisao et al. \cite{56} it was reported that the most critical point for carbon deposition occurs about one quarter down the fuel channel. This is caused by two partly compensating effects: oxygen is moved to the anode side in the electrochemical reactions, which shifts the gas composition away from the carbon deposition region, and the cooling of the cell caused by the endothermal steam reforming reduces the temperature, which increases the carbon deposition region. No carbon deposition was observed for S/C ratios higher than 1.5–1.6 on Ni-YSZ in an SOFC \cite{52,57}, but higher S/C ratios are needed to avoid carbon deposition from higher hydrocarbons \cite{48,51,58,59}. The lower the fuel utilization the higher S/C ratio is needed to avoid carbon deposition \cite{52}.

In the industrial steam reforming process carbon deposition is normally avoided by using a relatively high S/C ratio. However, in SOFCs the S/C ratio should be kept as low as possible since water is a product in the electrochemical reactions, and as such a higher steam content in the fuel will decrease the reversible cell voltage \((U_{\text{rev}})\), as seen from the Nernst equation below.

\[
U_{\text{rev}} = -\frac{\Delta G}{2F} + \frac{R_T}{2F} \ln \left( \frac{P_{\text{H}_2}^2 P_{\text{H}_2O}}{P_{\text{H}_2} P_{\text{H}_2O}^2} \right)
\]

A lowering of the S/C ratio in industrial steam reforming will result in a reduction in equipment cost, so methods for avoiding carbon depositions at low S/C have long been searched for \cite{47}.

In situ microscopy studies reported by Sehested \cite{38,60} show that step sites on the Ni catalyst particles are the most active nucleation
sites for both carbon formation and steam reforming. This is backed up by density functional theory calculations [61,62] and is in line with the observation that potassium, sulfur and gold reduce carbon formation by blocking these step sites [13,14,47,63–65]. Blocking the step sites also significantly reduces the steam reforming rate, which makes this method one of the most promising ones for reducing carbon deposition in SOFCs with internal steam reforming. New approaches to lowering carbon deposition by adding different promoters (Sn, Mo, Li, n-butanethiol, Mg, Ca, Sr, Ce, Ru, Rh, Pd, Pt) to the Ni-YSZ anode, are regularly reported in literature [54,66–69].

3.2. Effect of current

It has been shown that a sufficiently high cell current prevents carbon deposition, even for a cell fueled by methane with 3% H₂O (S/C = 0.03) [70–73]. Lin et al. [70] suggested that deposited carbon is reoxidised by the oxygen ions passing through the electrolyte, but another possible explanation is that backflow of steam produced in the electrochemical reactions increases the local S/C ratio to values were elemental carbon is not formed. The necessary minimum cell current density is greatly dependent on temperature. At 700 °C a current of approximately 0.1 A cm⁻² is needed while at 800 °C, 1.8 A cm⁻² is needed. The minimum cell current density is, most likely, highly dependent on the total flow, and this should also be investigated (the flow used by Lin et al. [70] was 30 sccm on a anode area of 2.8 cm² with a thickness of 0.7–1 mm). Such a high current density will with present day state of the art cells mean that one has to operate at very low voltage unlikely to be optimal from an overall cost point of view. It has been shown that it is possible to decrease the necessary current with up to a factor 3 by applying an inert barrier layer on the anode support. This is most likely caused by increased mass transport limitations, which in turn should also decrease the rate of the electrochemical reactions. A further investigation of the effect of such an inert layer would be very interesting. There are, however some fundamental difficulties, with using pure methane fuel and relying on current to prevent carbon deposition. Natural gas contains higher hydrocarbons, which have a much higher tendency for carbon deposition, meaning that some degree of external purification is needed. Also, it is highly problematic if a commercial cell is not tolerant towards sudden drops in current. The possibility of direct electrochemical oxidation of methane in SOFC has been shown [74], however with high polarization resistance. Recently, some groups have reported fast direct electrochemical oxidation of methane [75–77], however, it has been debated [78] whether it is direct electrochemical oxidation of methane or rather oxidation via an indirect route, e.g. cracking of methane with subsequent oxidation of carbon or possibly via partial steam reforming followed by electrochemical oxidation of hydrogen and CO.

3.3. Finetuning of catalyst

In SOFC systems running on natural gas with internal steam reforming, some degree of pre-reforming is necessary to avoid carbon formation due to higher hydrocarbons and decrease the methane concentration to a level that result in acceptable temperature and concentration gradients in the SOFC stack [18,79]. There is, however, potential for significant improvement of the system efficiency by lowering the degree of pre-reforming and reducing the temperature and concentration gradients in the stack. A possible strategy, is to lower the reforming rate to the same level as the electrochemical reactions. In fact, the general tendency of today’s SOFC research is to lower the operating temperature [80–82] and since the steam reforming reaction has a high activation energy (58–228 kJ mol⁻¹, see Table 5), the reaction rate decreases rapidly with temperature. The present lower temperature limit for efficient operation of an SOFC is around 650–700 °C [25,82]. In order to illustrate the temperature dependency of internal steam reforming, order of magnitude calculations were made based on the steam reforming rate by Wei et al. [40] (\( \eta_\text{S/R} \approx 102.2 \text{~kJ mol}^{-1} \)), which is later used as a reference expression. The calculations are made for a 1 cm² Ni-YSZ anode with thickness = 500 μm. Ni content = 50% (w/w), Ni particle size = 1 μm and porosity = 50%, Gas composition: 50/50 methane and water and no mass transport limitation for steam reforming. The resulting rate of hydrogen production from steam reforming is shown in Table 1. The efficiency factor in Table 1 is calculated from Eq. (5) and describes how big a fraction of the available catalyst material that is being fully used, i.e. an efficiency factor = 1 corresponds to full usage of the catalyst [42].

\[
\eta = \frac{\tan h(\phi)}{\phi}
\]

where \( \phi \) is the Thiele modulus:

\[
\phi = L \sqrt{\frac{k}{D}}
\]

where \( L \) is the anode thickness, \( k \) is the rate constant (m² s⁻¹) and \( D \) is the diffusion coefficient (m² s⁻¹). The diffusion coefficient of methane is assumed to be 10⁻⁵ m² s⁻¹, \( \eta_\text{S/R, prod} \) is the theoretical current that corresponds to a consumption of hydrogen in the same rate as it is produced from the steam reforming reaction, calculated from:

\[
\eta_\text{S/R, prod} = 2F_k \text{Ni,S/R, prod}
\]

where \( F_k \) is the Faraday constant.

These calculations illustrates how the rate of the steam reforming reaction compares to the rate of electrochemical reactions. For optimal operation, without hydrogen in the inlet gas, \( \eta_\text{S/R, prod} \) should probably be a little higher than the operating current. This means that at temperatures 600–700 °C the rate of steam reforming rate is in a range where it should be possible to reduce it to the desired level by finetuning the catalyst. It should be noted however, that during the calculation of \( \eta_\text{S/R, prod} \) it was assumed that the steam reforming rate was not limited by diffusion. The \( \eta \) values show that this assumption is only valid at low temperatures, meaning that at high temperatures the actual rate will be lower than the one calculated here.

Another theoretical possibility for decreasing the steam reforming rate, by changing the conditions, is to have a low S/C ratio in the fuel inlet, so that the conversion of methane will be controlled by equilibrium and thereby the amount of water produced in the electrochemical reaction. However, this will result in significant carbon deposition in the cell as described in Section 3.1.

Up to now, alternative materials has been hampered by low electronic conduction. For example, Georges et al. [15] has presented a strontium doped lanthanum chromite impregnated with ruthenium catalyst (LSRuC), which operates at S/C ratios down to 0.08 without carbon deposition. Unfortunately, this material has very poor anode properties, so this study can only be considered a proof of concept, not a solution.
Rostrup-Nielsen et al. [14] conclude that the catalytic steam reforming of methane does not take place at the same catalytic sites as the electrochemical conversion of hydrogen. It might therefore be possible to further decrease the steam reforming reaction rate by selectively blocking the catalytic sites without significantly lowering the cell performance. Several possible methods for doing this originating from the research on preventing poisoning of industrial reforming catalysts are described in the following sections.

3.3.1. Particle size

The size of nickel particles in the anode support will influence the steam reforming rate because the large particles give a smaller surface area for the same nickel content and thereby less active sites for catalysis. If the particle size in the active anode is also increased it can however result in a smaller triple phase boundary between anode, electrolyte and gas, which is the active area for the anode reaction [83–85]. It was shown by Simwonis et al. [86] that the nickel particle size also influences the electrical conductivity of the anode and that the particle size increases during operation by agglomeration, which is in fact one of the major anode degradation mechanisms [38,86,87]. This means that an increase in Ni particle size in order to reduce the steam reforming reaction rate may result in a reduction in cell performance. Note however that nickel particle size in SOFC anodes is in general much larger than in industrial steam reforming catalysts.

3.3.2. Sulfur

Several studies on the effects of sulfur on the fuel cell performance of Ni-YSZ anodes operating in hydrogen have been reported in literature [64,88–94]. Operating an engine cell to ppm levels of sulfur in the anode stream results in an immediate voltage drop (few minutes up to few hours) followed by a slower decay of the voltage occurring over the following hundred hours [89]. In hydrogen under the studied current loads (less than 1A cm⁻²) the effect of the sulfur poisoning seems fully reversible—the cell voltage returns slowly (over 10 to few hundred hours) to its original value after removal of the sulfur [89,90]. The effects of sulfur on Ni catalysts and SOFC anodes has recently been reviewed by Hansen and Nielsen [95]. The poisoning is due to adsorption of sulfur on sites active in the electrochemical reaction [95]. Both the temperature dependence and the dependence on sulfur concentration of the experimentally observed voltage losses can be accounted for by assuming that the loss scales in a linear manner with the temperature dependence and the dependence on sulfur content active in the electrochemical reaction [95]. This means that an increase in Ni particle size in order to reduce the steam reforming reaction rate may result in a reduction in cell performance. Note however that nickel particle size in SOFC anodes is in general much larger than in industrial steam reforming catalysts.

3.3.3. Alkali and earth alkali metals

Rostrup-Nielsen and Christiansen [63] reported that the rate of catalytic steam reforming over 7–9% Ni on Mg/Al-spinel is significantly reduced by addition of alkali metals. An explanation of this is suggested from DFT calculations, which show that inserting of step sites will significantly reduce catalyst activity [61,62] and alkali metals absorb to step sites. The reduction in activity was shown to be a factor 2–5 depending on the alkali metal. Alkali poisoning is thus a promising method for finetuning of catalytic activity in SOFCs.

Kikuchi and coworkers [54,58] investigated the change in carbon deposition and steam reforming rate when adding CaO, MgO, SO and CeO₂ to Ni-YSZ anodes in the temperature range 600–800 °C. CaO and SO decreased carbon deposition with 30–50% while Mg increased it with up to 20%, low amounts of CeO₂ (0.2% w/w) decreased the carbon deposition (~50%) while high amounts (2%, w/w) increased carbon deposition (~25%). In most cases the addition of the alkaline earth metals to Ni-YSZ resulted in a slight increase in steam reforming rate, with the following 3 exceptions: A high amount of SO almost removed the catalytic effect of nickel (whereas low amounts increased activity), small addition of MgO reduced reforming rate by about 40% and high amounts of CeO₂ decreased reforming rate with up to 75%. From this it can be concluded that MgO and CeO₂ in the right amounts could possibly be used for reducing steam reforming rate in SOFC’s, but it has to be considered that both of these increase carbon deposition. It should be noted that the Ni-YSZ in these investigations contained 75–80% Ni (w/w), which is very high for an SOFC anode.

3.3.4. Modified Ni-YSZ anodes and Ni substitution

The suggestions for finetuning the anode catalyst in the previous sections by larger particles and poisoning by sulfur or alkali metals have the disadvantage that the electrochemical reactions are also influenced. Another method for lowering the steam reforming rate is modification of Ni-YSZ or using entirely different anode materials. Note, however, that other requirements also have to be considered, such as low electric resistance, high porosity and a thermal expansion coefficient similar to the active anode, electrolyte and cathode.

A promising work on modifying the anode was presented by Boder and Dittmeyer [79], who reported that replacing some of the nickel in the anode with copper reduces the steam reforming rate with a factor 4–20 without significant reduction in electrochemical performance. Further investigations into this direction could be rewarding.

An SOFC with an anode catalyst layer consisting of Ir impregnated Ceria on top an active anode of Ni-YSZ is reported by Klein et al. [12] to operate on pure methane for almost 30 h without showing signs of degradation, i.e. carbon deposition. The power production during this experiment was only about 55 mW m⁻², so the performance of this type of cell has to be greatly improved in order to be relevant. Ru and Pt additives have also been reported to prevent carbon deposition on Ni-YSZ for internal steam reforming with C/H₂ as low as 0.1 [54,101].

Gorte and coworkers [102–104] report the use of Cu–CeO₂–YSZ. It is applicable for higher hydrocarbons but has lower affinity toward hydrogen oxidation in the triple phase boundary. A fuel cell with Ni-YSZ as the active anode and Co–Ni–SDC as support material and steam reforming catalyst has been tested with pure methane as the fuel with no observed carbon deposition. The cell performances were however relatively poor, with a maximum power density of 0.35 W cm⁻², which decreased significantly with time [105]. Finally, a Ni-YSZ anode coated with a layer of catalytically inert YSZ was proposed to reduce the steam reforming rate due to mass transport, but there is disagreement about the effect on the electrical efficiency [70–72,106–108]. On a side note, these find-
general Langmuir–Hinshelwood kinetics.

\[ P = kP_0 \left( 1 - \frac{T}{T_r} \right) \]

where \( k \) is the overall rate constant, \( P \) is the pressure, \( T \) is the temperature, and \( T_r \) is the reference temperature. The reactions are reversible, and the equilibrium constants are included in the subscripts.

The kinetic behaviour of the steam reforming reaction has been extensively studied on Ni supported model and industrial catalysts [21,37,39–41,43]. More recently, also the kinetics over Ni-YSZ anodes have been reported [9,79,109]. The reported kinetics seem reasonably and this should be kept in mind when evaluating kinetic expressions. Subsequently a review of the available studies carried out on SOFC anodes is given in Section 4.4. An overview of the used kinetic expression and references can be found in Tables 2–4 for the model and industrial catalysts and in Tables 5 and 6 for the SOFC anode studies. When trying to compare kinetics reported for different SOFC anodes and between anodes and model systems, it should be noted that the microstructure of the Ni particles in Ni-YSZ may not be stable. Firstly, the Ni grain size distribution has been reported to have large fractions in two different sizes, the large Ni particles (0.3–2 \( \mu m \)) which are needed in SOFC anodes to ensure a high electrical conductivity, and small Ni particles (10–30 nm), which have a significant influence on the catalytic activity [9]. Secondly, sintering both increases particle size of the small particles, and removes some highly active reaction sites, for both small and large particles [9]. Thirdly, it has been shown that Ni particles are highly dynamic and can dramatically change structure during operation [60]. These effects are very difficult to describe accurately and this should be kept in mind when evaluating kinetic expressions.

### 4. Steam reforming kinetics

The kinetic behaviour of the steam reforming reaction has been extensively studied on Ni supported model and industrial catalysts [21,37,39–41,43]. More recently, also the kinetics over Ni-YSZ anodes have been reported [9,79,109]. The reported kinetics seem to be significantly different, but this may be because the reaction conditions vary a lot in the different studies. Moreover, due to the high temperatures applied, mass and heat transport effects are difficult to control. A full kinetic analysis over a wide range of conditions has only been given in a few cases. The studies can be grouped in three according to which type of kinetic expression is used in the analysis of the experiments:

- General Langmuir–Hinshelwood kinetics.
- First order reaction with respect to methane.
- Power law expressions derived from data fitting.

First investigations on industrial and model catalyst systems shall be discussed in Sections 4.1–4.3 for the three types of kinetic expressions. Subsequently a review of the available studies carried out on SOFC anodes is given in Section 4.4. An overview of the used kinetic expression and references can be found in Tables 2–4 for the model and industrial catalysts and in Tables 5 and 6 for the SOFC anode studies. When trying to compare kinetics reported for different SOFC anodes and between anodes and model systems, it should be noted that the microstructure of the Ni particles in Ni-YSZ may not be stable. Firstly, the Ni grain size distribution has been reported to have large fractions in two different sizes, the large Ni particles (0.3–2 \( \mu m \)) which are needed in SOFC anodes to ensure a high electrical conductivity, and small Ni particles (10–30 nm), which have a significant influence on the catalytic activity [9]. Secondly, sintering both increases particle size of the small particles, and removes some highly active reaction sites, for both small and large particles [9]. Thirdly, it has been shown that Ni particles are highly dynamic and can dramatically change structure during operation [60]. These effects are very difficult to describe accurately and this should be kept in mind when evaluating kinetic expressions.

### 4.1. Langmuir–Hinshelwood kinetics

The classical approach of Langmuir–Hinshelwood kinetics is derived from the reaction of surface species. Mainly two mech-

### Table 2

Langmuir–Hinshelwood steam reforming kinetics reported for Ni catalysts. (The constants in the table are: \( k \) overall rate constants, \( P \) equilibrium constants, the subscript \( P \) adsorption of the denoted species and a roman numeral in the subscripts refers to reactions 1–11. (1–Q, Kr) describes the approach to equilibrium of reaction \( i \) where \( Q \) is defined in Eq. (6), and at equilibrium \( P \) is.

<table>
<thead>
<tr>
<th>RDS</th>
<th>Expression</th>
<th>Support</th>
<th>( T ) [°C]</th>
<th>( P_{out} ) [bar]</th>
<th>S/C</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>A) Classical</td>
<td>( r = \frac{k}{P_0} \left( 1 - \frac{T}{T_r} \right) )</td>
<td>MgAl2O4</td>
<td>500–575</td>
<td>3–15</td>
<td>3–5</td>
<td>[39]</td>
</tr>
<tr>
<td>B) Classical</td>
<td>( r = \frac{k}{P_0} \left( 1 - \frac{T}{T_r} \right) )</td>
<td>YSZ-CeO</td>
<td>700–1000</td>
<td>-</td>
<td>2–7</td>
<td>[111]</td>
</tr>
<tr>
<td>C) Classical</td>
<td>( r = k \left( 1 + K_{ad,CH} \right) )</td>
<td>YSZ</td>
<td>700–1000</td>
<td>-</td>
<td>3–7</td>
<td>[110]</td>
</tr>
<tr>
<td>D) CH2O ( \lambda ) ( \lambda ) CH4 + H2</td>
<td>( r = \frac{k}{P_0} \left( 1 + K_{ad,CH} \right) )</td>
<td>Ni foil</td>
<td>700–800</td>
<td>1</td>
<td>1.6–25</td>
<td>[37]</td>
</tr>
<tr>
<td>E) 1, 7</td>
<td>( r = k \left( 1 + K_{ad,CH} \right) )</td>
<td>YSZ</td>
<td>700–1000</td>
<td>1</td>
<td>0–2</td>
<td>[73]</td>
</tr>
<tr>
<td>F) 1, 7</td>
<td>( r = k \left( 1 + K_{ad,CH} \right) )</td>
<td>ZrO2</td>
<td>700–1000</td>
<td>1</td>
<td>1–3</td>
<td>[113]</td>
</tr>
</tbody>
</table>

*Where \( k \) is the overall rate constant, \( P \) is the pressure, \( T \) is the temperature, and \( T_r \) is the reference temperature.*

### Table 3

First order steam reforming kinetics reported for Ni catalysts.

<table>
<thead>
<tr>
<th>Expression</th>
<th>Support</th>
<th>( T ) [°C]</th>
<th>( P_{out} ) [bar]</th>
<th>S/C</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r = kP_{CH} )</td>
<td>none</td>
<td>700–900</td>
<td>1</td>
<td>-</td>
<td>[121]</td>
</tr>
<tr>
<td>( r = kP_{CH} \left( 1 + K_{ad,CH} \right) )</td>
<td>ZrO2-CeO</td>
<td>800–850</td>
<td>1</td>
<td>2–4</td>
<td>[122]</td>
</tr>
<tr>
<td> </td>
<td>CeO</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[50]</td>
</tr>
<tr>
<td> </td>
<td>MgO</td>
<td>600–700</td>
<td>1–15</td>
<td>0–10</td>
<td>[40]</td>
</tr>
<tr>
<td> </td>
<td>YSZ</td>
<td>650–950</td>
<td>-</td>
<td>2</td>
<td>[79]</td>
</tr>
<tr>
<td> </td>
<td>ZrO2</td>
<td>700–940</td>
<td>1.1–2.8</td>
<td>2.6–8</td>
<td>[109]</td>
</tr>
</tbody>
</table>

### Table 4

Power law steam reforming kinetics reported for Ni catalysts.

<table>
<thead>
<tr>
<th>Expression</th>
<th>Support</th>
<th>( T ) [°C]</th>
<th>( P_{out} ) [bar]</th>
<th>S/C</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>( kP_{CH} \lambda )</td>
<td>CGO</td>
<td>800–950</td>
<td>1</td>
<td>0.3</td>
<td>[123]</td>
</tr>
<tr>
<td>( kP_{CH} \lambda )</td>
<td>YSZ</td>
<td>850–900</td>
<td>1</td>
<td>1.3–2.5</td>
<td>[134]</td>
</tr>
<tr>
<td>( kP_{CH} \lambda )</td>
<td>ZrO2</td>
<td>800–1000</td>
<td>1</td>
<td>2–8</td>
<td>[65]</td>
</tr>
<tr>
<td>( kP_{CH} \lambda )</td>
<td>ZrO2</td>
<td>900–1000</td>
<td>1</td>
<td>1.5–2.5</td>
<td>[125]</td>
</tr>
<tr>
<td>( kP_{CH} \lambda )</td>
<td>YSZ</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[126]</td>
</tr>
</tbody>
</table>
anisotropic schemes have been considered. The classical mechanism, presented first by Xu and Froment [39], postulates that the reaction of adsorbed carbon and oxygen species is the rate determining step (RDS) as shown below.

- \( \text{CHO}^{+*} \rightarrow \text{CO}^{+} + \text{H}^{+} \)
- \( \text{CO}^{+} + \text{O}^{*} \rightarrow \text{CO}_{2}^{\text{eq}} \)
- \( \text{CHO}^{+} + \text{O}^{*} \rightarrow \text{CO}_{2}^{\text{eq}} + \text{H}^{+} \)

From this they conclude that the reaction rate is dependent on partial pressure of methane, water and hydrogen as shown in entry A in Table 2. Similar kinetics (without the strong hydrogen dependence) was used for Ni-YSZ, by Peters et al. [110] and Nakagawa et al. [111] as given in entry B and C in Table 2. The positive influence of water predicted by entries A, B and C is, however, rarely observed in literature. The value \( Q \) in expressions A, B and C is defined by:

\[
Q = \frac{\prod_{\text{reactants}}}{\prod_{\text{products}}} \tag{6}
\]

The term connected with \( Q \), which appear in some of the kinetic expressions accounts for the backwards reaction close to equilibrium. In more recent work it has been shown that dissociative adsorption of methane is the rate limiting step (step 1). This leads to the following model for the elementary reactions, which nowadays is often used to derive kinetic expressions for steam reforming [42,112,40].

1. \( \text{CH}_4 + 2\text{O} \rightarrow \text{CH}_4^{\text{eq}} + \text{H}^{+} \)
2. \( \text{CH}_4^{+} + \text{H}^{*} \rightarrow \text{CH}_4^{\text{eq}} + \text{H}^{*} \)
3. \( \text{CH}_4^{+} + \text{H}^{*} \rightarrow \text{CH}_4^{\text{eq}} + \text{H}^{*} \)
4. \( \text{CH}_4^{+} \rightarrow \text{C}^{*} + \text{H}^{*} \)
5. \( \text{H}_2\text{O} + 2\text{CH}_4 \rightarrow \text{H}_2\text{O} + \text{CH}_4^{\text{eq}} + \text{H}^{*} \)
6. \( \text{H}_2\text{O} + \text{CH}_4^{\text{eq}} \rightarrow \text{H}_2 + \text{CO}^{*} + \text{H}^{*} \)
7. \( \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}^{*} + \text{H}^{*} \)
8. \( \text{CH}_4^{+} \rightarrow \text{CHO}^{+} + \text{H}^{*} \)
9. \( \text{CHO}^{+} + \text{O}^{*} \rightarrow \text{CO}_{2}^{\text{eq}} + \text{H}^{*} \)
10. \( \text{CO}^{*} \rightarrow \text{CO}_{2}^{\text{eq}} + \text{H}^{*} \)
11. \( 2\text{H}_2 \rightarrow \text{H}_2 + \text{2} \)

It is generally agreed that Reaction 1 is an RDS, but there is great disagreement on whether or not reactions 5 and 7 should also be considered as RDS. The Langmuir–Hinshelwood expressions that can be derived from the elementary reactions in Eqs. (1)-(11) are used by Wei and Iglesia, shown in Eqs. (7) and (6).

\[
r_k = \eta_f \left(1 - \frac{Q_{\text{eq}}}{Q_{\text{eq}}^0}\right) \tag{7}
\]

where \( r_k \) is the net \( \text{CH}_4 \) conversion rate, \( \eta_f \) is the forward reaction rate, \( K \) is the equilibrium constant of the steam reforming reaction and \( Q \) is given by Eq. (6). The forward reaction rate was found to be first order in \( \text{CH}_4 \) and independent of the \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) content, resulting in the simple expression in Eq. (8) for all the examined catalysts. The first order dependence in methane is in agreement with the majority of the reported steam reforming kinetics, but the independence of other gasses is less commonly reported.

\[
\eta_f = k_{\text{a}} P_{\text{CH}_4} \tag{8}
\]

Wei and Iglesia also examined the steam reforming and water gas shift reactions by isotopic tracing of some of the elementary steps, showing that they are in quasi-equilibrium. The results are summarized in Fig. 3, underlining that the rate determining step is activation of the first C–H bond (reaction 1), resulting in a first order expression for steam reforming with water gas shift and hydrogen formation/dissociation in quasi-equilibrium.

More recently, Hecht et al. [112] reported a combined model and experimental study of internal steam reforming over Ni-YSZ. They conclude that their findings on Ni-YSZ are consistent with the result of a first order expression with activation of the first C–H bond, found by Wei and Iglesia. However, an overall reaction rate for the steam reforming reaction is not explicitly presented. The model in this work is described in more detail in Section 6.

A possible explanation for the many different expressions is given by density functional theory calculations, which show that reactions 1 and 7 are kinetically controlling, and that reaction 1 is rate controlling at high temperature while 7 (or another CO formation reaction) is rate controlling at low temperatures [114,115]. Hence the kinetic expression will change with operating conditions. Furthermore, it must be kept in mind that a large number of different plausible expressions can be derived from Langmuir–Hinshelwood kinetics with several constants in each expression. This means that an agreement to experimental data is not a definite proof for a mechanism.
Steam reforming kinetics and activation energies reported for steam reforming over Ni-YSZ SOFC anode/anode-supports.

### Table 5

<table>
<thead>
<tr>
<th>Expression</th>
<th>$E_a$ [kJ mol$^{-1}$]</th>
<th>$T$ [°C]</th>
<th>$P_{H_2}$ [bar]</th>
<th>S/C</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$</td>
<td>228.8</td>
<td>800–900</td>
<td>1</td>
<td>0–2</td>
<td>LH1 [73]</td>
</tr>
<tr>
<td>$k_2$</td>
<td>113–124</td>
<td>650–800</td>
<td>-</td>
<td>3–15</td>
<td>SLH1 [9]</td>
</tr>
<tr>
<td>$k_3$</td>
<td>63.3</td>
<td>650–950</td>
<td>-</td>
<td>2</td>
<td>SLH2 [79]</td>
</tr>
<tr>
<td>$k_4$</td>
<td>82</td>
<td>700–940</td>
<td>1.1–2.8</td>
<td>2.6–8</td>
<td>SLH3 [109]</td>
</tr>
<tr>
<td>$k_5$</td>
<td>74–98</td>
<td>800–1000</td>
<td>-</td>
<td>2–8</td>
<td>PL2 [65]</td>
</tr>
<tr>
<td>$k_6$</td>
<td>58</td>
<td>900–1000</td>
<td>-</td>
<td>1.5–2.5</td>
<td>PL2 [125]</td>
</tr>
<tr>
<td>$k_7$</td>
<td>95</td>
<td>850–900</td>
<td>1</td>
<td>1.5–2.5</td>
<td>PL3 [124]</td>
</tr>
<tr>
<td>$k_8$</td>
<td>191</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[126]</td>
</tr>
<tr>
<td>$k_9$</td>
<td>-</td>
<td>700–1000</td>
<td>1</td>
<td>3–7</td>
<td>[110]</td>
</tr>
<tr>
<td>$k_10$</td>
<td>-</td>
<td>700–950</td>
<td>1.5</td>
<td>3</td>
<td>[128,129]</td>
</tr>
<tr>
<td>$k_11$</td>
<td>205</td>
<td>600–700</td>
<td>-</td>
<td>2–3.5</td>
<td>[110]</td>
</tr>
</tbody>
</table>

Fig. 3. Sequence of elementary steps for steam reforming and water gas shift reaction on Ni catalysts, as found by isotopic analysis. $→$ irreversible step, $→$ reversible step. (A), quasi-equilibrated steps, $k_i$ is the rate constant and $K_i$ is the equilibrium constant for reaction (46), reproduced with permission from Elsevier.

### 4.3. Power law expressions

The kinetic expressions presented in Section 4.1 rely on several assumptions and simplifications (a single RDS, one dominating species on the surface, quasi-equilibrium, etc.). To have a model independent description, many of the measured kinetics are instead given by power law expressions without tracing back to a mechanism of elementary steps. Kinetic measurements of the steam reforming reaction are normally fitted to the following power law expression.

$$-r_{CH_4} = k_0 P_{CH_4}^{a} P_{H_2O}^{b} P_C^{c}$$

(9)

$γ$, $β$, and $λ$ are often found to be close to zero (see Table 4). The rate constant, $k_0$ as well as $α$ and $β$ vary between different studies. An overview of the reported power law expressions for steam reforming over Ni catalysts on either ceria or zirconia support is shown in Table 4. The reaction order with respect to methane is close to 1 for all expressions, in agreement with the expressions presented in Sections 4.1 and 4.2. There is, however, no agreement on the reaction order with respect to water. This may be due to the different conditions used in these studies. It is striking that many report the order to be negative.

Unfortunately, in many of the studies that present power law kinetics the experimental method does not follow the recommended practice for measuring catalytic reaction rates as described in “Concepts of Modern Catalysis and Kinetics” [42]. Some works do not comment on the possible effects of mass transport [124] and others have a high degree of conversion across the reactor (50–95%) giving strong temperature and concentration gradients along the reactor [65,125,123]. Temperature gradients imply that the actual temperature in the catalyst material will differ from the measured temperature and high concentration gradients mean that approach to equilibrium may influence the results. These uncontrolled effects are probably an additional cause for the disagreement on the reaction order with respect to water partial pressure. When using power law kinetics, it must be kept in mind that they are often used to describe measurements that are specific to the setup they are measured on, and in such cases they will probably not be representative for another system.

### 4.4. Kinetics over Ni-YSZ anode catalysts

Steam reforming kinetics for SOFCs have been investigated since the late 1980s but there is still no consensus on the kinetic expression [50,127]. In this section a comparison of the reported expressions is given as follows:

1. Reaction orders and experimental conditions.
   - Kinetic expressions (i.e. reaction orders) and activation energies are given in Table 5.
   - Experimental conditions of the compared expressions are summarized in Table 6.

2. Comparison of predicted rate under specific conditions normalized by:
   - Ni weight, Fig. 4.
   - Ni surface area, Fig. 5.
   - Geometric anode area, Fig. 6.

Besides the studies that are discussed here, additional experiments exist in the literature [8,79,110,113,126,131–133]. These studies were not included in this comparison because of insufficient information on experimental details to allow for appropriate calculations.

As can be seen in Table 5, there is a large spread in the reported activation energies ($E_a$), i.e., 58–229 kJ mol$^{-1}$, but the majority of the reported $E_a$ lies just below 100 kJ mol$^{-1}$, which also fits well...
Table 6
Ni-YSZ properties and measuring conditions for the compared expressions.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>LH1 [73]</td>
<td>cermet film</td>
<td>Precipitation</td>
<td>800–900</td>
<td>0.01</td>
<td>70</td>
<td>0.83</td>
<td>0.88</td>
<td>-</td>
</tr>
<tr>
<td>SLH1 [9]</td>
<td>PFR</td>
<td>Tape Casting</td>
<td>650–800</td>
<td>0.075–0.150</td>
<td>50</td>
<td>0.18</td>
<td>10–2000</td>
<td>-</td>
</tr>
<tr>
<td>SLH2 [79]</td>
<td>anode</td>
<td>Coat mix</td>
<td>650–950</td>
<td>0.04</td>
<td>65</td>
<td>1.2</td>
<td>0.4</td>
<td>-</td>
</tr>
<tr>
<td>SLH3 [109]</td>
<td>anode</td>
<td>-</td>
<td>750–950</td>
<td>1.4</td>
<td>20</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PL1 [65]</td>
<td>CSTR</td>
<td>4 different</td>
<td>800–1000</td>
<td>2.4–4.8</td>
<td>50–80</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PL2 [125]</td>
<td>anode</td>
<td>Spray paint</td>
<td>900–1000</td>
<td>0.04</td>
<td>60 vol.%</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PL3 [124]</td>
<td>anode</td>
<td>Screen print</td>
<td>850–900</td>
<td>0.05</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ref [40]</td>
<td>PFR</td>
<td>-</td>
<td>600–700</td>
<td>0.25–0.45</td>
<td>7</td>
<td>1.8</td>
<td>0.0067</td>
<td>-</td>
</tr>
</tbody>
</table>

* Estimated value, assuming spherical Ni particles.  
* Particle diameter of crushed anode.  
* ZrO$_2$ support.

with the value of 102 kJ mol$^{-1}$ reported by Wei and Iglesia [40] on an industrial steam reforming catalyst. There is, however, also a large spread in the activation energies reported for industrial steam reforming catalysts, for example the studies in Refs. [37,39,40,121] report values in the range 102–240 kJ mol$^{-1}$. In general the reported values seem to be higher than for Ni-YSZ.

A comparison with the activation energy of the electrode reactions is interesting in order to evaluate the idea of lowering the internal steam reforming rate by lowering the operating temperature and thereby spread the reforming reaction over a larger part of the cell, as described in Section 3.3. Barford et al. [134] report activation energies of the anode reaction in the order $E_A \approx 1eV \approx 100$ kJ mol$^{-1}$, meaning that it is similar to that of the steam reforming reaction. A decrease in operating temperature of a specific cell will therefore not have the desired effect on spreading the conversion of methane over a larger part of the cell area. However, a lowering of the SOFC operating temperature will only be industrially relevant if new cells are developed, with a higher electrochemical activity at the lower temperatures. New types of cells with improved electrodes could show a better balance between the rates of the steam reforming and the electrochemical processes if the modifications only affect the latter.

The abbreviations that are used in both Tables 5 and 6 and Figs. 4–6, denote classical Langmuir–Hinshelwood (LH), Simple Langmuir–Hinshelwood (SLH, first order with respect to methane), and Power Law (PL). Fig. 4 shows a comparison of the rates with respect to Ni content (weight), note that the reaction rate is on a logarithmic scale. LH1 is not included in the bottom plot, because the expression is not valid for this gas composition. The large difference between the values in Fig. 4 may be caused by differences in Ni particle size for the tested catalysts. The reported Ni particle sizes for SOFC anodes are in the range 0.3–3 μm [9,35,73,79,86,83], though Iwata et al. [83] report sintering up to 10 μm particles. The Ni particles in the alumina supported catalyst used as the reference have an average particle size of 6.7 nm [40]. The study by Bebelis et al. [73] further reports small (10–20 nm) particles on top of large particles. Hence, the rate expressions with respect to Ni content are very system specific and as such, they should only be used in connection with the system they have been measured on.

The reference (ref) refers to the kinetic expression reported by Wei and Iglesia [40] over Ni on alumina support and allows comparison with the kinetics for catalysts related to industrial steam reforming. In Figs. 5 and 6 the reforming rates per Ni area or per cell area are compared, as expected, the values are much closer to each other than those in Fig. 4, so a logarithmic scale is not suited for comparing these values. Instead the two first plots represent the same data, with the first plot being on a logarithmic scale to ease the comparison with Fig. 4. The optimal comparison of catalytic reactivity is with respect to active catalyst surface area. Unfortunately only three studies on Ni-YSZ report the Ni surface area and one of these, LH1, has an exceptionally high activation energy and is only valid at one of the gas compositions that are used for comparison.
Fig. 5. Comparison of the reaction rate, at ambient pressure, of steam reforming over Ni-YSZ reported in literature with respect to nickel surface area: LH1 [73], SLH1 [9], SLH2 [79], Ref. [46].

Fig. 6. Comparison of the reaction rate, at ambient pressure, of steam reforming over Ni-YSZ reported in literature with respect to geometric anode surface area: LH1 [73], PL2 [125], PL3 [124], SLH2 [79], SLH3 [109].
The reactivity predicted from these three expressions along with the reference (Ni on alumina) is shown in Fig. 5. Obviously some of the expressions that were orders of magnitudes apart in Fig. 4 are now relatively close, except for LH1 at high temperatures (note that this is very thick). It is especially worth noticing that the catalytic activity of the industrial catalyst is now very similar to that of the anodes, in spite of the big difference in nickel particle size, i.e. the majority of the difference when comparing based on mass is simply an effect of differences in Ni area. Only few of the kinetic studies on catalytic steam reforming over SOFC anodes explicitly report the Ni surface area, and if the Ni particle size is not given either, then an estimation of the surface is also not possible.

When comparing the measurements given as activity pr. geometric anode surface area as shown in Fig. 6, a surprisingly good correspondence is seen, especially when considering that the Ni content in these experiments range from 20 to 70 wt%. It should be noticed that all expressions in this comparison were measured over a planar cell structure, so it might not be valid for other configurations or other anode materials very different from the ones of the four studies.

The depth of the steam reforming reaction zone on Ni-YSZ anodes has been reported to be in the range 0.15–0.30 mm at 900°C[129,133,135,136]. No systematic variation with anode thickness is found in Fig. 5, there is, however, a tendency showing that thicker anodes give higher activity. The thickest anode SUH3 (1.4 mm) gives the highest rates pr. cell area and the thinnest anode LH1 (0.01 mm) gives the second lowest rates, which indicates that the reaction depth is larger than 0.01 mm. This is supported by the fact that the thinnest anode, LH1, has the highest rate per nickel area in Fig. 5.

The rate expression that gives the lowest activity and deviates most from the others is PL2, even though the anode used to determine this expression has a thickness of 40 μm, which is a medium value for this comparison. The experiments underlying this rate were conducted with a very high conversion of methane (85–96%). This was taken into account in the data treatment by treating the anode as an integral plug flow reactor, but because of the high conversion the result are highly sensitive to small changes in the outlet composition[125]. It is not reported whether or not the cooling of the catalyst material was considered during data treatment. Note also that the activation energy reported in this study is very low, which could indicate that some mass transfer limitations are not accounted for.

In future studies, the surface area of nickel should be determined, in order to both ease comparison with other experimental studies and to increase the value of the measurements with respect to SOFC modeling work. Until further experimental studies are available, it is reasonable to use a kinetic expression from the general Ni-based steam reforming or with respect to anode surface area in a first, rough SOFC model. The relative good agreement between rates measured on different anodes, means that these expressions should result in reasonable results as also indicated from the model work performed by Nagel et al.[137] where several different kinetic expressions were used in the same model with similar results.

Hecht et al.[112] studied steam reforming kinetics over Ni-YSZ by using a setup were the porous anode was supplied with methane, water and carbon dioxide on one side and a mixture of water and carbon dioxide on the other side. No dense electrolyte was present in this setup. In this way steam reforming could be investigated under SOFC conditions, including realistic diffusion through the anode. The experimental results were compared to a dusty gas model to describe diffusion and a system of 42 elementary reactions to describe the reforming kinetics. The model results fitted the measured data well indicating the suitability of the model. A comparison of the elementary reactions and the other rate expressions in Table 5 would be interesting, both with respect to the rate and the reaction order, but such a comparison is unfortunately not possible. Special notice should be given to the experimental setup used in this work, which is especially suited for measuring steam reforming kinetics for Ni-YSZ in an anode structure. Further experiments on this or similar setups would be valuable.

5. Water gas shift reaction

In SOFC modeling it is often assumed that the water gas shift reaction is at equilibrium at all time. Little work has been conducted to investigate this, but in several experimental works examining steam reforming kinetics, it is outlined that the water gas shift reaction was not at equilibrium[9,110,130,138,139]. Also Hecht et al.[112] include the elementary reactions of the water gas shift reaction in their model (see Section 4.4). Ahmed and Fger[138] examines the approach to the equilibrium of the reverse water gas shift reaction over a Ni/zirconia based anode. The inlet gas contains H2 and CO at different concentrations representing different levels of fuel utilization in an SOFC, but anode size and flow rates are not reported. The approach to equilibrium was defined as 100% \(1 - (P_{CO}/P_{CO2} - 1)\) and is reported to be in the range 80–90% for most fuel utilizations. A few works include an expression for the water gas shift reaction rate[128,130] and the previously described set of elementary reactions by Hecht et al.[112]. If the water gas shift reaction is not at equilibrium, then the potentials of the H2 oxidation and CO oxidation are not equal, which means that the reaction with the highest potential will drive the other reaction forward and thereby move the water gas shift reaction further toward equilibrium. The resulting cell voltage will lie between the two reaction potentials.

6. Modeling internal steam reforming

Modeling of SOFCs is being used widely, for a variety of different purposes. First of all there is the need for relative quick and cheap testing of new configurations and stack designs[10,140–145] as well as ideas for innovative system designs based on SOFCs[146–154]. These are the classical reasons for modeling. For SOFCs the further motivation comes from the fact that it is very difficult to measure the specific condition inside the cell or stack. Here modeling is an invaluable tool to evaluate concentration and temperature profiles and thereby to both avoid hotspots[155,156,126] and to determine optimal operation conditions[20,113,157–160]. An equally important use of models is as a tool in research both to interpret experimental observations[128,161,162] and to determine specific trouble areas where future research should be focused[142,161,163].

A large number of SOFC models exist that include either partial or complete internal steam reforming. A detailed rigorous model of a complete SOFC stack is highly computational demanding, so normally a SOFC model will focus on one aspect and models can roughly be divided into three categories based on the focus of the model.

Micromodels (electrode models) describe in great detail the catalytic, electrochemical and gas phase reactions in the porous electrodes, often taking into account mass and heat transfer effects as well as electrical conduction. This type of model will normally be one-dimensional and describes the performance of a cell in a single point with known bulk concentrations, this can be used to determine key issues for material research and micro structural optimization[112,163,161].

Cell/stack models examine the changes in composition and temperature in the gas channels of an SOFC and they will often have a simplified description of the electrodes and electrolyte in order to avoid excessive computations. These models are two- or three-dimensional and can be used to evaluate concentration and temperature profiles in the cell/stack, and thereby identify trou-
ble areas such as hotspots or areas with low S/C ratios. Single cell models can to some extent incorporate a micro structure model [20,112,137,154,164–166].

System models describe the performance of a complete stack, they are highly simplified and are normally focused on the interaction of the stack with the surroundings. These models are zero- or one-dimensional and intended to be incorporated in flow sheets in order to evaluate and optimize complete systems which includes an SOFC [167–172].

When modeling an SOFC with a significant amount of methane in the inlet, the steam reforming kinetics will have a deciding influence on both the gas composition and the temperature profile both of which are major parameters in determining both the local and overall performance of the cell or stack. This means that micro structure and cell/stack models need to have an accurate description of steam reforming in order to be accurate. System models will often use a thermodynamic description, instead of kinetic expressions to describe the effect of internal reforming [171,172].

Some models describe the reforming reaction by using assumptions such as: equilibrium at all time, or 75% of the remaining CH \(_4\) is converted in each finite element [172–178]. This approach should only be used for initial calculations for a new system or as an alternative to the thermodynamic description in system models.

The most widely used rate expression in SOFC modeling is the one found by Achenbach and Ronesche [109] (SIH3 in Fig. 6) [7,20,137,154,161,163,165,166,179]. The Ni content was smaller than typical in SOFCs (20% w/w on ZrO \(_2\)) [7,20,137,154,161,163,165,166,179]. The Ni content was smaller than typical in SOFCs (20% w/w on ZrO \(_2\)) did not match the electrochemical specifications of an SOFC anode and was rather thick. From the comparison in Fig. 6 it can be seen that this expression gives a reaction rate a bit higher than average, but it is a valid choice for flow models.

Another rate expression, often used in modelling, is that found by Lehner et al. [128] given in entry 10, Table 5, for example in modeling studies in Refs. [142–145,180–182]. It corresponds to the expression by Xu and Fronetti [19] on industrial catalyst. It assumes first order dependence both on methane and water. The latter is rarely observed experimentally, especially at conditions relevant for steam reforming in SOFCs (see Section 4).

In recent literature, several micro structure model works have used a complete set of elementary reactions (42 reactions), with separate kinetic expressions, to describe the catalyzed steam reforming and water gas shift reactions [112,141,159,164,183]. The accuracy of this type of model will primarily depend on how well the gas diffusion and micro structure of the anode are described. This method requires high computer power and since the kinetic data sets are taken from different studies, a comparison with the experimental data would be highly rewarding.

6.1. Recommendations

Until a consensus on the steam reforming kinetics is reached, the best choice for a steam reforming rate expression for use in a model is the use of a kinetic expression measured on the specific cell under the reaction conditions that are relevant for the model, as done by several research groups [112,126,135,162]. If this is not possible, we recommend an expression with a reaction order of methane close to 1, and \( E_A \) around 100 kJ mol\(^{-1}\), possibly a bit lower. The dependency of water is disputed, but it seems that if there is a dependency it is slightly negative.

In micro structure models it is necessary to use a steam reforming rate with respect to Ni surface area. Only few experimental works report this for Ni-YSZ. There seems to be a close correlation to industrial steam reforming for these kinetics and the thoroughly examined expression reported by Wei and Igelisa [40] appears to be a valid choice for this type of model, even though the study was not performed on Ni-YSZ.

7. Conclusion

Optimal operation of SOFCs with internal steam reforming requires that the steam reforming reaction and the electrochemical reactions progress at similar rates. Order of magnitude calculations show that at the temperatures targeted in SOFCs today (\( \approx 700^\circ \text{C} \)), the difference between the rates are now so small that it should be possible to lower the reforming rate to the same level as the electrochemical. Much work is being done on detuning the SOFC anode material in order to achieve this, and an elegant solution would be to use the sulfur that is already present in the natural gas, to reduce the internal reforming rate by blocking the active nickel step sites.

Unfortunately, sulfur increases the long-term degradation of the cell voltage and therefore it may be more viable to block the step sites with alkali metals. A completely different approach that also seems promising is to replace some of the nickel with copper. This seems to lower the catalytic activity, without having a significant influence on cell performance and, furthermore, it increases the resistance toward carbon poisoning. When considering this type of work, it is important to keep in mind that the operating temperature of SOFCs is generally being lowered, so the detuning of the catalyst must be done with consideration to the intended operating temperature.

Another approach for optimizing internal steam reforming utilization is to carefully control the operating conditions so that existing stacks can withstand the temperature gradients that arise. This requires precise modeling, and therefore an overview of steam reforming kinetics on SOFCs was given and discussed. There are large differences in the reported steam reforming kinetics, which is reflected by the number of kinetic expressions that exist for both industrial steam reforming catalysts and on Ni-YSZ for SOFCs. Recent improved understanding of the elementary steps by surface science studies, in situ electron microscopy and DFT calculations have given the possibility to give an atomic level view and to develop new structure models. These verify a strong positive dependence on the partial pressure of methane and a negative influence of water under conditions that are relevant for internal steam reforming in SOFCs.

SOFC models incorporating internal steam reforming have only recently been developed. Even though their number is rapidly increasing they only use a few experimental data sets. Five studies were compared with respect to the geometric surface area of the anode (Fig. 6). It is worth noticing that these anodes showed similar overall reaction rates, in spite of relatively large structural differences. Only three studies on Ni-YSZ could be compared with respect to the surface area of nickel (Fig. 5). The comparison showed a relatively good agreement, but nothing conclusive.

There is a surprising lack of detailed investigations of the catalytic activity of Ni-YSZ with respect to steam reforming, where the nickel surface area and particle size are reported and the common practice for measuring catalytic activity is followed. Such thorough experimental studies are needed to increase the precision of SOFC models with internal steam reforming.

References

Article II

Article in preparation
Abstract

The reaction rate of methane steam reforming over Ni-YSZ anode material for SOFCs has been investigated in a packed bed reactor on two different Ni-YSZ samples. The measurements were performed in the temperature range 600-800 °C and variations in the partial pressure of all reactants and products were studied. In agreement with other kinetic measurements reported in literature, it was found that the steam reforming rate was mostly first order in methane concentration. Hence, the methane dissociation is the rate limiting step. Slight dependencies of other gases were also observed, all other than CO were described adequately by an approach to equilibrium. The CO dependency was described by an adsorption term, which does only have a significant effect at low temperatures.

Furthermore, a previously unreported dynamic behavior of the reaction rate was observed. In particular, a slow deactivation over several days after startup, and a complete regain of the original activity after operation without methane. These dynamic effects did not only effect the reaction rate, but also the activation energy. The extent of this behavior has been examined closer and samples of Ni-YSZ were subjected to different defined reaction conditions and examined with several characterization techniques. The investigations did not give a conclusive explanation for the dynamic behavior of the catalyst. It is tentatively ascribed to changes in the catalyst structure.

Keywords: Steam reforming, Kinetics, SOFC, Ni-YSZ, TEM, XRD, EXAFS, HT-22970

1. Introduction

The steam reforming reaction (Reaction 1) is highly endothermic with a reaction enthalpy of 206 kJ/mol at 25 ºC, whereas the water gas shift reaction (Reaction 2) occurring simultaneously is slightly exothermic with a reaction enthalpy of -41 kJ/mol at 25 ºC [1].

\[ \text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons 3\text{H}_2 + \text{CO} \]  
(1)

\[ \text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \]  
(2)

When having partial internal steam reforming in an SOFC, the waste heat from the electrochemical reactions is used to supply the energy for the endothermic reforming reaction. This also decreases the need for cooling of the SOFC stack, which is normally obtained through a high air flow at the cathode side. Reducing the required air flow and using waste heat for the steam reforming significantly increase the overall efficiency of the SOFC system and thereby reduces cost, of operation.

A literature review of studies of internal steam reforming in SOFCs has been published recently [2]. With the present SOFC technology and operating temperatures, the steam reforming reaction is much faster than the electrochemical reactions. This means that internal steam reforming causes rapid cooling at the anode inlet, resulting in large temperature gradients, reduced efficiency and even, in some cases, physical destruction of the cell due to mechanical stress caused by the large temperature gradient.
Careful control is needed in order to fully utilize the advantages of internal steam reforming and for this purpose it is necessary to have a model that can predict the temperature gradients in an SOFC stack. The precision of such a model will be highly dependent on the reforming rate, but the review [2] showed that only few experimental studies of the steam reforming rate over Ni-YSZ have been published so far and there is little agreement in the reported kinetic expressions [3–9].

2. Experimental

Three different catalysts have been tested, an industrial SOFC Ni-YSZ anode from Topsoe Fuel Cell A/S, an experimental steam reforming catalyst (HT-22970) delivered from Haldor Topsøe A/S consisting of Ni on a MgAl2O4 spinel support, and a model anode material with a Ni content of ≈ 42% w/w, which is similar to the industrial anode. The preparation of the model anode material is described in [10], where it is designated ”Sample E”. The kinetic measurements were conducted in a packed bed reactor made of quartz glass as described by Jensen et al. [11]. The reactor is illustrated in Figure 1. The quartz reactor is 65 cm high, with a diameter of 2.6 cm, the catalyst bed has a diameter of 1.7 cm and the typical bed height is around 2 cm. The catalyst bed is placed on a porous quartz frit where the holes has a diameter of 100-160 μm. So in order to avoid particles getting stuck in the frit a layer of around 0.5 cm quartz wool was placed between the frit and the bed. The distance from the thermocouple to the bottom of the bed is 2-2.5 cm.

The bed consists primarily of inert alumina and amounts to approximately 4 g. At high temperature (700-800°C) around 0.1g catalyst was used and at low temperatures (600-700°C) around 0.4g catalyst was put into the reactor. The catalyst materials were supplied by Topsoe Fuel Cell A/S and Risø-DTU. The sieve fraction of the particles was 180-250 μm. The secondary inlet is mixed with the primary inlet just above the catalyst bed, which means that the effect of CO and CO2 on the reaction rate can be investigated at conditions where the water gas shift reaction is not at equilibrium. The inlets contain the following gases.

primary inlet: CH4, H2O, N2 and CO2

secondary inlet: H2 and CO

A small amount of hydrogen is added through the secondary inlet in all experiments, both to maintain a reducing environment and to avoid having a dead volume in the secondary inlet tube. CO and CO2 are only
added in the experiments that investigate the influence of these species. The water is supplied by leading nitrogen through a heated bubble flask which is kept at 80°C.

Gas flows are controlled with Mass Flow Controllers (MFC) of the type “LOW ΔP FLOW” and “EL-FLOW” from Bronkhorst HI-TEC. The MFCs has analogue control and are controlled with a Gilibrator 2 soap bubble flow meter from Gilian with a specified measuring range of 20-6000 ml/min. Temperature measurements were made with K-type thermo couples.

Table 1: Overview of the gas composition at standard conditions and the range each gas is varied in.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Standard range kPa</th>
<th>kPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>16</td>
<td>8-20</td>
</tr>
<tr>
<td>H₂O</td>
<td>33</td>
<td>24-39</td>
</tr>
<tr>
<td>H₂</td>
<td>8</td>
<td>8-24</td>
</tr>
<tr>
<td>CO</td>
<td>0</td>
<td>0-8</td>
</tr>
<tr>
<td>CO₂</td>
<td>0</td>
<td>0-8</td>
</tr>
</tbody>
</table>

In order to test for mass transport effects, both particle size and total gas flow was varied, neither of these changes had a significant effect on the reactivity, and mass transport limitations is therefore assumed to be negligible. The efficiency of the heat transfer was estimated by comparing the measured temperature at similar conditions with and without steam reforming taking place, and it is estimated that the temperature gradient over the bed is < 5°C. The majority of the measurements had a methane conversion between 5 and 10% mole/mole and all were in the range 4-15% and during data treatment it was assumed that the partial pressures were constant in the bed, using an average value of the inlet and outlet concentrations. A blind test was made where the reactor was loaded with quartz wool and the alumina powder used to dilute the catalyst material. The inert material was treated according to the standard procedure, including reduction procedure, and no activity was observed.

The oxidation state and average coordination number of the Ni particles was determined by X-ray absorption spectroscopy (XAS) in transmission mode at the ANKA-XAS beamline at Karlsruhe Institute of Technology (KIT). The spectra were recorded around the Ni K-edge between 8.2 keV and 9.4 keV. The raw data were energy-calibrated, background corrected, and normalised using the WinXAS 3.0 software [12]. Further the data were Fourier-transformed in k-space between 3 and 15 Å⁻¹. Data fitting was performed in R-space on the Fourier transformed k¹-weighted EXAFS functions (Fourier transform in the range 3.0 - 15 Å⁻¹, S₀² = 0.825). Theoretical scattering amplitudes and phase shifts of the Ni-Ni and the Ni-O shell (only first shell) were calculated using the FEFF code [13].

3. Dynamic Behavior

During the kinetic measurements, it was observed that the catalytic steam reforming activity of Ni-YSZ exhibits a long term dynamic behavior under different operating conditions.

At 750°C and low methane concentrations an initial rapid activation of the catalyst was followed by a short deactivation period, see Figure 2(a), which is normal catalyst behavior. However, after a few hours of apparent steady state, the catalyst was slowly reactivated over a period of several days as shown in Figure 2(b).

In his thesis work, J.G. Jakobsen [14] reported a similar behavior for steam reforming over 5% Rhodium on a MgAl₂O₄ support although this occurred significantly faster and was seen at 500-600°C during a temperature cycle instead of stable operation.

Figure 3 shows two startups similar to those in Figures 2(a) and 2(b), but at high methane concentration and T = 640°C and 750°C, respectively. Here it is seen that there is a long deactivation period (just over one week at low temperature) and no subsequent reactivation was observed.

A slow approach to steady state was also observed after a change in hydrogen concentration. For all gases except hydrogen, a new steady state was achieved rapidly after a concentration change. After a change in hydro-
Figure 2: Approach to steady state after startup over crushed anode material in the packed bed reactor at $T = 750^\circ C$ and low methane concentration $\approx 7.3$ kPa. (a) The first 4 hours, (b) on a longer time scale.

Figure 3: Approach to steady state after startup over crushed anode material in the packed bed reactor at two different temperatures and high methane concentration. (a) $640^\circ C$, (b) $740^\circ C$. 
gen concentration it took several hours, or even days to achieve a new steady state, depending on temperature.

Similar tests were made with the experimental steam reforming catalyst (HT-22970) from Haldor Topsøe A/S and no long term dynamic effect was observed. First of all this shows that the observed dynamic effects is an actual property of the catalyst, not an effect from the setup or experimental method. Secondly it means that the dynamic effect is either caused by the support material, Yttria stabilized Zirconia, interactions between the support and catalyst, or by the fact that the SOFC anode contains very large Ni-particles with diameters up to 2 μm.

Furthermore, it was found that the activity that is lost during the stabilization period could be regained by passing a water rich gas (including H2) through the catalyst bed with no methane in the gas. In Figure 4 it is shown that 1 hour exposure to a water rich gas did not have any effect, but 16 hours exposure resulted in more than a doubling of the catalytic activity.

![Figure 4: A test of the reactivation of catalytic activity of Ni-YSZ in the packed bed reactor with crushed anode material. T = 790°C, PCH4 = 15 kPa, PO2 = 30 kPa, PCH4 = 7 kPa. The three plots show the sum of CO and CO2 in the outlet for the catalyst after rate determination experiments, and after respectively 1 hour and 16 hours with no methane in a water rich environment.](image)

Three explanations for the long-term dynamic behavior exhibited by Ni-YSZ when used as a steam reforming catalyst were considered on the basis of literature: 1) Poisoning of the catalyst surface [15–17]. 2) Changes in Ni particle size, by formation of Ni nano particles and subsequent sintering [5, 18]. 3) Changes in Ni particle sphericity resulting in a change in the number of step sites, which has been shown to account for the majority of the catalytic activity [17, 19–21].

4. Characterization of Ni-YSZ Model catalyst

In order to examine the different possible explanations for the catalyst behavior, four samples of the model Ni-YSZ catalyst were prepared for characterization. The first was an as-sintered sample. The second sample was reduced. The third sample was reduced, and then run at standard gas conditions at 800°C until the activity was stable. The fourth sample was reduced, stabilized as the second sample and then subject to a gas consisting of 7.6% H2, 31.5% H2O and balance N2 at a total pressure of 1.1 bar for 16 hours at 800°C in order to achieve the regain of activity shown in Figure 4. These samples were not diluted by inert material during operation.

The samples were first examined with Scanning Electron Microscopy (SEM), which indicated that the samples had different particle size distributions, but the results were not conclusive. Because of this, further examinations were made with Transmission Electron Microscopy (TEM), as described in Section 4.1. It should be noted that it was necessary to crush the samples further down prior to investigation with TEM. The samples were also studied with low-voltage scanning electron microscopy, by courtesy of Karl Thydén from Risø-DTU, the method for this technique has previously been described by Thydén et al. [22]. The overall structure of the samples were found to be very similar both to each other and to a standard SOFC anode from Risø-DTU, meaning that any structural differences between the samples must be found on the nano scale. Clusters of nano scale particles were also observed, in accordance with the trends found in the TEM images as described in Section 4.1.

Because of the large span in Ni particle size (2 nm to >1 μm) it is impractical to determine the particle size distribution from microscopy. It was instead attempted to obtain an average crystallite size from X-Ray Diffraction (XRD) by using the Scherrer formula. The average Ni crystallite size were found to be in the range 200-300 nm. Within the experimental uncertainty no difference in the Ni crystallite size could be detected in the different samples. The XRD patterns did however show that there as expected was no crystalline NiO present in any of the reduced samples.

4.1. Transmission Electron Microscopy

In addition to the TEM images, dark field imaging was used to ease the observation of small particles. Some of the particles were also investigated by Energy-dispersive X-ray spectroscopy (EDX), in order to distinguish between Ni (or NiO) and YSZ particles. The areas
where EDX was performed are marked on the TEM images with numbered circles, and the measured compositions are given in the figure caption. The sample holder is made of copper and carbon, so these two materials are removed from the composition, oxygen is also omitted from the composition because it is not quantified correctly by the EDX.

Normally, TEM images can be used to determine particle size distribution of the catalytically active material, but for this catalyst there is a huge span in the size of the Ni particles, i.e. 2-3 orders of magnitude (2 nm but also >1 μm). This means that if a particle size distribution was to be measured with TEM it would require many measurements in order to achieve statistical precision. It should also be kept in mind that the amount of sample examined with TEM is very limited, and as such it can not be guaranteed that the results are fully representative.

Figure 5 shows images taken on the reduced model anode material and a bimodal particle size distribution can be seen. Both the dark field imaging in Figures 5(c) and 5(d) as well as the higher magnification in Figures 5(b) show clusters of particles in the size <10 nm. Such clusters were not seen in the as-sintered sample (no images of this sample is included here). EDX measurements could not be performed on such small sample areas as the nano particles represent, but it is assumed that the nano particles are residue, left behind when a Ni/NiO particle is reduced in size during reduction. This has been described previously by King et al. [5] and has very recently been shown with in situ TEM by Jeangros et. al [18]. Such clusters of nano particles were observed on several of the larger particles in the reduced sample and they are most likely the cause for the high initial activity of the catalyst.

The TEM images of the deactivated sample (Figure 6) show clear signs of sintering. The particles in Figures 6(b), 6(c), 6(d) varying in size from 5 nm to 200 nm are clearly larger and less abundant than in just reduced sample, in particular, it was not possible to find any nano particle clusters as the one seen in Figure 5(b). Nevertheless, the dark field images in Figures 6(c), 6(d) and the image in Figure 6(b) show that there are still nm scale particles present, just fewer of them. So after the initial reduction in activity of the model anode material, the Ni particle size span from 5 nm to 2 μm. The images further indicates that it is no longer only a bimodal distribution of nm particles and μm particles, there are also Ni particles in all sizes in between.

Figure 7 shows representative TEM images of the reactivated sample, which, after the initial deactivation has been subjected to H2O/H2 without methane in order to recover the activity of the catalyst, as described earlier.

The TEM images of the reactivated sample seems to show more Ni nano particles than the deactivated sample and even clusters of 5-10 nm particles was observed as seen in Figure 7(b) and 7(c). This looks very similar to the clusters seen in the freshly reduced sample in Figure 5. In order to quantify these observations a count of the nano particles observed in a series of 10 dark field images was made for each sample. The samples are crushed further just before TEM measurements, and since the YSZ particles are agglomerates of 50-100 nm particles, it was chosen only to consider particles smaller than 50 nm. The particle count was normalized by setting the count for the just reduced sample to 1, and the count for the deactivated and reactivated samples were found to be 0.51 and 0.74 respectively. Keep in mind that these numbers should only serve as a rough quantification of an observed trend.

A possible explanation for such a re-dispersion has been given by Ruckenstein and Hu [23] who suggested the following three step mechanism from experimental observations: “(1) extension of films from the crystallites, (2) coalescence of the films surrounding neighboring crystallites, and (3) further extension of the films.”

Figure 7(d), apparently show flat Ni particles on the surface of a larger particle, this supports the theory that a change in the Ni particle shape increases the number of step sites and thereby increases the reaction rate. Recently reported density functional theory calculations showed that these step sites are approximately a 100 times more active than terrace sites [21], so they have a significant impact on the overall reaction rate.

It is well known that small Ni particles are very dynamic [19], the same is known for copper particles on zinc oxide [24, 25], where it has been shown that the reaction rate is higher during methanol synthesis if the CO/CO2 ratio is high. This, under certain conditions results in deactivation followed by reactivation, similar to what is reported in this study, although in a much smaller time frame. Furthermore, Ruckenstein and Hu [23] have reported a mechanism for the re-dispersion of Ni particles in steam which is shown to occur via the following three steps (1) the extension of films from the crystallites, (2) the coalescence of the films surrounding neighboring crystallites, and (3) further extension of the films over the entire substrate. It should however be noted that these observations were also made with zirconia as the support material, so there it is possible that part of the behavior is induced by interaction between Ni and zirconia.

These previous studies along with the observations
made in the TEM images shown here, leads to the conclusion that the dynamic behavior of Ni-YSZ is most likely caused by a combination of three types of restructur-ting, i.e. sintering, re-dispersion and changes in particle shape, changing the amount of the highly active step sites.

4.2. X-ray Absorption Spectroscopy

The X-ray absorption near edge spectroscopy (XANES) data are given in Figure 8. They show that the spectrum of the Ni-YSZ fuel cell anodes is very similar to nickel foil and even after exposure to air most of the nickel is in reduced state (>97%). Also the wiggly part (EXAFS region) is very similar to the pure nickel foil indicating large nickel particles as observed in transmission electron microscopy. However, Figure 8(b) shows that the backscattering is smaller in the Fourier transformed EXAFS spectra, which is especially fine for the reactivated catalyst.

This is also reflected in the Fourier transformed EXAFS data, see Figure 8(b), where not only first shell but also the high Ni shells are well observed. The backscat-tering is highest in the reduced and the deactivated Ni-YSZ sample. This supports that restructuring occurs
Table 2: Fit of the EXAFS data at the Ni K-edge. CN: coordination number; R: interatomic distance; $\sigma^2$: Debye Waller factor; $\Delta E_0$: energy shift.

<table>
<thead>
<tr>
<th>sample</th>
<th>CN</th>
<th>R</th>
<th>$\sigma^2$</th>
<th>$\Delta E_0$</th>
<th>Residual</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni foil</td>
<td>12</td>
<td>2.849</td>
<td>0.0055</td>
<td>7.6</td>
<td>-</td>
</tr>
<tr>
<td>reduced</td>
<td>10.9</td>
<td>2.483</td>
<td>0.0065</td>
<td>6.4</td>
<td>1.8</td>
</tr>
<tr>
<td>deactivated</td>
<td>9.8</td>
<td>2.481</td>
<td>0.0055</td>
<td>6.3</td>
<td>1.0</td>
</tr>
<tr>
<td>reactivated</td>
<td>7.0</td>
<td>2.484</td>
<td>0.0055</td>
<td>7.0</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Data fitting of the first shell gives a similar picture indicating that most Nickel neighbors are found for the reduced Ni-YSZ. This is surprising if considering the conclusions from electron microscopy. Note that there are several effects that may influence the number of nearest Ni neighbors: small particle sizes, disorder but also partial oxidation / dissolution of oxygen/carbon may decrease the coordination number. It seems that the reduced sample is the one which is most defined and therefore gives a coordination number closer to 12 with an average particle size >5 nm. The reactivated sample during the reactivation process.
has a significantly smaller coordination number which would correspond to a much smaller particle size which is in contradiction to TEM and XRD results. Therefore this rate indicates a stronger disorder due to e.g. oxygen dissolved during air exposure, but also carbonaceous species that lead to deactivation. Most interesting is that the reactivated sample has a significantly lower coordination number, which is probably due to redispersion as is also indicated by TEM.

5. Kinetic Studies

The rate order determinations for the different gas species over the model anode are shown in Figure 9 at 650°C and in Figure 10 at 700°C. The methane rate order has also been determined at other temperatures, and the results are shown in Table 3, along with the values from Figures 9 and 10.

Methane has an apparent rate order of around 0.9, the water partial pressure has no effect on the reaction rate, and the rate of all other species are close to zero. It can be seen that there is some significant deviation between
Table 3: Measured rate order of methane at different temperatures

<table>
<thead>
<tr>
<th>T [°C]</th>
<th>reaction order</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>0.78</td>
</tr>
<tr>
<td>625</td>
<td>0.84</td>
</tr>
<tr>
<td>650</td>
<td>0.91</td>
</tr>
<tr>
<td>675</td>
<td>0.91</td>
</tr>
<tr>
<td>700</td>
<td>0.87</td>
</tr>
<tr>
<td>725</td>
<td>0.94</td>
</tr>
<tr>
<td>775</td>
<td>0.80</td>
</tr>
<tr>
<td>800</td>
<td>0.80</td>
</tr>
</tbody>
</table>

the measured data points in some of the data series, especially at 700°C. It is, however, still worth noticing that the reaction order for CO is measured as -0.14 at 650°C and 0.10 at 700°C. This change with temperature supports the recent result from first principle calculations, showing that the dominant elementary reaction change with temperature [29]. There are however also other possible explanations, such as an increase in the species adsorbed on the catalyst at lower temperatures or a change in the approach to equilibrium. For the sake of the power law expression, the rate order is set as a mean of the observed rates, i.e. 0 for CO and the resulting power law expression is shown in Equation 3. In section 6 a more thorough discussion of such effects is made while determining the reaction mechanism and the corresponding kinetic expression.

$$r = k P_{\text{CH}_4}^{0.9} P_{\text{H}_2}^{-0.2} P_{\text{CO}_2}^{0.2}$$

(3)

Figure 11 shows an Arrhenius plot for the kinetic constant obtained with the power law expression, giving an activation energy of 185 kJ/mol and a pre-exponential factor of 139 mol/(s g Pa^{0.9}).

5.1. Temperature Dependence at Non-Steady State

There is a large span in the observed activation energies, 58-229 kJ/mol, reported for methane steam reforming in literature [2]. Possible reasons for these large differences, are for example transport limitations, differences in catalyst structure, lack of an approach to equilibrium term, rate determining step changes with temperature or species covering the surface resulting in different observed kinetic expressions at different conditions.

The long term dynamic behavior presented in this paper presents a new possible explanation for these large deviations. Lacking knowledge of a slow approach to steady state can have a large influence on the observed
activation energy. In order to illustrate this, measurements were made with fast changes of temperature. A model anode sample was reduced, and then operated with standard gas conditions at 800°C until the activity has stabilized. After this, three series of temperature changes were made, with different holding time at each temperature before the activity measurement was taken. One with 60 min waiting period, one with 30 min waiting period and one where the reactor was continuously cooled from 800°C to 650°C with a rate of approximately 5°C/min. After each series, the temperature was kept at 800°C until stability had been reached again.

Figure 12 shows the Arrhenius plot for the three measurement series for the reaction constant with respect to the power law expression in Equation 3. The observed activation energy of the three measurement series are close to each other. This is because the approach to steady state after a change in temperature is so slow that the change in activity after an hour is not significant, meaning that only the initial jump in activity is effecting these three series. This initial jump in activity takes approximately 5 minutes, and this small time delay is most likely causing the curvature seen in the series with no holding time. The observed activation energies in these fast measurement series are 76 kJ/mol with no holding time, 73 kJ/mol with 30 min holding time, and 72 kJ/mol with 60 min holding time. This is less than half of the 185 kJ/mole obtained when waiting for stability at each temperature. It is likely that the activation energy found with fast temperature changes is the activation energy of the reaction, and the increased activation energy found when waiting for stability is caused by reversible structural changes in the catalyst. It is, however, surprising that the activation energy found in these measurements are lower at longer holding time.

These two different activation energies for the reactivity, combined with the dynamic behavior described in section 3, may very well be the reason for the large variations in the activation energy values reported in literature. The measurements made here with fast temperature changes were made after the initial deactivation had been completed at 800°C. If measurements are carried out while the deactivation is taking place, the observed activation energy will depend on whether temperature changes are performed by increasing or decreasing temperature, as well as how fast the temperature changes are made.
Figure 9: Measured dependencies of the different gas species over the model Ni-YSZ catalyst at 650°C. The corresponding fit data are given in the text in each of the graphs.
Figure 10: Measured dependencies of the different gas species over the model Ni-YSZ catalyst at 700°C. The corresponding fit data are given in the text in each of the graphs.
6. Kinetic Expressions

A great number of elementary reactions are known to take place during catalytic steam reforming of methane [26, 27]. It is however often estimated that the 9 elementary reactions shown below are sufficient to give a complete understanding of the mechanism [14, 28, 29].

1. \( CH_4 + 2' \rightarrow CH_2^+ + H^+ \)
2. \( CH_2^+ + CO \rightarrow CH_2O + H^+ \)
3. \( CH_2^+ + \cdot \cdot \cdot \rightarrow CH_2^+ + H^+ \)
4. \( CH^+ + \cdot \cdot \cdot \rightarrow C^+ + H^+ \)
5. \( H_2O + 2' \rightarrow HO^+ + H^+ \)
6. \( HO^+ + \cdot \cdot \cdot \rightarrow O^+ + H^+ \)
7. \( C^+ + O^+ \rightarrow CO^+ \cdot \cdot \cdot \)
8. \( CO^+ \rightarrow CO + \cdot \cdot \cdot \)
9. \( 2H^+ \rightarrow H_2 + 2' \)

It is generally agreed, that Reaction 1 is a rate limiting step. Both experimental studies and Density Functional Theory (DFT) calculations have shown that there is two rate determining steps, Reaction 7 being the second one [3, 29]. Furthermore, the dissociation of water, Reaction 5, has also been proposed as a rate determining step [30, 31, 32].

Assuming that the surface is clean from adsorbents and Reaction 7 is the rate limiting step, results in the kinetic expression shown in Equation 4.

\[
r = k \frac{P_{CH_4} P_{H_2O}}{P_{H_2}} \left(1 - \frac{Q}{K_{eq}}\right) \theta^2
\]  

(4)

Where \( K_{eq} \) is the equilibrium constant for the steam reforming reaction and \( Q \) is defined as shown in Equation 5. The term \((1-Q/K)\) is referred to as the approach to equilibrium term and when equilibrium is reached the rate becomes 0 because \( Q = K \). \( \theta \), is the fraction of free surface sites, which is equal to 1 according to the assumption of clean surface.

\[
Q = \frac{P_{H_2}^0 P_{CO}}{P_{CH_4} P_{H_2O}}
\]  

(5)

Equation 4 shows a negative third order dependency on hydrogen, coming from the assumption that equation 1-6 is in quasi-equilibrium. There are no experimental observations showing a negative third order dependency on hydrogen, neither in literature nor in this study, therefore Reaction 7 is not considered a rate limiting step.

Assuming a clean catalyst surface and that Reaction 1 is the the only rate limiting step, results in the the following kinetic expression.

\[
r = k P_{CH_4} \left(1 - \frac{Q}{K_{eq}}\right)
\]  

(6)

If the dissociation of water is also assumed to be rate limiting, the resulting kinetic expression will also have a first order dependence on the partial pressure of water. Even though a few studies report such a dependence [7, 31, 32], most experimental studies of steam reforming kinetics, including the measurements in this paper, do not observe any dependence of water partial pressure. In this work Reaction 5 is therefore not considered a rate limiting step.

The assumption that the catalyst surface is completely clean and available for reaction is not always valid, meaning that the free surface area, \( \theta \), is not equal to 1. Even though the temperatures used in this study are rather high, it is observed that the reaction rate has a low order dependence on both \( H_2 \), \( CO \) and \( CO_2 \), which could be an indication of some degree of surface coverage, especially at lower temperature. Equation 7 shows the kinetic expression where \( CO \) is the most abundant species on the surface area.

\[
r = \frac{Q^2 k_{CH_4} P_{CH_4} \left(1 - \frac{Q}{K_{eq}}\right)}{1 + k_{CO} P_{CO}}
\]  

(7)

6.1. Intrinsic Kinetics

Kinetic expressions with clean surface and with either \( H_2 \), \( CO \) or \( H+CO \) as most abundant species has been fitted to the reaction rates measured over the model anode. It was found, however that several different sets of parameter values could give similar fit to the experimental data, a summary of some different best fits is given in Table 4. The deviation values given in the table is an average of the deviation between each measurement point and the corresponding model point, calculated from Equation 8.

\[
err = \frac{|r_{measured} - r_{model}|}{r_{measured}} \times 100\%
\]  

(8)

A comparison of the power law and clean surface expressions in Table 4 show that the approach to equilibrium term accounts for a large part of the deviations in the power law expression, introducing this term gives much better quality of the fit. Especially the deviation of the measurements with \( CO_2 \) changes, get a better representation when the approach to equilibrium term is included, going from 97.1% to 19.6% average deviation.
The majority of this improve comes from the fact that the observed CO₂ dependency change with temperature, which is described poorly by the power law expression. Apparently only the CO dependence is not completely described by the clean surface expression, i.e. a deviation of 58% compared to 16.9% and 19.6% for H₂ and CO₂ and 18.9% overall deviation. This could indicate that CO covers a significant part of the catalyst surface.

Even though the approach to equilibrium term seems to account for the dependency on H₂ and CO₂, expressions with adsorption of both species has been tested, since the three species are connected through the water gas shift reaction. The expression with CO₂ and H₂ adsorption are not included in Table 4, since none of them gave a noteworthy improved fit to the data.

The different parameter values found for the expression assuming CO as the most abundant surface species in Table 4, exemplifies an inherent weakness in micro kinetic models. Several different sets of parameter values was found which all give a good fit to the experimental data, illustrating that the large number of model parameters enables a fit, even though the underlying assumptions may not be correct. The best fit was obtained with a small negative or positive activation energy. Even a fit with EA,CO = 0 (i.e. temperature independent) gave a good fit. It is expected that the activation energy of adsorption of gasses is negative, since adsorption is normally reported to decrease with increasing temperature. On this basis, the expression shown in Equation 9 was chosen. In literature, the activation energy of CO adsorption is reported to be around -115 kJ/mol [26, 33], but this does not fit with the data presented in this paper. It has, however, also been shown that Eₐ,CO is highly dependent on the support material [34].

\[
    r = \frac{110 \text{ mole} \exp\left(-\frac{199 \text{kJ/mole}}{RT}\right) P_{\text{CH}_4} \left(1 - \frac{Q}{K_c}\right)}{\left(1 + 1.7 \times 10^{-6} P_{\text{H}_2}\exp\left(\frac{26 \text{kJ/mol}}{RT}\right) P_{\text{CO}}\right)^2} \tag{9}
\]

This expression was also determined fitted to the kinetic measurements for the industrial anode material, as shown in Equation 10, with an overall deviation from experimental data of 19%.

\[
    r = \frac{100 \text{ mole} \exp\left(-\frac{195 \text{kJ/mol}}{RT}\right) P_{\text{CH}_4} \left(1 - \frac{Q}{K_c}\right)}{\left(1 + 4.6 \times 10^{-7} P_{\text{H}_2}\exp\left(\frac{232 \text{kJ/mol}}{RT}\right) P_{\text{CO}}\right)^2} \tag{10}
\]

The deviation for the power law expression determined from the industrial anode measurements is 41.4% and for the clean surface expression it is 21%. The average deviation for the final expression over the industrial anode is 4 percentage points higher than that over the model anode.

Assuming an average Ni particle size of 250 nm and that all Ni particles are spherical and only have single point contact with other particles, the Ni surface area of the model anode and industrial anode material is estimated to be 0.16 m²/g. From this estimate a comparison is made of the expressions obtained in this study with expressions found in literature, see Figure 13. A more thorough comparison of the rate expressions reported in literature is given in [2]. The rate expression measured by Wei and Iglesia [35] is measured over a classical steam reforming catalyst, and is included in Figure 13 as a reference. It is seen that the rates obtained in this paper is in the same range as those previously reported in literature, though in the high end of the range, especially at high temperatures. Furthermore, it is seen that the rate measured for the industrial anode and the model anode are almost identical.

<table>
<thead>
<tr>
<th>most abundant species</th>
<th>Parameter values</th>
<th>Deviation</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ACH₄</td>
<td>EACCH₄</td>
<td>ACO</td>
<td>EACO</td>
<td>overall %</td>
</tr>
<tr>
<td>power law</td>
<td>139</td>
<td>185</td>
<td>-</td>
<td>-</td>
<td>45.7</td>
</tr>
<tr>
<td>clean surface</td>
<td>227</td>
<td>205</td>
<td>-</td>
<td>-</td>
<td>18.9</td>
</tr>
<tr>
<td>CO</td>
<td>100</td>
<td>197</td>
<td>4.60E-07</td>
<td>-41</td>
<td>15</td>
</tr>
<tr>
<td>CO</td>
<td>110</td>
<td>198</td>
<td>1.70E-06</td>
<td>-26</td>
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<tr>
<td>CO</td>
<td>103</td>
<td>197</td>
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<tr>
<td>CO</td>
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<td>198</td>
<td>5.50E-04</td>
<td>18</td>
<td>14.4</td>
</tr>
</tbody>
</table>

Table 4: Summary of the different kinetic expressions fitted to the experimental data, the first four columns show the values of the pre-exponential factor and activation energy for respectively, methane dissociation and CO adsorption. The last five columns show the average deviation between the kinetic expression and the experimental data for all data points and data with varying H₂O content, H₂ content and CO content and CO₂ content, respectively.
7. Conclusion

A long term dynamic behavior of Ni-YSZ, when used as a steam reforming catalyst has been discovered. This includes an initial deactivation over days or even weeks depending on conditions. This initial loss of activity was completely recovered by prolonged exposure to H$_2$O/H$_2$ without methane. Furthermore, a slow approach to steady state (3-30 hours) after changes in temperature and hydrogen content was observed.

Characterization of the catalyst indicated that the dynamic behavior is caused by changes in Ni particle structure through the following mechanisms: During reduction, the shrinking NiO/Ni particles deposits Ni nano particles, which gives a high initial activity but gives a slow deactivation because of sintering. The regain of catalytic activity caused by exposure to H$_2$O/H$_2$ without methane is most likely caused by a re-dispersion of the Ni nano particles or removal of poisons, such as carbonaceous species. The slow approach to steady-state after changes in temperature and hydrogen content was tentatively ascribed to changes in Ni particle sphericity. These explanations are, however, not satisfactorily proven, so further investigations are needed, preferably with in-situ techniques, since the Ni particle structure are likely to change during cooling of the samples.

The activation energy was measured both with and without waiting for steady state at each temperature, giving 195-198 kJ/mol and 71-76 kJ/mol, respectively. This was done in order to illustrate that the dynamic behavior reported in this article may very well explain the large differences in the activation energies reported in literature.

Finally, the steam reforming rate was measured over both an industrial Ni-YSZ anode and a model anode material. The activity of the two samples were near identical and was best described by assuming methane dissociation as the rate limiting step and CO as the most abundant species on the catalyst surface.

8. Acknowledgment

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References


Article III

Article in preparation
Methane Steam Reforming over Ni-YSZ Solid Oxide Fuel Cell Anode in Stack Configuration

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Abstract

The kinetics of catalytic steam reforming of methane over a Ni-YSZ anode for Solid Oxide Fuel Cells (SOFC) have been measured in a stack configuration. In order to decrease the degree of conversion, a single cell stack with reduced area was used. Measurements were performed in the temperature range 600-800°C and with variations in the partial pressure of all reactants and products. The obtained rate measurements have been fitted to a power law expression. A simple model is used to predict methane conversion in a stack configuration from intrinsic kinetics. These predictions are compared with the stack measurements presented here, and a very good correspondence is obtained.

Keywords: steam reforming, Kinetics, Solid oxide fuel cells, Ni-YSZ

1. Introduction

The major advantage of partial internal steam reforming in an SOFC is that the waste heat from the electrochemical reactions is used to supply the energy for the endothermic reforming reaction (Reaction 1) with a reaction enthalpy of 206 kJ/mol at 25 °C. The overall reaction is still endothermic when taking into account the exothermic water gas shift reaction (Reaction 2) having a reaction enthalpy of -41 kJ/mol at 25 °C [1].

\[ \text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons 3\text{H}_2 + \text{CO} \] (1)

\[ \text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \] (2)

A further advantage of internal reforming is the decreased need for cooling via air flow at the cathode side, which can significantly increase system efficiency.

The rate of catalytic steam reforming of methane over an industrial SOFC anode is very high [2]. This is caused by the combined effect of high operating temperature, a highly active catalyst material, and a high catalyst content. The result is a rapid cooling, due to the reaction enthalpy, at the anode inlet giving large temperature gradients which decreases the stack efficiency and in the worst case can result in cell cracking, due to thermal stress. So in order to achieve optimal operation of SOFC systems with internal steam reforming, it is necessary to have a good understanding and control of the amount reforming taking place in the cell, this requires a good model representation of the stack, which has also received much attention lately [3–10]. The accuracy of such models depend on the accuracy of the kinetic expression used to predict the steam reforming rate and the purpose of this work is to obtain such an expression measured directly in a stack configuration. Furthermore, it would be highly advantageous to be able to predict the reforming rate in different stack configurations. In rigorous models describing both the flow in the gas channels and the diffusion through the anode the observed reforming rate can be predicted by using an intrinsic kinetic expression. Such a model will however require heavy computations if used as a stack model. In Section 4 a simple method for predicting reforming rate in a stack is presented and validated.

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2. Experimental

The setup is an "Evaluator C50" from FuelCon [11], which has undergone some modifications to fit the purpose of these experiments. Dry gas flows are controlled with Mass Flow Controllers (MFC) of the type "LOW ΔP FLOW" and "EL-FLOW" from Bronkhorst HI-TEC, which are calibrated using a Gilibrator 2 soap bubble flow meter from Gilian with a specified measuring range of 20-6000 ml/min. Water vapour is added by bubbling nitrogen through a bubble flask at 90°C. Temperature measurements were made with K-type thermocouples for the temperature range -40 to 850°C.

Two IR-analyzers of the type NGA 2000 Analyzer from Fisher-Rosemount, were used interchangeably. The analyzers only measure CO and CO$_2$ contents, the contents of the other species were calculated from a mass balance, as verified by full gas analysis by GC. The analyzers have a measurement error of 1% of the given measuring limit.

The stacks were reduced by the following procedure: Heating to 860°C in N$_2$. At 860°C the gas was changed to 20% H$_2$ in N$_2$ for at least 4 hours, hereafter the sample was cooled to the test temperature and measurements were started.

The first attempt of measuring the steam reforming kinetics were made on a 5-cell SOFC 10cmx10cm standard stack from Topsøe Fuel Cell A/S. It was found that the methane was completely converted, even at the highest flows that the setup could deliver.

Therefore a special stack was made, also by Topsøe Fuel Cell A/S, with only a single crossflow cell. Three quarters of the cell was cut away so that number of the cathode flow channels were removed, and the length of the anode flow channels were shortened, as illustrated in Figure 1.

A further decrease in cell area would have been preferred, but removing part of the cell significantly reduced the robustness of the cells, and several modified cells cracked under conditions that a normal stack could easily withstand. Furthermore, removing more than 3/4 of the cell could result in a gas flow pattern significantly different from that of full cell.

Four thermocouples were placed in the gas distribution plates close to the flow channels, in order to monitor the temperature gradient. One at each of corner of the fuel inlet side and one at the corner with fuel outlet and air inlet, and finally one at the fuel outlet and halfway through the air channel. The temperature used in later calculations is an average of these four measurements. The cathode side was only fed with nitrogen, both in order to avoid mixing of air with the anode gas, and to avoid electrochemical reactions in the cell. It is desired to avoid the electrochemical reactions, since the steam reforming reaction can be studied better, when no other reactions are taking place.

The rate measurements on the quartercell stack was performed at flows, much higher than what is used during normal operation of an SOFC. $F_{\text{tot}} \approx 2$ Nl/min. This was done in order to decrease the degree of conversion of methane. The pressure and temperature were, $T = 600-700$°C, $P = 1.1-1.25$ atm.

Table 1 shows the standard gas composition as well as the range each gas species is varied in at the inlet.

![Figure 1: Illustration of the orientation of the quartercell with respect to flow directions.](image)

<table>
<thead>
<tr>
<th>Gas</th>
<th>Standard range (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>12</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>56</td>
</tr>
<tr>
<td>H$_2$</td>
<td>7</td>
</tr>
<tr>
<td>CO</td>
<td>0</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 1: Overview of the gas composition at standard conditions and the range each gas is varied in.

3. Results

During the rate measurements on the quartercell stack it was observed that the catalytic activity had a slow approach to equilibrium after start-up and after changes in temperature or hydrogen partial pressure. This behavior has also been found during kinetic measurements on a Ni-YSZ anode catalyst in a flow reactor [12], with the only difference being that the response time is longer in the stack measurements. The reason for this...
is that changes in the catalytic activity at the anode inlet will effect the temperature profile and gas composition, and thereby the catalytic activity further down the anode flow channels. An important note on this dynamic behavior is that if the activation energy is examined without waiting for steady state after each temperature change, the value will be underestimated with a factor 2-3 [12]. All measurements reported in this paper are obtained after steady-state has been achieved at the relevant temperature. Figures 2 and 3 show the the influence on the flow rate by varying the gas composition at respectively 650°C and 750°C. The measurements of the rate order of CO at 650°C where subject to experimental problems and is not included.

The observed reaction order of all species except methane is seen to be close to zero, in agreement with the majority of the expressions reported in literature [2, 13–15]. There is also seen a weak dependence on H2, -0.2 at 650°C and 0.1 at 750°C, this could be due to restructuring of the catalyst [12]. The influence of methane partial pressure has been tested at several temperatures, and the observed rate orders are shown in Table 2. A power law expression is fit to the measured data using a methane rate order of 0.7. It should be noted that this rate expression is only intended as a direct description of the observed conversions and as such, mass transport limitations and temperature gradients have not been taken into account. Such effects will be accounted for in the next section, i.e. the rate constant is calculated from Equation 3. The change in methane concentration through the cell is taken into account by using a logarithmic mean of the the inlet and outlet concentrations, even though this is only accurate when there is a first order dependency.

$$k = \frac{r_{obs}}{A_{ano} \cdot \text{logmean}(P_{CH4})^{0.7}} \quad (3)$$

$$r_{obs}$$ is the observed rate and $$A_{ano}$$ is the geometric anode area ($$\approx 23cm^2$$). An Arrhenius plot of the rate constant for this kinetic expression is shown in Figure 4, resulting in the rate expression in Equation 4.

$$r = 2 \cdot 10^4 \frac{\text{mole}}{s \cdot m^2 \cdot \text{Pa}} \cdot \exp(-166.1 \frac{kJ}{mol} R_g P_{CH4})^{0.7} \quad (4)$$

The average deviation between the model and the measurement points is 20.6%.

### 4. Predicting Rate from Intrinsic Kinetics

Kinetic measurements in a stack configuration are subject to mass transport limitations and temperature

<table>
<thead>
<tr>
<th>T [°C]</th>
<th>reaction order</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>0.63</td>
</tr>
<tr>
<td>625</td>
<td>0.56</td>
</tr>
<tr>
<td>650</td>
<td>0.75</td>
</tr>
<tr>
<td>675</td>
<td>0.80</td>
</tr>
<tr>
<td>725</td>
<td>0.63</td>
</tr>
<tr>
<td>750</td>
<td>0.65</td>
</tr>
<tr>
<td>775</td>
<td>0.71</td>
</tr>
<tr>
<td>800</td>
<td>0.73</td>
</tr>
</tbody>
</table>

Table 2: Measured rate order of CH4 at different temperatures

Figure 4: Arrhenius plot for measured rate constants on the quarter cell stack.
Figure 2: Measured dependencies of the different gas species over the quarter cell stack at 650°C
Figure 3: Measured dependencies of the different gas species over the quarter cell stack at 750°C
gradients. This means that a rate expression obtained on a stack is not necessarily valid for a stack with a different configuration. In detailed models with a complete description of mass and energy transport this problem can be avoided by using intrinsic kinetics. This type of model requires massive computations, and as such are not viable for flow sheet models. Here a simple approach to predicting steam reforming kinetics in a stack from intrinsic kinetics is presented and validated against the stack measurements. The cell/stack is described by the design equation for a packed bed reactor as shown in Equation 5 [16] and the differential equation is solved using ode45 in matlab.

\[ \frac{dX_{CH_4}}{W_{cat}} = \frac{r_{eff}}{N_{CH_4,in}} \]  

(5)

\[ X_{CH_4} \text{ is the conversion of methane, } W_{cat} \text{ is the catalyst weight, } N_{CH_4,in} \text{ is the molar inlet flow of methane and } r_{eff} \text{ is the effective reaction rate described by Equation 6.} \]

\[ r_{eff} = \eta \star r_{int} \]  

(6)

\[ \eta \text{ is the efficiency factor, calculated from Equation 7. } \eta \text{ describes how big a fraction of the available catalyst material that is being fully used, i.e. an efficiency factor } = 1 \text{ corresponds to full usage of the catalyst [17].} \]

\[ \eta = \frac{Tanh(\phi)}{\phi} \]  

(7)

Where \( \phi \) is the Thiele modulus:

\[ \phi = L \sqrt{\frac{k}{D}} \]  

(8)

\( L \) is the anode thickness, \( k \) is the rate constant (s\(^{-1}\)) and \( D \) is the effective diffusion coefficient (m\(^2\)s\(^{-1}\)) of methane. The diffusion coefficient is assumed to be temperature independent and set to 10\(^{-5}\)m\(^2\)s\(^{-1}\). This estimations is based on calculations of both the knudsen diffusion and the binary diffusion coefficients as described by Reid et al. [18]. It should be noted that the model results are rather sensitive to the estimate of the diffusion coefficient, so if a more sophisticated model is made, a description of the diffusion as a function of temperature and gas composition should be included.

The intrinsic rate \( r_{int} \) is calculated from an expression obtained in a plug-flow reactor under differential conversion and without mass transfer limitations [12]. The expression is shown in Equation 9.

\[ r_{int} = \frac{100 \text{ mole } P_{CH_4} exp\left(\frac{-195.1}{R_T}\right) P_{CH_4} \left(1 - \frac{Q_{SR}}{Q_{SR}}\right)}{\left(1 + 4.6 \cdot 10^{-7} P_{Ar} exp\left(\frac{32 \text{ atm}}{R_T}\right) P_{CO}\right)^2} \]  

(9)

The majority of the kinetic expression reported in literature for steam reforming over Ni-YSZ report an activation energy in the range 58-135 kJ/mol \([3, 13–15, 19–21]\), and only a few report values around 200 kJ/mol \([22–24]\).

The high activation energy both in Equation 9 and 4 is a result of waiting for the slow approach to steady state at each temperature, which has not been reported in the previous studies. The expressions presented here, is consequently not a good representation of the steam reforming rate in a stack just after startup or a temperature change. Instead they describe the reforming rate in a stack operating at steady state for long periods of time.

Figure 5 shows a comparison of the measured conversion and the conversion predicted by the model. Figure 5(a) show the entire range of obtained values, while Figure 5(b) show a zoom at low conversion.
Considering the simplicity of the model, it gives a surprisingly good prediction of the conversion in the stack, with an average deviation between model data and measurements of 44.6%. With the only inputs being the inlet gas composition, the efficiency factor calculated from the structure of the anode, the temperature, and an intrinsic rate expression. It can furthermore be seen from the figures that the major deviations are at low conversion while higher conversions have a better fit. The measurements that deviate most from the model in Figure 5(b) is with methane concentration changes at 675°C (four points overestimated by model) and 625°C (four points underestimated by model). It is also these measurements that deviate from the trend in the Arrhenius plot in Figure 4. The error does not seem to be systematic and is ascribed to experimental uncertainty.

The major strength of the results reported here, is that they are part of a study where the reaction rate has been measured under similar conditions, both in a stack setup with realistic mass transport limitations, and in a plug-flow reactor with no mass transport limitations [12]. The results are given high credibility from the fact that the two series of measurements can be correlated through a simple description of the expected mass transport in the stack.

5. Conclusion

The rate of methane steam reforming over an SOFC Ni-YSZ anode has been measured in the temperature range 600-800°C and with variations in the partial pressure of all reactants and products. The activity was observed to have a long-term dynamic behavior similar to that found for packed bed measurements of the same catalyst [12]. Furthermore, a simple method for predicting methane conversion in a stack from an intrinsic expression was presented. The method was validated against the quarter stack measurements and was found to give a surprisingly good representation of the observed methane conversion. The simplicity of this method makes it ideal for simple SOFC stack models, for flow sheeting purposes.

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